Electronic Supplementary Information for

An odorless, one-pot synthesis of nitroaryl thioethers *via* S_NAr reactions through the *in situ* generation of *S*-alkylisothiouronium salts

Guo-ping Lu* and Chun Cai

Chemical Engineering College, Nanjing University of Science & Technology, Nanjing, Jiangsu 210094, P. R. China

* Corresponding Author E-mail: glu@njust.edu.cn

1 Experimental

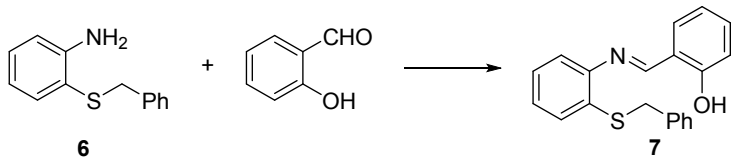
1.1 General

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are identified by appropriate technique such as mp, ^{1}H NMR, and compared with previously reported data. All unknown compounds are characterized by ^{1}H NMR, ^{13}C NMR, MS and elemental analyses. Melting points were determined uncorrected. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm. Elemental analyses are performed on a Yanagimoto MT3CHN recorder. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection.

1.2 Experimental Procedure

General procedures for the synthesis of nitroaryl thioethers from organic halides, thiourea and aryl fluorides in water: A mixture of organic halide **1** 0.75 mmol, nitroaryl fluoride **2** 0.50 mmol, thiourea 1.50 mmol and base 1.50 mmol in 2 wt.% aqueous Triton X-100 solution (1.0 mL) is stirred at 40-80 ^{o}C for 8-24 h. Upon completion, the reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles are removed in *vacuo* to afford the crude product. The extent of conversions is determined by GC. Sometimes, further column chromatography on silica gel affords the pure desired product **3**.

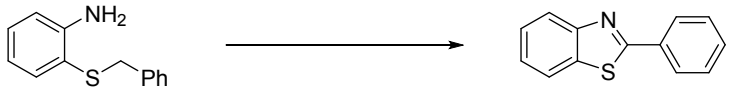
General procedure for the synthesis of anilines 6, 9 and 11 *via* a two-step one-pot process: A mixture of organic halide 0.75 mmol, aryl fluoride 0.5 mmol, thiourea 1.5 mmol and NEt_3 (K_2CO_3 for **11**) 1.5 mmol in 2 wt.% aqueous Triton X-100 solution (1.0 mL) is stirred at 50 ^{o}C (80 ^{o}C for **11**) for 8-24 h. Upon completion, zinc power 2.5 mmol and AcOH 2.5 mmol are employed in aqueous medium, and the mixture is allowed to stir at room temperature for another 8 h. Then, the reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles are removed in *vacuo* to afford the crude product. The extent of conversions is determined by GC. Further column chromatography on silica gel affords the pure desired product.



6 **7**

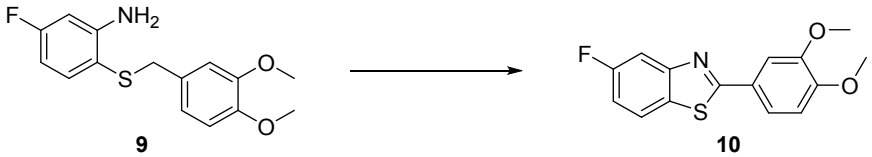
A mixture of **6** 0.50 mmol and salicylaldehyde 0.50 mmol in ethanol (1.0 mL) is

stirred at room temperature for 30 min. The solution is then kept undisturbed for 6 hours at room temperature. The yellow crystalline product **7** that formed was filtered off washed several times with ethanol and dried in a vacuum.



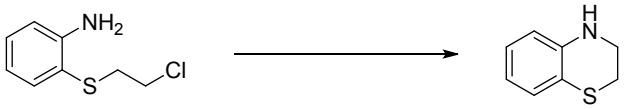
6 **8**

A mixture of **6** 0.50 mmol, $FeBr_2$ 0.05 mmol and DTBP 2.00 mmol in toluene is stirred at 110 °C for 16 h. Upon completion, the reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles are removed in *vacuo* to afford the crude product. The extent of conversions is determined by GC. Further column chromatography on silica gel affords the pure desired product **8**.



9 **10**

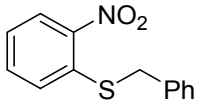
A mixture of **9** 0.50 mmol, $FeBr_2$ 0.05 mmol and DTBP 2.00 mmol in toluene (1 mL) is stirred at 110 °C for 16 h. Upon completion, the reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles are removed in *vacuo* to afford the crude product. The extent of conversions is determined by GC. Further column chromatography on silica gel affords the pure desired product **10**.



11 **12**

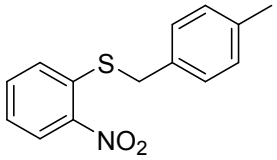
A mixture of **11** 0.50 mmol, NaI 0.60 mmol and K_2CO_3 1.00 mmol in DMF (1 mL) is stirred at 90 °C for 16 h. Upon completion, the reaction mixture is diluted with EtOAc (10.0 mL), and washed by water (10×3 mL). The collected organic phase is filtered through a bed of silica gel layered over Celite, and removed in *vacuo* to afford the product **12**.

2 Characterization Data



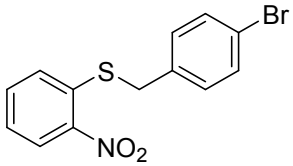
Chemical Formula: $C_{13}H_{11}NO_2S$
Mass: 245

Benzyl(2-nitrophenyl)sulfane **3a,** light yellow solid, mp: 82-84 °C (lit. 82-83).[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.19 (s, 2H), 7.22-7.24 (t, *J* = 7.5 Hz, 1H), 7.27-7.29 (t, *J* = 7.5 Hz, 1H), 7.32-7.35 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.49-7.52 (t, *J* = 7.5 Hz, 1H), 8.19 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.6, 123.8, 125.1, 126.0, 126.8, 127.9, 128.1, 132.7, 134.0, 136.9, 144.7. MS (ESI) *m/z*: 245 [M^+].



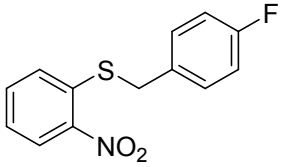
Chemical Formula: $C_{14}H_{13}NO_2S$
Mass: 259

(4-Methylbenzyl)(2-nitrophenyl)sulfane **3b,** light yellow solid, mp: 101-103 °C.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.34 (s, 3H), 4.17 (s, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.23-7.26 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.50-7.54 (t, *J* = 7.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.2, 36.3, 123.7, 125.1, 126.0, 128.0, 128.5, 130.9, 132.6, 136.6, 137.1, 144.8. MS (ESI) *m/z*: 259 [M^+].



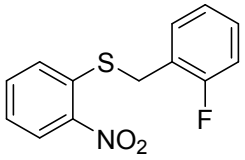
Chemical Formula: $C_{13}H_{10}BrNO_2S$
Mass: 323

(4-Bromobenzyl)(2-nitrophenyl)sulfane **3c,** light yellow solid, mp: 135-137 °C.[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.14 (s, 2H), 7.24-7.29 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.44-7.45 (t, *J* = 6.5 Hz, 2H). 7.50-7.53 (t, *J* = 7.5 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.0, 120.8, 124.0, 125.1, 126.1, 129.7, 131.0, 132.6, 133.2, 136.1, 145.0. MS (ESI) *m/z*: 323 [M^+].



Chemical Formula: $C_{13}H_{10}FNO_2S$
Mass: 263
Elemental Analysis: C, 59.30; H, 3.83;
F, 7.22; N, 5.32; O, 12.15; S, 12.18

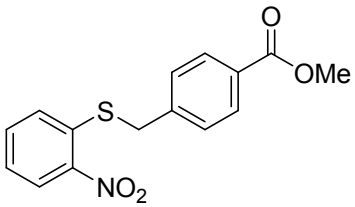
(4-Fluorobenzyl)(2-nitrophenyl)sulfane **3d,** light yellow solid, mp: 78-80 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.17 (s, 2H), 7.01-7.04 (t, *J* = 8.5 Hz, 2H), 7.25-7.28 (m, 1H), 7.36-7.43 (m, 3H), 7.51-7.54 (m, 1H), 8.20 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 35.9, 114.8 (d, *J* = 21 Hz, 1C), 124.0, 125.1, 126.1, 129.6, 129.7, 132.5, 136.3, 145.1, 160.3-162.3 (d, *J* = 245 Hz, 1C). MS (ESI) *m/z*: 263 [M^+]. Anal. Calcd for $C_{13}H_{10}FNO_2S$: C, 59.30; H, 3.83%, N, 5.32%. Found: C, 59.51; H, 4.21%; N, 5.12%.



Chemical Formula: $C_{13}H_{10}FNO_2S$
Mass: 263
Elemental Analysis: C, 59.30; H, 3.83;
F, 7.22; N, 5.32; O, 12.15; S, 12.18

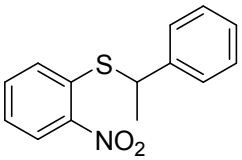
(2-Fluorobenzyl)(2-nitrophenyl)sulfane **3e,** light yellow solid, mp: 71-73 °C. ^{1}H NMR ($CDCl_3$,

500 MHz) δ 4.24 (s, 2H), 7.06-7.13 (m, 2H), 7.26-7.30 (m, 2H), 7.42-7.47 (m, 2H), 7.53-7.56 (t, *J* = 7.5 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.3, 114.6 (d, *J* = 22 Hz, 1C), 121.3 (d, *J* = 14 Hz, 1C), 123.5, 124.0, 125.1, 126.1, 128.6, 128.7, 130.0, 132.6, 136.2, 145.1, 159.0-160.9 (d, *J* = 246 Hz, 1C). MS (ESI) *m/z*: 263 [M^+]. Anal. Calcd for $C_{13}H_{10}FNO_2S$: C, 59.30; H, 3.83%, N, 5.32%. Found: C, 59.28; H, 3.60%; N, 5.44%.



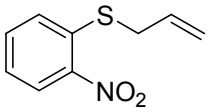
Chemical Formula: $C_{15}H_{13}NO_4S$
Mass: 303

Methyl 4-((2-nitrophenylthio)methyl)benzoate **3f,** light yellow solid, mp: 141-143 °C.[4] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.91 (s, 3H), 4.23 (s, 2H), 7.25-7.28 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.48-7.52 (m, 3H), 8.99 (d, *J* = 8.0 Hz, 2H), 8.19-8.20 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.4, 51.2, 124.1, 125.1, 126.2, 128.0, 128.7, 129.1, 132.6, 136.8, 139.5, 145.2, 165.7. MS (ESI) *m/z*: 303 [M^+].



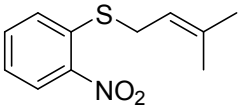
Chemical Formula: $C_{14}H_{13}NO_2S$
Mass: 259

(2-Nitrophenyl)(1-phenylethyl)sulfane **3g,** light yellow solid, mp: 90-92 °C (lit. 91-93).[5] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.69 (d, *J* = 7.0 Hz, 3H), 4.52-4.56 (q, *J* = 7.0 Hz, 1H), 7.18-7.25 (m, 2H), 7.30-7.33 (t, *J* = 7.5 Hz. 2H), 7.37-7.44 (m, 4H), 8.06 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.0, 45.1, 124.2, 124.6, 126.2, 126.6, 127.8, 128.2, 131.9, 134.8, 141.2, 146.3. MS (ESI) *m/z*: 259 [M^+].



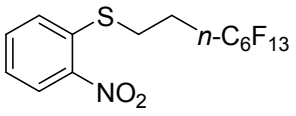
Chemical Formula: $C_9H_9NO_2S$
Mass: 195

Allyl(2-nitrophenyl)sulfane **3h,** light yellow oil.[6] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.58 (d, *J* = 7.0 Hz, 2H), 5.17 (d, *J* = 10.0 Hz, 1H), 5.30 (d, *J* = 17.5 Hz, 1H), 5.80-5.88 (m, 1H), 7.18-7.21 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.46-7.49 (m, 1H), 8.12-8.14 (m, 1H). ^{13}C NMR ($CDCl_3$ 125 MHz) δ 34.6, 118.5, 123.7, 125.1, 126.2, 130.8, 132.3, 136.1, 145.4. MS (ESI) *m/z*: 195 [M^+].



Chemical Formula: $C_{11}H_{13}NO_2S$
Mass: 223

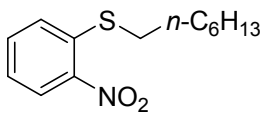
(3-Methylbut-2-enyl)(2-nitrophenyl)sulfane **3i,** light yellow oil.[7] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.74 (s, 3H), 1.76 (s, 3H), 3.59 (d, *J* = 7.5 Hz, 2H), 5.29-5.32 (t, *J* = 7.5 Hz, 1H), 7.22-7.25 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.52-7.55 (m, 1H), 8.19 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.0, 24.7, 30.0, 115.9, 123.4, 125.1, 126.1, 132.4, 137.5, 137.8, 145.0. MS (ESI) *m/z*: 223 [M^+].



Chemical Formula: $C_{14}H_8F_{13}NO_2S$
Mass: 501
Elemental Analysis: C, 33.55; H, 1.61;
F, 49.27; N, 2.79; O, 6.38; S, 6.40

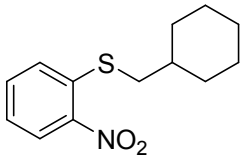
(2-Nitrophenyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfane **3j,** light yellow oil. ^{1}H NMR

($CDCl_3$, 500 MHz) δ 2.46 (m, 2H), 3.22-3.25 (m, 2H), 7.34-7.37 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.63-7.66 (m, 1H), 8.24-8.26 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.1, 29.2-29.5 (m), 49.9, 124.4, 125.2, 125.4, 132.9, 134.4, 145.6. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -126.1, -123.3, -122.8, -121.8, -114.2, -80.8. MS (ESI) *m/z*: 501 [M^+]. Anal. Calcd for $C_{14}H_8F_{13}NO_2S$: C, 33.55; H, 1.61%, N, 2.79%. Found: C, 33.19; H, 1.94%; N, 3.13%.



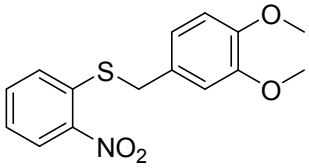
Chemical Formula: $C_{13}H_{19}NO_2S$
Mass: 253
Elemental Analysis: C, 61.63; H, 7.56; N, 5.53; O, 12.63; S, 12.66

Heptyl(2-nitrophenyl)sulfane **3k,** light yellow oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.87-0.90 (t, *J* = 7.0 Hz, 3H), 1.28-1.37 (m, 6H), 1.45-1.50 (m, 2H), 1.71-1.77 (m, 2H), 2.94-2.97 (t, *J* = 7.5 Hz, 2H), 7.23-7.26 (m, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.53-7.55 (m, 1H), 8.19-8.21 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.0, 21.6, 26.9, 27.9, 28.1, 30.7, 31.4, 123.3, 125.1, 125.6, 132.3, 137.3, 145.1. MS (ESI) *m/z*: 253 [M^+]. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56%, N, 5.53%. Found: C, 61.59; H, 7.87%; N, 5.14%.



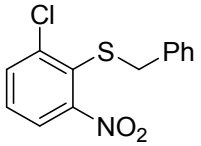
Chemical Formula: $C_{13}H_{17}NO_2S$
Mass: 251
Elemental Analysis: C, 62.12; H, 6.82; N, 5.57; O, 12.73; S, 12.76

(Cyclohexylmethyl)(2-nitrophenyl)sulfane **3l,** light yellow oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.97-1.05 (m, 2H), 1.10-1.23 (m, 3H), 1.57-1.69 (m, 4H), 1.87-1.90 (m, 2H), 2.76 (d, *J* = 8.5 Hz, 2H), 7.14-7.17 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.45-7.48 (t, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.0, 25.2, 32.2, 35.8, 38.7, 123.2, 125.1, 125.7, 132.3, 137.6, 145.2. MS (ESI) *m/z*: 251 [M^+]. Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12%; H, 6.82%, N, 5.57%. Found: C, 61.91; H, 6.56%; N, 5.38%.



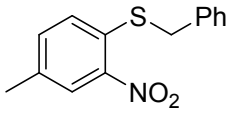
Chemical Formula: $C_{15}H_{15}NO_4S$
Mass: 305
Elemental Analysis: C, 59.00; H, 4.95; N, 4.59; O, 20.96; S, 10.50

(3,4-Dimethoxybenzyl)(2-nitrophenyl)sulfane **3m,** light yellow solid, mp: 96-98 °C. ^1H NMR ($CDCl_3$, 500 MHz) δ 3.87 (s, 6H), 4.16 (s, 2H), 6.79-6.84 (d, *J* = 8.0 Hz, 1H), 6.93-6.96 (m, 2H), 7.24-7.27 (m, 1H), 7.45-7.54 (m, 2H), 8.19 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.7, 56.0 (2C), 111.4, 112.2, 121.5, 124.9, 126.1, 127.2, 127.3, 133.6, 137.9, 146.1, 148.8, 149.3. MS(ESI) *m/z*: 305 [M^+]. Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 59.00%; H, 4.95%, N, 4.59%. Found: C, 59.32; H, 4.56%; N, 4.97%.



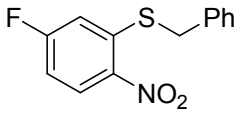
Chemical Formula: $C_{13}H_{10}ClNO_2S$
Mass: 279

Benzyl(2-chloro-6-nitrophenyl)sulfane **3n**, light yellow solid, mp: 86-88 °C.[8] ^1H NMR ($CDCl_3$, 500 MHz) δ 4.12 (s, 2H), 7.17-7.19 (m, 2H), 7.22-7.24 (m, 3H), 7.34-7.37 (t, *J* = 8.0 Hz, 1H), 7.42-7.44 (m, 1H), 7,61-7.63 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 39.1, 120.5, 125.8, 126.7, 127.6, 128.1, 129.1, 131.7, 135.2, 141.1, 155.6. MS (ESI) *m/z*: 279 [M^+].



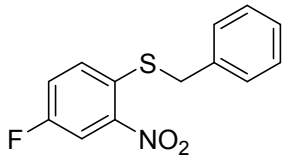
Chemical Formula: $C_{14}H_{13}NO_2S$
Mass: 259

Benzyl(4-methyl-2-nitrophenyl)sulfane **3o**, light yellow solid, mp: 94-96 °C (lit. 96-98 °C).[9] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.40 (s, 3H), 4.19 (s, 2H), 7.28-7.36 (m, 5H), 7.42 (d, *J* = 7.5 Hz, 2H), 8.02 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.5, 36.7, 125.2, 126.2, 126.7, 127.8, 128.1, 132.9, 133.5, 134.3, 134.4, 145.1. MS (ESI) *m/z*: 259 [M^+].



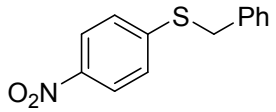
Chemical Formula: $C_{13}H_{10}FNO_2S$
Mass: 263
Elemental Analysis: C, 59.30; H, 3.83;
F, 7.22; N, 5.32; O, 12.15; S, 12.18

Benzyl(5-fluoro-2-nitrophenyl)sulfane **3p** light yellow solid, mp: 74-76 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.17 (s, 2H), 6.91-6.94 (m, 1H), 7.14-7.16 (dd, *J* = 9.5, 2.0 Hz, 1H), 7.30-7.44 (m, 5H), 8.28-8.31 (dd, *J* = 9.0, 5.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.7, 110.9-111.1 (d, *J* = 24 Hz, 1C), 112.2-112.5 (d, *J* = 28 Hz, 1C), 127.0, 128.0, 128.1, 133.2, 140.6, 141.1, 163.2-165.2 (d, *J* = 258 Hz, 1C). MS(ESI) *m/z*: 263 [M^+]. Anal. Calcd for $C_{13}H_{10}NO_2S$: C, 59.30%; H, 3.83%, N, 5.32%. Found: C, 59.08; H, 4.12%; N, 5.26%.



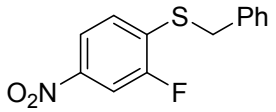
Chemical Formula: $C_{13}H_{10}FNO_2S$
Mass: 263

Benzyl(4-fluoro-2-nitrophenyl)sulfane **3q,** light yellow solid, mp: 76-78 °C.[10] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.19 (s, 2H), 7.25-7.43 (m, 7H), 7.89-7.92 (dd, *J* = 8.5, 3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 38.12, 113.2-113.4 (d, *J* = 26 Hz, 1C), 121.3-121.5 (d, *J* = 23 Hz, 1C), 128.0, 129.0, 129.1, 129.3, 132.7, 135.0, 146.8, 158.5-160.5 (d, *J* = 248 Hz, 1C). MS(ESI) *m/z*: 263 [M^+].



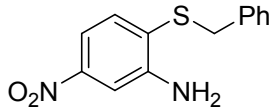
Chemical Formula: $C_{13}H_{11}NO_2S$
Mass: 245

Benzyl(4-nitrophenyl)sulfane **3r,** light yellow solid, mp: 120-122 °C (lit. 123 °C).[11] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.05 (s, 2H), 7.29-7.35 (m, 5H), 7.39 (d, *J* = 7.5 Hz, 2H), 8.09 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.1, 122.9, 125.7, 126.8, 127.7, 127.9, 134.5, 144.3, 146.2. MS (ESI) *m/z*: 245 [M^+].



Chemical Formula: $C_{13}H_{10}FNO_2S$
Mass: 263

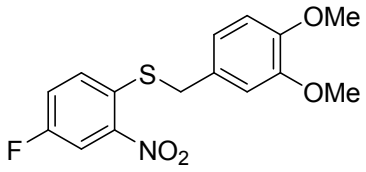
Benzyl(2-fluoro-4-nitrophenyl)sulfane **3s,** light yellow solid, mp: 122-124 °C (lit. 126 °C).[10] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.25 (s, 2H), 7.18-7.38 (m, 6H), 7.87-7.90 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 7.92-7.94 (dd, *J* = 8.5, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 35.6, 109.7-109.9 (d, *J* = 26 Hz, 1C), 118.0, 126.9, 127.4, 127.5, 133.5, 133.6, 134.2, 145.1, 157.0-159.0 (d, *J* = 248 Hz, 1C). MS (ESI) *m/z*: 263 [M^+].



Chemical Formula: $C_{13}H_{12}N_2O_2S$
Mass: 260

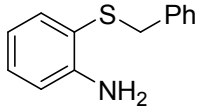
2-(Benzylthio)-5-nitroaniline **3t,** light yellow solid, mp: 158-160 °C.[12] ^{1}H NMR ($CDCl_3$, 500

MHz) δ 4.03 (s, 2H), 4.50 (br s, 2H), 7.18-7.20 (t, *J* = 6.0 Hz, 2H), 7.24-7.30 (m, 4H), 7.44-7.46 (dd, *J* = 8.5, 2,5 Hz, 1H), 7.51 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.8, 107.6, 111.7, 125.0, 126.6, 127.6, 127.5, 133.6, 136.0, 146.9, 147.4. MS (ESI) *m/z*: 260 [M^+].



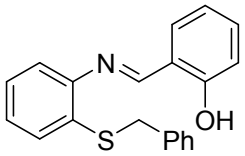
Chemical Formula: $C_{15}H_{14}FNO_4S$
Mass: 323
Elemental Analysis: C, 55.72; H, 4.36; F, 5.88; N, 4.33; O, 19.79; S, 9.92

(3,4-Dimethoxybenzyl)(5-fluoro-2-nitrophen**y**l)sulfane **3w,** light yellow solid, mp: 92-94 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.97 (s, 6H), 4.25 (s, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 7.02-7.03 (m, 2H), 7.36-7.40 (m, 1H), 7.52-7.55 (dd, *J* = 9.0, 5.0 Hz, 1H), 7.98-8.01 (dd, *J* = 8.5, 3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 37.0, 54.9 (2C), 110.3, 111.0, 112.0-112.2 (d, *J* = 26 Hz, 1C), 120.1, 120.2-120.4 (d, *J* = 25 Hz, 1C), 126.1, 128.3, 131.7, 145.7, 147.8, 148.3, 157.4-159.4 (d, *J* = 248 Hz, 1C). MS(ESI) *m/z*: 323 [M^+]. Anal. Calcd for $C_{15}H_{14}FNO_4S$: C, 55.72%; H, 4.36%, N, 4.33%. Found: C, 56.01; H, 3.97%; N, 4.14%.



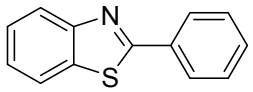
Chemical Formula: $C_{13}H_{13}NS$
Mass: 215

2-(Benzylthio)aniline **6,** light green solid, mp: 48-50 °C (lit. 45-46 °C).[13] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.93 (s, 2H), 4.19 (br s, 2H), 6.64-6.67 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 7.12-7.19 (m, 3H), 7.24-7.29 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 38.7, 113.9, 116.5, 117.5, 126.1, 127.4, 127.9, 129.1, 135.5, 137.4, 147.6. MS (ESI) *m/z*: 215 [M^+].



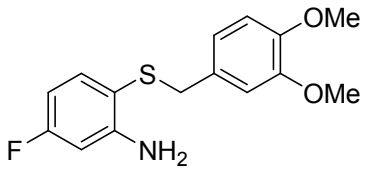
Chemical Formula: $C_{20}H_{17}NOS$
Mass: 319

(*E*)-2-((2-(Benzylthio)phenylimino)methyl)phenol **7,** yellow solid, mp: 218-220 °C.[13] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.12 (s, 2H), 6.93-6.96 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 7.14-7.40 (m, 10H), 8.54 (s, 1H), 13.19 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.8, 116.5, 116.8, 118.0, 118.3, 125.9, 126.2, 126.3, 127.5, 127.9, 128.1, 131.3, 131.5, 132.4, 135.9, 146.2, 160.2, 161.1. MS (ESI) *m/z*: 319 [M^+].



Chemical Formula: $C_{13}H_9NS$
Mass: 211

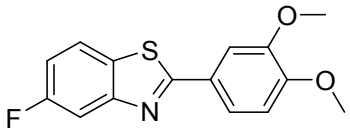
2-Phenylbenzo[*d*]thiazole **8,** white solid, mp: 112-114 °C (lit. 115 °C).[14] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.43 (t, J = 7.5 Hz, 1H), 7.50-7.53 (m, 4H), 7.92 (d, J = 8.0 Hz, 4H), 8.09-8.13 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 120.6, 122.3, 124.2, 125.3, 126.6, 128.0, 130.0, 132.7, 134.1, 153.2, 167.1. MS (ESI) *m/z*: 211 [M^+].



Chemical Formula: $C_{15}H_{16}FNO_2S$
Mass: 293
Elemental Analysis: C, 61.41; H, 5.50; F, 6.48; N, 4.77; O, 10.91; S, 10.93

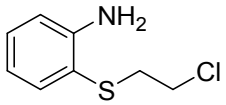
2-(3,4-Dimethoxybenzylthio)-4-fluoroaniline **9,** light yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ

3.69 (s, 3H), 3.72 (s, 2H), 3.76 (s, 3H), 4.42 (s, 2H), 6.23-6.27 (m, 1H), 6.31-6.33 (dd, *J* = 10.5, 2.5 Hz, 1H), 6.51 (d, *J* = 1.5 Hz, 1H), 6.58-6.60 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 7.04-7.07 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 39.6, 55.7, 55.9, 101.1-101.3 (d, *J* = 25 Hz, 1C), 105.1-105.2 (d, *J* = 21 Hz, 1C), 111.2, 112.2-112.3 (d, *J* = 23 Hz, 1C), 121.1, 130.9, 138.7, 138.8, 150.6-150.7 (d, *J* = 10 Hz, 1C), 163.4-165.4 (d, *J* = 244 Hz, 1C). MS(ESI) *m/z*: 293 [M^+]. Anal. Calcd for $C_{15}H_{16}FNO_2S$: C, 61.41%; H, 5.50%, N, 4.77%. Found: C, 61.13; H, 5.22%; N, 4.38%.



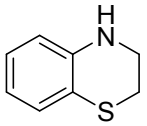
Chemical Formula: $C_{15}H_{12}FNO_2S$
Mass: 289

2-(3,4-Dimethoxyphenyl)-5-fluorobenzo[d]thiazole **10,** white solid, mp: 108-110 °C (lit. 110 °C).[15] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.94 (s, 3H), 4.01 (s, 3H), 6.91 (d, *J* = 8.5 Hz, 1H), 7.09-7.13 (m, 1H), 7.55-7.57 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.67-7.71 (m, 2H), 7.75-7.78 (dd, *J* = 9.0, 5.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 56.1, 56.2, 109.0-109.2 (d, *J* = 24 Hz, 1C), 109.9, 111.1, 113.4-113.6 (d, *J* = 25 Hz, 1C), 121.3, 122.1-122.2 (d, *J* = 9 Hz, 1C), 126.5, 130.4, 149.5, 151.9, 155.1-155.2 (d, *J* = 11 Hz, 1C), 161.1-163.0 (d, *J* = 243 Hz, 1C), 170.5. MS(ESI) *m/z*: 289 [M^+].



Chemical Formula: $C_8H_{10}ClNS$
Mass: 187

2-(2-Chloroethylthio)aniline **11,** light green oil.[16] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.04-3.07 (t, *J* = 7.5 Hz, 2H), 3.58-3.61 (t, *J* = 8.0 Hz, 2H), 4.19 (br s, 2H), 6.70-6.77 (m, 2H), 7.16-7.19 (m, 1H), 7.40-7.42 (dd, *J* = 7.5, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 35.8, 41.8, 114.2, 114.7, 117.7, 129.6, 135.7, 147.7. MS (ESI) *m/z*: 187 [M^+].



Chemical Formula: C_8H_9NS
Mass: 151

3,4-Dihydro-2*H*-benzo[*b*][1,4]thiazine **12,** light yellow oil.[16] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.06-3.08 (m, 2H), 3.61-3.64 (m, 2H), 4.00 (br, 1H), 6.47-6.49 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.64-6.67 (m, 1H), 6.91-6.94 (m, 1H), 7.02-7.04 (dd, *J* = 7.5, 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.1, 41.4, 114.4, 115.0, 117.1, 124.6, 126.7, 140.8. MS (ESI) *m/z*: 151 [M^+].

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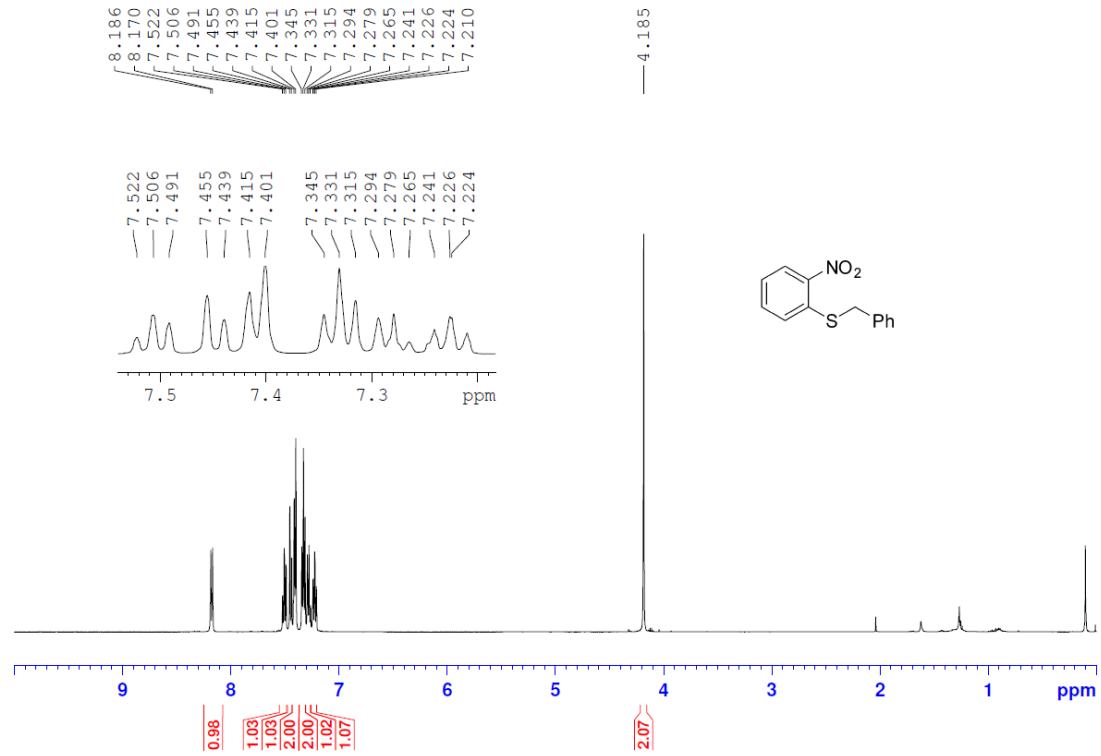
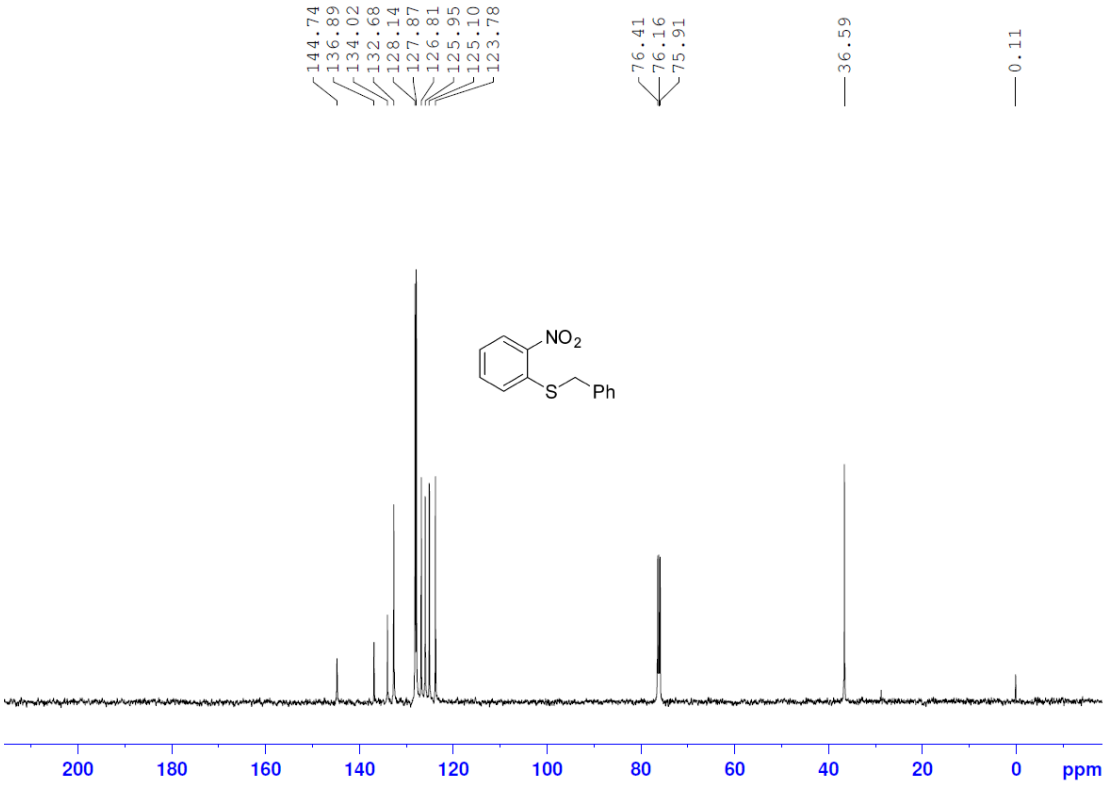
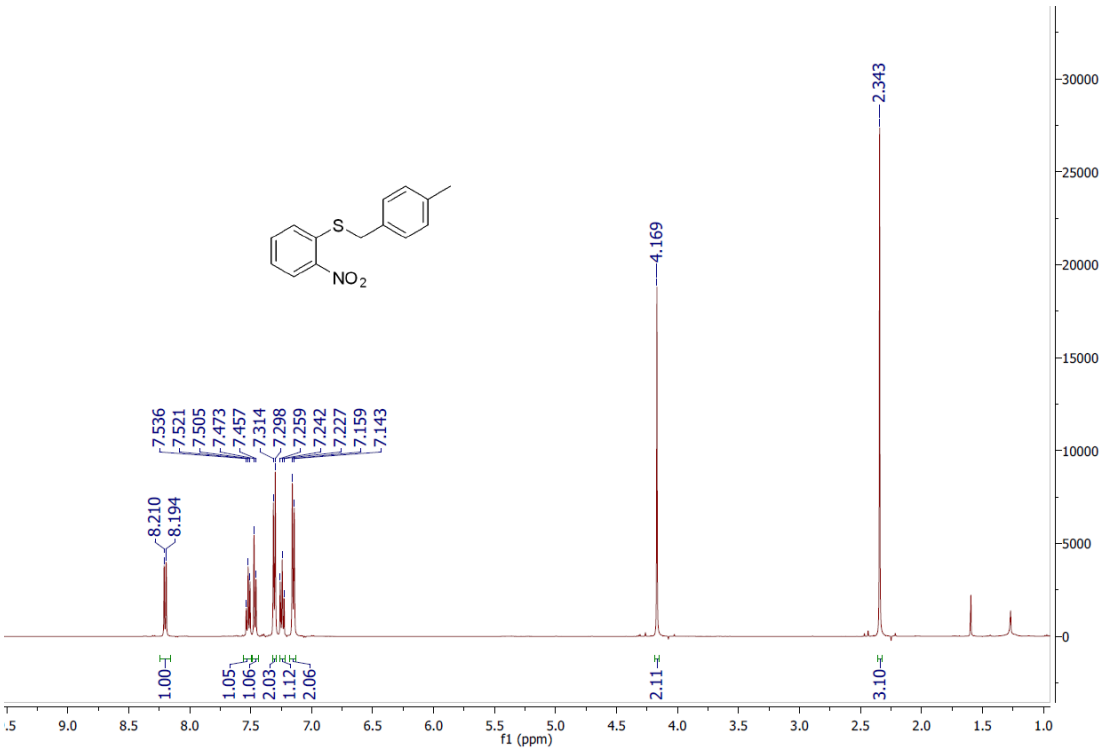
3 NMR Spectra of All Products



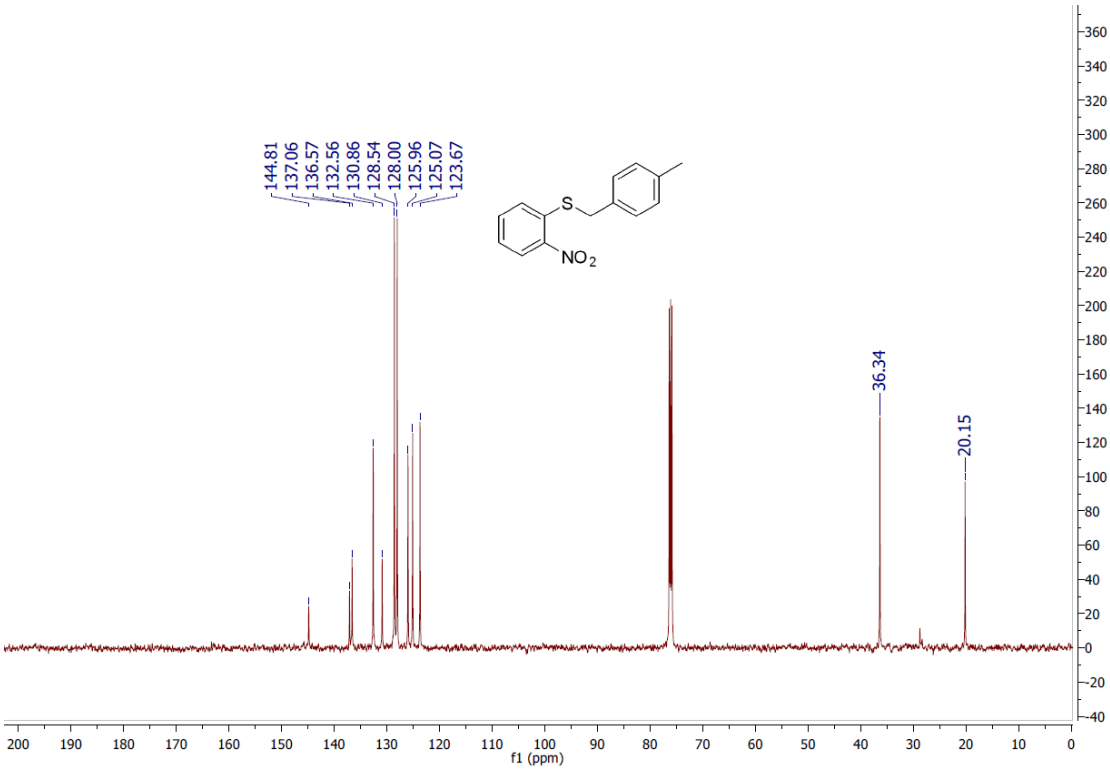
^{1}H NMR **3a**



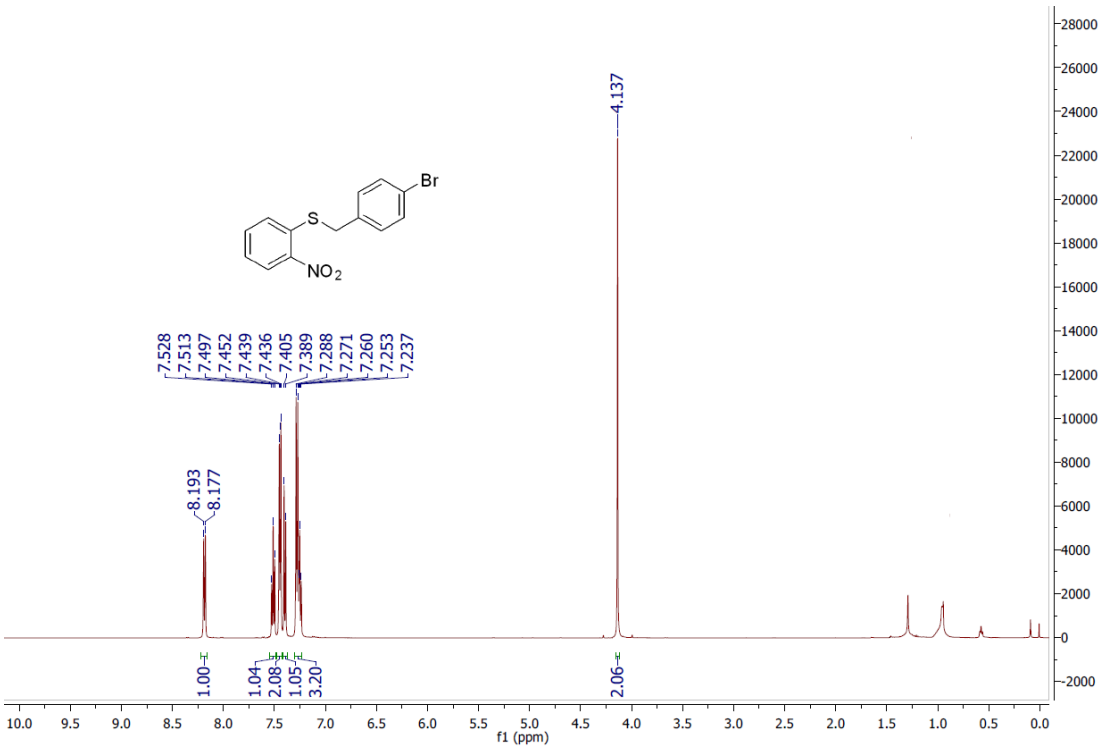
^{13}C NMR **3a**



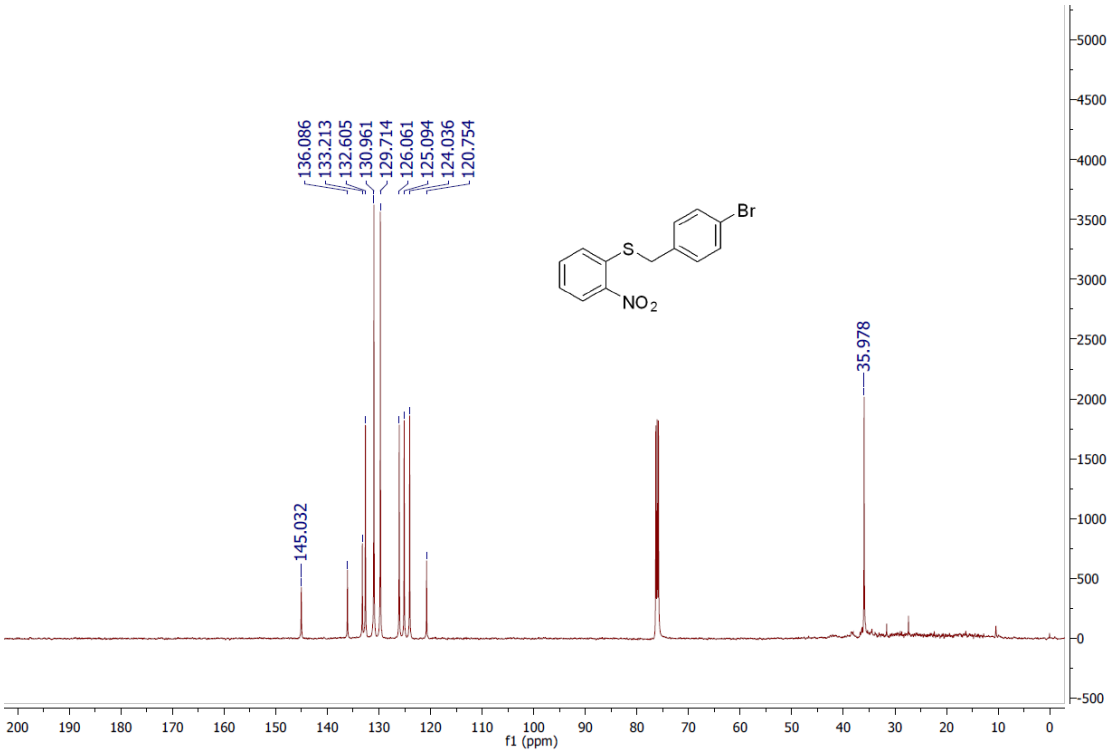
^{1}H NMR **3b**



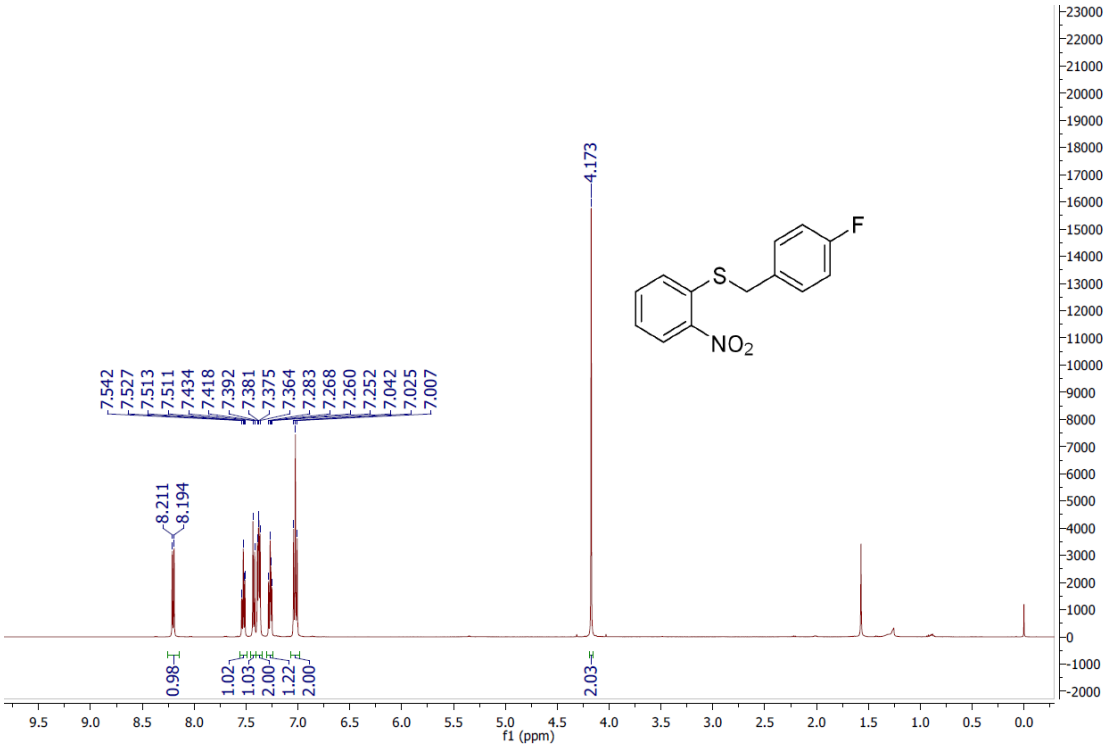
^{13}C NMR **3b**



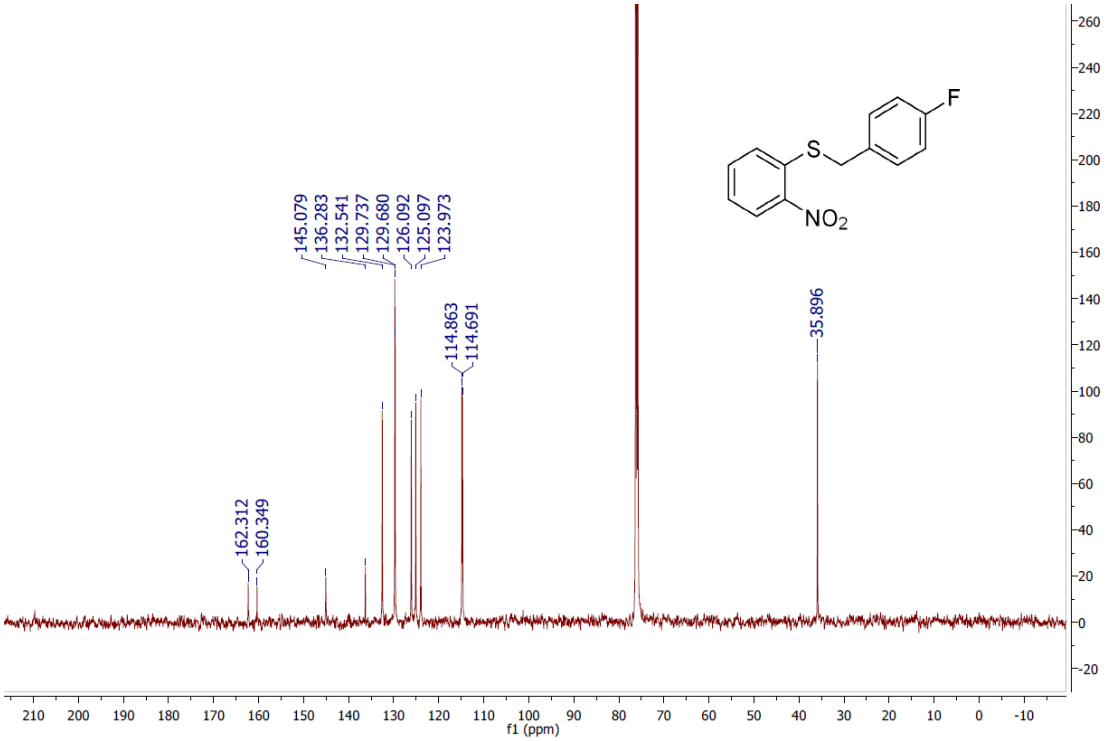
^{1}H NMR **3c**



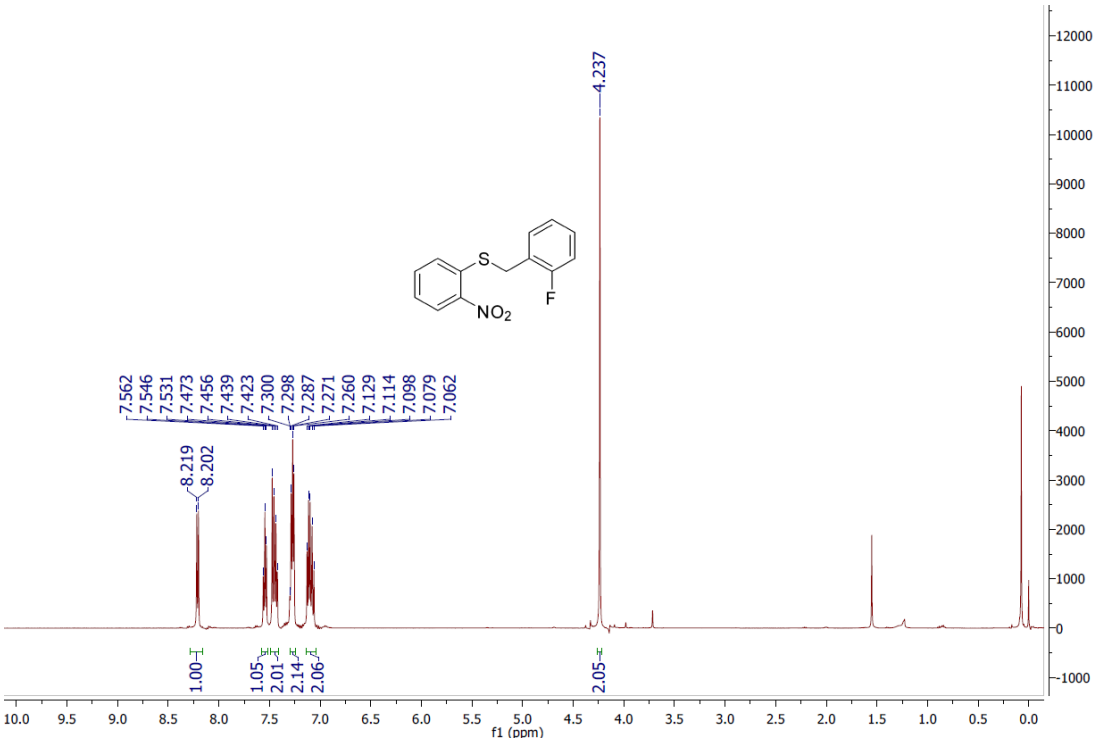
^{13}C NMR **3c**



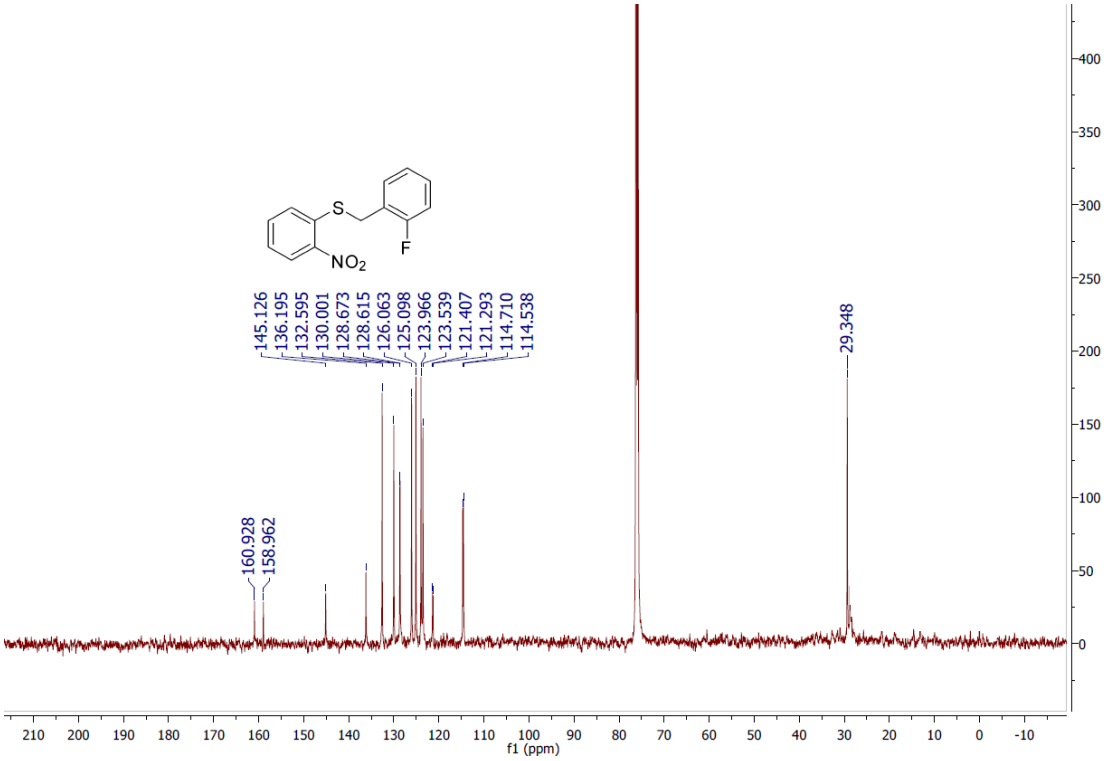
^{1}H NMR **3d**



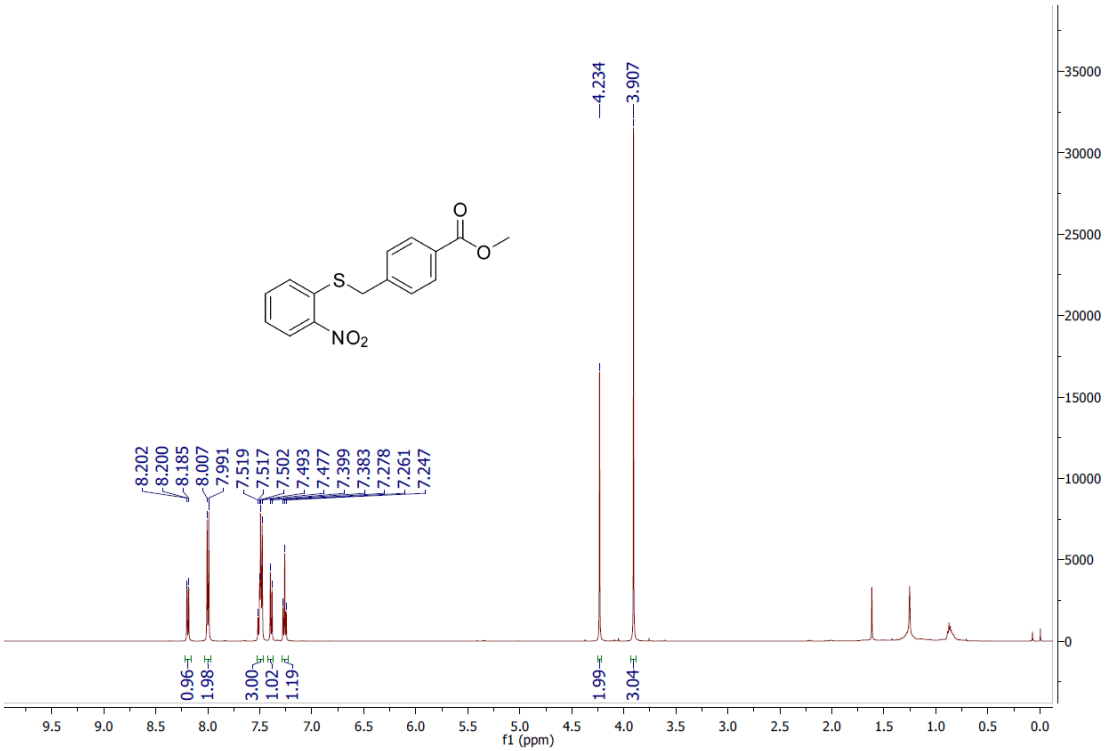
^{13}C NMR **3d**



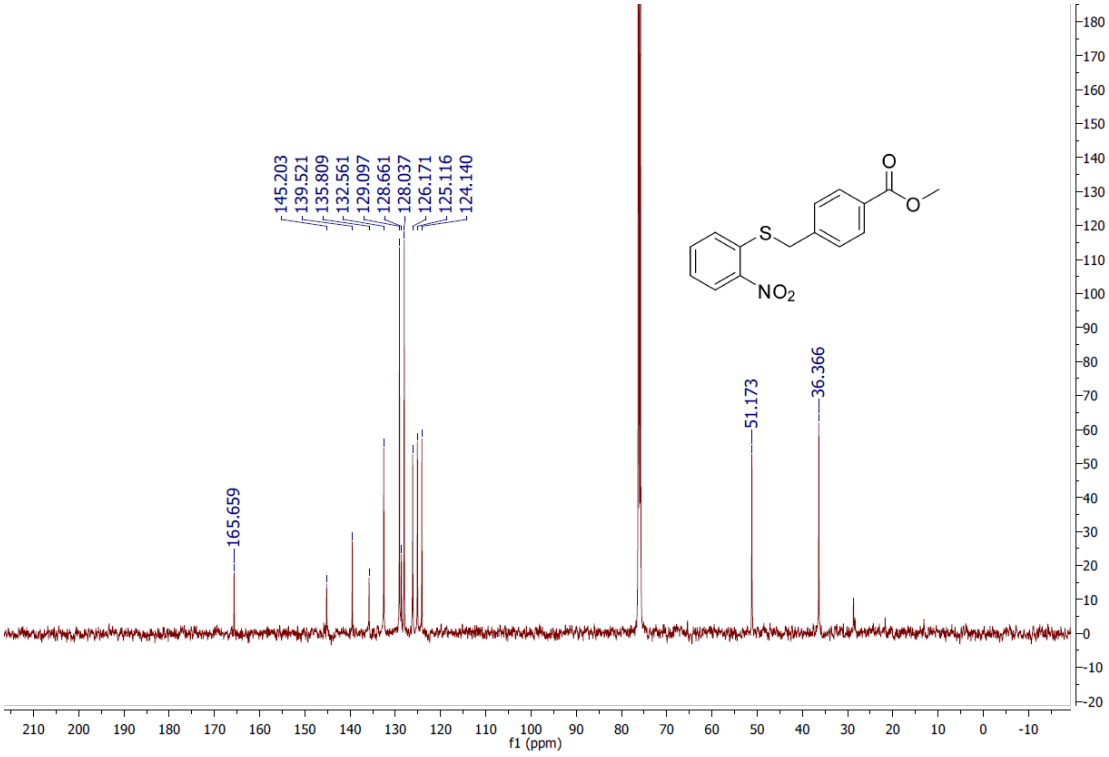
^{1}H NMR **3e**



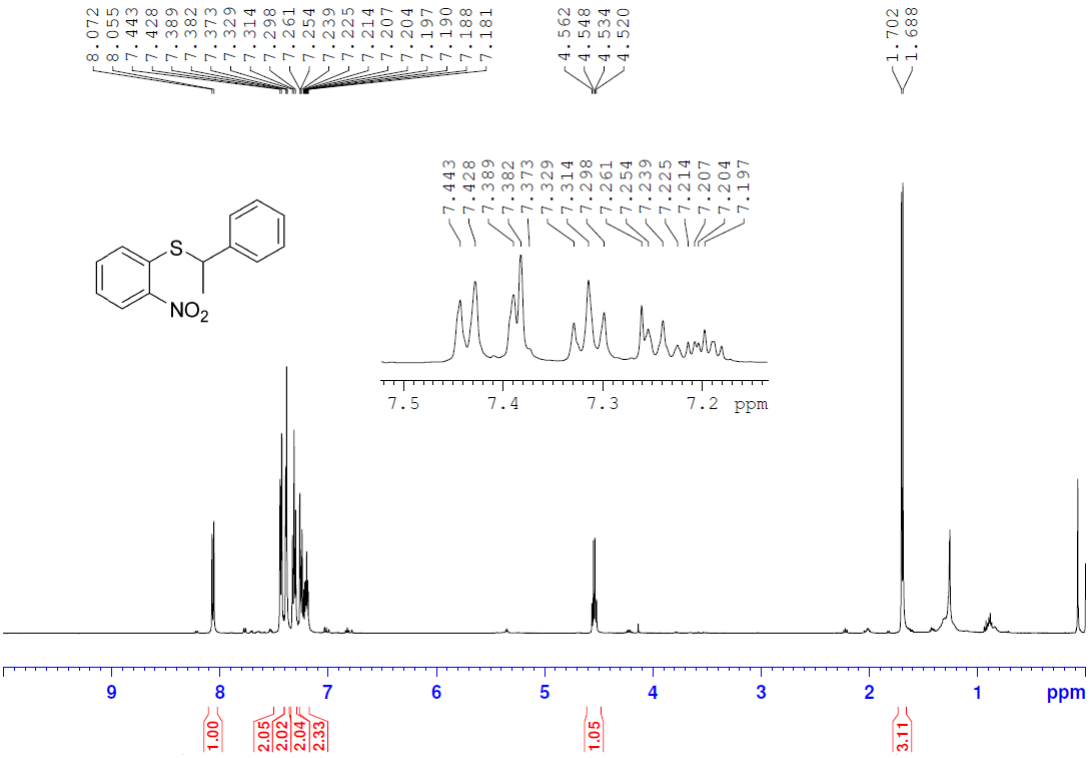
^{13}C NMR **3e**



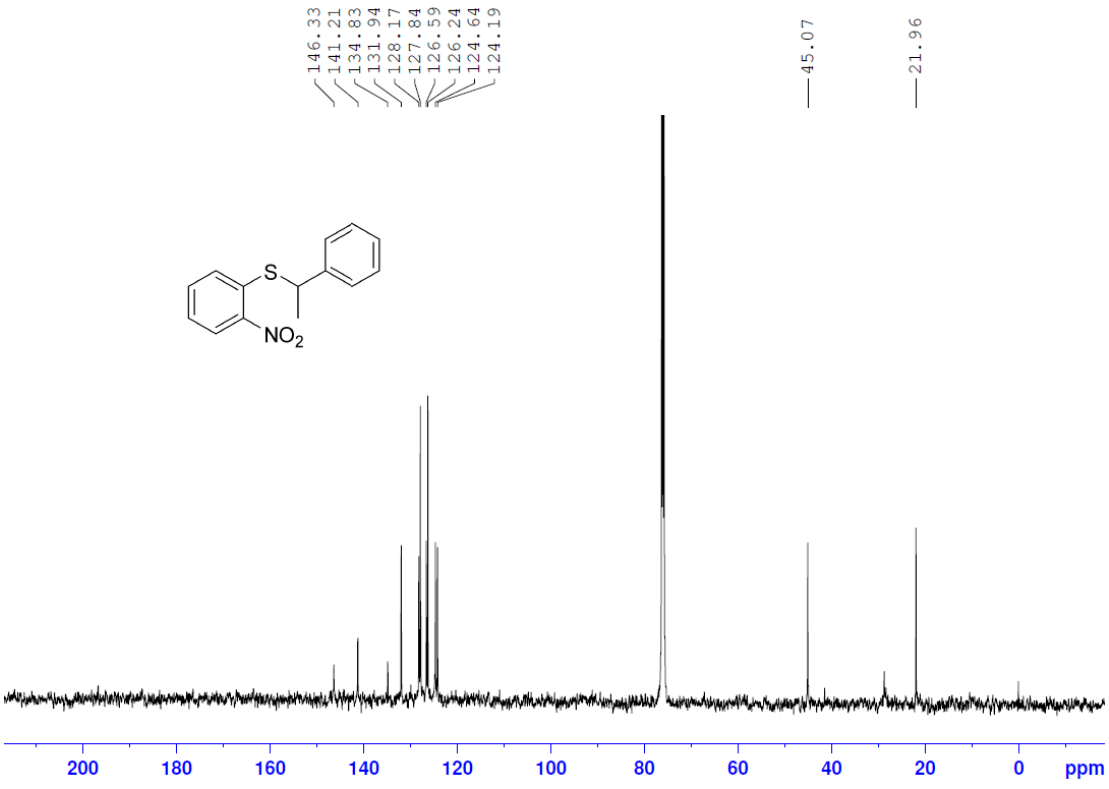
^{1}H NMR **3f**



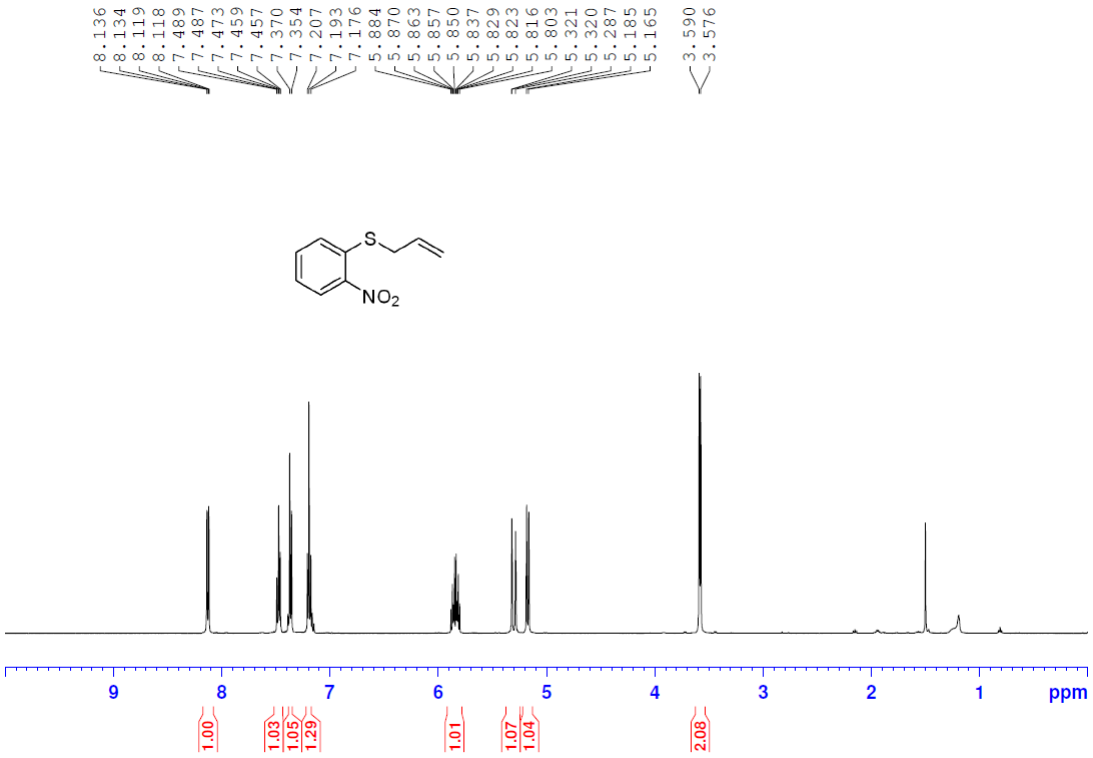
^{13}C NMR **3f**



^{1}H NMR **3g**



^{13}C NMR **3g**



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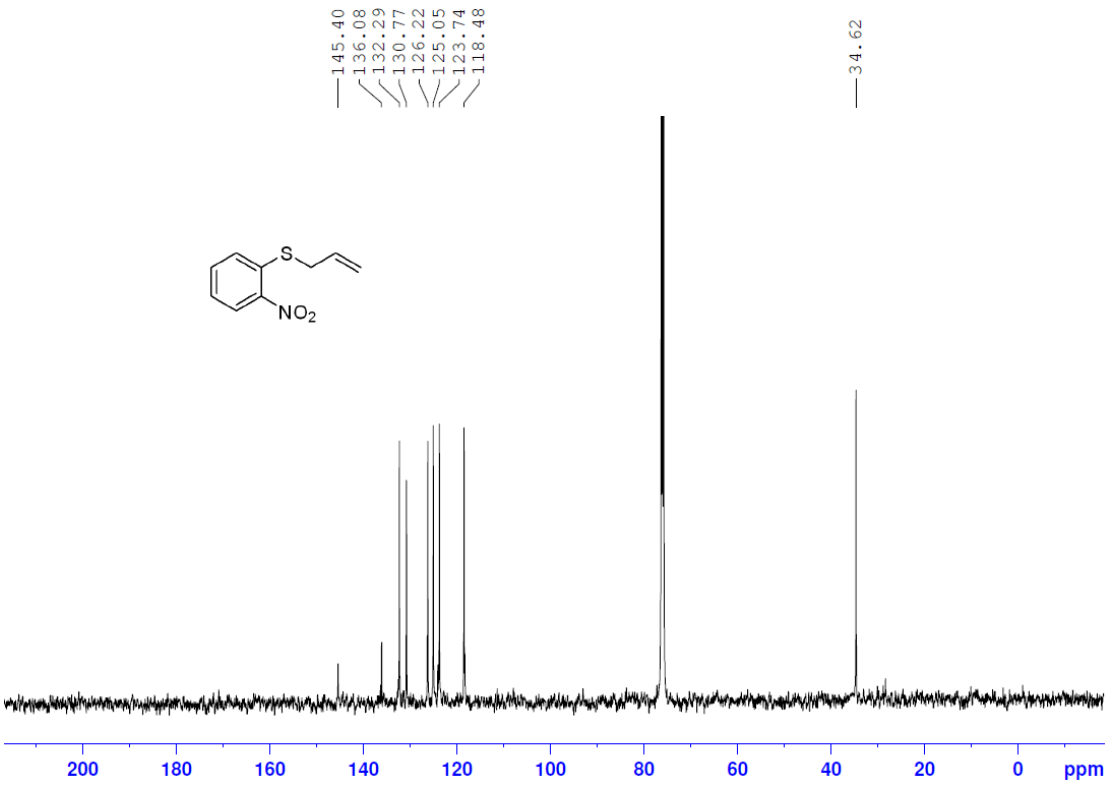
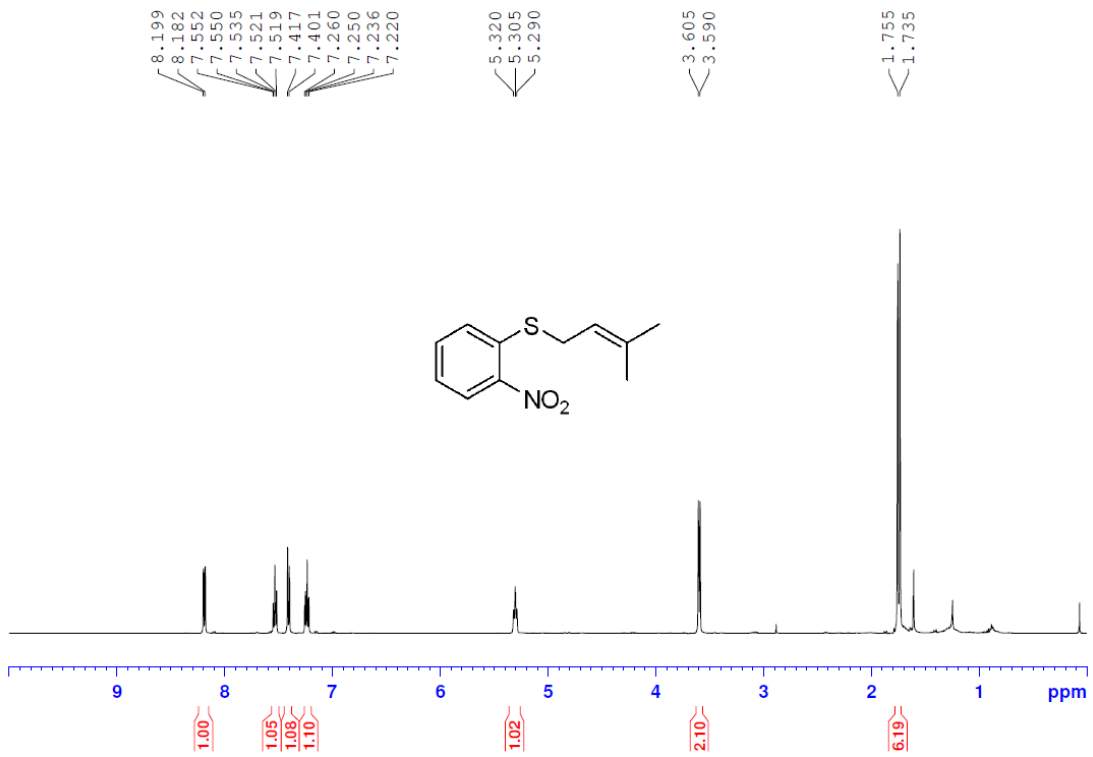


^{13}C NMR **3h**



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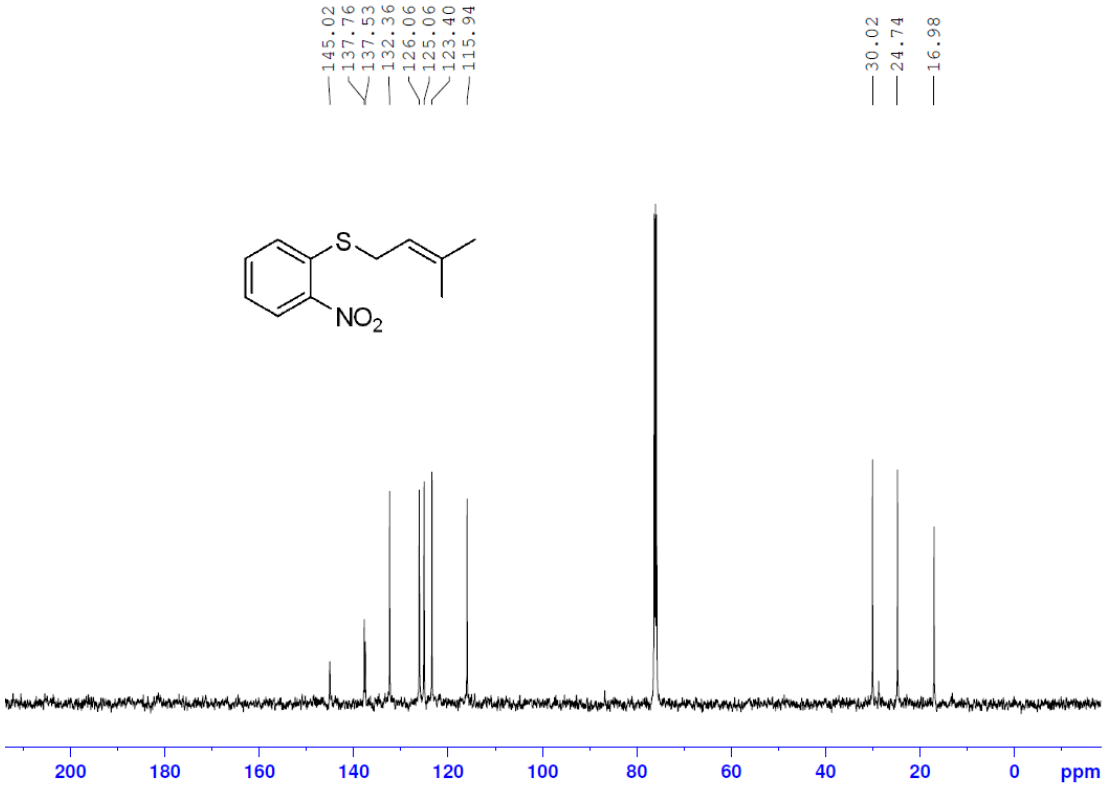
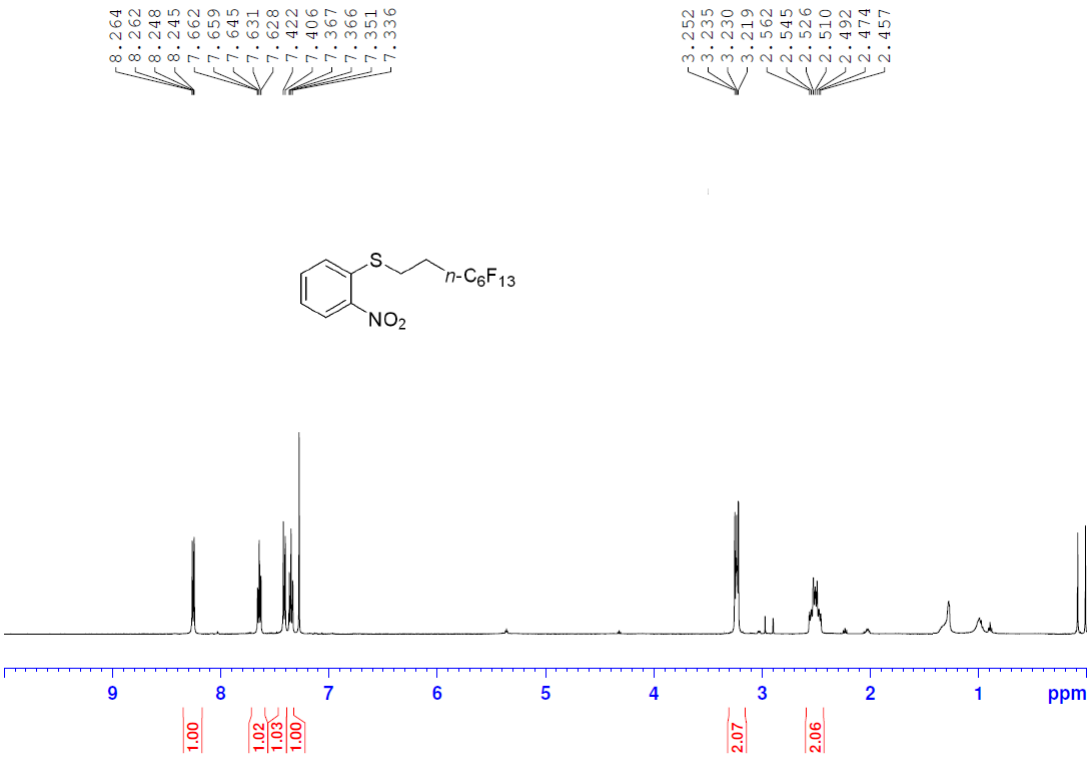
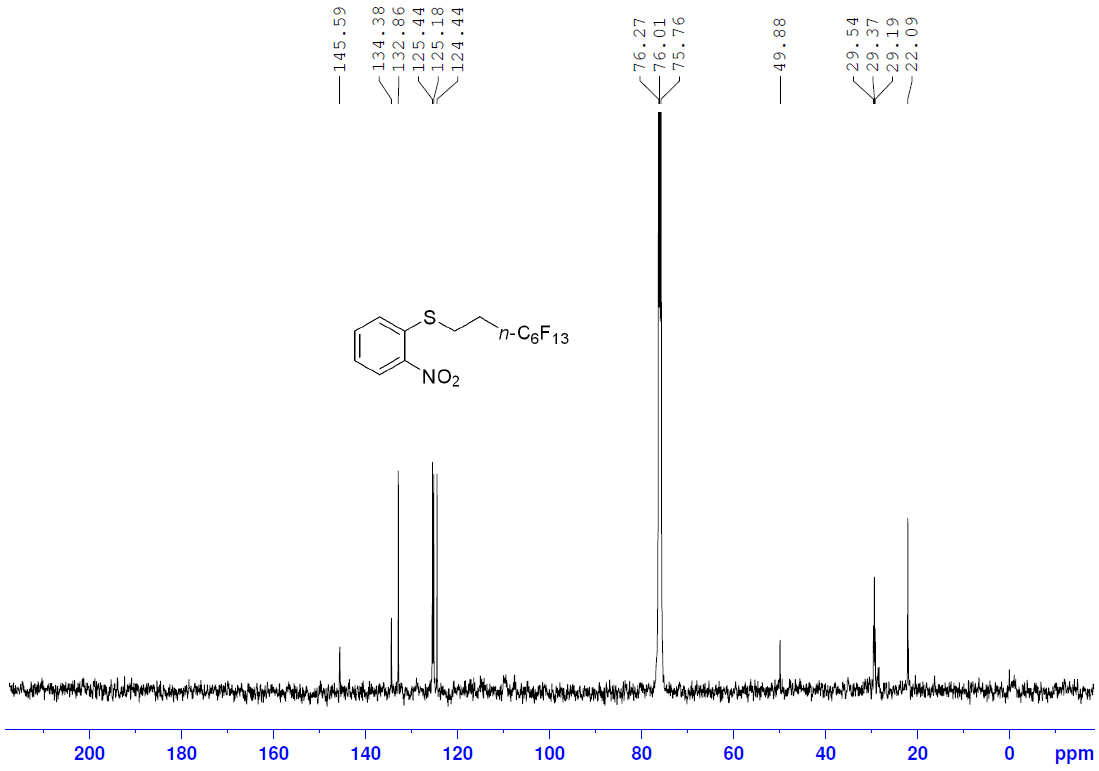


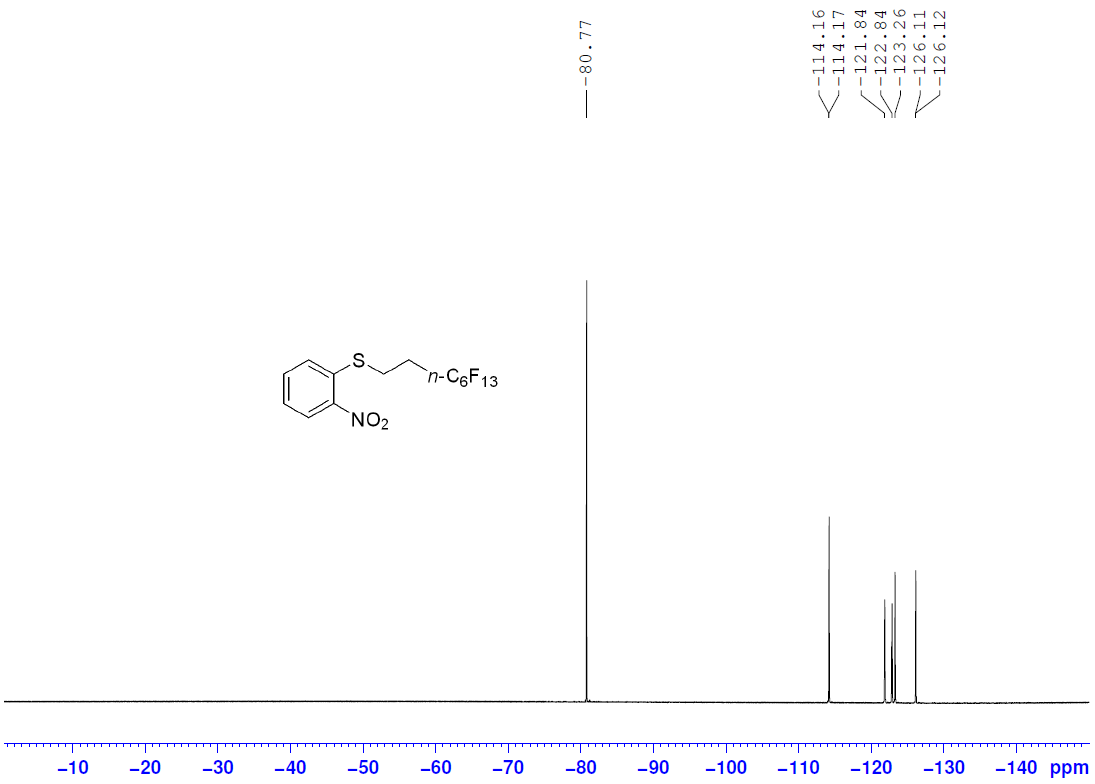
^{13}C NMR **3i**



^{1}H NMR **3j**



^{13}C NMR **3j**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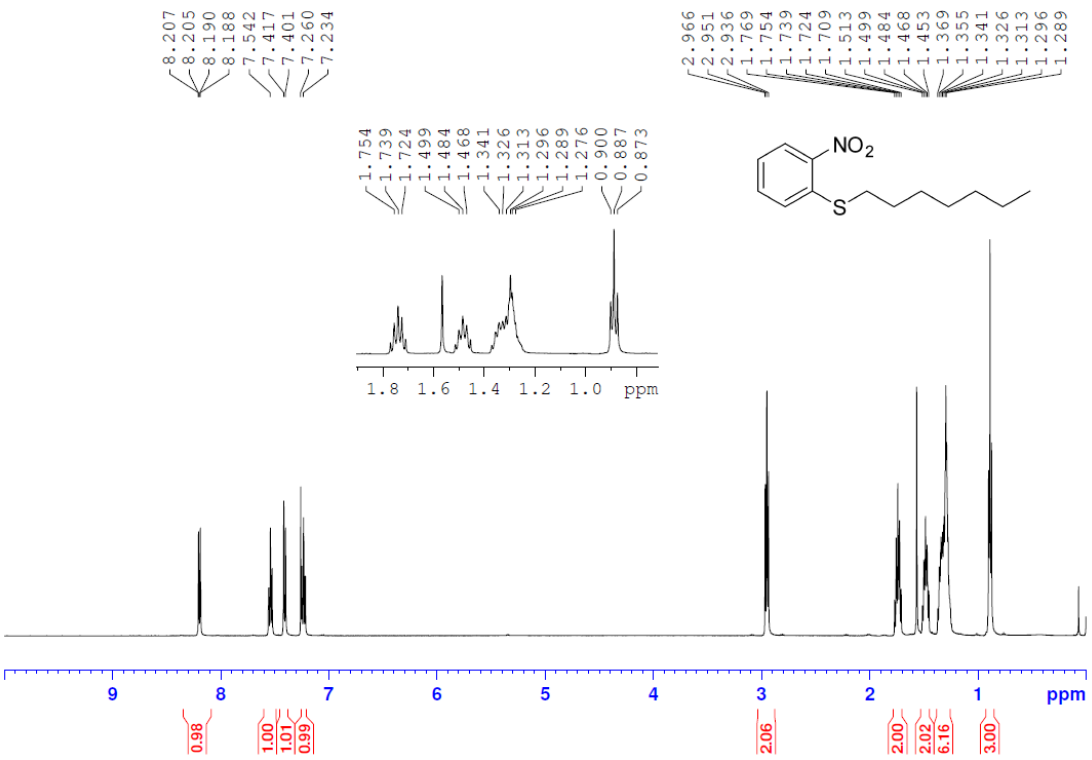
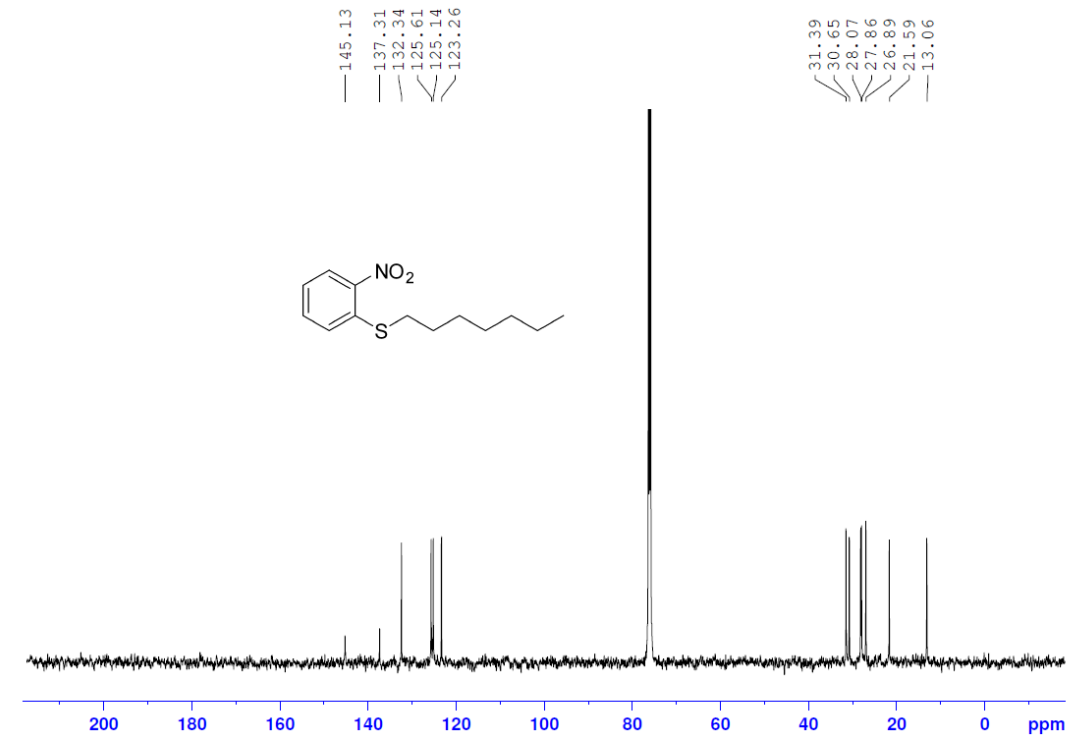
-114.16
-114.17
-121.84
-122.84
-123.26
-126.11
-126.12
S
n-C6F13
NO2
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm

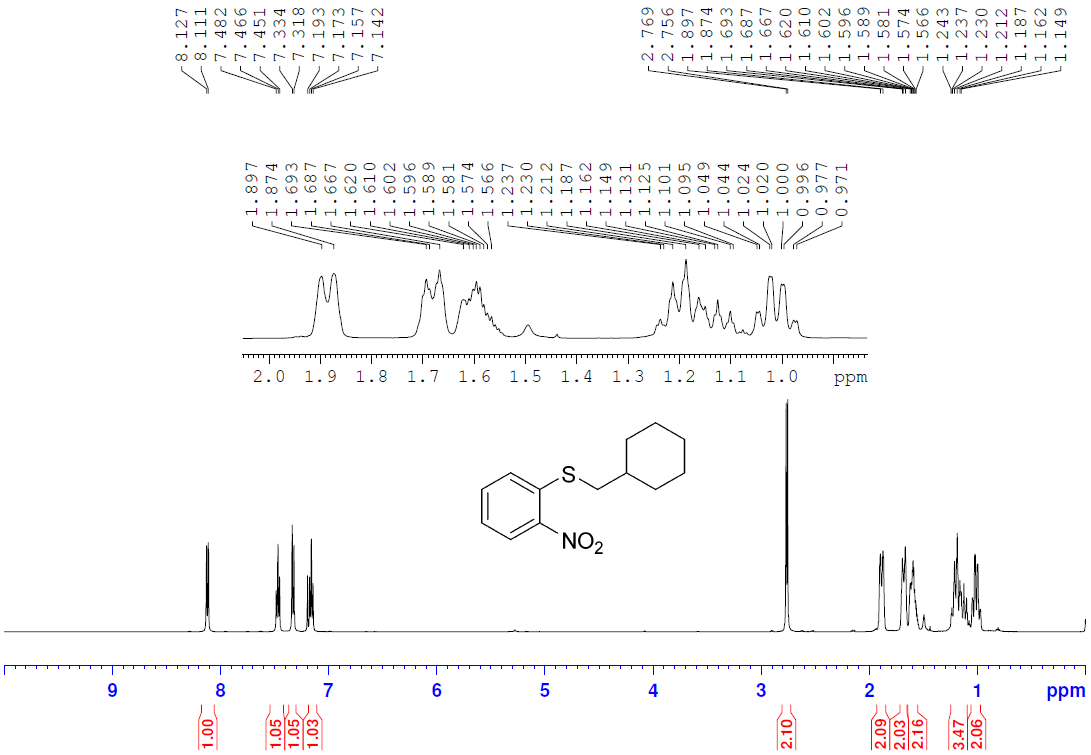
^{19}F NMR **3j**



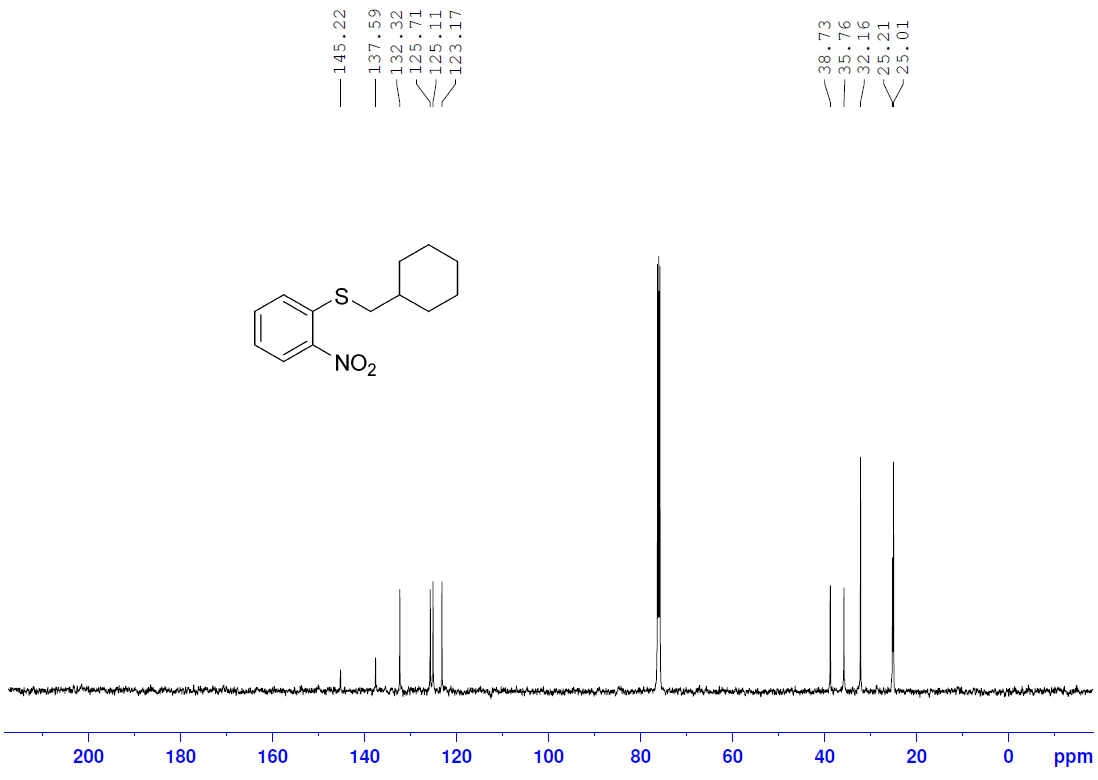
^{1}H NMR **3k**



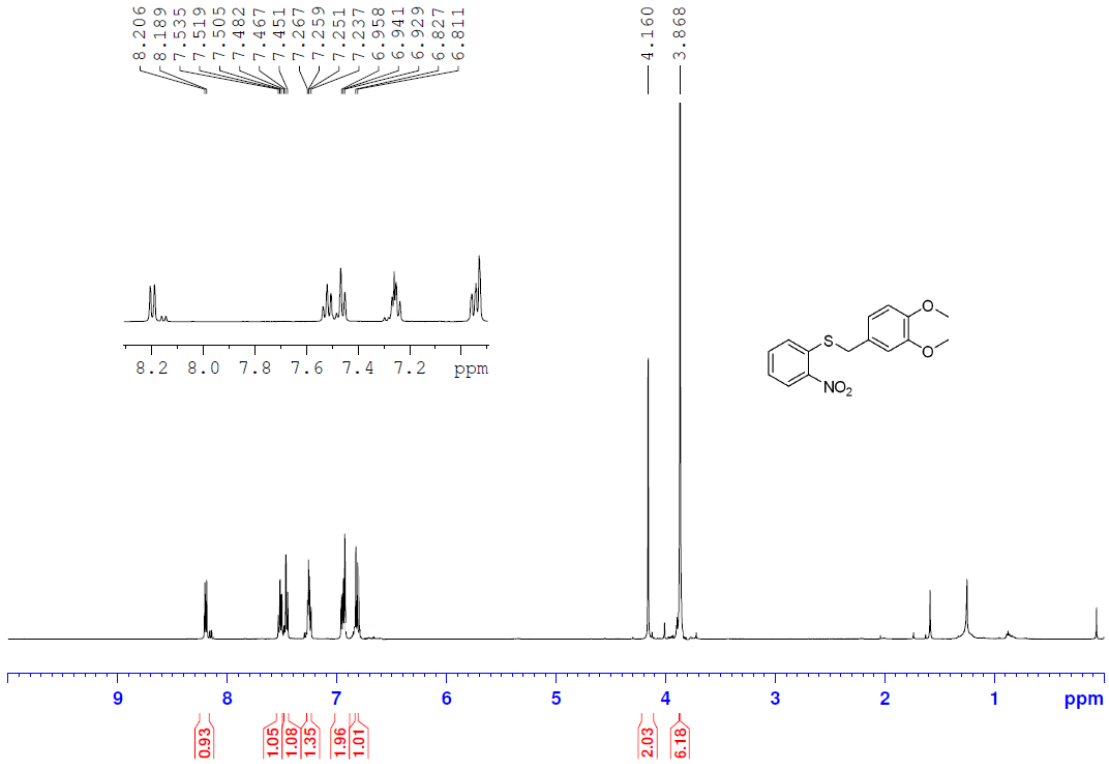
^{13}C NMR **3k**



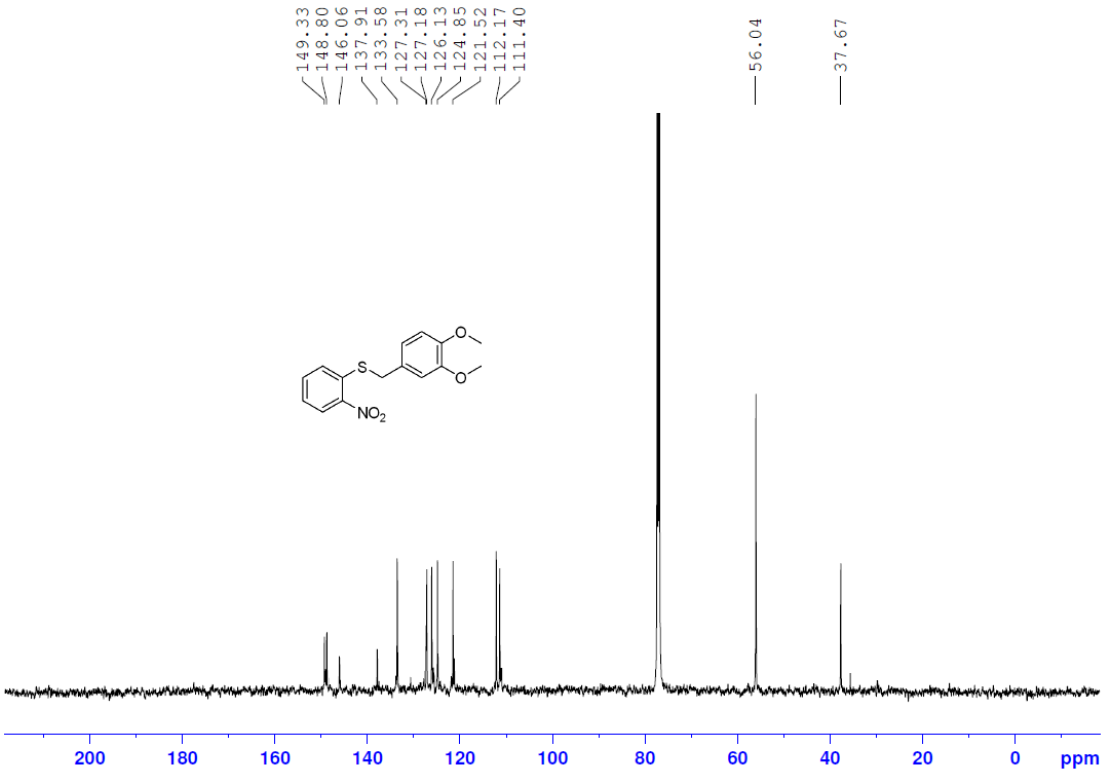
^{1}H NMR **3l**



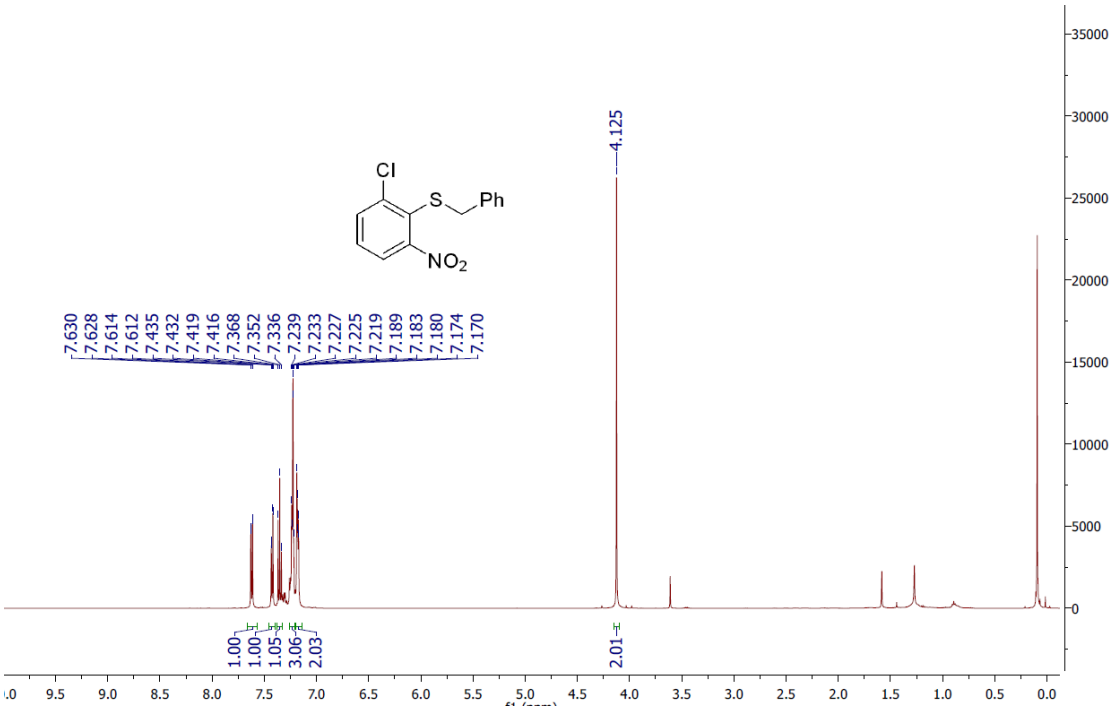
^{13}C NMR **3l**



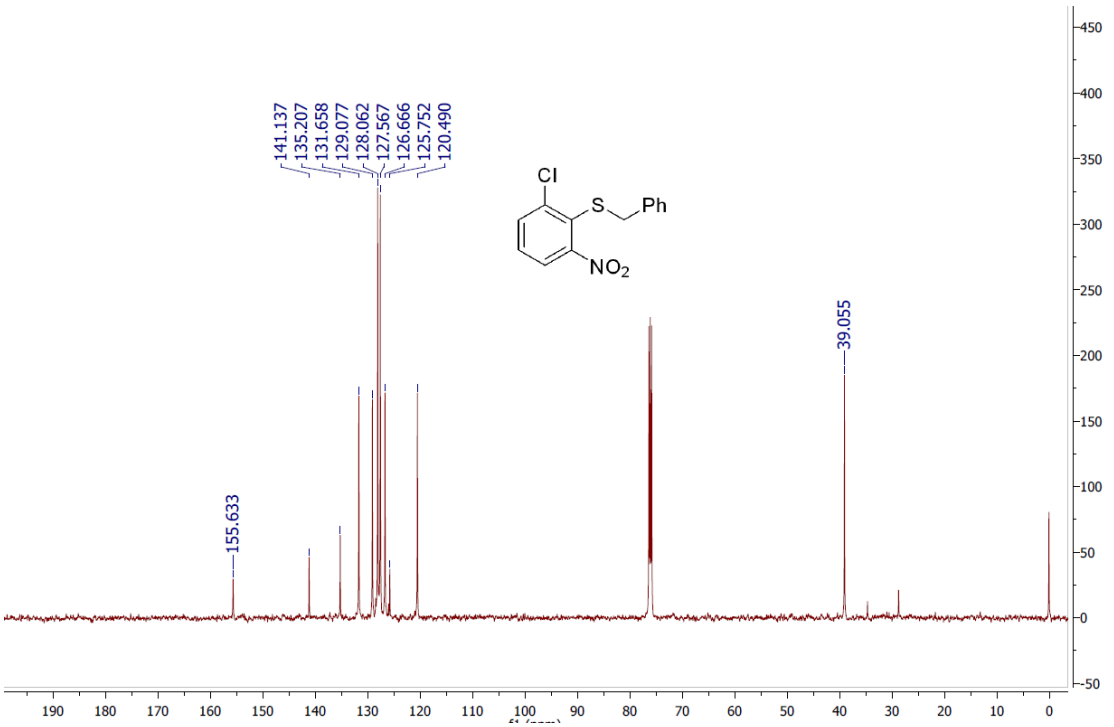
^{1}H NMR **3m**



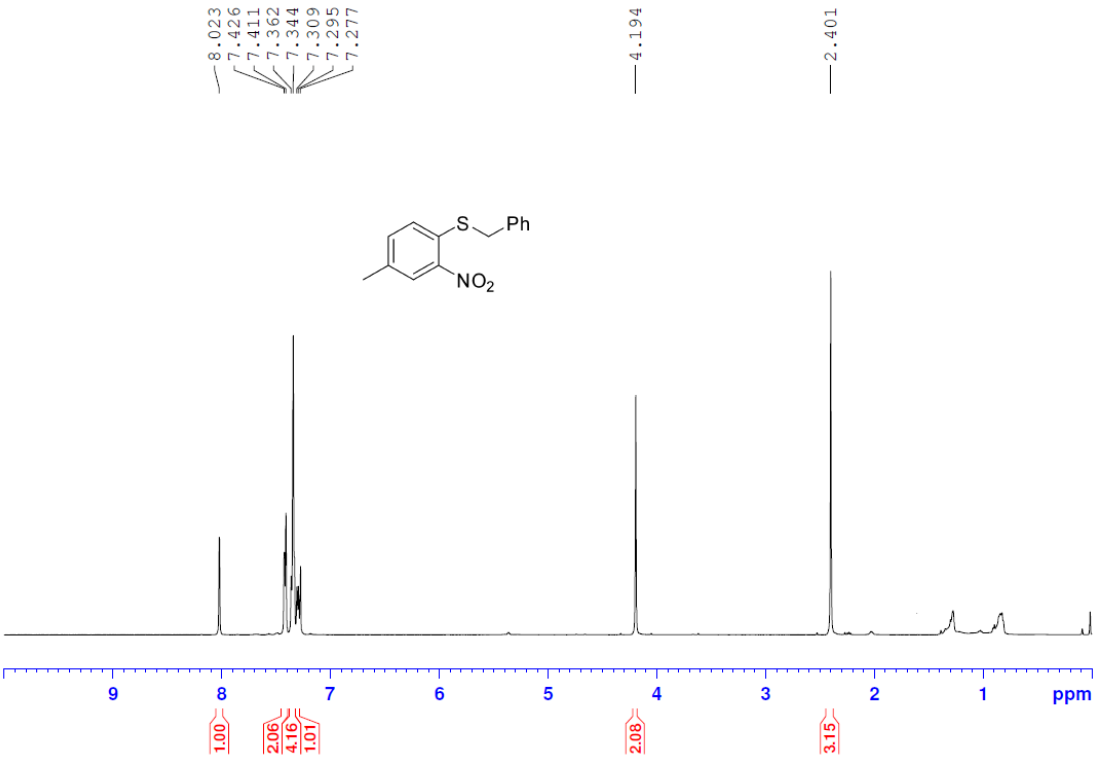
^{13}C NMR **3m**



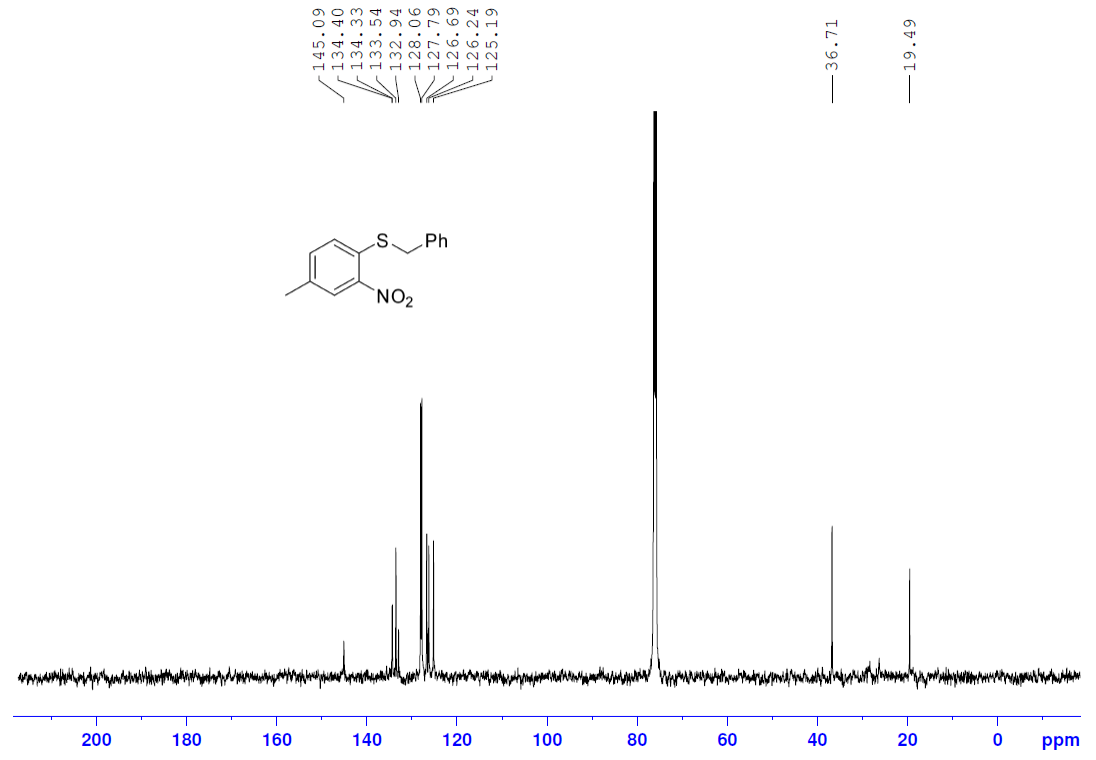
^{1}H NMR **3n**



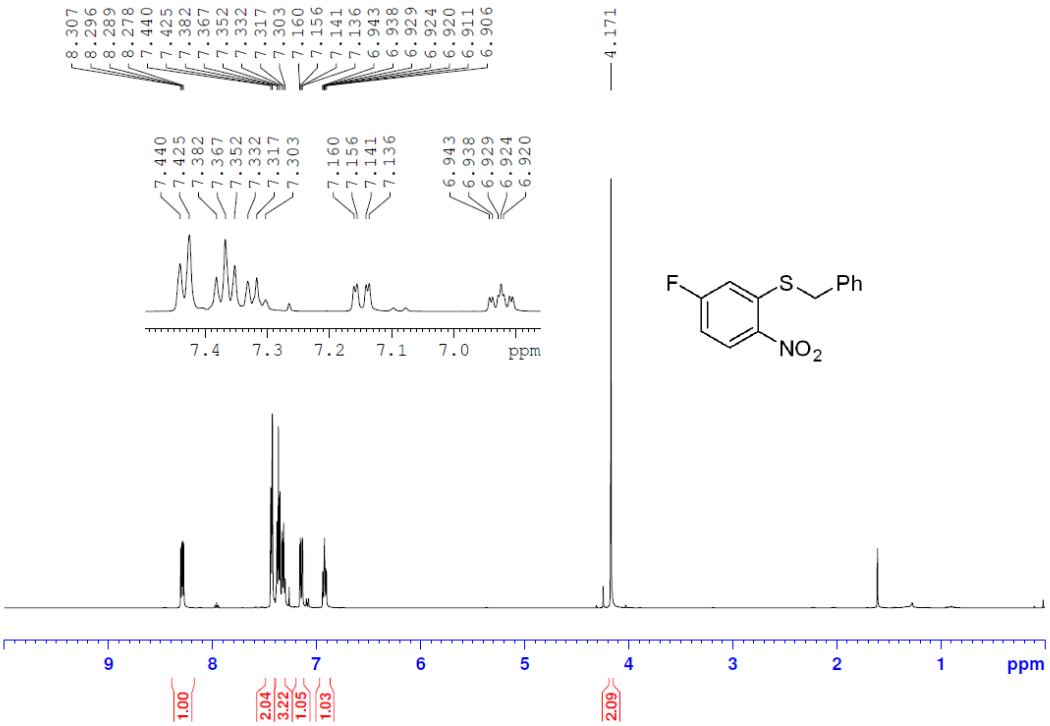
^{13}C NMR **3n**



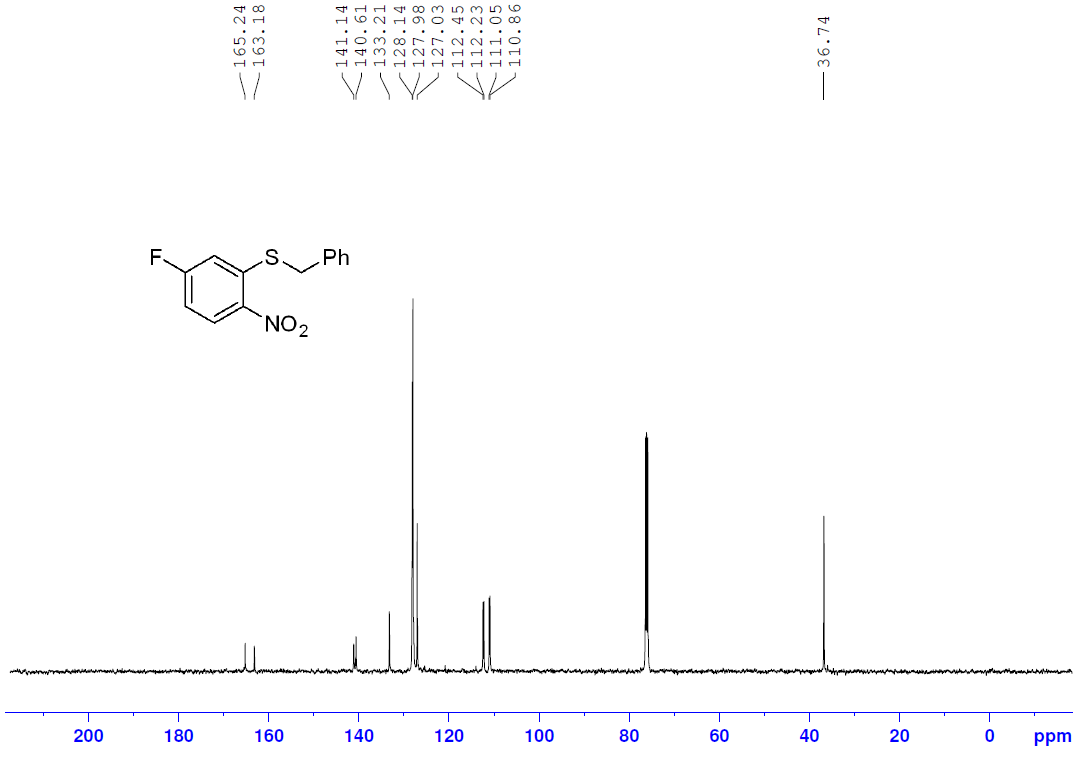
^{1}H NMR **3o**



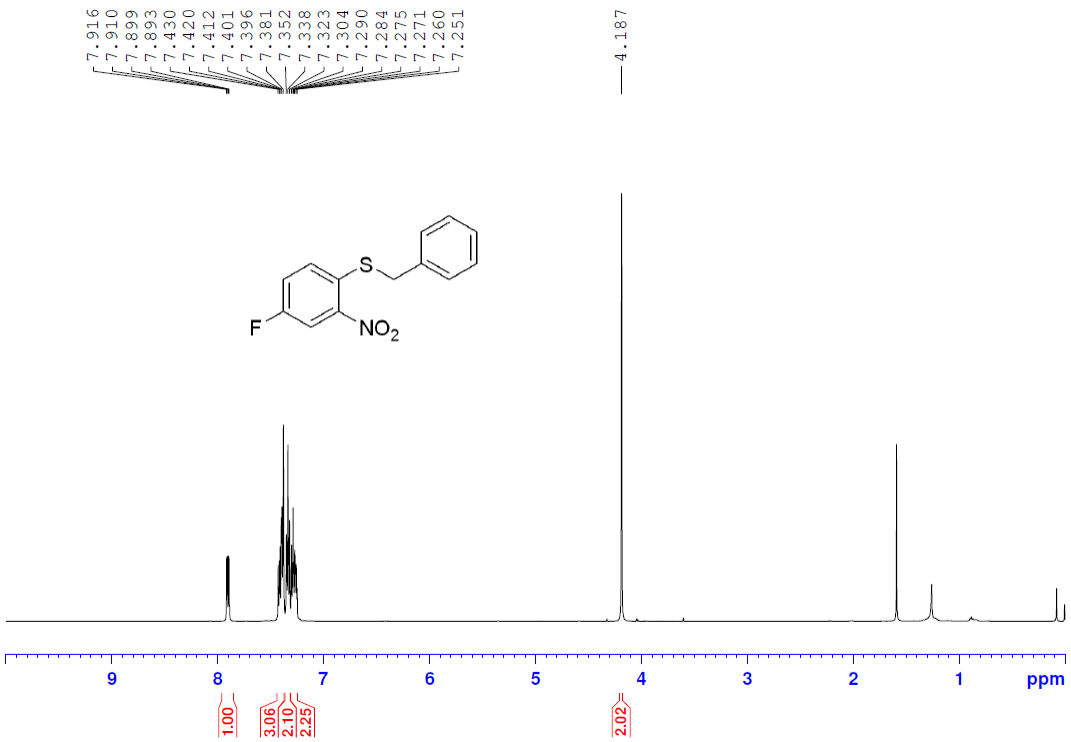
^{13}C NMR **3o**



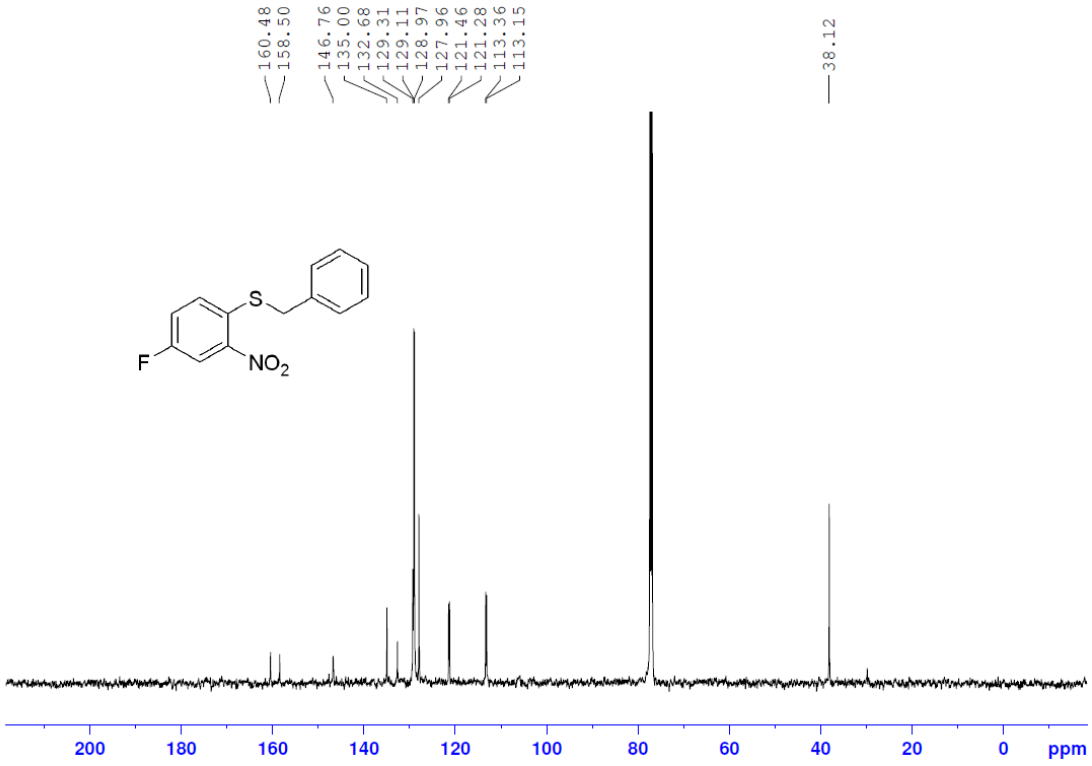
^{1}H NMR **3p**



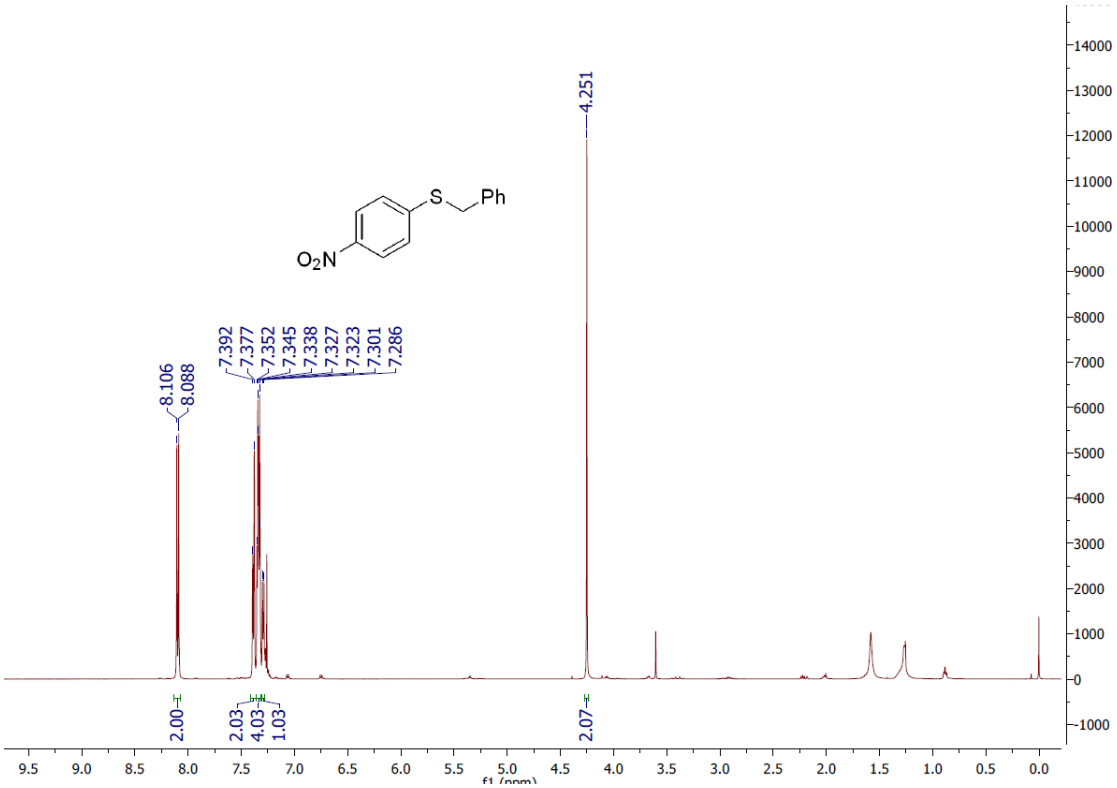
^{13}C NMR **3p**



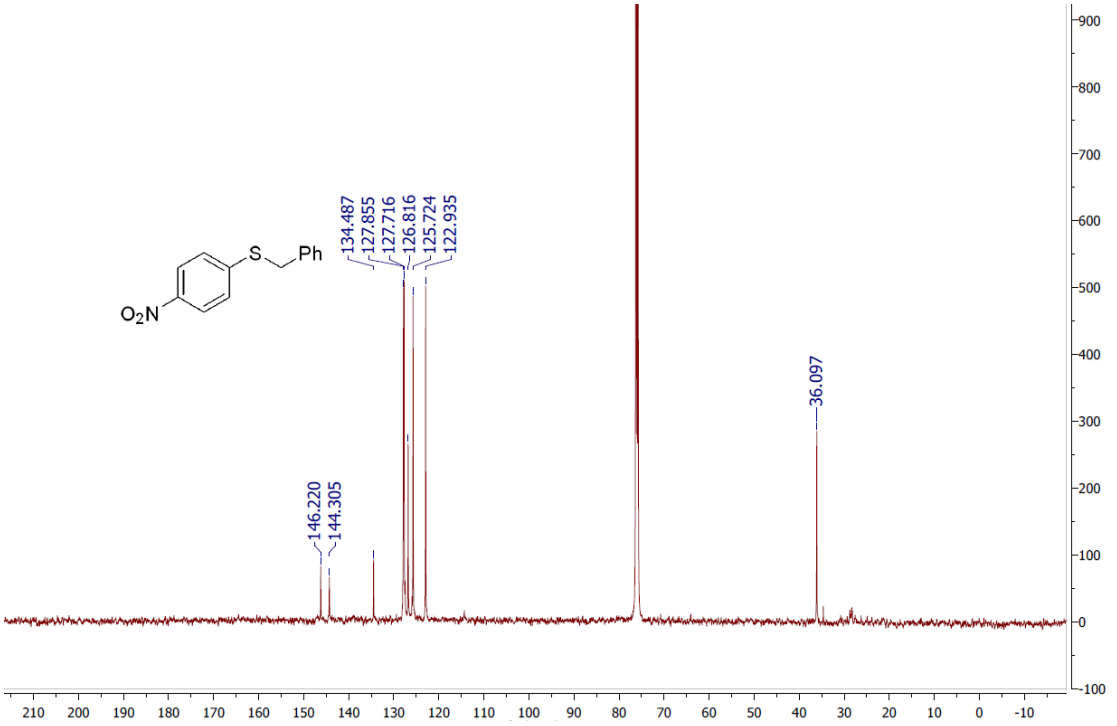
^{1}H NMR **3q**



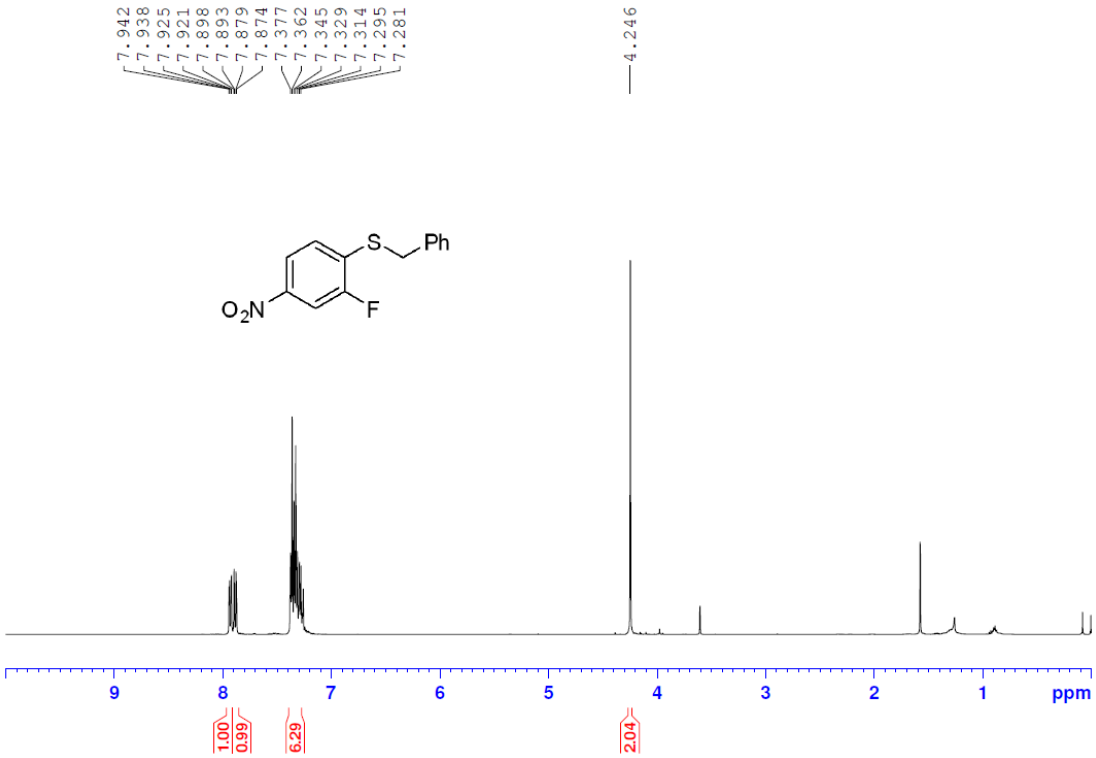
^{13}C NMR **3q**



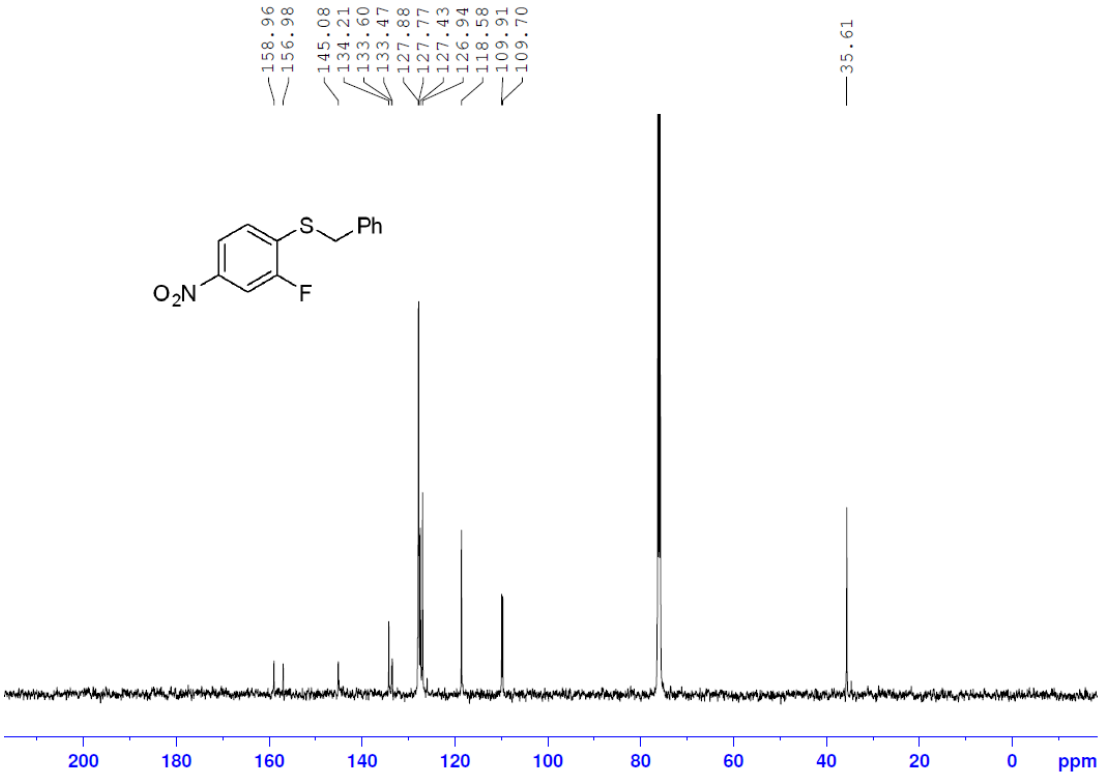
^{1}H NMR **3r**



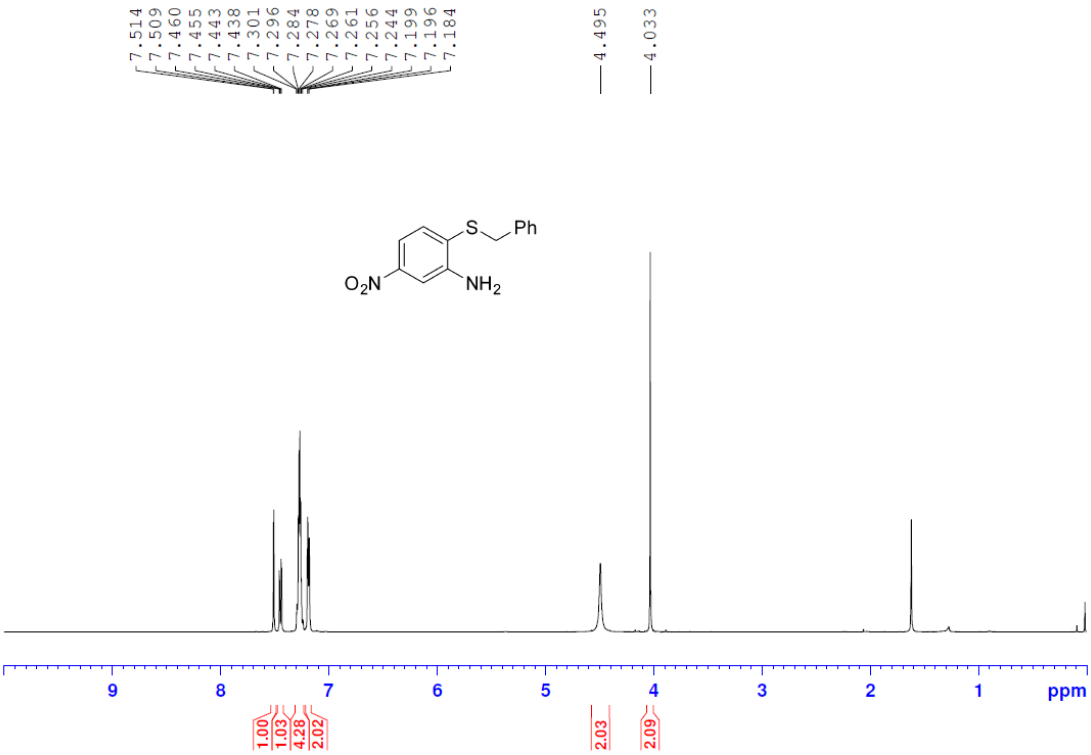
^{13}C NMR **3r**



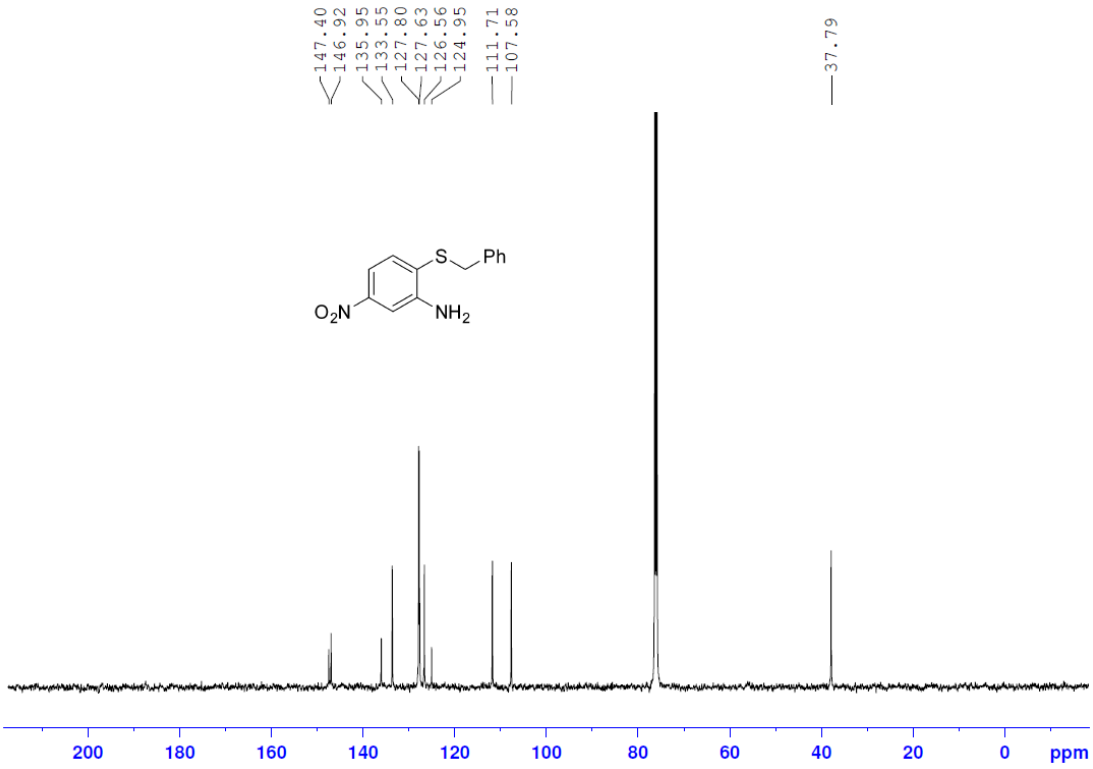
^{1}H NMR **3s**



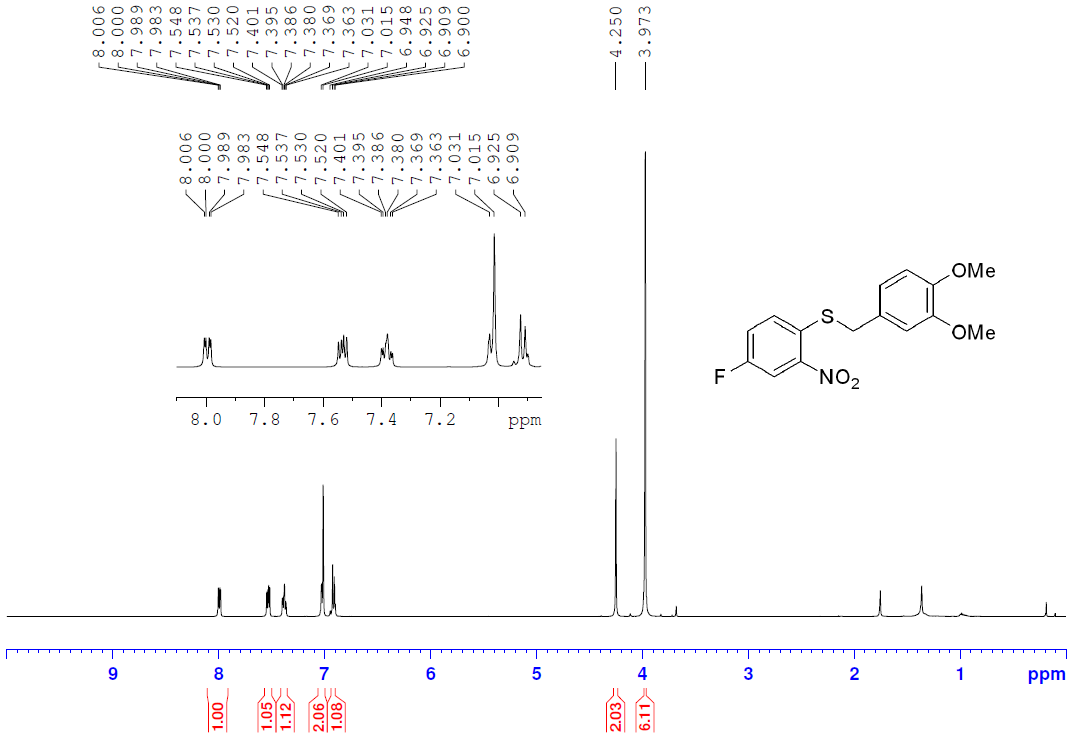
^{13}C NMR **3s**



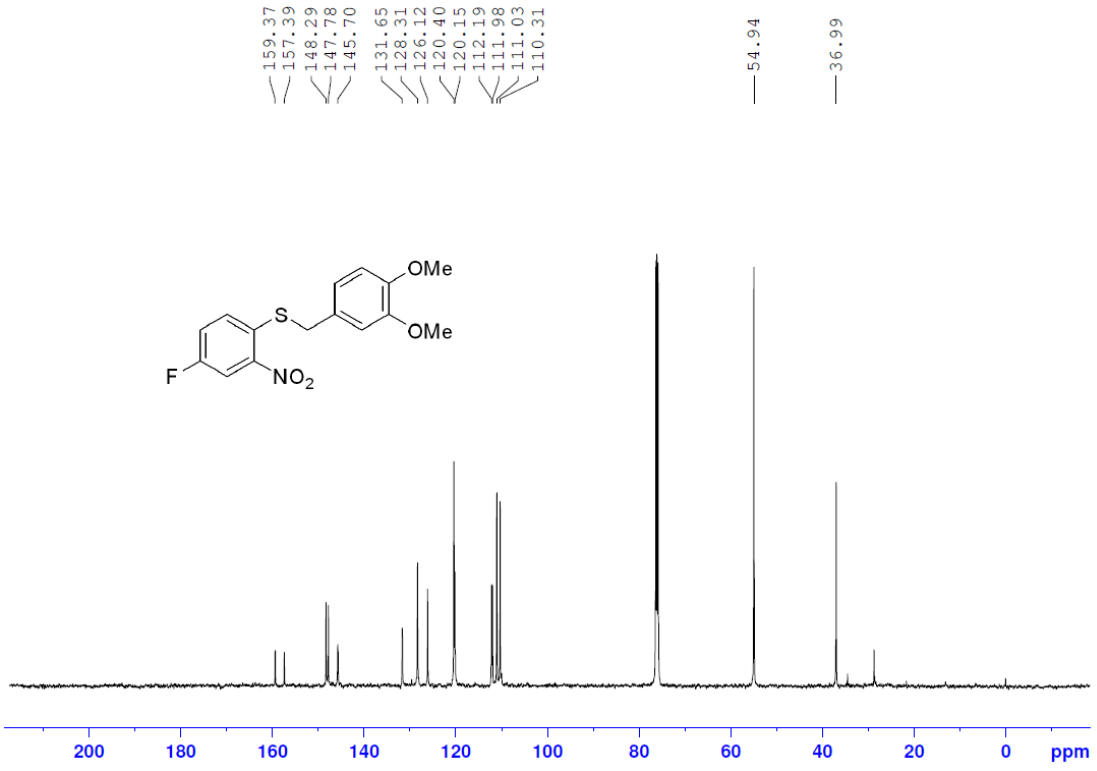
^{1}H NMR **3t**



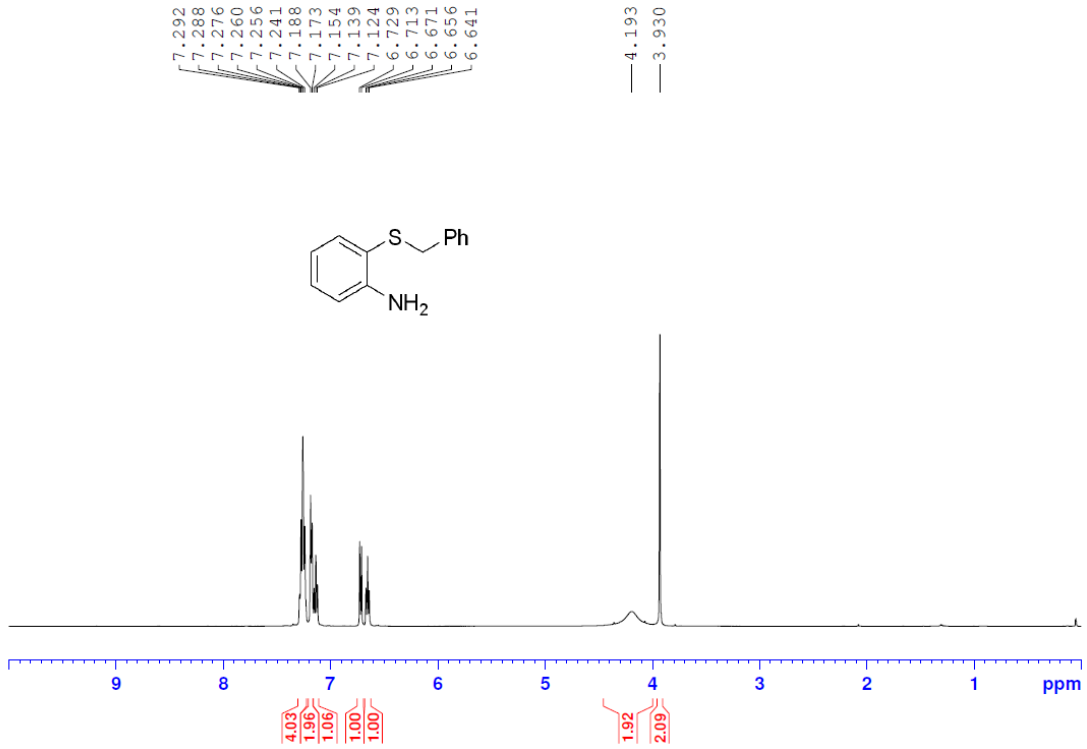
^{13}C NMR **3t**



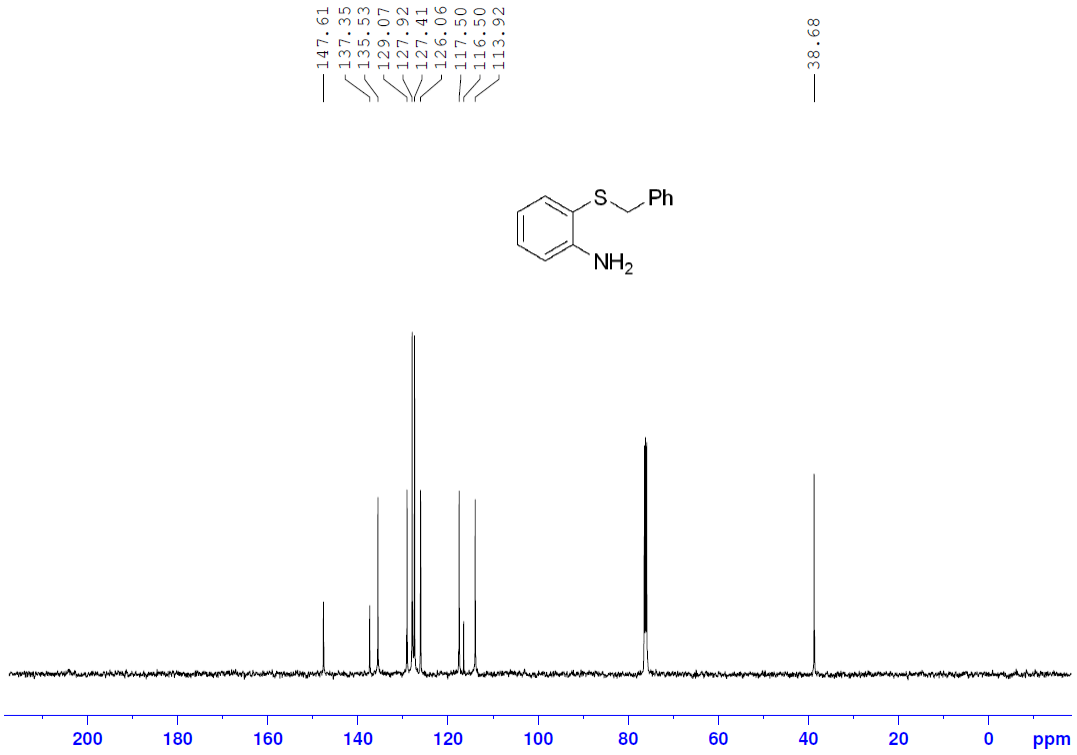
^{1}H NMR **3w**



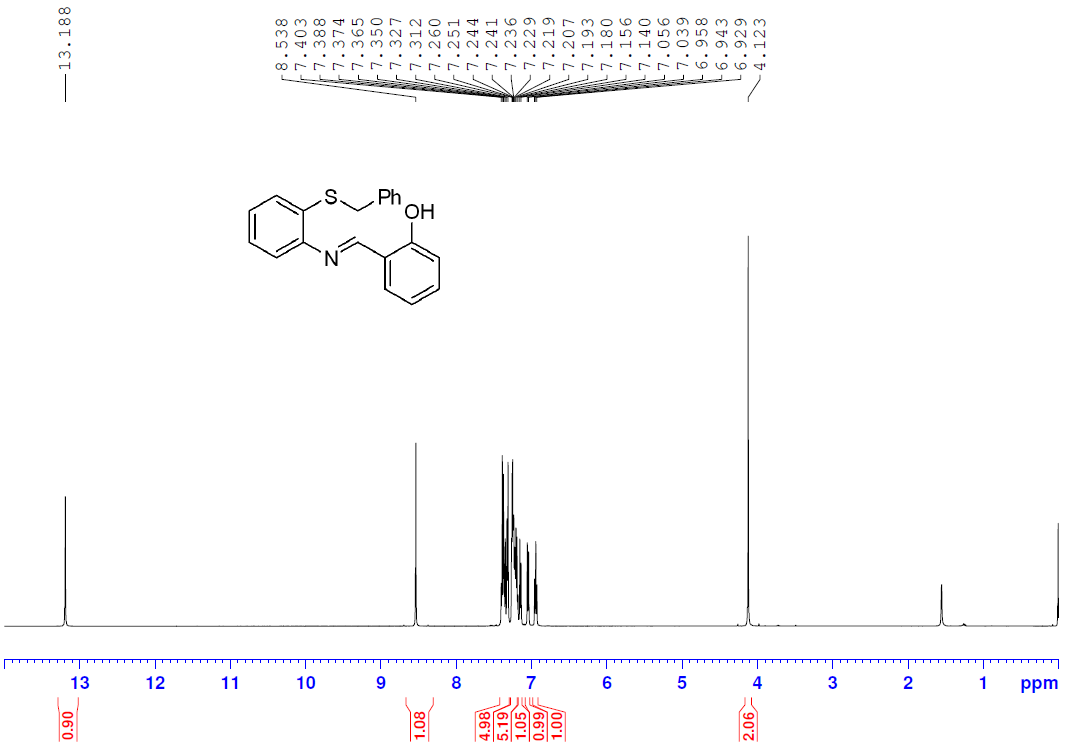
^{13}C NMR **3w**



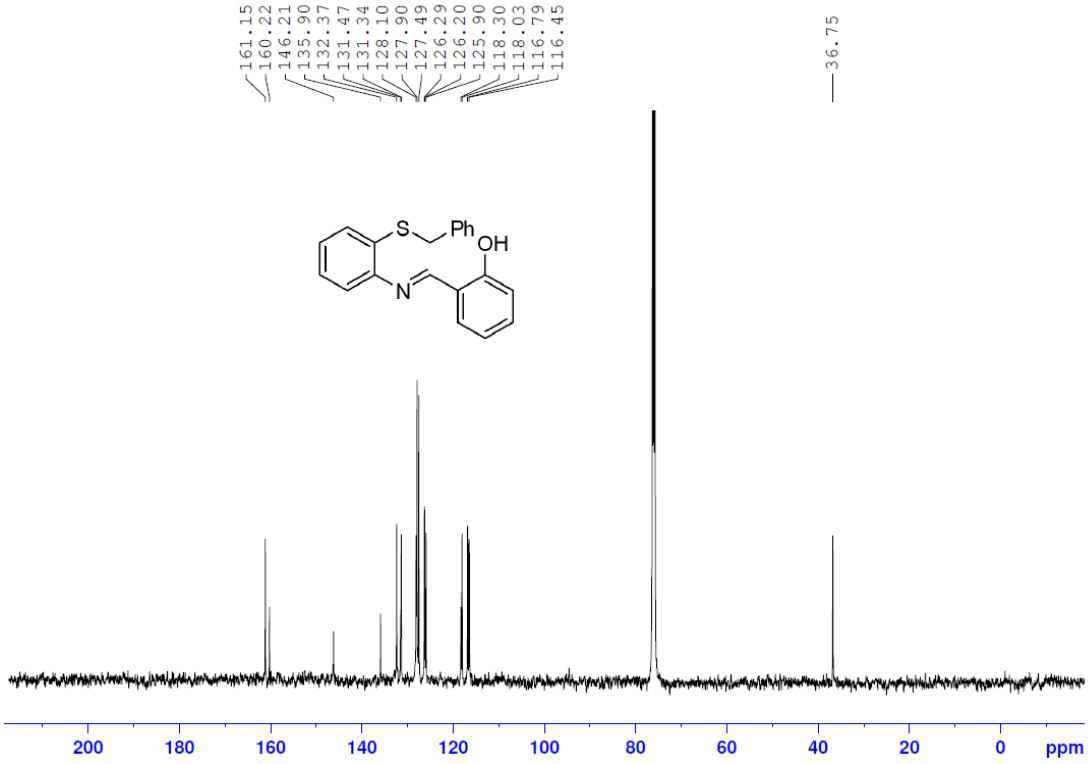
^{1}H NMR **6**



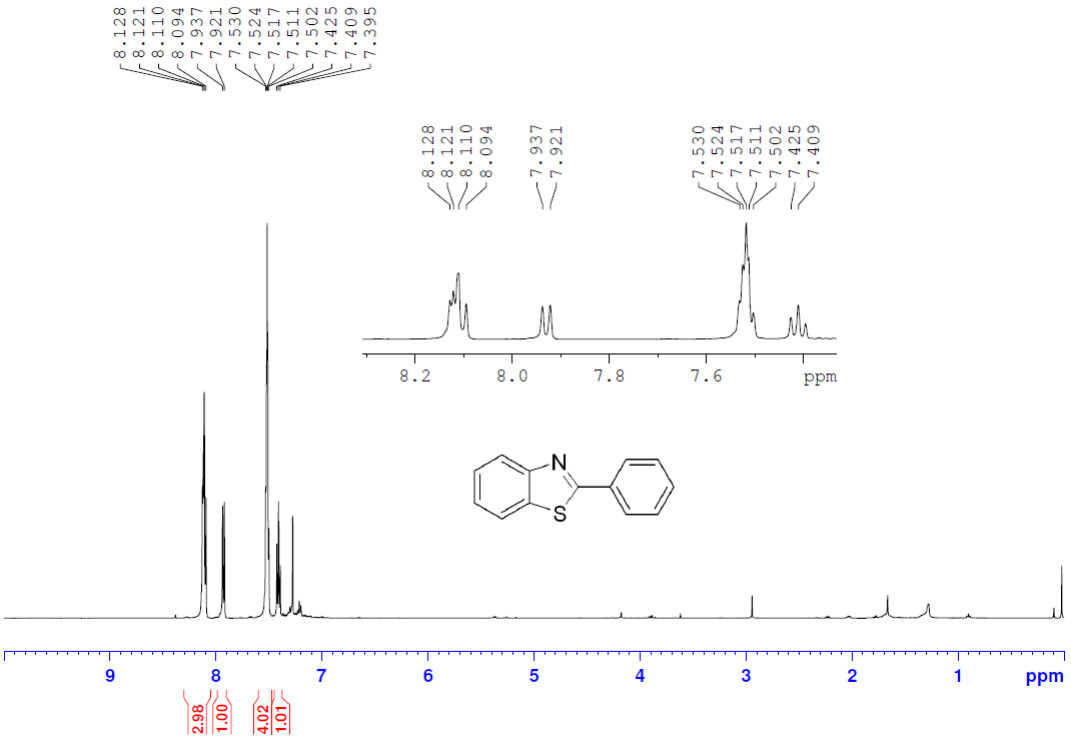
^{13}C NMR **6**



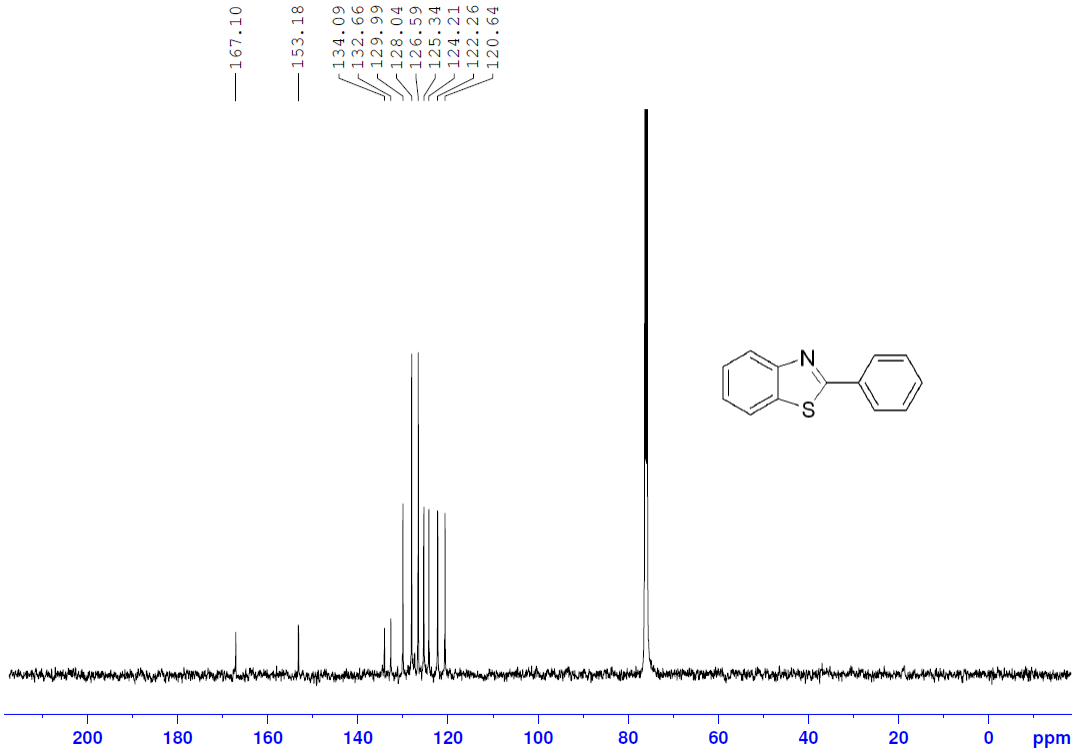
^{1}H NMR **7**



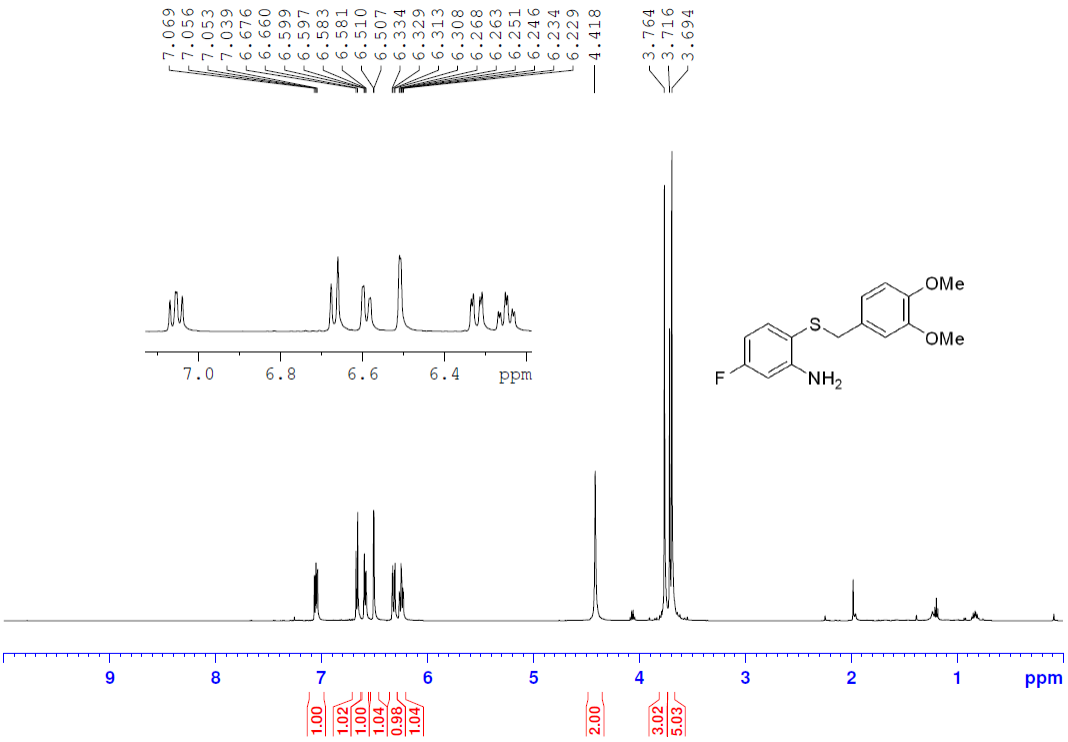
^{13}C NMR **7**



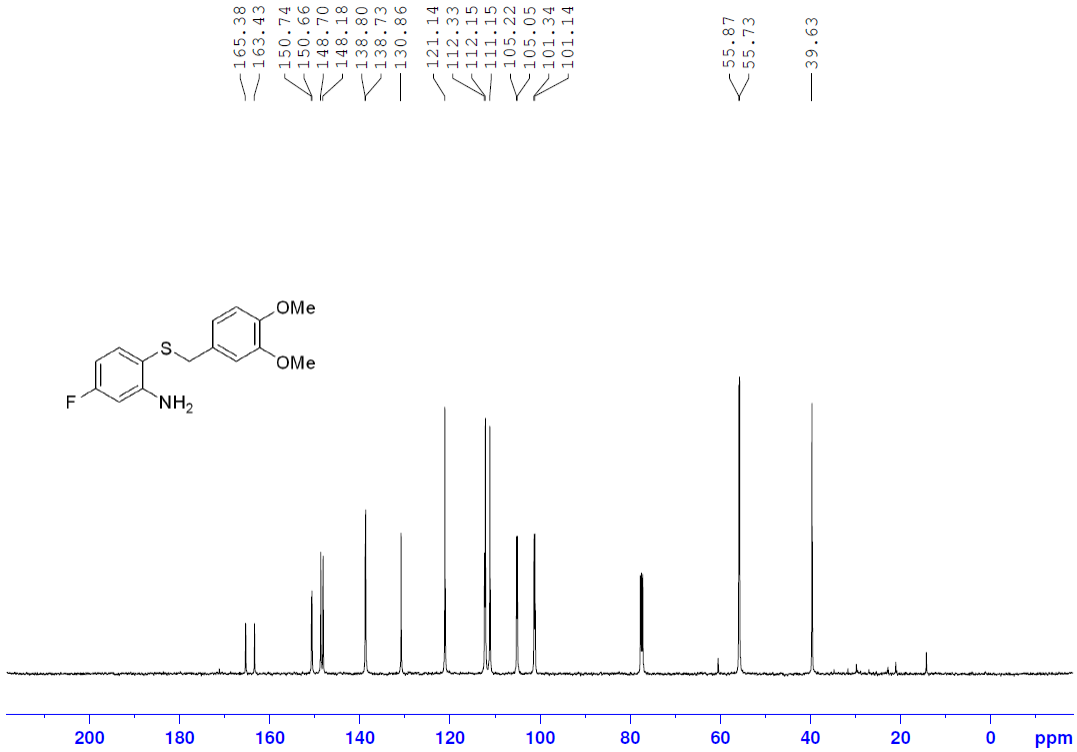
^{1}H NMR **8**



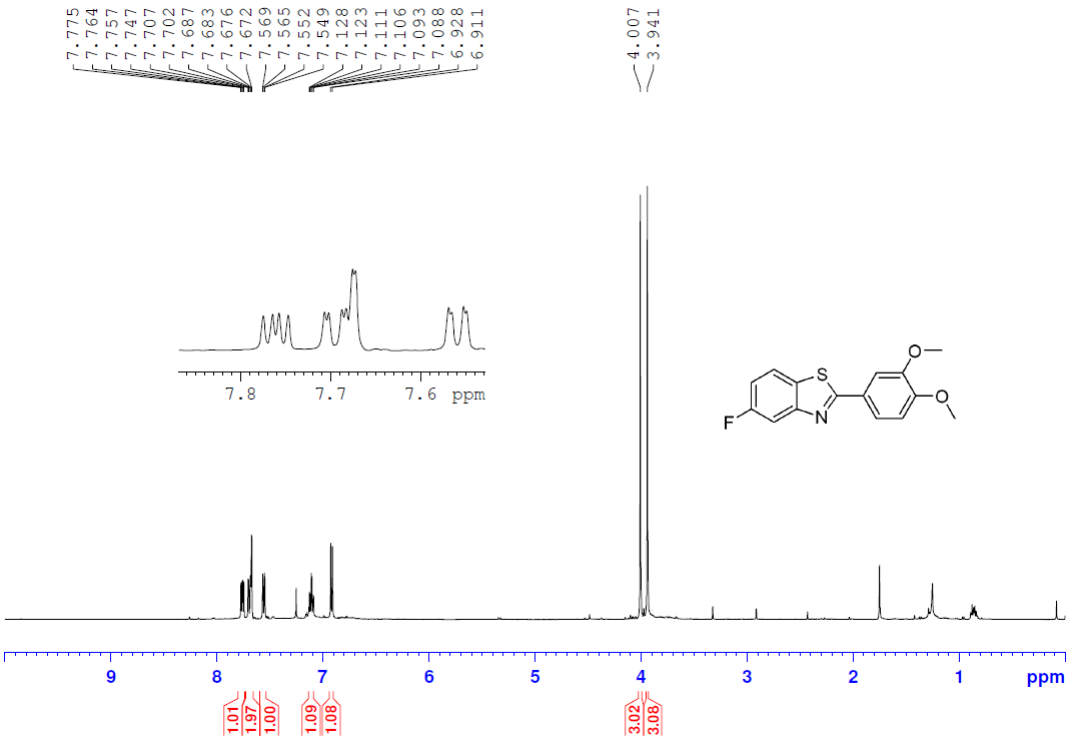
^{13}C NMR **8**



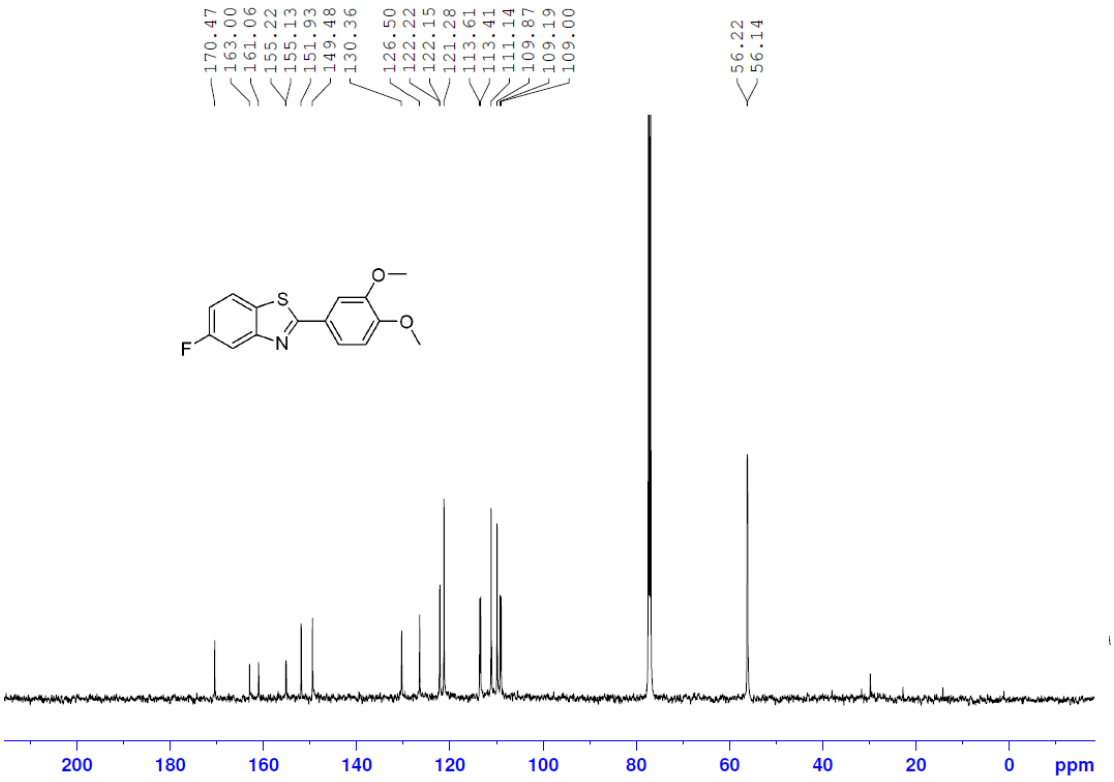
^{1}H NMR **9**



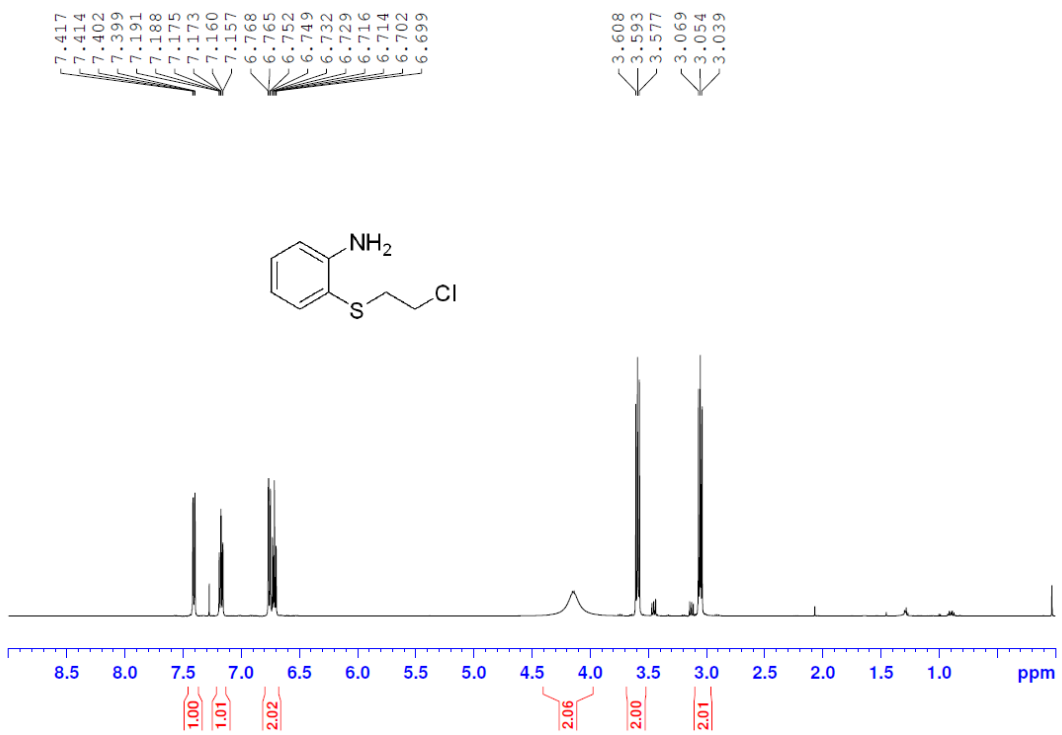
^{13}C NMR **9**



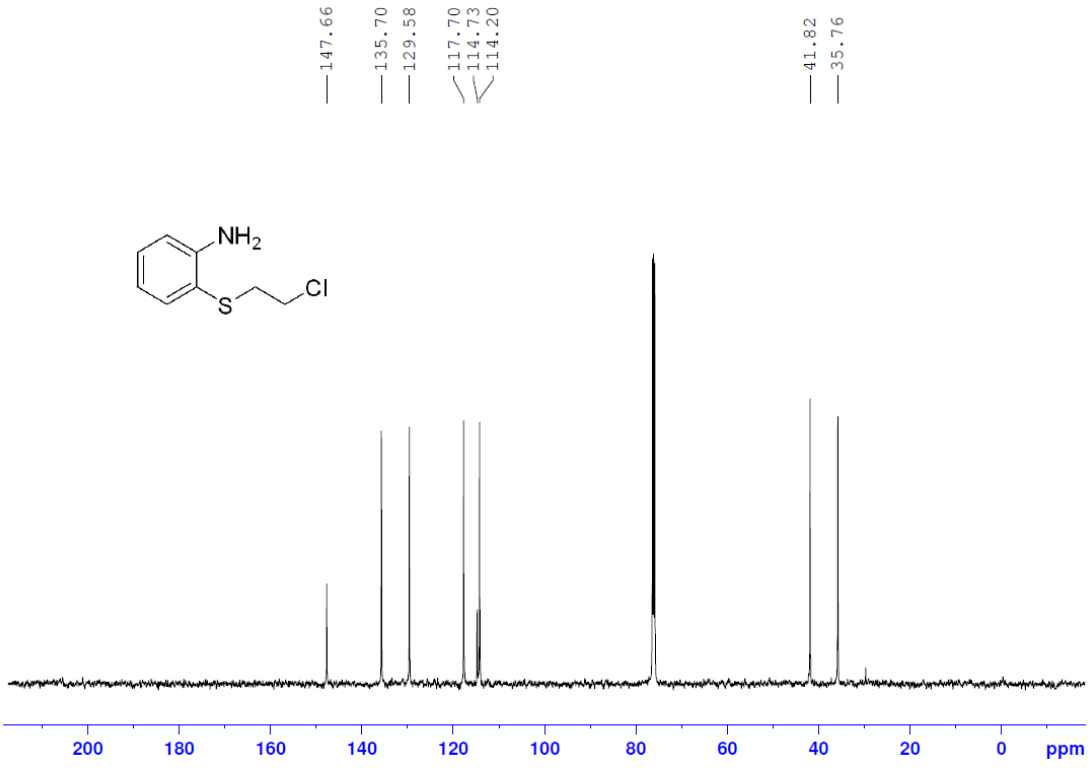
^{1}H NMR **10**



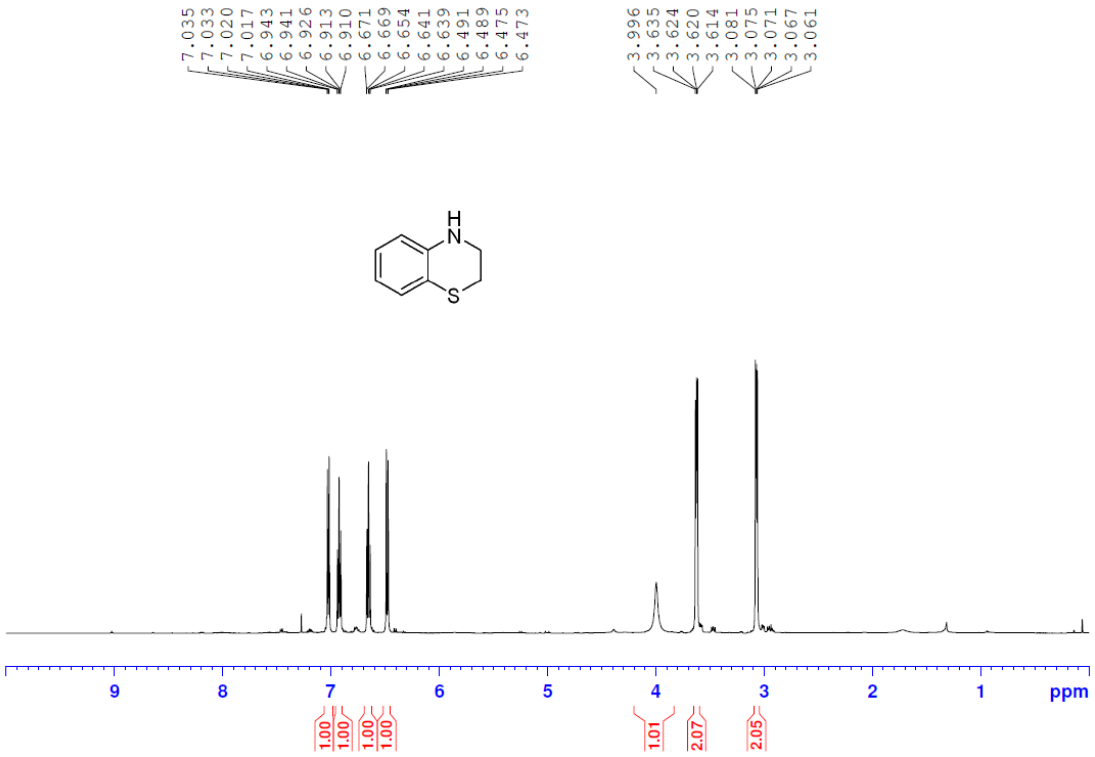
^{13}C NMR **10**



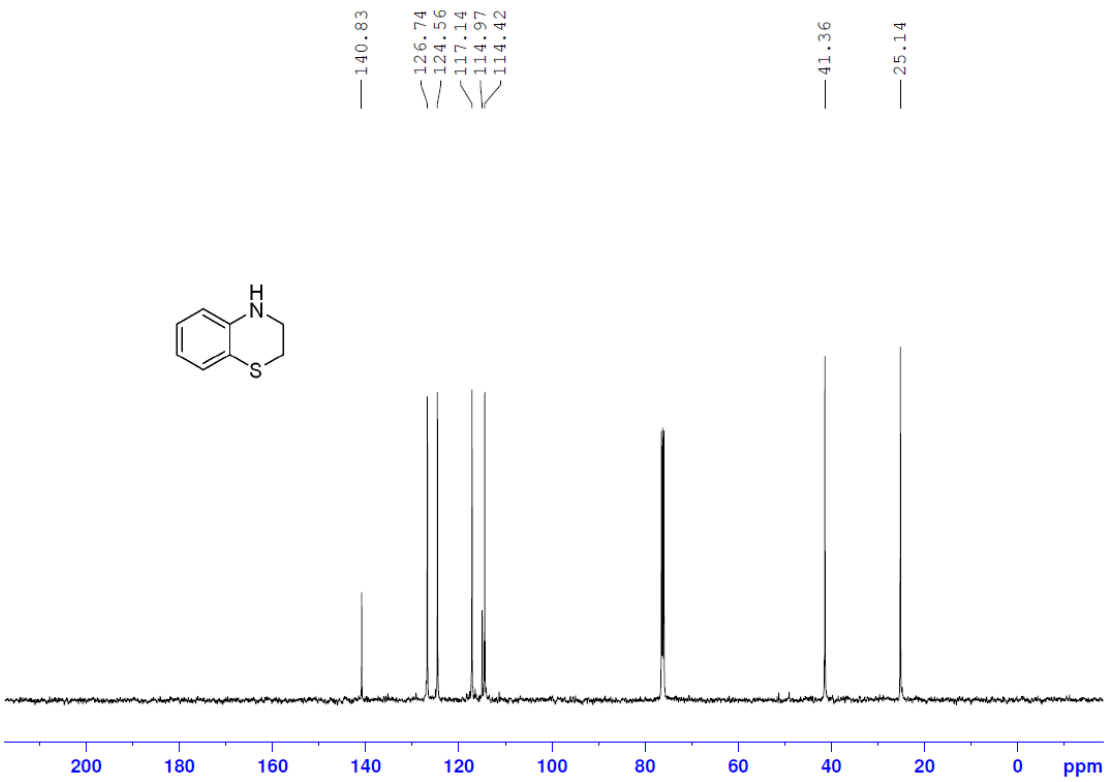
^{1}H NMR **11**



^{13}C NMR **11**



^{1}H NMR **12**



^{13}C NMR **12**