Support Information.

Scandium-Catalyzed Chemoselective Carbene Insertion into N−H over S−H: Access to *o*-Alkylamine-Diaryl Disulfides

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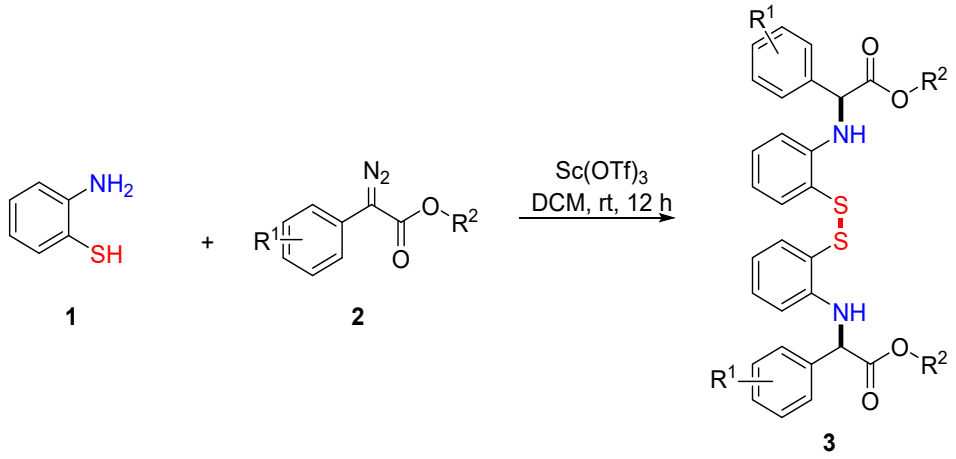
1. General information

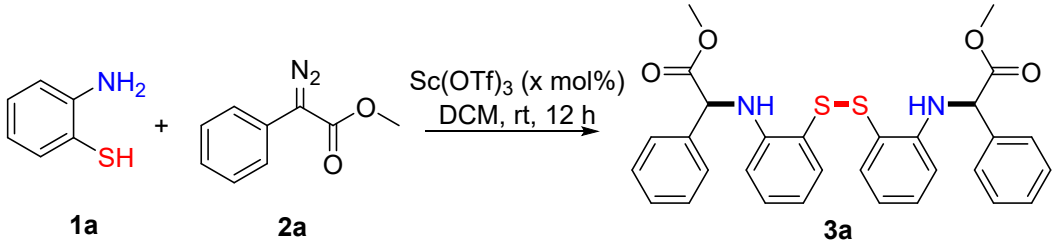
All chemicals and reagents were used of commercial grade and were used without further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200–300 mesh silica gel. All yields refer to isolated products after purification. The intermediates and the products synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker DRX-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or Bruker DRX-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) using $CDCl_3$ as solvents. The following abbreviation were used to explain the multiplicities: (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (sept) = septuplet, (dd) = double doublet, (dt) = double triplet, (dq) = double quartet, (ddd) = double double doublet, (m) = multiplet; Chemical shifts (δ) are expressed in parts per million (ppm) and *J* values are given in hertz (Hz). HRMS was performed on an Agilent LC/MSD TOF instrument. The melting points were measured by the XT-4A melting point apparatus without correction.

2. General Procedure for preparing *o*-alkylamine-diaryl disulfides



Under an air atmosphere, 2-aminobenzenethiol **1** (0.3 mmol, 1.0 equiv), the diazoester compound **2** (0.3 mmol, 1.0 equiv), $Sc(OTf)_3$ (2 mol%, 0.006 mmol), and DCM (2.0 mL) were added to a 10 mL of reaction tube. The mixture was stirred at room temperature and monitored using thin-layer chromatography (TLC). After stirring for 12 hours, the reaction was quenched with a saturated solution of sodium chloride (10 mL) and then extracted three times with 20 mL of ethyl acetate (EtOAc). The organic layers were combined, dried over sodium sulfate (Na_2SO_4), filtered, and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel yielding the product **3**. The products were further characterized by nuclear magnetic resonance (**NMR**) spectroscopy and high-resolution mass spectrometry (**HRMS**).

Table S1. Optimization of catalyst amounts

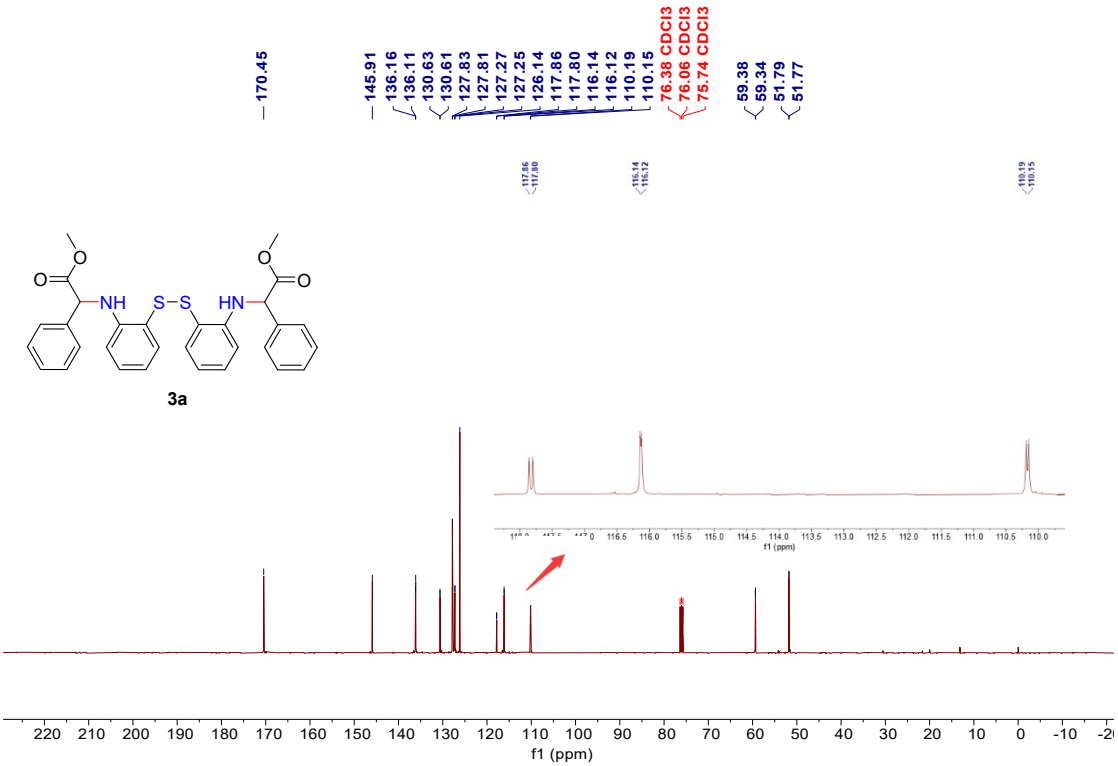


1a **2a** **3a**

entry	$Sc(OTf)_3$(x mol%)	yield of **3a**
1	0	0
2	1	77
3	**2**	**96**
4	3	88
5	5	91
6	8	90
7	10	83

[a] In a 10 mL reaction tube, o-aminobenzene thiol **1a** (0.3 mmol, 1.0 eq.), methyl 2-diazo-2-phenylacetate **2a** (0.3 mmol, 1.0 eq.), base (0.3 mmol, 1.0 eq.), catalyst (x mol%), solvent 2 mL, under air atmosphere (1 atm), stirred for 12 h. [b]rt = room temperature. [c]Isolated yield based on **1a**.

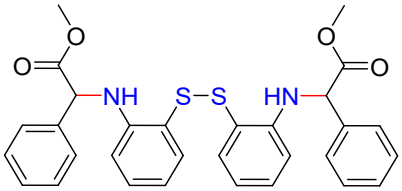
Figure S1. The discovery of diastereoisomers.



During the experimental process, we observed the appearance of diastereoisomers in the products and analyzed the ratio of diastereoisomers. Taking product **3a** as an example, we found a noticeable splitting in the peak corresponding to a chiral carbon in its ^{13}C NMR spectrum. At the chemical shift of 110.8 ppm, we identified and marked two peaks at the chemical shifts of 117.86 ppm and 117.80 ppm. We analyzed the ratio of its components and ultimately determined that the diastereoisomers ratio was 1:1.

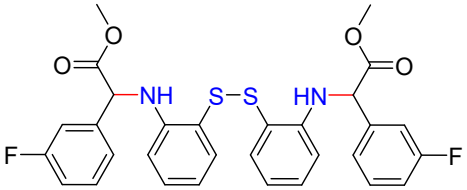
3. Spectroscopic Data of 3

Dimethyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)
3a



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3a** as Yellow solid; Mp: 168.9 - 170.4 °C; yield: 96%, 78 mg, 1:1 dr; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.1 Hz, 2H), 7.32 (m, 6H), 7.18 – 7.01 (m, 4H), 6.48 h(q, *J* = 7.0 Hz, 2H), 6.35 (d, *J* = 5.9 Hz, 2H), 6.29 (q, *J* = 7.2, 6.1 Hz, 2H), 5.09 (q, *J* = 6.6, 5.9 Hz, 2H), 3.73 (t, *J* = 5.5 Hz, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.5, 145.9, 136.1, 130.6, 127.8, 127.3, 126.1, 117.9, 116.1, 110.2, 59.3, 51.8; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{30}H_{29}N_2O_4S_2$ $[M+H]^+$, 545.1563; found, 545.1567.

Dimethyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(3-fluorophenyl) acetate)
3b

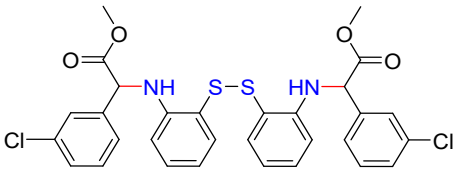


Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3b** as Yellow solid; Mp: 264.1 - 266.0°C; yield: 88%, 78 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 3H), 7.13 (dd, *J* = 16.0, 8.2 Hz, 3H), 7.07 (t, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 2H), 6.51 (d, *J* = 6.6 Hz, 2H), 6.35 (s, 2H), 6.25 (d, *J* = 8.6 Hz, 2H), 5.06 (s, 2H), 3.75 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 170.9, 163.1(d, J_{C-F} = 246.0 Hz), 146.8, 140.0, 137.2, 131.8, 130.4(d, J_{C-F} = 3.8 Hz), 122.9, 119.2(d, J_{C-F} = 7.5 Hz), 117.6, 115.4(d, J_{C-F} = 21.3 Hz), 114.3(d, J_{C-F} = 22.5 Hz), 111.3, 60.1, 53.0; **^{19}F NMR** (376 MHz, Chloroform-d) δ -134.71;

HRMS (TOF-ESI$^+$): m/z calcd for $C_{30}H_{27}F_2N_2O_4S_2$ $[M+H]^+$, 581.1375; found, 581.1376.

Dimethyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(3-chlorophenyl) acetate)

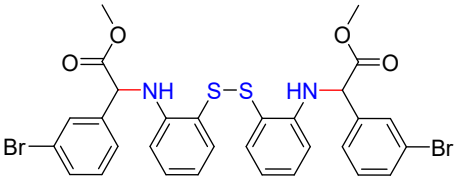
3c



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3c** as Yellow solid; Mp: 230.6 - 232.4 °C; yield: 90%, 83 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.49 (s, 2H), 7.33 (d, *J* = 32.4 Hz, 2H), 7.27 (d, *J* = 6.2 Hz, 4H), 7.15 – 7.03 (m, 4H), 6.50 (s, 2H), 6.35 (s, 2H), 6.24 (d, *J* = 8.1 Hz, 2H), 5.03 (s, 2H), 3.75 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 170.9, 146.8, 139.5, 137.3, 134.8, 131.8, 130.2, 128.6, 127.5, 125.4, 117.6, 111. 3, 59.7, 53.1; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{30}H_{27}Cl_2N_2O_4S_2$ [M+H]+, 613.0784; found, 613.0756.

Dimethyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(3-bromophenyl) acetate)

3d

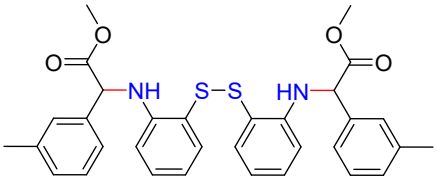


Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3d** as Yellow solid; Mp: 388.2 - 390.1 °C; yield: 91％, 96 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ7.24 (s, 2H), 7.16 (dd, *J* = 15.2, 7.0 Hz, 4H), 7.04 (d, *J* = 7.3 Hz, 2H), 6.99 (t, *J* = 6.9 Hz,

4H), 6.40 (s, 2H), 6.24 (d, J = 6.9 Hz, 4H), 4.97 (t, J = 6.3 Hz, 2H), 3.66 (d, J = 7.4 Hz, 6H), 2.26 (s, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 170.9, 146.8, 139.8, 139.7, 137.3, 131.8, 131.6, 130.4, 125.8, 123.0, 119.2, 117.6, 111.3, 60.1, 53.1; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{30}H_{27}Br_2N_2O_4S_2$ $[M+H]^+$, 702.9754; found, 702.9757.

Dimethyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(m-tolyl)acetate)

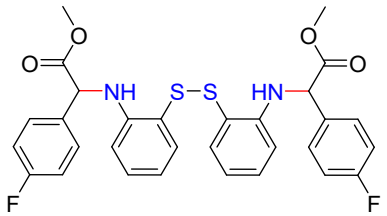
3e



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3e** as Yellow solid; Mp: 362.9 - 364.8 °C; yield: 85%; 73mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.24 (s, 2H), 7.16 (dd, J = 15.3, 7.0 Hz, 4H), 7.04 (d, J = 7.4 Hz, 2H), 7.02 – 6.96 (m, 4H), 6.39 (q, J = 6.5 Hz, 2H), 6.24 (d, J = 6.8 Hz, 4H), 4.97 (t, J = 6.3 Hz, 2H), 3.66 (d, J = 7.4 Hz, 6H), 2.26 (d, J = 3.1 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 170.7, 146.1, 137.6, 136.2, 130.7, 128.1, 127.7, 126.8, 123.4, 117.9, 116.1, 110.2, 59.6, 51.8, 20.5; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{32}H_{33}N_2O_4S_2$ $[M+H]^+$, 573.1876; found, 573.1873.

Dimethyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(4-fluorophenyl) acetate)

3f

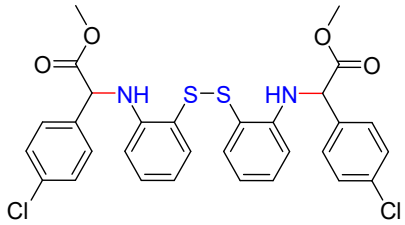


Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3f** as Yellow solid; Mp:

237.9 - 239.6 °C; yield: 90%,78 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 2H), 7.37 – 7.33 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 6.96 (t, *J* = 8.5 Hz, 2H), 6.55 – 6.47 (m, 2H), 6.32 (t, *J* = 5.7 Hz, 2H), 6.25 (t, *J* = 8.2 Hz, 2H), 5.05 (dd, *J* = 10.3, 5.5 Hz, 2H), 3.74 (d, *J* = 9.2 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ171.3, 162.7(d, $J_{C\text{-}F}$ = 248.8 Hz), 146.8, 137.2, 133.0, 131.7(d, *J* = 6.0 Hz), 128.9, 119.3, 117.5, 115.9(d, *J* = 22.5 Hz), 111.3, 59.8, 52.9; **^{19}F NMR** (376 MHz, Chloroform-d) δ -123.36; **HRMS** (TOF-ESI^{+}): m/z calcd for $C_{30}H_{27}F_2N_2O_4S_2$ $[M+H]^+$, 581.1375; found, 581.1377.

Dimethyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(4-chlorophenyl) acetate)

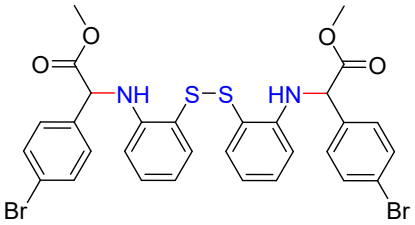
3g



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3g** as Yellow solid; Mp: 358.7 - 360.7 °C; yield: 92%, 84 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 4H), 7.25 (s, 2H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 2H), 6.52 (dt, *J* = 13.0, 7.4 Hz, 2H), 6.33 (t, *J* = 6.4 Hz, 2H), 6.22 (t, *J* = 8.9 Hz, 2H), 5.03 (dd, *J* = 10.9, 5.5 Hz, 2H), 3.74 (d, *J* = 9.4 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.1, 146.7, 137.2, 135.8, 134.2, 131.7, 131.6, 129.1, 128.6, 119.3, 117.6, 111.6, 59.8, 53.0,; **HRMS** (TOF-ESI^{+}): m/z calcd for $C_{30}H_{27}N_2O_4S_2$ $[M+H]^+$, 613.0784; found, 613.0788.

Dimethyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(4-bromophenyl)acetate)

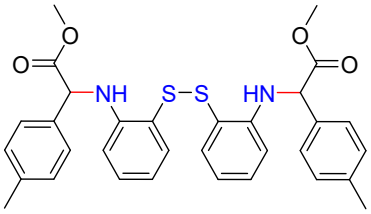
3h



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3h** as Yellow solid; Mp: 221.7 - 223.4 °C, yield: 90%, 95 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.18 (s, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.9 Hz, 2H), 6.45 (dd, *J* = 13.0, 6.0 Hz, 2H), 6.26 (t, *J* = 6.6 Hz, 2H), 6.14 (t, *J* = 8.8 Hz, 2H), 4.94 (dd, *J* = 10.5, 5.4 Hz, 2H), 3.67 (d, *J* = 9.4 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.0, 146.7, 137.2, 136.3, 132.0, 131.7, 128.9, 122.4, 119.2, 117.6, 111.2, 59.9, 53.0; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{30}H_{27}Br_2N_2O_4S_2$ $[M+H]^+$, 702.9754; found, 702.9759.

Dimethyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(p-tolyl)acetate)

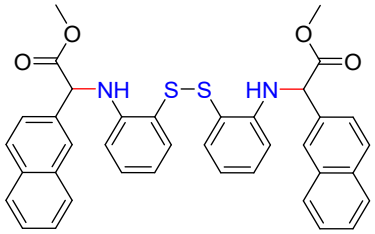
3i



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3i** as; Yellow solid; Mp: 369.4 - 371.4 °C; yield: 88%, 76 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.09 (dd, *J* = 23.5, 7.0 Hz, 8H), 6.48 (s, 2H), 6.30 (s, 4H), 5.04 (d, *J* = 6.2 Hz, 2H), 3.73 (t, *J* = 7.4 Hz, 6H), 2.32 (s, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.7, 147.1, 138.1, 137.2, 131.7, 129.6, 127.1, 117.2, 111.2, 60.3, 52.8, 21.2; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{32}H_{33}N_2O_4S_2$ $[M+H]^+$, 573.1876; found, 573.1879.

Dimethyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(naphthalen-2-yl)acetate)

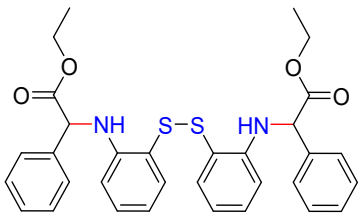
3j



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3j** as Yellow solid; Mp: 197.9-199.77 °C; yield: 92%, 89 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 12.1 Hz, 2H), 7.82 (s, 8H), 7.47 (s, 4H), 7.10 (s, 2H), 7.01 (s, 2H), 6.47 (d, *J* = 19.6 Hz, 4H), 6.32 (s, 2H), 5.23 (d, *J* = 19.2 Hz, 2H), 3.72 (d, *J* = 10.5 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.5, 147.1, 137.3, 134.8, 133.3, 131.7, 128.8, 128.1, 127.7, 126.6, 124.9, 199.1, 117.3, 111.4, 60.7, 52.9; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{38}H_{33}N_2O_4S_2$ $[M+H]^+$, 645.1876; found, 645.1879.

Diethyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

3k

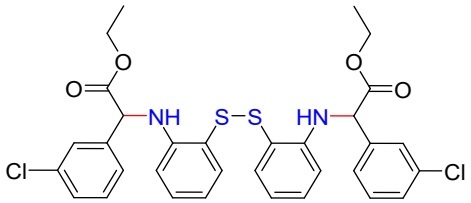


Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3k** as Yellow solid; Mp: 200.9 - 202.5 °C; yield: 93%, 80 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ7.49 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.30 (q, *J* = 9.8, 8.8 Hz, 6H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.06 (q, *J* = 7.7 Hz, 3H), 6.47 (q, *J* = 7.0 Hz, 2H), 6.36 (t, *J* = 5.7 Hz, 2H),

6.30 (t, *J* = 8.2 Hz, 2H), 5.10 – 5.04 (m, 2H), 4.27 – 4.20 (m, 2H), 4.18 – 4.12 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 6H).; **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.0, 147.1, 137.4, 137.2, 131.7, 128.8, 128.2, 127.2, 117.1, 111.3, 61.9, 60.6, 14.1; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{32}H_{33}N_2O_4S_2$ $[M+H]^+$, 573.1876; found, 573.1879.

Diethyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(3-chlorophenyl)acetate)

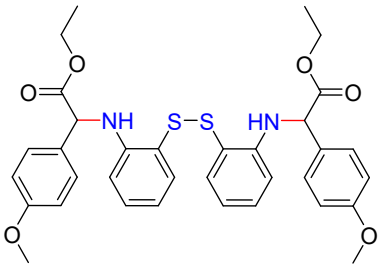
3l



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3l** as Yellow solid; Mp: 384.9 - 386.7 °C; yield: 88%, 84 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.51 (s, 2H), 7.26 (s, 6H), 7.08 (d, *J* = 7.9 Hz, 4H), 6.51 (s, 2H), 6.37 (s, 2H), 6.25 (s, 2H), 5.04 (s, 2H), 4.22 (dt, *J* = 30.6, 7.4 Hz, 4H), 1.24 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 170.3, 146.8, 139.6, 137.3, 134.7, 131.8, 130.1, 128.5, 127.4, 125.3, 119.0, 117.4, 111.3, 62.2, 60.2, 14.1; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{32}H_{31}Cl_2N_2O_4S_2$ $[M+H]^+$, 641.1097; found, 641.1098.

Diethyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-(4-methoxyphenyl) acetate)

3m

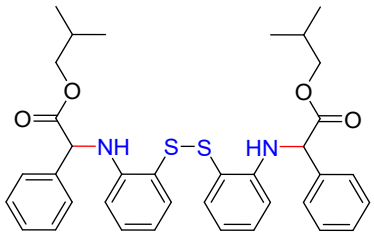


Following the general procedure, purification by flash chromatography on silica gel

(eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3m** as Yellow solid; Mp: 200.5 - 212.1 °C; yield: 90%, 85 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 9.0 Hz, 4H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.89 (t, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 7.3 Hz, 4H), 6.76 – 6.70 (m, 4H), 5.24 (s, 2H), 4.20 (td, *J* = 11.3, 10.8, 5.3 Hz, 4H), 3.71 (s, 6H), 1.19 (d, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 172.2, 159.8, 145.0, 132.9, 127.8, 126.4, 125.7, 121.6, 121.2, 113.8, 111.9, 80.0, 62.9, 55.3, 14.0; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{34}H_{37}N_2O_4S_2$ $[M+H]^+$, 633.2088; found, 633.2089.

Diisobutyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

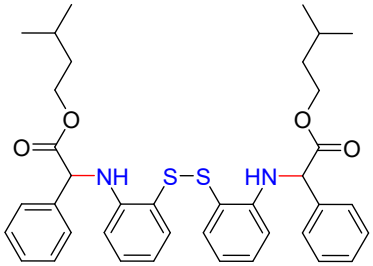
3n



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3n** as Yellow solid; Mp: 174.3 - 176.1 °C; yield: 88%, 83 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.34 – 7.28 (m, 6H), 7.07 (dd, *J* = 22.2, 7.3 Hz, 4H), 6.46 (d, *J* = 6.8 Hz, 2H), 6.40 (s, 2H), 6.30 (t, *J* = 7.6 Hz, 2H), 5.09 (t, *J* = 6.7 Hz, 2H), 3.95 (t, *J* = 6.9 Hz, 2H), 3.92 – 3.87 (m, 2H), 1.89 (dt, *J* = 13.4, 6.8 Hz, 2H), 0.83 (t, *J* = 6.4 Hz, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.0, 147.1, 137.5, 137.2, 131.7, 128.8, 128.2, 127.2, 117.1 111.3, 71.7, 60.7, 27.7, 18.9; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{36}H_{41}N_2O_4S_2$ $[M+H]^+$, 629.2502; found, 629.2505.

Diisopentyl2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

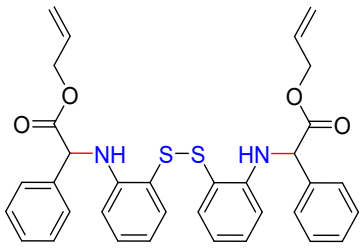
3o



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3o** as Yellow solid; Mp: 196.2-198.1 °C; yield: 89%, 88 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.3 Hz, 4H), 7.32 (dt, *J* = 13.5, 7.1 Hz, 6H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 2H), 6.56 (t, *J* = 7.6 Hz, 2H), 6.50 (t, *J* = 7.5 Hz, 2H), 5.05 (d, *J* = 6.0 Hz, 2H), 4.32 (s, 4H), 4.16 (t, *J* = 6.7 Hz, 4H), 1.48 (d, *J* = 7.1 Hz, 2H), 0.84 (dd, *J* = 17.2, 6.6 Hz, 12H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.1, 148.9, 147.0, 137.1, 137.0, 131.7, 131.5, 128.8, 128.3, 127.2, 118.1, 117.2, 115.3, 111.2, 64.5, 60.7, 37.1, 22.4, 22.3; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{38}H_{45}N_2O_4S_2$ $[M+H]^+$, 657.2815; found, 657.2819.

Diallyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

3p

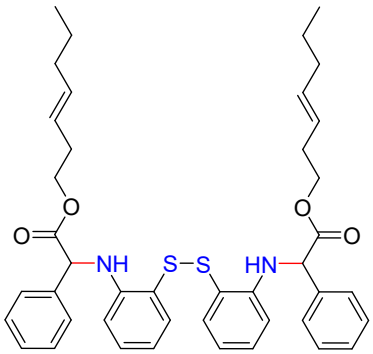


Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3p** as Yellow solid; Mp: 165.9-167.6 °C; yield: 87%, 78 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.47 (s, 2H), 7.34 (d, *J* = 7.5 Hz, 4H), 7.16 – 7.08 (m, 6H), 6.67 (d, *J* = 8.2 Hz, 2H), 6.53 (dt, *J* = 23.5, 7.8 Hz, 4H), 6.32 (s, 2H), 5.83 (ddt, *J* = 17.0, 11.3, 5.6 Hz, 2H), 5.18 (d,

J = 11.7 Hz, 4H), 5.09 (d, *J* = 5.6 Hz, 2H), 4.63 (s, 4H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 170.1, 148.9, 147.0, 137.2, 137.0, 131.8, 131.6, 128.9, 128.4, 127.3, 118.5, 118.2, 117.3, 115.3, 111.3, 66.2, 60.6; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{34}H_{33}N_2O_4S_2$ $[M+H]^+$, 597.1876; found, 597.1877.

Di((E)-hept-3-en-1-yl)2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

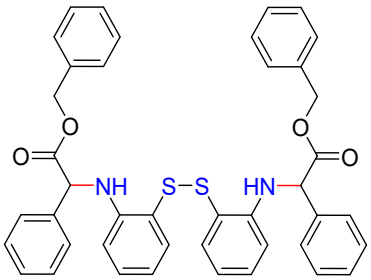
3q



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3q** as Yellow solid; Mp: 192.5 - 194.1 °C; yield: 85%, 90 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.1 Hz, 4H), 7.31 (dd, *J* = 13.4, 7.1 Hz, 6H), 7.11 (ddd, *J* = 25.2, 17.9, 7.1 Hz, 8H), 6.69 (t, *J* = 10.5 Hz, 2H), 6.56 (t, *J* = 7.8 Hz, 2H), 6.52 – 6.44 (m, 2H), 6.30 (d, *J* = 7.4 Hz, 4H), 5.45 (q, *J* = 8.4 Hz, 2H), 5.20 (d, *J* = 9.0 Hz, 2H), 5.06 (t, *J* = 6.7 Hz, 2H), 4.32 (s, 4H), 4.11 (dd, *J* = 14.8, 7.1 Hz, 4H), 2.33 (d, *J* = 7.2 Hz, 4H), 2.00 (t, *J* = 7.5 Hz, 4H), 0.95 (t, *J* = 7.7 Hz, 6H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.1, 148.9, 147.0, 137.3, 137.1, 137.0, 136.8, 134.8, 131.7, 131.5, 128.8, 128.3, 127.2, 123.2, 118.6, 118.1, 117.3, 115.3, 111.3, 65.4, 60.6, 26.6, 20.6, 14.2; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{42}H_{49}N_2O_4S_2$ $[M+H]^+$, 709.3128; found, 709.3135.

Dibenzyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

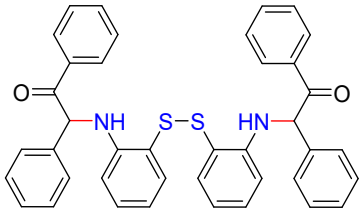
3r



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.4) afforded **3r** as Yellow solid; Mp: 213.7 - 215.2 °C; yield: 90%, 94 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 6.9 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 5.4 Hz, 12H), 7.18 (s, 4H), 7.09 (dd, *J* = 16.6, 7.6 Hz, 2H), 7.02 (t, *J* = 7.9 Hz, 2H), 6.46 (d, *J* = 6.6 Hz, 2H), 6.35 (s, 2H), 6.31 – 6.23 (m, 2H), 5.19 (t, *J* = 11.7 Hz, 2H), 5.12 (t, *J* = 11.6 Hz, 4H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 170.9, 147.0, 137.2, 137.2, 135.4, 131.7, 131.6, 128.9, 128.5, 128.3, 127.9, 127.3, 119.0, 117.3, 111.3, 67.3, 60.7; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{42}H_{37}N_2O_4S_2$ $[M+H]^+$, 697.2189; found, 697.2196.

Diphenyl 2,2'-((disulfanediylbis(2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

3s

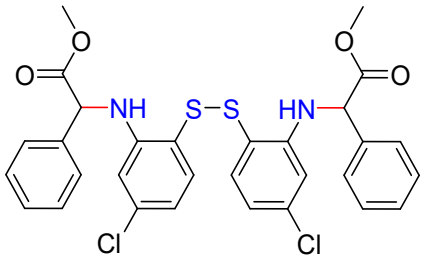


Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.4) afforded **3s** as Yellow solid; Mp: 230.0 - 231.8 °C; yield: 82%, 78 mg, 1:1 dr; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.8 Hz, 4H), 7.49 (t, *J* = 7.4 Hz, 3H), 7.38 (d, *J* = 7.8 Hz, 8H), 7.33 (s, 7H), 7.25 (s, 6H), 6.88 (s, 2H), 5.21 (s, 2H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 193.7, 172.1, 138.4, 138.3, 134.8, 133.4, 129.2, 129.0, 128.9, 128.8, 128.7, 128.62, 128.59, 128.54, 128.49, 127.4, 127.3, 78.3, 56.6; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{40}H_{33}N_2O_4S_2$

[M+H]$^+$, 669.1878; found, 669.1880.

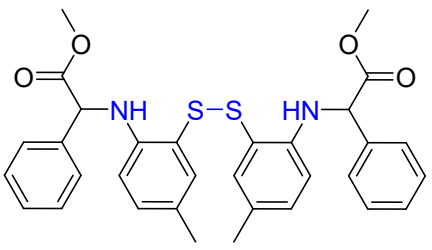
dimethyl 2,2'-((disulfanediylbis(5-chloro-2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

3t



Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3t** as Yellow solid; Mp: 220.2 - 223.3℃; yield: 90%, 83 mg, 1:1 dr; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37 (d, *J* = 10.1 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 3H), 7.30 – 7.24 (m, 5H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.41 (td, *J* = 8.1, 2.1 Hz, 2H), 6.32 (d, *J* = 5.7 Hz, 2H), 6.17 (dd, *J* = 7.7, 2.1 Hz, 2H), 4.92 (dd, *J* = 11.6, 5.6 Hz, 2H), 3.69 – 3.65 (m, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.2, 146.7, 137.0, 136.8, 135.4, 128.0, 127.8, 127.6, 126.6, 126.1, 116.4, 116.1, 110.1, 59.1, 52.0; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{42}H_{37}N_2O_4S_2$ [M+H]$^+$, 612.0784; found, 612.0789.

dimethyl 2,2'-((disulfanediylbis(4-methyl-2,1-phenylene))bis(azanediyl))bis(2-phenylacetate)

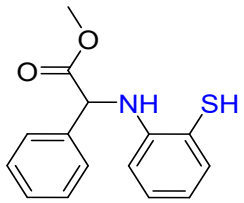


3u

Following the general procedure, purification by flash chromatography on silica gel (eluent: $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.4) afforded **3u** as Yellow solid; Mp: 180.9 - 183.3℃; yield: 90%, 77 mg, 1:1 dr; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.40 (d, *J* = 7.9 Hz, 4H), 7.29 – 7.22 (m, 6H), 6.49 – 6.43 (m, 4H), 6.36 (d, *J* = 7.9 Hz, 2H), 4.93 (s, 2H), 3.64 (s, 6H), 2.09 (s, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.2, 144.2, 136.6, 131.0, 128.6, 127.9, 127.3, 126.3, 120.4, 114.7, 113.9, 61.2, 51.8, 19.6; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{42}H_{37}N_2O_4S_2$ $[M+H]^+$, 573.1876; found, 573.1879.

methyl 2-((2-mercaptophenyl)amino)-2-phenylacetate

5



Yellow solid; Mp: 194.1-195.8 ℃; yield: 51%, 42 mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 15:1, R_f = 0.3; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 7.15 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.97 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.82 – 6.76 (m, 2H), 5.79 (d, *J* = 8.0 Hz, 1H), 3.70 (s, 3H); **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.2, 146.6, 135.6, 131.7, 128.1, 128.0, 127.7, 127.0, 117.5, 116.1, 115.5, 67.3, 52.5; **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{15}H_{15}NO_2S$ $[M+H]^+$, 273.0896; found, 273.0895.

4. General informationX-ray Structure and Data of **3a**

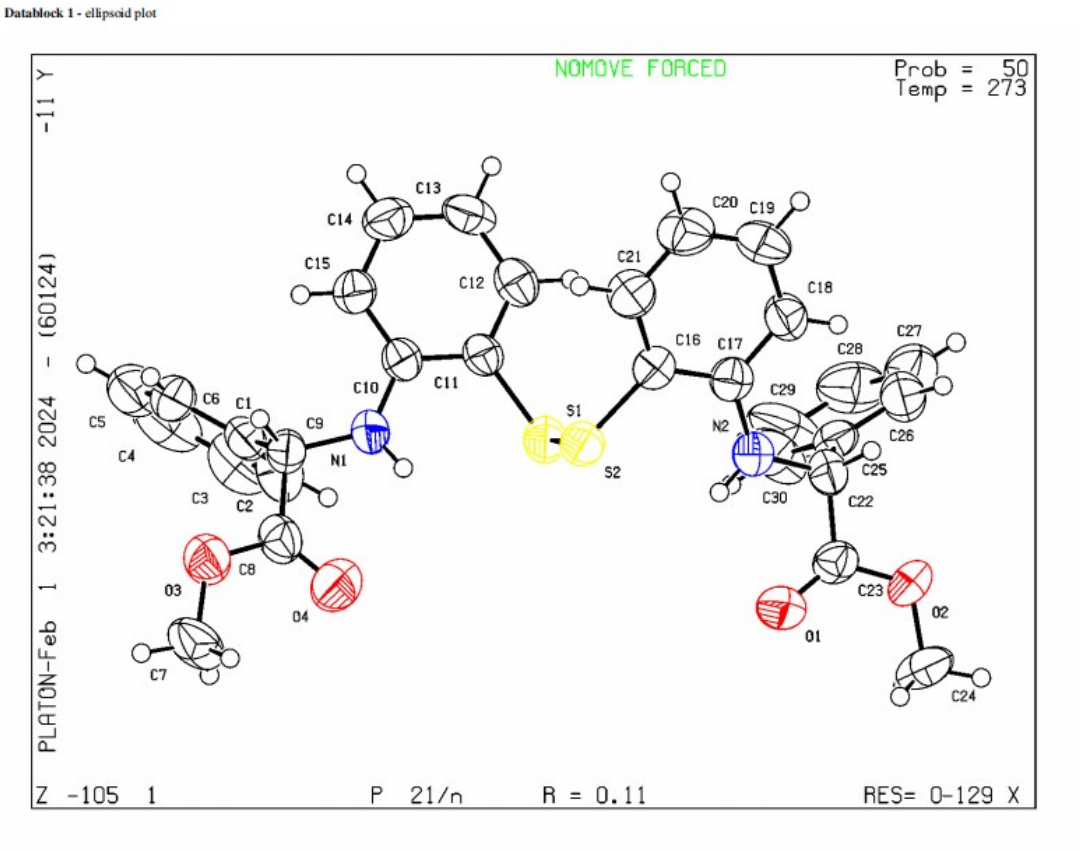


Figure S2. X-Ray crystal structure of **3a**, ellipsoids was drawn at the 50% probability level

Table S2. Crystal data and structure refinement for 3a

Datablock: 1

Bond precision: C-C = 0.0064 A Wavelength=0.71073

Cell: a=8.2168(12) b=12.1811(18) c=28.132(4)
alpha=90 beta=93.702(5) gamma=90
Temperature: 273 K

	Calculated	Reported
Volume	2809.9(7)	2809.9(7)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C30 H28 N2 O4 S2	C30 H28 N2 O4 S2
Sum formula	C30 H28 N2 O4 S2	C30 H28 N2 O4 S2
Mr	544.66	544.66
Dx,g cm-3	1.288	1.288
Z	4	4
Mu (mm-1)	0.227	0.227
F000	1144.0	1144.0
F000'	1145.46	
h,k,lmax	9,14,33	9,14,33
Nref	4966	4962
Tmin,Tmax	0.968,0.978	0.622,0.746
Tmin'	0.956	

Correction method= # Reported T Limits: Tmin=0.622 Tmax=0.746
AbsCorr = MULTI-SCAN

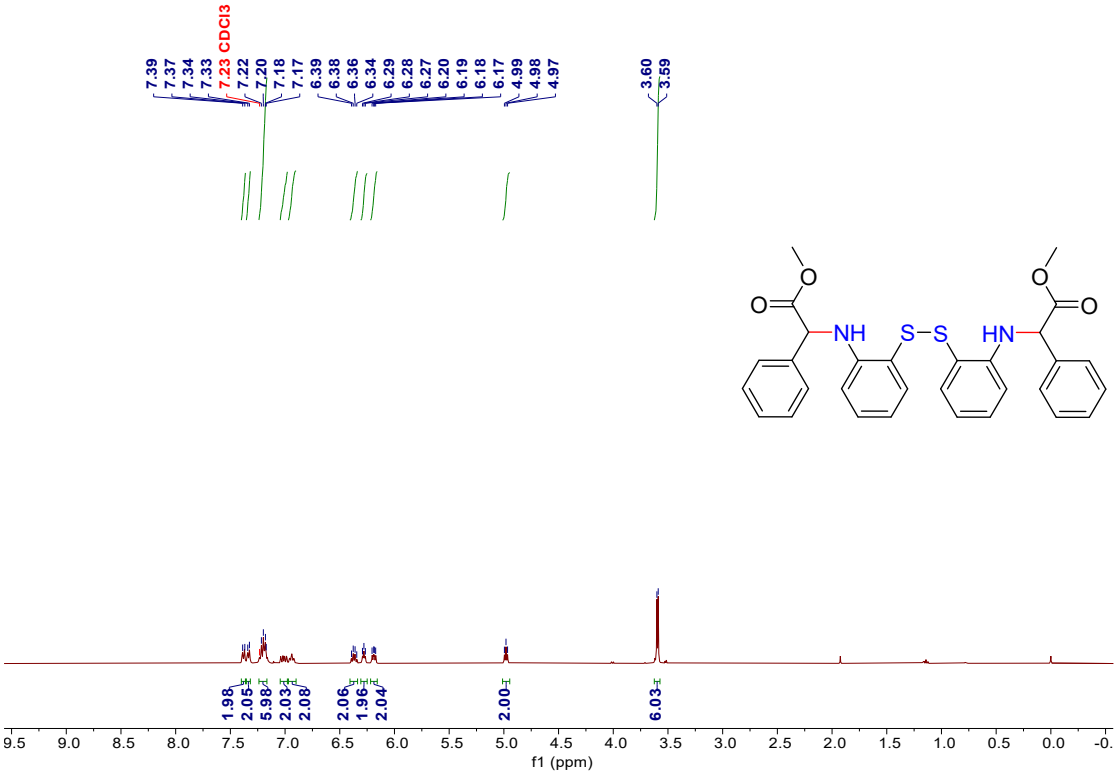
Data completeness= 0.999 Theta(max)= 24.999

R(reflections)= 0.1110(2791) wR2(reflections)= 0.1720(4962)

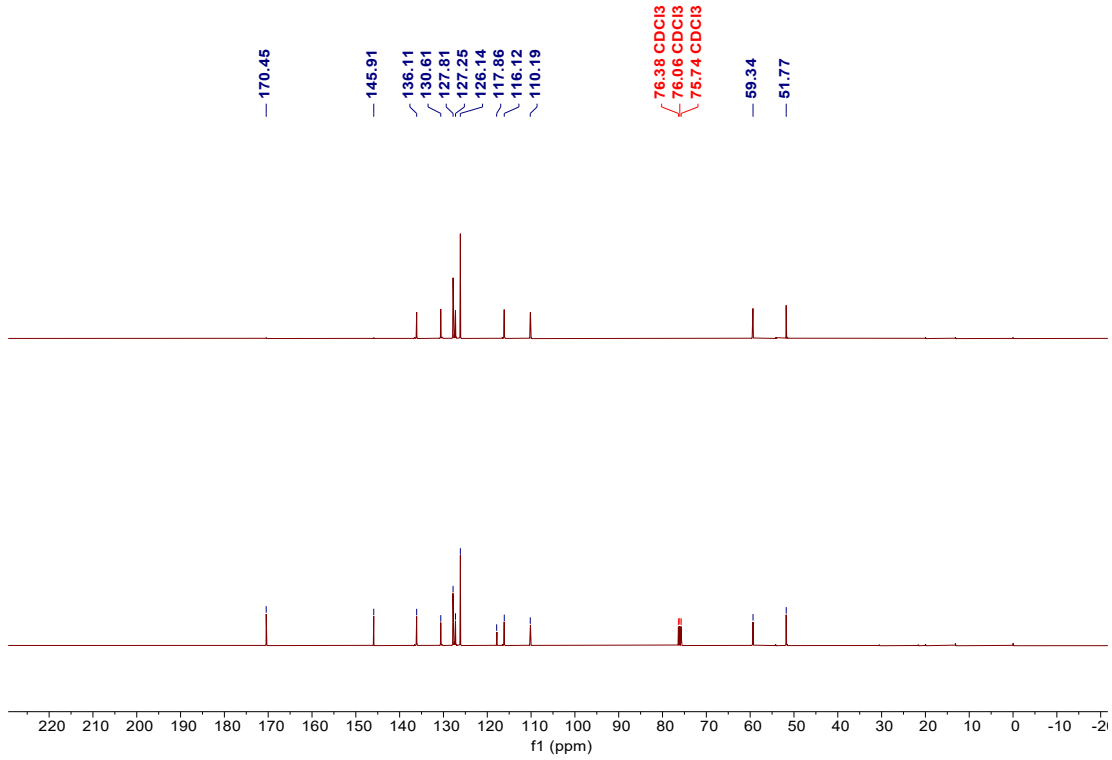
S = 1.092 Npar= 297

Compound **3a** (15mg) was add to a 5mL sample bottle, following to add DCM (1mL), n-hexane (2.5mL), then seal the bottle with a parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model：Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.

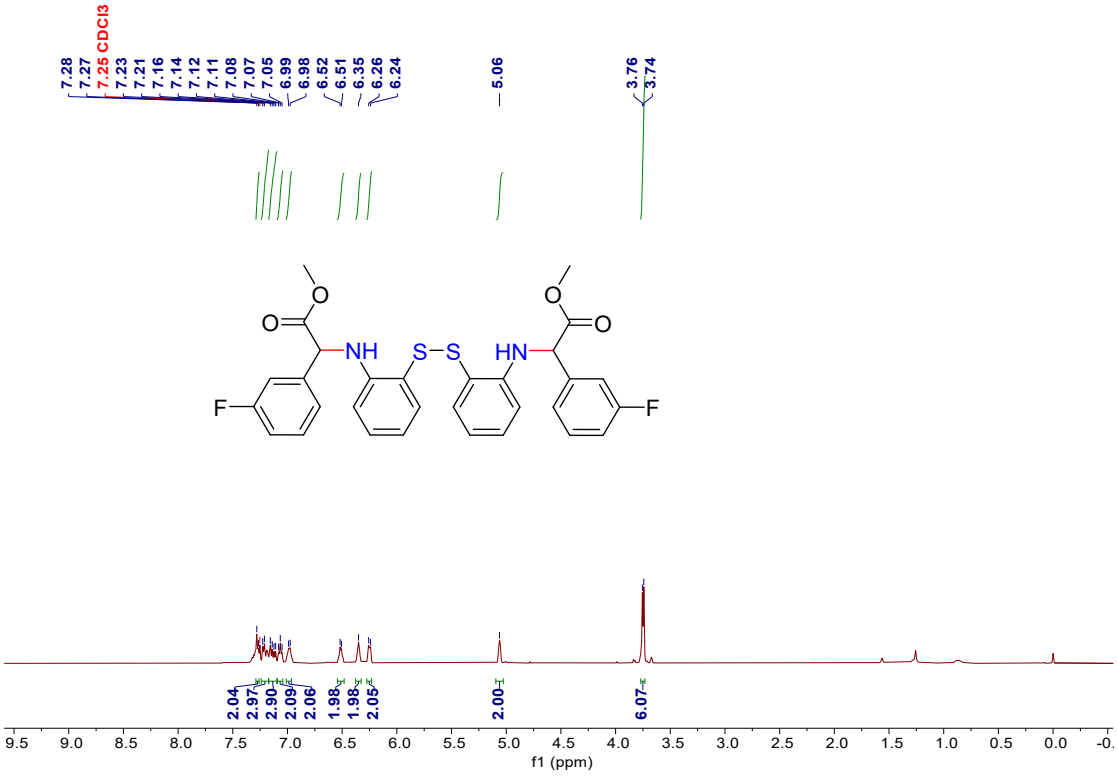
5. ^{1}H NMR and ^{13}C NMR Spectra of Compounds



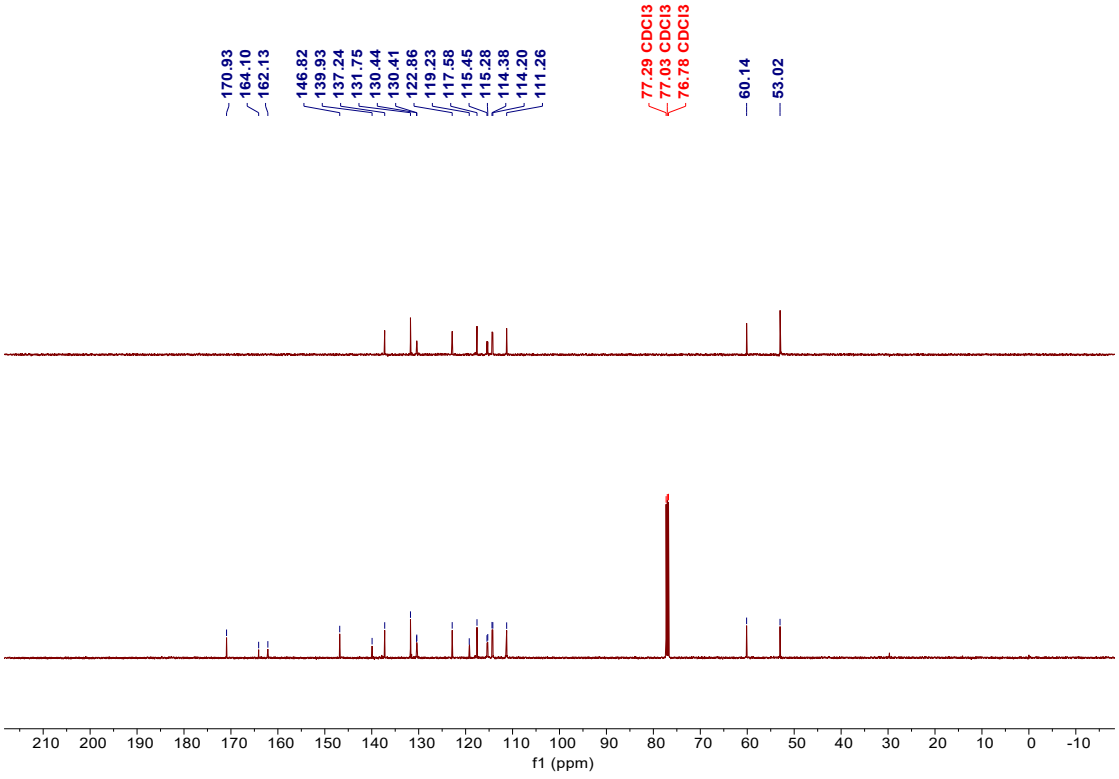
^{1}H-NMR (400 MHz, CDCl3) spectrum of compound (**3a**)



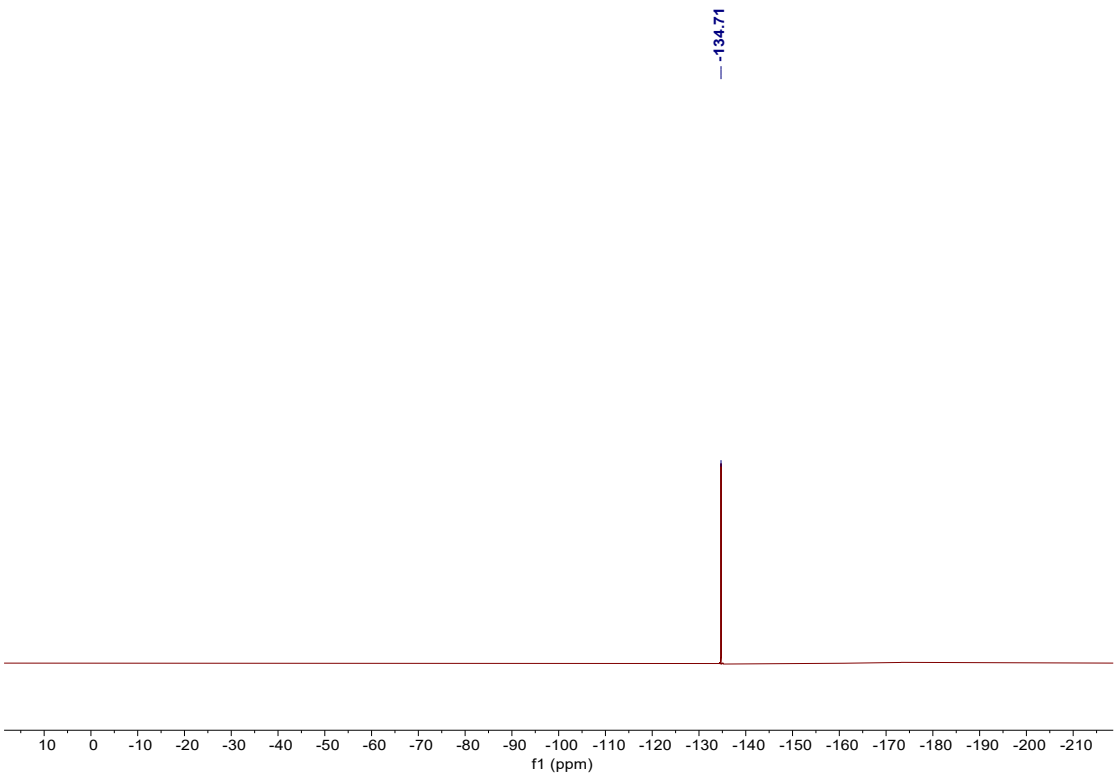
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of compound **(3a)**



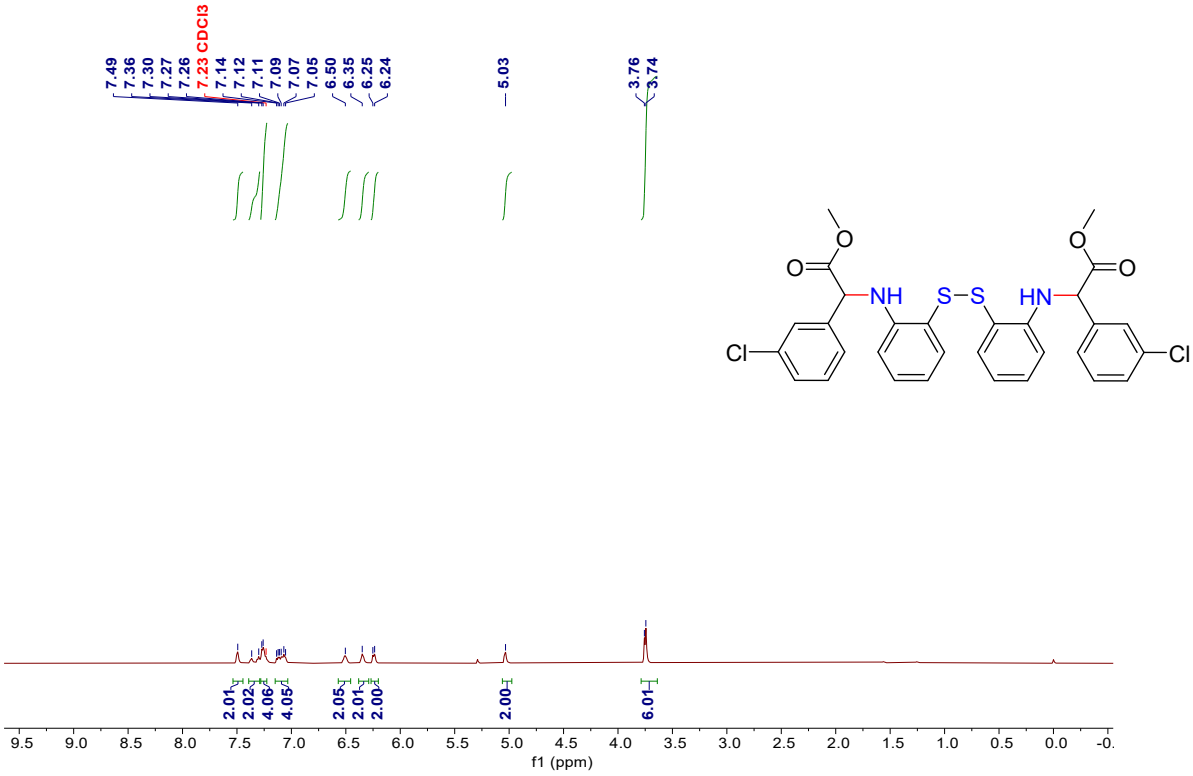
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3b**)



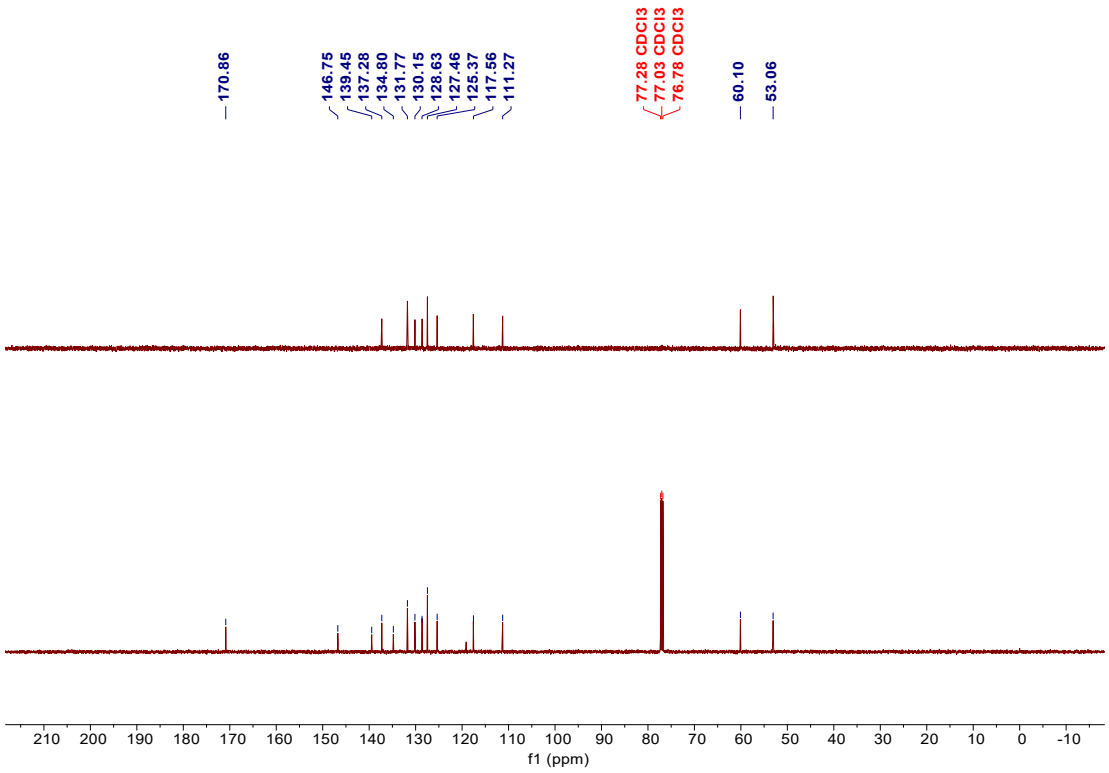
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3b)**



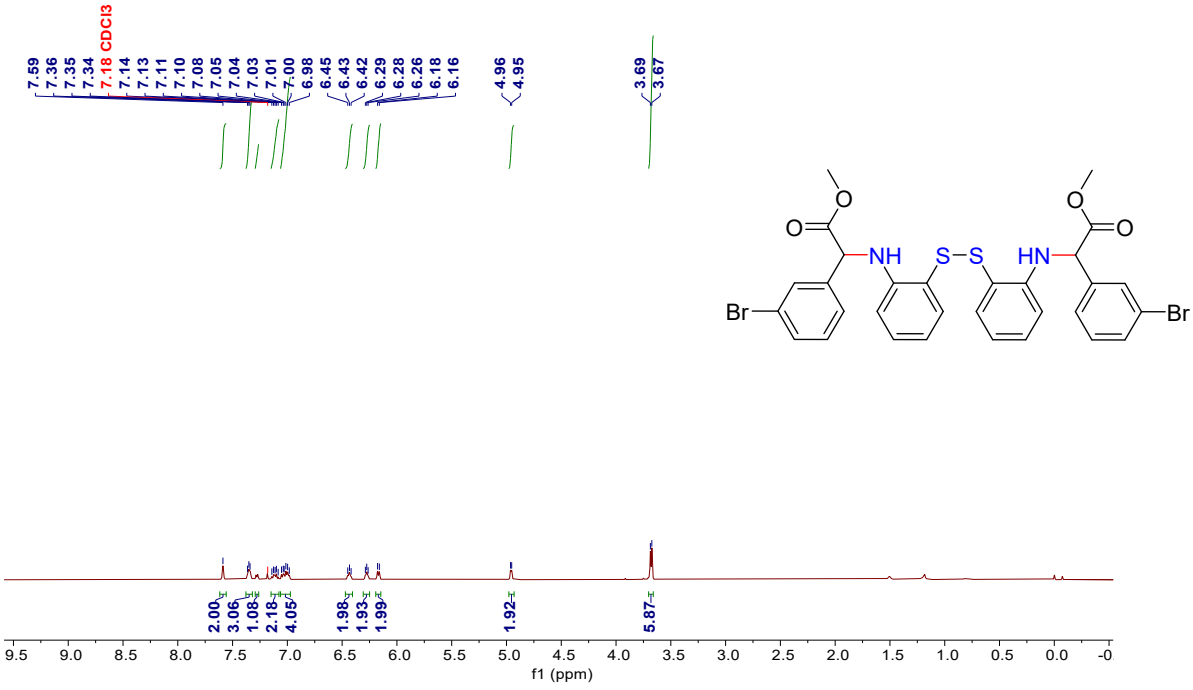
^{19}F-NMR (376MHz, CDCl3) spectrum of compound (**3b**)



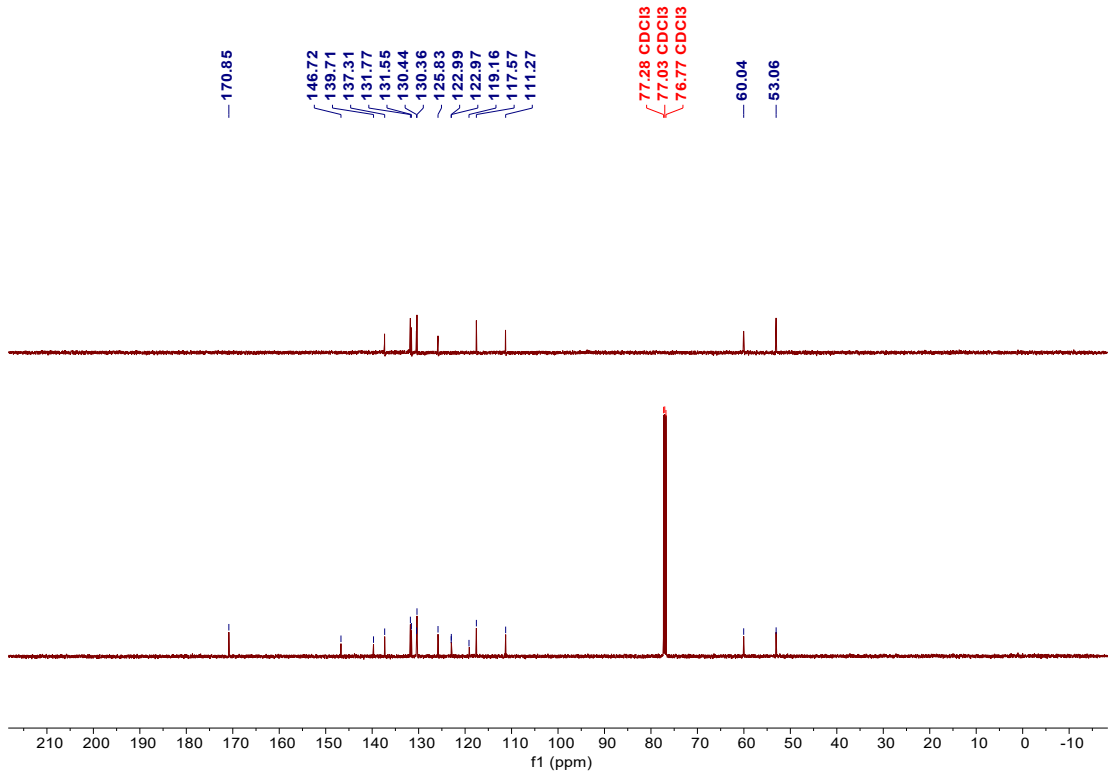
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3c**)



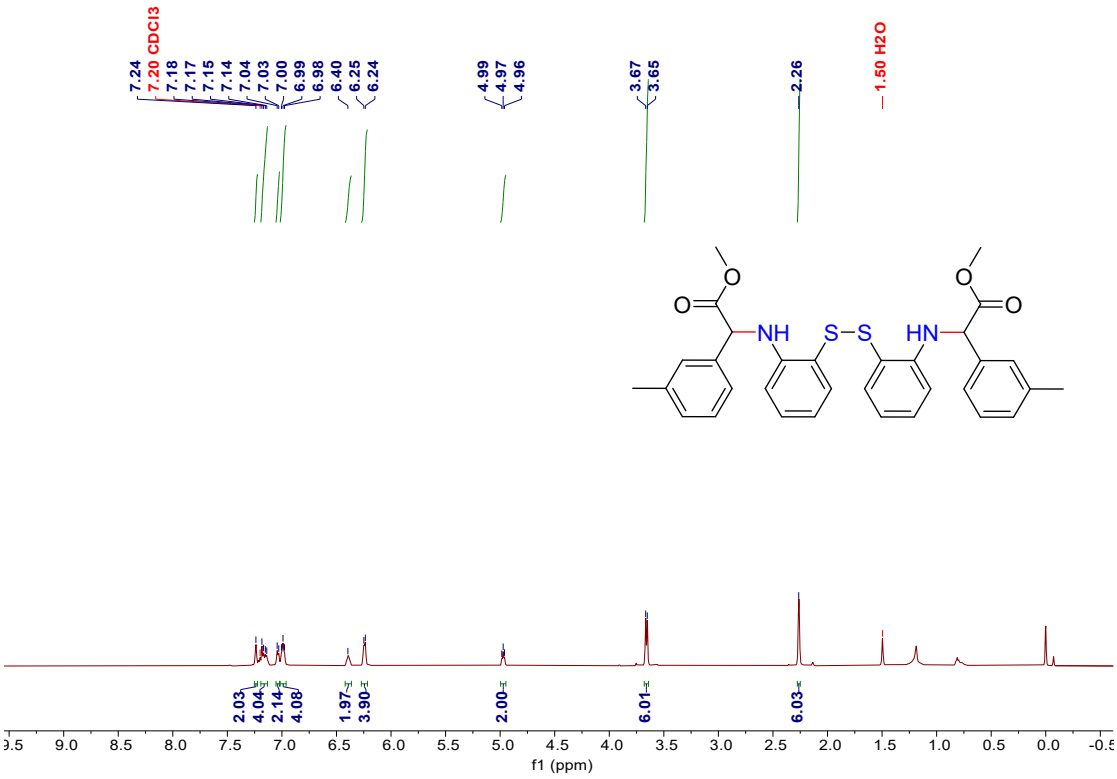
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3c)**



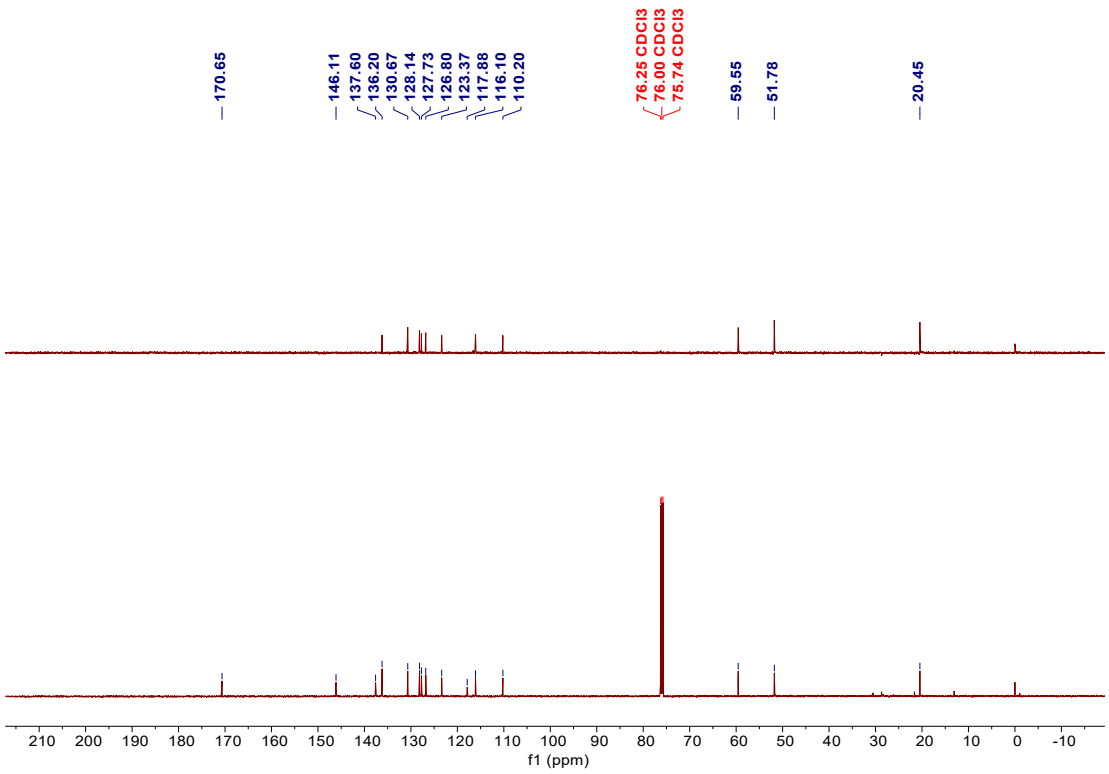
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3d**)



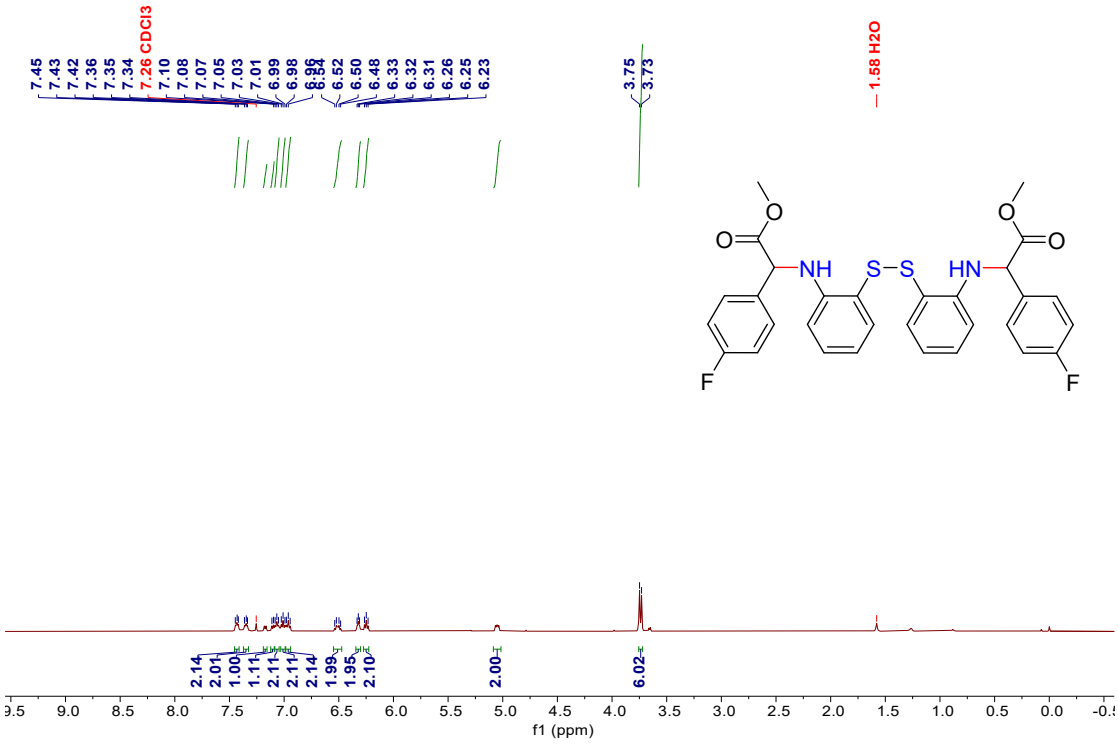
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3d)**



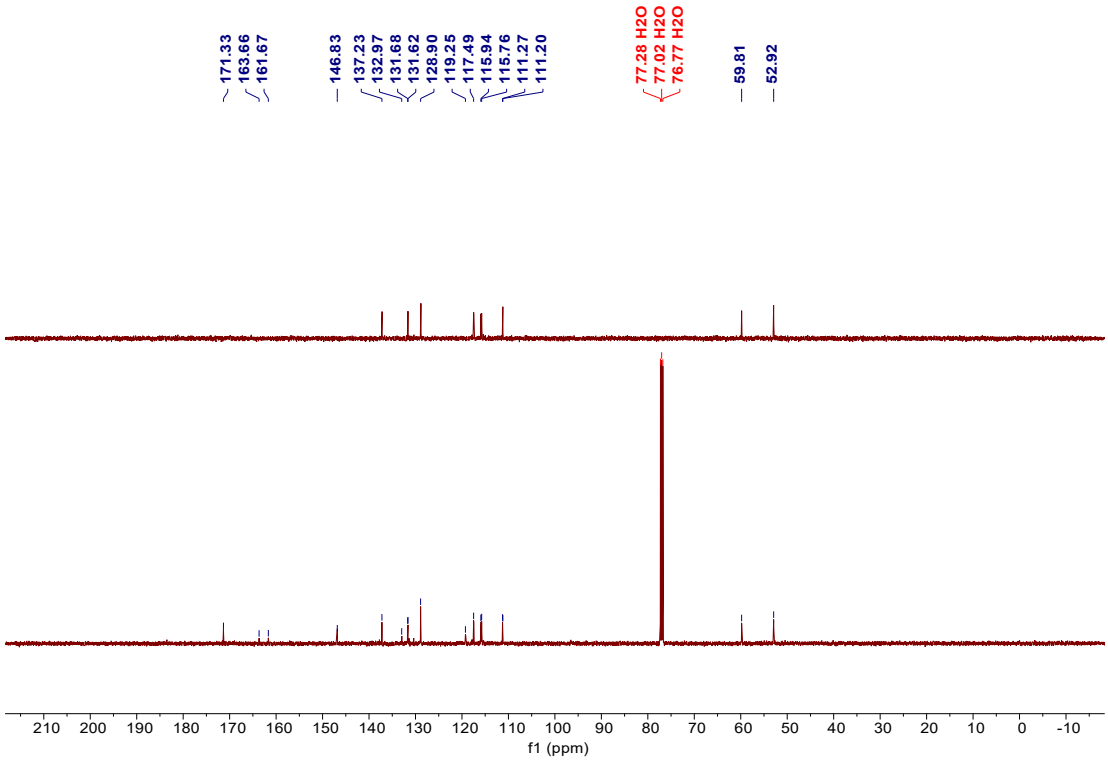
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3e**)



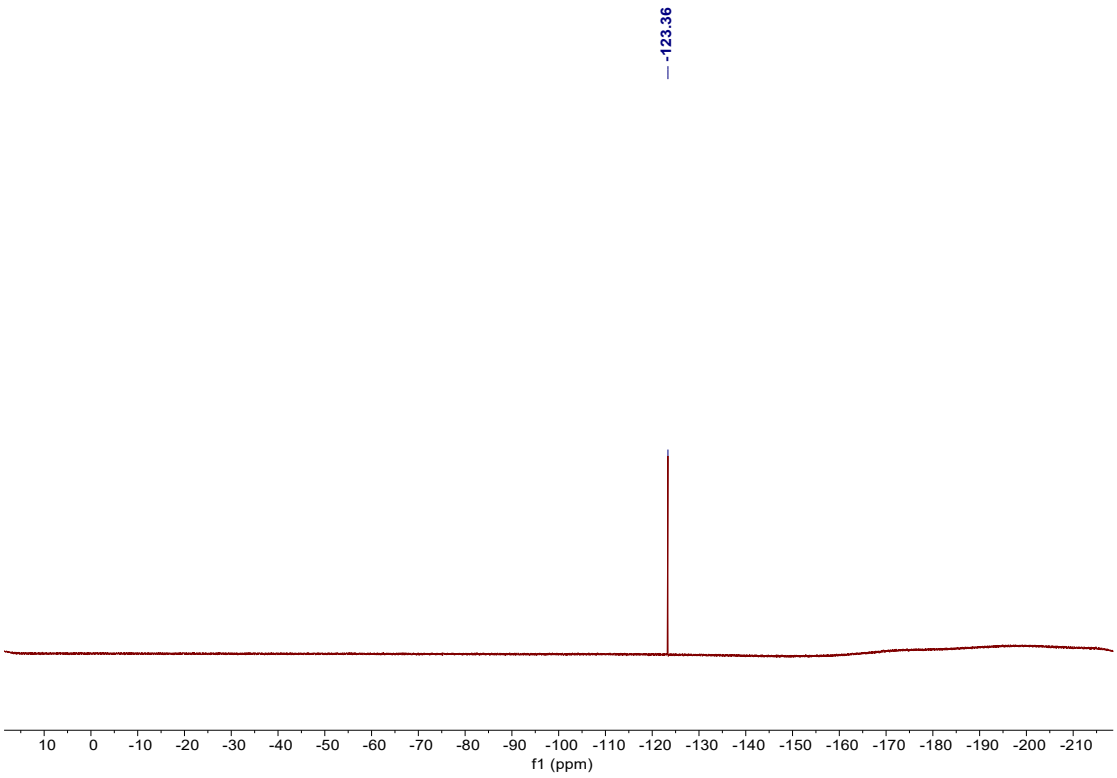
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3e)**



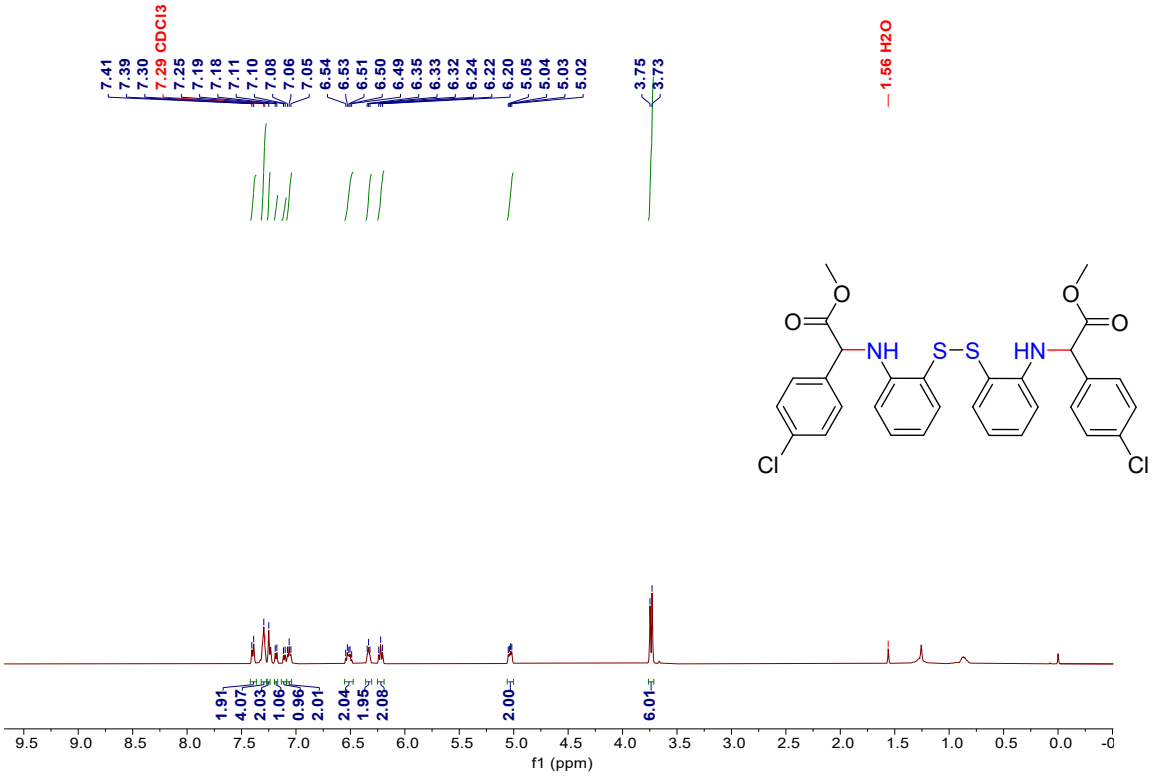
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3f**)



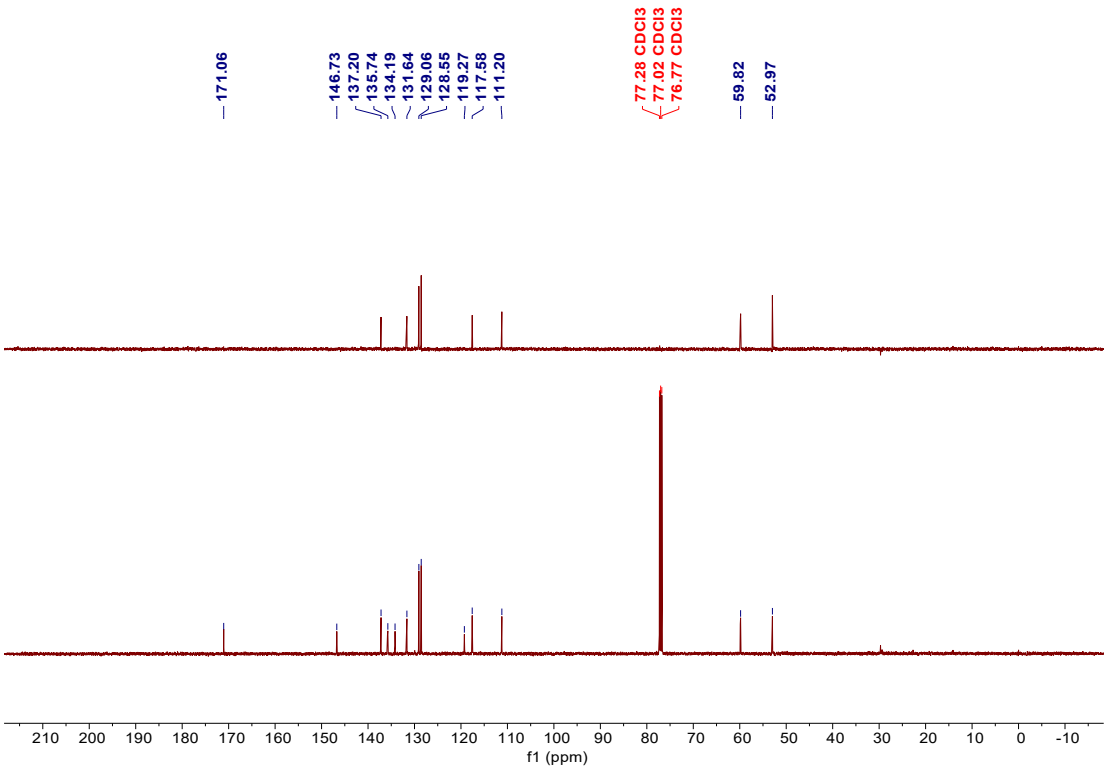
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3f)**



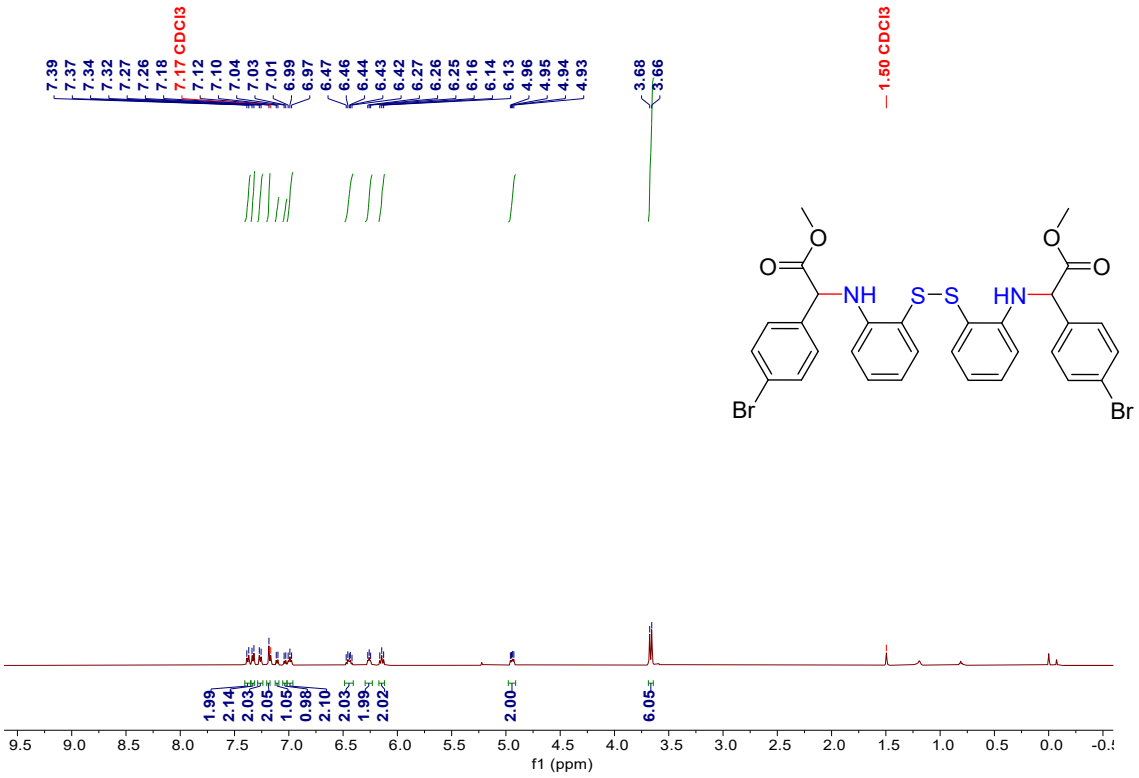
^{19}F-NMR (376MHz, CDCl3) spectrum of compound **(3f)**



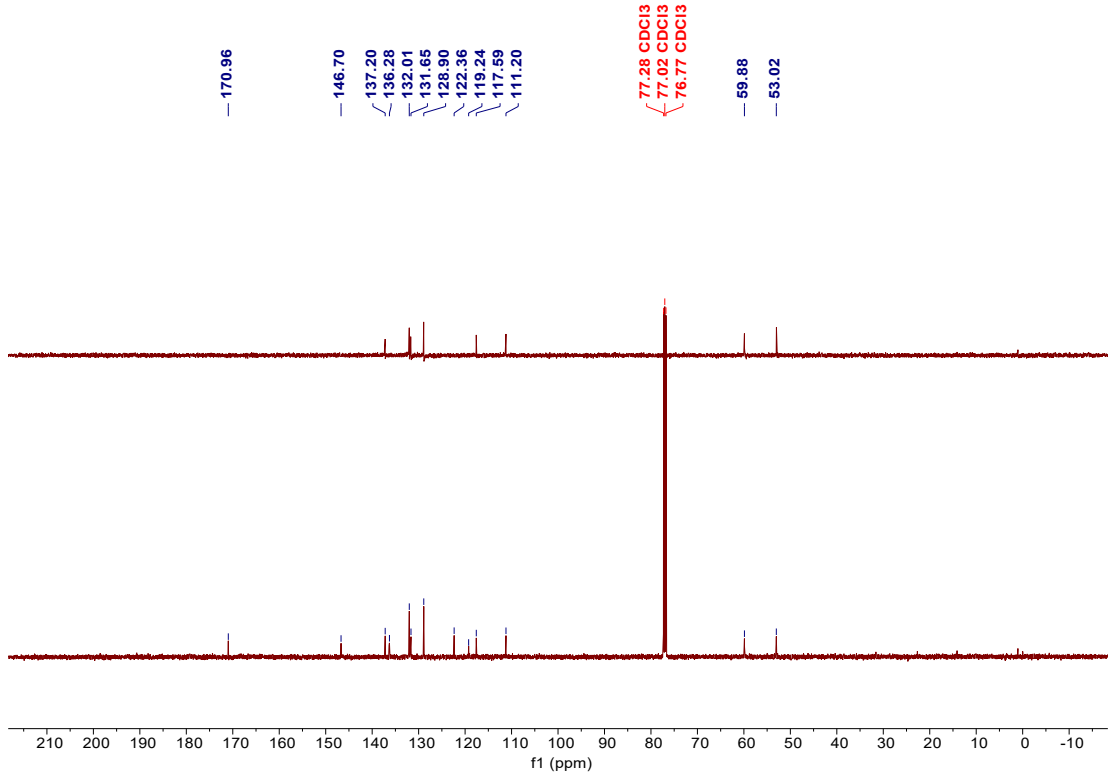
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3g**)



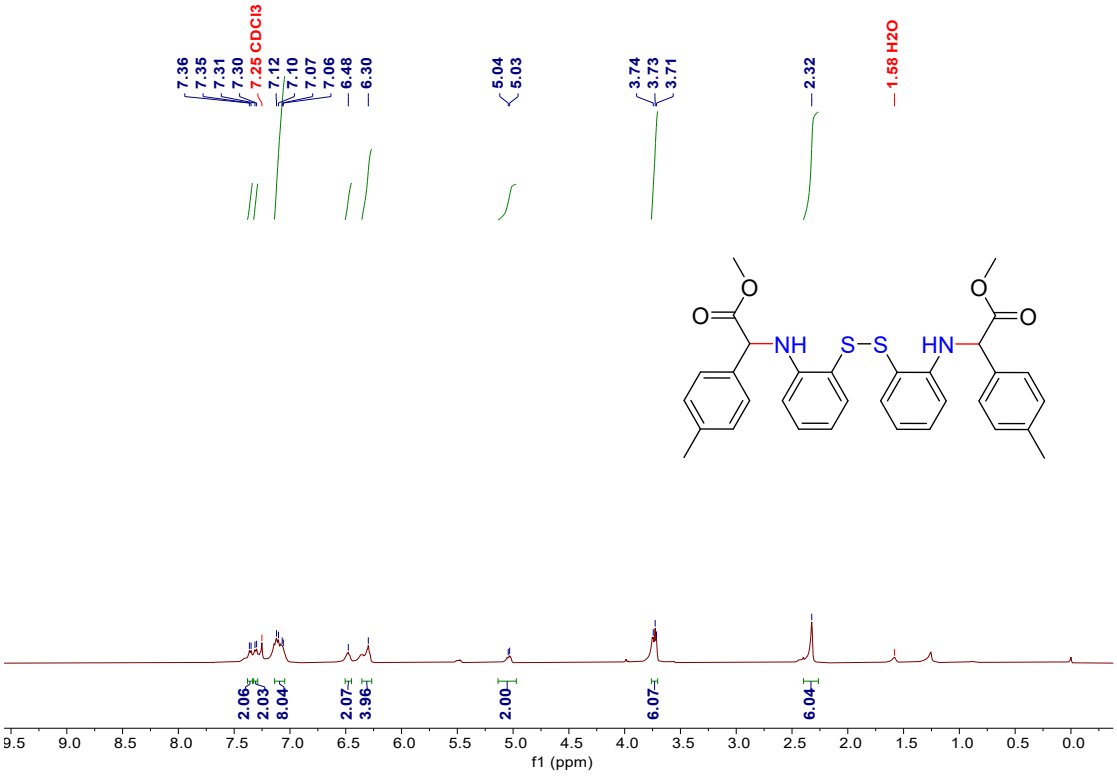
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound (**3g**)



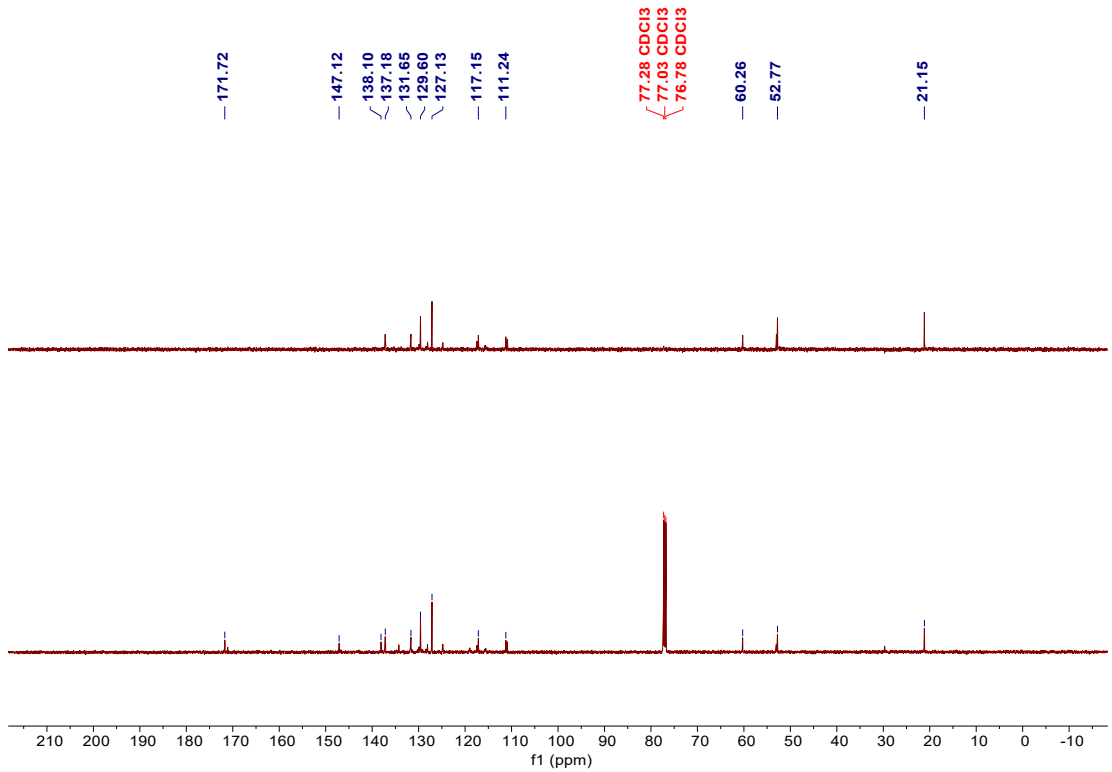
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3h**)



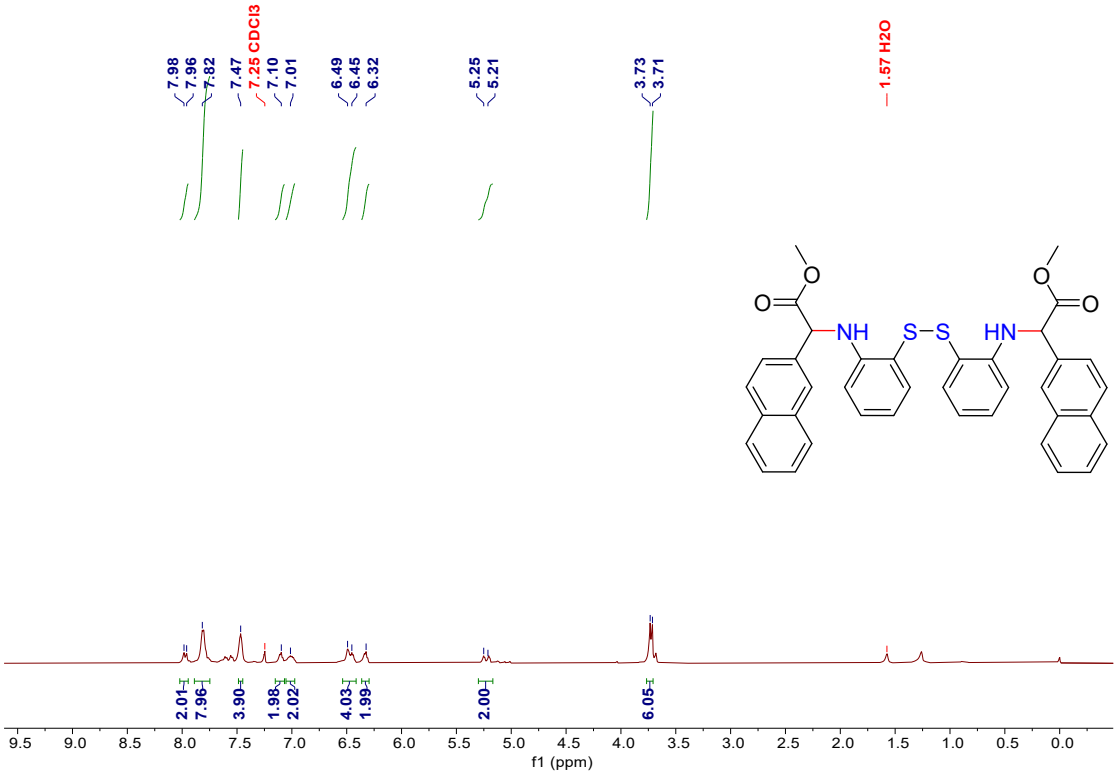
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3h)**



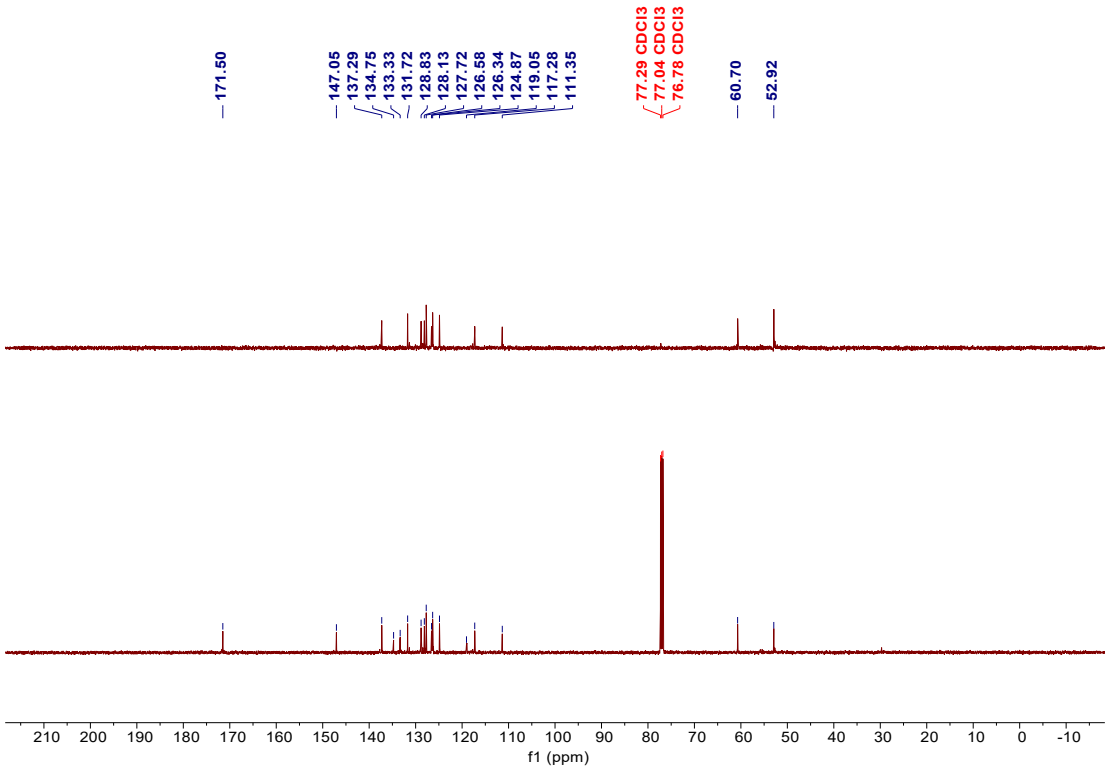
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3i**)



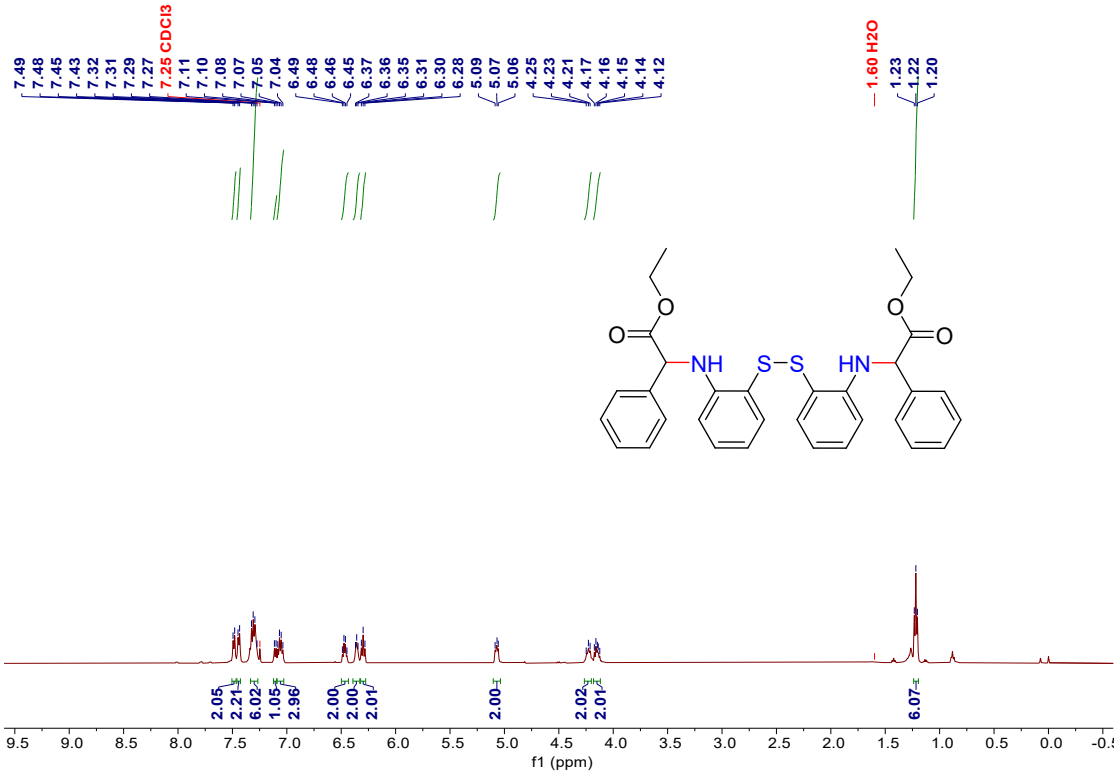
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3i)**



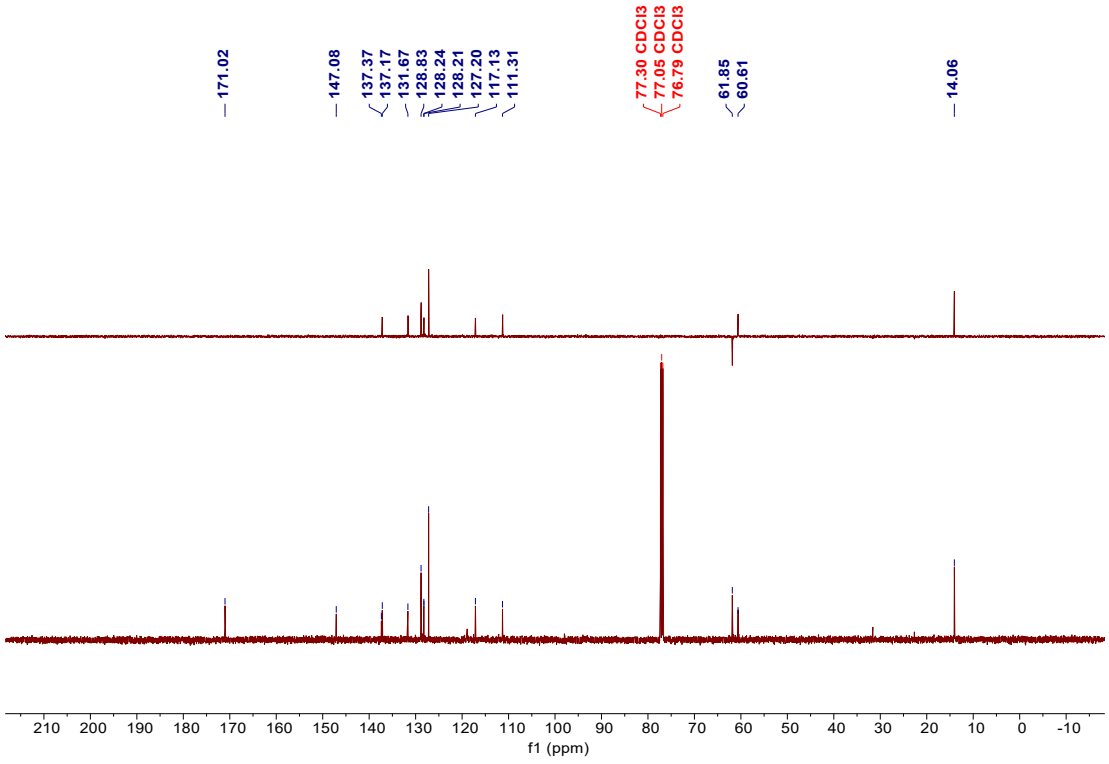
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3j**)



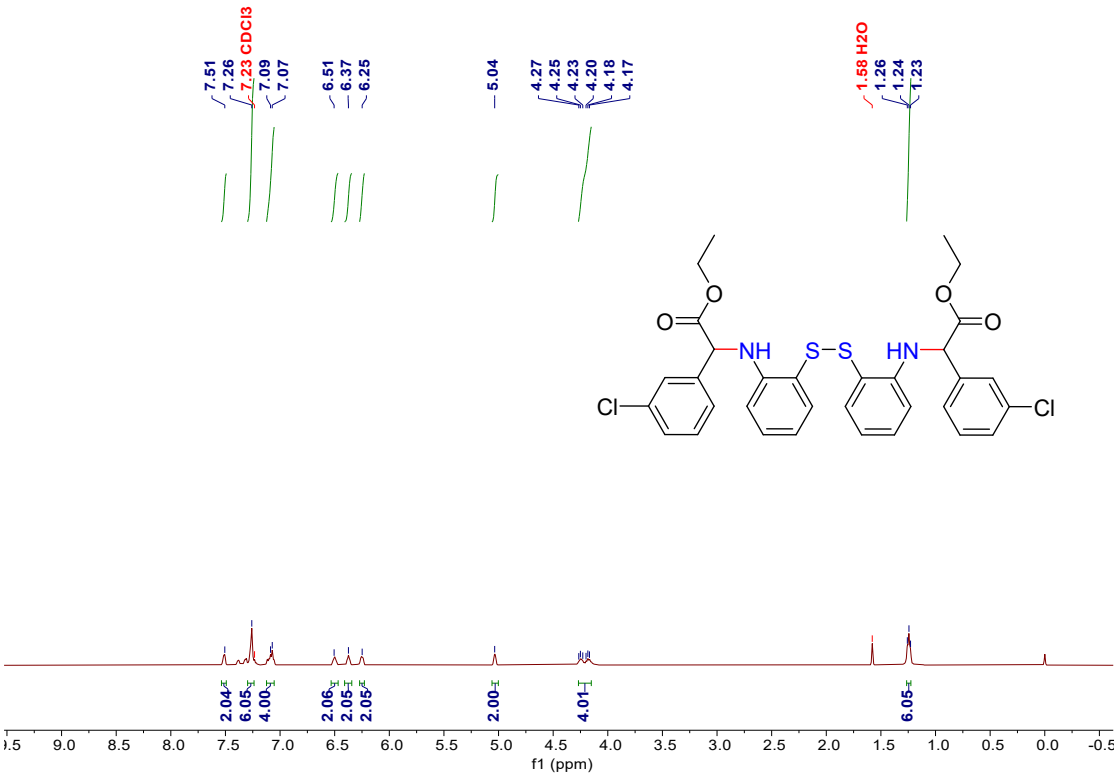
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3j)**



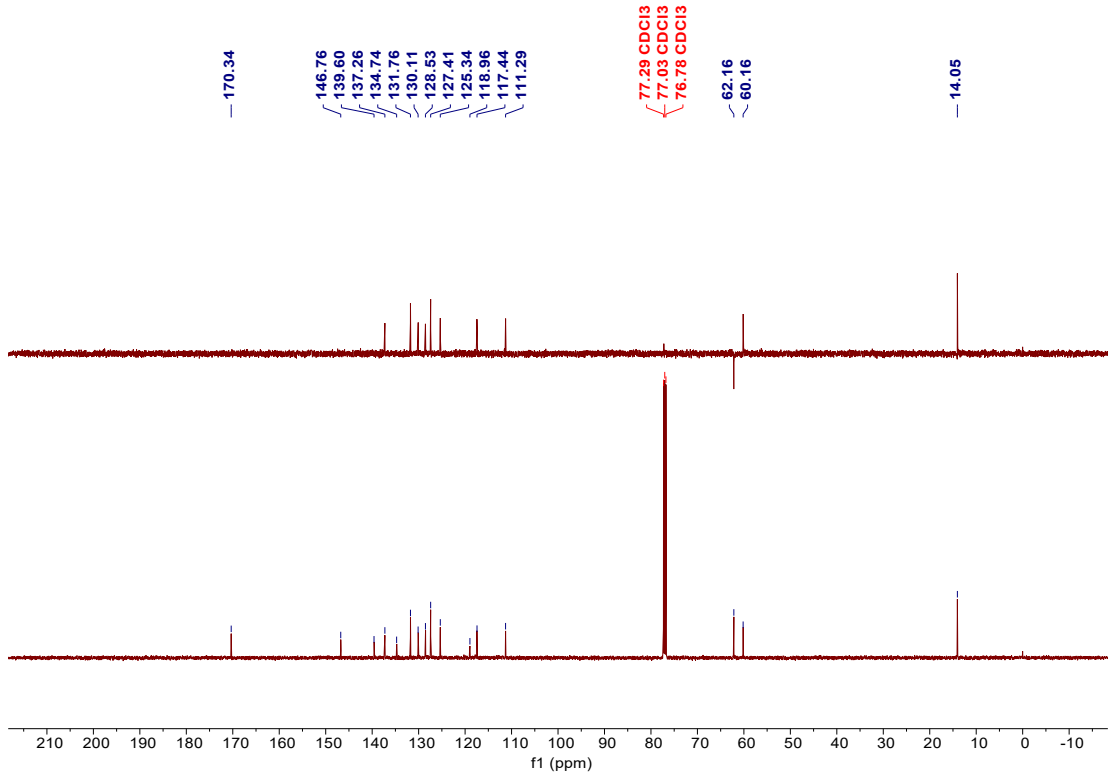
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3k**)



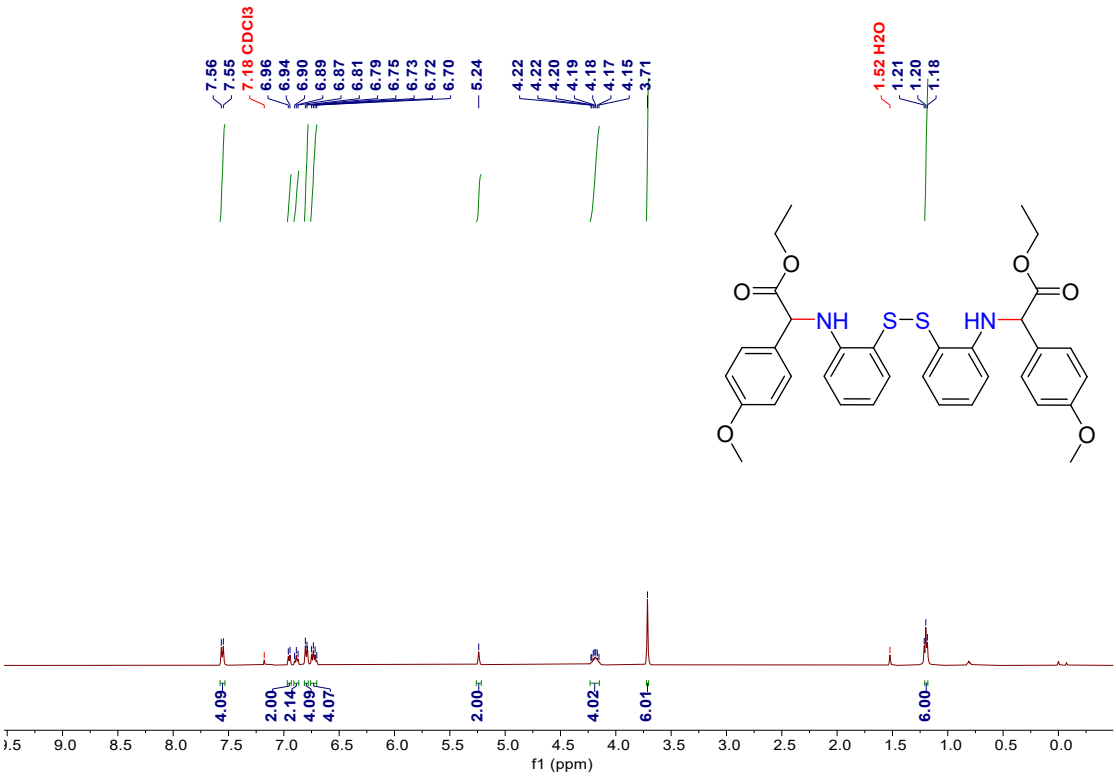
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3k)**



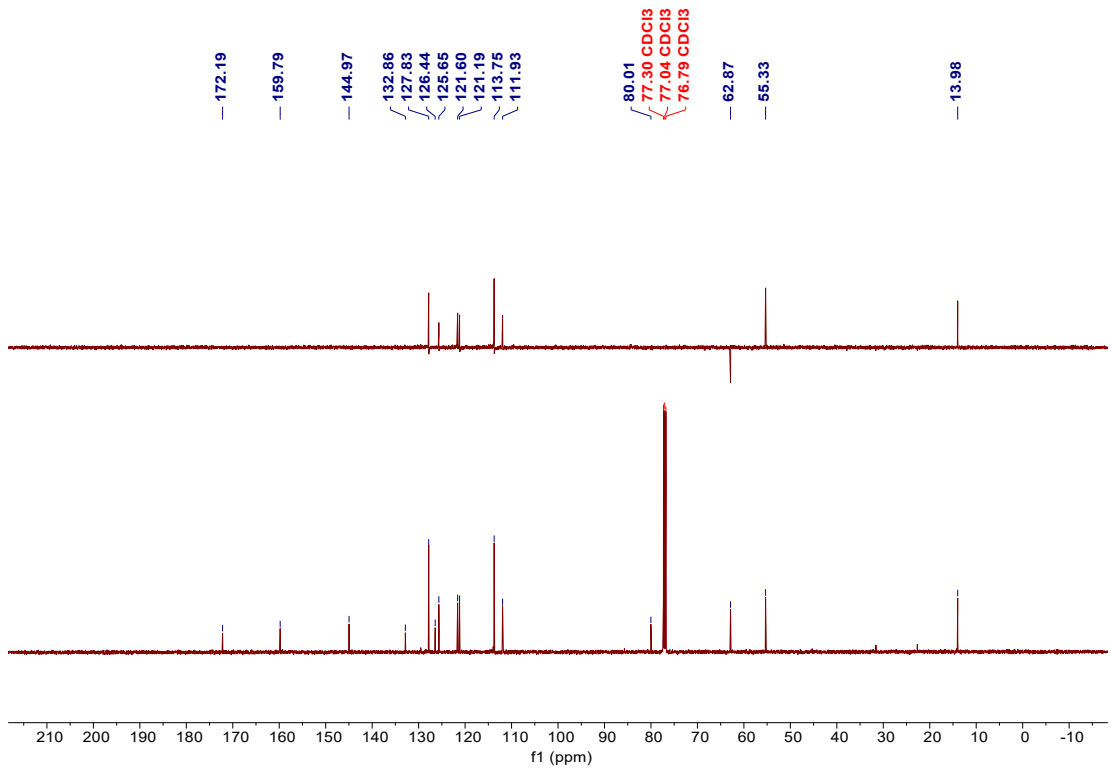
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3l**)



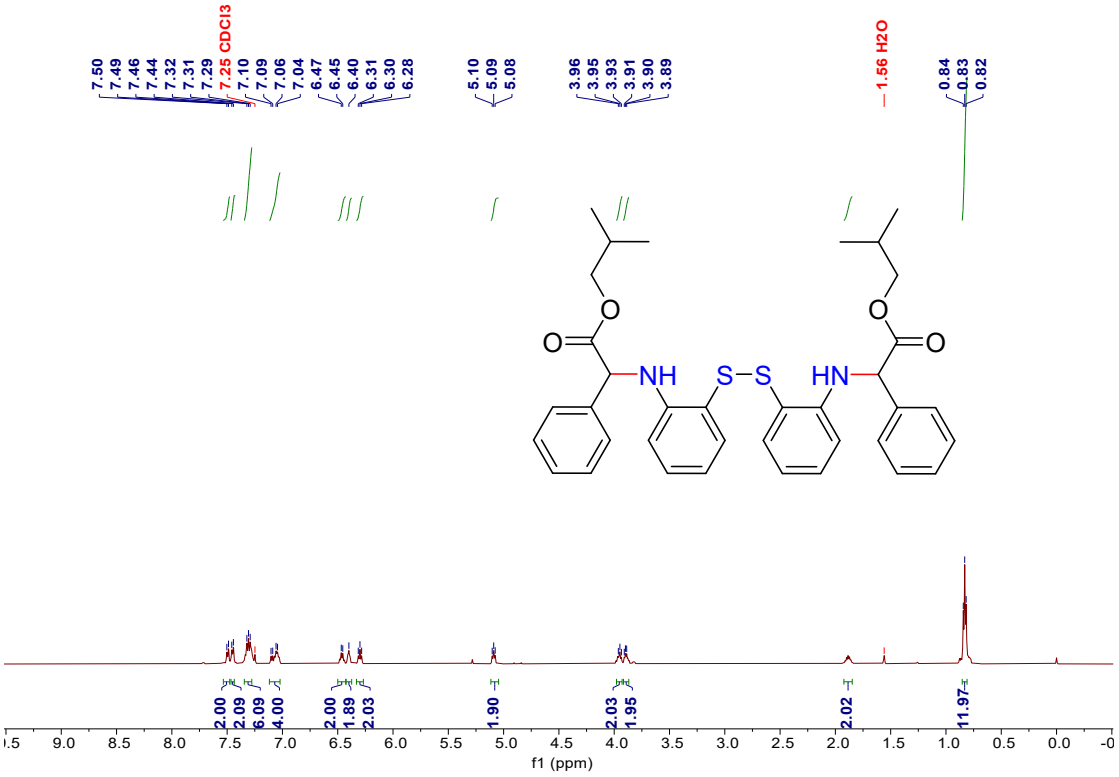
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3l)**



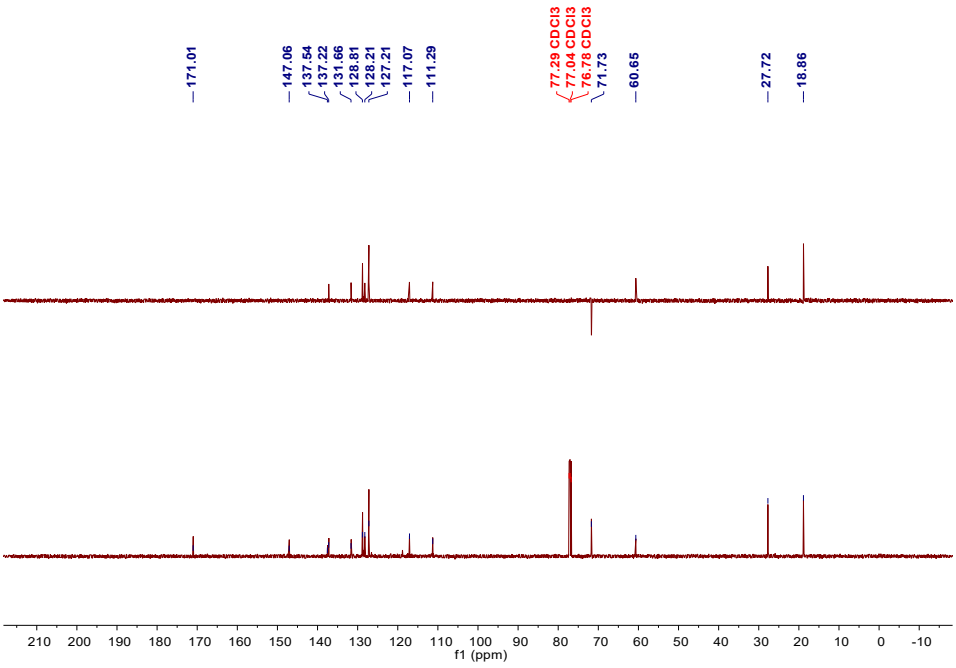
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3m**)



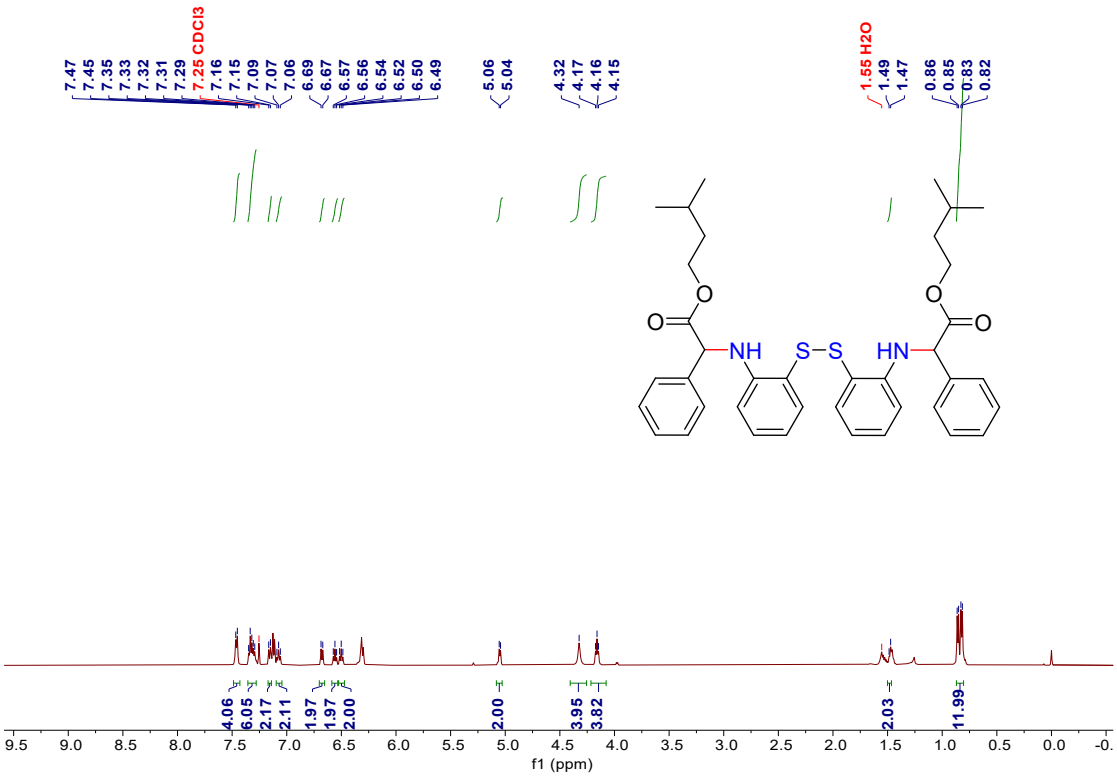
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3m)**



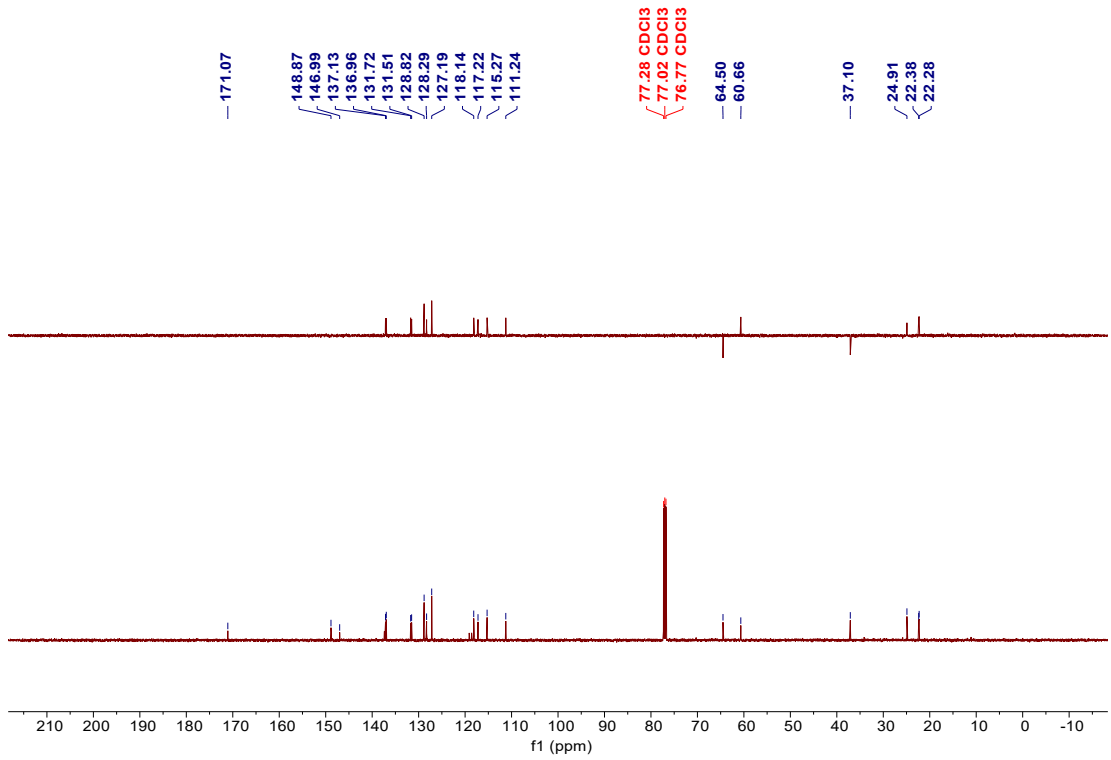
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3n**)



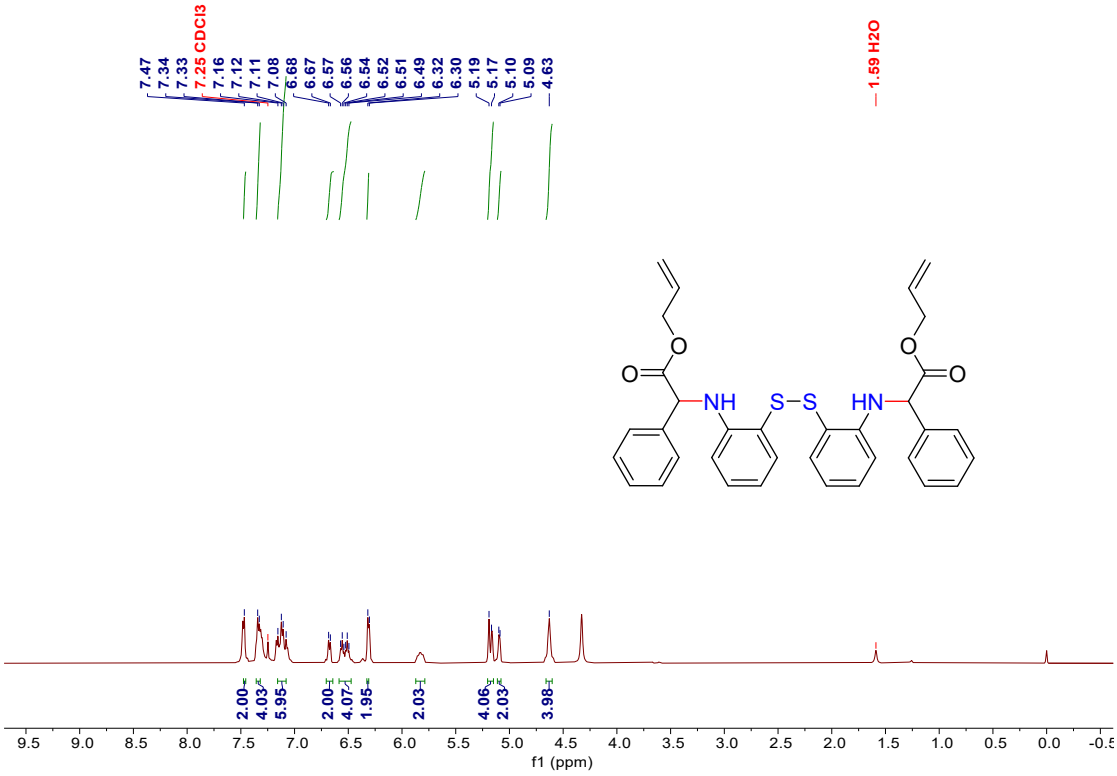
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3n)**



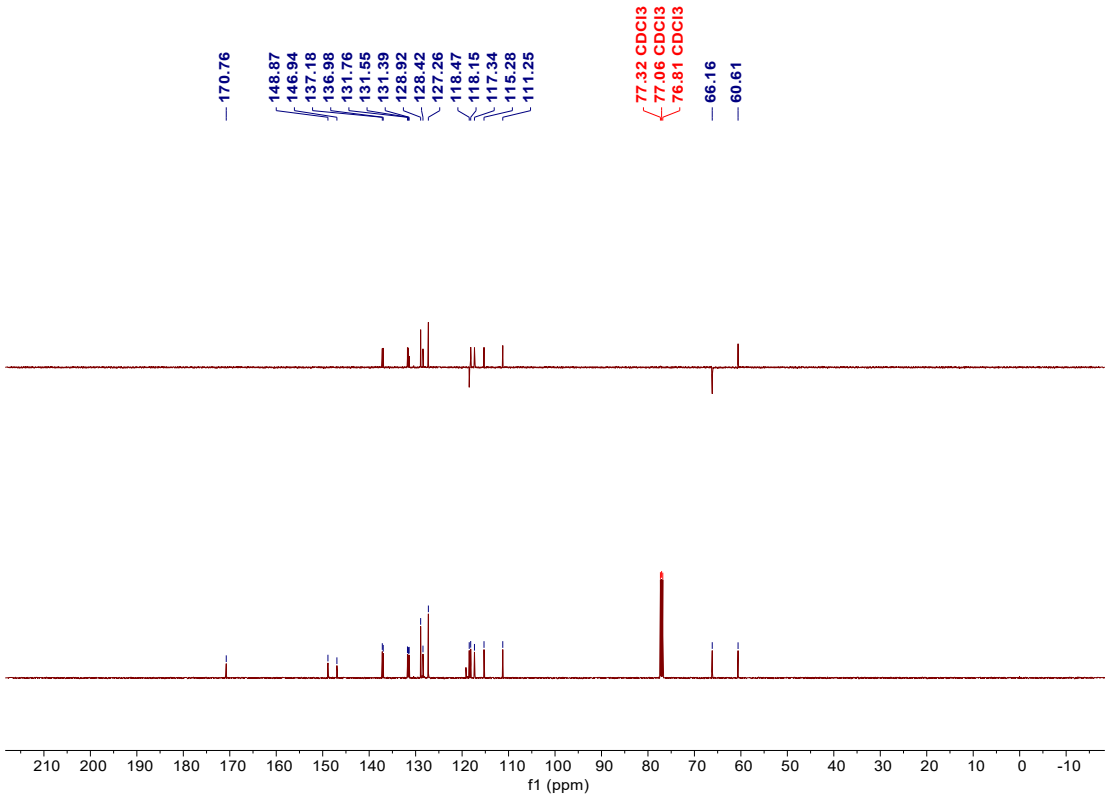
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3o**)



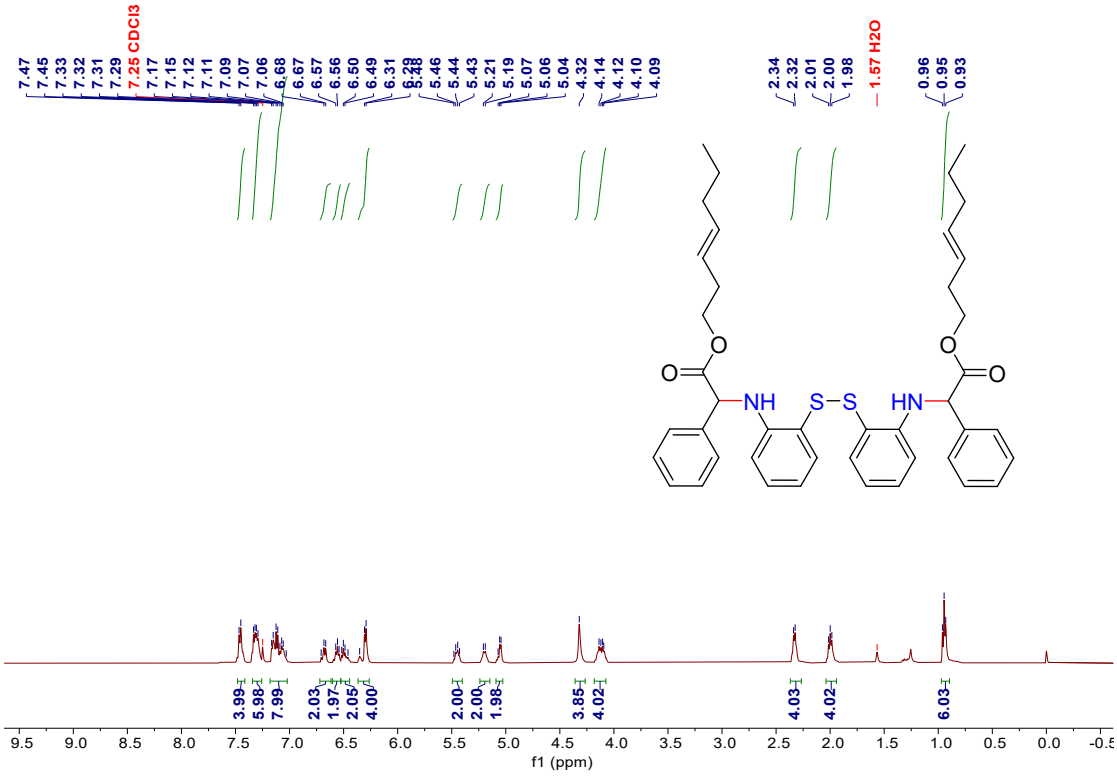
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3o)**



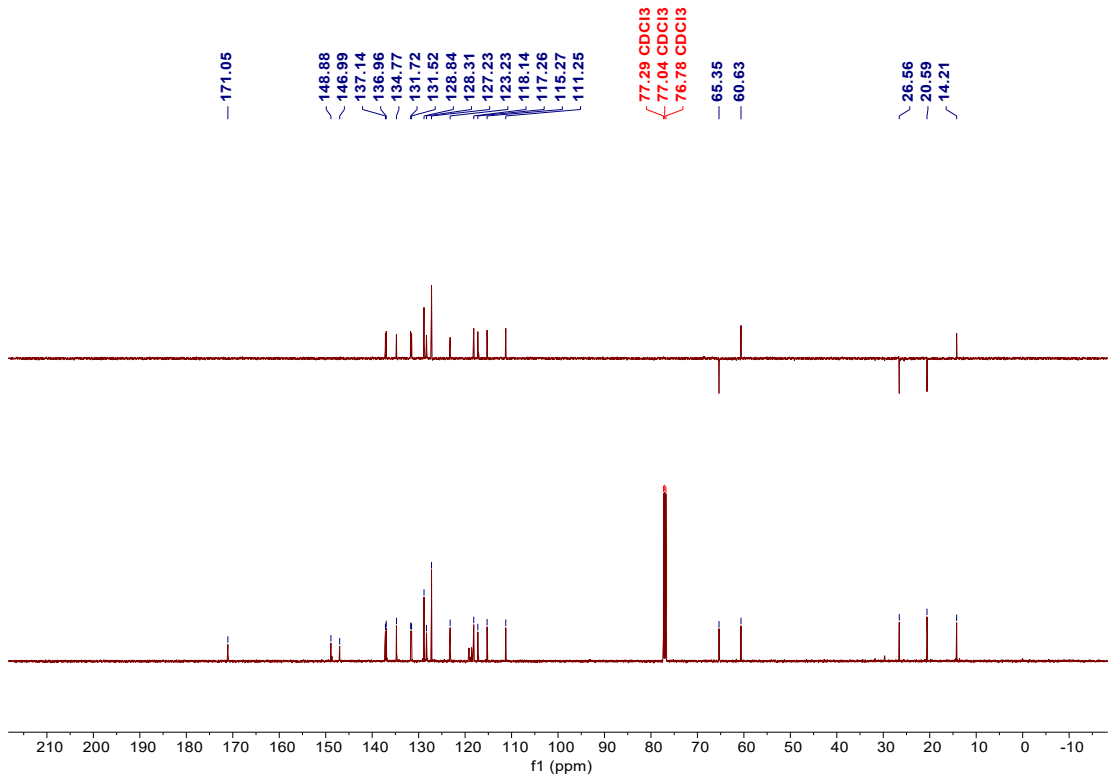
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3p**)



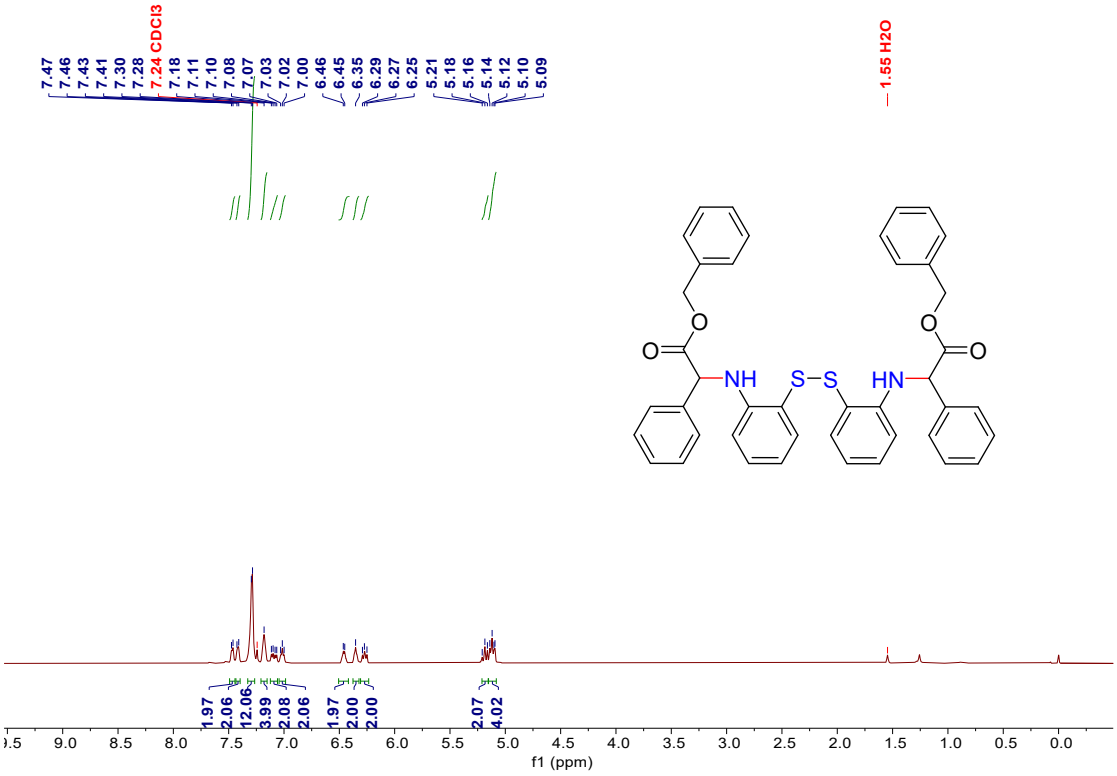
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3p)**



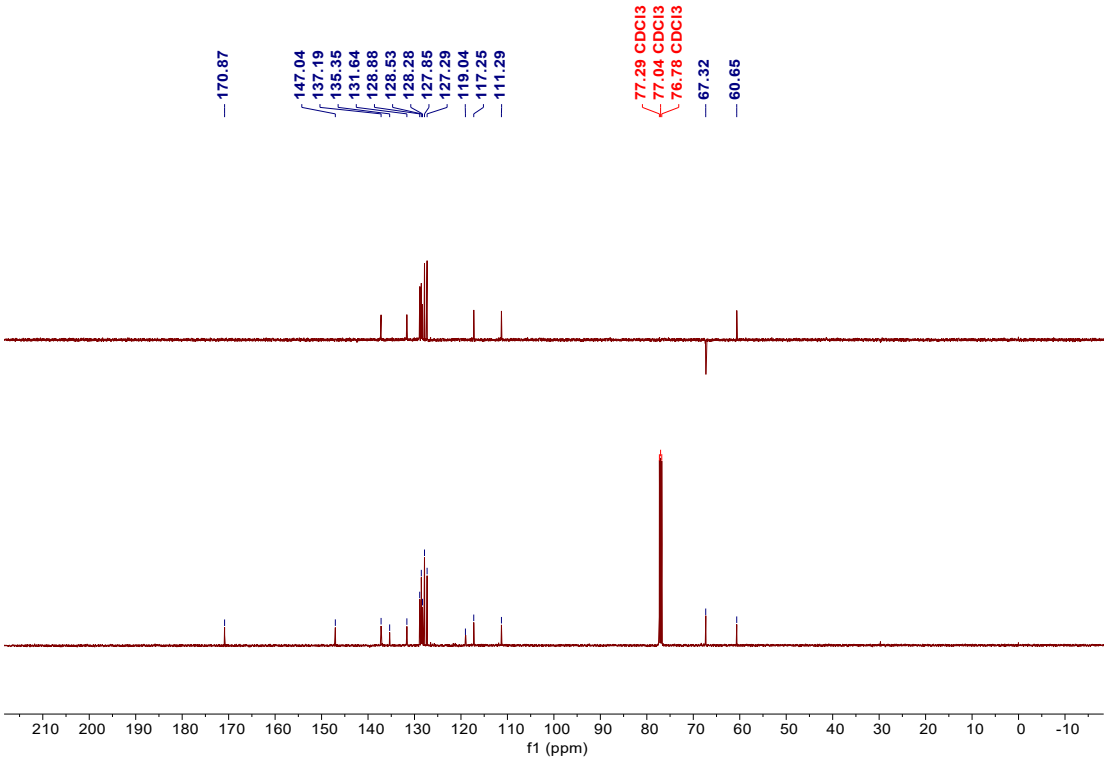
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3q**)



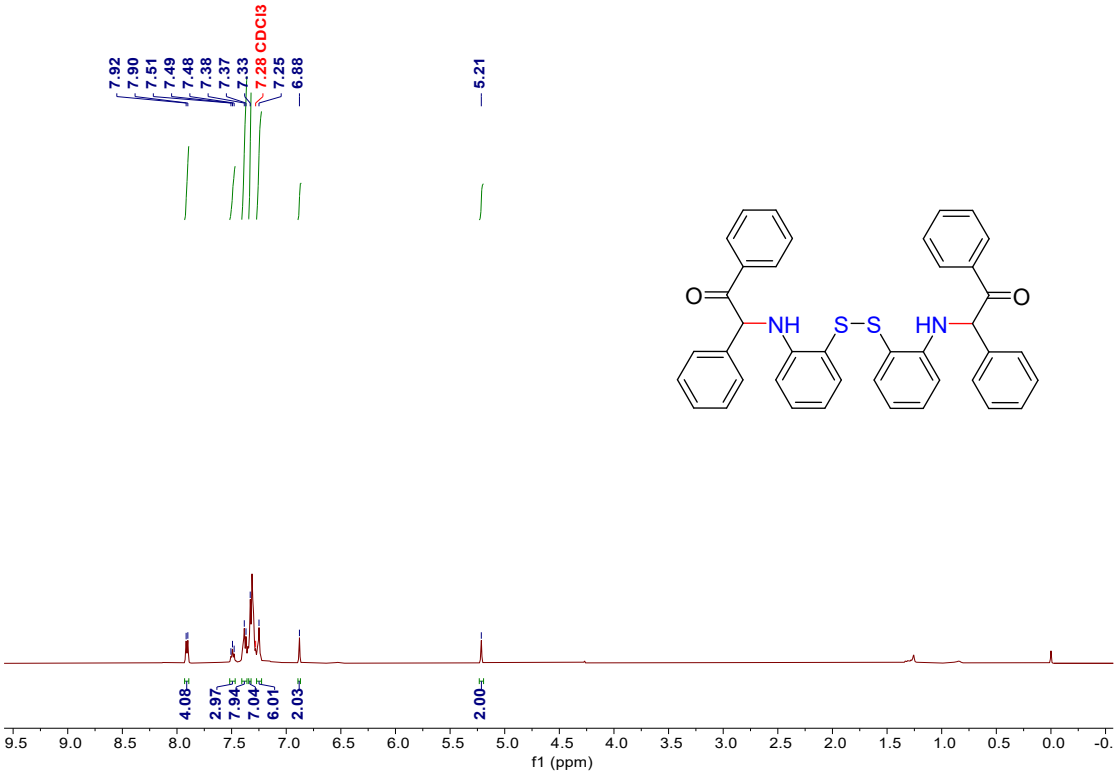
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound **(3q)**



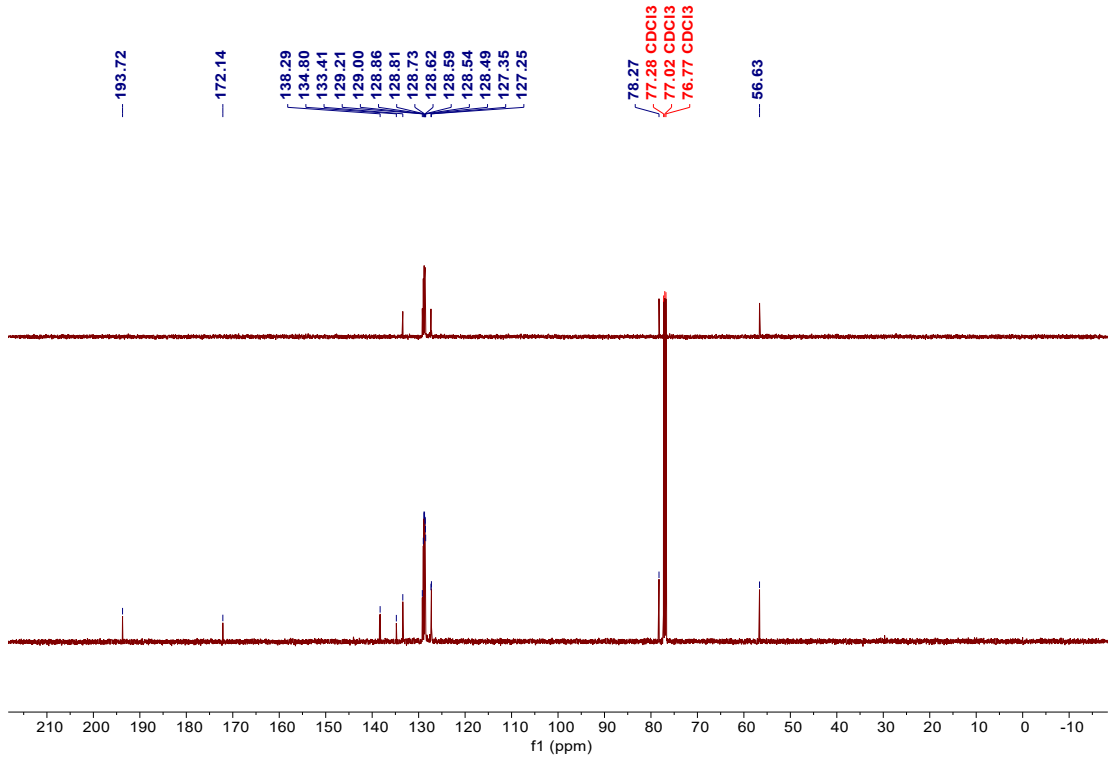
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3r**)



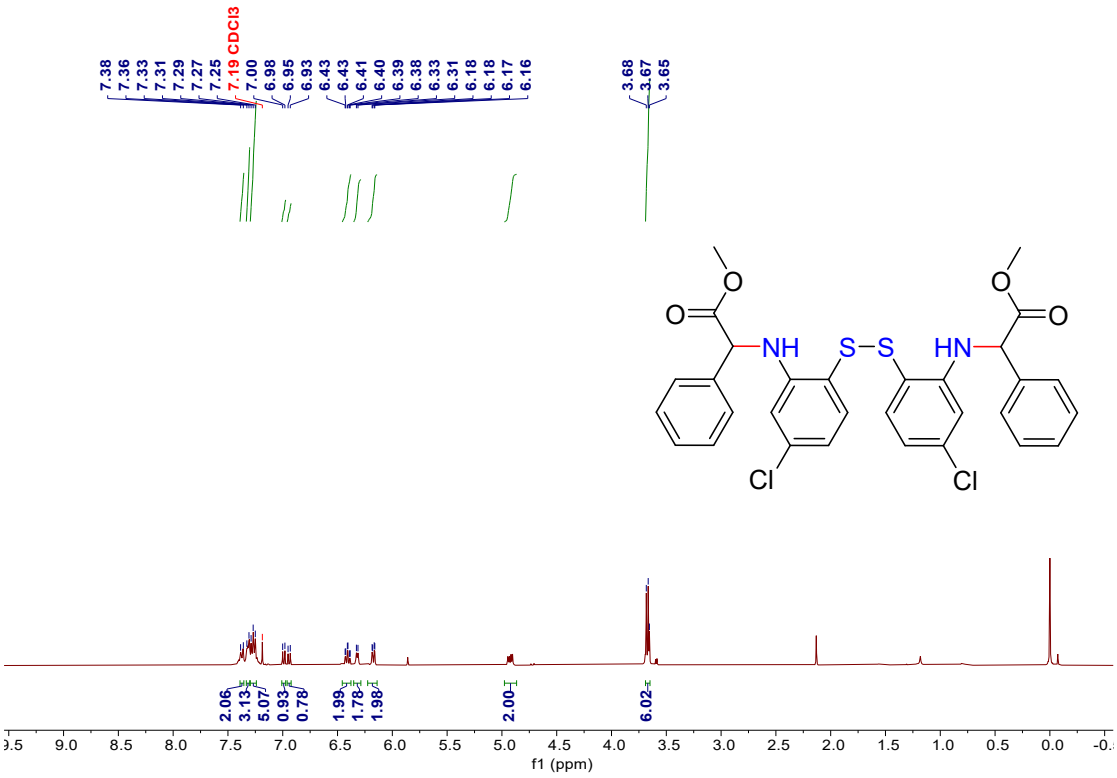
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound (**3r**)



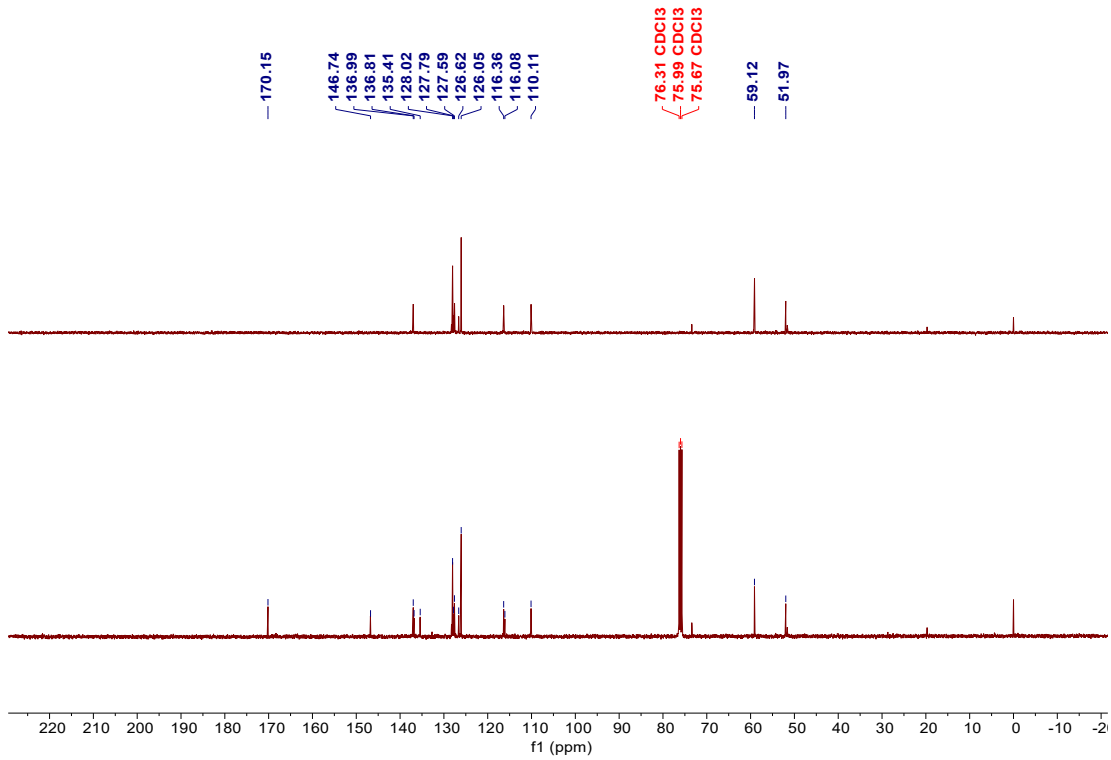
^{1}H-NMR (500 MHz, CDCl3) spectrum of compound (**3s**)



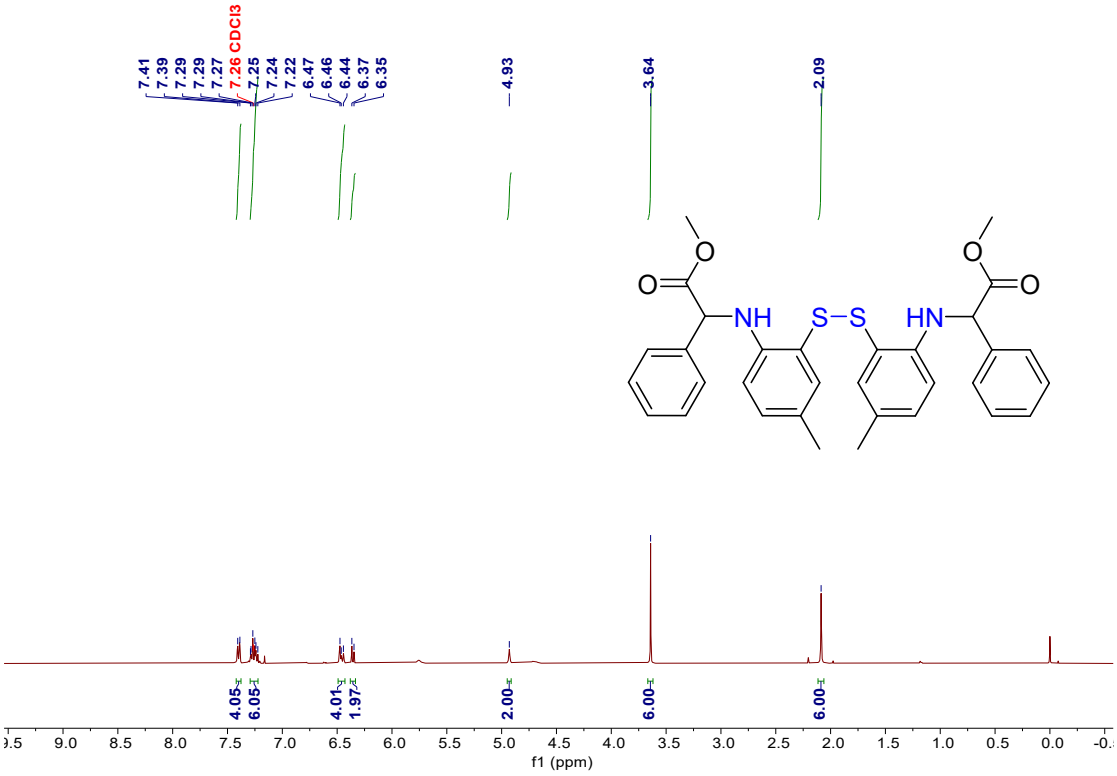
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound (**3s**)



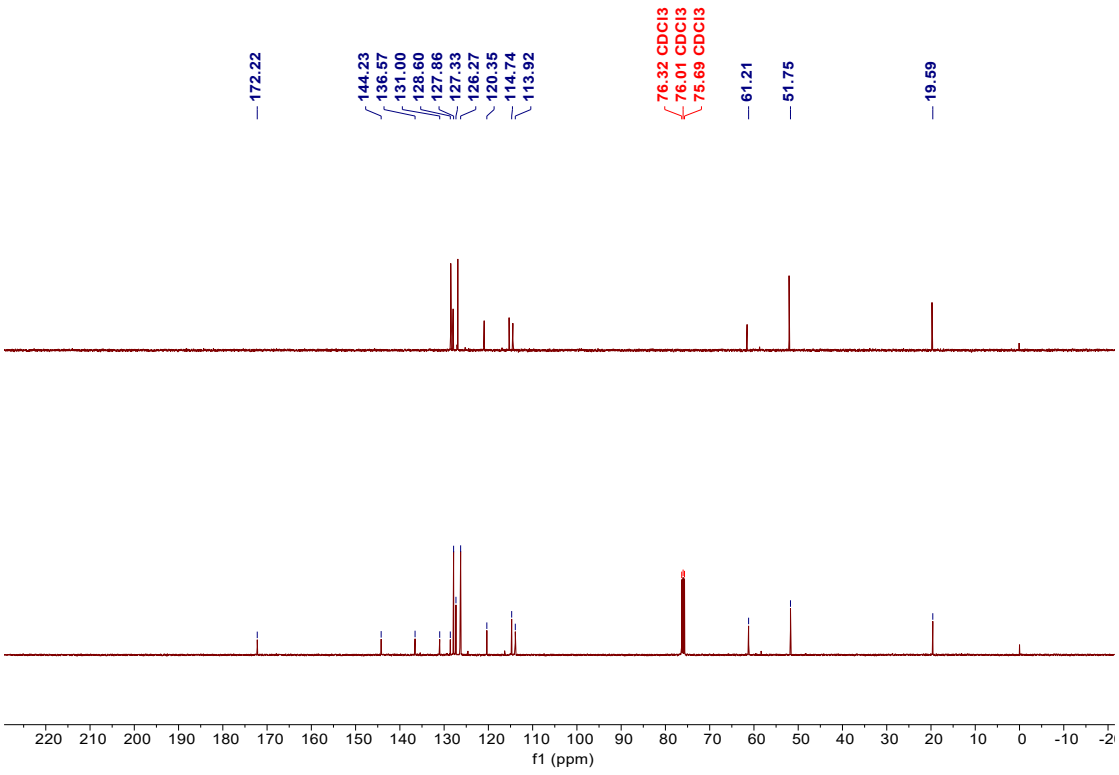
^{1}H-NMR (400 MHz, CDCl3) spectrum of compound (**3t)**



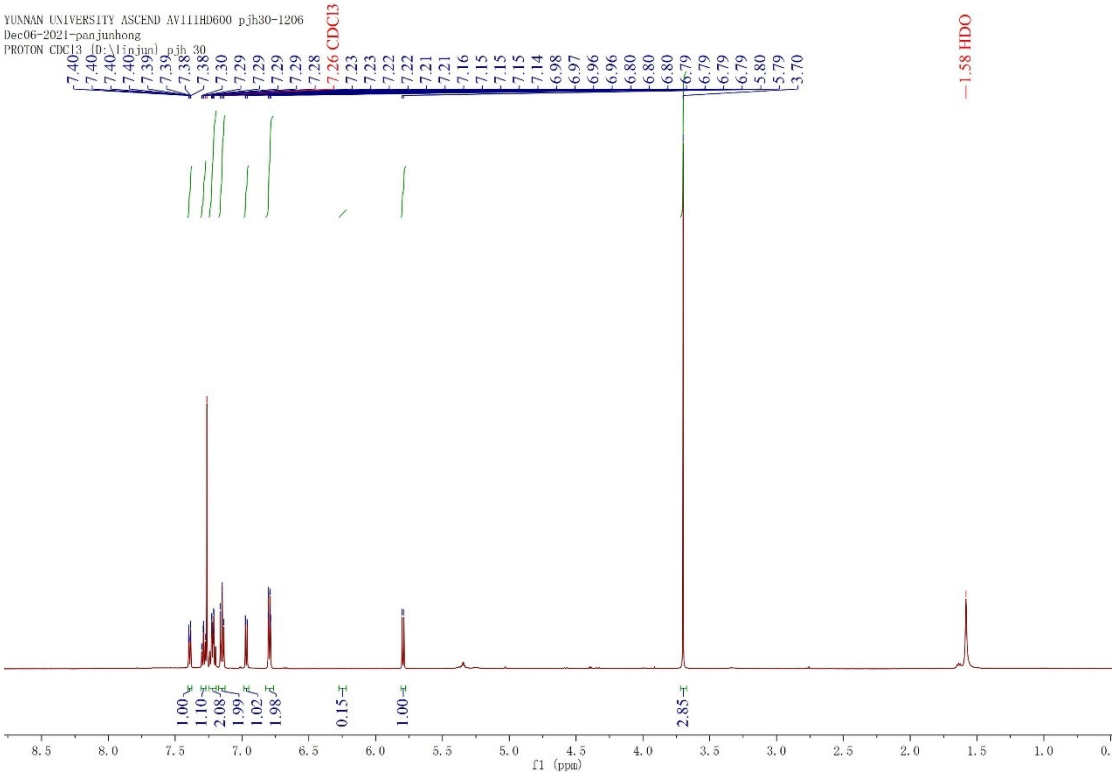
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of compound (**3t**)



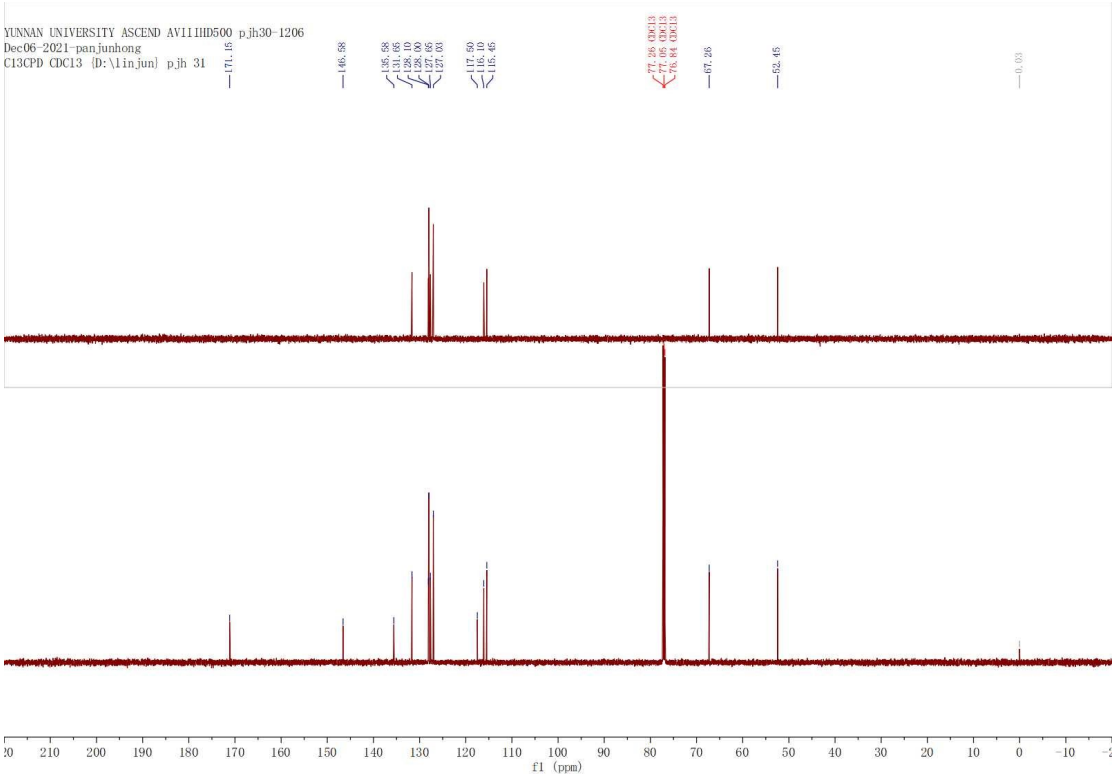
^{1}H-NMR (400 MHz, CDCl3) spectrum of compound (**3u)**



^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of compound (**3u**)



^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of compound (**5**)



^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of compound (**5**)