Supporting Information for

Alkyl- and aryl-thioalkylation of olefins with organotrifluoroborates by photoredox catalysis

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Contents

Materials and methods

[Ir(dF(CF$_3$)ppy)$_2$(bpy)](PF$_6$) (**4**)[1a], [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) (**5**)[1b], [Ru(bpy)$_3$](PF$_6$)$_2$ (**6**)[1c], and potassium (1,3-dithian-2-yl)trifluoroborate (**1a**)[2] were prepared according to the reported literature procedures. Electron-deficient alkenes **2a**, **2b**, **2c**, **2e**, **2g**, and **2i** were purchased from TCI. **2d** was purchased from Wako. **2f** was purchased from SynQuest. **2h** was purchased from Aldrich. Reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. CD_3OD (99.8 atom % D) and Acetone-*d*$_6$ (99.9 atom % D) were purchased from Cambridge Isotope Laboratories, and CD_3OH (99.8 atom % D) was purchased from ISOTEC. Solvents were dried by standard procedures (acetone (K_2CO_3)), distilled and stored under N_2 atmosphere. Methanol (dehydrated solvent KANTO CHEMICAL CO., INC.) was degassed with ultrasonic bath, and stored under N_2 atmosphere. Thin-layer chromatography was performed on Merck TLC plate with 60 F_{254}. Recycled gel permeation chromatography (GPC) was performed by LC-9201 on Japan Analytical Industry Co. Ltd. Visible light irradiation was conducted with a Relyon LED lamp (3 W × 2; λ_{max}= 425 ± 15 nm). The NMR spectra were acquired on Bruker AVANCE-400 (400 MHz) and Bruker AVANCE-500 (500 MHz). NMR chemical shifts were referred to residual protio impurities in the deuterated solvent. ^{19}F-NMR chemical shifts were referenced to external 1,4-difluorobenzene (-118.8 ppm in DMSO-*d*$_6$)[3], and trifluoroacetic acid (-77.8 ppm in CD_3OD[4], -76.6 ppm in $CDCl_3$). All ^{11}B-NMR chemical shifts were referenced to external boron trifluoride diethyl etherate (0.0 ppm). Electrochemical measurements were recorded on a Hokutodenkou HZ-5000 analyzer (observed in 0.002 M MeCN; [NBu$_4$](PF$_6$) = 0.1 M; Ag/AgCl = electrode; reported with respect to the [FeCp$_2$]/[FeCp$_2$]$^+$ couple). UV-vis spectra and luminescence spectra were obtained on a JASCO V-670DS and HITACHI F-7000, respectively. HRMS (ESI-TOF Mass) spectra were obtained with a Bruker micrOTOF II. Elemental analysis was carried out by a MICRO CORDER JM10. GC-MS analyses were carried out using a GC-MS system (Shimadzu GC-MS Parvum 2, capillary column: Rxi®-5ms (30 m × 0.25 mm × 0.25 μm)).

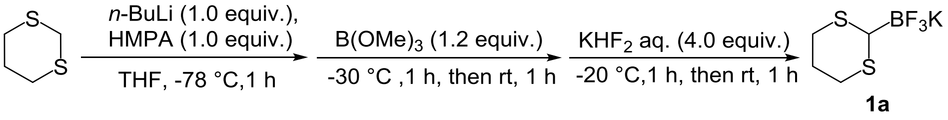
Reaction apparatus

Irradiation of visible light was performed with a Relyon LED lamp (3 W × 2; λ_{max} = 425 ± 15 nm) (left).

Cylindrical vessel was used for photoreaction under sunlight (right)

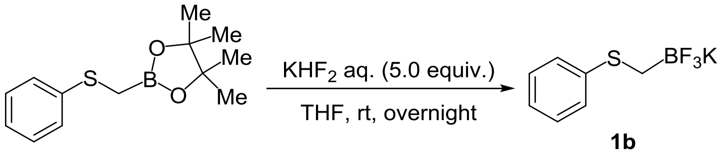
Procedure for the synthesis of organotrifluoroborates

Potassium (1,3-dithian-2-yl)trifluoroborate (1a)



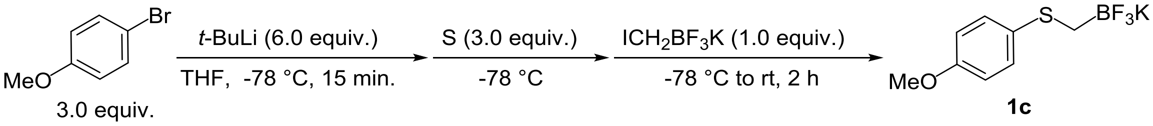
According to the literature[2], 1,3-dithiane (2.40 g, 20.0 mmol), dry THF (40.0 mL), a 1.55 M hexane solution of *n*-BuLi (13.0 mL, 20.0 mmol), HMPA (3.6 mL, 20.0 mmol), $B(OMe)_3$ (2.7 mL, 24.0 mmol), and a saturated KHF_2 aq. (6.24 g, 80.0 mmol, water = 20.0 mL) afforded **1a** as a white solid in 47% yield (2.11 g, 9.3 mmol). **^{1}H NMR** (500 MHz, CD_3OD) δ 3.49 (br, 1H; SC*H*S), 2.82 (m, 2H; SC*H*HCH$_2$), 2.65 (m, 2H; SCH*H*CH$_2$), 2.08 (m, 1H; SCH$_2$C*H*H), 1.88 (m, 1H; SCH$_2$CH*H*). **^{13}C NMR** (125 MHz, CD_3OD) δ 40.0 (S*C*HS), 31.5 (S*C*H$_2$CH$_2$), 28.2 (SCH$_2$*C*H$_2$). **^{11}B NMR** (160 MHz, CD_3OD) δ 3.14 (apparent q). **^{19}F NMR** (470 MHz, CD_3OD) δ -147.65 (apparent q). **HRMS (ESI-TOF):** calculated for $[C_4H_7BF_3S_2]^-$ requires 187.0041, found 187.0044.

Potassium phenylthiomethyltrifluoroborate (1b)



To a solution of 4,4,5,5,-tetramethyl-2-phenylsulfanylmethyl-1,3,2-dioxaborolane (1.00 g, 4.0 mmol) in THF (25.0 mL) at room temperature, then a saturated KHF_2 aq. (1.56 g, 20.0 mmol, water = 5.0 mL) was added. Then, the reaction mixture was stirred for 12 h. The suspension was concentrated and dried *in vacuo*. The residue was dissolved in dry acetone and filtered. After the solvent was removed, the residue was washed with Et_2O and dried *in vacuo*. The product was obtained as a white solid in 95% (0.88 g, 3.8 mmol). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.17 (4H; *phenyl*), 6.97 (1H; *phenyl*), 1.62 (apparent d, SC*H$_2$*). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 143.5 (*phenyl*), 128.3 (*phenyl*), 124.7 (*phenyl*), 122.8 (*phenyl*), 20.7 (S*C*H$_2$). **^{11}B NMR** (160 MHz, DMSO-d_6) δ 3.86 (apparent br.q). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -135.6 (br). **HRMS (ESI-TOF):** calculated for $[C_7H_7BF_3S]^-$ requires 191.0320, found 191.0318. **Elemental Anal.:** calculated for $C_7H_7BF_3SK$: C 36.54, H 3.07. Found: C 36.28, H 3.04.

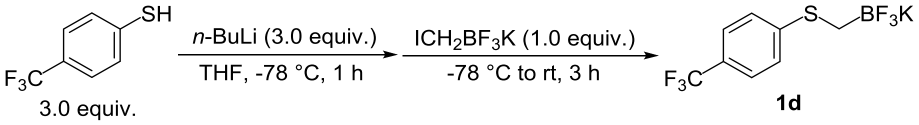
Potassium 4-methoxyphenylthiomethyltrifluoroborate (1c)



To a solution of 4-bromoanisole (0.45 g, 2.4 mmol) in dry THF (6.0 mL) was added a 1.61 M pentane solution of *t*-BuLi (3.0 ml, 4.8 mmol) at -78 ˚C for 15 min., and the mixture was stirred for 15 min. at -78 ˚C under N_2 atmosphere. Then, sulfur powder (0.08 g, 2.4 mmol) was added in one portion. After the reaction mixture changed to a yellow clear solution, a solution of potassium iodomethyltrifluoroborate (0.20 g, 0.8 mmol) in dry THF (6.0 mL) was slowly added and then the reaction mixture was gradually warmed up to room temperature for 2 h. After the reaction was completed, it was quenched with 1.5 M KHF_2 aq. (4.0 mL) and then the suspension was concentrated and dried *in vacuo*. The residue was dissolved in dry acetone and filtered. After the solvent was removed, the residue was washed with Et_2O and dried *in vacuo*. The product was obtained as a white solid in 59% yield (0.21 g, 0.5 mmol). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.07 (d, *J* = 9.0 Hz, 2H; *phenyl*), 6.81 (d, *J* = 9.0 Hz, 2H; *phenyl*), 3.70 (s, 3H; OC*H$_3$*), 1.62 (apparent d, 2H; SC*H$_2$*). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 156.5 (*phenyl*), 134.4 (*phenyl*), 127.2 (*phenyl*), 114.7 (*phenyl*), 55.5 (O*C*H$_3$), 22.8 (S*C*H$_2$). **^{11}B NMR** (160

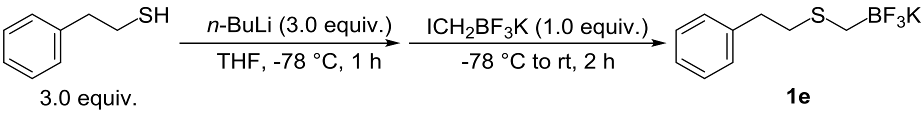
MHz, DMSO-d_6) δ 3.75 (br). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -135.8 (br). **HRMS (ESI-TOF):** calculated for $[C_8H_9BF_3OS]^-$ requires 221.0426, found 221.0426.

Potassium 4-trifluoromethylphenylthiomethyltrifluoroborate (1d)



To a solution of 4-trifluoromethyl benzenethiol (1.07 g, 6.0 mmol) in dry THF (15.0 mL) was added a 1.55 M hexane solution of *n*-BuLi (4.0 ml, 6.0 mmol) at -78 ˚C for 10 min., and the mixture was stirred for 1 h at -78 ˚C under N_2 atmosphere. A solution of potassium iodomethyltrifluoroborate (0.50 g, 2.0 mmol) in dry THF (15.0 mL) was gradually added and then the reaction mixture was slowly warmed up to room temperature for 3 h. After the reaction was completed, it was quenched with 1.5 M KHF_2 aq. (10.0 mL) and then the suspension was concentrated and dried *in vacuo*. The residue was dissolved in dry acetone and filtered. After the solvent was removed, the residue was washed with Et_2O and dried *in vacuo*. The product was obtained as a white solid in 90% yield (0.54 g, 1.8 mmol). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.51 (d, *J* = 8.5 Hz, 2H; *phenyl*), 7.32 (d, *J* = 8.5 Hz, 2H; *phenyl*), 1.68 (q, *J* = 5.5 Hz, 2H; SCH_2). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 150.0 (*phenyl*), 124.8 (q, *J* = 269.4 Hz, CF_3), 125.0 (q, *J* = 3.6 Hz, *phenyl*), 124.8 (*phenyl*), 123.1 (q, *J* = 31.5 Hz, *phenyl*), 22.6 (SCH_2). **^{11}B NMR** (160 MHz, DMSO-d_6) δ 3.77 (br). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -59.9 (s, CF_3), -135.8 (br, BF_3K). **HRMS (ESI-TOF):** calculated for $[C_8H_6BF_6S]^-$ requires 259.0194, found 259.0189.

Potassium phenethylthiomethyltrifluoroborate (1e)



To a solution of 2-phenylethanethiol (1.66 g, 12.0 mmol) in dry THF (30.0 mL) was added a 1.55 M hexane solution of *n*-BuLi (8.0 ml, 12.0 mmol) at -78 ˚C for 20 min, and the mixture was stirred for 1 h at -78 ˚C under N_2 atmosphere. A solution of potassium iodomethyltrifluoroborate (0.99 g, 4.0 mmol) in dry THF (30.0 mL) was slowly added and then the reaction mixture was gradually warmed up to room temperature for 2 h. After the reaction was completed, it was quenched with 1.5 M KHF_2 aq. (20.0 mL) and then the suspension was concentrated and dried *in vacuo*. The residue was dissolved in dry acetone and filtered. After the solvent was removed, the residue was washed with Et_2O and dried *in vacuo*. The product was obtained as a white solid in 92% yield (0.94 g, 3.7 mmol). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.22 (2H; *phenyl*), 7.15 (3H; *phenyl*), 2.75 (m, 2H; phenyl-CH_2), 2.53 (m, 2H; phenyl-CH_2CH_2), 1.32 (q, *J* = 5.5 Hz, 2H; SCH_2BF_3K). **^{13} C NMR** (125 MHz, DMSO-d_6) δ 141.5 (*phenyl*), 128.4 (*phenyl*), 128.2 (*phenyl*), 125.8 (*phenyl*), 36.0 (phenyl-CH_2), 35.6 (phenyl-CH_2CH_2), 22.3 (SCH_2). **^{11}B NMR** (160 MHz, DMSO-d_6) δ 3.94 (br). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -135.7 (br). **HRMS (ESI-TOF):** calculated for $[C_9H_{11}BF_3S]^-$ requires 219.0634, found 219.0629.

Typical NMR experimental procedure (Table 1)

Under N_2 atmosphere, Ir photocatalyst **4** (1.0 mg, 1.0 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (11.3 mg, 0.05 mmol), tetraethylsilane ($SiEt_4$) as an internal standard, CD_3OD (0.40 mL), and acrylonitrile (**2a**) (5.3 mg, 0.10 mmol) were added to an NMR tube. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamp: λ = 425 ± 15 nm).

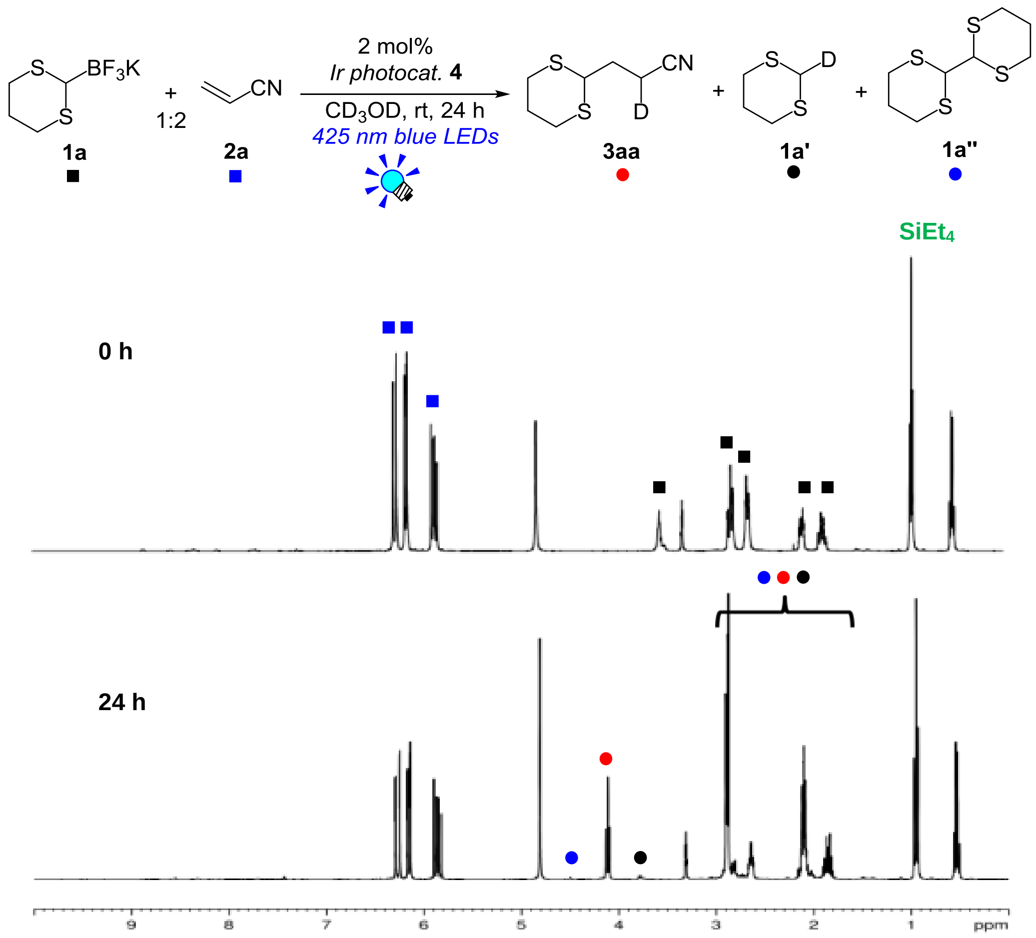
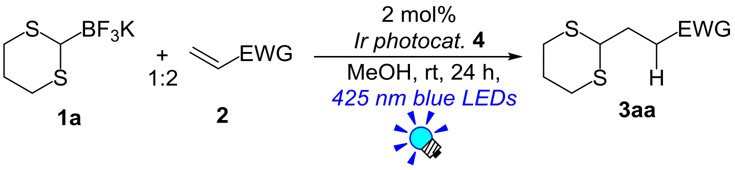


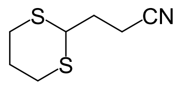
Figure S1 ^{1}**H NMR spectra for the photocatalytic reaction of 1a with 2a**

General procedure for the photocatalytic reaction of potassium (1,3-dithian-2-yl)trifluoroborate (1a) with electron-deficient alkenes (Table 2)



A 20 mL Schlenk tube was charged with Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.5 mg, 0.25 mmol), dry methanol (2.0 mL), and electron-deficient alkene **2** (0.50 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamp: λ = 425 ± 15 mm). After the reaction was completed, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by the recycled gel permeation chromatography (GPC).

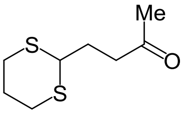
3-(1,3-Dithian-2-yl)propanenitrile (3aa)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.4 mg, 0.25 mmol) and acrylonitrile (**2a**) (26.5 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3aa** (34.6 mg, 80% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 4.11 (t, *J* = 7.2 Hz, 1H; SC*H*S), 2.89 (m, 4H; SCH_2CH$_2$), 2.60 (t, *J* = 7.2 Hz, 2H; CH$_2$CH_2CN), 2.14 (m, 3H; SCH$_2$C*H*H and CH_2CH$_2$CN), 1.94 (m, 1H; SCH$_2$CH*H*). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 118.7 (*C*N), 45.2 (S*C*HS), 31.1 (*C*H$_2$CH$_2$CN), 29.8 (S*C*H$_2$CH$_2$), 25.7 (SCH$_2$*C*H$_2$), 14.9 (*C*H$_2$CN). **HRMS (ESI-TOF):** calculated for $[C_7H_{11}NS_2+Na]^+$ requires 196.0225, found 196.0221.

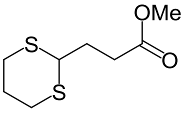
4-(1,3-Dithian-2-yl)butan-2-one (3ab)



According to the general procedure, Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.8 mg, 0.25 mmol) and 3-buten-2-one (**2b**) (35.4 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3ab** (37.1 mg, 78% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 4.05 (t, *J* =7.2 Hz, 1H; SC*H*S), 2.84 (m, 4H; SCH_2CH$_2$), 2.68 (t, *J* = 7.2 Hz, 2H; CH$_2$CH_2C=O), 2.16 (s, 3H; CH_3C=O), 2.09 (m, 3H; SCH$_2$C*H*H and CH_2CH$_2$C=O), 1.89 (m, 1H; SCH$_2$CH*H*). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 207.5 (*C*=O), 46.5 (S*C*HS), 40.2 (CH$_2$*C*H$_2$C=O), 30.2 (*C*H$_3$C=O), 30.1 (S*C*H$_2$CH$_2$), 29.1 (*C*H$_2$CH$_2$C=O), 26.0 (SCH$_2$*C*H$_2$). **HRMS (ESI-TOF):** calculated for $[C_8H_{14}OS_2+Na]^+$ requires 213.0378, found 213.0372.

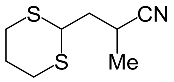
Methyl 3-(1,3-Dithian-2-yl)propanoate (3ac)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.5 mg, 0.25 mmol) and methyl acrylate (**2c**) (43.1 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3ac** (36.6 mg, 71% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 4.06 (t, *J* = 7.2 Hz, 1H; SC*H*S), 3.69 (s, 3H; OCH_3), 2.85 (m, 4H; SCH_2CH$_2$), 2.56 (t, *J* = 7.2 Hz, 2H; CH$_2$CH_2C=O), 2.12 (m, 3H; SCH$_2$C*H*H and CH_2CH$_2$C=O), 1.88 (m, 1H; SCH$_2$CH*H*). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 173.2 (*C*=O), 51.9 (O*C*H$_3$), 46.3 (S*C*HS), 31.1 (CH$_2$*C*H$_2$C=O), 30.4 (*C*H$_2$CH$_2$C=O), 29.9 (S*C*H$_2$CH$_2$), 25.9 (SCH$_2$*C*H$_2$). **HRMS (ESI-TOF):** calculated for $[C_8H_{14}O_2S_2+Na]^+$ requires 229.0327, found 229.0322.

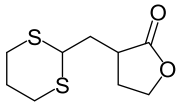
3-(1,3-Dithian-2-yl)-2-methylpropanenitrile (3ad)



According to the general procedure, Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (57.3 mg, 0.25 mmol) and methacrylonitrile (**2d**) (34.0 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3ad** (30.4 mg, 64% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, rt) δ 4.19 (dd, *J* = 9.9 Hz, *J* = 5.2 Hz, 1H; SC*H*S), 3.03 (m, 1H; C*H*CN), 2.90 (m, 4H; $\mathrm{S}\mathit{CH}_2\mathrm{CH}_2$), 2.12 (m, 2H; SCHC*H*H and $\mathrm{SCH_2C}\mathit{H}\mathrm{H}$), 1.91 (m, 2H; SCHCH*H* and $\mathrm{SCH_2CH}\mathit{H}$), 1.36 (d, *J* = 6.4 Hz, 3H; $\mathrm{CHC}\mathit{H}_3$). **^{13}C NMR** (100 MHz, $\mathrm{CDCl_3}$, rt) δ 122.0 (*C*N), 44.4 (S*C*HS), 39.5 ($\mathit{C}\mathrm{H_2CHCN}$), 30.1 ($\mathrm{S}\mathit{C}\mathrm{H_2CH_2}$), 30.0 ($\mathrm{S}\mathit{C}\mathrm{H_2CH_2}$), 25.8 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$), 23.2 (*C*HCN), 18.1 ($\mathrm{CH}\mathit{C}\mathrm{H_3}$). **HRMS (ESI-TOF):** calculated for $[\mathrm{C_8H_{13}NS_2{+}Na}]^+$ requires 210.0382, found 210.0377.

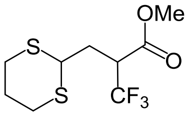
3-((1,3-Dithian-2-yl)methyl)dihydrofuran-2(3H)-one (3ae)



According to the general procedure, Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.6 mg, 0.25 mmol) and α-methylene-γ-butyrolactone (**2e**) (49.2 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3ae** (42.6 mg, 78% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, rt) δ 4.32 (dt, *J* = 9.0 Hz, *J* = 2.0 Hz, 1H; OC*H*H), 4.19 (m, 2H; SC*H*S and OCH*H*), 2.88 (m, 5H; $\mathrm{S}\mathit{CH}_2\mathrm{CH}_2$ and $\mathrm{C{=}OC}\mathit{H}\mathrm{CH_2}$), 2.47 (m, 2H; $\mathrm{SCHC}\mathit{H}_2\mathrm{CH}$), 2.08 (m, 1H; $\mathrm{SCH_2C}\mathit{H}\mathrm{H}$), 1.92 (m, 3H; $\mathrm{SCH_2CH}\mathit{H}$ and $\mathrm{OCH_2C}\mathit{H}_2$). **^{13}C NMR** (100 MHz, $\mathrm{CDCl_3}$, rt) δ 178.6 (*C*=O), 66.5 ($\mathrm{O}\mathit{C}\mathrm{H_2}$), 44.9 (S*C*HS), 37.0 ($\mathrm{SCHCH_2}\mathit{C}\mathrm{H}$), 36.3 ($\mathrm{SCH}\mathit{C}\mathrm{H_2}$), 29.7(2C; $\mathrm{S}\mathit{C}\mathrm{H_2CH_2}$), 29.5 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$), 25.9 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$). **HRMS (ESI-TOF):** calculated for $[\mathrm{C_9H_{14}O_2S_2{+}Na}]^+$ requires 241.0327, found 241.0322.

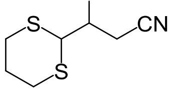
Methyl 2-((1,3-dithian-2-yl)methyl)-3,3,3-trifluoropropanoate (3af)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.5 mg, 0.25 mmol) and methyl 2-(trifluoromethyl) acrylate (**2f**) (77.2 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3af** (54.6 mg, 80% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, rt) δ 3.93 (dd, *J* = 8.9 Hz, *J* = 6.3 Hz, 1H; SC*H*S), 3.81 (s, 3H; $\mathrm{OC}\mathit{H}_3$), 3.52 (m, 1H; $\mathrm{C}\mathit{H}\mathrm{CF_3}$), 2.84 (m, 4H; $\mathrm{S}\mathit{CH}_2\mathrm{CH}_2$), 2.52 (m, 1H; SCHC*H*HCH), 2.26 (m, 1H; SCHCH*H*CH), 2.10 (m, 1H; $\mathrm{SCH_2C}\mathit{H}\mathrm{H}$), 1.94 (m, 1H; $\mathrm{SCH_2CH}\mathit{H}$). **^{13}C NMR** (125 MHz, $\mathrm{CDCl_3}$, rt) δ 167.4 (q, *J* = 3.1 Hz; *C*=O), 124.5 (q, *J* = 266.1 Hz; $\mathit{C}\mathrm{F_3}$), 53.2 ($\mathrm{O}\mathit{C}\mathrm{H_3}$), 47.6 (q, *J* = 27.8 Hz; $\mathit{C}\mathrm{HCF_3}$), 43.3 (S*C*HS), 31.6 (d, *J* = 1.8 Hz; $\mathrm{SCH}\mathit{C}\mathrm{H_2}$), 29.1 ($\mathrm{S}\mathit{C}\mathrm{H_2CH_2}$), 28.9 ($\mathrm{S}\mathit{C}\mathrm{H_2CH_2}$), 25.6 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$). **^{19}F NMR** (470 MHz, $\mathrm{CDCl_3}$) δ -68.0 (d, *J* = 8.5 Hz; $\mathrm{C}\mathit{F}_3$). **HRMS (ESI-TOF):** calculated for $[\mathrm{C_9H_{13}F_3O_2S_2{+}Na}]^+$ requires 297.0201, found 297.0197.

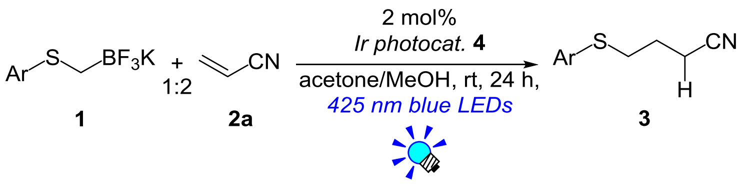
2-(1,3-Dithian-2-yl)succinonitrile (3ai)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.6 mg, 0.25 mmol) and fumaronitrile (**2i**) (39.0 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3ai** (42.5 mg, 86% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

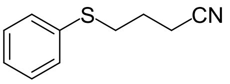
^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, rt) δ 4.15 (d, *J* = 7.2 Hz, 1H; SC*H*S), 3.44 (apparent q, 1H; CNC*H*), 3.02 (m, 4H; $\mathrm{S}\mathit{CH}_2\mathrm{CH}_2$ and $\mathrm{CHC}\mathit{H}_2\mathrm{CN}$), 2.87 (m, 2H; $\mathrm{S}\mathit{CH}_2\mathrm{CH}_2$), 2.14 (m, 1H; $\mathrm{SCH_2C}\mathit{H}\mathrm{H}$), 2.03 (m, 1H; $\mathrm{SCH_2CH}\mathit{H}$). **^{13}C NMR** (125 MHz, $\mathrm{CDCl_3}$, rt) δ 116.9 (*C*NCH), 115.3 ($\mathrm{CH_2}\mathit{C}\mathrm{N}$), 44.1 (S*C*HS), 34.8 (CN*C*H), 28.3 ($\mathrm{S}\mathit{C}\mathrm{H_2CH_2}$), 28.2 ($\mathrm{S}\mathit{C}\mathrm{H_2CH_2}$), 24.6 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$), 19.9 ($\mathrm{CN}\mathit{C}\mathrm{H_2}$). **HRMS (ESI-TOF):** calculated for $[\mathrm{C_8H_{10}N_2S_2{+}Na}]^+$ requires 221.0178, found 221.0173.

General procedure for the photocatalytic reaction of arylthiomethyltrifluoroborates with acrylonitrile (2a) (Scheme 2)



A 20 mL Schlenk tube was charged with Ir photocatalyst **4** (5.0 mg, 5.0 μmol), arylthiomethyltrifluoroborate **1** (0.25 mmol), dry methanol (1.0 mL), dry acetone (1.0 mL) and acrylonitrile (**2a**) (26.5 mg, 0.50 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamp: $\lambda = 425 \pm 15$ nm). After the reaction was completed, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by the recycled gel permeation chromatography (GPC).

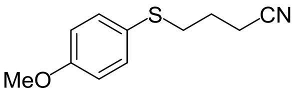
4-(Phenylthio)butanenitrile (3ba)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium phenylthiomethyltrifluoroborate (**1b**) (57.5 mg, 0.25 mmol) and acrylonitrile (**2a**) (26.7 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3ba** (14.2 mg, 32% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.29 (5H; *phenyl*), 3.04 (t, *J* = 7.0 Hz, 2H; SCH_2), 2.52 (t, *J* = 7.0 Hz, 2H; CH_2CN), 1.96 (apparent quint, 2H; CH_2CH_2CN). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 134.8 (*phenyl*), 130.3 (*phenyl*), 129.3 (*phenyl*), 126.9 (*phenyl*), 119.2 (*C*N), 32.7 (SCH_2), 24.9 (CH_2CH_2CN), 16.0 (CH_2CN). **HRMS (ESI-TOF):** calculated for $[C_{10}H_{11}NS+Na]^+$ requires 200.0504, found 200.0510.

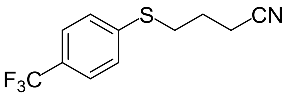
4-((4-Methoxyphenyl)thio)butanenitrile (3ca)



According to the general procedure, Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium 4-methoxyphenylthiomethyltrifluoroborate (**1c**) (65.0 mg, 0.25 mmol) and acrylonitrile (**2a**) (26.6 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3ca** (8.0 mg, 15% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.32 (d, *J* = 8.5 Hz, 2H; *phenyl*), 6.86 (d, *J* = 8.5 Hz, 2H; *phenyl*), 3.80 (s, 3H; CH_3O), 2.92 (t, *J* = 6.5 Hz, 2H; SCH_2), 2.51 (t, *J* = 6.5 Hz, 2H; CH_2CN), 1.90 (apparent quint, 2H; SCH_2CH_2). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 159.6 (*phenyl*), 134.1 (*phenyl*), 124.8 (*phenyl*), 119.3 (*C*N), 114.9 (*phenyl*), 55.5 (CH_3O), 34.7 (SCH_2), 25.0 (CH_2CH_2CN), 15.9 (CH_2CN). **HRMS (ESI-TOF):** calculated for $[C_{11}H_{13}NOS+Na]^+$ requires 230.0610, found 230.0607.

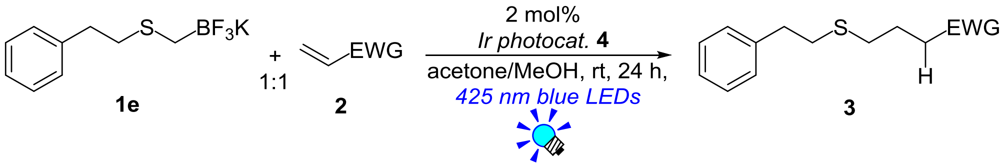
4-((4-(Trifluoromethyl)phenyl)thio)butanenitrile (3da)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium 4-trifluoromethylphenylthiomethyltrifluoroborate (**1d**) (74.5 mg, 0.25 mmol) and acrylonitrile (**2a**) (26.6 mg, 0.50 mmol) with irradiation of blue LEDs afforded **3da** (26.1 mg, 43% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

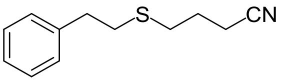
^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.55 (d, *J* = 8.0 Hz, 2H; *phenyl*), 7.40 (d, *J* = 8.0 Hz, 2H; *phenyl*), 3.12 (t, *J*= 7.0 Hz, 2H; SCH_2), 2.53 (t, *J* = 7.0 Hz, 2H; CH_2CN), 2.02 (apparent quint, 2H; CH_2CH_2CN). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 140.5 (*phenyl*), 128.4 (*phenyl*), 126.1 (q, *J* = 3.6 Hz; *phenyl*), 124.1 (q, *J* = 270.1 Hz; CF_3), 123.1 (*phenyl*), 118.9 (*C*N), 31.4 (S*C*H_2), 24.7 (*C*H_2CH_2CN), 16.2 (*C*H_2CN). **^{19}F NMR** (500 MHz, $CDCl_3$) δ -62.5 (s; C*F_3*). **HRMS (ESI-TOF):** calculated for $[C_{11}H_{10}F_3NS+Na]^+$ requires 268.0378, found 268.0375.

General procedure for the photocatalytic reaction of potassium phenethylthiomethyltrifluoroborate (1e) with electron-deficient alkenes (Scheme 2 and Table 3)



A 20 mL Schlenk tube was charged with Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (64.5 mg, 0.25 mmol), dry methanol (1.0 mL), dry acetone (1.0 mL), and electron-deficient alkene **2** (0.25 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamp: $\lambda = 425 \pm 15$ mm). After the reaction was completed, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by the recycled gel permeation chromatography (GPC).

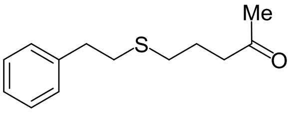
4-(Phenethylthio)butanenitrile (3ea)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (64.8 mg, 0.25 mmol) and acrylonitrile (**2a**) (13.8 mg, 0.25 mmol) with irradiation of blue LEDs afforded **3ea** (43.1 mg, 84% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.27 (5H; *phenyl*), 2.89 (m, 2H; phenyl-C*H*$_2$), 2.78 (m, 2H; phenyl-CH$_2$C*H*$_2$), 2.65 (t, *J* = 7.2 Hz, 2H; C*H*$_2$CH$_2$CH$_2$CN), 2.48 (t, *J* = 7.2 Hz, 2H; C*H*$_2$CN), 1.92 (apparent quint, 2H; CH$_2$C*H*$_2$CH$_2$CN). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 140.3 (*phenyl*), 128.7 (*phenyl*), 128.6 (*phenyl*), 126.6 (*phenyl*), 119.3 (*C*N), 36.3 (phenyl-*C*H$_2$), 33.8 (phenyl-CH$_2$*C*H$_2$), 30.9 (*C*H$_2$CH$_2$CH$_2$CN), 25.3 (*C*H$_2$CH$_2$CN), 16.1 (*C*H$_2$CN). **HRMS (ESI-TOF):** calculated for $[C_{12}H_{15}NS+Na]^+$ requires 228.0817, found 228.0816.

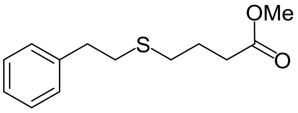
4-(Phenethylthio)butan-2-one (3eb)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (64.4 mg, 0.25 mmol) and 3-buten-2-one (**2b**) (17.4 mg, 0.25 mmol) with irradiation of blue LEDs afforded **3eb** (41.1 mg, 74% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.26 (5H; *phenyl*), 2.89 (m, 2H; phenyl-C*H*$_2$), 2.77 (m, 2H; phenyl-CH$_2$C*H*$_2$), 2.55 (m, 4H; C*H*$_2$CH$_2$C*H*$_2$C=O), 2.14 (s, 3H; C*H*$_3$C=O), 1.88 (apparent quint, 2H; SCH$_2$C*H*$_2$CH$_2$C=O). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 208.3 (*C*=O), 140.6 (*phenyl*), 128.6 (*phenyl*), 128.6 (*phenyl*), 126.5 (*phenyl*), 42.2 (*C*H$_2$C=O), 36.4 (phenyl-*C*H$_2$), 33.5 (phenyl-CH$_2$*C*H$_2$), 31.6 (*C*H$_2$CH$_2$CH$_2$C=O), 30.2 (*C*H$_3$C=O), 23.2 (CH$_2$*C*H$_2$CH$_2$C=O). **HRMS (ESI-TOF):** calculated for $[C_{13}H_{18}OS+Na]^+$ requires 245.0971, found 245.0967.

Methyl 3-(phenethylthio)propanoate (3ec)

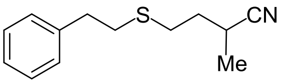


According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (64.6 mg, 0.25 mmol) and methyl acrylate (**2c**) (21.5 mg, 0.25 mmol) with irradiation of blue LEDs afforded **3ec** (42.3 mg, 71% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.26 (5H; *phenyl*), 3.68 (s, 3H; OC*H*$_3$), 2.89 (m, 2H; phenyl-C*H*$_2$), 2.77 (m, 2H; phenyl-CH$_2$C*H*$_2$), 2.57 (t, *J* = 7.2 Hz, 2H; C*H*$_2$C=O), 2.44 (t, *J* = 7.3 Hz, 2H; C*H*$_2$CH$_2$CH$_2$C=O), 1.92 (apparent quint, 2H; C*H*$_2$CH$_2$C=O). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 173.7 (*C*=O), 140.7 (*phenyl*), 128.7

(*phenyl*), 128.6 (*phenyl*), 126.5 (*phenyl*), 51.7 ($\mathrm{O}C\mathrm{H_3}$), 36.5 (phenyl-$C\mathrm{H_2}$), 33.6 (phenyl-$\mathrm{CH_2}C\mathrm{H_2}$), 33.0 ($C\mathrm{H_2CH_2CH_2C{=}O}$), 31.7 ($C\mathrm{H_2C{=}O}$), 24.9 ($C\mathrm{H_2CH_2C{=}O}$). **HRMS (ESI-TOF):** calculated for $[\mathrm{C_{13}H_{18}O_2S+Na}]^+$ requires 261.0920, found 261.0922.

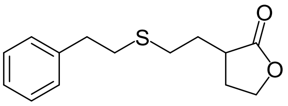
2-Methyl-4-(phenethylthio)butanenitrile (3ed)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (65.1 mg, 0.25 mmol) and methacrylonitrile (**2d**) (17.0 mg, 0.25 mmol) with irradiation of blue LEDs afforded **3ed** (33.7 mg, 60% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, rt) δ 7.26 (5H; *phenyl*), 2.90 (m, 2H; phenyl-$\mathrm{C}H_2$), 2.82 (m, 3H; phenyl-$\mathrm{CH_2C}H_2$ and $\mathrm{C}H\mathrm{CN}$), 2.67 (m, 2H; $\mathrm{C}H_2\mathrm{CH_2CHCN}$), 1.83 (m, 2H; $\mathrm{C}H_2\mathrm{CHCN}$), 1.33 (d, J = 7.0 Hz, 3H; $\mathrm{CHC}H_3$). **^{13}C NMR** (125 MHz, $\mathrm{CDCl_3}$, rt) δ 140.3 (*phenyl*), 128.6 (*phenyl*), 128.6 (*phenyl*), 126.6 (*phenyl*), 122.5 (CN), 36.3 (phenyl-$C\mathrm{H_2}$), 33.9 (phenyl-$\mathrm{CH_2}C\mathrm{H_2}$), 33.9 ($C\mathrm{H_2CHCN}$), 29.6 ($C\mathrm{H_2CH_2CHCN}$), 24.5 ($C$HCN), 17.9 ($\mathrm{CH}C\mathrm{H_3}$). **HRMS (ESI-TOF):** calculated for $[\mathrm{C_{13}H_{17}NS+Na}]^+$ requires 242.0974, found 242.0976.

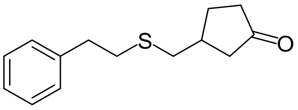
3-(2-(Phenethylthio)ethyl)dihydrofuran-2(3H)-one (3ee)



According to the general procedure, Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (65.6 mg, 0.25 mmol) and α-methylene-γ-butyrolactone (**2e**) (25.0 mg, 0.25 mmol) with irradiation of blue LEDs afforded **3ee** (40.1 mg, 63% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, rt) δ 7.26 (5H; *phenyl*), 4.36 (m, 1H; $\mathrm{OC}H\mathrm{HCH_2}$), 4.19 (m, 1H; $\mathrm{OCH}H\mathrm{CH_2}$), 2.90 (m, 2H; phenyl-$\mathrm{C}H_2$), 2.80 (m, 2H; phenyl-$\mathrm{CH_2C}H_2$), 2.73 (m, 3H; $\mathrm{C}H\mathrm{C{=}O}$ and $\mathrm{SC}H_2\mathrm{CH_2CH}$), 2.54 (m, 1H; $\mathrm{OCH_2C}H\mathrm{H}$), 2.17 (m, 1H; $\mathrm{OCH_2CH}H$), 1.82 (m, 1H; $\mathrm{SCH_2C}H\mathrm{HCH}$), 1.72 (m, 1H; $\mathrm{SCH_2CH}H\mathrm{CH}$). **^{13}C NMR** (125 MHz, $\mathrm{CDCl_3}$, rt) δ 179.2 (C=O), 140.5 (*phenyl*) 128.6 (*phenyl*), 128.6 (*phenyl*) 126.6 (*phenyl*), 66.6 ($\mathrm{O}C\mathrm{H_2CH_2}$), 38.0 (phenyl-$C\mathrm{H_2}$), 36.3 (phenyl-$\mathrm{CH_2}C\mathrm{H_2}$), 33.4 ($C$HC=O), 30.1 ($\mathrm{SCH_2}C\mathrm{H_2CH}$), 29.8 ($\mathrm{S}C\mathrm{H_2CH_2CH}$), 28.8 ($\mathrm{OCH_2}C\mathrm{H_2}$). **HRMS (ESI-TOF):** calculated for $[\mathrm{C_{14}H_{18}O_2S+Na}]^+$ requires 273.0920, found 273.0916.

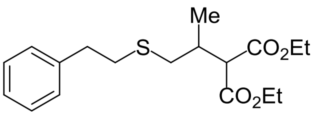
3-((Phenethylthio)methyl)cyclopentan-1-one (3eg)



According to the general procedure, Ir photocatalyst **4** (12.0 mg, 12.0 μmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (129.0 mg, 0.50 mmol) and 2-cyclopenten-1-one (**2g**) (19.9 mg, 0.25 mmol) with irradiation of blue LEDs afforded 3eg (23.6 mg, 41% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, rt) δ 7.26 (5H; *phenyl*), 2.90 (m, 2H; phenyl-$\mathrm{C}H_2$), 2.80 (m, 2H; phenyl-$\mathrm{CH_2C}H_2$), 2.63 (d, J = 8.5 Hz, 2H; $\mathrm{SC}H_2\mathrm{CH}$), 2.43 (m, 2H; $\mathrm{CHC}H\mathrm{HC{=}O}$, $\mathrm{C}H\mathrm{CH_2C{=}O}$), 2.33 (m, 1H; $\mathrm{CH_2C}H\mathrm{HC{=}O}$), 2.20 (m, 2H; $\mathrm{C}H\mathrm{HCH_2C{=}O}$ and $\mathrm{CH_2CH}H\mathrm{C{=}O}$), 1.97 (m, 1H; $\mathrm{CHC}H\mathrm{HC{=}O}$), 1.65 (m, 1H; $\mathrm{CH}H\mathrm{CH_2C{=}O}$). **^{13}C NMR** (125 MHz, $\mathrm{CDCl_3}$, rt) δ 218.6 (C=O), 140.5 (*phenyl*), 128.6 (*phenyl*), 128.6 (*phenyl*), 126.6 (*phenyl*), 44.7 ($\mathrm{CH}C\mathrm{H_2C{=}O}$), 38.4 ($\mathrm{CHCH_2}C\mathrm{H_2C{=}O}$), 37.8 ($\mathrm{S}C\mathrm{H_2CH}$), 37.2 ($\mathrm{SCH_2}C\mathrm{H}$), 36.6 (phenyl-$C\mathrm{H_2}$), 34.5 (phenyl-$\mathrm{CH_2}C\mathrm{H_2}$), 28.9 ($C\mathrm{H_2CH_2C{=}O}$)**.** **HRMS (ESI-TOF):** calculated for $[\mathrm{C_{14}H_{18}OS+Na}]^+$ requires 257.0971, found 257.0976.

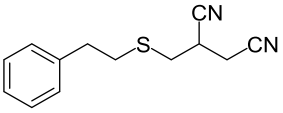
Diethyl 2-(1-(phenethylthio)propan-2-yl)malonate (3eh)



According to the general procedure, Ir photocatalyst **4** (12.5 mg, 12.5 μmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (129.1 mg, 0.50 mmol) and diethyl ethylidenemalonate (**2h**) (46.6 mg, 0.25 mmol) with irradiation of blue LEDs afforded **3eh** (52.5 mg, 62% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.26 (5H; *phenyl*), 4.19 (m, 4H; $OC\mathit{H_2}CH_3$), 3.48 (d, *J* = 8.7 Hz, 1H; C=OC*H*), 2.88 (m, 2H; phenyl-C*H₂*), 2.79 (m, 3H; phenyl-$CH_2C\mathit{H_2}$ and $CH_3C\mathit{H}$), 2.46 (m, 2H; $SC\mathit{H_2}CH$), 1.268 (t, *J* = 8.9 Hz, 3H; $OCH_2C\mathit{H_3}$), 1.265 (t, *J* = 8.9 Hz, 3H; $OCH_2C\mathit{H_3}$), 1.11 (d, *J* = 8.2 Hz, 3H; $CHC\mathit{H_3}$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 168.8 (*C*=O), 168.5 (*C*=O), 140.6 (*phenyl*) 128.6 (*phenyl*), 128.5(*phenyl*) 126.4 (*phenyl*), 61.5 ($O\mathit{C}H_2CH_3$), 61.4 ($O\mathit{C}H_2CH_3$), 56.0 (C=O*C*H), 37.1 ($SCH_2\mathit{C}H$), 36.4 (phenyl-$\mathit{C}H_2$), 34.0 (phenyl-$CH_2\mathit{C}H_2$), 33.7 ($S\mathit{C}H_2CH$), 16.9 ($\mathit{C}H_3CH$), 14.2 ($OCH_2\mathit{C}H_3$), 14.2 ($OCH_2\mathit{C}H_3$). **HRMS (ESI-TOF):** calculated for $[C_{18}H_{26}O_4S+Na]^+$ requires 361.1444, found 361.1450.

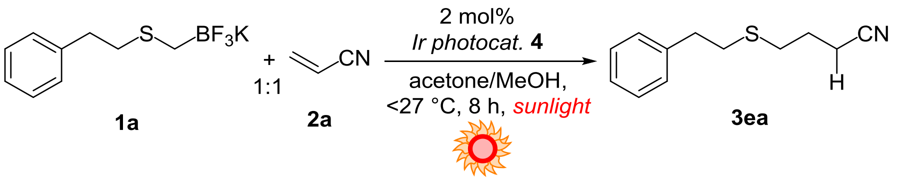
2-((Phenethylthio)methyl)succinonitrile (3ei)



According to the general procedure, Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (64.5 mg, 0.25 mmol) and fumaronitrile (**2i**) (19.5 mg, 0.25 mmol) with irradiation of blue LEDs afforded **3ei** (49.0 mg, 85% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.27 (5H; *phenyl*), 2.93 (m, 5H; phenyl-C*H₂*, phenyl-$CH_2C\mathit{H_2}$ and C*H*CN), 2.88 (m, 1H; SC*H*HCHCN), 2.82 (m, 3H; SCH*H*CHCN and $CHC\mathit{H_2}CN$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 139.7 (*phenyl*), 128.9 (*phenyl*), 128.8 (*phenyl*), 127.1 (*phenyl*), 118.2 (*C*NCH), 115.4 ($CH_2\mathit{C}N$), 36.4 (phenyl-$\mathit{C}H_2$), 34.9 (phenyl-$CH_2\mathit{C}H_2$), 33.7 ($S\mathit{C}H_2CHCN$), 29.5 (CN*C*H), 20.0 ($\mathit{C}H_2CN$). **HRMS (ESI-TOF):** calculated for $[C_{13}H_{14}N_2S+Na]^+$ requires 253.0770, found 253.0769.

Sunlight-driven reaction



Cylindrical vessel was used for photocatalytic reaction under sunlight. Cylindrical vessel was charged with Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**1e**) (64.5 mg, 0.25 mmol), dry methanol (1.0 mL), dry acetone (1.0 mL) and acrylonitrile (**2a**) (13.4 mg, 0.25 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction mixture was exposed to sunlight for 8 h (in June 28th, 2014) below 27 ˚C. After workup, **3ea** was obtained as pale yellow oil in 75% yield (38.5 mg, 0.19 mmol).

Luminescence quenching experiments

Emission spectra for the Ir photocatalyst **4** in a deaerated solution whose concentration was adjusted so as to show the absorbance 0.1 at excitation wavelength were recorded at room temperature. Ir photocatalyst **4** excited at 379 nm in DMSO exhibited band at 479 nm. General experimental procedure: a solution of the Ir photocatalyst **4** was prepared and degassed three times via freeze-pump-thaw cycle in a 1 cm quartz cell equipped with a sphere moiety for freeze. The solution of quencher was added to the solution of the Ir photocatalyst **4** before measurement of emission intensities.

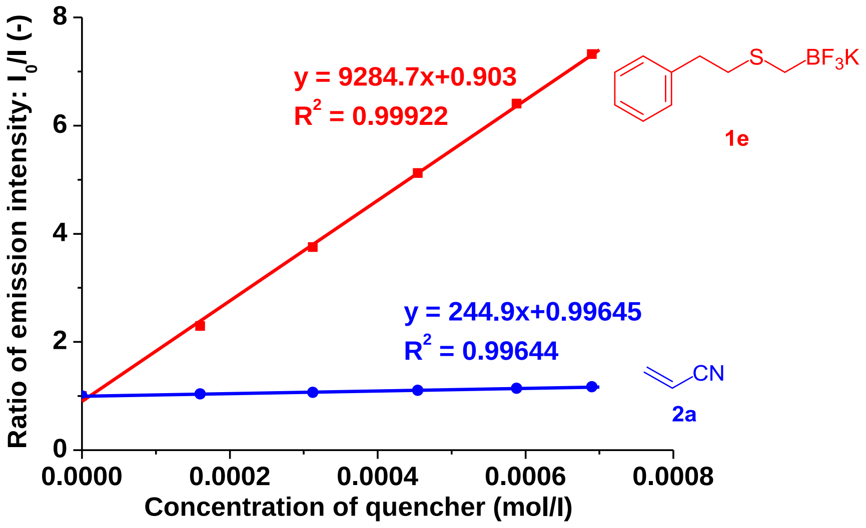
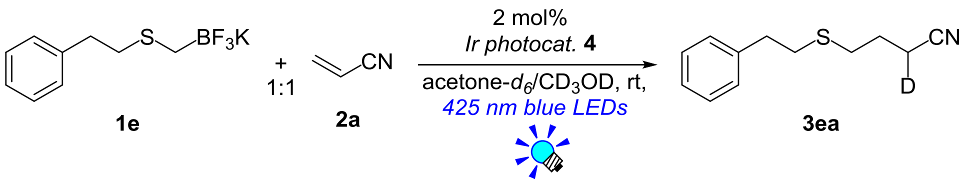


Figure S2. Stern-Volmer plots for 1e and 2a

Time profile for photocatalytic C-C bond formation of potassium phenethylthiomethyltrifluoroborate (1e) with acrylonitrile (2a)



According to the typical NMR experiment procedure, the photocatalytic C–C bond formation of **1e** with **2a** using Ir photocatalyst **4** was performed with/without visible light irradiation. The time profile is shown in Figure S3. As a result, continuous irradiation of visible light is essential for efficient reaction. Furthermore, the result of this experiment suggests that radical chain propagation mechanism is not main component in this reaction.

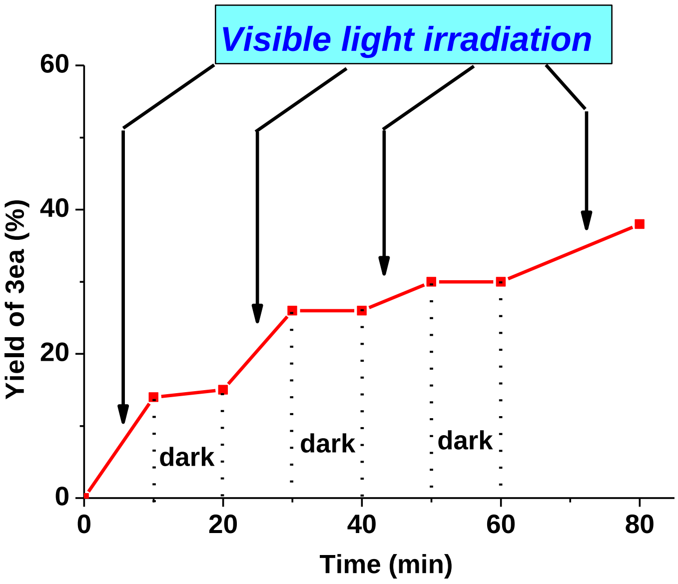


Figure S3. Dependence of thioalkylation on constant irradiation

Cyclic voltammograms

Electrochemical measurements were recorded on Hokutodenkou HZ-5000 analyzer (observed in 0.002 M MeCN; $[NBu_4](PF_6)$ = 0.1 M; Ag/AgCl = electrode; reported with respect to the $[FeCp_2]/[FeCp_2]^+$ couple).

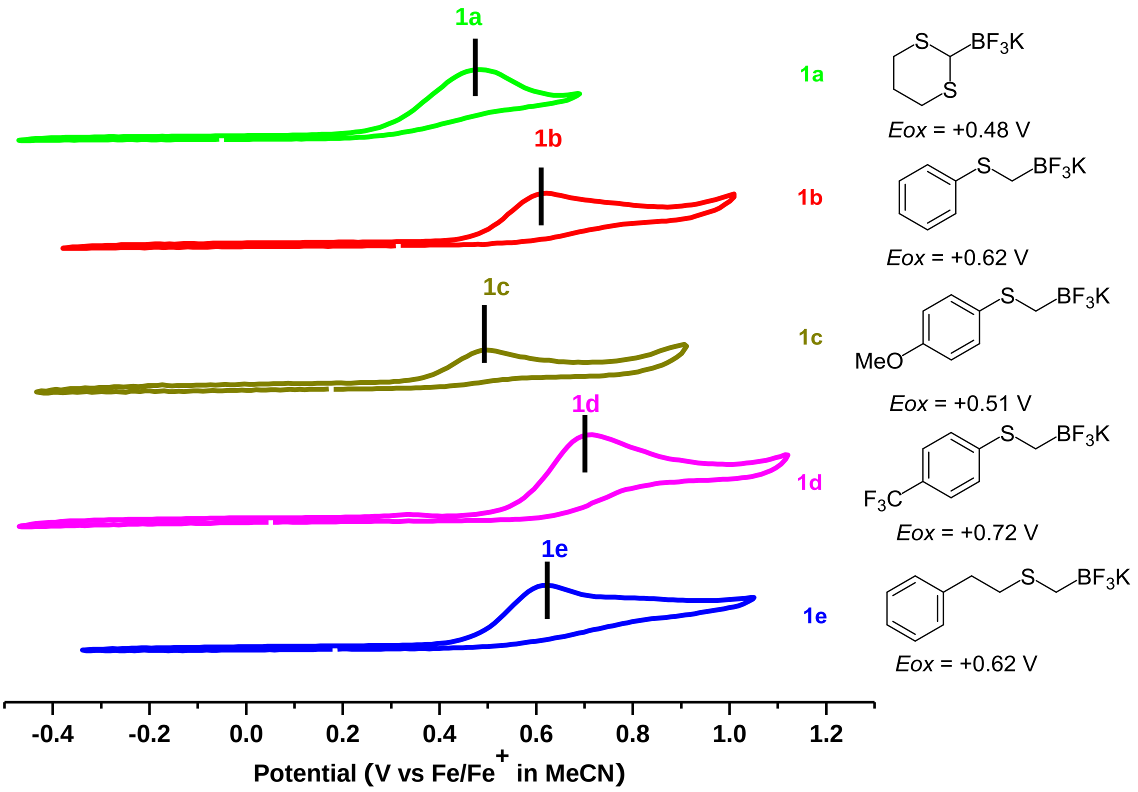
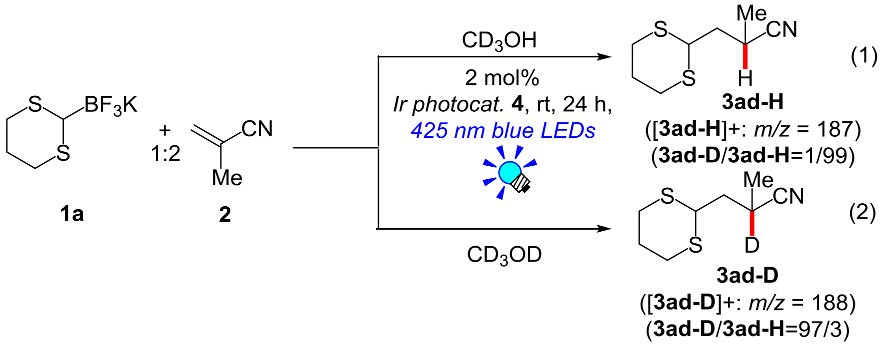


Figure S4. CV traces for 1a, 1b, 1c, 1d and 1e

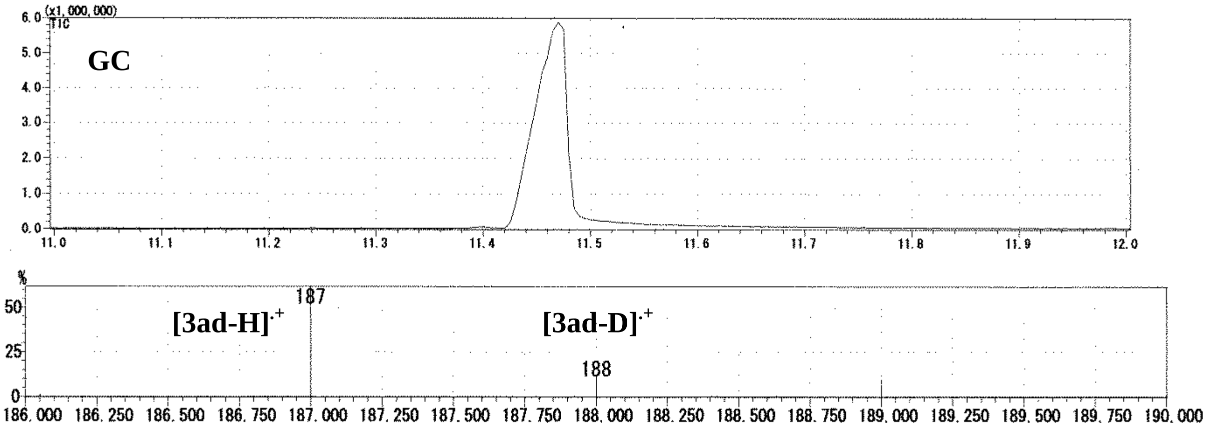
Isotope incorporation experiments



According to the typical NMR experimental procedure, the isotope incorporation experiments (1) and (2) were conducted by using CD_3OH and CD_3OD, respectively. GC-MS analyses of (1) and (2) were carried out using a GC-MS system (Shimadzu GC-MS Parvum 2, capillary column: Rxi®-5ms (30 m × 0.25 mm × 0.25 μm)). With helium as carrier gas at 1.2 mL min^{-1} through column, the injection in the GC system was performed in split mode and the injector temperature was 250 ˚C. The GC oven temperature was held at 50 ˚C for 4 min, increased to 250 ˚C by a temperature ramp of 10 ˚C min^{-1} and held for 10 min. The ion source temperature was 230 ˚C. Mass spectral analyses were carried out in full scan mode. The peaks of **3ad-H** and **3ad-D** were detected at

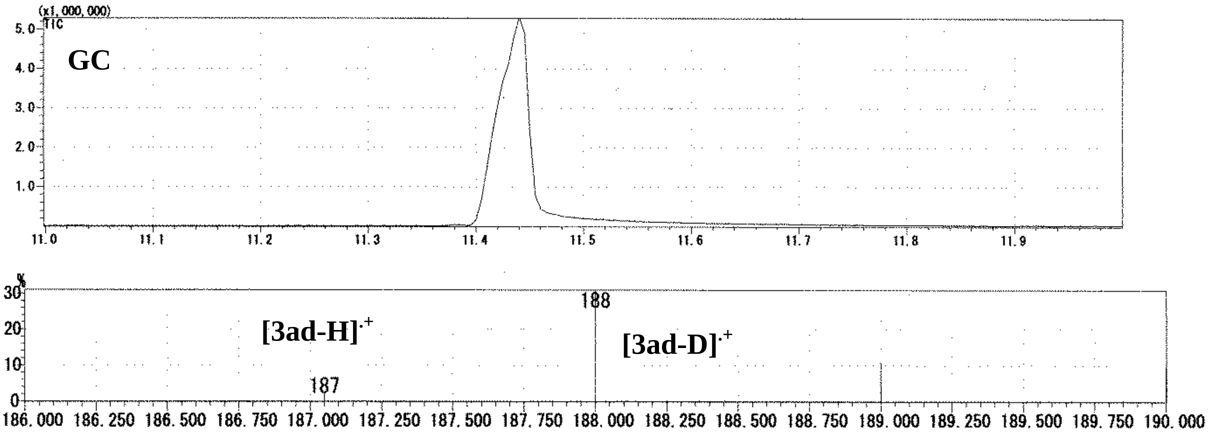
11.44 min. On the basis of absolute intensity of isotope peaks in MS spectra, the ratios of **3ad-D**/**3ad-H** were calculated.

(1)



Absolute intensity: 187(434775), 188(48164), 189(42506)

(2)



Absolute intensity: 187(12859), 188(414460), 189(56308)

Figure S5 GC-MS spetra of (1) and (2)

References

[1] a) D. Hanss, J. C. Freys, G. Bernardinelli and O. S. Wenger, *Eur. J. Inorg. Chem*. **2009**, 4850. b) M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, Jr. G. G. Malliaras and S. Bernhard, *Chem. Mater*. **2005**, *17*, 5712. c) H. B. Ross, M. Boldaji, D. P. Rillema, C. B. Blanton and R. P. White, *Inorg. Chem*. **1989**, *28*, 1013.

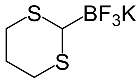
[2] A.S. Vieira, P. F. Fiorante, J. Z. Schpector, D. Alves, G. V. Botteselle and H. A. Stefani, *Tetrahedron*. **2008**, *64*, 7234.

[3] J. Bieron and F. Dinan, *J. Org. Chem.* **1989**, *54*, 3019.

[4] K. Liu, P. Lee, S. Wang, Y. Cheng, J. Fang and C. Wong, *Bioorg. Med. Chem.* **2011**, *19*, 479

^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra

^{1}H NMR of



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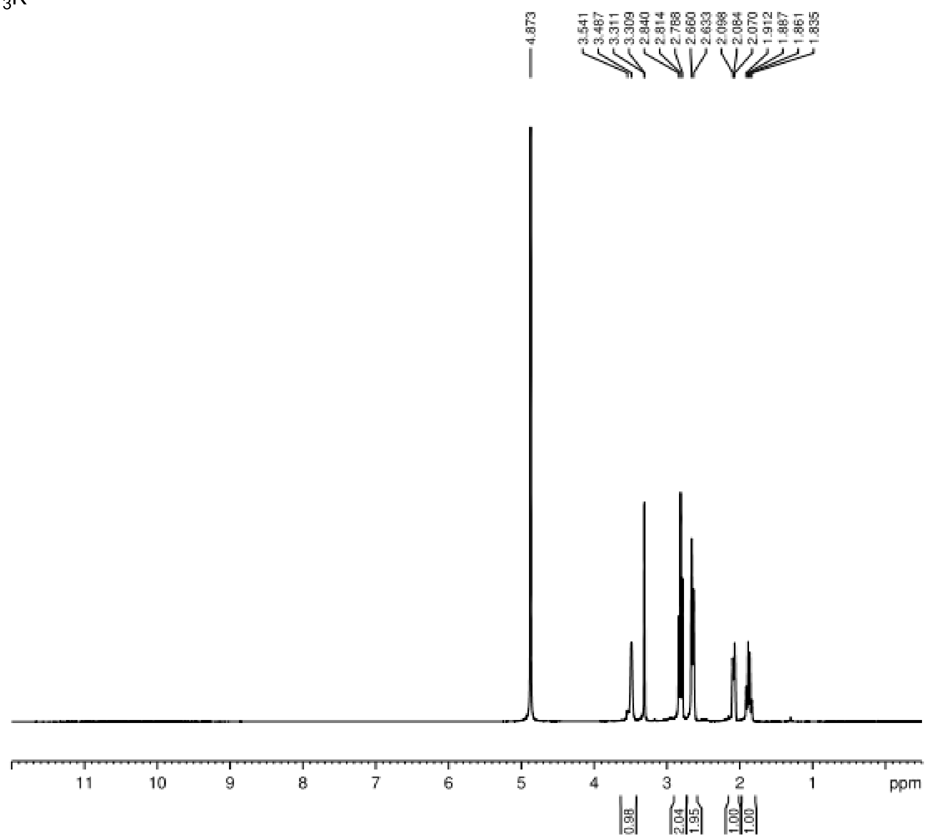

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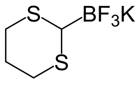

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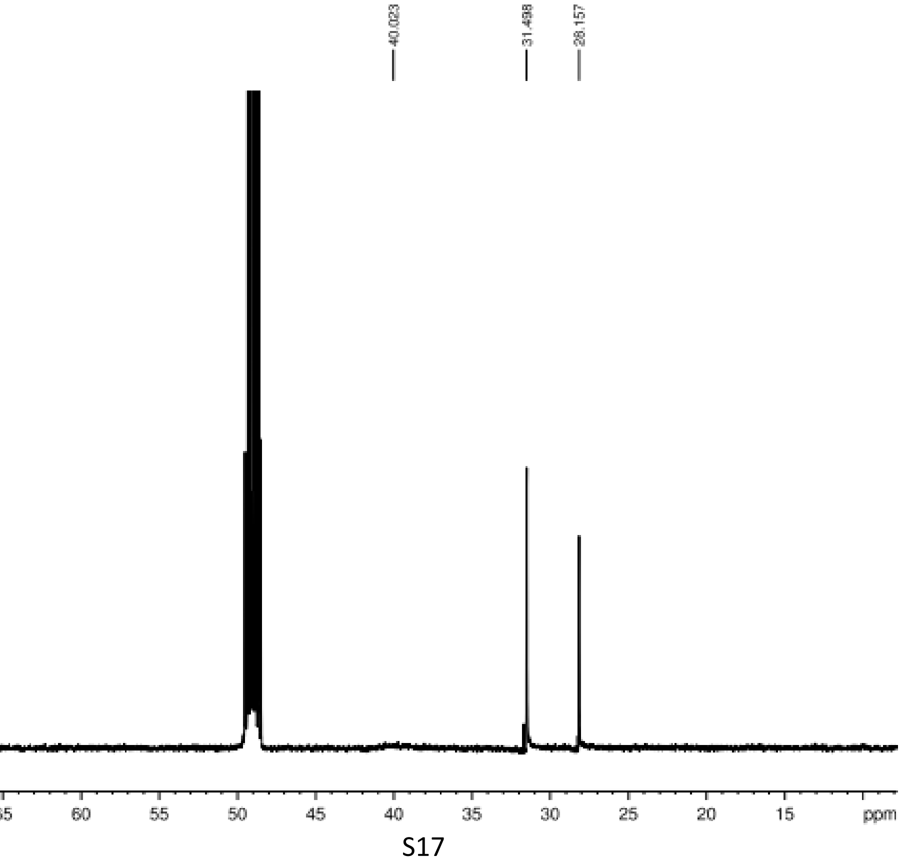

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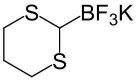

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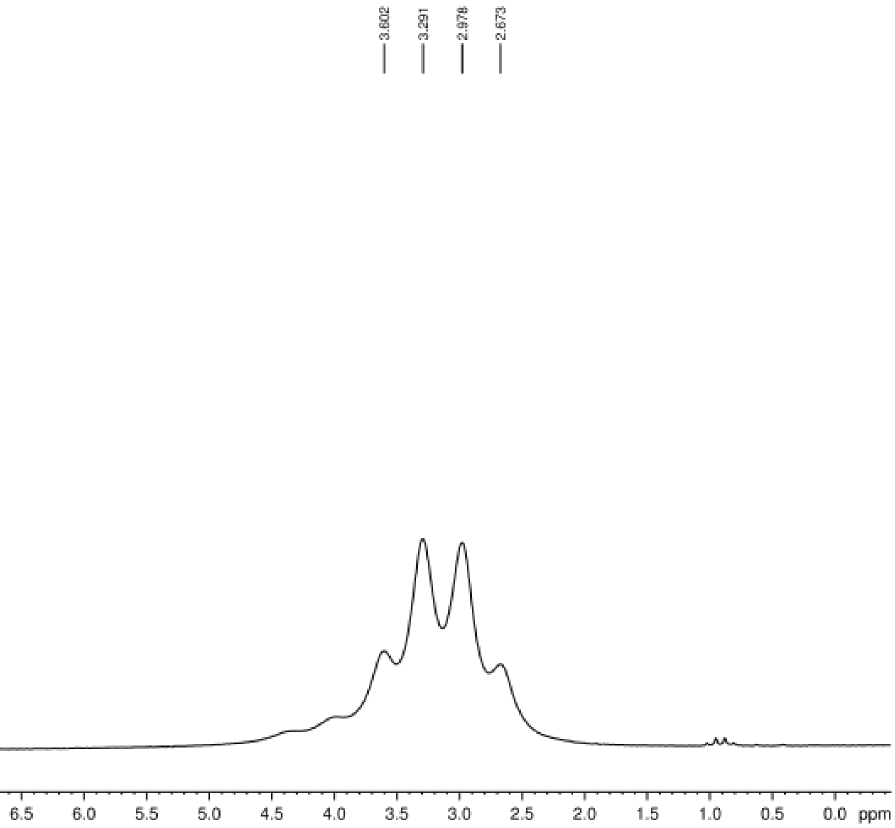

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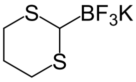

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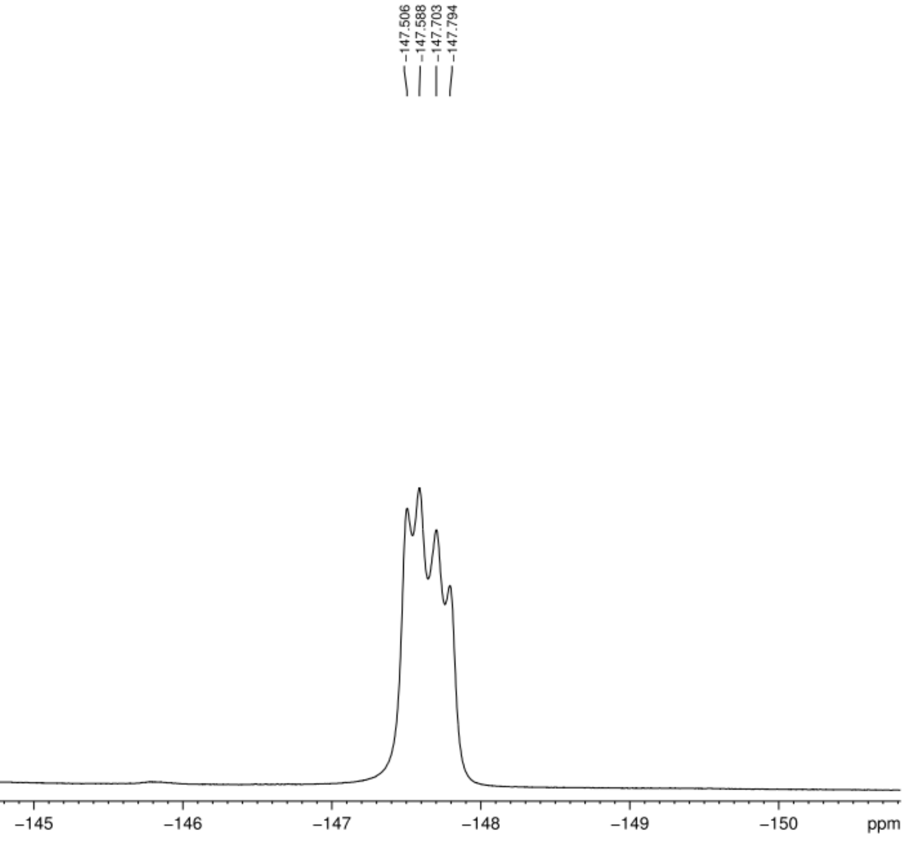

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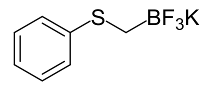

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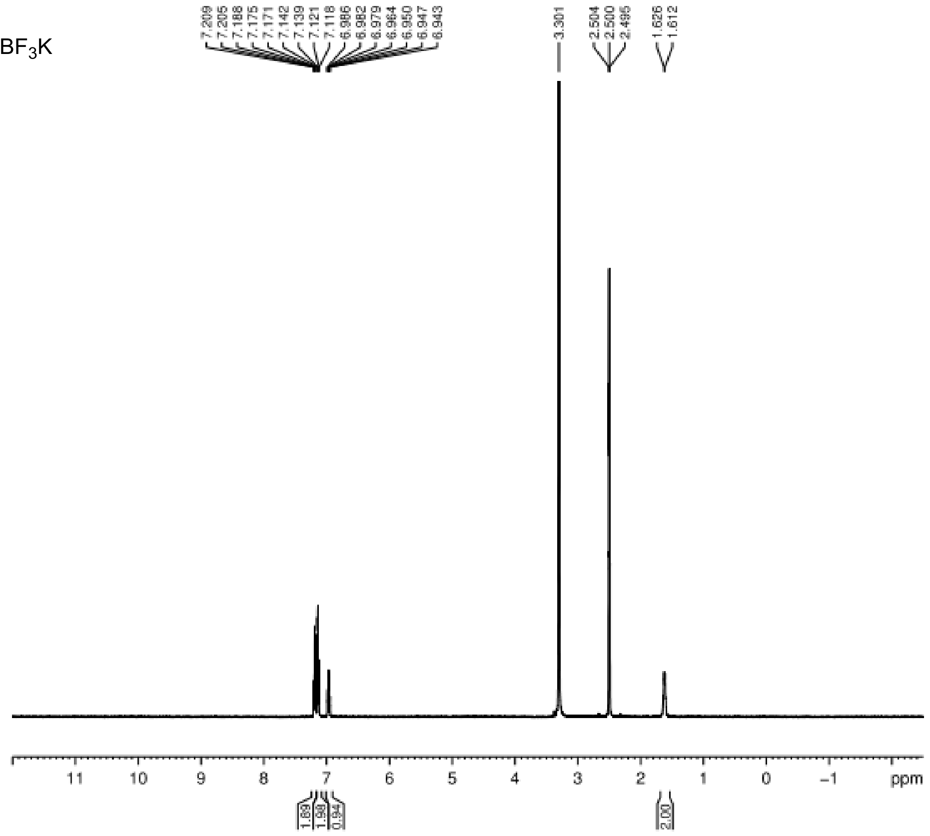

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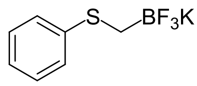

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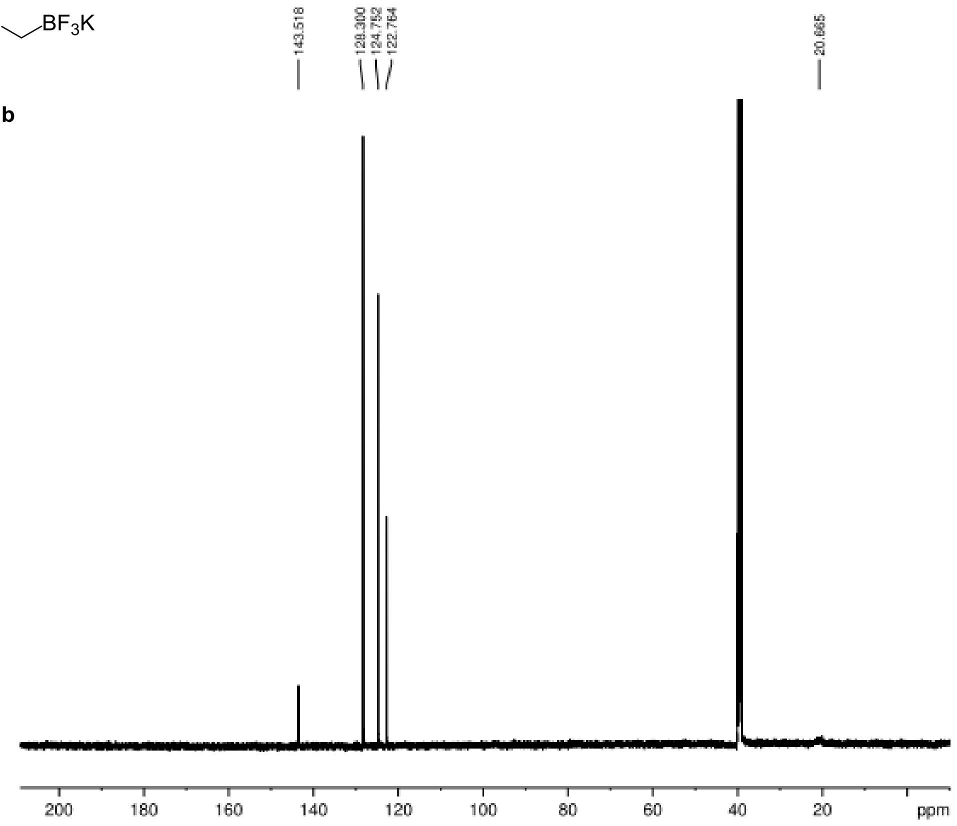

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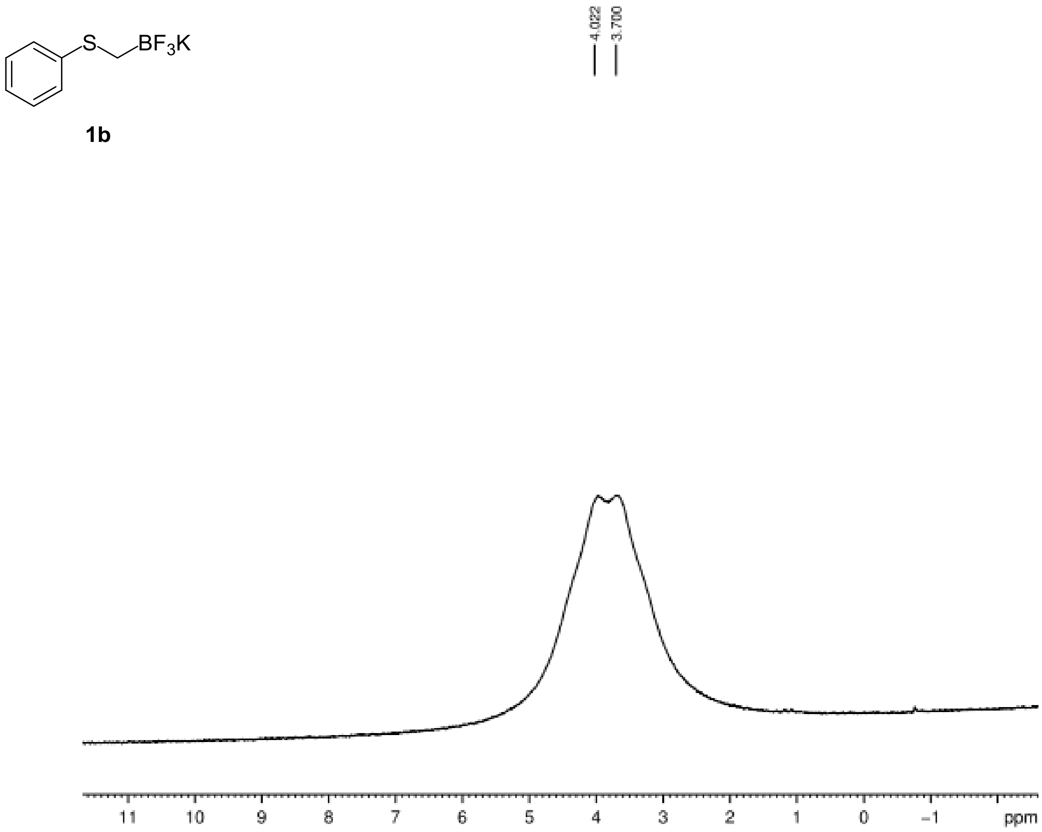

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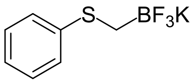

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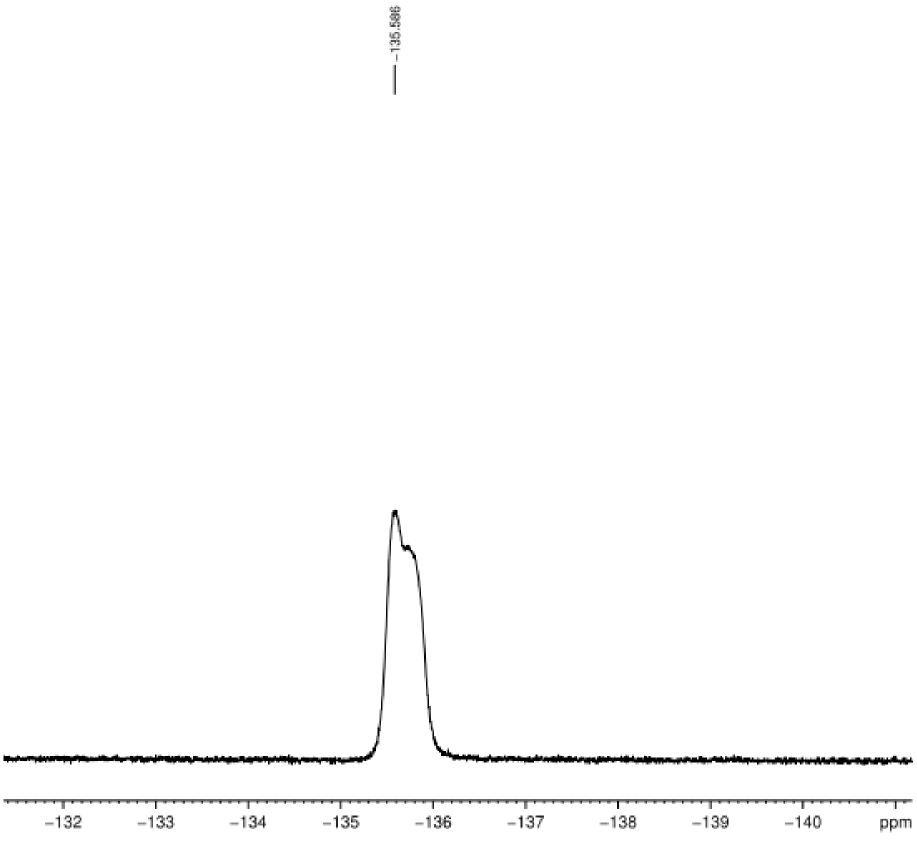

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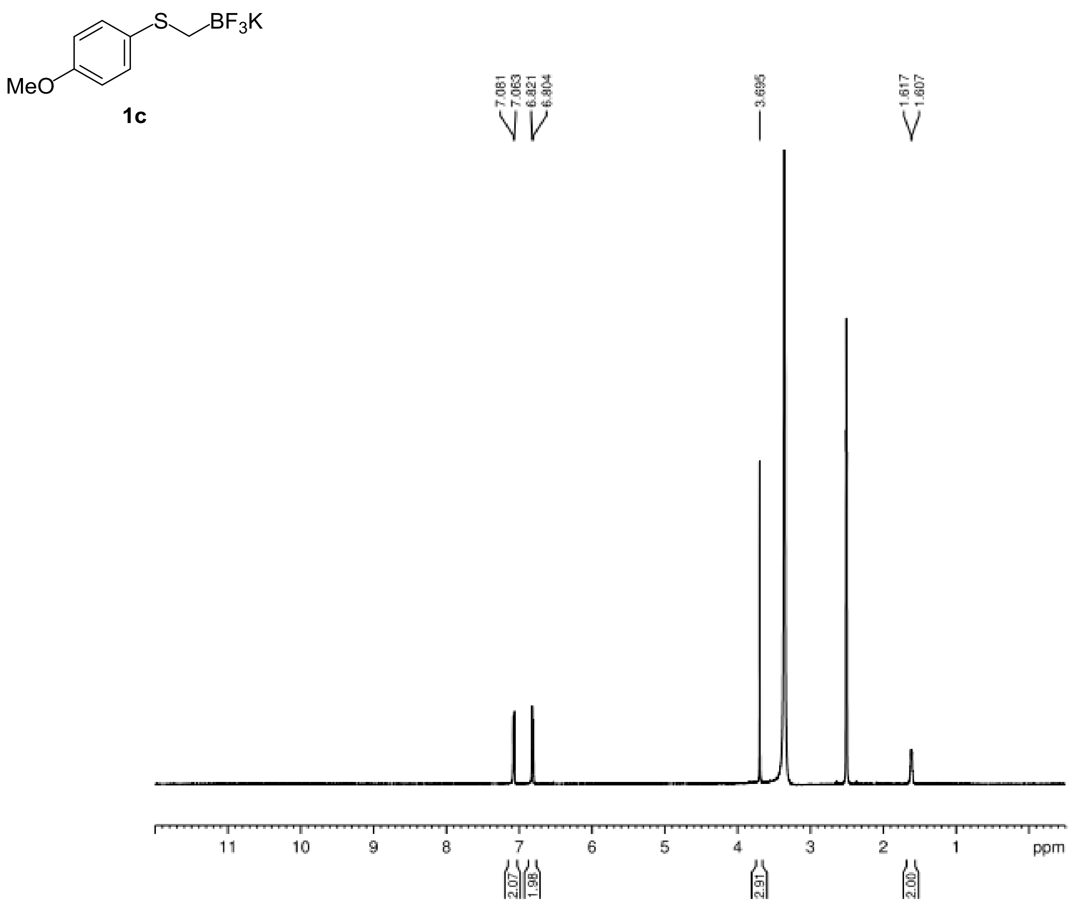
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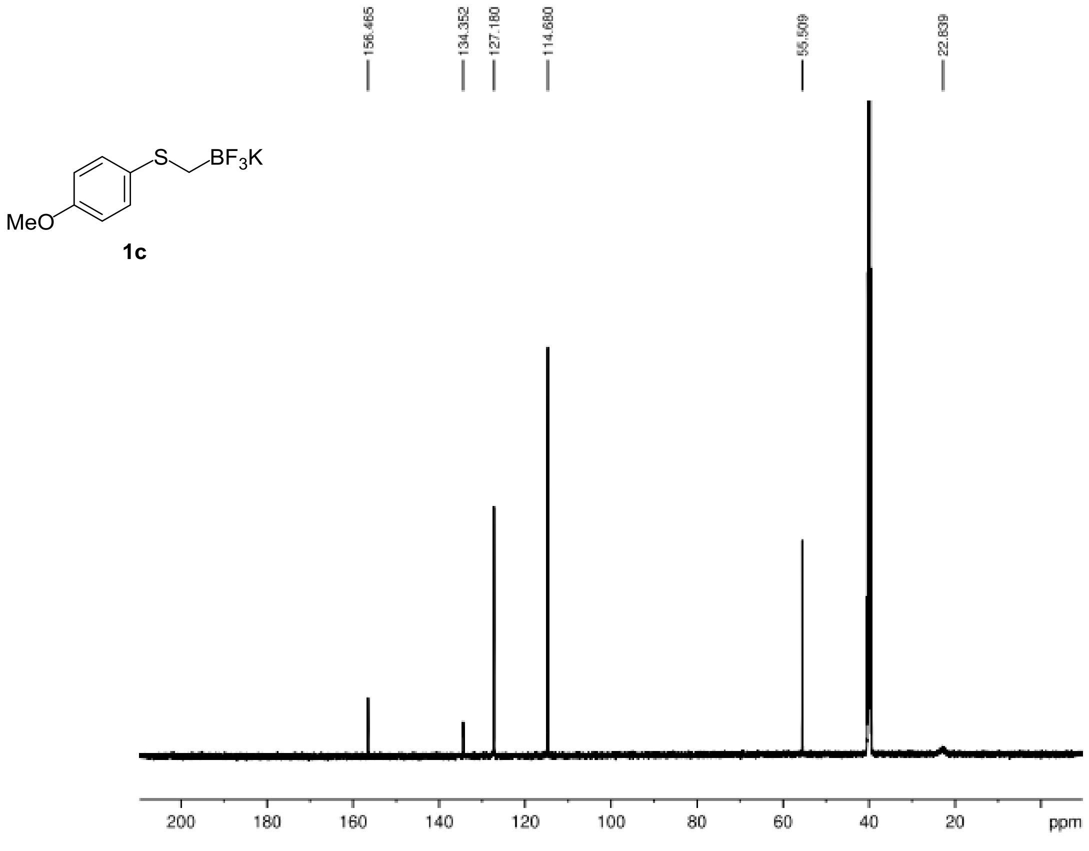
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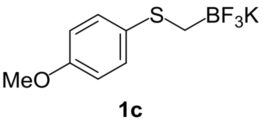

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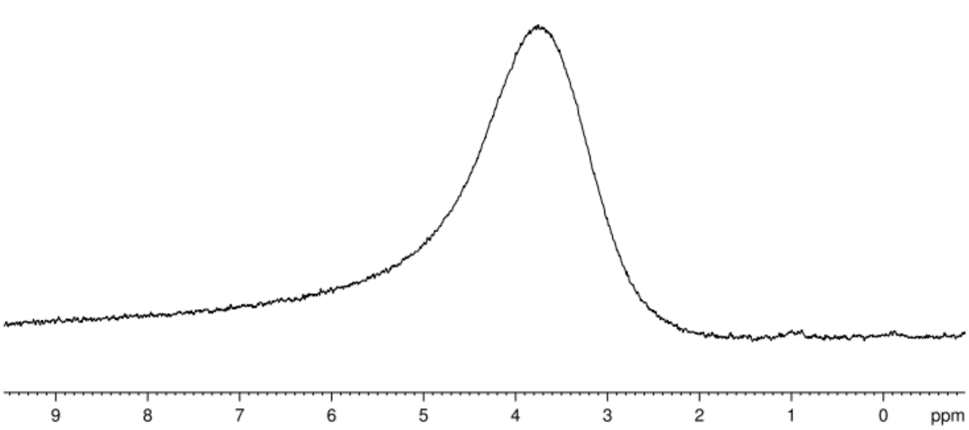

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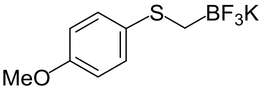

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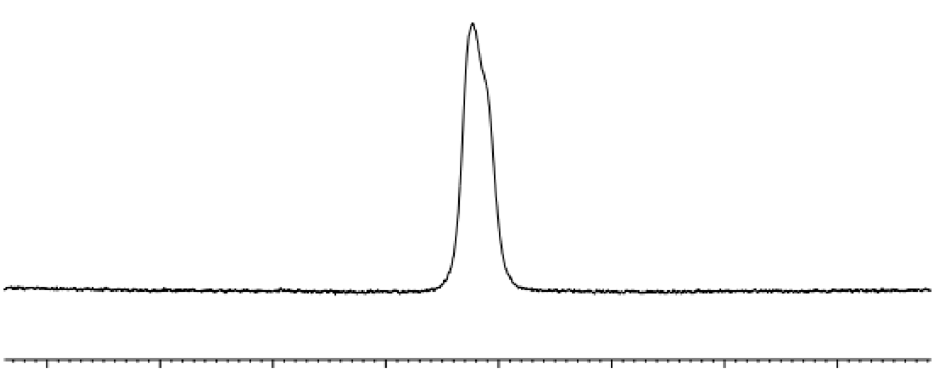

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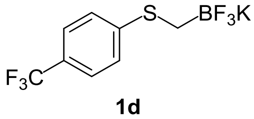

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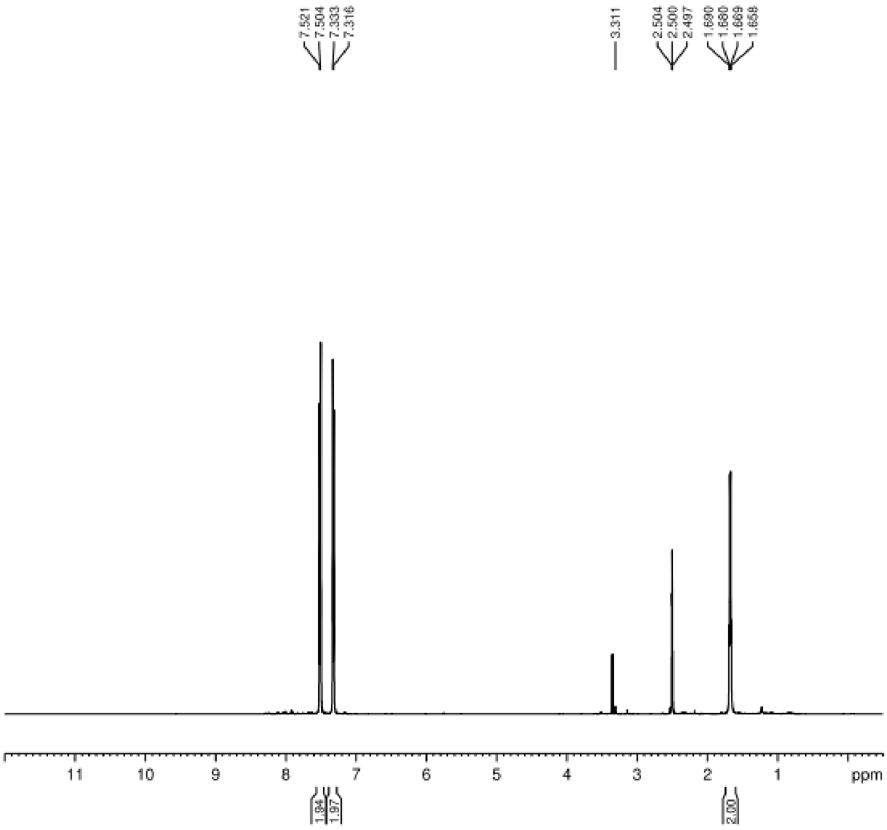

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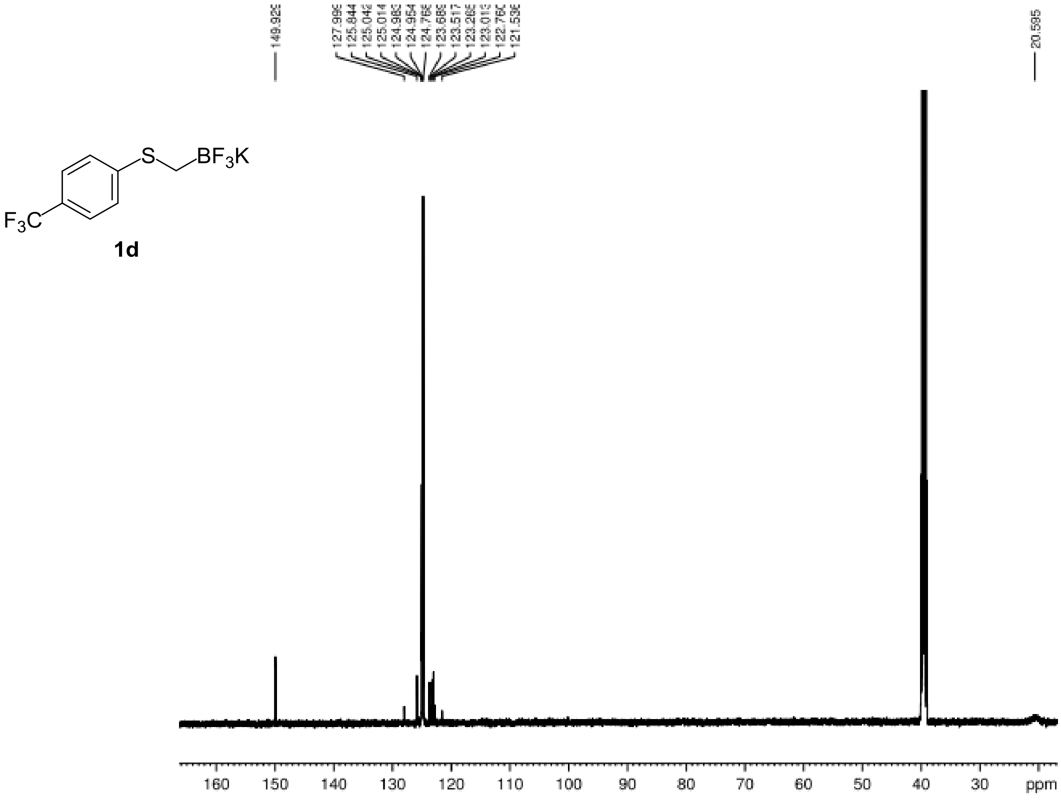

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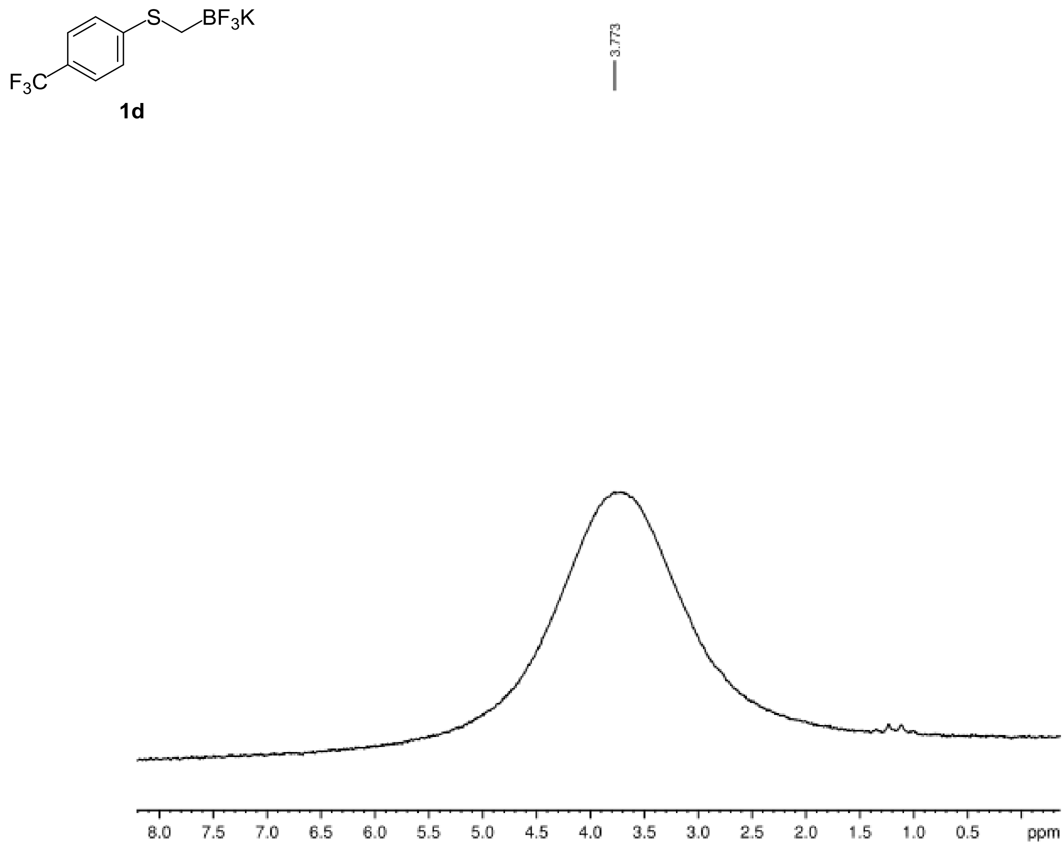

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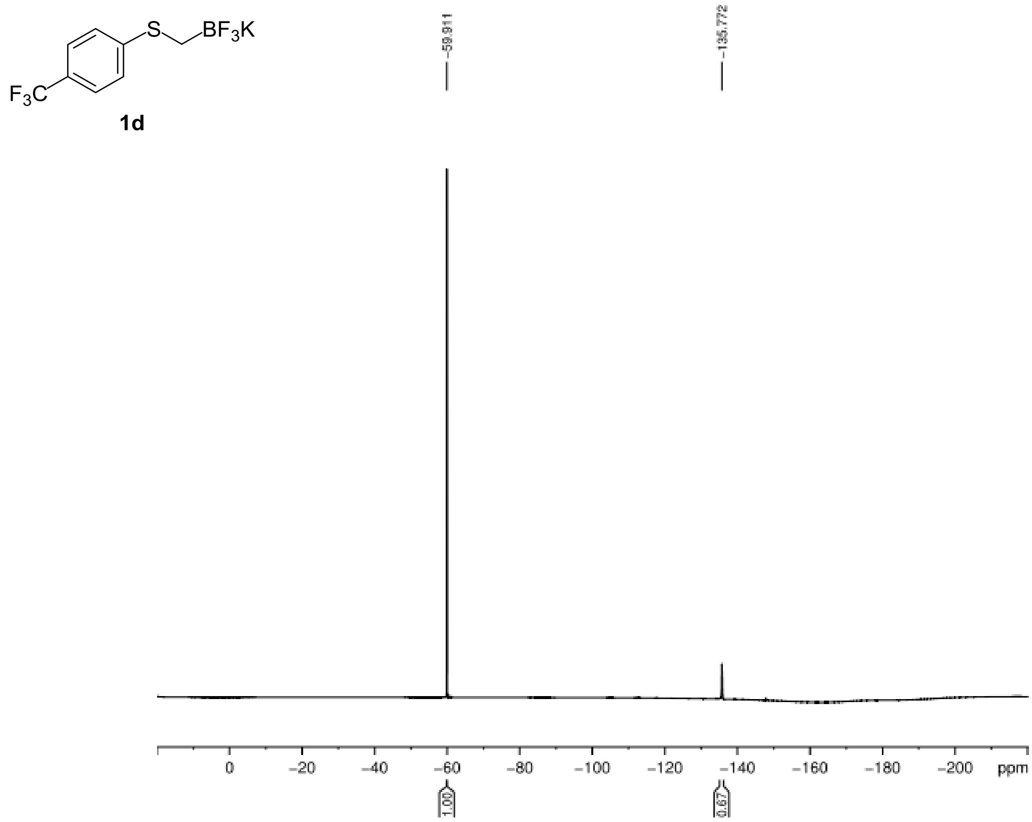

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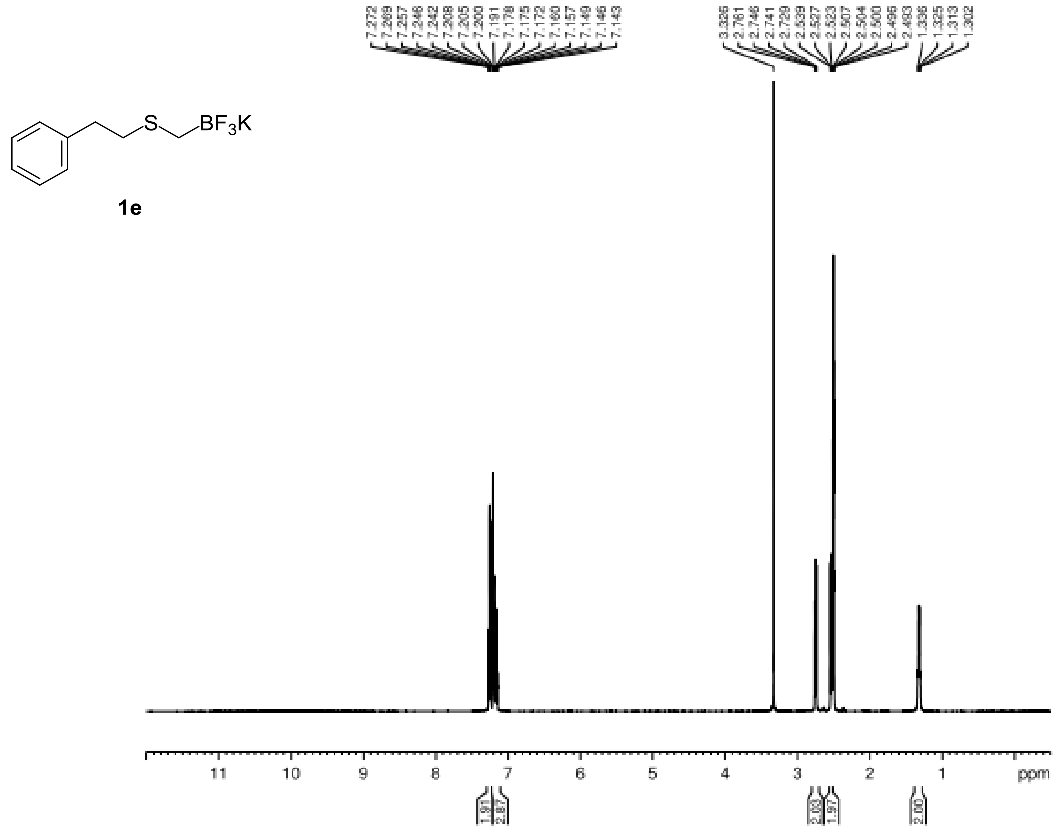

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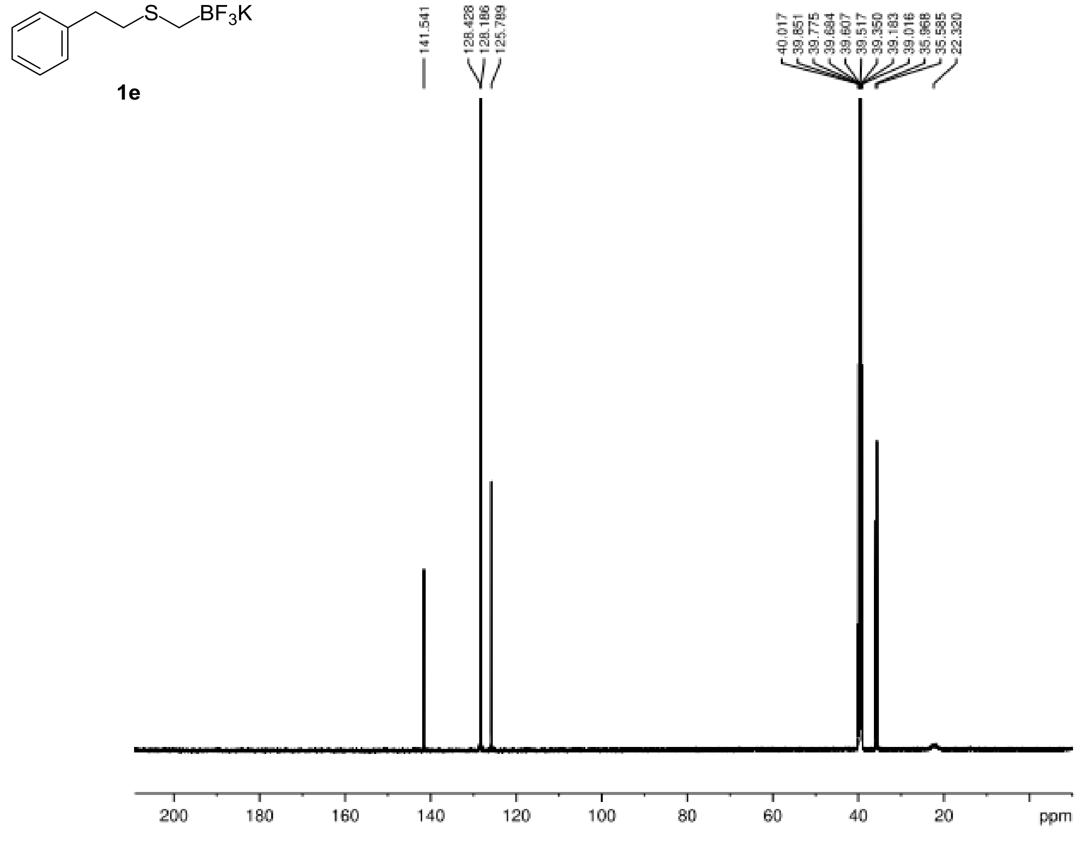

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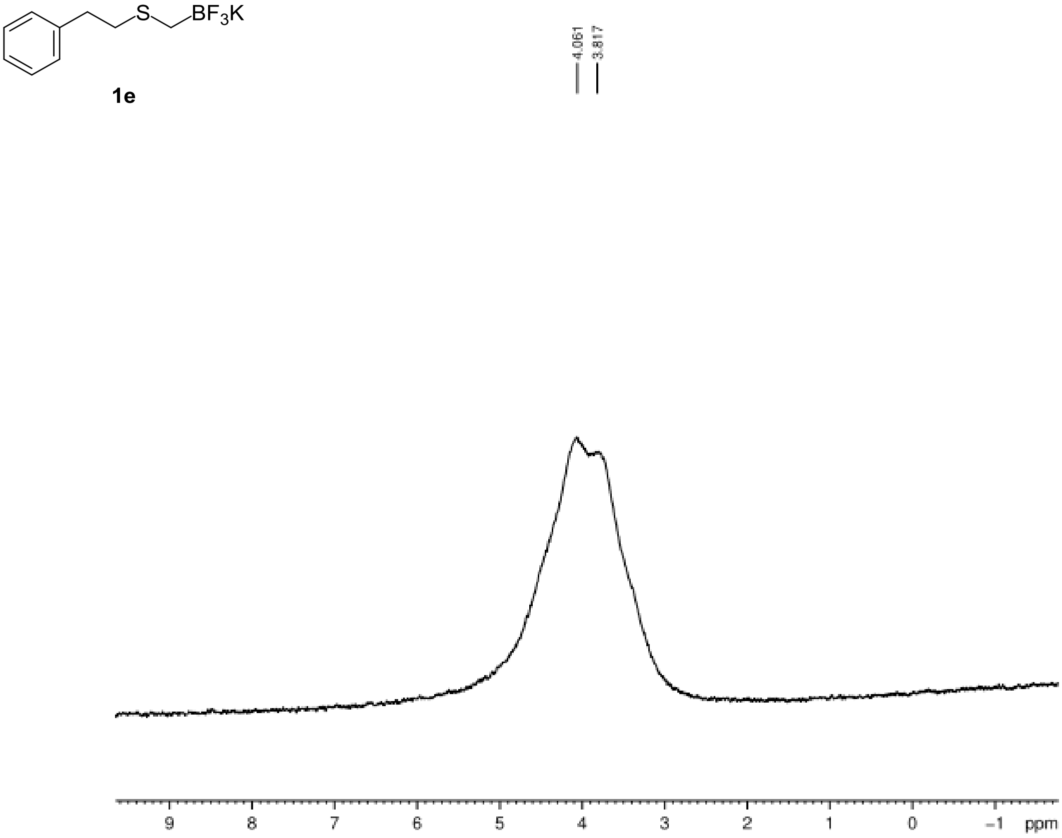

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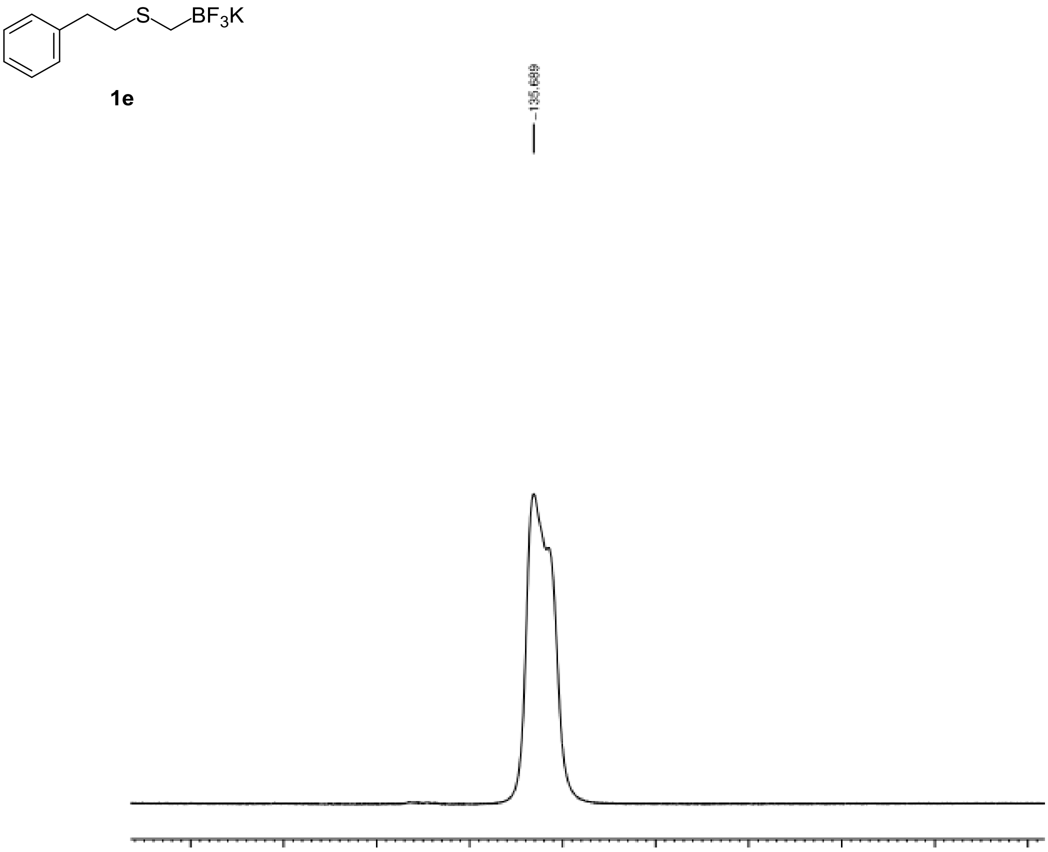

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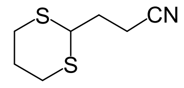

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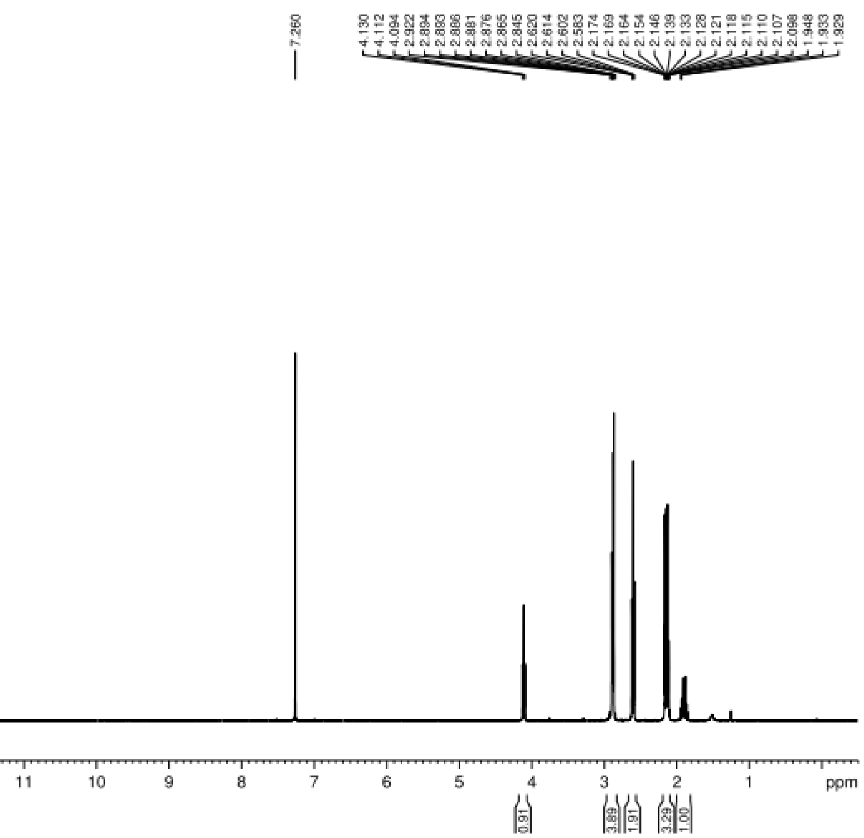

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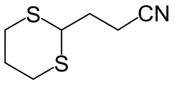

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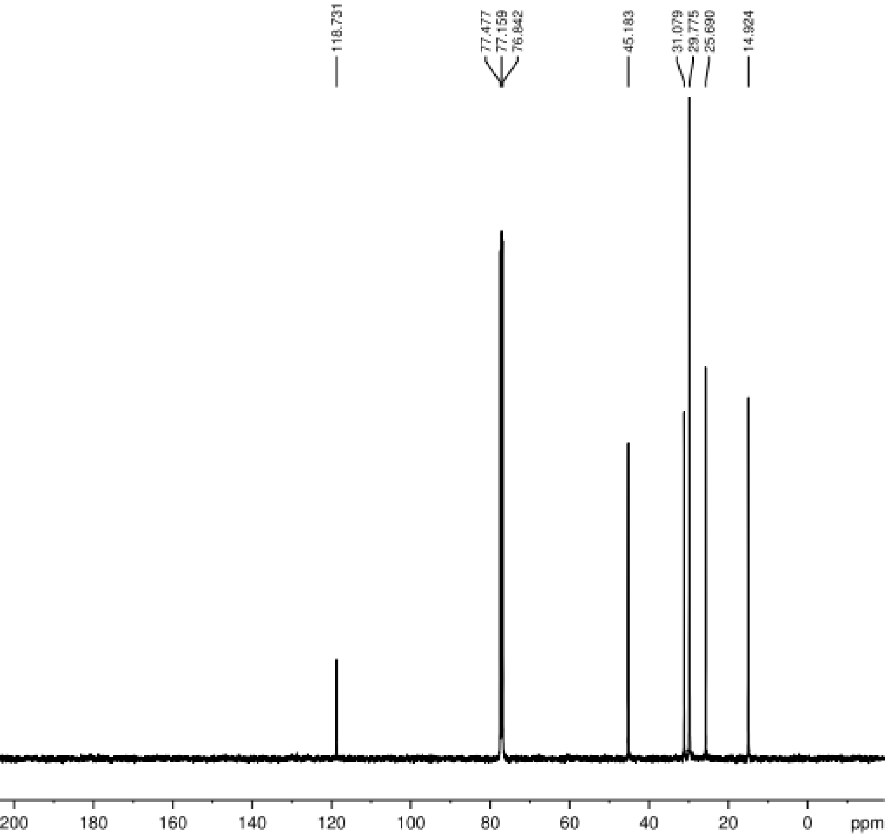

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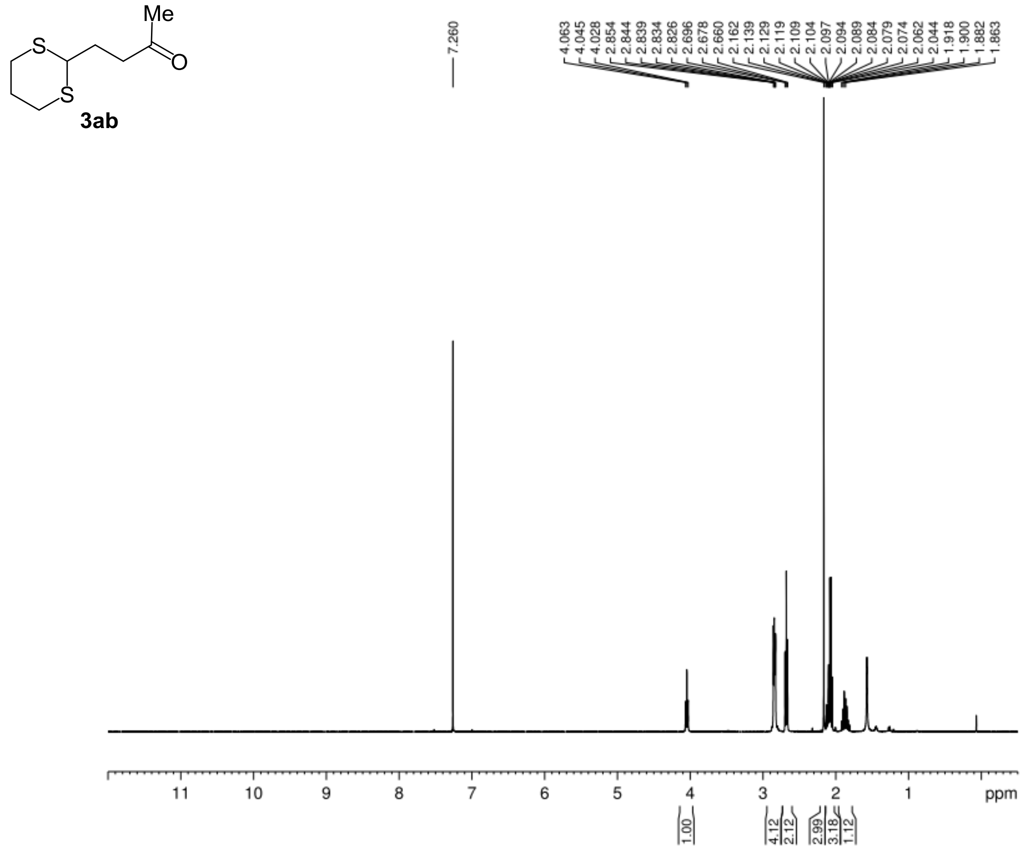
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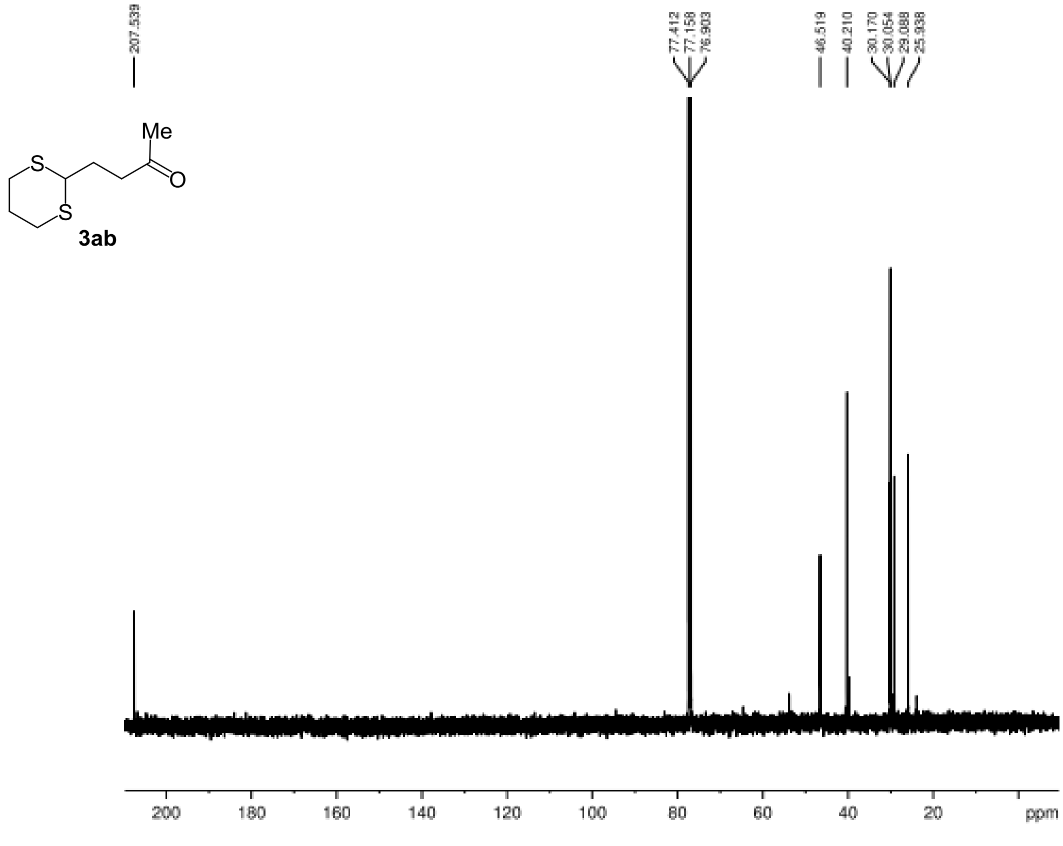
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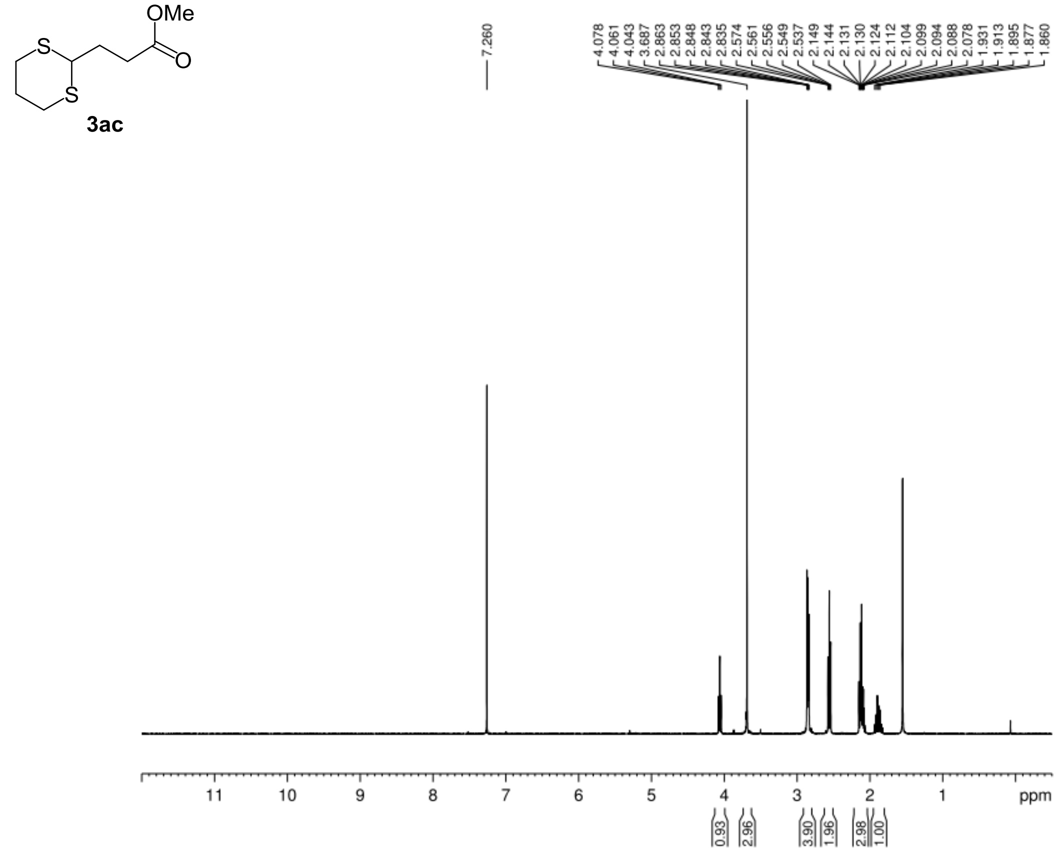

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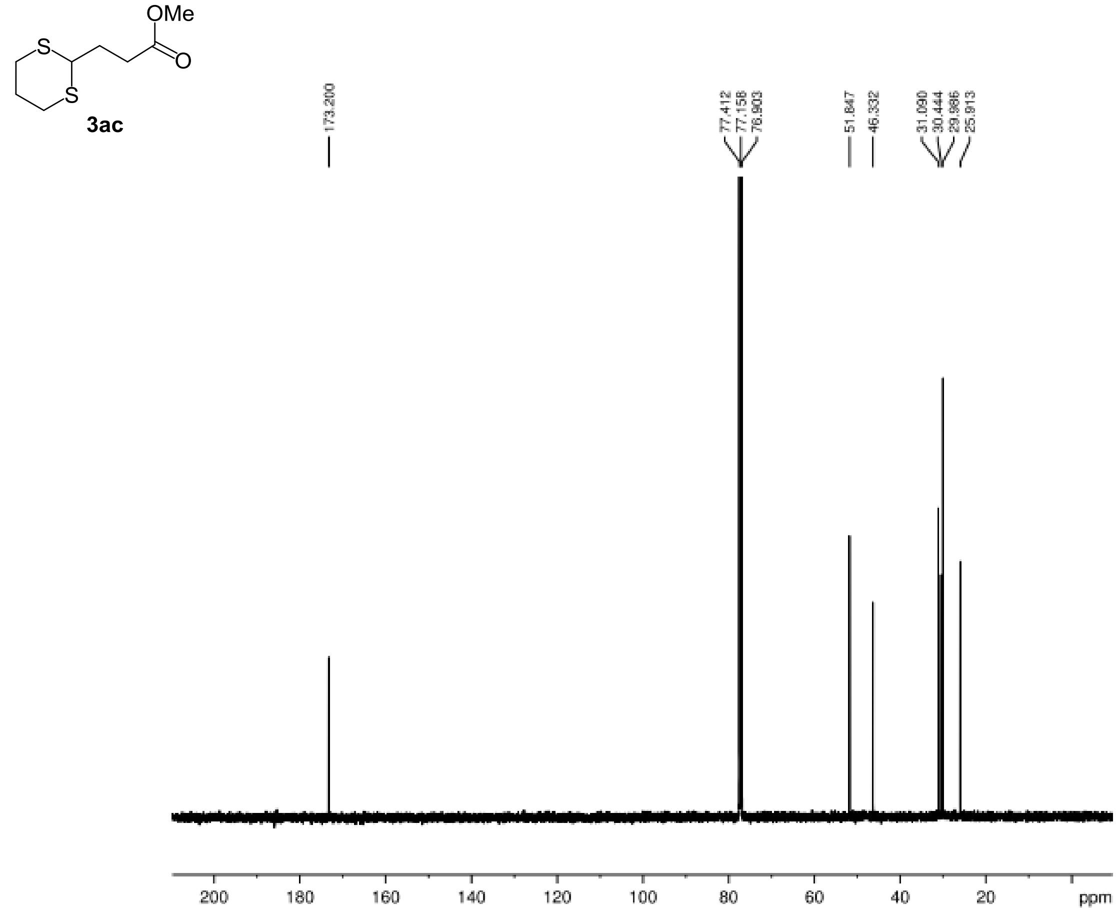

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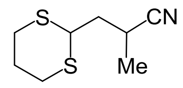

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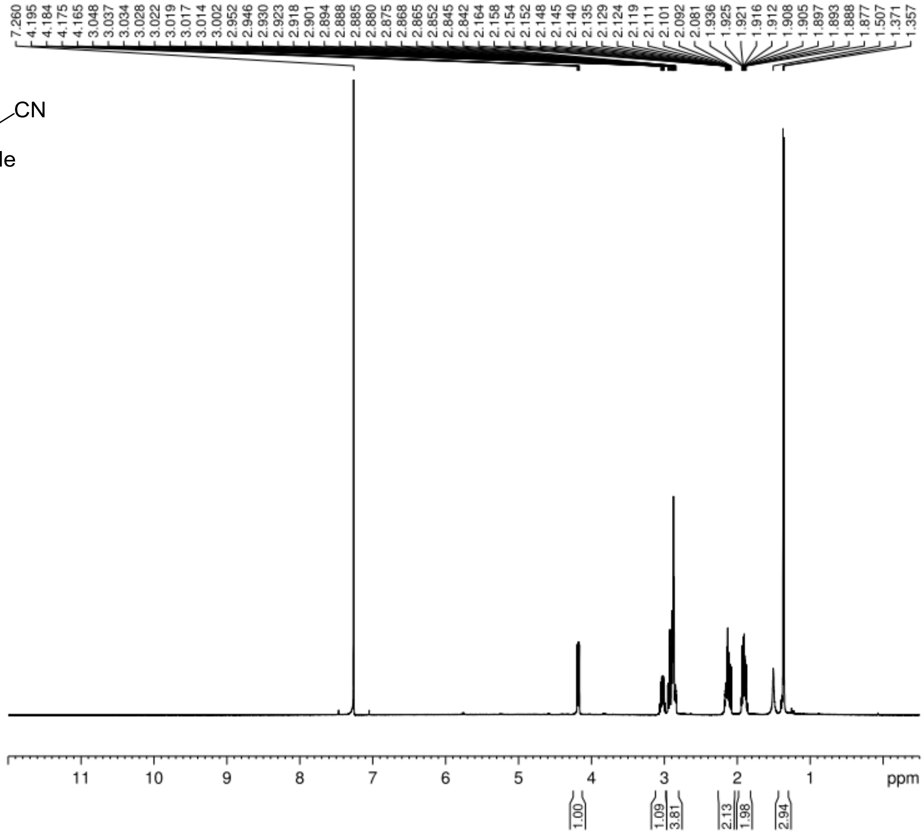

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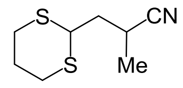

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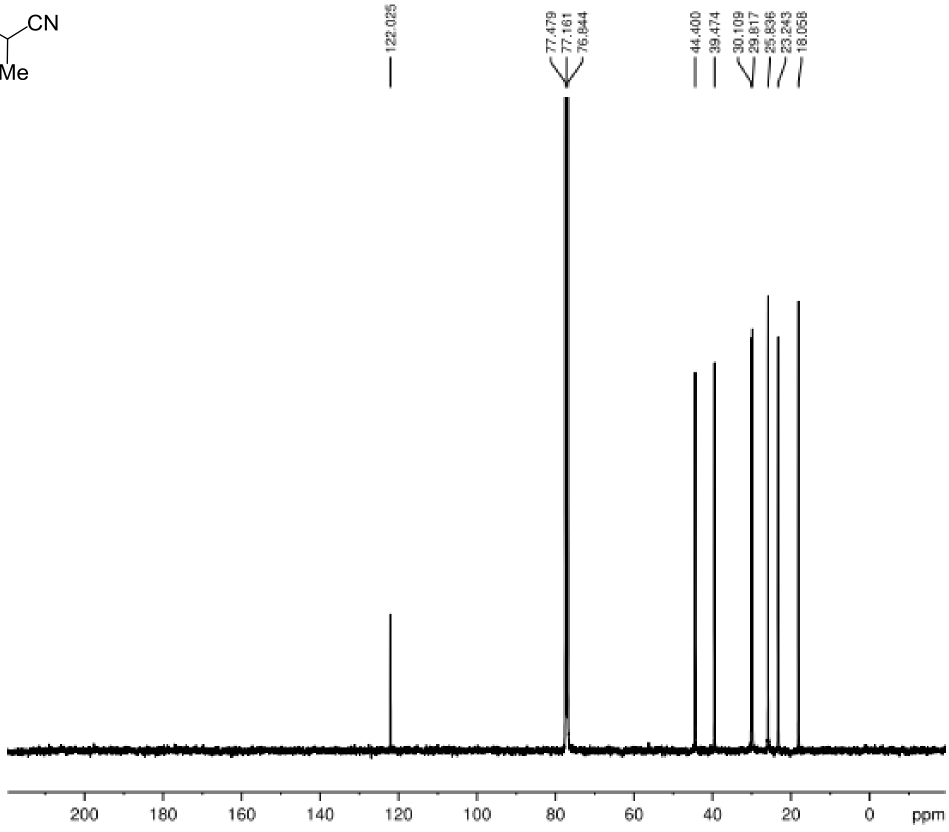

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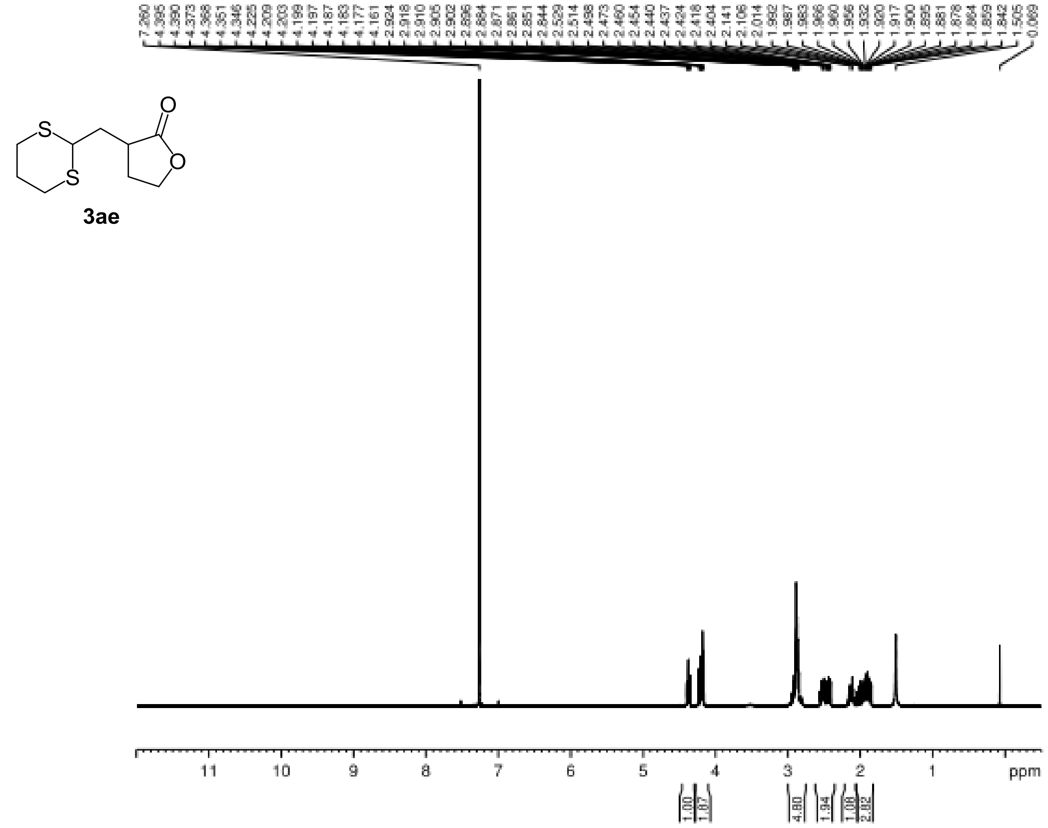

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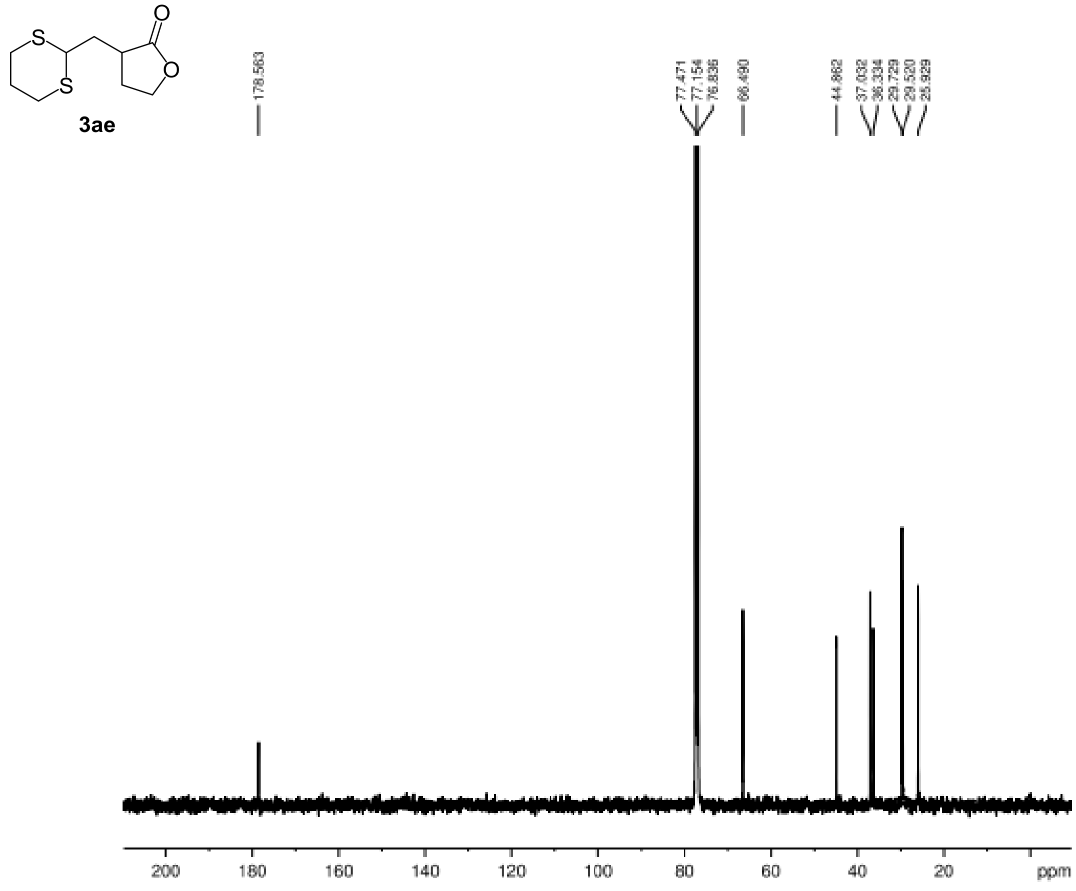

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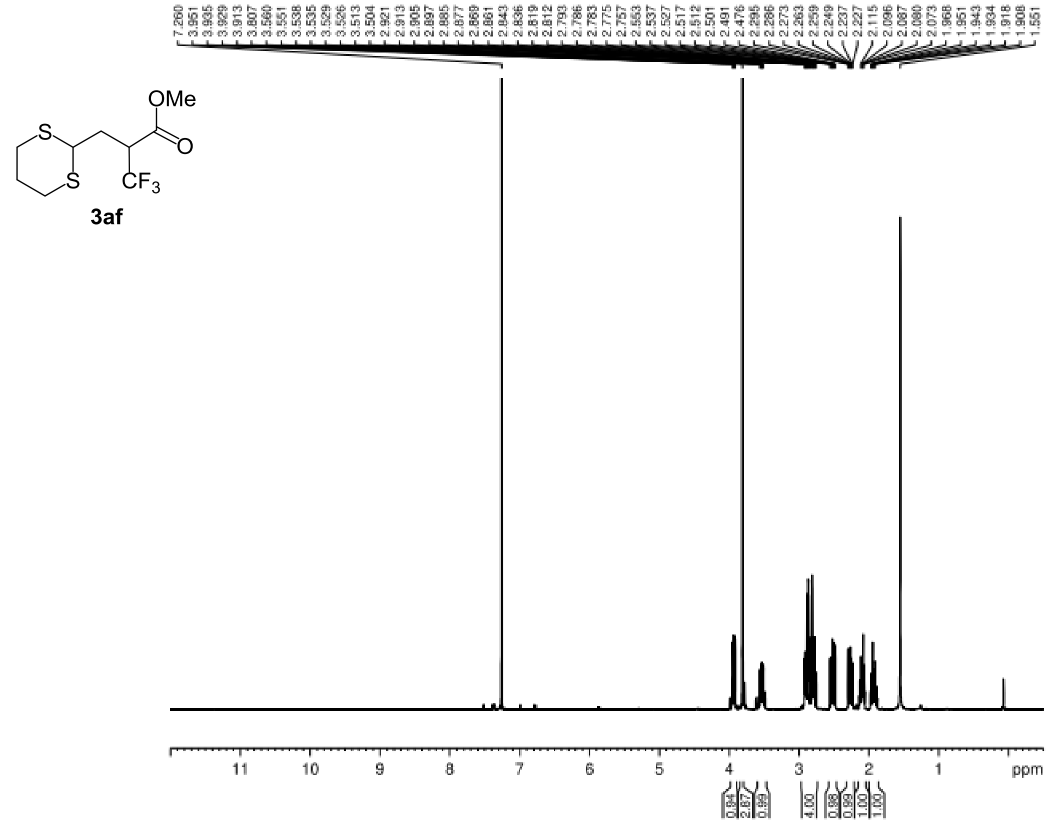

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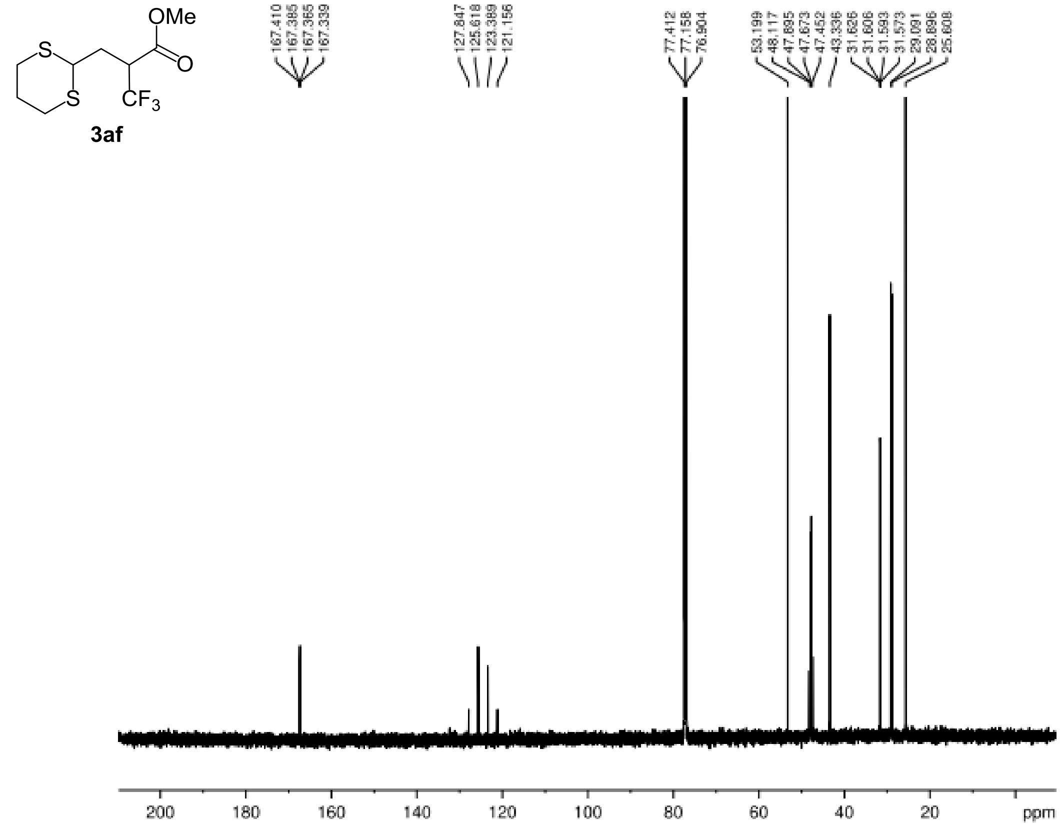

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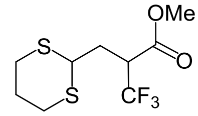

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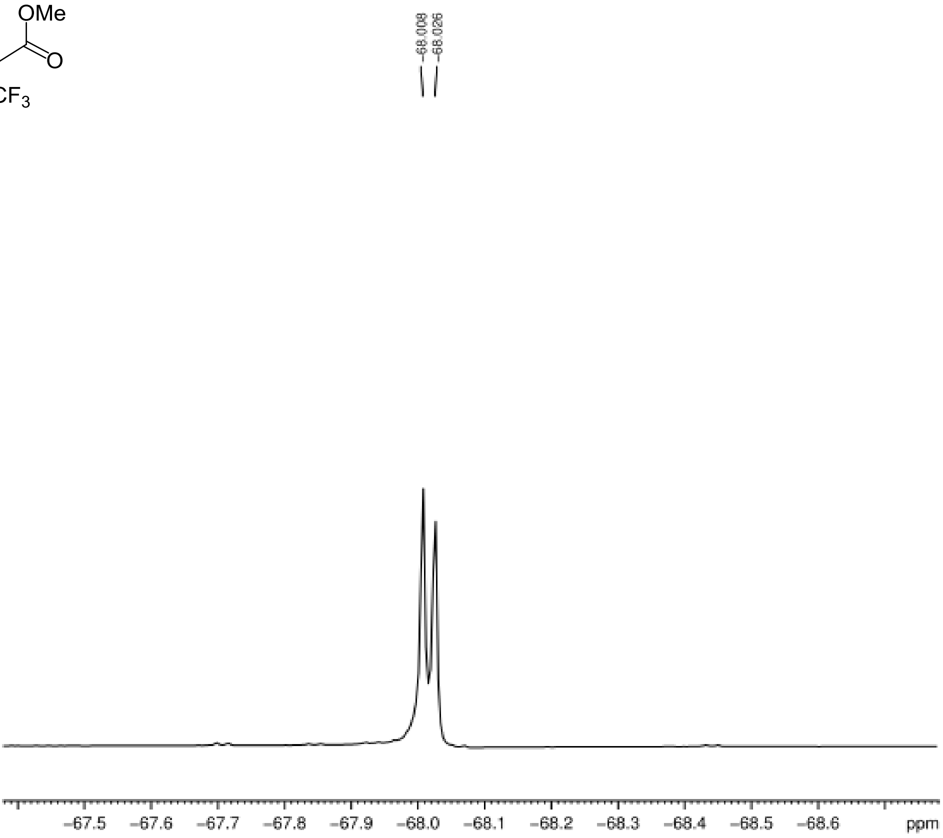

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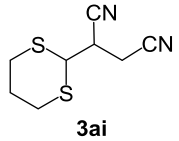

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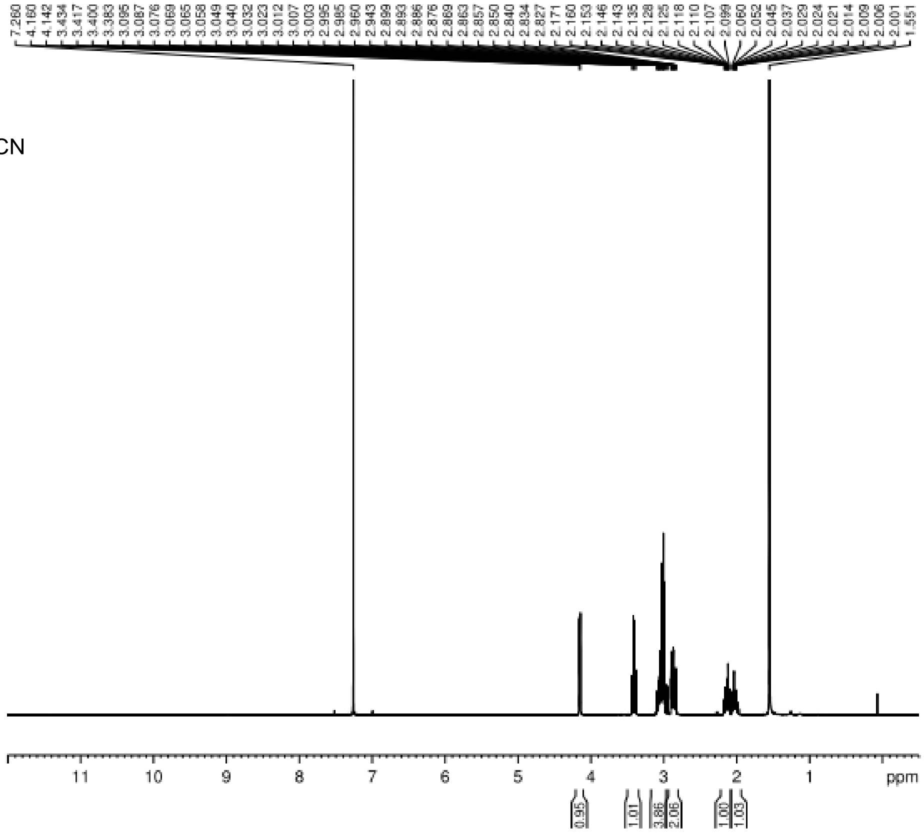

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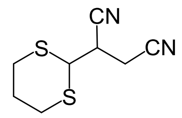

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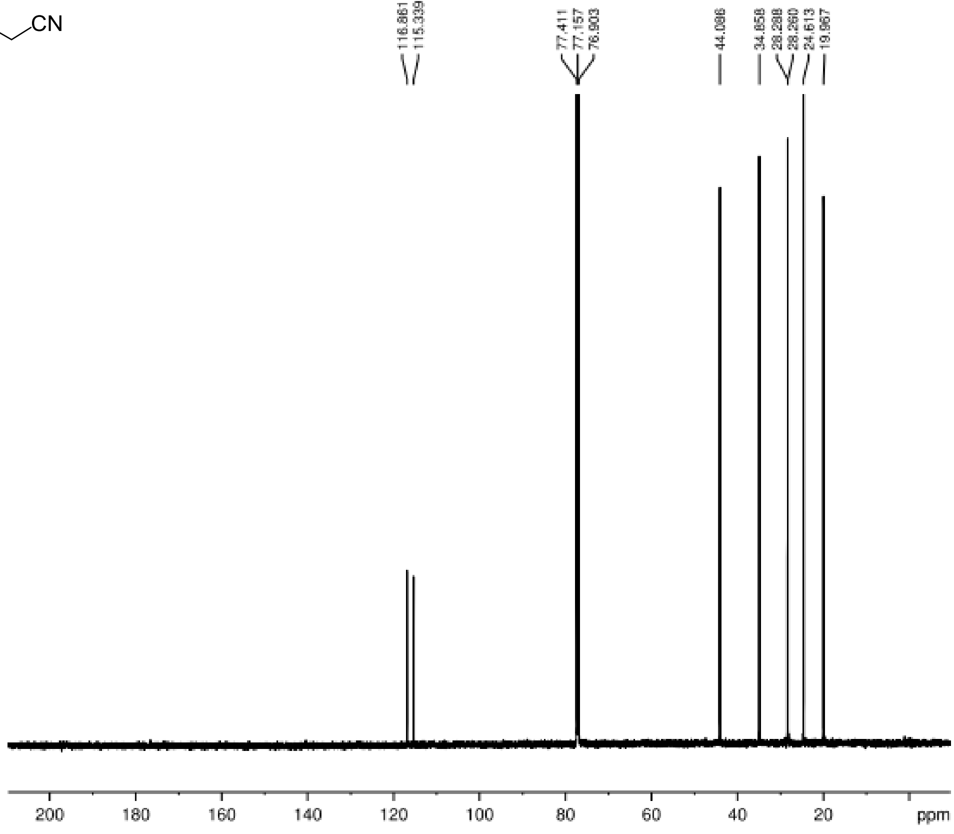

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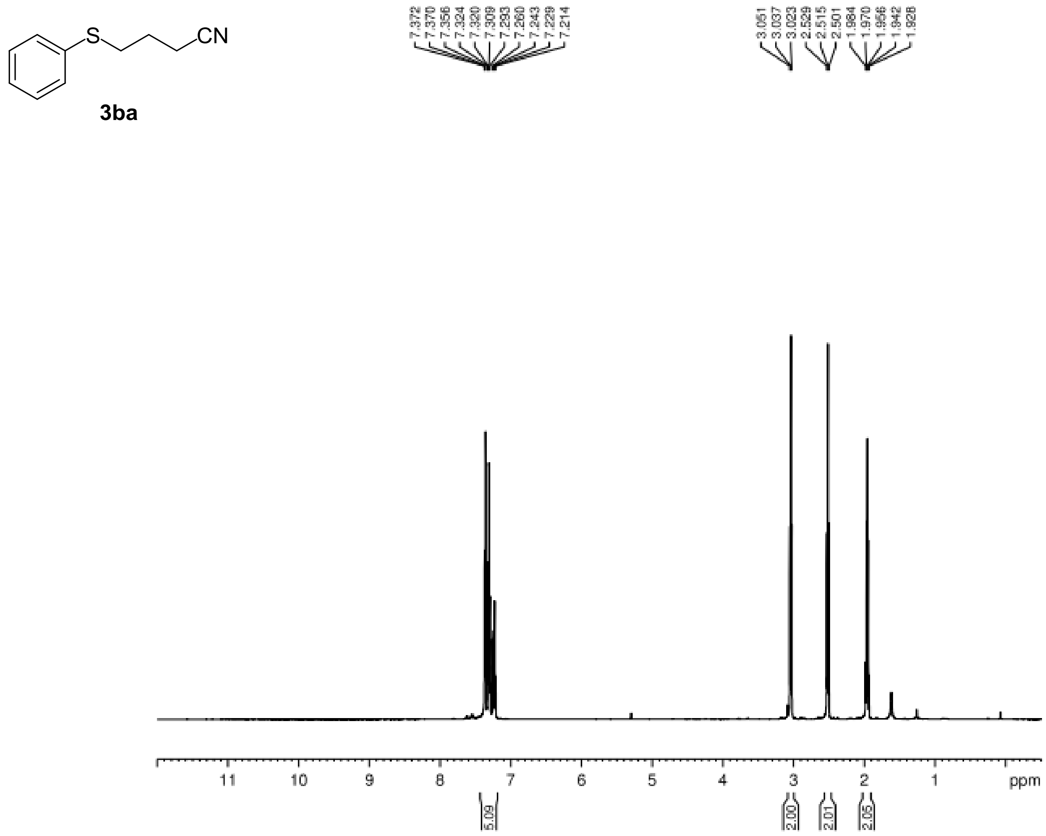

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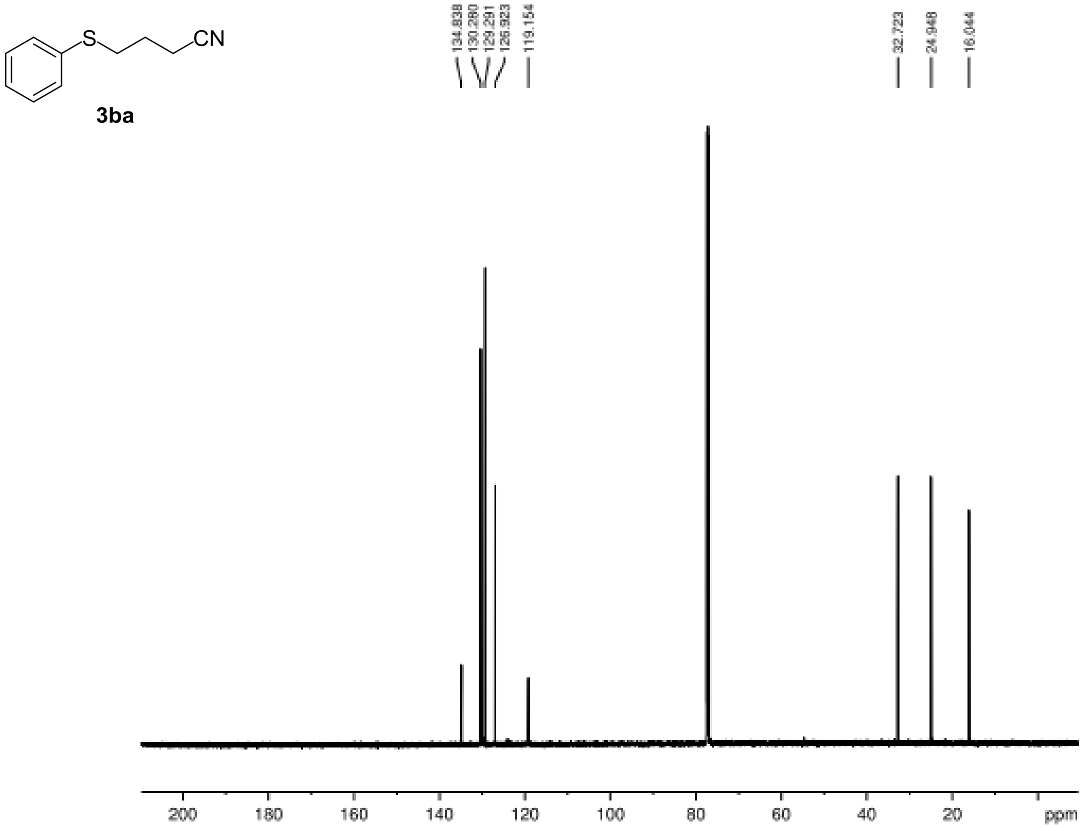

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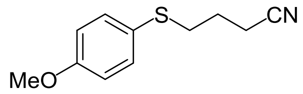

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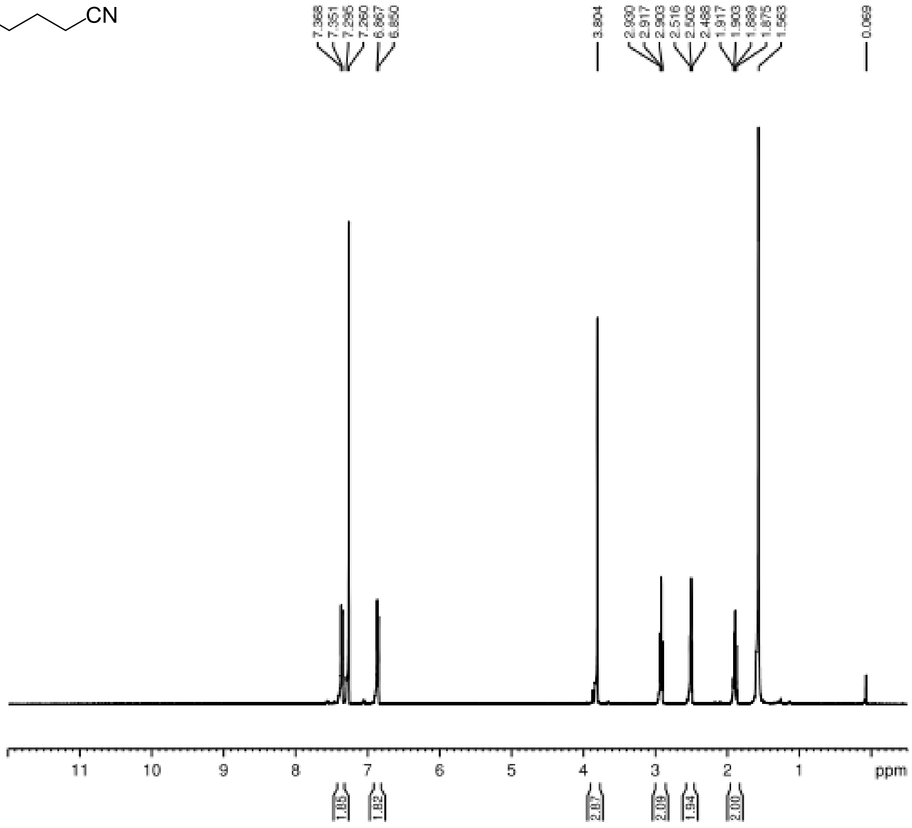

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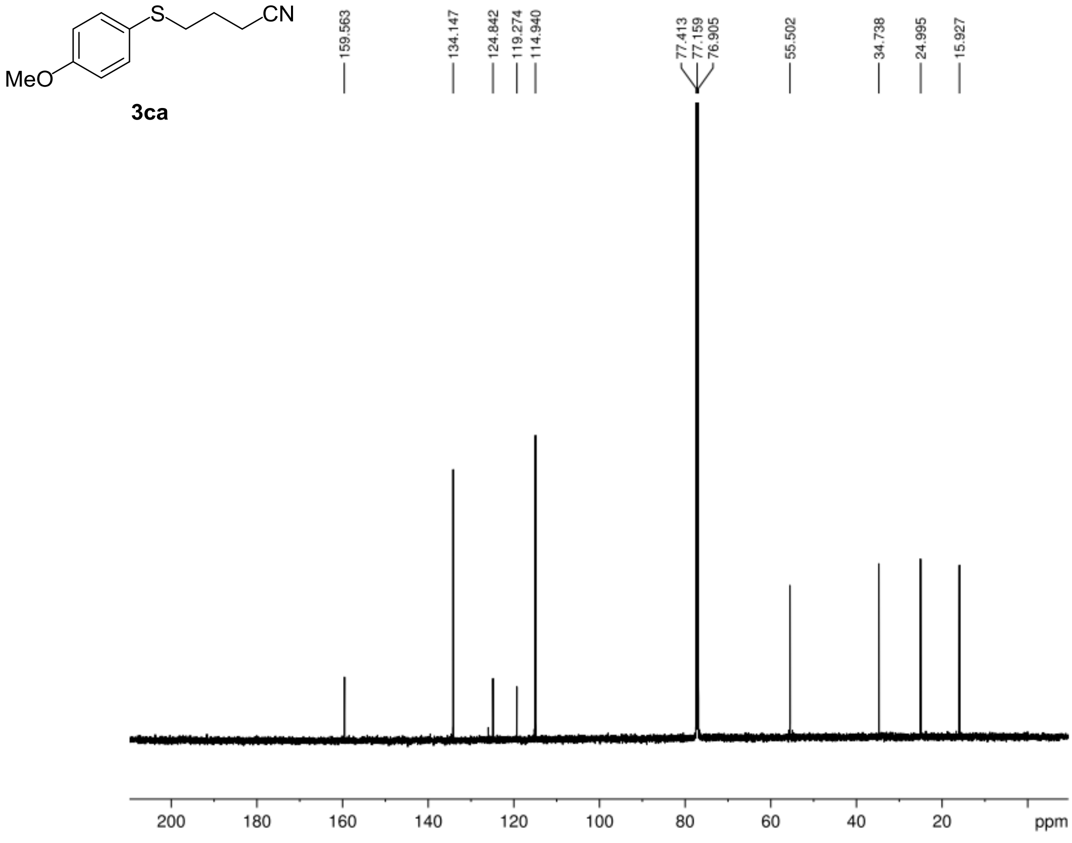

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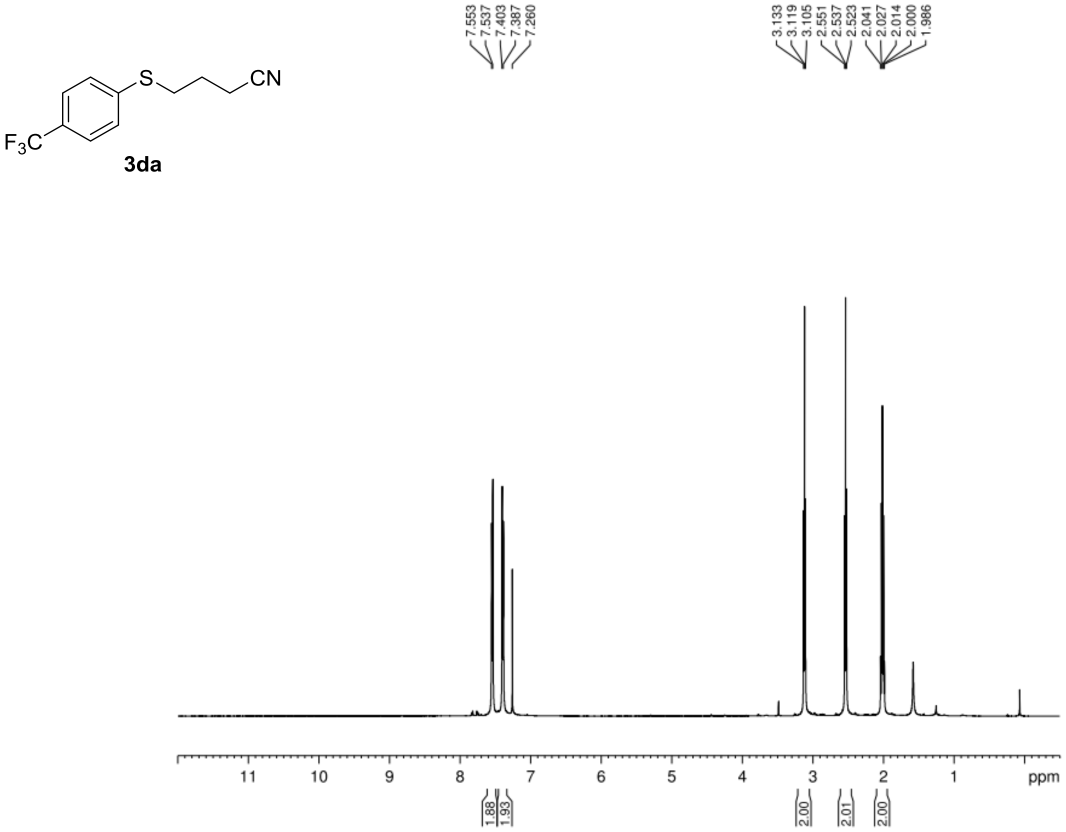

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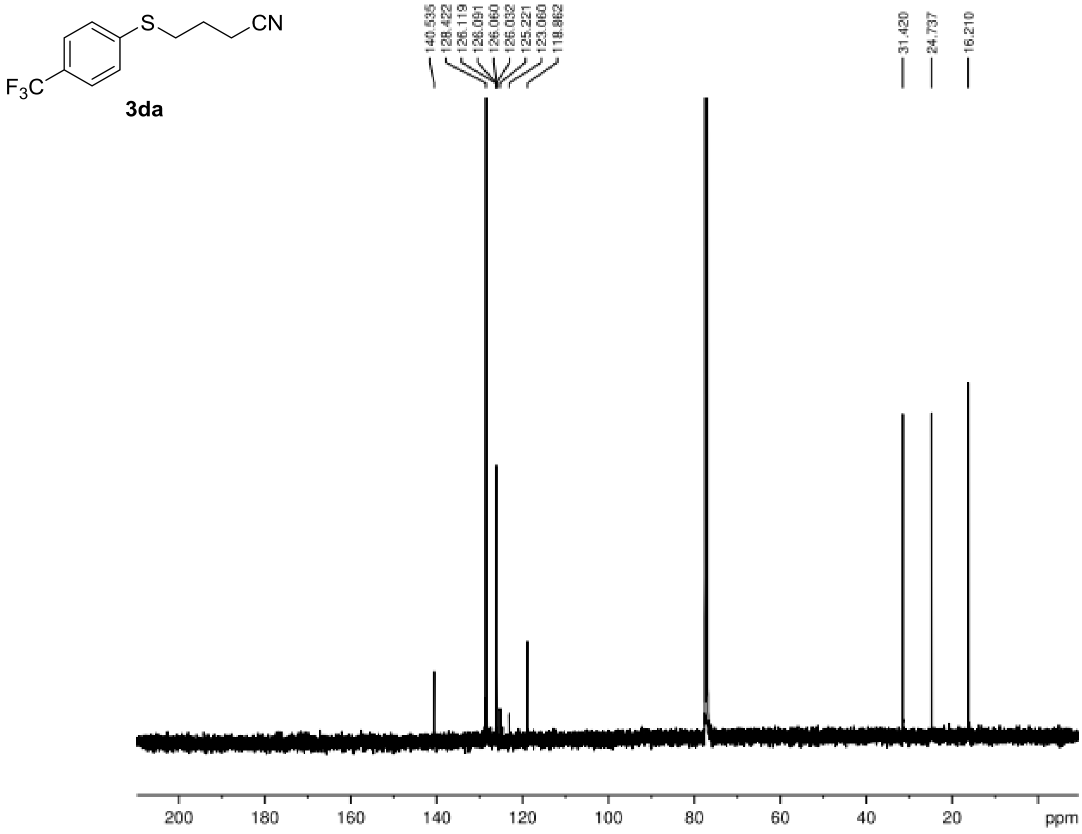
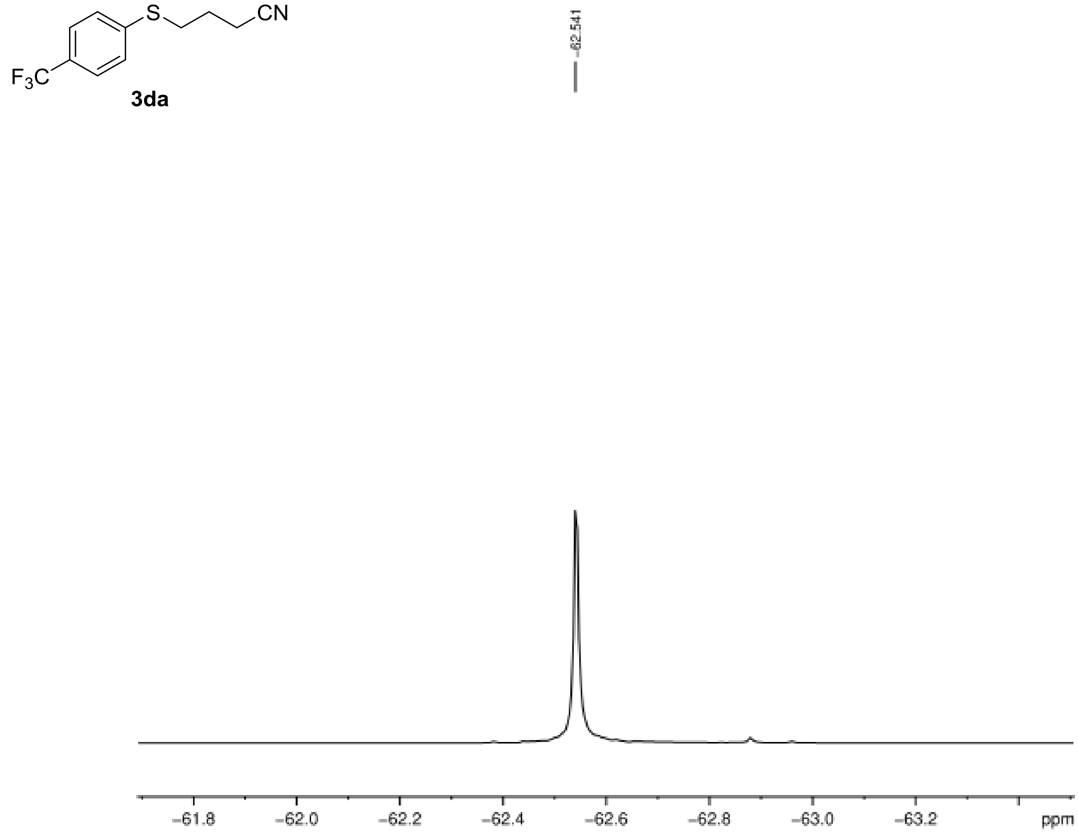


^{19}F NMR spectra



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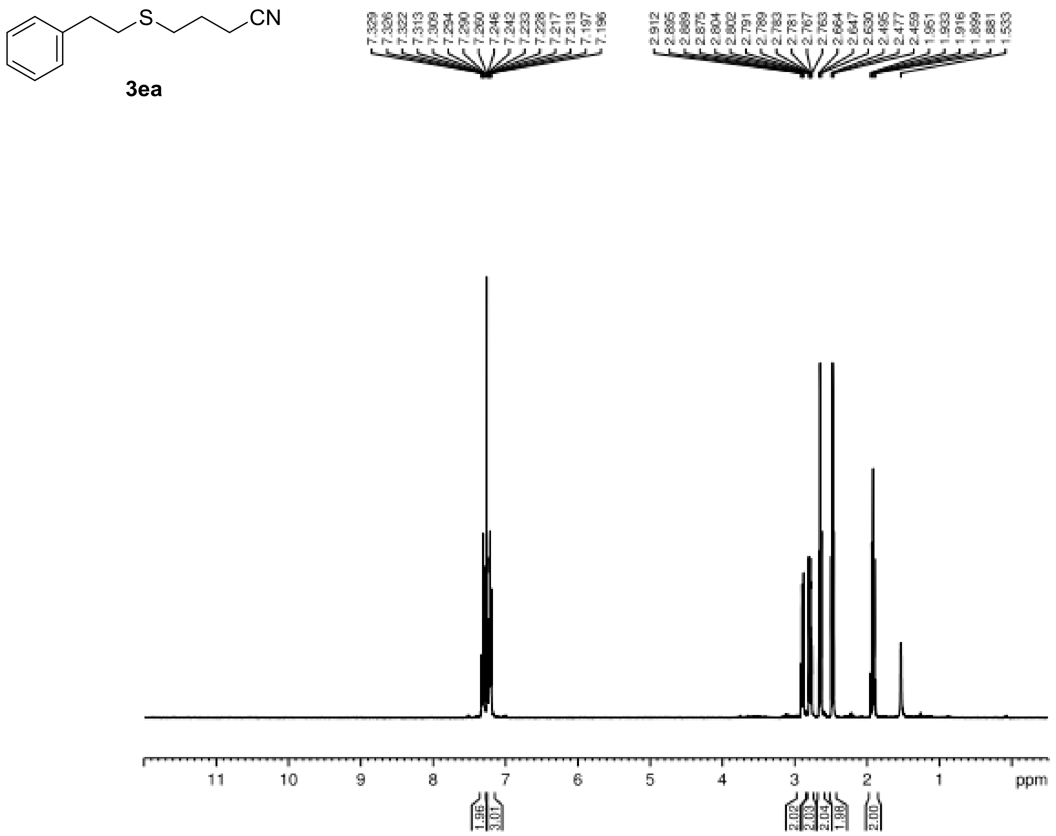

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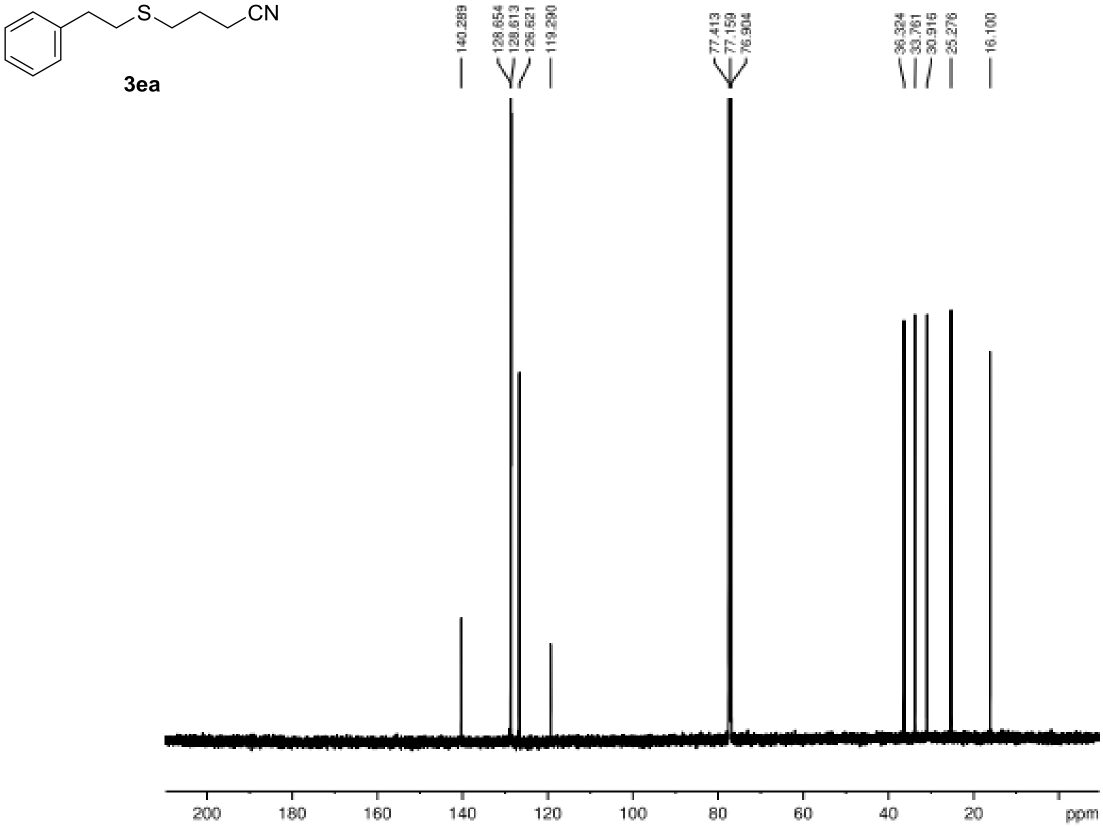

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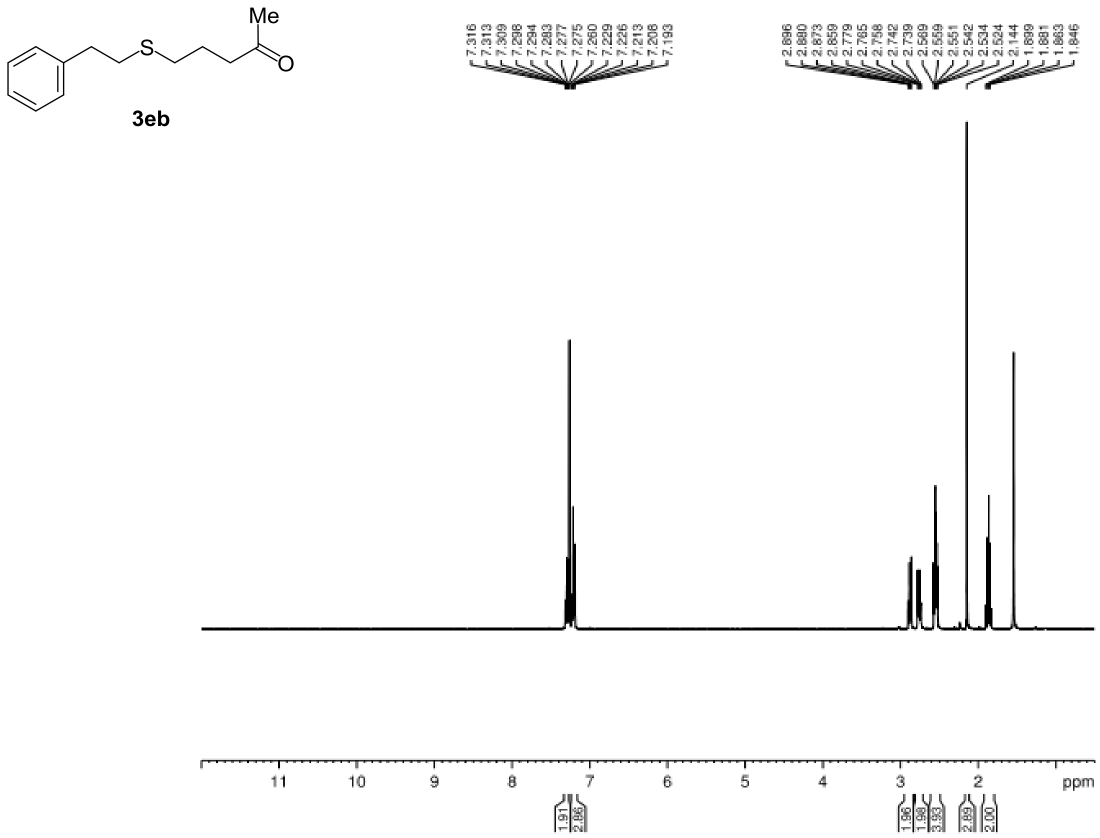

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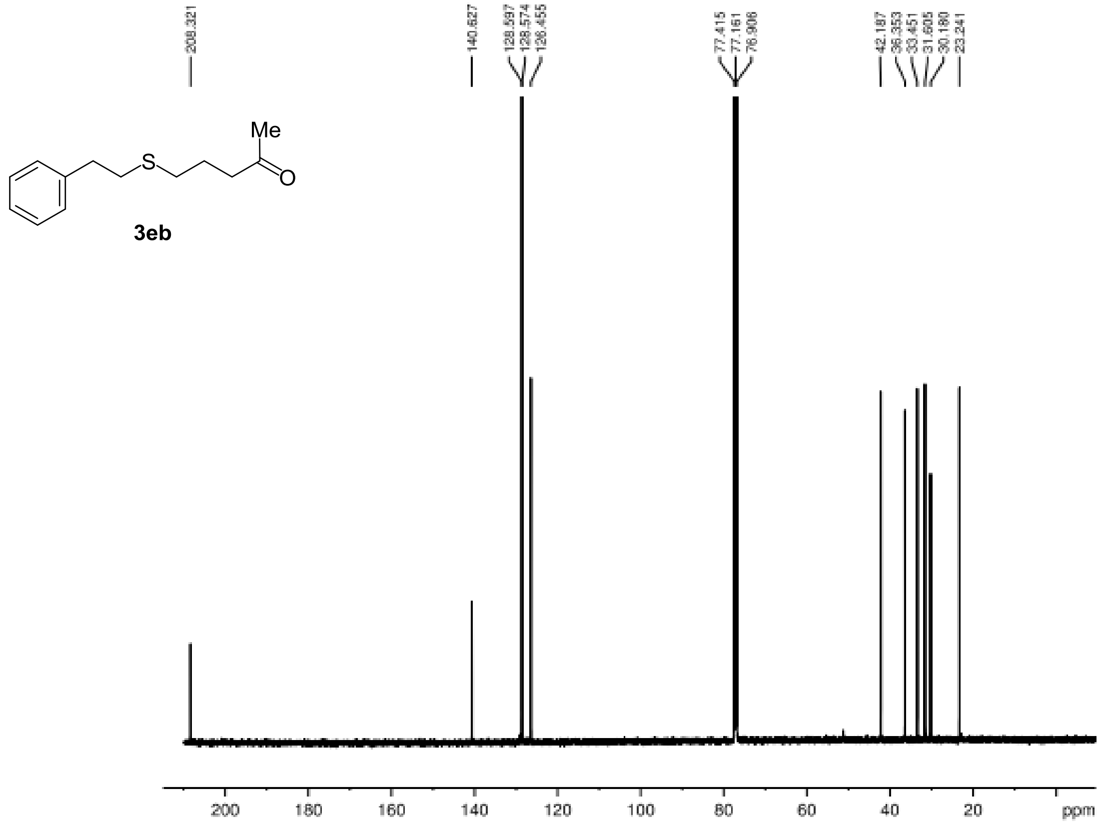

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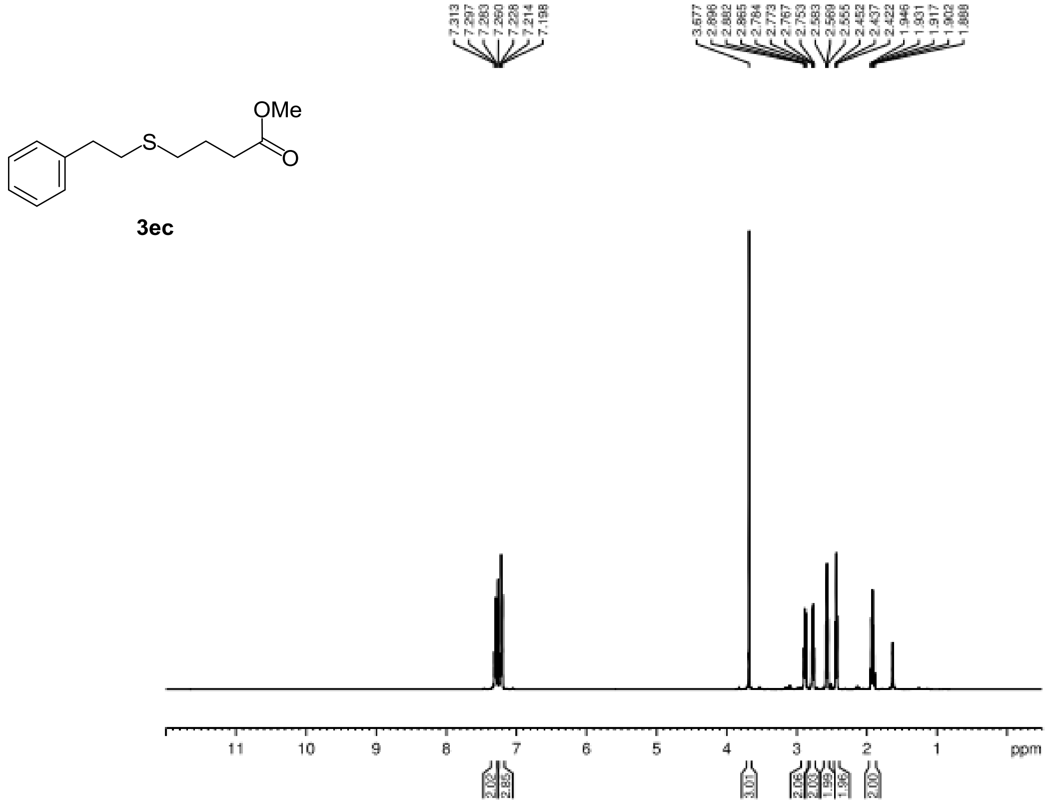

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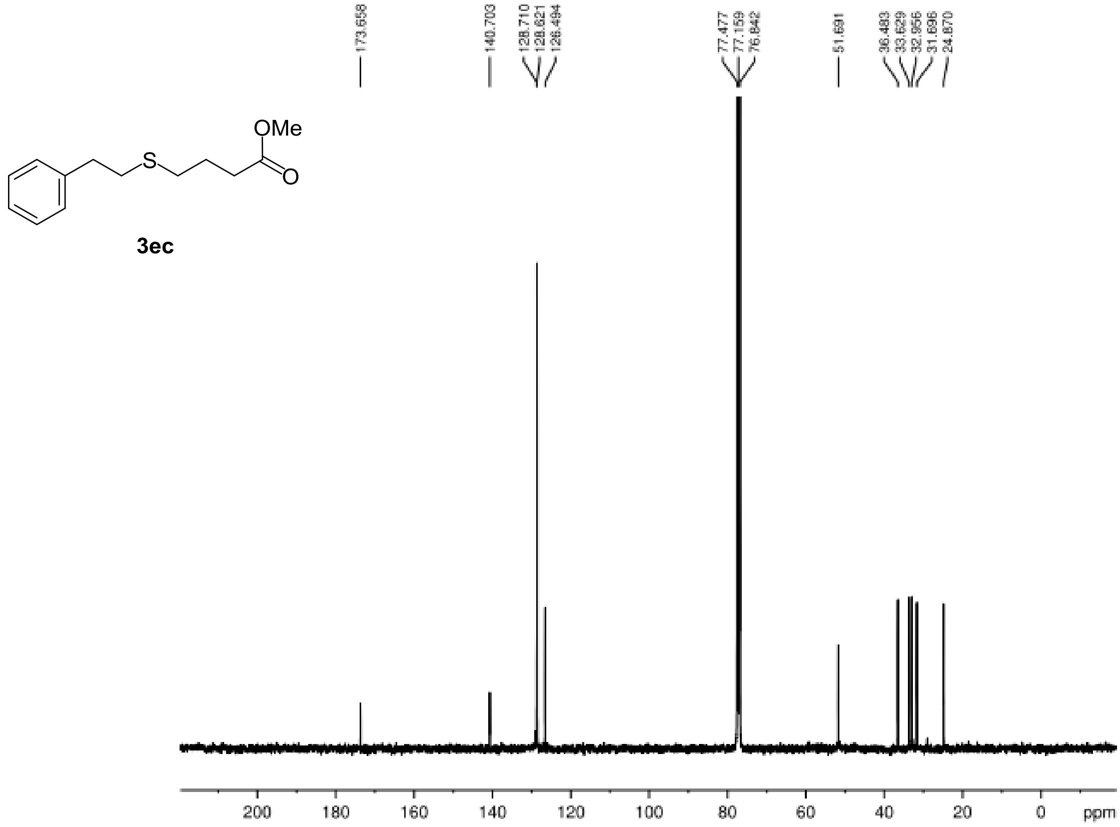

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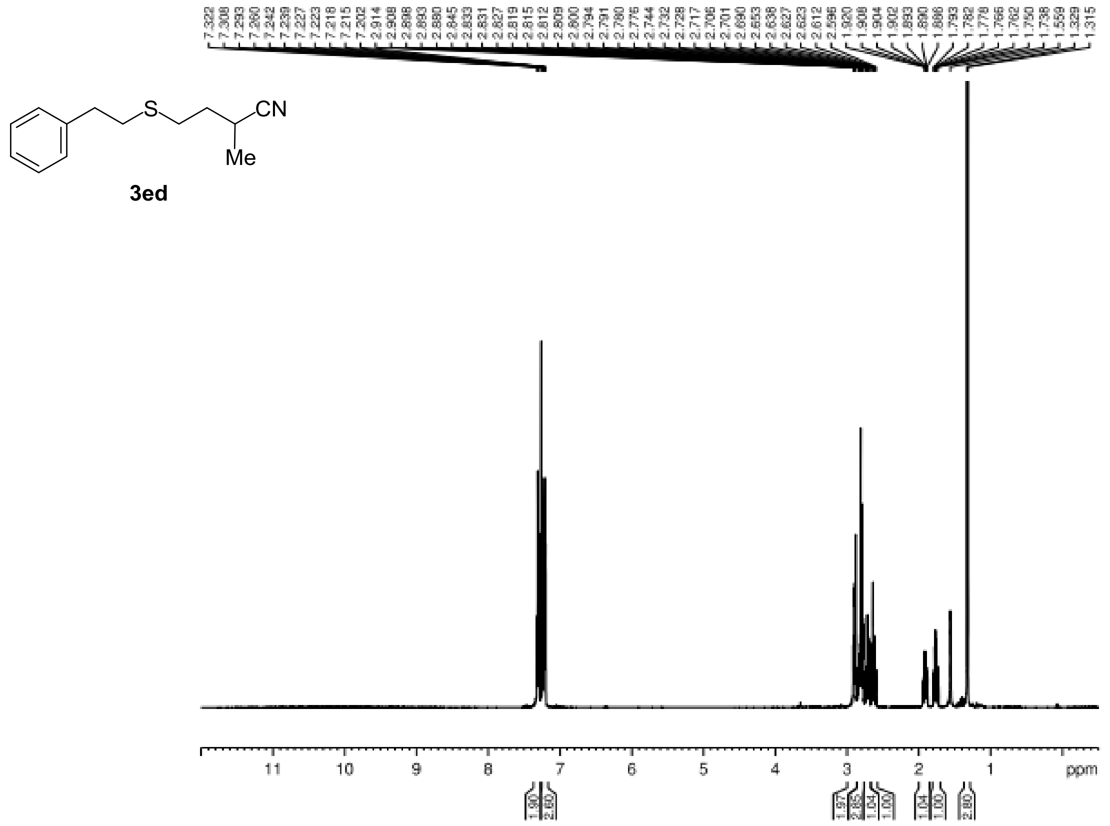

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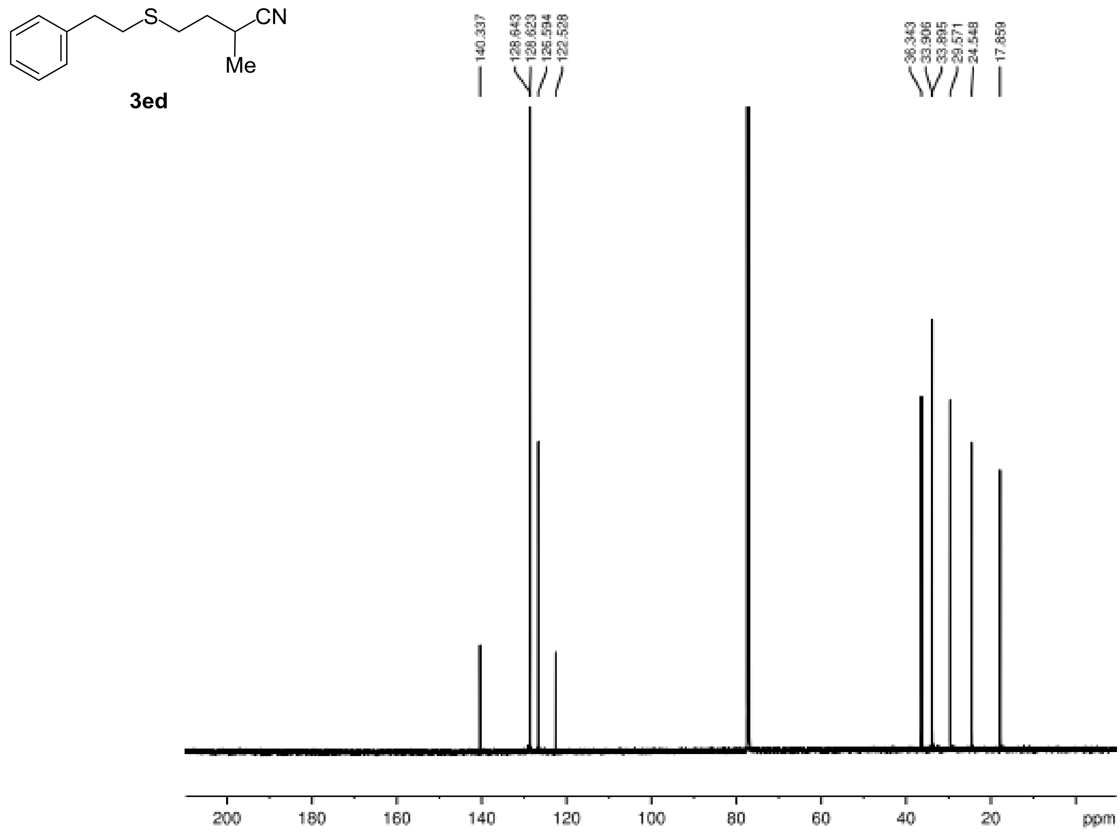

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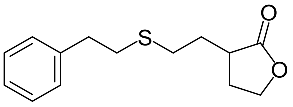

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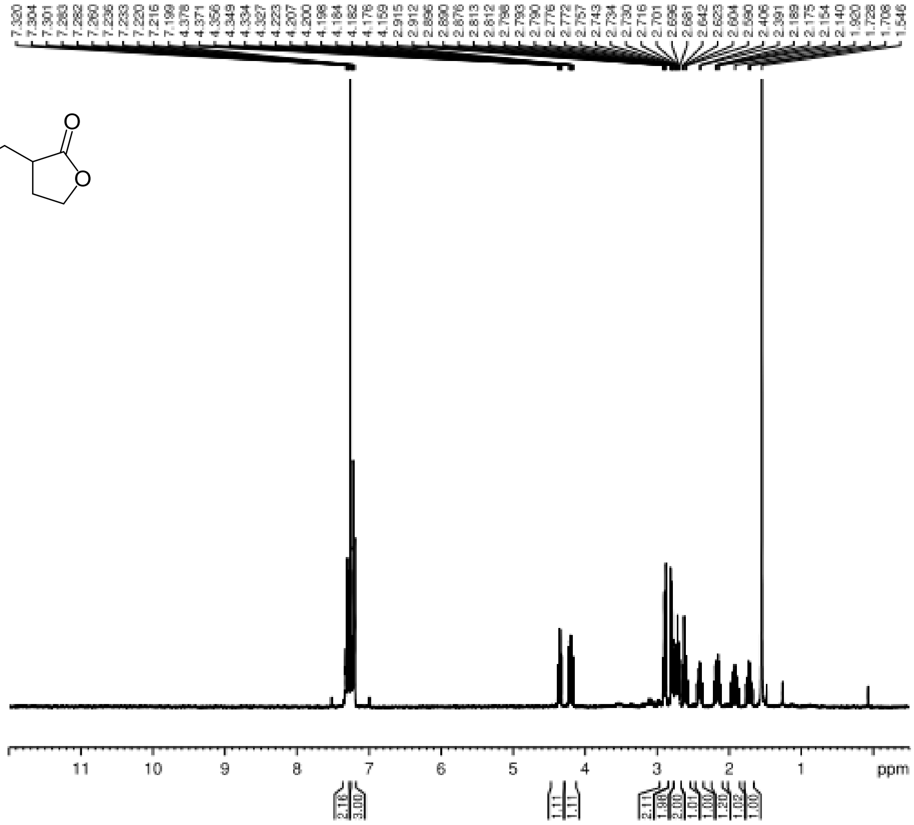

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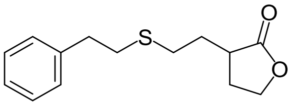

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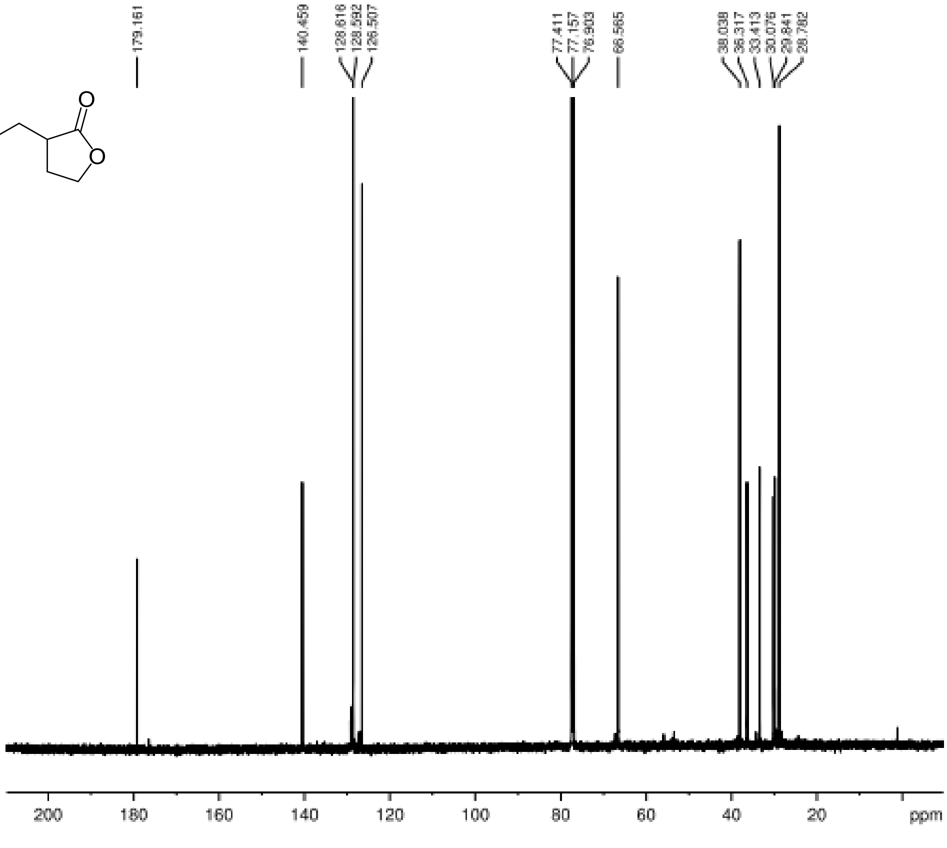

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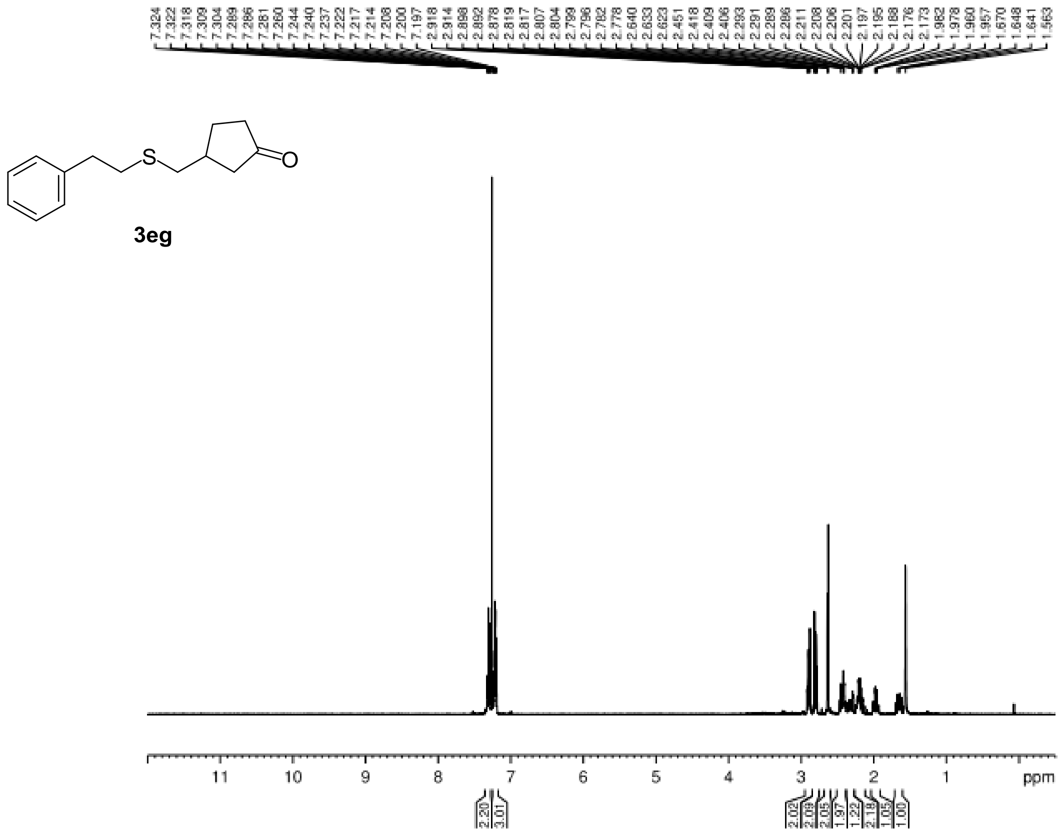

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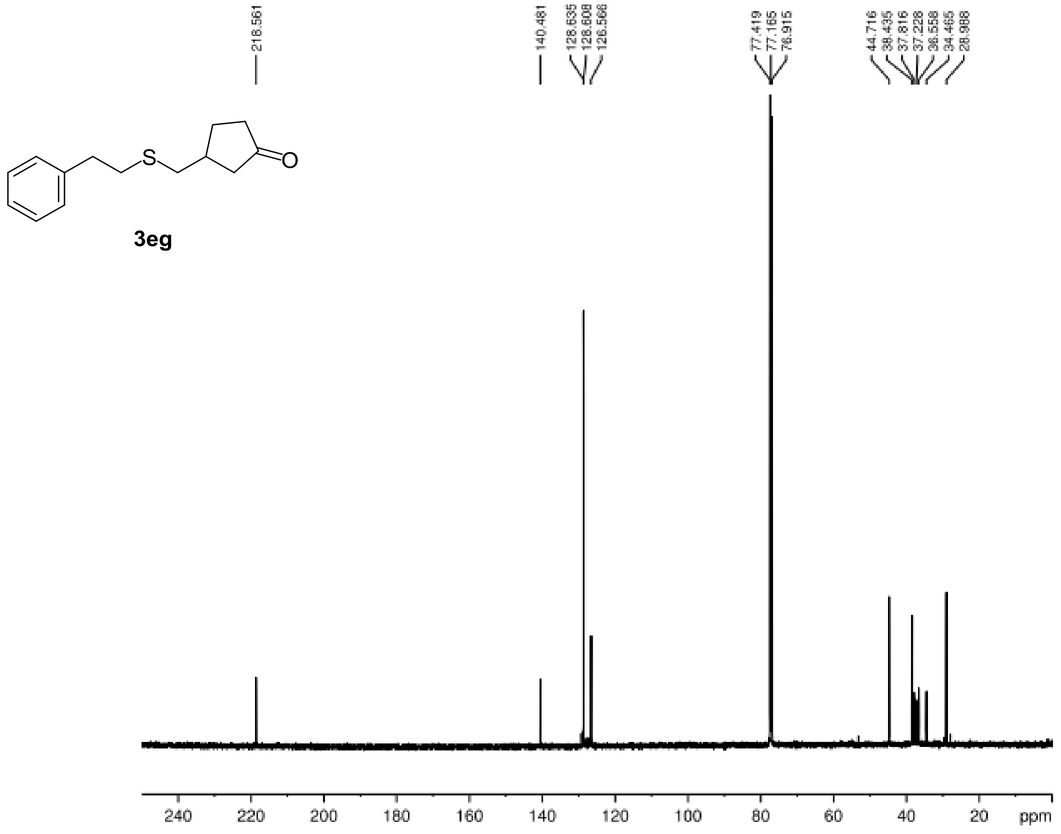

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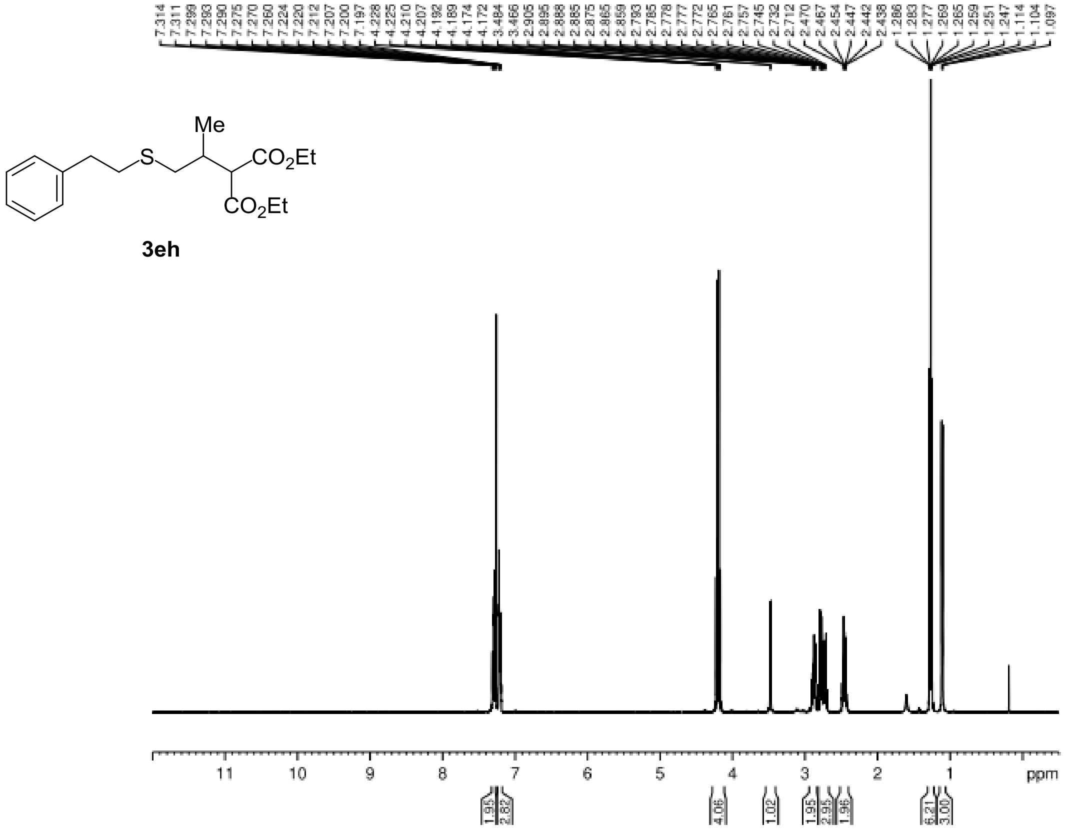

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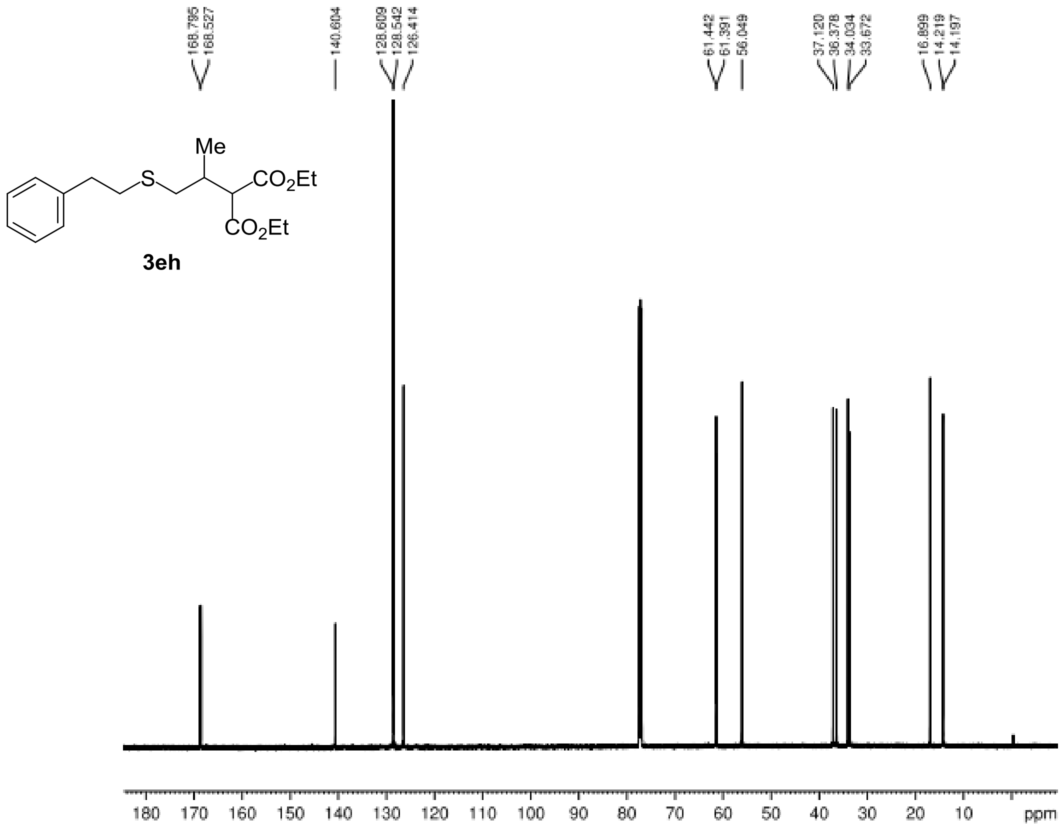

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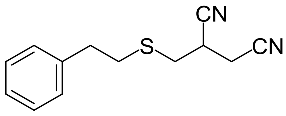

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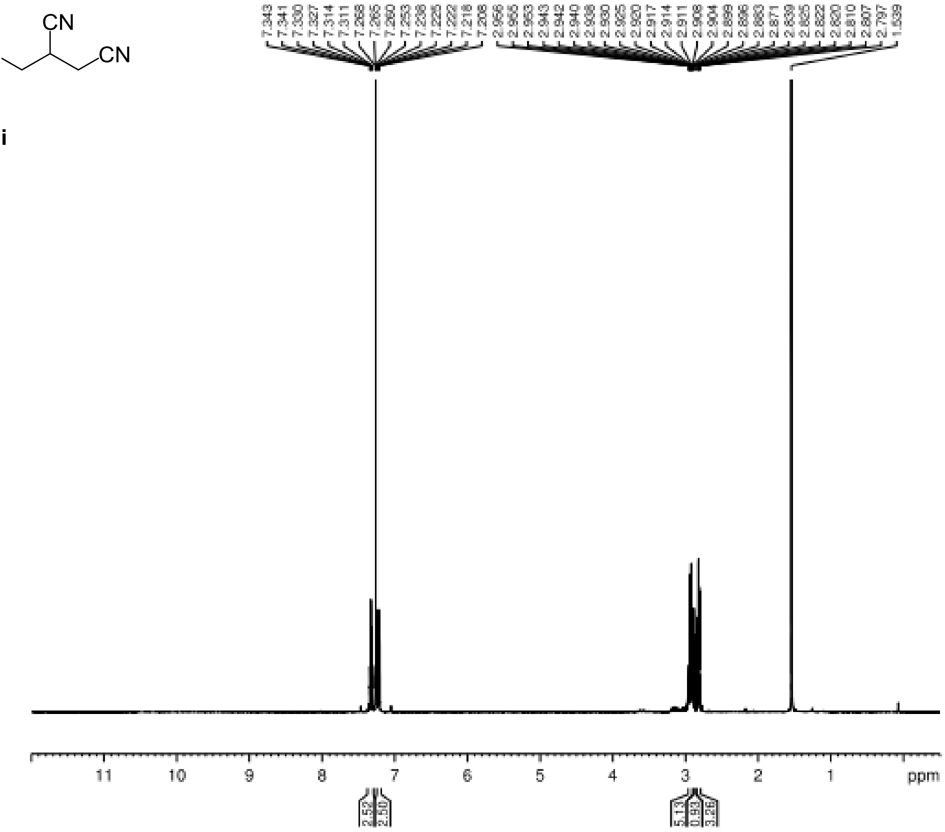

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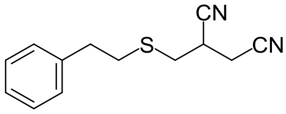

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