Supporting Information

Synthesis of β-Amino Diaryldienones Using the Mannich Reaction

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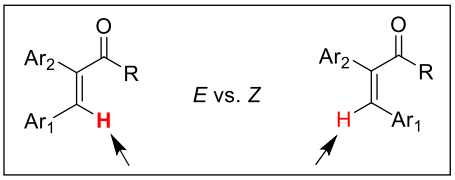
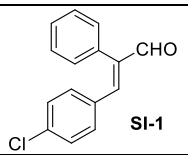
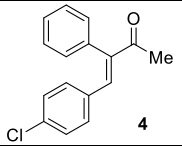
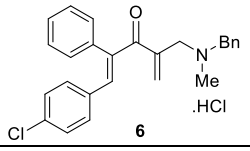
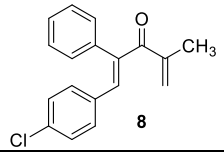
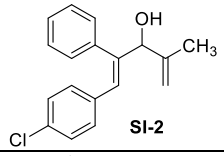
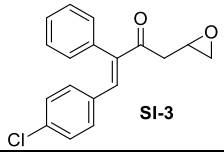
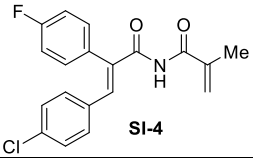
General Materials and Methods

All solvents and reagents were purchased from commercial sources and used without further purification unless otherwise noted. Acetonitrile (MeCN), toluene, dichloromethane (DCM), diethyl ether (Et_2O), and THF (THF) used for the reactions were dried by distillation over calcium hydride (MeCN, toluene, DCM) or sodium (Et_2O, THF). All reactions were performed under an inert atmosphere of dry argon and monitored by thin layer chromatography (TLC) on pre-coated EMD silica gel 60 F_{254} TLC aluminum sheets and visualized with a UV lamp. Flash column chromatography was performed on SiliaFlash P60 (SiliCycle Inc.) silica gel (40−63 μm, 60 Å pore size). NMR spectra were obtained on Bruker AV400 and AV500 instruments at the UCLA MIC Magnetic Resonance Laboratory. NMR data were analyzed using the MestReNova NMR software (Mestrelab Research S. L., version 11.0.2). Chemical shifts (δ) are expressed in ppm and are internally referenced for ^{1}H NMR ($CHCl_3$ 7.26 ppm, DMSO-d_6 2.50 ppm) and ^{13}C NMR ($CDCl_3$ 77.16 ppm, DMSO-d_6 39.52 ppm). DART-MS spectra were collected on a Thermo Exactive Plus MSD (Thermo Scientific) equipped with an ID-CUBE ion source and a VAPUR Interface (IonSense). Both the source and MSD were controlled by Excalibur, version 3.0. The analyte was spotted onto OpenSpot sampling cards (IonSense) using DCM or chloroform as the solvent. Ionization was accomplished using He plasma with no additional ionization agents. Melting points were recorded on a Büchi® B-545 melting point apparatus. Analytical HPLC was performed on a 2.0 × 50 mm Waters Corp. 1.5 μm C_{18} analytical HPLC column. A linear gradient of mobile phase was used over 5 min from 5 – 95% MeCN/water containing 0.2% HCOOH. The flow rate was 0.4 mL/min and the peaks were detected by a LCT-Premier ESI-TOF mass spectrometer in the positive ion mode. X-ray single crystal analysis was

performed on a Bruker dual source (micro-focus Cu and Mo) single crystal x-ray diffractometer with an Apex-11 detector (more information on p. S29).

Table S1. Stereochemistry of the diaryl-substituted enone versus the NMR chemical shift of the enone proton.

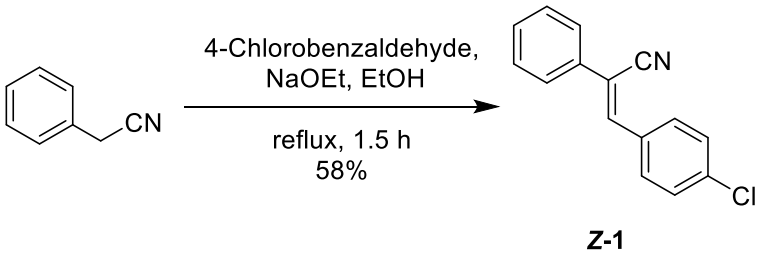


Entry	Compound	^{1}H chemical shift of enone proton (ppm)†	Structure‡
i	***E*-SI-1**	7.34	
ii	***Z*-SI-1**	7.78	
iii*	**4** (*E*)	7.58	
iv	***E*-6**	7.40	
v	***Z*-6**	7.10	
vi*	***E*-8**	7.11	
vii	***Z*-8**	7.02	
viii	***E*-SI-2**	6.71	
ix*	***Z*-SI-2**	6.87	
x*	**SI-3** (*E*)	7.61	
xi*	***E*-SI-4**	7.88	
xii*	***Z*-SI-4**	6.88	

*Stereochemistry confirmed by x-ray crystallography (see pp. S29 – S31). †All measurements in $CDCl_3$. ‡ Corresponding stereoisomer shown for ii, v, vii, ix, and xii.

For acrylaldehyde systems[1] of structure **SI-1** and for dienol systems with structure **SI-2**, the alkene proton for the *Z* isomer appears downfield of that of the *E* isomer. However, when the alkene is conjugated to a ketone or an imide (entries iv - vii, xi, and xii), an opposite trend is observed. A clear downfield shift is observed for the alkene proton in the *E*-isomer, which reaches almost a 1 ppm difference in the imide systems of structure **SI-4**. This may be the result of a deshielding magnetic anisotropic effect by the carbonyl groups towards the enone proton in these systems.

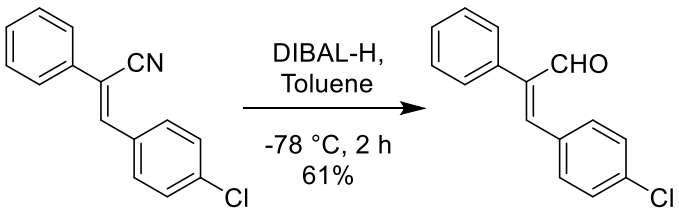
Experimental Procedures



***Z*-1**

(*Z*)-3-(4-Chlorophenyl)-2-phenylacrylonitrile (*Z*-1)[2]

To a mixture of benzyl cyanide (10.0 mL, 84.9 mmol, 1.0 eq) and 4-chlorobenzaldehyde (12.1 g, 84.9 mmol, 1.0 eq) in absolute ethanol at 23 °C was added a freshly prepared solution of sodium ethoxide in ethanol (100 mL of a 1.27 M solution, 127.0 mmol, 1.5 eq). The resultant mixture was heated at reflux for 1.5 h, and then gradually cooled to 0 °C. The resultant precipitate was filtered, washed with ice-cold absolute ethanol, and dried in vacuo to yield the acrylonitrile ***Z*-1** (11.9 g, 49.6 mmol, 58%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.50 – 7.40 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 136.6, 134.3, 132.3, 130.6, 129.6, 129.4, 129.3, 126.1, 117.9, 112.4.

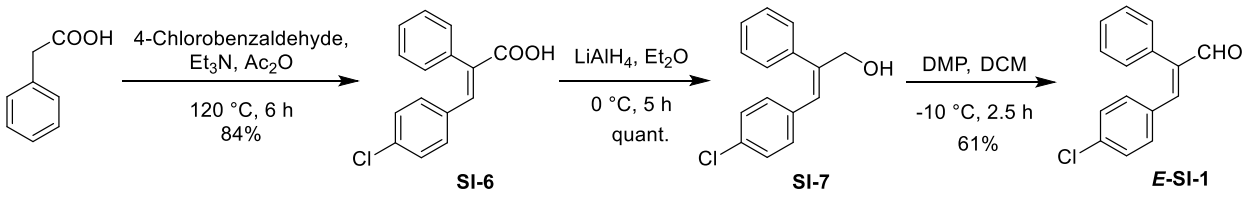


***Z*-1** ***Z*-SI-1**

(*Z*)-3-(4-Chlorophenyl)-2-phenylacrylaldehyde (*Z*-SI-1)

To a cooled (-78 °C) solution of the acrylonitrile ***Z*-1** (10.0 g, 41.7 mmol, 1.0 eq) in toluene was added a 1.0 M solution of DIBAL-H (43.8 mL, 43.8 mmol, 1.05 eq). The resultant suspension was stirred for 2 h at -78 °C. The reaction was quenched by the addition of 5 mL of 5% H_2SO_4 (aq) at -78 °C, and the reaction allowed to warm to 0 °C while stirring. To this was added a

further 5% H_2SO_4 (aq, 145 mL) and Et_2O (100 mL), and the mixture stirred vigorously for 30 min at 0 °C. After separating the layers, the aqueous layer was extracted with Et_2O (150 mL × 2). The combined organic layers were washed with brine (300 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel, using a mobile phase gradient of 0 to 5% of EtOAc/hexanes to yield the enal ***Z*-SI-1** (6.2 g, 25.6 mmol, 61%) as a pale yellow solid. Melting point 90.7 – 91.7 °C; R_f 0.52 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.78 (s, 1H), 7.45 – 7.37 (m, 7H), 7.37 – 7.34 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 145.5, 141.7, 136.1, 136.0, 132.6, 131.6, 123.0, 128.9, 128.7, 128.6; HRMS m/z calcd. for $C_{15}H_{12}ClO$ $[M+H]^+$ 243.0571, found 243.0565.



(*E*)-3-(4-Chlorophenyl)-2-phenylacrylic acid (SI-6)[3]

To phenylacetic acid (8.0 g, 58.2 mmol, 1.0 eq) and 4-chlorobenzaldehyde (8.3 g, 58.2 mmol, 1.0 eq) in a flask was added a mixture of acetic anhydride and triethylamine (v/v 1:1, 15 mL each). The resultant suspension was stirred at 120 °C for 6 h. Then it was cooled to 23 °C and conc. HCl (15 mL) and water (45 mL) were added whilst stirring. The flask was then left in a fridge overnight, and the resultant precipitate filtered and washed with water. The crude product was recrystallized from ethanol/water to yield the acrylic acid **SI-6** as an off-white solid (12.6 g, 48.7 mmol, 84%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34 (s, 1H), 7.27 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 7.15 (d, J = 8.6 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.92 (d, J = 8.6 Hz, 2H); ^{13}C NMR

(126 MHz, DMSO-d_6) δ 170.2, 144.3, 140.3, 136.1, 131.1, 130.8, 129.5, 129.3, 127.9, 127.6, 125.9.

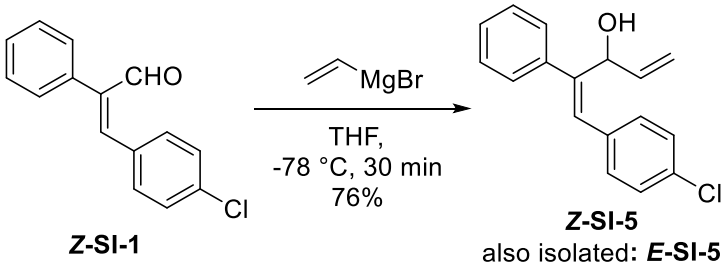
(*E*)-3-(4-Chlorophenyl)-2-phenylprop-2-en-1-ol (SI-7)

To a solution of the acrylic acid **SI-6** (5.1 g, 19.7 mmol, 1.0 eq) in Et_2O (60 mL) at 0 °C, was added lithium aluminum hydride (1.58 g, 39.4 mmol, 2.0 eq) in small portions. The resultant solution was stirred at 23 °C for 1.5 h and then quenched by the slow addition of water (8 mL). To this flask was added Et_2O, 15% aq. NaOH solution and water (50 mL each), and the solution stirred for 15 min at 23 °C. It was then filtered through a plug of celite, and the celite washed with further Et_2O. Layers were separated in the filtrate, and the aqueous layer extracted with further Et_2O (50 mL × 2). The combined organic layers were washed with brine (150 mL), dried over anhydrous $MgSO_4$, filtered, and volatiles removed in vacuo to yield the α-hydroxy alkene **SI-7** (4.81 g, 19.7 mmol, quant.) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 3H), 7.20 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 1.5 Hz, 1H), 4.46 (d, *J* = 1.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 138.2, 135.1, 132.6, 130.6, 129.1, 128.8, 128.3, 127.9, 125.2, 68.4; HRMS m/z calcd. for $C_{15}H_{12}ClO$ $[M\text{-}OH]^+$ 227.0622, found 227.0616.

(*E*)-3-(4-Chlorophenyl)-2-phenylacrylaldehyde (*E*-SI-1)[4]

To a cooled solution (ice-water bath) of the α-hydroxy alkene **SI-7** (4.57 g, 18.7 mmol, 1.0 eq) dissolved in DCM (90 mL) was added Dess-Martin periodinane (8.80 g, 20.5 mmol, 1.1 eq) in three portions. The resultant mixture was stirred at 4 °C for 2.5 h. Then 20 mL of saturated aq. $NaHCO_3$ solution was added to the flask and stirred for 5 min. Flask contents were then partitioned between further DCM (60 mL) and saturated $NaHCO_3$ (aq, 80 mL). The organic layer was removed and washed with saturated $NaHCO_3$ (aq, 50 mL × 3) and brine (50 mL). It was then

dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mobile phase gradient of 3 – 10% EtOAc/hexanes to give the enal ***E*-SI-1** (2.79 g, 11.5 mmol, 61%) as a yellowish solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.44 – 7.38 (m, 3H), 7.34 (s, 1H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.13 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 148.5, 142.3, 136.4, 133.1, 132.6, 132.0, 129.4, 129.1, 129.0, 128.7.



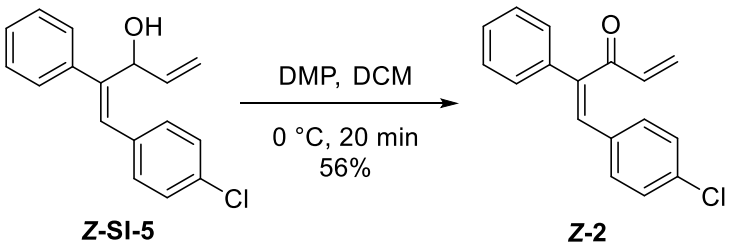
(*Z*)-1-(4-Chlorophenyl)-2-phenylpenta-1,4-dien-3-ol (***Z*-SI-5**)

A solution of enal ***Z*-SI-1** (5.78 g, 23.9 mmol, 1.0 eq) in THF (75 mL) was cooled to -78 °C. To this was added a solution of vinylmagnesium bromide (32.9 mL of a 0.80 M solution in THF, 26.3 mmol, 1.1 eq) and the reaction left to stir for 30 min at -78 °C. To this mixture was added saturated NH_4Cl (aq, 2 mL) and the mixture allowed to warm to 0 °C. The contents were then partitioned between saturated NH_4Cl (aq, 145 mL), water (50 mL), and DCM (200 mL). The aqueous layer was further extracted with DCM (150 mL × 2). The combined organic layers were washed with brine (200 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel, using a mobile phase gradient of 0 to 10% of EtOAc/hexanes to yield the alcohol ***Z*-SI-5** (4.93 g, 18.2 mmol, 76%) as a pale yellow oil. R_f 0.31 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.42 – 7.30 (m, 7H), 6.76 (s, 1H), 6.07 (ddd, *J* = 17.2, 10.5, 4.8 Hz, 1H), 5.42 (br tt, *J* = 4.8, 1.8 Hz, 1H), 5.33 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.22 (dt, *J* = 10.5, 1.6 Hz, 1H), 2.28 (d, *J* = 4.9 Hz,

1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.7, 139.3, 135.1, 133.2, 130.4, 130.3, 128.5, 128.5, 128.1, 127.6, 116.1, 71.0; HRMS m/z calcd. for $C_{17}H_{14}ClO$ $[M-H]^-$ 269.0728, found 269.0728.

(*E*)-1-(4-Chlorophenyl)-2-phenylpenta-1,4-dien-3-ol (***E*-SI-5**)

A small amount of the ***E*** isomer, ***E*-SI-5**, was also isolated from the above synthesis of ***Z*-SI-5**. R_f 0.17 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 3H), 7.20 – 7.15 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.68 (s, 1H), 5.92 (ddd, *J* = 17.1, 10.4, 5.9 Hz, 1H), 5.26 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.17 (dt, *J* = 10.4, 1.3 Hz, 1H), 4.98 – 4.93 (br m, 1H), 1.92 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 138.6, 137.9, 135.0, 132.7, 130.6, 129.4, 128.9, 128.2, 127.8, 126.1, 116.2, 78.0; HRMS m/z calcd. for $C_{17}H_{14}Cl$ $[M-OH]^+$ 253.0778, found 253.0767.

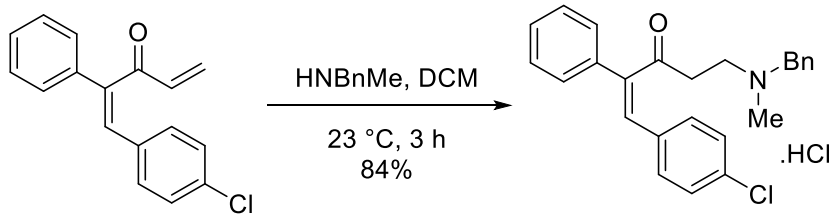


***Z*-SI-5** ***Z*-2**

(*Z*)-1-(4-Chlorophenyl)-2-phenylpenta-1,4-dien-3-one (***Z*-2**)

A solution of the alcohol ***Z*-SI-5** (1.0 g, 3.7 mmol, 1.0 eq) in DCM (30 mL) was cooled in an ice-water bath. To this was added Dess-Martin periodinane (1.7 g, 4.1 mmol, 1.1 eq) and the reaction left to stir for 20 min at 0 °C. To this mixture was added a saturated $NaHCO_3$ (aq, 25 mL) and the mixture stirred for 10 min. The contents were then partitioned between DCM (70 mL) and saturated $NaHCO_3$ (aq, 75 mL), and the layers were separated. The organic layer was washed with saturated $NaHCO_3$ (aq, 50 mL × 2), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel, using a mobile phase gradient of 0 to 3% of EtOAc/hexanes to yield the dienone ***Z*-2** (560.0 mg, 2.1

mmol, 56%) as a yellow oil. R_f 0.38 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 5H), 7.30 – 7.22 (m, 4H), 7.07 (s, 1H), 6.41 (dd, *J* = 17.6, 10.3 Hz, 1H), 6.23 (dd, *J* = 17.6, 1.1 Hz, 1H), 5.90 (dd, *J* = 10.3, 1.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 141.6, 137.7, 137.1, 134.25, 134.19, 132.4, 130.2, 129.3, 128.97, 128.87, 128.6, 126.6; HRMS m/z calcd. for $C_{17}H_{14}ClO$ $[M+H]^+$ 269.0728, found 269.0707.

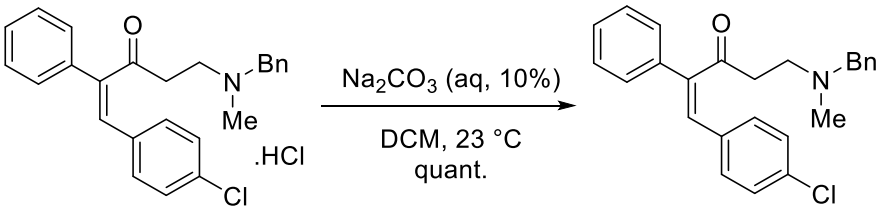


***Z*-2** ***Z*-3.HCl**

(*Z*)-5-(Benzyl(methyl)amino)-1-(4-chlorophenyl)-2-phenylpent-1-en-3-one hydrochloride (*Z*-3.HCl)

To the dienone ***Z*-2** (109.8 mg, 0.41 mmol, 1.05 eq) in DCM (1.5 mL) was added a solution of *N*-benzylmethylamine (0.78 mL of a 0.50 M solution in DCM, 0.39 mmol, 1.0 eq), and the resultant solution stirred at 23 °C for 3 h. Then the reaction mixture was diluted with 10 mL DCM and shaken with a 1 N solution of HCl (aq, 10 mL). The layers were immediately separated, and the aqueous layer extracted with DCM (5 mL × 2). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and volatiles removed in vacuo. The residue was triturated with Et_2O (3 × 3mL) and dried in vacuo to yield the β-amino diarylenone hydrochloride salt ***Z*-3.HCl** (147.0 mg, 0.34 mmol, 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.74 (m, 1H), 7.51 – 7.40 (m, 5H), 7.40 – 7.34 (m, 5H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.97 (s, 1H), 4.11 (d, *J* = 13.4 Hz, 1H), 3.94 (d, *J* = 12.2 Hz, 1H), 3.41 – 3.05 (m, 4H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 143.6, 135.9, 134.8, 134.1, 131.2,

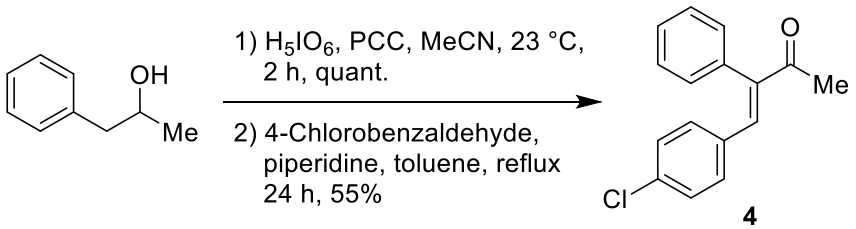
130.4, 130.0, 129.6, 129.21, 129.18, 129.1, 129.0, 128.0, 126.7, 60.2, 50.0, 39.6, 38.5; HRMS m/z calcd. for $C_{25}H_{25}ClNO$ $[M+H]^+$ 390.1619, found 390.1599.



***Z*-3.HCl** ***Z*-3**

(*Z*)-5-(Benzyl(methyl)amino)-1-(4-chlorophenyl)-2-phenylpent-1-en-3-one (***Z*-3**)

The hydrochloride ***Z*-3.HCl** (147.0 mg, 0.34 mmol) from above was dissolved in 5 mL of DCM and stirred for 10 min at 23 °C with a solution of 10% Na_2CO_3 (aq, 5 mL). The layers were separated, and the aqueous layer extracted with further DCM (5 mL × 2). The combined organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, and the volatiles were removed in vacuo to yield the β-amino diarylenone ***Z*-3** (133.0 mg, 0.34 mmol, quantitative) as a yellow waxy oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.38 – 7.30 (m, 4H), 7.29 – 7.22 (m, 6H), 7.17 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.87 (s, 1H), 3.39 (s, 2H), 2.76 – 2.60 (m, 4H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 144.3, 138.7, 137.1, 134.3, 134.2, 130.1, 129.1, 129.0, 128.9, 128.6, 128.33, 128.30, 127.1, 126.8, 62.4, 52.0, 42.0, 41.9; HRMS m/z calcd. for $C_{25}H_{25}ClNO$ $[M+H]^+$ 390.1619, found 390.1593.

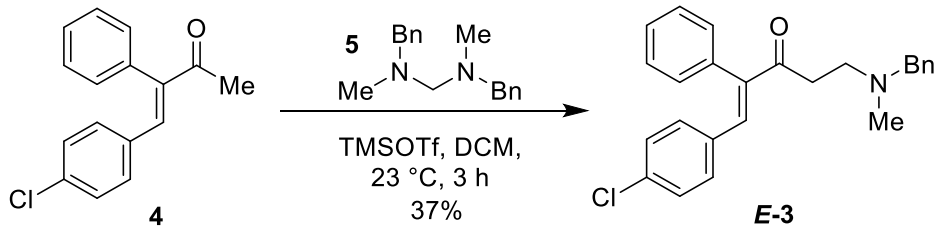


4

(*E*)-4-(4-Chlorophenyl)-3-phenylbut-3-en-2-one (4)[5]

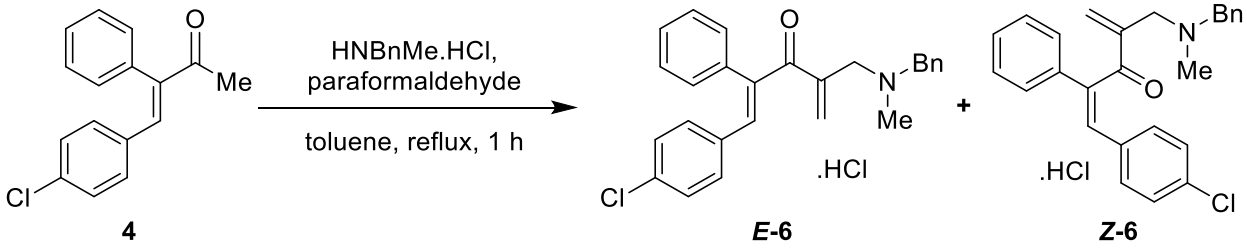
Periodic acid (21.50 g, 92.4 mmol, 1.1 eq) was added to MeCN (250 mL) while stirring at 23 °C, and the suspension stirred vigorously for 15 min. Then the flask was placed in an ice-bath and 1-phenyl-2-propanol, (12.0 mL, 84.0 mmol, 1.0 eq) was added. To this cooled solution was added pyridinium chlorochromate (370.1 mg, 1.7 mmol, 0.02 eq) in MeCN (60 mL), dropwise over 5 min. The resultant creamy yellow suspension was stirred at 0 °C for 1 h and at 23 °C for 1 h. Then the reaction mixture was diluted with ethyl acetate (EtOAc, 300 mL) and washed with a mixture of brine/water (1:1, 200 mL). The organic layer was then washed with a saturated solution of Na_2SO_3 (200 mL × 2) and brine (200 mL), dried over anhydrous $MgSO_4$, filtered, and the solvent removed in vacuo to obtain 1-phenylacetone, (11.2 g, 83.5 mmol, quantitative) as a yellow oil. R_f 0.24 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 3.69 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 134.3, 129.4, 128.8, 127.1, 51.0, 29.3.

To a solution of phenylacetone (5.0 g, 37.3 mmol, 1.0 eq) and 4-chlorobenzaldehyde (5.32 g, 37.3 mmol, 1.0 eq) in toluene (120 mL) was added piperidine (0.15 mL, 1.5 mmol, 0.04 eq), and the resultant mixture heated at reflux for 24 h. Then the solvent was removed in vacuo and the residue purified by column chromatography using a mobile phase gradient of 0 to 10% EtOAc/hexanes to yield the diarylenone **4** (5.3 g, 20.6 mmol, 55%) as an off-white solid. R_f 0.18 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.45 – 7.35 (m, 3H), 7.16 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 141.4, 137.4, 136.7, 135.3, 133.2, 132.1, 129.5, 129.3, 128.7, 128.3, 28.2.



(*E*)-5-(Benzyl(methyl)amino)-1-(4-chlorophenyl)-2-phenylpent-1-en-3-one (***E*-3**)

Ketone **4** (200.0 mg, 0.78 mmol, 1.0 eq) and *N*,*N*'-dibenzyl-*N*,*N*'-dimethylmethanediamine[6] (0.25 mL, 0.93 mmol, 1.2 eq) were dissolved in DCM (5 mL) and cooled in an ice-water bath. To this was slowly added TMSOTf (0.17 mL, 0.93 mmol, 1.2 eq), and the resultant mixture allowed to warm to 23 °C and stir for 3 h. Then the reaction mixture was diluted with further DCM (10 mL), and washed with saturated $NaHCO_3$ (aq, 10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel buffered with 1% triethylamine in hexanes, using a mobile phase gradient of 0 – 20% Et_2O/hexanes to yield the β-amino diarylenone ***E*-3** (114.0 mg, 0.29 mmol, 37%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.45 – 7.38 (m, 2H), 7.36 – 7.27 (m, 5H), 7.27 – 7.22 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 3.65 (s, 2H), 2.29 (s, 3H), 2.25 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 141.4, 137.4 (2C), 136.7, 135.2, 133.2, 132.1, 129.5, 129.3, 129.0, 128.7, 128.3, 128.3, 126.9, 59.5, 40.6, 28.2; HRMS m/z calcd. for $C_{25}H_{25}ClNO$ $[M+H]^+$ 390.1619, found 390.2527.



(*E*)-4-((Benzyl(methyl)amino)methyl)-1-(4-chlorophenyl)-2-phenylpenta-1,4-dien-3-one hydrochloride (***E*-6**)

The enone **4** (300.0 mg, 1.2 mmol, 1.0 eq), paraformaldehyde (222.9 mg, 7.2 mmol, 6.0 eq), and *N*-benzylmethylamine hydrochloride (405.3 mg, 2.6 mmol, 2.2 eq) were dissolved in toluene (3 mL) and heated at reflux for 1 h. Then the reaction was quenched with the addition of 1 mL of 10% Na_2CO_3 (aq) while stirring. The solution was then partitioned between Et_2O (5 mL) and 10% Na_2CO_3 (aq, 6 mL). The layers were separated, and the aqueous layer was extracted with further Et_2O (4 mL × 2). The combined organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel buffered with 1% triethylamine in hexanes, using a mobile phase gradient of 3:100 to 15:100 mL of Et_2O/hexanes to yield the **free base of *E*-6** as a yellow colored oil (330.9 mg, 0.82 mmol). R_f 0.18 (20% Et_2O/hexanes on silica buffered with 1% triethylamine in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 3H), 7.29 (m, 4H), 7.23 (m, 2H), 7.21 – 7.16 (m, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.86 (q, *J* = 1.3 Hz, 1H), 5.84 (q, *J* = 1.2 Hz, 1H), 3.54 (s, 2H), 3.31 (t, *J* = 1.2 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 146.8, 141.5, 139.2, 137.5, 136.1, 134.8, 133.5, 131.6, 129.7, 128.9 (2C), 128.6, 128.3, 128.2, 127.1, 125.0, 62.1, 59.3, 42.5.

A small amount of the *Z*-isomer of the free base **6** (***Z*-6**) was also obtained in this reaction as described below.

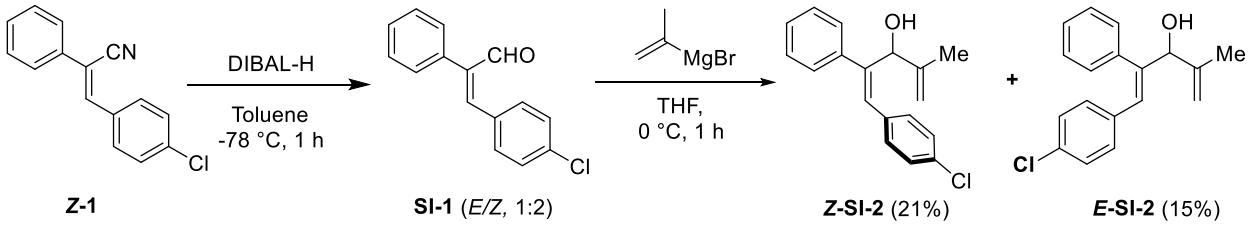
The **free base of *E*-6** above was dissolved in DCM (7 mL) and shaken vigorously with 1 N HCl (aq, 5 mL) to form the hydrochloride salt. The aqueous layer was extracted with further DCM (5 mL × 2). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield the diaryldienone hydrochloride ***E*-6** (327.0 mg, 0.75 mmol, 62% from **4**) as a white solid. Melting point 165.8 – 166.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.76 (m, 1H), 7.69 – 7.63 (m, 2H), 7.47 – 7.43 (m, 3H), 7.40 (s, 1H), 7.39 – 7.35 (m, 3H), 7.18 – 7.13

(m, 4H), 7.12 (s, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.59 (s, 1H), 4.28 (dd, *J* = 13.1, 4.9 Hz, 1H), 4.19 (dd, *J* = 13.1, 5.5 Hz, 1H), 4.00 (dd, *J* = 13.1, 4.5 Hz, 1H), 3.93 (dd, *J* = 13.1, 6.8 Hz, 1H), 2.65 (d, *J* = 4.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 139.8, 139.5, 138.4, 136.6, 135.6, 135.6, 132.6, 132.0, 131.5, 130.4, 129.6, 129.4, 129.3, 128.8, 128.7, 128.5, 60.4, 53.9, 39.7; HRMS m/z calcd. for $C_{26}H_{25}ClNO$ $[M+H]^+$ 402.1619, found 402.1610; Analytical HPLC t_R = 3.45 min.

(*Z*)-4-((Benzyl(methyl)amino)methyl)-1-(4-chlorophenyl)-2-phenylpenta-1,4-dien-3-one hydrochloride (***Z*-6**)

The **free base of *Z*-6** was isolated from the same reaction that generated the **free base of *E*-6** above, as an orange colored oil (108.8 mg, 0.27 mmol). R_f 0.32 (20% Et_2O/hexanes on silica buffered with 1% triethyamine in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.38 – 7.34 (m, 3H), 7.34 – 7.25 (m, 5H), 7.20 (s, 4H), 7.02 (s, 1H), 6.19 (d, *J* = 1.2 Hz, 1H), 6.11 (d, *J* = 1.4 Hz, 1H), 3.49 (s, 2H), 3.29 (t, *J* = 1.3 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 145.5, 141.9, 139.3, 138.2, 134.5, 134.0, 131.0, 130.1, 129.0, 128.85, 128.80, 128.6, 128.5, 128.4, 127.1, 126.4, 62.5, 56.3, 42.3.

The free base above was converted to the hydrochloride using the procedure outlined for ***E*-6**, to obtain the diaryldienone hydrochloride ***Z*-6** (96.4 mg, 0.22 mmol, 18% from **4**) as a white solid. Melting point 162.0 – 162.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.63 (m, 1H), 7.63 – 7.57 (m, 2H), 7.48 – 7.43 (m, 3H), 7.41 – 7.31 (m, 6H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.10 (m, 3H), 6.72 (s, 1H), 4.16 (dd, *J* = 13.1, 4.3 Hz, 1H), 4.01 (dd, *J* = 13.0, 5.7 Hz, 1H), 3.92 – 3.85 (m, 2H), 2.47 (d, *J* = 4.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 141.8, 140.7, 137.01, 136.98, 134.7, 134.2, 131.4, 130.4, 130.1, 129.9, 129.6, 129.3, 129.1 (2C), 128.3, 126.2, 60.1, 51.4, 39.1; HRMS m/z calcd. for $C_{26}H_{25}ClNO$ $[M+H]^+$ 402.1619, found 402.1613.



***Z*-1** **SI-1** (*E*/*Z*, 1:2) ***Z*-SI-2** (21%) ***E*-SI-2** (15%)

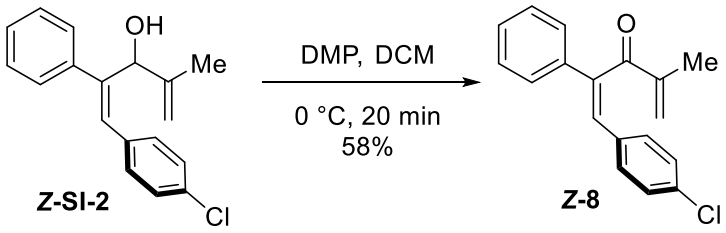
1-(4-Chlorophenyl)-4-methyl-2-phenylpenta-1,4-dien-3-ol (SI-2)

To a cooled (-78 °C) solution of the acrylonitrile ***Z*-1** (2.0 g, 8.3 mmol, 1.0 eq) in toluene was added a 1.0 M solution of DIBAL-H (10.0 mL, 10.0 mmol, 1.2 eq). The resultant suspension was stirred for 1 h at -78 °C. The reaction was allowed to warm to 0 °C and quenched by the addition of 5 mL of 5% H_2SO_4 (aq) at 0 °C. To this was added a further 5% H_2SO_4 (aq, 45 mL) and Et_2O (50 mL), and the mixture stirred vigorously for 30 min at 0 °C. After separating the layers, the aqueous layer was extracted with Et_2O (50 mL × 2). The combined organic layers were washed with brine (75 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude enal **SI-1** (2:1, *E*:*Z*) thus obtained was used for the next step without further purification.

A solution of the crude enal **SI-1** above (8.3 mmol, 1.0 eq) in THF (40 mL) was cooled to 0 °C. To this was added a solution of isopropenylmagnesium bromide (18.3 mL of a 0.50 M solution in THF, 9.1 mmol, 1.1 eq) and the reaction left to stir for 1 h at 0 °C. To this mixture was added saturated NH_4Cl (aq, 5 mL) and the reaction contents partitioned between saturated NH_4Cl (aq, 50 mL), water (50 mL), and DCM (100 mL). The aqueous layer was further extracted with DCM (100 mL × 2). The combined organic layers were washed with brine (150 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel, using a mobile phase gradient of 0 to 10% of EtOAc/hexanes to yield the alcohols ***Z*-SI-2** (485.0 mg, 1.7 mmol, 21%) and ***E*-SI-2** (364.4 mg, 1.3 mmol, 15%).

***Z*-SI-2**: Yellow Solid. Melting point 65.9 – 66.9 °C; ^{1}H NMR δ 7.57 – 7.53 (m, 2H), 7.36 – 7.34 (m, 4H), 7.34 – 7.29 (m, 3H), 6.87 (s, 1H), 5.26 (d, *J* = 5.6 Hz, 1H), 5.10 (s, 1H), 4.95 (q, *J* = 1.6 Hz, 1H), 1.89 (d, *J* = 5.6 Hz, 1H), 1.63 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR δ 145.6, 142.5, 139.6, 135.4, 133.3, 131.8, 130.3, 128.7, 128.3, 128.2, 127.8, 111.4, 73.2, 20.1; HRMS m/z calcd. for $C_{18}H_{16}Cl$ $[M\text{-}OH]^+$ 267.0935, found 267.0921.

***E*-SI-2**: Pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 3H), 7.15 – 7.11 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.71 (s, 1H), 4.91 (s, 2H), 4.89 (d, *J* = 4.8 Hz, 1H), 1.86 (d, *J* = 4.4 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 142.9, 138.0, 135.1, 132.6, 130.6, 129.2, 128.8, 128.2, 127.8, 126.6, 113.3, 80.6, 18.4; HRMS m/z calcd. for $C_{18}H_{16}Cl$ $[M\text{-}OH]^+$ 267.0935, found 267.0920.

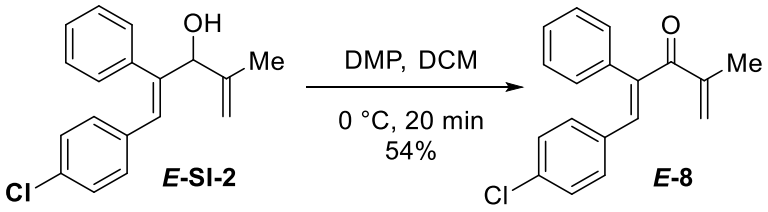


***Z*-SI-2** ***Z*-8**

(*Z*)-1-(4-Chlorophenyl)-4-methyl-2-phenylpenta-1,4-dien-3-one (*Z*-8)

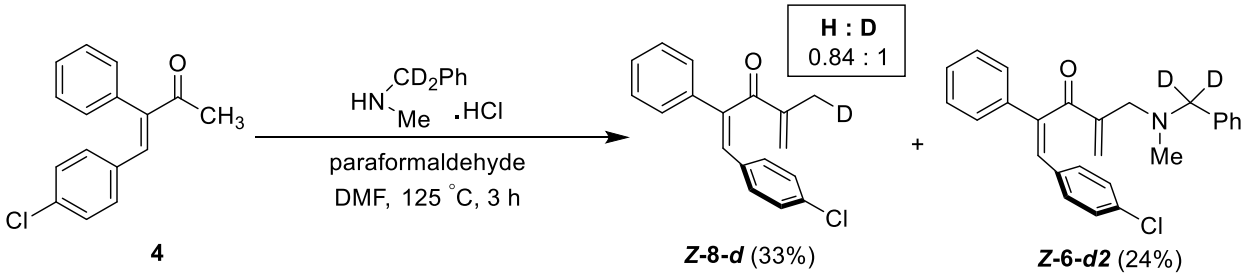
A solution of the alcohol ***Z*-SI-2** (450.9 mg, 1.58 mmol, 1.0 eq) in DCM (10 mL) was cooled in an ice-water bath. To this was added Dess-Martin periodinane (738.7 mg, 1.74 mmol, 1.1 eq) and the reaction left to stir for 20 min at 0 °C. To this mixture was added a saturated $NaHCO_3$ (aq, 3 mL) and the mixture stirred for 5 min. The contents were then partitioned between DCM (40 mL) and saturated $NaHCO_3$ (aq, 50 mL), and the layers were separated. The aqueous layer was extracted with further DCM (20 mL × 2). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel, using a mobile phase gradient of 0 to 3% of

EtOAc/hexanes to yield the dienone ***Z*-8** (258.3 mg, 0.91 mmol, 58%) as a pale-yellow wax. ^{1}H NMR δ 7.42 – 7.29 (m, 5H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.02 (s, 1H), 5.99 (s, 1H), 5.81 (s, 1H), 1.94 (s, 3H); ^{13}C NMR δ 201.5, 144.4, 141.8, 138.2, 134.6, 134.0, 130.3, 130.0, 129.0, 128.9, 128.5, 128.4, 126.3, 17.0; HRMS m/z calcd. for $C_{18}H_{16}ClO$ $[M+H]^+$ 283.0884, found 283.0864.



(*E*)-1-(4-Chlorophenyl)-4-methyl-2-phenylpenta-1,4-dien-3-one (*E*-8)

Using the same procedure outlined for ***Z*-8** above, the isomer ***E*-8** was obtained as a white solid (54%). Melting point 93.2 – 93.9 °C; ^{1}H NMR δ 7.37 – 7.31 (m, 3H), 7.21 – 7.17 (m, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.11 (s, 1H), 6.99 (d, *J* = 8.3 Hz, 2H), 5.84 (p, *J* = 1.0 Hz, 1H), 5.81 (p, *J* = 1.5 Hz, 1H), 2.00 (dd, *J* = 1.5, 0.9 Hz, 3H); ^{13}C NMR δ 199.0, 144.3, 141.3, 136.4, 136.3, 134.6, 133.5, 131.5, 129.4, 129.0, 128.6, 128.2, 126.4, 18.8; HRMS m/z calcd. for $C_{18}H_{16}ClO$ $[M+H]^+$ 283.0884, found 283.0863.



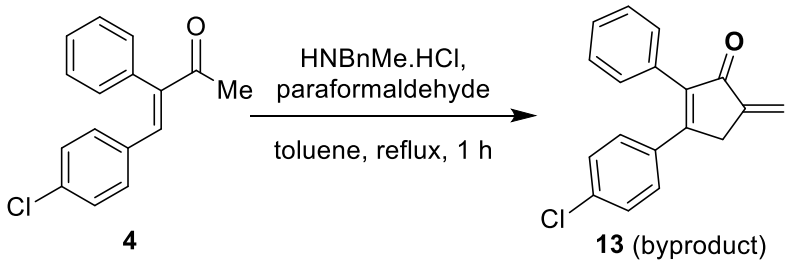
(*Z*)-1-(4-Chlorophenyl)-4-(methyl-*d*)-2-phenylpenta-1,4-dien-3-one (*Z*-8-*d*, H:D 0.84:1 mixture)

The enone **4** (77.0 mg, 0.30 mmol, 1.0 eq), paraformaldehyde (30.3 mg, 0.98 mmol, 3.3 eq), and *N*-methyl-1-phenylmethan-d_2-amine hydrochloride[7] (100.0 mg, 0.63 mmol, 2.1 eq) were dissolved in dimethylformamide (1 mL) and heated at 125 °C for 3 h. Then the volatiles were removed in vacuo and the remaining contents partitioned between Et_2O (7 mL) and 10% Na_2CO_3 (aq, 7 mL). The layers were separated, and the aqueous layer was extracted with further Et_2O (5 mL × 2). The combined organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel buffered with 1% triethylamine in hexanes, using a mobile phase gradient of 3:100 to 15:100 mL of Et_2O/hexanes to yield ***Z*-8-*d*** (H:D 0.84:1 mixture) as a yellow-colored wax (28.4 mg, 0.10 mmol, 33%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 5H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.02 (s, 1H), 5.99 (t, *J* = 0.9 Hz, 1H), 5.83 – 5.80 (m, 1H), 1.95 (s, 1.34H, -CH_3), 1.94 – 1.92 (br m, 1.07H, -CH_2D); ^{2}H NMR (77 MHz, $CDCl_3$) δ 1.94 (t, *J* = 2.2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.53, 201.51, 144.39, 144.36, 141.9, 138.2, 134.6, 134.0, 130.3, 130.0, 129.0, 128.9, 128.5, 128.4, 126.3, 17.0 (CH_3), 16.7 (t, J = 19.7 Hz, -CH_2D); HRMS m/z calcd. for $C_{18}H_{15}DClO$ $[M+H]^+$ 284.0947, found 284.0935; HRMS m/z calcd. for $C_{18}H_{16}ClO$ $[M+H]^+$ 283.0884, found 283.0873.

(*Z*)-1-(4-Chlorophenyl)-4-((methyl(phenylmethyl-*d*$_2$)amino)methyl)-2-phenylpenta-1,4-dien-3-one (*Z*-6-*d*$_2$)

From the same reaction (above) that yielded ***Z*-8-*d***, compound ***Z*-6-*d*$_2$** was isolated as a pale-yellow wax (28.8 mg, 71.3 μmol, 24%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 3H), 7.32 – 7.27 (m, 5H), 7.20 (s, 4H), 7.02 (s, 1H), 6.19 (q, *J* = 1.2 Hz, 1H), 6.11 (q, *J* = 1.5 Hz, 1H), 3.29 (s, 2H), 2.06 (s, 3H); ^{2}H NMR (77 MHz, $CDCl_3$) δ 3.46 (s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.9, 145.5, 141.9, 138.2, 134.5, 134.0, 131.0, 130.1, 129.0, 128.84, 128.82,

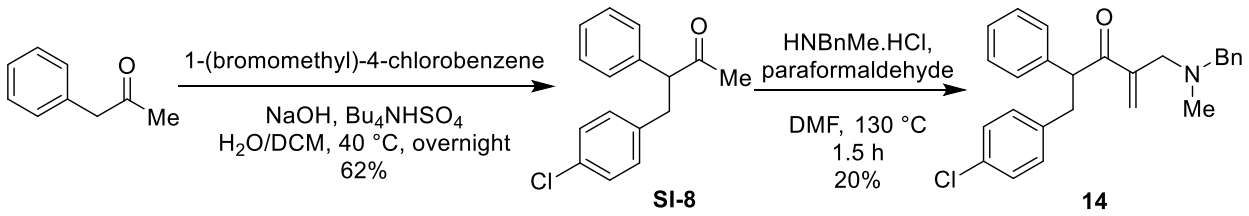
128.6, 128.5, 128.4, 128.3, 127.1, 126.4, 61.7 (weak p, J = 19.2 Hz), 56.2, 42.2; HRMS m/z calcd. for $C_{26}H_{23}D_2ClNO$ $[M+H]^+$ 404.1745, found 404.1740.



4 **13** (byproduct)

3-(4-Chlorophenyl)-5-methylene-2-phenylcyclopent-2-en-1-one (**13**)

The enone **4** (1.0 g, 3.9 mmol, 1.0 eq), paraformaldehyde (0.72 g, 23.4 mmol, 6.0 eq), and *N*-benzylmethylamine hydrochloride (1.36 g, 8.6 mmol, 2.2 eq) were dissolved in toluene (8 mL) and heated at reflux for 1 h. Then the reaction was quenched with the addition of 1 mL of 10% Na_2CO_3 (aq) while stirring. The solution was then partitioned between Et_2O (30 mL) and 10% Na_2CO_3 (aq, 30 mL). The layers were separated, and the aqueous layer was extracted with further Et_2O (10 mL × 2). The combined organic layers were washed with brine (30 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel buffered with 1% triethylamine in hexanes using a mobile phase gradient of 3:100 to 15:100 mL of Et_2O/hexanes. The fractions containing **13** were further purified by preparative TLC on silica gel using a mobile phase of 15% EtOAc/hexanes to give cyclopentenone **13** as an off-white solid (10.4 mg, 37.0 µmol, 0.9 %). R_f 0.16 (10% Et_2O/hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.31 – 7.22 (m, 7H), 6.31 – 6.26 (m, 1H), 5.61 – 5.57 (m, 1H), 3.97 – 3.21 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 160.5, 142.0, 141.3, 136.2, 133.7, 132.3, 129.8, 129.5, 129.0, 128.8, 128.4, 117.6, 35.2; HRMS m/z calcd. for $C_{18}H_{14}ClO$ $[M+H]^+$ 281.0728, found 281.0716.



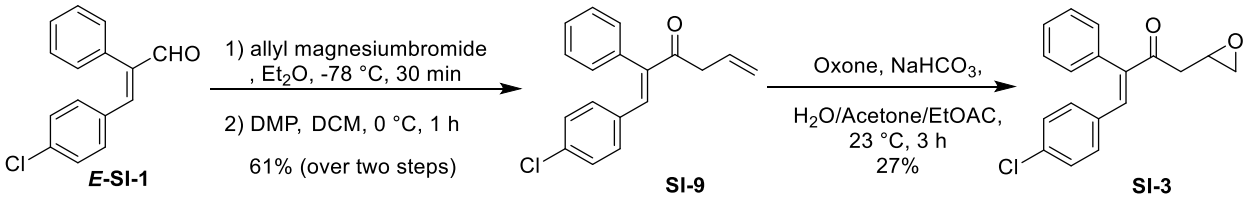
4-(4-Chlorophenyl)-3-phenylbutan-2-one (**SI-8**)[8]

To a flask containing phenylacetone (0.52 mL, 3.9 mmol, 1.0 eq) and sodium hydroxide (0.17 g, 4.3 mmol, 1.1 eq) was added 1-(bromomethyl)-4-chlorobenzene (964.0 mg, 4.7 mmol, 1.2 eq). To this was added 2 mL each of water and DCM. After commencing stirring, tetrabutylammonium bisulfate (1.32 mg, 3.9 mmol, 1.0 eq) was added and the resultant solution stirred overnight at 40 °C. The reaction mixture was then diluted with water (5 mL) and extracted with Et_2O (3 mL × 3). The combined organic layers were washed with brine (3 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mobile phase gradient of 0 – 4% EtOAc/hexanes to give ketone **SI-8** (630.0 mg, 2.4 mmol, 62%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 3H), 7.18 – 7.12 (m, 4H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.85 (t, *J* = 7.4 Hz, 1H), 3.37 (dd, *J* = 13.9, 7.3 Hz, 1H), 2.86 (dd, *J* = 13.9, 7.5 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 138.3, 138.2, 132.0, 130.5, 129.1, 128.5 (2C), 127.7, 61.6, 37.8, 29.6.

2-((Benzyl(methyl)amino)methyl)-5-(4-chlorophenyl)-4-phenylpent-1-en-3-one (**14**)

The ketone **SI-8** (50.0 mg, 0.19 mmol, 1.0 eq), paraformaldehyde (19.9 mg, 0.64 mmol, 3.3 eq), and *N*-benzylmethylamine hydrochloride (67.8 mg, 0.43 mmol, 2.2 eq) were dissolved in anhydrous DMF (3 mL) and heated at 130 °C for 1.5 h. Then volatiles were removed in vacuo and the residue partitioned between Et_2O (5 mL) and 10% Na_2CO_3 (aq, 6 mL). The layers were separated, and the aqueous layer was extracted with further Et_2O (3 mL × 2). The combined

organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by preparative scale TLC using a mobile phase of Et_2O:hexanes:triethyamine (25:75:2) to yield the β-aminoenone **14** (15.1 mg, 37.4 µmol, 20%) as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.54 – 12.45 (m, 1H), 12.45 – 12.37 (m, 1H), 7.56 – 7.47 (m, 4H), 7.45 – 7.38 (m, 6H), 7.32 – 7.27 (m, 3H), 7.25 – 7.20 (m, 3H), 7.19 – 7.09 (m, 9H), 7.04 (s, 1H), 7.02 – 6.96 (m, 4H), 6.69 (s, 2H), 4.62 (dd, *J* = 8.4, 6.6 Hz, 2H), 4.00 (ddd, *J* = 13.6, 9.6, 4.3 Hz, 2H), 3.92 – 3.71 (m, 6H), 3.38 (dt, *J* = 13.7, 8.4 Hz, 2H), 2.98 (dd, *J* = 13.7, 6.5 Hz, 2H), 2.30 (d, *J* = 4.7 Hz, 3H), 2.25 (d, *J* = 4.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.32, 199.25, 138.4, 138.0, 137.9, 137.6, 137.5, 136.7, 136.5, 132.53, 132.50, 131.3, 130.6, 130.5, 130.3, 130.3, 129.51, 129.48, 128.7, 128.43, 128.37, 128.1, 128.0, 127.9, 59.9, 59.7, 54.8, 54.7, 52.4, 52.3, 39.3, 39.2, 38.9, 38.4; HRMS m/z calcd. for $C_{26}H_{27}ClNO$ $[M+H]^+$ 404.1776, found 404.1767.



(*E*)-1-(4-Chlorophenyl)-2-phenylhexa-1,5-dien-3-one (SI-9)

The enal ***E*-SI-1** (2.79 g, 11.5 mmol, 1.0 eq) was dissolved in 50 mL of Et_2O and then cooled to -78 °C. To this was slowly added a 1.0 M solution of allyl magnesium bromide in Et_2O (14.9 mL, 14.9 mmol 1.3 eq), and the solution stirred for 30 min at -78 °C. Then 2.5 mL of saturated aq. NH_4Cl solution was added and the solution allowed to warm to 23 °C whilst stirring. The reaction mixture was then diluted with saturated NH_4Cl (aq, 75 mL), water (30 mL), and DCM (100 mL). After layer separation, the aqueous layer was extracted with further DCM (30 mL × 2). The combined organic layers were washed with brine (100 mL), dried over anhydrous

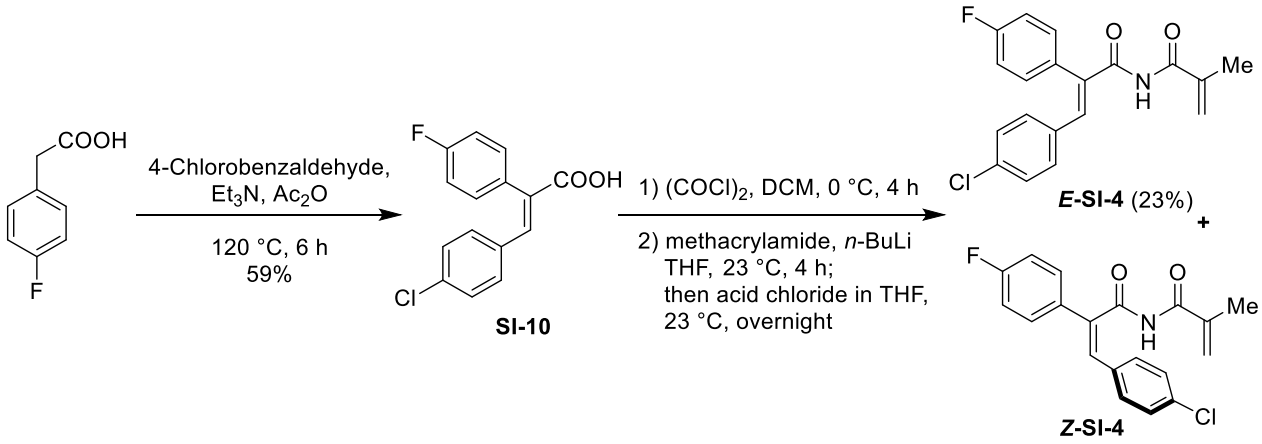
$MgSO_4$, filtered, and the volatiles removed in vacuo to give the crude alcohol (2.77 g) as a yellowish solid.

The crude alcohol above (2.72 g, 9.6 mmol, 1.0 eq) was dissolved in 70 mL of DCM, and the resultant solution cooled in an ice-water bath. To that was added Dess-Martin periodinane (4.91 g, 11.5 mmol, 1.2 eq) in three portions, and the reaction mixture stirred at 0 °C for 1 h. Then 30 mL of saturated aq. $NaHCO_3$ solution was added to the flask and stirred for 5 min. Flask contents were then partitioned between further DCM (150 mL), saturated $NaHCO_3$ (aq, 150 mL), and water (20 mL). The organic layer was removed and washed with saturated $NaHCO_3$ (aq, 50 mL × 2), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mobile phase gradient of 0 – 3% EtOAc/hexanes to give the alkene **SI-9** (1.98 g, 7.0 mmol, 61%) as an off-white solid. Melting point 75.6 – 77.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.48 – 7.37 (m, 3H), 7.17 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 5.96 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.15 (dq, *J* = 10.2, 1.4 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.5 Hz, 1H), 3.31 (dt, *J* = 6.8, 1.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 140.7, 137.2, 136.6, 135.3, 133.2, 132.2, 131.3, 129.7, 129.4, 128.7, 128.4, 118.6, 45.0; HRMS m/z calcd. for $C_{18}H_{16}ClO$ $[M+H]^+$ 283.0884, found 283.0877.

(*E*)-4-(4-Chlorophenyl)-1-(oxiran-2-yl)-3-phenylbut-3-en-2-one (**SI-3**)

To a solution of the alkene **SI-9** in acetone/EtOAc/water (10:10:5 mL) cooled in an ice-water bath, was added $NaHCO_3$ (5.21 g, 62.0 mmol, 25 eq) whilst stirring. To this suspension was added oxone (6.0 g, 9.8 mmol, 3.93 eq) in three portions (2.0 g each, at 1 h intervals). After stirring the solution at 0 °C for 3 hours, the reaction mixture was partitioned between EtOAc (80 mL) and saturated sodium thiosulfate (aq, 100 mL). The aqueous layer was extracted with further

EtOAc (20 mL × 2). The combined organic layers were washed with saturated $NaHCO_3$ (aq, 100 mL × 2), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel using a mobile phase gradient of 10 – 20% EtOAc/hexanes. The product containing fractions were combined and volatiles removed in vacuo. Residue was dissolved in to chloroform and concentrated in vacuo to near dryness. Resultant concentrated solution was diluted with hexanes, and the flask left in a refrigerator, where the product crystallizes out. Filtration of the solution and washing the product with hexanes gives the oxirane **SI-3** (203.3 mg, 0.68 mmol, 27%) as white needle-like crystals. Melting point 85.9 – 86.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.46 – 7.38 (m, 3H), 7.19 – 7.15 (m, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 3.34 (tdd, *J* = 5.6, 4.0, 2.7 Hz, 1H), 2.90 – 2.82 (m, 2H), 2.68 (dd, *J* = 17.5, 5.3 Hz, 1H), 2.45 (dd, *J* = 4.8, 2.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5, 140.6, 137.6, 136.2, 135.5, 133.0, 132.3, 129.6, 129.5, 128.7, 128.5, 48.5, 47.0, 43.6; HRMS m/z calcd. for $C_{18}H_{16}ClO_2$ $[M+H]^+$ 299.0833, found 299.0830; Analytical HPLC t_R = 4.37 min.



(*E*)-3-(4-Chlorophenyl)-2-(4-fluorophenyl)acrylic acid (**SI-10**)[9]

To 4-fluorophenylacetic acid (15.0 g, 95.4 mmol, 1.0 eq) and 4-chlorobenzaldehyde (13.61 g, 95.4 mmol, 1.0 eq) in a flask was added a mixture of acetic anhydride and triethylamine (v/v 1:1,

37.5 mL each). The resultant suspension was stirred at 120 °C for 6 h. Then it was cooled to 23 °C and 75 mL of conc. HCl and 225 mL of water were added whilst stirring. The flask was then left at 23 °C overnight, and the resultant precipitate filtered and washed with water. This crude product was recrystallized from ethanol/water (left at 23 °C overnight to complete precipitation) to yield acrylic acid **SI-10** as a pale-brown solid (15.50 g, 56.0 mmol, 59%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.84 (br s, 1H), 7.76 (s, 1H), 7.30 (d, J = 8.6 Hz, 2H), 7.22 – 7.19 (m, 4H), 7.07 (d, J = 8.6 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.0, 161.7 (d, J = 244.4 Hz), 138.1, 133.6, 133.3, 133.0, 131.8, 131.7 (d, J = 8.2 Hz), 128.5, 128.14, 128.08, 115.5 (d, J = 21.3 Hz).

(*E*)-3-(4-Chlorophenyl)-2-(4-fluorophenyl)-*N*-methacryloylacrylamide (***E*-SI-4**)

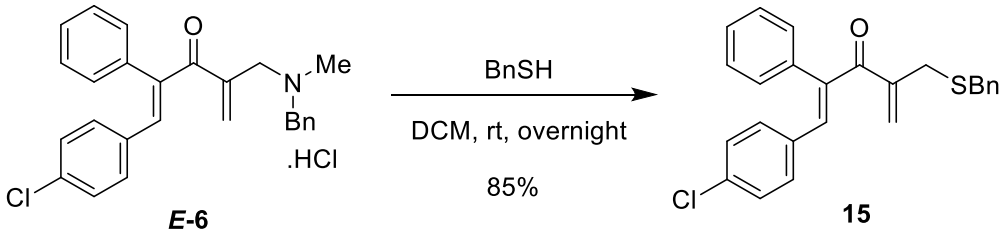
The acrylic acid **SI-10** (15.0 g, 54.2 mmol, 1.0 eq) was suspended in dichloromethane (225 mL) and the flask cooled to 0 °C. To this was added oxalyl chloride (5.62 mL, 65.1 mmol, 1.2 eq) followed by anhydrous DMF (1.0 mL, slowly), and the solution left to stir at 0 °C for 4 h. Then the volatiles were removed in vacuo to yield the crude acid chloride as a brown waxy solid.

In a separate flask cooled in a Dry Ice-acetone bath, *n*-BuLi (21.5 mL of a 2.40 M solution in hexanes, 51.5 mmol, 0.95 eq) was added to a suspension of methacrylamide (4.47 g, 51.5 mmol, 0.95 eq) in tetrahydrofuran (250 mL), and stirring continued for further 4 h at 23 °C. Then the acid chloride synthesized above was slowly added to the flask as a solution in tetrahydrofuran (50 mL). The resultant mixture was stirred overnight at 23 °C, and then partitioned between EtOAc (500 mL) and saturated NH_4Cl/water (400:100 mL). The organic layer was separated and washed sequentially with saturated $NaHCO_3$/water (200:200 mL) and brine (300 mL). Then it was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel using a mobile phase gradient of 0 – 20%

EtOAc/hexanes, followed by a gradient of 15 – 20% EtOAc/hexanes containing 2% triethylamine additive. The isolated pale-yellow solid was then further purified by recrystallization in dichloromethane/hexanes to yield the *N*-methacryloylacrylamide ***E*-SI-4** as a white solid (4.04, 11.8 mmol, 23%). Melting point 146.2 – 146.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.88 (s, 1H), 7.30 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.23 (t, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 5.40 (q, *J* = 1.6 Hz, 1H), 5.32 (d, *J* = 1.1 Hz, 1H), 1.83 (t, *J* = 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 164.1, 163.2 (d, *J* = 250.8 Hz), 140.1, 140.0, 135.8, 133.2, 132.6, 131.9, 131.8 (d, *J* = 8.1 Hz), 130.7 (d, *J* = 3.8 Hz), 128.9, 121.9, 117.6 (d, *J* = 21.6 Hz), 18.2; HRMS m/z calcd. for $C_{19}H_{16}ClFNO_2$ $[M+H]^+$ 344.0848, found 344.0830; Analytical HPLC t_R = 4.26 min.

(*Z*)-3-(4-Chlorophenyl)-2-(4-fluorophenyl)-*N*-methacryloylacrylamide (*Z*-SI-4)

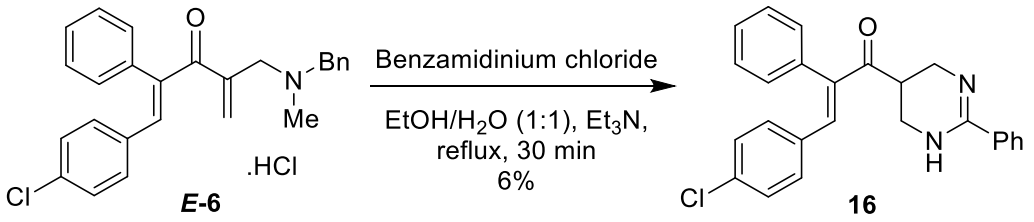
The *Z*-isomer (***Z*-SI-4**) can be isolated from the same reaction chromatographed above that gave ***E*-SI-4**. Off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 7.48 (dd, *J* = 8.9, 5.2 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.08 (t, *J* = 8.7 Hz, 2H), 6.88 (s, 1H), 5.48 (q, *J* = 1.6 Hz, 1H), 5.46 (q, *J* = 1.0 Hz, 1H), 1.83 (dd, *J* = 1.6, 0.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 165.1, 163.1 (d, *J* = 248.6 Hz), 139.3, 137.3, 134.5, 133.9, 132.4 (d, *J* = 3.4 Hz), 129.7, 129.1, 128.62, 128.61 (d, *J* = 8.1 Hz), 123.1, 116.0 (d, *J* = 21.7 Hz), 18.2; HRMS m/z calcd. for $C_{19}H_{16}ClFNO_2$ $[M+H]^+$ 344.0848, found 344.0845.



***E*-6** **15**

(*E*)-4-((Benzylthio)methyl)-1-(4-chlorophenyl)-2-phenylpenta-1,4-dien-3-one (**15**)

To a solution of the hydrochloride ***E*-6** (60.0 mg, 0.14 mmol, 1.0 eq) in DCM (1.5 mL) was added a 1.0 M solution of benzyl mercaptan in DCM (0.08 mL, 82.0 µmol, 0.6 eq), and the solution stirred at 23 °C for 3 h. Then the volatiles were removed in vacuo, and the residue passed through silica gel (0 to 8% EtOAc/hexanes). After concentrating the product containing fractions, it was purified by preparative scale TLC on silica gel using a mobile phase of 50% DCM/hexanes to give compound **15** (28.2 mg, 69.6 µmol, 85%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 3H), 7.32 – 7.29 (m, 4H), 7.25 – 7.19 (m, 4H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 5.80 (d, *J* = 0.7 Hz, 1H), 5.72 (q, *J* = 1.0 Hz, 1H), 3.66 (s, 2H), 3.37 (d, *J* = 1.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 144.5, 141.3, 138.0, 137.8, 136.1, 134.9, 133.4, 131.7, 129.6, 129.2, 129.1, 128.69, 128.67, 128.3, 127.3, 125.5, 36.3, 32.7; HRMS m/z calcd. for $C_{25}H_{22}ClOS$ $[M+H]^+$ 405.1074, found 405.1054.



(*E*)-3-(4-Chlorophenyl)-2-phenyl-1-(2-phenyl-1,4,5,6-tetrahydropyrimidin-5-yl)prop-2-en-1-one (**16**)

Benzamidinium chloride (hydrate, 35.4 mg, 0.22 mmol, 1.0 eq) and the diaryldienone hydrochloride ***E*-6** (96.2 mg, 0.22 mmol, 1.0 eq) were dissolved in to a 1:1 mixture of EtOH/H_2O (3 mL). To this was added triethylamine (0.13 mL, 0.93 mmol, 4.2 eq) and the mixture heated at reflux for 30 min. After cooling the reaction mixture back to 23 °C volatiles were removed in vacuo and the residue partitioned between DCM and 10% aq. Na_2CO_3 (4 mL each). The aqueous layer was extracted with further DCM (2 mL × 2). The combined organic layers were washed

with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by preparative scale TLC using a mobile phase of MeOH: DCM:triethyamine (5:95:2). Thus obtained white solid was suspended in chloroform (1 mL), filtered, and volatiles removed in vacuo to yield the tetrahydropyrimidinyl derivative **16** (5.7 mg, 14.2 µmol, 6%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.59 (s, 1H), 7.45 – 7.31 (m, 6H), 7.19 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.64 (dd, *J* = 13.0, 4.6 Hz, 2H), 3.57 (dd, *J* = 13.4, 9.6 Hz, 2H), 3.26 (tt, *J* = 9.5, 4.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.7, 154.5, 140.8, 137.9, 136.13, 136.09, 135.5, 133.1, 132.2, 130.2, 129.6, 129.5, 128.7, 128.60, 128.58, 126.3, 45.0, 39.2; HRMS m/z calcd. for $C_{25}H_{22}ClN_2O$ $[M+H]^+$ 401.1415, found 401.1399.

Crystal Structures

X-ray Single Crystal Analysis

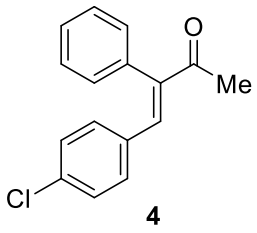
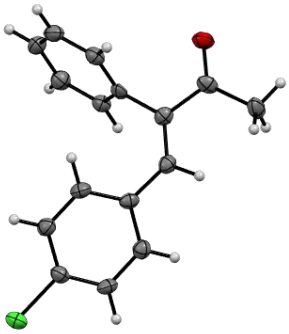
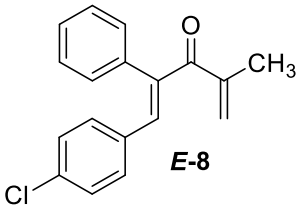
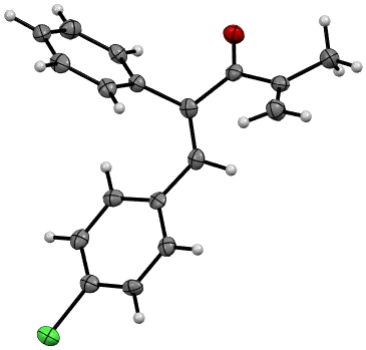
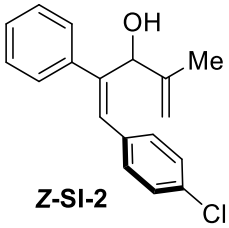
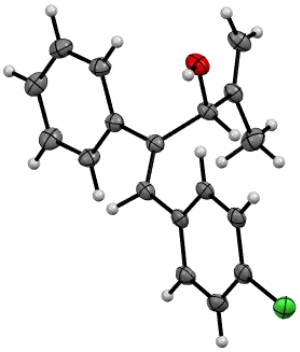
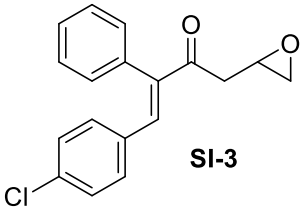
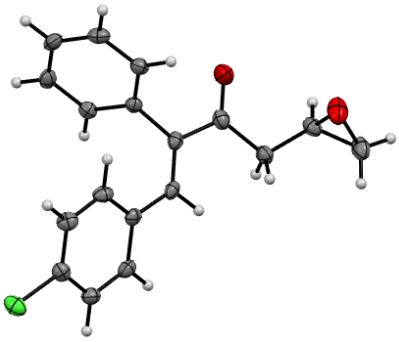
In a typical experiment, a selected crystal of the compound was mounted on a Bruker dual source (micro-focus Cu and Mo) single crystal x-ray diffractometer with Apex-11 detector. The diffraction data were measured at 100(2) K.

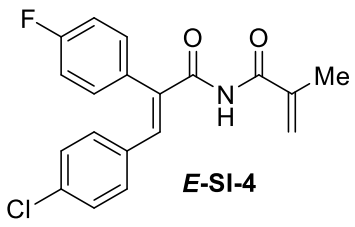
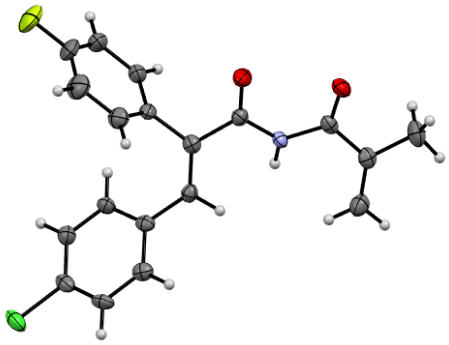
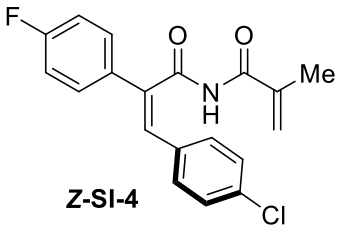
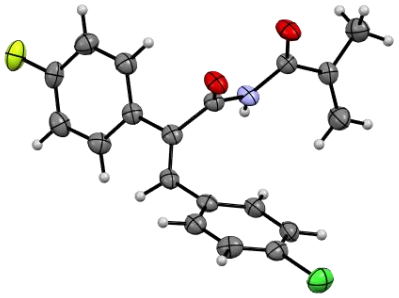
The structures were solved and refined using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions. The deposition numbers (Cambridge structural database) and selected crystallographic parameters for all the compounds are compiled in **Table S2**, and the corresponding crystal structures tabulated in **Table S3**.

Table S2. Single-Crystal X-ray Diffraction Parameters and Crystal Data.

	4	***E*-8**	***Z*-SI-2**	**SI-3**	***E*-SI-4**	***Z*-SI-4**
Deposition Number	CCDC 1896680	CCDC 1896679	CCDC 1896681	CCDC 1896682	CCDC 1896684	CCDC 1896683
Formula	$C_{16}H_{13}ClO$	$C_{18}H_{15}ClO$	$C_{18}H_{17}ClO$	$C_{18}H_{15}ClO_2$	$C_{19}H_{15}ClFNO_2$	$C_{19}H_{15}ClFNO_2$
FW	256.71	282.75	284.76	298.77	343.78	343.78
Crystal System	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P $2_1/n$	P $2_1/c$	$P\bar{1}$	P $2_1/n$	P $2_1/c$	P $2_1/c$
a (Å)	5.9388(3)	5.8817(6)	14.2826(6)	5.76710(10)	8.5700(13)	8.7741(2)
b (Å)	22.8069(11)	28.002(3)	15.7328(6)	8.3553(2)	26.883(4)	17.0251(4)
c (Å)	9.7824(5)	8.7384(8)	15.9073(6)	30.0196(7)	8.6441(14)	22.6707(5)
α (º)	90	90	105.171(2)	90	90	90
β (º)	105.541(3)	97.955(6)	91.882(3)	94.7320(10)	104.374(11)	91.4711(17)
γ (º)	90	90	114.330(2)	90	90	90
V ($Å^3$)	1276.5(1)	1425.4(2)	3103.0(2)	1441.59	1929.15	3385.43
Z	Z: 4 Z': 0	Z: 4 Z': 0	Z: 8 Z': 0	Z: 4 Z': 0	Z: 4 Z': 0	Z: 8 Z': 0
R-Factor (%)	5.63	7.58	5.16	4.3	5.8	4.11

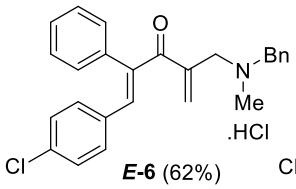
Table S3. Crystal structures for the compounds **4**, ***E*-8**, ***Z*-SI-2**, **SI-3**, and **SI-4** (*E*/*Z*).

Compound	Crystal Structure
 **4**	
 ***E*-8**	
 ***Z*-SI-2**	
 **SI-3**	

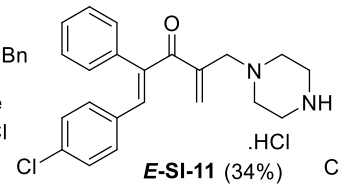
 ***E*-SI-4**	
 ***Z*-SI-4**	

Substrate scope for β-amino diaryldienone synthesis

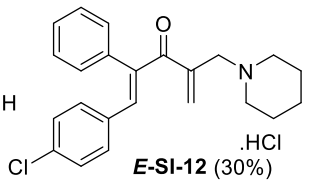
*All compounds synthesized (from the corresponding methyl ketones)[10, 11] and purified according to the general procedure outlined for ***E*-6** and ***Z*-6**. Unless otherwise specified, all are white to off-white solids isolated as the hydrochloride salt.



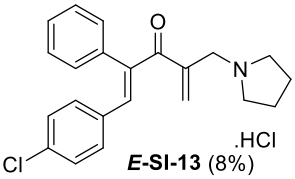
***E*-6** (62%)
***Z*-6** (18%)



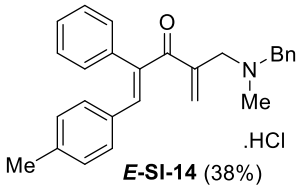
***E*-SI-11** (34%)



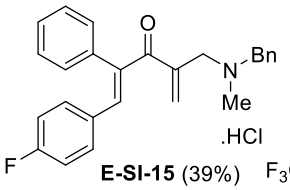
***E*-SI-12** (30%)
***Z*-SI-12** (3%)



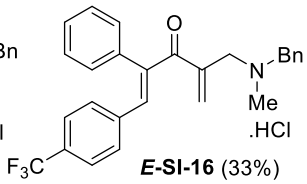
***E*-SI-13** (8%)



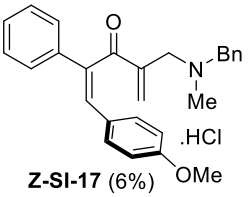
***E*-SI-14** (38%)
***Z*-SI-14** (18%)



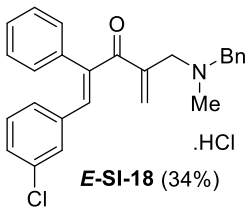
E-SI-15 (39%)
Z-SI-15 (20%)



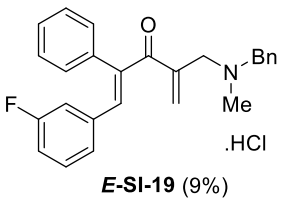
***E*-SI-16** (33%)
***Z*-SI-16** (10%)



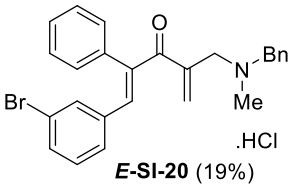
Z-SI-17 (6%)



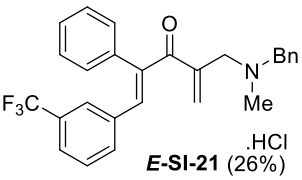
***E*-SI-18** (34%)



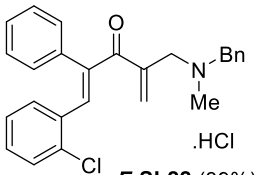
***E*-SI-19** (9%)



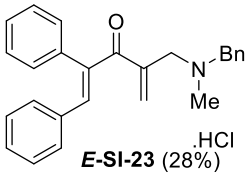
***E*-SI-20** (19%)
***Z*-SI-20** (7%)



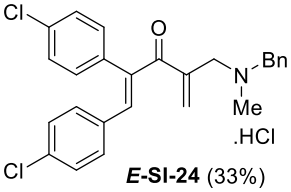
***E*-SI-21** (26%)
***Z*-SI-21** (7%)



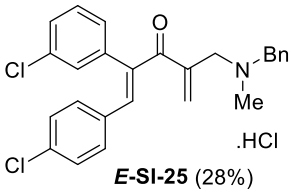
***E*-SI-22** (39%)



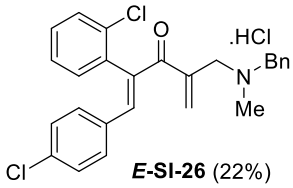
***E*-SI-23** (28%)
***Z*-SI-23** (11%)



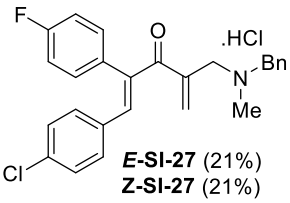
***E*-SI-24** (33%)



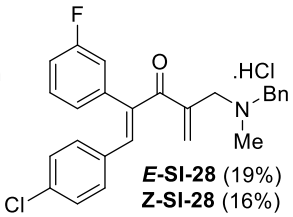
***E*-SI-25** (28%)



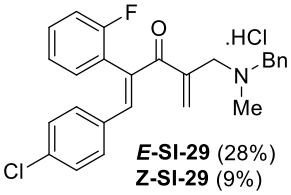
***E*-SI-26** (22%)



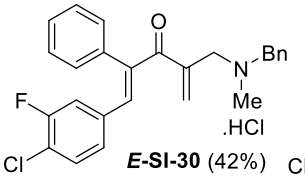
***E*-SI-27** (21%)
***Z*-SI-27** (21%)



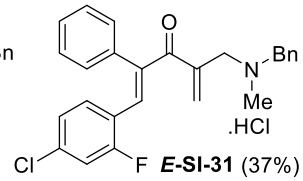
***E*-SI-28** (19%)
***Z*-SI-28** (16%)



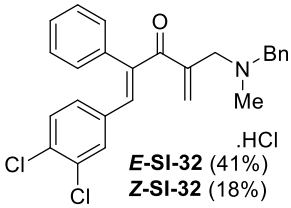
***E*-SI-29** (28%)
***Z*-SI-29** (9%)



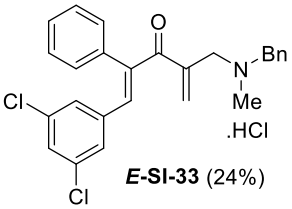
***E*-SI-30** (42%)



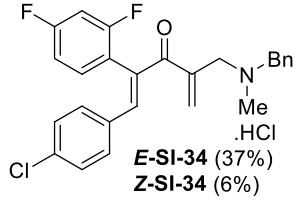
***E*-SI-31** (37%)



***E*-SI-32** (41%)
***Z*-SI-32** (18%)



***E*-SI-33** (24%)



***E*-SI-34** (37%)
***Z*-SI-34** (6%)

**Lack of *Z* isomer yields for some compounds in this figure does not necessarily represent lack of *Z* isomer formation.

Characterization data for β-amino diaryldienones

Compound	NMR data[1] and melting points[2]	Formula[3] m/z (calc.)	m/z (meas.)
***E*-6**	^{1}H NMR δ 12.76 (m, 1H), 7.69 – 7.63 (m, 2H), 7.47 – 7.43 (m, 3H), 7.40 (s, 1H), 7.39 – 7.35 (m, 3H), 7.18 – 7.13 (m, 4H), 7.12 (s, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.59 (s, 1H), 4.28 (dd, *J* = 13.1, 4.9 Hz, 1H), 4.19 (dd, *J* = 13.1, 5.5 Hz, 1H), 4.00 (dd, *J* = 13.1, 4.5 Hz, 1H), 3.93 (dd, *J* = 13.1, 6.8 Hz, 1sH), 2.65 (d, *J* = 4.9 Hz, 3H); ^{13}C NMR δ 196.8, 139.8, 139.5, 138.4, 136.6, 135.62, 135.55, 132.6, 132.0, 131.5, 130.4, 129.6, 129.4, 129.3, 128.8, 128.7, 128.5, 60.4, 53.9, 39.7; Melting point 165.8 – 166.0 °C.	$C_{26}H_{25}ClNO$ 402.1619	402.1610
***Z*-6**	^{1}H NMR δ 12.63 (m, 1H), 7.63 – 7.57 (m, 2H), 7.48 – 7.43 (m, 3H), 7.41 – 7.31 (m, 6H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.10 (m, 3H), 6.72 (s, 1H), 4.16 (dd, *J* = 13.1, 4.3 Hz, 1H), 4.01 (dd, *J* = 13.0, 5.7 Hz, 1H), 3.92 – 3.85 (m, 2H), 2.47 (d, *J* = 4.3 Hz, 3H); ^{13}C NMR δ 199.5, 141.8, 140.7, 137.01, 136.98, 134.7, 134.2, 131.4, 130.4, 130.1, 129.9, 129.6, 129.3, 129.1 (2C), 128.3, 126.2, 60.1, 51.4, 39.1; Melting point 162.0 – 162.3 °C.	$C_{26}H_{25}ClNO$ 402.1619	402.1613
***E*-SI-11**	^{1}H NMR δ 13.18 (m, 1H), 7.42 – 7.35 (m, 3H), 7.33 (s, 1H), 7.25 (s, 1H), 7.19 – 7.14 (m, 4H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.65 (s, 1H), 4.29 (t, *J* = 12.1 Hz, 2H), 3.96 (s, 2H), 3.95 (d, *J* = 12.2 Hz, 2H), 3.36 (d, *J* = 12.2 Hz, 2H), 3.03 – 2.92 (m, 2H); ^{13}C NMR δ 196.7, 139.5, 139.4 (2C), 135.7, 135.6, 135.5, 132.5, 131.9, 129.4, 129.2, 128.8, 128.8, (one low-field carbon is overlapped), 63.7, 55.7, 52.1; Melting point 171.5 – 172.1 °C.	$[M-H]^-$ $C_{22}H_{22}ClN_2O$ 365.1426	365.1175
***E*-SI-12**	^{1}H NMR δ 12.22 (m, 1H), 7.40 - 7.34 (m, 3H), 7.31 (s, 1H), 7.28 (s, 1H), 7.19 – 7.13 (m, 4H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.64 (s, 1H), 3.92 (d, *J* = 5.3 Hz, 2H), 3.46 (br d, *J* = 12.1 Hz, 2H), 2.76 – 2.65 (m, 2H), 2.35 – 2.22 (m, 2H), 1.92 – 1.79 (m, 3H), 1.46 – 1.34 (m, 1H); ^{13}C NMR δ 196.9, 139.5, 139.3, 139.0, 136.1, 135.6, 135.5, 132.6, 131.9, 129.3, 129.2, 128.8, 128.7, 55.1, 53.4, 22.7, 22.2.	$C_{23}H_{25}ClNO$ 366.1619	366.1608
***Z*-SI-12**	^{1}H NMR δ 12.09 (m, 1H), 7.42 (s, 1H), 7.40 – 7.35 (m, 3H), 7.33 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.16 – 7.11 (m, 3H), 6.71 (s, 1H), 3.83 (d, *J* = 5.8 Hz, 2H), 3.20 (d, *J* = 11.7 Hz, 2H), 2.54	$C_{23}H_{25}ClNO$ 366.1619	366.1608

	(tdd, *J* = 12.3, 8.9, 2.9 Hz, 2H), 2.24 – 2.12 (m, 2H), 1.81 – 1.72 (m, 2H), 1.45 – 1.31 (m, 2H); ^{13}C NMR δ 199.5, 142.3, 140.9, 136.9, 136.7, 134.6, 134.4, 130.0, 129.8, 129.3, 129.1, 129.0, 126.2, 53.1, 52.3, 22.6, 22.1.		
***E*-SI-13**	^{1}H NMR δ 12.55 (m, 1H), 7.42 – 7.33 (m, 3H), 7.35 – 7.31 (m, 3H), 7.29 – 7.26 (m, 2H), 7.15 – 7.11 (m, 3H), 6.63 (d, *J* = 0.9 Hz, 1H), 3.93 (d, *J* = 5.7 Hz, 2H), 3.57 – 3.49 (m, 2H), 2.78 – 2.65 (m, 2H), 2.22 – 2.12 (m, 2H), 2.09 – 1.99 (m, 2H); ^{13}C NMR δ 199.6, 140.8, 140.2, 137.9, 137.0, 134.6, 134.4, 130.1, 129.9, 129.3, 129.10, 129.07, 126.2, 53.5, 50.8, 23.4.	$C_{22}H_{23}ClNO$ 352.1463	352.1442
***E*-SI-14**	^{1}H NMR δ 12.68 (m, 1H), 7.69 – 7.63 (m, 2H), 7.47 – 7.42 (m, 4H), 7.41 – 7.32 (m, 3H), 7.20 – 7.15 (m, 2H), 7.13 (s, 1H), 6.98 (s, 4H), 6.58 (s, 1H), 4.30 (dd, *J* = 13.2, 4.4 Hz, 1H), 4.18 (dd, *J* = 13.1, 5.2 Hz, 1H), 4.00 (dd, *J* = 13.2, 4.2 Hz, 1H), 3.95 (dd, *J* = 12.9, 6.4 Hz, 1H), 2.65 (d, *J* = 4.2 Hz, 3H), 2.28 (s, 3H); ^{13}C NMR δ 197.0, 142.0, 140.3, 138.1, 137.7, 136.7, 136.2, 131.5, 131.2, 130.9, 130.3, 129.5, 129.4, 129.3, 129.2, 128.6, 128.4, 60.2, 54.1, 39.5, 21.5.	$C_{27}H_{28}NO$ 382.2165	382.2143
***Z*-SI-14**	^{1}H NMR δ 12.53 (m, 1H), 7.61 – 7.56 (m, 2H), 7.47 – 7.42 (m, 3H), 7.39 – 7.31 (m, 6H), 7.20 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 1H), 4.10 (dd, *J* = 13.0, 4.3 Hz, 1H), 3.95 – 3.89 (m, 3H), 2.46 (d, *J* = 4.6 Hz, 3H), 2.20 (s, 3H); ^{13}C NMR δ 200.1, 141.2, 139.2, 138.9, 137.4, 137.2, 133.0, 131.7, 131.4, 130.3, 129.6, 129.5, 129.2, 128.8, 128.6, 126.3, (one low-field carbon is overlapped), 59.8, 51.7, 39.2, 21.3.	$C_{27}H_{28}NO$ 382.2165	382.2144
***E*-SI-15**	^{1}H NMR δ 12.71 (m, 1H), 7.69 – 7.62 (m, 2H), 7.49 – 7.41 (m, 4H), 7.41 – 7.32 (m, 3H), 7.19 – 7.13 (m, 2H), 7.13 – 7.06 (m, 3H), 6.86 (t, *J* = 8.7 Hz, 2H), 6.57 (s, 1H), 4.29 (dd, *J* = 13.1, 3.8 Hz, 1H), 4.19 (dd, *J* = 13.0, 4.3 Hz, 1H), 4.00 (dd, *J* = 13.3, 3.3 Hz, 1H), 3.94 (dd, *J* = 13.0, 5.7 Hz, 1H), 2.65 (d, *J* = 3.1 Hz, 3H); ^{13}C NMR δ 196.8, 163.25 (d, *J* = 251.8 Hz), 140.4, 138.7 (d, *J* = 1.9 Hz), 138.0, 136.7, 135.7, 132.9 (d, *J* = 8.4 Hz), 131.5, 130.4, 130.31, 130.28, 129.6, 129.4, 129.3, 128.6, 115.7 (d, *J* = 21.6 Hz), 60.3, 54.1, 39.6.	$C_{26}H_{25}FNO$ 386.1915	386.1906
***Z*-SI-15**	Purity > 85%. ^{1}H NMR δ 12.59 (m, 1H), 7.63 – 7.56 (m, 2H), 7.48 – 7.42 (m, 3H), 7.41 – 7.30 (m, 6H), 7.20 – 7.15 (m, 2H), 7.14 (s, 1H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.73 (s, 1H), 4.17 (dd, *J* = 13.1, 4.0 Hz, 1H),	$C_{26}H_{25}FNO$ 386.1915	386.1905

	4.02 (dd, *J* = 13.1, 5.3 Hz, 1H), 3.95 – 3.85 (m, 2H), 2.46 (d, *J* = 3.9 Hz, 3H); ^{13}C NMR δ 199.6, 162.6 (d, *J* = 250.0 Hz), overlap of impurity peaks, 116.0 (d, *J* = 21.83 Hz), 60.1, 51.4, 39.0.		
***E*-SI-16**	^{1}H NMR δ 12.77 (m, 1H), 7.68 – 7.63 (m, 2H), 7.47 – 7.44 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.39 (s, 1H), 7.38 – 7.34 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.14 (m, 3H), 6.63 (s, 1H), 4.28 (d, *J* = 13.9 Hz, 1H), 4.20 (d, *J* = 14.0 Hz, 1H), 4.01 (d, *J* = 13.7 Hz, 1H), 3.94 (d, *J* = 13.2 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR δ 196.7, 141.1, 139.1, 138.3, 137.7, 136.6, 135.2, 131.5, 130.9 (q, *J* = 32.7 Hz), 130.7, 130.4, 129.6, 129.4, 129.2, 128.9, 128.5, 125.4 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.2 Hz), 60.4, 53.6, 39.7.	$C_{27}H_{25}F_3NO$ 436.1883	436.1860
***Z*-SI-16**	^{1}H NMR δ 12.68 (m, 1H), 7.61 – 7.56 (m, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.43 (m, 3H), 7.42 – 7.34 (m, 6H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (s, 1H), 6.73 (s, 1H), 4.14 (dd, *J* = 13.0, 4.5 Hz, 1H), 4.02 (dd, *J* = 13.0, 5.7 Hz, 1H), 3.93 – 3.84 (m, 2H), 2.44 (d, *J* = 4.7 Hz, 3H); ^{13}C NMR δ 199.0, 142.18, 142.15, 139.3, 137.0, 136.7, 131.4, 130.46, 130.46 (q, *J* = 32.8 Hz), 129.7, 129.6, 129.42, 129.41, 128.9, 128.2, 126.3, 125.8 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.3 Hz), 60.2, 51.3, 39.0.	$C_{27}H_{25}F_3NO$ 436.1883	436.1860
***Z*-SI-17**	^{1}H NMR δ 12.53 (m, 1H), 7.62 – 7.57 (m, 2H), 7.47 – 7.42 (m, 3H), 7.39 – 7.29 (m, 6H), 7.16 (s, 1H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.74 (s, 1H), 4.16 (dd, *J* = 13.0, 4.3 Hz, 1H), 4.00 – 3.91 (m, 3H), 3.70 (s, 3H), 2.49 (d, *J* = 4.7 Hz, 3H); ^{13}C NMR δ 200.3, 159.9, 141.1, 138.2, 137.6, 137.2, 131.4 (2C), 130.3, 130.1, 129.5, 129.2, 128.6, 128.5, 128.3, 126.2, 114.3, (one low-field carbon is overlapped), 59.9, 55.3, 51.7, 39.2.	$C_{27}H_{28}NO_2$ 398.2120	398.2110
***E*-SI-18**	^{1}H NMR δ 12.80 (m, 1H), 7.69 – 7.62 (m, 2H), 7.48 – 7.43 (m, 3H), 7.40 – 7.35 (m, 3H), 7.30 (s, 1H), 7.22 – 7.15 (m, 4H), 7.11 (t, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 1.9 Hz, 1H), 6.99 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.63 (s, 1H), 4.28 (dd, *J* = 13.2, 4.7 Hz, 1H), 4.18 (dd, *J* = 13.1, 5.3 Hz, 1H), 4.00 (dd, *J* = 13.2, 4.3 Hz, 1H), 3.93 (dd, *J* = 13.0, 6.7 Hz, 1H), 2.64 (d, *J* = 4.5 Hz, 3H); ^{13}C NMR δ 196.7, 140.3, 138.9, 138.8, 136.6, 136.0, 135.3, 134.4, 131.5, 130.4, 130.4, 129.7, 129.6, 129.5, 129.3, 129.2, 128.83, 128.76, 128.5, 60.3, 53.7, 39.6; Melting point 143.6 – 144.5 °C.	$C_{26}H_{25}ClNO$ 402.1619	402.1599
***E*-SI-19**	^{1}H NMR δ 12.76 (m, 1H), 7.68 – 7.63 (m, 2H), 7.48 – 7.43 (m, 3H), 7.40 – 7.33 (m, 4H), 7.20 – 7.14 (m,	$C_{26}H_{25}FNO$	386.1895

	4H), 6.94 (dd, *J* = 8.6, 2.4 Hz, 2H), 6.72 (dt, *J* = 10.2, 2.1 Hz, 1H), 6.63 (s, 1H), 4.29 (dd, *J* = 13.1, 4.8 Hz, 1H), 4.18 (dd, *J* = 13.1, 5.4 Hz, 1H), 4.00 (dd, *J* = 13.2, 4.4 Hz, 1H), 3.94 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.65 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR δ 196.8, 162.5 (q, *J* = 246.2 Hz), 140.1, 139.1 (q, *J* = 2.6 Hz), 138.8, 136.6, 136.3 (q, *J* = 7.8 Hz), 135.3, 131.5, 130.4, 130.0 (q, *J* = 8.4 Hz), 129.6, 129.4, 129.2, 128.8, 128.5, 126.8 (q, *J* = 2.9 Hz), 116.9 (q, *J* = 22.6 Hz), 116.6 (q, *J* = 21.4 Hz), 60.3, 53.7, 39.6.	386.1915	
***E*-SI-20**	^{1}H NMR δ 12.76 (m, 1H), 7.68 – 7.62 (m, 2H), 7.49 – 7.41 (m, 3H), 7.41 – 7.32 (m, 4H), 7.29 (s, 1H), 7.21 (d, *J* = 1.7 Hz, 1H), 7.19 – 7.13 (m, 3H), 7.08 – 6.99 (m, 2H), 6.62 (s, 1H), 4.28 (dd, *J* = 13.1, 4.6 Hz, 1H), 4.19 (dd, *J* = 13.0, 5.2 Hz, 1H), 4.00 (dd, *J* = 13.2, 4.2 Hz, 1H), 3.94 (dd, *J* = 13.0, 6.6 Hz, 1H), 2.64 (d, *J* = 4.4 Hz, 3H); ^{13}C NMR δ 196.7, 140.3, 138.9, 138.7, 136.6, 136.2, 135.3, 133.3, 132.4, 131.5, 130.4, 130.0, 129.6, 129.3, 129.2, 129.1, 128.8, 128.5, 122.5, 60.3, 53.7, 39.6.	$C_{26}H_{25}BrNO$ 446.1114	446.1118
***Z*-SI-20**	^{1}H NMR δ 12.64 (m, 1H), 7.65 – 7.59 (m, 2H), 7.48 – 7.43 (m, 3H), 7.42 – 7.35 (m, 4H), 7.35 – 7.30 (m, 4H), 7.18 – 7.14 (m, 2H), 7.12 (s, 1H), 6.69 (s, 1H), 4.16 (dd, *J* = 13.0, 4.6 Hz, 1H), 4.04 (dd, *J* = 13.0, 5.8 Hz, 1H), 3.98 – 3.85 (m, 2H), 2.49 (d, *J* = 4.9 Hz, 3H); ^{13}C NMR δ 199.4, 141.4, 141.3, 137.9, 137.2, 136.9, 131.6, 131.5, 131.1, 130.6, 130.4, 129.6, 129.6, 129.3, 129.2, 128.4, 127.4, 126.3, 122.9, 60.3, 51.5, 39.1.	$C_{26}H_{25}BrNO$ 446.1114	446.1118
***E*-SI-21**	^{1}H NMR δ 12.80 (m, 1H), 7.69 – 7.64 (m, 2H), 7.49 – 7.43 (m, 4H), 7.39 (s, 1H), 7.38 – 7.36 (m, 3H), 7.32 – 7.29 (m, 3H), 7.19 – 7.15 (m, 3H), 6.64 (s, 1H), 4.29 (dd, *J* = 13.1, 4.6 Hz, 1H), 4.20 (dd, *J* = 13.1, 5.2 Hz, 1H), 4.01 (dd, *J* = 13.2, 4.1 Hz, 1H), 3.94 (dd, *J* = 13.1, 6.7 Hz, 1H), 2.65 (d, *J* = 4.4 Hz, 3H); ^{13}C NMR δ 196.6, 140.7, 139.0, 138.4, 136.6, 135.1, 135.0, 133.8, 131.5, 130.9 (q, *J* = 32.4 Hz), 130.4, 129.6, 129.4, 129.1, 129.0, 128.9, 128.5, 127.1 (q, *J* = 3.9 Hz), 125.9 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 272.4 Hz), 60.4, 53.7, 39.6; Melting point 136.4 – 136.9 °C.	$C_{27}H_{25}F_3NO$ 436.1883	436.1884
***Z*-SI-21**	^{1}H NMR δ 12.65 (m, 1H), 7.64 – 7.58 (m, 2H), 7.51 – 7.33 (m, 13H), 7.18 (s, 1H), 6.70 (s, 1H), 4.16 (dd, *J* = 13.0, 4.6 Hz, 1H), 4.05 (dd, *J* = 13.0, 5.7 Hz, 1H), 3.88 (dd, *J* = 13.4, 7.0 Hz, 1H), 3.83 (dd, *J* = 13.4, 4.8 Hz, 1H), 2.46 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR	$C_{27}H_{25}F_3NO$ 436.1883	436.1859

	δ 199.4, 141.8, 141.7, 137.1, 136.8, 136.5, 132.0, 131.5, 131.2 (q, *J* = 32.4 Hz), 130.4, 129.7, 129.58, 129.56, 129.4, 129.3, 128.3, 126.3, 125.2 (q, *J* = 3.7 Hz), 125.0 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.6 Hz), 60.3, 51.3, 38.9.		
***E*-SI-22**	^{1}H NMR δ 12.78 (m, 1H), 7.68 – 7.63 (m, 2H), 7.47 – 7.43 (m, 3H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.33 (s, 1H), 7.30 – 7.27 (m, 3H), 7.19 – 7.11 (m, 3H), 6.94 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.79 (s, 1H), 4.31 (dd, *J* = 13.1, 4.6 Hz, 1H), 4.16 (dd, *J* = 13.1, 5.6 Hz, 1H), 4.03 (dd, *J* = 13.2, 4.6 Hz, 1H), 3.98 (dd, *J* = 13.1, 6.5 Hz, 1H), 2.64 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR δ 196.8, 140.7, 139.9, 136.6, 135.9, 134.8, 134.8, 133.2, 131.5, 131.1, 130.4, 130.1, 129.7, 129.6, 129.4, 129.0, 128.6, 128.5, 126.5, 60.1, 53.2, 39.2; Melting point 155.7 – 156.5 °C.	$C_{26}H_{25}ClNO$ 402.1619	402.1600
***E*-SI-23**	^{1}H NMR δ 12.72 (m, 1H), 7.69 – 7.62 (m, 2H), 7.47 – 7.42 (m, 3H), 7.41 (s, 1H), 7.39 – 7.33 (m, 3H), 7.25 – 7.21 (m, 1H), 7.21 – 7.14 (m, 5H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.62 (s, 1H), 4.30 (dd, *J* = 13.1, 4.4 Hz, 1H), 4.18 (dd, *J* = 13.1, 5.3 Hz, 1H), 4.01 (dd, *J* = 13.1, 4.2 Hz, 1H), 3.95 (dd, *J* = 13.1, 6.5 Hz, 1H), 2.65 (d, *J* = 4.3 Hz, 3H); ^{13}C NMR δ 197.0, 141.2, 139.0, 138.2, 136.7, 135.9, 134.1, 131.5, 130.8, 130.3, 129.7, 129.6, 129.4, 129.2, 128.54, 128.52, 128.49, 60.2, 53.9, 39.5.	$C_{26}H_{26}NO$ 368.2009	368.1998
***Z*-SI-23**	Purity > 88%. ^{1}H NMR δ 12.55 (m, 1H), 7.62 – 7.57 (m, 2H), 7.46 – 7.42 (m, 3H), 7.40 – 7.30 (m, 7H), 7.25 – 7.14 (m, 5H), 6.72 (s, 1H), 4.14 (dd, *J* = 13.1, 4.5 Hz, 1H), 3.97 (dd, *J* = 13.0, 5.9 Hz, 1H), 3.93 – 3.84 (m, 2H), 2.41 (d, *J* = 4.7 Hz, 3H); ^{13}C NMR δ 199.8, impurity overlap in the aromatic region, 60.0, 51.5, 39.0.	$C_{26}H_{26}NO$ 368.2009	368.1998
***E*-SI-24**	^{1}H NMR δ 12.79 (m, 1H), 7.68 – 7.64 (m, 2H), 7.49 (s, 1H), 7.47 – 7.44 (m, 3H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.09 (s, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.56 (s, 1H), 4.28 (dd, *J* = 13.2, 4.4 Hz, 1H), 4.21 (dd, *J* = 13.0, 4.7 Hz, 1H), 4.01 (dd, *J* = 13.1, 3.6 Hz, 1H), 3.92 (dd, *J* = 13.0, 6.6 Hz, 1H), 2.66 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR δ 196.4, 140.9, 138.2, 138.1, 136.7, 136.0, 134.8, 133.9, 132.3, 132.0, 131.5, 130.9, 130.4, 129.60, 129.58, 129.0, 128.4, 60.5, 54.0, 39.8; Melting point 148.6 – 149.2 °C;	$C_{26}H_{24}Cl_2NO$ 436.1230	436.1200

***E*-SI-25**	^{1}H NMR δ 12.80 (m, 1H), 7.68 – 7.63 (m, 2H), 7.51 (s, 1H), 7.48 – 7.44 (m, 3H), 7.37 – 7.29 (m, 3H), 7.21 – 7.16 (m, 3H), 7.10 (s, 1H), 7.08 – 7.03 (m, 3H), 6.57 (s, 1H), 4.28 (dd, *J* = 13.3, 4.3 Hz, 1H), 4.21 (dd, *J* = 13.1, 4.8 Hz, 1H), 4.01 (dd, *J* = 13.1, 3.7 Hz, 1H), 3.93 (dd, *J* = 13.0, 6.4 Hz, 1H), 2.67 (d, *J* = 3.9 Hz, 3H); ^{13}C NMR δ 196.2, 141.2, 138.2, 137.8, 137.3, 136.6, 136.1, 135.1, 132.1, 132.0, 131.5, 130.6, 130.4, 129.6, 129.4, 129.0, 128.9, 128.4, 127.7, 60.5, 54.0, 39.8; Melting point 143.6 – 143.8 °C.	$C_{26}H_{24}Cl_2NO$ 436.1230	436.1200
***E*-SI-26**	^{1}H NMR δ 12.71 (m, 1H), 7.69 (s, 1H), 7.68 – 7.63 (m, 2H), 7.48 – 7.42 (m, 4H), 7.35 (td, *J* = 7.7, 1.7 Hz, 1H), 7.26 (td, *J* = 7.5, 1.3 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.10 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.63 (s, 1H), 4.29 (br s, 1H), 4.22 (br s, 1H), 3.99 (br s, 2H), 2.67 (s, 3H); ^{13}C NMR δ 195.8, 143.1, 137.9, 137.2, 136.3, 136.2, 135.3, 133.6, 132.3, 131.9, 131.8, 131.5, 130.29, 130.25, 130.1, 129.5, 128.9, 128.6, 127.7, 60.3, 54.3, 39.7; Melting point 194.3 – 194.6 °C.	$C_{26}H_{24}Cl_2NO$ 436.1230	436.1203
***E*-SI-27**	^{1}H NMR δ 12.91 – 12.74 (m, 1H), 7.70 – 7.64 (m, 2H), 7.49 – 7.44 (m, 4H), 7.20 – 7.12 (m, 4H), 7.11 – 7.03 (m, 5H), 6.58 (s, 1H), 4.28 (dd, *J* = 13.1, 4.8 Hz, 1H), 4.21 (dd, *J* = 13.1, 5.3 Hz, 1H), 4.01 (dd, *J* = 13.1, 4.2 Hz, 1H), 3.92 (dd, *J* = 13.0, 6.9 Hz, 1H), 2.66 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR δ 196.7, 162.8 (d, *J* = 248.9 Hz), 140.8, 138.3, 138.2, 136.7, 135.9, 132.4, 132.0, 131.5, 131.4 (d, *J* = 3.4 Hz), 131.3 (d, *J* = 8.1 Hz), 130.5, 129.6, 128.9, 128.4, 116.5 (d, *J* = 21.7 Hz), 60.5, 54.1, 39.8; Melting point 160.6 – 160.8 °C.	$C_{26}H_{24}ClFNO$ 420.1525	420.1519
***Z*-SI-27**	^{1}H NMR δ 12.77 – 12.55 (m, 1H), 7.63 – 7.57 (m, 2H), 7.49 – 7.43 (m, 3H), 7.37 (s, 1H), 7.32 (dd, *J* = 8.5, 5.1 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.04 (m, 5H), 6.70 (s, 1H), 4.14 (dd, *J* = 13.0, 4.4 Hz, 1H), 4.02 (dd, *J* = 13.0, 5.7 Hz, 1H), 3.87 (d, *J* = 5.6 Hz, 2H), 2.47 (d, *J* = 4.6 Hz, 3H); ^{13}C NMR δ 199.3, 163.2 (d, *J* = 250.0 Hz), 141.7, 139.6, 137.0, 134.8, 134.1, 133.1 (d, *J* = 3.4 Hz), 131.5, 130.5, 130.2, 129.9, 129.6, 129.2, 128.3, 128.2 (d, *J* = 8.4 Hz), 116.4 (d, *J* = 21.8 Hz), 60.2, 51.5, 39.2.	$C_{26}H_{24}ClFNO$ 420.1525	420.1520
***E*-SI-28**	^{1}H NMR δ 12.90 – 12.72 (m, 1H), 7.69 – 7.64 (m, 2H), 7.50 (s, 1H), 7.47 – 7.43 (m, 3H), 7.35 (td, *J* = 8.0, 5.9 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 7.6 Hz,	$C_{26}H_{24}ClFNO$ 420.1525	420.1520

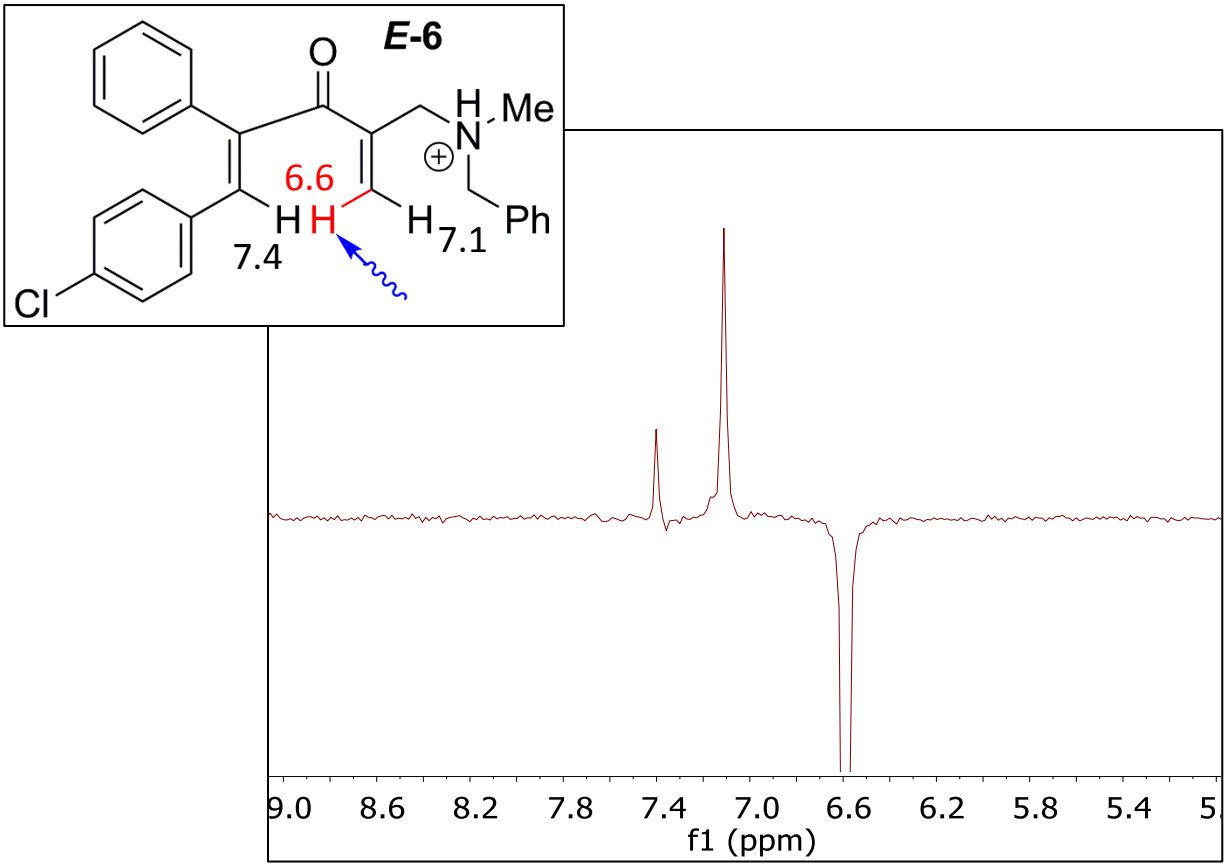
	2H), 6.90 (dt, *J* = 9.3, 2.0 Hz, 1H), 6.58 (s, 1H), 4.28 (dd, *J* = 13.1, 5.0 Hz, 1H), 4.21 (dd, *J* = 13.1, 5.3 Hz, 1H), 4.01 (dd, *J* = 13.1, 4.2 Hz, 1H), 3.93 (dd, *J* = 13.1, 6.9 Hz, 1H), 2.66 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR δ 196.2, 163.2 (d, *J* = 248.0 Hz), 141.0, 138.3, 138.0 (d, *J* = 1.9 Hz), 137.6 (d, *J* = 7.8 Hz), 136.6, 136.0, 132.2, 132.0, 131.5, 131.0 (d, *J* = 8.5 Hz), 130.5, 129.6, 129.0, 128.4, 125.2 (d, *J* = 3.1 Hz), 116.5 (d, *J* = 21.9 Hz), 115.7 (d, *J* = 20.9 Hz), 60.5, 54.0, 39.8.		
***Z*-SI-28**	^{1}H NMR δ 12.74 – 12.62 (m, 1H), 7.63 – 7.56 (m, 2H), 7.48 – 7.43 (m, 3H), 7.40 (s, 1H), 7.38 – 7.31 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.16 – 7.09 (m, 4H), 7.08 – 7.02 (m, 2H), 6.70 (s, 1H), 4.15 (dd, *J* = 13.0, 4.6 Hz, 1H), 4.02 (dd, *J* = 13.0, 5.8 Hz, 1H), 3.89 (d, *J* = 5.9 Hz, 2H), 2.47 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR δ 198.9, 163.2 (d, *J* = 247.6 Hz), 141.9, 139.4 (d, *J* = 2.3 Hz), 139.0 (d, *J* = 7.6 Hz), 137.0, 135.0, 133.8, 131.4, 131.1, 131.0 (d, *J* = 8.3 Hz), 130.5, 129.9, 129.6, 129.2, 128.3, 122.0 (d, *J* = 2.9 Hz), 116.1 (d, *J* = 21.3 Hz), 113.3 (d, *J* = 22.8 Hz), 60.2, 51.4, 39.1; Melting point 65.1 – 66.9 °C.	$C_{26}H_{24}ClFNO$ 420.1525	420.1521
***E*-SI-29**	^{1}H NMR δ 12.80 – 12.68 (m, 1H), 7.68 – 7.65 (m, 2H), 7.64 (s, 1H), 7.48 – 7.43 (m, 3H), 7.41 – 7.34 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.15 – 7.08 (m, 5H), 7.06 (s, 1H), 6.54 (s, 1H), 4.30 (dd, *J* = 13.1, 4.8 Hz, 1H), 4.19 (dd, *J* = 13.1, 5.5 Hz, 1H), 4.01 (dd, *J* = 13.1, 4.4 Hz, 1H), 3.95 (dd, *J* = 13.1, 6.8 Hz, 1H), 2.66 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR δ 195.9, 159.9 (d, *J* = 246.5 Hz), 142.8, 137.9, 136.3, 136.1, 133.6, 132.4, 131.7, 131.6 (d, *J* = 3.1 Hz), 131.5, 131.0 (d, *J* = 8.1 Hz), 130.4, 129.6, 129.0, 128.5, 125.0 (d, *J* = 3.5 Hz), 123.7 (d, *J* = 15.9 Hz), 116.4 (d, *J* = 21.5 Hz), 60.3, 54.2, 39.6; Melting point 173.2 – 173.8 °C.	$C_{26}H_{24}ClFNO$ 420.1525	420.1514
***Z*-SI-29**	^{1}H NMR δ 12.59 – 12.47 (m, 1H), 7.64 – 7.59 (m, 2H), 7.47 – 7.42 (m, 4H), 7.35 (tdd, *J* = 7.7, 5.3, 1.6 Hz, 1H), 7.28 (s, 1H), 7.26 – 7.22 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.10 – 7.01 (m, 3H), 6.71 (s, 1H), 4.26 (dd, *J* = 13.1, 4.4 Hz, 1H), 4.00 (dd, *J* = 13.1, 6.2 Hz, 1H), 3.85 (d, *J* = 5.8 Hz, 2H), 2.52 (d, *J* = 4.9 Hz, 3H); ^{13}C NMR δ 198.5, 159.6 (d, *J* = 248.0 Hz), 140.5, 136.4 (d, *J* = 1.4 Hz), 135.2 (d, *J* = 2.9 Hz), 134.7, 134.1, 131.5, 131.0 (d, *J* = 8.6 Hz), 130.3 (2C), 130.0, 129.9 (d, *J* = 3.2 Hz), 129.6, 129.2, 128.6, 126.1 (d, *J* = 13.3 Hz), 125.2 (d, *J* = 3.2 Hz), 116.3 (d, *J* = 22.1 Hz), 59.9, 52.0, 38.9.	$C_{26}H_{24}ClFNO$ 420.1525	420.1513

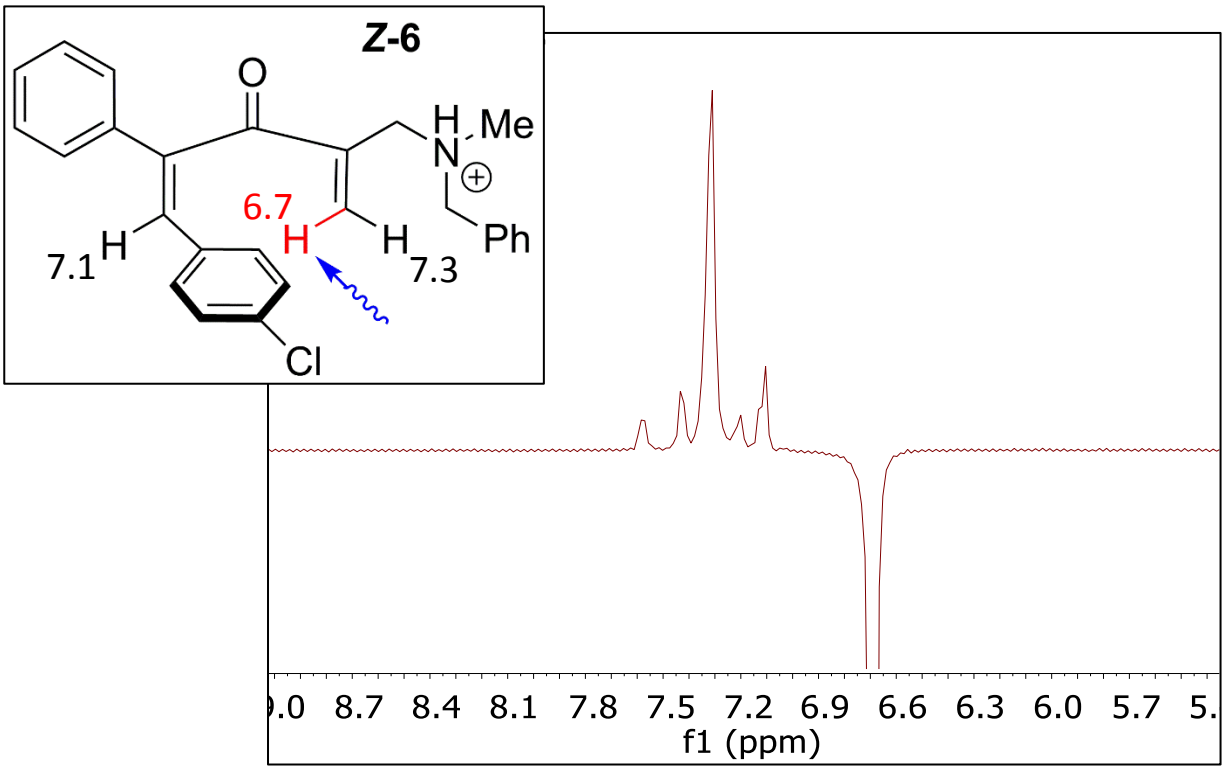
***E*-SI-30**	^{1}H NMR δ 12.76 (m, 1H), 7.70 – 7.62 (m, 2H), 7.47 – 7.43 (m, 3H), 7.40 – 7.37 (m, 3H), 7.35 (s, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.11 (s, 1H), 6.90 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.81 (dd, *J* = 10.4, 1.9 Hz, 1H), 6.59 (s, 1H), 4.23 (m, 2H), 3.96 (m, 2H), 2.64 (s, 3H); ^{13}C NMR δ 196.5, 157.8 (d, *J* = 249.3 Hz), 140.5, 138.8, 138.1, 136.6, 135.0, 134.7 (d, *J* = 7.1 Hz), 131.5, 130.7, 130.4, 129.6, 129.5, 129.1, 129.0, 128.5, 127.4 (d, *J* = 3.5 Hz), 122.3 (d, *J* = 17.8 Hz), 118.0 (d, *J* = 22.4 Hz), 60.4, 53.8, 39.8; Melting point 151.2 – 151.4 °C.	$C_{26}H_{24}ClFNO$ 420.1525	420.1514
***E*-SI-31**	^{1}H NMR δ 12.73 (m, 1H), 7.69 – 7.62 (m, 2H), 7.47 – 7.42 (m, 3H), 7.37 – 7.32 (m, 3H), 7.28 (d, *J* = 9.5 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.07 (dd, *J* = 9.9, 2.0 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.74 (t, *J* = 8.2 Hz, 1H), 6.65 (s, 1H), 4.29 (dd, *J* = 13.1, 4.7 Hz, 1H), 4.17 (dd, *J* = 13.1, 5.5 Hz, 1H), 4.01 (dd, *J* = 13.2, 4.5 Hz, 1H), 3.93 (dd, *J* = 13.1, 6.7 Hz, 1H), 2.64 (d, *J* = 4.7 Hz, 3H); ^{13}C NMR δ 196.5, 160.9 (d, *J* = 254.7 Hz), 141.2, 139.6, 136.5, 136.2 (d, *J* = 10.6 Hz), 135.1, 131.5, 131.2 (d, *J* = 3.1 Hz), 130.4, 130.1 (d, *J* = 4.6 Hz), 129.6, 129.3, 129.1, 128.9, 128.5, 124.5 (d, *J* = 3.5 Hz), 121.1 (d, *J* = 12.5 Hz), 116.7 (d, *J* = 25.4 Hz), 60.2, 53.3, 39.3; Melting point 167.8 – 168.0 °C.	$C_{26}H_{24}ClFNO$ 420.1525	420.1510
***E*-SI-32**	^{1}H NMR δ 12.77 (m, 1H), 7.68 – 7.62 (m, 2H), 7.48 – 7.41 (m, 3H), 7.41 – 7.34 (m, 3H), 7.31 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.14 (m, 3H), 7.12 (s, 1H), 6.92 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.59 (s, 1H), 4.27 (dd, *J* = 13.1, 4.7 Hz, 1H), 4.19 (dd, *J* = 13.1, 5.2 Hz, 1H), 4.00 (dd, *J* = 13.1, 4.1 Hz, 1H), 3.92 (dd, *J* = 13.0, 6.7 Hz, 1H), 2.65 (d, *J* = 4.6 Hz, 3H); ^{13}C NMR δ 196.5, 140.6, 138.9, 137.8, 136.6, 135.1, 134.2, 133.5, 132.7, 132.2, 131.5, 130.4, 130.4, 129.7, 129.6, 129.5, 129.1, 129.0, 128.4, 60.4, 53.7, 39.7.	$C_{26}H_{24}Cl_2NO$ 436.1230	436.1220
***Z*-SI-32**	^{1}H NMR δ 12.69 (m, 1H), 7.63 – 7.59 (m, 2H), 7.48 – 7.43 (m, 4H), 7.40 – 7.30 (m, 6H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.71 (s, 1H), 4.17 (dd, *J* = 13.1, 4.4 Hz, 1H), 4.05 (dd, *J* = 12.9, 5.7 Hz, 1H), 3.97 – 3.85 (m, 2H), 2.51 (d, *J* = 4.6 Hz, 3H); ^{13}C NMR δ 199.2, 142.0, 141.8, 137.0, 136.7, 135.6, 133.0, 132.9, 131.5, 131.0, 130.5, 130.0, 129.6, 129.4, 129.4, 128.6, 128.3, 128.0, 126.2, 60.3, 51.4, 39.1.	$C_{26}H_{24}Cl_2NO$ 436.1230	436.1219
***E*-SI-33**	^{1}H NMR δ 12.79 (m, 1H), 7.69 – 7.63 (m, 2H), 7.48 – 7.43 (m, 3H), 7.41 – 7.37 (m, 3H), 7.23 – 7.19 (m,	$C_{26}H_{24}Cl_2NO$	436.1232

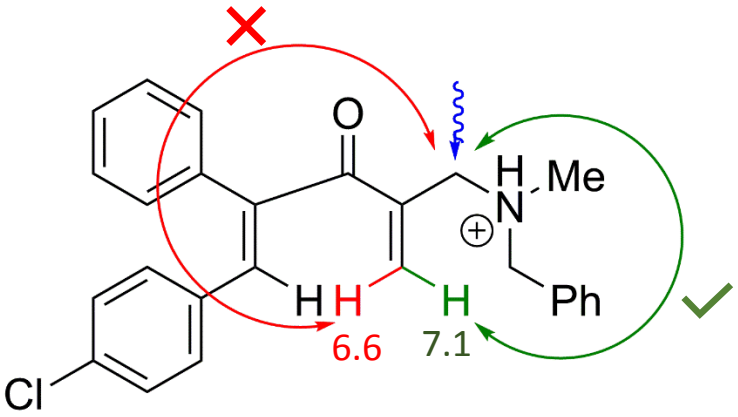
	2H), 7.19 – 7.13 (m, 3H), 6.95 (d, *J* = 1.8 Hz, 2H), 6.62 (s, 1H), 4.32 – 4.24 (m, 1H), 4.19 (dd, *J* = 13.4, 4.8 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.96 – 3.89 (m, 1H), 2.64 (d, *J* = 4.1 Hz, 3H); ^{13}C NMR δ 196.4, 141.5, 139.4, 137.2, 136.7, 136.5, 135.0, 134.7, 131.5, 130.4, 129.6, 129.5, 129.1, 129.0, 128.6 (one low-field carbon is overlapped), 128.4, 60.4, 53.5, 39.7.	436.1230	
***E*-SI-34**	^{1}H NMR δ 12.88 – 12.74 (m, 1H), 7.70 (s, 1H), 7.69 – 7.64 (m, 2H), 7.49 – 7.43 (m, 3H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.15 – 7.08 (m, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 7.05 (s, 1H), 6.92 – 6.84 (m, 2H), 6.54 (s, 1H), 4.29 (dd, *J* = 13.3, 4.4 Hz, 1H), 4.21 (dd, *J* = 13.2, 4.8 Hz, 1H), 4.02 (dd, *J* = 13.1, 3.6 Hz, 1H), 3.93 (dd, *J* = 13.1, 6.4 Hz, 1H), 2.67 (d, *J* = 3.9 Hz, 3H); ^{13}C NMR δ 195.9, 163.4 (dd, *J* = 251.67, 11.87 Hz), 160.1 (dd, *J* = 249.06, 11.99 Hz), 143.6, 137.9, 136.3, 132.6, 132.6 (dd, *J* = 9.52, 4.71 Hz), 132.2, 131.7, 131.5, 130.4, 129.6, 129.1, 128.5, one carbon overlapped, 119.7 (dd, *J* = 16.24, 4.11 Hz), 112.4 (dd, *J* = 21.38, 3.53 Hz), 104.9 (t, *J* = 25.50 Hz), 60.4, 54.3, 39.8; Melting point 65.8 – 66.9 °C.	$C_{26}H_{23}ClF_2NO$ 438.1431	438.1418
***Z*-SI-34**	^{1}H NMR δ 12.61 – 12.46 (m, 1H), 7.64 – 7.58 (m, 2H), 7.49 – 7.39 (m, 4H), 7.29 (s, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.20 (s, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.95 (ddd, *J* = 9.0, 6.5, 2.7 Hz, 1H), 6.81 (td, *J* = 9.8, 2.5 Hz, 1H), 6.69 (s, 1H), 4.30 – 4.20 (m, 1H), 4.05 – 3.96 (m, 1H), 3.87 – 3.80 (m, 2H), 2.51 (br s, 3H); ^{13}C NMR δ 198.4, 163.4 (dd, *J* = 252.71, 12.77 Hz), 159.8 (dd, *J* = 250.76, 12.10 Hz), 140.5, 136.4, 135.3, 134.7, 134.2, 134.0, 131.4, 131.0 (m), 130.4, 130.0, 129.6, 129.2, 128.5, 122.5 (m), 112.5 (d, *J* = 24.32 Hz), 104.8 (t, *J* = 25.93 Hz), 59.9, 52.0, 39.0.	$C_{26}H_{23}ClF_2NO$ 438.1431	438.1417

1. Unless otherwise specified, the NMR data are given in chloroform-*d* at 500 MHz for ^{1}H NMR, and at 126 MHz for ^{13}C NMR. 2. Some of these hydrochloride salts have amorphous characteristics (e.g., ***E*-SI-14**, ***E*-SI-15**, ***Z*-SI-15**, ***Z*-SI-16**), and some (e.g., ***E*-SI-20**) were too hygroscopic to record melting point data. 3. Unless otherwise specified, formula is for $[M+H]^+$ where M represents the compound in its charge neutral form.

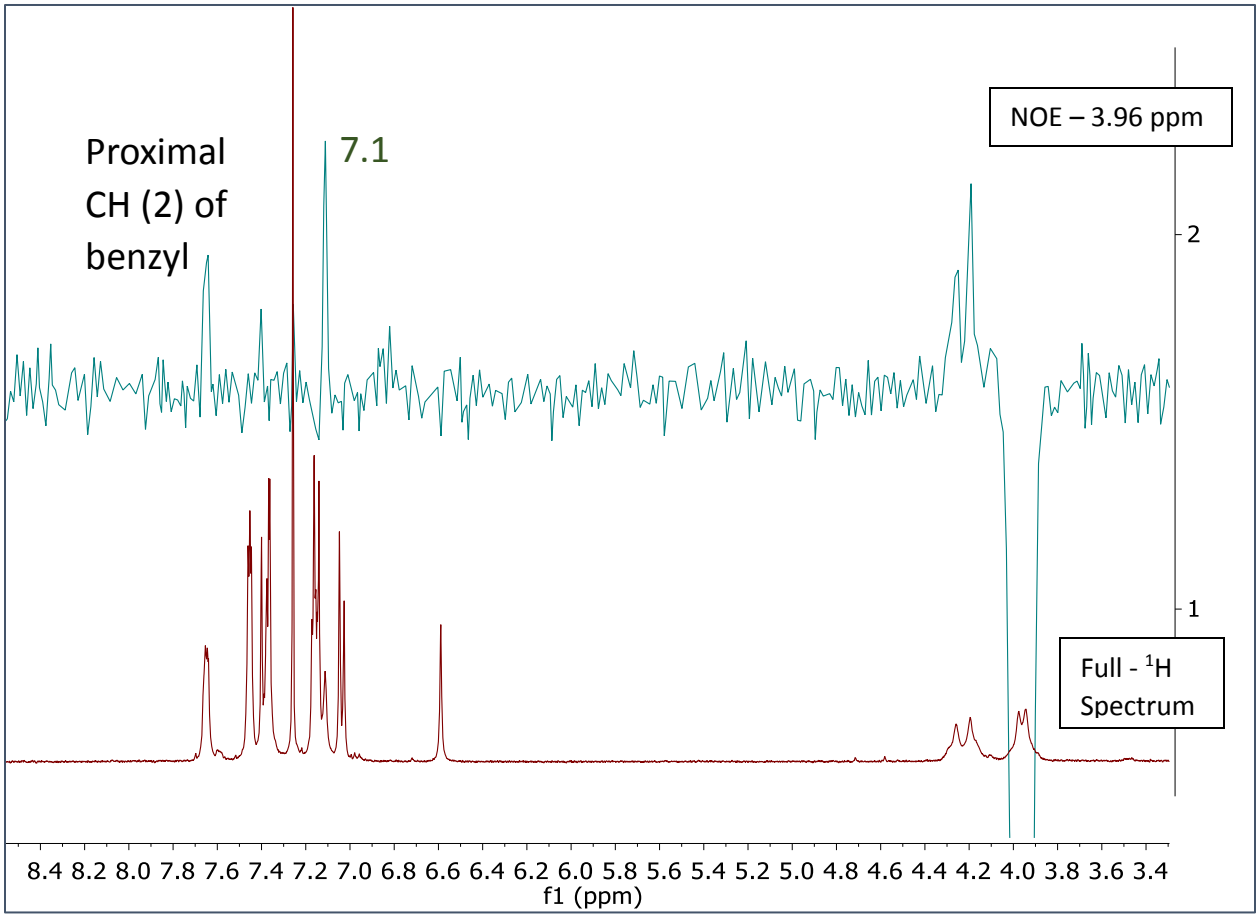
Key NOE Data for *E*-6 vs. *Z*-6





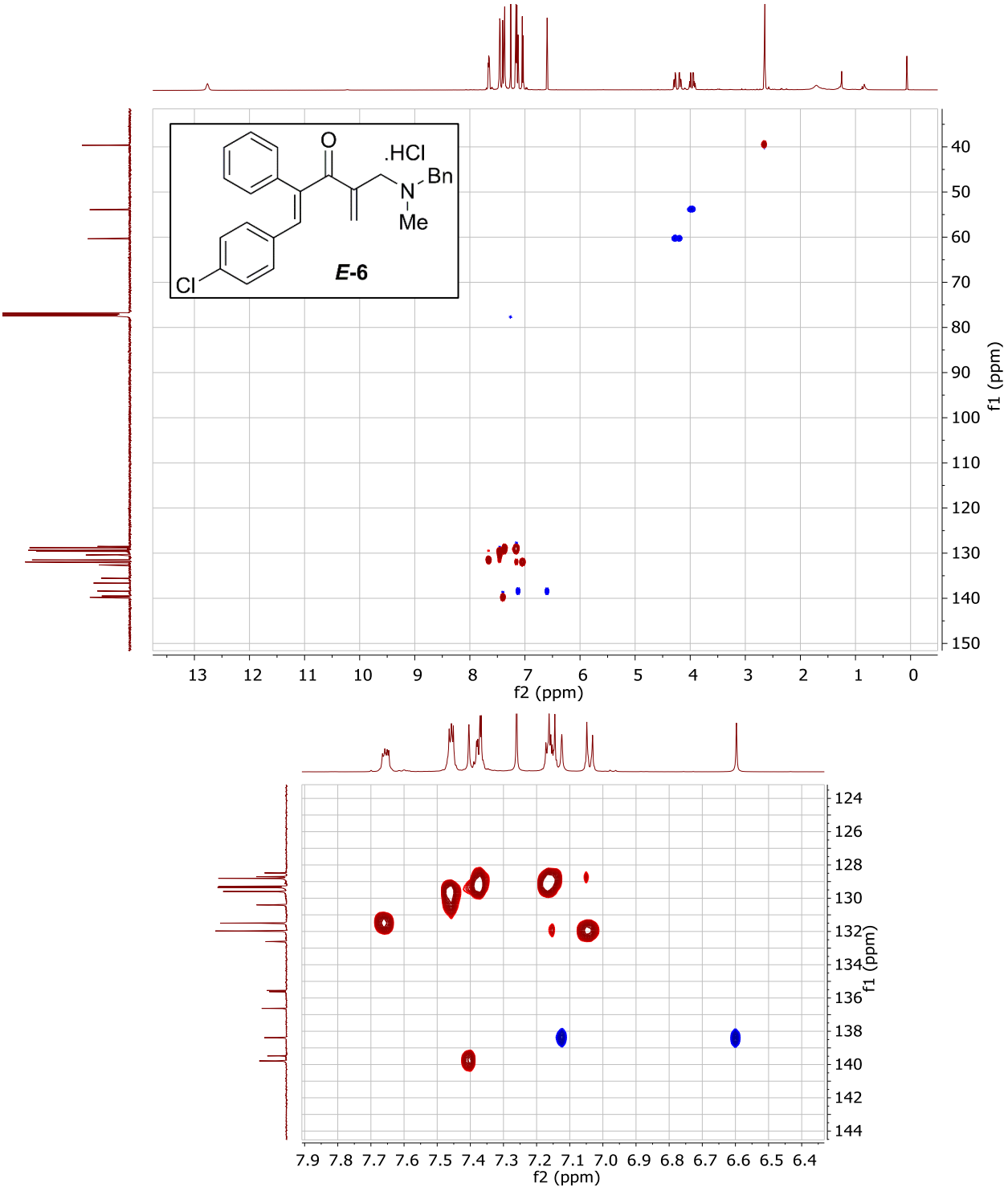

O
H
N
Me
Ph
Cl
H
H
H
6.6
7.1

***E*-6**

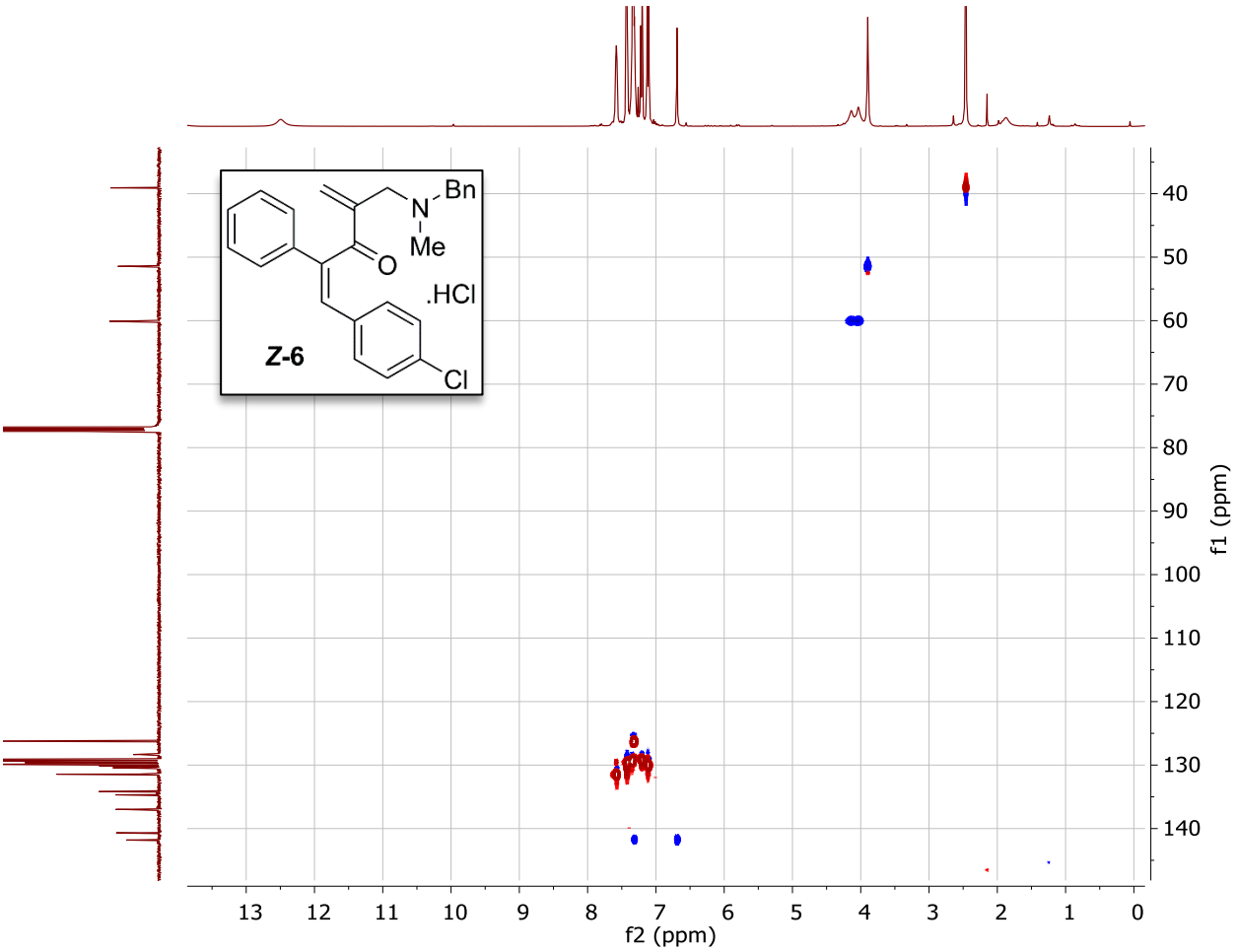

Proximal
CH (2) of
benzyl
7.1
NOE – 3.96 ppm
2
1
Full - ^{1}H
Spectrum
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
f1 (ppm)

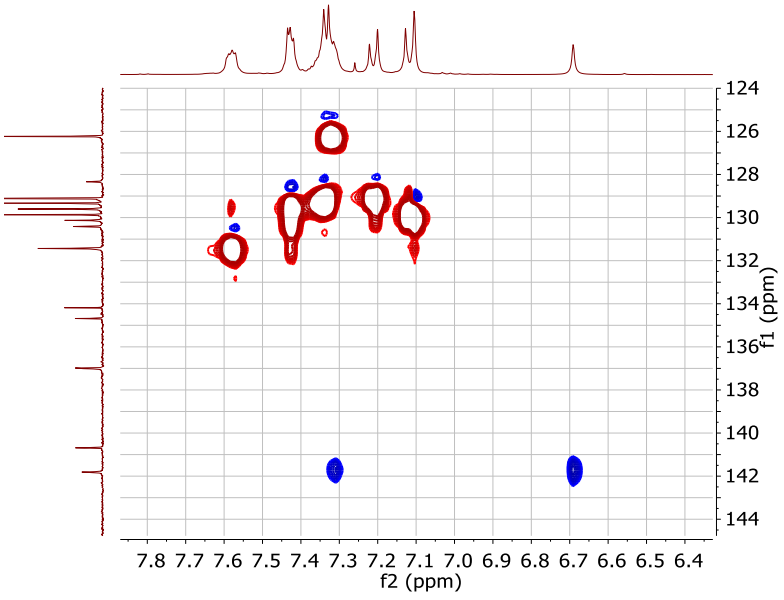
2D-NMR Spectra

HSQC – *E*-6

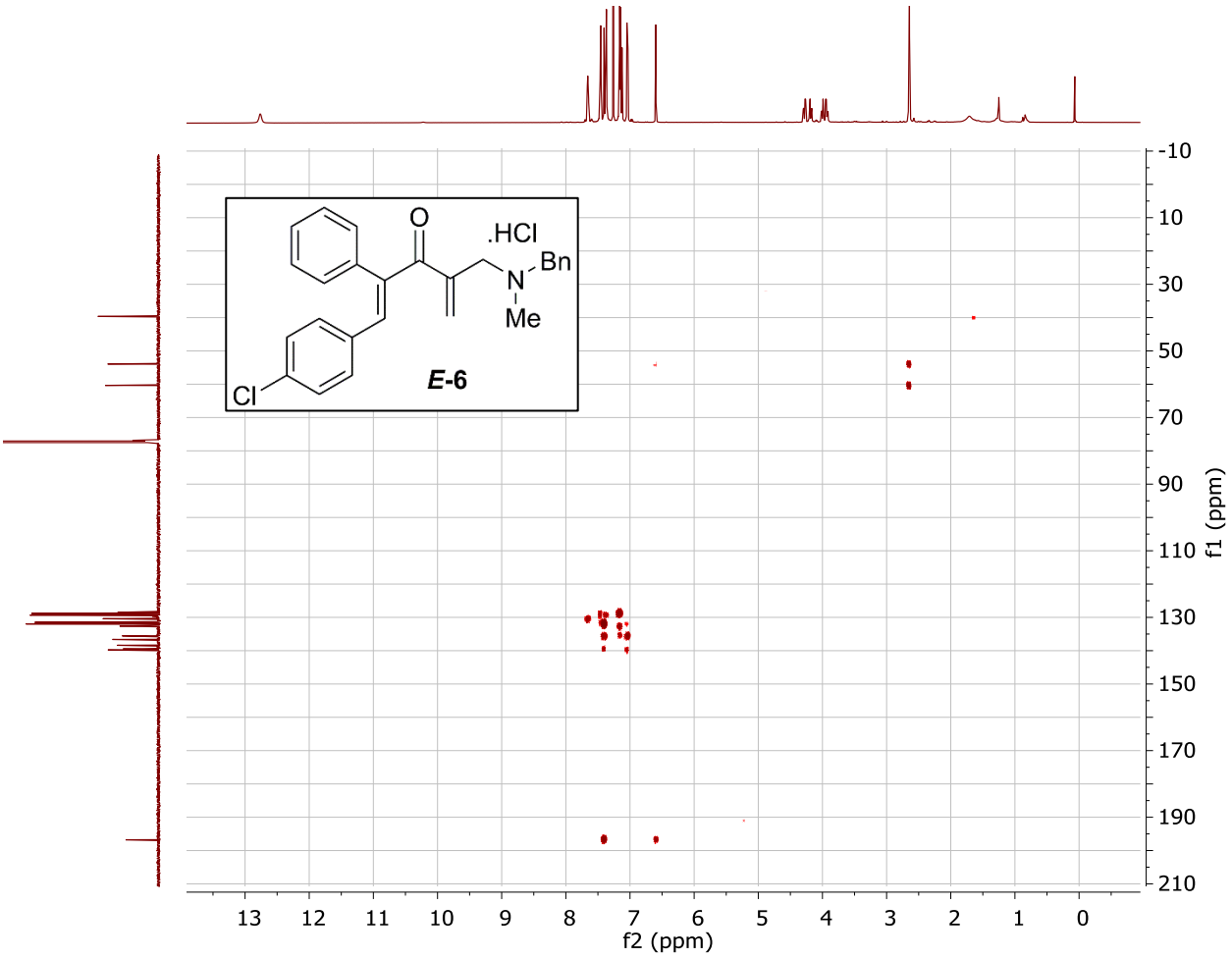


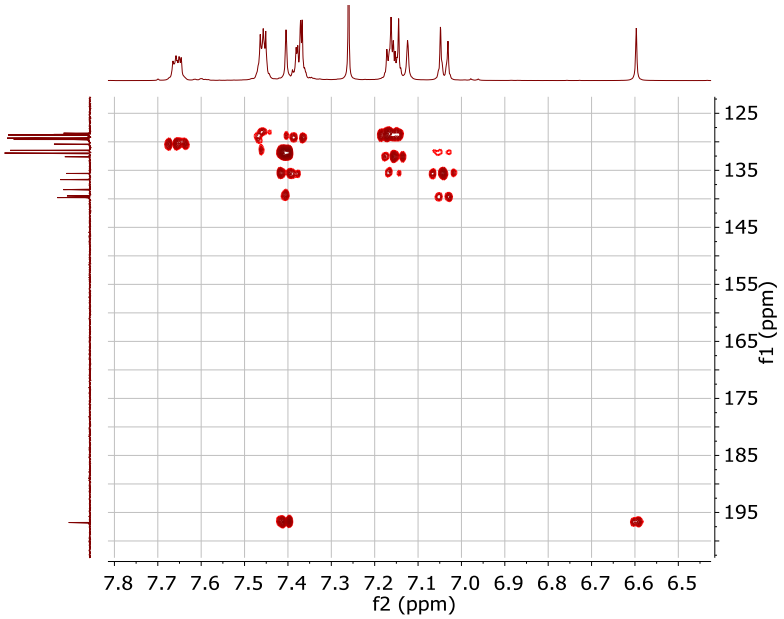
HSQC – Z-6



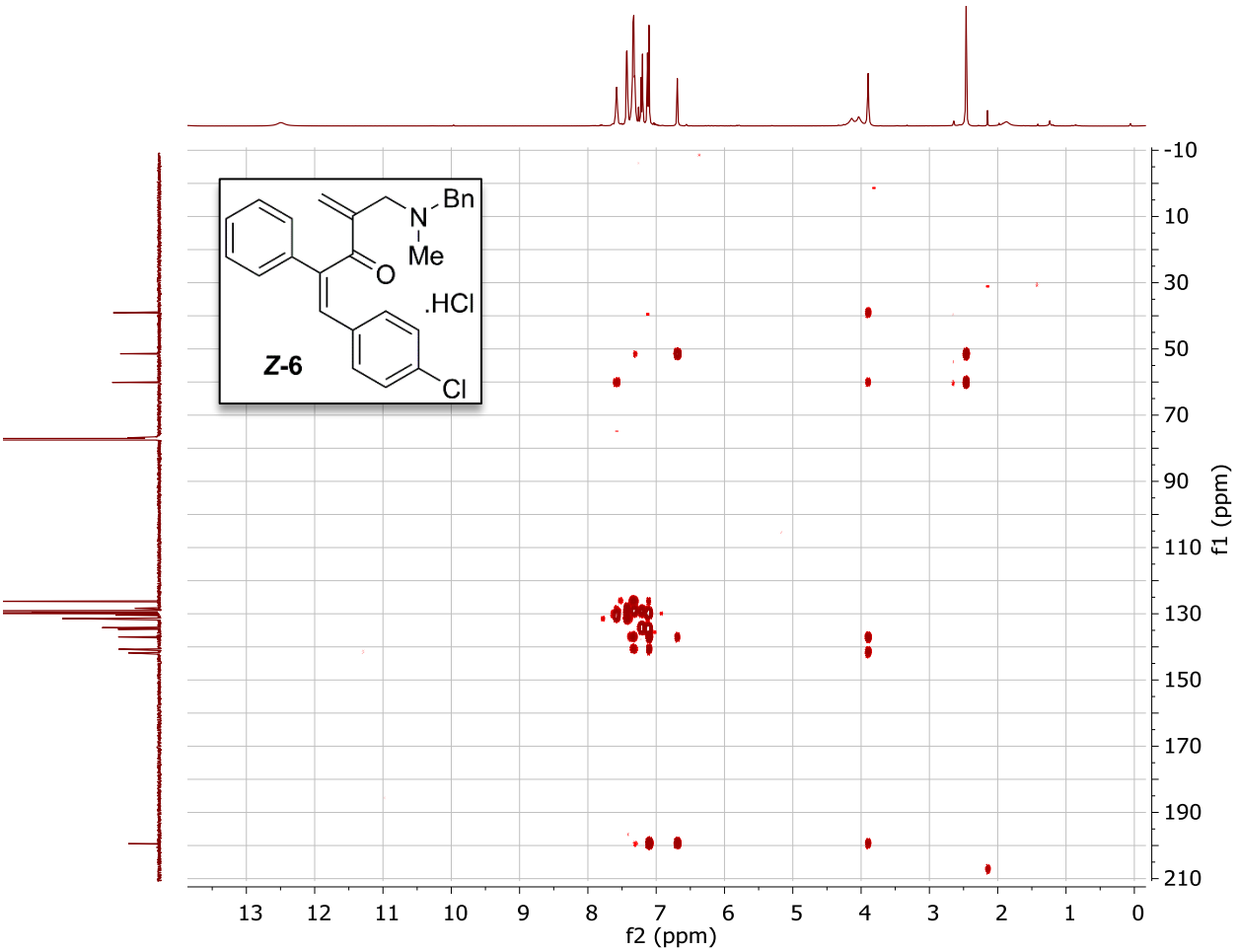


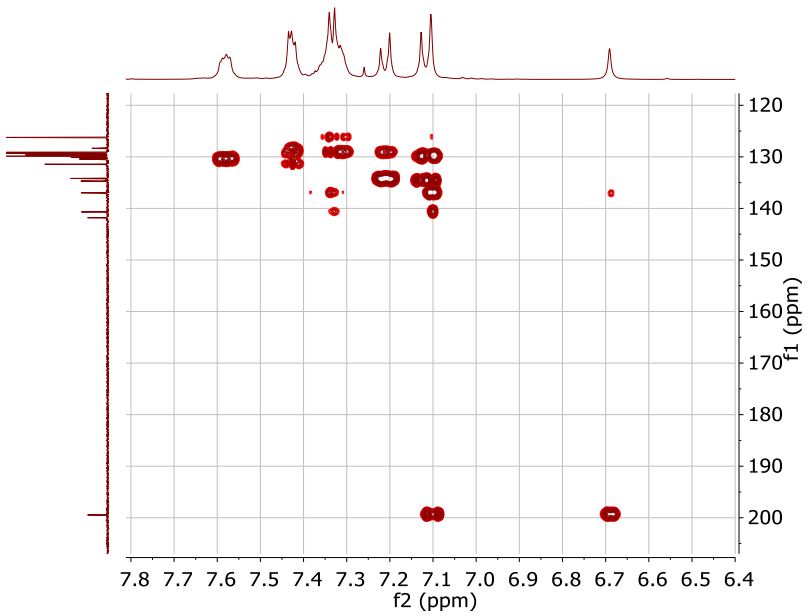
HMBC – *E*-6


O
.HCl
Bn
N
Me
Cl
E-6
-10
10
30
50
70
90
110
130
150
170
190
210
f1 (ppm)
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f2 (ppm)

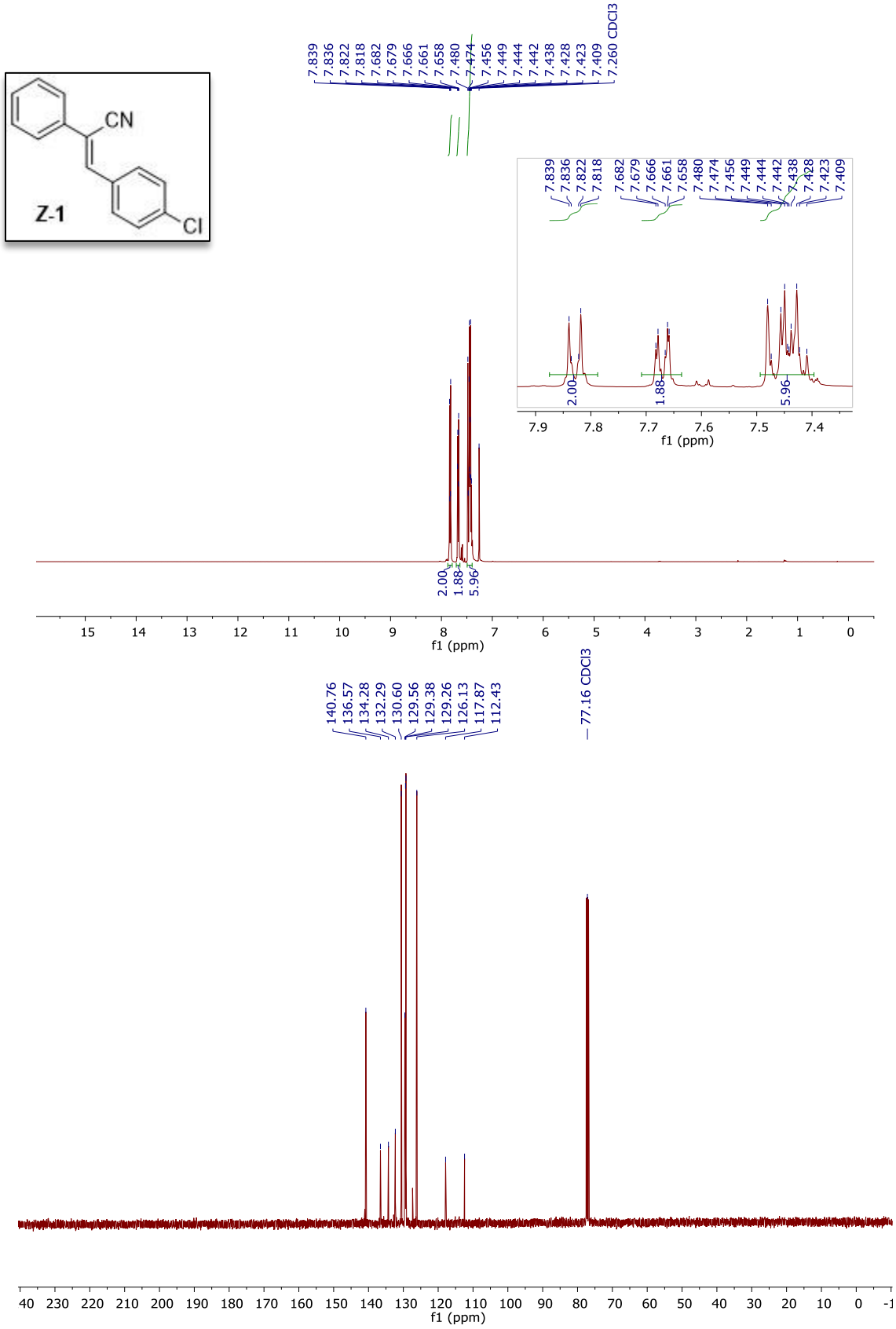

125
135
145
155
165
175
185
195
f1 (ppm)
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
f2 (ppm)

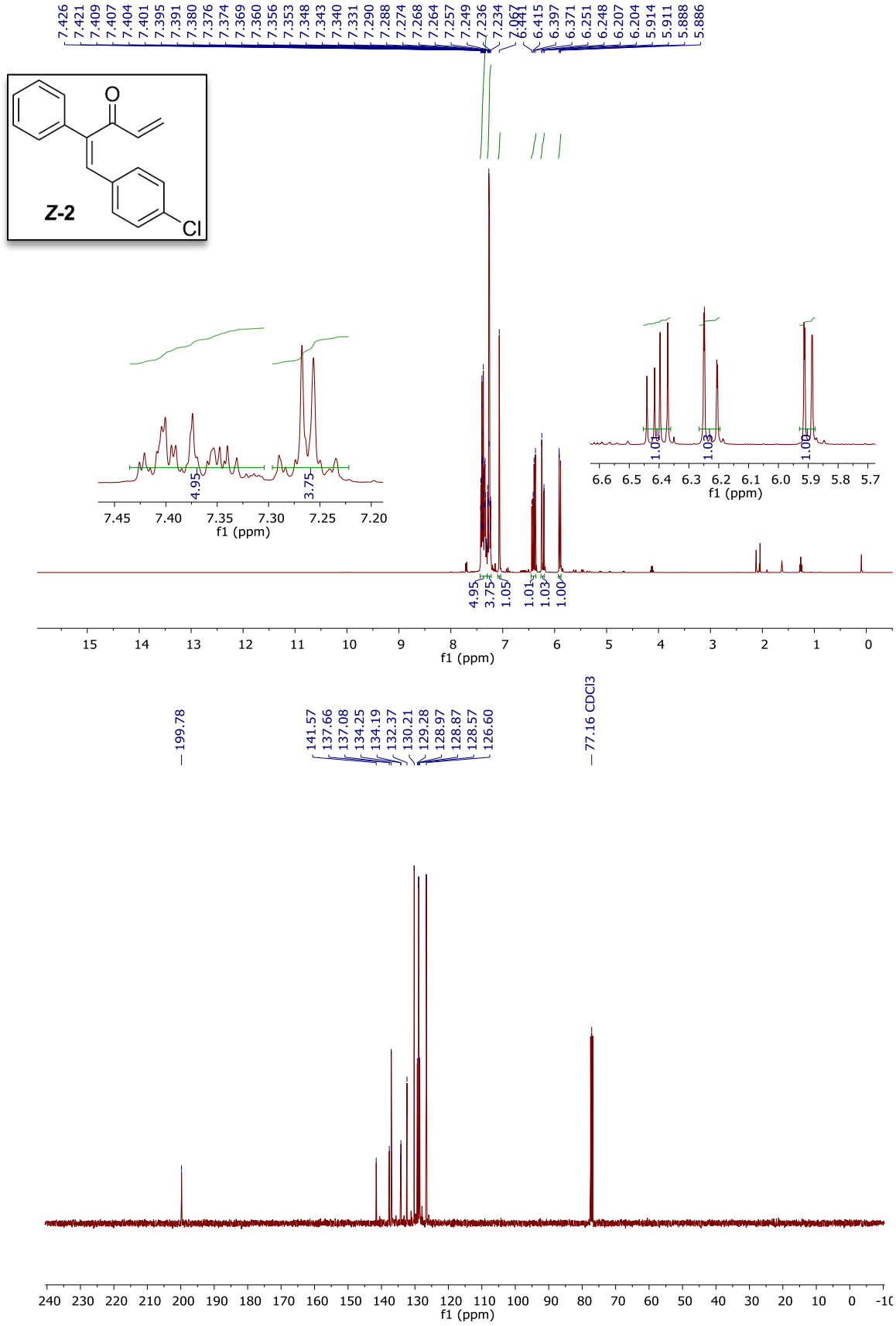
HMBC – *Z*-6

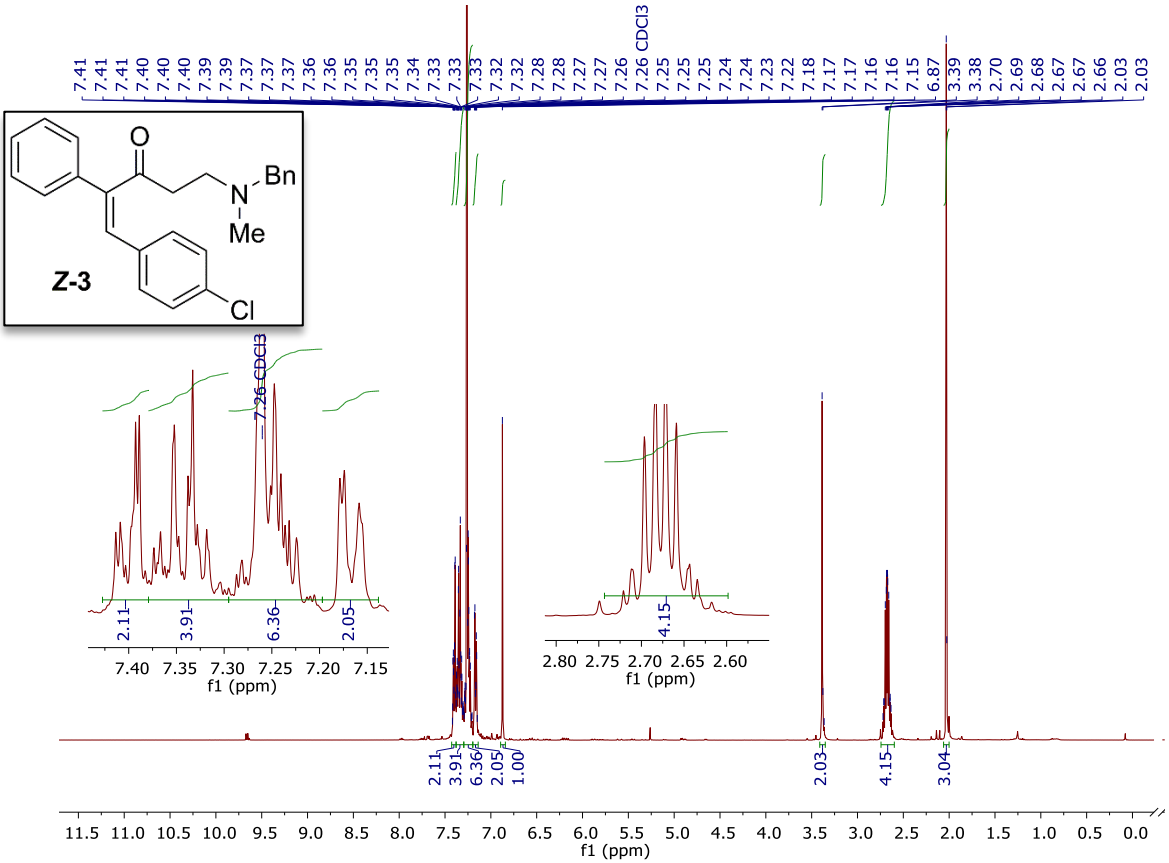

Bn
N
Me
O
.HCl
Cl
Z-6
-10
10
30
50
70
90
110
130
150
170
190
210
f1 (ppm)
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f2 (ppm)

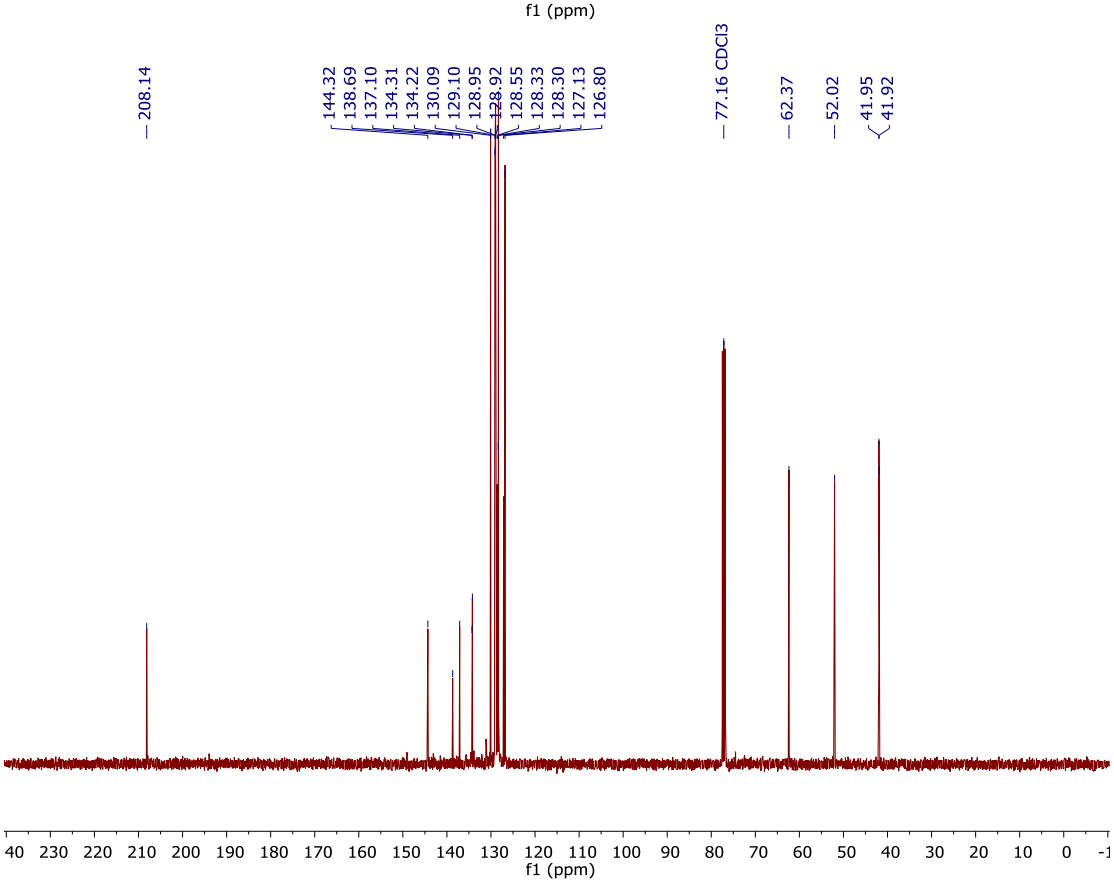

120
130
140
150
160
170
180
190
200
f1 (ppm)
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
f2 (ppm)

^{1}H, ^{2}H and ^{13}C NMR Spectra




7.426
7.421
7.409
7.407
7.404
7.401
7.395
7.391
7.380
7.376
7.374
7.369
7.360
7.356
7.353
7.348
7.343
7.340
7.331
7.290
7.288
7.274
7.268
7.264
7.257
7.249
7.236
7.234
7.067
6.441
6.415
6.397
6.371
6.251
6.248
6.207
6.204
5.914
5.911
5.888
5.886
O
Z-2
Cl
4.95
3.75
1.05
1.01
1.03
1.00
f1 (ppm)
199.78
141.57
137.66
137.08
134.25
134.19
132.37
130.21
129.28
128.97
128.87
128.57
126.60
77.16 CDCl3
f1 (ppm)


Z-3
O
N
Bn
Me
Cl
7.26 CDCl3
2.11
3.91
6.36
2.05
4.15
f1 (ppm)
1.00
2.03
3.04


208.14
144.32
138.69
137.10
134.31
134.22
130.09
129.10
128.95
128.92
128.55
128.33
128.30
127.13
126.80
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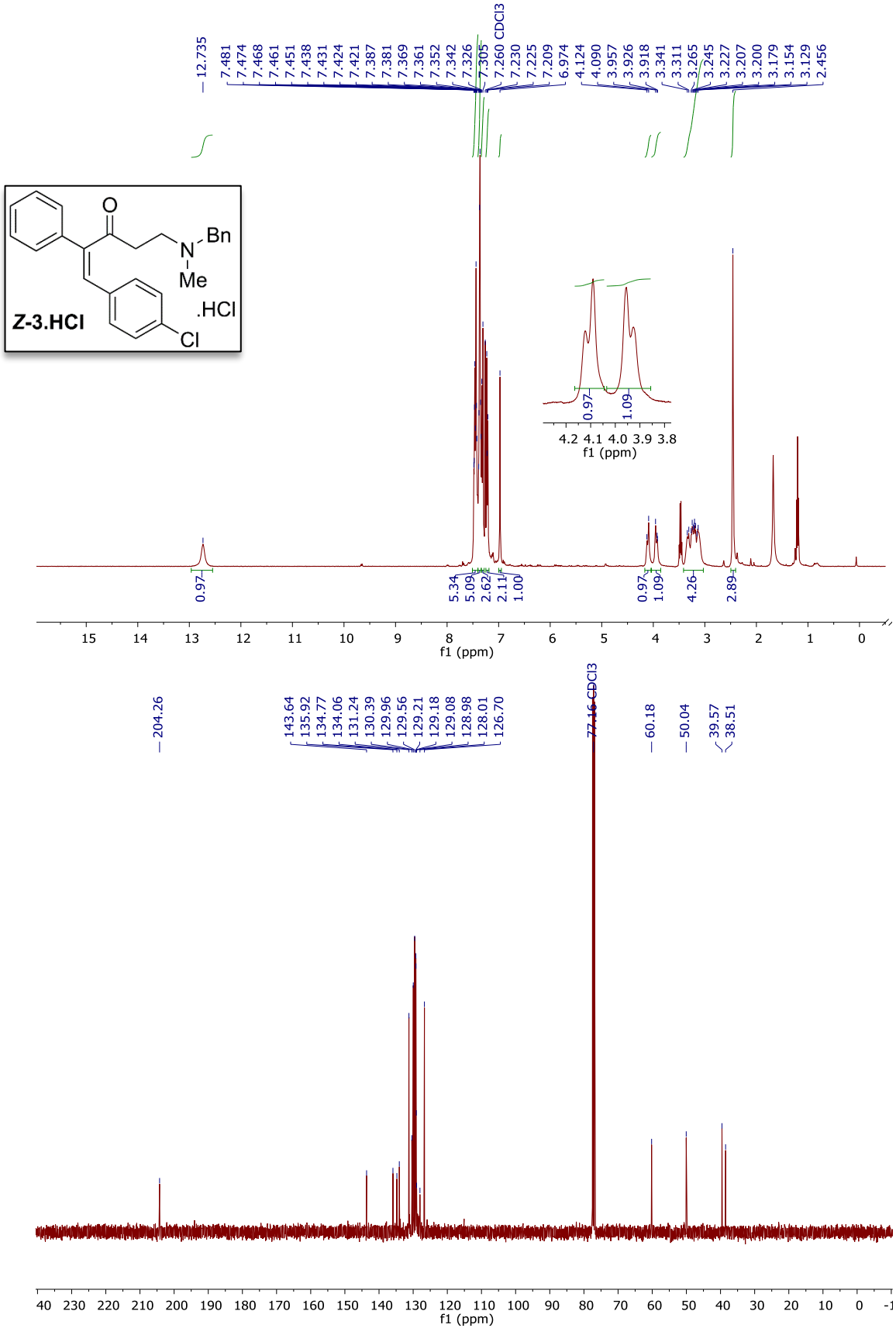
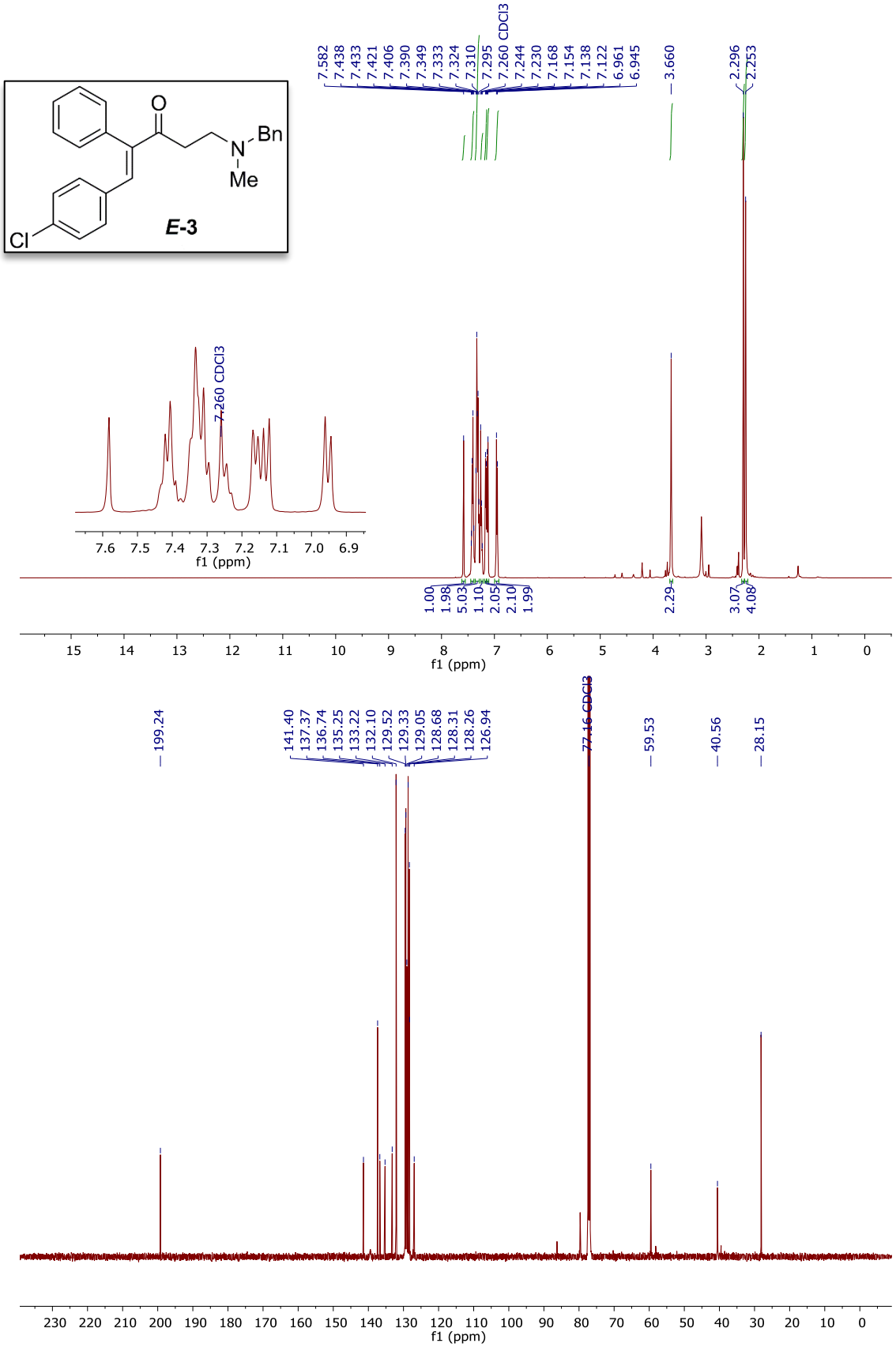
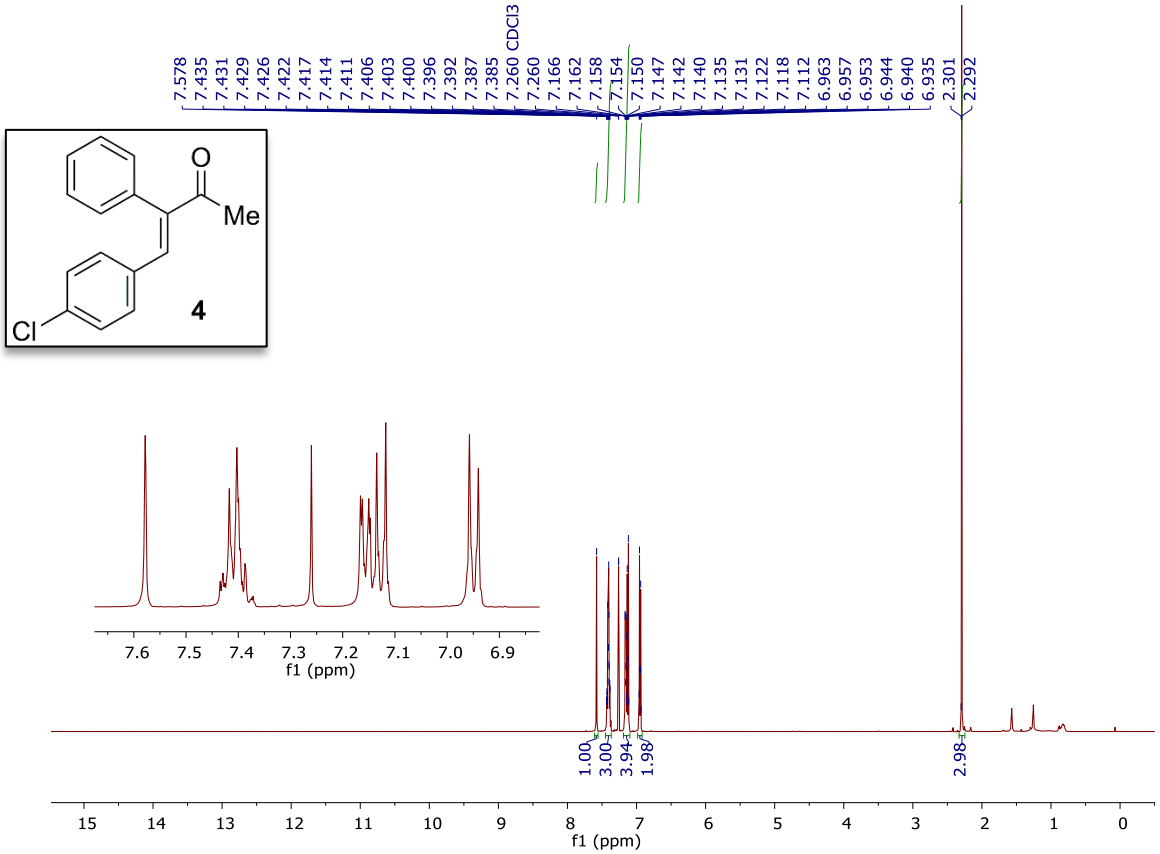
62.37
52.02
41.95
41.92
f1 (ppm)


12.735
7.481
7.474
7.468
7.461
7.451
7.438
7.431
7.424
7.421
7.387
7.381
7.369
7.361
7.352
7.342
7.326
7.305
7.260 CDCl3
7.230
7.225
7.209
6.974
4.124
4.090
3.957
3.926
3.918
3.341
3.311
3.265
3.245
3.227
3.207
3.200
3.179
3.154
3.129
2.456
O
N
Bn
Me
.HCl
Cl
Z-3.HCl
0.97
1.09
4.2 4.1 4.0 3.9 3.8
f1 (ppm)
0.97
5.34
5.09
2.62
2.11
1.00
0.97
1.09
4.26
2.89
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
204.26
143.64
135.92
134.77
134.06
131.24
130.39
129.96
129.56
129.21
129.18
129.08
128.98
128.01
126.70
77.16 CDCl3
60.18
50.04
39.57
38.51
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
N
Bn
Me
Cl
E-3
7.582
7.438
7.433
7.421
7.406
7.390
7.349
7.333
7.324
7.310
7.295
7.260 CDCl3
7.244
7.230
7.168
7.154
7.138
7.122
6.961
6.945
3.660
2.296
2.253
1.00
1.98
5.03
1.10
2.05
2.10
1.99
2.29
3.07
4.08
f1 (ppm)
199.24
141.40
137.37
136.74
135.25
133.22
132.10
129.52
129.33
129.05
128.68
128.31
128.26
126.94
77.16 CDCl3
59.53
40.56
28.15
f1 (ppm)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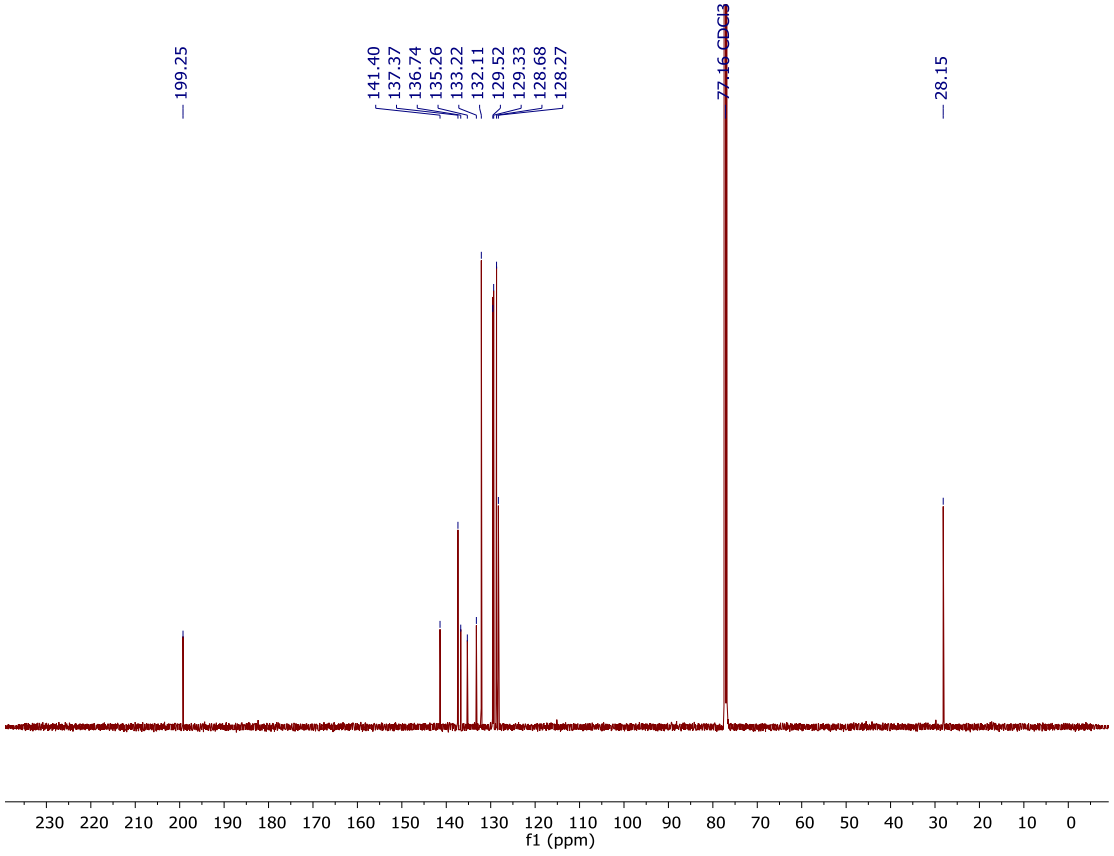
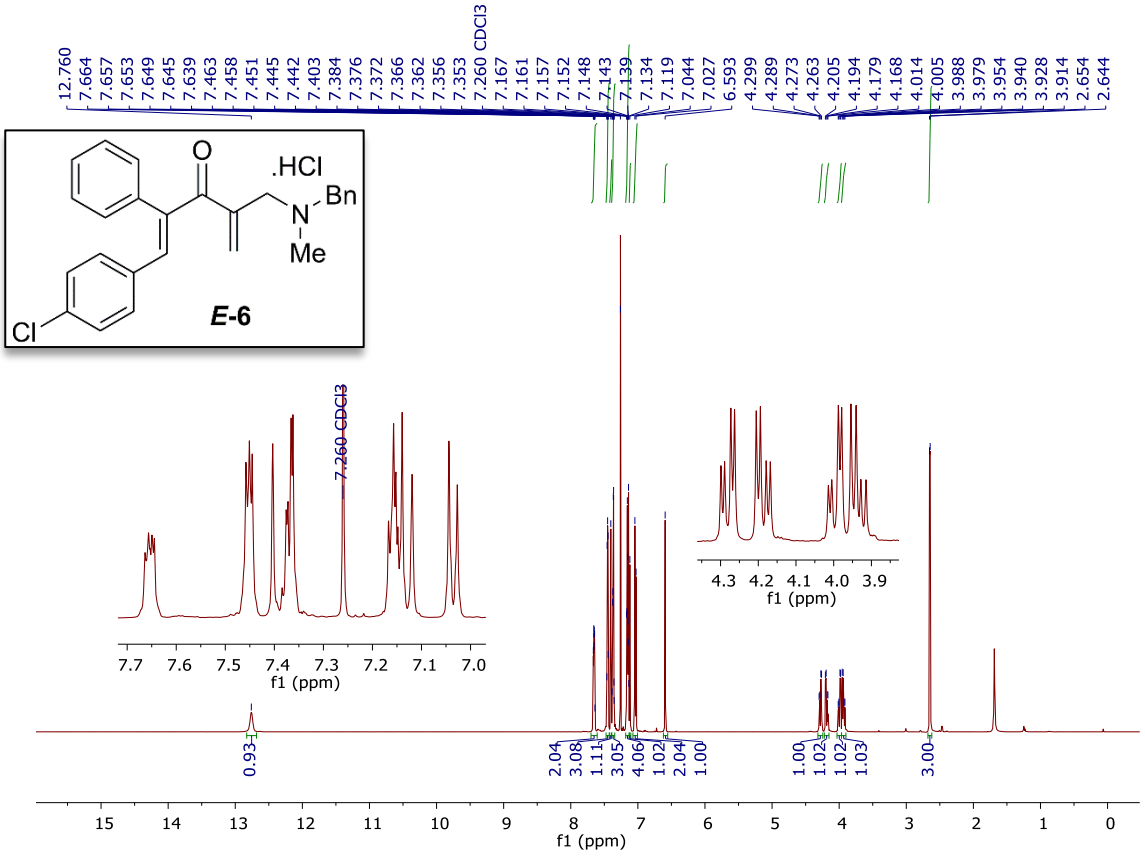
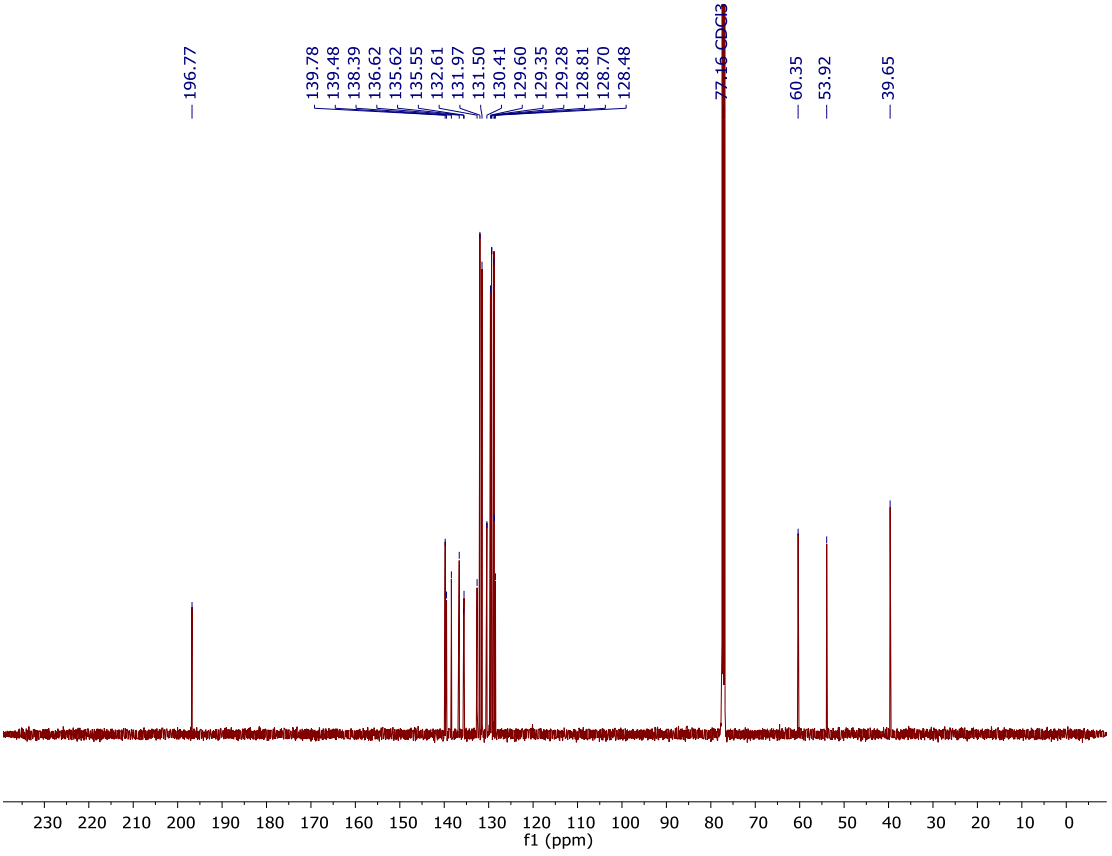
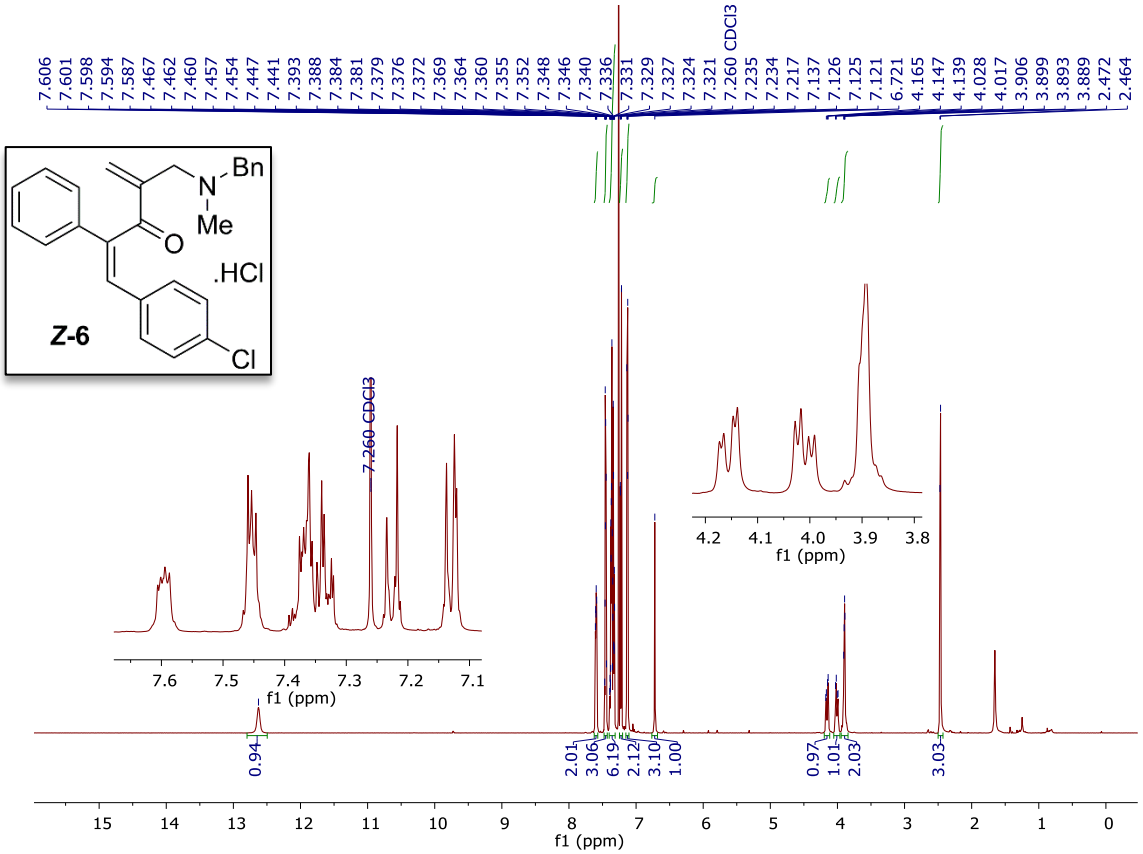
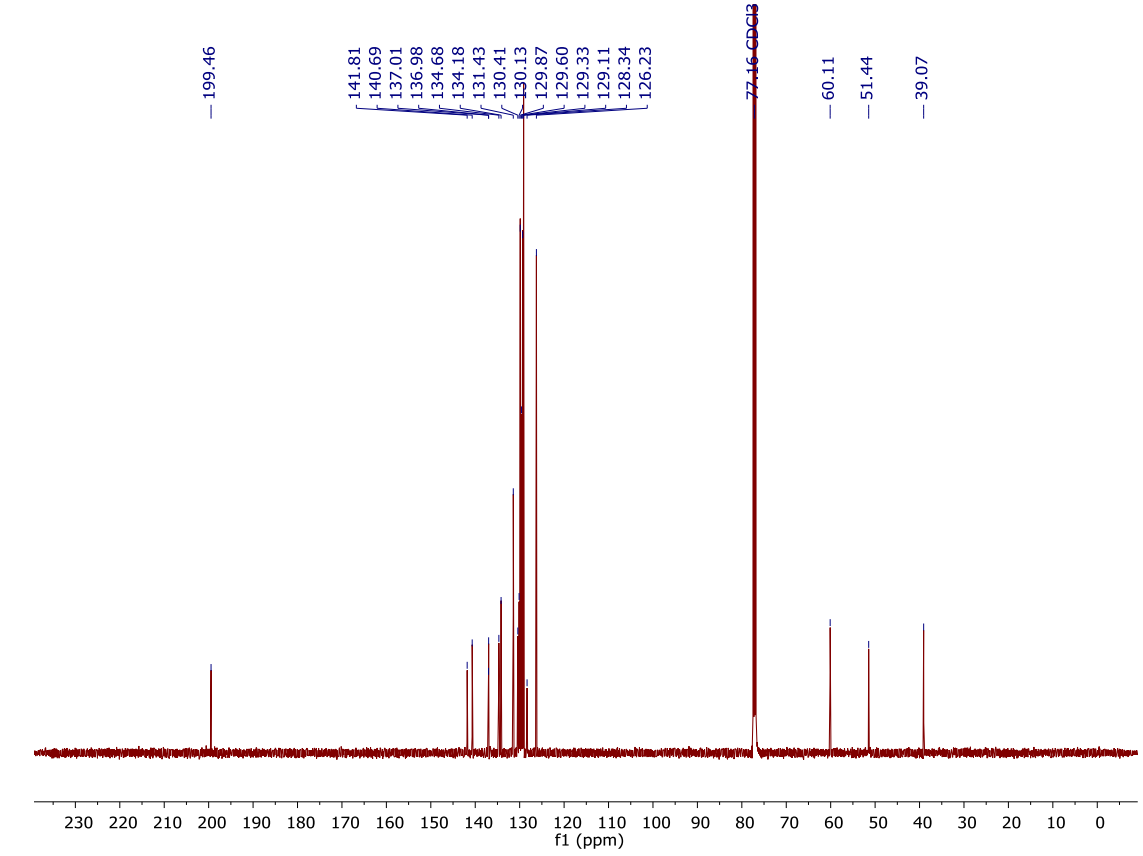
7.435
7.431
7.429
7.426
7.422
7.417
7.414
7.411
7.406
7.403
7.400
7.396
7.392
7.387
7.385
7.260 CDCl3
7.260
7.166
7.162
7.158
7.154
7.150
7.147
7.142
7.140
7.135
7.131
7.122
7.118
7.112
6.963
6.957
6.953
6.944
6.940
6.935
2.301
2.292
O
Me
Cl
4
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.00
3.00
3.94
1.98
2.98
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

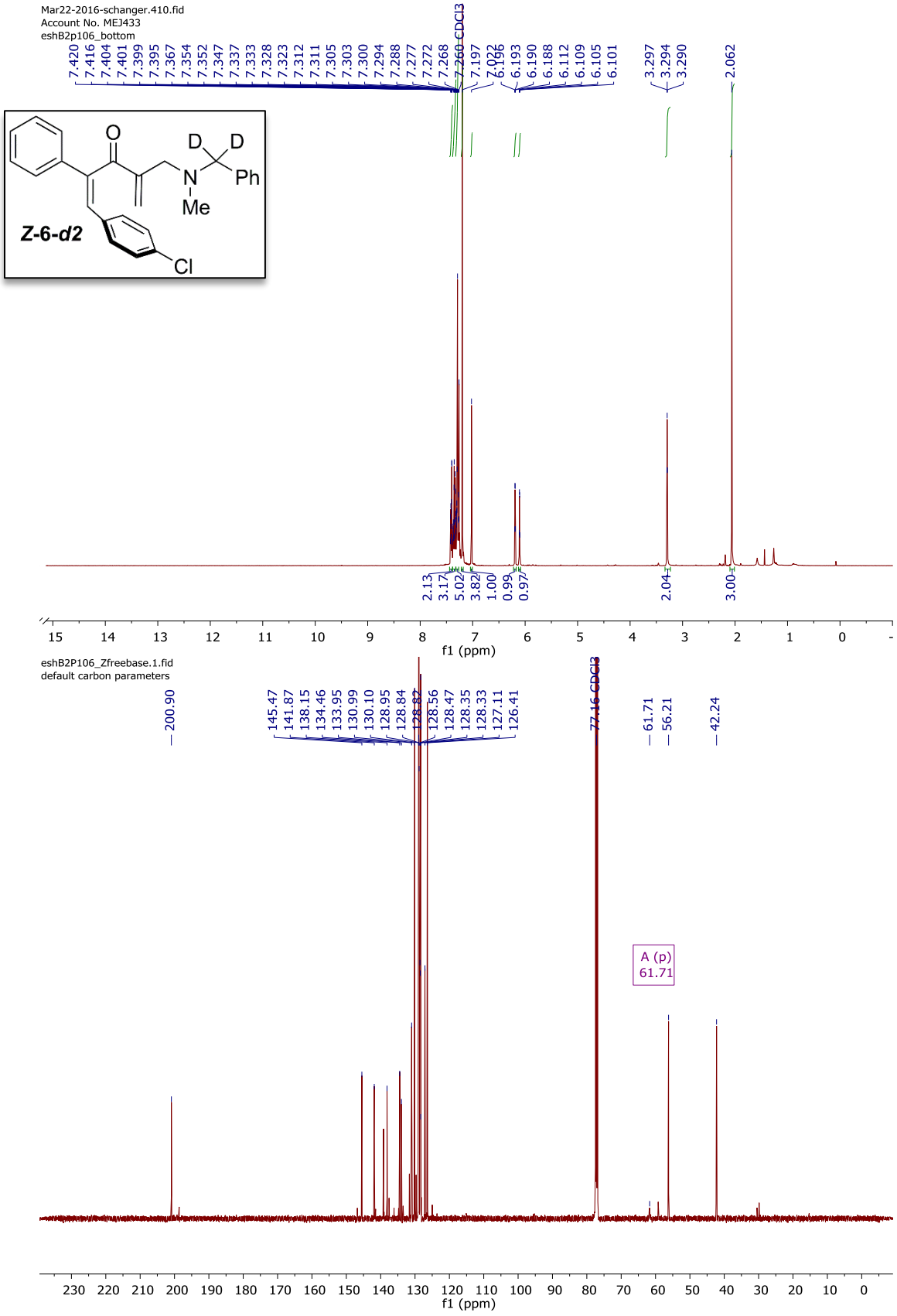

199.25
141.40
137.37
136.74
135.26
133.22
132.11
129.52
129.33
128.68
128.27
77.16 CDCl3
28.15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

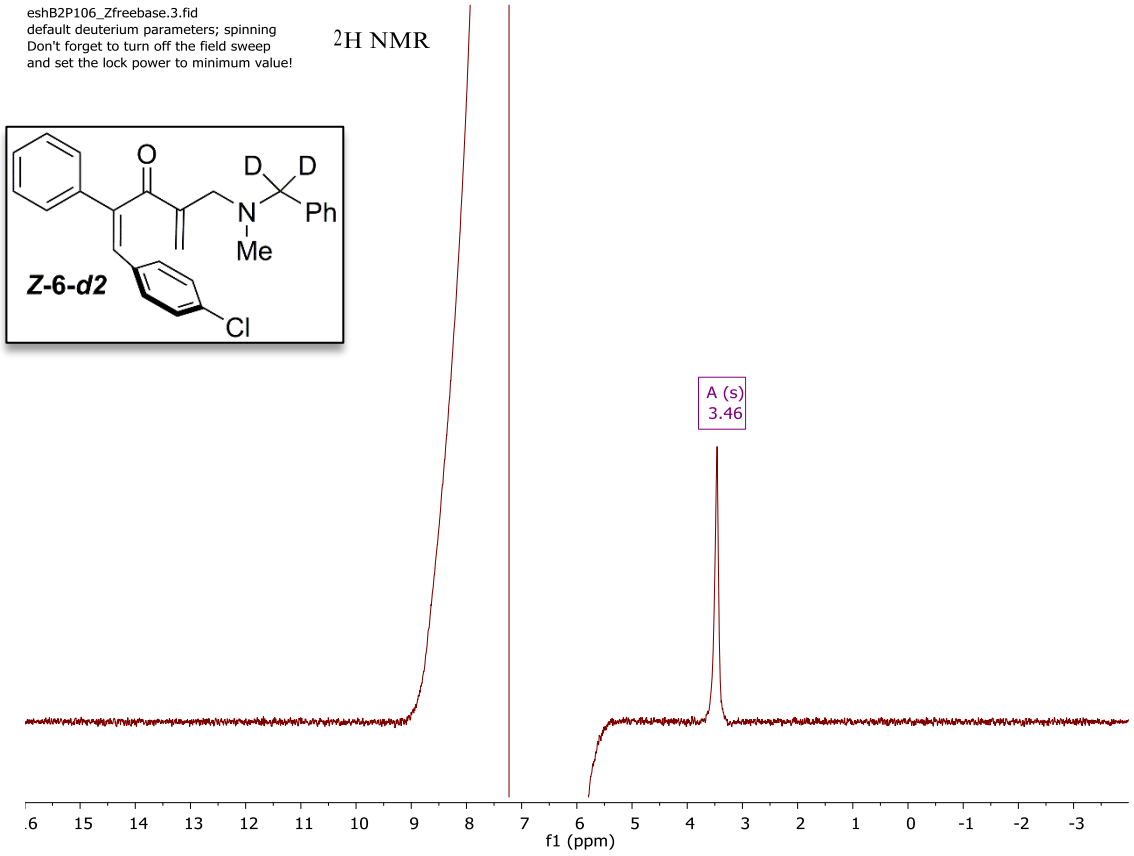

12.760
7.664
7.657
7.653
7.649
7.645
7.639
7.463
7.458
7.451
7.445
7.442
7.403
7.384
7.376
7.372
7.366
7.362
7.356
7.353
7.260 CDCl3
7.167
7.161
7.157
7.152
7.148
7.143
7.139
7.134
7.119
7.044
7.027
6.593
4.299
4.289
4.273
4.263
4.205
4.194
4.179
4.168
4.014
4.005
3.988
3.979
3.954
3.940
3.928
3.914
2.654
2.644
O
.HCl
Bn
N
Me
Cl
E-6
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
0.93
2.04
3.08
1.11
3.05
4.06
1.02
2.04
1.00
1.00
1.02
1.02
1.03
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

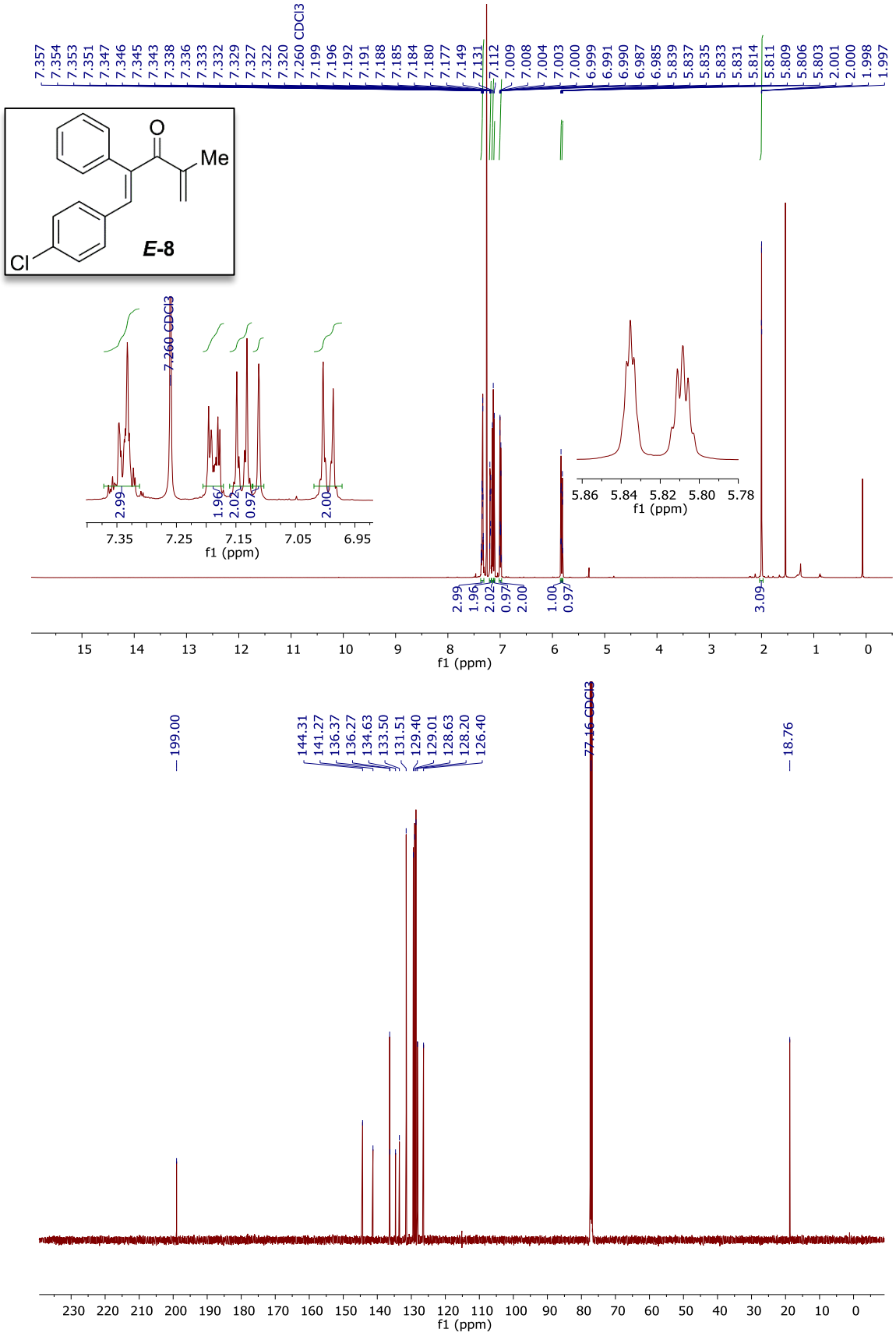

196.77
139.78
139.48
138.39
136.62
135.62
135.55
132.61
131.97
131.50
130.41
129.60
129.35
129.28
128.81
128.70
128.48
77.16 CDCl3
60.35
53.92
39.65
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

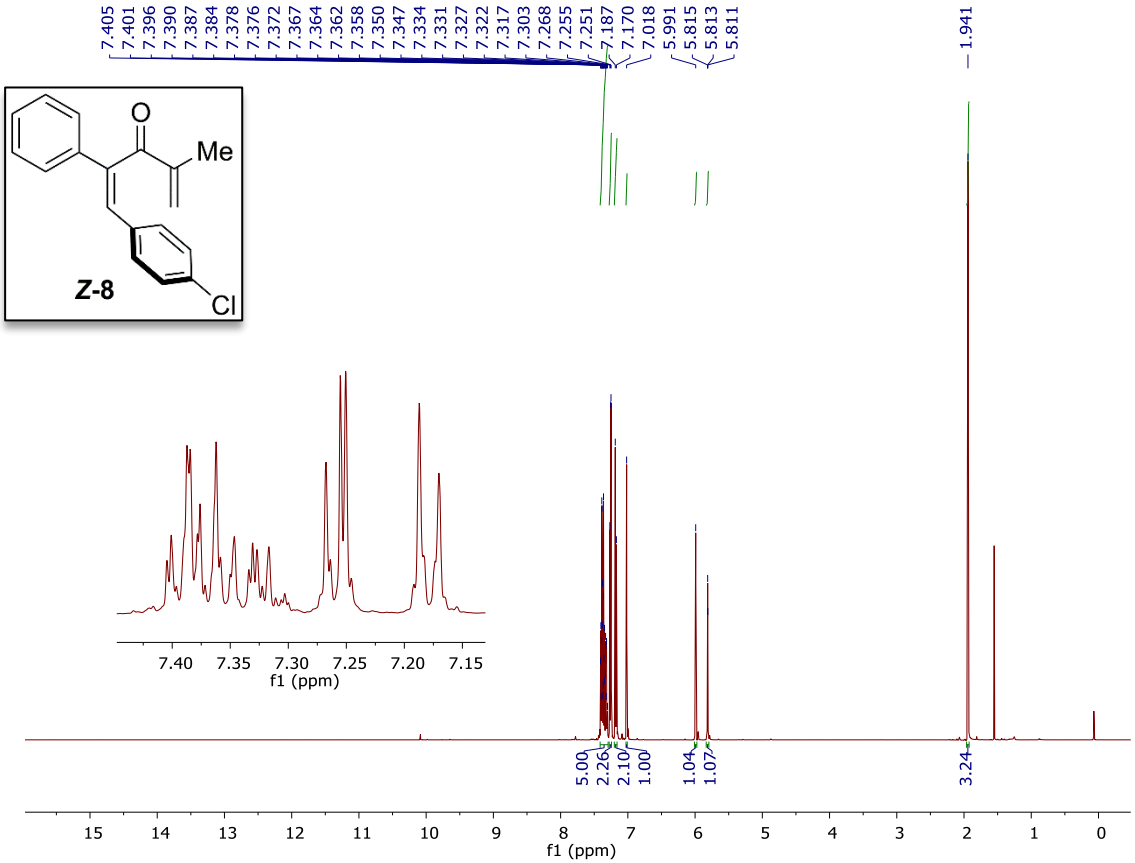

7.606 7.601 7.598 7.594 7.587 7.467 7.462 7.460 7.457 7.454 7.447 7.441 7.393 7.388 7.384 7.381 7.379 7.376 7.372 7.369 7.364 7.360 7.355 7.352 7.348 7.346 7.340 7.336 7.331 7.329 7.327 7.324 7.321 7.260 CDCl3 7.235 7.234 7.217 7.137 7.126 7.125 7.121 6.721 4.165 4.147 4.139 4.028 4.017 3.906 3.899 3.893 3.889 2.472 2.464
Bn
N
Me
O
.HCl
Cl
Z-6
7.260 CDCl3
f1 (ppm)
0.94
2.01
3.06
6.19
2.12
3.10
1.00
0.97
1.01
2.03
3.03
f1 (ppm)

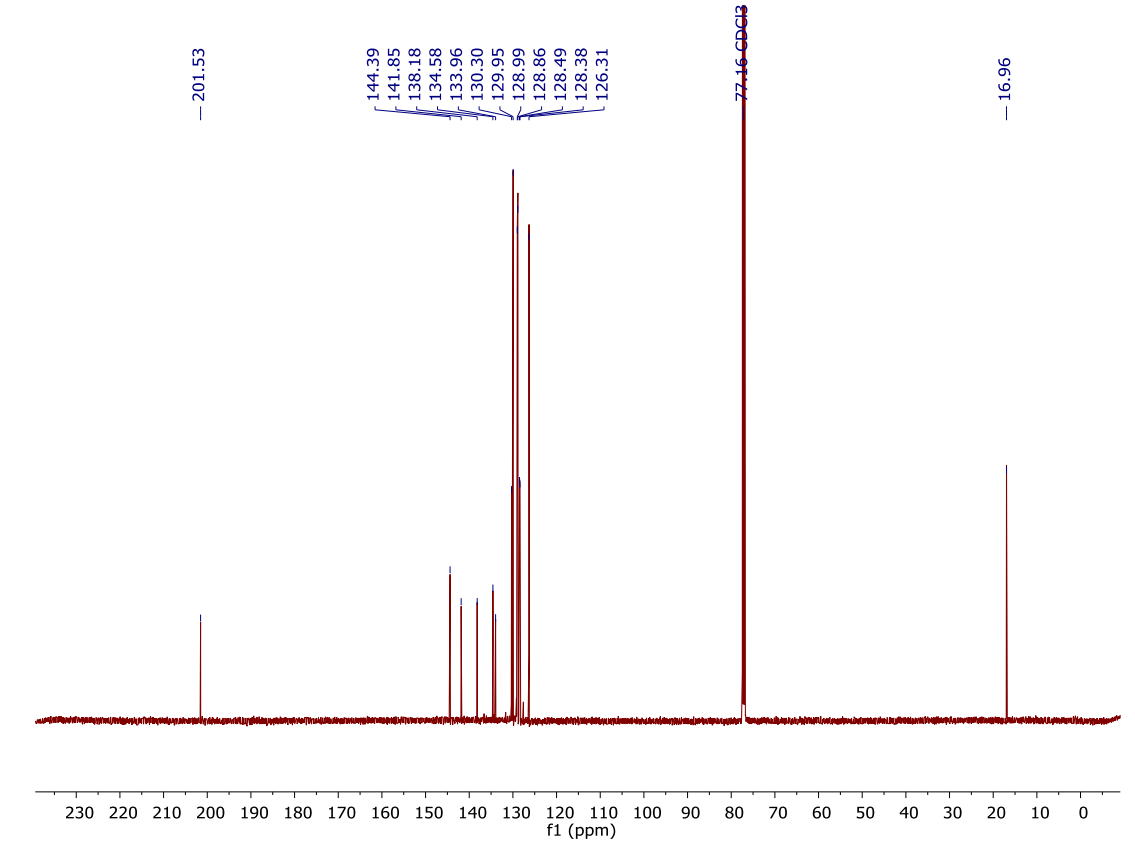

199.46
141.81 140.69 137.01 136.98 134.68 134.18 131.43 130.41 130.13 129.87 129.60 129.33 129.11 128.34 126.23
77.16 CDCl3
60.11
51.44
39.07
f1 (ppm)

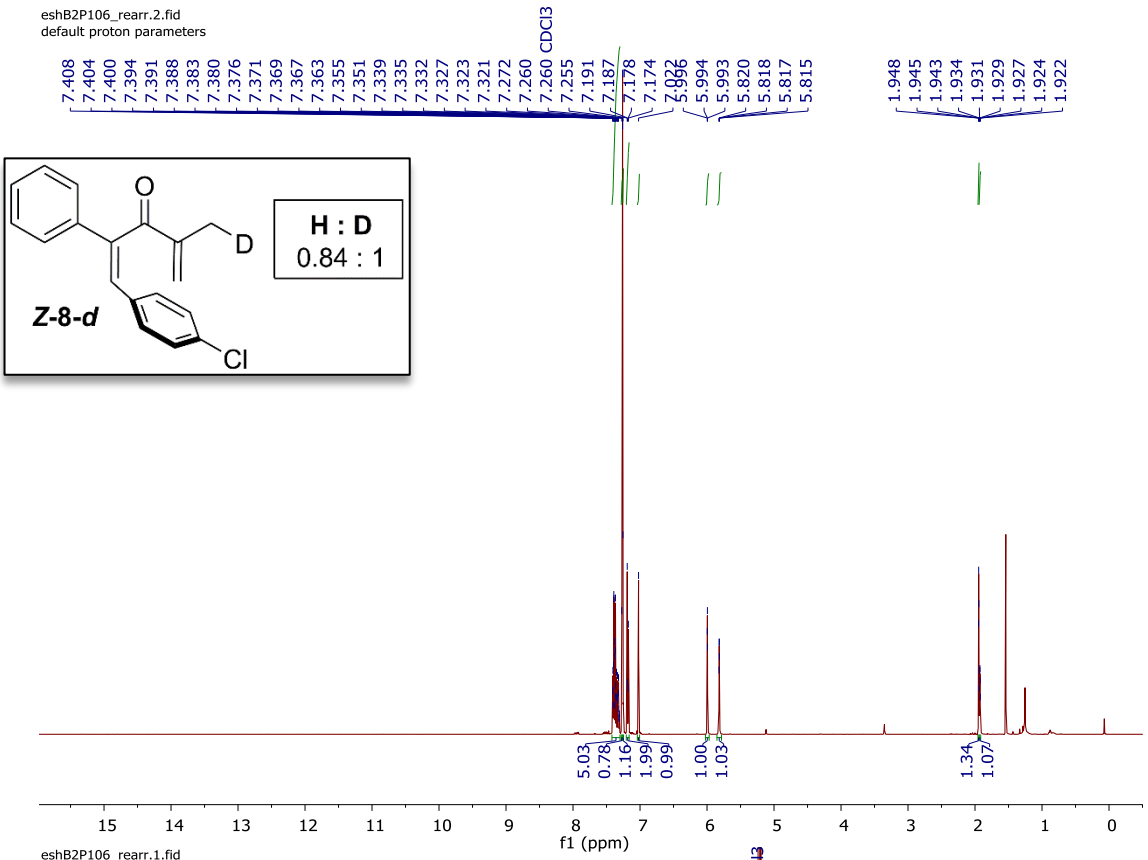

Mar22-2016-schanger.410.fid
Account No. MEJ433
eshB2p106_bottom
7.420 7.416 7.404 7.401 7.399 7.395 7.367 7.354 7.352 7.347 7.337 7.333 7.328 7.323 7.312 7.311 7.305 7.303 7.300 7.294 7.288 7.277 7.272 7.268 7.260 CDCl3 7.197 7.022 7.006 6.193 6.190 6.188 6.112 6.109 6.105 6.101 3.297 3.294 3.290 2.062
O
D D
N
Ph
Me
Z-6-d2
Cl
2.13 3.17 5.02 3.82 1.00 0.99 0.97 2.04 3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
eshB2P106_Zfreebase.1.fid
default carbon parameters
200.90
145.47 141.87 138.15 134.46 133.95 130.99 130.10 128.95 128.84 128.82 128.56 128.47 128.35 128.33 127.11 126.41
77.16 CDCl3
61.71 56.21 42.24
A (p)
61.71
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

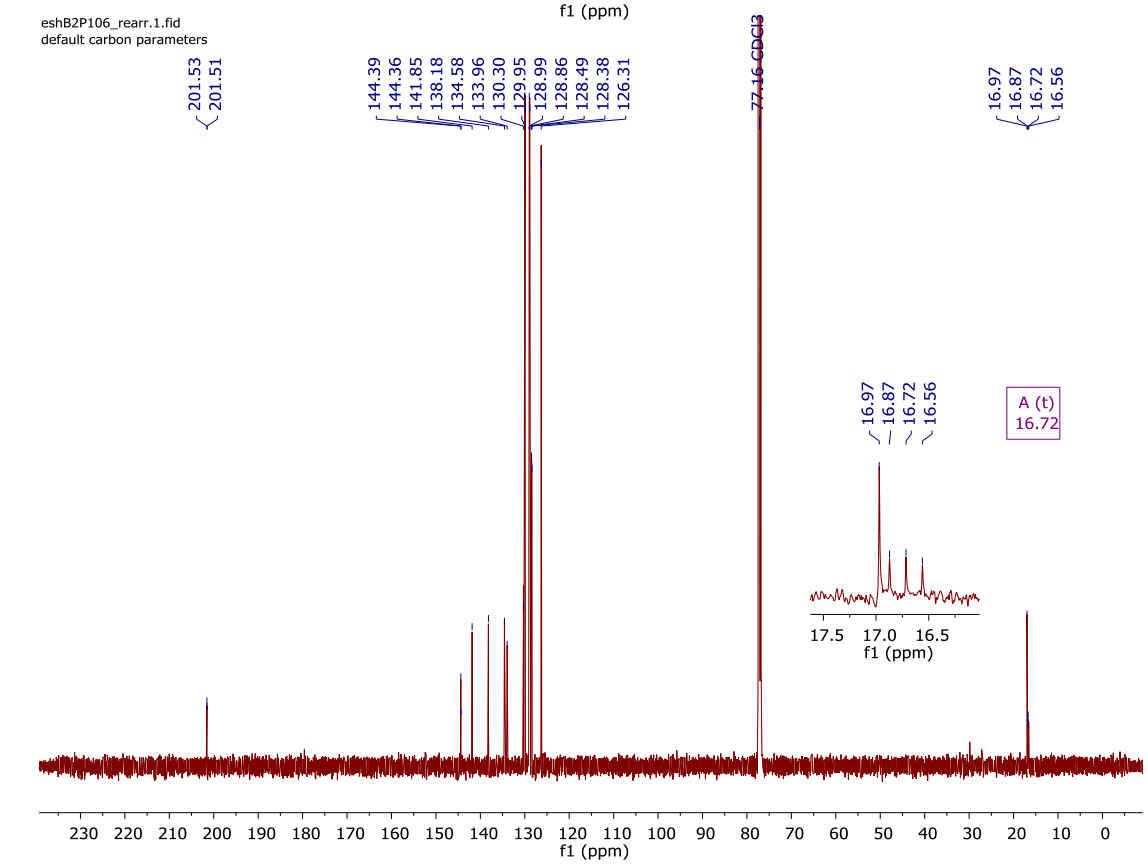

eshB2P106_Zfreebase.3.fid
default deuterium parameters; spinning
Don't forget to turn off the field sweep
and set the lock power to minimum value!
2H NMR
O
D
D
N
Ph
Me
Z-6-d2
Cl
A (s)
3.46
.6
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


7.357
7.354
7.353
7.351
7.347
7.346
7.345
7.343
7.338
7.336
7.333
7.332
7.329
7.327
7.322
7.320
7.260 CDCl3
7.199
7.196
7.192
7.191
7.188
7.185
7.184
7.180
7.177
7.149
7.131
7.112
7.009
7.008
7.004
7.003
7.000
6.999
6.991
6.990
6.987
6.985
5.839
5.837
5.835
5.833
5.831
5.814
5.811
5.809
5.806
5.803
2.001
2.000
1.998
1.997
O
Me
Cl
E-8
7.260 CDCl3
2.99
1.96
2.02
0.97
2.00
7.35
7.25
7.15
7.05
6.95
f1 (ppm)
5.86
5.84
5.82
5.80
5.78
f1 (ppm)
2.99
1.96
2.02
0.97
2.00
1.00
0.97
3.09
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
199.00
144.31
141.27
136.37
136.27
134.63
133.50
131.51
129.40
129.01
128.63
128.20
126.40
77.16 CDCl3
18.76
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.405
7.401
7.396
7.390
7.387
7.384
7.378
7.376
7.372
7.367
7.364
7.362
7.358
7.350
7.347
7.334
7.331
7.327
7.322
7.317
7.303
7.268
7.255
7.251
7.187
7.170
7.018
5.991
5.815
5.813
5.811
1.941
O
Me
Cl
Z-8
7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
5.00
2.26
2.10
1.00
1.04
1.07
3.24
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

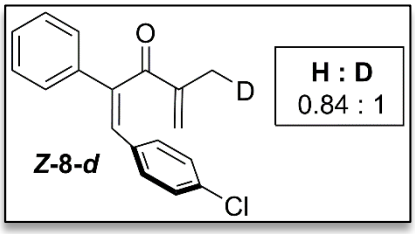

201.53
144.39
141.85
138.18
134.58
133.96
130.30
129.95
128.99
128.86
128.49
128.38
126.31
77.16 CDCl3
16.96
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

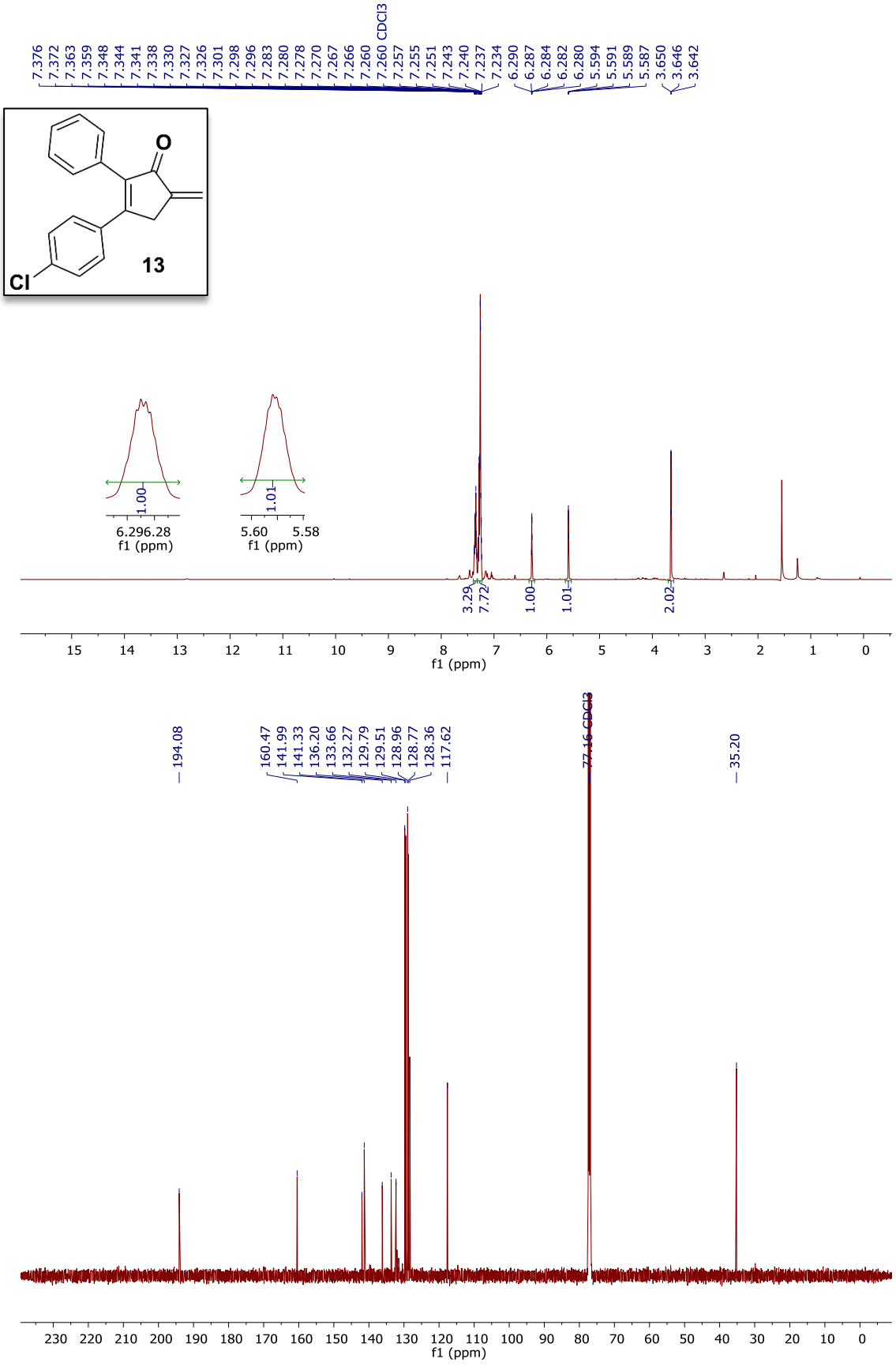

eshB2P106_rearr.2.fid
default proton parameters
7.408 7.404 7.400 7.394 7.391 7.388 7.383 7.380 7.376 7.371 7.369 7.367 7.363 7.355 7.351 7.339 7.335 7.332 7.327 7.323 7.321 7.272 7.260 7.260 CDCl3 7.255 7.191 7.187 7.178 7.174 7.022 5.994 5.993 5.820 5.818 5.817 5.815
1.948 1.945 1.943 1.934 1.931 1.929 1.927 1.924 1.922
O
D
Cl
Z-8-d
H : D
0.84 : 1
5.03 0.78 1.16 1.99 0.99 1.00 1.03 1.34 1.07
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

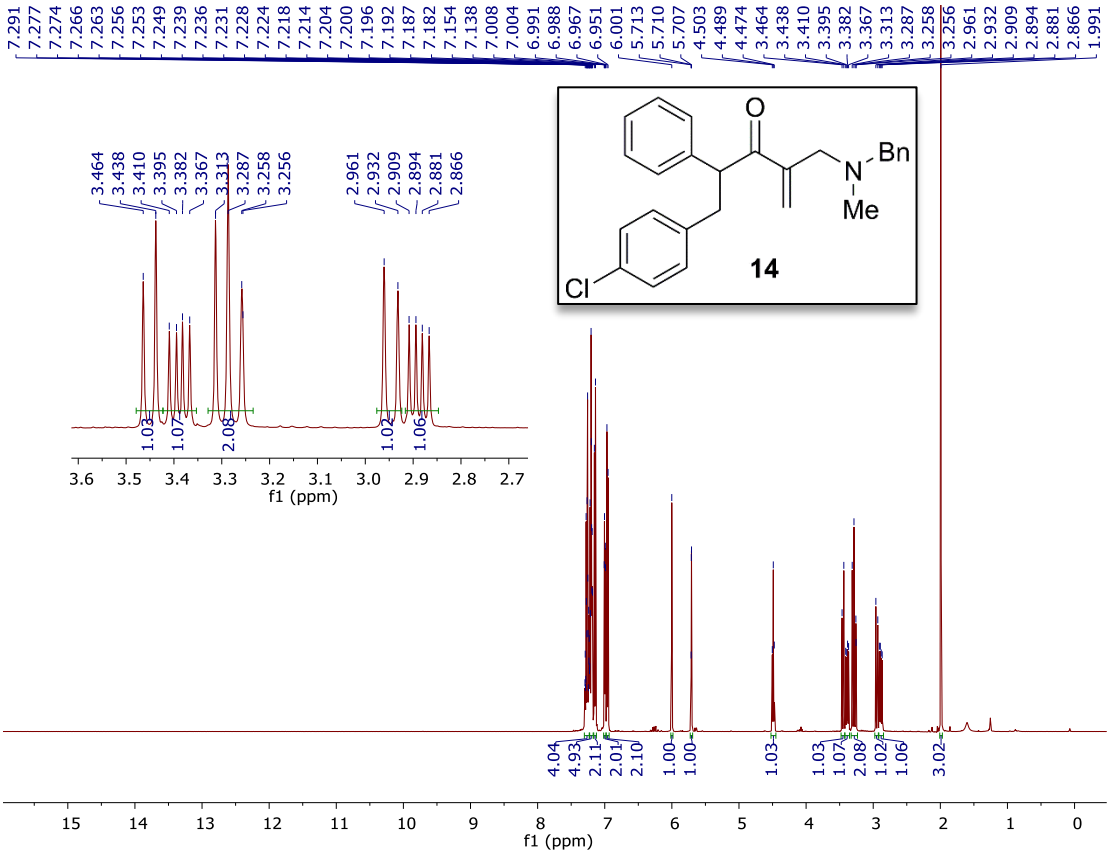

eshB2P106_rearr.1.fid
default carbon parameters
201.53 201.51
144.39 144.36 141.85 138.18 134.58 133.96 130.30 129.95 128.99 128.86 128.49 128.38 126.31
77.16 CDCl3
16.97 16.87 16.72 16.56
A (t)
16.72
17.5 17.0 16.5
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

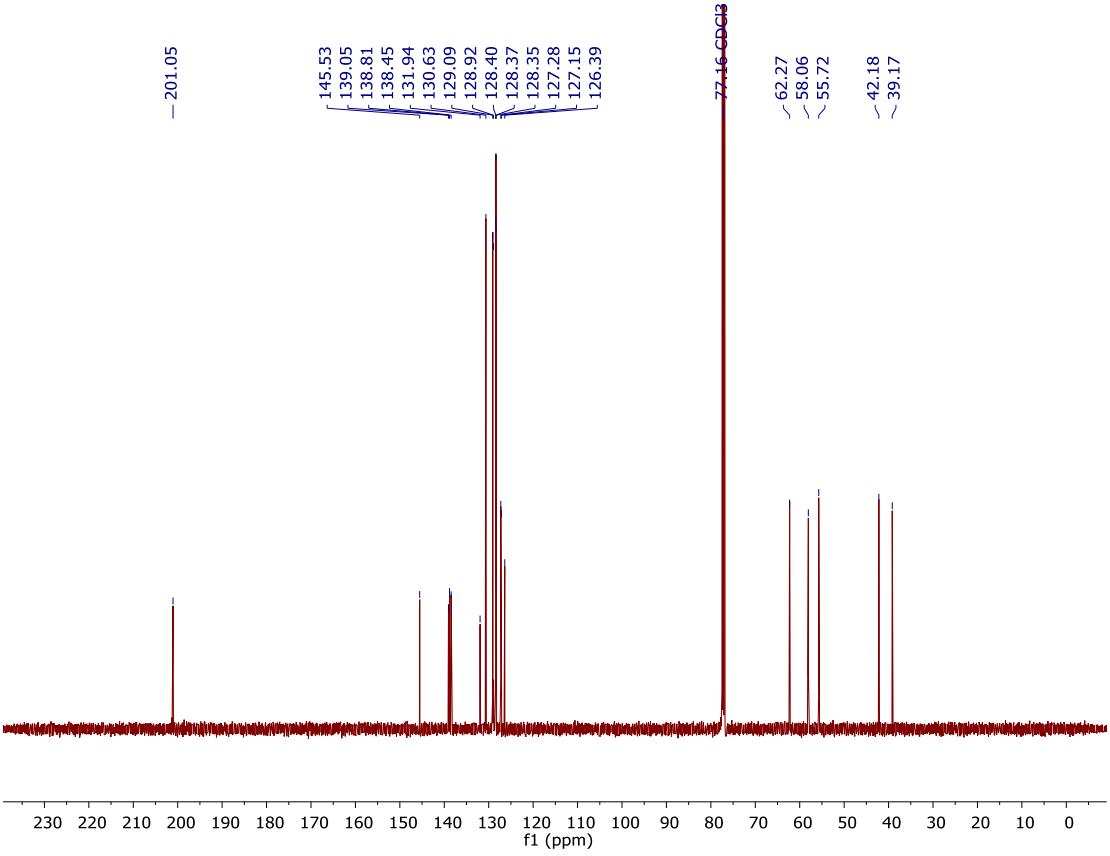
eshB2P106_rearr.3.fid
default deuterium parameters; spinning
Don't forget to turn off the field sweep
and set the lock power to minimum value!

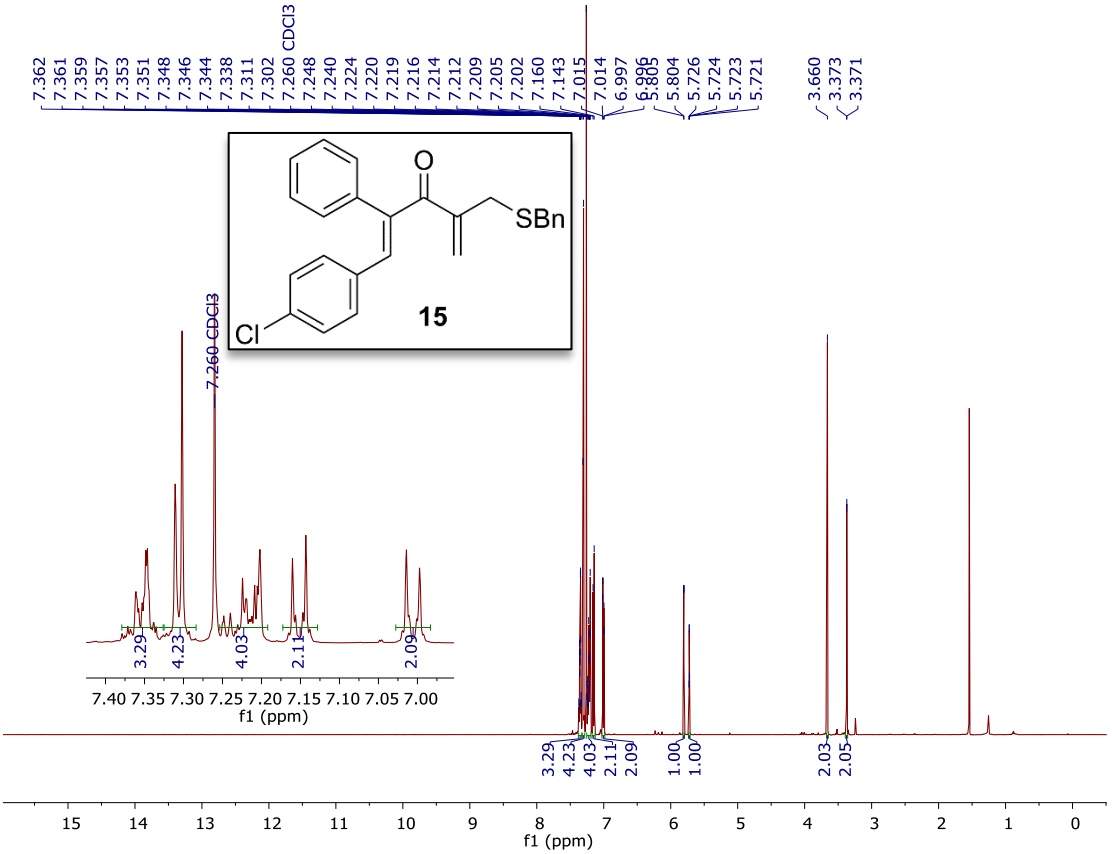
^{2}H NMR

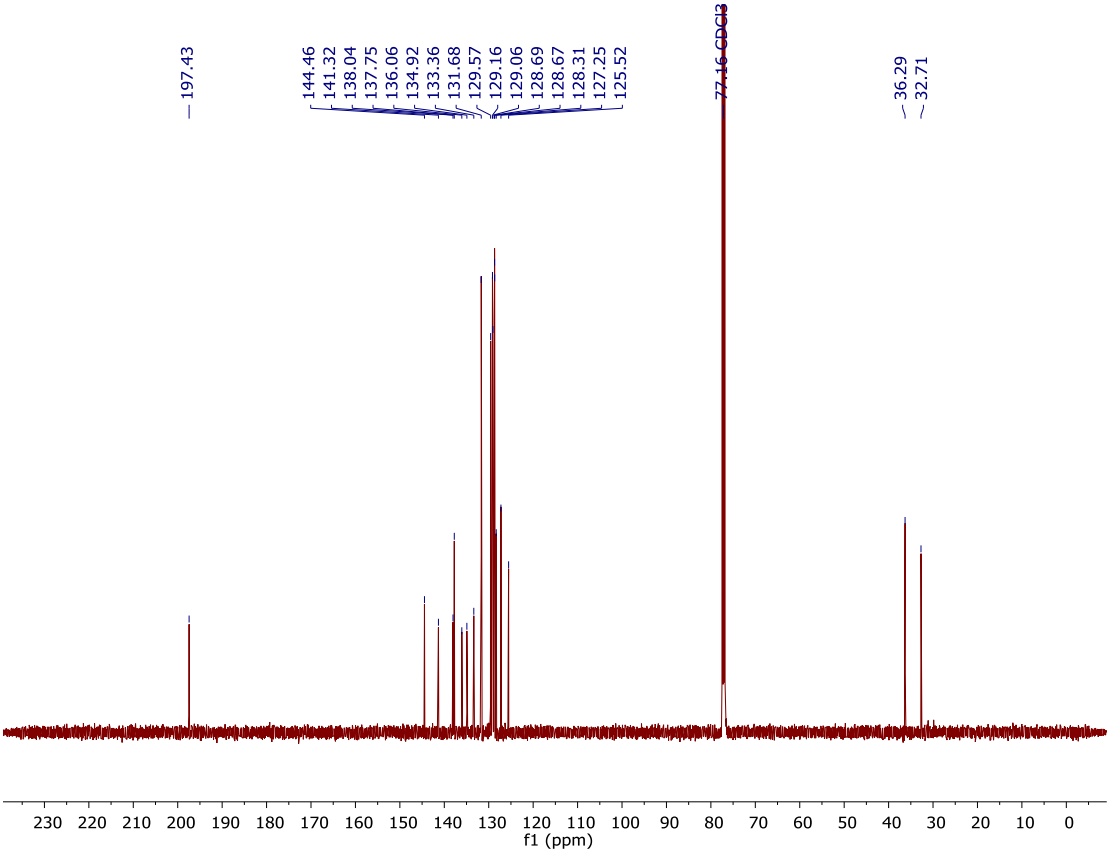


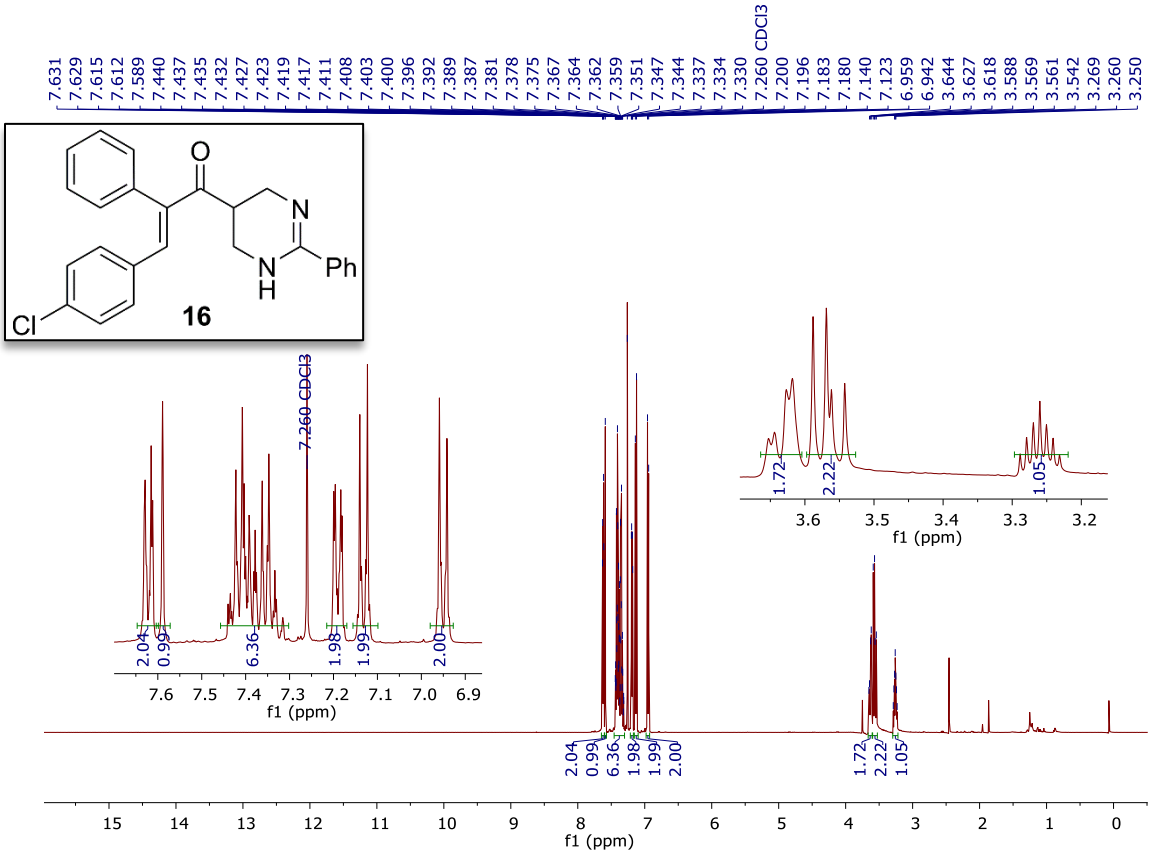

7.376
7.372
7.363
7.359
7.348
7.344
7.341
7.338
7.330
7.327
7.326
7.301
7.298
7.296
7.283
7.280
7.278
7.270
7.267
7.266
7.260
7.260 CDCl3
7.257
7.255
7.251
7.243
7.240
7.237
7.234
6.290
6.287
6.284
6.282
6.280
5.594
5.591
5.589
5.587
3.650
3.646
3.642
O
Cl
13
1.00
6.296.28
f1 (ppm)
1.01
5.60
5.58
f1 (ppm)
3.29
7.72
1.00
1.01
2.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
194.08
160.47
141.99
141.33
136.20
133.66
132.27
129.79
129.51
128.96
128.77
128.36
117.62
77.16 CDCl3
35.20
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

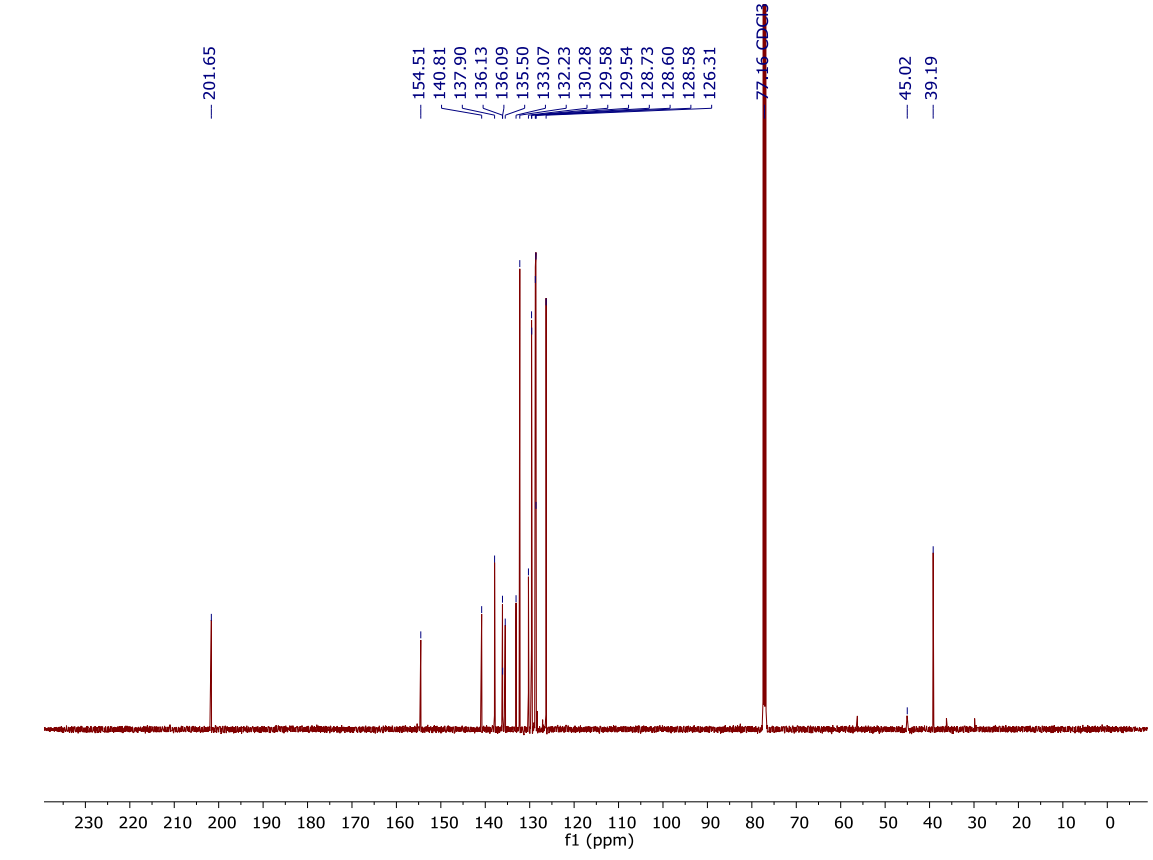

7.291 7.277 7.274 7.266 7.263 7.256 7.253 7.249 7.239 7.236 7.231 7.228 7.224 7.218 7.214 7.204 7.200 7.196 7.192 7.187 7.182 7.154 7.138 7.008 7.004 6.991 6.988 6.967 6.951 6.001 5.713 5.710 5.707 4.503 4.489 4.474 4.464 3.438 3.410 3.395 3.382 3.367 3.313 3.287 3.258 3.256 2.961 2.932 2.909 2.894 2.881 2.866 1.991
O
N
Bn
Me
Cl
14
1.03 1.07 2.08 1.02 1.06
4.04 4.93 2.11 2.01 2.10 1.00 1.00 1.03 1.03 1.07 2.08 1.02 1.06 3.02
f1 (ppm)

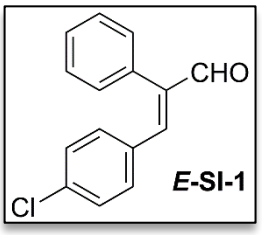

201.05
145.53 139.05 138.81 138.45 131.94 130.63 129.09 128.92 128.40 128.37 128.35 127.28 127.15 126.39
77.16 CDCl3
62.27 58.06 55.72 42.18 39.17
f1 (ppm)


7.362
7.361
7.359
7.357
7.353
7.351
7.348
7.346
7.344
7.338
7.311
7.302
7.260 CDCl3
7.248
7.240
7.224
7.220
7.219
7.216
7.214
7.212
7.209
7.205
7.202
7.160
7.143
7.015
7.014
6.997
6.996
6.995
5.804
5.726
5.724
5.723
5.721
3.660
3.373
3.371
O
SBn
Cl
15
7.260 CDCl3
3.29
4.23
4.03
2.11
2.09
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
3.29
4.23
4.03
2.11
2.09
1.00
1.00
2.03
2.05
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


197.43
144.46
141.32
138.04
137.75
136.06
134.92
133.36
131.68
129.57
129.16
129.06
128.69
128.67
128.31
127.25
125.52
77.16 CDCl3
36.29
32.71
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.631 7.629 7.615 7.612 7.589 7.440 7.437 7.435 7.432 7.427 7.423 7.419 7.417 7.411 7.408 7.403 7.400 7.396 7.392 7.389 7.387 7.381 7.378 7.375 7.367 7.364 7.362 7.359 7.351 7.347 7.344 7.337 7.334 7.330 7.260 CDCl3 7.200 7.196 7.183 7.180 7.140 7.123 6.959 6.942 3.644 3.627 3.618 3.588 3.569 3.561 3.542 3.269 3.260 3.250
O
N
N
H
Ph
Cl
16
7.260 CDCl3
2.04 0.99 6.36 1.98 1.99 2.00
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.72 2.22 1.05
3.6 3.5 3.4 3.3 3.2
f1 (ppm)
2.04 0.99 6.36 1.98 1.99 2.00 1.72 2.22 1.05
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


201.65
154.51 140.81 137.90 136.13 136.09 135.50 133.07 132.23 130.28 129.58 129.54 128.73 128.60 128.58 126.31
77.16 CDCl3
45.02 39.19
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CHO
Cl
E-SI-1

9.766
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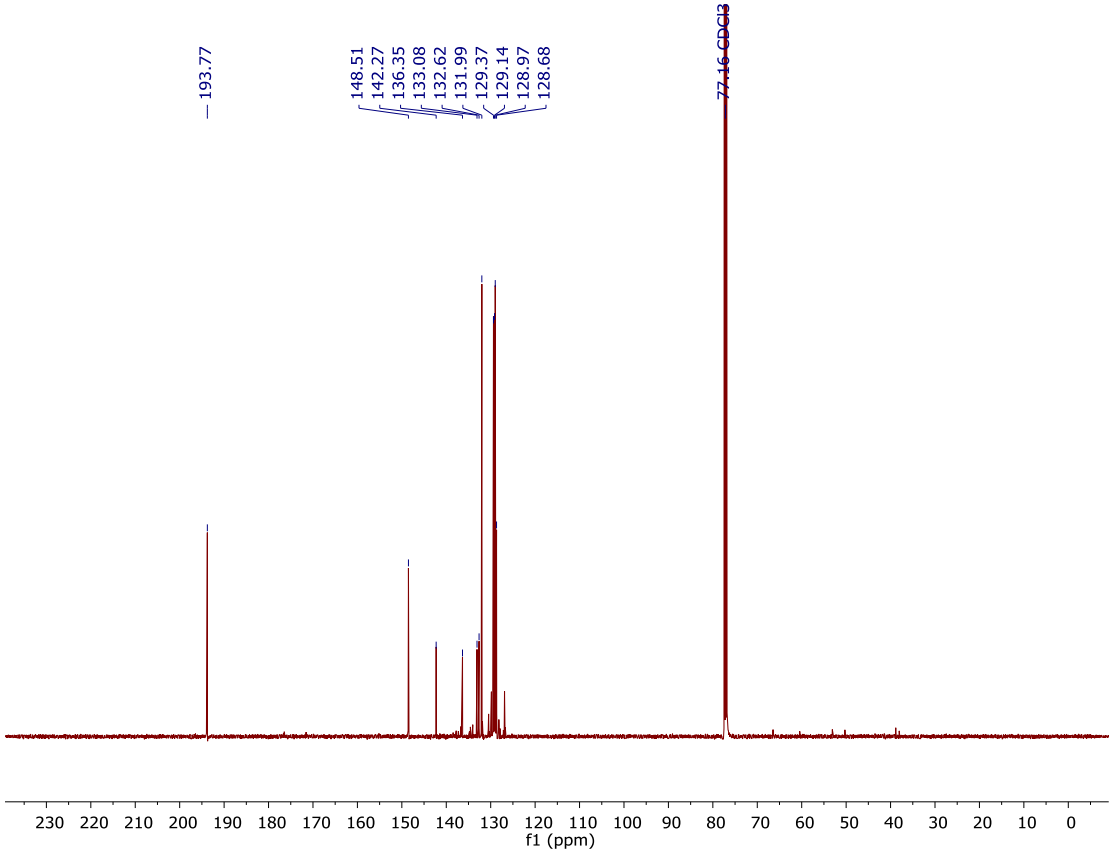
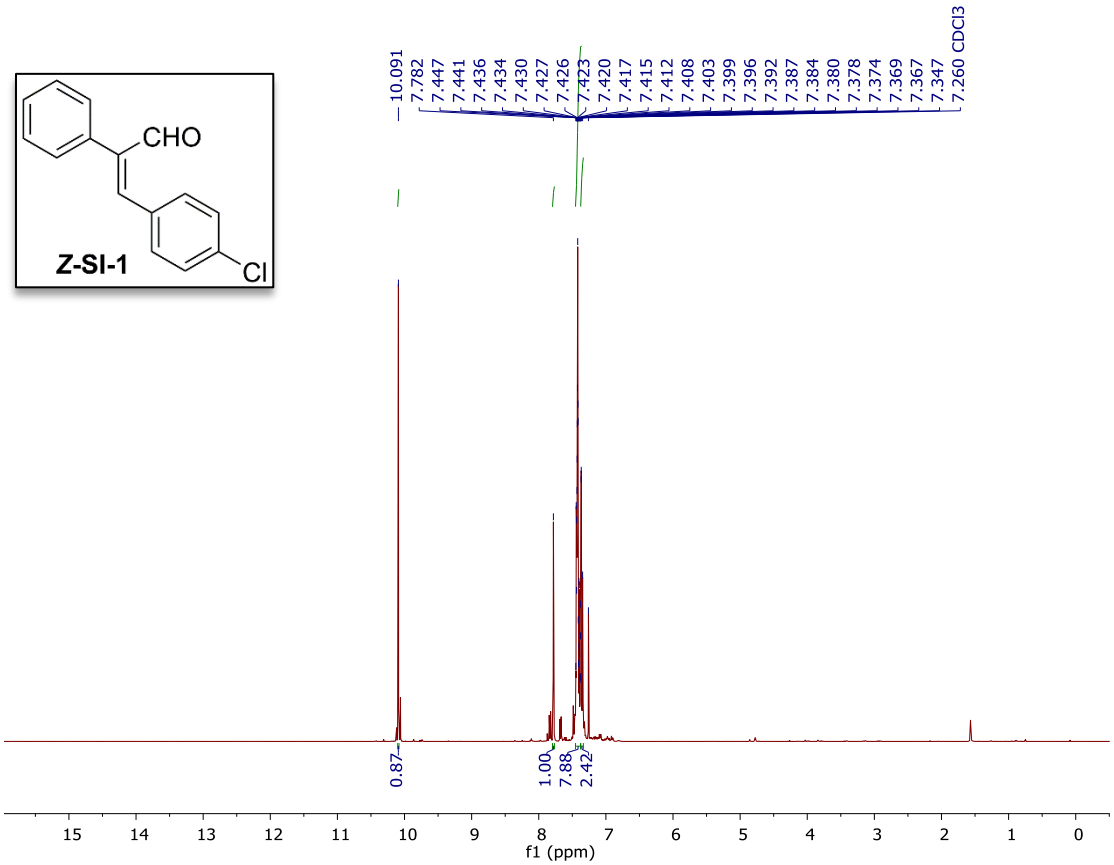
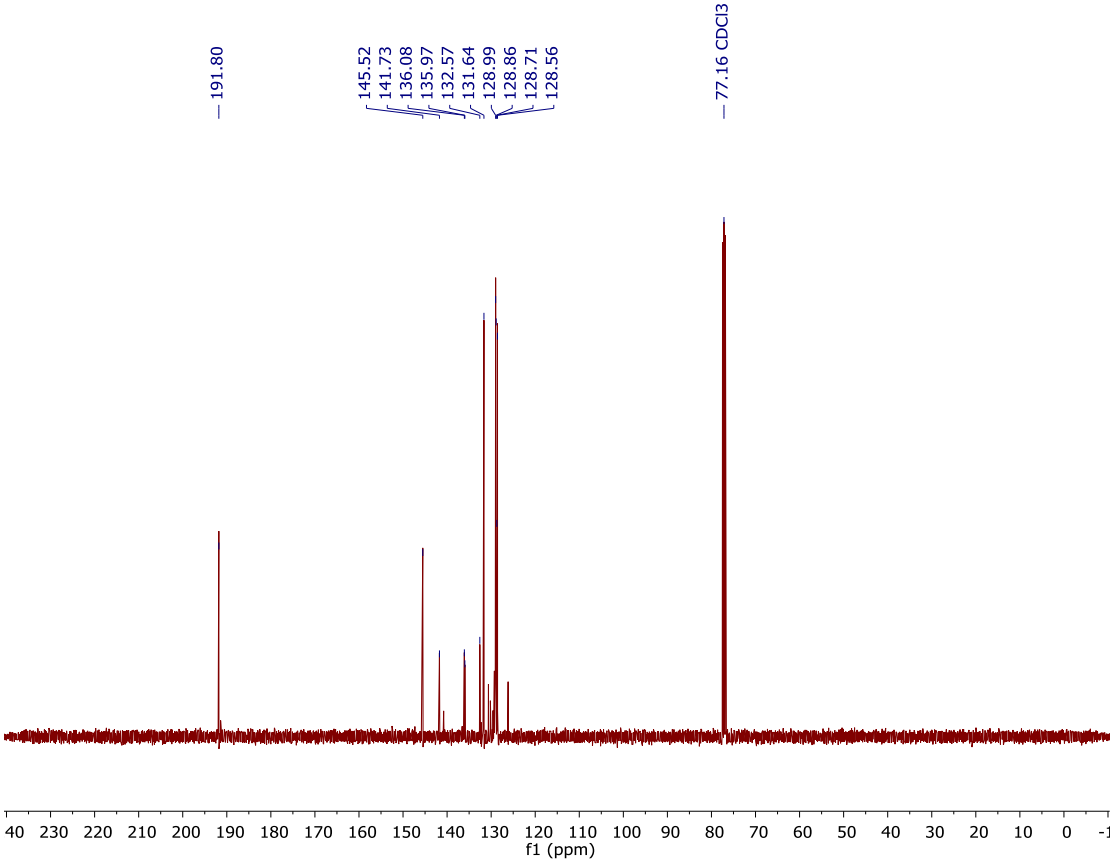
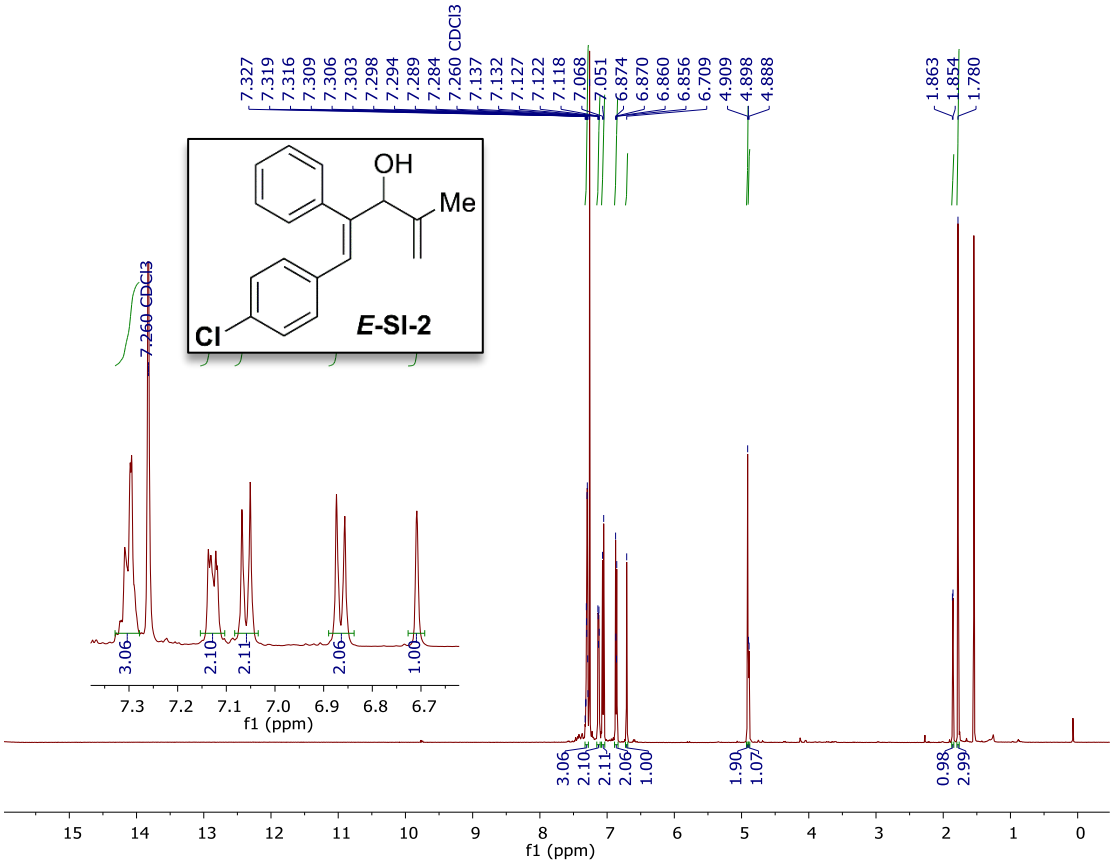
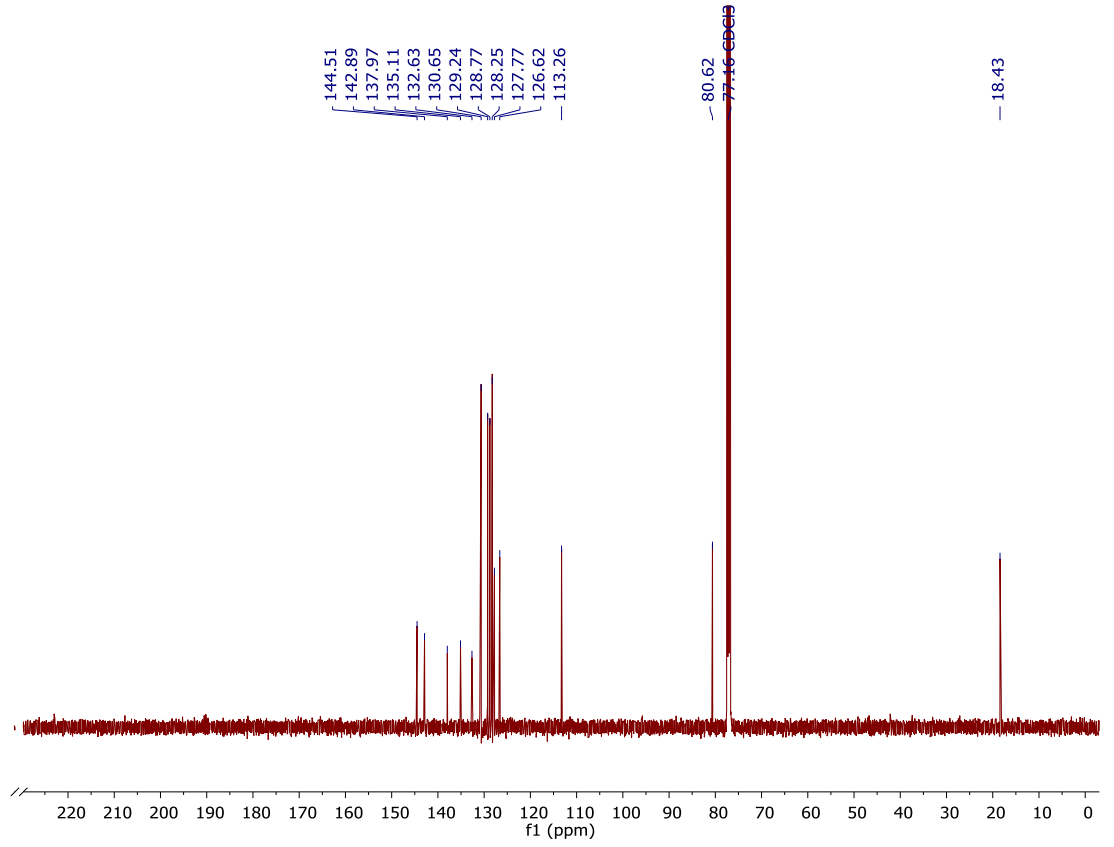
7.434
7.431
7.428
7.423
7.419
7.416
7.411
7.407
7.403
7.401
7.395
7.393
7.391
7.386
7.340
7.260 CDCl3
7.213
7.195
7.185
7.181
7.177
7.173
7.169
7.166
7.160
7.137
7.120
1.00
3.36
1.22
2.06
2.19
2.10
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
7.260 CDCl3
3.36
1.22
2.06
2.19
2.10
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)

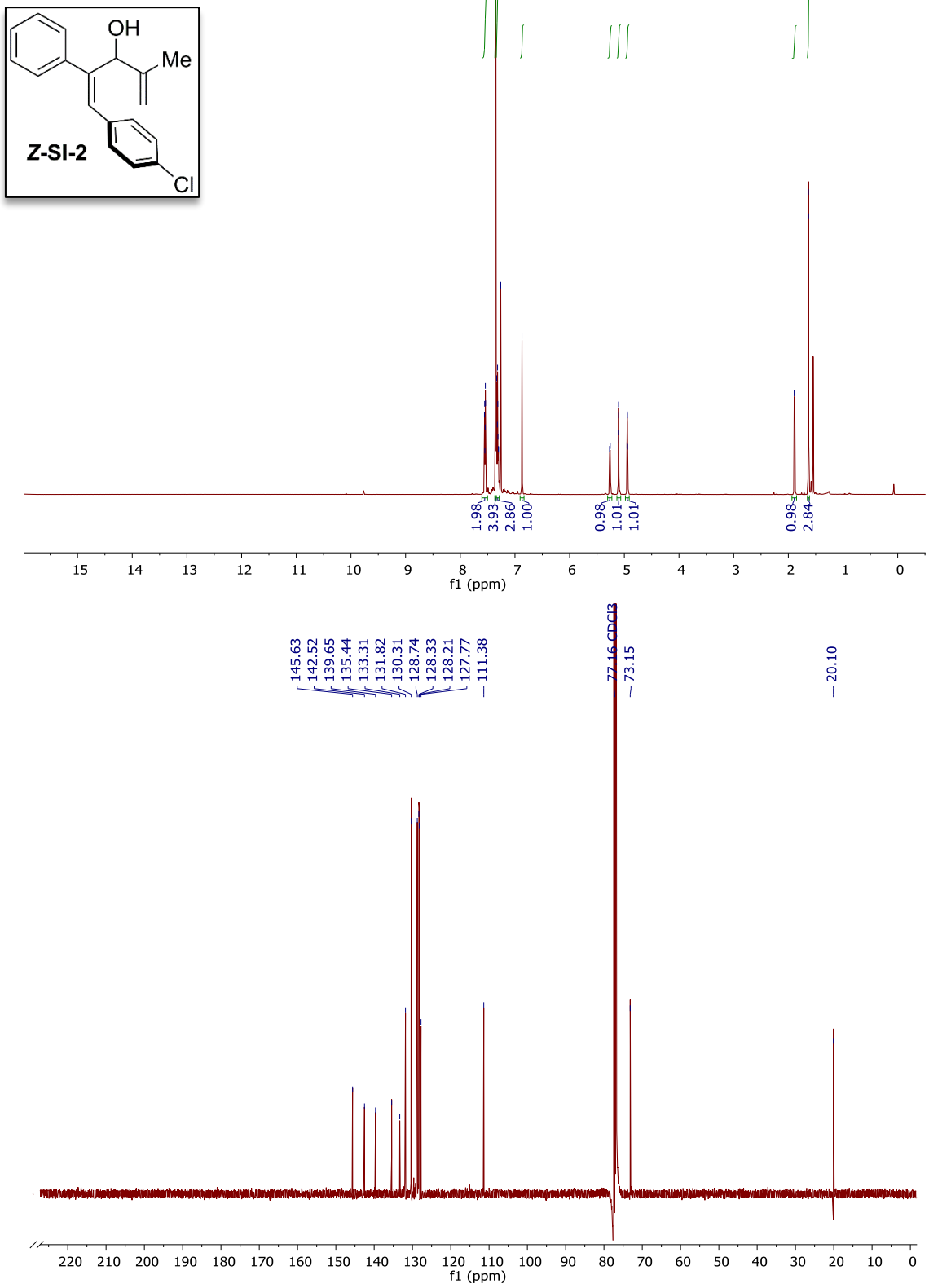

193.77
148.51
142.27
136.35
133.08
132.62
131.99
129.37
129.14
128.97
128.68
77.16 CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

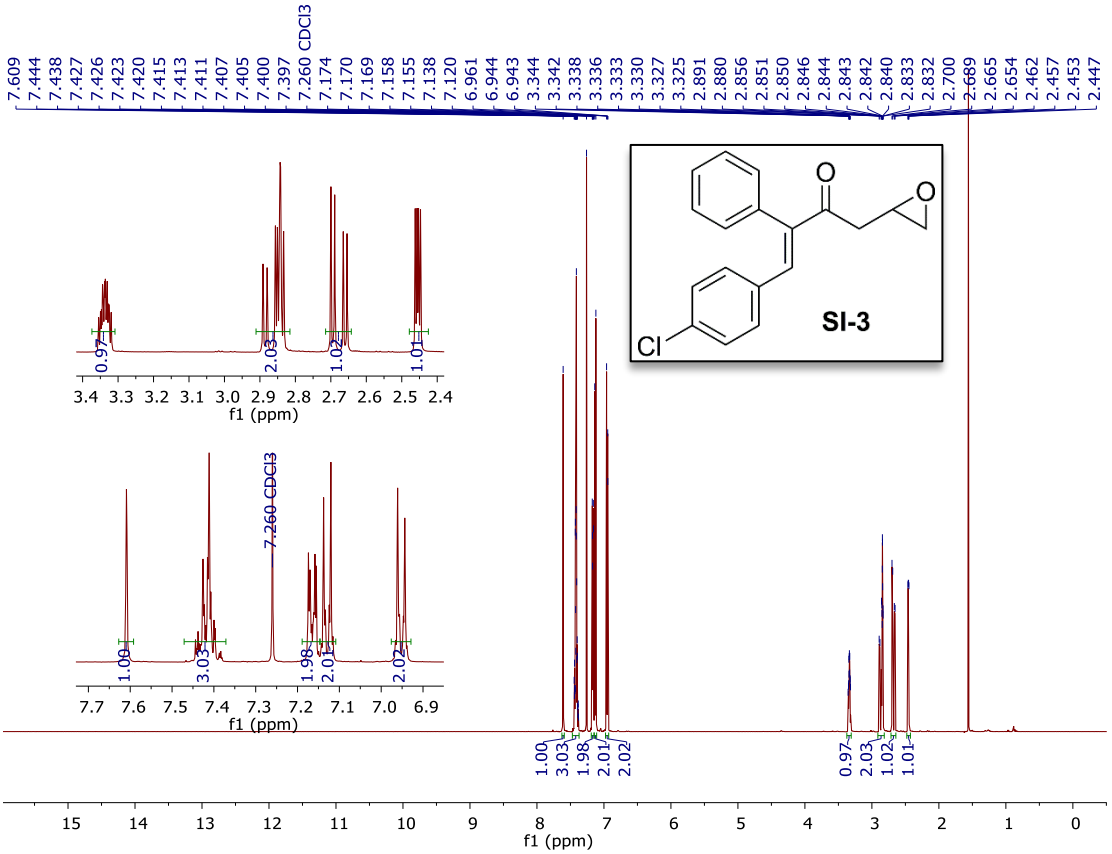

CHO
Cl
Z-SI-1
10.091
7.782
7.447
7.441
7.436
7.434
7.430
7.427
7.426
7.423
7.420
7.417
7.415
7.412
7.408
7.403
7.399
7.396
7.392
7.387
7.384
7.380
7.378
7.374
7.369
7.367
7.347
7.260 CDCl3
0.87
1.00
7.88
2.42
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

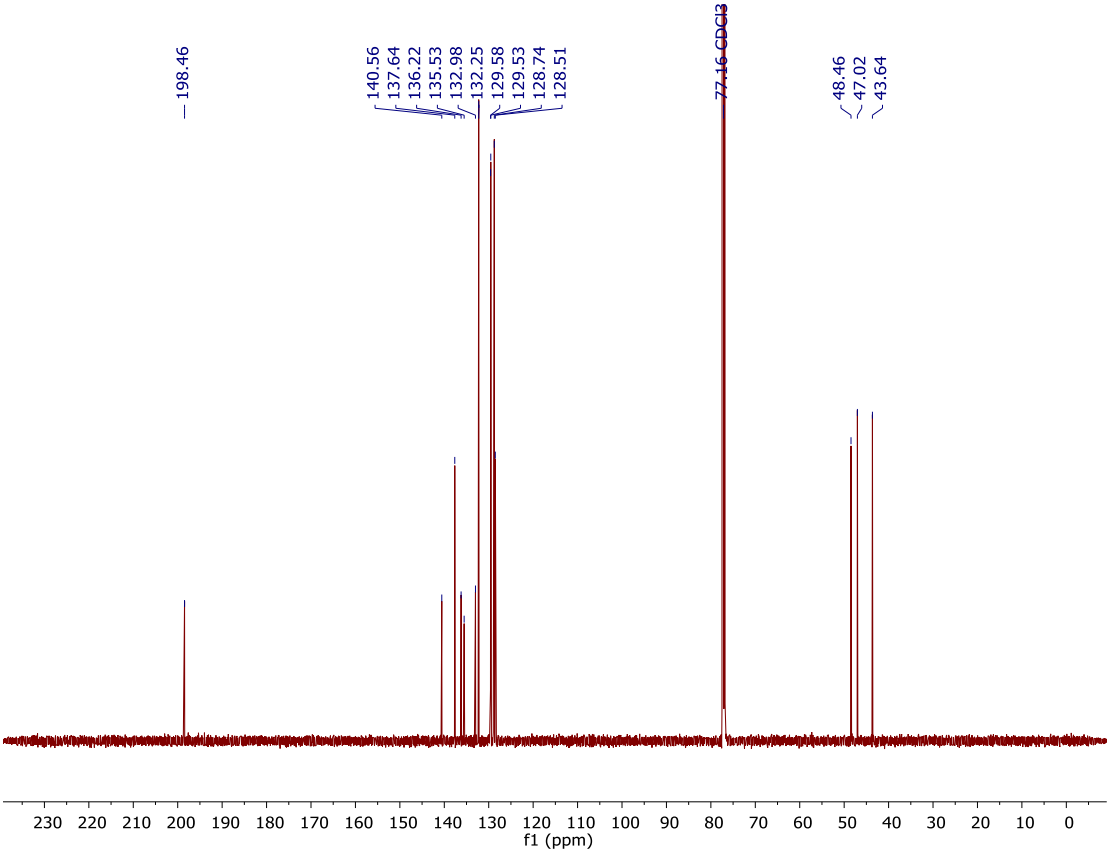

191.80
145.52
141.73
136.08
135.97
132.57
131.64
128.99
128.86
128.71
128.56
77.16 CDCl3
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

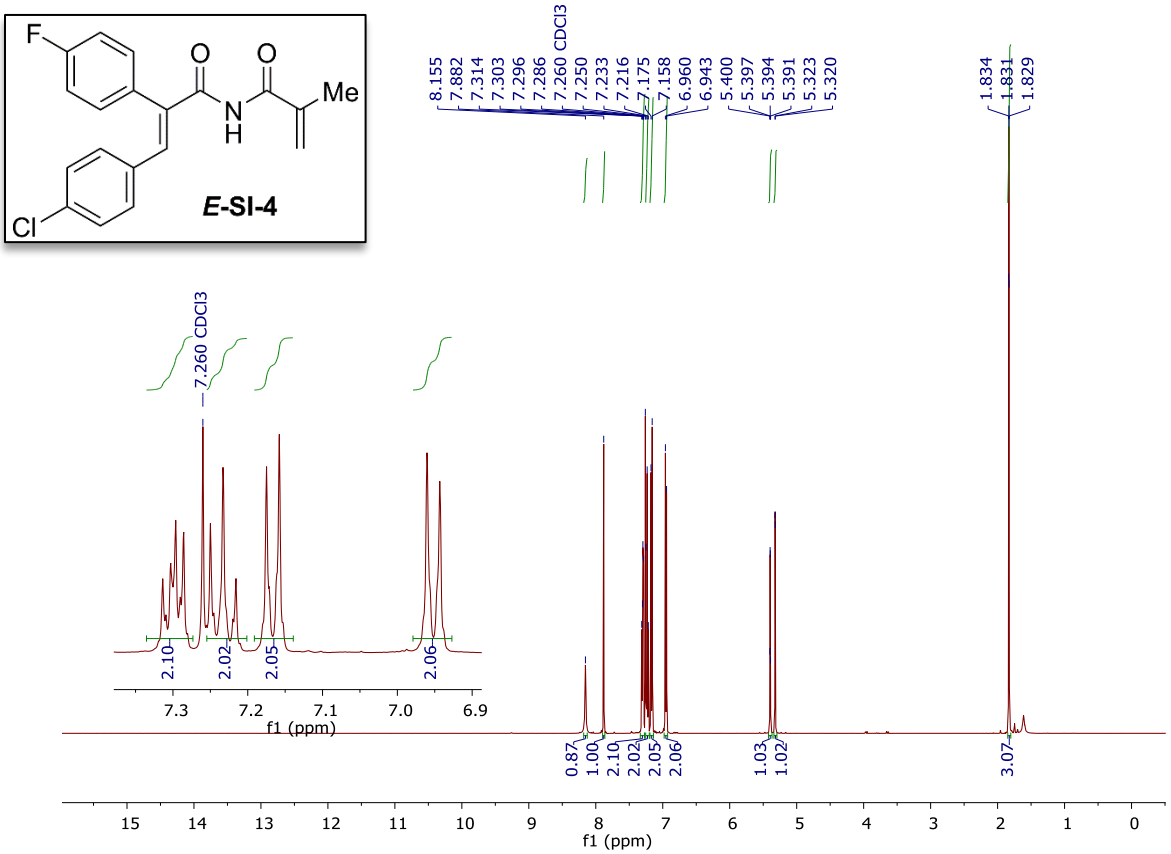

7.327
7.319
7.316
7.309
7.306
7.303
7.298
7.294
7.289
7.284
7.260 CDCl3
7.137
7.132
7.127
7.122
7.118
7.068
7.051
6.874
6.870
6.860
6.856
6.709
4.909
4.898
4.888
1.863
1.854
1.780
OH
Me
Cl
E-SI-2
3.06
2.10
2.11
2.06
1.00
1.90
1.07
0.98
2.99
f1 (ppm)

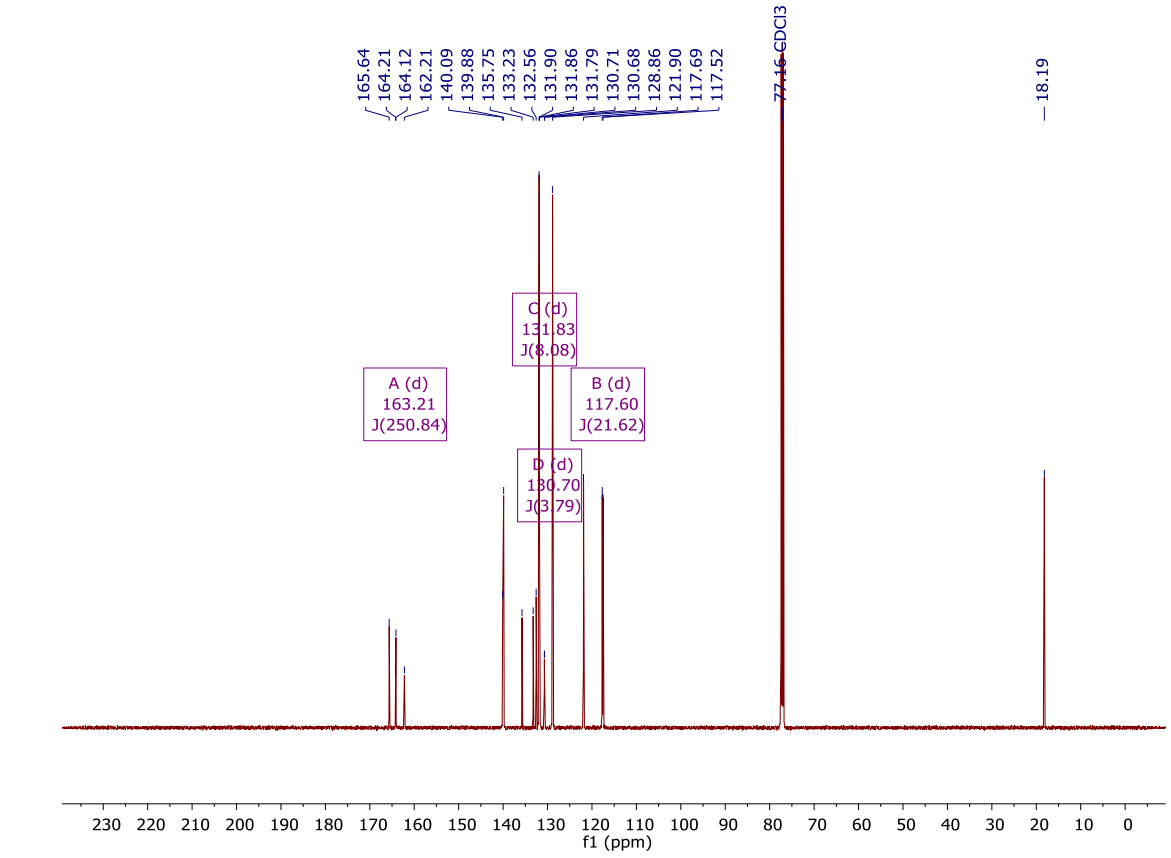

144.51
142.89
137.97
135.11
132.63
130.65
129.24
128.77
128.25
127.77
126.62
113.26
80.62
77.16 CDCl3
18.43
f1 (ppm)

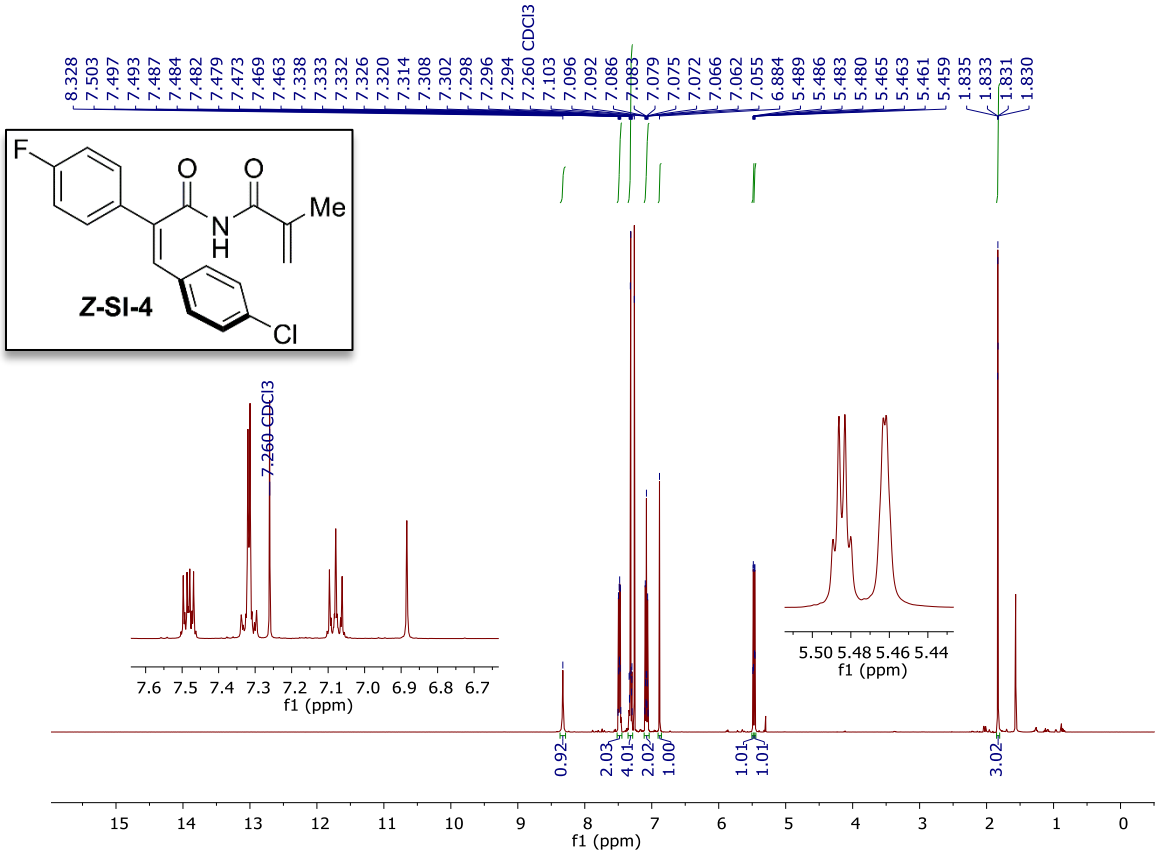

OH
Me
Cl
Z-SI-2
7.558
7.555
7.551
7.545
7.542
7.539
7.352
7.334
7.323
7.319
7.315
7.312
7.302
7.301
7.260
CDCl3
6.872
5.270
5.258
5.108
5.105
5.103
5.101
4.951
4.948
4.944
4.941
1.893
1.882
1.634
1.631
1.98
3.93
2.86
1.00
0.98
1.01
1.01
0.98
2.84
f1 (ppm)
145.63
142.52
139.65
135.44
133.31
131.82
130.31
128.74
128.33
128.21
127.77
111.38
77.16
CDCl3
73.15
20.10
f1 (ppm)

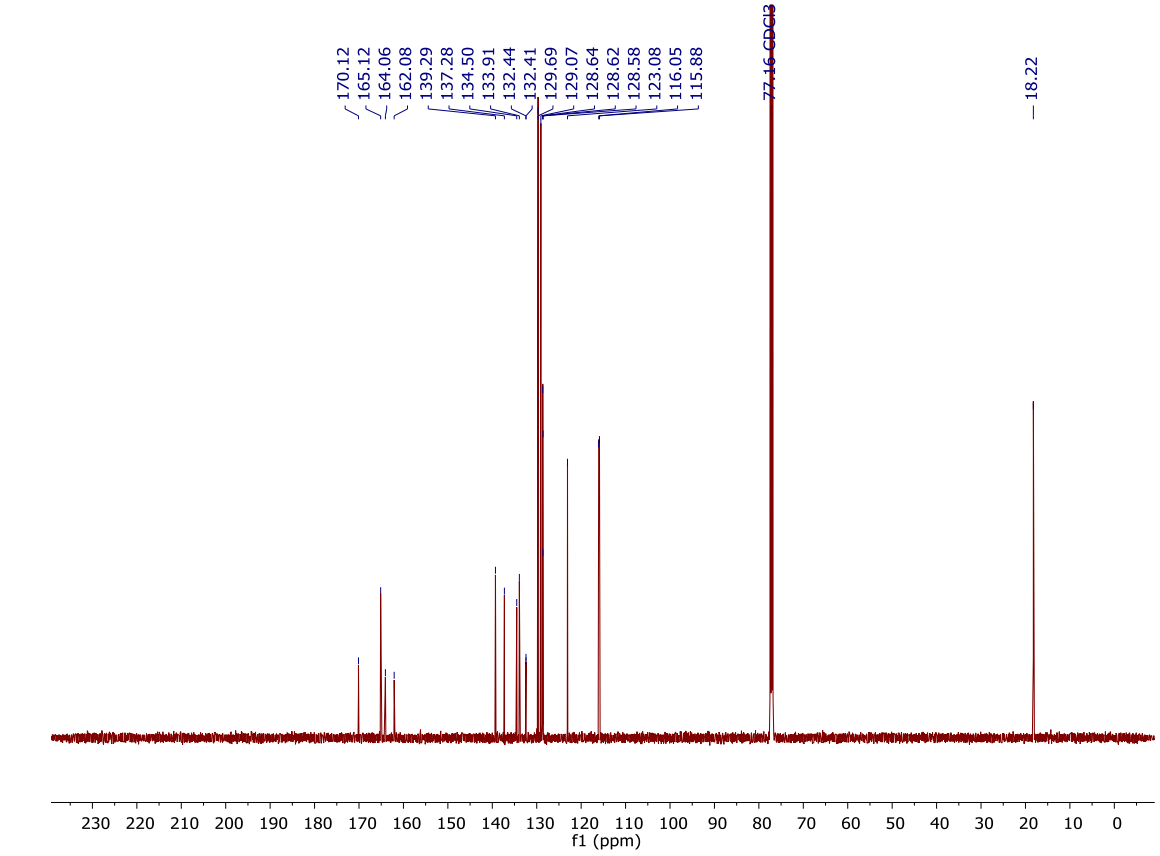

7.609 7.444 7.438 7.427 7.426 7.423 7.420 7.415 7.413 7.411 7.407 7.405 7.400 7.397 7.260 CDCl3 7.174 7.170 7.169 7.158 7.155 7.138 7.120 6.961 6.944 6.943 3.344 3.342 3.338 3.336 3.333 3.330 3.327 3.325 2.891 2.880 2.856 2.851 2.850 2.846 2.844 2.843 2.842 2.840 2.833 2.832 2.700 2.689 2.665 2.654 2.462 2.457 2.453 2.447
O
O
Cl
SI-3
0.97 2.03 1.02 1.01
3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4
f1 (ppm)
1.00 3.03 1.98 2.01 2.02
0.97 2.03 1.02 1.01
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

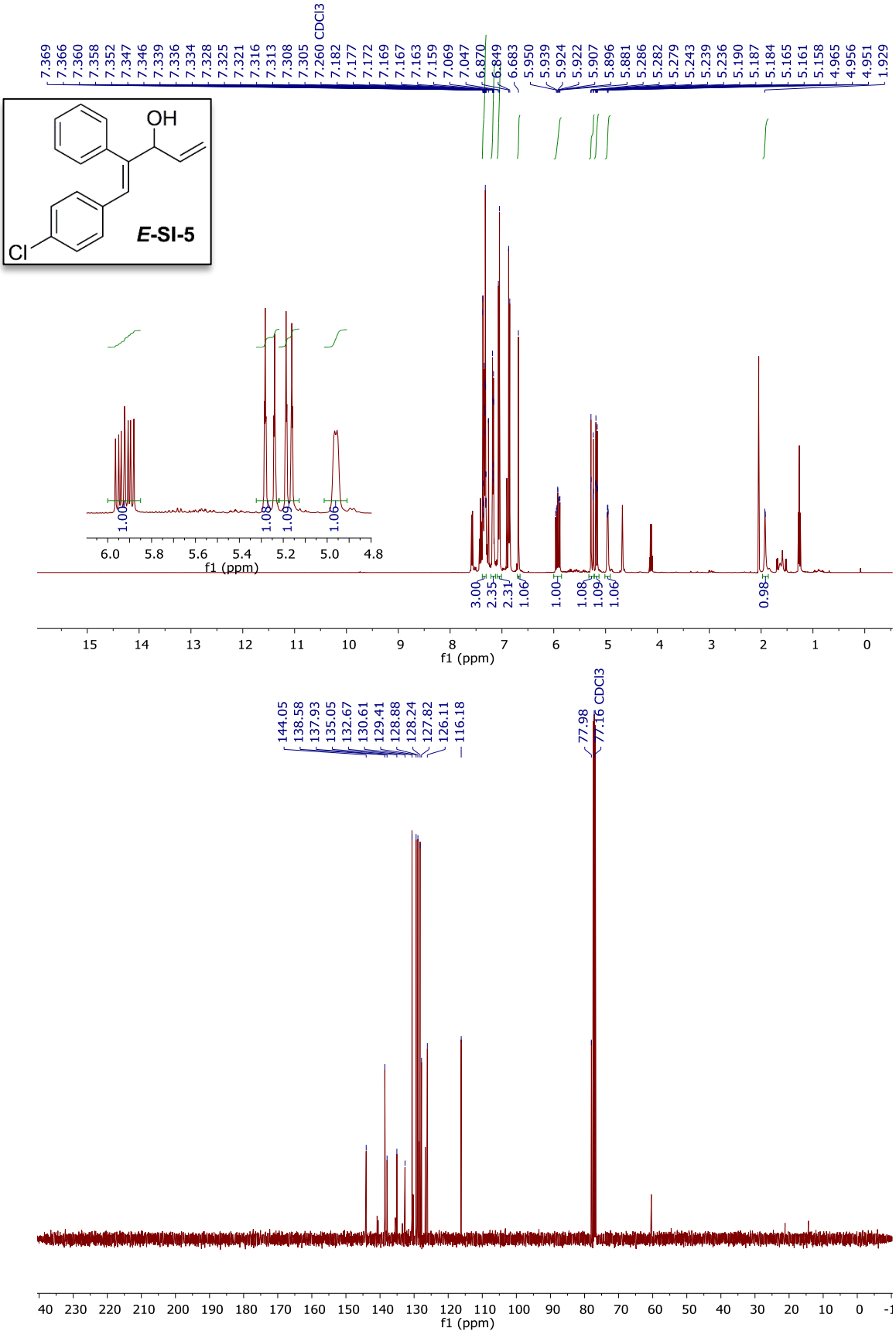

198.46
140.56 137.64 136.22 135.53 132.98 132.25 129.58 129.53 128.74 128.51
77.16 CDCl3
48.46 47.02 43.64
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

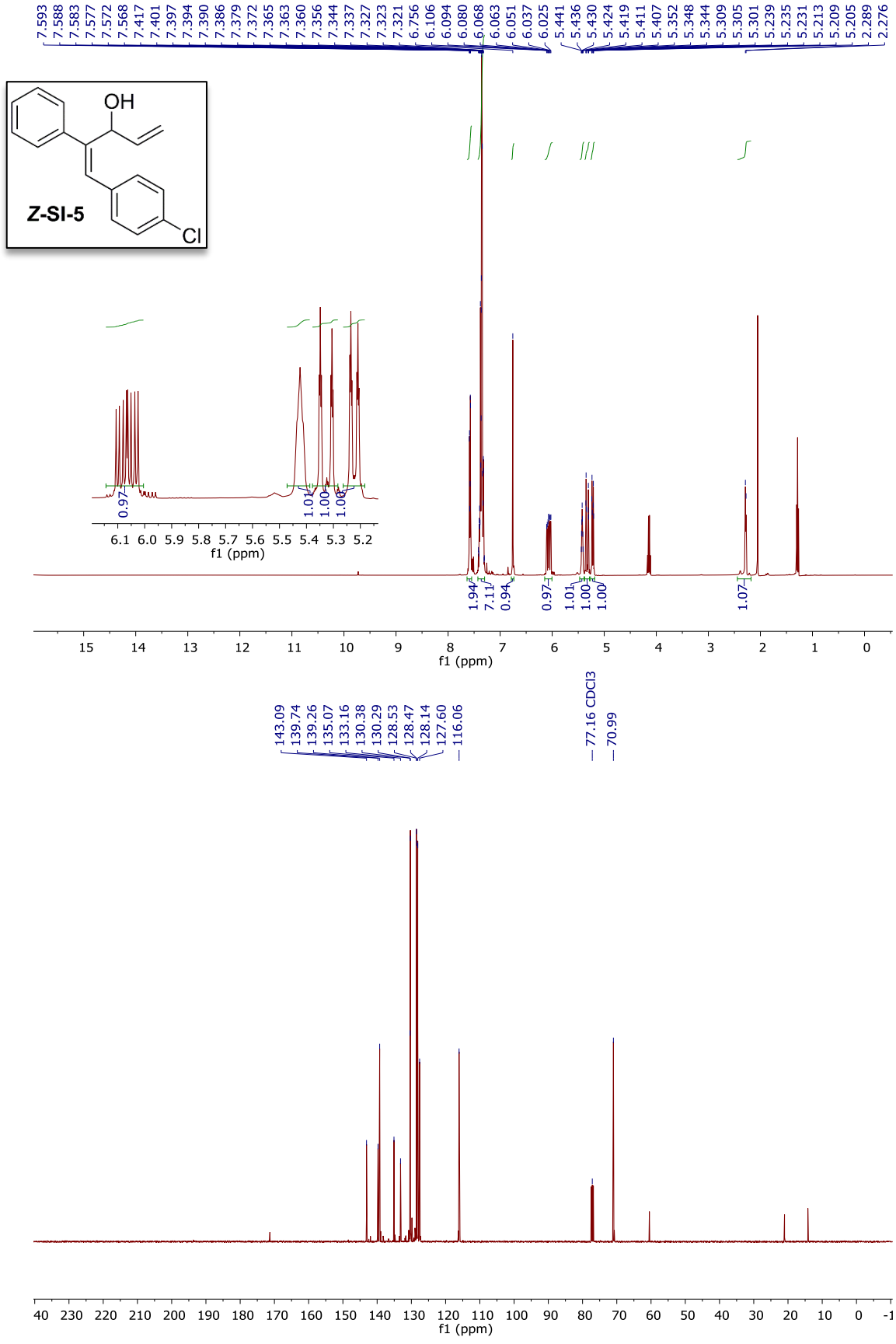

F
O
O
N
H
Me
Cl
E-SI-4
8.155
7.882
7.314
7.303
7.296
7.286
7.260 CDCl3
7.250
7.233
7.216
7.175
7.158
6.960
6.943
5.400
5.397
5.394
5.391
5.323
5.320
1.834
1.831
1.829
7.260 CDCl3
2.10
2.02
2.05
2.06
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
0.87
1.00
2.10
2.02
2.05
2.06
1.03
1.02
3.07
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


165.64
164.21
164.12
162.21
140.09
139.88
135.75
133.23
132.56
131.90
131.86
131.79
130.71
130.68
128.86
121.90
117.69
117.52
77.16 CDCl3
18.19
C (d)
131.83
J(8.08)
A (d)
163.21
J(250.84)
B (d)
117.60
J(21.62)
D (d)
130.70
J(3.79)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.328
7.503
7.497
7.493
7.487
7.484
7.482
7.479
7.473
7.469
7.463
7.338
7.333
7.332
7.326
7.320
7.314
7.308
7.302
7.298
7.296
7.294
7.260 CDCl3
7.103
7.096
7.092
7.086
7.083
7.079
7.075
7.072
7.066
7.062
7.055
6.884
5.489
5.486
5.483
5.480
5.465
5.463
5.461
5.459
1.835
1.833
1.831
1.830
F
O
O
N
H
Me
Cl
Z-SI-4
7.260 CDCl3
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
5.50 5.48 5.46 5.44
f1 (ppm)
0.92
2.03
4.01
2.02
1.00
1.01
1.01
3.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


170.12
165.12
164.06
162.08
139.29
137.28
134.50
133.91
132.44
132.41
129.69
129.07
128.64
128.62
128.58
123.08
116.05
115.88
77.16 CDCl3
18.22
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.369
7.366
7.360
7.358
7.352
7.347
7.346
7.339
7.336
7.334
7.328
7.325
7.321
7.316
7.313
7.308
7.305
7.260 CDCl3
7.182
7.177
7.172
7.169
7.167
7.163
7.159
7.069
7.047
6.870
6.849
6.683
5.950
5.939
5.924
5.922
5.907
5.896
5.881
5.286
5.282
5.279
5.243
5.239
5.236
5.190
5.187
5.184
5.165
5.161
5.158
4.965
4.956
4.951
1.929
OH
Cl
E-SI-5
1.00
1.08
1.09
1.06
6.0
5.8
5.6
5.4
5.2
5.0
4.8
f1 (ppm)
3.00
2.35
2.31
1.06
1.00
1.08
1.09
1.06
0.98
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
144.05
138.58
137.93
135.05
132.67
130.61
129.41
128.88
128.24
127.82
126.11
116.18
77.98
77.16 CDCl3
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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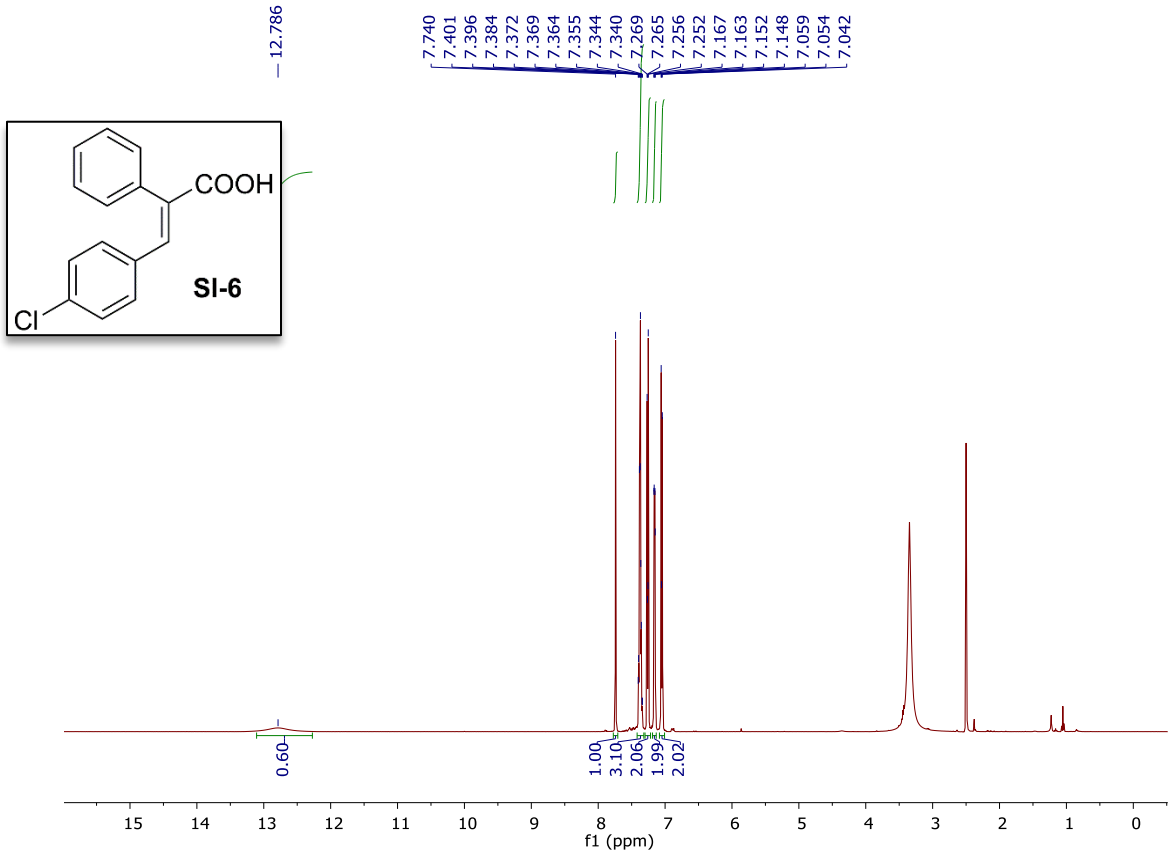
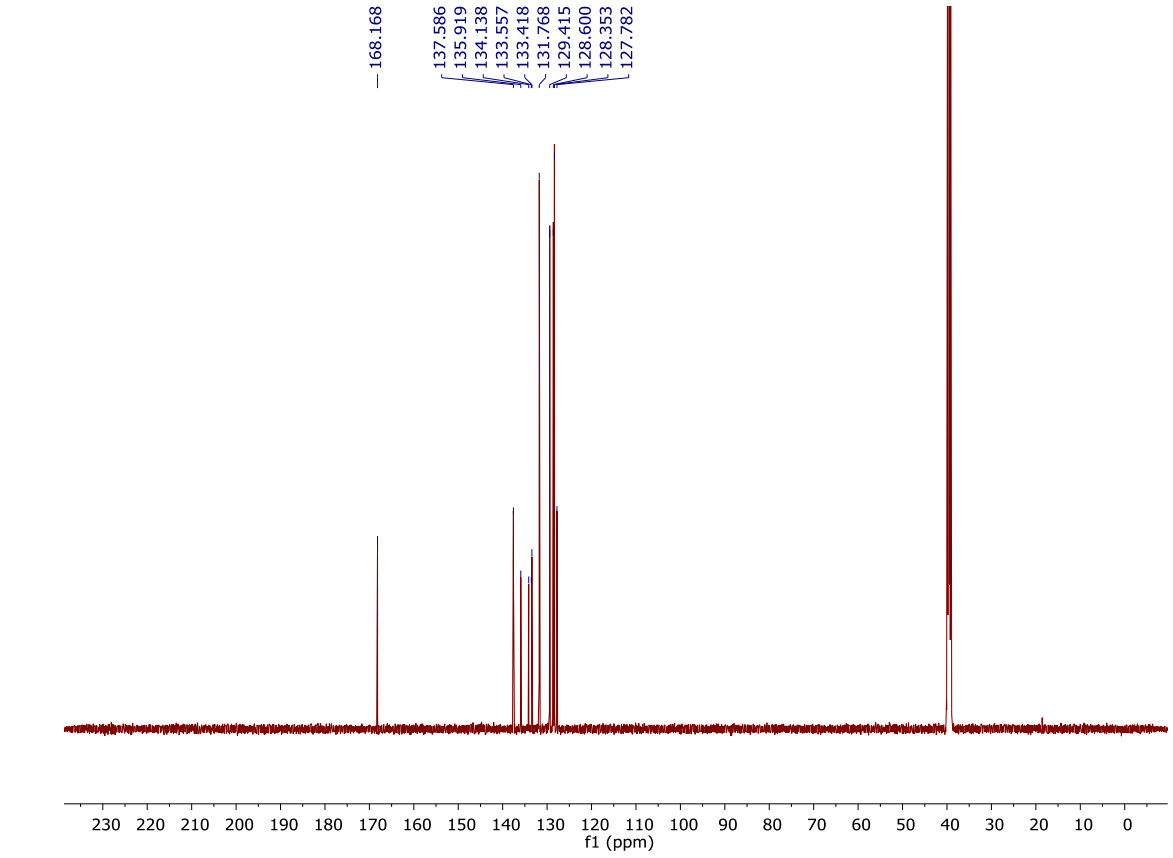
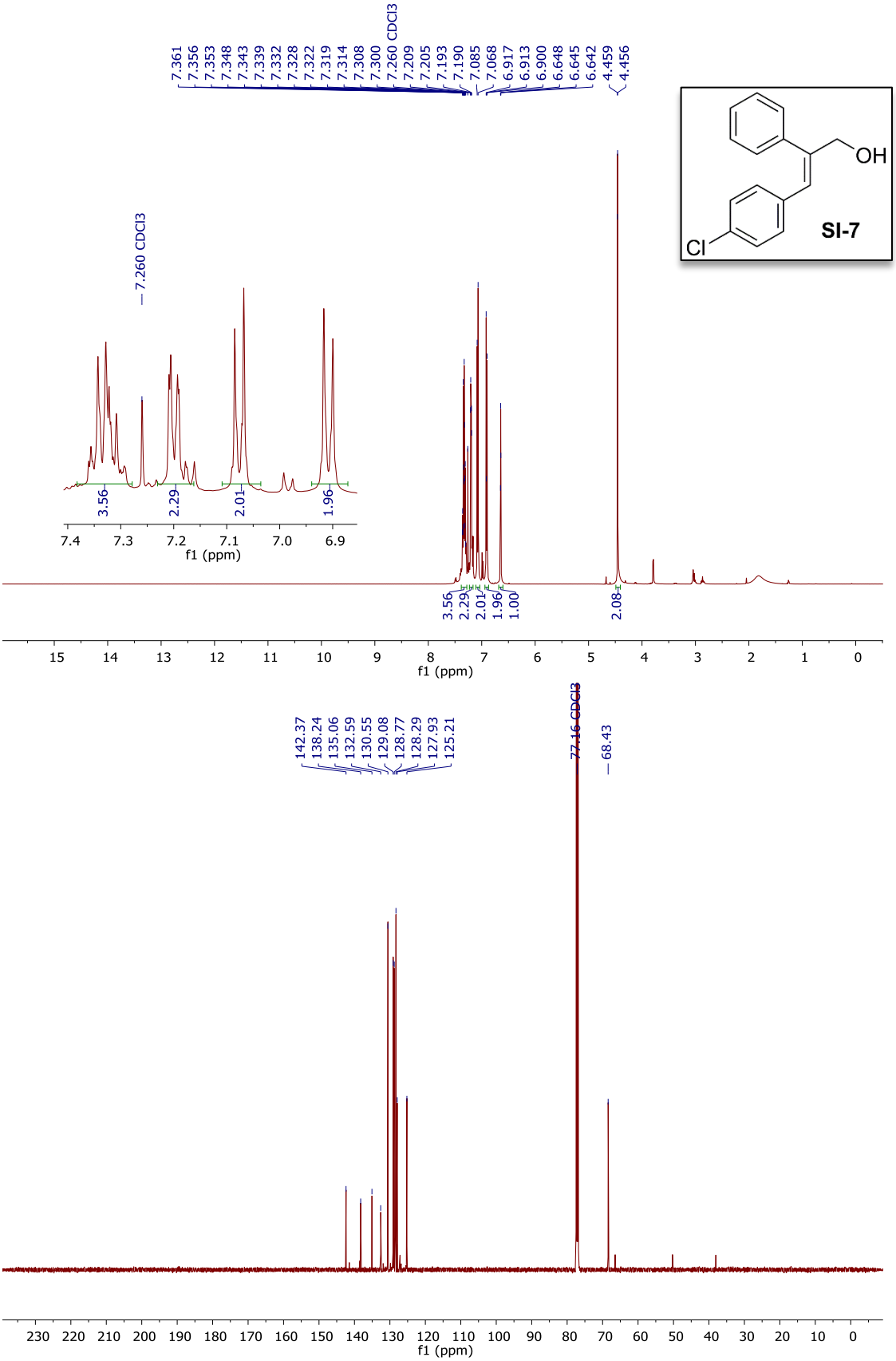
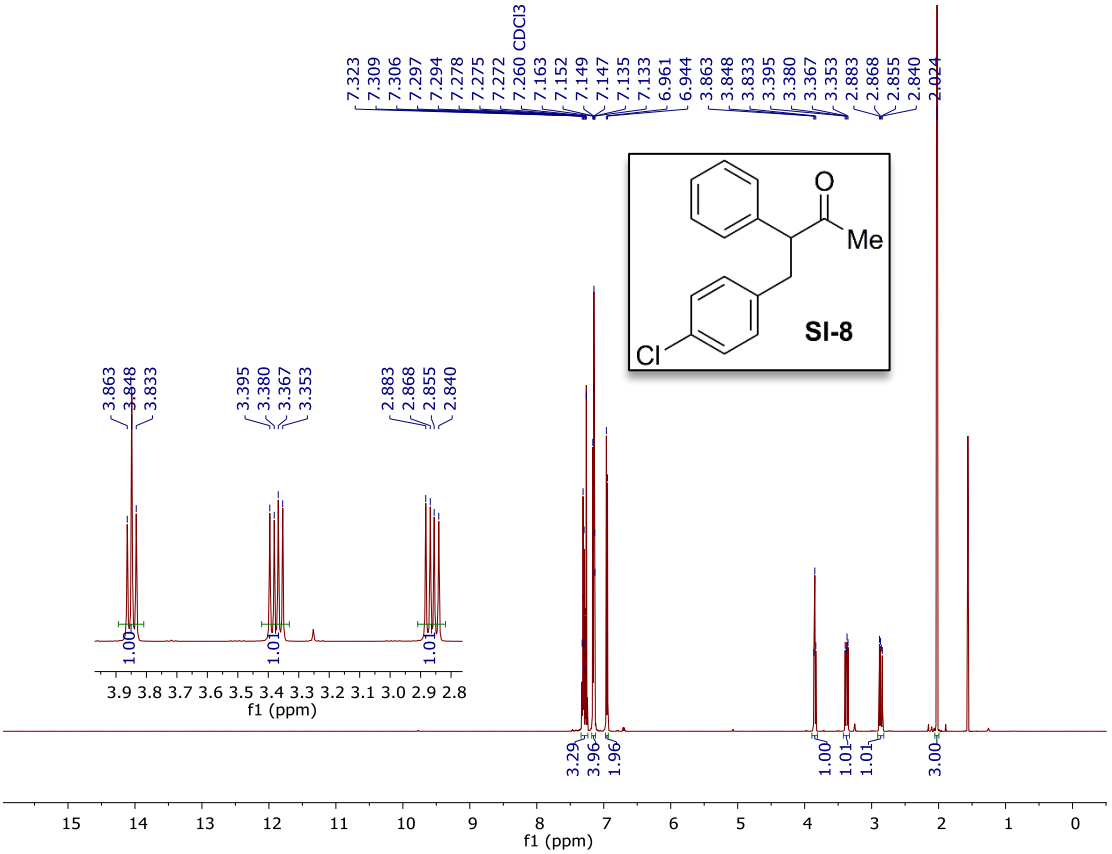
7.588
7.583
7.577
7.572
7.568
7.417
7.401
7.397
7.394
7.390
7.386
7.379
7.372
7.365
7.363
7.360
7.356
7.344
7.337
7.327
7.323
7.321
6.756
6.106
6.094
6.080
6.068
6.063
6.051
6.037
6.025
5.441
5.436
5.430
5.424
5.419
5.411
5.407
5.352
5.348
5.344
5.309
5.305
5.301
5.239
5.235
5.231
5.213
5.209
5.205
2.289
2.276
OH
Z-SI-5
Cl
0.97
1.01
1.00
1.08
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2
f1 (ppm)
1.94
7.11
0.94
0.97
1.01
1.00
1.00
1.07
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
143.09
139.74
139.26
135.07
133.16
130.38
130.29
128.53
128.47
128.14
127.60
116.06
77.16 CDCl3
70.99
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


12.786
7.740
7.401
7.396
7.384
7.372
7.369
7.364
7.355
7.344
7.340
7.269
7.265
7.256
7.252
7.167
7.163
7.152
7.148
7.059
7.054
7.042
COOH
Cl
SI-6
0.60
1.00
3.10
2.06
1.99
2.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


168.168
137.586
135.919
134.138
133.557
133.418
131.768
129.415
128.600
128.353
127.782
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.361
7.356
7.353
7.348
7.343
7.339
7.332
7.328
7.322
7.319
7.314
7.308
7.300
7.260 CDCl3
7.209
7.205
7.193
7.190
7.085
7.068
6.917
6.913
6.900
6.648
6.645
6.642
4.459
4.456
OH
Cl
SI-7
7.260 CDCl3
3.56
2.29
2.01
1.96
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
3.56
2.29
2.01
1.96
1.00
2.08
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
142.37
138.24
135.06
132.59
130.55
129.08
128.77
128.29
127.93
125.21
77.16 CDCl3
68.43
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.323
7.309
7.306
7.297
7.294
7.278
7.275
7.272
7.260 CDCl3
7.163
7.152
7.149
7.147
7.135
7.133
6.961
6.944
3.863
3.848
3.833
3.395
3.380
3.367
3.353
2.883
2.868
2.855
2.840
2.024
O
Me
Cl
SI-8
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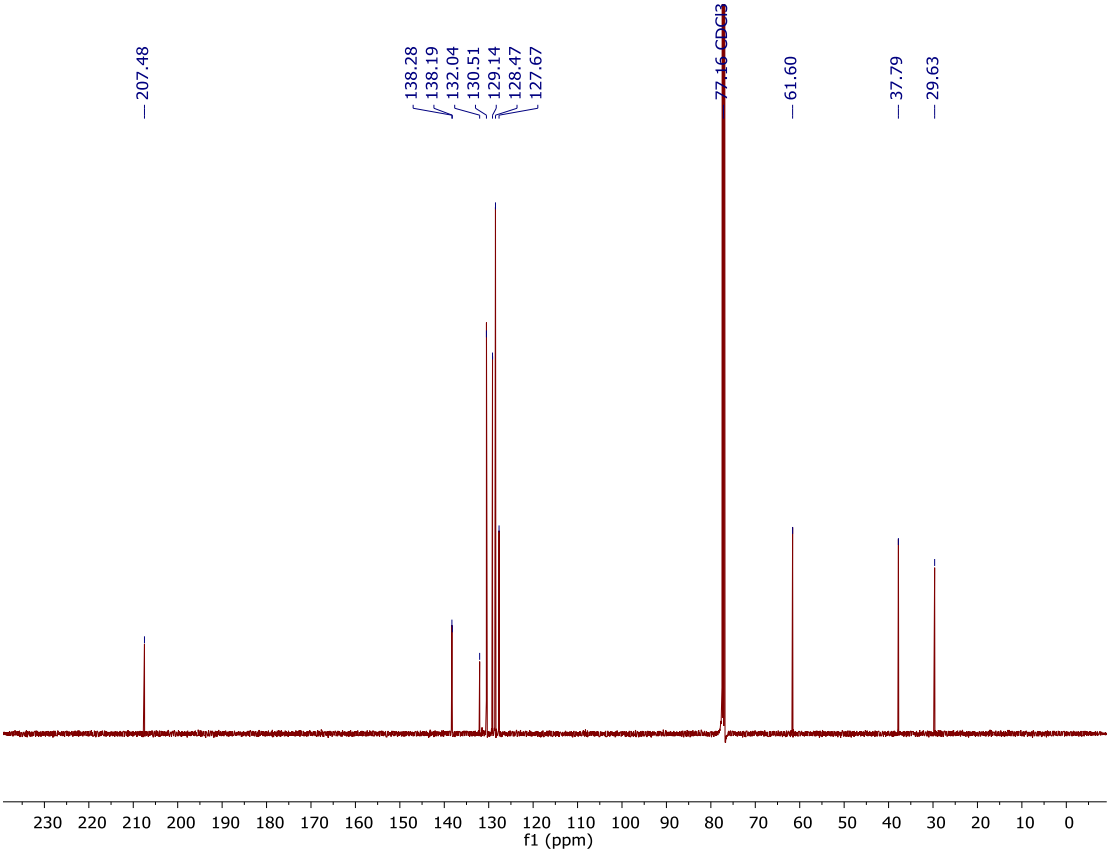
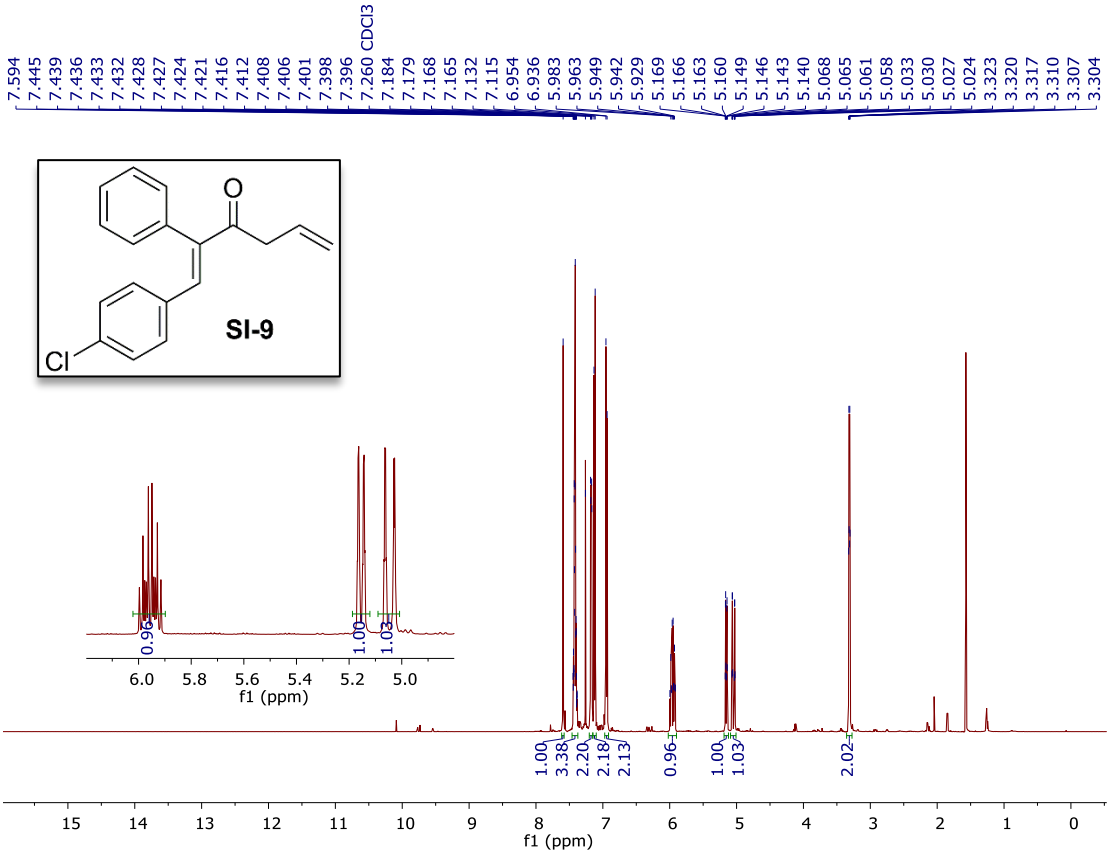
1.01
1.01
3.29
3.96
1.96
1.00
1.01
1.01
3.00
f1 (ppm)


207.48
138.28
138.19
132.04
130.51
129.14
128.47
127.67
77.16 CDCl3
61.60
37.79
29.63
f1 (ppm)


7.594
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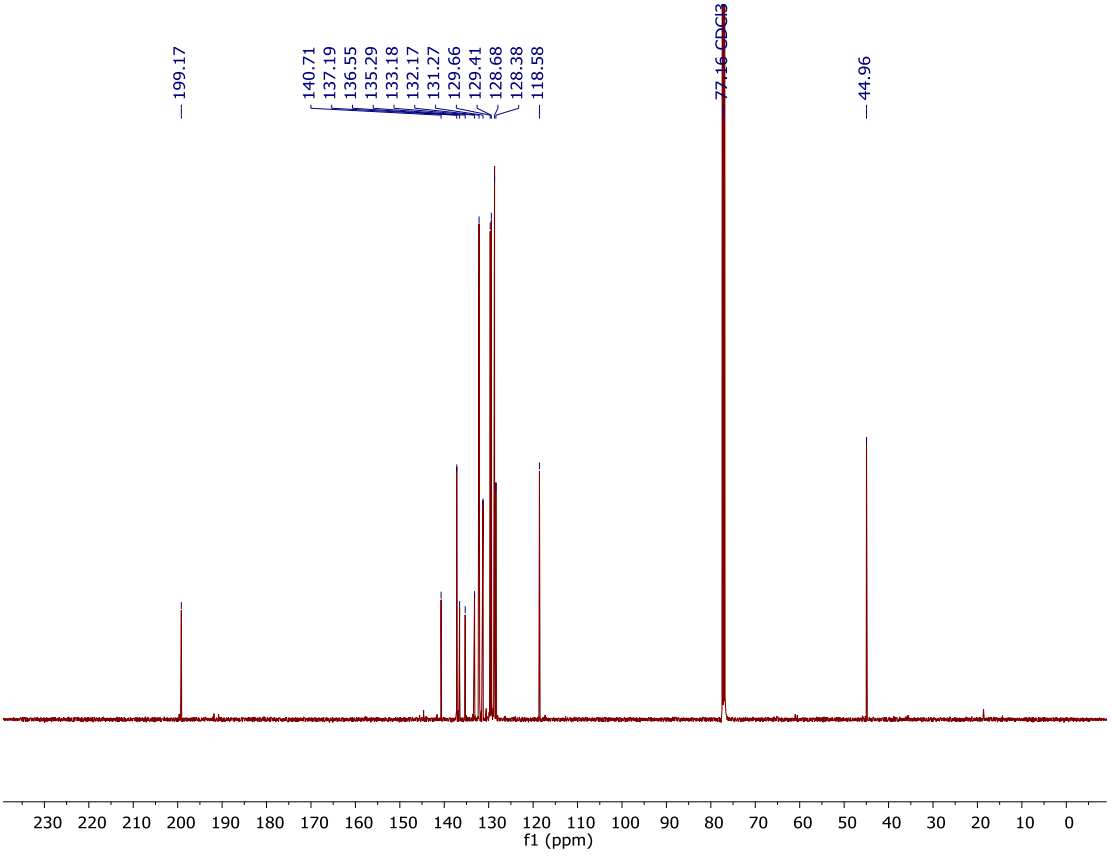
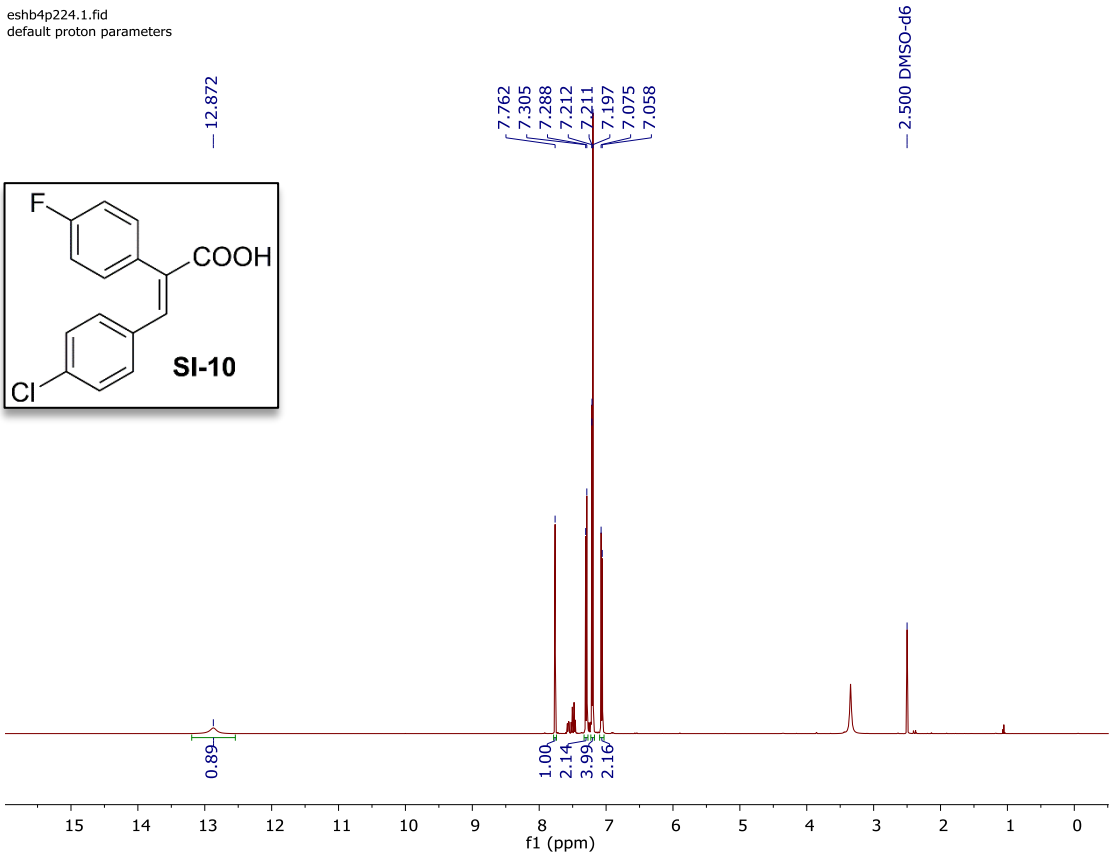
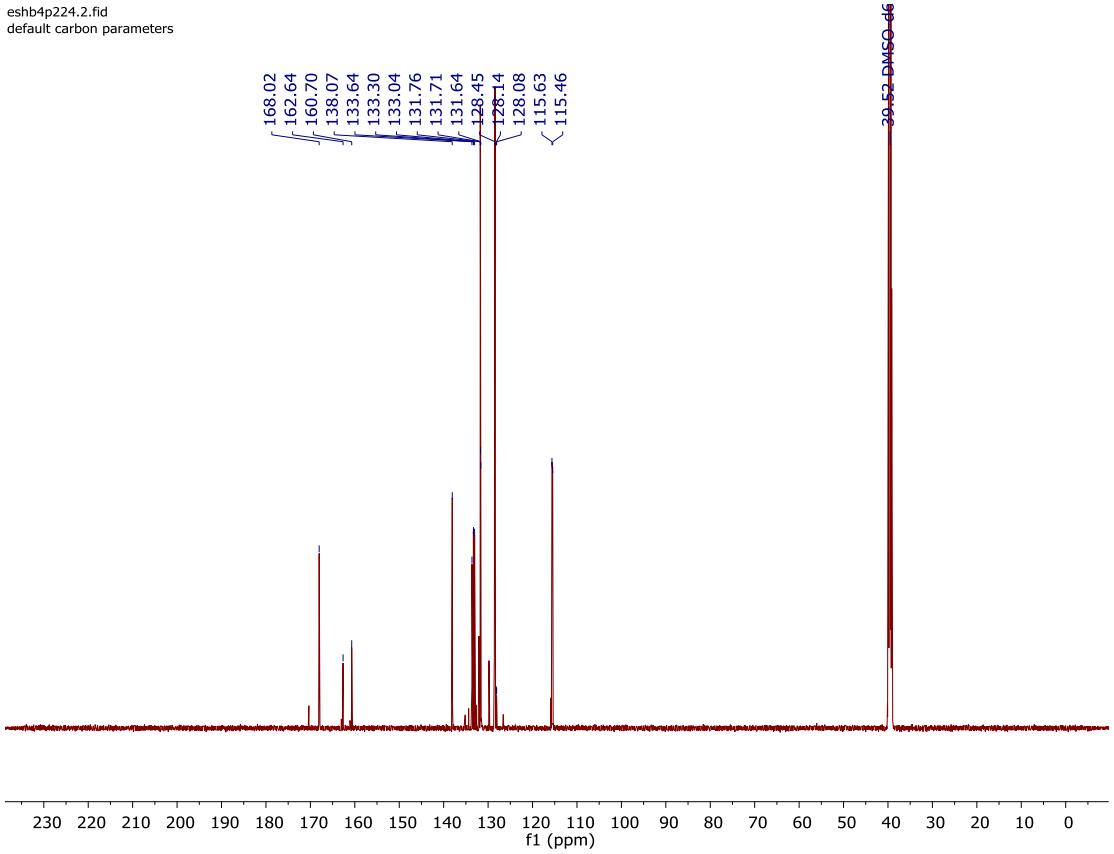
7.439
7.436
7.433
7.432
7.428
7.427
7.424
7.421
7.416
7.412
7.408
7.406
7.401
7.398
7.396
CDCl3
7.260
7.184
7.179
7.168
7.165
7.132
7.115
6.954
6.936
5.983
5.963
5.949
5.942
5.929
5.169
5.166
5.163
5.160
5.149
5.146
5.143
5.140
5.068
5.065
5.061
5.058
5.033
5.030
5.027
5.024
3.323
3.320
3.317
3.310
3.307
3.304
O
Cl
SI-9
0.96
1.00
1.02
6.0
5.8
5.6
5.4
5.2
5.0
f1 (ppm)
1.00
3.38
2.20
2.18
2.13
0.96
1.00
1.03
2.02
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


199.17
140.71
137.19
136.55
135.29
133.18
132.17
131.27
129.66
129.41
128.68
128.38
118.58
77.16 CDCl3
44.96
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


eshb4p224.1.fid
default proton parameters
12.872
7.762
7.305
7.288
7.212
7.211
7.197
7.075
7.058
2.500 DMSO-d6
F
COOH
Cl
SI-10
0.89
1.00
2.14
3.99
2.16
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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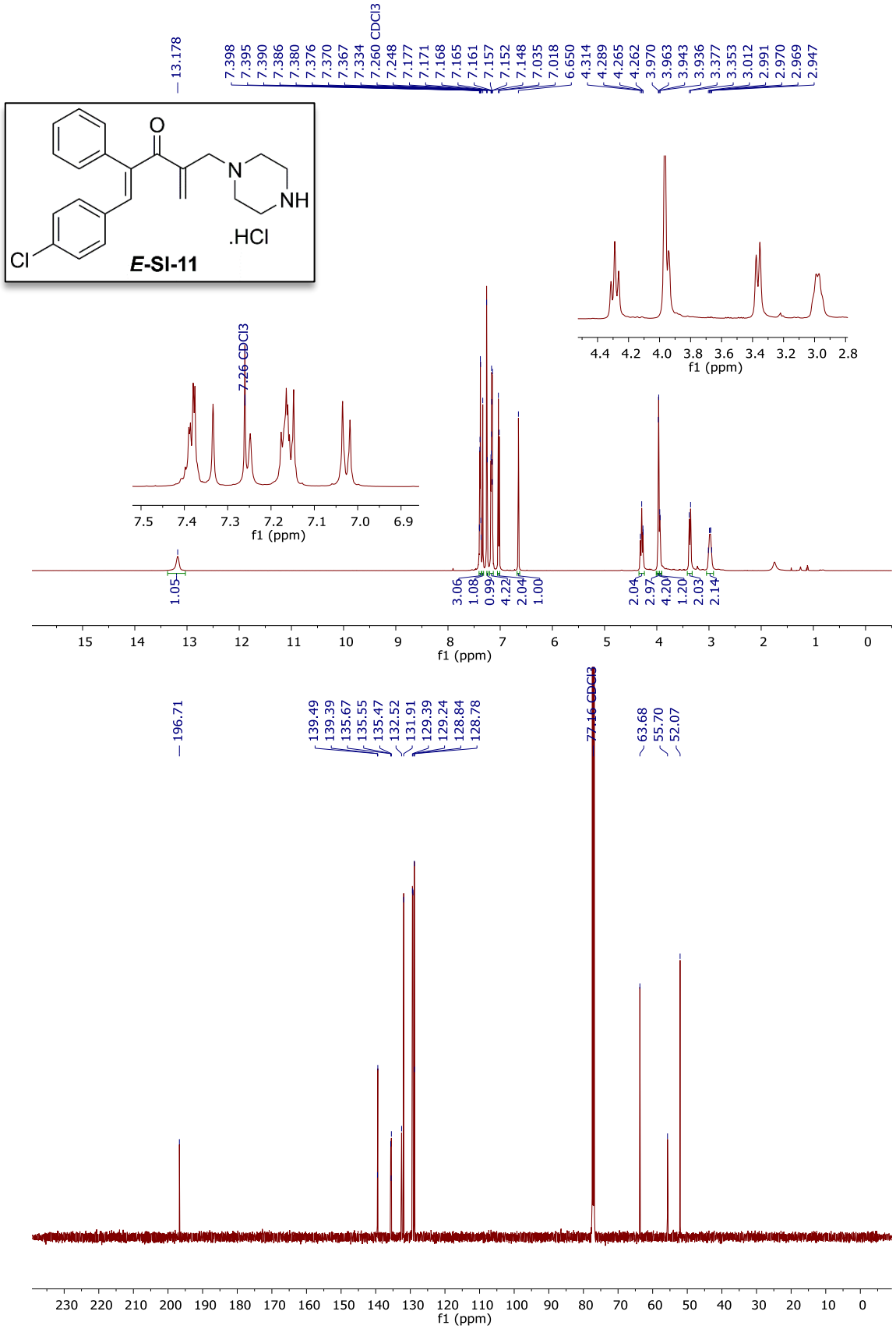
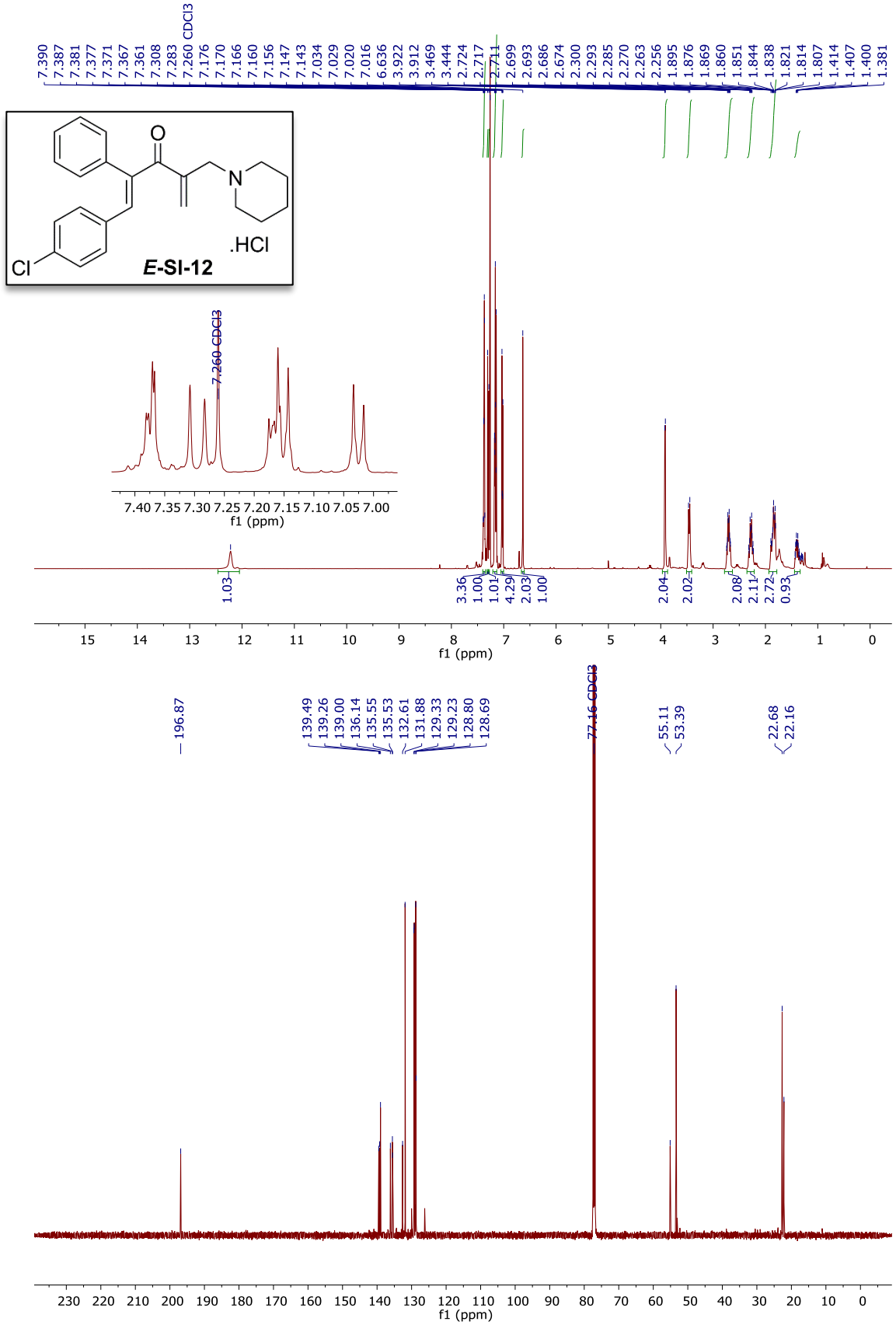
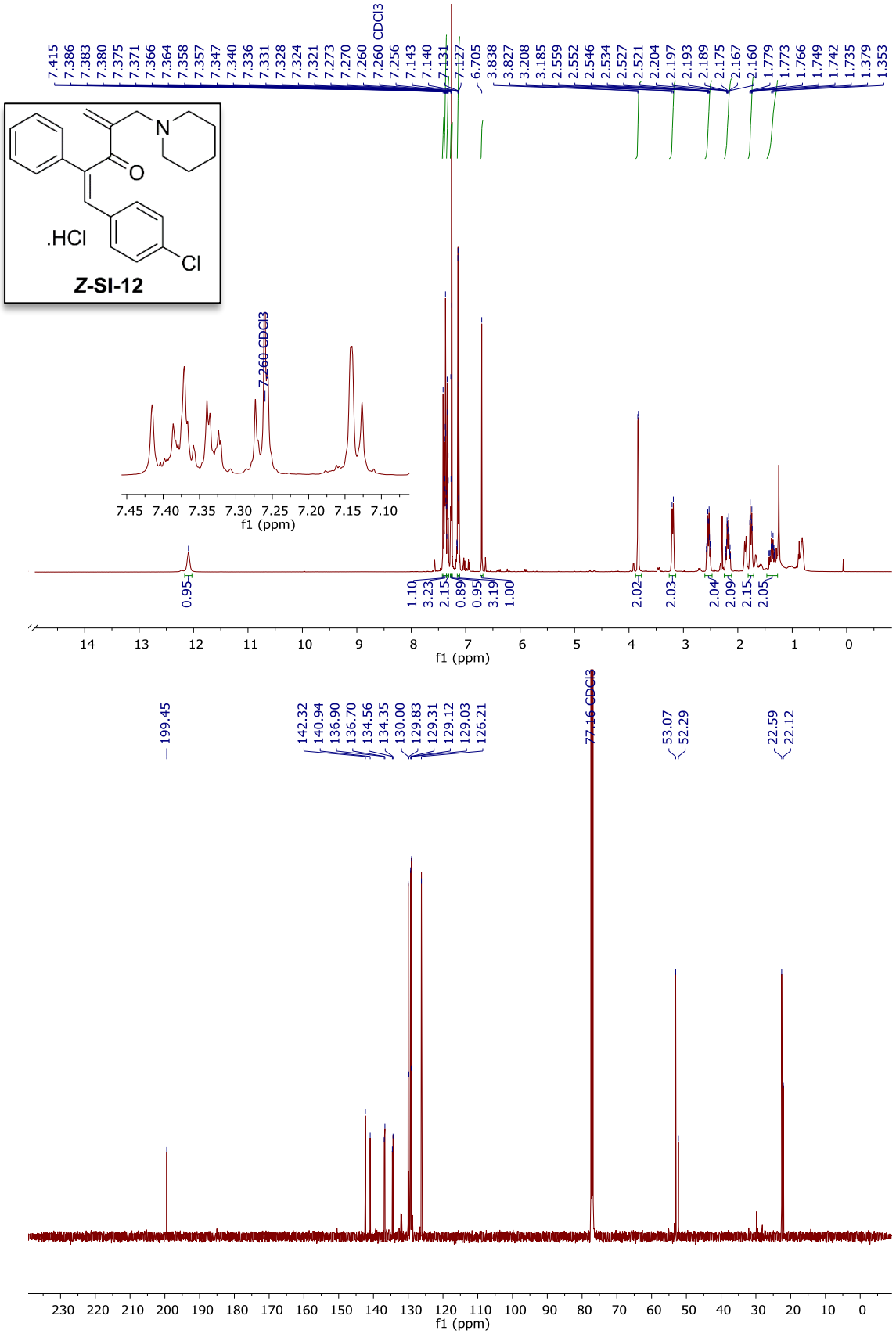
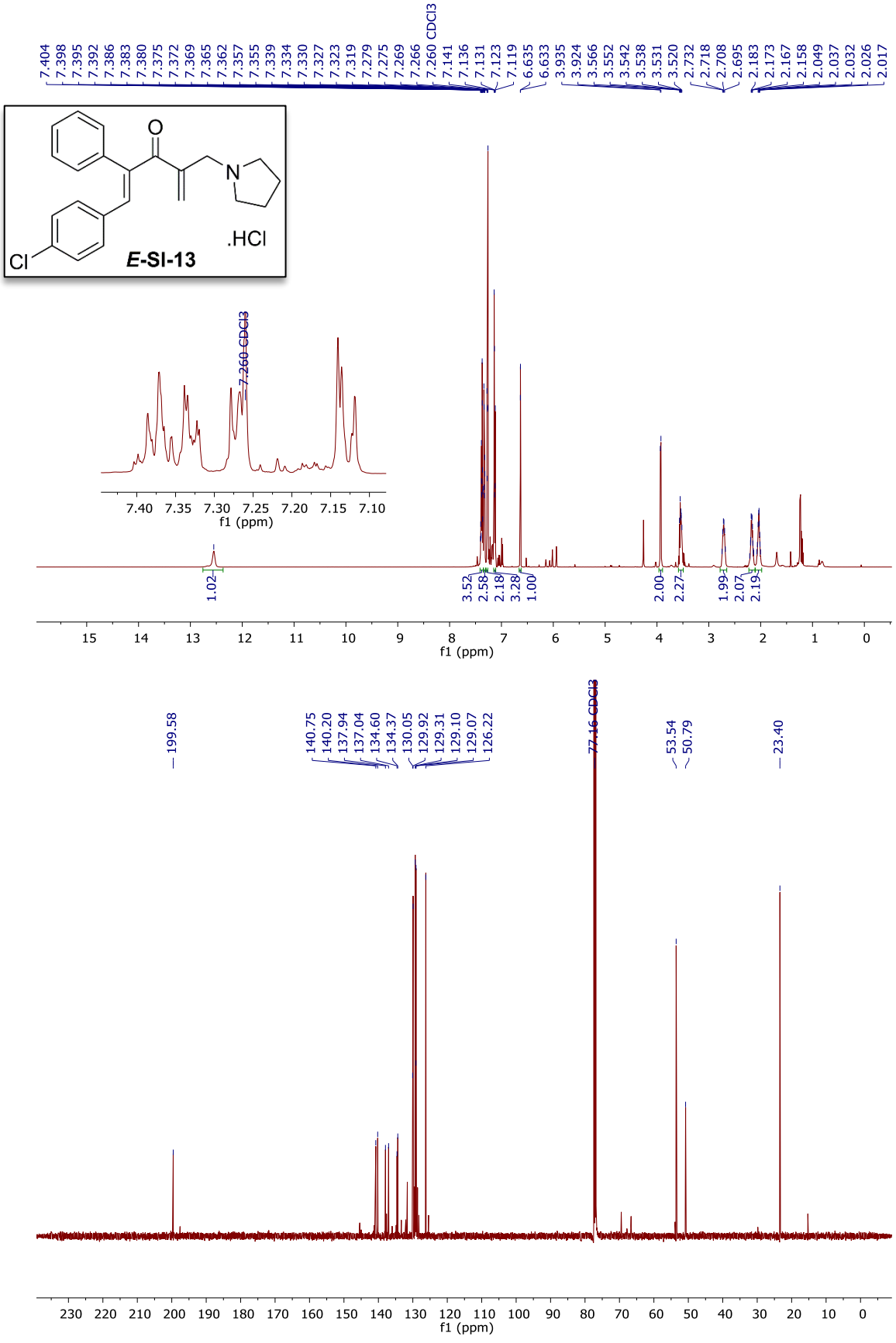
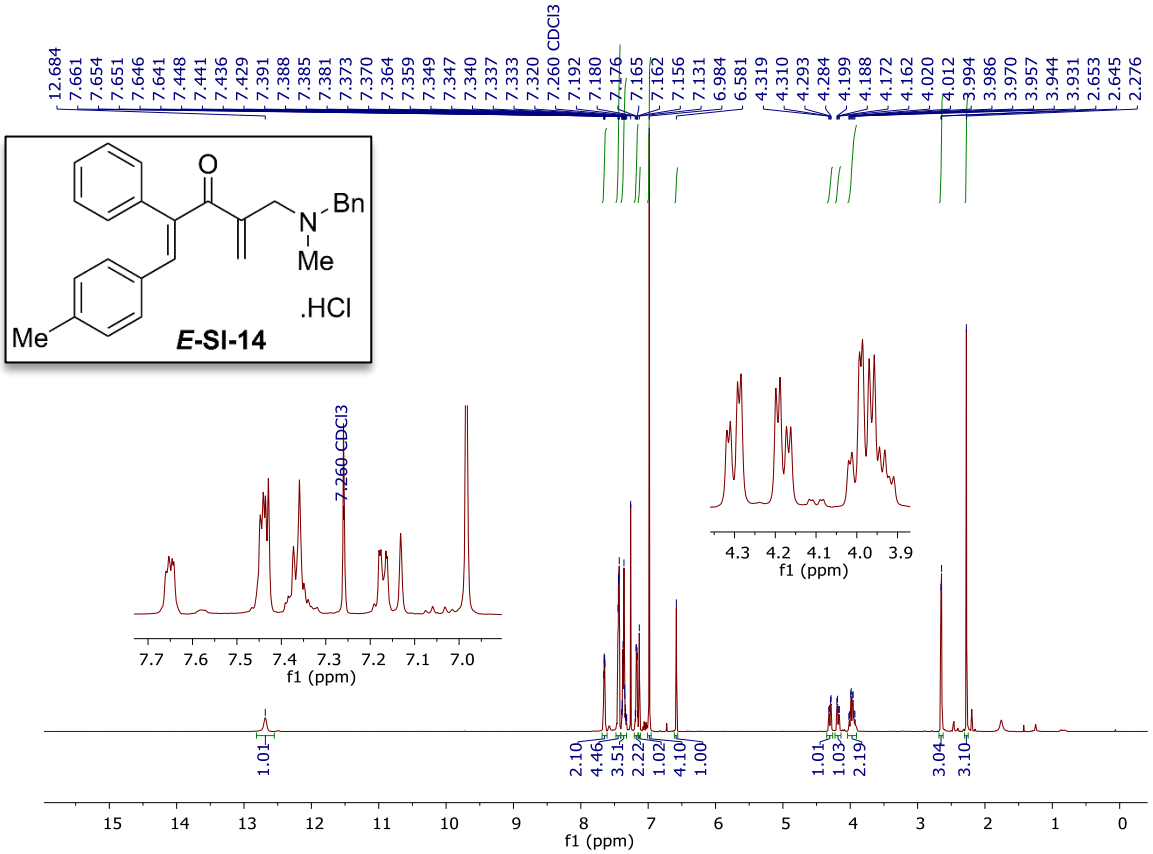
default carbon parameters
168.02
162.64
160.70
138.07
133.64
133.30
133.04
131.76
131.71
131.64
128.45
128.14
128.08
115.63
115.46
39.52 DMSO-d6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

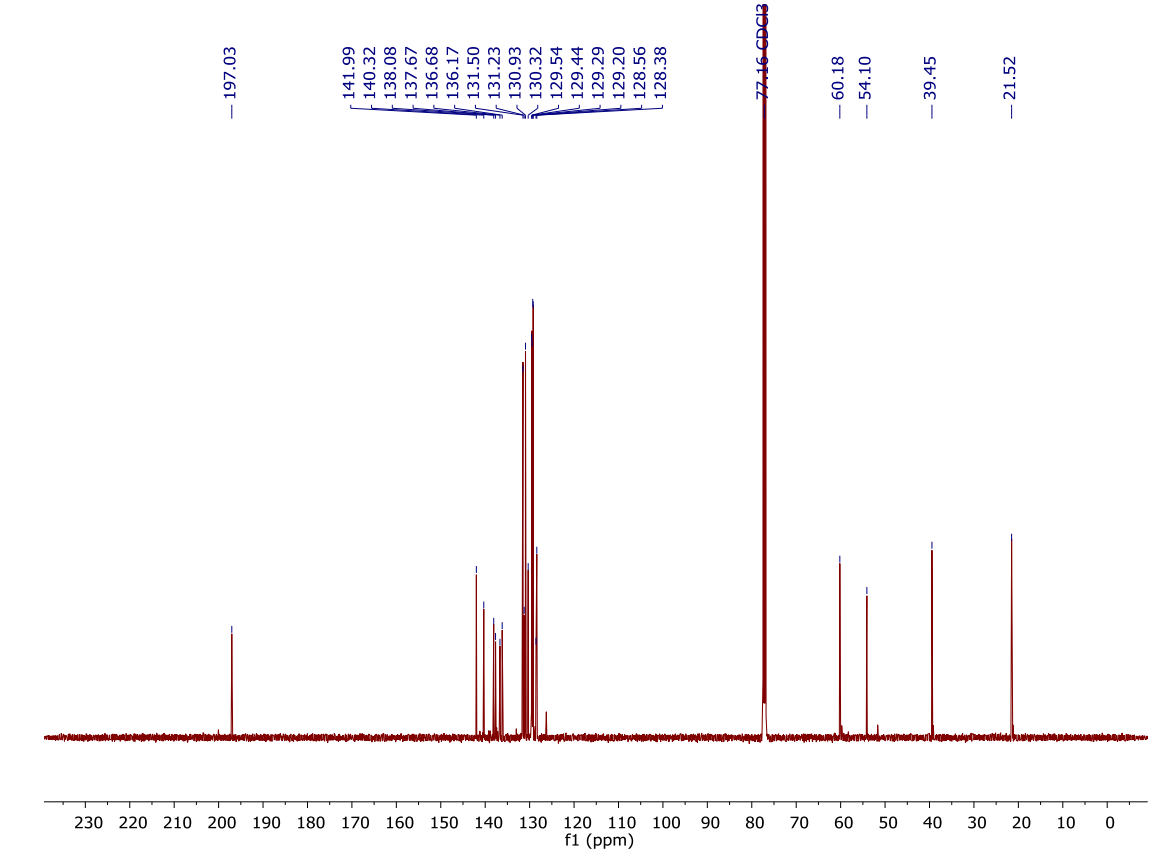

13.178
7.398
7.395
7.390
7.386
7.380
7.376
7.370
7.367
7.334
7.260 CDCl3
7.248
7.177
7.171
7.168
7.165
7.161
7.157
7.152
7.148
7.035
7.018
6.650
4.314
4.289
4.265
4.262
3.970
3.963
3.943
3.936
3.377
3.353
3.012
2.991
2.970
2.969
2.947
O
N
NH
.HCl
Cl
E-SI-11
7.26 CDCl3
f1 (ppm)
1.05
3.06
1.08
0.99
4.22
2.04
1.00
2.04
2.97
4.20
1.20
2.03
2.14
196.71
139.49
139.39
135.67
135.55
135.47
132.52
131.91
129.39
129.24
128.84
128.78
77.16 CDCl3
63.68
55.70
52.07

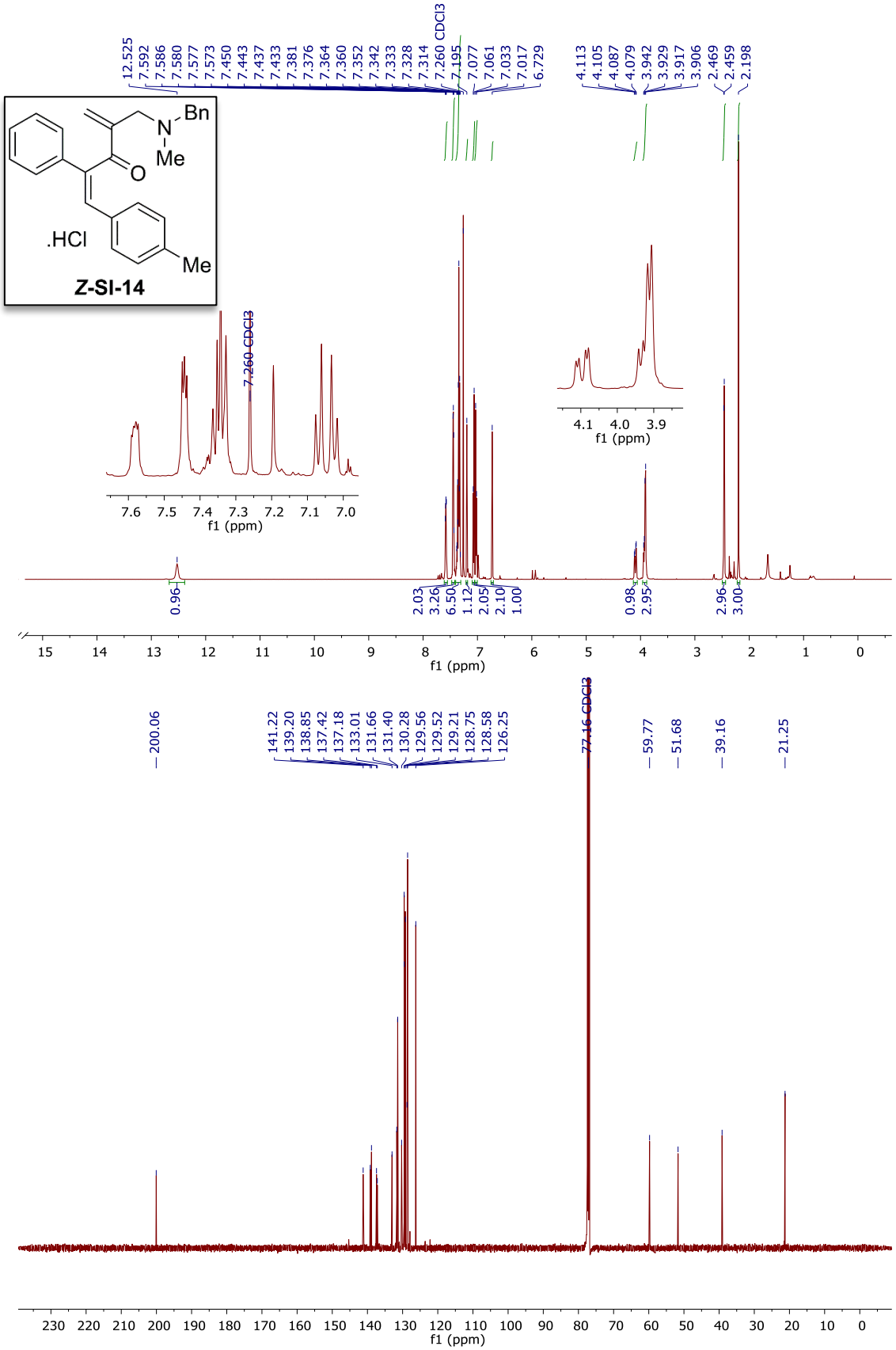

7.390 7.387 7.381 7.377 7.371 7.367 7.361 7.308 7.283 7.260 CDCl3 7.176 7.170 7.166 7.160 7.156 7.147 7.143 7.034 7.029 7.020 7.016 6.636 3.922 3.912 3.469 3.444 2.724 2.717 2.711 2.699 2.693 2.686 2.674 2.300 2.293 2.285 2.270 2.263 2.256 1.895 1.876 1.869 1.860 1.851 1.844 1.838 1.821 1.814 1.807 1.414 1.407 1.400 1.381
O
N
.HCl
Cl
E-SI-12
7.260 CDCl3
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
1.03 3.36 1.00 1.01 4.29 2.03 1.00 2.04 2.02 2.08 2.11 2.72 0.93
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.87
139.49 139.26 139.00 136.14 135.55 135.53 132.61 131.88 129.33 129.23 128.80 128.69
77.16 CDCl3
55.11 53.39
22.68 22.16
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

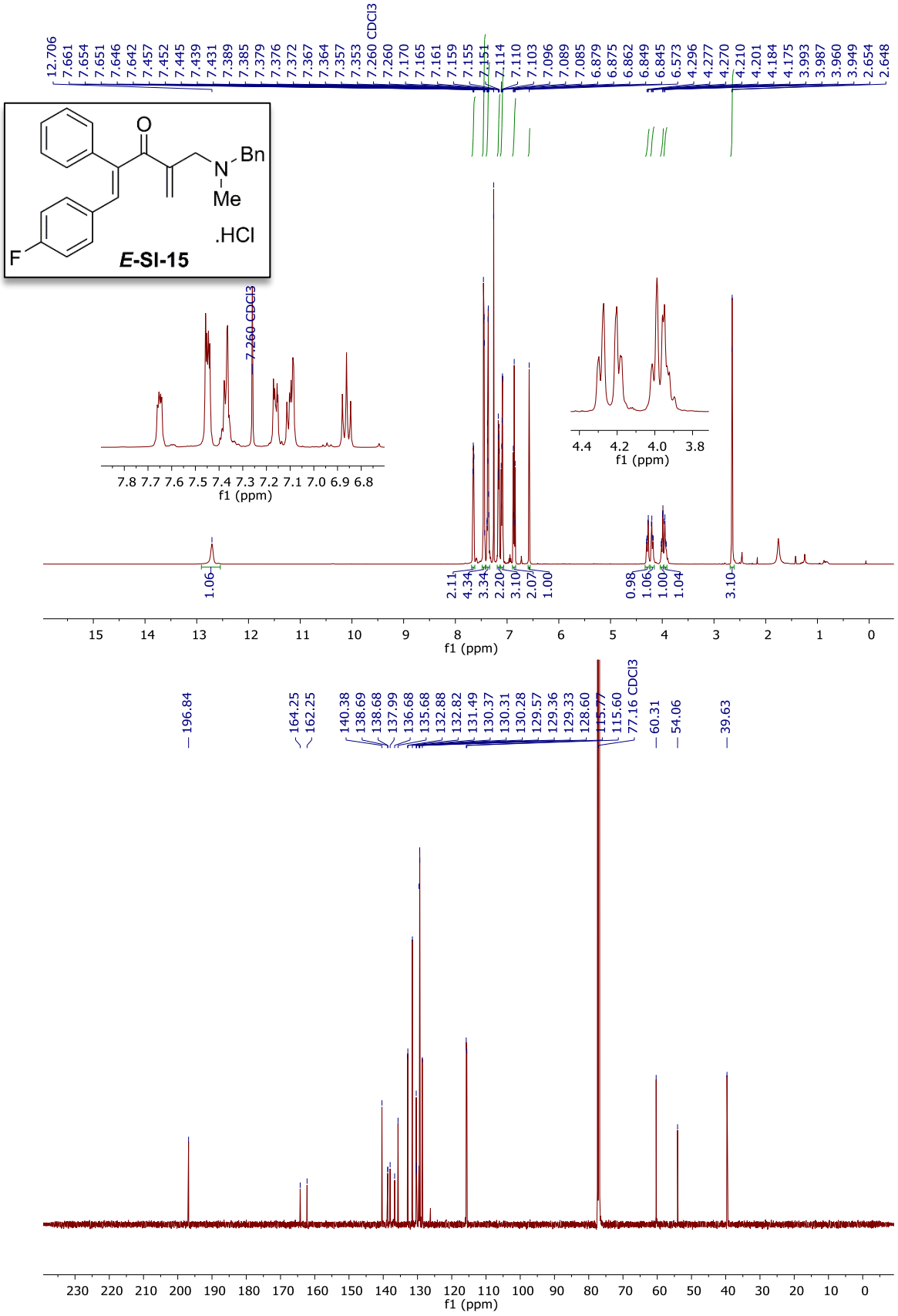

7.415
7.386
7.383
7.380
7.375
7.371
7.366
7.364
7.358
7.357
7.347
7.340
7.336
7.331
7.328
7.324
7.321
7.273
7.270
7.260 CDCl3
7.260
7.256
7.143
7.140
7.131
7.127
6.705
3.838
3.827
3.208
3.185
2.559
2.552
2.546
2.534
2.527
2.521
2.204
2.197
2.193
2.189
2.175
2.167
2.160
1.779
1.773
1.766
1.749
1.742
1.735
1.379
1.353
N
O
.HCl
Cl
Z-SI-12
7.260 CDCl3
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
0.95
1.10
3.23
2.15
0.89
0.95
3.19
1.00
2.02
2.03
2.04
2.09
2.15
2.05
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
199.45
142.32
140.94
136.90
136.70
134.56
134.35
130.00
129.83
129.31
129.12
129.03
126.21
77.16 CDCl3
53.07
52.29
22.59
22.12
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

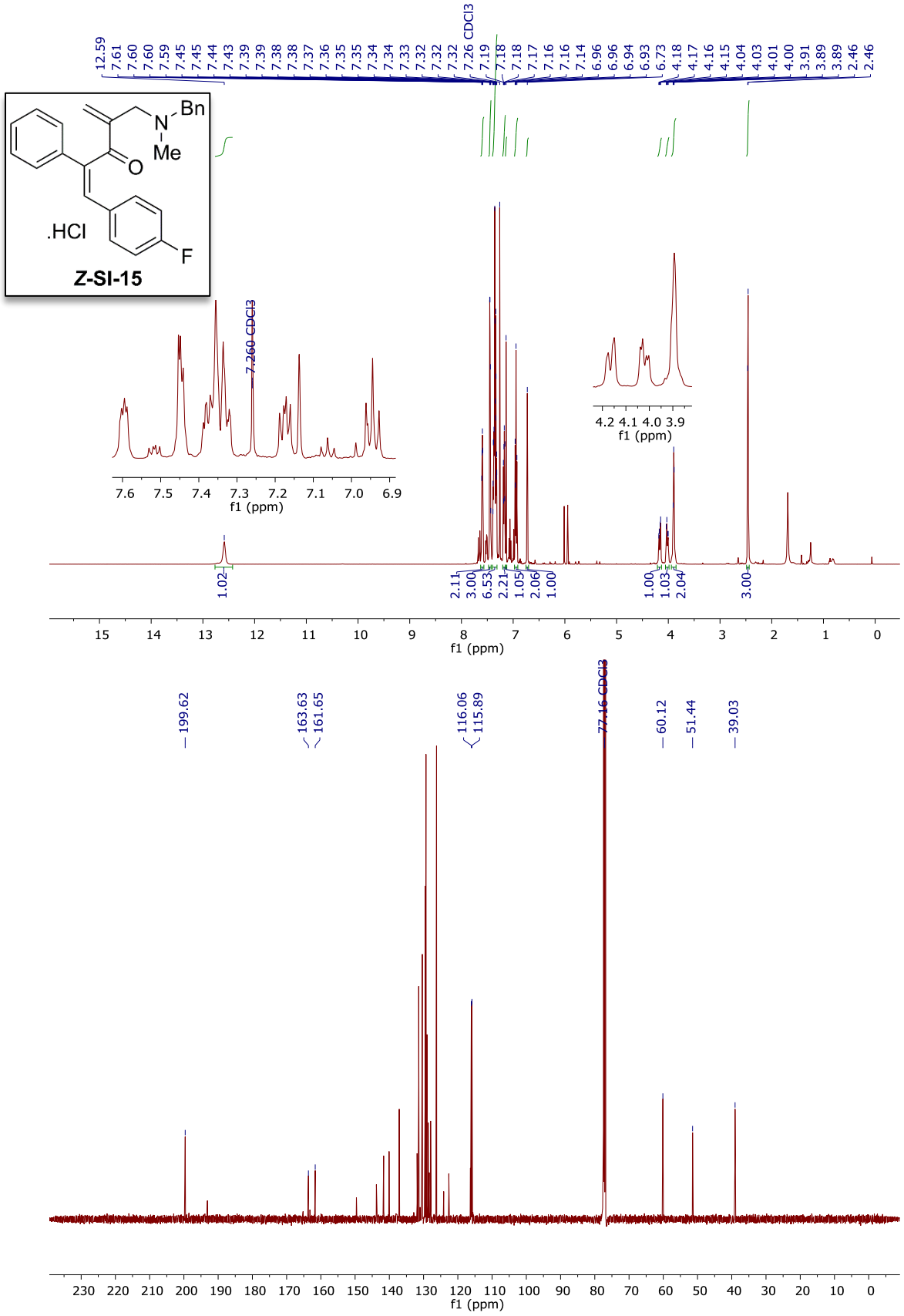

7.404 7.398 7.395 7.392 7.386 7.383 7.380 7.375 7.372 7.369 7.365 7.362 7.357 7.355 7.339 7.334 7.330 7.327 7.323 7.319 7.279 7.275 7.269 7.266 7.260 CDCl3 7.141 7.136 7.131 7.123 7.119 6.635 6.633 3.935 3.924 3.566 3.552 3.542 3.538 3.531 3.520 2.732 2.718 2.708 2.695 2.183 2.173 2.167 2.158 2.049 2.037 2.032 2.026 2.017
O
N
.HCl
Cl
E-SI-13
7.260 CDCl3
7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
1.02
3.52 2.58 2.18 3.28 1.00
2.00 2.27
1.99 2.07 2.19
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
199.58
140.75 140.20 137.94 137.04 134.60 134.37 130.05 129.92 129.31 129.10 129.07 126.22
77.16 CDCl3
53.54 50.79
23.40
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

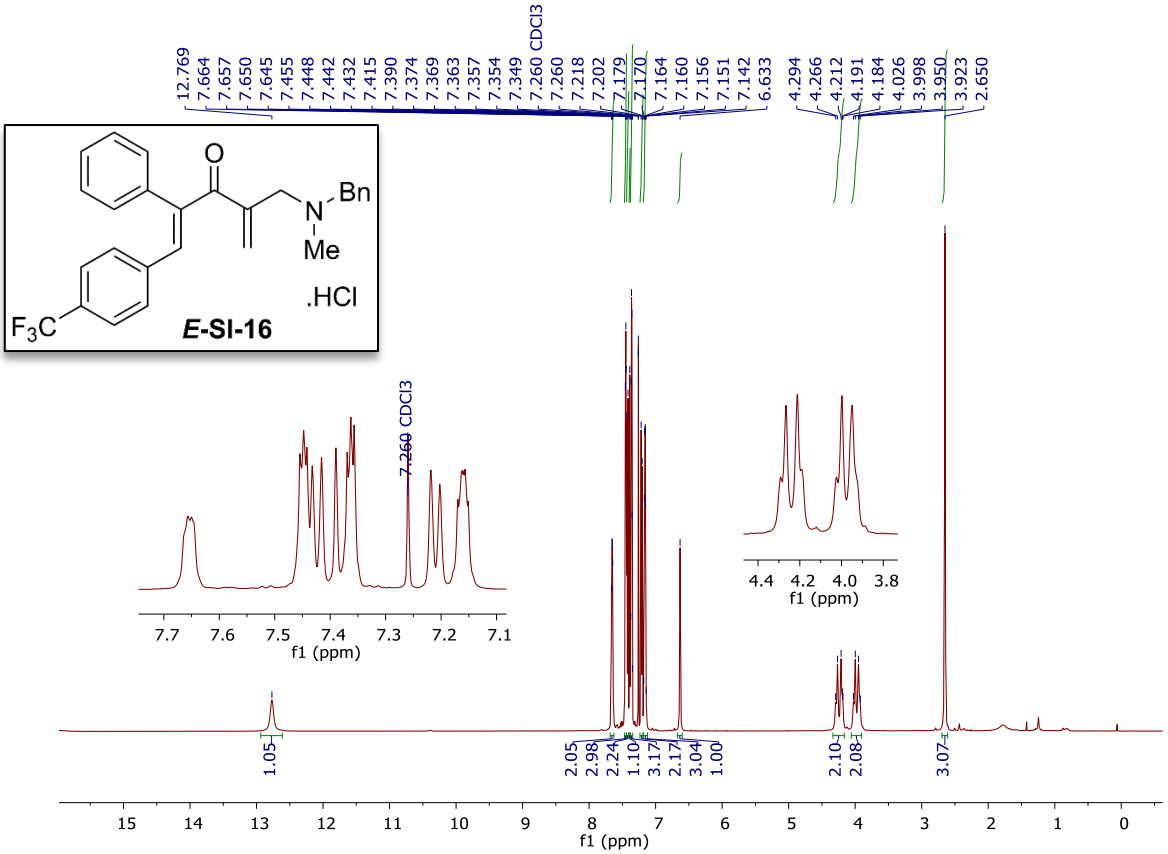

12.684
7.661
7.654
7.651
7.646
7.641
7.448
7.441
7.436
7.429
7.391
7.388
7.385
7.381
7.373
7.370
7.364
7.359
7.349
7.347
7.340
7.337
7.333
7.320
7.260 CDCl3
7.192
7.180
7.176
7.165
7.162
7.156
7.131
6.984
6.581
4.319
4.310
4.293
4.284
4.199
4.188
4.172
4.162
4.020
4.012
3.994
3.986
3.970
3.957
3.944
3.931
2.653
2.645
2.276
O
N
Bn
Me
.HCl
Me
E-SI-14
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
1.01
2.10
4.46
3.51
2.22
1.02
4.10
1.00
1.01
1.03
2.19
3.04
3.10
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

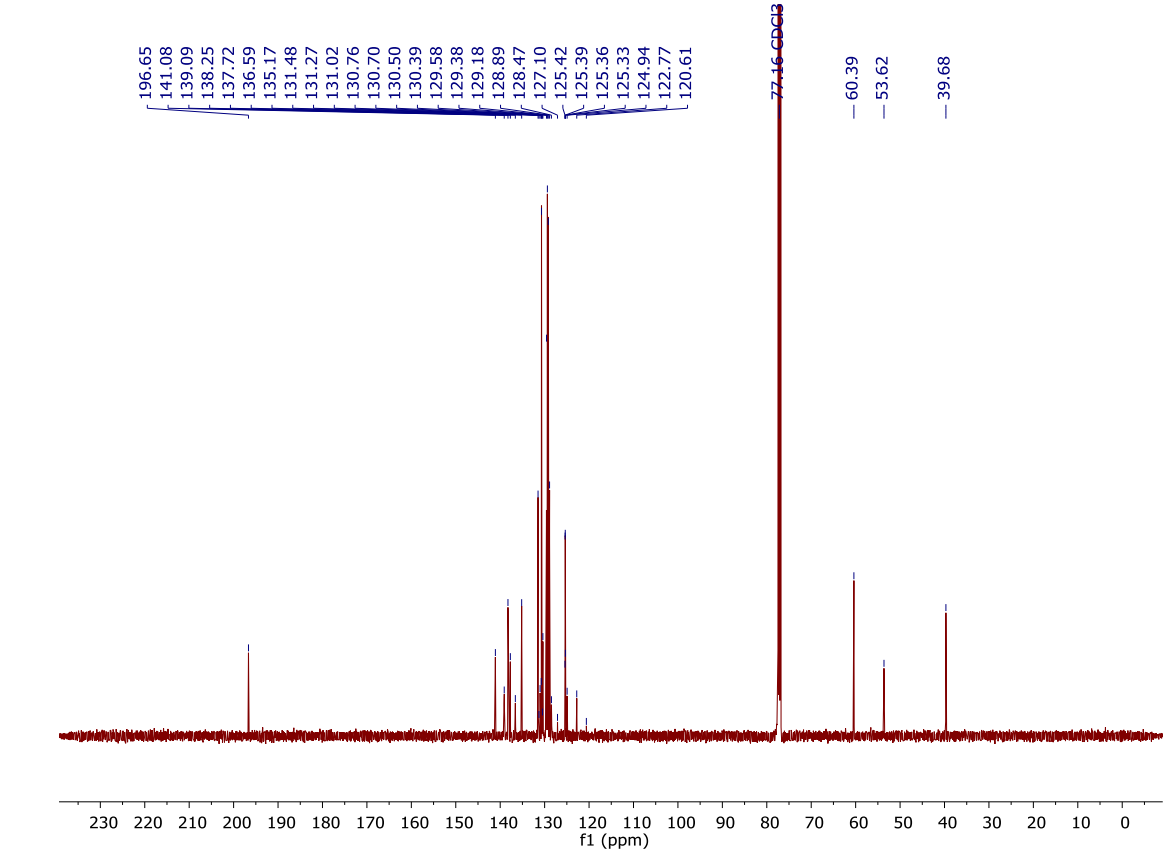

197.03
141.99
140.32
138.08
137.67
136.68
136.17
131.50
131.23
130.93
130.32
129.54
129.44
129.29
129.20
128.56
128.38
77.16 CDCl3
60.18
54.10
39.45
21.52
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

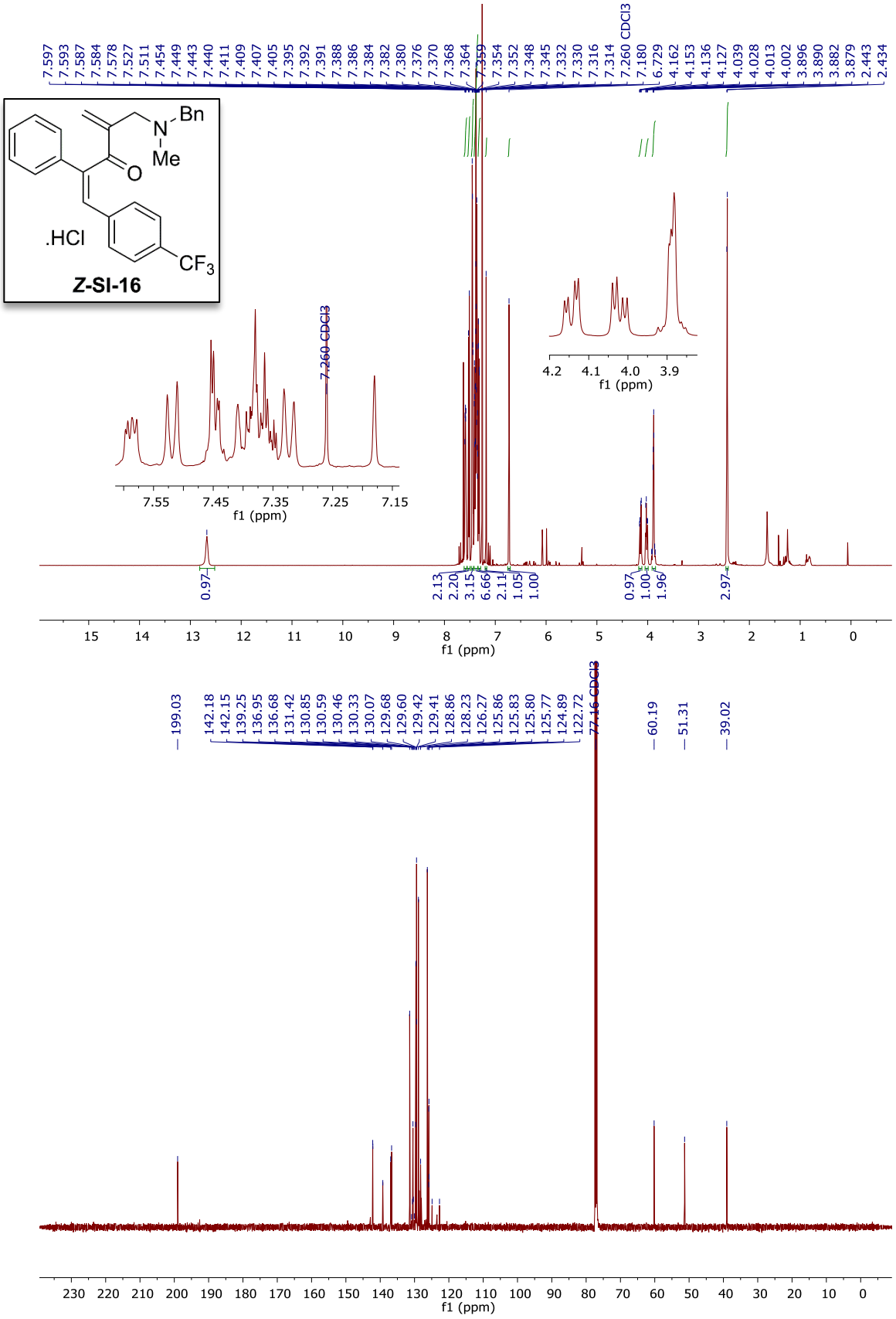

12.525
7.592
7.586
7.580
7.577
7.573
7.450
7.443
7.437
7.433
7.381
7.376
7.364
7.360
7.352
7.342
7.333
7.328
7.314
7.260 CDCl3
7.195
7.077
7.061
7.033
7.017
6.729
4.113
4.105
4.087
4.079
3.942
3.929
3.917
3.906
2.469
2.459
2.198
Bn
N
Me
O
.HCl
Me
Z-SI-14
7.260 CDCl3
f1 (ppm)
f1 (ppm)
0.96
2.03
3.26
6.50
1.12
2.05
2.10
1.00
0.98
2.95
2.96
3.00
f1 (ppm)
200.06
141.22
139.20
138.85
137.42
137.18
133.01
131.66
131.40
130.28
129.56
129.52
129.21
128.75
128.58
126.25
77.16 CDCl3
59.77
51.68
39.16
21.25
f1 (ppm)

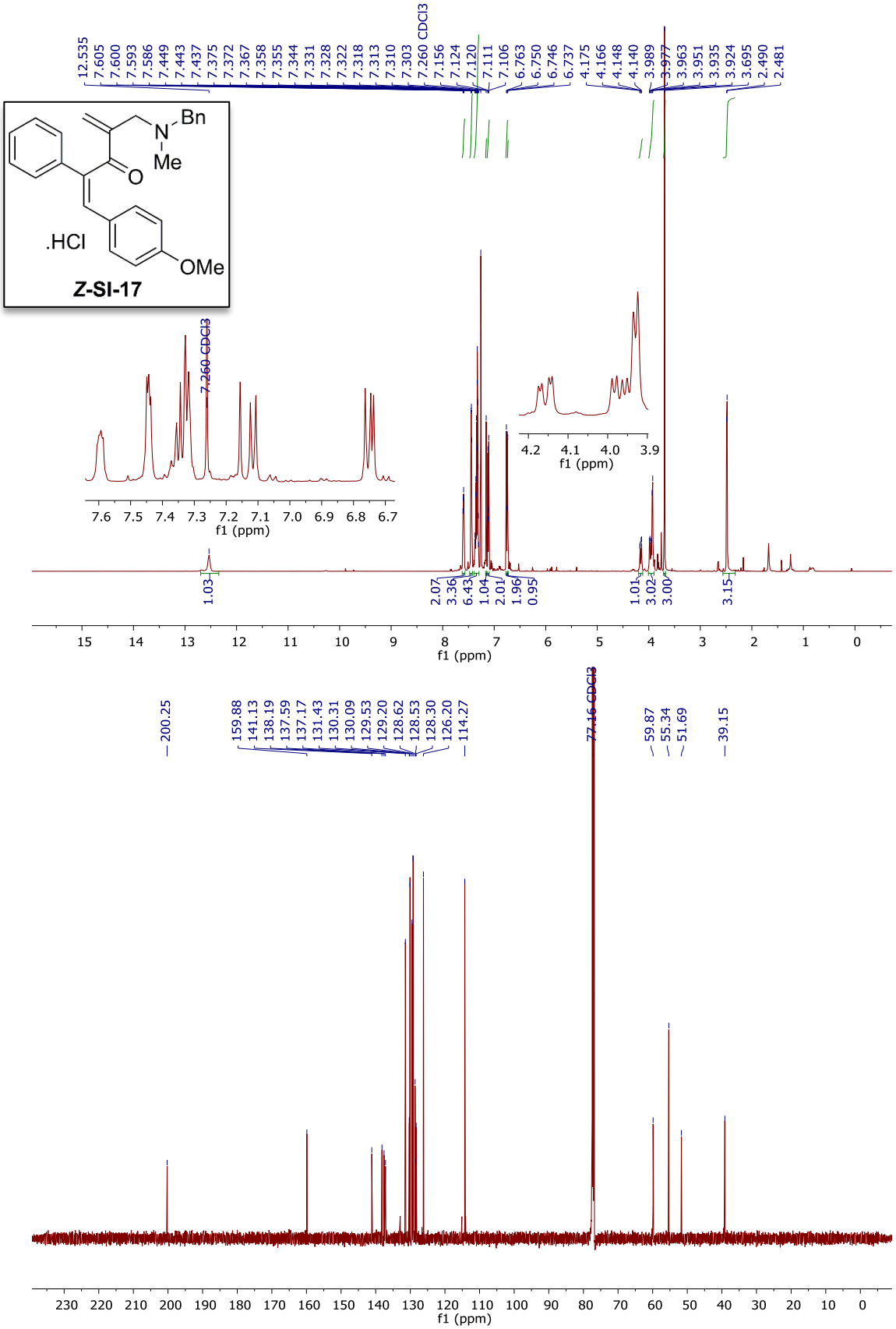

12.706
7.661
7.654
7.651
7.646
7.642
7.457
7.452
7.445
7.439
7.431
7.389
7.385
7.379
7.376
7.372
7.367
7.364
7.357
7.353
7.260 CDCl3
7.260
7.170
7.165
7.161
7.159
7.155
7.151
7.114
7.110
7.103
7.096
7.089
7.085
6.879
6.875
6.862
6.849
6.845
6.573
4.296
4.277
4.270
4.210
4.201
4.184
4.175
3.993
3.987
3.960
3.949
2.654
2.648
O
N
Bn
Me
.HCl
F
E-SI-15
7.260 CDCl3
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
4.4 4.2 4.0 3.8
f1 (ppm)
1.06
2.11
4.34
3.34
2.20
3.10
2.07
1.00
0.98
1.06
1.00
1.04
3.10
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.84
164.25
162.25
140.38
138.69
138.68
137.99
136.68
135.68
132.88
132.82
131.49
130.37
130.31
130.28
129.57
129.36
129.33
128.60
115.77
115.60
77.16 CDCl3
60.31
54.06
39.63
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Bn
N
Me
O
.HCl
F
Z-SI-15
12.59
7.61
7.60
7.60
7.59
7.45
7.45
7.44
7.43
7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.26 CDCl3
7.19
7.18
7.18
7.17
7.16
7.16
7.14
6.96
6.96
6.94
6.93
6.73
4.18
4.17
4.16
4.15
4.04
4.03
4.01
4.00
3.91
3.89
3.89
2.46
2.46
7.260 CDCl3
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
4.2 4.1 4.0 3.9
f1 (ppm)
1.02
2.11
3.00
6.53
2.21
1.05
2.06
1.00
1.00
1.03
2.04
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
199.62
163.63
161.65
116.06
115.89
77.16 CDCl3
60.12
51.44
39.03
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.769
7.664
7.657
7.650
7.645
7.455
7.448
7.442
7.432
7.415
7.390
7.374
7.369
7.363
7.357
7.354
7.349
7.260 CDCl3
7.260
7.218
7.202
7.179
7.170
7.164
7.160
7.156
7.151
7.142
6.633
4.294
4.266
4.212
4.191
4.184
4.026
3.998
3.950
3.923
2.650
O
N
Bn
Me
.HCl
F3C
E-SI-16
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
4.4 4.2 4.0 3.8
f1 (ppm)
1.05
2.05
2.98
2.24
1.10
3.17
2.17
3.04
1.00
2.10
2.08
3.07
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


196.65
141.08
139.09
138.25
137.72
136.59
135.17
131.48
131.27
131.02
130.76
130.70
130.50
130.39
129.58
129.38
129.18
128.89
128.47
127.10
125.42
125.39
125.36
125.33
124.94
122.77
120.61
77.16 CDCl3
60.39
53.62
39.68
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Bn
N
Me
O
.HCl
CF3
Z-SI-16
7.260 CDCl3
f1 (ppm)
77.16 CDCl3
f1 (ppm)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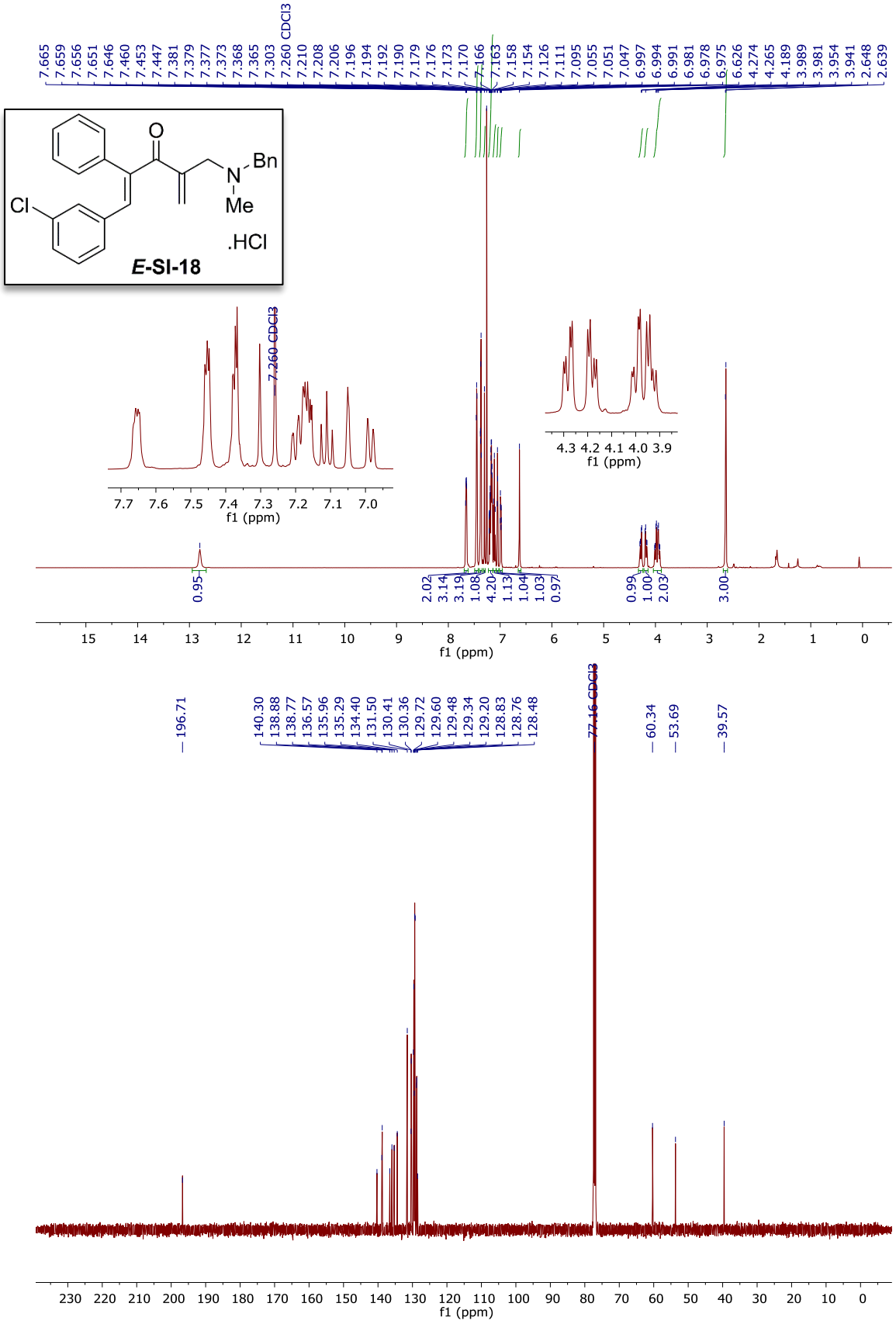
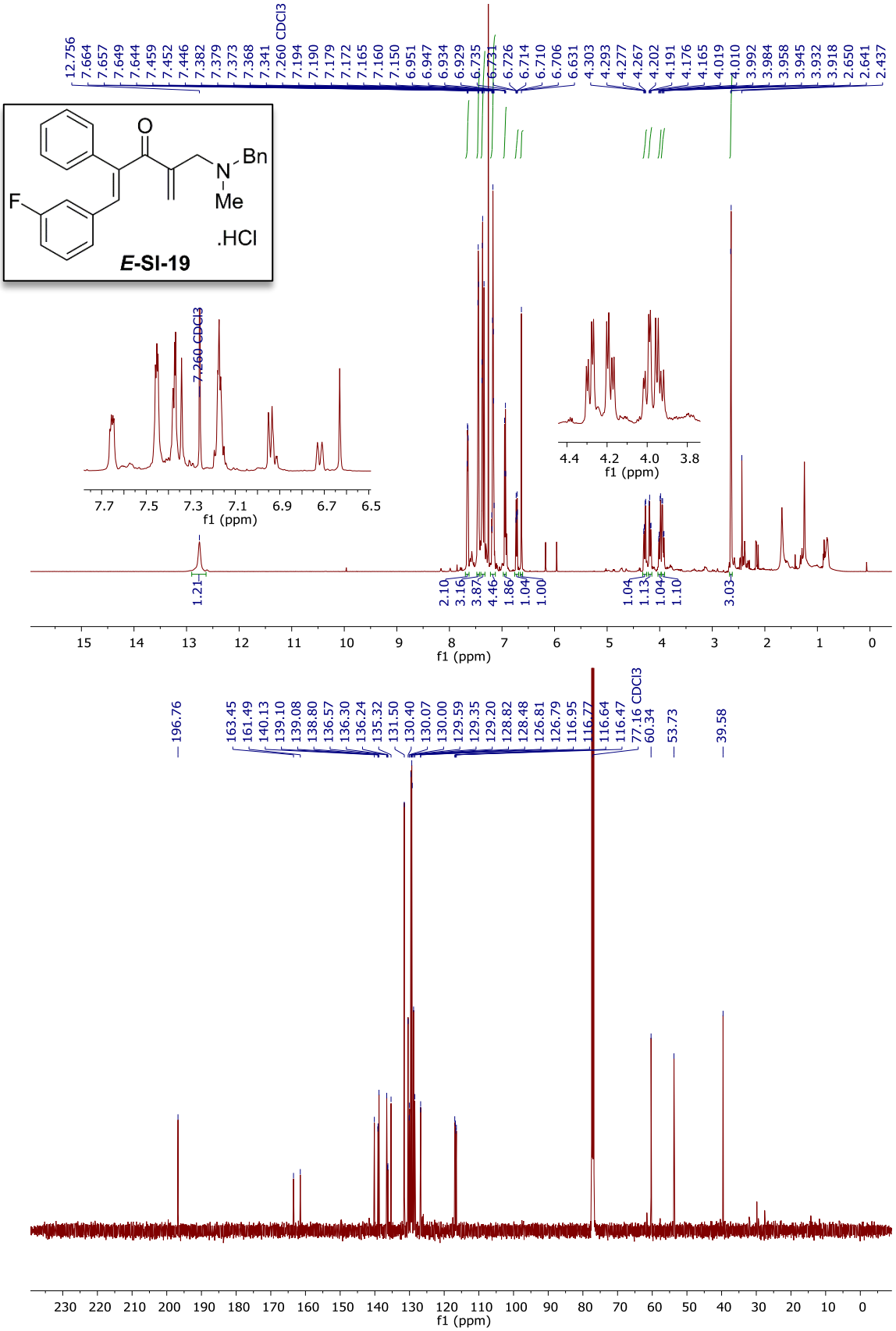
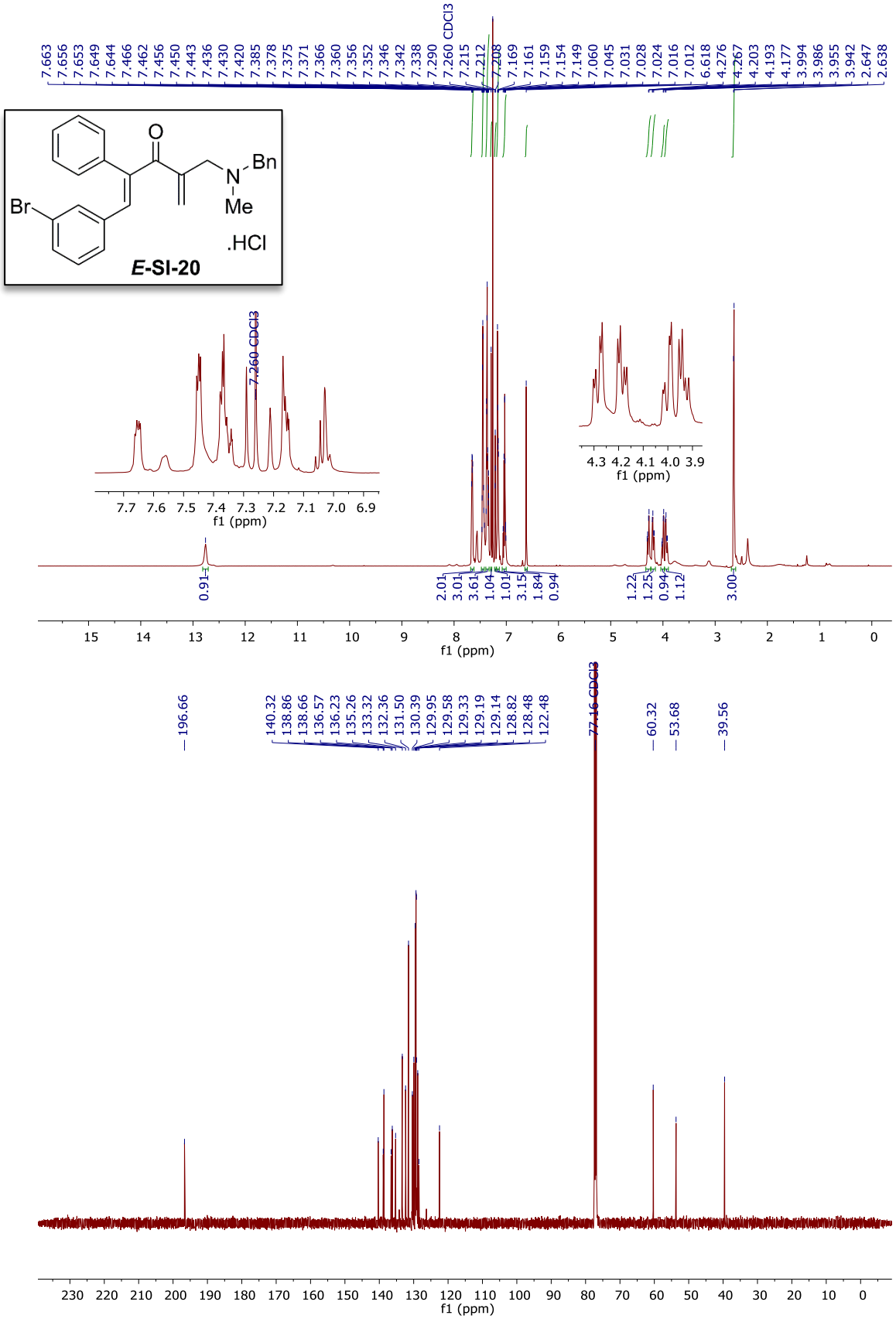
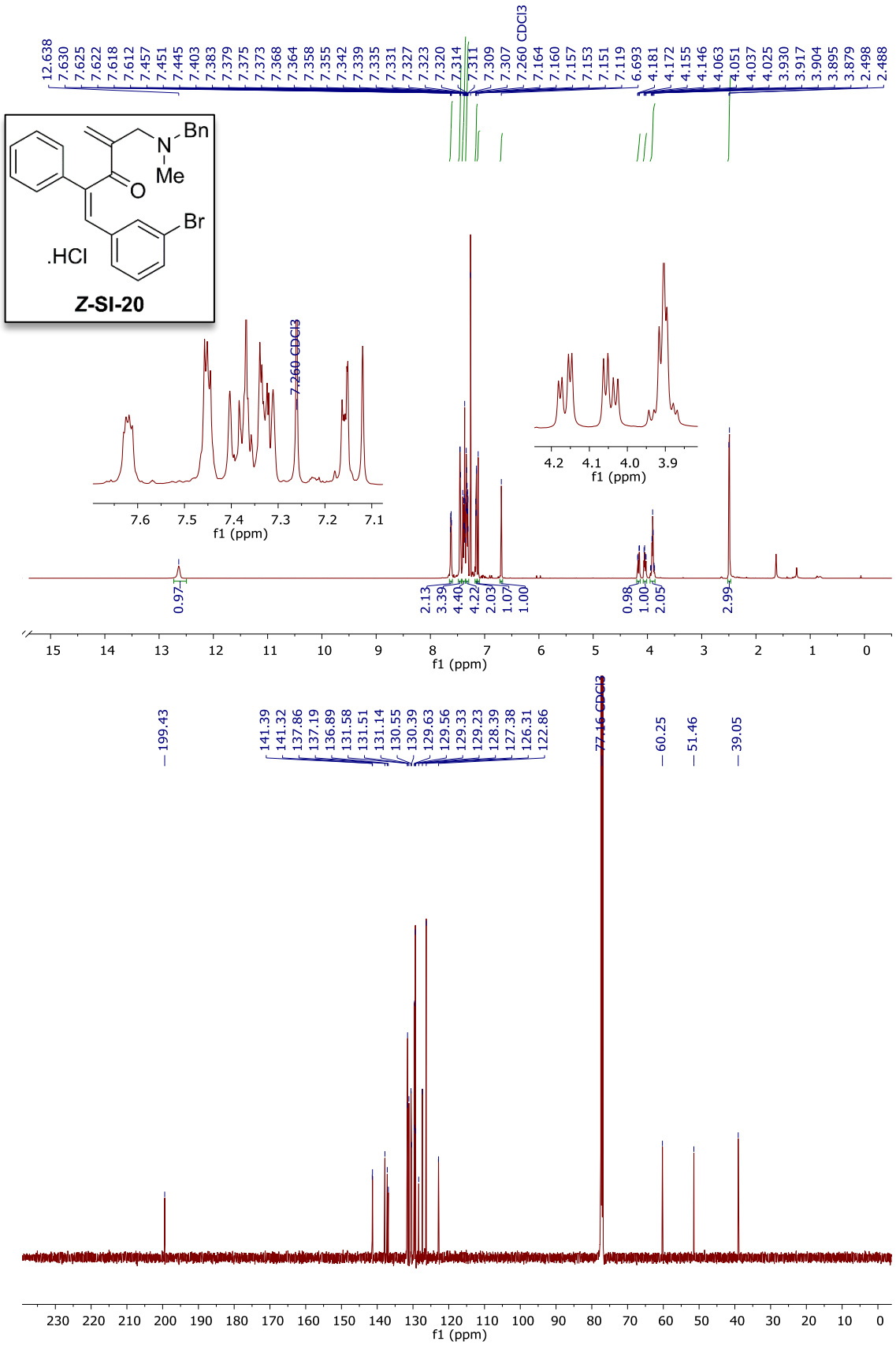
7.600
7.593
7.586
7.449
7.443
7.437
7.375
7.372
7.367
7.358
7.355
7.344
7.331
7.328
7.322
7.318
7.313
7.310
7.303
7.260 CDCl3
7.156
7.124
7.120
7.111
7.106
6.763
6.750
6.746
6.737
4.175
4.166
4.148
4.140
3.989
3.977
3.963
3.951
3.935
3.924
3.695
2.490
2.481
Bn
N
Me
O
.HCl
OMe
Z-SI-17
7.260 CDCl3
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
4.2 4.1 4.0 3.9
f1 (ppm)
1.03
2.07
3.36
6.43
1.04
2.01
1.96
0.95
1.01
3.02
3.00
3.15
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
200.25
159.88
141.13
138.19
137.59
137.17
131.43
130.31
130.09
129.53
129.20
128.62
128.53
128.30
126.20
114.27
77.16 CDCl3
59.87
55.34
51.69
39.15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.665 7.659 7.656 7.651 7.646 7.460 7.453 7.447 7.381 7.379 7.377 7.373 7.368 7.365 7.303 7.260 CDCl3 7.210 7.208 7.206 7.196 7.194 7.192 7.190 7.179 7.176 7.173 7.170 7.166 7.163 7.158 7.154 7.126 7.111 7.095 7.055 7.051 7.047 6.997 6.994 6.991 6.981 6.978 6.975 6.626 4.274 4.265 4.189 3.989 3.981 3.954 3.941 2.648 2.639
O
N
Bn
Me
Cl
.HCl
E-SI-18
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
0.95 2.02 3.14 3.19 1.08 4.20 1.13 1.04 1.03 0.97 0.99 1.00 2.03 3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.71 140.30 138.88 138.77 136.57 135.96 135.29 134.40 131.50 130.41 130.36 129.72 129.60 129.48 129.34 129.20 128.83 128.76 128.48 77.16 CDCl3 60.34 53.69 39.57
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.756
7.664
7.657
7.649
7.644
7.459
7.452
7.446
7.382
7.379
7.373
7.368
7.341
7.260 CDCl3
7.194
7.190
7.179
7.172
7.165
7.160
7.150
6.951
6.947
6.934
6.929
6.735
6.731
6.726
6.714
6.710
6.706
6.631
4.303
4.293
4.277
4.267
4.202
4.191
4.176
4.165
4.019
4.010
3.992
3.984
3.958
3.945
3.932
3.918
2.650
2.641
2.437
O
N
Bn
Me
F
.HCl
E-SI-19
7.260 CDCl3
7.7 7.5 7.3 7.1 6.9 6.7 6.5
f1 (ppm)
4.4 4.2 4.0 3.8
f1 (ppm)
1.21
2.10
3.16
3.87
4.46
1.86
1.04
1.00
1.04
1.13
1.04
1.10
3.03
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.76
163.45
161.49
140.13
139.10
139.08
138.80
136.57
136.30
136.24
135.32
131.50
130.40
130.07
130.00
129.59
129.35
129.20
128.82
128.48
126.81
126.79
116.95
116.77
116.64
116.47
77.16 CDCl3
60.34
53.73
39.58
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.663 7.656 7.653 7.649 7.644 7.466 7.462 7.456 7.450 7.443 7.436 7.430 7.420 7.385 7.378 7.375 7.371 7.366 7.360 7.356 7.352 7.346 7.342 7.338 7.290 7.260 CDCl3 7.215 7.212 7.208 7.169 7.161 7.159 7.154 7.149 7.060 7.045 7.031 7.028 7.024 7.016 7.012 6.618 4.276 4.267 4.203 4.193 4.177 3.994 3.986 3.955 3.942 2.647 2.638
O
N
Bn
Me
Br
.HCl
E-SI-20
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
0.91
2.01 3.01 3.61 1.04 1.01 3.15 1.84 0.94
1.22 1.25 0.94 1.12
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.66
140.32 138.86 138.66 136.57 136.23 135.26 133.32 132.36 131.50 130.39 129.95 129.58 129.33 129.19 129.14 128.82 128.48 122.48
77.16 CDCl3
60.32
53.68
39.56
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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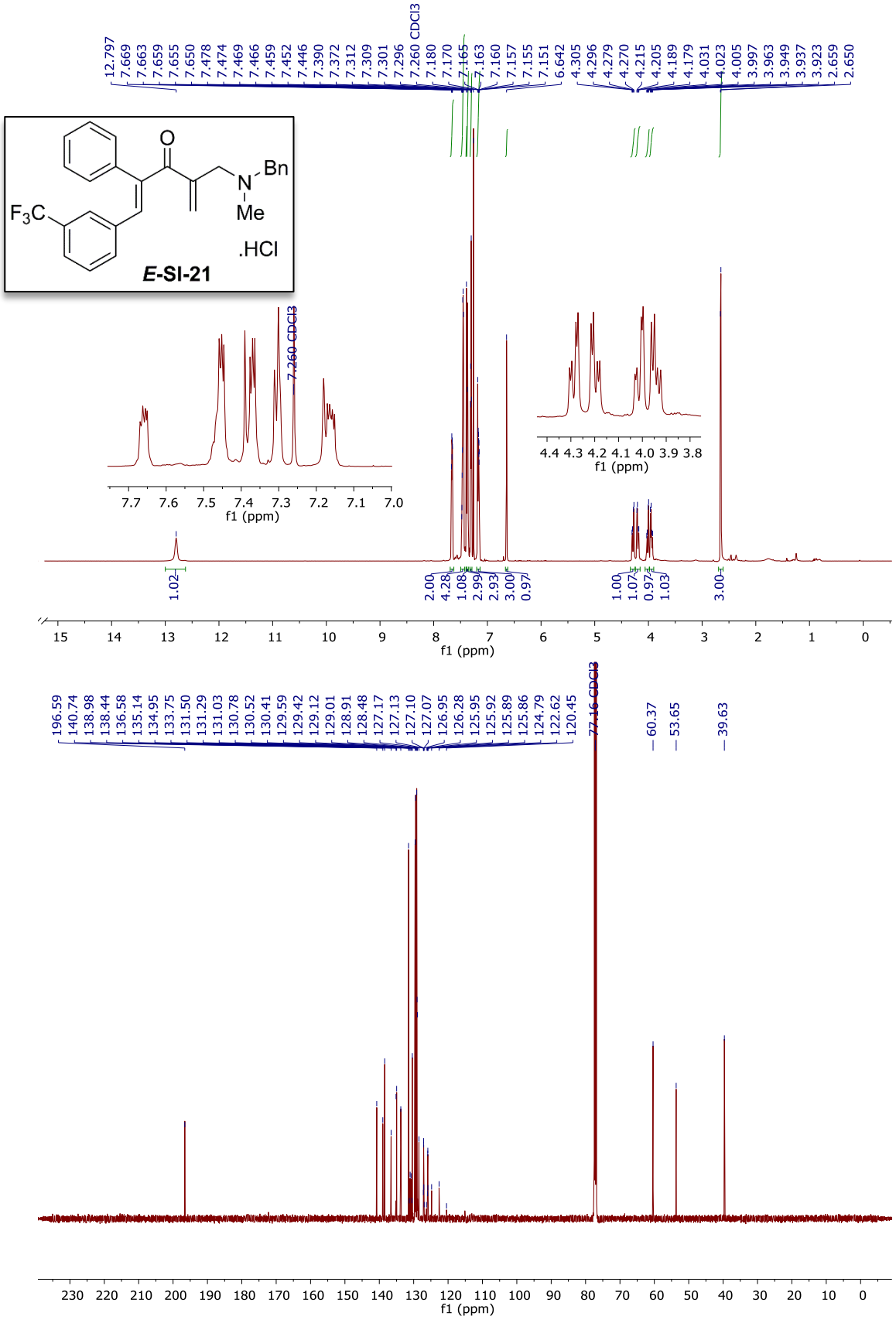
7.625
7.622
7.618
7.612
7.457
7.451
7.445
7.403
7.383
7.379
7.375
7.373
7.368
7.364
7.358
7.355
7.342
7.339
7.335
7.331
7.327
7.323
7.320
7.314
7.311
7.309
7.307
7.260 CDCl3
7.164
7.160
7.157
7.153
7.151
7.119
6.693
4.181
4.172
4.155
4.146
4.063
4.051
4.037
4.025
3.930
3.917
3.904
3.895
3.879
2.498
2.488
N
Bn
Me
O
Br
.HCl
Z-SI-20
f1 (ppm)
0.97
2.13
3.39
4.40
4.22
2.03
1.07
1.00
0.98
1.00
2.05
2.99
199.43
141.39
141.32
137.86
137.19
136.89
131.58
131.51
131.14
130.55
130.39
129.63
129.56
129.33
129.23
128.39
127.38
126.31
122.86
77.16 CDCl3
60.25
51.46
39.05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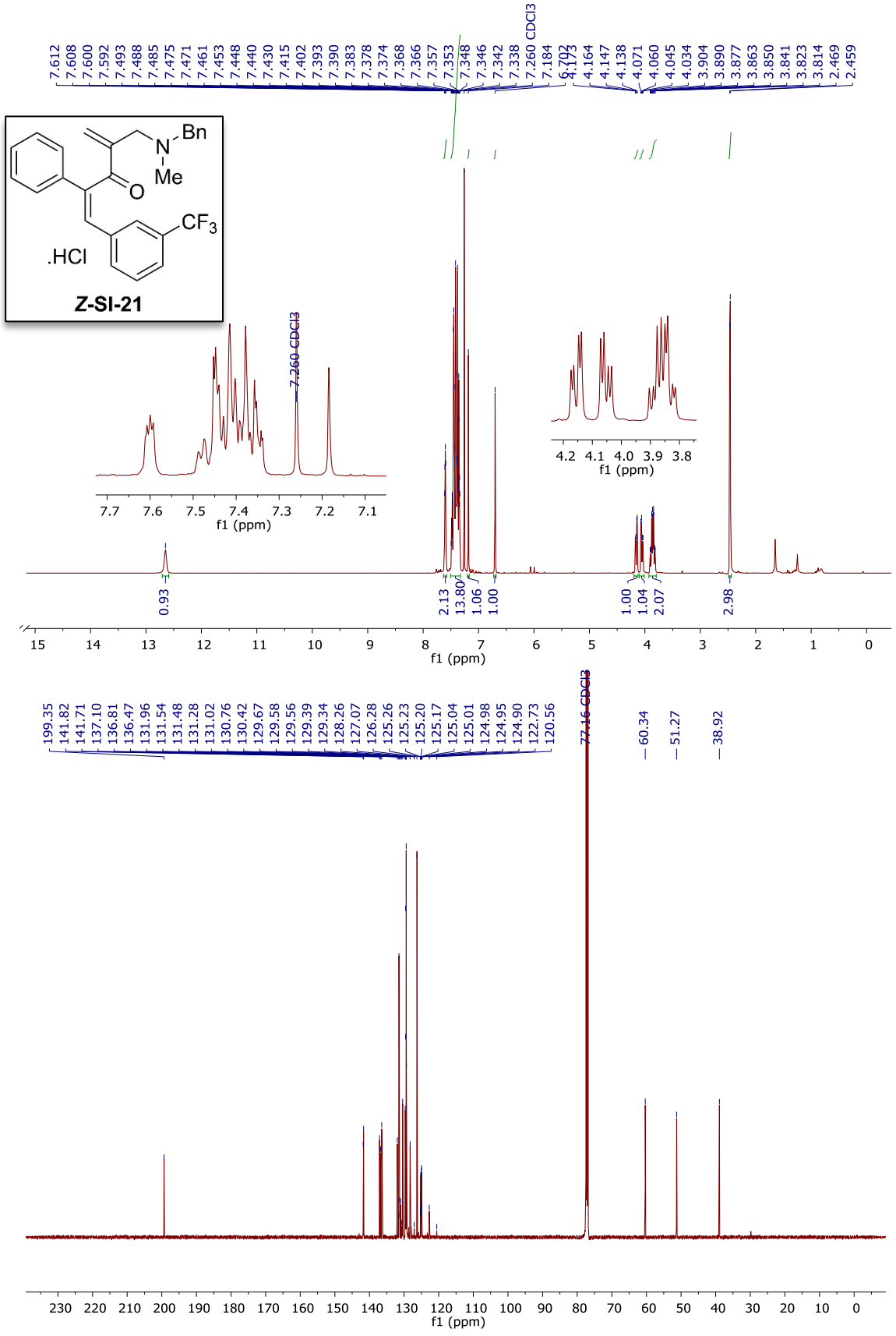
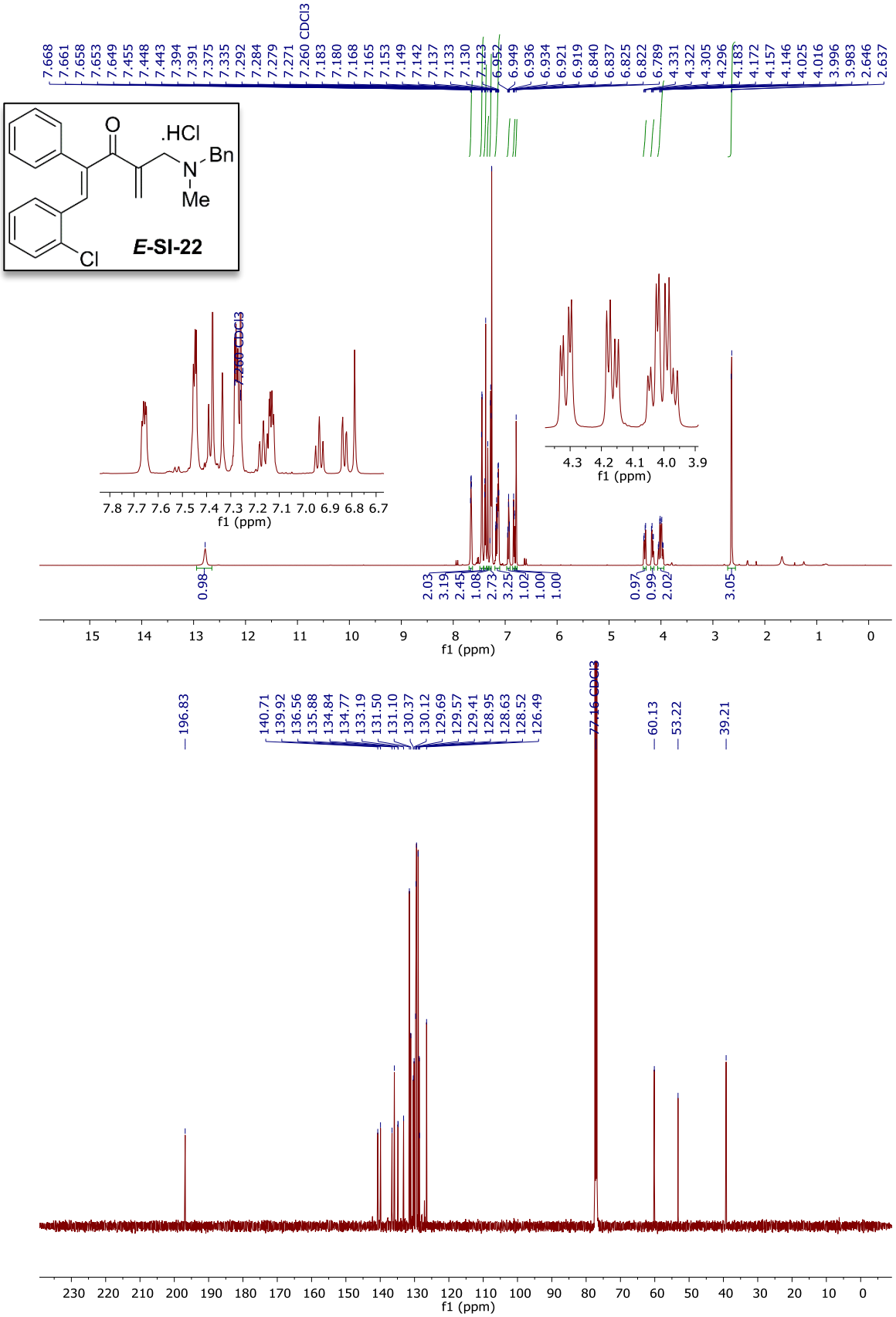
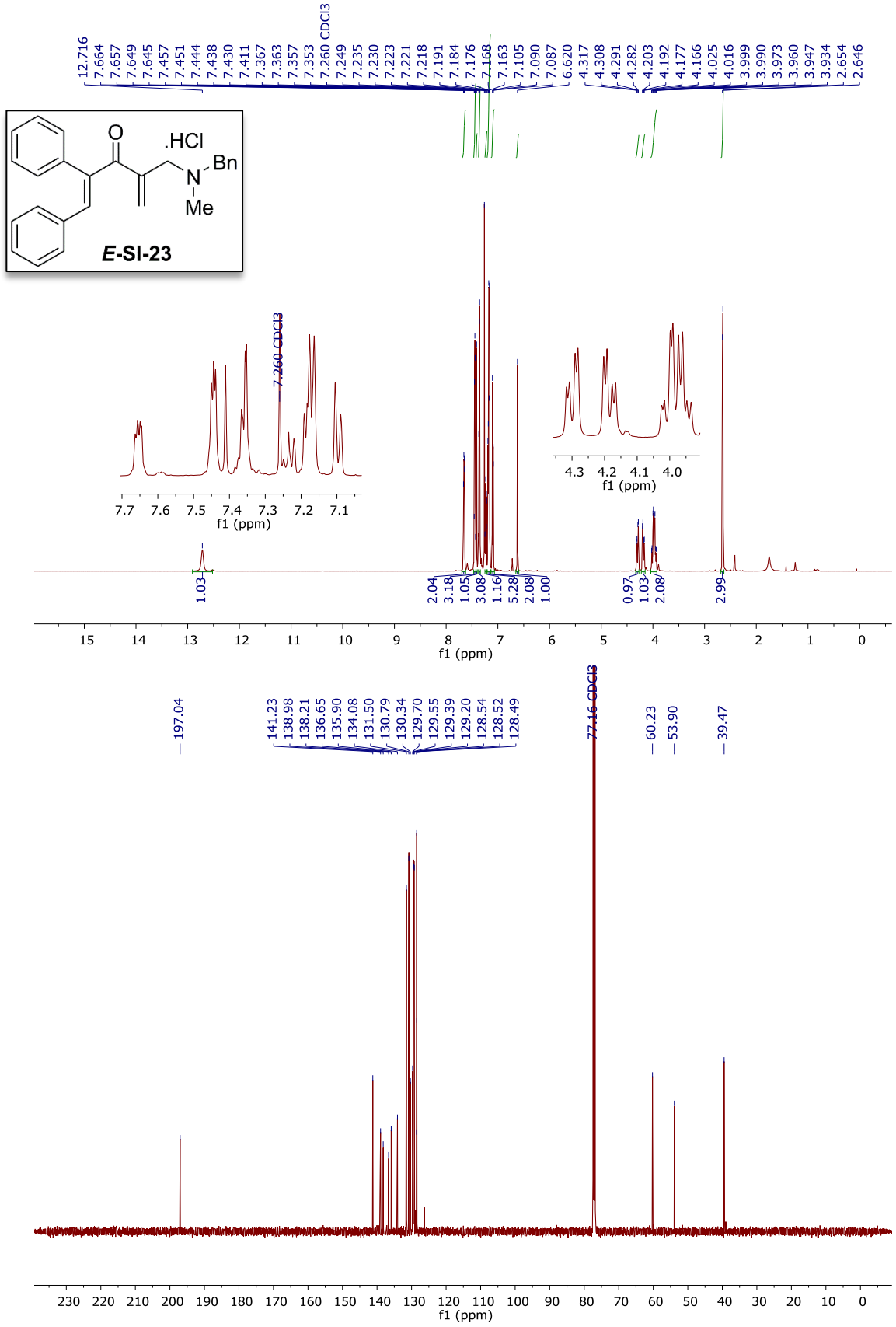
7.663
7.659
7.655
7.650
7.478
7.474
7.469
7.466
7.459
7.452
7.446
7.390
7.372
7.312
7.309
7.301
7.296
7.260 CDCl3
7.180
7.170
7.165
7.163
7.160
7.157
7.155
7.151
6.642
4.305
4.296
4.279
4.270
4.215
4.205
4.189
4.179
4.031
4.023
4.005
3.997
3.963
3.949
3.937
3.923
2.659
2.650
O
N
Bn
Me
F3C
.HCl
E-SI-21
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
4.4 4.3 4.2 4.1 4.0 3.9 3.8
f1 (ppm)
1.02
2.00
4.28
1.08
2.99
2.93
3.00
0.97
1.00
1.07
0.97
1.03
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.59
140.74
138.98
138.44
136.58
135.14
134.95
133.75
131.50
131.29
131.03
130.78
130.52
130.41
129.59
129.42
129.12
129.01
128.91
128.48
127.17
127.13
127.10
127.07
126.95
126.28
125.95
125.92
125.89
125.86
124.79
122.62
120.45
77.16 CDCl3
60.37
53.65
39.63
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.612 7.608 7.600 7.592 7.493 7.488 7.485 7.475 7.471 7.461 7.453 7.448 7.440 7.430 7.415 7.402 7.393 7.390 7.383 7.378 7.374 7.368 7.366 7.357 7.353 7.348 7.346 7.342 7.338 7.260 CDCl3 7.184 4.173 4.164 4.147 4.138 4.071 4.060 4.045 4.034 3.904 3.890 3.877 3.863 3.850 3.841 3.823 3.814 2.469 2.459
Bn
N
Me
O
CF3
.HCl
Z-SI-21
7.260 CDCl3
f1 (ppm)
0.93
2.13
13.80
1.06
1.00
1.00
1.04
2.07
2.98
f1 (ppm)
199.35 141.82 141.71 137.10 136.81 136.47 131.96 131.54 131.48 131.28 131.02 130.76 130.42 129.67 129.58 129.56 129.39 129.34 128.26 127.07 126.28 125.26 125.23 125.20 125.17 125.04 125.01 124.98 124.95 124.90 122.73 120.56
77.16 CDCl3
60.34
51.27
38.92
f1 (ppm)


7.668 7.661 7.658 7.653 7.649 7.455 7.448 7.443 7.394 7.391 7.375 7.335 7.292 7.284 7.279 7.271 7.260 CDCl3 7.183 7.180 7.168 7.165 7.153 7.149 7.142 7.137 7.133 7.130 7.123 6.952 6.949 6.936 6.934 6.921 6.919 6.840 6.837 6.825 6.822 6.789 4.331 4.322 4.305 4.296 4.183 4.172 4.157 4.146 4.025 4.016 3.996 3.983 2.646 2.637
O
.HCl
Bn
N
Me
Cl
E-SI-22
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
0.98 2.03 3.19 2.45 1.08 2.73 3.25 1.02 1.00 1.00 0.97 0.99 2.02 3.05
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.83 140.71 139.92 136.56 135.88 134.84 134.77 133.19 131.50 131.10 130.37 130.12 129.69 129.57 129.41 128.95 128.63 128.52 126.49 77.16 CDCl3 60.13 53.22 39.21
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.657
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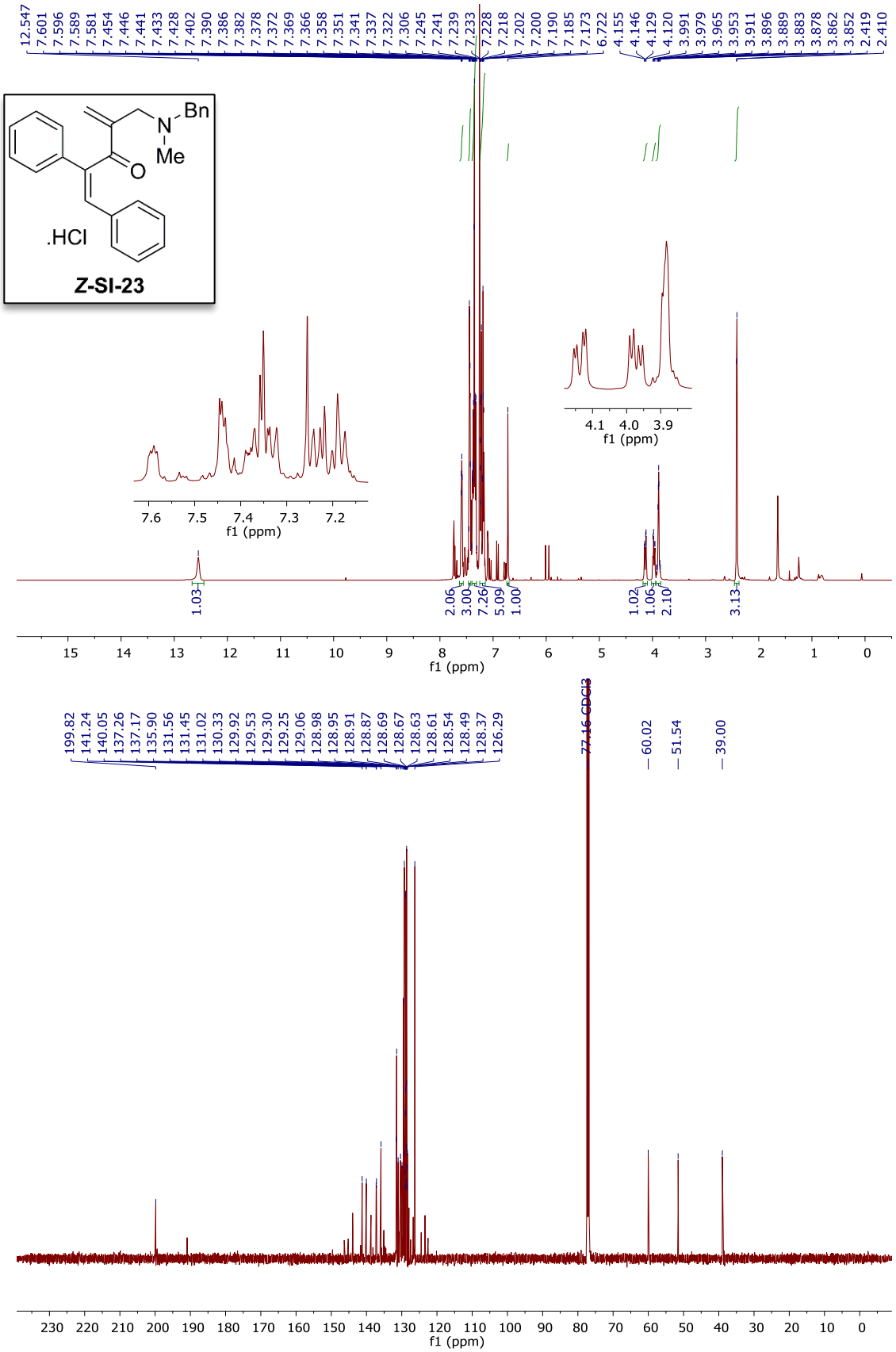
7.645
7.457
7.451
7.444
7.438
7.430
7.411
7.367
7.363
7.357
7.353
7.260 CDCl3
7.249
7.235
7.230
7.223
7.221
7.218
7.191
7.184
7.176
7.168
7.163
7.105
7.090
7.087
6.620
4.317
4.308
4.291
4.282
4.203
4.192
4.177
4.166
4.025
4.016
3.999
3.990
3.973
3.960
3.947
3.934
2.654
2.646
O
.HCl
N
Bn
Me
E-SI-23
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
4.3 4.2 4.1 4.0
f1 (ppm)
1.03
2.04
3.18
1.05
3.08
1.16
5.28
2.08
1.00
0.97
1.03
2.08
2.99
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
197.04
141.23
138.98
138.21
136.65
135.90
134.08
131.50
130.79
130.34
129.70
129.55
129.39
129.20
128.54
128.52
128.49
77.16 CDCl3
60.23
53.90
39.47
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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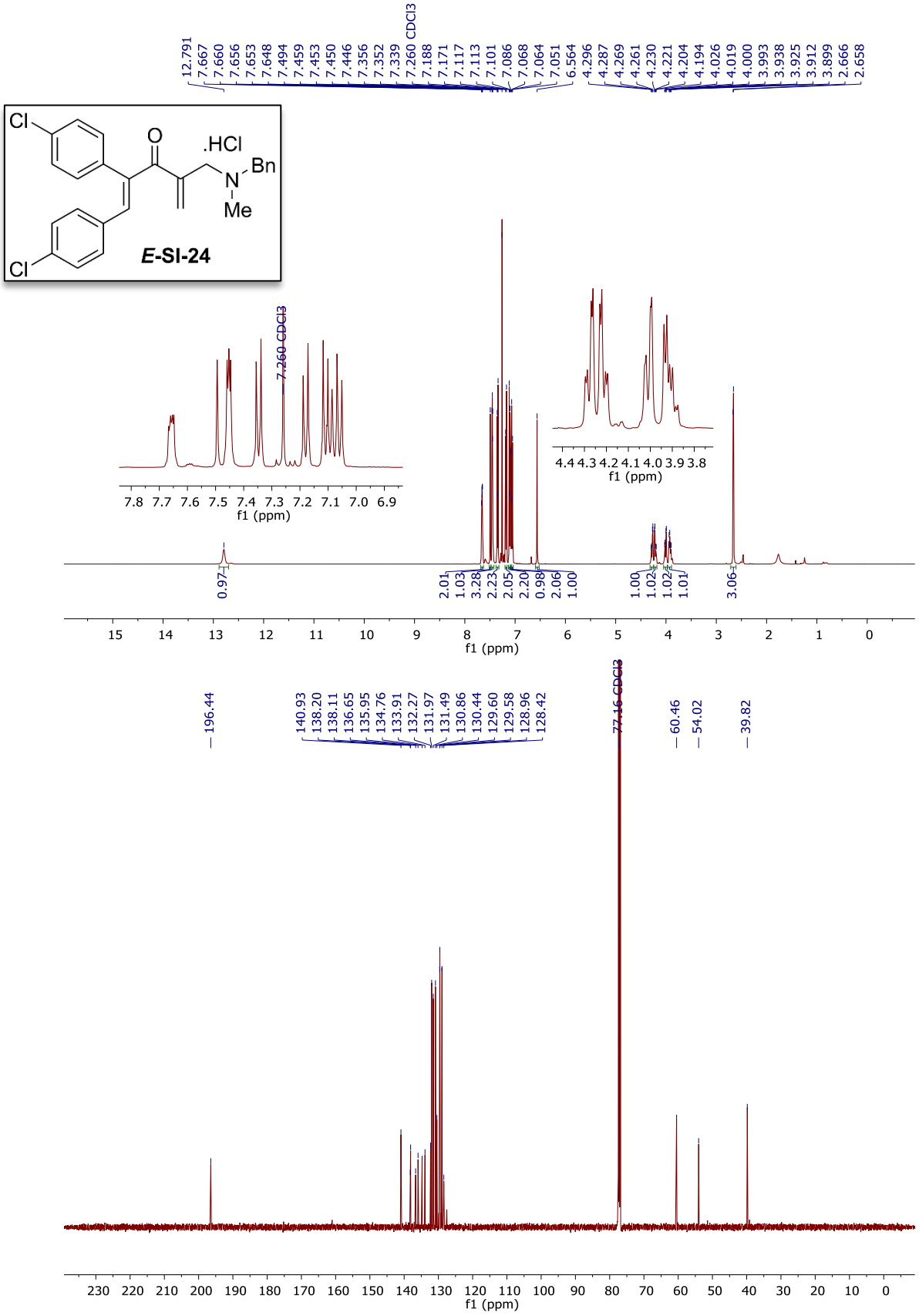
7.596
7.589
7.581
7.454
7.446
7.441
7.433
7.428
7.402
7.390
7.386
7.382
7.378
7.372
7.369
7.366
7.358
7.351
7.341
7.337
7.322
7.306
7.245
7.241
7.239
7.233
7.228
7.218
7.202
7.200
7.190
7.185
7.173
6.722
4.155
4.146
4.129
4.120
3.991
3.979
3.965
3.953
3.911
3.896
3.889
3.883
3.878
3.862
3.852
2.419
2.410
Bn
N
Me
O
.HCl
Z-SI-23
7.6 7.5 7.4 7.3 7.2
f1 (ppm)
4.1 4.0 3.9
f1 (ppm)
1.03
2.06
3.00
7.26
5.09
1.00
1.02
1.06
2.10
3.13
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
199.82
141.24
140.05
137.26
137.17
135.90
131.56
131.45
131.02
130.33
129.92
129.53
129.30
129.25
129.06
128.98
128.95
128.91
128.87
128.69
128.67
128.63
128.61
128.54
128.49
128.37
126.29
77.16 CDCl3
60.02
51.54
39.00
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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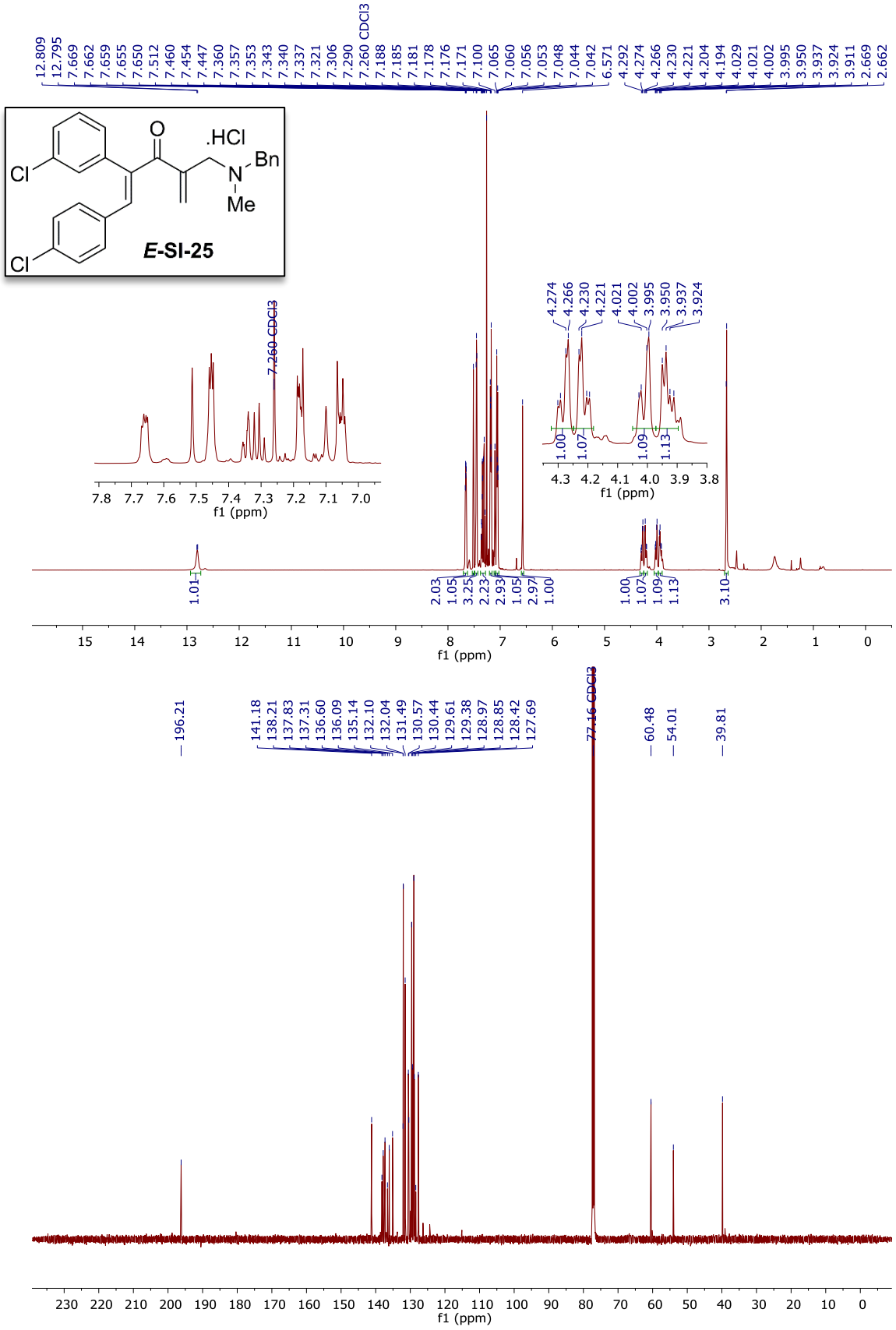
7.656
7.653
7.648
7.494
7.459
7.453
7.450
7.446
7.356
7.352
7.339
7.260 CDCl3
7.188
7.171
7.117
7.113
7.101
7.086
7.068
7.064
7.051
6.564
4.296
4.287
4.269
4.261
4.230
4.221
4.204
4.194
4.026
4.019
4.000
3.993
3.938
3.925
3.912
3.899
2.666
2.658
Cl
O
.HCl
Bn
N
Me
Cl
E-SI-24
7.260 CDCl3
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
4.4 4.3 4.2 4.1 4.0 3.9 3.8
f1 (ppm)
0.97
2.01
1.03
3.28
2.23
2.05
2.20
0.98
2.06
1.00
1.00
1.02
1.02
1.01
3.06
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.44
140.93
138.20
138.11
136.65
135.95
134.76
133.91
132.27
131.97
131.49
130.86
130.44
129.60
129.58
128.96
128.42
77.16 CDCl3
60.46
54.02
39.82
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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12.795
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7.659
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7.650
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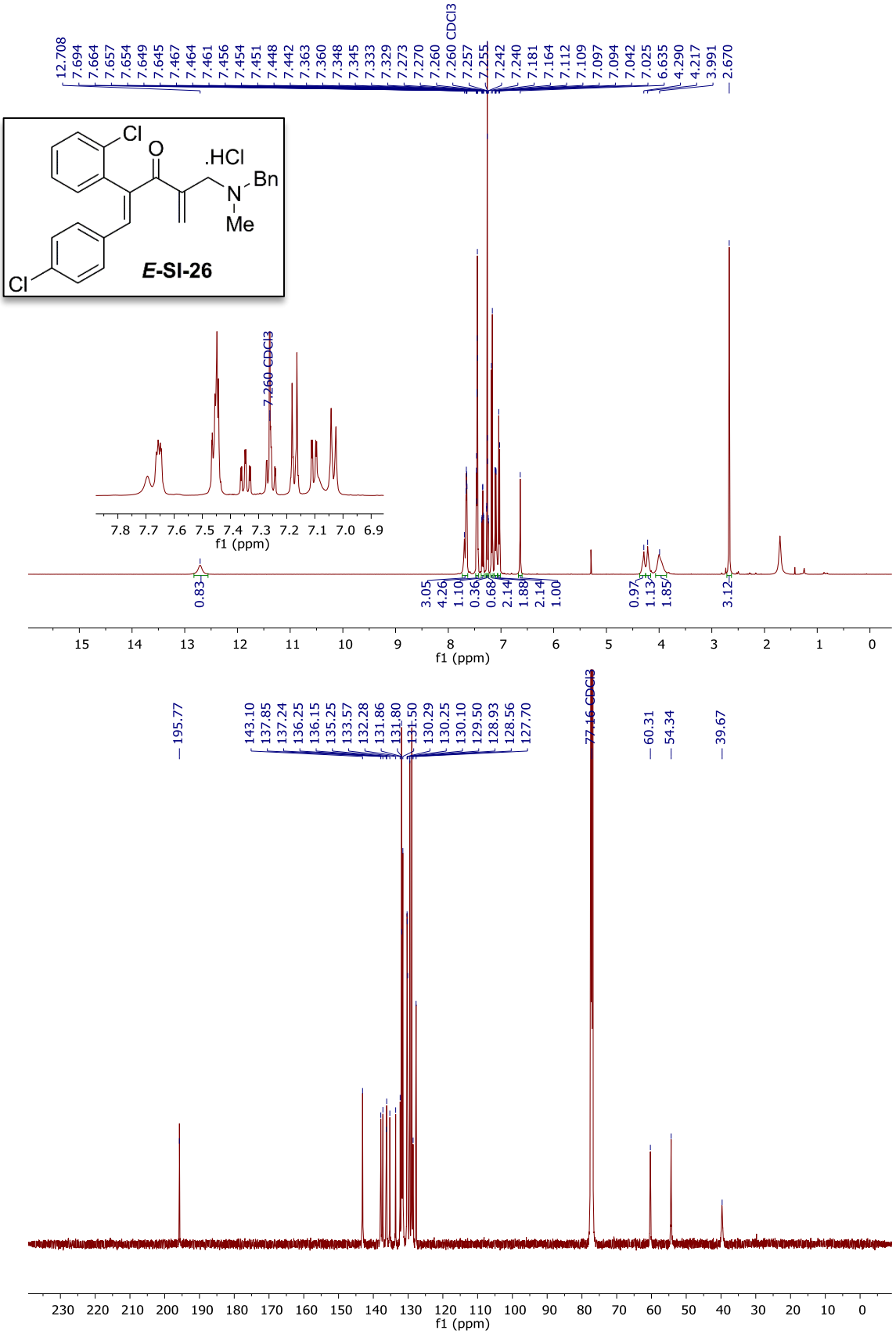
7.454
7.447
7.360
7.357
7.353
7.343
7.340
7.337
7.321
7.306
7.290
7.260 CDCl3
7.188
7.185
7.181
7.178
7.176
7.171
7.100
7.065
7.060
7.056
7.053
7.048
7.044
7.042
6.571
4.292
4.274
4.266
4.230
4.221
4.204
4.194
4.029
4.021
4.002
3.995
3.950
3.937
3.924
3.911
2.669
2.662
O
.HCl
Cl
N
Bn
Me
Cl
E-SI-25
f1 (ppm)
1.01
2.03
1.05
3.25
2.23
2.93
1.05
2.97
1.00
1.00
1.07
1.09
1.13
3.10
196.21
141.18
138.21
137.83
137.31
136.60
136.09
135.14
132.10
132.04
131.49
130.57
130.44
129.61
129.38
128.97
128.85
128.42
127.69
77.16 CDCl3
60.48
54.01
39.81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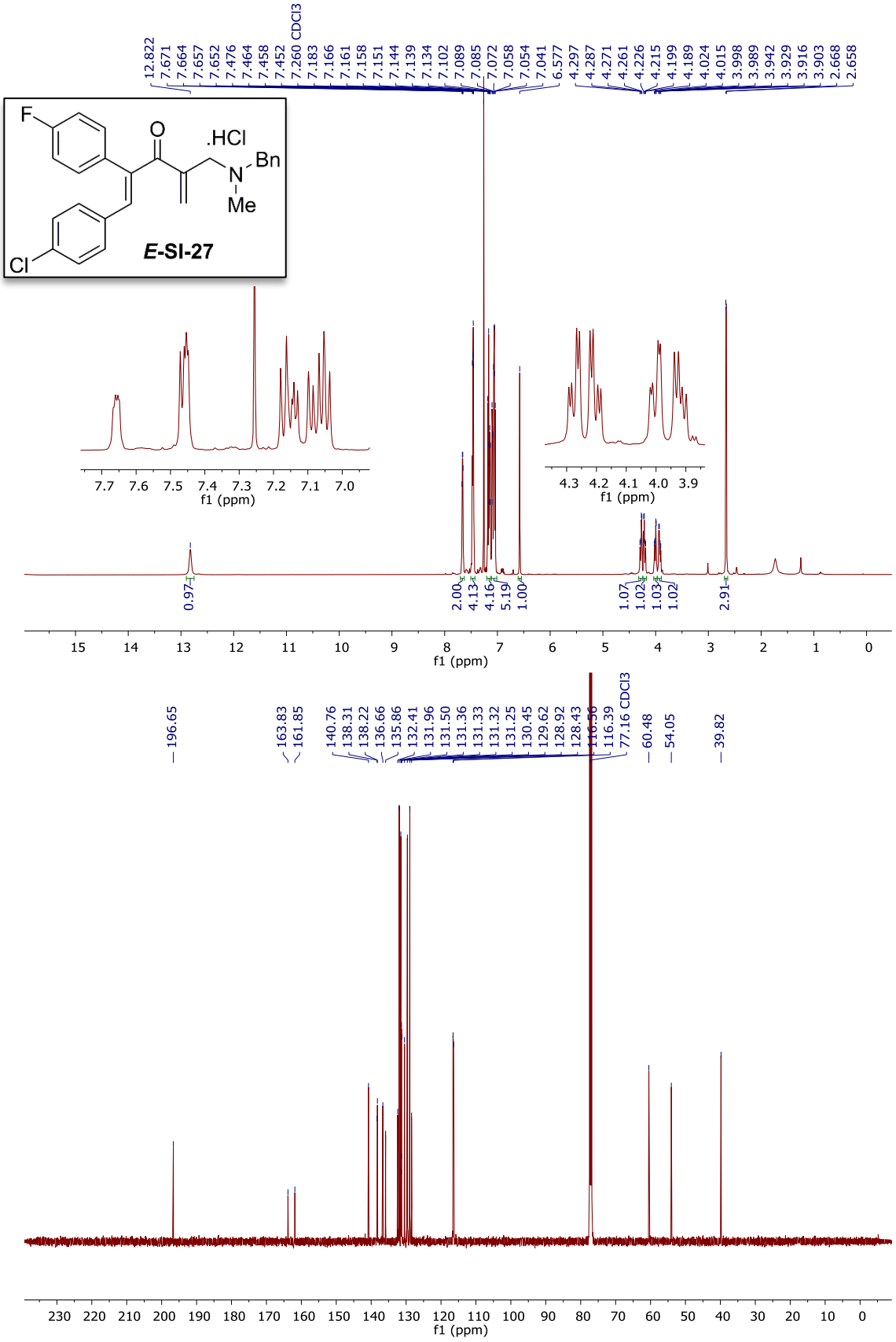
7.657
7.654
7.649
7.645
7.467
7.464
7.461
7.456
7.454
7.451
7.448
7.442
7.363
7.360
7.348
7.345
7.333
7.329
7.273
7.270
7.260
7.260 CDCl3
7.257
7.255
7.242
7.240
7.181
7.164
7.112
7.109
7.097
7.094
7.042
7.025
6.635
4.290
4.217
3.991
2.670
Cl
O
.HCl
Bn
N
Me
Cl
E-SI-26
7.260 CDCl3
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
0.83
3.05
4.26
1.10
0.36
0.68
2.14
1.88
2.14
1.00
0.97
1.13
1.85
3.12
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
195.77
143.10
137.85
137.24
136.25
136.15
135.25
133.57
132.28
131.86
131.80
131.50
130.29
130.25
130.10
129.50
128.93
128.56
127.70
77.16 CDCl3
60.31
54.34
39.67
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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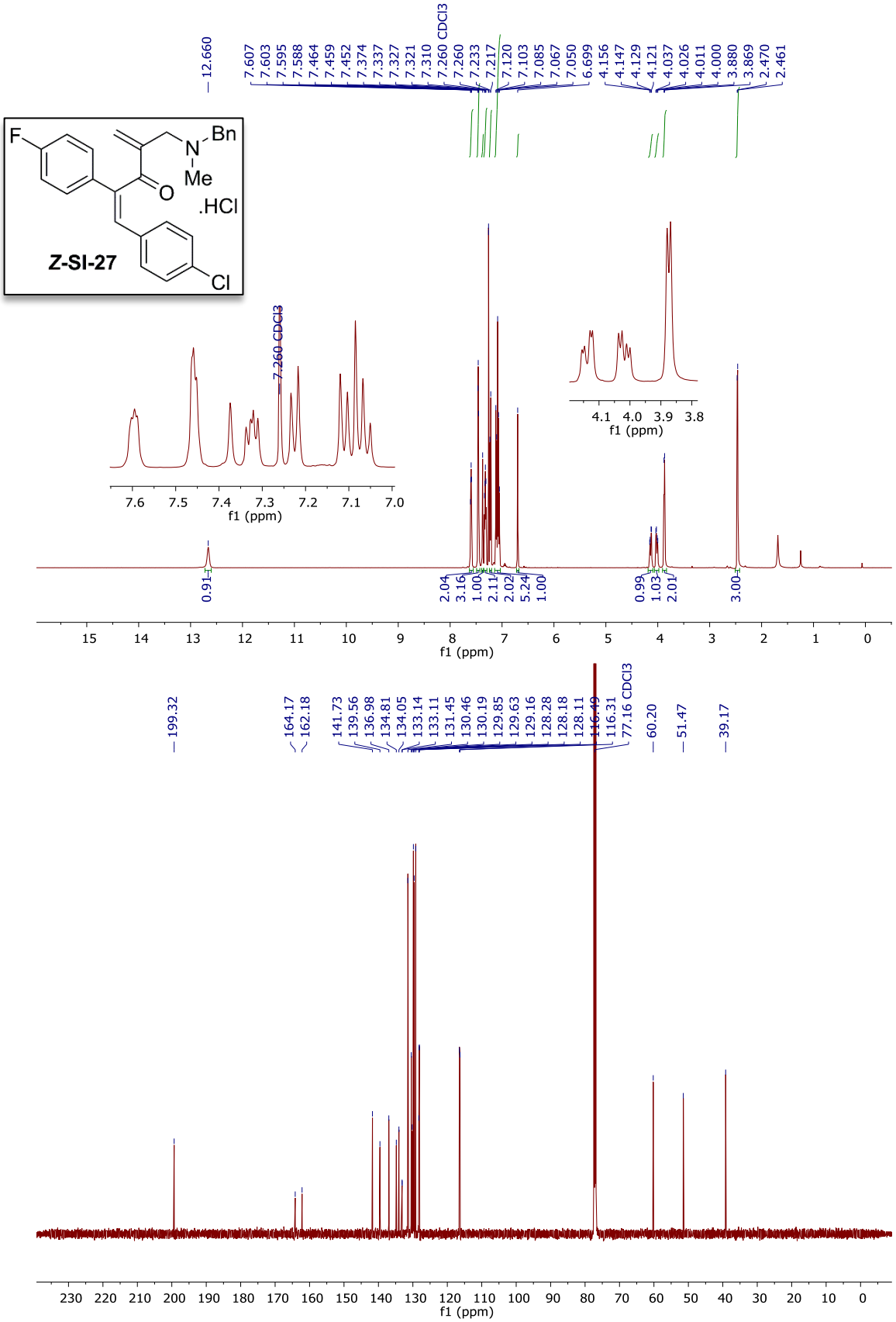
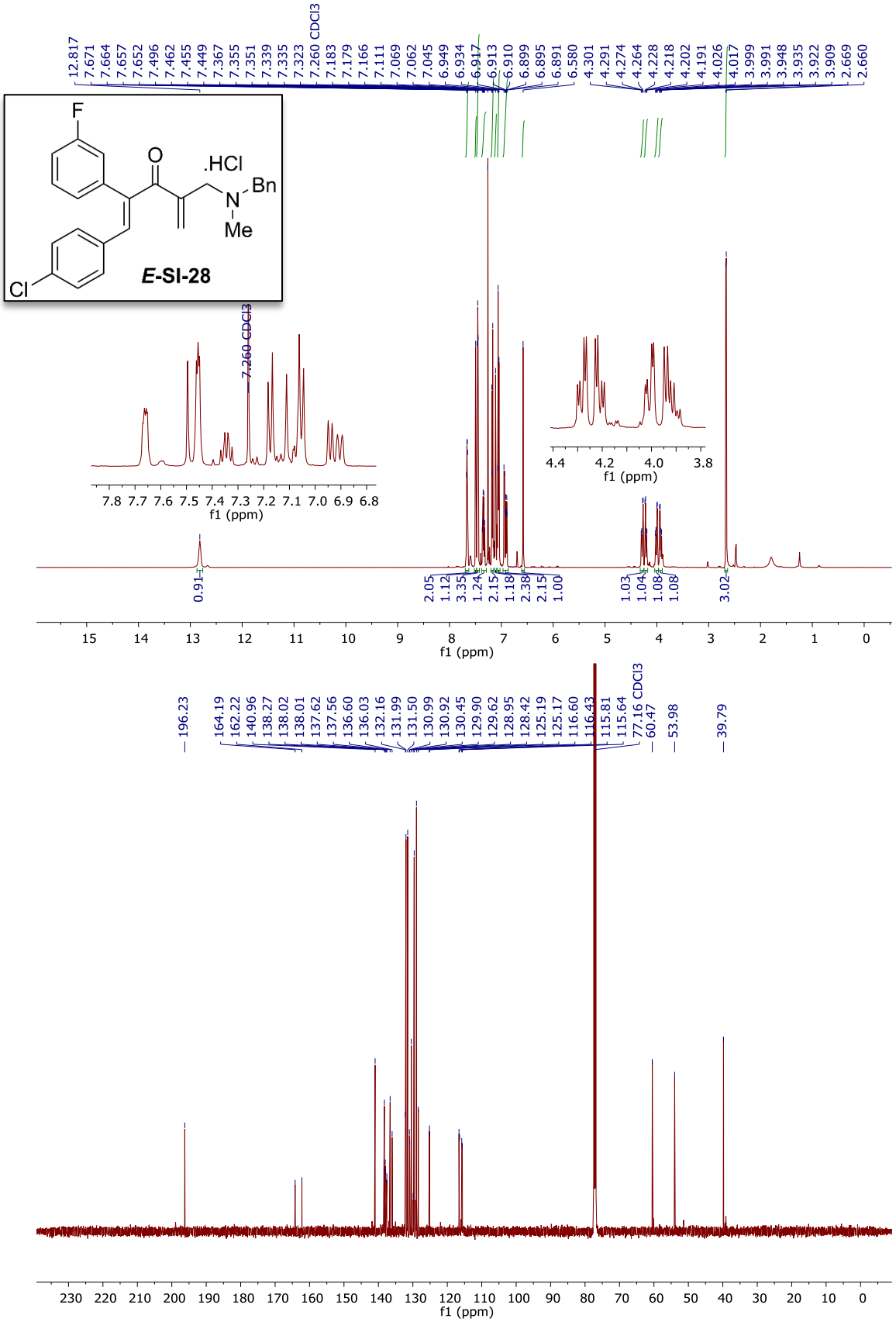
7.671
7.664
7.657
7.652
7.476
7.464
7.458
7.452
7.260 CDCl3
7.183
7.166
7.161
7.158
7.151
7.144
7.139
7.134
7.102
7.089
7.085
7.072
7.058
7.054
7.041
6.577
4.297
4.287
4.271
4.261
4.226
4.215
4.199
4.189
4.024
4.015
3.998
3.989
3.942
3.929
3.916
3.903
2.668
2.658
F
O
.HCl
Bn
N
Me
Cl
E-SI-27
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
0.97
2.00
4.13
4.16
5.19
1.00
1.07
1.02
1.03
1.02
2.91
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.65
163.83
161.85
140.76
138.31
138.22
136.66
135.86
132.41
131.96
131.50
131.36
131.33
131.32
131.25
130.45
129.62
128.92
128.43
116.56
116.39
77.16 CDCl3
60.48
54.05
39.82
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.660
7.607
7.603
7.595
7.588
7.464
7.459
7.452
7.374
7.337
7.327
7.321
7.310
7.260 CDCl3
7.260
7.233
7.217
7.120
7.103
7.085
7.067
7.050
6.699
4.156
4.147
4.129
4.121
4.037
4.026
4.011
4.000
3.880
3.869
2.470
2.461
F
N
Bn
Me
O
.HCl
Z-SI-27
Cl
7.260 CDCl3
7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
4.1 4.0 3.9 3.8
f1 (ppm)
0.91
2.04
3.16
1.00
2.11
2.02
5.24
1.00
0.99
1.03
2.01
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
199.32
164.17
162.18
141.73
139.56
136.98
134.81
134.05
133.14
133.11
131.45
130.46
130.19
129.85
129.63
129.16
128.28
128.18
128.11
116.49
116.31
77.16 CDCl3
60.20
51.47
39.17
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.335
7.323
7.260 CDCl3
7.183
7.179
7.166
7.111
7.069
7.062
7.045
6.949
6.934
6.917
6.913
6.910
6.899
6.895
6.891
6.580
4.301
4.291
4.274
4.264
4.228
4.218
4.202
4.191
4.026
4.017
3.999
3.991
3.948
3.935
3.922
3.909
2.669
2.660
F
O
.HCl
Bn
N
Me
Cl
E-SI-28
7.260 CDCl3
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
4.4 4.2 4.0 3.8
f1 (ppm)
0.91
2.05
1.12
3.35
1.24
2.15
1.18
2.38
2.15
1.00
1.03
1.04
1.08
1.08
3.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.23
164.19
162.22
140.96
138.27
138.02
138.01
137.62
137.56
136.60
136.03
132.16
131.99
131.50
130.99
130.92
130.45
129.90
129.62
128.95
128.42
125.19
125.17
116.60
116.43
115.81
115.64
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53.98
39.79
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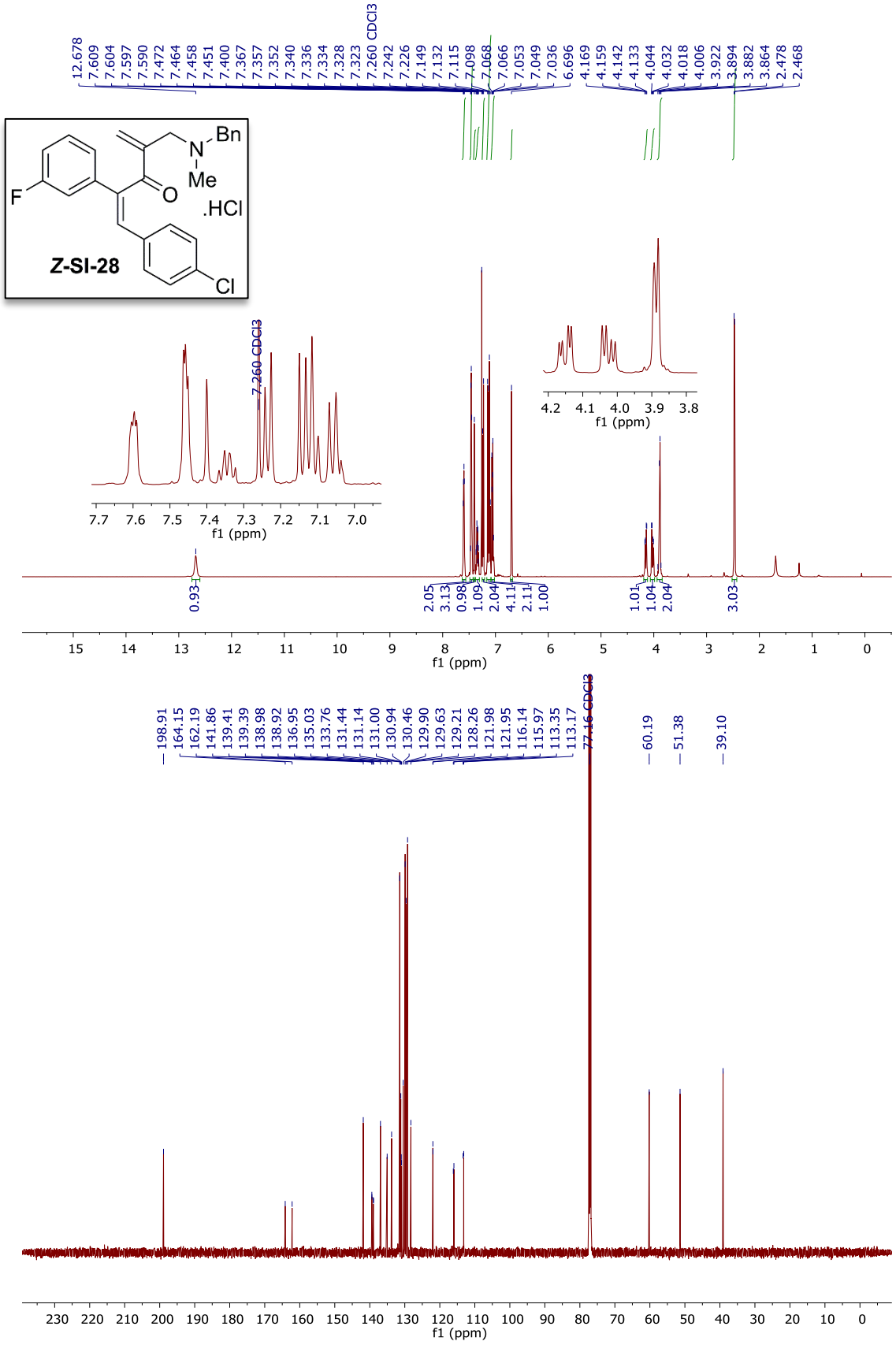
f1 (ppm)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7.352
7.340
7.336
7.334
7.328
7.323
7.260 CDCl3
7.242
7.226
7.149
7.132
7.115
7.098
7.068
7.066
7.053
7.049
7.036
6.696
4.169
4.159
4.142
4.133
4.044
4.032
4.018
4.006
3.922
3.894
3.882
3.864
2.478
2.468
Bn
N
Me
O
F
.HCl
Cl
Z-SI-28
7.260 CDCl3
f1 (ppm)
0.93
2.05
3.13
0.98
1.09
2.04
4.11
2.11
1.00
1.01
1.04
2.04
3.03
f1 (ppm)
198.91
164.15
162.19
141.86
139.41
139.39
138.98
138.92
136.95
135.03
133.76
131.44
131.14
131.00
130.94
130.46
129.90
129.63
129.21
128.26
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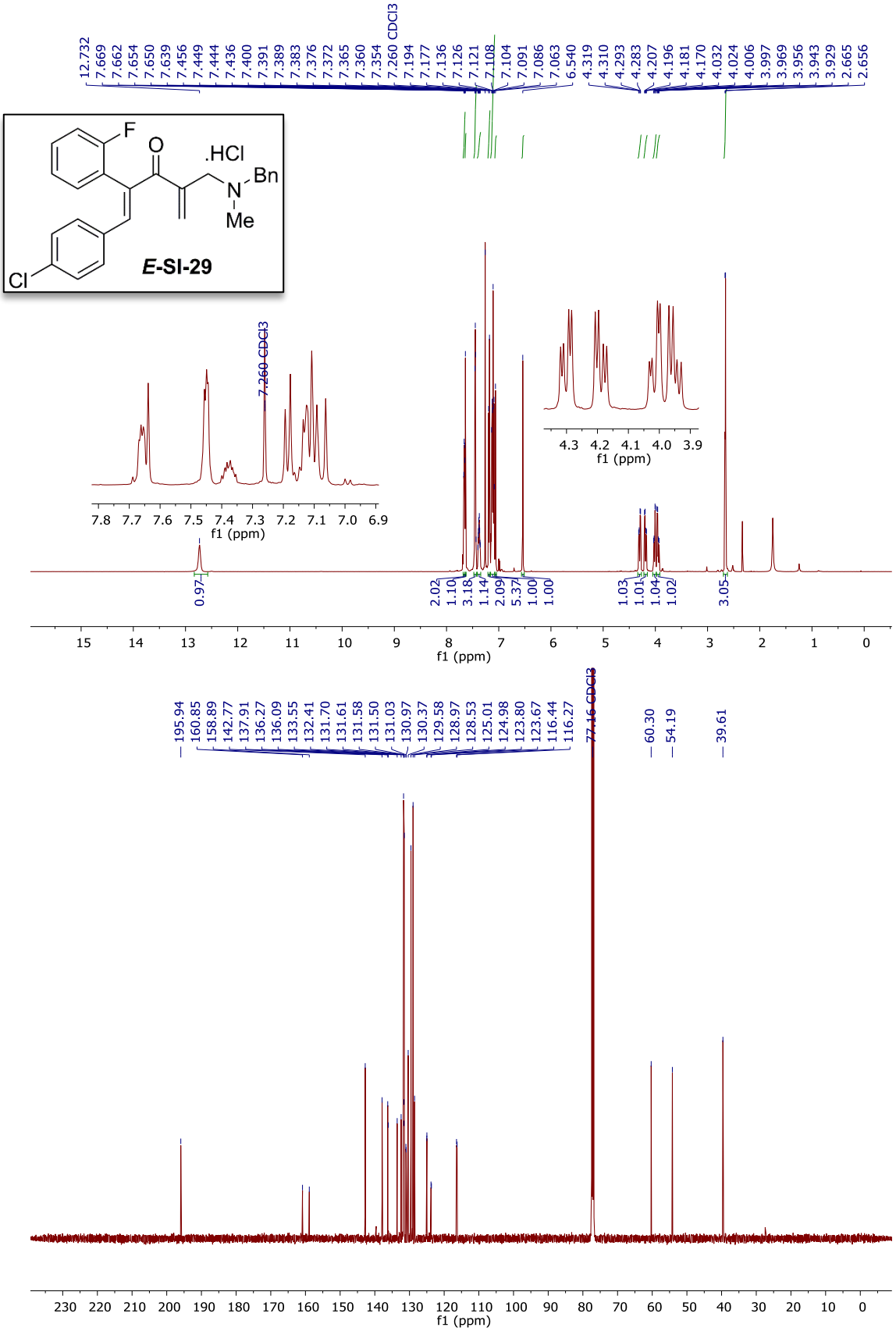
121.95
116.14
115.97
113.35
113.17
77.16 CDCl3
60.19
51.38
39.10
f1 (ppm)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7.449
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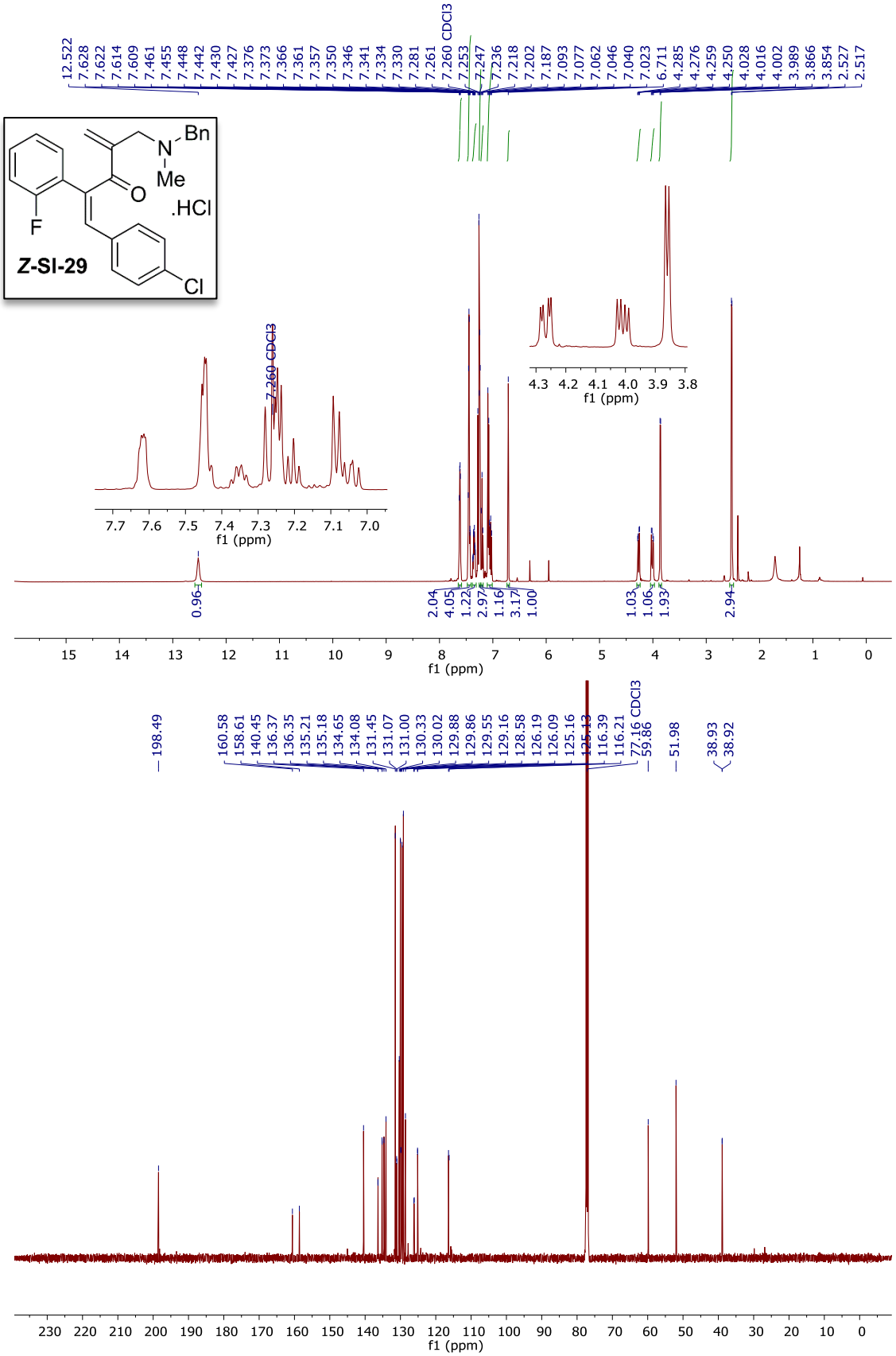
7.436
7.400
7.391
7.389
7.383
7.376
7.372
7.365
7.360
7.354
7.260 CDCl3
7.194
7.177
7.136
7.126
7.121
7.108
7.104
7.091
7.086
7.063
6.540
4.319
4.310
4.293
4.283
4.207
4.196
4.181
4.170
4.032
4.024
4.006
3.997
3.969
3.956
3.943
3.929
2.665
2.656
F
O
.HCl
Bn
N
Me
Cl
E-SI-29
7.260 CDCl3
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
0.97
2.02
1.10
3.18
1.14
2.09
5.37
1.00
1.00
1.03
1.01
1.04
1.02
3.05
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
195.94
160.85
158.89
142.77
137.91
136.27
136.09
133.55
132.41
131.70
131.61
131.58
131.50
131.03
130.97
130.37
129.58
128.97
128.53
125.01
124.98
123.80
123.67
116.44
116.27
77.16 CDCl3
60.30
54.19
39.61
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.448
7.442
7.430
7.427
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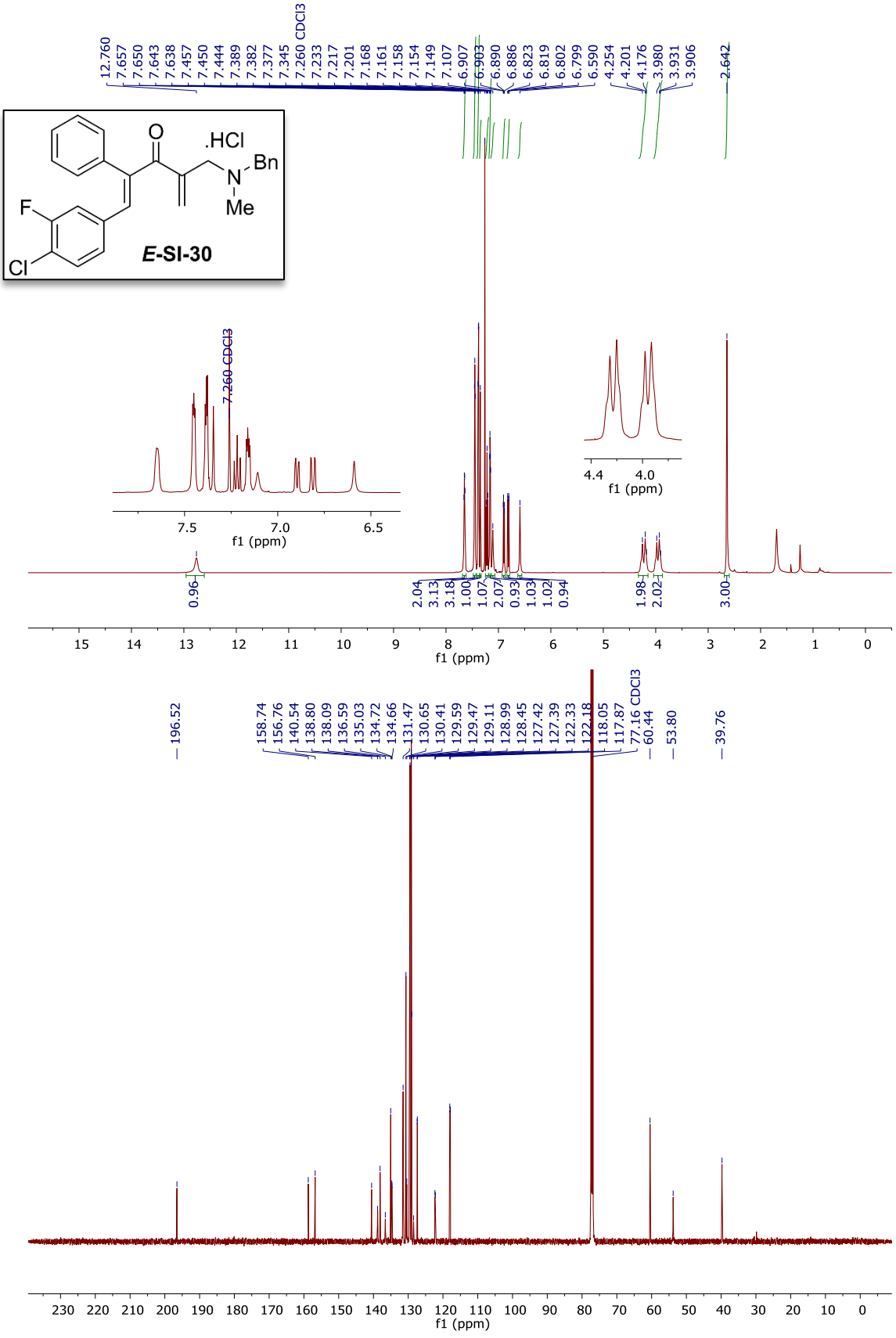
7.373
7.366
7.361
7.357
7.350
7.346
7.341
7.334
7.330
7.281
7.261
7.260 CDCl3
7.253
7.247
7.236
7.218
7.202
7.187
7.093
7.077
7.062
7.046
7.040
7.023
6.711
4.285
4.276
4.259
4.250
4.028
4.016
4.002
3.989
3.866
3.854
2.527
2.517
Bn
N
Me
O
.HCl
F
Z-SI-29
Cl
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
4.3 4.2 4.1 4.0 3.9 3.8
f1 (ppm)
0.96
2.04
4.05
1.22
2.97
1.16
3.17
1.00
1.03
1.06
1.93
2.94
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
198.49
160.58
158.61
140.45
136.37
136.35
135.21
135.18
134.65
134.08
131.45
131.07
131.00
130.33
130.02
129.88
129.86
129.55
129.16
128.58
126.19
126.09
125.16
125.13
116.39
116.21
77.16 CDCl3
59.86
51.98
38.93
38.92
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.643
7.638
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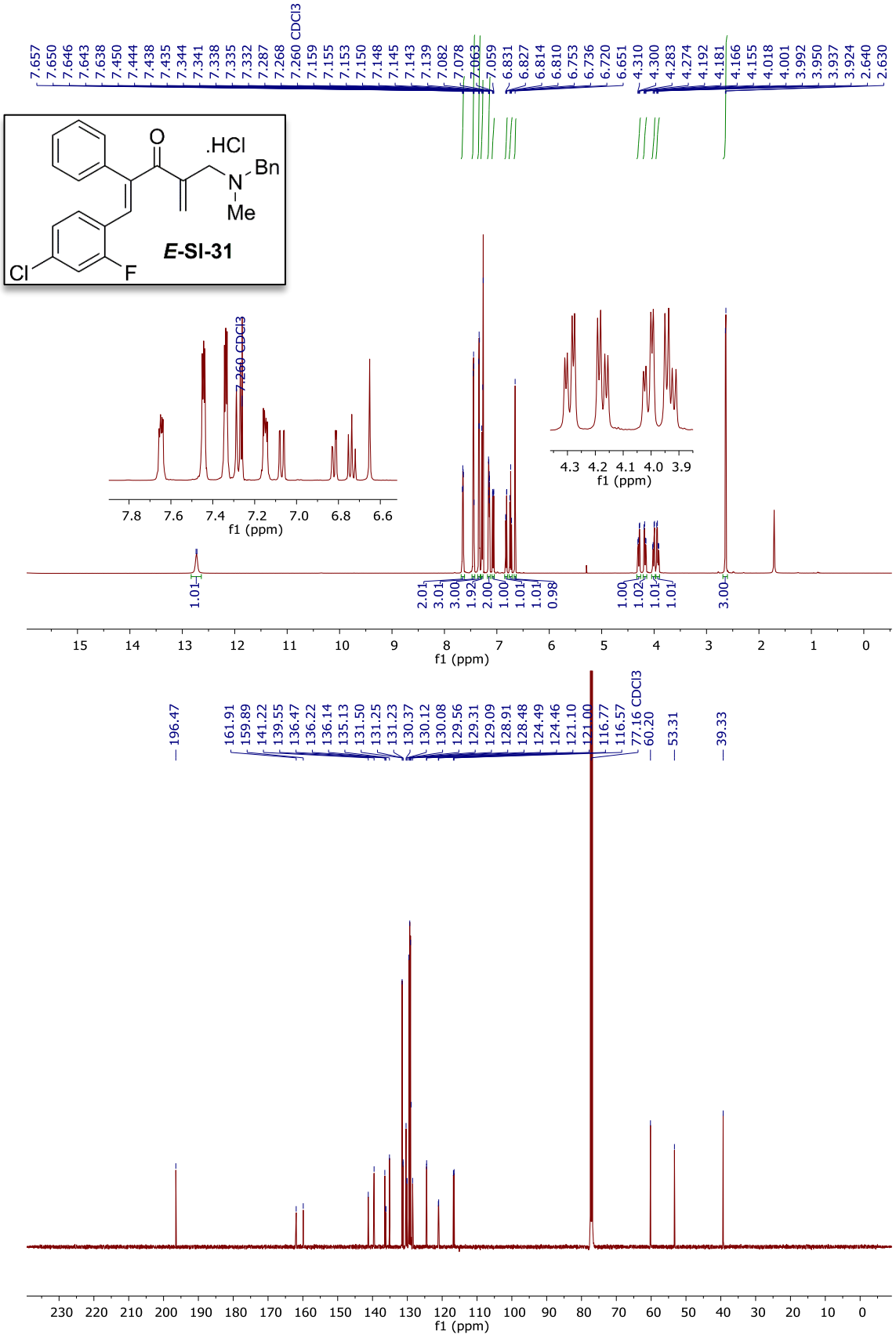
7.450
7.444
7.389
7.382
7.377
7.345
7.260 CDCl3
7.233
7.217
7.201
7.168
7.161
7.158
7.154
7.149
7.107
6.907
6.903
6.890
6.886
6.823
6.819
6.802
6.799
6.590
4.254
4.201
4.176
3.980
3.931
3.906
2.642
O
.HCl
Bn
N
Me
F
Cl
E-SI-30
7.260 CDCl3
7.5
7.0
6.5
f1 (ppm)
4.4
4.0
f1 (ppm)
0.96
2.04
3.13
3.18
1.00
1.07
2.07
0.93
1.03
1.02
0.94
1.98
2.02
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.52
158.74
156.76
140.54
138.80
138.09
136.59
135.03
134.72
134.66
131.47
130.65
130.41
129.59
129.47
129.11
128.99
128.45
127.42
127.39
122.33
122.18
118.05
117.87
77.16 CDCl3
60.44
53.80
39.76
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.643
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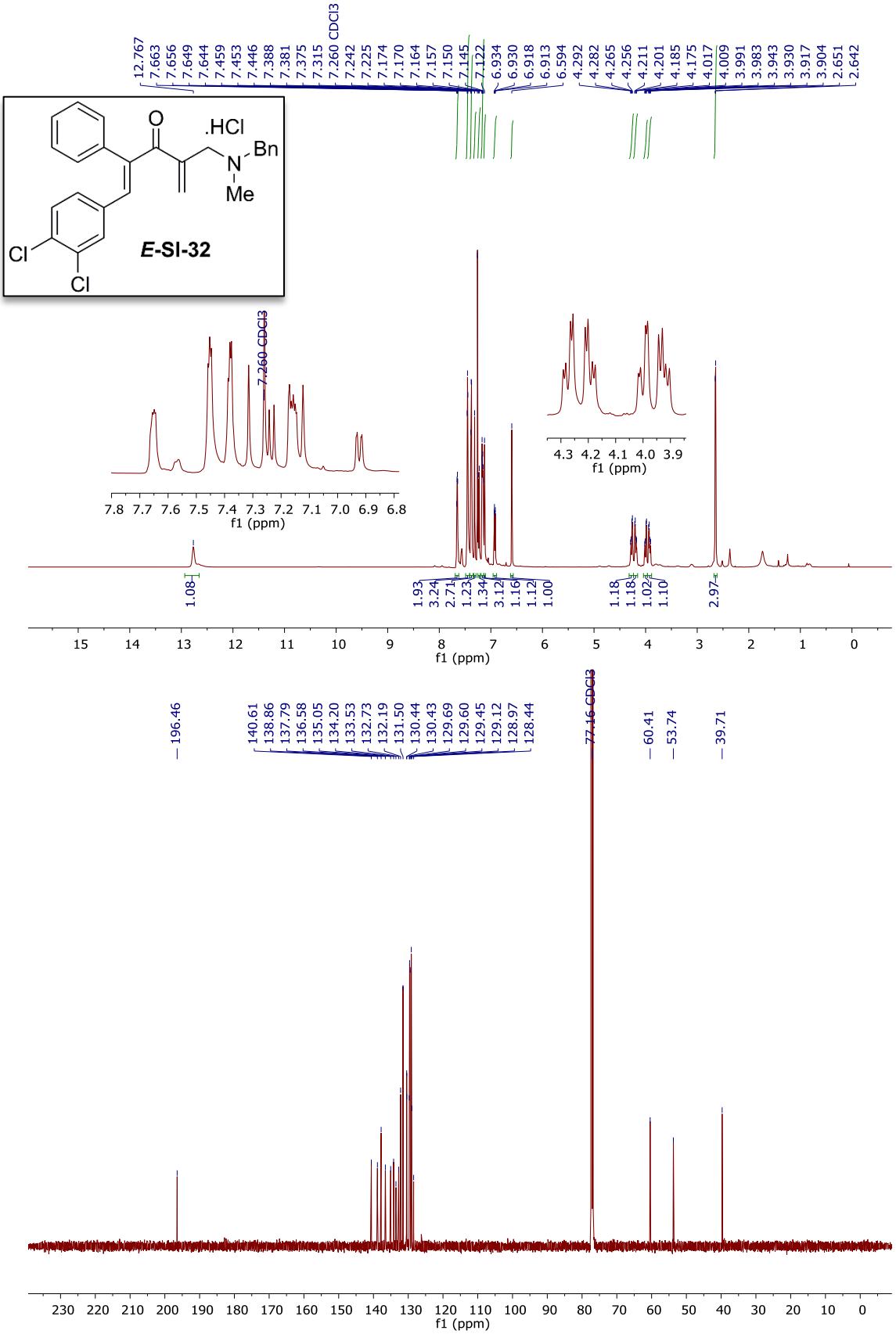
7.450
7.444
7.438
7.435
7.344
7.341
7.338
7.335
7.332
7.287
7.268
7.260 CDCl3
7.159
7.155
7.153
7.150
7.148
7.145
7.143
7.139
7.082
7.078
7.063
7.059
6.831
6.827
6.814
6.810
6.753
6.736
6.720
6.651
4.310
4.300
4.283
4.274
4.192
4.181
4.166
4.155
4.018
4.001
3.992
3.950
3.937
3.924
2.640
2.630
O
.HCl
Bn
N
Me
E-SI-31
Cl
F
7.260 CDCl3
7.8 7.6 7.4 7.2 7.0 6.8 6.6
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
1.01
2.01
3.01
3.00
1.92
2.00
1.00
1.01
1.01
0.98
1.00
1.02
1.01
1.01
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.47
161.91
159.89
141.22
139.55
136.47
136.22
136.14
135.13
131.50
131.25
131.23
130.37
130.12
130.08
129.56
129.31
129.09
128.91
128.48
124.49
124.46
121.10
121.00
116.77
116.57
77.16 CDCl3
60.20
53.31
39.33
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.644
7.459
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7.446
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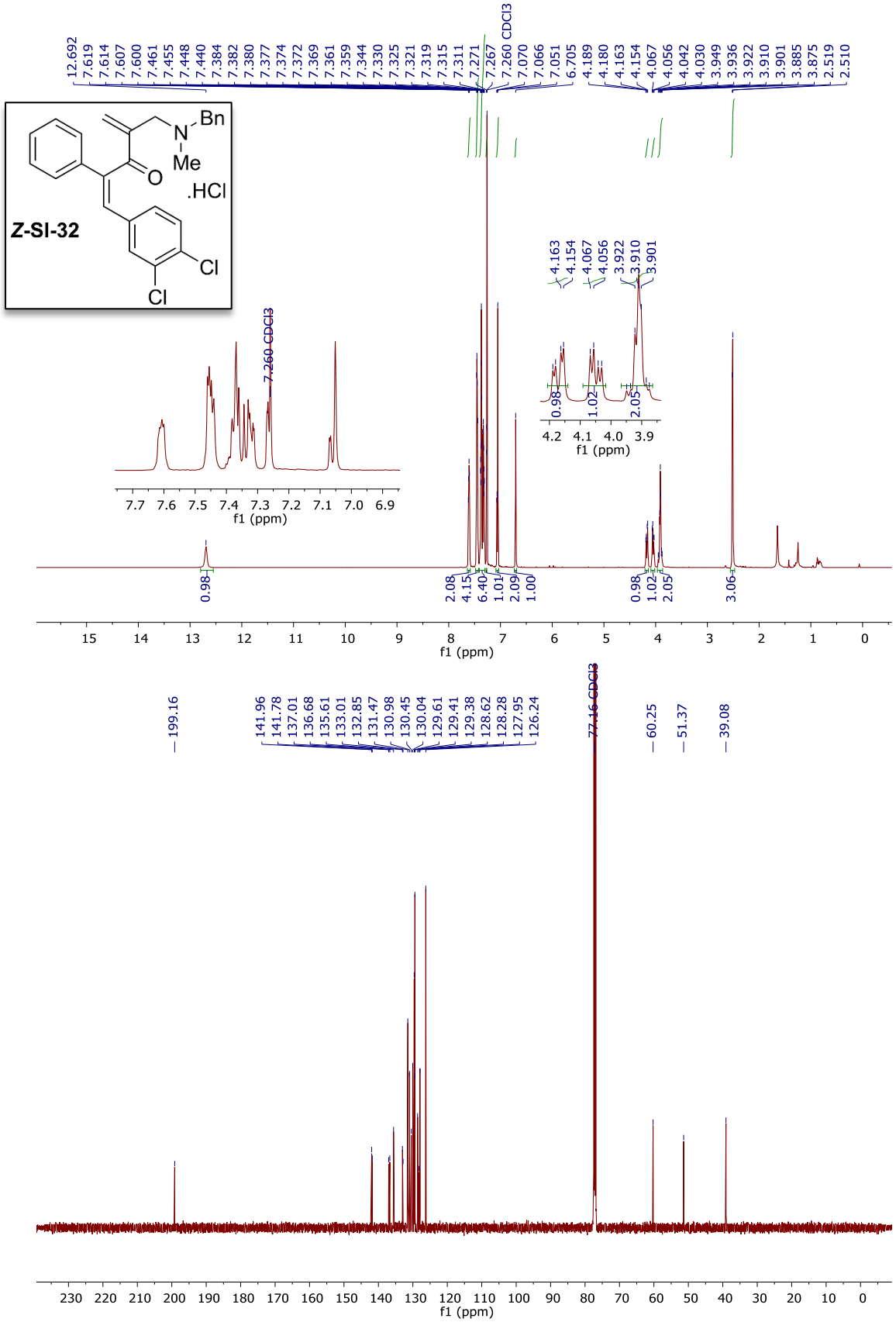
7.315
7.260 CDCl3
7.242
7.225
7.174
7.170
7.164
7.157
7.150
7.145
7.122
6.934
6.930
6.918
6.913
6.594
4.292
4.282
4.265
4.256
4.211
4.201
4.185
4.175
4.017
4.009
3.991
3.983
3.943
3.930
3.917
3.904
2.651
2.642
O
.HCl
N
Bn
Me
Cl
Cl
E-SI-32
7.260 CDCl3
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
4.3 4.2 4.1 4.0 3.9
f1 (ppm)
1.08
1.93
3.24
2.71
1.23
1.34
3.12
1.16
1.12
1.00
1.18
1.18
1.02
1.10
2.97
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.46
140.61
138.86
137.79
136.58
135.05
134.20
133.53
132.73
132.19
131.50
130.44
130.43
129.69
129.60
129.45
129.12
128.97
128.44
77.16 CDCl3
60.41
53.74
39.71
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Z-SI-32
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N
Me
O
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Cl
Cl
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7.607
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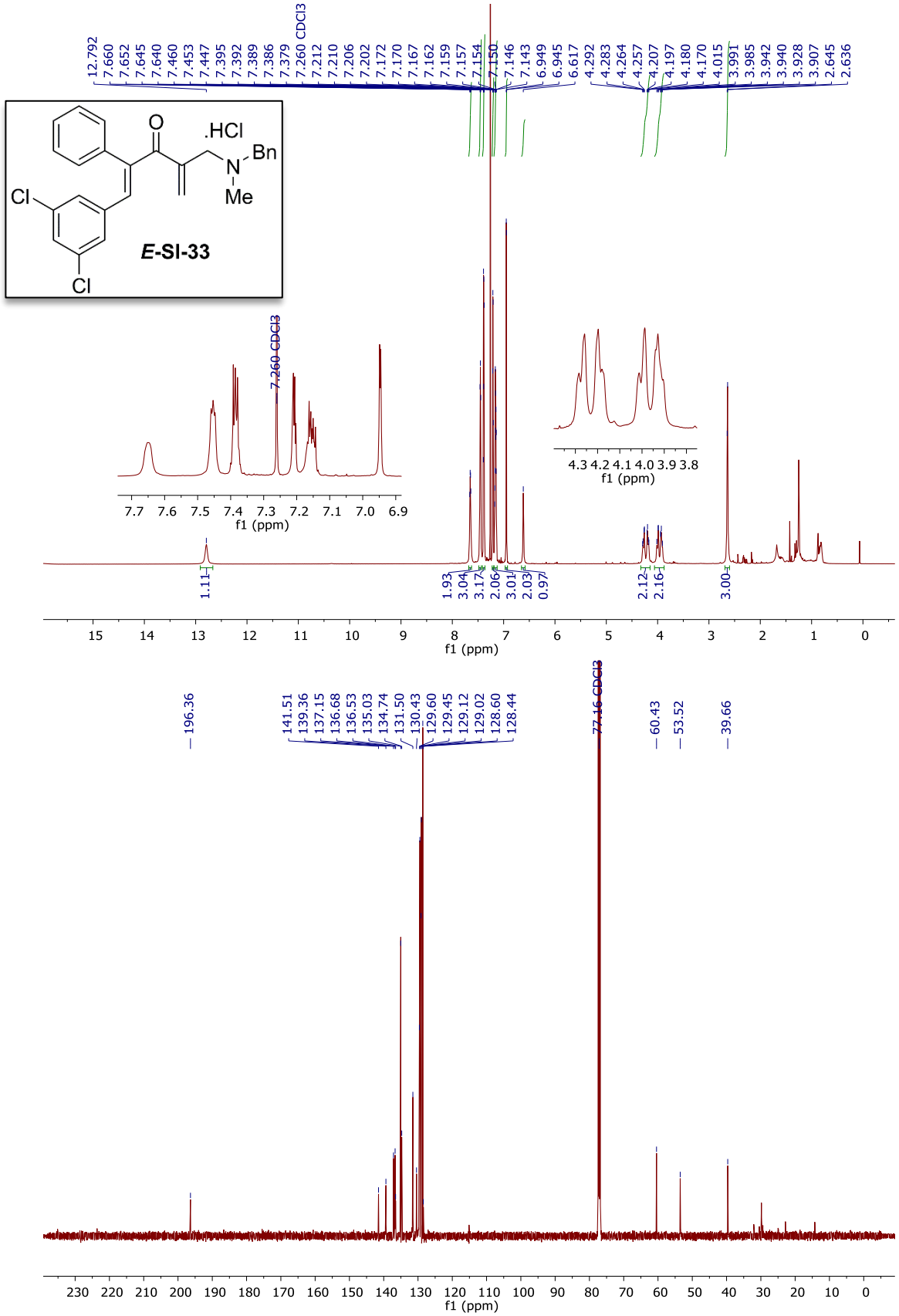
7.448
7.440
7.384
7.382
7.380
7.377
7.374
7.372
7.369
7.361
7.359
7.344
7.330
7.325
7.321
7.319
7.315
7.311
7.271
7.267
7.260 CDCl3
7.070
7.066
7.051
6.705
4.189
4.180
4.163
4.154
4.067
4.056
4.042
4.030
3.949
3.936
3.922
3.910
3.901
3.885
3.875
2.519
2.510
f1 (ppm)
0.98
2.08
4.15
6.40
1.01
2.09
1.00
0.98
1.02
2.05
3.06
199.16
141.96
141.78
137.01
136.68
135.61
133.01
132.85
131.47
130.98
130.45
130.04
129.61
129.41
129.38
128.62
128.28
127.95
126.24
77.16 CDCl3
60.25
51.37
39.08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7.392
7.389
7.386
7.379
7.260 CDCl3
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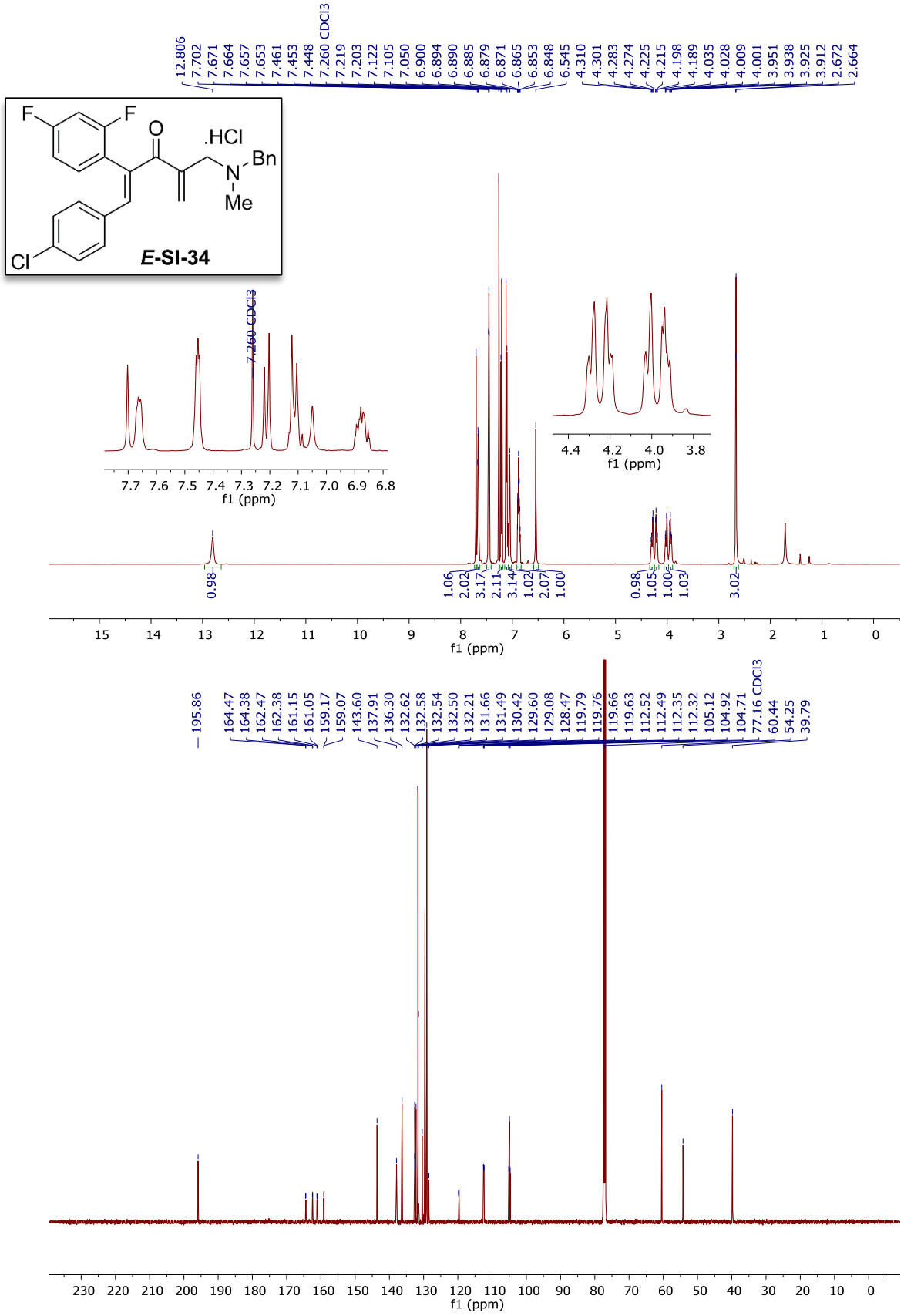
7.210
7.206
7.202
7.172
7.170
7.167
7.162
7.159
7.157
7.154
7.150
7.146
7.143
6.949
6.945
6.617
4.292
4.283
4.264
4.257
4.207
4.197
4.180
4.170
4.015
3.991
3.985
3.942
3.940
3.928
3.907
2.645
2.636
O
.HCl
Bn
N
Me
Cl
Cl
E-SI-33
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
4.3 4.2 4.1 4.0 3.9 3.8
f1 (ppm)
1.11
1.93
3.04
3.17
2.06
3.01
2.03
0.97
2.12
2.16
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
196.36
141.51
139.36
137.15
136.68
136.53
135.03
134.74
131.50
130.43
129.60
129.45
129.12
129.02
128.60
128.44
77.16 CDCl3
60.43
53.52
39.66
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.653
7.461
7.453
7.448
7.260 CDCl3
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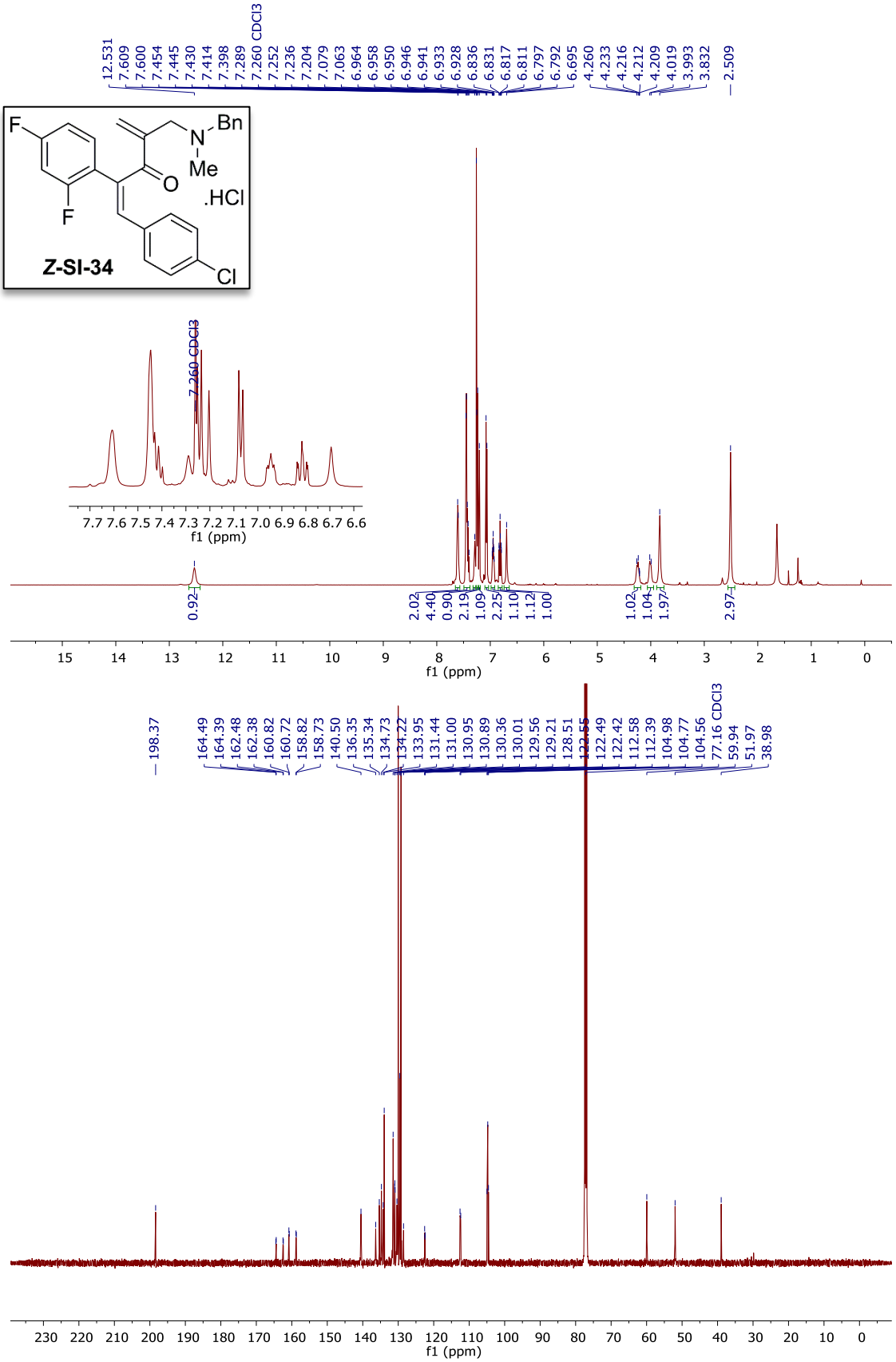
7.203
7.122
7.105
7.050
6.900
6.894
6.890
6.885
6.879
6.871
6.865
6.853
6.848
6.545
4.310
4.301
4.283
4.274
4.225
4.215
4.198
4.189
4.035
4.028
4.009
4.001
3.951
3.938
3.925
3.912
2.672
2.664
F
F
O
.HCl
Bn
N
Me
Cl
E-SI-34
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
4.4 4.2 4.0 3.8
f1 (ppm)
0.98
1.06
2.02
3.17
2.11
3.14
1.02
2.07
1.00
0.98
1.05
1.00
1.03
3.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
195.86
164.47
164.38
162.47
162.38
161.15
161.05
159.17
159.07
143.60
137.91
136.30
132.62
132.58
132.54
132.50
132.21
131.66
131.49
130.42
129.60
129.08
128.47
119.79
119.76
119.66
119.63
112.52
112.49
112.35
112.32
105.12
104.92
104.71
77.16 CDCl3
60.44
54.25
39.79
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.609
7.600
7.454
7.445
7.430
7.414
7.398
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7.260 CDCl3
7.252
7.236
7.204
7.079
7.063
6.964
6.958
6.950
6.946
6.941
6.933
6.928
6.836
6.831
6.817
6.811
6.797
6.792
6.695
4.260
4.233
4.216
4.212
4.209
4.019
3.993
3.832
2.509
F
N
Bn
Me
O
.HCl
F
Cl
Z-SI-34
7.260 CDCl3
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
0.92
2.02
4.40
0.90
2.19
1.09
2.25
1.10
1.12
1.00
1.02
1.04
1.97
2.97
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
198.37
164.49
164.39
162.48
162.38
160.82
160.72
158.82
158.73
140.50
136.35
135.34
134.73
134.22
133.95
131.44
131.00
130.95
130.89
130.36
130.01
129.56
129.21
128.51
122.55
122.49
122.42
112.58
112.39
104.98
104.77
104.56
77.16 CDCl3
59.94
51.97
38.98
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

References

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