Stereospecific Decarboxylative Benzylation of Enolates: Development and Mechanistic Insight

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Supporting Information

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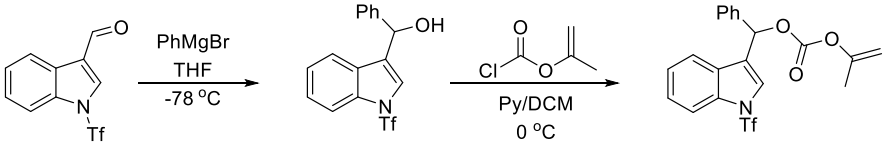
1. General Information

All reactions were run under an argon atmosphere using standard Schlenk techniques or an inert atmosphere glove box. All glassware were oven or flame dried prior to use. Toluene and THF were dried over sodium and distilled in the presence of benzophenone. Dried toluene was taken to the glove box in a Schlenk flask with activated molecular sieves. CH_2Cl_2 was dried over alumina. Other commercially available solvents were used without additional purification. All palladium catalysts and ligands were purchased from Strem and stored in the glove box under an argon atmosphere. Compound purification was effected by flash chromatography using 230x400 mesh, 60Å porosity silica obtained from Sorbent Technologies.

^1H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance 400 or a Bruker Avance 500 DRX spectrometer equipped with a QNP cryoprobe and referenced to residual protio solvent signals. Structural assignments were based on ^1H, ^{13}C, DEPT-135, COSY, HSQC. Mass spectrometry was run using EI or ESI techniques. Chiral HPLC analysis was performed by LC-10ATVP Shimadzu HPLC using Chiralpak AD, AS-H, AD-H and Chiralcell OD-H, OD chiral columns (0.46cm∅x25cm), eluting with hexane/iso-propanol mixture. All HPLC data are provided in a separate document. Optical rotations were measured on a Autopol® IV automatic polarimeter using a 5 cm cell and sodium D line (589 nm) at ambient temperature in the solvent and concentration indicated

2. Preparation and Spectral Data of Materials

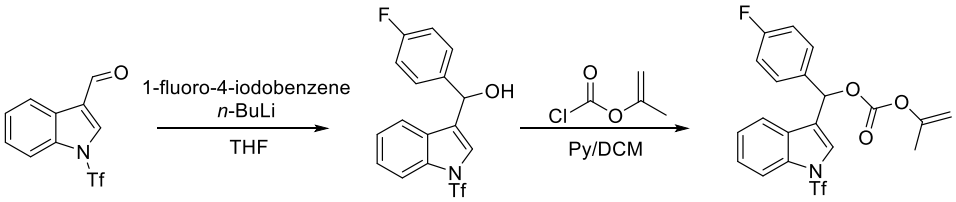
Substrates were prepared with the procedures shown below. The N-Tf indole-3-carboxaldehyde was synthesised via the reported process[1].



Standard procedure 1: N-Tf indole-3-carboxaldehyde (832 mg, 3 mmol) was dissolved into THF (15 ml). After the mixture was cooled to -78 °C, phenylmagnesium bromide (1.5 eq, 4.5 mmol) was added dropwise. The mixture was allowed to stirring at this temperature for 30 min. Then the reaction was quenched with NH_4Cl(aq.) and organic layer was separated. The aqueous layer was extracted with EtOAc 3 times. The combined organic layer was dried by $MgSO_4$. Removed the solvent on rotary evaporator, the corresponding secondary benzoic alcohol could be purified by column chromatography (978 mg, 92% yield).

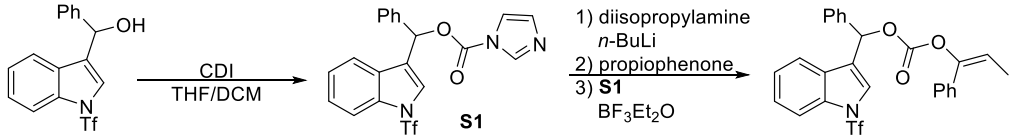
Then product of last step (711 mg, 2 mmol) was re-dissolved into DCM. Pyridine (483 uL, 6 mmol) was added and the mixture was cooled to 0 °C in a ice bath. After that, isopropenylchloroformate (289 mg, 2.4 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and monitored by TLC. After the starting material completely converted, the product was isolated by column

chromatography (705 mg, 80% yield).



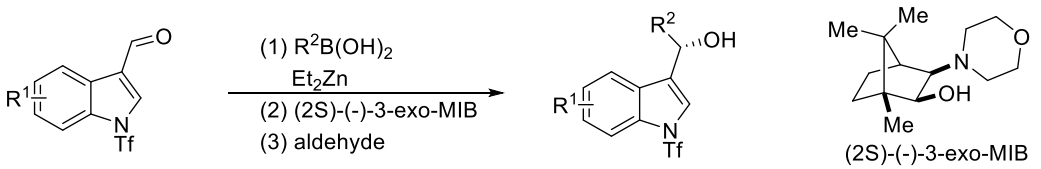
Standard procedure 2: 1-Fluoro-4-iodobenzene (666 mg, 3 mmol) was dissolved into THF (15 ml). After the mixture was cooled to -78 ^{o}C, *n*-BuLi (1.2 ml, 2.5 N in hexane) was added dropwise. The mixture was allowed to stirring at -78 ^{o}C for 30 min. N-Tf indole-3-carboxaldehyde (554 mg,2 mmol) was added with 5 ml THF, further stirring for 30 min before quenched with NH_4Cl(aq.). Organic layer was separated. The aqueous layer was extracted with EtOAc 3 times. The combined organic layer was dried by $MgSO_4$. Removed the solvent on rotary evaporator, the corresponding secondary alcohol could be purified by column chromatography (636 mg, 85% yield).

Then procedure of next step was as same as procedure 1.



Standard procedure 3[2]**:** CDI (1.62 g, 10 mmol) was dissolved into THF (20 mL), cooled to 0 ^{o}C in a ice bath. Phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-methanol (1.76 g, 5 mmol) was added slowly dropwise with 20 mL DCM via syringe. After completely added, the mixture was allowed to warm to room temperature and continuous stired for 3 hs and monitored by TLC. When the starting material totally disappeared, the solvent was removed via rotary evaporator and the desired product was purified by column chromatography (2.04 g, 90% yield). The 1H-imidazole-1-carboxylate intermediate **S1** can stored at 4 ^{o}C for more than 7 days without obviously decomposition.

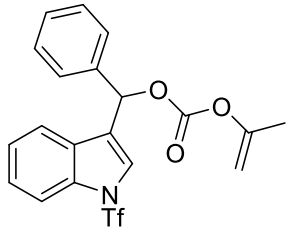
Diisopropylamine (313 uL, 2.2 mmol) was dissolved into THF (5 mL), cooled to -78 ^{o}C before *n*-BuLi (880 uL, 2.2 mmol, 2.5 N in hexane) was added via syringe. The mixture was stirred at this temperature for 10 min, then propiophenone (269 mg, 2 mmol) was added. This mixture was allowed to stir at -78 ^{o}C for 30 min. A separate flask was charged with a THF solution of 1H-imidazole-1-carboxylate intermediate **S1** (450 mg, 1 mmol), also cooled to -78 ^{o}C followed by the addition of BF_3Et_2O (303 uL, 2.4 mmol). After stirring at this temperature for 15 min, the enolate mixture was transferred into the solution of 1H-imidazole-1-carboxylate and $BF_3.Et_2O$ quickly. Then the mixture was further stirred at -78 ^{o}C for 30 min. After 1H-imidazole-1-carboxylate intermediate totally disappeared, the reaction was quench by H_2O, extrated with EtOAc 3 times. The combined organic layer was dried by $MgSO_4$. The solvent was removed on a rotary evaporator and the corresponding enol carbonate could be purified by column chromatography using 6:1 pentane:diethyl ether (388 mg, 76% yield, E/Z = 50:1).



Standard procedure for the preparation of enantioenriched diarylmethanols[3]: To a flame dried Schlenk flask was added phenyl boronic acid (731 mg, 6 mmol) and toluene (10 mL). Then diethyl zinc (18 mL, 18 mmol, 1.0 M in hexanes) was added and the solution was heated at 60 °C for 24 hours in an oil bath. After 24 hours, it was removed from the oil bath and cooled to room temperature. Then a solution of (2*S*)-(–)-3-exo-MIB (59.8 mg, 0.25 mmol) in toluene (5 mL) was added to the reaction mixture and was allowed to stir for one hour at room temperature before the addition of corresponding N-Tf indole-3-carboxaldehyde (2.5 mmol, 692 mg). Then the reaction mixture was allowed to stir for 12 hours and the resulting mixture was quenched with 1N HCl acid and the product was extracted with EtOAc. The combined organics were washed with brine and dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified via flash chromatography over silica gel to isolate enantioenriched secondary alcohol in 87% yield.

Characterization Data of Substrates

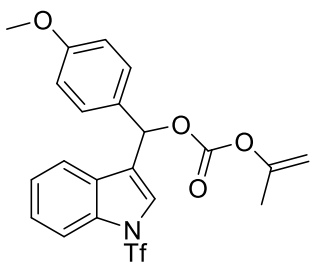
Phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



402 mg, white solid, mp. 65-67 °C, 92% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.81 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.37 – 7.34 (m, 1H), 7.34 – 7.27 (m, 5H), 7.23 – 7.19 (m, 1H), 6.88 (s, 1H), 4.76 – 4.72 (m, 1H), 4.63 (dd, *J* = 1.8, 1.1 Hz, 1H), 1.87 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.90, 152.12, 136.84, 135.92, 129.12, 128.89, 128.54, 127.27, 126.29, 125.04, 124.35, 124.02, 120.81, 119.50 (q, *J* = 322.0 Hz), 113.92, 102.04, 74.81, 19.10. ATR-IR: 1759, 1451, 1420, 1271, 1233, 1209, 1150, 1113 cm^{-1}. HRMS for: $C_{16}H_{11}F_3NO_2S$ $[M\text{-}C_4H_5O_3]^+$: calcd 338.0468 , found 338.0504.

The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed.

(4-Methoxyphenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate

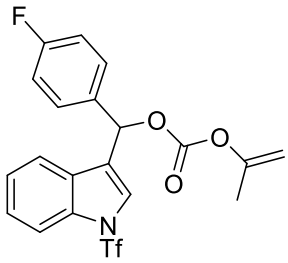


197 mg, yellow oil, 42% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.81 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.21 (ddd, *J* = 8.2, 7.2, 0.9 Hz, 1H), 6.86 – 6.81 (m, 3H), 4.74 – 4.61 (m, 2H), 3.73 (s, 3H), 1.87 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.17, 152.89, 152.12, 135.90, 129.05, 128.82, 128.54, 126.23, 124.99, 124.24, 123.92, 120.81, 119.50 (q, *J* =

321.3 Hz), 114.21, 113.89, 102.02, 74.80, 55.25, 19.12. ATR-IR: 1752, 1643, 1514, 1418, 1207, 1175, 1148, 991, 745 cm^{-1}. HRMS for: $C_{17}H_{13}F_3NO_3S$ $[M-C_4H_5O_3]^+$: calcd 368.0563, found 368.0596.

The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

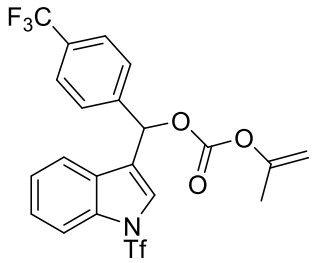
(4-Fluorophenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



398 mg, colorless oil, 85% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.93 (d, J = 8.4 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.44 (ddd, J = 8.4, 7.3, 1.2 Hz, 1H), 7.39 (d, J = 6.5 Hz, 2H), 7.33 (td, J = 7.6, 0.9 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.95 (s, 1H), 4.85 (d, J = 1.5 Hz, 1H), 4.75 (dd, J = 1.8, 1.1 Hz, 1H), 1.98 (d, J = 0.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.03 (d, J = 247.5 Hz), 152.86, 152.05, 135.93, 132.73 (q, J = 3.8 Hz), 129.40 (q, J = 8.8 Hz), 128.32, 126.40, 125.09, 124.21, 123.72, 120.69, 119.49 (q, J = 322.5 Hz), 116.92 (q, J = 35.0 Hz), 113.99, 102.14, 74.23, 19.11. ATR-IR: 1759, 1676, 1607, 1510, 1451, 1422, 1273, 1234, 1209, 1150, 1113, 991, 747, 611 cm^{-1}. HRMS for: $C_{16}H_{10}F_4NO_2S$ $[M-C_4H_5O_3]^+$: calcd 356.0363, found 356.0371.

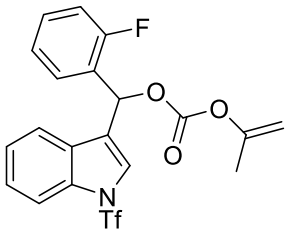
The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

Prop-1-en-2-yl-((4-(trifluoromethyl)phenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl) carbonate



White solid, mp. 75-76 °C, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.93 (d, J = 8.3 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.47 – 7.41 (m, 3H), 7.34 (td, J = 7.7, 0.9 Hz, 1H), 4.85 (d, J = 1.6 Hz, 1H), 4.75 (dd, J = 1.8, 1.1 Hz, 1H), 1.98 (d, J = 0.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.88, 152.02, 140.86 (q, J = 2.0 Hz), 135.95, 131.24 (q, J = 32.0 Hz), 128.19, 127.49, 126.53, 125.96 (q, J = 4.0 Hz), 125.20, 124.69, 123.78 (q, J = 270.0 Hz), 123.13, 120.64, 119.49 (q, J = 322.0 Hz), 114.04, 102.16, 73.92, 19.04. ATR-IR: 1759, 1422, 1325, 1273, 1234, 1209, 1167, 1150, 1130, 1113, 1069, 990, 746, 610 cm^{-1}.

(2-Fluorophenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate

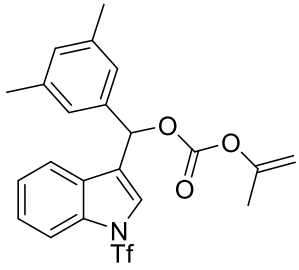


Yellow solid, mp. 58-61 °C, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.81 (d, J = 8.4 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.44 (td, J = 7.6, 1.7 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.30 – 7.24 (m, 3H), 7.17 (s, 1H), 7.12 (td, J = 7.6, 1.0 Hz, 1H), 7.06 – 7.01 (m, 1H), 4.75 (d, J = 1.5 Hz, 1H), 4.64 (dd, J = 1.8, 1.1 Hz, 1H), 1.88 (d, J = 0.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.98 (d, *J* = 247.5 Hz), 152.93, 151.91, 135.87, 130.94 (d, *J* = 31.0 Hz), 128.45, 128.24 (d, *J* = 2.5 Hz), 126.42, 125.19, 124.73 (d, *J* = 3.8 Hz), 124.60 (d, *J* = 12.5 Hz), 124.28, 123.27, 120.55, 119.51 (q, *J* = 322.5 Hz), 116.04 (d, *J* = 21.3 Hz), 113.99, 102.16, 68.73 (q, *J* = 3.8 Hz), 19.11. ATR-IR: 1761, 1674, 1491, 1451, 1422, 1271, 1233, 1207, 1148, 1113, 990, 758, 606 cm^{-1}. HRMS for: $C_{16}H_{10}F_4NO_2S$ $[M\text{-}C_4H_5O_3]^+$: calcd 356.0363, found 356.0368.

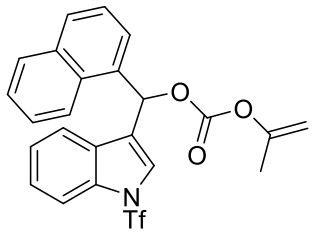
The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

(3,5-Dimethylphenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



White solid, mp. 63-65 ºC, 6:1 pentane:diethyl ether.. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 7.91 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.44 – 7.38 (m, 1H), 7.38 – 7.29 (m, 2H), 7.13 – 7.06 (m, 2H), 7.01 (s, 1H), 6.90 (s, 1H), 4.84 (d, *J* = 1.4 Hz, 1H), 4.73 (dd, *J* = 1.7, 1.2 Hz, 1H), 2.33 (s, 6H), 1.98 (d, *J* = 0.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.92, 152.14, 138.49, 136.67, 135.90, 130.81, 128.65, 126.22, 125.03, 125.00, 124.32, 124.18, 120.83, 119.52 (q, *J* = 322.0 Hz), 113.89, 102.00, 74.94, 21.29, 19.13. ATR-IR: 1759, 1672, 1611, 1451, 1420, 1271, 1233, 1207, 1150, 1111, 990, 839, 746, 610 cm^{-1}. HRMS for: $C_{22}H_{21}F_3NO_5S$ $[M+H]^+$: calcd 468.1093, found 468.1230.

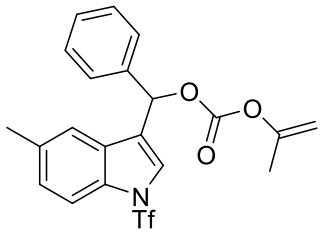
Naphthalen-1-yl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



392 mg, white oil, 80% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* (ppm) = 8.02 – 7.96 (m, 1H), 7.78 (dd, *J* = 8.4, 5.1 Hz, 3H), 7.66 – 7.58 (m, 2H), 7.44 – 7.36 (m, 4H), 7.28 (dd, *J* = 8.2, 7.5 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 4.73 (s, 1H), 4.60 (d, *J* = 0.8 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.89, 151.28, 134.85, 132.90, 131.16, 129.43, 128.99, 127.98, 127.80, 125.76, 125.30, 125.05, 124.76, 124.19, 124.11, 123.02, 122.09, 119.68, 118.40 (q, *J* = 321.3 Hz), 112.90, 101.02, 71.36, 18.04. ATR-IR: 1755, 1674, 1451, 1422, 1275, 1233, 1207, 1150, 1113, 988, 779, 746, 615 cm^{-1}. HRMS for: $C_{20}H_{13}F_3NO_2S$ $[M\text{-}C_4H_5O_3]^+$: calcd 388.0614, found 388.0637.

The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

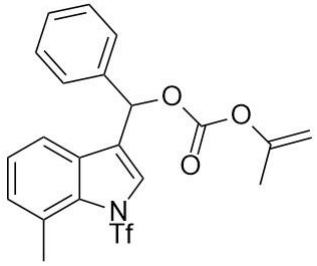
(5-Methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate



372 mg, white solid, mp. 71-73 ºC, 82% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.77 (d, *J* = 9.0 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.30 (s, 1H), 7.22 (d, *J* = 6.8 Hz, 2H), 6.94 (s, 1H), 4.83 (d, *J* = 1.5 Hz, 2H), 4.72 (s, 1H), 2.39 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.96, 152.19, 136.92, 134.99, 134.12, 129.12, 128.92, 128.81, 127.68, 127.29, 124.49, 123.88, 120.63, 119.56 (q, *J* = 322.0 Hz), 113.59, 102.06, 74.84, 21.38, 19.15. ATR-IR: 1759, 1418, 1273, 1233, 1204, 1153, 1142, 1111, 1090, 991, 698, 625, 586 cm^{-1}. HRMS (ESI) for: $C_{17}H_{13}F_3NO_2S$ $[M\text{-}C_4H_5O_3]^+$: calcd 352.0614, found 352.0619.

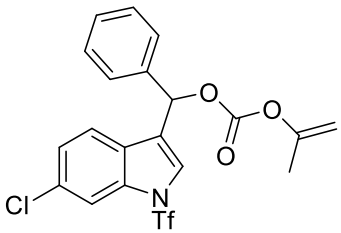
The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

(7-Methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate



Beige solid, mp. 62.1-64.9 °C, 5:1 hexane:ethyl acetate. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 2H), 7.42 – 7.39 (m, 1H), 7.39 – 7.35 (m, 2H), 7.28 (t, *J* = 4.7 Hz, 1H), 7.21 (s, 1H), 7.20 (d, *J* = 1.1 Hz, 1H), 6.93 (s, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 4.72 – 4.70 (m, 1H), 2.68 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.93, 152.15, 136.80, 135.72, 130.66, 130.53, 129.10, 128.88, 127.34, 125.74, 125.47, 123.84, 118.63, 102.04, 74.80, 21.85 (d, *J* = 1.8 Hz), 19.14. ATR-IR: 1758, 1419, 1270, 1231, 1207, 1112, 1083, 739, 724 cm^{-1}. HRMS for: $C_{21}H_{18}F_3NO_5S$ $[M]^+$: calcd 453.0858, found 453.0864.

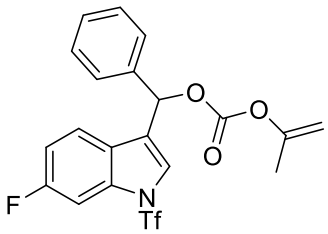
(6-Chloro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate



398 mg, white solid, mp. 101-103 ºC, 84% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.93 (d, *J* = 1.7 Hz, 1H), 7.48 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.95 (s, 1H), 4.84 (d, *J* = 1.5 Hz, 1H), 4.74 (dd, *J* = 1.8, 1.1 Hz, 1H), 1.97 (d, *J* = 0.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.86, 152.04, 136.57, 136.23, 132.55, 129.22, 128.94, 127.19, 127.01, 125.84, 124.80, 123.76, 121.65, 119.38 (q, *J* = 321.3 Hz), 114.21, 102.08, 74.53, 19.06. ATR-IR: 1759, 1422, 1269, 1233, 1209, 1152, 1121, 1074, 993, 625, 602 cm^{-1}. HRMS for: $C_{16}H_{10}ClF_3NO_2S$ $[M\text{-}C_4H_5O_3]^+$: calcd 372.0073, found 372.0087.

The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

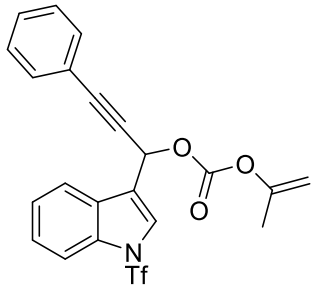
(6-Fluoro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate



White solid, mp. 72-74 ºC, 6:1 pentane:diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.63 (dd, *J* = 9.2, 2.2 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 – 7.35 (m, 5H), 7.06 (td, *J* = 8.9, 2.3 Hz, 1H), 6.93 (s, 1H), 4.83 (d, *J* = 1.5 Hz, 1H), 4.73 (dd, *J* = 1.7, 1.1 Hz, 1H), 1.96 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.52 (d, *J* = 245.0 Hz), 152.87, 152.09, 136.63, 136.20 (d, *J* = 12.5 Hz), 129.24, 128.96, 127.21, 124.79 (d, *J* = 1.3 Hz), 124.62 (d, *J* = 3.8 Hz), 123.76, 121.87 (d, *J* = 8.8 Hz), 119.42 (q, *J* = 321.3 Hz), 113.66 (d, *J* = 25.0 Hz), 102.12, 101.74 (d, *J* = 28.8 Hz), 74.63, 19.11. ATR-IR: 1759, 1676, 1616, 1578, 1489, 1271, 1234, 1209, 1148, 1098, 1001, 905 cm^{-1}. $C_{16}H_{10}F_4NO_2S$ $[M\text{-}C_4H_5O_3]^+$: calcd 356.0363, found 356.0380.

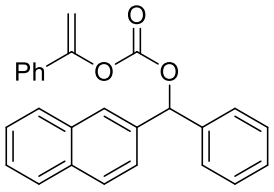
The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

3-Phenyl-1-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)prop-2-yn-1-yl prop-1-en-2-yl carbonate



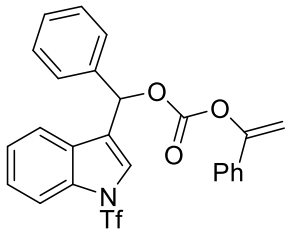
Yellowish oil, 6:1 pentane:diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.88 – 7.81 (m, 2H), 7.56 (s, 1H), 7.42 – 7.33 (m, 4H), 7.28 – 7.21 (m, 3H), 6.72 (d, *J* = 0.7 Hz, 1H), 4.81 – 4.77 (m, 1H), 4.66 (dd, *J* = 1.8, 1.1 Hz, 1H), 1.91 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.98, 152.02, 136.02, 132.05, 129.37, 128.45, 128.17, 126.56, 125.64, 125.26, 121.37, 120.99, 120.93, 119.51 (q, *J* = 322.0 Hz), 114.01, 102.19, 88.19, 82.77, 63.09, 19.16. ATR-IR: 1759, 1678, 1491, 1451, 1422, 1323, 1267, 1234, 1209, 1150, 1113, 756, 613 cm^{-1}. HRMS for: $C_{22}H_{16}F_3NNaO_5S$ $[M+Na]^+$: calcd 486.0593, found 486.0518.

Naphthalen-2-yl(phenyl)methyl (1-phenylvinyl) carbonate



285 mg, colorless oil, 75% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 0.5 Hz, 1H), 7.86 – 7.80 (m, 3H), 7.52 – 7.46 (m, 4H), 7.44 – 7.40 (m, 3H), 7.39 – 7.35 (m, 2H), 7.35 – 7.28 (m, 3H), 6.90 (s, 1H), 5.45 (d, *J* = 2.5 Hz, 1H), 5.15 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.37, 152.48, 139.09, 136.53, 133.78, 133.03, 133.02, 129.09, 128.60, 128.55, 128.51, 128.29, 128.18, 127.66, 127.09, 126.39, 126.37, 126.03, 124.86, 124.62, 101.87, 81.60. ATR-IR: 1755, 1672, 1271, 1207, 1167, 1125, 1086, 936, 853, 816, 698 cm^{-1}. HRMS for: $C_{26}H_{20}NaO_3$ $[M+Na]^+$: calcd 403.1305, found 403.1346.

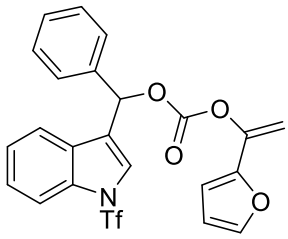
Phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl (1-phenylvinyl) carbonate



366 mg, white solid, mp. 97-100 °C, 73% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.91 (d, *J* = 8.3 Hz, 1H), 7.46 (m, 5H), 7.43 – 7.39 (m, 4H), 7.35 – 7.28 (m, 5H), 6.97 (s, 1H), 5.45 (d, *J* = 2.6 Hz, 1H), 5.15 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.33, 151.32, 135.60, 134.88, 132.58, 128.20, 128.16, 127.88, 127.59, 127.47, 126.27, 125.29, 124.03, 123.77, 123.40, 122.85, 119.79, 118.46 (q, *J* = 321.3 Hz), 112.90, 100.94, 74.21. ATR-IR: 1765, 1418, 1279, 1229, 1148, 1111, 990, 746, 698, 606 cm^{-1}. HRMS for: $C_{16}H_{11}F_3NO_2S$ $[M\text{-}C_9H_7O_3]^+$: calcd 338.0463, found 338.0504.

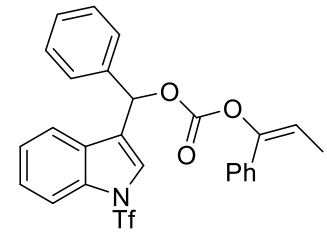
The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

1-(Furan-2-yl)vinyl (phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl) carbonate



373 mg, yellow oil, 76% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.95 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.51 – 7.48 (m, 1H), 7.47 – 7.38 (m, 6H), 7.33 (td, *J* = 7.8, 0.9 Hz, 1H), 7.05 (s, 1H), 6.37 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.33 (d, *J* = 3.4 Hz, 1H), 5.49 (d, *J* = 2.7 Hz, 1H), 5.10 (d, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.23, 147.77, 144.72, 143.27, 136.54, 135.88, 129.21, 128.90, 128.44, 127.28, 126.32, 125.04, 124.41, 123.78, 120.79, 119.47 (q, *J* = 322.5 Hz), 113.90, 111.32, 107.77, 100.17, 75.44. ATR-IR: 1765, 1451, 1418, 1233, 1209, 1148, 1111, 990, 745, 604, 579 cm^{-1}. HRMS for: $C_{23}H_{16}F_3NNaO_6S$ $[M+Na]^+$: calcd 514.0593, found 514.0590.

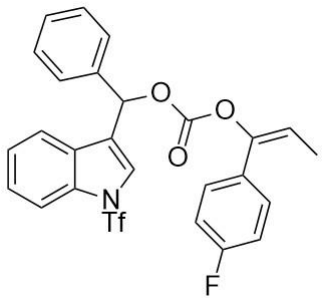
(*E*)-phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl-(1-phenylprop-1-en-1-yl) carbonate



418 mg, pale yellow solid, mp. 88-91 °C, 81% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.80 (d, *J* = 8.4 Hz, 1H), 7.35 (m, 3H), 7.31 – 7.25 (m, 6H), 7.22 (s, 1H), 7.20 – 7.14 (m, 4H), 6.87 (s, 1H), 5.75 (q, *J* = 7.0 Hz, 1H), 1.58 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.10, 147.44, 136.74, 135.94, 134.46, 129.18, 128.92, 128.60, 128.54, 128.32, 127.26, 126.35, 125.08, 124.39, 124.21, 124.04, 120.84, 119.52 (q, *J* = 321.3 Hz), 113.95, 112.98, 75.23, 11.22. ATR-IR: 1763, 1451, 1418, 1148, 1111, 991, 953, 746, 698, 606, 579 cm^{-1}. HRMS for: $C_{16}H_{11}F_3NO_2S$ $[M\text{-}C_{10}H_9O_3]^+$: calcd 338.0463, found 338.0467.

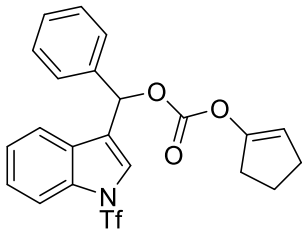
The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

(*E*)-(4-fluorophenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl-(1-phenylprop-1-en-1-yl) carbonate



White solid, mp. 102.4-105.6 °C, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.44 – 7.37 (m, 5H), 7.34 – 7.27 (m, 4H), 6.99 – 6.91 (m, 3H), 5.77 (q, *J* = 7.0 Hz, 1H), 1.68 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.65, 161.67, 152.00, 146.62, 136.66, 135.94, 129.22, 128.92, 128.49, 127.23, 126.37, 126.15, 126.09, 125.06, 124.39, 123.93, 120.77, 115.64, 115.47, 113.97, 112.86 (d, *J* = 2.1 Hz), 75.34, 11.17. ATR-IR: 1762, 1607, 1510, 1451, 1420, 1233, 1112, 992, 843, 665, 452 cm^{-1}. HRMS for $C_{26}H_{19}F_4NO_5S$ $[M+Na]^+$: calcd 556.0818, found 556.0812.

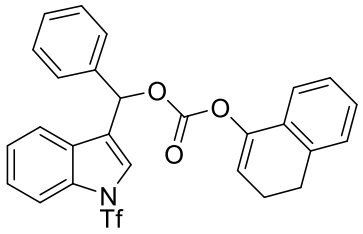
Cyclopent-1-en-1-yl (phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl) carbonate



177 mg, colorless oil, 38% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* (ppm) = 7.89 (d, *J* = 8.4 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.44 – 7.38 (m, 5H), 7.36 (s, 1H), 7.32 – 7.28 (m, 1H), 6.95 (s, 1H), 5.48 (d, *J* = 1.8 Hz, 1H), 2.54 – 2.32 (m, 4H), 1.95 (dt, *J* = 14.9, 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.81, 150.77, 136.81, 135.94, 129.19, 128.94, 128.56, 127.37, 126.32, 125.08, 124.43, 123.93, 120.86, 119.52 (q, *J* = 322.5 Hz), 113.95, 112.68, 74.88, 30.60, 28.48, 20.91. ATR-IR: 1763, 1418, 1233, 1213, 1148, 1111, 745, 610 cm^{-1}. HRMS for: $C_{16}H_{11}F_3NO_2S$ $[M-C_6H_7O_3]^+$: calcd 338.0463, found 338.0497.

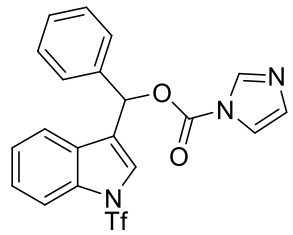
The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

3,4-Dihydronaphthalen-1-yl (phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl) carbonate



211 mg, pale yellow solid, mp. 128-131 ºC, 40% yield, 6:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* (ppm) = 7.91 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.46 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.44 – 7.39 (m, 4H), 7.35 (s, 1H), 7.33 – 7.29 (m, 1H), 7.20 – 7.13 (m, 2H), 7.09 (td, *J* = 7.3, 1.8 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.99 (s, 1H), 5.81 (t, *J* = 4.7 Hz, 1H), 2.86 (t, *J* = 8.1 Hz, 2H), 2.44 (ddd, *J* = 9.2, 7.4, 4.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.72, 146.19, 136.78, 136.34, 135.96, 129.85, 129.22, 128.96, 128.58, 128.20, 127.66, 127.38, 126.49, 126.36, 125.10, 124.45, 124.00, 120.89, 120.47, 119.53 (q, *J* = 322.5 Hz), 115.37, 113.97, 75.25, 27.32, 21.94. ATR-IR: 1765, 1451, 1418, 1225, 1148, 1111, 1007, 745, 619 cm-1. HRMS for: $C_{27}H_{20}F_3NNaO_5S$ $[M+Na]^+$: calcd 550.0906 , found 550.0882.

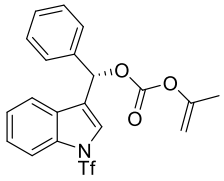
Phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl-1H-imidazole-1-carboxylate

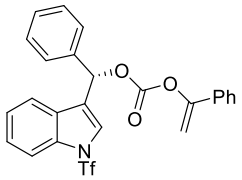


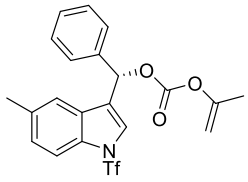
404 mg, yellowish oil, 90% yield, 5:1 hexane:ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.19 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.53 – 7.40 (m, 8H), 7.34 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 3.1 Hz, 2H), 7.09 (d, J = 0.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.87, 137.11, 135.95, 135.87, 131.04, 129.62, 129.17, 128.38, 127.18, 126.64, 125.32, 125.15, 123.00, 120.60, 119.45 (q, J = 321.3 Hz), 118.16, 114.11, 74.80. ATR-IR: 1761, 1472, 1391, 1316, 1288, 1240, 1173, 1001, 764, 746 cm^{-1}. HRMS for: $C_{16}H_{11}F_3NO_2S$ [M- $C_4H_5O_3$]: calcd 338.0463, found 338.0469.

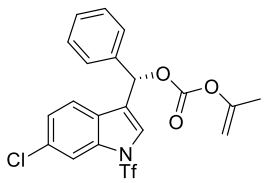
The molecular ion peak wasn't found in standard high resolution mass spectrometry, instead the diarylmethane cation was observed .

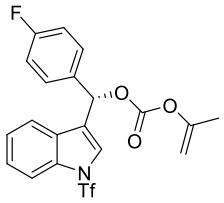
HPLC analysis for enantioenriched materials

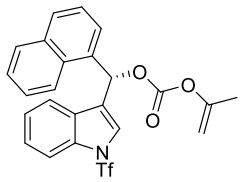
(*S*)-phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate	
	HPLC analysis: 85% ee (Chiralcel AD, 99.8:0.2 Hexanes/isopropanol, 0.2 mL/min, 254 nm, major R_t = 51.6 min, minor R_t = 58.9 min)

(*S*)-phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl (1-phenylvinyl) carbonate	
	HPLC analysis: 30% ee (Chiralcel AD-H, 98:2 Hexanes/isopropanol, 0.5 mL/min, 254 nm, major R_t = 26.0 min, minor R_t = 33.4 min)

(*S*)-(5-methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate	
	HPLC analysis: 90% ee (Chiralcel AD-H, 99.6:0.4 Hexanes/isopropanol, 0.2 mL/min, 254 nm, major R_t = 37.9 min, minor R_t = 43.4 min)

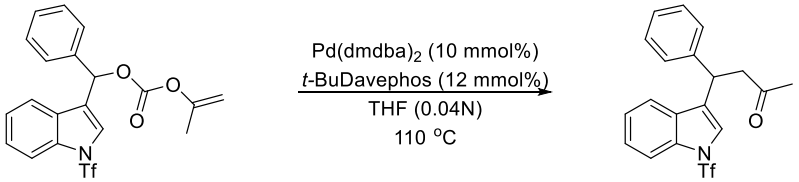
(*S*)-(6-chloro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate	
	HPLC analysis: 90% ee (Chiralcel AD-H, 99.6:0.4 Hexanes/isopropanol, 0.2 mL/min, 254 nm, major R_t = 44.1 min, minor R_t = 51.6 min)

(*S*)-(4-fluorophenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate	
	HPLC analysis: 85% ee (Chiralcel AD-H, 99.6:0.4 Hexanes/isopropanol, 0.2 mL/min, 254 nm, major R_t = 43.5 min, minor R_t = 47.3 min)

(*S*)-naphthalen-1-yl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate	
	HPLC analysis: 66% ee (Chiralcel AD-H, 99.6:0.4 Hexanes/isopropanol, 0.2 mL/min, 254 nm, major R_t = 34.3 min, minor R_t = 44.2 min)

3. General Procedure and Spectral Data of Products

3.1 General Procedure

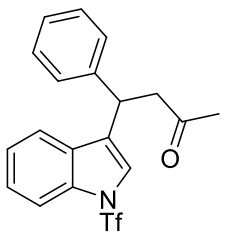


In a glove box, under an argon atmosphere, a flame dried 25 mL microwave vial with a stir bar was charged with secondary benzylic enol carbonate **1a** (88 mg, 0.2 mmol), Pd(dmdba)$_2$ (10 mmol%, 16.6 mg, 0.02 mmol), *t*-BuDavephos (12 mmol%, 8.4 mg, 0.024 mmol) and THF (5 mL, 0.04N). The vial was carefully sealed with a cap and removed from glove box and stirring under 110 ^{o}C until the material totally converted as judged by TLC. ***Note***: heating the vial results in pressure buildup and normal precaution should be taken. After cooling the mixture to room temperature, the solvent was removed under vacuum and the crude product was purified by column chromatography.

1.5 mmol scale reaction: Following the same protocol as described above, the reaction was increased to a 1.5 mmol scale. In a glove box, under an argon atmosphere, a 60 mL Fischer-Porter reaction vessel containing a stir bar was charged with secondary benzylic enol carbonate **1a** (0.659 g, 1.5 mmol), Pd(dmdba)$_2$ (10 mol %, 0.122 g, 0.15 mmol), *t*-Bu-Davephos (12 mol %, 0.062 g, 0.18 mmol) and THF (37.5 mL, 0.04 N). The vessel was sealed, removed from the glove box, and stirred in an oil bath heated to 110 ^{o}C behind a protective blast shield. After 48 hours at 110 ^{o}C, the vessel was removed from the heat, and the solvent was removed under vacuum. Crude ^{1}H NMR indicated complete conversion of starting material to product. The crude product was purified by flash column chromatography with a solvent system of hexane and ethyl acetate (5:1). Removal of solvent from the combined fractions produced 486 mg of product (82%).

3.2 Characterization Data of Products

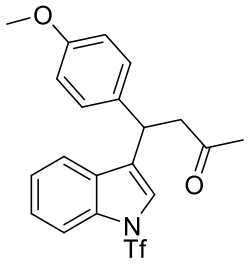
(2a): 4-Phenyl-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



68 mg, colorless oil, 36 h, 86% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.75 (d, J = 8.4 Hz, 1H), 7.38 – 7.25 (m, 2H), 7.23 – 7.20 (m, 1H), 7.19 – 7.15 (m, 3H), 7.13 – 7.08 (m, 3H), 4.68 (t, J = 7.2 Hz, 1H), 3.14 – 3.03 (m, 2H), 1.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 205.84, 141.49, 135.94, 130.28, 129.14, 128.91, 127.78, 127.20, 126.10, 124.86, 122.19, 120.81, 119.68 (q, J = 322.5 Hz), 113.86, 49.12, 37.56, 30.68. ATR-IR: 1719, 1451, 1416, 1360, 1282, 1231, 1206, 1148, 1113, 1022, 990, 745, 702, 611 cm^{-1}. HRMS: Calcd for $C_{19}H_{16}F_3NNaO_3S$ $[M+Na]^+$: 418.0695. Found: 418.0690.

(2b):

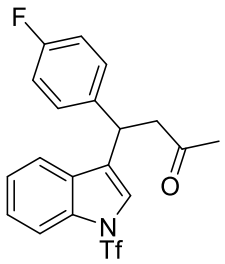
4-(4-methoxyphenyl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



71 mg, colorless oil, 24 h, 84% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.78 (d, J = 8.3 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.20 – 7.16 (m, 1H), 7.14 – 7.04 (m, 3H), 6.79 – 6.70 (m, 2H), 4.65 (t, J = 7.0 Hz, 1H), 3.69 (s, 3H), 3.08 (dd, J = 7.3, 2.6 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 206.01, 158.52, 135.88, 133.30, 130.18, 128.70, 128.44, 125.99, 124.75, 121.93, 120.76, 119.58 (q, J = 322.5 Hz), 114.17, 113.80, 55.19, 49.20, 36.75, 30.78. ATR-IR: 1719, 1609, 1512, 1451, 1414, 1522, 1233, 1206, 1148, 1111, 1032, 749, 611 cm^{-1} . HRMS: Calcd for $C_{20}H_{18}F_3NNaO_4S$ $[M+Na]^+$: 448.0801. Found: 448.0807.

(2c):

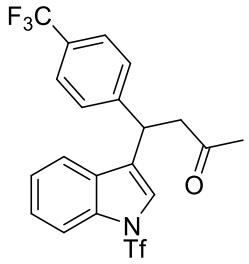
4-(4-fluorophenyl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



65 mg, colorless oil, 48 h, 79% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.87 (d, J = 8.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.28 – 7.22 (m, 3H), 7.18 (s, 1H), 7.04 – 6.92 (m, 2H), 4.78 (t, J = 7.2 Hz, 1H), 3.18 (qd, J = 16.9, 7.2 Hz, 2H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ205.52, 161.75 (d, J = 243.8 Hz), 137.13 (d, J = 3.8 Hz), 135.88, 129.97, 129.27 (d, J = 7.5 Hz), 127.95, 126.14, 124.82, 122.04, 120.61, 119.57 (q, J = 321.3 Hz), 115.72 (d, J = 21.3 Hz), 113.86, 49.07, 36.66, 30.71. ATR-IR: 1719, 1605, 1508, 1451, 1416, 1283, 1233, 1206, 1148, 1113, 746, 611 cm^{-1}. HRMS: Calcd for $C_{18}H_{19}FN_2O$ $[M+NH_4\text{-}Tf]^+$: 298.1481. Found: 298.1493.

(2d):

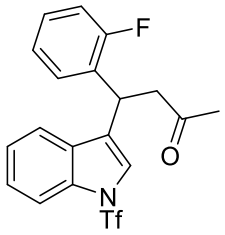
4-(4-(trifluoromethyl)phenyl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



63 mg, colorless oil, 72 h, 68% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.87 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.1 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.35 – 7.26 (m, 2H), 7.22 (s, 1H), 4.87 (t, J = 7.1 Hz, 1H), 3.29 – 3.15 (m, 2H), 2.14 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.02, 145.57, 135.87, 129.80, 129.42 (q, J = 32.5 Hz), 128.18, 127.22, 126.31, 125.85 (q, J = 3.8 Hz), 124.93, 123.95 (q, J = 270.0 Hz), 122.27, 120.45, 119.56 (q, J = 322.5 Hz), 113.94, 48.75, 37.01, 30.62.. ATR-IR: 1721, 1618, 1451, 1416, 1325, 1233, 1207, 1165, 1150, 1113, 1069, 1018, 743, 610 cm^{-1}. HRMS : Calcd for $C_{19}H_{16}F_3NNaO$ $[M+Na\text{-}Tf]^+$: 354.1082. Found: 354.1849.

(2e):

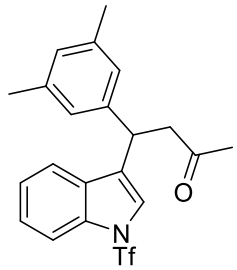
4-(2-fluorophenyl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



36 mg, colorless oil, 72 h, 43% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.55 (dd, *J* = 9.2, 2.2 Hz, 1H), 7.28 – 7.16 (m, 7H), 6.96 (td, *J* = 8.9, 2.3 Hz, 1H), 4.72 (t, *J* = 7.2 Hz, 1H), 3.19 – 3.10 (m, 2H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.67, 162.47 (d, *J* = 6.3 Hz), 141.26, 136.14 (q, *J* = 12.5 Hz), 128.96, 127.93, 127.69, 127.30, 126.53, 126.51, 122.32, 121.77 (q, *J* =8.8 Hz), 119.56 (q, *J* = 322.5 Hz), 113.35 (q, *J* = 23.8 Hz), 101.68 (q, *J* = 28.7 Hz), 49.11, 37.47, 30.72. ATR-IR: 1714, 1614, 1487, 1416, 1269, 1233, 1207, 1148, 1098, 997, 901, 746, 702 cm^{-1}. HRMS: Calcd for $C_{19}H_{19}F_4N_2O_3S$ $[M+NH_4]^+$: 431.1047. Found: 431.1043.

(2f):

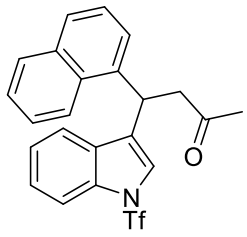
4-(3,5-Dimethylphenyl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



47 mg, white foam, 72 h, 56% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.86 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.28 (dd, *J* = 10.2, 3.1 Hz, 1H), 7.18 (s, 1H), 6.87 (s, 2H), 6.85 (s, 1H), 4.70 (t, *J* = 7.1 Hz, 1H), 3.21 – 3.13 (m, 2H), 2.26 (s, 6H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.91, 141.23, 138.27, 135.83, 130.33, 128.82, 128.36, 125.96, 125.41, 124.78, 121.97, 120.74, 119.56 (q, *J* = 321.3 Hz), 113.76, 49.26, 37.33, 30.66, 21.30. ATR-IR: 1715, 1643, 1416, 1231, 1206, 1148, 1111, 745, 646, 610, 579 cm^{-1}. HRMS: Calcd for $C_{21}H_{20}F_3NNaO_3S$ $[M+Na]^+$: 446.1014. Found: 446.1001.

(2g):

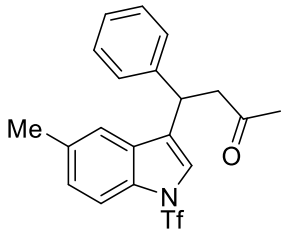
4-(Naphthalen-1-yl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



62 mg, colorless oil, 48 h, 70% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.14 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.46 (dddd, *J* = 23.0, 7.9, 6.9, 1.3 Hz, 2H), 7.25 (dt, *J* = 8.7, 4.3 Hz, 2H), 7.19 – 7.13 (m, 2H), 7.09 (ddd, *J* = 8.0, 6.4, 0.9 Hz, 2H), 5.56 (dd, *J* = 7.9, 6.0 Hz, 1H), 3.21 (ddd, *J* = 23.1, 17.5, 7.0 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.76, 137.16, 135.92, 134.14, 130.88, 130.25, 129.18, 128.10, 127.92, 126.64, 126.08, 125.87, 125.41, 124.81, 124.73, 122.92, 122.69, 120.70, 119.57 (q, *J* = 322.5 Hz), 113.82, 48.81, 32.72, 30.45. ATR-IR: 1714, 1451, 1416, 1360, 1283, 1231, 1206, 1165, 1148, 1113, 1030, 793, 746, 613 cm^{-1}. HRMS: Calcd for $C_{23}H_{18}F_3NNaO_3S$ $[M+Na]^+$: 468.0852. Found: 468.0871.

(2i):

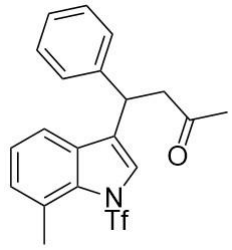
4-(5-Methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one



74 mg, white foam, 36 h, 90% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.65 (d, J = 9.0 Hz, 1H), 7.26 – 7.19 (m, 4H), 7.17 – 7.13 (m, 1H), 7.08 (dd, J = 11.7, 6.7 Hz, 3H), 4.68 (t, J = 7.0 Hz, 1H), 3.10 (dd, J = 7.3, 2.3 Hz, 2H), 2.29 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.83, 141.38, 134.64, 133.99, 130.37, 128.84, 127.97, 127.65, 127.38, 127.11, 122.19, 120.48, 119.60 (q, J = 322.5 Hz), 113.45, 49.20, 37.40, 30.70, 21.35. ATR-IR: 1717, 1414, 1231, 1206, 1153, 1113, 700, 633, 617, 584 cm^{-1}. HRMS : Calcd for $C_{20}H_{18}F_3NNaO_3S$ $[M+Na]^+$: 432.0892. Found: 432.0896.

(2j):

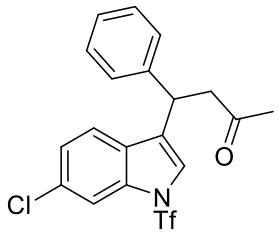
4-(7-Methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one



71 mg, beige solid, mp. 74.3-77.0 °C, 48 h, 87% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 6H), 7.22 (s, 1H), 7.18 – 7.12 (m, 2H), 4.74 (t, J = 7.2 Hz, 1H), 3.24 – 3.10 (m, 2H), 2.66 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.76, 141.44, 135.67, 132.42, 130.28, 128.84, 127.99, 127.69, 127.10, 125.72, 125.27, 125.15, 118.56, 49.18, 37.40, 30.73, 21.82 (d, J = 1.6 Hz). ATR-IR: 1718, 1414, 1230, 1204, 1145, 1110, 1083, 535, 467 cm^{-1}. HRMS: Calcd for $C_{20}H_{18}F_3NNaO_3S$ $[M+Na]^+$: 432.0857, Found: 432.0868.

(2k):

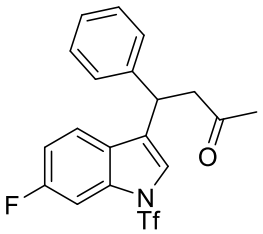
4-(6-Chloro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one



78 mg, white solid, mp. 139-141 ^{o}C, 72 h, 91% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.80 (d, J = 1.6 Hz, 1H), 7.24 – 7.14 (m, 8H), 7.11 (d, J = 0.5 Hz, 1H), 4.67 (t, J = 6.9 Hz, 1H), 3.10 (dd, J = 7.2, 1.1 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.56, 141.11, 136.19, 132.27, 128.94, 128.72, 127.86, 127.63, 127.30, 125.57, 122.50, 121.55, 119.78 (q, J = 322.5 Hz), 114.14, 49.03, 37.36, 30.71. ATR-IR: 1717, 1418, 1285, 1207, 1152, 1119, 1072, 991, 814, 702, 627, 602 cm^{-1}. HRMS: Calcd for $C_{18}H_{20}ClN_2O$ $[M+H]^+$: 315.1264. Found: 315.1288.

(2l):

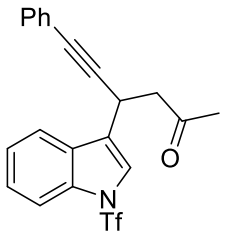
4-(6-Fluoro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one



69 mg, yellowish oil, 72 h, 83% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.50 (dd, J = 9.3, 2.2 Hz, 1H), 7.24 – 7.14 (m, 6H), 7.10 (s, 1H), 6.91 (td, J = 8.9, 2.3 Hz, 1H), 4.66 (t, J = 6.9 Hz, 1H), 3.09 (dd, J = 7.2, 1.9 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

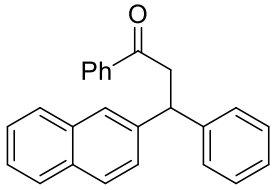
δ 205.58, 162.41 (d, *J* = 244.0 Hz), 141.21, 136.10 (d, *J* = 12.0 Hz), 128.90, 127.88, 127.63, 127.24, 126.47 (d, *J* = 1.0 Hz), 122.26 (d, *J* = 4.1 Hz), 121.70 (d, *J* = 10.0 Hz), 119.51(q, *J* = 322.0 Hz), 113.27 (d, *J* = 24.0 Hz), 101.64 (d, *J* = 39.0 Hz), 49.06, 37.43, 30.64. ATR-IR: 1717, 1487, 1418, 1233, 1207, 1148, 1099, 478, 465, 403 cm^{-1}. HRMS: Calcd for $C_{19}H_{19}F_4N_2O_3S$ $[M+NH_4]^+$: 431.1503. Found: 431.1573.

(2m): 6-Phenyl-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)hex-5-yn-2-one



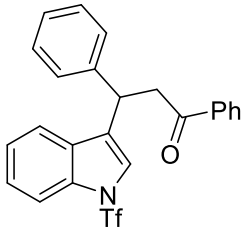
37 mg, yellow oil, 48 h, 44% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* (ppm) = 7.84 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.37 – 7.31 (m, 5H), 7.25 – 7.21 (m, 3H), 4.60 (ddd, *J* = 8.0, 5.8, 0.7 Hz, 1H), 3.10 (dd, *J* = 16.9, 8.1 Hz, 1H), 2.99 (dd, *J* = 16.9, 5.8 Hz, 1H), 2.16 (s, 3H).. ^{13}C NMR (125 MHz, $CDCl_3$) δ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.91, 136.01, 131.71, 129.15, 128.35, 128.32, 126.16, 124.88, 124.63, 123.27, 122.73, 120.41, 119.56 (q, *J* = 322.5 Hz), 114.12, 88.13, 83.05, 48.85, 30.63, 24.62. ATR-IR: 1721, 1451, 1416, 1362, 1281, 1233, 1206, 1148, 1111, 988, 758, 610 cm^{-1}. HRMS (ESI): Calcd for $C_{25}H_{24}LiN_2O_2S$ $[M+Li-Tf]^+$: 293.1186. Found: 293.1147.

(2n): 3-(Naphthalen-2-yl)-1,3-diphenylpropan-1-one (4ad) [CAS : 1198215-04-1]



59 mg, colorless oil, 72 h, 88% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* (ppm) = 8.03 – 7.91 (m, 2H), 7.83 – 7.68 (m, 4H), 7.56 (ddd, *J* = 6.8, 4.0, 1.2 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.36 – 7.27 (m, 4H), 7.22 – 7.17 (m, 1H), 5.02 (t, *J* = 7.3 Hz, 1H), 3.92 – 3.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.91, 143.96, 141.52, 136.99, 133.42, 133.10, 132.15, 128.61, 128.59, 128.56, 128.25, 128.04, 127.94, 127.74, 127.53, 126.73, 126.43, 125.99, 125.73, 125.51, 45.93, 44.54. ATR-IR: 1714, 1597, 1249, 1182, 1074, 1022, 600 cm^{-1}. HRMS : Calcd for $C_{25}H_{20}NaO$ $[M+Na]^+$: 359.1406. Found: 359.1414.

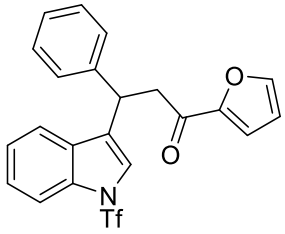
(2o): 1,3-Diphenyl-3-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)propan-1-one



87 mg, white solid, mp. 107-109 °C, 15 h, 95% yield, hexane and ethyl acetate (5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* (ppm) = 7.96 – 7.91 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.38 – 7.26 (m, 6H), 7.24 – 7.18 (m, 2H), 5.03 (t, *J* = 7.0 Hz, 1H), 3.74 (d, *J* = 7.1 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) *δ* (ppm) 197.18, 141.63, 136.67, 135.88, 133.39, 130.31, 128.84, 128.69, 128.30, 128.01, 127.77, 127.10, 126.00, 124.78, 122.22, 120.77, 119.56 (q, *J* = 322.5 Hz), 113.81, 44.31, 37.59. ATR-IR: 1686, 1451, 1414, 1283, 1231, 1206, 1148, 1111, 991, 617 cm^{-1}. HRMS: Calcd for $C_{24}H_{18}F_3NNaO_3S$ $[M+Na]^+$: 480.0857. Found: 480.0865.

(2p):

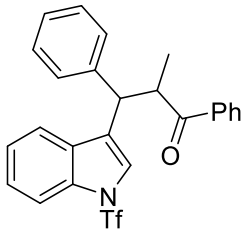
1-(Furan-2-yl)-3-phenyl-3-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)propan-1-one



89 mg, yellow solid, mp. 127-130 ºC, 15 h, 99% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.40 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.37 – 7.24 (m, 7H), 7.24 – 7.19 (m, 1H), 7.17 (dd, *J* = 3.6, 0.7 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.97 (t, *J* = 7.3 Hz, 1H), 3.59 (ddd, *J* = 38.9, 16.3, 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 186.47, 152.68, 146.62, 141.39, 135.89, 130.30, 128.86, 128.04, 127.80, 127.18, 126.04, 124.81, 122.38, 120.83, 119.60 (q, *J* = 322.5 Hz), 117.46, 113.81, 112.54, 43.95, 37.66. ATR-IR: 1670, 1570, 1468, 1414, 1287, 1231, 1204, 1148, 1113, 700, 617 cm^{-1}. HRMS : Calcd for $C_{22}H_{16}F_3NNaO_4S$ $[M+Na]^+$: 470.0644. Found: 470.0640.

(2q):

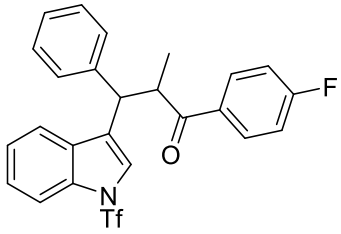
2-Methyl-1,3-diphenyl-3-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)propan-1-one



90 mg, white solid, mp. 144-146 ºC, 15 h, 95% yield, d.r. = 3:1, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.90 (dd, *J* = 8.4, 1.2 Hz, 2H, minor), 7.81 (d, *J* = 8.2 Hz, 1H, major), 7.80 – 7.74 (m, 2H, major), 7.67 (d, *J* = 8.2 Hz, 1H, minor), 7.55 (dd, *J* = 7.2, 0.7 Hz, 1H, major), 7.52 (d, *J* = 1.3 Hz, 2H, minor), 7.47 – 7.42 (m, 1H, major+minor), 7.41 – 7.18 (m, 7H, major+minor), 7.17 – 7.14 (m, 2H, minor), 7.08 – 7.03 (m, 2H, major), 7.00 – 6.93 (m, 1H, major+minor), 4.65 (d, *J* = 10.8 Hz, 1H, major), 4.60 (d, *J* = 10.9 Hz, 1H, minor), 4.35 (dq, *J* = 10.9, 6.9 Hz, 1H, major), 4.15 (dd, *J* = 10.9, 7.0 Hz, 0H, minor), 1.22 (d, *J* = 6.9 Hz, 3H, major), 1.05 (d, *J* = 7.0 Hz, 3H, minor). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 202.69, 202.57, 140.92, 140.13, 136.54, 136.10, 135.62, 135.47, 133.53, 133.11, 130.82, 130.62, 128.93, 128.79, 128.61, 128.54, 128.06, 127.96, 126.95, 126.79, 126.07, 125.98, 124.88, 124.73, 122.55, 121.25, 120.76, 120.52, 119.60 (q, *J* = 321.3 Hz), 119.35 (q, *J* = 321.3 Hz), 113.87, 113.52, 45.12, 45.09, 44.85, 44.77, 17.72, 17.65. ATR-IR: 1684, 1676, 1449, 1414, 1283, 1231, 1206, 1148, 1111, 970, 743, 700 cm^{-1}. HRMS : Calcd for $C_{25}H_{20}F_3NNaO_3S$ $[M+Na]^+$: 494.1008. Found: 494.1003.

(2r):

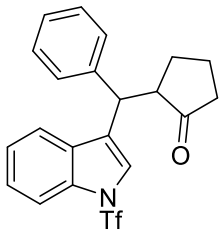
1-(4-Fluorophenyl)-2-methyl-3-phenyl-3-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)propan-1-one



81 mg, white foam, 24 h, 83% yield, d.r. = 3.5:1, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.92 – 7.81 (m, 3H), 7.61 (d, J = 7.7 Hz, 1H), 7.42 (s, 1H), 7.39 – 7.35 (m, 1H), 7.34 – 7.30 (m, 1H), 7.25 (dd, J = 4.7, 4.1 Hz, 2H), 7.13 (t, J = 7.7 Hz, 2H), 7.09 – 6.98 (m, 3H), 4.69 (d, J = 10.9 Hz, 1H), 4.37 (dq, J = 11.0, 6.8 Hz, 1H), 1.29 (d, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 201.19, 165.71 (d, J = 253.8 Hz), 140.78, 135.62, 132.95 (d, J = 2.5 Hz), 130.79, 130.71 (d, J = 10.0 Hz), 128.57, 127.93, 126.89, 126.81, 126.12, 124.91, 122.49, 120.47, 119.60 (q, J = 322.5 Hz), 115.72 (d, J = 21.3 Hz), 113.88, 45.24, 44.78, 17.62. ATR-IR: 1684, 1676, 1449, 1414, 1283, 1231, 1206, 1148, 1111, 970, 743, 700 cm^{-1}. HRMS: Calcd for $C_{25}H_{19}F_4NNaO_3S$ $[M+Na]^+$: 512.0914. Found: 512.1005.

(2s):

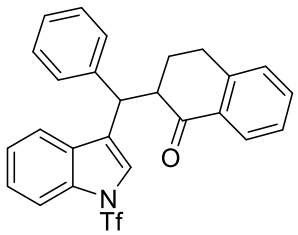
2-(Phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl)cyclopentan-1-one



75 mg, colorless oil, 18 h, 89% yield, d.r. = 2:1, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.89 (d, J = 8.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.28 – 7.23 (m, 3H), 7.19 (td, J = 7.6, 0.9 Hz, 1H), 7.15 – 7.08 (m, 3H), 4.95 – 4.90 (m, 1H), 2.94 – 2.85 (m, 1H), 2.39 – 2.25 (m, 2H), 1.90 – 1.77 (m, 3H), 1.73 – 1.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.01, 138.88, 135.77, 130.61, 129.13, 128.57, 127.68, 127.23, 125.98, 124.73, 122.55, 121.23, 119.69 (q, J = 322.5 Hz), 113.71, 52.77, 41.27, 38.35, 26.00, 20.60. ATR-IR: 1715, 1416, 1267, 1231, 1206, 1153, 1113, 750, 700, 660, 633, 617 cm^{-1}. HRMS: Calcd for $C_{21}H_{18}F_3NNaO_3S$ $[M+Na]^+$: 444.0852. Found: 444.0865.

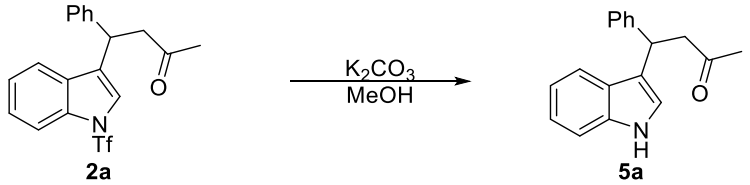
(2t):

2-(phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl)-3,4-dihydronaphthalen-1(2H)-one



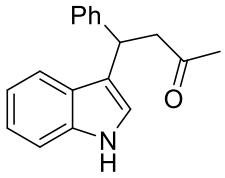
91 mg, yellow oil, 18 h, 94% yield, hexane and ethyl acetate (5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.92 (dd, J = 7.9, 1.2 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.38 (td, J = 7.5, 1.4 Hz, 1H), 7.29 (d, J = 0.7 Hz, 1H), 7.27 – 7.19 (m, 5H), 7.18 – 7.11 (m, 5H), 5.14 (dd, J = 5.5, 1.1 Hz, 1H), 3.25 (ddd, J = 12.4, 5.5, 4.1 Hz, 1H), 2.97 (ddt, J = 16.9, 8.6, 5.6 Hz, 2H), 2.12 (dq, J = 13.0, 4.2 Hz, 1H), 1.70 – 1.61 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 197.54, 143.37, 139.47, 135.69, 133.46, 132.59, 130.84, 129.10, 128.66, 128.51, 127.89, 127.70, 127.06, 126.73, 125.89, 124.67, 122.04, 121.04, 119.64 (q, J = 322.5 Hz), 113.70, 51.62, 40.49, 28.84, 26.43. ATR-IR: 1686, 1599, 1451, 1414, 1279, 1231, 1206, 1148, 1113, 990, 745, 704, 608, 577, 527 cm^{-1}. HRMS : Calcd for $C_{26}H_{20}F_3NNaO_3S$ $[M+Na]^+$: 506.1008. Found: 506.1025.

3.3 Removal of the Tf protecting group.



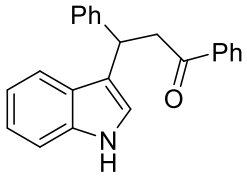
Procedure: To an oven-dried 10 mL flask with a stir bar under Ar atmosphere, the ketone product **2a** (79 mg, 0.2 mmol), K_2CO_3 (138 mg, 1 mmol), 3 ml MeOH was added. The resulting mixture was stirred at 65 °C until the **2a** totally disappeared (about 4 h). The mixture was filtered and washed with EtOAc. The filtrate was concentrated in vacuum and the residue was purified via flash column chromatography (diethyl ether:pentane = 1:5) to give the product **5a** in 97% yield as colorless oil.

4-(1H-indol-3-yl)-4-phenylbutan-2-one (3a) [CAS : 21909-35-3]



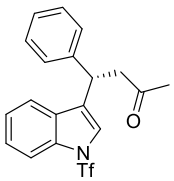
51 mg, colorless oil, 4 h, 97% yield, 5:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.03 – 7.97 (b, 1H), 7.39 (dd, J = 7.9, 0.7 Hz, 1H), 7.24 (ddd, J = 11.2, 8.8, 4.4 Hz, 5H), 7.18 – 7.06 (m, 2H), 6.99 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H), 6.96 – 6.89 (m, 1H), 4.80 (t, J = 7.6 Hz, 1H), 3.17 (ddd, J = 44.3, 16.1, 7.6 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 207.72, 143.89, 136.51, 128.44, 127.65, 126.45, 126.34, 122.13, 121.31, 119.37, 118.73, 111.12, 50.28, 38.32, 30.35. ATR-IR: 1707, 1493, 1454, 1416, 1356, 1337, 1240, 1161, 1099, 1011, 739, 700, 472 cm^{-1} . HRMS : Calcd for $C_{18}H_{17}NNaO$ $[M+Na]^+$: 286.1602. Found: 286.1673.

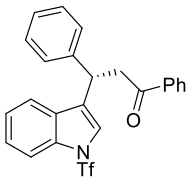
3-(1H-indol-3-yl)-1,3-diphenylpropan-1-one (3o) [CAS : 5884-15-1]

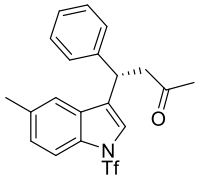


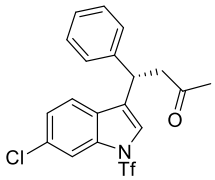
63 mg, colorless oil, 4 h, 98% yield, 5:1 pentane:diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.98 (s, 1H), 7.94 (dd, J = 8.3, 1.2 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.48 – 7.41 (m, 3H), 7.38 – 7.34 (m, 2H), 7.32 (d, J = 8.2 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.21 – 7.13 (m, 2H), 7.05 – 7.00 (m, 1H), 6.99 (d, J = 2.3 Hz, 1H), 5.08 (t, J = 7.2 Hz, 1H), 3.78 (ddd, J = 24.4, 16.7, 7.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 198.54, 144.18, 137.06, 136.56, 133.00, 128.55, 128.41, 128.08, 127.80, 126.58, 126.27, 122.12, 121.38, 119.52, 119.37, 119.26, 111.08, 45.16, 38.16. ATR-IR: 1682, 1597, 1493, 1449, 1416, 1231, 1206, 1153, 746, 700 cm^{-1} . HRMS: Calcd for $C_{23}H_{19}NNaO$ $[M+Na]^+$: 348.1364. Found: 348.1384.

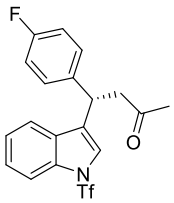
HPLC analysis for enantioenriched products

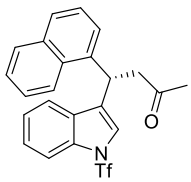
(*S*)-4-phenyl-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one	
	HPLC analysis: 80% ee (Chiralcel OD-H, 98:2 Hexanes/isopropanol, 0.5 mL/min, 254 nm, major R_t = 29.1 min, minor R_t = 49.2 min)

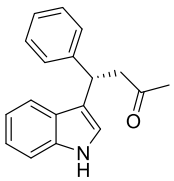
(*S*)-1,3-diphenyl-3-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)propan-1-one	
	HPLC analysis: 31% ee (Chiralcel AD-H, 99:1 Hexanes/isopropanol, 0.5 mL/min, 254 nm, major R_t = 25.2 min, minor R_t = 30.0 min)

(*S*)-4-(5-methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one	
	HPLC analysis: 91% ee (Chiralcel AD-H, 98:2 Hexanes/isopropanol, 0.5 mL/min, 254 nm, major R_t = 24.4 min, minor R_t = 31.8 min)

(*S*)-4-(6-chloro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one	
	HPLC analysis: 90% ee (Chiralcel OD, 98:2 Hexanes/isopropanol, 0.5 mL/min, 254 nm, major R_t = 40.8 min, minor R_t = 73.3 min)

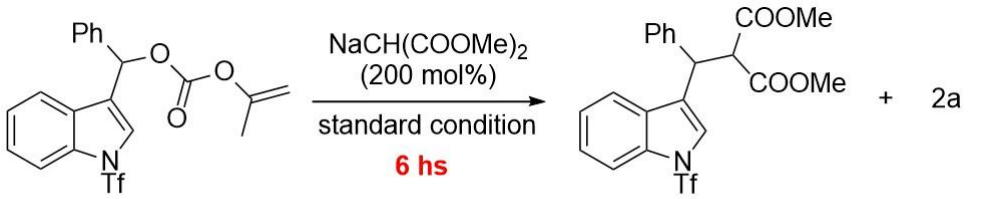
(*S*)-4-(4-fluorophenyl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one	
	HPLC analysis: 83% ee (Chiralcel OD, 99:1 Hexanes/isopropanol, 0.2 mL/min, 254 nm, major R_t = 77.7 min, minor R_t = 89.2 min)

(*S*)-4-(naphthalen-1-yl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one	
	HPLC analysis: 63% ee (Chiralcel AD-H, 98:2 Hexanes/isopropanol, 0.2 mL/min, 254 nm, major R_t = 17.7 min, minor R_t = 13.5 min)

(*S*)-4-(1H-indol-3-yl)-4-phenylbutan-2-one	
	HPLC analysis: 81% ee (Chiralcel AD-H, 95:5 Hexanes/isopropanol, 0.5 mL/min, 254 nm, major R_t = 73.2 min, minor R_t = 67.0 min)

4. Crossover studies

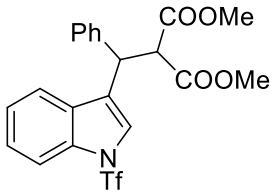
Nucleophile obstruction experiment:



Crude ^{1}H NMR Ratio: 1 : 0.53

Procedure: In a glove box, under an argon atmosphere, a flame dried 25 mL microwave vial with a stir bar was charged with dimethyl malonate and 5 mL THF. NaH was added and stirred for 10 min until no more gas generated. After that, secondary benzylic enol carbonate **1a** (88 mg, 0.2 mmol), $Pd(dmdba)_2$ (10 mmol%, 0.02 mmol), *t*-BuDavephos (12 mmol%, 0.024 mmol) was added. The vial was carefully sealed with a cap and removed from glove box and stirring under 110 ^oC until the material totally disappeared. The conversion and ratio of products determined by ^{1}H NMR spectroscopy of the crude mixture. After the solvent was removed under vacuum, the malonate substitution product was separated by column chromatography.

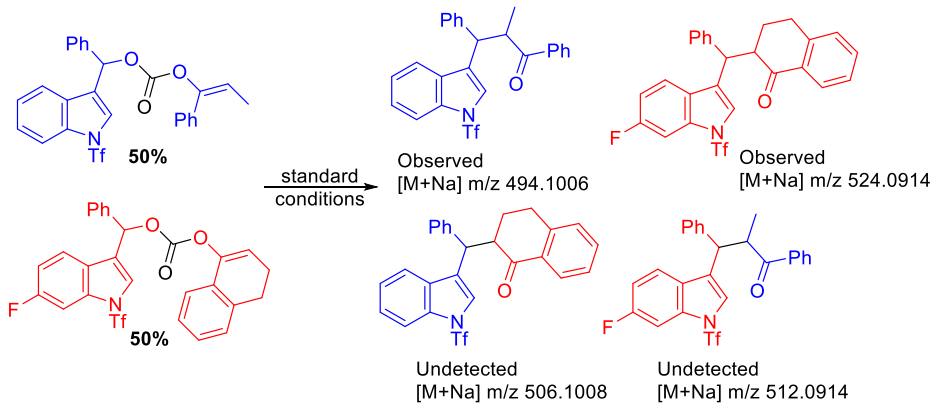
Dimethyl 2-(phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl)malonate (4a)

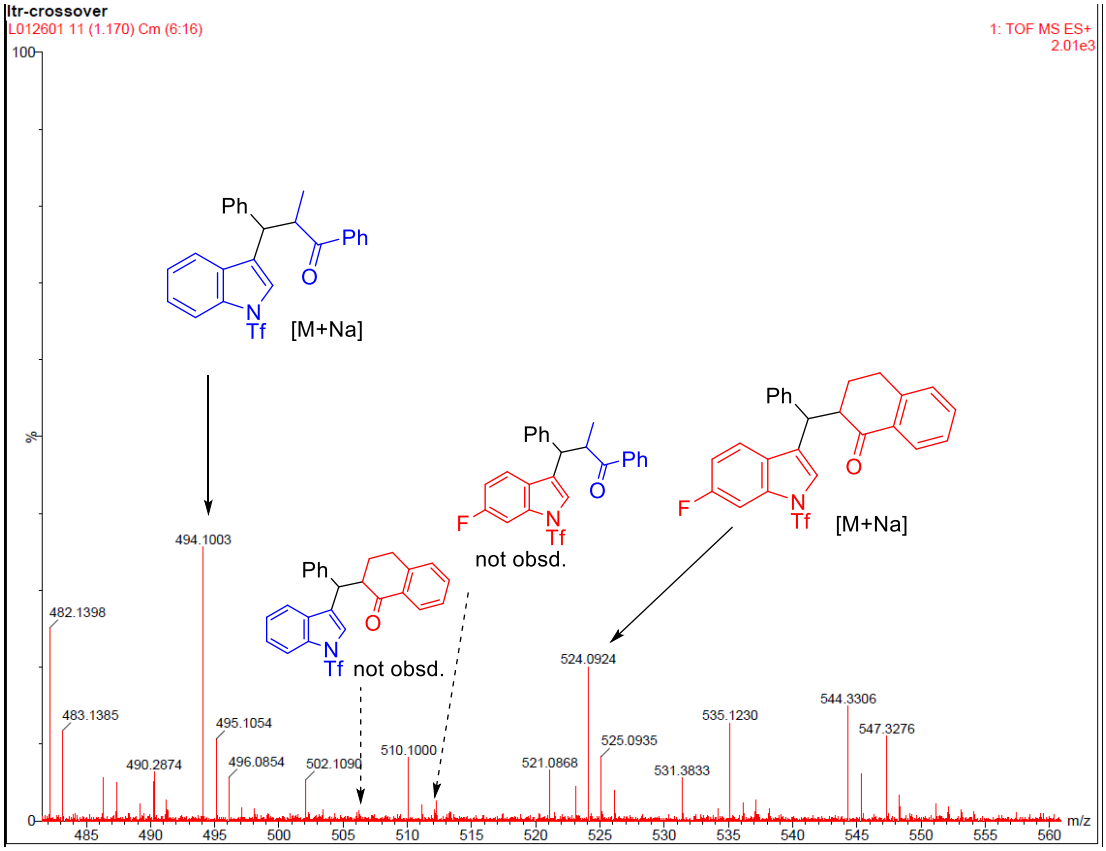


64 mg, colorless oil, 6 h, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.85 (d, J = 8.3 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.39 (s, 1H), 7.37 – 7.32 (m, 3H), 7.30 – 7.25 (m, 3H), 7.22 (ddd, J = 7.1, 3.9, 1.4 Hz, 1H), 5.05 – 5.01 (m, 1H), 4.25 (d, J = 11.6 Hz, 1H), 3.65 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.71, 167.31, 138.14, 135.55, 130.03, 128.76, 128.17, 127.71, 126.23, 126.04, 124.88, 121.66, 120.52, 119.53 (q, J = 322.5 Hz), 113.69, 57.18, 52.80, 52.66, 42.38. ATR-IR: 1759, 1738, 1451, 1416, 1263, 1233, 1202, 1167, 1150, 1113, 990, 755, 579 cm^{-1}. HRMS: Calcd for $C_{21}H_{18}F_3KNO_6S$ $[M+K]^+$: 508.0439. Found: 508.0451.

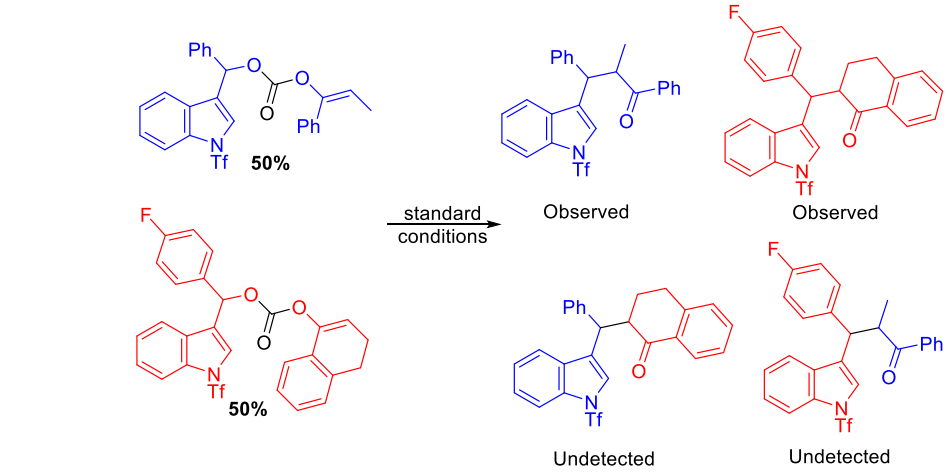
Crossover experiments:

Procedure: In a glove box, under an argon atmosphere, a flame dried 25 mL microwave vial with a stir bar was charged with secondary benzylic enol carbonate **1q** (52 mg, 0.1 mmol, 50%), **S5** or **S6** (54 mg, 0.1 mmol, 50%), $Pd(dmdba)_2$ (10 mmol%, 0.02 mmol, 16.6 mg), *t*-BuDavephos (12 mmol%, 0.024 mmol, 8.4 mg) and THF (5 ml, 0.04N). The vial was carefully sealed with a cap and removed from glove box and stirring under 110 ^oC until the materials totally converted. The reaction mixture was directly loaded on HRMS.


50%
standard conditions
Observed
[M+Na] m/z 494.1006
Observed
[M+Na] m/z 524.0914
50%
Undetected
[M+Na] m/z 506.1008
Undetected
[M+Na] m/z 512.0914


ltr-crossover
L012601 11 (1.170) Cm (6:16)
1: TOF MS ES+
2.01e3
[M+Na]
not obsd.
not obsd.
[M+Na]
494.1003
482.1398
483.1385
490.2874
495.1054
496.0854
502.1090
510.1000
521.0868
524.0924
525.0935
531.3833
535.1230
544.3306
547.3276
m/z

^{13}C NMR Analysis of Crossover:



Crude ^{13}C spectra for the coupling of individual enol carbonates and the crossover experiment (bottom). No additional peaks for crossover products are observed.

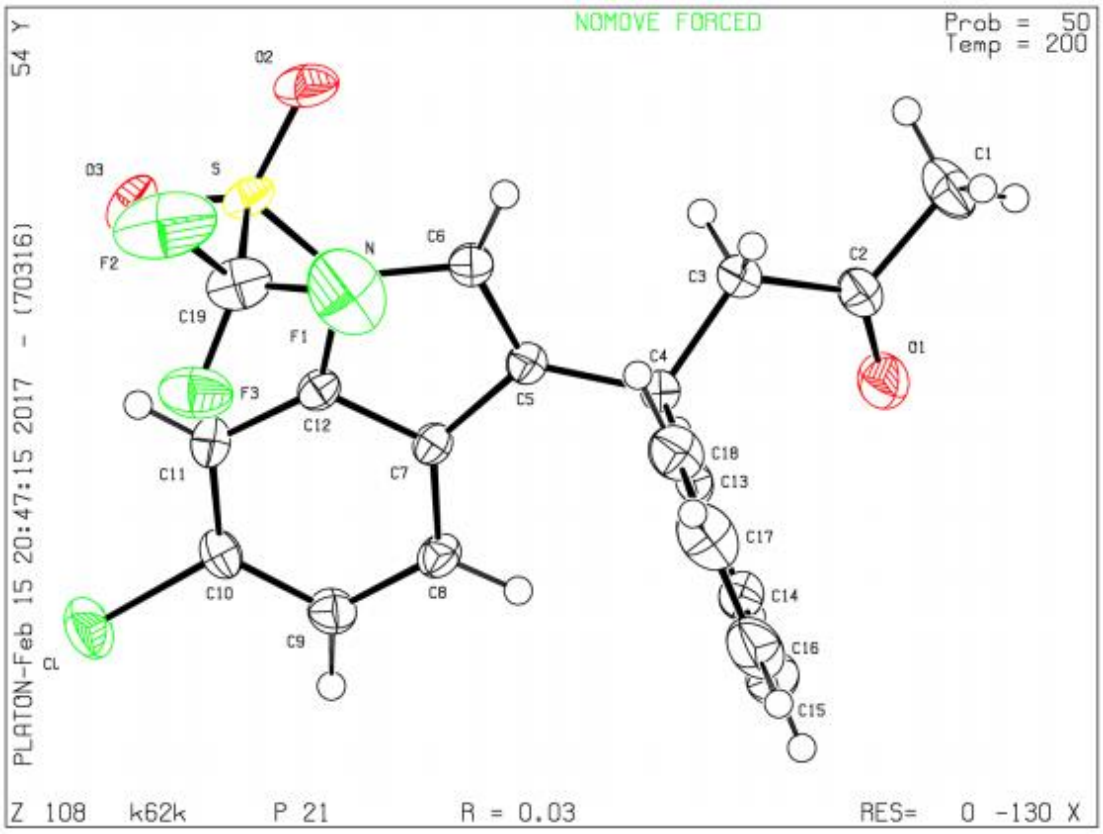
References:

(1) Chen, X. B.; Fan, H. Q.; Zhang, S. L.; Yu, C. G.; Wang, W. *Chem. Eur. J.* **2016**, *22*, 716.

(2) Mendis, S. N.; Tunge, J. A. *Chem. Commun.* **2016**, *52*, 7695.

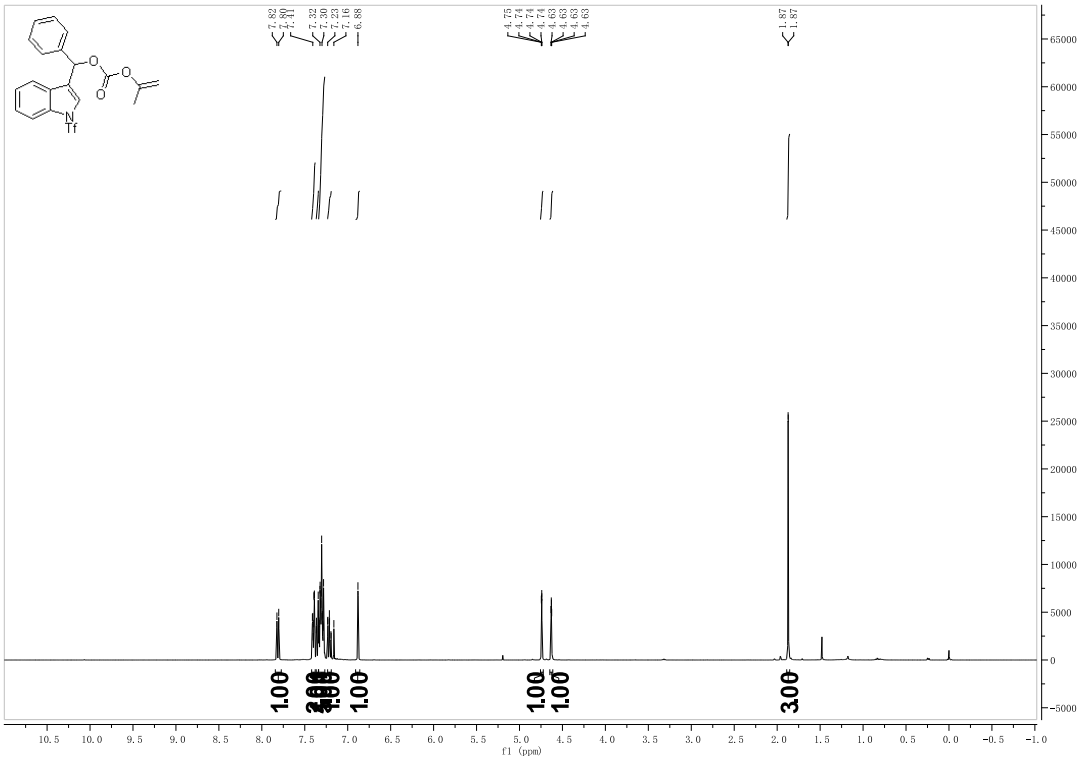
(3) Mendis, S. N.; Tunge, J. A. *Org. Lett.* **2015**, *17*, 5164.

5. X-Ray Structure of Products (*S*)-2k

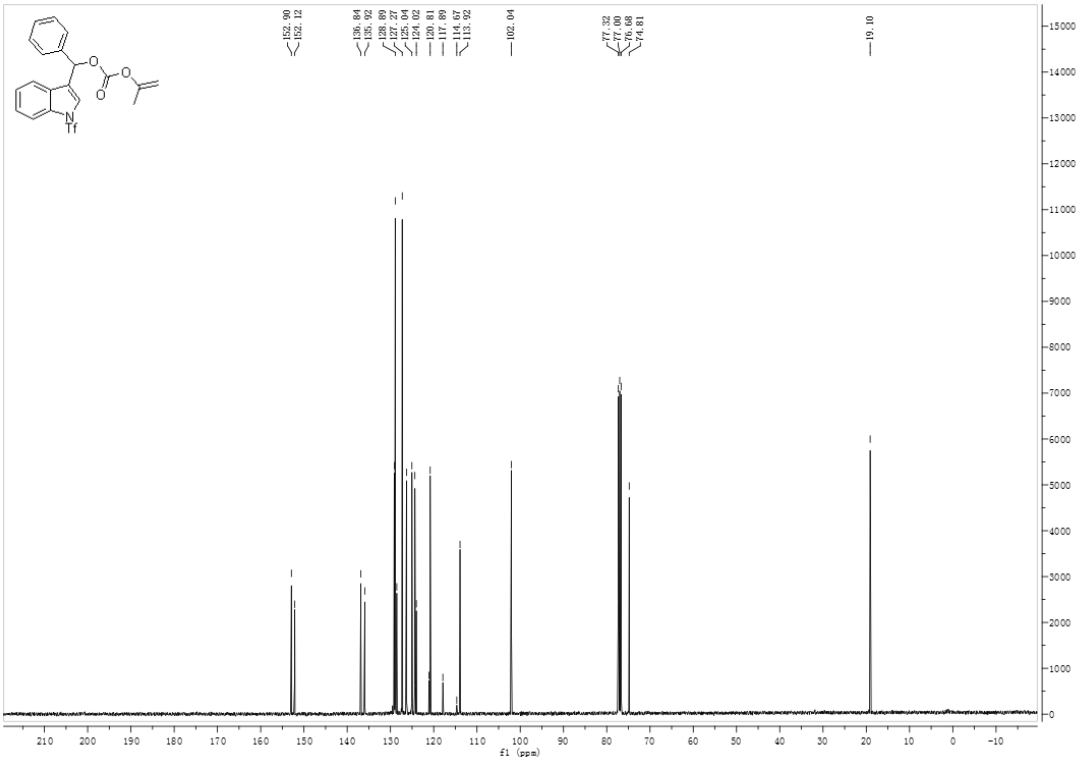


6. Copies of ^{1}H NMR and ^{13}C NMR Spectra

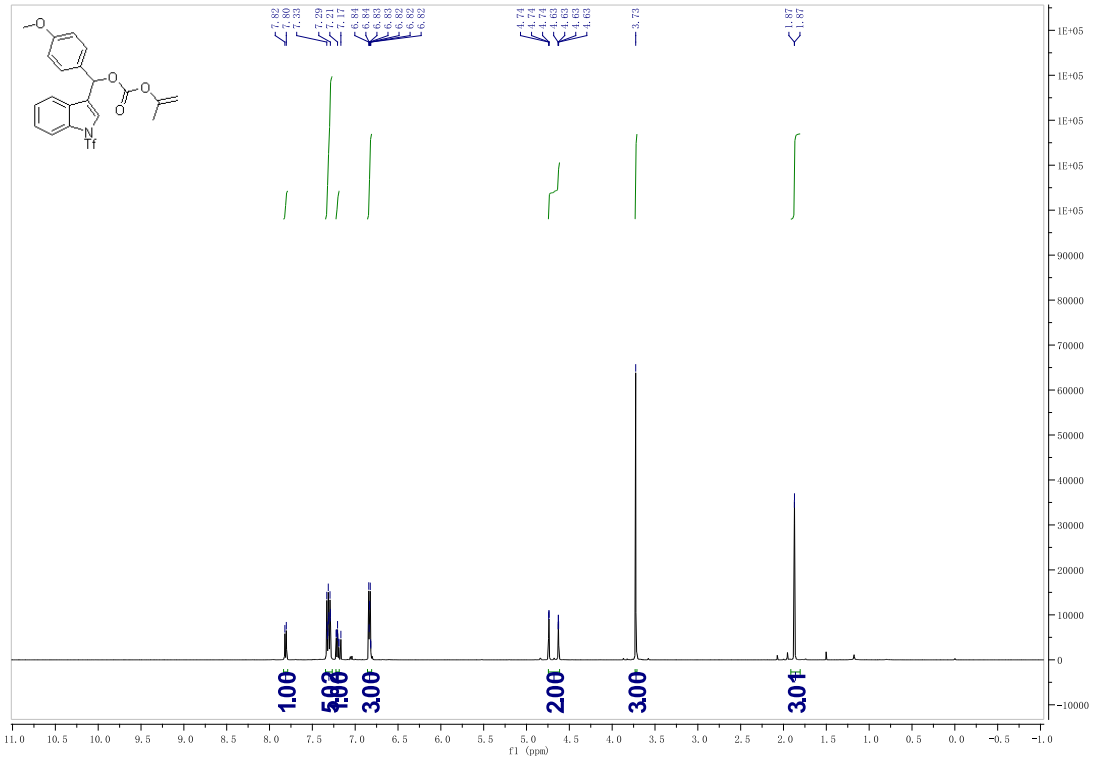
^{1}H NMR Spectra of **1a**



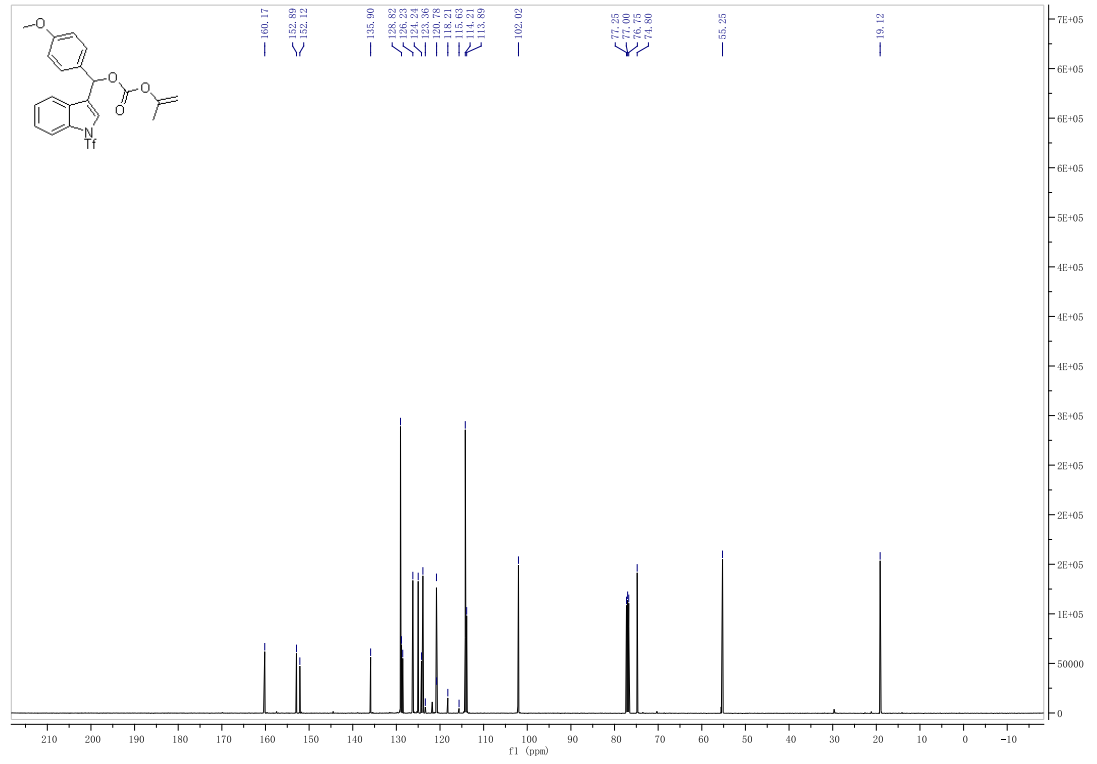
^{13}C NMR Spectra of **1a**



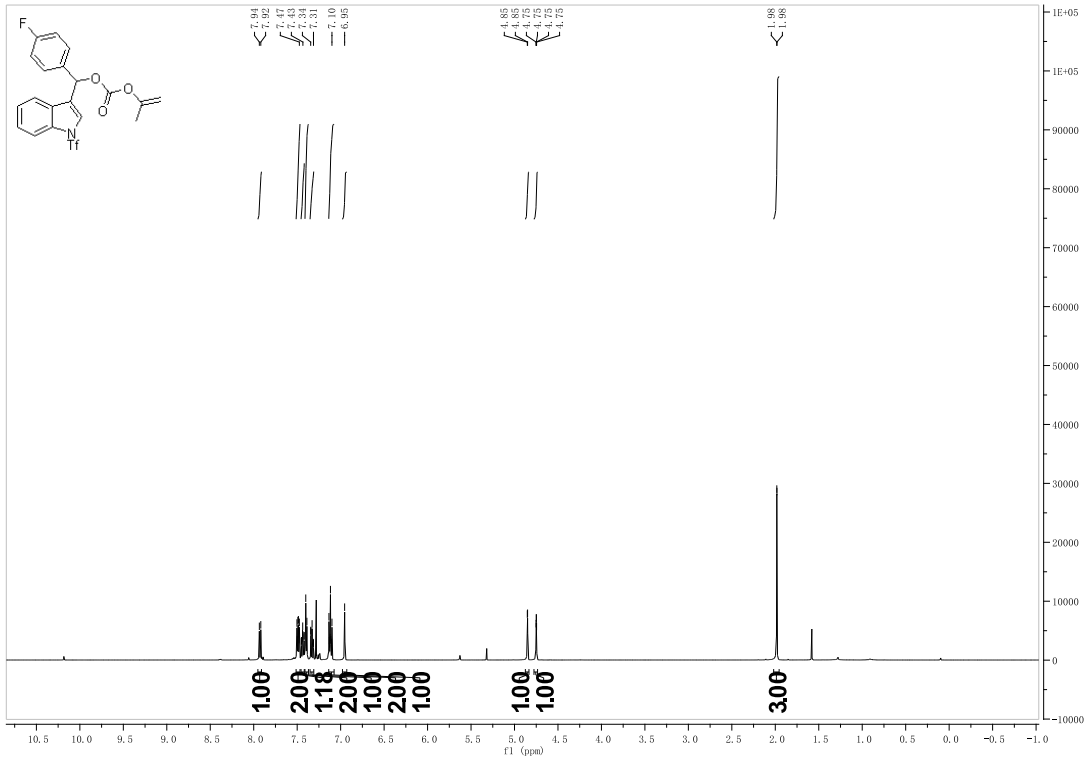
^{1}H NMR Spectra of **1b**



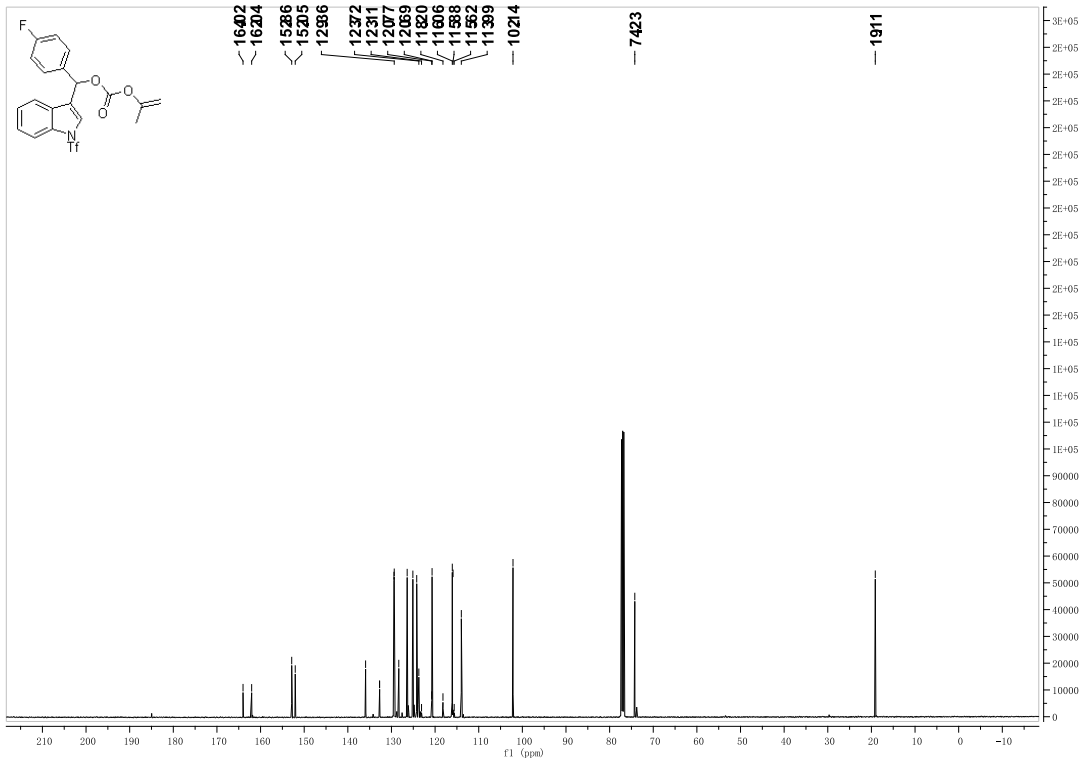
^{13}C NMR Spectra of **1b**



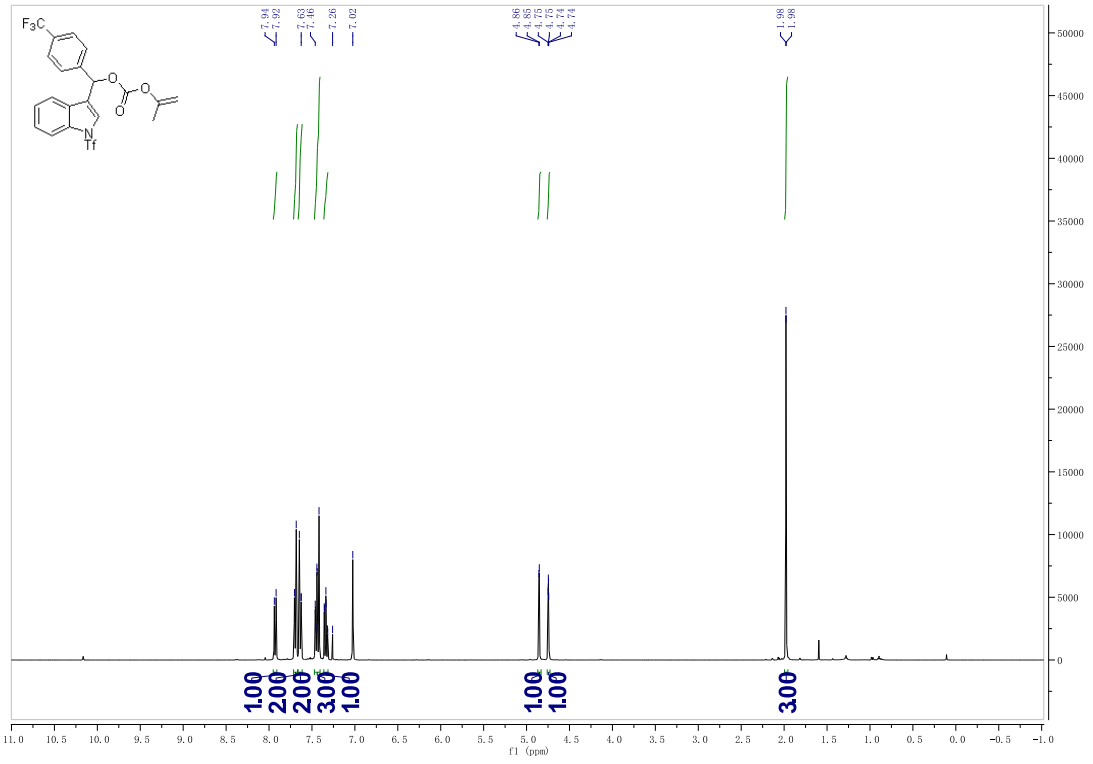
^{1}H NMR Spectra of **1c**



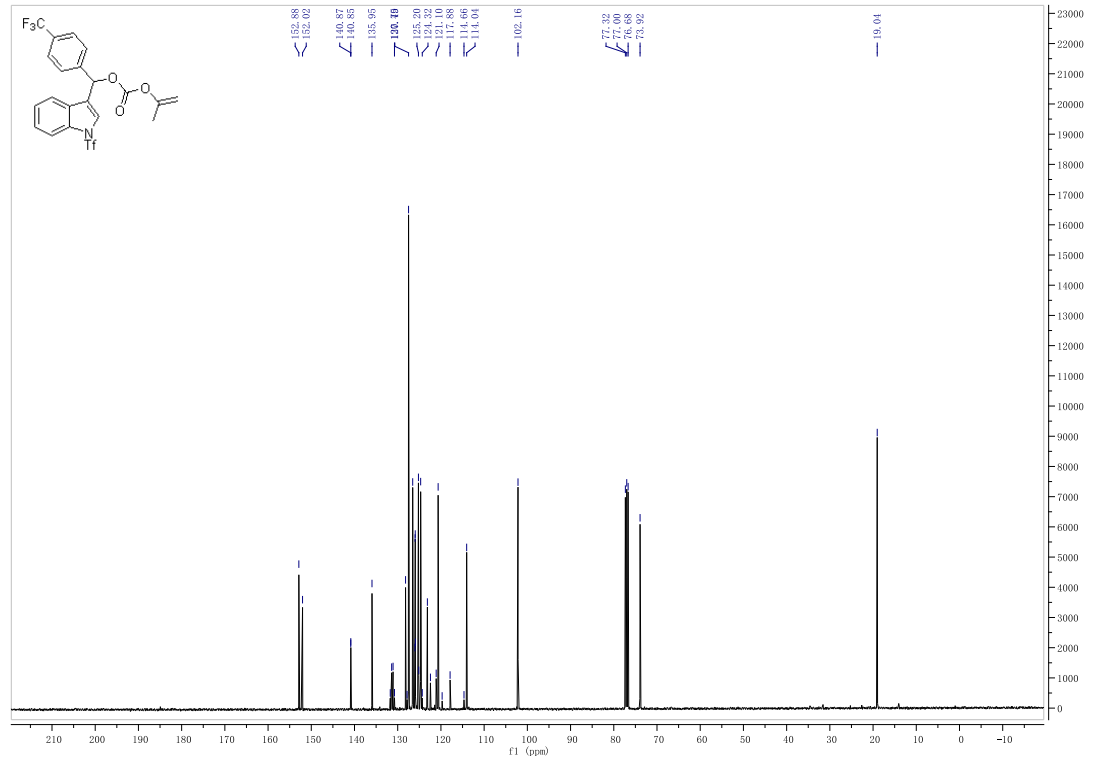
^{13}C NMR Spectra of **1c**



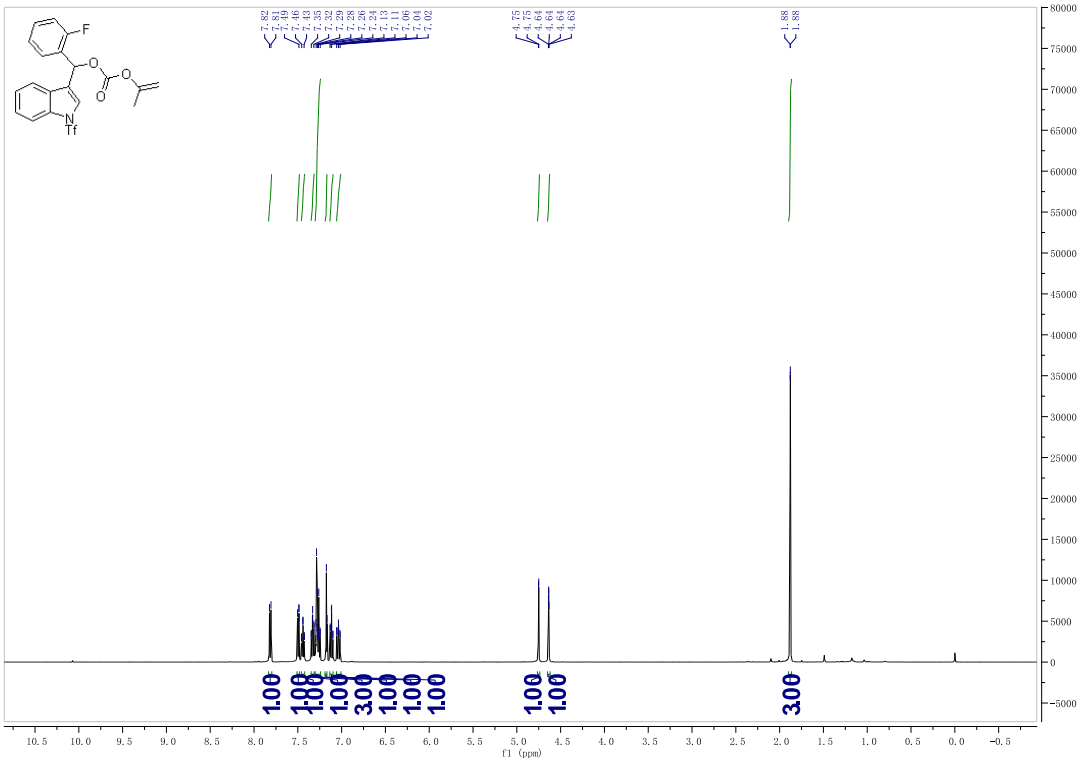
^{1}H NMR Spectra of **1d**



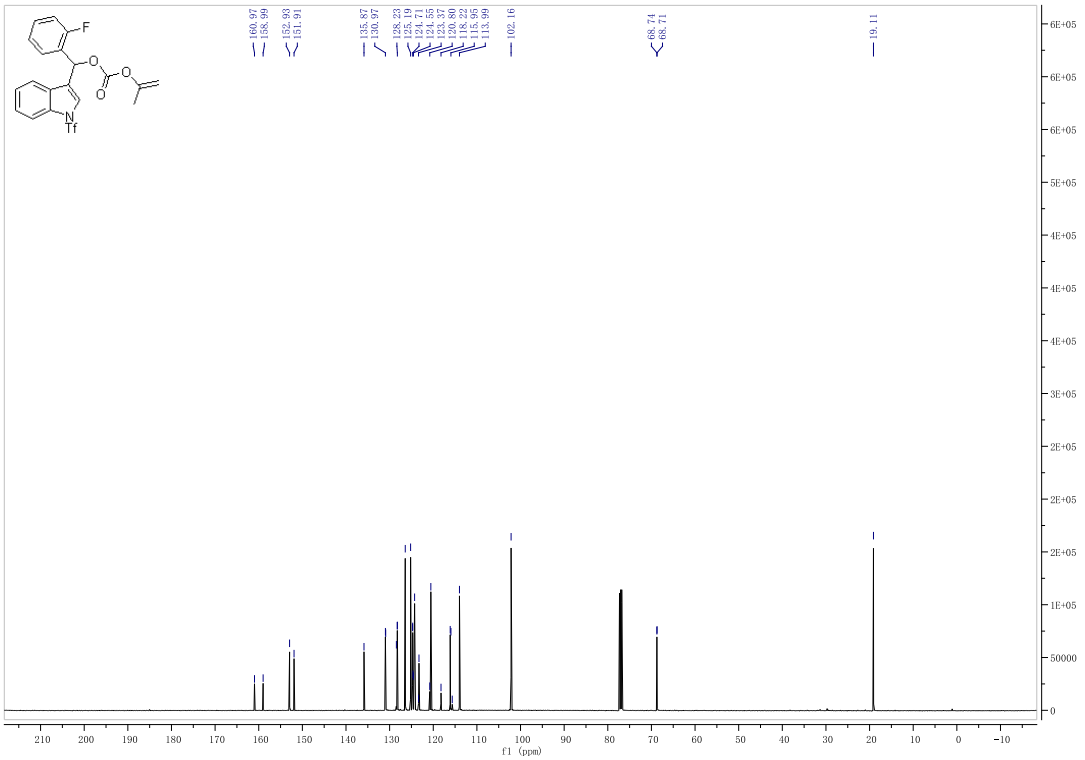
^{13}C NMR Spectra of **1d**



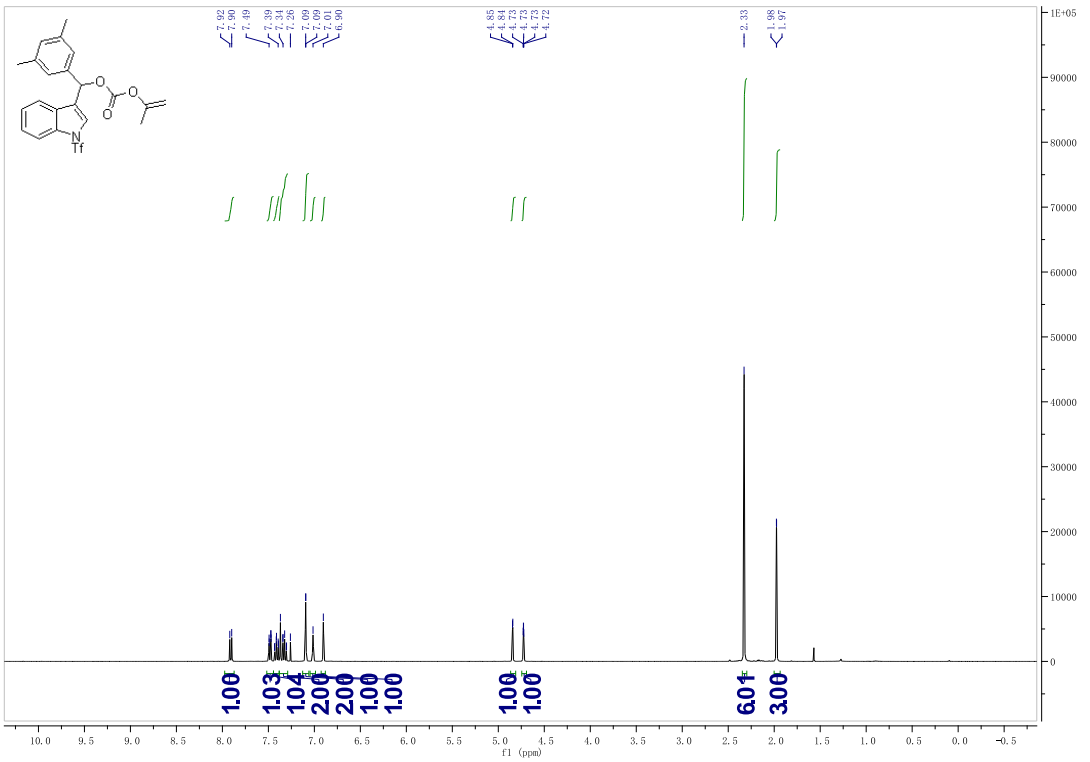
^{1}H NMR Spectra of **1e**



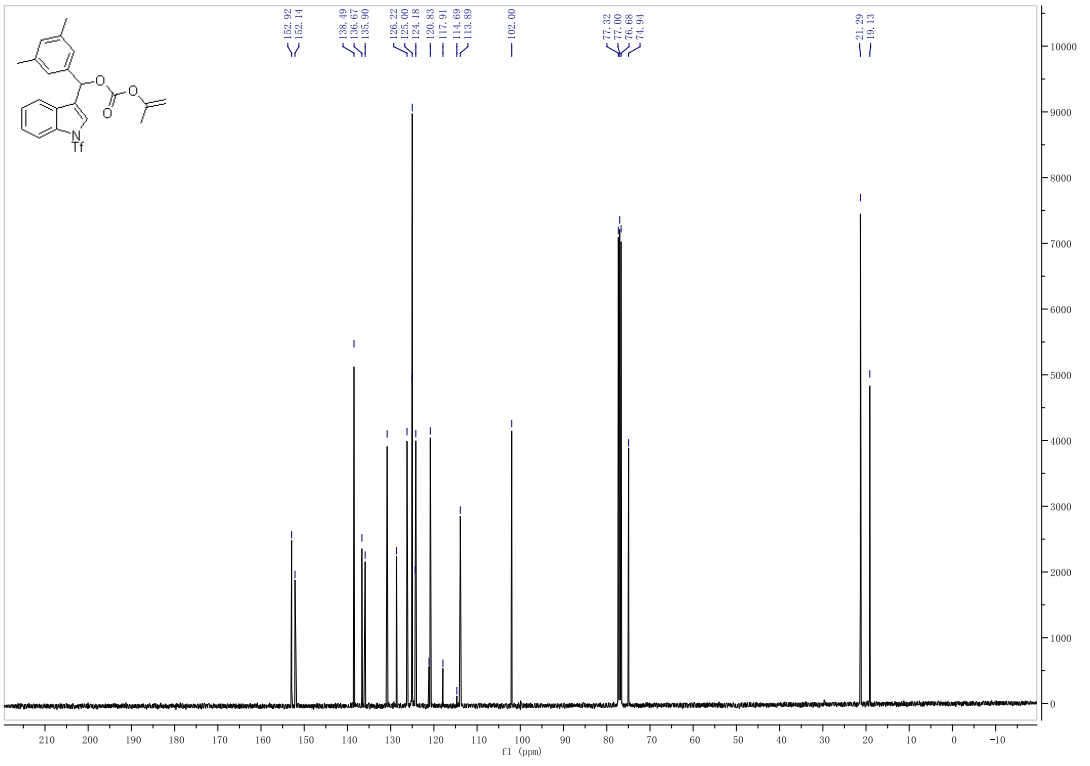
^{13}C NMR Spectra of **1e**



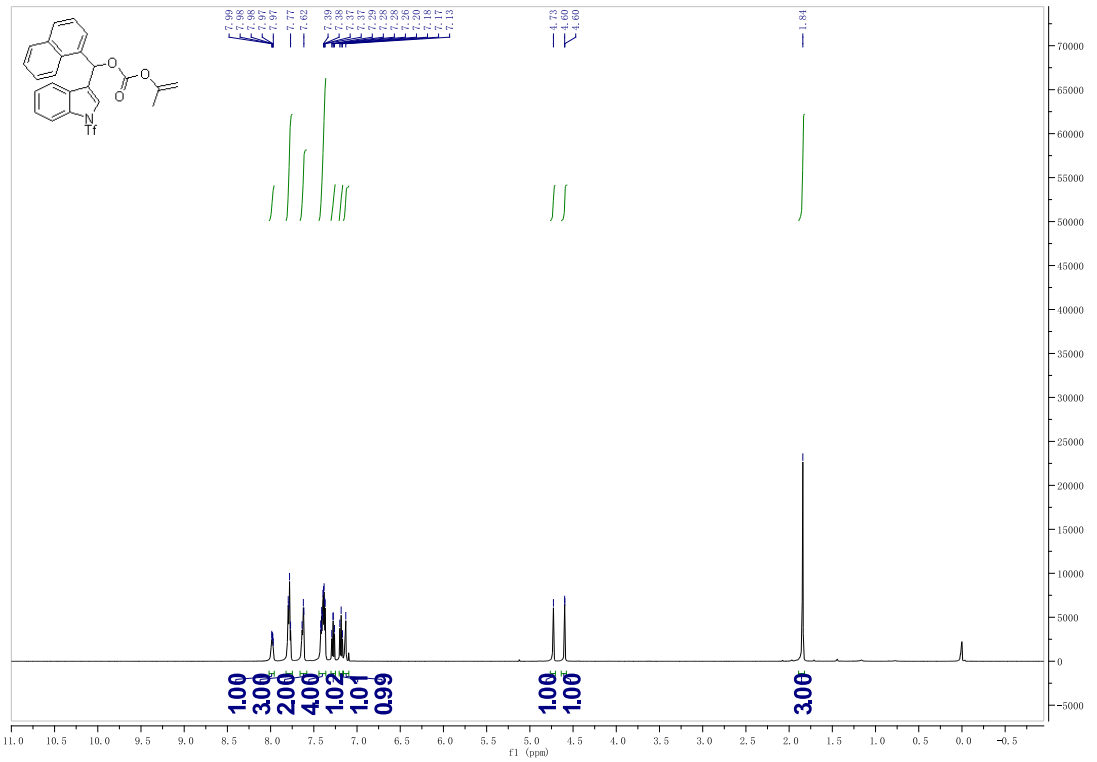
^{1}H NMR Spectra of **1f**



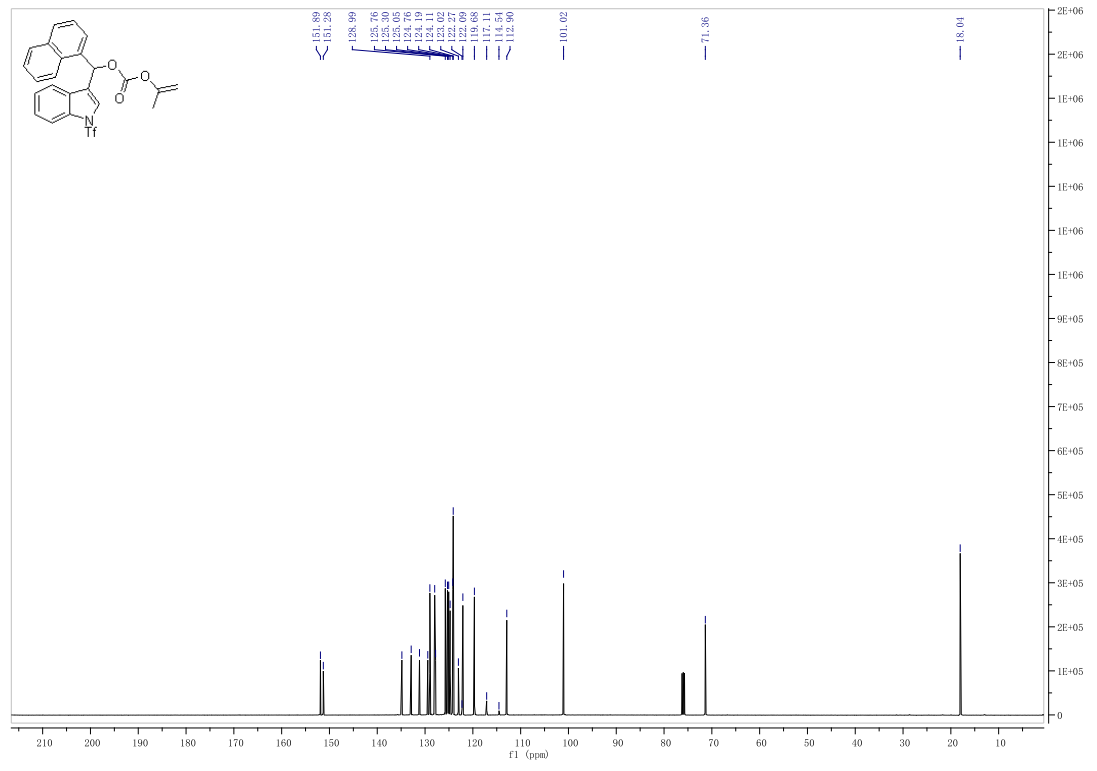
^{13}C NMR Spectra of **1f**



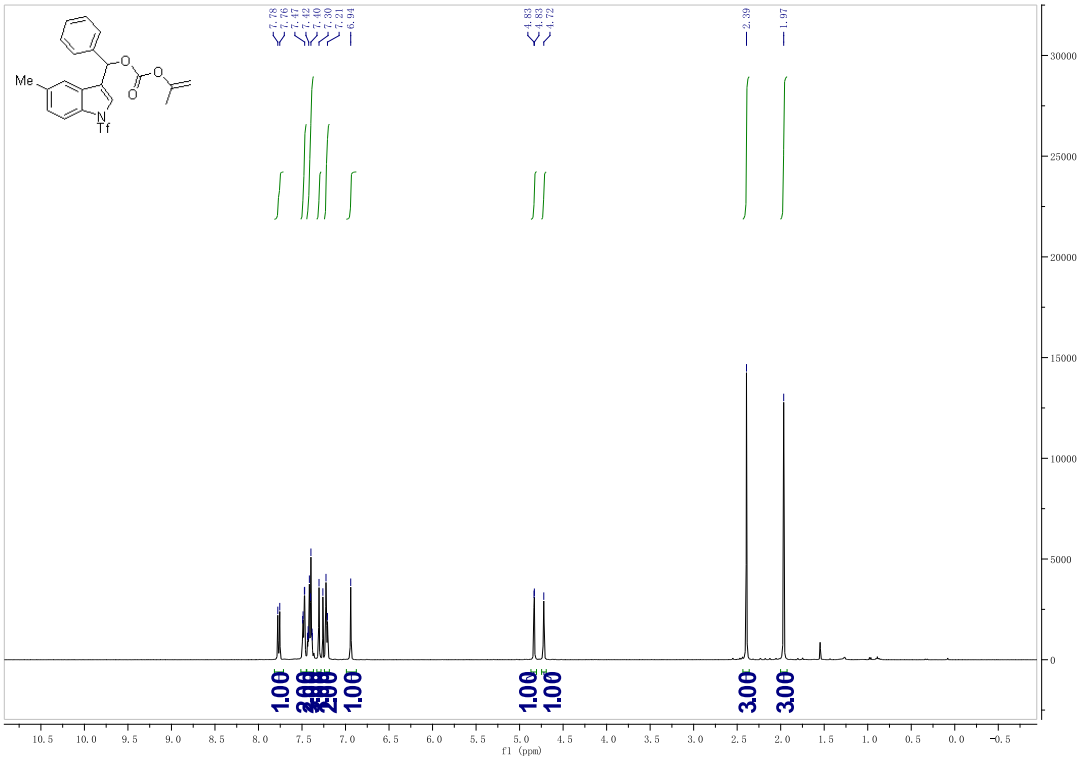
^{1}H NMR Spectra of **1g**



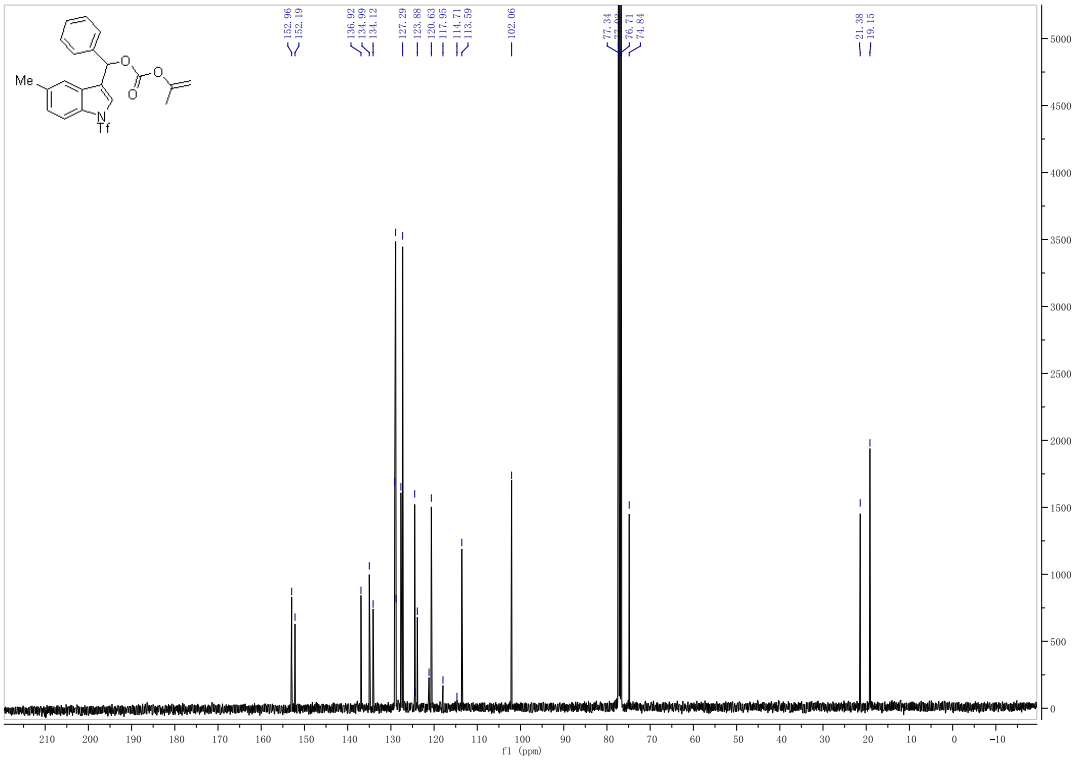
^{13}C NMR Spectra of **1g**



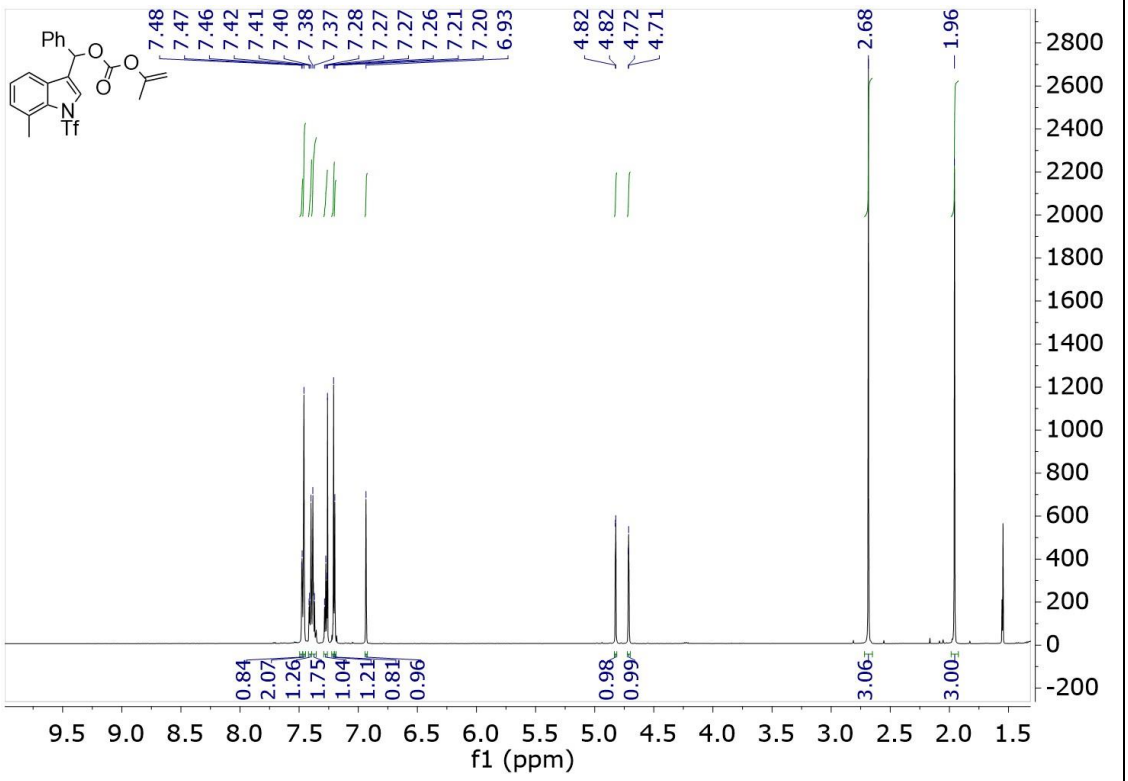
^{1}H NMR Spectra of **1i**



^{13}C NMR Spectra of **1i**



^{1}H NMR Spectra of **1j**



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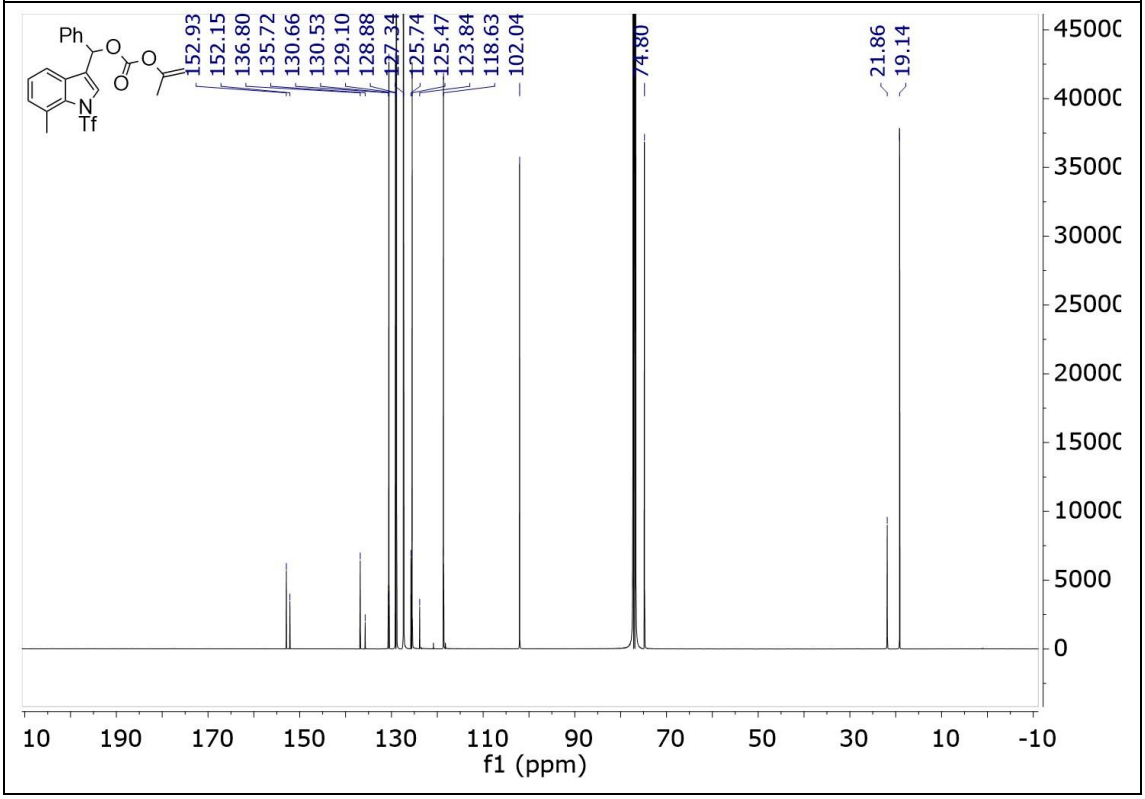
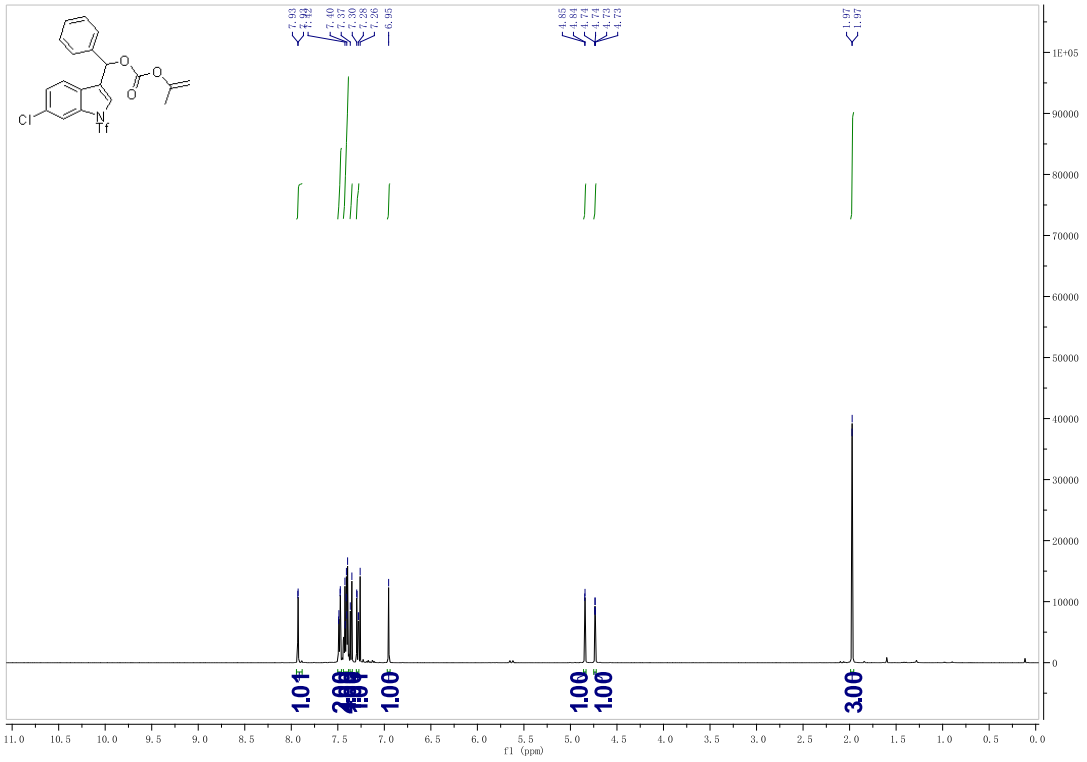
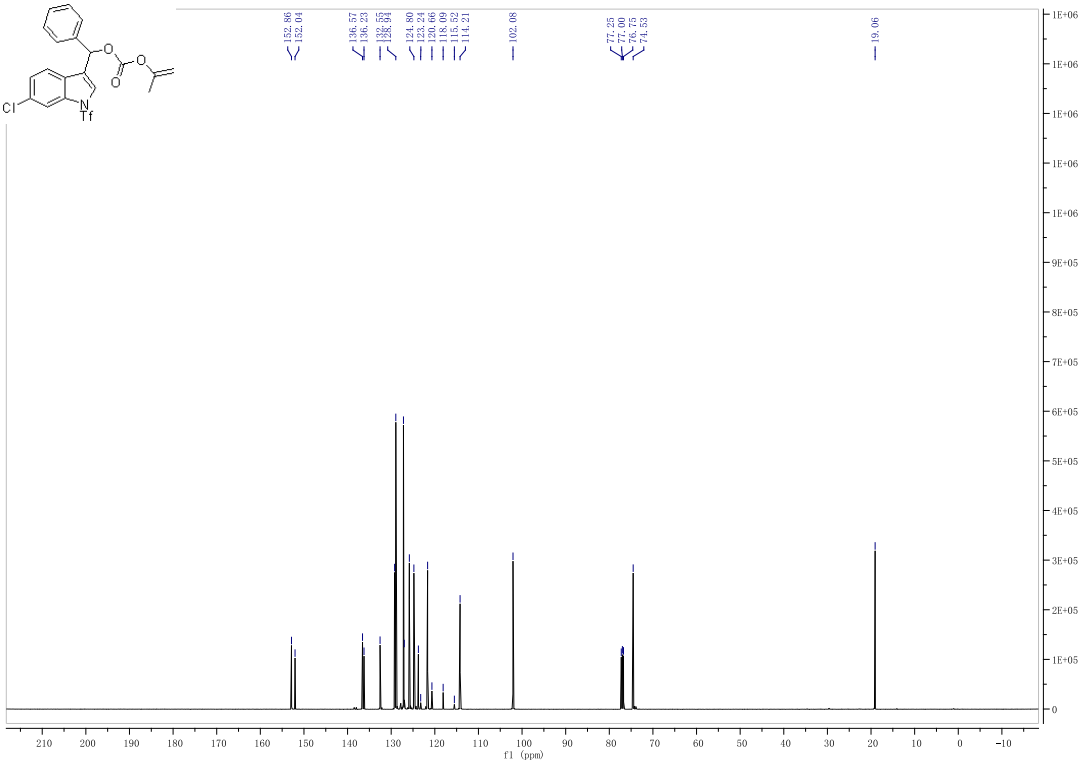


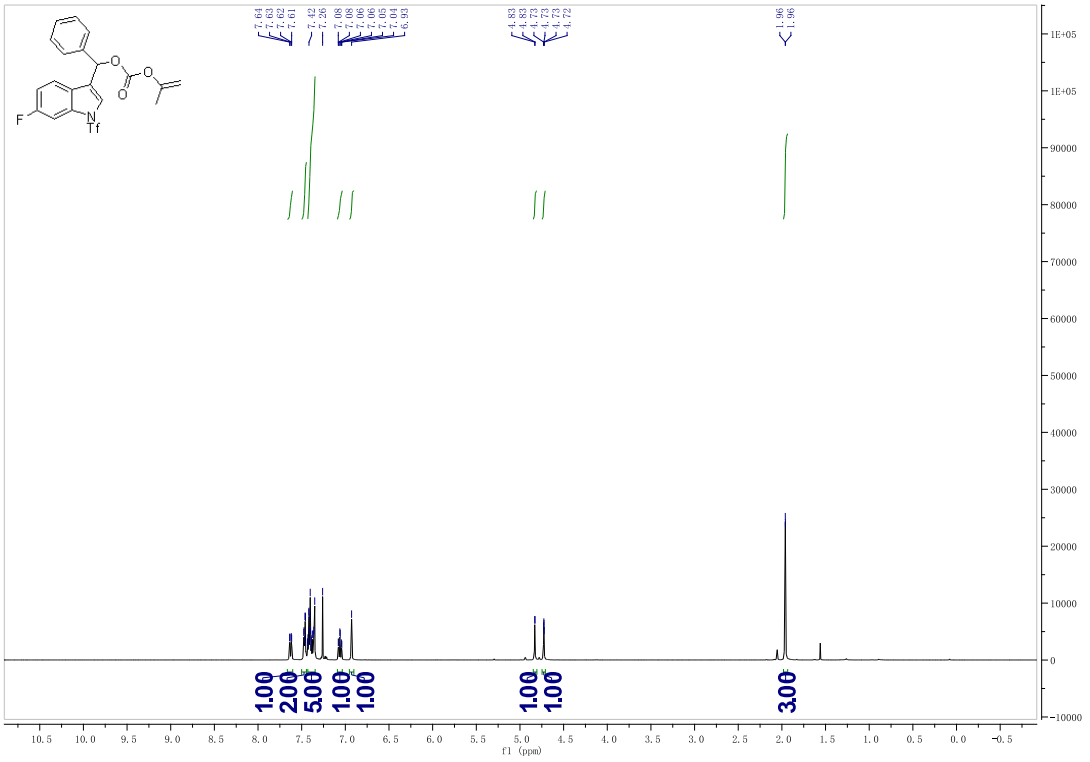
^{1}H NMR Spectra of **1k**



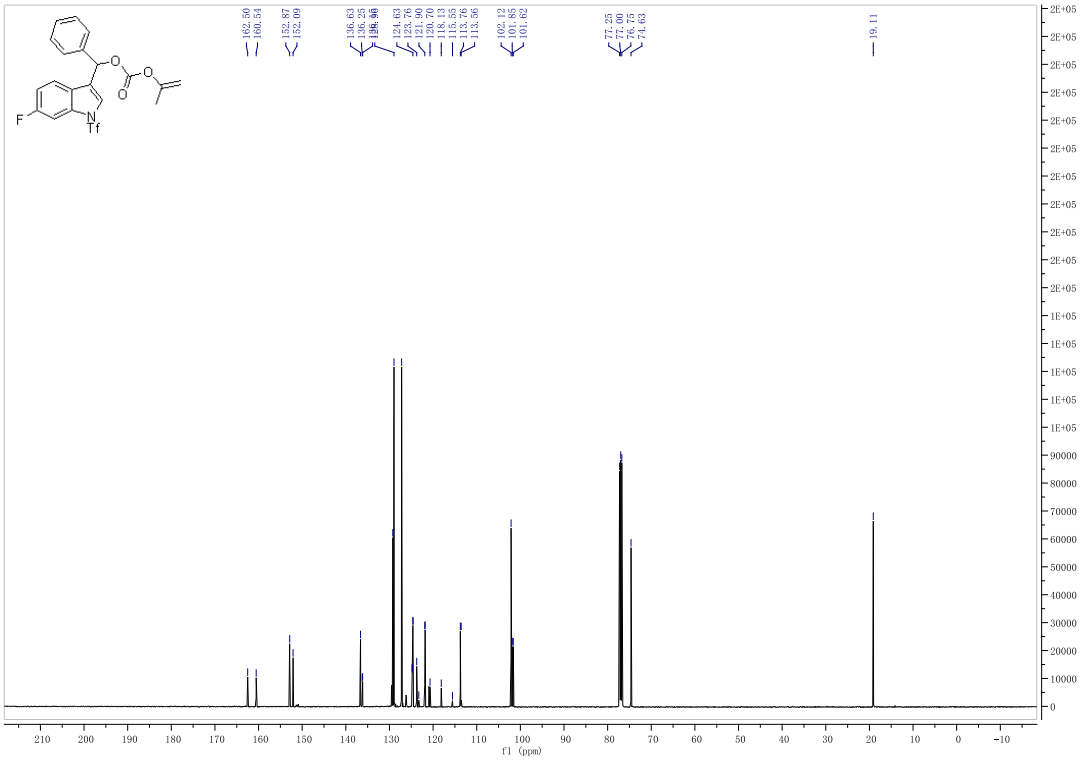
^{13}C NMR Spectra of **1k**



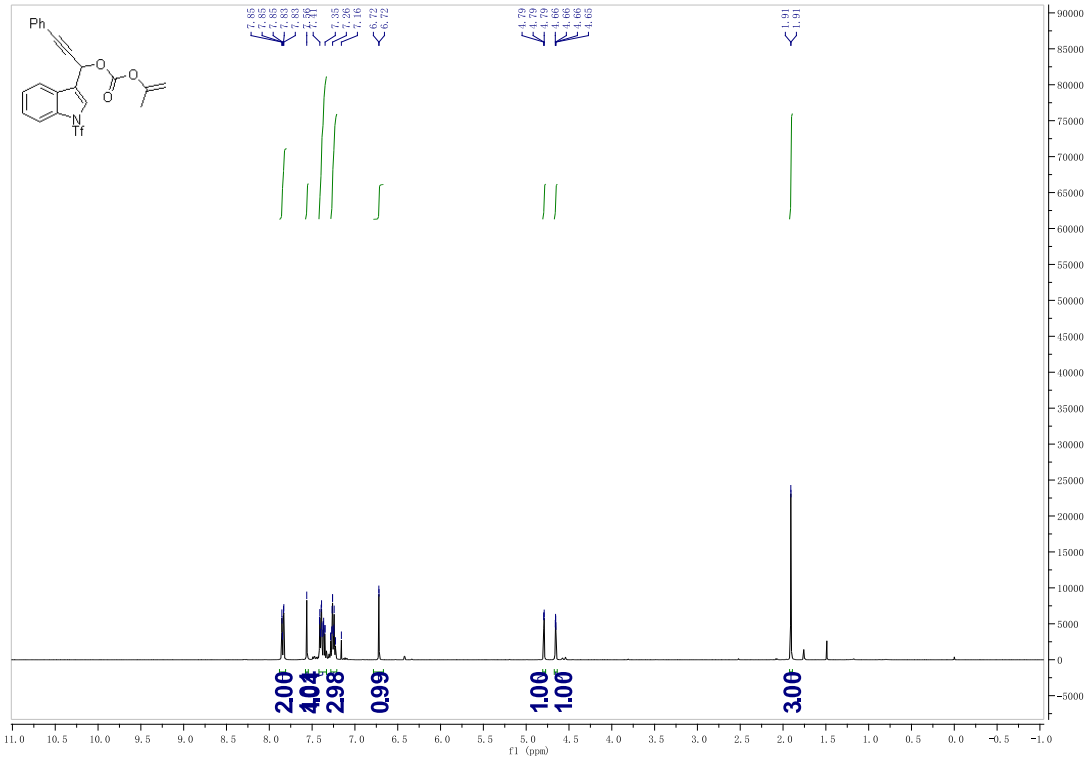
^{1}H NMR Spectra of **1l**



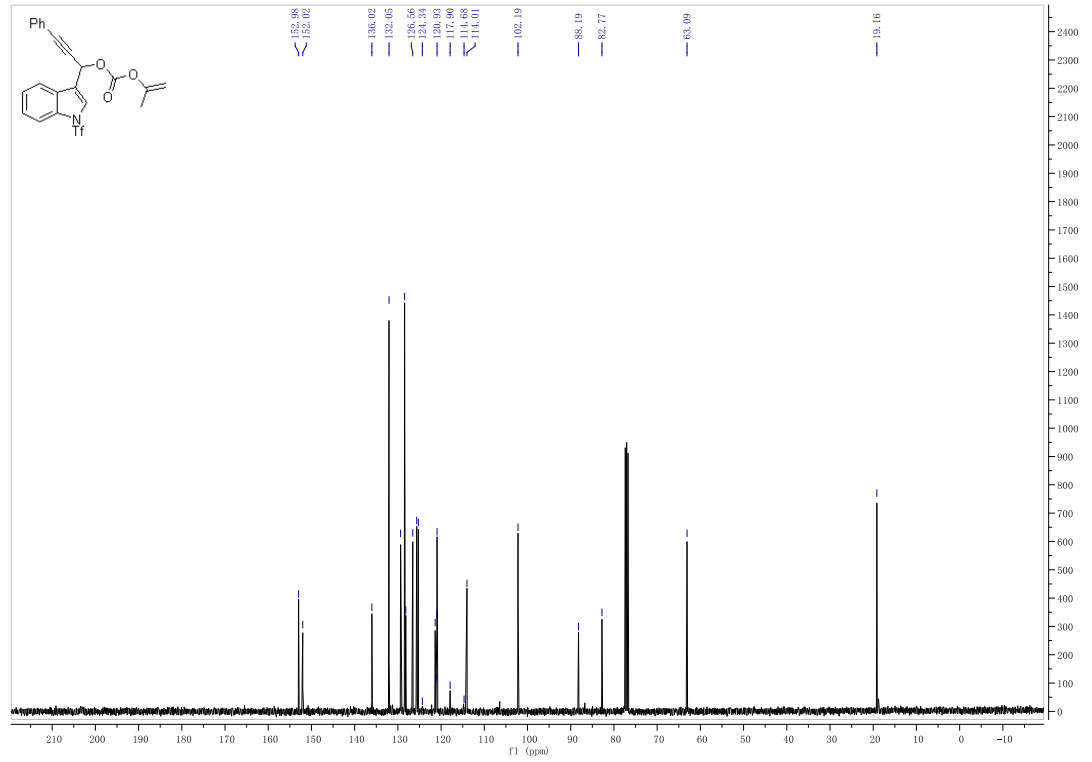
^{13}C NMR Spectra of **1l**



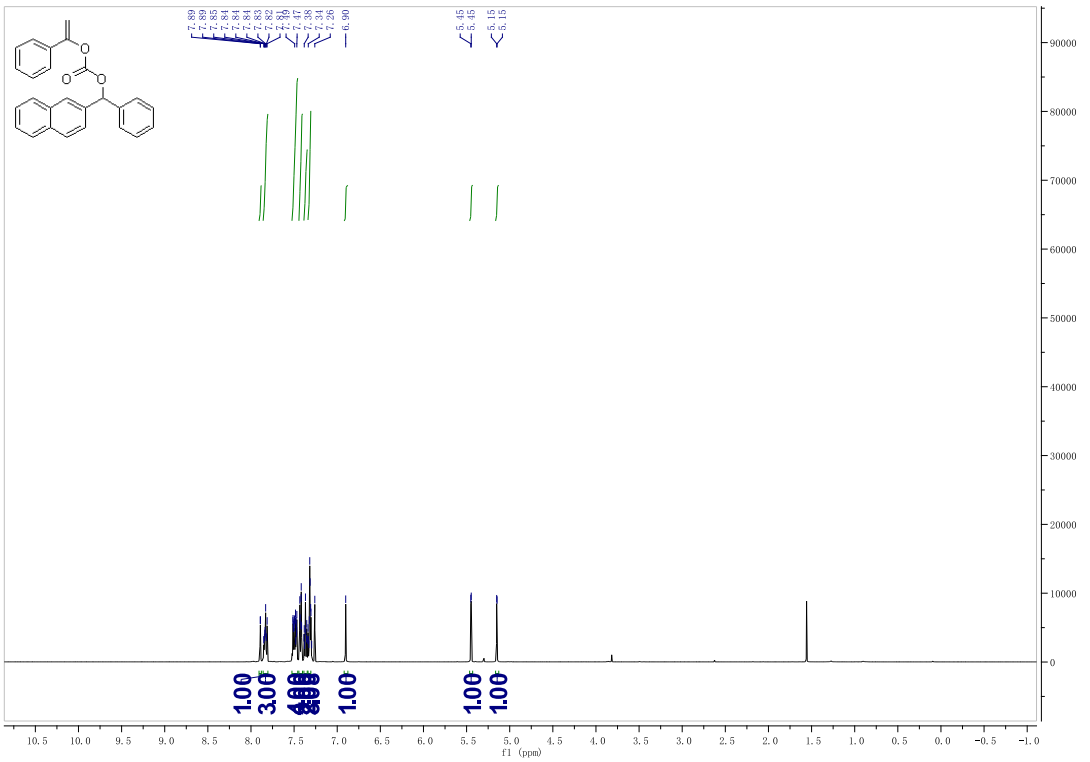
^{1}H NMR Spectra of **1m**



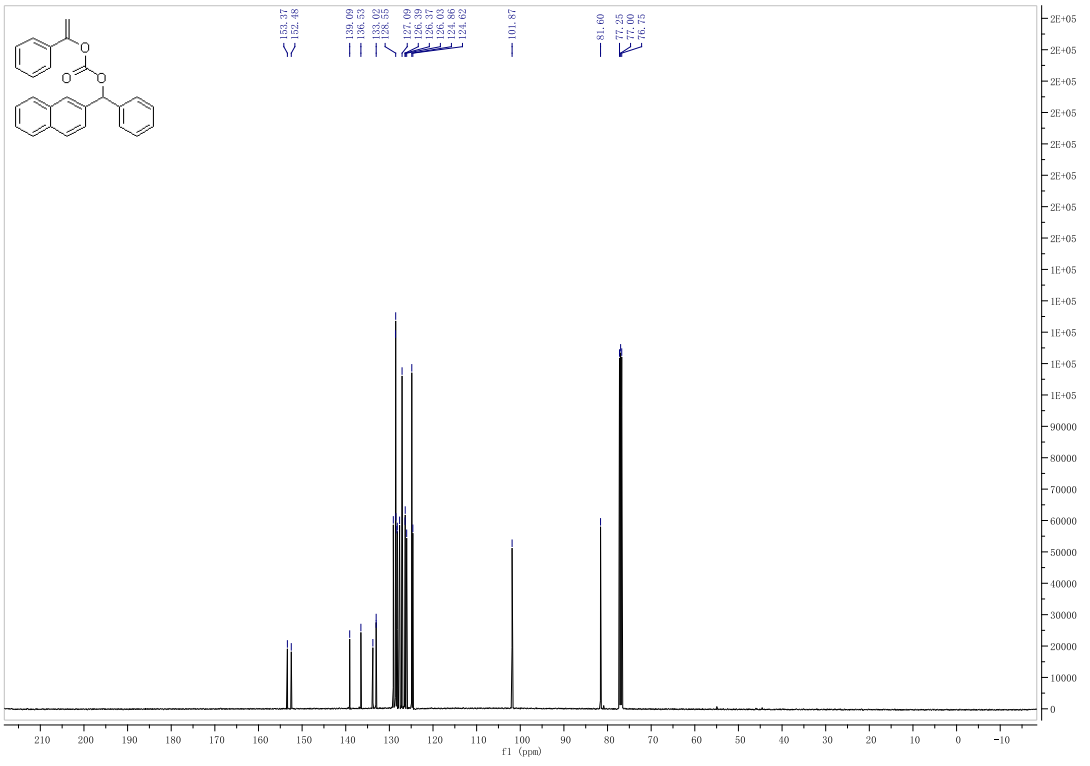
^{13}C NMR Spectra of **1m**



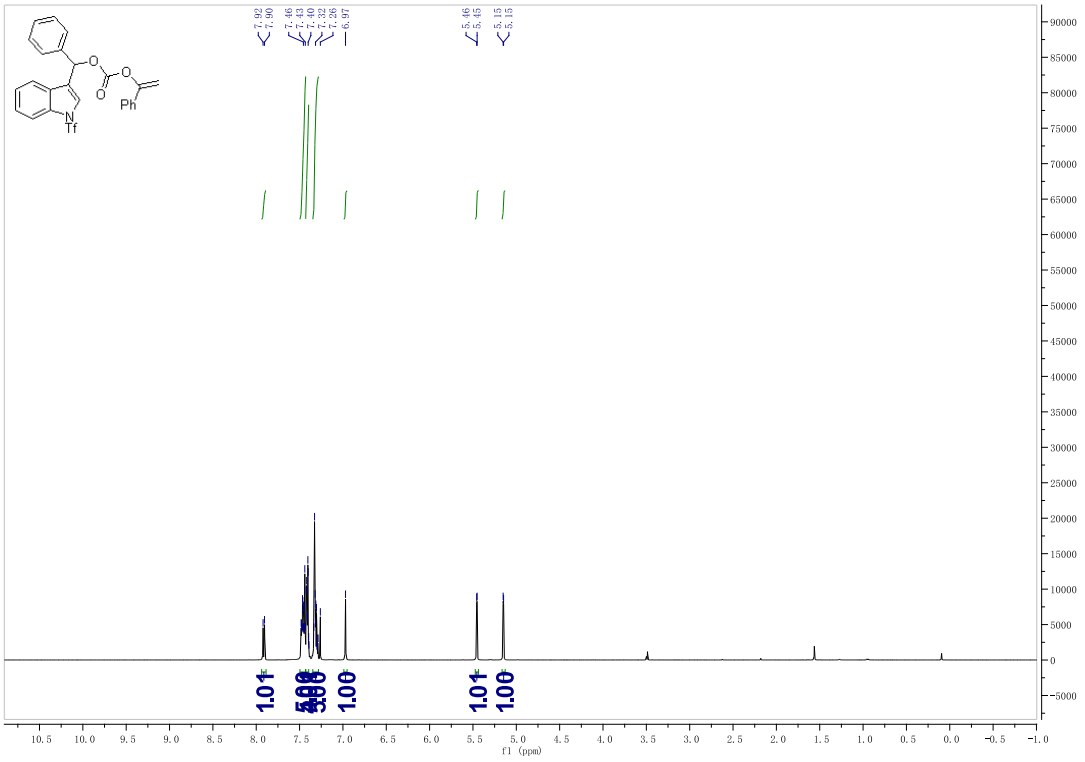
^{1}H NMR Spectra of **1n**



^{13}C NMR Spectra of **1n**



^{1}H NMR Spectra of **1o**



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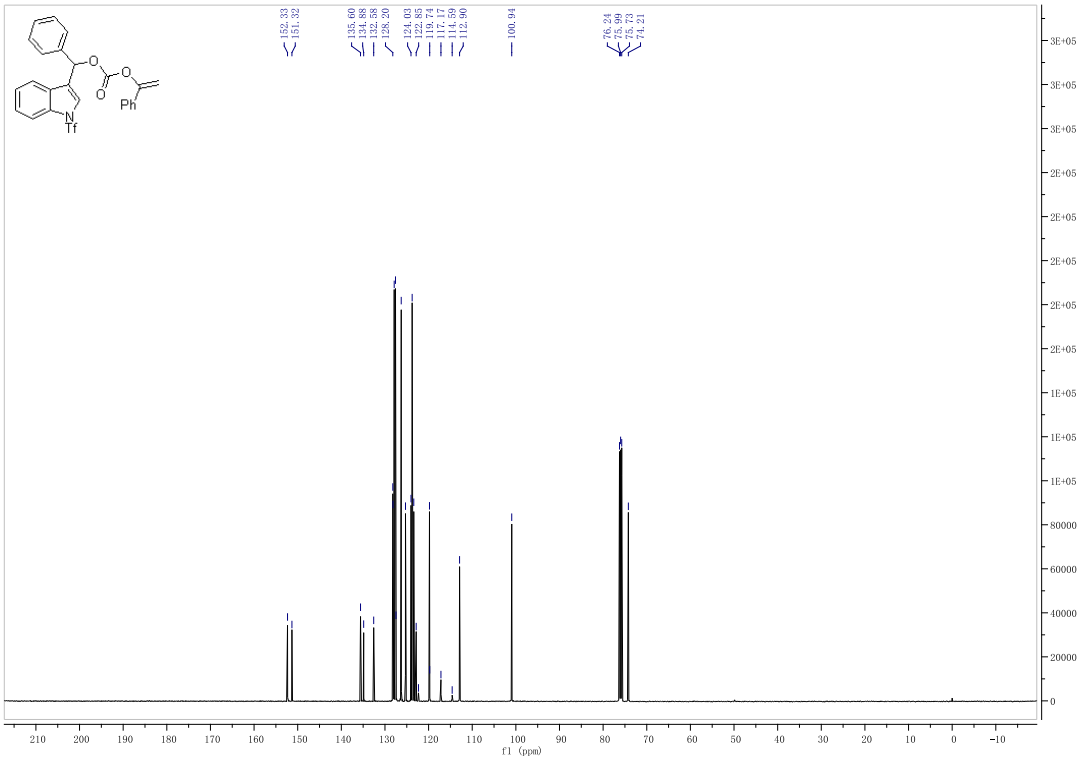
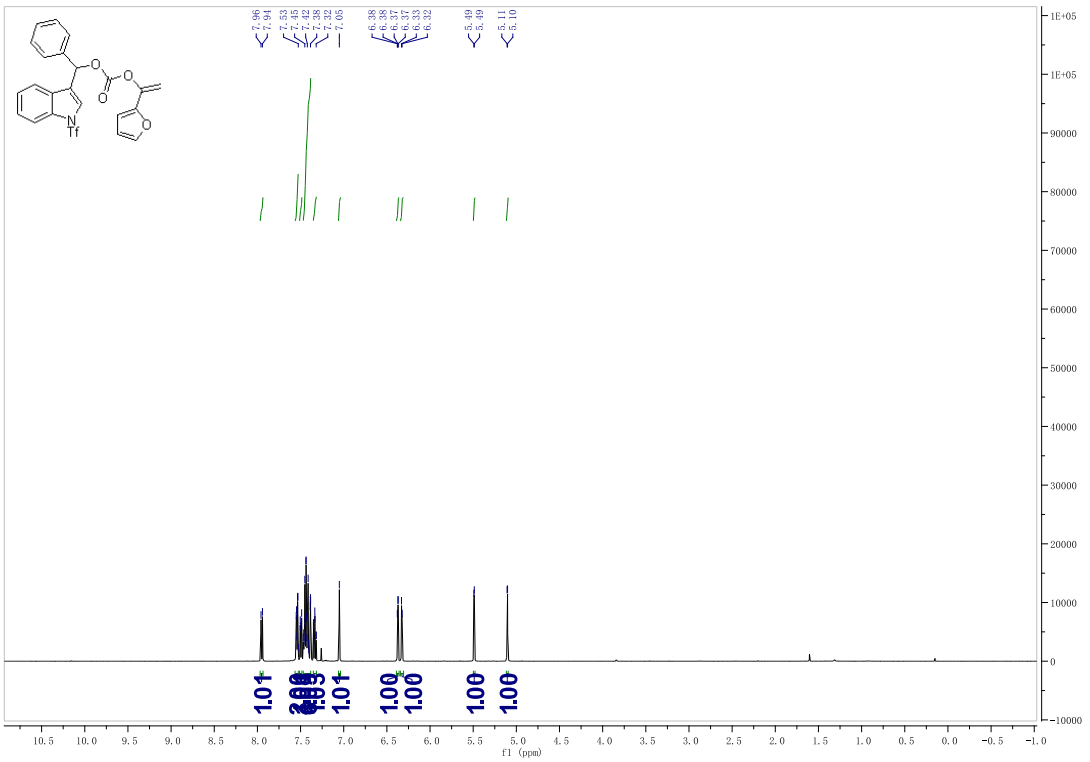
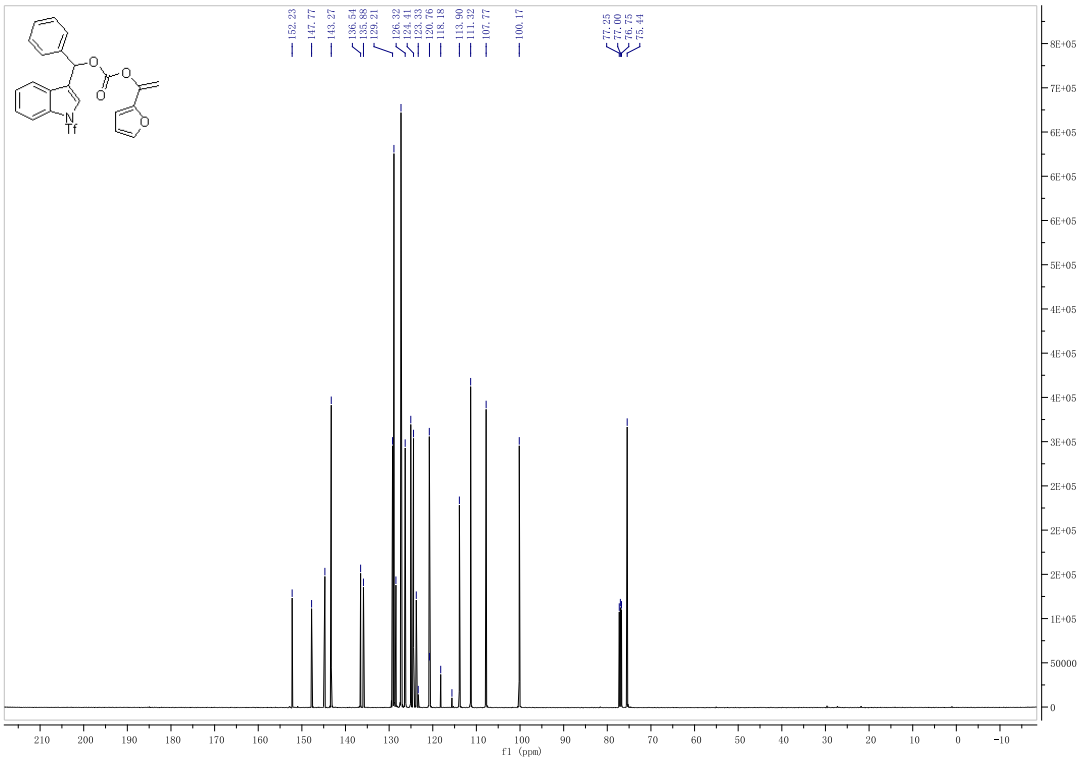


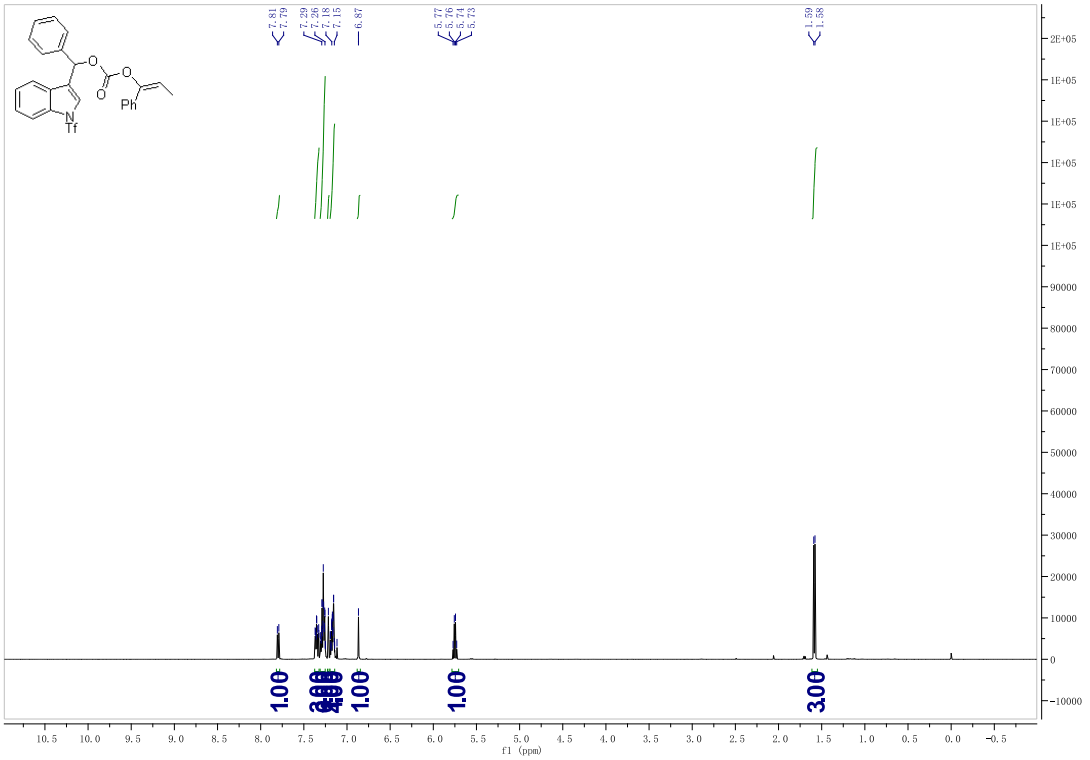
^{1}H NMR Spectra of **1p**



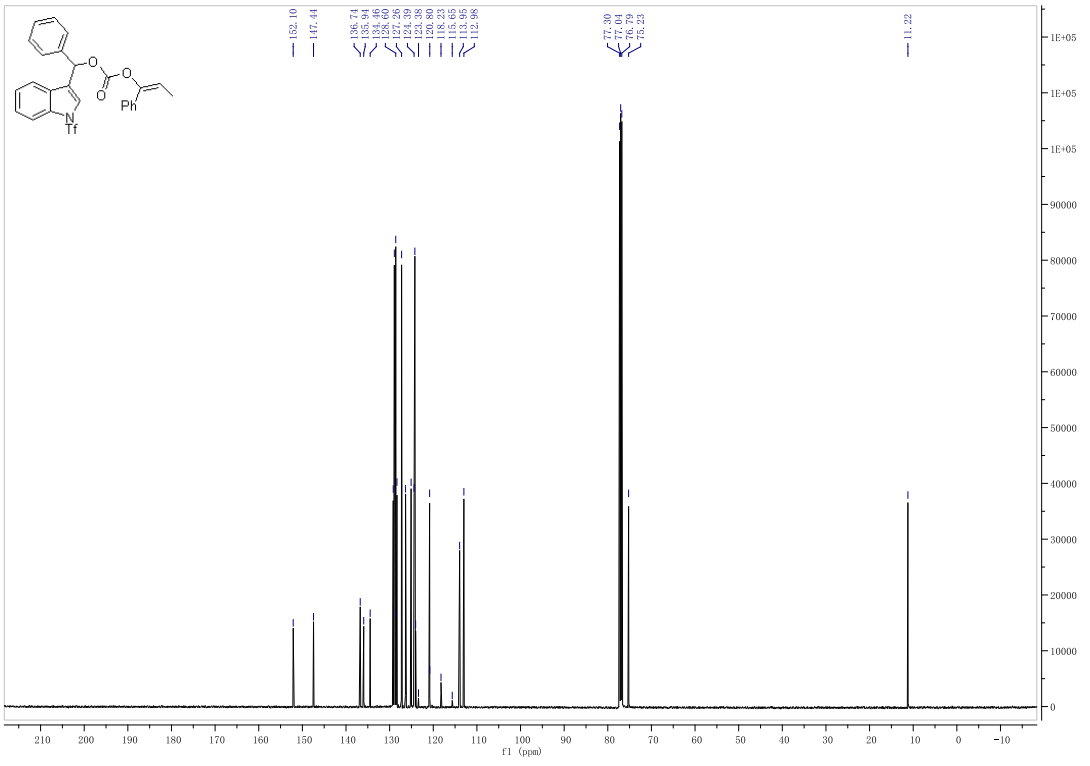
^{13}C NMR Spectra of **1p**



^{1}H NMR Spectra of **1q**



^{13}C NMR Spectra of **1q**



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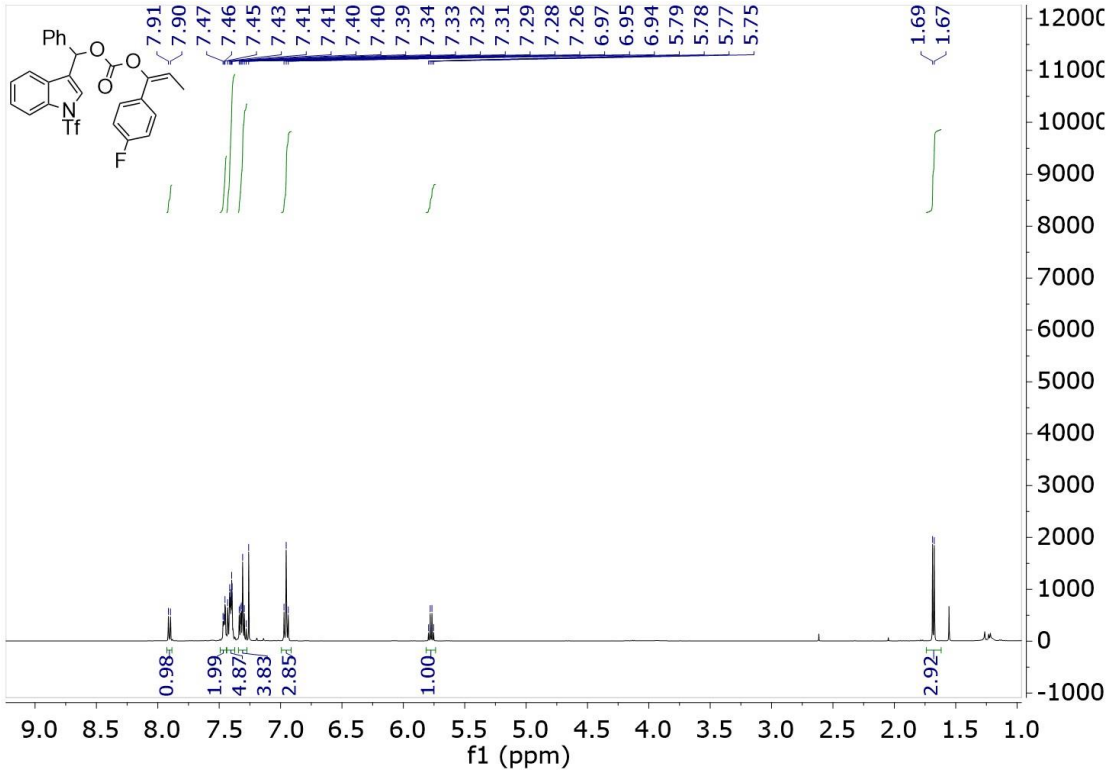

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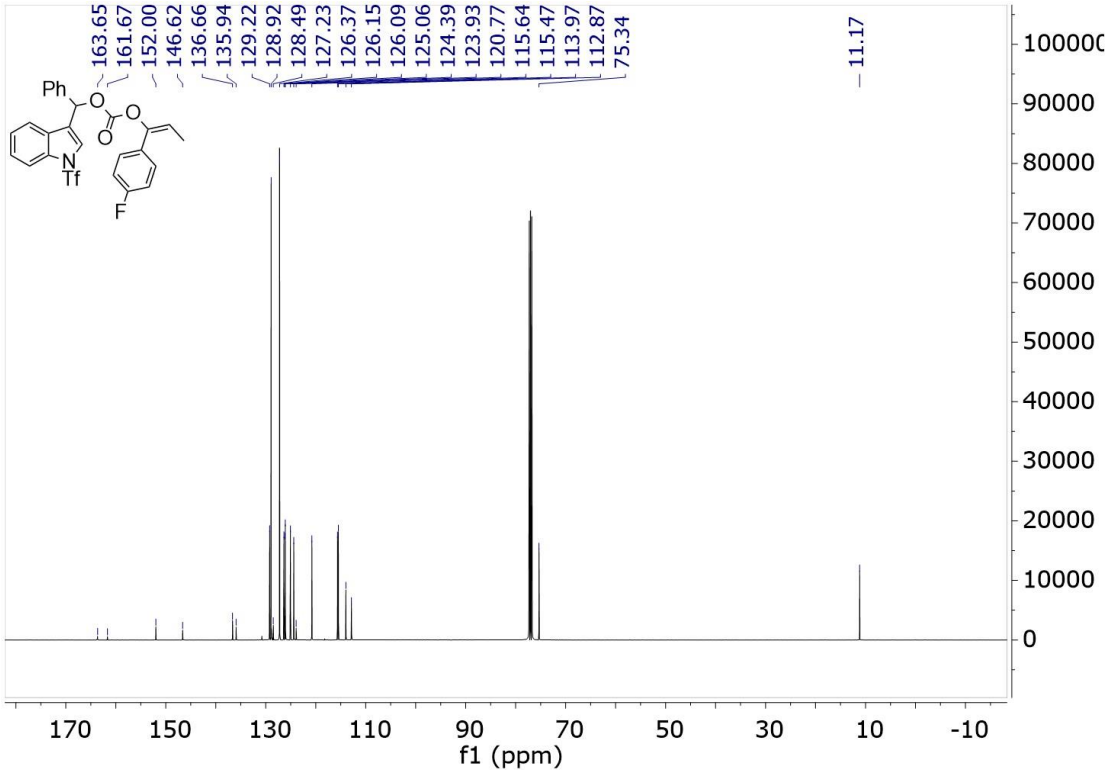
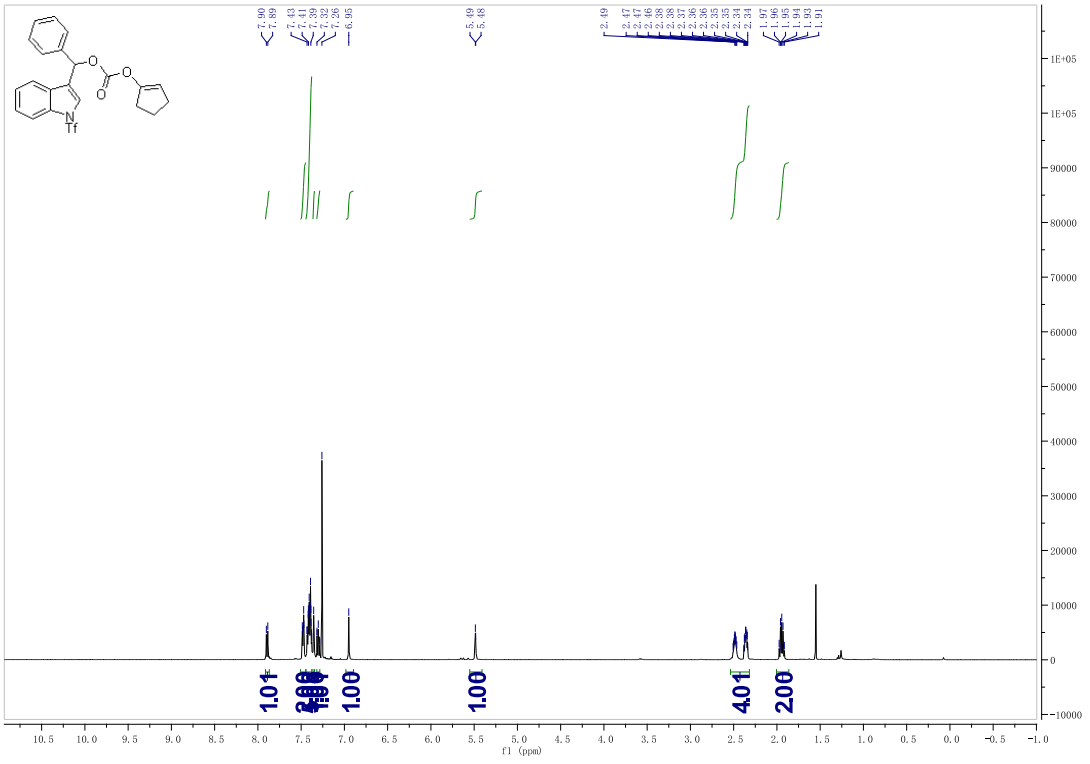


^{1}H NMR Spectra of **1s**



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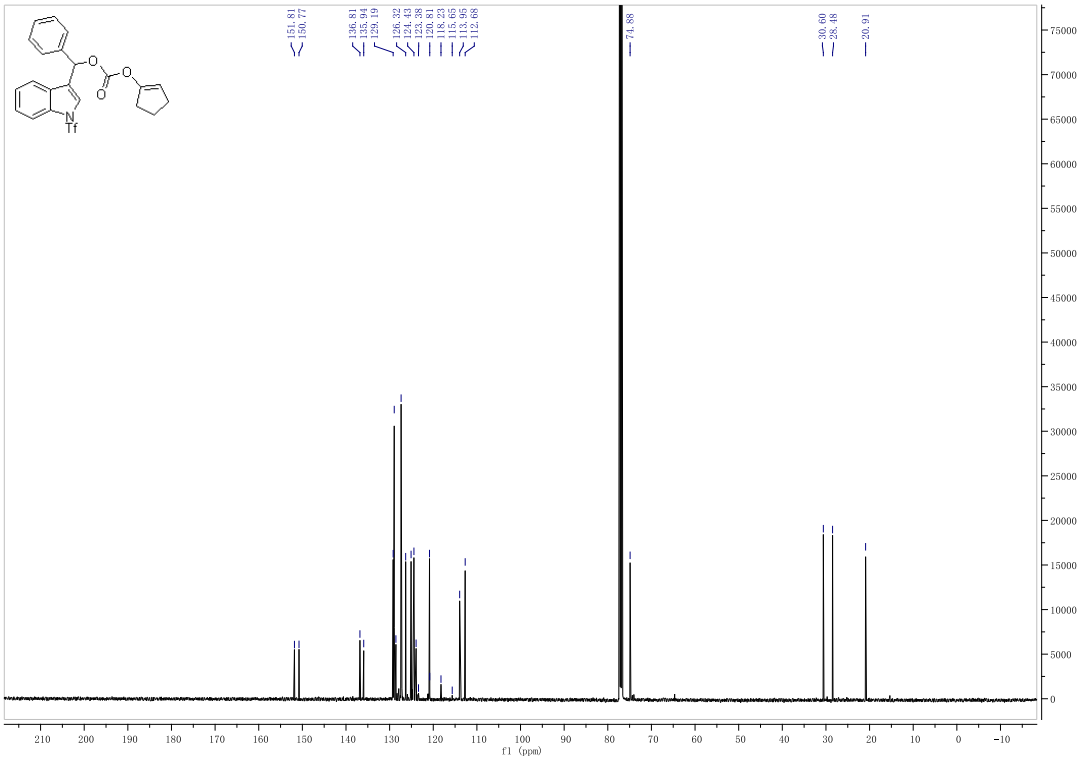
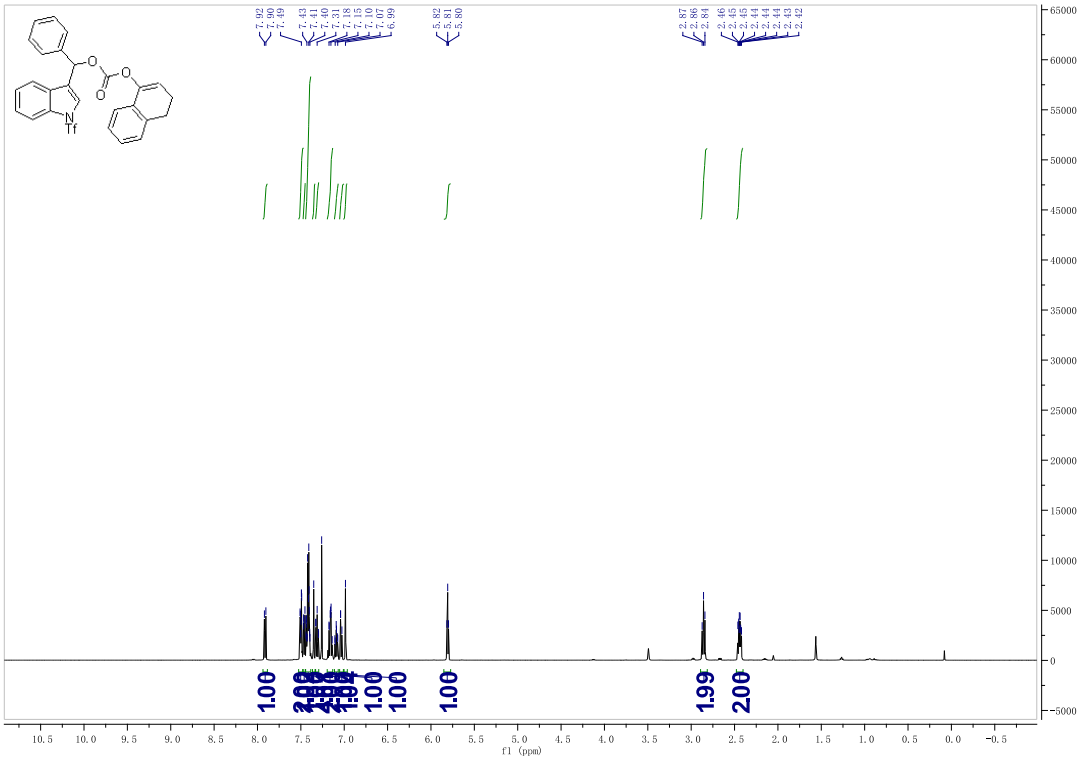


^{1}H NMR Spectra of **1t**



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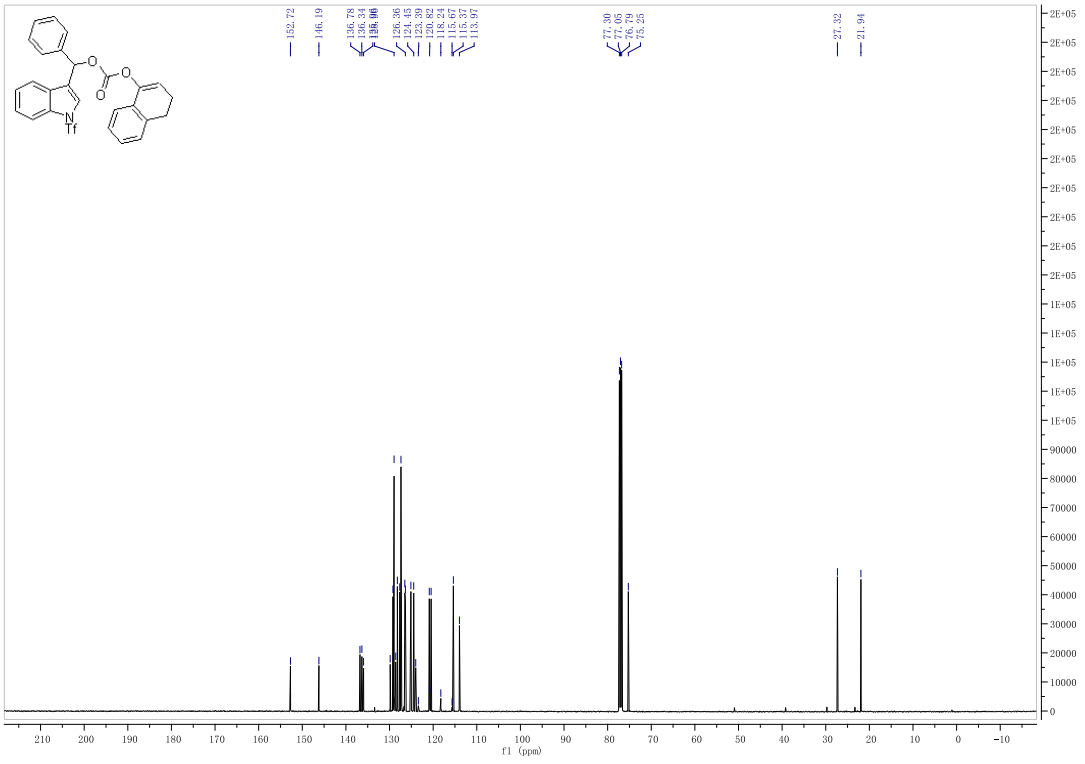
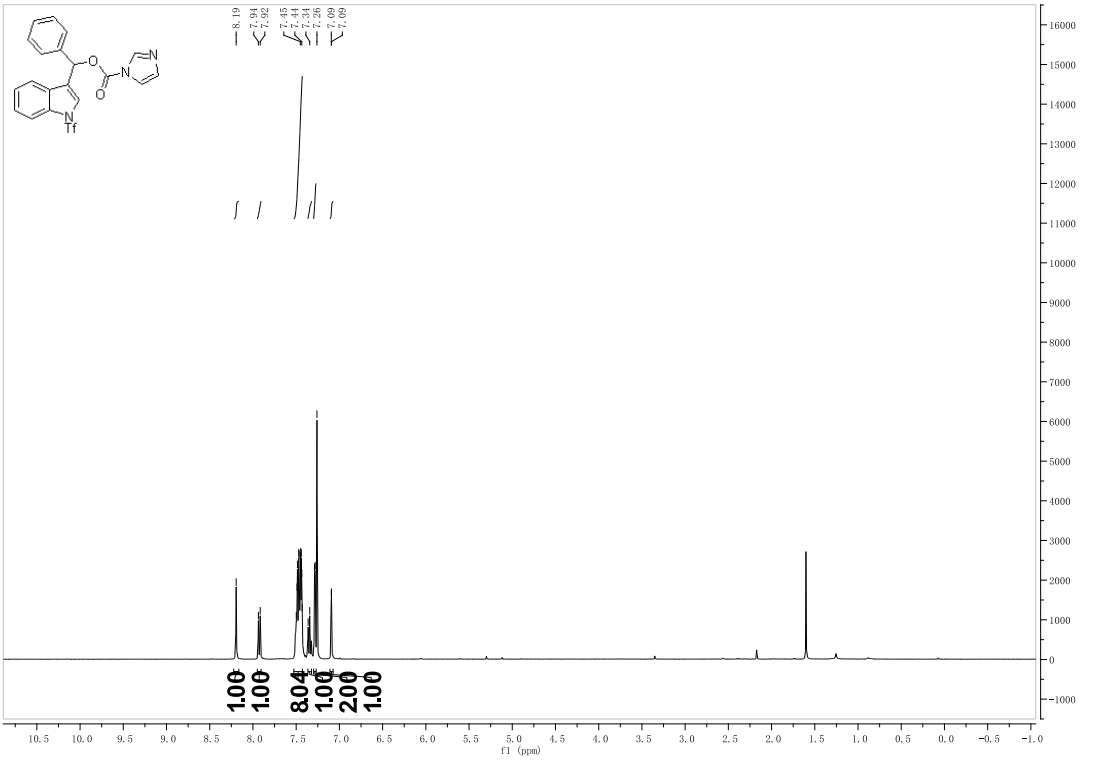
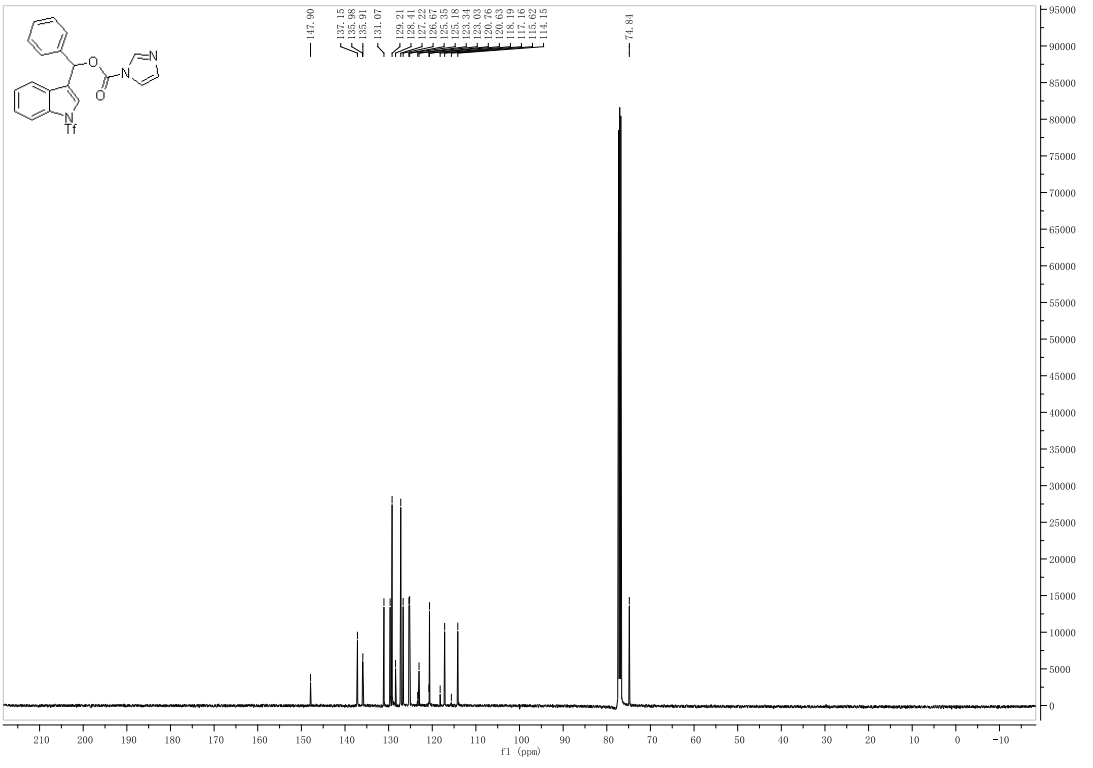


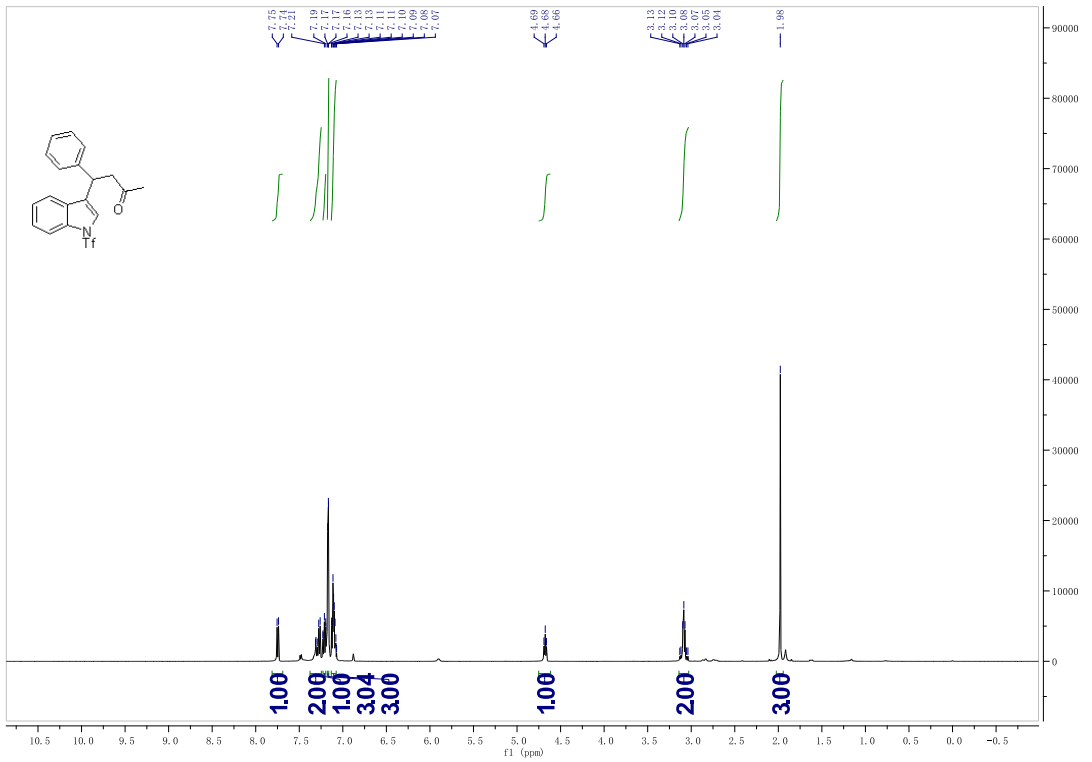
^{1}H NMR Spectra of **S1**



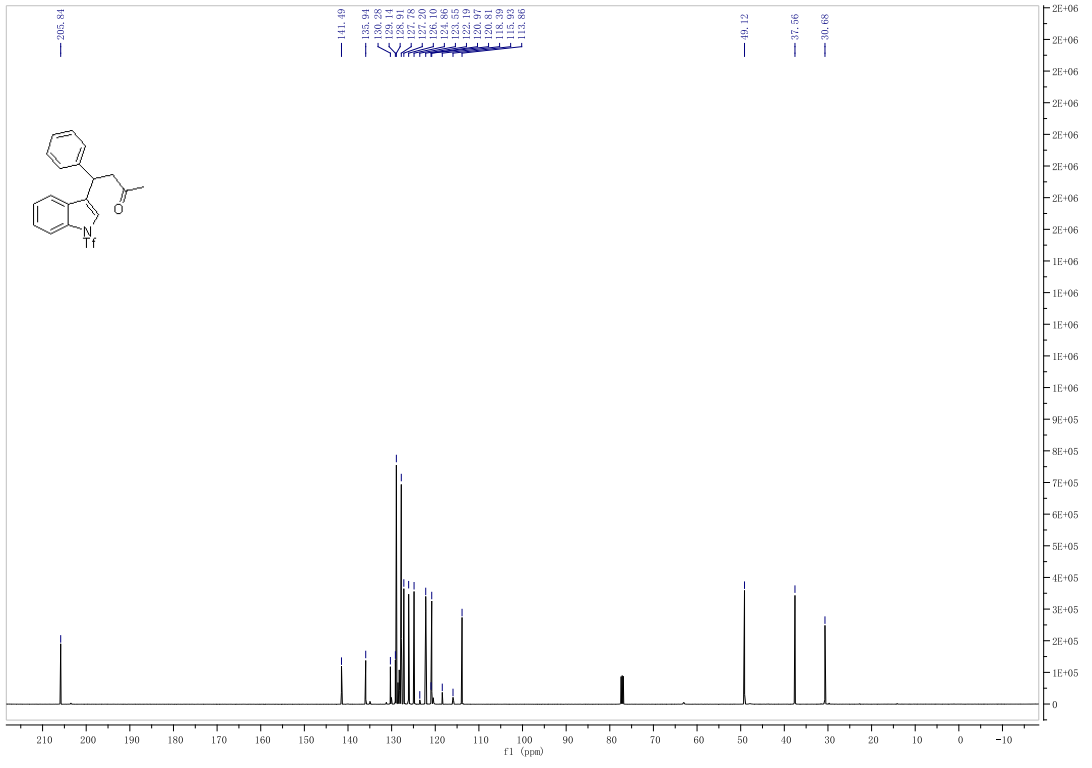
^{13}C NMR Spectra of **S1**



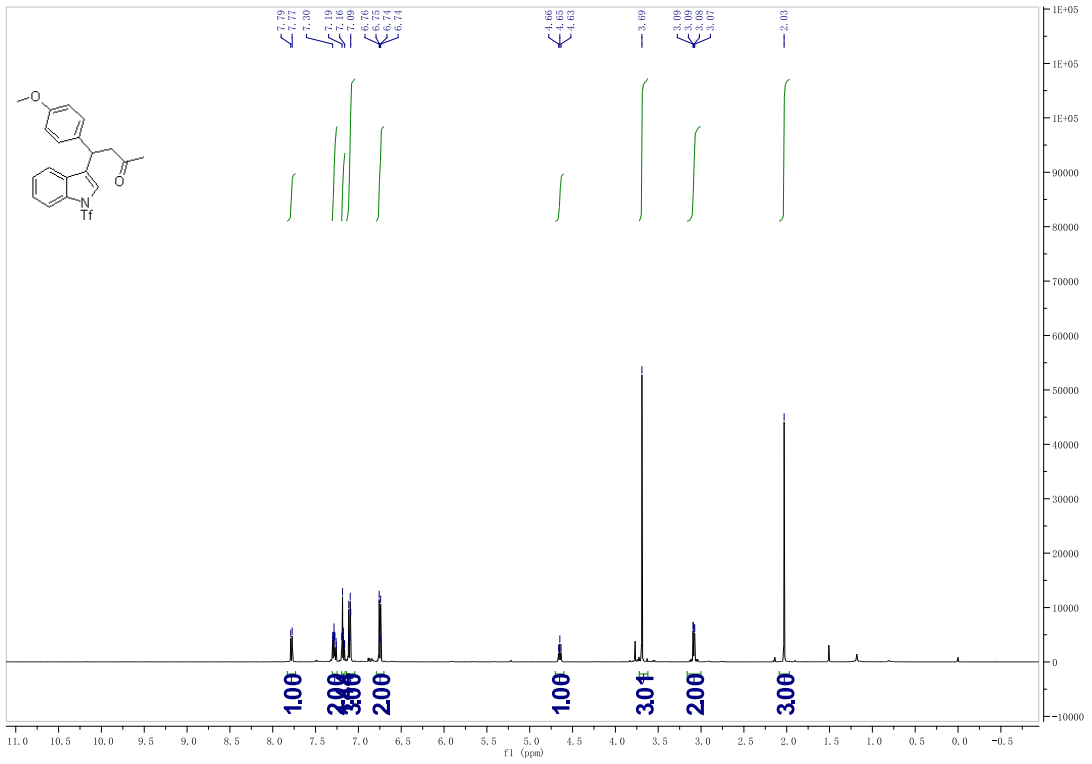
^{1}H NMR Spectra of **2a**



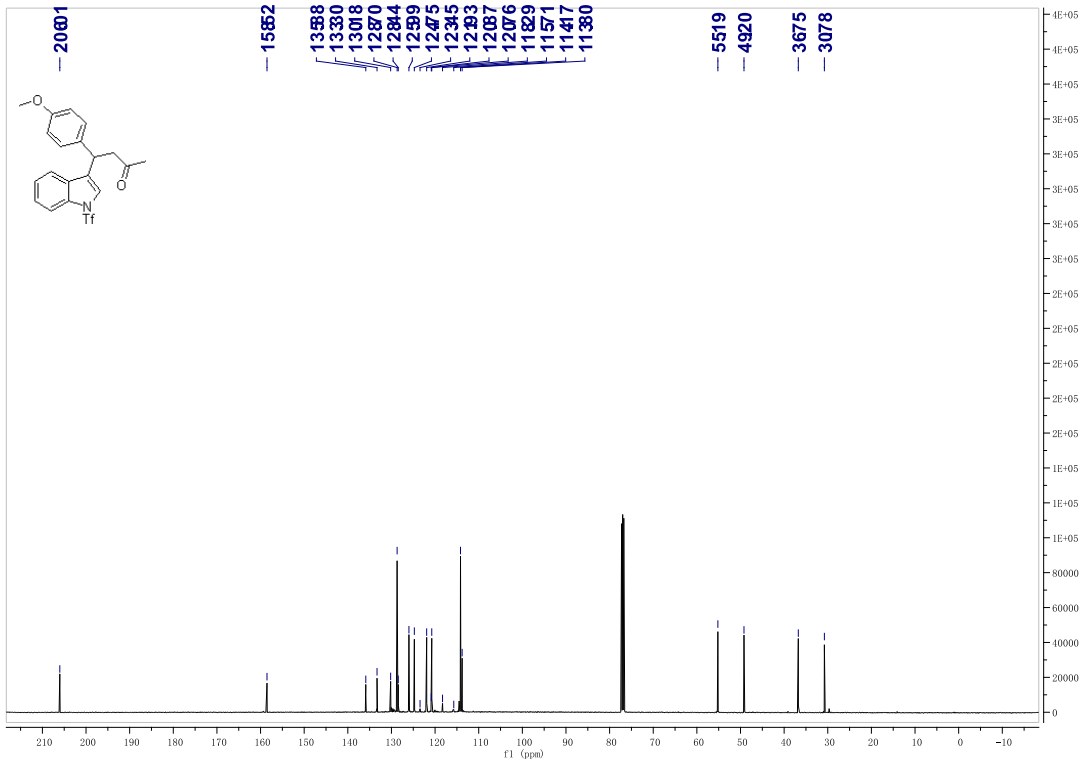
^{13}C NMR Spectra of **2a**



^{1}H NMR Spectra of **2b**



^{13}C NMR Spectra of **2b**



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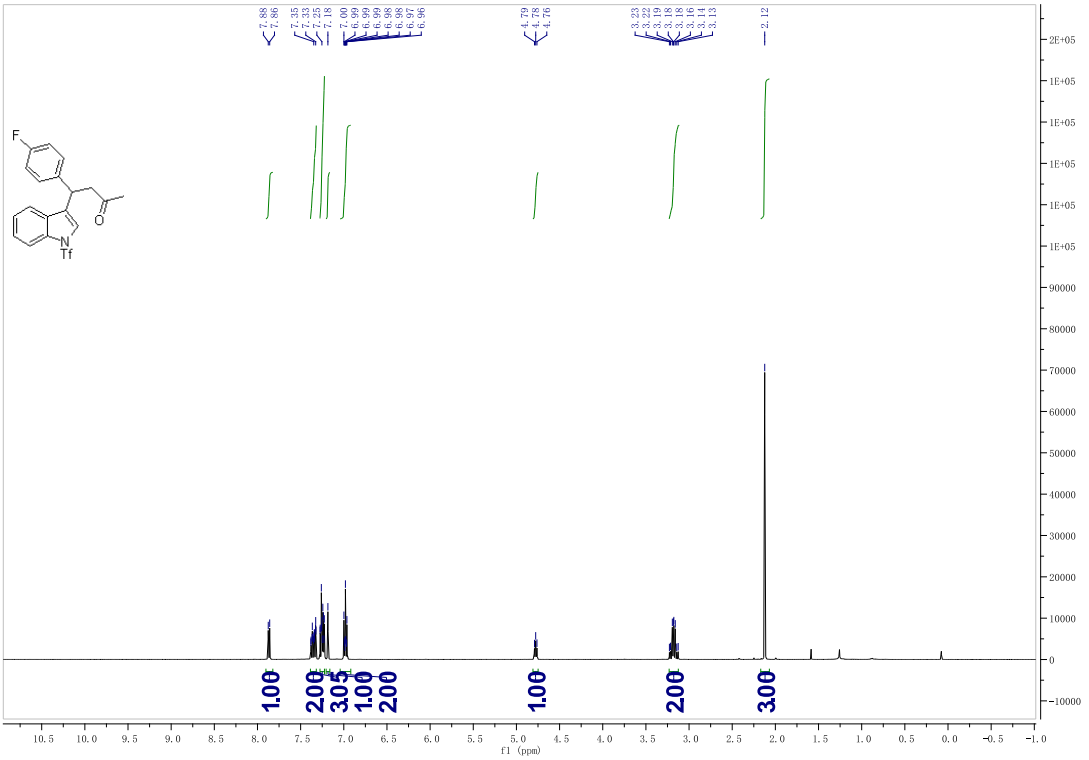
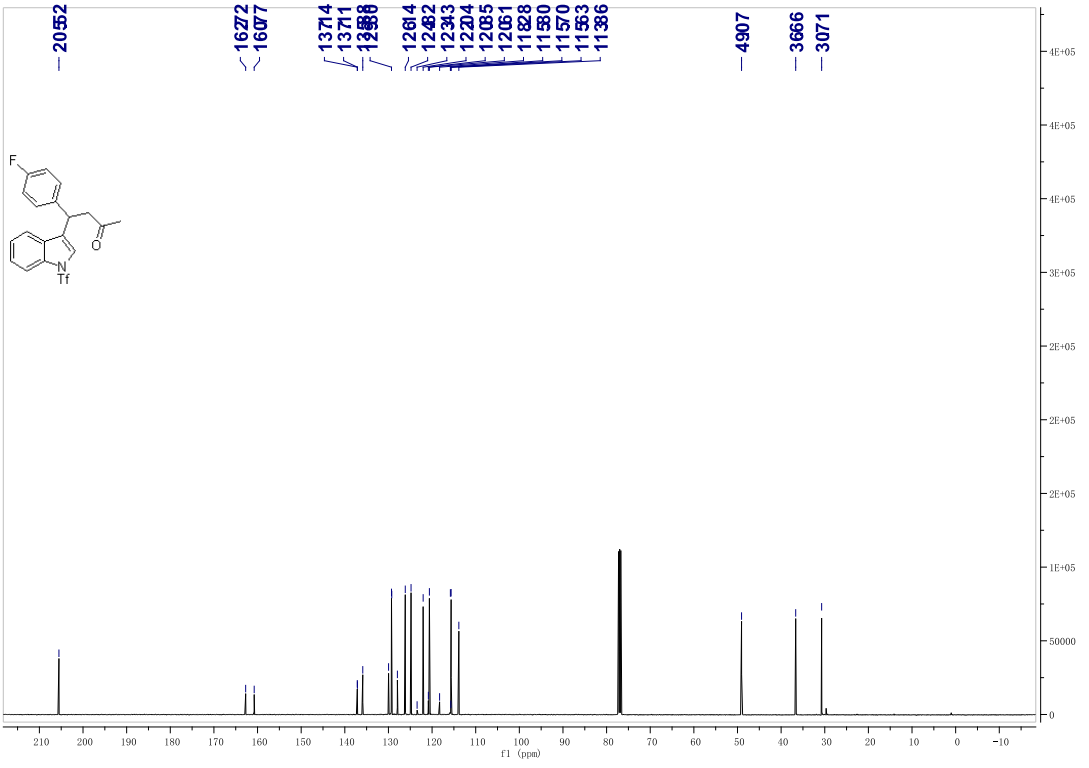


^{13}C NMR Spectra of **2c**



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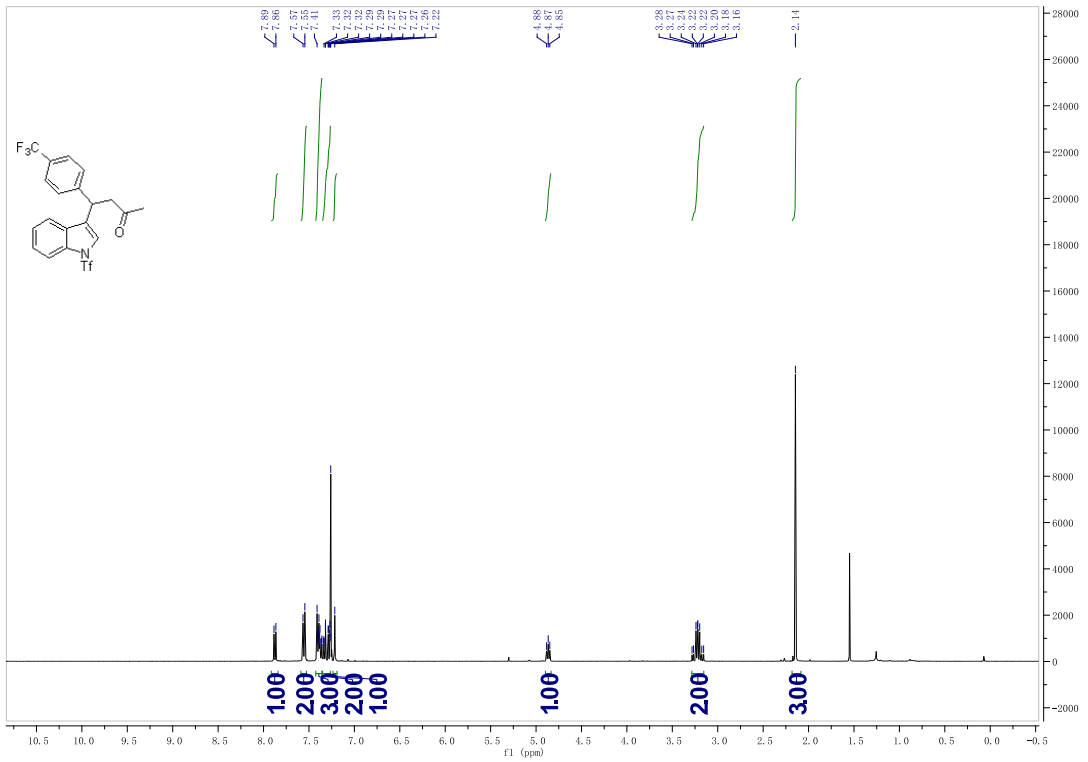

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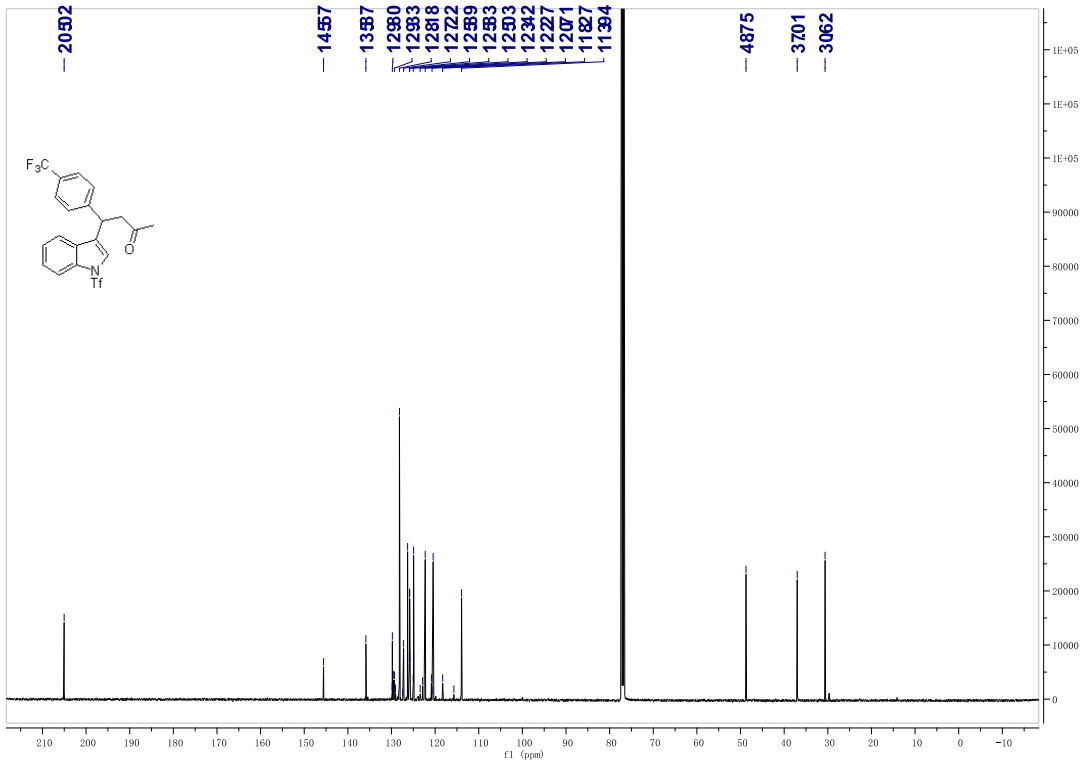

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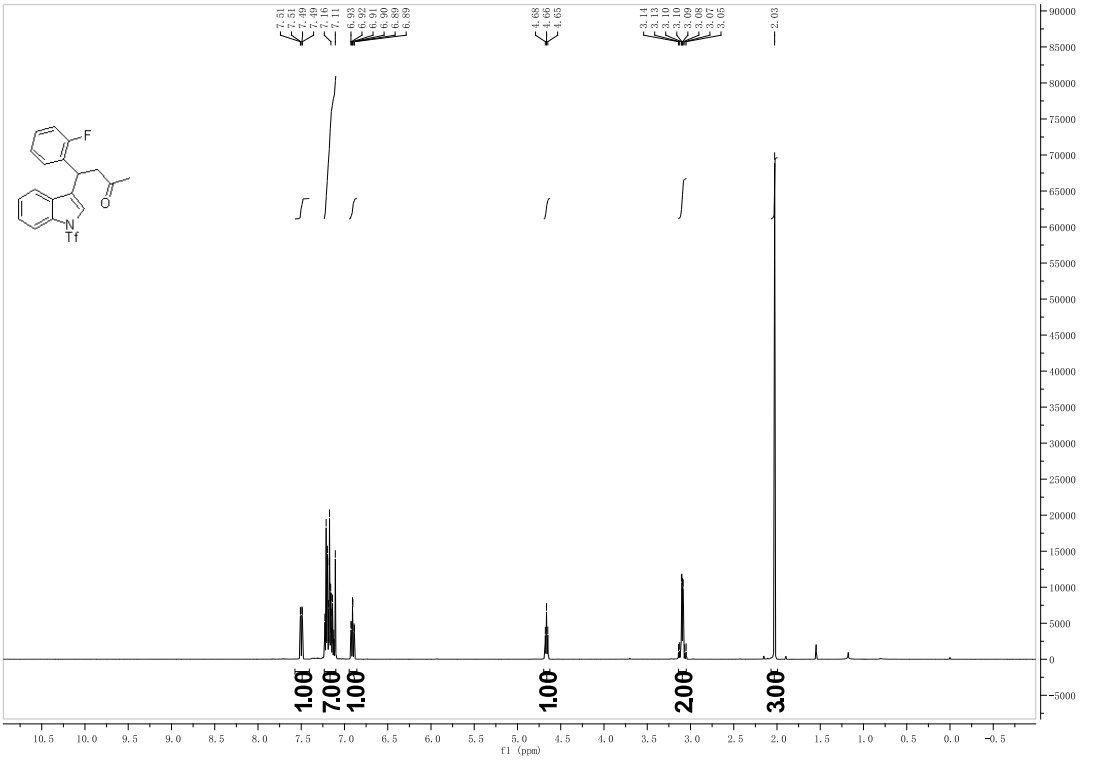

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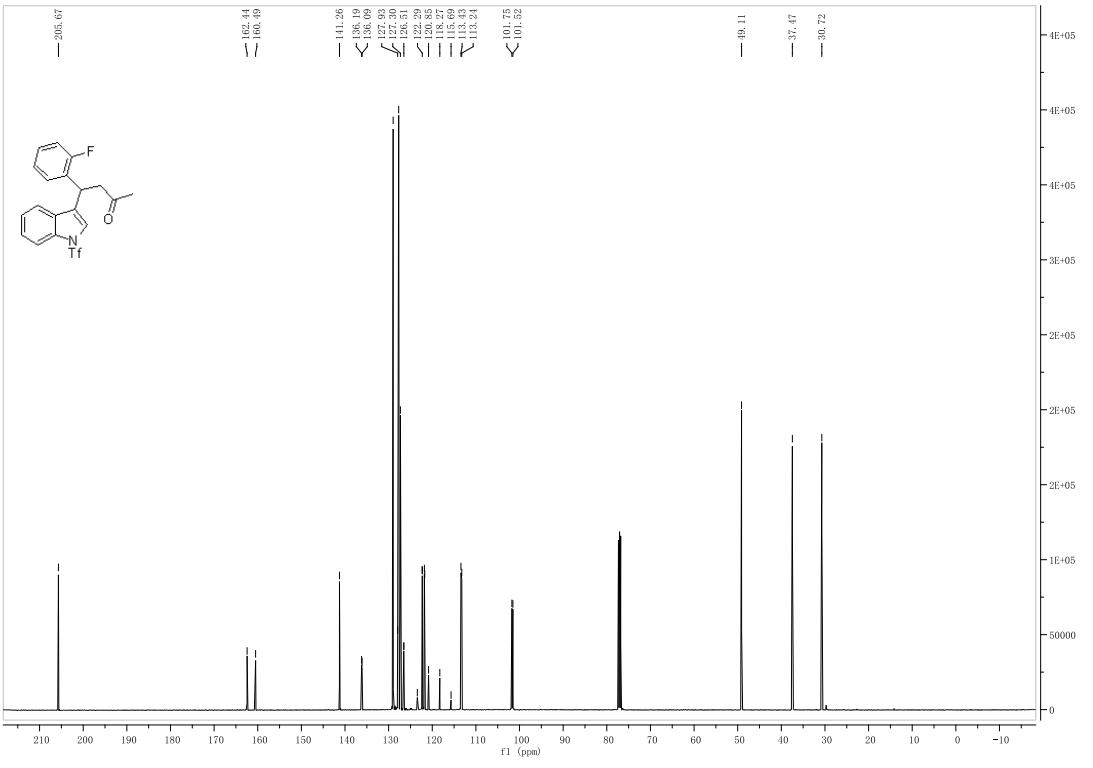
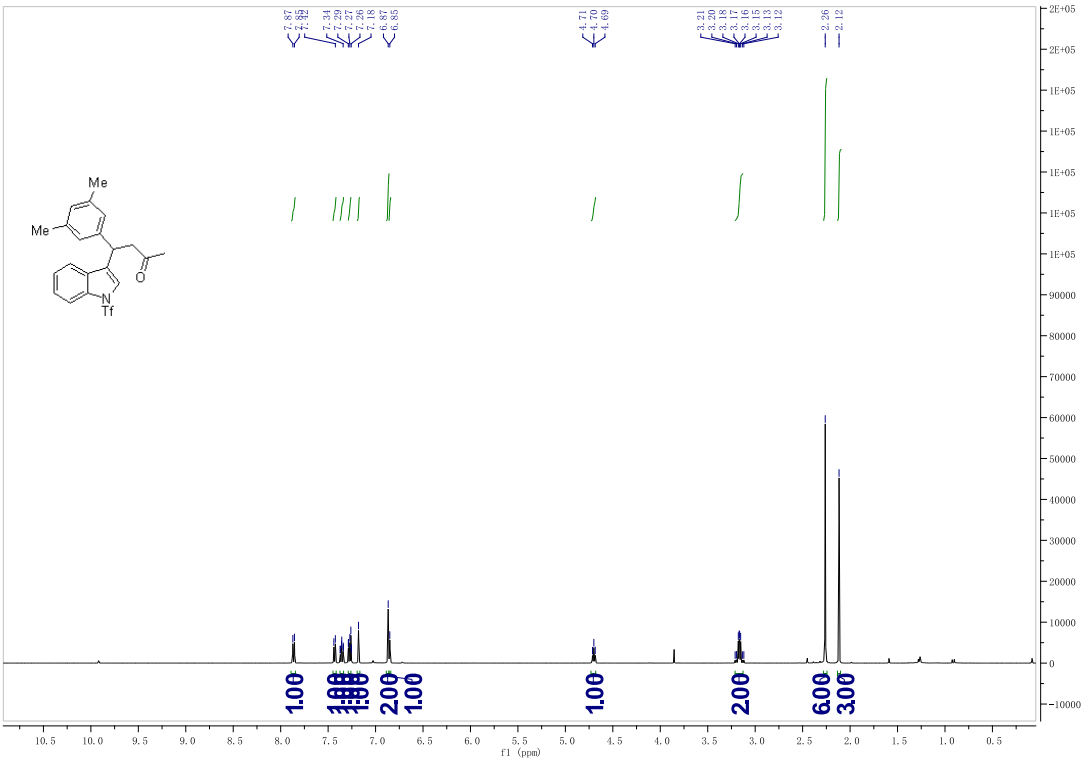
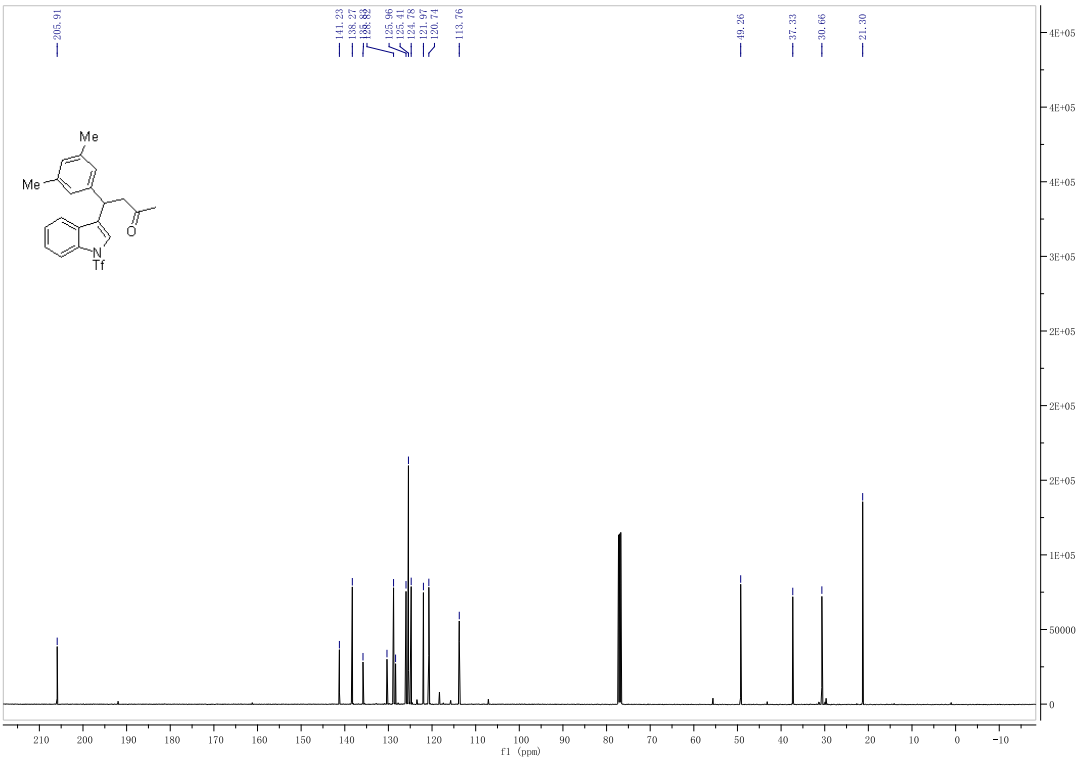


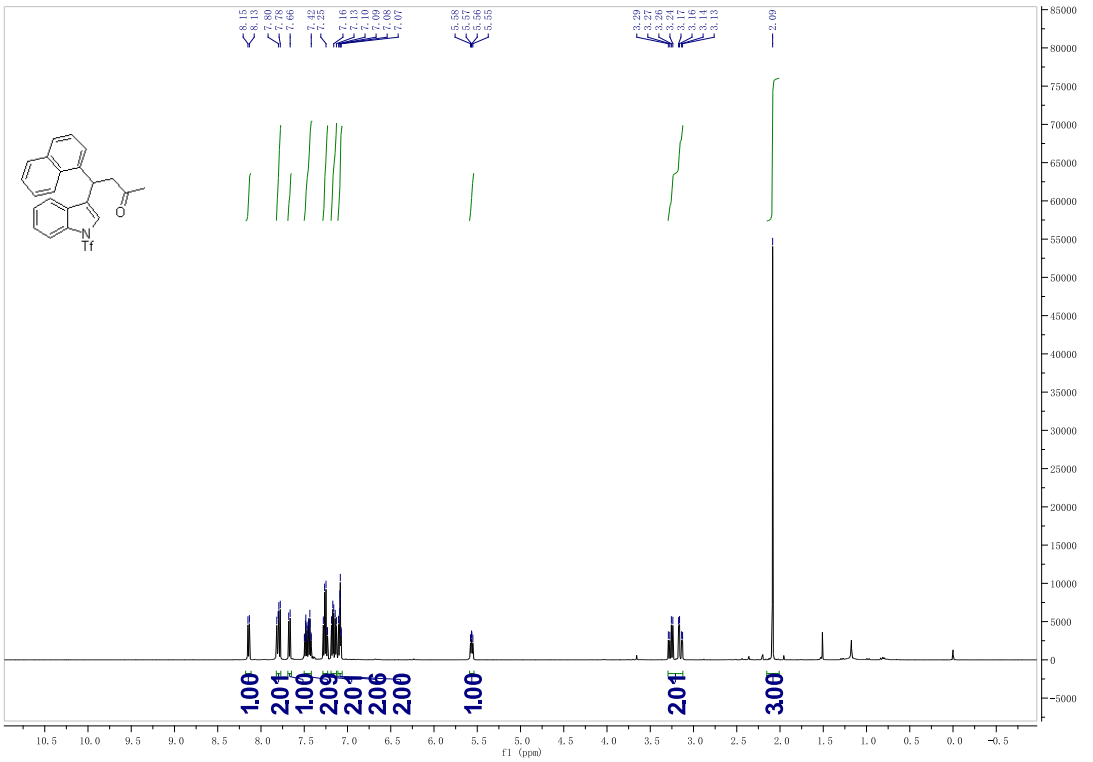
^{1}H NMR Spectra of **2f**



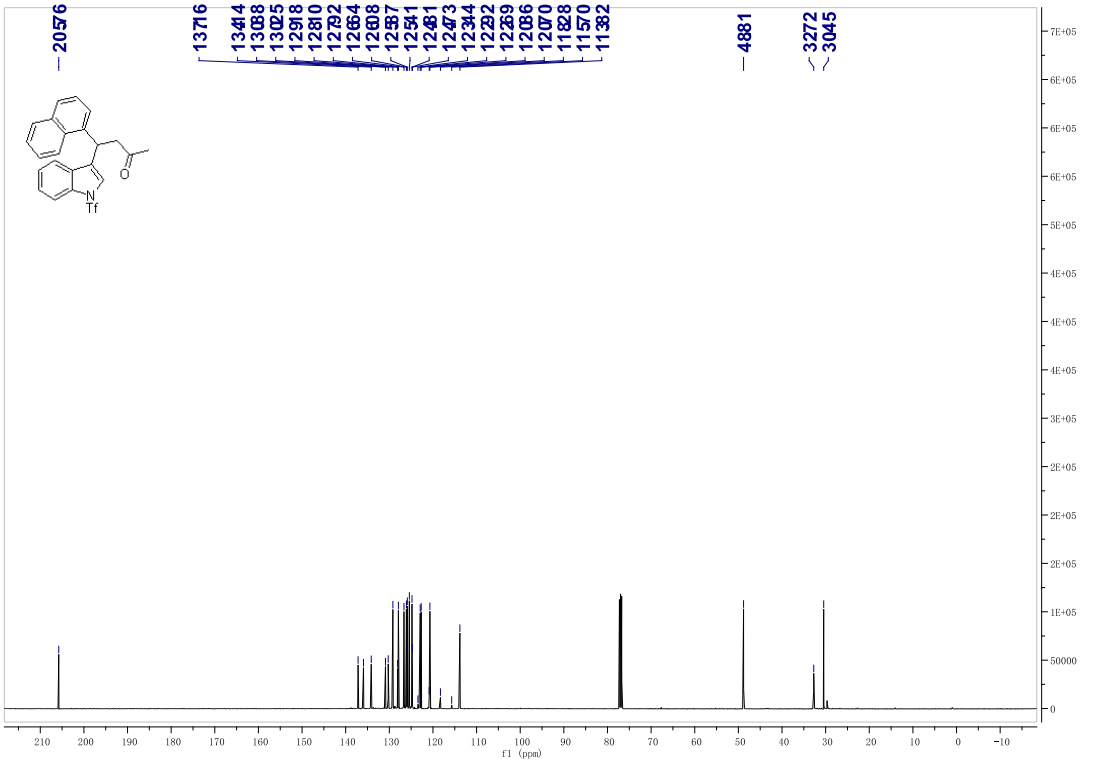
^{13}C NMR Spectra of **2f**



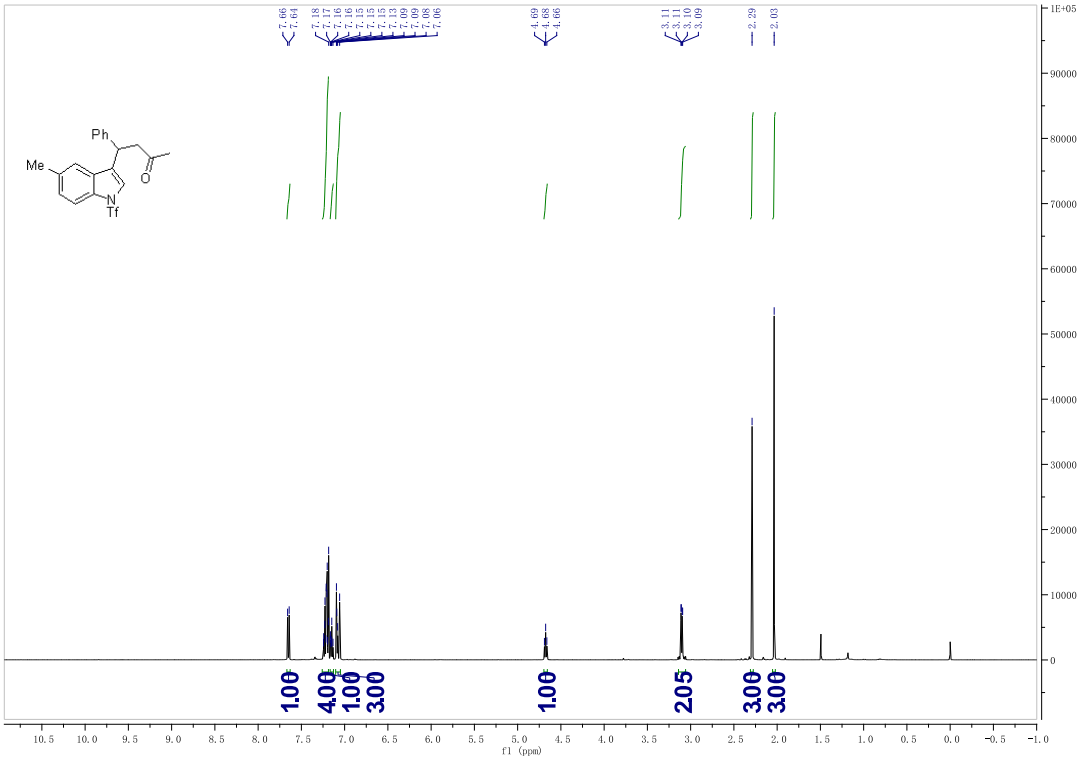
^{1}H NMR Spectra of **2g**



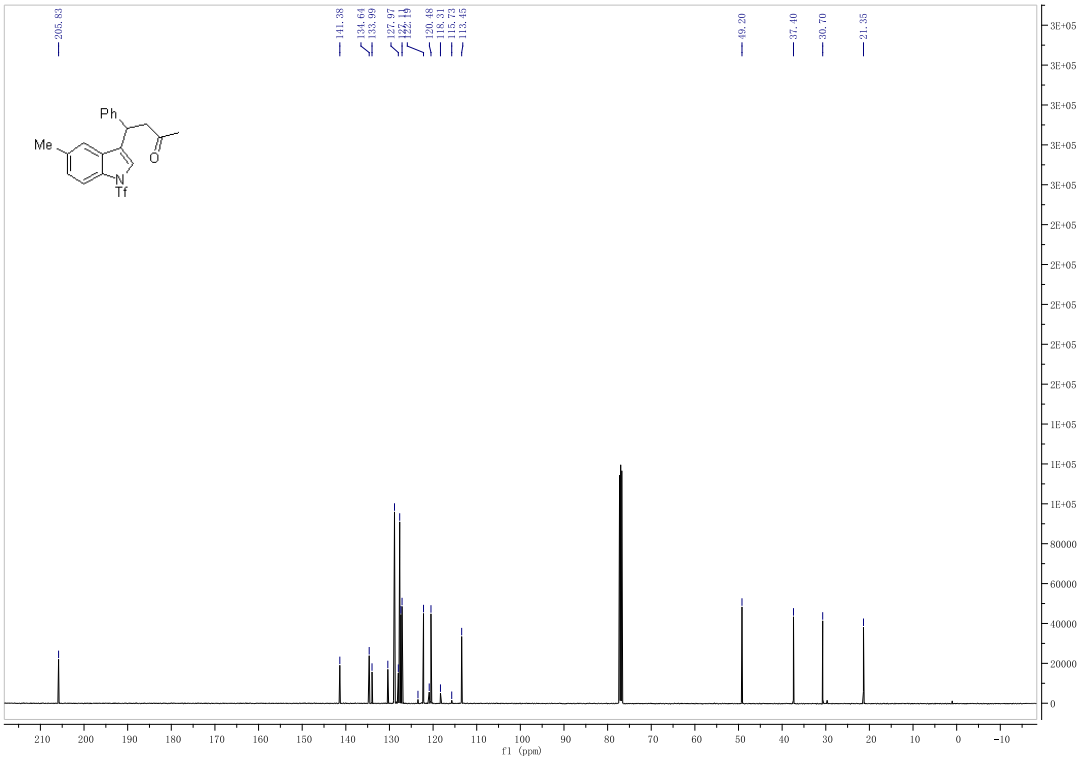
^{13}C NMR Spectra of **2g**



^{1}H NMR Spectra of **2i**



^{13}C NMR Spectra of **2i**



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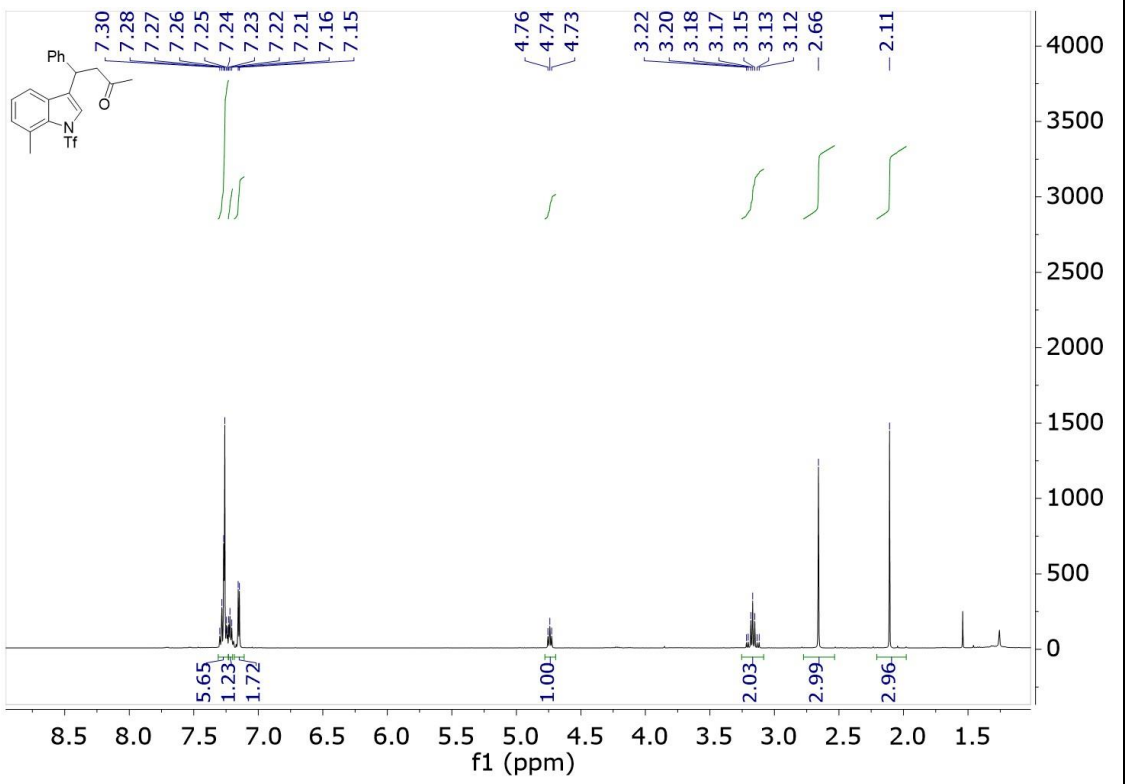

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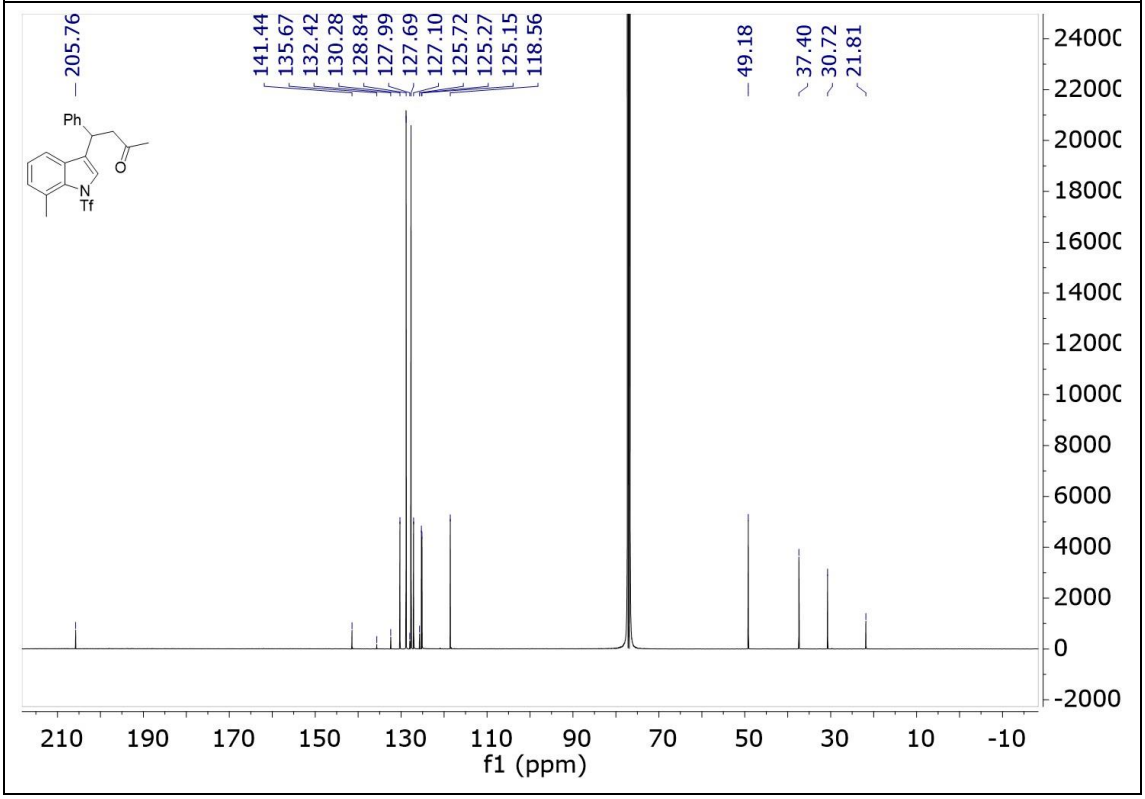

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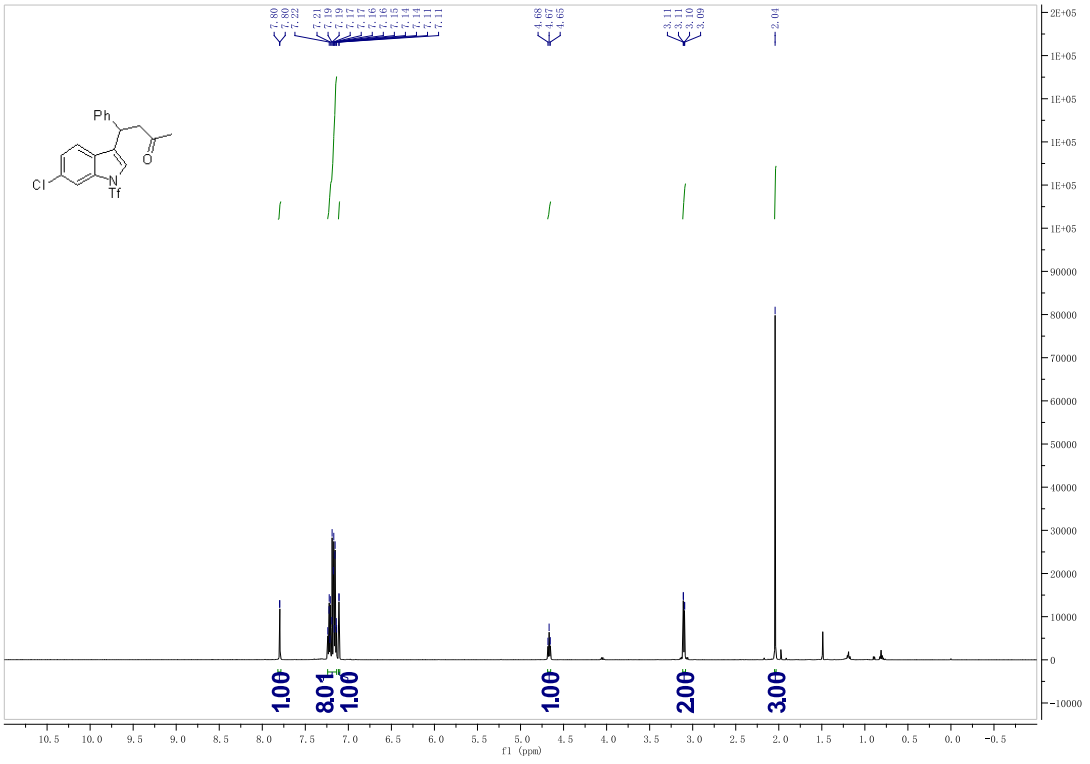
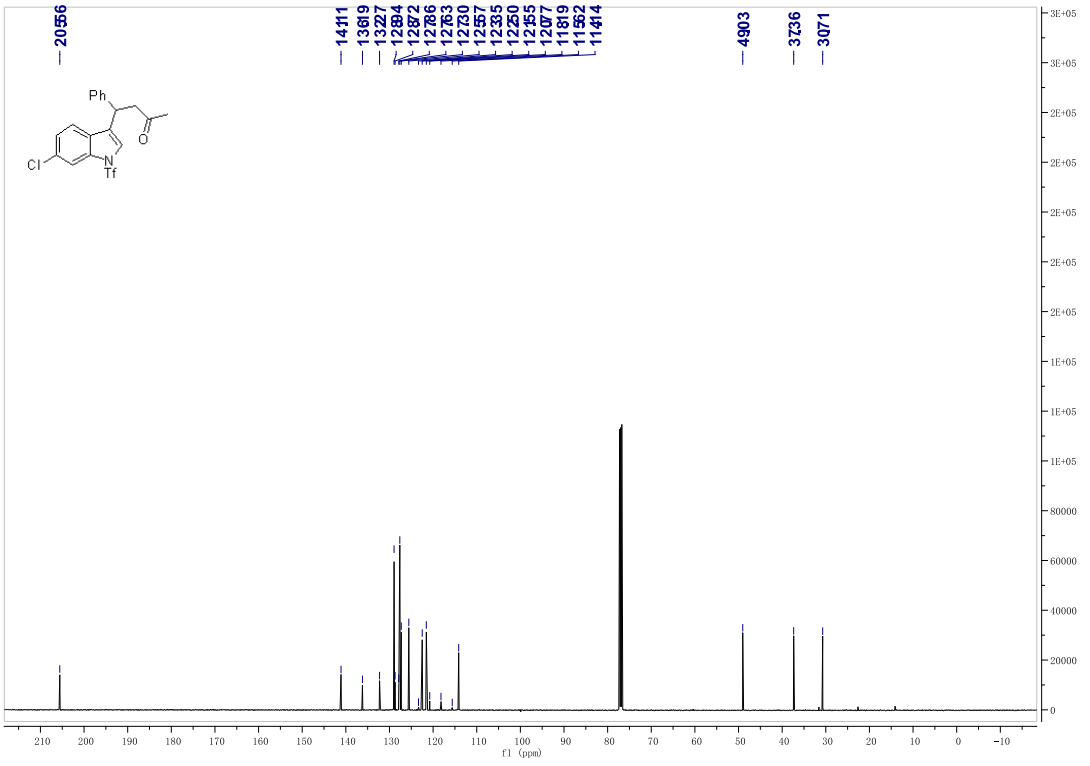
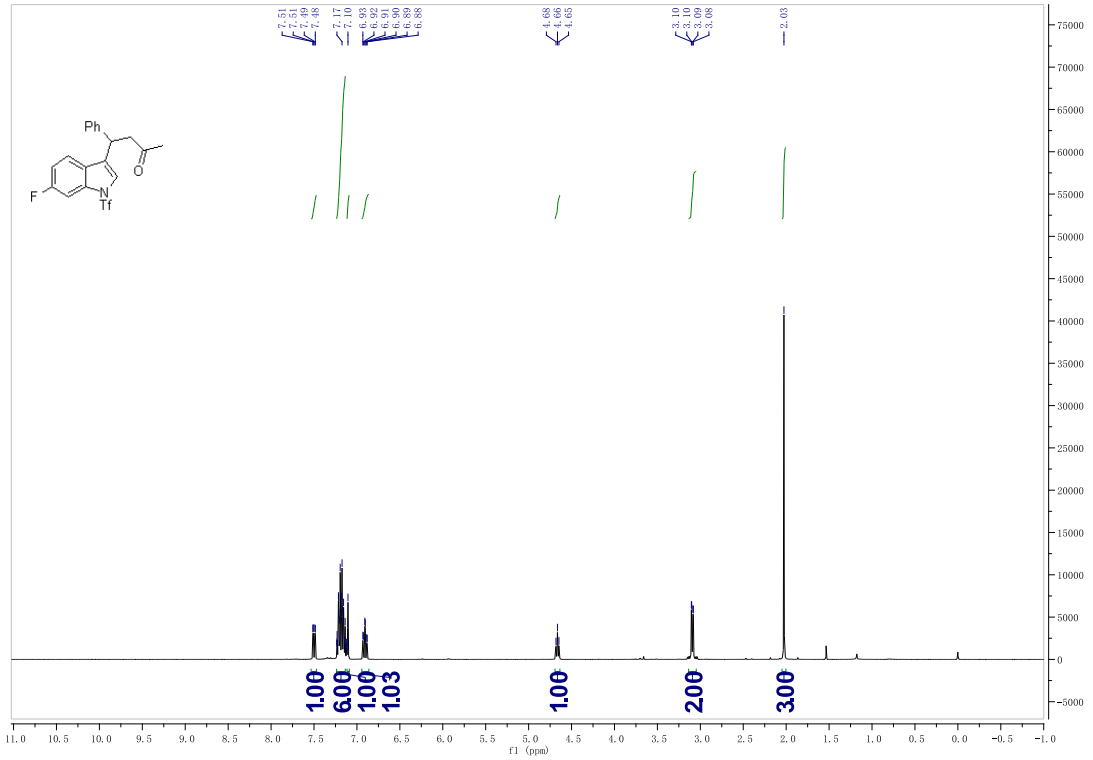


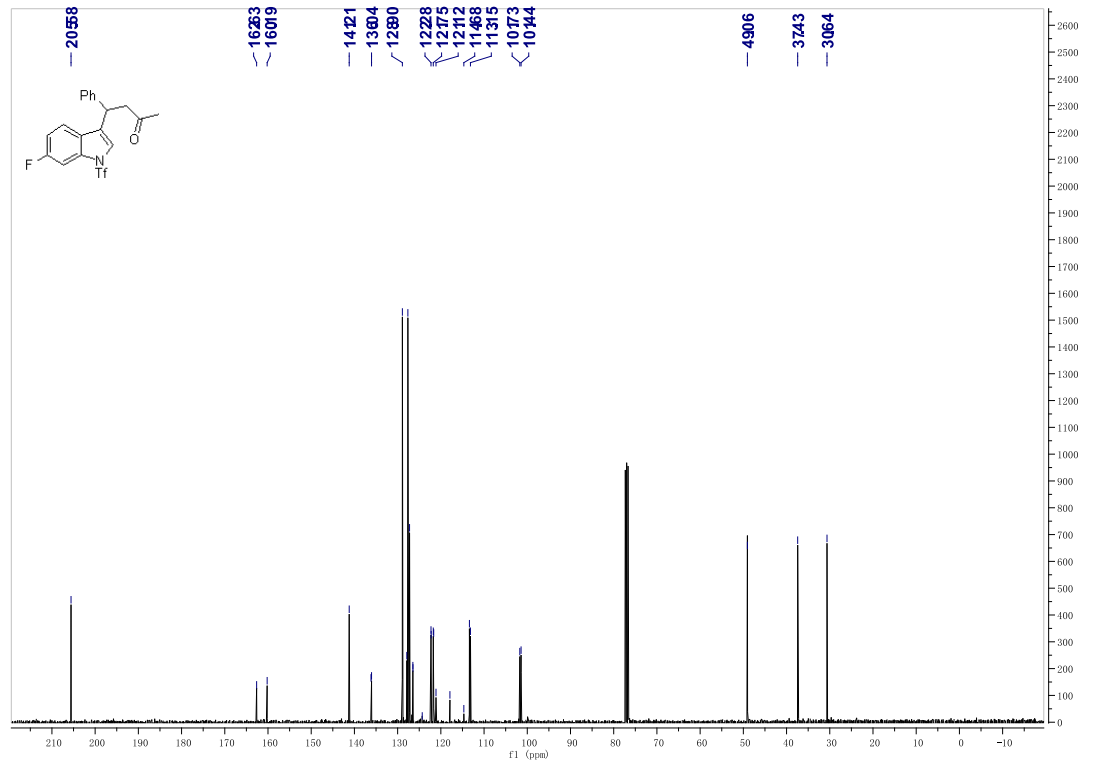
^{13}C NMR Spectra of **2k**



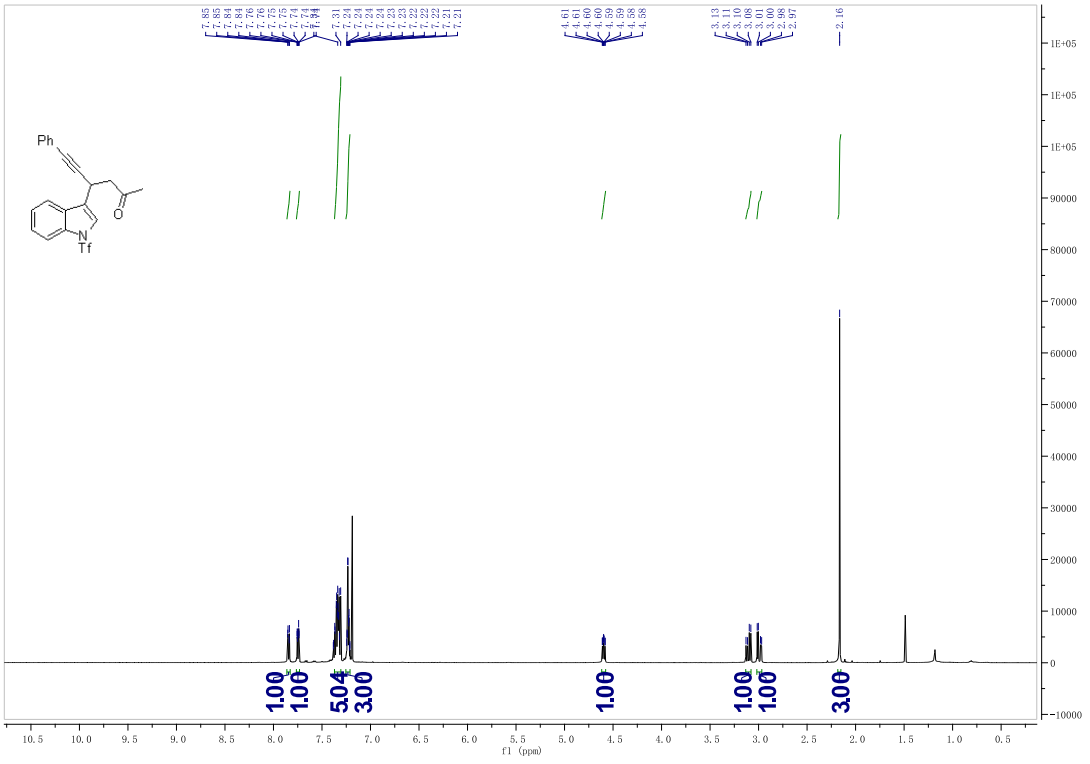
^{1}H NMR Spectra of **2l**



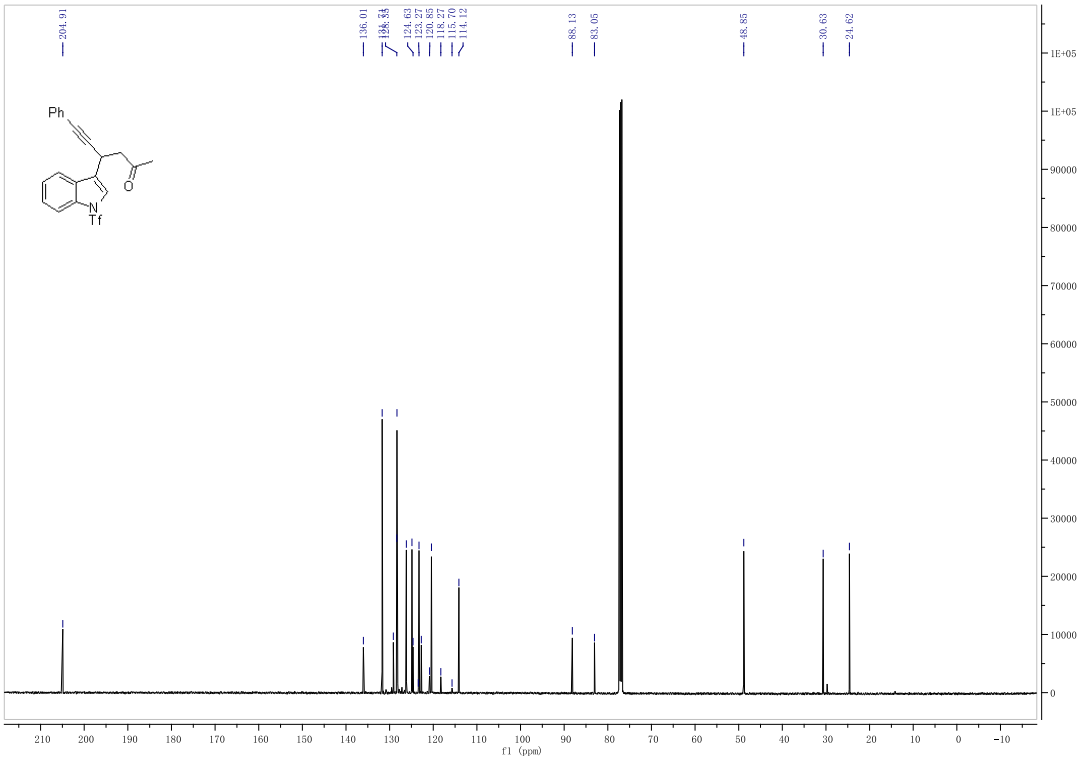
^{13}C NMR Spectra of **2l**



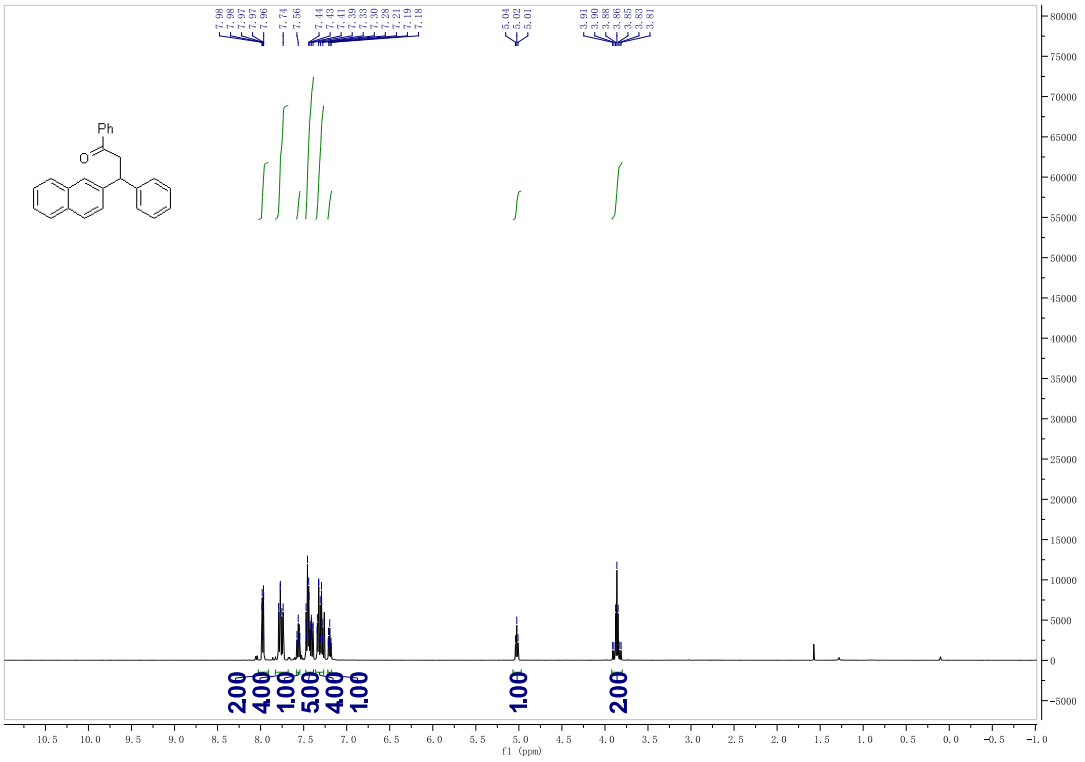
^{1}H NMR Spectra of **2m**



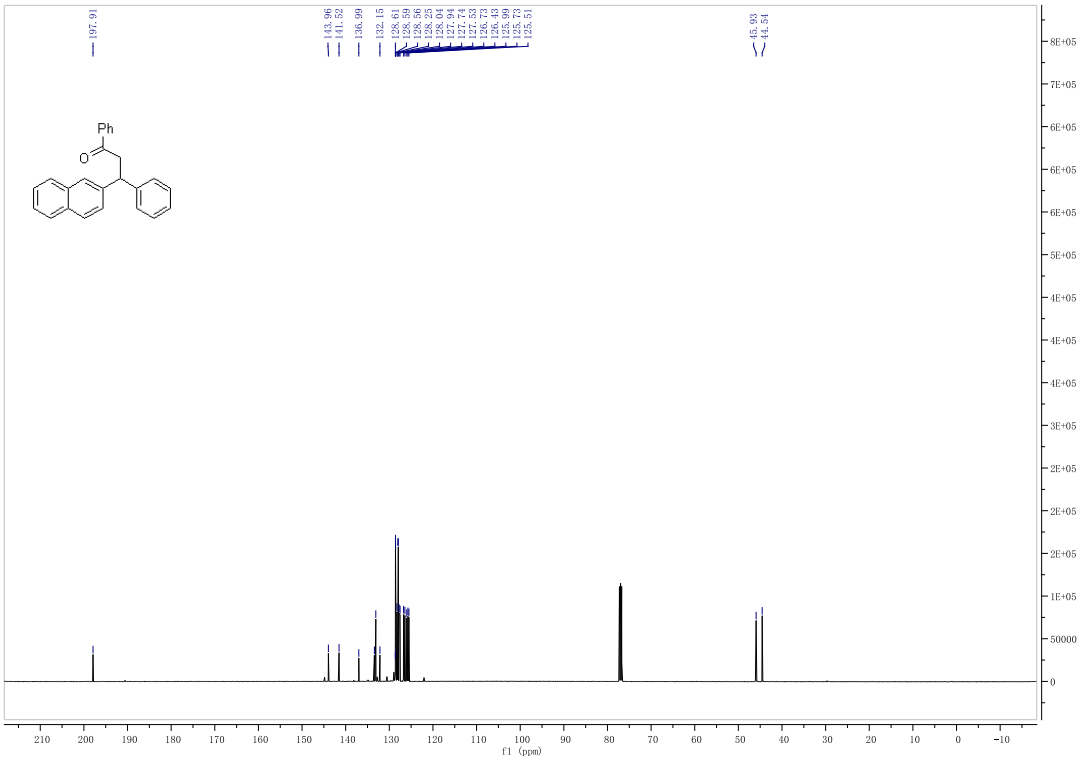
^{13}C NMR Spectra of **2m**



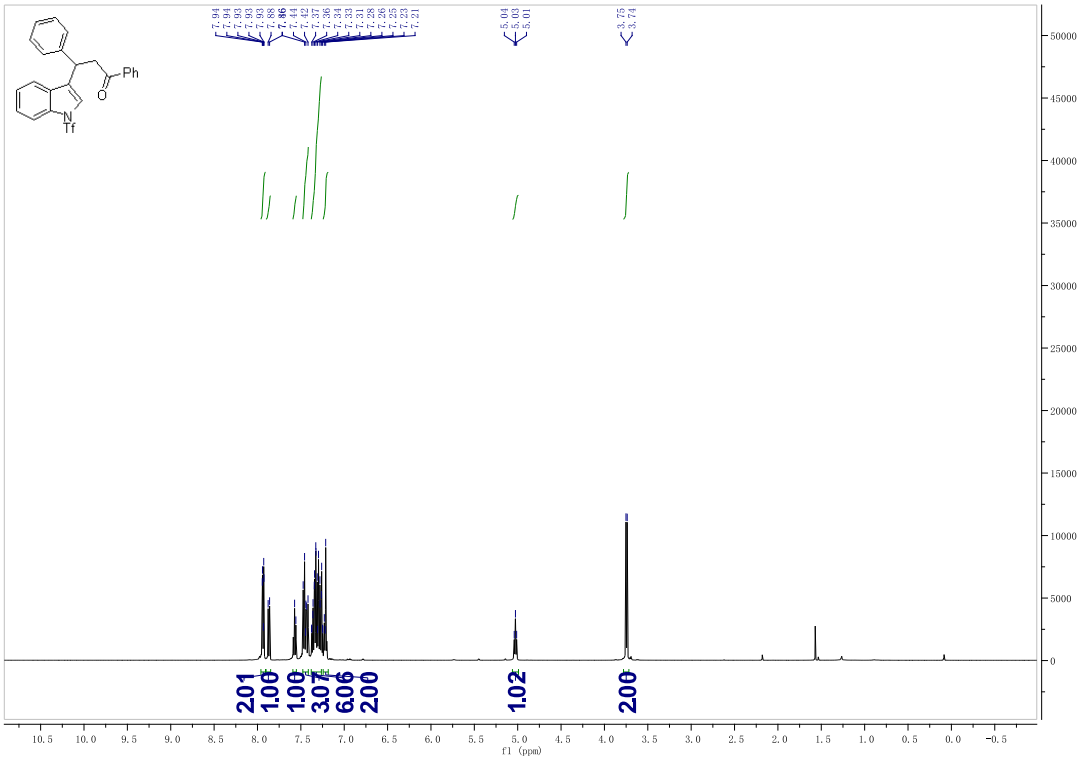
^{1}H NMR Spectra of **2n**



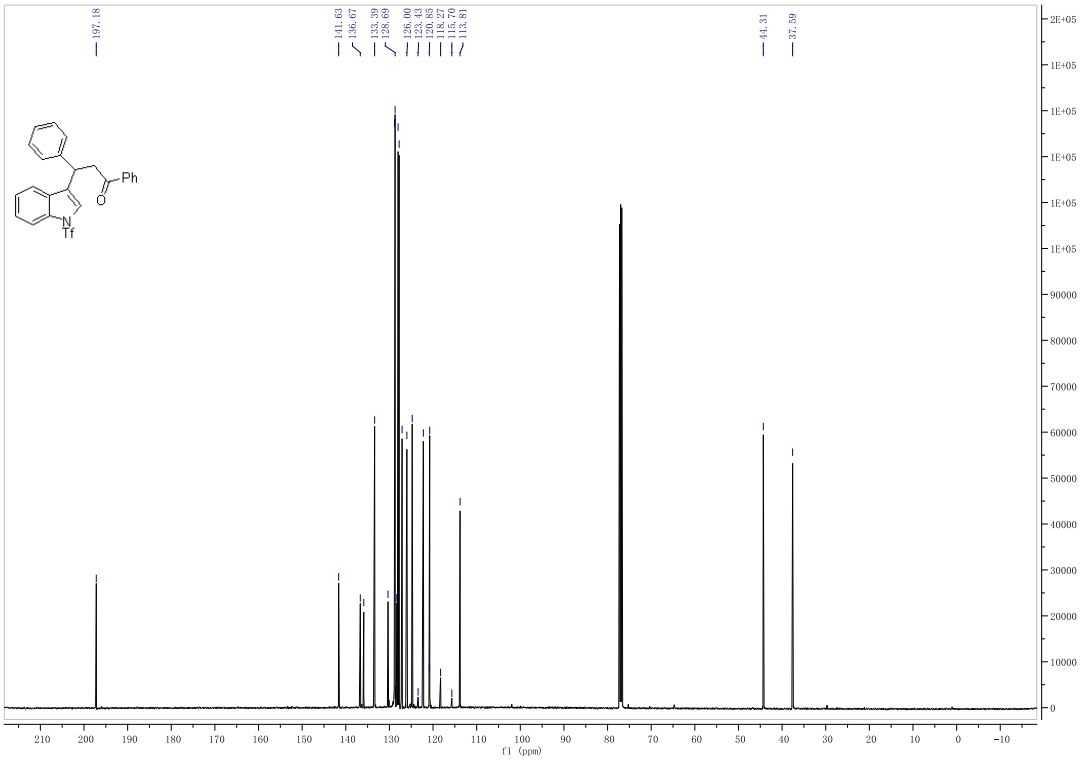
^{13}C NMR Spectra of **2n**



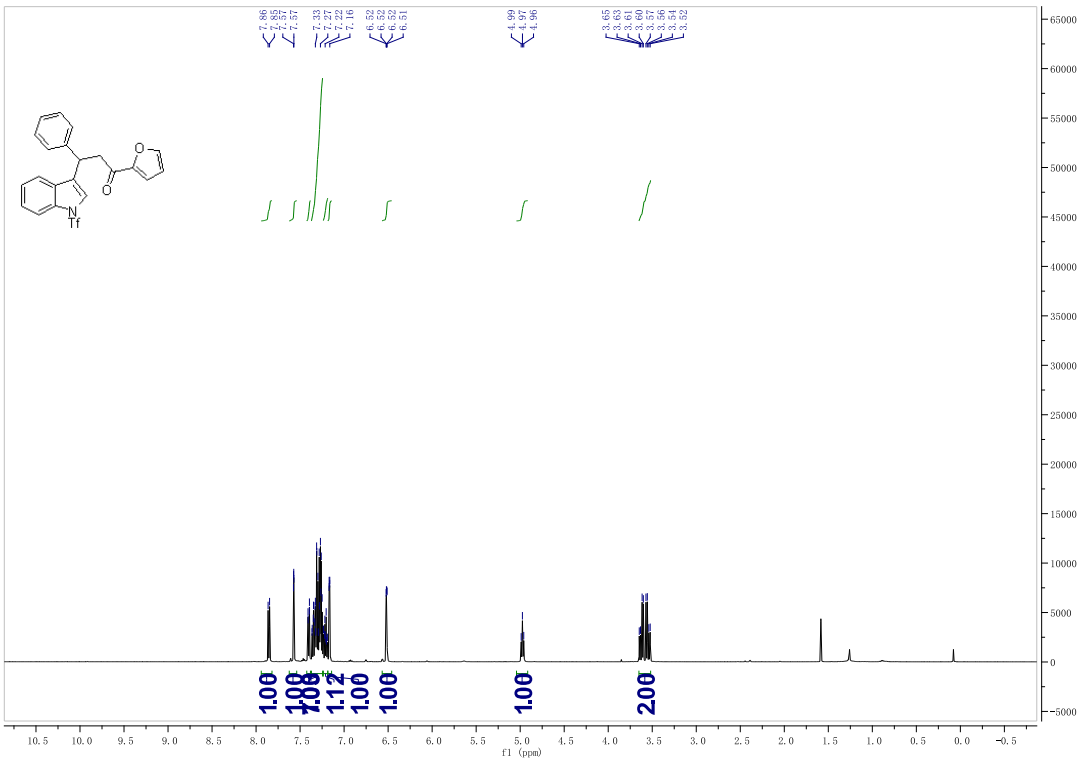
^{1}H NMR Spectra of **2o**



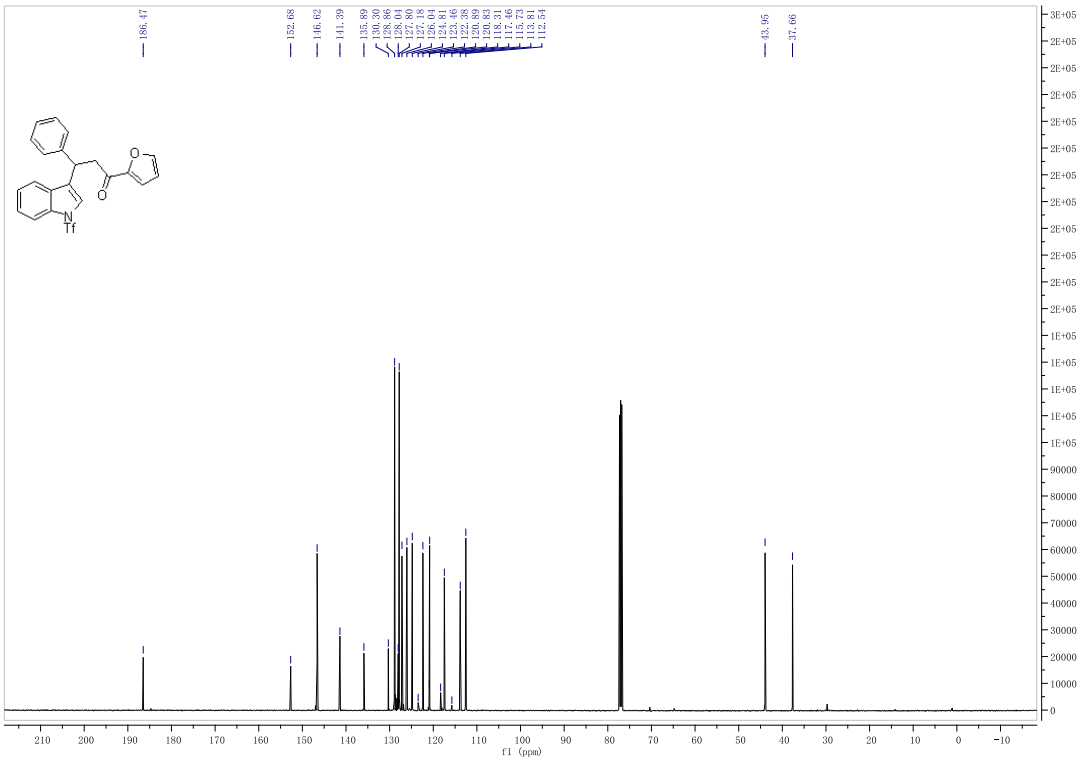
^{13}C NMR Spectra of **2o**



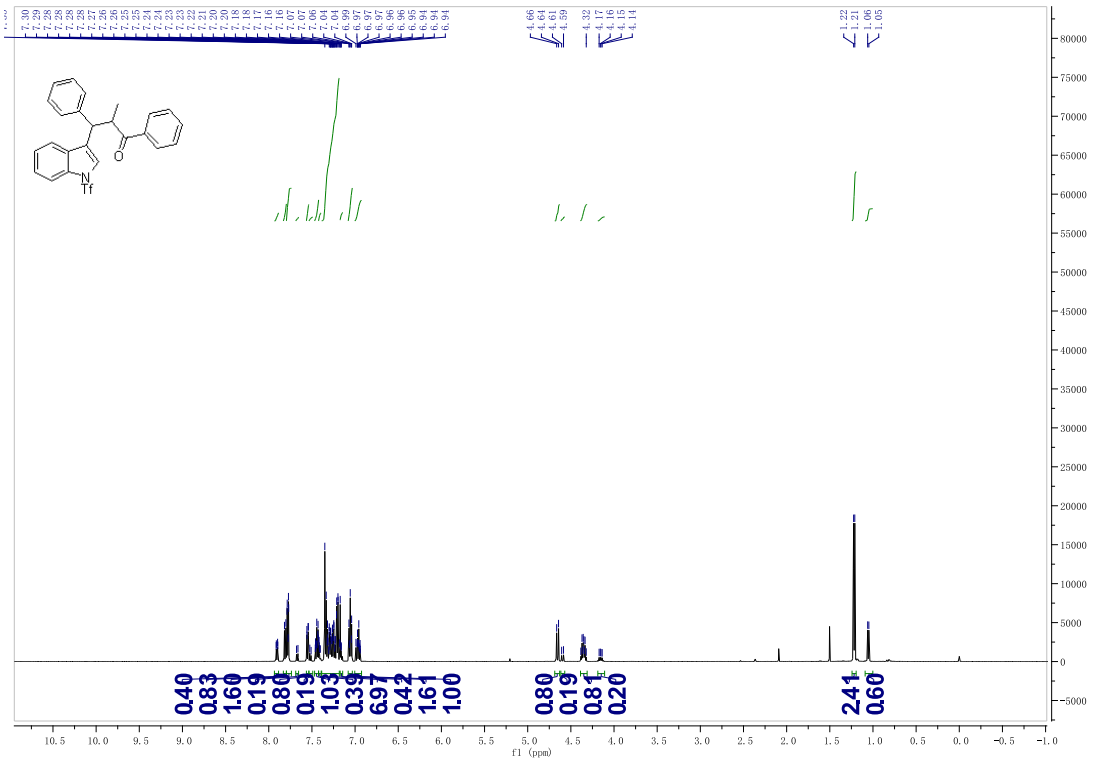
^{1}H NMR Spectra of **2p**



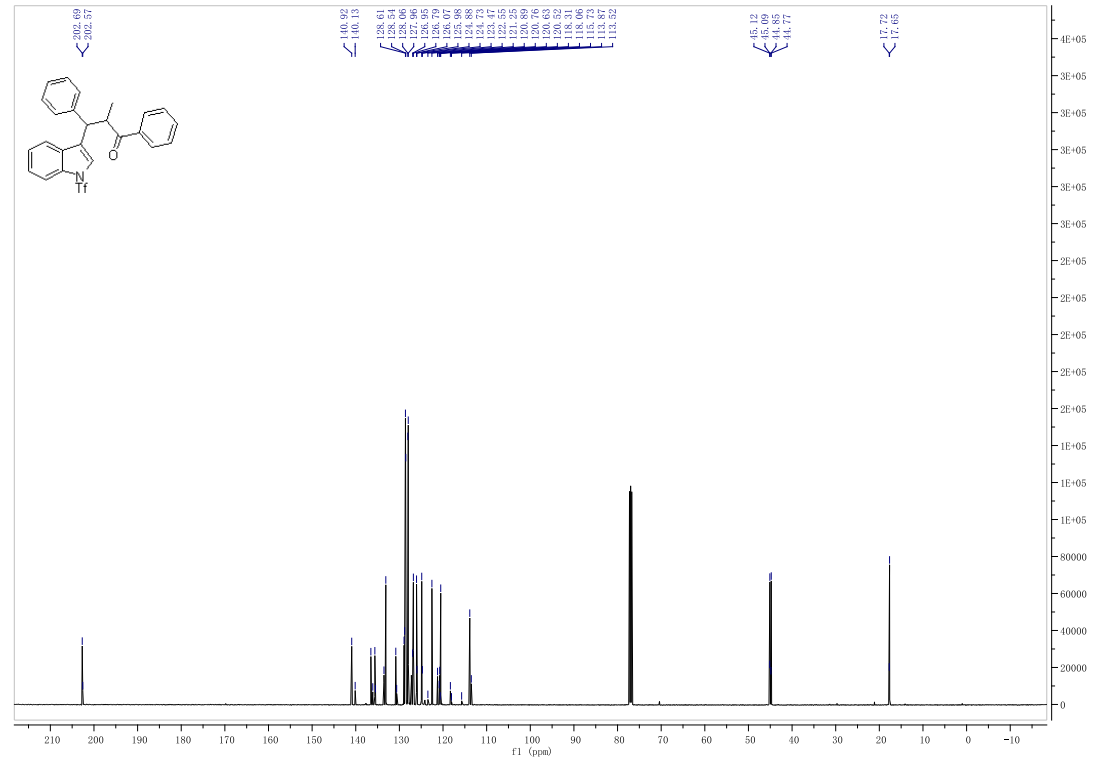
^{13}C NMR Spectra of **2p**



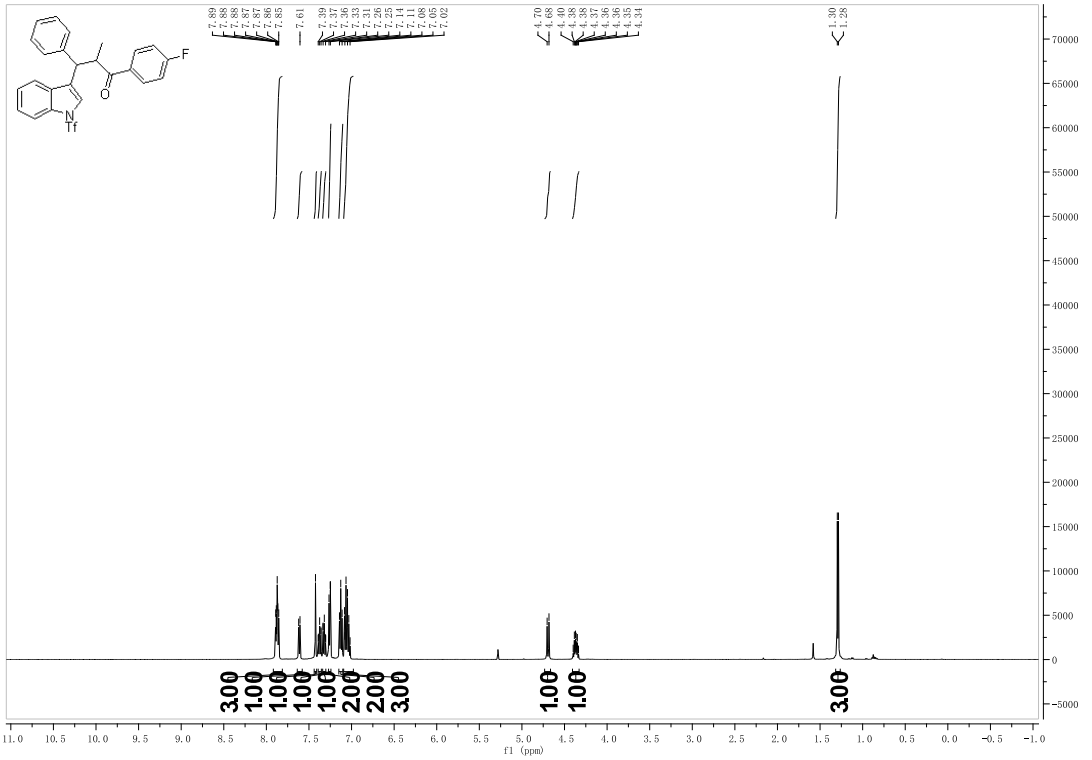
^{1}H NMR Spectra of **2q**



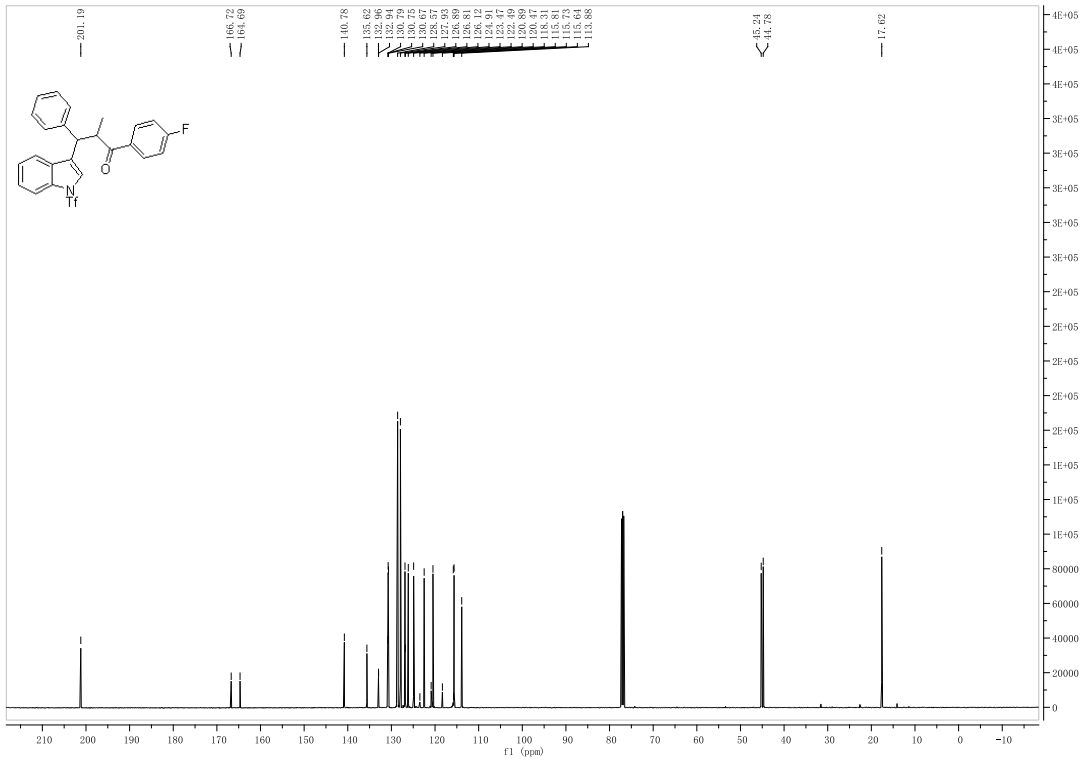
^{13}C NMR Spectra of **2q**



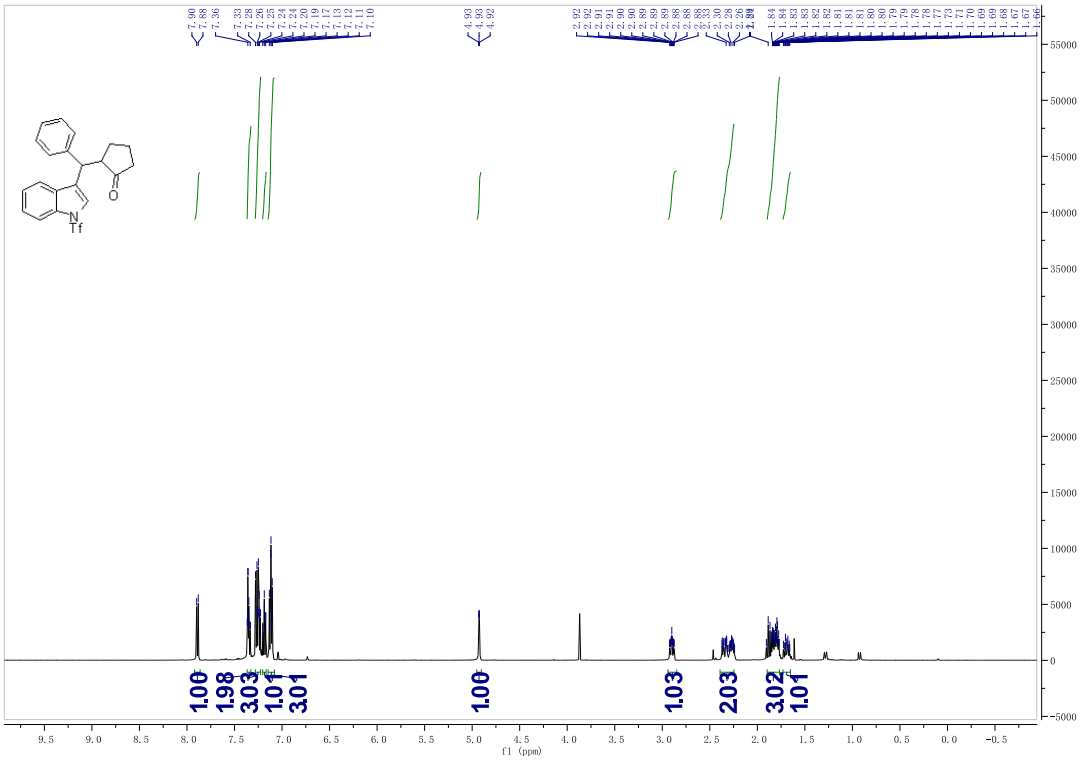
^{1}H NMR Spectra of **2r**



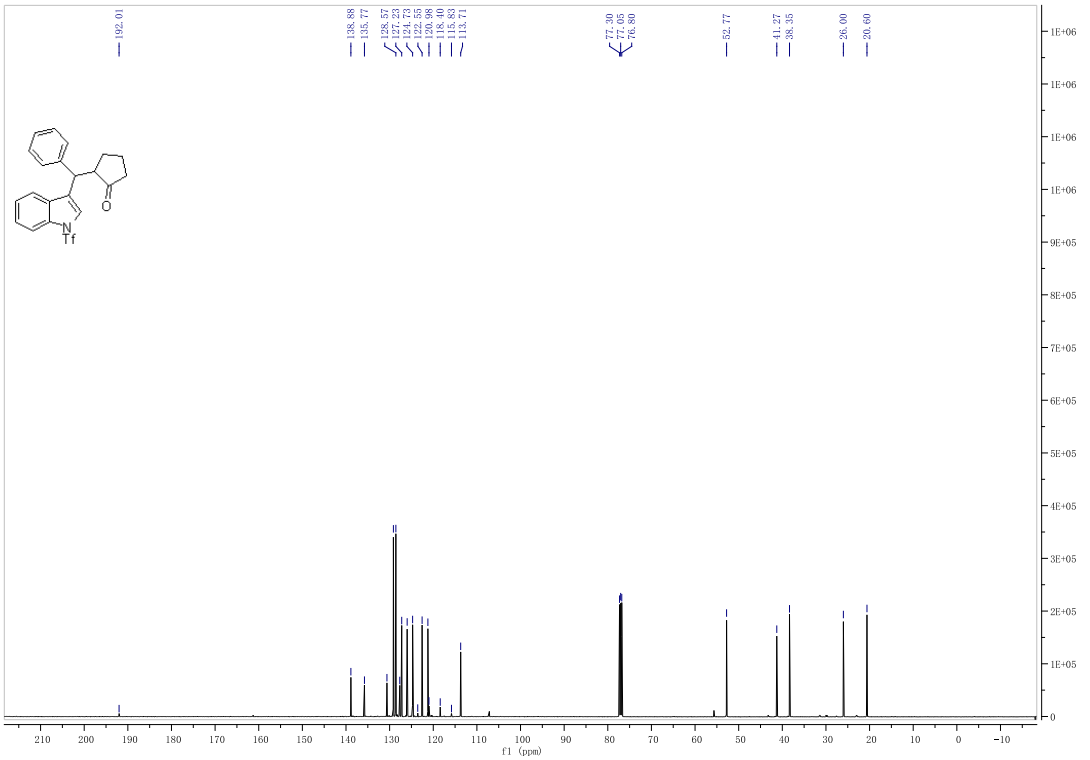
^{13}C NMR Spectra of **2r**



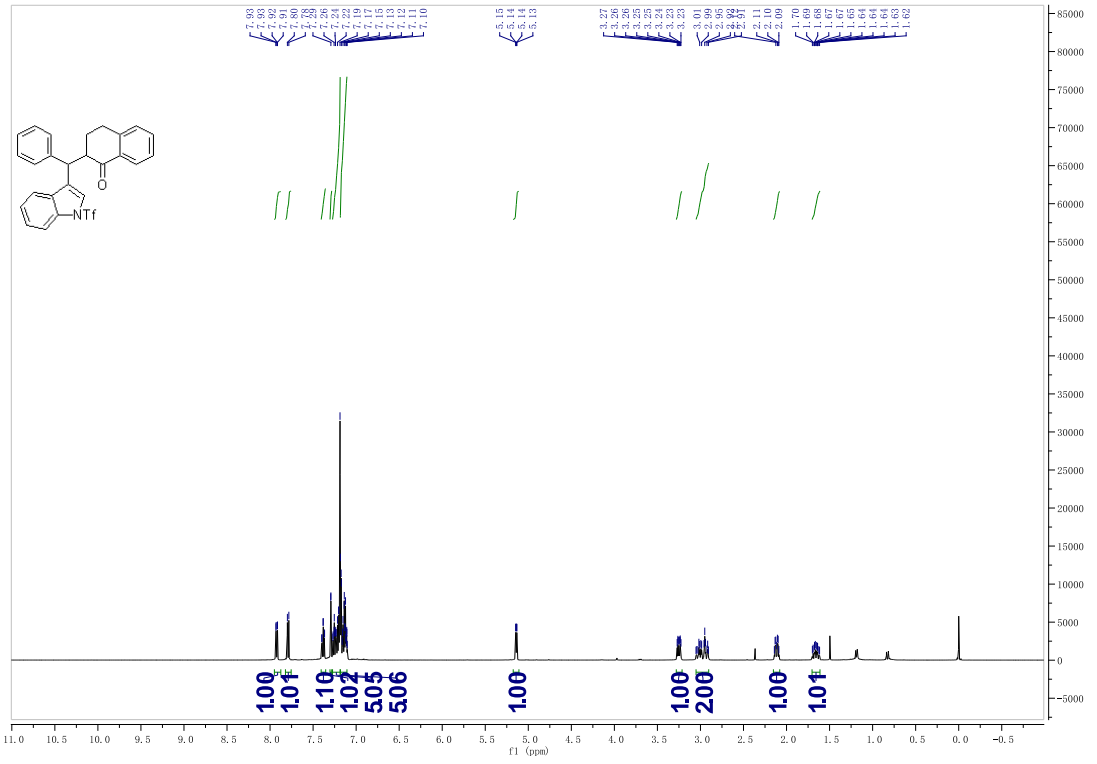
^{1}H NMR Spectra of **2s**



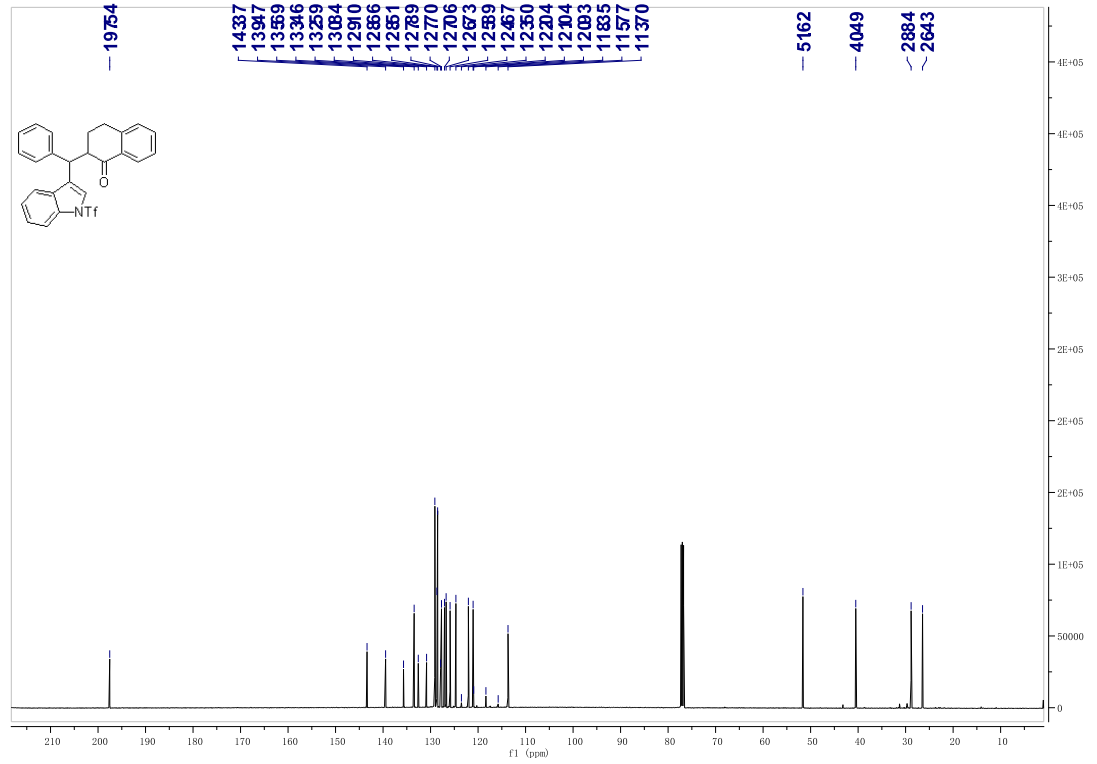
^{13}C NMR Spectra of **2s**



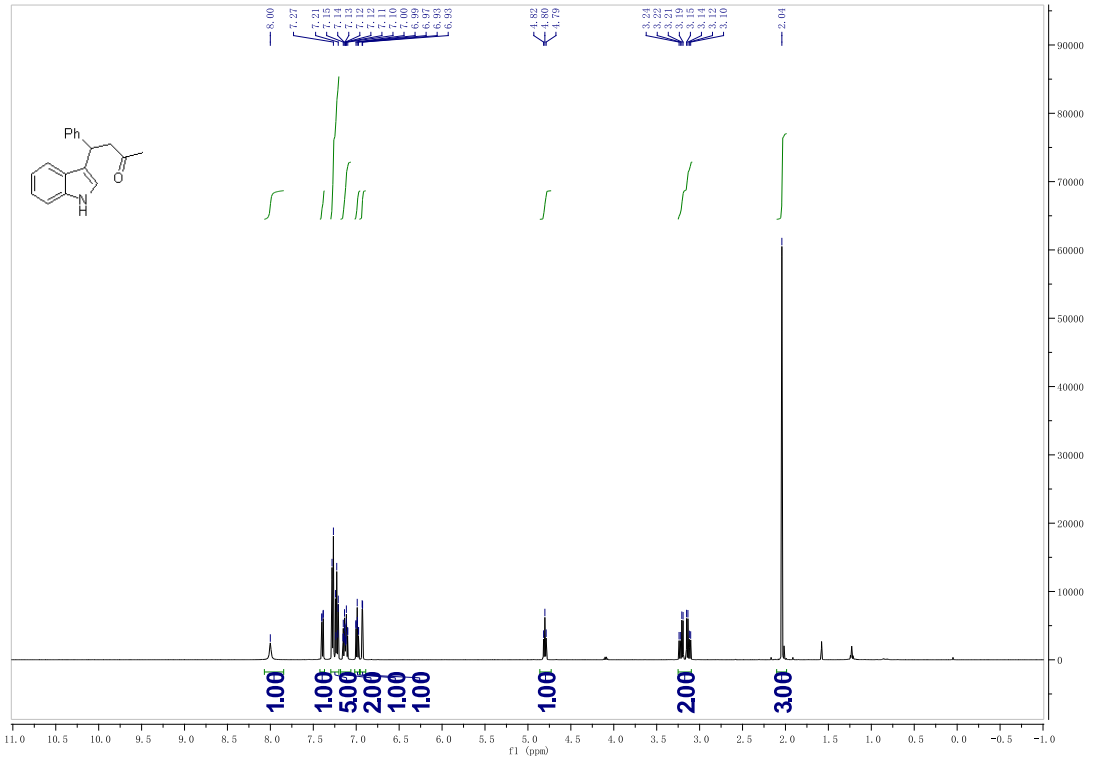
^{1}H NMR Spectra of **2t**



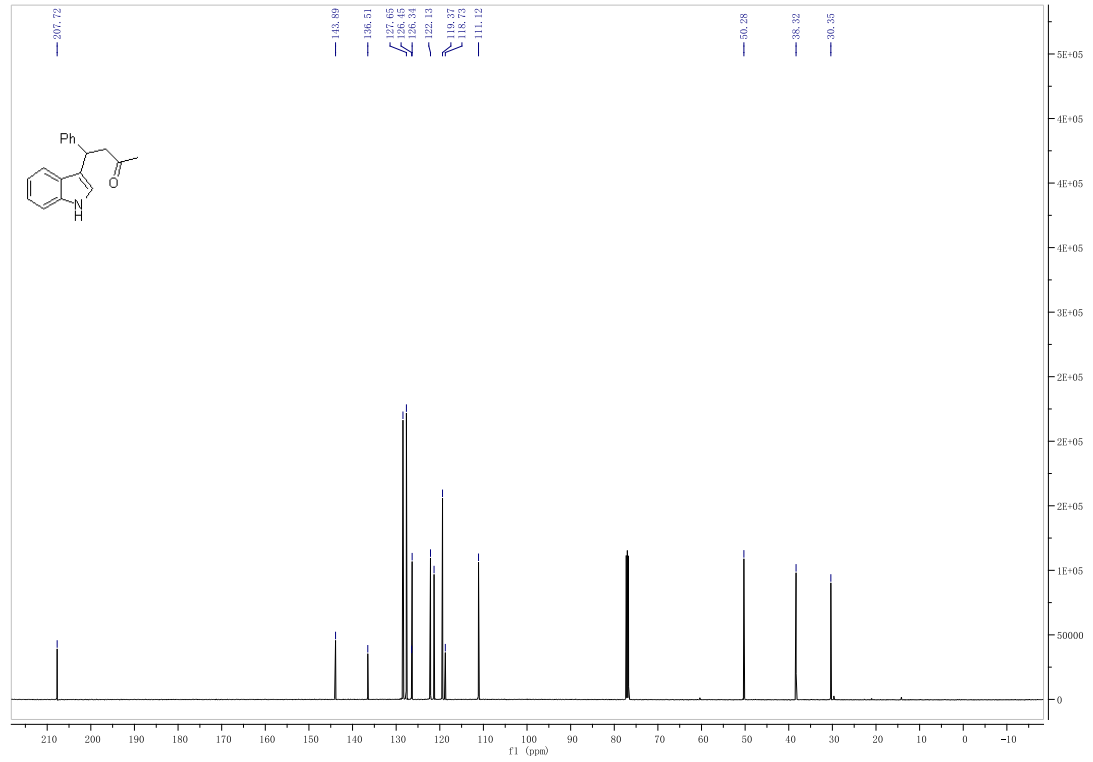
^{13}C NMR Spectra of **2t**



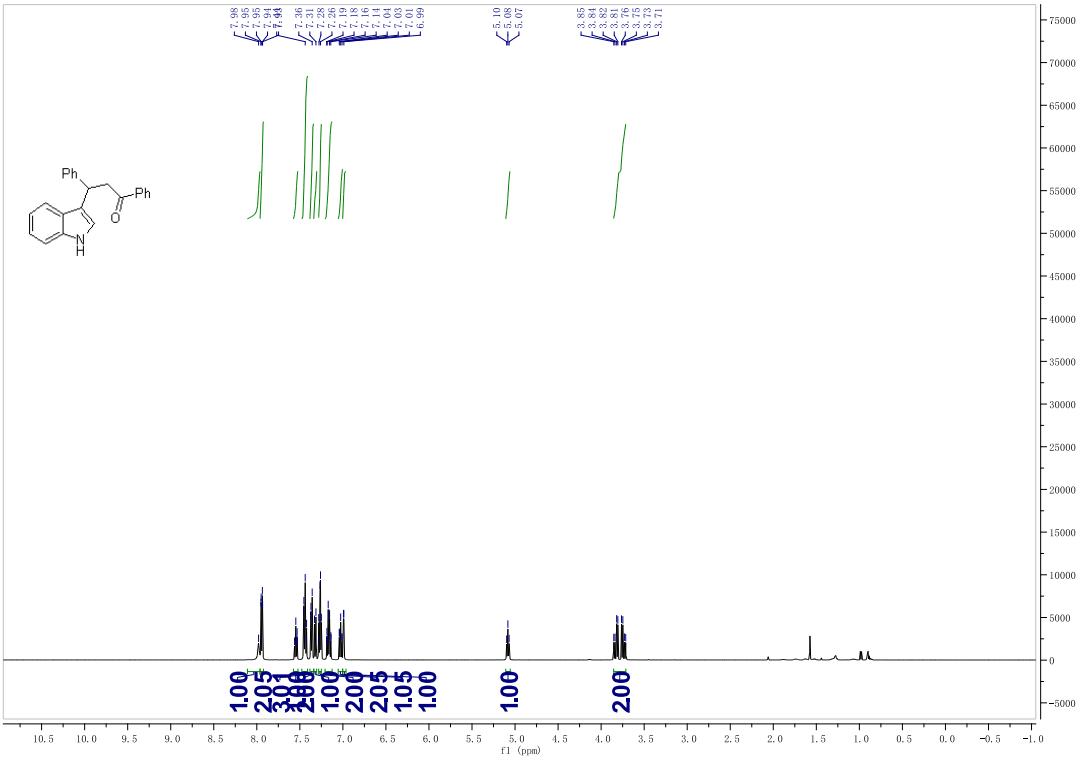
^{1}H NMR Spectra of **3a**



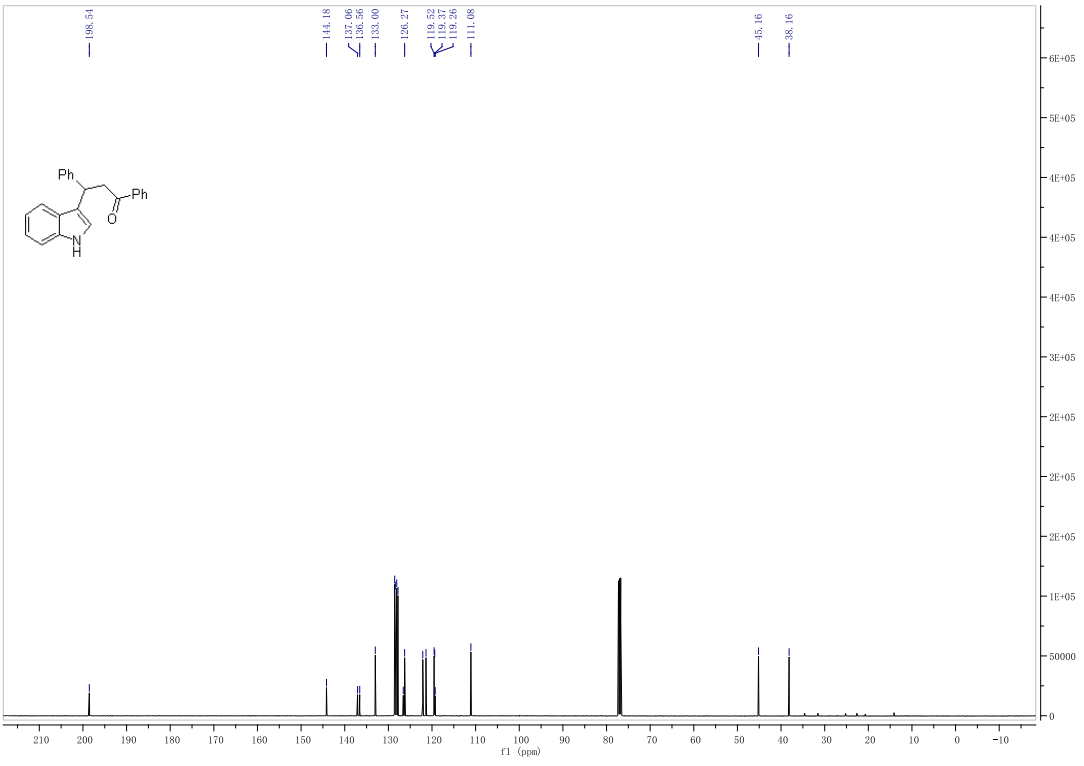
^{13}C NMR Spectra of **3a**



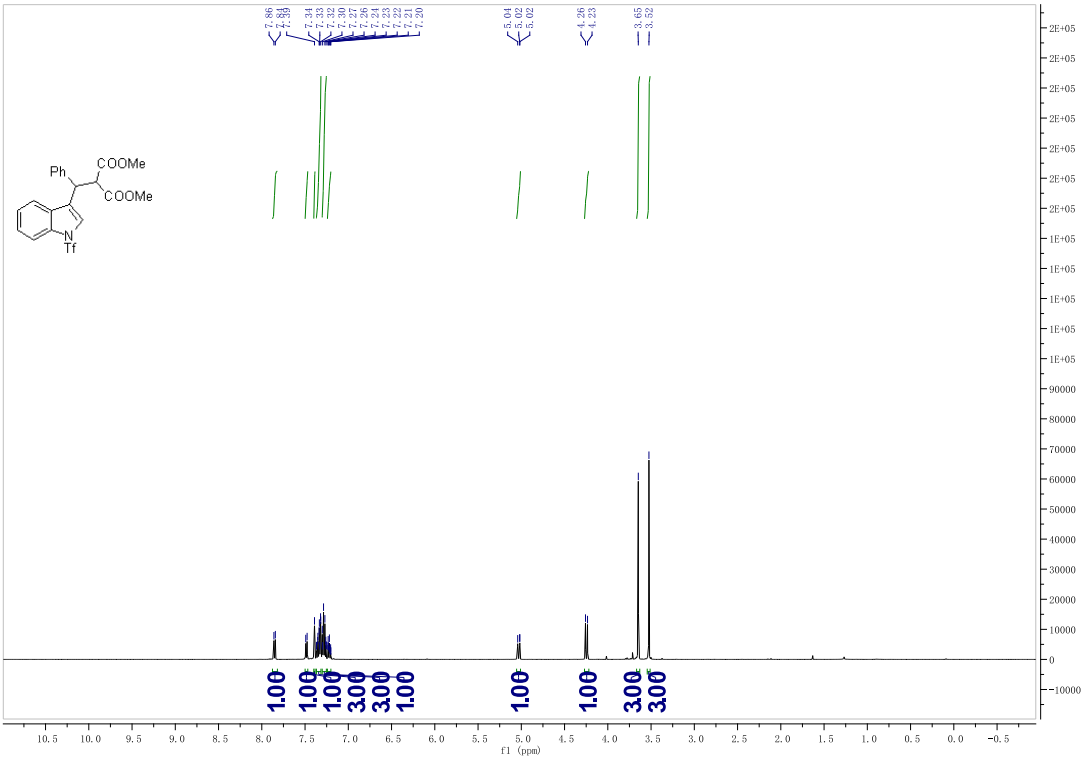
^{1}H NMR Spectra of **3o**



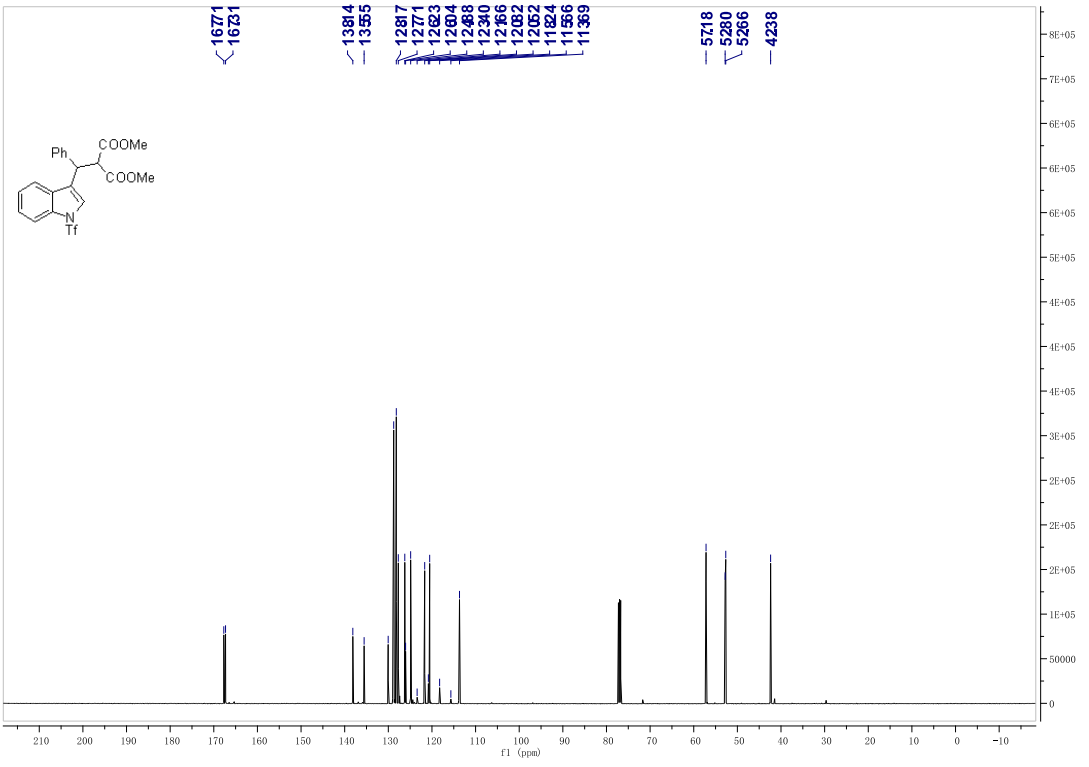
^{13}C NMR Spectra of **3o**



^{1}H NMR Spectra of **4a**

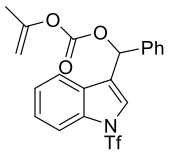


^{13}C NMR Spectra of **4a**



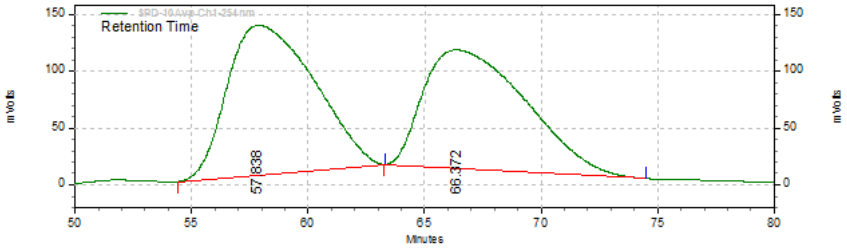
8. Copies of HPLC Spectra

Phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



Area % Report

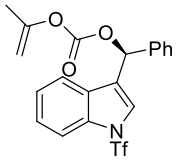
Data File: C:\EZStart\Data\Tian-Ren\LTR-167E AD 99.8-0.2@0.2 12.13.16.dat
Method: C:\EZStart\Methods\Shehani\99.8-0.2 at 0.2.met
Acquired: 12/13/2016 4:09:46 PM
Printed: 2/14/2017 10:39:07 PM



SPD-10Avp
Ch1-254nm
Results

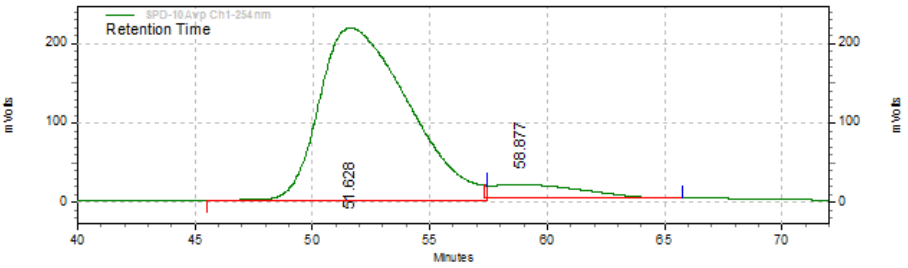
Retention Time	Area	Area %	Height	Height %
57.838	34018184	51.46	131673	55.83
66.372	32090597	48.54	104187	44.17
Totals				
	66108781	100.00	235860	100.00

(*S*)-phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



Area % Report

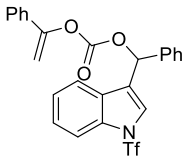
Data File: C:\EZStart\Data\Tian-Ren\LTR-235E AD 99.8-0.2@0.2 12.13.16.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 12/13/2016 5:44:01 PM
Printed: 2/25/2017 1:02:07 PM



SPD-10Avp
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
51.628	57758498	92.59	217954	92.72
58.877	4619501	7.41	17121	7.28
Totals				
	62377999	100.00	235075	100.00

Phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl (1-phenylvinyl) carbonate



Area % Report

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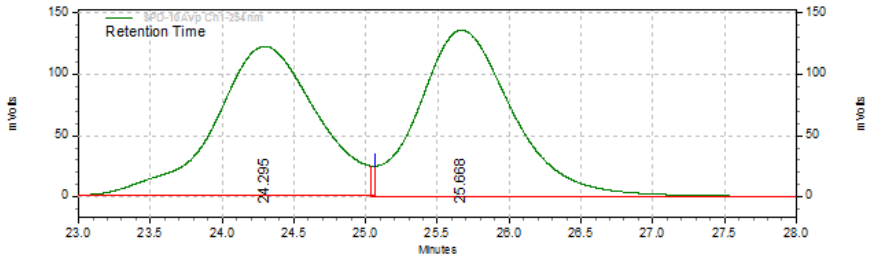
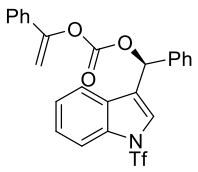
Method: C:\EZStart\Methods\Shehani\99-1 at 0.5.met
Acquired: 2/23/2017 4:49:43 PM
Printed: 2/23/2017 5:22:29 PM



SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
24.295	6073645	49.46	121499	47.27
25.668	6205754	50.54	135553	52.73
Totals				
	12279399	100.00	257052	100.00

(*S*)-phenyl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl (1-phenylvinyl) carbonate



Area % Report

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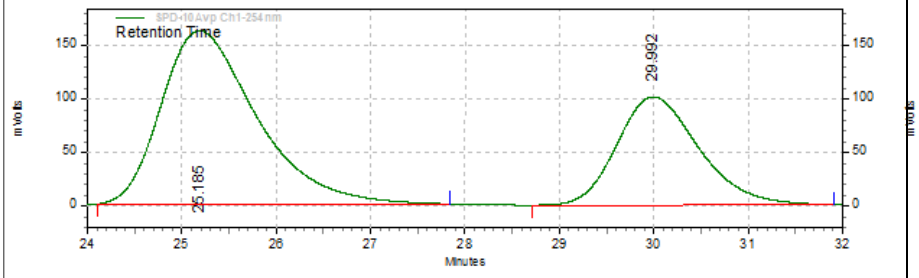
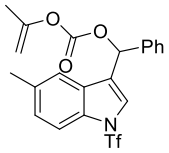
Acquired: 2/22/2017 10:11:22 PM
Printed: 2/25/2017 8:51:34 PM



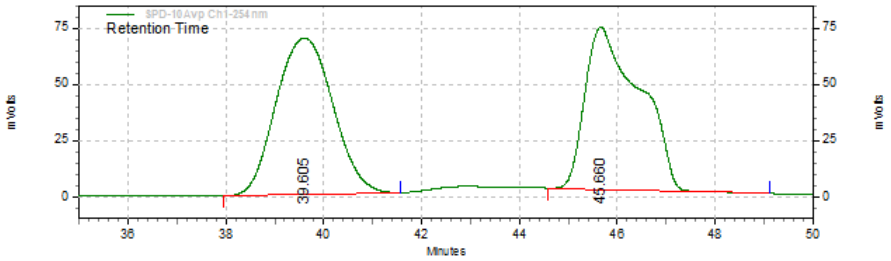
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
25.185	11379580	65.09	162058	61.61
29.992	6103613	34.91	100999	38.39
Totals				
	17483193	100.00	263057	100.00

(5-methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate



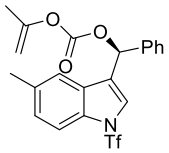
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr-239 AD-H 99.6-0.4@0.2 12.31.16.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 12/31/2016 4:19:42 PM
Printed: 2/15/2017 12:39:43 PM



SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
39.605	5613187	49.96	69487	49.09
45.660	5622225	50.04	72072	50.91
Totals				
	11235412	100.00	141559	100.00

(*S*)-(5-methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate



Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr-284 AD-H 99.6-0.4@0.2 12.31.16.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
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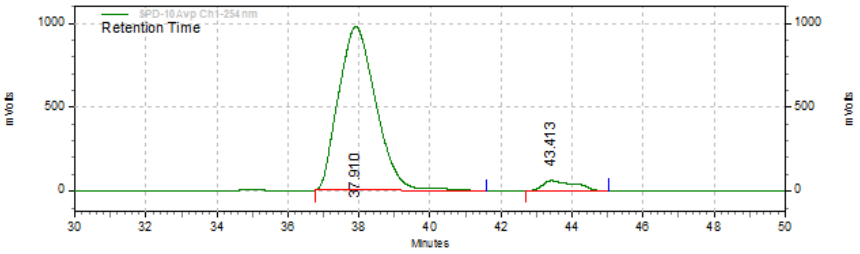
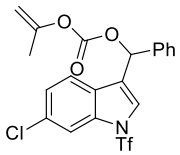


SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
37.910	71001755	95.09	975134	94.26
43.413	3666503	4.91	59340	5.74
Totals				
	74668258	100.00	1034474	100.00

(6-chloro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate



Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr-250c AD-H 99.6-0.4@0.2 12.31.16.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
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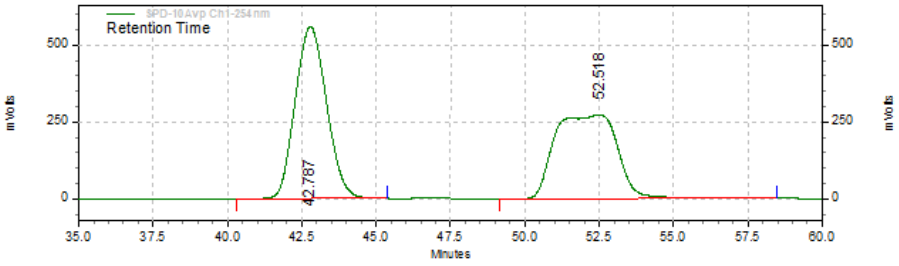
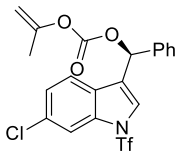


SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
42.787	41006785	50.64	558236	67.17
52.518	39976282	49.36	272876	32.83
Totals				
	80983067	100.00	831112	100.00

(*S*)-(6-chloro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)(phenyl)methyl prop-1-en-2-yl carbonate



Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr-283b AD-H 99.6-0.4@0.2 12.31.16.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
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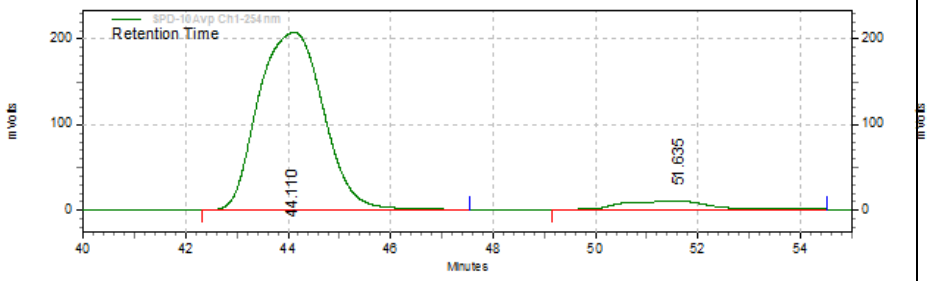
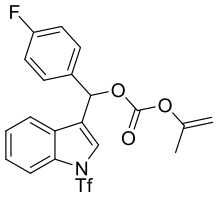


SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
44.110	18185022	94.21	207062	95.63
51.635	1117307	5.79	9473	4.37
Totals				
	19302329	100.00	216535	100.00

(4-Fluorophenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



Area % Report

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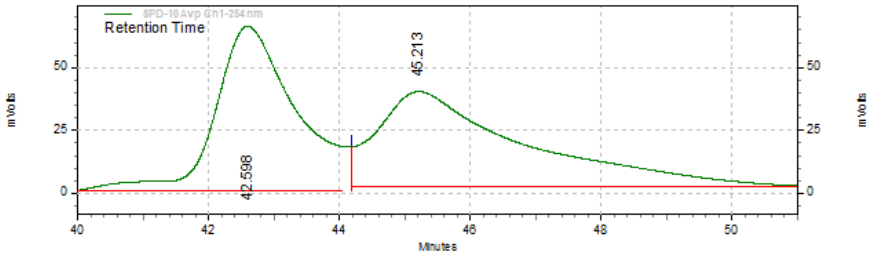
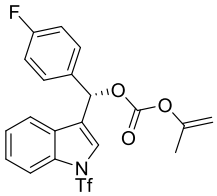


SPD-10Avp Ch1-254nm Results

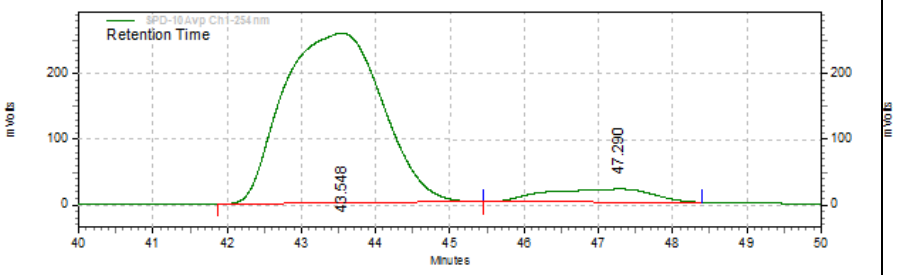
Retention Time	Area	Area %	Height	Height %
42.598	5671472	49.44	65663	63.58
45.213	5800829	50.56	37619	36.42
Totals	11472301	100.00	103282	100.00

(*S*)-(4-fluorophenyl)(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



Area % Report

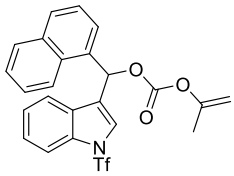
Data File: C:\EZStart\Data\Tian-Ren\ltr-285 AD-H 99.6-0.4@0.2 12.31.16.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 12/31/2016 9:31:30 PM
Printed: 2/15/2017 12:46:30 PM



SPD-10Avp Ch1-254nm Results

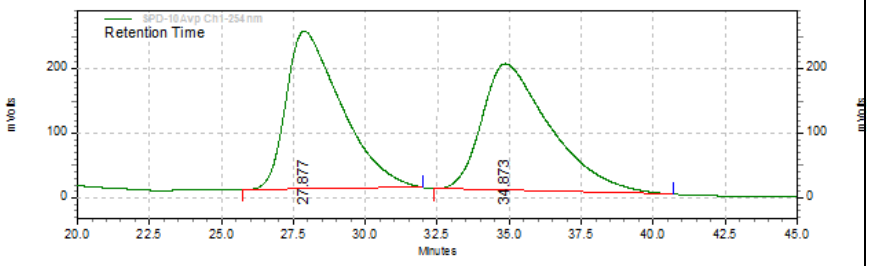
Retention Time	Area	Area %	Height	Height %
43.548	23990425	92.16	259049	92.81
47.290	2040752	7.84	20069	7.19
Totals	26031177	100.00	279118	100.00

Naphthalen-1-yl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



Area % Report

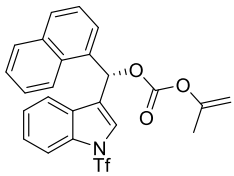
Data File: C:\EZStart\Data\Tian-Ren\ltr-267 AD-H 99.6-0.4@0.2 01.01.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/1/2017 1:27:58 PM
Printed: 2/15/2017 1:10:36 PM



SPD-10Avp Ch1-254nm Results

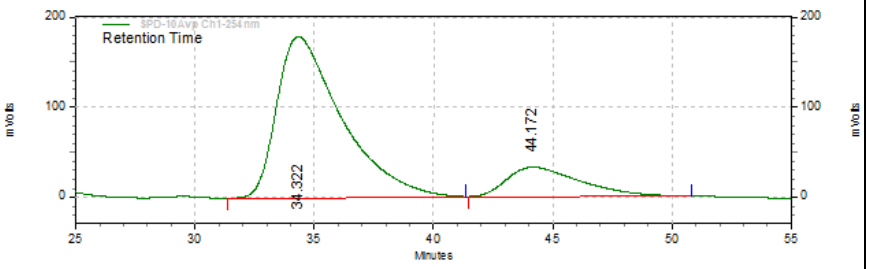
Retention Time	Area	Area %	Height	Height %
27.877	32630182	50.10	244350	55.48
34.873	32500148	49.90	196112	44.52
Totals				
	65130330	100.00	440462	100.00

(S)-naphthalen-1-yl(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)methyl prop-1-en-2-yl carbonate



Area % Report

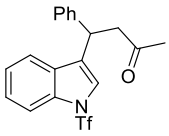
Data File: C:\EZStart\Data\Tian-Ren\ltr-290 AD-H 99.6-0.4@0.2 01.03.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/3/2017 11:50:30 AM
Printed: 2/15/2017 1:11:34 PM



SPD-10Avp Ch1-254nm Results

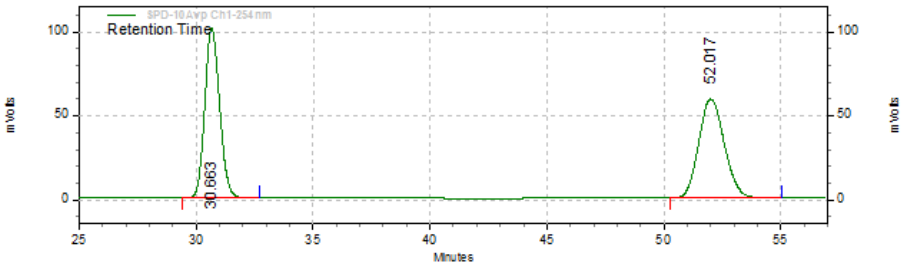
Retention Time	Area	Area %	Height	Height %
34.322	33701119	83.16	178769	84.70
44.172	6826720	16.84	32282	15.30
Totals				
	40527839	100.00	211051	100.00

4-Phenyl-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



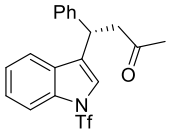
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\LTR-238 OD-H 98-2@0.5 12.11.16.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 12/11/2016 8:03:07 PM
Printed: 2/15/2017 12:36:13 PM



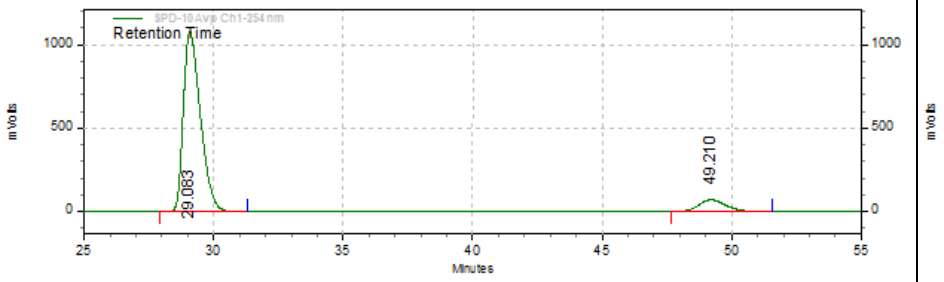
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
30.663	4439904	50.02	101140	63.31
52.017	4436261	49.98	58602	36.69
Totals				
	8876165	100.00	159742	100.00

(*S*)-4-phenyl-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



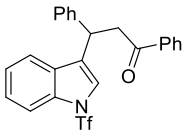
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\LTR-235 OD-H 98-2@0.5 12.11.16.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 12/11/2016 6:07:41 PM
Printed: 2/15/2017 12:37:30 PM



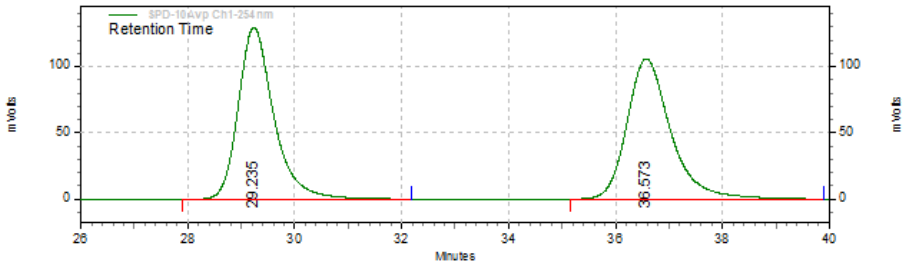
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
29.083	49096333	90.76	1077483	93.94
49.210	4999016	9.24	69522	6.06
Totals				
	54095349	100.00	1147005	100.00

1,3-Diphenyl-3-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)propan-1-one



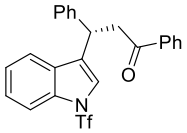
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr309-2 AD-H 98-2@0.5 02.21.17.dat
Method: C:\EZStart\Methods\Shehani\99-1 at 0.5.met
Acquired: 2/21/2017 4:26:44 PM
Printed: 2/23/2017 5:27:40 PM



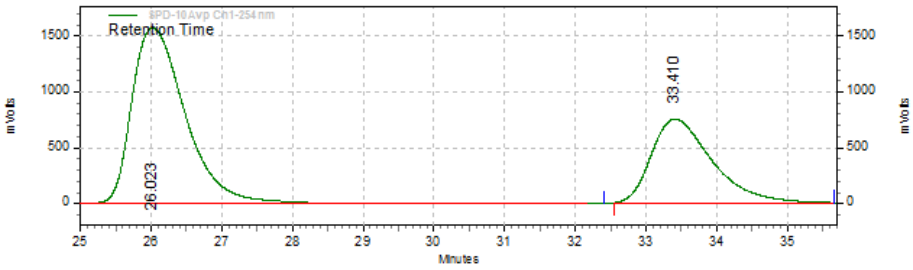
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
29.235	6002229	49.90	129729	55.04
36.573	6027119	50.10	105980	44.96
Totals				
	12029348	100.00	235709	100.00

(*S*)-1,3-diphenyl-3-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)propan-1-one



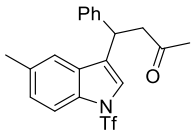
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr367 AD-H 98-2@0.5 02.21.17.dat
Method: C:\EZStart\Methods\Old Methods\10% wash.met
Acquired: 2/21/2017 6:03:54 PM
Printed: 2/25/2017 8:36:13 PM



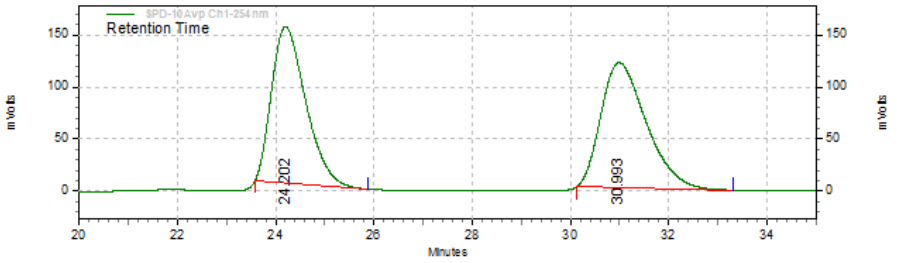
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
26.023	82797004	65.08	1571002	67.72
33.410	44418756	34.92	748797	32.28
Totals				
	127215760	100.00	2319799	100.00

4-(5-Methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one



Area % Report

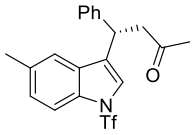
Data File: C:\EZStart\Data\Tian-Ren\ltr-239 OD 98-2@0.5 01.01.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/2/2017 9:20:59 PM
Printed: 2/15/2017 1:34:09 PM



SPD-10Avp Ch1-254nm Results

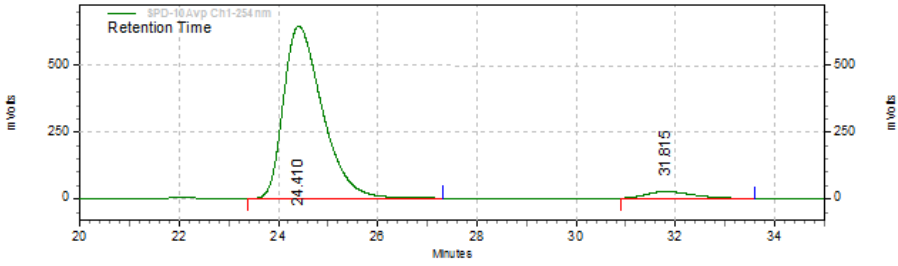
Retention Time	Area	Area %	Height	Height %
24.202	7225009	48.41	149867	55.50
30.993	7700151	51.59	120178	44.50
Totals				
	14925160	100.00	270045	100.00

(*S*)-4-(5-methyl-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one



Area % Report

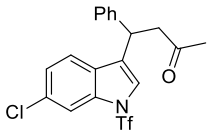
Data File: C:\EZStart\Data\Tian-Ren\ltr-287 AD-H 98-2@0.5 01.03.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/3/2017 3:19:42 PM
Printed: 2/15/2017 1:06:45 PM



SPD-10Avp Ch1-254nm Results

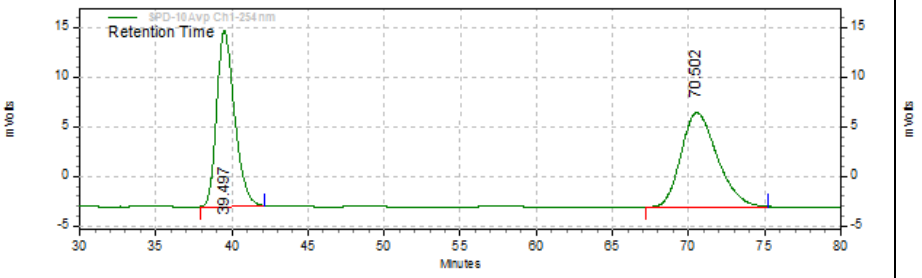
Retention Time	Area	Area %	Height	Height %
24.410	35038623	95.53	645471	96.24
31.815	1640145	4.47	25236	3.76
Totals				
	36678768	100.00	670707	100.00

4-(6-Chloro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one



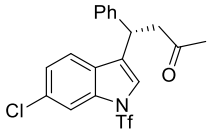
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr-259b OD 98-2@0.5 01.04.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/4/2017 4:10:12 PM
Printed: 2/15/2017 1:40:29 PM



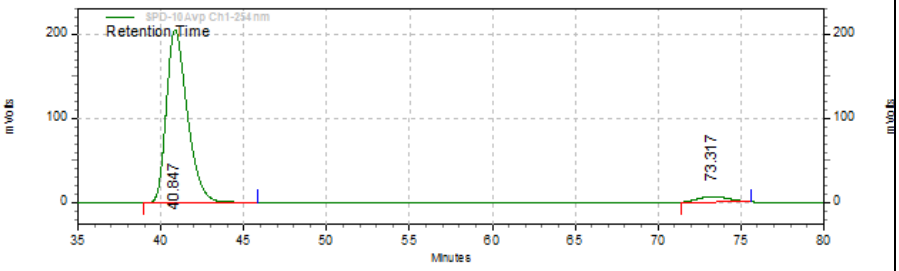
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
39.497	1446384	47.95	17750	65.15
70.502	1570001	52.05	9493	34.85
Totals				
	3016385	100.00	27243	100.00

(*S*)-4-(6-chloro-1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)-4-phenylbutan-2-one



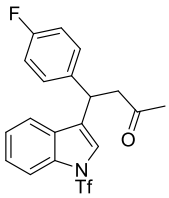
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr-286b OD 98-2@0.5 01.04.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/4/2017 5:52:58 PM
Printed: 2/15/2017 1:42:56 PM



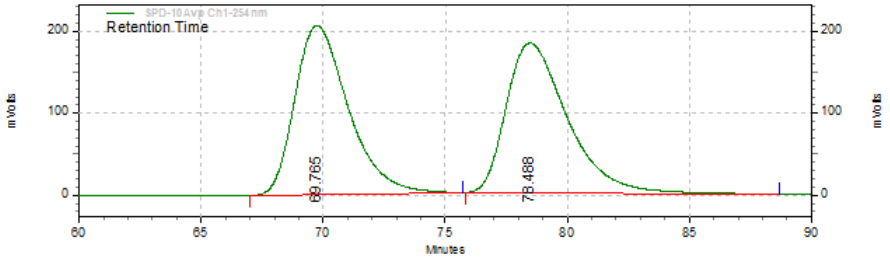
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
40.847	18048919	95.27	205147	96.77
73.317	895841	4.73	6837	3.23
Totals				
	18944760	100.00	211984	100.00

4-(4-Fluorophenyl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



Area % Report

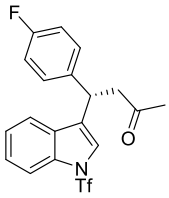
Data File: C:\EZStart\Data\Tian-Ren\ltr-255A OD 99-1@0.2 01.06.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/6/2017 2:47:08 PM
Printed: 2/15/2017 12:58:03 PM



SPD-10Avp
Ch1-254nm
Results

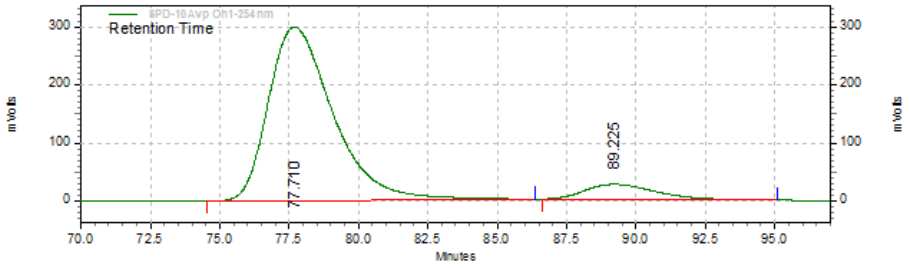
Retention Time	Area	Area %	Height	Height %
69.765	31431205	49.76	205957	53.00
78.488	31733810	50.24	182632	47.00
Totals				
	63165015	100.00	388589	100.00

(*S*)-4-(4-fluorophenyl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



Area % Report

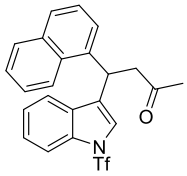
Data File: C:\EZStart\Data\Tian-Ren\ltr-288 OD 99-1@0.2 01.06.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/6/2017 4:51:54 PM
Printed: 2/15/2017 12:54:37 PM



SPD-10Avp
Ch1-254nm
Results

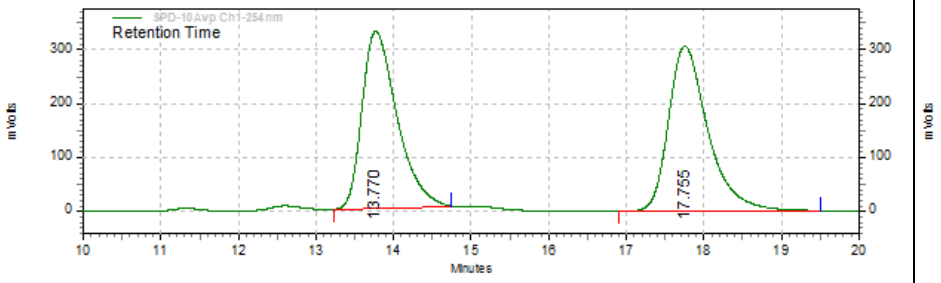
Retention Time	Area	Area %	Height	Height %
77.710	48339668	91.31	298552	92.00
89.225	4603338	8.69	25957	8.00
Totals				
	52943006	100.00	324509	100.00

4-(Naphthalen-1-yl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



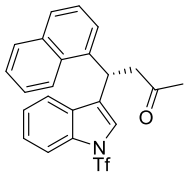
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr-291 AD-H 98-2@0.5 01.06.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/6/2017 9:22:07 PM
Printed: 2/15/2017 1:13:15 PM



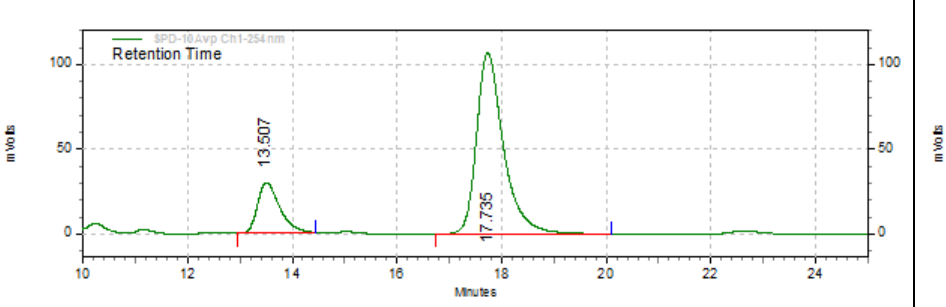
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
13.770	10304803	48.90	328815	51.81
17.755	10766673	51.10	305885	48.19
Totals				
	21071476	100.00	634700	100.00

(*S*)-4-(naphthalen-1-yl)-4-(1-((trifluoromethyl)sulfonyl)-1H-indol-3-yl)butan-2-one



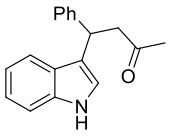
Area % Report

Data File: C:\EZStart\Data\Tian-Ren\ltr-295 AD-H 98-2@0.5 01.06.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/6/2017 8:44:19 PM
Printed: 2/15/2017 1:14:11 PM



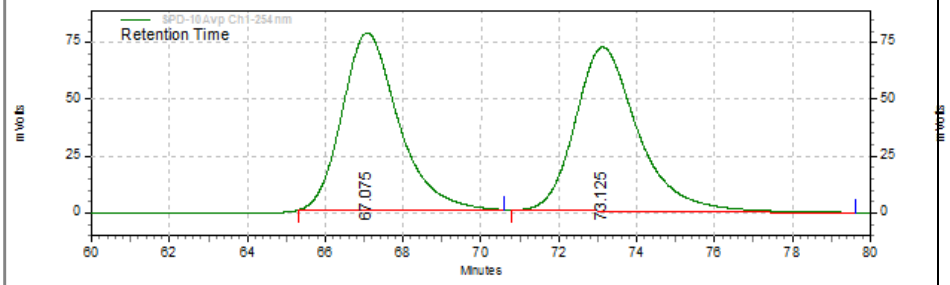
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
13.507	873800	18.54	29625	21.66
17.735	3839121	81.46	107128	78.34
Totals				
	4712921	100.00	136753	100.00

4-(1H-indol-3-yl)-4-phenylbutan-2-one



Area % Report

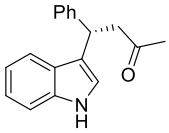
Data File: C:\EZStart\Data\Tian-Ren\LTR-320 AD-H 95-5@0.5 01.12.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/12/2017 2:33:26 PM
Printed: 2/15/2017 1:49:06 PM



SPD-10Avp Ch1-254nm Results

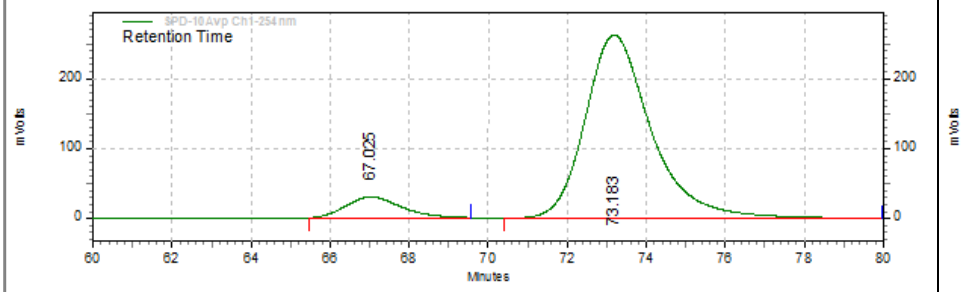
Retention Time	Area	Area %	Height	Height %
67.075	7828791	49.33	77842	52.00
73.125	8040514	50.67	71857	48.00
Totals				
	15869305	100.00	149699	100.00

(*S*)-4-(1H-indol-3-yl)-4-phenylbutan-2-one



Area % Report

Data File: C:\EZStart\Data\Tian-Ren\LTR-317 AD-H 95-5@0.5 01.12.17.dat
Method: C:\EZStart\Methods\Mary\90-10@0.8.met
Acquired: 1/12/2017 4:48:06 PM
Printed: 2/15/2017 1:50:30 PM



SPD-10Avp Ch1-254nm Results

Retention Time	Area	Area %	Height	Height %
67.025	2895568	8.69	29949	10.27
73.183	30429588	91.31	261809	89.73
Totals				
	33325156	100.00	291758	100.00