Supporting Information

Silver-Copper Co-catalyzed Cascade Intramolecular Cyclization/Desulfinamide/Dehydrogenation: One-Pot Synthesis of Substituted Carbazoles

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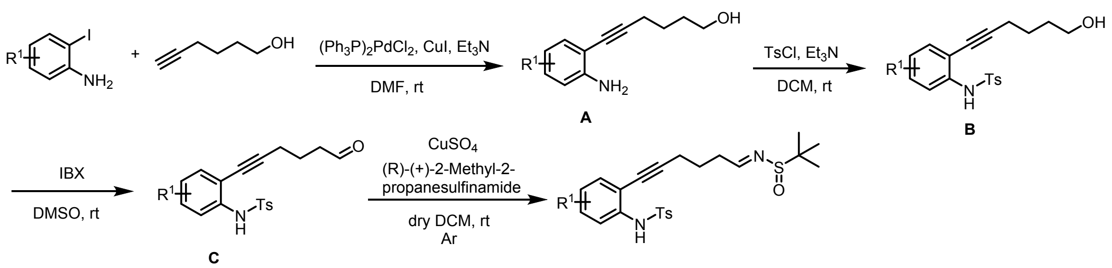
1. General procedure for the synthesis of substrate

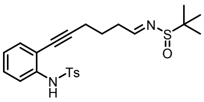


To a three-necked flask were added $(PPh_3)_2PdCl_2$ (5.0 mol%), CuI (5.0 mol%), DMF, Et_3N (4.0 equiv), and 2-iodoaniline (1.0 equiv). After degassing with argon and four evacuation/backfill-cycles with argon, 5-hexyn-1-ol was then added and the resulting mixture was stirring at room temperature. The reaction was complete as monitored by TLC. Then it was diluted with saturated aqueous NH_4Cl and EtOAc. The aqueous phase was extracted with an additional of EtOAc, and the combined organic layers were washed with water. The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the product **A**.

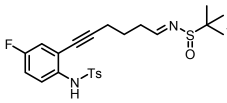
To a flask were added **A** (1.0 equiv)/DCM, pyridine (2.0 equiv) and TsCl (1.2 equiv) sequentially at room temperature. The reaction was complete as monitored by TLC. H_2O were added to the resulting mixture. After separation of the organic layer, the water layer was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **B.**

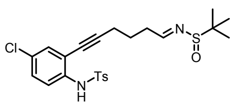
To a flask were added **B** (1.0 equiv)/DMSO and IBX (3.0 equiv) sequentially at room temperature. The reaction was complete as monitored by TLC. H_2O and EtOAc were added to the resulting mixture. The aqueous phase was extracted with an additional of EtOAc, and the combined organic layers were washed with water. The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo yielding the crude extract **C** without further purification**.**

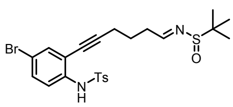
To a flask were added **C** (1.0 equiv), (R)-(+)-2-Methyl-2-propanesulfinamide (1.2 equiv) and $CuSO_4$ (3.0 equiv). After degassing with argon and four evacuation/backfill-cycles with argon, dry DCM was then added, and the resulting mixture was stirring at room temperature. After 48 h, the reaction was stopped and filtrated through Celite, washing with DCM. The solution was evaporated with a rotary evaporator to remove the solvent, yielding the crude extract which was further purified by flash column (eluent: petroleum ether/ethyl acetate) to yield the desired product as a yellow oil.



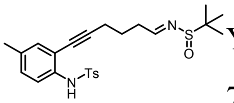
Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.28 – 7.18 (m, 5H), 6.99 (t, J = 7.2 Hz, 1H), 2.71 – 2.63 (m, 2H), 2.53 (t, J = 6.8 Hz, 2H), 2.37 (s, 3H), 1.99 – 1.91 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 144.0, 137.6, 136.2, 132.1, 129.6, 129.1, 127.2, 124.3, 119.5, 114.6, 96.2, 76.4, 56.7, 35.0, 24.3, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{23}H_{29}N_2O_3S_2$ $[M+H]^+$ 445.1614, found 445.1618.

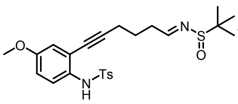

Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, J = 4.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.54 (dd, J = 8.8, 5.2 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.02 (s, 1H), 6.95 (d, J = 8.4 Hz, 2H), 2.64 (td, J = 7.2, 4.4 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.97 – 1.89 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 159.3 (d, $J_{C\text{-}F}$ = 243.6 Hz), 144.1, 136.0, 133.7, 129.6, 127.2, 122.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 118.5 (d, $J_{C\text{-}F}$ = 24.2 Hz), 117.0 (d, $J_{C\text{-}F}$ = 9.8 Hz), 116.3 (d, $J_{C\text{-}F}$ = 22.5 Hz), 96.9, 75.6, 56.7, 35.0, 24.1, 22.4, 21.6, 19.0, HRMS (ESI) calcd for $C_{23}H_{28}FN_2O_3S_2$ $[M+H]^+$ 463.1520, found 463.1526.

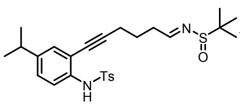

Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (t, J = 4.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.8 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.15 (s, 1H), 2.73 – 2.63 (m, 2H), 2.55 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H), 2.01 – 1.92 (m, 2H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 144.3, 136.2, 136.0, 131.8, 129.7, 129.6, 129.2, 127.2, 121.2, 116.5, 97.5, 75.3, 56.8, 35.0, 24.1, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{23}H_{28}ClN_2O_3S_2$ $[M+H]^+$ 479.1224, found 479.1232.

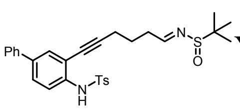

Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, J = 4.0 Hz, 1H), 7.65 (d, J = 7.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 1H), 7.39 (s, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 7.2 Hz, 2H), 7.14 (s, 1H), 2.69 – 2.62 (m, 2H), 2.53 (t, J = 6.8 Hz, 2H), 2.39 (s, 3H), 2.01 – 1.89 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 144.3, 136.7, 135.9, 134.6, 132.1, 129.7, 127.2, 121.0, 117.0, 116.4, 97.6, 76.7, 56.7, 35.0, 24.1, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{23}H_{28}BrN_2O_3S_2$

[M+H]$^{+}$ 523.0719, found 523.0721.

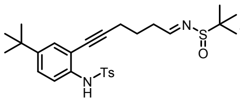

Yellow Oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 (t, J = 4.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 12.0 Hz, 2H), 7.04 (d, J = 8.4 Hz, 1H), 2.69 – 2.62 (m, 2H), 2.50 (t, J = 7.2 Hz, 2H), 2.36 (s, 3H), 2.22 (s, 3H), 1.97 – 1.87 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.4, 143.9, 136.3, 135.0, 134.3, 132.5, 129.9, 129.6, 127.3, 120.2, 114.9, 95.6, 76.6, 56.7, 35.0, 24.3, 22.4, 21.6, 20.6, 19.1, HRMS (ESI) calcd for $C_{24}H_{31}N_2O_3S_2$ [M+H]$^{+}$ 459.1771, found 459.1779.


Yellow Oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 (t, J = 4.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 9.2 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.95 (s, 1H), 6.82 (dd, J = 8.8, 3.2 Hz, 1H), 6.76 (d, J = 2.8 Hz, 1H), 3.74 (s, 3H), 2.63 (td, J = 7.2, 4.4 Hz, 2H), 2.46 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.97 – 1.82 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.3, 156.7, 143.7, 136.2, 130.6, 129.4, 127.2, 123.4, 117.3, 116.4, 115.4, 95.5, 76.5, 56.7, 55.5, 35.0, 24.2, 22.4, 21.6, 19.0, HRMS (ESI) calcd for $C_{24}H_{31}N_2O_4S_2$ [M+H]$^{+}$ 475.1720, found 475.1721.

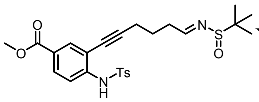

Yellow Oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.15 – 7.06 (m, 3H), 2.83 – 2.74 (m, 1H), 2.70 – 2.63 (m, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.00 – 1.89 (m, 2H), 1.22 (s, 9H), 1.17 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.4, 145.1, 143.8, 136.4, 135.2, 129.9, 129.6, 127.4, 127.2, 120.0, 114.6, 95.4, 76.7, 56.7, 35.0, 33.3, 24.3, 23.8, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{26}H_{35}N_2O_3S_2$ [M+H]$^{+}$ 487.2084, found 487.2089.


Yellow Oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (t, J = 4.4 Hz, 1H),

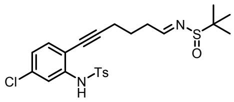
7.71 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.8 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.40 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.25 – 7.19 (m, 3H), 2.72 – 2.64 (m, 2H), 2.55 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.03 – 1.91 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 144.1, 139.4, 137.2, 136.7, 136.2, 130.6, 129.7, 128.9, 127.8, 127.6, 127.3, 126.7, 119.8, 114.9, 96.2, 76.4, 56.8, 35.0, 24.3, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{29}H_{33}N_2O_3S_2$ $[M+H]^+$ 521.1927, found 521.1931.



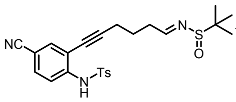
Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.8 Hz, 1H), 7.27 (d, J = 0.8 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.10 (s, 1H), 2.70 – 2.64 (m, 2H), 2.52 (t, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.91 – 1.99 (m, 2H), 1.24 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 147.3, 143.9, 136.5, 135.0, 129.6, 128.9, 127.2, 126.4, 119.3, 114.1, 95.3, 76.9, 56.7, 35.0, 34.3, 31.2, 24.3, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{27}H_{37}N_2O_3S_2$ $[M+H]^+$ 501.2240, found 501.2246



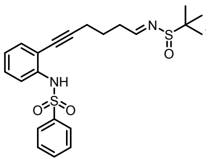
Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.0 Hz, 1H), 7.96 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.8 Hz, 1H), 7.46 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 3.87 (s, 3H), 2.74 – 2.67 (m, 2H), 2.59 (t, J = 7.2 Hz, 2H), 2.38 (s, 3H), 2.06 – 1.94 (m, 2H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 165.8, 144.5, 141.4, 135.8, 133.8, 130.4, 129.8, 127.3, 125.5, 117.3, 113.5, 97.4, 75.5, 56.7, 52.2, 35.0, 24.2, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{25}H_{31}N_2O_5S_2$ $[M+H]^+$ 503.1669, found 503.1675.



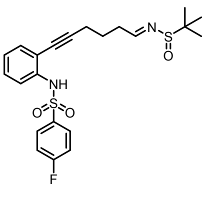
Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 2.0 Hz, 1H), 7.27 (s, 1H), 7.24 (d, J = 4.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 1H), 6.97 (dd, J = 8.4, 2.0 Hz, 1H), 2.67 (td, J = 6.8, 4.4 Hz, 2H), 2.54 (t, J = 7.2 Hz, 2H), 2.39 (s, 3H), 2.00 – 1.91 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 144.4, 138.6, 135.9, 134.8, 132.9, 129.8, 127.2, 124.4, 119.2, 112.6, 97.2, 75.5, 56.7, 35.0, 24.2, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{23}H_{28}ClN_2O_3S_2$ $[M+H]^+$ 479.1224, found 479.1224.



Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.4 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.62 – 7.55 (m, 3H), 7.47 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 6.4 Hz, 2H), 2.72 – 2.65 (m, 2H), 2.60 (t, J = 7.2 Hz, 2H), 2.40 (s, 3H), 2.05 – 1.93 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 144.9, 141.4, 135.9, 135.6, 132.6, 130.0, 127.2, 117.8, 117.8, 114.3, 107.2, 99.2, 74.4, 56.7, 35.0, 24.1, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{24}H_{28}N_3O_3S_2$ $[M+H]^+$ 470.1567, found 470.1565.

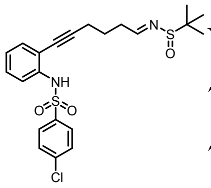


Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, J = 4.4 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.59 – 7.50 (m, 2H), 7.45 – 7.39 (m, 2H), 7.29 – 7.19 (m, 3H), 7.01 (td, J = 7.6, 1.2 Hz, 1H), 2.70 – 2.62 (m, 2H), 2.51 (t, J = 7.2 Hz, 2H), 1.98 – 1.88 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 139.1, 137.4, 133.1, 132.1, 129.1, 129.0, 127.2, 124.5, 120.0, 114.9, 96.2, 76.3, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcd for $C_{22}H_{27}N_2O_3S_2$ $[M+H]^+$ 431.1458, found 431.1466.

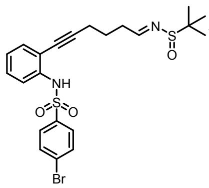


Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.29 – 7.21 (m, 3H), 7.13 – 7.07 (m, 2H), 7.04 (td, J = 7.6, 0.8 Hz, 1H), 2.70 – 2.64 (m, 2H), 2.52 (t, J = 7.2 Hz, 2H), 2.01 – 1.89 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.3 (d, $J_{C\text{-}F}$ = 254 Hz), 137.1, 135.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 132.3, 130.0 (d, $J_{C\text{-}F}$ = 9.4 Hz), 129.2, 124.8, 120.3, 116.2 (d, $J_{C\text{-}F}$ = 22.5 Hz), 115.2, 96.3, 76.2, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcd for $C_{22}H_{26}FN_2O_3S_2$

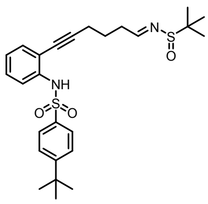
$[M+H]^+$ 449.1363, found 449.1369.



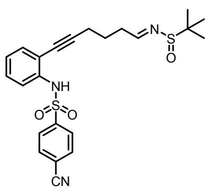
Yellow Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.55 (d, J = 8.4 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.31 – 7.23 (m, 2H), 7.20 (s, 1H), 7.05 (td, J = 7.6, 0.8 Hz, 1H), 2.67 (td, J = 7.6, 4.4 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.00 – 1.87 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 139.7, 137.6, 137.0, 132.3, 129.3, 129.2, 128.6, 124.9, 120.3, 115.2, 96.3, 76.3, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcd for $C_{22}H_{26}ClN_2O_3S_2$ $[M+H]^+$ 465.1068, found 465.1071.



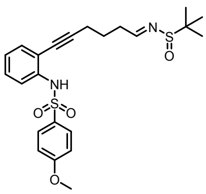
Yellow Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.4 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.58 – 7.53 (m, 3H), 7.31 – 7.23 (m, 2H), 7.20 (s, 1H), 7.05 (td, J = 7.6, 0.8 Hz, 1H), 2.70 – 2.63 (m, 2H), 2.51 (t, J = 7.2 Hz, 2H), 1.99 – 1.90 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 138.2, 137.0, 132.3, 132.3, 129.2, 128.7, 128.2, 124.9, 120.3, 115.2, 96.3, 76.3, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcd for $C_{22}H_{26}BrN_2O_3S_2$ $[M+H]^+$ 509.0563, found 509.0562.



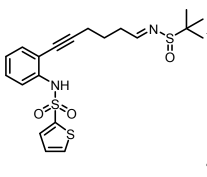
Yellow Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.30 – 7.19 (m, 3H), 7.00 (td, J = 7.6, 0.8 Hz, 1H), 2.72 – 2.65 (m, 2H), 2.53 (t, J = 7.2 Hz, 2H), 2.01 – 1.90 (m, 2H), 1.29 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 157.0, 137.7, 136.2, 132.1, 129.1, 127.0, 126.0, 124.0, 119.0, 114.2, 96.2, 76.4, 56.7, 35.2, 35.0, 31.0, 24.3, 22.4, 19.1, HRMS (ESI) calcd for $C_{26}H_{35}N_2O_3S_2$ $[M+H]^+$ 487.2084, found 487.2092.



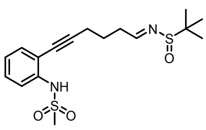
Yellow Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.32 (s, 1H), 7.31 – 7.27 (m, 2H), 7.13 – 7.04 (m, 1H), 2.68 (td, J = 7.2, 4.4 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 2.05 – 1.87 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 143.3, 136.4, 132.7, 132.5, 129.3, 127.8, 125.4, 120.8, 117.2, 116.8, 115.6, 96.5, 76.2, 56.8, 35.0, 24.3, 22.4, 19.1, HRMS (ESI) calcd for $C_{23}H_{26}N_3O_3S_2$ $[M+H]^+$ 456.1410, found 456.1415.



Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.17 (s, 1H), 7.00 (td, J = 7.6, 1.2 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.71 – 2.64 (m, 2H), 2.54 (t, J = 7.2 Hz, 2H), 2.01 – 1.91 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 163.2, 137.7, 132.1, 130.7, 129.4, 129.1, 124.2, 119.5, 114.5, 114.1, 96.2, 76.4, 56.7, 55.6, 35.0, 24.3, 22.4, 19.1, HRMS (ESI) calcd for $C_{23}H_{29}N_2O_4S_2$ $[M+H]^+$ 461.1563, found 461.1573.

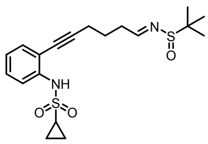


Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.54 (dd, J = 4.8, 1.2 Hz, 1H), 7.48 (dd, J = 4.0, 1.2 Hz, 1H), 7.34 – 7.25 (m, 3H), 7.06 (td, J = 7.6, 0.8 Hz, 1H), 6.99 (dd, J = 4.8, 4.0 Hz, 1H), 2.67 (td, J = 7.6, 4.4 Hz, 2H), 2.53 (t, J = 7.2 Hz, 2H), 2.01 – 1.89 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 139.5, 137.1, 132.8, 132.6, 132.1, 129.1, 127.3, 124.9, 120.3, 115.2, 96.3, 76.2, 56.7, 35.0, 24.2, 22.4, 19.1, HRMS (ESI) calcd for $C_{20}H_{25}N_2O_3S_3$ $[M+H]^+$ 437.1022, found 437.1026.

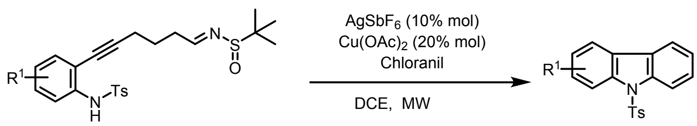


Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.4 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.42 (dd, J = 8.0, 1.6 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.11 (td, J = 7.6, 1.0 Hz, 1H), 7.04 (s, 1H), 3.02 (s, 3H), 2.75 – 2.69 (m, 2H), 2.61 (t, J = 7.2 Hz, 2H), 2.06 – 1.95 (m, 2H), 1.21 (s, 9H); ^{13}C NMR

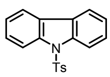
(100 MHz, $CDCl_3$) δ 168.3, 137.7, 132.5, 129.5, 124.6, 119.1, 114.5, 96.8, 76.4, 56.7, 39.6, 35.0, 24.3, 22.4, 19.2, HRMS (ESI) calcd for $C_{17}H_{25}N_2O_3S_2$ $[M+H]^+$ 369.1301, found 369.1305.


Yellow Oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.4 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.41 (dd, J = 8.0, 1.6 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.10 (td, J = 7.6, 1.2 Hz, 1H), 6.98 (s, 1H), 2.75 – 2.69 (m, 2H), 2.61 (t, J = 7.2 Hz, 2H), 2.51 – 2.43 (m, 1H), 2.06 – 1.96 (m, 2H), 1.21 (s, 9H), 1.20 – 1.17 (m, 2H), 0.99 – 0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 137.9, 132.3, 129.3, 124.5, 120.1, 115.0, 96.4, 76.7, 56.7, 35.0, 30.1, 24.4, 22.4, 19.2, 5.8, HRMS (ESI) calcd for $C_{19}H_{27}N_2O_3S_2$ $[M+H]^+$ 395.1458, found 395.1459.

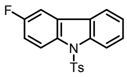
2. General procedure for the synthesis of products



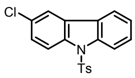
To a microwave rotor were added DCE, substrate (1.0 equiv), $Cu(OAc)_2$ (20 mol%), $AgSbF_6$ (10 mol %) and chloranil (0.6 equiv) sequentially. The mixture was heated at 80 ºC in microwave for 2.5 h. After the reaction was complete as monitored by TLC. CH_2Cl_2 and H_2O were added to the resulting mixture. After separation of the organic layer, the water layer was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, evaporated, and purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product as a solid.


Pale grey solid; yield: 86%; mp: 134-135 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 7.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H),

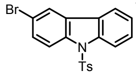
7.48 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 7.34 (td, J = 7.6, 0.8 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 138.4, 134.9, 129.7, 127.4, 126.5, 126.4, 123.9, 120.0, 115.2, 21.5, HRMS (ESI) calcd for $C_{19}H_{16}NO_2S$ $[M+H]^+$ 322.0896, found 322.0902.



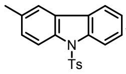
White solid; yield: 82%; mp: 171-172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 8.28 (dd, J = 9.2, 4.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.39 – 7.33 (m, 1H), 7.20 (td, J = 8.8, 2.4 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, $J_{C\text{-}F}$ = 240.6 Hz), 145.0, 139.2, 134.7, 134.5 (d, $J_{C\text{-}F}$ = 1.3 Hz), 129.7, 128.0, 127.8 (d, $J_{C\text{-}F}$ = 9.6 Hz), 126.5, 125.9 (d, $J_{C\text{-}F}$ = 3.6 Hz), 124.0, 120.2, 116.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 115.47, 114.8 (d, $J_{C\text{-}F}$ = 24.6 Hz), 106.2 (d, $J_{C\text{-}F}$ = 4.0 Hz), 21.5, HRMS (ESI) calcd for $C_{19}H_{15}FNO_2S$ $[M+H]^+$ 340.0802, found 340.0803.



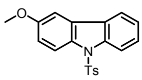
White solid; yield: 84%; mp: 135-136 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.43 (dd, J = 9.2, 2.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.9, 136.7, 134.7, 129.8, 129.7, 128.1, 127.8, 127.4, 126.5, 125.3, 124.2, 120.2, 119.9, 116.3, 115.3, 21.5, HRMS (ESI) calcd for $C_{19}H_{15}ClNO_2S$ $[M+H]^+$ 356.0507, found 356.0504.



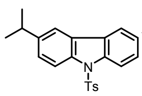
White solid; yield: 83%; mp: 143-144 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 2.0 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.57 (dd, J = 8.8, 2.0 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.7, 137.1, 134.6, 130.1, 129.8, 128.3, 128.2, 126.5, 125.2, 124.2, 122.9, 120.2, 117.3, 116.6, 115.3, 21.6, HRMS (ESI) calcd for $C_{19}H_{15}BrNO_2S$ [M+H]$^+$ 400.0001, found 400.0001.



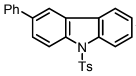
White solid; yield: 56%; mp: 121-122 ºC. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.49 – 7.41 (m, 1H), 7.36 – 7.31 (m, 1H), 7.29 (dd, J = 8.4, 1.2 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.7, 138.7, 136.5, 135.0, 133.6, 129.6, 128.6, 127.2, 126.6, 126.5, 123.8, 120.1, 119.9, 115.2, 114.9, 21.5, 21.3, HRMS (ESI) calcd for $C_{19}H_{15}NO_2S$ [M+H]$^+$ 356.0507, found 356.0504.

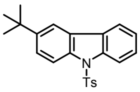


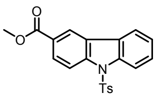
White solid; yield: 48%; mp: 129-130 ºC. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.52 – 7.44 (m, 1H), 7.37 – 7.30 (m, 2H), 7.09 – 7.05 (m, 3H), 3.89 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.8, 144.7, 139.1, 134.8, 132.7, 129.6, 127.6, 127.4, 126.6, 126.5, 123.8, 119.9, 116.3, 115.5, 115.3, 103.2, 55.8, 21.5, HRMS (ESI) calcd for $C_{20}H_{17}NNaO_3S$ [M+Na]$^+$ 374.0821, found 374.0825.

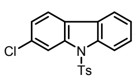


White solid; yield: 74%; mp: 94-95 ºC. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.73 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 3.11 – 2.98 (m, 1H), 2.25 (s, 3H), 1.32 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.74, 144.72, 138.6, 136.7, 135.1, 129.6, 127.1, 126.6, 126.5, 126.4, 126.3, 123.7, 119.9, 117.3, 115.1, 114.9, 34.0, 24.3, 21.5, HRMS (ESI) calcd for $C_{22}H_{22}NO_2S$ [M+H]$^+$ 364.1366, found 364.1370.

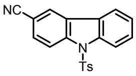
White solid; yield: 70%; mp: 139-140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.8 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 1.6 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.75 – 7.70 (m, 3H), 7.69 – 7.64 (m, 2H), 7.54 – 7.45 (m, 3H), 7.41 – 7.34 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 140.9, 138.8, 137.8, 137.3, 135.0, 129.7, 128.9, 127.6, 127.3, 127.3, 126.9, 126.8, 126.5, 126.4, 124.0, 120.1, 118.4, 115.4, 115.2, 21.6, HRMS (ESI) calcd for $C_{25}H_{20}NO_2S$ $[M+H]^+$ 398.1209, found 398.1211.

White solid; yield: 72%; mp: 158-159 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.8 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.71 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 8.8 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.24 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 144.7, 138.6, 136.3, 135.1, 129.7, 127.1, 126.7, 126.5, 126.0, 125.2, 123.7, 119.8, 116.3, 115.1, 114.6, 34.8, 31.7, 21.5, HRMS (ESI) calcd for $C_{23}H_{24}NO_2S$ $[M+H]^+$ 378.1522, found 378.1525.

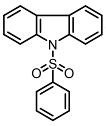
White solid; yield: 84%; mp: 176-177 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.35 (dd, J = 16.0, 8.8 Hz, 2H), 8.18 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 3.97 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.3, 141.2, 138.9, 134.8, 129.8, 128.7, 128.0, 126.5, 126.3, 125.8, 125.7, 124.3, 122.0, 120.4, 115.1, 114.7, 52.3, 21.6, HRMS (ESI) calcd for $C_{21}H_{18}NO_4S$ $[M+H]^+$ 380.0951, found 380.0948.

White solid; yield: 85%; mp: 170-171 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.35 (dd, J = 14.4, 7.6 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2,

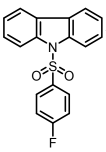
138.8, 138.5, 134.8, 133.1, 129.8, 127.7, 126.5, 125.5, 124.9, 124.4, 124.1, 120.7, 120.0, 115.4, 115.1, 21.6, HRMS (ESI) calcd for $C_{19}H_{15}ClNO_2S$ $[M+H]^+$ 356.0507, found 356.0507.



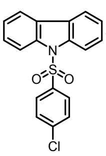
White solid; yield: 82%; mp: 189-190 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.8 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 1.2 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.76 (dd, J = 8.8, 1.6 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 8.2 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 140.4, 138.8, 134.6, 130.6, 130.0, 128.9, 126.7, 126.5, 124.6, 124.5, 124.5, 120.4, 119.1, 115.7, 115.1, 107.3, 21.6, HRMS (ESI) calcd for $C_{20}H_{15}N_2O_2S$ $[M+H]^+$ 347.0849, found 347.0853.



White solid; yield: 81%; mp: 134-135 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 2H), 7.90 – 7.87 (m, 2H), 7.82 – 7.77 (m, 2H), 7.48 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.35 (td, J = 7.6, 0.8 Hz, 2H), 7.32 – 7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.9, 133.8, 129.0, 127.5, 126.5, 126.4, 124.0, 120.0, 115.2, HRMS (ESI) calcd for $C_{18}H_{14}NO_2S$ $[M+H]^+$ 308.0740, found 308.0741.

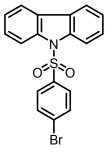


White solid; yield: 80%; mp: 152-153 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 7.2 Hz, 2H), 7.84 – 7.76 (m, 2H), 7.49 (ddd, J = 8.8, 7.6, 1.2 Hz, 2H), 7.40 – 7.33 (m, 2H), 6.96 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, $J_{C\text{-}F}$ = 255.3 Hz), 138.3, 133.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.3 (d, $J_{C\text{-}F}$ = 9.6 Hz), 127.6, 126.6, 124.2, 120.1, 116.4 (d, $J_{C\text{-}F}$ = 22.7 Hz), 115.2, HRMS (ESI) calcd for $C_{18}H_{13}FNO_2S$ $[M+H]^+$ 326.0646, found 326.0651.

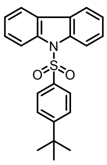


White solid; yield: 83%; mp: 135-136 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30

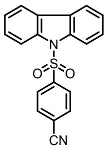
(d, J = 8.4 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.53 – 7.46 (m, 2H), 7.41 – 7.34 (m, 2H), 7.29 – 7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 138.2, 136.1, 129.4, 127.8, 127.6, 126.6, 124.3, 120.2, 115.2, HRMS (ESI) calcd for $C_{18}H_{13}ClNO_2S$ $[M+H]^+$ 342.0350, found 326.0351.



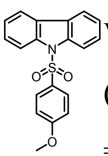
White solid; yield: 81%; mp: 145-146 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.49 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 7.45 – 7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.7, 132.4, 129.1, 127.9, 127.6, 126.6, 124.3, 120.2, 115.2, HRMS (ESI) calcd for $C_{18}H_{13}BrNO_2S$ $[M+H]^+$ 385.9845, found 385.9839.



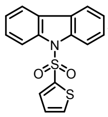
White solid; yield: 78%; mp: 184-185 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.80 – 7.73 (m, 1H), 7.50 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 7.39 – 7.30 (m, 4H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 138.4, 135.2, 127.4, 126.4, 126.3, 126.1, 123.8, 120.0, 115.0, 35.1, 30.9, HRMS (ESI) calcd for $C_{22}H_{22}NO_2S$ $[M+H]^+$ 364.1366, found 364.1371.



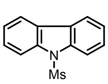
White solid; yield: 72%; mp: 181-182 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 138.0, 132.8, 127.8, 127.0, 126.8, 124.8, 120.4, 117.5, 116.9, 115.2, HRMS (ESI) calcd for $C_{19}H_{13}N_2O_2S$ $[M+H]^+$ 333.0692, found 333.0637.



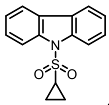
White solid; yield: 77%; mp: 175-176 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.77 – 7.70 (m, 2H), 7.48 (ddd, J = 8.8, 7.6, 1.2 Hz, 2H), 7.39 – 7.31 (m, 2H), 6.75 – 6.65 (m, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 138.4, 129.5, 128.7, 127.4, 126.4, 123.9, 120.0, 115.2, 114.2, 55.5, HRMS (ESI) calcd for $C_{19}H_{16}NO_3S$ $[M+H]^+$ 338.0845, found 338.0842.



White solid; yield: 74%; mp: 157-158 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 7.6 Hz, 2H), 7.58 (dd, J = 4.0, 1.2 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.45 – 7.36 (m, 3H), 6.88 (dd, J = 4.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.3, 132.9, 132.5, 127.5, 127.3, 126.8, 124.4, 120.1, 115.5, HRMS (ESI) calcd for $C_{16}H_{12}NO_2S_2$ $[M+H]^+$ 314.0304, found 314.0304.



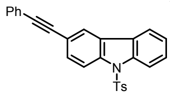
White solid; yield: 60%; mp: 108-109 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 7.2 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.45 – 7.40 (m, 2H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 127.6, 126.3, 124.2, 120.2, 114.7, 38.7, HRMS (ESI) calcd for $C_{13}H_{11}NNaO_2S$ $[M+Na]^+$ 268.0403, found 268.0407.



White solid; yield: 65%; mp: 59-60 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.39 – 7.33 (m, 2H), 7.28 (td, J = 7.6, 0.8 Hz, 2H), 2.48 – 2.41 (m, 1H), 1.24 – 1.18 (m, 2H), 0.74 – 0.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 127.4, 126.2, 123.8, 120.2, 114.8, 30.2, 5.2, HRMS (ESI) calcd for $C_{15}H_{14}NO_2S$ $[M+H]^+$ 272.0740, found 272.0742.

3. Scale-up Synthesis and Further Transformations

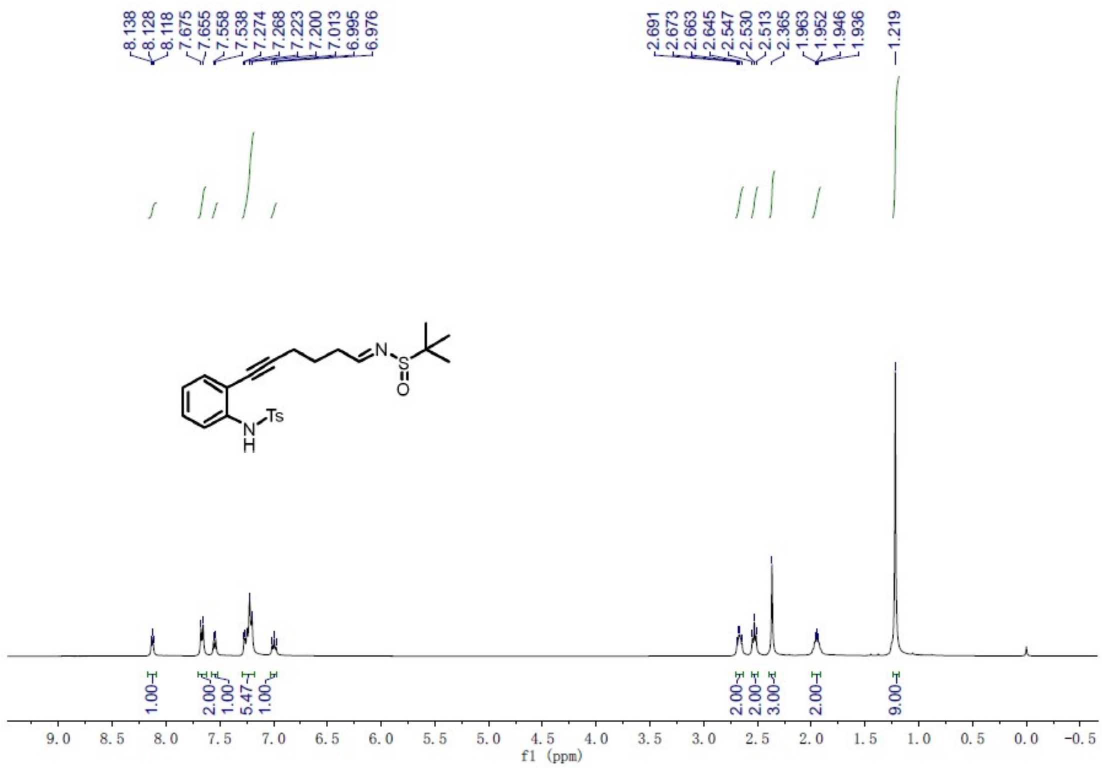
Under nitrogen, to a round flask containing **2d**, $Pd(PPh_3)_2Cl_2$ (5 mol%), and CuI (5 mol%) were added acetonitrile, piperidine (V/V = 2:1, 0.75 M) and phenylacetylene (1.1 eq). The reaction mixture was stirred and heated to reflux for 12 hours. After the reaction mixture was cooled down to room temperature, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was then extracted with ethyl acetate. All organic fractions were combined and washed with water and brine, dried over Na_2SO_4 and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to afford product **2d′**.



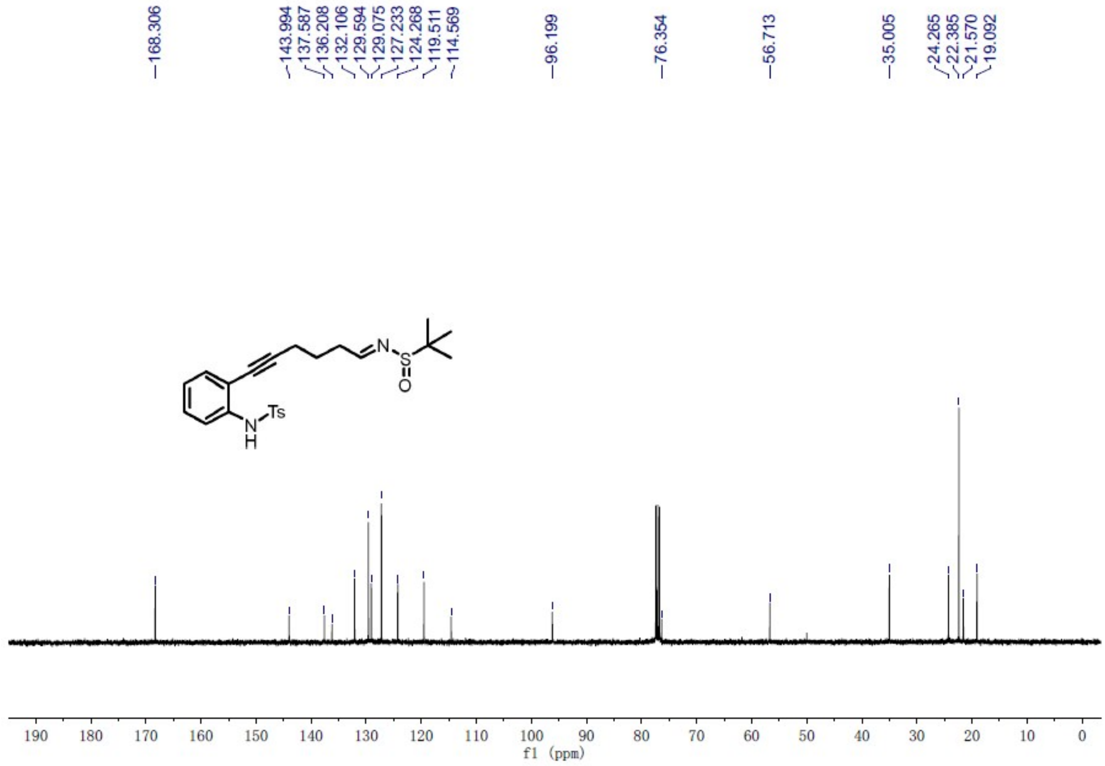
Yellow solid; yield: 82%; mp: 72-73 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, J = 8.4, 4.0 Hz, 2H), 8.08 (d, J = 1.0 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.66 (dd, J = 8.8, 1.6 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.42 – 7.33 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 138.8, 137.9, 134.8, 131.6, 130.8, 129.8, 128.4, 128.3, 127.9, 126.6, 126.5, 125.8, 124.2, 123.3, 123.2, 120.2, 118.9, 115.2, 115.2, 89.3, 89.2, 21.5, HRMS (ESI) calcd for $C_{27}H_{19}NNaO_2S$ $[M+Na]^+$ 444.1029, found 444.1032.

4. NMR spectra

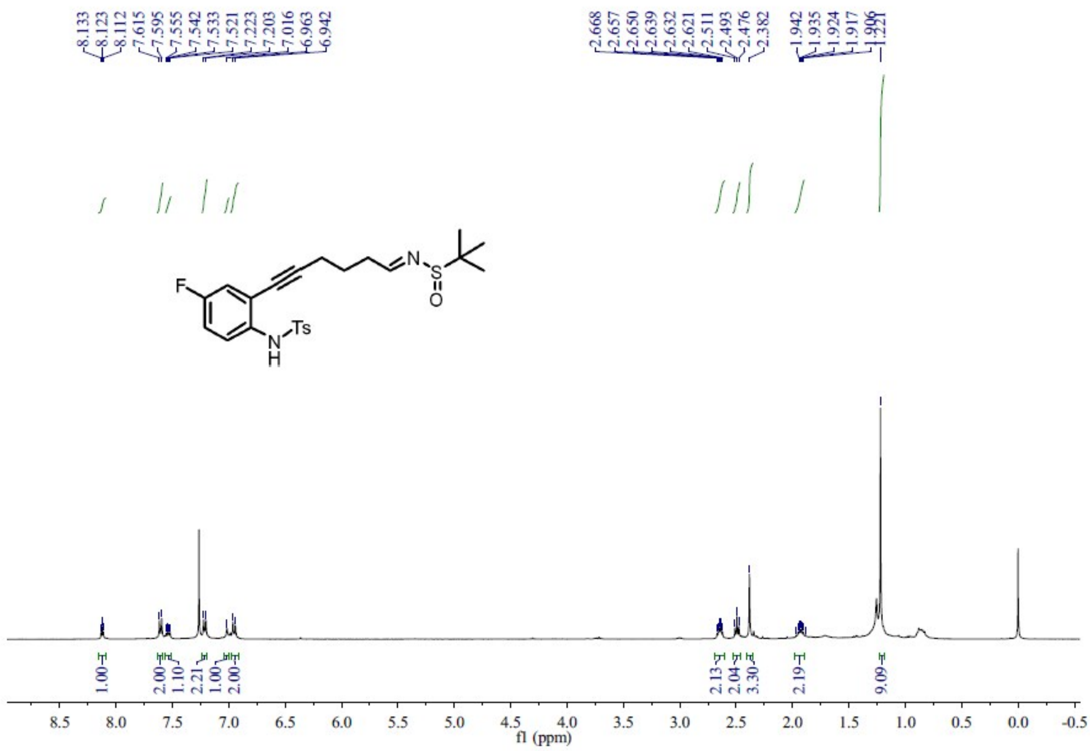
^{1}H NMR spectrum of 1a



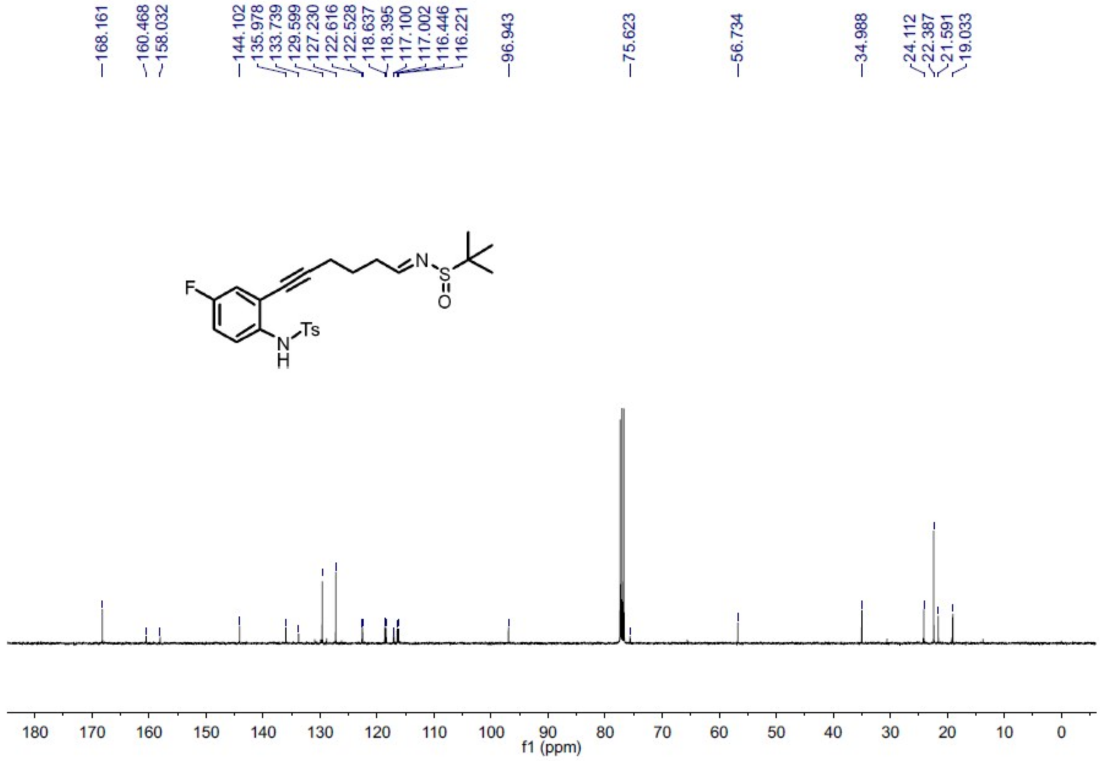
^{13}C NMR spectrum of 1a



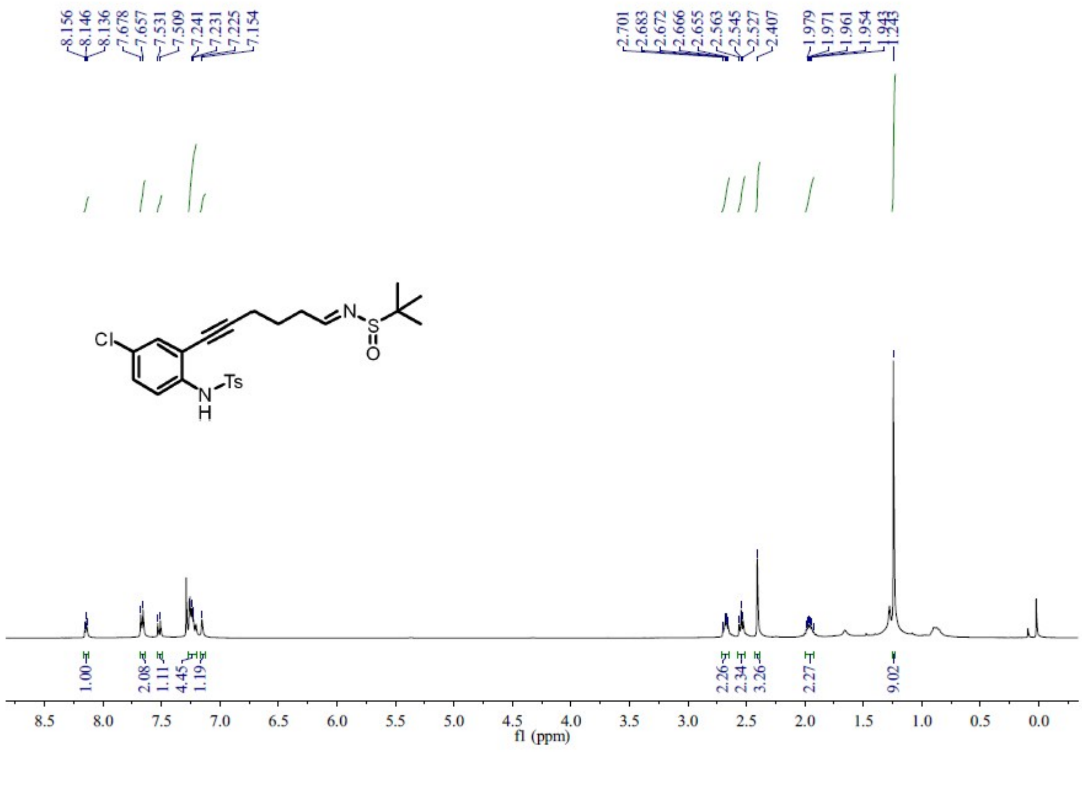
^{1}H NMR spectrum of 1b



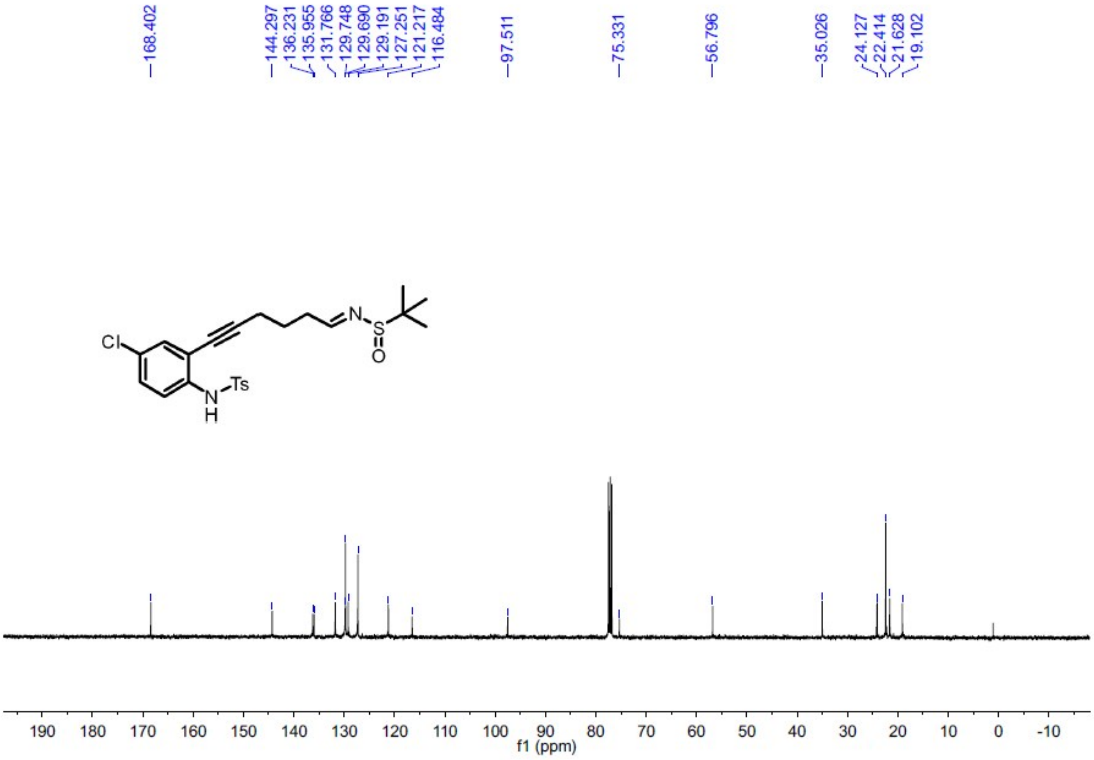
^{13}C NMR spectrum of 1b



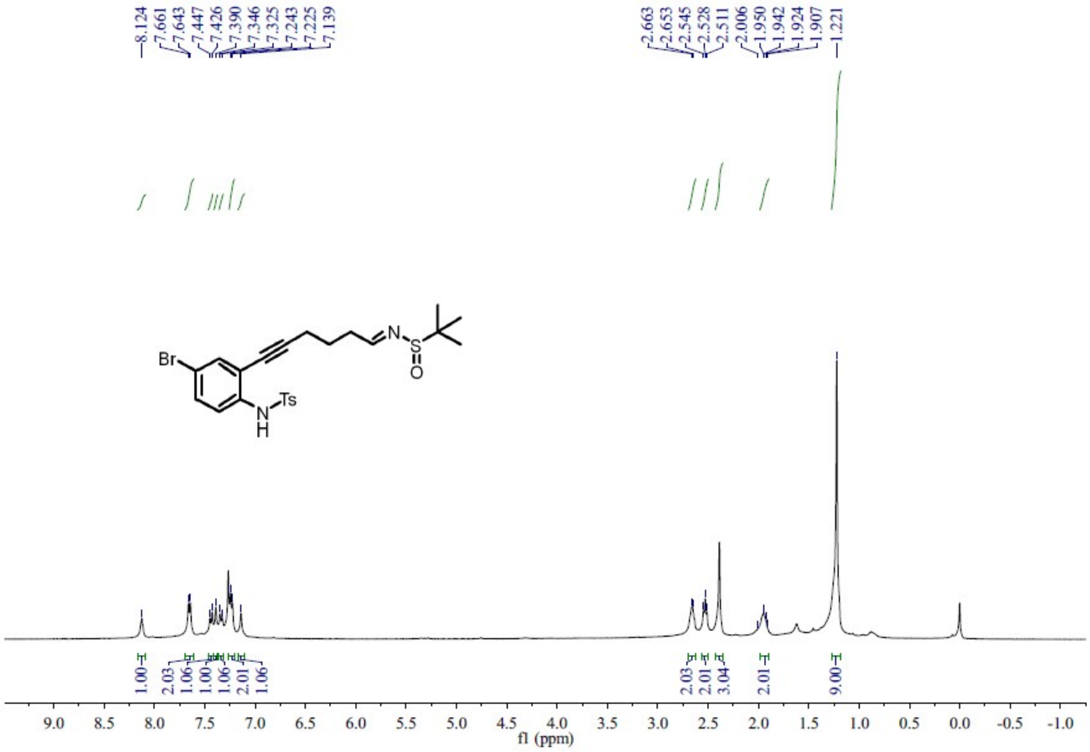
^{1}H NMR spectrum of 1c



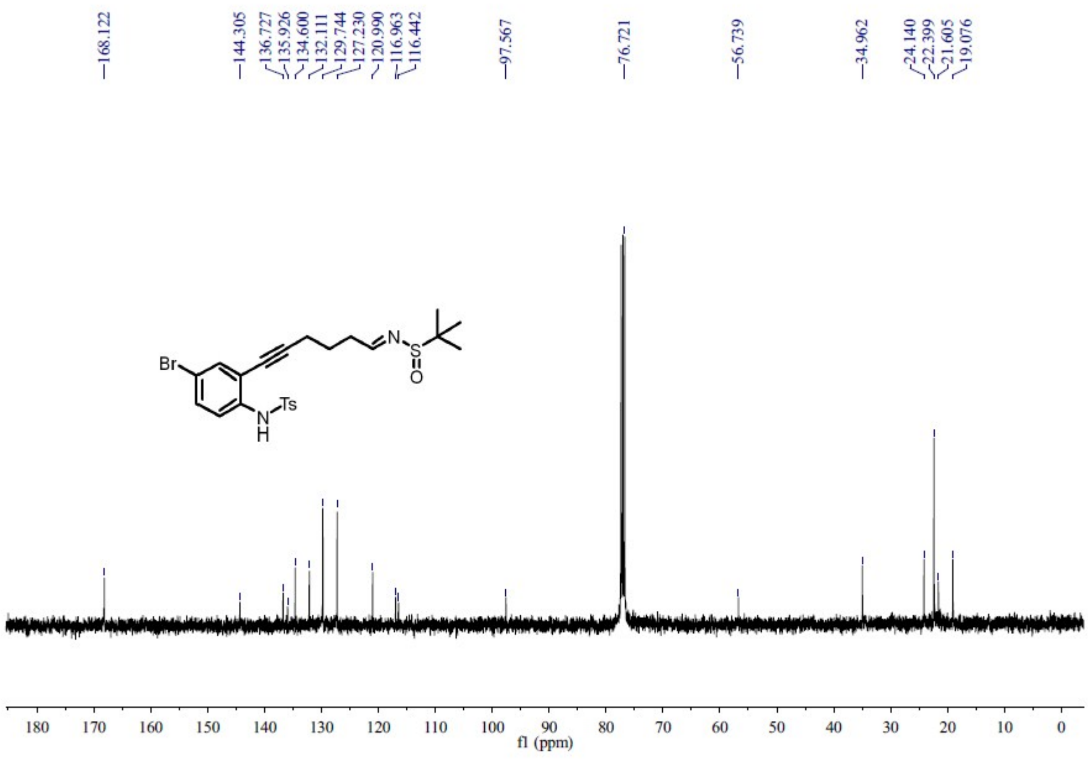
^{13}C NMR spectrum of 1c



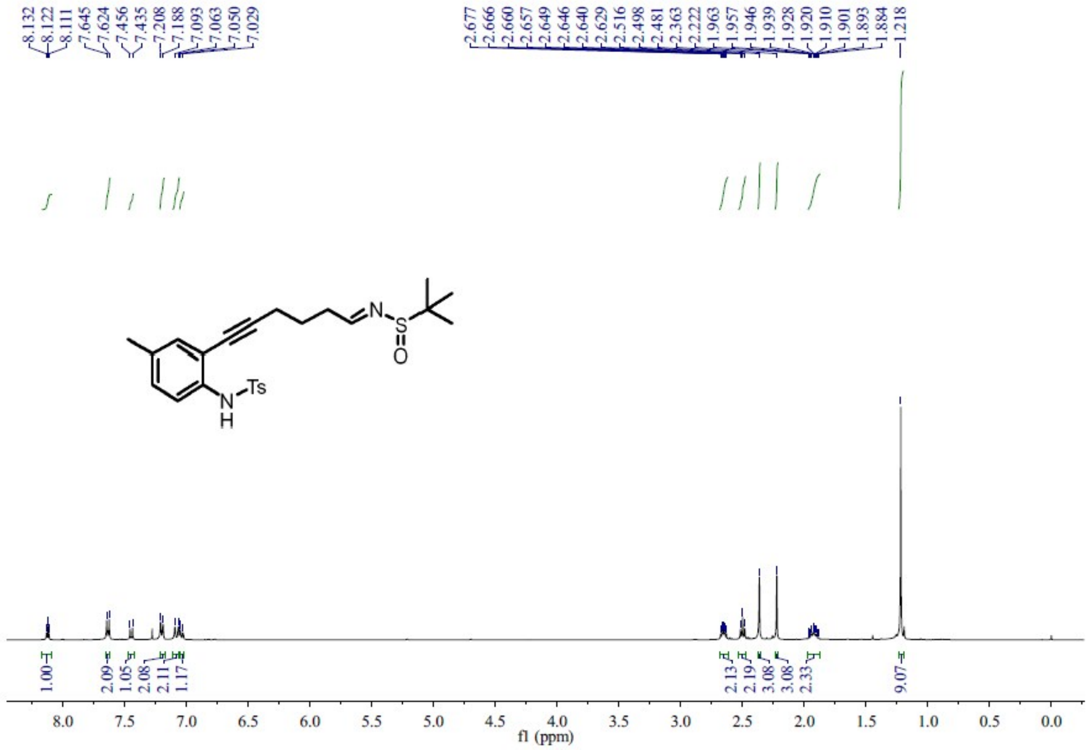
^{1}H NMR spectrum of 1d



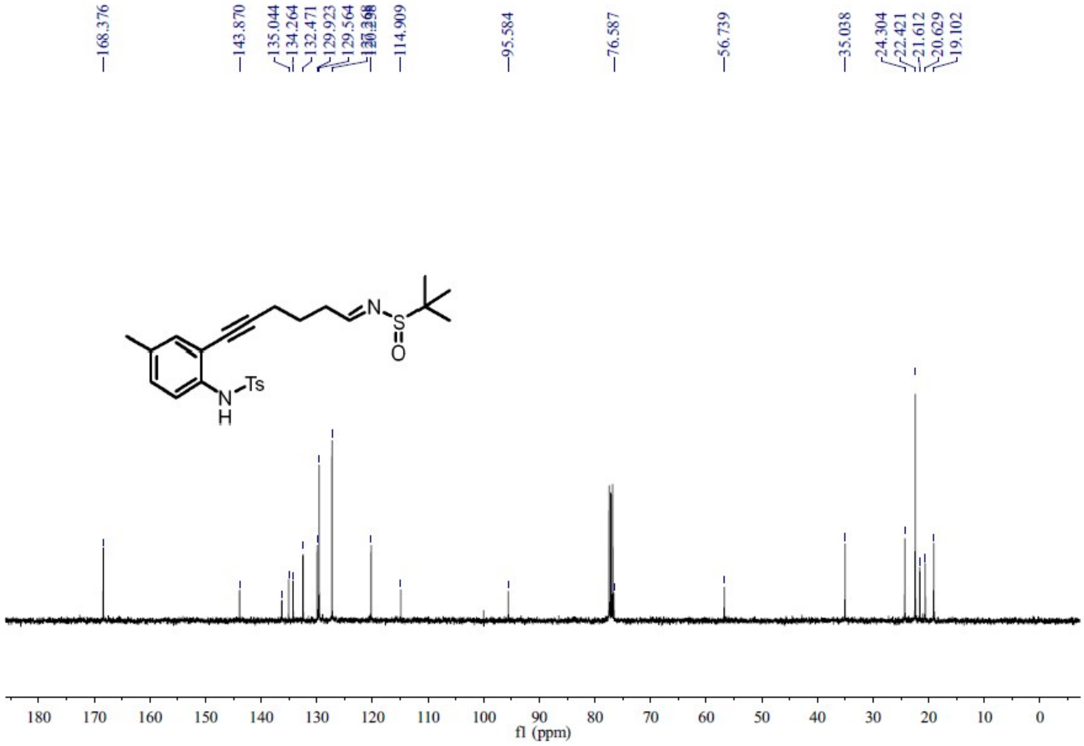
^{13}C NMR spectrum of 1d



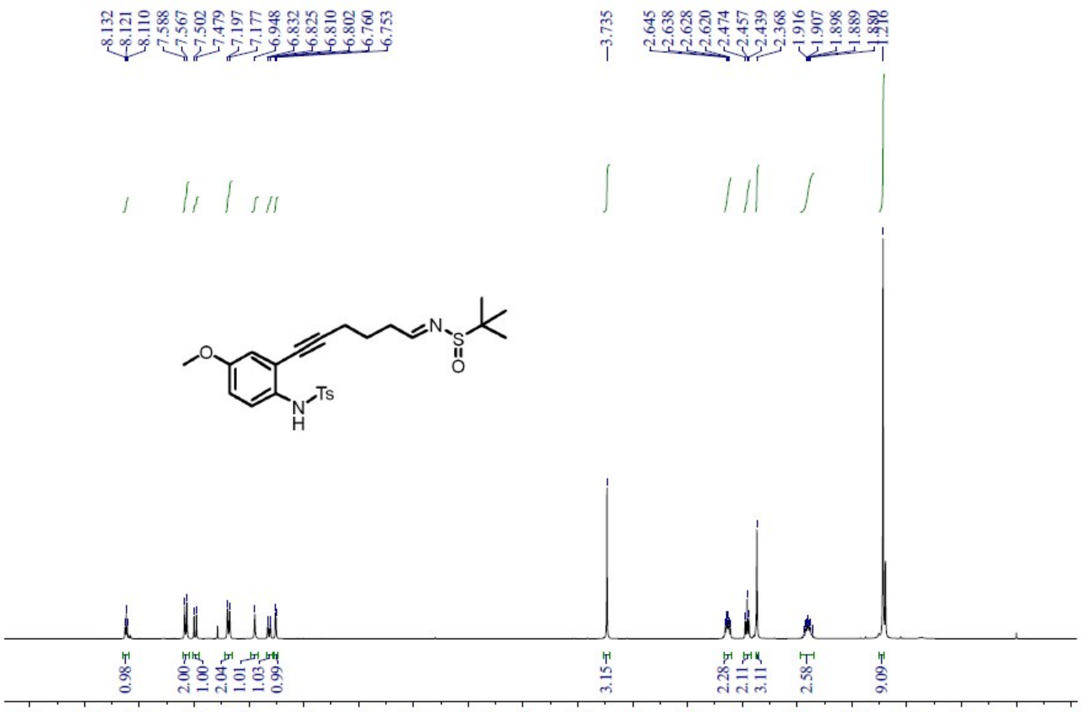
^1H NMR spectrum of 1e



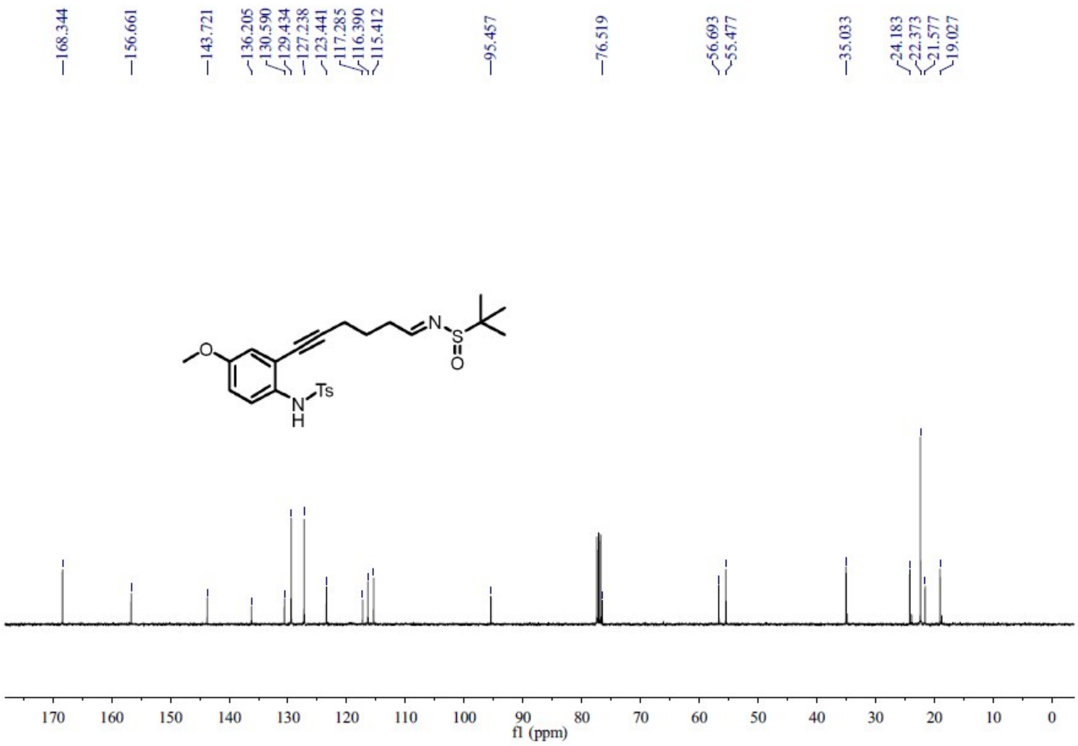
^{13}C NMR spectrum of 1e



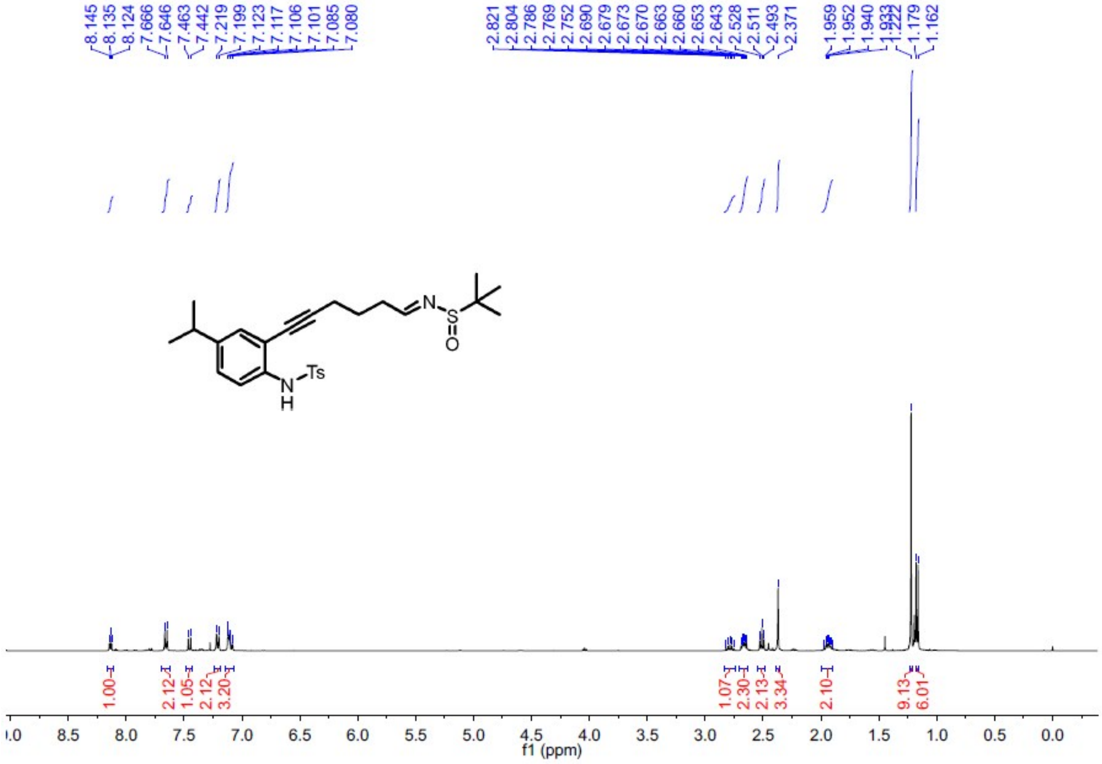
^{1}H NMR spectrum of 1f



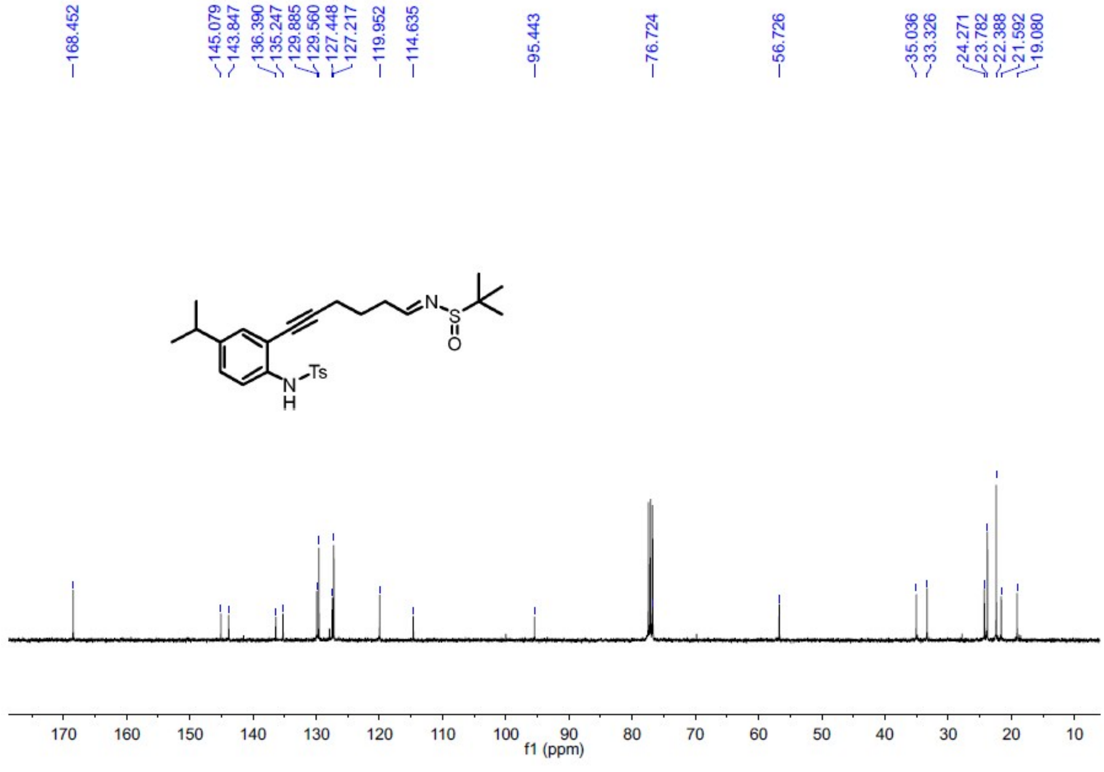
^{13}C NMR spectrum of 1f



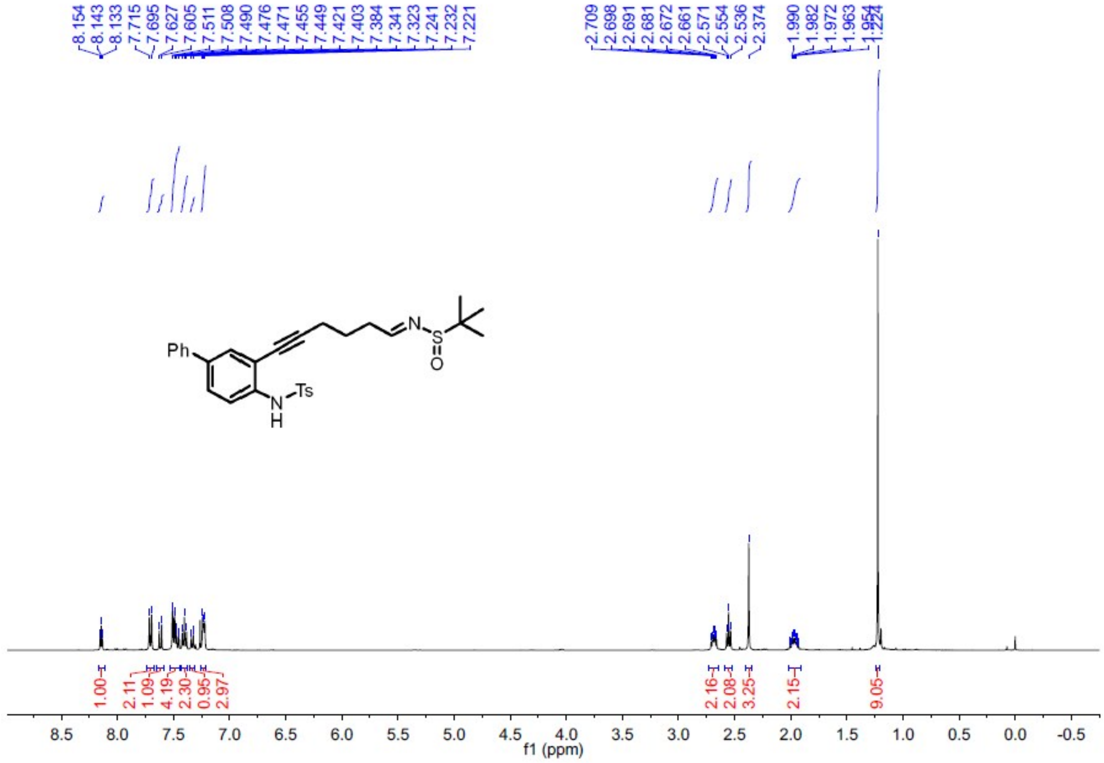
^{1}H NMR spectrum of 1g



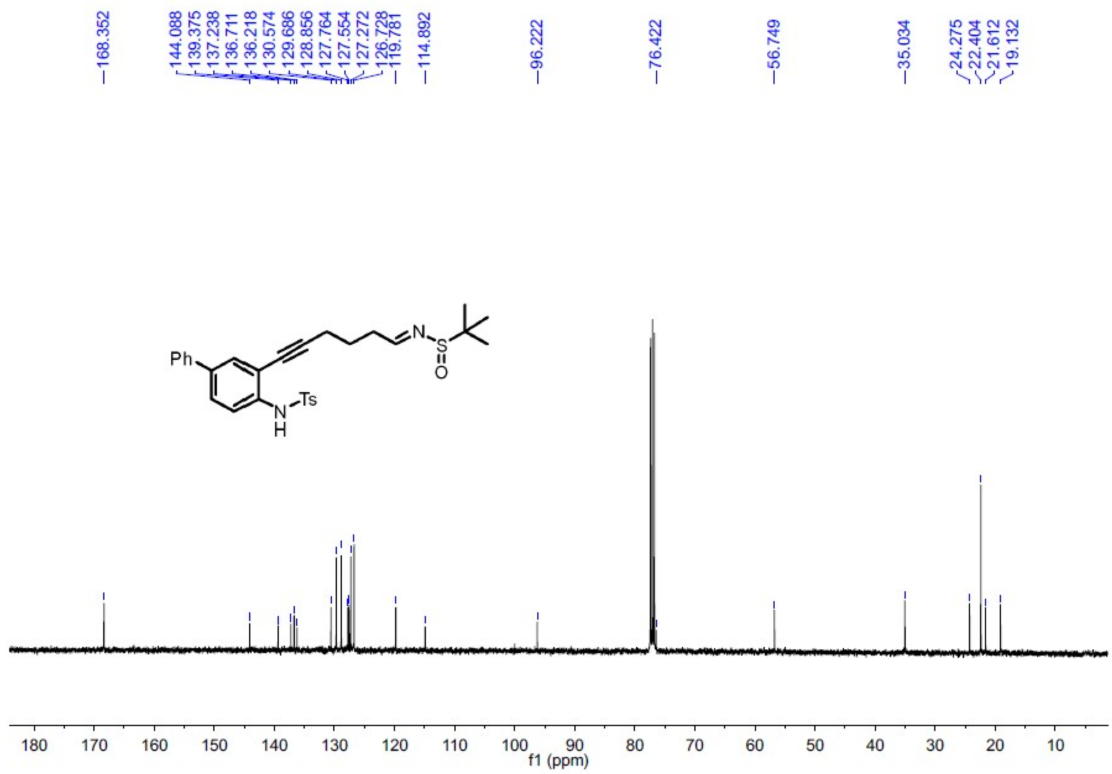
^{13}C NMR spectrum of 1g



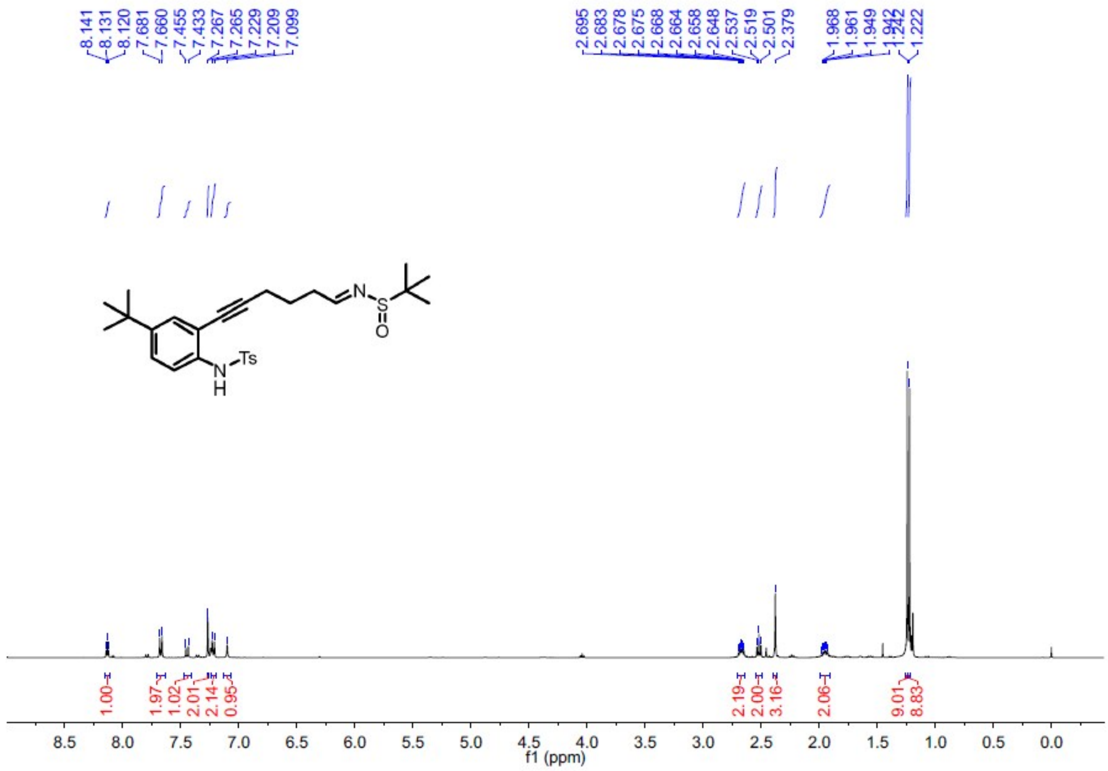
^{1}H NMR spectrum of 1h



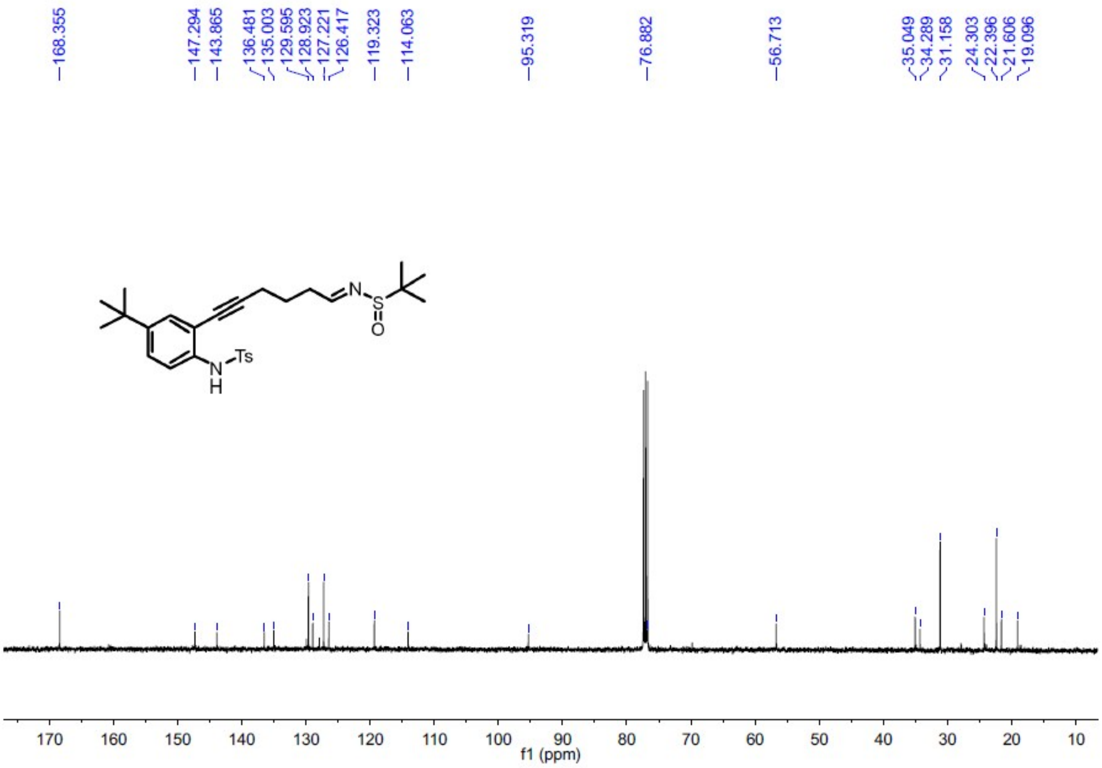
^{13}C NMR spectrum of 1h



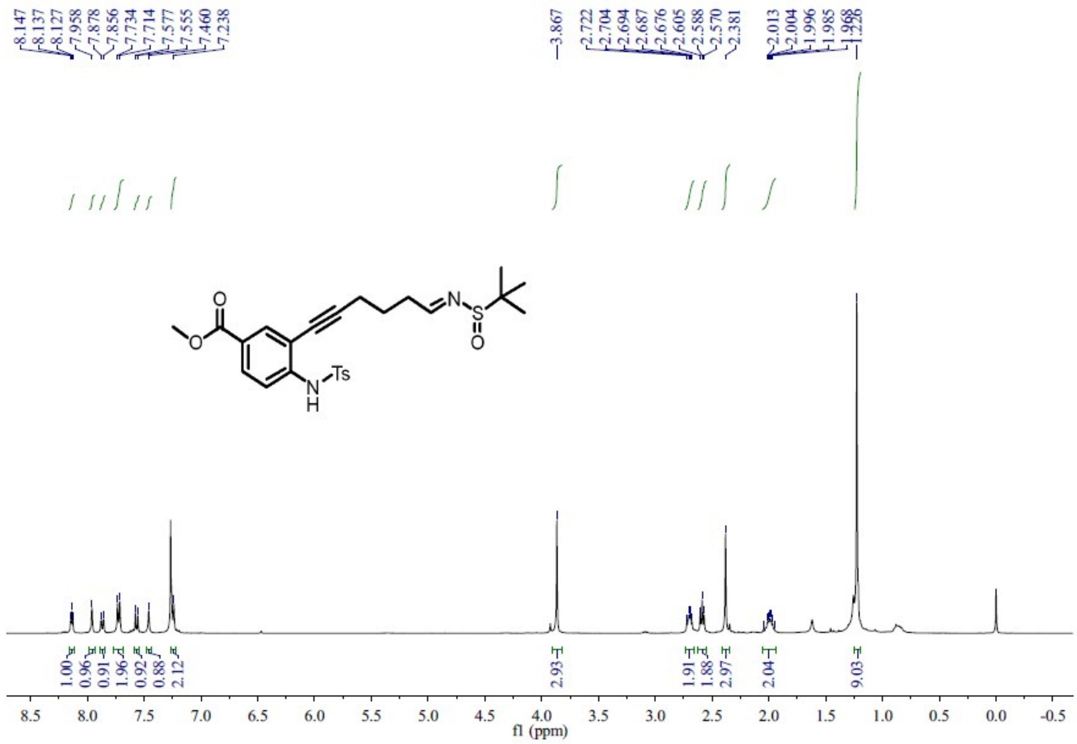
^{1}H NMR spectrum of 1i



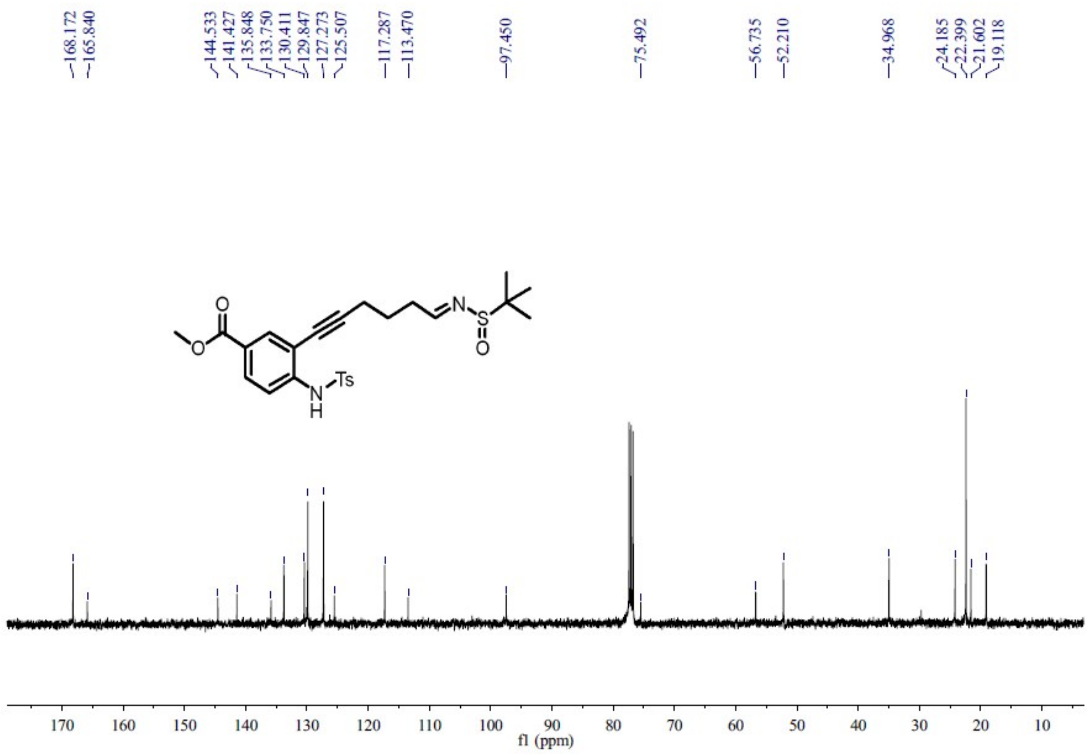
^{13}C NMR spectrum of 1i



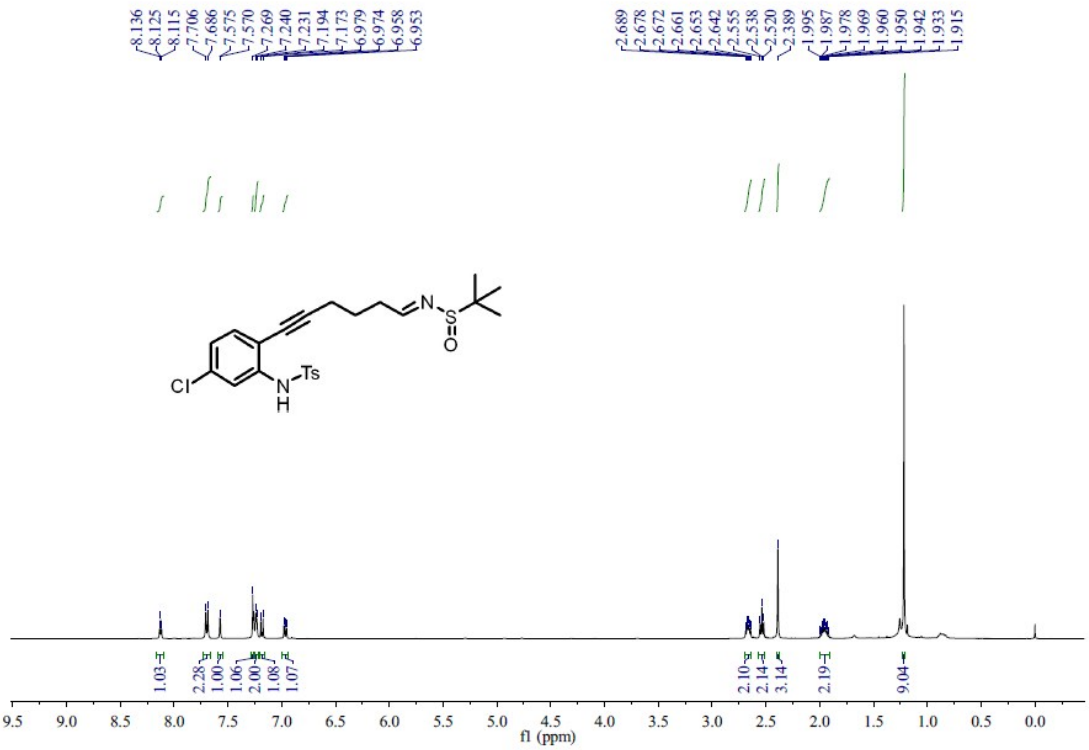
^{1}H NMR spectrum of 1j



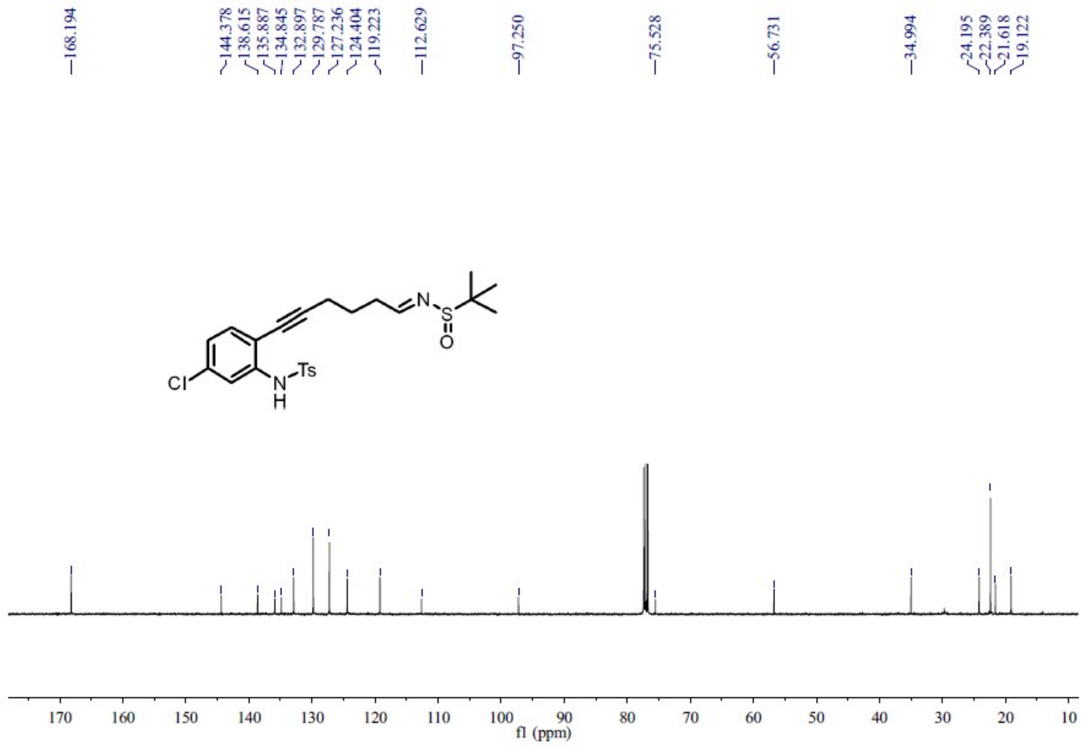
^{13}C NMR spectrum of 1j



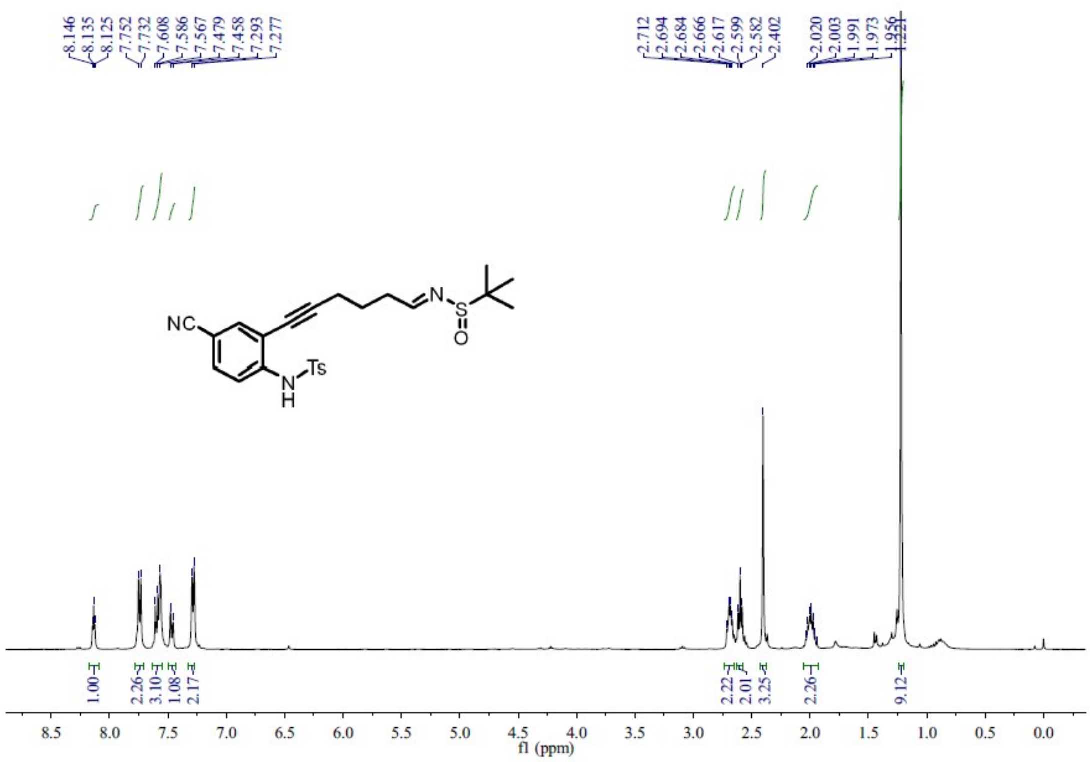
^{1}H NMR spectrum of 1k



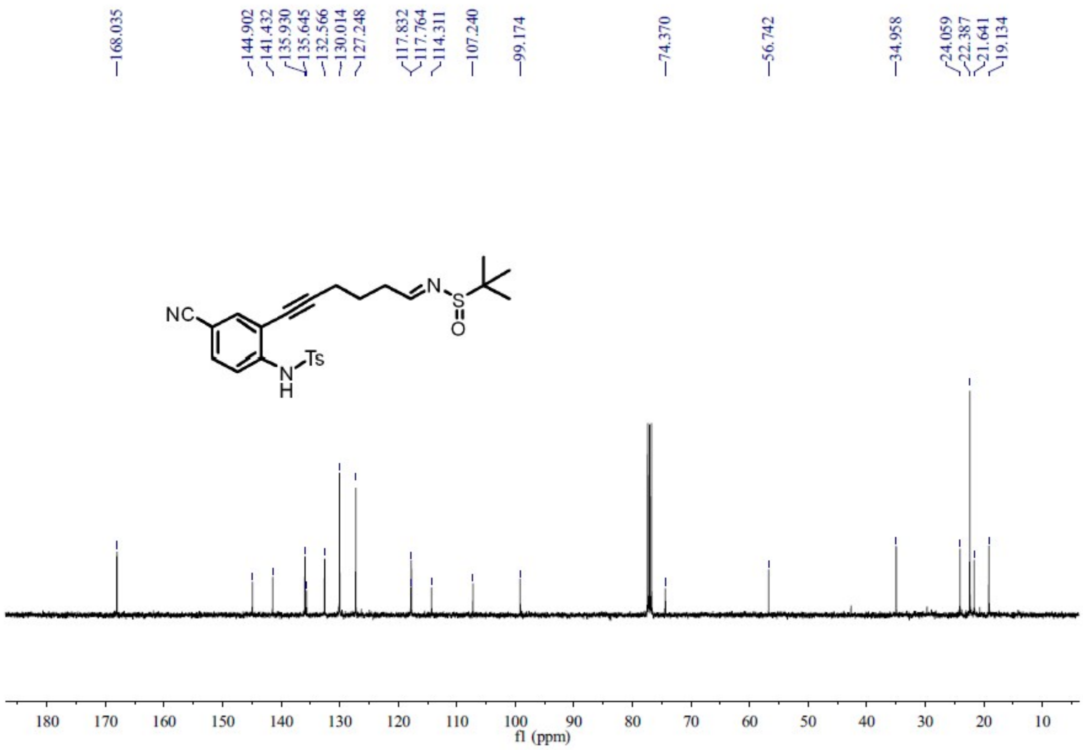
^{13}C NMR spectrum of 1k



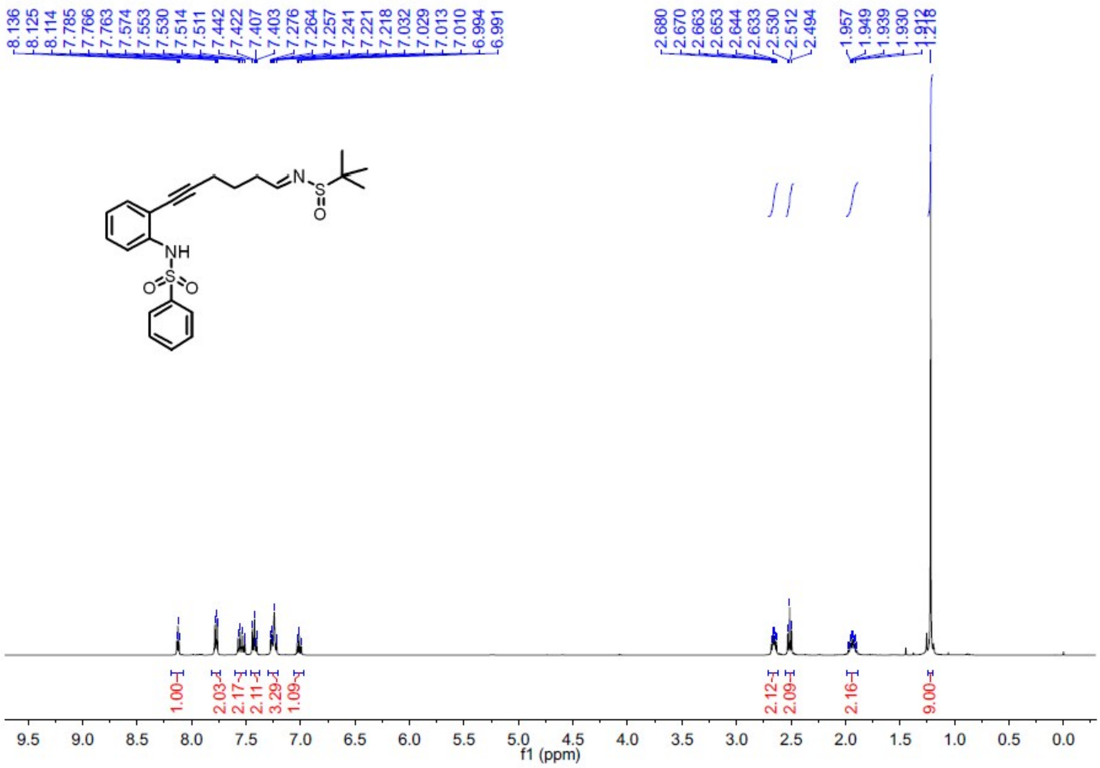
^{1}H NMR spectrum of 1l



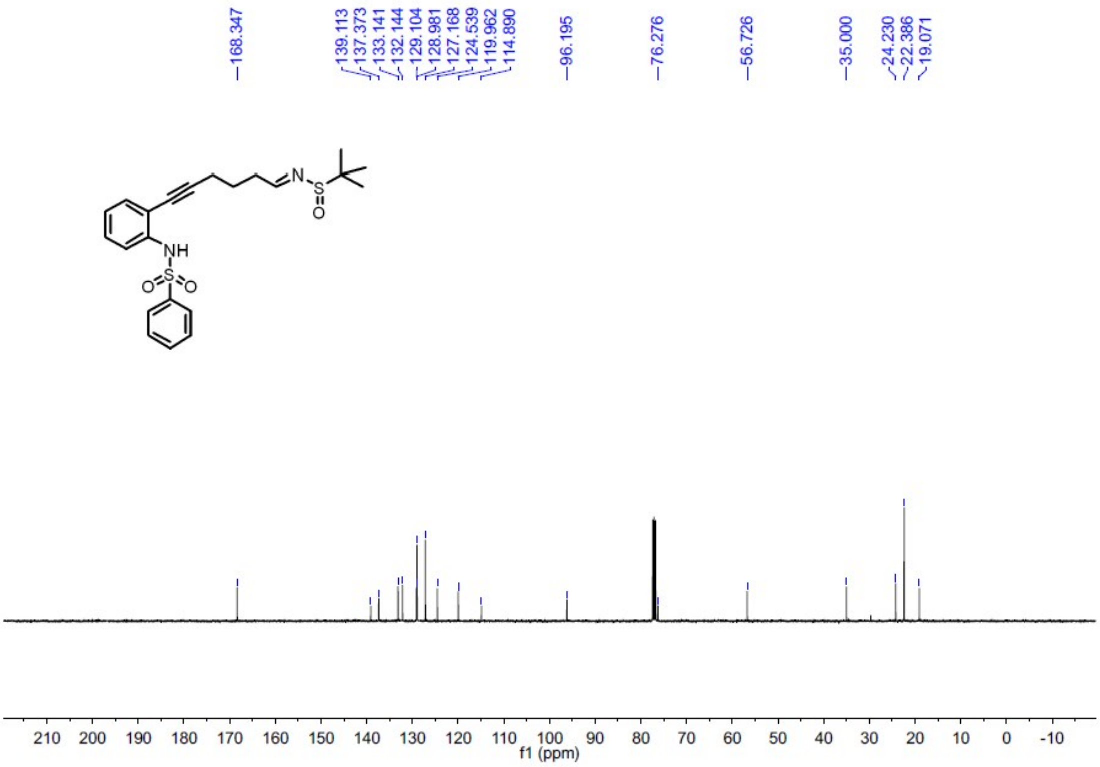
^{13}C NMR spectrum of 1l



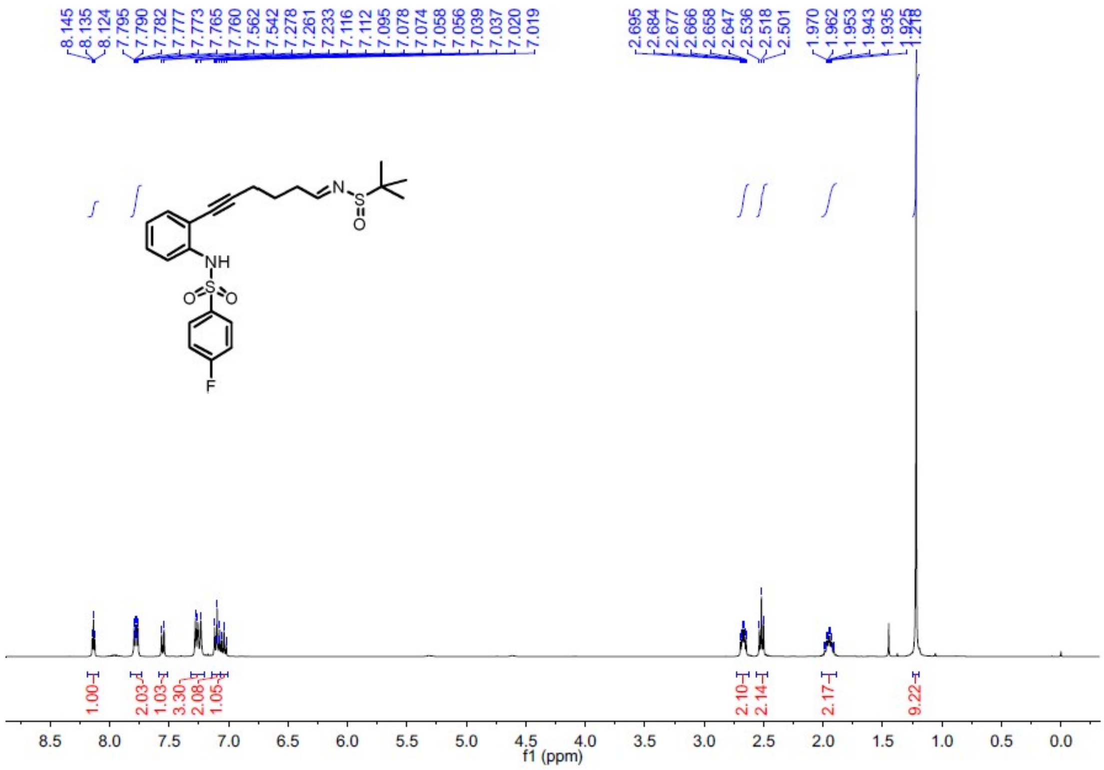
^{1}H NMR spectrum of 1m



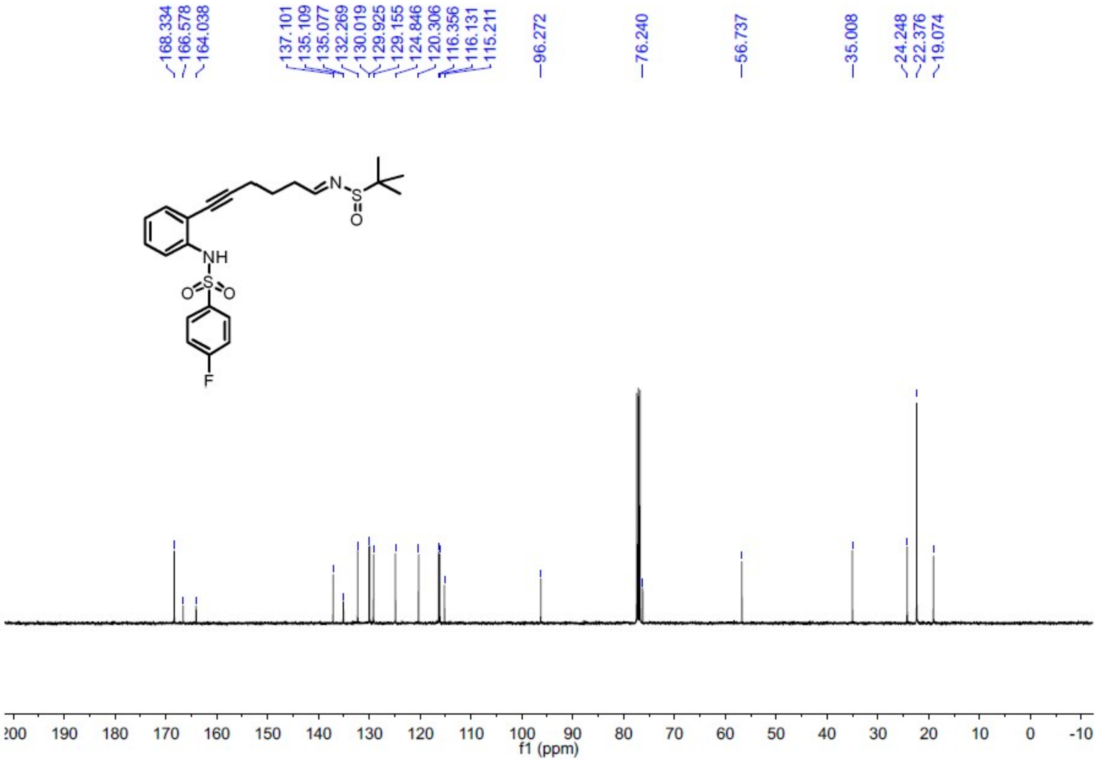
^{13}C NMR spectrum of 1m



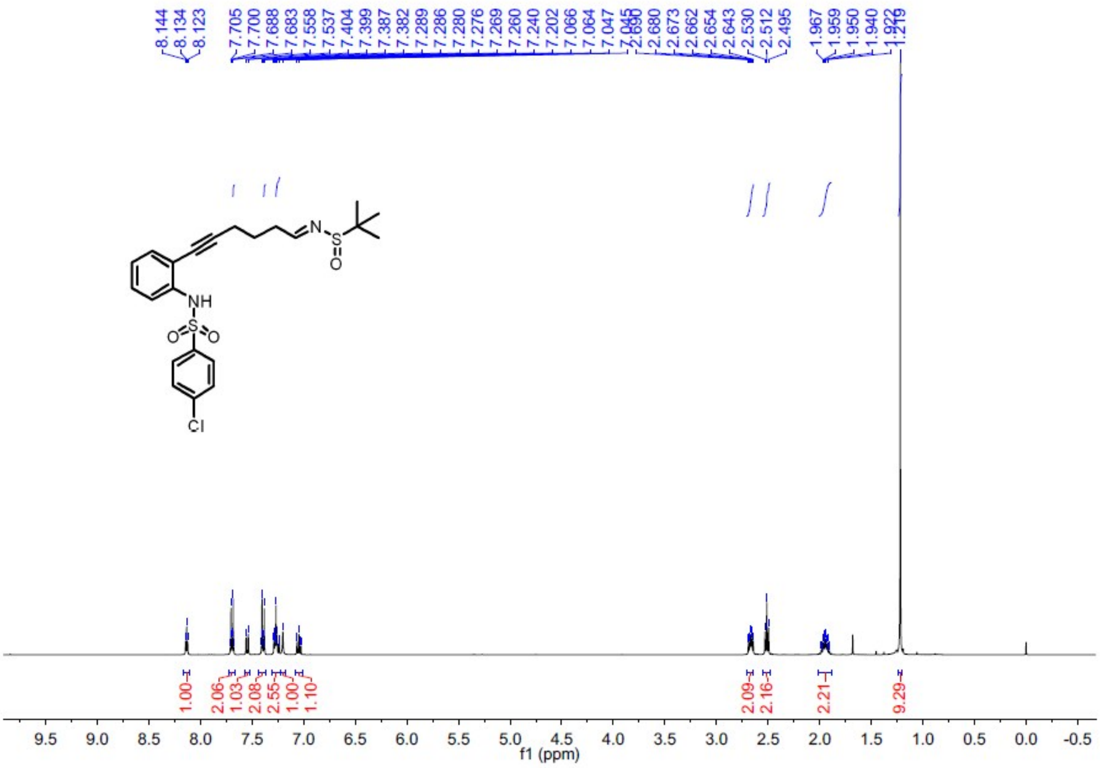
[1]H NMR spectrum of 1n



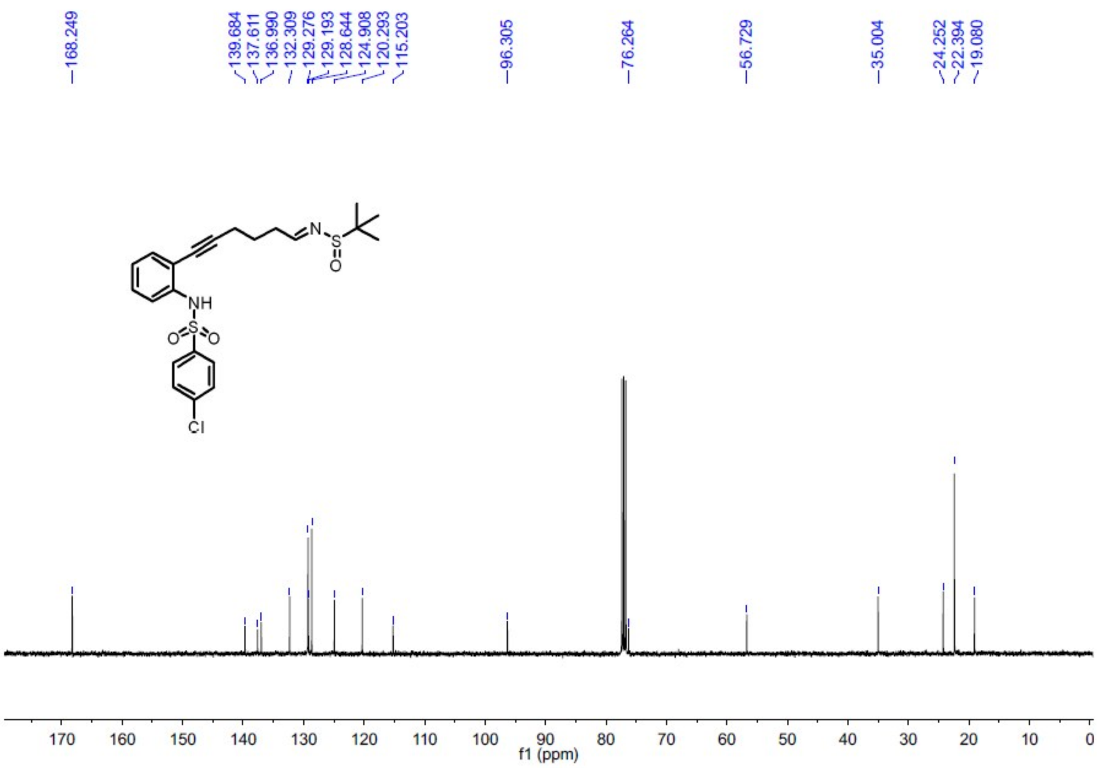
[13]C NMR spectrum of 1n



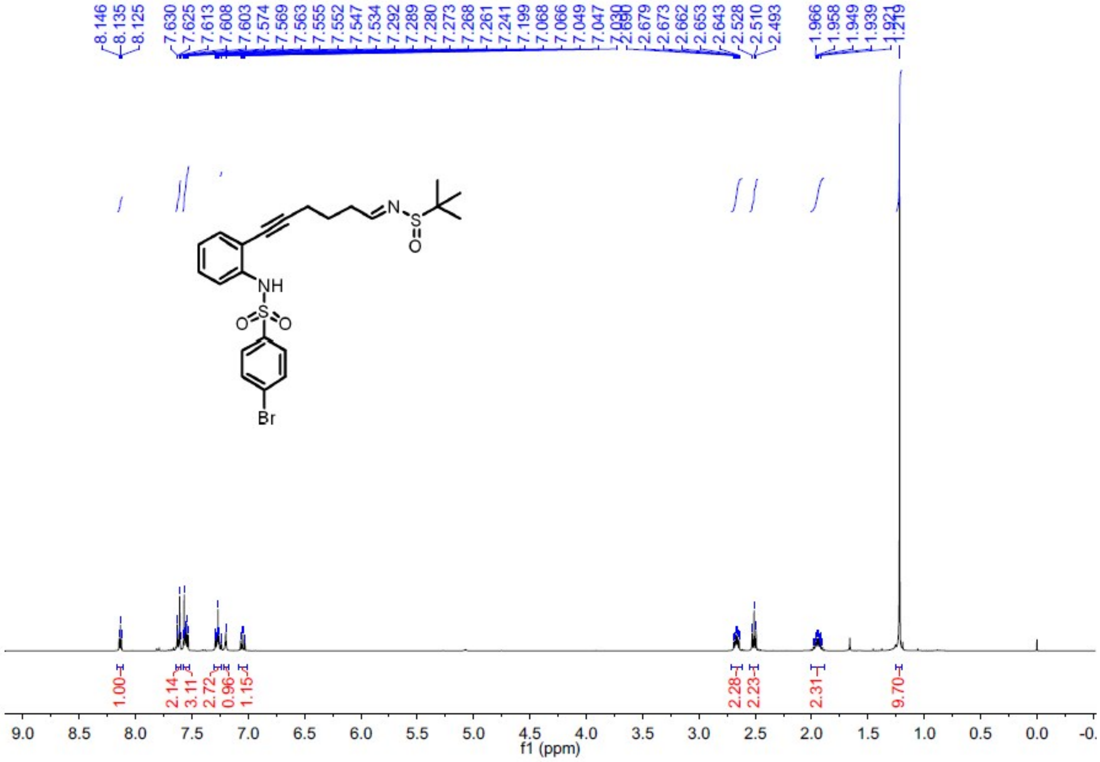
^{1}H NMR spectrum of 1o



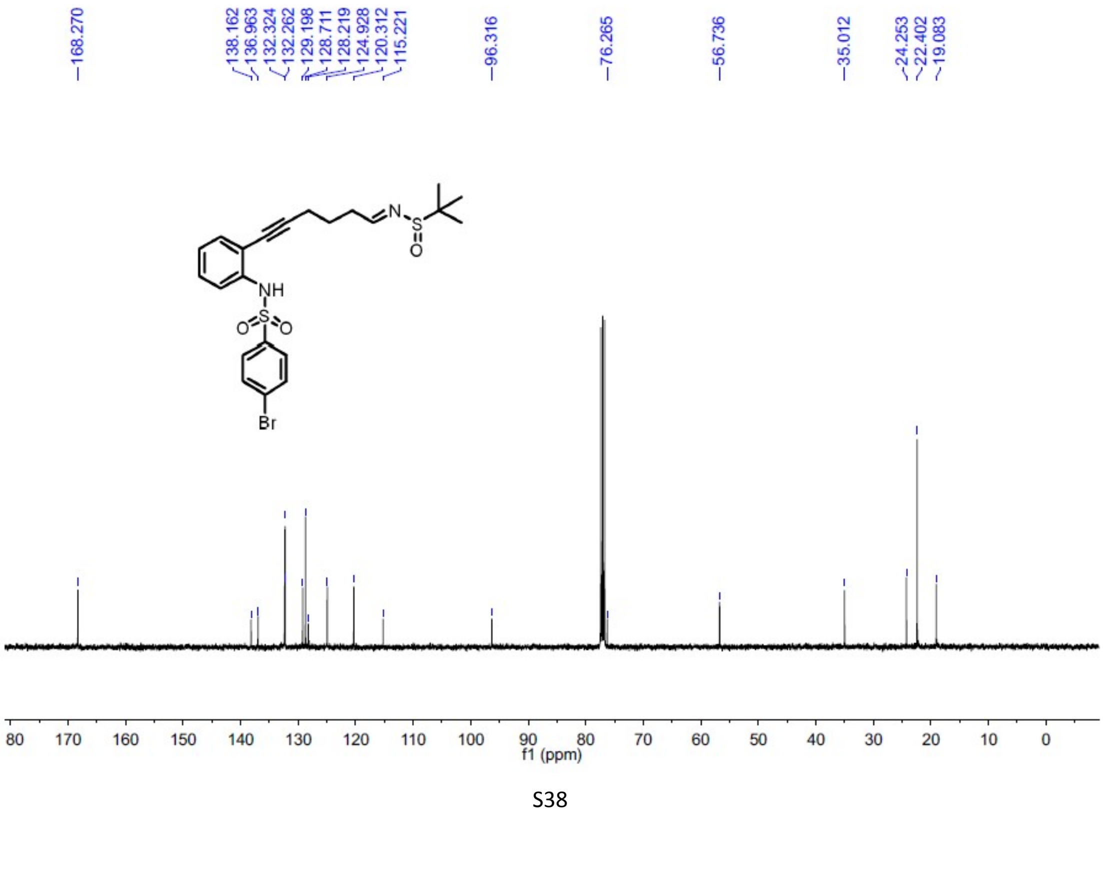
^{13}C NMR spectrum of 1o



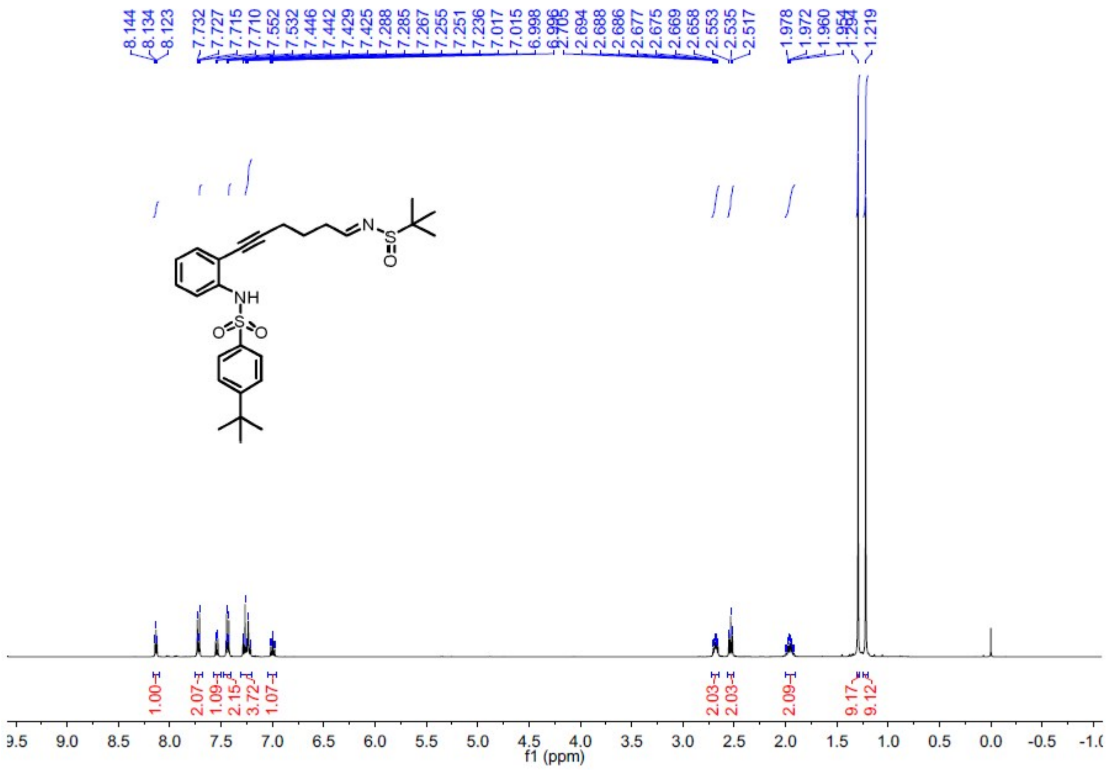
^{1}H NMR spectrum of 1p



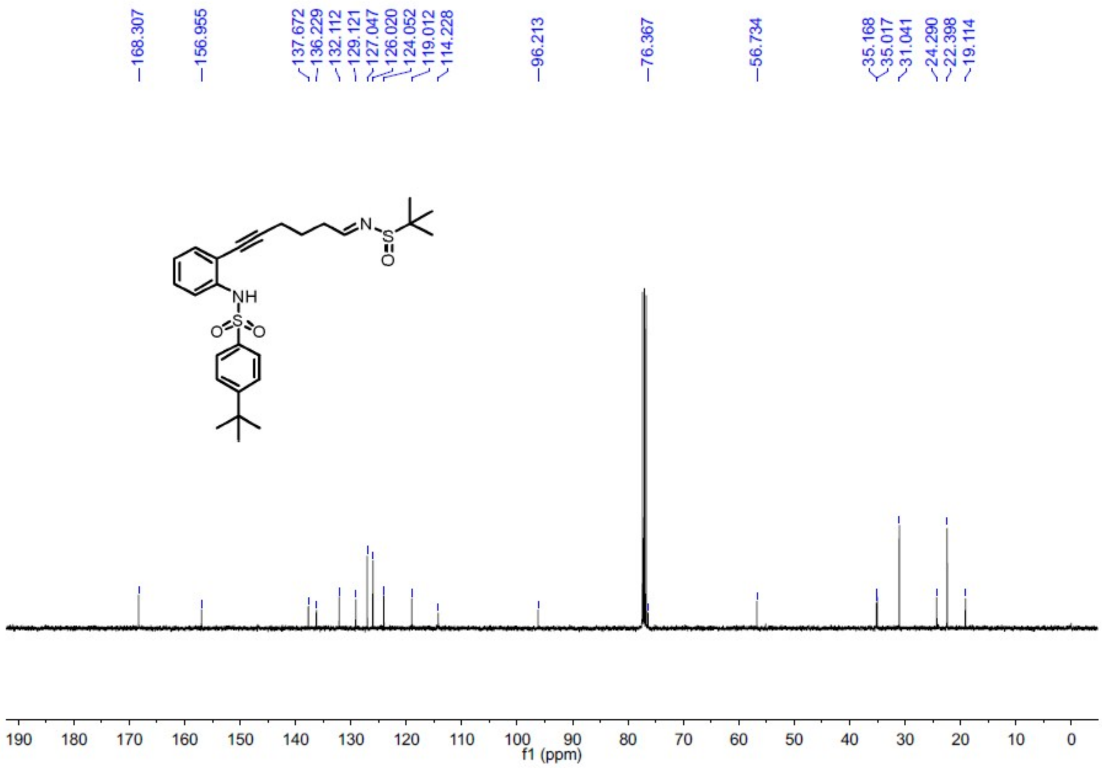
^{13}C NMR spectrum of 1p



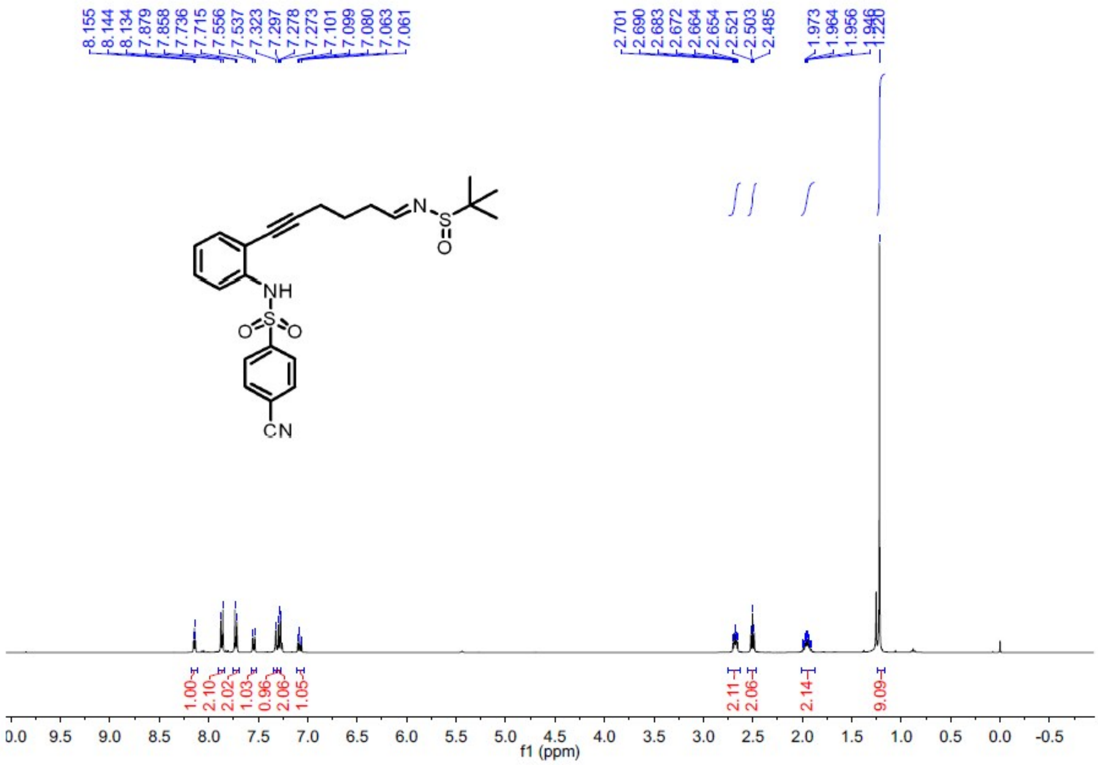
^{1}H NMR spectrum of 1q



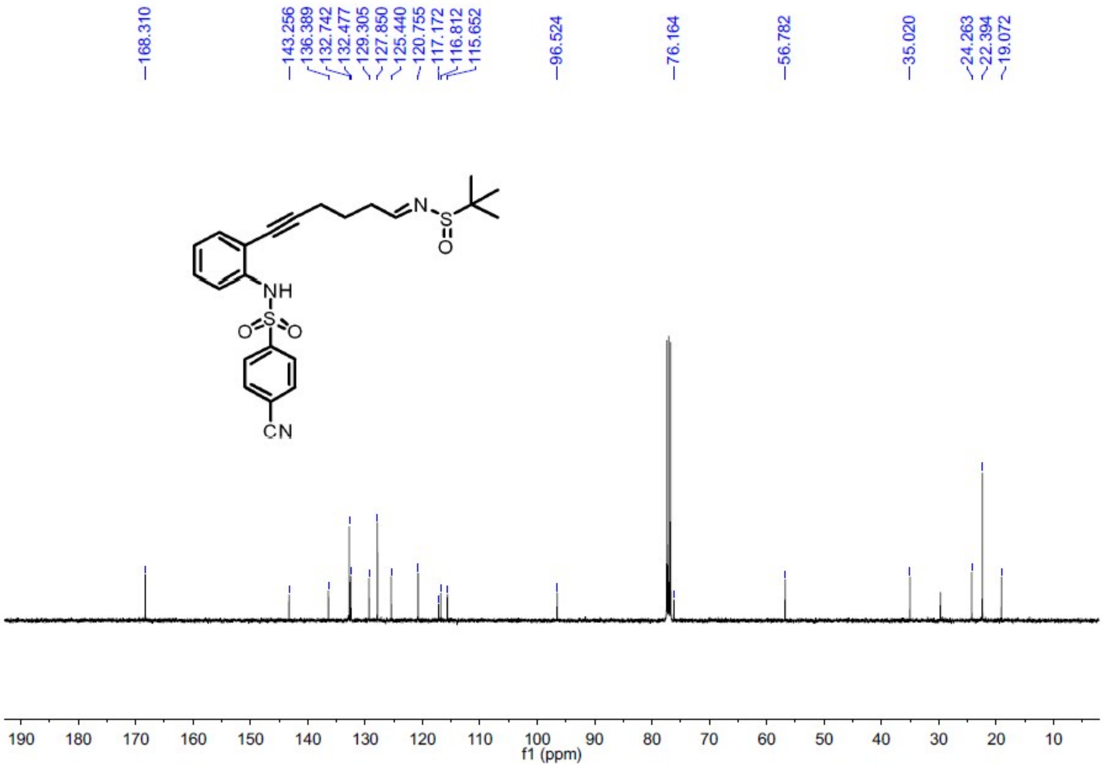
^{13}C NMR spectrum of 1q



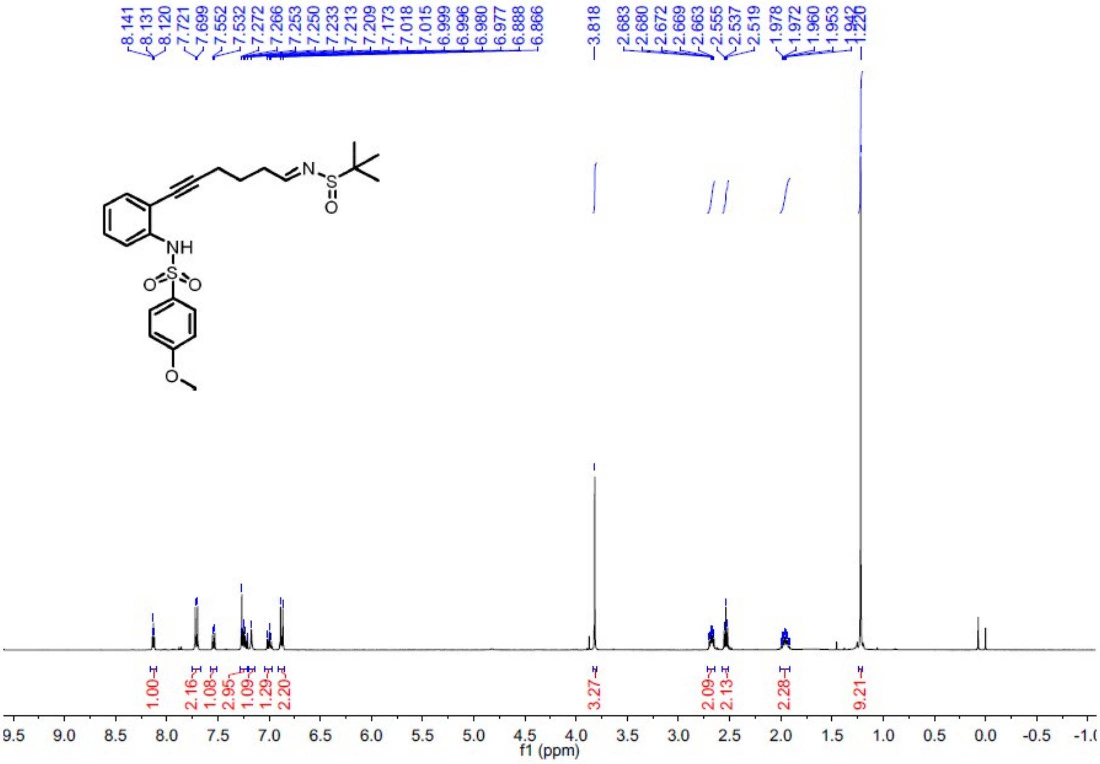
^{1}H NMR spectrum of 1r



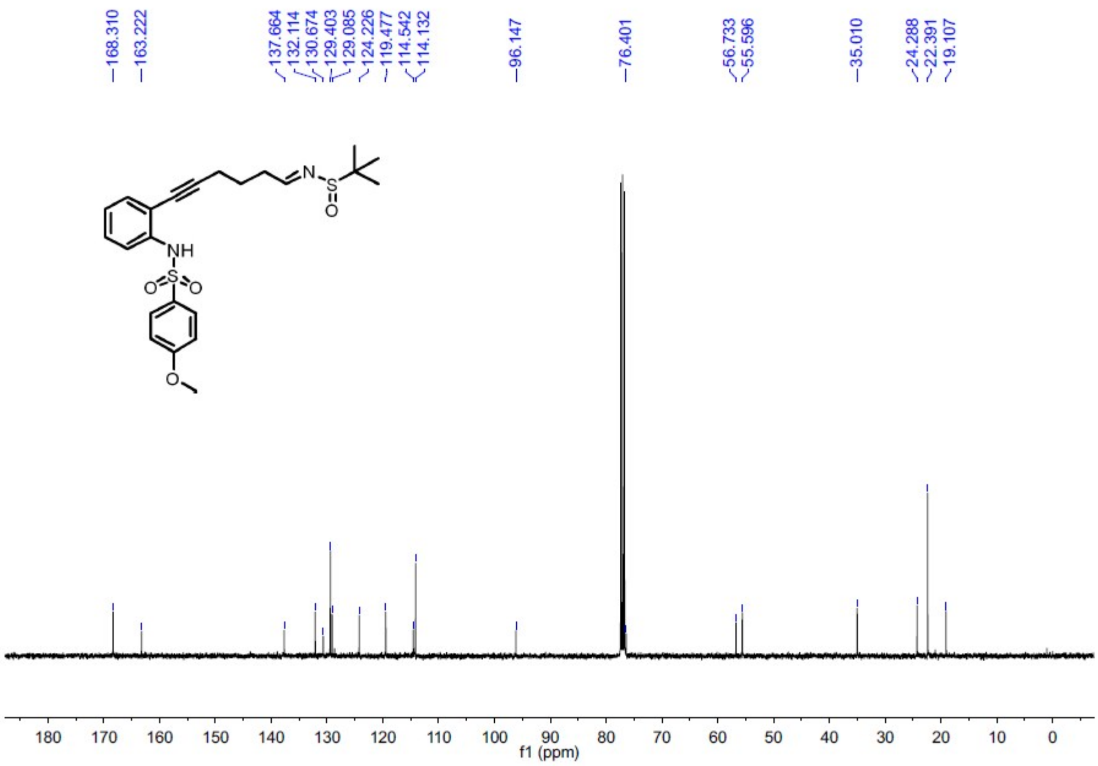
^{13}C NMR spectrum of 1r



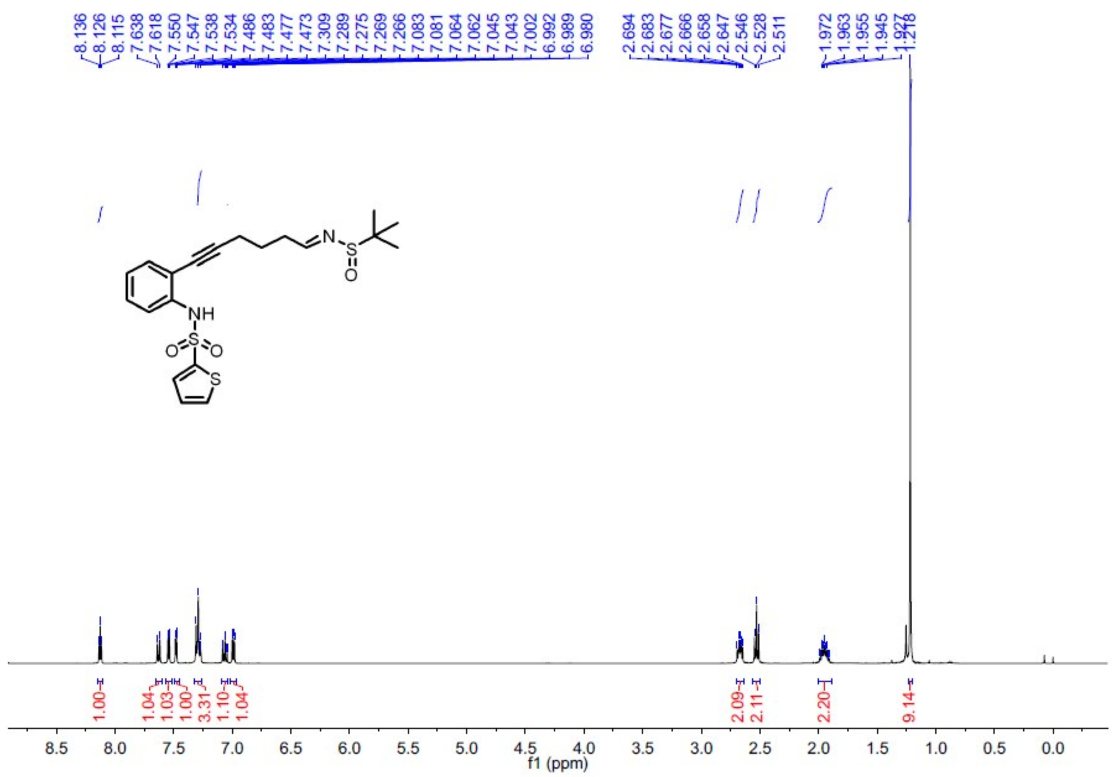
^{1}H NMR spectrum of 1s



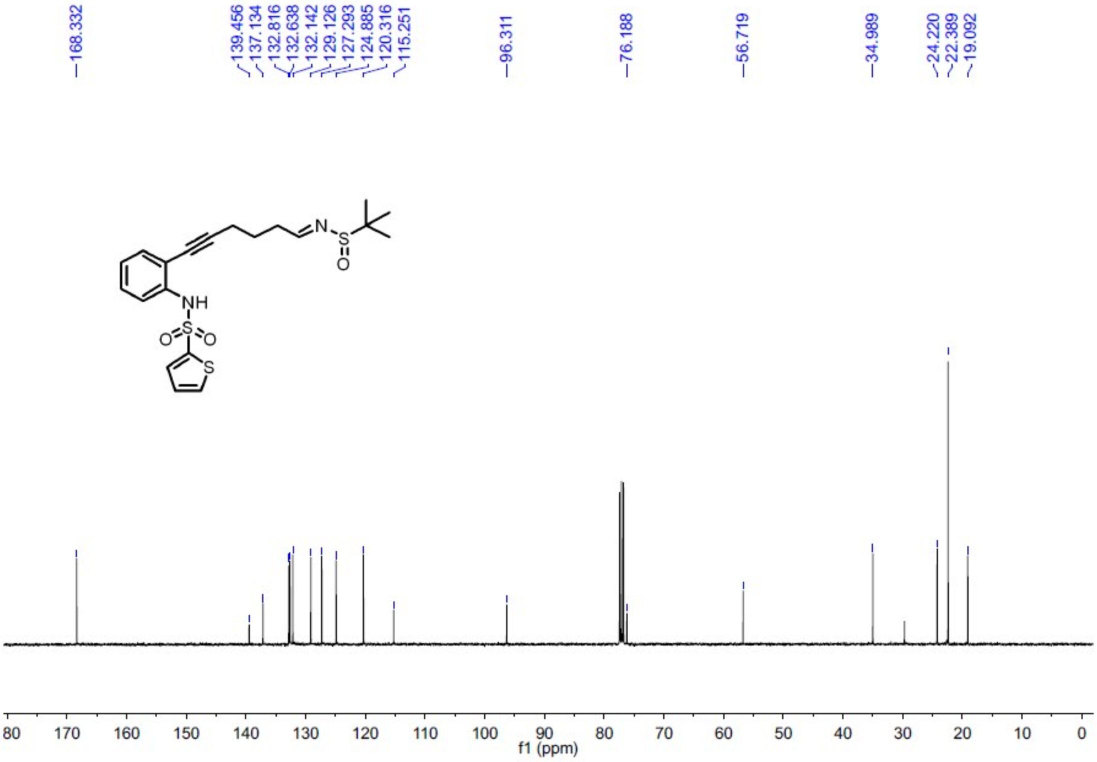
^{13}C NMR spectrum of 1s



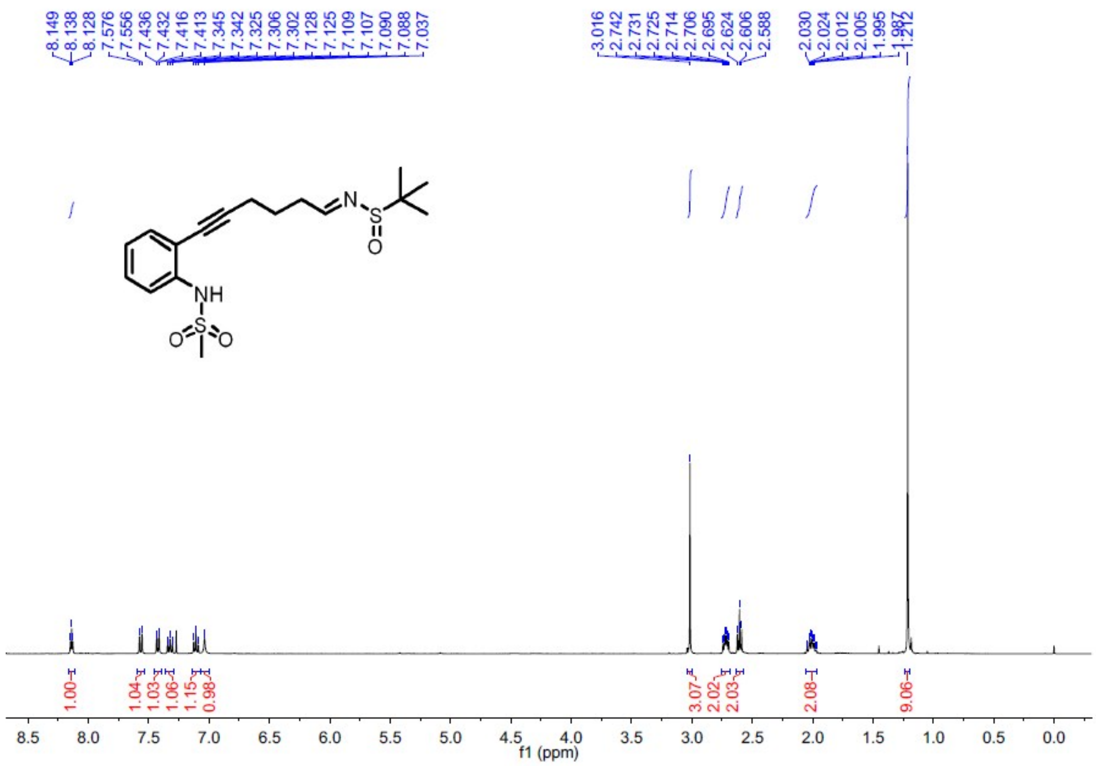
^{1}H NMR spectrum of 1t



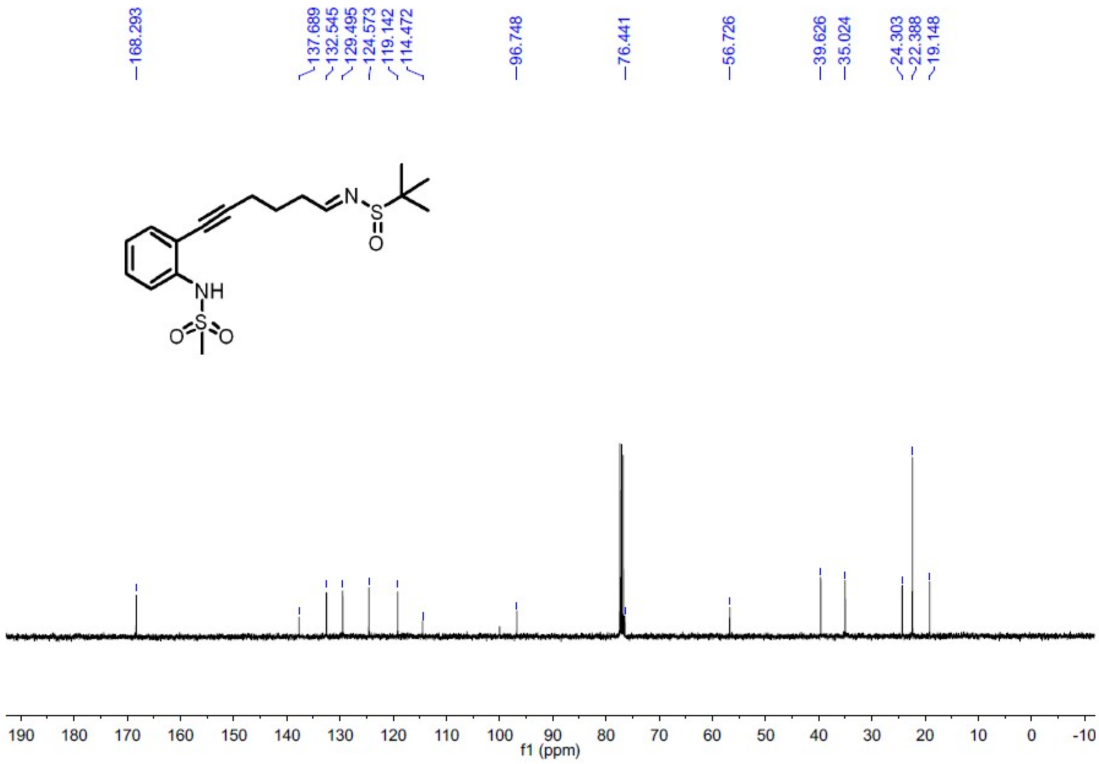
^{13}C NMR spectrum of 1s



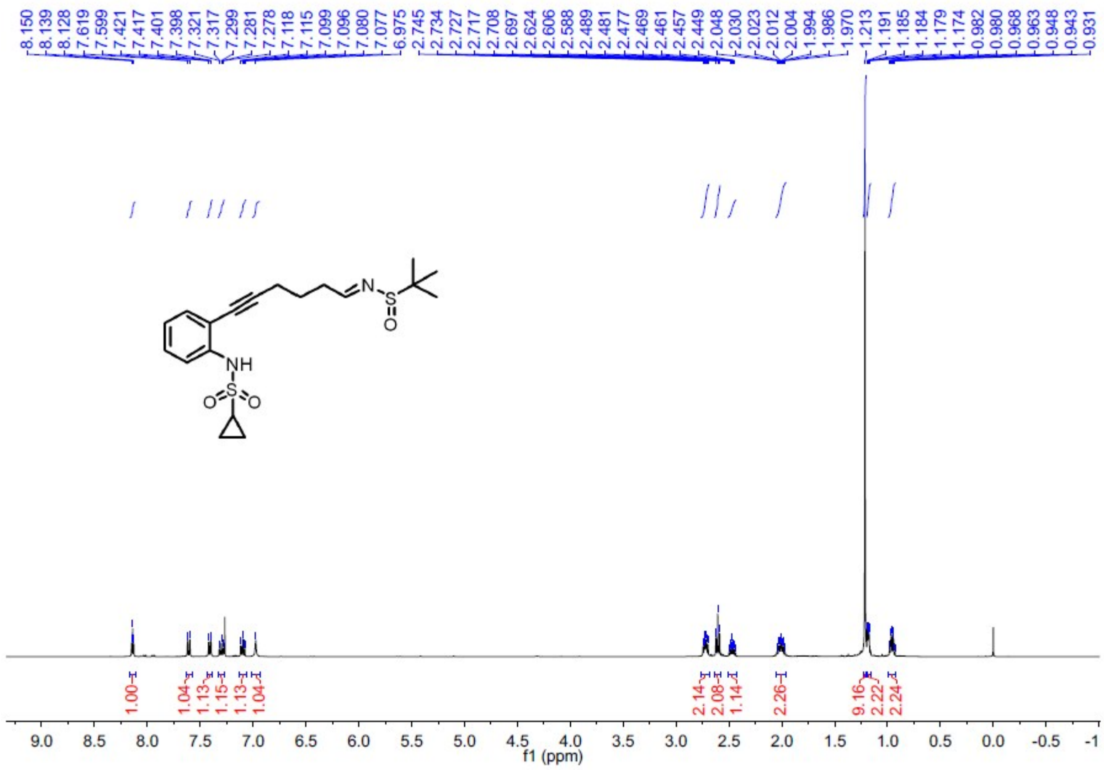
^1H NMR spectrum of 1u



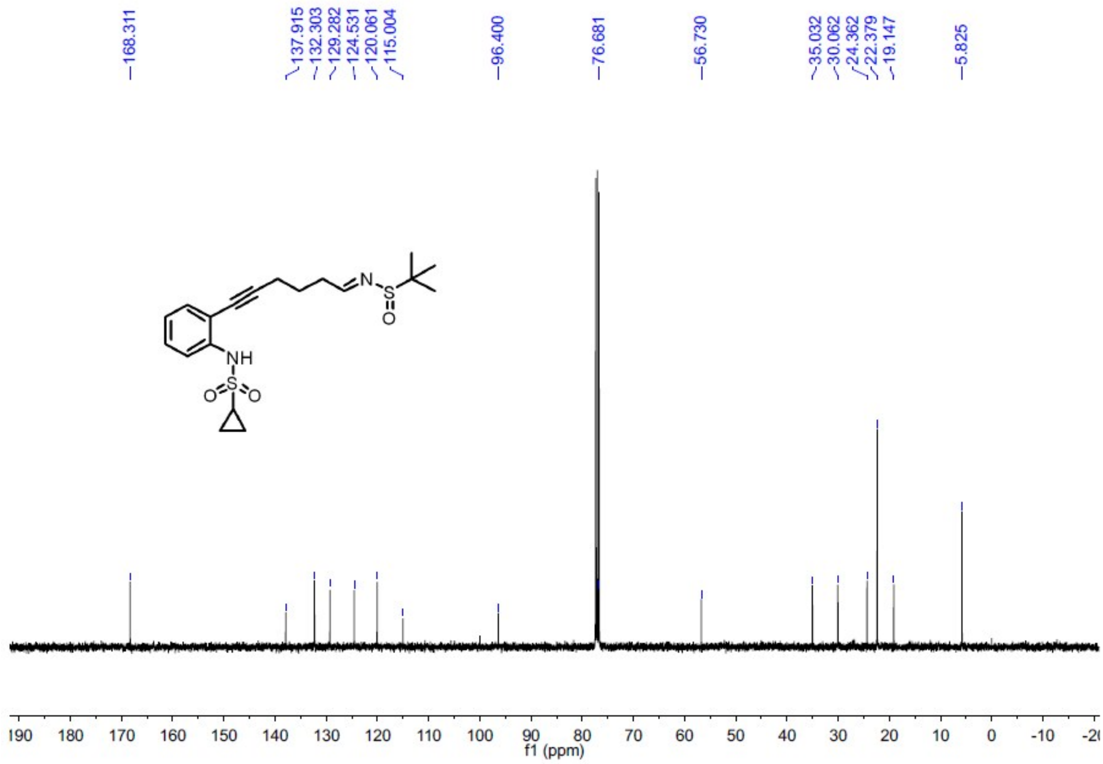
^{13}C NMR spectrum of 1u



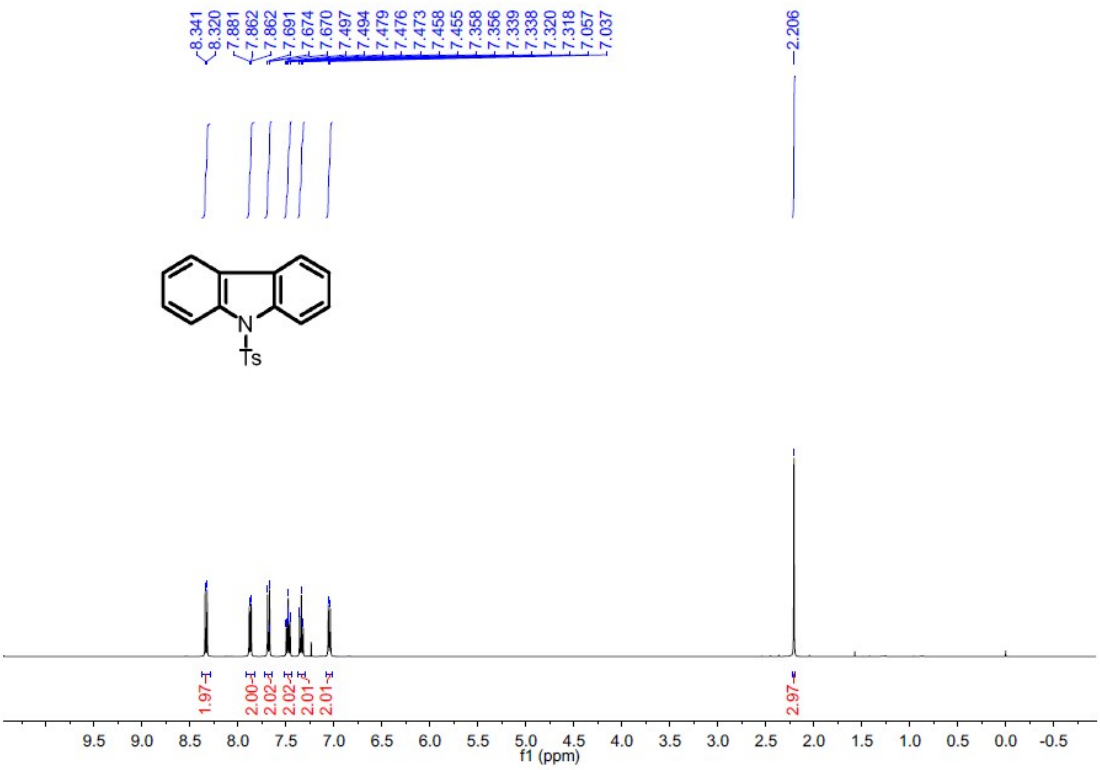
^{1}H NMR spectrum of 1v



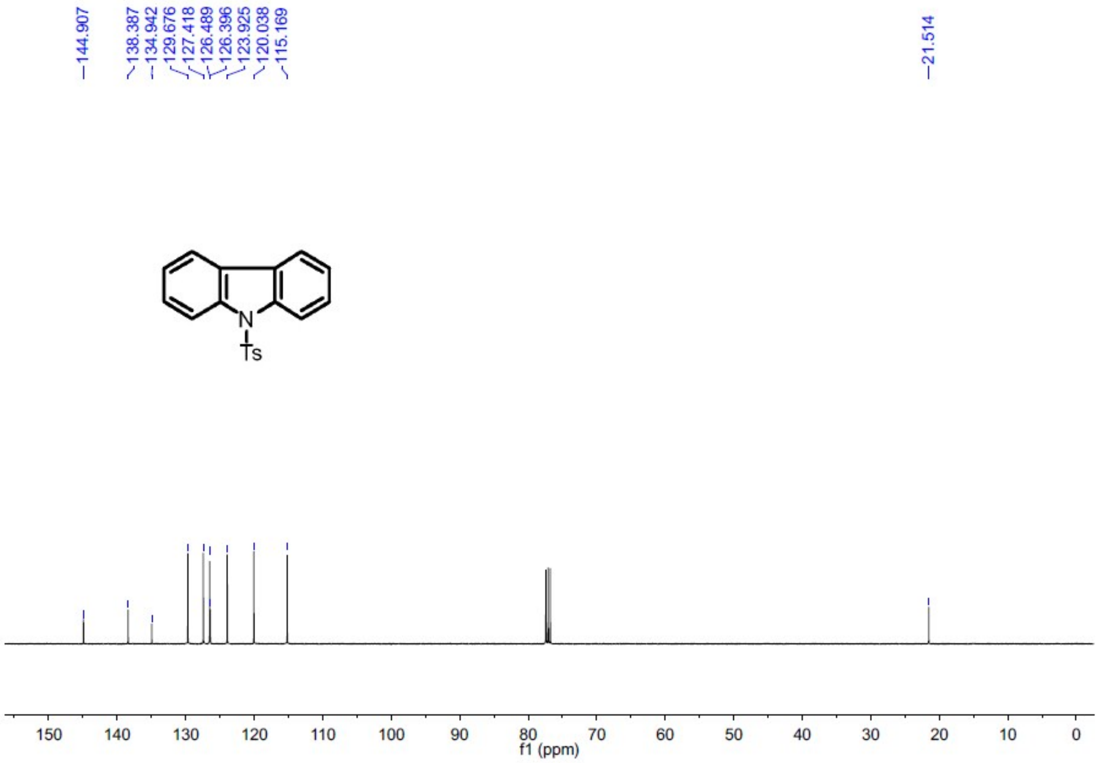
^{13}C NMR spectrum of 1v



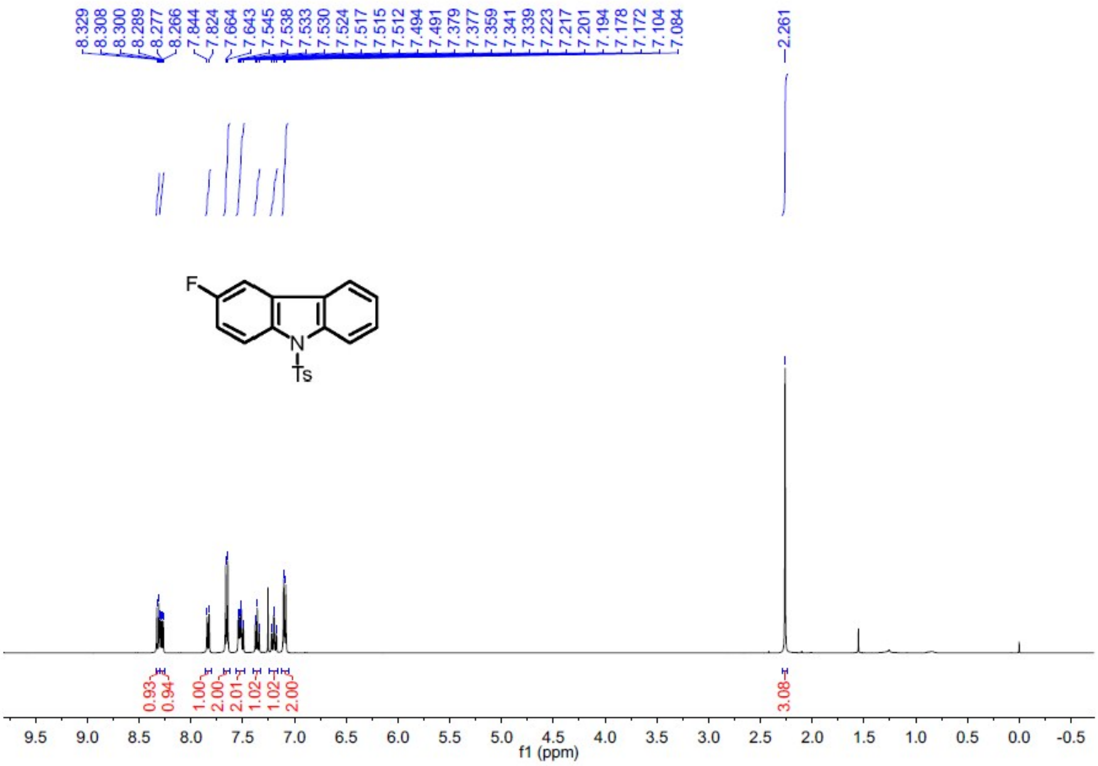
^{1}H NMR spectrum of 2a



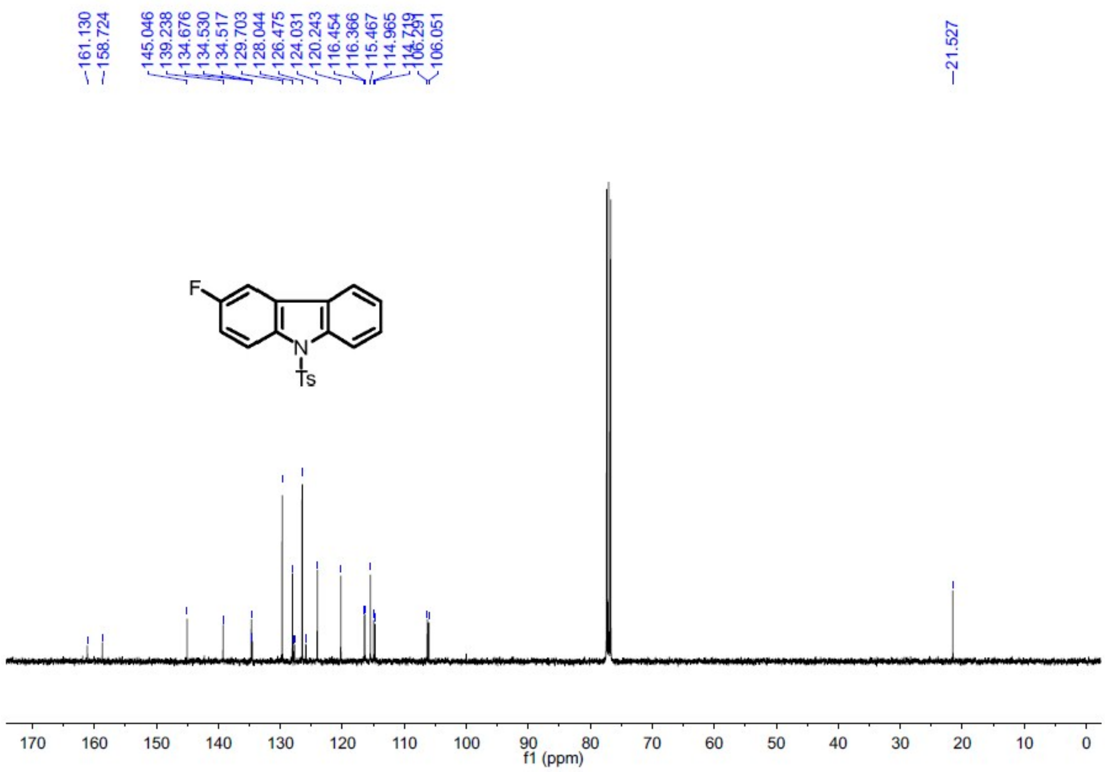
^{13}C NMR spectrum of 2a



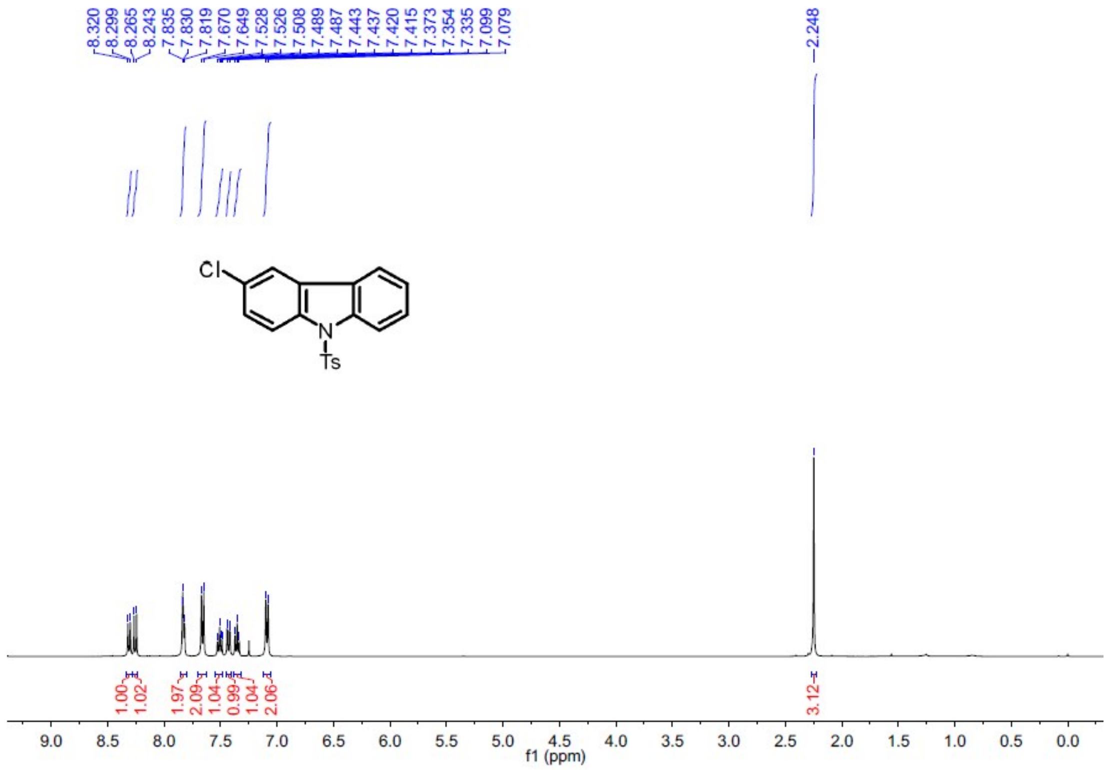
^{1}H NMR spectrum of 2b



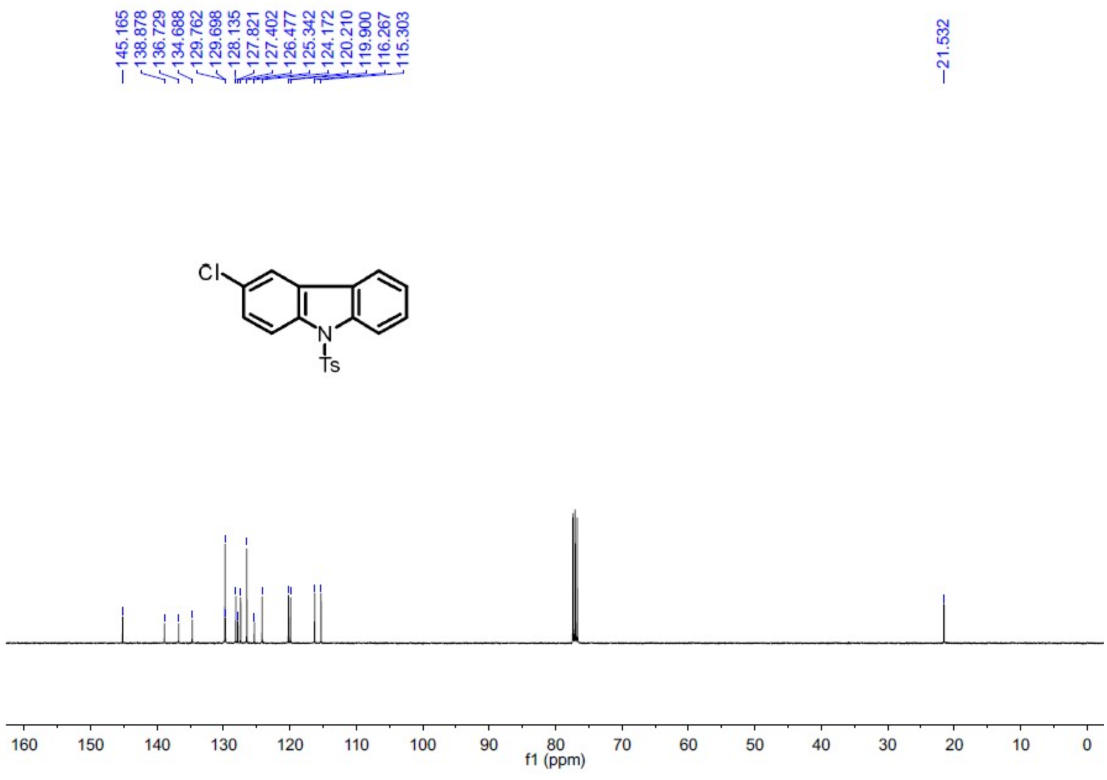
^{13}C NMR spectrum of 2b



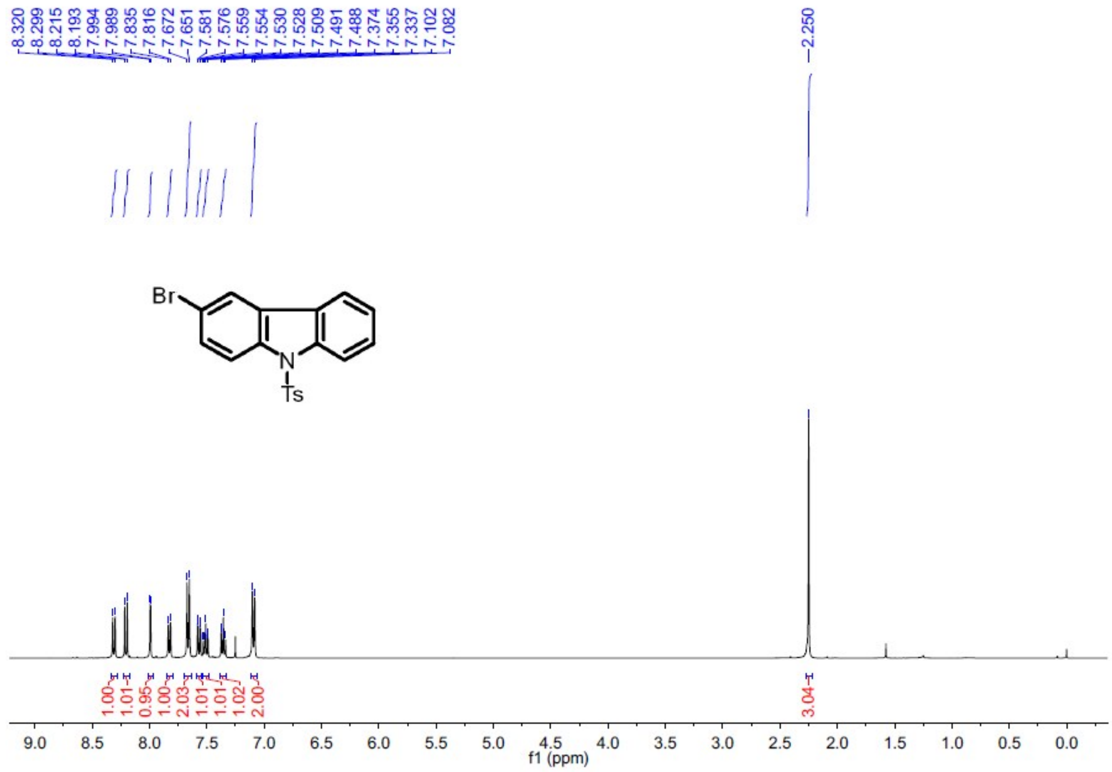
^{1}H NMR spectrum of 2c



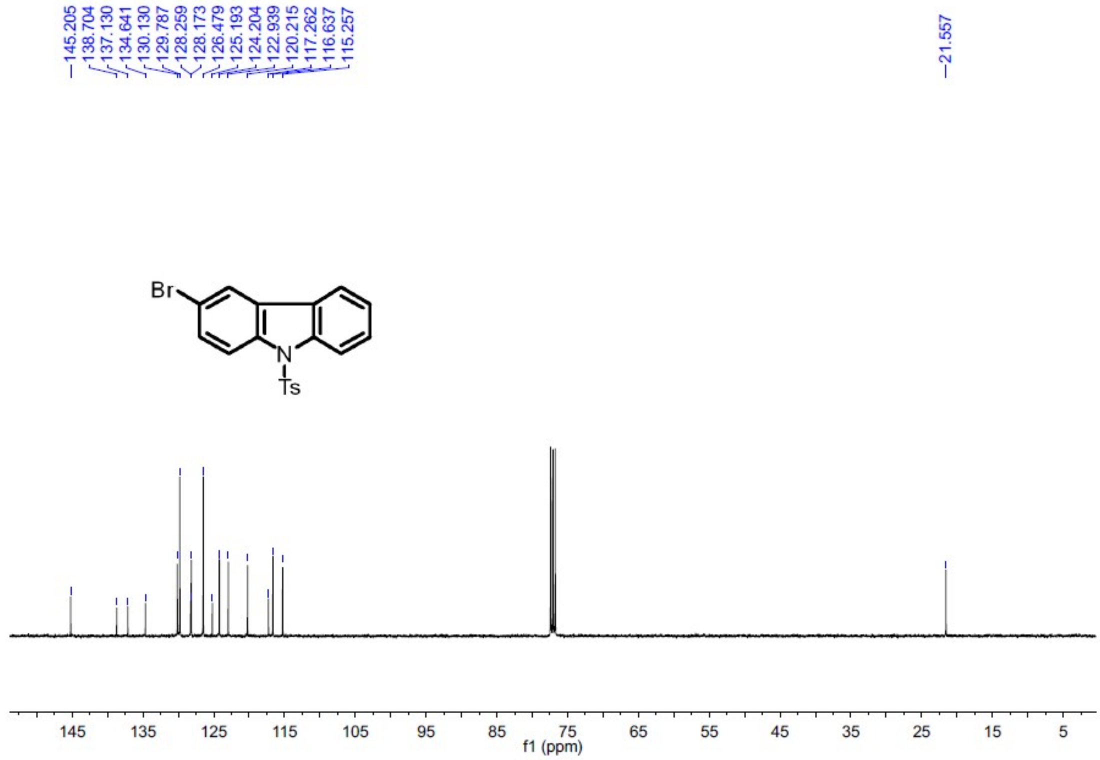
^{13}C NMR spectrum of 2c



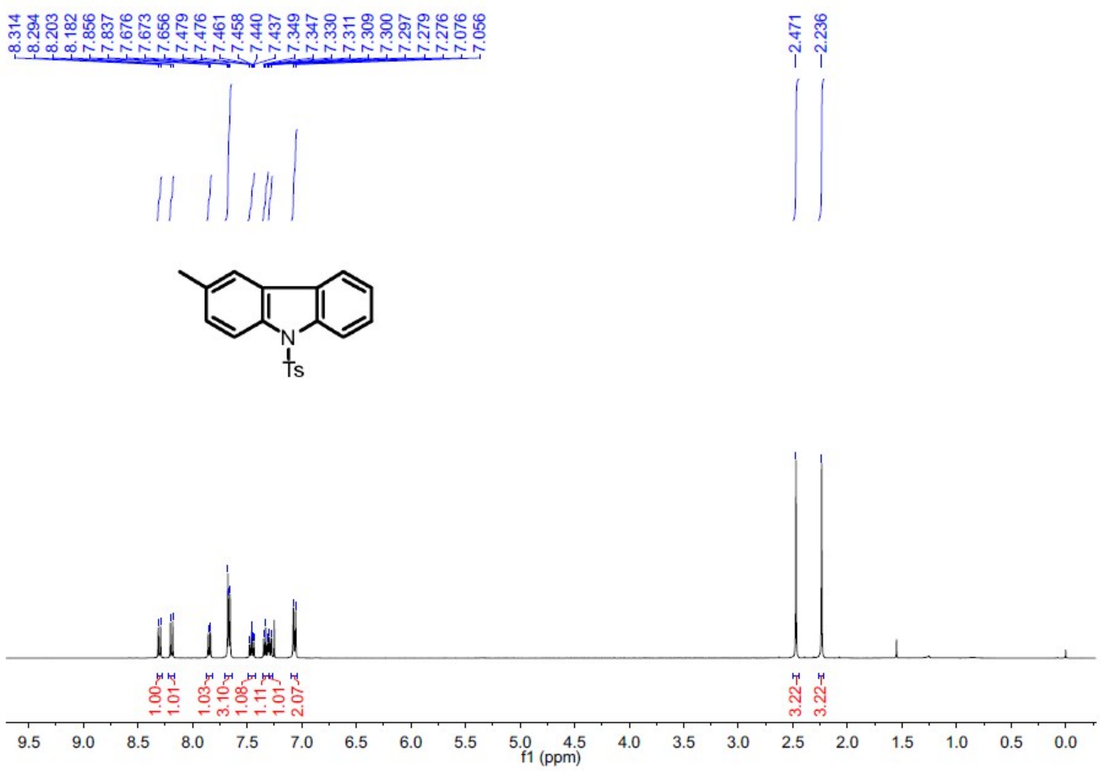
^{1}H NMR spectrum of 2d



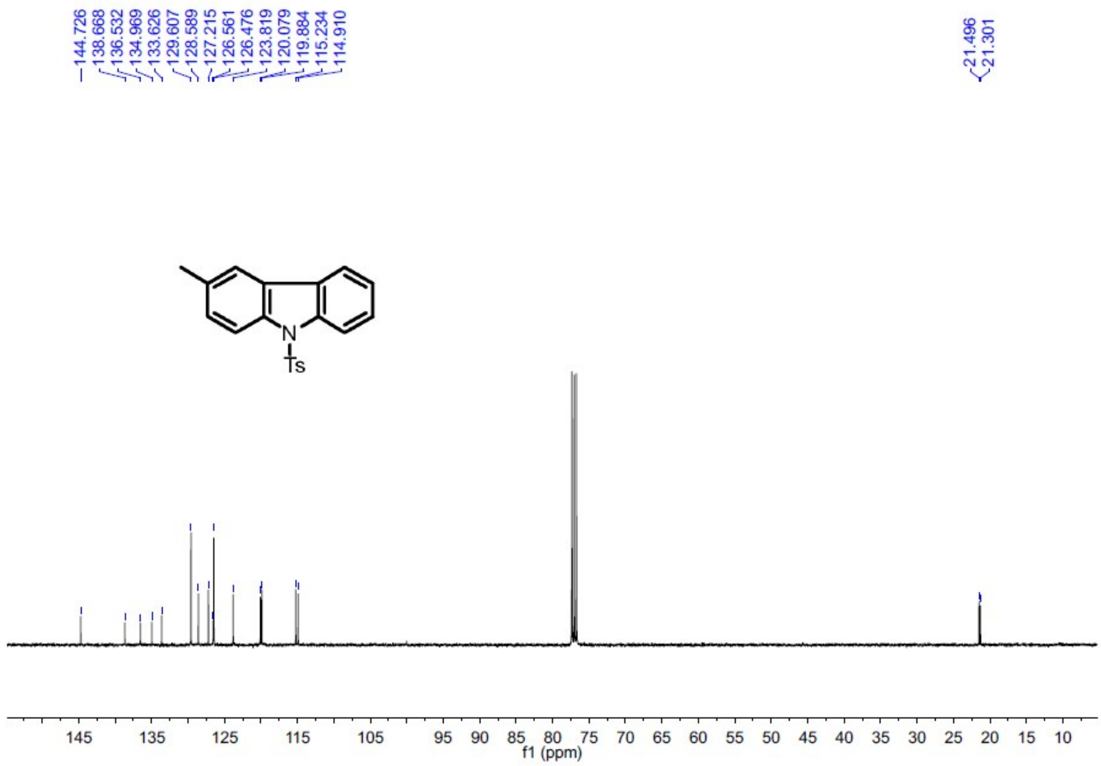
^{13}C NMR spectrum of 2d



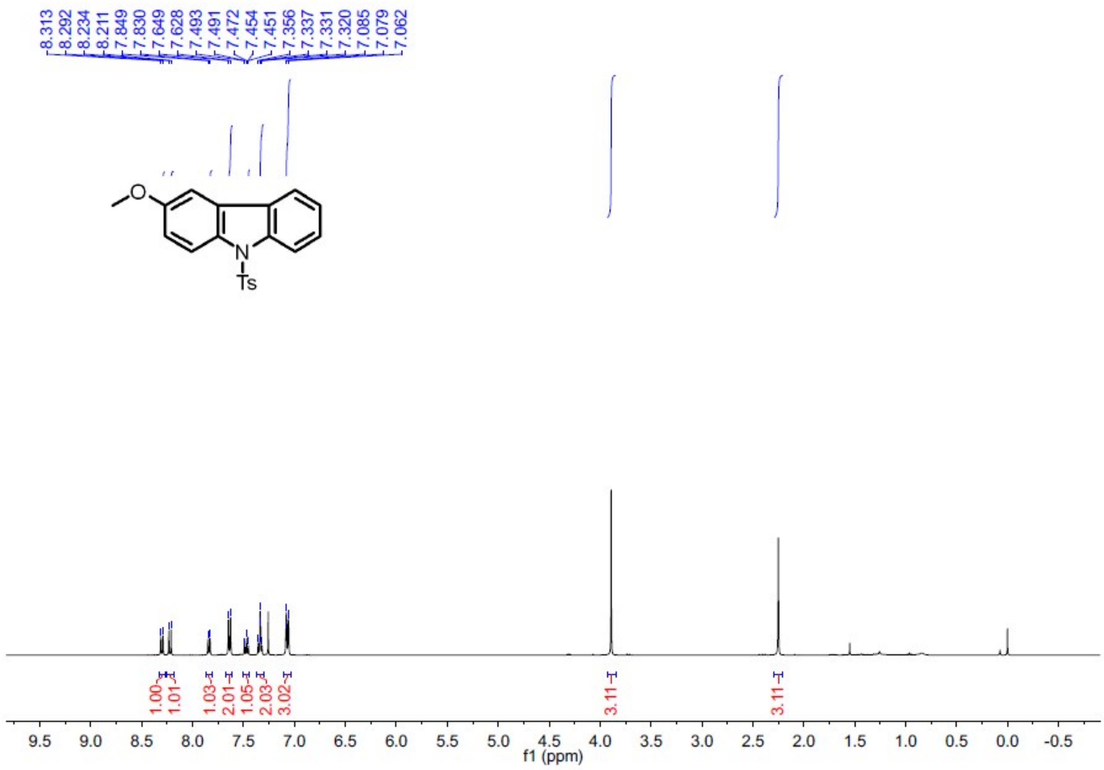
¹H NMR spectrum of 2e



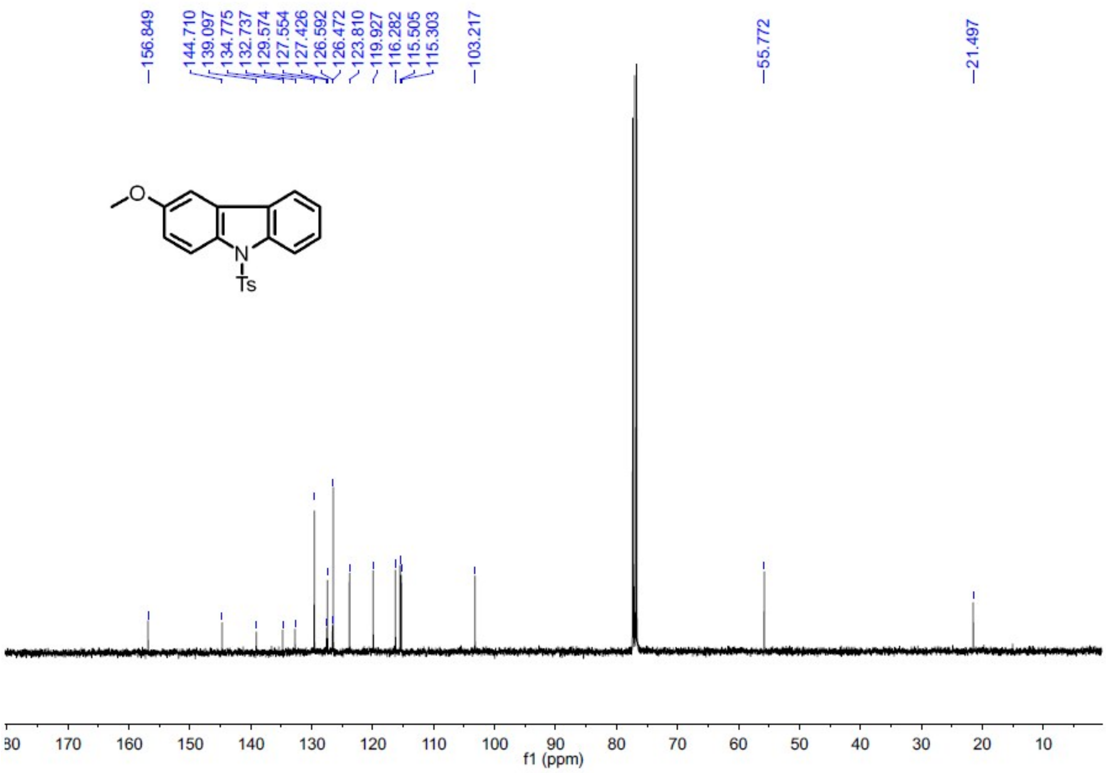
^{13}C NMR spectrum of 2e



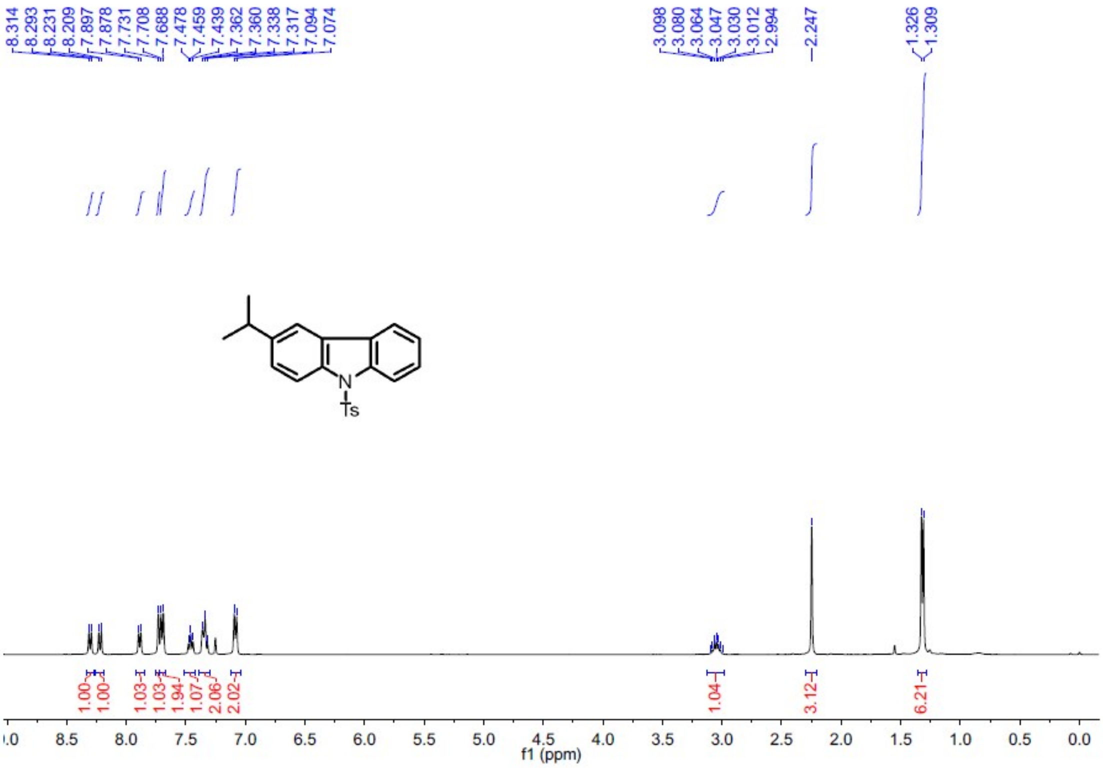
^{1}H NMR spectrum of 2f



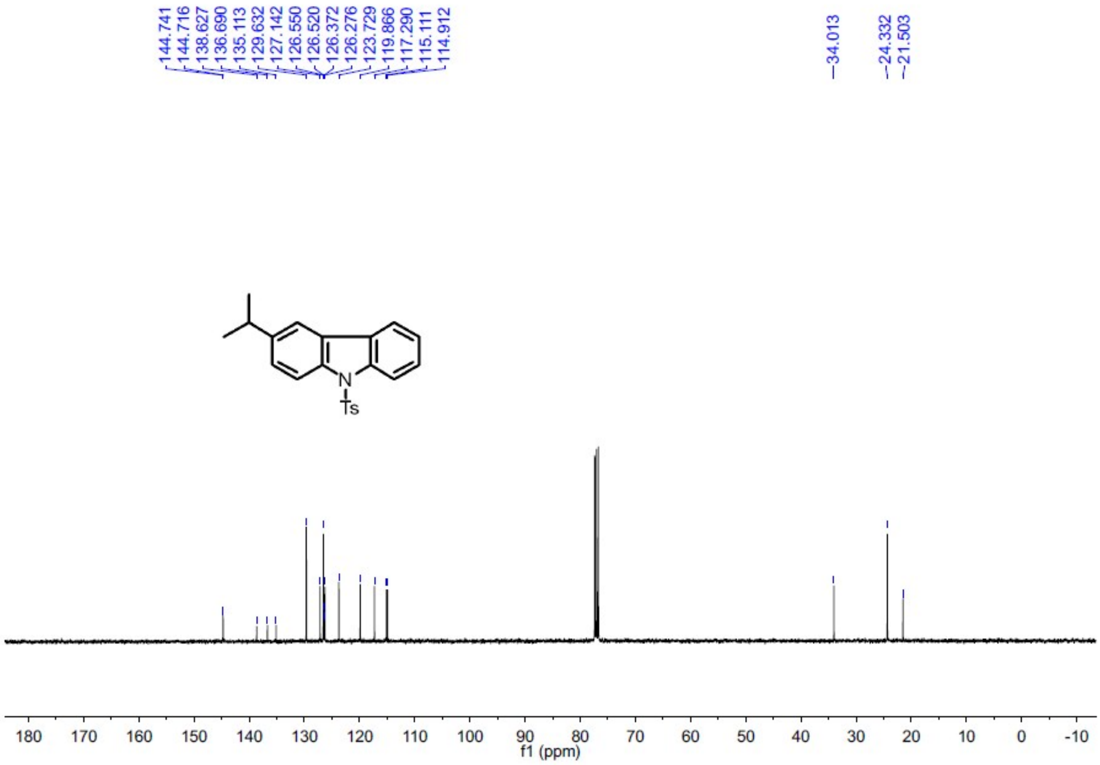
^{13}C NMR spectrum of 2f



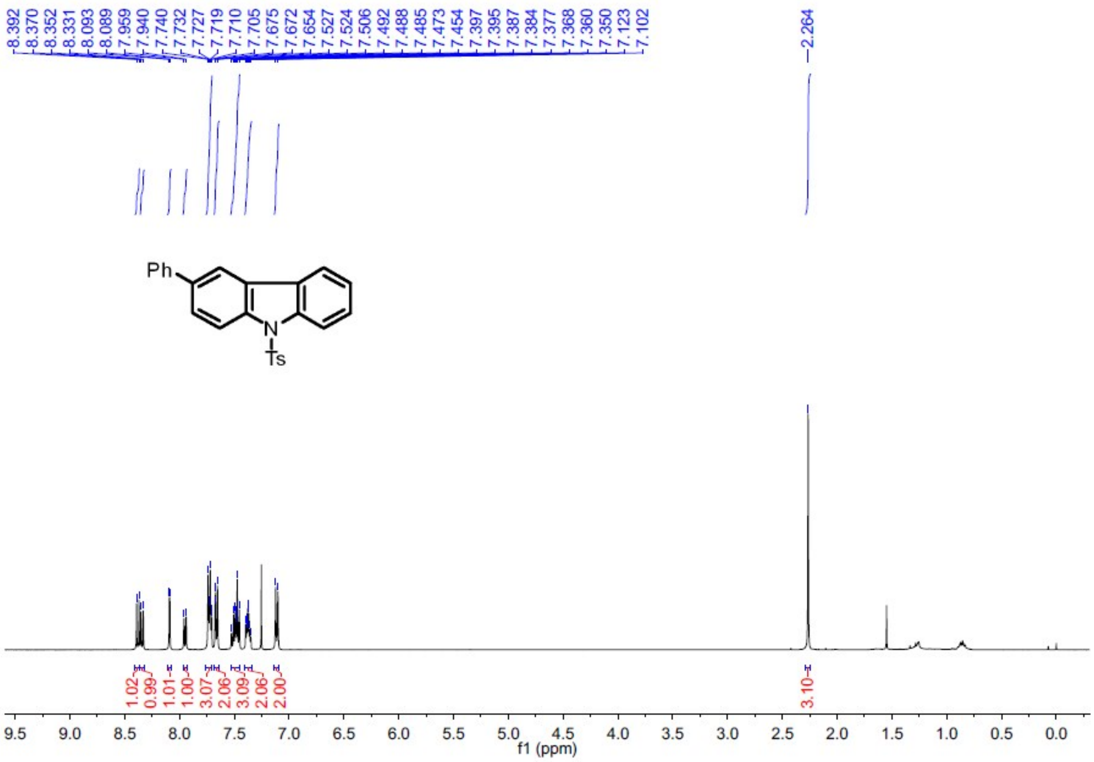
^{1}H NMR spectrum of 2g



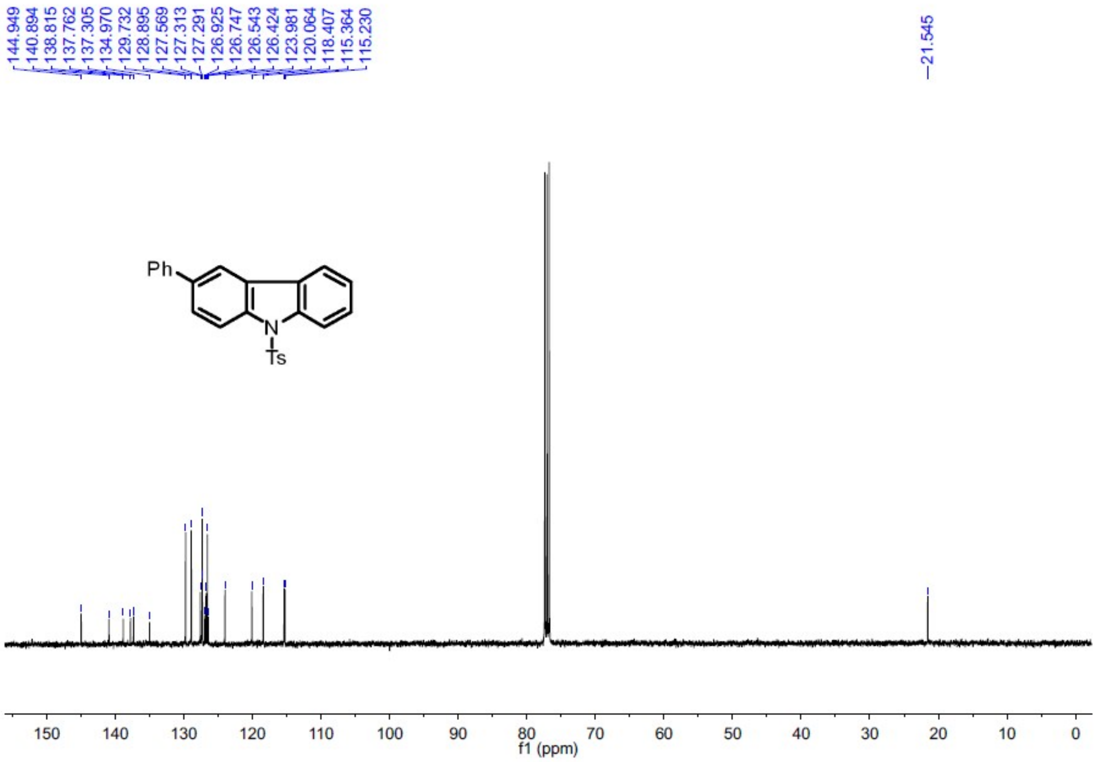
^{13}C NMR spectrum of 2g



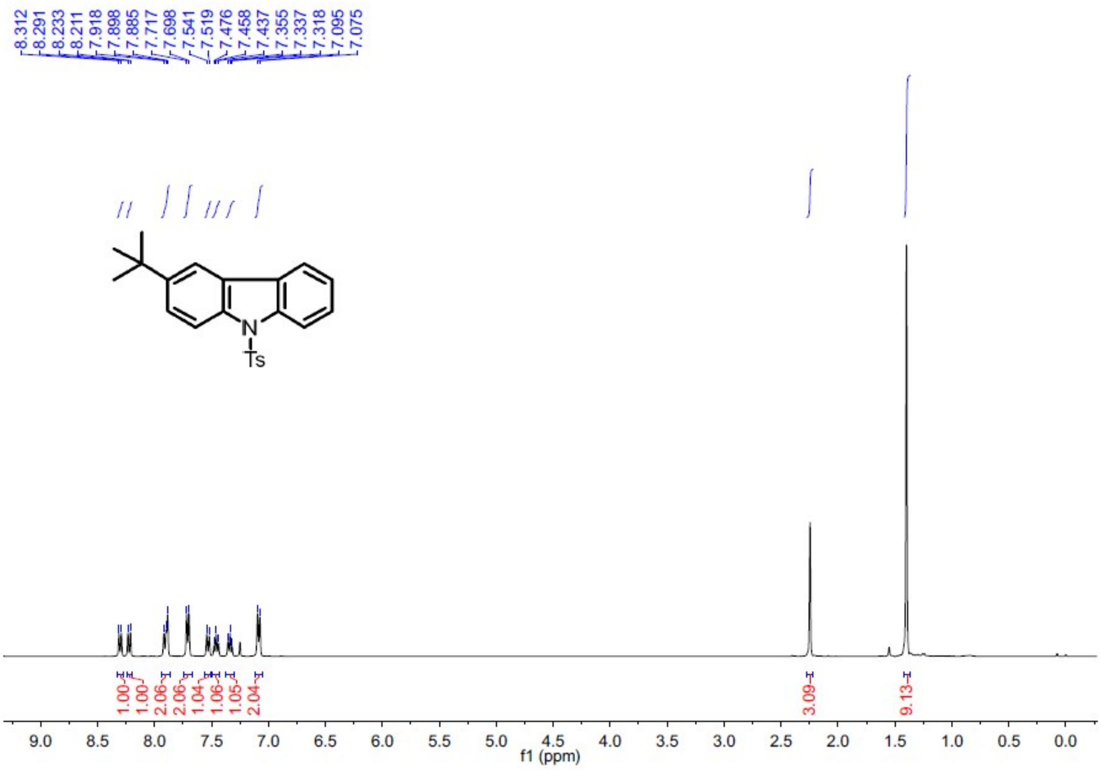
^{1}H NMR spectrum of 2h



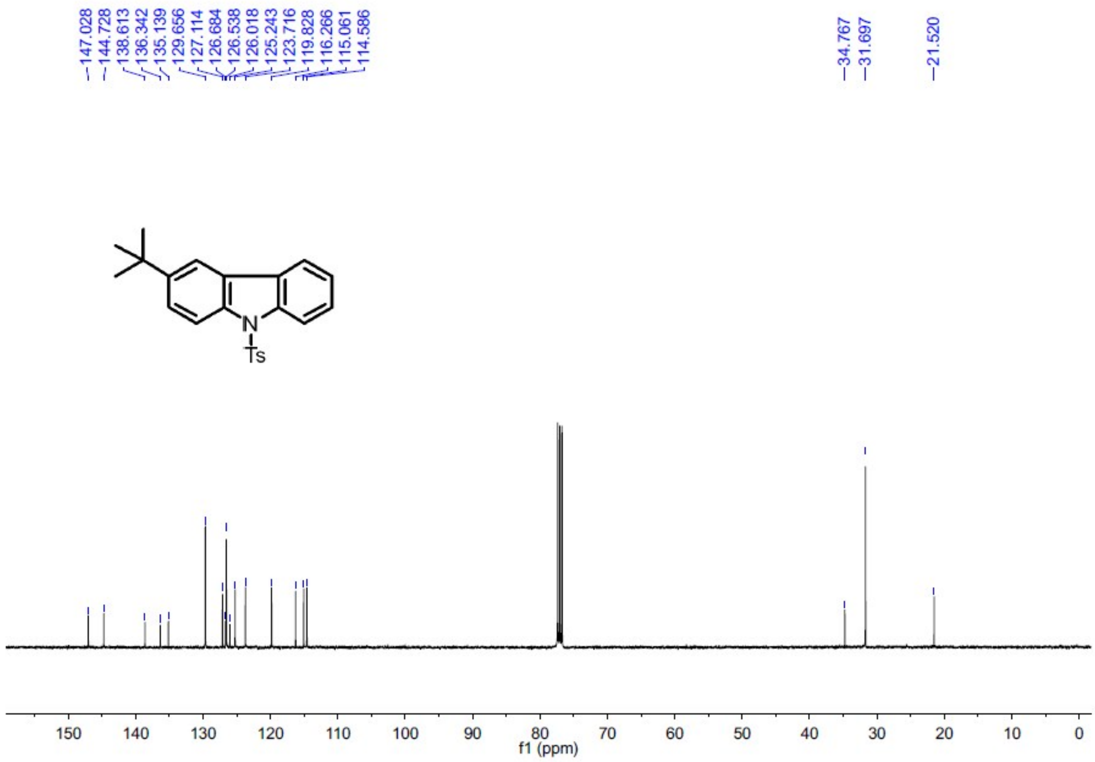
^{13}C NMR spectrum of 2h



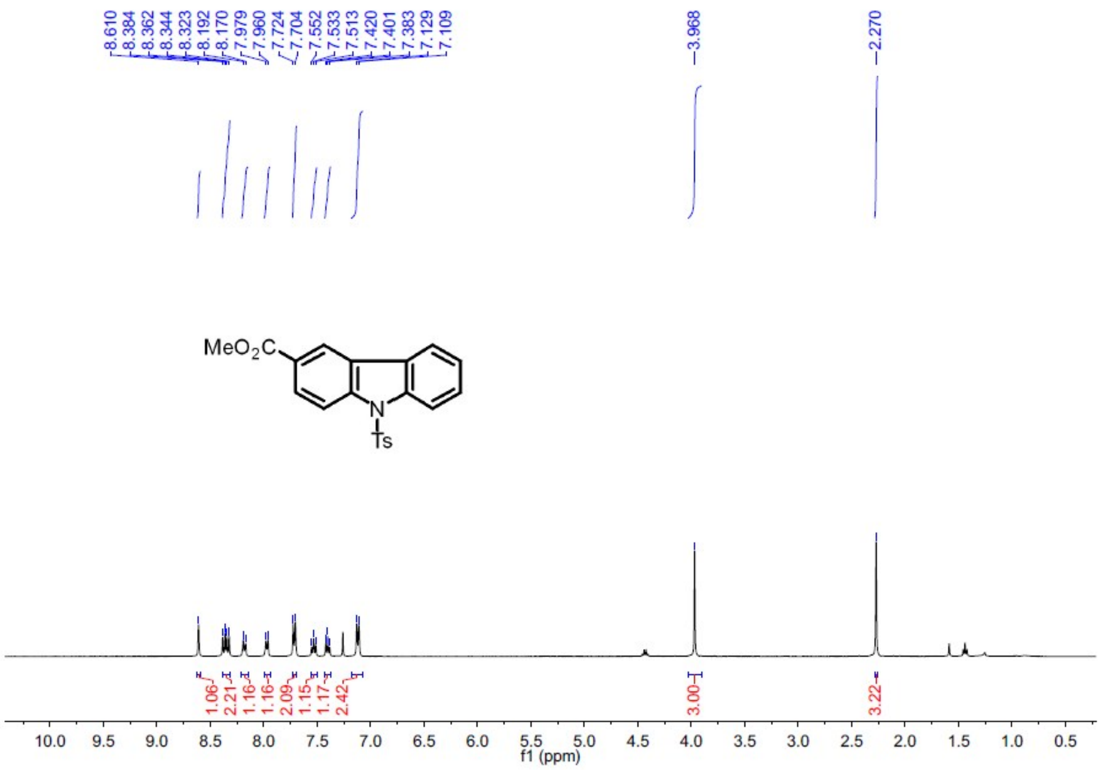
^{1}H NMR spectrum of 2i



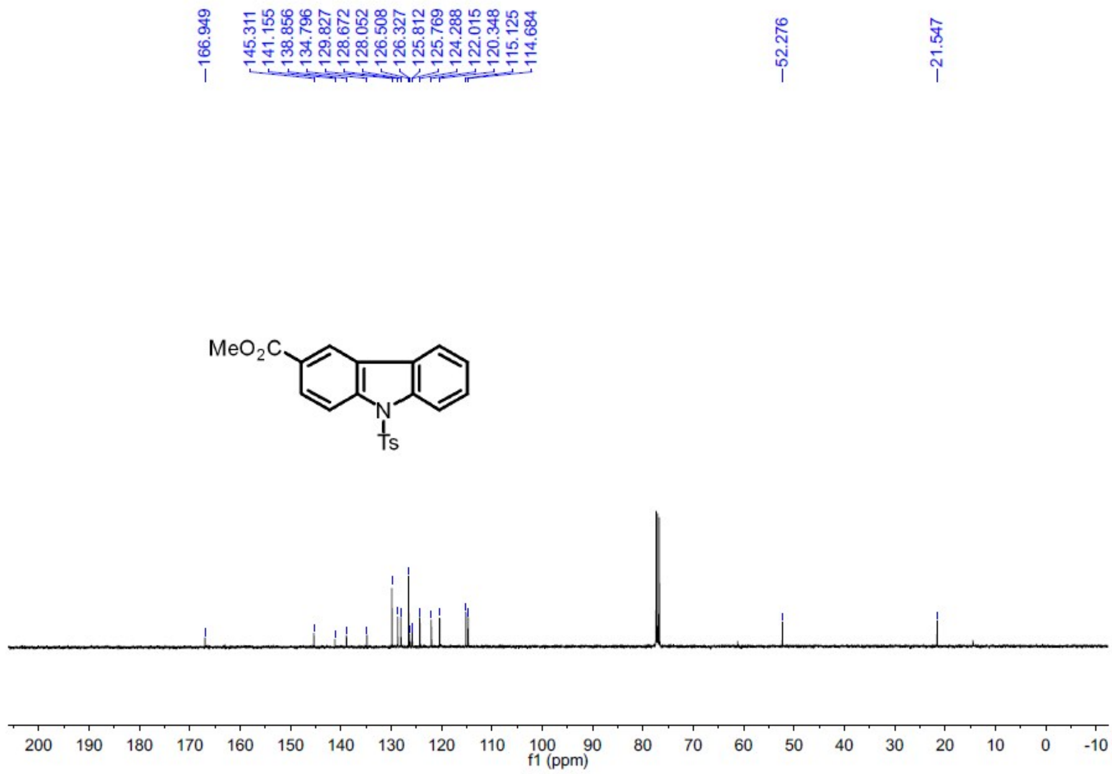
^{13}C NMR spectrum of 2i



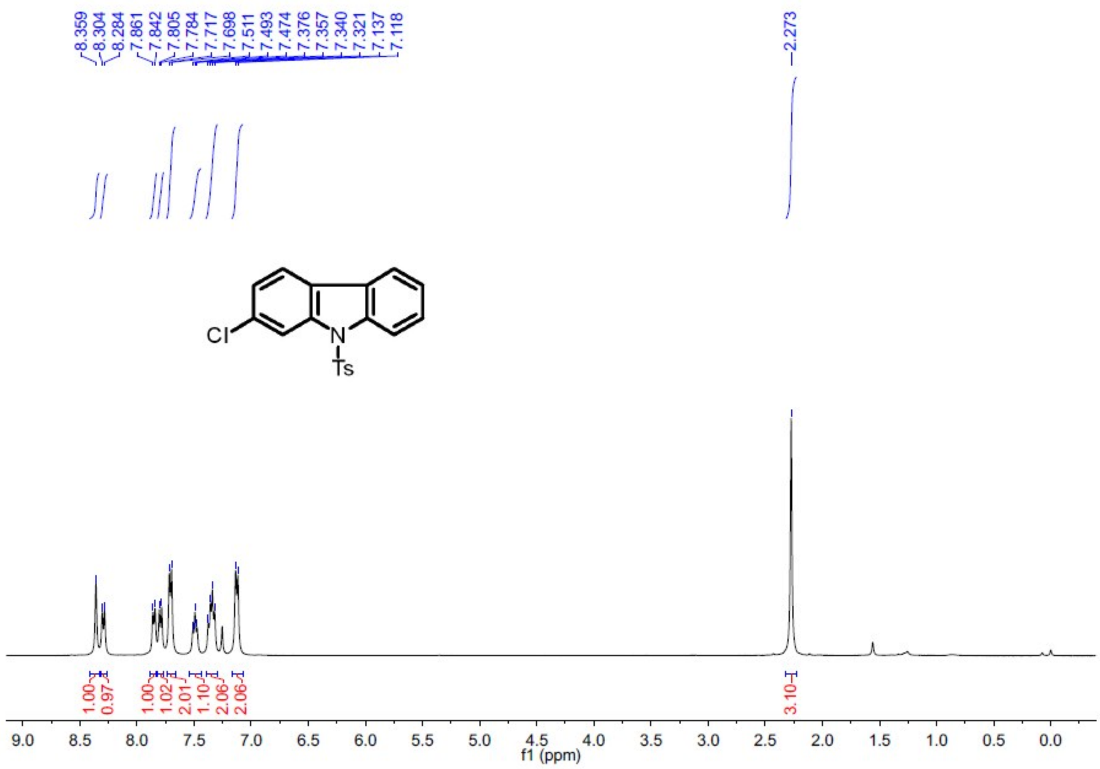
^1H NMR spectrum of 2j



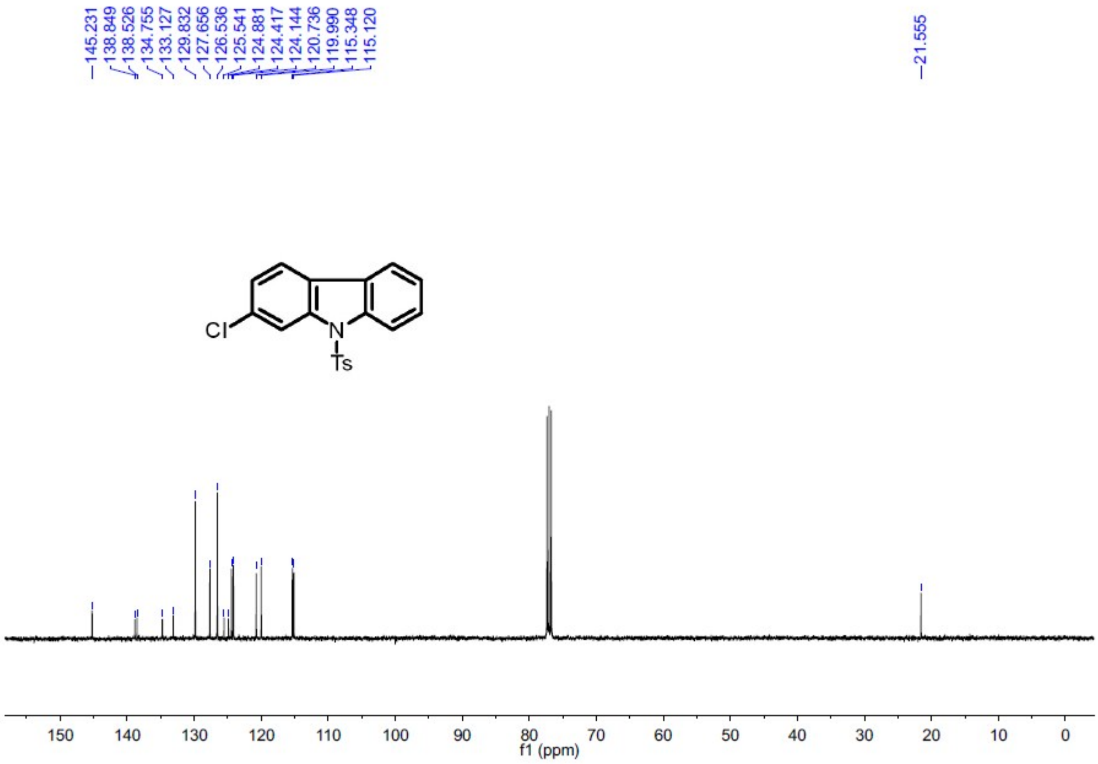
^{13}C NMR spectrum of 2j



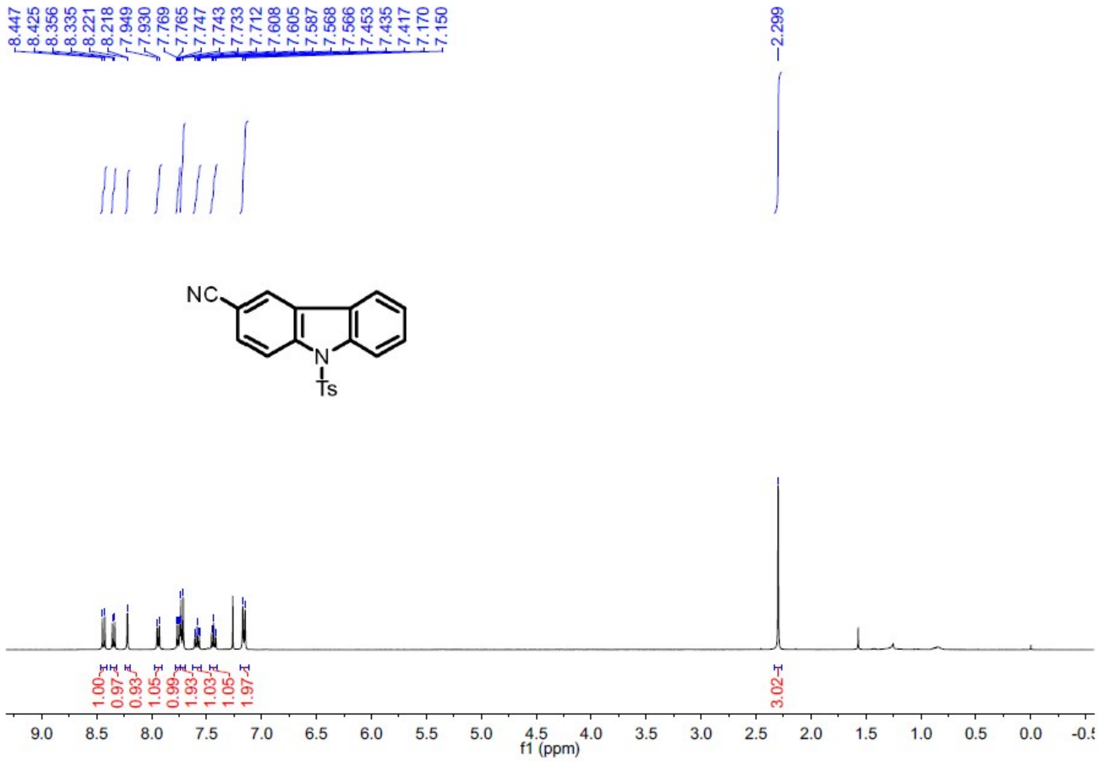
^{1}H NMR spectrum of 2k



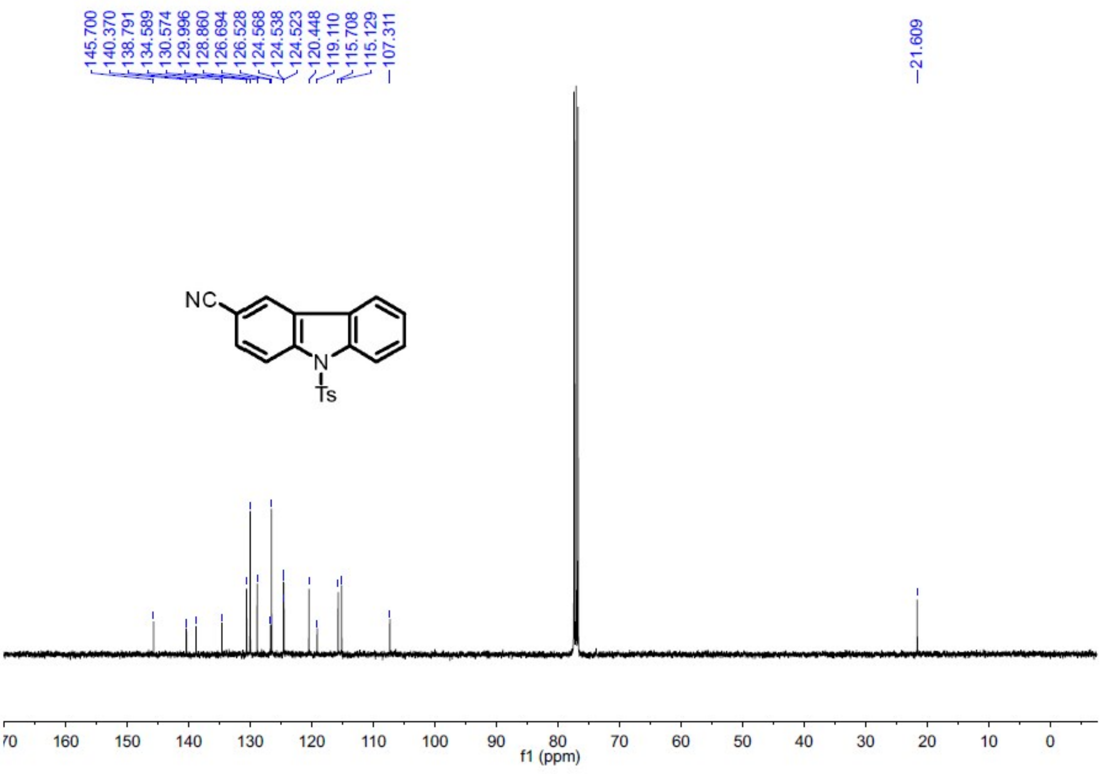
^{13}C NMR spectrum of 2k



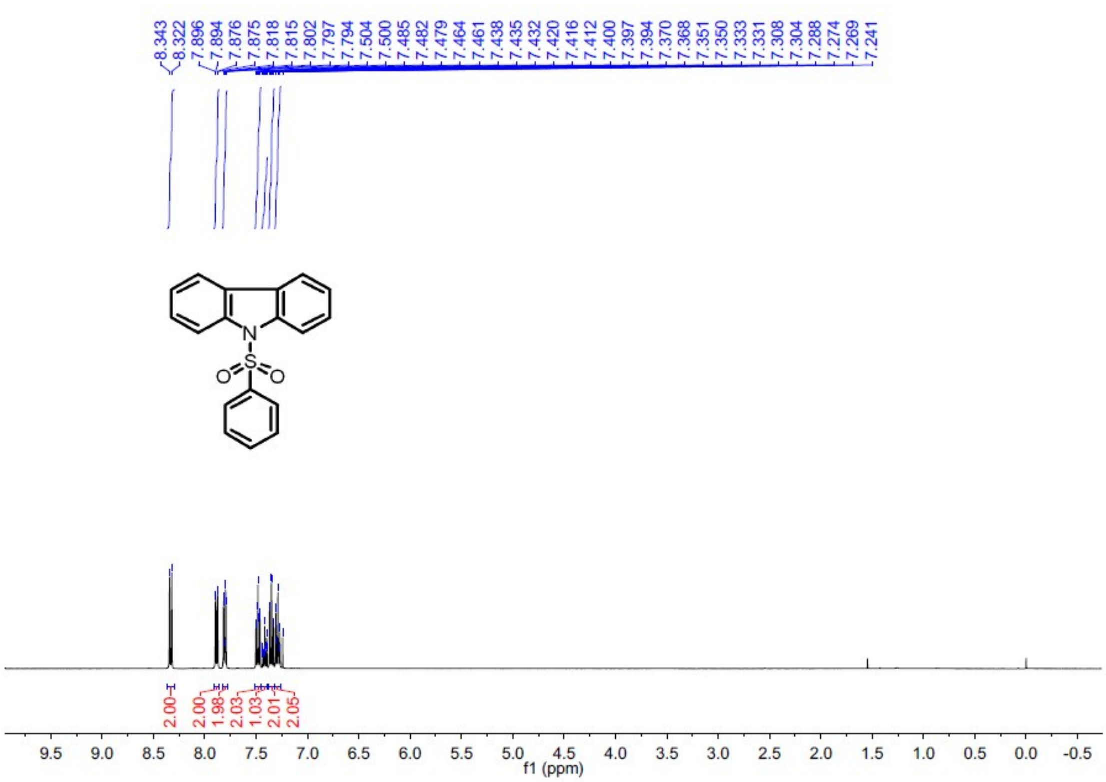
^{1}H NMR spectrum of 2l



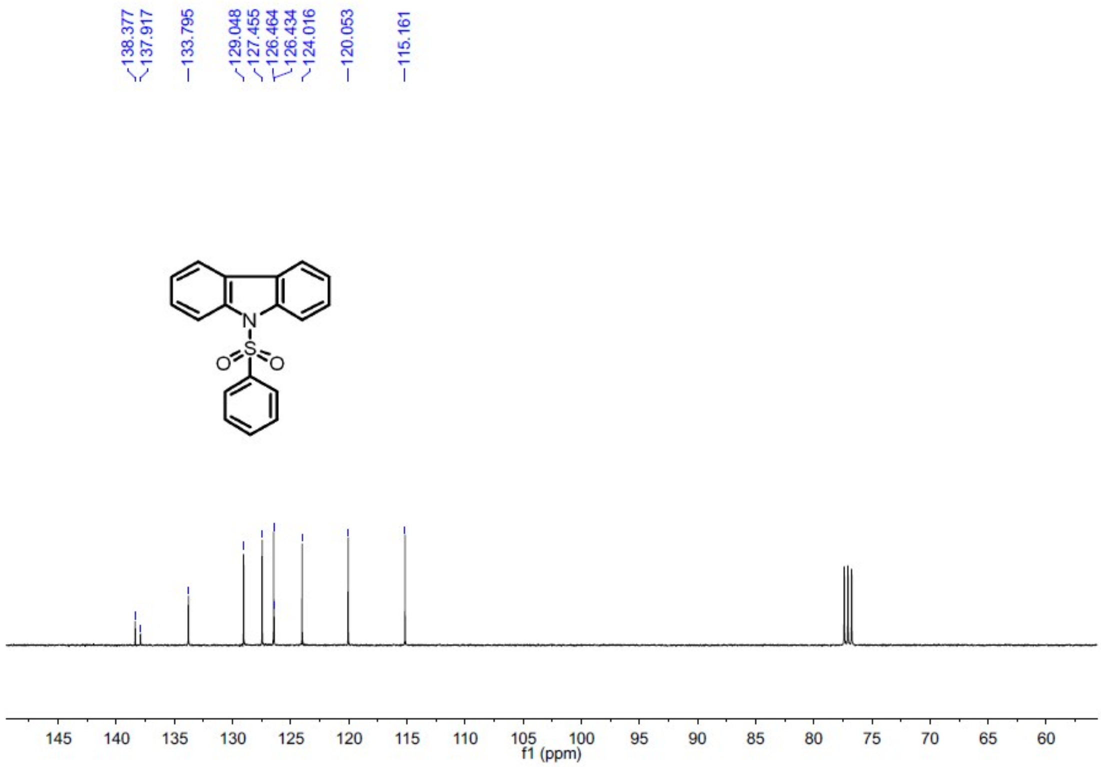
^{13}C NMR spectrum of 2l



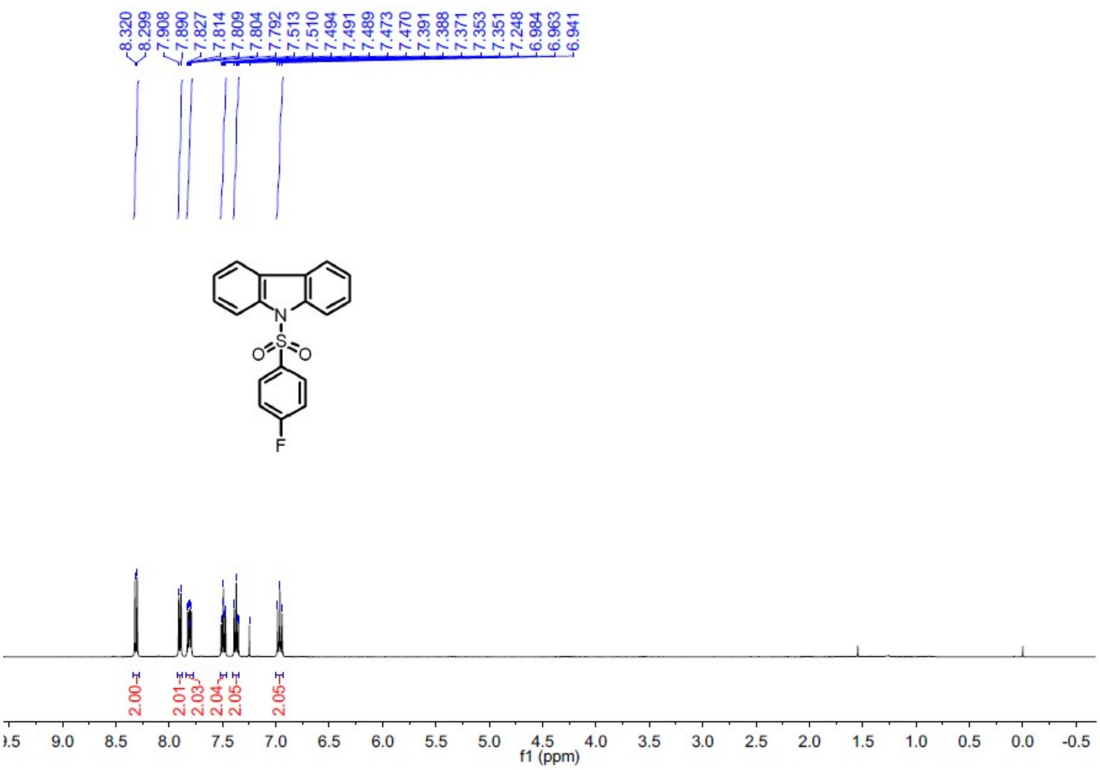
^{1}H NMR spectrum of 2m



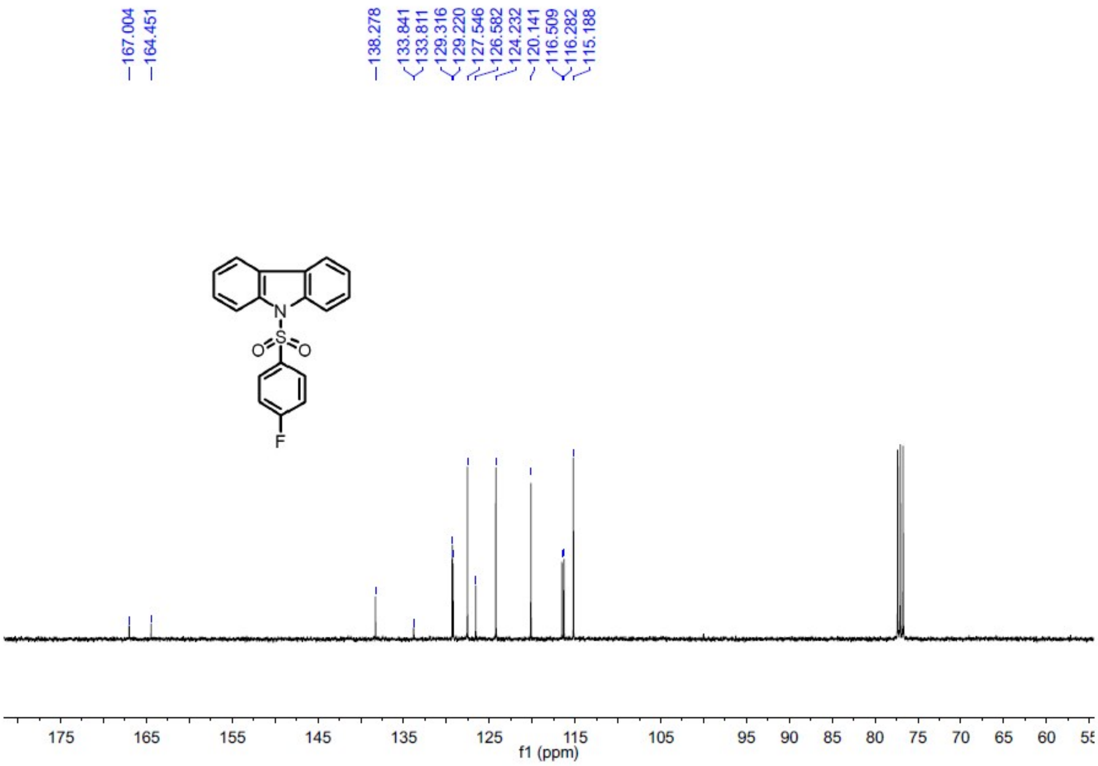
^{13}C NMR spectrum of 2m



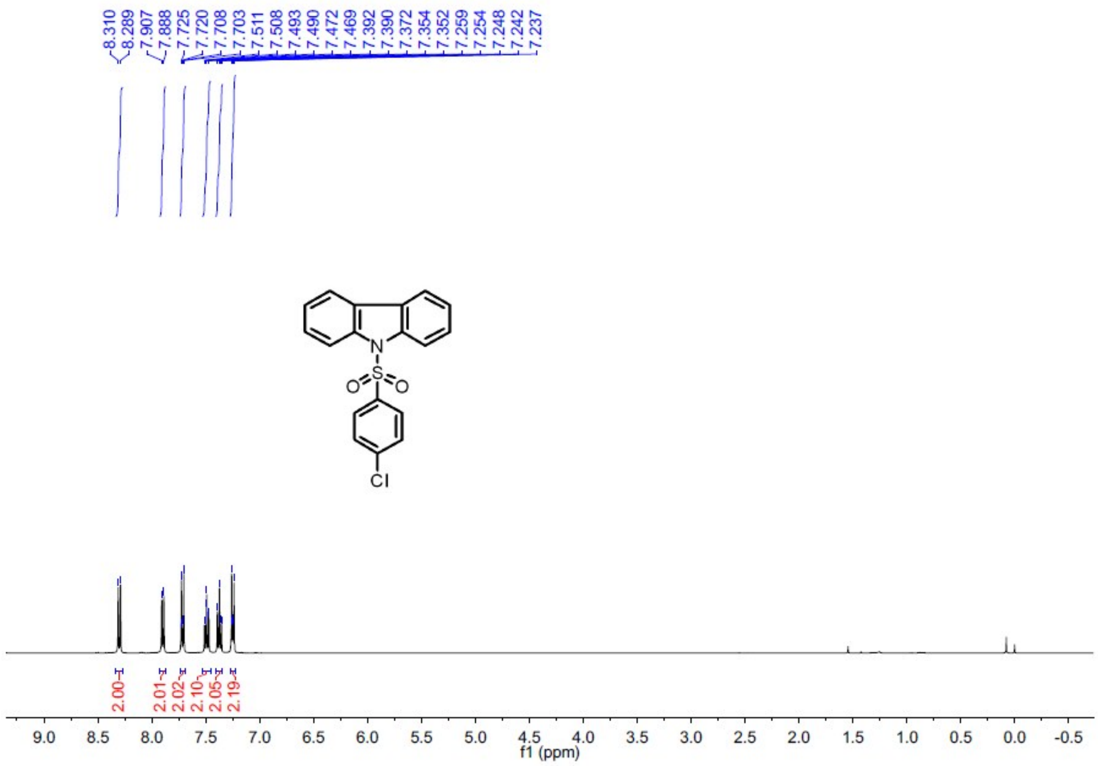
^{1}H NMR spectrum of 2n



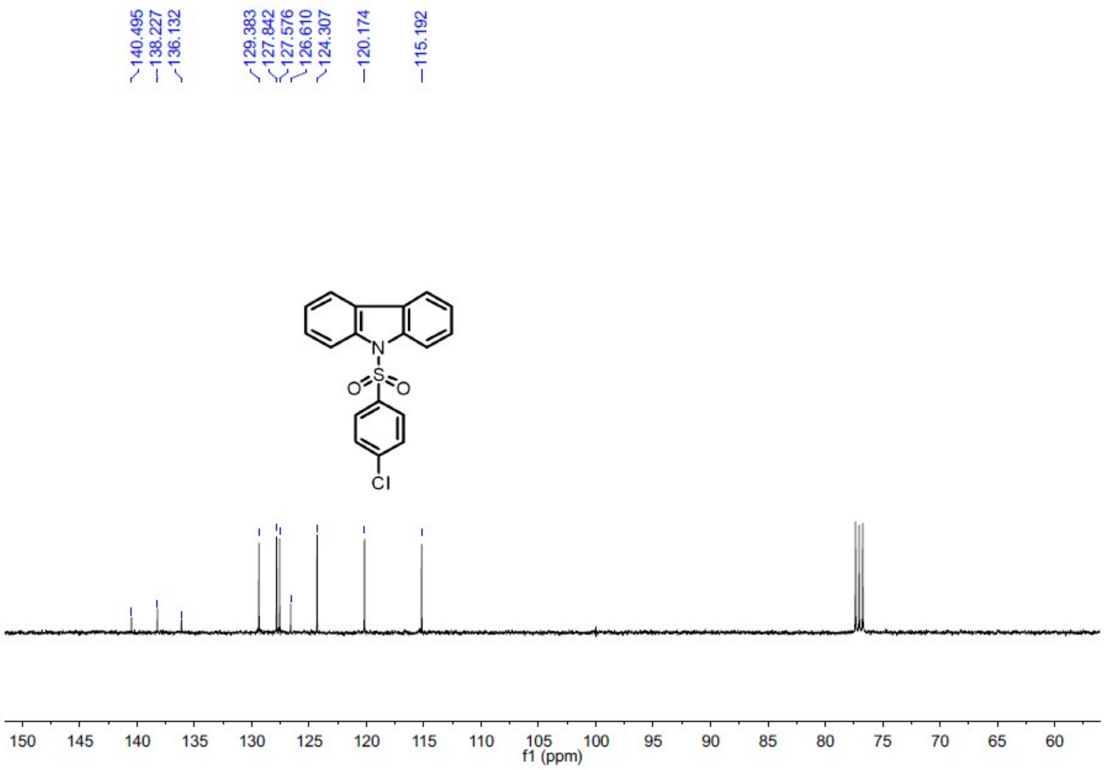
^{13}C NMR spectrum of 2n



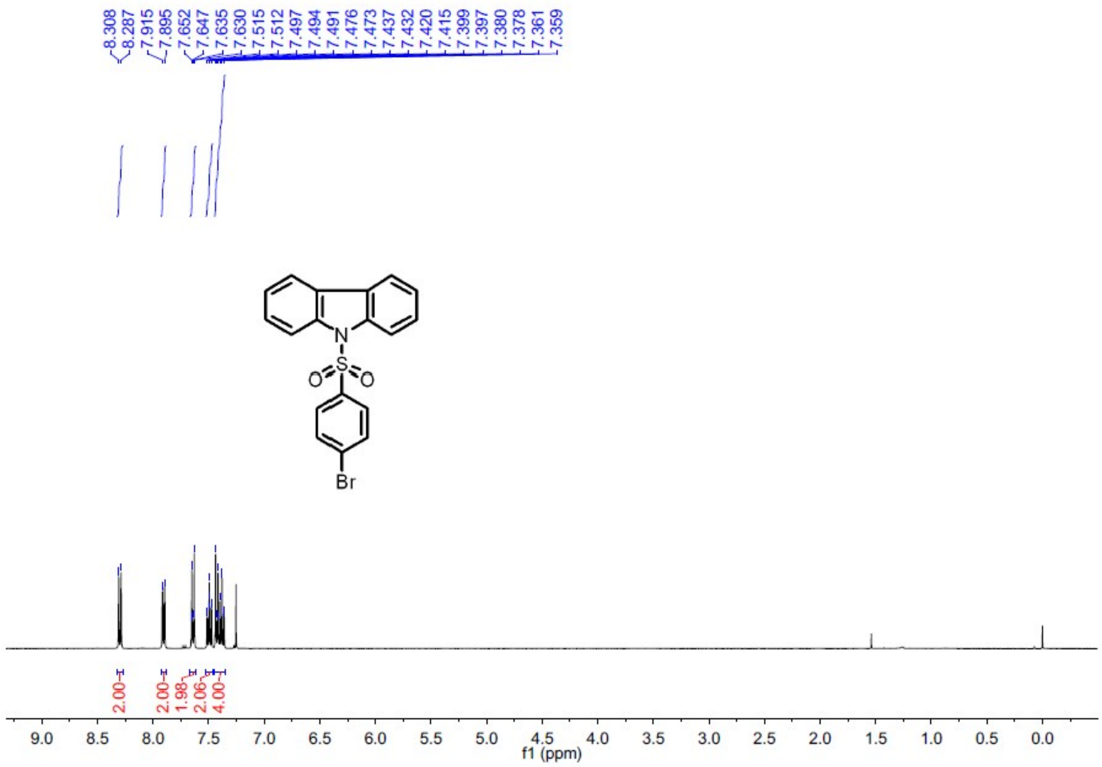
^{1}H NMR spectrum of 2o



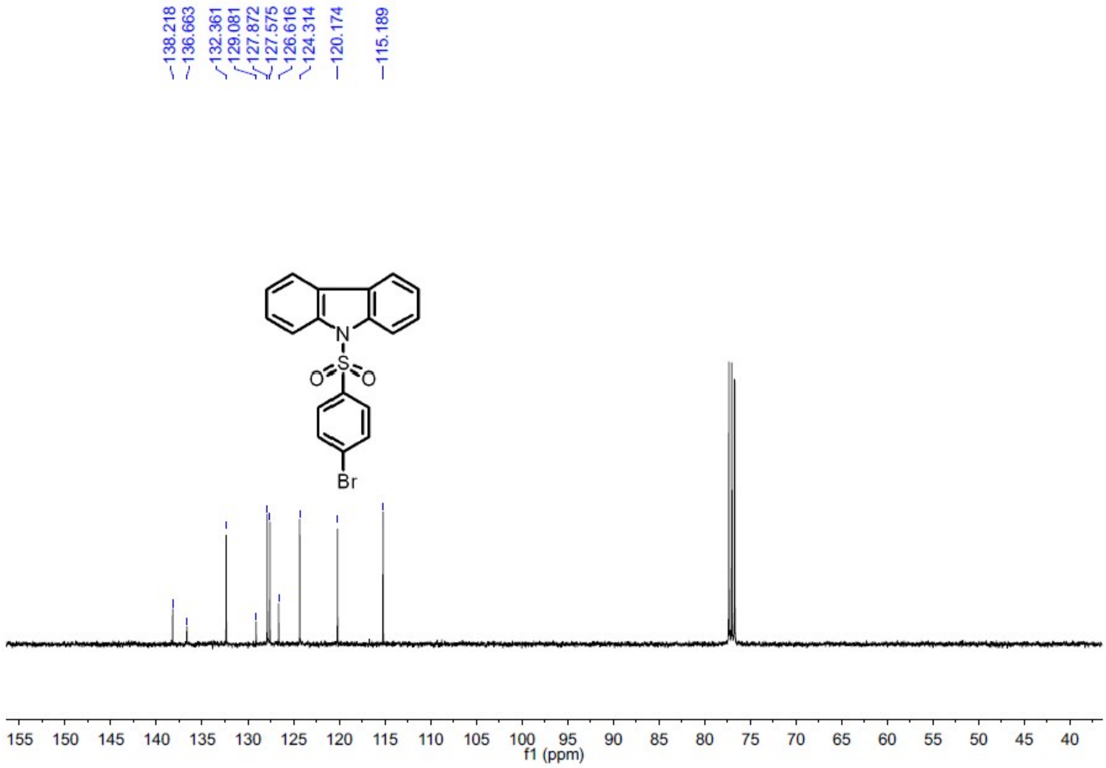
^{13}C NMR spectrum of 2o



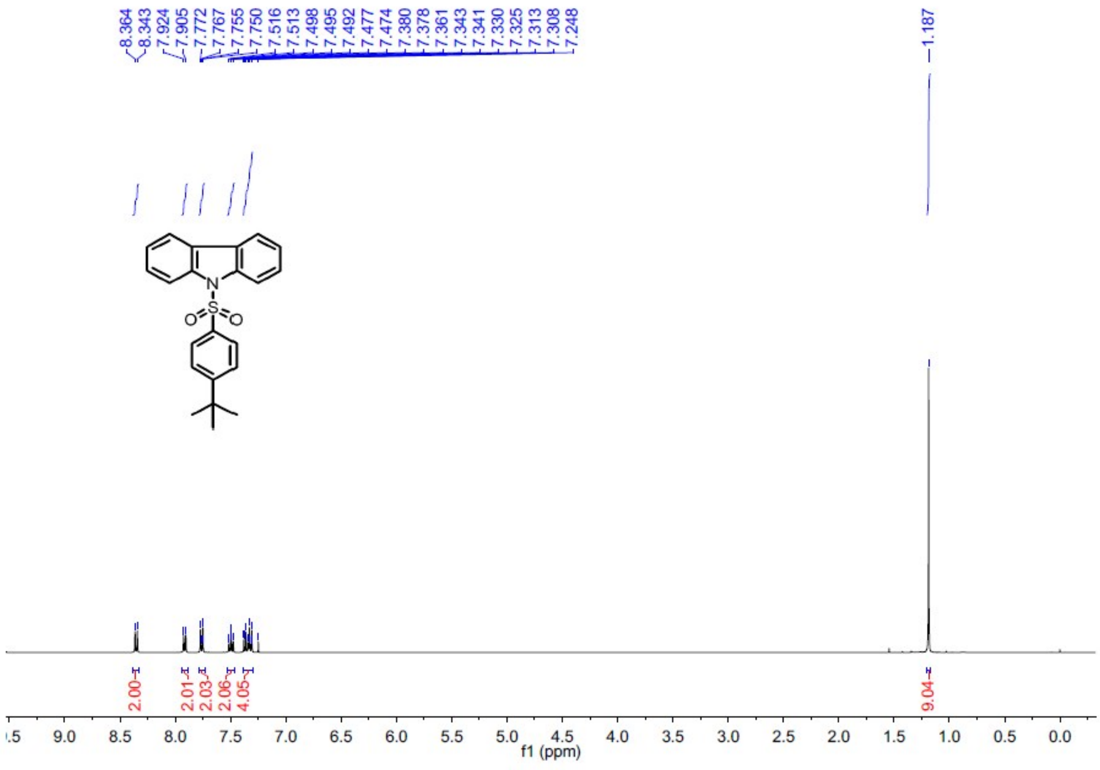
[1]H NMR spectrum of 2p



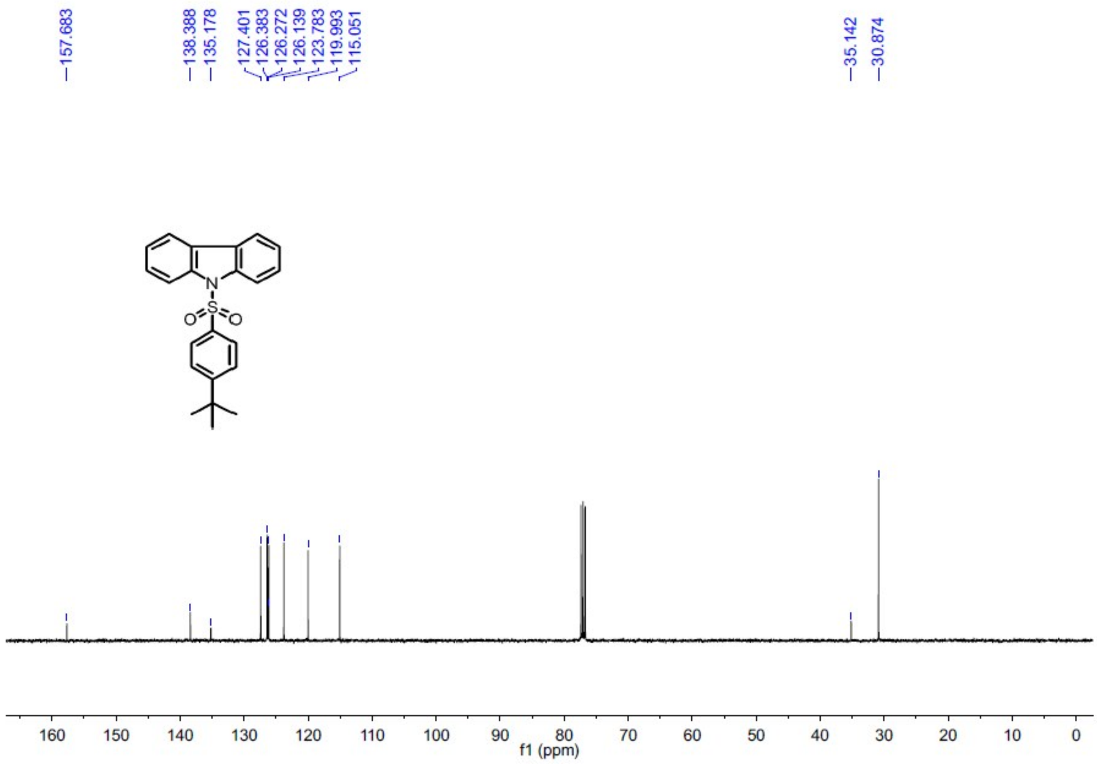
[13]C NMR spectrum of 2p



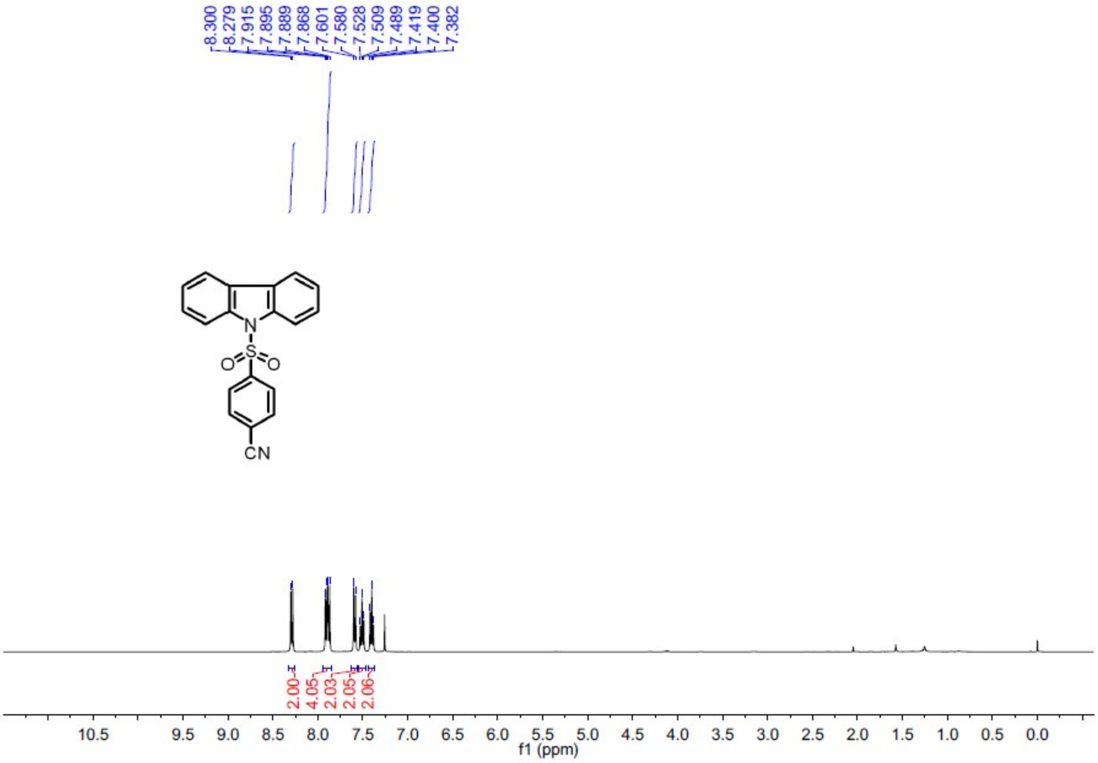
^1H NMR spectrum of 2q



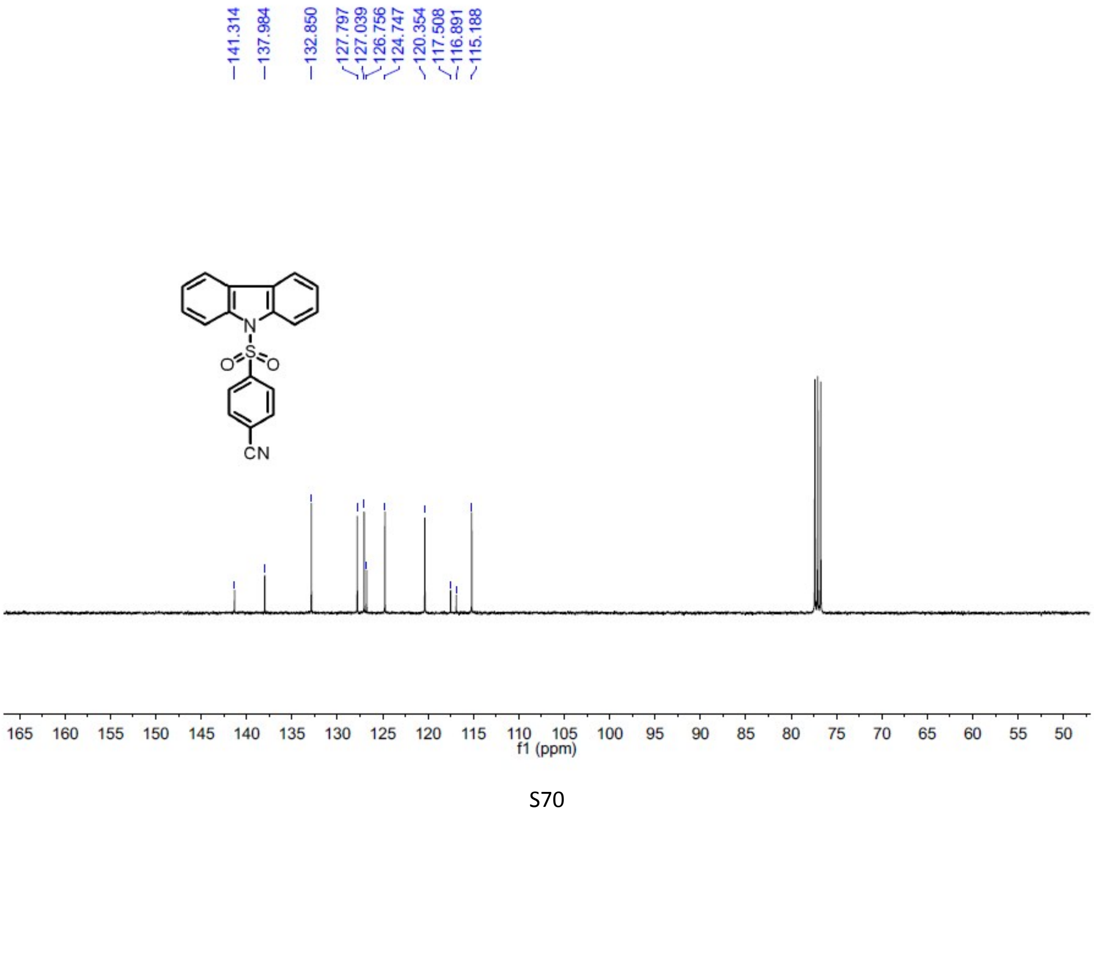
^{13}C NMR spectrum of 2q



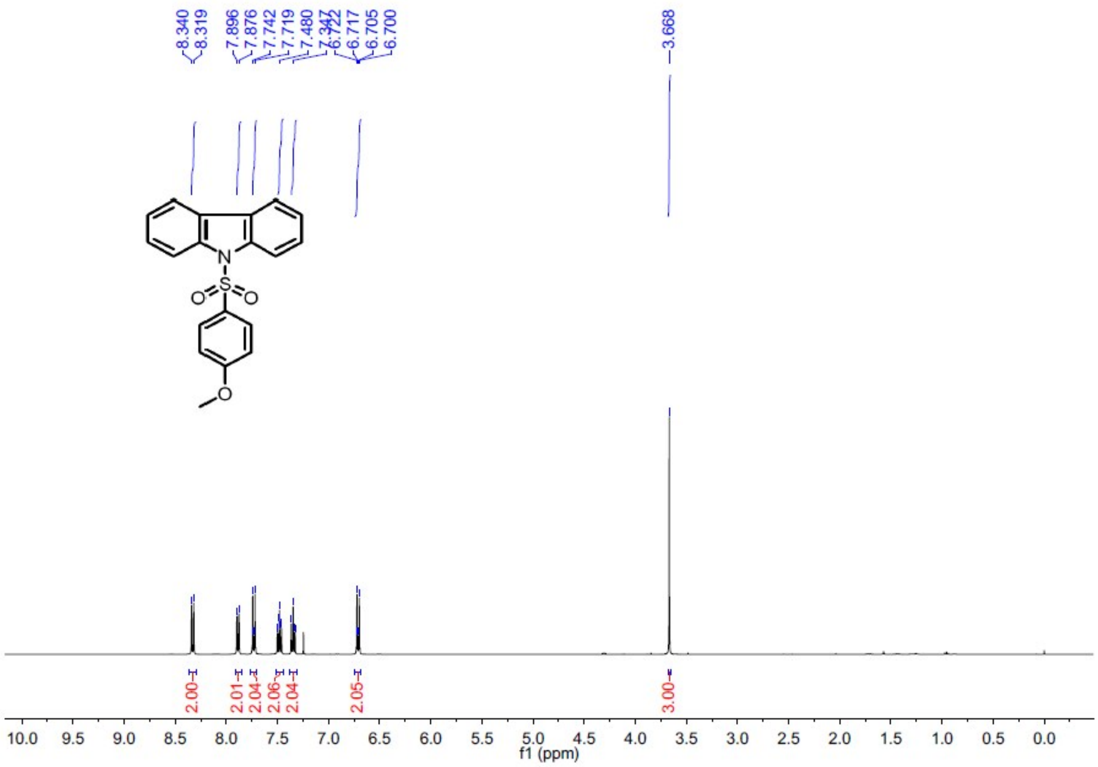
^{1}H NMR spectrum of 2r



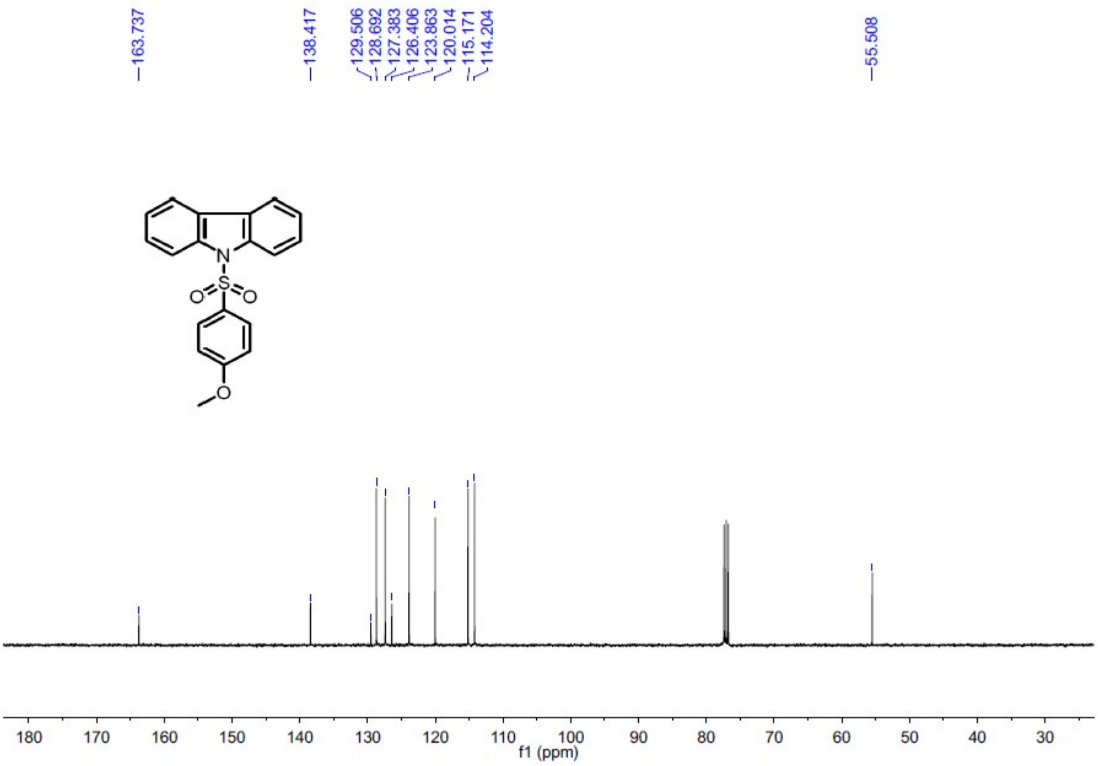
^{13}C NMR spectrum of 2r



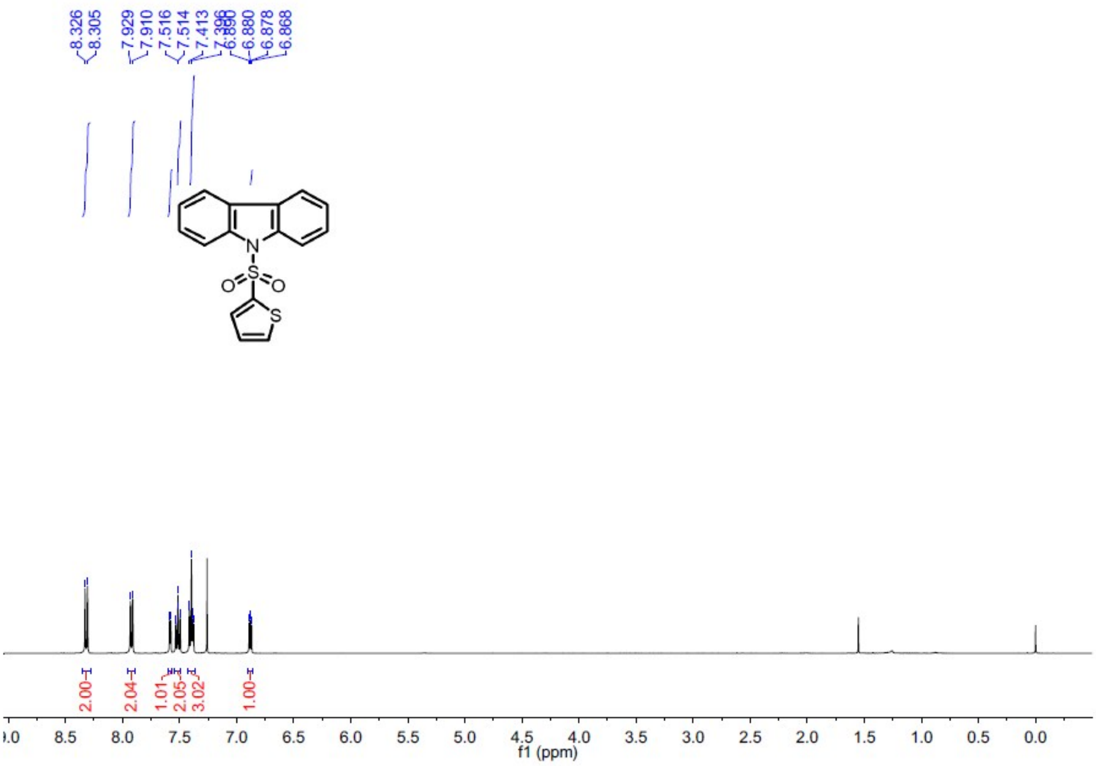
^{1}H NMR spectrum of 2s



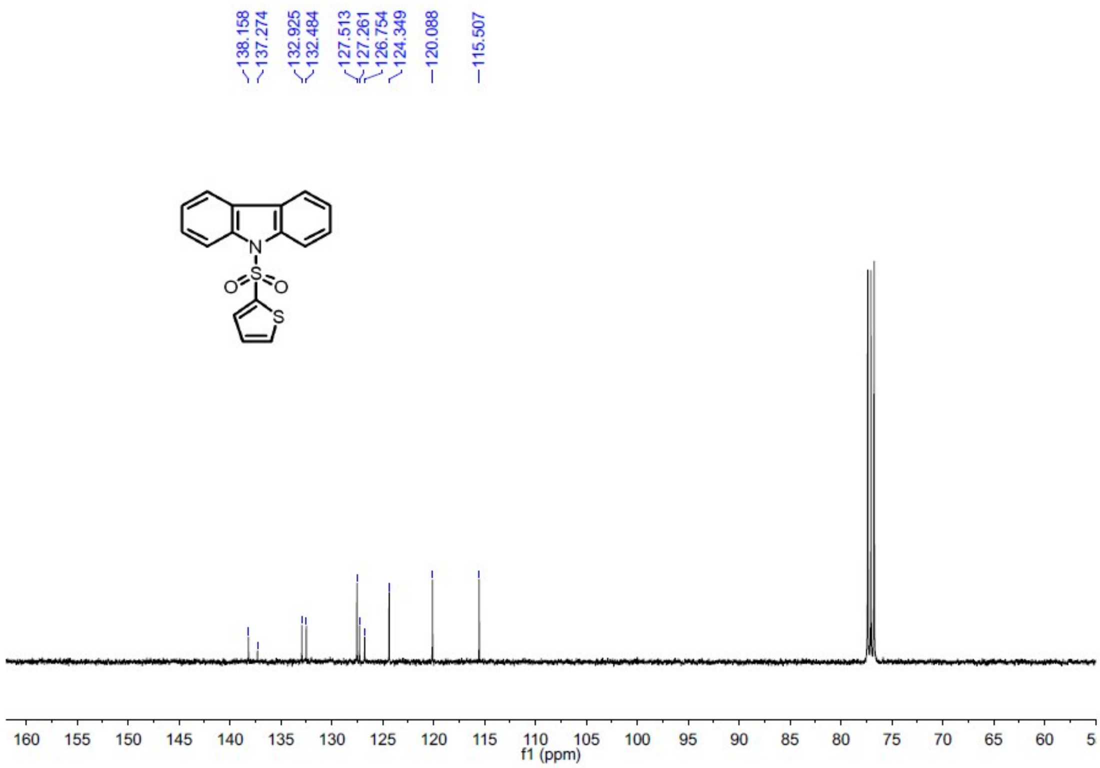
^{13}C NMR spectrum of 2s



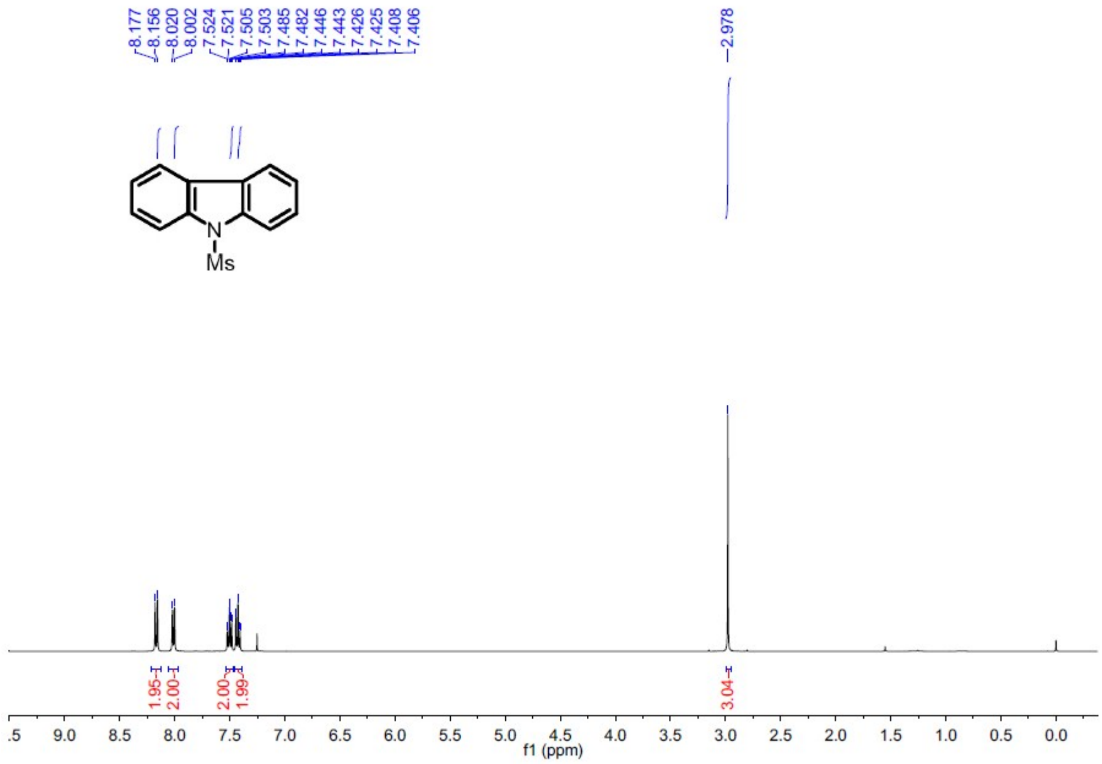
^{1}H NMR spectrum of 2t



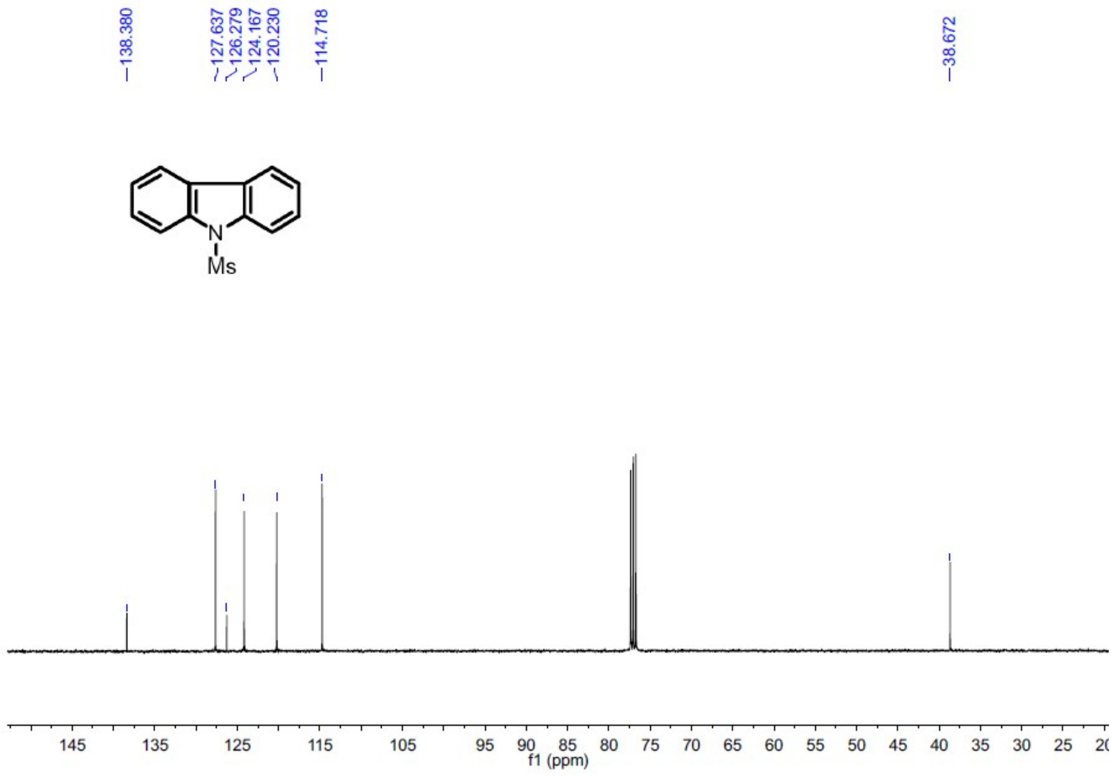
^{13}C NMR spectrum of 2t



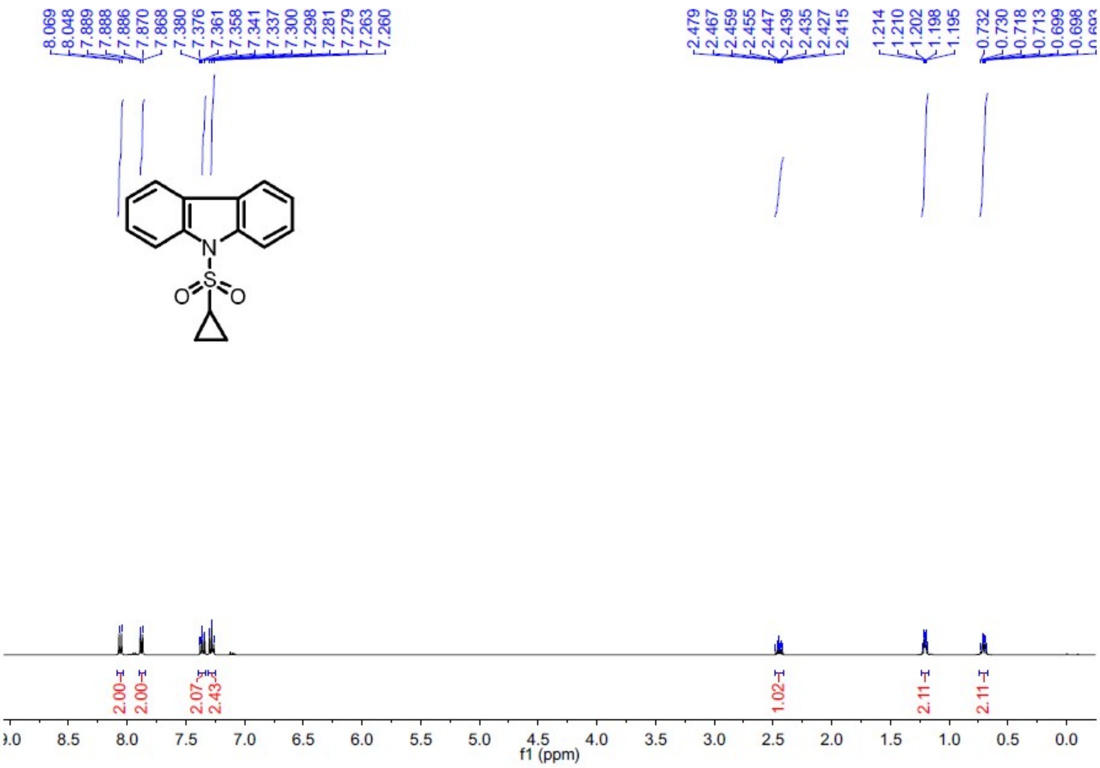
^{1}H NMR spectrum of 2u



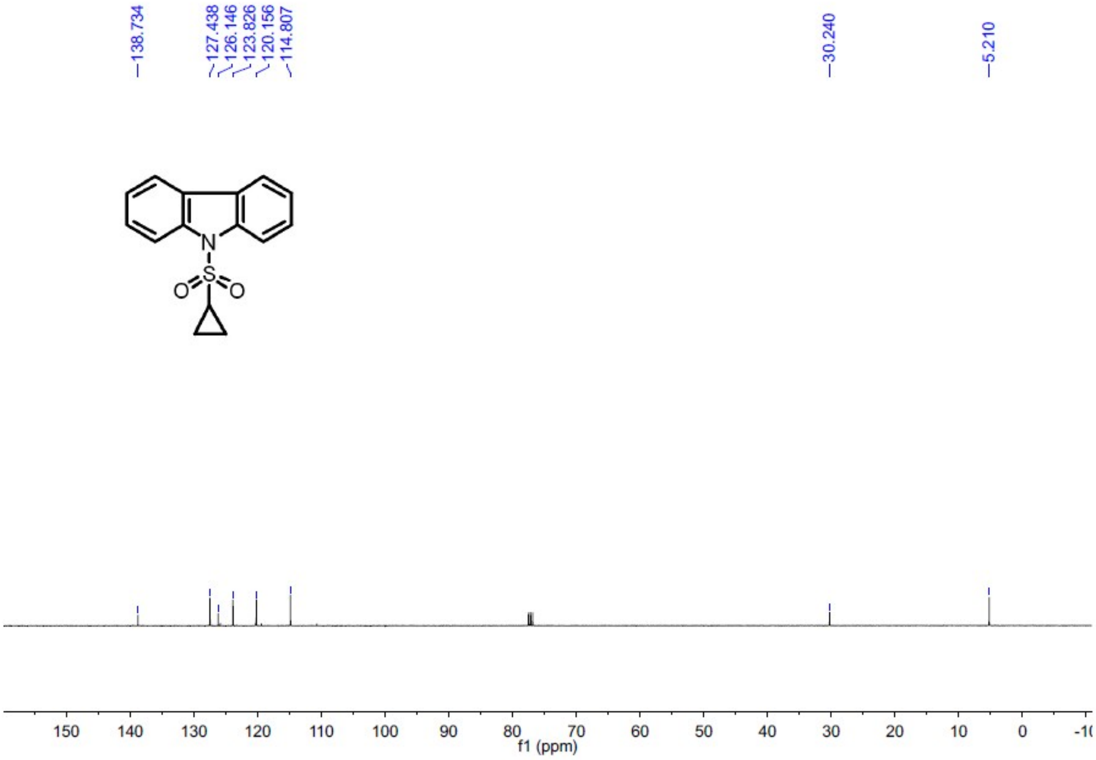
^{13}C NMR spectrum of 2u



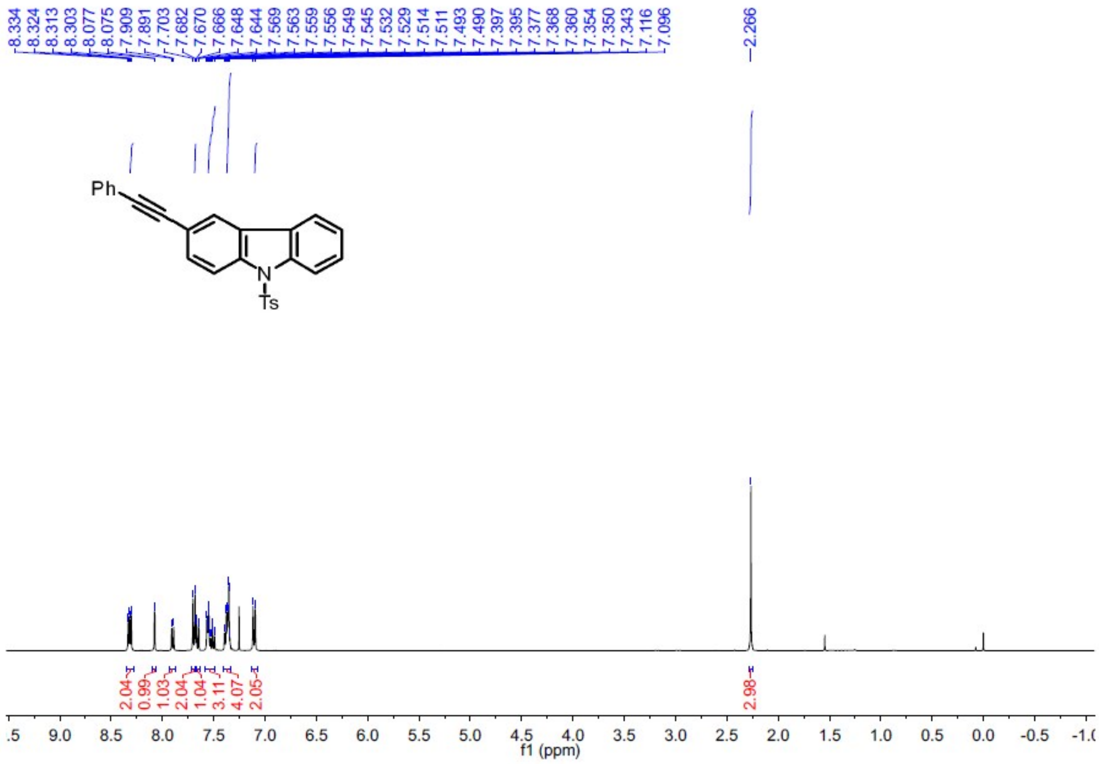
^{1}H NMR spectrum of 2v



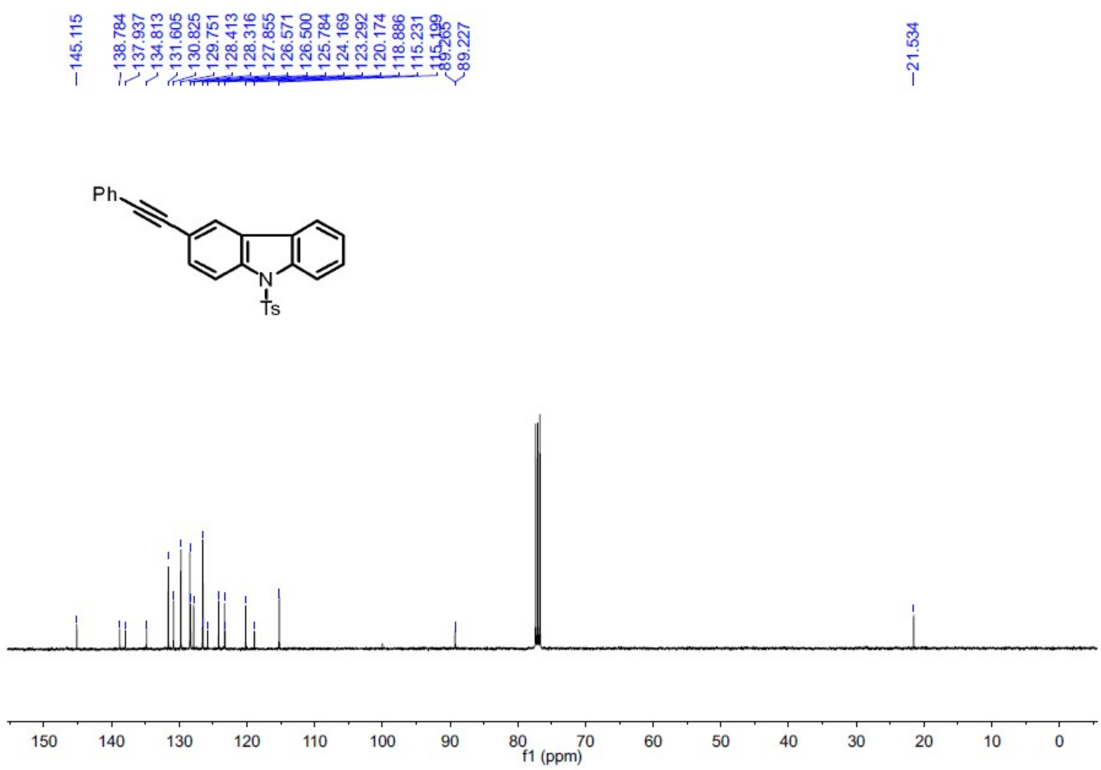
^{13}C NMR spectrum of 2v



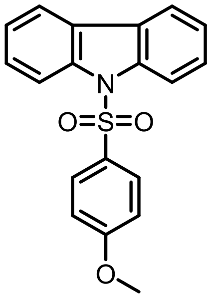
^{1}H NMR spectrum of 2d′



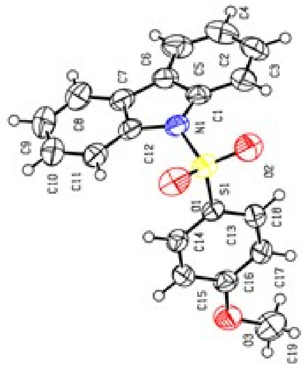
^{13}C NMR spectrum of 2d′



5. X-ray single crystal data for product



2s



structure of 2s

Identification code	**2s**
Empirical formula	$C_{19}H_{15}NO_3S$
Formula weight	337.38
Temperature	113(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 17.5290(4) Å alpha = 90 deg. b = 10.1840(2) Å beta = 99.753(2) deg. c = 18.2727(4) Å gamma = 90 deg.
Volume	3214.79(13) Å ^{3}
Z, Calculated density	8, 1.394 Mg/m^3
Absorption coefficient	0.218 mm^{-1}
F(000)	1408
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	3.53 to 35.68 deg.

Limiting indices	-28<=h<=27, -16<=k<=16, -28<=l<=29
Reflections collected / unique	49049 / 14126 [R(int) = 0.0435]
Completeness to theta = 27.90	94.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9743 and 0.9577
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14126 / 0 / 435
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1437
R indices (all data)	R1 = 0.0990, wR2 = 0.1653
Largest diff. peak and hole	0.261 and -0.306 e. Å $^{-3}$