Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

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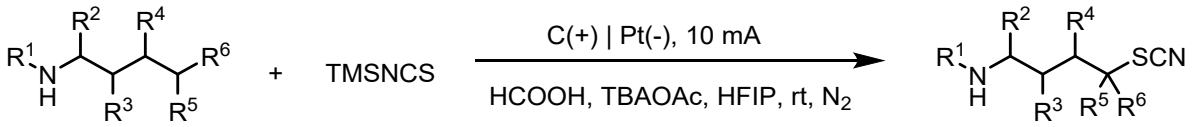
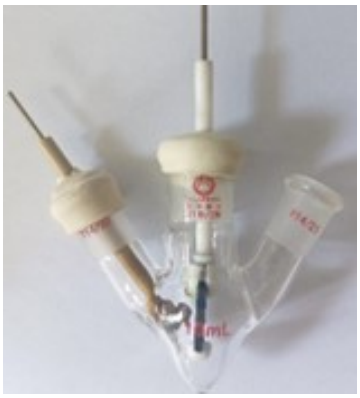
1. General information

All reagents and solvents were commercially available and used as received. The electrochemical instrument is HONGSHENGFENG DPS-305BM. Column chromatography was performed on silica gel (200-300 mesh). NMR spectra were recorded in $CDCl_3$ on Bruker AV-500 MHz spectrometers. The chemical shifts (δ) are reported in parts per million (ppm) relative to the residue signal of $CDCl_3$ (δ/ppm = 7.26 for ^1H NMR and δ/ppm = 77.16 for ^{13}C NMR). The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. The coupling constants *J* have been given in Hertz (Hz). HRMS were obtained on an Ultima Global spectrometer with an ESI source. Cyclic voltammograms (CV) were performed with a CS electrochemical workstation (CS300H, CorrTest).

2. General procedure



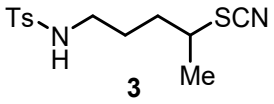
Procedure: To a 10 mL three-necked flask equipped with a carbon plate anode (3 cm x 1 cm x 0.3 cm, about 1.5 cm immersion depth in solution) and a platinum plate cathode (1 cm x 1 cm x 0.1 mm) was charged with substrate (0.2 mmol, 1.0 equiv.), TMSNCS (0.3 mmol, 1.5 equiv.), HCOOH (0.4 mmol, 2.0 equiv.), TBAOAc (0.1 mmol, 0.5 equiv.) and HFIP (5 mL). The electrolysis was carried out at room temperature using a constant current of 10 mA under N_2 for 2-8 h (3.7-14.9 F/mol). After completion of the reaction, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate to give the product.



At the beginning of the reaction At the end of the reaction

Figure S1. Electrolysis cell for small scale reaction

3. Characterization data

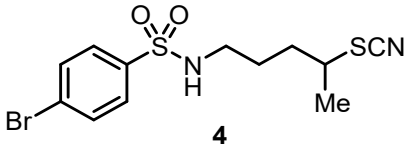


3

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4.5 h (8.4 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **3** (38 mg, 63% yield) as a yellow oil. The spectra matched with the previous report. [1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 4.48 (t, *J* = 6.5 Hz, 1H), 3.23 – 3.16 (m, 1H), 2.98 (q, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 1.79 – 1.71 (m, 2H), 1.69 – 1.61 (m, 2H), 1.48 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.9, 130.0, 127.2, 111.1, 45.2, 42.6, 34.0, 27.3, 22.1, 21.7.



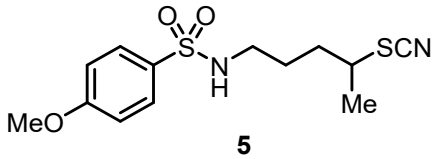
4

The reaction was conducted following the general procedure in a 0.2 mmol scale for 6 h (11.2 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **4** (37 mg, 51% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 4.85 (t, *J* = 6.3 Hz, 1H), 3.24 – 3.17 (m, 1H), 2.98 (q, *J* = 6.6 Hz, 2H), 1.77 – 1.72 (m, 2H), 1.68 – 1.60 (m, 2H), 1.49 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 132.7, 128.7, 128.0, 111.1, 45.1, 42.7, 34.0, 27.3, 22.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{15}BrN_2O_2S_2Na$, 384.9651, found 384.9651.



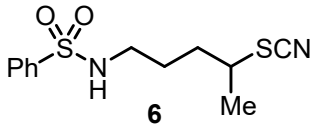
5

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **5** (41 mg, 65% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.71 (s, 1H), 3.87 (s, 3H), 3.23 – 3.16 (m, 1H), 2.95 (q, *J* = 6.6 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.67 – 1.62 (m, 2H), 1.48 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 131.4, 129.3, 114.5, 111.2, 55.8, 45.2, 42.6, 34.0, 27.2, 22.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{18}N_2O_3S_2Na$, 337.0651, found 337.0652.



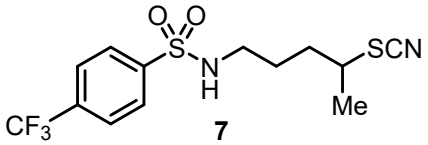
6

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4.5 h (8.4 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **6** (35 mg, 61% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 5.04 (s, 1H), 3.22 – 3.15 (m, 1H), 2.97 (t, *J* = 6.7 Hz, 2H), 1.75 – 1.69 (m, 2H), 1.66 – 1.56 (m, 2H), 1.46 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 132.9, 129.4, 127.1, 111.2, 45.1, 42.6, 33.9, 27.2, 22.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{16}N_2O_2S_2Na$, 307.0545, found 307.0554.



7

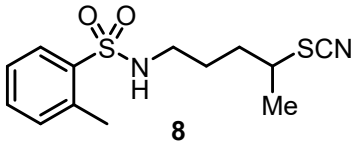
The reaction was conducted following the general procedure in a 0.2 mmol scale for 8 h (14.9 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **7** (24 mg, 34% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 4.80 (s, 1H), 3.25 – 3.18 (m, 1H), 3.07 – 3.02 (m, 2H), 1.79 – 1.72 (m, 2H), 1.71 – 1.62 (m, 2H), 1.49 (d, J = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 134.7 (q, $J_{C\text{-}F}$ = 34.9 Hz), 127.7, 126.6 (d, $J_{C\text{-}F}$ = 3.9 Hz), 123.3 (q, $J_{C\text{-}F}$ = 272.9 Hz), 111.1, 45.1, 42.8, 34.0, 27.4, 22.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.14.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{15}F_3N_2O_2S_2Na$, 375.0419, found 375.0421.



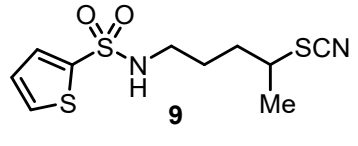
8

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **8** (31 mg, 52% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 6.9 Hz, 2H), 4.94 (s, 1H), 3.19 – 3.12 (m, 1H), 2.97 (q, J = 6.5 Hz, 2H), 2.64 (s, 3H), 1.75 – 1.68 (m, 2H), 1.65 – 1.57 (m, 2H), 1.45 (d, J = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.1, 133.0, 132.8, 129.5, 126.4, 111.1, 45.1, 42.4, 34.0, 27.4, 22.0, 20.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{18}N_2O_2S_2Na$, 321.0702, found 321.0710.



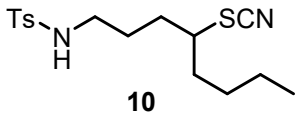
9

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **9** (32 mg, 55% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.11 (t, J = 4.4 Hz, 1H), 4.85 (t, J = 6.4 Hz, 1H), 3.26 – 3.19 (m, 1H), 3.07 (q, J = 6.5 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.70 – 1.62 (m, 2H), 1.50 (d, J = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 132.4, 132.2, 127.7, 111.2, 45.2, 42.9, 34.0, 27.2, 22.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{30}N_3O_4S_2$, 291.0290, found 291.0298.



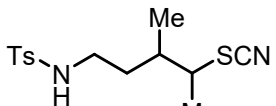
10

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **10** (39 mg, 58% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.98 (t, *J* = 6.3 Hz, 1H), 3.00 – 2.93 (m, 3H), 2.42 (s, 3H), 1.82 – 1.77 (m, 1H), 1.73 – 1.57 (m, 5H), 1.48 – 1.42 (m, 1H), 1.35 – 1.26 (m, 3H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 136.8, 129.9, 127.2, 111.2, 51.2, 42.6, 35.2, 32.4, 29.0, 27.0, 22.3, 21.6, 14.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{25}N_2O_2S_2$, 341.1352, found 341.1352.

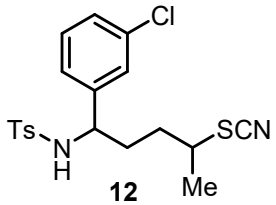


11

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **11** (32 mg, 51% yield, dr = 1:1) as a yellow oil. The spectra matched with the previous report.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.86 (s, 1H), 3.38 – 3.28 (m, 1H), 3.05 – 2.97 (m, 1H), 2.95 – 2.90 (m, 1H), 2.43 (s, 3H), 1.95 – 1.88 (m, 1H), 1.69 – 1.62 (m, 1H), 1.44 – 1.37 (m, 4H), 0.95 (dd, *J* = 6.3, 3.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.8, 130.0, 127.2, 112.2, 112.0, 51.2, 50.7, 41.0, 40.9, 35.8, 35.7, 33.6, 21.7, 19.2, 17.4, 15.33, 15.26.



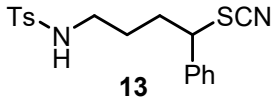
12

The reaction was conducted following the general procedure in a 0.2 mmol scale for 3.5 h (6.5 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **12** (42 mg, 52% yield, dr = 3:2) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.14 – 7.10 (m, 4H), 6.95 – 6.93 (m, 1H), 6.83 (d, *J* = 5.6 Hz, 1H), 5.46 (s, 1H), 4.23 – 4.19 (m, 1H), 3.21 – 3.13 (m, 1H), 2.37 (s, 3H), 1.92 – 1.75 (m, 3H), 1.65 – 1.55 (m, 1H), 1.45 – 1.43 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 142.3, 142.2, 137.3, 134.7, 130.2, 130.1, 129.6, 128.0, 127.9, 127.1, 126.9, 126.8, 124.6, 111.0, 57.7, 57.3, 45.3, 45.0, 34.8, 34.7, 33.5, 33.3, 22.3, 22.1, 21.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{21}ClN_2O_2S_2Na$, 431.0625, found 431.0631.

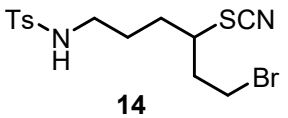


13

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4 h (7.5 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **13** (59 mg, 82% yield) as a colorless oil. The spectra matched with the previous report. [1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.23 (m, 7H), 4.83 (s, 1H), 4.26 (t, *J* = 7.8 Hz, 1H), 2.93 (q, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 2.21 – 2.09 (m, 2H), 1.55 – 1.45 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 137.9, 136.8, 129.9, 129.3, 129.2, 127.5, 127.2, 111.6, 53.0, 42.4, 32.7, 27.6, 21.7.

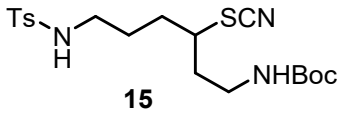


14

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **14** (41 mg, 52% yield) as a colorless oil. The spectra matched with the previous report. [1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 4.83 (t, *J* = 6.4 Hz, 1H), 3.55 (t, *J* = 6.2 Hz, 2H), 3.00 – 2.97 (m, 1H), 2.99 (q, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.20 (q, *J* = 6.4 Hz, 2H), 1.91 – 1.70 (m, 3H), 1.69 – 1.56 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.9, 130.0, 127.2, 109.9, 48.7, 42.5, 37.7, 32.2, 29.9, 27.2, 21.7.



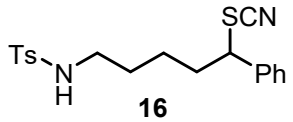
15

The reaction was conducted following the general procedure with 12 mA in a 0.2 mmol scale for 6 h (13.4 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to afford **15** (36 mg, 42% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.26 (s, 1H), 4.82 (s, 1H), 3.32 – 3.21 (m, 2H), 3.11 – 3.03 (m, 1H), 2.97 – 2.92 (m, 2H), 2.42 (s, 3H), 1.97 – 1.83 (m, 4H), 1.77 – 1.67 (m, 2H), 1.42 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 143.7, 137.1, 129.9, 127.2, 110.8, 79.9, 47.9, 42.2, 38.0, 36.5, 31.9, 28.5, 27.0, 21.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{29}N_3O_4S_2Na$, 450.1497, found 450.1503.



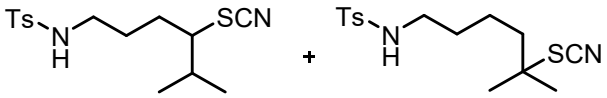
16

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4 h (7.5 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **16** (59 mg, 79% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.26 (m, 7H), 4.90 (t, *J* = 6.2 Hz, 1H), 4.25 (t, *J* = 7.7 Hz, 1H), 2.87 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 2.10 – 2.04 (m, 2H), 1.51 – 1.46 (m, 2H), 1.38 – 1.32 (m, 1H), 1.28 – 1.23 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 138.1, 137.0, 129.8, 129.2, 129.1, 127.5, 127.2, 111.7, 53.4, 42.8, 35.2, 29.0, 24.5, 21.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{22}N_2O_2S_2Na$, 397.1015, found 397.1022.

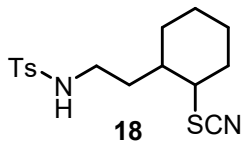


17

The reaction was conducted following the general procedure in a 0.2 mmol scale for 8 h (14.9 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **17** (35 mg, 53% yield, rr = 3:1) as a yellow oil. The spectra matched with the previous report. [1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.00 (t, *J* = 6.3 Hz, 0.74H), 4.93 (t, *J* = 6.2 Hz, 0.22H), 3.04 – 2.87 (m, 2.87H), 2.42 (s, 3H), 2.05 – 1.94 (m, 0.86H), 1.88 – 1.70 (m, 1.95H), 1.68 – 1.54 (m, 2.22H), 1.52 – 1.35 (m, 2.45H), 0.99 (dd, *J* = 19.4, 6.7 Hz, 4.77H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.70, 143.67, 136.9, 136.8, 129.93, 129.91, 127.2, 112.3, 112.2, 58.7, 55.78, 55.74, 42.9, 42.6, 42.3, 33.4, 29.7, 28.8, 27.5, 22.1, 21.64, 21.60, 20.1, 18.7.

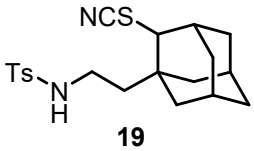


18

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to afford **18** (43 mg, 63% yield, dr = 1.2:1) as a colorless oil. The spectra matched with the previous report. [1]

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.75 (dd, *J* = 8.3, 2.3 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 4.84 (t, *J* = 6.5 Hz, 0.47H), 4.76 (t, *J* = 6.3 Hz, 0.55H), 3.77 – 3.76 (m, 0.47H), 3.11 – 2.92 (m, 2H), 2.80 – 2.74 (m, 0.56H), 2.44 (s, 3H), 2.25 – 2.20 (m, 0.56H), 2.09 – 2.03 (m, 0.54H), 1.98 – 1.64 (m, 5H), 1.56 – 1.45 (m, 2.27H), 1.41 – 1.32 (m, 1H), 1.30 – 1.16 (m, 2.33H), 1.05 – 0.97 (m, 0.63H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 143.7, 136.79, 136.76, 130.0, 129.9, 127.24, 127.20, 112.9, 111.3, 54.6, 54.0, 40.5, 40.4, 40.0, 37.5, 35.1, 33.9, 33.1, 31.8, 29.8, 27.6, 26.5, 24.9, 24.5, 21.7, 21.4.

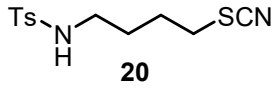


19

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to afford **19** (72 mg, 92% yield) as a yellow oil. The spectra matched with the previous report. [1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.70 (t, *J* = 6.1 Hz, 1H), 3.64 (s, 1H), 3.06 – 2.89 (m, 2H), 2.43 (s, 3H), 2.28 – 2.27 (m, 1H), 1.97 – 1.88 (m, 4H), 1.75 – 1.68 (m, 2H), 1.65 – 1.54 (m, 5H), 1.49 – 1.36 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 136.8, 129.9, 127.3, 113.1, 62.6, 42.0, 40.7, 37.8, 37.7, 36.54, 36.45, 34.5, 31.1, 27.64, 27.58, 21.7.



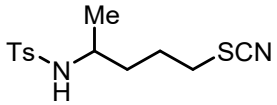
20

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **20** (30 mg, 53% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 4.91 (s, 1H), 2.96 (q, J = 6.0 Hz, 2H), 2.90 (t, J = 7.0 Hz, 2H), 2.43 (s, 3H), 1.86 – 1.80 (m, 2H), 1.66 – 1.60 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.8, 130.0, 127.2, 112.2, 42.4, 33.5, 27.9, 27.0, 21.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{16}N_2O_2S_2Na$, 307.0545, found 307.0551.



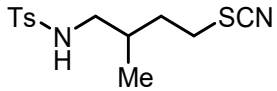
21

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **21** (29 mg, 48% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 4.62 (d, J = 8.5 Hz, 1H), 3.34 – 3.29 (m, 1H), 2.86 (t, J = 8.6 Hz, 2H), 2.43 (s, 3H), 1.85 – 1.75 (m, 2H), 1.58 – 1.47 (m, 2H), 1.00 (d, J = 5.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 138.0, 130.0, 127.1, 112.3, 49.3, 35.6, 33.6, 26.1, 21.8, 21.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{18}N_2O_2S_2Na$, 321.0702, found 321.0708.



22

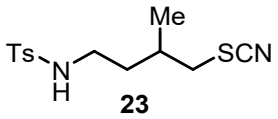
The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **22** (35 mg, 59% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.94 (s, 1H),

3.00 – 2.94 (m, 1H), 2.90 – 2.85 (m, 1H), 2.82 (t, *J* = 5.2 Hz, 2H), 2.43 (s, 3H), 1.92 – 1.86 (m, 1H), 1.82 – 1.76 (m, 1H), 1.65 – 1.59 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.8, 130.0, 127.1, 112.3, 48.4, 34.1, 32.1, 31.6, 21.7, 17.3.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{18}N_2O_2S_2Na$, 321.0702, found 321.0712.



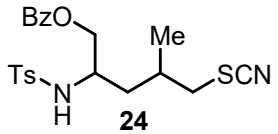
23

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4.5 h (8.4 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **23** (24 mg, 41% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.77 (t, *J* = 5.0 Hz, 1H), 3.04 – 2.98 (m, 1H), 2.97 – 2.90 (m, 2H), 2.83 – 2.79 (m, 1H), 2.43 (s, 3H), 2.01 – 1.94 (m, 1H), 1.71 – 1.64 (m, 1H), 1.46 – 1.39 (m, 1H), 1.02 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.8, 130.0, 127.2, 112.7, 41.0, 40.8, 34.9, 31.4, 21.7, 18.3.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{18}N_2O_2S_2Na$, 321.0702, found 321.0710.



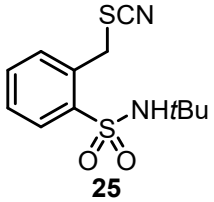
24

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **24** (47 mg, 54% yield, dr = 1.7:1) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.75 – 7.71 (m, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.21 – 7.15 (m, 2H), 5.26 (s, 1H), 4.23 – 4.03 (m, 2H), 3.73 – 3.63 (m, 1H), 3.00 – 2.82 (m, 2H), 2.34 (s, 1.09H), 2.31 (s, 1.87H), 2.20 – 2.02 (m, 1H), 1.78 – 1.72 (m, 1H), 1.60 – 1.54 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 1.80H), 0.97 (d, *J* = 6.6 Hz, 1.05H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 166.4, 143.8, 137.8, 137.6, 133.5, 130.0, 129.8, 129.4, 129.2, 128.6, 128.5, 127.0, 126.9, 112.9, 112.7, 66.8, 65.9, 51.1, 51.0, 41.5, 40.5, 38.4, 37.9, 30.7, 30.4, 21.7, 19.1, 18.2.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{24}N_2O_4S_2Na$, 455.1070, found 455.1066.



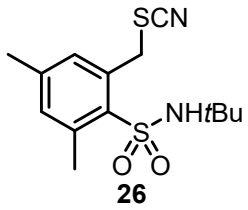
25

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4 h (7.5 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **25** (29 mg, 51% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.56 – 7.50 (m, 2H), 4.74 (s, 1H), 4.57 (s, 2H), 1.27 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 133.8, 133.4, 132.3, 130.0, 129.4, 112.8, 55.9, 35.8, 30.3.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{16}N_2O_2S_2Na$, 307.0551, found 307.0558.



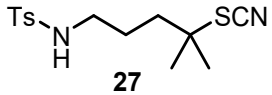
26

The reaction was conducted following the general procedure in a 0.2 mmol scale for 3.5 h (6.5 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **26** (36 mg, 57% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.08 (s, 1H), 4.64 (s, 1H), 4.52 (s, 2H), 2.68 (s, 3H), 2.37 (s, 3H), 1.24 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 139.5, 136.2, 135.9, 135.1, 131.8, 113.9, 55.5, 39.2, 30.3, 22.1, 21.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{20}N_2O_2S_2Na$, 335.0864, found 335.0874.

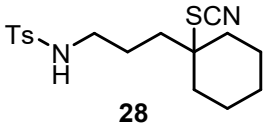


27

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4 h (7.5 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **27** (24 mg, 38% yield) as a yellow oil. The spectra matched with the previous report.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.95 (t, *J* = 6.1 Hz, 1H), 2.95 (q, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 1.73 – 1.64 (m, 2H), 1.66 – 1.55 (m, 2H), 1.44 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 136.9, 130.0, 127.2, 111.7, 55.4, 43.1, 39.8, 28.9, 25.4, 21.6.

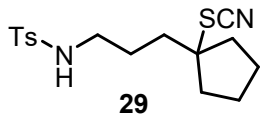


28

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4.5 h (8.4 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **28** (37 mg, 52% yield) as a yellow oil. The spectra matched with the previous report. [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.78 (s, 1H), 2.97 (q, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.83 – 1.80 (m, 2H), 1.76 – 1.71 (m, 5H), 1.60 – 1.53 (m, 7H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 137.0, 129.9, 127.2, 111.6, 61.0, 43.3, 38.9, 36.4, 25.4, 24.3, 22.3, 21.7.

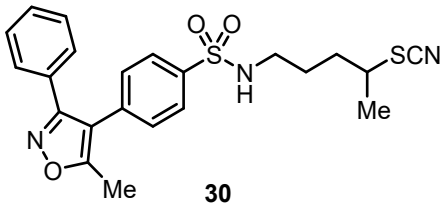


29

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4.5 h (8.4 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **29** (43 mg, 64% yield) as a yellow oil. The spectra matched with the previous report. [1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.67 (s, 1H), 2.98 (q, *J* = 6.6 Hz, 2H), 2.43 (s, 3H), 1.95 – 1.78 (m, 6H), 1.78 – 1.63 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 136.9, 123.0, 127.2, 112.3, 66.8, 43.2, 39.2, 38.4, 26.5, 23.9, 21.7.



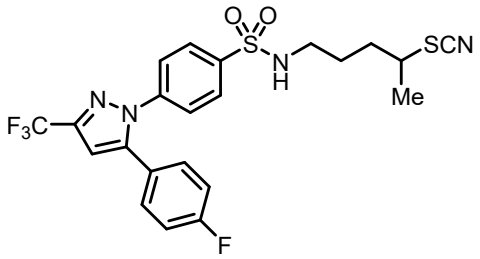
30

The reaction was conducted following the general procedure in a 0.2 mmol scale for 5 h (9.3 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **30** (60 mg, 68% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.49 – 7.29 (m, 7H), 4.91 (t, J = 6.5 Hz, 1H), 3.26 – 3.19 (m, 1H), 3.03 (q, J = 6.6 Hz, 2H), 2.49 (s, 3H), 1.97 – 1.73 (m, 2H), 1.72 – 1.61 (m, 2H), 1.49 (d, J = 6.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 161.2, 139.2, 135.5, 130.5, 129.9, 128.9, 128.6, 127.5, 114.6, 111.1, 45.2, 42.7, 34.0, 27.4, 22.1, 11.9.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{23}N_3O_3S_2Na$, 464.1073, found 464.1077.



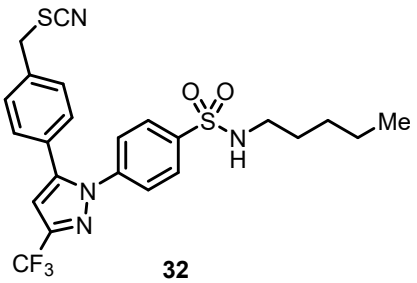
31

The reaction was conducted following the general procedure with TFA (0.4 mmol, 2.0 equiv.) in a 0.2 mmol scale for 3 h (5.6 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford **31** (43 mg, 42% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.08 (t, J = 8.4 Hz, 2H), 6.76 (s, 1H), 4.90 (t, J = 6.3 Hz, 1H), 3.24 – 3.19 (m, 1H), 2.98 (q, J = 6.7 Hz, 2H), 1.77 – 1.66 (m, 4H), 1.49 (d, J = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5 (d, $J_{C\text{-}F}$ = 251.3 Hz), 144.4 (q, $J_{C\text{-}F}$ = 35.1 Hz), 142.5, 139.8, 131.0 (d, $J_{C\text{-}F}$= 8.4 Hz), 128.3, 128.2 (q, $J_{C\text{-}F}$ = 282.0 Hz), 125.8, 124.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 116.5 (d, $J_{C\text{-}F}$ = 22.1 Hz), 111.1, 106.8, 45.2, 42.7, 34.0, 27.4, 22.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{20}F_4N_4O_2S_2Na$, 535.0856, found 535.0859.



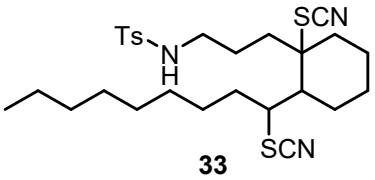
32

The reaction was conducted following the general procedure in a 0.2 mmol scale for 4 h (7.5 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford **32** (77 mg, 76% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 1H), 4.82 (s, 1H), 4.16 (s, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.28 – 1.22 (m, 4H), 0.86 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.33 (q, $J_{C\text{-}F}$ = 38.5 Hz), 144.29, 142.2, 140.1, 136.2, 129.8, 129.7, 128.3, 125.7, 121.1 (q, $J_{C\text{-}F}$= 269.2 Hz), 111.4, 106.8, 43.4, 37.6, 29.3, 28.7, 22.2, 14.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{23}F_3N_4O_2S_2Na$, 531.1107, found 531.1112.



33

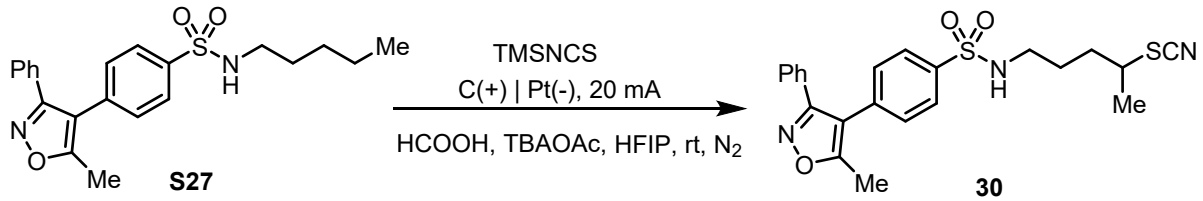
The reaction was conducted following the general procedure in a 0.2 mmol scale for 2 h (3.7 F/mol). The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to afford **33** (57 mg, 53% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.82 (t, *J* = 6.4 Hz, 1H), 3.53 (t, *J* = 6.4 Hz, 1H), 2.88 (q, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 2.04 – 1.93 (m, 2H), 1.71 (t, *J* = 12.0 Hz, 2H), 1.62 – 1.51 (m, 2H), 1.42 (q, *J* = 7.1 Hz, 4H), 1.36 – 1.15 (m, 18H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 137.1, 129.7, 127.1, 110.5, 110.4, 55.6, 55.5, 43.2, 31.8, 31.2, 31.1, 29.5, 29.3, 29.2, 29.0, 28.9, 28.8, 28.7, 27.2, 27.1, 26.4, 22.7, 21.6, 14.2.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{27}H_{41}N_3O_2S_3Na$, 558.2253, found 558.2263.

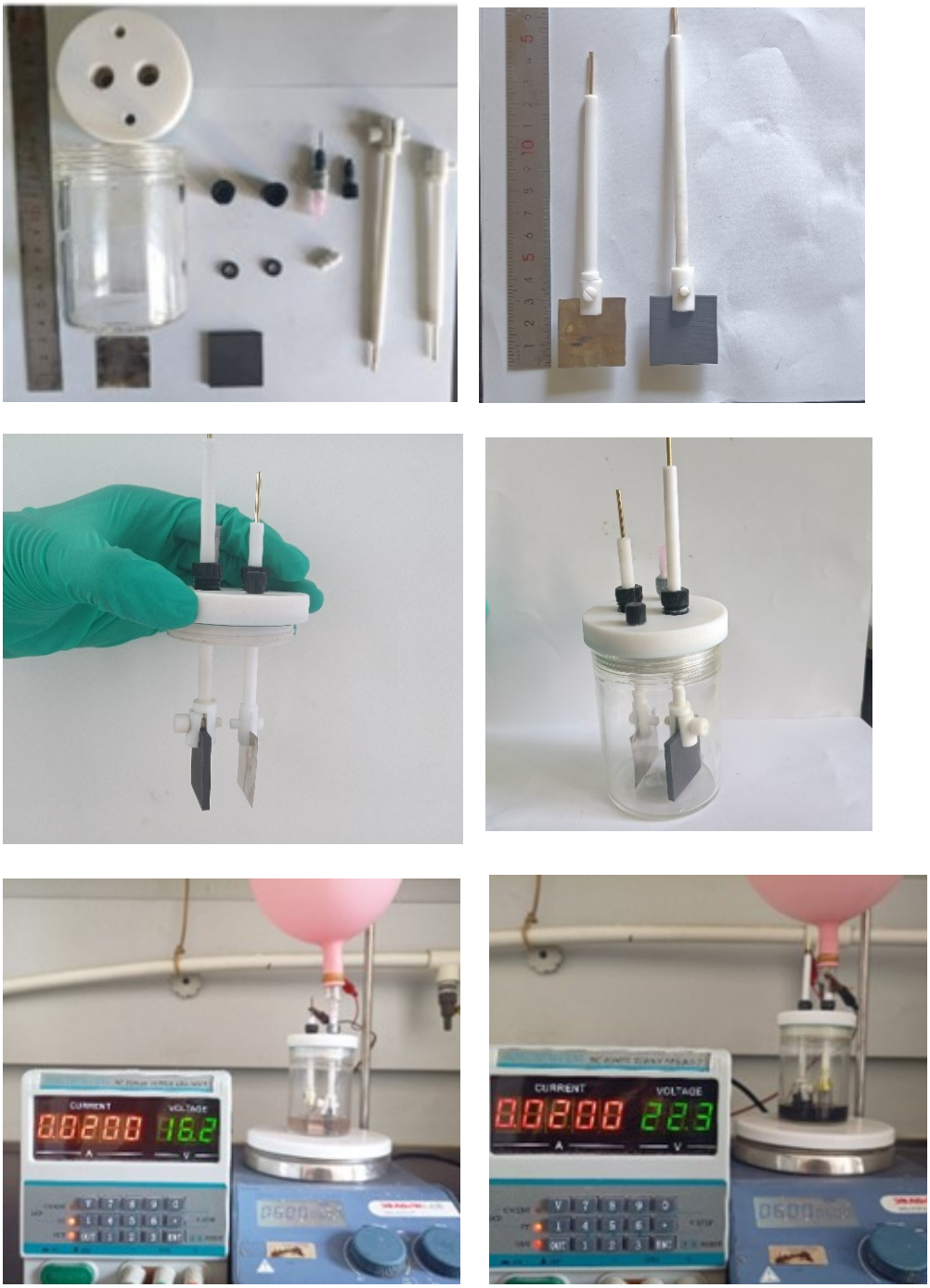
4. Scaled-up reaction



S27 **30**

To a 150 mL beaker-type cell equipped with a carbon plate anode (3 cm x 3 cm x 0.3 cm, about 1.5 cm immersion depth in solution) and a platinum plate cathode (3 cm x 3 cm x 0.1 mm, about 1.5 cm immersion depth in solution) was charged with **S27** (0.38 g, 1.0 mmol, 1.0 equiv.), TMSNCS (0.20 g, 1.5 mmol, 1.5 equiv.), HCOOH (92 mg, 2.0 mmol, 2.0 equiv.), TBAOAc

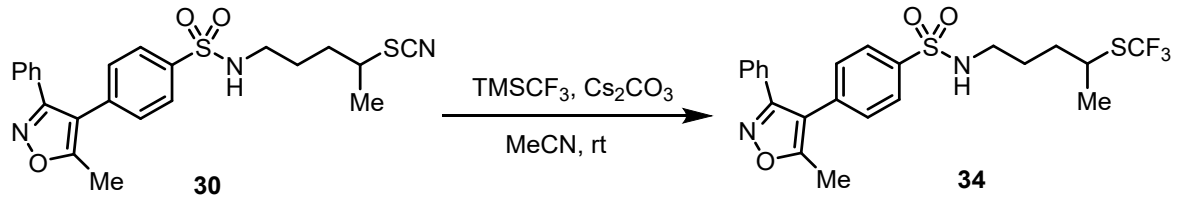
(0.15 g, 0.5 mmol, 0.5 equiv.) and HFIP (20 mL). The electrolysis was carried out at room temperature using a constant current of 20 mA under N_2 for 15 h (11.2 F/mol). After completion of the reaction, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1) to give **30** as a yellow oil (0.28 g, 64% yield).



At the beginning of the reaction At the end of the reaction

Figure S2. Electrolysis cell for large scale reaction

5. Follow-up transformations

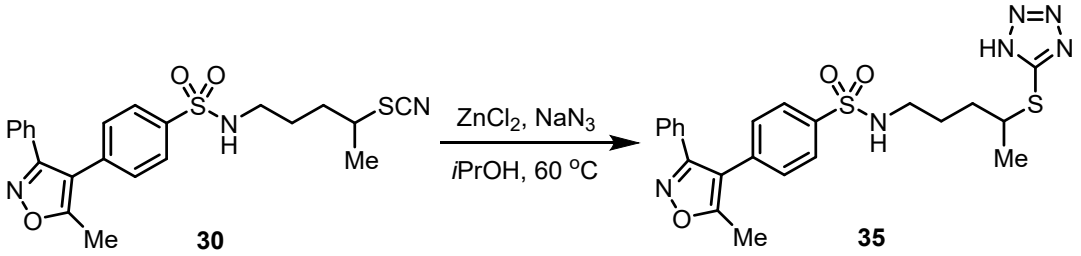


To a solution of **30** (88 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (1.5 mL) was added $TMSCF_3$ (57 mg, 0.4 mmol, 2.0 equiv.) and Cs_2CO_3 (65 mg, 0.2 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature for 5 h. After completion of the reaction (monitored by TLC), water (5 mL) was added to quench the reaction and the mixture was extracted with DCM. The organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to give **34** (72 mg, 74% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.9 Hz, 2H), 7.45 – 7.28 (m, 7H), 4.70 (s, 1H), 3.26 (q, J = 6.3 Hz, 1H), 3.03 (d, J = 5.3 Hz, 2H), 2.49 (s, 3H), 1.69 – 1.62 (m, 4H), 1.39 (d, J = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 161.3, 139.4, 135.5, 131.2 (q, $J_{C\text{-}F}$ = 304.5 Hz), 130.5, 129.9, 128.9, 128.6, 127.5, 114.6, 43.0, 40.8, 33.9, 27.0, 22.5, 11.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{24}F_3N_2O_3S_2$, 485.1175, found 485.1169.

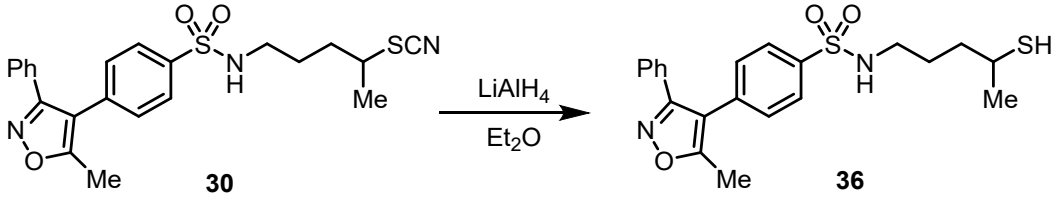


To a solution of **30** (88 mg, 0.2 mmol, 1.0 equiv.), $ZnCl_2$ (27 mg, 0.2 mmol, 1.0 equiv.) in *i*PrOH (1.0 mL) was added NaN_3 (33 mg, 0.5 mmol, 2.5 equiv.) in one portion. The reaction mixture was stirred at 60 ℃ for 15 h. After cooling, the mixture was acidified with 10% HCl. The aqueous layer was extracted with ethyl acetate. The organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel with (DCM/MeOH = 8:1) to give **35** (66 mg, 68% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 4.6 Hz, 2H), 7.36 – 7.22 (m, 7H), 3.63 (s, 1H), 3.01 (s, 3H), 2.45 (s, 3H), 1.76 (s, 1H), 1.62 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 161.0, 156.9, 139.0, 135.1, 130.3, 129.8, 128.8, 128.5, 127.6, 114.5, 42.0, 41.4, 33.6, 25.7, 20.5, 11.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{25}N_6O_3S_2$, 485.1424, found 485.1434.



To a solution of **30** (88 mg, 0.2 mmol, 1.0 equiv.) was added dry Et_2O (3 mL) under N_2, and the suspension was cooled to 0 ℃. A solution of $LiAlH_4$ (15 mg, 0.4 mmol, 2.0 equiv.) in dry Et_2O (3 mL) was slowly added, and the reaction was stirred at 0 ℃ for 20 min. After completion of the reaction (monitored by TLC), the mixture was quenched by dropwise addition of 0.5 M HCl, diluted with H_2O and extracted with ethyl acetate. The organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (6:1) to give **36** (79 mg, 95% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.40 – 7.28 (m, 7H), 4.96 (t, J = 6.3 Hz, 1H), 3.01 (q, J = 6.4 Hz, 2H), 2.87 – 2.81 (m, 1H), 2.48 (s, 3H), 1.67 – 1.54 (m, 3H), 1.49 – 1.43 (m, 1H), 1.40 (d, J = 6.5 Hz, 1H), 1.28 (d, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 161.2, 139.3, 135.2, 130.4, 129.8, 128.8, 128.6, 128.5, 127.5, 114.6, 43.0, 37.6, 35.2, 27.6, 25.9, 11.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{25}N_2O_3S_2$, 417.1301, found 417.1299.

6. Mechanism study

Cyclic voltammetry experiments

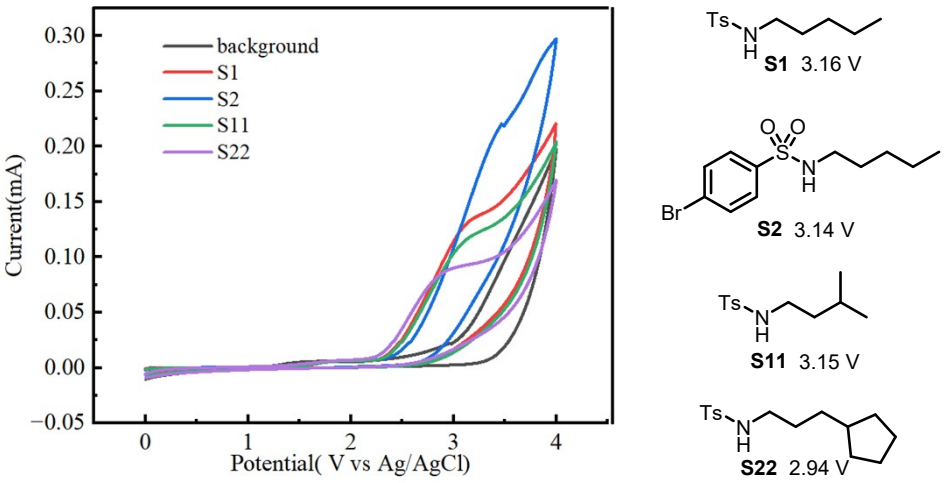
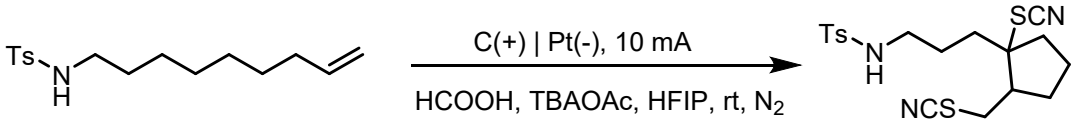


Figure S3. Cyclic voltammograms for sulfonamides

Cyclic voltammograms (CV) were performed with a CS electrochemical workstation (CS300H, CorrTest, China). CV analysis conditions: working electrode: glassy carbon disk; counter electrode: Pt wire; reference electrode: The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution; solvent: HFIP (5 mL); scan rate: v = 100 mV/s; c = 0.005 M; supporting electrolyte: nBu$_4$NBF$_4$ (0.1 M).

Radical probe experiments



S26 **37**

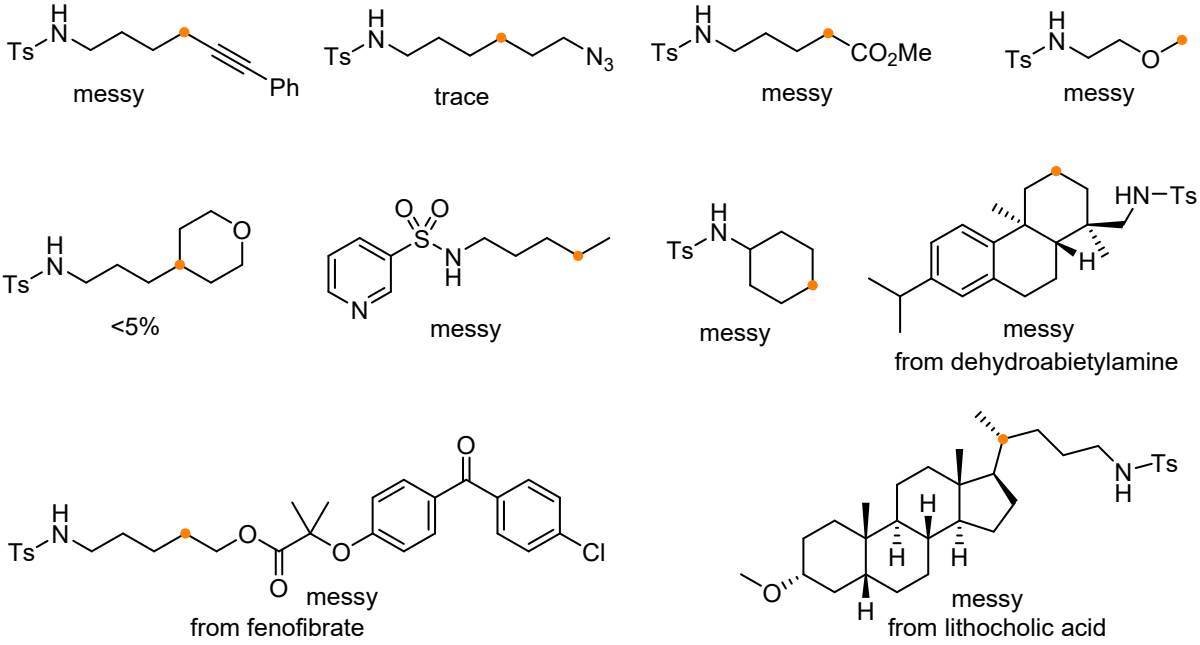
To a 10 mL three-necked flask equipped with a carbon plate anode (3 cm x 1 cm x 0.3 cm, about 1.5 cm immersion depth in solution) and a platinum plate cathode (1 cm x 1 cm x 0.1 mm) was charged with **S26** (59 mg, 0.2 mmol, 1.0 equiv.), TMSNCS (39 mg, 0.3 mmol, 1.5 equiv.), HCOOH (18 mg, 0.4 mmol, 2.0 equiv.), TBAOAc (30 mg, 0.1 mmol, 0.5 equiv.) and HFIP (5 mL). The electrolysis was carried out at room temperature using a constant current of 10 mA under N_2 for 2 h (3.7 F/mol). After completion of the reaction, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to give **37** as a yellow oil (51 mg, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 4.86 (t, J = 6.3 Hz, 1H), 3.35 – 3.31 (m, 2H), 2.89 (q, J = 6.7 Hz, 2H), 2.41 (s, 3H), 2.04 – 1.93 (m, 1H), 1.77 – 1.69 (m, 1H), 1.62 – 1.49 (m, 1H), 1.47 – 1.37 (m, 3H), 1.30 – 1.23 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 137.0, 129.8, 127.1, 111.1, 109.3, 50.8, 50.0, 43.1, 39.1, 33.2, 29.4, 28.6, 26.6, 26.3, 21.6.

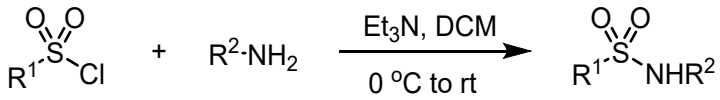
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{23}N_3O_2S_3Na$, 432.0845, found 432.0848.

7. Unsuccessful substrates

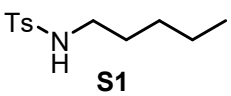


8. Synthesis of substrates

General procedure for the synthesis of sulfonamide (GP1)

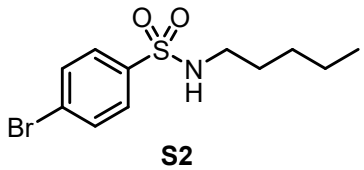


To a round bottom flask was added sulfonyl chloride (3 mmol, 1.0 equiv.) and dry DCM (12 mL), the mixture was cooled to 0 °C. Amine (3.3 mmol, 1.1 equiv.) and Et_3N (3.6 mmol, 1.2 equiv.) were added into the solution. The reaction mixture was warmed to room temperature and the stirring was continued until the starting material was consumed completely as indicated by TLC. The reaction mixture was quenched with 1.0 M HCl and extracted with DCM. The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding sulfonamide.



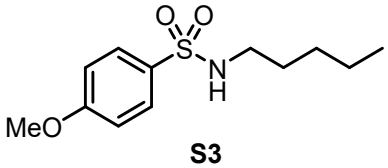
S1

Following **GP1** with tosyl chloride and amylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S1** (0.67 g, 92%) as a yellow oil. [3]



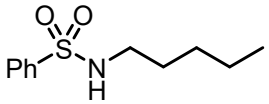
S2

Following **GP1** with 4-bromobenzenesulfonyl chloride and amylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S2** (0.69 g, 75%) as a yellow oil. [4]



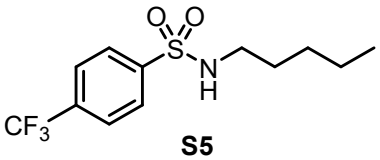
S3

Following **GP1** with 4-methoxybenzenesulfonyl chloride and amylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S3** (0.66 g, 86%) as a yellow oil. [5]



S4

Following **GP1** with benzenesulfonyl chloride and amylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S4** (0.61 g, 89%) as a colorless oil. [5]



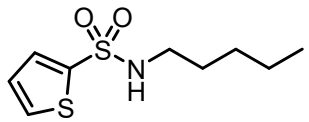
S5

Following **GP1** with 4-(trifluoromethyl)benzene sulfonyl chloride and amylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S5** (0.80 g, 90%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 4.96 (t, J = 6.1 Hz, 1H), 2.96 (q, J = 6.8 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.26 – 1.20 (m, 4H), 0.82 (t, J = 6.8 Hz, 3H).

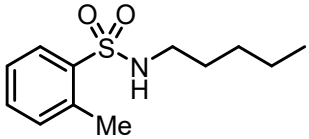
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 134.4 (q, $J_{C\text{-}F}$ = 33.1 Hz), 127.7, 126.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.4 (q, $J_{C\text{-}F}$ = 272.8 Hz), 43.4, 29.4, 28.7, 22.2, 13.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{17}F_3NO_2S$, 296.0927, found 296.0933.



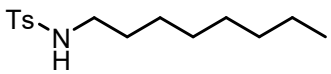
S6

Following **GP1** 2-thiophenesulfonyl chloride and amylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S6** (0.60 g, 86%) as a colorless oil. [6]



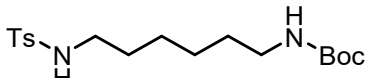
S7

Following **GP1** *o*-toluenesulfonyl chloride and amylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S7** (0.57 g, 79%) as a colorless oil. [6]



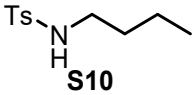
S8

Following **GP1** tosyl chloride and octylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S8** (0.76 g, 90%) as a colorless oil. [7]



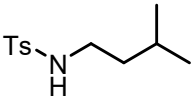
S9

Following **GP1** tosyl chloride and *N*-Boc-1,6-diaminohexane. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to give **S9** (0.94 g, 85%) as a white solid.



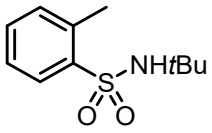
S10

Following **GP1** with tosyl chloride and butylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S10** (0.61 g, 90%) as a yellow oil. [8]



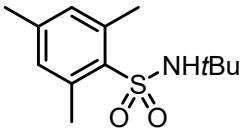
S11

Following **GP1** with tosyl chloride and isoamylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S11** (0.59 g, 82%) as a yellow oil. [9]



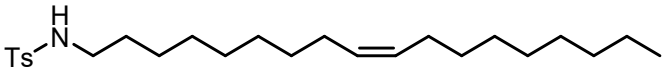
S12

Following **GP1** with *o*-toluenesulfonyl chloride and tert-butylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give **S12** (0.55 g, 80%) as a white solid. [10]



S13

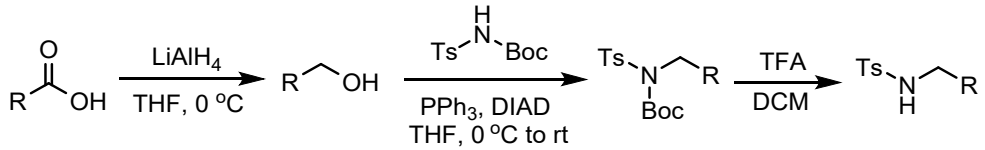
Following **GP1** with mesitylene-2-sulfonyl chloride and tert-butylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) to give **S13** (0.60 g, 79%) as a white solid. [11]



S14

Following **GP1** tosyl chloride and oleylamine. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S14** (1.02 g, 81%) as a white solid. [12]

General procedure for the synthesis of sulfonamide (GP2)

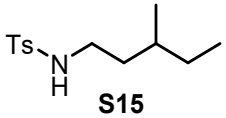


To a round bottom flask was added the acid (3 mmol, 1.0 equiv.) and dry THF (12 mL), the mixture was cooled to 0 °C. $LiAlH_4$ (0.17 g, 4.5 mmol, 1.5 equiv.) was added into the solution under N_2. The reaction mixture was warmed to room temperature and the stirring was continued until the starting material was consumed completely as indicated by TLC. The reaction mixture was quenched carefully with water at 0 °C and allowed to stir for about 10 min. The mixture was filtered and extracted with ethyl acetate. The organic extracts were combined, washed with

brine, and dried over anhydrous Na_2SO_4. The organic layer was concentrated in vacuo to obtain the alcohol.

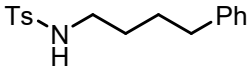
To a round bottom flask was added alcohol, PPh_3 (1.1 equiv.), tert-butyl tosylcarbamate (1.1 equiv.) and dry THF (12 mL). The mixture was stirred for 10 min then cooled to 0 ℃. DIAD (1.1 equiv.) was added and the mixture was stirred overnight at room temperature. Upon completion, the mixture was concentrated and purified by column chromatography on silica gel to give the Boc-protected amide.

To a round bottom flask was added Boc-protected amide and DCM (0.25 M), then TFA (5.0 equiv.) was added. The reaction was stirred for 3 h at room temperature. The mixture was concentrated and purified by column chromatography on silica gel to give the corresponding amide.



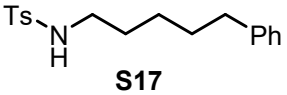
S15

Following **GP2** with 3-methylpentanoic acid. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S15** (0.60 g, 78%) as a colorless oil. [13]



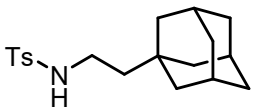
S16

Following **GP2** with 4-phenylbutyric acid. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to give **S16** (0.64 g, 70%) as a white solid. [3]



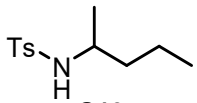
S17

Following **GP2** with 5-phenylvaleric acid. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S17** (0.74 g, 78%) as a white solid. [14]



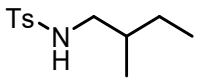
S18

Following **GP2** with 1-adamantaneacetic acid. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S18** (0.65 g, 65%) as a white solid. [14]



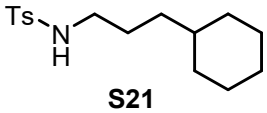
S19

Following **GP2** with 2-pentanol. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S19** (0.45 g, 62%) as a colorless oil. [13]



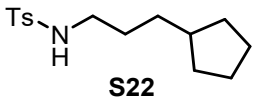
S20

Following **GP2** with 2-methyl-1-butanol. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S20** (0.53 g, 73%) as a colorless oil. [16]



S21

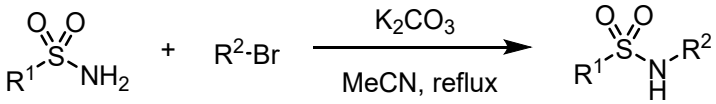
Following **GP2** with cyclohexanepropionic acid. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S21** (0.56 g, 63%) as a white solid. [14]



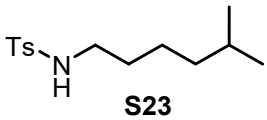
S22

Following **GP2** with 3-cyclopentylpropionic acid. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S22** (0.48 g, 57%) as a white solid. [13]

General procedure for the synthesis of sulfonamide (GP3)

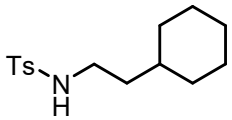


To a round bottom flask was added alkyl bromide (3 mmol, 1.0 equiv.), sulfonamide (6 mmol, 2.0 equiv.), K_2CO_3 (0.83 g, 6 mmol, 2.0 equiv.) and MeCN (12 mL). The reaction mixture was heated to reflux for 5 h. The mixture was filtrated through celite and concentrated in vacuo. The crude was purified by column chromatography on silica gel to give the corresponding amide.



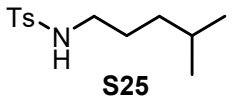
S23

Following **GP3** with *p*-toluenesulfonamide and 1-bromo-5-methylhexane. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S23** (0.63 g, 78%) as a colorless oil. [13]



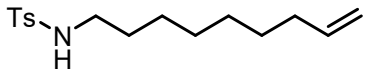
S24

Following **GP3** with *p*-toluenesulfonamide and 1-bromo-2-cyclohexyl. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S24** (0.53 g, 63%) as a white solid. [4]



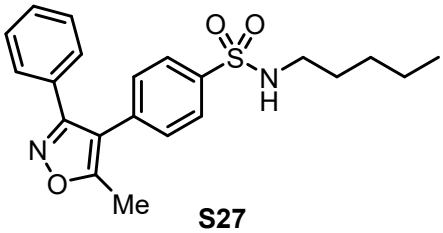
S25

Following **GP3** with *p*-toluenesulfonamide and 1-bromo-4-methylpentane. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S25** (0.57 g, 75%) as a colorless oil. [7]



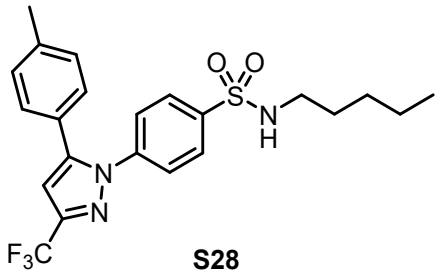
S26

Following **GP3** with *p*-toluenesulfonamide and 9-bromo-1-decene. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S26** (0.71 g, 80%) as a white solid. [17]



S27

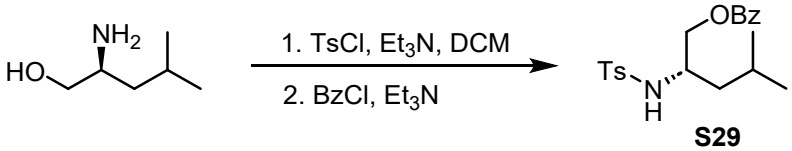
Following **GP3** with valdecoxib and 1-bromopentane. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to give **S27** (0.75 g, 65%) as a white solid.



S28

Following **GP3** with celecoxib and 1-bromopentane. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to give **S28** (0.69 g, 51%) as a white solid.

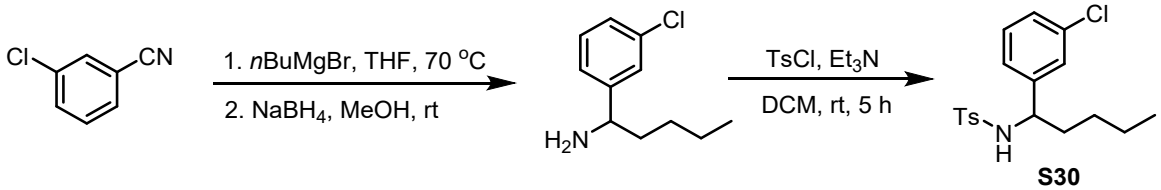
(S)-4-methyl-2-((4-methylphenyl) sulfonamido) pentyl benzoate (S29)



S29

To a round bottom flask was added L(+)-Leucinol (0.35 g, 3 mmol, 1.0 equiv.) and dried DCM (6 mL). The mixture was cooled to 0 ºC, Et_3N (1.25 mL, 9 mmol, 3.0 equiv.) and tosyl chloride (0.57 g, 3 mmol, 1.0 equiv.) were added slowly. The reaction was warmed to room temperature and stirred overnight. After completion, the solvent was evaporated and the residue was dissolved in dried DCM (6 mL), then Et_3N (1.25 mL, 9 mmol, 3.0 equiv.) and BzCl (0.51 g, 3.6 mmol, 1.2 equiv.) were added. The reaction mixture was warmed to room temperature and stirred for 8 h. The mixture was quenched by water and extracted with DCM. The organic layers were combined, washed with brine, and dried over anhydrous Na_2SO_4. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to give **S29** (0.57 g, 51%) as a yellow solid. [18]

***N*-(1-(3-chlorophenyl) pentyl)-4-methylbenzenesulfonamide (S30)**



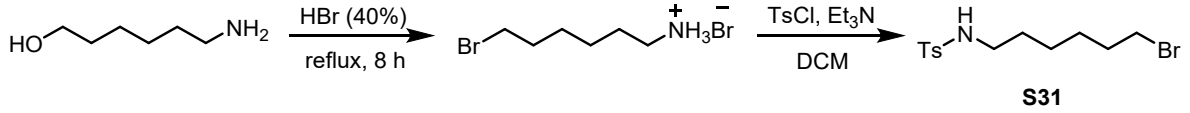
S30

To a solution of *n*BuMgBr (15 mmol, 3.0 equiv.) in THF (20 mL) was added 3-chlorobenzonitrile (0.69 g, 5 mmol, 1.0 equiv.). The reaction mixture was heated at 70 ℃ for 4 h under vigorous stirring. After cooling to room temperature, a solution of sodium borohydride (0.38 g, 10 mmol, 2.0 equiv.) in MeOH (25 mL) was added to the reaction mixture. After stirring for 15 min, the mixture was quenched with aqueous NaOH solution (1.0 M), and extracted with

ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated to give the crude amine.

The last step was following **GP1** with 1-(3-chlorophenyl) pentan-1-amine (0.65 g, 3.3 mmol, 1.1 equiv.) and tosyl chloride (0.57 g, 3 mmol, 1.0 equiv.). The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) to give **S30** (0.66 g, 63%) as a yellow oil. [19]

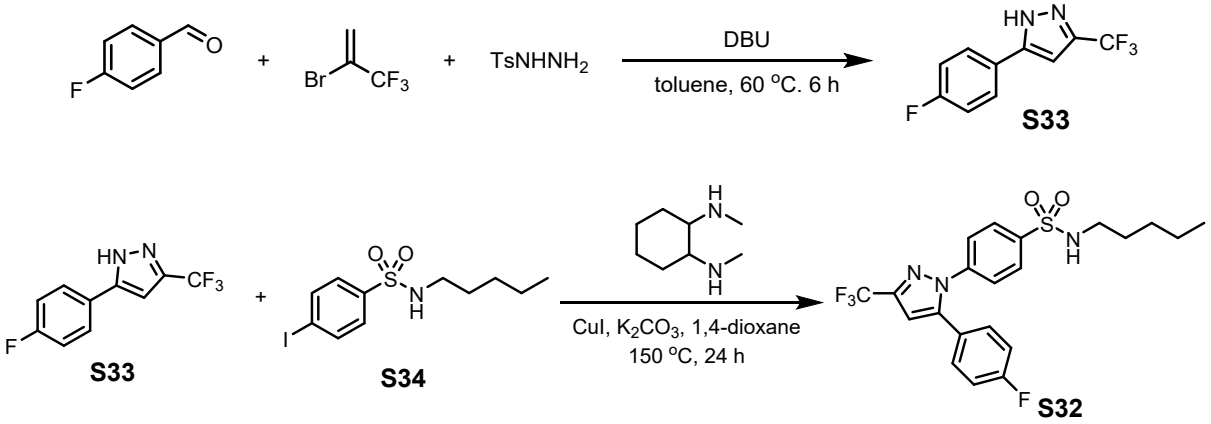
***N*-(6-bromohexyl)-4-methylbenzenesulfonamide (S31)**



To a round bottom flask was added 6-aminohexanol (0.70 g, 5 mmol) and 40% HBr (6 mL). The mixture was refluxed for 8 h, and concentrated to give 6-bromohexylamine hydrobromide (1.14 g, 88%) as a yellow solid.

The last step was following **GP1** with 6-bromohexan-1-aminium bromide (0.85 g, 3.3 mmol, 1.1 equiv.) and tosyl chloride (0.57 g, 3 mmol, 1.0 equiv.). The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to give **S31** (0.83 g, 83%) as a yellow solid. [20]

4-(5-(4-fluorophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)-*N*-pentylbenzenesulfonamide (S32)



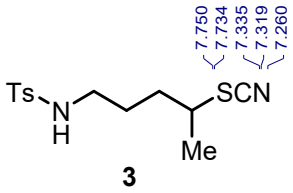
To a round bottom flask was added 4-fluorobenzaldehyde (0.37 g, 3 mmol, 1.0 equiv.), 4-methylbenzenesulfonohydrazide (0.67 g, 3.6 mmol, 1.2 equiv.), 1,8-diazabicyclo[5.4.0]undec-7-ene (1.37 g, 9 mmol, 3.0 equiv.), 2-bromo-3,3,3-trifluoropropene (1.05 g, 6 mmol, 2.0 equiv.), and toluene (18 mL). The resulting mixture was vigorously stirred at 60 ℃ for 6 h. The reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic layers

were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S33** (0.50 g, 72%) as a yellow solid.

The **S34** was synthesized following **GP1** with 4-iodobenzenesulfonyl chloride (3.63 g, 12 mmol, 1.0 equiv.) and amylamine (1.15 g, 13.2 mmol, 1.1 equiv.). The crude was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give **S34** (4.15 g, 98%) as a white solid.

To a Schlenk tube was added **S33** (0.46 g, 2 mmol, 1.0 equiv.), **S34** (3.18 g, 9 mmol, 4.5 equiv.), CuI (0.19 g, 1 mmol, 0.5 equiv.), K_2CO_3 (0.55 g, 4 mmol, 2.0 equiv.) and 1,4-dioxane (8 mL). *N*, *N*'-dimethyl-1,2-cyclohexanediamine (0.14 g, 1 mmol, 1.0 equiv.) was slowly injected into the system under Ar. The resulting mixture was vigorously stirred at 150 ℃ for 24 h under Ar. The mixture was concentrated in vacuo and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to give **S32** (0.30 g, 33%) as a colorless oil.

9. Copies of NMR spectra

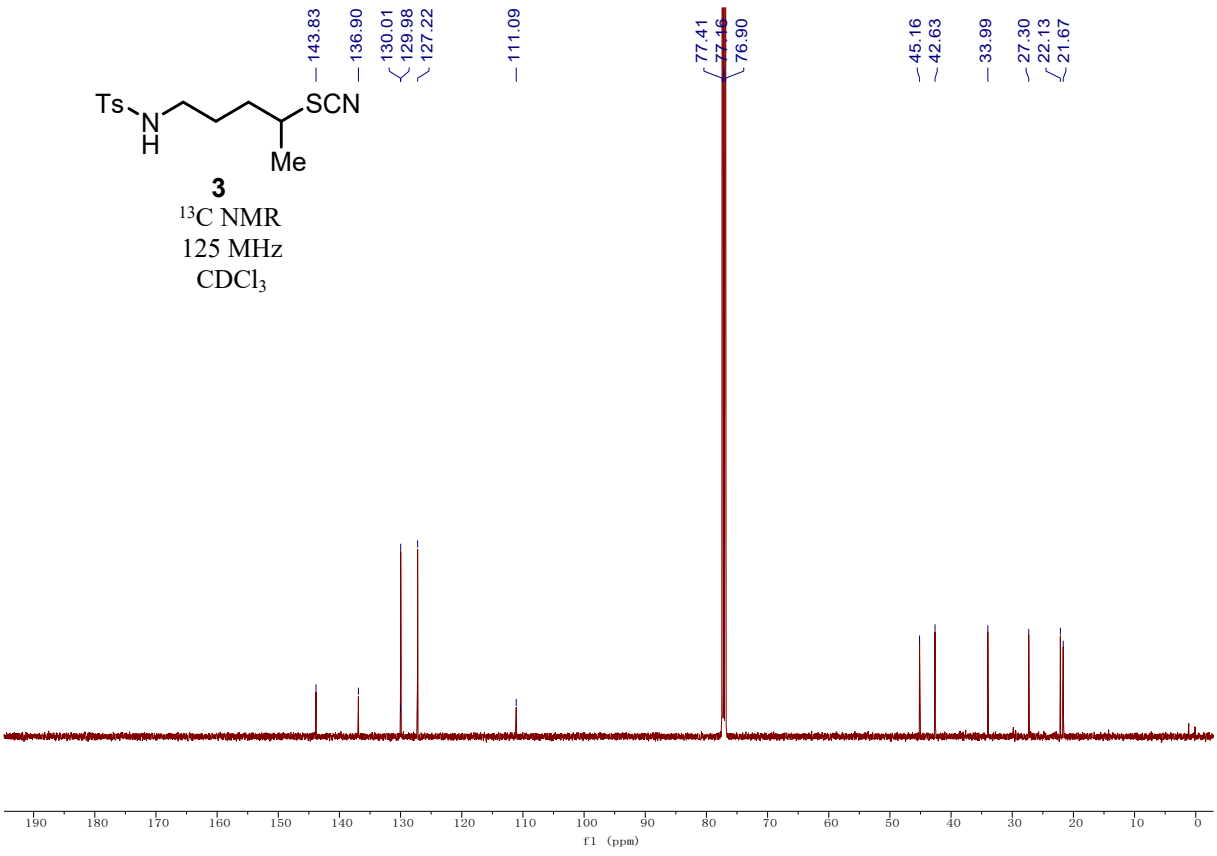


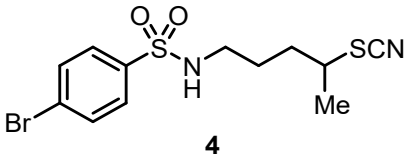
3

^{1}H NMR
500 MHz
$CDCl_3$

3

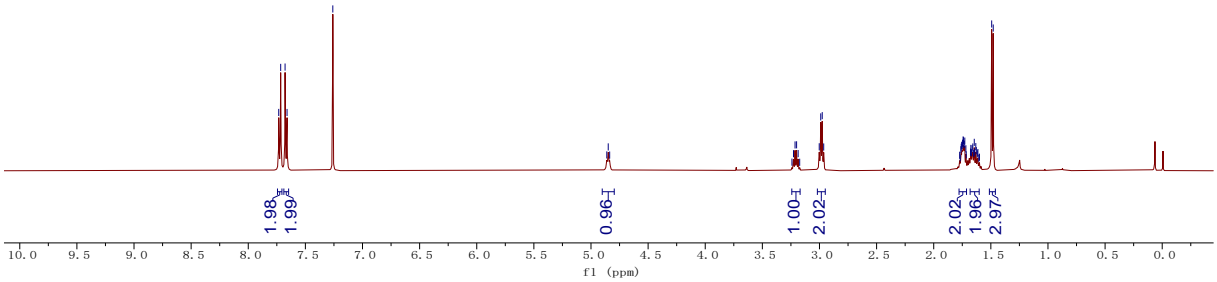
^{13}C NMR
125 MHz
$CDCl_3$

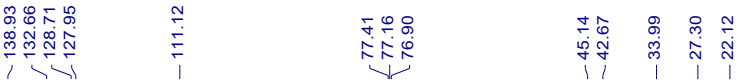


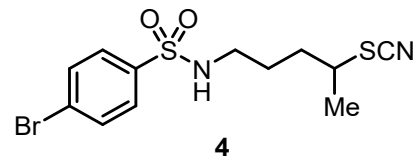


4

^{1}H NMR
500 MHz
$CDCl_3$

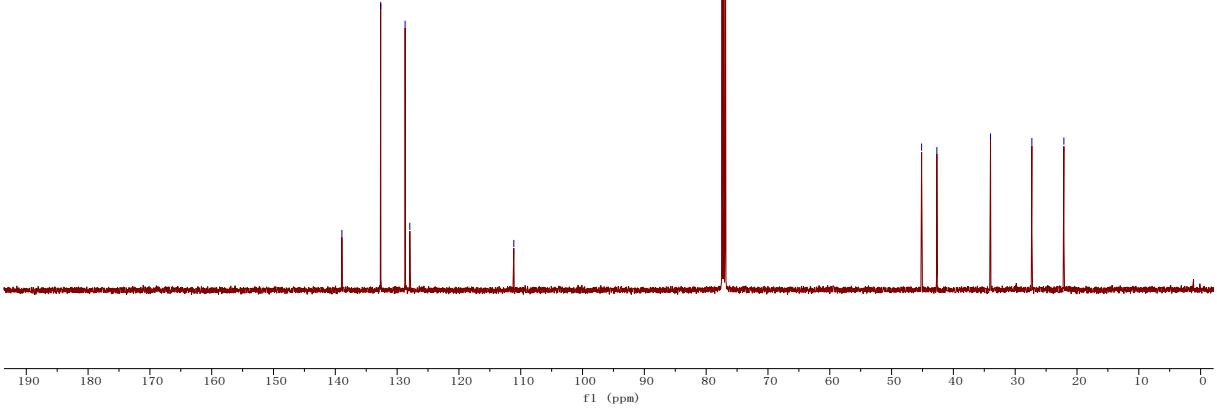


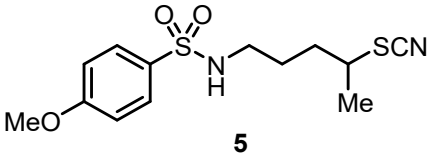




4

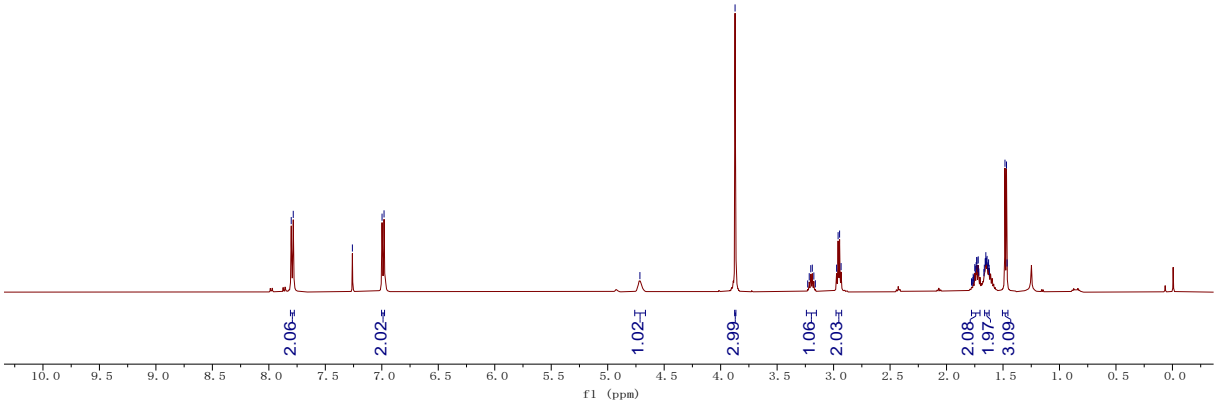
^{13}C NMR
125 MHz
$CDCl_3$

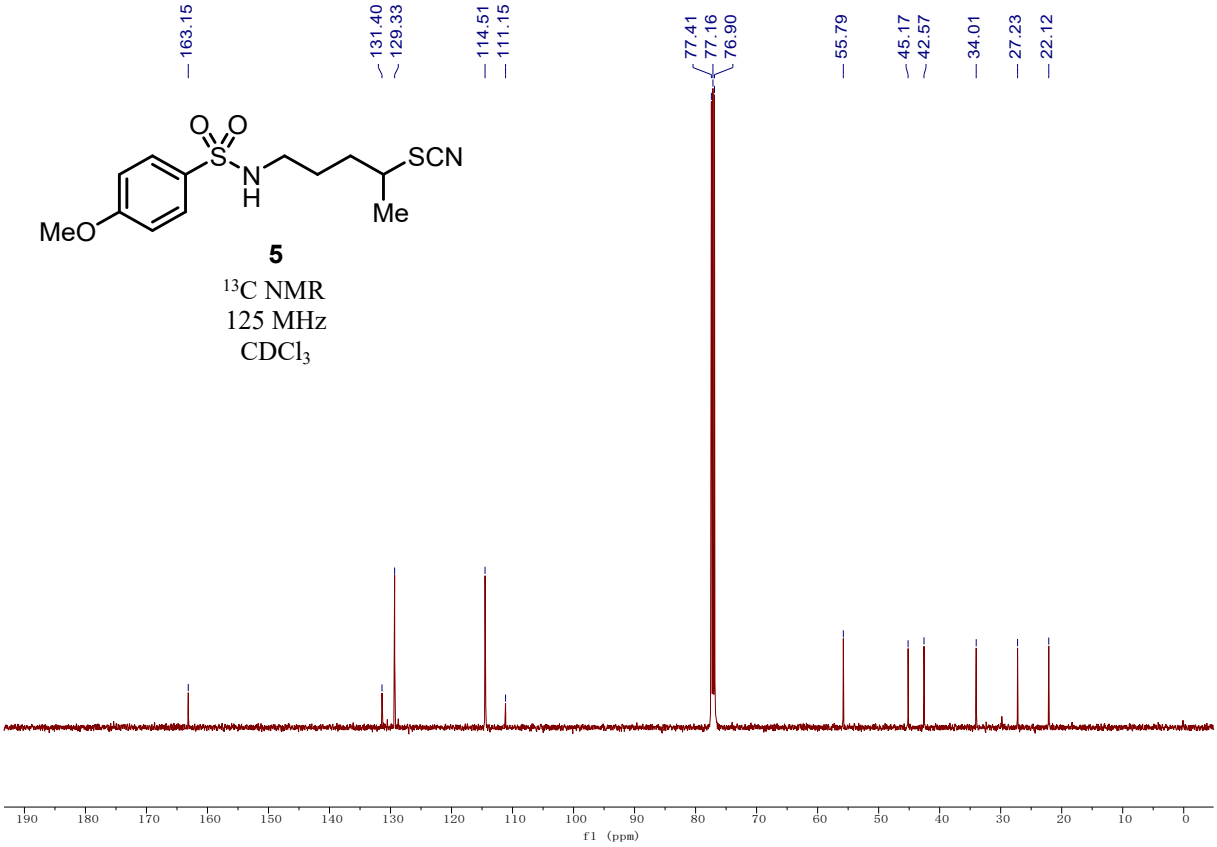




5

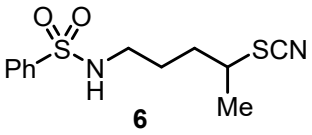
^{1}H NMR
500 MHz
$CDCl_3$





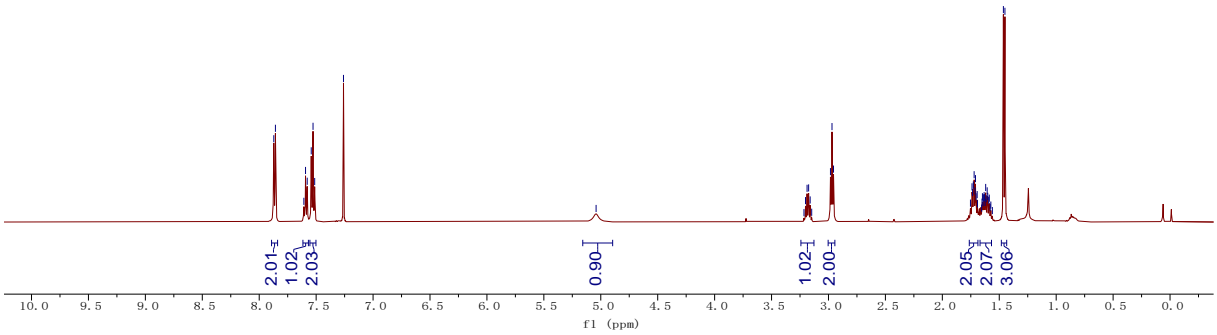
5

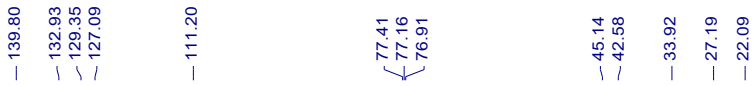
^{13}C NMR
125 MHz
$CDCl_3$

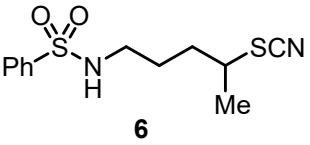


6

^{1}H NMR
500 MHz
$CDCl_3$

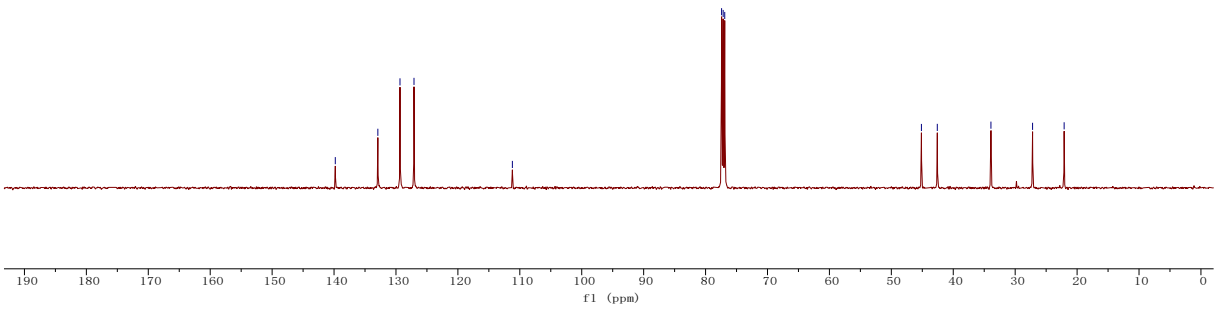


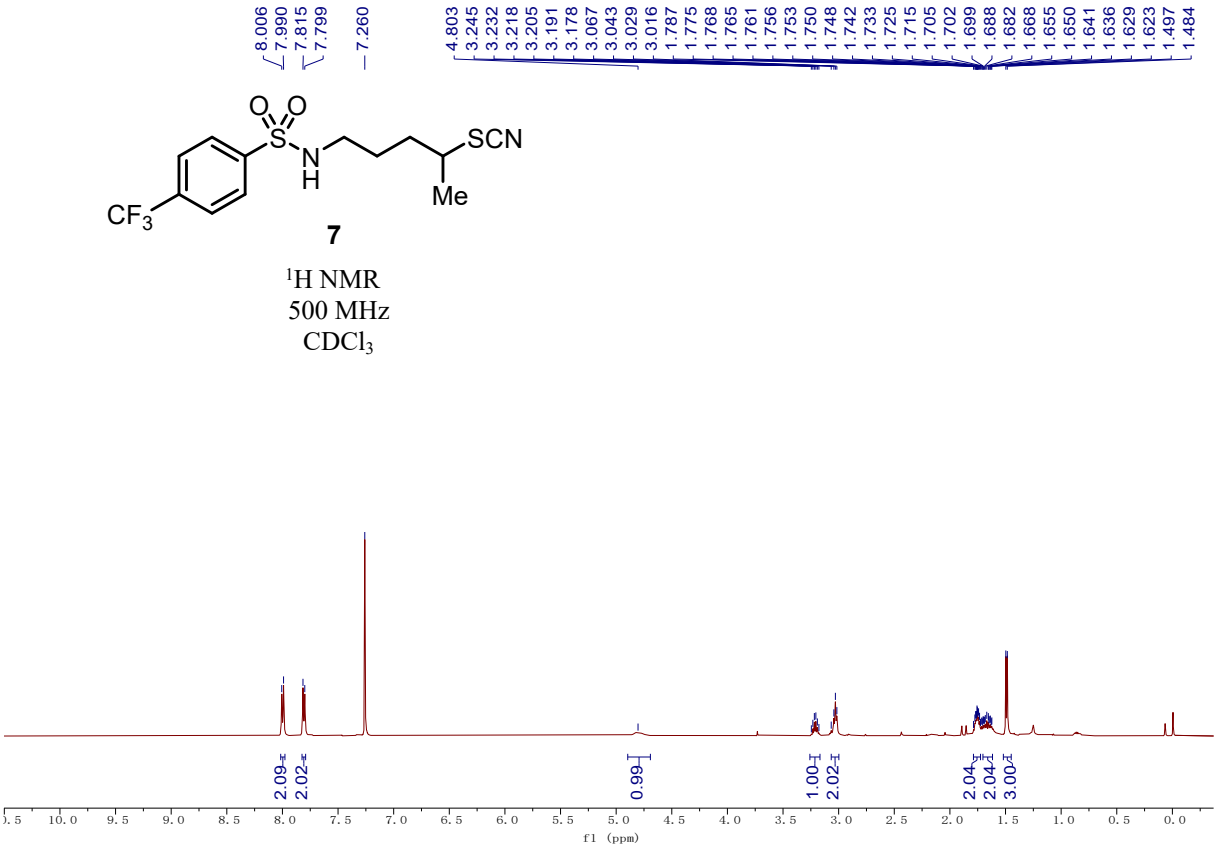




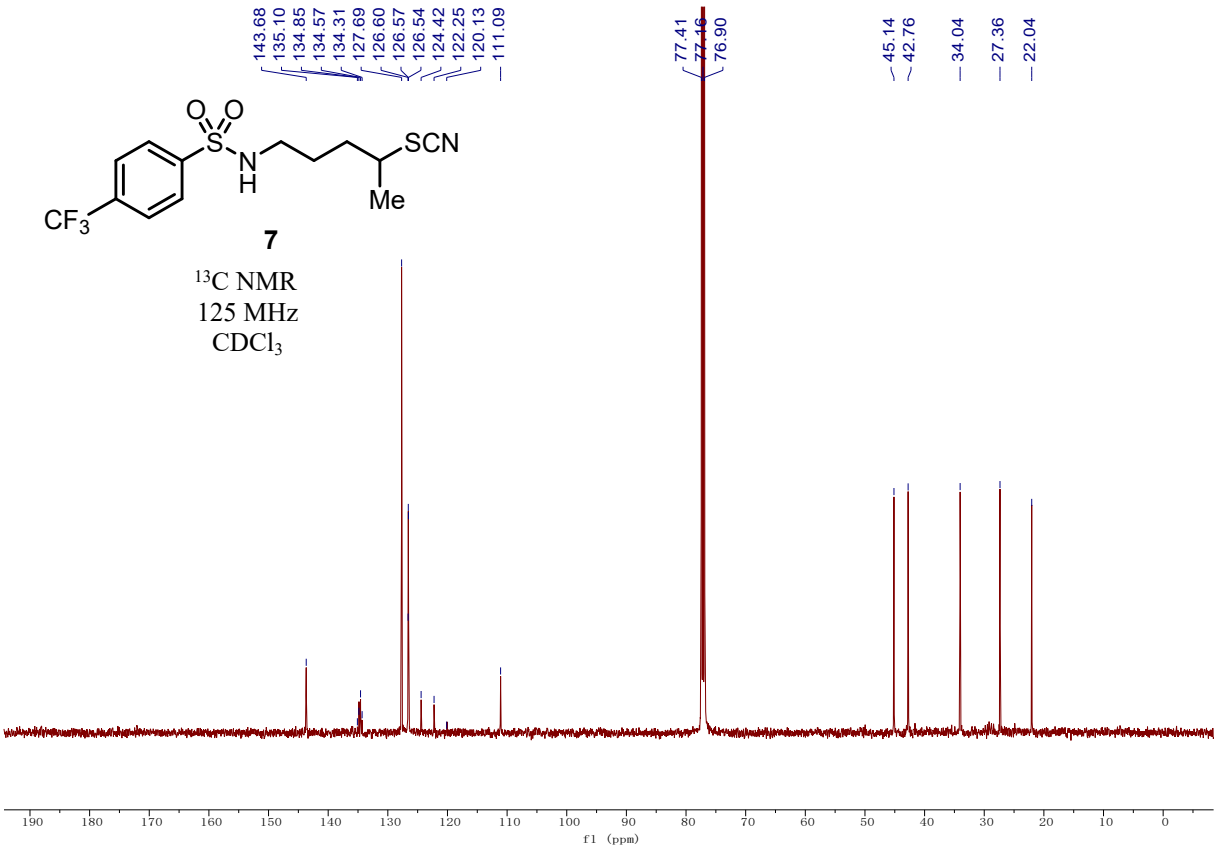
6

^{13}C NMR
125 MHz
$CDCl_3$

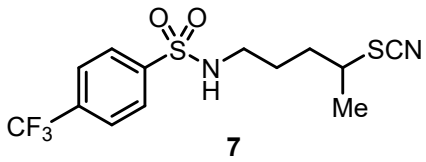




^{1}H NMR
500 MHz
$CDCl_3$

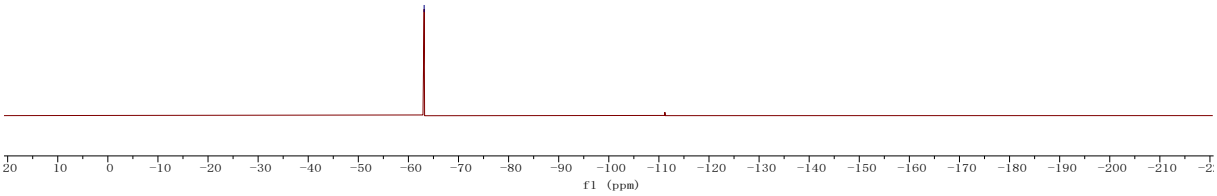


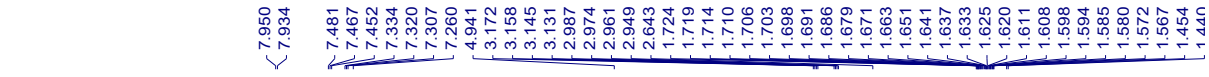
^{13}C NMR
125 MHz
$CDCl_3$

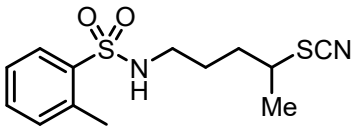


7

^{19}F NMR
376 MHz
$CDCl_3$

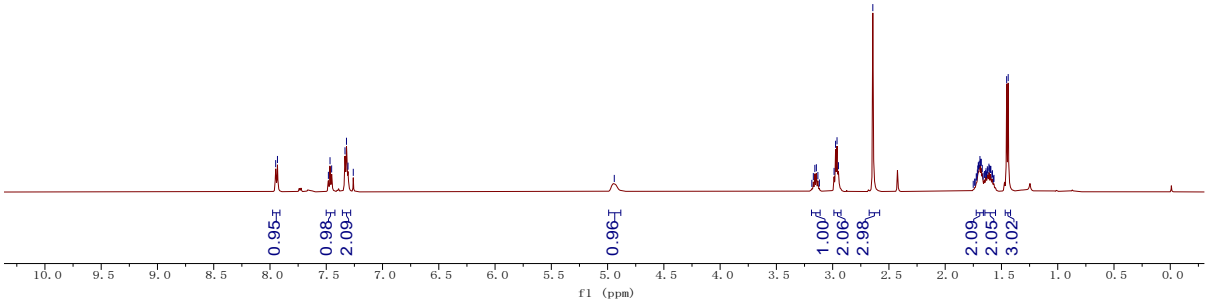


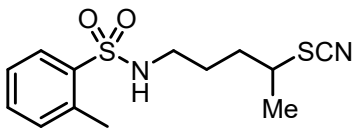




8

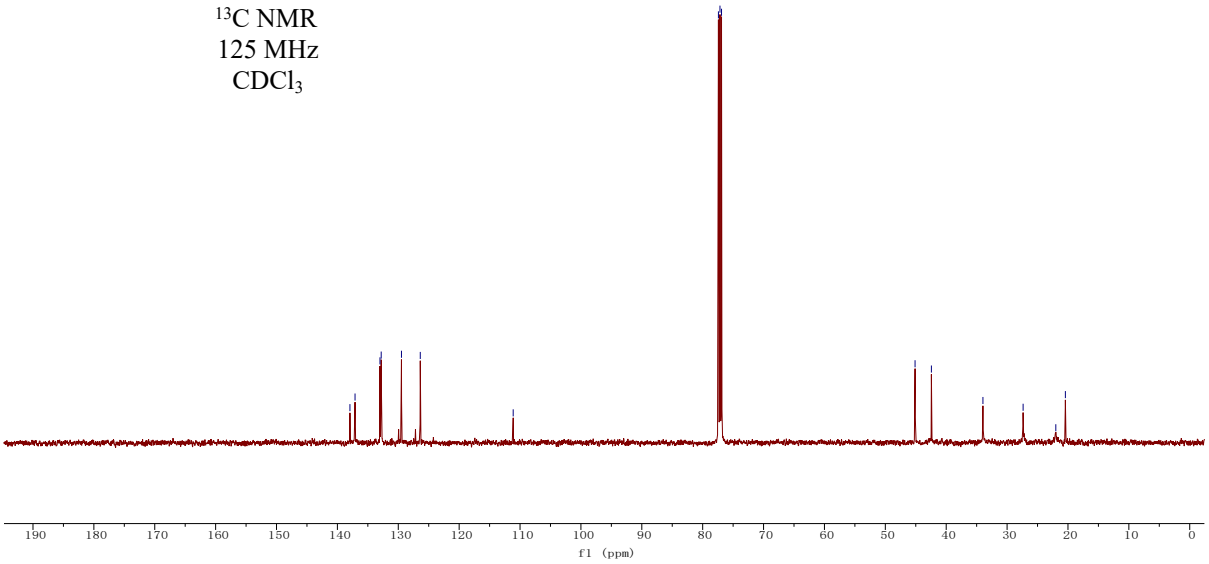
^{1}H NMR
500 MHz
$CDCl_3$

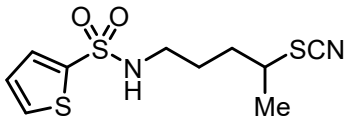




8

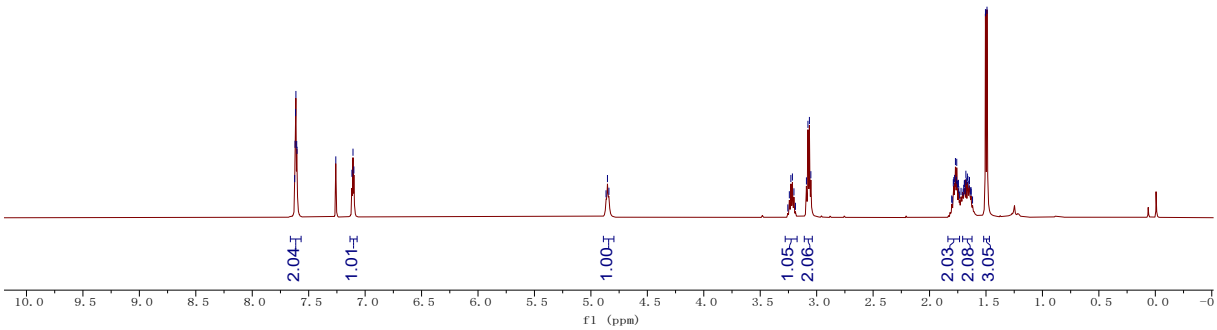
^{13}C NMR
125 MHz
$CDCl_3$

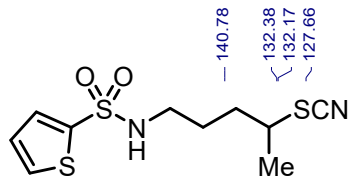




9

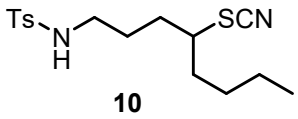
^{1}H NMR
500 MHz
$CDCl_3$





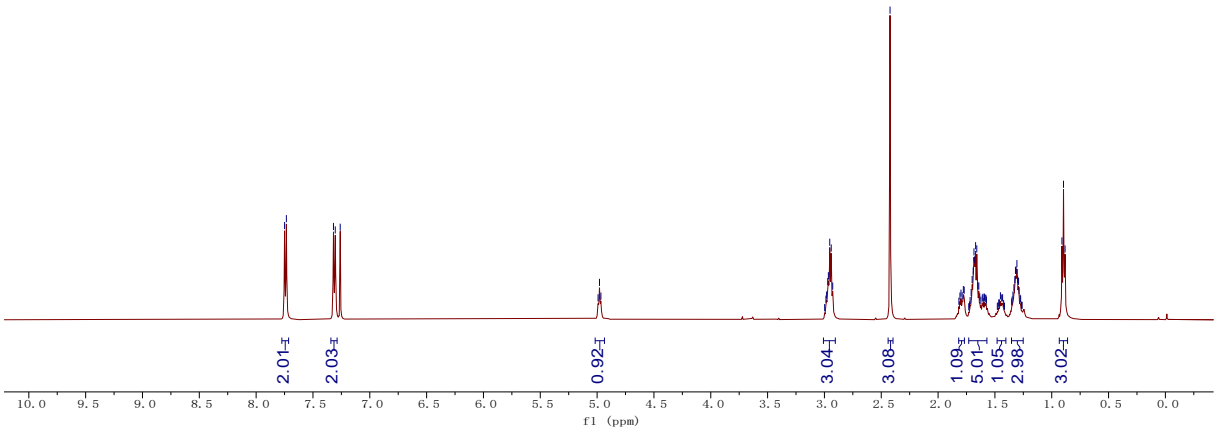
9

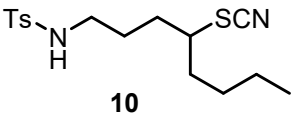
^{13}C NMR
125 MHz
$CDCl_3$



10

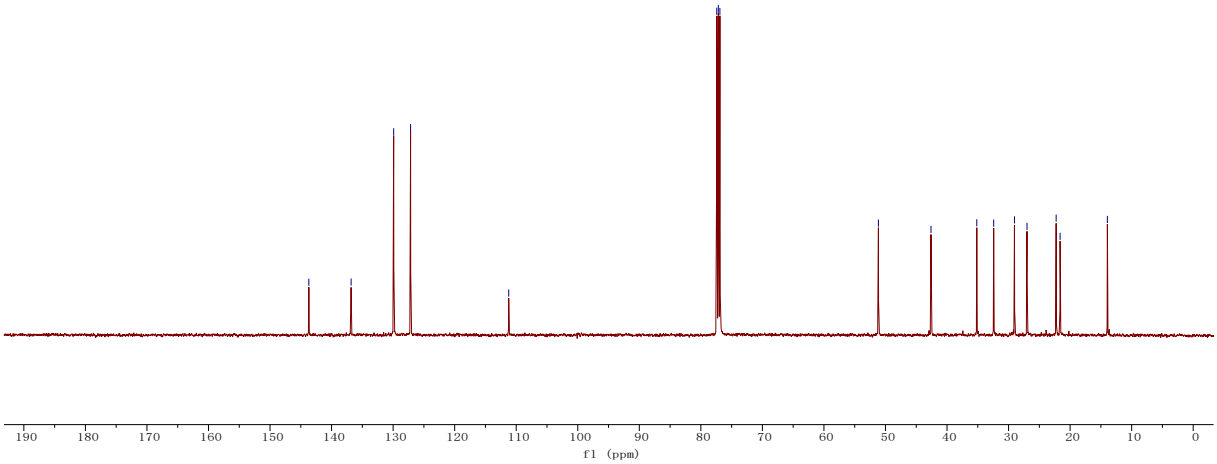
^{1}H NMR
500 MHz
$CDCl_3$

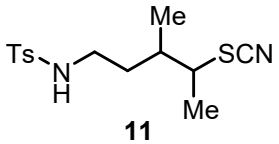




10

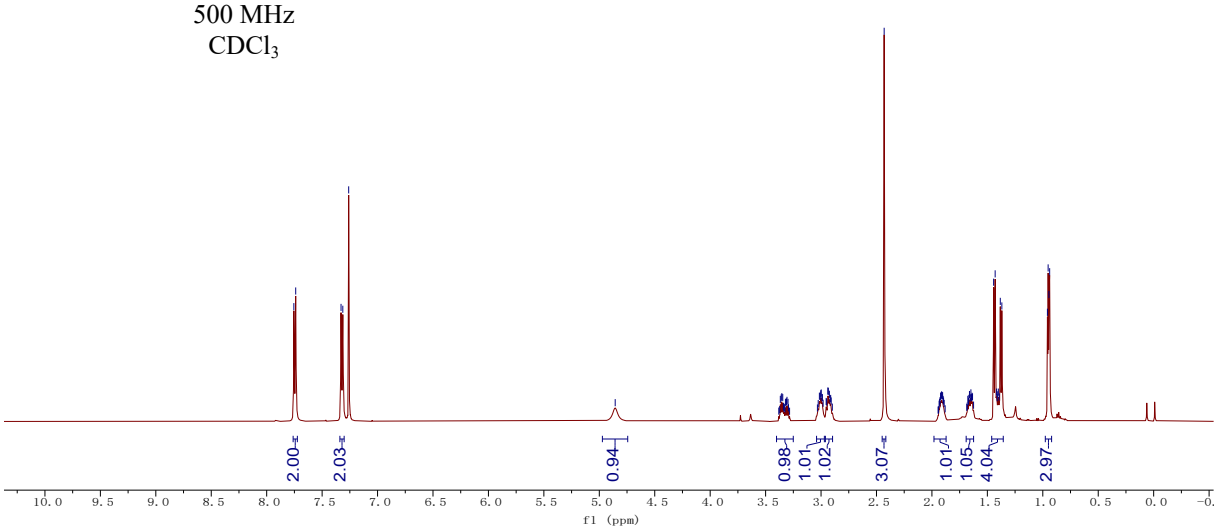
^{13}C NMR
125 MHz
$CDCl_3$

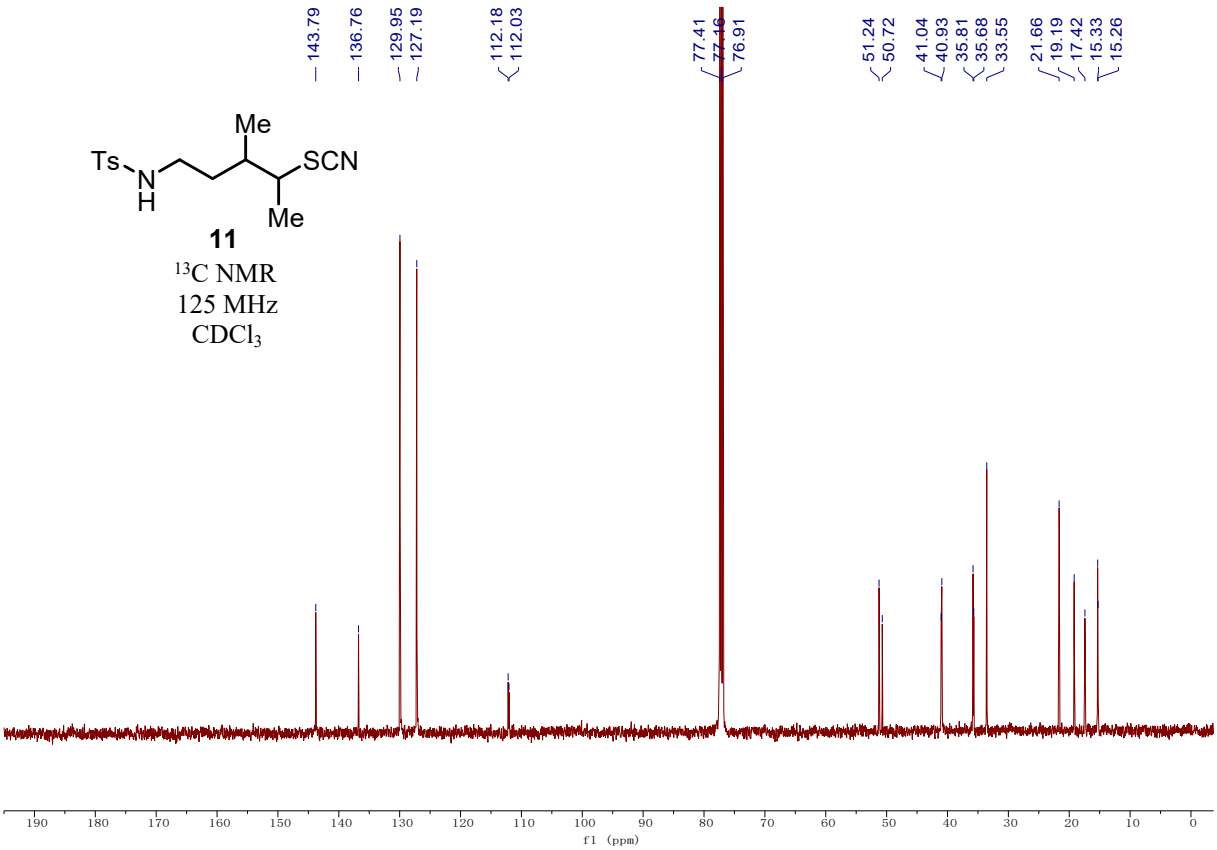




11

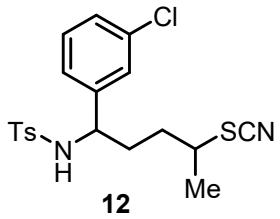
^{1}H NMR
500 MHz
$CDCl_3$





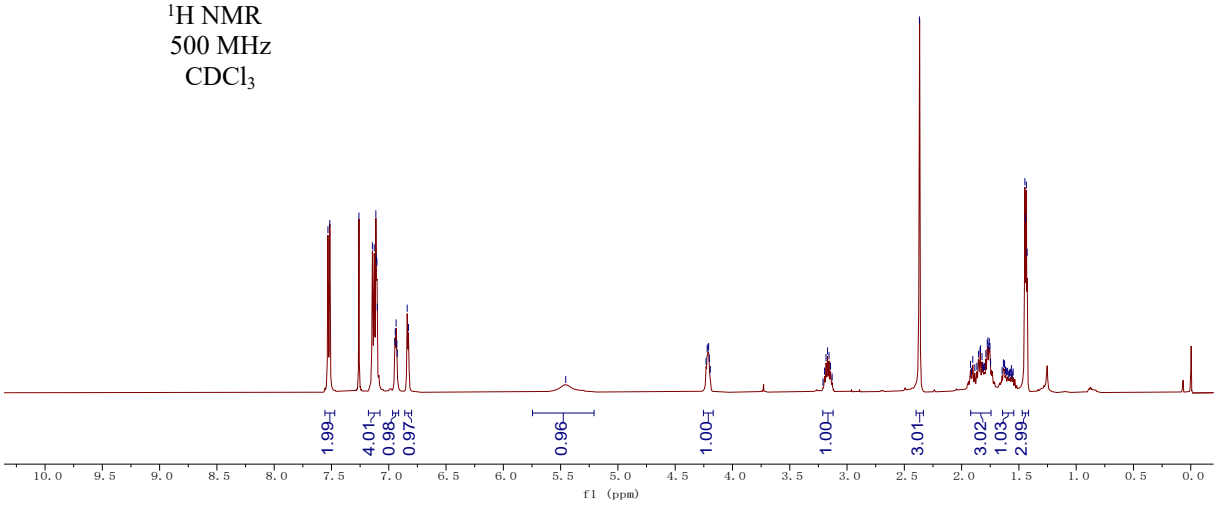
11

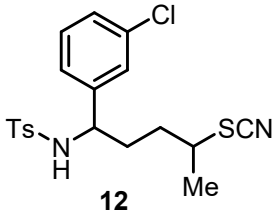
^{13}C NMR
125 MHz
$CDCl_3$



12

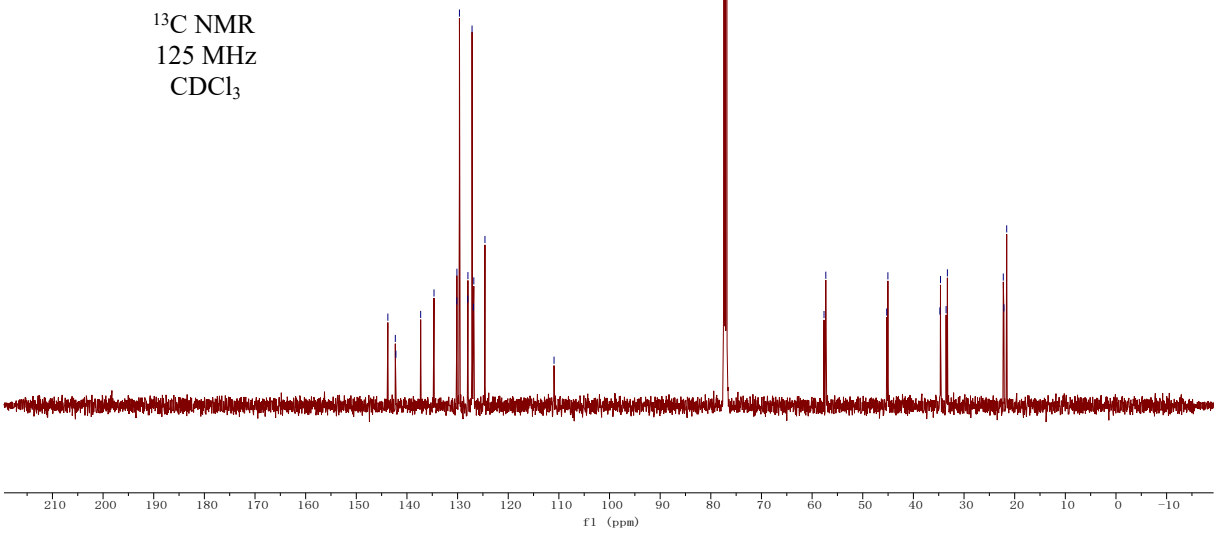
^{1}H NMR
500 MHz
$CDCl_3$

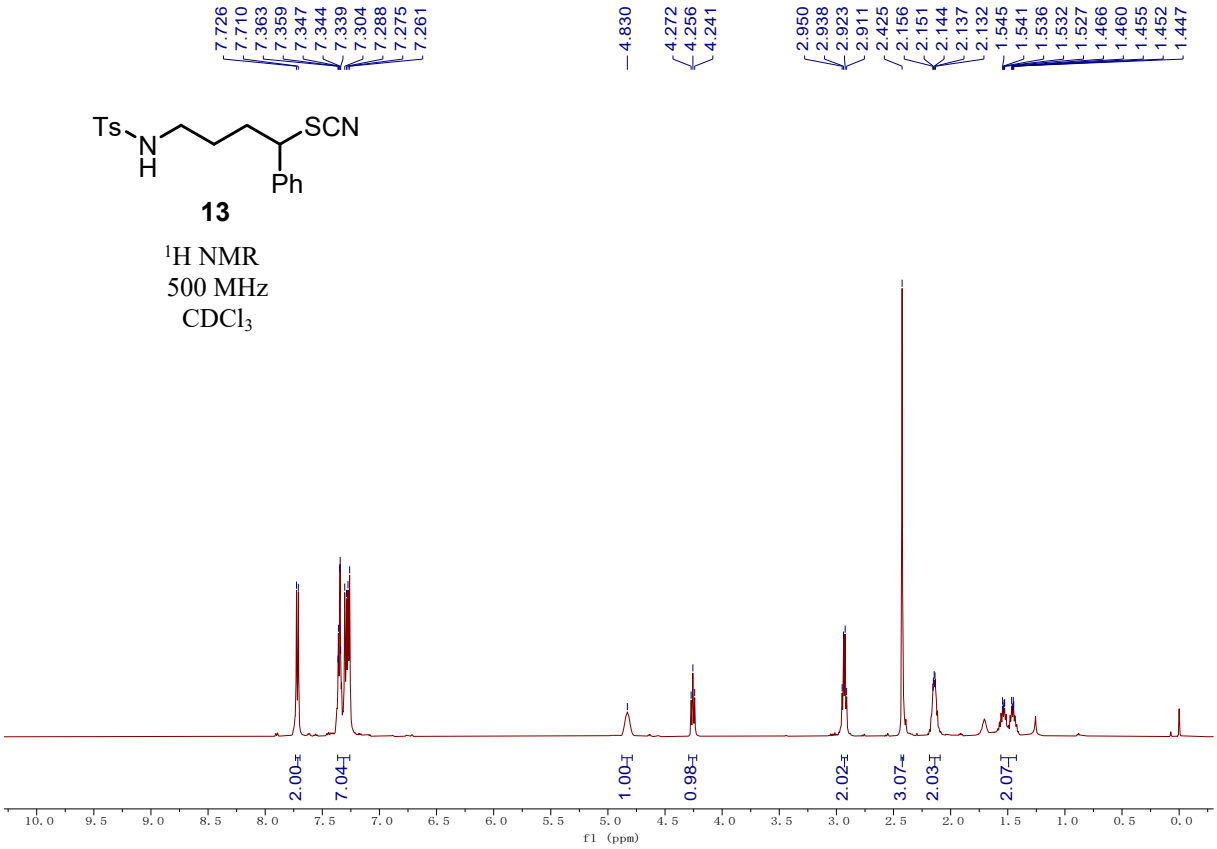




12

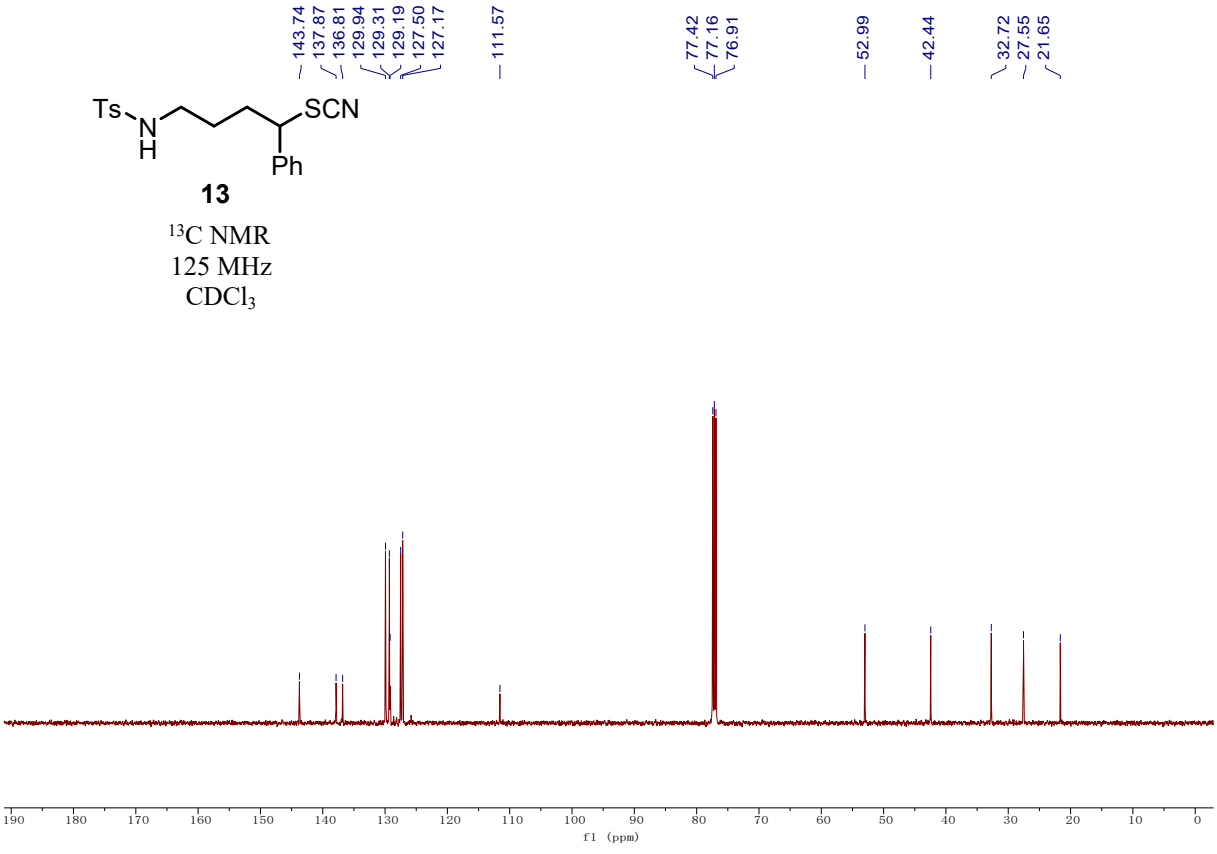
^{13}C NMR
125 MHz
$CDCl_3$





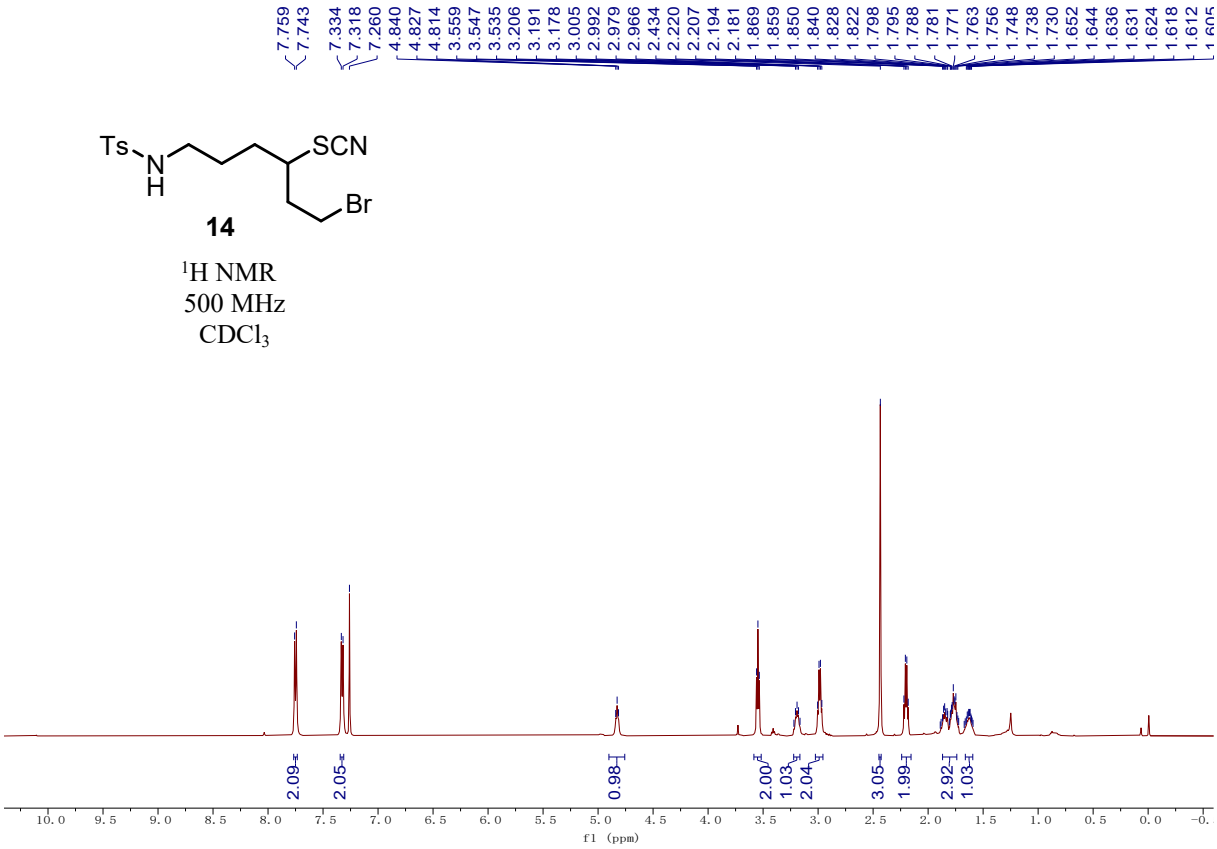
13

^{1}H NMR
500 MHz
$CDCl_3$

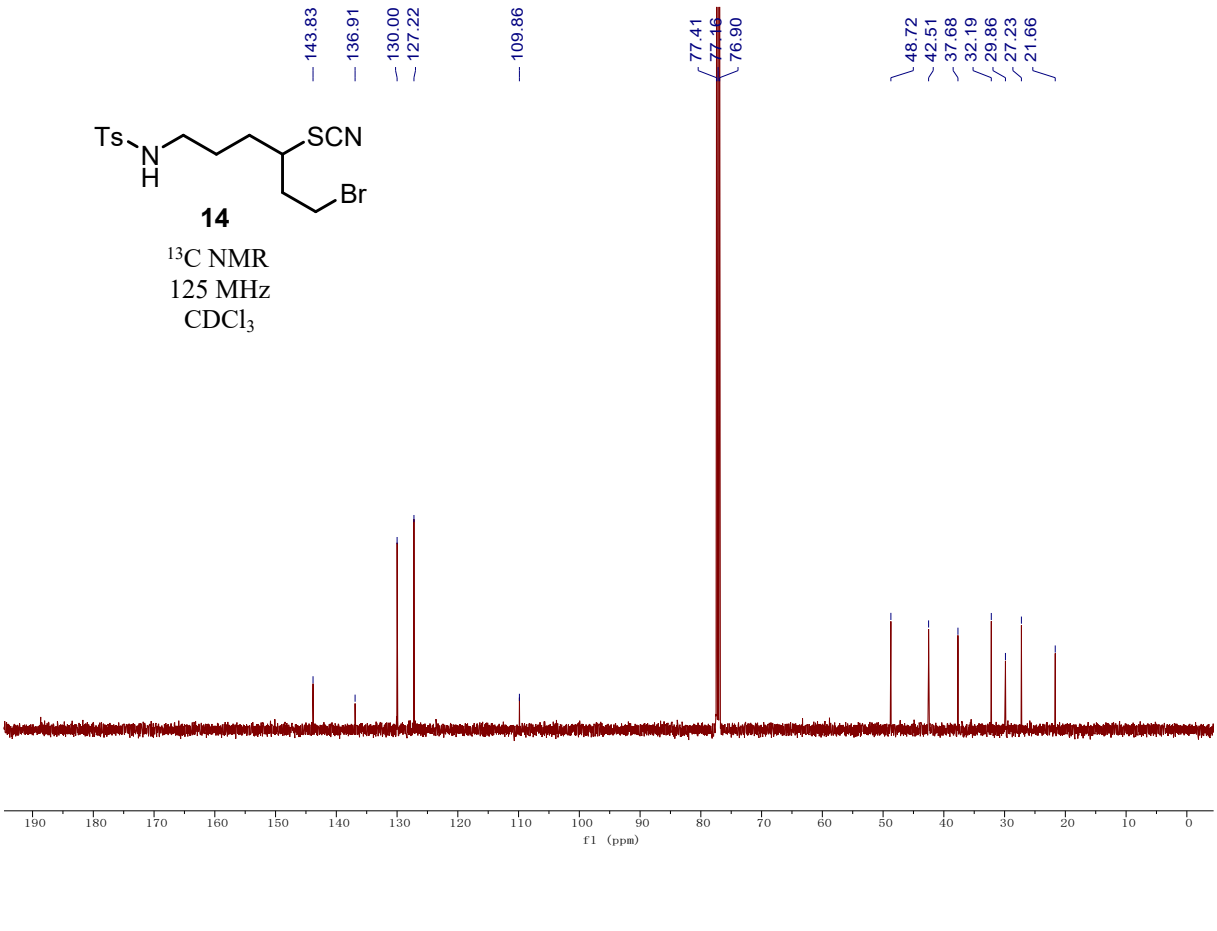


13

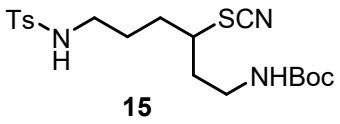
^{13}C NMR
125 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$

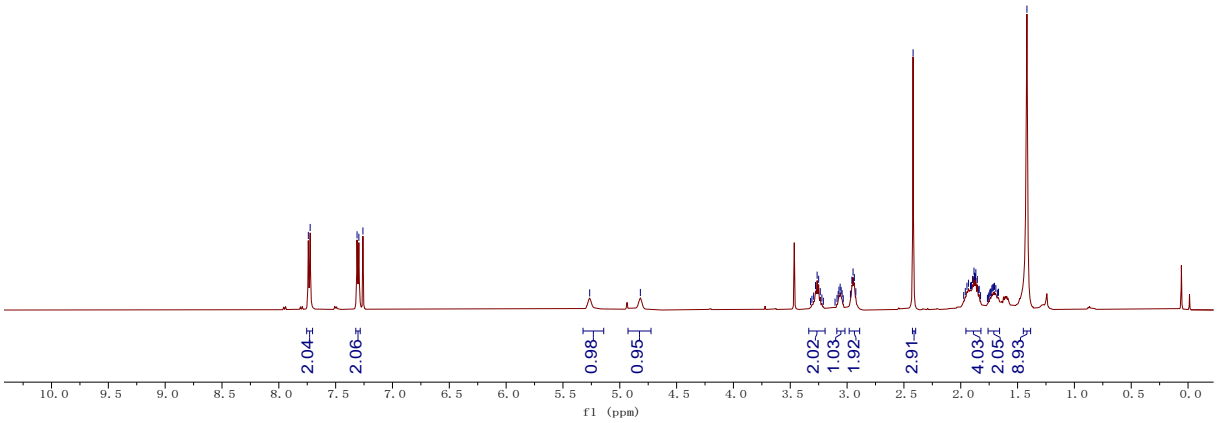


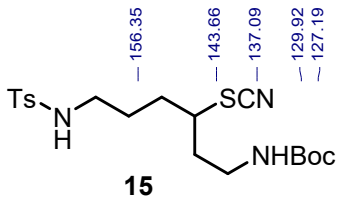
^{13}C NMR
125 MHz
$CDCl_3$



15

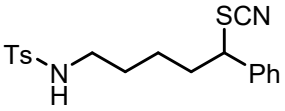
^{1}H NMR
500 MHz
$CDCl_3$





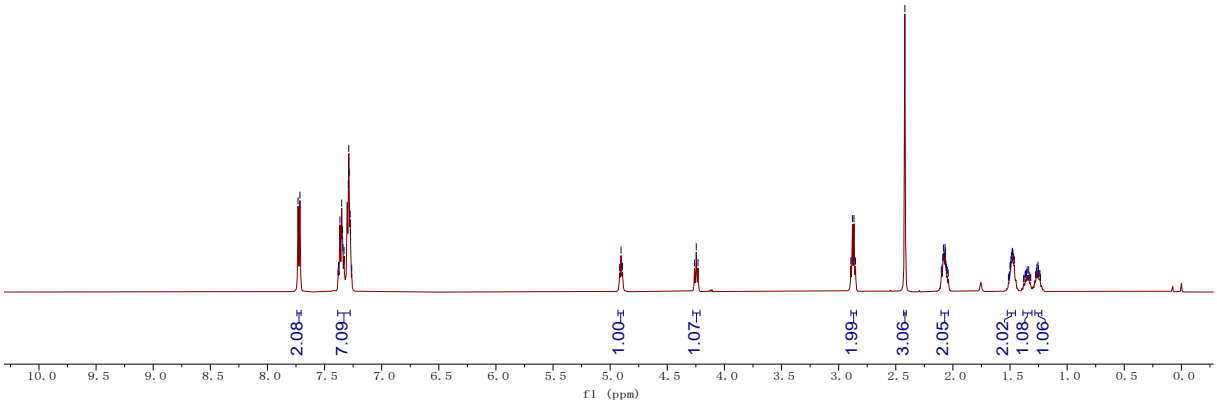
15

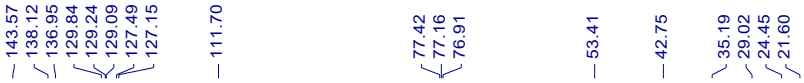
^{13}C NMR
125 MHz
$CDCl_3$

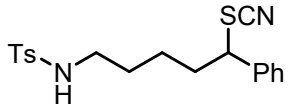


16

^{1}H NMR
500 MHz
$CDCl_3$

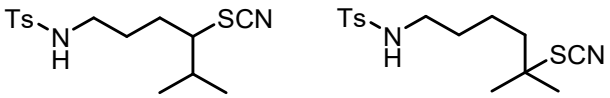






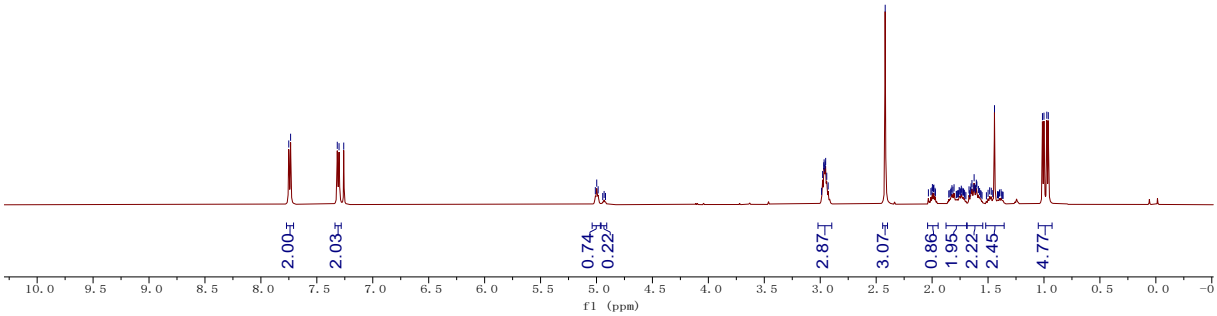
16

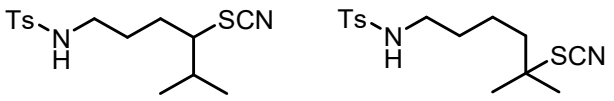
^{13}C NMR
125 MHz
$CDCl_3$



17

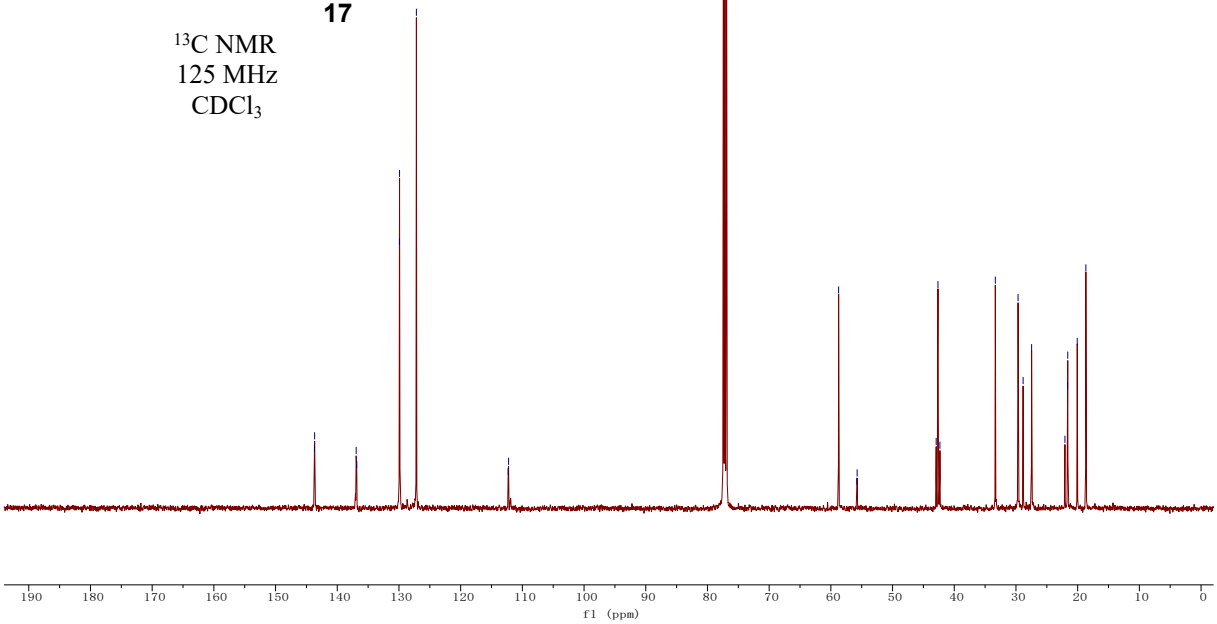
^{1}H NMR
500 MHz
$CDCl_3$

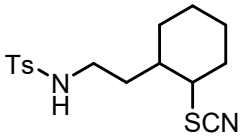




17

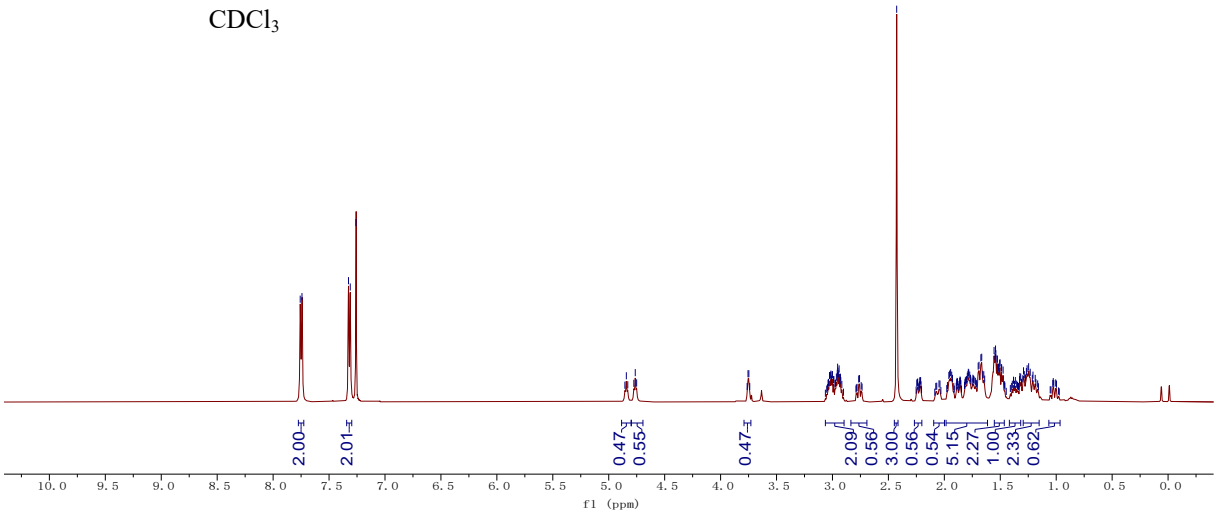
^{13}C NMR
125 MHz
$CDCl_3$

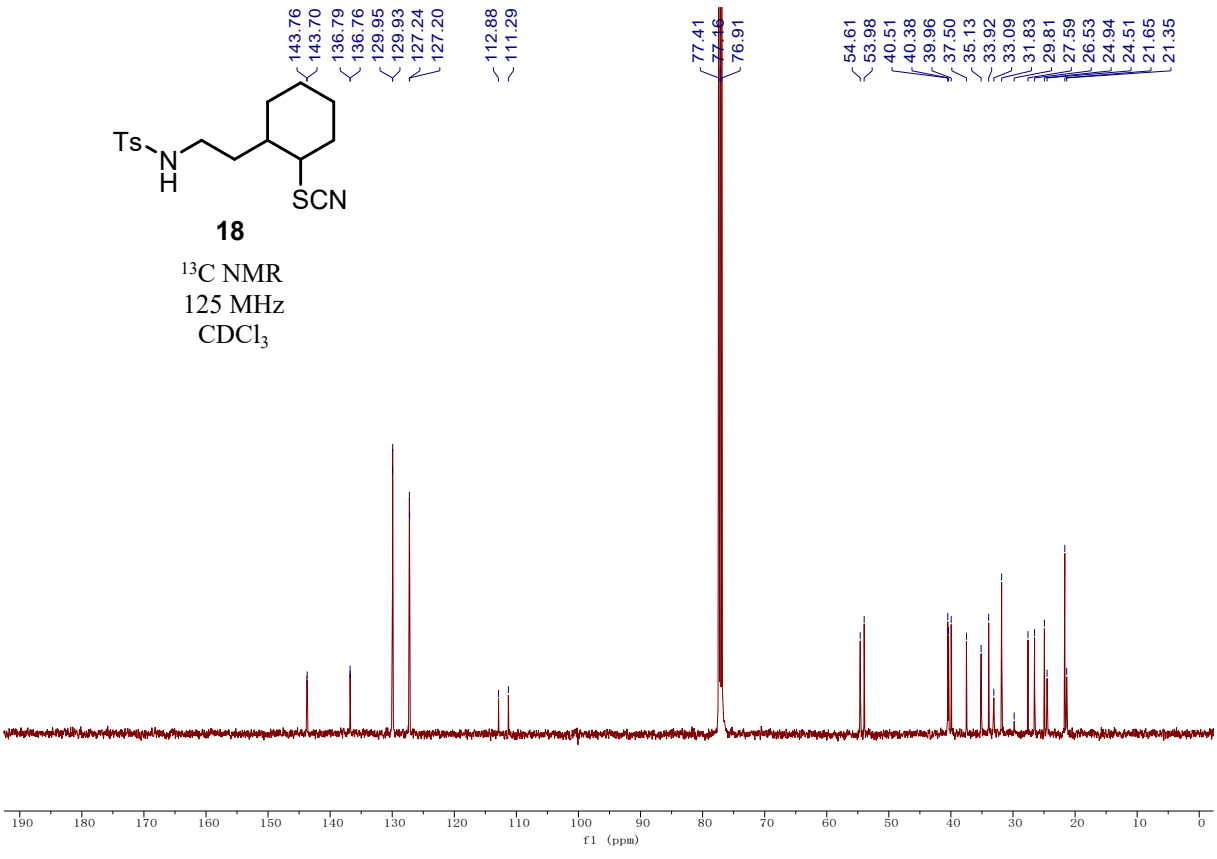




18

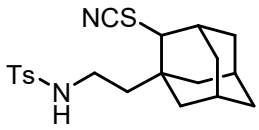
^{1}H NMR
500 MHz
$CDCl_3$





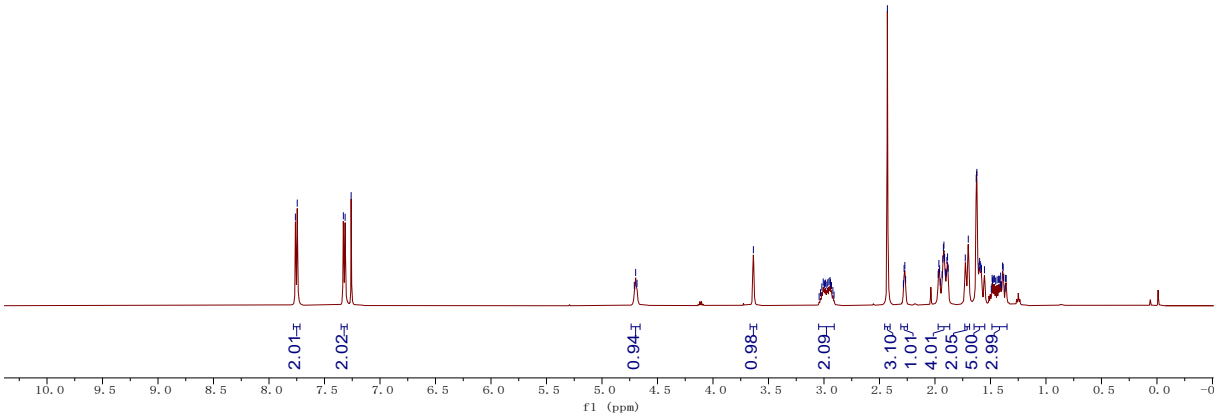
18

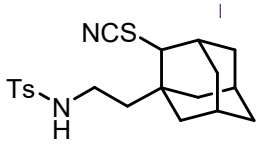
^{13}C NMR
125 MHz
$CDCl_3$



19

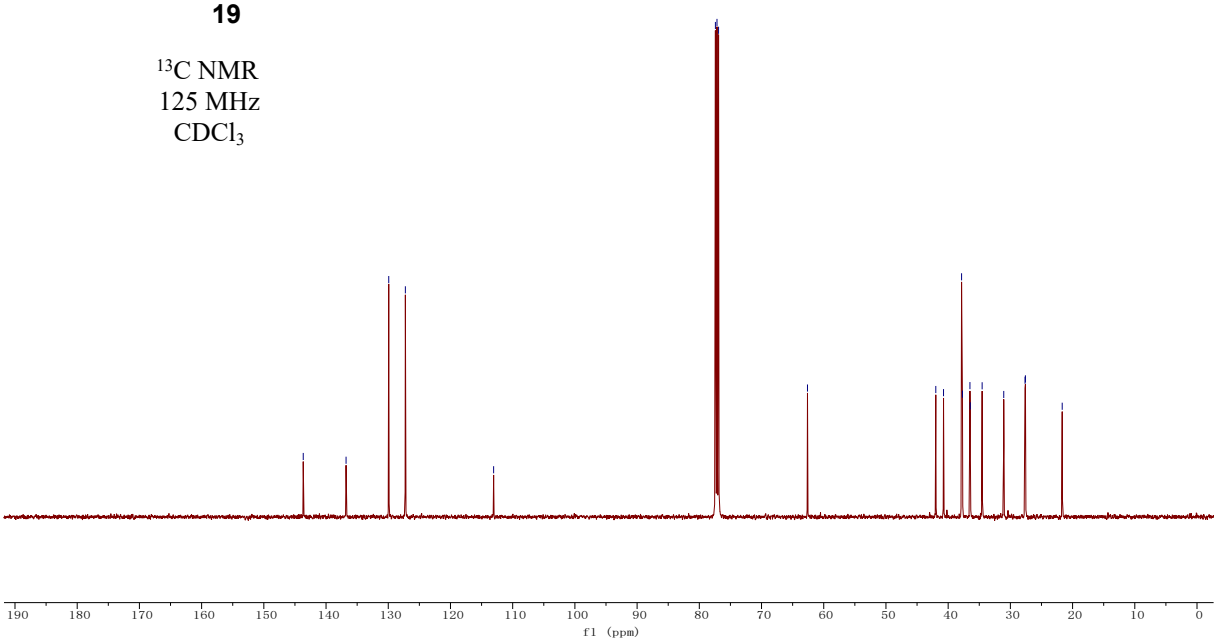
^{1}H NMR
500 MHz
$CDCl_3$

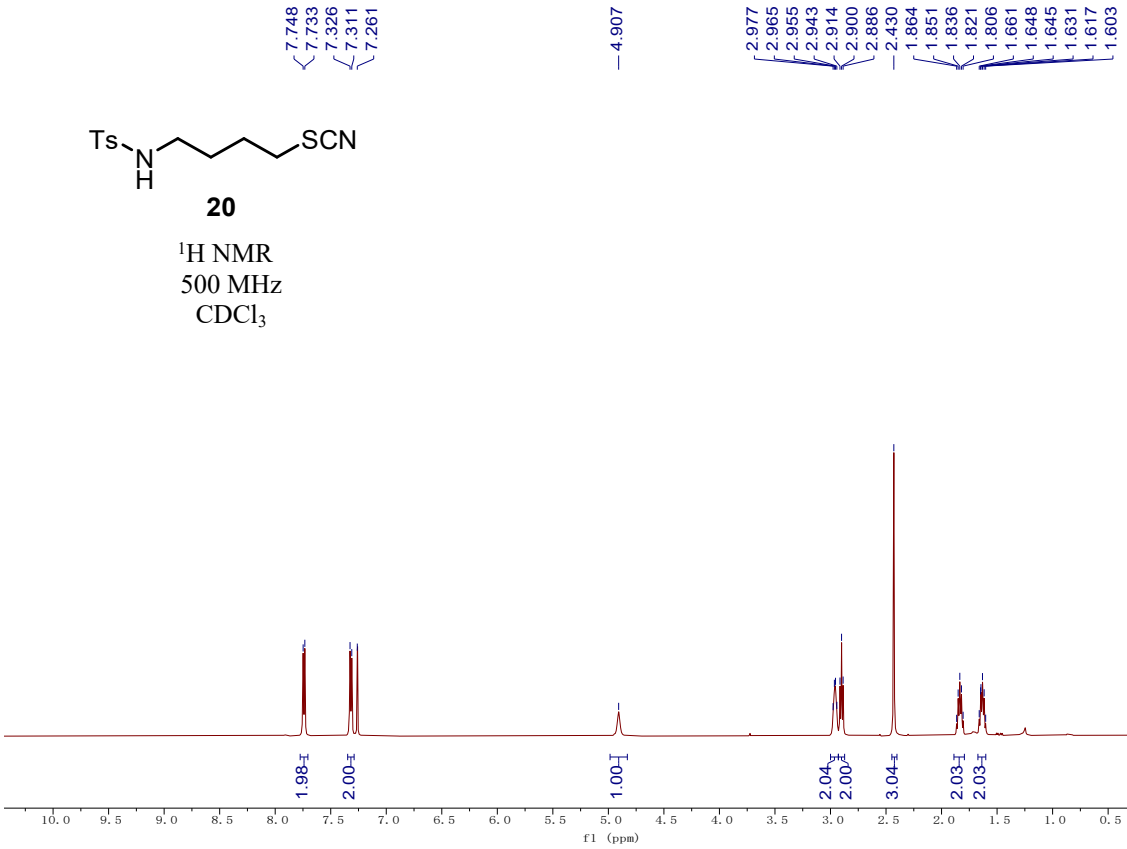




19

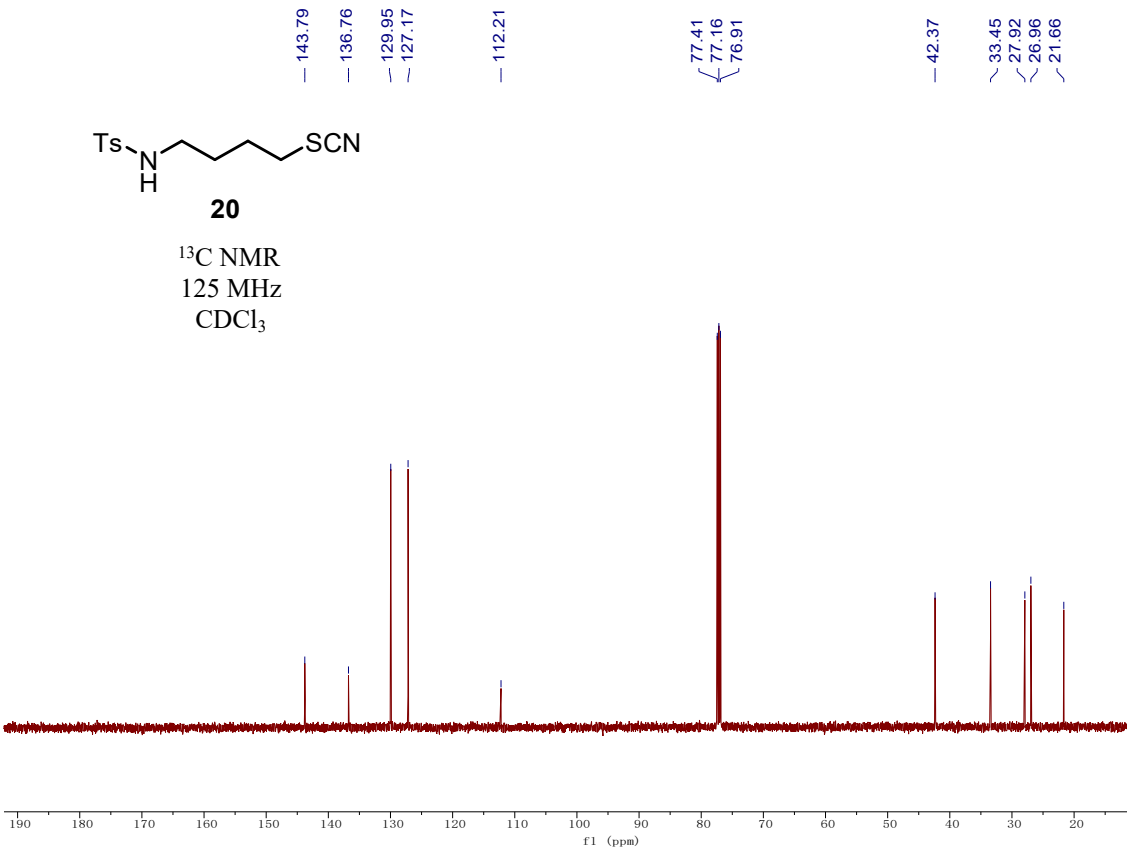
^{13}C NMR
125 MHz
$CDCl_3$





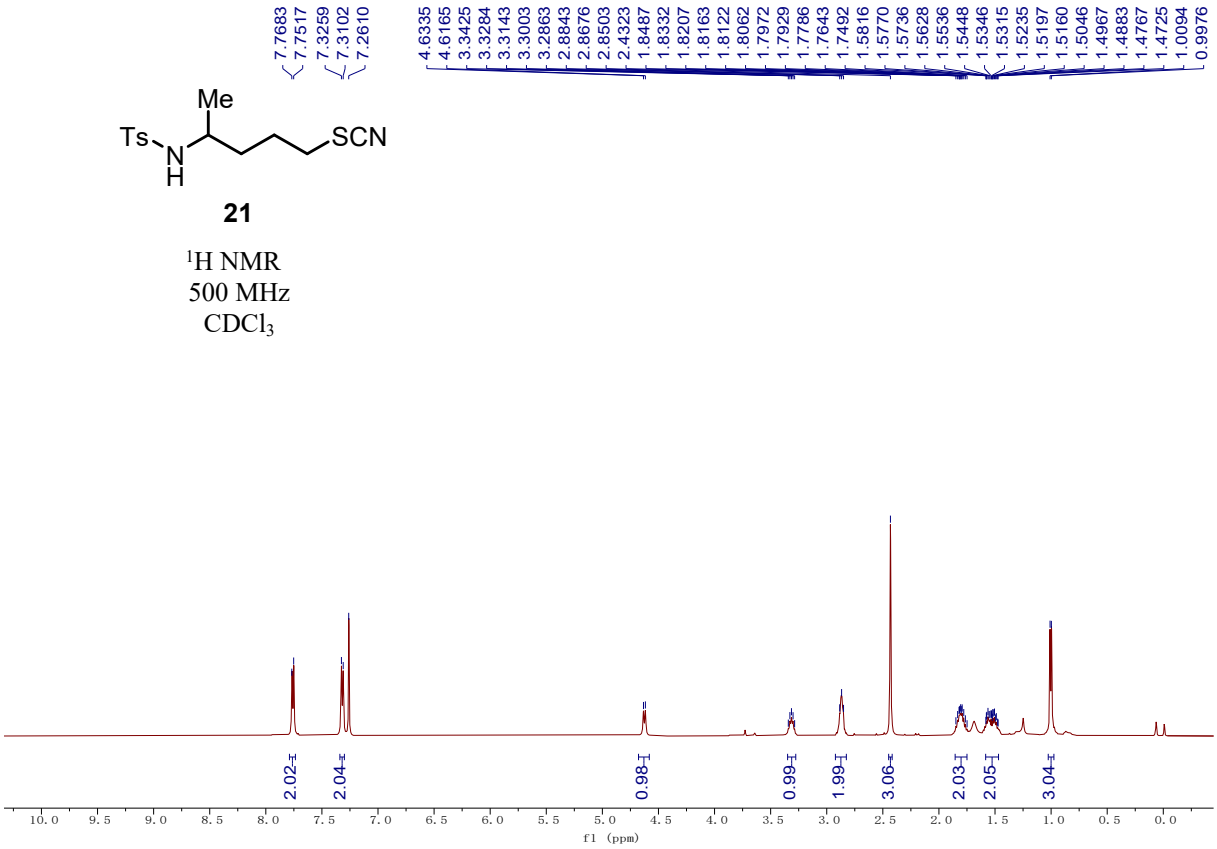
20

^{1}H NMR
500 MHz
$CDCl_3$



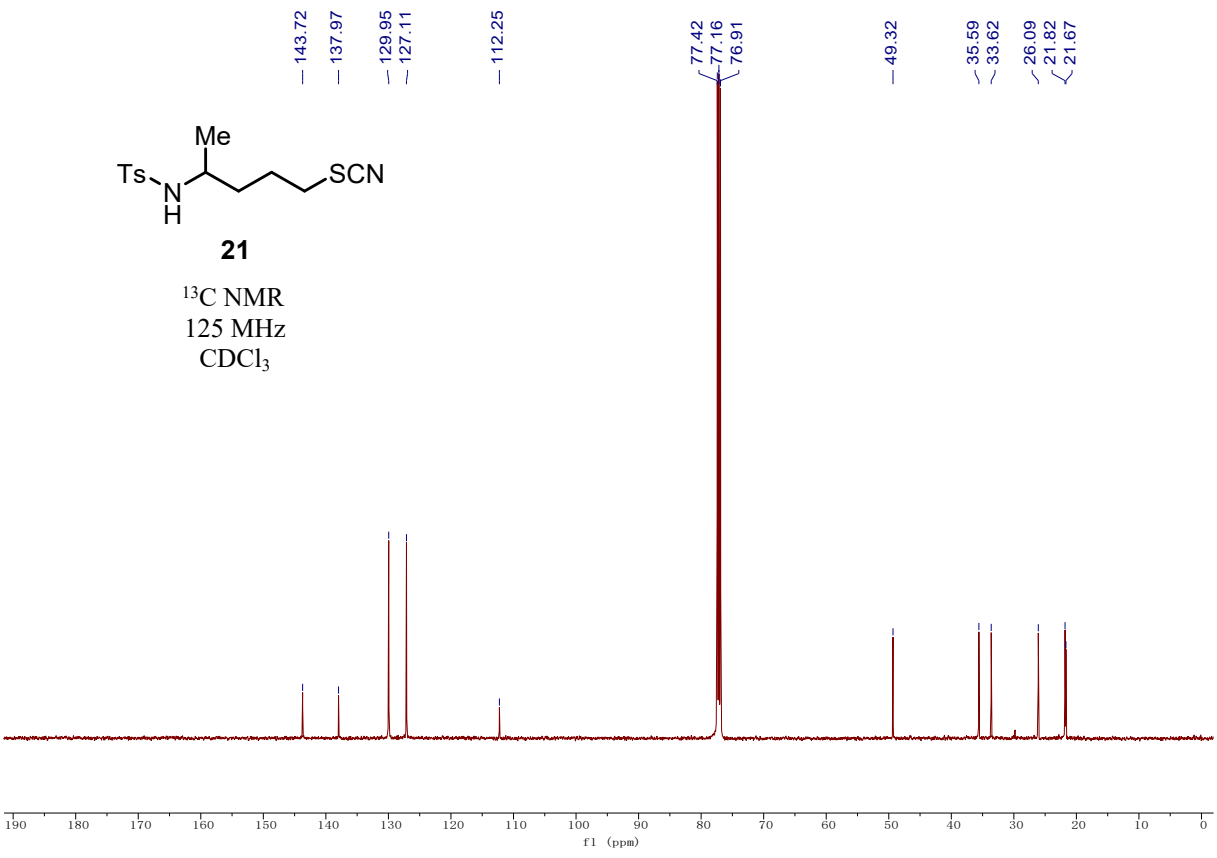
20

^{13}C NMR
125 MHz
$CDCl_3$



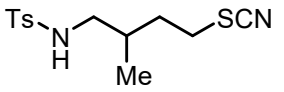
21

^{1}H NMR
500 MHz
$CDCl_3$



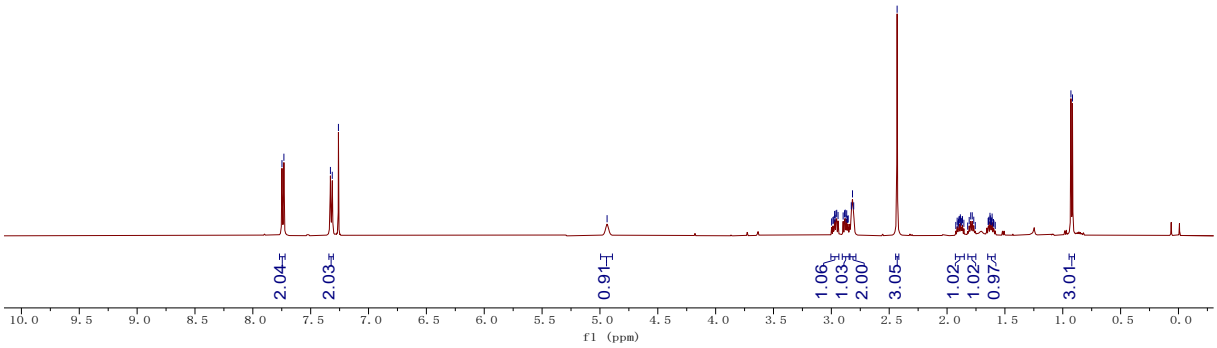
21

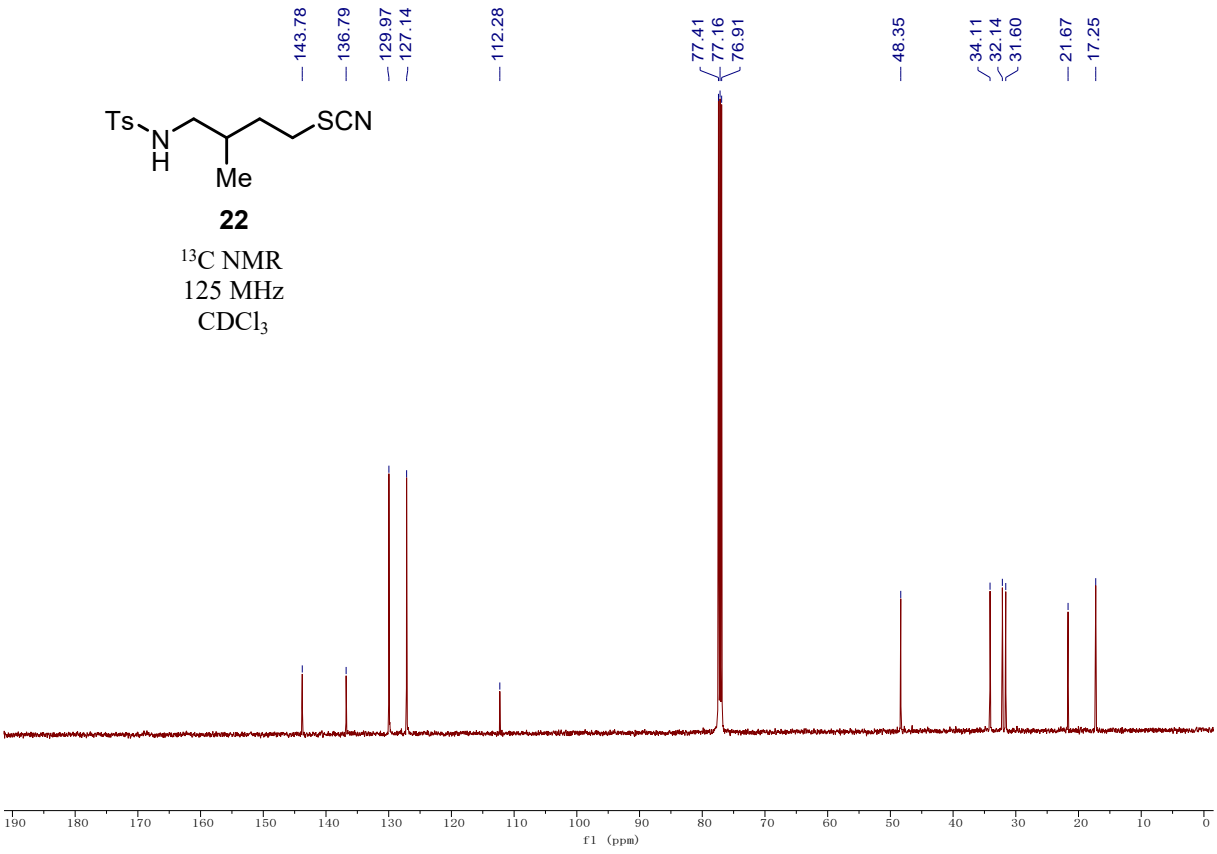
^{13}C NMR
125 MHz
$CDCl_3$



22

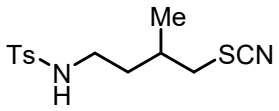
^{1}H NMR
500 MHz
$CDCl_3$





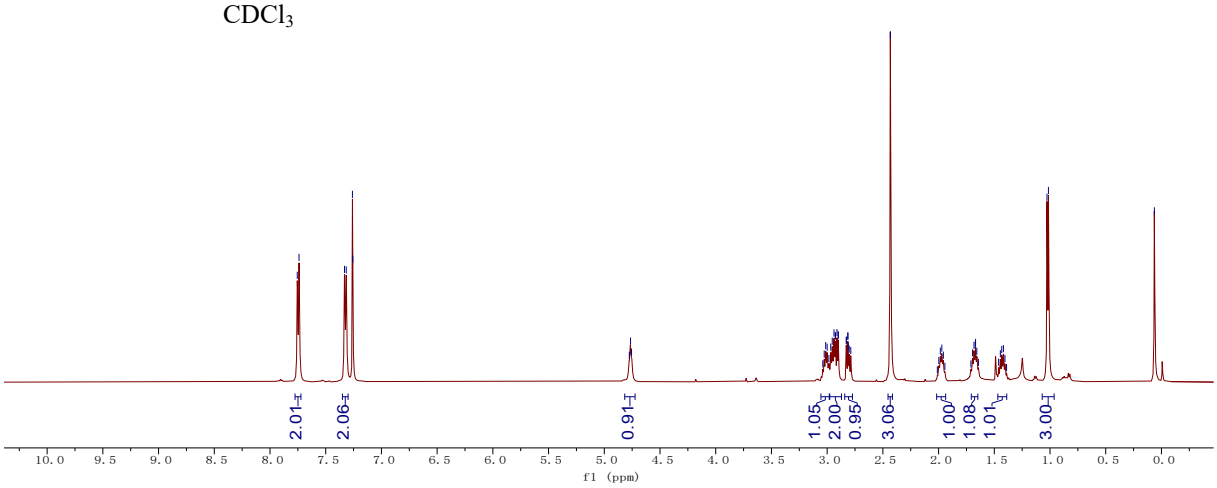
22

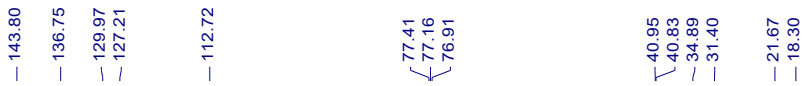
^{13}C NMR
125 MHz
$CDCl_3$

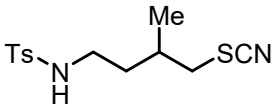


23

^{1}H NMR
500 MHz
$CDCl_3$

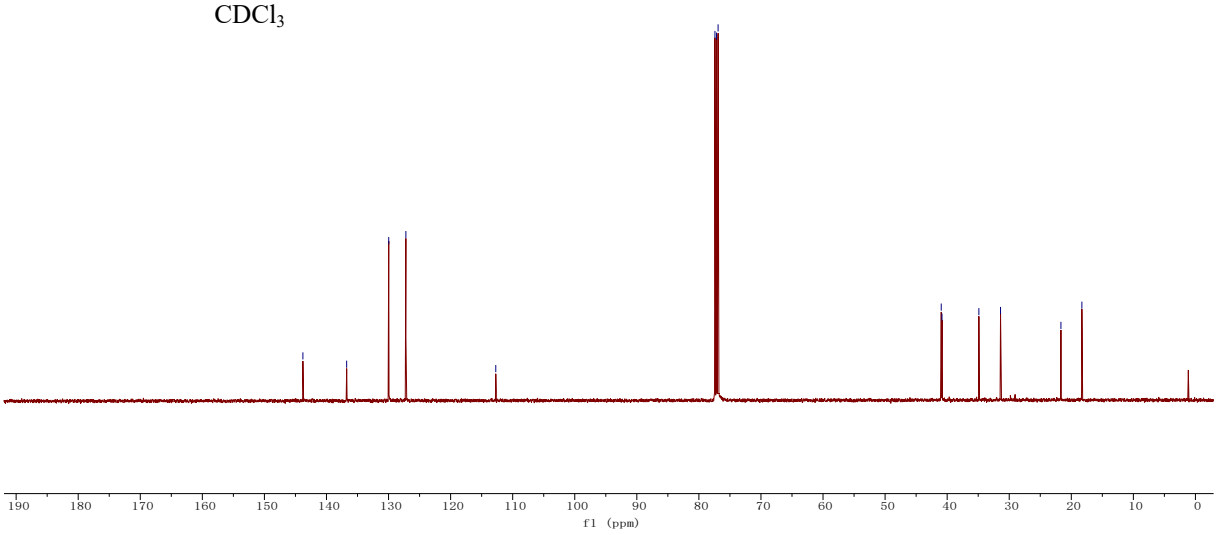


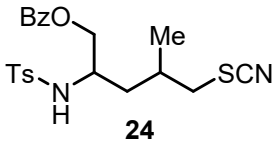




23

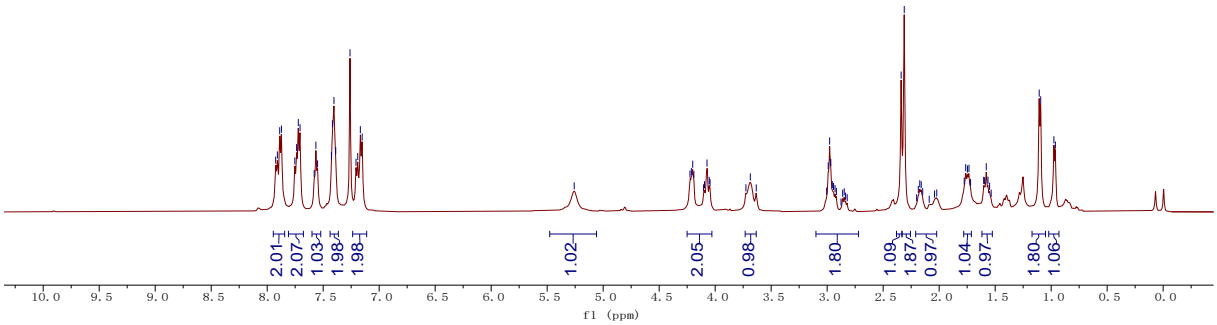
^{13}C NMR
125 MHz
$CDCl_3$

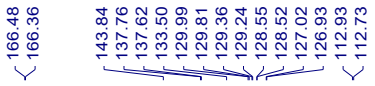




24

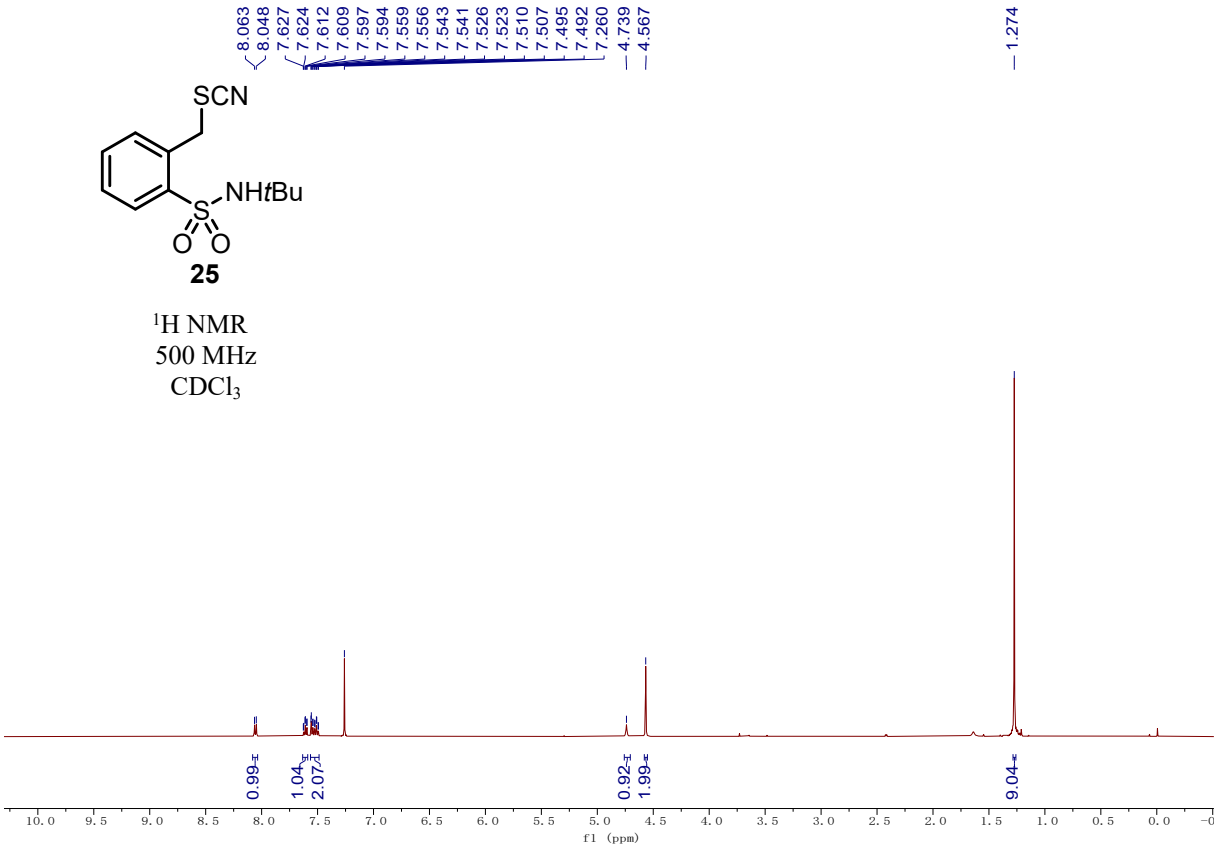
^{1}H NMR
500 MHz
$CDCl_3$





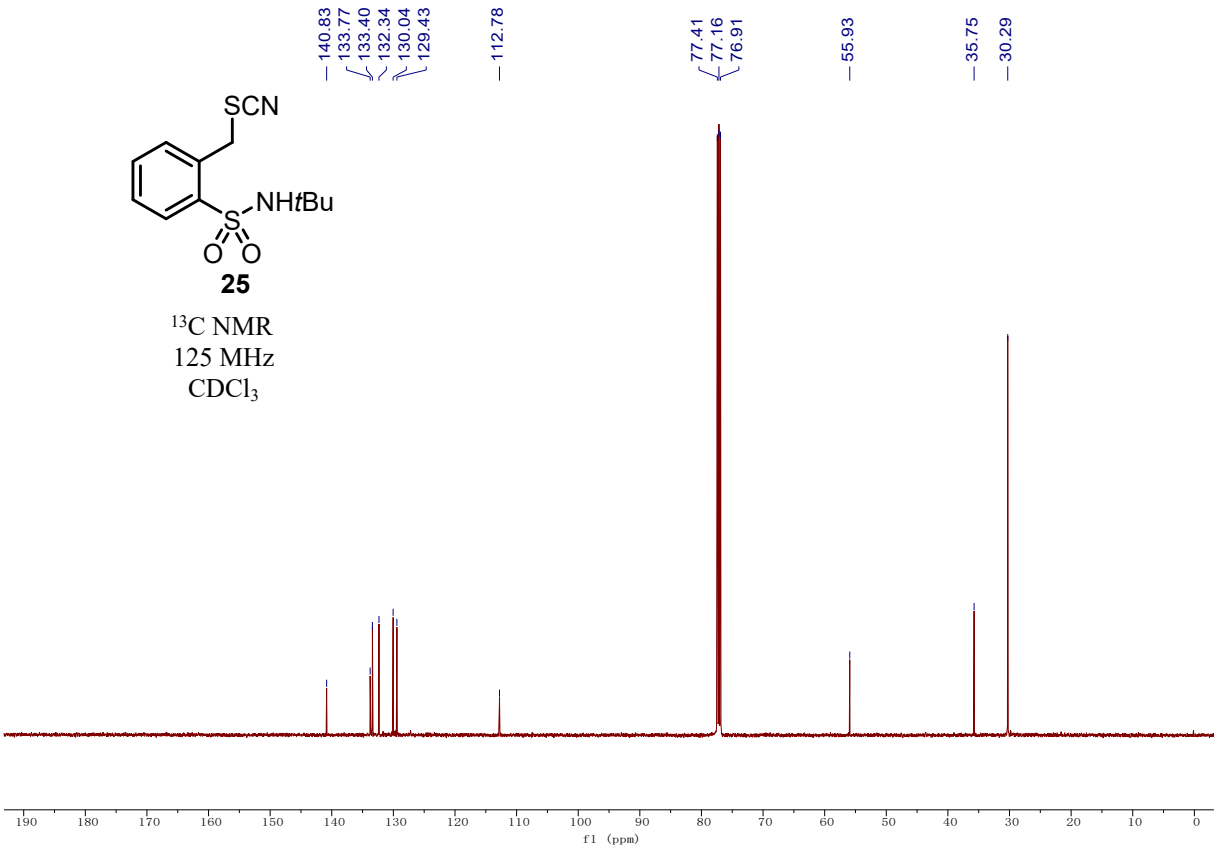
24

^{13}C NMR
125 MHz
$CDCl_3$



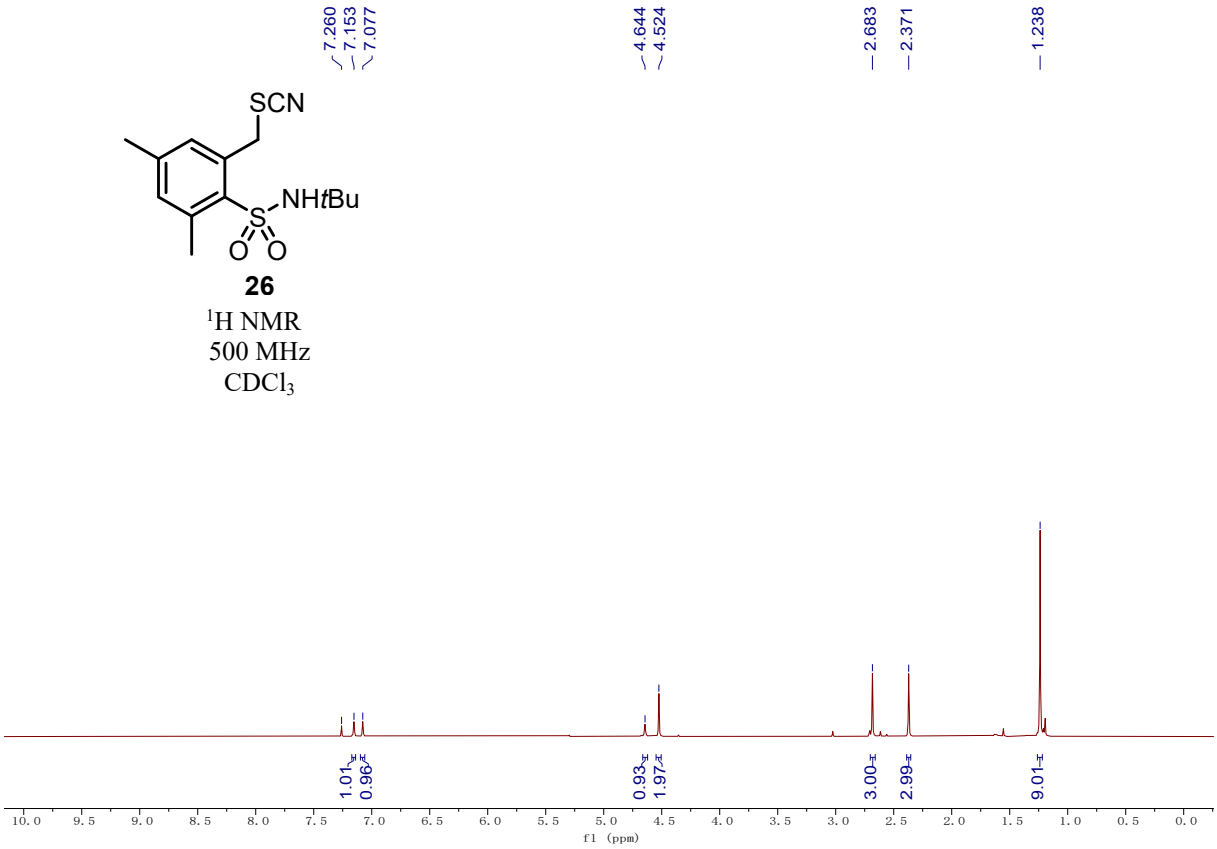
25

^{1}H NMR
500 MHz
$CDCl_3$



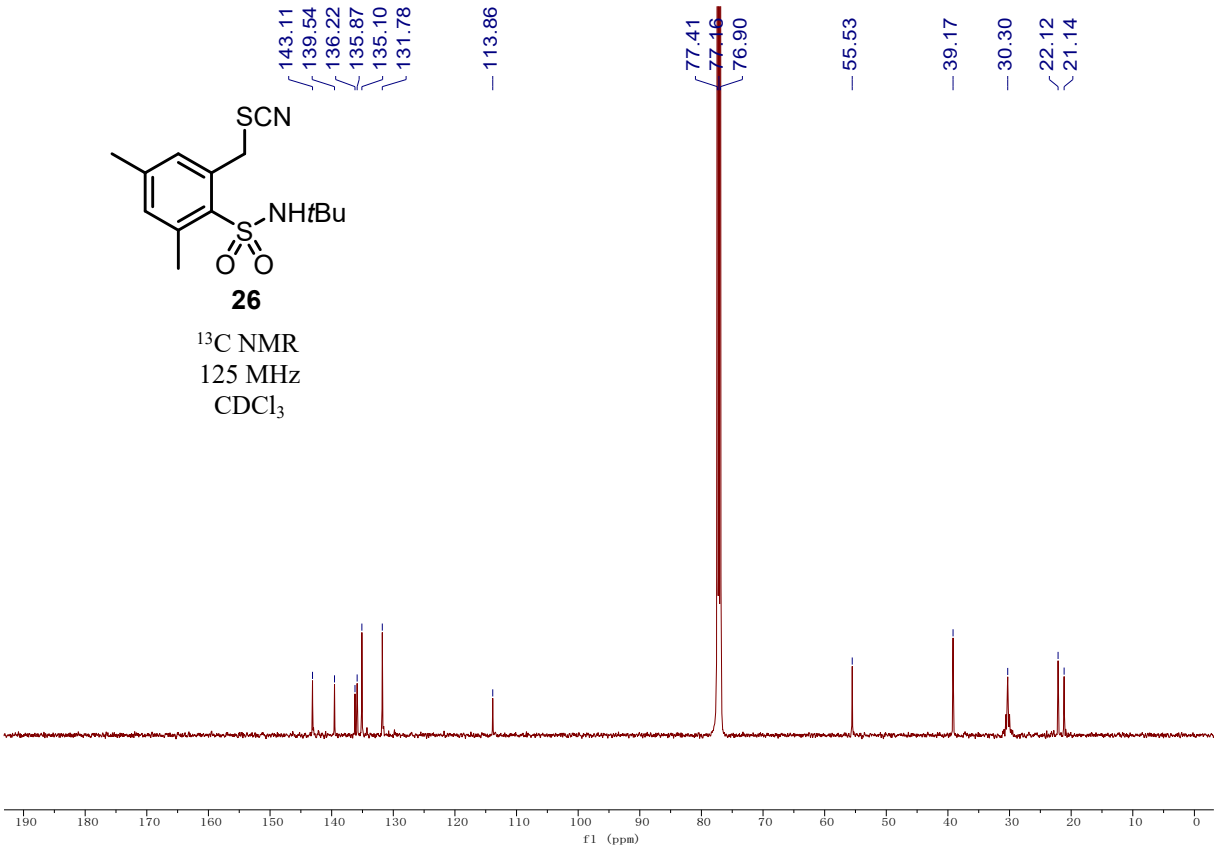
25

^{13}C NMR
125 MHz
$CDCl_3$



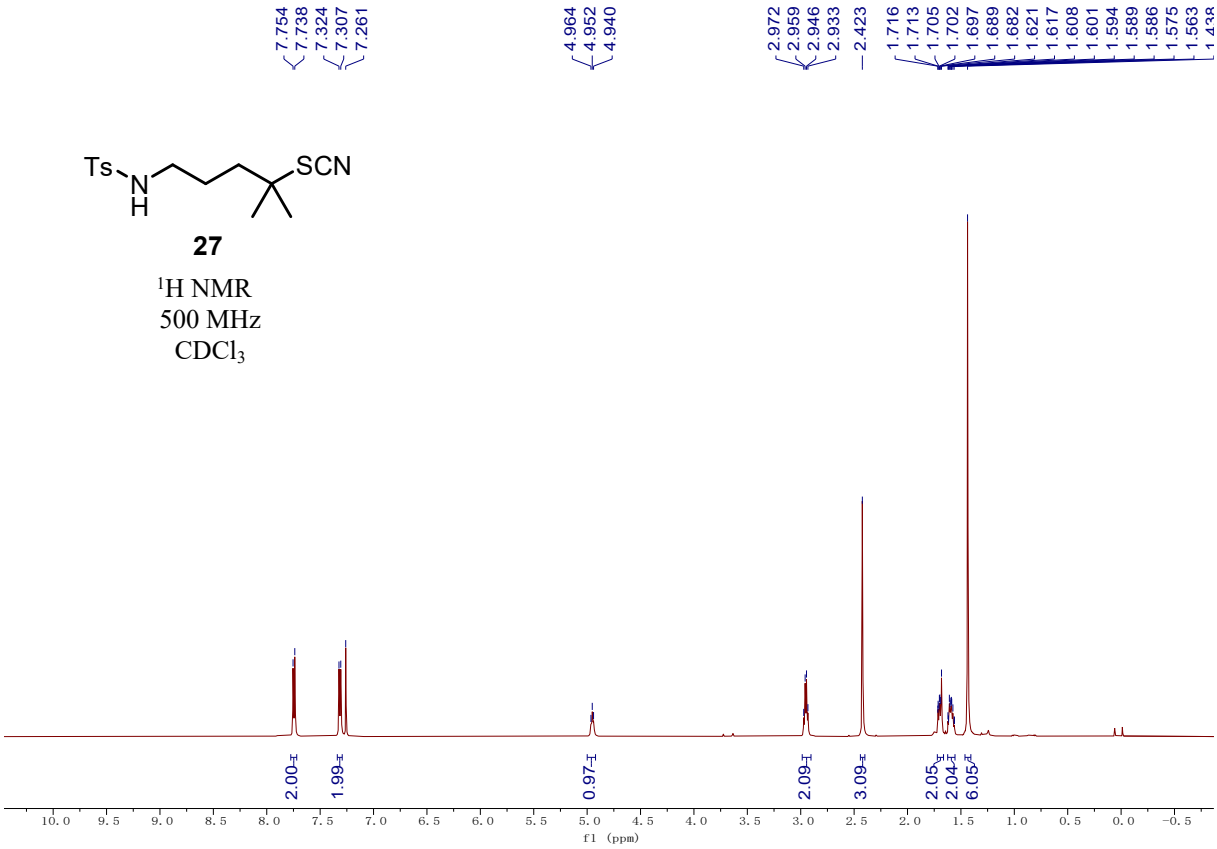
26

^{1}H NMR
500 MHz
$CDCl_3$



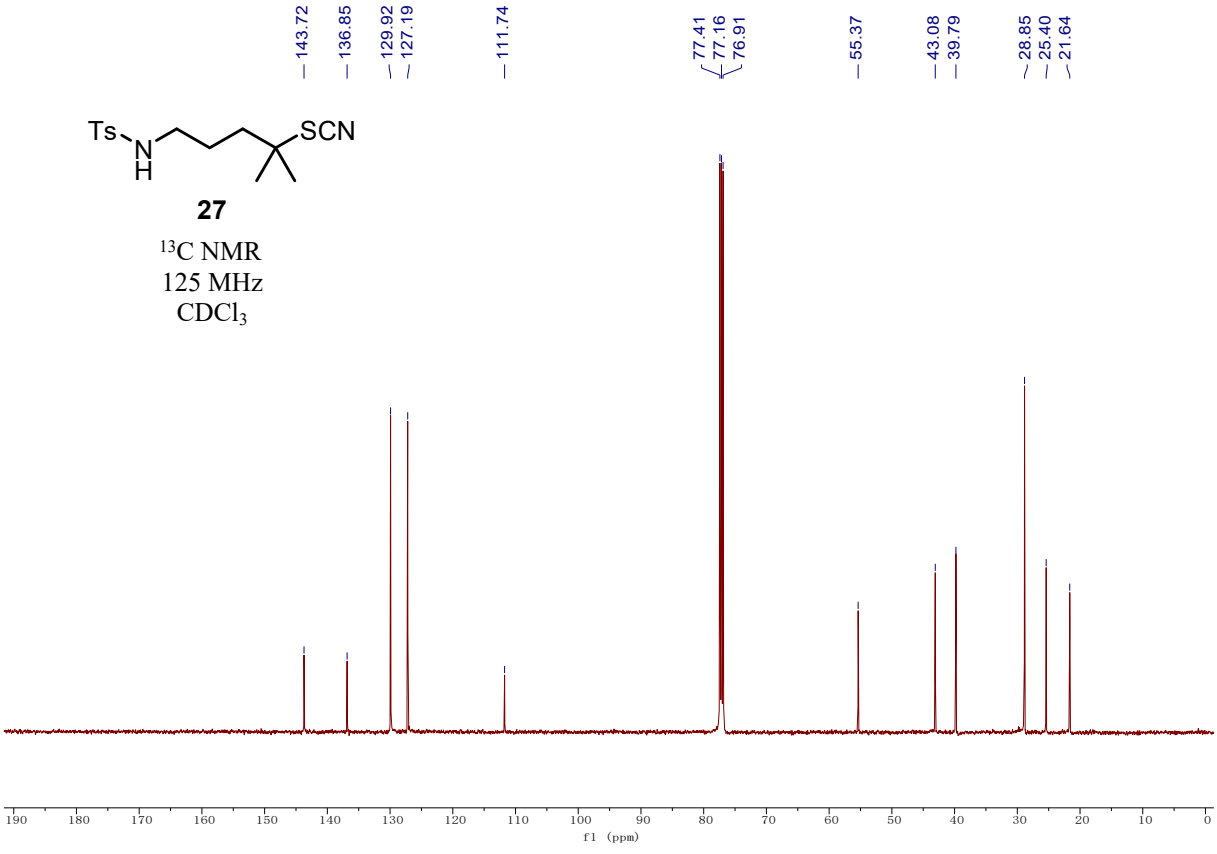
26

^{13}C NMR
125 MHz
$CDCl_3$



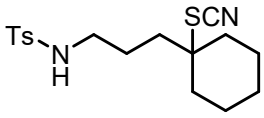
27

^{1}H NMR
500 MHz
$CDCl_3$



27

^{13}C NMR
125 MHz
$CDCl_3$



28

^{1}H NMR
400 MHz
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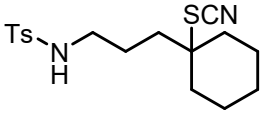
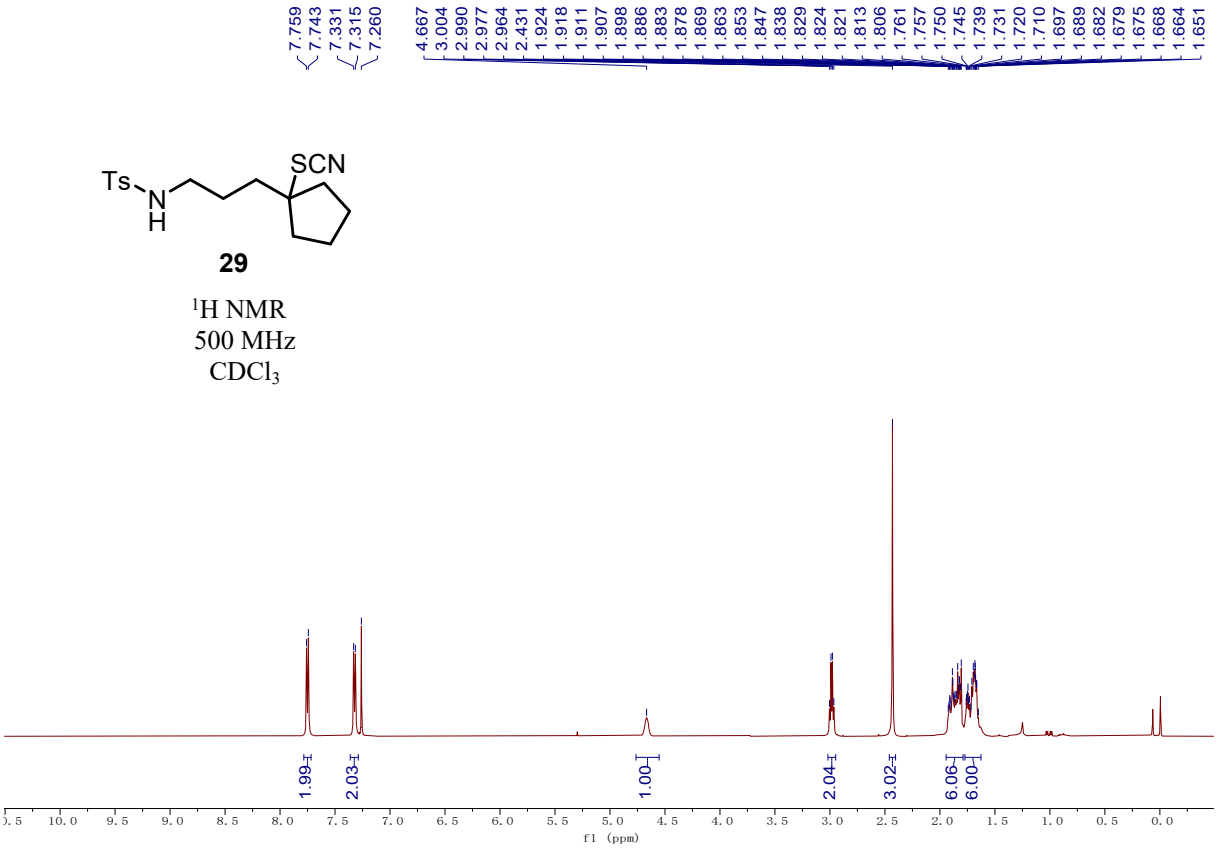


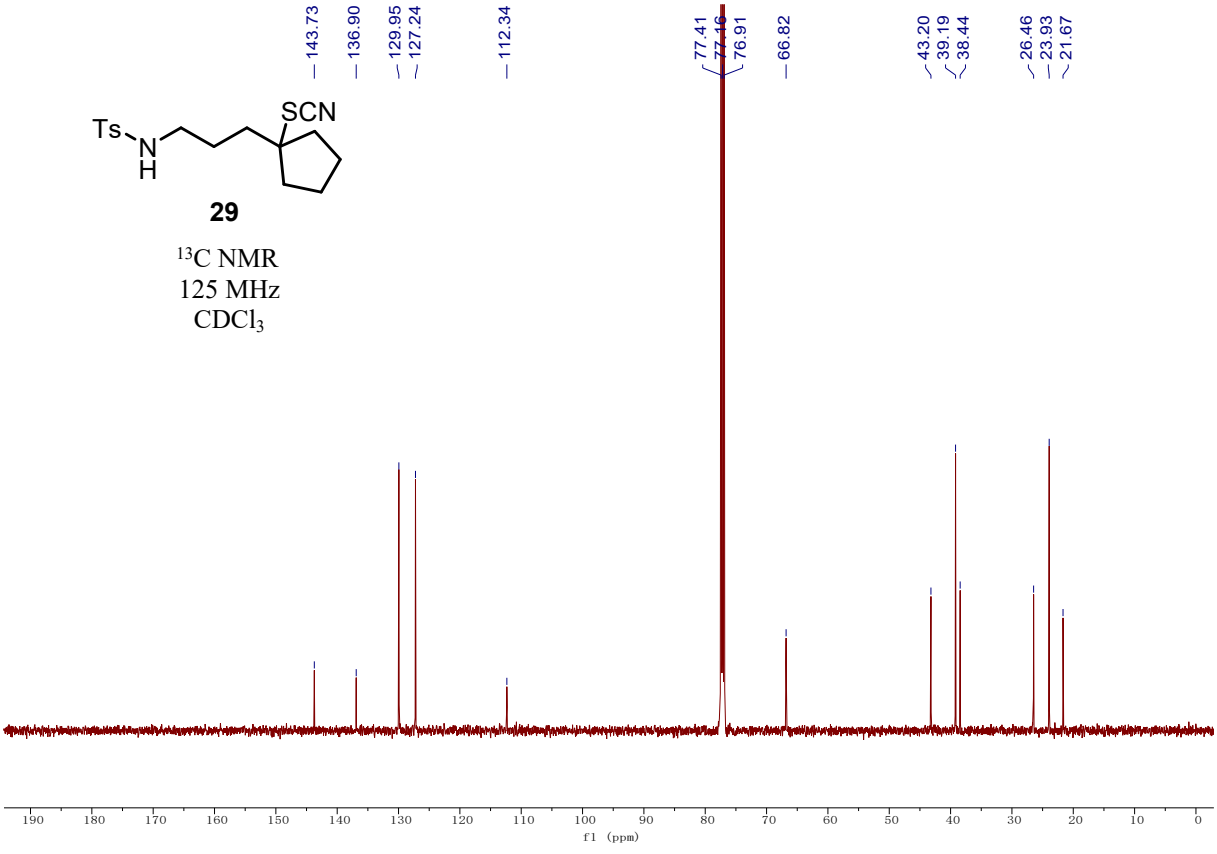
28

^{13}C NMR
125 MHz
$CDCl_3$



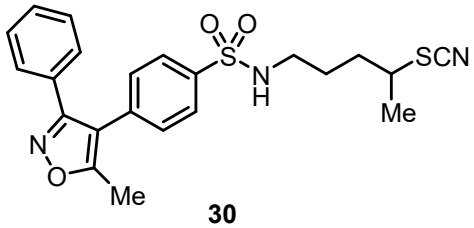
29

^{1}H NMR
500 MHz
$CDCl_3$



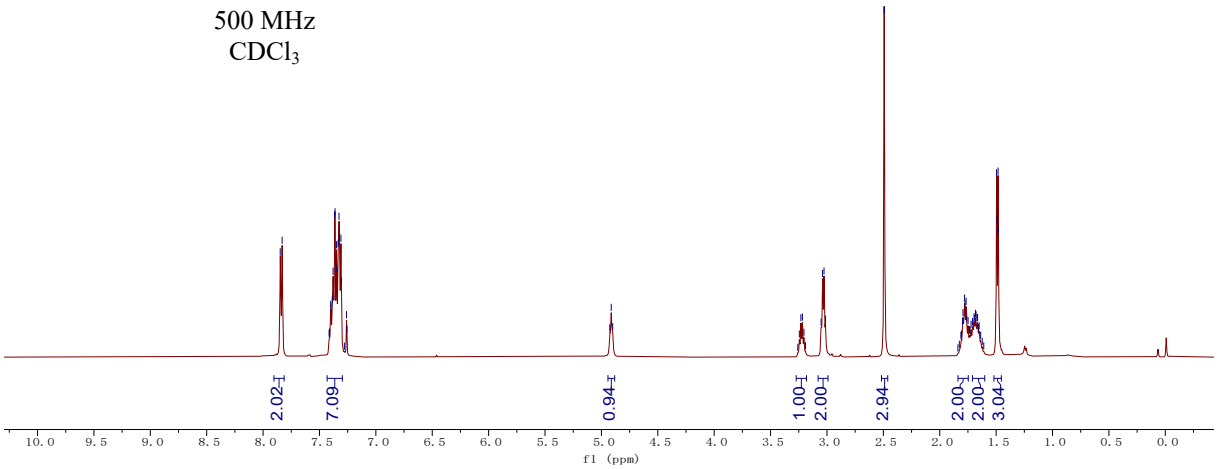
29

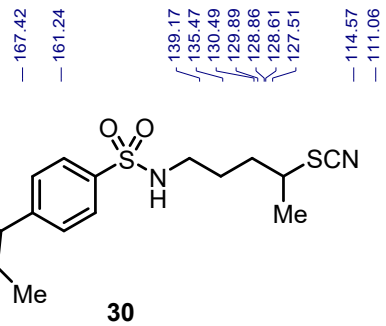
^{13}C NMR
125 MHz
$CDCl_3$



30

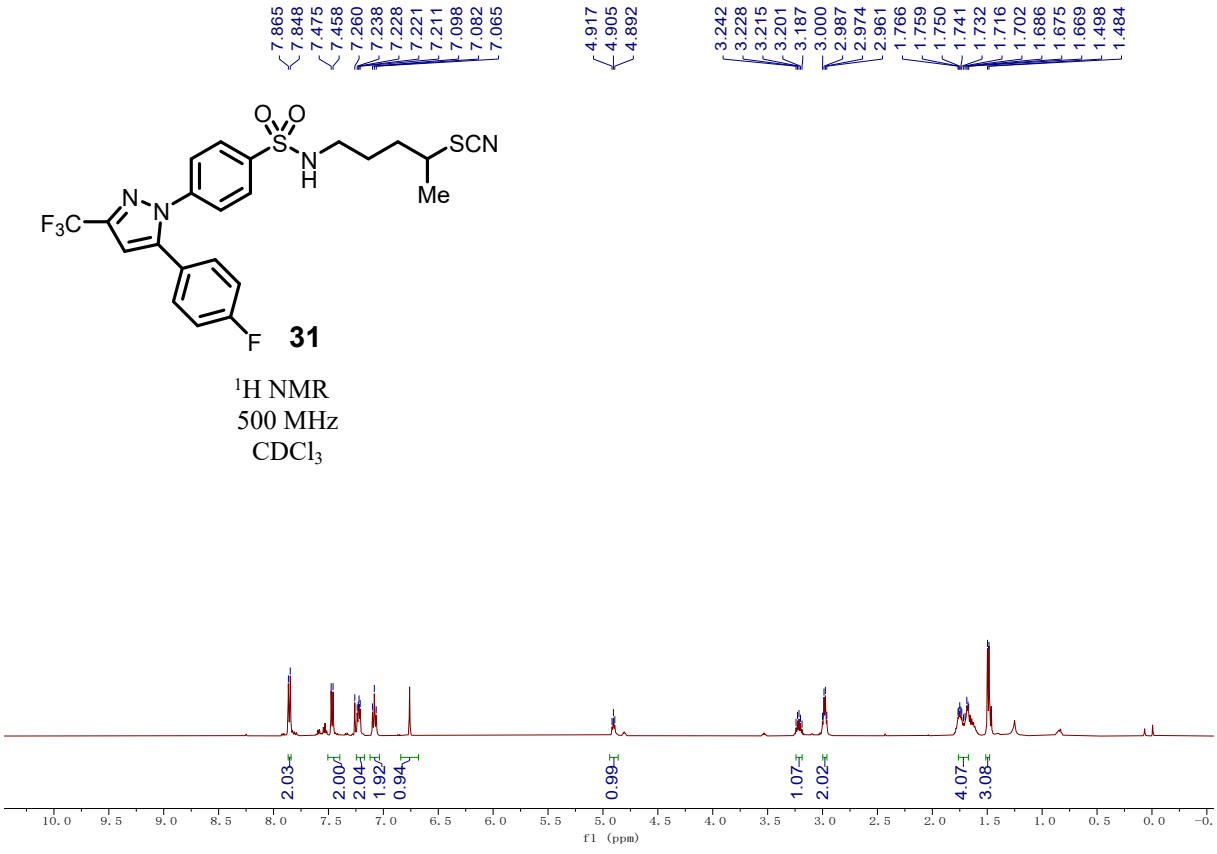
^{1}H NMR
500 MHz
$CDCl_3$



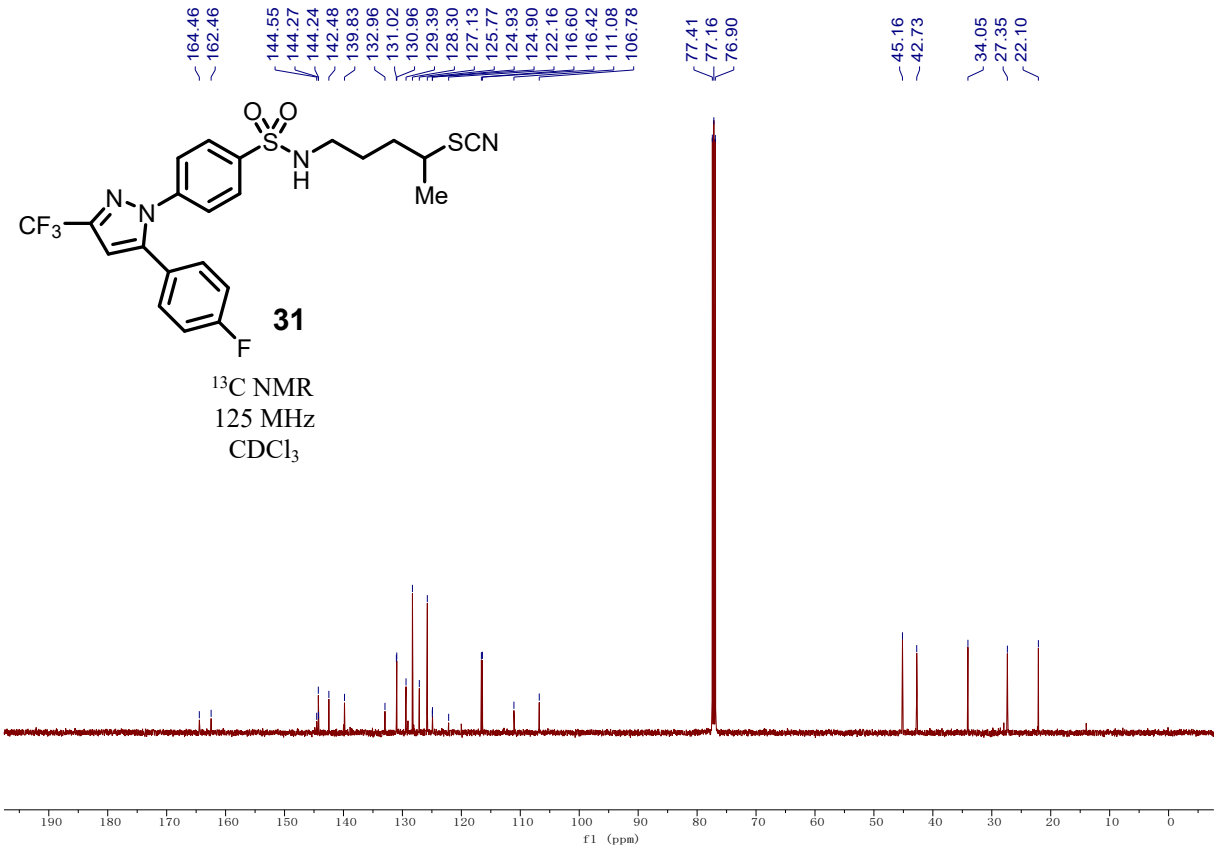


30

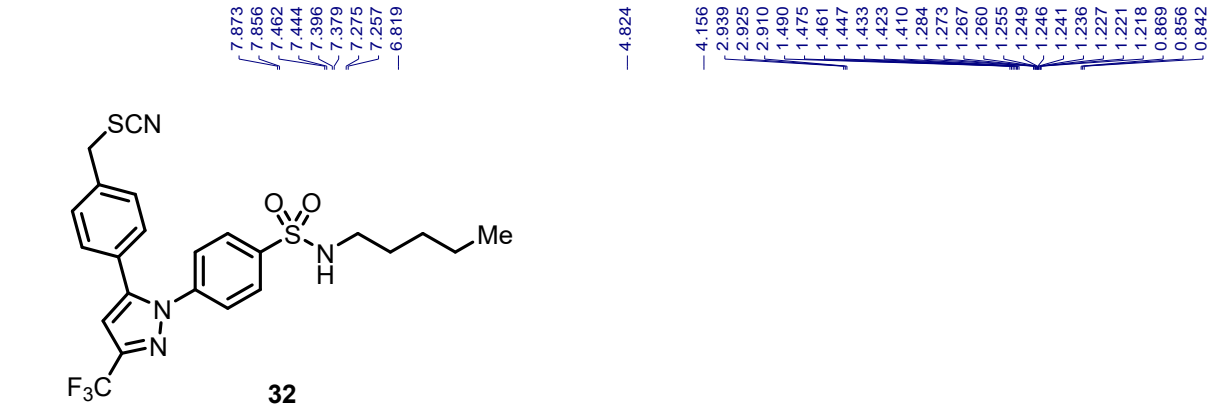
^{13}C NMR
125 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



^{13}C NMR
125 MHz
$CDCl_3$



32

^{1}H NMR
500 MHz
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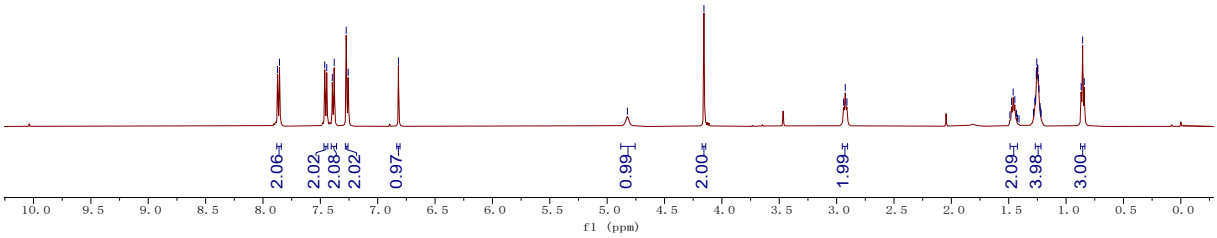

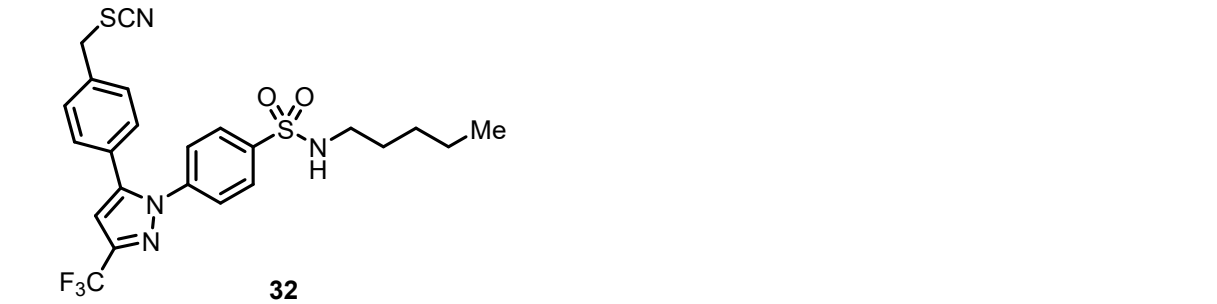

32

^{13}C NMR
125 MHz
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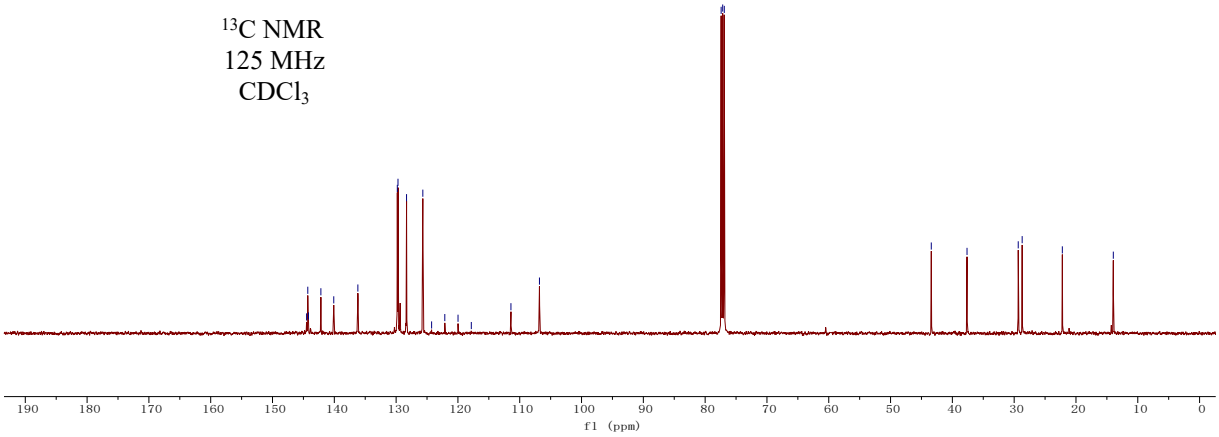
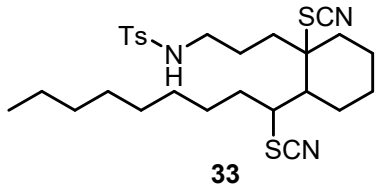
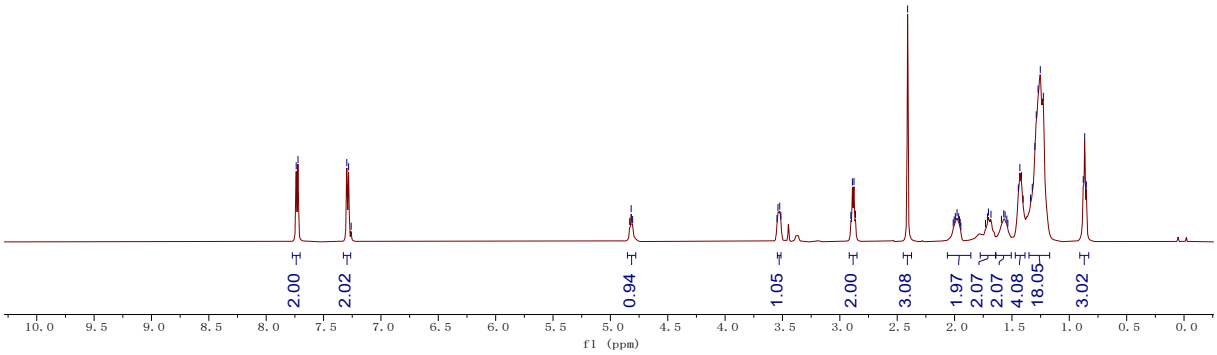
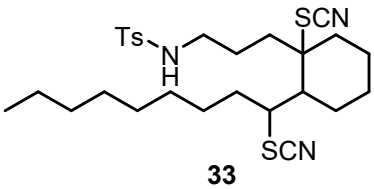




33

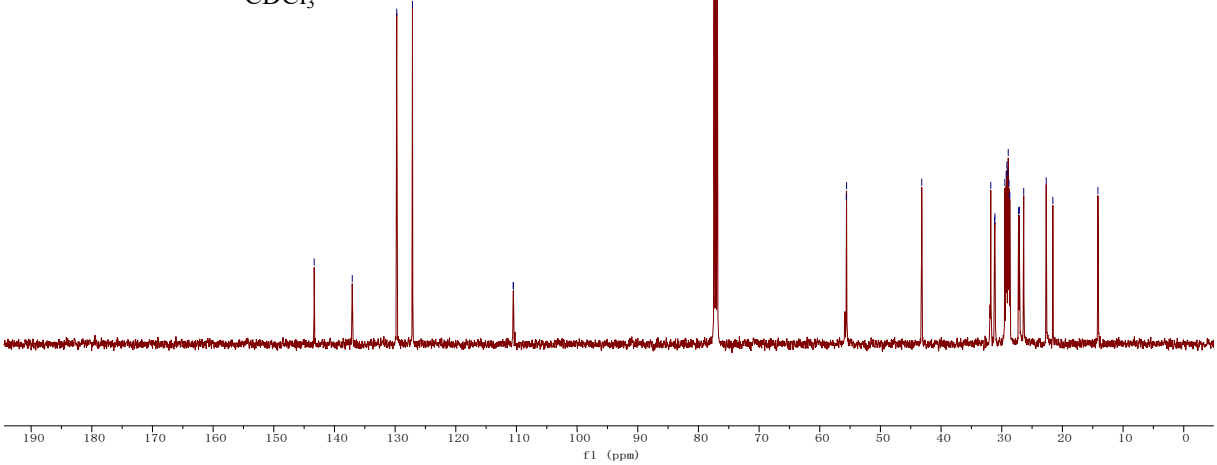
^{1}H NMR
500 MHz
$CDCl_3$

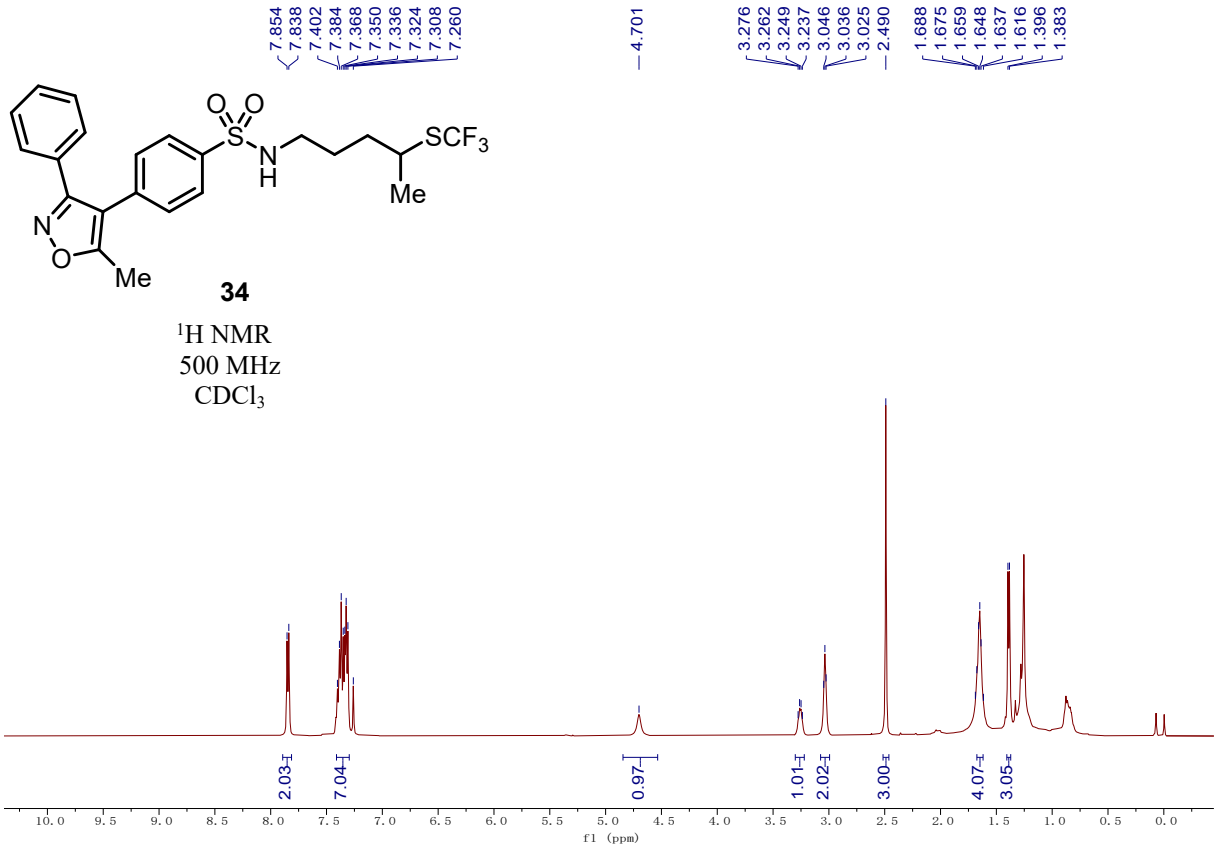




33

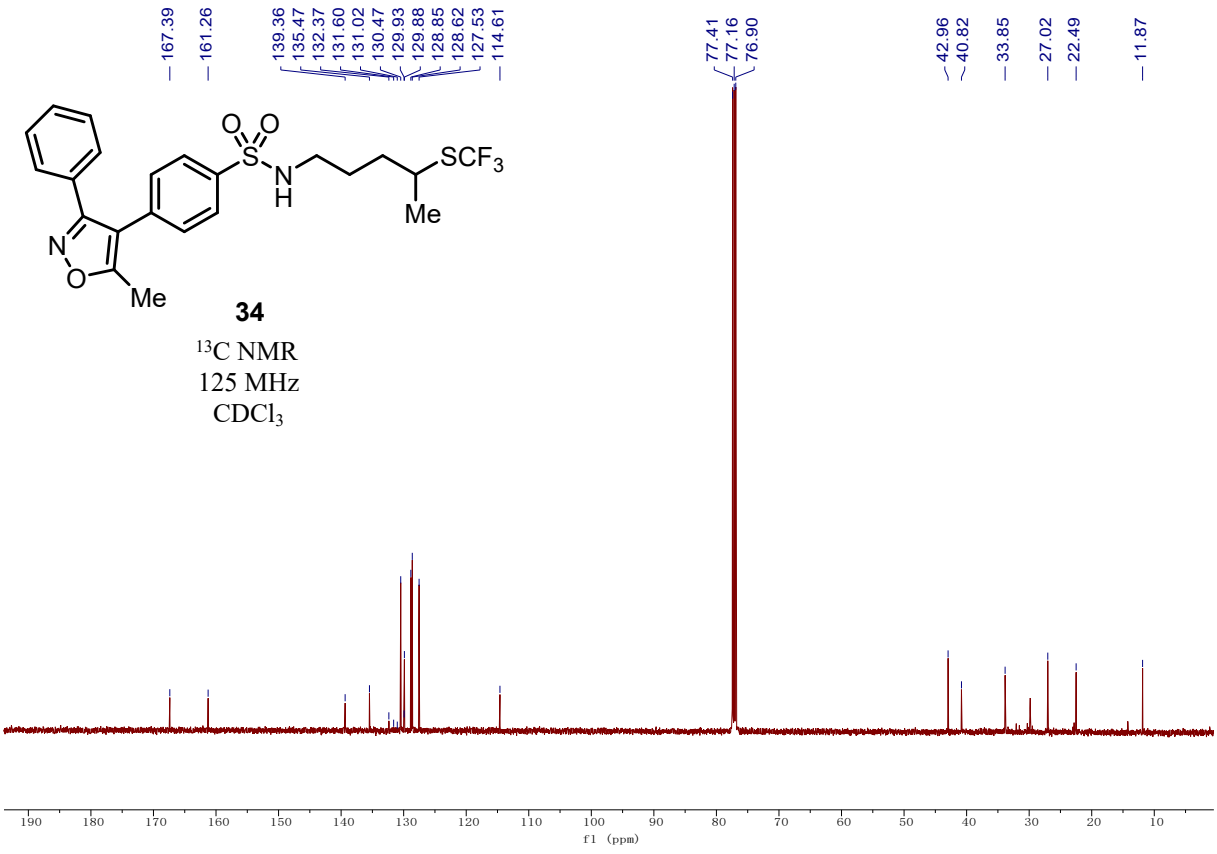
^{13}C NMR
125 MHz
$CDCl_3$





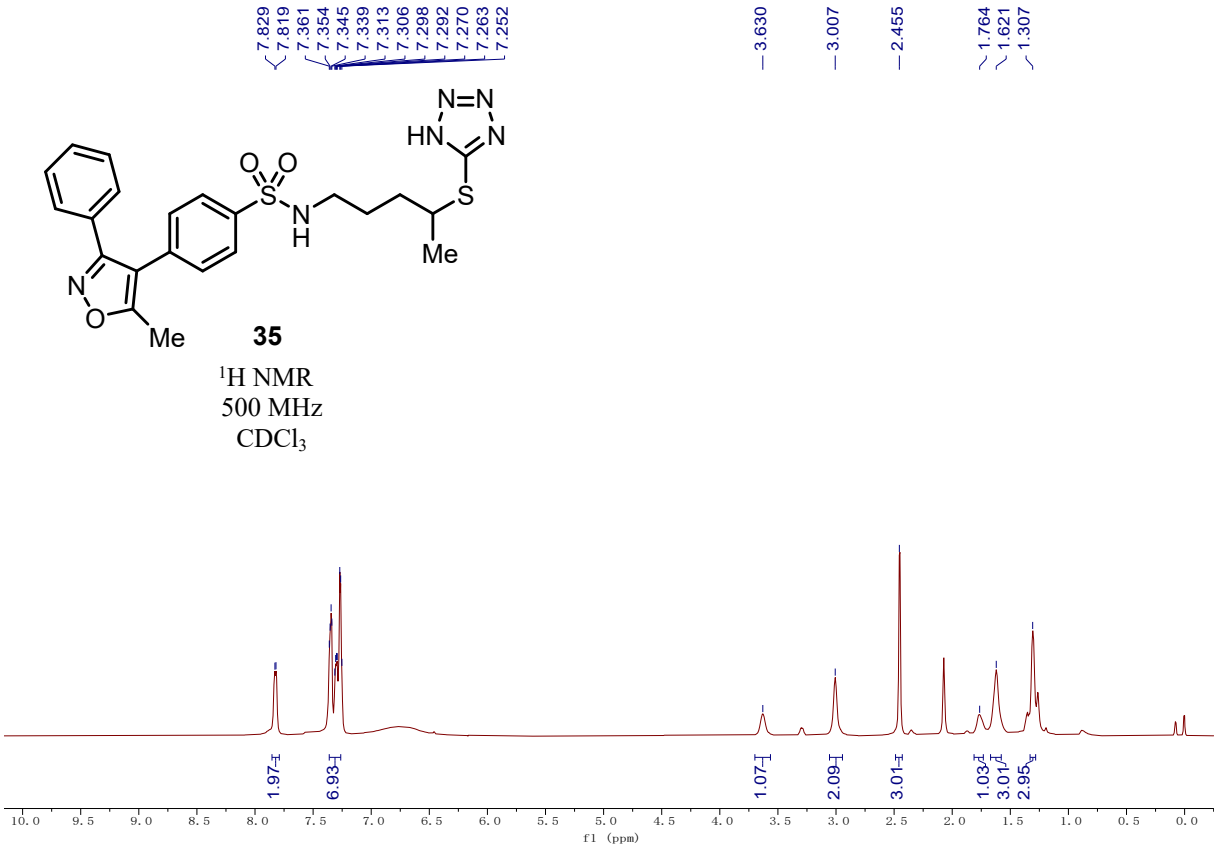
34

^{1}H NMR
500 MHz
$CDCl_3$



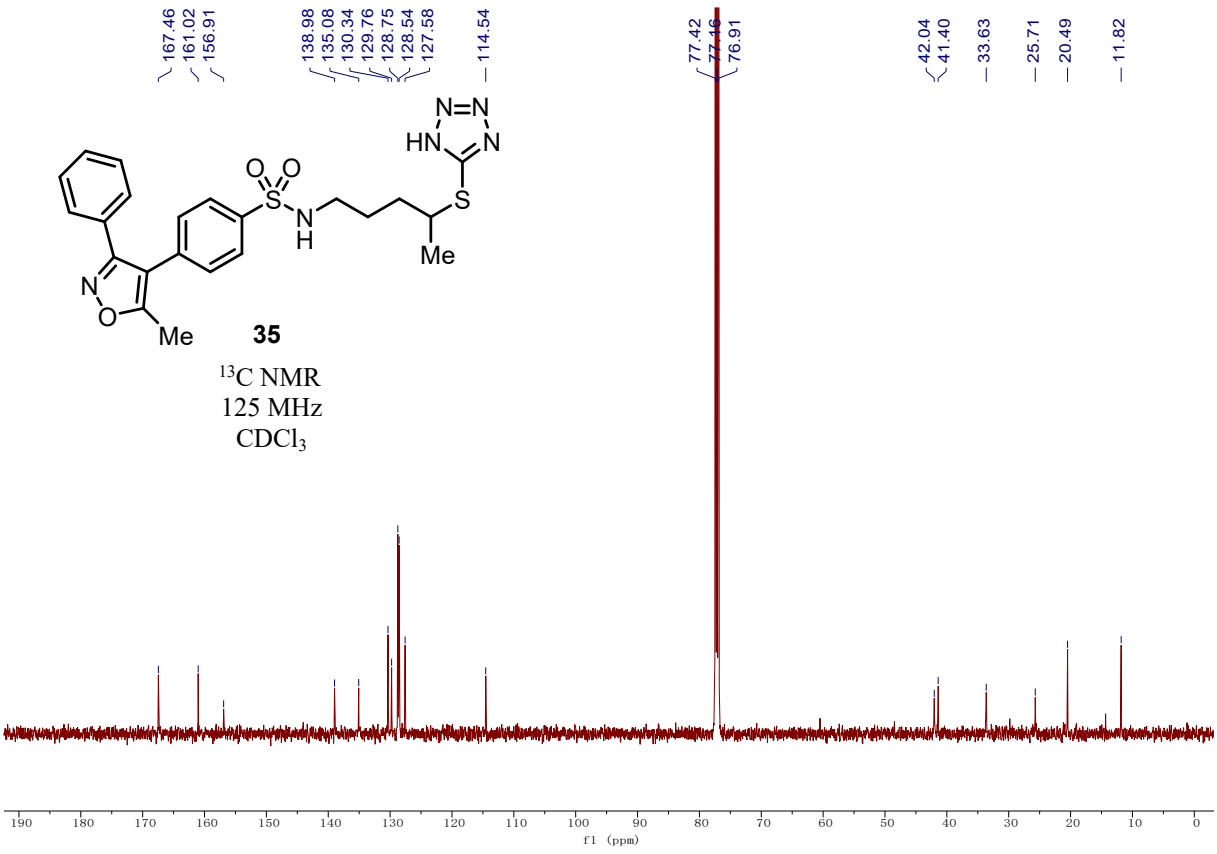
34

^{13}C NMR
125 MHz
$CDCl_3$



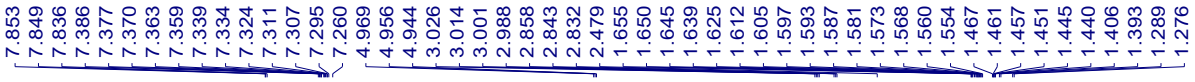
35

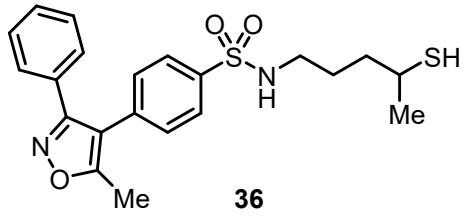
^{1}H NMR
500 MHz
$CDCl_3$



35

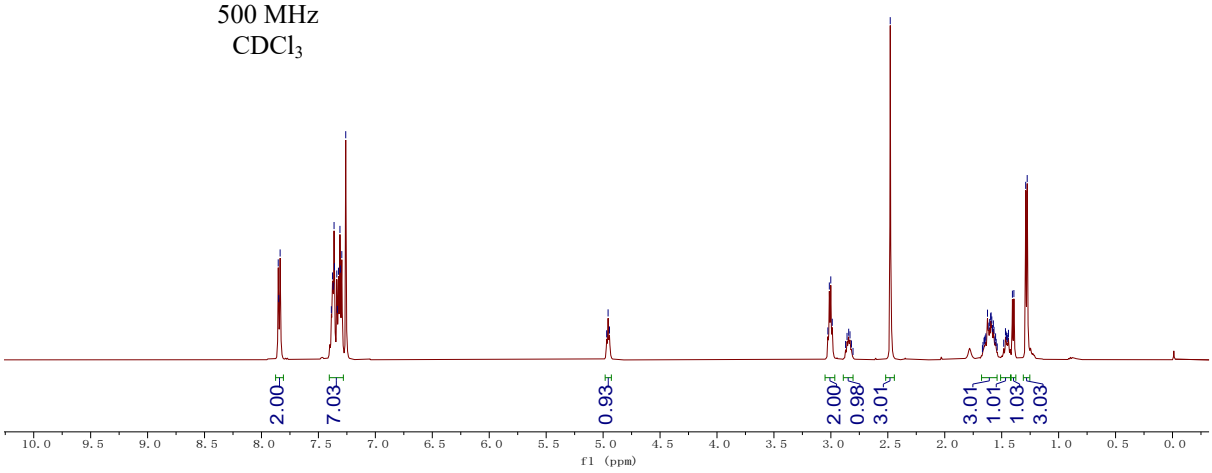
^{13}C NMR
125 MHz
$CDCl_3$

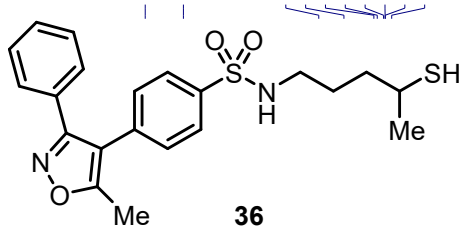




36

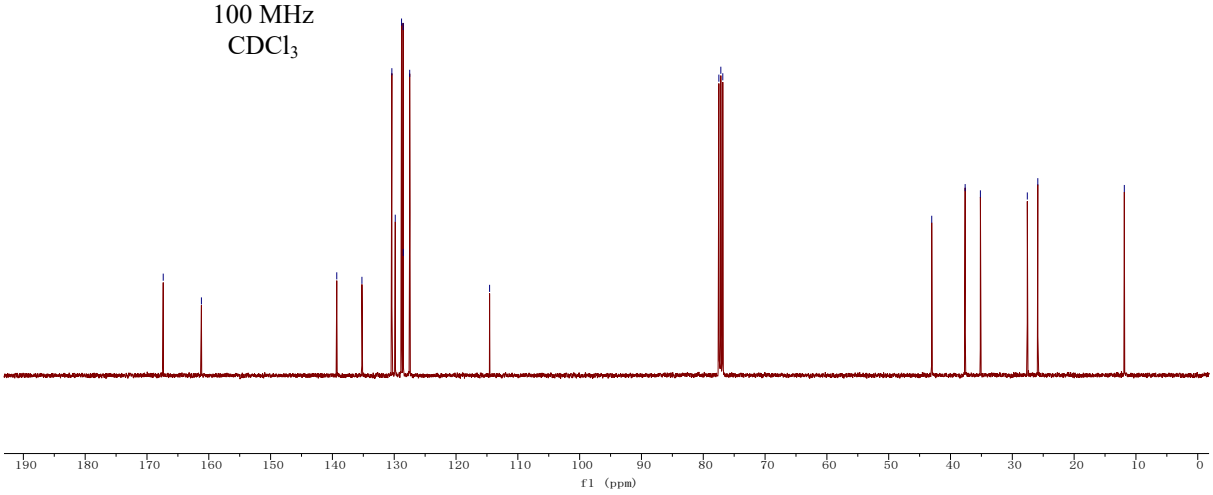
^{1}H NMR
500 MHz
$CDCl_3$

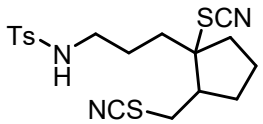




36

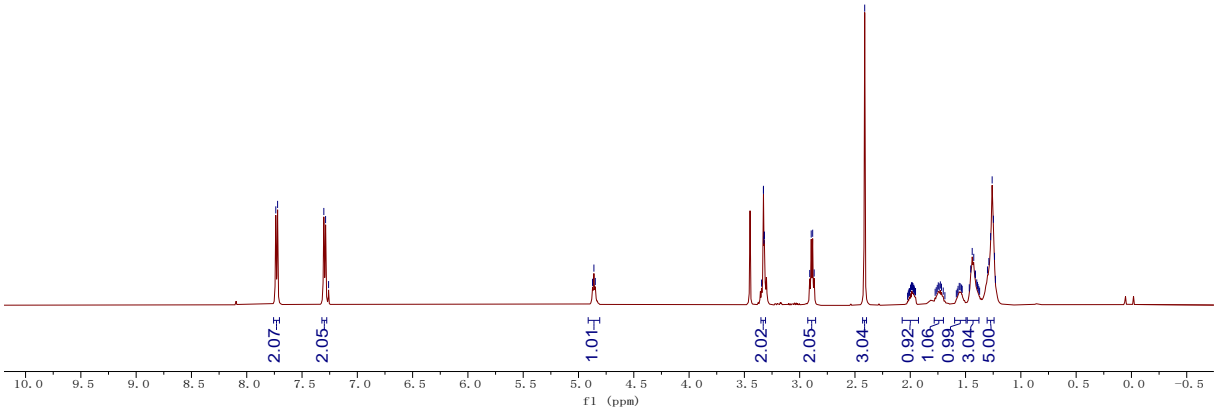
^{13}C NMR
100 MHz
$CDCl_3$

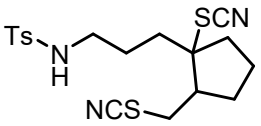




37

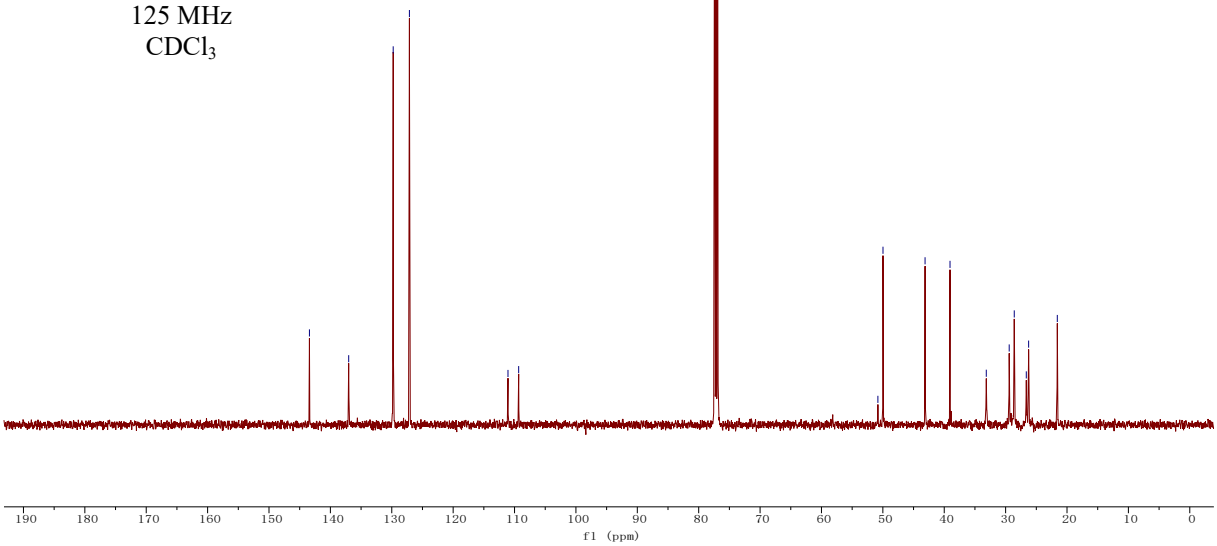
^{1}H NMR
500 MHz
$CDCl_3$





37

^{13}C NMR
125 MHz
$CDCl_3$



10.Theoretical calculations

Computational details:

All calculations were performed using Gaussian 16, Revision A.03 package.[21] All of the reactants, intermediates, transition states, products were optimized by the DFT with the M06-2X functional.[22] For geometry optimizations and frequency calculations, BS-I basis set system was employed. In BS-I, we employed 6-31+G(d) basis sets for all atoms. All the stationary structures were characterized with no imaginary frequency and the transition state structures (TSs) were characterized with a single imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed on the TSs. The solvent effect of hexafluoro-propan-2-ol (HFIP) (ε = 16.7) was evaluated through the SMD method,[23] in which a better basis system BS-II was used. In BSII, we employed def2-TZVP basis sets for all atoms. All reported energies are free energies at a concentration of 1 M and a temperature of 298.15 K.

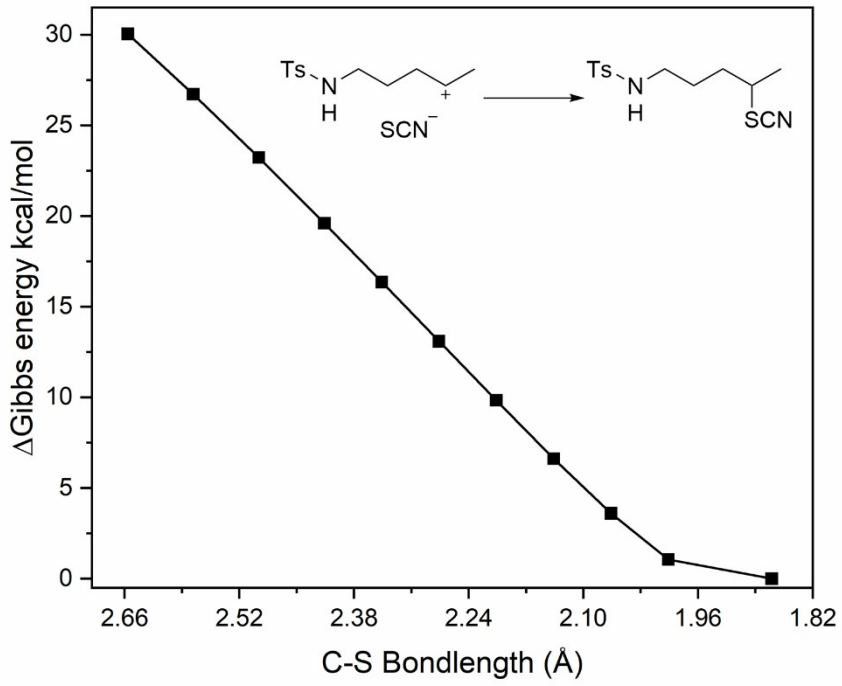


Figure S4. The scanned energy change along with the formation of C-S bond.

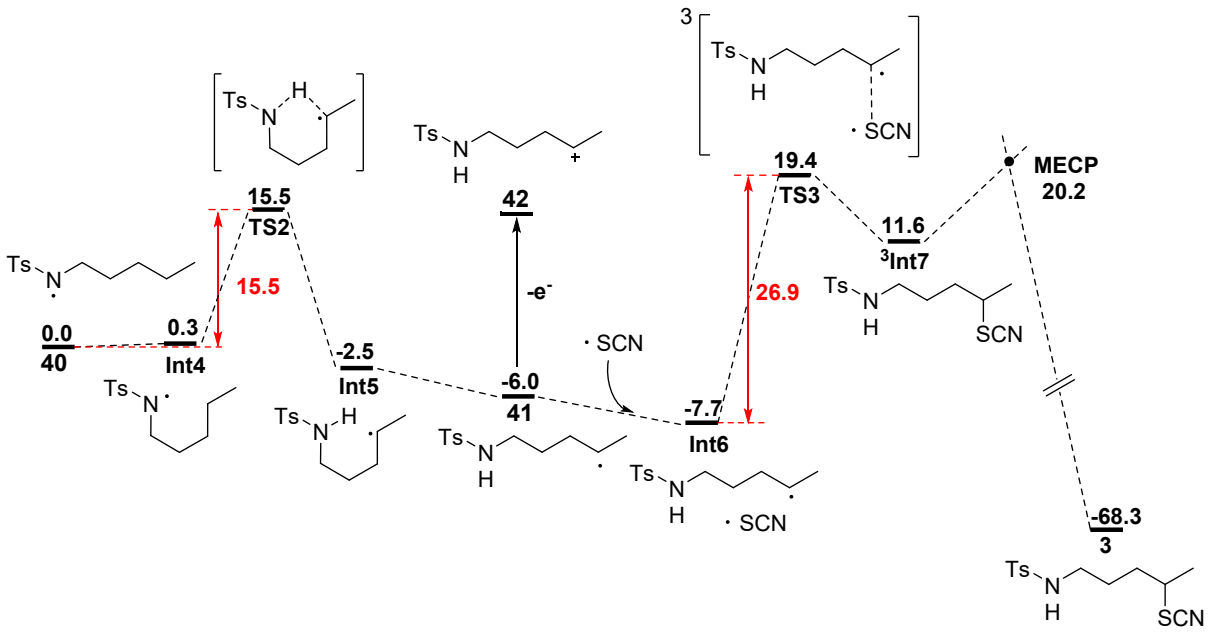


Figure S5. DFT calculated Gibbs free energy profiles for the radical coupling process (in kcal/mol).

Cartesian coordinates of the optimized structures

1

E = -1071.7237480 a.u.

0 1

S	-2.90105100	0.72786200	-2.33081300
O	-2.06398100	0.54367100	-3.50861900
O	-4.31824100	1.04623000	-2.46355500
C	-2.77834100	-0.70290200	-1.28411300
C	-1.54333600	-1.33757100	-1.15180900
C	-1.44954500	-2.45569900	-0.33503400
C	-2.57141600	-2.94885300	0.34832600
C	-3.79427600	-2.29371900	0.19284900
C	-3.90837600	-1.16858200	-0.62445200
H	-0.67978900	-0.95713600	-1.68930600
H	-0.49362400	-2.96227900	-0.22600800
H	-4.67267000	-2.66847600	0.71142900
H	-4.85859200	-0.66203600	-0.76315500
C	-2.44687900	-4.17154800	1.22046300
H	-3.38704500	-4.39319700	1.73168300
H	-2.17104000	-5.04761200	0.62389200
H	-1.67003100	-4.03375900	1.97954300
N	-2.11478500	1.88847900	-1.41883000
H	-1.67531300	2.54607400	-2.06392000
C	-2.89957600	2.53004000	-0.35728700
H	-3.25132500	1.73664400	0.31364000
H	-3.78506800	3.03629000	-0.76350600
C	-2.02152500	3.50625300	0.41522200
H	-1.63209500	4.26944000	-0.27401500
H	-1.15390800	2.96709100	0.81487300
C	-2.78456600	4.19158600	1.54732200
H	-3.17802900	3.42986100	2.23540600
H	-3.65751600	4.71795100	1.13637500
C	-1.92279300	5.18057700	2.33111500
H	-1.05067300	4.65407400	2.74046800
H	-1.53054600	5.94129200	1.64336200
C	-2.69355100	5.85802600	3.46225700
H	-3.07123400	5.11754200	4.17608700
H	-2.06257000	6.56258300	4.01241100
H	-3.55411400	6.41232100	3.07160900

3

E = -1562.08245935 a.u.

0 1

S	-1.75297400	0.94202200	-1.84571900
O	-0.97085900	0.59294100	-3.01920800
O	-2.86725000	1.87630900	-1.88726300
C	-2.36944200	-0.57143900	-1.13285600
C	-1.61633900	-1.73843200	-1.26763000
C	-2.07994400	-2.91046400	-0.68412400
C	-3.28746800	-2.93580300	0.02836200
C	-4.02541800	-1.75507100	0.13811300
C	-3.57551200	-0.56838700	-0.44045300
H	-0.69579200	-1.72507300	-1.84445700
H	-1.50467000	-3.82692800	-0.79139300
H	-4.97058200	-1.76283000	0.67442100
H	-4.16006700	0.34481300	-0.38193800
C	-3.77681100	-4.22205100	0.64229600
H	-4.70337100	-4.06918100	1.20117100
H	-3.96772600	-4.97361000	-0.13098100
H	-3.03042800	-4.63789500	1.32684600
N	-0.66516600	1.57003700	-0.75980800
C	-1.14950200	2.02651700	0.54645800
H	-0.35260800	1.83418000	1.27263600
H	-2.01796100	1.43248300	0.86832200
C	-1.50055500	3.51167500	0.52601400
H	-2.24378600	3.68620700	-0.25974500

H	-0.60214700	4.07472700	0.24768300
C	-2.04484800	3.96715700	1.87907900
H	-1.30093900	3.80429400	2.67292900
H	-2.91664900	3.35235700	2.14274600
C	-2.51305000	5.42293300	1.92798500
H	-3.19356400	5.61886100	1.09305900
C	-3.17341700	5.76910300	3.25439700
H	-2.48821400	5.58025300	4.08719000
H	-3.48499400	6.81630500	3.29098800
H	-4.06399500	5.14492200	3.38770600
H	0.20190300	1.04153500	-0.76480400
S	-1.00988100	6.47023200	1.62967100
C	-1.72811000	8.00431100	1.74618800
N	-2.20977100	9.05710800	1.82832100

47

E = -1071.05852649 a.u.

0 2

S	-3.77704400	0.57119100	-0.95606900
O	-3.32998300	1.06463000	-2.25408300
O	-5.18031900	0.65377800	-0.56578400
C	-3.22623000	-1.09834300	-0.75920200
C	-2.12863100	-1.54004000	-1.49246600
C	-1.69350300	-2.84946400	-1.31854800
C	-2.33878300	-3.71213500	-0.42439700
C	-3.44409300	-3.23825800	0.29071200
C	-3.89562200	-1.93166700	0.13121600
H	-1.64126400	-0.87037000	-2.19427500
H	-0.84300000	-3.21119900	-1.89060500
H	-3.96225100	-3.90316900	0.97665400
H	-4.76100600	-1.56246000	0.67277700
C	-1.83881900	-5.11960700	-0.22511000
H	-2.63416600	-5.77634800	0.13708200
H	-1.44606100	-5.53629800	-1.15677500
H	-1.02910500	-5.13803800	0.51322600
N	-2.87311600	1.37566500	0.23074100
C	-3.16940400	2.79406500	0.25147400
H	-4.25023000	2.92978400	0.42417200
H	-2.96630700	3.21513000	-0.74745000
C	-2.34843700	3.49904000	1.32293900
H	-1.28333800	3.32759400	1.12437400
H	-2.56753800	3.04239000	2.29592900
C	-2.63857700	4.99784800	1.36972000
H	-3.70977900	5.15961900	1.55760600
H	-2.42690300	5.44448000	0.38755600
C	-1.82476100	5.72513900	2.43914000
H	-2.03736500	5.27878800	3.41942200
H	-0.75540200	5.56288900	2.25061900
C	-2.11940600	7.22310500	2.48003800
H	-3.17807800	7.40756800	2.69376000
H	-1.52889700	7.72761500	3.25080000
H	-1.88769000	7.69345800	1.51798200

48

E = -1071.0592089 a.u

0 2

S	-2.41318900	0.73475000	-2.36530400
O	-1.35440200	0.50007200	-3.33405100
O	-3.76109000	1.11632500	-2.75327500
C	-2.55172000	-0.72024800	-1.34399400
C	-1.43559100	-1.53804500	-1.16997400
C	-1.53439400	-2.64339900	-0.33329500
C	-2.73218100	-2.94419200	0.32953900
C	-3.83533900	-2.10965700	0.13225700
C	-3.75519300	-0.99666100	-0.70351400
H	-0.51583100	-1.31637900	-1.70376100
H	-0.67233500	-3.29221800	-0.19793500
H	-4.77354500	-2.33620100	0.63192000
H	-4.61657600	-0.35826400	-0.87651600
C	-2.82319700	-4.15936800	1.21637300
H	-3.76850800	-4.18205900	1.76440800
H	-2.75520900	-5.07768900	0.62311400
H	-2.00567200	-4.17729800	1.94393300
N	-1.84622300	1.94654100	-1.37752200
C	-2.64291700	2.31957400	-0.20694600
H	-2.63646700	1.52562500	0.55684600
H	-3.67376700	2.44944200	-0.55123000
C	-2.11837800	3.62285000	0.38334300
H	-2.15671300	4.39996700	-0.38878700
H	-1.06378900	3.50438200	0.66732400
C	-2.92007100	4.05895500	1.61073000
H	-2.88826800	3.26888400	2.37681400
H	-3.98567500	4.14690900	1.32719700
C	-2.43490600	5.34185700	2.20024100
H	-1.99826100	6.07888200	1.53076800
C	-2.89943500	5.77609500	3.54881400
H	-2.81110300	4.96224300	4.27994600
H	-2.32808200	6.63109900	3.92081100
H	-3.96152900	6.07338000	3.54053200
H	-0.85412600	1.80990600	-1.19107200

49

E = -1070.80997156 a.u

1 1

S	-2.59746200	1.33266300	0.29107500
O	-1.86950400	2.10960100	-0.71434900
O	-3.89440100	1.84199200	0.74212600
C	-2.70361200	-0.34067200	-0.22832800
C	-1.98130900	-0.74675900	-1.34606600
C	-2.07845000	-2.07708900	-1.74819200
C	-2.88187700	-2.98497300	-1.05262600
C	-3.59910700	-2.53618000	0.06883900
C	-3.51876700	-1.21819300	0.49028900
H	-1.36973000	-0.03539300	-1.89182700
H	-1.52403800	-2.41068700	-2.62033700
H	-4.23098600	-3.23381100	0.61178400
H	-4.07991200	-0.86884000	1.35178200
C	-2.99336600	-4.42030300	-1.49041400
H	-4.02447800	-4.65780400	-1.77172500
H	-2.34990400	-4.62849800	-2.34780600
H	-2.71136500	-5.09659300	-0.67734000
N	-1.68754600	1.26564600	1.70304600
C	-1.92436800	2.34530600	2.64792400
H	-1.18366000	2.22825800	3.44326400

H	-2.91140800	2.20313900	3.08856300
C	-1.77633400	3.79850800	2.08095700
H	-1.31999500	3.71898900	1.08301400
H	-1.11479700	4.41623300	2.68957900
C	-3.23026000	4.53537700	2.10224200
H	-3.27190700	5.14074200	3.00601300
H	-4.02395800	3.79722400	2.00018800
C	-2.87058000	5.19721700	0.89838100
H	-2.18303400	6.04263200	0.97488000
C	-3.32583400	4.82129900	-0.43689800
H	-3.91264200	3.90360600	-0.45433400
H	-3.96750200	5.67742500	-0.72680600
H	-2.51221400	4.80239100	-1.16896000
H	-0.70522500	1.09615400	1.48943200

50

E = -1070.88612727 a.u

1 1

S	0.33790600	-1.35010800	-0.39947700
O	-0.71575200	-2.28074800	-0.08152800
O	1.62110200	-1.73019900	-0.93446500
C	-0.27869300	0.10565300	-1.13915300
C	-1.65305700	0.35364700	-1.10619100
C	-2.11769500	1.53697900	-1.66588200
C	-1.23709500	2.45785400	-2.25303800
C	0.13624200	2.16733400	-2.27454800
C	0.62975500	0.99106700	-1.72698300
H	-2.33616500	-0.37314600	-0.67629400
H	-3.18355300	1.74560900	-1.65973800
H	0.82348800	2.86614400	-2.74270200
H	1.68810600	0.74981100	-1.77570100
C	-1.75863100	3.71539700	-2.88951700
H	-2.70038200	4.03207000	-2.43571700
H	-1.03720500	4.53191400	-2.80782100
H	-1.94413500	3.54254800	-3.95590400
N	0.82862600	-0.72458300	1.27531500
C	1.51885900	-1.82028000	2.06306800
H	2.55921400	-1.88417300	1.74522400
H	1.00269700	-2.75591700	1.82690500
C	1.27076900	-1.39447000	3.50245200
H	1.94661100	-0.57947300	3.78499500
H	1.43322000	-2.22156900	4.19613900
C	-0.18680100	-0.92539100	3.46122600
H	-0.45029600	-0.27812500	4.30090500
H	-0.85819100	-1.78892400	3.47408700
C	-0.32166600	-0.17144300	2.12574300
H	-1.24479600	-0.44383100	1.60831400
C	-0.18533300	1.33965000	2.22571600
H	-1.03683900	1.74219800	2.77986000
H	0.72684200	1.61973900	2.76586500
H	-0.17693800	1.81101000	1.23626400
H	1.50593600	0.02777100	1.09633700

Int1

E = -1860.78916107 a.u

-1 1

S	-4.22844700	1.45332500	-2.15791300
O	-4.06499800	1.43483200	-3.60956000
O	-5.57591100	1.47845400	-1.57882500
C	-3.45438500	-0.03785200	-1.51873900
C	-2.08933200	-0.23472700	-1.74140900
C	-1.49506700	-1.39397100	-1.25517500
C	-2.23642400	-2.35527300	-0.55455100
C	-3.59596900	-2.12533100	-0.33837400
C	-4.21062700	-0.96501500	-0.81360000
H	-1.50515900	0.52577900	-2.26217100
H	-0.43143000	-1.55417200	-1.41998300
H	-4.18263400	-2.85839900	0.21150200
H	-5.26513400	-0.76952700	-0.64410600
C	-1.56570800	-3.60752500	-0.04555300
H	-2.26838600	-4.23683300	0.50898600
H	-1.16140700	-4.20096300	-0.87330300
H	-0.73014400	-3.36458200	0.62020100
N	-3.35717300	2.70159700	-1.59778200
H	-2.32860100	2.70394600	-2.03137500
C	-3.32444700	2.89381900	-0.14982600
H	-2.81274600	2.05514500	0.35513000
H	-4.35121500	2.93760300	0.23289000
C	-2.58224400	4.19191900	0.15203100
H	-3.12129600	5.02163200	-0.32315200
H	-1.59316700	4.14714100	-0.32174400
C	-2.44147300	4.44268300	1.65130600
H	-1.89504300	3.60704200	2.11297300
H	-3.43703600	4.45729600	2.12080000
C	-1.71735100	5.74968900	1.97093400
H	-0.72707600	5.73514400	1.49787300
H	-2.26391400	6.58514100	1.51357900
C	-1.57008500	5.99128000	3.47239500
H	-1.00215200	5.18033100	3.94322000
H	-1.04997200	6.93188400	3.68378400
H	-2.55168200	6.03293100	3.95929200
C	-0.46647900	4.60329800	-3.78218500
C	-0.92473000	3.13495300	-3.75781700
H	-1.90559800	3.13304700	-4.28233500
C	-0.00736800	2.27372700	-4.63940100
O	-0.95524500	2.66050300	-2.49803200
F	-1.30656800	5.35336900	-3.04698200
F	-0.45639200	5.14603800	-5.02320800
F	0.76474300	4.78574700	-3.27531400
F	0.00908200	2.66006600	-5.93673600
F	1.27265800	2.26944800	-4.22648100
F	-0.42483700	0.99644800	-4.62721600

Int2

E = -1860.79147925 a.u

-1 1

S	-3.88817700	1.51587000	-2.20771500
O	-3.58324400	1.46325600	-3.64806100
O	-5.30554000	1.55918200	-1.80277400
C	-3.28132000	-0.04904900	-1.53823400
C	-1.95904800	-0.41726400	-1.79702200
C	-1.46402100	-1.60222000	-1.26675200
C	-2.26768200	-2.43061700	-0.46979900
C	-3.58196100	-2.03895900	-0.21673900

C	-4.09267700	-0.84989000	-0.74595600
H	-1.33151000	0.22733000	-2.40843600
H	-0.43503600	-1.89279100	-1.47101300
H	-4.21780100	-2.66912700	0.40234600
H	-5.11537800	-0.53623300	-0.55889900
C	-1.70952900	-3.71382400	0.09558200
H	-2.45820300	-4.24097000	0.69486500
H	-1.38172000	-4.38827800	-0.70365500
H	-0.84108900	-3.51972800	0.73532800
N	-3.00244800	2.65808200	-1.56470300
H	-1.56627900	2.75298200	-2.12606200
C	-3.23169600	2.92614000	-0.15381100
H	-2.98093900	2.05212600	0.47943500
H	-4.29039000	3.16032600	0.03626700
C	-2.36381200	4.10605100	0.27407100
H	-2.60713500	4.96460300	-0.36565200
H	-1.30981600	3.86509900	0.07972800
C	-2.54972800	4.47405800	1.74411800
H	-2.31544400	3.60267400	2.37395100
H	-3.60716000	4.71301400	1.93223400
C	-1.68376800	5.65445900	2.18219500
H	-0.62877800	5.41618800	1.99271300
H	-1.91852000	6.52488200	1.55522600
C	-1.87418900	6.01422300	3.65498500
H	-1.61901400	5.16468200	4.29938600
H	-1.24656500	6.86162700	3.95199500
H	-2.91790500	6.28081200	3.85913500
C	-0.68799200	4.67732700	-4.14239500
C	-0.94214600	3.18402900	-3.92005200
H	-1.99561100	2.98863100	-4.17764300
C	-0.09338700	2.32155200	-4.85230100
O	-0.64752900	2.84589200	-2.61756600
F	-1.43632700	5.39948500	-3.29838700
F	-1.00655600	5.07413300	-5.39235400
F	0.59263700	5.02973300	-3.93715500
F	-0.32765400	2.58742400	-6.15312300
F	1.22652100	2.48430800	-4.65415000
F	-0.36220300	1.02425800	-4.65910100

Int3

E = -1071.16695153 a.u

-1 1

S	-2.76089500	0.86329100	-2.34899500
O	-1.94697500	0.53012900	-3.53106000
O	-4.20958100	1.09035900	-2.58015100
C	-2.74718100	-0.66407900	-1.36078000
C	-1.56332500	-1.39873500	-1.26053300
C	-1.50806800	-2.52132300	-0.44275500
C	-2.62558300	-2.93015300	0.29977600
C	-3.79859800	-2.18345600	0.19409500
C	-3.86374100	-1.05616300	-0.63135600
H	-0.70096900	-1.07651100	-1.83815900
H	-0.58536600	-3.09677700	-0.37528500
H	-4.67743200	-2.48769100	0.76069800
H	-4.78044900	-0.48197400	-0.73325800
C	-2.54933200	-4.15202600	1.18332300
H	-3.50563400	-4.33833700	1.68238600
H	-2.29296500	-5.04705900	0.60427600
H	-1.78332500	-4.03565900	1.95915200
N	-2.04490700	1.95574600	-1.48821900
C	-2.81739400	2.43296200	-0.35810800
H	-2.98371800	1.64252100	0.40565300
H	-3.82028000	2.78798300	-0.65342500
C	-2.06412700	3.58042200	0.31016600
H	-1.90877200	4.37084700	-0.43658100
H	-1.06605600	3.22204900	0.59681500
C	-2.78646400	4.14670100	1.53053300
H	-2.94145800	3.34644900	2.26999400
H	-3.78986900	4.48991200	1.23673300
C	-2.03835100	5.30180700	2.19514600
H	-1.03578900	4.96047900	2.48695800
H	-1.88715200	6.10293700	1.45896200
C	-2.76719200	5.85858700	3.41767300
H	-2.90391500	5.07942300	4.17689900
H	-2.21793600	6.68639200	3.88041100
H	-3.76230900	6.22733000	3.14219100

Int4

E = -1071.05905903 a.u

0 2

S	-3.24320800	0.14206800	-1.10180200
O	-2.02245900	0.46071100	-1.83584100
O	-4.54214500	0.60358300	-1.57814700
C	-3.31458800	-1.60617300	-0.84332100
C	-2.13127400	-2.33627700	-0.82908800
C	-2.19562500	-3.70869800	-0.60380800
C	-3.42175500	-4.34854800	-0.39730900
C	-4.59490300	-3.58356000	-0.42117900
C	-4.55252500	-2.21213900	-0.64383000
H	-1.18334600	-1.83622700	-1.00241300
H	-1.27907500	-4.29227700	-0.59261800
H	-5.55400600	-4.07170000	-0.26710500
H	-5.45875600	-1.61532000	-0.67534400
C	-3.49243900	-5.83735600	-0.17542100
H	-3.91020600	-6.33929300	-1.05506900
H	-2.50203900	-6.25909700	0.01344000
H	-4.13553700	-6.07764000	0.67671100
N	-3.03288800	0.72031800	0.47357200
C	-3.00062100	2.17123400	0.50893100
H	-4.04645300	2.51341500	0.44396600
H	-2.48676100	2.57813700	-0.37460600
C	-2.35285100	2.64622300	1.80673100
H	-2.97535500	2.32743000	2.65044900
H	-2.35574900	3.74288900	1.80434900
C	-0.92905100	2.10999200	1.99308600
H	-0.98371700	1.02782800	2.16248900
H	-0.50873500	2.55148600	2.90622600
C	0.01426400	2.38633100	0.81726300
H	1.00230900	1.98151300	1.06716300
H	-0.32156300	1.83420700	-0.07044000
C	0.14968100	3.87142200	0.48108500
H	0.44225800	4.44859300	1.36658500
H	0.90689700	4.03344800	-0.29177900
H	-0.79083800	4.29263300	0.10848100

Int5

E = -1071.05746534 a.u

0 2

S	-3.16048100	0.12340800	-1.42249400
O	-2.16761600	0.28510500	-2.48103800
O	-4.51379200	0.62837700	-1.60915100
C	-3.21947200	-1.60046000	-0.99975900
C	-2.27590000	-2.46645400	-1.53678700
C	-2.33877500	-3.81963000	-1.20225500
C	-3.32999000	-4.30394500	-0.34698000
C	-4.27096400	-3.40339400	0.17513300
C	-4.22477400	-2.05409700	-0.14583800
H	-1.51789500	-2.08377200	-2.21318400
H	-1.60809000	-4.50744600	-1.61930100
H	-5.05070500	-3.77151300	0.83753400
H	-4.95469700	-1.35402400	0.24950600
C	-3.40684200	-5.76634500	0.00880200
H	-4.34372000	-6.20501200	-0.35069100
H	-2.57934200	-6.32738700	-0.43262500
H	-3.37377500	-5.90728100	1.09407300
N	-2.61853400	0.78411900	0.02433800
C	-2.78517300	2.24708300	0.13164800
H	-3.80714200	2.47960300	-0.17520200
H	-2.09571500	2.76652300	-0.54741600
C	-2.55612000	2.68607400	1.57570500
H	-3.37006200	2.30332200	2.20096400
H	-2.61389800	3.78089400	1.60695300
C	-1.21382100	2.21077900	2.16114800
H	-1.26465700	1.13130700	2.34673200
H	-1.09852800	2.67679900	3.15543000
C	-0.02622600	2.52727800	1.30592400
H	0.78883500	1.81023900	1.26790400
H	-1.63498800	0.52615500	0.13377700
C	0.24939700	3.93094100	0.87847500
H	0.50607500	4.56903300	1.74077100
H	1.08298900	3.98298500	0.17336200
H	-0.62305800	4.39509000	0.40154600

Int6

E = -1561.98696634 a.u

0 3

S	-2.26465600	0.64095100	-2.23880900
O	-1.21943100	0.08916800	-3.08411300
O	-3.65171800	0.73359600	-2.66558200
C	-2.24485600	-0.29128000	-0.71343400
C	-1.07541600	-0.96492800	-0.34330800
C	-1.03265800	-1.63990500	0.87033400
C	-2.13535300	-1.64018800	1.73256800
C	-3.29604700	-0.95208800	1.33825600
C	-3.36174700	-0.28752100	0.10851600
H	-0.22092900	-0.95730300	-1.01352600
H	-0.12731100	-2.16706100	1.15991300
H	-4.16909100	-0.96461700	1.98629500
H	-4.26892900	0.21891400	-0.20788000
C	-2.07949800	-2.37614500	3.04467600
H	-2.94574600	-2.14391400	3.66973200
H	-2.06300600	-3.45874700	2.87794300
H	-1.17497500	-2.11280600	3.60162900
N	-1.78697900	2.17671300	-1.84347700
C	-2.67464600	2.97333400	-0.99149900
H	-2.80896600	2.51518900	0.00108200
H	-3.65039200	3.01335000	-1.48396600
C	-2.09960400	4.37679300	-0.83530100
H	-2.10566700	4.87372000	-1.81112200
H	-1.05179800	4.30661600	-0.51187600
C	-2.88707600	5.19009000	0.20029000
H	-3.96314200	5.12257700	-0.01604200
H	-2.62560400	6.25522700	0.08185000
C	-2.62382800	4.75358000	1.60661400
H	-1.58179800	4.67776800	1.91172200
C	-3.67205400	4.87916800	2.66064700
H	-4.61344900	4.41511300	2.33928100
H	-3.36513000	4.40810000	3.59935600
H	-3.90349300	5.93355100	2.88632900
H	-0.82011400	2.16659800	-1.51477500
S	-2.15020000	1.32413900	2.95519200
C	-1.04968400	1.62049500	1.76039900
N	-0.27892300	1.82479000	0.90100300

^{3}Int7

E = -1561.94888648 a.u

0 3

S	-2.13796700	0.61148800	-2.75491900
O	-1.03072400	0.42307300	-3.67940000
O	-3.39149100	1.23482200	-3.14940000
C	-2.54073900	-1.00722800	-2.11073400
C	-1.40769200	-1.74130900	-1.50821700
C	-1.45675800	-1.95198600	-0.16556100
C	-2.65415200	-1.69450400	0.58558200
C	-3.87424800	-1.40091400	-0.13915400
C	-3.86201600	-1.15026900	-1.46894700
H	-0.56275400	-2.03793900	-2.12147800
H	-0.61181800	-2.40469600	0.34994100
H	-4.81673400	-1.44128800	0.40405800
H	-4.76633300	-0.98668400	-2.04542200
C	-2.69820200	-1.88297800	2.06799300
H	-3.56883100	-2.47968800	2.36623600
H	-1.79573500	-2.37604200	2.43920700
H	-2.78622900	-0.91871900	2.58863200
N	-1.50826600	1.53297400	-1.51801600
C	-2.33834500	1.86078600	-0.36054600
H	-2.34417700	1.04063800	0.37430500
H	-3.36206700	1.99187800	-0.72615700
C	-1.84311200	3.14822200	0.29123200
H	-1.86754100	3.95285200	-0.45272500
H	-0.79354700	3.02298600	0.58789900
C	-2.70181100	3.51692400	1.50086600
H	-2.66184400	2.72032900	2.25803900
H	-3.75162800	3.59138100	1.18644600
C	-2.34977300	4.85088300	2.16200800
H	-2.30316600	5.63837900	1.40280700
C	-3.33268000	5.22283600	3.26243100
H	-3.37301300	4.43829800	4.02498300

H -3.06079600	6.16463100	3.74636400
H -4.33224900	5.33971900	2.82944000
H -0.55521300	1.24358100	-1.30680400
S -0.62749700	4.67121800	2.83017200
C -0.43899700	6.22187300	3.49534500
N -0.30376300	7.27858900	3.95569800

Int8

E = -1070.8080104 a.u

1 1

S 0.84942200	-1.54363200	-0.55374600
O -0.12516400	-2.61856100	-0.50234400
O 2.02902500	-1.56454700	-1.39516300
C -0.06179800	-0.05196500	-0.91956800
C -1.44826300	-0.11536800	-1.06837400
C -2.14325600	1.04632900	-1.39461300
C -1.47149000	2.26199300	-1.60816600
C -0.07431100	2.28795700	-1.48099000
C 0.63704000	1.13793000	-1.14946400
H -1.96067300	-1.06494000	-0.94112000
H -3.22258600	1.00639400	-1.51564500
H 0.46278100	3.21304300	-1.67373300
H 1.72297600	1.15060000	-1.09164400
C -2.22983900	3.49144000	-2.02851100
H -3.23283400	3.51182300	-1.59503500
H -1.70484200	4.40587800	-1.74227600
H -2.34221900	3.50179700	-3.11855700
N 1.44222300	-1.27174700	1.01147800
C 0.81525000	-1.97300600	2.14333200
H 1.57139000	-2.56935500	2.66022000
H 0.06020100	-2.66829400	1.76358400
C 0.18088800	-0.97962500	3.12149400
H 0.95140400	-0.38365800	3.62177300
H -0.34894000	-1.53533200	3.90048900
C -0.81397900	-0.07929800	2.39073700
H -1.45085500	0.47206100	3.13180800
H -1.54303700	-0.63512000	1.78893200
C -0.33435800	1.08985000	1.67619000
H -1.01875000	1.52892500	0.94676300
C 0.87626000	1.82739300	2.03144300
H 0.97155600	2.77392100	1.50259200
H 0.89940700	1.98160600	3.12162500
H 1.73716600	1.17649000	1.81899600
H 2.45335000	-1.39297200	0.96031900

TS1

E = -1860.78908299 a.u

-1 1

S -4.10719100	1.45861000	-2.17587400
O -3.90706300	1.43027900	-3.62569700
O -5.47450200	1.49577300	-1.64009200
C -3.38583200	-0.05741600	-1.52646600
C -2.03123700	-0.30710800	-1.75963100
C -1.46786100	-1.47495500	-1.25845700
C -2.23140100	-2.39631200	-0.52814900
C -3.57946900	-2.11648400	-0.30150000
C -4.16167200	-0.94614900	-0.79422200
H -1.43155300	0.41932000	-2.30733400
H -0.41267700	-1.67511100	-1.43411100
H -4.18336500	-2.81845900	0.27002300
H -5.20770700	-0.71340800	-0.61914800
C -1.59567000	-3.65901700	-0.00018400
H -2.31400300	-4.25642200	0.56943200
H -1.21417600	-4.27972000	-0.81878200
H -0.74947300	-3.42987700	0.65713900
N -3.22009600	2.67103100	-1.59749400
H -2.11301900	2.67491400	-2.04106500
C -3.25123200	2.88481800	-0.15485100
H -2.76257400	2.05422500	0.38721100
H -4.29194900	2.93638400	0.19050100
C -2.52423400	4.18796200	0.16381000
H -3.03993600	5.00878200	-0.35109600
H -1.51259700	4.14070700	-0.25958700
C -2.45633100	4.46454400	1.66365000
H -1.93161100	3.63834000	2.16593400
H -3.47371500	4.48366700	2.08335000
C -1.75221300	5.77913400	1.99678300
H -0.73970700	5.76084400	1.57314400
H -2.27806800	6.60487900	1.49931900
C -1.67911000	6.04640900	3.49937000
H -1.13198400	5.24593100	4.01104500
H -1.17353500	6.99280500	3.72020000
H -2.68352800	6.09152700	3.93685600
C -0.51016000	4.61093800	-3.83819400
C -0.95208600	3.14092700	-3.77824900
H -1.96796700	3.11864900	-4.22313600
C -0.08586800	2.27514100	-4.70081700
O -0.89356400	2.67371400	-2.50823700
F -1.29525200	5.35457900	-3.04088600
F -0.60239500	5.14650200	-5.07762100
F 0.75597500	4.80277600	-3.43066200
F -0.13811800	2.66164100	-5.99586500
F 1.21355100	2.27334300	-4.35416300
F -0.50199600	0.99963200	-4.66214700

TS2

E = -1071.02789331 a.u

0 2

S -3.37105400	0.55077100	-1.14166200
O -2.27985000	0.99262400	-2.01015900
O -4.75095100	0.84412200	-1.51372200
C -3.18910700	-1.19227200	-0.86858500
C -1.96347100	-1.79634700	-1.12127800
C -1.82654300	-3.16311300	-0.88301900
C -2.89780000	-3.92027200	-0.40226700
C -4.12205200	-3.28106400	-0.16151200
C -4.27753400	-1.92005000	-0.39177700
H -1.14112900	-1.20442900	-1.51242700
H -0.87445600	-3.64824500	-1.08122300
H -4.96365200	-3.86242100	0.20727400
H -5.22512300	-1.42000200	-0.21590200
C -2.75802100	-5.40162500	-0.16235100
H -3.36058800	-5.96880700	-0.88008700
H -1.71911400	-5.72526900	-0.26486200

H	-3.10271200	-5.67112300	0.84096700
N	-3.15462500	1.12841500	0.42261300
C	-3.20920800	2.59766800	0.48021500
H	-4.26477300	2.88934600	0.48200300
H	-2.74728500	3.04585700	-0.40951500
C	-2.51167200	3.10237400	1.76314300
H	-3.25153400	3.23357700	2.55773000
H	-2.10516600	4.09604800	1.54791900
C	-1.39752100	2.16153700	2.28378700
H	-1.82684200	1.47121800	3.01655900
H	-0.63798700	2.75474500	2.81273700
C	-0.75677100	1.34412200	1.18108600
H	-0.28538300	0.41985000	1.52735400
H	-1.87158000	0.93134500	0.66762500
C	0.02955100	2.07987400	0.12506900
H	0.95270100	2.48820700	0.56118800
H	0.30490400	1.42272500	-0.70397500
H	-0.53470900	2.91877000	-0.29454000

TS3

E = -1561.94527427 a.u

0 3

S	-2.67624600	0.73573600	-2.19578700
O	-1.88867500	0.05228700	-3.20575200
O	-4.07913100	1.07162300	-2.38835000
C	-2.54017600	-0.18850200	-0.67725200
C	-1.46271200	-1.05270400	-0.50398900
C	-1.28144400	-1.66843400	0.73112400
C	-2.14293300	-1.40997600	1.80127400
C	-3.23273000	-0.55494500	1.59401300
C	-3.44651500	0.04767200	0.35541100
H	-0.77607100	-1.22826500	-1.32642400
H	-0.44037900	-2.34205600	0.87236200
H	-3.93188400	-0.37166300	2.40676200
H	-4.31629800	0.67450000	0.17937200
C	-1.88813800	-2.01515800	3.15699000
H	-2.81677800	-2.13745400	3.72124000
H	-1.40505400	-2.99227200	3.07151600
H	-1.22451200	-1.36715700	3.74175900
N	-1.90253200	2.18545900	-1.88833200
C	-2.56887500	3.04842500	-0.91045200
H	-2.83783500	2.47120100	-0.01549900
H	-3.49953700	3.40982800	-1.35952900
C	-1.67391600	4.21048100	-0.50473100
H	-1.49107500	4.84991400	-1.37509400
H	-0.69822800	3.82519400	-0.18303000
C	-2.28472300	5.06369800	0.62103100
H	-3.19013000	5.55645600	0.23711200
H	-1.57469400	5.86391800	0.85342900
C	-2.66745200	4.34531000	1.91666300
H	-2.37123800	4.91451600	2.80514100
C	-4.11024200	3.88049300	2.03188600
H	-4.40870600	3.25271500	1.18667100
H	-4.28984400	3.32413400	2.95750100
H	-4.77157100	4.75692500	2.03740900
H	-0.91973700	2.00762600	-1.66675100
S	-1.54155500	2.66233000	2.25297900
C	-0.32810300	1.57975100	1.38795700
N	0.32006200	1.33406200	0.43909500

TS4

E = -1070.80800768 a.u

1 1

S	-3.53433000	1.84273300	-1.31378100
O	-4.49717300	0.75677600	-1.28568600
O	-2.33829000	1.83894600	-2.13193800
C	-4.45304200	3.32775800	-1.68500800
C	-5.84065900	3.26126500	-1.81627900
C	-6.54205000	4.42152200	-2.13544100
C	-5.87540200	5.63796400	-2.35852400
C	-4.47658200	5.66665800	-2.24854900
C	-3.75906200	4.51860900	-1.92390900
H	-6.34967200	2.31073100	-1.68250900
H	-7.62265700	4.37924800	-2.24361000
H	-3.94371000	6.59248600	-2.44928600
H	-2.67254900	4.53290200	-1.87941800
C	-6.64055400	6.86576400	-2.77162200
H	-7.64240500	6.88000600	-2.33533400
H	-6.11876600	7.78135500	-2.48304400
H	-6.75577300	6.88033000	-3.86131000
N	-2.97236200	2.11386700	0.26386700
C	-3.62000500	1.41216300	1.38307400
H	-2.88238800	0.79019700	1.89674800
H	-4.38905200	0.74014300	0.98954500
C	-4.23613100	2.40834400	2.37017300
H	-3.45473400	2.98866800	2.87189500
H	-4.77389200	1.85677200	3.14658200
C	-5.21768100	3.32825100	1.64452300
H	-5.83745400	3.89250300	2.39054600
H	-5.95910100	2.78584100	1.04621900
C	-4.71887900	4.48713600	0.92781100
H	-5.38715200	4.92360300	0.18197600
C	-3.50439900	5.21521000	1.28755300
H	-3.41704600	6.17666000	0.78445200
H	-3.44623300	5.32890900	2.38017100
H	-2.65259300	4.56910800	1.02439100
H	-1.96024900	1.99325300	0.23218100

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