Supporting Information for:

Chiral Diene as Ligands for the Synthesis of Axially Chiral Compounds via Palladium Catalyzed Suzuki-Miyaura Coupling Reaction

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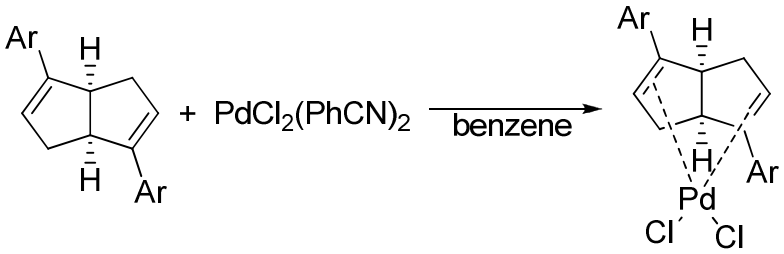
Table of Contents

1. General

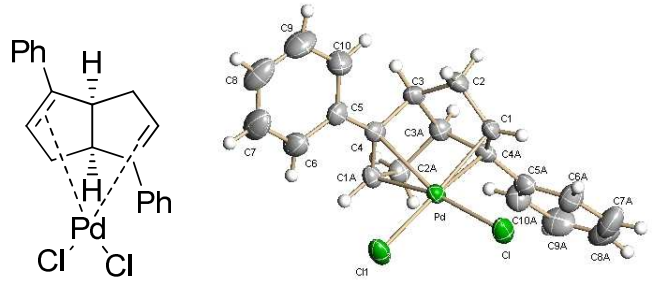
All moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Toluene was distilled from sodium under nitrogen. Cs_2CO_3 (Sinopharm Chemical Reagent Co., Ltd), 4-methyl-1-naphthaleneboronic acid (Accela ChemBio Inc.), 1-naphthaleneboronic acid (Acros), 1-bromo-2-methylnaphthalene (Acros) were used as received. NMR spectra were recorded on a Bruker 400 MHz. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR and residual $CHCl_3$ (δ 77.00) for ^{13}C NMR. The *in situ* IR experiments were performed on a React IR iC10 from Mettler-Toledo AutoChem fitted with a SiComp probe. Optical rotations were measured on a JASCO P-1030 polarimeter.

Diene ligands,[1] $PdCl_2(PhCN)_2$,[2] **3b**[3] were synthesized following the literature procedures.

2. General procedure for the synthesis of [$PdCl_2$(diene)] complexes

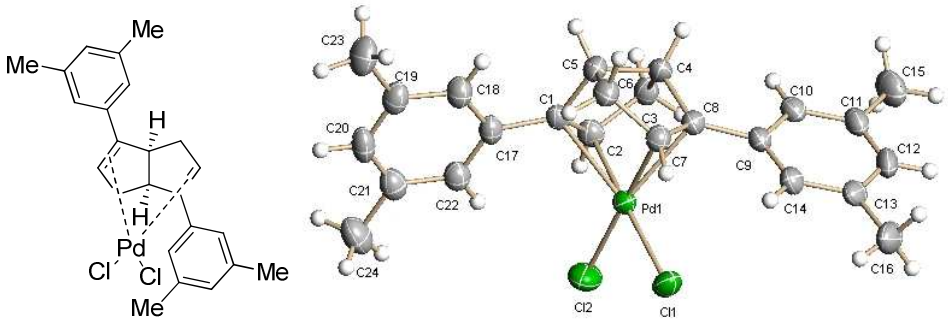


To a solution of $PdCl_2(PhCN)_2$ (153.4 mg, 0.4 mmol) in dry benzene (4 ml) at room temperature under argon atmosphere was added the solution of diene (0.4 mmol) in dry benzene (8 ml). The mixture was stirred overnight. The precipitate was filterd, residue was recrystallized from ether and chloroform to give the [$PdCl_2$(diene)] complexes.



2a. 55% yield, ^1H NMR (300 MHz, $CDCl_3$): δ 2.77 (d, 2H, J = 16.2Hz), 3.20 (s, 2H), 3.62 (d, 2H, J =16.2Hz), 6.79 (s, 2H), 7.14-7.53 (m, 6H), 8.06 (d, 4H, J = 6.9).

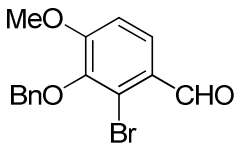
[1] Z.-Q. Wang, C.-G. Feng, M.-H. Xu, G.-Q. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 5336.
[2] Braunstein, P.; Bender, R.; Jud, J. *Inorg. Synth.* **1989**, *26*, 341.
[3] Schulte, B.; Froehlich, R.; Studer, A. *Tetrahedron* **2008**, *64*, 11852.



2d. 63% yield, 1H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 12H), 2.71 (d, 2H, J =14.8Hz), 3.12 (s, 2H), 3.58 (d, 2H, J =16.0Hz), 6.72 (s, 2H), 7.15 (s, 2H), 7.67 (s, 4H).

3. Synthesis of starting materials

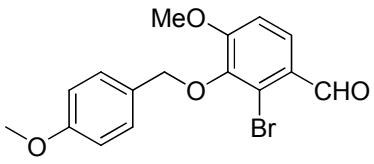
3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde (**3c**) [4]



A round-bottomed flask was charged with 3-Hydroxy-4-methoxybenzaldehyde (15.21g, 0.1 mol) and acetic acid (150 ml). The mixture was cooled to 0 ^{o}C and Bromine (5 ml in 20 ml acetic acid, 0.1 mol) was added dropwise. The solution was warmed gradually to ambient temperature and stirred for 3h. After reaction finished, the solution was poured into ice water (200 ml) and stirred for 30 min. The precipitate was filtered and recrystallization from hot acetic acid gave 2-bromo-3-hydroxy-4-methoxybenzaldehyde as a white solid (16.2 g, 70% yield).

A solution of 2-bromo-3-hydroxy-4-methoxybenzaldehyde (4.62 g, 20 mmol, 1.0 equiv), potassium carbonate (6.92 g, 50 mmol, 2.5 equiv), BnBr (4.8 ml, 40 mmol, 2.0 equiv) in acetone (20 ml) was refluxed for 3 h. The solution was diluted with ethyl acetate and filtered, filtrate was concentrated and the residue was purified by flash chromatography on silica gel to give the title compound as a white solid (3.68 g, 58%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 5.05 (s, 2H), 6.97 (d, J = 8.8Hz, 1H), 7.25-7.56 (m, 5H), 7.75 (d, J = 8.8 Hz, 1H), 10.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.27, 74.78, 110.94, 123.45, 126.53, 127.46, 128.28, 128.37, 128.46, 136.63, 145.15, 158.74, 190.93.

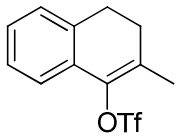
2-bromo-4-methoxy-3-(4-methoxybenzyloxy)benzaldehyde (**3d**)



(4) Cheng, B.; Zhang, S.; Zhu, L.; Zhang, J.; Li, Q.; Shan, A.; He, L. *Synthesis* **2009**, 2501.

A solution of 2-bromo-3-hydroxy-4-methoxybenzaldehyde (924 mg, 4 mmol, 1.0 equiv), potassium carbonate (1.2 g, 8 mmol, 2.0 equiv), 4-methoxybenzyl chloride (813 uL, 6 mmol, 1.5 equiv) in DMF (5 ml) was refluxed for 3 h. The solution was diluted with ethyl acetate and filtered, filtrate was concentrated and the residue was purified by flash chromatography on silica gel to give the title compound as a white solid (912 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ3.81 (s, 3H), 3.95 (s, 3H), 4.99 (s, 2H), 6.89-6.97 (m, 3H), 7.44-7.46 (m, 2H), 7.72-7.74 (m, 1H), 10.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.24, 56.25, 74.55, 110.89, 113.75, 123.53, 126.43, 127.42, 128.75, 130.29, 145.10, 158.77, 159.74, 190.99. ESI-MS: 373.0 $[M+Na]^+$. HRMS calcd for $C_{16}H_{15}BrO_4Na$ $[M+Na]^+$ 373.00459, found 373.00528.

2-methyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (**3e**)



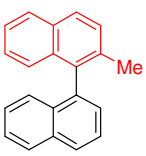
To a mixture of 2,6-lutidine (1.1 mL, 9.5 mmol, 1.9 equiv), triflic anhydride (1.9 mL, 11.2 mmol, 2.2 equiv) and CH_2Cl_2 (20 mL) under nitrogen at -78 ^{o}C was add a solution of 2-Methyl-1-tetralone (760 uL, 5 mmol, 1.0 equiv) in CH_2Cl_2 (5 ml). The mixture was allowed to warm to ambient temperature and stirred for 24 h, the solvent was removed, and the residue was diluted with petroleum ether and washed with 1N HCl, saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated, the residue was purified by flash chromatography on silica gel to give the title compound as a white solid (912 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ2.00 (s, 3H), 2.43 (t, J = 8.0Hz, 2H), 2.85 (t, J = 8.0Hz, 2H), 7.13-7.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.52, 27.12, 29.77, 118.59(q, J = 320 Hz), 120.18, 126.68, 127.32, 128.00, 129.51, 129.71, 135.18, 140.93. EI-MS (m/z): 292(M^+). HRMS m/z calcd for $C_{12}H_{11}F_3O_3S$ 292.0381 found 292.0386.

4. *In situ* IR experiment

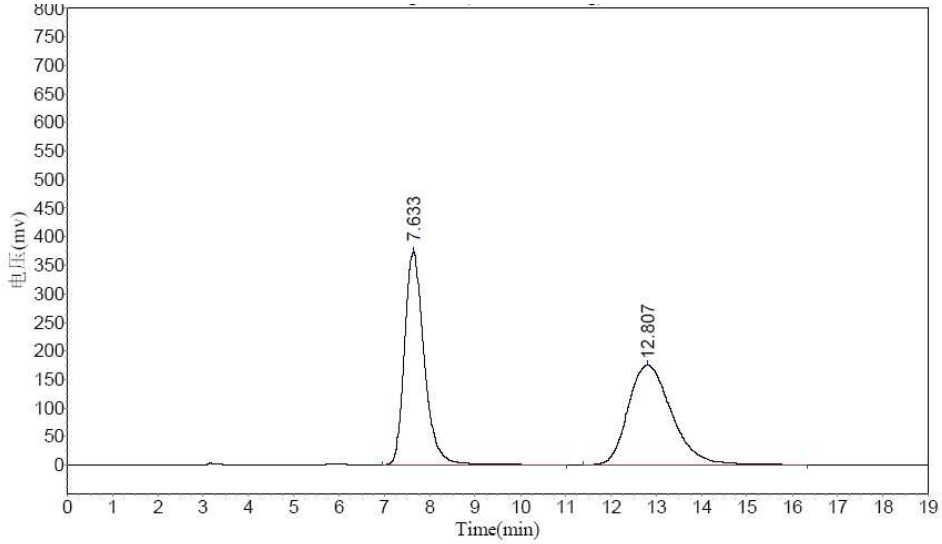
An oven dried self-prepared three-necked micro reactor with a magnetic stirrer was charged with 3d (98.4 mg, 0.2 mmol, 1 eq), 1-naphthaleneboronic acid (68.8 mg, 0.4 mmol, 2 eq). The reactor was allowed to be vacuumed and purged with nitrogen for three times. 2 ml dry toluene was injected via a syringe. The mixture was reacted at room temperature for 15 minutes and then 2-bromo-3-methylbenzaldehyde (40 mg, 0.2 mmol, 1 eq) was added. 45 minutes later, 1 equiv 1-naphthaleneboronic acid was added. The whole reaction progress was monitored by in situ IR.

5. General Procedure for the Suzuki-Miyaura coupling reaction

A dry schlenk tube was charged with aryl halide (alkenyl triflate) (0.2 mmol, 1.0 equiv), arylboronic acid (0.3 mmol, 1.5 equiv), Cs_2CO_3 (163 mg, 0.5 mmol), $PdCl_2$(diene) (0.01 mmol, 5 mol%), diene (0.03 mmol, 15 mol%), dry toluene (1.5 mL). The mixture was degassed using Freeze-Pump-Thaw cycling with liguid nitrogen, and then stirred at indicated temperature until consumption of the aryl (alkenyl triflate) (monitored by TLC). To the Mixture was add water (10 mL), extracted with ethyl acetate. Organic phase was dried over $MgSO_4$, filtered, concentrated, the residue was purified by flash chromatography on silica gel using petroleum ether or petroleum ether-ethyl acetate mixtures as eluents.

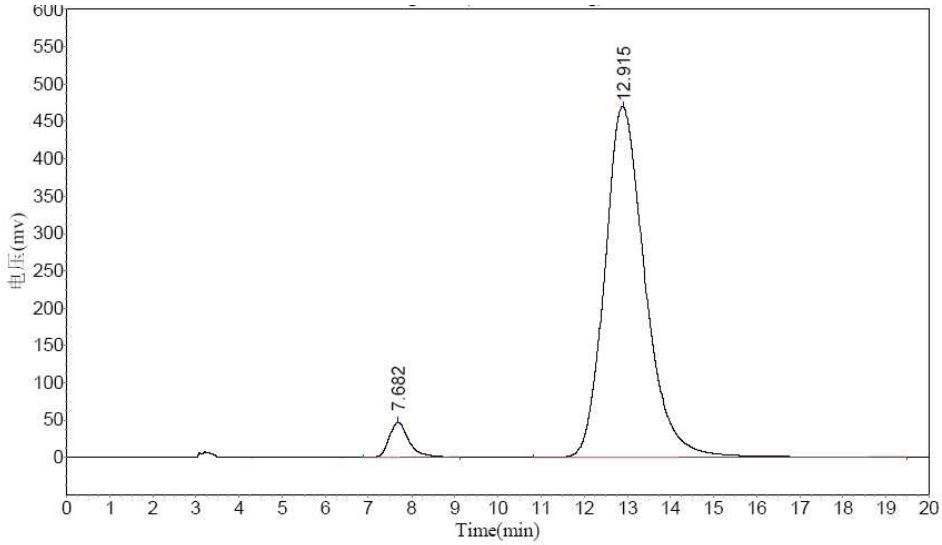


5a 78% yield, $[\alpha]^{23}_{D}$ +41.8 (c 0.90, $CHCl_3$) for 90% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ2.10 (s, 3H), 7.13-7.28 (m, 4H), 7.36-7.50 (m, 4H), 7.58-7.62 (m, 1H), 7.87 (dd, 2H, J = 8.8Hz, 2.4Hz), 7.94 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.48, 124.80, 125.63, 125.85, 125.88, 126.00, 126.11, 126.26, 127.54, 127.62, 127.73, 127.76, 128.26, 128.59, 132.00, 132.59, 133.48, 133.76, 134.38, 136.07, 137.50. EI-MS (m/z): 268(M^+). HRMS m/z calcd for $C_{21}H_{16}$ 268.1252 found 268.1255. HPLC: Chiralcel OJ-H Column (250 mm); detected at 224 nm; n-hexane / i-propanol = 95/5; flow = 1.0 mL/min; Retention time: 7.7 min (minor), 12.9 min (major).



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.633	373788.406	11345272.000	49.1462
2		12.807	175249.328	11739461.000	50.8538
Total			549037.734	23084733.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.682	46981.867	1495948.125	4.6740
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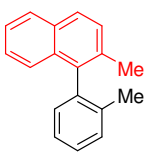
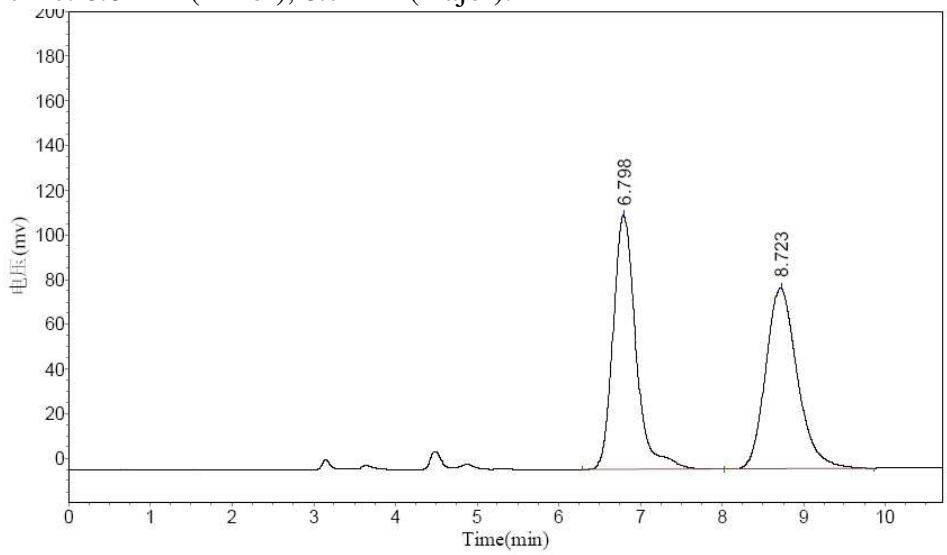
Total			516835.773	32005960.125	100.0000

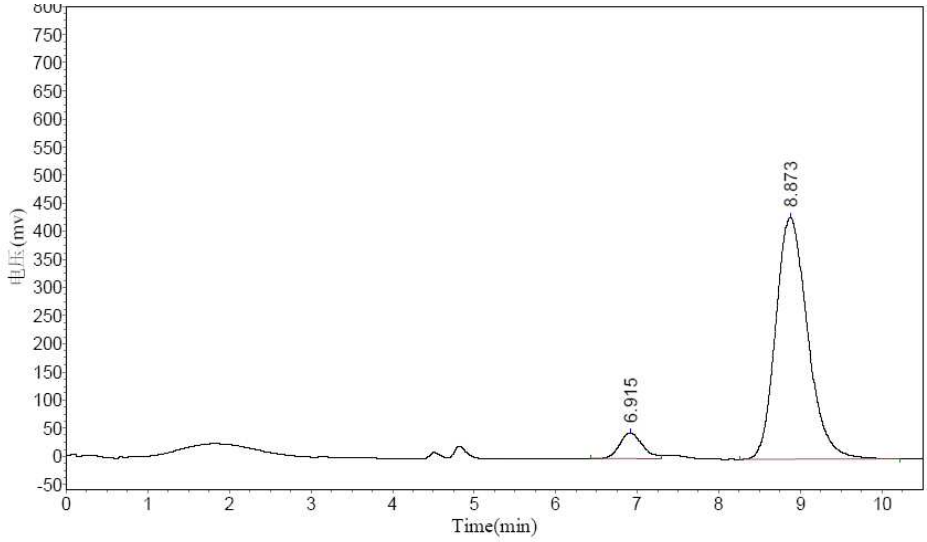


5b 90% yield, $[\alpha]^{23}_{D}$ +2.2 (c 2.48, $CHCl_3$) for 84% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ1.90(s, 3H), 2.15(s, 3H), 7.09-7.41(m, 8H), 7.74-7.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.51, 20.29, 124.74, 125.71, 125.87, 125.93, 127.09, 127.39, 127.81, 128.57, 129.71, 130.03, 132.01, 132.56, 133.05, 136.79, 137.49, 139.20. EI-MS (m/z): 232(M^+). HRMS m/z calcd for $C_{18}H_{16}$ 232.1252 found 232.1253. HPLC: Chiralcel OJ-H Column (250 mm); detected at 224 nm; n-hexane / i-propanol = 98/2; flow = 1.0 mL/min; Retention time: 6.8 min (minor), 8.7 min (major).



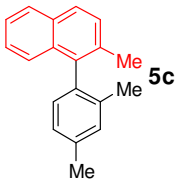
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.798	113584.297	2195824.250	50.1212
2		8.723	80782.125	2185202.250	49.8788
Total			194366.422	4381026.500	100.000



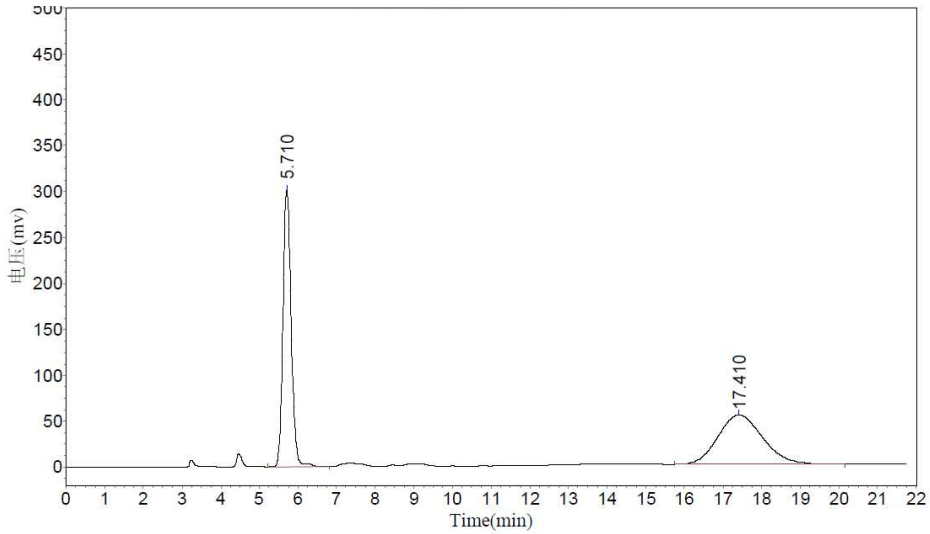
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.915	45435.887	903030.875	7.1750
2		8.873	429894.313	11682838.000	92.8250
Total			475330.199	12585868.875	100.0000



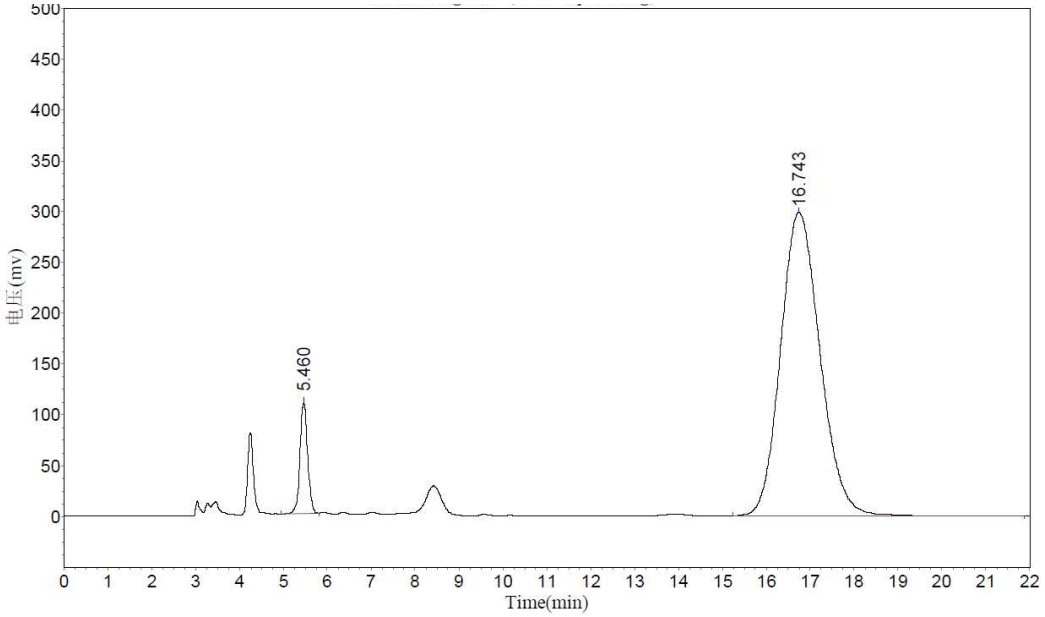
5c

97% yield, $[\alpha]^{23}_{D}$ -1.8 (c 0.39, $CHCl_3$) for 87% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ1.88(s, 3H), 2.16(s, 3H), 2.42(s, 3H), 6.98-7.42(m, 7H), 7.75-7.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ19.43, 20.34, 21.20, 124.67, 125.79, 125.82, 126.66, 126.97, 127.79, 128.57, 129.93, 130.76, 132.04, 132.80, 133.25, 136.17, 136.58, 136.86, 137.56. EI-MS (m/z): 246(M^+). HRMS m/z calcd for $C_{19}H_{18}$ 246.1409 found 246.1412. HPLC: Chiralcel OJ-H Column (250 mm); detected at 224 nm; n-hexane / i-propanol = 98/2; flow = 1.0 mL/min; Retention time: 5.7 min (minor), 17.4 min (major).



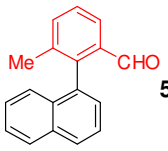
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.710	301659.563	4440791.500	50.5035
2		17.410	53797.895	4352240.500	49.4965
Total			355457.457	8793032.000	100.0000

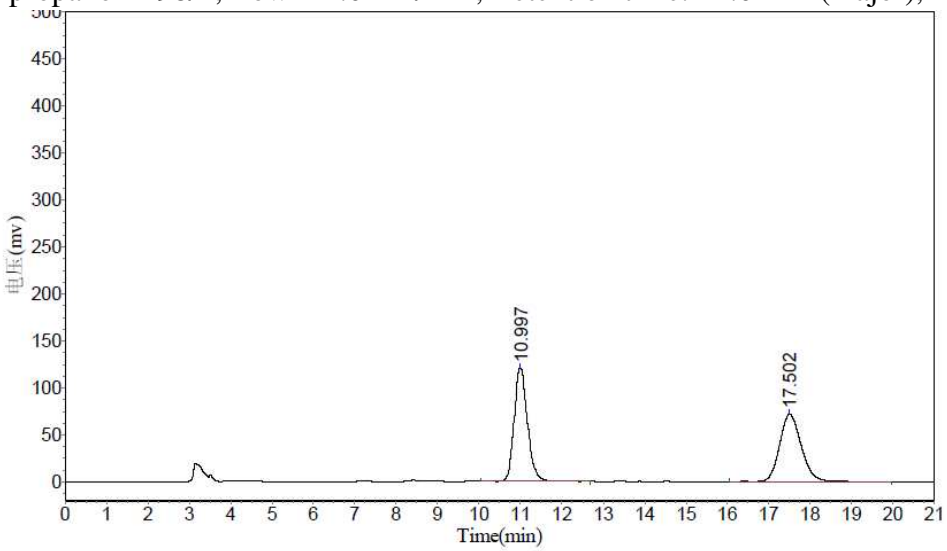


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.460	109252.555	1319261.500	6.6362
2		16.743	298312.469	18560560.000	93.3638
Total			407565.023	19879821.500	100.0000

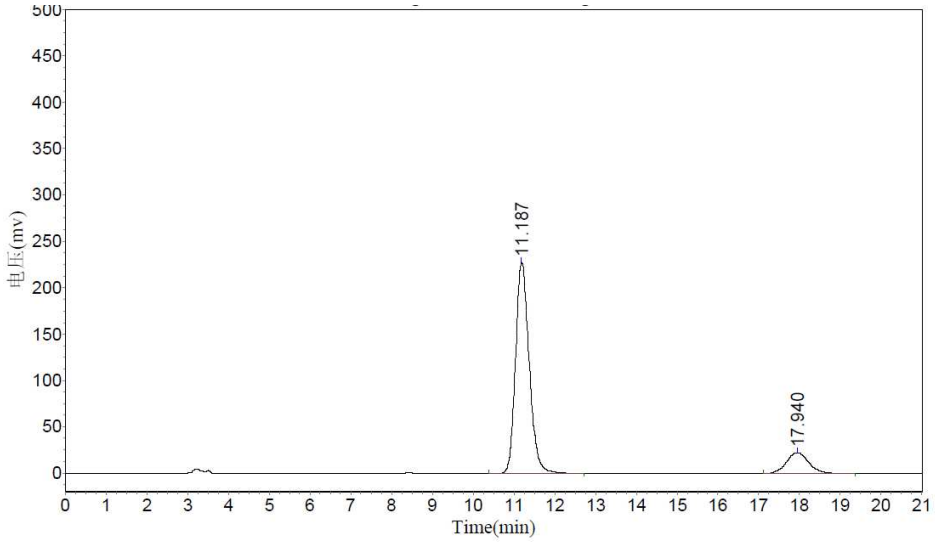


5d 90% yield, $[\alpha]^{23}_{D}$ -47.8 (c 0.63,$CHCl_3$) for 73% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 3H), 7.27-7.59 (m, 7H), 7.94 (d, 3H, J =8.4 Hz), 9.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.44, 124.53, 125.13, 125.49, 126.14, 126.66, 127.75, 127.92, 128.32, 128.37, 132.32, 133.36, 134.27, 135.06, 135.36, 138.22, 143.53, 192.35. ESI-MS: 247.2 $[M+H]^+$, 269.1 $[M+Na]^+$, 285.0 $[M+K]^+$. HRMS calcd for $C_{18}H_{15}O$ $[M+H]^+$ 247.11174, found 247.11177. HPLC: Chiralpak AS-H Column (250 mm); detected at 224 nm; n-hexane / i-propanol = 98/2; flow = 1.0 mL/min; Retention time: 11.0 min (major), 17.5 min (minor).



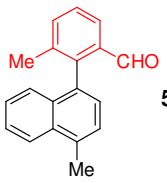
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.997	120772.586	2687360.000	50.9055
2		17.502	71752.406	2591755.500	49.0945
Total			192524.992	5279115.500	100.0000

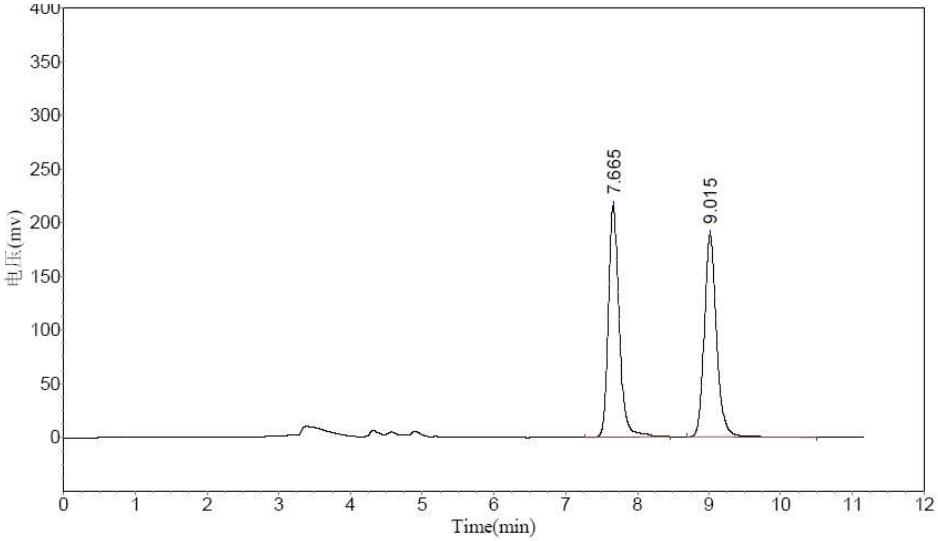


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.187	227106.031	5267437.000	86.5822
2		17.940	22351.143	816304.063	13.4178
Total			249457.174	6083741.063	100.0000

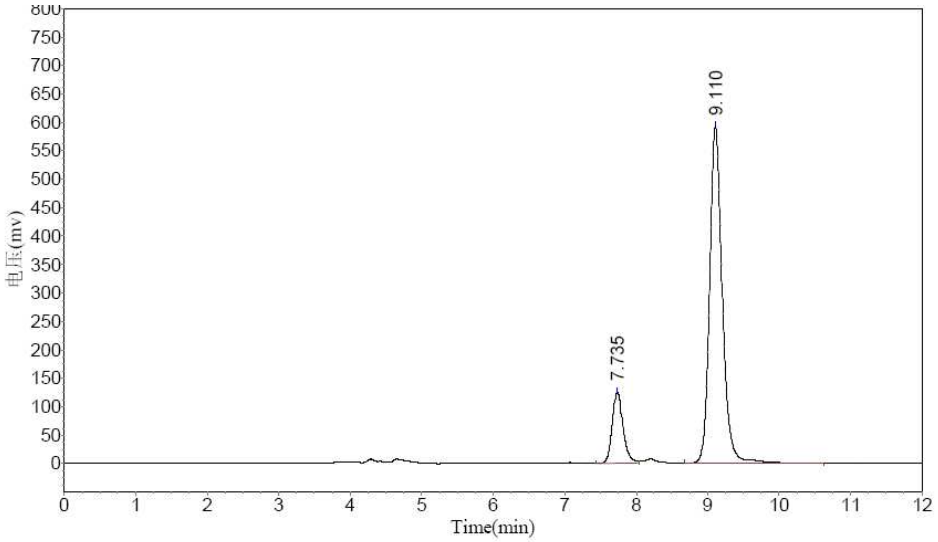


5e 99% yield, $[\alpha]^{23}_{D}$ -49.6 (c 1.10, $CHCl_3$) for 70% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.77 (s, 3H), 7.21-7.57 (m, 7H), 7.93 (d, 1H, J =8.4 Hz), 8.09 (d, 1H, J =8.4 Hz), 9.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.48, 19.54, 124.55, 124.60, 126.00, 126.25, 126.32, 127.59, 127.87, 132.48, 132.54, 132.62, 134.80, 135.29, 135.34, 138.47, 143.97, 192.67. EI-MS (m/z): 260(M^+). HRMS m/z calcd for $C_{19}H_{16}O$ 260.1201 found 260.1204. HPLC: Chiralpak AD-H Column (250 mm); detected at 224 nm; n-hexane / i-propanol = 98/2; flow = 0.7 mL/min; Retention time: 7.7 min (minor), 9.1 min (major).



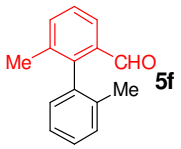
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.665	215583.156	2252061.500	50.0333
2		9.015	188472.219	2249064.000	49.9667
Total			404055.375	4501125.500	100.0000

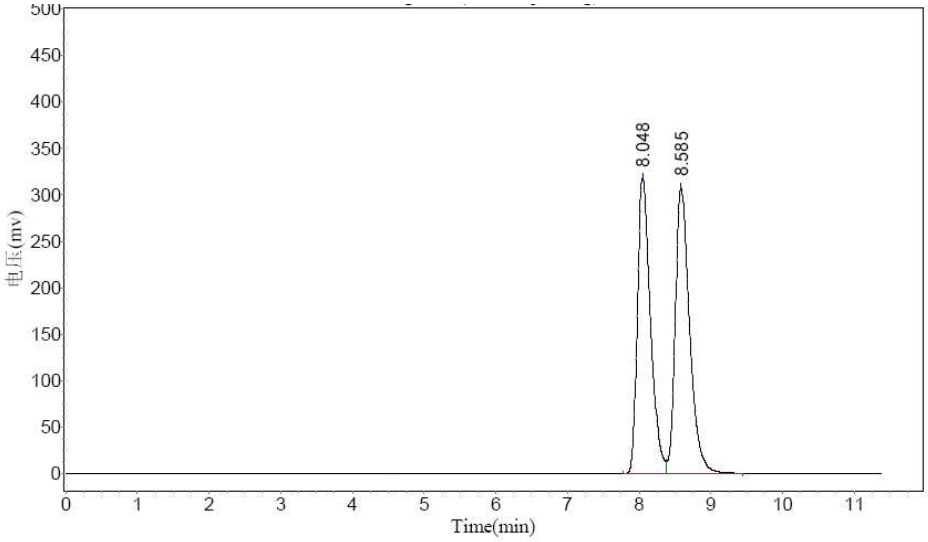


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.735	125196.250	1313788.375	15.2518
2		9.110	592474.313	7300194.500	84.7482
Total			717670.563	8613982.875	100.0000

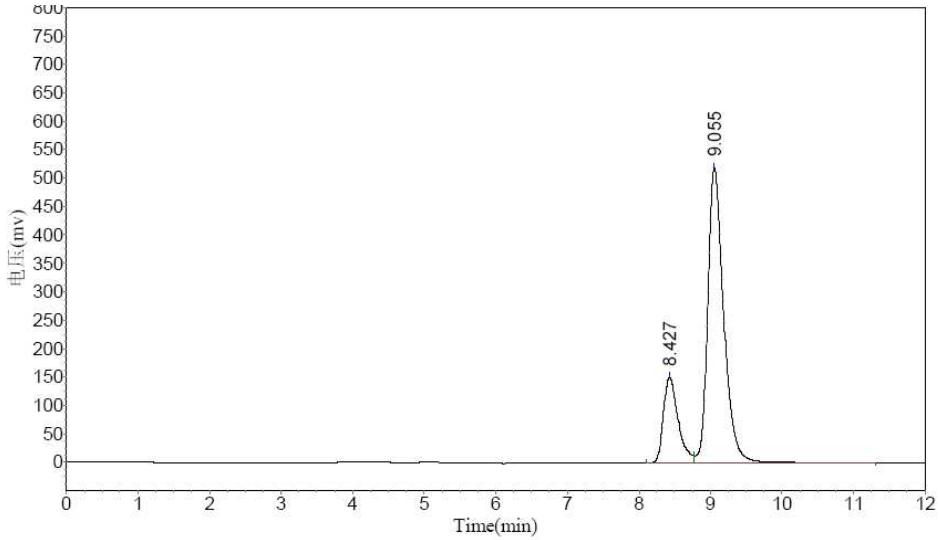


90% yield, $[\alpha]^{23}_{D}$ +4.8 (c 1.10,$CHCl_3$) for 58% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.04 (s, 3H), 7.10 (d, 1H, J =7.6 Hz), 7.25-7.54 (m, 5H), 7.86 (d, 1H, J =7.6 Hz), 9.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.39, 19.82, 124.57, 125.89, 127.57, 128.07, 129.56, 130.04, 133.98, 135.48, 136.09, 136.26, 137.20, 144.98, 192.56. EI-MS (m/z): 210(M^+). HRMS m/z calcd for $C_{15}H_{14}O$ 210.1045 found 210.1049. HPLC: Chiralcel OJ-H Column (250 mm); detected at 254 nm; n-hexane / i-propanol = 98/2; flow = 0.7 mL/min; Retention time: 8.4 min (minor), 9.1 min (major).



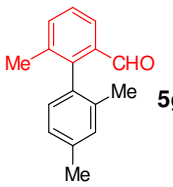
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.048	318346.219	4050214.250	48.6163
2		8.585	307533.063	4280773.500	51.3837
Total			625879.281	8330987.750	100.0000

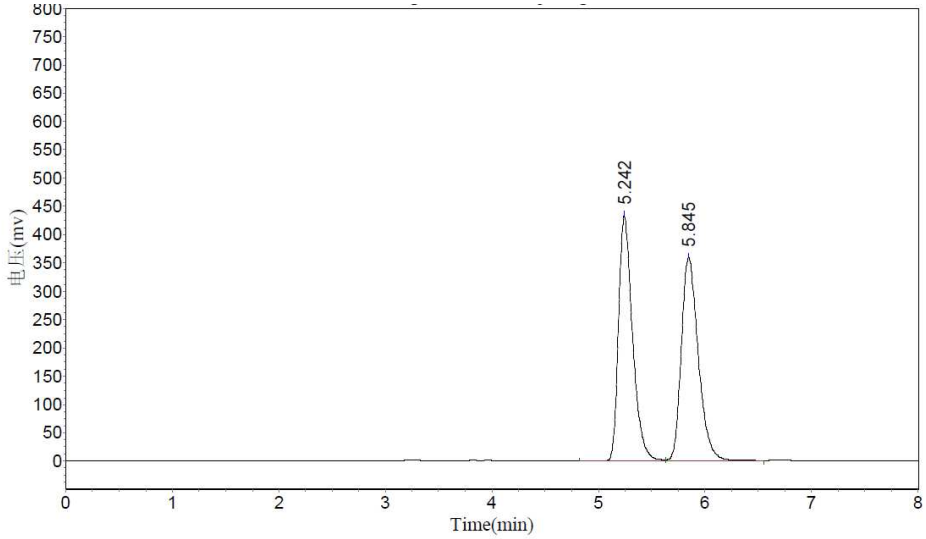


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.427	150975.453	2151111.250	21.0509
2		9.055	519573.531	8067500.000	78.9491
Total			670548.984	10218611.250	100.0000

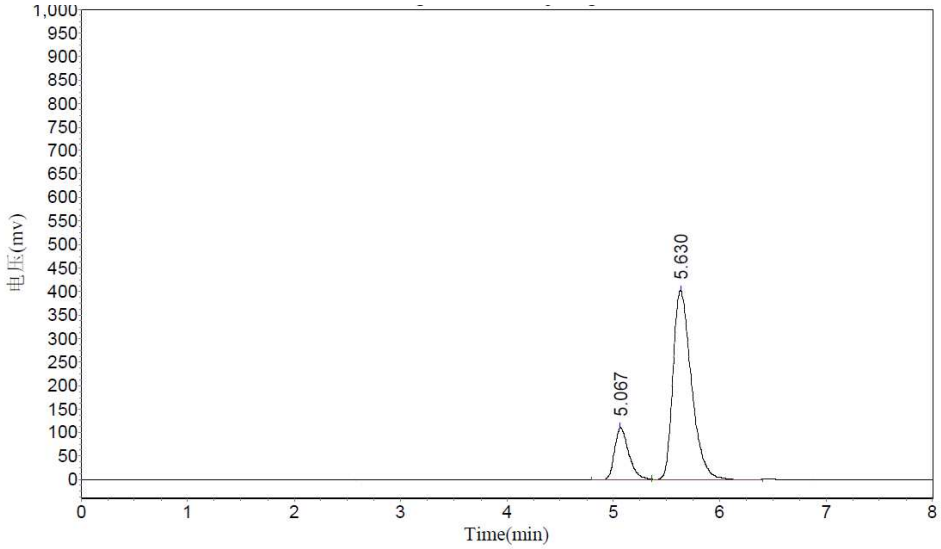


5g 97% yield, $[\alpha]^{27}_{D}$ +7.7 (c 0.73,$CHCl_3$) for 65% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 3H), 2.03 (s, 3H), 2.39 (s, 3H), 6.97 (d, 1H, J = 7.8 Hz), 7.08 (d, 1H, J = 7.6Hz), 7.12 (s, 1H), 7.38 (t, 1H, J = 7.6Hz), 7.51 (d, 1H, J = 7.6 Hz), 7.84 (d, 1H, J = 7.8 Hz), 9.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.46, 19.78, 21.13, 124.57, 126.65, 127.48, 129.56, 130.85, 133.27, 134.27, 135.44, 135.94, 137.50, 137.74, 145.20, 192.88. EI-MS (m/z): 224(M^+). HRMS m/z calcd for $C_{16}H_{16}O$ 224.1206 found 224.1205. HPLC: Chiralcel OJ-H Column (250 mm); detected at 254 nm; n-hexane / i-propanol = 98/2; flow = 1.0 mL/min; Retention time: 5.2 min (minor), 5.8 min (major).



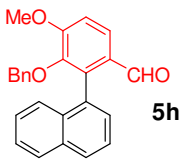
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.242	433745.531	3955397.500	49.7265
2		5.845	359697.063	3998905.500	50.2735
Total			793442.594	7954303.000	100.0000



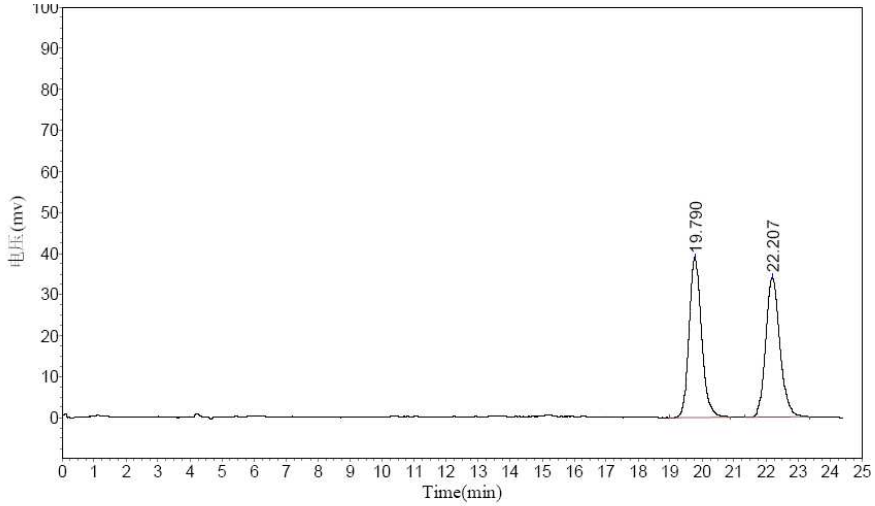
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.067	110429.914	1018898.500	17.3324
2		5.630	402887.188	4859686.500	82.6676
Total			513317.102	5878585.000	100.0000



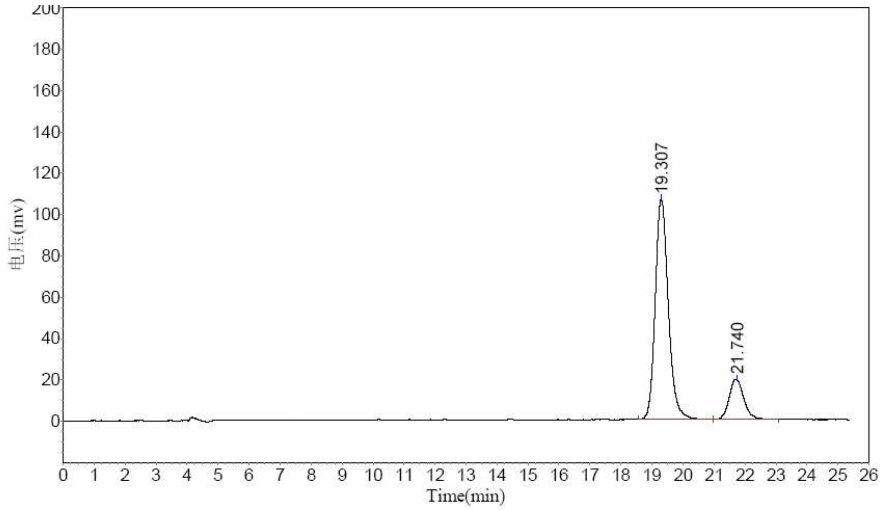
5h

93% yield, $[\alpha]^{23}_{D}$ -93.0 (c 0.94, $CHCl_3$) for 65% ee. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.03 (s, 3H), 4.64(q, 2H, J =10.5Hz), 6.63 (d, 2H, J = 7.2Hz), 7.01-7.18(m, 4H), 7.33-7.54 (m, 5H), 7.90-7.96 (m, 3H), 9.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.01, 74.82, 111.64, 124.58, 124.89, 125.91, 125.99, 126.58, 127.58, 127.76, 127.87, 128.17, 128.49, 128.58, 128.89, 131.03, 132.98, 133.25, 136.71, 139.02, 145.56, 157.98, 190.87. ESI-MS: 369.2 $[M+H]^+$, 391.2 $[M+Na]^+$, 407.1 $[M+K]^+$. HRMS calcd for $C_{25}H_{10}O_3Na$ $[M+Na]^+$ 391.13101, found 391.13190. HPLC: Chiralpak AD-H Column (250 mm); detected at 254 nm; n-hexane / i-propanol = 95/5; flow = 0.7 mL/min; Retention time: 19.3 min (major), 21.7 min (minor).



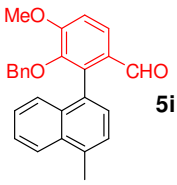
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.790	38921.547	1059796.500	50.1420
2		22.207	34025.203	1053793.875	49.8580
Total			72946.750	2113590.375	100.0000



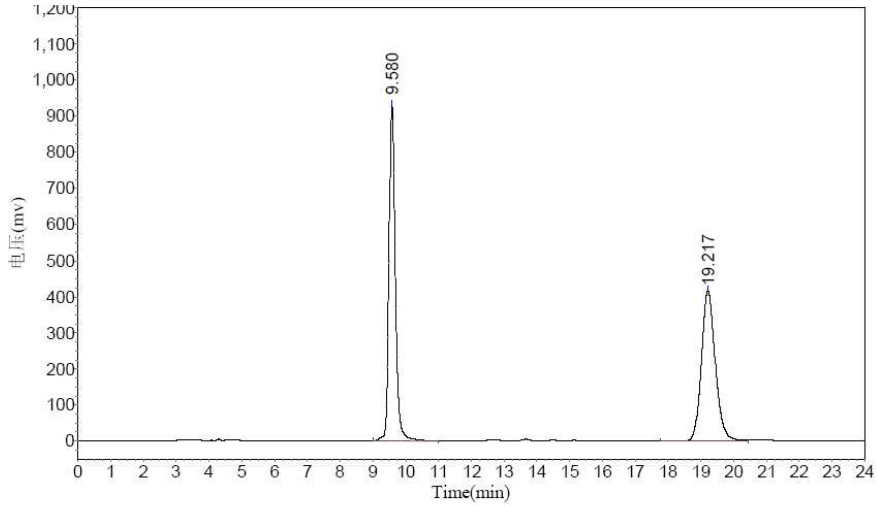
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.307	106311.133	3131625.250	82.7432
2		21.740	19676.945	653125.813	17.2568
Total			125988.078	3784751.063	100.0000



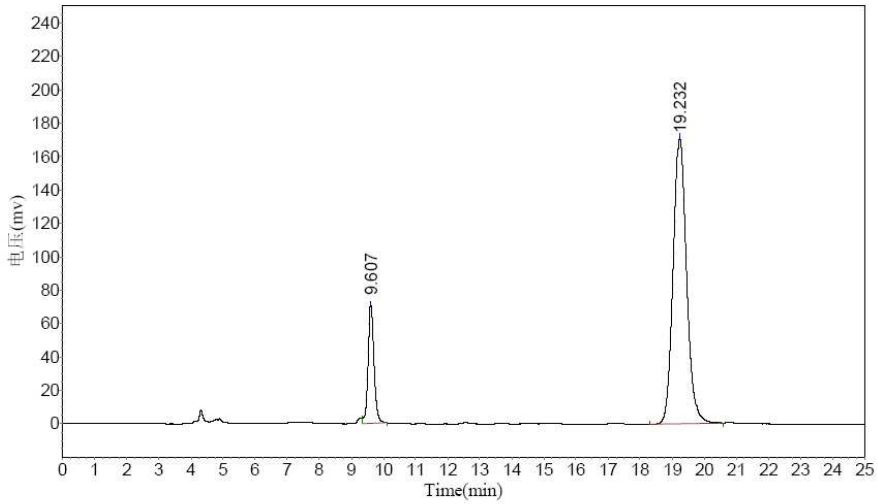
5i

97% yield, $[\alpha]^{23}_{D}$ -86.0 (c 0.65,$CHCl_3$) for 69% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (s, 3H), 4.00 (s, 3H), 4.63(q, 2H, J =10.8Hz), 6.64(d, 2H, J =7.2 Hz), 7.02-7.51 (m, 9H), 7.93 (d, 1H, J =8.8 Hz), 8.06 (d, 1H, J =8.4 Hz), 9.38 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.50, 55.99, 74.83, 111.55, 124.31, 124.51, 125.71, 125.81, 126.17, 126.60, 127.50, 127.74, 127.81, 128.35, 129.08, 129.22, 132.44, 133.06, 134.89, 136.87, 139.37, 145.74, 157.96, 191.05. EI-MS (m/z): 382(M^+). HRMS m/z calcd for $C_{26}H_{22}O_3$ 382.1569 found 382.1572. HPLC: Chiralpak AD-H Column (250 mm); detected at 224 nm; n-hexane / i-propanol = 90/10; flow = 0.7 mL/min; Retention time: 9.6 min (minor), 19.2 min (major).



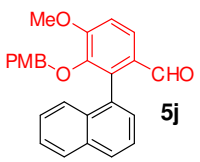
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.580	930502.188	12569088.000	50.5919
2		19.217	417682.781	12274986.000	49.4081
Total			1348184.969	24844074.000	100.0000



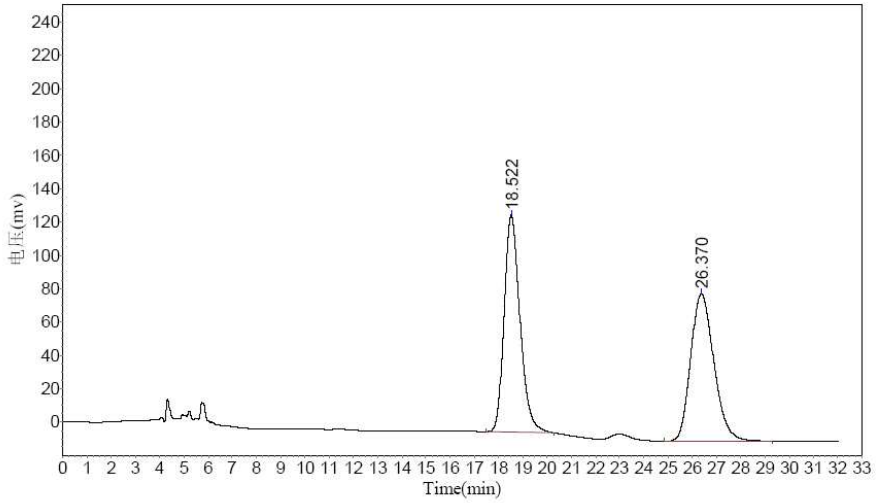
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.607	70480.875	920754.313	15.6452
2		19.232	171007.094	4964454.000	84.3548
Total			241487.969	5885208.313	100.0000



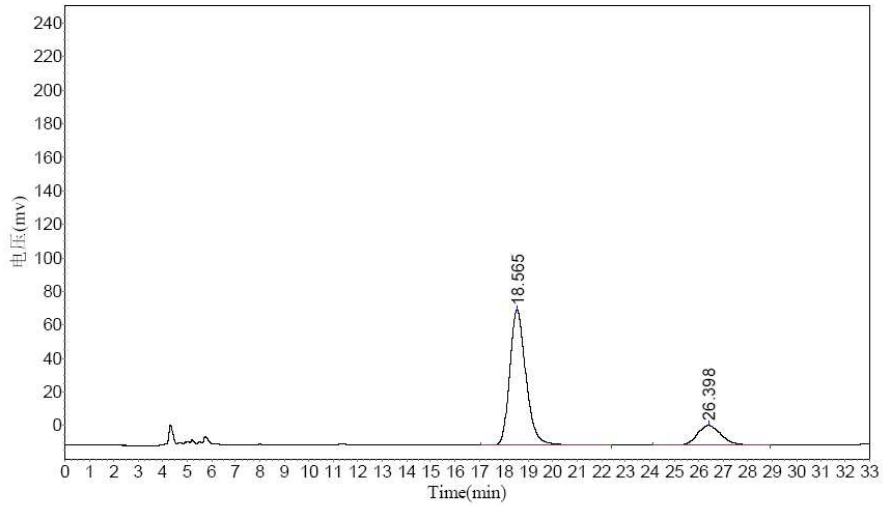
5j

83% yield, $[\alpha]^{23}_{D}$ -94.1 (c 1.00, $CHCl_3$) for 65% ee. ^1H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, 3H), 3.99 (s, 3H), 4.58(q, 2H, J =10.4Hz), 6.54 (s, 4H), 7.13(d, 1H, J =8.8 Hz), 7.32-7.52 (m, 5H), 7.89-7.94 (m, 3H), 9.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.06, 55.99, 74.44, 111.59, 113.23, 124.47, 124.86, 125.92, 125.94, 126.53, 128.11, 128.42, 128.62, 128.88, 129.51, 131.09, 132.97, 133.20, 139.04, 145.44, 158.03, 159.10, 190.89. EI-MS (m/z): 398(M^+). HRMS m/z calcd for $C_{26}H_{22}O_4$ 398.1518, found 398.1514. HPLC: Chiralcel OD-H Column (250 mm); detected at 224 nm; n-hexane / i-propanol = 90/10; flow = 0.7 mL/min; Retention time: 18.6 min (major), 26.4 min (minor).



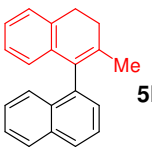
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.522	129917.797	5921815.000	50.0900
2		26.370	88557.477	5900542.500	49.9100
Total			218475.273	11822357.500	100.0000



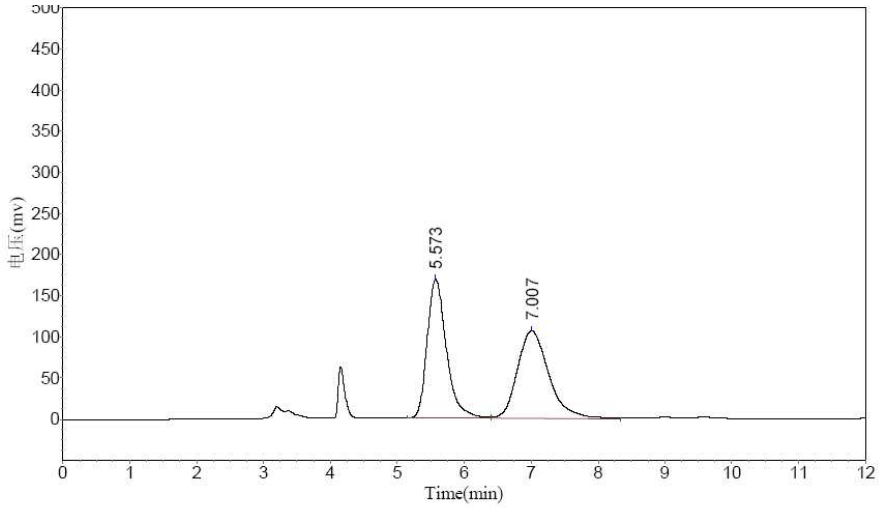
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.565	80606.516	3737229.000	82.2510
2		26.398	11773.524	806457.000	17.7490
Total			92380.040	4543686.000	100.0000



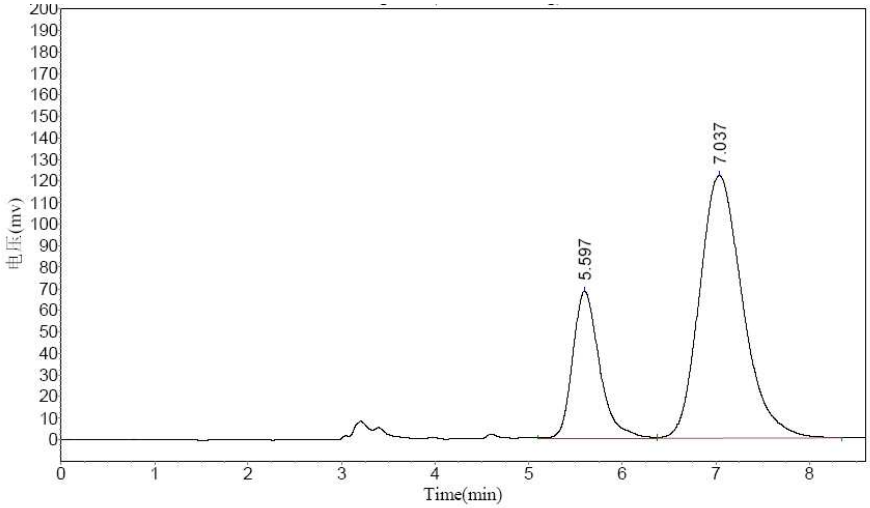
5k

72% yield, $[\alpha]^{23}_{D}$ -24.7 (c 0.88, $CHCl_3$) for 48% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 1.61(s, 3H), 2.51(m, 2H), 3.00(m, 2H) ,6.36 (d, 1H, J = 7.6 Hz) 6.87 (t, 1H, J = 7.4 Hz) , 7.03 (t, 1H, J = 7.4 Hz), 7.16-7.54 (m, 5H) , 7.69 (d, 1H, J = 8.4 Hz), 8.76 (q, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.42, 28.38, 30.18, 125.10, 125.68, 125.70, 125.82, 125.90, 126.00, 126.26, 127.01, 127.16, 127.64, 128.23, 131.47, 132.50, 133.76, 134.48, 135.80, 136.83, 137.58. EI-MS (m/z): 270(M^+). HRMS m/z calcd for $C_{21}H_{18}$ 270.1409 found 270.1413. HPLC: Chiralcel OJ-H Column (250 mm); detected at 224 nm; n-hexane / i-propanol = 95/5; flow = 0.7 mL/min; Retention time: 5.6 min (minor), 7.0 min (major).



Results

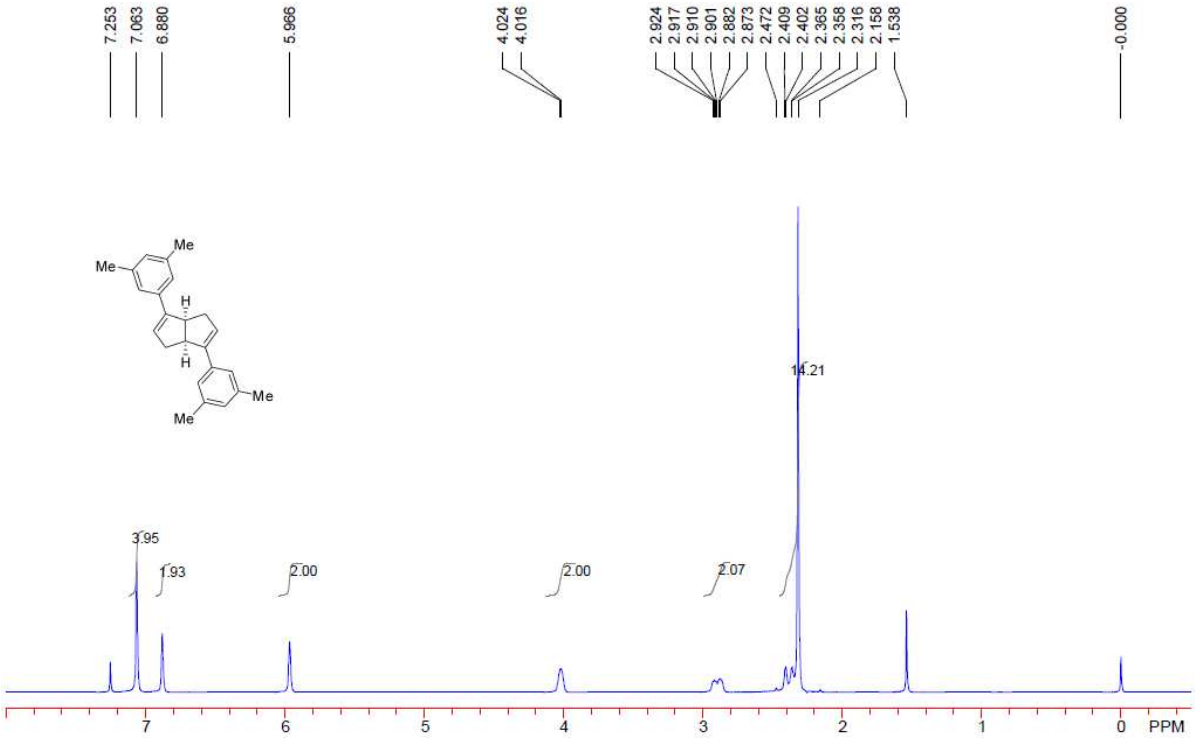
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.573	169145.406	3393637.250	49.3788
2		7.007	106644.914	3479024.750	50.6212
Total			275790.320	6872662.000	100.0000

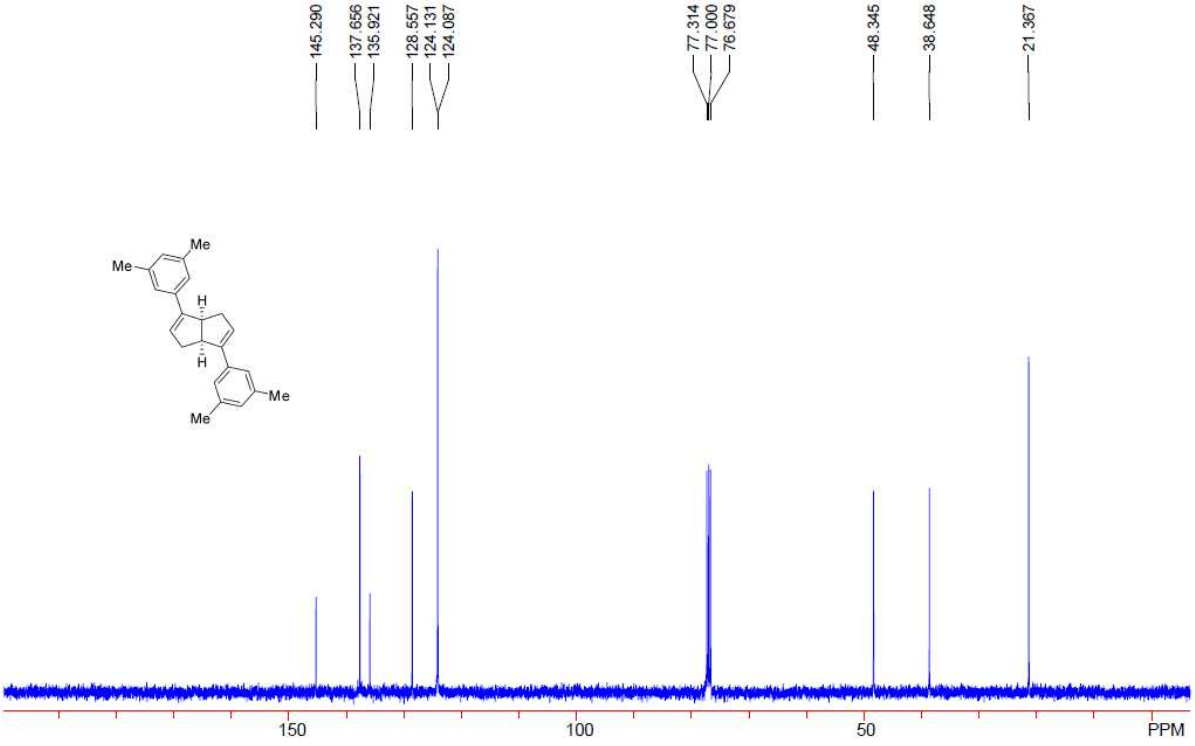


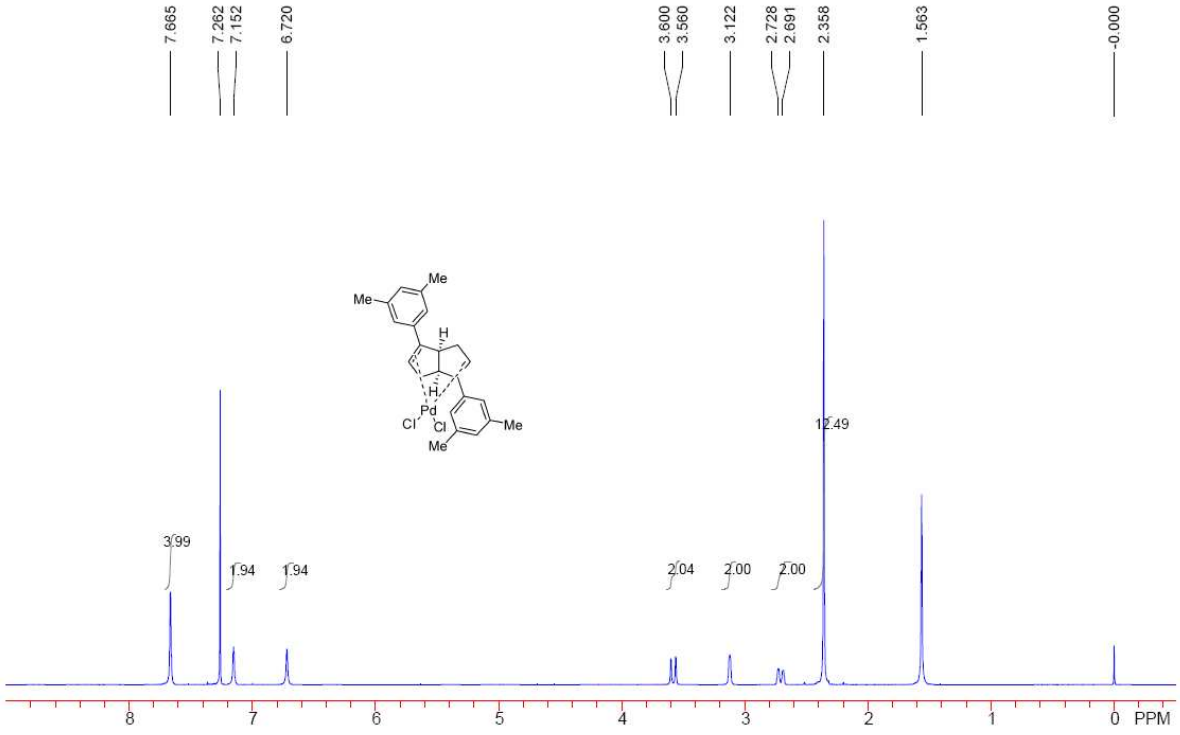
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.597	68363.977	1370081.000	25.9787
2		7.037	122005.805	3903791.000	74.0213
Total			190369.781	5273872.000	100.0000

6. ^{1}HNMR and ^{13}CNMR Spectra of Compounds 1d, 2d, 5



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Cl
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5
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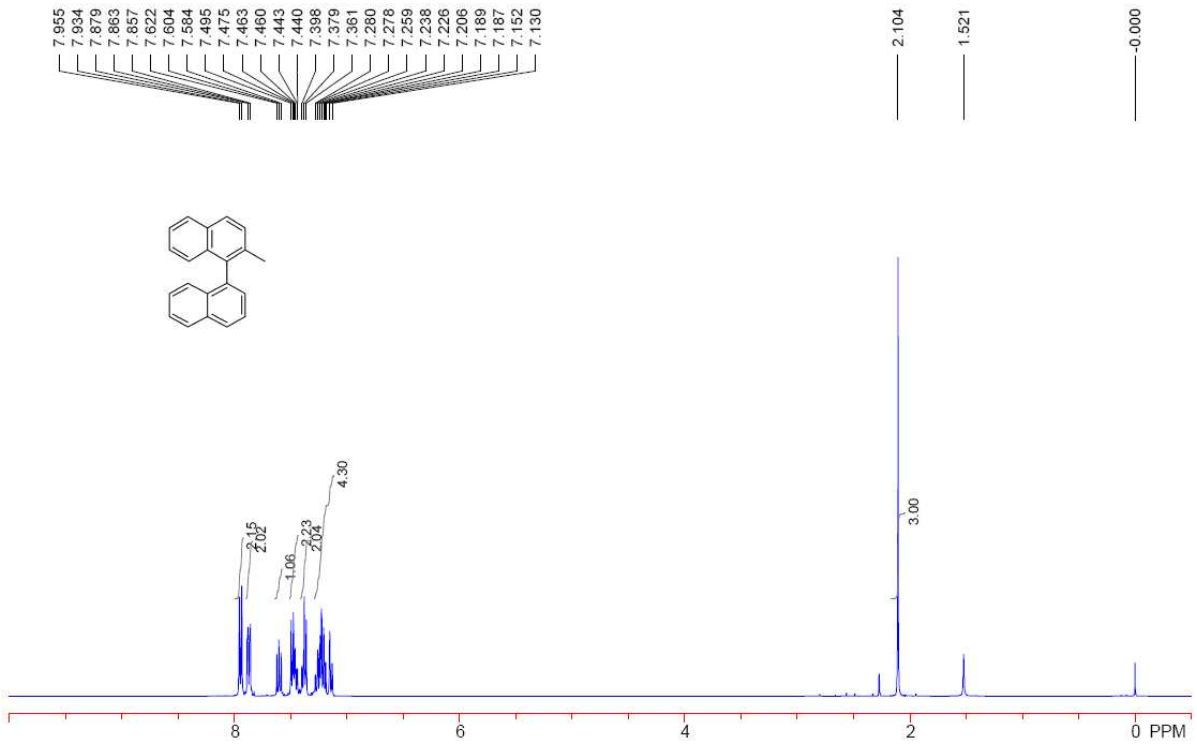
PPM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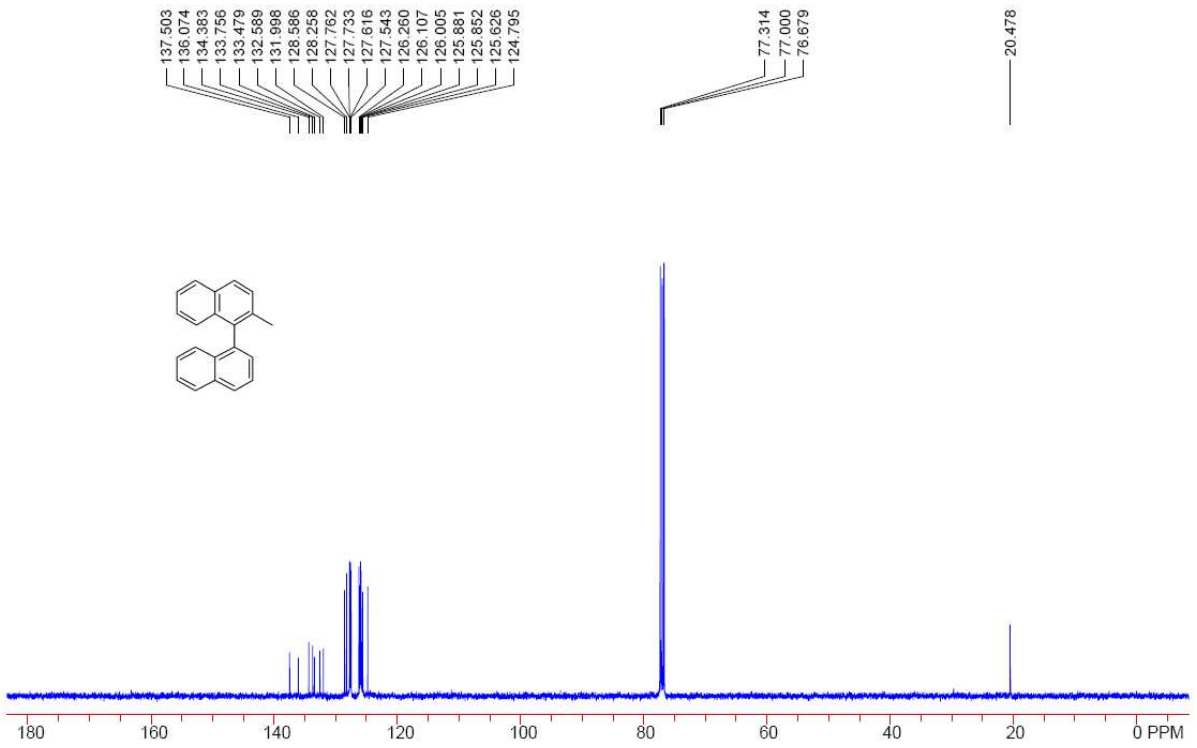
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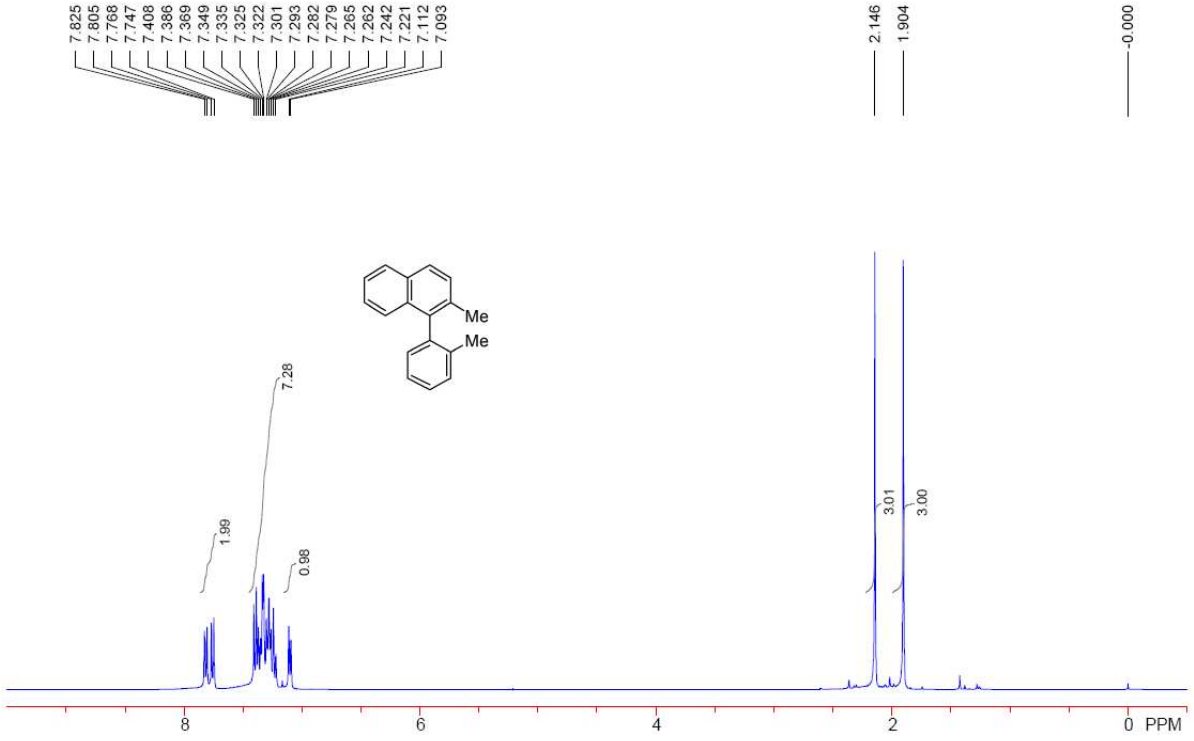
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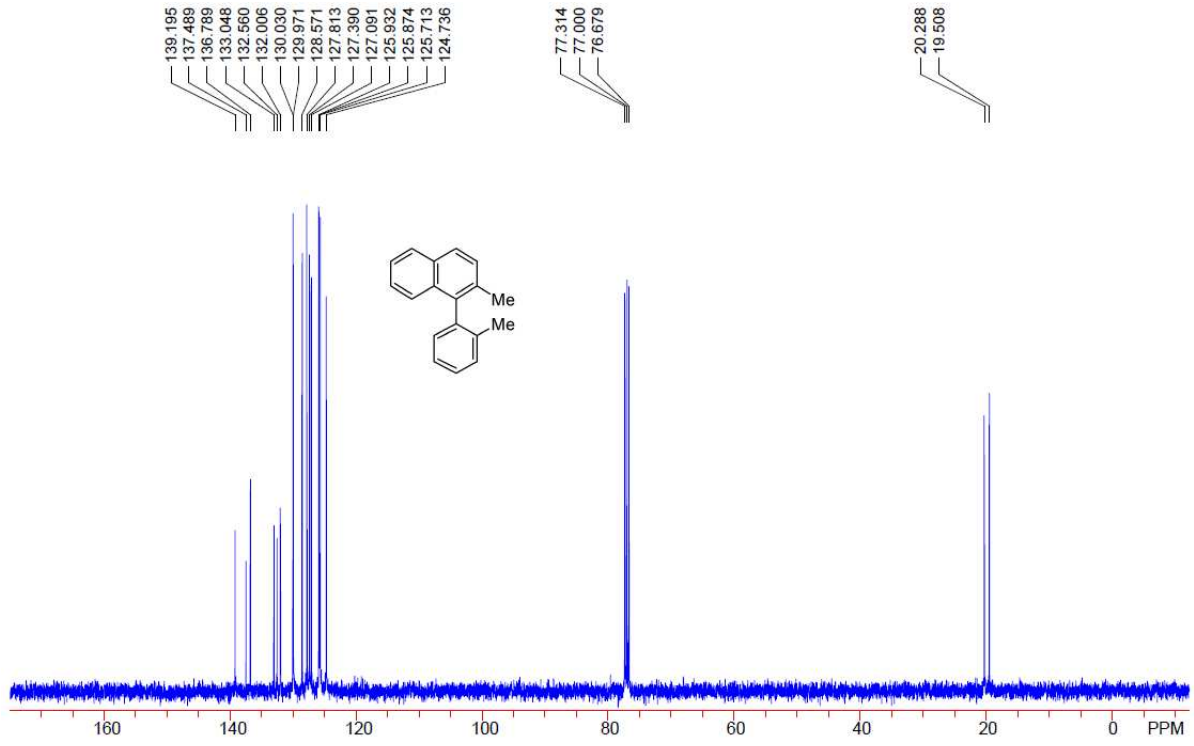
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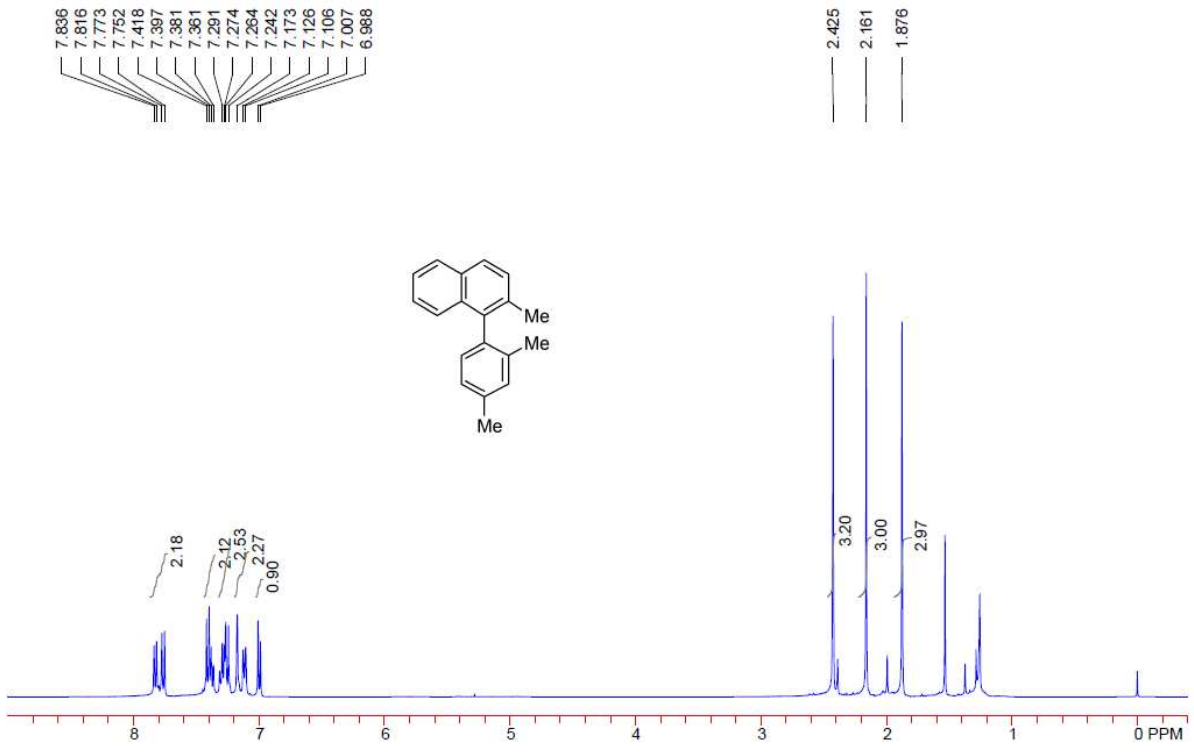
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6
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2
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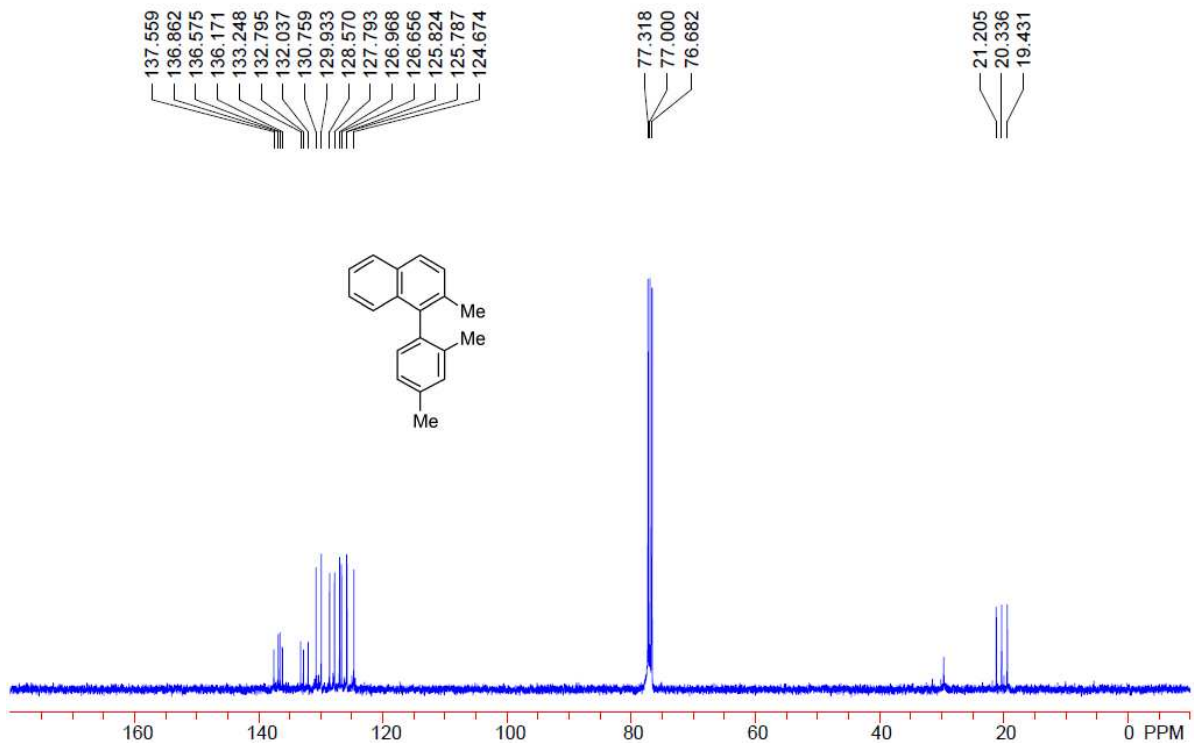
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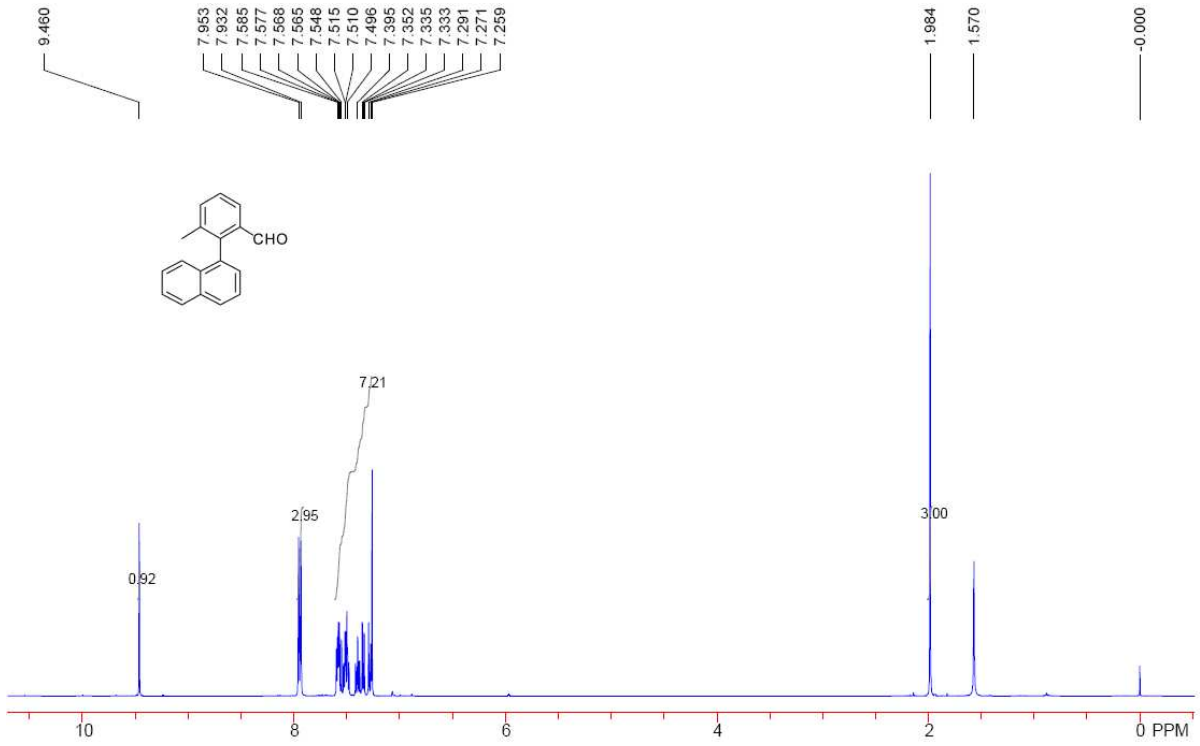
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7.548
7.515
7.510
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7.395
7.352
7.335
7.333
7.291
7.271
7.259
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1.570
-0.000
CHO
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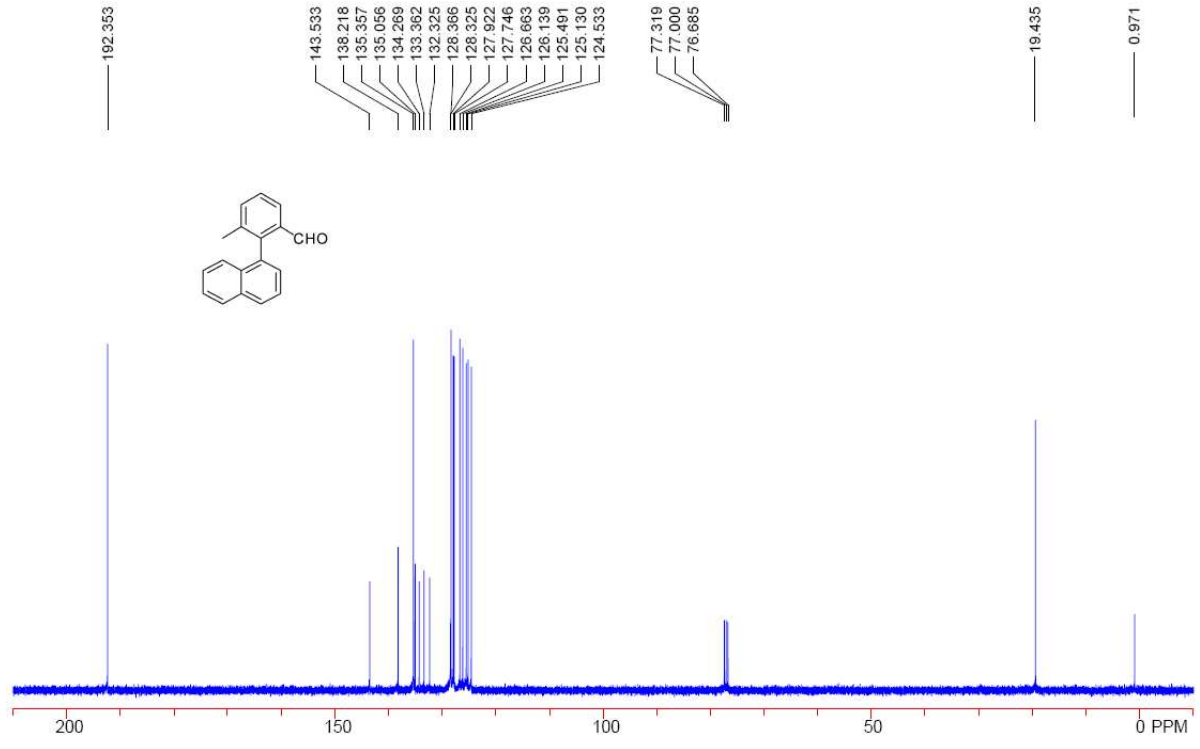
2.95
3.00
0.92
10
8
6
4
2
0 PPM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138.218
135.357
135.056
134.269
133.362
132.325
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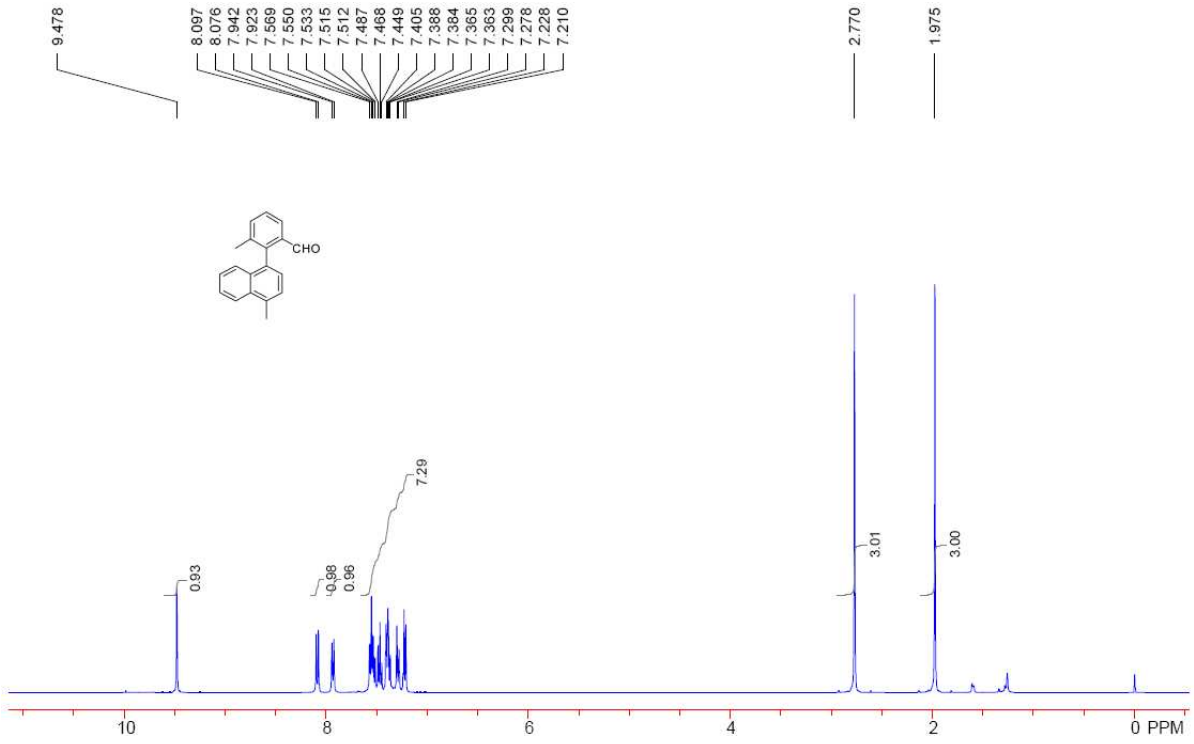
128.325
127.922
127.746
126.663
126.139
125.491
125.130
124.533
77.319
77.000
76.685
19.435
0.971
CHO
200
150
100
50
0 PPM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8.076
7.942
7.923
7.569
7.550
7.533
7.515
7.512
7.487
7.468
7.449
7.405
7.388
7.384
7.365
7.363
7.299
7.278
7.228
7.210
2.770
1.975
CHO
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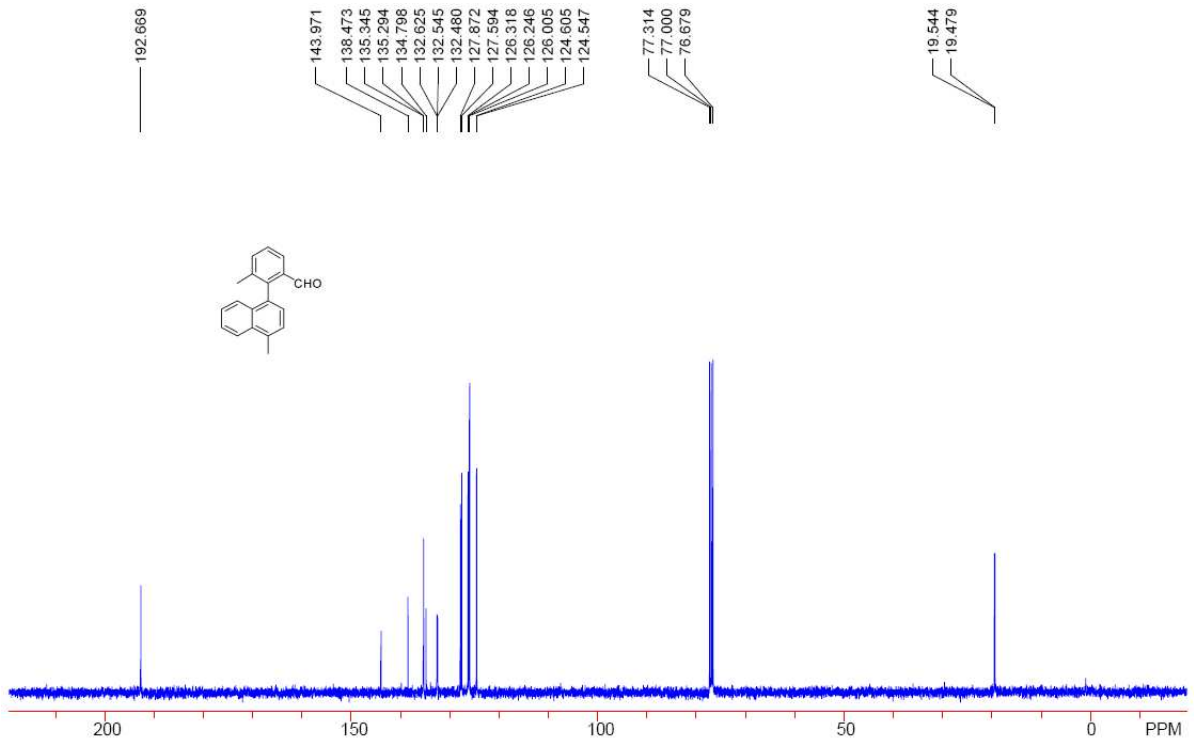
0.98
0.96
7.29
3.01
3.00
10
8
6
4
2
0 PPM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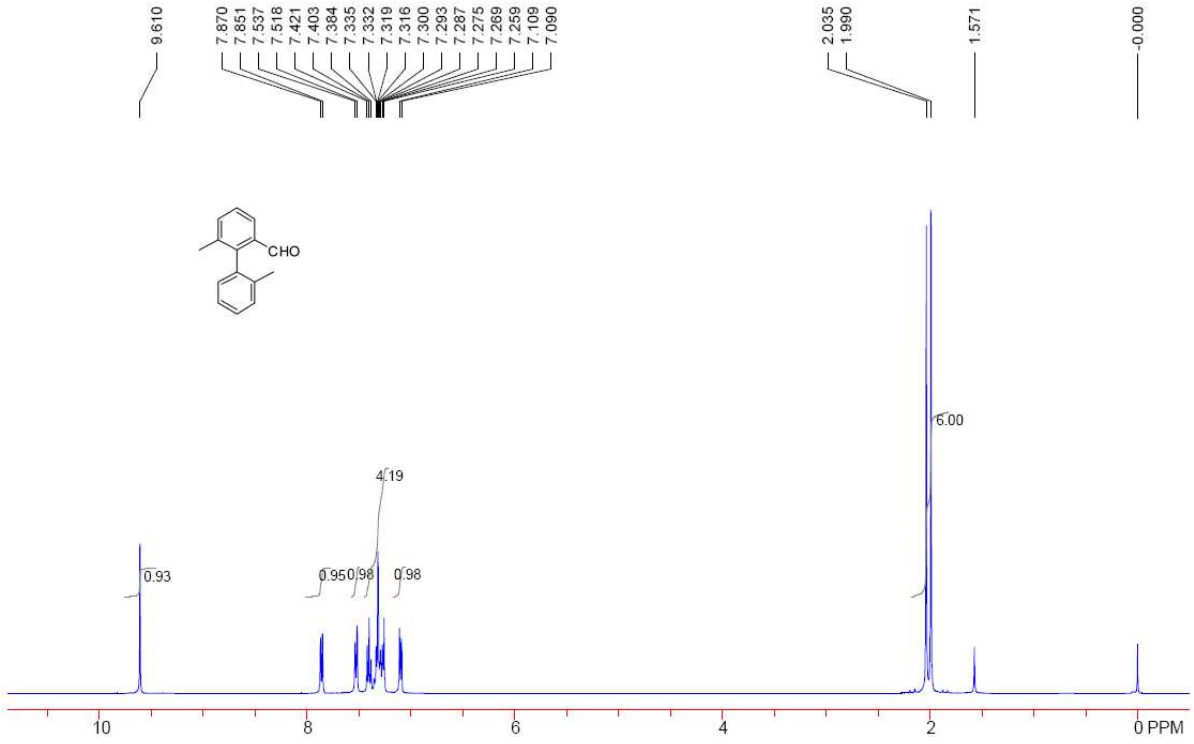
143.971
138.473
135.345
135.294
134.798
132.625
132.545
132.480
127.872
127.594
126.318
126.246
126.005
124.605
124.547
77.314
77.000
76.679
19.544
19.479
CHO
200
150
100
50
0
PPM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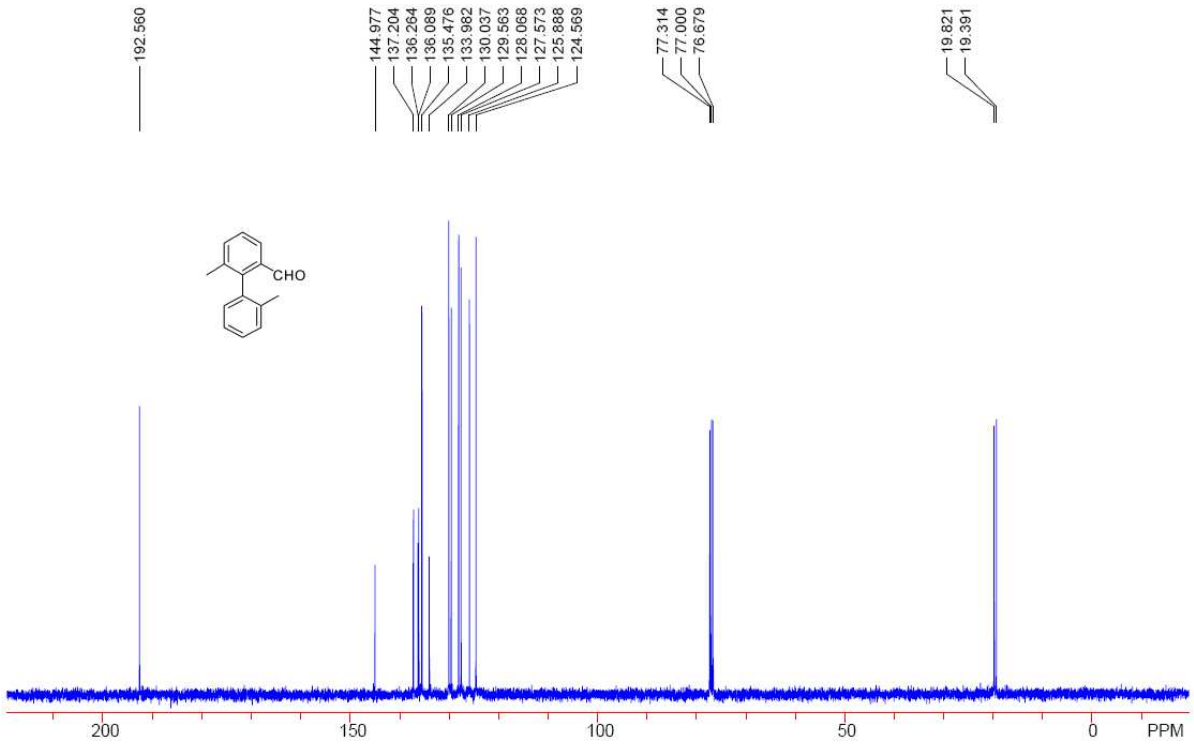
7.870
7.851
7.537
7.518
7.421
7.403
7.384
7.335
7.332
7.319
7.316
7.300
7.293
7.287
7.275
7.269
7.259
7.109
7.090
2.035
1.990
1.571
-0.000
CHO
6.00
4.19
0.93
0.95
0.98
0.98
10
8
6
4
2
0 PPM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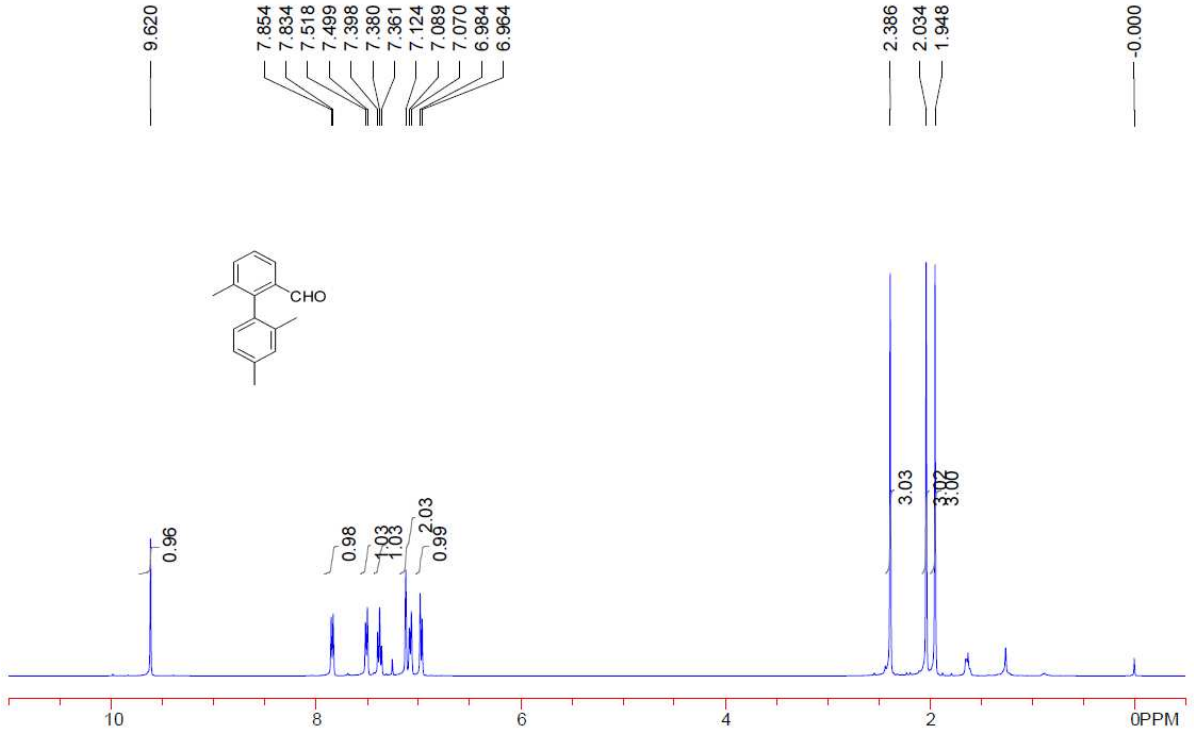
144.977
137.204
136.264
136.089
135.476
133.982
130.037
129.563
128.068
127.573
125.888
124.569
77.314
77.000
76.679
19.821
19.391
CHO
200
150
100
50
0
PPM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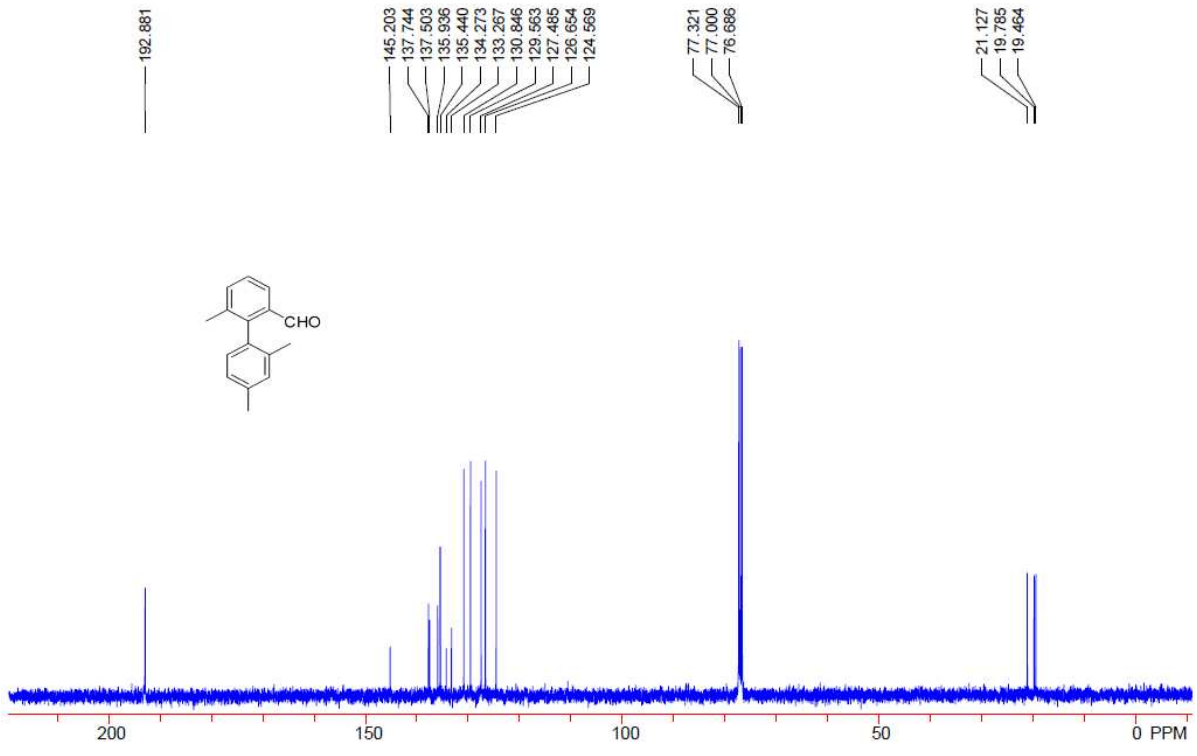
7.834
7.518
7.499
7.398
7.380
7.361
7.124
7.089
7.070
6.984
6.964
2.386
2.034
1.948
-0.000
CHO
0.96
0.98
1.03
1.03
2.03
0.99
3.03
3.02
3.00
10
8
6
4
2
0PPM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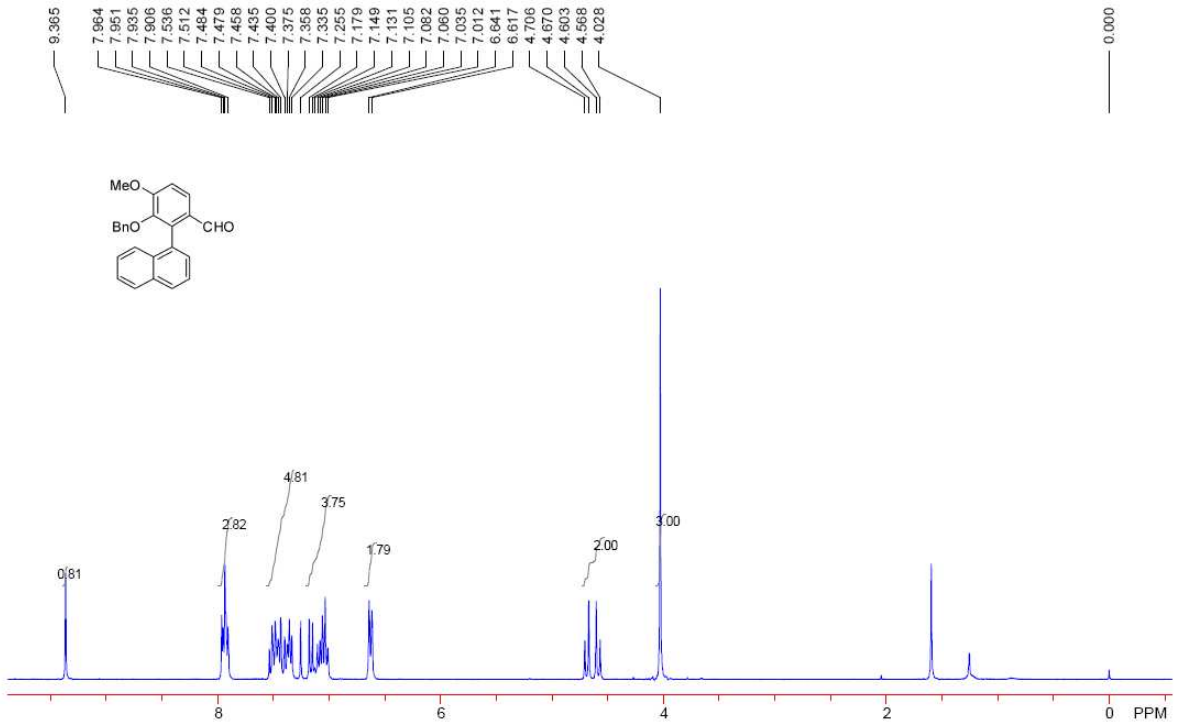
134.273
133.267
130.846
129.563
127.485
126.654
124.569
77.321
77.000
76.686
21.127
19.785
19.464
CHO
200
150
100
50
0 PPM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7.951
7.935
7.906
7.536
7.512
7.484
7.479
7.458
7.435
7.400
7.375
7.358
7.335
7.255
7.179
7.149
7.131
7.105
7.082
7.060
7.035
7.012
6.641
6.617
4.706
4.670
4.603
4.568
4.028
0.000
MeO
BnO
CHO
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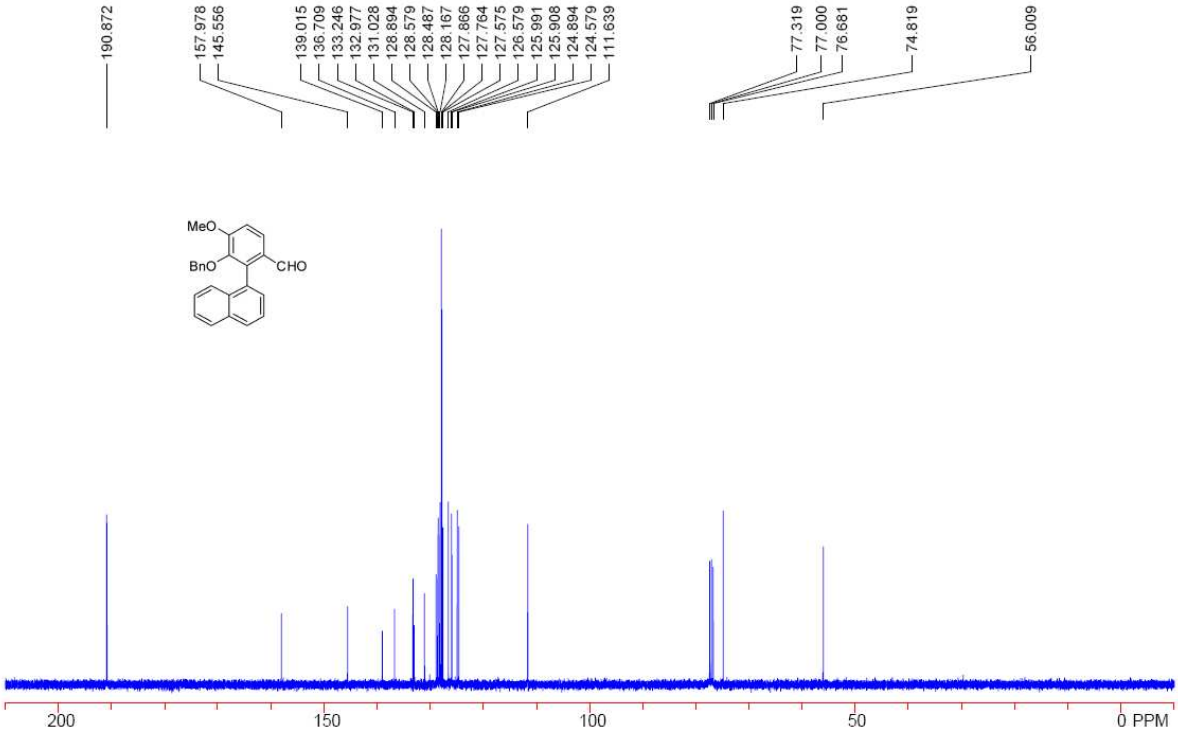
2.82
4.81
3.75
1.79
2.00
3.00
8
6
4
2
0
PPM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127.866
127.764
127.575
126.579
125.991
125.908
124.894
124.579
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76.681
74.819
56.009
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BnO
CHO
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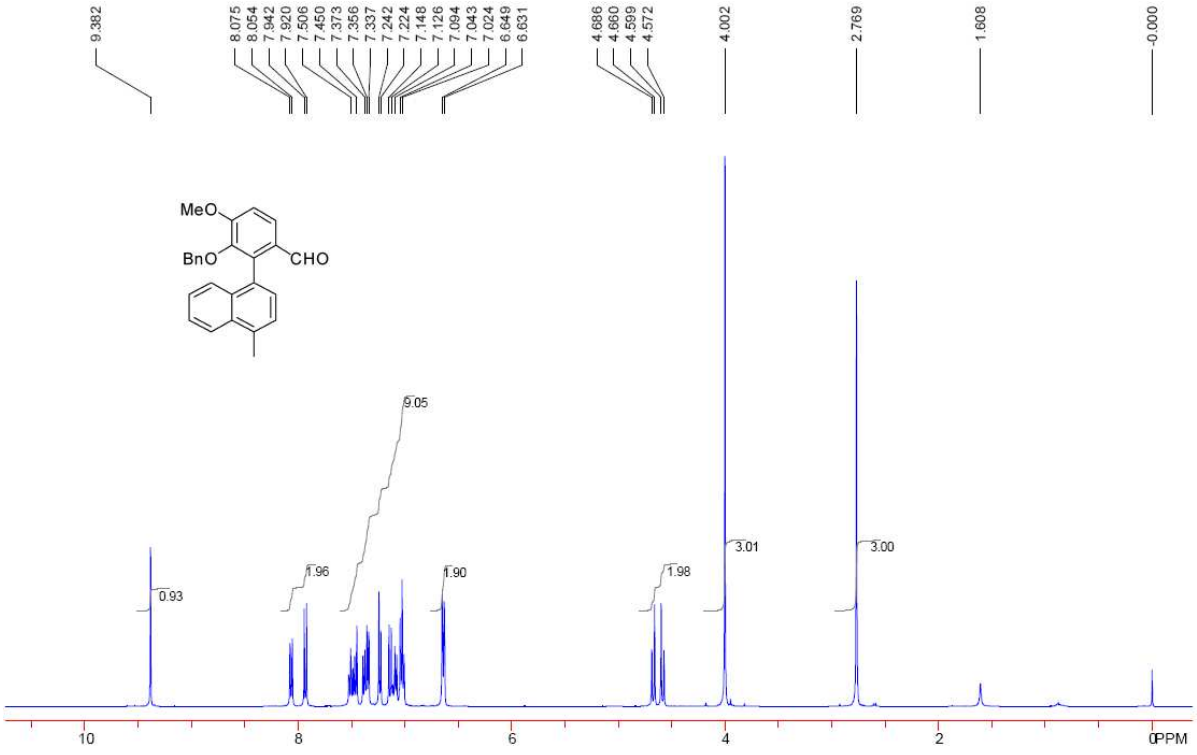
150
100
50
0
PPM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8.054
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7.920
7.506
7.450
7.373
7.356
7.337
7.242
7.224
7.148
7.126
7.094
7.043
7.024
6.649
6.631
4.686
4.660
4.599
4.572
4.002
2.769
1.608
-0.000
MeO
BnO
CHO
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3.01
3.00
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1.90
1.98
0.93
10
8
6
4
2
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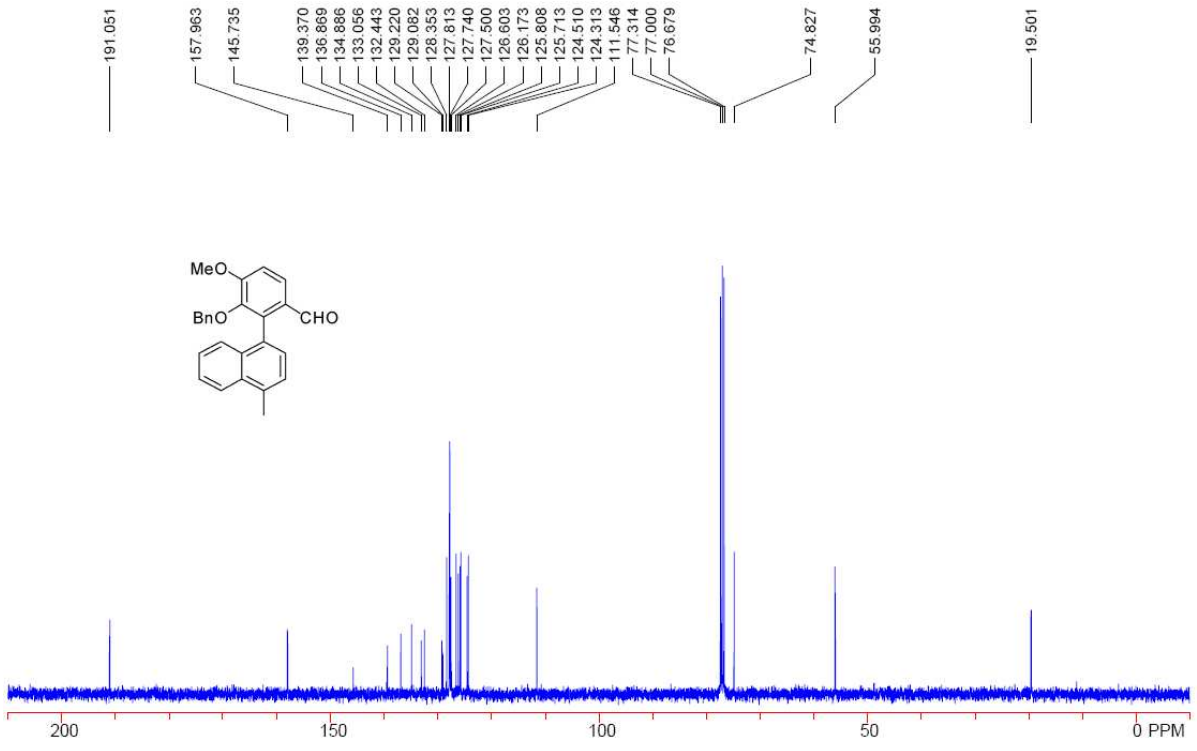
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132.443
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129.082
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127.813
127.740
127.500
126.603
126.173
125.808
125.713
124.510
124.313
111.546
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74.827
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BnO
CHO
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150
100
50
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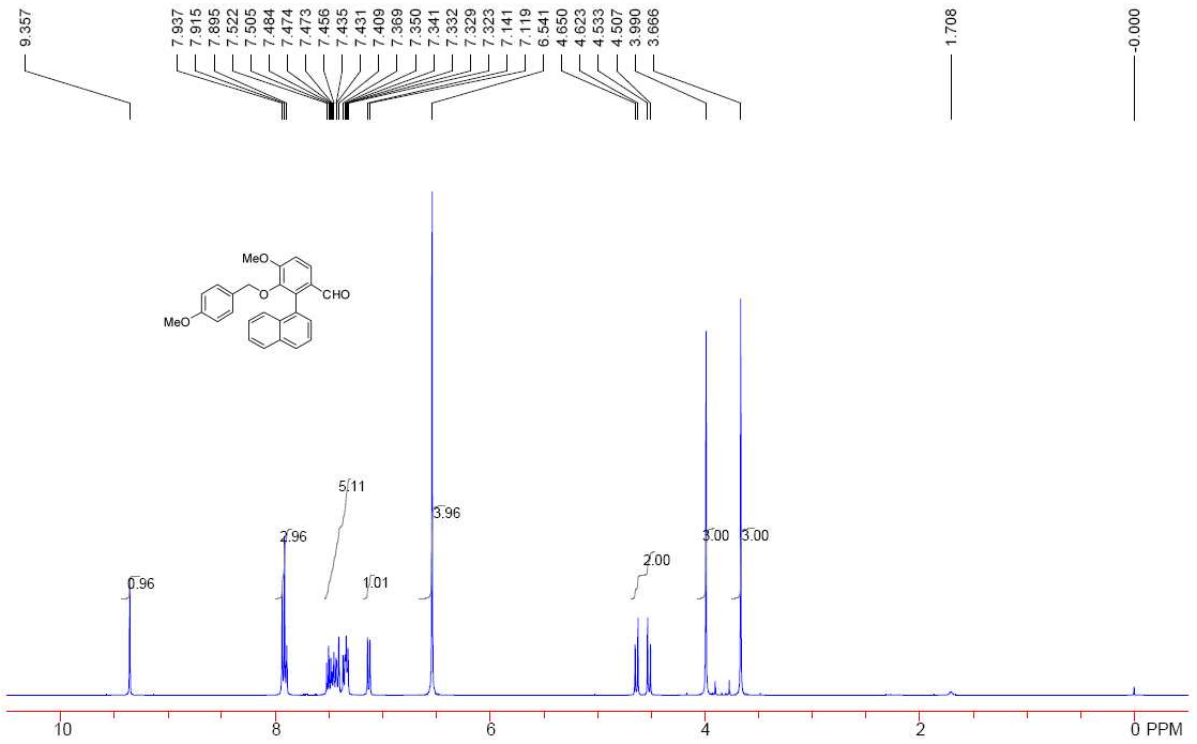
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7.505
7.484
7.474
7.473
7.456
7.435
7.431
7.409
7.369
7.350
7.341
7.332
7.329
7.323
7.141
7.119
6.541
4.650
4.623
4.533
4.507
3.990
3.686
1.708
0.000
MeO
CHO
MeO
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3.00
3.00
2.00
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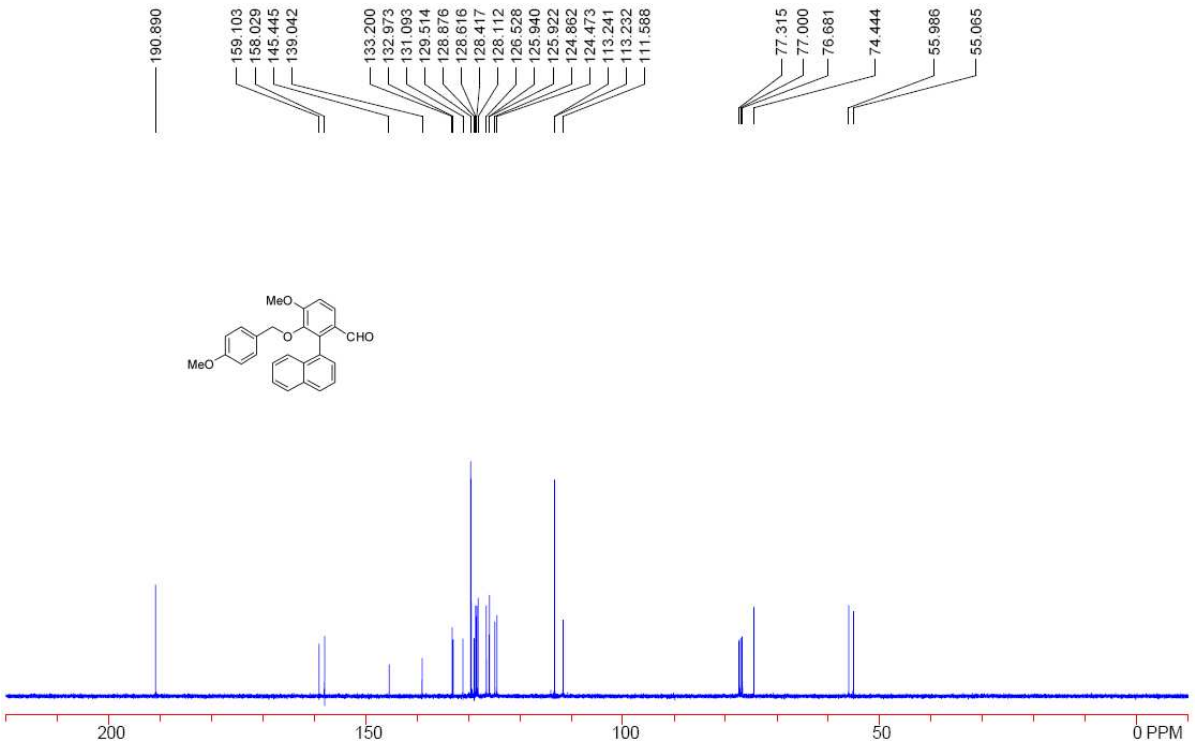
1.01
10
8
6
4
2
0 PPM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128.876
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128.417
128.112
126.528
125.940
125.922
124.862
124.473
113.241
113.232
111.588
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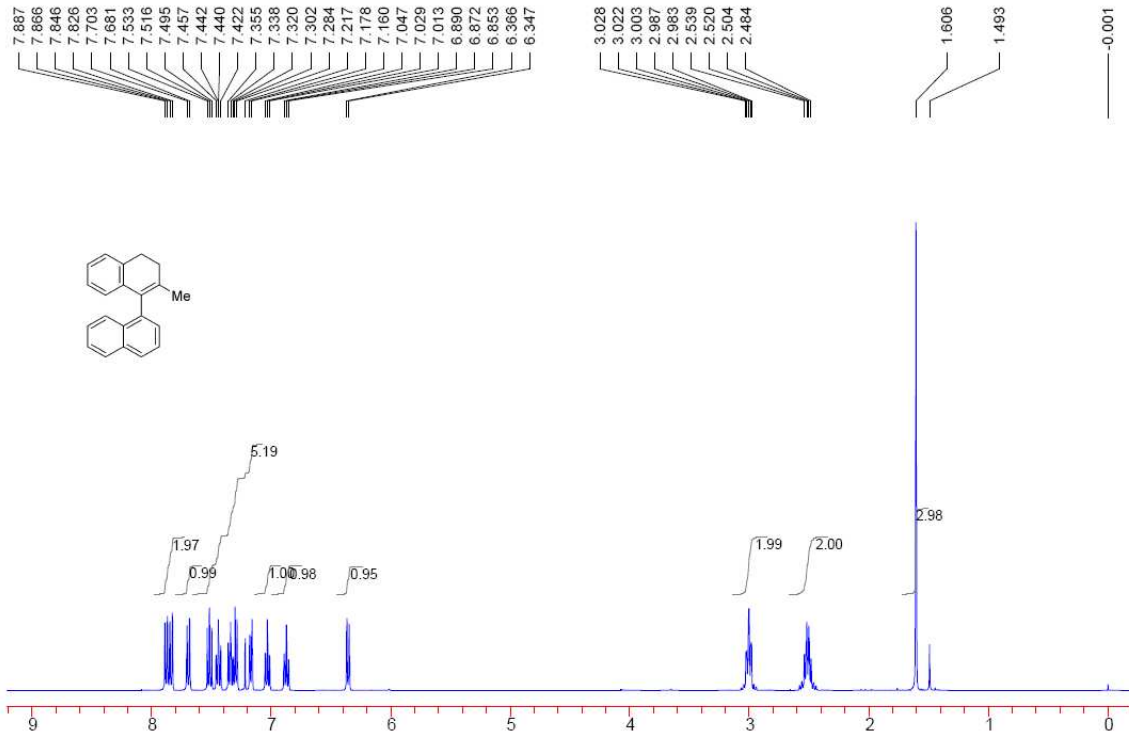
74.444
55.986
55.065
MeO
CHO
MeO
200
150
100
50
0 PPM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7.440
7.422
7.355
7.338
7.320
7.302
7.284
7.217
7.178
7.160
7.047
7.029
7.013
6.890
6.872
6.853
6.366
6.347
3.028
3.022
3.003
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2.983
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2.520
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2.484
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1.493
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Me
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1.97
0.99
1.00
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1.99
2.00
2.98
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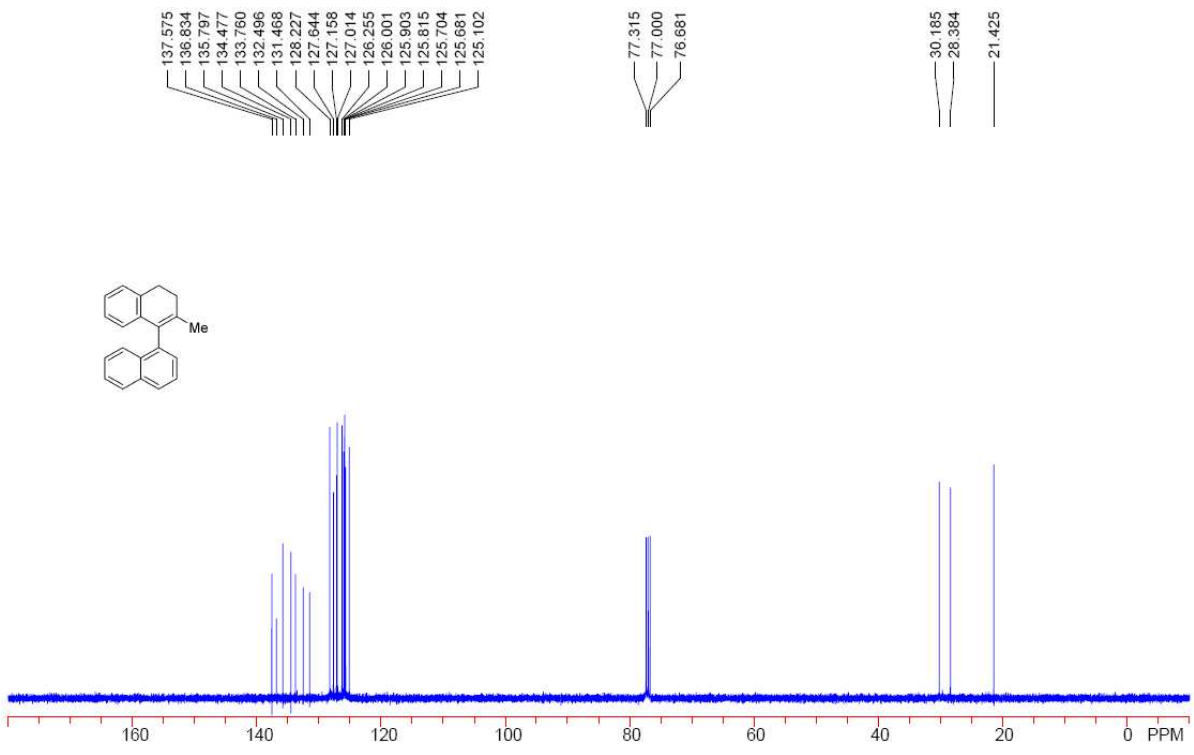
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126.001
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125.815
125.704
125.681
125.102
77.315
77.000
76.681
30.185
28.384
21.425
Me
160
140
120
100
80
60
40
20
0
PPM