Divergent Process for the Decarboxylative Thiocyanation and Isothiocyanation of Alkyl Carboxylic Acids Promoted by Visible Light

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Supporting Information

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1. General information

All the glassware used was oven-dried (100 °C for 16 h) and the reactions were carried out under argon unless otherwise stated. Analytical thin layer chromatography was performed on silica gel aluminum plates with F-254 indicator and visualized by UV light (254 nm). Thiocyanate compounds were revealed using chemical staining with a $KMnO_4$ solution. Flash chromatography on silica gel was performed using 0.040 – 0.063 mm silica. ^{1}H NMR spectra were recorded on a Bruker DXP 300 MHz or 400 MHz spectrometer at 300.1 MHz or 400.2 MHz, ^{13}C NMR spectra at 75.5 MHz or 100.7 MHz, ^{19}F NMR spectra at 282.4 MHz Chemical shifts (δ) are quoted in parts per million (ppm) relative to residual solvent peak for $CDCl_3$ (δ_H = 7.26 ppm; δ_C = 77.0 ppm; or relative to external $CFCl_3$: δ = 0.0 ppm). Coupling constants (J) are quoted in Hz. The following abbreviations were used to show the multiplicities: br s: broad singlet, s: singlet, d: doublet, t: triplet, q: quadruplet, dd: doublet of doublet, qd: quadruplet of doublet, m: multiplet. High-resolution mass spectrometry (HRMS) was carried out on an electrospray ionization mass spectrometer with a micro-TOF analyzer. Infrared spectra were recorded on a Perkin Elmer FT-IR spectrometer Paragon 100 (ATR), the wave numbers (σ) of recorded IR-signals (ATR) are quoted in cm^{-1}. Melting points were measured on a STUART SMP3 melting point apparatus in open capillaries or on a Heizbank System Köfler WME and were uncorrected.

2. Materials

The UV-lamp used was a Kessil™ H150 (34 W, 456 nm) and the reaction was carried inside a mirror box (Figure S1 & S2). The temperature of the reaction was measured to be approximately 50 °C (+/- 2 °C) using a thermometer probe in a reaction tube (Figure S3). Chlorobenzene and dichloromethane were distilled over calcium hydride and stored under argon prior to use. Toluene was distilled over sodium/benzophenone. Anhydrous acetonitrile, methanol and dimethylsulfoxide were purchased from Acros Organics (Solvents Extra Dry Over Molecular Sieve, AcroSeal®). Chlorobenzene was degassed daily before use (Freeze-Pump-Thaw). Other solvents were purchased from Sigma Aldrich or Fisher Scientific and used without further drying. *tert*-butyl hypochlorite and silver selenocyanate were prepared as described in the literature.[1,2] Other carboxylic acids were purchased from Sigma Aldrich, Fisher Scientific, Apollo Scientific or TCI Chemicals and used without further purification. Substrates **1c**,[3] **1f**,[4] **1i**,[5,6] **1r**,[7] **1x**,[8] **1ah**,[9] **1ak**,[10] **1al**,[11] **1am**,[12] **1aw**[13] were synthesized according to literature procedures. The sources *N*-thiocyanatosaccharin **I**,[14] *N*-thiocyanatophthalimide **II**,[15] and *N*-selenocyanatosaccharin **III**[2] were prepared according to the literature. Synthesized thiocyanated compounds were stored under argon at -20 °C.

Figure S1: Picture of the mirror box.

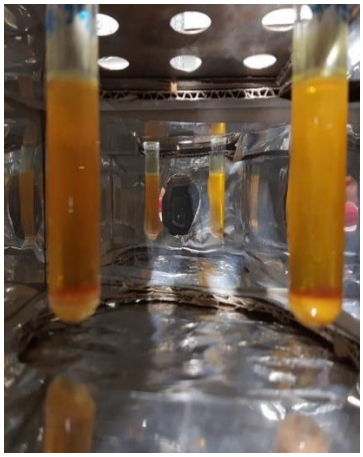


Figure S2: Inside view of the mirror box.

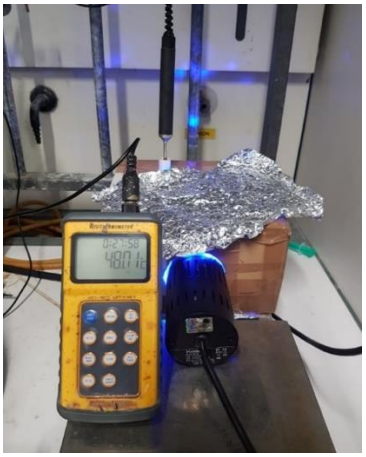
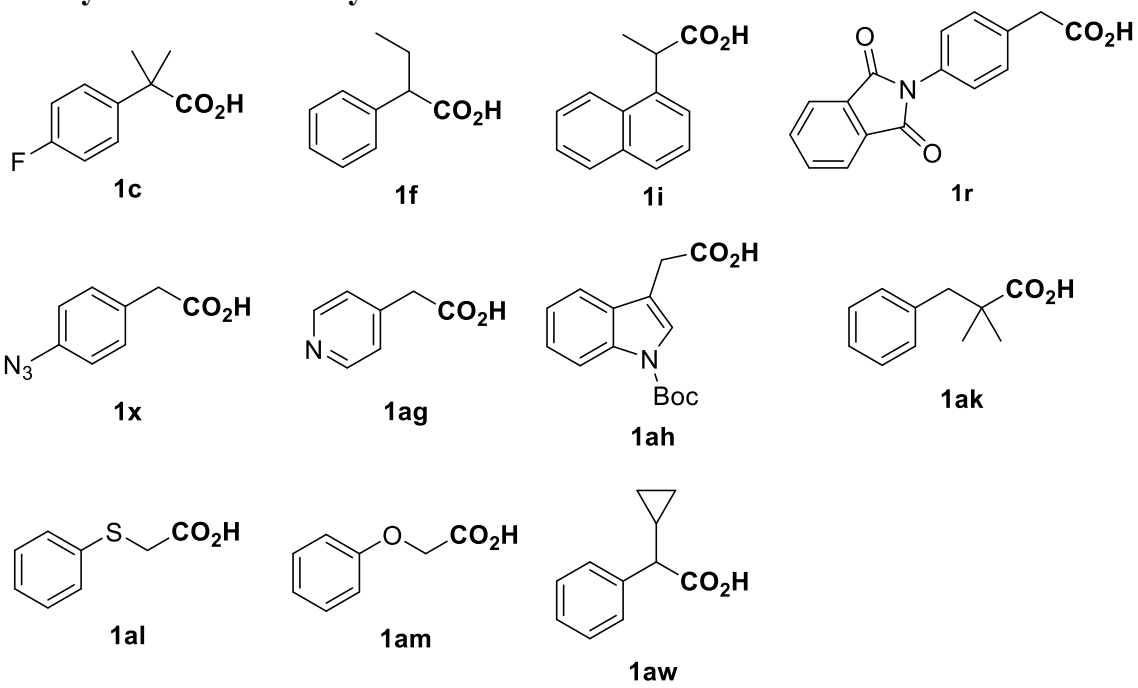


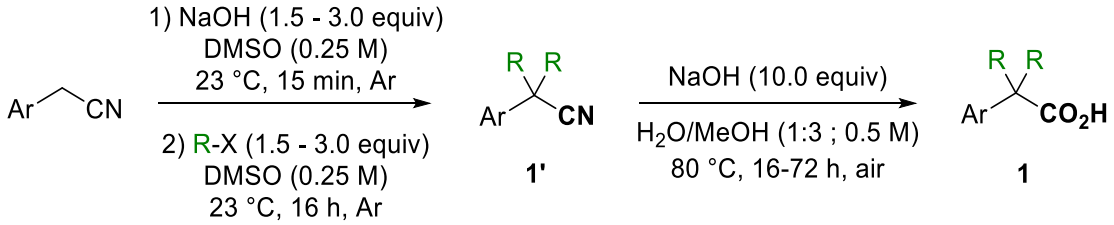
Figure S3: Apparatus with a temperature probe.

3. Synthesis of the carboxylic acids 1

List of synthesized carboxylic acids

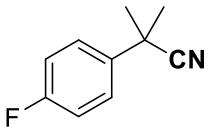


General procedure for the synthesis of 1c, 1f and 1i



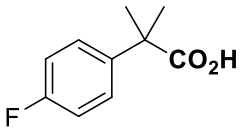
From a modified known procedure.[3] In an oven-dried reaction flask under argon was added sodium hydroxide (2.40 g, 60.0 mmol, 3.0 equiv) to a solution of the arylacetonitrile (20.0 mmol, 1.0 equiv) in dry DMSO (0.25 M). The solution mixture was stirred at 23 °C for 15 min and turned orange/red. Alkyl halide (60.0 mmol, 3.0 equiv) was added. The reaction mixture was stirred at 23 °C for 16 h, then diluted with water (100 mL). The aqueous layers were extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with water (5 × 20 mL), brine (20 mL), and dried over $MgSO_4$. Removal of the solvent under vacuum yielded the corresponding products **1'** as colorless oils, which were used in the second step without any further purification.

From a known procedure.[3] In a round-bottom flask under air was added sodium hydroxide (8.0 g, 200.0 mmol, 10.0 equiv) to a solution of **1'** (20.0 mmol, 1.0 equiv) in a water/methanol mixture (1:3 ratio, 0.5 M). The solution mixture was stirred at reflux for 16 h to 72 h. When TLC (eluent: *n*-pentane/ethyl acetate, 7:3) showed full completion of the reaction, the solution was acidified with an aqueous HCl solution (2 M) until pH = 2. The solution was then extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. The solvents were evaporated under vacuum to yield the corresponding arylacetic acids **1c**, **1f** and **1i** as white solids.



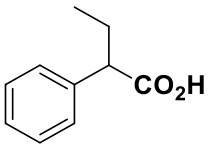
1c'

2-(4-Fluorophenyl)-2-methylpropanenitrile **1c'** was synthesized following the general procedure. The product was obtained as a colorless oil and was sufficiently pure for the next step (1.66 g, 99%). R_f (*n*-pentane/ethyl acetate, 9:1): 0.90. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.52 – 7.38 (m, 2H), 7.16 – 7.00 (m, 2H), 1.72 (s, 6H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ -114.50 – -114.62 (m). NMR data were in accordance with the literature.[16]



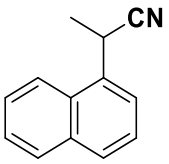
1c

2-(4-Fluorophenyl)-2-methylpropanoic acid **1c** was synthesized following the general procedure on a 8.9 mmol scale and obtained as a white solid (1.48 g, 91%). R_f (*n*-pentane/ethyl acetate/AcOH, 90:9:1): 0.32. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.08 – 6.97 (m, 2H), 1.59 (s, 6H). **^{19}F NMR** (282.4 MHz, CDCl3) δ -116.51 – -116.63 (m). NMR data were in accordance with the literature.[3]



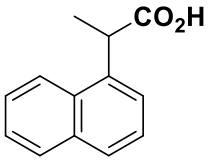
1f

2-Phenylbutyric acid **1f** was synthesized from commercially available α-ethylbenzene acetonitrile following the second step of the general procedure on a 10.0 mmol scale and obtained as a white solid (1.58 g, 96%). **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 12.07 (s, 1H), 7.40 – 7.27 (m, 5H), 3.47 (t, J = 7.7 Hz, 1H), 2.22 – 2.04 (m, 1H), 1.92 – 1.74 (m, 1H), 0.92 (t, J = 7.4 Hz, 3H). NMR data were in accordance with the literature.[4]



1i'

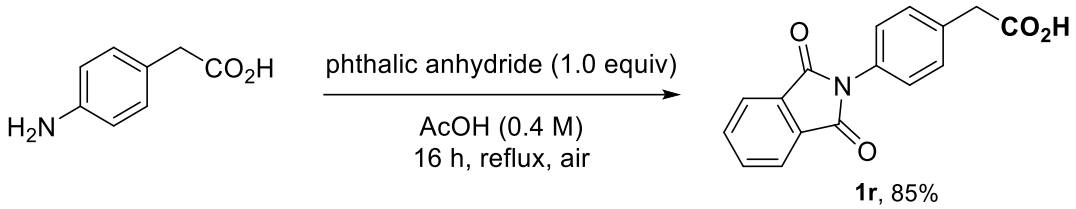
2-(Naphthalen-1-yl)propanenitrile **1i'** was synthesized following the general procedure on a 5.0 mmol scale. The product was not purified for next step and obtained as a colorless oil (0.88 g, 97%). R_f (*n*-pentane/ethyl acetate, 9:1): 0.87. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.85 (d, J = 8.3 Hz, 1H), 7.71 (d, J = 7.1 Hz, 1H), 7.64 – 7.47 (m, 3H), 4.64 (q, J = 7.2 Hz, 1H), 1.80 (d, J = 7.2 Hz, 3H). NMR data were in accordance with the literature.[5]



1i

2-(Naphthalen-1-yl)propanoic acid **1i** was synthesized following the general procedure on a 5.0 mmol scale and obtained as a white solid (0.95 g, 95%). **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 8.12 (d, J = 8.1 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.81 (d, J = 0.9 Hz, 1H), 7.60 – 7.44 (m, 4H), 4.57 (q, J = 7.1 Hz, 1H), 1.70 (d, J = 7.1 Hz, 3H). NMR data were in accordance with the literature.[6]

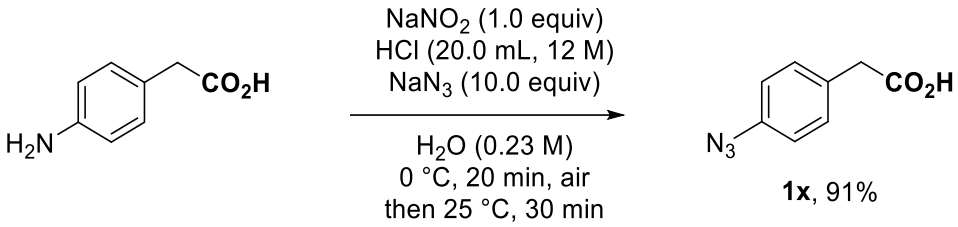
Synthesis of 4-*N*-phthaloylphenylacetic acid 1r



1r, 85%

Following a known procedure.[7] In a 50 mL round bottom flask was added phthalic anhydride (1.48 g, 10 mmol, 1.0 equiv) to a solution of 4-aminophenylacetic acid (1.51 g, 10 mmol, 1.0 equiv) in glacial acetic acid (25.0 mL, 0.4 M) under air atmosphere. The mixture was refluxed for 16 h. The reaction mixture was cooled down to 0 °C and the white precipitate was filtered, then recrystallized from ethanol to yield **1r** as a white solid (2.39 g, 85%). mp: 180-181 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.83 – 7.76 (m, 2H), 7.49 – 7.40 (m, 4H), 3.72 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 170.4, 129.2, 127.9, 126.5, 124.9, 121.4, 118.6, 35.2. **IR** (neat, cm^{-1}): ν 2894, 1697, 1517, 1383, 1299, 1254, 1119, 1080, 959, 885. **HRMS** (ESI^+) calcd for $C_{11}H_{16}NO_4$ *m/z* 282.0766 $[M+H^+]^+$, Found 282.0761 (Δ 1.8 ppm).

Synthesis of 4-azidophenylacetic acid 1x

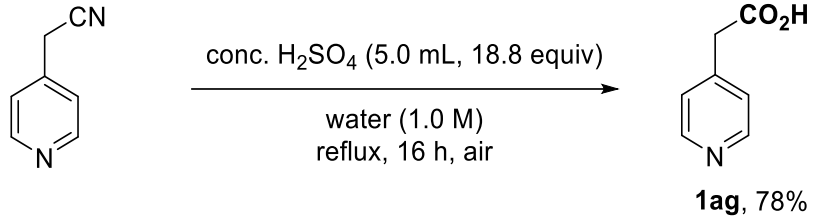


1x, 91%

Following a known procedure.[8] In a 250 mL three-necked round bottom flask was dissolved 4-aminophenylacetic acid (2.0 g, 13.2 mmol, 1.0 equiv) in a concentrated aqueous HCl solution (20.0 mL, 12 M) at 0 °C. An aqueous solution of sodium nitrite (913 mg, 13.2 mmol, 1.0 equiv) in water (70.0 mL) was slowly added for 15 min. The reaction mixture was stirred at 0 °C for 20 min. A solution of sodium azide (8.60 mL, 132 mmol, 10.0 equiv) in water (200 mL) was then slowly added for 10 min. The reaction mixture was then warm up at room temperature and stirred for an additional 30 min. The crude reaction mixture was diluted with EtOAc (40 mL) and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and the residual solvents were evaporated under vacuum to yield the 4-azidophenylacetic acid **1x** as a light brown solid (2.14 g, 91%). **^{1}H NMR** (300.1 MHz, $CDCl_3$)

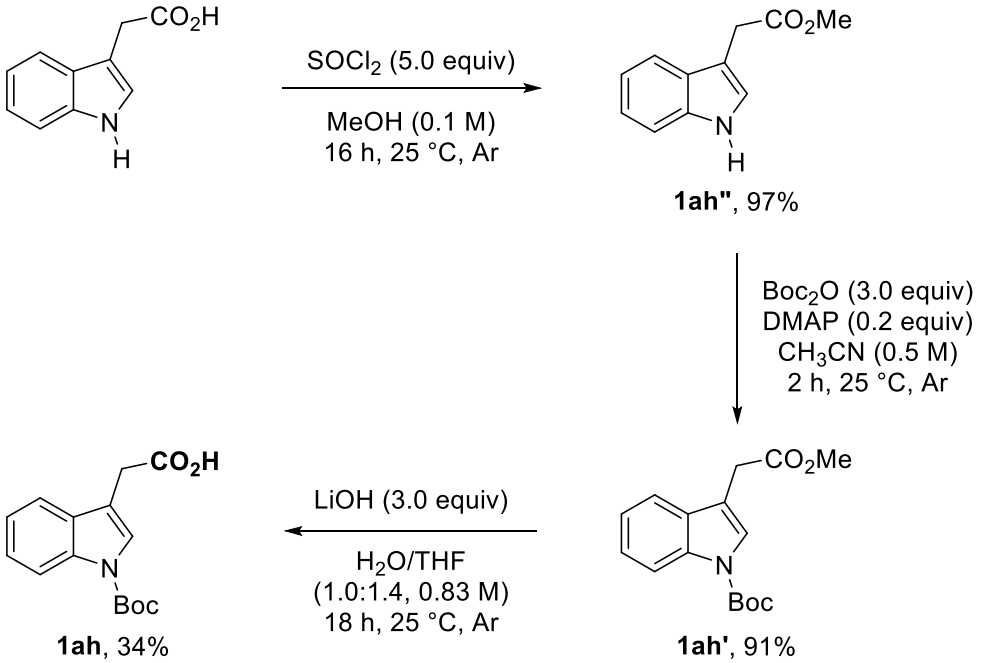
δ 11.53 (br s, 1H), 7.31 – 7.22 (m, 2H), 7.04 – 6.95 (m, 2H), 3.63 (s, 2H). NMR data were in accordance with the literature.[8]

Synthesis of 3-pyridylacetic acid 1ag



In a 50 mL round bottom flask, 3-pyridylacetonitrile (591 mg, 5.0 mmol, 1.0 equiv) was added to distilled water (5.0 mL, 1.0 M) at 23 °C under air. The mixture was placed in an ice bath and a concentrated H_2SO_4 solution (5.0 mL, 94.0 mmol, 18.8 equiv) was slowly added. The solution was then stirred at reflux for 16h. The reaction mixture was neutralized to around pH = 7 with a saturated aqueous solution of $NaHCO_3$ and the residual solvents were evaporated under vacuum at 60 °C. The solid residue was transferred to a fritted glass and washed with methanol (3 × 30 mL). Solvents were evaporated and the crude product was purified by flash chromatography on silica gel (height = 15 cm, width = 2 cm, eluent: ethyl acetate/acetic acid, 95:5) to yield 3-pyridylacetic acid **1ag** as a white solid (535 mg, 78%). R_f (eluent: ethyl acetate/acetic acid, 95:5): 0.24. **^{1}H NMR** (300.1 MHz, DMSO-d_6) δ 7.88 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 3.67 (s, 2H). **^{13}C NMR** (75.5 MHz, DMSO-d_6) δ 173.4, 149.4, 146.9, 124.8, 20.5.

Synthesis of *N*-Boc-3-indolaecetic acid 1ah



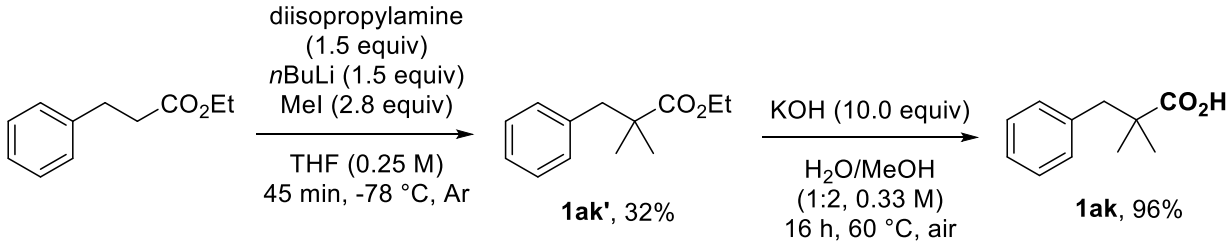
Following a known procedure.[9] In a 100 mL flame-dried round bottom flask was slowly added Thionyl chloride (1.82 mL, 25.0 mmol, 5.0 equiv) to a solution of 3-Indoleacetic acid (0.88 g, 5.0 mmol, 1.0 equiv) in dry methanol (50 mL, 0.1 M) at 0 °C under argon. The reaction mixture was stirred for 16 h at 25 °C. The solvents and thionyl chloride excess were removed under

vacuum and the residue (purple oil) was diluted with EtOAc (30 mL). The organic layer was washed whith a NH_4Cl saturated solution (25 mL), a $NaHCO_3$ saturated solution (25 mL) and brine (20 mL). The organic layer was dried over Na_2SO_4 and the solvents were evaporated under vacuum to give **1ah"** as a brown oil (0.91 g, 97%).

In a 25 mL flame-dried round bottom flask were added di-*tert*-Butyldicarbonate (3.18 g, 14.5 mmol, 3.0 equiv) and 4-(Dimethylamino)pyridine (119 mg, 0.97 mmol, 0.2 equiv) to a solution of **1ah"** (910 mg, 4.85 mmol, 1.0 equiv) in acetonitrile (9.7 mL, 0.5 M) at 25 °C under argon atmosphere. The reaction mixture was stirred at 25 °C for 2 h. The solvents were removed under vacuum and the residue (yellow oil) was diluted with EtOAc (30 mL) and washed whith a NH_4Cl saturated solution (25 mL), a $NaHCO_3$ saturated solution (25 mL) and brine (20 mL). The residual solvents were dried over $MgSO_4$ and evaporated under vacuum. The crude was purified by flash chromatography on silica gel (height = 10 cm, width = 2 cm, eluent: hexane/ethyl acetate, 9:1) to yield **1ah'** as a colorless oil (1.27 g, 91%), which contained traces of residual Boc_2O.

In a 250 mL round bottom flask was added lithium hydroxide monohydrate (317 mg, 13.2 mmol, 5.0 equiv) to a solution of **1ah'** (1.25 g, 4.4 mmol, 1.0 equiv) in a H_2O/THF mixture (1.0:1.4, 53 mL, 0.83 M) at 25 °C under argon atmosphere. The reaction mixture was stirred at 25 °C for 18 h. The solvents were partially removed under vacuum and the residue (yellow oil) was acidified with a hydrochloric acid solution (2 M, 30 mL) until pH 2 then extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water (25 mL) and brine (20 mL). After drying over Na_2SO_4, the solvents were removed and the crude was purified by flash chromatography on silica gel (height = 10 cm, width = 2 cm, eluent: hexane/ethyl acetate/AcOH 65:30:5) to yield **1ah** as a white solid (413 mg, 34%). **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 11.20 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.64 (s, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.33 – 7.27 (m, 1H), 3.79 (s, 2H), 1.71 (s, 9H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 177.4, 149.5, 135.3, 129.8, 124.6, 124.5, 122.6, 118.9, 115.2, 112.3, 83.6, 30.7, 28.0. NMR data were in accordance with the literature.[9]

Synthesis of 2,2-Dimethyl-3-phenylpropanoic acid 1ak

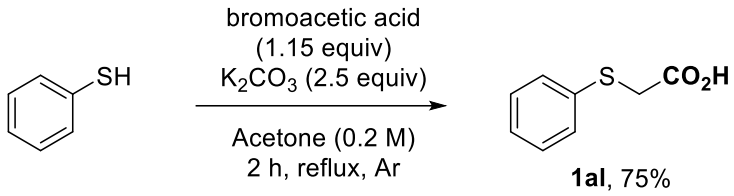


Following a known procedure.[10] In a 100 mL flame-dried round bottom flask was slowly added *n*-butyllithium (6.67 mL, 15.0 mmol, 2.25 M in hexane, 1.5 equiv) to a solution of diisopropyamine (2.10 mL, 15.0 mmol, 1.5 equiv) in dry THF (40.0 mL, 0.25 M) at –78 °C under argon. After 10 min, ethyl-3-phenylpropionate (1.78 g, 10 mmol, 1.0 equiv) was added and the reaction is stirred for 10 min at –78 °C. Iodomethane (1.74 mL, 28 mmol, 2.8 equiv) was slowly added over 10 min. The reaction mixture was stirred at –78 °C for 30 min, then reverse-quenched into an ice-cold hydrochloric acid bath (50 mL, 2 M). The aqueous phase was transferred to a separatory funnel and extracted with diethylether (2 × 30 mL). The organic layers were dried over anhydrous Na_2SO_4 and then evaporated under vacuum. The crude

reaction mixture (brown oil) was reacted a second time by following the same protocol. After that, the crude reaction mixture was purified by flash chromatography on silica gel (height = 20 cm, width = 2 cm, eluent: Hexane/ethyl acetate, 98:2) to produce **1ak'** as a colorless oil (0.67 g, 32%) containing minor impurities. **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.25 – 7.09 (m, 5H), 4.11 (q, J = 7.1 Hz, 2H), 2.85 (s, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.17 (s, 6H).

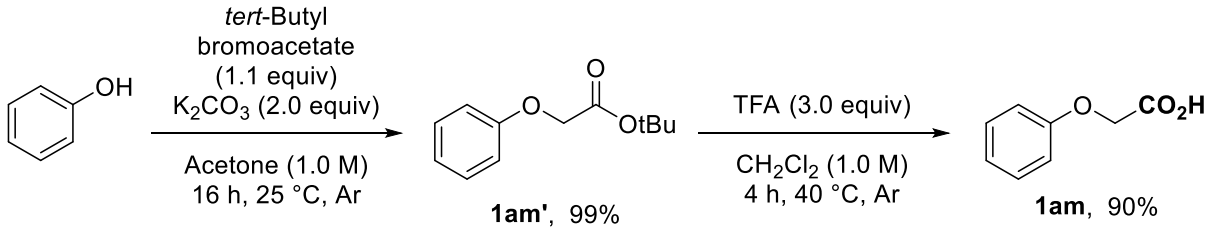
In a 50 mL round bottom flask was sadded potassium hydroxide (1.86 g, 32.0 mmol, 10.0 equiv) to a solution of **1ak'** (0.67 g, 3.2 mmol, 1.0 equiv) in a water/methanol (1:2, 30 mL, 0.33 M) at 25 °C under air. The reaction mixture was stirred at 60 °C for 16 h, then cooled at room temperature and quenched with an hydrochloric acid aqueous solution (20 mL, 2 M) until pH 2. The aqueous phase was transferred to a separatory funnel and extracted with ethyl acetate (3 × 15 mL). The organic layers were dried over anhydrous Na_2SO_4 and then evaporated under vacuum to give **1ak** as a light yellow solid (0.510 g, 96%). **^{1}H NMR** (400.2 MHz, MeOD) δ 7.27 – 7.17 (m, 5H), 2.85 (s, 2H), 1.15 (s, 6H).

Synthesis of (phenylthio)methylcarboxylic acid 1al



Adapted from a known procedure.[11] In a 50 mL flame-dried round bottom flask was added potassium carbonate (1.73 g, 12.5 mmol, 2.5 equiv) to a solution of thiophenol (0.51 mL, 5.0 mmol, 1.0 equiv) in acetone (25.0 mL, 0.2 M) and the reaction mixture was stirred at 25 °C for 10 min under argon. Bromoacetic acid (0.80 g, 5.75 mmol, 1.15 equiv) was then added and the reaction mixture was stirred for 2 h at reflux. The reaction mixture was quenched with a hydrochloric acid aqueous solution (10 mL, 2.0 M) until pH 2, then transferred to a separatory funnel and partitioned between water (50 mL) and Ethyl acetate (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (3 × 10 mL) and brine (20 mL) and dried over anhydrous Na_2SO_4. The solvents were evaporated under vacuum the crude reaction mixture was purified by flash chromatography on silica gel (height = 10 cm, width = 2 cm, eluent: Hexane/ethyl acetate, 8:2 then hexane/ethyl acetate/AcOH 65:30:5) to produce **1al** as a white solid (632 mg, 75%). **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.22 (m, 1H), 3.68 (s, 2H). NMR data were in accordance with the literature.[11]

Synthesis of (phenyloxy)methylcarboxylic acid 1am

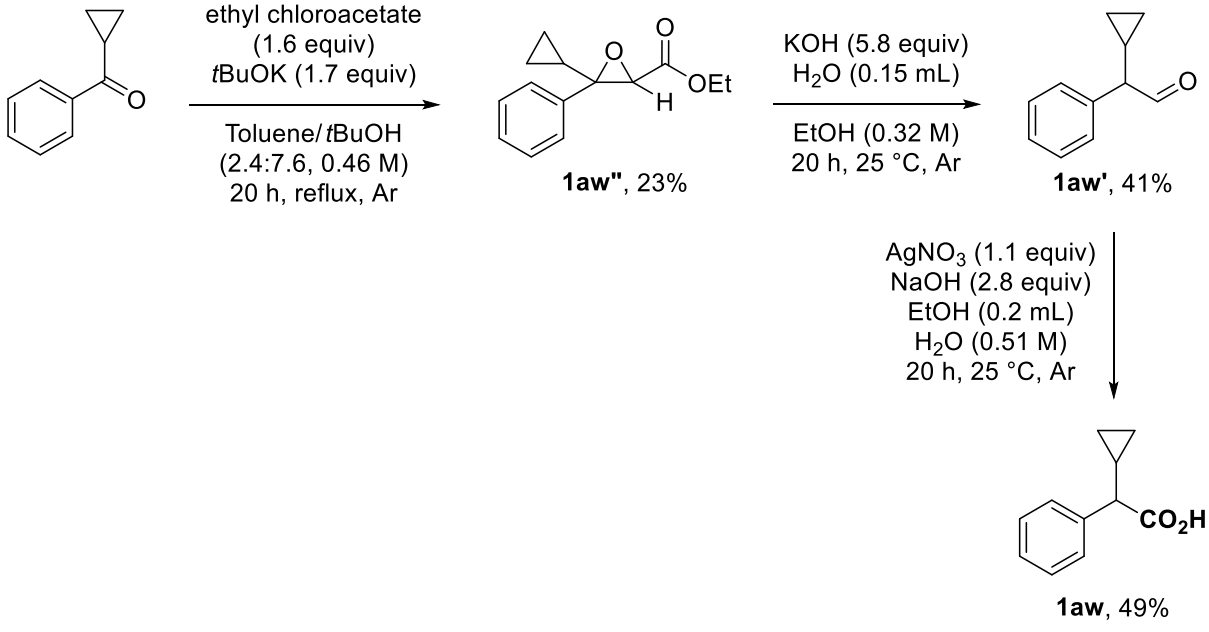


Following a known procedure.[12] In a 50 mL flame-dried round bottom flask was slowly added *tert*-butylbromoacetate (3.25 mL, 22.0 mmol, 1.1 equiv) to a mixture of phenol (1.76 mL, 20.0

mmol, 1.0 equiv) and potassium carbonate (5.53 g, 40.0 mmol, 2.0 equiv) in acetone (20.0 mL, 1.0 M) at 0 °C under argon. The reaction mixture was stirred for 16 h at 25 °C. The reaction mixture was then filtered to remove carbonate salts and the white solid was washed with acetone (2 × 10 mL). The filtrate was evaporated under vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (height = 7 cm, width = 2 cm, eluent: Hexane/ethyl acetate, 9:1) to produce **1am'** as a white solid (4.10 g, 99%). **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.8, 7.3 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.90 (dd, J = 8.8, 1.1 Hz, 2H), 4.51 (s, 2H), 1.49 (s, 9H).

Following the same procedure,[12] in a 50 mL flame-dried round bottom flask was added trifluoroacetic acid (4.59 mL, 60.0 mmol, 3.0 equiv) to a solution of **1am'** (4.10 g, 20.0 mmol, 1.0 equiv) in dichloromethane (20.0 mL, 1.0 M) at 25 °C under argon. The reaction mixture was stirred for 4 h at 40 °C and monitored by TLC. The reaction mixture was then transferred to a separatory funnel and partitioned between water (10 mL) and dichloromethane (10 mL). The organic layer was washed with water (3 × 10 mL) and brine (10 mL) and dried over anhydrous Na_2SO_4. The solvents were evaporated under vacuum to give a light brown solid as crude (containing traces of the starting material). This solid was dissolved in an aqueous NaOH solution (25 mL, 1 M) and the aqueous layer was washed with dichloromethane (2 × 10 mL). The solution was acidified to pH ~ 2 and white crystals formed. Filtration and washing with cold water followed by drying afforded the expected acid **1am** as a white solid (2.73 g, 90%). **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.31 (t, J = 7.8 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 8.1 Hz, 2H), 4.68 (s, 2H). NMR data were in accordance with the literature.[12]

Synthesis of 2-cyclopropyl-2-phenylacetic acid 1aw



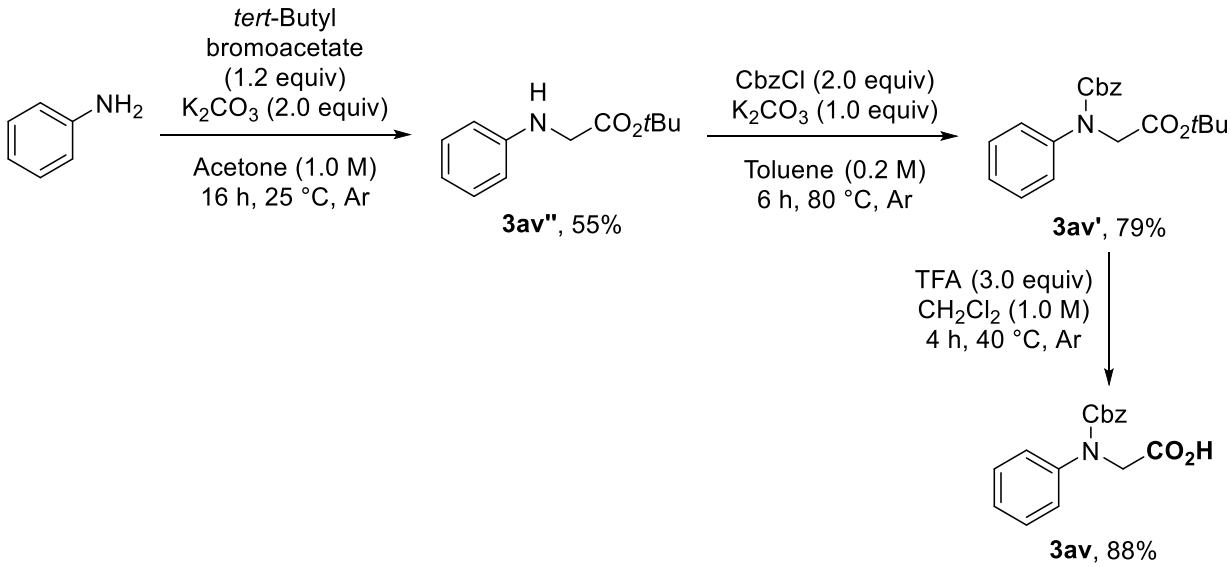
Following a known procedure.[13] In a 100 mL oven-dried round bottom flask was added *tert*-butoxide (6.33 g, 56.4 mmol, 1.7 equiv) portion wise potassium to a solution of ethyl chloroacetate (5.72 mL, 53.4 mmol, 1.6 equiv) and 1-cyclopropyl-1-phenyl ketone (4.88 g, 33.4 mmol, 1.0 equiv) in toluene (17.5 mL) and *tert*-butyl alcohol (55 mL) at - 5 °C under argon. The reaction mixture was allowed to warm up slowly to room temperature and was stirred for 20 h at reflux. The mixture was then diluted with water (200 mL) and the aqueous

layer was extracted with *n*-pentane (3 × 80 mL). The organic layer was washed with water (2 × 80 mL) and brine (80 mL). The combined organic layers were dried over $MgSO_4$ and the residual solvents were evaporated under vacuum. The crude reaction mixture was purified by flash chromatography on silica gel (height = 20 cm, width = 5 cm, eluent: *n*-pentane/ethyl acetate, 97:3) to produce **1aw"** as a colorless oil (1.75 g, 23%).

Following a known procedure.[13] The synthesized intermediate **1aw"** (1.75 g, 7.53 mmol, 1.0 equiv) was added to a solution of potassium hydroxide (2.46 g, 43.8 mmol, 5.8 equiv) in ethanol (23.4 mL) and water (0.15 mL). The resulting mixture was stirred at room temperature for 20 h, acidified with an aqueous HCl solution (1 M), and stirred at 22 °C for 4 h. The aqueous layer was extracted with *n*-pentane (3 × 20 mL), and the combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (20 mL), brine (20 mL) and dried over $MgSO_4$. The residual solvents were evaporated under vacuum. The crude was purified by flash chromatography on silica gel (height = 12 cm, width = 3 cm, eluent: *n*-pentane/ethyl acetate, 97:3) to yield 2-cyclopropyl-2-phenyl acetaldehyde **1aw'** as a yellow oil (502 mg, 41%), which contained an inseparable impurity.

Following a known procedure.[13] In a 25 mL round bottom flask, 2-cyclopropyl-2-phenyl acetaldehyde **1aw'** (500 mg, 3.12 mmol, 1.0 equiv) was added to a solution of silver nitrate (593 mg, 3.53 mmol, 1.13 equiv) and sodium hydroxide (356 mg, 8.89 mmol, 2.85 equiv) in water (6.06 mL) and ethanol (0.2 mL). The solution was stirred at room temperature for 24 h, filtered through Celite, and washed with an aqueous NaOH solution (2 × 10 mL; 1 M). The solution was acidified with an aqueous HCl solution (2 M) until pH = 3 and the aqueous layer was extracted with diethyl ether (3 × 15 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and the residual solvents were evaporated under vacuum. The crude mixture was purified by flash chromatography on silica gel (height = 10 cm, width = 1 cm, eluent: dichloromethane/methanol, 98:2) to produce **1aw** as a white solid (270 mg, 49%) **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 10.81 (s, 1H), 7.42 – 7.27 (m, 5H), 2.81 (d, J = 10.0 Hz, 1H), 1.54 – 1.39 (m, 1H), 0.76 – 0.65 (m, 1H), 0.64 – 0.51 (m, 1H), 0.47 – 0.36 (m, 1H), 0.25 – 0.14 (m, 1H). NMR data were in accordance with the literature.[13]

Synthesis of *N*-Phenyl-*N*-[(phenylmethoxy)carbonyl]glycine



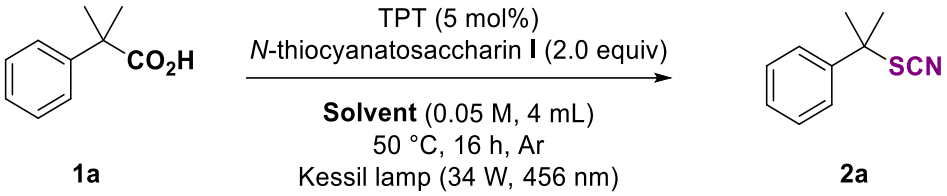
In a 25 mL flame-dried round bottom flask was slowly added *tert*-butylbromoacetate (1.77 mL, 12.0 mmol, 1.2 equiv) to a mixture of aniline (0.911 mL, 10.0 mmol, 1.0 equiv) and potassium carbonate (2.76 g, 20.0 mmol, 2.0 equiv) in acetone (10.0 mL, 1.0 M) at 0 °C under argon. The reaction mixture was stirred for 16 h at 25 °C. The reaction mixture was then filtered to remove carbonate salts and the white solid was washed with acetone (2 × 10 mL). The filtrate was evaporated under vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (height = 7 cm, width = 2 cm, eluent: Hexane/ethyl acetate, 9:1 to 8:2 gradient) to produce **3av"** as a colorless oil (1.15 g, 55%). **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.19 (dd, J = 8.6, 7.3 Hz, 2H), 6.74 (tt, J = 7.3, 1.1 Hz, 1H), 6.61 (dd, J = 8.6, 1.1 Hz, 2H), 3.80 (s, 2H), 1.49 (s, 9H).

From a known procedure.[17] In a 50 mL flame-dried round bottom flask was slowly added benzylchloroformate (1.43 mL, 10.0 mmol, 2.0 equiv) to a mixture of **3av"** (1.04 g, 5.0 mmol, 1.0 equiv) and potassium carbonate (0.69 g, 5.0 mmol, 1.0 equiv) in toluene (25.0 mL, 0.2 M) at 25 °C under argon. The reaction mixture was stirred for 6 h at 80 °C. The reaction mixture was cooled at room temperature, transferred to a separatory funnel, and partitioned between water (20 mL) and EtOAc (5 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (2 × 20 mL) and dried over anhydrous Na_2SO_4. The solvents were evaporated under vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (height = 10 cm, width = 3.5 cm, eluent: Hexane/ethyl acetate, 95:5 to 8:2 gradient) to produce **3av'** as a colorless oil (1.35 g, 79%). **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.45 – 7.18 (m, 10H), 5.18 (s, 2H), 4.24 (s, 2H), 1.43 (s, 9H). the compound contains some ethyl acetate but was used in the next step without further drying.

In a 10 mL flame-dried microwave reaction tube was added trifluoroacetic acid (0.46 mL, 6.0 mmol, 3.0 equiv) to a solution of **3av'** (683 mg, 2.0 mmol, 1.0 equiv) in dichloromethane (2.0 mL, 1.0 M) at 25 °C under argon. The reaction mixture was stirred for 4 h at 40 °C and monitored by TLC. The reaction mixture was then transferred to a separatory funnel and partitioned between water (10 mL) and dichloromethane (10 mL). The organic layer was washed with water (3 × 10 mL) and brine (10 mL) and dried over anhydrous Na_2SO_4. The solvents were evaporated under vacuum and the crude reaction mixture was passed through a short pad of silica gel (height = 5 cm, width = 2 cm, eluent: DCM/MeOH, 100:0, then 95:5) to give **3av** as a very sticky oil (502 mg, %). **^{1}H NMR** (400.2 MHz, MeOD) δ 7.56 – 7.15 (m, 10H), 5.14 (s, 2H), 4.34 (s, 2H). **^{13}C NMR** (100.7 MHz, MeOD) δ 171.5, 155.8, 136.3, 128.6, 128.1, 127.7, 127.2, 126.7, 67.3, 51.8, 26.9. **IR** (neat, cm^{-1}): ν 3063, 3033, 1700, 1494, 1358, 1322, 1278, 1154, 1074, 1022. **HRMS** ($APCI^+$) calcd for $C_{16}H_{15}O_4$ *m/z* 177.0948 $[M+H]^+$, Found 286.10824 (Δ 3.01 ppm).

4. Optimization of the reaction conditions

Table S1: Optimization of the solvent

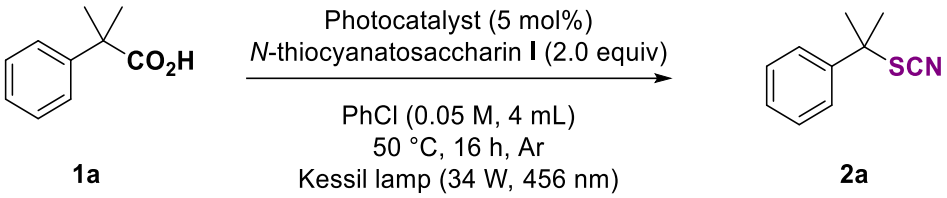


1a **2a**

Entry N°	*Solvent*	***2a*** *^{1}H NMR Yield*	***2a*** *isolated yield*
1	**PhCl**	**63**	**32**
2	Benzene	0	N.D.
3	PhMe	0	N.D.
4	Acetonitrile)	N.D.	23
5	CH_2Cl_2	21	15
6	THF	N.D.	0
7	1,1,2,2-tetrachloroethane	4	N.D.
8	1,2-dichloroethane	5	N.D.
9	$PhCl_2$	61	N.D.
10	$CHCl_3$	5	N.D.

Standard conditions: substrate **1a** (0.2 mmol, 1 equiv), *N*-thiocyanatosaccharin (0.4 mmol, 2 equiv), and TPT (5 mol%) in solvent (4 mL, 0.05 M) at 50 °C under argon atmosphere and UV Light (Kessil Lamp, 34 W) for 16 h. ^{1}H NMR were calculated with 1,1,2,2-tetrachloroethane (0.2 mmol, 1 equiv) as standard. N.D.: not determined.

Table S2: Optimization of the photocatalyst

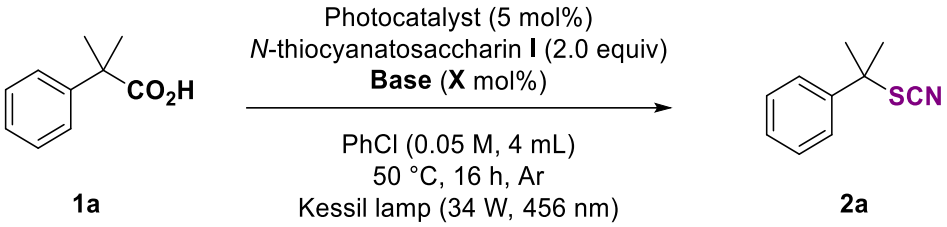


1a **2a**

Entry N°	*Photocatalyst*	*Catalytic charge (mol%)*	***2a*** *^{1}H NMR Yield*
1	TPT	5	63
2	4-CzIPN	5	0
3	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$	5	0
4	$Acr.Mes.ClO_4$	5	58
5	**TPT**	**2.5**	**64**
6	TPT	10	52

Standard conditions: substrate **1a** (0.2 mmol, 1 equiv), *N*-thiocyanatosaccharin (0.4 mmol, 2 equiv), and Photocatalyst (2.5 to 10 mol%) in PhCl (4 mL, 0.05 M) at 50 °C under argon atmosphere and UV Light (Kessil Lamp, 34 W) for 16 h. ^{1}H NMR were calculated with 1,1,2,2-tetrachloroethane (0.2 mmol, 1 equiv) as standard.

Table S3: Optimization of the base and reaction time

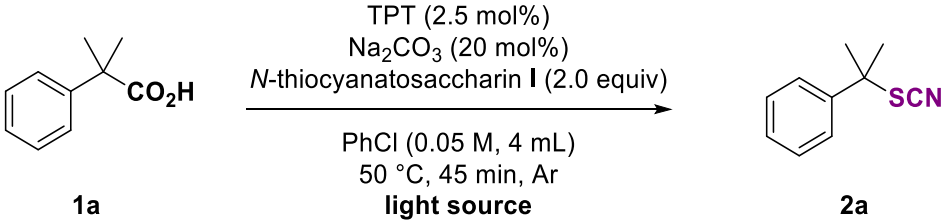


1a **2a**

Entry N°	*Base*	*X mol%*	*time*	***2a*** *^{1}H NMR Yield*
1	DBU	20	16 h	16
2	Et_3N	20	16 h	16
3	Cs_2CO_3	20	16 h	56
4	Na_2CO_3	20	16 h	74
5	K_3PO_4	20	16 h	45
6	Na_2CO_3	30	16 h	73
7	Na_2CO_3	10	16 h	68
8	Na_2CO_3	20	1 h	77
9	**Na_2CO_3**	**20**	**45 min**	**87**

Standard conditions: substrate **1a** (0.2 mmol, 1 equiv), *N*-thiocyanatosaccharin (0.4 mmol, 2 equiv), base (10 to 30 mol%) and TPT (2.5 mol%) in PhCl (4 mL, 0.05 M) at 50 °C under argon atmosphere and UV Light (Kessil Lamp, 34 W) for 45 min to 16 h. ^{1}H NMR were calculated with 1,1,2,2-tetrachloroethane (0.2 mmol, 1 equiv) as standard.

Table S4: Optimization of the light source

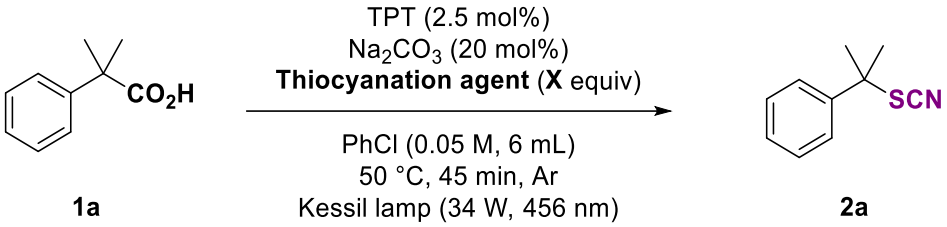


1a **2a**

Entry N°	*Light source λ (nm)*	*Light source power (W)*	***2a*** *^{1}H NMR Yield*
1	390	40	58
2	425	17	67
3	440	40	73
4	456	40	85
5	**456**	**34**	**87**
6	467	40	64

Standard conditions: substrate **1a** (0.2 mmol, 1 equiv), *N*-thiocyanatosaccharin (0.4 mmol, 2 equiv), and TPT (2.5 mol%) in PhCl (4 mL, 0.05 M) at 50 °C under argon atmosphere and UV Light (Kessil Lamp, 34 W) for 45 min. ^{1}H NMR were calculated with 1,1,2,2-tetrachloroethane (0.2 mmol, 1 equiv) as standard.

Table S5: Optimization of the thiocyanate source

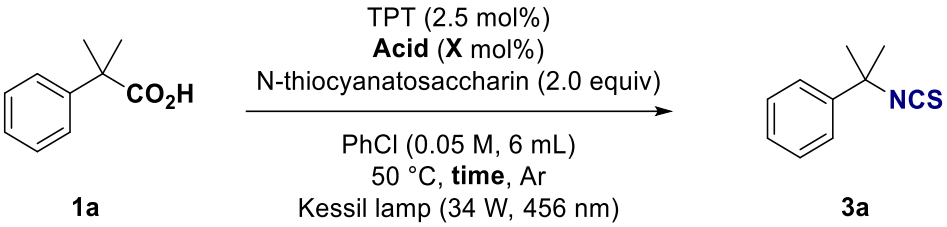


1a **2a**

Entry N°	*Thiocyanate source*	*X equiv*	***2a*** *^{1}H NMR Yield*
1	***N*-thiocyanatosaccharin**	**2.0**	**87**
2	*N*-thiocyanatosuccinimide	2.0	20
3	*N*-thiocyanatophthalimide	2.0	8
4	KSCN	2.0	0
5	NaSCN	2.0	0
6	NH_4SCN	2.0	0
7	NH_4SCN / $K_2S_2O_8$	2.0 / 2.0	0
8	TMSNCS	2.0	0
9	*N*-thiocyanatosaccharin	1.5	70
10	*N*-thiocyanatosaccharin	2.5	85

Standard conditions: substrate **1a** (0.3 mmol, 1 equiv), Thiocyanate source (0.6 mmol, 2 equiv), and TPT (2.5 mol%) in PhCl (6 mL, 0.05 M) at 50 °C under argon atmosphere and UV Light (Kessil Lamp, 34 W) for 45 min. ^{1}H NMR were calculated with 1,1,2,2-tetrachloroethane (0.3 mmol, 1 equiv) as standard.

Table S6: Optimization of the isomerization conditions

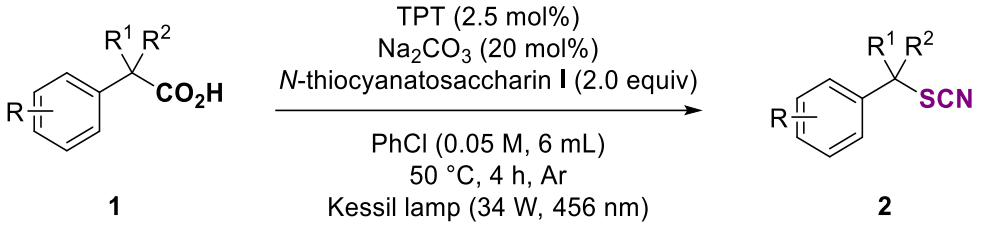


1a **3a**

Entry N°	*Acid*	*X mol%*	*time*	***3a*** *^{1}H NMR Yield*
1	AcOH	20	45 min	48
2	PivOH	20	45 min	33
3	$MesCO_2H$	20	45 min	29
4	H_2SO_4	20	45 min	0
5	TFA	20	45 min	38
6	AcOH	150	45 min	2
7	**AcOH**	**20**	**4 h**	**91**

Standard conditions: substrate **1a** (0.3 mmol, 1 equiv), *N*-thiocyanatosaccharin (0.6 mmol, 2 equiv), acid (20 to 150 mol%) and TPT (2.5 mol%) in PhCl (6 mL, 0.05 M) at 50 °C under argon atmosphere and UV Light (Kessil Lamp, 34 W) for 45 min to 4 h. ^{1}H NMR were calculated with 1,1,2,2-tetrachloroethane (0.3 mmol, 1 equiv) as standard.

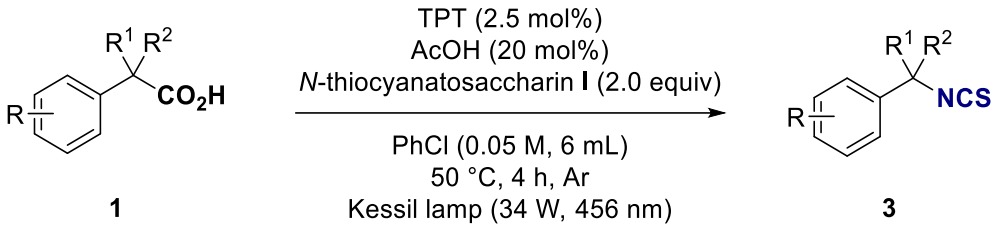
5. General procedure for the decarboxylative thiocyanation reaction



1 **2**

In a 10 mL oven-dried reaction tube equipped with a stirring bar was added carboxylic acid **1** (0.3 mmol, 1.0 equiv), sodium carbonate (6.4 mg, 0.06 mmol, 0.2 equiv), triphenylpyrylium tetrafluoroborate (3.0 mg, 0.0075 mmol, 0.025 equiv) and *N*-thiocyanatosaccharin **I** (144.0 mg, 0.6 mmol, 2.0 equiv). The tube was flushed three times with argon and freshly distilled and degassed (Freeze-Pump-Thaw) chlorobenzene (6.0 mL) was added. The tube was sealed and the heterogeneous reaction mixture (the photocatalyst and the *N*-thiocyanatosaccharin were partially soluble in chlorobenzene) was stirred at ~50 °C for 45 min under UV light irradiation (Kessil lamp, 34 W, 456 nm). The yield of the reaction was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) as an internal standard.
Due to the high volatility of the product, filtration was performed on a short pad of silica (height = 5 cm, width = 2 cm) eluted with *n*-pentane to remove chlorobenzene, then with diethylether or ethyl acetate (70 mL) to afford the desired product **2**. The solvent was evaporated and the crude reaction mixture was purified by flash chromatography on silica gel to give the corresponding isothiocyanate **2**.

6. General procedure for the decarboxylative isothiocyanation reaction

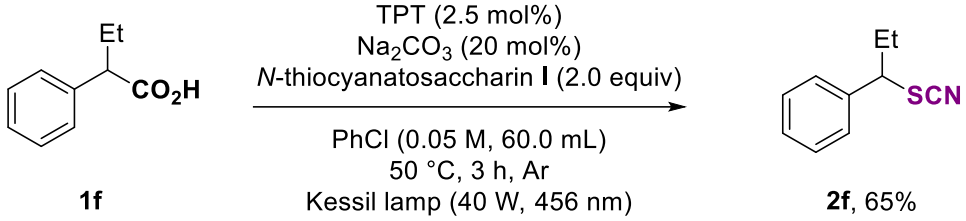


1 **3**

In a 10 mL oven-dried reaction tube equipped with a stirring bar was added carboxylic acid **1** (0.3 mmol, 1.0 equiv), triphenylpyrylium tetrafluoroborate (3.0 mg, 0.0075 mmol, 0.025 equiv) and *N*-thiocyanatosaccharin **I** (144.0 mg, 0.6 mmol, 2.0 equiv). The tube was flushed three times with argon and freshly distilled and degassed (Freeze-Pump-Thaw) chlorobenzene (6.0 mL) was added followed by acetic acid (3.5 µL, 0.06 mmol, 0.2 equiv). The tube was sealed and the heterogeneous reaction mixture (the photocatalyst and the *N*-thiocyanatosaccharin were partially soluble in chlorobenzene) was stirred at ~50 °C for 4 h under UV light irradiation (Kessil lamp, 34 W, 456 nm). The yield of the reaction was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) as an internal standard.
Due to the high volatility of the product, filtration was performed on a short pad of silica (height = 5 cm, width = 2 cm) eluted with *n*-pentane to remove chlorobenzene, then with diethylether or ethyl acetate (70 mL) to afford the desired product **3**. In some cases, no further purification was necessary. Otherwise, diethylether or ethyl acetate was evaporated and the crude reaction mixture was purified by flash chromatography on silica gel to give the corresponding isothiocyanate **3**.

7. Reaction scale-up in batch and continuous flow

Large-scale experiment:

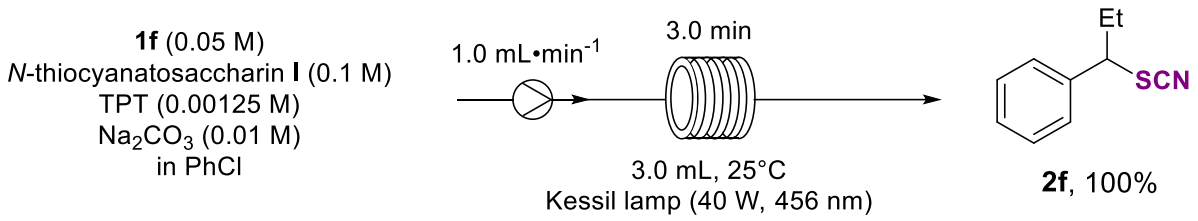


1f **2f**, 65%

In a 100 mL flame-dried reaction tube equipped with a stirring bar was added carboxylic acid **1f** (492 mg, 3.0 mmol, 1.0 equiv), sodium carbonate (64 mg, 0.6 mmol, 0.2 equiv), triphenylpyrylium tetrafluoroborate (30.0 mg, 0.075 mmol, 0.025 equiv) and *N*-thiocyanatosaccharin **I** (1.44 g, 6.0 mmol, 2.0 equiv). The flask was flushed with argon and freshly distilled and degassed (Freeze-Pump-Thaw) chlorobenzene (60.0 mL) was added. The flask was surrounded with aluminum foil and the heterogeneous reaction mixture was stirred at ~50 °C for 3h min under UV light irradiation (Kessil lamp, 40 W, 456 nm). After 3h, the conversion checked by ^{1}H NMR using 1,1,2,2-tetrachloroethane (0.32 mL, 3.0 mmol, 1.0 equiv) as an internal standard. The reaction media was filtrated on a large pad of silica (height = 5 cm, width = 10 cm) eluted with hexanes to remove chlorobenzene, then with ethyl acetate (250 mL) to afford the desired crude product **2f**. The solvent was evaporated and the crude reaction mixture was purified by flash chromatography on silica gel flash chromatography on silica gel (height = 10 cm, width = 2 cm, eluent: hexanes/ethyl acetate 95:5) to produce a yellowish oil (346 mg, 65%).

Figure S4 : Photo of the large-scale experiment. Distance flask-lamp : 3 cm.

Continuous flow experiment:



In a 100 mL flame-dried reaction tube equipped with a stirring bar was added carboxylic acid **1f** (328.0 mg, 2.0 mmol, 1.0 equiv), sodium carbonate (42.0 mg, 0.4 mmol, 0.2 equiv), triphenylpyrylium tetrafluoroborate (9.9 mg, 0.025 mmol, 0.025 equiv) and *N*-thiocyanatosaccharin **I** (961.0 mg, 0.6 mmol, 2.0 equiv). The flask was purged with argon and freshly distilled and degassed (freeze-pump-thaw) chlorobenzene (40.0 mL) was added. The reaction mixture was stirred at 23 °C for 10 min and transferred to a 30 mL syringe.
The solution was injected with a syringe pump (1.0 mL.min^{-1}) into a 3.0 mL PFA reactor (d = 1.0 mm) placed in an aluminum-covered box and irradiated with a blue LED Kessil lamp (40 W, 456 nm). The exiting slug flow was collected in an open flask, ($V_{collected}$ = 20.0 mL; the first 5.0 mL were discarded). The crude reaction mixture was purified by flash chromatography on silica gel flash chromatography on silica gel (height = 10 cm, width = 2 cm, eluent: hexanes/ethyl acetate 95:5) to give a yellowish oil (177 mg, 100%).

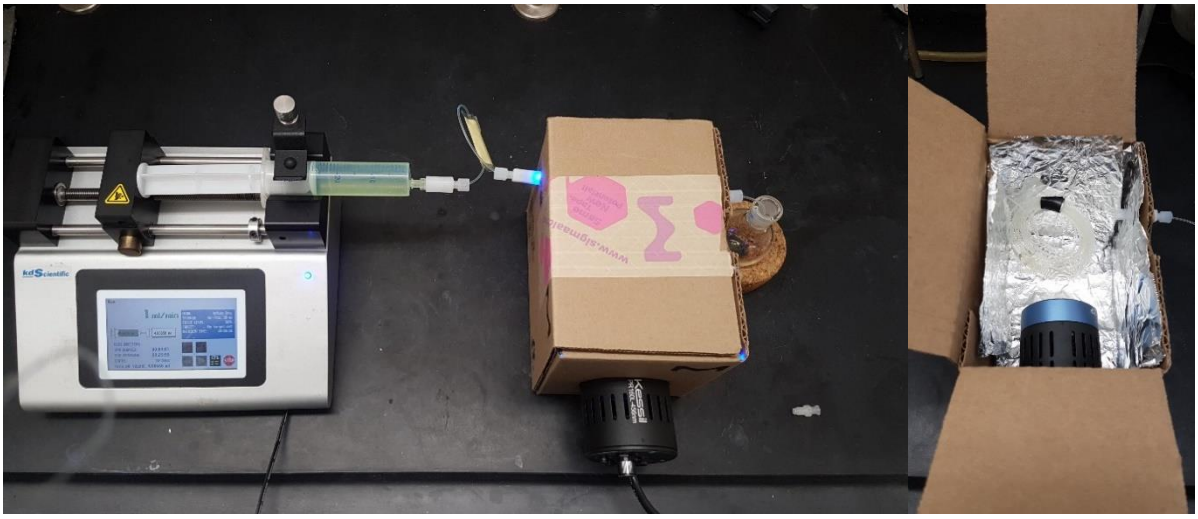


Figure S5 : Photos of the continuous flow montage (left) and inside of the aluminum box (right).

8. Reluctant substrates

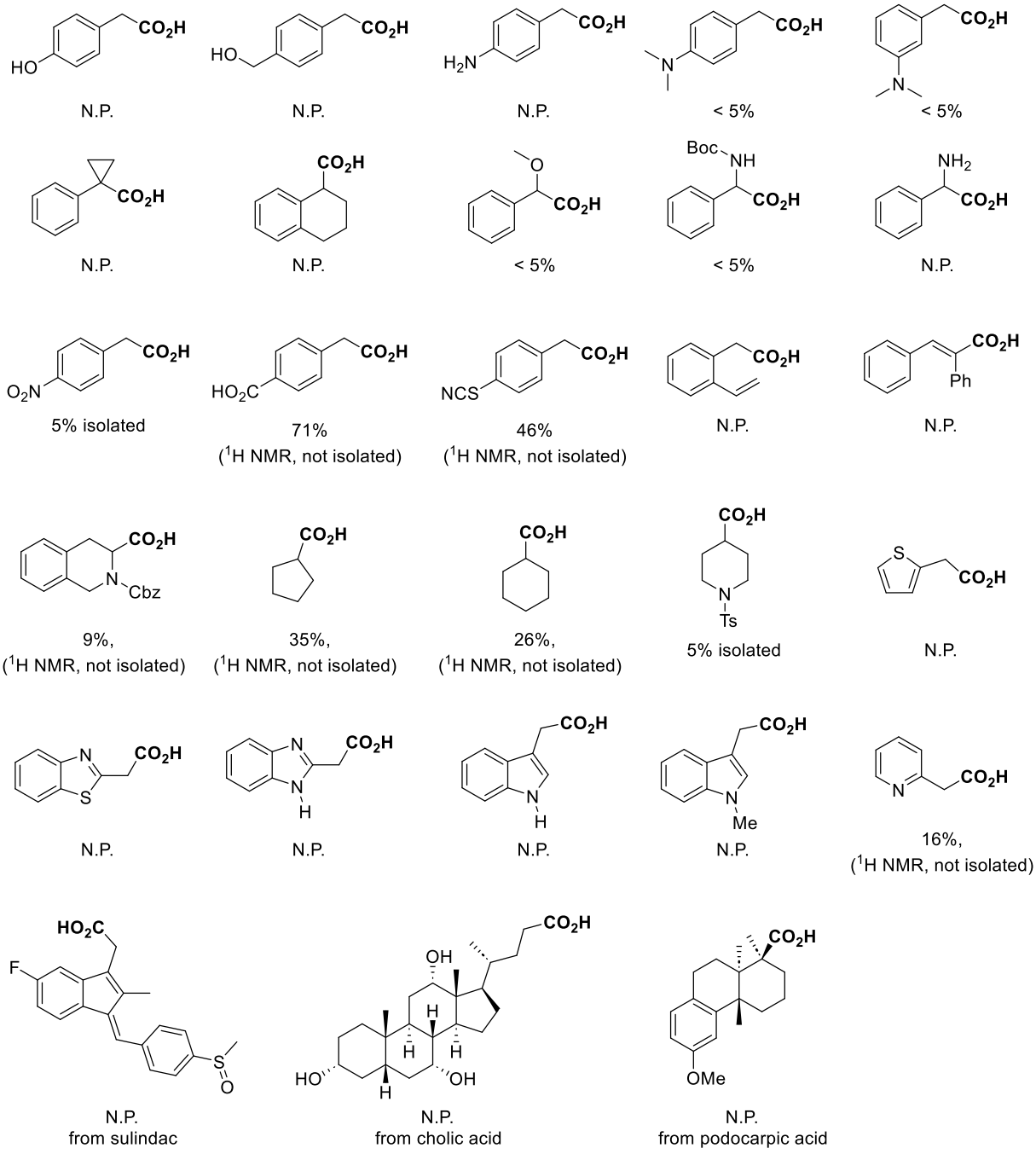
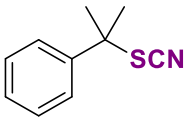


Figure S6 : List of reluctant substrates

N.P. = no product detected

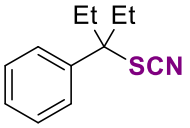
^{1}H NMR yields were determined using 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) as an internal standard.

9. Purification and characterization data of the products 2



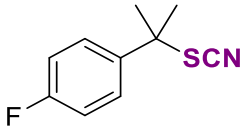
2a

(2-Thiocyanatopropan-2-yl)benzene **2a** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 97:3) to produce a colorless oil (38.4 mg, 73%). The same procedure was used on a 0.2 mmol scale to give **2a** in similar yield (27.3 mg, 72%). Note that in that case no pre-filtration on a short pad was necessary. R_f (*n*-pentane/diethyl ether, 95:5): 0.60. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 2H), 7.45 – 7.30 (m, 3H), 2.00 (s, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 141.9, 128.8, 128.4, 125.9, 112.0, 56.5, 30.3. **IR** (neat, cm^{-1}): *v* 2976, 2928, 2148, 1496, 1449, 1372, 1254, 1126, 1097. **HRMS** (EI^+) calcd for $C_{10}H_{11}NS$ *m/z* 177.0612 $[M]^+$, Found 177.0620 (Δ 4.5 ppm).



2b

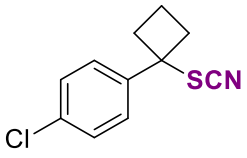
(1-Thiocyanato-1-ethylpropyl)benzene **2b** was synthesized following the general procedure and purified by flash chromatography on alumina (height = 20 cm, width = 0.5 cm, eluent: Hexane/ethyl acetate 100:0 to 95:5 gradient) to produce a colorless oil (37.0 mg, 60%). R_f (Hexane/ethyl acetate, 9:1): 0.56. **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.35 – 7.27 (m, 1H), 2.24 (q, J = 6.9 Hz, 4H), 0.94 (t, J = 6.9 Hz, 6H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 139.9, 128.7, 127.9, 126.7, 111.7, 66.8, 31.9, 9.0. **IR** (neat, cm^{-1}): *v* 2973, 2938, 2149, 1495, 1455, 1446, 1381, 1092, 1080, 836. **HRMS** (ESI^+) calcd for $C_{12}H_{15}NS$ *m/z* 311.9971 $[M+Ag]^+$, Found 311.9951 (Δ 1.96 ppm). Note: The compound isomerizes when purified on silica gel.



2c

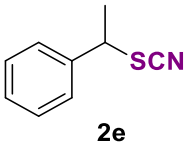
1-Fluoro-4-(2-thiocyanatopropan-2-yl)benzene **2c** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 98:2) to produce a colorless oil (43.3 mg, 74%). The same procedure was used on a 0.2 mmol scale to give **2c** in similar yield (25.2 mg, 70%). Note that in that case no pre-filtration on a short pad was necessary. R_f (*n*-pentane/diethyl ether, 95:5): 0.64. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.60 – 7.45 (m, 2H), 7.15 – 7.00 (m, 2H), 1.98 (s, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 162.4 (d, J = 248.7 Hz), 138.0 (d, J = 3.4 Hz), 127.9 (d, J = 8.3 Hz), 115.7 (d, J = 21.6 Hz), 111.7, 55.9, 30.4. **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ -116.51 – -

116.63 (m). **IR** (neat, cm^{-1}): *v* 2985, 2936, 2062, 1602, 1511, 1254, 1234, 1163, 1099, 834. **HRMS** (EI^+) calcd for $C_{10}H_{10}FNS$ *m/z* 195.0518 $[M]^+$, Found 195.0522 (Δ 2.0 ppm).



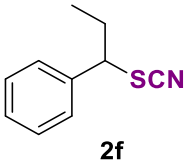
2d

1-Chloro-4-(1-thiocyanatocyclobutyl)benzene **2d** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 20 cm, width = 1 cm, eluent: Hexane/ethyl acetate 95:5) to produce a colorless oil (54.3 mg, 81%). R_f (Hexane/ethyl acetate, 9:1): 0.52. **^{1}H NMR** (400.2 MHz, $CDCl_3$) *δ* 7.39 – 7.33 (m, 2H), 7.28 – 7.22 (m, 2H), 2.87 – 2.77 (m, 2H), 2.74 – 2.65 (m, 2H), 2.49 – 2.36 (m, 1H), 2.05 – 1.92 (m, 1H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) *δ* 141.9, 134.1, 128.9, 127.2, 111.8, 58.4, 35.3, 16.1. **IR** (neat, cm^{-1}): *v* 2993, 2954, 2150, 1491, 1464, 1432, 1282, 1091, 1012, 828. **HRMS** (ESI^+) calcd for $C_{11}H_{10}ClNS$ *m/z* 246.01147 $[M+Na]^+$, Found 246.01193 (Δ 1.87 ppm).



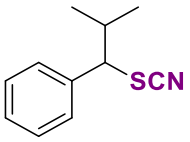
2e

1-(Thiocyanatoethyl)benzene **2e** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 96:4) to produce a colorless oil (46.0 mg, 94%). R_f (*n*-pentane/diethyl ether, 95:5): 0.48. **^{1}H NMR** (300.1 MHz, $CDCl_3$) *δ* 7.45 – 7.31 (m, 5H), 4.61 (q, *J* = 7.0 Hz, 1H), 1.88 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) *δ* 139.0, 129.0, 128.9, 127.0, 111.7, 48.4, 21.9. **IR** (neat, cm^{-1}): *v* 2976, 2151, 1494, 1454, 1380, 1217, 1046, 1027, 974, 765. **HRMS** (EI^+) calcd for C_9H_9NS *m/z* 163.0456 $[M]^+$, Found 163.0455 (Δ -0.2 ppm).



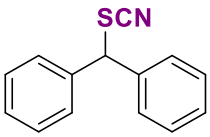
2f

1-(Thiocyanatopropyl)benzene **2f** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 95:5) to produce a colorless oil (52.3 mg, 99%). R_f (*n*-pentane/diethyl ether, 95:5): 0.50. **^{1}H NMR** (300.1 MHz, $CDCl_3$) *δ* 7.46 – 7.29 (m, 5H), 4.26 (dd, *J* = 8.6, 6.9 Hz, 1H), 2.34 – 2.06 (m, 2H), 0.99 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) *δ* 138.1, 129.0, 128.8, 127.4, 111.7, 55.2, 29.0, 12.0. **IR** (neat, cm^{-1}): *v* 2971, 2935, 2876, 2150, 1493, 1454, 1383, 1079, 906, 833. **HRMS** (EI^+) calcd for $C_{10}H_{11}N_2O_3S$ *m/z* 177.0612 $[M]^+$, Found 177.0620 (Δ 4.3 ppm). Characterization data were in accordance with the literature.[18]



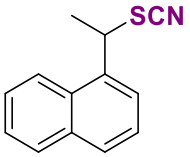
2g

1-(Thiocyanatoisobutyl)benzene **2f** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 95:5) to produce a colorless oil (50.1 mg, 87%). R_f (*n*-pentane/diethyl ether, 95:5): 0.54. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 4.08 (d, J = 9.1 Hz, 1H), 2.45 – 2.26 (m, 1H), 1.18 (d, J = 6.6 Hz, 3H), 0.90 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.5, 128.9, 128.6, 127.8, 112.1, 61.8, 33.6, 21.2, 20.5. **IR** (neat, cm^{-1}): ν 3031, 2965, 2932, 2151, 1493, 1462, 1454, 1390, 1220, 1115. **HRMS** (CI^+) calcd for $C_{11}H_{13}NS$ *m/z* 191.0769 $[M]^+$, Found 191.0761 (Δ -0.8 ppm). Characterization data were in accordance with the literature.[19]



2h

(Thiocyanatomethylene)dibenzene **2h** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 95:5) to produce a yellowish oil (52.7 mg, 78%). R_f (*n*-pentane/ethyl acetate, 9:1): 0.57. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 10H), 5.84 (s, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 137.4, 129.0, 128.8, 128.2, 111.7, 57.4. **IR** (neat, cm^{-1}): ν 2985, 2158, 1718, 1604, 1465, 1271, 1248, 1271, 1248, 1027. **HRMS** (EI^+) calcd for $C_{13}H_{11}$ *m/z* 167.0861 $[M\text{-}SCN]^+$, Found 167.0856 (Δ -3.0 ppm).

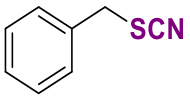


2i

2-(1-Thiocyanatoethyl)naphthalene **2i** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 85:15) to produce a white off solid (60.8 mg, 95%). R_f (*n*-pentane/diethyl ether, 8:2): 0.43. mp: 89-90 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 8.08 (d, J = 8.5 Hz, 1H), 7.96 – 7.83 (m, 2H), 7.70 – 7.45 (m, 4H), 5.40 (q, J = 6.9 Hz, 1H), 2.12 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 133.9, 133.7, 130.2, 129.8, 129.3, 127.0, 126.2, 125.3, 124.5, 122.2, 111.8, 43.9, 22.0. **IR** (neat, cm^{-1}): ν 2975, 2149, 1597, 1511, 1445, 1379, 1200, 1167, 1038, 800. **HRMS** (EI^+) calcd for $C_{12}H_{11}$ *m/z* 155.0861 $[M\text{-}SCN]^+$, Found 155.0849 (Δ -7.7 ppm). Characterization data were in accordance with the literature.[20]

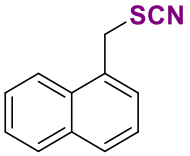
2j

9*H*-Fluoren-9-yl thiocyanate **2j** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 9:1) to produce a sticky yellow oil (48.8 mg, 73%). R_f (*n*-pentane/ethyl acetate, 9:1): 0.52. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.56 – 7.34 (m, 3H), 5.40 (s, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 141.2, 140.6, 129.8, 128.2, 125.4, 120.6, 111.5, 49.8. **IR** (neat, cm^{-1}): *v*3065, 2924, 2152, 2022, 1713, 1610, 1600, 1450, 1189, 917. **HRMS** (CI^+) calcd for $C_{14}H_9NS$ *m/z* 223.0456 $[M]^+$, Found 223.0450 (Δ -2.76 ppm).



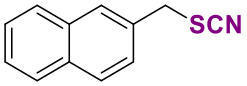
2k

1-(Thiocyanatomethyl)benzene **2k** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether, 97:3) to produce a white solid (31.2 mg, 70%). R_f (*n*-pentane/diethyl ether 95:5): 0.61. mp: 40-41 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 4.16 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 134.3, 129.1, 128.9, 128.9, 111.9, 38.3. **IR** (neat, cm^{-1}): *v* 2926, 2146, 1721, 1492, 1455, 1426, 1244, 1204, 1147, 1074. **HRMS** (EI^+) calcd for C_8H_7NS *m/z* 149.0299 $[M]^+$, Found 149.0298 (Δ -0.8 ppm). Characterization data were in accordance with the literature.[21]



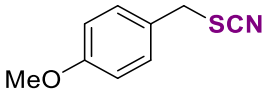
2l

1-(Thiocyanatomethyl)naphthalene **2l** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 85:15) to produce a white solid (43.1 mg, 72%). R_f (*n*-pentane/diethyl ether, 8:2): 0.45. mp: 84-85 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 8.03 – 7.84 (m, 3H), 7.69 – 7.41 (m, 4H), 4.66 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 134.0, 130.6, 130.2, 129.4, 129.2, 128.6, 127.0, 126.3, 125.3, 122.7, 112.0, 36.4. **IR** (neat, cm^{-1}): *v* 3006, 2149, 1594, 1510, 1395, 1247, 1233, 1168, 804, 780. **HRMS** (EI^+) calcd for $C_{12}H_9NS$ *m/z* 199.0456 $[M+H^+]^+$, Found 199.0451 (Δ -2.4 ppm). Characterization data were in accordance with the literature.[22]



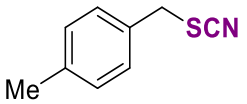
2m

2-(Thiocyanatomethyl)naphthalene **2m** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 85:15) to produce a white solid (31.1 mg, 52%). R_f (*n*-pentane/diethyl ether, 8:2): 0.43. mp: 94-96 °C. **^{1}H NMR**(300.1 MHz, $CDCl_3$) δ 1H NMR (300 MHz, CDCl3) δ 7.92 – 7.79 (m, 4H), 7.58 – 7.41 (m, 4H), 4.33 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 133.1, 133.1, 131.5, 129.2, 128.4, 128.0, 127.8, 126.8, 126.7, 126.0, 111.9, 38.7. **IR** (neat, cm^{-1}): *v* 3023, 2145, 1597, 1507, 1423, 1240, 1126, 965, 867, 828, 753. **HRMS** (EI^+) calcd for $C_{12}H_9NS$ *m/z* 199.0456 $[M]^+$, Found 199.0448 (Δ –4.9 ppm). Characterization data were in accordance with the literature.[22]



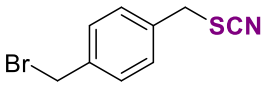
2n

1-Methoxy-4-(thiocyanatomethyl)benzene **2n** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 85:15) to produce a yellow oil containing 5% of 4-methoxybenzaldehyde as impurity (35.0 mg, 57%). R_f (*n*-pentane/ethyl acetate, 85:15): 0.37. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 6.90 (d, J = 8.7 Hz, 2H), 4.15 (s, 2H), 3.81 (s, 3H). **IR** (neat, cm^{-1}): *v* 2933, 2151, 1610, 1509, 1463, 1301, 1224, 1153 1022, 832. **HRMS** (CI^+) calcd for C_9H_9NOS *m/z* 179.0405 $[M]^+$, Found 179.0396 (Δ -4.8 ppm). Characterization data were in accordance with the literature.[23]



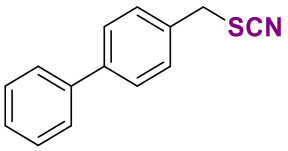
2o

4-Methyl-1-(thiocyanatomethyl)benzene **2o** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 95:5) to produce a colorless oil (35.7 mg, 73%). R_f (*n*-pentane/diethyl ether, 95:5): 0.59. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 2H), 7.28 – 7.22 (m, 2H), 4.23 (s, 2H), 2.46 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.9, 131.2, 129.8, 128.9, 112.1, 38.3, 21.2. **IR** (neat, cm^{-1}): *v* 3027, 2923, 2153, 1610, 1489, 1429, 1371, 1242, 1233, 789. **HRMS** (EI^+) calcd for C_9H_9NS *m/z* 163.0456 $[M]^+$, Found 163.0448 (Δ -4.7 ppm). Characterization data were in accordance with the literature.[22]



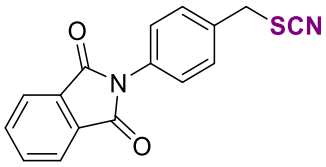
2p

1-Bromomethyl-4-(thiocyanatomethyl)benzene **2p** was synthesized following the general procedure but no base was added and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 9:1) to produce a white sticky solid (50.3 mg, 69%). R_f (*n*-pentane/diethyl ether, 9:1): 0.43. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 4.49 (s, 2H), 4.14 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.5, 134.5, 129.8, 129.4, 111.7, 37.8, 32.6. **IR** (neat, cm^{-1}): ν 3676, 2989, 2902, 2157, 1425, 1394, 1226, 1075, 1066, 1057. **HRMS** (EI^+) calcd for $C_9H_8{}^{79}BrNS$ *m/z* 240.9561 $[M]^+$, Found 240.9552 (Δ -3.9 ppm).



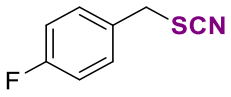
2q

1-Phenyl-4-(thiocyanatomethyl)benzene **2q** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 9:1) to produce a white off solid (40.0 mg, 59%). mp: 93-95 °C. R_f (*n*-pentane/ethyl acetate, 9:1): 0.56. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 4H), 7.50 – 7.33 (m, 5H), 4.22 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 141.1, 139.6, 133.3, 129.0, 128.3, 127.1, 127.1, 126.4, 111.4, 37.3. (Acetone-d_6 was added to improve the solubility) **IR** (neat, cm^{-1}): ν 3032, 2149, 1487, 1429, 1407, 1243, 1006, 843, 769. **HRMS** (EI^+) calcd for $C_{13}H_{11}$ *m/z* 167.0861 $[M\text{-}SCN]^+$, Found 167.0858 (Δ -1.8 ppm). Characterization data were in accordance with the literature.[20]



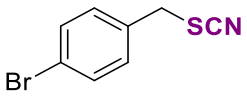
2r

1-Phthaloyl-4-(thiocyanatomethyl)benzene **2r** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 85:15) to produce a white solid (37.9 mg, 42%). mp: 137-140 °C. R_f (*n*-pentane/ethyl acetate, 9:1): 0.26.**^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.83 – 7.75 (m, 2H), 7.51 (s, 4H), 4.21 (s, 2H).**^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 166.9, 134.5, 134.0, 132.2, 131.5, 129.7, 126.9, 123.8, 111.7, 37.8.**IR** (neat, cm^{-1}): ν 2159, 1710, 1518, 1381, 1247, 1117, 1079, 885, 832, 793. **HRMS** (ESI^+) calcd for $C_{16}H_{14}N_3O_2S$ *m/z* 312.0807 $[M+H^+]^+$, Found 312.0792 (Δ -4.8 ppm).



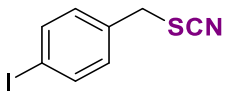
2s

1-Fluoro-4-(thiocyanatomethyl)benzene **2s** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 97:3) to produce a colorless oil (34.0 mg, 68%). R_f (*n*-pentane/diethyl ether, 97:3): 0.62. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.13 – 7.03 (m, 2H), 4.14 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 162.9 (d, J = 248.7 Hz), 130.8 (d, J = 8.5 Hz), 130.2 (d, J = 3.3 Hz), 116.2 (d, J = 21.9 Hz), 111.7, 37.5. **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ -112.60 – -121.04 (m). **IR** (neat, cm^{-1}): ν 2934, 2154, 1600, 1508, 1427, 1223, 1159, 1095, 1016, 835, 722. **HRMS** (EI^+) calcd for C_8H_6FNS *m/z* 167.0205 $[M]^+$, Found 167.0205 (Δ -0.3 ppm). Characterization data were in accordance with the literature.[19]



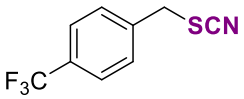
2t

1-Bromo-4-(thiocyanatomethyl)benzene **2t** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 90:10) to produce a colorless oil (43.0 mg, 63%). R_f (*n*-pentane/diethyl ether, 90:10): 0.46. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.51 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 4.08 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 133.4, 132.3, 130.6, 123.1, 111.5, 37.5. **IR** (neat, cm^{-1}): ν 2930, 2153, 1590, 1487, 1404, 1245, 1102, 1070, 1012, 829, 815. **HRMS** (EI^+) calcd for $C_8H_6{}^{79}BrNS$ *m/z* 226.9404 $[M]^+$, Found 226.9403 (Δ -0.8 ppm). calcd for $C_8H_6{}^{81}BrNS$ *m/z* 228.9384 $[M]^+$, Found 228.9380 (Δ -1.8 ppm). Characterization data were in accordance with the literature.[24]



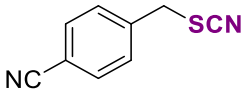
2u

1-Iodo-4-(thiocyanatomethyl)benzene **2u** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 90:10) to produce a yellow oil (58.8 mg, 71%). R_f (*n*-pentane/diethyl ether, 90:10): 0.47. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 4.07 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.2, 134.0, 130.7, 111.5, 94.8, 37.6. **IR** (neat, cm^{-1}): ν 2924, 2152, 1585, 1483, 1399, 1243, 1059, 1007, 825, 798. **HRMS** (CI^+) calcd for $C_8H_6{}^{127}INS$ *m/z* 274.9271 $[M]^+$, Found 274.9266 (Δ 1.9 ppm). Characterization data were in accordance with the literature.[25]



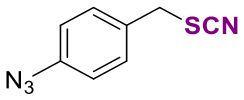
2v

1-Trifluoromethyl-4-(thiocyanatomethyl)benzene **2v** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 95:5) to produce a colorless oil (29.2 mg, 53%). R_f (*n*-pentane/diethyl ether, 95:5): 0.51. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 4.17 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.5 – 138.3 (m), 131.0 (q, 138.4 (d, J = 1.5 Hz, J = 32.7 Hz), 129.3, 126.1 (q, J = 3.8 Hz), 123.7 (q, J = 272.9 Hz), 111.3, 37.4. **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ -62.80. **IR** (neat, cm^{-1}): ν 2930, 2156, 1418, 1321, 1166, 1120, 1107, 1065, 1019, 846, 825. **HRMS** (ESI^+) calcd for $C_9H_6F_3NS$ *m/z* 217.0173 $[M+H^+]^+$, Found 217.0178 (Δ 2.1 ppm).



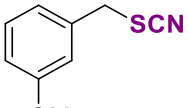
2w

4-(Thiocyanatomethyl)benzonitrile **2w** was synthesized following the general procedure (4 h instead of 45 min) and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 8:2) to produce a white solid (23.5 mg, 45%). mp: 77-79 °C. R_f (*n*-pentane/ethyl acetate, 8:2): 0.37. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 4.15 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 139.7, 132.9, 129.7, 118.1, 112.8, 111.0, 37.3. **IR** (neat, cm^{-1}): ν 2918, 2226, 2156, 1724, 1502, 1412, 1248, 1107, 848, 829. **HRMS** (CI^+) calcd for $C_9H_7N_2S$ *m/z* 175.0330 $[M+H^+]^+$, Found 175.0336 (Δ -3.4 ppm). Characterization data were in accordance with the literature.[26]



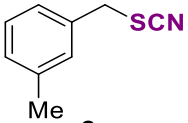
2x

1-Azido-4-(thiocyanatomethyl)benzene **2x** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 8:2) to produce a light brown oil (34.8 mg, 61%). R_f (*n*-pentane/diethyl ether, 9:1): 0.22. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.36 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 4.14 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 140.8, 130.9, 130.5, 119.7, 111.7, 37.8. **IR** (neat, cm^{-1}): ν 2105, 1607, 1505, 1422, 1283, 1245, 1184, 1128, 1110, 831. **HRMS** (EI^+) calcd for $C_8H_6N_4S$ *m/z* 190.0313 $[M]^+$, Found 190.0323 (Δ 5.3 ppm).



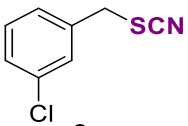
2y

1-Methoxy-3-(thiocyanatomethyl)benzene **2y** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 8:2) to produce a colorless oil (35.1 mg, 65%). R_f (*n*-pentane/diethyl ether, 9:1): 0.30. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 1H), 6.98 – 6.86 (m, 3H), 4.13 (s, 2H), 3.82 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 159.9, 135.7, 130.1, 121.1, 114.4, 114.3, 111.9, 55.2, 38.2. **IR** (neat, cm^{-1}): *v* 2931, 2152, 1609, 1511, 1463, 1304, 1239, 1176 1028, 831. **HRMS** (CI^+) calcd for $C_9H_{10}NOS$ *m/z* 180.0483 $[M+H^+]^+$, Found 180.0484 (Δ 0.6 ppm).



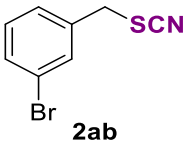
2z

3-Methyl-1-(thiocyanatomethyl)benzene **2z** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 95:5) to produce a colorless oil (31.3 mg, 64%). R_f (*n*-pentane/diethyl ether, 95:5): 0.54. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 139.0, 134.1, 129.7, 129.6, 129.0, 126.0, 112.1, 38.4, 21.3. **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.9, 131.2, 129.8, 128.9, 112.1, 38.3, 21.2. **IR** (neat, cm^{-1}): *v* 2932, 2154, 1489, 1462, 1427, 1242, 1165, 788, 704. **HRMS** (EI^+) calcd for C_9H_9NS *m/z* 163.0456 $[M]^+$, Found 163.0448 (Δ -4.7 ppm). Characterization data were in accordance with the literature.[22]



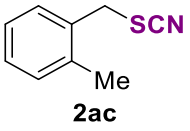
2aa

1-Chloro-3-(thiocyanatomethyl)benzene **2aa** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 9:1) to produce a colorless oil (40.2 mg, 72%). R_f (*n*-pentane/diethyl ether, 9:1): 0.44. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 3H), 7.26 – 7.18 (m, 1H), 4.07 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 136.2, 134.8, 130.4, 129.1, 128.9, 127.1, 111.5, 37.4. **IR** (neat, cm^{-1}): *v* 2989, 2154, 1575, 1475, 1432, 1245, 1205, 1078, 883, 787. **HRMS** (EI^+) calcd for $C_8H_6{}^{35}ClNS$ *m/z* 182.9910 $[M]^+$, Found 182.9917 (Δ 3.9 ppm). Characterization data were in accordance with the literature.[22]



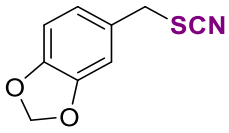
2ab

1-Bromo-3-(thiocyanatomethyl)benzene **2ab** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 9:1) to produce a light brown oil (51.8 mg, 76%). R_f (*n*-pentane/diethyl ether, 9:1): 0.45. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.34 – 7.23 (m, 2H), 4.10 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 136.5, 132.0, 131.8, 130.6, 127.6, 122.9, 111.4, 37.4. **IR** (neat, cm^{-1}): *v* 2971, 2153, 1569, 1474, 1429, 1243, 1202, 1071, 890, 848. **HRMS** (EI^+) calcd for $C_8H_6{}^{79}BrNS$ *m/z* 226.9404 $[M]^+$, Found 226.9401 (Δ -1.4 ppm). (EI^+) calcd for $C_8H_6{}^{81}BrNS$ *m/z* 228.9384 $[M]^+$, Found 228.9380 (Δ -1.8 ppm). Characterization data were in accordance with the literature.[22]



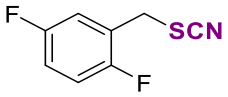
2ac

2-Methyl-1-(thiocyanatomethyl)benzene **2ac** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 95:5) to produce a colorless oil (32.9 mg, 67%). R_f (*n*-pentane/diethyl ether, 95:5): 0.54. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 4H), 4.20 (s, 2H), 2.39 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 136.8, 131.9, 131.0, 130.3, 129.3, 126.7, 111.9, 36.6, 19.0. **IR** (neat, cm^{-1}): *v* 2923, 2152, 1495, 1462, 1427, 1242, 765, 742, 724. **HRMS** (EI^+) calcd for C_9H_9NS *m/z* 163.0456 $[M]^+$, Found 163.0448 (Δ -4.7 ppm). Characterization data were in accordance with the literature.[22]



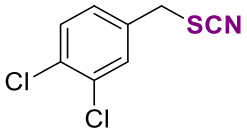
2ad

1,3-Benzodioxol-5-yl-methyl thiocyanate **2ad** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 8:2) to produce a colorless oil (15.7 mg, 27%). R_f (*n*-pentane/ethyl acetate, 9:1): 0.24. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 6.86 – 6.76 (m, 3H), 5.99 (s, 2H), 4.11 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 148.2, 127.8, 122.9, 112.0, 109.1, 108.6, 101.5, 38.7. One carbon signal overlaps and is missing. **IR** (neat, cm^{-1}): *v* 2921, 2152, 1502, 1489, 1445, 1249, 1191, 1099, 1035, 924, 809. **HRMS** (CI^+) calcd for $C_9H_8NO_2S$ *m/z* 194.0276 $[M+H^+]^+$, Found 194.0268 (Δ 4.1 ppm).



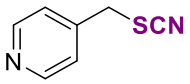
2ae

1,4-Difluoro-2-(thiocyanatomethyl)benzene **2ae** was synthesized following the general procedure (4 h instead of 45 min) and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 9:1) to produce a colorless oil (21.7 mg, 39%). R_f (*n*-pentane/diethyl ether, 9:1): 0.42. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.10 – 6.92 (m, 3H), 4.07 (d, J = 1.2 Hz, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 161.6 – 153.6 (m), 124.2 – 122.5 (m), 112.0 – 115.7 (m), 111.2, 32.0 – 30.6 (m). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ -117.62 – -117.76 (m), -122.78 – -122.93 (m). **IR** (neat, cm^{-1}): ν 2931, 2156, 1497, 1431, 1248, 1210, 1196, 1143, 959, 871, 817. **HRMS** (EI^+) calcd for $C_8H_5F_2NS$ *m/z* 185.0111 $[M]^+$, Found 185.0112 (Δ 0.8 ppm).



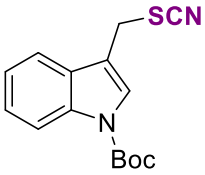
2af

1,2-Dichloro-4-(thiocyanatomethyl)benzene **2af** was synthesized following the general procedure (4 h instead of 45 min) and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 8:2) to produce a sticky colorless oil (29.4 mg, 45%). R_f (*n*-pentane/diethyl ether, 9:1): 0.24. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.22 (dd, J = 8.3, 2.1 Hz, 1H), 4.08 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 134.5, 133.3, 133.2, 131.1, 130.8, 128.2, 111.2, 36.9. **IR** (neat, cm^{-1}): ν 2154, 1471, 1424, 1397, 1242, 1207, 1132, 1031, 897, 822. **HRMS** (EI^+) calcd for $C_8H_5{}^{35}Cl_2NS$ *m/z* 216.9520 $[M]^+$, Found 216.9518 (Δ -0.9 ppm).



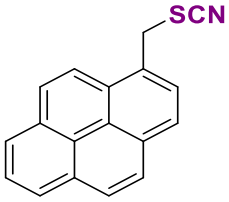
2ag

4-Thiocyanatomethyl-pyridine **2ag** was synthesized following the general procedure (16 h instead of 45 min) and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: dichloromethane/methanol 95:5) to produce a light brown oil (26.4 mg, 59%). Isolated with an inseparable minor impurity. R_f (dichloromethane/methanol 9:1): 0.62. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 8.64 (d, J = 5.9 Hz, 2H), 7.28 (d, J = 5.9 Hz, 2H), 4.06 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 150.5, 143.2, 123.4, 110.9, 36.4. **IR** (neat, cm^{-1}): ν 3032, 2155, 1600, 1563, 1414, 1256, 1218, 1069, 993, 834. **HRMS** (CI^+) calcd for $C_7H_7N_2S$ *m/z* 151.0330 $[M+H^+]^+$, Found 151.0328 (Δ -1.0 ppm). The compound degrades to a black sticky solid, even stored under argon and at -20 °C but was stable enough for analysis.



2ah

1,1-Dimethylethyl 3-(thiocyanatomethyl)-1*H*-indole-1-carboxylate **2ah** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 20 cm, width = 1 cm, eluent: Hexane/ethyl acetate 95:5) to produce an orange oil (25.1 mg, 29%). R_f (Hexane/ethyl acetate, 9:1): 0.52. **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 8.17 (d, J = 9.9 Hz, 1H), 7.70 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 4.38 (d, J = 0.8 Hz, 2H), 1.68 (s, 9H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 149.2, 135.7, 128.2, 125.8, 125.2, 123.0, 118.7, 115.7, 113.2, 112.1, 84.4, 30.0, 28.1. **IR** (neat, cm^{-1}): ν 2979, 2931, 2153, 1736, 1476, 1365, 1308, 1272, 1154, 1084. **HRMS** ($APCI^-$) calcd for $C_{15}H_{16}N_2O_2S$ *m/z* 166.0327 $[M-H]^-$, Found 287.0857 (Δ -0.3 ppm).

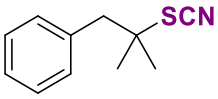


2ai

1-(Thiocyanatomethyl)pyrene **2ai** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 85:15) to produce a white solid (67.2 mg, 82%). R_f (*n*-pentane/diethyl ether, 8:2): 0.43. mp: 112-114 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 8.34 – 7.86 (m, 9H), 4.93 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 132.1, 131.1, 130.5, 128.8, 128.8, 128.3, 128.1, 127.2, 126.5, 126.3, 126.0, 125.8, 125.0, 124.9, 124.5, 121.8, 112.0, 36.9. **IR** (neat, cm^{-1}): ν 3038, 2150, 1587, 1441, 1245, 1224, 1135, 847, 829, 818. **HRMS** (EI^+) calcd for $C_{18}H_{11}NS$ *m/z* 273.0612 $[M]^+$, Found 273.0617 (Δ 1.6 ppm).

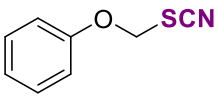
2aj

1-Adamantyl-thiocyanate **2aj** was synthesized following the general procedure (16 h instead of 45 min) and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 9:1) to produce a white solid (15.2 mg, 39%). mp: 65-67 °C. R_f (*n*-pentane/diethyl ether, 9:1): 0.69. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 2.17 (br s, 3H), 2.11 – 2.03 (m, 6H), 1.80 – 1.65 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 110.9, 54.0, 43.6, 35.4, 30.3. **IR** (neat, cm^{-1}): ν 2985, 2805, 2151, 1605, 1465, 1271, 1248, 1027. **HRMS** (CI^+) calcd for $C_{11}H_{16}NS$ *m/z* 194.1003 $[M+H^+]^+$, Found 194.1011 (Δ 3.9 ppm). Characterization data were in accordance with the literature.[27]



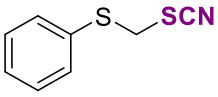
2ak

1,1-Dimethyl-2-phenylethyl thiocyanate **2ak** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 20 cm, width = 1 cm, eluent: Hexane/ethyl acetate 96:4) to produce a colorless oil (32.6 mg, 57%). The product was obtained in mixture with the compound **2g** (**2ak**/**2g** ratio 4:1) and could not be separated by regular chromatography. R_f (Hexane/ethyl acetate, 9:1): 0.45. **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 3H), 7.24 – 7.20 (m, 2H), 3.04 (s, 2H), 1.52 (s, 6H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 135.6, 130.6, 128.3, 127.4, 111.9, 55.7, 48.5, 28.6. **IR** (neat, cm^{-1}): *v* 3029, 2969, 2928, 2149, 1496, 1454, 1389, 1370, 1203, 1112, 1154. **HRMS** (ESI^+) calcd for $C_{11}H_{13}NS$ *m/z* 209.11070 $[M+NH_4]^+$, Found 209.11052 (Δ –0.82 ppm).



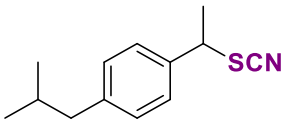
2al

Phenoxymethyl thiocyanate **2al** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 20 cm, width = 1 cm, eluent: Hexane/ethyl acetate 8:2) to produce light yellow oil (42.5 mg, 85%). R_f (Hexane/ethyl acetate, 8:2): 0.47. **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.18 – 7.11 (m, 1H), 7.05 – 7.00 (m, 2H), 5.62 (s, 2H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 155.1, 129.9, 129.9, 123.9, 116.8, 116.8, 110.5, 73.1. **IR** (neat, cm^{-1}): *v* 3063, 2158, 1592, 1489, 1290, 1191, 1173, 1047, 999, 814. **HRMS** (API^+) calcd for C_8H_7NOS *m/z* 166.0327 $[M+H]^+$, Found 166.0341 (Δ 1.4 ppm).



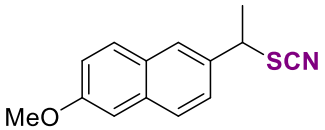
2am

Phenylthiomethyl thiocyanate **2am** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 20 cm, width = 1 cm, eluent: Hexane/ethyl acetate 85:15) to produce light yellow oil (29.7 mg, 55%). R_f (Hexane/ethyl acetate, 8:2): 0.60. **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.43 – 7.36 (m, 3H), 4.41 (s, 2H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 132.5, 131.6, 129.5, 129.0, 111.1, 41.6. **IR** (neat, cm^{-1}): *v* 3058, 2997, 2153, 1582, 1481, 1439, 1388, 1203, 1047, 1024. **HRMS** (ESI^+) calcd for $C_8H_7NS_2$ *m/z* 203.99121 $[M+Na]^+$, Found 203.99151 (Δ 1.48 ppm).



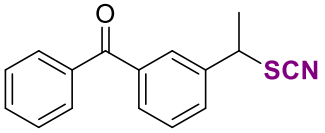
2an

4-Isobutyl-1-(1-thiocyanatoethyl)benzene **2an** was synthesized following modified conditions from the general procedure. No base was added and the reaction time was reduced to 20 min. The crude was purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 9:1) to produce a colorless oil (51.3 mg, 78%). R_f (*n*-pentane/ethyl acetate, 9:1): 0.58. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.28 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 4.61 (q, J = 7.0 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.96 – 1.76 (m, 4H), 0.90 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 142.7, 136.1, 129.7, 126.8, 112.0, 48.5, 45.0, 30.1, 22.3, 22.0. **IR** (neat, cm^{-1}): ν 2955, 2927, 2151, 1512, 1465, 1451, 1382, 1219, 1046, 848. **HRMS** (EI^+) calcd for $C_{13}H_{17}NS$ *m/z* 219.1082 $[M]^+$, Found 219.1084 (Δ 1.2 ppm).



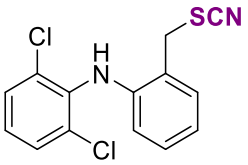
2ao

2-Methoxy-6-(1-thiocyanatoethyl)naphthalene **2ao** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 8:2) to produce a sticky oil (43.8 mg, 60%). R_f (*n*- pentane/ethyl acetate, 8:2): 0.57. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.84 – 7.67 (m, 3H), 7.55 – 7.42 (m, 1H), 7.28 – 7.12 (m, 2H), 4.78 (q, J = 7.0 Hz, 1H), 3.94 (s, 3H), 1.98 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 158.3, 134.6, 133.8, 129.5, 128.4, 127.8, 126.1, 125.0, 119.5, 111.8, 105.7, 55.3, 49.0, 22.0. **IR** (neat, cm^{-1}): ν 2932, 2147, 2042, 1604, 1483, 1392, 1265, 1235, 1196, 1028, 853. **HRMS** (EI^+) calcd for $C_{14}H_{13}NOS$ *m/z* 243.0718 $[M]^+$, Found 243.0718 (Δ -0.1 ppm).



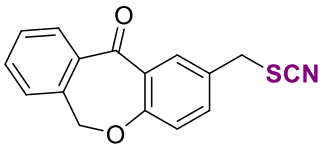
2ap

Phenyl(3-(1-thiocyanatoethyl)phenyl)methanone **2ap** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 9:1) to produce a white solid (63.7 mg, 79%). mp: 92-96 °C. R_f (*n*-pentane/ethyl acetate, 8:2): 0.71. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 4H), 7.67 – 7.58 (m, 2H), 7.57 – 7.45 (m, 3H), 4.65 (q, J = 7.0 Hz, 1H), 1.89 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 195.9, 139.7, 138.3, 137.0, 132.8, 130.9, 130.6, 130.1, 129.1, 128.6, 128.4, 111.3, 47.9, 21.7. **IR** (neat, cm^{-1}): ν 3022, 2152, 1656, 1597, 1447, 1316, 1283, 1202, 1178, 950, 786. **HRMS** (ESI^+) calcd for $C_{16}H_{13}NOS$ *m/z* 267.0718 $[M]^+$, Found 267.0695 (Δ -8.6 ppm).



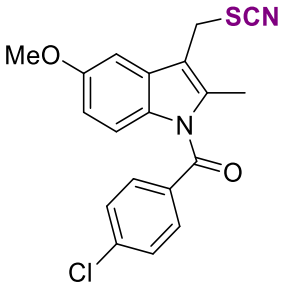
2aq

2,6-Dichloro-*N*-(2-(thiocyanatomethyl)phenyl)aniline **2aq** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 7:3) to produce a white solid (59.2 mg, 64%). R_f (*n*-pentane/ethyl acetate, 8:2): 0.34. mp: 104-106 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 3H), 7.25 – 7.19 (m, 1H), 7.09 – 6.97 (m, 2H), 6.59 (d, J = 8.1 Hz, 1H), 5.89 (br s, 1H), 4.42 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 142.2, 137.0, 131.1, 130.1, 129.7, 128.9, 124.9, 123.4, 122.7, 118.8, 111.5, 36.0. **IR** (neat, cm^{-1}): ν 3344, 2158, 1587, 1500, 1449, 1409, 1301, 1280, 1251, 1190. **HRMS** (ESI^-) calcd for $C_{14}H_9{}^{35}Cl_2N_2S$ *m/z* 306.9864 $[M-H]^-$, Found 306.9852 (Δ -3.9 ppm).



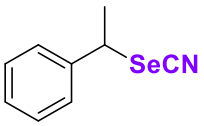
2ar

2-(Thiocyanatomethyl)dibenzo[*b*,*e*]oxepin-11(6*H*)-one **2ar** was synthesized following modified conditions from the general procedure. No base was added and the reaction time was reduced to 20 min. The crude was purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 85:15) to produce a white solid (53.2 mg, 62%). R_f (*n*-pentane/ethyl acetate, 8:2): 0.42. mp: 137-138 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 8.22 (d, J = 2.4 Hz, 1H), 7.89 (dd, J = 7.6, 1.3 Hz, 1H), 7.62 – 7.45 (m, 3H), 7.41 – 7.35 (m, 1H), 7.09 (d, J = 8.5 Hz, 1H), 5.22 (s, 2H), 4.19 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 190.4, 161.5, 140.2, 135.5, 135.2, 133.0, 132.7, 129.5, 129.4, 128.0, 127.9, 125.4, 121.9, 111.7, 73.6, 37.6. **IR** (neat, cm^{-1}): ν 2975, 2146, 2060, 1677, 1589, 1478, 1357, 1217, 1152, 1087, 1013. **HRMS** (EI^+) calcd for $C_{16}H_{11}NO_2S$ *m/z* 281.0511 $[M]^+$, Found 281.0519 (Δ 3.0 ppm).



2as

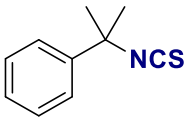
(4-Chlorophenyl)(5-methoxy-2-methyl-3-(thiocyanatomethyl)-1*H*-indol-1-yl)methanone **2as** was synthesized following modified conditions from the general procedure. No base was added and the reaction time was reduced to 20 min. The crude was purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate 8:2) to produce a white solid (61.2 mg, 55%). R_f (*n*-pentane/ethyl acetate 8:2): 0.31. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.68 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 2.4 Hz, 1H), 6.82 (d, J = 9.0 Hz, 1H), 6.70 (dd, J = 9.1, 2.5 Hz, 1H), 4.77 (s, 2H), 3.87 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.3, 156.2, 139.7, 136.4, 133.3, 131.3, 130.7, 129.2, 129.0, 115.1, 112.7, 112.4, 100.6, 55.8, 39.4, 13.1. **IR** (neat, cm^{-1}): ν 2151, 1640, 1607, 1597, 1483, 1303, 1199, 1142, 1012, 843. **HRMS** (EI^+) calcd for $C_{15}H_{20}{}^{35}ClNO_2S$ *m/z* 313.0903 $[M\text{-}SCN]^+$, Found 313.0890 (Δ -4.2 ppm).



6

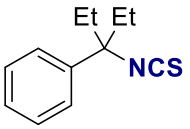
(2-Selenocyanatopropan-2-yl)benzene **6** was synthesized following the general procedure using the *N*-selenocyanatosaccharin instead of **I** and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether 95:5) to produce a colorless oil (54.7 mg, 87%). R_f (*n*-pentane/diethyl ether, 9:1): 0.61. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 5H), 4.92 (q, J = 7.0 Hz, 1H), 2.06 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 139.5, 129.2, 128.9, 127.2, 102.6, 45.6, 22.8. **IR** (neat, cm^{-1}): ν 2968, 2926, 2147, 1495, 1454, 1379, 1204, 1164, 1026, 764. Characterization data were in accordance with the literature.[28]

10.Purification and characterization data of the products 3



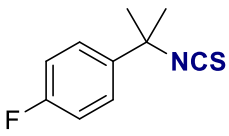
3a

(2-Isothiocyanatopropan-2-yl)benzene **3a** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane) to produce a colorless oil (49.5 mg, 93%). The same procedure was used on a 0.2 mmol scale to give **3a** in similar yield (32.3 mg, 91%). R_f (*n*-pentane/diethyl ether, 95:5): 0.81. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.48 – 7.28 (m, 5H), 1.79 (s, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 143.9, 128.7, 127.7, 124.2, 63.8, 31.9. **IR** (neat, cm^{-1}): *v* 2983, 2058, 1990, 1496, 1448, 1367, 1255, 1161, 1002. **HRMS** (EI^+) calcd for $C_{10}H_{11}NS$ *m/z* 177.0612 $[M]^+$, Found 177.0624 (Δ 6.6 ppm).



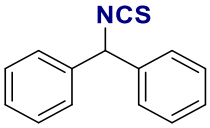
3b

(1-Isothiocyanato-1-ethylpropyl)benzene **3b** was synthesized following the general procedure and purified by flash chromatography on alumina (height = 20 cm, width = 1 cm, eluent: Hexane/ethyl acetate 98:2) to produce a light yellow oil (47.9 mg, 78%). R_f (Hexane/ethyl acetate, 9:1): 0.83. **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.32 – 7.26 (m, 3H), 2.14 – 1.93 (m, 4H), 0.84 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 140.5, 128.5, 127.4, 125.3, 72.8, 36.3, 8.7. **IR** (neat, cm^{-1}): *v* 3035, 2957, 2924, 1961, 1497, 1455, 1375, 1226, 1066, 747. **HRMS** (AP^+) calcd for C_8H_7NOS *m/z* 206.1003 $[M+H]^+$, Found 206.0997 (Δ -0.6 ppm).



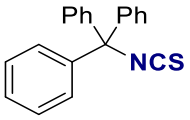
3c

4-Fluoro-1-(2-isothiocyanatopropan-2-yl)benzene **3c** was synthesized following the general procedure and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/diethyl ether, 97:3). colorless oil (50.4 mg, 86%). R_f (*n*-pentane/diethyl ether 95:5): 0.82. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 1H), 7.10 – 6.99 (m, 1H), 1.77 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 162.0 (d, *J* = 246.8 Hz), 139.8, 126.1 (d, *J* = 8.1 Hz), 115.4 (d, *J* = 21.6 Hz), 63.3, 32.0. **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ -114.84 – -114.96 (m). **IR** (neat, cm^{-1}): *v* 2985, 2062, 1602, 1511, 1254, 1235, 1163, 1099, 834. **HRMS** (ESI^+) calcd for $C_{10}H_{10}FNS$ *m/z* 195.0518 $[M]^+$, Found 195.0529 (Δ 5.4 ppm).



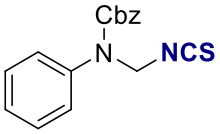
3h

(Isothiocyanatomethylene)dibenzene **3h** was synthesized following the general procedure and was obtained by filtration on a short pad of silica gel (height = 5 cm, width = 2 cm, eluent: *n*-pentane (30 mL), then diethyl ether (70 mL)). After evaporation of solvent, **3f** was produced as a white solid (38.5 mg, 57%). R_f (pentane/diethyl ether, 97:3): 0.83. mp: 57-59 °C. **^{1}H NMR (300.1 MHz, CDCl$_3$)** δ 7.43 – 7.28 (m, 10H), 5.99 (s, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 139.2, 128.9, 128.3, 126.6, 64.6. **IR** (neat, cm^{-1}): *v* 3031, 2062, 1494, 1453, 1342, 1280, 1029, 856. **HRMS** (EI$^+$) calcd for $C_{13}H_{11}$ *m/z* 167.0861 [M-NCS]$^+$, Found 167.0847 (Δ 8.3 ppm).



3at

1-Isothiocyanato-1,1,1-triphenyl-methane **3at** was synthesized following the general procedure and was obtained by filtration on a short pad of silica gel (height = 5 cm, width = 2 cm, eluent: *n*-pentane (30 mL), then diethyl ether (70 mL)). After evaporation of the solvents, **3ao** was produced as a white solid (61.5 mg, 68%). R_f (*n*-pentane/diethyl ether, 97:3): 0.85. mp: 137-138 °C **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 9H), 7.25 – 7.13 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 143.0, 128.3, 128.1, 128.0, 76.8. **IR** (neat, cm^{-1}): *v* 3040, 2110, 2054, 1490, 1444, 1201, 1184, 1150, 1032, 895, 826. **HRMS** (EI$^+$) calcd for $C_{19}H_{15}$ *m/z* 243.1174 [M-NCS]$^+$, Found 243.1175 (Δ 0.6 ppm).

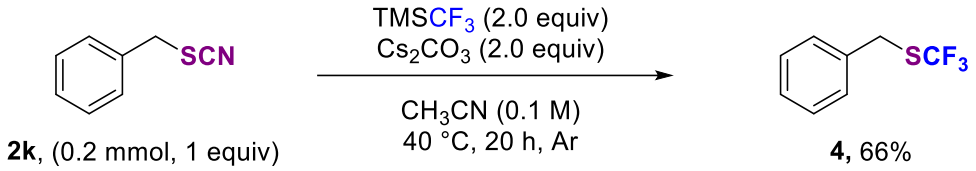


3av

(1-Isothiocyanato-1-ethylpropyl)benzene **3at** was synthesized following the general procedure for thiocyanation and purified by flash chromatography on alumina (height = 20 cm, width = 1 cm, eluent: Hexane/ethyl acetate 93:7) to produce a colorless oil (47.3 mg, 53%). R_f (Hexane/ethyl acetate, 9:1): 0.49. **^{1}H NMR** (400.2 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 10H), 5.28 – 5.18 (m, 4H). **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 154.7, 140.2, 135.7, 129.5, 128.6, 128.3, 128.0, 126.9, 68.3, 60.7. ^{13}C signals for some carbons overlap. **IR** (neat, cm^{-1}): *v* 3034, 2020, 1709, 1597, 1535, 1453, 1398, 1358, 1314, 1271. **HRMS** (ESI$^+$) calcd for $C_{16}H_{14}N_2O_2S$ *m/z* 316.11142 [M+NH_4]$^+$, Found 316.11121 (Δ –0.69 ppm).

11.Post-functionalization reactions

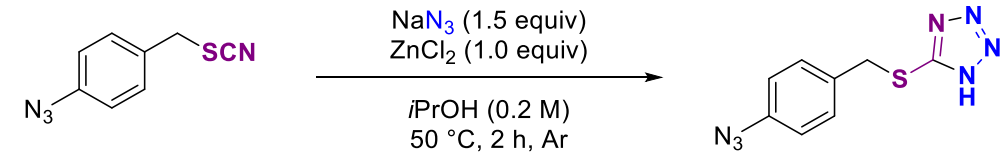
Thiocyanate conversion to SCF_3



2k, (0.2 mmol, 1 equiv) **4,** 66%

Following a known procedure,[29] in a 10 mL oven-dried reaction tube were charged benzyl thiocyanate (29.8 mg, 0.2 mmol, 1.0 equiv) and cesium carbonate (131 mg, 0.4 mmol, 2.0 equiv) in acetonitrile (2 mL, 0.1 M) under argon atmosphere. $TMSCF_3$ (59 µL, 0.4 mmol, 2.0 equiv) was added and the tube was sealed and flushed 3 times with argon. The reaction mixture was stirred at 40 °C for 20 h and the reaction was monitored by TLC (eluent: *n*-pentane/ethyl acetate, 9:1). The solution was cooled at room temperature diluted with water (20 mL) and extracted with EtOAc (3 × 10 mL). The organic phase was washed with brine (10 mL) and dried over $MgSO_4$ to produce **4** as a light brown oil (25.4 mg, 66%). **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 4.13 (s, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 135.0, 130.6 (q, J = 306.8 Hz), 128.9, 128.9, 128.0, 34.3 (q, J = 2.4 Hz). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ -42.17. Characterization data were in accordance with the literature.[30]

Synthesis of tetrazole via [2+3] Cycloaddition



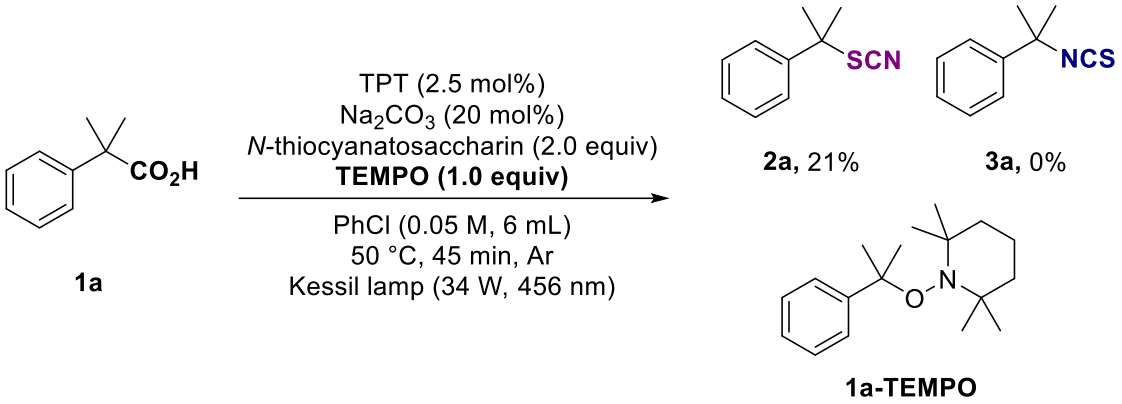
2x, (0.2 mmol, 1 equiv) **5,** 74%

Following a known procedure,[29] in a 10 mL oven-dried reaction tube were added sodium azide (19.5 mg, 0.3 mmol, 1.5 equiv) and zinc chloride (27.3 mg, 0.2 mmol, 1.0 equiv) to a solution of 4-azidobenzyl thiocyanate (38.0 mg, 0.2 mmol, 1.0 equiv) in isopropanol (1 mL, 0.2 M) under argon atmosphere. The reaction mixture was stirred at 50 °C for 2 h and the reaction was monitored by TLC (eluent: *n*-pentane/ethyl acetate, 9:1). The white suspension was diluted with EtOAc (15 mL) and transferred to a separatory funnel, then washed with an EDTA solution (10 mL) to remove zinc salts and brine (10 mL). The crude product was purified by flash chromatography on silica gel (height = 10 cm, width = 1 cm, eluent: ethyl acetate/methanol, 100:0 to 95:5) to produce **5** as a white solid (34.5 mg, 74%). mp: 94-97 °C. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 4.07 (s, 2H). ^{1}H signal of NH wasn't detected. **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 148.6, 132.2, 129.8, 128.7, 127.0, 62.0. **IR** (neat, cm^{-1}): ν 3467, 3083, 2132, 1595, 1533, 1367, 1255, 1161, 1002, 812. **HRMS** (EI^+) calcd for $C_8H_7N_6S$ *m/z* 219.0453 $[M]^+$, Found 219.0459 (Δ 2.7 ppm).

12.Mechanistic studies

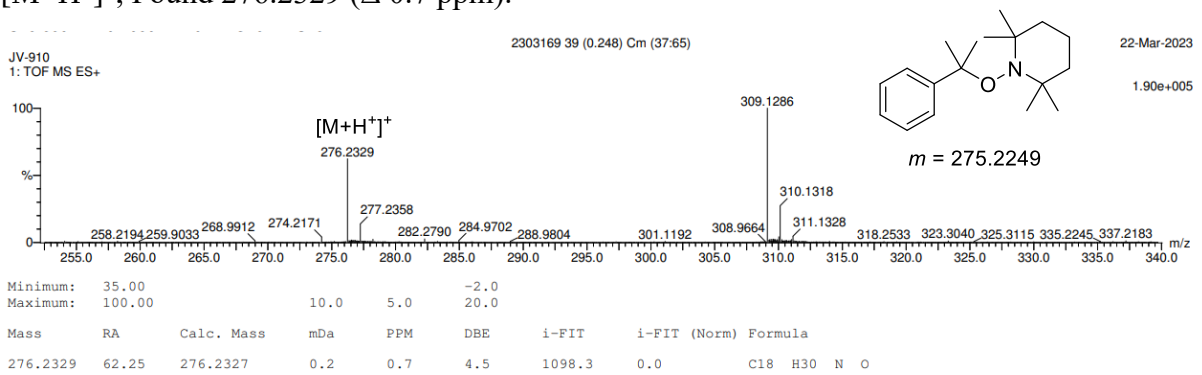
(1) Radical trap experiments

Experiment with TEMPO



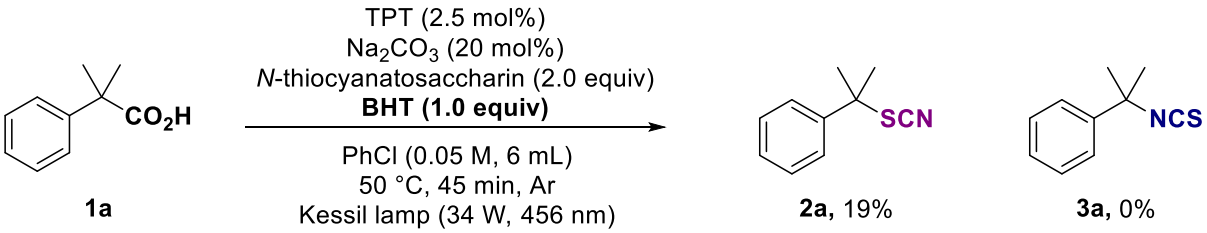
In a 10 mL oven-dried sealable reaction tube equipped with a stirring bar was added phenylisobutyric acid (49.3 mg, 0.3 mmol, 1.0 equiv), sodium carbonate (6.4 mg, 0.06 mmol, 0.2 equiv), triphenylpyrylium tetrafluoroborate (3.0 mg, 0.025 equiv) and *N*-thiocyanatosaccharin (144.0 mg, 0.6 mmol, 2.0 equiv). The tube was flushed three times with argon and freshly distilled and degassed (freeze-pump-thaw) chlorobenzene (6.0 mL) was added. 2,2,6,6-tetramethylpiperidine-*N*-oxyl (31.2 mg, 0.3 mmol, 1.0 equiv) was quickly added and the tube was sealed and the heterogenous reaction mixure was stirred at ~ 50 °C for 45 min under UV light irradiation (Kessil lamp, 34 W, 456 nm). The yield of the reaction was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (32 μL, 0.3 mmol, 1.0 equiv) as an internal standard.

The adduct **1a-TEMPO** was detected by **HRMS** (ESI$^+$) calcd for $C_{18}H_{30}NO$ *m/z* 276.2327 $[M+H^+]^+$, Found 276.2329 (Δ 0.7 ppm).



Minimum:	35.00			-2.0			
Maximum:	100.00		10.0	5.0	20.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
276.2329	62.25	276.2327	0.2	0.7	4.5	1098.3	0.0	C18 H30 N O

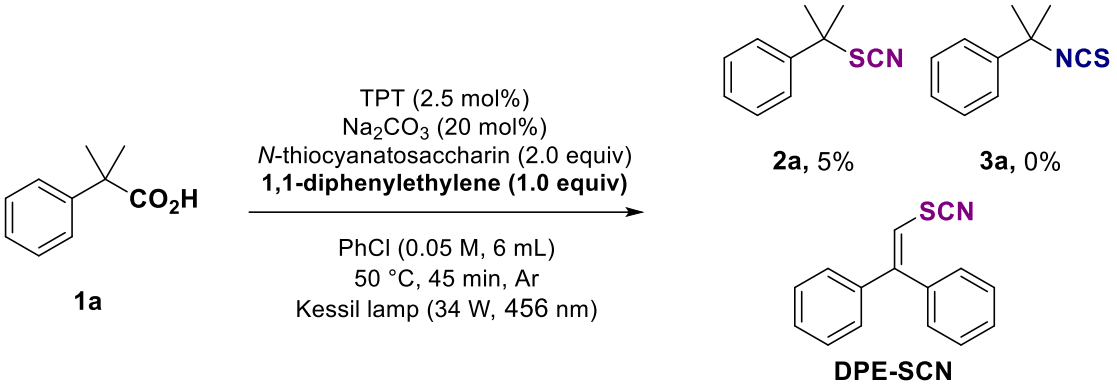
Experiment with BHT



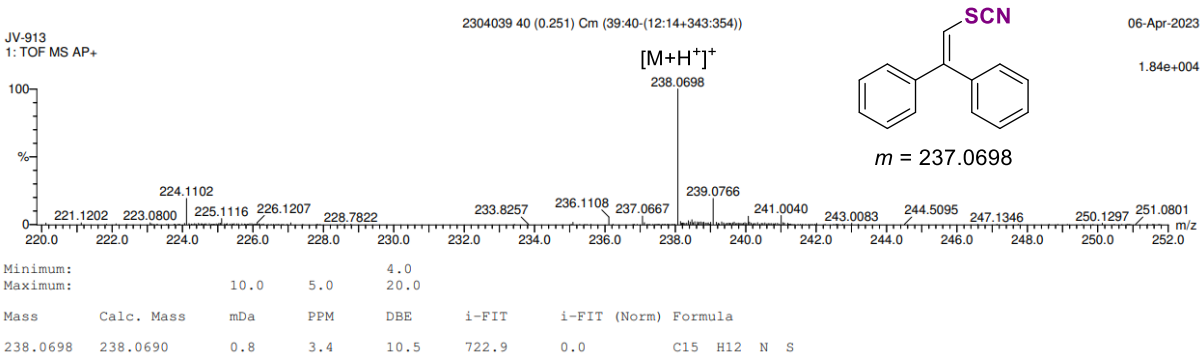
In a 10 mL oven-dried sealable reaction tube equipped with a stirring bar was added phenylisobutyric acid (49.3 mg, 0.3 mmol, 1.0 equiv), sodium carbonate (6.4 mg, 0.06 mmol,

0.2 equiv), triphenylpyrylium tetrafluoroborate (3.0 mg, 0.025 equiv) and *N*-thiocyanatosaccharin (144.0 mg, 0.6 mmol, 2.0 equiv). The tube was flushed three times with argon and freshly distilled and degassed (Freeze-Pump-Thaw) chlorobenzene (6.0 mL) was added. 3,5-di-tert-4-butylhydroxytoluene (44.1 mg, 0.3 mmol, 1.0 equiv) was quickly added and the tube was sealed and the heterogenous reaction mixture was stirred at ~50 °C for 45 min under UV light irradiation (Kessil lamp, 34 W, 456 nm). The yield of the reaction was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) as an internal standard. No adduct was detected by HRMS.

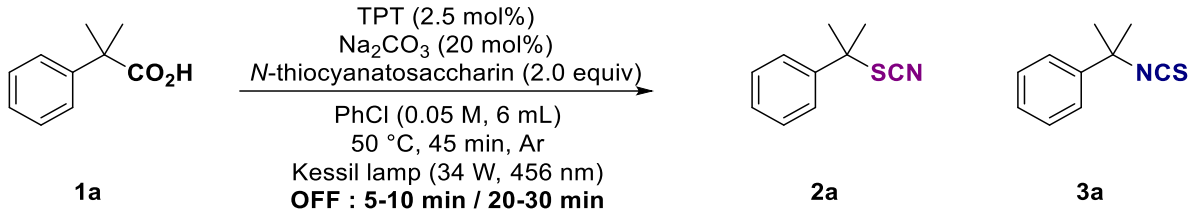
Experiment with 1,1-diphenylethylene



In a 10 mL oven-dried sealable reaction tube equipped with a stirring bar was added phenylisobutyric acid (49.3 mg, 0.3 mmol, 1.0 equiv), sodium carbonate (6.4 mg, 0.06 mmol, 0.2 equiv), triphenylpyrylium tetrafluoroborate (3.0 mg, 0.025 equiv) and *N*-thiocyanatosaccharin (144.0 mg, 0.6 mmol, 2.0 equiv). The tube was flushed three times with argon and freshly distilled and degassed (Freeze-Pump-Thaw) chlorobenzene (6.0 mL) was added. 1,1-diphenylethylene (35 µL, 0.3 mmol, 1.0 equiv) was added, the tube was sealed and the heterogenous reaction mixture was stirred at ~50 °C for 45 min under UV light irradiation (Kessil lamp, 34 W, 456 nm). The yield of the reaction was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) as an internal standard.
The adduct **DPE-SCN** was detected by **HRMS** (ESI$^+$) calcd for $C_{15}H_{12}NS$ *m/z* 238.0690 $[M+H^+]^+$, Found 238.0698 (Δ 3.4 ppm).



(2) Light ON/OFF experiments



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

In a 10 mL oven-dried reaction tube equipped with a stirring bar was added phenylisobutyric acid (49.3 mg, 0.3 mmol, 1.0 equiv), sodium carbonate (6.4 mg, 0.06 mmol, 0.2 equiv), triphenylpyrylium tetrafluoroborate (3.0 mg, 0.025 equiv) and *N*-thiocyanatosaccharin (144.0 mg, 0.6 mmol, 2.0 equiv). The tube was flushed three times with argon and freshly distilled and degassed (Freeze-Pump-Thaw) chlorobenzene (6.0 mL) and 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) were added and the tube was sealed and the heterogenous reaction mixture was stirred at ~50 °C for 45 min under UV light irradiation (Kessil lamp, 34 W, 456 nm). The reaction tube was covered with aluminum foil between 5-10 min and 20-30 min. The reaction was followed by ^{1}H NMR at 5, 10, 20, 30 and 45 min by taking 10 µL of the reaction mixture kept in the dark (aluminum foil), diluted in $CDCl_3$ (0.35 mL) and analyzed by ^{1}H NMR.

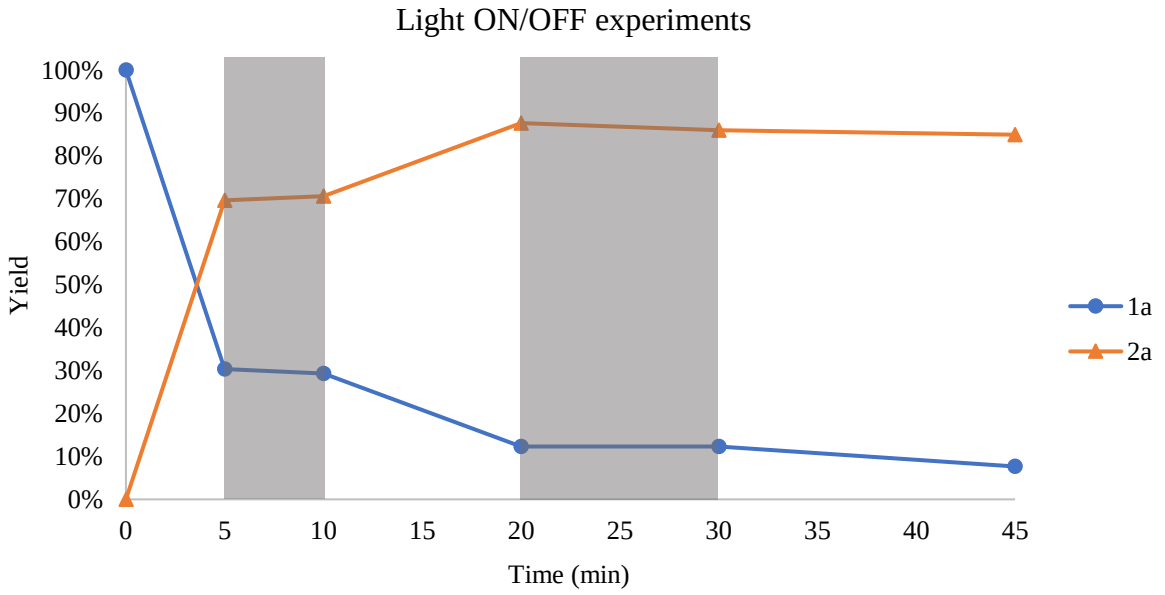
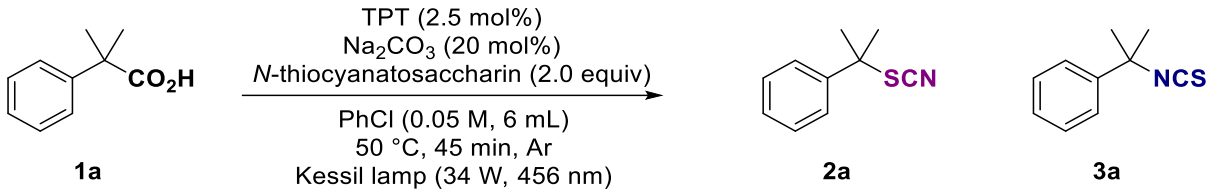


Figure S7

The results of the ON/OFF experiments indicated that the mechanism involved in the decarboxylative thiocyanation process is photoinduced.

(3) Kinetic studies

The kinetic study was performed under our standard conditions.



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

In a 10 mL oven-dried reaction tube equipped with a stirring bar was added phenylisobutyric acid **1a** (49.3 mg, 0.3 mmol, 1.0 equiv), sodium carbonate (6.4 mg, 0.06 mmol, 0.2 equiv), triphenylpyrylium tetrafluoroborate (3.0 mg, 0.025 equiv) and *N*-thiocyanatosaccharin (144.0 mg, 0.6 mmol, 2.0 equiv). The tube was flushed three times with argon and freshly distilled and degassed (Freeze-Pump-Thaw) chlorobenzene (6.0 mL) and 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) were added and the tube was sealed and the heterogenous reaction mixture was stirred at ~50 °C for 45 min under UV light irradiation (Kessil lamp, 34 W, 456 nm). The reaction was followed by ^{1}H NMR at 1, 3, 5, 10, 15, 20, 30 and 45 min by taking 10 µL of the reaction mixture, kept in the dark (aluminum foil), diluted in $CDCl_3$ (0.35 mL) and analyzed by ^{1}H NMR.

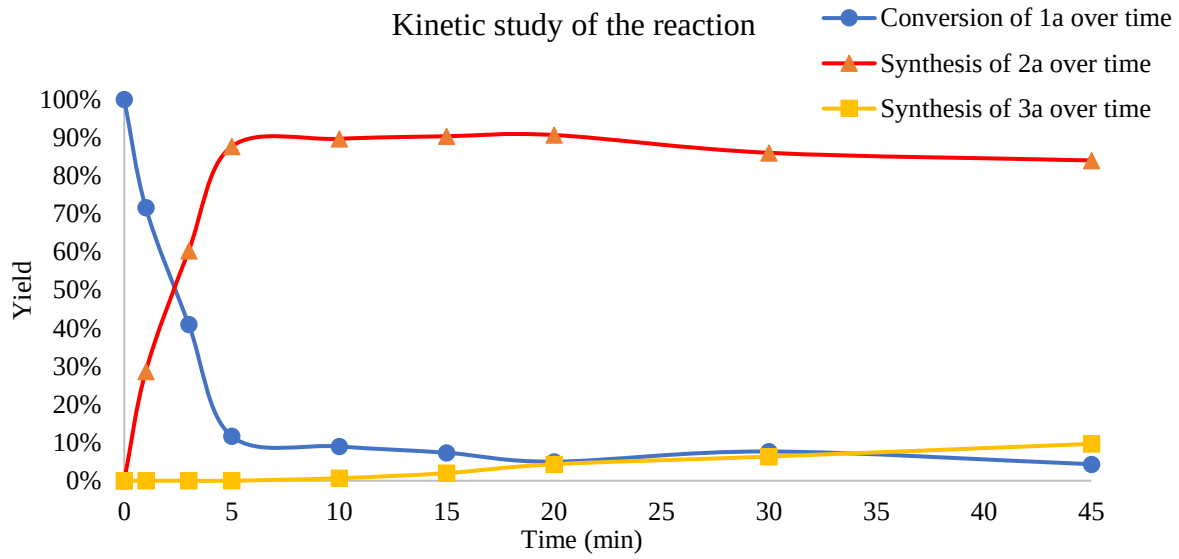


Figure S8

The kinetic study of the reaction with **1a** (Figure S6) showed that the formation of the thiocyanate **2a** was very fast (87% yield after 5 min). Note the incubation time for the formation of **3a**. This suggests that **3a** may result from the isomerization of **2a**.

The kinetic study of the reaction was also performed with substrate **1i** under our standard conditions (Figure S7). In this case, no isothiocyanation product was observed. The reaction was slower and the yield after 1 min is ~ 7%.

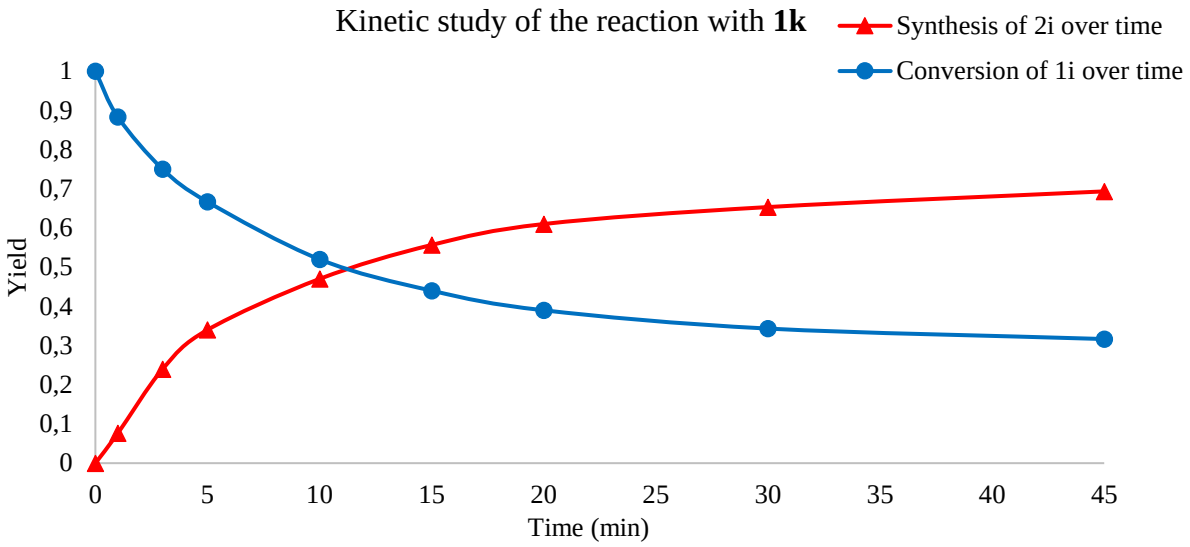
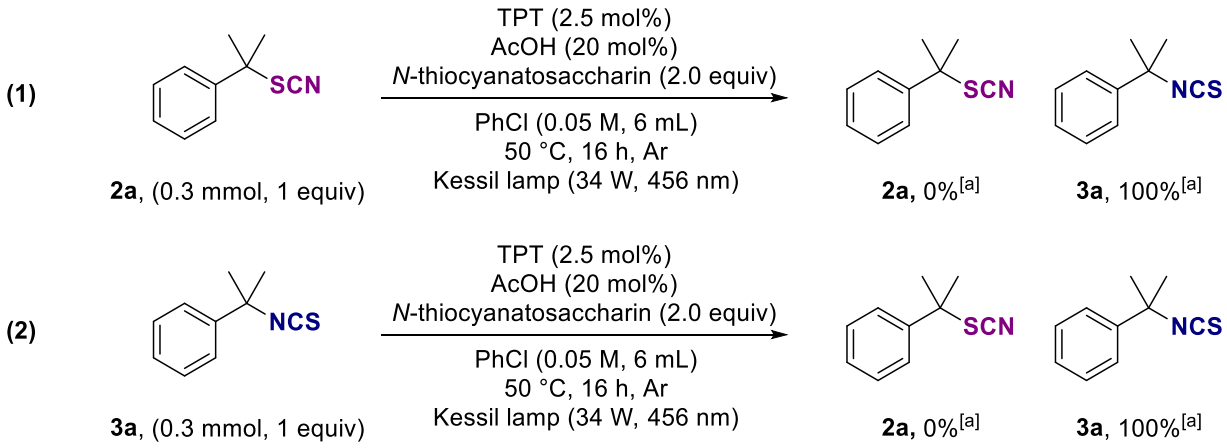


Figure S9

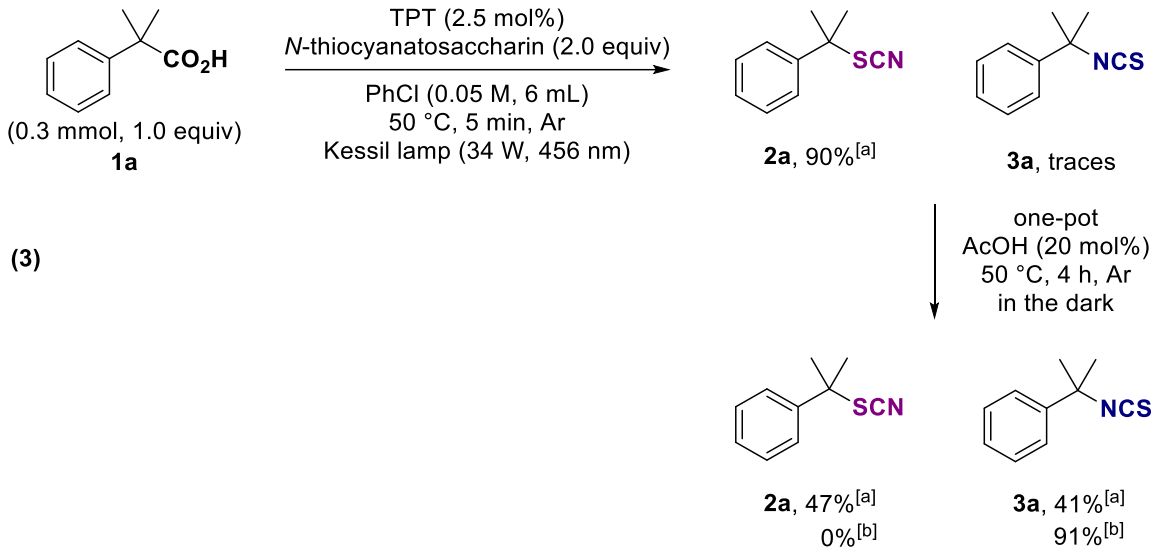
(4) Isomerization studies

To confirm this hypothesis, reactions were performed under our standard isomerization conditions for 16 h using either **2a** (equation 1) or **3a** (equation 2) as starting materials. In the first case, **2a** was isomerized into **3a** in a quantitative manner. Conversely **3a** remained unchanged during the reaction (equation 2).



[a] The ^{1}H NMR yield were measured using 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) as an internal standard.

To further confirm these results, a one-pot reaction was conducted (equation 3). After 15 min of reaction under our standard conditions, **2a** was obtained in 90% ^{1}H NMR yield. The reaction mixture was then stirred in the dark for 4 h after the addition of acetic acid (20 mol%) to give a mixture of **2a** (47%) and **3a** (41%).



[a] The ^{1}H NMR yield were measured using 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) as an internal standard. [b] ^{1}H NMR yield obtained under our standard isothiocyanation conditions (with light).

Please note that the formation of **3a** was slower in the absence of UV light compared to the results obtained under standard isothiocyanation conditions (with UV light irradiation).

(5) Quantum Yield measurement

Procedure for the determination of the photon flux of the lamp

From known procedures of Yoon[31], Glorius,[32] and Poisson[33] the photon flux of the UV-lamp (17W, λmax = 425 nm) was measured by standard ferrioxalate actinometry. A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (20 mg) and sodium acetate (4.5 g) in a sulfuric acid solution (0.5 M, 20 mL). A solution of ferrioxalate (0.006 M) was prepared by dissolving potassium ferrioxalate hydrate (36 mg) in a sulfuric acid solution (0.05 M, 10 mL). Both solutions were covered with aluminum foil.

In a reaction tube, was charged a sample of the ferrioxalate solution (1000 µL). The sample was irradiated at λ = 425 nm for 90 s. The lamp was then turned off and the phenanthroline solution (175 µL) was added. The resulting solution was stirred for 1 h in the dark. The absorption of the sample was then measured at 510 nm. The absorption of a non-irradiated sample was measured. The average of the absorption in case of 3 experiments (irradiated and non-irradiated) was determined and used to calculate the ferrioxalate conversion using the equation **(4)**.

$$(4)\quad \mathrm{n}(Fe^{2+}) = \frac{V\,.\Delta A\,(510nm)}{l\,.\varepsilon} \qquad \mathrm{n}(Fe^{2+}) = \frac{0.001175\,.1.11}{1\,.11100} = 1.18\,10^{-6}\,mol$$

In our study, V is the total volume of the solution (0.001175 L). ΔA is the difference in absorption at 510 nm measured between the irradiated and non-irradiated solutions, l is the length of the quartz cuvette (1.0 cm), and ε is the molar absorption coefficient of the ferrioxalate actinometer at 510 nm (11100 L.cm^{-1}.mol^{-1}). The calculated conversion is 1.18 10^{-6} mol.

$$(5)\quad \mathrm{f} = 1 - 10^{-A}$$

The photon flux (Φq) was calculated with the equation **(6)** where Φ_{Fe} is the photoreaction quantum yield for the ferrioxalate actinometer (1.12 at λ_{ex} = 416 nm),[34] t is the sample

irradiation time (90 s) and f is the fraction of absorbed light (calculated 0.86 with equation **(5)**). The photon flux was found to be 1.36 10^{-8} einstein.s^{-1}.

$$(6)\quad \Phi_p = \frac{n\,(Fe^{2+})}{\Phi_{Fe}\,.t\,.f} \qquad \Phi_p = \frac{1.18\ 10^{-6}}{1.12\ .90\ .0.86} = 1.36\ 10^{-8}\ einstein.s^{-1}$$

Quantum yield determination

The quantum yield of the reaction was determined with the equation **(7)**. The average yield of **2k** was 6.4% (over 3 experiments: 5.4%, 6.2%, 7.6%) after 1 min of reaction, using phenylacetic acid as substrate under our standard conditions. This value corresponds to a conversion of 1.92 10^{-5} mol. The absorption of the reaction mixture at λ = 425 nm was > 2 giving f_R = 0.99 (with equation **(5)**).

$$(7)\quad \Phi = \frac{n_{2i}}{\Phi_p.t.f_R} \qquad \Phi = \frac{1.92\ 10^{-5}}{1.36\ 10^{-8}\ .60\ .0.99} = 22.5$$

The quantum yield with those data was determined to be 22.5. Such value suggested a photoinduced radical chain process.

(6) Cyclic voltammetry experiments

A cyclic voltammetry cell was equipped with a 100 µm platine electrode (measure), a saturated calomel electrode (reference) and a platine electrode (auxiliary). The experiments were realized in acetonitrile (15 mL) with *n*Bu_4PF_6 as electrolyte (0.1 M) under argon. After blank measurement, *N*-thiocyanatosaccharin (36.0 mg, 0.15 mmol, 10 mM) or phenylisobutyric acid (24.6 mg, 0.15 mmol, 10 mM) were added to the solution and the mixture was stirred and degassed with argon for 5 min. The stirring was then stopped and the voltammograms were recorded between -2500 and 3000 mV with a scan rate of 700 mV/s.

Voltammogram of *N*-thiocyanatosaccharin I

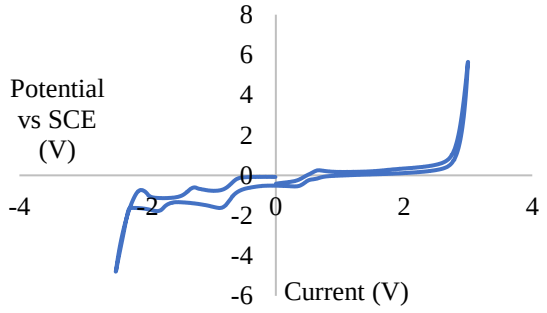


Figure S8: Voltammogram of **I**

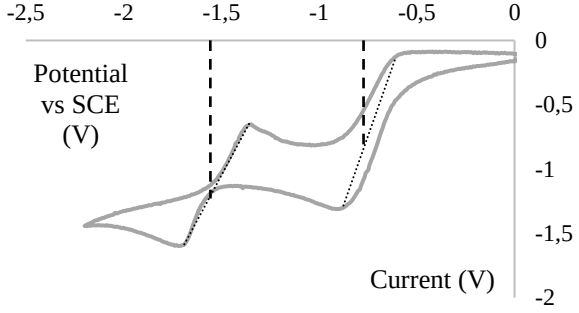


Figure S9: Zoom of the -2.2 V to 0 V area

The oxidation potential was attributed to the presence of oxygen and observed despite the fact that the voltametric cell was degassed several times with argon. Two reversible reduction events were observed and reduction potentials of -0.8 V and -1.6 V vs SCE were determined (Figure S9).

Voltammogram of Phenylisobutyric acid 1a

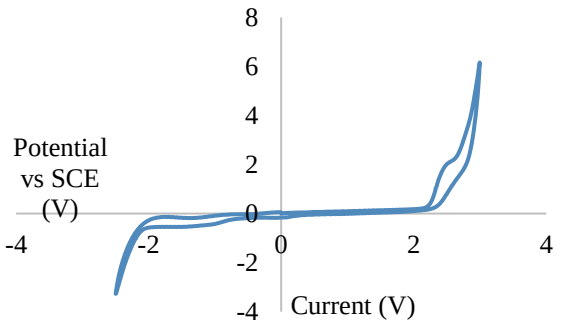


Figure S10: Voltammogram of **1a**

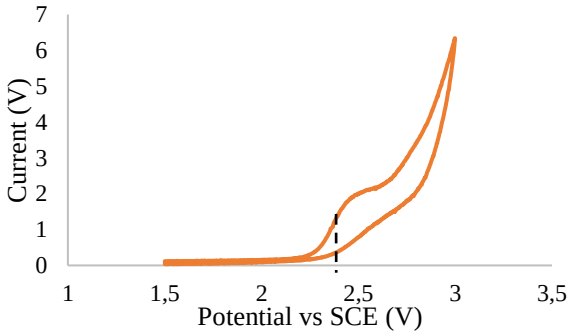


Figure S11: Zoom of the 1.5 V to 3 V area

An oxidation potential for the phenylisobutyric acid of + 2.4 V vs SCE was measured (Figure S11). No clear reduction potential was observed.

Voltammogram of Phenylisobutyric acid 1a with Na_2CO_3 (1 equiv)

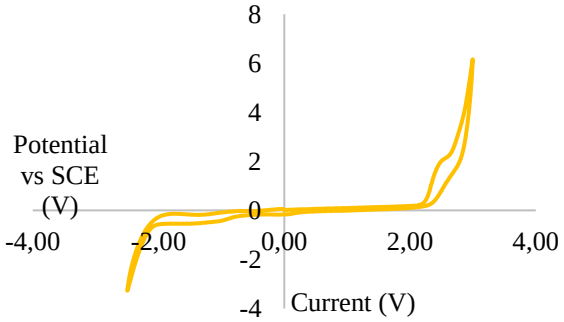


Figure S12: Voltammogram of **1a** + **Na_2CO_3**

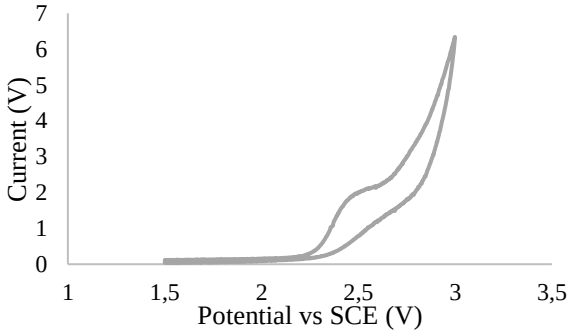
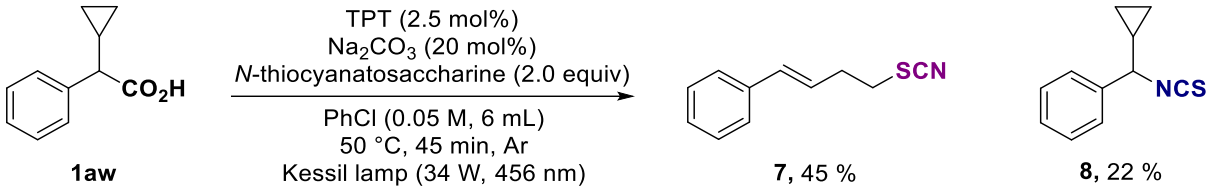


Figure S13: Zoom of the 1.5 V to 3 V area

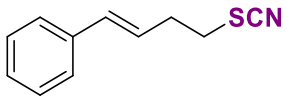
In the presence of Na_2CO_3 (1 equiv) no difference was observed and the oxidation potential of + 2.4 V vs SCE was measured (Figure S13).

(7) Radical clock experiments



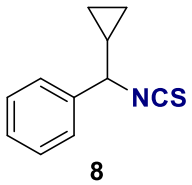
1aw | **7**, 45 % | **8**, 22 %

In a 10 mL oven-dried sealable reaction tube equipped with a stirring bar was added 2-cyclopropyl-2-phenylacetic acid (52.9 mg, 0.3 mmol, 1.0 equiv), sodium carbonate (6.4 mg, 0.06 mmol, 0.2 equiv), triphenylpyrylium tetrafluoroborate (3.0 mg, 0.025 equiv) and *N*-thiocyanatosaccharin (144.0 mg, 0.6 mmol, 2.0 equiv). The tube was flushed three times with argon and freshly distilled and degassed (Freeze-Pump-Thaw) chlorobenzene (6.0 mL). 1,1,2,2-tetrachloroethane (32 µL, 0.3 mmol, 1.0 equiv) were added, the tube was sealed and the heterogenous reaction mixture was stirred at ~50 °C under UV light irradiation (Kessil lamp, 34 W, 456 nm). After filtration through a silica pad, the crude reaction mixture was purified by flash chromatography on silica gel (Biotage 25 g, eluent: *n*-pentane/ethyl acetate = 9:1 to 7:3). The compound **7** was isolated in 45% yield along with **8** (22%).



7

(4-Thiocyanatobut-1-en-1-yl)benzene **7** was obtained under our standard reaction conditions starting from **1aw** and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate = 90:10 to 70:30) to produce a colorless oil (25.0 mg, 44%). R_f (*n*-pentane/ethyl acetate 8:2) = 0.56. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 6.55 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.8, 7.0 Hz, 1H), 3.09 (t, J = 7.1 Hz, 2H), 2.74 (qd, J = 7.1, 1.4 Hz, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 136.6, 133.7, 128.6, 127.7, 126.2, 125.0, 112.1, 33.7, 33.2. **IR** (neat, cm^{-1}): ν 3028, 2926, 2154, 1724, 1493, 1449, 1287, 1151, 967. **HRMS** (CI^+) calcd for $C_{11}H_{12}NS$ *m/z* 190.0690 $[M+H^+]^+$, Found 190.0692 (Δ 0.8 ppm).



8

(Cyclopropyl(isothiocyanato)methyl)benzene **8** was was obtained under our standard reaction conditions starting from **1aw** and purified by flash chromatography on silica gel (height = 15 cm, width = 1 cm, eluent: *n*-pentane/ethyl acetate = 90:10 to 70:30) to produce a colorless oil (12.5 mg, 22%). R_f (*n*-pentane/ethyl acetate 8:2) = 0.78. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.25 – 7.09 (m, 5H), 4.07 (d, J = 7.9 Hz, 1H), 1.28 – 1.13 (m, 1H), 0.60 – 0.34 (m, 3H), 0.32 – 0.23 (m, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 138.7, 128.8, 128.3, 126.1, 65.7, 19.0, 4.1, 3.9. **IR** (neat, cm^{-1}): ν 3026, 2062, 1494, 1453, 1375, 1298, 1287, 1023, 950. **HRMS** (EI^+) calcd for $C_{11}H_{11}NS$ *m/z* 189.0612 $[M]^+$, Found 189.0621 (Δ 4.7 ppm). Characterization data were in accordance with the literature.[20]

13.References

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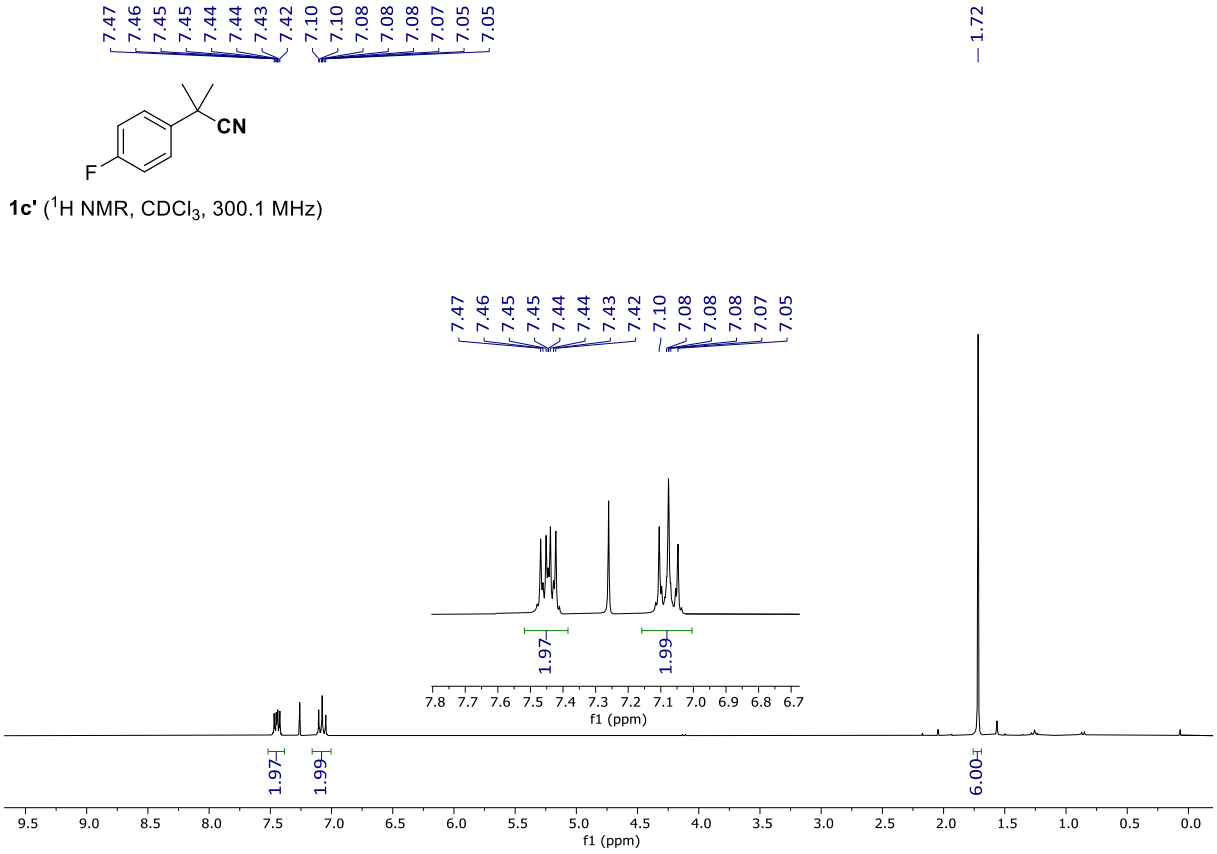
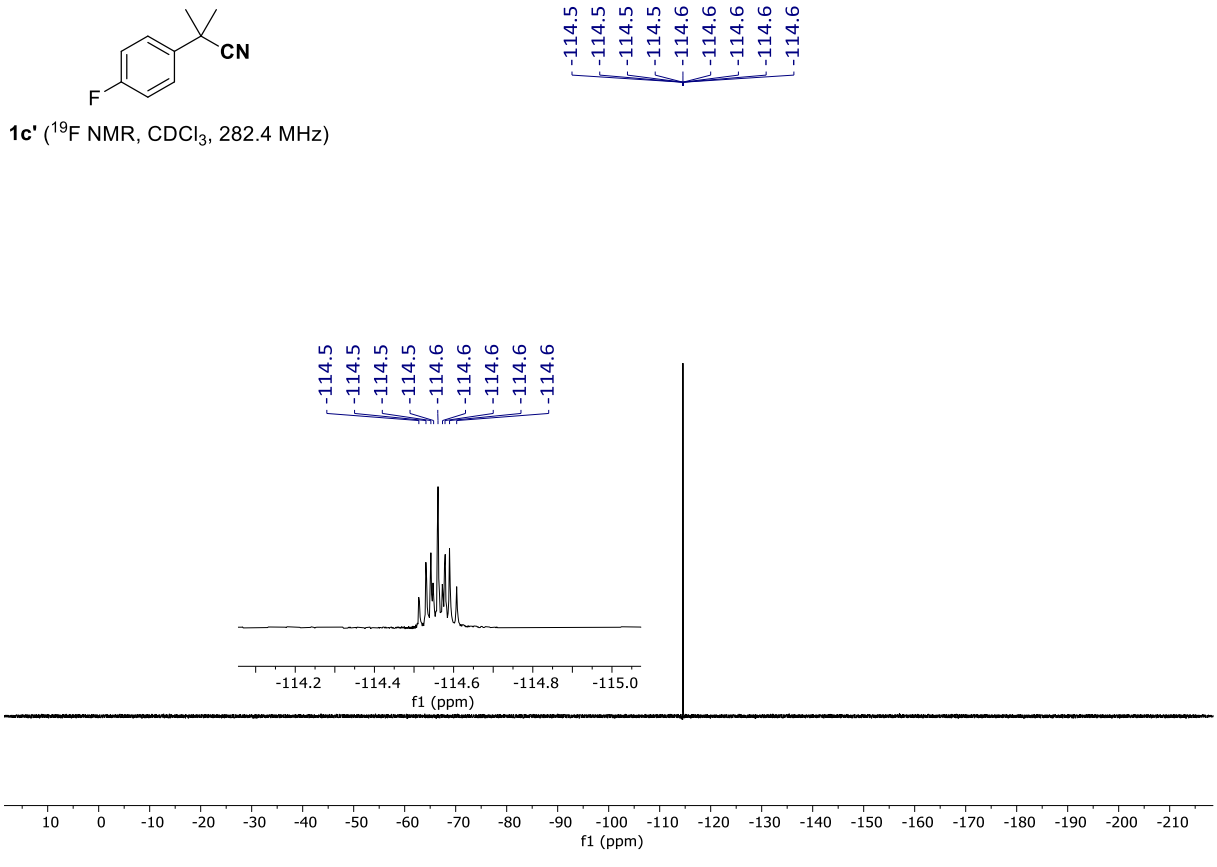
14.NMR Spectra



1c' (^{1}H NMR, $CDCl_3$, 300.1 MHz)



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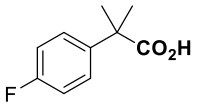

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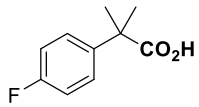

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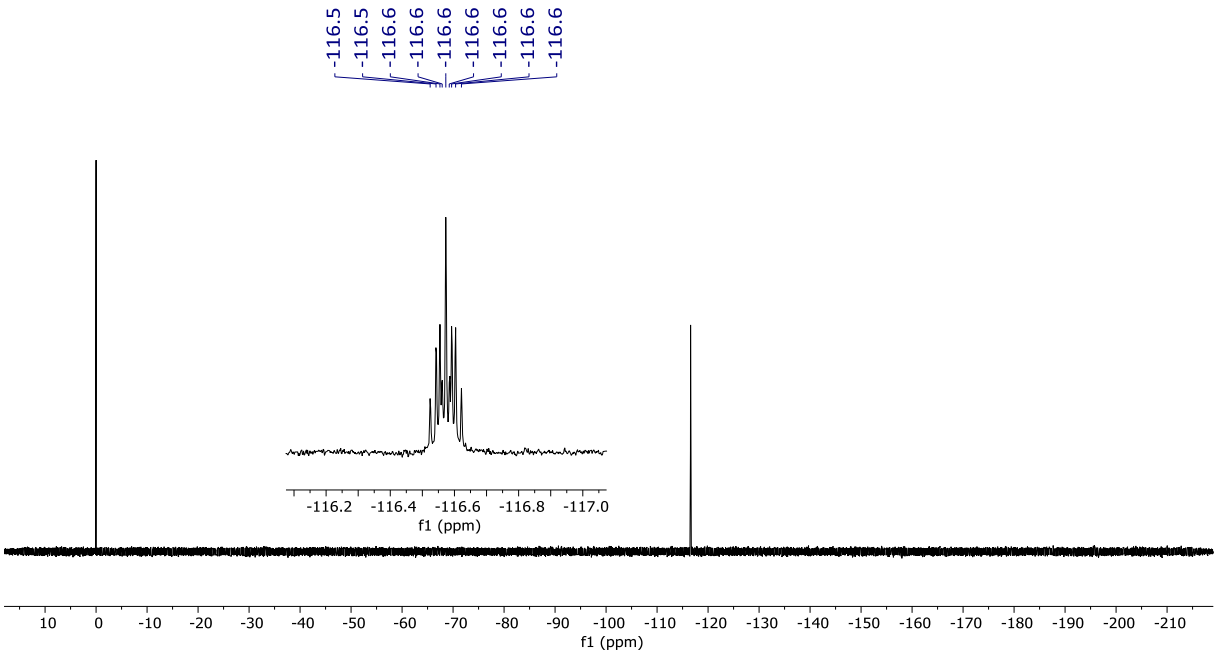

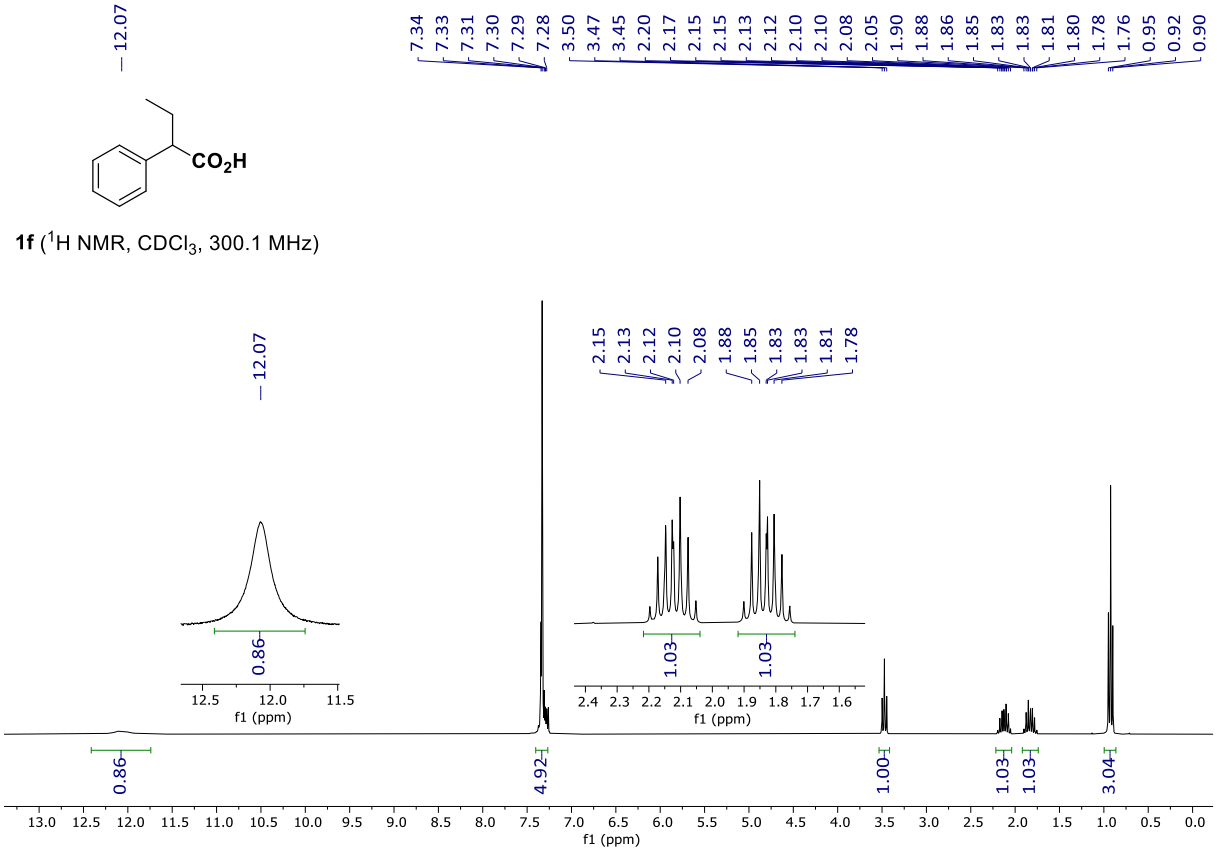

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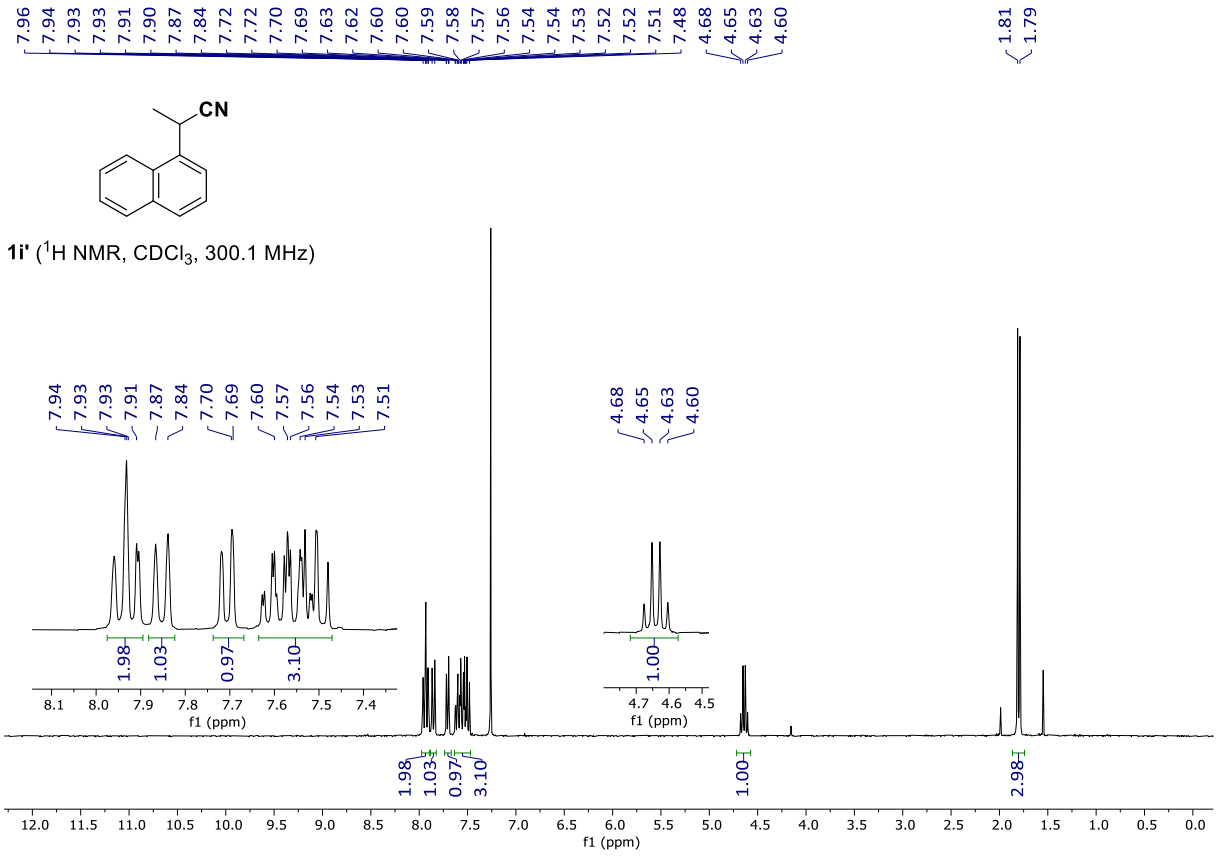

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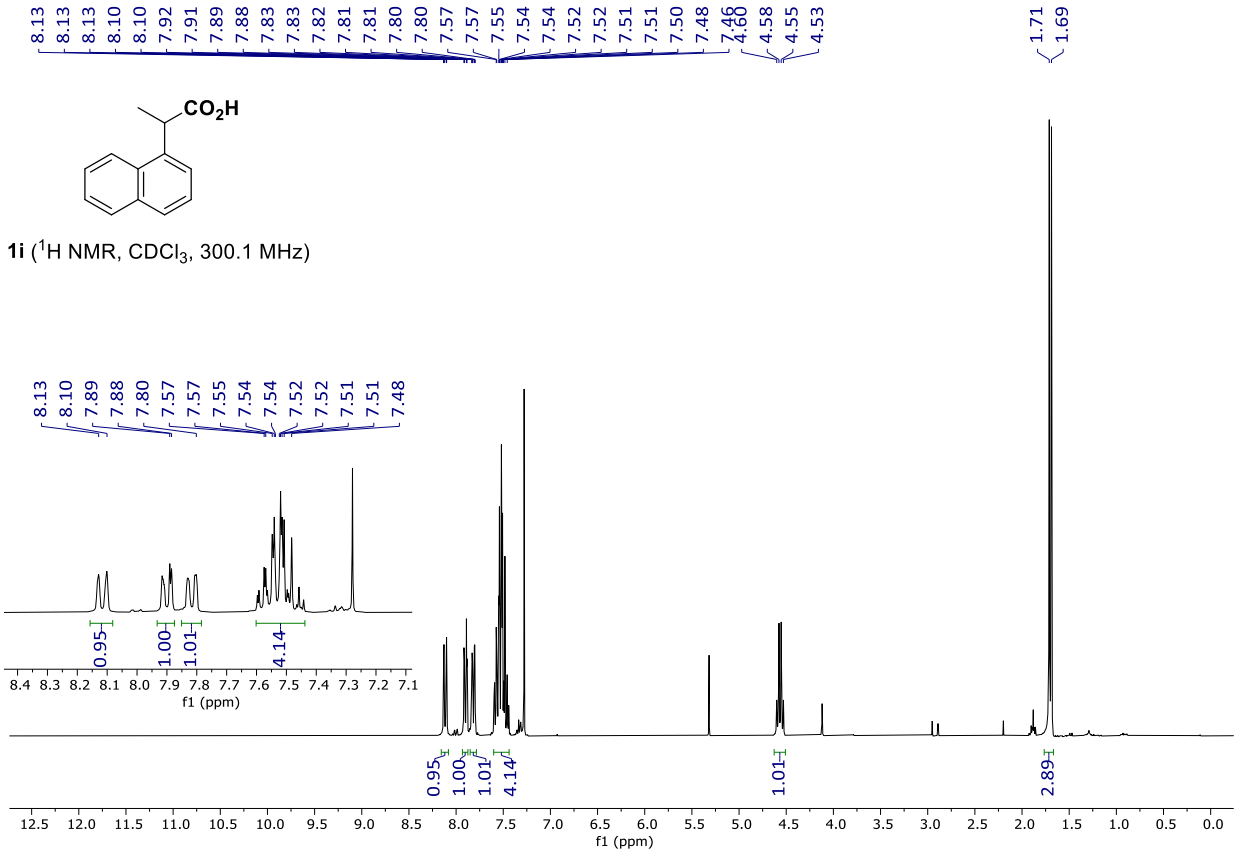

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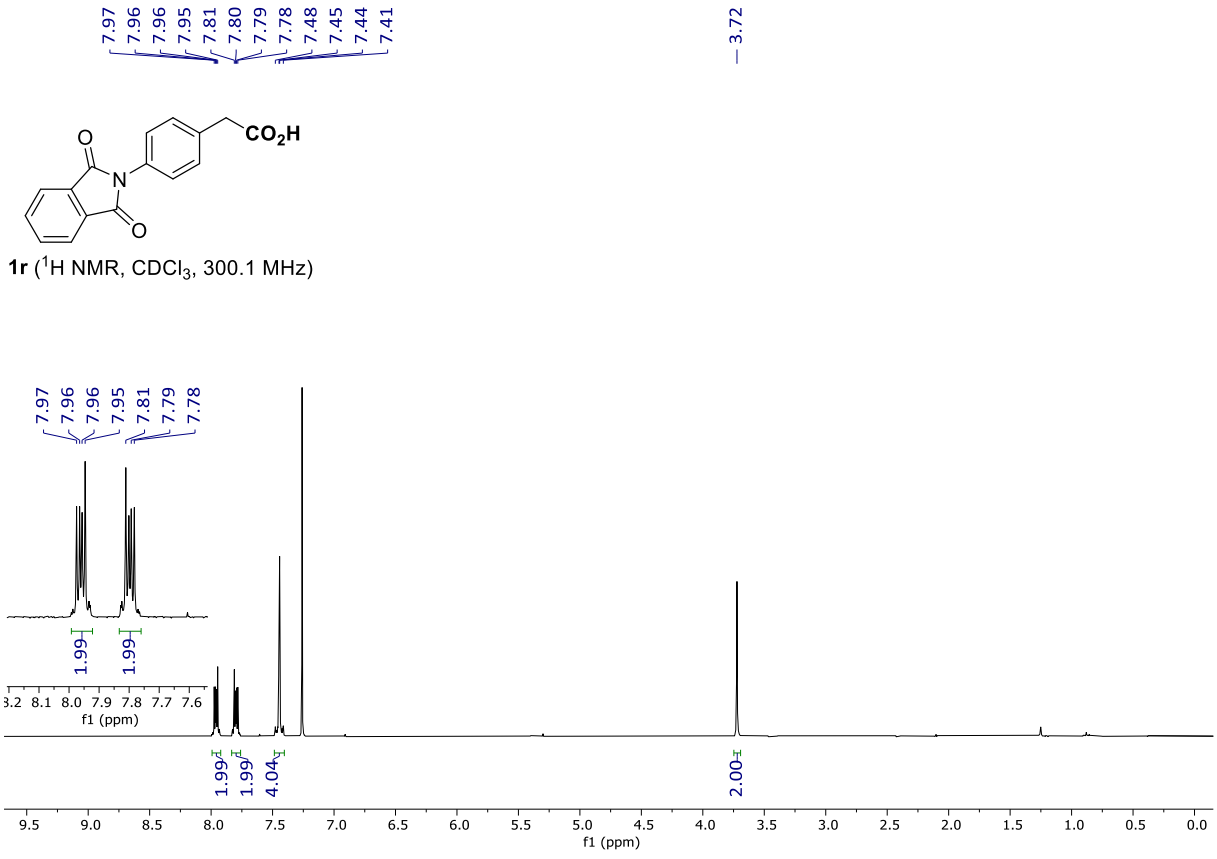

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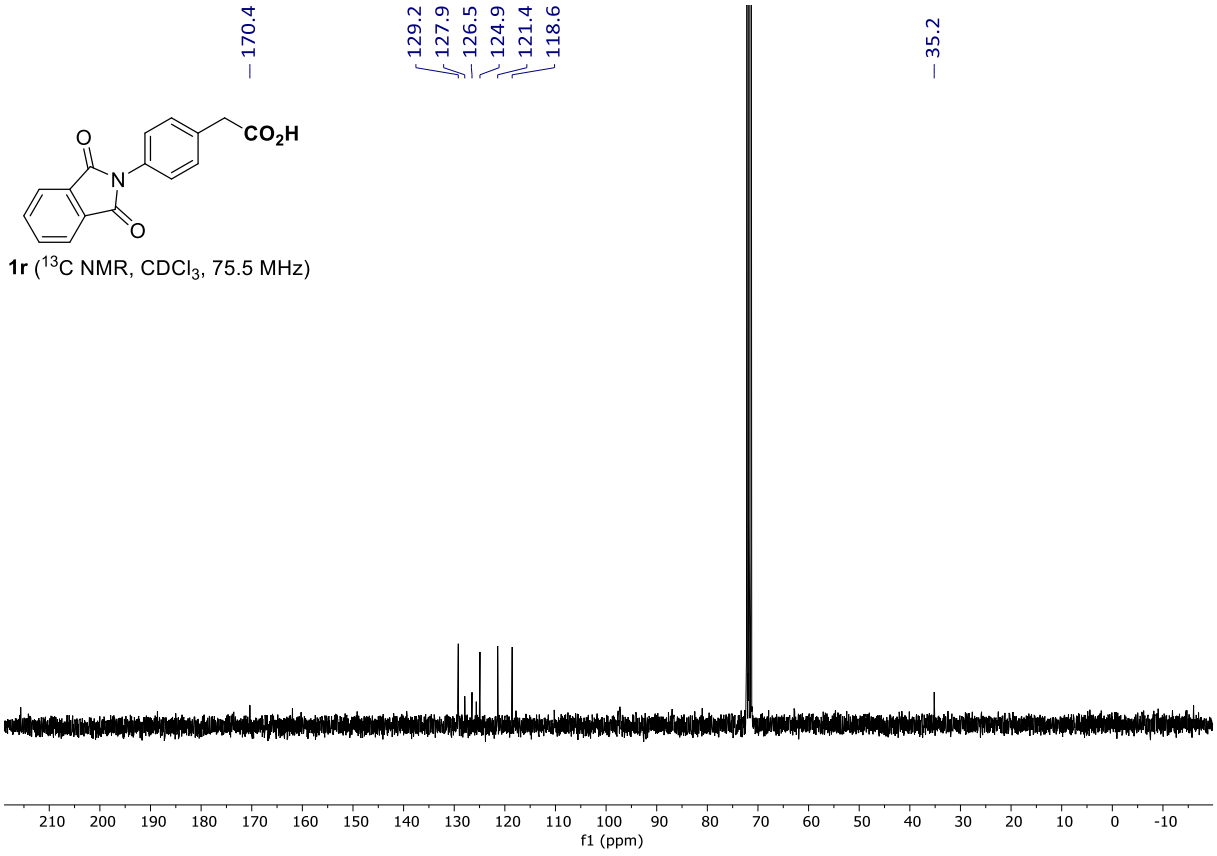

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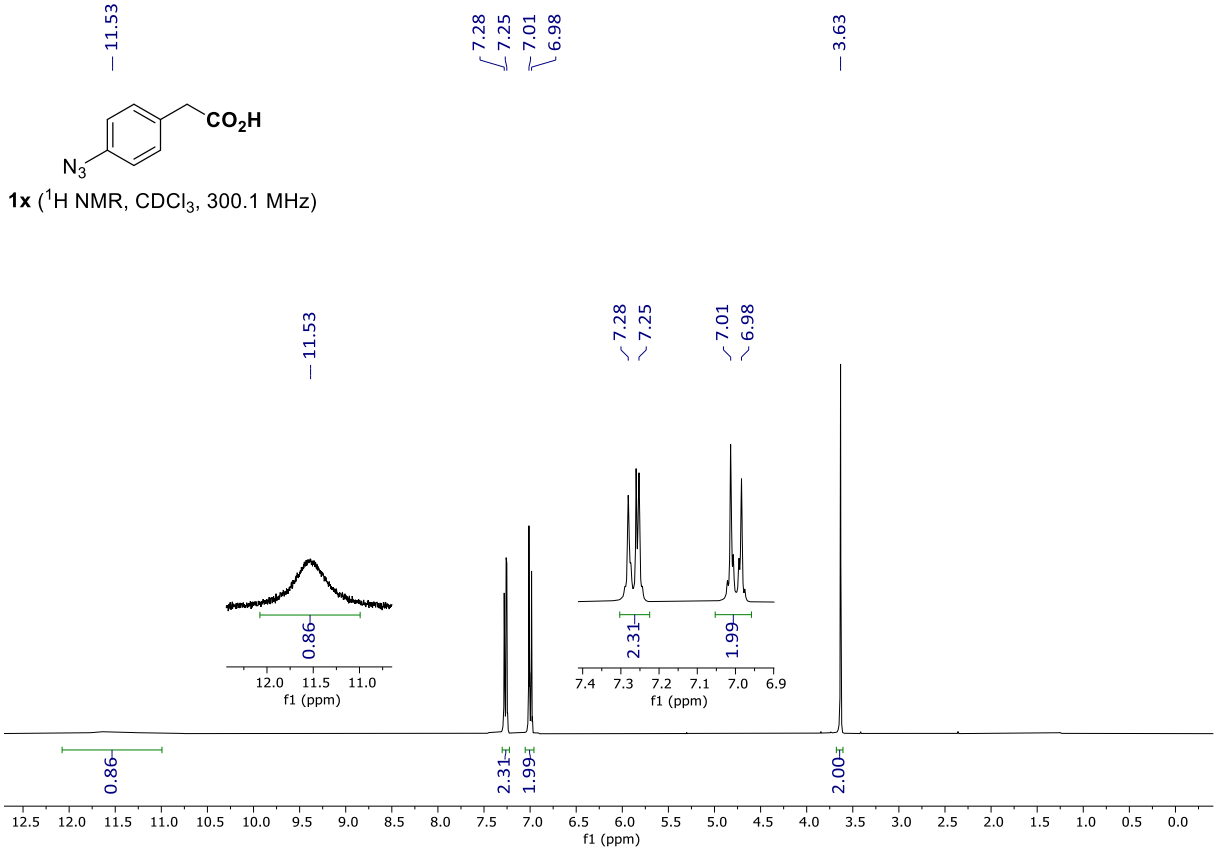

1x (^{1}H NMR, $CDCl_3$, 300.1 MHz)

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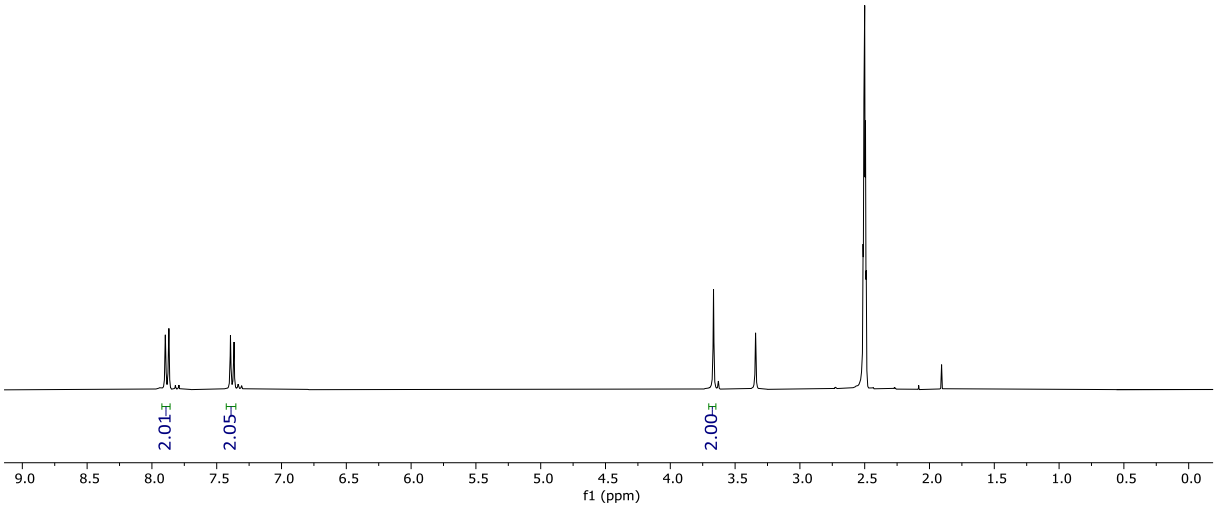

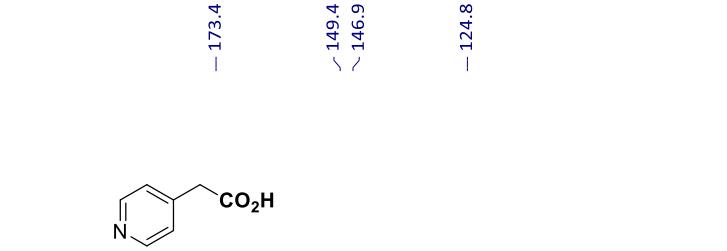

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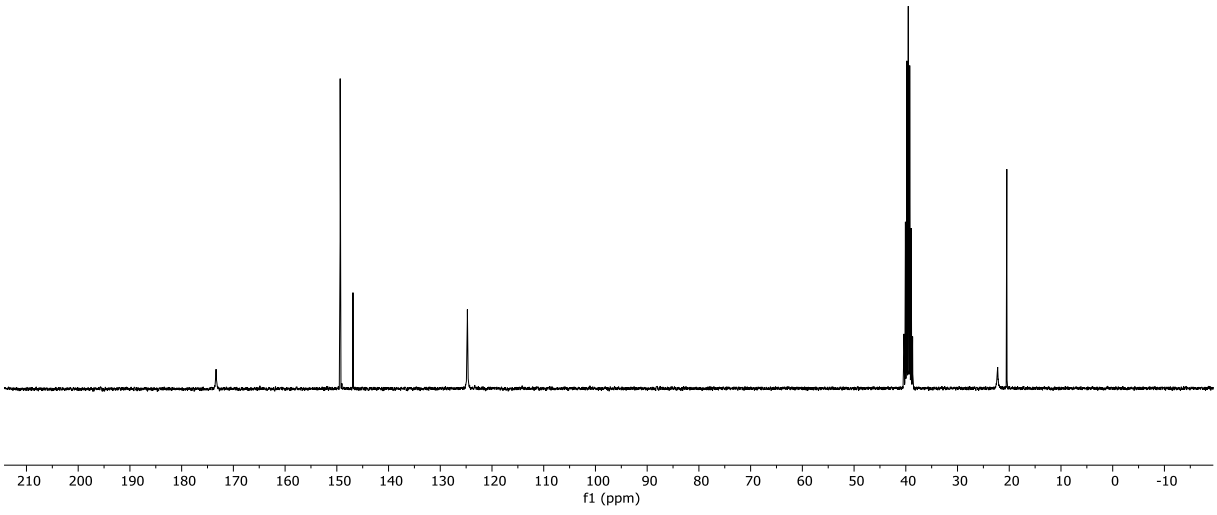
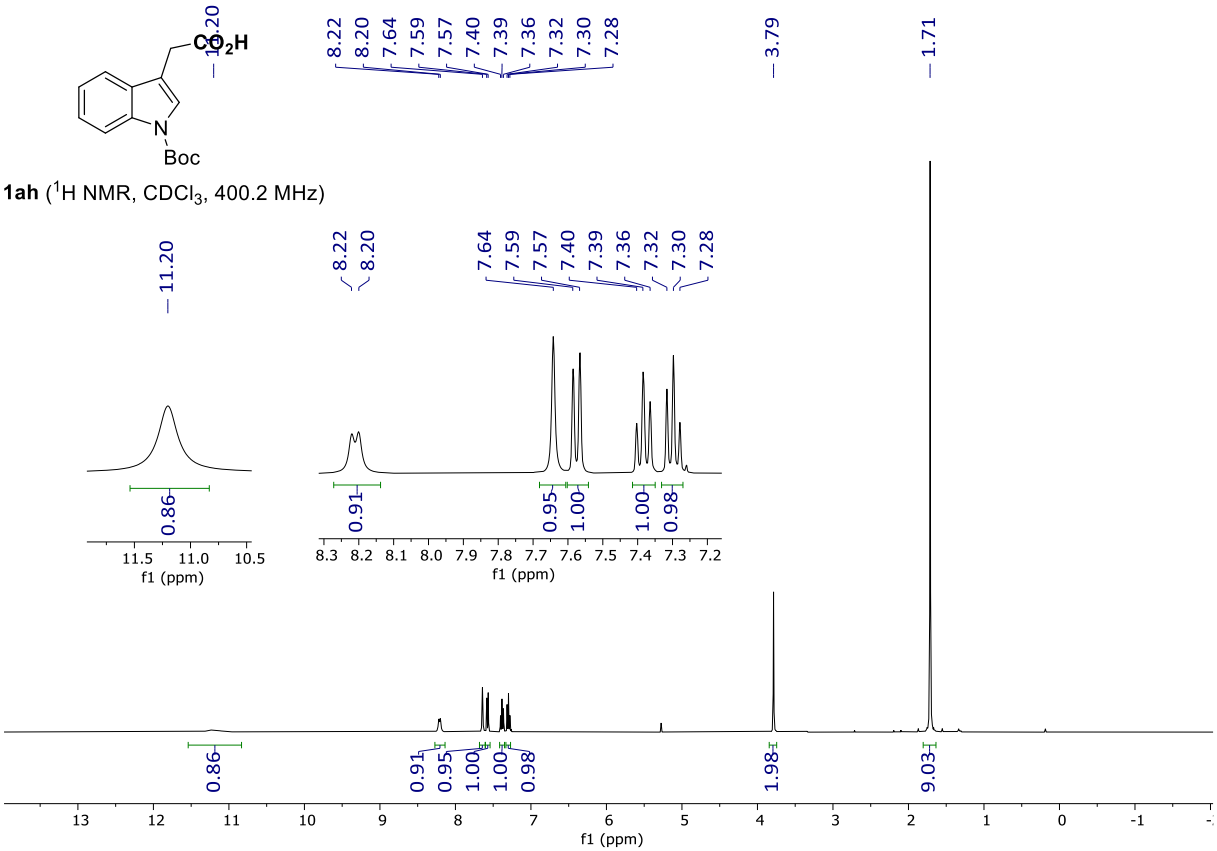
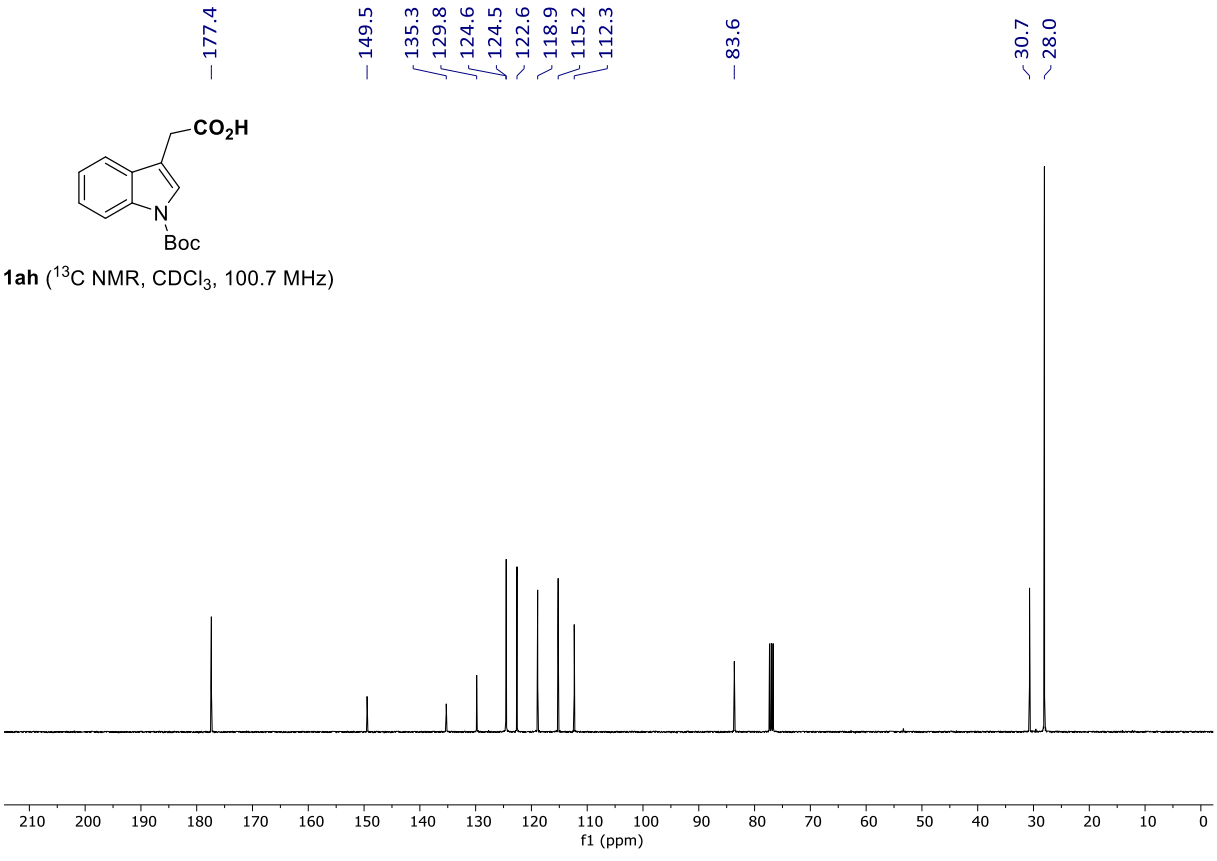




1ah (^{1}H NMR, $CDCl_3$, 400.2 MHz)



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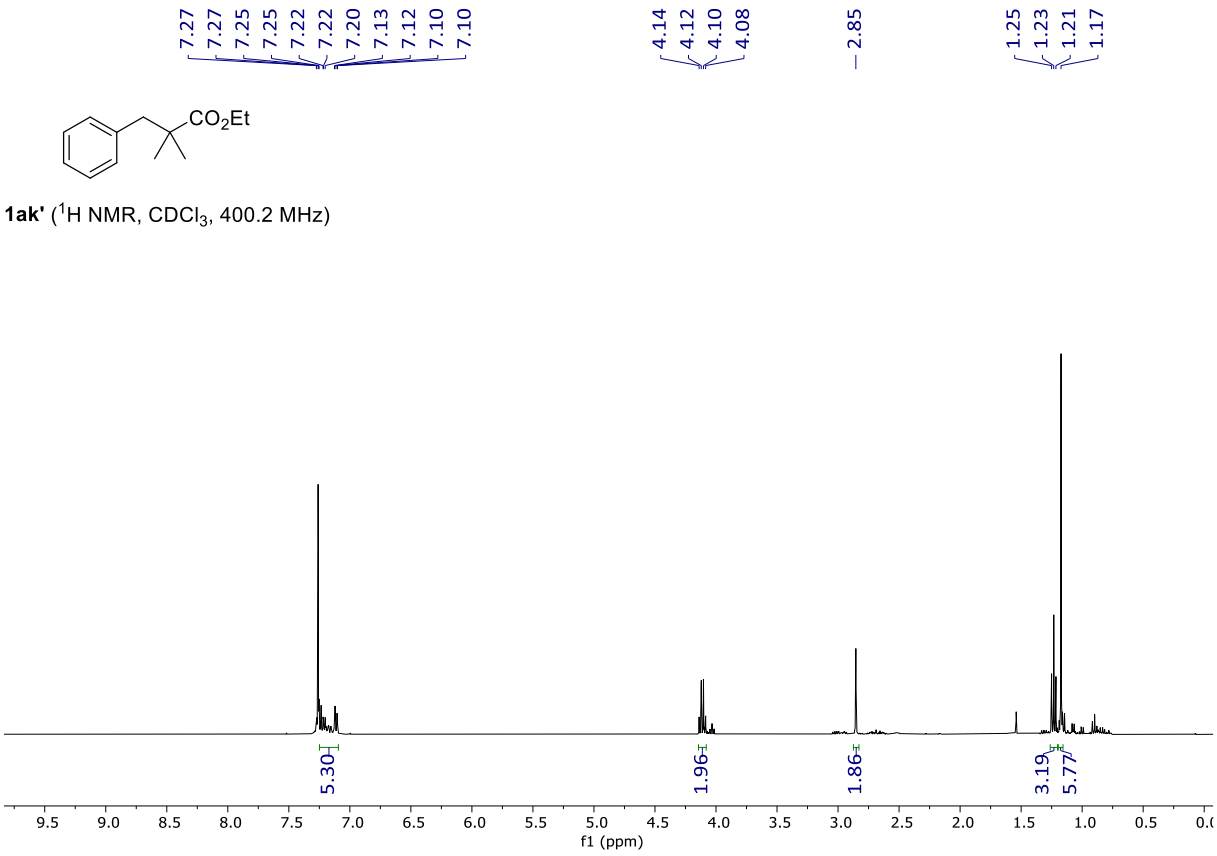

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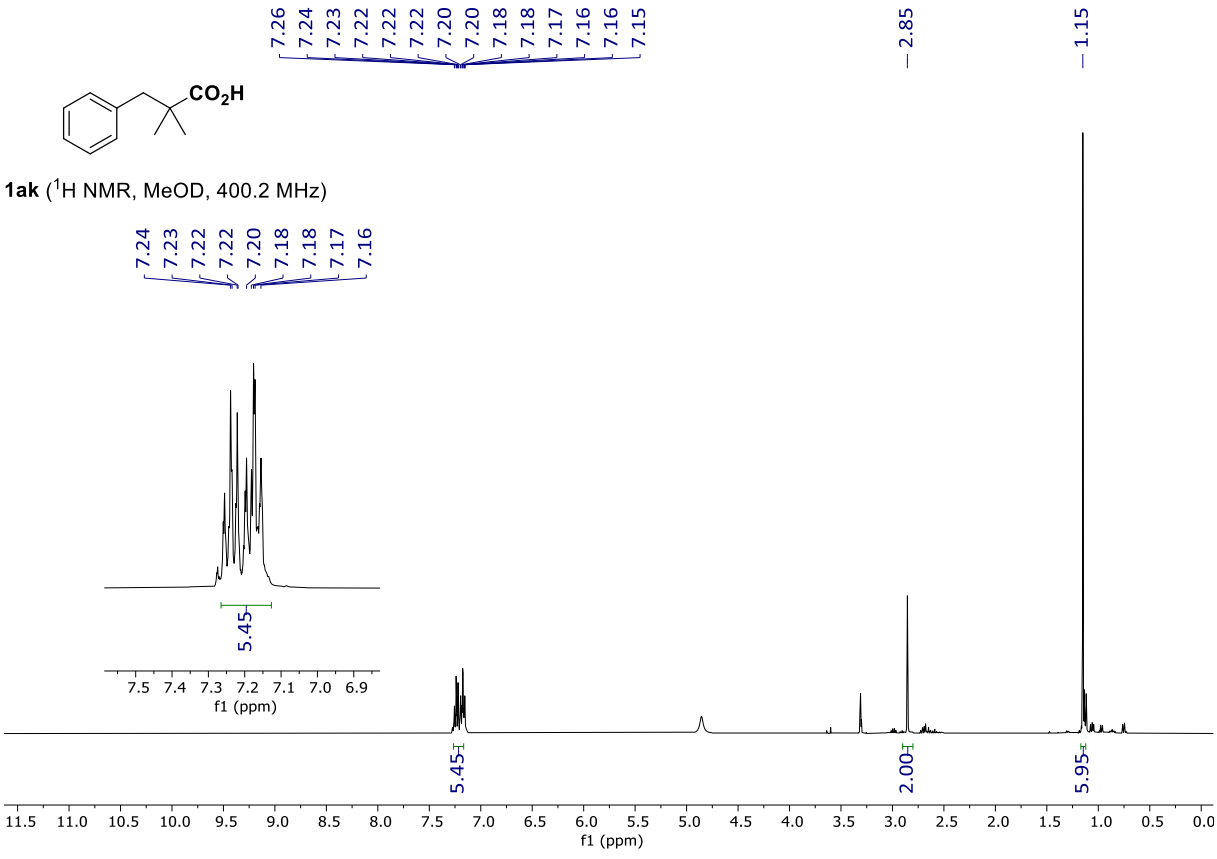

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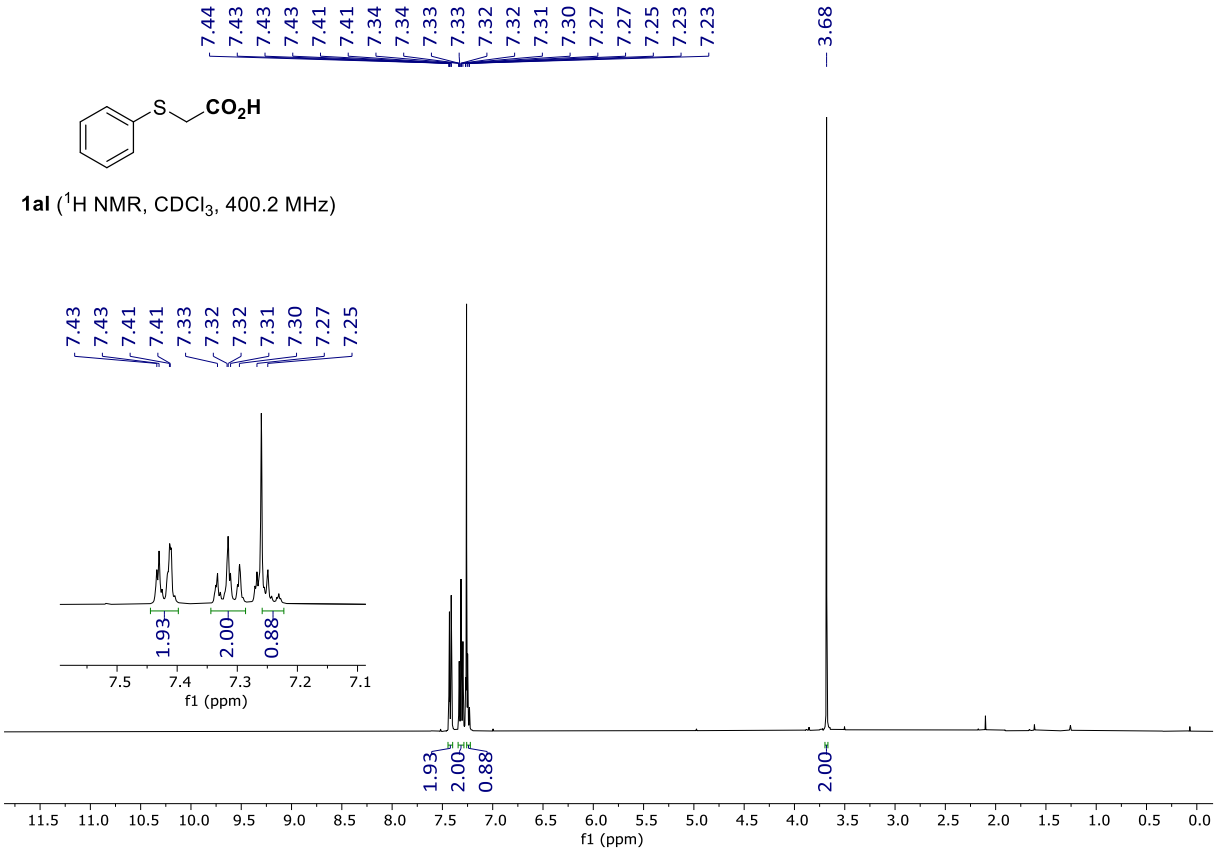

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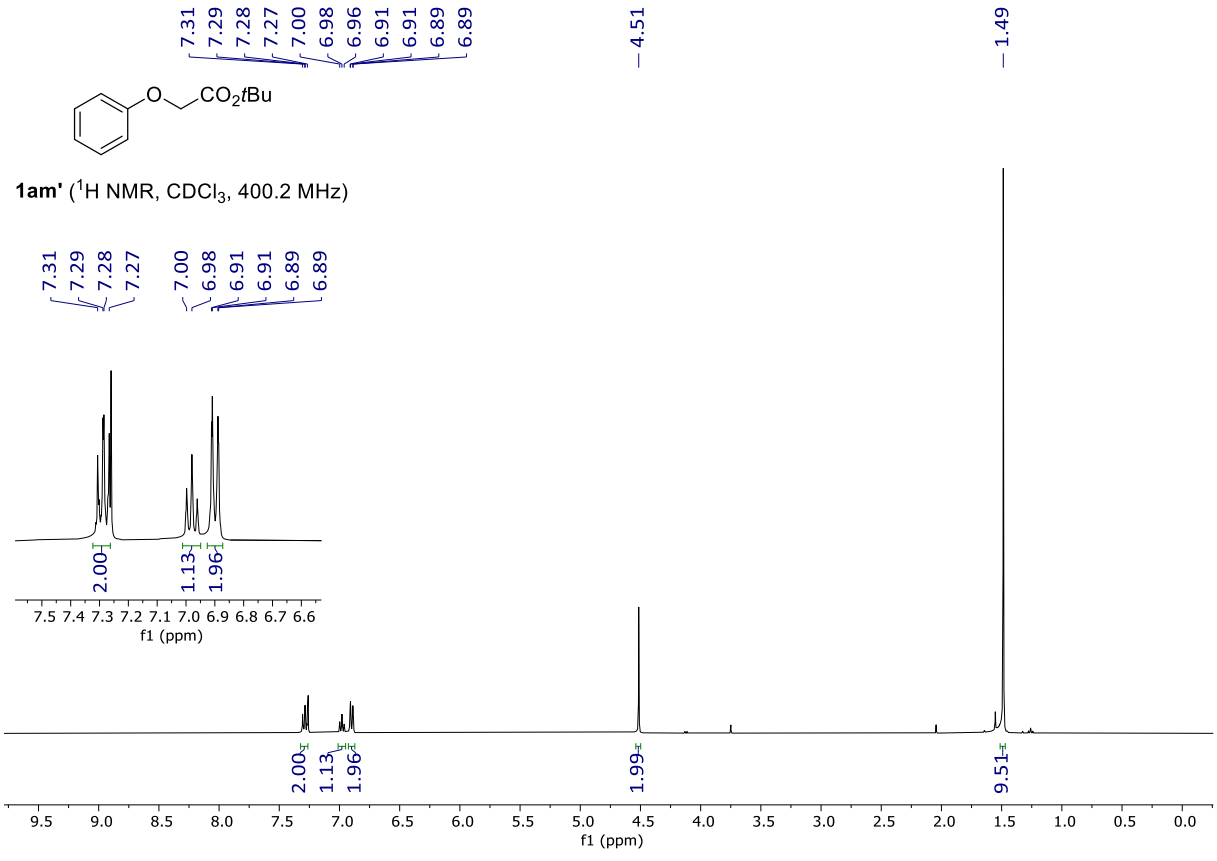
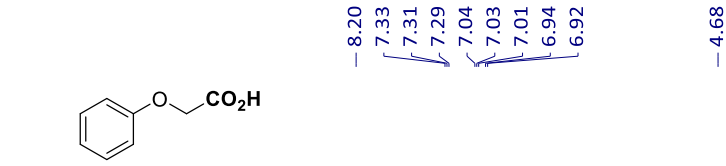


1am' (^{1}H NMR, $CDCl_3$, 400.2 MHz)



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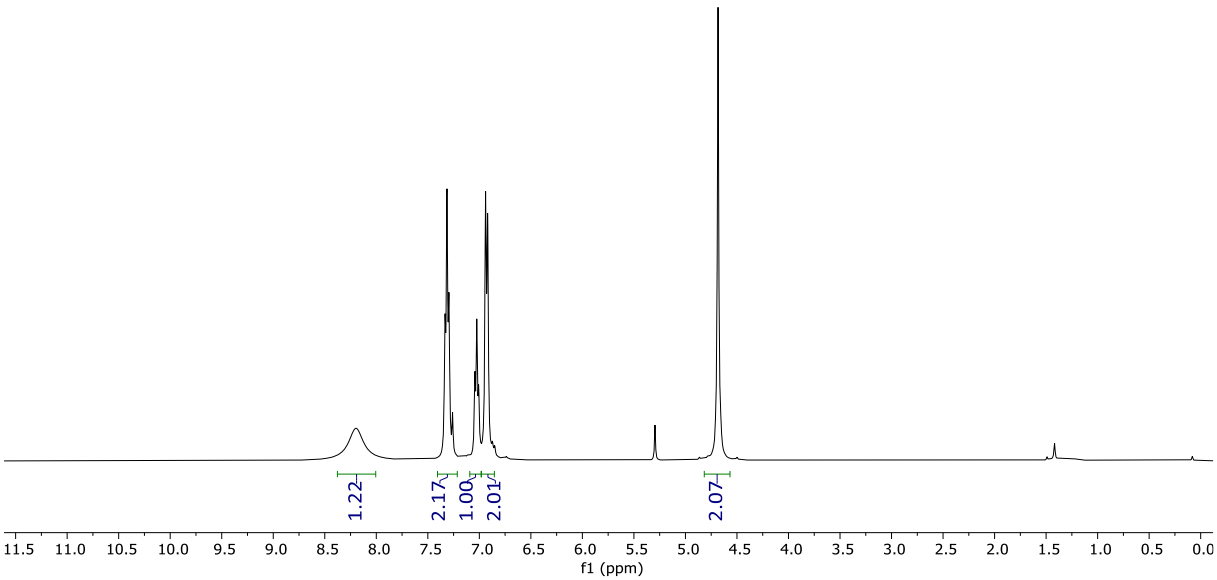
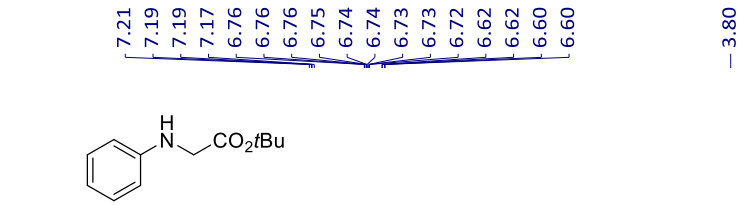
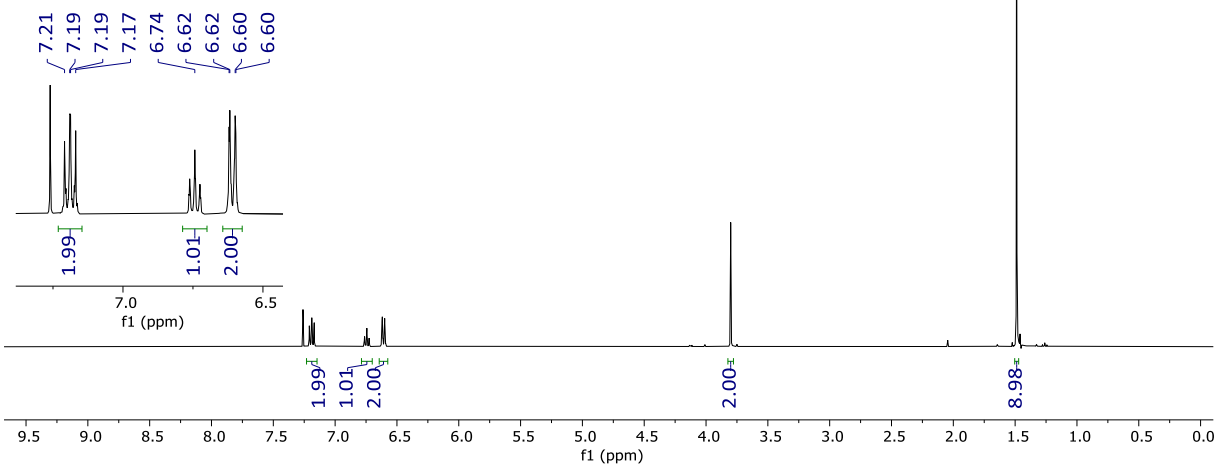
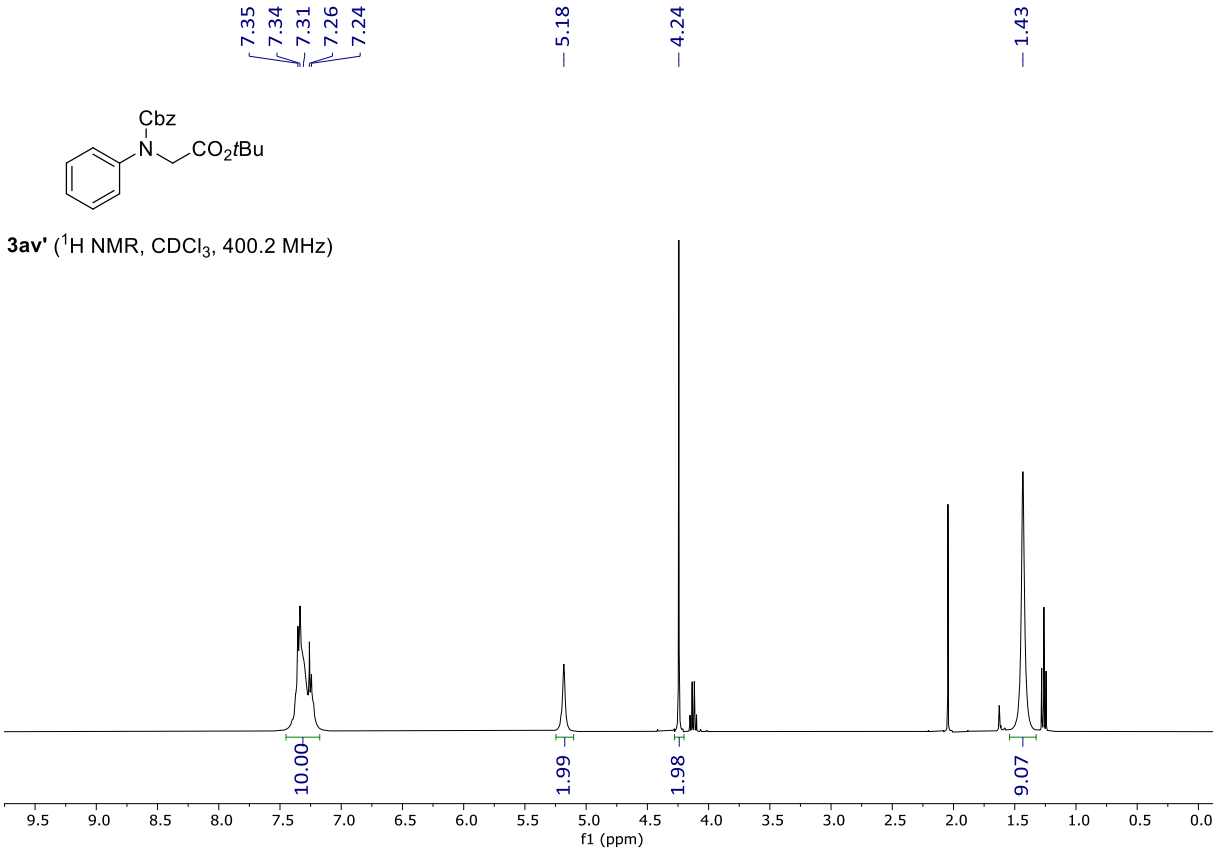




3av" (^{1}H NMR, $CDCl_3$, 400.2 MHz)





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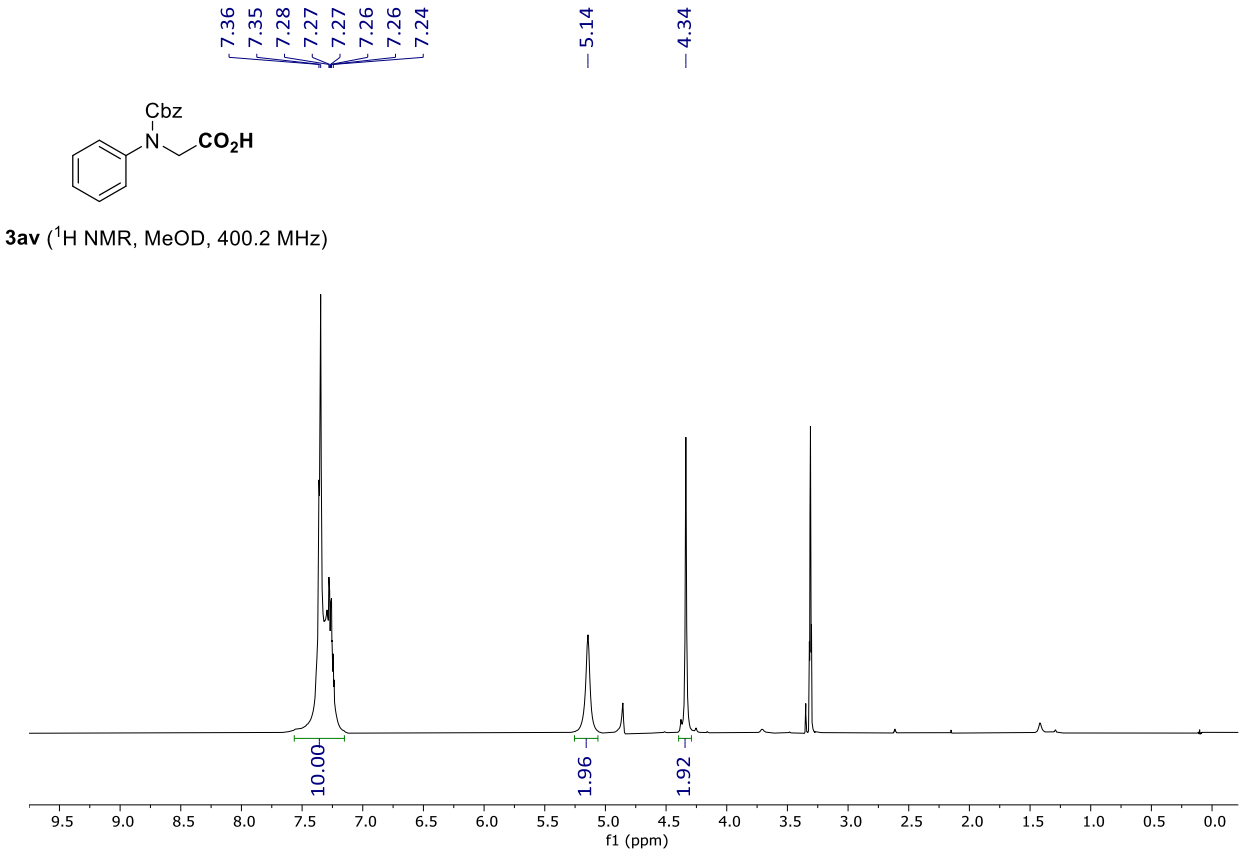
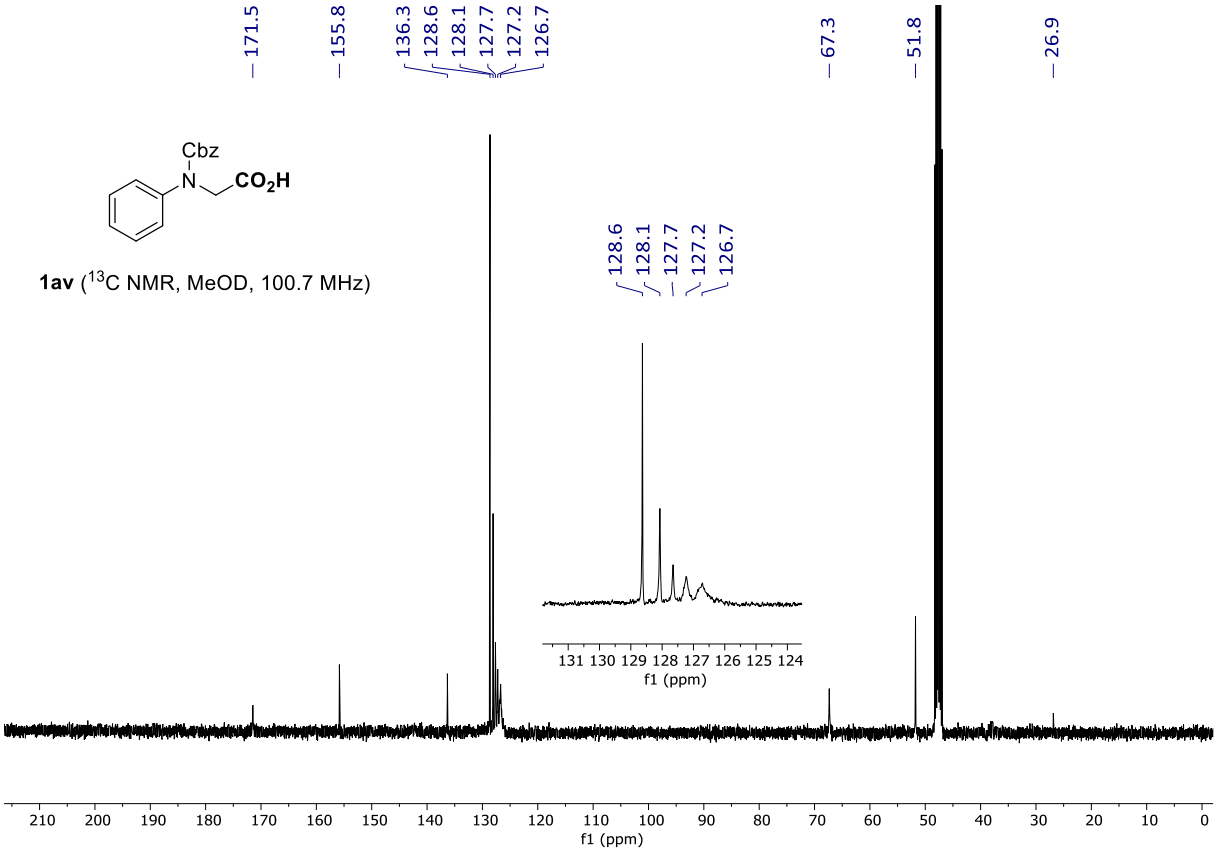
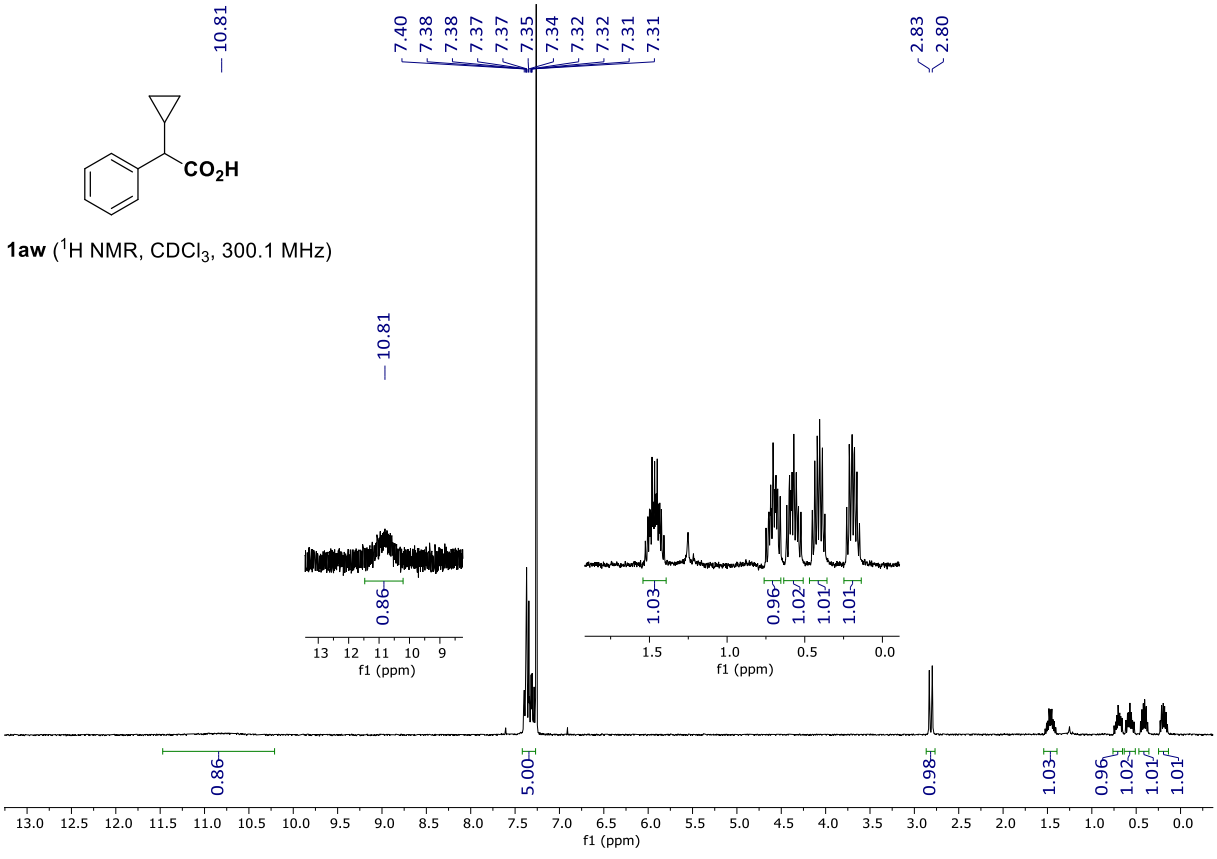
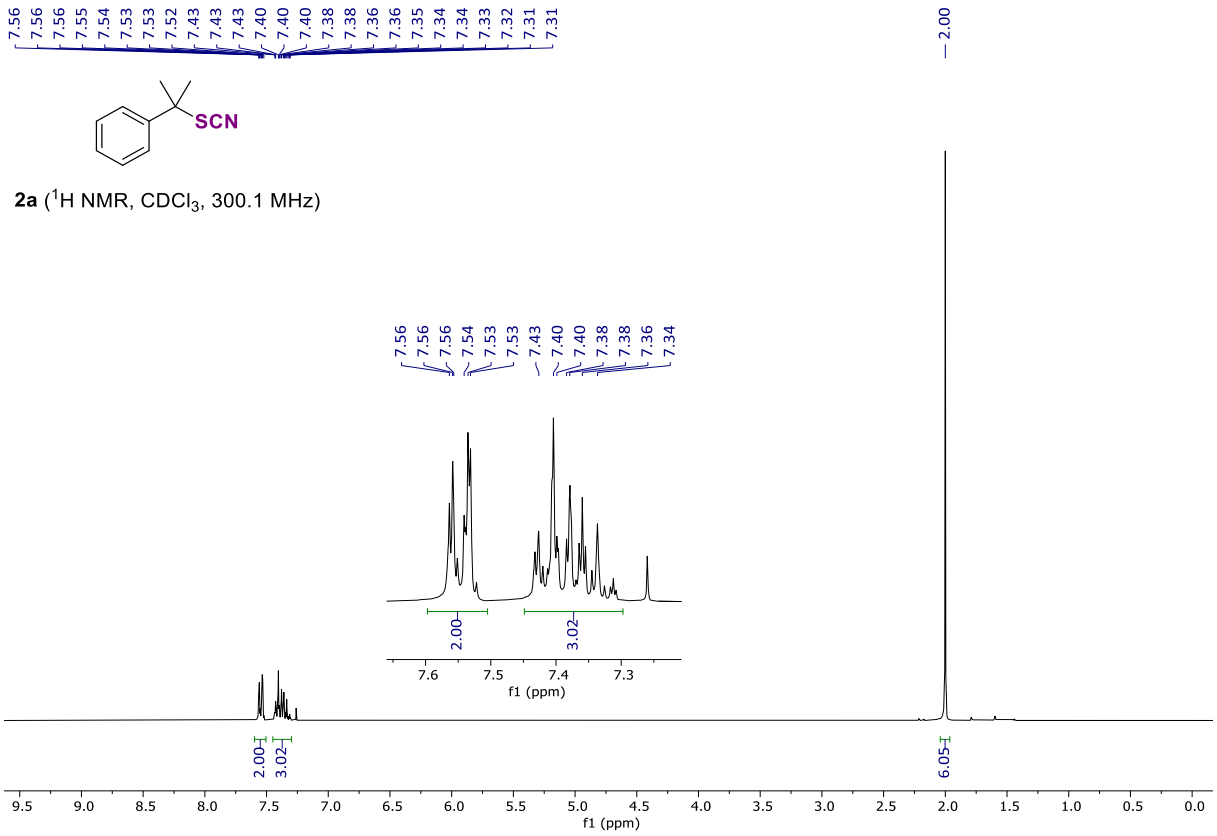


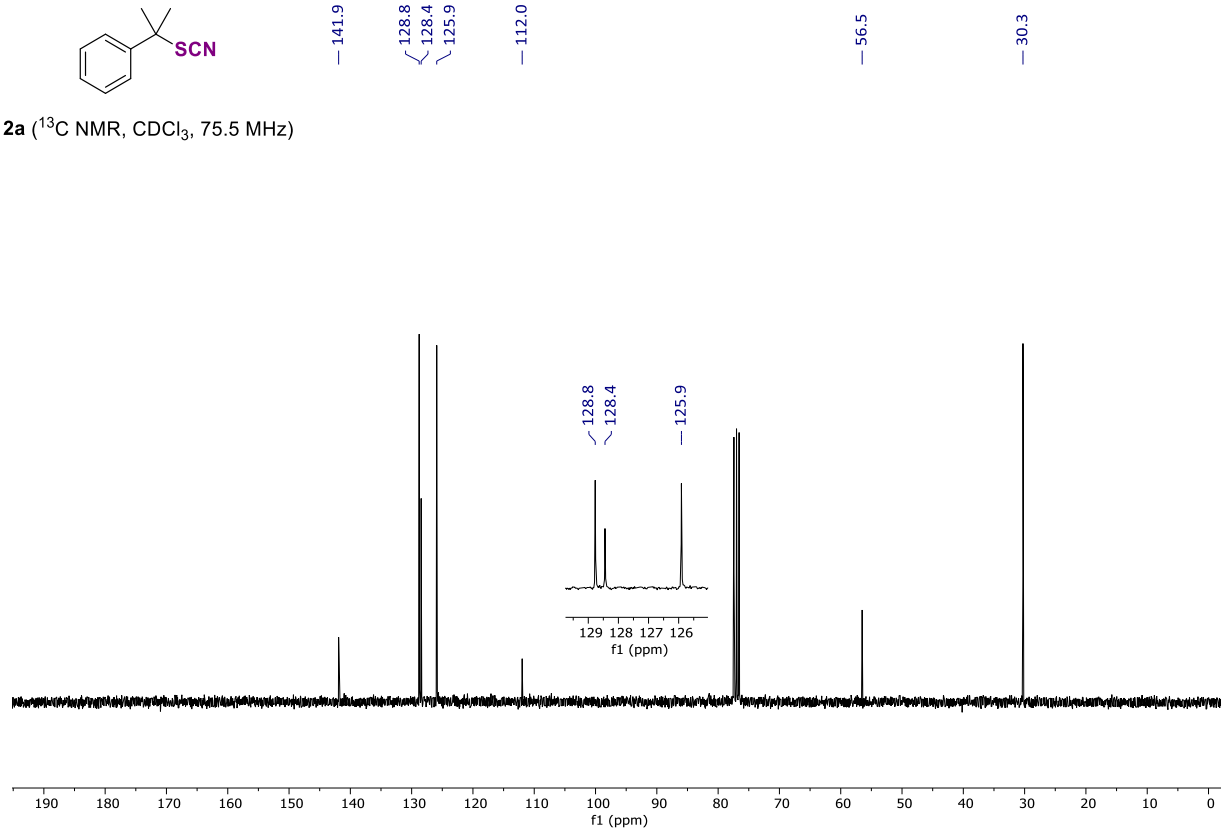
3av (^{1}H NMR, MeOD, 400.2 MHz)


171.5
155.8
136.3
128.6
128.1
127.7
127.2
126.7
67.3
51.8
26.9
Cbz
N
CO2H
1av (13C NMR, MeOD, 100.7 MHz)
f1 (ppm)

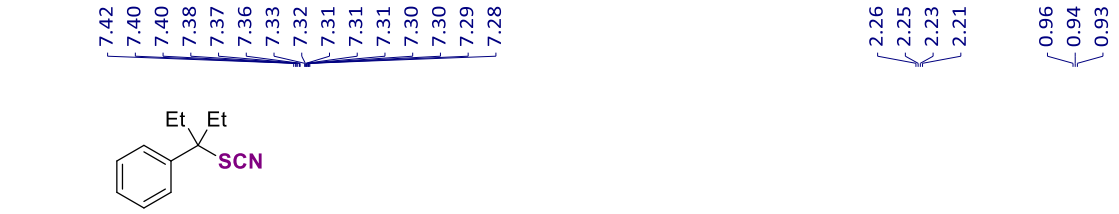

10.81
7.40
7.38
7.38
7.37
7.37
7.35
7.34
7.32
7.32
7.31
7.31
2.83
2.80
CO2H
1aw (1H NMR, CDCl3, 300.1 MHz)
0.86
1.03
0.96
1.02
1.01
1.01
f1 (ppm)



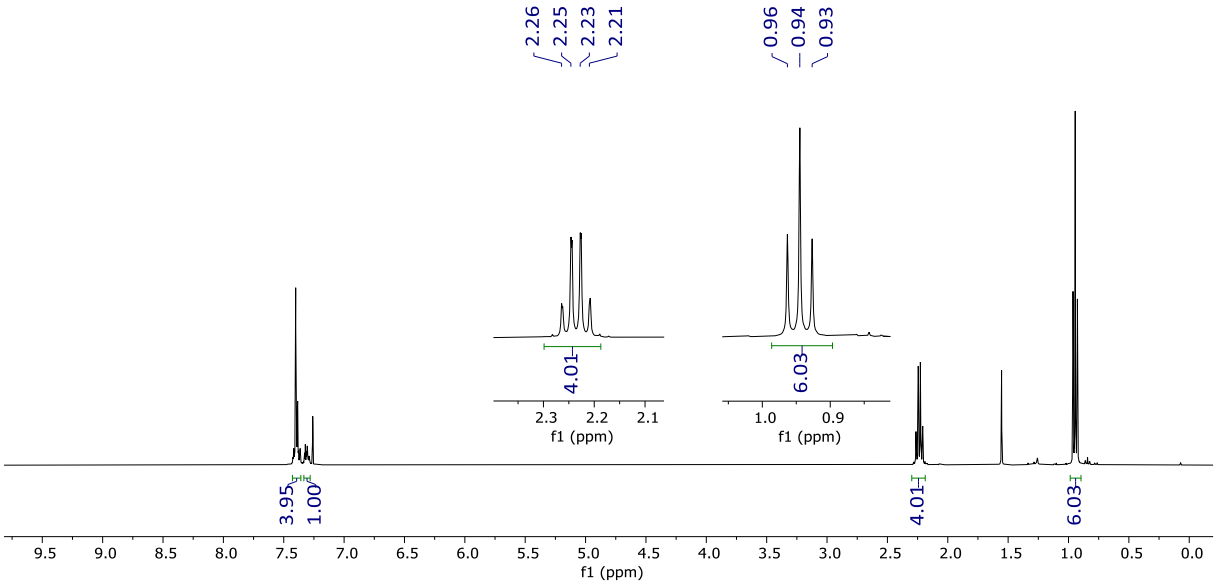
2a (^{1}H NMR, $CDCl_3$, 300.1 MHz)

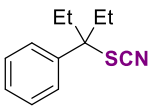


2a (^{13}C NMR, $CDCl_3$, 75.5 MHz)



2b (^{1}H NMR, $CDCl_3$, 400.2 MHz)





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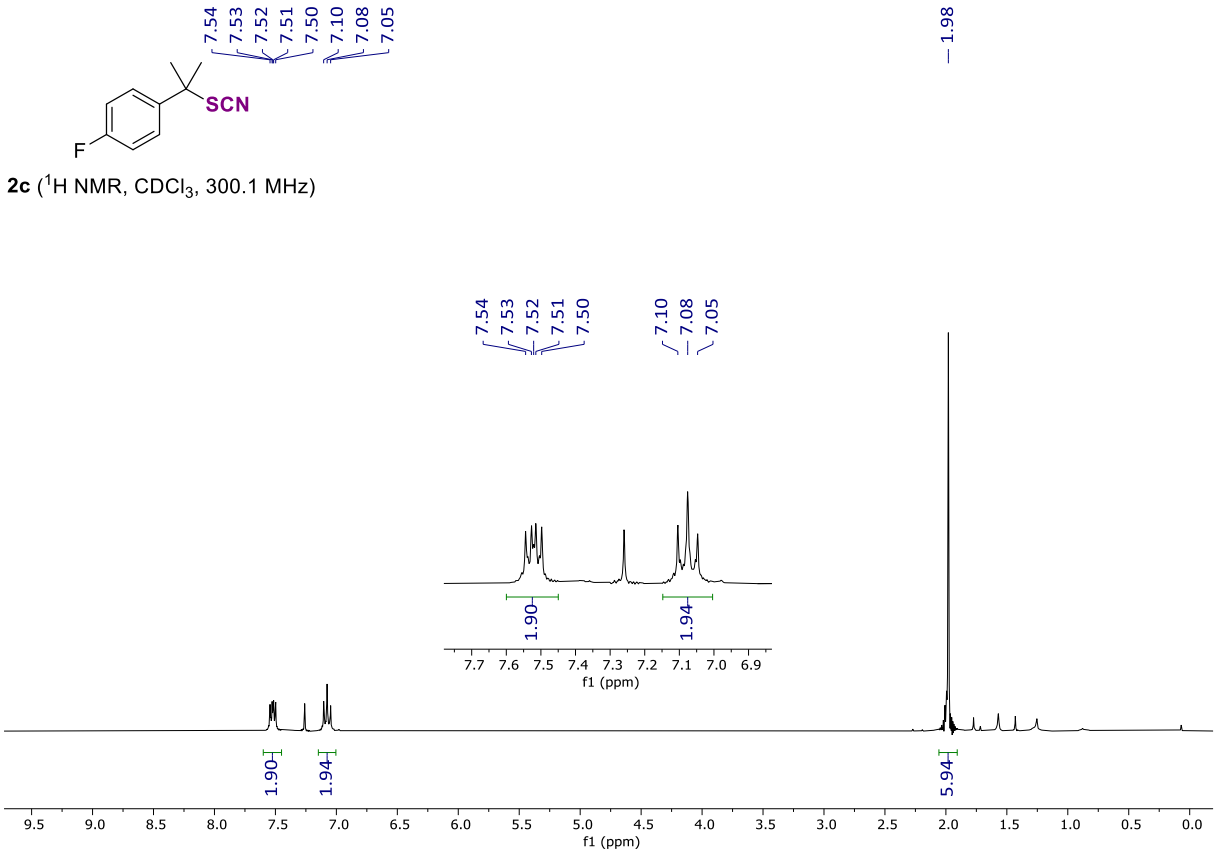

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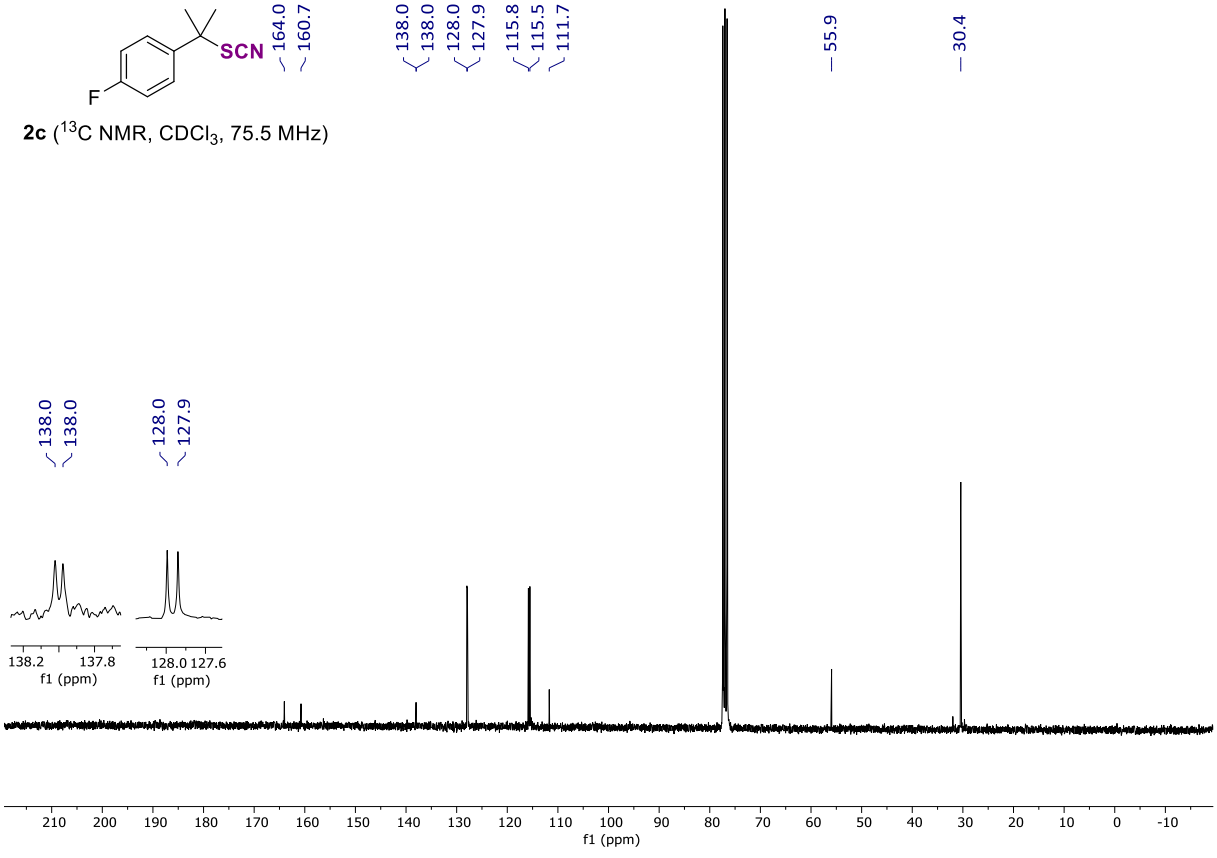
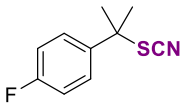
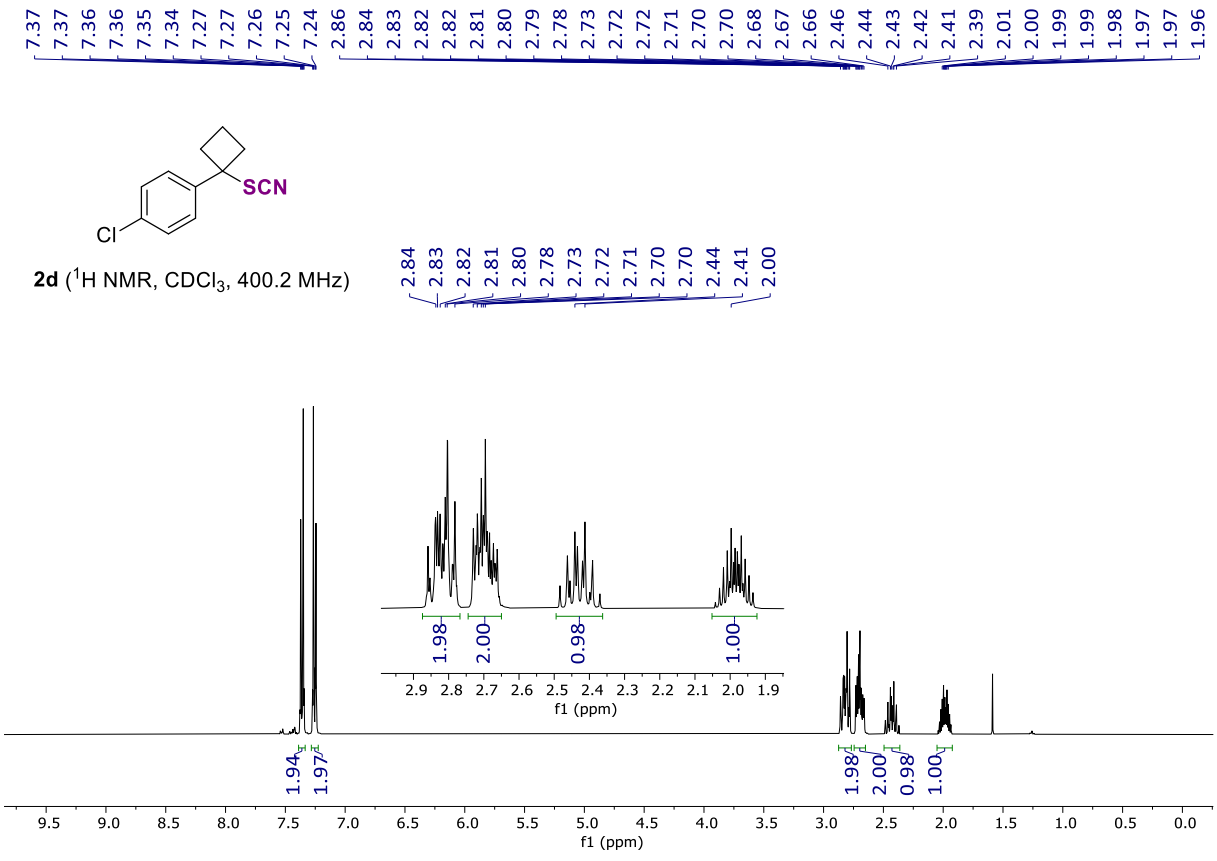


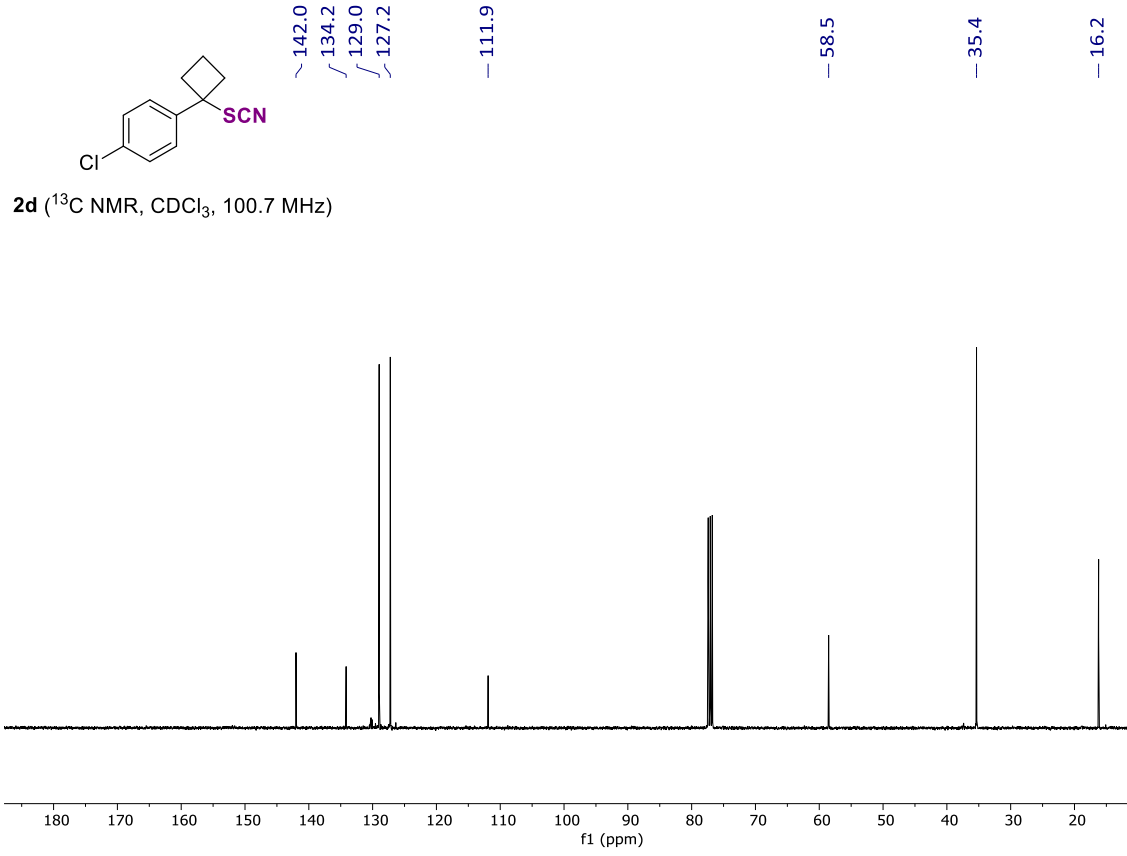
2c (^{13}C NMR, $CDCl_3$, 75.5 MHz)



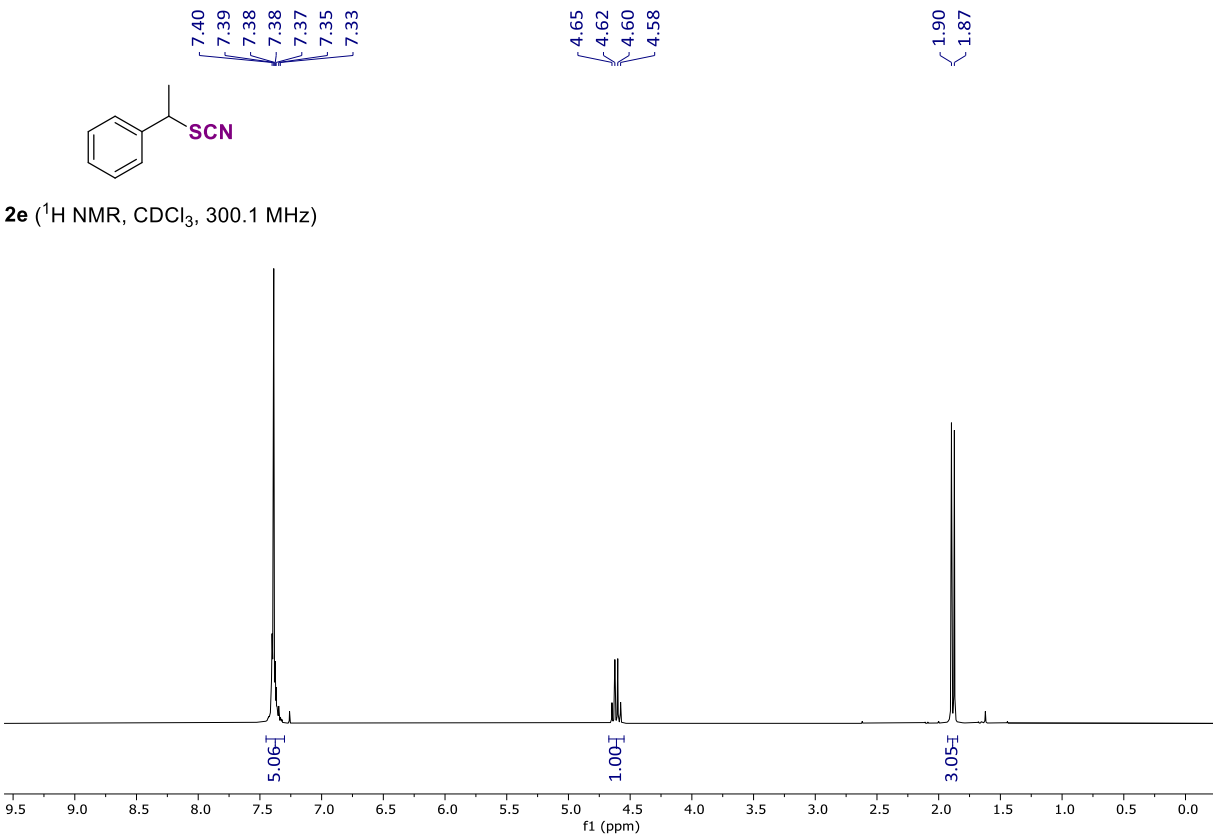
2c (^{19}F NMR, $CDCl_3$, 282.4 MHz)



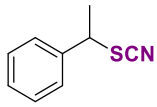
2d (^{1}H NMR, $CDCl_3$, 400.2 MHz)



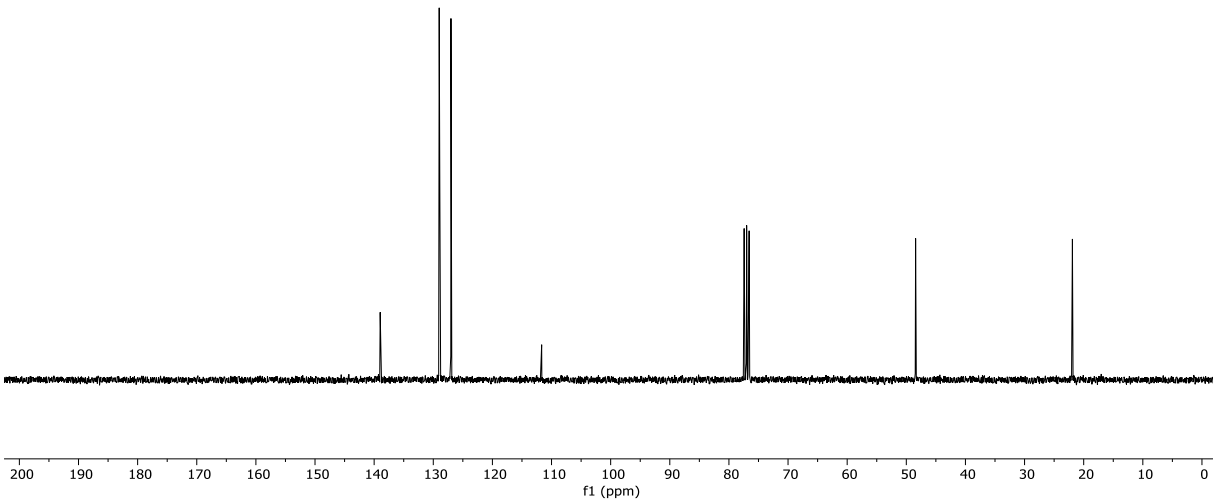
2d (^{13}C NMR, $CDCl_3$, 100.7 MHz)

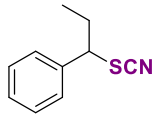


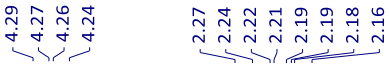
2e (^{1}H NMR, $CDCl_3$, 300.1 MHz)



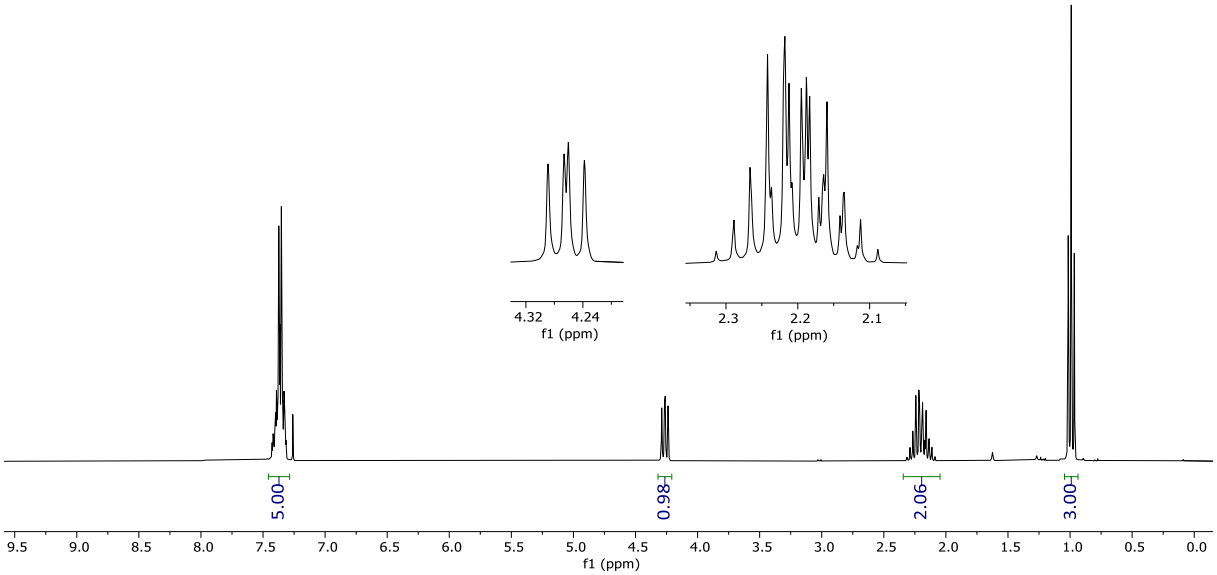
2e (^{13}C NMR, $CDCl_3$, 75.5 MHz)

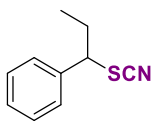




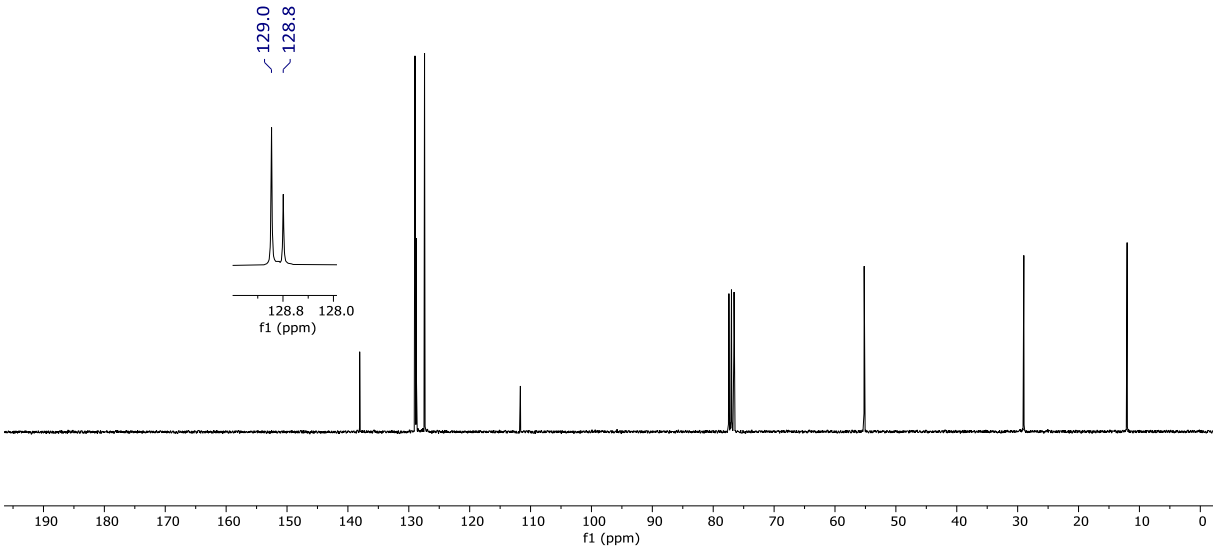


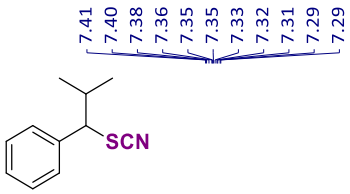
2f (^{1}H NMR, $CDCl_3$, 300.1 MHz)



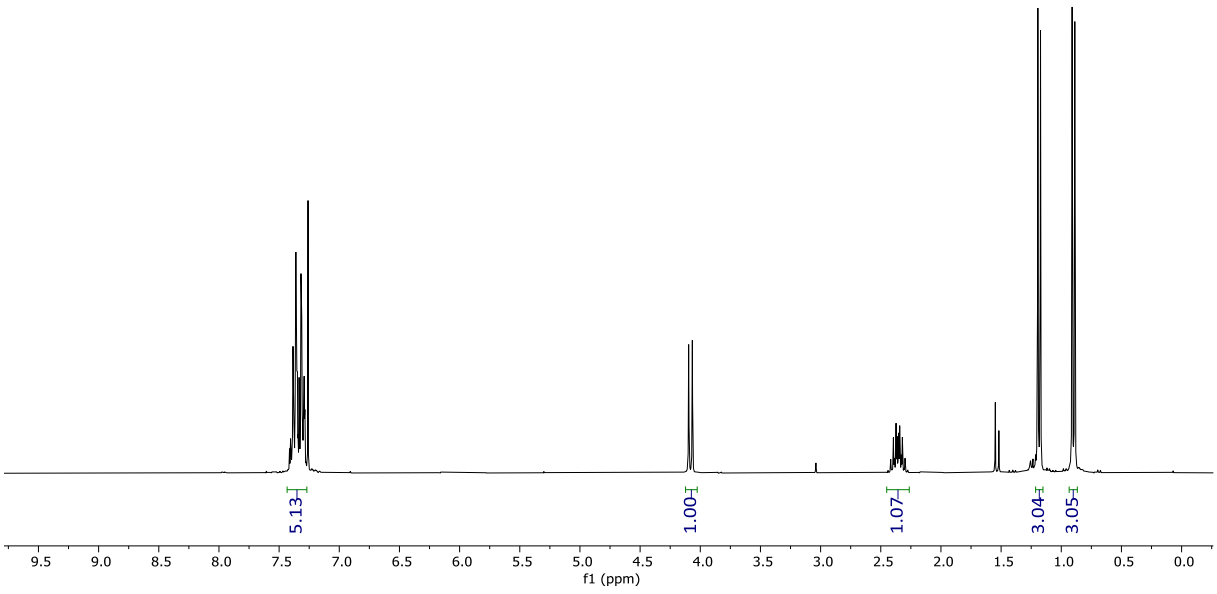


2f (^{13}C NMR, $CDCl_3$, 75.5 MHz)

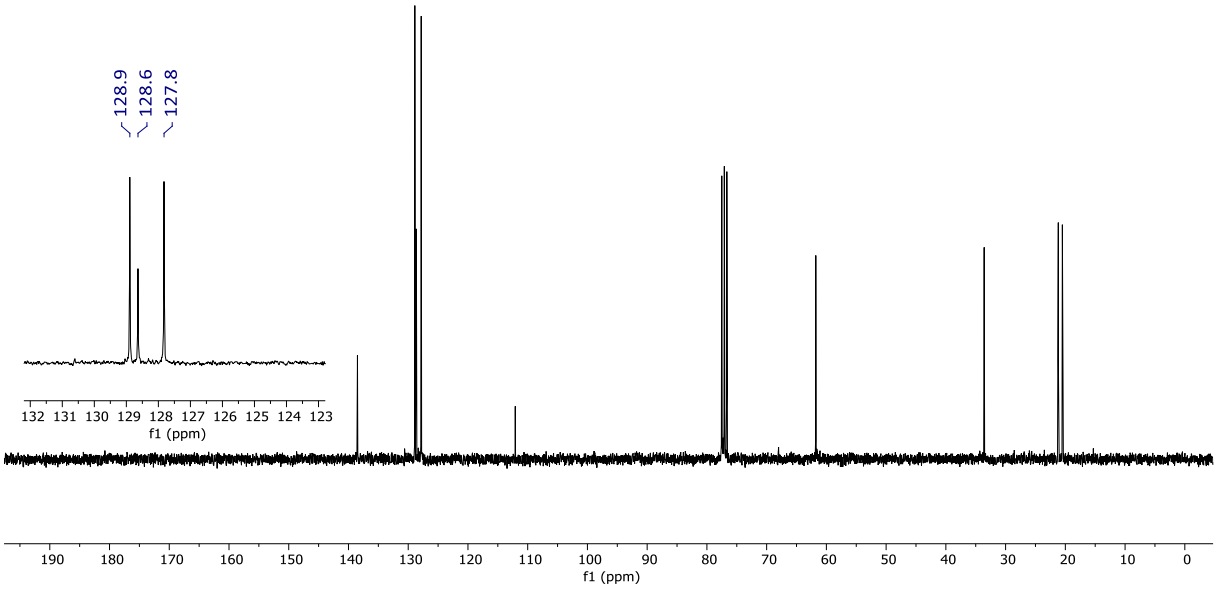


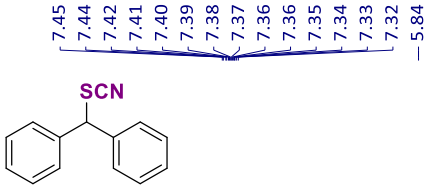


2g (^{1}H NMR, $CDCl_3$, 300.1 MHz)

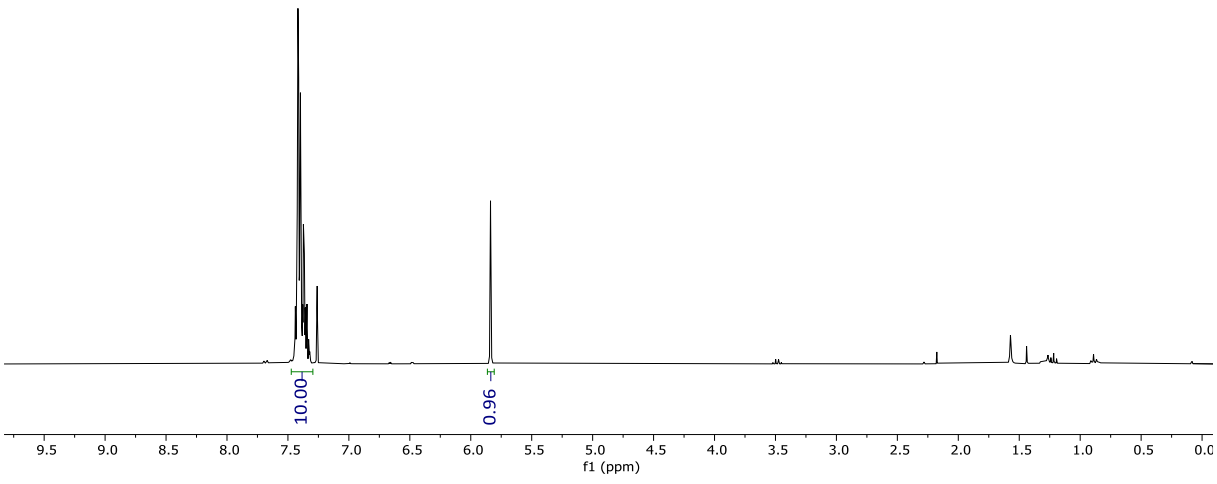


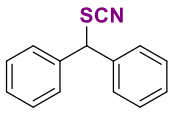
2g (^{13}C NMR, $CDCl_3$, 75.5 MHz)



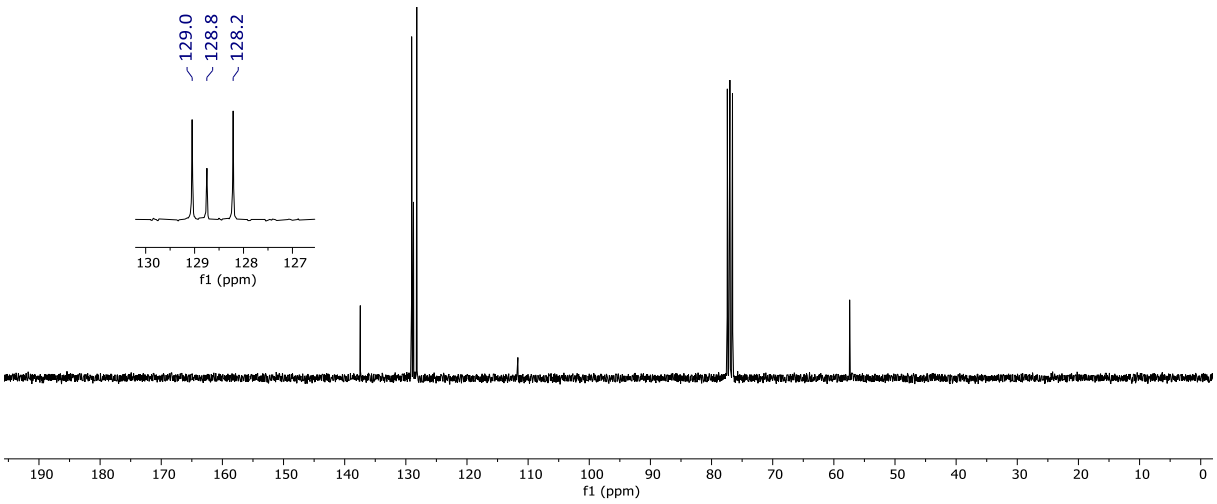


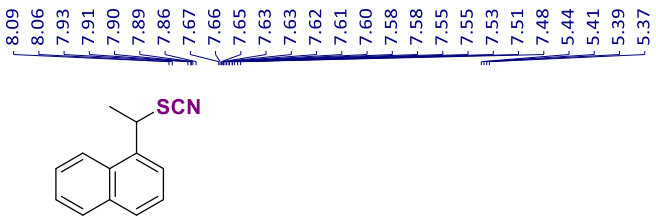
2h (^{1}H NMR, $CDCl_3$, 300.1 MHz)



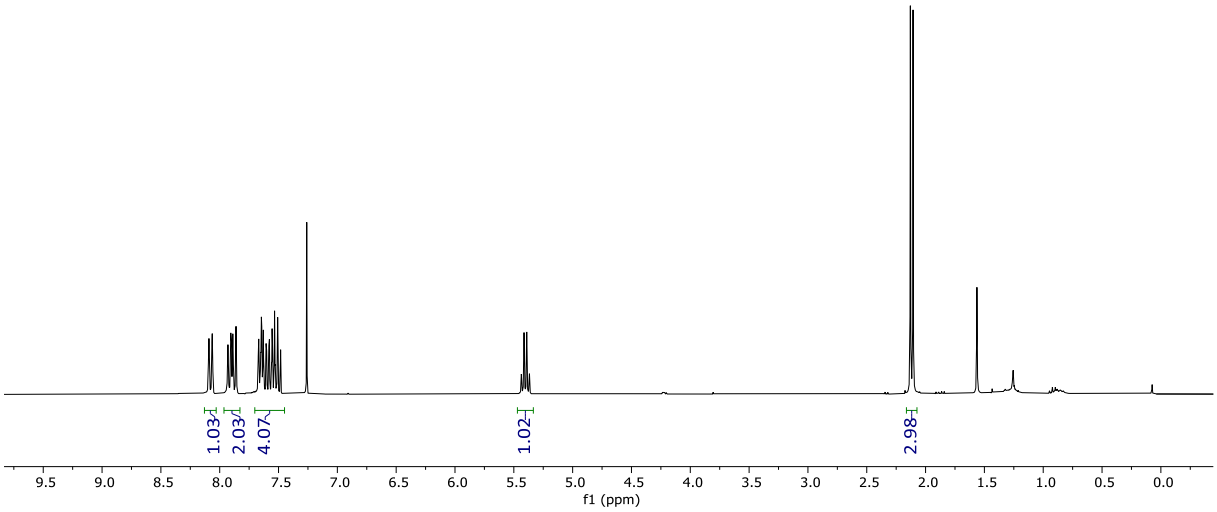


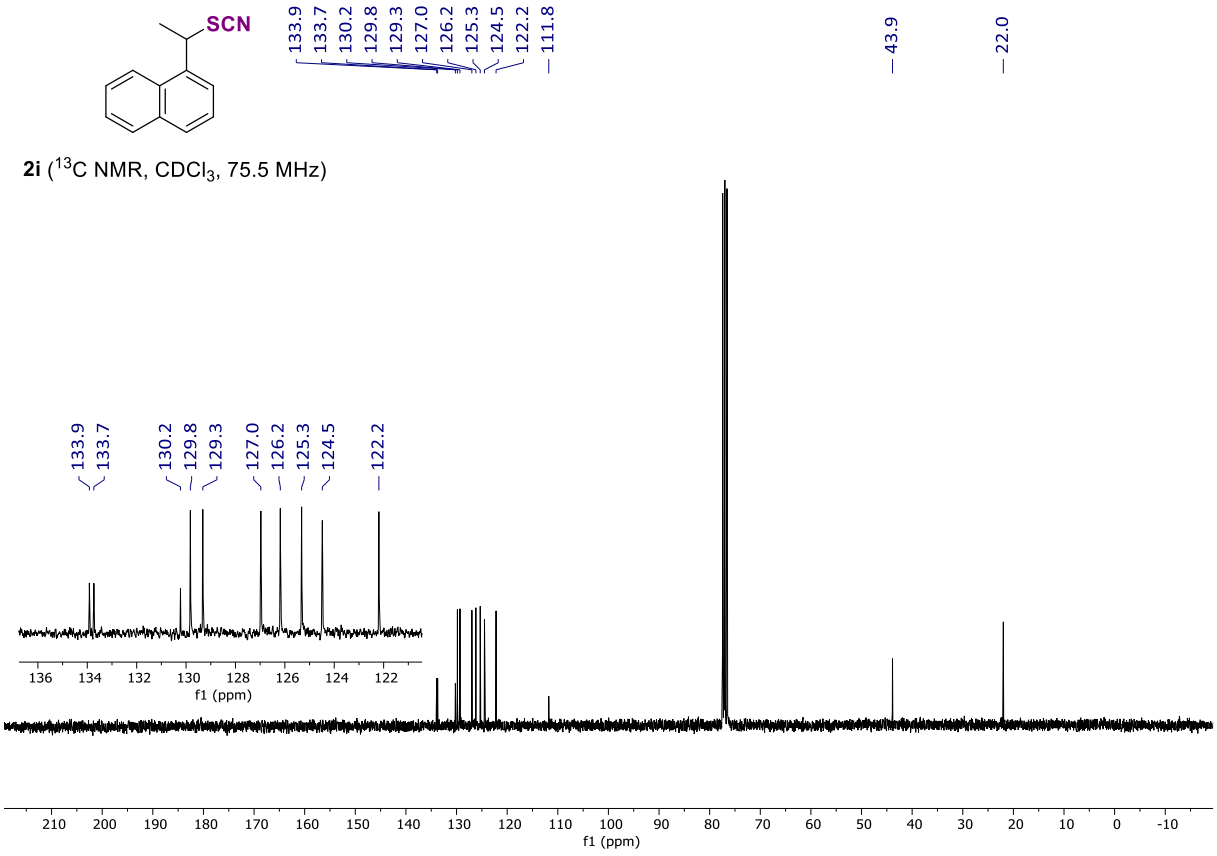
2h (^{13}C NMR, $CDCl_3$, 75.5 MHz)



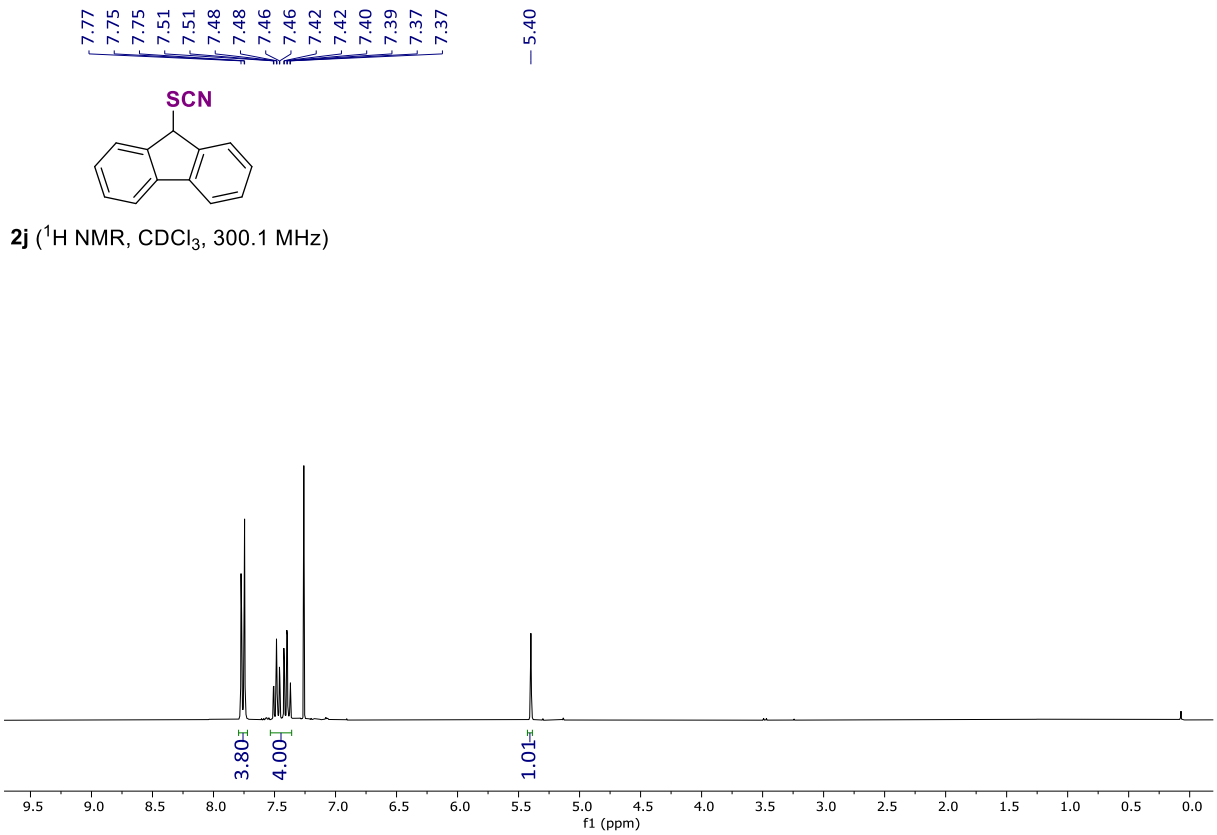


2i (^{1}H NMR, $CDCl_3$, 300.1 MHz)

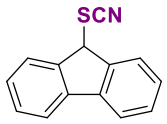




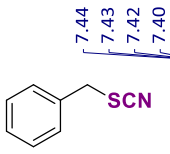
2i (^{13}C NMR, $CDCl_3$, 75.5 MHz)



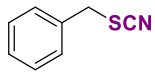
2j (^{1}H NMR, $CDCl_3$, 300.1 MHz)



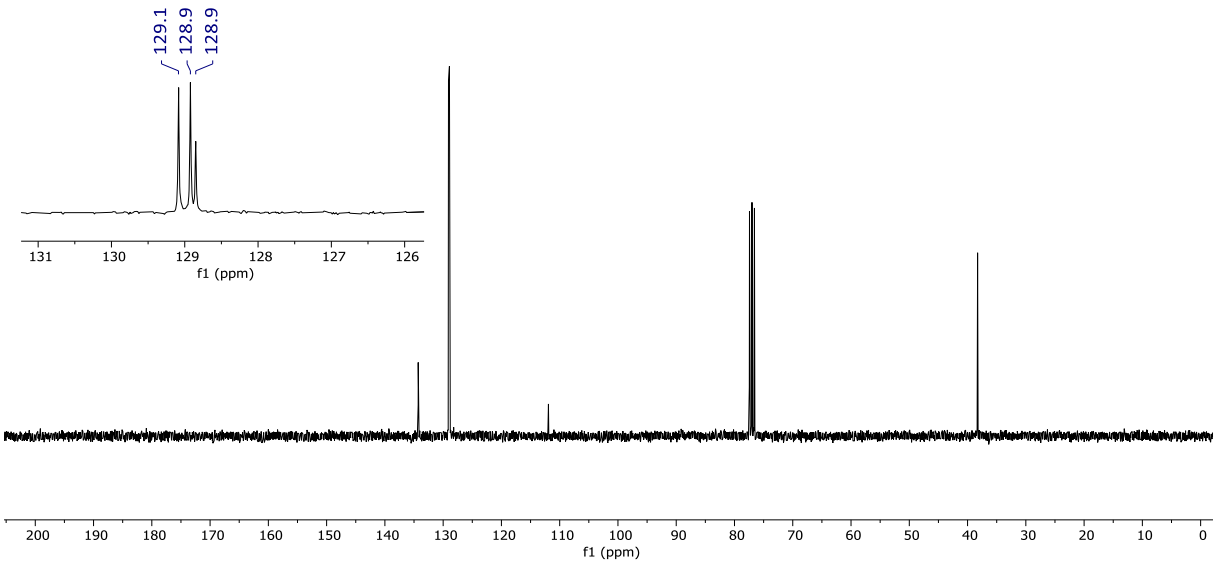
2j (^{13}C NMR, $CDCl_3$, 75.5 MHz)

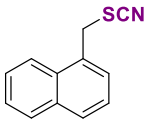


2k (^{1}H NMR, $CDCl_3$, 300.1 MHz)

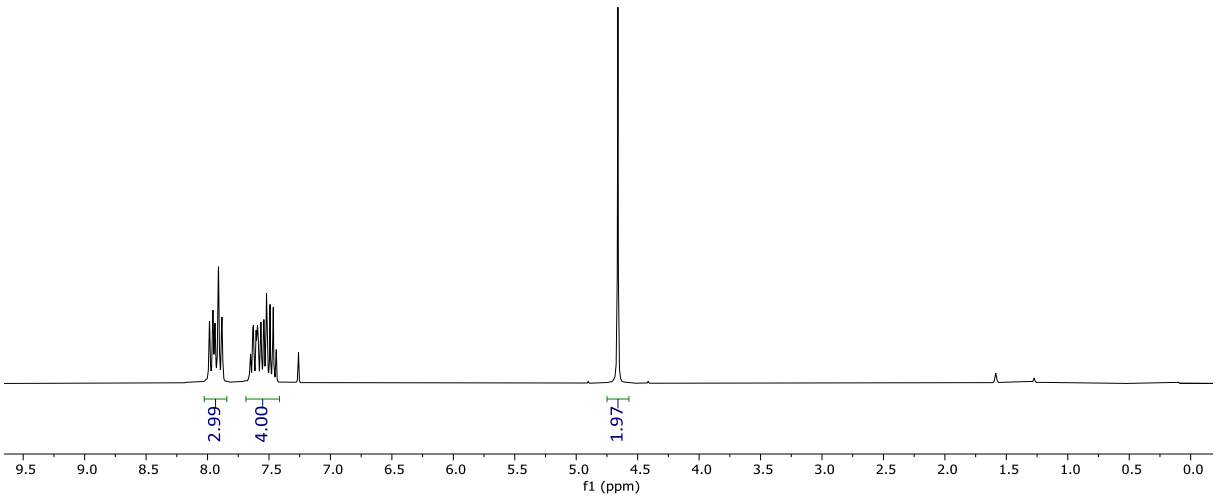


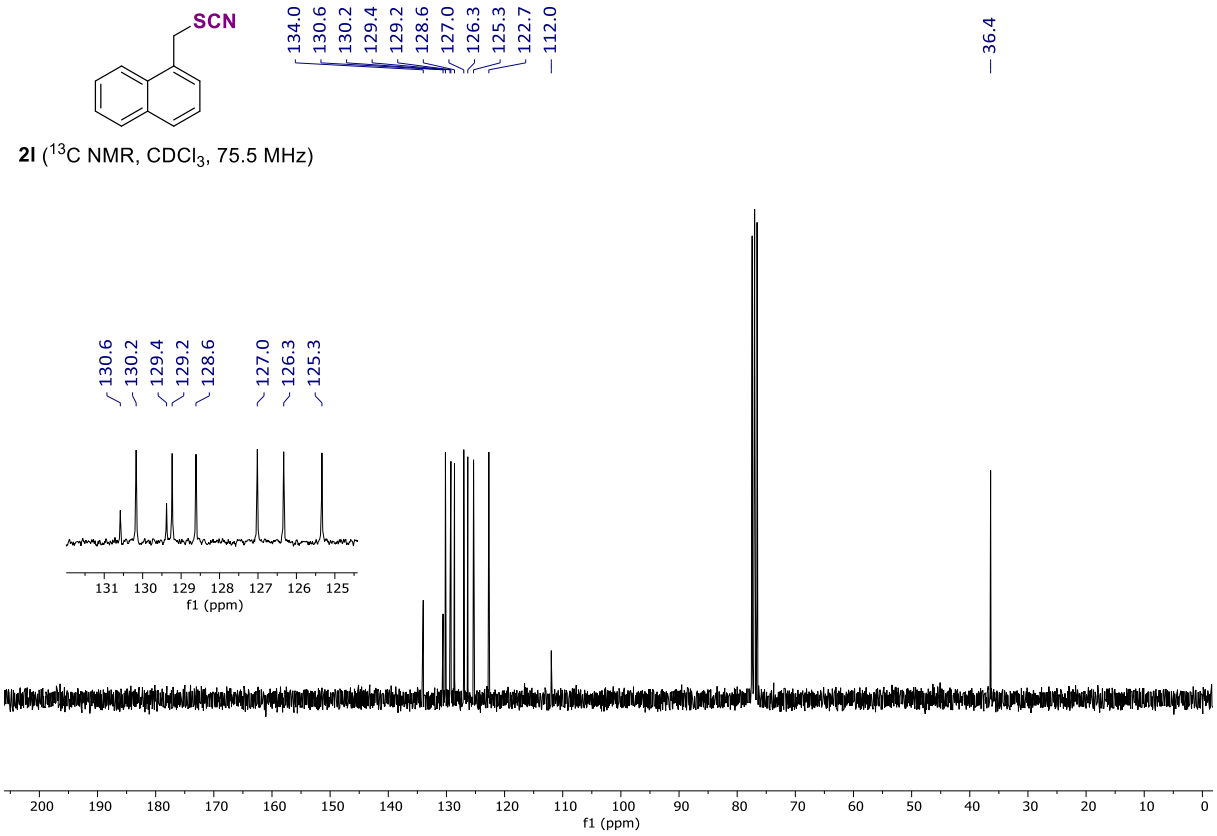
2k (^{13}C NMR, $CDCl_3$, 75.5 MHz)



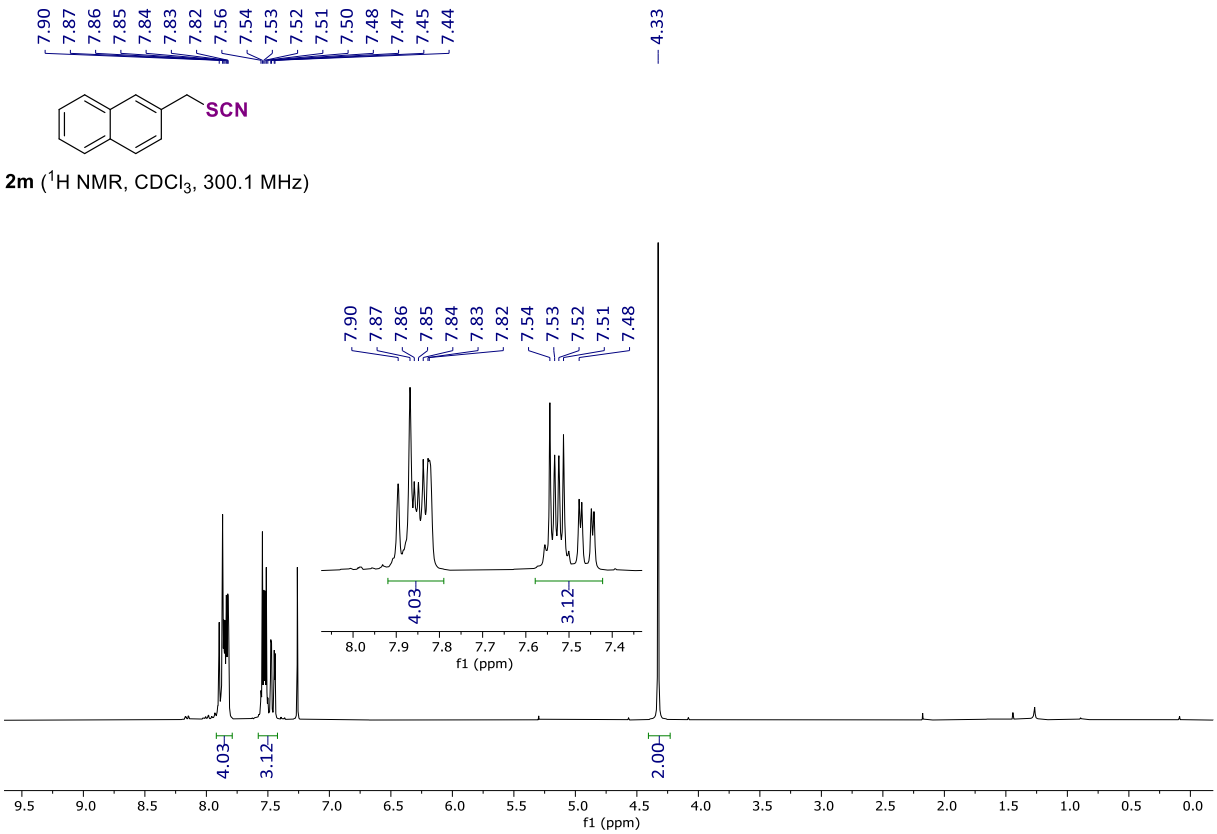


2l (^{1}H NMR, $CDCl_3$, 300.1 MHz)

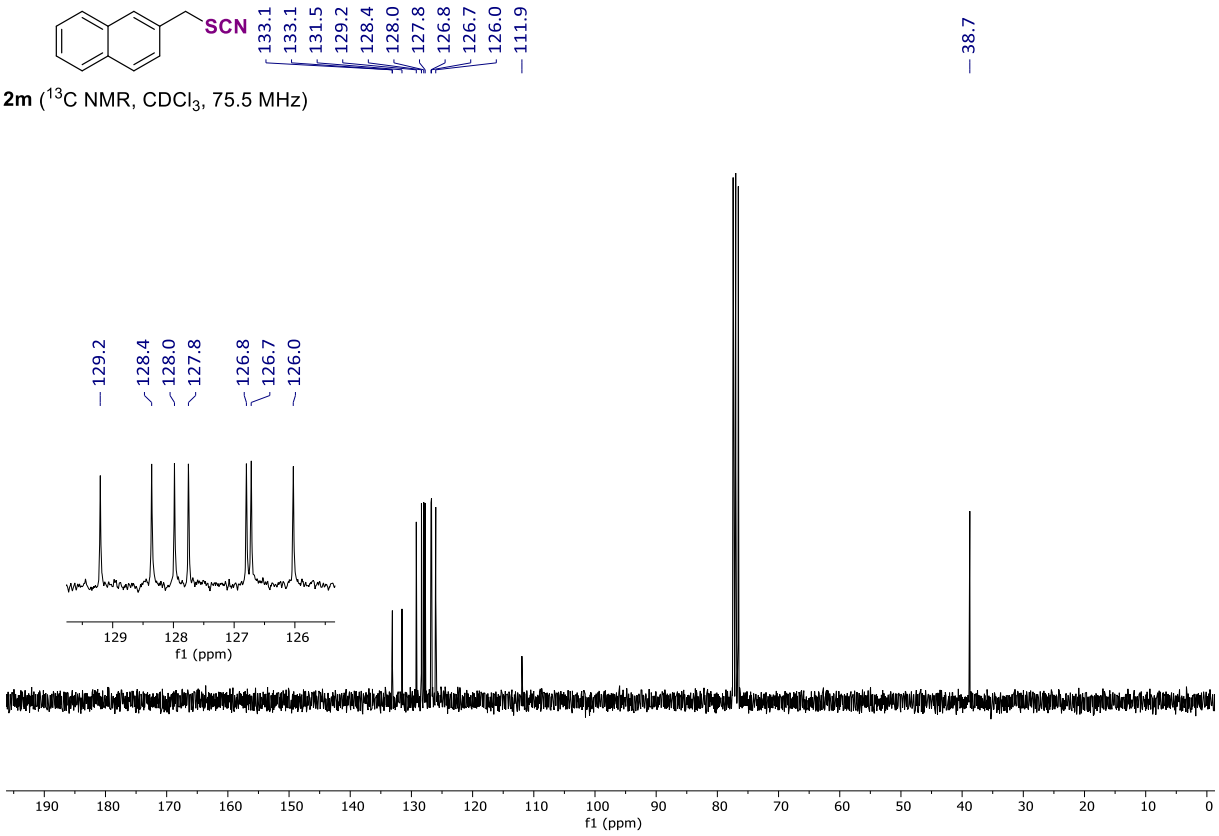




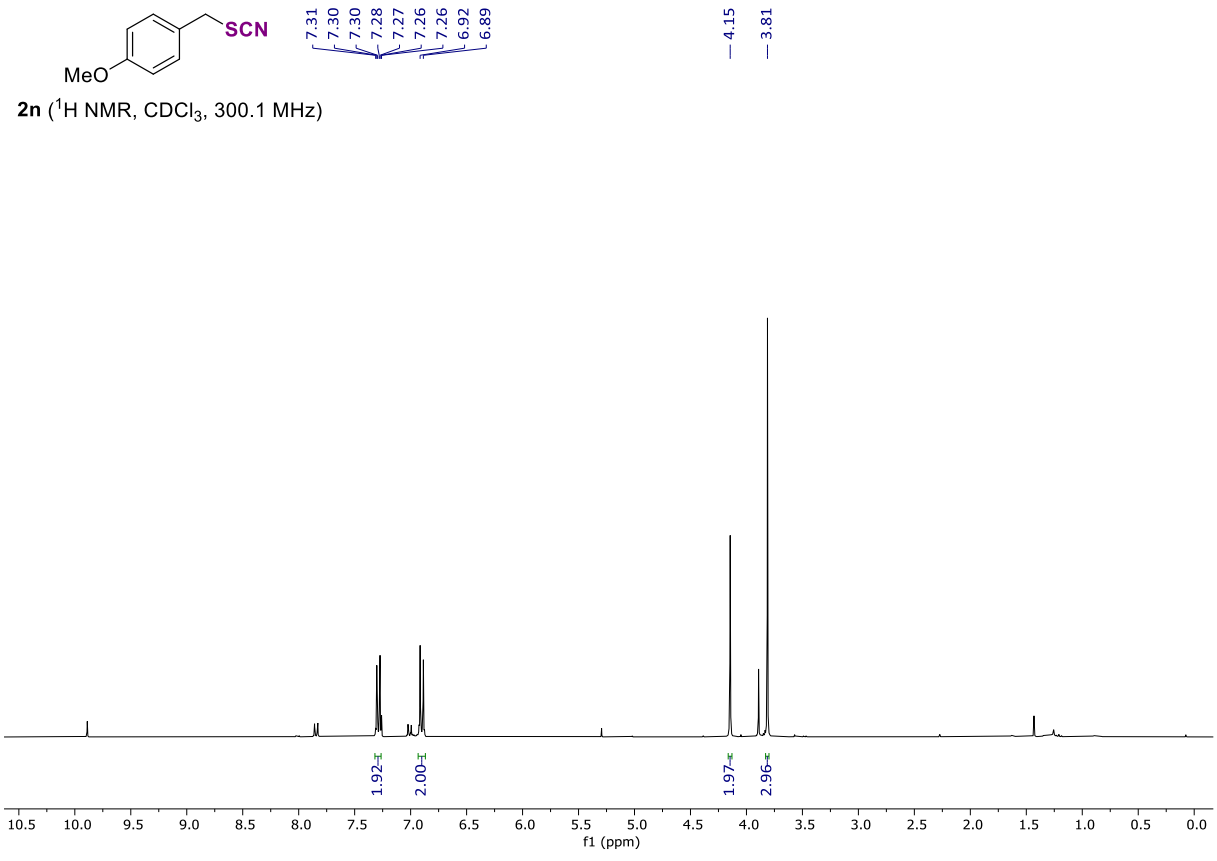
2l (^{13}C NMR, $CDCl_3$, 75.5 MHz)



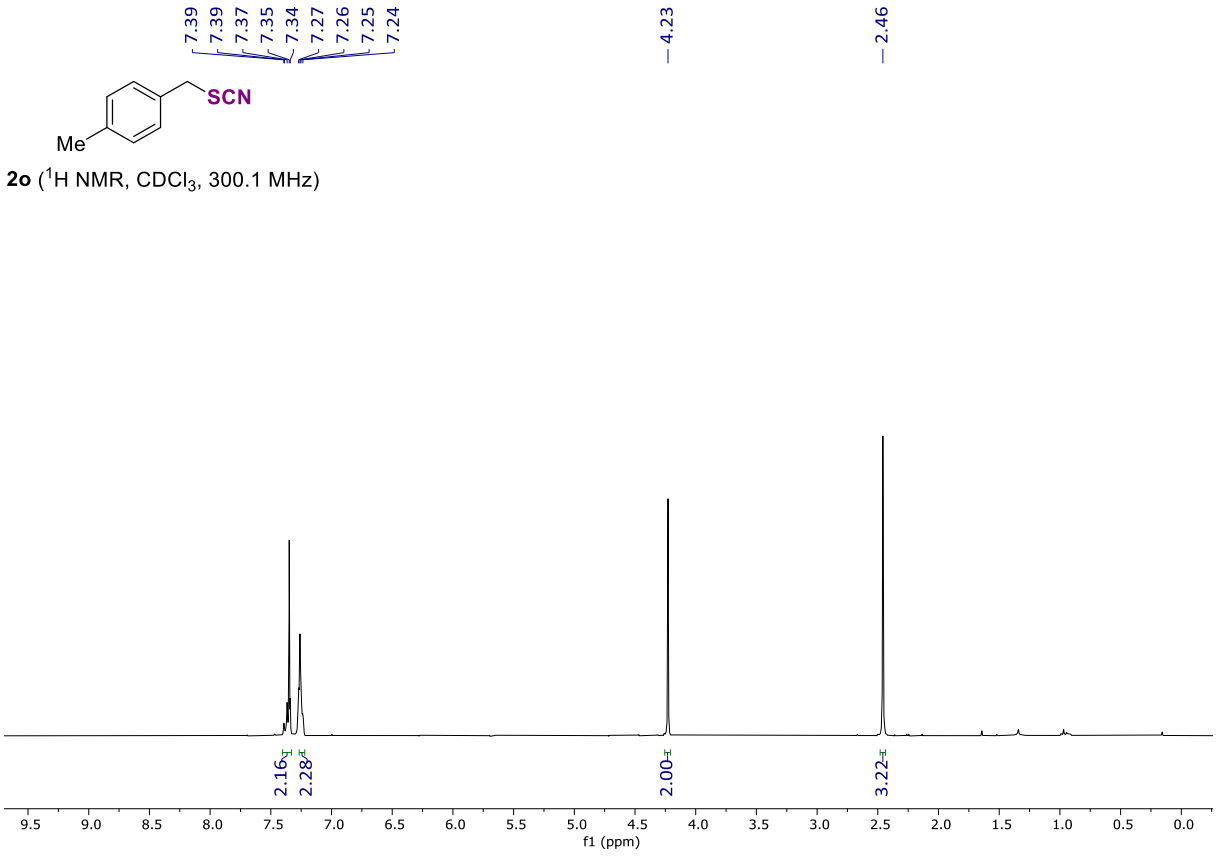
2m (^{1}H NMR, $CDCl_3$, 300.1 MHz)



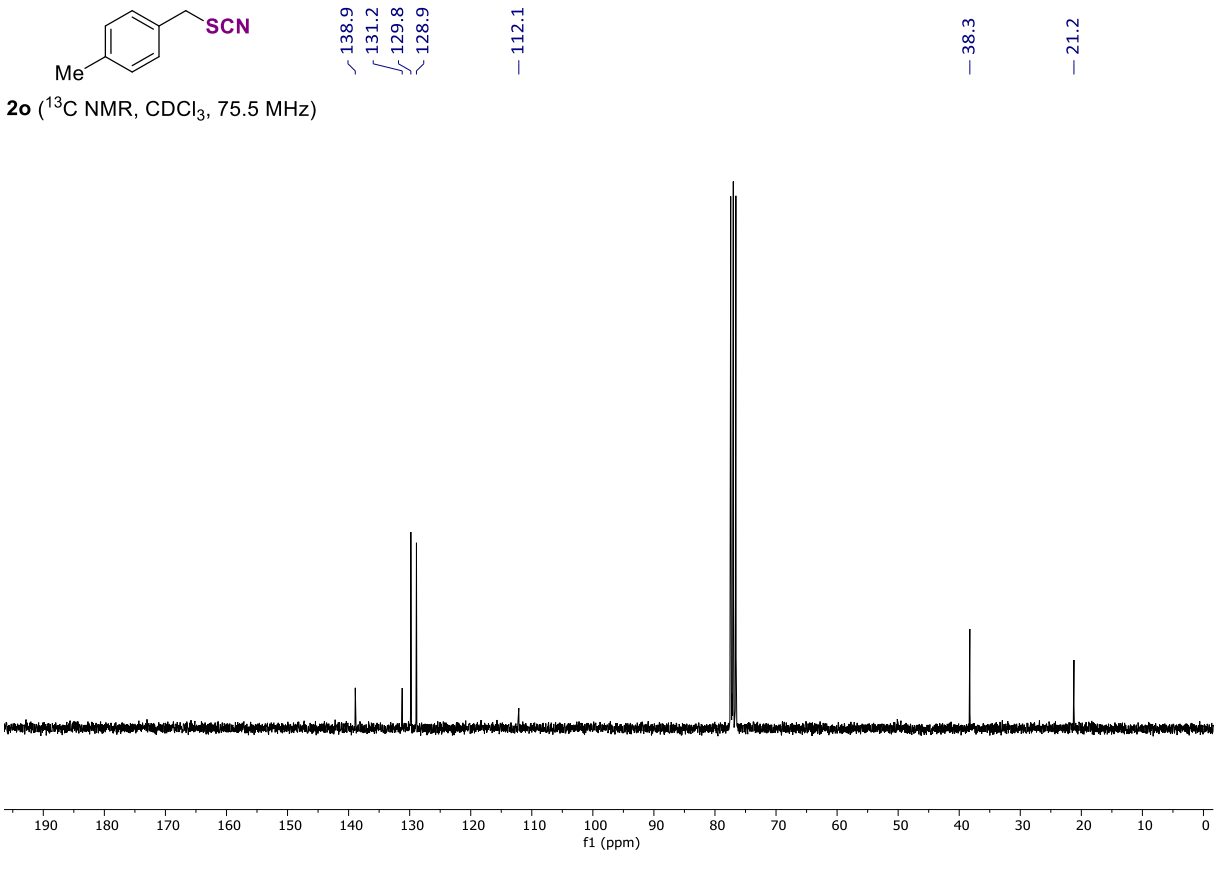
2m (^{13}C NMR, $CDCl_3$, 75.5 MHz)



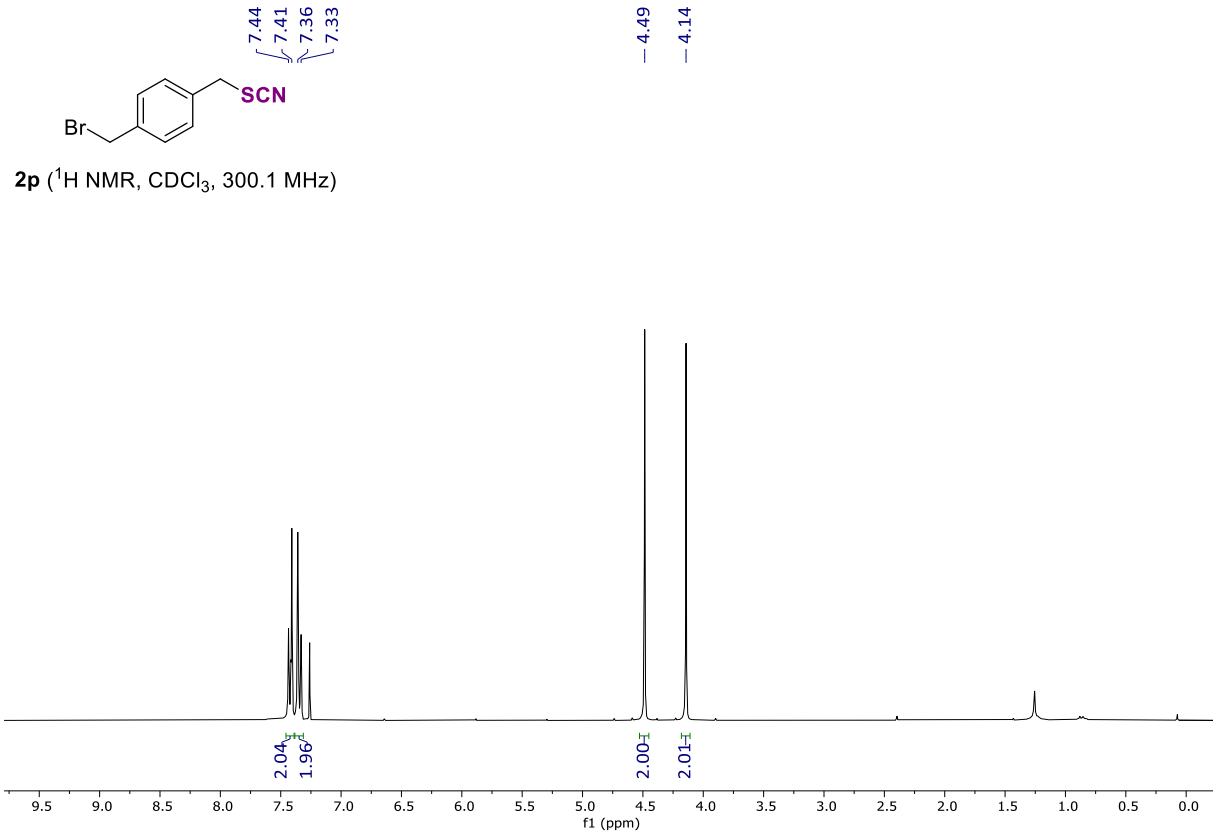
2n (^{1}H NMR, $CDCl_3$, 300.1 MHz)



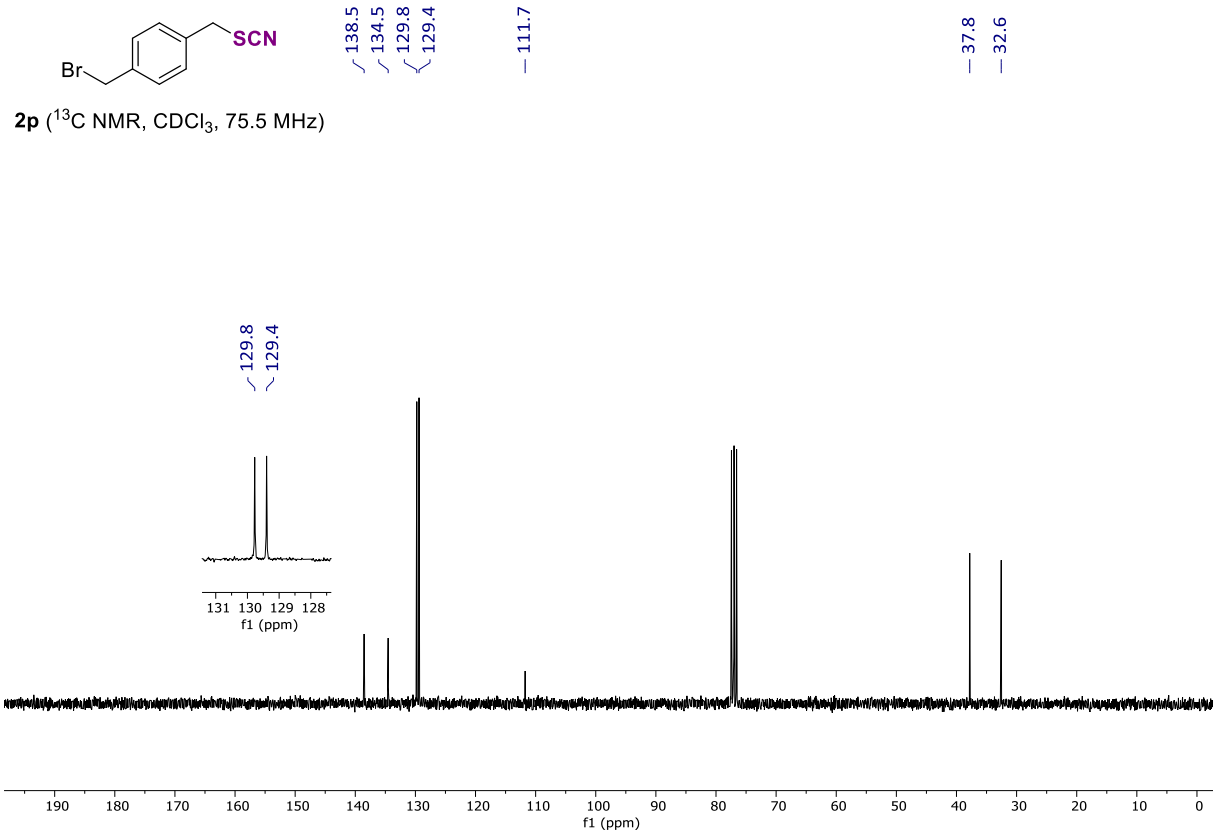
2o (^{1}H NMR, $CDCl_3$, 300.1 MHz)



2o (^{13}C NMR, $CDCl_3$, 75.5 MHz)

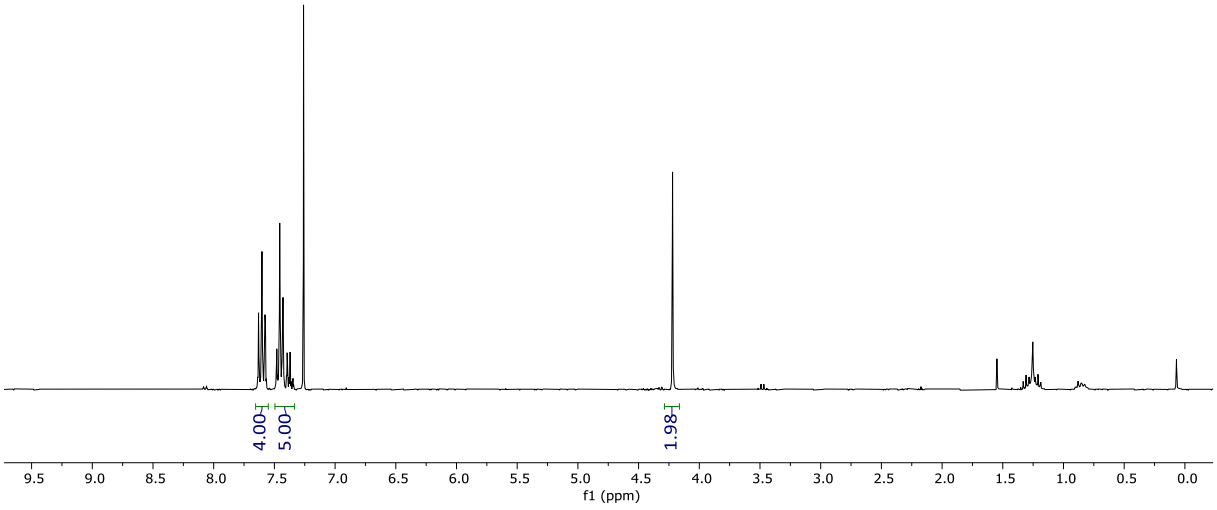


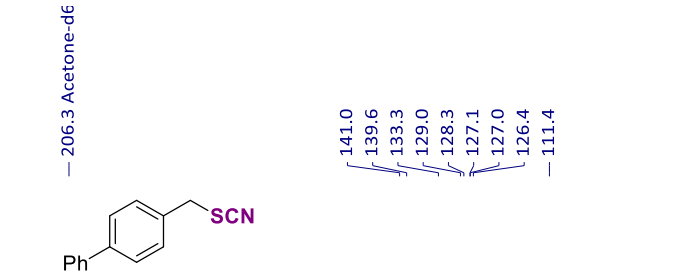
2p (^{1}H NMR, $CDCl_3$, 300.1 MHz)



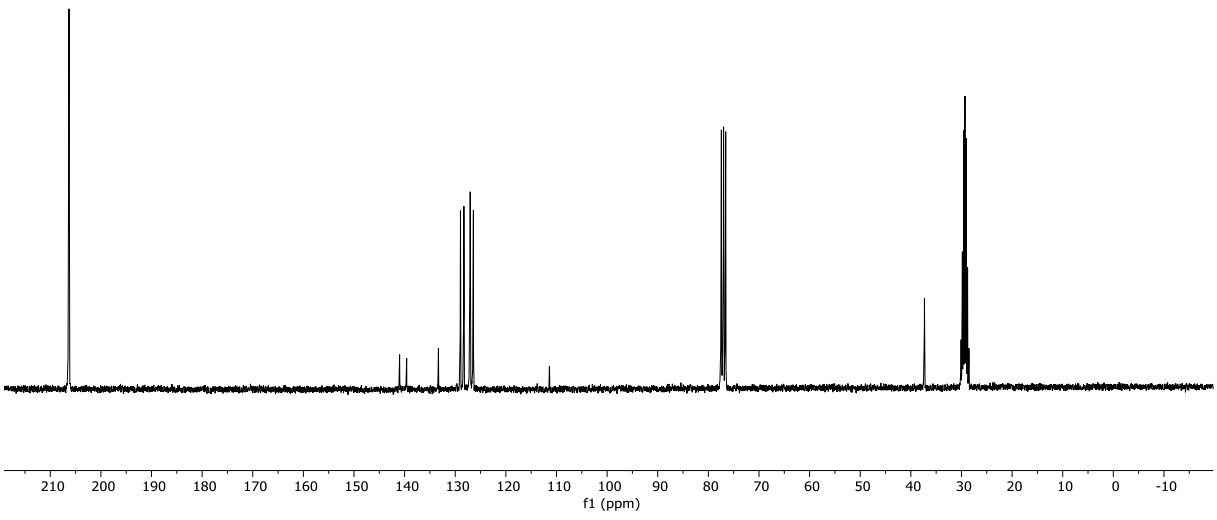
2p (^{13}C NMR, $CDCl_3$, 75.5 MHz)

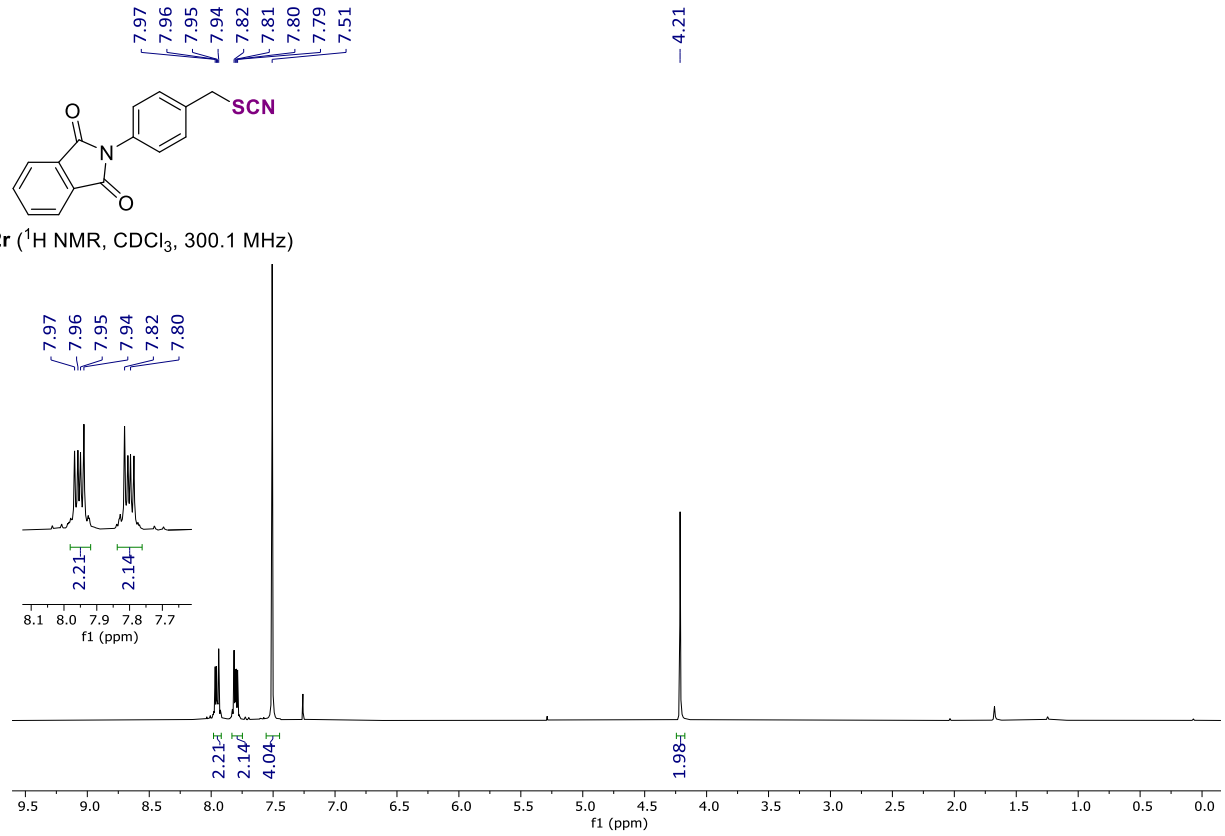
2q (^{1}H NMR, $CDCl_3$, 300.1 MHz)



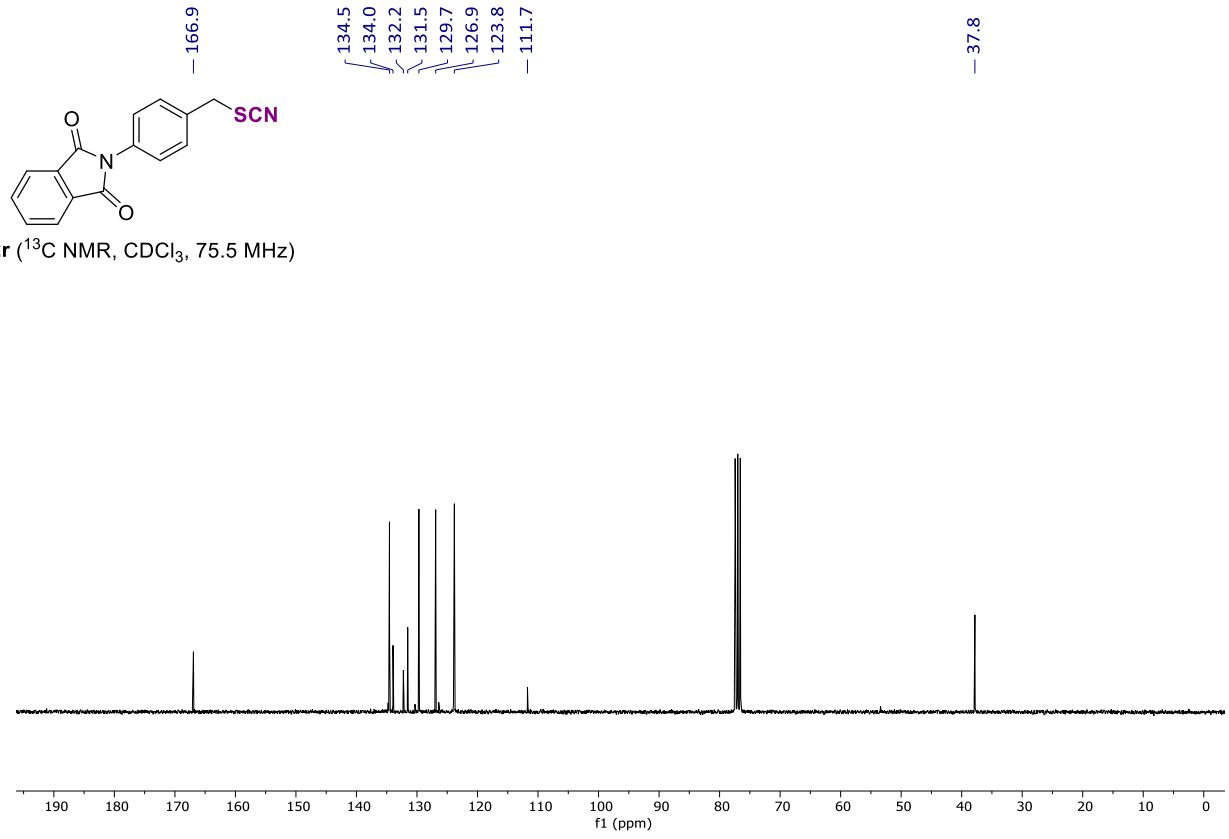


2q (^{13}C NMR, $CDCl_3$, 75.5 MHz)

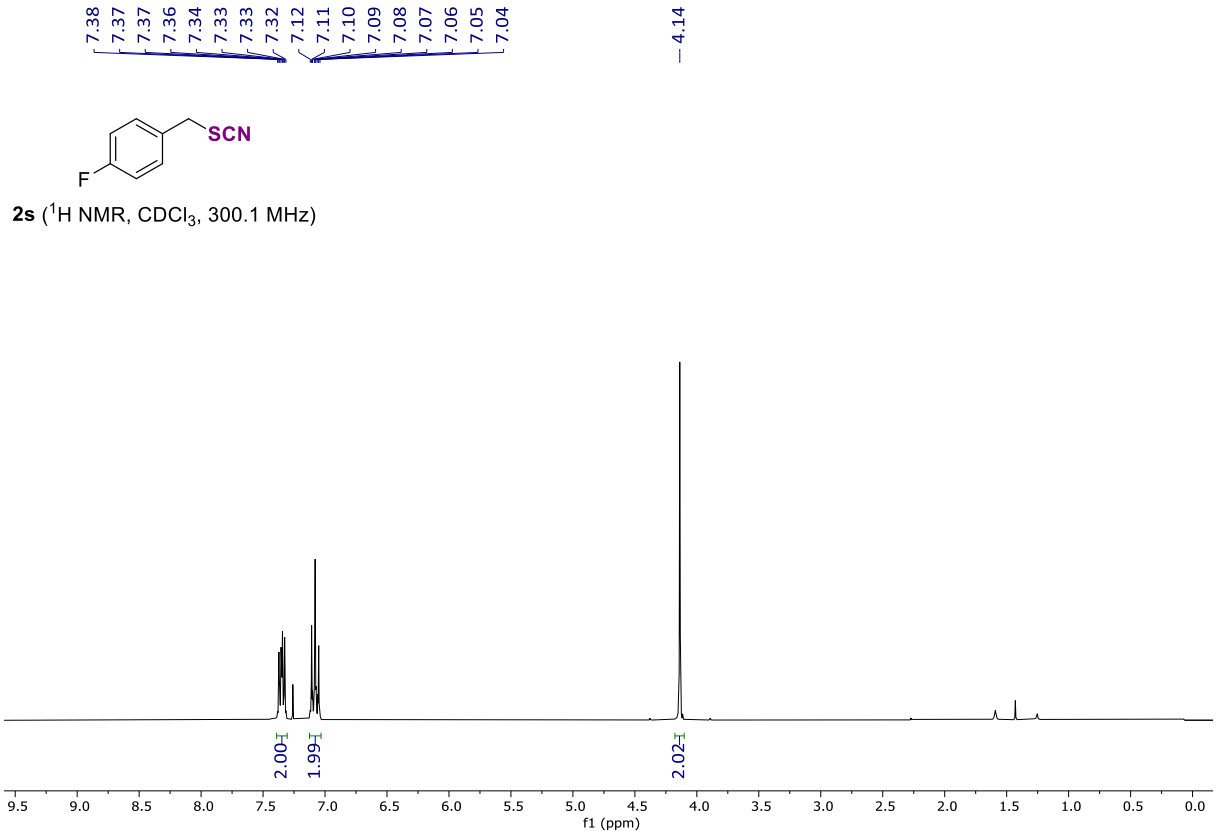




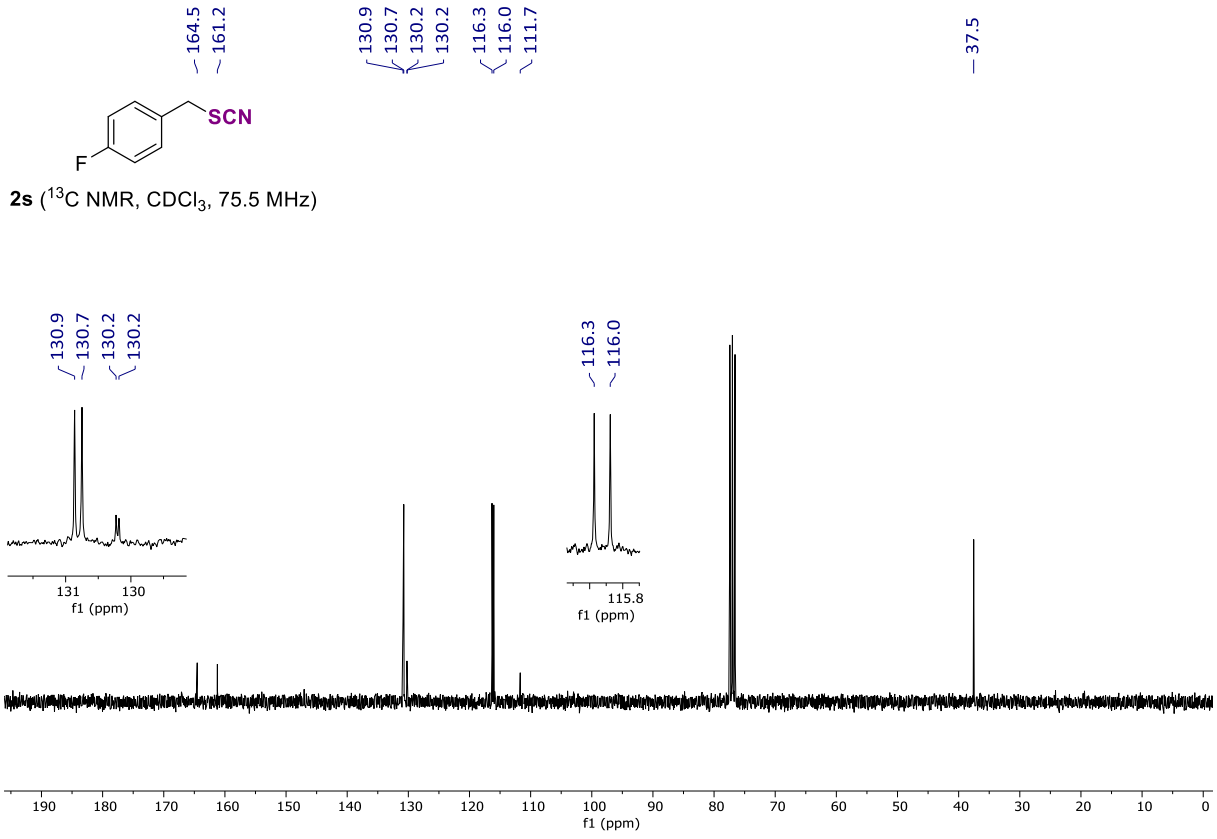
2r (^{1}H NMR, $CDCl_3$, 300.1 MHz)



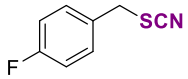
2r (^{13}C NMR, $CDCl_3$, 75.5 MHz)

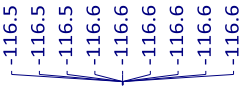


2s (^{1}H NMR, $CDCl_3$, 300.1 MHz)

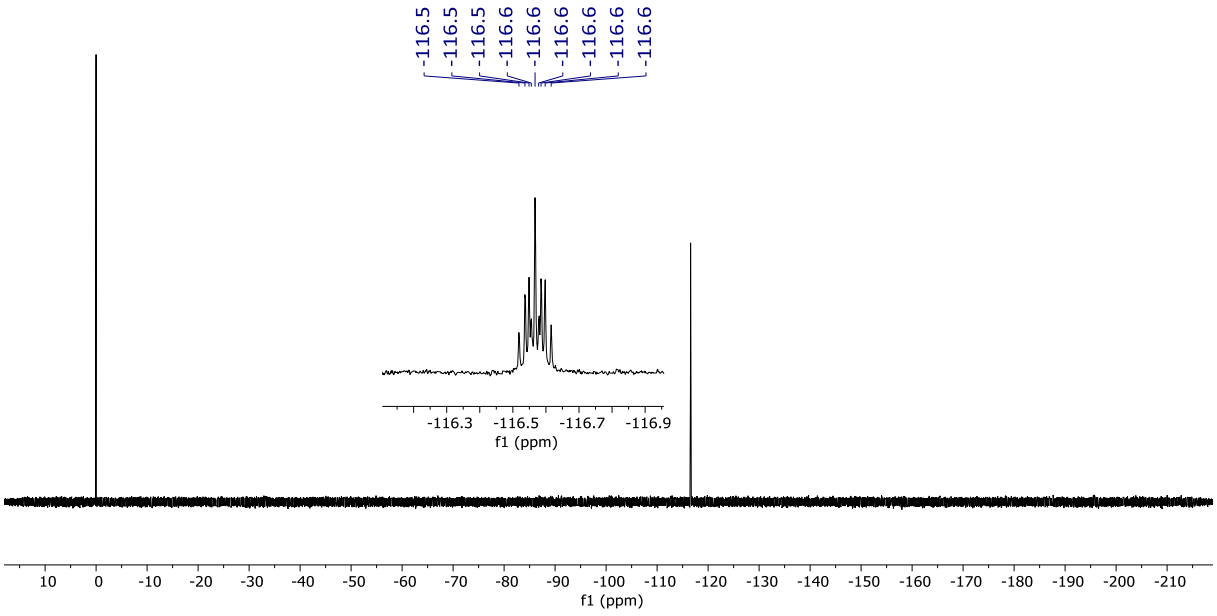


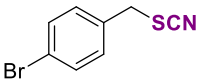
2s (^{13}C NMR, $CDCl_3$, 75.5 MHz)



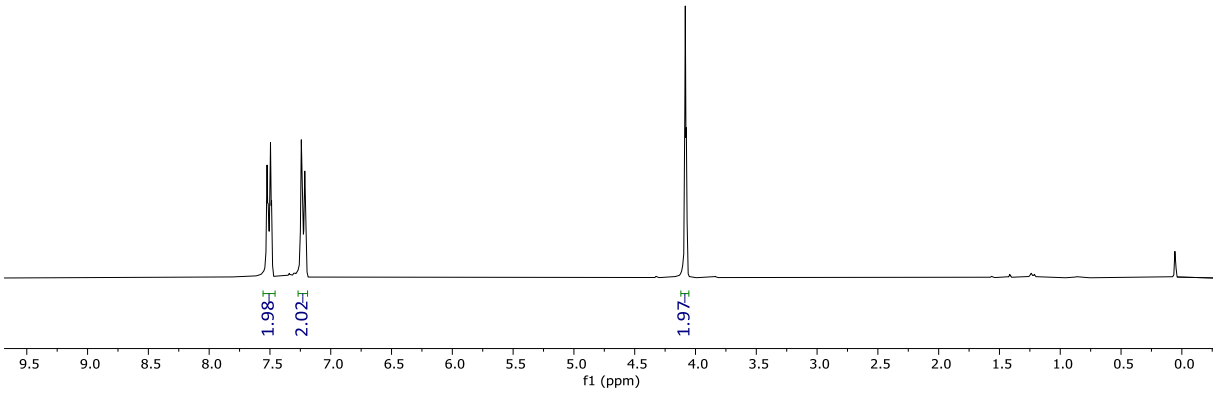


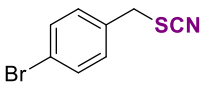
2s (^{19}F NMR, $CDCl_3$, 282.4 MHz)



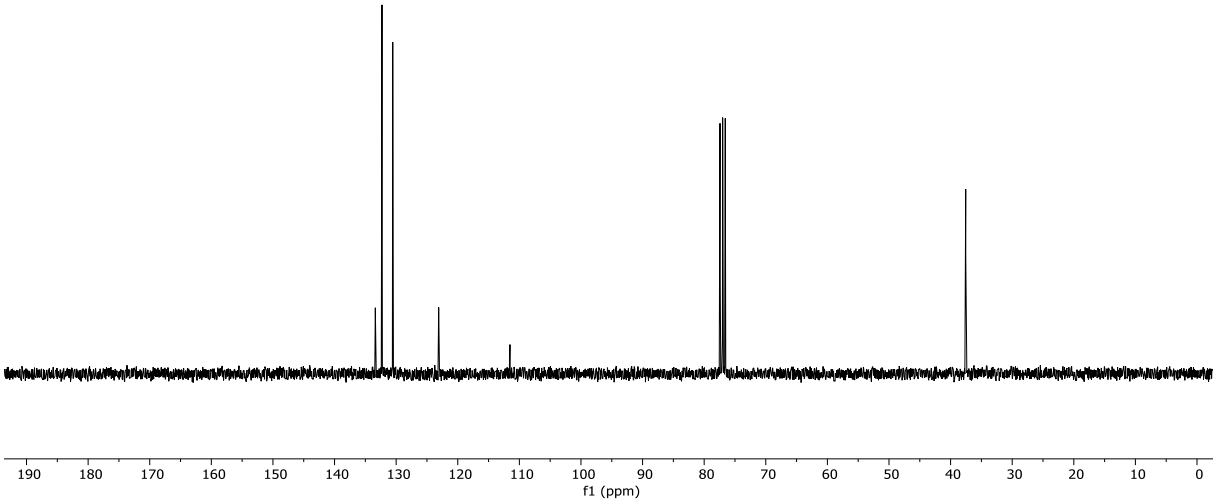


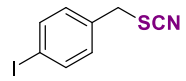
2t (^{1}H NMR, $CDCl_3$, 300.1 MHz)



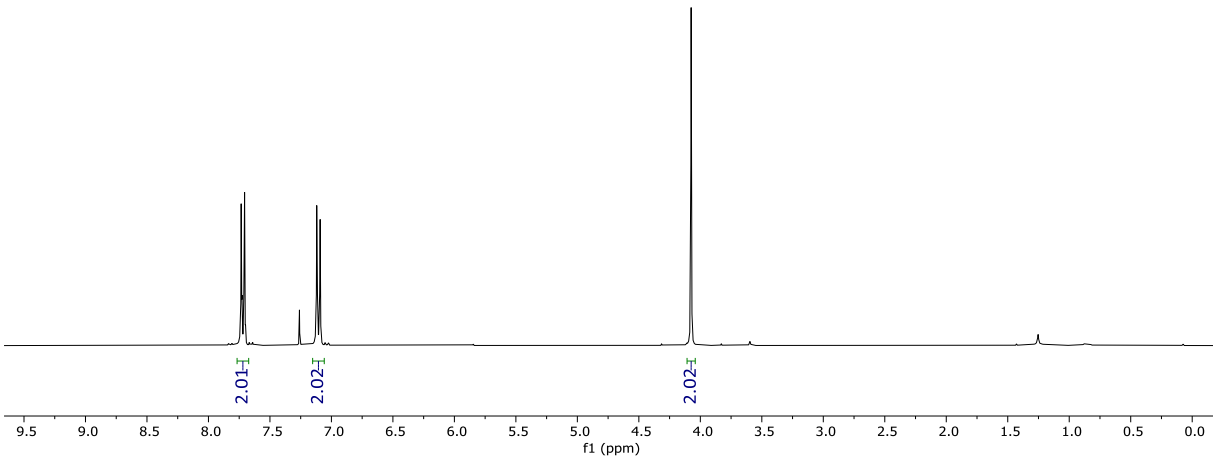


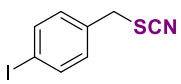
2t (^{13}C NMR, $CDCl_3$, 75.5 MHz)



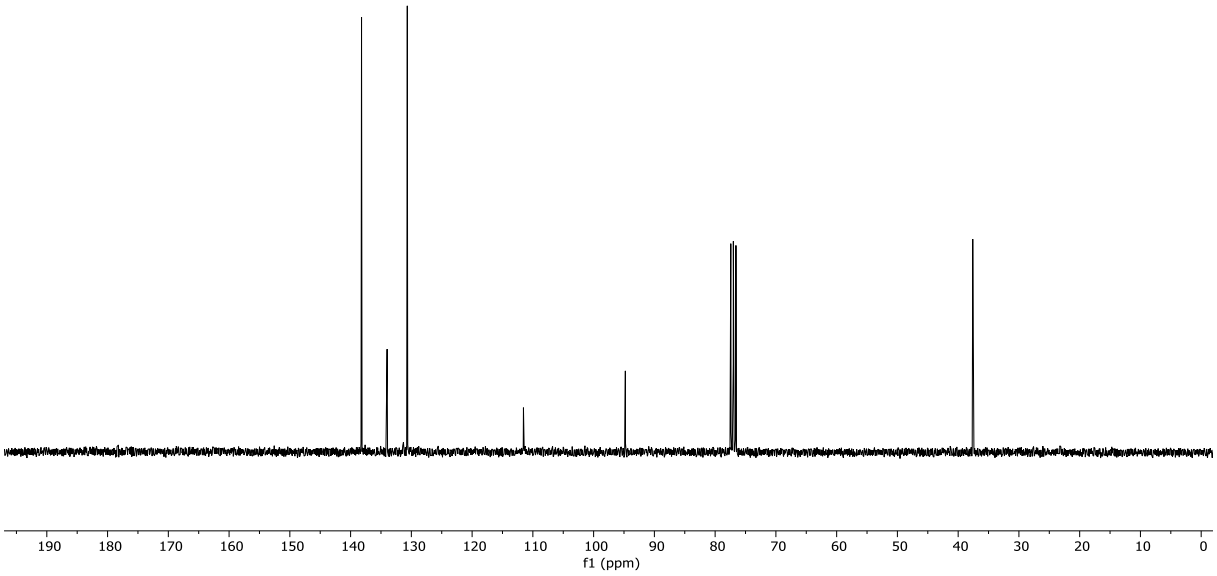


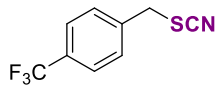
2u (^{1}H NMR, $CDCl_3$, 300.1 MHz)



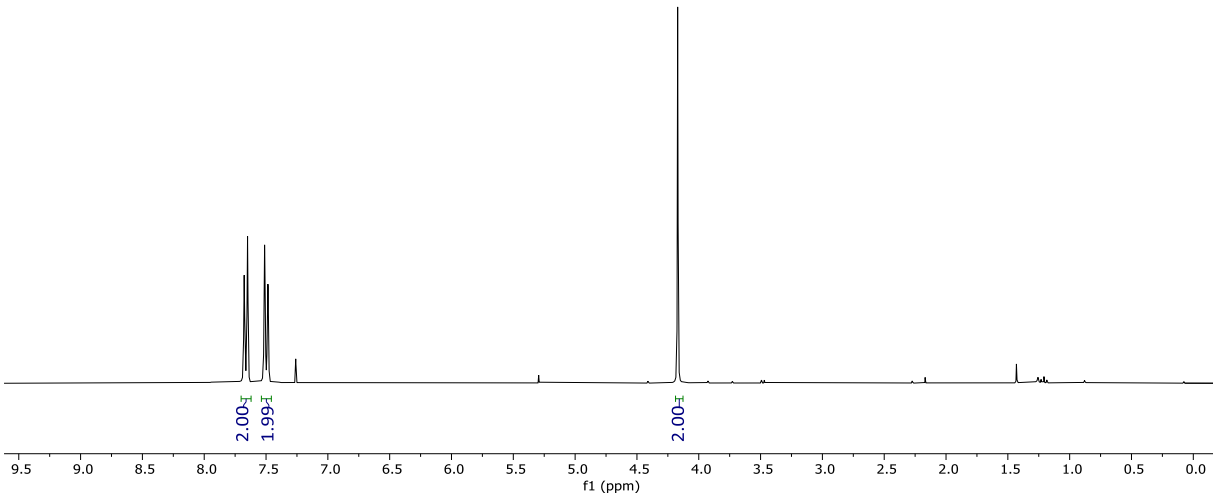


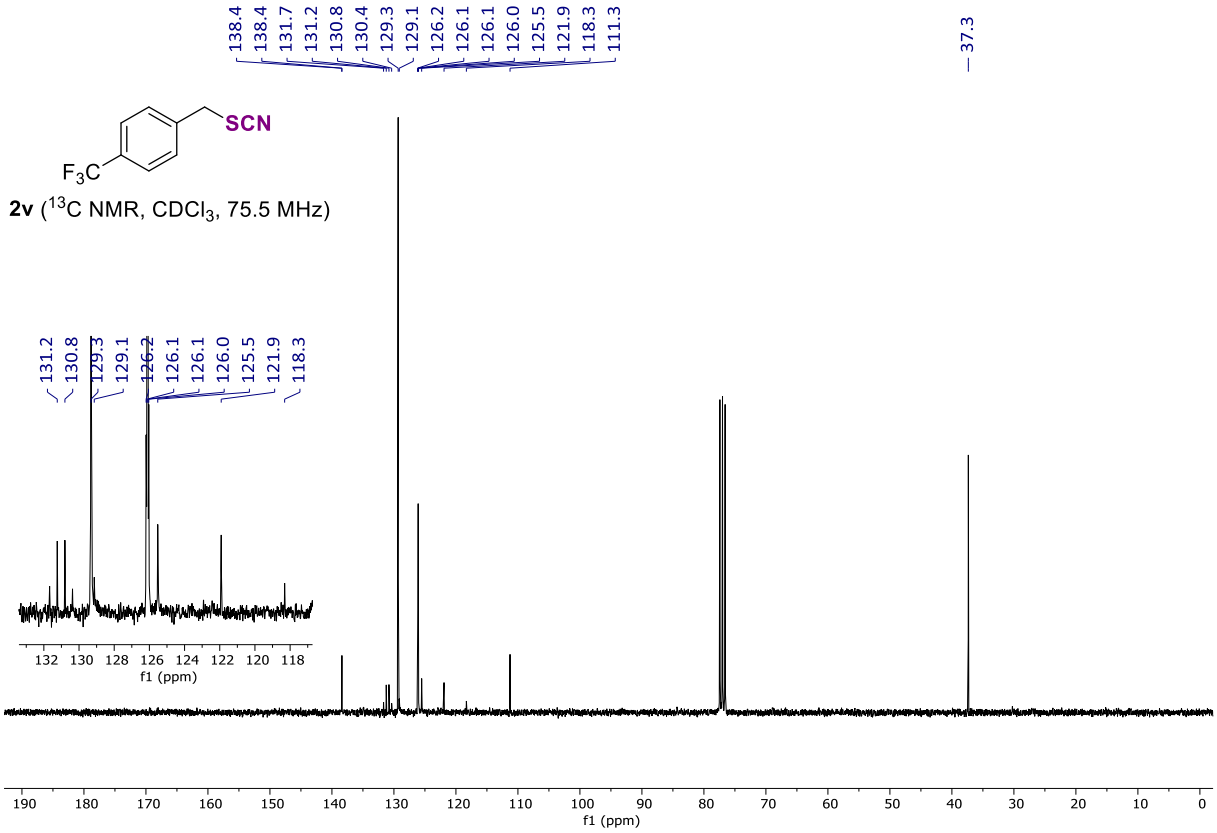
2u (^{13}C NMR, $CDCl_3$, 75.5 MHz)



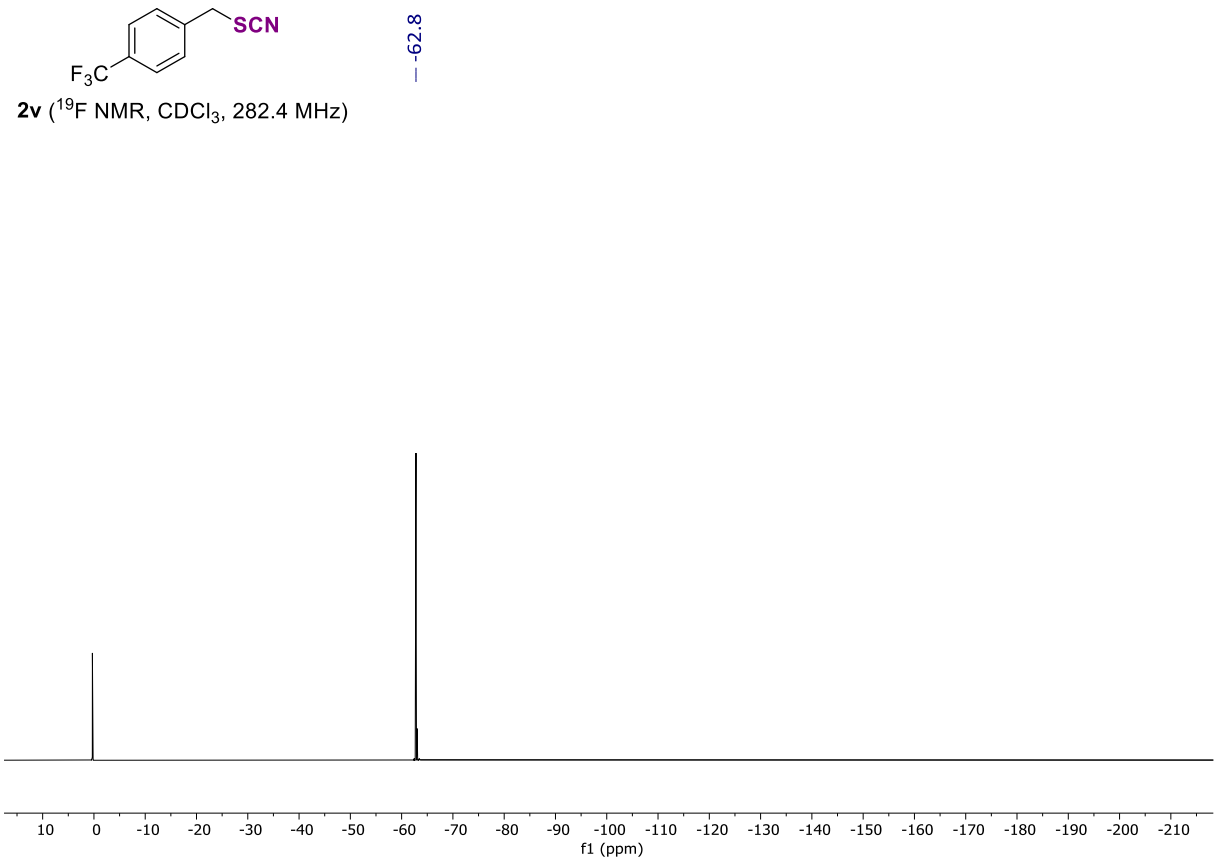


2v (^{1}H NMR, $CDCl_3$, 300.1 MHz)

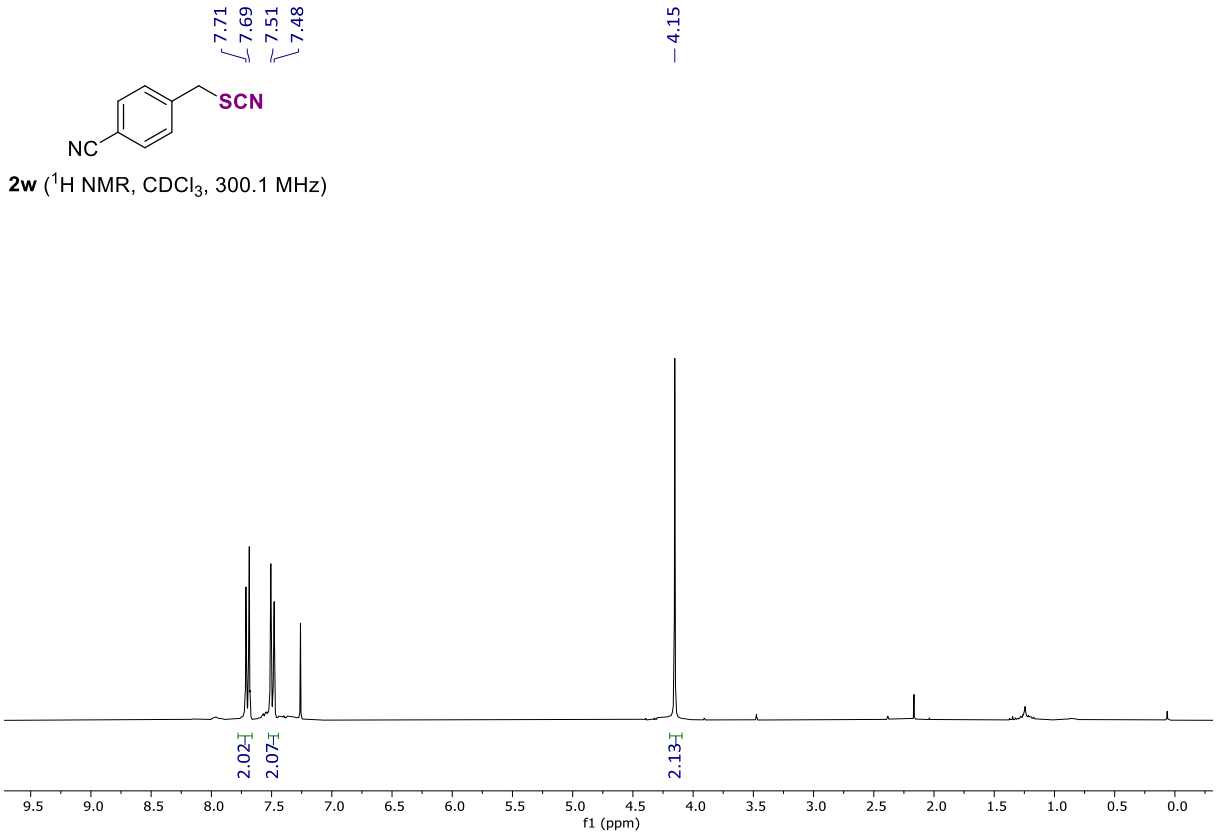




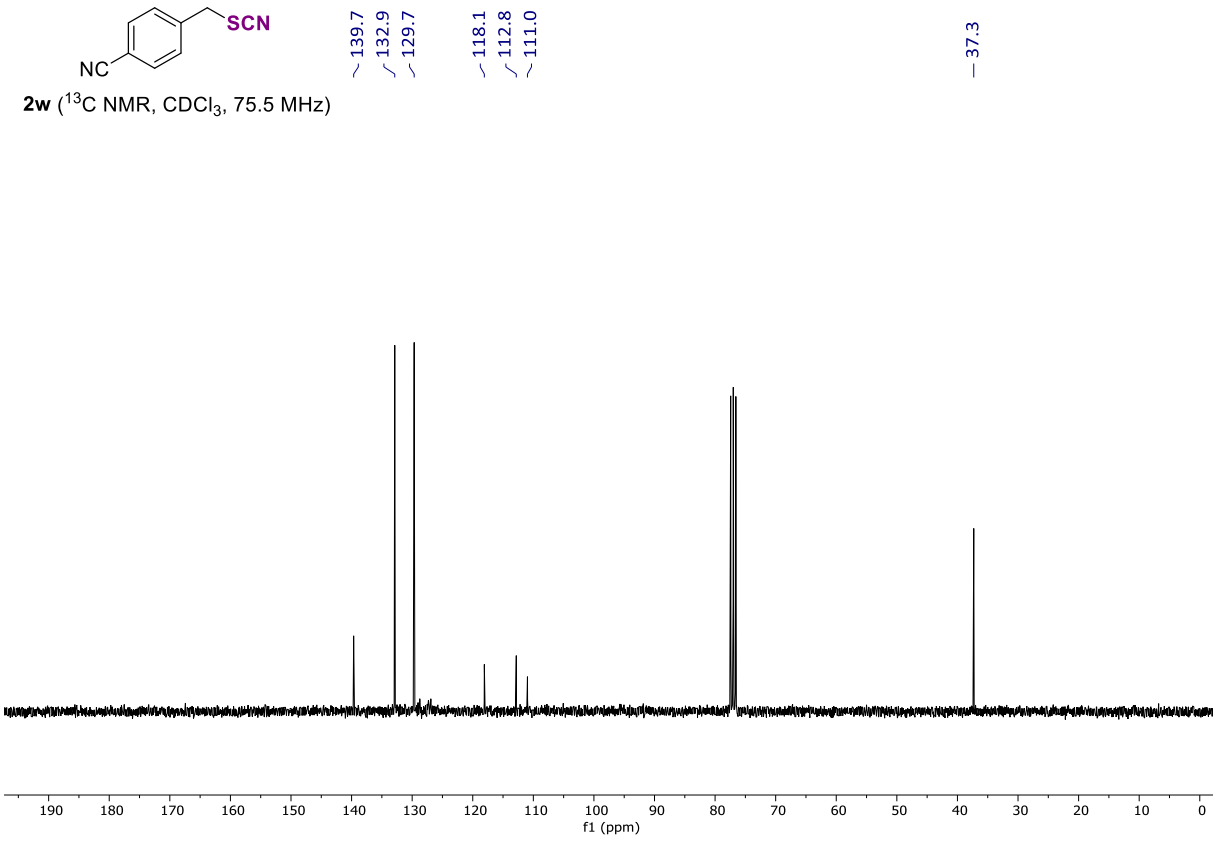
2v (^{13}C NMR, $CDCl_3$, 75.5 MHz)



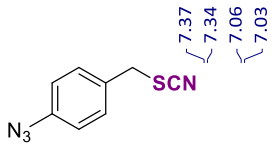
2v (^{19}F NMR, $CDCl_3$, 282.4 MHz)



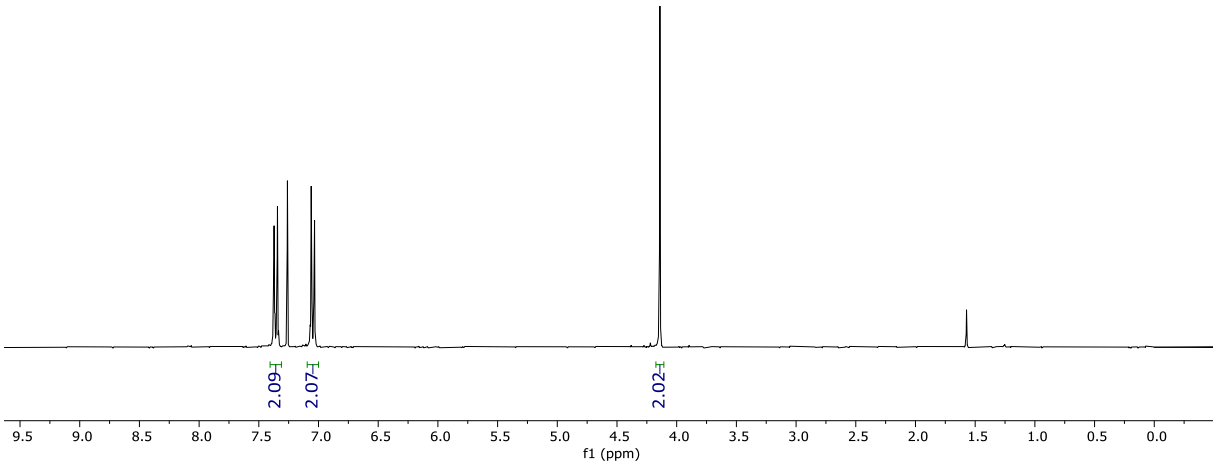
2w (^{1}H NMR, $CDCl_3$, 300.1 MHz)

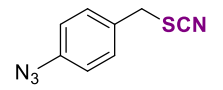


2w (^{13}C NMR, $CDCl_3$, 75.5 MHz)

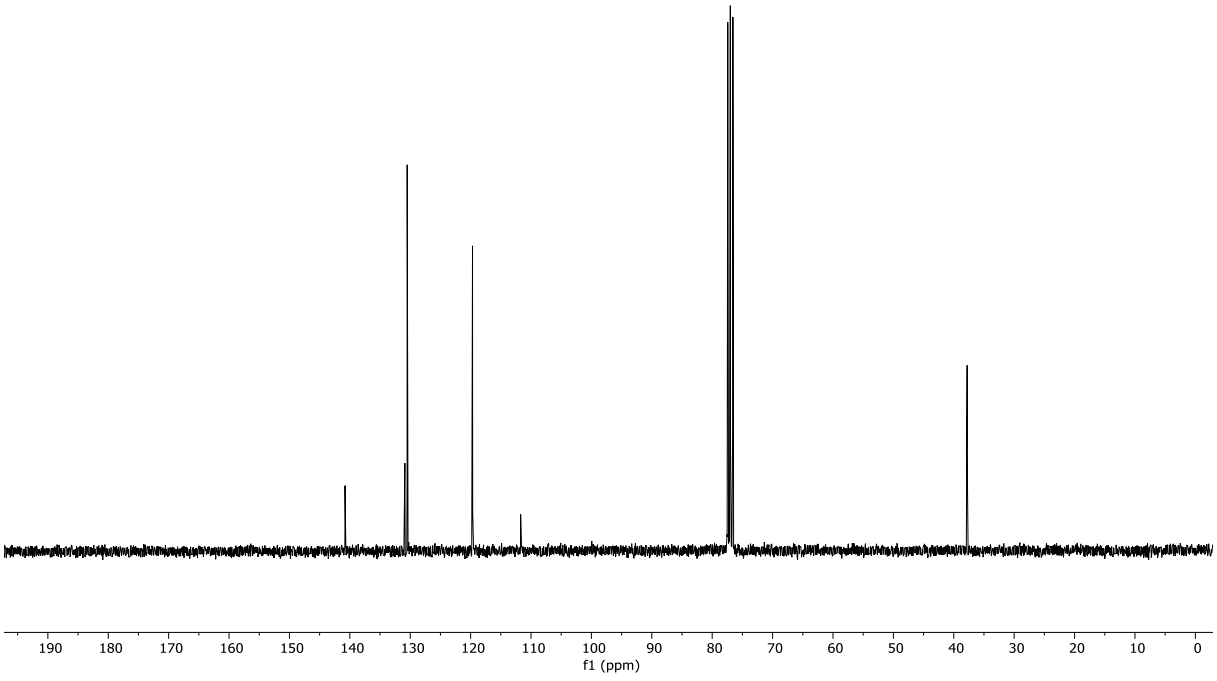


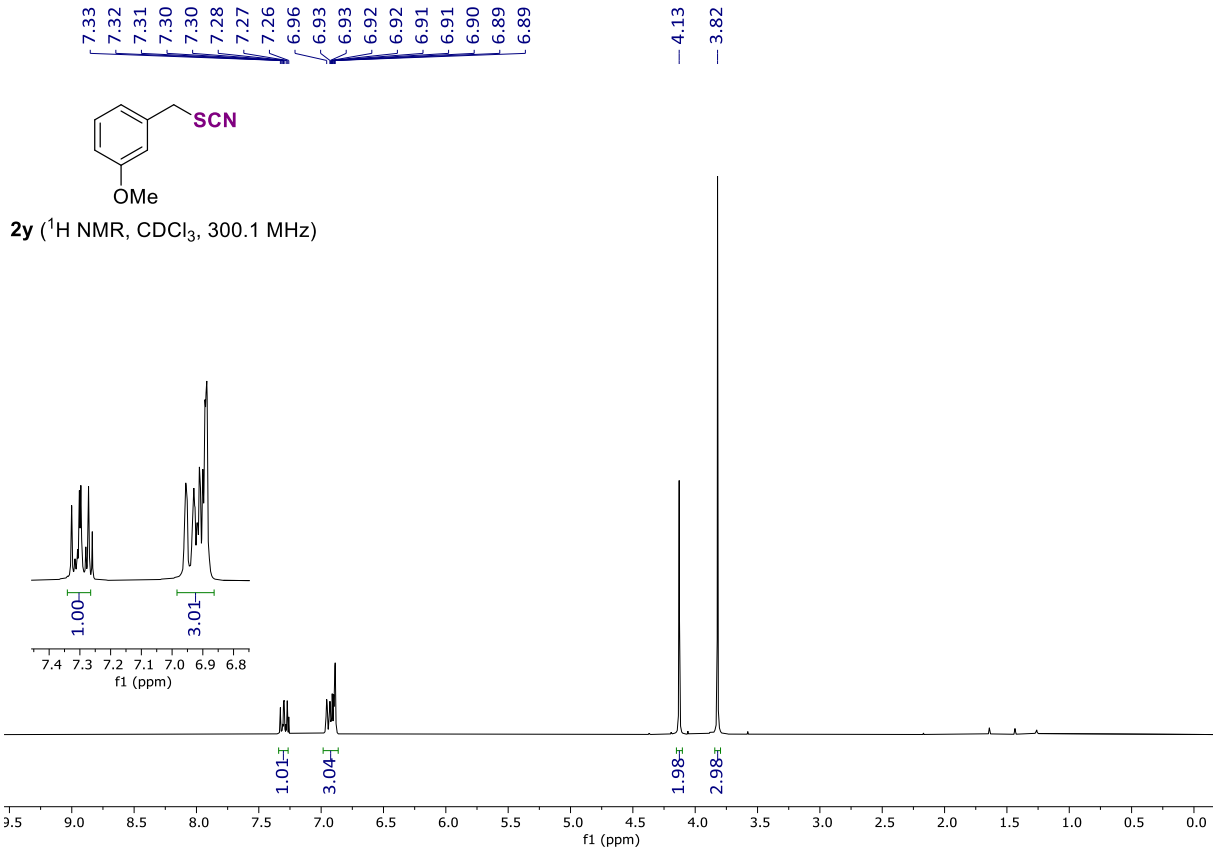
2x (^{1}H NMR, $CDCl_3$, 300.1 MHz)



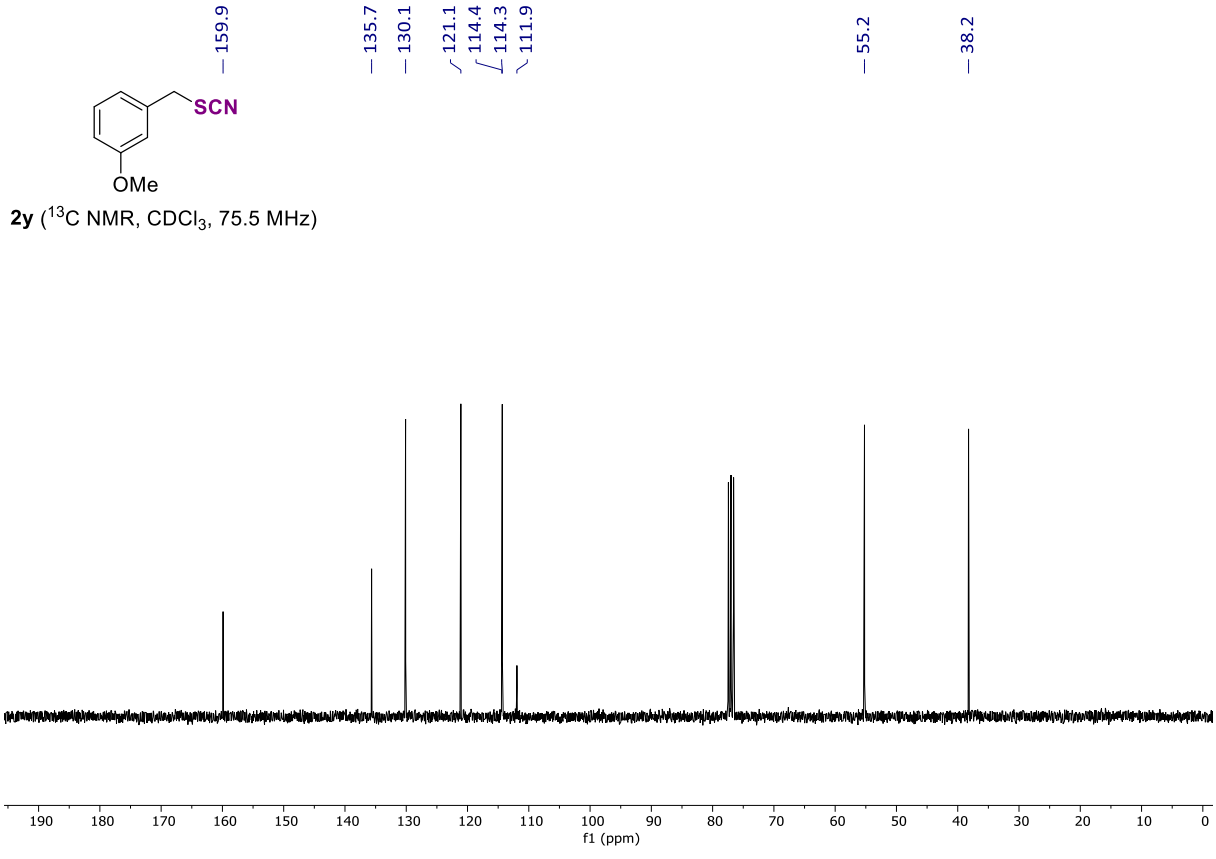


2x (^{13}C NMR, $CDCl_3$, 75.5 MHz)

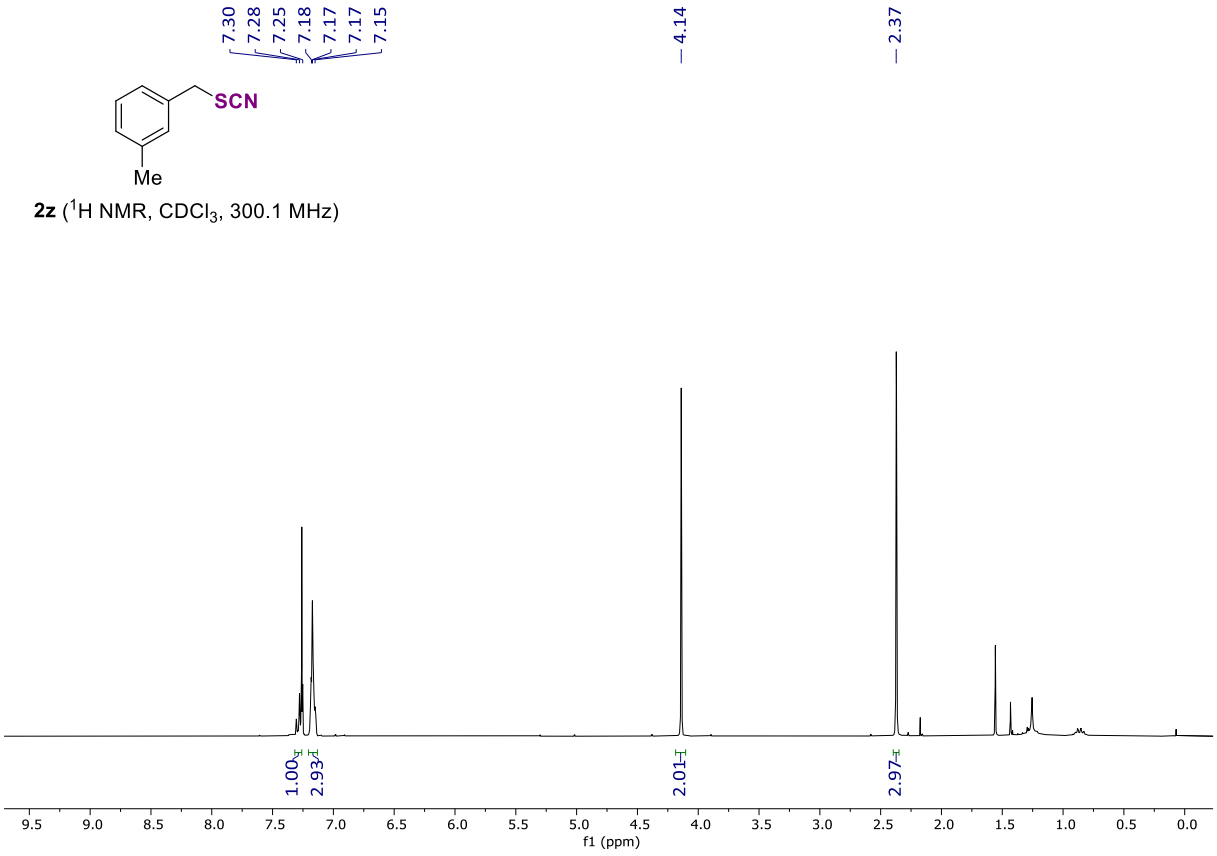




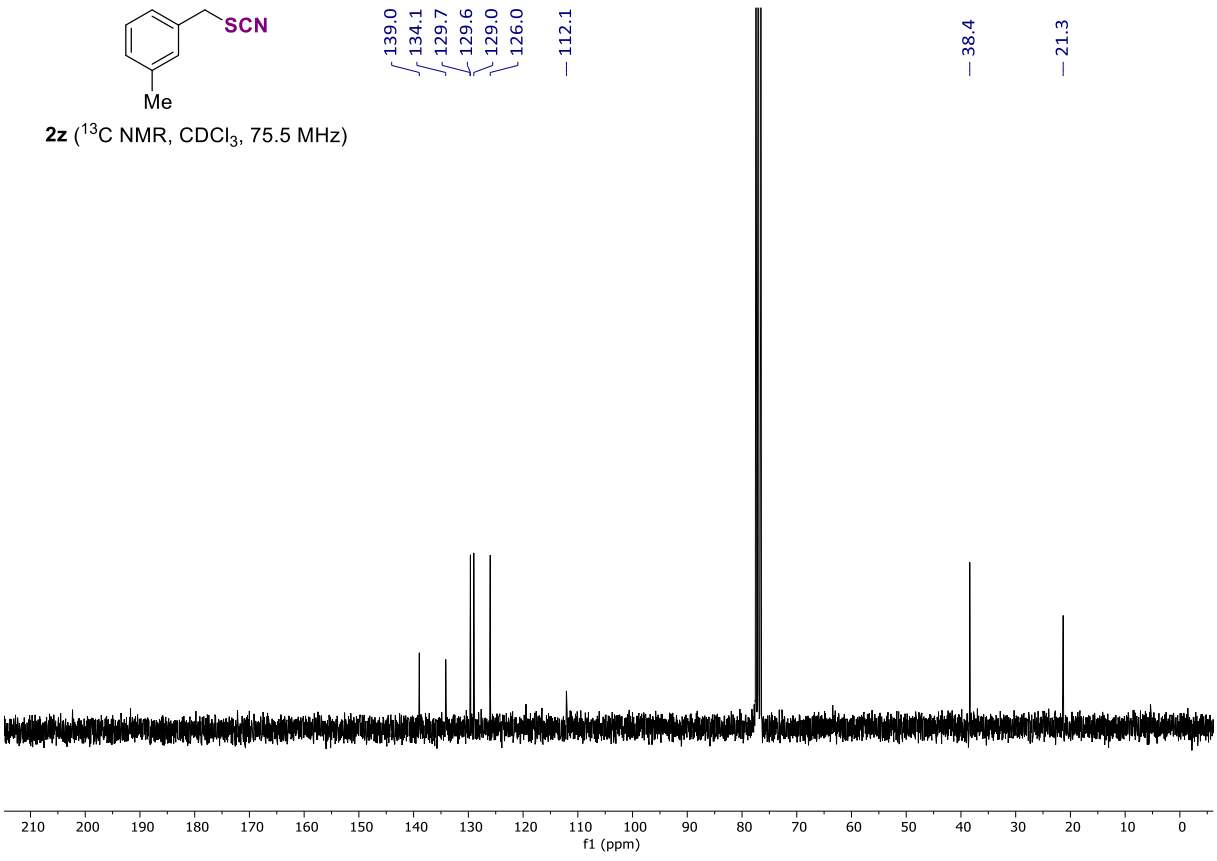
2y (^{1}H NMR, $CDCl_3$, 300.1 MHz)



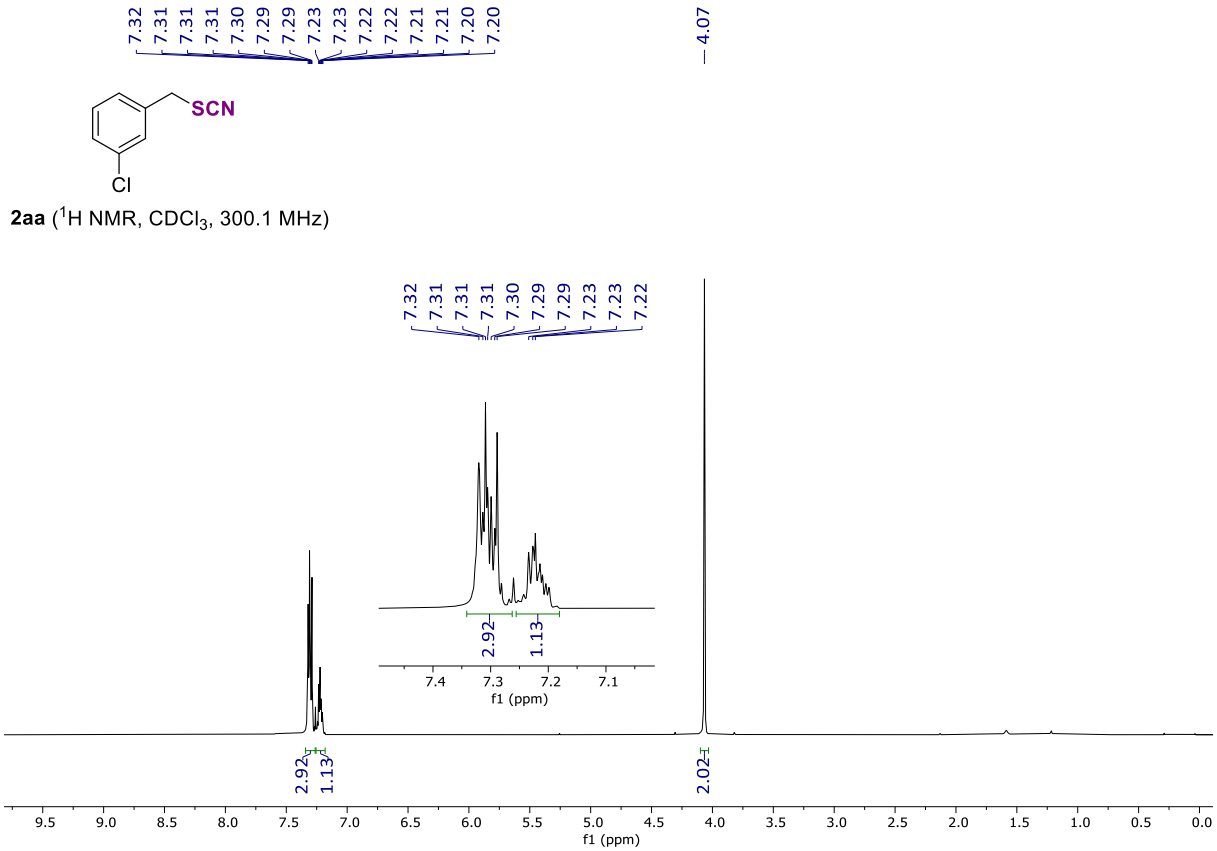
2y (^{13}C NMR, $CDCl_3$, 75.5 MHz)



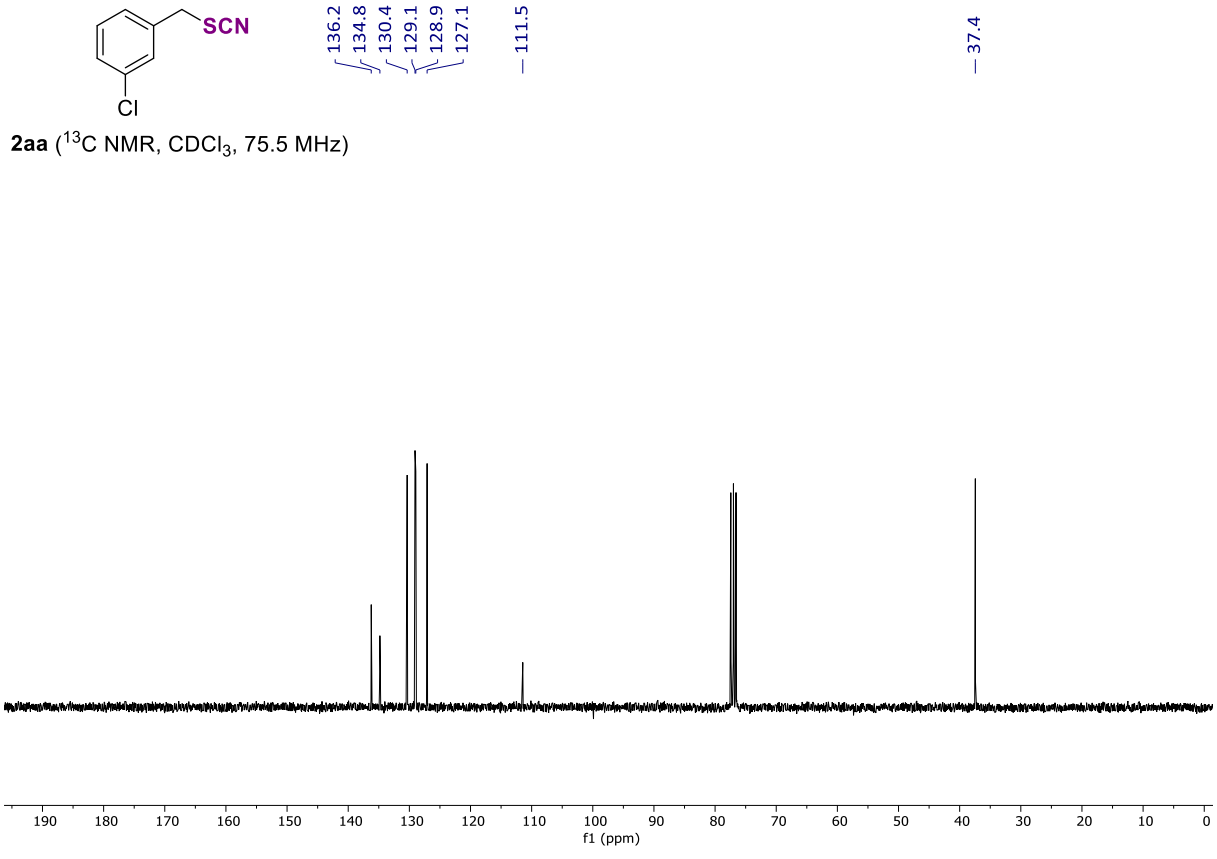
2z (^{1}H NMR, $CDCl_3$, 300.1 MHz)



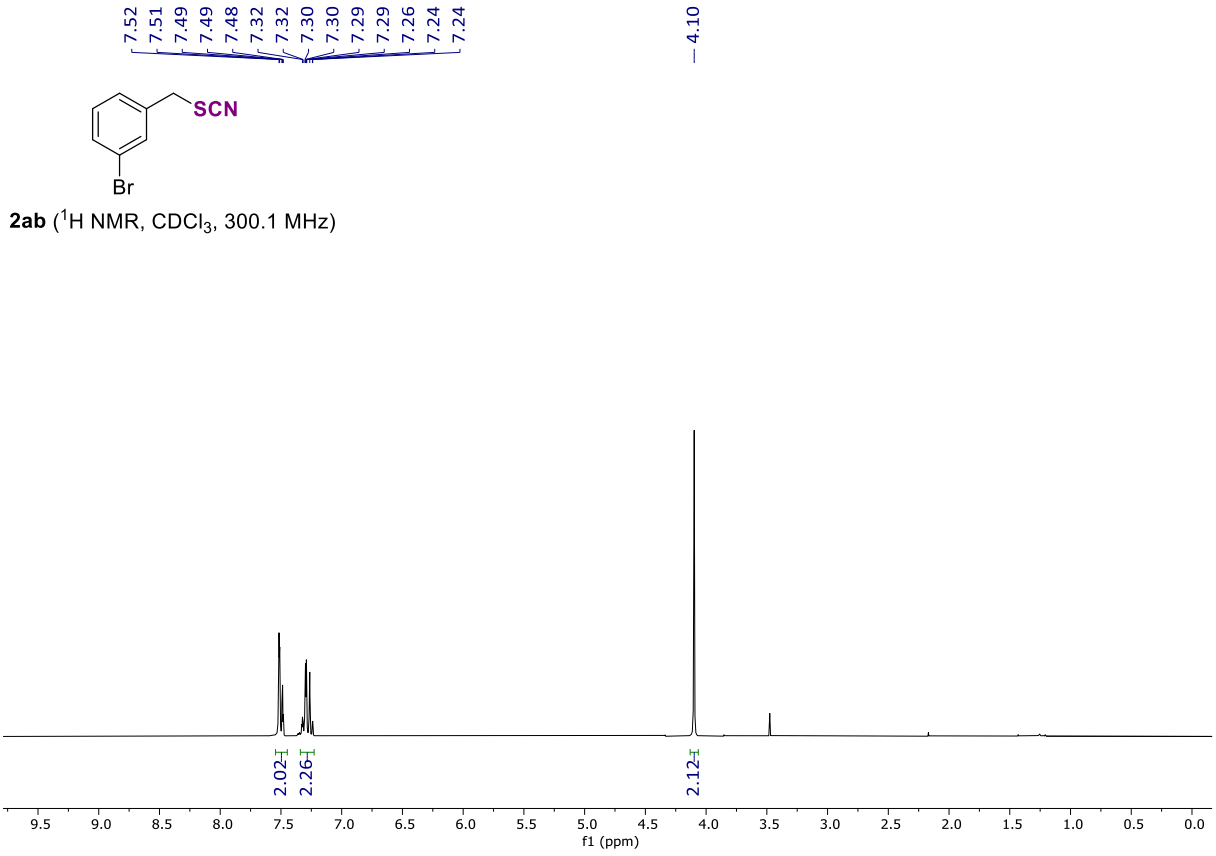
2z (^{13}C NMR, $CDCl_3$, 75.5 MHz)



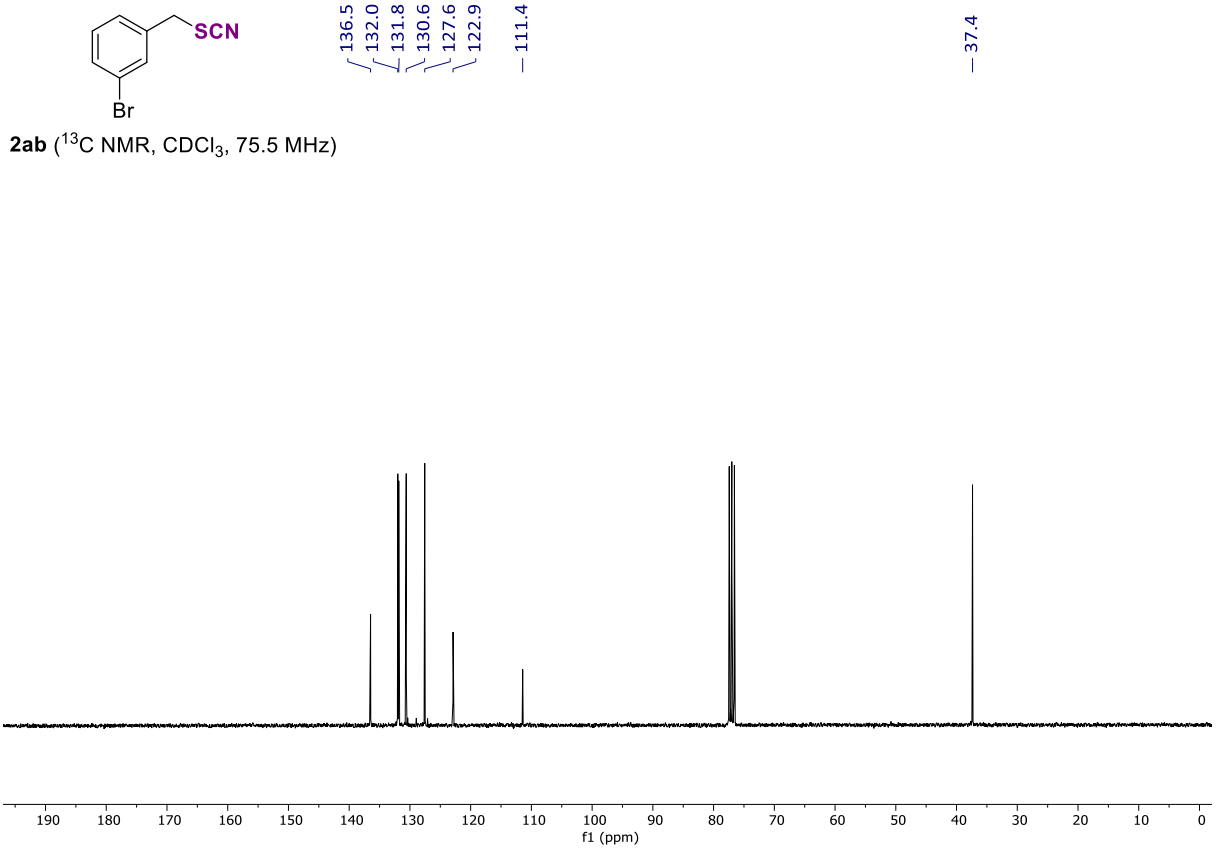
2aa (^{1}H NMR, $CDCl_3$, 300.1 MHz)



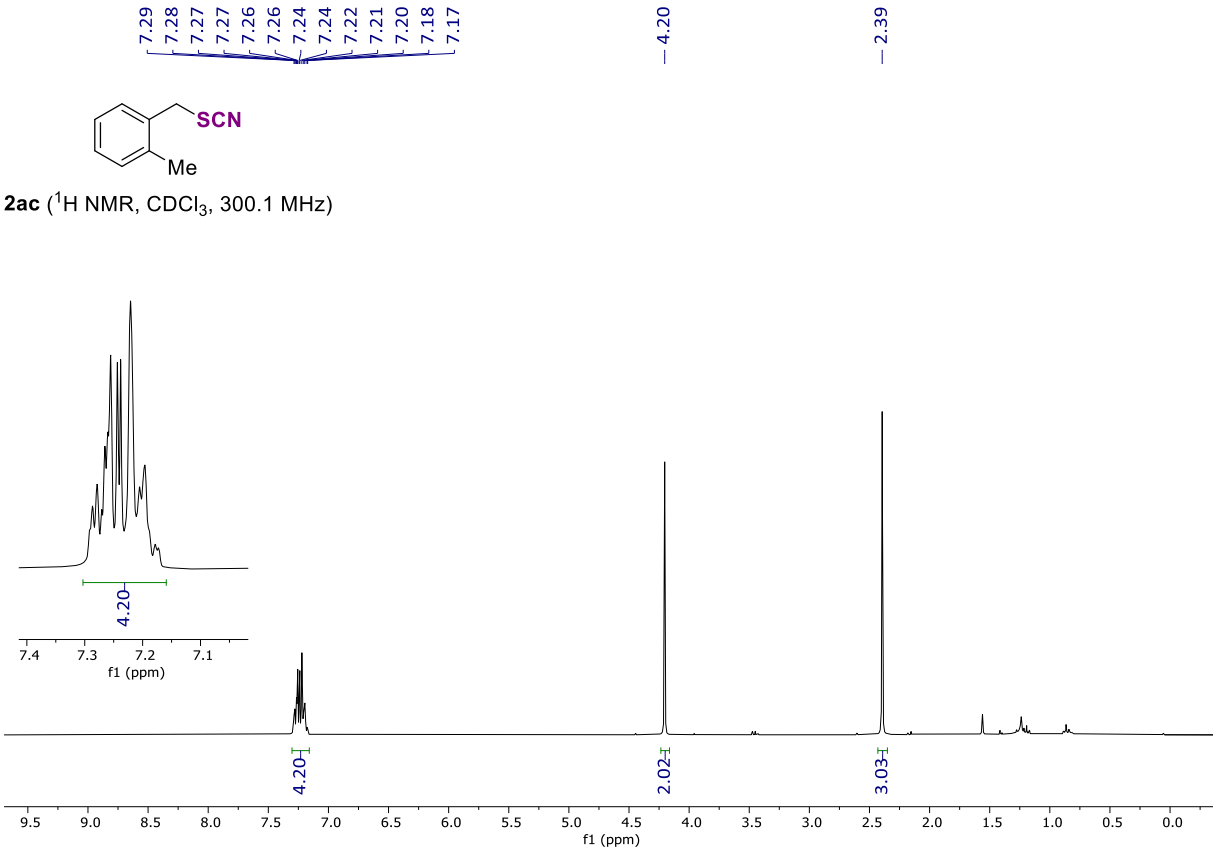
2aa (^{13}C NMR, $CDCl_3$, 75.5 MHz)



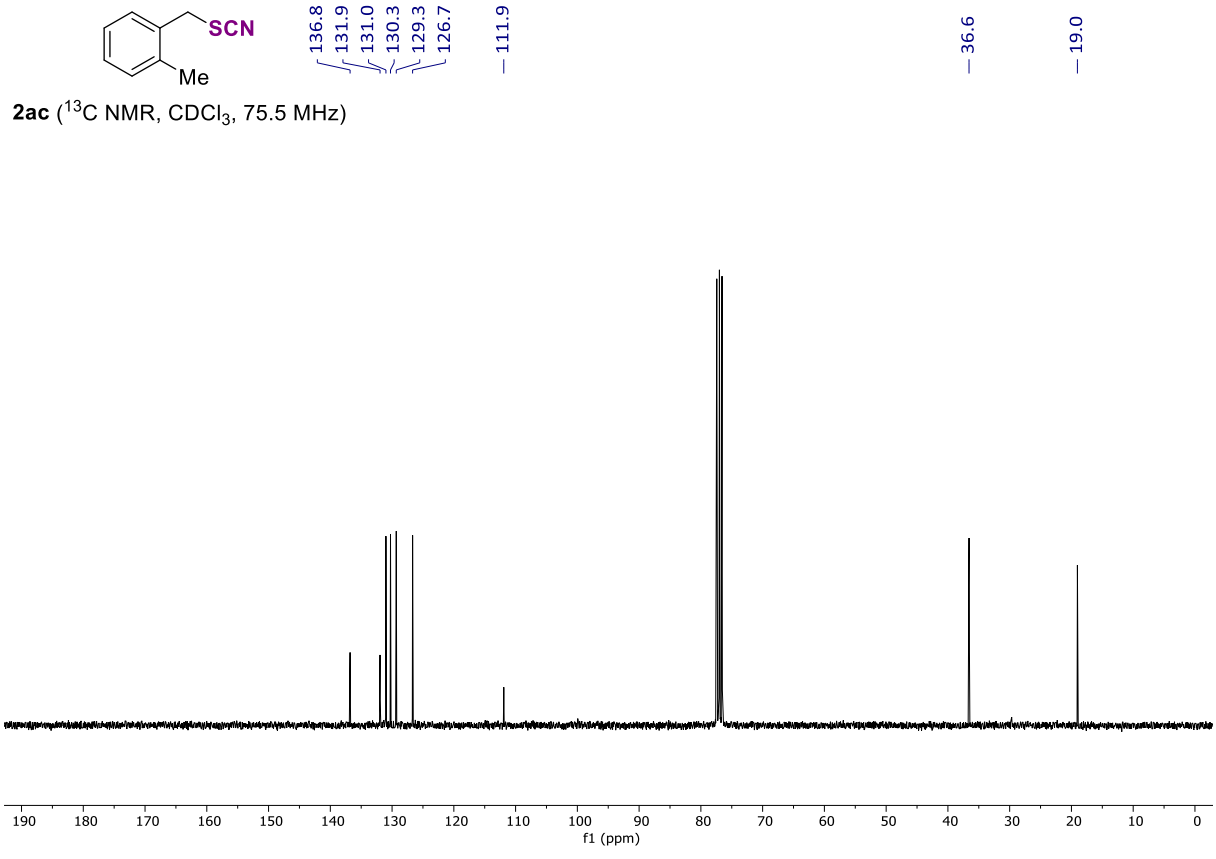
2ab (^{1}H NMR, $CDCl_3$, 300.1 MHz)



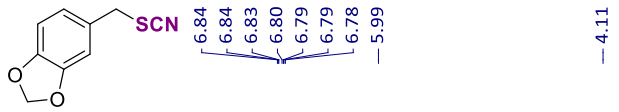
2ab (^{13}C NMR, $CDCl_3$, 75.5 MHz)



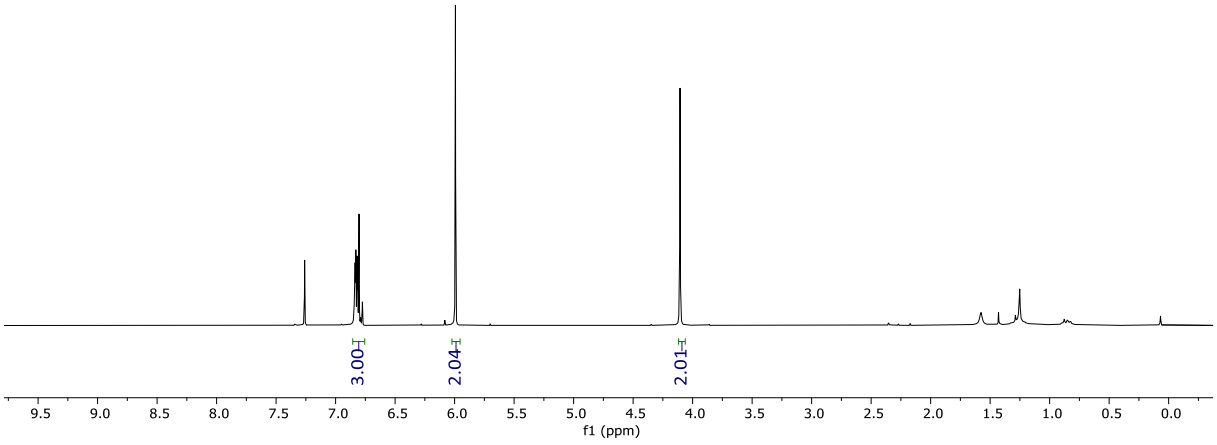
2ac (^{1}H NMR, $CDCl_3$, 300.1 MHz)



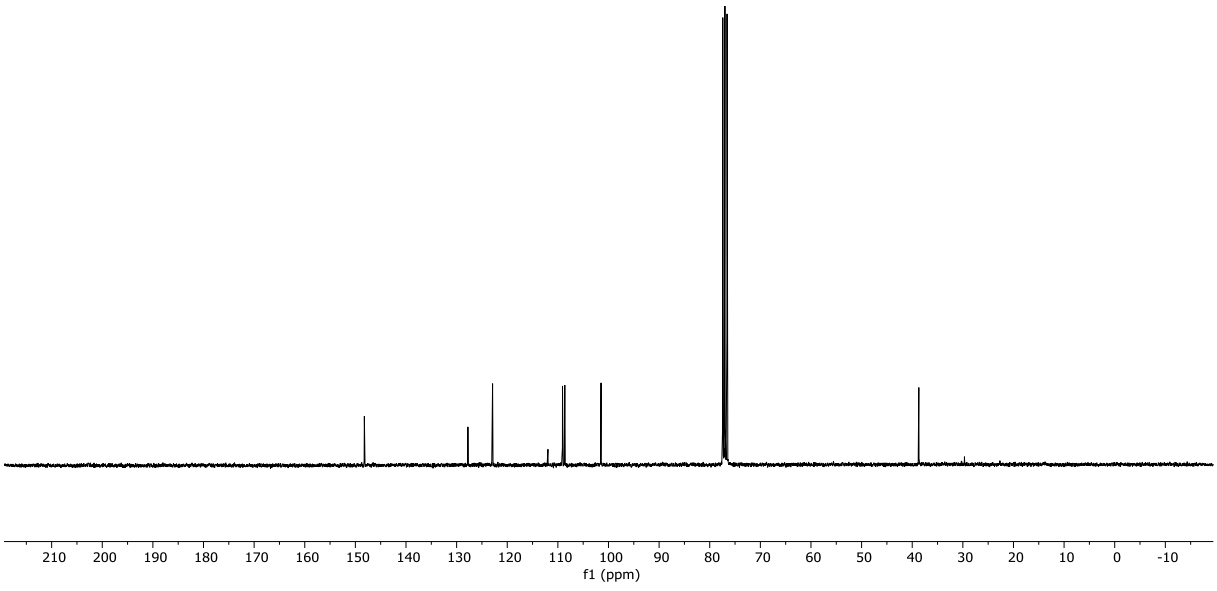
2ac (^{13}C NMR, $CDCl_3$, 75.5 MHz)

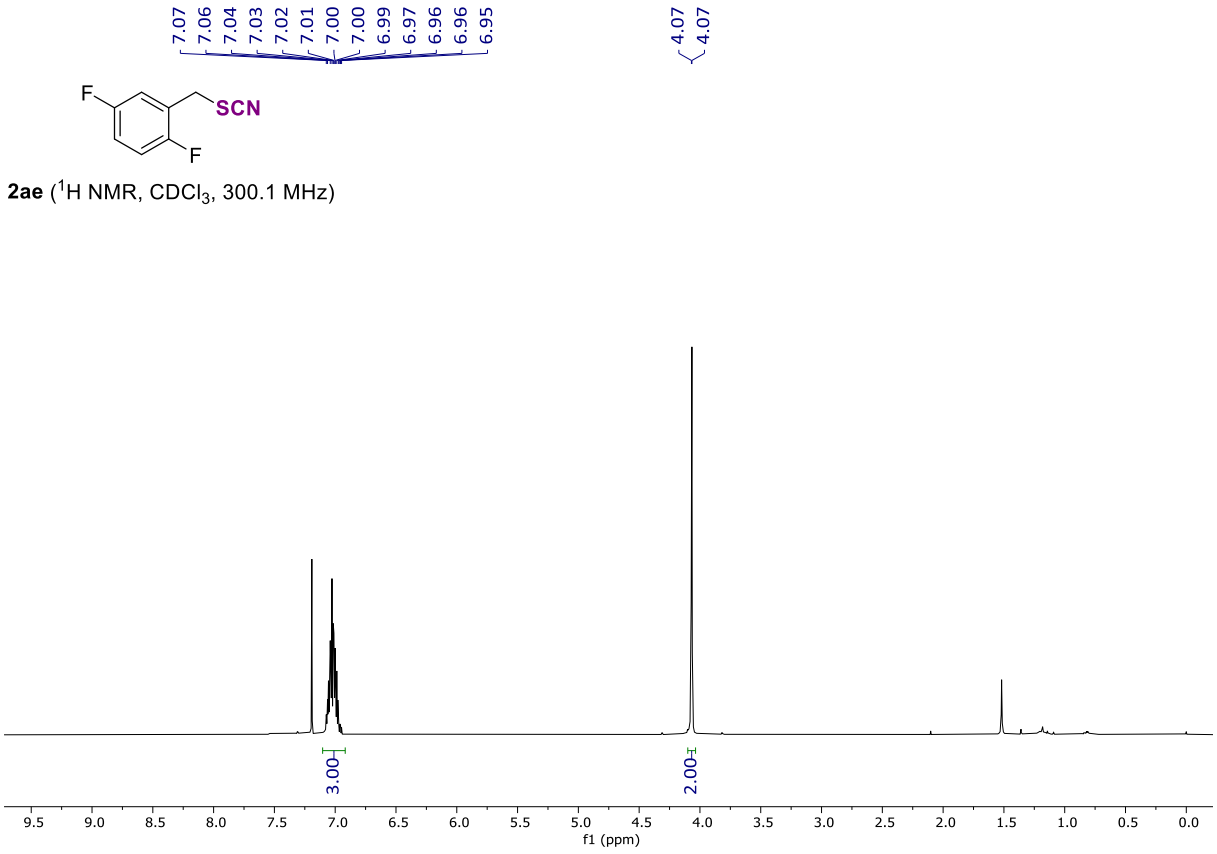


2ad (^{1}H NMR, $CDCl_3$, 300.1 MHz)

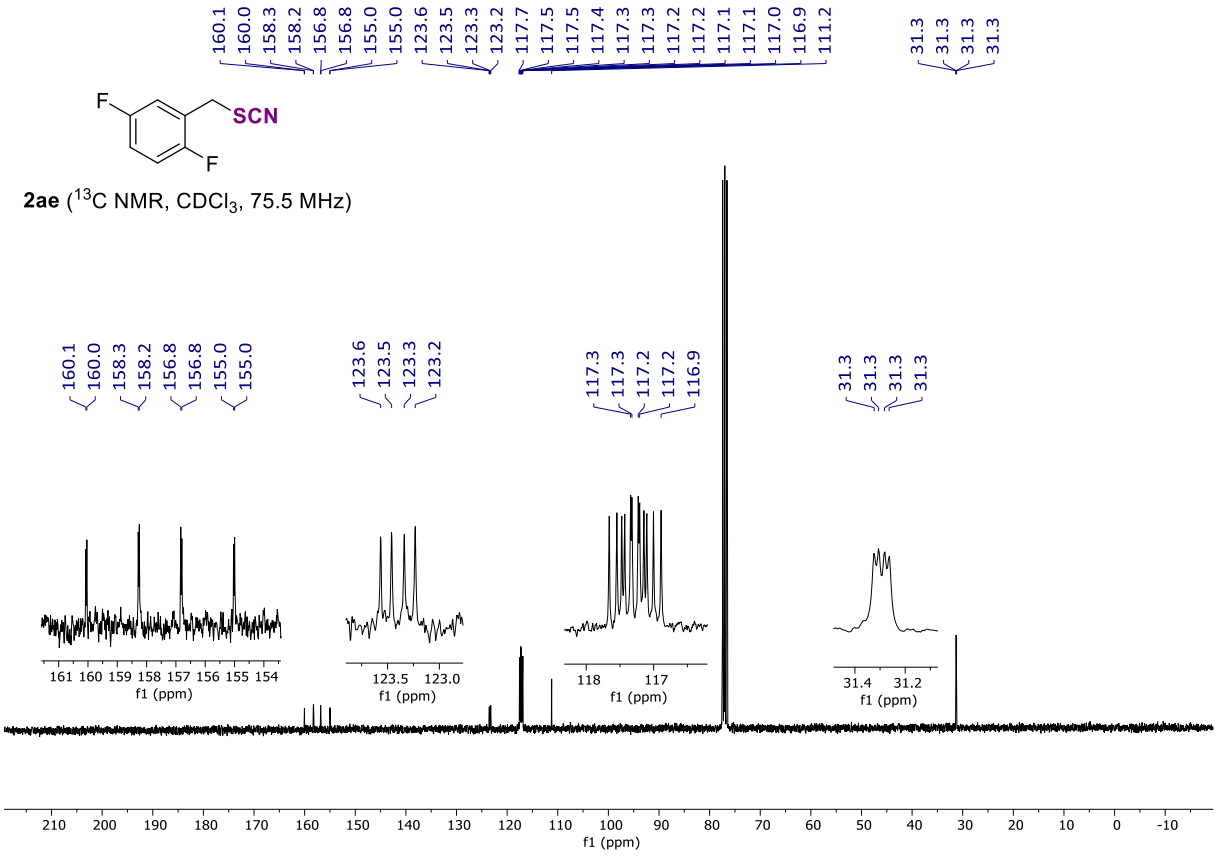


2ad (^{13}C NMR, $CDCl_3$, 75.5 MHz)

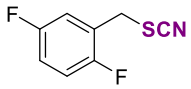


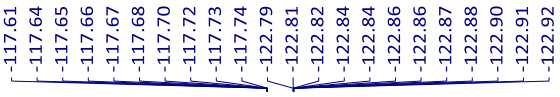


2ae (^{1}H NMR, $CDCl_3$, 300.1 MHz)

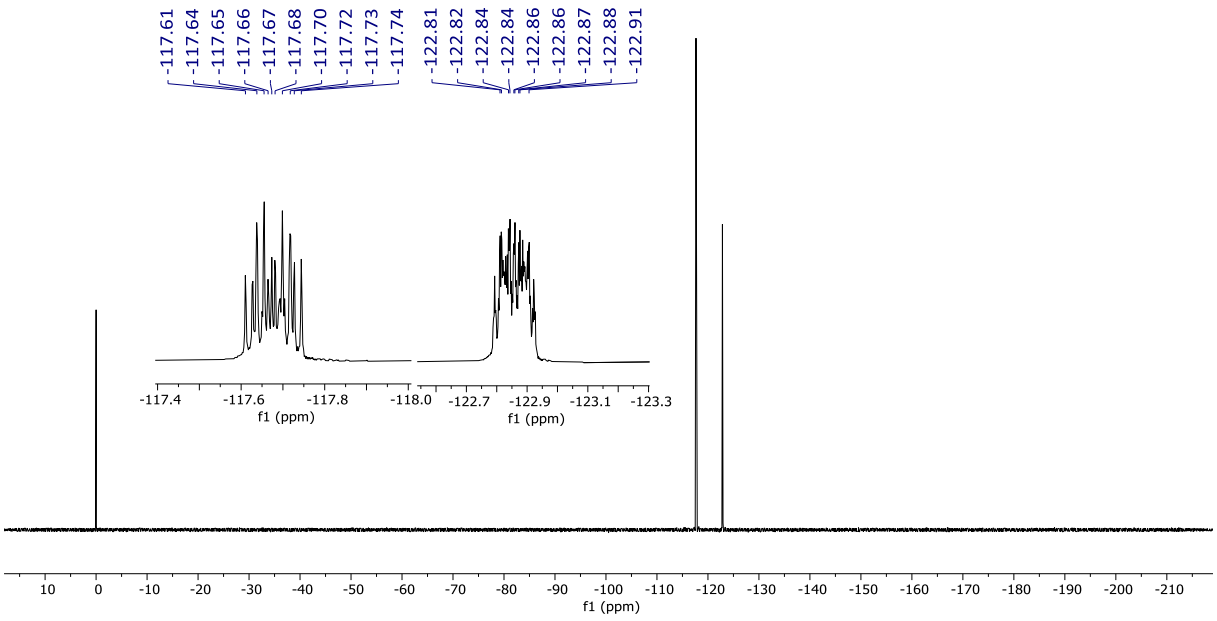


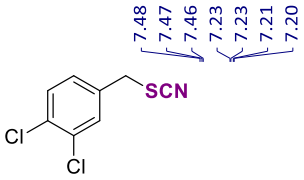
2ae (^{13}C NMR, $CDCl_3$, 75.5 MHz)



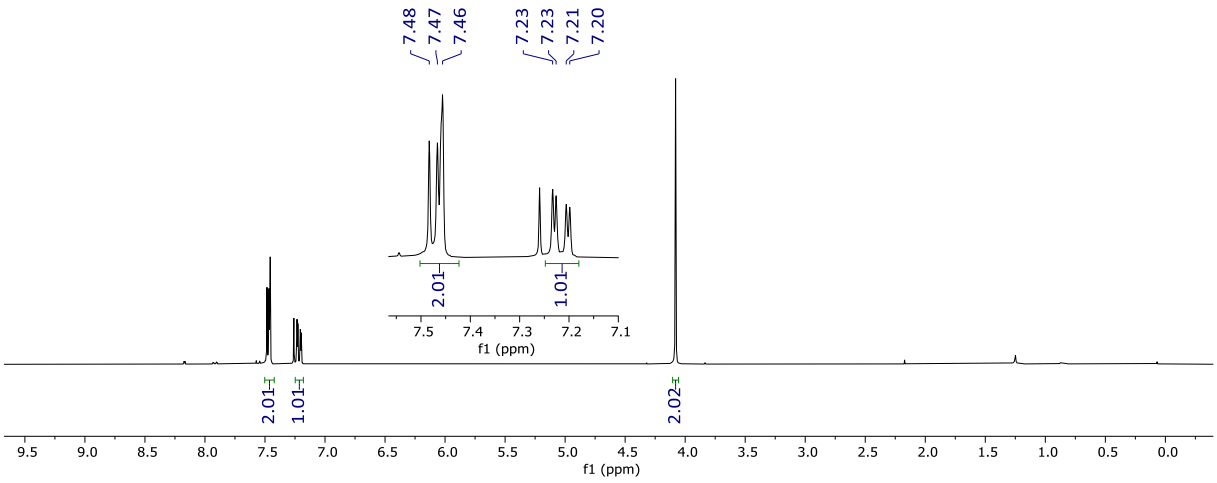


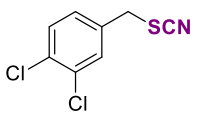
2ae (^{19}F NMR, $CDCl_3$, 282.4 MHz)



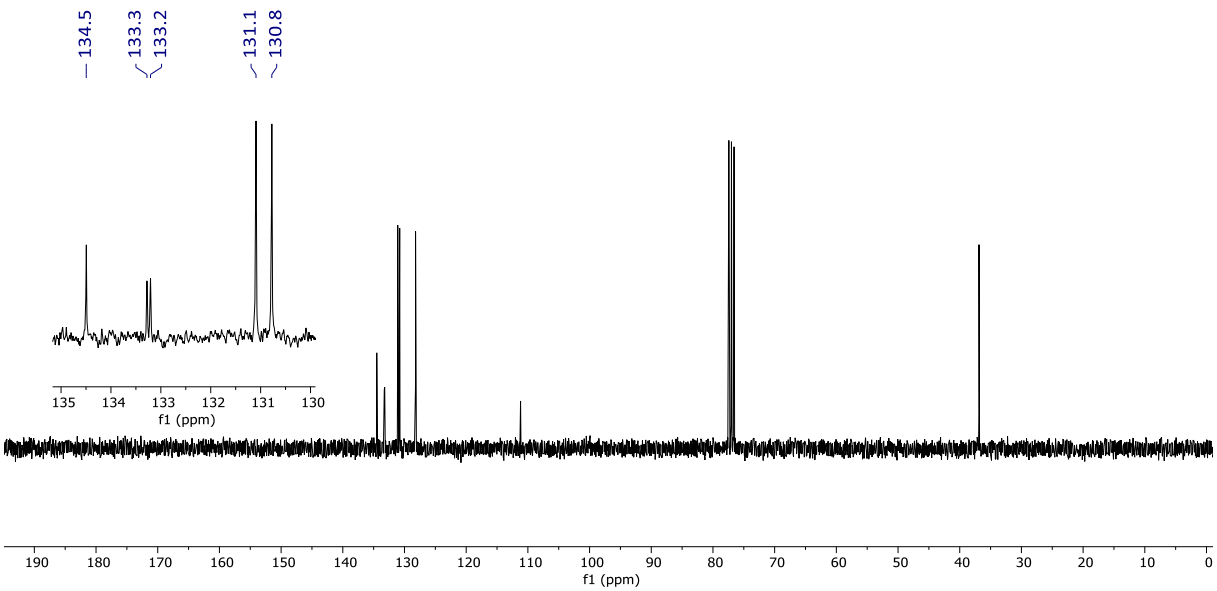


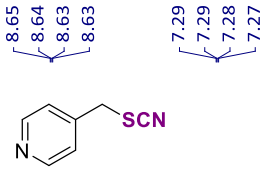
2af (^{1}H NMR, $CDCl_3$, 300.1 MHz)



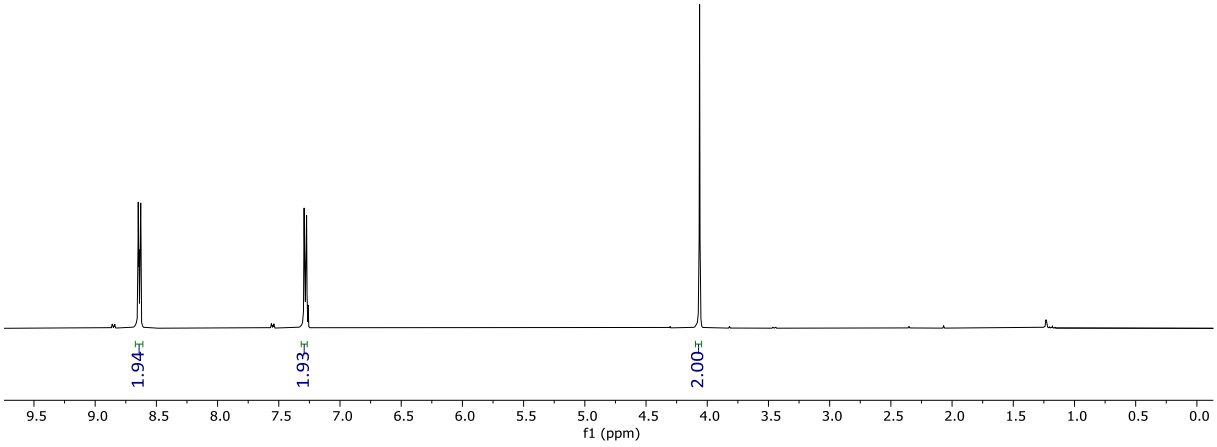


2af (^{13}C NMR, $CDCl_3$, 75.5 MHz)

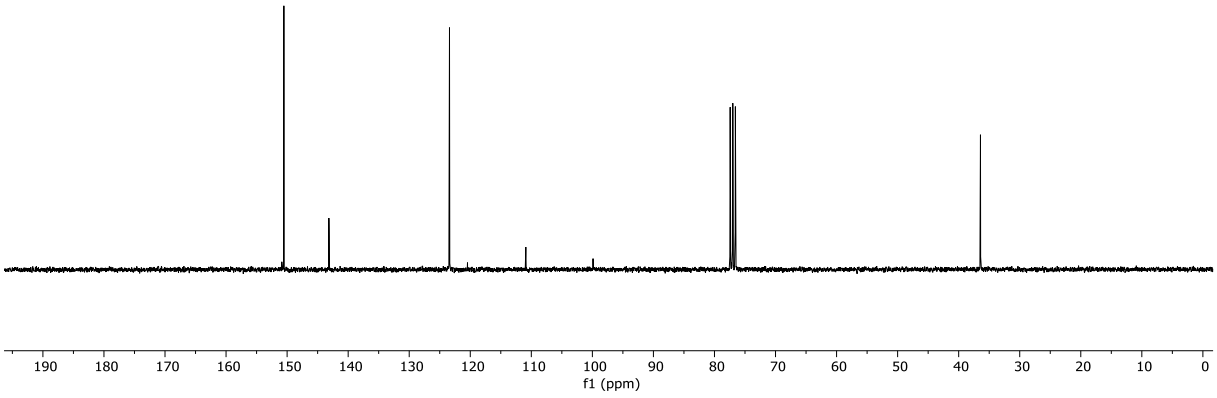


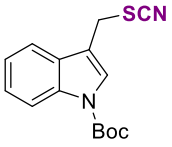


2ag (^{1}H NMR, $CDCl_3$, 300.1 MHz)

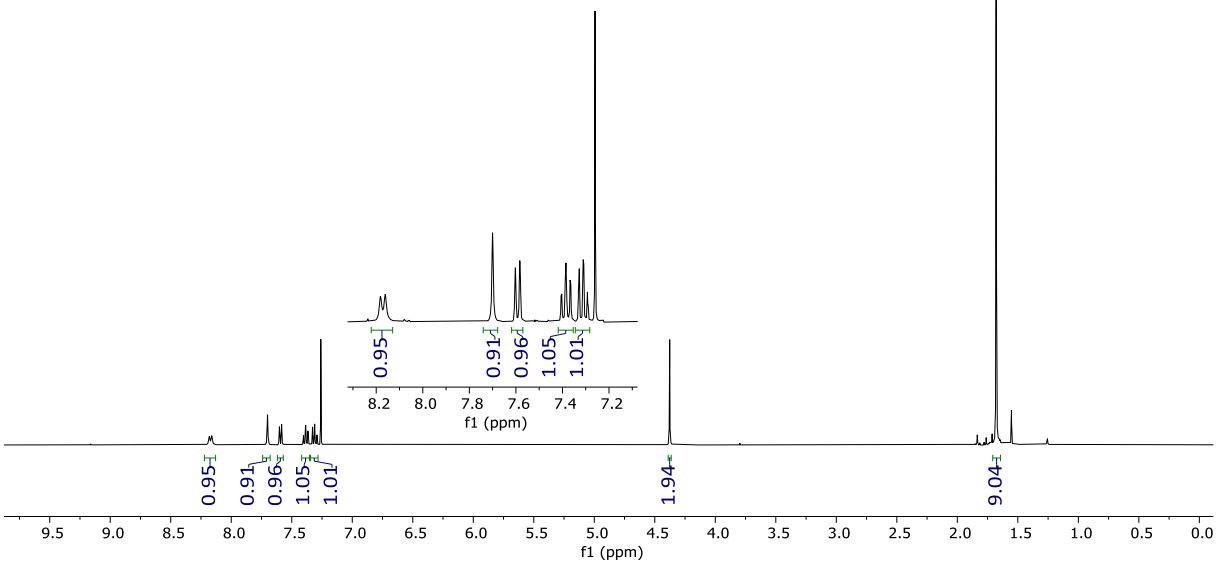


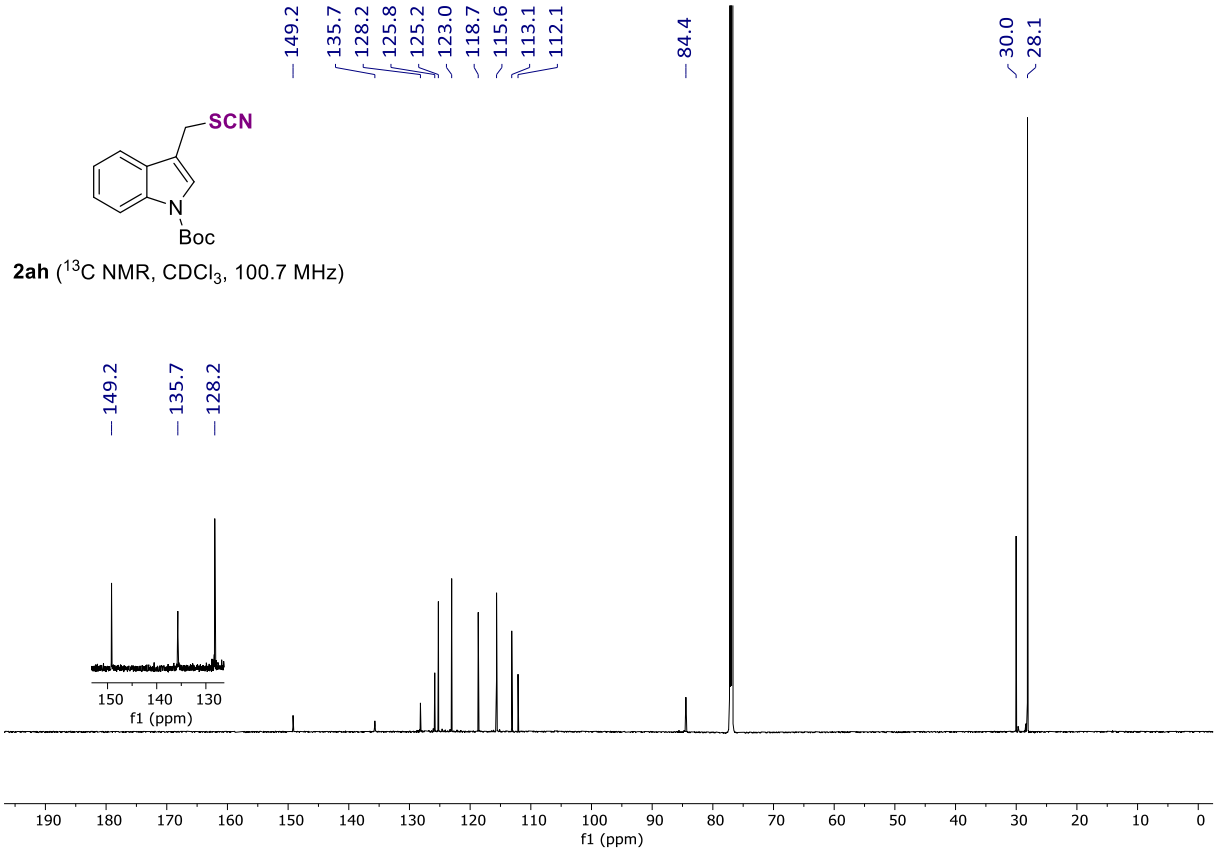
2ag (^{13}C NMR, $CDCl_3$, 75.5 MHz)



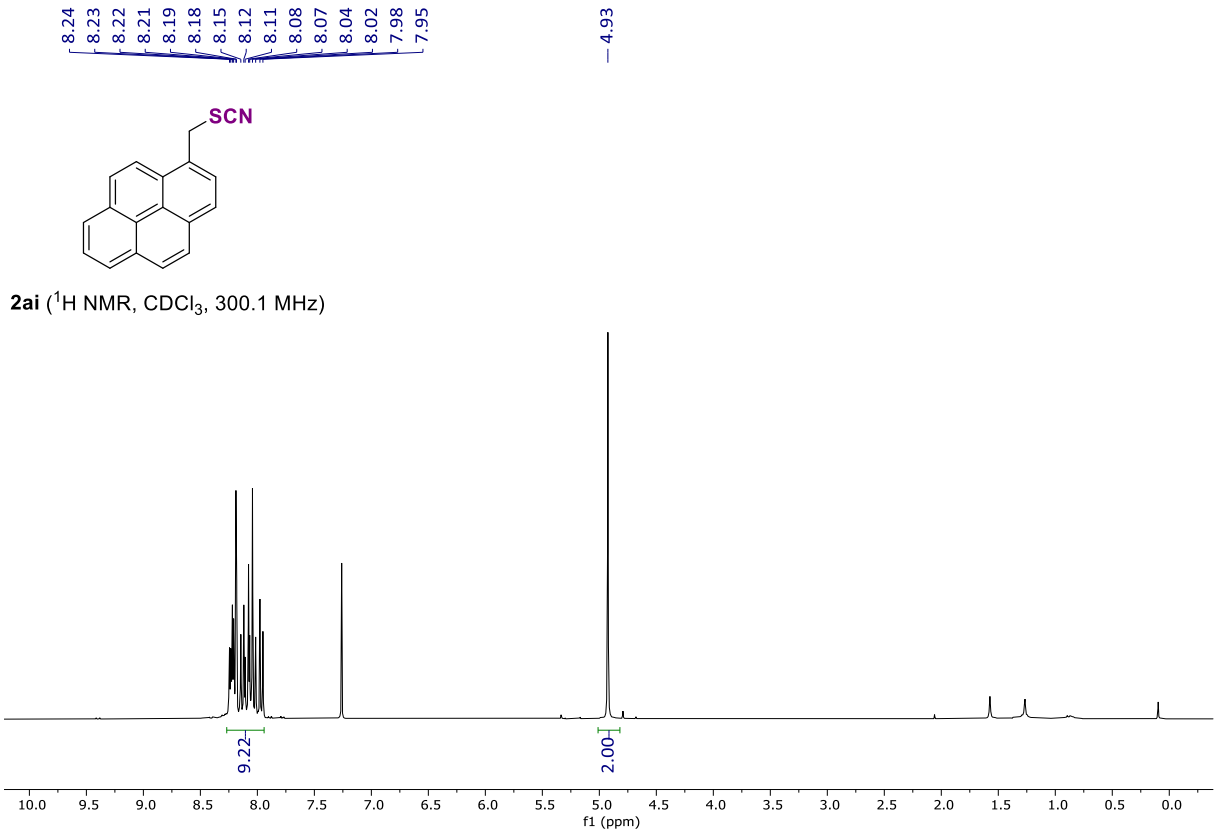


2ah (^{1}H NMR, $CDCl_3$, 400.2 MHz)

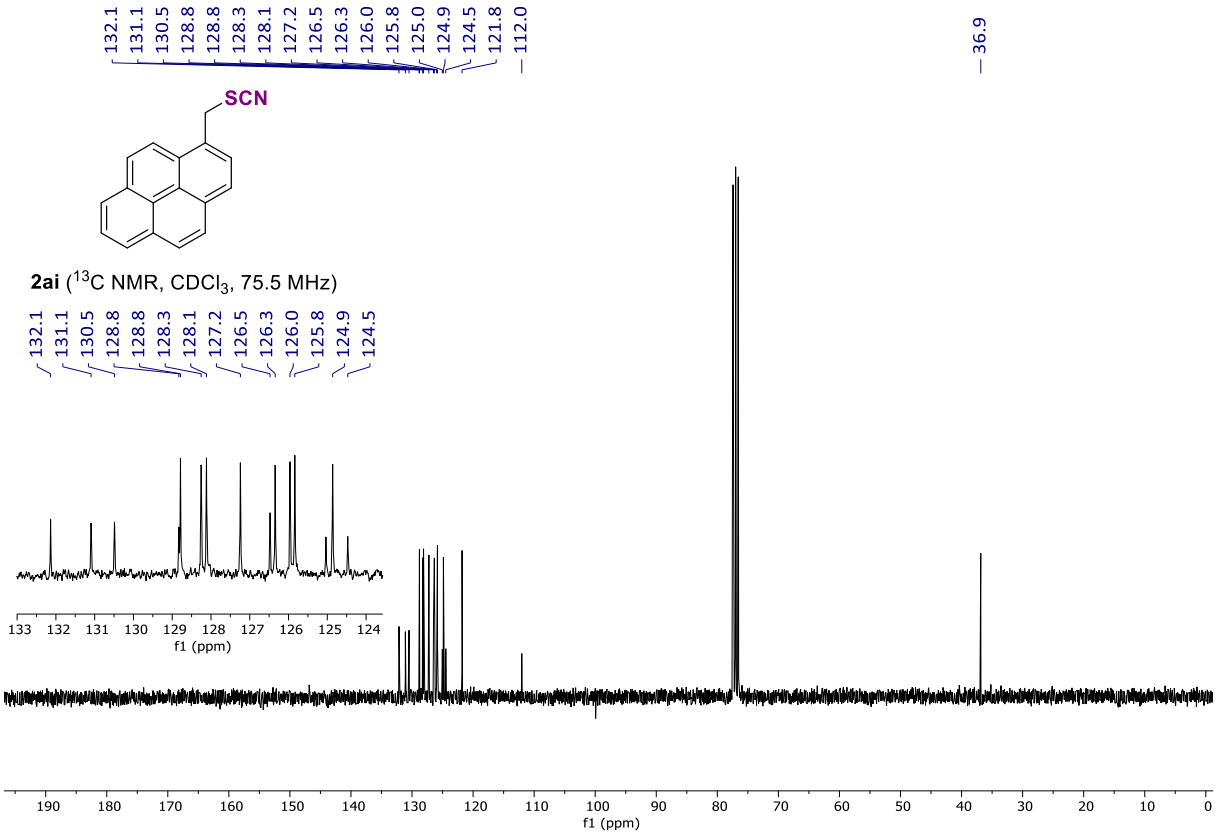




2ah (^{13}C NMR, $CDCl_3$, 100.7 MHz)



2ai (^{1}H NMR, $CDCl_3$, 300.1 MHz)

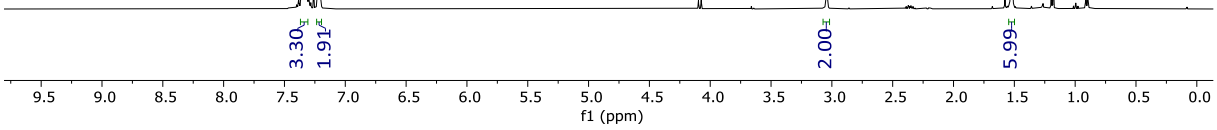


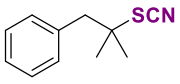
2ai (^{13}C NMR, $CDCl_3$, 75.5 MHz)

2aj (^{1}H NMR, $CDCl_3$, 300.1 MHz)

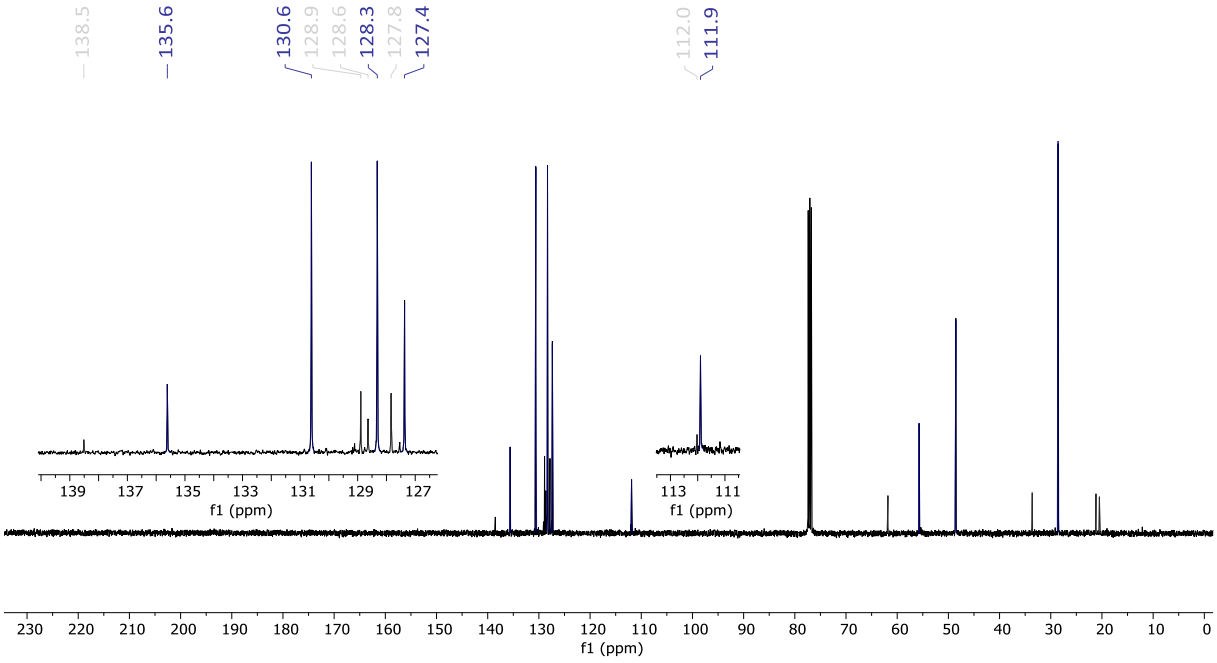
2aj (^{13}C NMR, $CDCl_3$, 75.5 MHz)

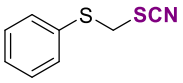
2ak (^{1}H NMR, $CDCl_3$, 400.2 MHz)



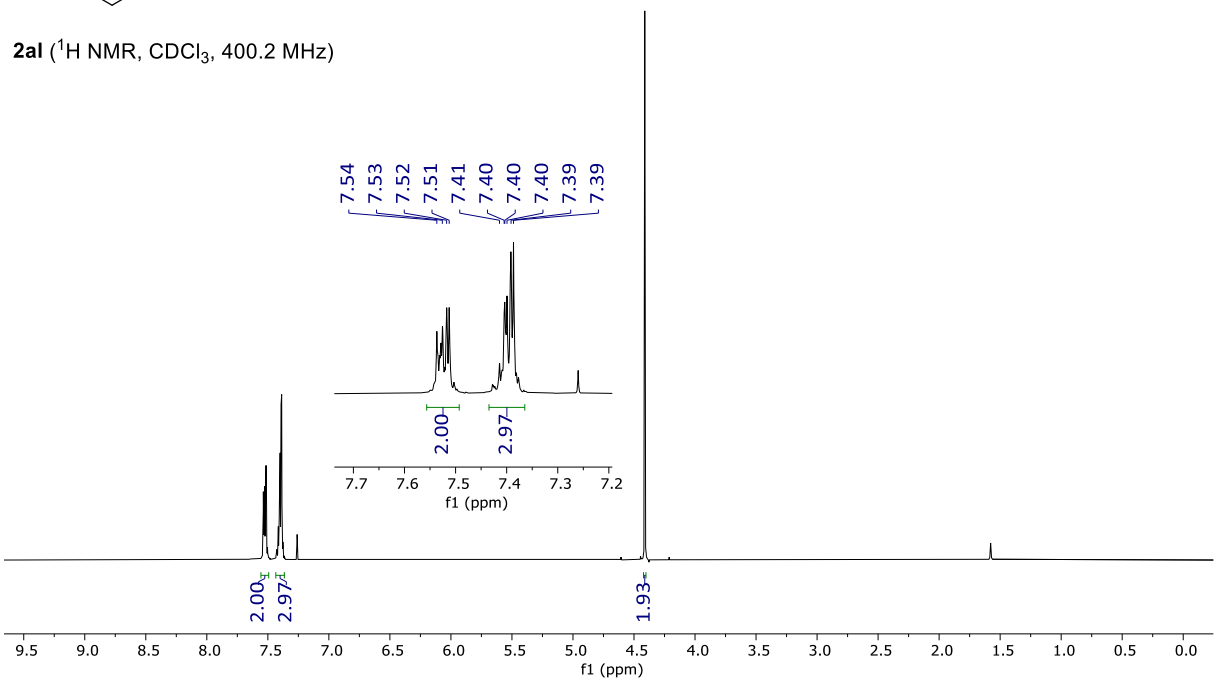


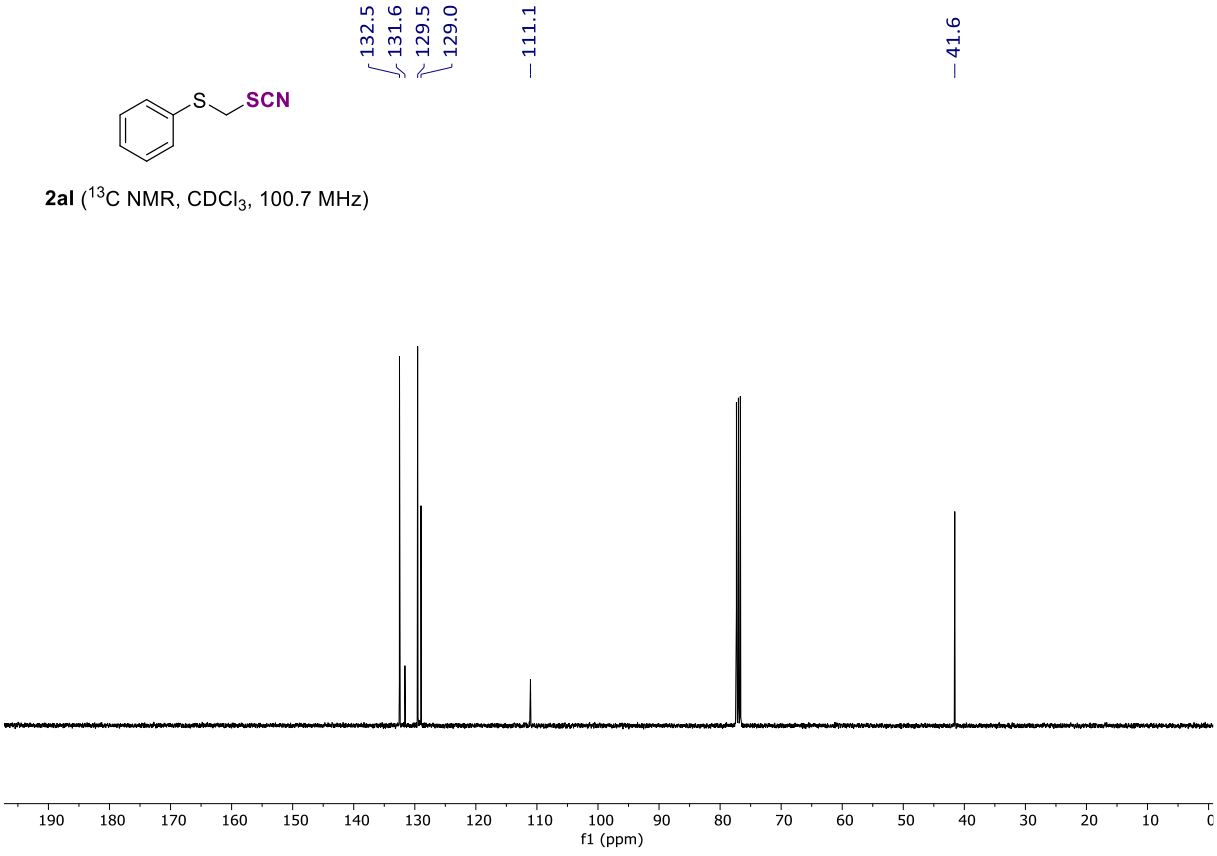
2ak (^{13}C NMR, $CDCl_3$, 100.7 MHz)



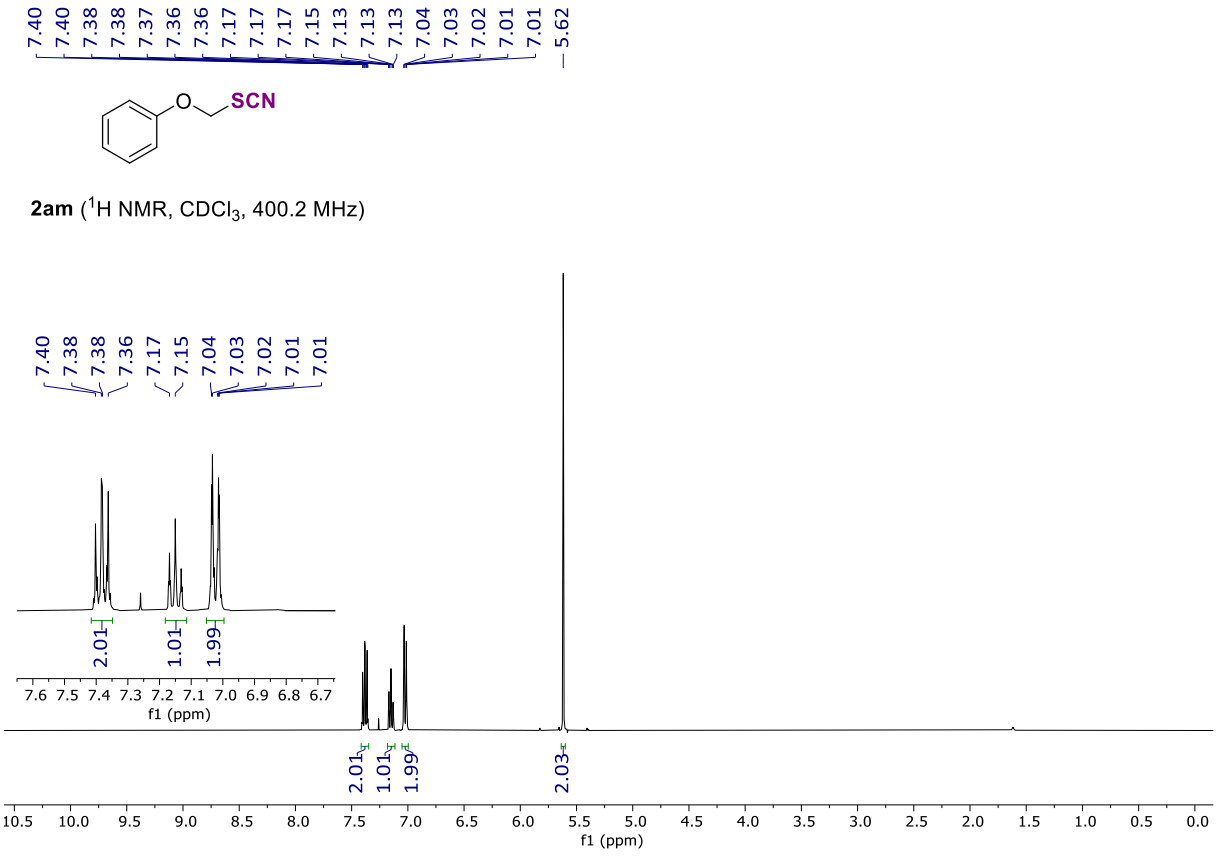


2al (^{1}H NMR, $CDCl_3$, 400.2 MHz)

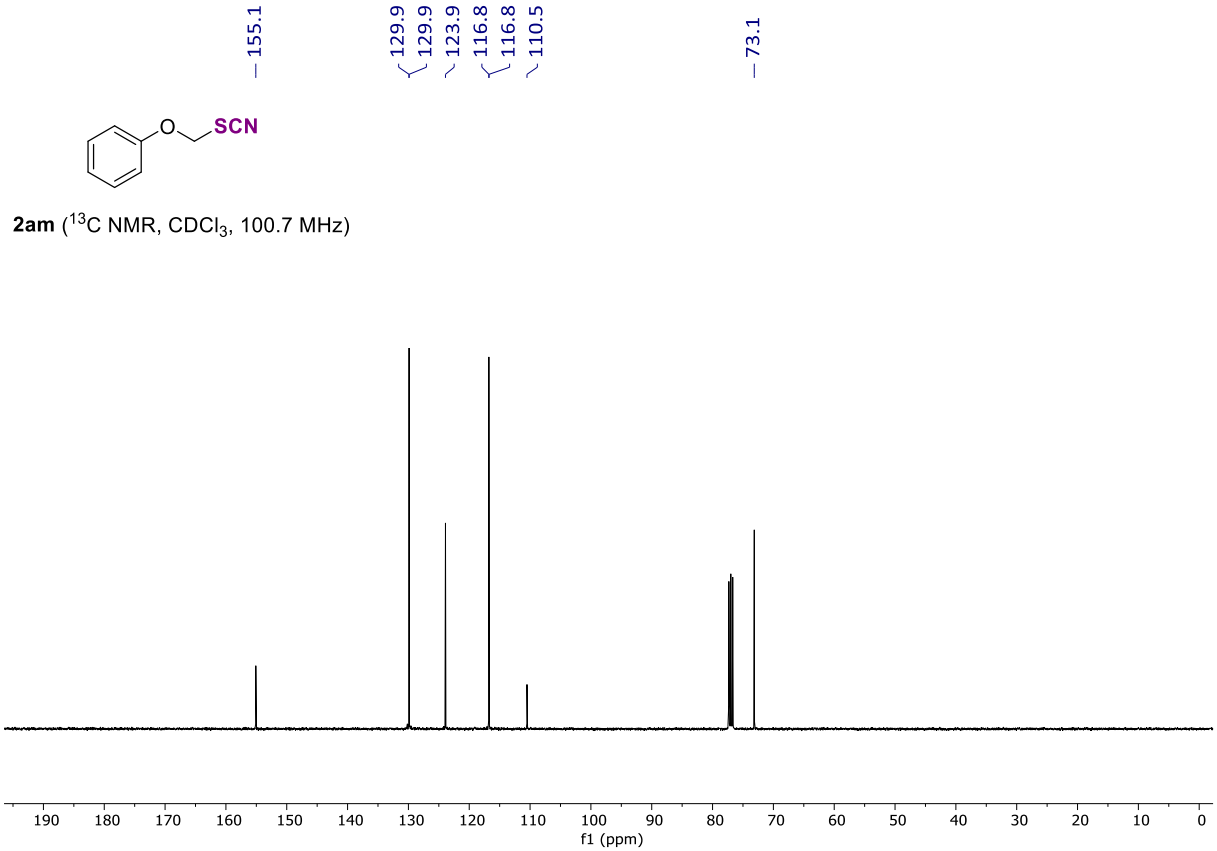




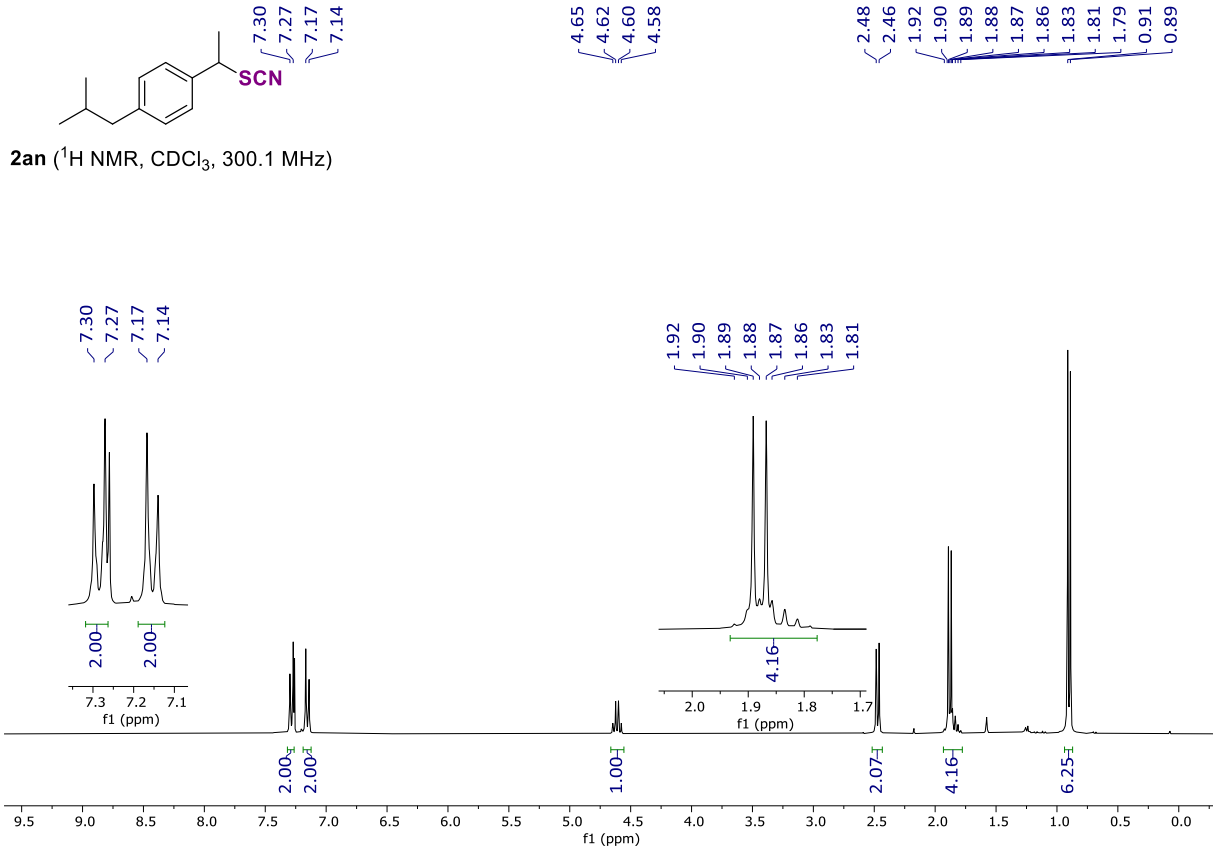
2al (^{13}C NMR, $CDCl_3$, 100.7 MHz)



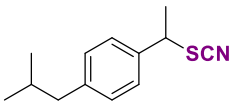
2am (^{1}H NMR, $CDCl_3$, 400.2 MHz)



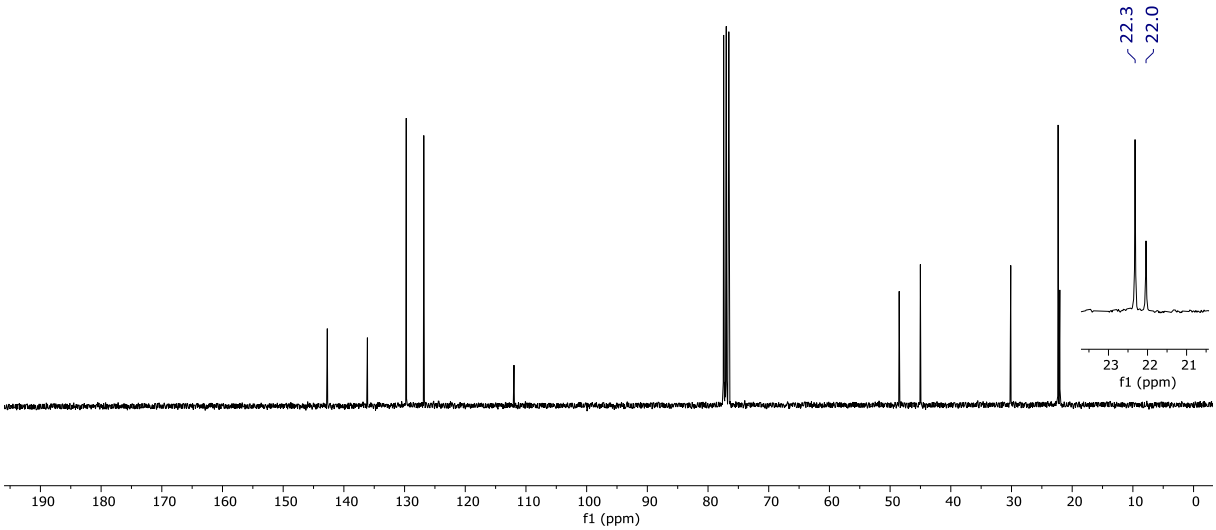
2am (^{13}C NMR, $CDCl_3$, 100.7 MHz)

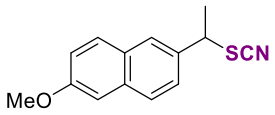


2an (^{1}H NMR, $CDCl_3$, 300.1 MHz)

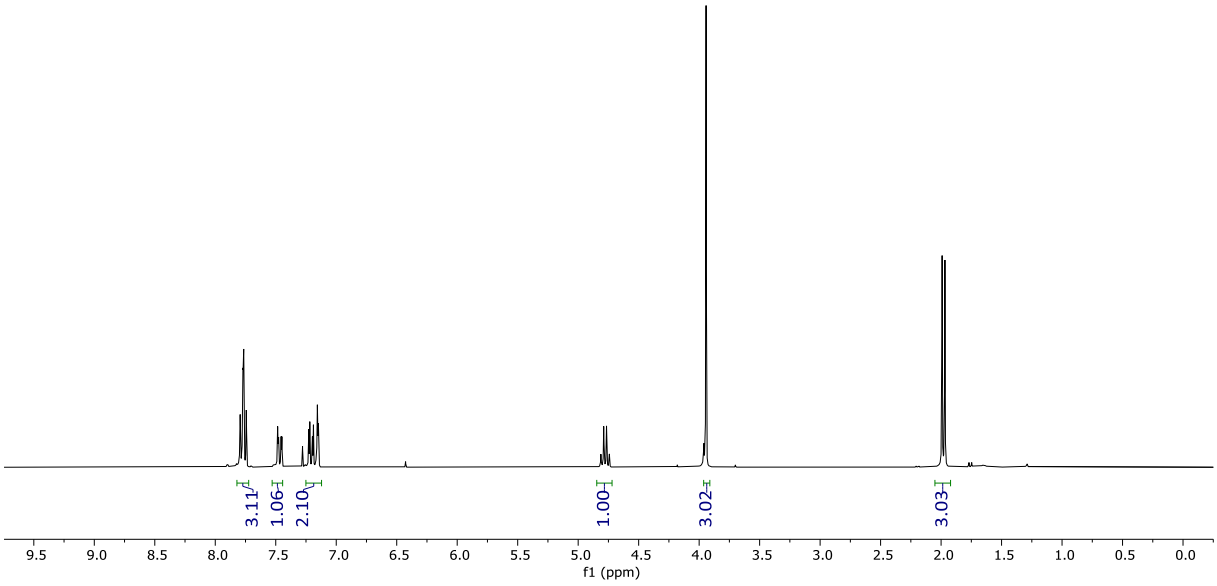


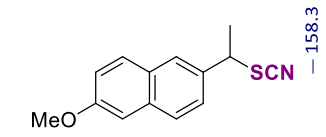
2an (^{13}C NMR, $CDCl_3$, 75.5 MHz)



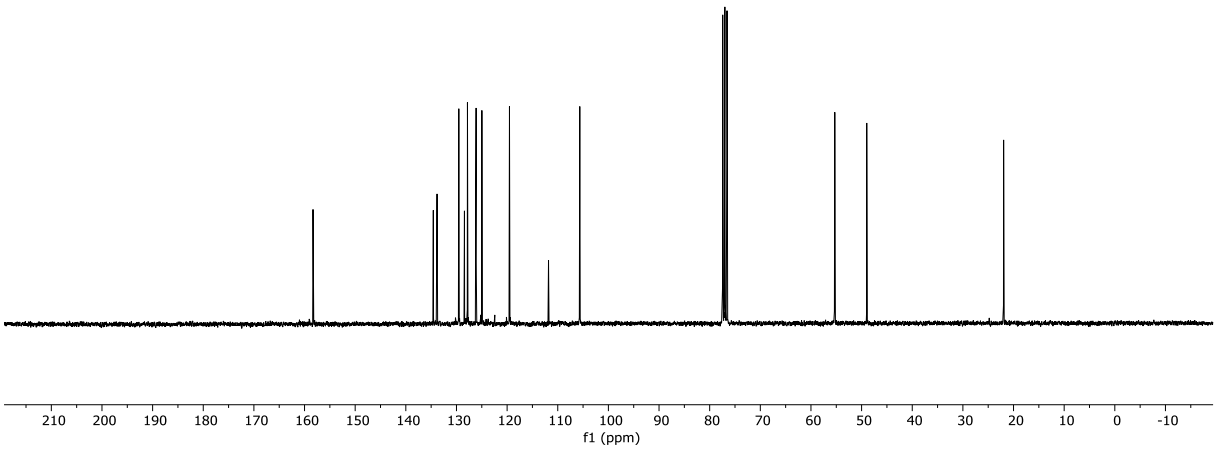


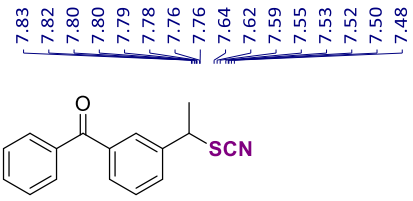
2ao (^{1}H NMR, $CDCl_3$, 300.1 MHz)



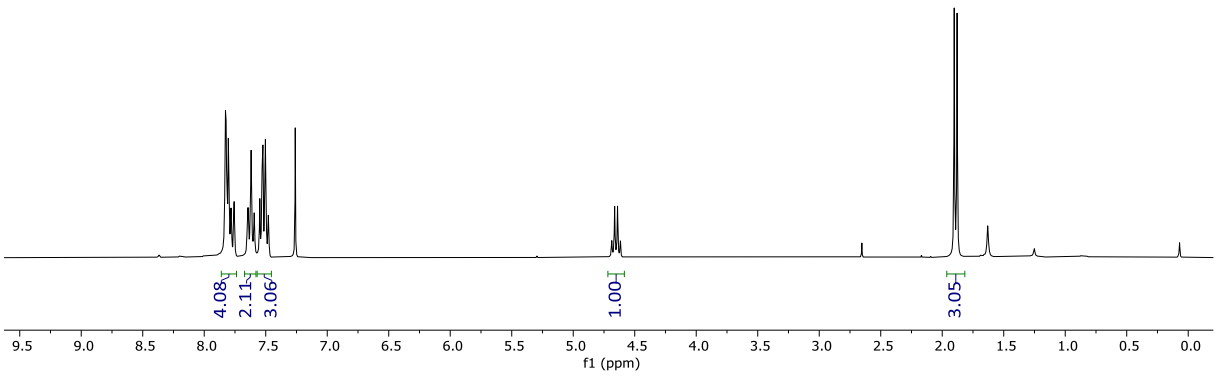


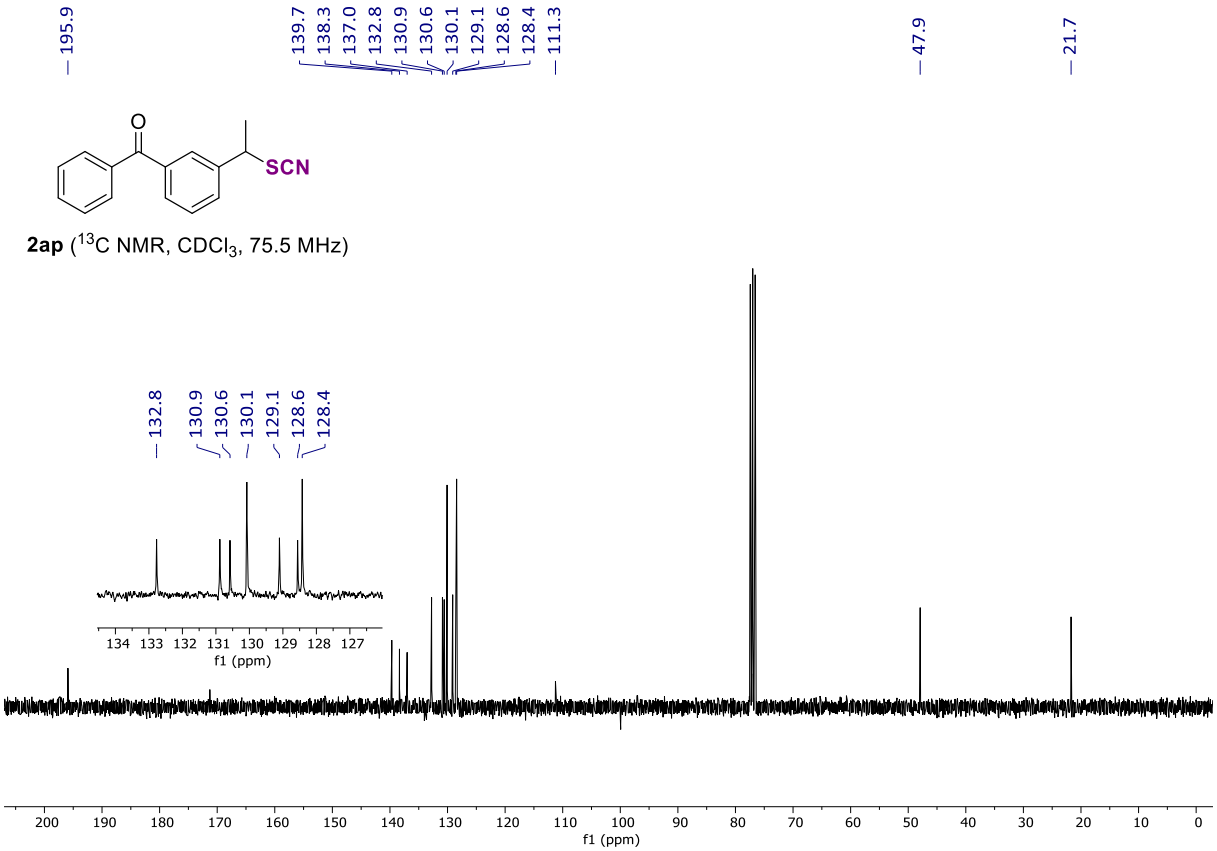
2ao (^{13}C NMR, $CDCl_3$, 75.5 MHz)



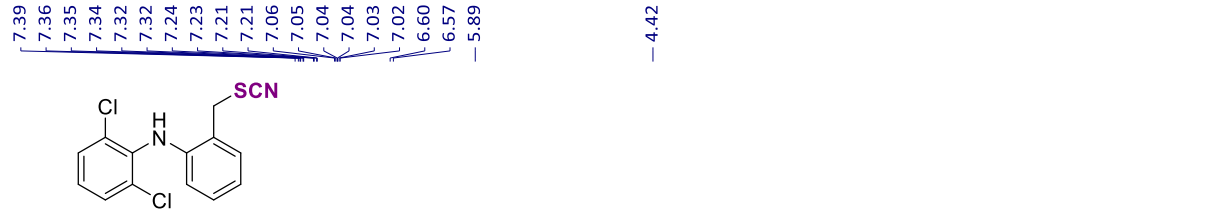


2ap (^{1}H NMR, $CDCl_3$, 300.1 MHz)

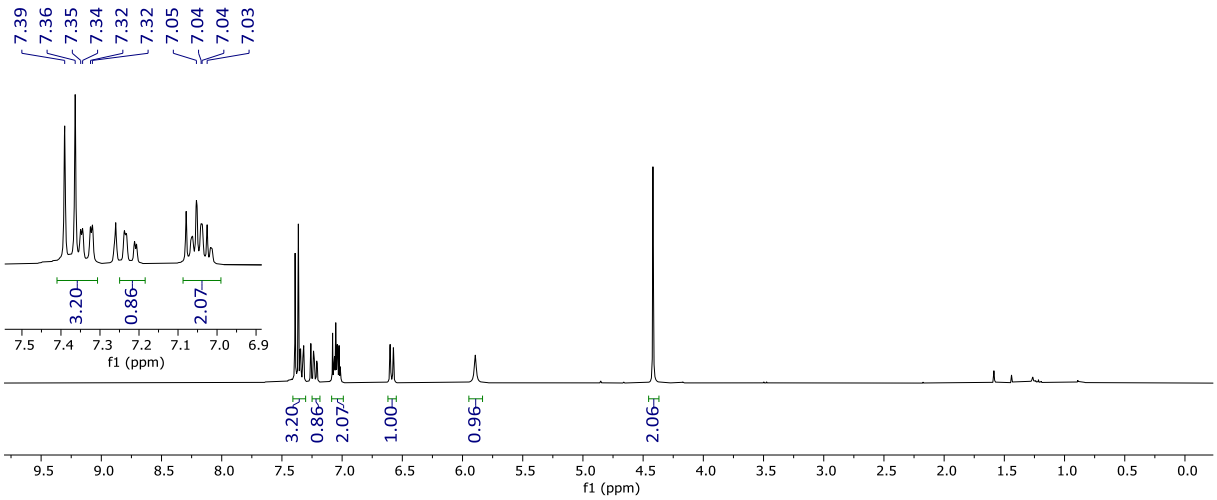


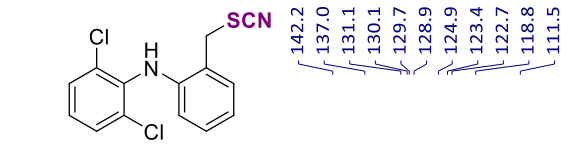


2ap (^{13}C NMR, $CDCl_3$, 75.5 MHz)

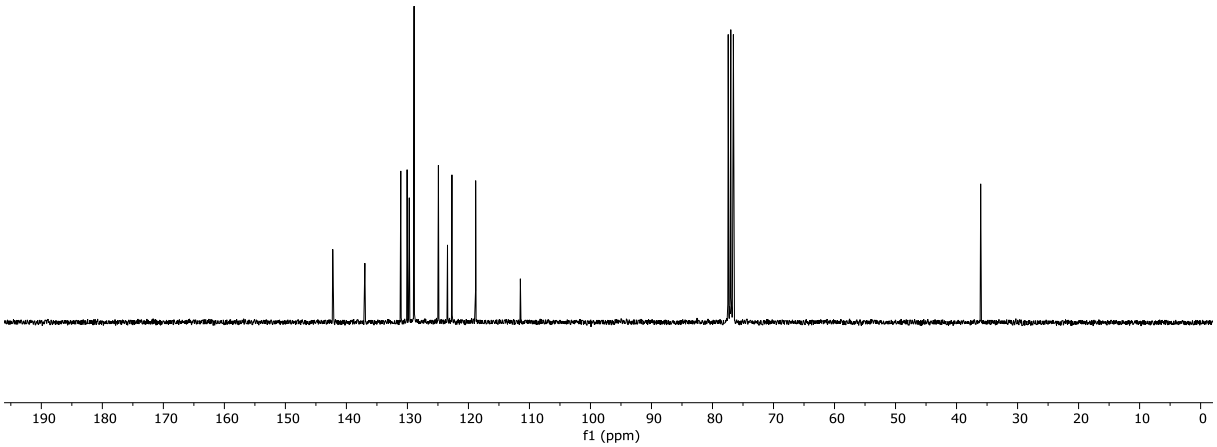


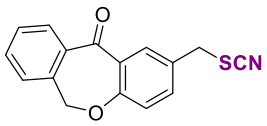
2aq (^{1}H NMR, $CDCl_3$, 300.1 MHz)



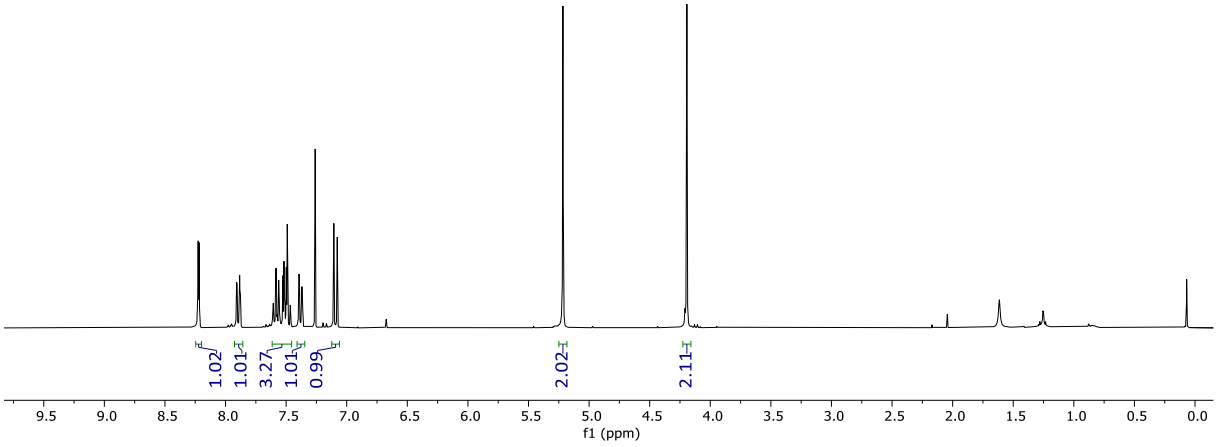


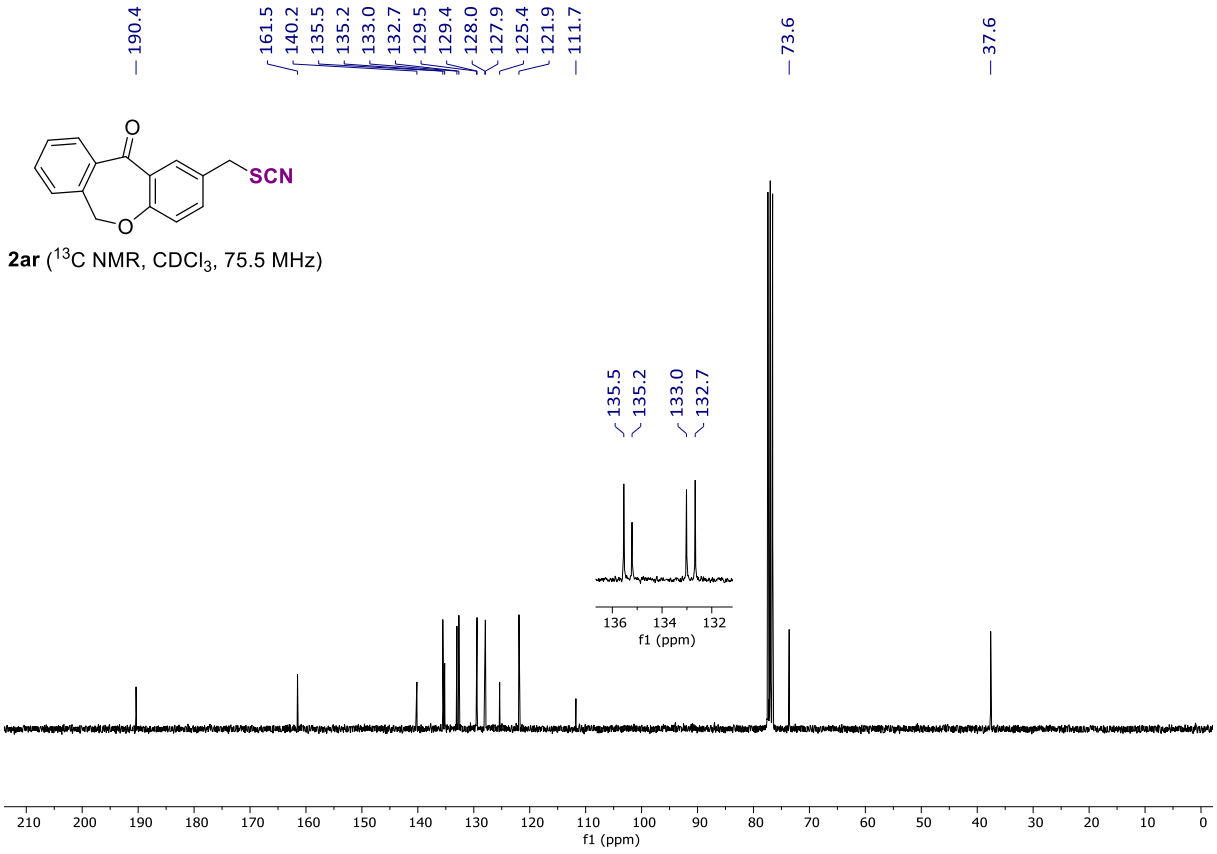
2aq (^{13}C NMR, $CDCl_3$, 75.5 MHz)



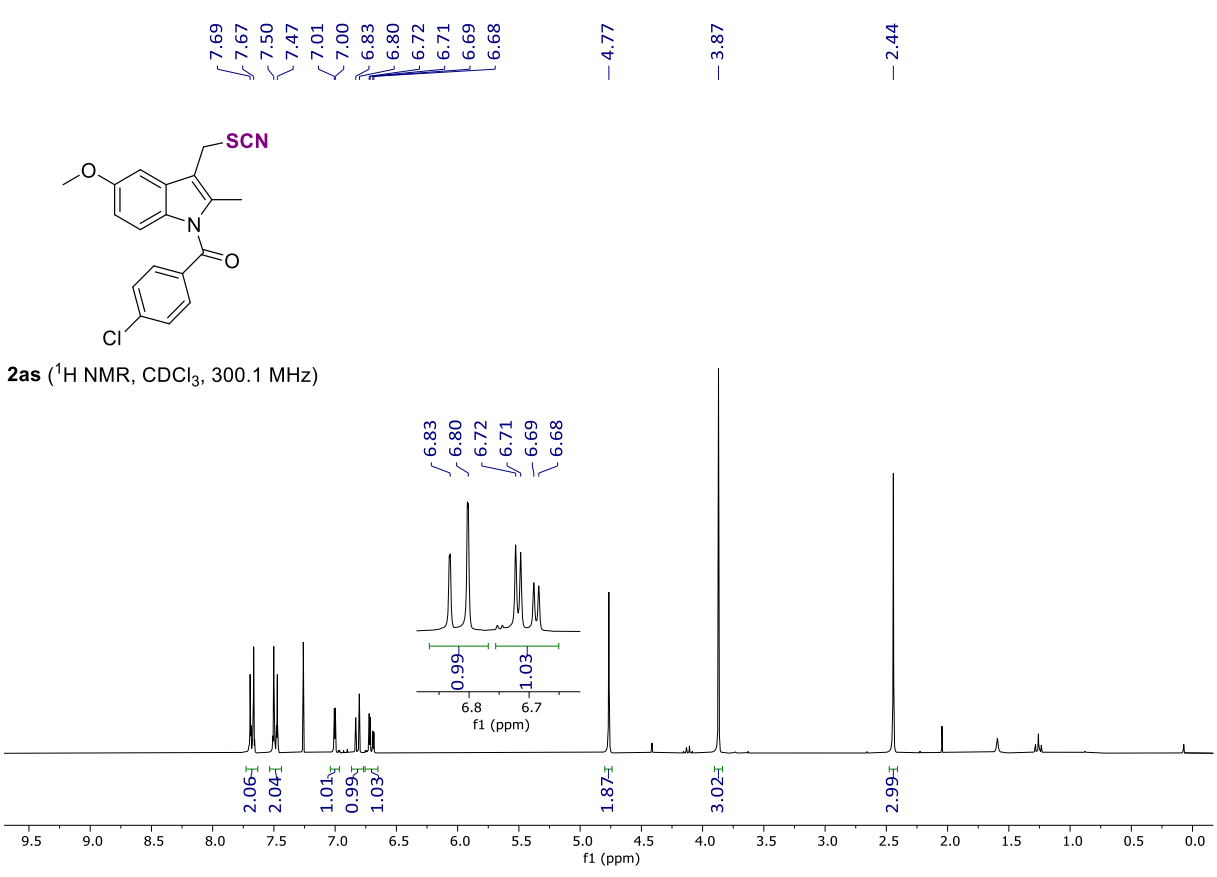


2ar (^{1}H NMR, $CDCl_3$, 300.1 MHz)

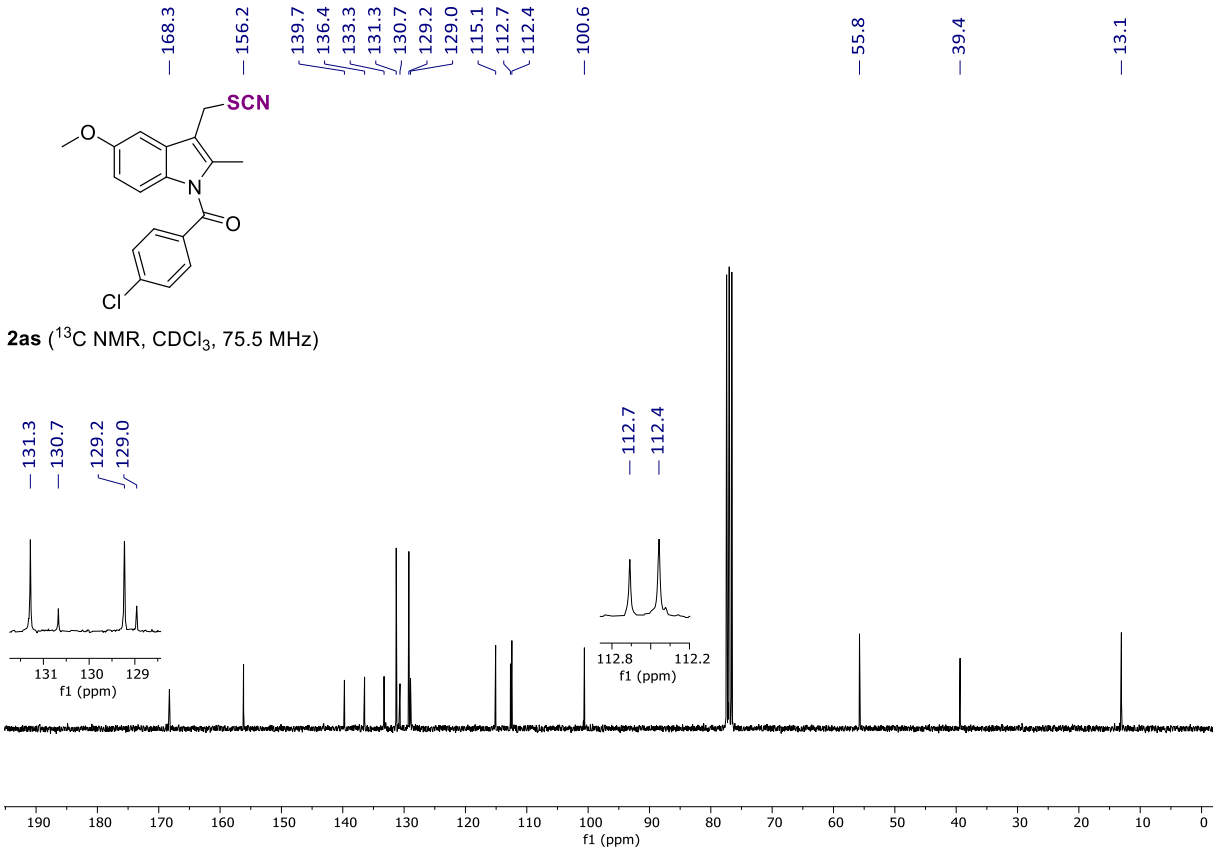




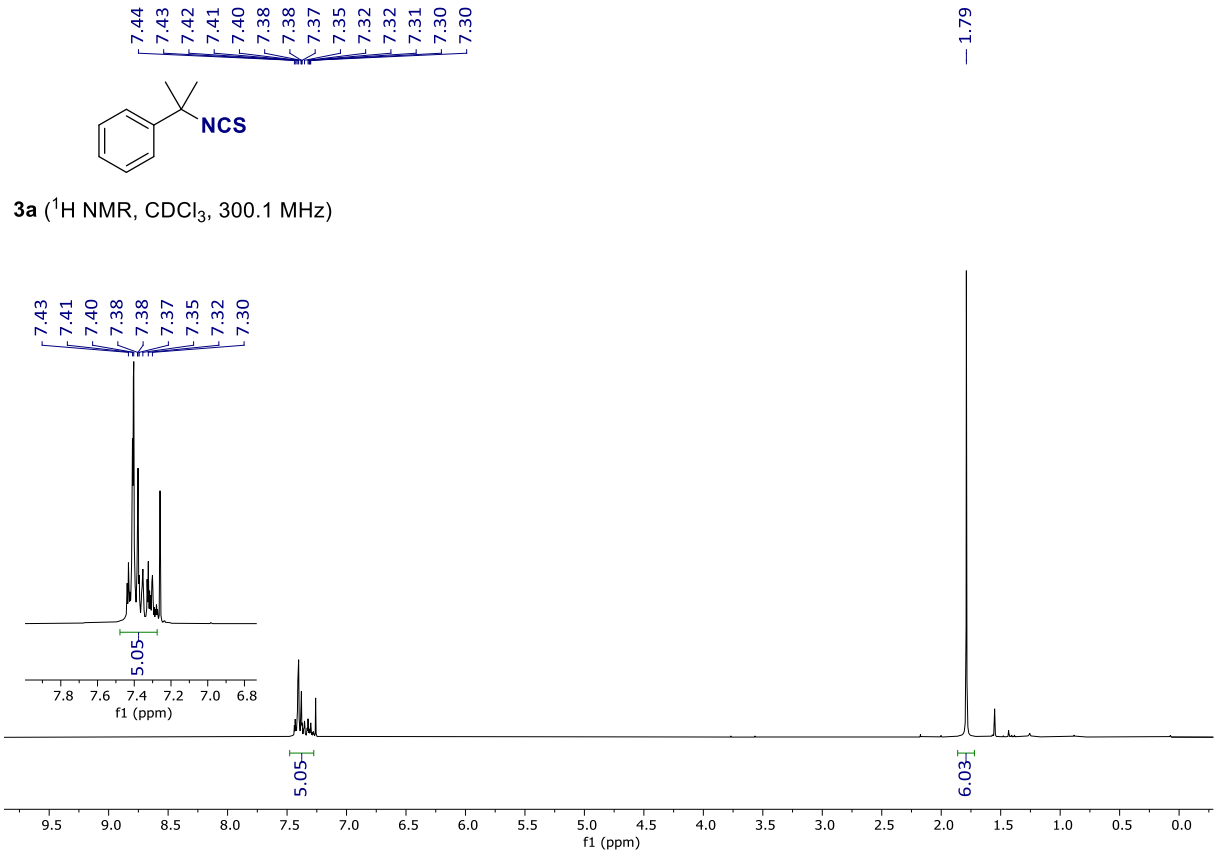
2ar (^{13}C NMR, $CDCl_3$, 75.5 MHz)



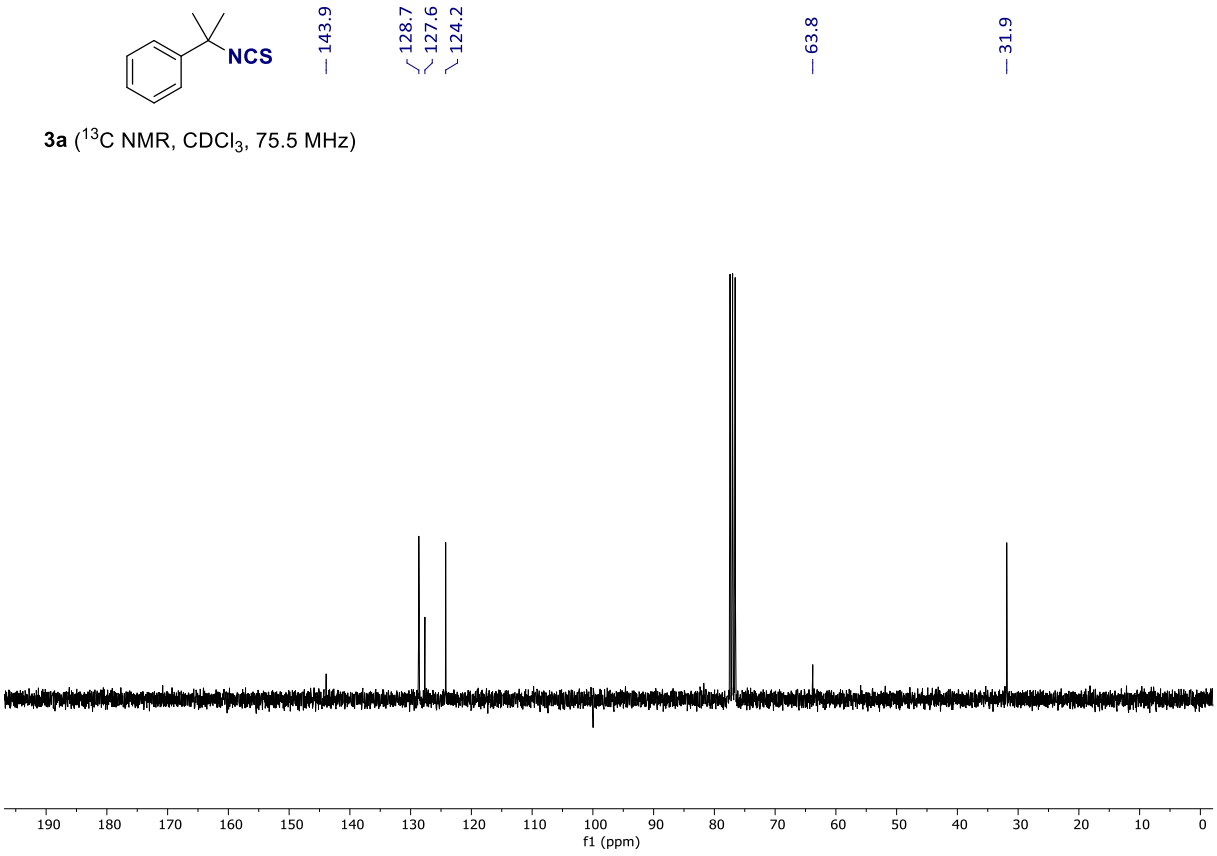
2as (^{1}H NMR, $CDCl_3$, 300.1 MHz)



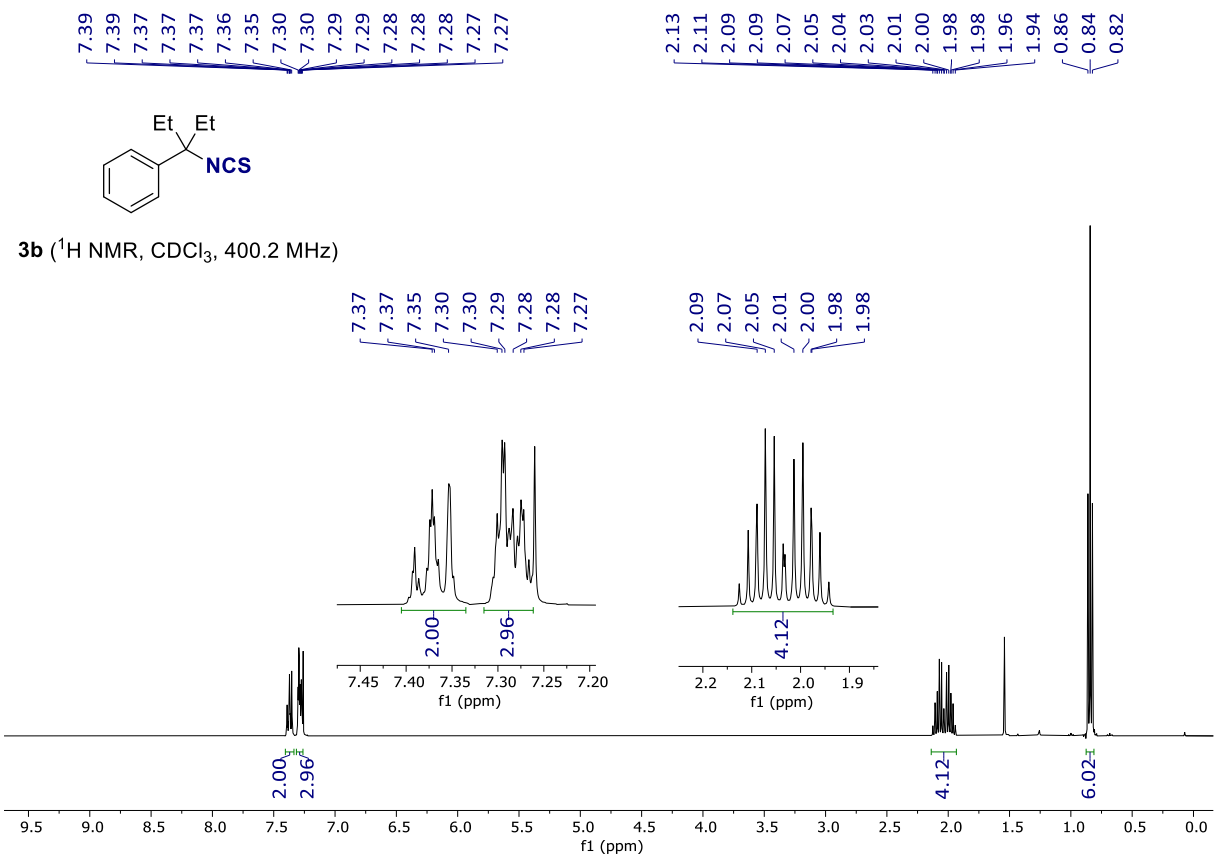
2as (^{13}C NMR, $CDCl_3$, 75.5 MHz)



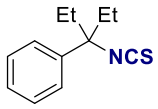
3a (^{1}H NMR, $CDCl_3$, 300.1 MHz)



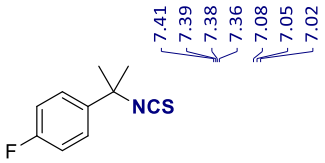
3a (^{13}C NMR, $CDCl_3$, 75.5 MHz)



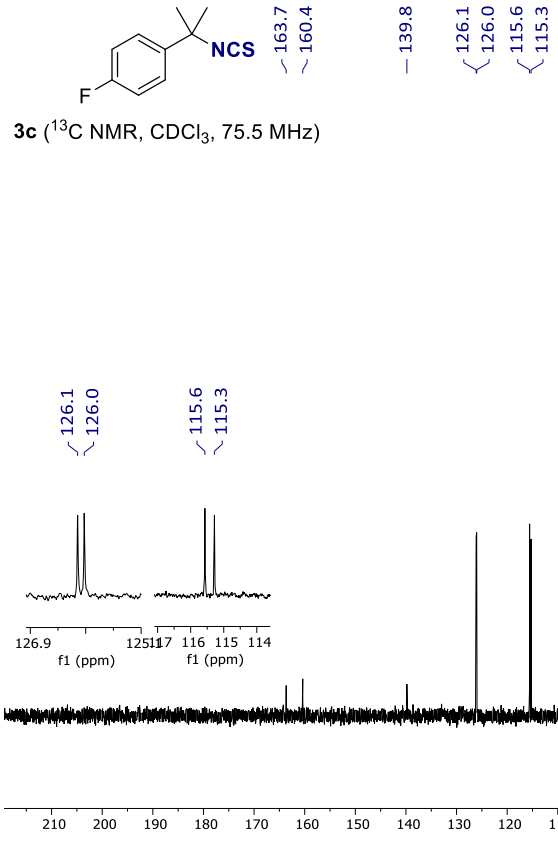
3b (^{1}H NMR, $CDCl_3$, 400.2 MHz)



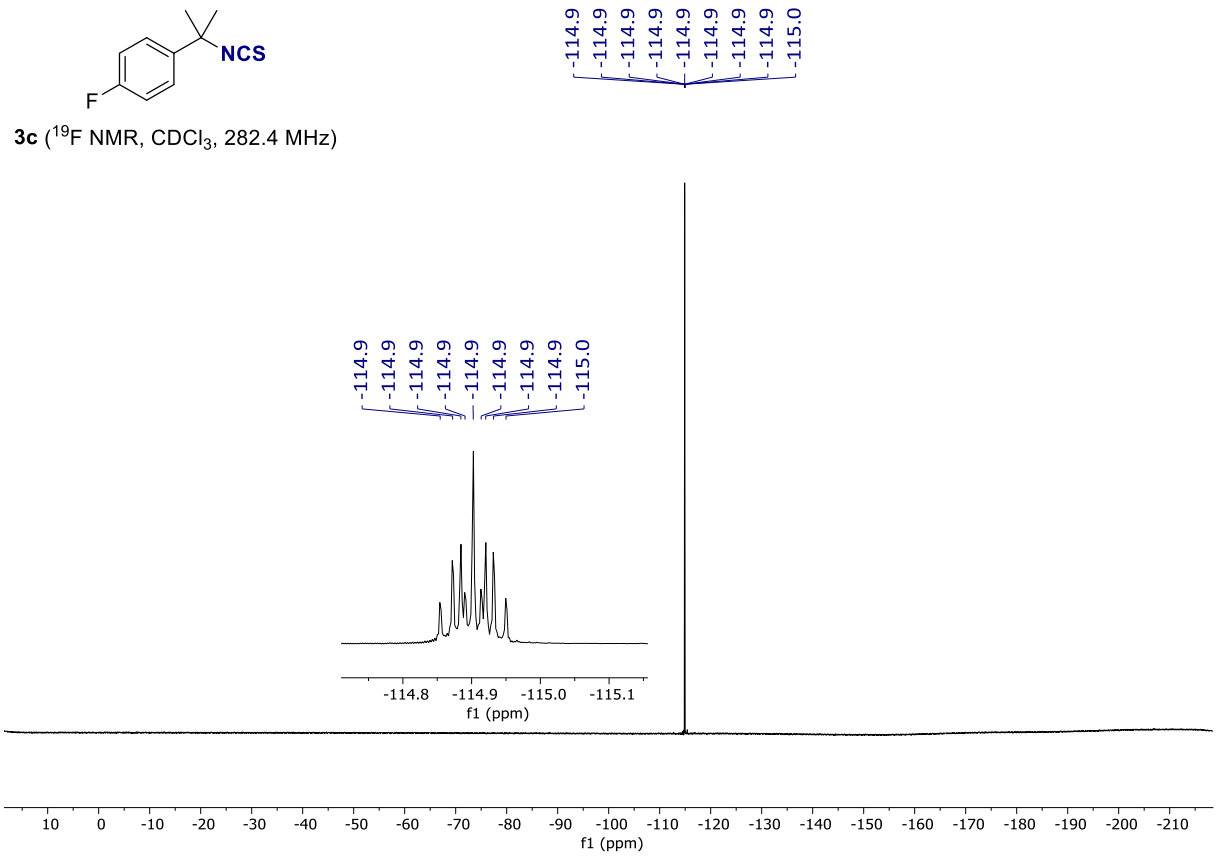
3b (^{13}C NMR, $CDCl_3$, 100.7 MHz)



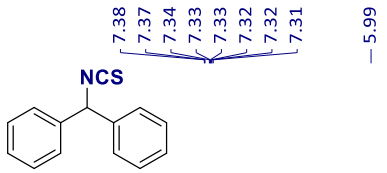
3c (^{1}H NMR, $CDCl_3$, 300.1 MHz)



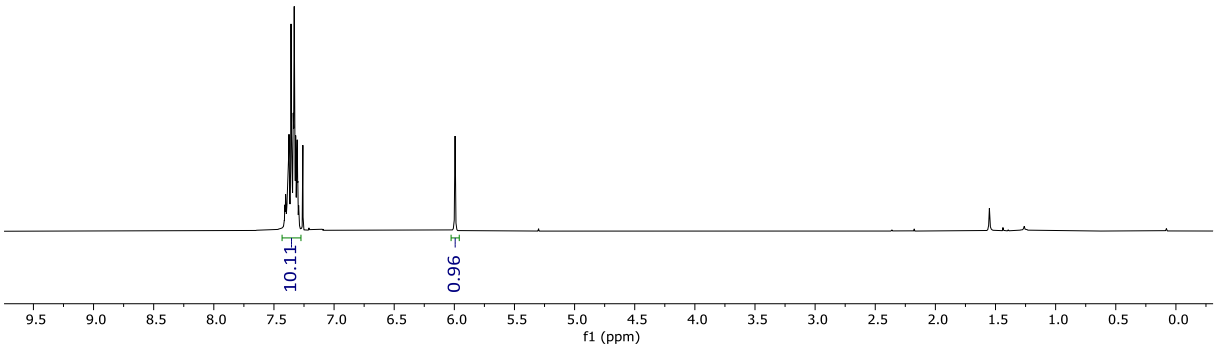
3c (^{13}C NMR, $CDCl_3$, 75.5 MHz)

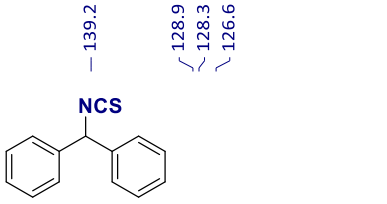


3c (^{19}F NMR, $CDCl_3$, 282.4 MHz)

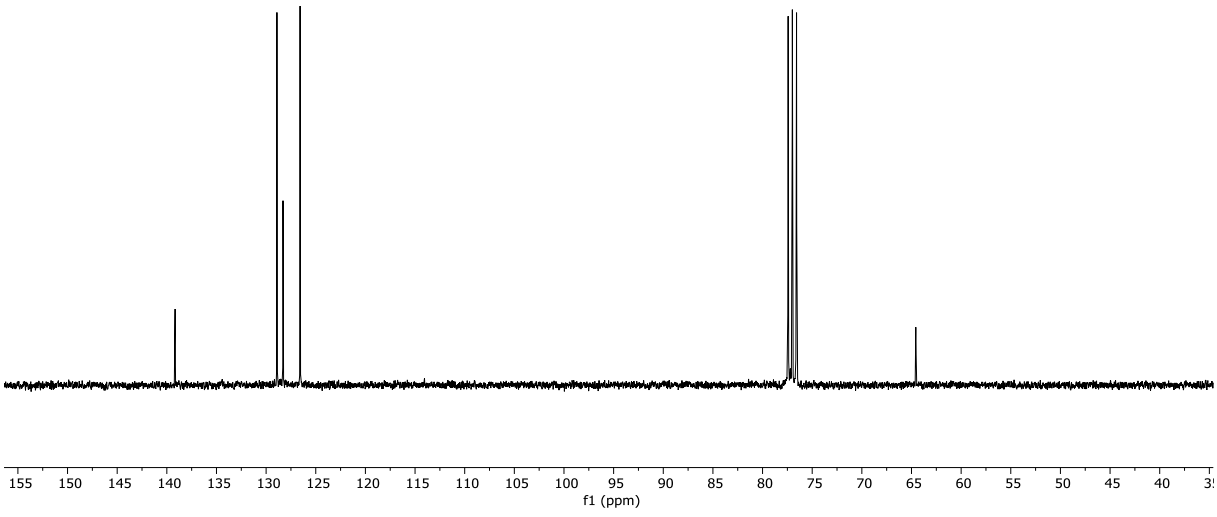


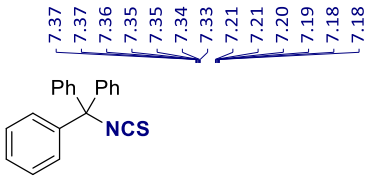
3h (^{1}H NMR, $CDCl_3$, 300.1 MHz)



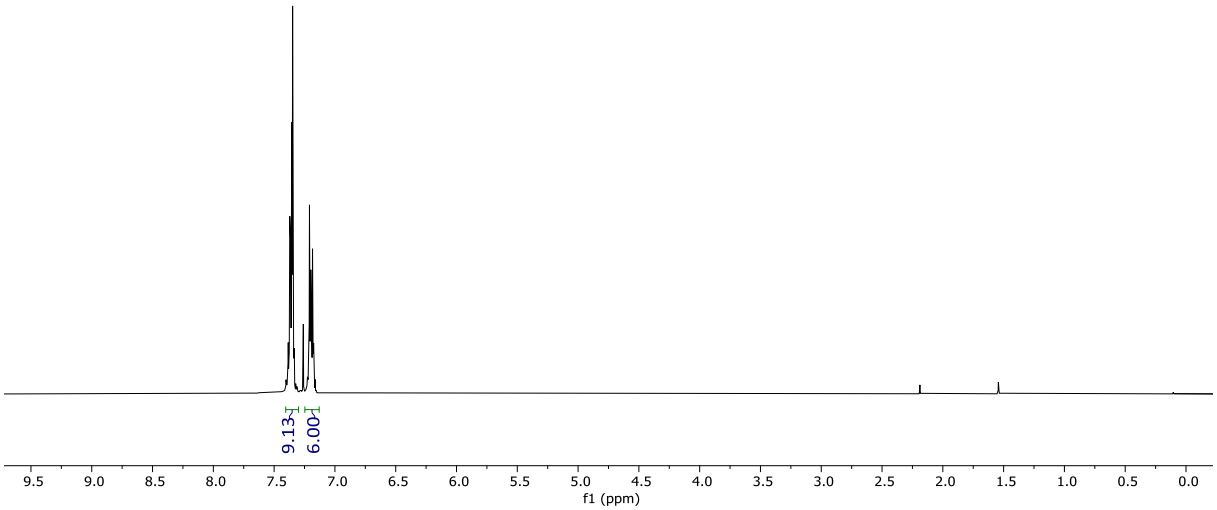


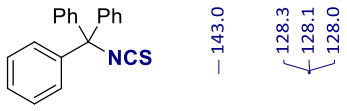
3h (^{13}C NMR, $CDCl_3$, 75.5 MHz)



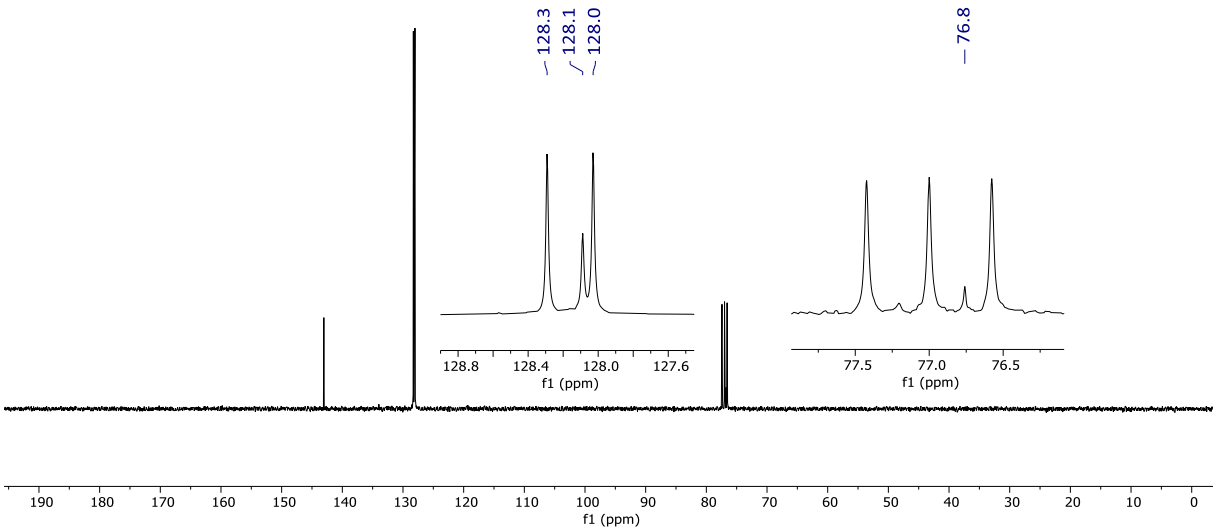


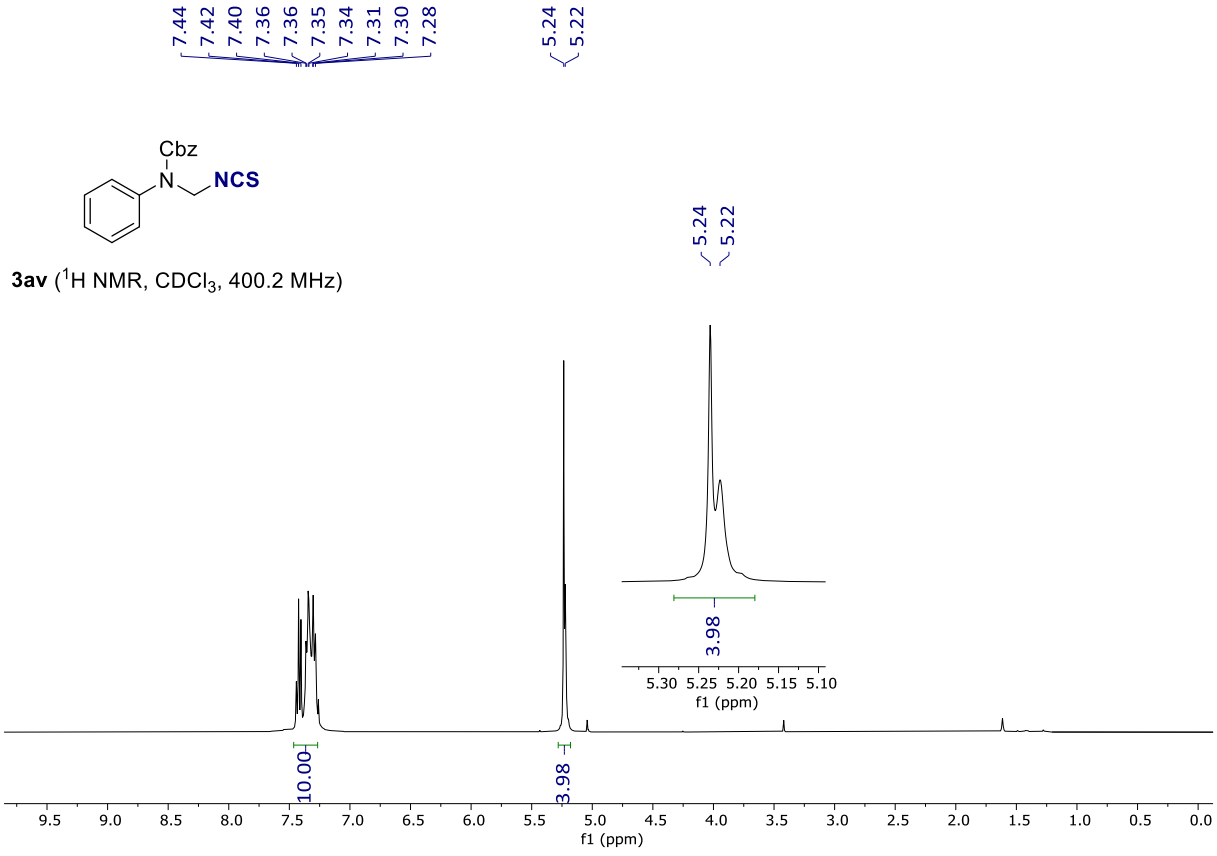
3at (^{1}H NMR, $CDCl_3$, 300.1 MHz)

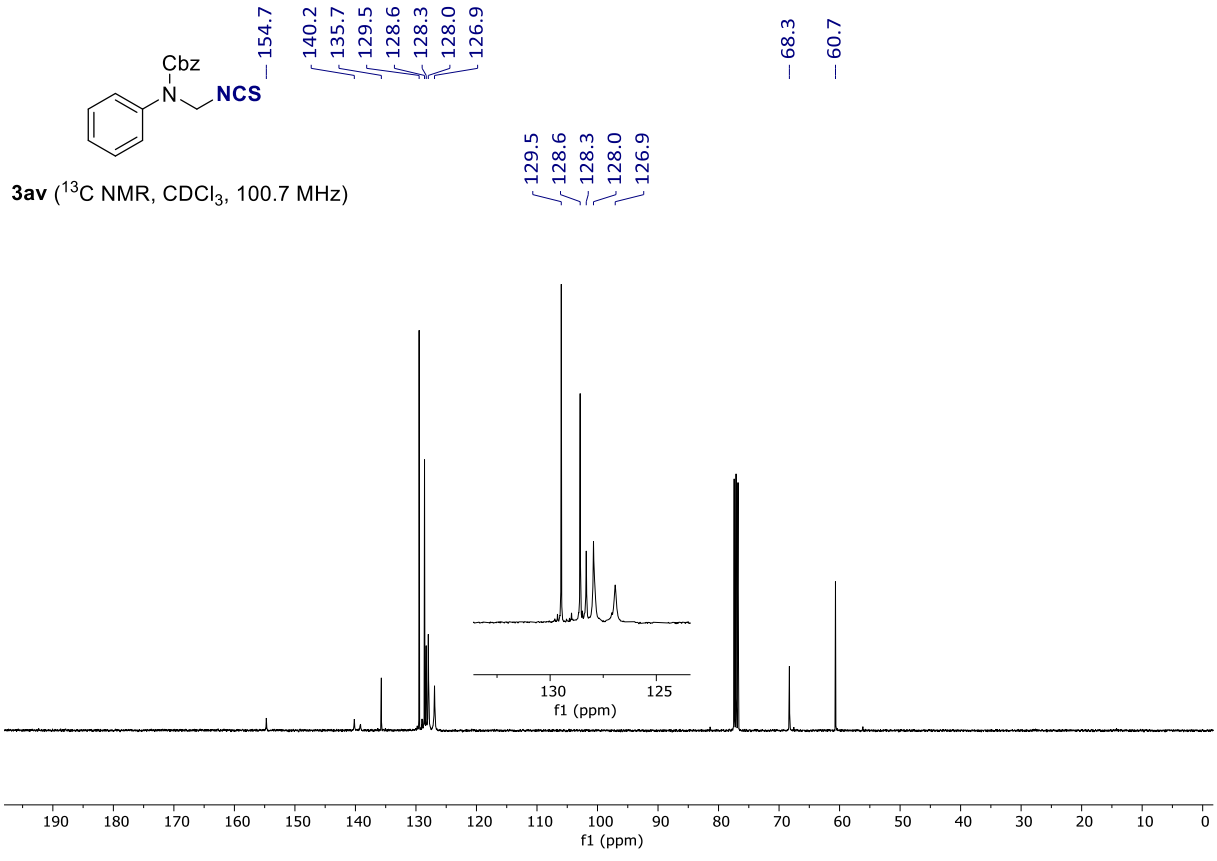


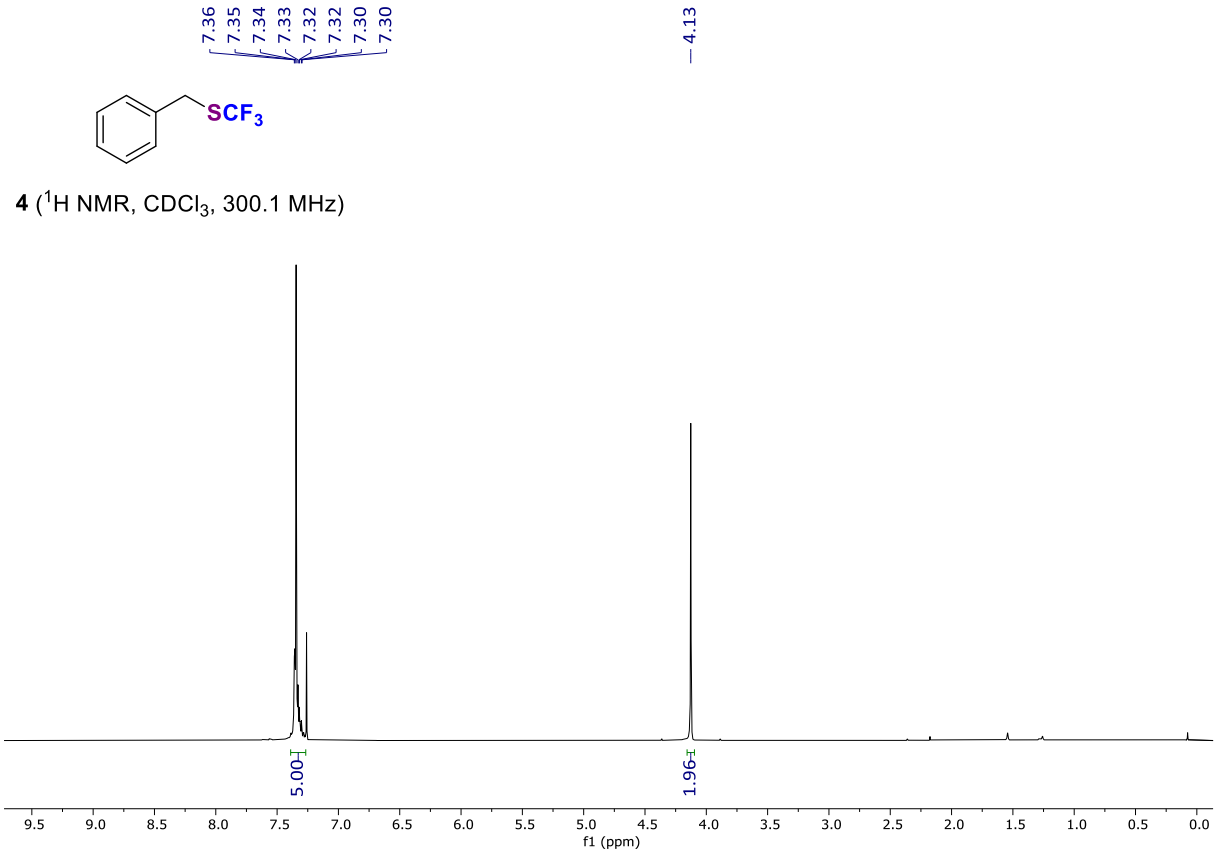


3at (^{13}C NMR, $CDCl_3$, 75.5 MHz)

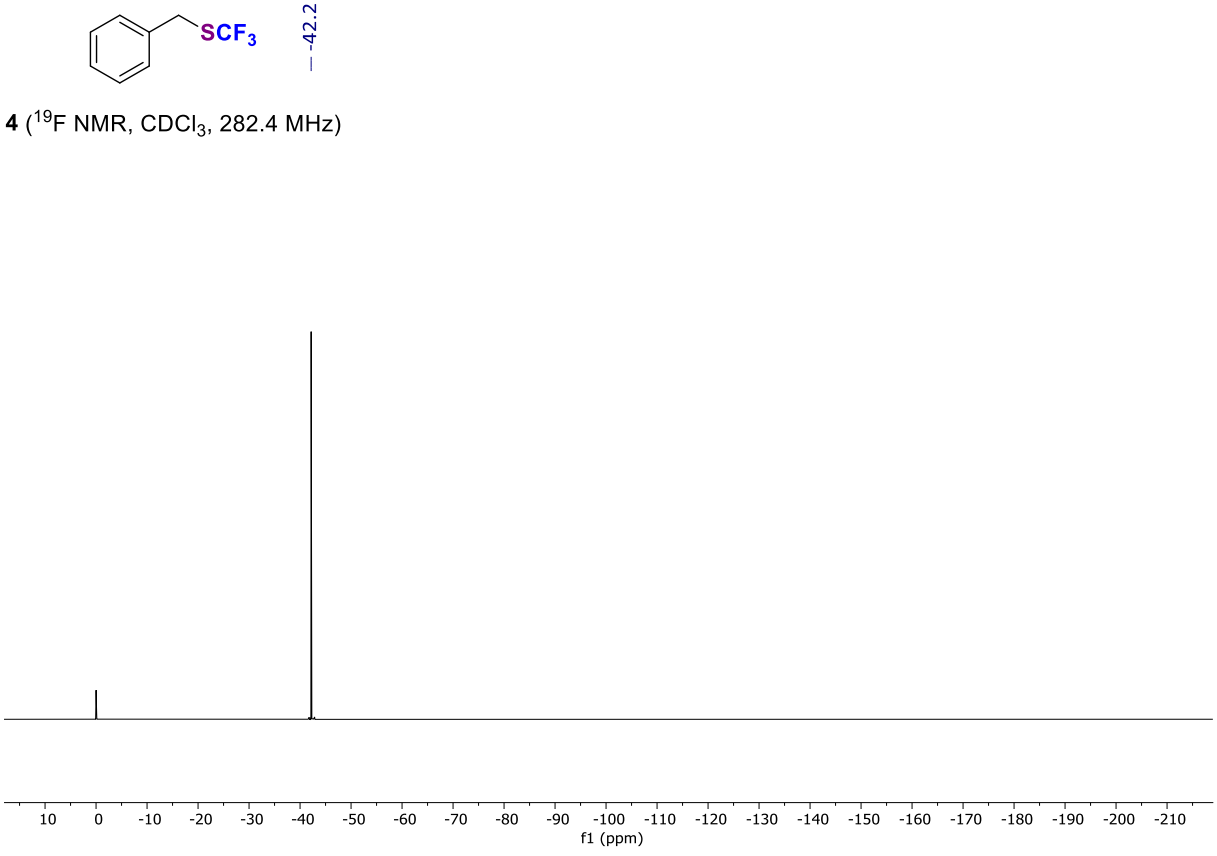



7.44
7.42
7.40
7.36
7.36
7.35
7.34
7.31
7.30
7.28
5.24
5.22
Cbz
N
NCS
3av (1H NMR, CDCl3, 400.2 MHz)
10.00
3.98
3.98
f1 (ppm)

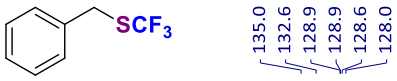

154.7
140.2
135.7
129.5
128.6
128.3
128.0
126.9
68.3
60.7
Cbz
N
NCS
129.5
128.6
128.3
128.0
126.9
3av (13C NMR, CDCl3, 100.7 MHz)
f1 (ppm)



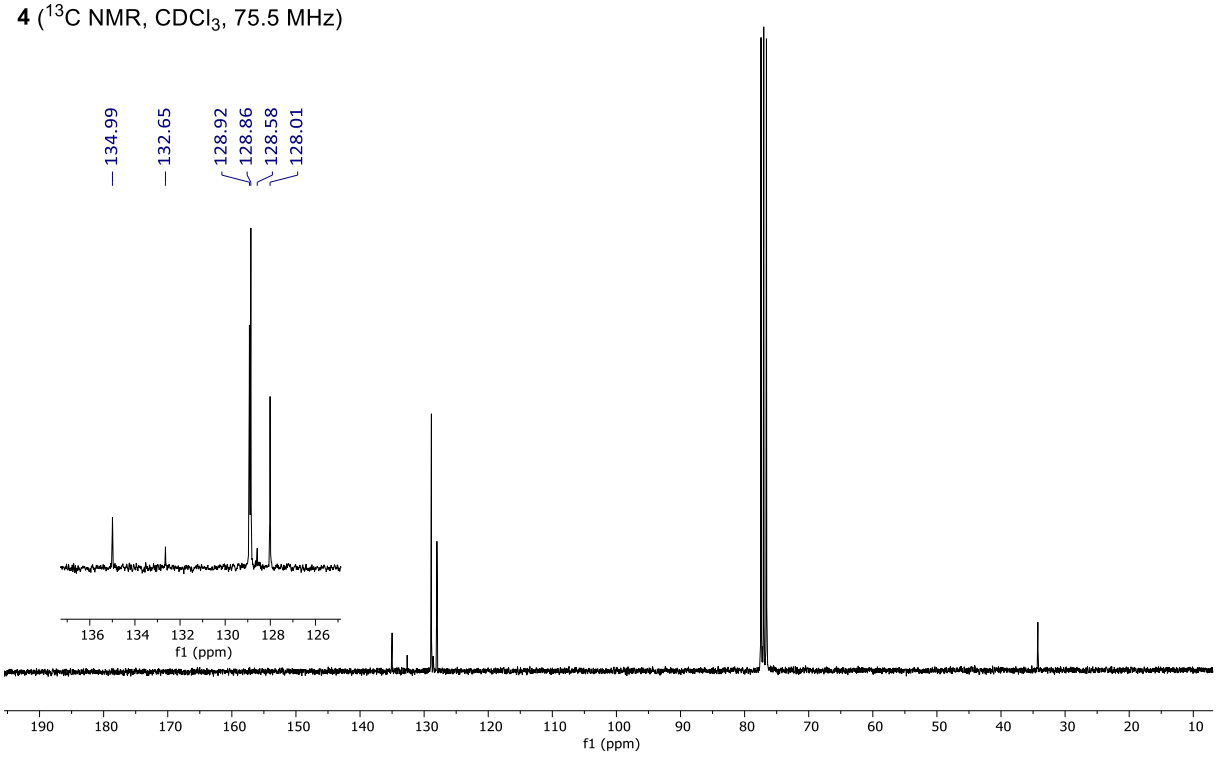
4 (^{1}H NMR, $CDCl_3$, 300.1 MHz)

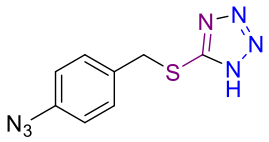


4 (^{19}F NMR, $CDCl_3$, 282.4 MHz)

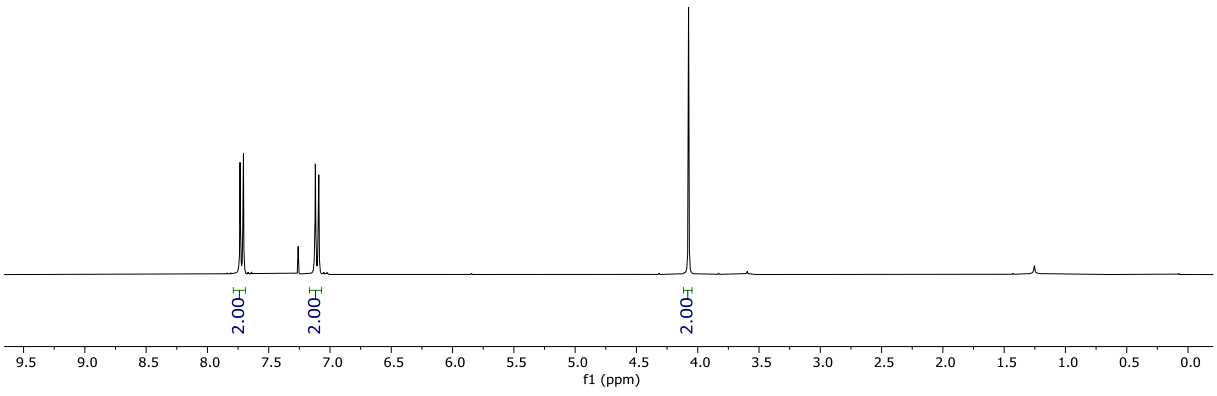


4 (^{13}C NMR, $CDCl_3$, 75.5 MHz)

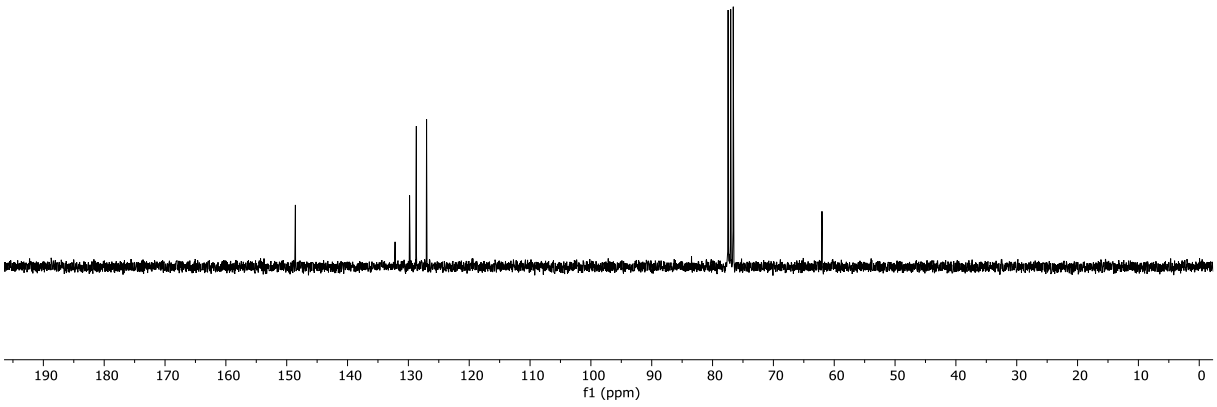


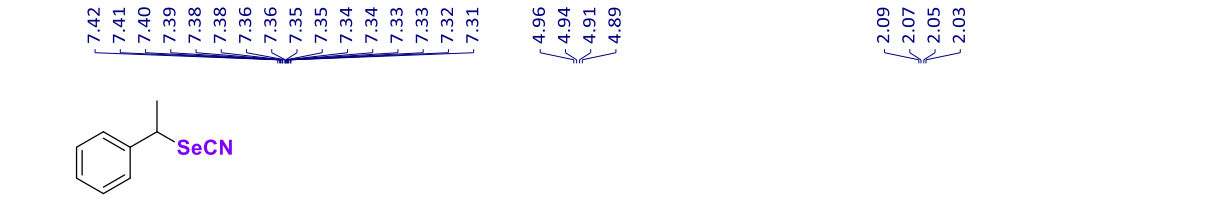


5 (^{1}H NMR, $CDCl_3$, 300.1 MHz)

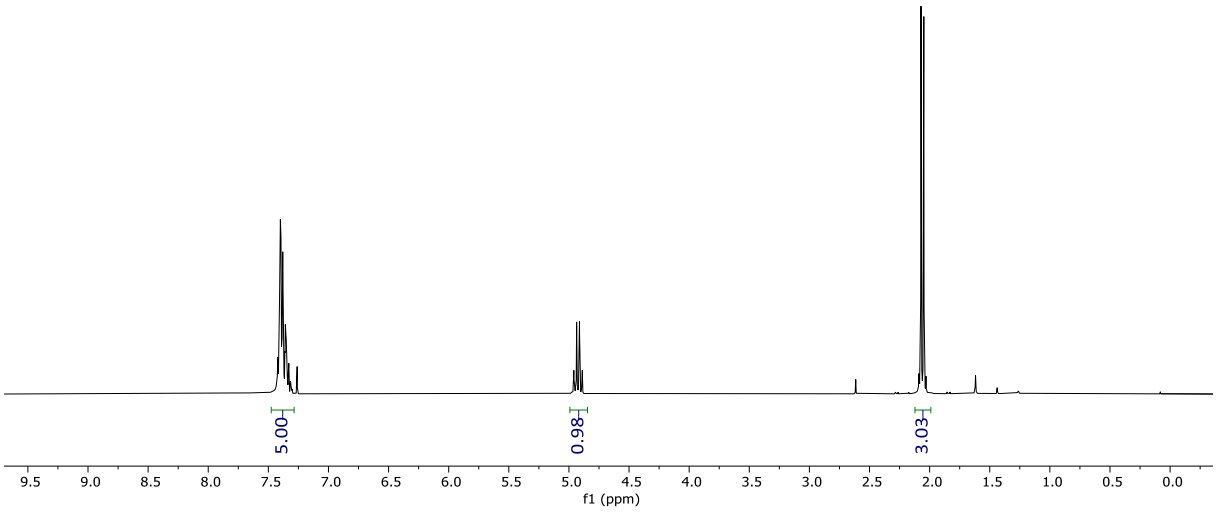


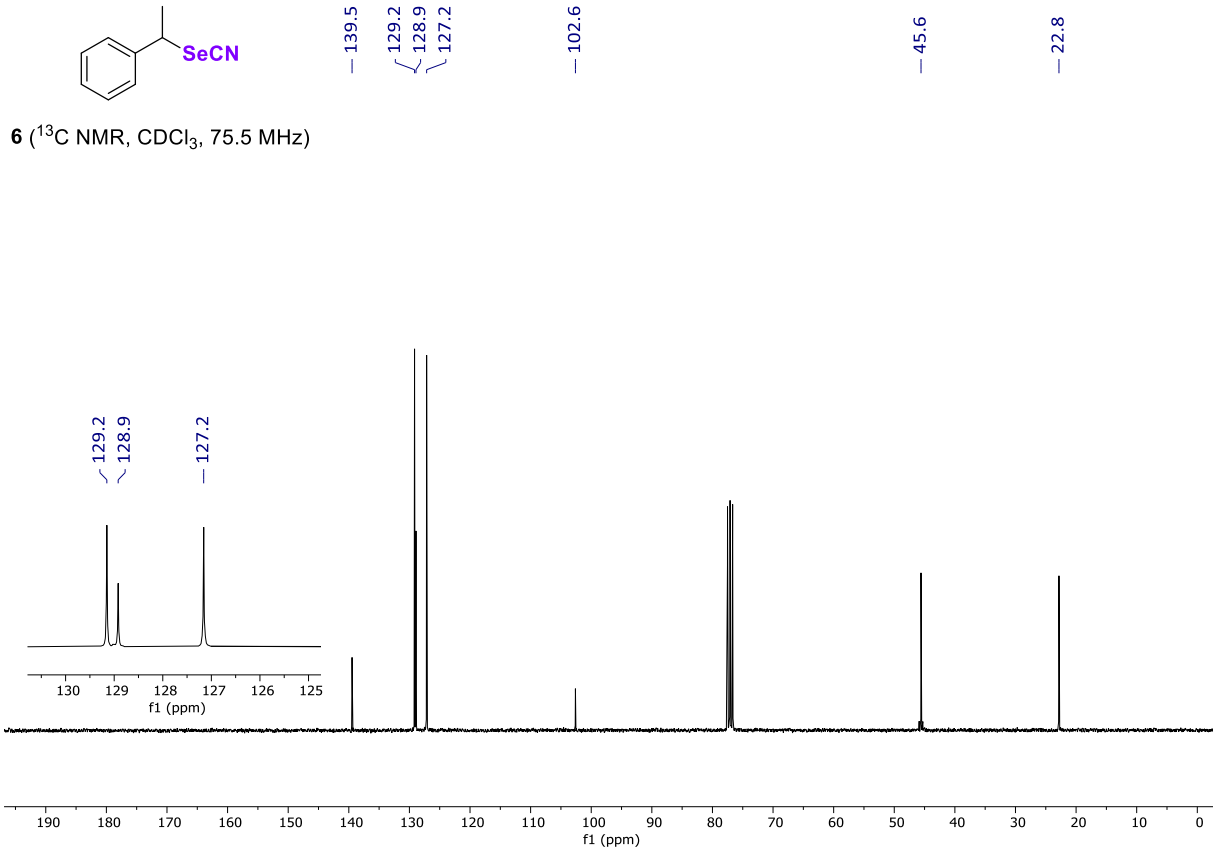
5 (^{13}C NMR, $CDCl_3$, 75.5 MHz)



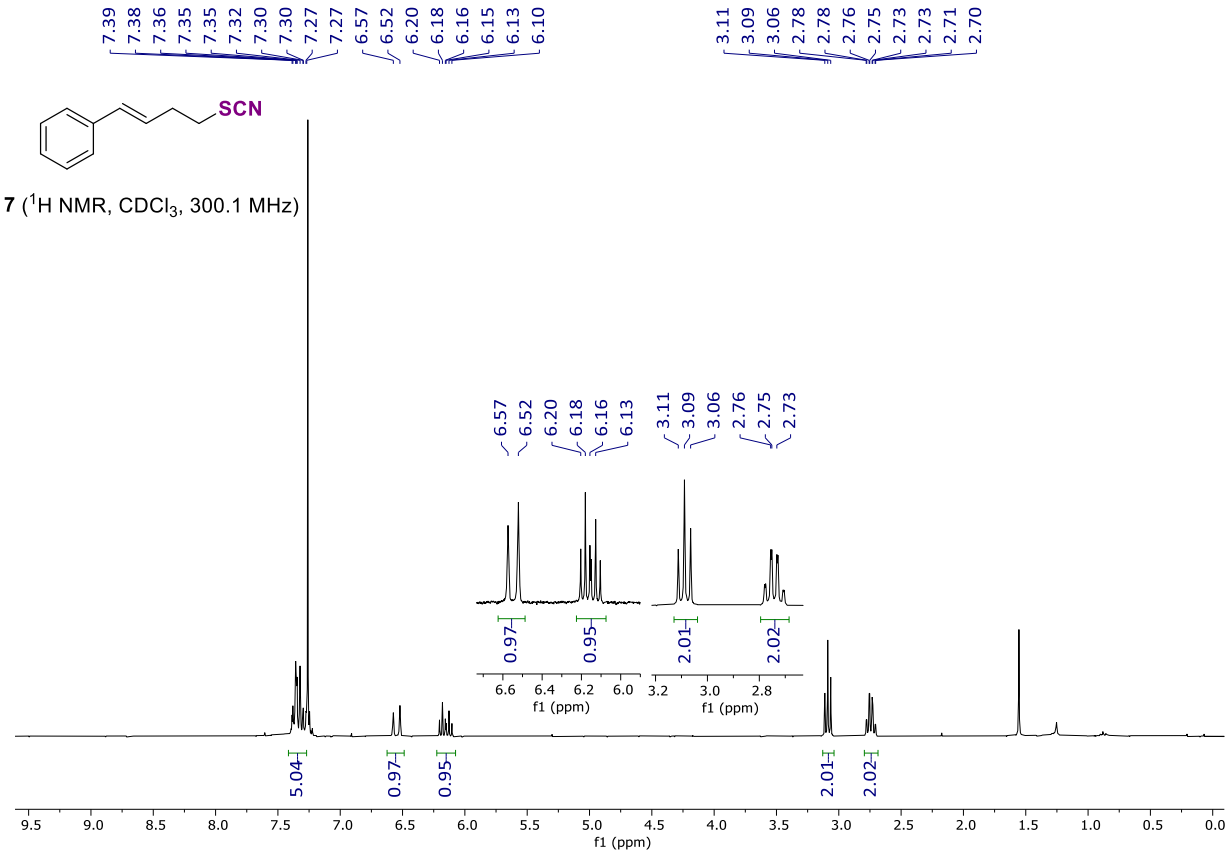


6 (^{1}H NMR, $CDCl_3$, 300.1 MHz)

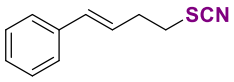


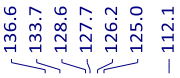


6 (^{13}C NMR, $CDCl_3$, 75.5 MHz)

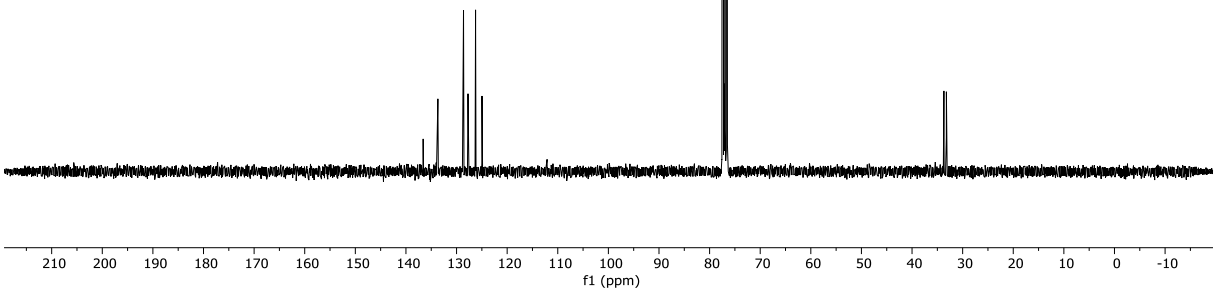


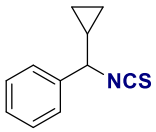
7 (^{1}H NMR, $CDCl_3$, 300.1 MHz)



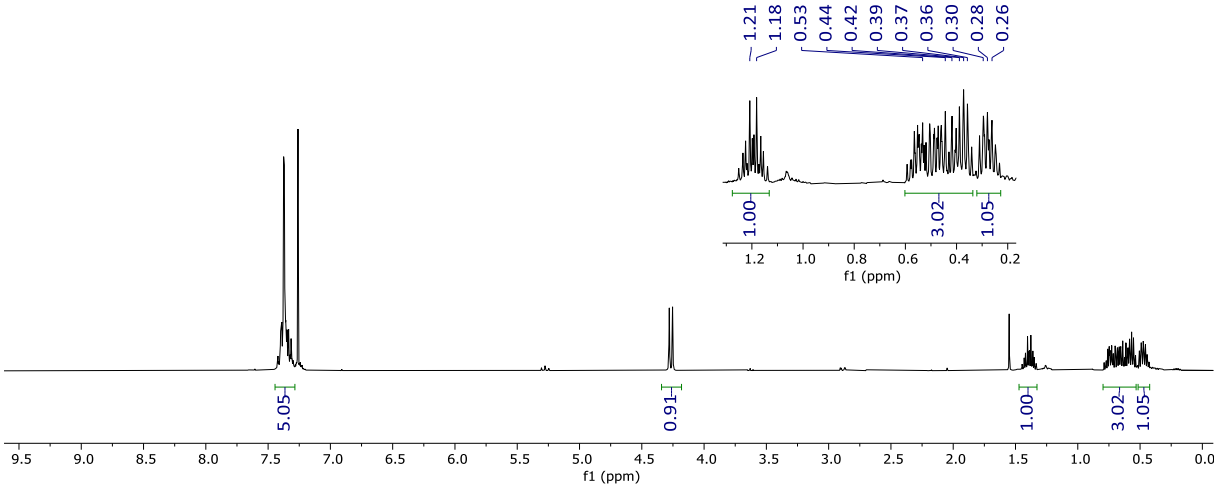


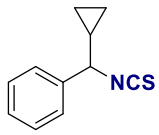
7 (^{13}C NMR, $CDCl_3$, 75.5 MHz)





8 (^{1}H NMR, $CDCl_3$, 300.1 MHz)





8 (^{13}C NMR, $CDCl_3$, 75.5 MHz)