Support information

Silver-Catalyzed Cascade Cyclization for the Synthesis of 4-Aminotetrahydrocarbazole

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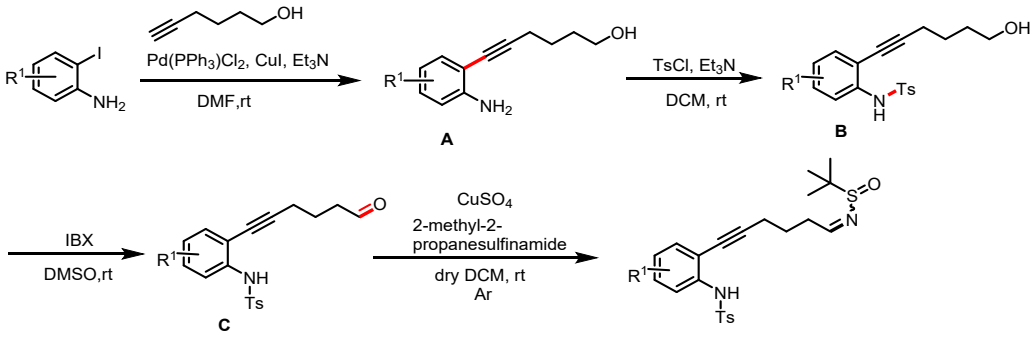
1. General procedure for the synthesis of substrate 1a-1u



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 stirred 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 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 product **A**.

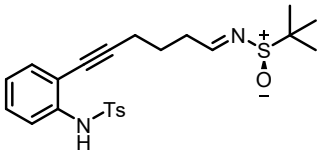
To a flask were added **A** (1.0 equiv)/DCM, pyridine (2.0 equiv), and TsCl (1.2equiv) sequentially at room temperature. The reaction was complete as monitored by TLC. H_2O was added to the resulting mixture. After the separation of the organic layer, the water layer was extracted with DCM. The combined 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 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), methyl-2-propanesulfinamide (1.2 equiv),

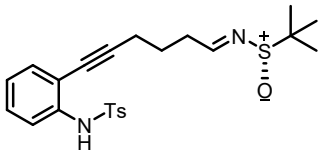
and $CuSO_4$ (3.0 equiv). After degassing with argon and four evacuation/backfill cycles with argon, dry DCM was then added, and the resulting mixture was stirred at room temperature. After 48 h, the reaction was stopped and filtrated through Celite, washing with DCM. The solution was evaporated with 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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1a)



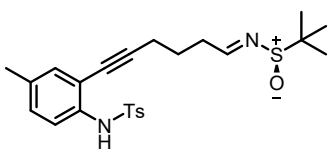
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.28 – 7.18 (m, 5H), 6.99 (t, J = 7.2 Hz, 1H), 2.71 – 2.63 (m, 2H), 2.53 (t, J = 6.8 Hz, 2H), 2.37 (s, 3H), 1.99 – 1.91 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 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.

(*S*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1b)



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); HRMS (ESI) calcd for $C_{23}H_{29}N_2O_3S_2$ $[M+H]^+$ 445.1614, found 445.1619.

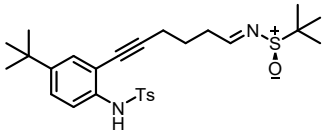
(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)-4-methylphenyl)-4-methylbenzenesulfonamide (1c)



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,

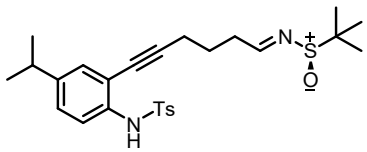
2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 12.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 2.69 – 2.62 (m, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.22 (s, 3H), 1.97 – 1.87 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 168.4, 143.9, 136.3, 135.0, 134.3, 132.5, 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.

(*R*)-*N*-(4-(tert-butyl)-2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1d)



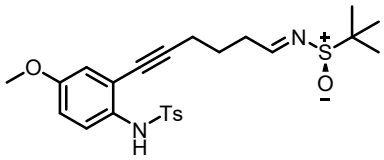
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, *J* = 4.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.27 (d, *J* = 0.8 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 2.70 – 2.64 (m, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.91 – 1.99 (m, 2H), 1.24 (s, 9H), 1.22 (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

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)-4-isopropylphenyl)-4-methylbenzenesulfonamide (1e)



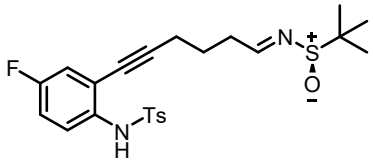
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.13 (t, *J* = 4.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.06 (m, 3H), 2.83 – 2.74 (m, 1H), 2.70 – 2.63 (m, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 2.00 – 1.89 (m, 2H), 1.22 (s, 9H), 1.17 (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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (1f)



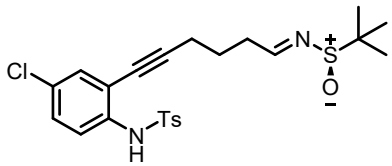
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, J = 4.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 9.2 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.95 (s, 1H), 6.82 (dd, J = 8.8, 3.2 Hz, 1H), 6.76 (d, J = 2.8 Hz, 1H), 3.74 (s, 3H), 2.63 (td, J = 7.2, 4.4 Hz, 2H), 2.46 (t, J = 7.2 Hz, 2H), 2.37 (s, 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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)-4-fluorophenyl)-4-methylbenzenesulfonamide (1g)



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.

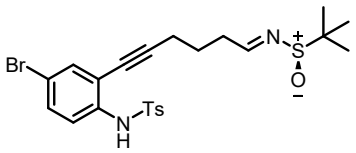
(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)-4-chlorophenyl)-4-methylbenzenesulfonamide (1h)



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 168.1, 150.2, 144.3, 136.2, 131.7, 129.7, 129.2, 127.2, 120.9,

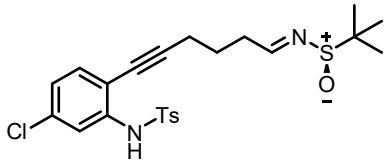
116.6, 116.2, 97.4, 77.4, 56.8, 35.0, 24.1, 22.4, 21.6, 19.1, HRMS (ESI) calcd for $C_{23}H_{28}ClN_2O_3S_2$ $[M+H]^+$ 479.1224, found 479.1232.

(*R*)-*N*-(4-bromo-2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1i)



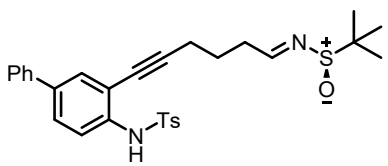
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, J = 4.0 Hz, 1H), 7.65 (d, J = 7.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 1H), 7.39 (s, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 7.2 Hz, 2H), 7.14 (s, 1H), 2.69 – 2.62 (m, 2H), 2.53 (t, J = 6.8 Hz, 2H), 2.39 (s, 3H), 2.01 – 1.89 (m, 2H), 1.22 (s, 9H); ^{13}C 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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)-5-chlorophenyl)-4-methylbenzenesulfonamide (1j)



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.

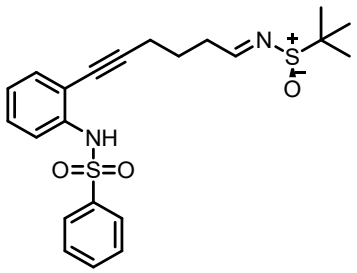
(*R*)-*N*-(3-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (1k)



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,

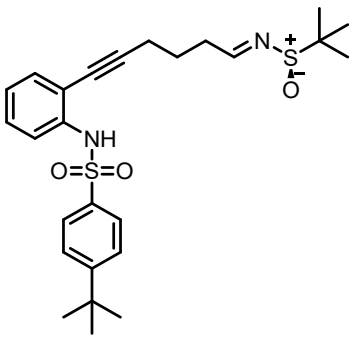
2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.19 (m, 3H), 2.72 – 2.64 (m, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 2.03 – 1.91 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 144.1, 139.4, 137.2, 136.7, 136.2, 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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)benzenesulfonamide (1l)



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.

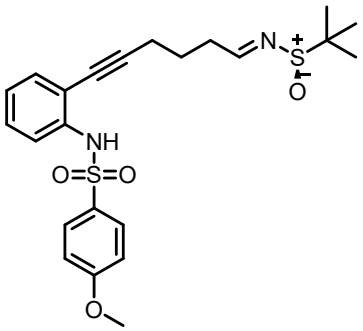
(*R*)-4-(*tert*-butyl)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)benzenesulfonamide (1m)



Yellow oil. ^{1}H 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),

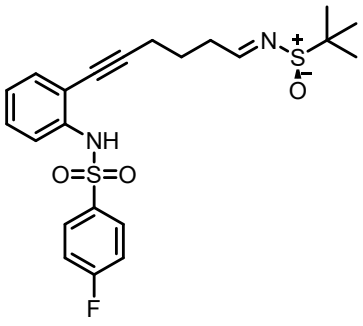
1.29 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 157.0, 137.7, 136.2, 132.1, 129.1, 127.0, 126.0, 124.0, 119.0, 114.2, 96.2, 76.4, 56.7, 35.2, 35.0, 31.0, 24.3, 22.4, 19.1, HRMS (ESI) calcd for $C_{26}H_{35}N_2O_3S_2$ $[M+H]^+$ 487.2084, found 487.2092.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)-4-methoxybenzenesulfonamide (1n)



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.

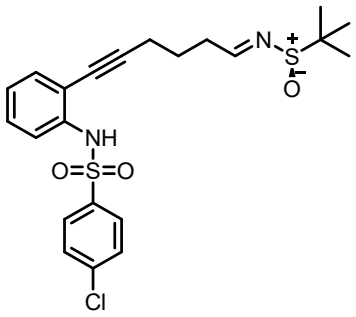
(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)-4-fluorobenzenesulfonamide (1o)



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

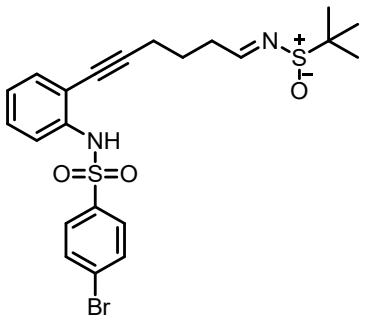
$C_{22}H_{26}FN_2O_3S_2$ $[M+H]^+$ 449.1363, found 449.1369.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)-4-chlorobenzenesulfonamide (1p)



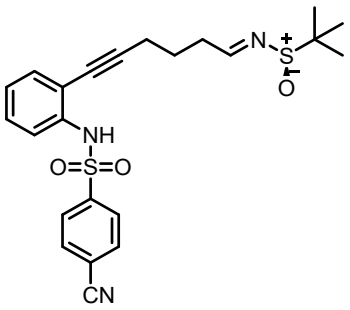
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.55 (d, J = 8.4 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.31 – 7.23 (m, 2H), 7.20 (s, 1H), 7.05 (td, J = 7.6, 0.8 Hz, 1H), 2.67 (td, J = 7.6, 4.4 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.00 – 1.87 (m, 2H), 1.22 (s, 9H); ^{13}C 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.

(*R*)-4-bromo-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)benzenesulfonamide (1q)



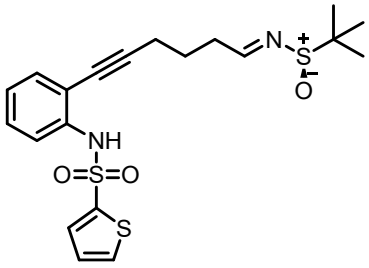
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.4 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.58 – 7.53 (m, 3H), 7.31 – 7.23 (m, 2H), 7.20 (s, 1H), 7.05 (td, J = 7.6, 0.8 Hz, 1H), 2.70 – 2.63 (m, 2H), 2.51 (t, J = 7.2 Hz, 2H), 1.99 – 1.90 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)-4-cyanobenzenesulfonamide (1r)



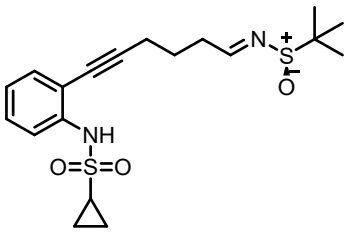
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.32 (s, 1H), 7.31 – 7.27 (m, 2H), 7.13 – 7.04 (m, 1H), 2.68 (td, J = 7.2, 4.4 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 2.05 – 1.87 (m, 2H), 1.22 (s, 9H); ^{13}C 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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)thiophene-2-sulfonamide (1s)



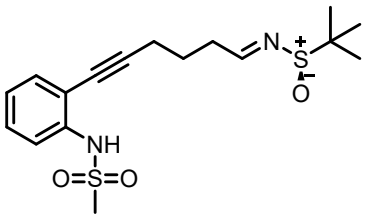
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 4.4 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.54 (dd, J = 4.8, 1.2 Hz, 1H), 7.48 (dd, J = 4.0, 1.2 Hz, 1H), 7.34 – 7.25 (m, 3H), 7.06 (td, J = 7.6, 0.8 Hz, 1H), 6.99 (dd, J = 4.8, 4.0 Hz, 1H), 2.67 (td, J = 7.6, 4.4 Hz, 2H), 2.53 (t, J = 7.2 Hz, 2H), 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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)cyclopropanesulfonamide (1t)



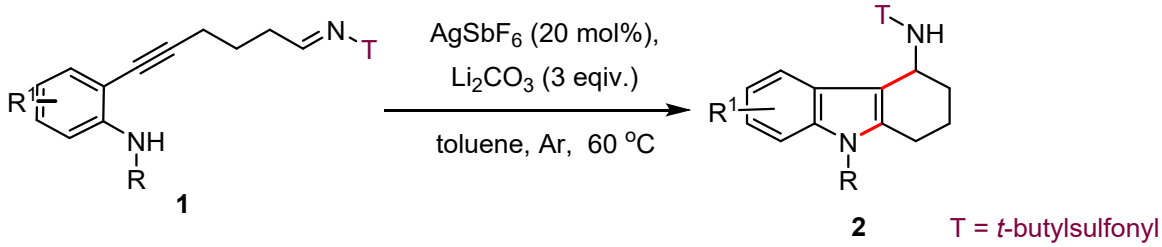
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 4.4 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.41 (dd, J = 8.0, 1.6 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.10 (td, J = 7.6, 1.2 Hz, 1H), 6.98 (s, 1H), 2.75 – 2.69 (m, 2H), 2.61 (t, J = 7.2 Hz, 2H), 2.51 – 2.43 (m, 1H), 2.06 – 1.96 (m, 2H), 1.21 (s, 9H), 1.20 – 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.

(*R*)-*N*-(2-(6-((tert-butylsulfinyl)imino)hex-1-yn-1-yl)phenyl)methanesulfonamide 1u



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.

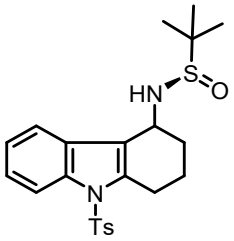
2. **General procedure for the synthesis of substrate 2a-2u**



1 **2**

The reaction substrate **1** (1 equiv), $AgSbF_6$ (20 mol %), Li_2CO_3 (3 equiv) and toluene (5.0 mL) were added sequentially to a Schlenk tube. The reaction mixture was stirred at 60℃ under argon. When TLC indicated complete consumption of the starting material, DCM and H_2O were added to the reaction mixture. After the separation of the organic layer, the water layer was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, the filtrate was evaporated, and the residue was purified via column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the desired product.

(+)/(-)-(*R*)-2-methyl-*N*-(9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)propane-2-sulfinamide (2a)

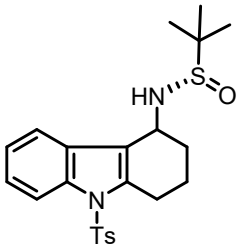


yield: 85 %.

(+)-2a: Yellow oil; $[\alpha]_D^{25}$= + 60 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.23 – 7.21 (m, 3H), 4.64 – 4.62 (m, 1H), 3.47 –3.45 (m, 1H), 3.18 – 3.14 (m, 1H), 2.88 – 2.80 (m, 1H), 2.35 (s, 3H), 2.20–1.91 (m, 4H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 137.7, 136.3, 136.2, 130.0, 128.8, 126.5, 124.2, 123.3, 119.2, 118.2, 114.3, 56.4, 50.5, 31.5, 24.4, 22.8, 21.6, 18.6.

(-)-2a: Yellow oil; $[\alpha]_D^{25}$= – 56 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.65 (m, 3H), 7.32 – 7.25 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.71 (s, 1H), 3.34 (s, 1H), 3.24 (d, *J* = 17.6 Hz, 1H), 2.86 – 2.73 (m, 1H), 2.35 (s, 3H), 2.00 – 1.75 (m, 4H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 138.2, 136.2, 136.0, 130.0, 128.0, 126.5, 124.5, 123.9, 118.7, 117.3, 114.3, 55.4, 46.4, 29.9, 24.4, 22.6, 21.6, 17.7. HRMS (ESI) calcd for $C_{23}H_{28}N_2O_3S_2Na$ $[M+Na]^+$ 467.1434, found 467.1438（High resolution of **2a-1** and **2a-2** mixtures, the same for the following compounds）.

(+)/(-)-(*S*)-2-methyl-*N*-(9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)propane-2-sulfinamide

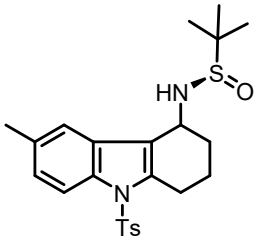


yield:77 %.

(+)-2b: Yellow oil; $[\alpha]_D^{25}$= + 56 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.34 – 7.28 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.73 (d, *J* = 2.0 Hz, 1H), 3.32 (s, 1H), 3.30 – 3.22 (m, 1H), 2.88 – 2.75 (m, 1H), 2.38 (s, 3H), 2.00 – 1.76 (m, 4H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 138.2, 136.2, 136.1, 130.0, 128.0, 126.5, 124.5, 123.9, 118.7, 117.3, 114.3, 55.4, 46.3, 29.9, 24.4, 22.6, 21.6, 17.7.

(-)-2b: Yellow oil; $[\alpha]_D^{25}$= - 60 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.30 (m, 1H), 7.27 – 7.21 (m, 3H), 4.73 – 4.57 (m, 1H), 3.39 (d, *J* = 10.4 Hz, 1H), 3.22 – 3.16 (m, 1H), 2.95 – 2.78 (m, 1H), 2.38 (s, 3H), 2.26 – 1.93 (m, 4H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 137.7, 136.3, 136.2, 130.0, 128.8, 126.5, 124.2, 123.3, 119.2, 118.3, 114.3, 56.3, 50.4, 31.5, 24.4, 22.7, 21.6, 18.6. HRMS (ESI) calcd for $C_{23}H_{28}N_2O_3S_2Na$ $[M+Na]^+$ 467.1434, found 467.1437.

(+)/(-)-(*R*)-2-methyl-*N*-(6-methyl-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)propane-2-sulfinamide



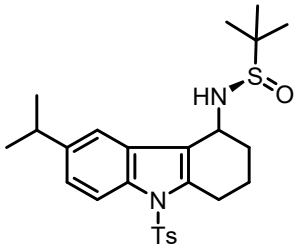
yield: 72%.

(+)-2c: Colorless oil; $[\alpha]_D^{25}$= + 56（*c* =0.1, $CHCl_3$）. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.46 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0, Hz, 1H), 4.68 (s, 1H), 3.29 – 3.18 (m, 2H), 2.84 – 2.70 (m, 1H), 2.42 (s, 3H), 2.35 (s, 3H), 2.03 – 1.69 (m, 4H) 1.18 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 138.3, 136.1, 134.4, 133.6, 129.9, 128.3, 126.5 125.8, 118.5, 117.1, 114.0, 55.4, 46.2, 29.7, 24.5, 22.6, 21.6, 21.4, 17.6.

(-)-2c: Colorless oil; $[\alpha]_D^{25}$= - 52 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 2H),

7.10 (d, J = 8.4, 1H), 4.64 – 4.55 (m, 1H), 3.34 (d, J = 10.4 Hz, 1H), 3.18 – 3.09 (m, 1H), 2.89 – 2.78 (m, 1H), 2.22 – 1.22 (m, 4H), 1.22 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 137.6, 136.2, 134.5, 132.8, 129.9, 129.0, 126.5, 125.5, 119.4, 118.2, 114.0, 56.4, 50.7, 31.6, 24.4, 22.7, 21.6, 21.3, 18.8. HRMS (ESI) calcd for $C_{24}H_{30}N_2O_3S_2Na$ $[M+Na]^+$ 481.1590, found 481.1594.

(+)/(-)-(*R*)-*N*-(6-isopropyl-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

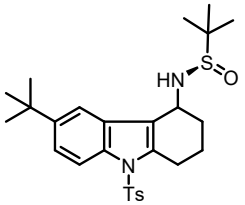


yield: 79%.

(+)-2d: Yellow oil; $[\alpha]_D^{25}$= + 48 (c =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.17 – 7.14 (m, 1H), 4.69 (s, 1H), 3.29 (s, 1H), 3.23 – 3.15 (m, 1H), 3.03 – 2.92 (m, 1H), 2.82 – 2.71 (m, 1H), 2.34 (s, 3H), 2.03 – 1.69 (m, 4H), 1.25 (dd, J = 7.2, 1.2 Hz, 6H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 138.2, 136.3, 134.6, 129.9, 128.1, 126.6, 123.3, 117.2, 116.0, 114.1, 55.3, 46.3, 34.0, 29.9, 24.4, 23.7, 22.6, 21.6, 17.8.

(-)-2d: Yellow oil; $[\alpha]_D^{25}$= –52 (c =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.20 –7.17 (m, 2H), 7.18 – 7.13 (m, 1H), 4.66 (s, 1H), 3.27 (s, 1H), 3.23 – 3.17 (m, 1H), 3.05 – 2.92 (m, 1H), 2.82 – 2.71 (m, 1H), 2.34 (s, 3H), 2.03 – 1.69 (m, 4H), 1.26 (dd, J = 7.2, 1.2 Hz, 6H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 138.4, 136.4, 134.6, 130.1, 128.3, 126.7, 123.5, 117.2, 116.1, 114.1, 55.4, 46.5, 34.0, 30.1, 24.5, 23.6, 22.6, 21.4, 17.8. HRMS (ESI) calcd for $C_{26}H_{35}N_2O_3S_2$ $[M+H]^+$ 487.2089, found 487.2088.

(+)/(-)-(*R*)-*N*-(6-(tert-butyl)-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

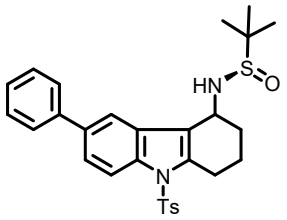


yield: 75%.

(+)-2e: Yellow oil; $[\alpha]_D^{25}$= + 70 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.73 – 7.71 (m, 3H), 7.37 – 7.34 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 1H), 3.33 (s, 1H), 3.25 – 3.16 (m, 1H), 2.82 – 2.73 (m, 1H), 2.36 (s, 3H), 2.03 – 1.76 (m, 4H), 1.36 (s, 9H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 144.8, 138.1, 136.2, 134.2, 130.0, 127.8, 126.6, 122.2, 117.3, 115.1, 113.7, 55.3, 46.4, 34.8, 31.8, 30.1, 24.4, 22.6, 21.6, 17.9.

(-)-2e: Yellow oil; $[\alpha]_D^{25}$= –62 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.46 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.68 – 4.59 (m, 1H), 3.35 (d, *J* = 10.4 Hz, 1H), 3.19 – 3.12 (m, 1H), 2.88 – 2.75 (m, 1H), 2.37 (s, 3H), 2.30 – 1.81. (m, 4H), 1.33 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.8, 137.6, 136.3, 134.2, 130.0, 128.4, 126.6, 122.2, 118.2, 115.3, 113.8, 56.3, 50.6, 34.7, 31.7, 31.4, 24.6, 22.8, 21.6, 18.5. HRMS (ESI) calcd for $C_{27}H_{36}N_2O_3S_2Na$ $[M+Na]^+$ 523.2060, found 523.2065.

(+)/(-)-(*R*)-2-methyl-*N*-(6-phenyl-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)propane-2-sulfinamide



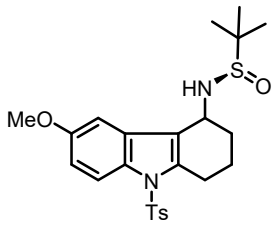
yield: 72%.

(+)-2f: Yellow oil; $[\alpha]_D^{25}$= + 64 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.56 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.76 (s, 1H), 3.35 – 3.21 (m, 2H), 2.87 – 2.74 (m, 1H), 2.36 (s, 3H), 2.04 – 1.76 (m, 4H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 140.8, 138.8, 137.0, 136.1, 135.6, 130.0, 128.9, 128.6, 127.2, 127.0, 126.6, 123.8, 117.6, 116.8, 114.5, 55.4, 46.4, 29.9, 24.5, 22.6, 21.6, 17.7.

(-)-2f: Yellow oil; $[\alpha]_D^{25}$= – 68 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.58 – 7.55 (m, 2H), 7.52 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.24 (s, 2H), 4.71 – 4.62 (m, 1H), 3.40 (d, *J* = 10.4 Hz, 1H), 3.21 – 3.12 (m, 1H), 2.93 – 2.82 (m, 1H), 2.37 (s, 3H), 2.23 – 1.93 (m, 4H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 141.2, 138.3, 136.6, 136.1, 135.7, 130.0, 129.3, 128.8, 127.6, 127.4, 126.6, 123.7, 118.4, 117.7, 114.5, 56.3, 50.8,

31.6, 24.4, 22.8, 21.6, 18.8. HRMS (ESI) calcd for $C_{29}H_{32}N_2O_3S_2$ $[M+Na]^+$ 543.1747, found 543.1750.

(+)/(-)-(*R*)-*N*-(6-methoxy-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

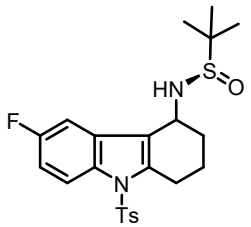


yield: 68%.

(+)-2g: Yellow oil; $[\alpha]_D^{25}$= +30 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.89 – 6.70 (m, 1H), 4.66 (s, 1H), 3.84 (s, 3H), 3.29 (s, 1H), 3.24 – 3.17 (m, 1H), 2.84 – 2.71 (m, 1H), 2.35 (s, 3H), 1.97 – 1.89 (m, 3H), 1.81 – 1.75 (m, 1H), 1.18 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 144.8, 138.7, 136.0, 130.5, 129.9, 129.0, 126.4, 117.5, 115.3, 113.6, 100.8, 55.8, 55.4, 46.7, 30.4, 24.5, 22.6, 21.6, 18.0.

(-)-2g: Yellow oil; $[\alpha]_D^{25}$= – 34 (*c* =0.1, $CHCl_3$). ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.90 – 6.70 (m, 1H), 4.64 – 4.54 (m, 1H), 3.79 (s, 3H), 3.36 (d, *J* = 8.4 Hz, 1H), 3.14 (dt, *J* = 18.4, 4.8 Hz, 1H), 2.88 – 2.76 (m, 1H), 2.36 (s, 3H), 2.24 – 2.17 (m, 1H), 2.08 – 1.99 (m, 1H), 1.95 – 1.86 (m, 2H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 144.8, 138.4, 136.0, 130.7, 129.9, 129.8, 126.4, 118.3, 115.3, 112.9, 101.8, 56.3, 55.6, 50.5, 31.5, 24.5, 22.8, 21.6, 18.6. HRMS (ESI) calcd for $C_{24}H_{30}N_2O_4S_2Na$ $[M+Na]^+$ 497.1539, found 497.1542.

(+)/(-)-(*R*)-*N*-(6-fluoro-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide



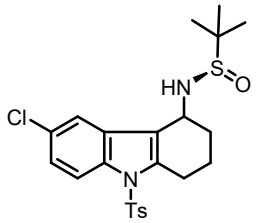
yield: 70%.

(+)-2h: Yellow oil; $[\alpha]_D^{25}$= + 54 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.03 – 6.97 (m, 1H), 4.64 (s, 1H), 3.25 – 3.21 (m, 2H), 2.85 –

2.73 (m, 1H), 2.37 (s, 3H), 2.04 – 1.89 (m, 3H), 1.82 – 1.74 (m, 1H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, (d, J = 250.2), 145.1, 140.0, 135.8, 132.4, 130.0, 126.5, 122.2, 117.3, 115.4 (d, J = 9.0), 112.2 (d, J = 25.3), 104.7 (d, J = 24.2), 55.4, 46.5, 30.1, 24.5, 22.6, 21.6, 17.7.

(-)-2h: Yellow oil; $[\alpha]_D^{25}$= - 46 (c =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 9.2, 4.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.14 (dd, J = 8.8, 2.4 Hz, 1H), 7.02 – 6.98 (m, 1H), 4.61 – 4.52 (m, 1H), 3.33 (d, J = 8.4 Hz, 1H), 3.17 – 3.10 (m, 1H), 2.90 – 2.78 (m, 1H), 2.38 (s, 3H), 2.23 – 2.15 (m, 1H), 2.12 – 2.03 (m, 1H), 1.96 – 1.88 (m, 2H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, J = 254.2), 145.1, 139.4, 135.9, 132.8, 130.0, 126.5, 123.4, 118.2, 115.4 (d, J = 9.0) 111.9 (d, J = 26.3), 105.1, (d, J = 24.6), 56.4, 50.6, 31.5, 24.4, 22.7, 21.6, 18.7. HRMS (ESI) calcd for $C_{23}H_{27}FN_2O_3S_2Na$ $[M+Na]^+$485.1339, found 485.1343.

(+)/(-)-(*R*)-*N*-(6-chloro-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

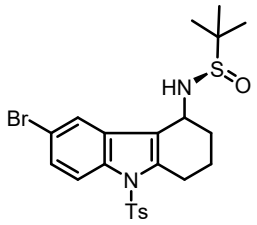


yield:78%.

(+)-2i: Yellow oil; $[\alpha]_D^{25}$= + 56 (c =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.26 – 7.22 (m, 3H), 4.65 – 4.62 (m, 1H), 3.28 – 3.18 (m, 2H), 2.82 – 2.73 (m, 1H), 2.37 (s, 3H), 2.04 – 1.76 (m, 4H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.8, 135.7, 134.6, 130.1, 129.7, 129.4, 126.5, 124.6, 118.5, 116.8, 115.3, 55.5, 46.5, 30.0, 24.4, 22.6, 21.7, 17.7.

(-)-2i: Yellow oil; $[\alpha]_D^{25}$= - 62 (c =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 2.4 Hz, 1H), 7.27 (s, 1H), 7.25 – 7.22 (m, 2H), 4.59 – 4.54 (m, 1H), 3.34 (d, J = 8.4 Hz, 1H), 3.16 – 3.09 (m, 1H), 2.89 – 2.81 (m, 1H), 2.38 (s, 3H), 2.19 – 1.90 (m, 4H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.1, 135.9, 134.6, 130.1, 129.1, 126.5, 124.3, 119.2, 117.8, 115.3, 100.0, 56.5, 50.8, 31.7, 24.4, 22.8, 21.6, 18.9. HRMS (ESI) calcd for $C_{23}H_{27}ClN_2O_3S_2Na$ $[M+Na]^+$ 501.1044, found 501.1048.

(+)/(-)-(*R*)-*N*-(6-bromo-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

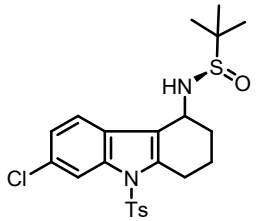


yield 68%.

(+)-2j: Yellow oil; $[\alpha]_D^{25}$= + 46 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.68 – 4.61 (m, 1H), 3.28 – 3.16 (m, 2H), 2.85 – 2.73 (m, 1H), 2.37 (s, 3H), 2.04 – 1.87 (m, 3H), 1.80 – 1.72 (m, 1H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.6, 135.8, 135.0, 130.1, 129.9, 127.3, 126.5, 121.5, 117.3, 116.6, 115.7, 55.5, 46.5, 30.0, 24.4, 22.6, 21.6, 17.7.

(-)-2j: Yellow oil; $[\alpha]_D^{25}$= - 42（*c* =0.1, $CHCl_3$）。^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.60 – 4.54 (m, 1H), 3.32 (d, *J* = 10.4 Hz, 1H), 3.12 (dt, *J* = 18.4, 5.2 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.38 (s, 3H), 2.16 – 2.10 (m, 2H), 1.93 – 1.87 (m, 2H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.9, 135.9, 135.0, 130.5, 130.1, 126.9, 126.5, 122.8, 117.8, 116.7, 115.7, 56.5, 50.8, 31.7, 24.3, 22.8, 21.6, 19.0. HRMS (ESI) calcd for $C_{23}H_{27}BrN_2O_3S_2Na$ $[M+Na]^+$ 545.0539, found 545.0542.

(+)/(-)-(*R*)-*N*-(7-chloro-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide



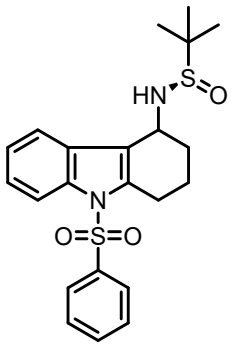
yield: 72 %.

(+)-2k:Yellow oil; $[\alpha]_D^{25}$= + 66 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.27 (s, 1H), 7.26 – 7.22 (m, 2H), 4.67 (s, 1H), 3.26 – 3.17 (m, 2H), 2.80 – 2.72 (m, 1H), 2.38 (s, 3H), 1.99 – 1.75 (m, 4H), 1.18 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 138.8, 136.6, 135.9, 130.5, 130.1, 126.6, 126.5, 124.4, 119.6, 117.0, 114.5, 55.5, 46.5, 30.1, 24.3, 22.6, 21.6, 17.7.

(-)-2k: Yellow oil; $[\alpha]_D^{25}$= - 68 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d,

J = 1.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.28 (s, 1H), 7.26 (s, 1H), 7.20 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.63 – 4.54 (m, 1H), 3.34 (d, *J* = 10.4 Hz, 1H), 3.15 – 3.10 (m, 1H), 2.86 – 2.78 (m, 1H), 2.39 (s, 3H), 2.18 – 1.91. (m, 4H), 1.20 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 138.3, 136.6, 135.9, 130.2, 130.1, 127.2, 126.6, 123.9, 119.9, 117.9, 114.5, 56.4, 50.2, 31.4, 24.3, 22.7, 21.7, 18.6. HRMS (ESI) calcd for $C_{23}H_{27}ClN_2O_3S_2Na$ $[M+Na]^+$ 501.1044, found 501.1047.

(+)/(-)-(*R*)-2-methyl-*N*-(9-(phenylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)propane-2-sulfinamide

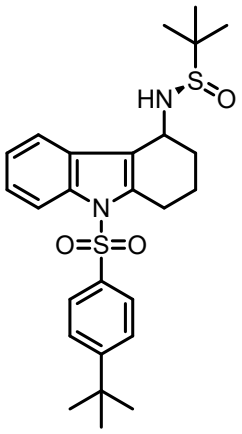


yield: 81 %。

(+)-2l: Yellow oil; $[\alpha]_D^{25}$= + 44 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.27 (m, 2H), 4.72 (s, 1H), 3.31 (s, 1H), 3.28 – 3.20 (m, 1H), 2.87 – 2.73 (m, 1H), 2.03 – 1.90 (m, 3H), 1.83 – 1.77 (m, 1H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.2, 136.2, 133.8, 129.4, 128.0, 126.5, 124.6, 124.0, 118.8, 117.5, 114.3, 55.4, 46.3, 29.9, 24.4, 22.6, 17.7.

(-)-2l: Yellow oil; $[\alpha]_D^{25}$= - 40 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.61 – 7.55 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.28 – 7.22 (m, 1H), 4.71 – 4.60 (m, 1H), 3.39 (d, *J* = 10.4 Hz, 1H), 3.19 (dt, *J* = 18.4, 4.8 Hz, 1H), 2.94 – 2.81 (m, 1H), 2.28 – 2.19 (m, 1H), 2.12 – 2.03 (m, 1H), 1.98 – 1.90 (m, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.6, 136.3, 133.8, 129.4, 128.8, 126.5, 124.3, 123.4, 119.2, 118.5, 114.3, 56.4, 50.4, 31.5, 24.4, 22.8, 18.6. HRMS (ESI) calcd for $C_{22}H_{26}N_2O_3S_2$ Na $[M+Na]^+$ 453.1277, found 453.1281.

(+)/(-)-(*R*)-*N*-(9-((4-(tert-butyl)phenyl)sulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

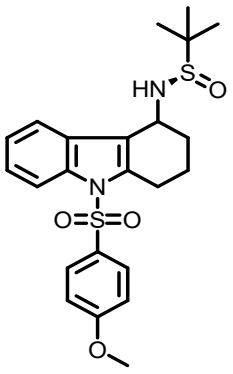


yield: 73 %.

(+)-2m: Yellow oil; $[\alpha]_D^{25}$= +46 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 1H), 7.77 – 7.71 (m, 3H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.26 (m, 2H), 4.73 (d, *J* = 2.4 Hz, 1H), 3.35 – 3.21 (m, 2H), 2.90 – 2.75 (m, 1H), 2.04 – 1.78 (m, 4H), 1.28 (s, 9H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 138.2, 136.2, 136.1, 127.9, 126.4, 126.4, 124.5, 123.8, 118.7, 117.1, 114.3, 55.4, 46.3, 35.3, 31.0, 29.9, 24.4, 22.6, 17.7.

(-)-2m: Yellow oil; $[\alpha]_D^{25}$= – 44 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.31 – 7.28 (m, 1H), 7.25 –7.21 (m, 1H), 4.69 – 4.60 (m, 1H), 3.36 (d, *J* = 10.4 Hz, 1H), 3.20 (d, *J* = 18.4 Hz, 1H), 2.92 – 2.82 (m, 1H), 2.21 – 1.95 (m, 4H), 1.28 (s, 9H), 1.21 (s, 9H). $^{13}CNMR$ (100 MHz, $CDCl_3$) δ 157.8, 137.7, 136.3, 128.7, 126.4, 126.4, 124.2, 123.2, 119.2, 118.1, 114.3, 56.3, 50.4, 35.3, 31.5, 31.0, 24.4, 22.8, 18.6. HRMS (ESI) calcd for $C_{26}H_{34}N_2O_3S_2Na$ $[M+Na]^+$ 509.1903, found 509.1907.

(+)/(-)-(*R*)-*N*-(9-((4-methoxyphenyl)sulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide



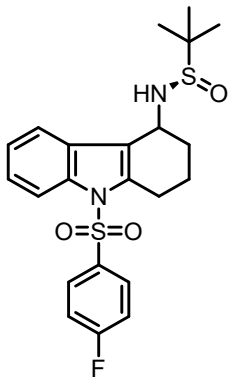
yield: 73 %.

(+)-2n: Yellow oil; $[\alpha]_D^{25}$= + 40 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.30 – 7.26 (m,

1H), 7.24 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.69 (s, 1H), 3.78 (s, 3H), 3.28 (s, 1H), 3.25 – 3.17 (m, 1H), 2.83 – 2.71 (m, 1H), 2.03 – 1.73 (m, 4H), 1.15 (s, 9H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 163.7, 138.2, 136.2, 130.6, 128.8, 128.0, 124.4, 123.8, 118.7, 117.2, 114.5, 114.3, 55.7, 55.4, 46.3, 29.9, 24.5, 22.6, 17.8.

(-)-2n: Yellow oil; $[\alpha]_D^{25}$= – 38 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 7.20 – 7.17 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.66 – 4.55 (m, 1H), 3.78 (s, 3H), 3.34 (d, *J* = 10.4 Hz, 1H), 3.17– 3.11 (m, 1H), 2.88 – 2.77 (m, 1H), 2.23 – 1.87 (m, 4H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 137.6, 136.2, 130.7, 128.7, 128.1, 124.2, 123.2, 119.2, 118.2, 114.5, 114.3, 56.3, 55.7, 50.5, 31.5, 24.4, 22.8, 18.6. HRMS (ESI) calcd for $C_{23}H_{28}N_2O_4S_2Na$ $[M+Na]^+$ 483.1383, found 483.1387.

(+)/(-)-(*R*)-*N*-(9-((4-fluorophenyl)sulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide



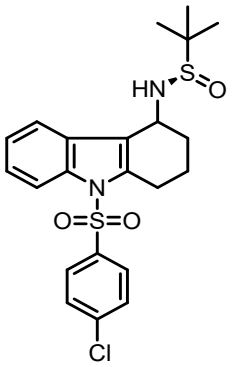
yield: 82 %.

(+)-2o: Yellow oil; $[\alpha]_D^{25}$= + 60 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.2, 1H), 7.87 – 7.80 (m, 2H), 7.73 –7.71 (m, 1H), 7.34 – 7.27 (m, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 4.76 – 4.69 (m, 1H), 3.31 – 3.18 (m, 2H), 2.86 – 2.73 (m, 1H), 2.05 – 1.90 (m, 3H), 1.82 – 1.73 (m, 1H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (d, *J* = 278.0), 138.1, 136.1, 129.3 (d, *J* = 10), 128.1, 124.7, 124.2, 118.9, 117.8, 116.9, 116.6, 114.2, 55.4, 46.3, 29.9, 24.5, 22.6, 17.8.

(-)-2o: Yellow oil; $[\alpha]_D^{25}$= - 56 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.14 (t, *J* = 8.4 Hz, 2H), 4.70 – 4.60 (m, 1H), 3.38 (d, *J* = 10.4 Hz, 1H), 3.18 (dt, *J* = 18.4, 4.8 Hz, 1H), 2.91 – 2.80 (m, 1H), 2.27 – 2.21 (m, 1H), 2.12 – 2.03 (m, 1H), 2.00 – 1.91 (m, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (d, *J* = 274.6), 137.5, 136.2, 129.3 (d, *J* = 10), 128.9, 124.5, 123.6, 119.4, 118.8,

116.8, 116.6, 114.3, 56.3, 50.4, 31.5, 24.4, 22.7, 18.6. HRMS (ESI) calcd for $C_{22}H_{25}FN_2O_3S_2Na$ $[M+Na]^+$ 471.1184, found 471.1188.

(+)/(-)-(*R*)-*N*-(9-((4-chlorophenyl)sulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

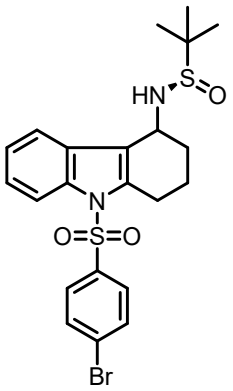


yield: 80 %.

(+)-2p: Yellow oil; $[\alpha]_D^{25}$= + 58 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.12 (m, 1H), 7.76 – 7.71 (m, 3H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.28 (m, 2H), 4.72 – 4.68(m, 1H), 3.29 (d, *J* = 1.6 Hz, 1H), 3.25 – 3.18 (m, 1H), 2.83 – 2.73 (m, 1H), 2.03 – 1.91 (m, 3H), 1.81 – 1.73 (m, 1H), 1.18 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 138.1, 137.3, 136.2, 129.7, 128.1, 127.9, 124.8, 124.3, 118.9, 118.0, 114.2, 55.4, 46.3, 29.9, 24.5, 22.6, 17.8.

(-)-2p: Yellow oil; $[\alpha]_D^{25}$= - 62 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.22 (m, 1H), 4.68 – 4.58 (m, 1H), 3.36 (d, *J* = 8.4 Hz, 1H), 3.15 (dt, *J* = 18.4, 4.8 Hz, 1H), 2.90 – 2.78 (m, 1H), 2.26 – 2.18 (m, 1H), 2.11 – 2.02 (m, 1H), 1.97 – 1.89 (m, 2H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 137.5, 137.4, 136.2, 129.7, 128.9, 127.9, 124.5, 123.7, 119.4, 119.0, 114.3, 56.4, 50.4, 31.4, 24.5, 22.8, 18.6. HRMS (ESI) calcd for $C_{22}H_{25}ClN_2O_3S_2Na$ $[M+Na]^+$ 487.0887, found 487.0892.

(+)/(-)-(*R*)-*N*-(9-((4-bromophenyl)sulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

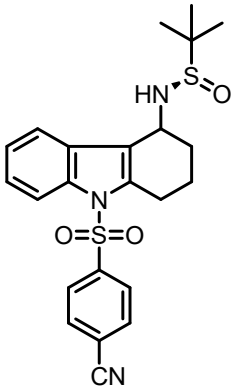


yield: 70 %.

(+)-2q: Yellow oil; $[\alpha]_D^{25}$= + 38 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0, 1H), 7.76 – 7.74 (m, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.29 (m, 2H), 4.73 – 4.71 (m, 1H), 3.32 (s, 1H), 3.27 – 3.19 (m, 1H), 2.86 – 2.75 (m, 1H), 2.06 – 1.81 (m, 4H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.9, 136.2, 132.7, 129.0, 128.1, 127.9, 124.8, 124.3, 118.9, 118.0, 114.2, 55.4, 46.4, 29.9, 24.5, 22.6, 17.8.

(-)-2q: Yellow oil; $[\alpha]_D^{25}$= - 38 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0, 1H), 7.77 – 7.74 (m, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.35 – 7.27 (m, 2H), 4.73 – 4.70 (m, 1H), 3.34 (s, 1H), 3.26 – 3.18 (m, 1H), 2.85 – 2.76 (m, 1H), 2.09 – 1.85 (m, 4H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.6, 136.1, 132.5, 129.1, 128.1, 127.8, 124.7, 124.3, 118.8, 118.2, 114.3, 55.5, 46.4, 29.8, 24.7, 22.6, 17.7. HRMS (ESI) calcd for $C_{22}H_{25}BrN_2O_3S_2Na$ $[M+Na]^+$ 531.0382, found 531.0388.

(+)/(-)-(*R*)-*N*-(9-((4-cyanophenyl)sulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide



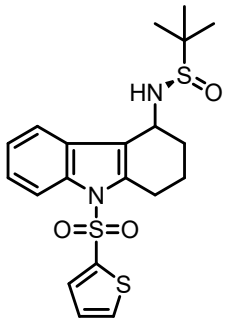
yield: 71 %.

(+)-2r: Yellow oil; $[\alpha]_D^{25}$= + 66 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 3H), 7.34 – 7.28 (m,

2H), 4.71 – 4.68(m, 1H), 3.31 (d, *J* = 1.6 Hz, 1H), 3.23 – 3.17 (m, 1H), 2.84 – 2.70 (m, 1H), 2.05 – 1.76 (m, 4H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.0, 136.0, 133.2, 128.3, 127.1, 125.1, 124.6, 119.2, 118.6, 117.5, 116.9, 114.2, 55.5, 46.4, 30.0, 24.5, 22.6, 17.7.

(-)-2r: Yellow oil; $[\alpha]_D^{25}$= - 64 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.23 (m, 1H), 4.69 – 4.58 (m, 1H), 3.38 (d, *J* = 8.4 Hz, 1H), 3.20 – 3.09 (m, 1H), 2.88 – 2.76 (m, 1H), 2.23 – 1.95 (m, 4H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 137.4, 136.1, 133.2, 129.0, 127.1, 124.8, 124.0, 119.6, 118.7, 117.6, 116.9, 114.2, 56.4, 50.3, 31.4, 24.5, 22.7, 18.6. HRMS (ESI) calcd for $C_{24}H_{27}N_3O_3S_2Na$ $[M+Na]^+$ 478.1235, found 478.1235.

(+)/(-)-(*R*)-2-methyl-*N*-(9-(thiophen-2-ylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)propane-2-sulfinamide

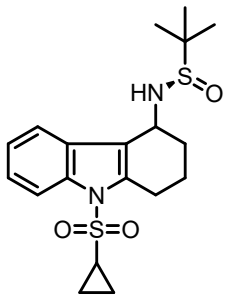


yield:76%.

(+)-2s: Yellow oil; $[\alpha]_D^{25}$= + 48 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0, 1H), 7.73 (d, *J* = 7.6. 1H), 7.64 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.54 (dd, *J* = 5.6, 1.2 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.00 (t, *J* = 4.8, 4.0 Hz, 1H), 4.72 (s, 1H), 3.31 (s, 1H), 3.30 – 3.23 (m, 1H), 2.93 – 2.82 (m, 1H), 2.05 – 1.92 (m, 3H), 1.83 – 1.77 (m, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.3, 135.9, 133.2, 132.6, 128.3, 127.5, 124.6, 124.3, 118.9, 118.1, 114.5, 55.4, 46.3, 29.9, 24.6, 22.6, 17.7.

(-)-2s: Yellow oil; $[\alpha]_D^{25}$= - 44 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 4.4 Hz,1H), 4.71 – 4.58 (m, 1H), 3.39 (d, *J* = 8.4 Hz, 1H), 3.20 (dt, *J* = 18.4, 4.8 Hz, 1H), 2.96 – 2.86 (m, 1H), 2.22 (dt, *J* = 8.4, 4.8 Hz, 1H), 2.12 – 2.03 (m, 1H), 2.00 – 1.91 (m, 2H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.7, 135.9, 133.2, 132.5, 129.1, 127.5, 124.4, 123.7, 119.3, 119.1, 114.5, 56.4, 50.4, 31.5, 24.5, 22.8, 18.6. HRMS (ESI) calcd for $C_{20}H_{24}N_2O_3S_2Na$ $[M+Na]^+$ 459.0841, found 459.0846.

(+)/(-)-(*R*)-*N*-(9-(cyclopropylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-2-methylpropane-2-sulfinamide

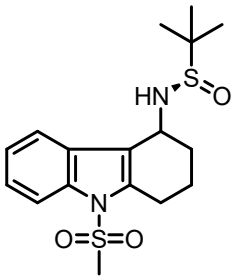


yield: 69%.

(+)-2t: Yellow oil; $[\alpha]_D^{25}$= + 48 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 1H), 7.81 – 7.76 (m, 1H), 7.32 – 7.28 (m, 2H), 4.80 (s, 1H), 3.37 (s, 1H), 3.21 – 3.11 (m, 1H), 2.85 – 2.71 (m, 1H), 2.63 – 2.56 (m, 1H), 2.07 – 1.83 (m, 4H), 1.40 – 1.34 (m, 2H), 1.21 (s, 9H), 1.03 – 0.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.3, 127.9, 124.4, 123.8, 118.8, 116.8, 113.9, 55.4, 46.3, 31.7, 29.9, 24.4, 22.6, 17.8, 5.8.

(-)-2t: Yellow oil; $[\alpha]_D^{25}$= – 40 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.2 Hz, 1H), 7.62 – 7.53 (m, 1H), 7.29 – 7.23 (m, 2H), 4.78 – 4.66 (m, 1H), 3.44 (d, *J* = 10.4 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.89 – 2.79 (m, 1H), 2.64 – 2.55 (m, 1H), 2.31 – 2.23 (m, 1H), 2.17 – 2.08 (m, 1H), 2.01 – 1.93 (m, 2H), 1.40 – 1.34 (m, 2H), 1.25（s, 9H), 1.04 – 0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.3, 128.7, 124.2, 123.2, 119.3, 117.8, 114.0, 56.4, 50.6, 31.7, 31.6, 24.4, 22.8, 18.7, 5.8. HRMS (ESI) calcd for $C_{19}H_{26}N_2O_3S_2Na$ $[M+Na]^+$ 417.1277, found 417.1282.

(+)/(-)-(*R*)-2-methyl-*N*-(9-(methylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)propane-2-sulfinamide



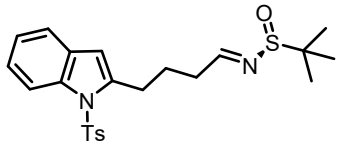
yield: 76%.

(+)-2u: Yellow oil; $[\alpha]_D^{25}$= + 64 (*c* =0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 1H), 7.81 – 7.77 (m, 1H), 7.33 – 7.30 (m, 2H), 4.79 (s, 1H), 3.38 (s, 1H), 3.18 – 3.11 (m, 1H), 3.07 (s, 3H), 2.85 – 2.75 (m, 1H), 2.09 – 1.84 (m, 4H), 1.21 (s,

9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.0, 128.0, 124.7, 124.1, 119.0, 117.2, 113.7, 55.5, 46.4, 40.9, 20.0, 24.3, 22.6, 17.7.

(-)-2u: Yellow oil; $[\alpha]_D^{25}$= – 62 (*c* =0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.30 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 4.71 – 4.65 (m, 1H), 3.42 (d, *J* = 8.4 Hz, 1H), 3.12 – 3.05 (m, 1H), 3.04 (s, 3H), 2.86 – 2.77 (m, 1H), 2.27 – 1.89 (m, 4H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.0, 128.8, 124.5, 123.5, 119.4, 118.2, 113.8, 56.4, 50.5, 41.0, 31.5, 24.3, 22.8, 18.6. HRMS (ESI) calcd for $C_{17}H_{24}N_2O_3S_2Na$ $[M+Na]^+$ 391.1121, found 391.1125.

(*R*,*E*)-2-methyl-*N*-(4-(1-tosyl-1H-indol-2-yl)butylidene)propane-2-sulfinamide



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 8.12 (t, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.40 (s, 1H), 3.08 (t, *J* = 7.6 Hz, 2H), 2.65 -2.61 (m, 2H), 2.17 – 2.03 (m, 2H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 144.7, 141.1, 137.2, 136.1, 129.8, 129.6, 127.2, 126.2, 124.0, 123.6, 120.2, 114.8, 109.3, 56.6, 35.5, 28.5, 24.7, 22.3, 21.5.

Synthesis of 3a

The product was prepared by treatment of **2a** with excess HCl in dioxane to afford the analytically pure product as yellow oil in >99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.15 (m, 1H), 3.11-3.06 (m, 1H), 2.90 – 2.84 (m, 1H), 2.31 (s, 3H), 1.94 – 1.82 (m, 3H), 1.70 – 1.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 136.4, 136.2, 136.2, 129.9, 129.2, 126.4, 124.0, 123.3, 121.6, 118.8, 114.4, 44.1, 32.9, 24.7, 21.6, 19.1. HRMS (ESI) calcd for $C_{19}H_{20}N_2O_2SNa$ $[M+Na]^+$ 363.1138, found 363.1140.

Synthesis of 4a

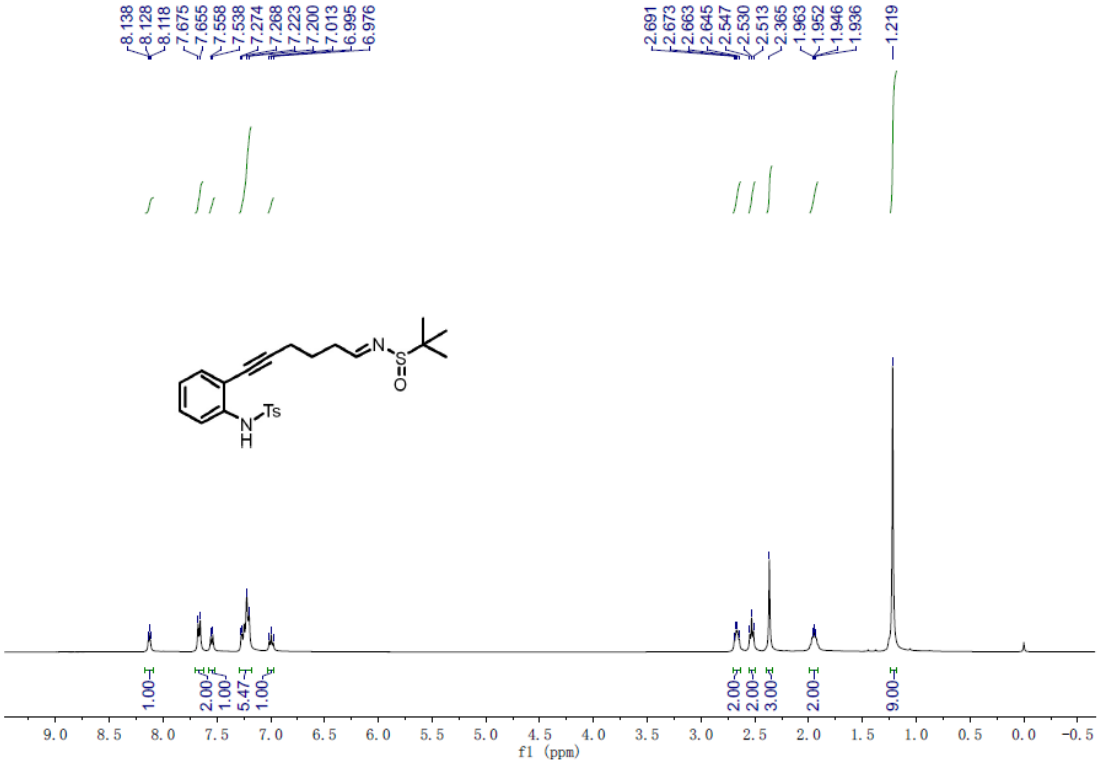
Potassium carbonate (166 mg, 1.2 mmol) and 2-bromoethanol (82 mg, 0.66 mmol) were added to a solution of compound **3a** (249 mg, 0.6 mmol) in acetonitrile (10 mL), and the mixture was heated to 80 ◦C and stirred for 2 h under an N_2 atmosphere. When the reaction was completed, as indicated by TLC, water (30 mL) was added to the residue. The mixture was filtered, concentrated, and purified by silica gel column chromatography using DCM/MeOH/$NH_3.H_2O$ (100:5:0.5, v/v/v) to

obtain compound **4a** (95% yield) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 3.95 (m, 1H), 3.69-3.62 (m, 2H), 3.12 – 3.07 (m, 1H), 2.96-283 (m, 3H), 2.34 (s, 3H), 1.97 – 1.72 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 136.3, 136.2, 129.9, 129.3, 126.4, 124.0, 123.3, 118.8, 114.4, 50.4, 44.2, 43.1, 29.7, 27.6, 24.7, 21.6, 18.9. HRMS (ESI) calcd for $C_{22}H_{25}ClN_2O_2S$ $[M+Na]^+$ 439.1217, found 439.1221.

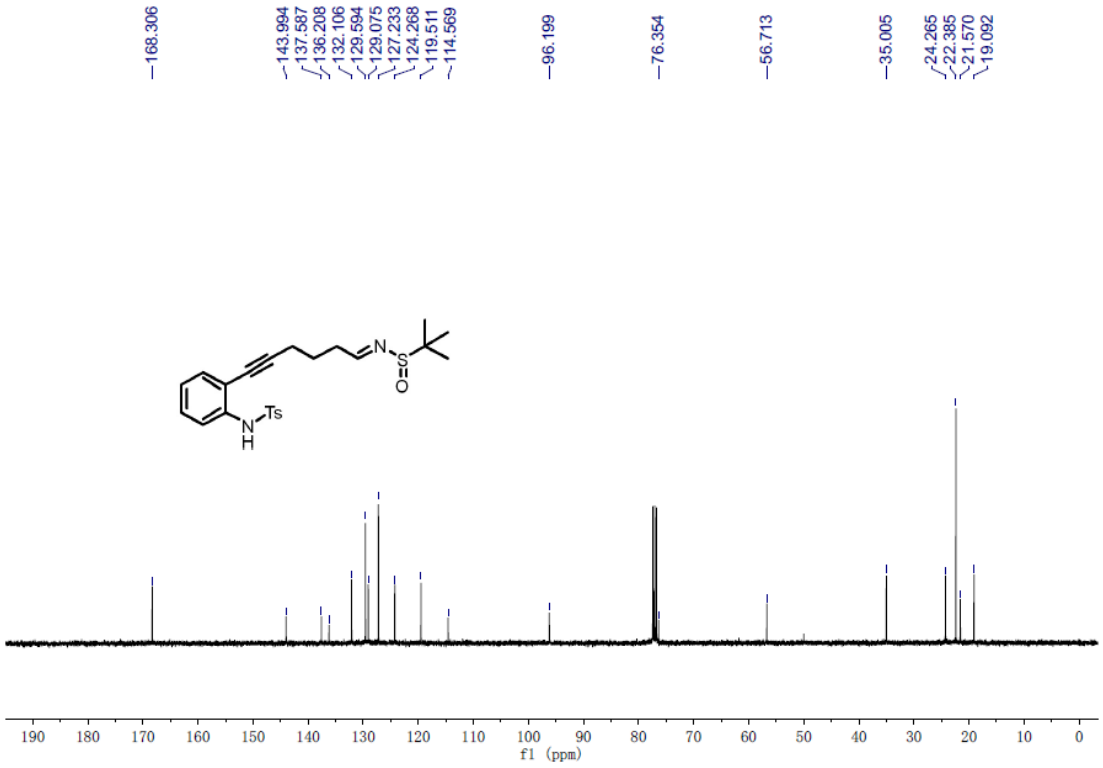
.

4. NMR spectra

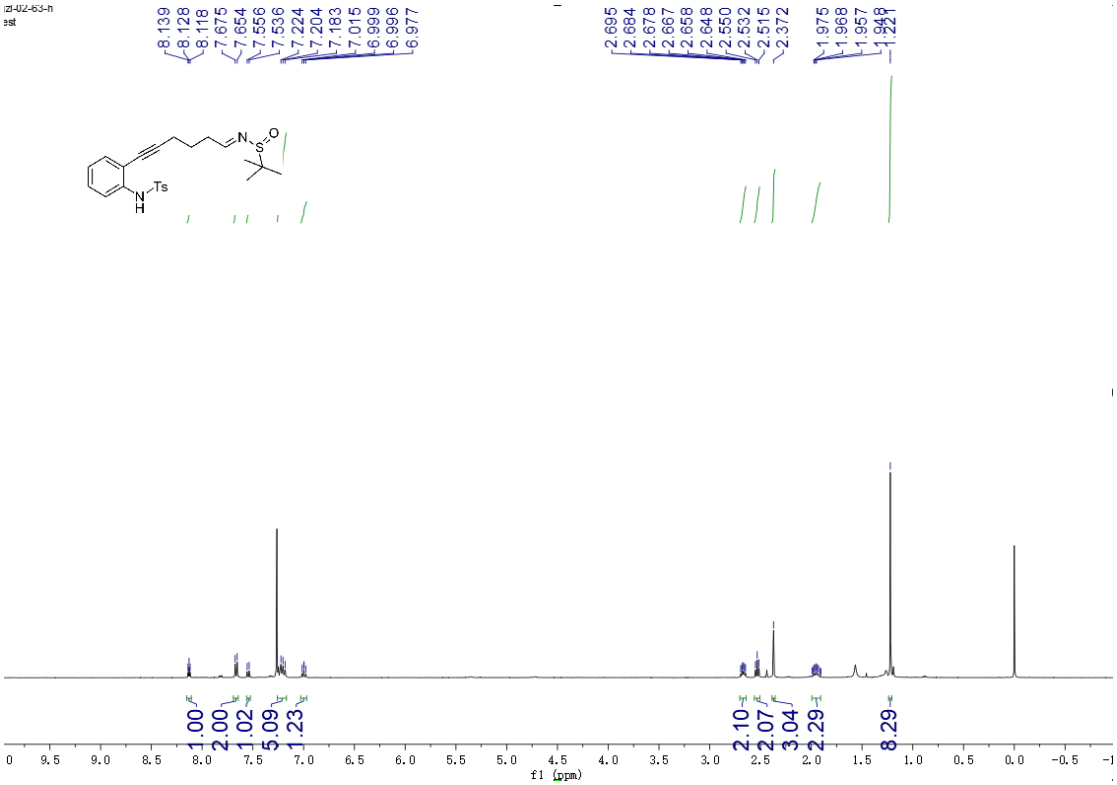
^{1}H NMR spectrum of 1a



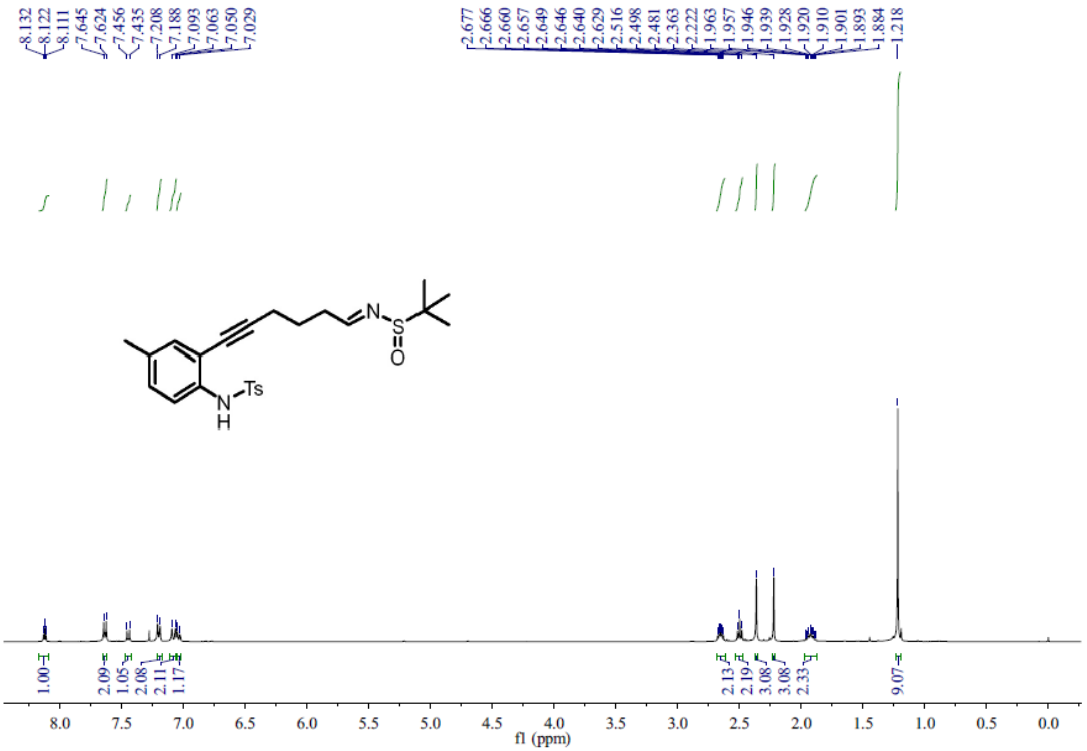
^{13}C NMR spectrum of 1a



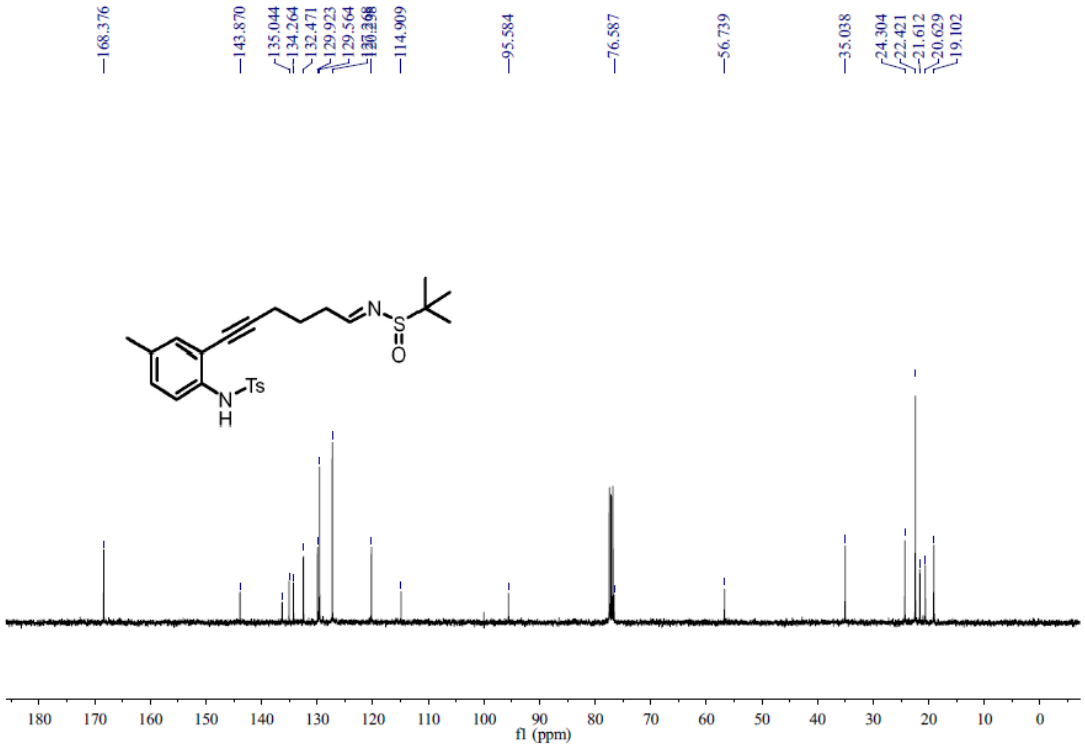
^{1}H NMR spectrum of 1b



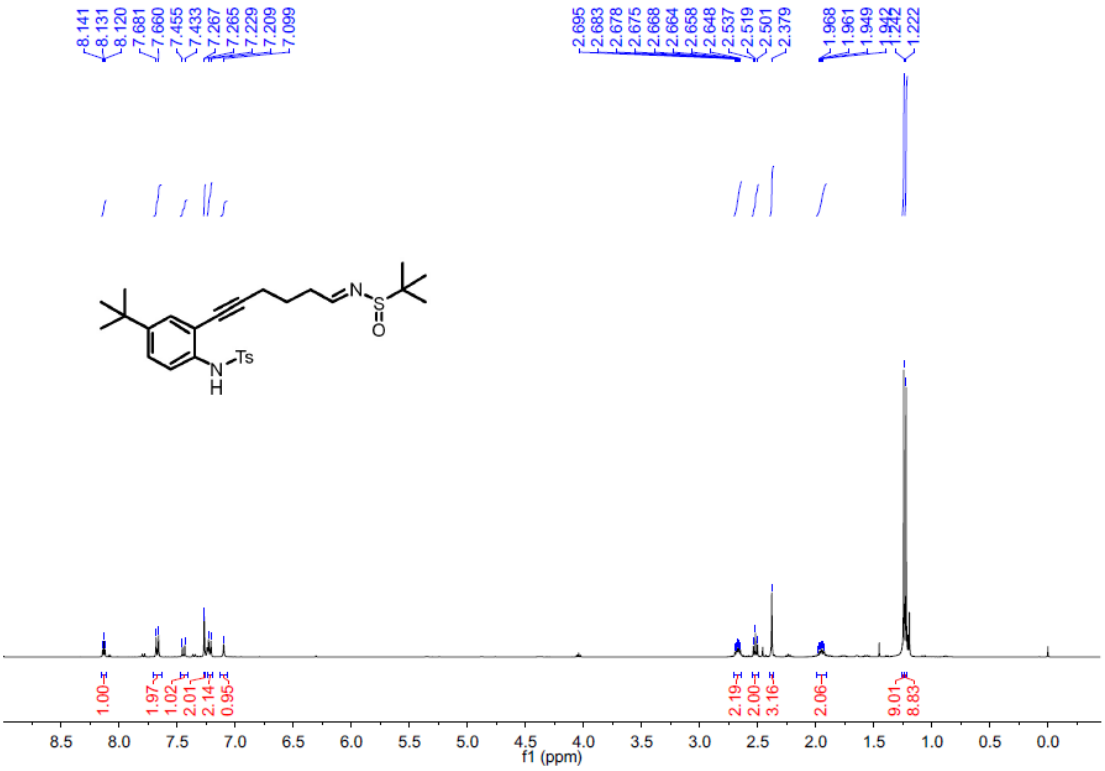
^{1}H NMR spectrum of 1c



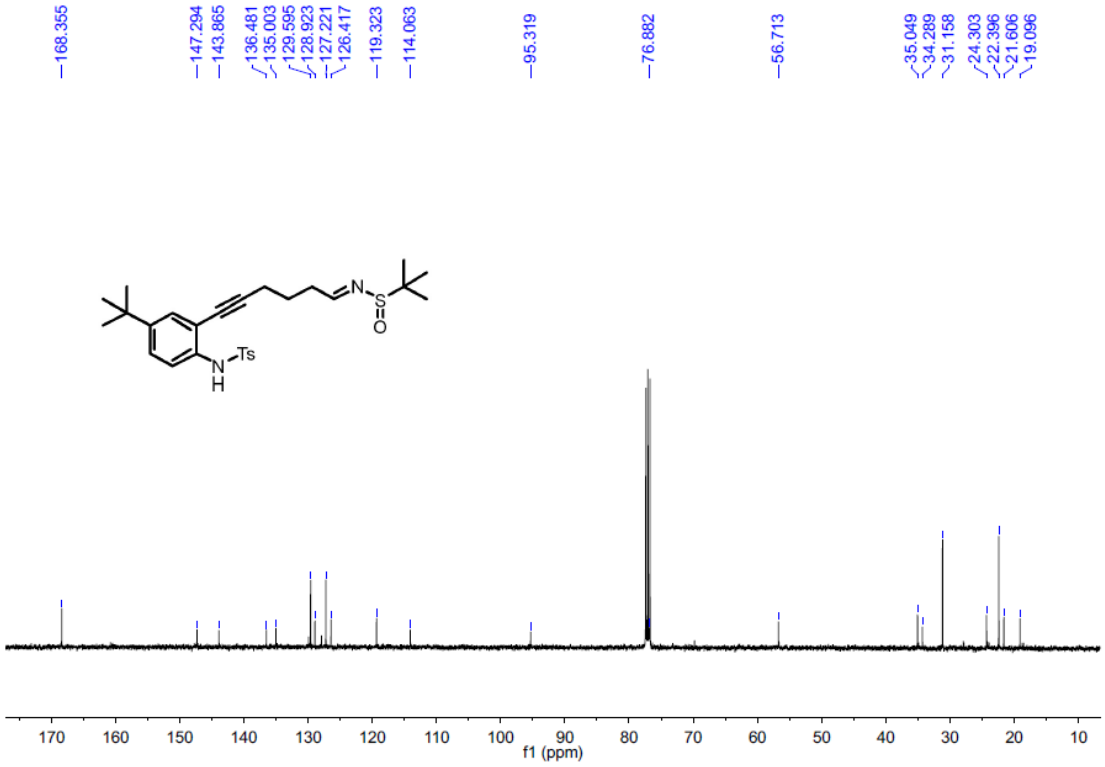
^{13}C NMR spectrum of 1c



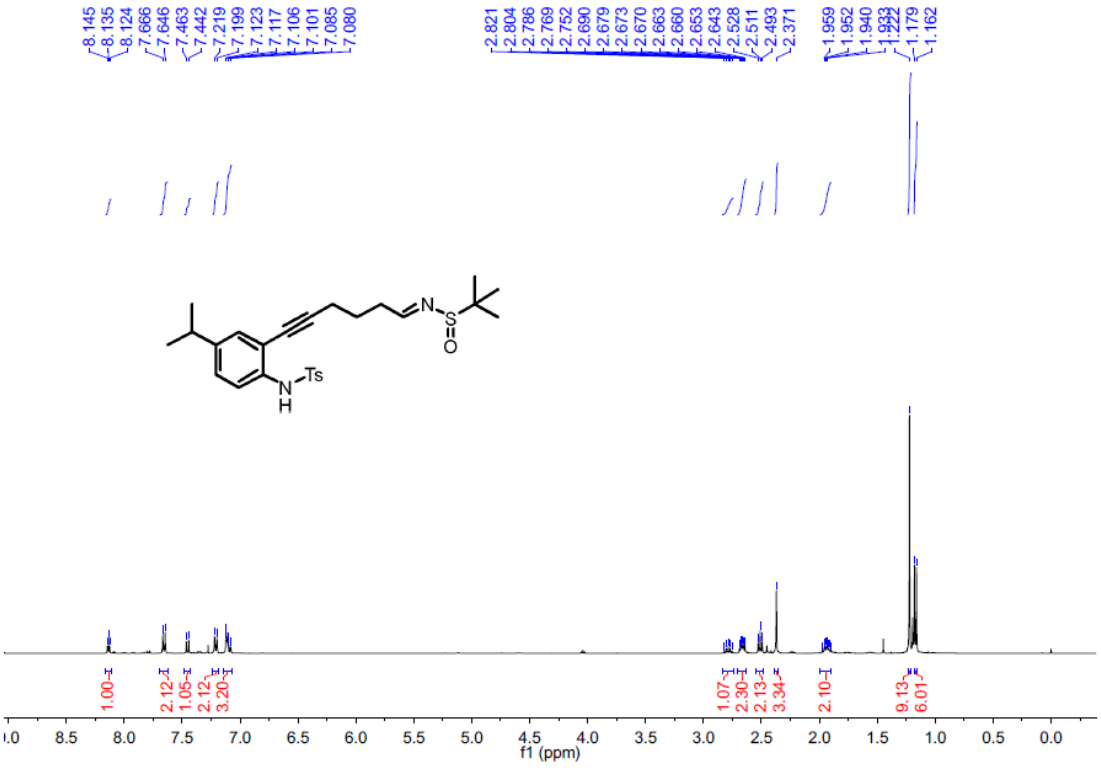
^{1}H NMR spectrum of 1d



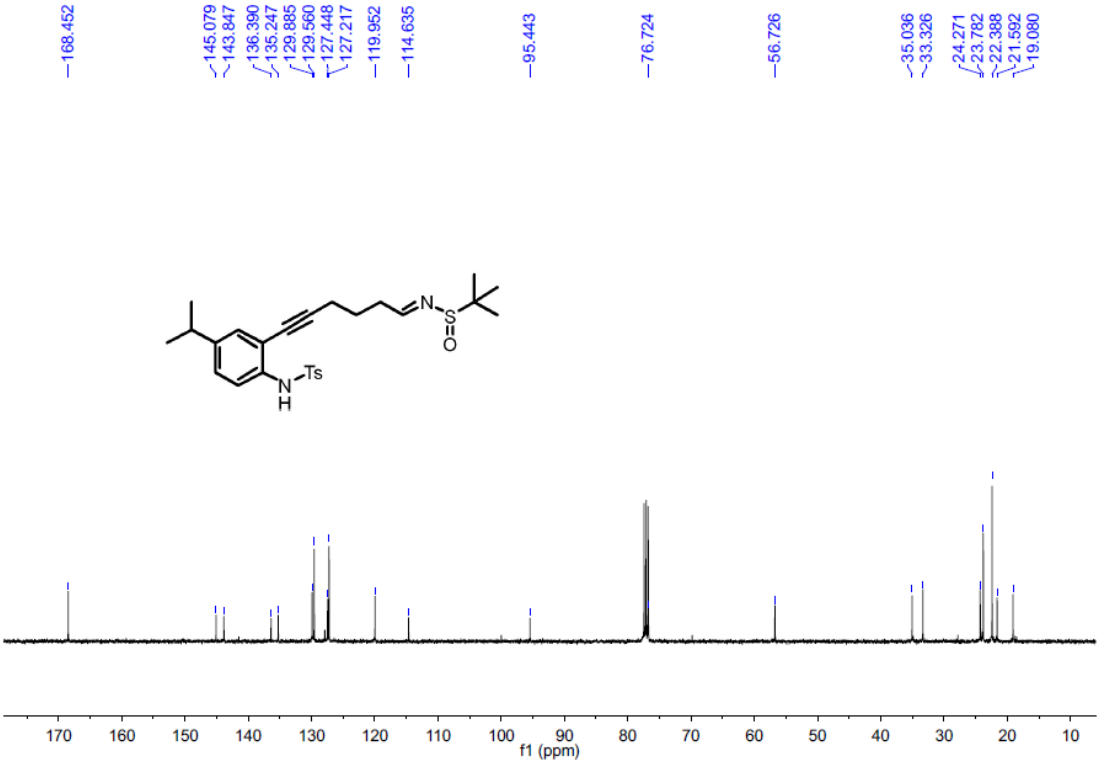
^{13}C NMR spectrum of 1d



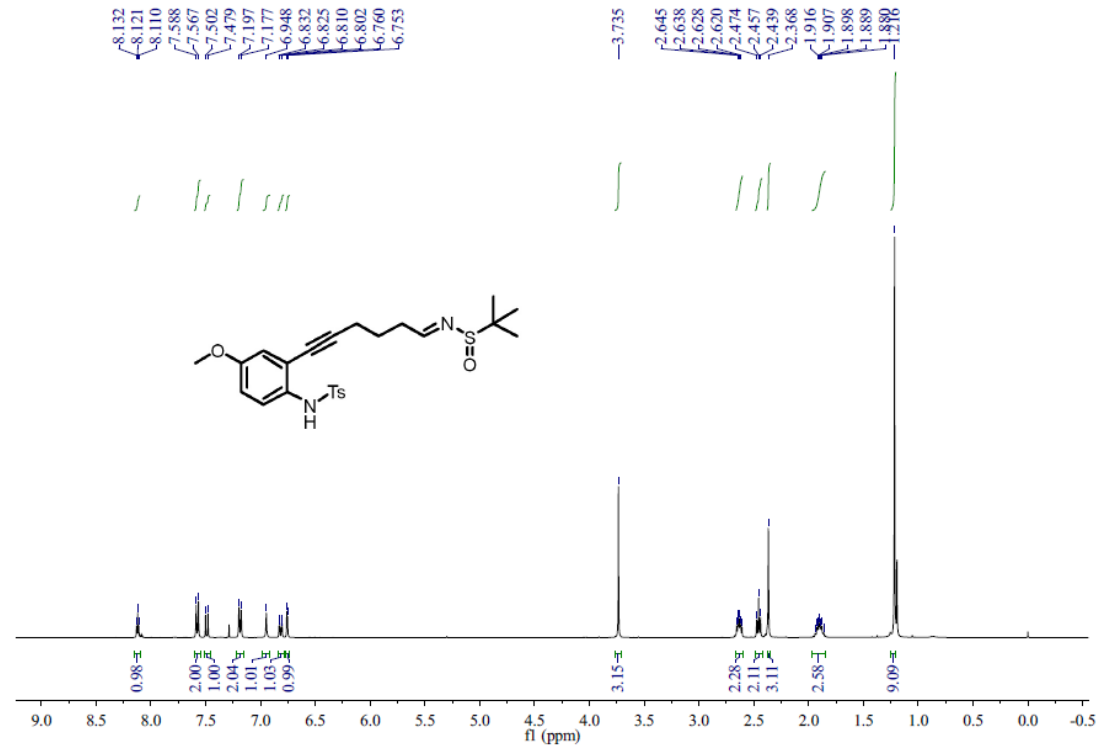
^{1}H NMR spectrum of 1e



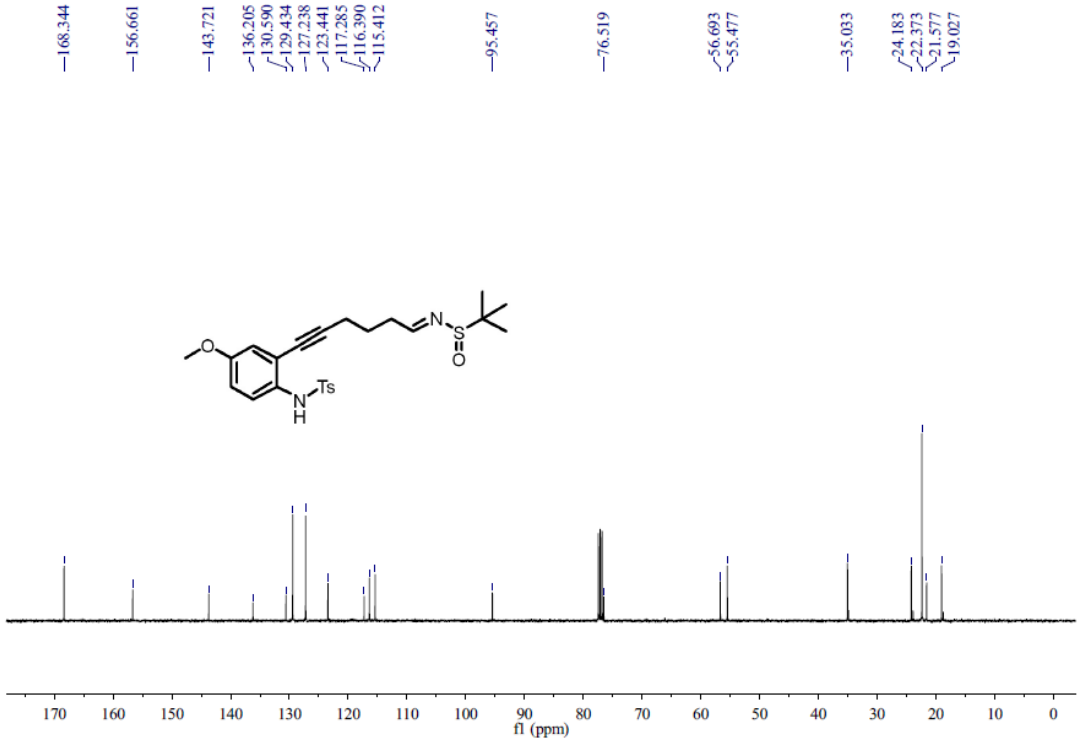
^{13}C NMR spectrum of 1e



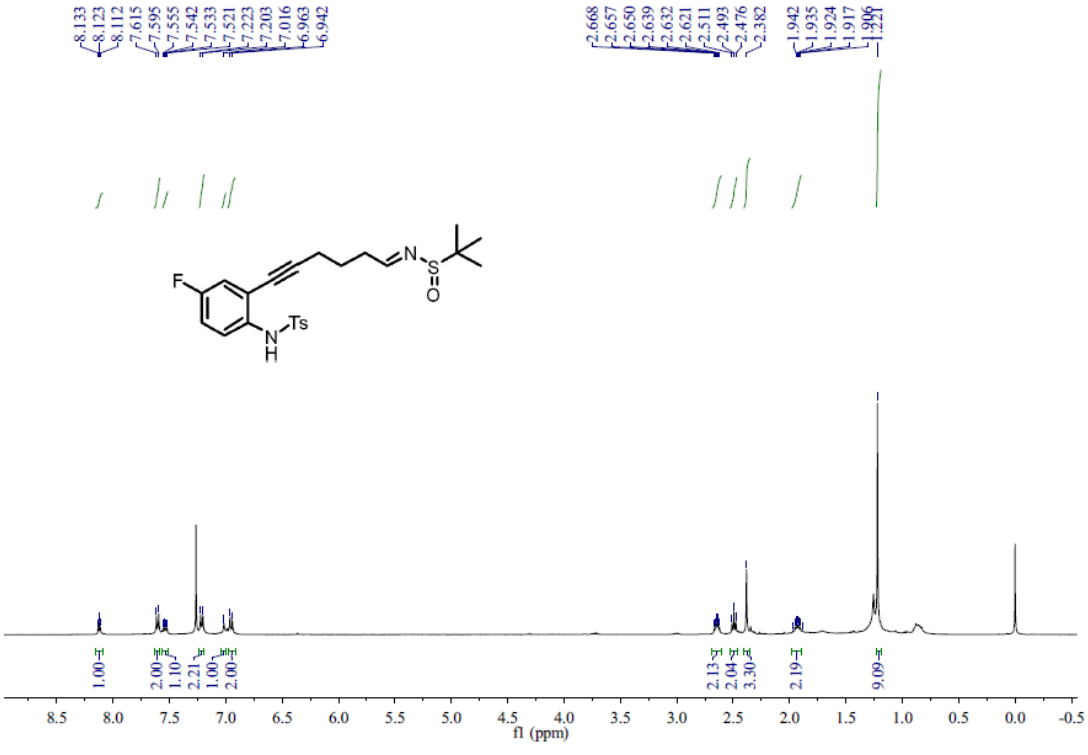
^{1}H NMR spectrum of 1f



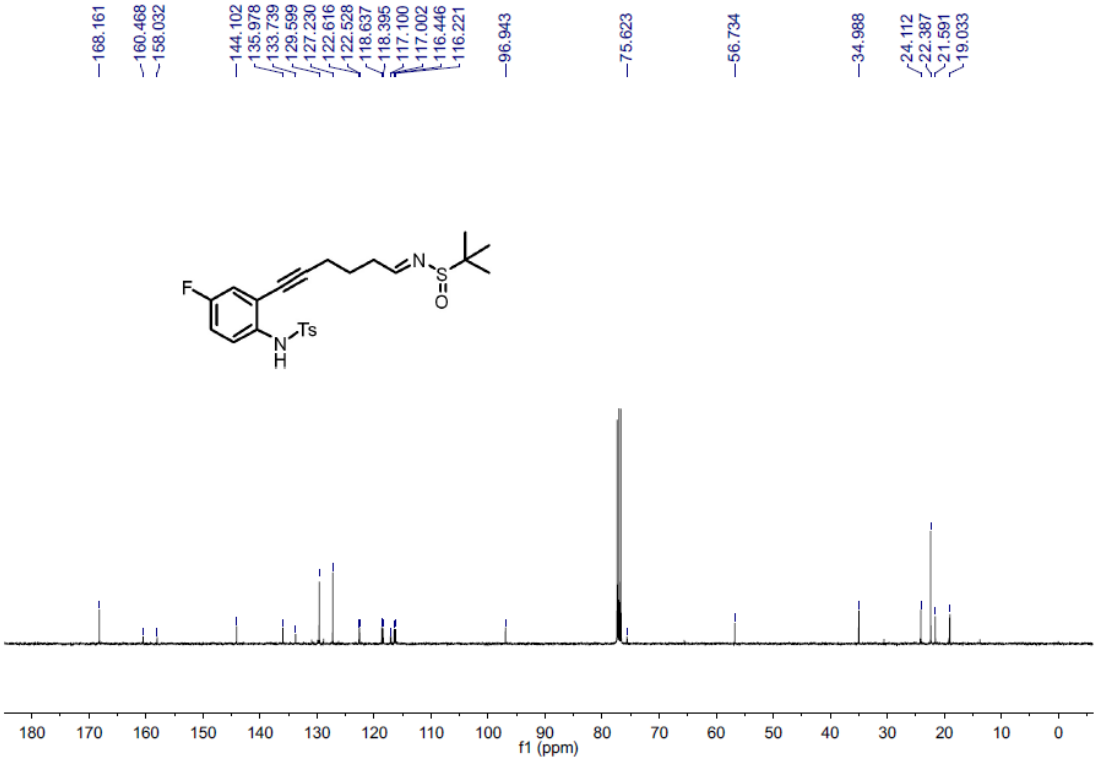
^{13}C NMR spectrum of 1f



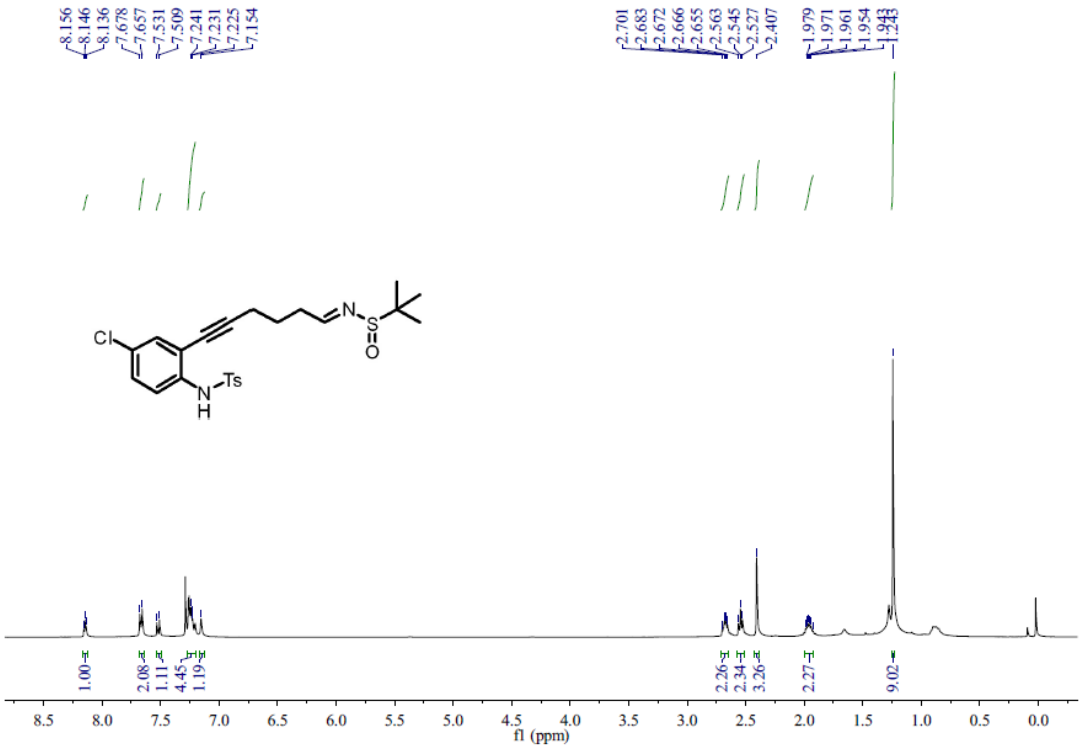
^{1}H NMR spectrum of 1g



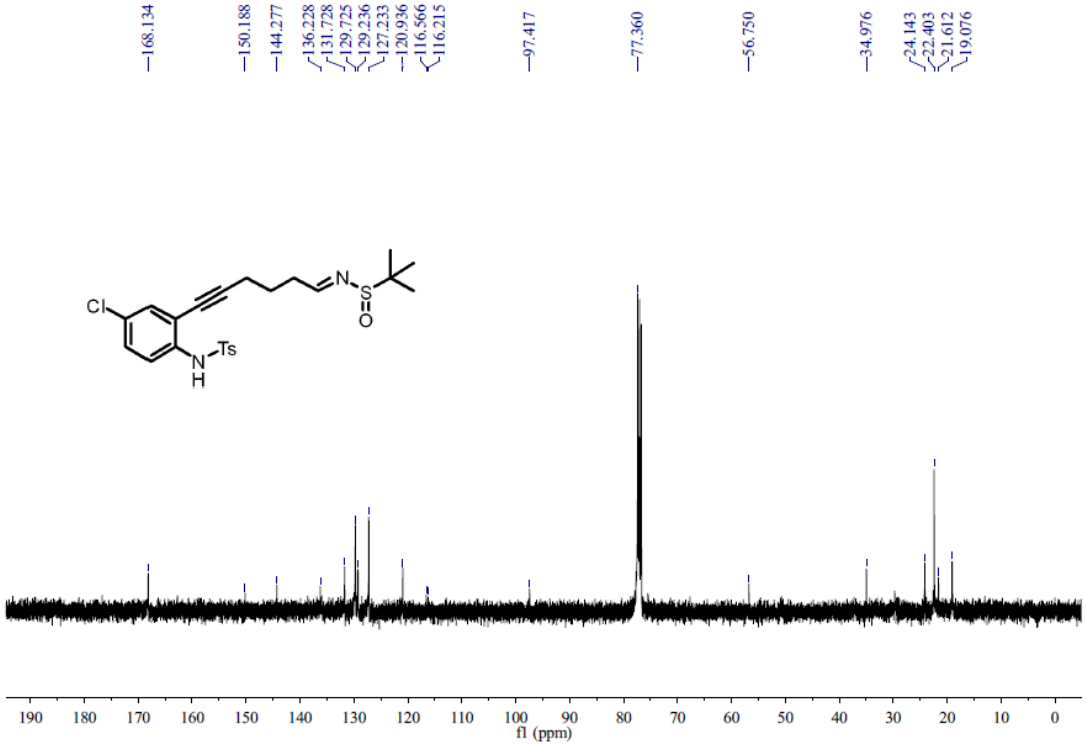
^{13}C NMR spectrum of 1g



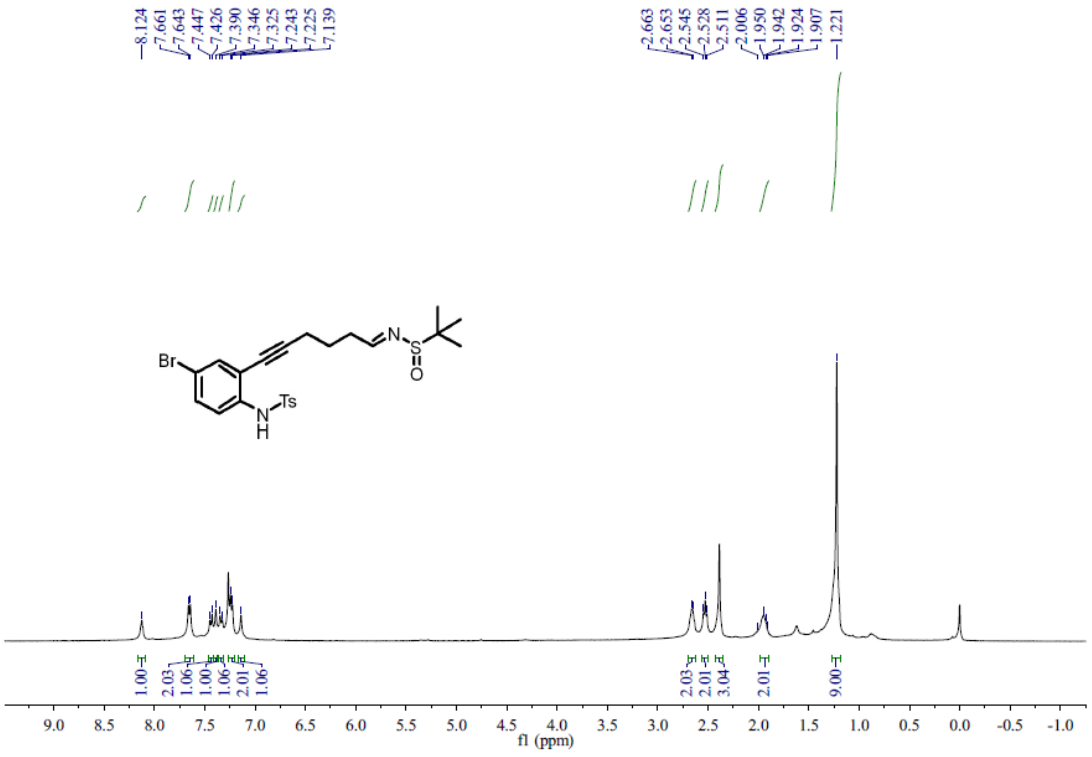
^{1}H NMR spectrum of 1h



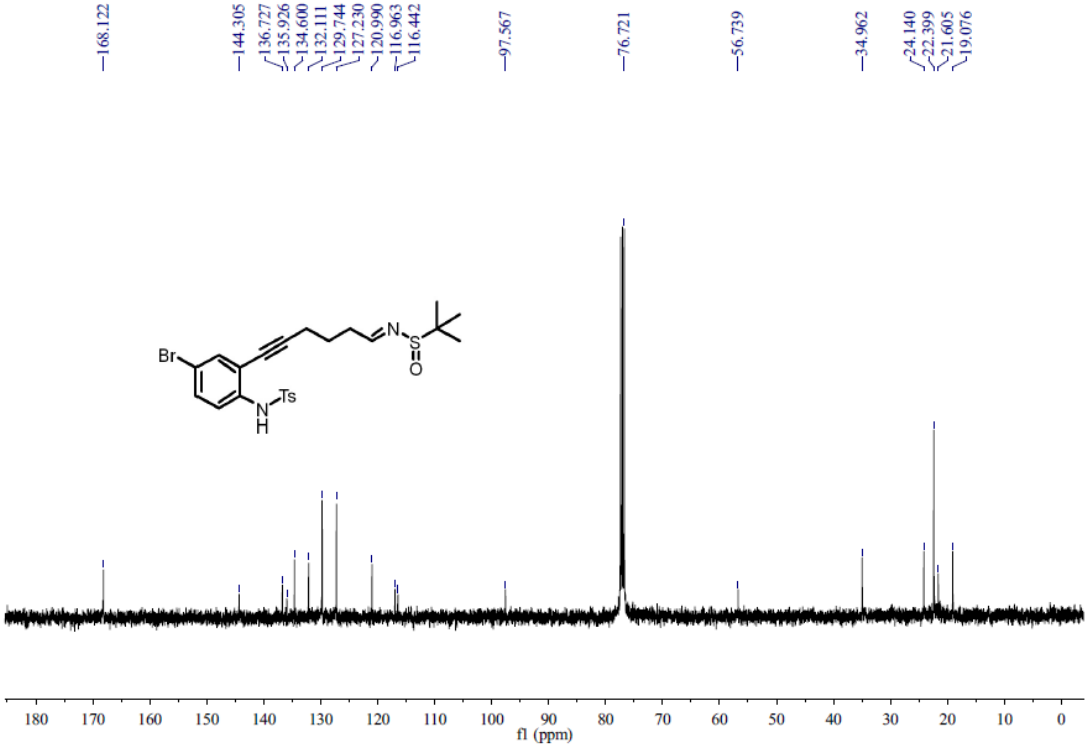
^{13}C NMR spectrum of 1h



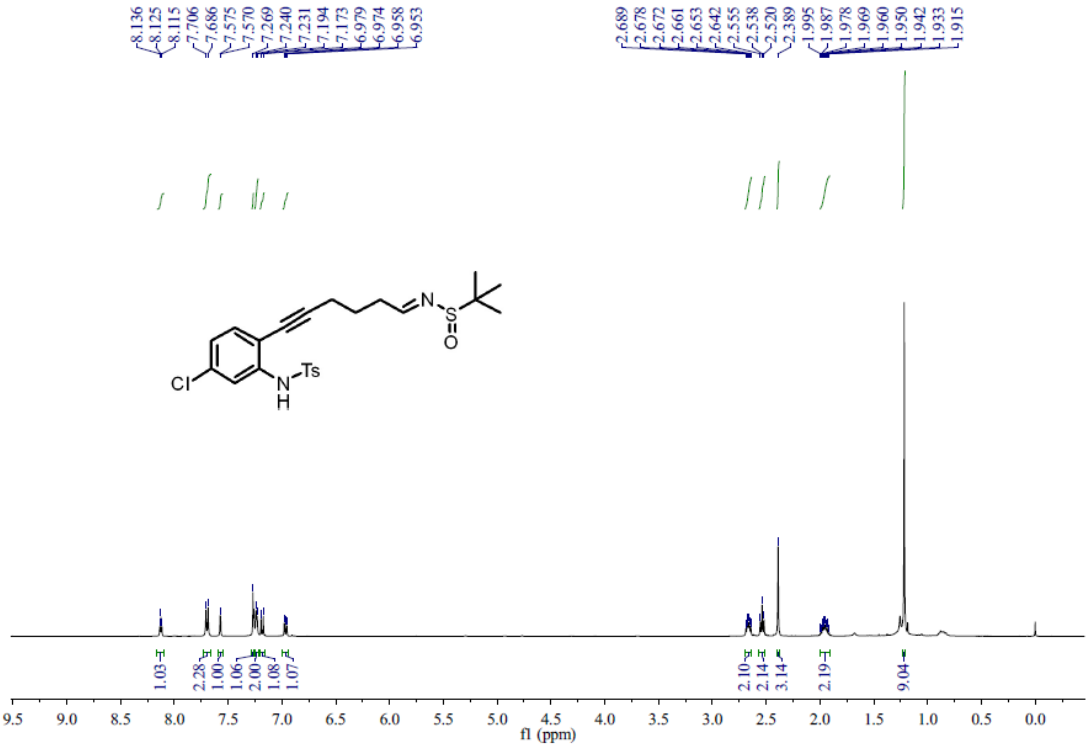
^{1}H NMR spectrum of 1i



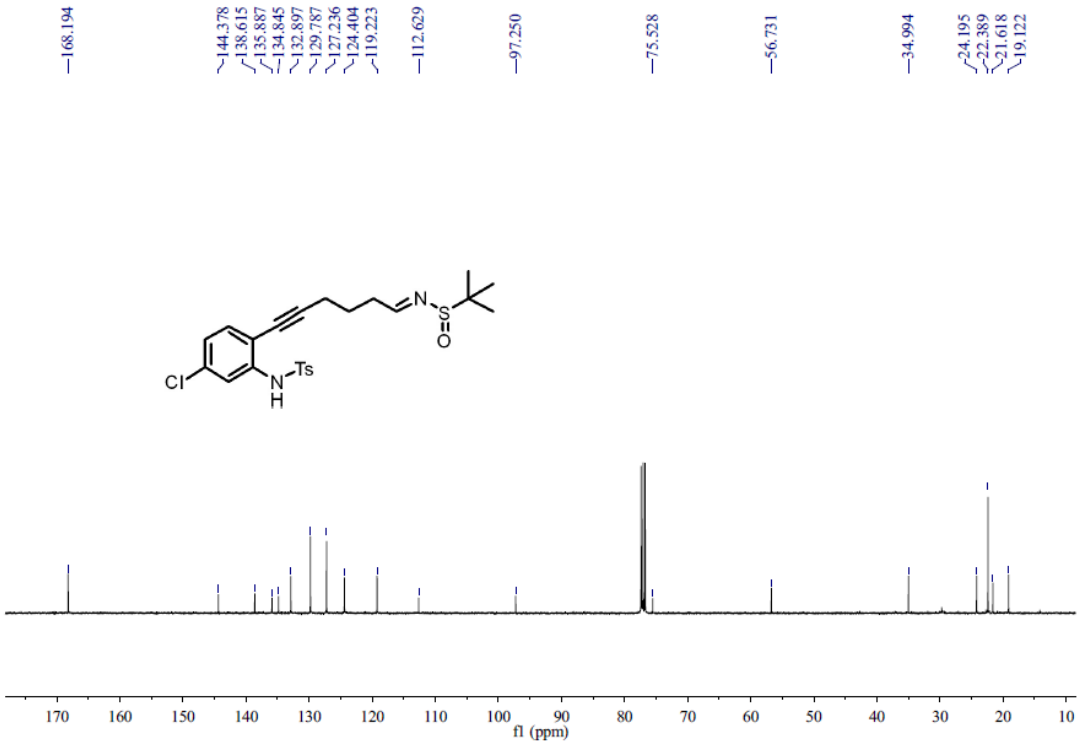
^{13}C NMR spectrum of 1i



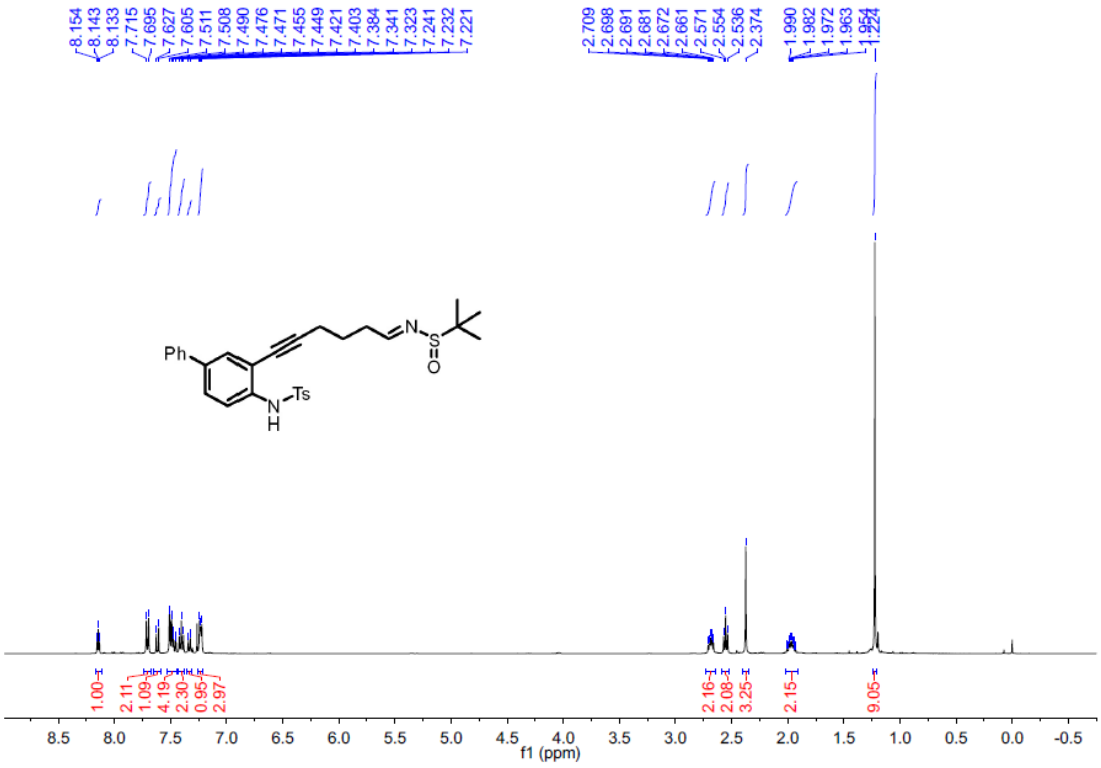
^{1}H NMR spectrum of 1j



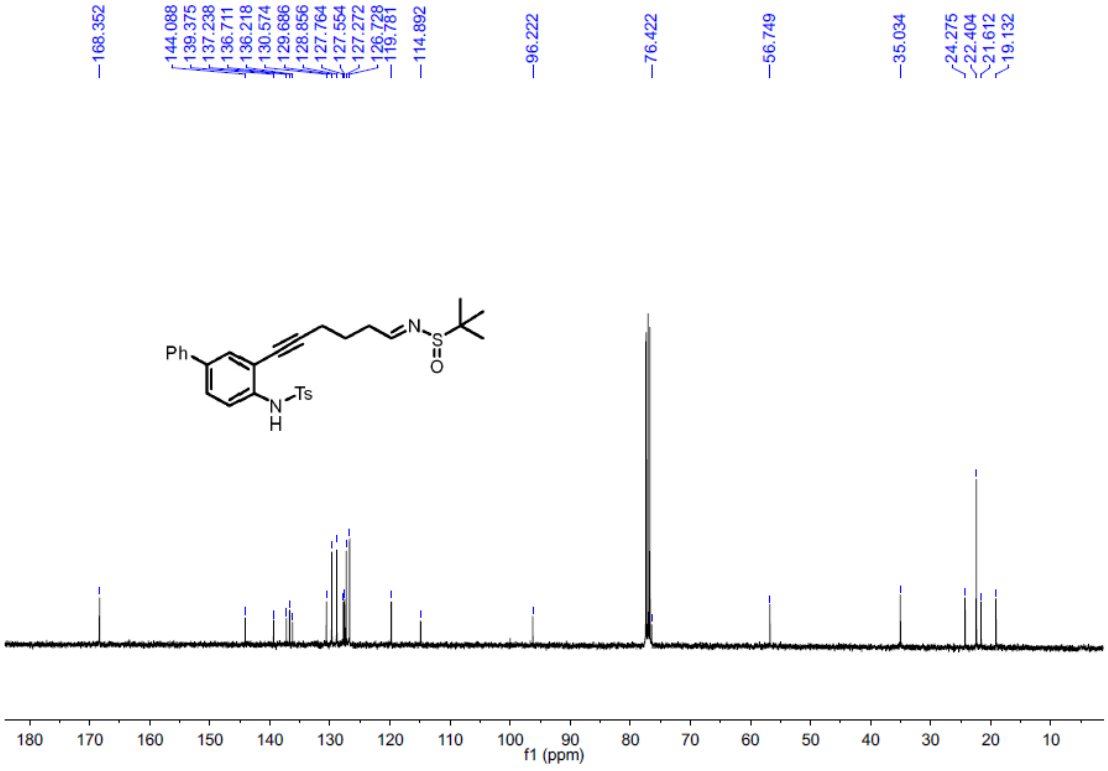
^{13}C NMR spectrum of 1j



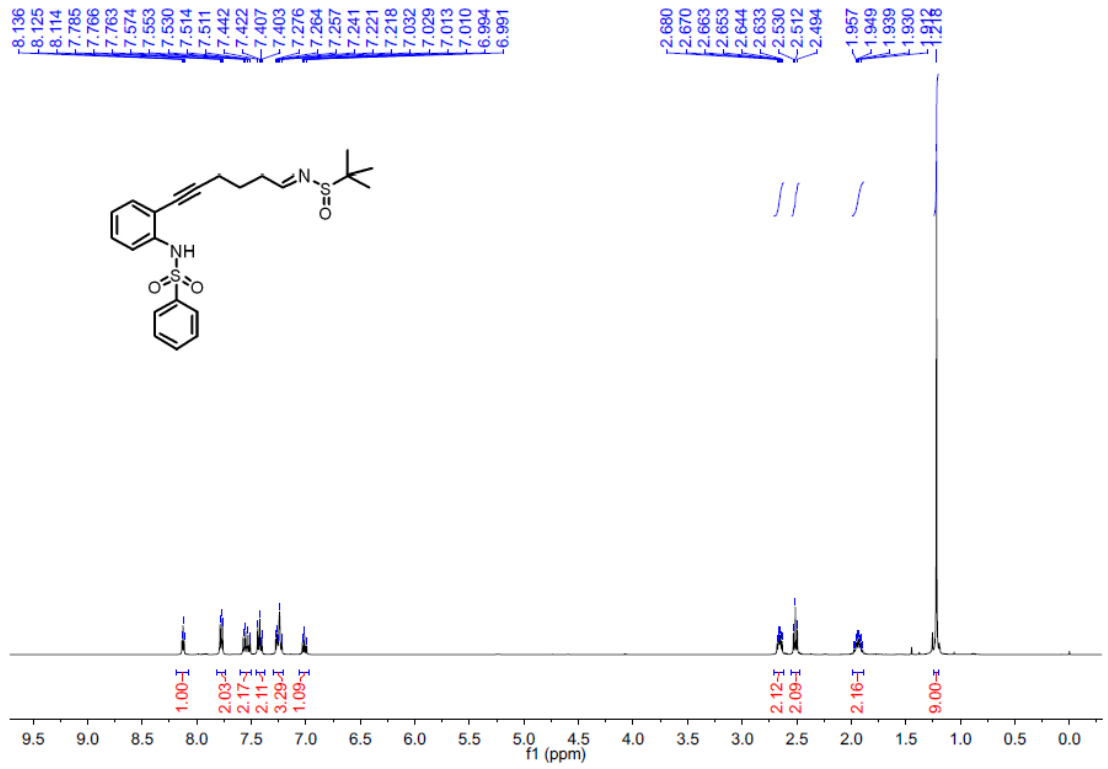
^{1}H NMR spectrum of 1k



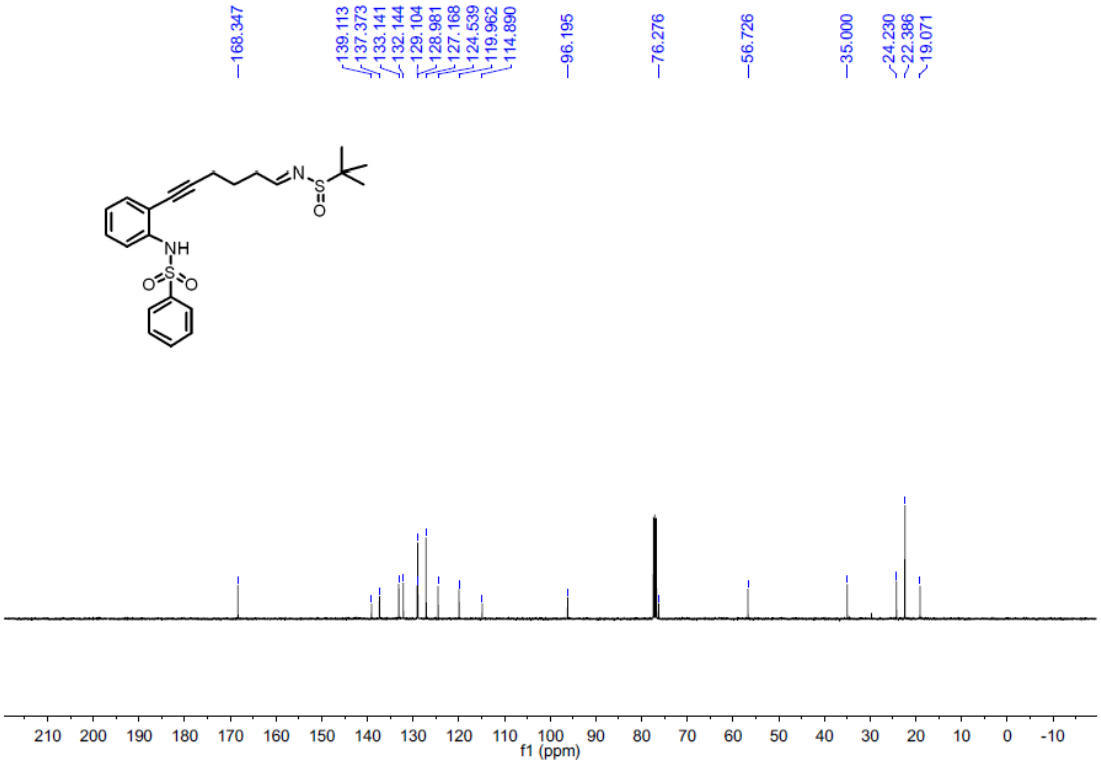
^{13}C NMR spectrum of 1k



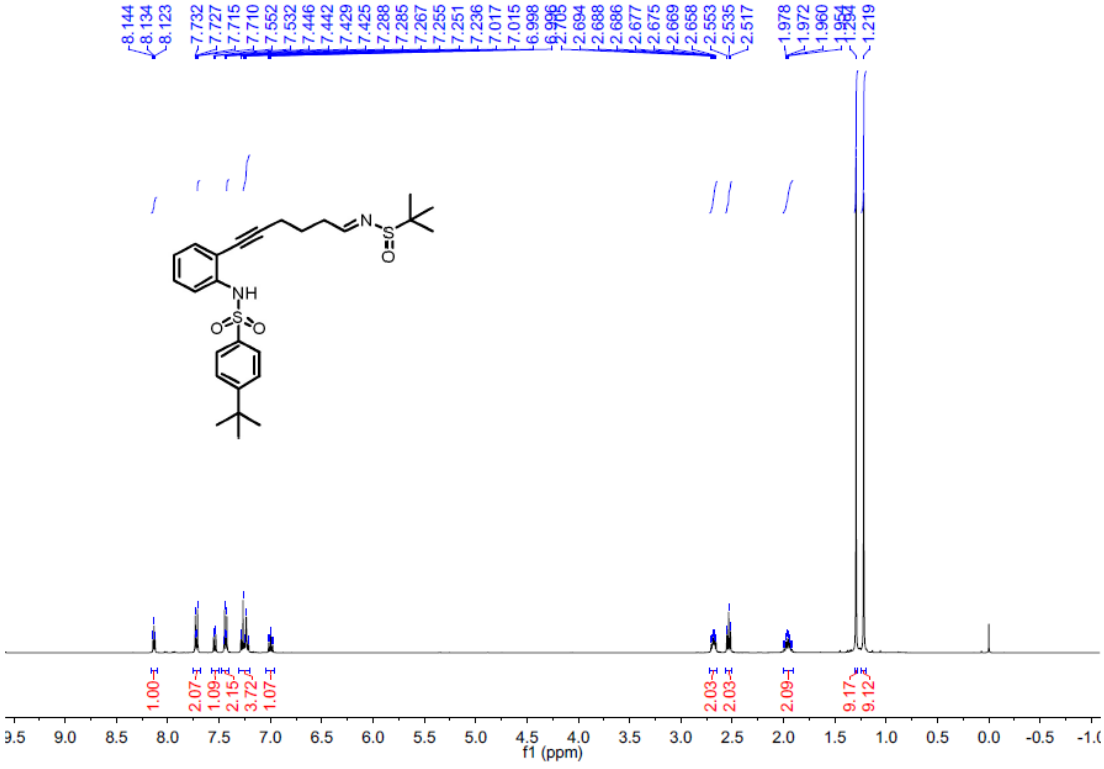
^{1}H NMR spectrum of 1l



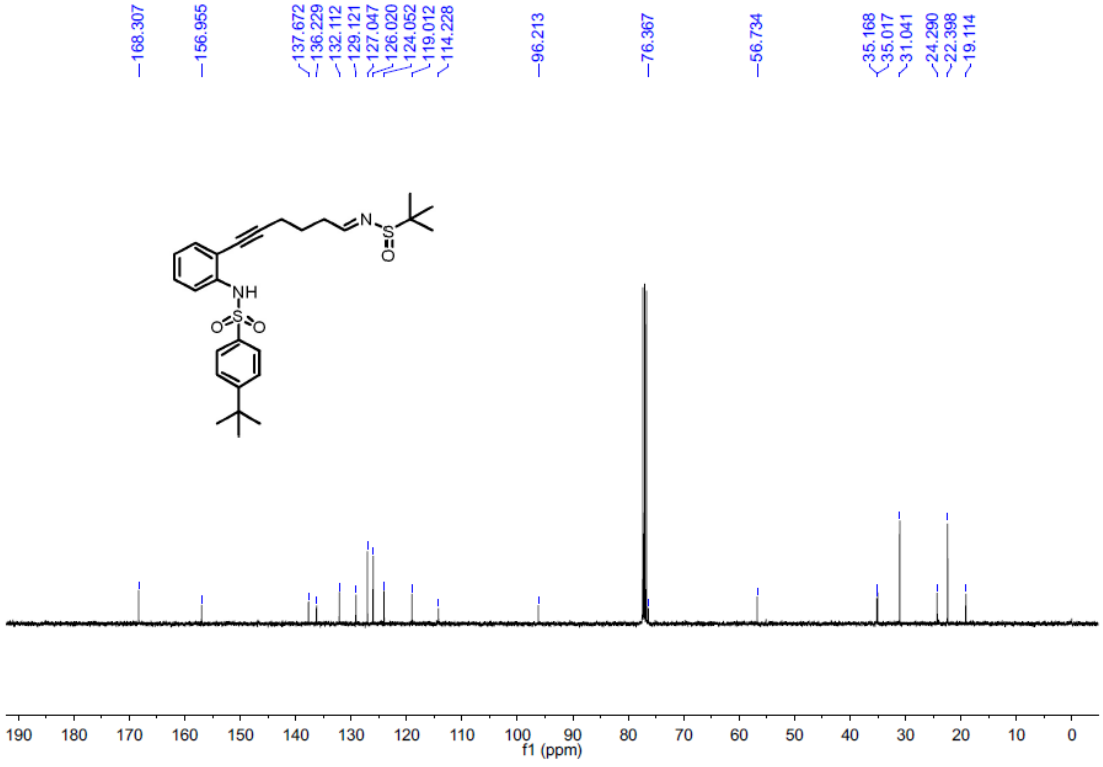
^{13}C NMR spectrum of 1l



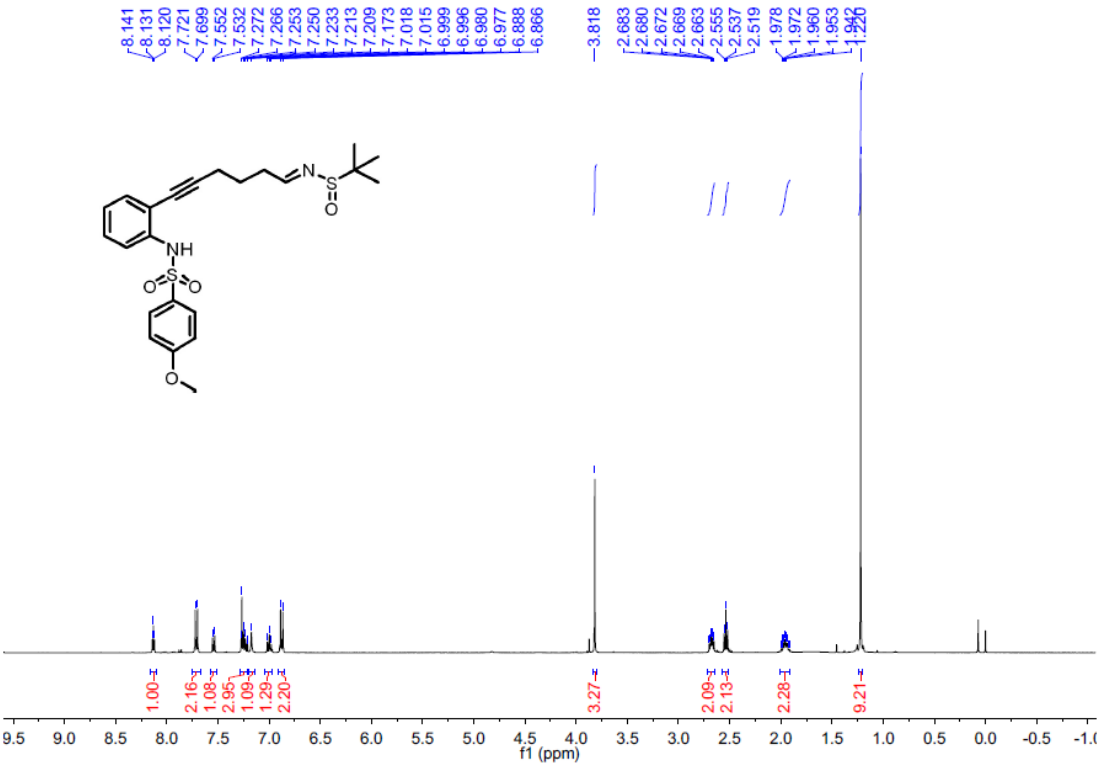
^{1}H NMR spectrum of 1m



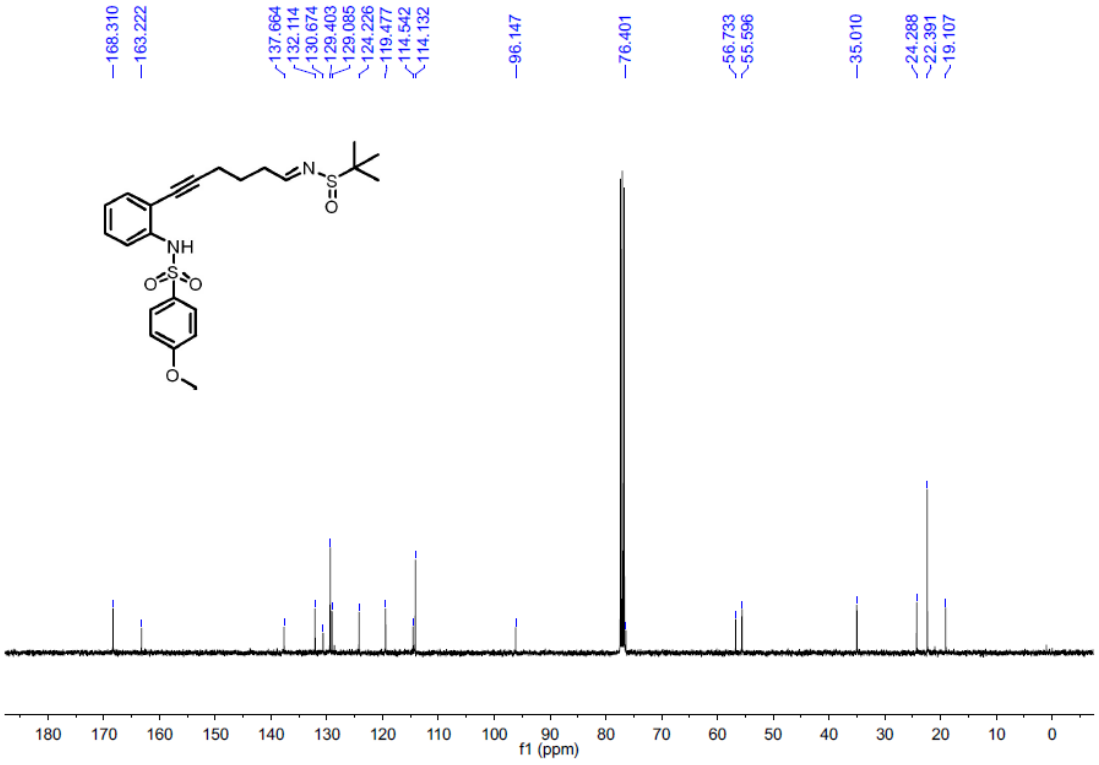
^{13}C NMR spectrum of 1m



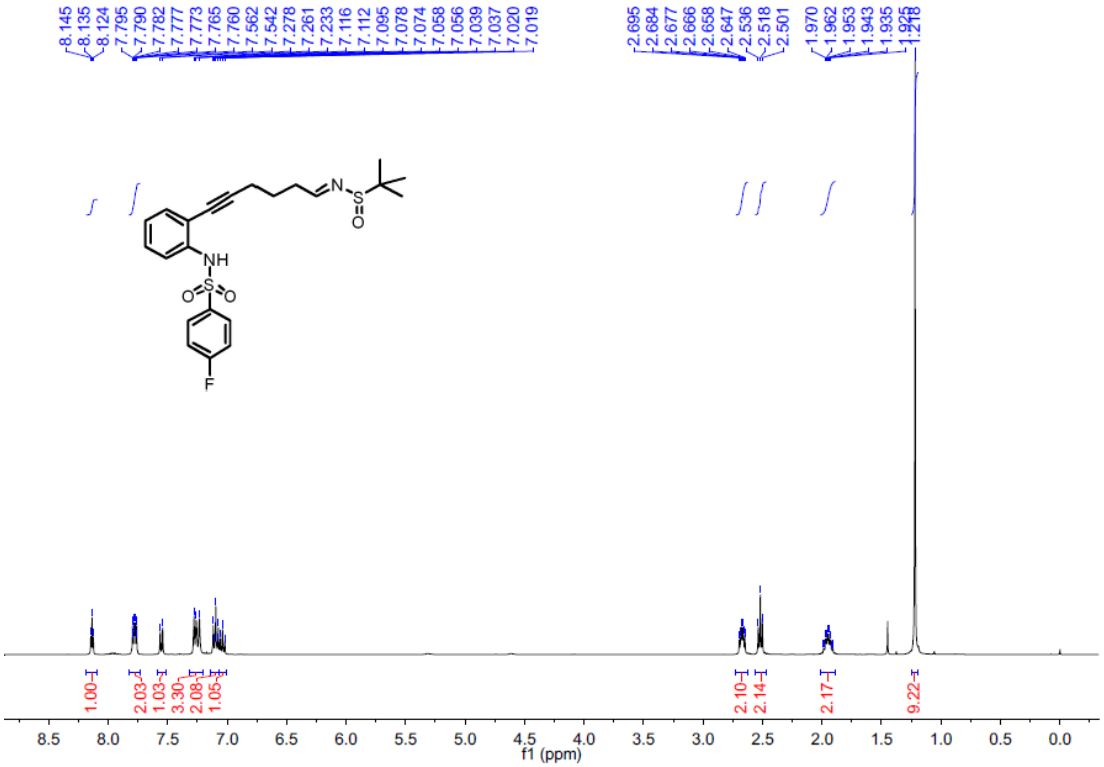
^{1}H NMR spectrum of 1n



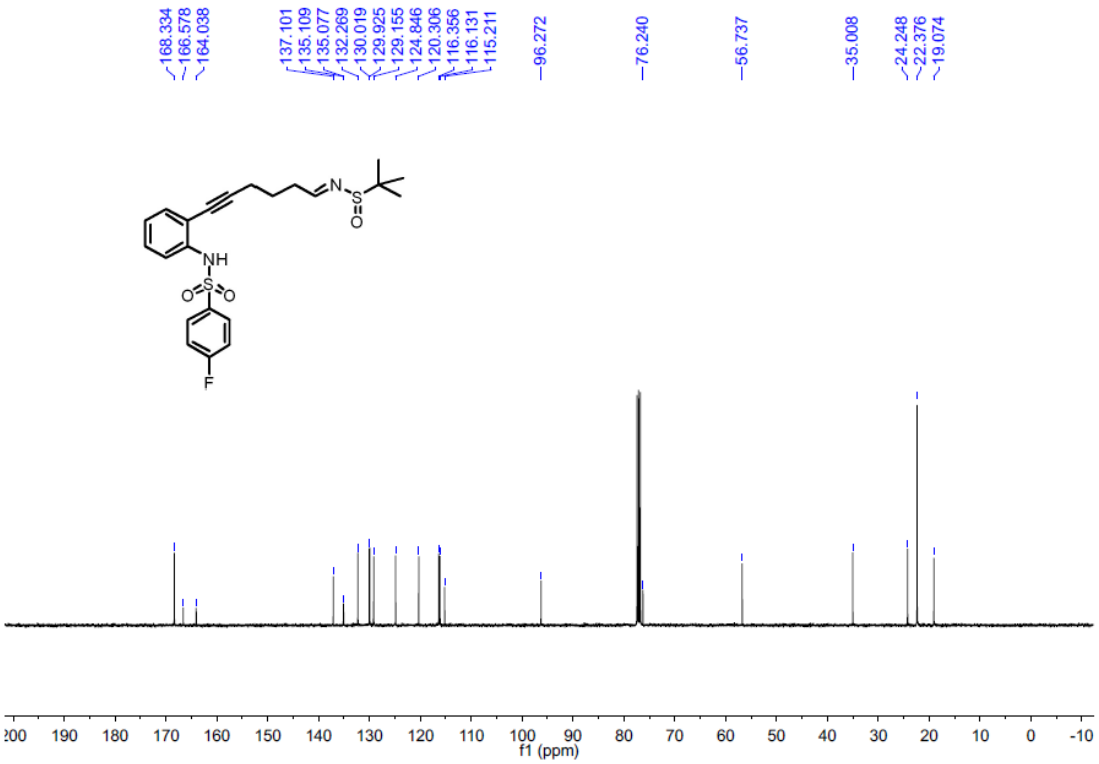
^{13}C NMR spectrum of 1n



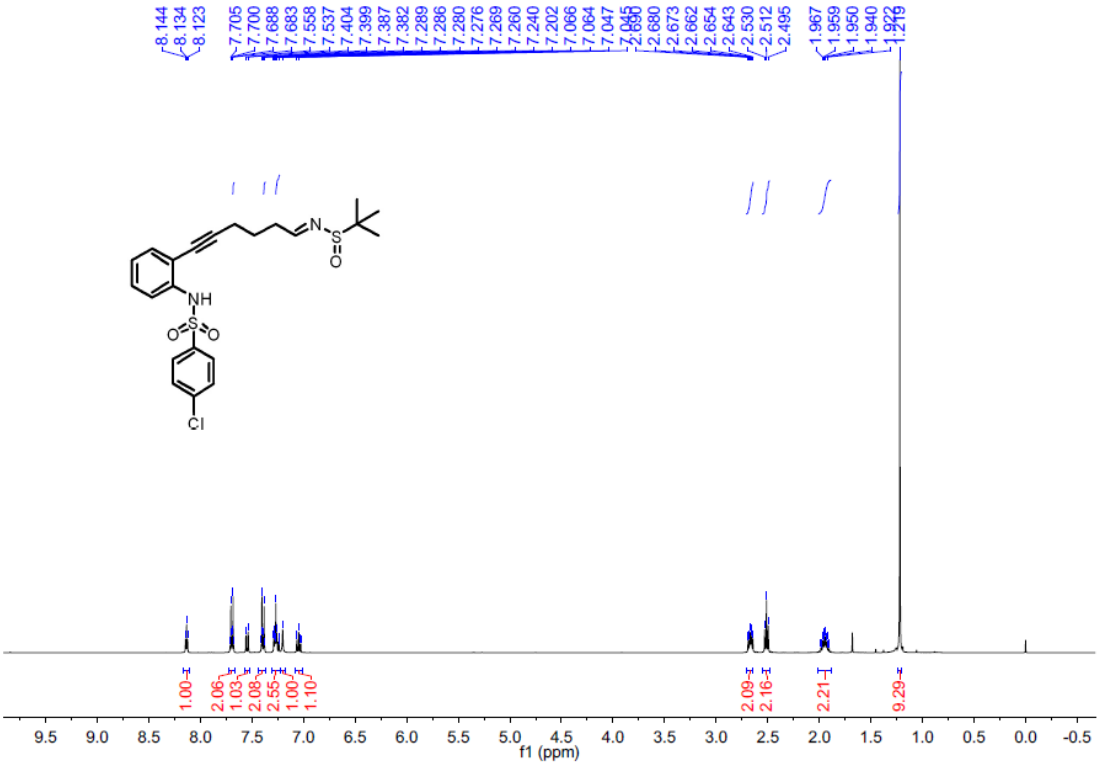
^{1}H NMR spectrum of 1o



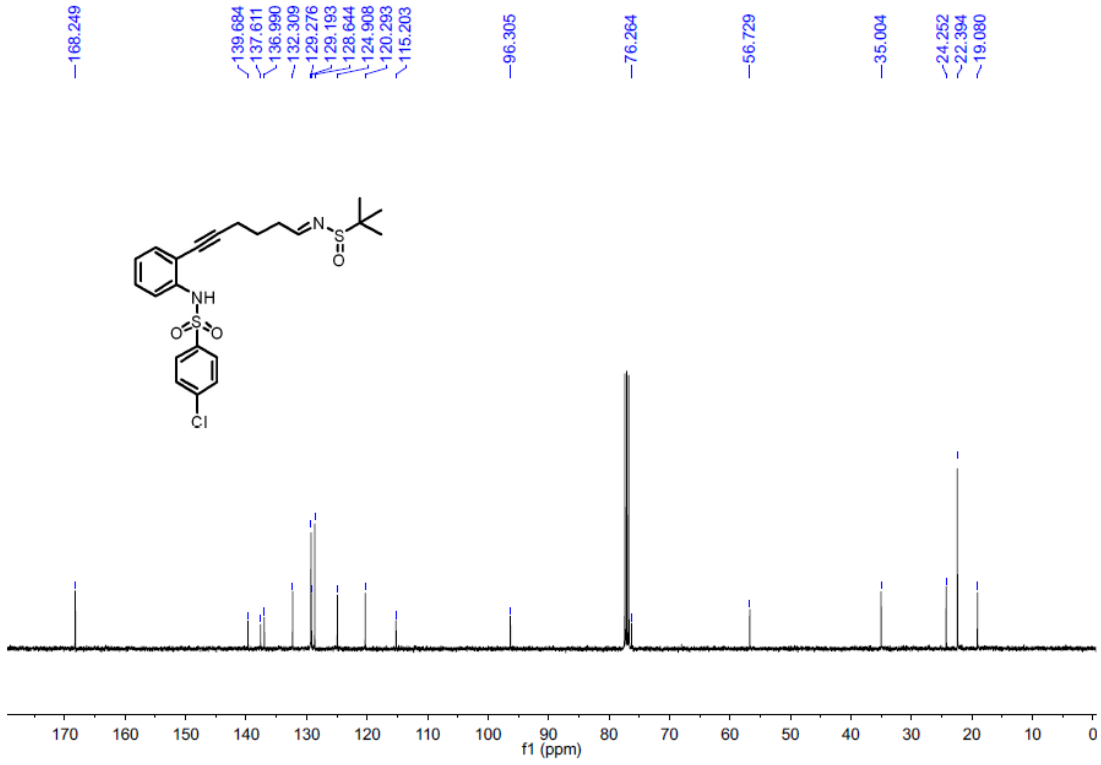
^{13}C NMR spectrum of 1o



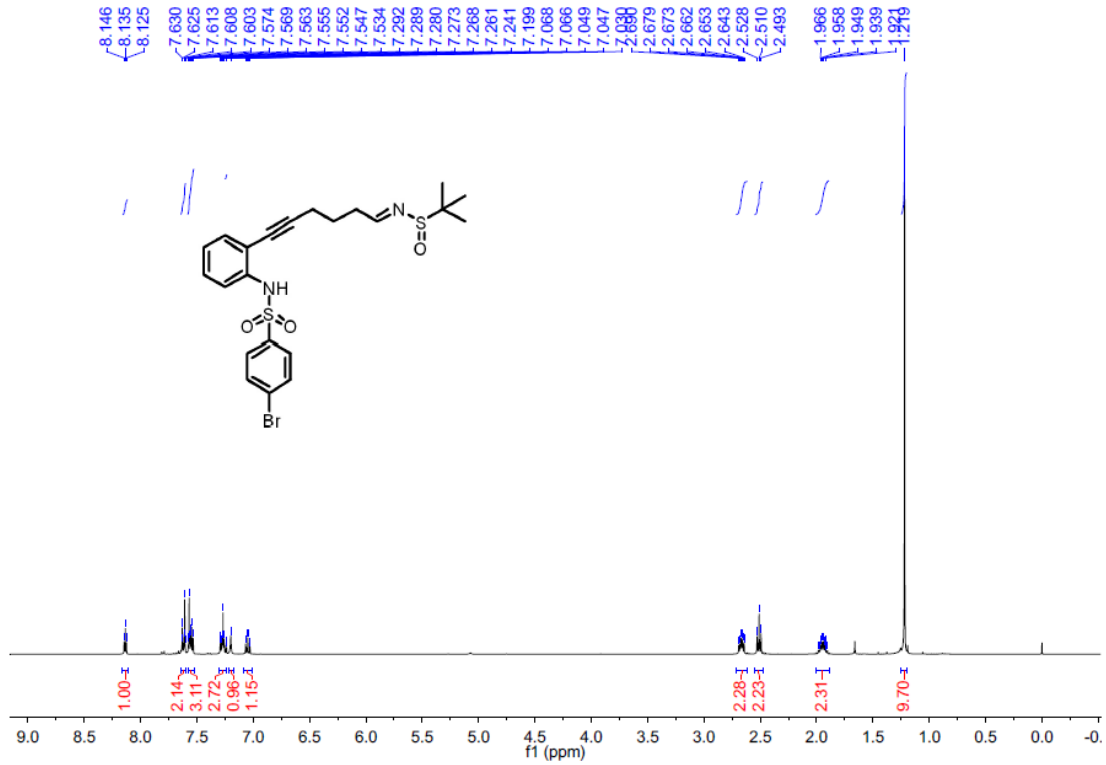
^{1}H NMR spectrum of 1p



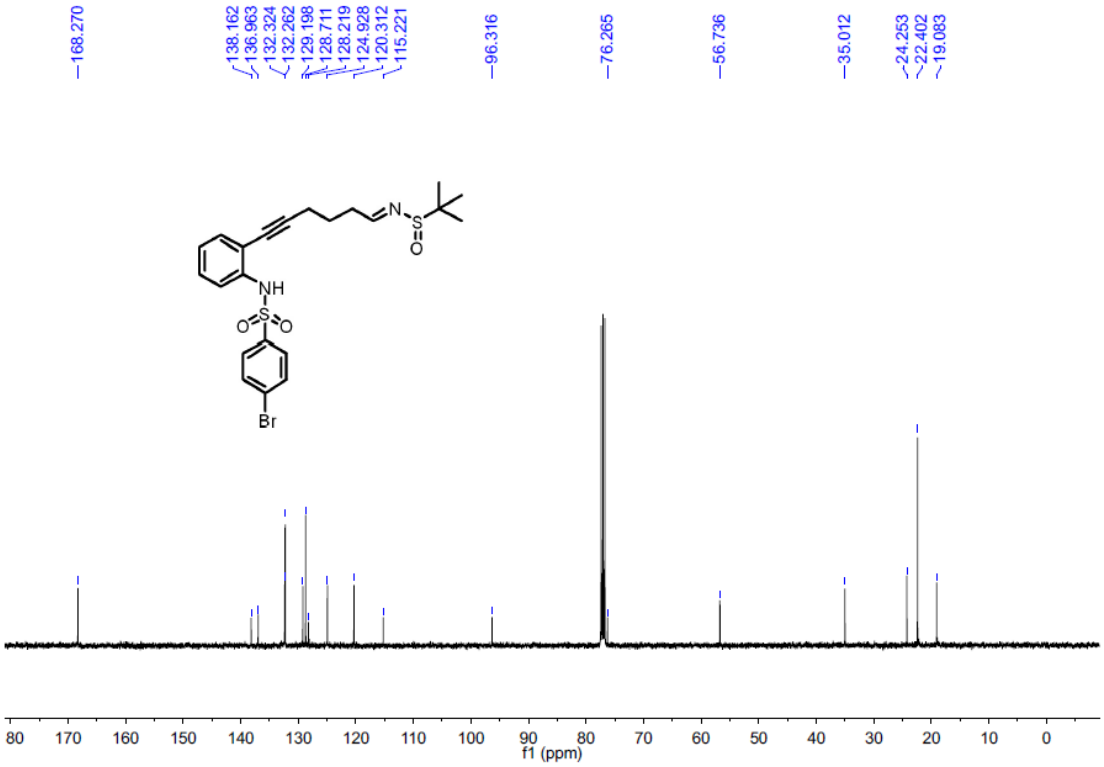
^{13}C NMR spectrum of 1p



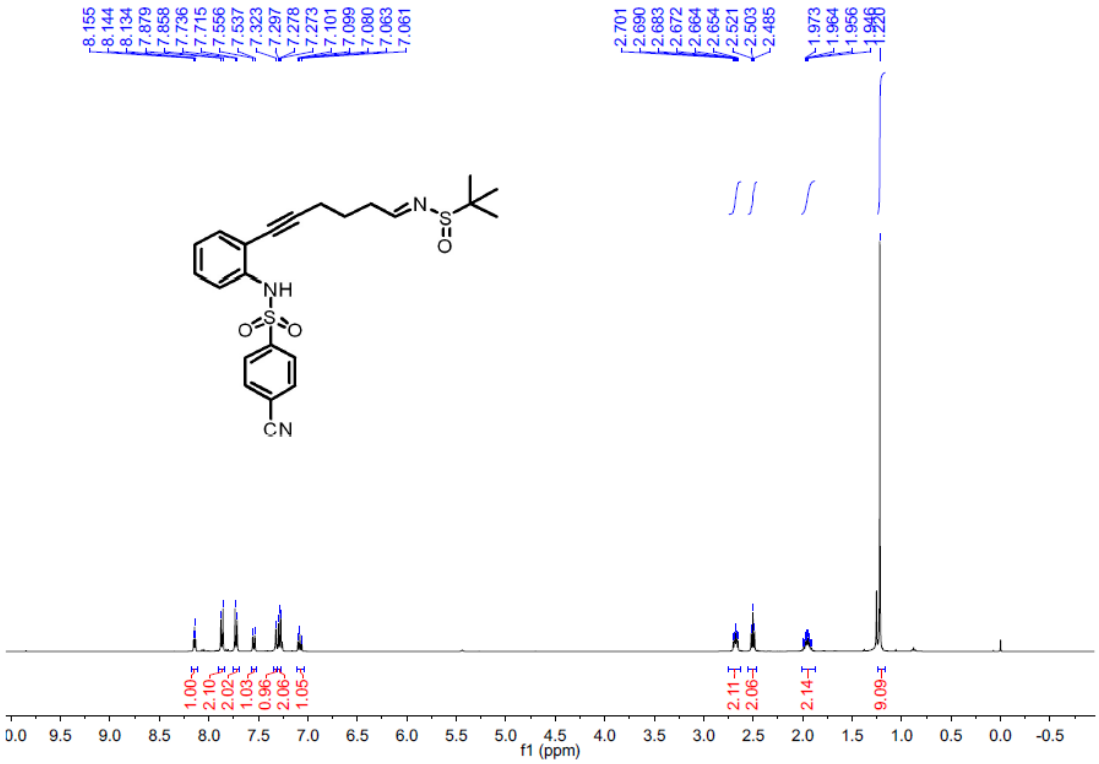
^{1}H NMR spectrum of 1q



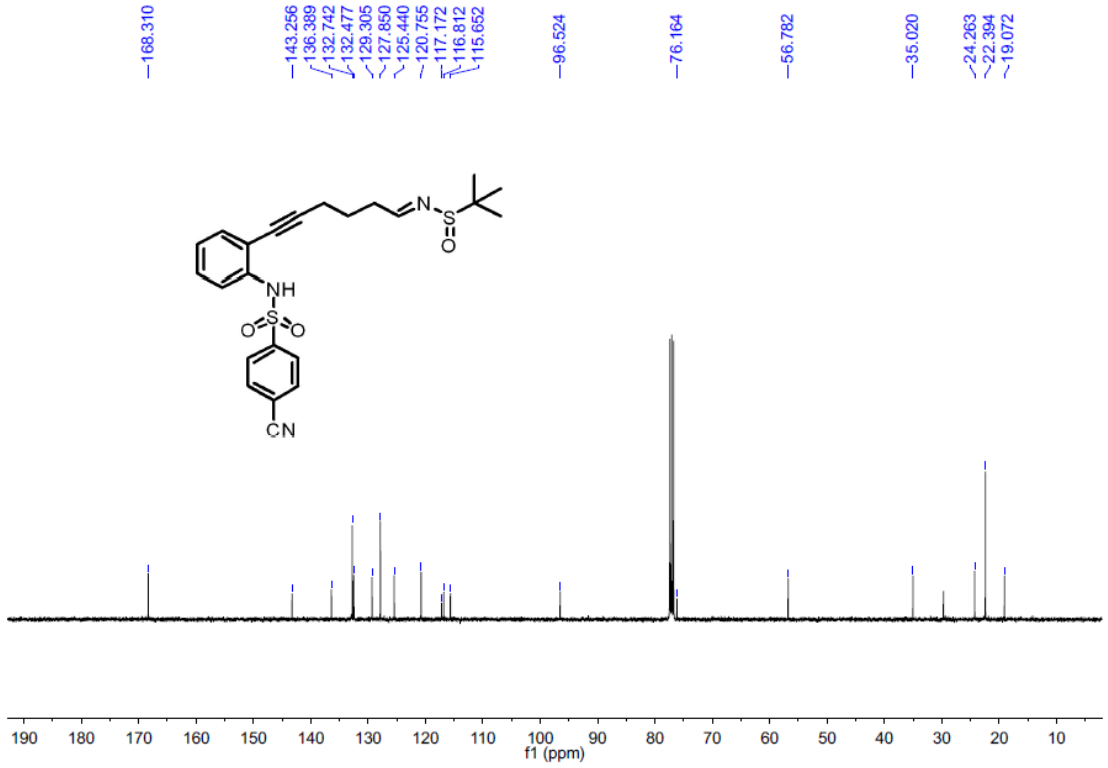
^{13}C NMR spectrum of 1q



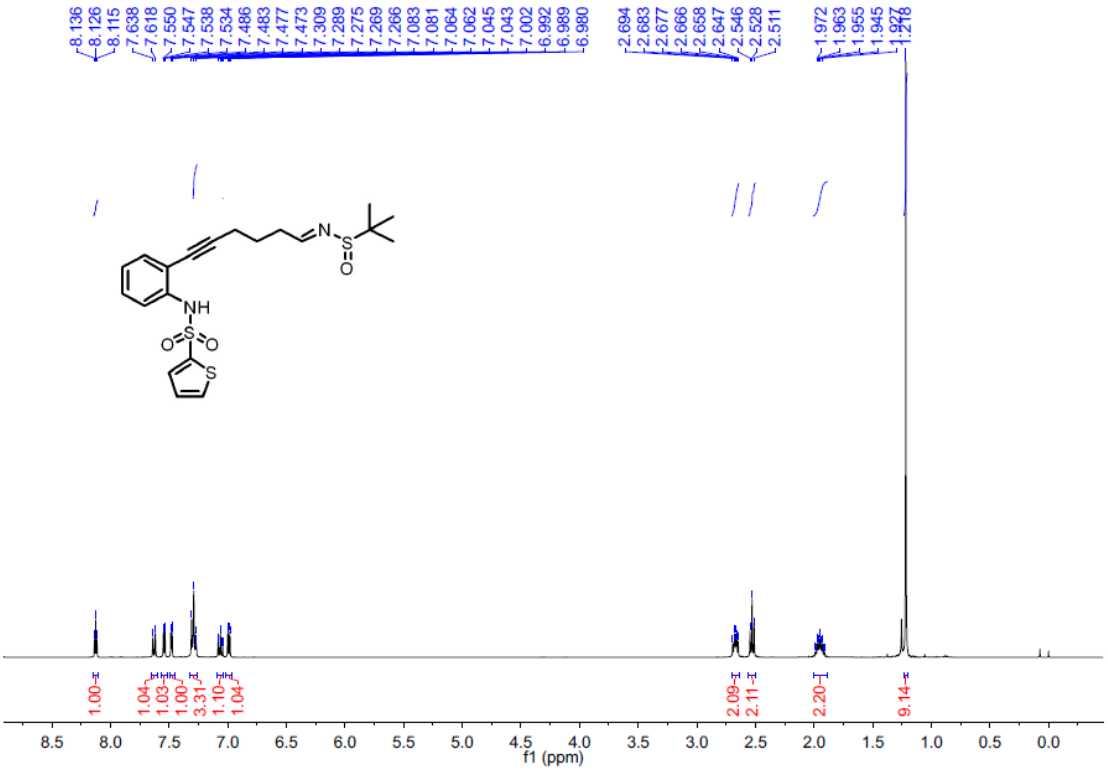
^{1}H NMR spectrum of 1r



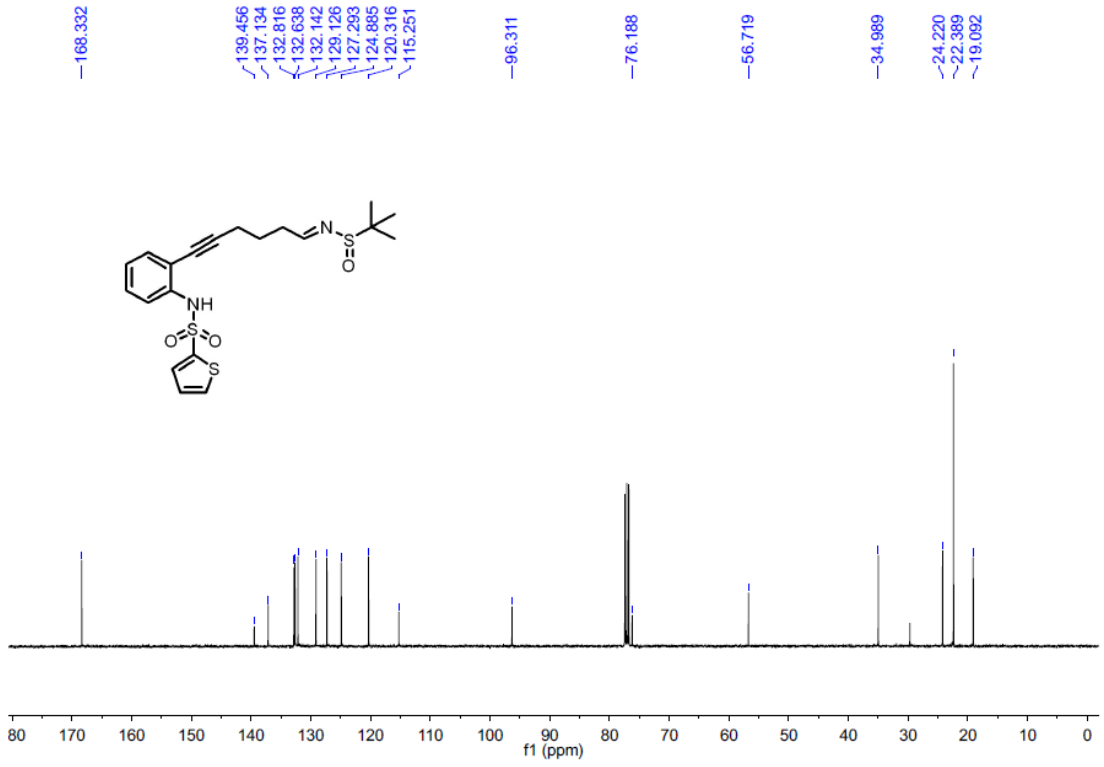
^{13}C NMR spectrum of 1r



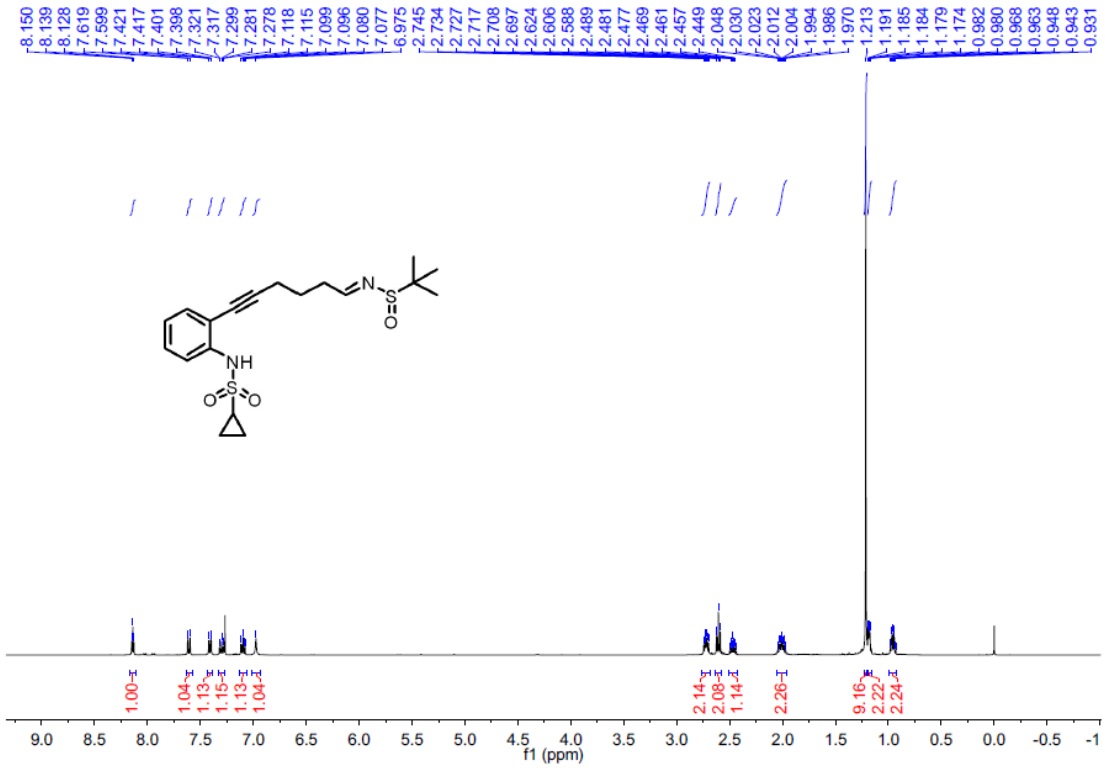
^{1}H NMR spectrum of 1s



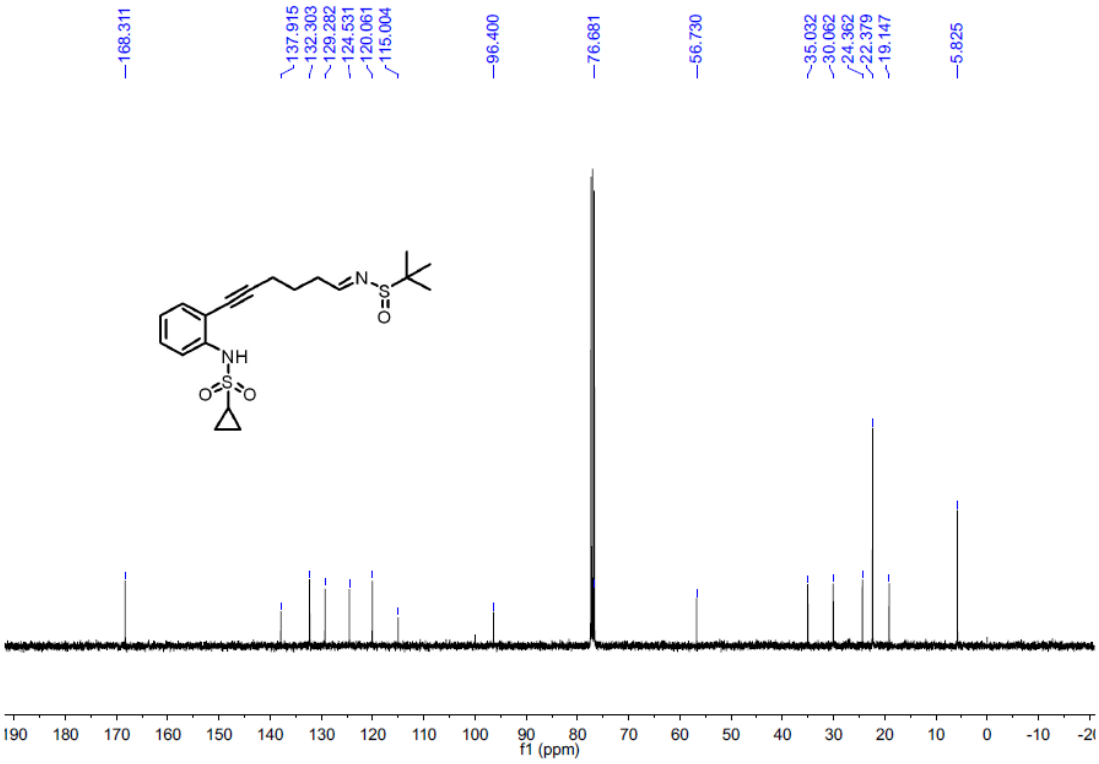
^{13}C NMR spectrum of 1s



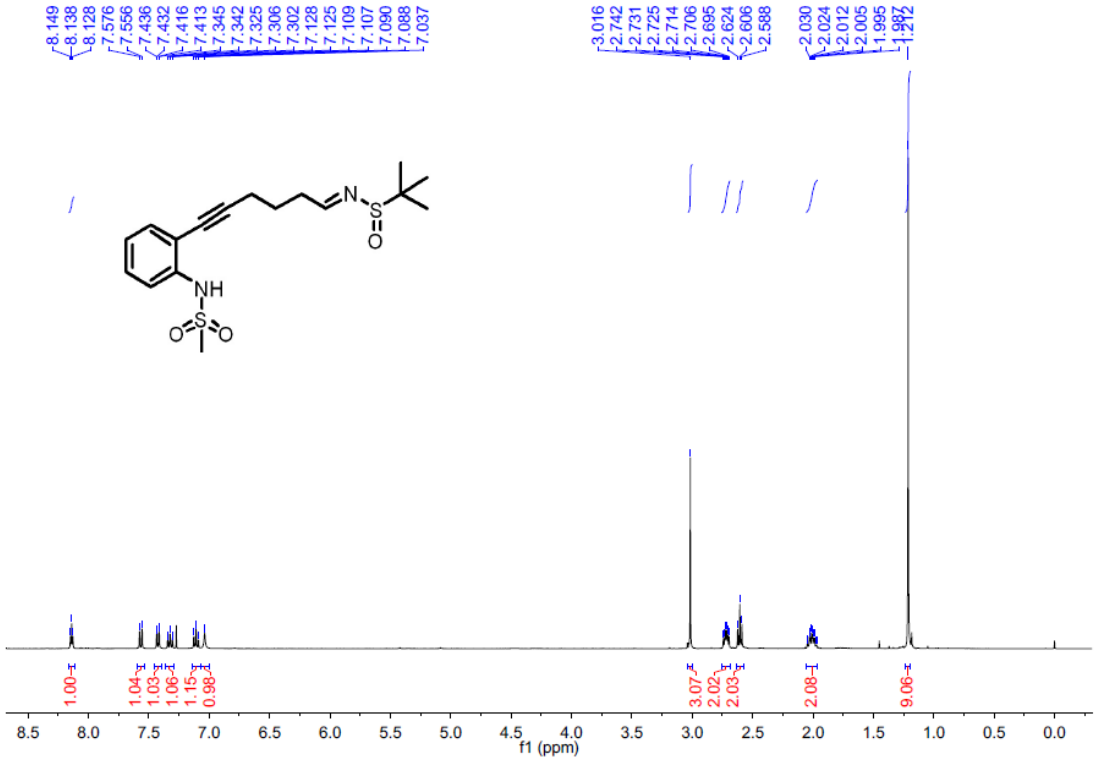
^{1}H NMR spectrum of 1t



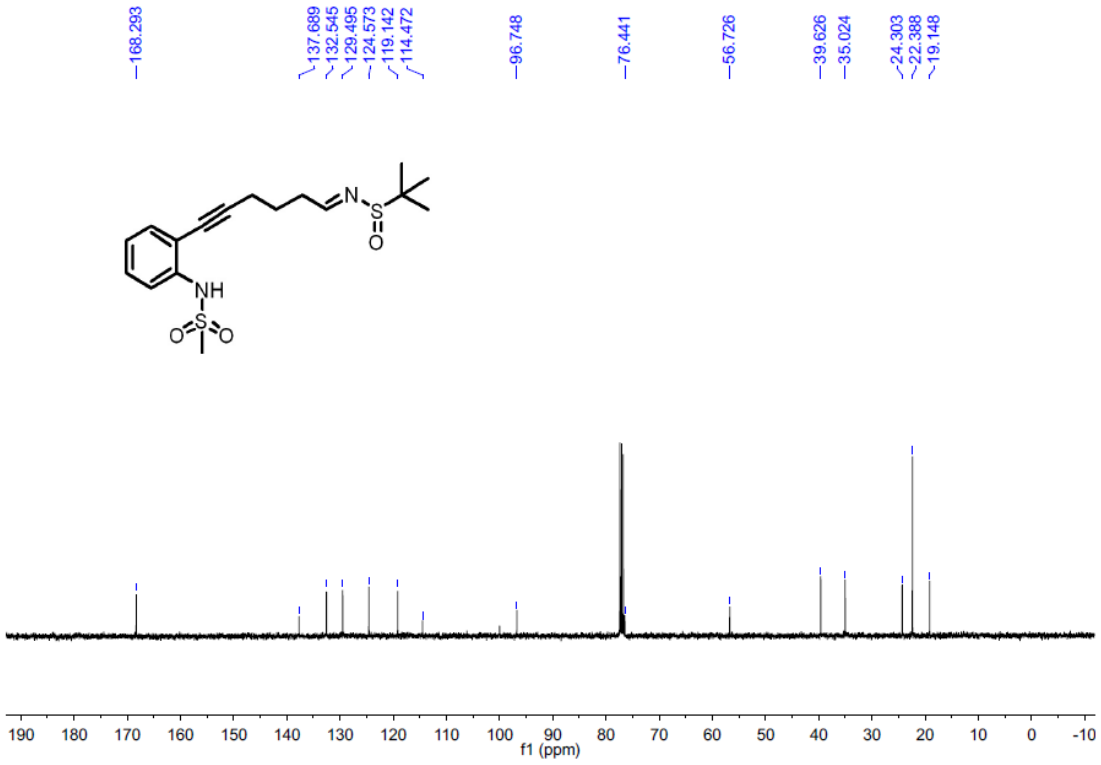
^{13}C NMR spectrum of 1t



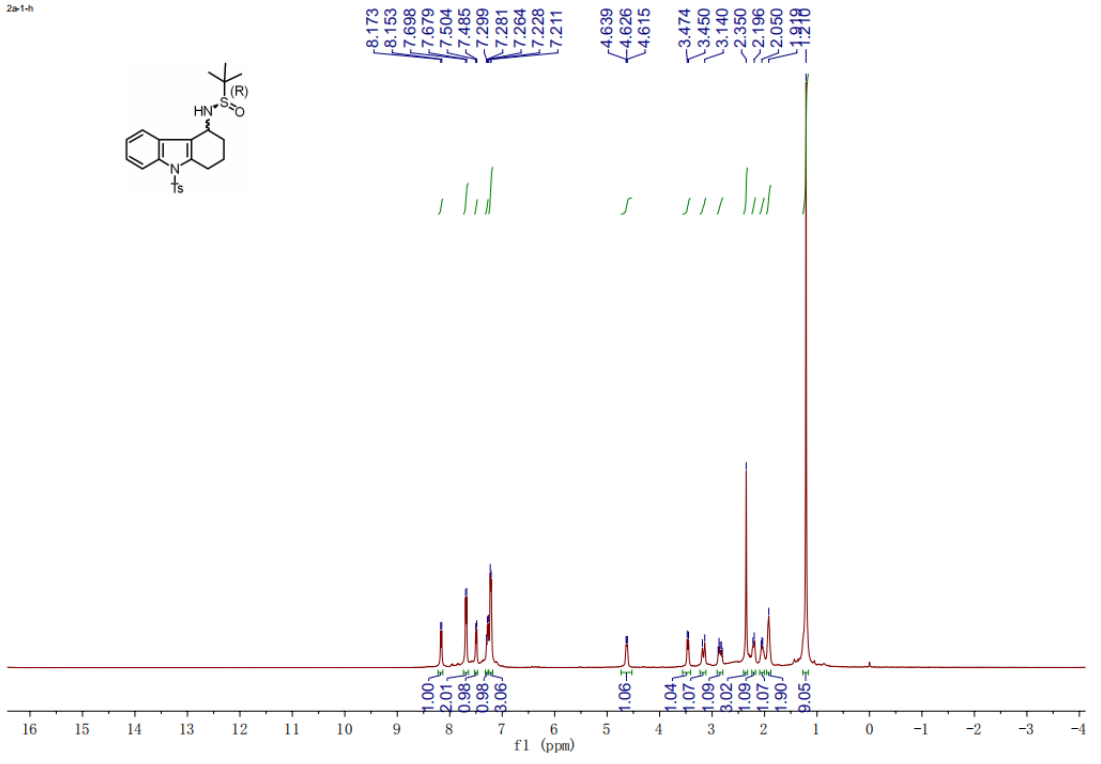
^{1}H NMR spectrum of 1u



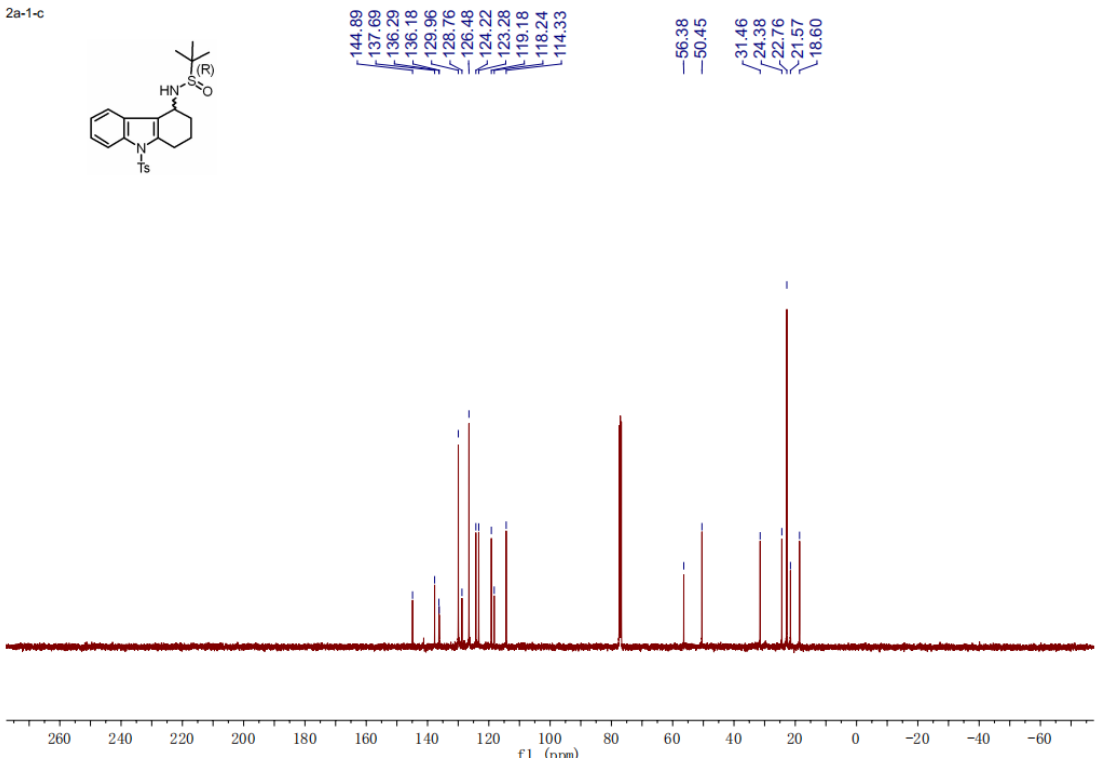
^{13}C NMR spectrum of 1u



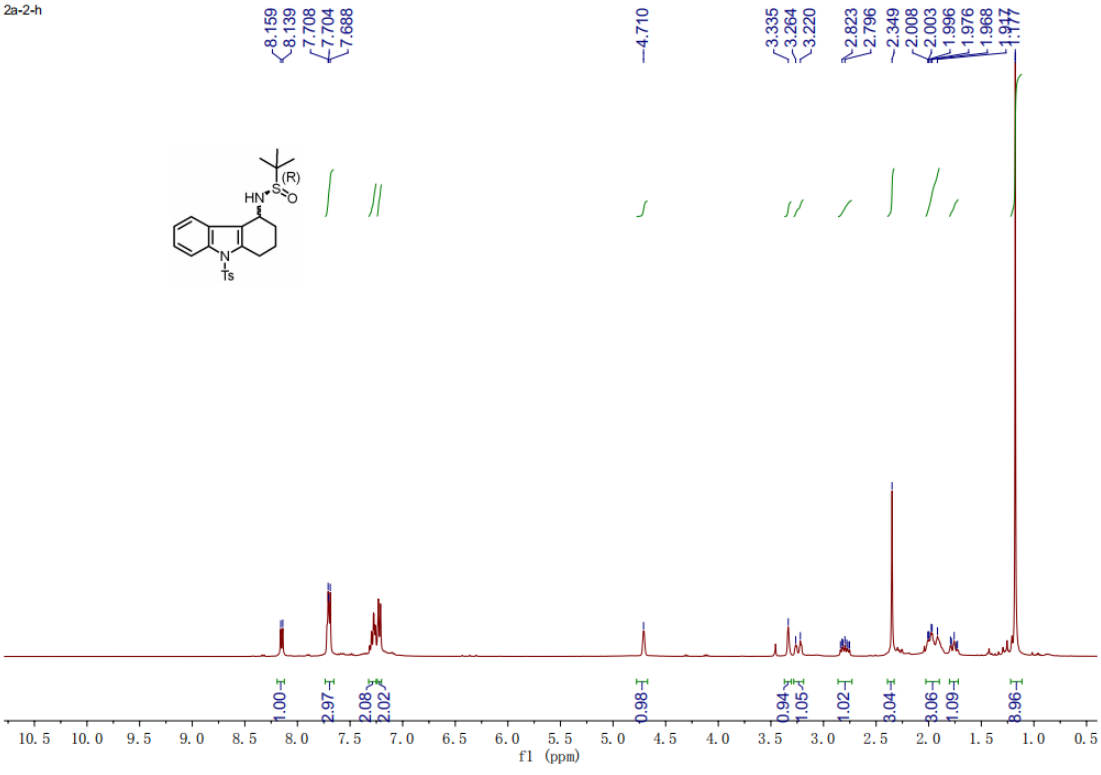
^{1}H NMR spectrum of (+)-2a



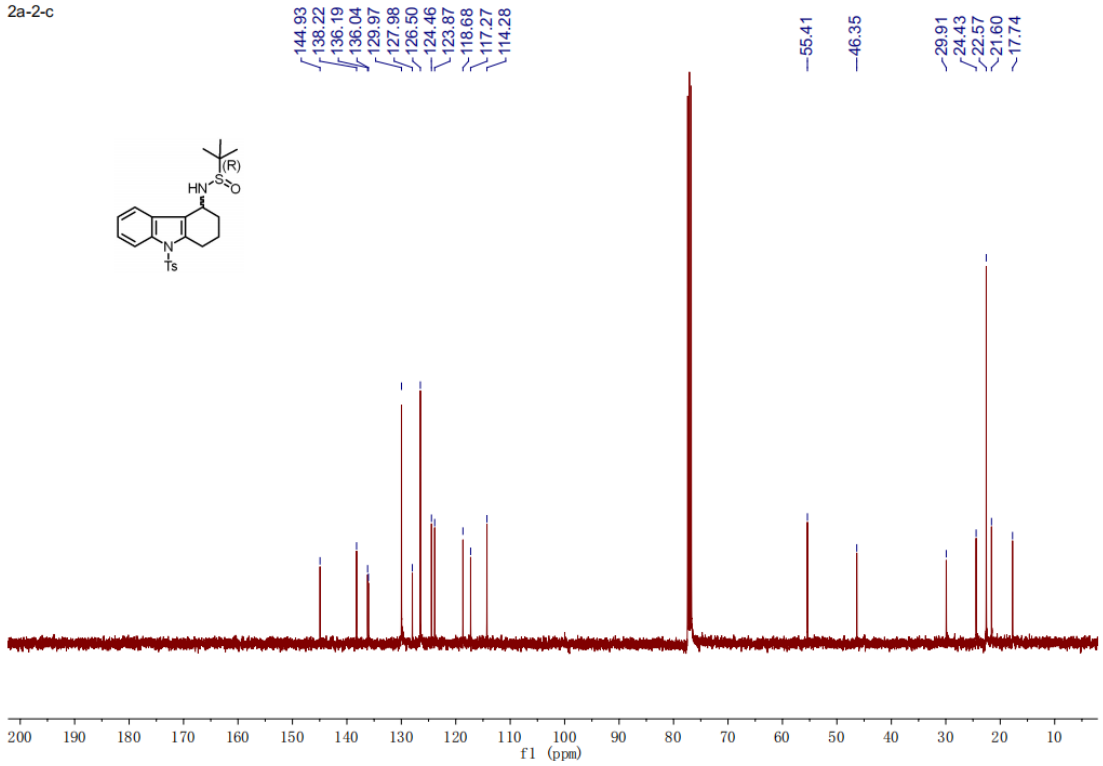
^{13}C NMR spectrum of (+)-2a



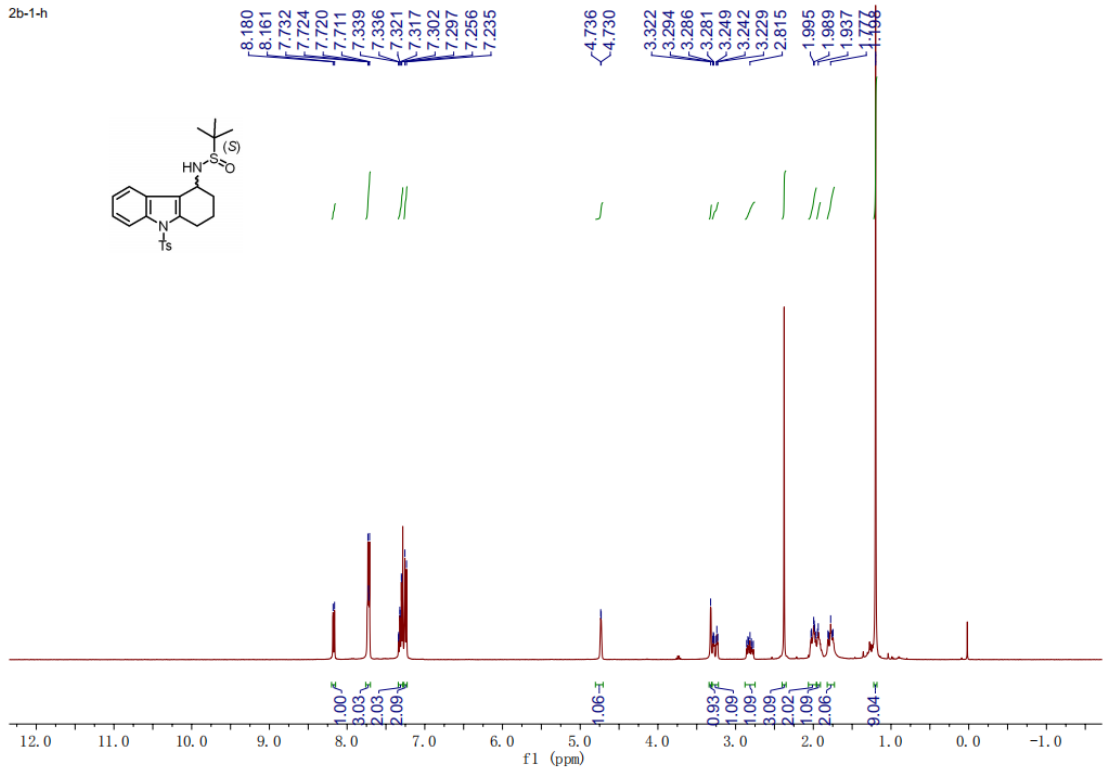
^{1}H NMR spectrum of (-)-2a



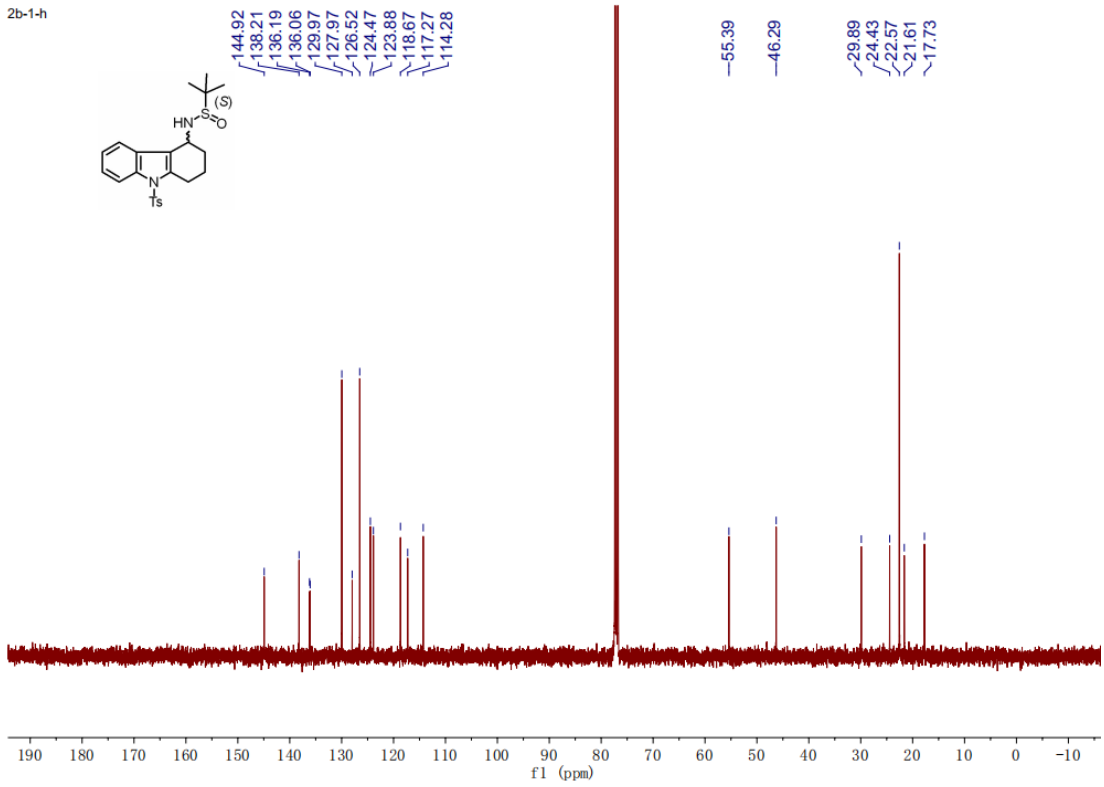
^{13}C NMR spectrum of (-)-2a



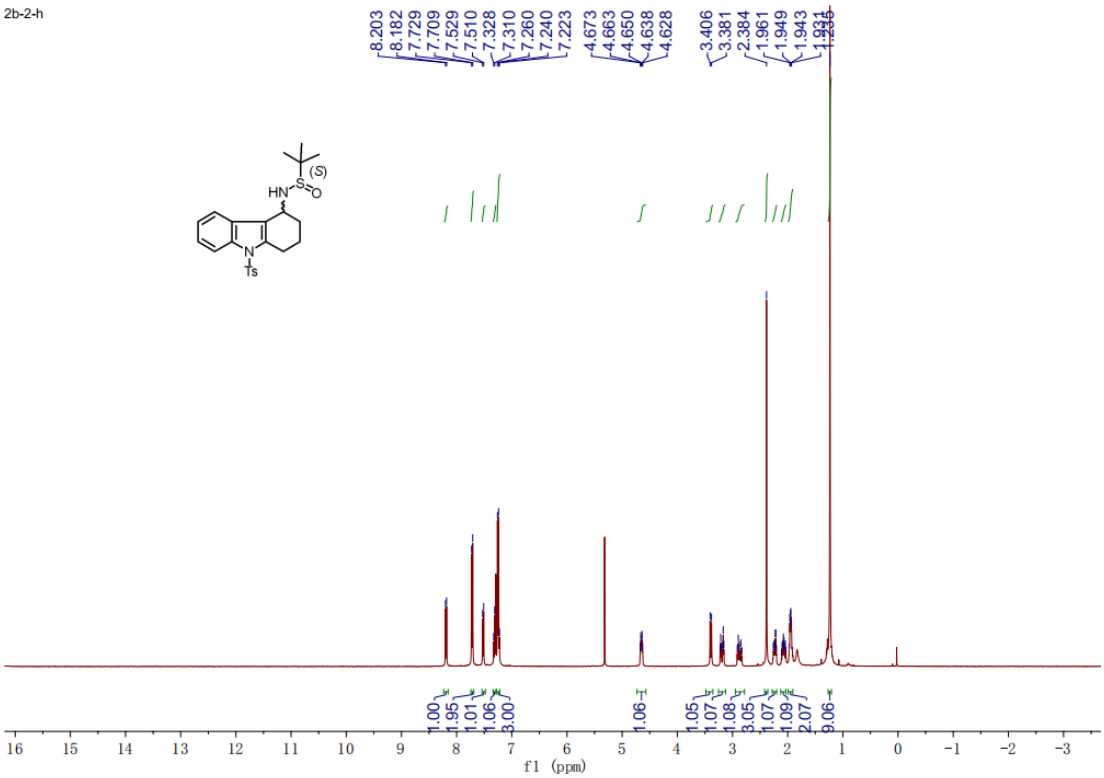
^{1}H NMR spectrum of (+)-2b



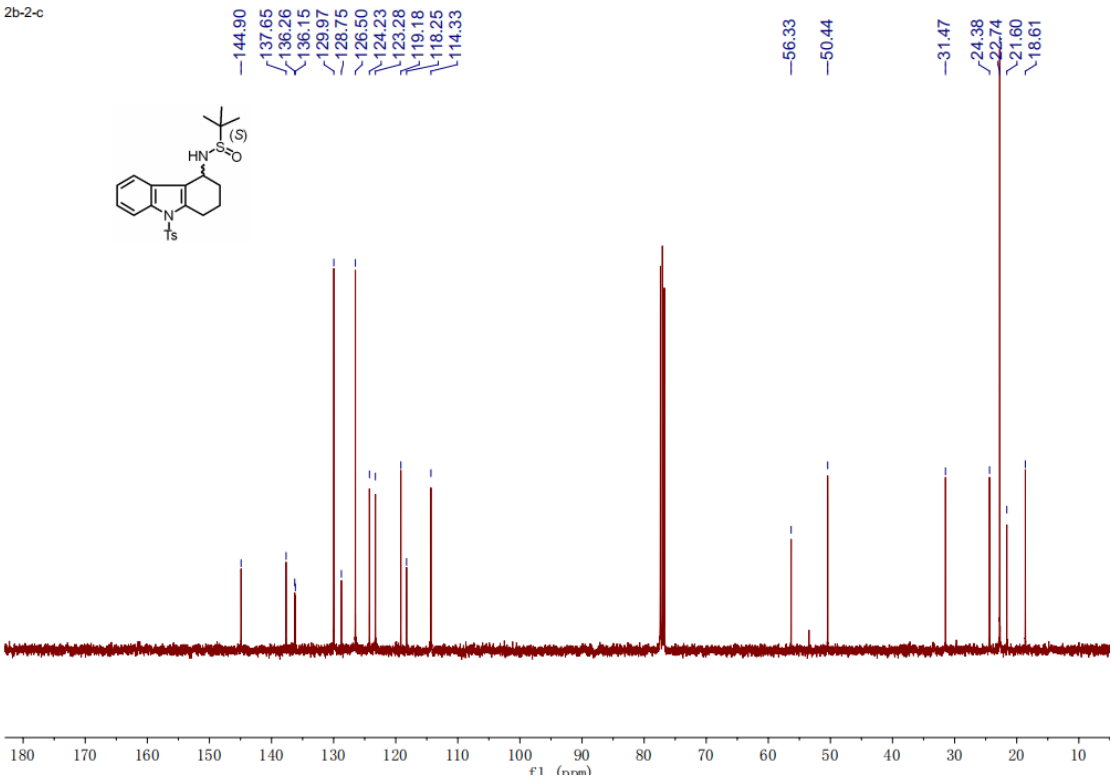
^{13}C NMR spectrum of (+)-2b



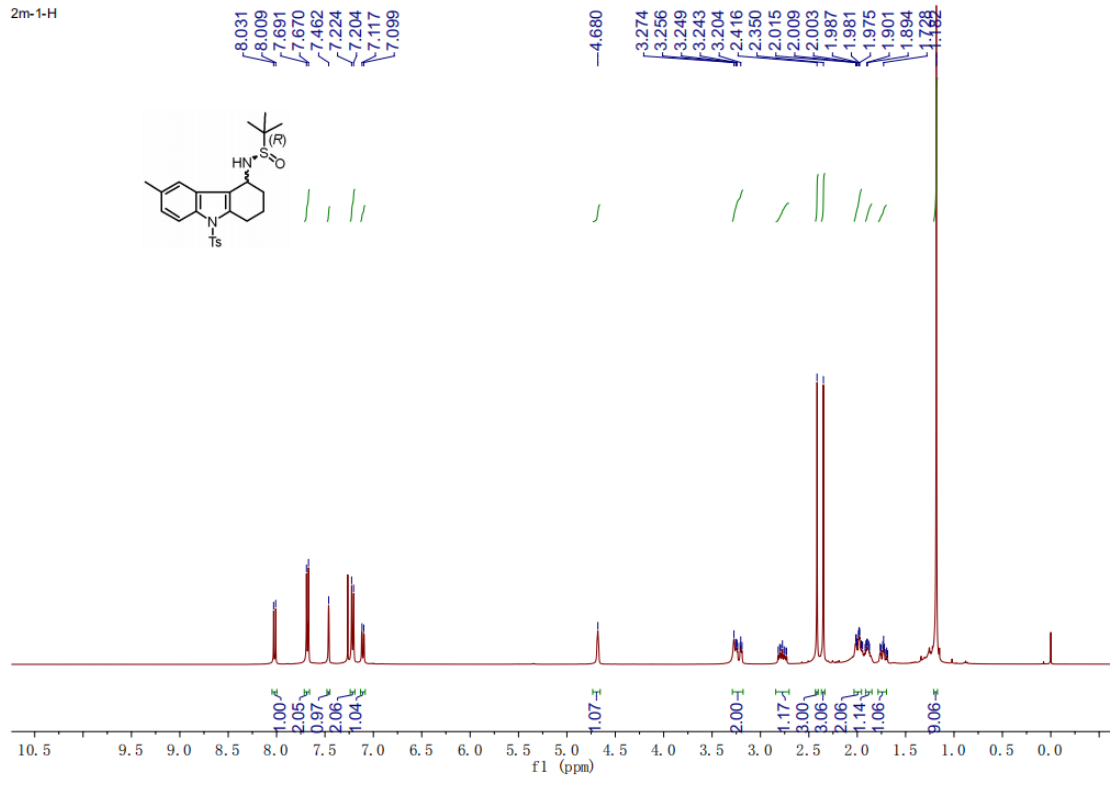
^{1}H NMR spectrum of (-)-2b



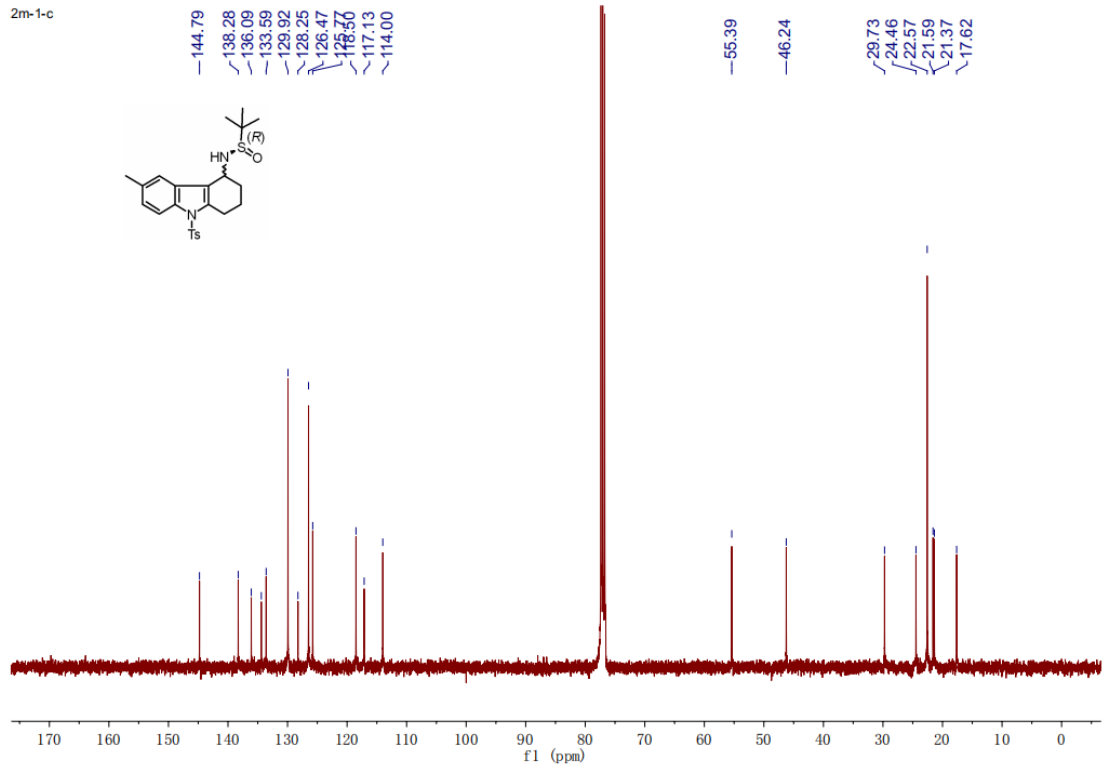
^{13}C NMR spectrum of (-)-2b



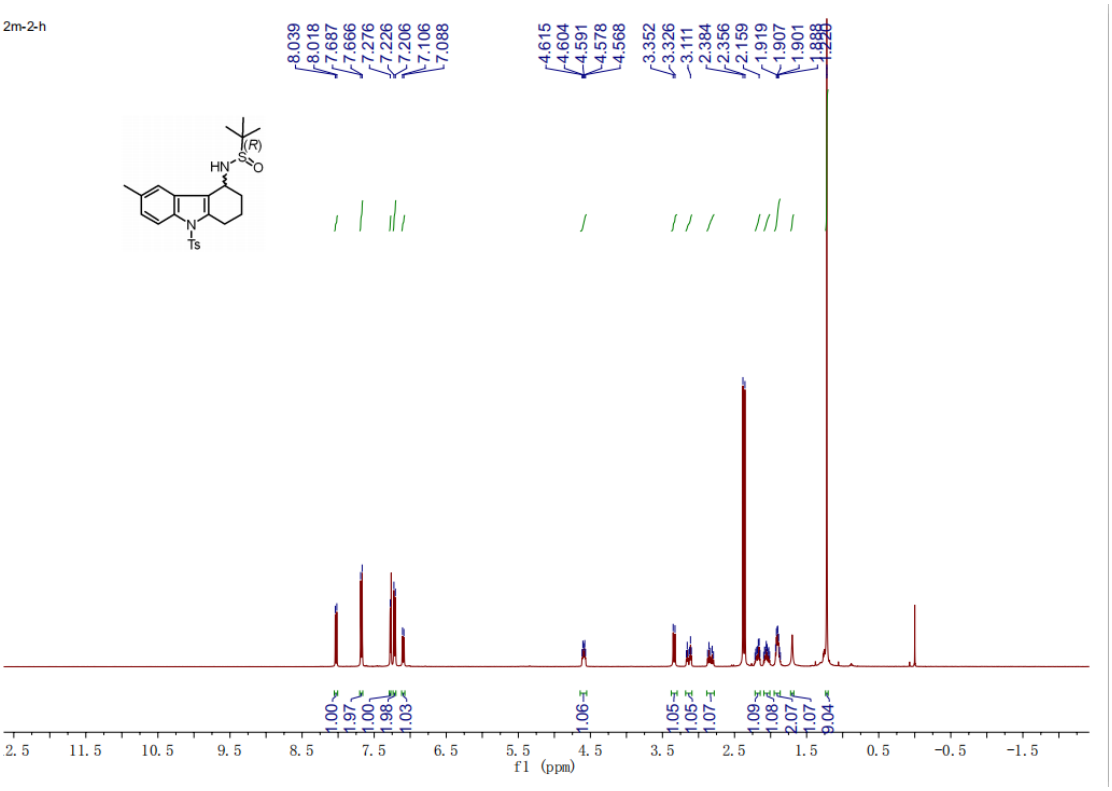
^{1}H NMR spectrum of (+)-2c



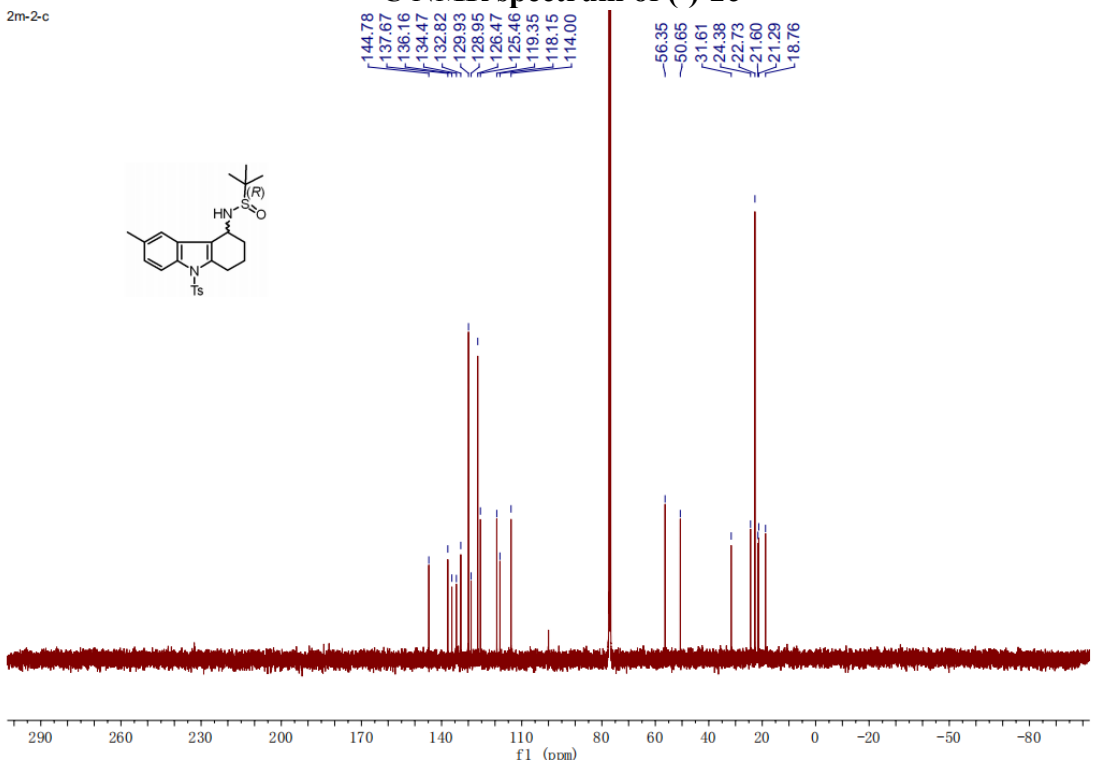
^{13}C NMR spectrum of (+)-2c



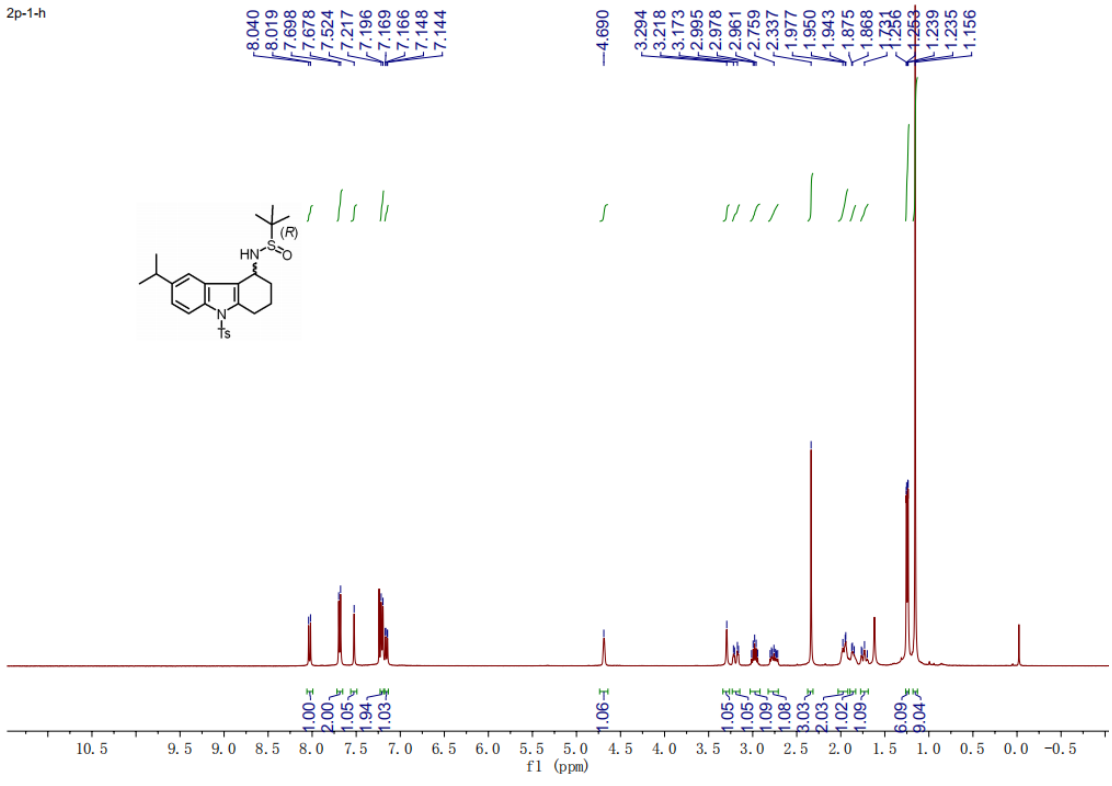
^{1}H NMR spectrum of (-)-2c



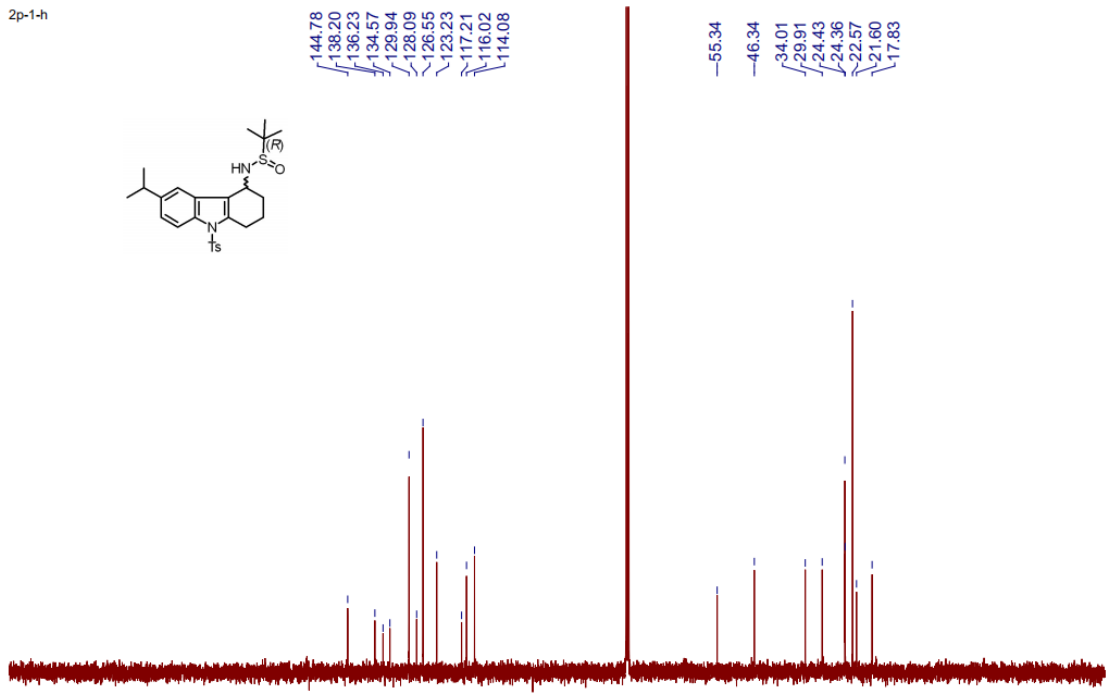
^{13}C NMR spectrum of (-)-2c



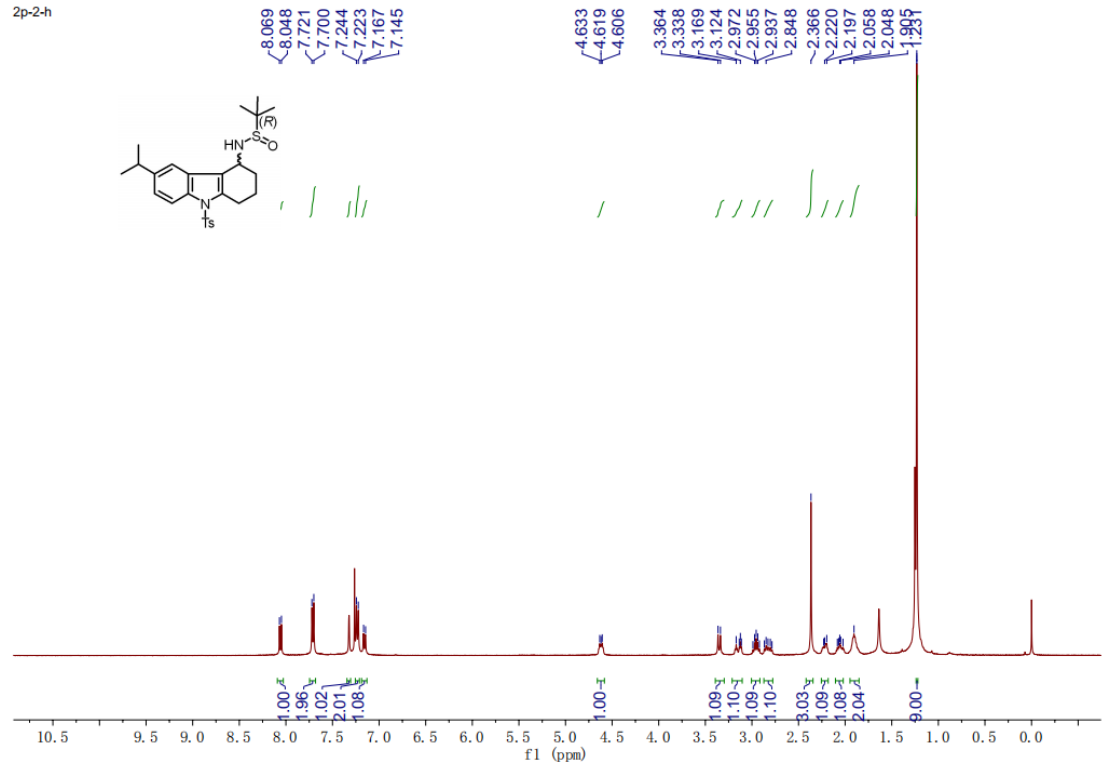
^{1}H NMR spectrum of (+)-2d



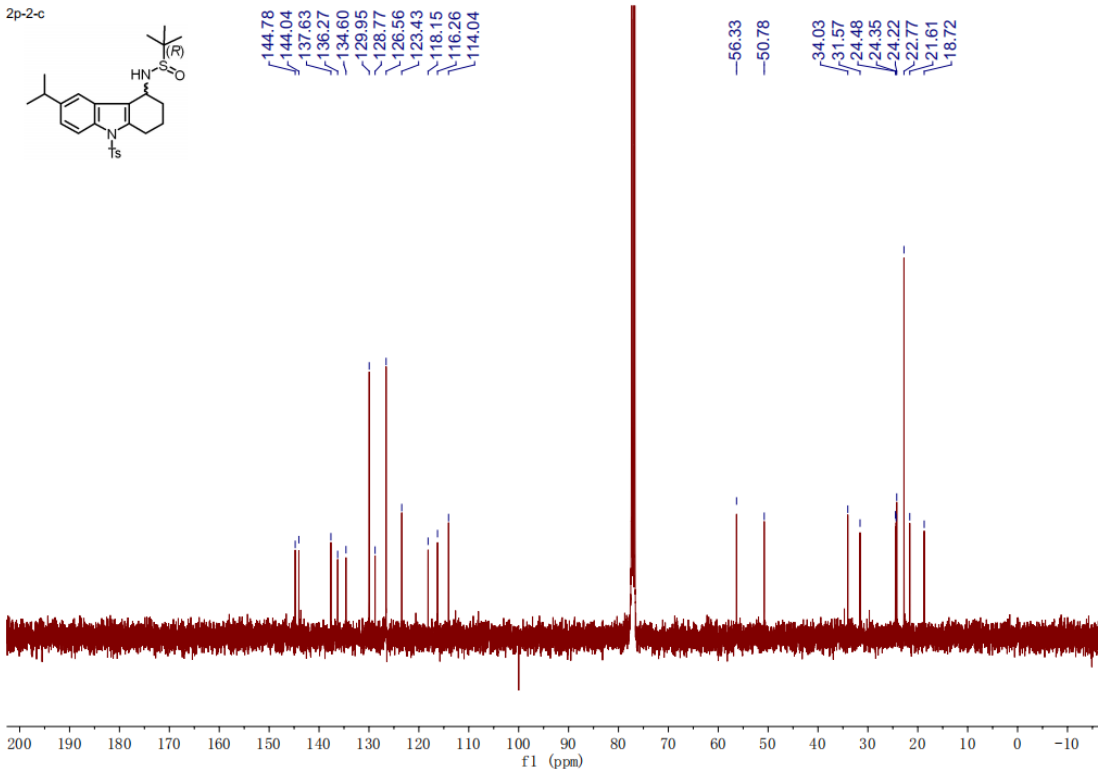
^{13}C NMR spectrum of (+)-2d



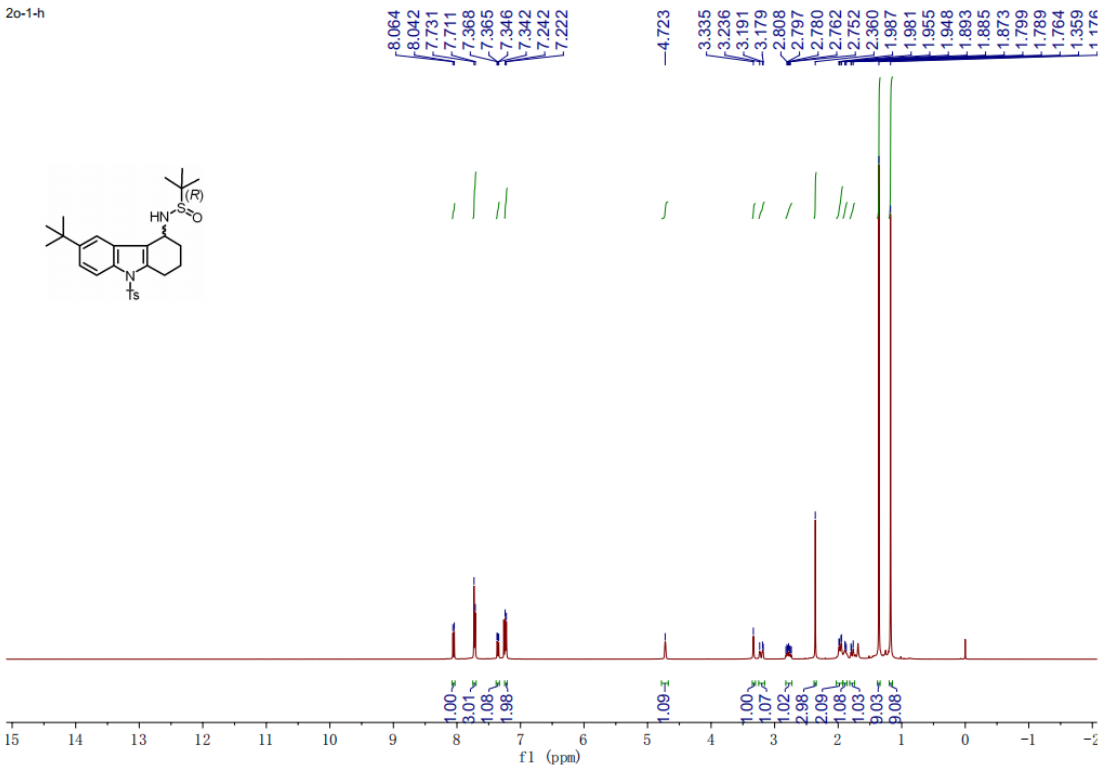
^{1}H NMR spectrum of (-)-2d



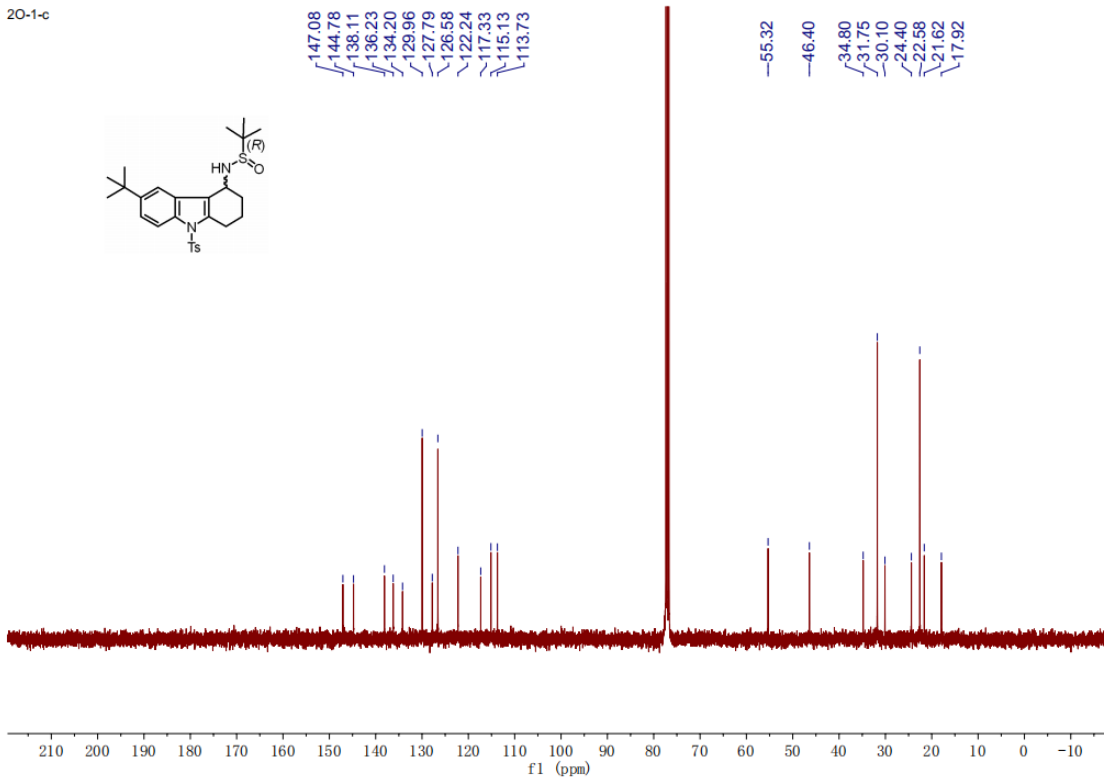
^{13}C NMR spectrum of (-)-2d



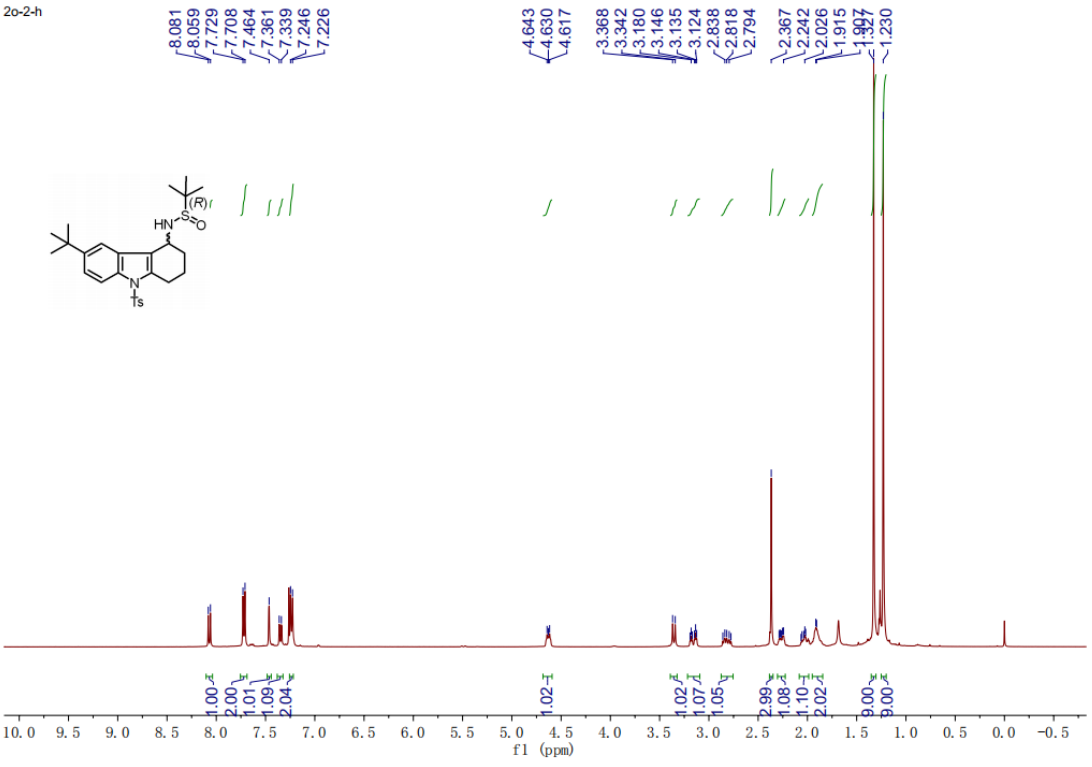
^{1}H NMR spectrum of (+)-2e



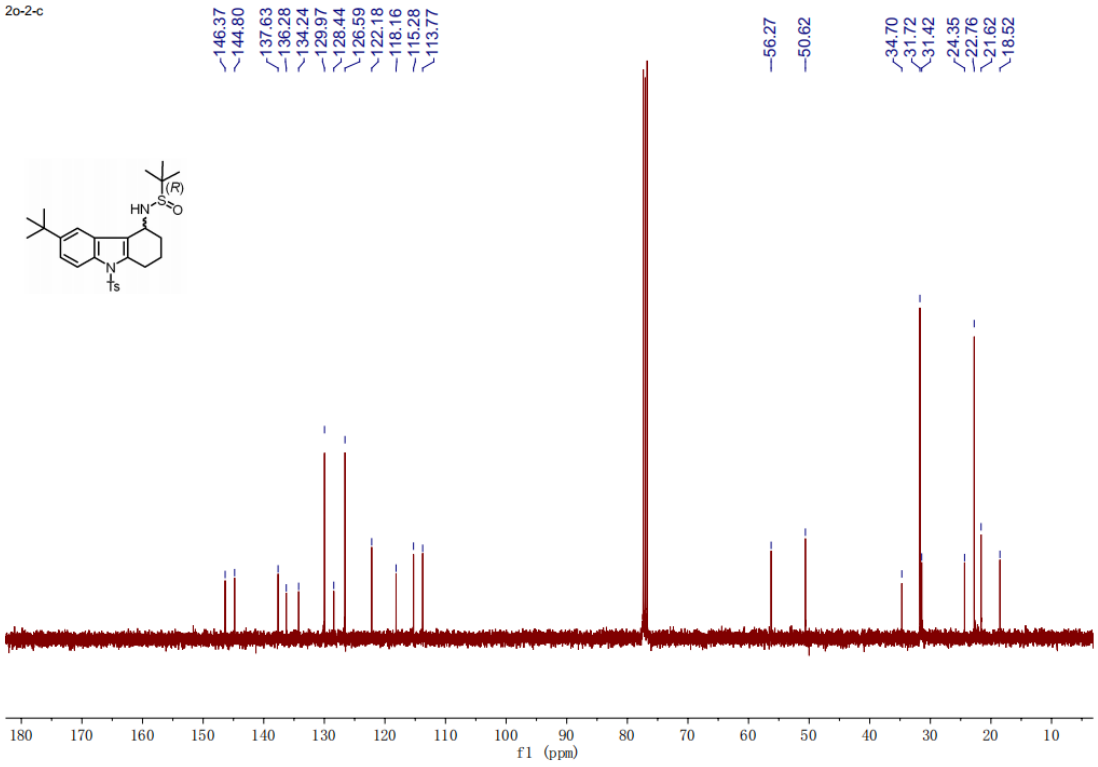
^{13}C NMR spectrum of (+)-2e



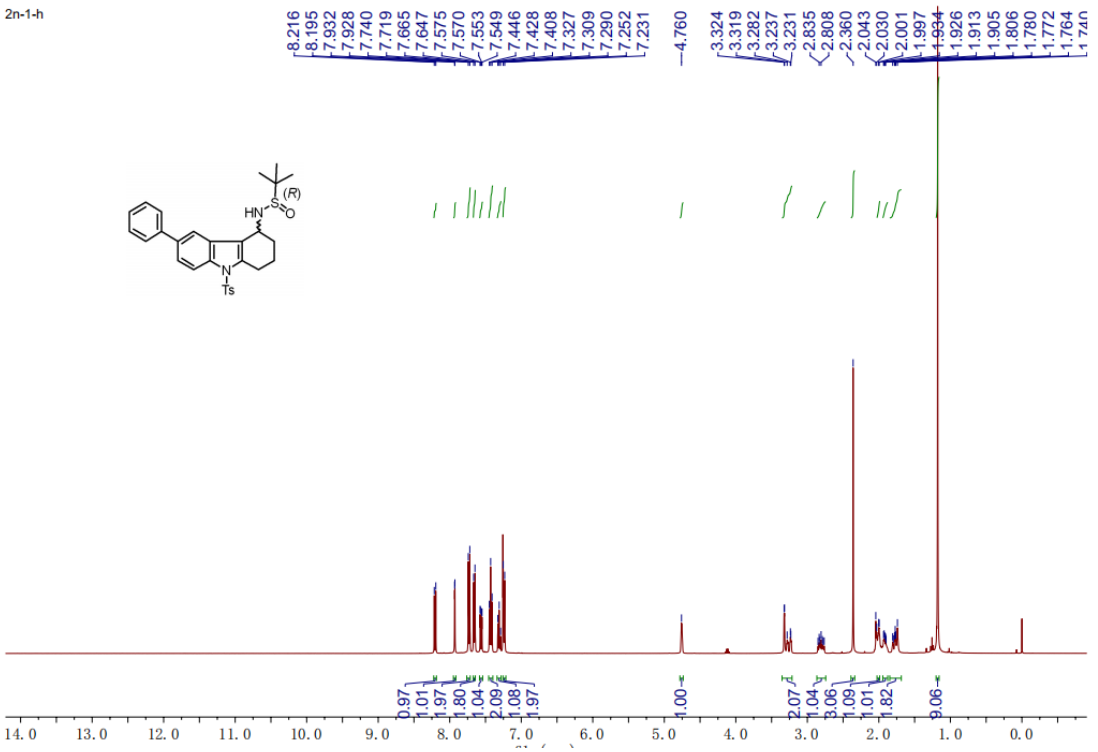
^{1}H NMR spectrum of (-)-2e



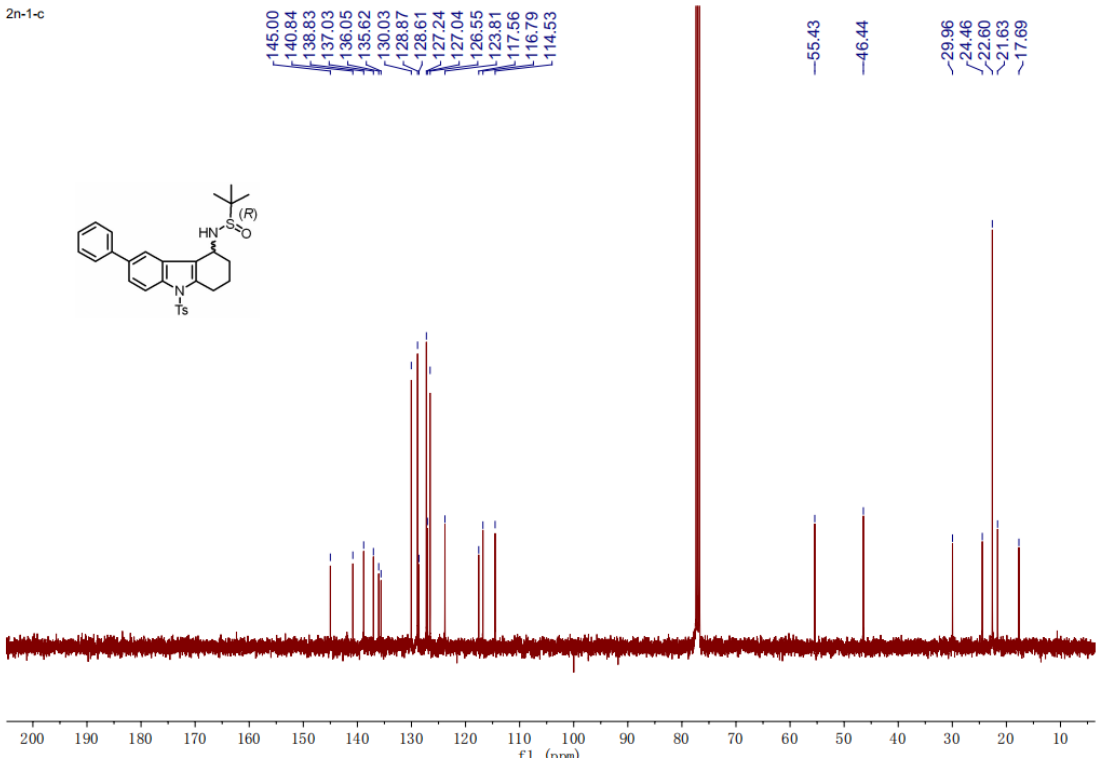
^{13}C NMR spectrum of (-)-2e



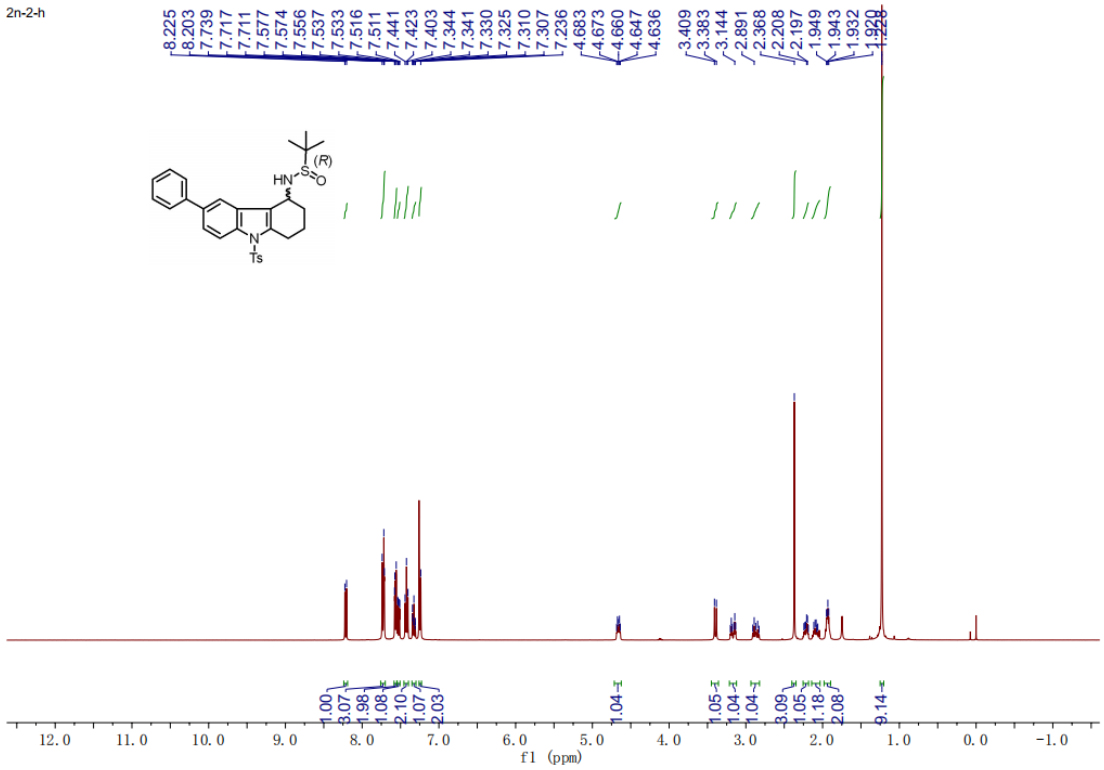
^{1}H NMR spectrum of (+)-2f



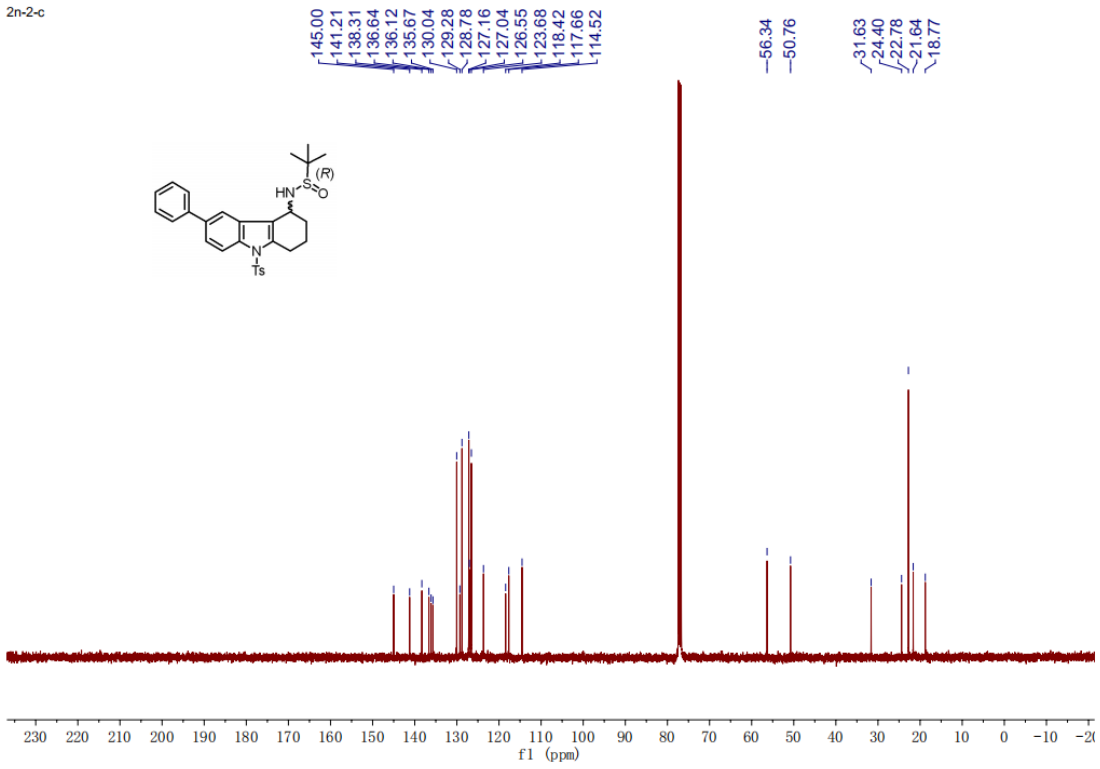
^{13}C NMR spectrum of (+)-2f



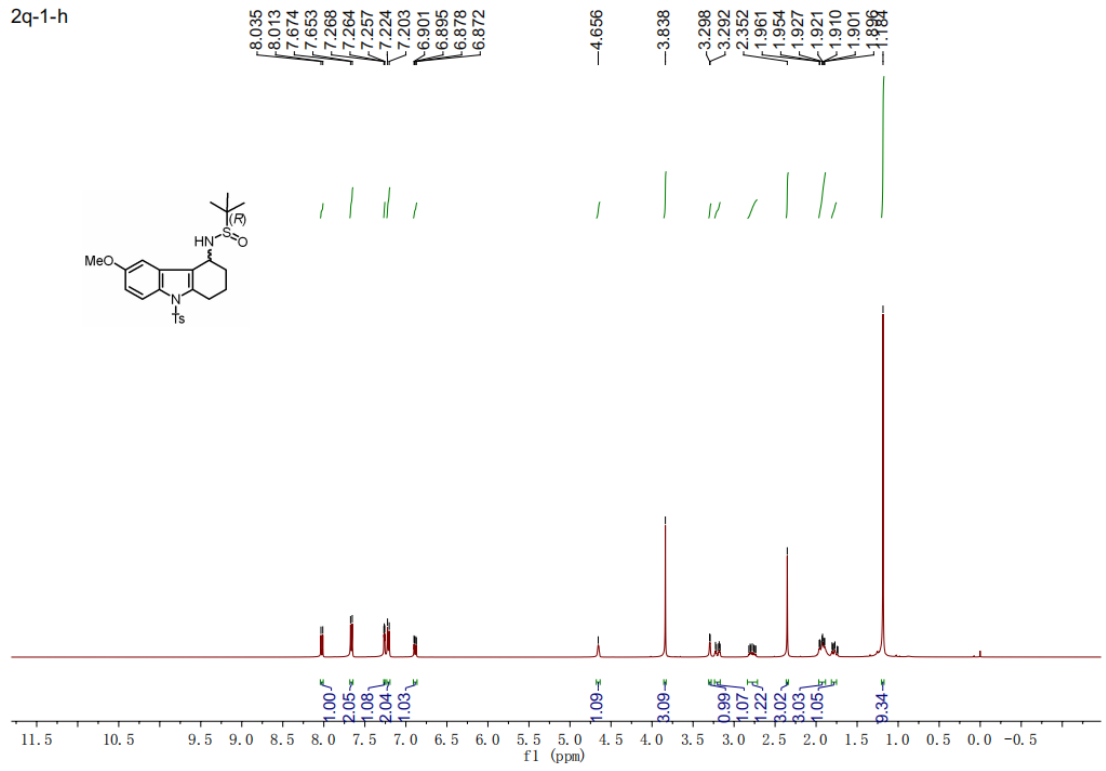
^{1}H NMR spectrum of (-)-2f



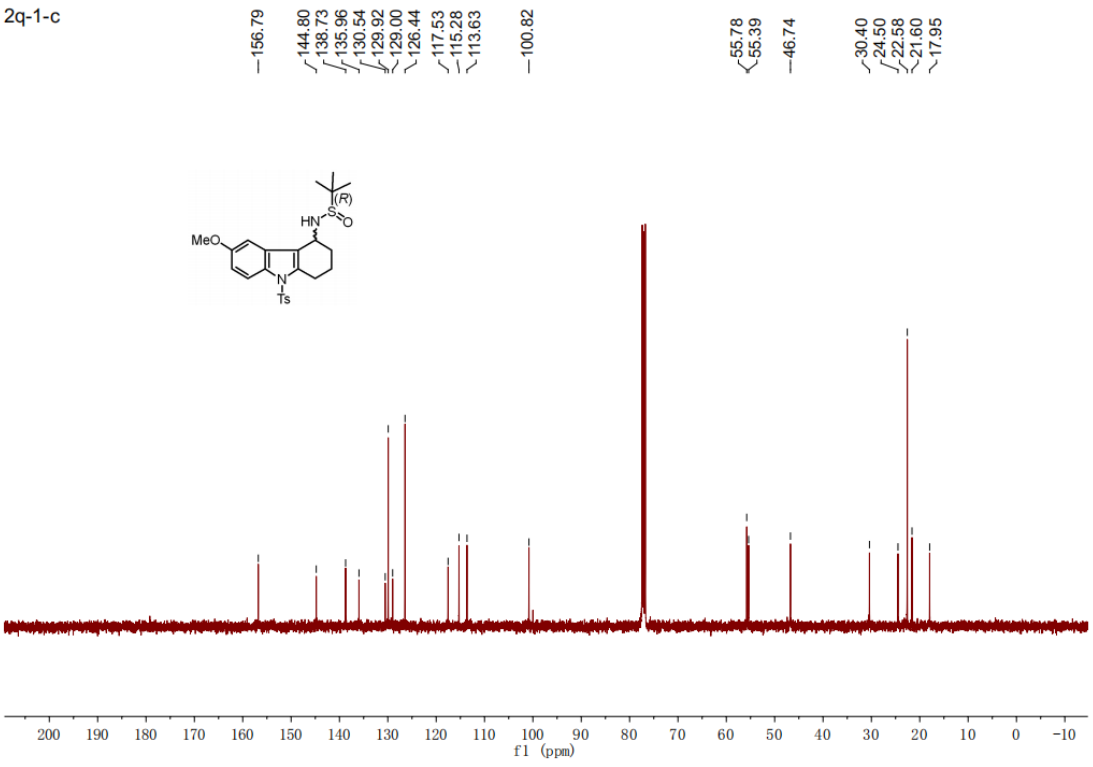
^{13}C NMR spectrum of (-)-2f



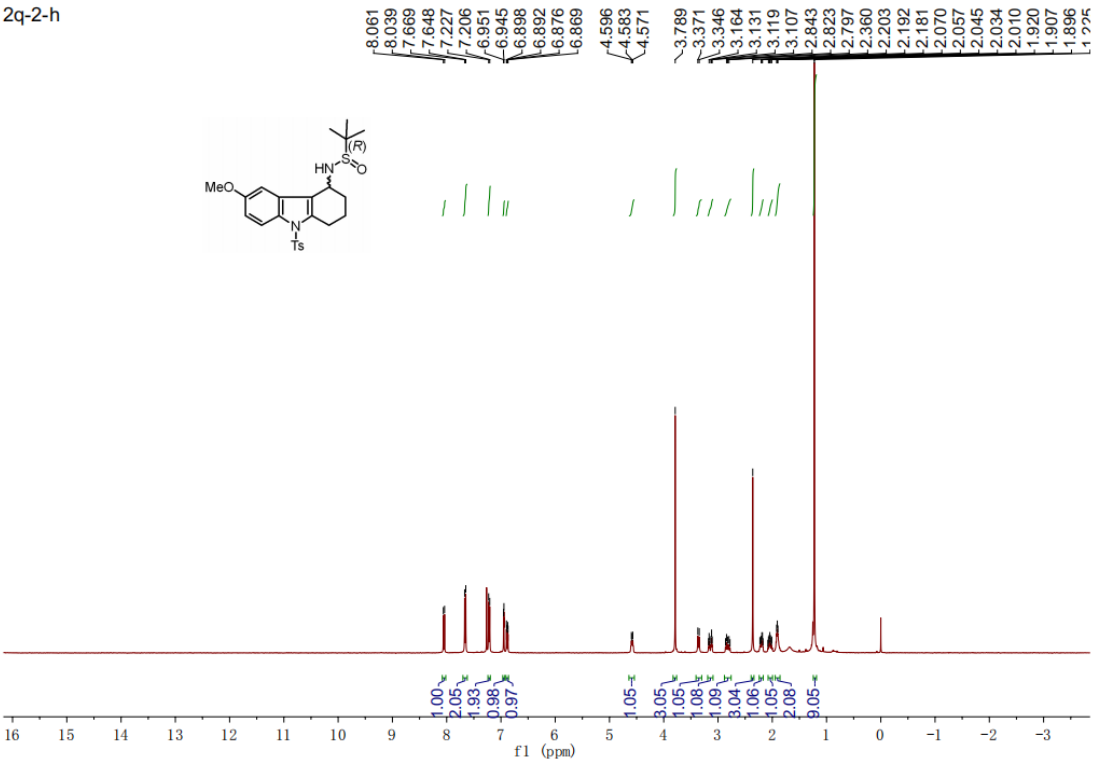
^{1}H NMR spectrum of (+)-2g



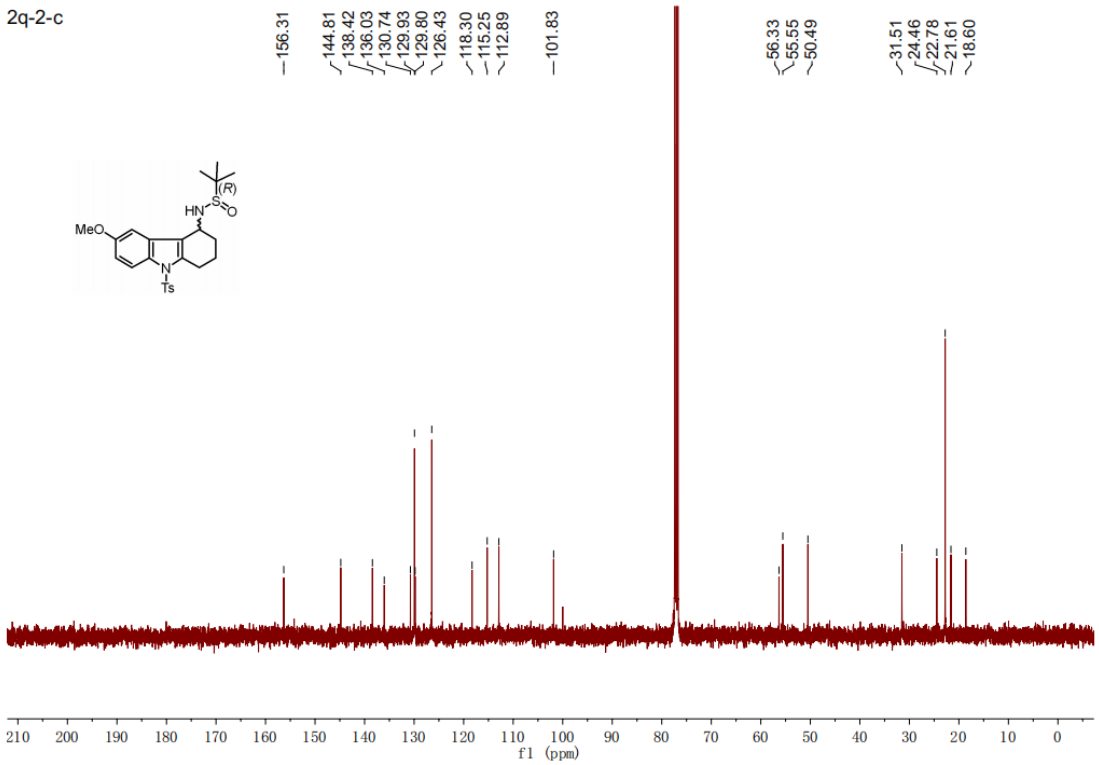
^{13}C NMR spectrum of (+)-2g



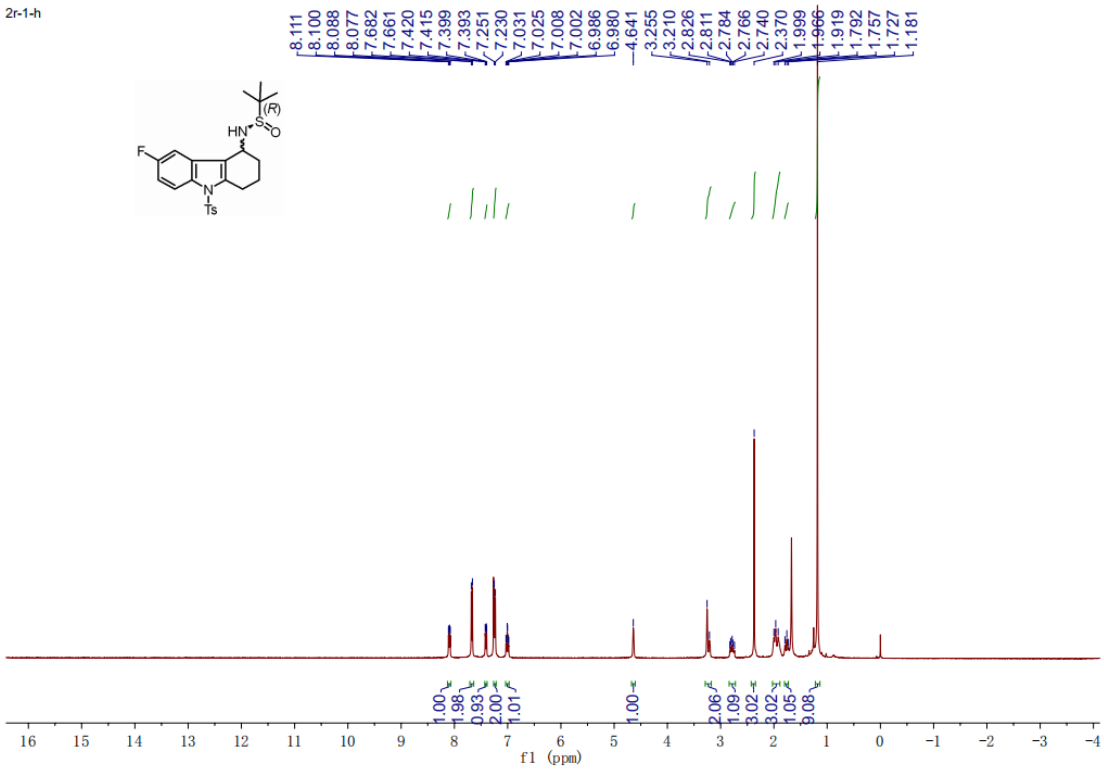
^{1}H NMR spectrum of (-)-2g



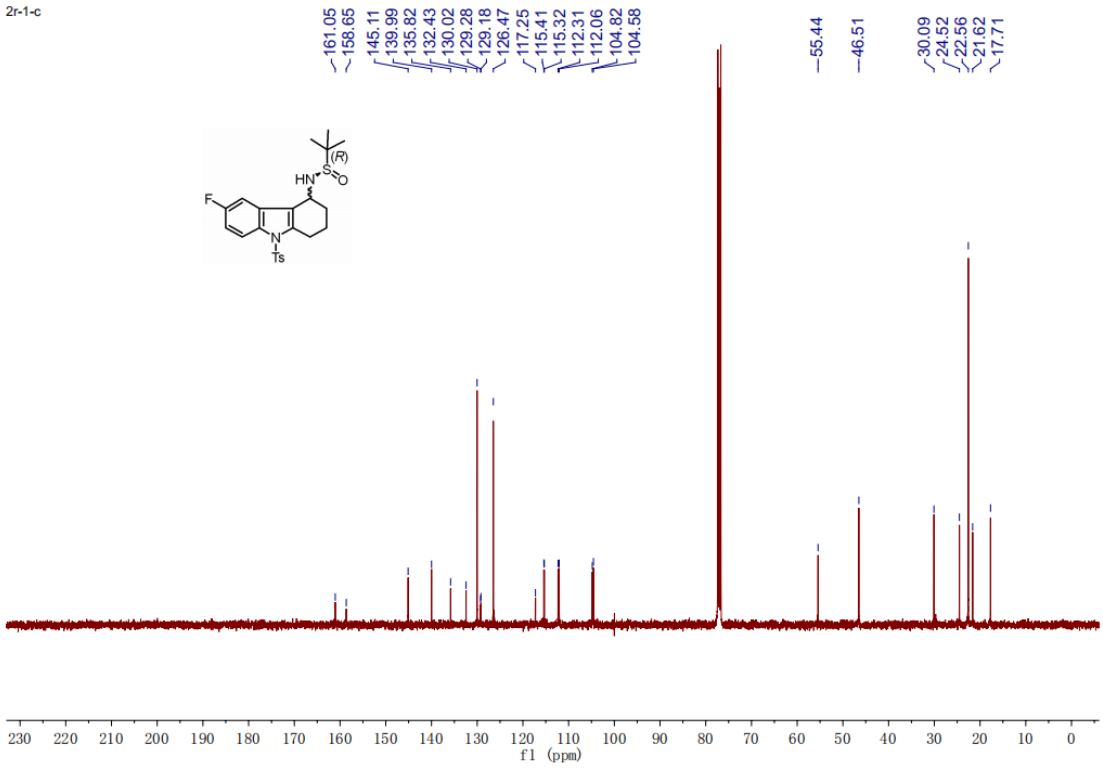
^{13}C NMR spectrum of (-)-2g



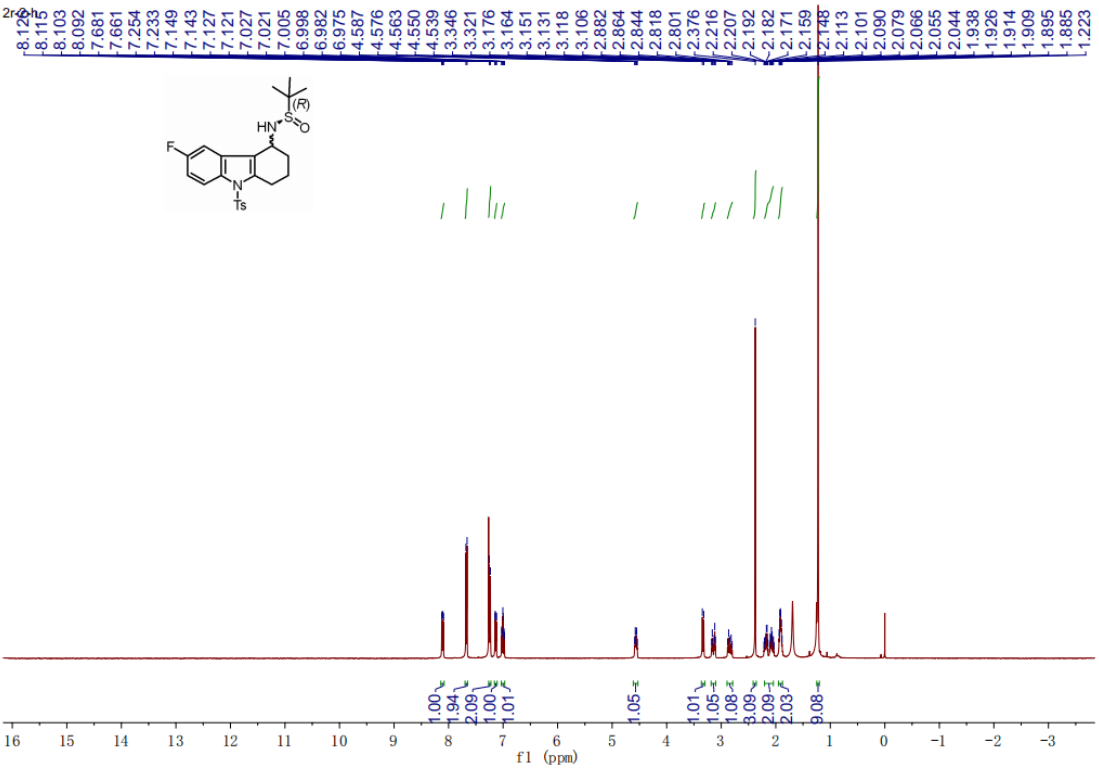
^{1}H NMR spectrum of (+)-2h



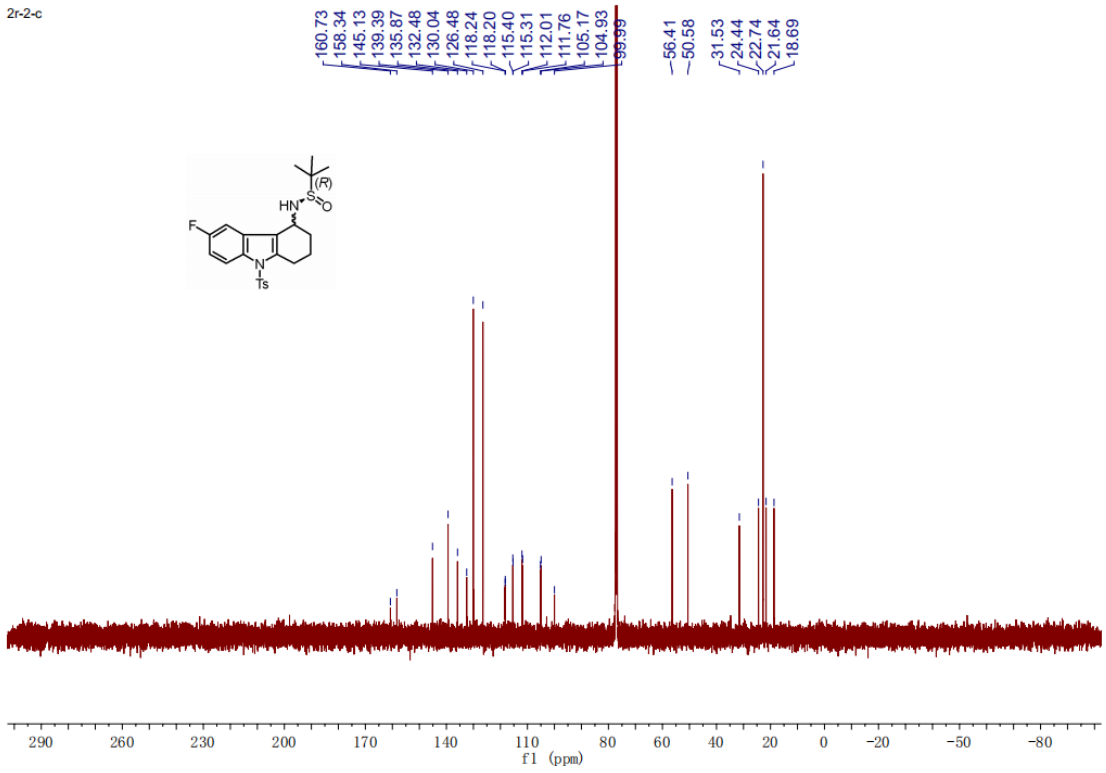
^{13}C NMR spectrum of (+)-2h



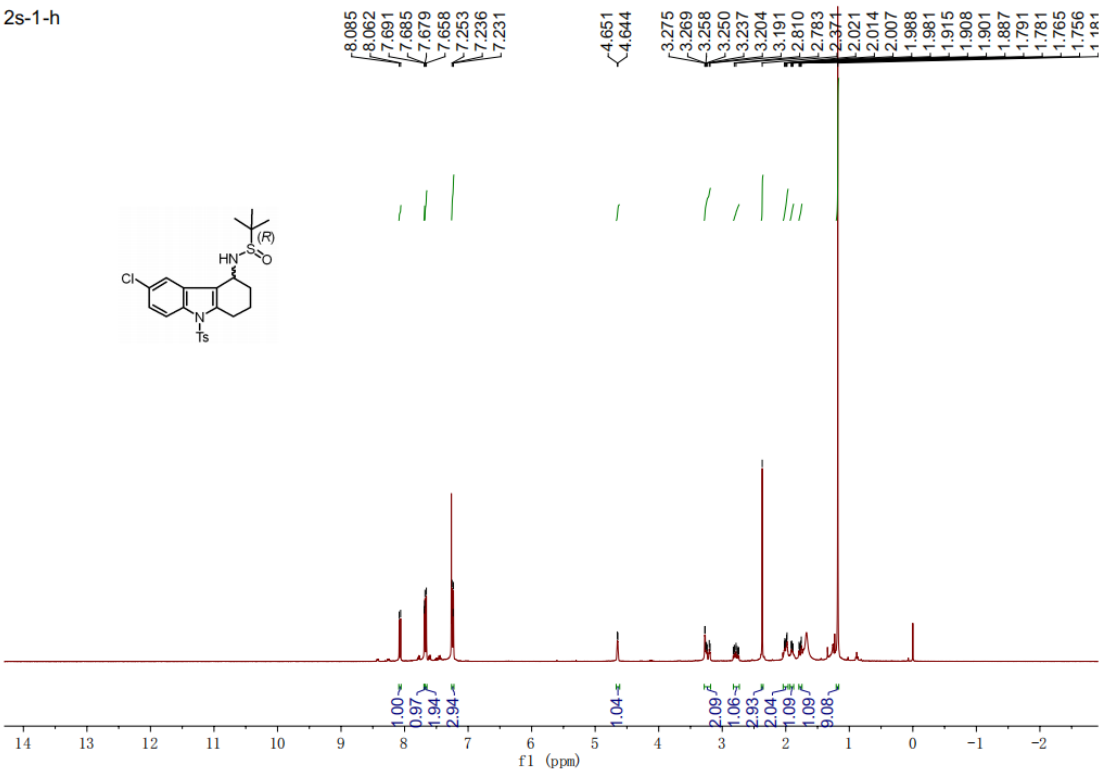
^{1}H NMR spectrum of (-)-2h



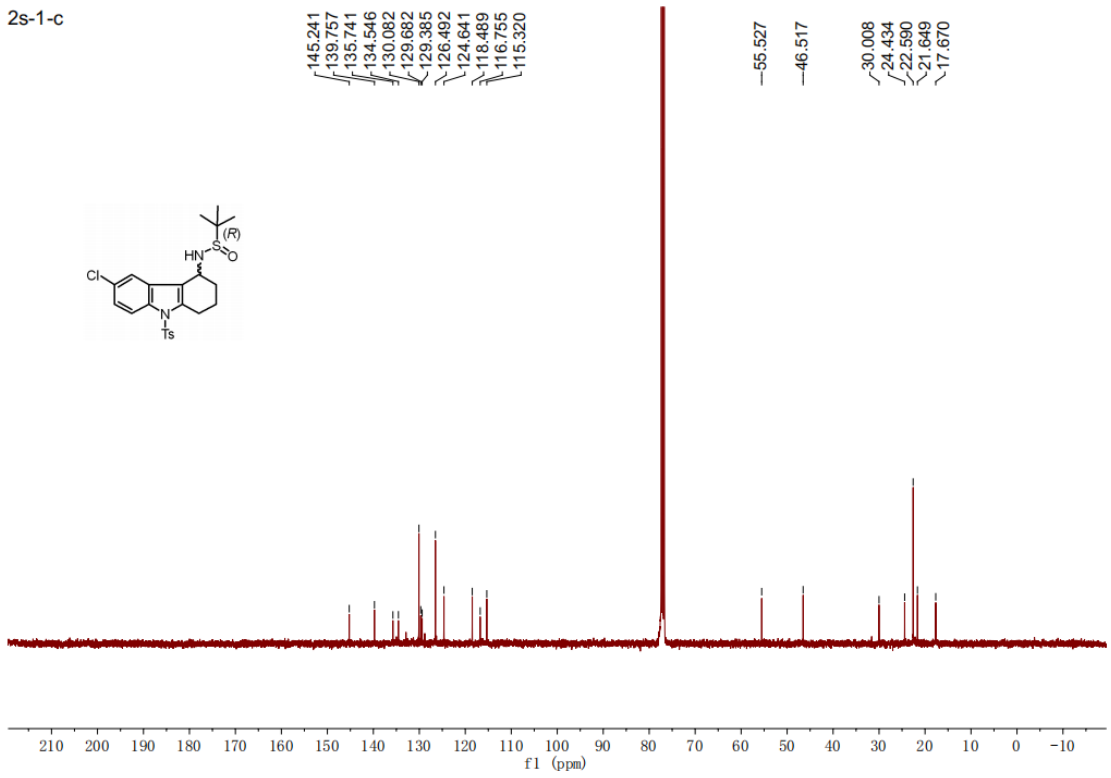
^{13}C NMR spectrum of (-)-2h



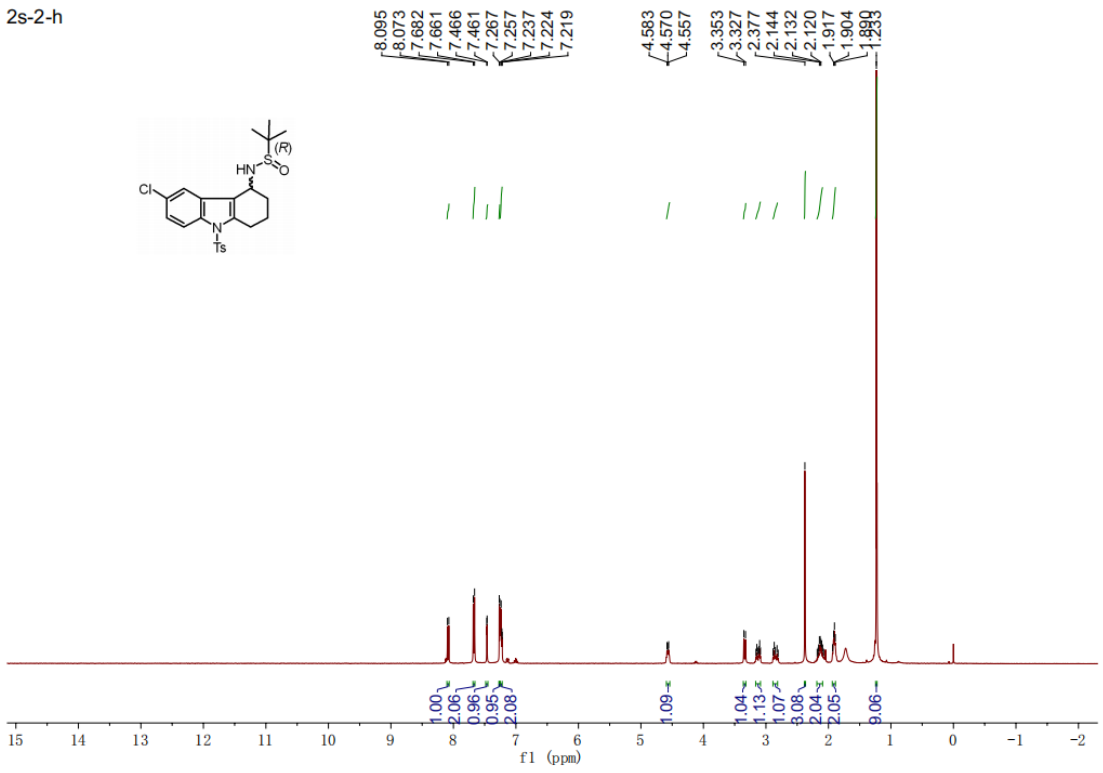
^{1}H NMR spectrum of (+)-2i



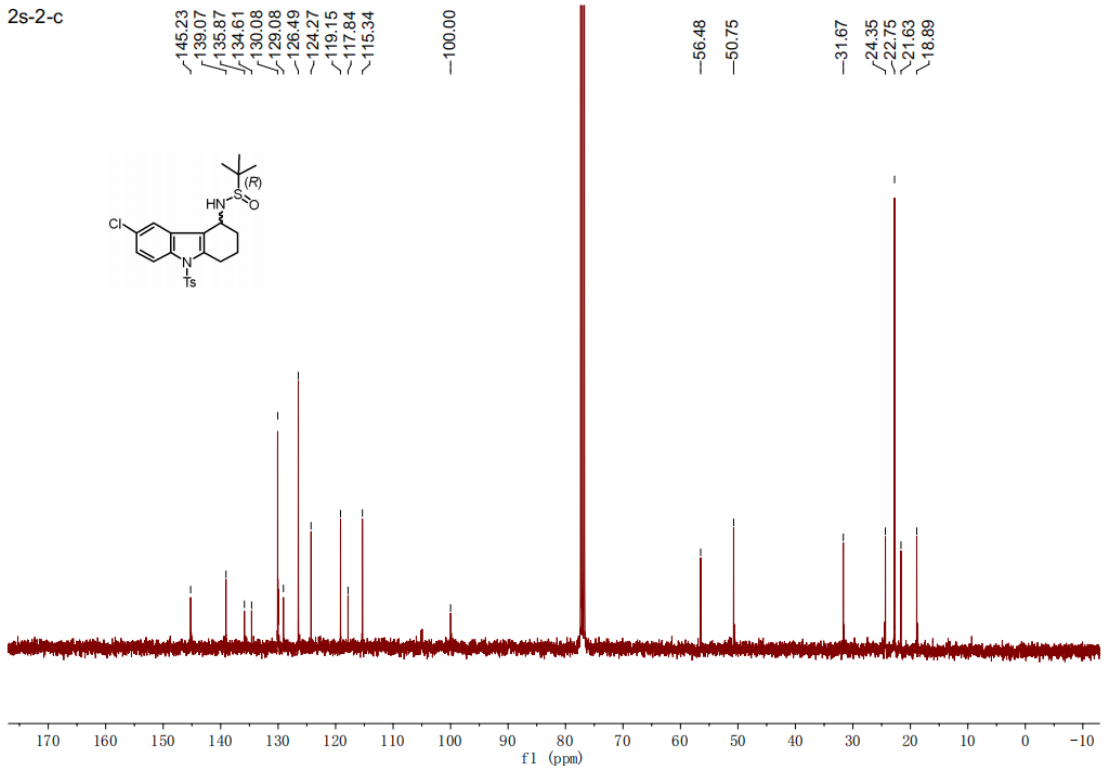
^{13}C NMR spectrum of (+)-2i



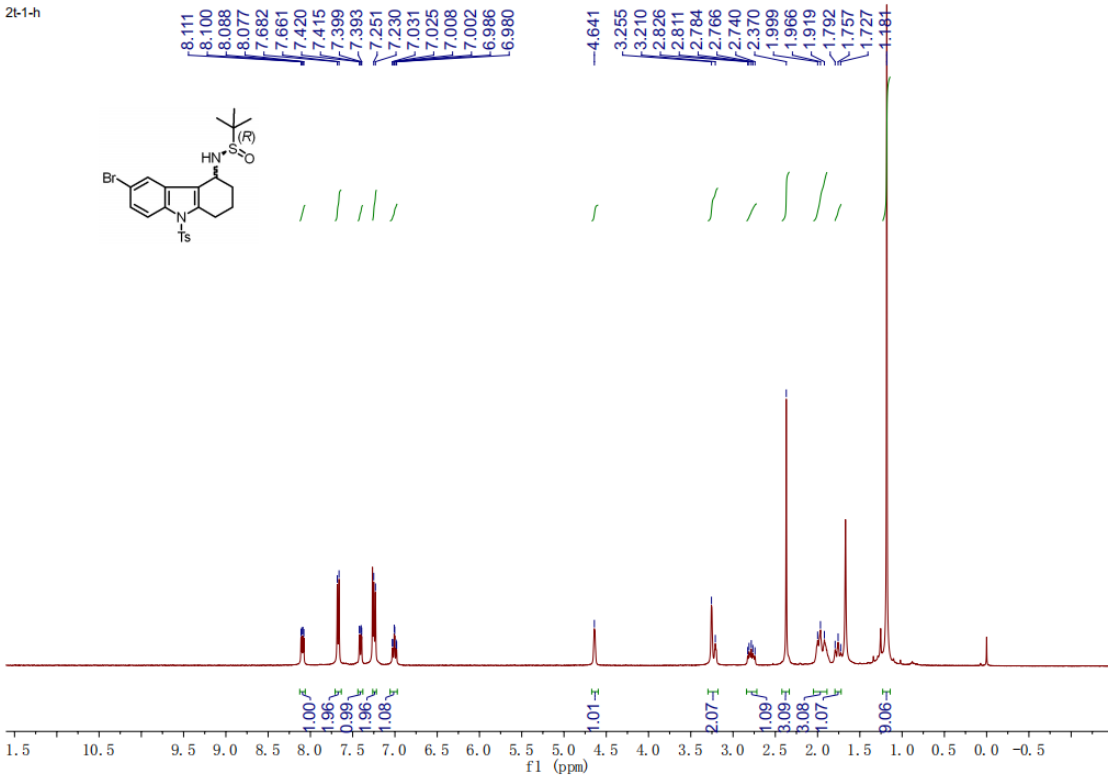
^{1}H NMR spectrum of (-)-2i



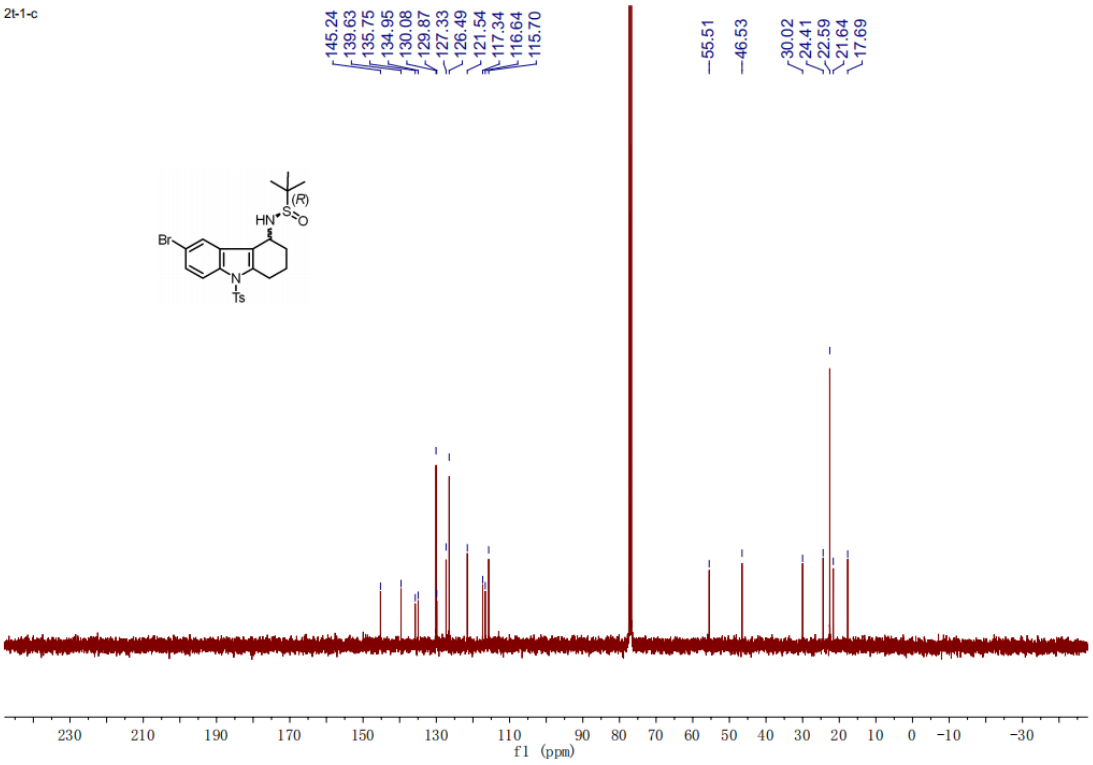
^{13}C NMR spectrum of (-)-2i



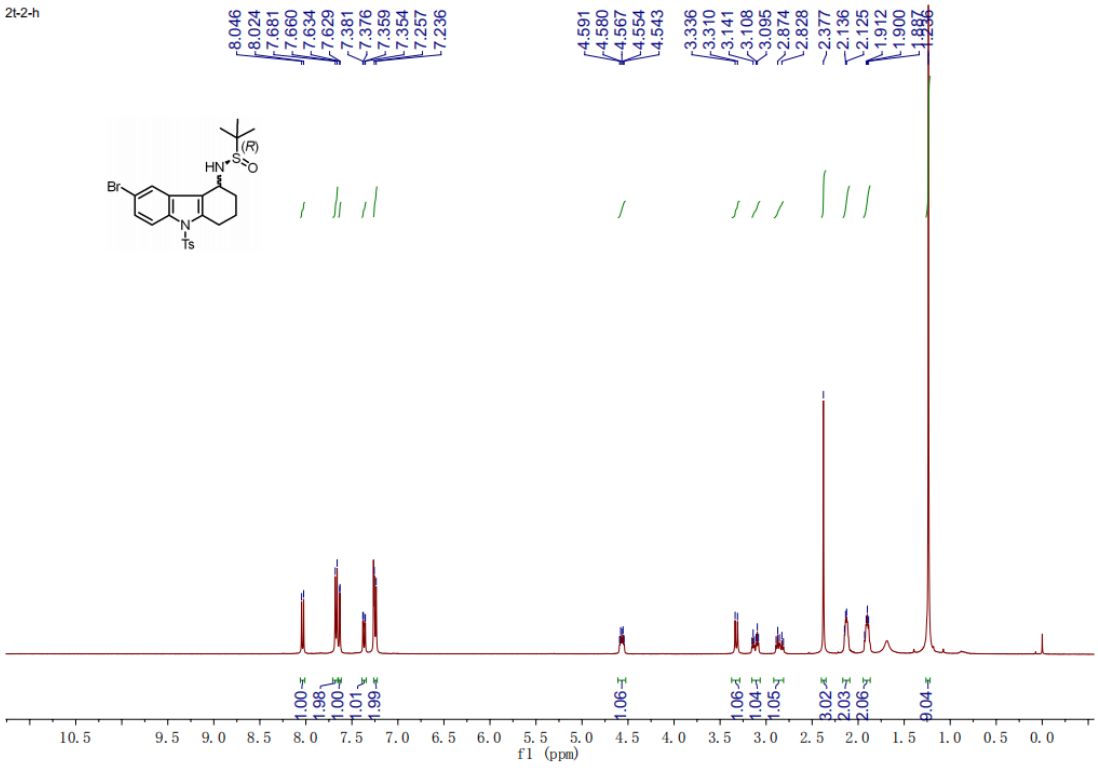
^{1}H NMR spectrum of (+)-2j



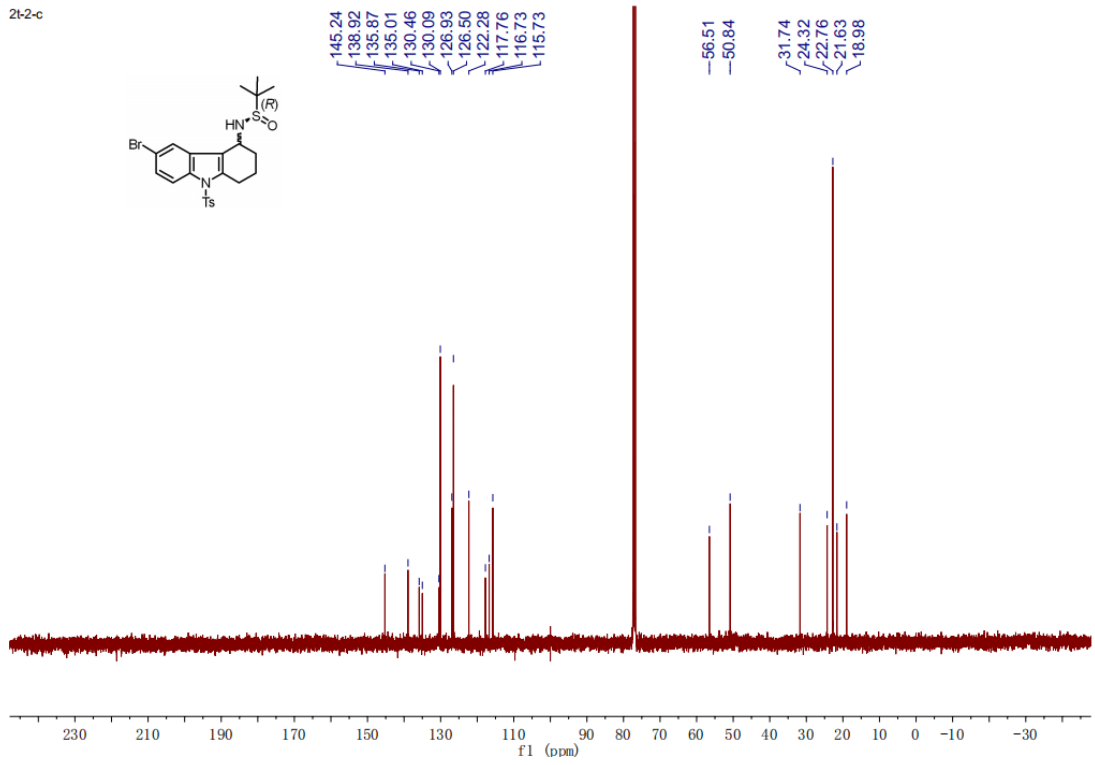
^{13}C NMR spectrum of (+)-2j



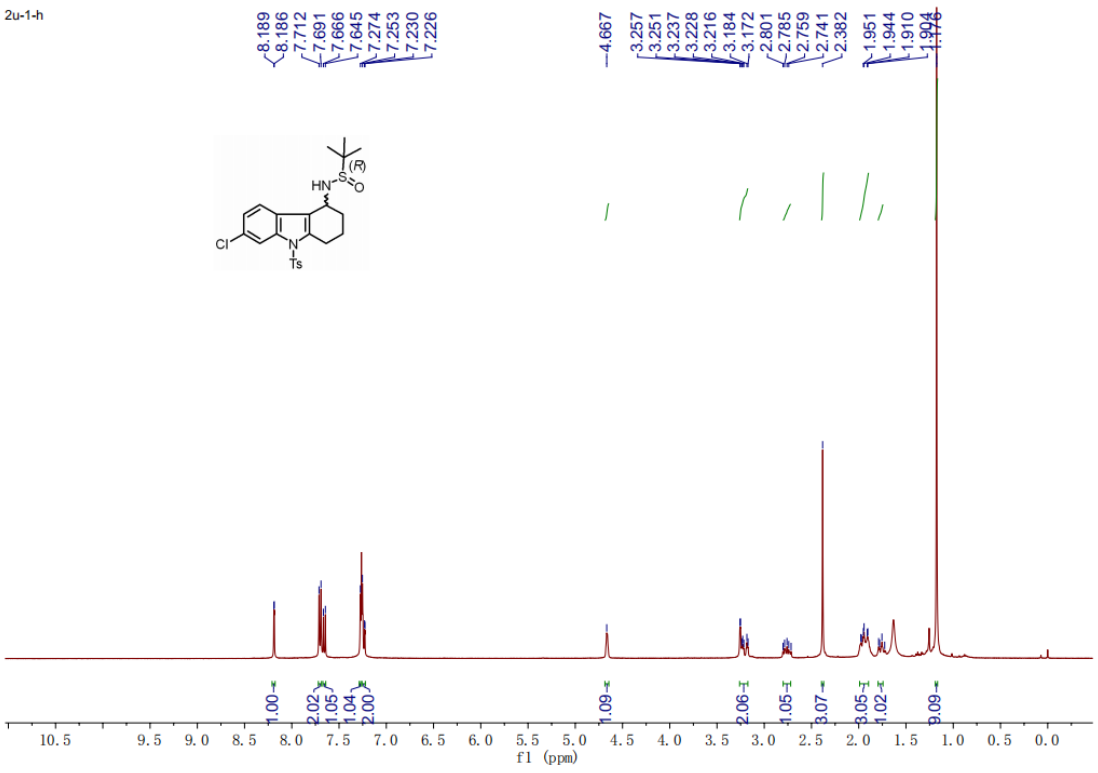
^{1}H NMR spectrum of (-)-2j



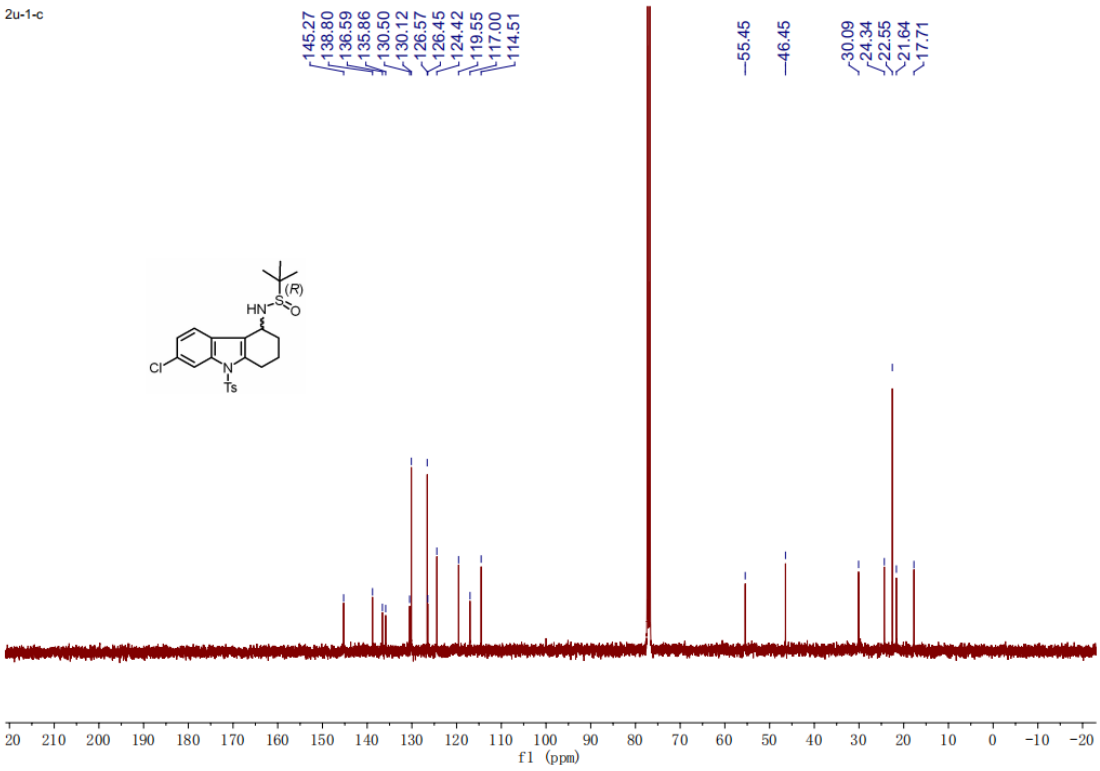
^{13}C NMR spectrum of (-)-2j



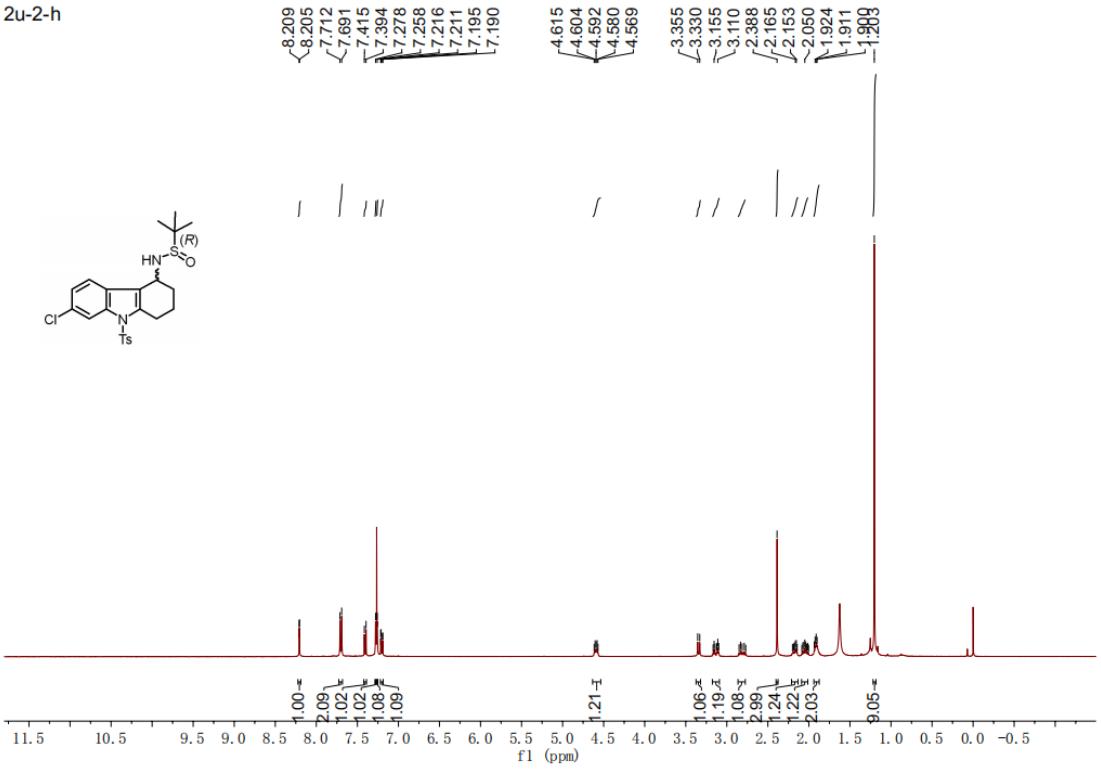
^{1}H NMR spectrum of (+)-2k



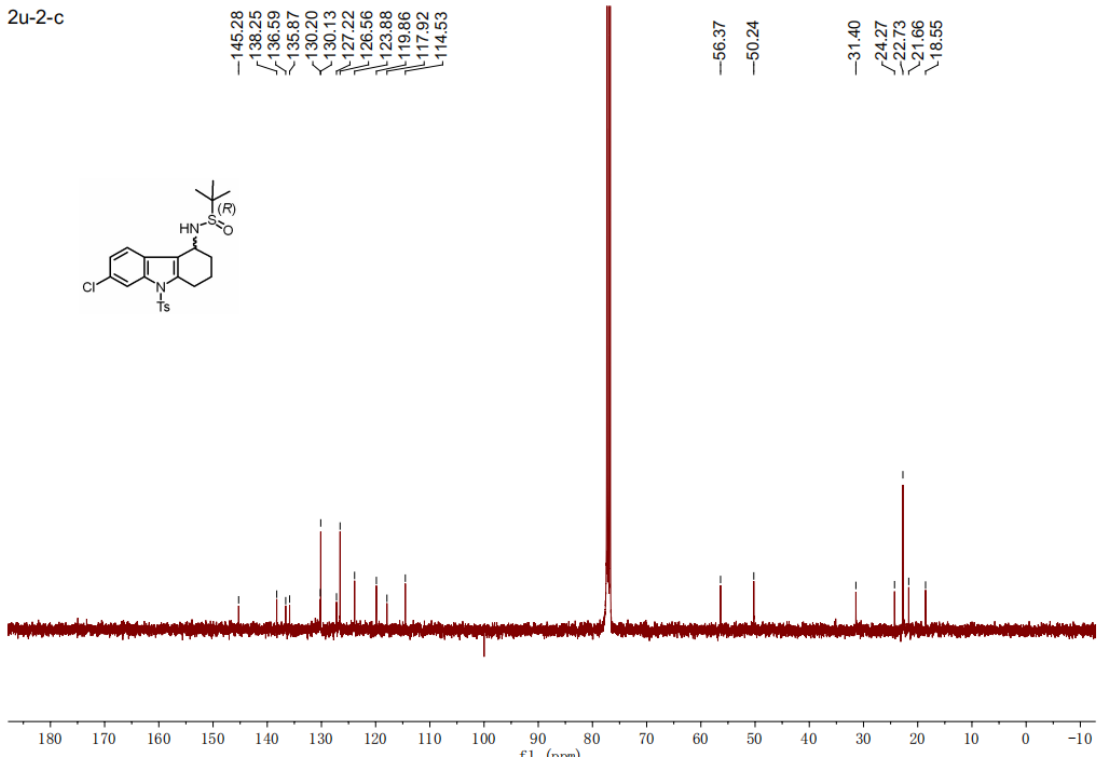
^{13}C NMR spectrum of (+)-2k



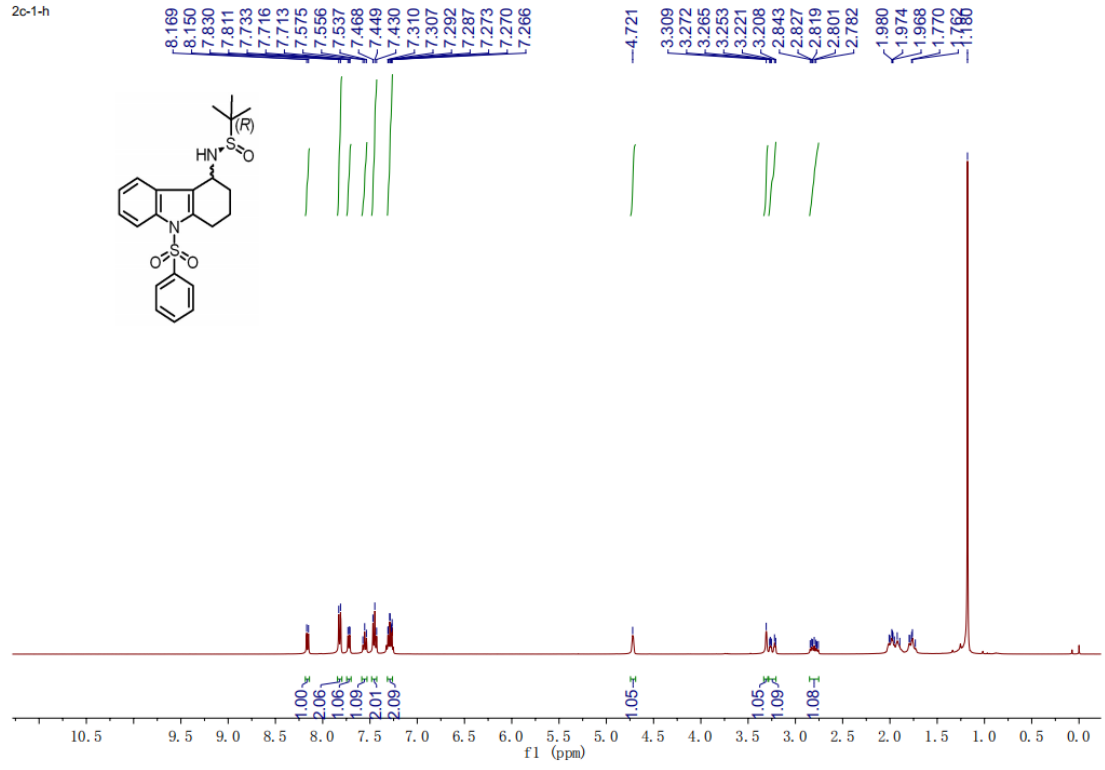
^{1}H NMR spectrum of (-)-2k



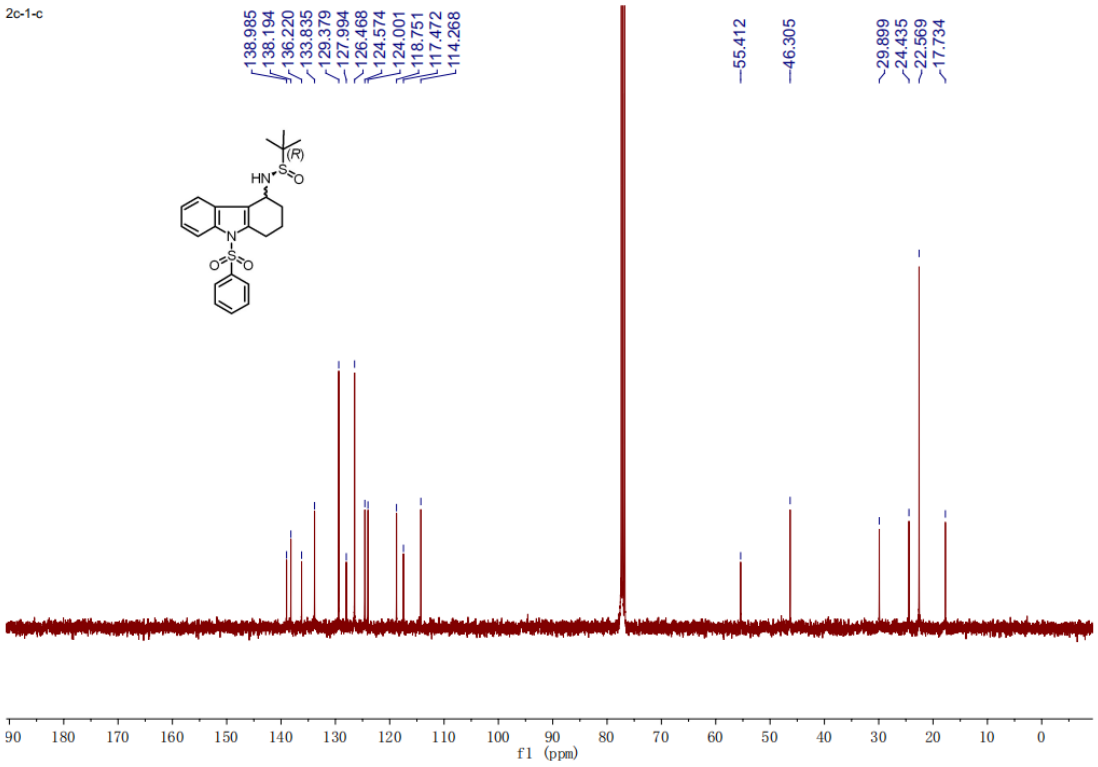
^{13}C NMR spectrum of (-)-2k



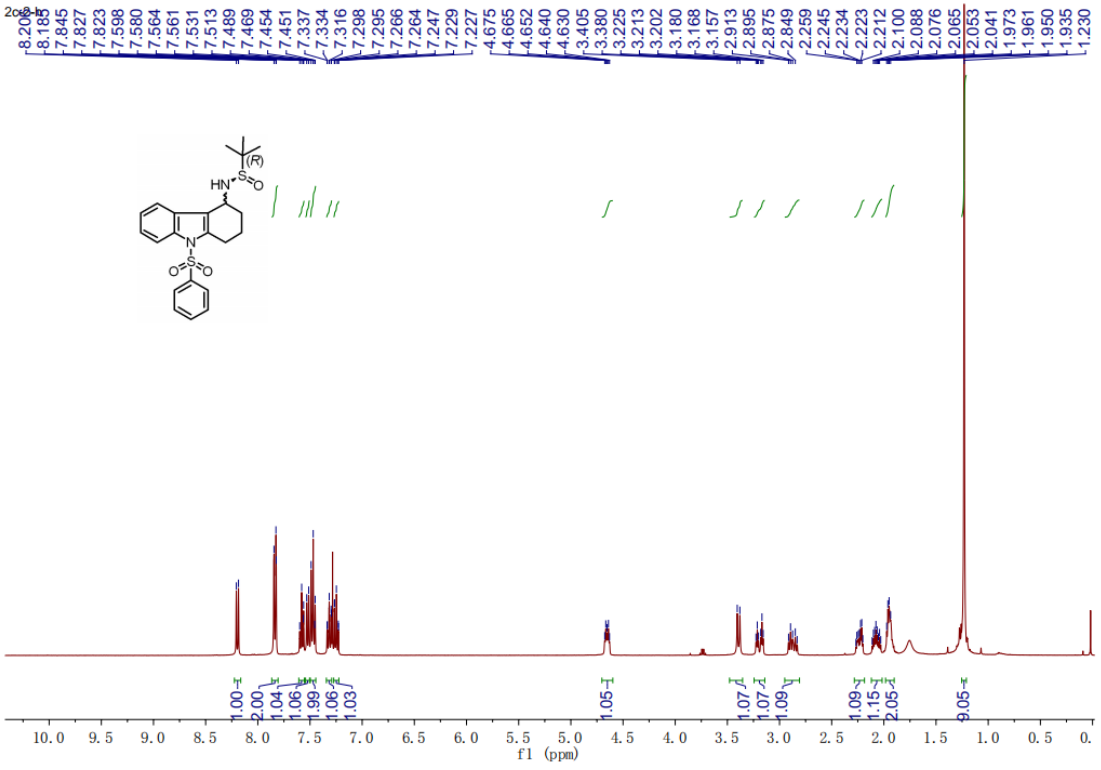
^{1}H NMR spectrum of (+)-2l



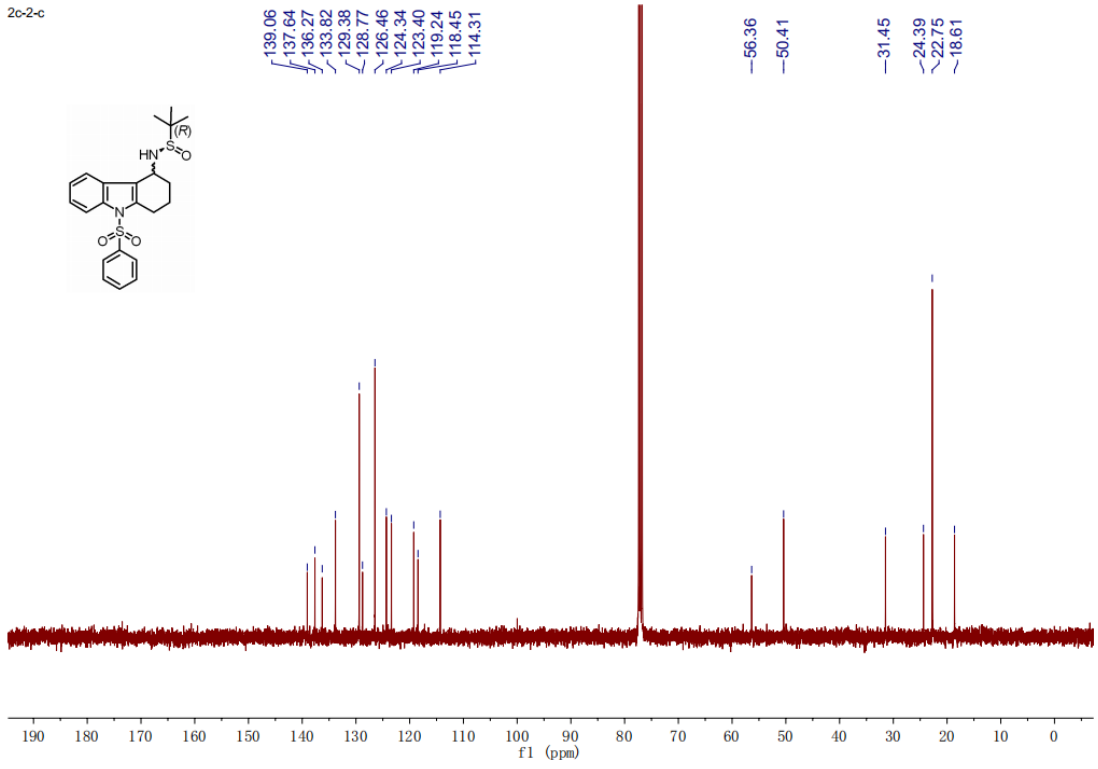
^{13}C NMR spectrum of (+)-2l



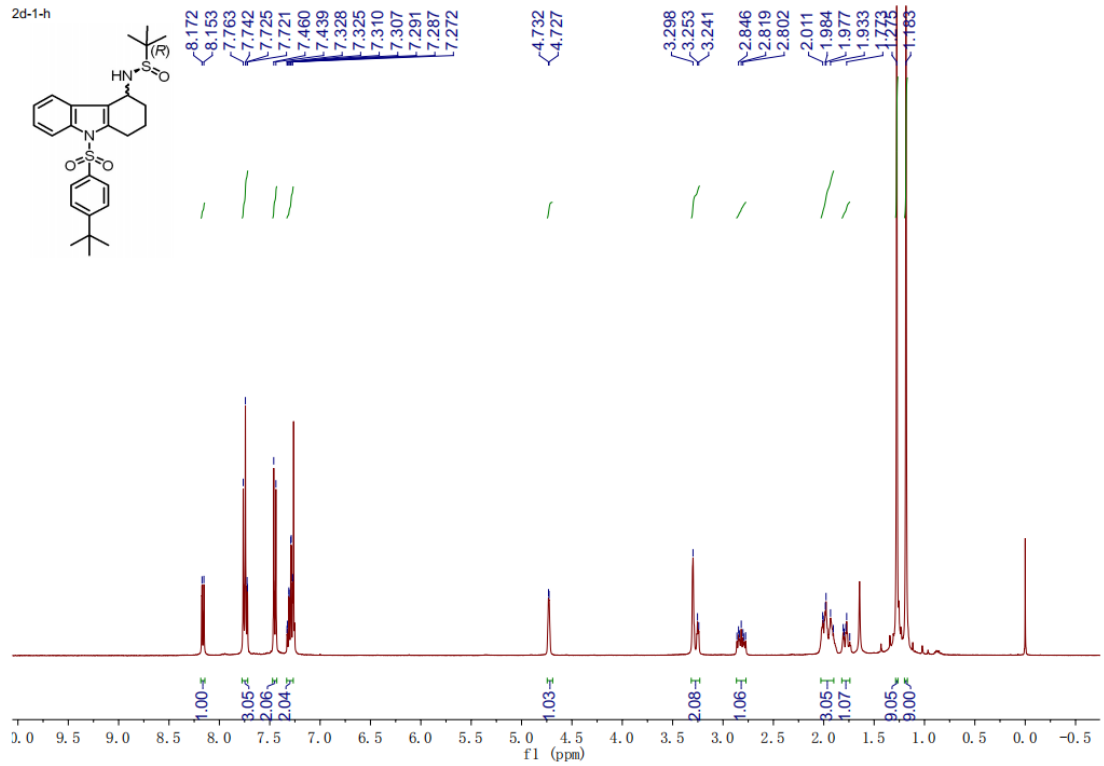
^{1}H NMR spectrum of (-)-2l



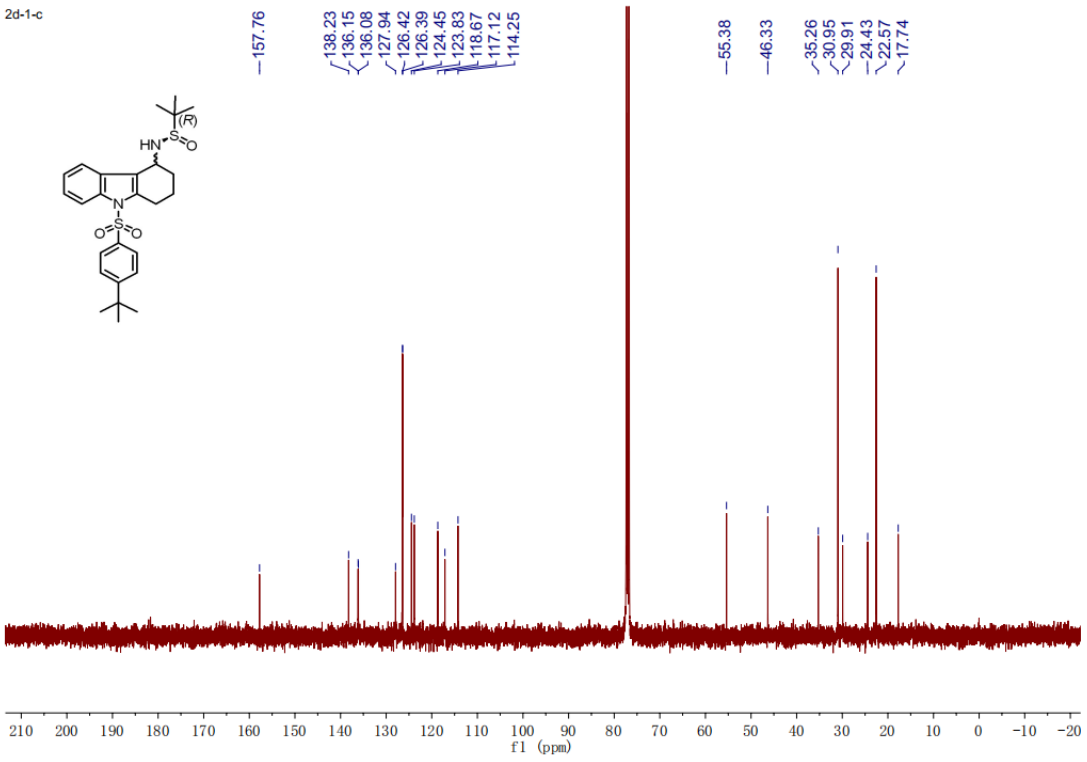
^{13}C NMR spectrum of (-)-2l



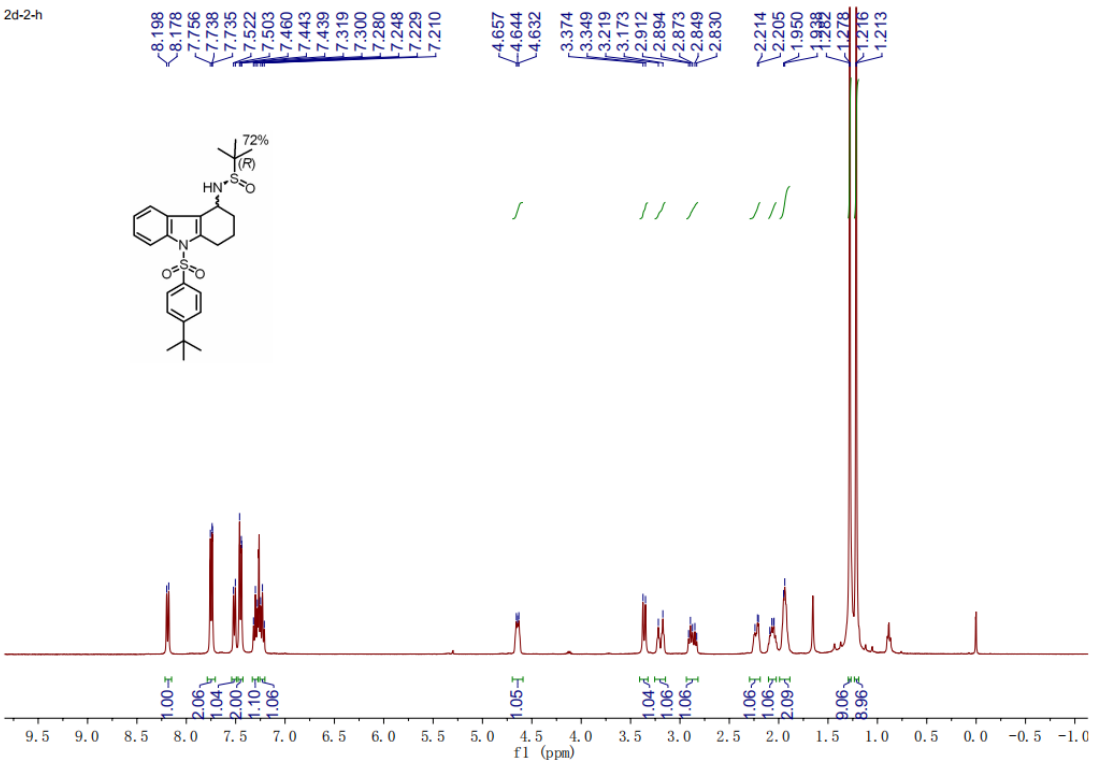
^{1}H NMR spectrum of (+)-2m



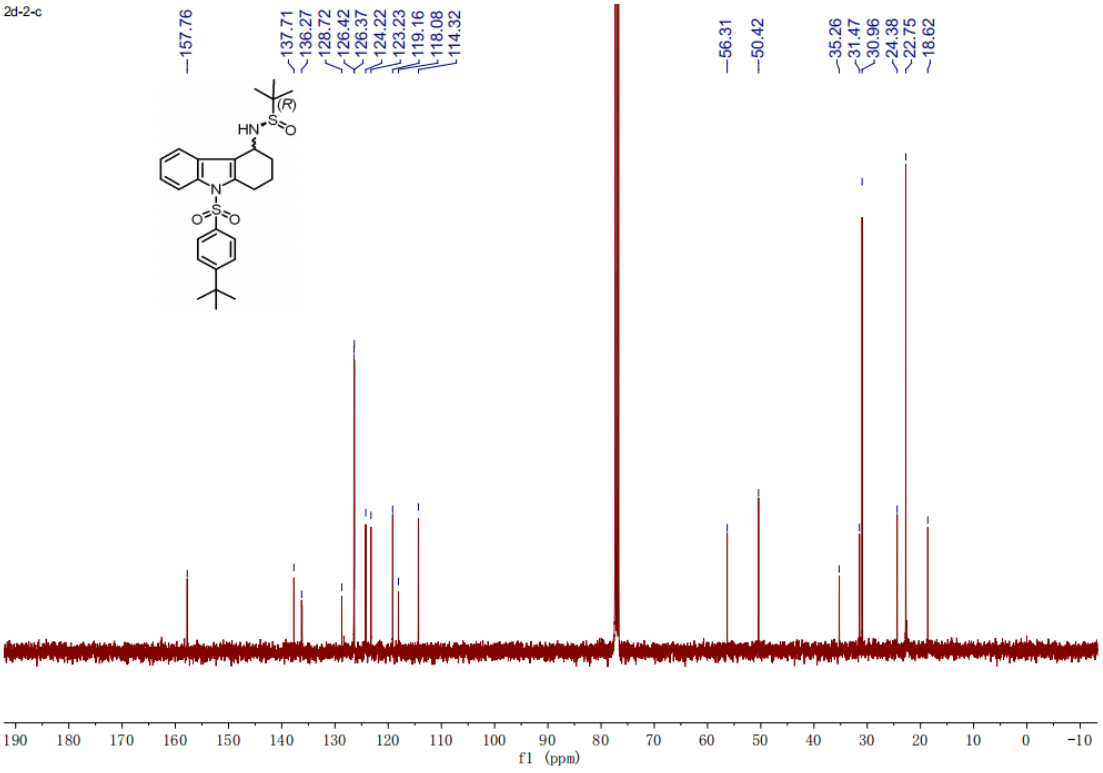
^{13}C NMR spectrum of (+)-2m



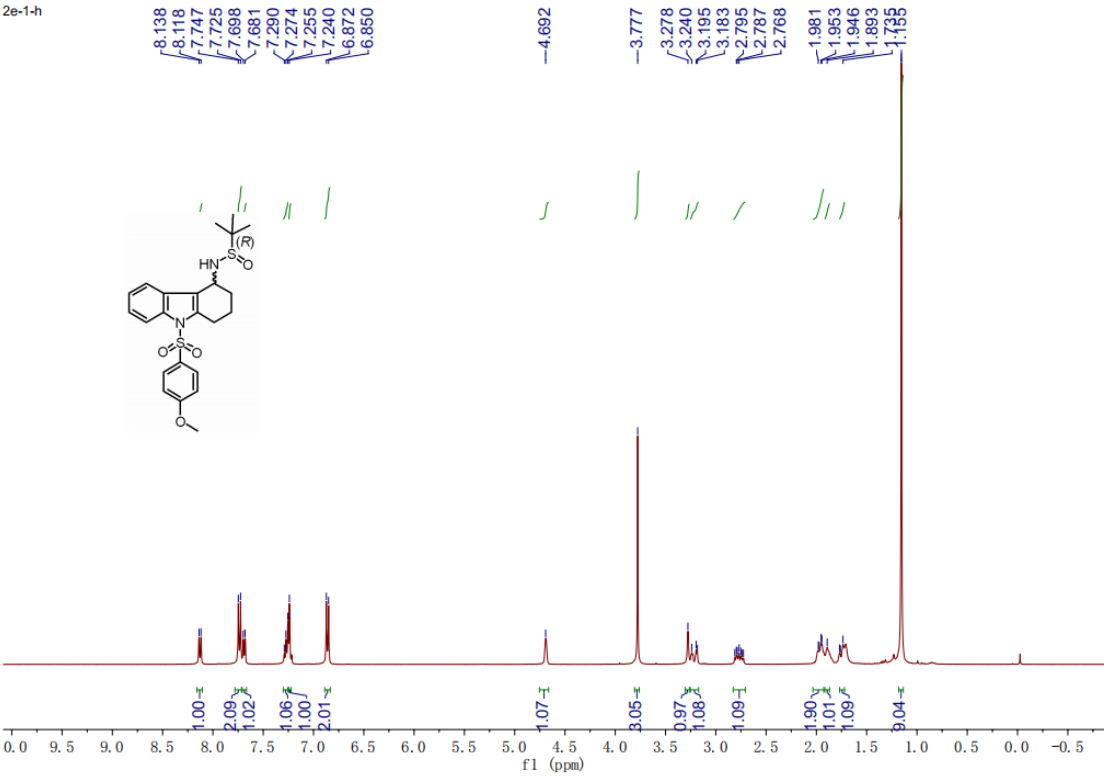
^{1}H NMR spectrum of (-)-2m



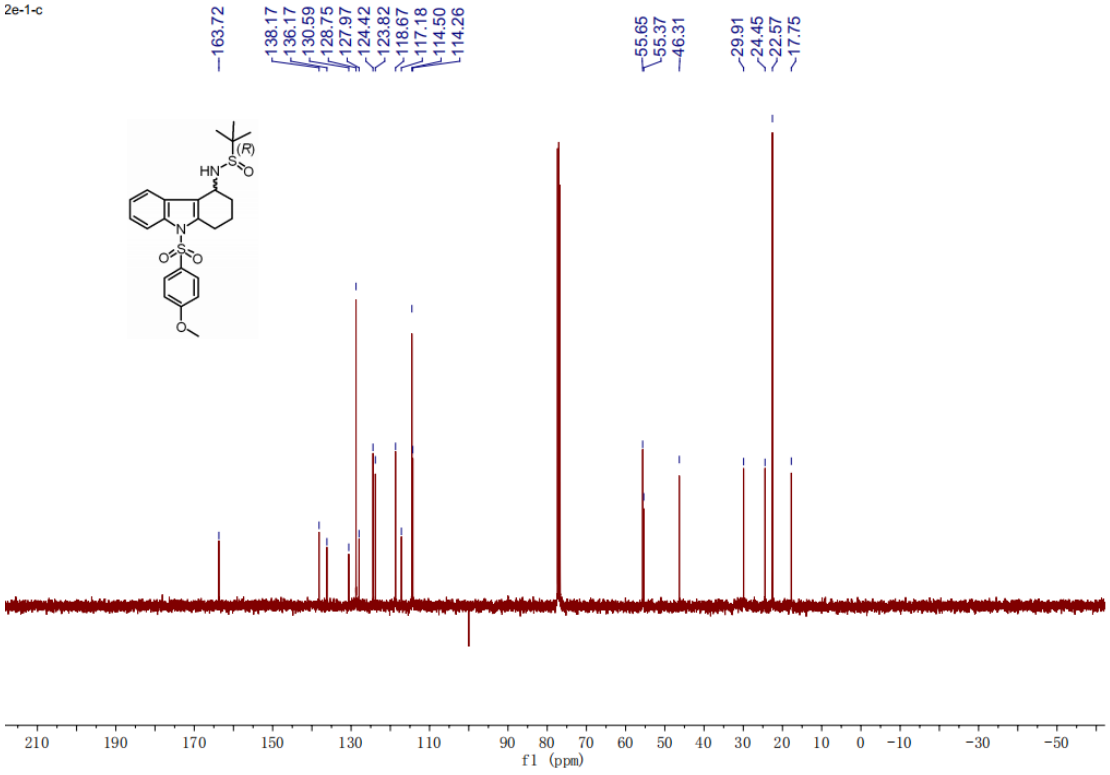
^{13}C NMR spectrum of (-)-2m



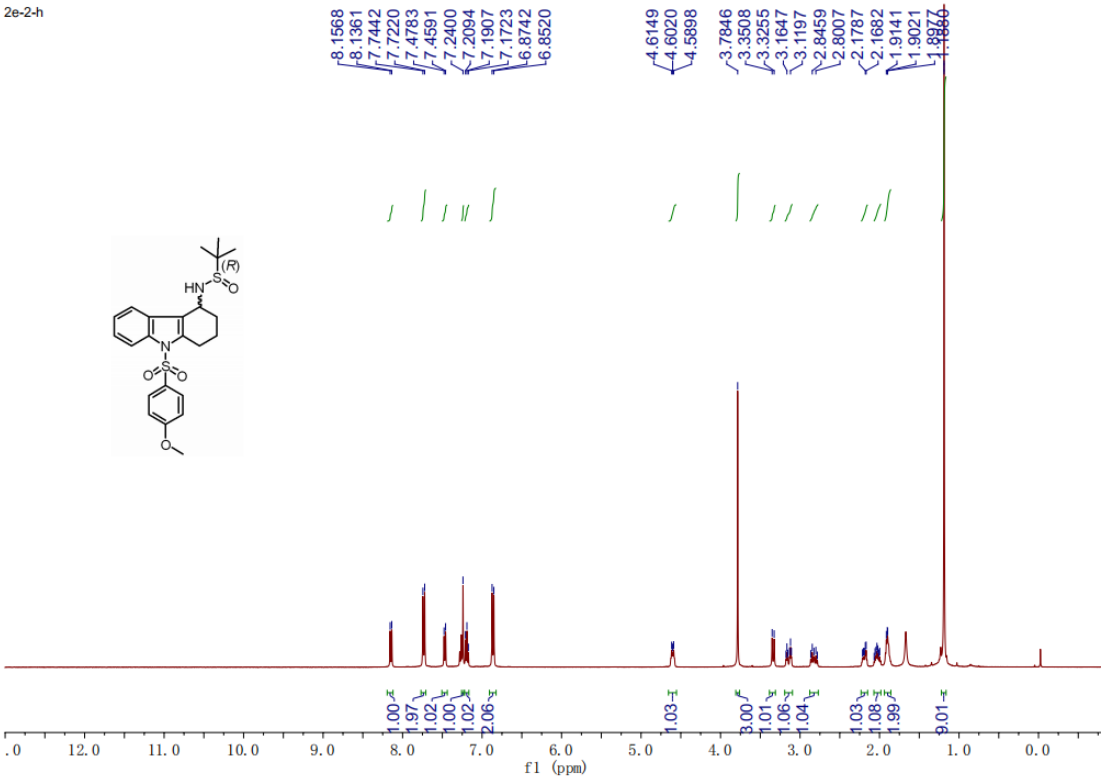
^{1}H NMR spectrum of (+)-2n



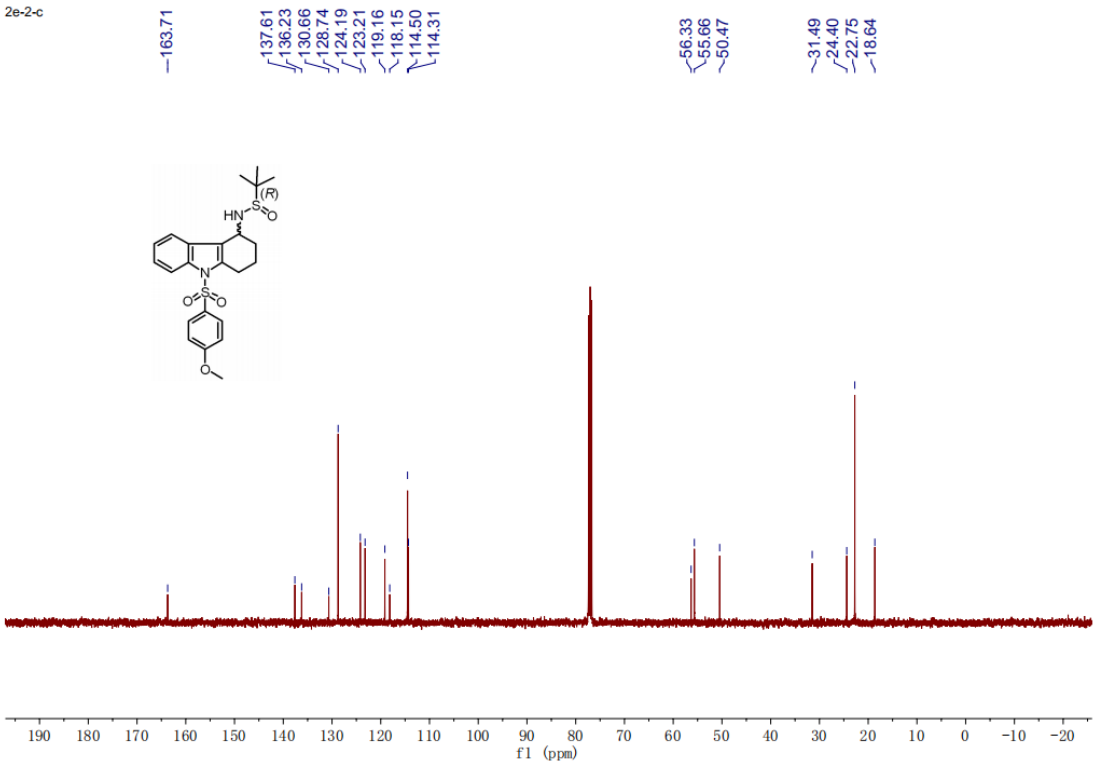
^{13}C NMR spectrum of (+)-2n



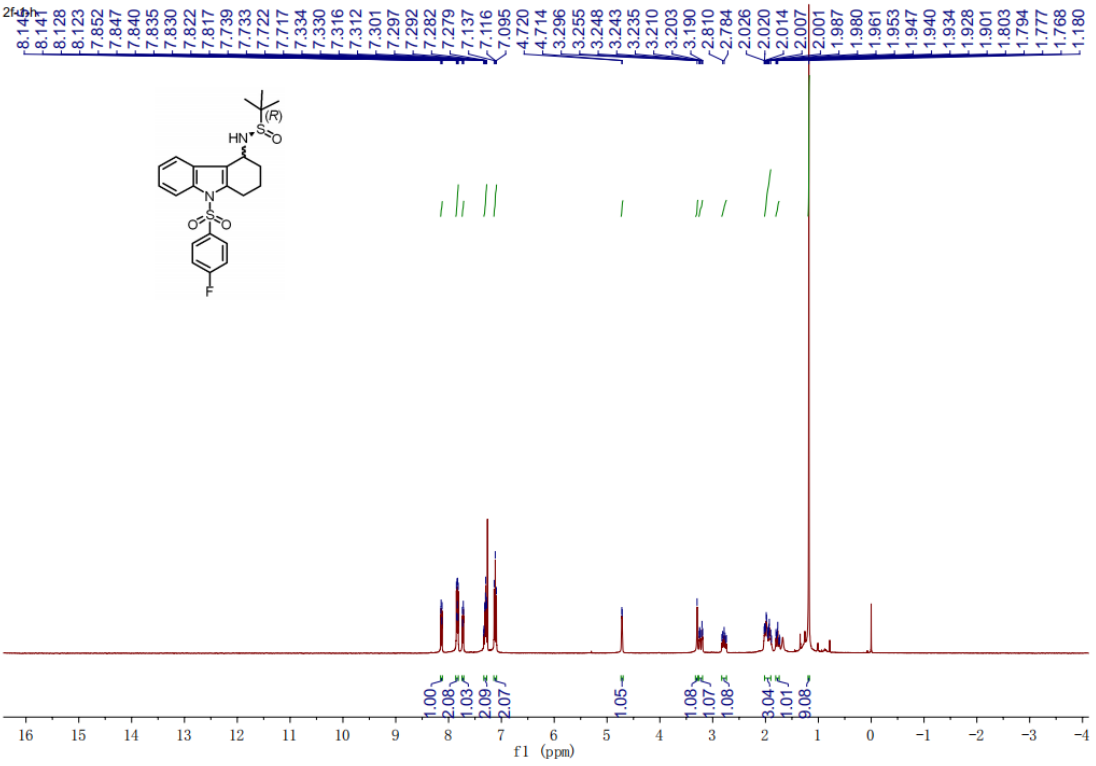
^{1}H NMR spectrum of (-)-2n



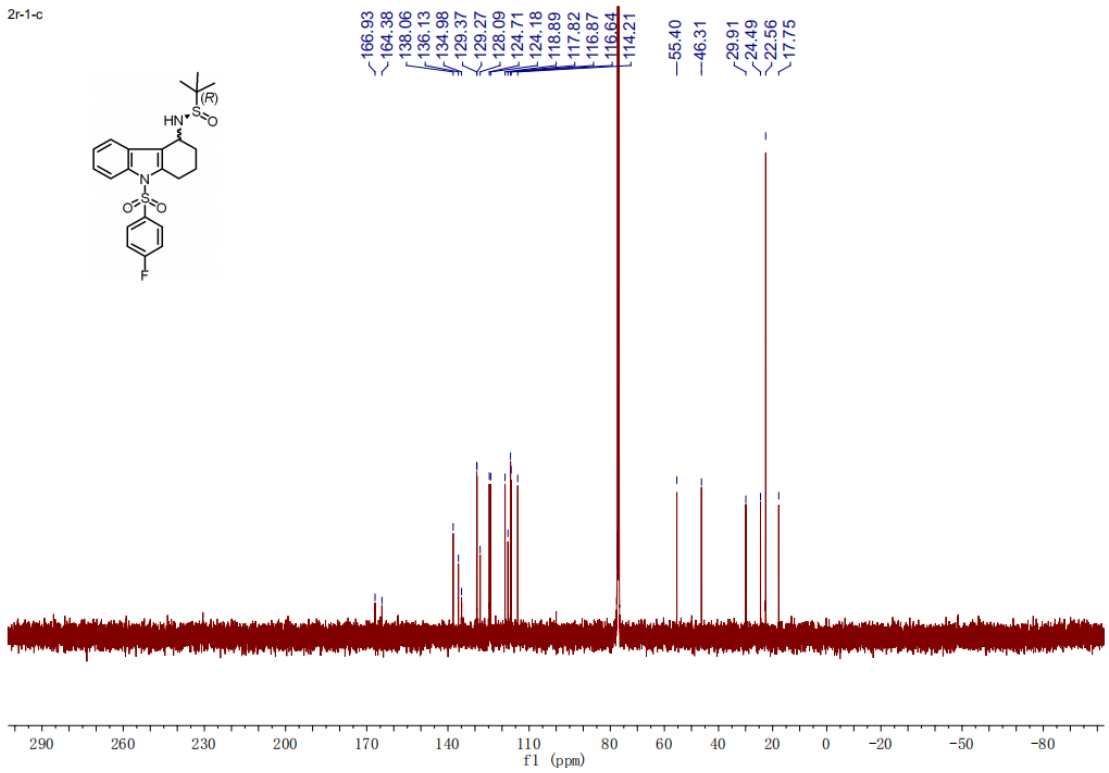
^{13}C NMR spectrum of (-)-2n



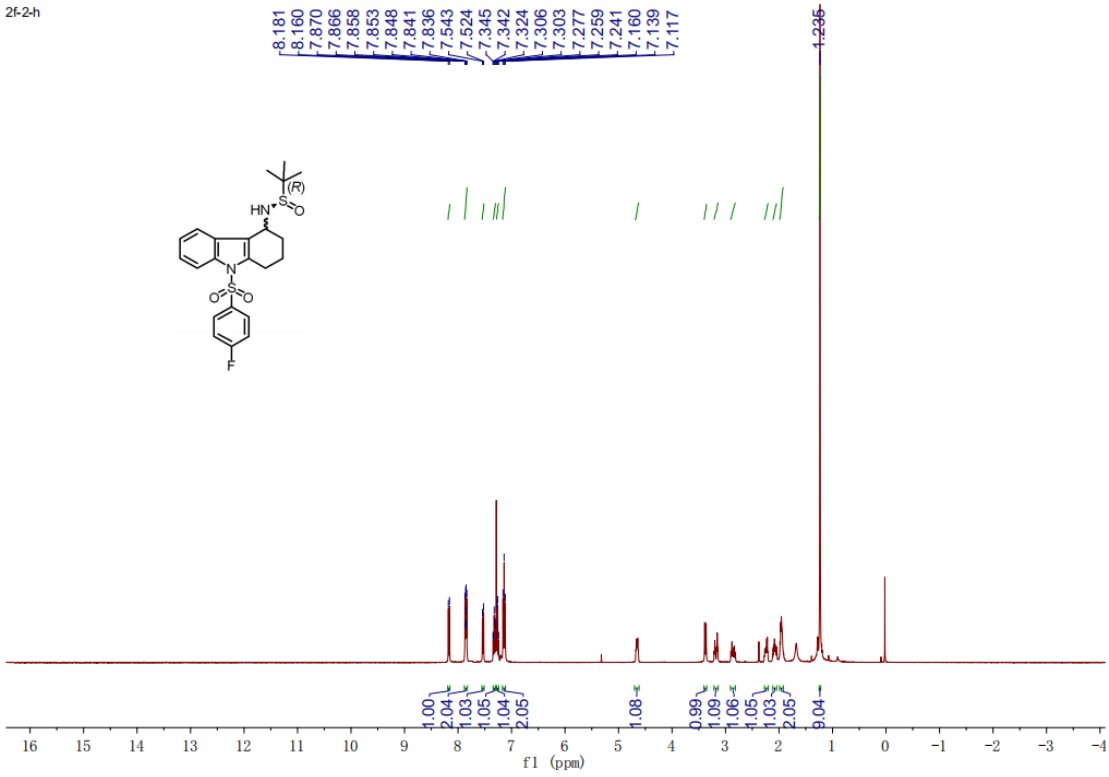
^{1}H NMR spectrum of (+)-2o



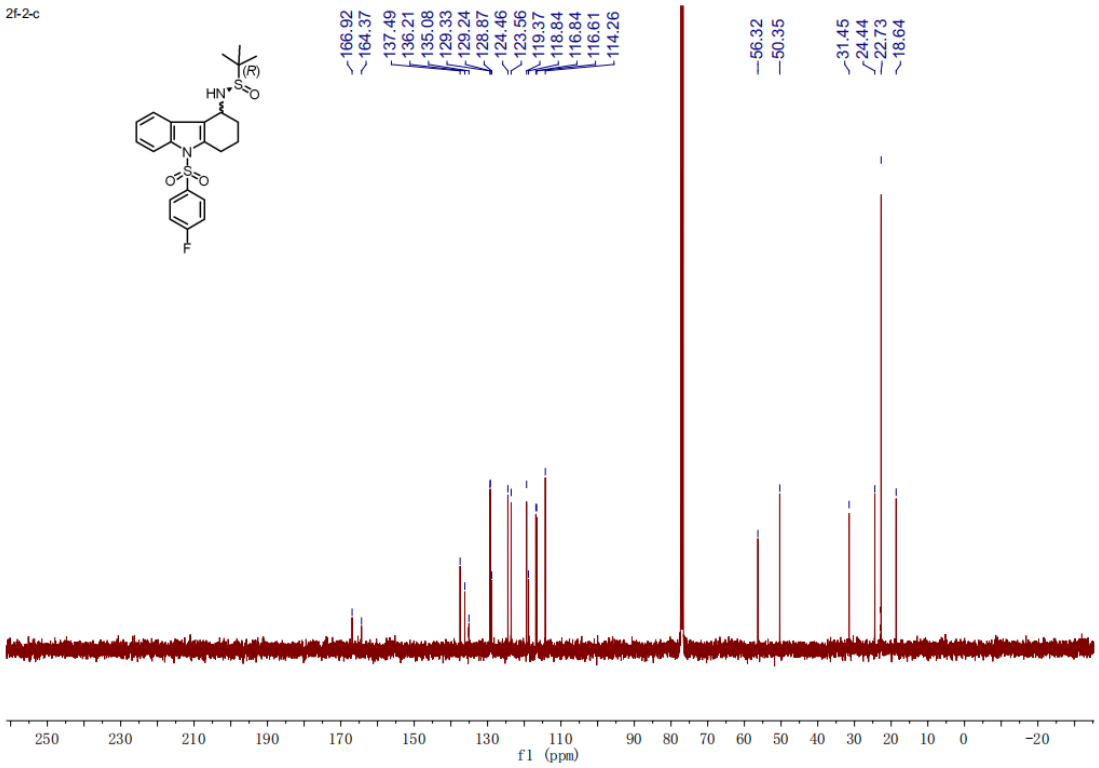
^{13}C NMR spectrum of (+)-2o



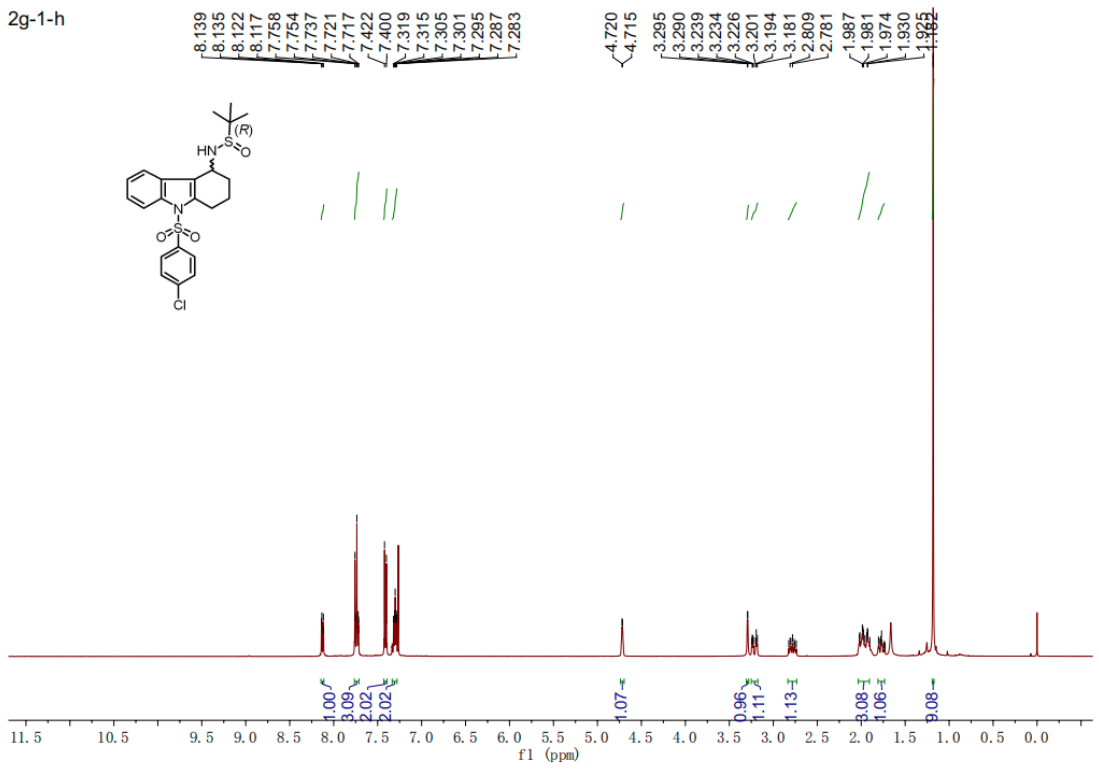
^{1}H NMR spectrum of (-)-2o



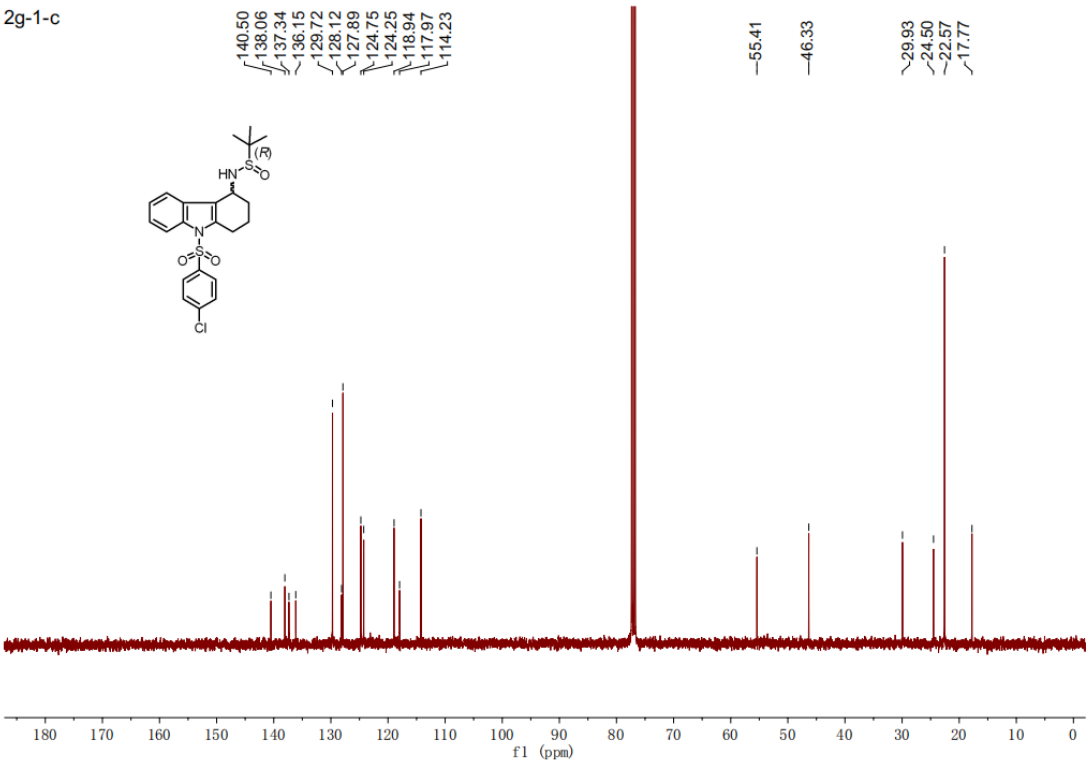
^{13}C NMR spectrum of (-)-2o



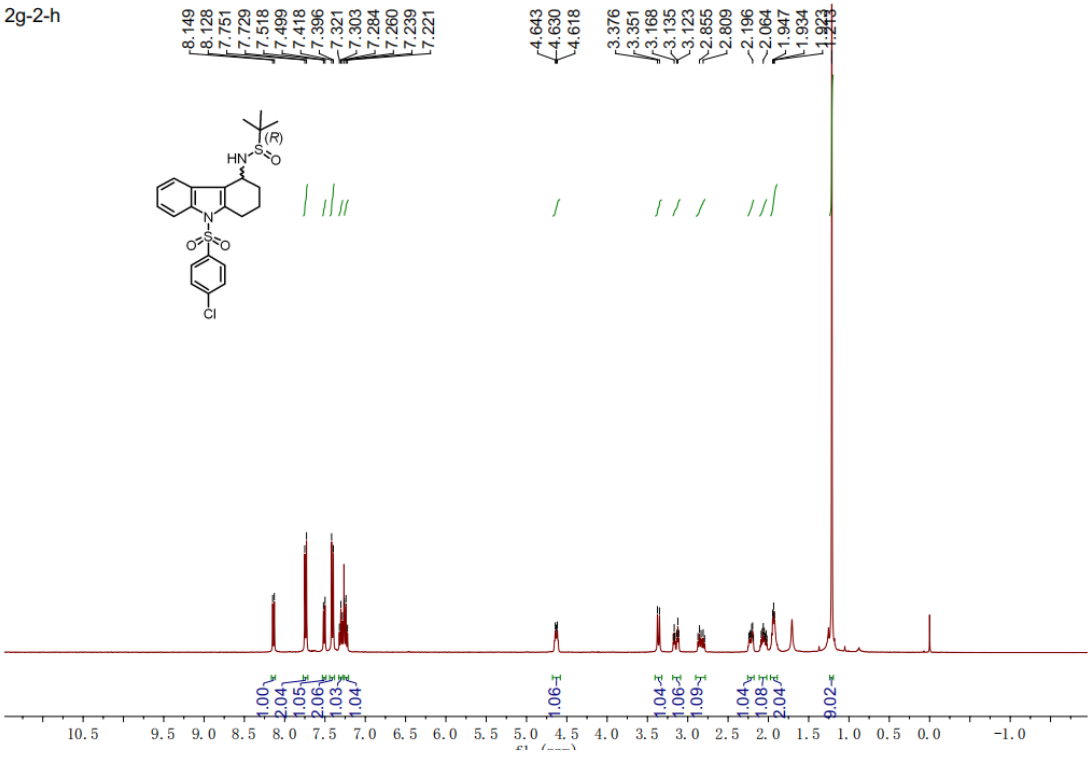
^{1}H NMR spectrum of (+)-2p



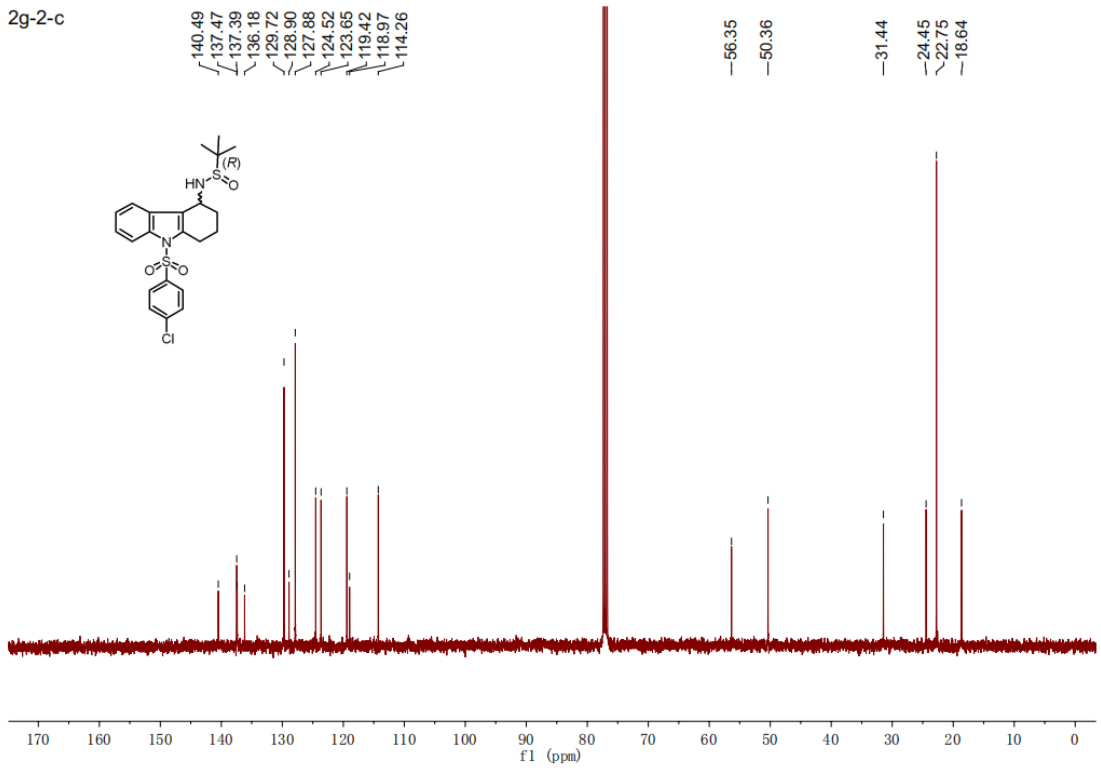
^{13}C NMR spectrum of (+)-2p



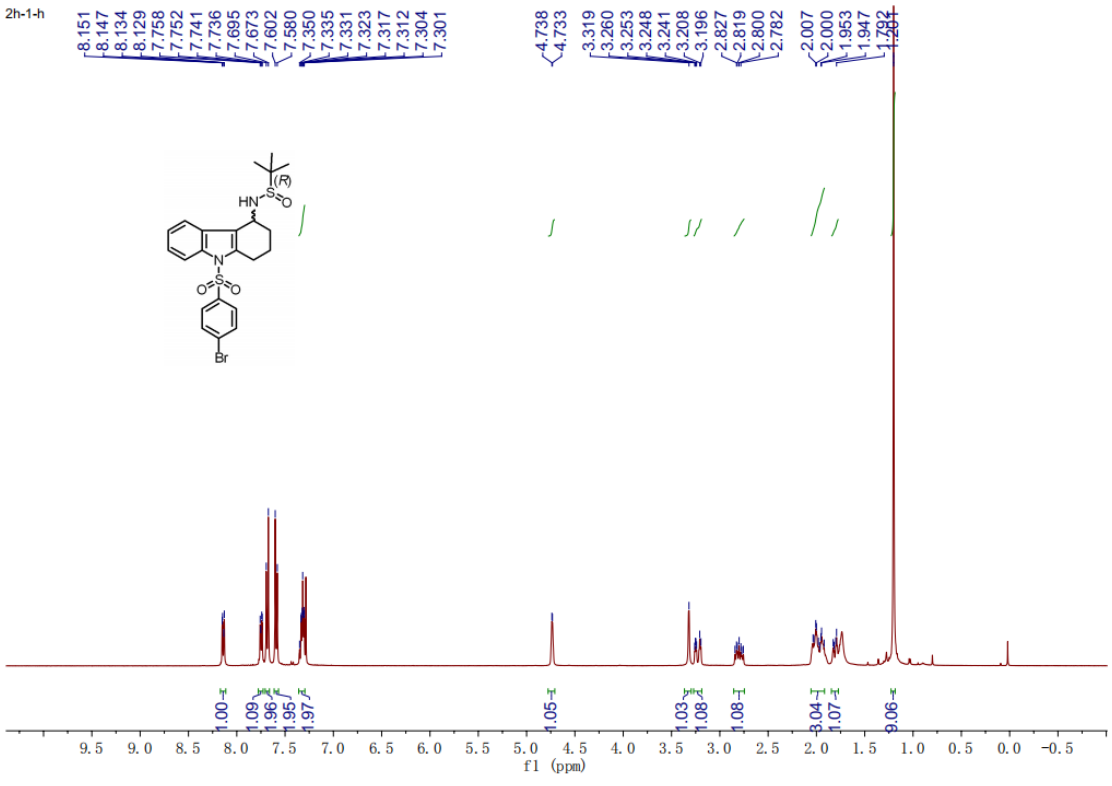
^{1}H NMR spectrum of (-)-2p



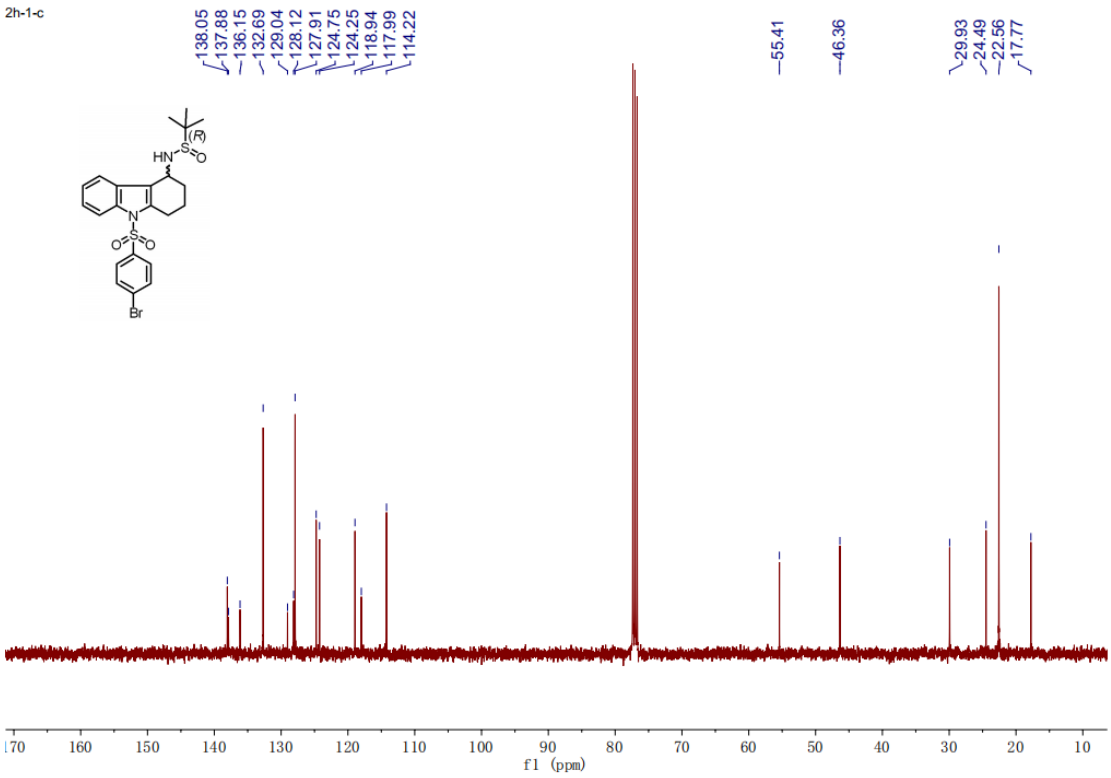
^{13}C NMR spectrum of (-)-2p



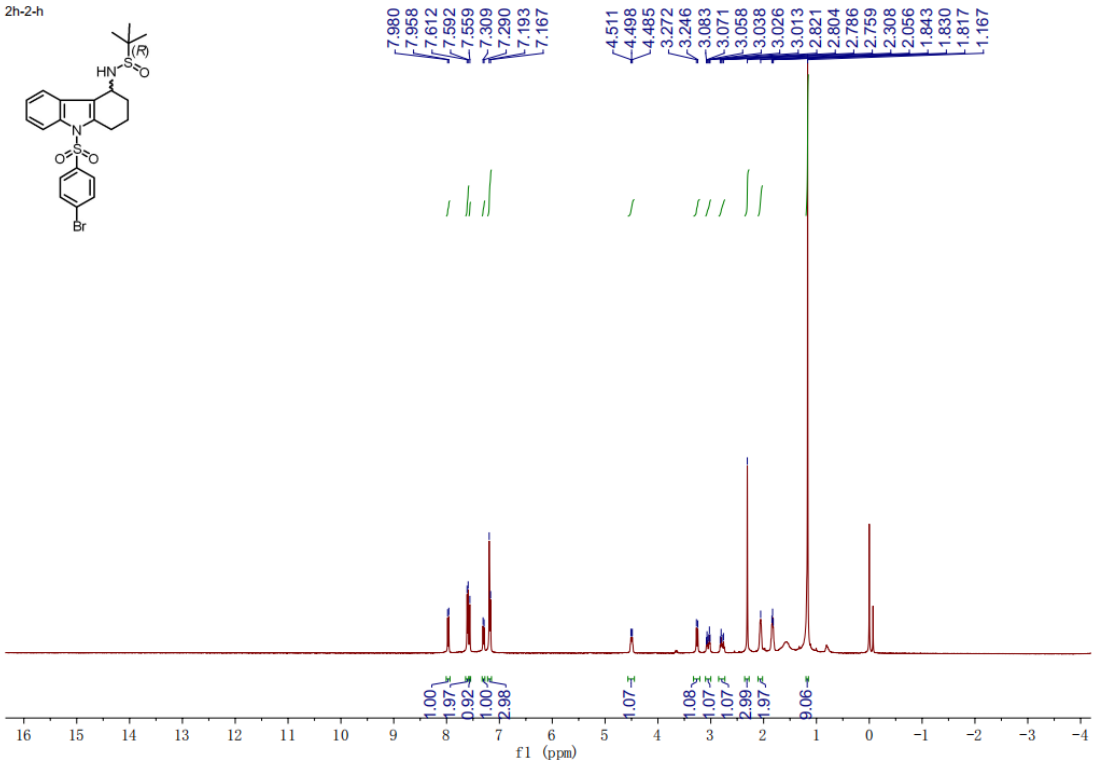
^{1}H NMR spectrum of (+)-2q



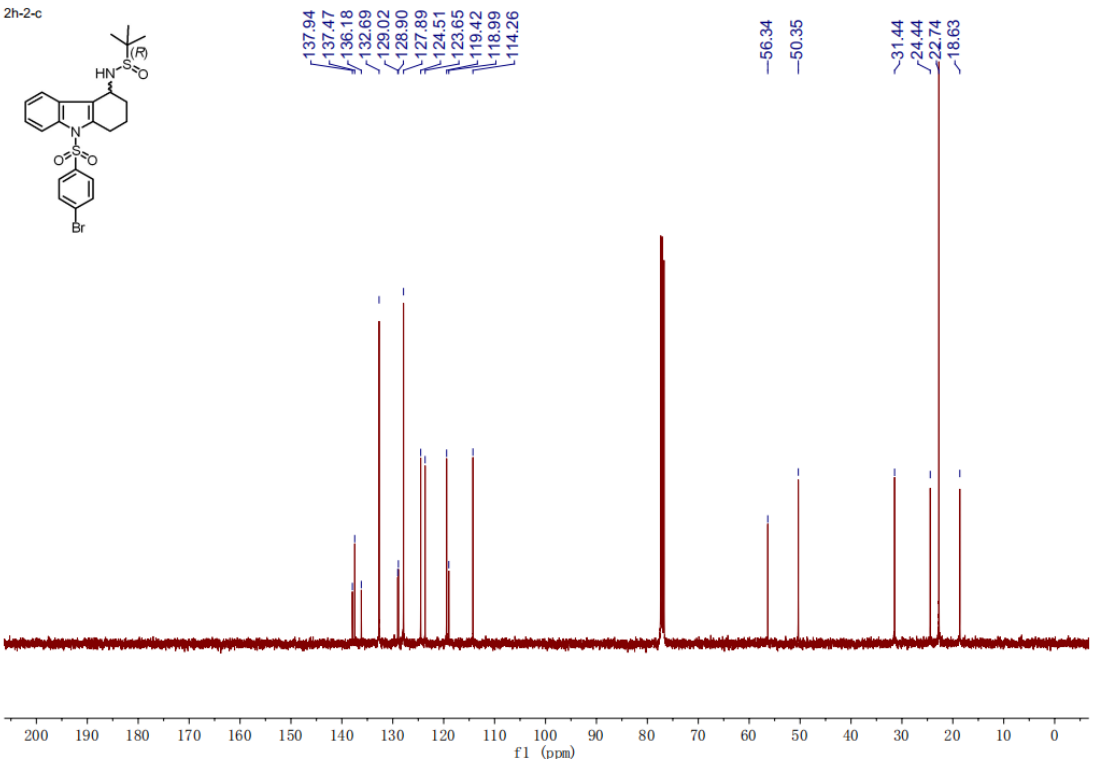
^{13}C NMR spectrum of (+)-2q



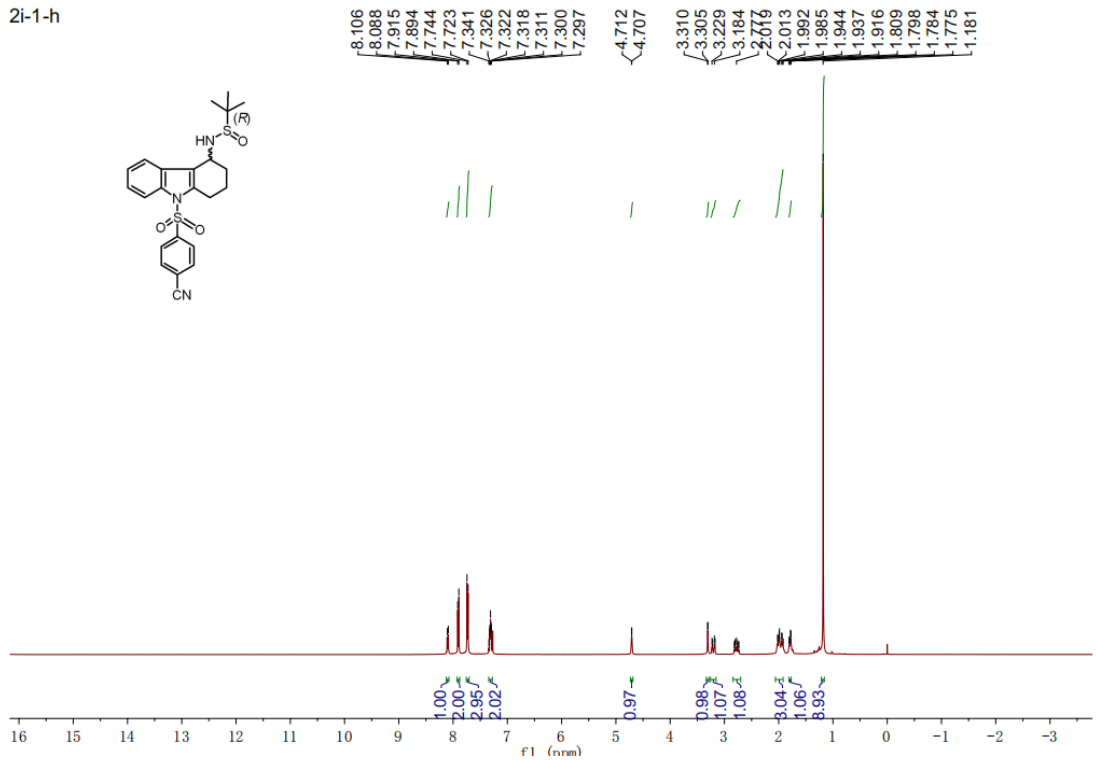
^{1}H NMR spectrum of (-)-2q



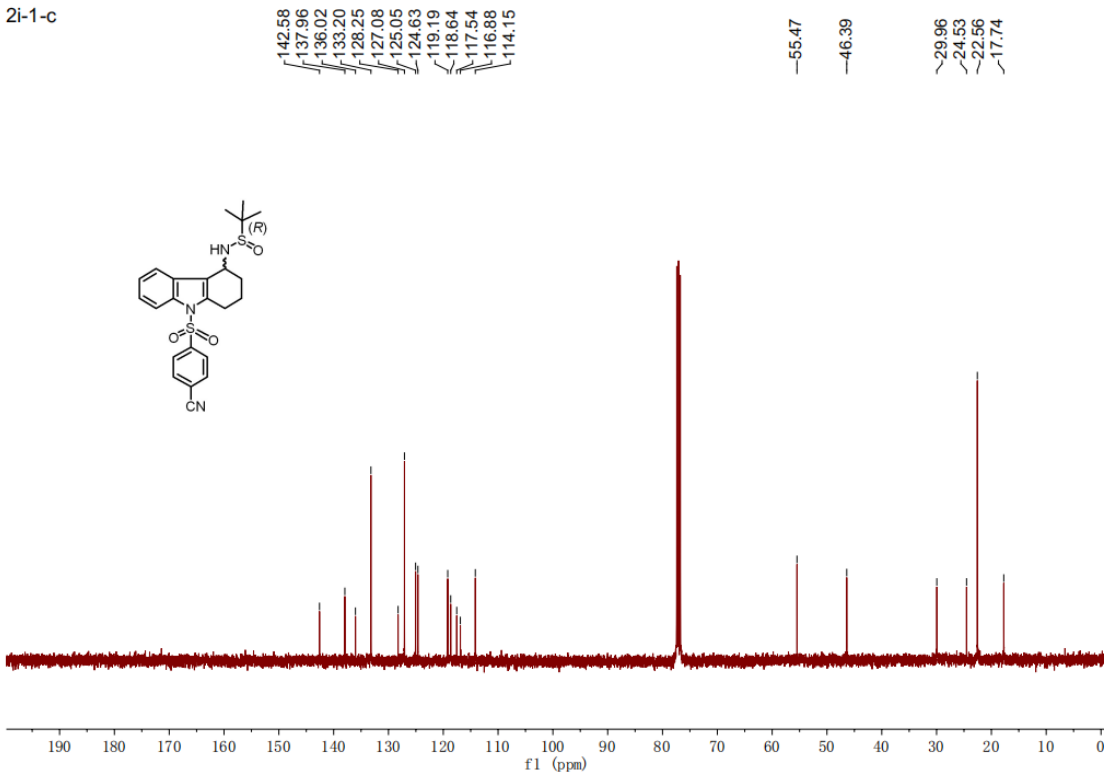
^{13}C NMR spectrum of (-)-2q



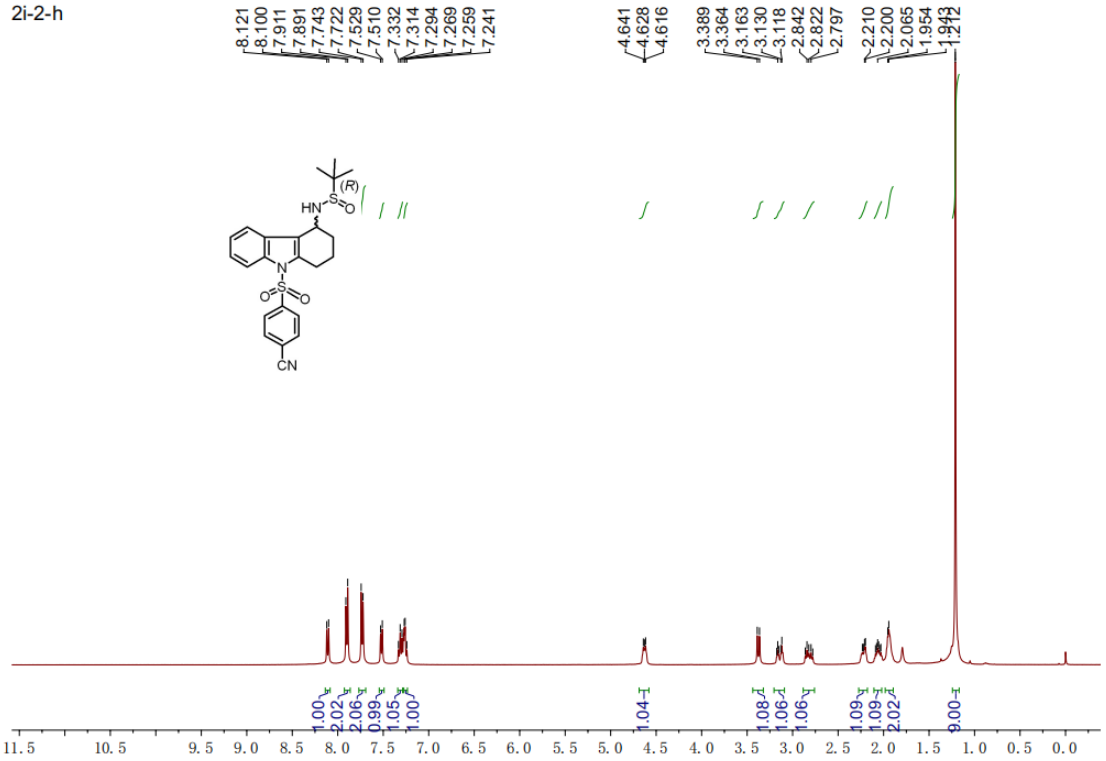
^{1}H NMR spectrum of (+)-2r



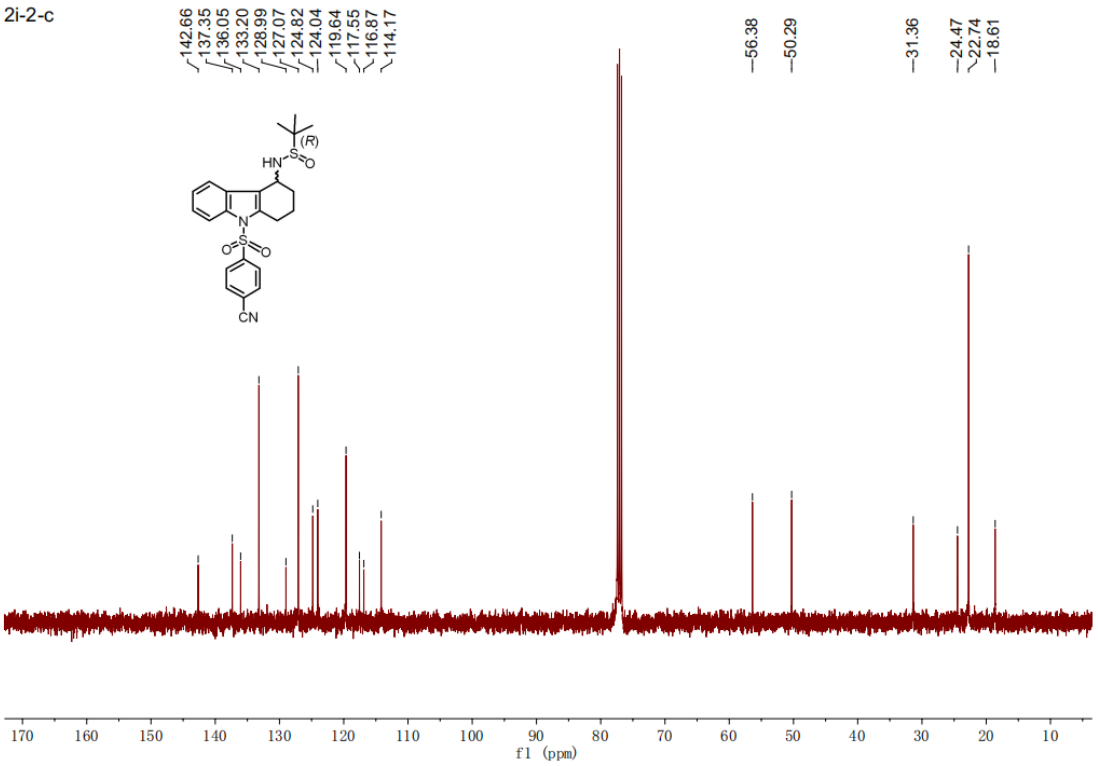
^{13}C NMR spectrum of (+)-2r



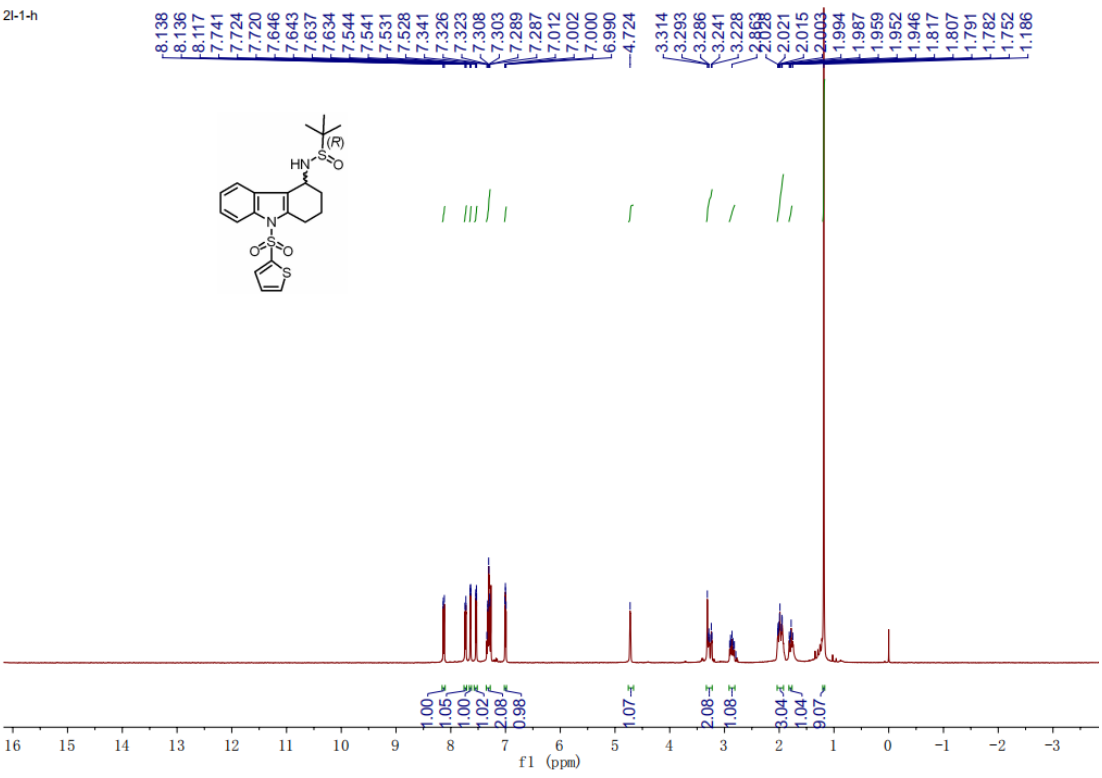
^{1}H NMR spectrum of (-)-2r



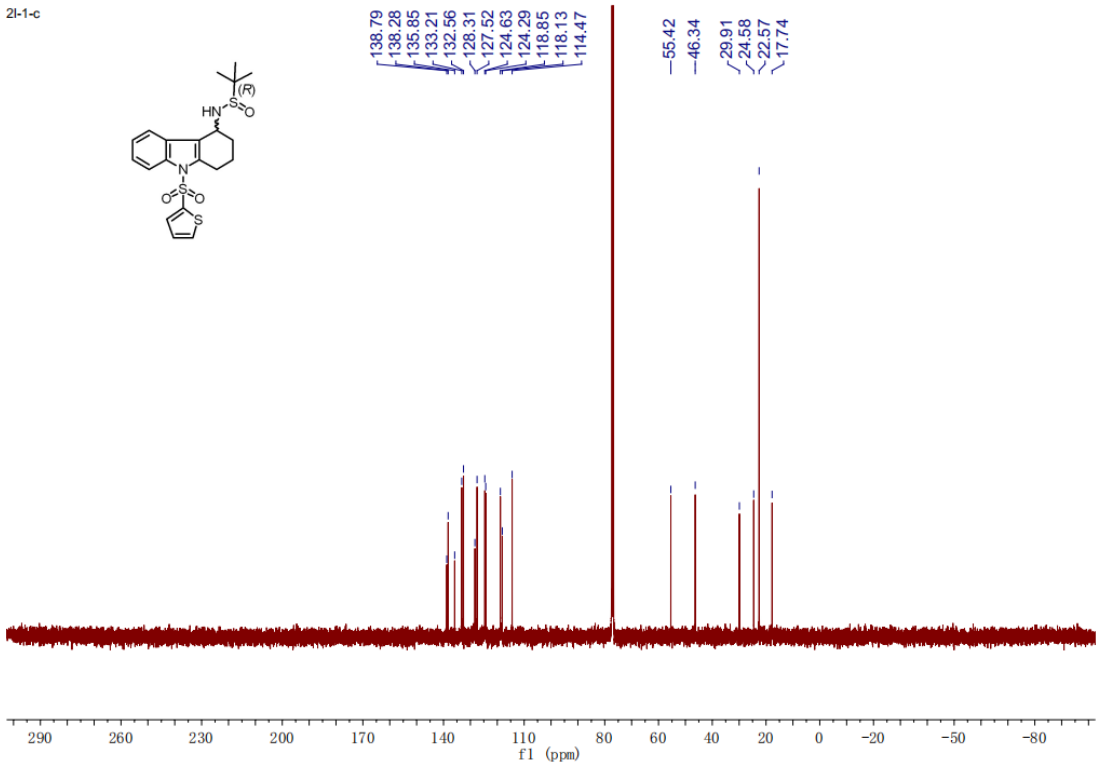
^{13}C NMR spectrum of (-)-2r



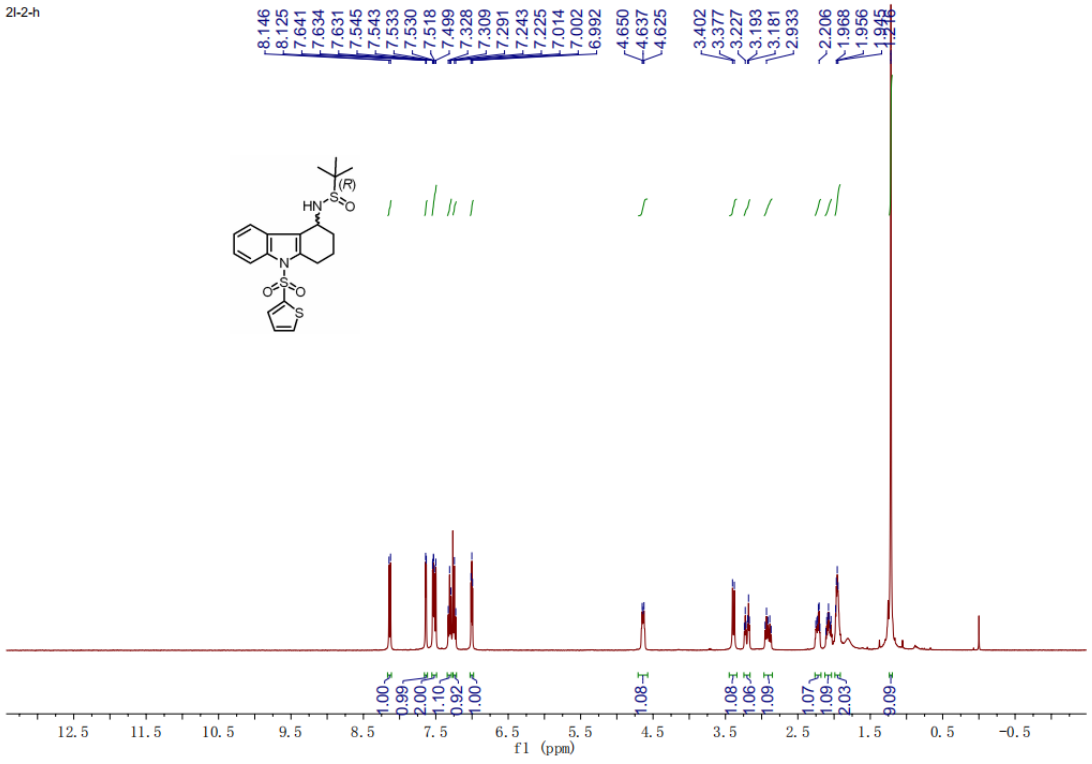
^{1}H NMR spectrum of (+)-2s



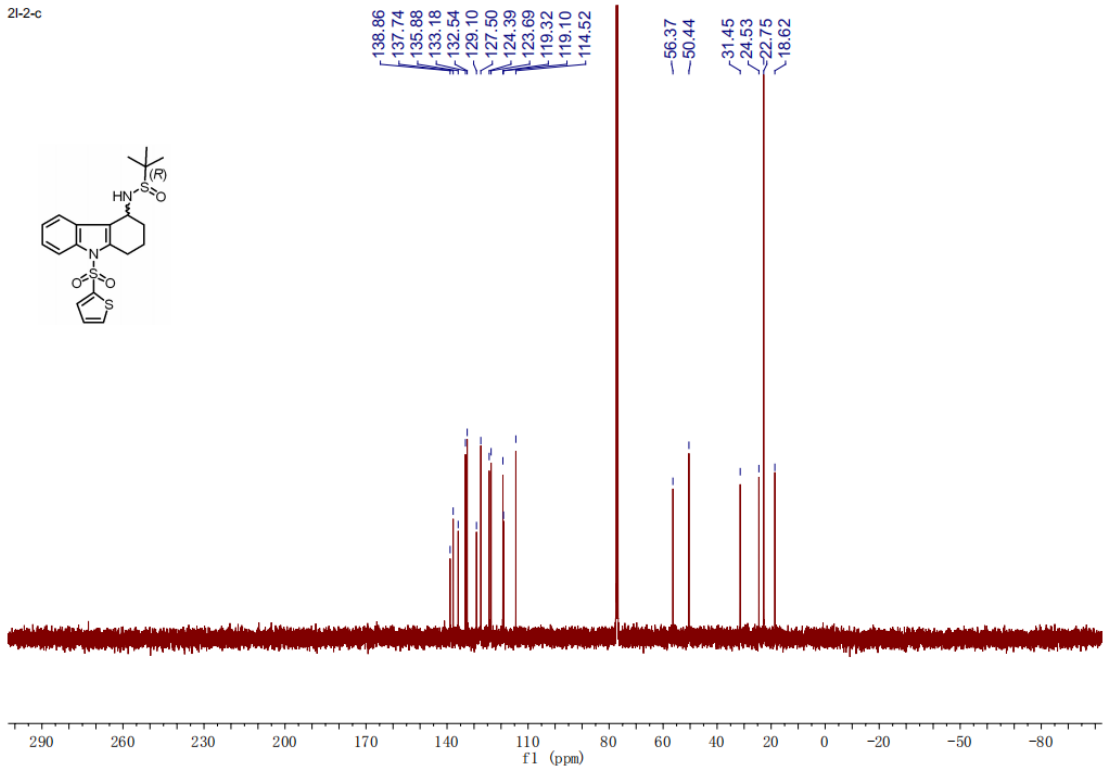
^{13}C NMR spectrum of (+)-2s



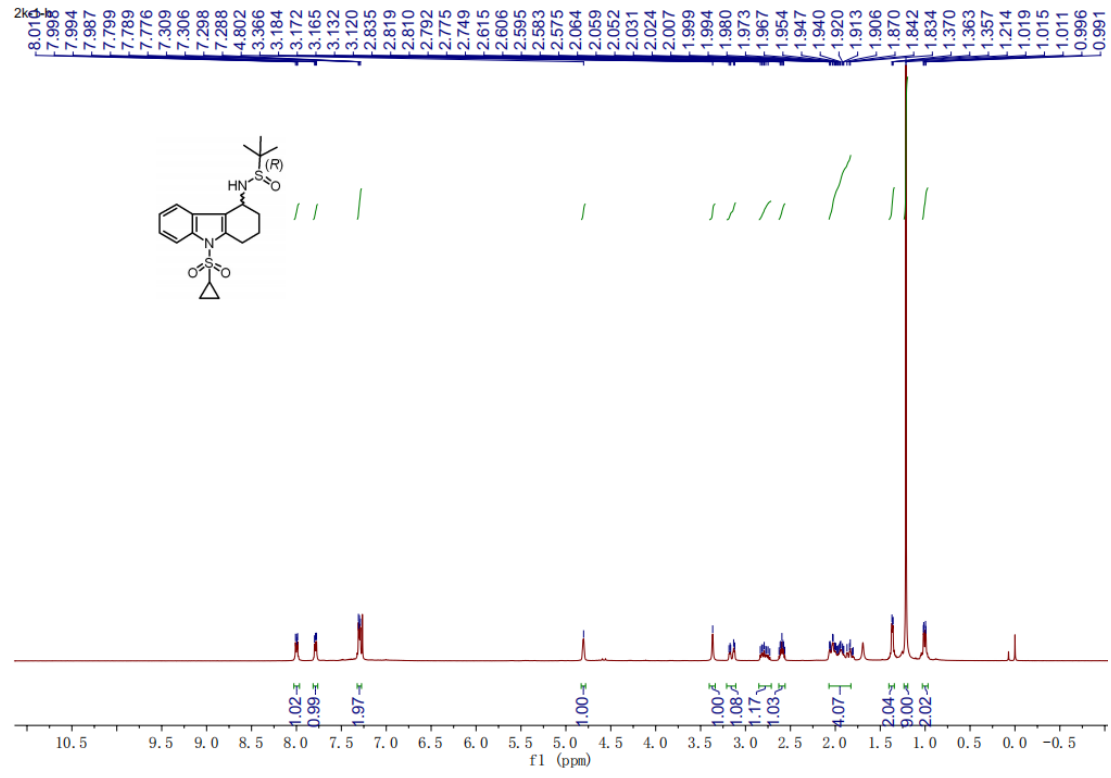
^{1}H NMR spectrum of (-)-2s



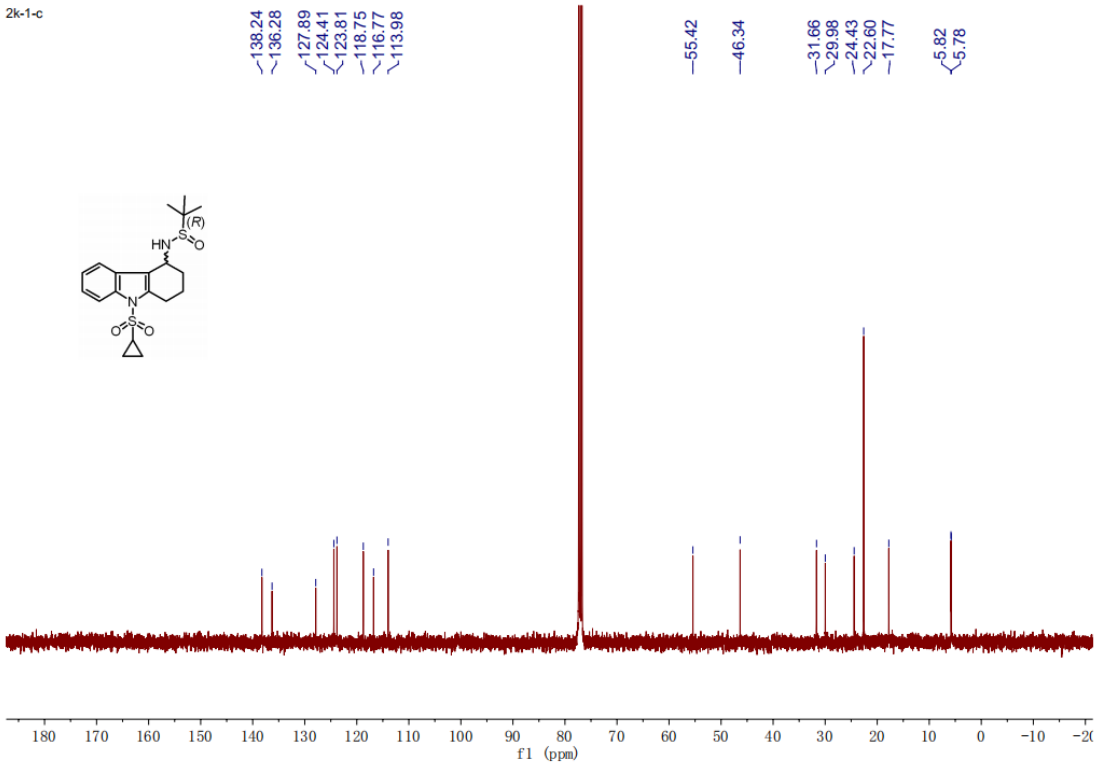
^{13}C NMR spectrum of (-)-2s



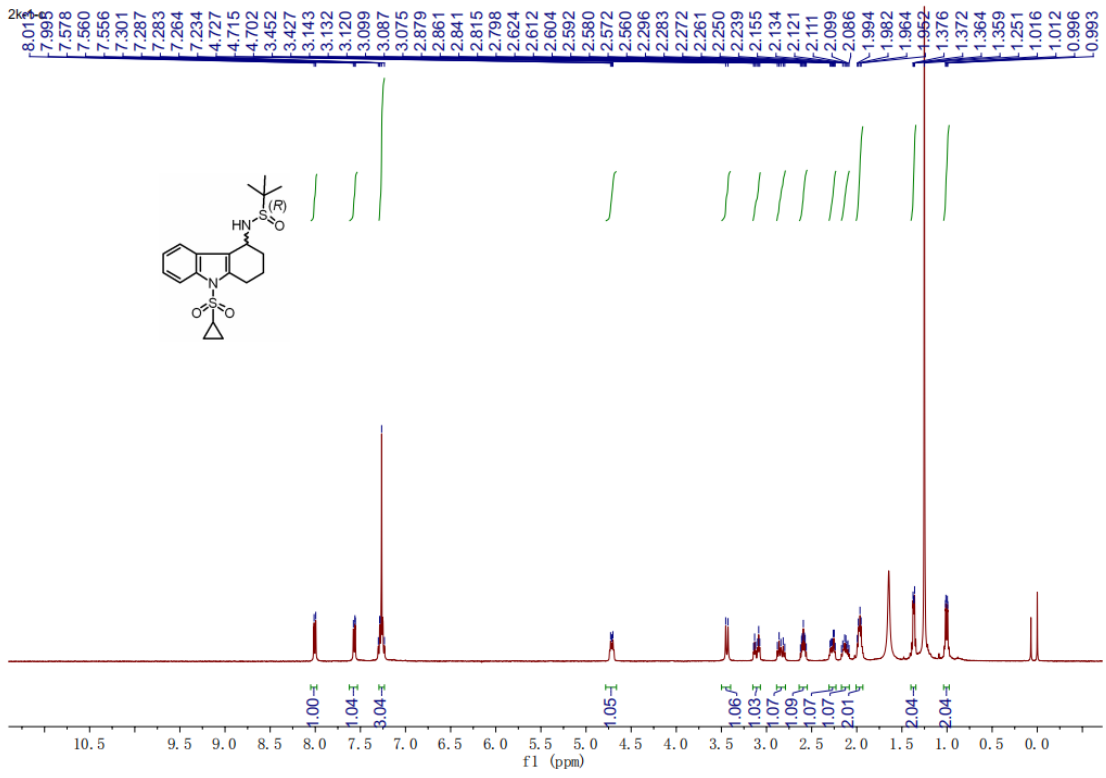
^{1}H NMR spectrum of (+)-2t



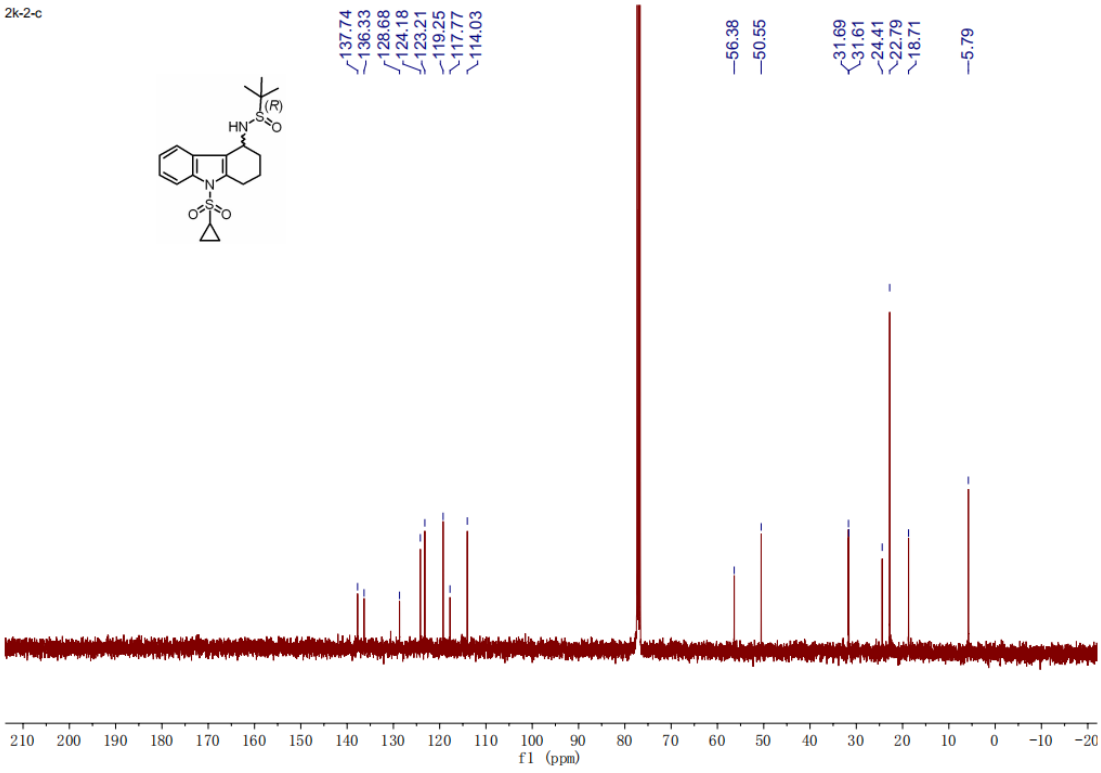
^{13}C NMR spectrum of (+)-2t



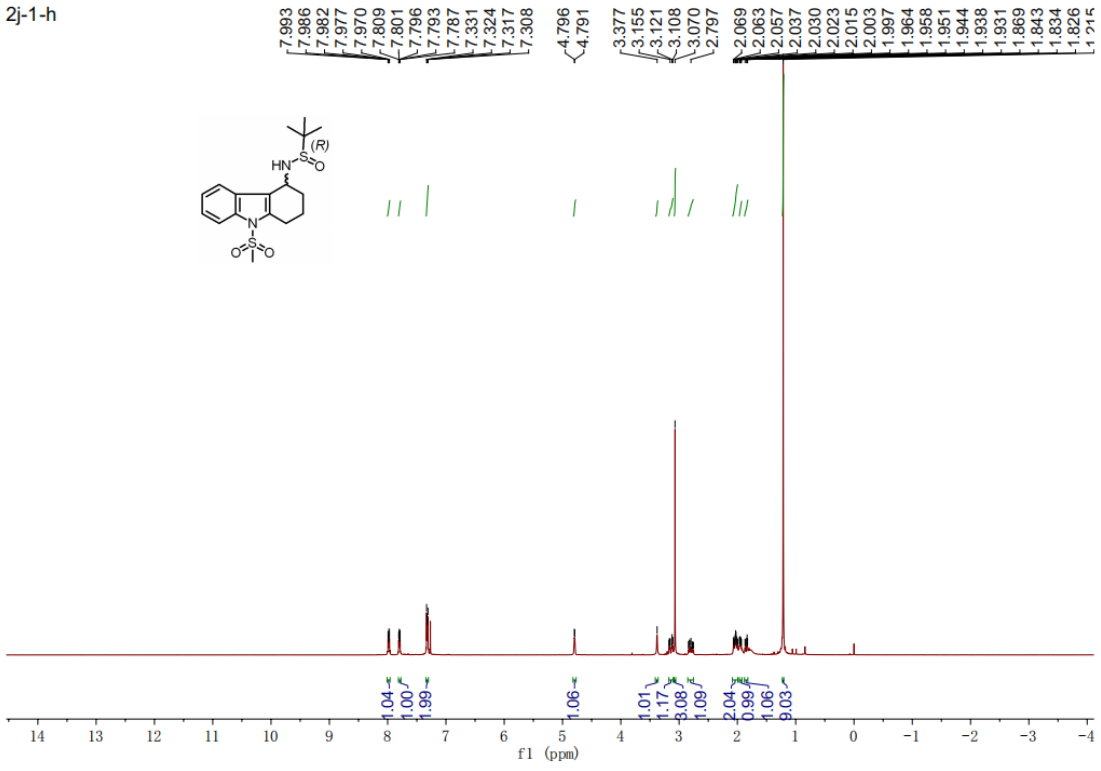
^{1}H NMR spectrum of (-)-2t



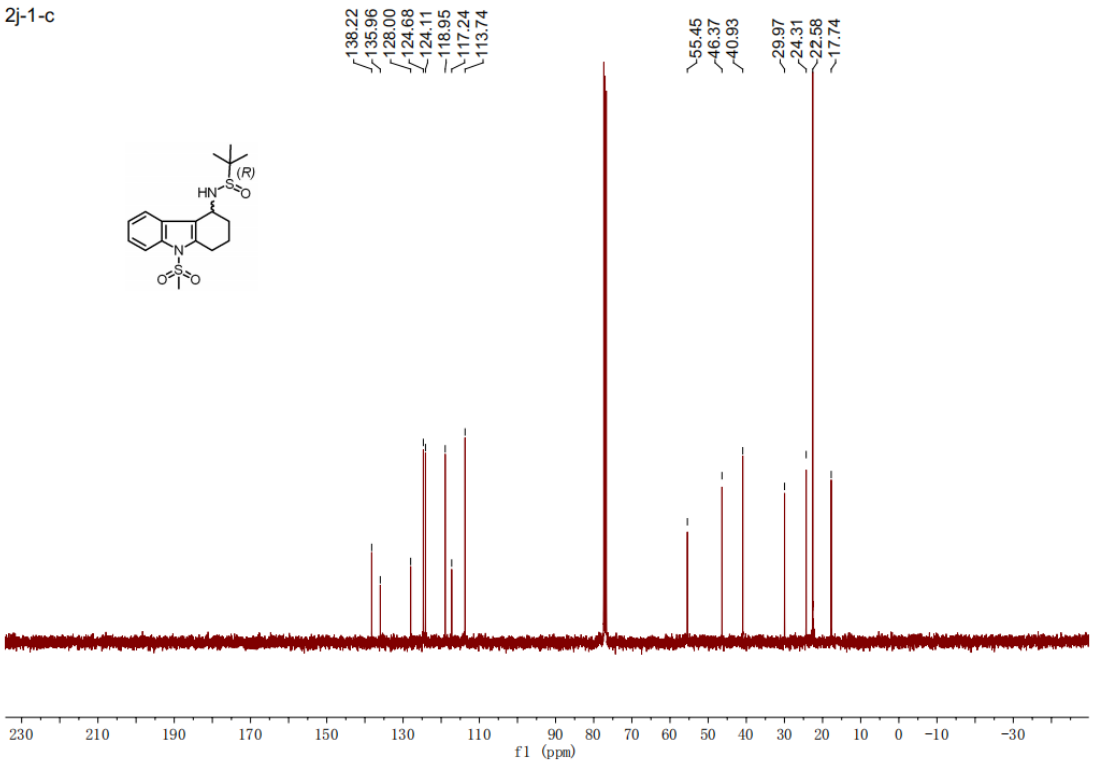
^{13}C NMR spectrum of (-)-2t



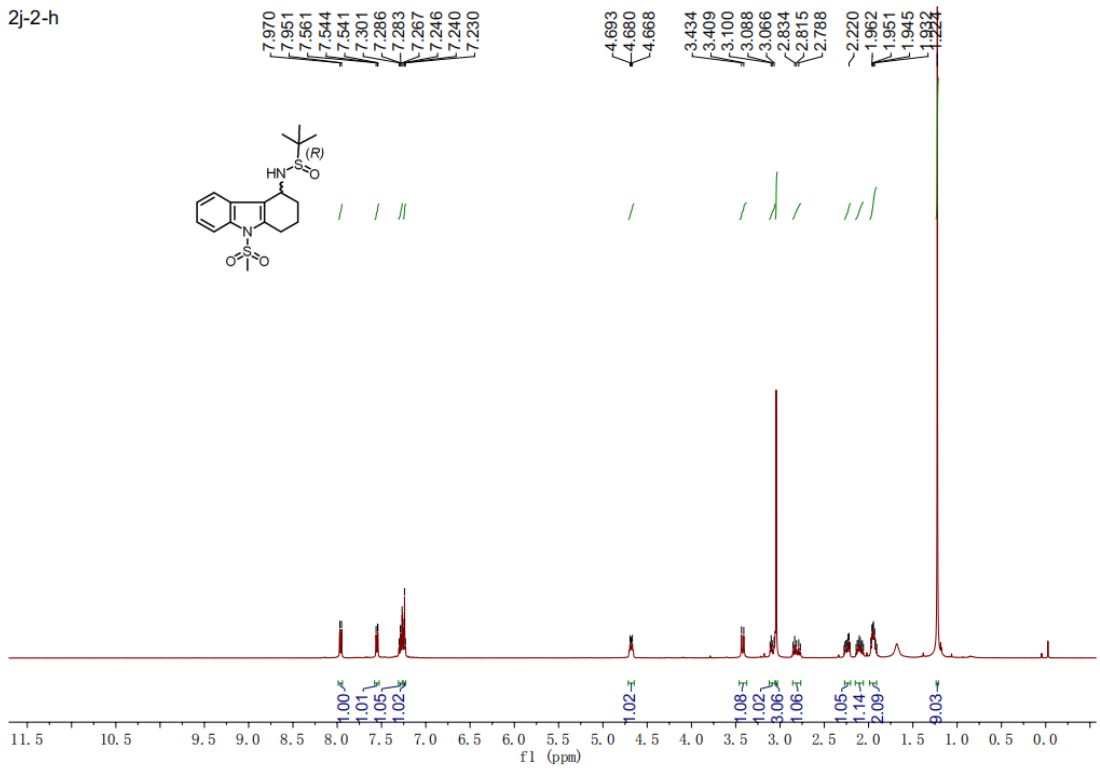
^{1}H NMR spectrum of (+)-2u



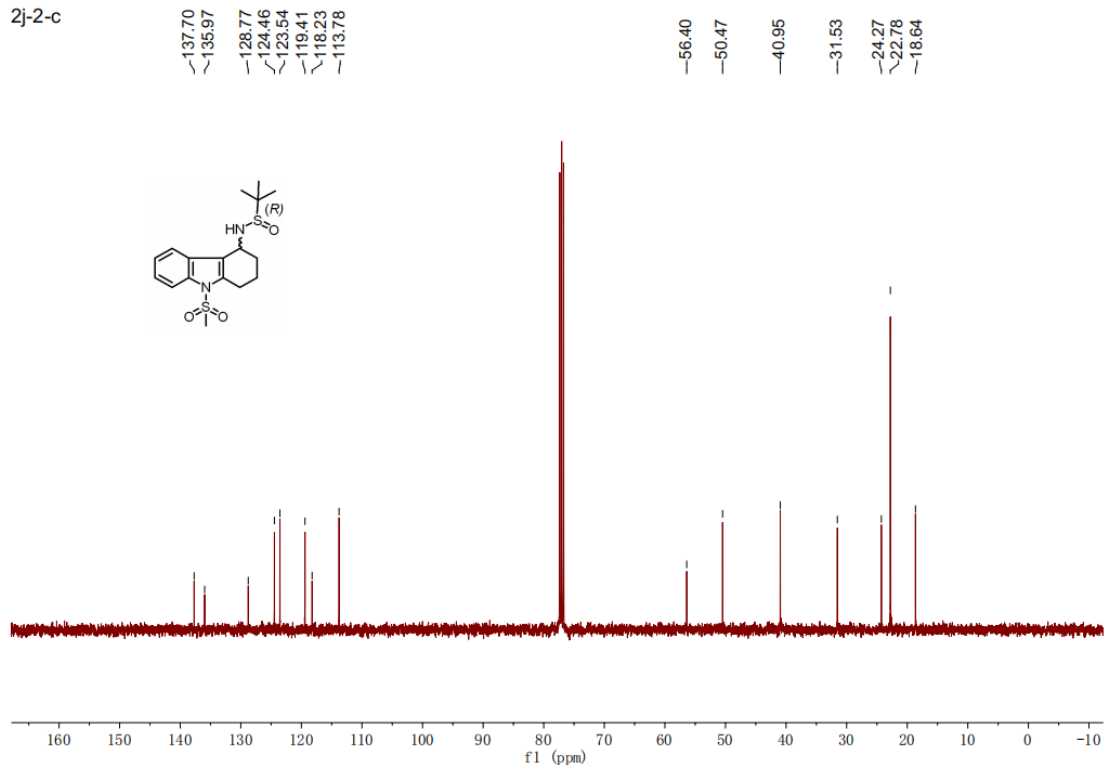
^{13}C NMR spectrum of (+)-2u



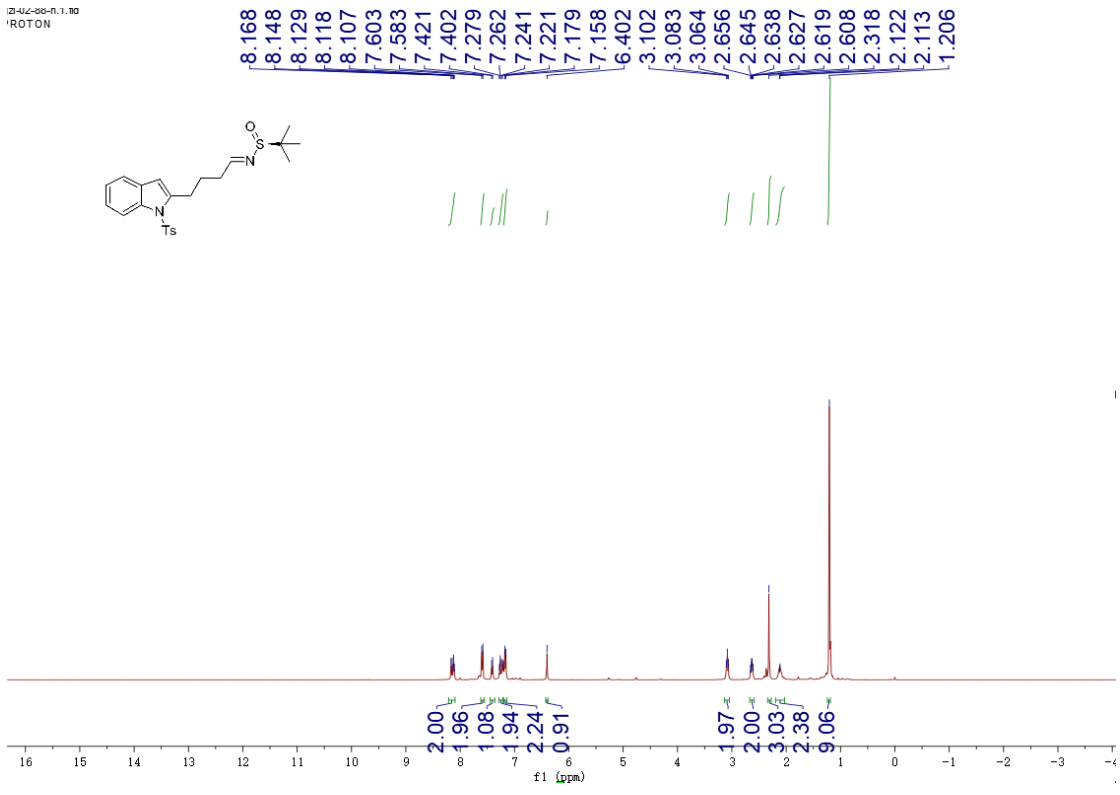
^{1}H NMR spectrum of (-)-2u



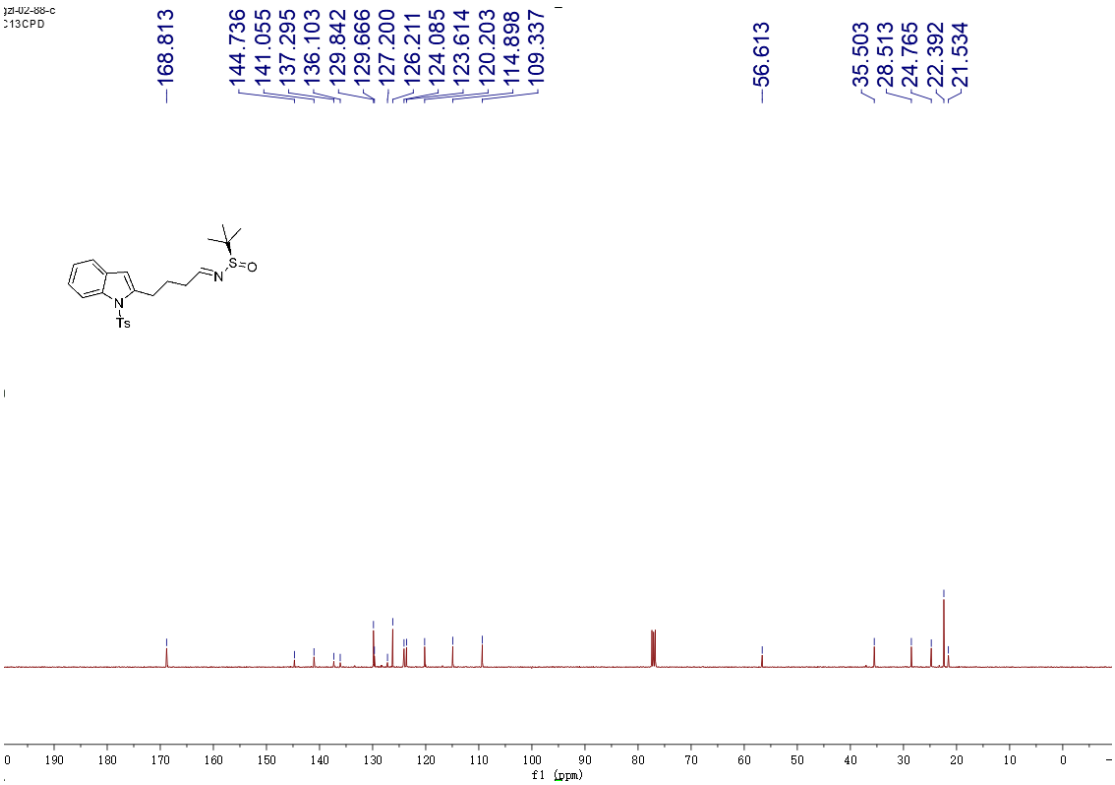
^{13}C NMR spectrum of (-)-2u



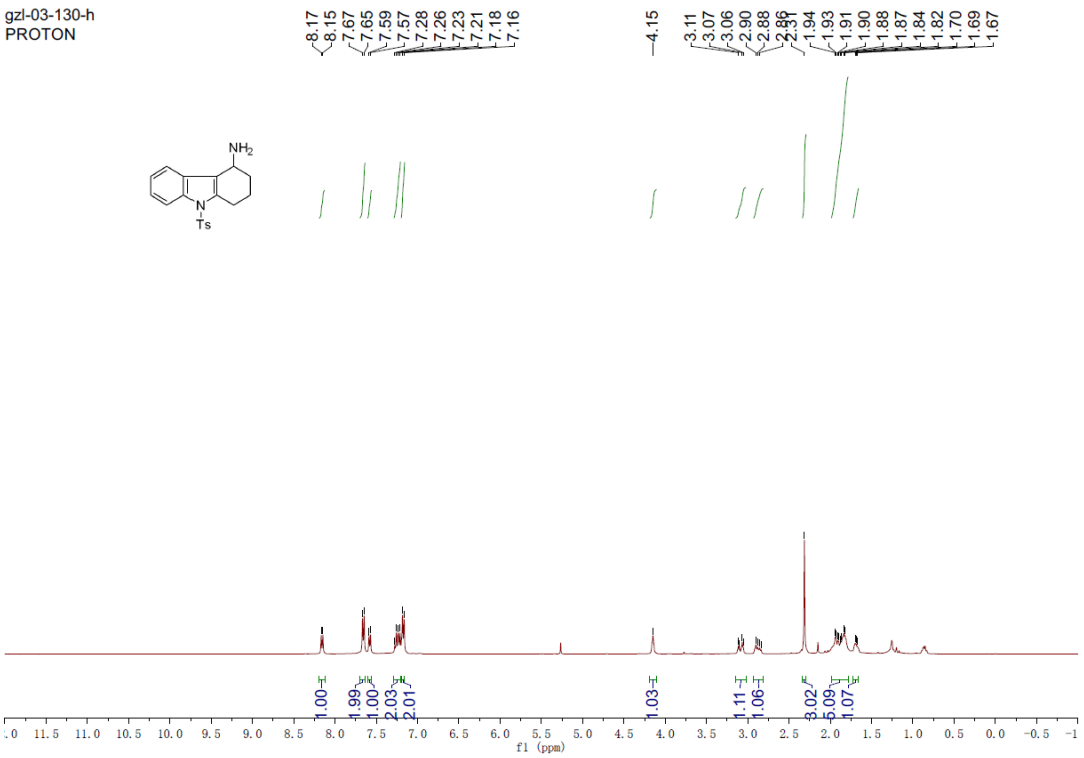
^{1}H NMR spectrum of 2a′



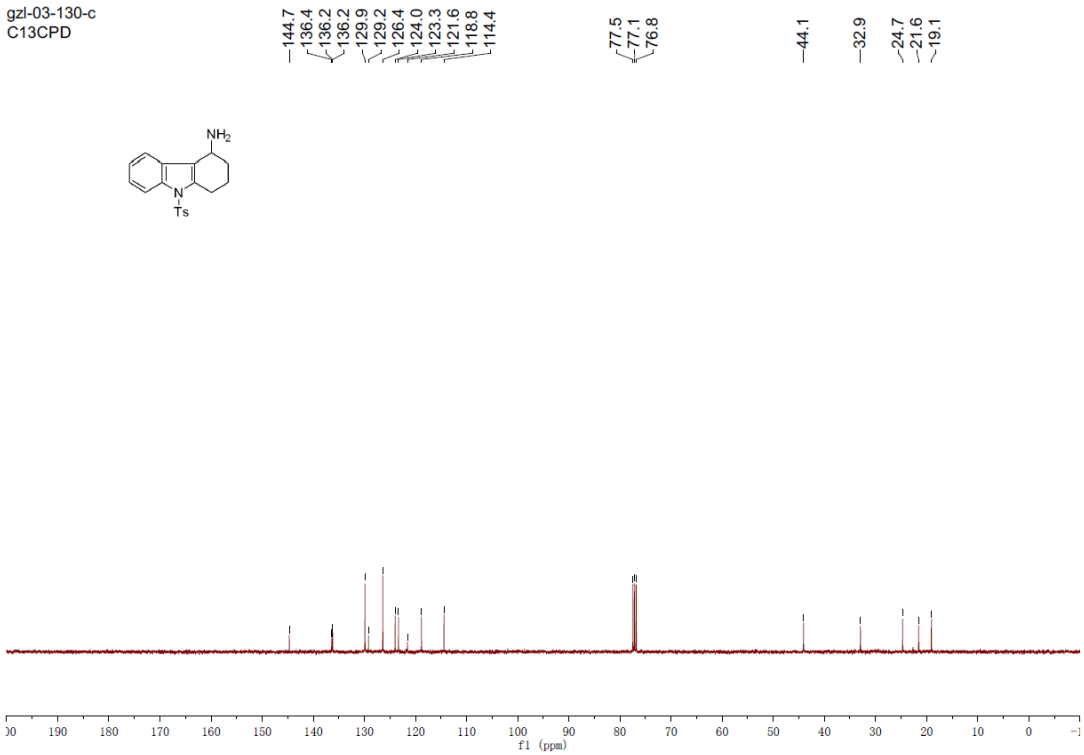
^{13}C NMR spectrum of 2a′



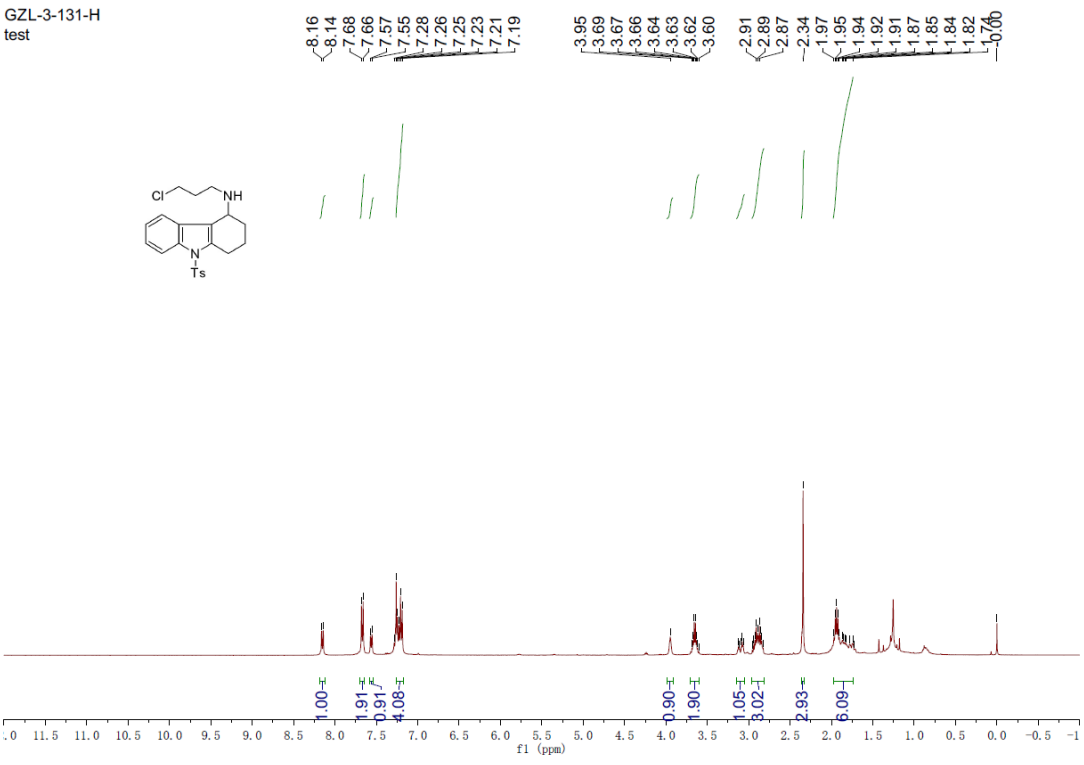
^{1}H NMR spectrum of 3a



^{13}C NMR spectrum of 3a



^{1}H NMR spectrum of 4a



^{13}C NMR spectrum of 4a