Visible-light-Driven, Fluoroalkylthiocyanation of Alkenes via Electron Donor-Accepter Complexes

Zebiao Li[a,b,†], Shan Wang[a,†], Yumei Huo[a], Bing Wang[b], Jun Yan[b], and Quanping Guo[a] [a,*]

[a] Key Laboratory of Preclinical Study for New Drugs of Gansu Province, School of Basic Medical Sciences, Lanzhou University, 199 West Donggang Road, Lanzhou 730000 (China).

[b] Changzhou Pharmaceutical Factory Co., LTD. Changzhou, China

Supporting Information

Table of Content:

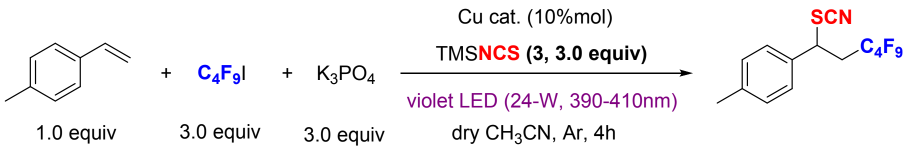
1. **General Information 1**
2. **Optimization of the reaction conditions 1**
3. **General procedure for the fluoroalkylthiocyanation of alkenes 3**
4. **Synthetic Applications 3**
5. **The Mechanistic Study. 4**
6. **References. 7**
7. **Characterization of products 8**
8. **NMR spectra of the products 22**

1. General Information

Unless otherwise statement, all the reactions were carried out under argon atmosphere. All solvents purified and dried according to standard methods prior to use. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker instrument (300 MHz, 75MHz, and 282 MHz) spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard unless otherwise noted. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quartet, coupling constant(s) in Hz integration). Data for ^{13}C NMR and ^{19}F NMR reported in terms of chemical shift (δ, ppm). HRMS obtained by the ESI ionization sources.

2. Optimization of the reaction conditions

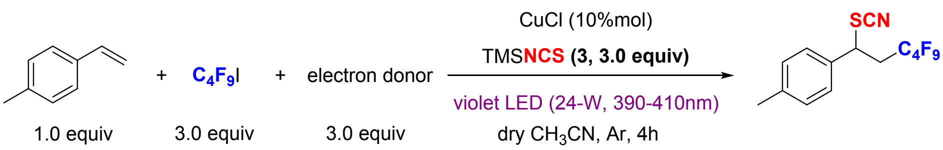
Table S1. Cu Catalysts Screening.



Entry	Cu cat.	Yield (%)[b]	Entry	Cu cat.	Yield (%)[b]
1	CuI	31%	5	$Cu(OTf)_2$	32%
2	CuBr	70%	6	$Cu(OAc)_2$	33%
3	CuCl	87%	7	$Cu(acac)_2$	48%
4	$Cu(CH_3CN)_4PF_6$	23%	8	CuF_2	25%

[a] Unless otherwise noted, the reactions were carried out by using **2a** (0.1 mmol), **1a** (3.0 equiv), **3** (3 equiv), K_3PO_4 (3 equiv), CH_3CN (1.0 mL), Cu catalyst (10 mol %), under Ar, and stirred at rt for 4 h under 24-W violet LED irradiation. [b] ^{1}H NMR yields with anisole internal standard. [c] isolated yield.

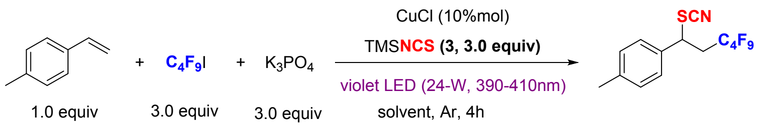
Table S2. Electron donor Screening.



Entry	electron donor	Yield (%)[b]	Entry	electron donor	Yield (%)[b]
1	DIPEA	0	6	Cs_2CO_3	2%
2	Et_3N	0	7	K_2CO_3	51%
3	iPr_2NH	10%	8	Na_2CO_3	52%
4	TMG	0	9	K_3PO_4	87%
5	t-BuOLi	0	10	$KHCO_3$	48%

[a] 0.1mmol scale. [b] ^{1}H NMR yields with anisole internal standard.

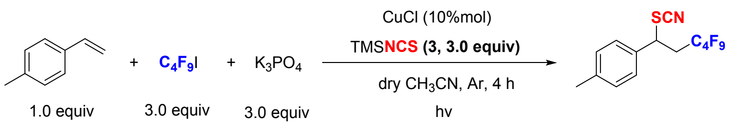
Table S3. Solvents Screening.



Entry	Solvent	Yield (%)b
1	CH_3CN	87%
2	DMF	0
3	DMSO	0
4	DCM	10%

[a]0.1mmol scale. [b] ^{1}H NMR yields with anisole internal standard

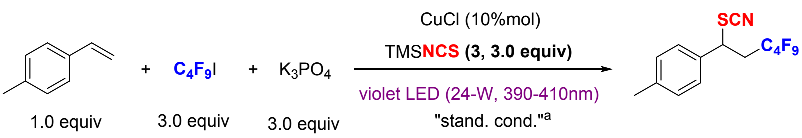
Table S4. Reactions under different wavelengths photo irradiation.



Entry	*hv*	Yield (%)b
1	390-410 nm	87%
2	254 nm	41%
3	blue LED	0
4	white LED	10%

[a]0.1mmol scale. [b] ^{1}H NMR yields with anisole internal standard

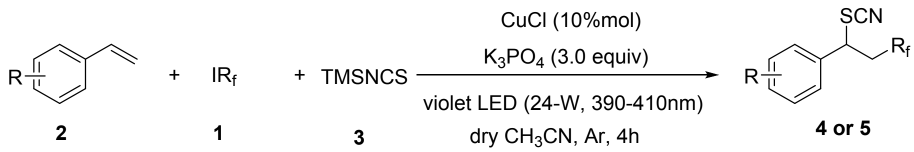
Table S5. Control experiment



Entry	Change from the "stand. cond."	Yield(%)[b]	Entry	Change from the "stand. cond."	Yield(%)[b]
1	10% K_3PO_4	0	10	$La(OTf)_3$ instead of CuCl	23
2	20% K_3PO_4	0	11	$Ni(OTf)_2$ instead of CuCl	22
3	50% K_3PO_4	0	12	$Al(OTf)_3$ instead of CuCl	22
4	1.0 equiv K_3PO_4	trace	13	$AlCl_3$ instead of CuCl	29
5	3.0 equiv K_3PO_4	87	14	$BF_3{\cdot}OEt_2$ instead of CuCl	12
6	50% PPh_3 instead of K_3PO_4	0	15	without CuCl	0
7	3.0 equiv PPh_3 instead of K_3PO_4	0	16	without K_3PO_4	0
8	3.0 equiv H_2O was added	0	17	without light	0
9	0.5 equiv H_2O was added	6	18	2.0 equiv TEMPO was added	0
10	$Fe(OTf)_3$ instead of CuCl	19	19	2.0 equiv BHT was added	0

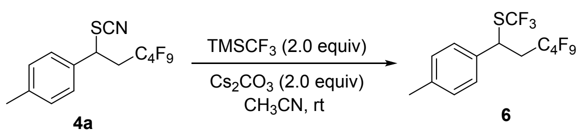
[a] Standerd condition, the reactions were carried out by using **2a** (0.1 mmol), **1a** (3.0 equiv), **3** (3 equiv), K_3PO_4 or other donor (3 equiv), solvent (1.0 mL), Lewis acid (10 mol %), under Ar, and stirred at rt for 4 h under 24-W violet LED irradiation. [b] ^{1}H NMR yields with anisole internal standard.

3. General procedure for the fluoroalkylthiocyanation of alkenes

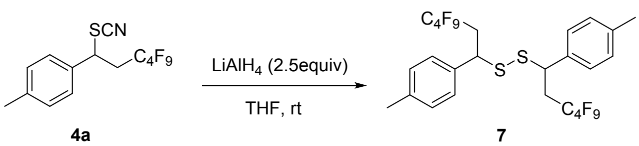


In a dried 10 ml glass test tube, CuCl (0.02 mmol, 2.8 mg), K_3PO_4 (0.6 mmol, 127 mg) were dissolved in CH_3CN (2.0 mL) under Ar atmosphere. Then styrene substrate **2** (0.2 mmol), perfluoroalkyl iodide **1** (IR_f, 0.6 mmol) and TMSNCS (**3**, 0.6 mmol, 78 mg) were added in turn. The glass test tube was transferred to a violet LED photoreactor (24 W, 390-410 nm) stirring for 4 h. After 4 h, the reaction was quenched by H_2O, extracted by EtOAc, dried over anhydrous sodium sulfate, concentrated in vacuo, and the residue was purified by column chromatography to afford the desired product.

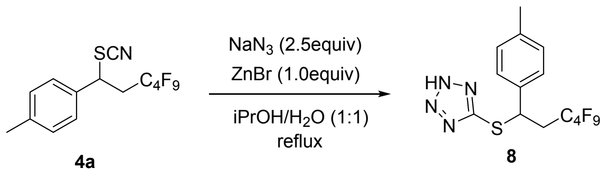
4. Synthetic Applications



4a (0.2 mmol, 79.1 mg), $TMSCF_3$ (0.4 mmol, 56.9 mg) and Cs_2CO_3 (0.4 mmol, 65.2 mg) were added into the solution of CH_3CN (5 ml) in a 10 ml round bottom flask equipped with a stir bar at room temperature under Ar atmosphere for 8 h. After 8 h, the reaction was quenched by H_2O, extracted by EtOAc, dried over anhydrous sodium sulfate, concentrated in vacuo, and the residue was purified by column chromatography to afford the product **6**.



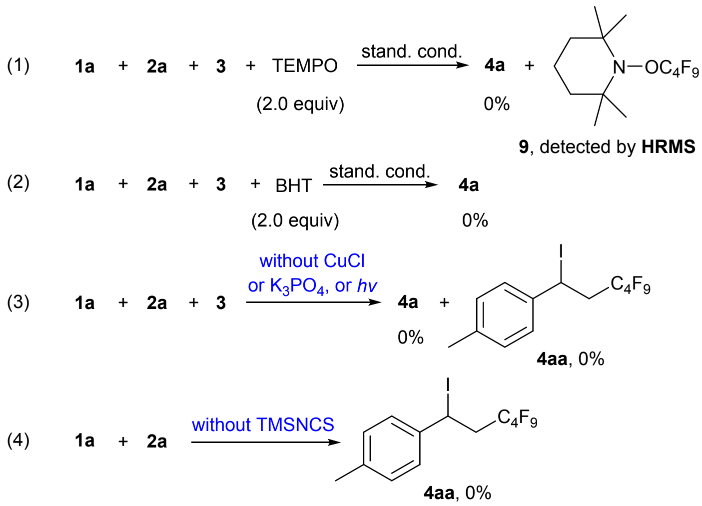
4a (0.2 mmol, 79.1 mg) and $LiAlH_4$ (0.5 mmol, 19 mg) were added into the solution of THF (5 ml) in a 10 ml round bottom flask equipped with a stir bar at room temperature for 5 h. After 5 h, the reaction was concentrated in vacuo and the residue was purified by column chromatography to afford the product **7**.

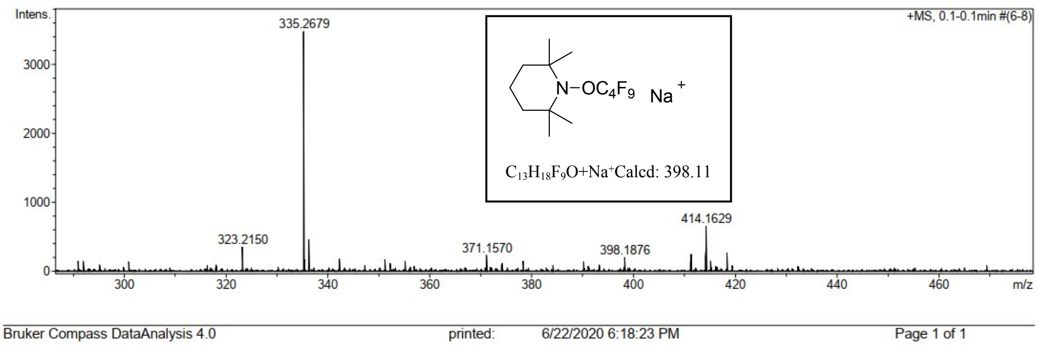


4a (0.2 mmol, 79.1 mg), NaN_3 (0.5 mmol, 32.4 mg) and ZnBr (0.2 mmol, 45 mg) were dissolved in iPrOH/H_2O (1:1, 10 ml) in 25 ml round bottom flask equipped with a stir bar at room temperature under Ar atmosphere, and then refluxed for 8 h. After 8 h, the reaction was cooled to room temperature, concentrated in vacuo and the residue was purified by column chromatography to afford the product **8**.

5. The Mechanistic Study.

5.1 Radical Trapping Experiments.





Discussion: In order to gain some mechanistic insights, radical trapping experiments were carried out. The reaction was completely shut down by 2,2,6,6-tetramethylpiperidin-1-oxyl (TMEPO) and butylated hydroxytoluene (BHT), respectively (eqns 1 and 2). Notably, when TMEPO was added, the radical trapping product **9** was detected by HRMS, which indicated the formation of fluoroalkyl radical (eqn 1). These results suggested that a radical pathway might be involved. The control experiment showed that no desired product **4a** was detected without CuCl, K_3PO_4, or light irradiation (Table 1, entries 15-17), indicating that the Cu salt, K_3PO_4, and light were all indispensable for the reaction. Furthermore, when the reaction was carried out in the absence of TMSNCS, the iodofluoroalkylation product (**4aa**) was not detected, which suggested that the ATRA pathway might not be involved in the aromatic alkenes reaction.

5.2 UV-Vis absorption experiment

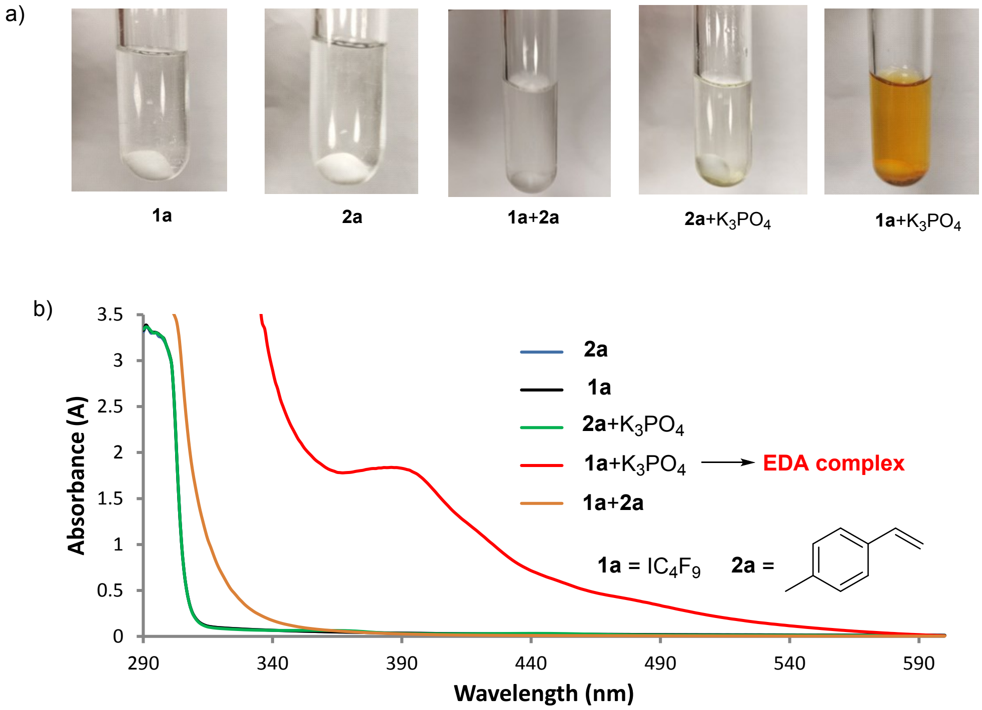


Figure S1. a) 0.1 M for each species in CH_3CN. Images showed the appearance of a yellow color upon the mixing of IC_4F_9 (**1a**) with K_3PO_4. b) UV-vis absorption spectra of the substrates in CH_3CN at concentrations of 0.1 M.

Disscussion: We first tested the -PO_4^{3-} anion for its ability to induce the formation of an EDA complex with perfluorobutyl iodide (IC_4F_9, **1a**) by UV/vis absorption spectroscope.When K_3PO_4 and **1a** were mixed in CH_3CN and stirred at room temperature for 1 h, an obviously yellow color was appeared (Scheme 1a). Meanwhile, the optical absorption spectrum of the mixture showed a significant bathochromic shift to visible spectral region, and a new absorption peak (λ_{max}) appeared at about 390nm (Scheme 1b). Under the same conditions, the mixture of **2a and** K_3PO_4 (**2a**+K_3PO_4) **or 1a** and **2a** (**1a**+**2a**) did not show bathochromic shift. These results suggested that the combination of K_3PO_4 and IC_4F_9 formed a new photoactive EDA complex.

5.3 Proposed mechanism.

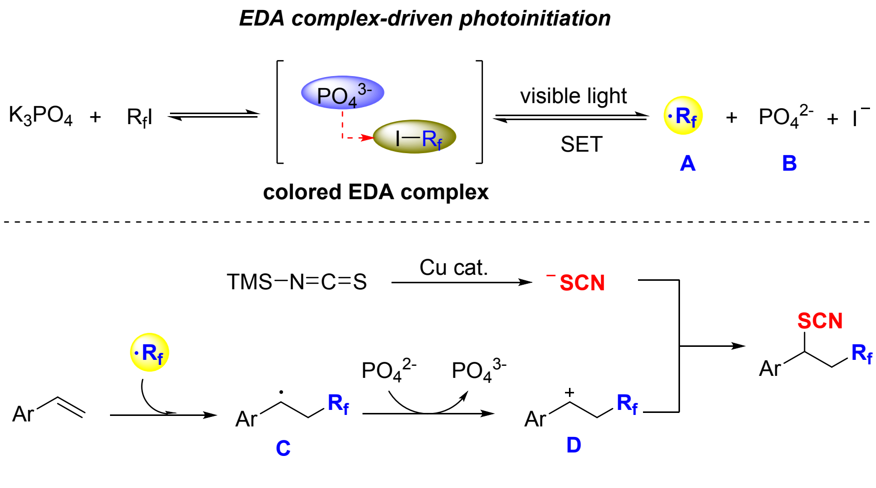


Figure S2. Proposed mechanism for aryl alkenes.

Disscussion: Based on the mechanistic investigations and previous reports,[1] a plausible mechanism was proposed (Figure S2). Firstly, K_3PO_4 and IR_f generate the colored EDA complex. Then, a visible-light-promoted electron transfer leads to the formation of the electron-deficient fluoroalkyl radical **A** through the reductive cleavage of the C−I bond within R_fI and K_3PO_4. The electrophilic fluoroalkyl radical is next trapped by the alkene and forms the benzylic intermediate **C**, which oxidized by PO_4^{2-} anion **B** to generate the carbocation species **D**, the carbocation intermediate **D** attracted by nucleophilic SCN anion to yield the desired product.

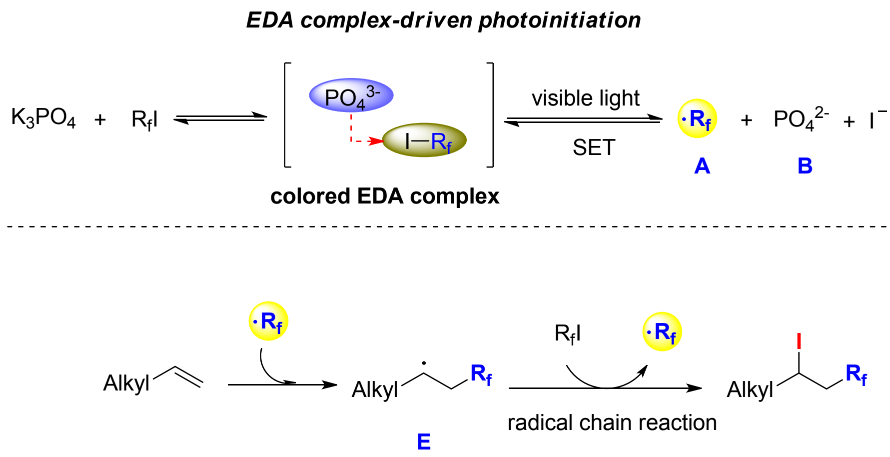
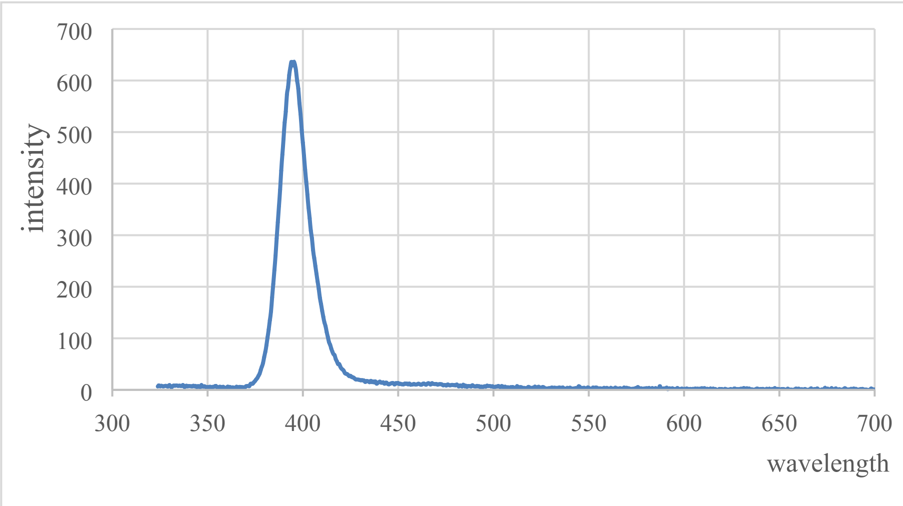


Figure S3. Proposed mechanism for unactivated alkenes.

Disscussion: For unactivated alkenes (Figure S3), firstly, K_3PO_4 and IR_f generate the colored EDA complex. Then, a visible-light-promoted electron transfer leads to the formation of the electron-deficient fluoroalkyl radical **A** through the reductive cleavage of the C−I bond within R_fI and K_3PO_4. The electrophilic fluoroalkyl radical is next trapped by the alkyl alkene and forms the radical intermediate **E**, which would undergo a radical chain mechanism and obtain the iodoperfluoroalkylation product through ATRA pathway.[2]

5.4 Measurement the wavelength of the LED light.

We also measured the wavelength of the LED light by ourselves (recorded on an AVANTES® AvaSpec-ULS2048 spectrometer instrument). The result was shown as follow:

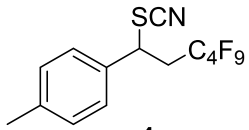


6. References.

(1) (a) R. Foster, Electron donor-acceptor complexes, *J. Phys. Chem.,* 1980, **84**, 2135. (b) S. V. Rosokha, and J. K. Kochi, Fresh look at electron-transfer mechanisms via the donor/acceptor bindings in the critical encounter complex, *Acc. Chem. Res*., 2008, **41**, 641. (c) C. G. S. Lima, T. de M. Lima, M. Duarte, I. D. Jurberg, M. W. Paixão, Organic synthesis enabled by light-irradiation of EDA complexes: theoretical background and synthetic applications, *ACS Catal.,* 2016, **6**, 1389. (d) S. V. Rosokha, J. K. Kochi, Fresh look at electron-transfer mechanisms via the donor/acceptor bindings in the critical encounter complex, *Acc. Chem. Res.,* 2008, **41**, 641. (e) G. E. M. Crisenza, D. Mazzarella, and P. Melchiorre, Synthetic methods driven by the photoactivity of electron donor–acceptor complexes, *J. Am. Chem. Soc.*, 2020, **142**, 5461.

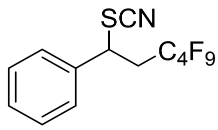
(2) (a) C. –J. Wallentin, J. D. Nguyen, P. Finkbeiner, C. R. J. Stephenson, Visible light-mediated atom transfer radical addition via oxidative and reductive quenching of photocatalysts, *J. Am. Chem. Soc.*, 2012, **134**, 8875; (b) R. Beniazza, R. Atkinson, C. Absalon, F. Castet, S. A. Denisov, N. D. McClenaghan, D. Lastécouerès, J.-M. Vincent, Benzophenone vs. copper/benzophenone in light-promoted atom transfer radical additions (ATRAs): highly effective iodoperfluoroalkylation of alkenes/alkynes and mechanistic studies, *Adv. Synth. Catal*. 2016, **358**, 2949; (c) Y. Wang, J. Wang, G.-X. Li, G. He, Chen, G. Halogen-bond-promoted photoactivation of perfluoroalkyl iodides: a photochemical protocol for perfluoroalkylation reactions, *Org. Lett.,* 2017, **19**, 1442.

7. Characterization of products



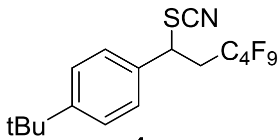
4a

1-methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 67.2 mg, yield:85%, light yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20–7.29 (m, 4H), 4.77 (dd, *J* = 6.0 Hz, 7.8Hz, 1H), 2.92–3.12 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.90, 133.40, 130.10, 127.05, 110.42, 45.29, 36.56 (t, *J* = 21.0 Hz), 21.17; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.05— -81.14 (m, 3F), -111.85— -114.27 (m, 2F), -124.23— -124.29 (m, 2F), -125.92— -126.03 (m, 2F); **HRMS (EI):** $C_{14}H_{10}F_9NS+Na^+$ Calcd: 418.0288, Found: 418.0276.



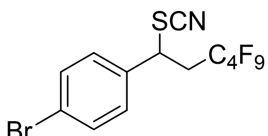
4b

(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 67.9 mg, yield:89%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37–7.45 (m, 5H), 4.77 (dd, *J* = 6.3 Hz, 8.1Hz, 1H), 2.95–3.12 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.46, 129.76, 129.48, 127.16, 110.25, 45.31, 36.42 (d, *J* = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (m, 3F), -111.88— -112.93 (m, 1F), -113.11— -114.15 (m, 1F), -124.23 (dd, *J* = 3.1 Hz, 7.3Hz 2F), -125.94 (d, *J* = 3.7 Hz 2F); **HRMS (EI):** $C_{13}H_8F_9NS+Na^+$ Calcd: 404.0131, Found: 404.0145.



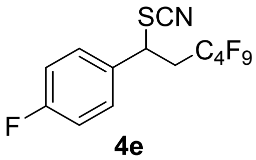
4c

1-(tert-butyl)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 76.1 mg, yield:87%, white solid, mp 43—45℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.26–7.32 (m, 2H), 4.77 (t, *J* = 6.9 Hz, 1H), 2.95–3.11 (m, 2H), 1.32 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.97, 133.37, 126.82, 126.40, 110.51, 45.14, 36.55, 34.77, 31.17; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03— -81.11 (m, 3F), -112.95— -112.23 (m, 2F), -124.17— -124.44 (m, 2F), -125.68— -126.03 (m, 2F); **HRMS (EI):** $C_{17}H_{16}F_9NS+Na^+$ Calcd: 460.0757, Found: 460.0758.



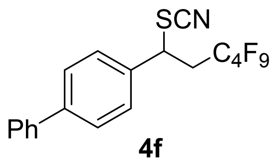
4d

1-bromo-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 72.7 mg, yield:79%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.75 (dd, J = 6.6 Hz, 7.8 Hz, 1H), 2.92–3.08 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 135.53, 132.72, 128.77, 124.00, 109.78, 44.65, 36.42 (t, J = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.95— -81.03 (m, 3F), -111.61— -114.04 (m, 2F), -124.13— -124.20 (m, 2F), -125.86— -125.97 (m, 2F); **HRMS (EI):**$C_{13}H_7BrF_9NS+Na^+$Calcd:481.9237, Found: 481.9321.



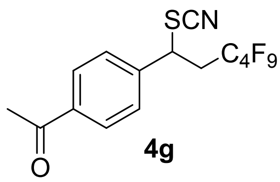
4e

1-fluoro-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 66.2 mg, yield:83%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35–7.39 (m, 2H), 7.08–7.17 (m, 2H), 4.78 (dd, J = 6.6 Hz, 7.8 Hz, 1H), 2.93–3.09 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.17 (d, J = 249.0 Hz), 132.34 (d, J = 3.0 Hz), 129.13 (d, J = 8.3 Hz), 116,74 (t, J = 10.5 Hz), 109.98, 44.60, 36.61 (t, J = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.01— -81.11 (m, 3F), -110.56 (s, 1F), -110.68— -113.22 (m, 1F), -114.08— -114.19 (m, 1F),-124.18— -124.29 (m, 2F), -125.90— -126.02 (m, 2F); **HRMS (EI):** $C_{13}H_7F_{10}NS+Na^+$ Calcd: 422.0037, Found: 422.0042.



4f

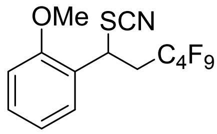
4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)-1,1'-biphenyl, 70.4 mg, yield:77%, yellow solid, mp 84-88℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57–7.63 (m, 4H), 7.43–7.48 (m, 4H), 7.34–7.41 (m, 1H), 4.82 (dd, J = 6.3 Hz, 7.5 Hz, 1H), 2.93–3.21 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.68, 139.82, 135.31, 128.93, 128.10, 127.94, 127.62, 127.13, 110.30, 45.16, 36.53 (t, J = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.01 (m, 3F), -111.71— -112.80 (s, 1F), -113.05— -114.12 (m, 1F), -124.18 (t, J = 2.8 Hz, 2F), -125.90 (d, J = 3.7 Hz); **HRMS (EI):** $C_{19}H_{12}F_9NS+Na^+$ Calcd: 480.0444, Found: 480.0454.



4g

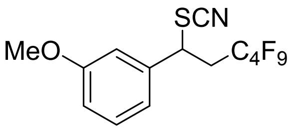
1-(4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)phenyl)ethan-1-one, 72.8 mg, yield:86%, white solid, mp 46—49℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 4.82 (t, J = 6.6 Hz, 1H), 2.97–3.11 (m, 2H), 2.63 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$)

δ 196.99, 141.39, 137.96, 129.39, 127.52, 109.67, 44.60, 36.24 (t, J = 21.0 Hz), 26.64; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.03— -81.11 (m, 3F), -111.61— -114.01 (m, 2F), -124.16— -124.25 (m, 2F), -125.92— -126.03 (m, 2F); **HRMS (EI):**$C_{15}H_{10}F_9NOS+Na^+$Calcd: 446.0237, Found: 446.0232.



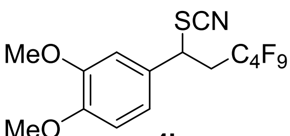
4h

1-methoxy-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 69.1 mg, yield:84%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.28–7.38 (m, 2H), 6.93–7.04 (m, 2H), 5.08 (dd, J = 6.3 Hz, 7.8 Hz, 1H), 3.91 (s, 3H), 2.90–3.24 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.37, 135.19, 130.84, 127.91, 124.85, 121.05, 111.29, 55.91, 40.83, 35.48 (t, J = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.96— -81.06 (m, 3F), -113.60— -113.83 (s, 2F), -124.27— -124.38 (m, 2F), -125.85— -125.98 (m, 2F); **HRMS (EI):** $C_{14}H_{10}F_9NOS+Na^+$ Calcd: 434.0237, Found: 434.0247.



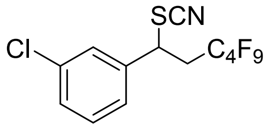
4i

1-methoxy-3-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 67.4 mg, yield:83%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (t, J = 7.8 Hz, 1H), 6.89–6.98 (m, 3H), 4.73 (dd, J = 6.3 Hz, 7.8 Hz, 1H), 3.83 (s, 3H), 2.88–3.16 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.14, 137.92, 130.59, 119.21, 114.85, 113.07, 110.32, 55.35, 45.26, 36.58 (t, J = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.01— -81.11 (m, 3F), -111.98— -113.26 (s, 1F), -114.15— -114.27 (m, 1F), -124.19— -124.30 (m,2F), -125.88— -126.06 (m, 2F); **HRMS (EI):** $C_{14}H_{10}F_9NOS+Na^+$ Calcd: 434.0237, Found: 434.0245.



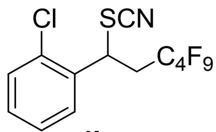
4j

1,2-dimethoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 64.1 mg, yield:73%, white solid, mp 50－54℃. ^{1}H NMR (300 MHz, CDCl3) δ 6.89 (s, 2H), 6.84 (s, 1H), 5.16 (dd, J = 3.6 Hz, 9.6Hz, 1H), 3.91 (d, J = 9.6 Hz 6H), 2.41–2.86 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.60, 149.56, 135.70, 130.24, 118.21, 111.37, 108.56, 55.98 (d, J = 4.5 Hz), 54.09, 39.18(t, J = 21.0 Hz), 18.37; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.05— -81.13 (m, 3F), -113.15— -115.40 (m, 2F), -124.40— -124.52 (m, 2F), -125.90— -126.02 (m, 2F); **HRMS (EI):**$C_{15}H_{12}F_9NO_2S+Na^+$Calcd: 464.0343, Found: 464.0337.



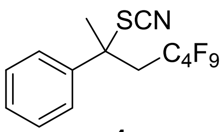
4k

1-chloro-3-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 73.1 mg, yield:88%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35–7.42 (m, 3H), 7.26–7.31 (m, 1H), 4.72 (t, J = 7.2 Hz, 1H), 2.92–3.08 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.48, 135.38, 130.78, 130.04, 127.39, 125.33, 109.71, 44.54, 36.45 (t, J = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.95— -81.04 (m, 3F), -113.73— -114.01 (m, 2F), -124.10— -124.18 (m, 2F), -125.86— -125.97 (m, 2F); **HRMS (EI):**$C_{13}H_7ClF_9NS+Na^+$Calcd: 437.9742, Found: 437.9736.



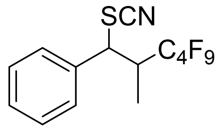
4l

1-chloro-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)benzene, 71.5 mg, yield:86%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45–7.50 (m, 2H), 7.35–7.41 (m, 2H), 5.24 (t, J = 7.2 Hz, 1H), 3.00–3.14 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ134.10, 133.27, 130.72, 130.55, 127.81, 109.82, 41.02, 35.58 (t, J = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.95— -81.04 (m, 3F), -113.25 (d, J = 11.6 Hz, 2F), -124.19— -124.28 (m, 2F), -125.85— -125.96 (m, 2F); **HRMS (EI):**$C_{13}H_7ClF_9NS+Na^+$Calcd: 437.9742, Found: 437.9736.



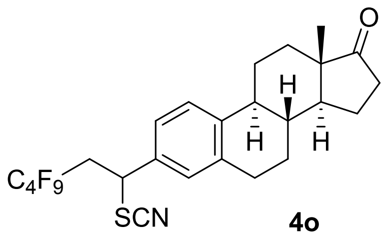
4m

(4,4,5,5,6,6,7,7,7-nonafluoro-2-thiocyanatoheptan-2-yl)benzene, 51.3 mg, yield:65%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50–7.54 (m, 2H), 7.39–7.46 (m, 3H), 3.29–3.46 (m, 1H), 2.90–3.08 (m, 1H), 2.28 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ138.21, 129.32, 129.16, 125.91, 110.60, 56.31, 41.77 (t, J = 19.5 Hz), 26.65 (d, J = 4.5 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.06 (s, 3F), -108.28— -109.36 (m, 1F), -111.97— -113.03 (m, 1F), -124.32— -124.37 (m, 2F), -125.67— -125.80 (m, 2F); **HRMS (EI):**$C_{14}H_{10}F_9NS+Na^+$Calcd: 418.0361, Found: 418.0363.



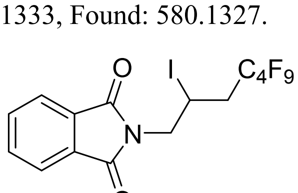
4n

(3,3,4,4,5,5,6,6,6-nonafluoro-2-methyl-1-thiocyanatohexyl)benzene, 59.3 mg, yield:75%, white liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30–7.37 (m, 5H), 4.90 (d, *J* = 3.9 Hz, 1H), 2.86–3.01 (m, 2H), 1.28 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.45, 128.24, 128.13, 128.00, 126.60, 109.62, 51.35 (d, *J* = 5.3 Hz), 41.02 (t, *J* = 20.3 Hz), 8.29 (d, *J* = 4.5 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.89 (t, *J* = 95.9 Hz 3F), -111.25— -112.41 (m, 1F), -116.43— -117.56 (m, 1F), -120.95— -122.33 (m, 2F), -124.58— -127.42 (m, 2F); **HRMS (EI):**$C_{13}H_7ClF_9NS+Na^+$Calcd: 418.0288, Found: 418.0282.



4o

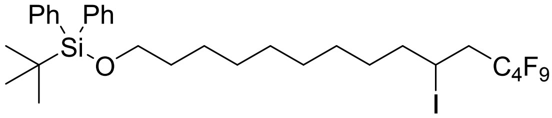
(8R,9S,13S,14S)-13-methyl-3-(3,3,4,4,5,5,6,6,6-nonafluoro-1-thiocyanatohexyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one, 94.8 mg, yield:85%, white liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 1H), 7.09–7.17 (m, 2H), 4.74 (t, *J* = 6.9 Hz, 1H), 2.93–3.11 (m, 4H), 1.96–2.57 (m, 7H), 1.43–1.72 (m, 6H), 1.40 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.62, 137.85, 133.87, 127.67 (d, *J* = 5.3 Hz), 126.46, 124.33 (d, *J* = 4.5 Hz), 110.49, 50.46, 47.91, 45.17, 44.34, 37.82, 36.76, 36.53, 36.23, 35.81, 31.52, 29.31, 26.24, 25.53, 21.56, 13.80; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.98— -81.06 (m, 3F), -111.96— -114.18 (m, 2F), -124.17— -124.27 (m, 2F), 125,86— -125.97 (m, 2F); **HRMS (EI):**$C_{25}H_{24}F_9NOS+Na^+$Calcd: 580.1333, Found: 580.1327.



4p

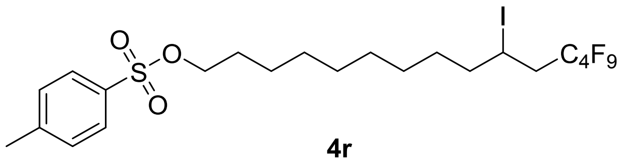
2-(4,4,5,5,6,6,8,8,8-nonafluoro-2-iodooctyl)isoindoline-1,3-dione, 72.5 mg, yield:68%, yellow liquid, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89–7.92 (m, 2H), 7.76–7.80 (m, 2H), 4.67–4.78 (m,1H), 4.18 (dd, *J* = 8.7 Hz, 5.4Hz, 1H), 3.99 (dd, *J* = 6.9 Hz, 7.5Hz, 1H), 2.84–3.02 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.65, 134.43, 131.56, 123.71, 45.83 (d, *J* = 2.3 Hz), 39.25 (d, *J* = 21.8 Hz), 13.14; **^{19}F NMR** (282 MHz, CDCl3) δ -81.07 — -81.15 (m, 3F), -111.78— -114.66 (m, 2F), -

124.44—-124.55 (m, 2F), -125.59—-126.07 (m, 2F); **HRMS (EI)**:$C_{15}H_9F_9INO_2$+Na^+Calcd: 555.9432, Found: 555.9426.



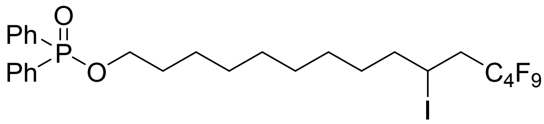
4q

tert-butyl((12,12,13,13,14,14,15,15,15-nonafluoro-10-iodopentadecyl)oxy)diphenylsilane, 113.2 mg, yield:75%, yellow liquid, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79–7.92 (m, 1H), 7.50–7.71 (m, 4H), 7.20–7.44 (m, 5H), 4.28–4.38 (m, 1H), 3.67 (t, *J* = 6.6 Hz, 2H), 2.69–2.97 (m, 2H), 1.71–1.85 (m, 2H), 1.52–1.60 (m, 3H), 1.28–1.36 (m, 11H), 1.06 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 135.62, 135.52, 134.21, 129.92, 129.50, 127.83, 127.78, 127.59, 64.08 (d, *J* = 12.0 Hz), 41.61 (t, *J* = 20.3 Hz), 40.35, 32.55 (d, *J* = 6.0 Hz), 29.75, 29.61, 29.50, 29.32, 28.51 (d, *J* = 1.5 Hz), 26.76 (t, *J* = 8.3 Hz), 25.76 (d, *J* = 1.5 Hz), 20.76, 19.22 (d, *J* = 3.8 Hz) **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.10— -81.17 (m, 3F), -111.27— -115.53 (m, 2F), -122.75— -124.66 (m, 2F), -125.63— -126.08 (m, 2F); **HRMS (EI)**: $C_{31}H_{40}F_9IOSi$+Na^+Calcd: 777.1647, Found: 777.1642.



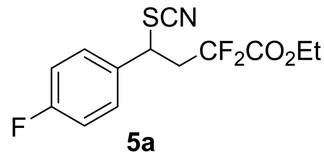
4r

12,12,13,13,14,14,15,15,15-nonafluoro-10-iodopentadecyl 4-methylbenzenesulfonate, 95.2 mg, yield:71%, yellow liquid, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.20–4.30 (m, 1H), 3.95 (t, *J* = 6.3 Hz, 2H), 2.62–2.93 (m, 2H), 2.38 (s, 3H), 1.66–1.77 (m, 2H), 1.51–1.59(m, 3H), 1.17–1.22(m, 11H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.64, 133.20, 129.80, 127.88, 70.66, 41.53 (t, *J* = 19.5 Hz), 40.25, 29.52, 29.24, 29.19, 28.85, 28.80, 28.42, 25.30, 21.63, 20.83; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.99— -81.06 (m, 3F), -111.43— -112.51 (m, 1F), -114.42— -115.48 (m, 1F), -124.53— -124.65 (m, 2F), -125.85— -126.00(m, 2F); **HRMS (EI)**: $C_{22}H_{28}F_9IO_3S$+Na^+Calcd: 693.0558, Found: 693.0552.



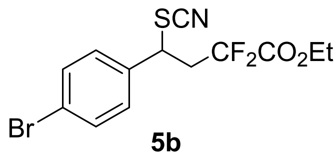
4s

12,12,13,13,14,14,15,15,15-nonafluoro-10-iodopentadecyl diphenylphosphinate, 108.9 mg, yield:76%, yellow liquid, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.78–7.86 (m, 4H), 7.28–7.55 (m, 6H), 4.30–4.36 (m, 1H), 4.03 (q, *J* = 6.6 Hz, 2H), 2.75–2.95 (m, 2H), 1.68–1.85 (m, 3H), 1.35–1.54 (m, 2H), 1.29 (s, 11H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 132.58, 132.08, 132.04, 131,68, 131.55, 130.77, 128.57, 128.40, 64.96 (d, J = 6.0 Hz), 41.50 (t, J = 21.0 Hz), 40.26, 30.51 (d, J = 6.0 Hz), 29.52, 29.32, 29.24, 29.04, 28.43, 25.56, 20.78; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.05— -81.12 (m, 3F), -111.52— -112.58 (m, 1F), -114.43— -115.49 (m, 1F), -124.61— -124.68 (m, 2F), -125.93— -126.03 (m, 2F); **HRMS (EI)**: $C_{27}H_{31}F_9IO_2P$+Na^+Calcd: 739.0860, Found: 739.0855.



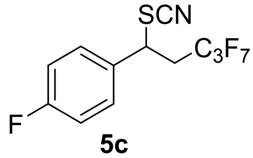
5a

ethyl 2,2-difluoro-4-(4-fluorophenyl)-4-thiocyanatobutanoate, 52.2 mg, yield:86%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34–7.39(m, 2H), 7.07–7.13(m, 2H), 4.69 (dd, J = 6.3 Hz, 2.1 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 2.88–3.14 (m, 2H), 1.30 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.75, 162.81, 161.44, 132.46 (d, J = 3.0 Hz), 129.46 (d, J = 8.3 Hz), 116.36 (d, J = 21.8 Hz), 113.84, 110.26, 63.49, 45.53 (d, J = 4.5 Hz), 40.20 (t, J = 24.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -102.89 (dd, J = 266.8 Hz, 252.6 Hz, 2F), -110.77 (s, 1F); **HRMS (EI):**$C_{13}H_{12}F_3NS$+Na^+Calcd: 326.0439, Found: 326.0433.



5b

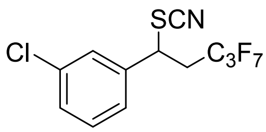
ethyl 4-(4-bromophenyl)-2,2-difluoro-4-thiocyanatobutanoate, 61.9 mg, yield:85%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 4.65 (dd, J = 6.3 Hz, 1.8 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.92–3.07 (m, 2H), 1.31(t, J = 7.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 135.69, 132.47, 129.10, 123.77, 110.99, 63.55, 45.57 (t, J = 4.5 Hz), 39.94 (t, J = 24.0 Hz), 13.79; **^{19}F NMR** (282 MHz, $CDCl_3$) δ **-**102.97 (dd, J = 265.1 Hz, 160.7 Hz, 2F); **HRMS (EI):**$C_{13}H_{12}BrF_2NO_2S$+Na^+Calcd: 385.9638, Found: 385.9632



5c

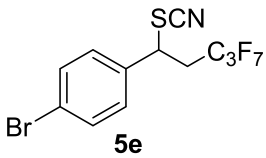
1-fluoro-4-(3,3,4,4,5,5,5-heptafluoro-1-thiocyanatopentyl)benzene, 62.2 mg, yield:89%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34–7.39 (m, 2H), 7.09–7.15 (m, 2H), 4.79 (dd, J = 4.8 Hz, 4.2Hz, 1H), 2.88–3.17 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.17 (d, J = 248.3 Hz), 132.19 (d, J = 14.1 Hz), 129.10 (d, J = 31.0 Hz), 116.60 (d, J = 81.8 Hz), 109.97, 45.96, 34.35 (d, J =

18.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.91— -76.04 (m, 3F), -77.00— -77.14 (m, 3F), -110.47，-185.26— -185.36 (m, 1F); **HRMS (EI):**$C_{12}H_7F_8NS+Na^+$Calcd: 372.0069, Found: 372.0064.



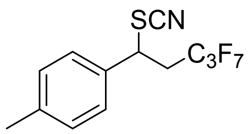
5d

1-chloro-3-(3,3,4,4,5,5,5-heptafluoro-1-thiocyanatopentyl)benzene, 62.8 mg, yield:86%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34–7.39 (m, 3H), 7.25–7.29 (m, 1H), 4.72 (dd, *J* = 5.4 Hz, 3.3Hz, 1H), 2.87–3.16 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.37, 135.34, 130.74, 130.04, 127.36, 125.25, 109.70, 45.87, 34.12 (d, *J* = 18.8 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -76.02— -76.12 (m, 3F), -76.93— -77.03 (m, 3F), -185.17— -185.28 (m, 1F); **HRMS (EI):**$C_{12}H_7ClF_7NS+Na^+$Calcd: 387.9774, Found: 387.9768.



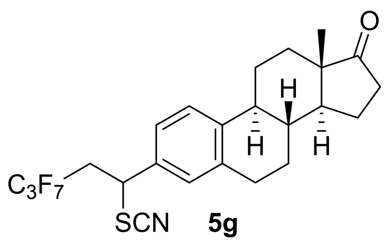
5e

1-bromo-4-(3,3,4,4,5,5,5-heptafluoro-1-thiocyanatopentyl)benzene, 70.5 mg, yield:86%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.73 (dd, *J* = 5.1 Hz, 3.9Hz, 1H), 2.87–3.17 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 135.38, 132.69, 128.72, 124.01, 109.79, 45.99, 34.09 (d, *J* = 18.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.90— -76.03 (m, 3F), -76.99— -77.11 (m, 3F), -185.42— -185.52 (m, 1F); **HRMS (EI):**$C_{12}H_7BrF_7NS+Na^+$Calcd: 431.9268, Found: 431.9263.



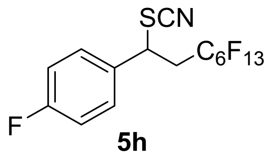
5f

1-(3,3,4,4,5,5,5-heptafluoro-1-thiocyanatopentyl)-4-methylbenzene, 59.4 mg, yield:86%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20–7.27 (m, 4H), 4.78 (dd, *J* = 4.8 Hz, 3.9 Hz, 1H), 2.88–3.20 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.93, 133.24, 130.09, 127.03, 110.42, 46.67, 34.29 (d, *J* = 18.0 Hz), 21.22; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.93— -76.05 (m, 3F), -76.99— -77.12 (m, 3F), -185.42— -185.52 (m, 1F); **HRMS (EI):**$C_{13}H_{10}F_7NS+Na^+$Calcd: 368.0320, Found: 368.0314



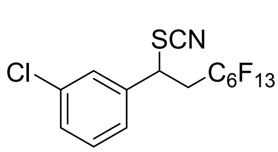
5g

(8R,9S,13S,14S)-3-(3,3,4,4,5,5,5-heptafluoro-1-thiocyanatopentyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one, 85.3 mg, yield:84%, white liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 1H), 7.08–7.16 (m, 2H), 4.75 (dd, *J* = 5.4 Hz, 3.0Hz, 1H), 2.91–3.20 (m, 4H), 1.96–2.57 (m, 7H), 1.43–1.69 (m, 6H), 0.92 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.62, 137.80, 133.77, 127.63 (d, *J* = 5.3 Hz), 126.42, 124.28 (d, *J* = 5.3 Hz), 110.49, 50.45, 47.90, 46.53, 44.33, 37.80, 35.81, 34.28, 34.03, 31.52, 29.31, 26.25, 25.52, 21.56, 13.80; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -76.02— -76.14 (m, 3F), -76.92— -77.05 (m, 3F), -185.51— -185.57 (m, 1F); **HRMS (EI):**$C_{24}H_{24}F_7NOS+Na^+$Calcd: 530.1365, Found: 530.1359.



5h

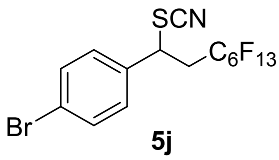
1-fluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-thiocyanatooctyl)benzene, 83.9 mg, yield:84%, white solid, mp 72—75°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36–7.41 (m, 2H), 7.09–7.16 (m, 2H), 4.80 (dd, *J* = 6.6 Hz, 7.5Hz, 1H), 2.93–3.09 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.18 (d, *J* = 249.0 Hz), 132.36 (d, *J* = 3.8 Hz), 129.14 (d, *J* = 8.3 Hz), 116,61 (d, *J* = 21.8 Hz), 109.99, 44.63, 36.70 (t, *J* = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.82— -80.90 (m, 3F), -110.57 (s, 1F), -111.58— -113.97 (m, 2F), -121.80— -121.98 (m, 2F), -122.90— -123.29 (m, 2F), -123.30— -123.37 (m, 2F), -126.18— -126.31 (m, 2F); **HRMS (EI):**$C_{15}H_7F_{14}NS+Na^+$Calcd: 521.9973, Found: 521.9968.



5i

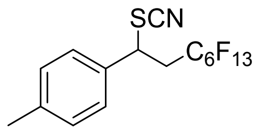
1-chloro-3-(3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1-thiocyanatononyl)benzene, 91.8 mg, yield:89%, white solid, mp 67—69°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34–7.39 (m, 3H), 7.27–7.31 (m, 2H), 4.72 (t, *J* = 7.2 Hz, 1H), 2.93–3.08 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.56, 135.53, 130.74, 129.99, 127.39, 125.33, 109.76, 44.52, 36.45 (t, *J* = 21.0 Hz); **^{19}F NMR** (282

MHz, $CDCl_3$) δ -80.97— -81.05 (m, 3F), -111.62— -112.67 (m, 1F), -112.84— -113.87 (m, 1F), -121.86— -121.95 (m, 2F), -123.00— -123.04 (m, 2F), -123.29— -123.41 (m, 2F), -126.28— -126.42 (m, 2F); **HRMS (EI):**$C_{15}H_7ClF_{13}NS+Na^+$Calcd: 537.9678, Found: 537.9672.



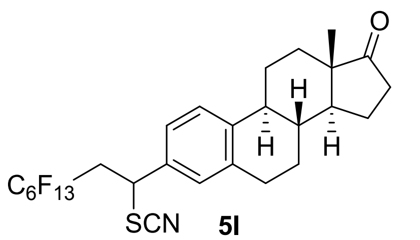
5j

1-bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-thiocyanatooctyl)benzene, 94.1 mg, yield:84%, yellow solid, mp 57－59℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.75 (dd, *J* = 6.6 Hz, 1.2Hz, 1H), 2.93–3.08 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 135.54, 132.72, 128.77, 123.99, 109.81, 44.67, 36.34 (d, *J* = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.81 (t, *J* = 9.9 Hz, 3F), -111.39— -112.44 (m, 1F), -112.78— -113.83 (m, 1F), -121.77— -121.85 (m, 2F), -122.87— -122.93 (m, 2F), -123.21— -123.33 (m, 2F), -126.14— -126.27 (m, 2F); **HRMS (EI):**$C_{15}H_7BrF_{13}NS+Na^+$Calcd: 581.9173, Found: 581.9167.



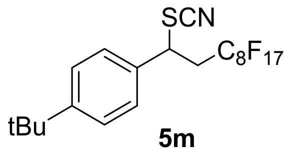
5k

1-methyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-thiocyanatooctyl)benzene, 86.2 mg, yield:87%, white solid, mp 66－69℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.25 (q, *J* = 8.4 Hz 4H), 4.77 (dd, *J* = 6.3 Hz, 1.5 Hz, 1H), 2.93–3.08 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.91, 133.38, 130.11, 127.05, 110.44, 45.31, 36.78 (d, *J* = 21.0 Hz), 21.22; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.83 (t, *J* = 10.2 Hz, 3F), -111.61— -112.71 (m, 1F), -112.96— -114.04 (m, 1F), -121.79— -121.88 (m, 2F), -122.94 (d, *J* = 3.7 Hz 2F), -123.27— -123.38 (m, 2F), -126.17— -126.28 (m, 2F); **HRMS (EI):**$C_{16}H_{10}F_{13}NS+Na^+$Calcd: 518.0224, Found: 518.0219.



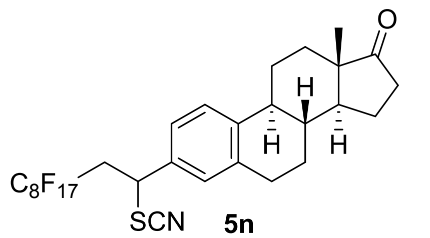
5l

(8R,9S,13S,14S)-13-methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-thiocyanatooctyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one, 113.1 mg, yield:86%, white solid, mp 137－140℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 1H), 7.09–7.17 (m, 2H), 4.74 (t, *J* = 6.6 Hz, 1H), 2.93–3.11 (m, 4H), 1.96–2.57 (m, 7H), 1.43–1.72 (m, 6H), 0.92 (s, 3H); **[13]C NMR** (75 MHz, $CDCl_3$) δ 141.62, 137.85, 133.90, 127.67 (d, *J* = 5.3 Hz), 126.46, 124.33 (d, *J* = 4.5 Hz), 110.49, 50.46, 47.91, 45.21, 44.35, 37.82, 36.59, 35.80, 31.52, 29.31, 26.24, 25.53, 21.56, 13.79; **[19]F NMR** (282 MHz, $CDCl_3$) δ -80.83 (t, *J* = 9.9 Hz, 3F), -111.74—-112.77 (m, 1F), -112.93— -114.01 (m, 1F), -121.80 (t, *J* = 10.7 Hz, 2F), -122.92 (d, *J* = 3.7 Hz, 2F), -123.25— -123.31 (m, 2F), -126.15— -126.28 (m, 2F); **HRMS (EI):**$C_{27}H_{24}F_{13}NOS+Na^+$Calcd: 680.1269, Found: 680.1263.



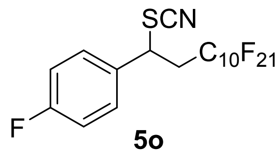
5m

1-(tert-butyl)-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-thiocyanatodecyl)benzene, 112.2 mg, yield:88%, white solid, mp 87－89℃. **[1]H NMR** (300 MHz, $CDCl_3$) δ 7.42–7.45 (m, 2H), 7.29–7.32 (m, 2H), 4.77 (t, *J* = 6.6 Hz, 1H), 2.90–3.12 (m, 2H), 1.32 (s, 9H); **[13]C NMR** (75 MHz, $CDCl_3$) δ 152.95, 133.39, 126.81, 126.38, 110.50, 45.14, 36.50 (d, *J* = 21.8 Hz), 34.74, 31.13; **[19]F NMR** (282 MHz, $CDCl_3$) δ -80.82 (t, *J* = 9.6 Hz, 3F), -112.73—-112.85 (m, 1F), -112.97— -113.18 (m, 1F), -121.61(d, *J* = 7.9 Hz, 2F), -121.97 (t, *J* = 7.3 Hz, 4F), -122.79 (d, *J* = 3.1 Hz, 2F), -123.27 (d, *J* = 13.5 Hz, 2F), -126.14— -126.26 (m, 2F); **HRMS (EI):** $C_{21}H_{16}F_{17}NS+Na^+$ Calcd: 660.0630, Found: 660.0650.



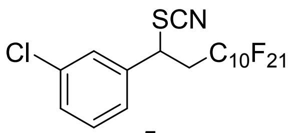
5n

(8R,9S,13S,14S)-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-thiocyanatodecyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one, 124.2 mg, yield:82%, yellow liquid. **[1]H NMR** (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 1H), 7.10–7.17 (m, 2H), 4.74 (t, *J* = 6.9 Hz, 1H), 2.56–3.08 (m, 4H), 1.97–2.54 (m, 7H), 1.43–1.97 (m, 6H), 0.93 (s, 3H); **[13]C NMR** (75 MHz, $CDCl_3$) δ 141.61, 137.84, 133.91, 127.67 (d, *J* = 5.3 Hz), 126.46, 124.33 (d, *J* = 5.3 Hz), 110.48, 50.46, 47.90, 45.18, 44.34, 37.82, 36.61, 35.80, 31.52, 29.30, 26.24, 25.53, 21.55, 13.78; **[19]F NMR** (282 MHz, $CDCl_3$) δ -80.83— -80.91 (m, 3F), -112.67— -112.78 (m, 1F), -112.94— -113.05 (m, 1F), -121.63 (d, *J* = 7.9 Hz, 2F), -121.98 (d, *J* = 7.6 Hz, 4F), -122.82 (s, 2F), -123.82 (s, 2F), -126.17— -126.28 (m, 2F); **HRMS (EI):**$C_{29}H_{24}F_{17}NOS+Na^+$Calcd: 780.1250, Found: 780.1199



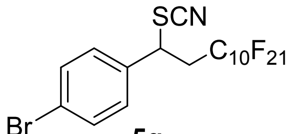
5o

1-fluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluoro-1-thiocyanatododecyl)benzene, 100.7 mg, yield:72%, white solid, mp 61—63℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36–7.41 (m, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 4.78(t, *J* = 7.2 Hz, 1H), 2.93–3.07 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.18 (d, *J* = 249.0 Hz), 132.36 (d, *J* = 3.0 Hz), 129.13 (d, *J* = 8.3Hz), 116.60 (d, *J* = 21.8 Hz), 109.97, 44.64, 36.71 (t, *J* = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.80— -80.96 (m, 3F), -110.59 (d, *J* = 14.1 Hz, 1F), -111.52— -112.58 (m, 1F), -112..88— -113.98 (m, 1F), -121.79 (d, *J* = 62.0 Hz 10F), -122.84 (s, 2F), -123.27 (s, 2F), -126.27 (d, *J* = 8.5 Hz 2F); **HRMS (EI):**$C_{19}H_7F_{22}NS+Na^+$Calcd: 721.9846, Found: 721.9840.



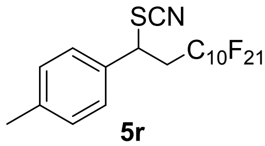
5p

1-chloro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluoro-1-thiocyanatododecyl)benzene, 111.65 mg, yield:78%, white solid, mp 69—73℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35–7.40 (m, 3H), 7.26–7.31 (m, 1H), 4.72(t, *J* = 6.9 Hz, 1H), 2.93–3.08 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.50, 135.38, 130.77, 130.04, 127.39, 125.32, 109.70, 44.57, 36.40 (d, *J* = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.77— -80.84 (m, 3F), -111.47— -112.53 (m, 1F), -112.75— -113.81 (m, 1F), -121.72 (d, *J* = 70.5 Hz 10F), -122.78 (s, 2F), -123.18 (s, 2F), -126.19 (s, 2F); **HRMS (EI):**$C_{19}H_7ClF_{21}NS+Na^+$Calcd: 737.9550, Found: 737.9545.



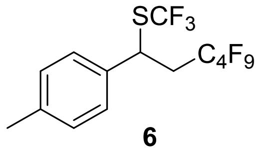
5q

1-bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluoro-1-thiocyanatododecyl)benzene, 117.1 mg, yield:77%, yellow solid, mp 98-100℃. **^{1}H NM R** (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 4.73 (t, *J* = 6.9 Hz, 1H), 2.93–3.08 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 135.54, 132.74, 128.78, 124.01, 109.81, 44.70, 36.53 (t, *J* = 21.0 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.70— -80.77 (m, 3F), -111.32— -112.37 (m, 1F), -112.75— -113.81 (m, 1F), -121.80 (s, 10F), -122.73 (s, 2F), -123.18 (s, 2F), -126.14 (s,2F); **HRMS (EI):**$C_{19}H_7BrF_{21}NS+Na^+$Calcd: 781.9045, Found: 781.9039.



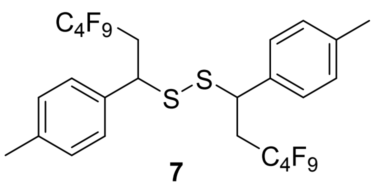
5r

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluoro-1-thiocyanatododecyl)-4-methylbenzene, 104.3 mg, yield:75%, white solid, mp 97-102℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 4.77 (t, *J* = 6.3 Hz, 1H), 2.93–3.11 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.90, 133.43, 130.10, 127.05, 110.41, 45.32, 36.66 (d, *J* = 20.3 Hz), 21.17; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.92 (t, *J* = 9.9Hz, 3F), -111.67— -112.74 (m, 1F), -113.00— -114.07 (m, 1F), -121.81 (d, *J* = 68.2 Hz 10F), -122.86 (s, 2F), -123.32 (s, 2F), -126.29 (s,2F); **HRMS (EI):**$C_{20}H_{10}F_{21}NS+Na^{+}$Calcd: 718.0096, Found: 718.0091.



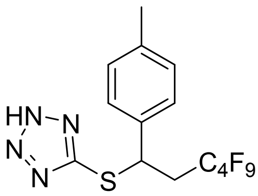
6

(3,3,4,4,5,5,6,6,6-nonafluoro-1-(p-tolyl)hexyl)(trifluoromethyl)sulfane, 53.4 mg, yield:61%, yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.4 Hz, 5.4 Hz, 4H), 4.75 (dd, *J* = 5.4 Hz, 3.3 Hz, 1H), 2.80–2.97 (m, 2H), 2.35 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.75, 135.03, 131.84, 129.86, 127.76, 127.02, 41.74, 37.68 (t, *J* = 20.3 Hz), 21.10; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.65 (s, 3F), -81.12— -81.20 (m, 3F), -111.75— -112.77 (m, 1F), -113.74— -114.80 (m, 1F), -124.51— -124.56 (m, 2F), -126.02— -126.12 (m, 2F).



7

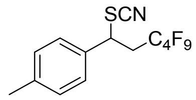
1,2-bis(3,3,4,4,5,5,6,6,6-nonafluoro-1-(p-tolyl)hexyl)disulfane,1,2-bis(3,3,4,4,5,5,6,6,6-nonafluoro-1-(p-tolyl)hexyl)disulfane, 125.4 mg, yield:85%, yellow solid, mp 79－81℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.08–7.17 (m, 4H), 6.98–7.06 (m, 4H), 3.64–3.74 (m, 2H), 2.54–2.80 (m, 4H), 2.28 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.49, 137.43, 134.33, 128.58, 128.53, 126.77, 126.64, 45.38, 45.06, 34.53, 34.25, 34.18, 33.97, 20.11, 20.09; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.06— -81.13 (m, 3F), -111.01— -112.08 (m, 2F), -113.17— -114.33 (m, 2F), -124.34— -124.43 (m, 4F), -124.44— -126.07 (m, 4F); **HRMS (EI):**$C_{26}H_{20}F_{18}S_2+Na^{+}$Calcd: 761.0617, Found: 761.0611.



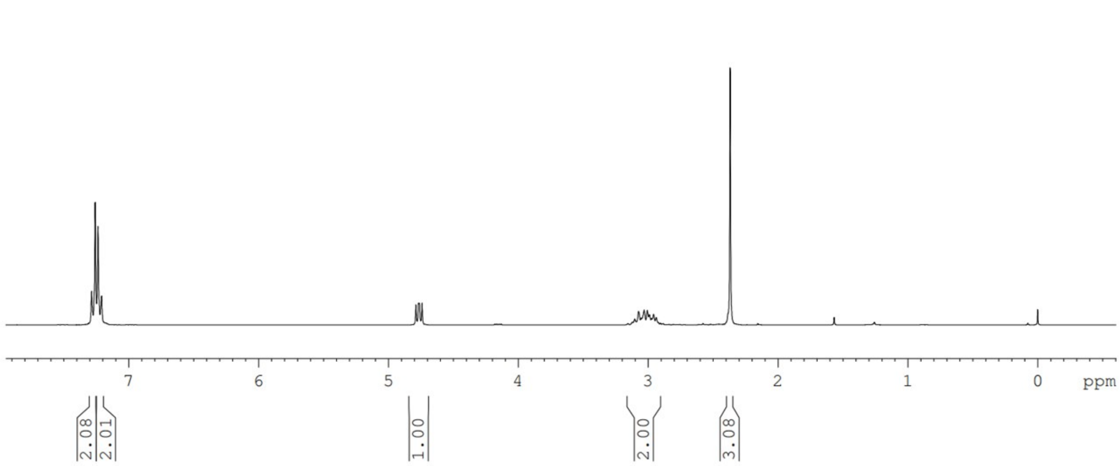
8

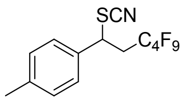
5-((3,3,4,4,5,5,6,6,6-nonafluoro-1-(p-tolyl)hexyl)thio)-2H-tetrazole, 60.5 mg, yield:69%, white solid, mp 82－85℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.8 Hz 3H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.18 (dd, *J* = 5.1 Hz, 4.2 Hz, 1H), 2.84–3.19 (m, 2H), 2.32 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.96, 138.92, 134.95, 129.83, 127.21, 44.78, 36.73 (t, *J* = 20.3 Hz), 21.15; **^{19}FNMR** (282 MHz, $CDCl_3$) δ -81.03— -81.09 (m, 3F), -111.35— -112.40 (m, 1F), -113.40— -114.45 (m, 1F), -124.34— -124.41 (m, 2F), -125.90— -126.03 (m, 2F); **HRMS (EI):**$C_{14}H_{11}F_9N_4S+H^+$Calcd: 439.0633, Found: 439.0639.

8. NMR spectra of the products

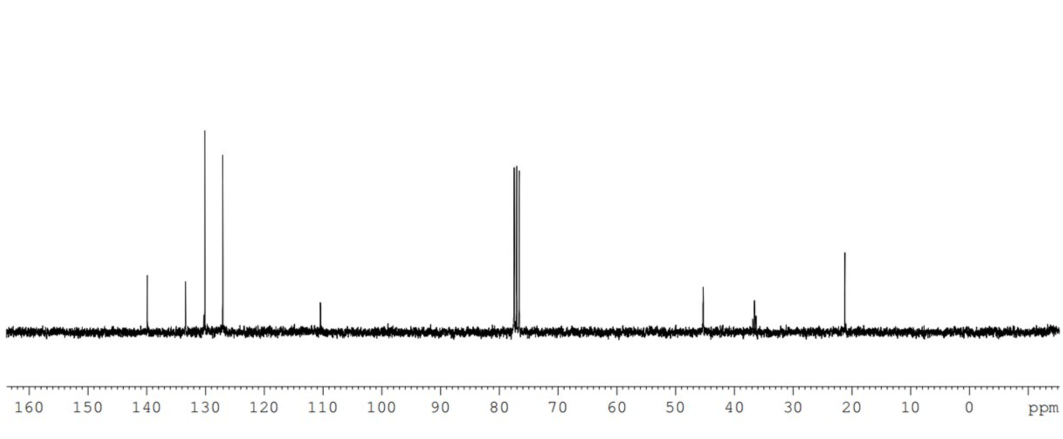


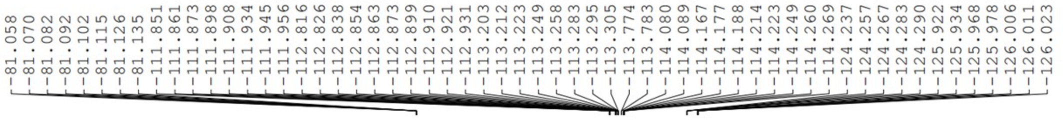
4a, ^{1}H NMR (300 MHz, $CDCl_3$)

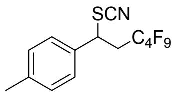




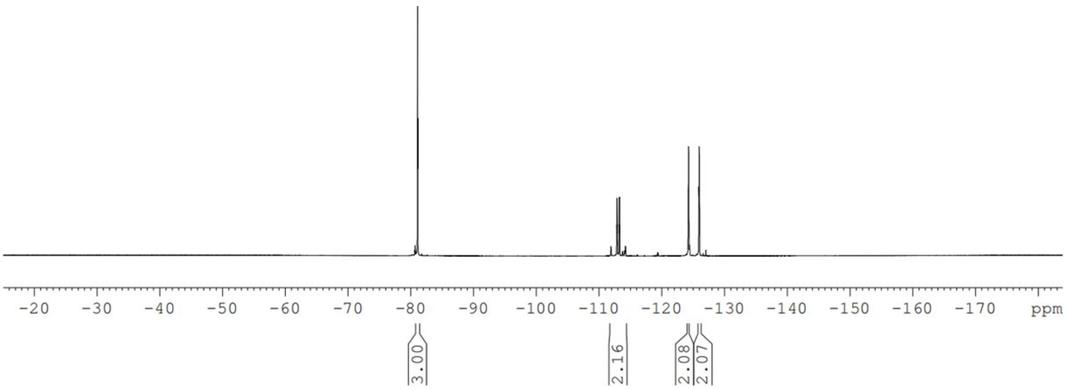
4a, ^{13}C NMR (75 MHz, $CDCl_3$)

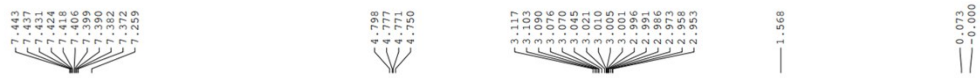


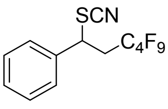




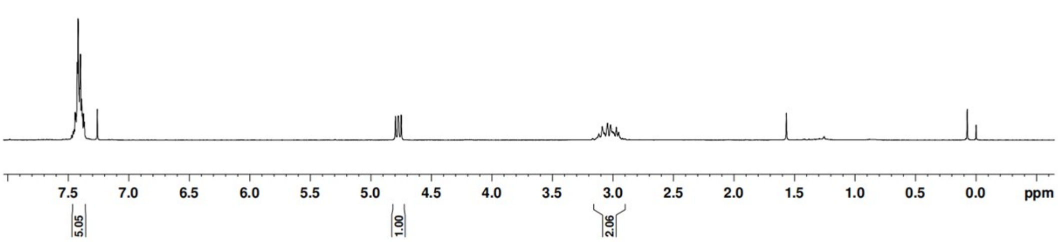
4a, ^{19}F NMR (282 MHz, $CDCl_3$)

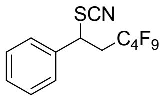




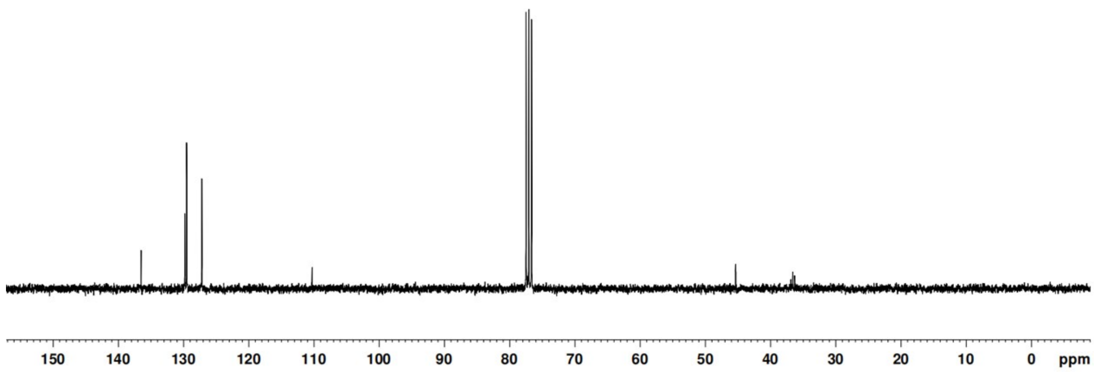


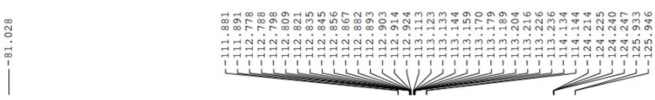
4b, ^{1}H NMR (300 MHz, $CDCl_3$)

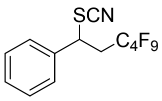




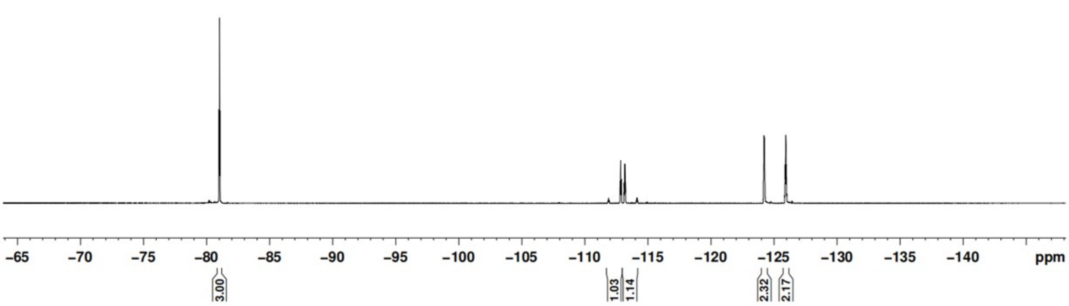
4b, ^{13}C NMR (75 MHz, $CDCl_3$)

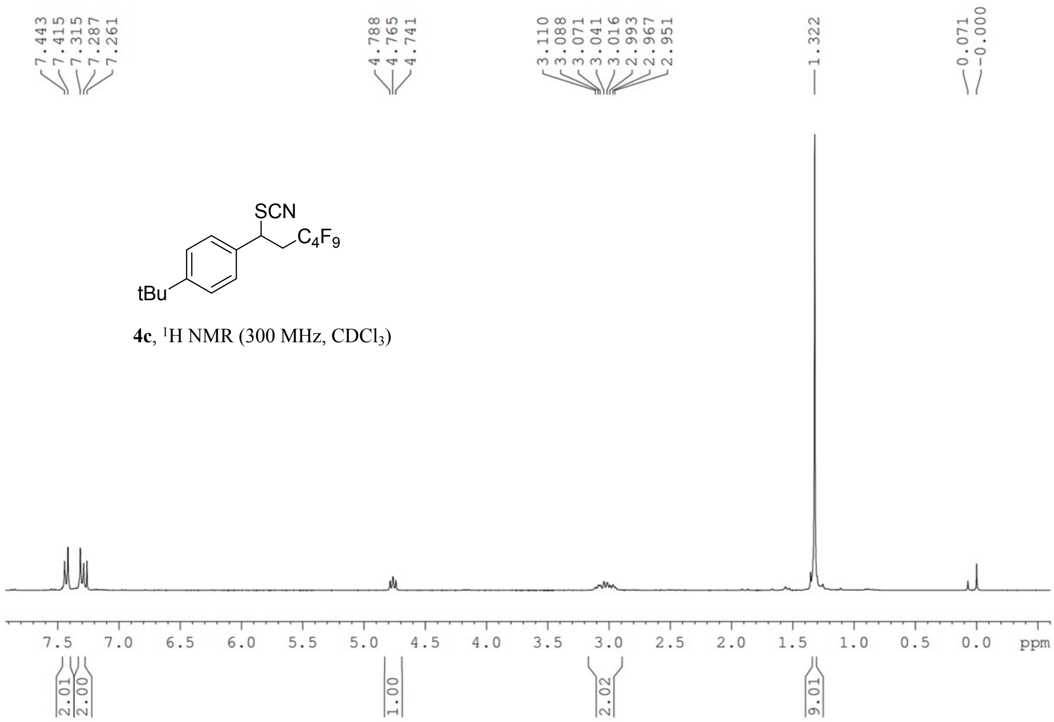




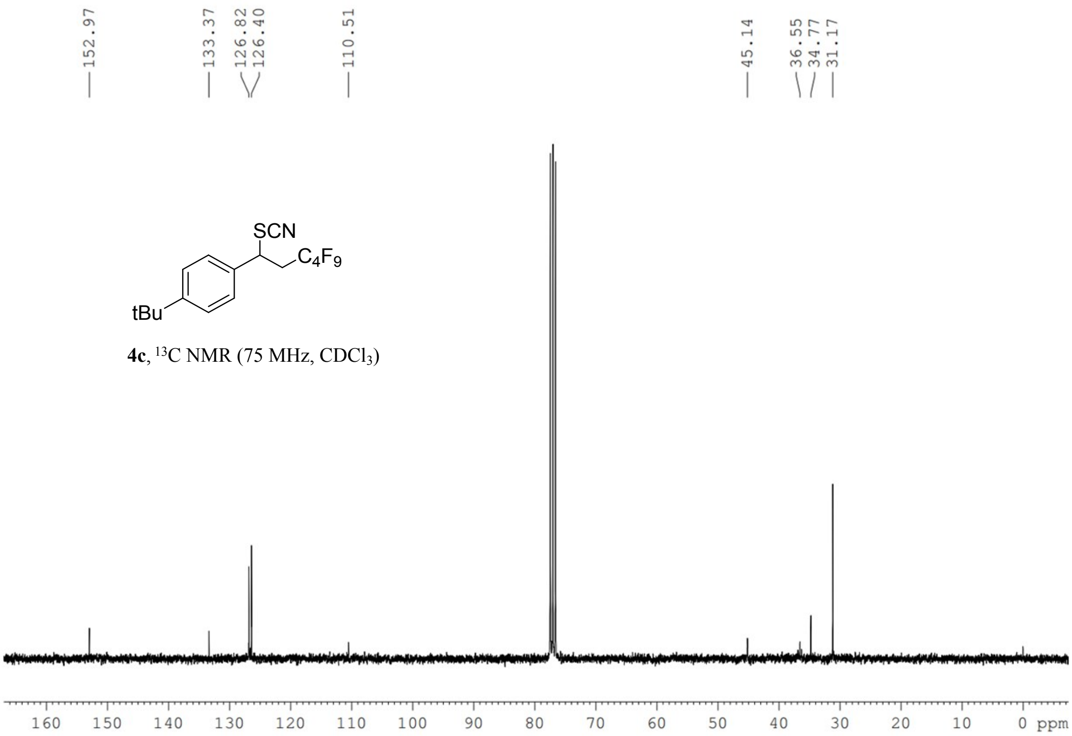


4b, ^{19}F NMR (282 MHz, $CDCl_3$)

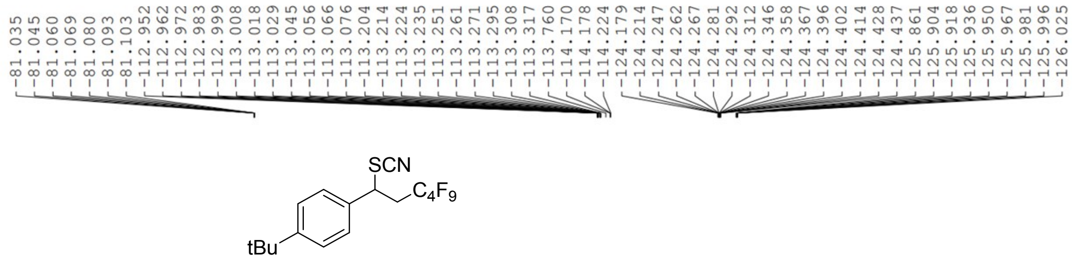




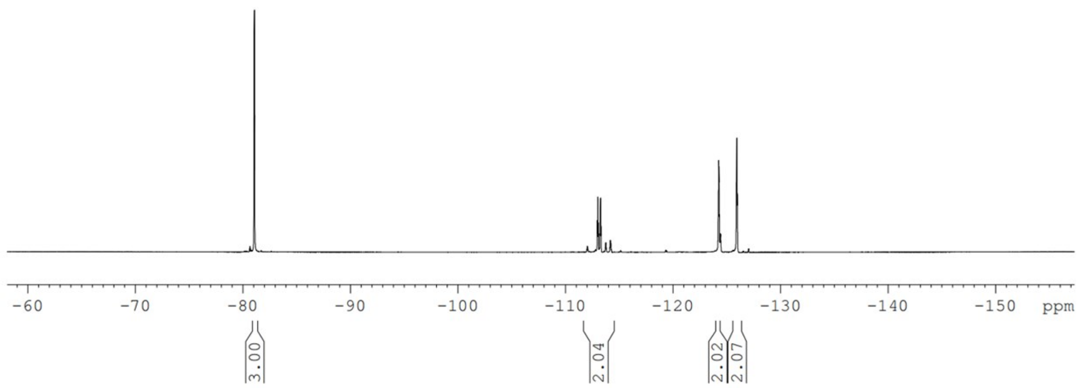
4c, ^{1}H NMR (300 MHz, $CDCl_3$)

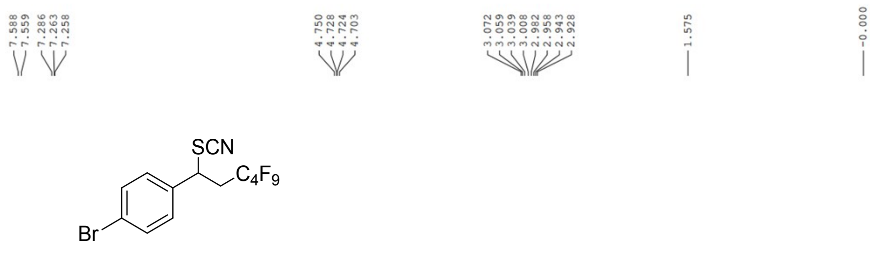


4c, ^{13}C NMR (75 MHz, $CDCl_3$)

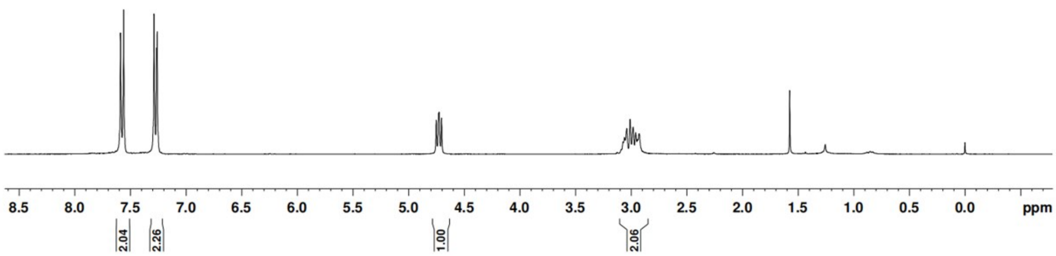


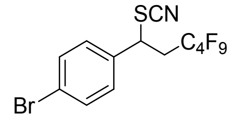
4c, ^{19}F NMR (282 MHz, $CDCl_3$)



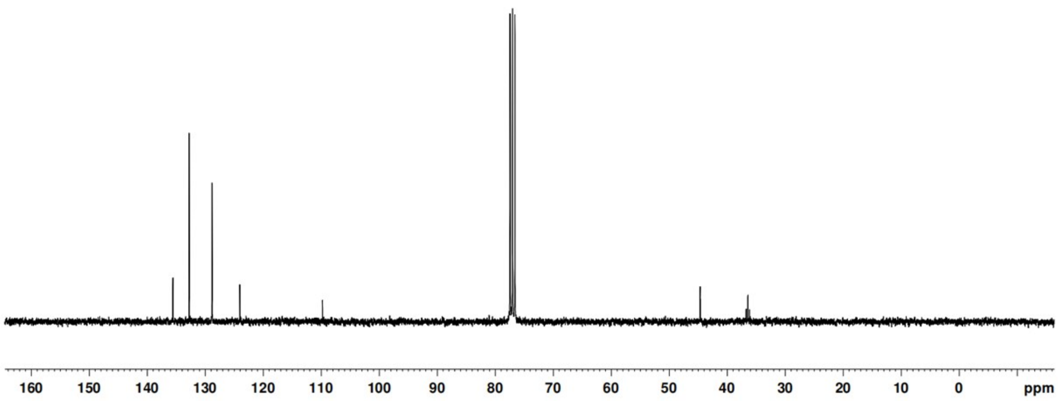


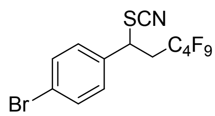
4d, ^{1}H NMR (300 MHz, $CDCl_3$)



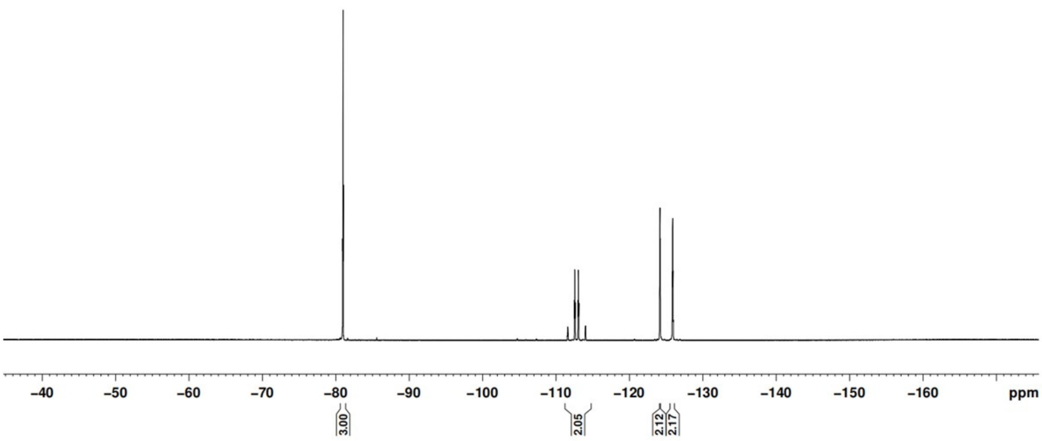


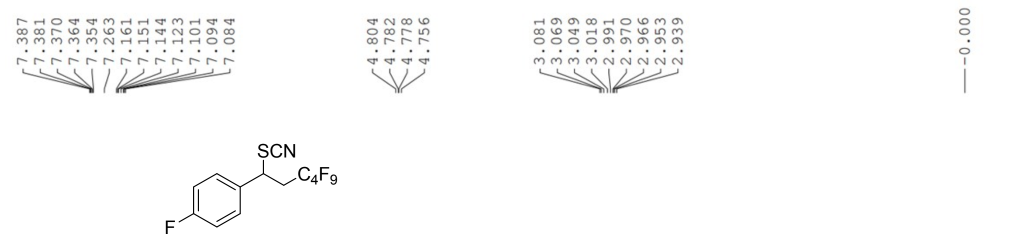
4d, ^{13}C NMR (75 MHz, $CDCl_3$)



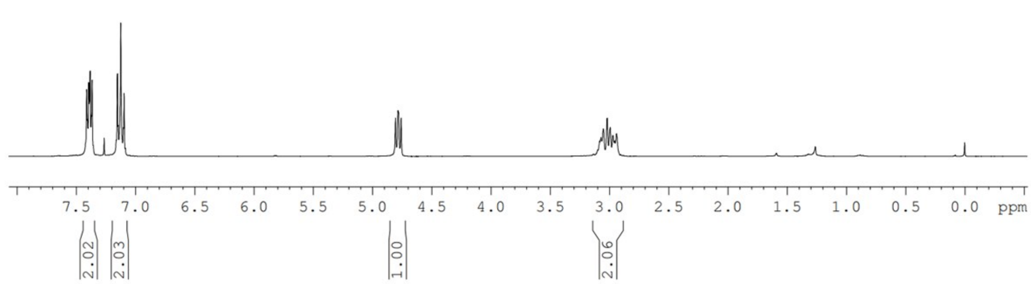


4d, ^{19}F NMR (282 MHz, $CDCl_3$)

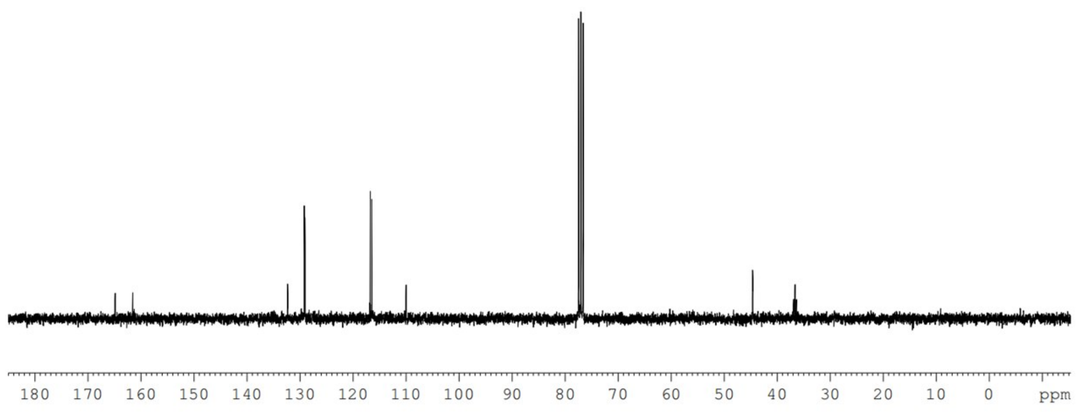


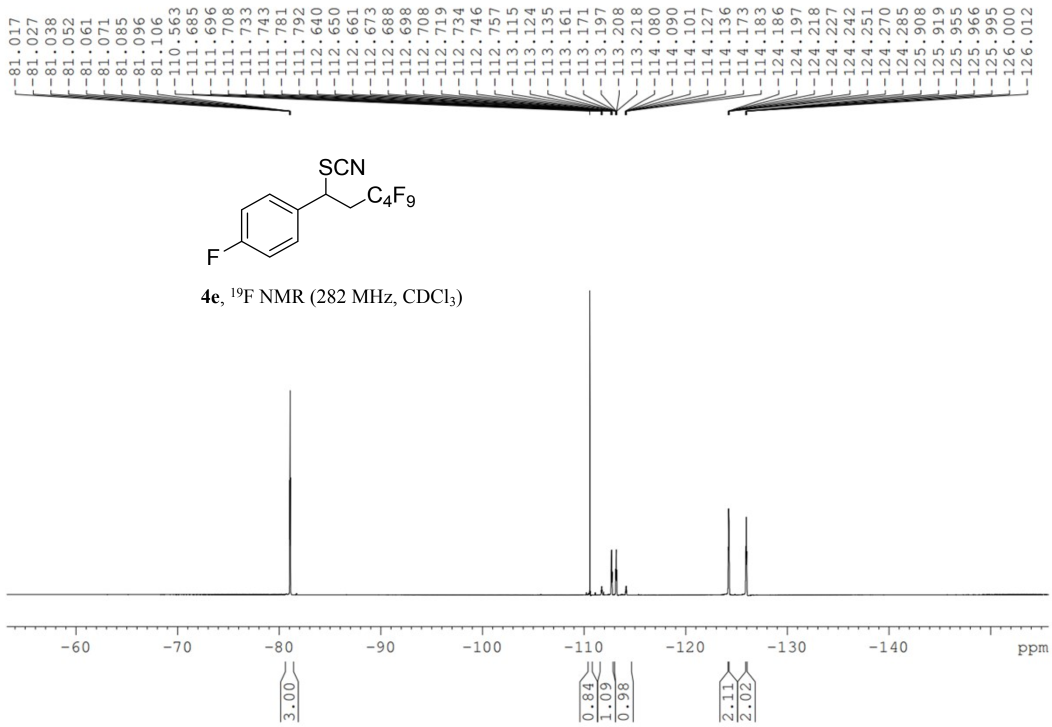


4e, ^{1}H NMR (300 MHz, $CDCl_3$)

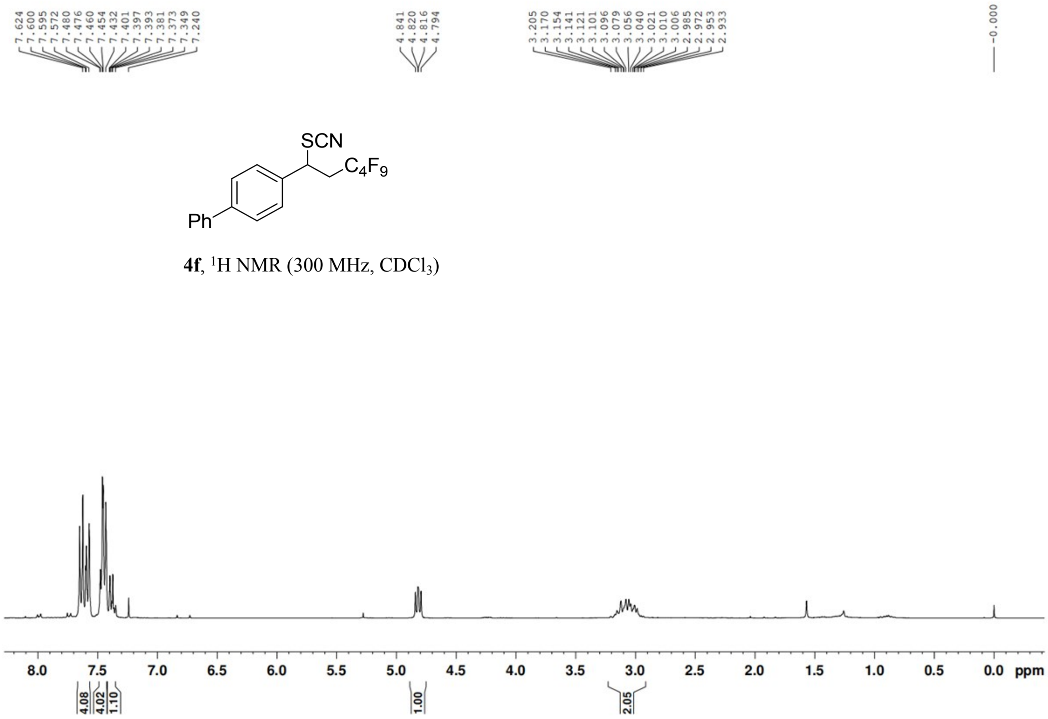


4e, ^{13}C NMR (75 MHz, $CDCl_3$)

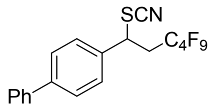




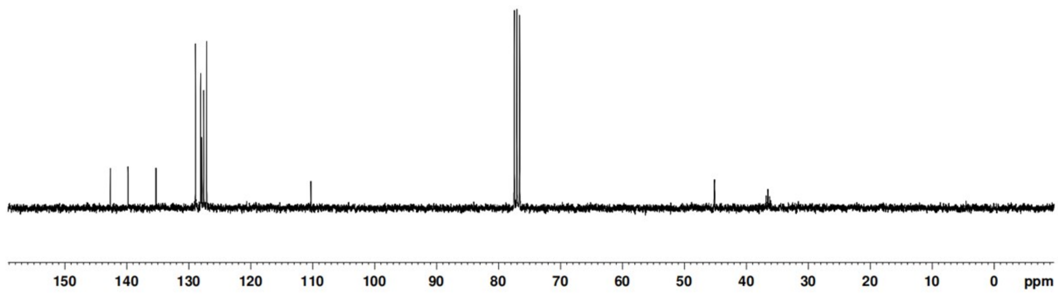
4e, ^{19}F NMR (282 MHz, $CDCl_3$)

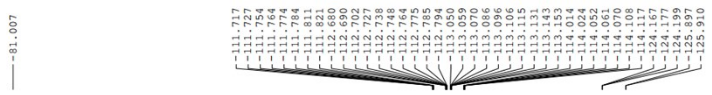


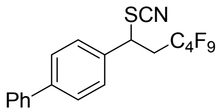
4f, ^{1}H NMR (300 MHz, $CDCl_3$)



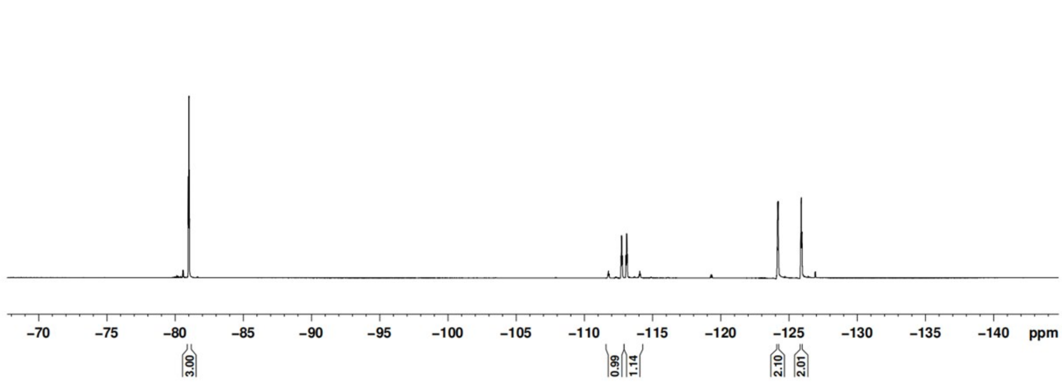
4f, ^{13}C NMR (75 MHz, $CDCl_3$)

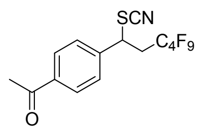




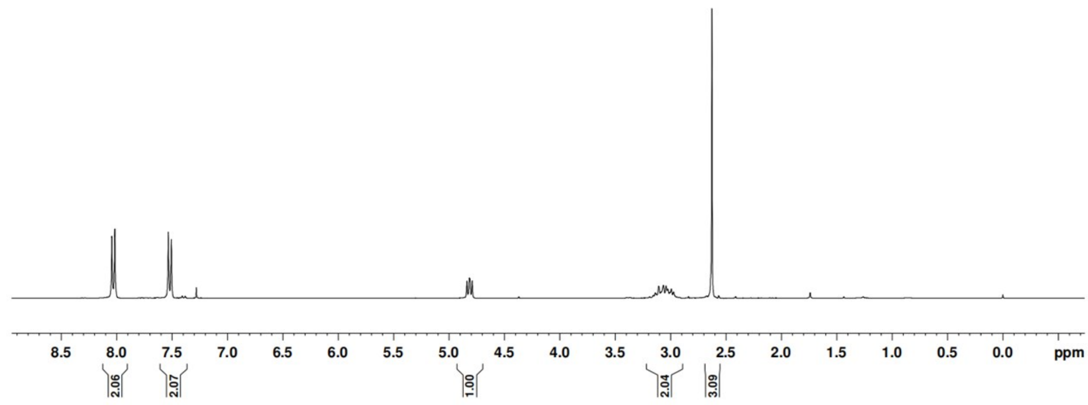


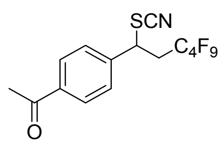
4f, ^{19}F NMR (282 MHz, $CDCl_3$)



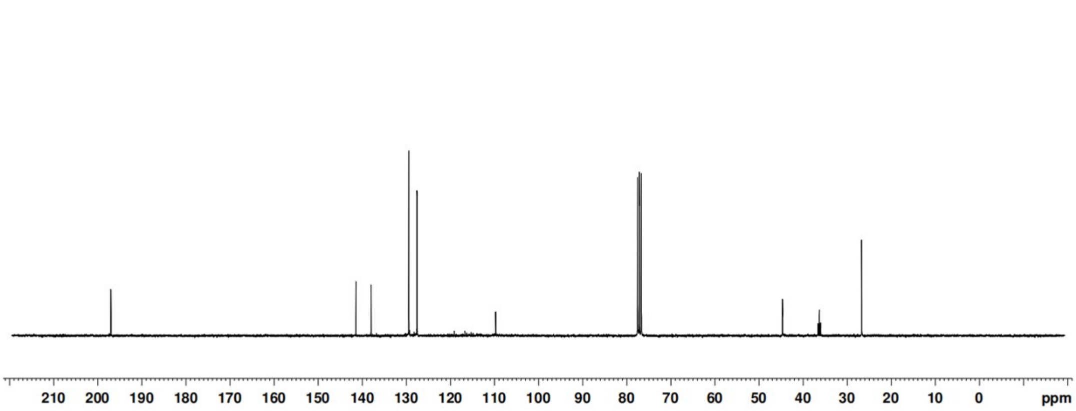


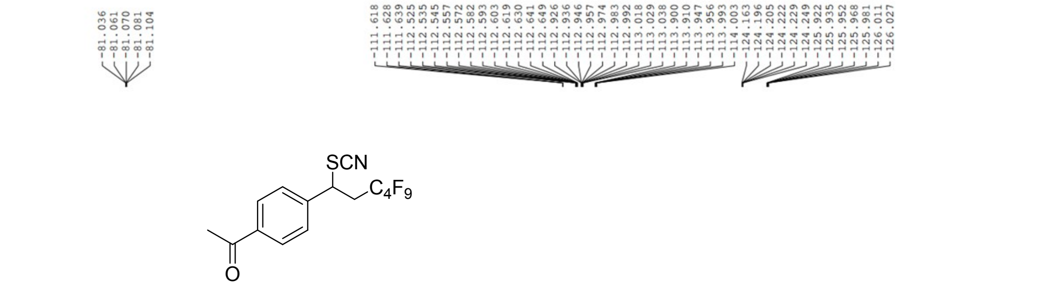
4g, ^{1}H NMR (300 MHz, $CDCl_3$)



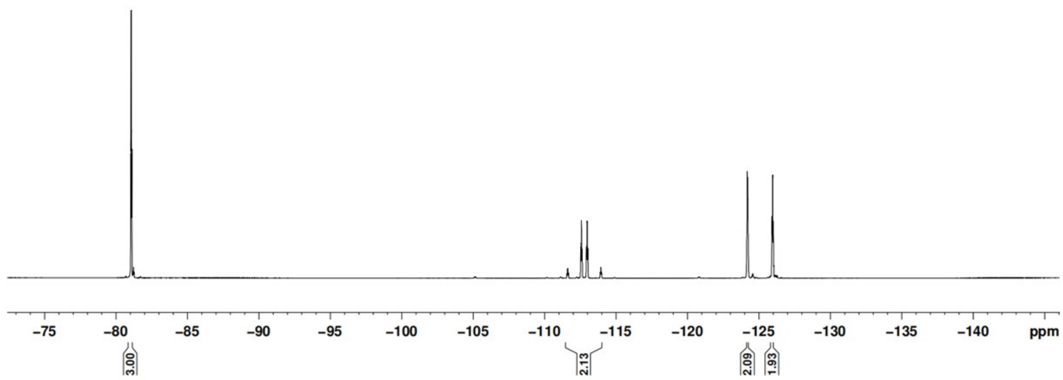


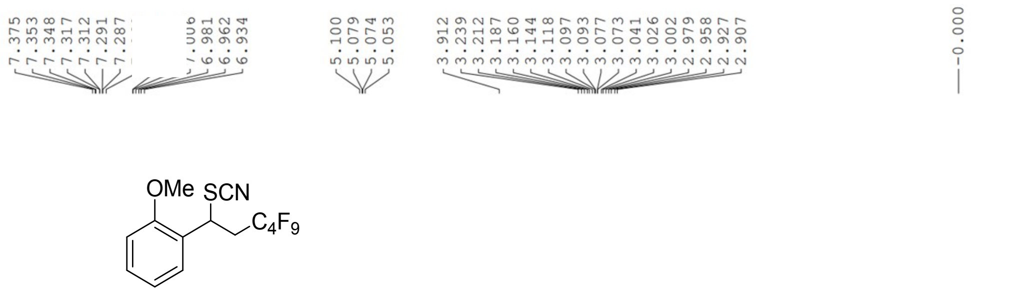
4g, ^{13}C NMR (75 MHz, $CDCl_3$)



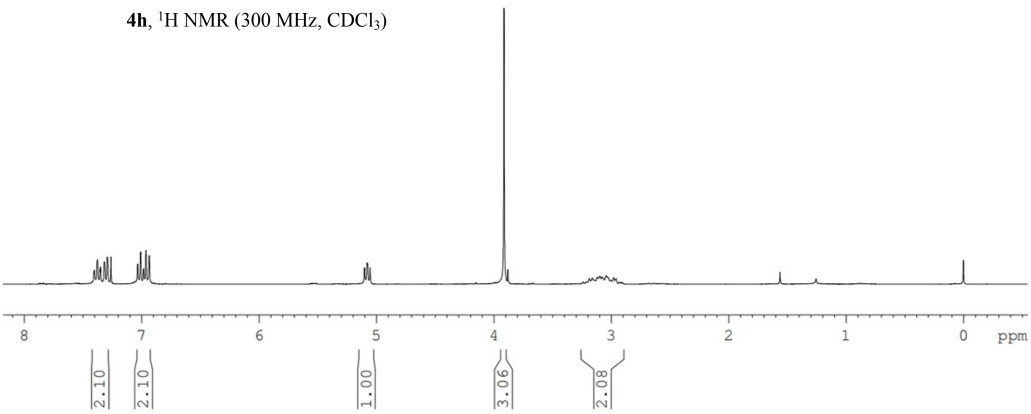


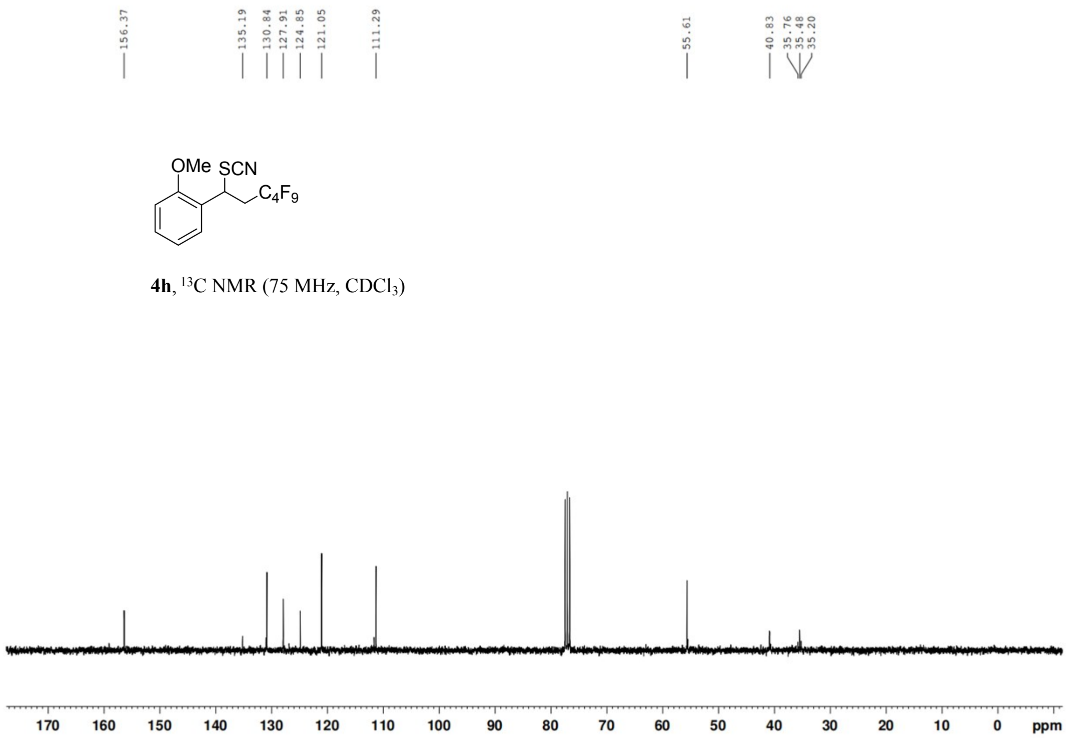
4g, ^{19}F NMR (282 MHz, $CDCl_3$)



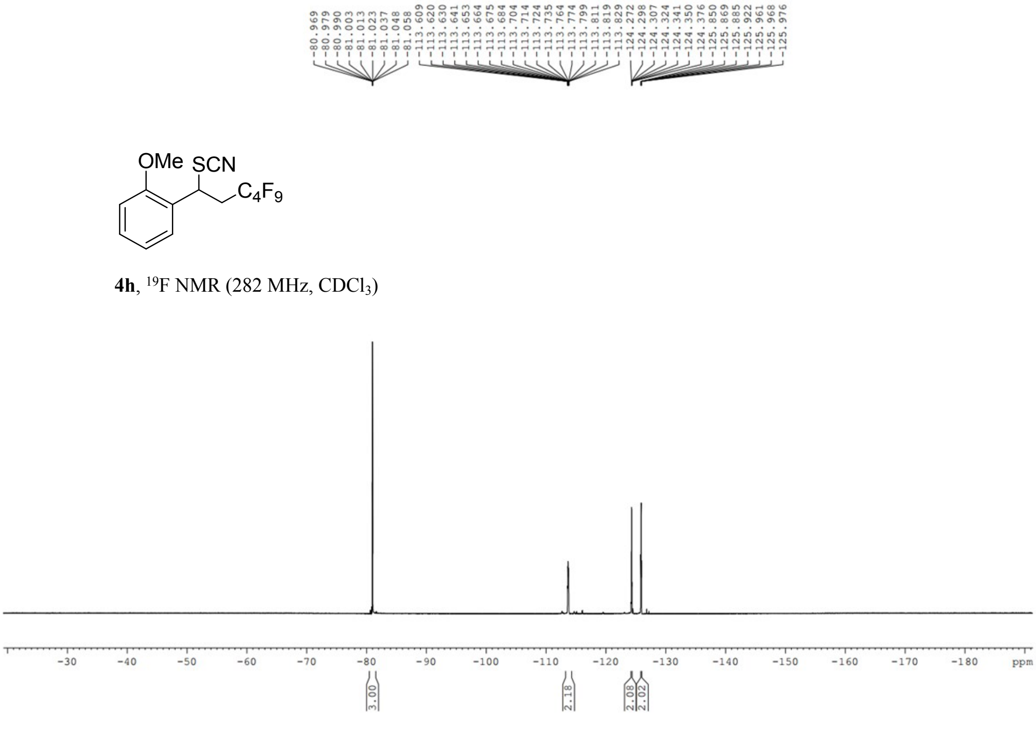


4h, ^{1}H NMR (300 MHz, $CDCl_3$)

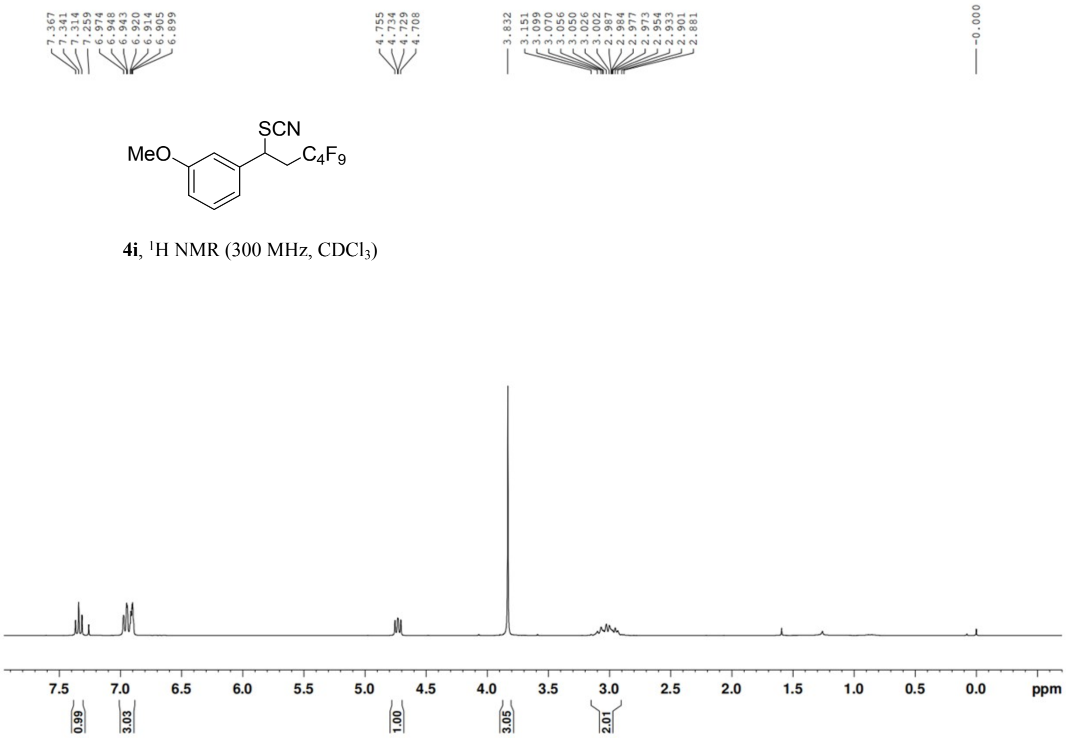




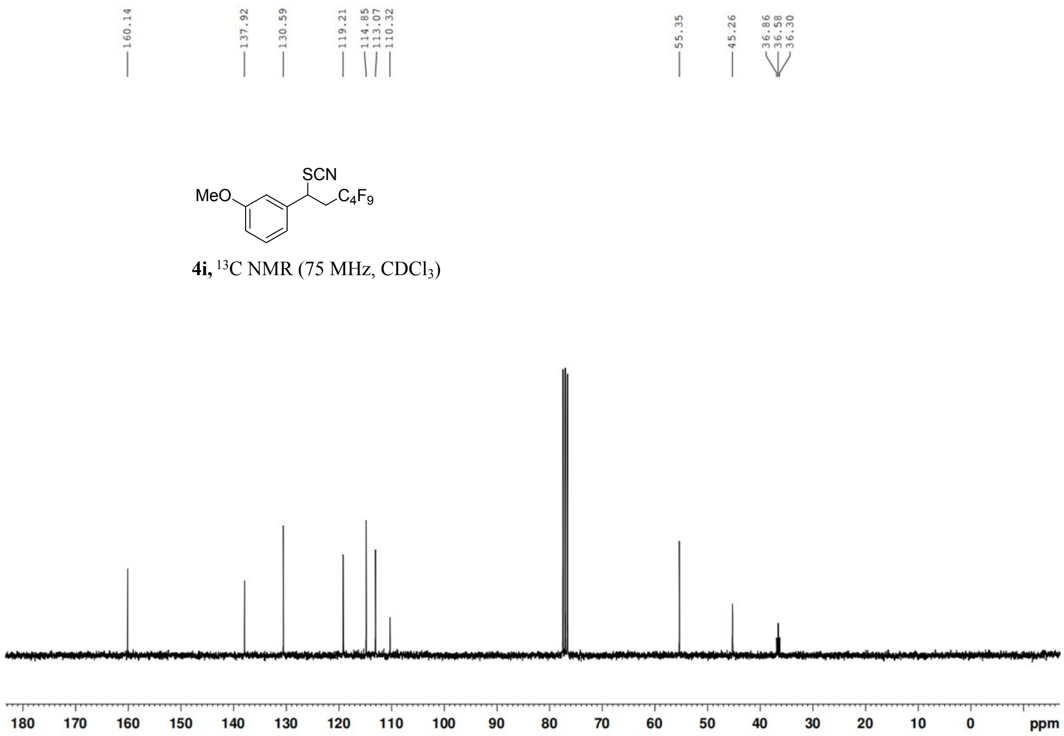
4h, ^{13}C NMR (75 MHz, $CDCl_3$)



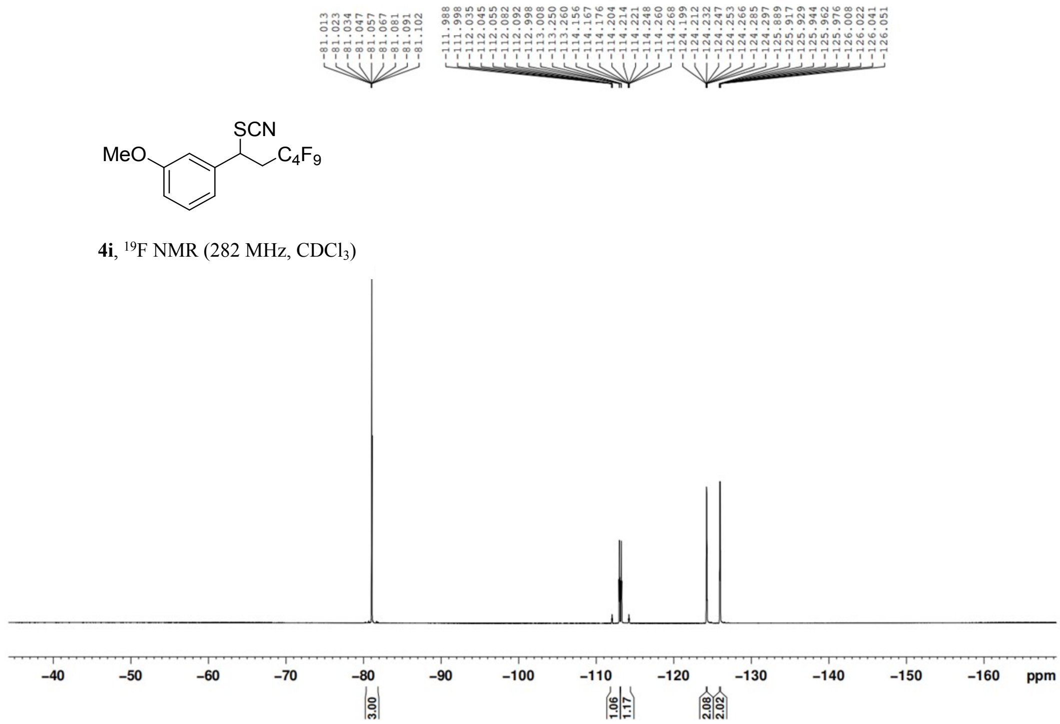
4h, ^{19}F NMR (282 MHz, $CDCl_3$)



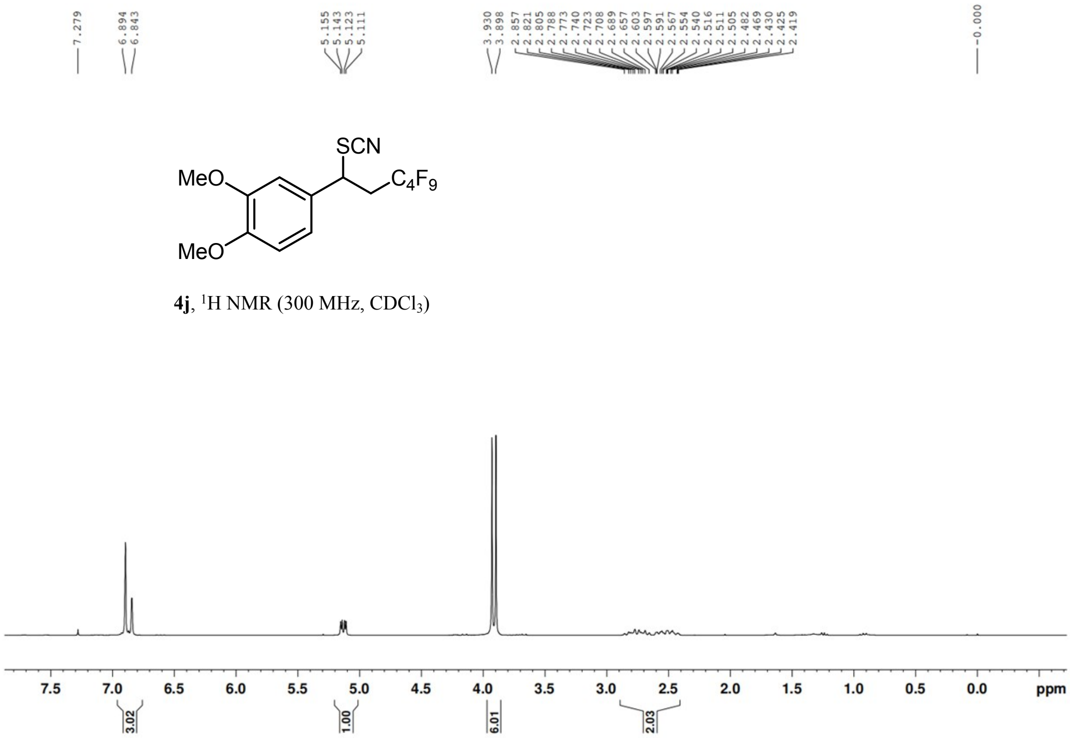
4i, ^{1}H NMR (300 MHz, $CDCl_3$)



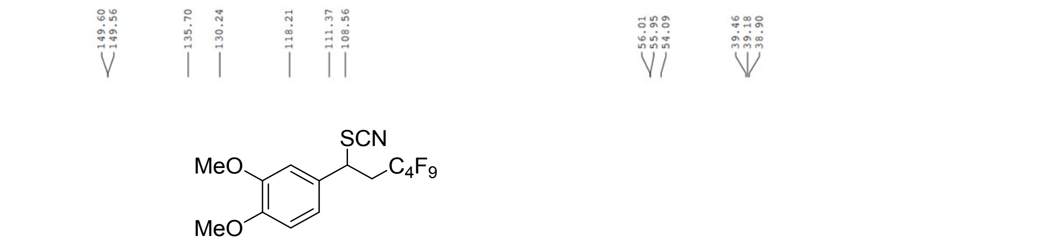
4i, ^{13}C NMR (75 MHz, $CDCl_3$)



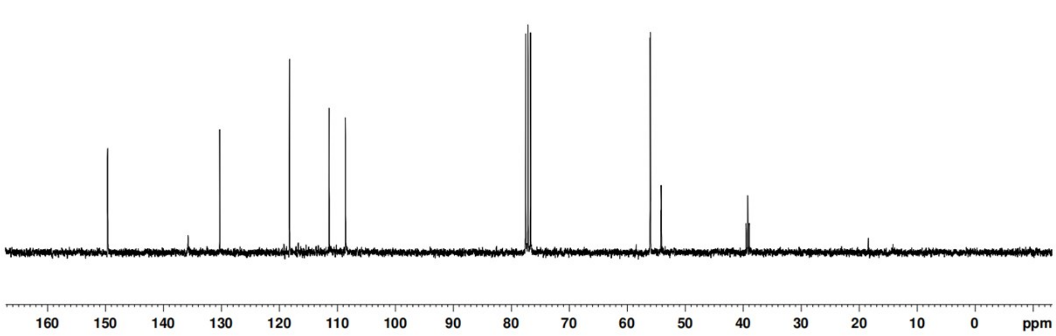
4i, ^{19}F NMR (282 MHz, $CDCl_3$)

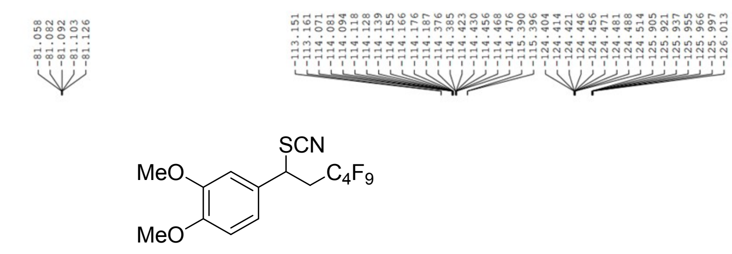


4j, ^{1}H NMR (300 MHz, $CDCl_3$)

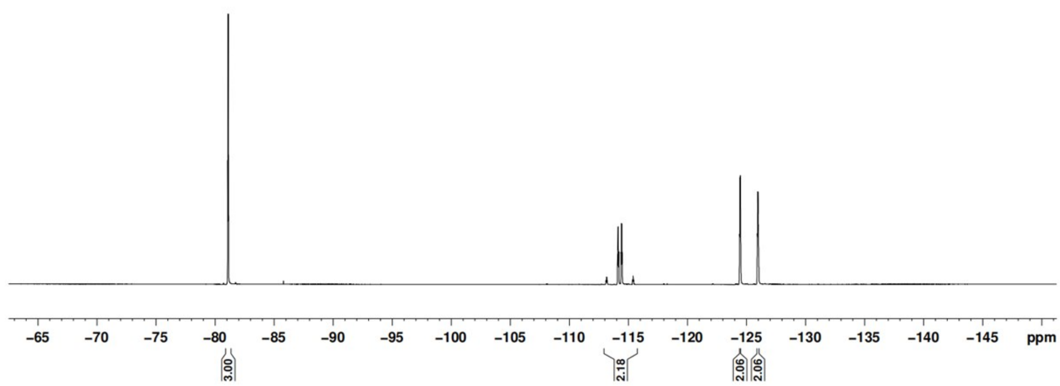


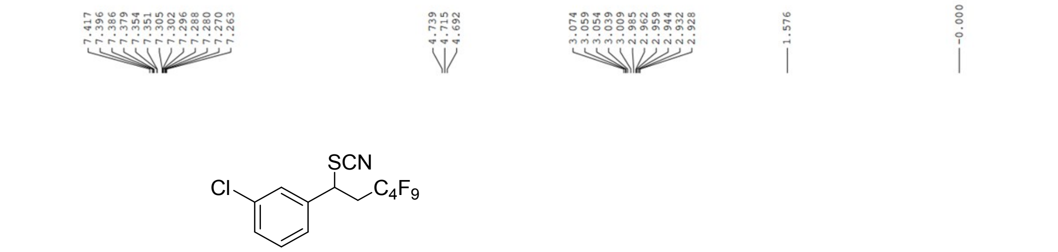
4j, ^{13}C NMR (75 MHz, $CDCl_3$)



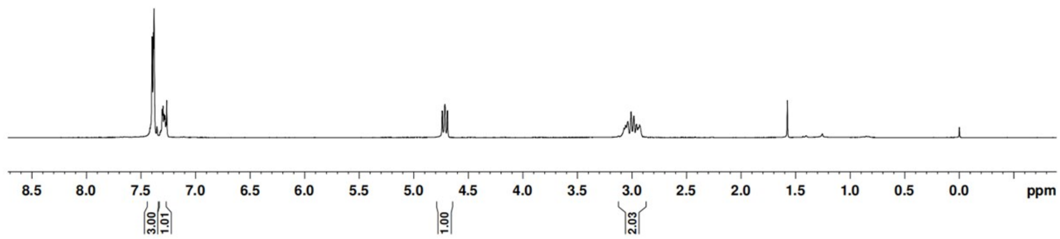


4j, ^{19}F NMR (282 MHz, $CDCl_3$)

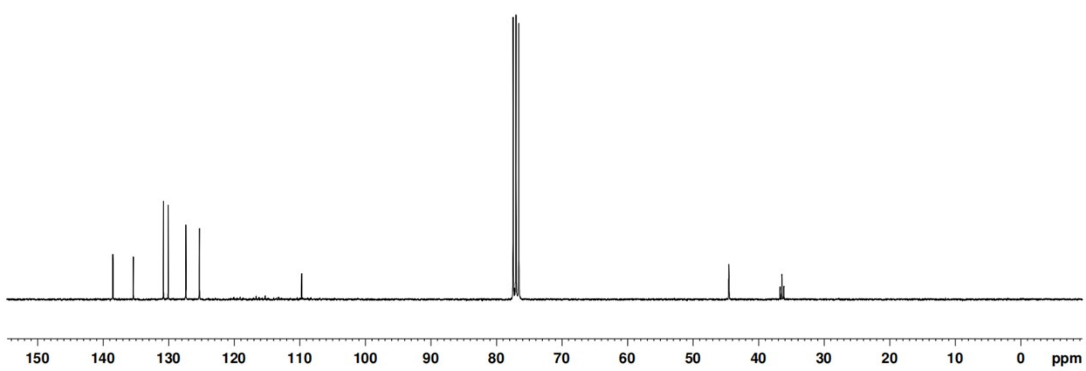


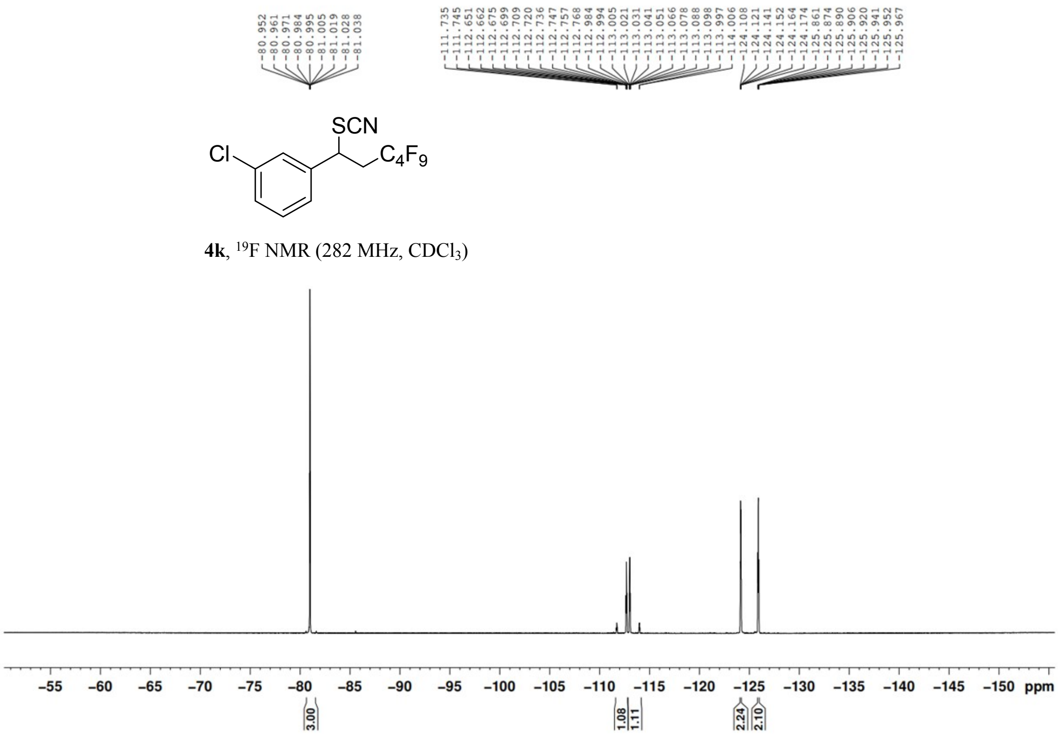


4k, ^{1}H NMR (300 MHz, $CDCl_3$)

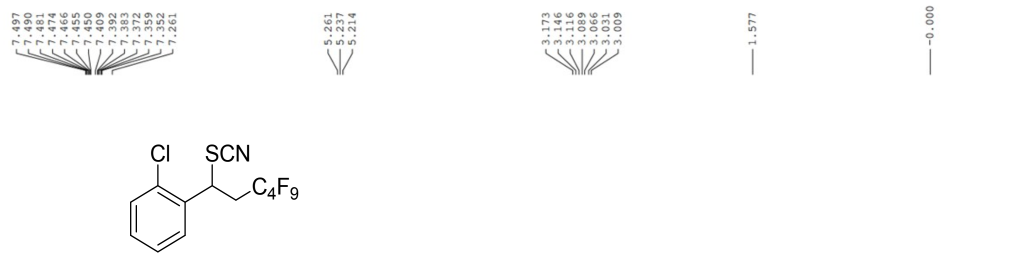


4k, ^{13}C NMR (75 MHz, $CDCl_3$)

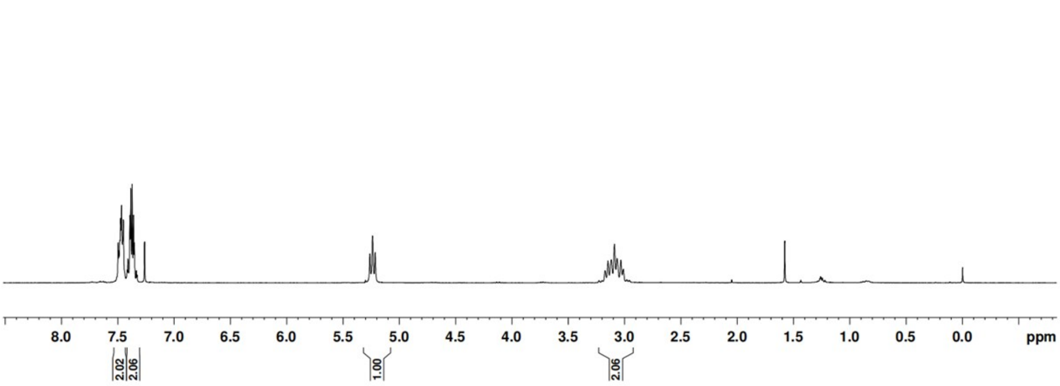


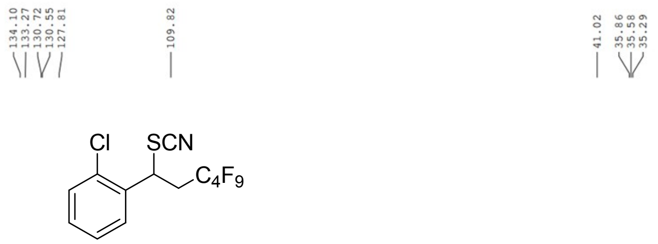


4k, ^{19}F NMR (282 MHz, $CDCl_3$)

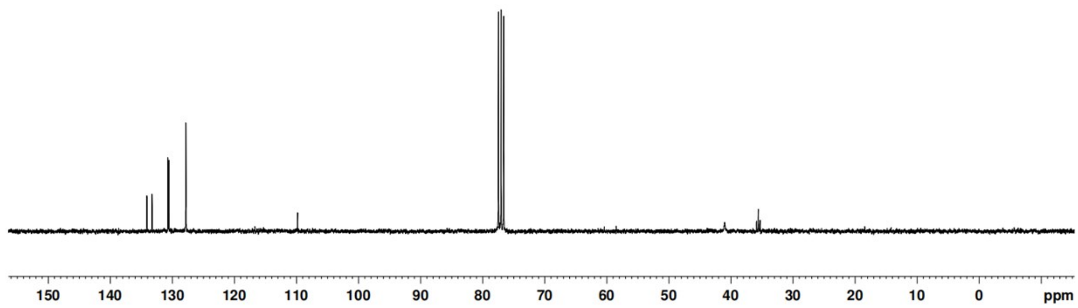


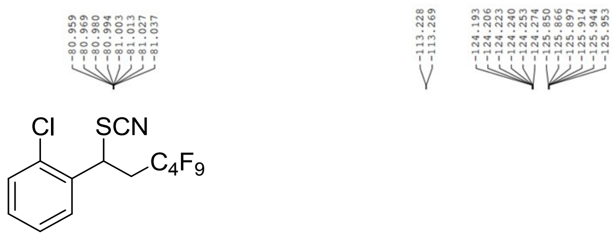
4l, ^{1}H NMR (300 MHz, $CDCl_3$)



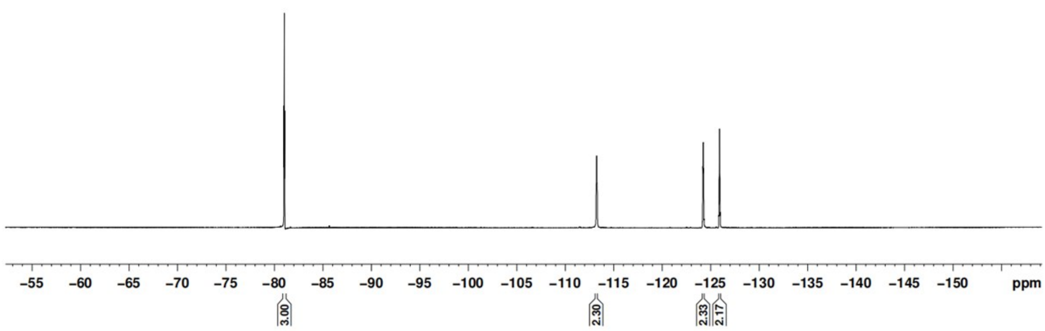


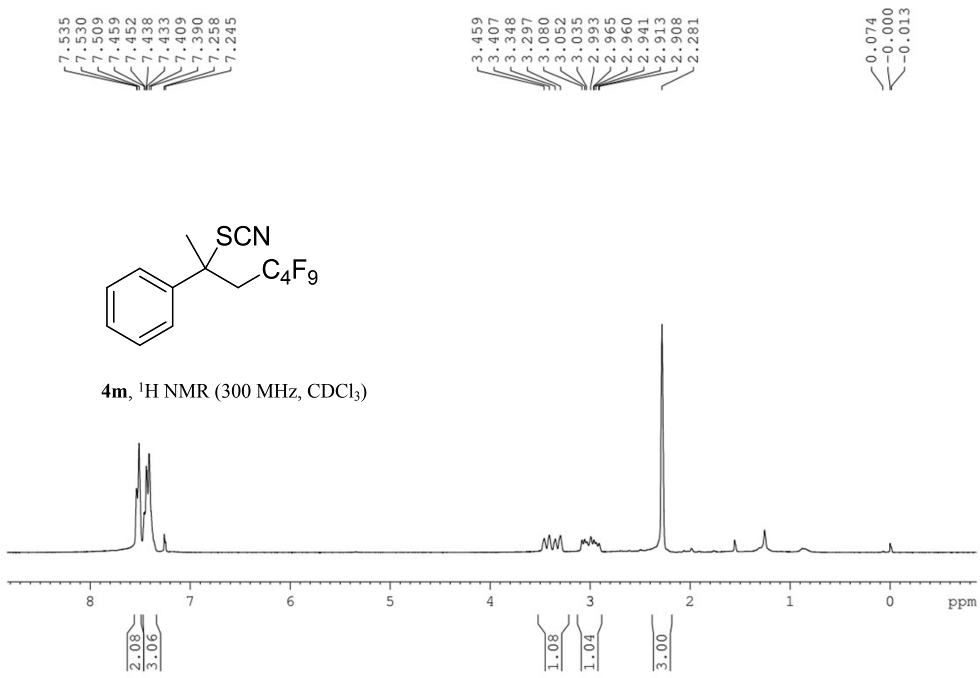
4l, ^{13}C NMR (75 MHz, $CDCl_3$)



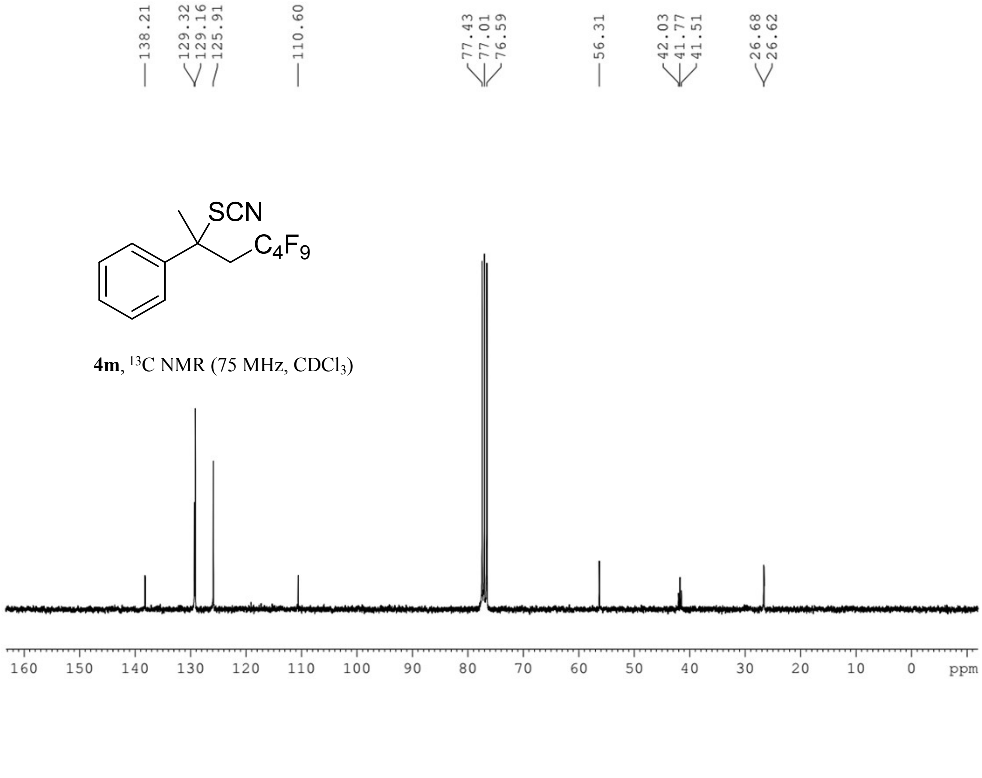


4l, ^{19}F NMR (282 MHz, $CDCl_3$)

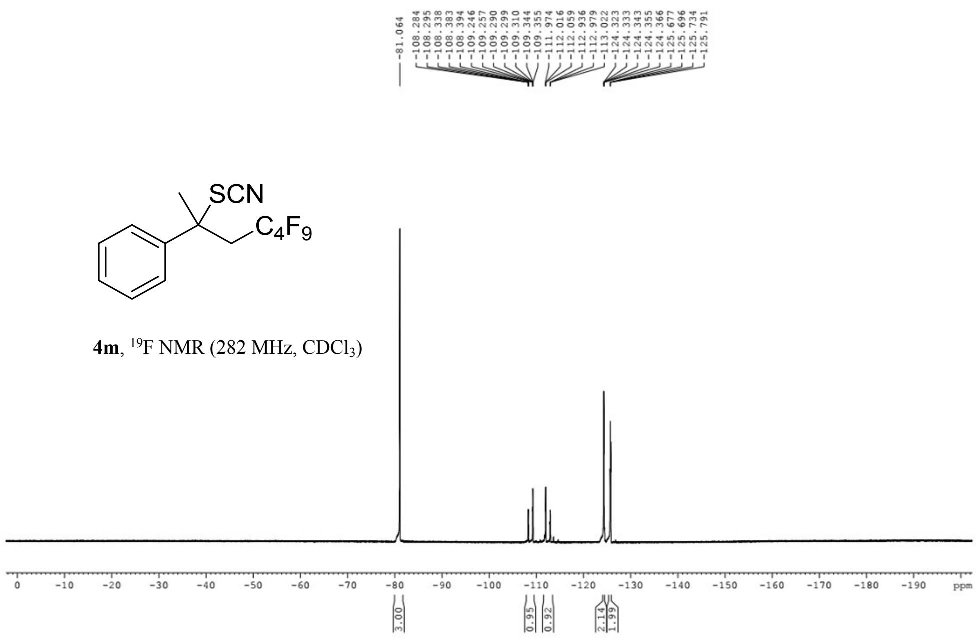




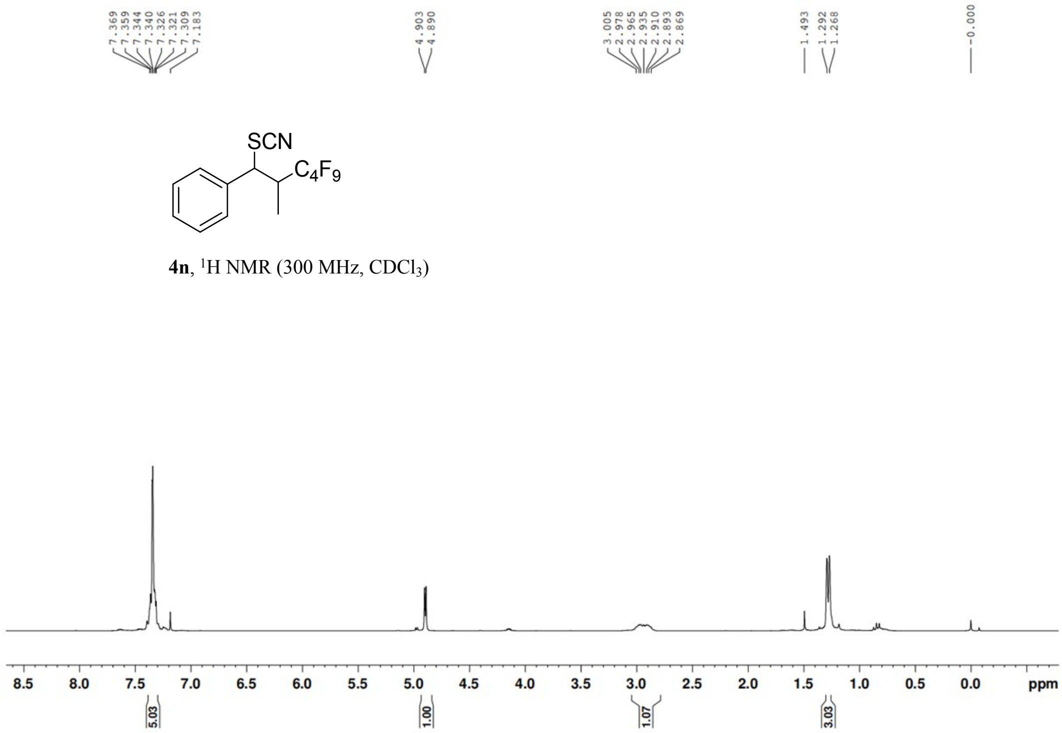
4m, ^{1}H NMR (300 MHz, $CDCl_3$)



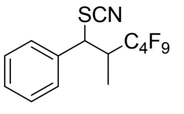
4m, ^{13}C NMR (75 MHz, $CDCl_3$)



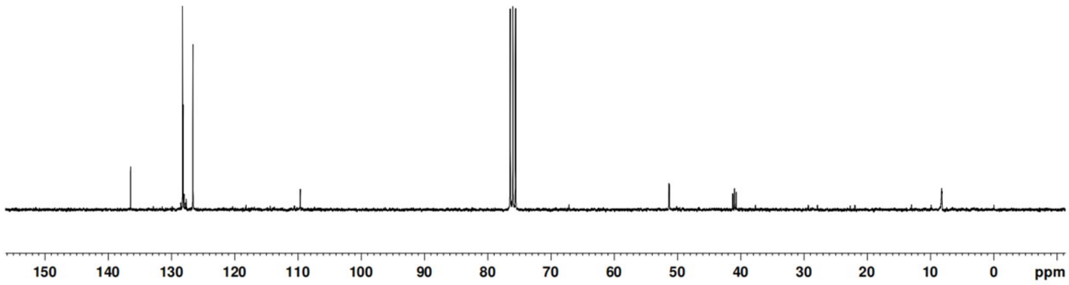
4m, ^{19}F NMR (282 MHz, $CDCl_3$)

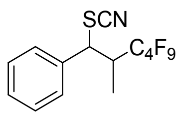


4n, ^{1}H NMR (300 MHz, $CDCl_3$)

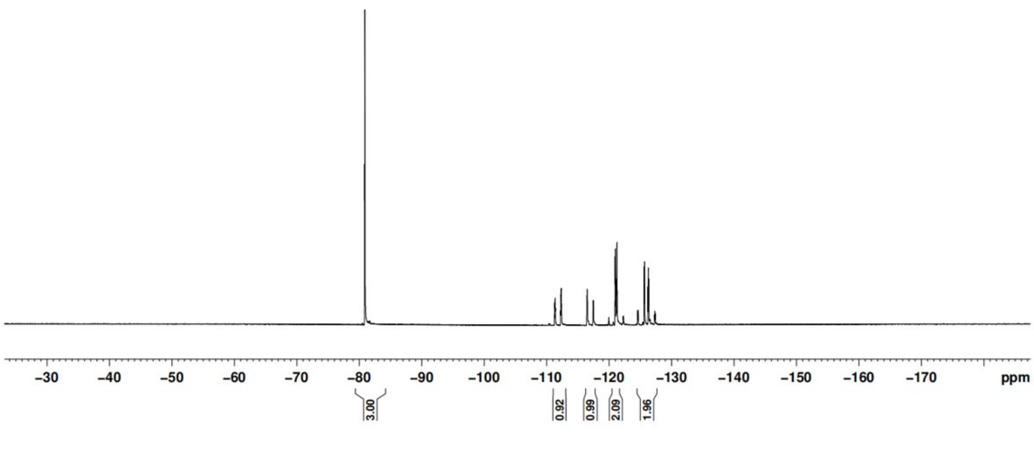


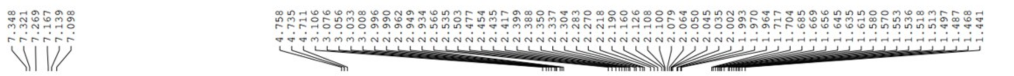
4n, ^{13}C NMR (75 MHz, $CDCl_3$)

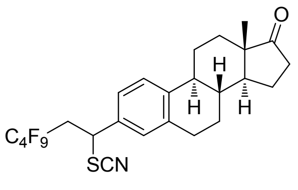




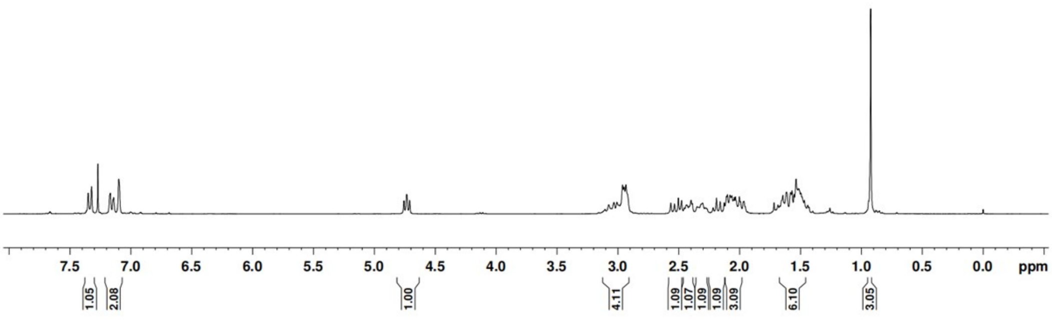
4n, ^{19}F NMR (282 MHz, $CDCl_3$)

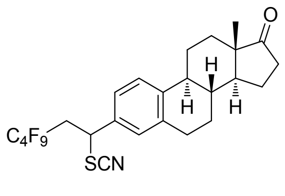




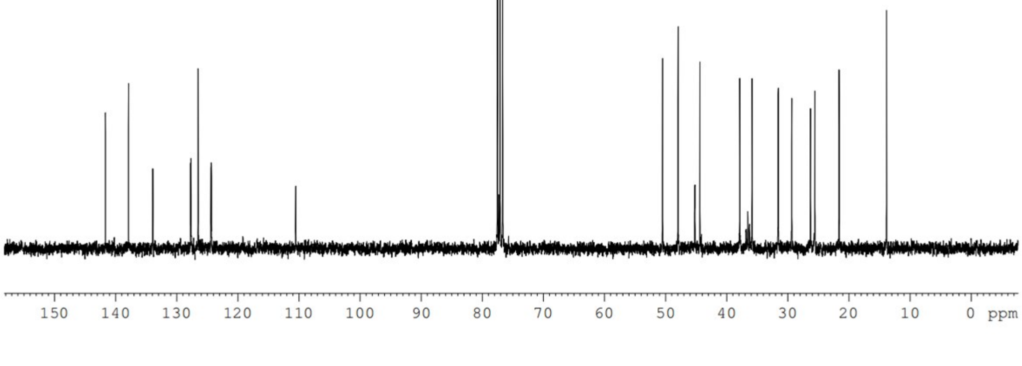


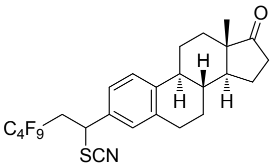
4o, ^{1}H NMR (300 MHz, $CDCl_3$)



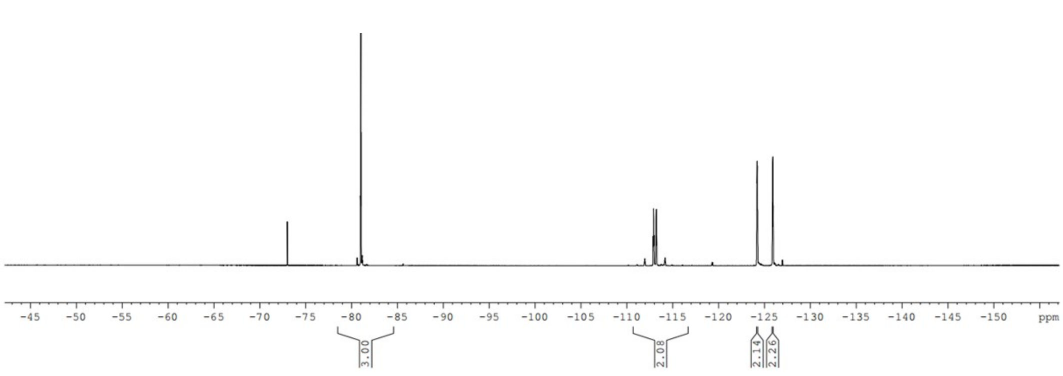


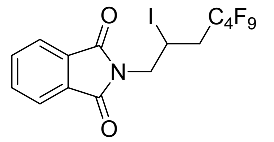
4o, ^{13}C NMR (75 MHz, $CDCl_3$)



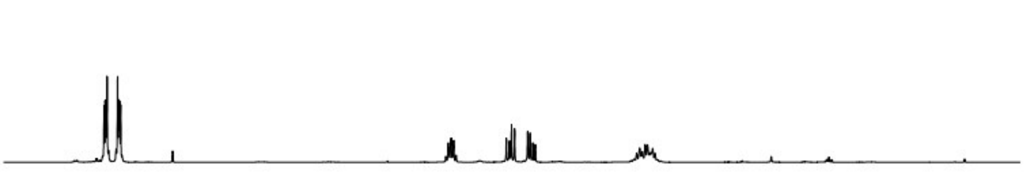


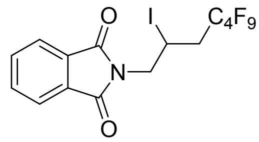
4o, ^{19}F NMR (282 MHz, $CDCl_3$)



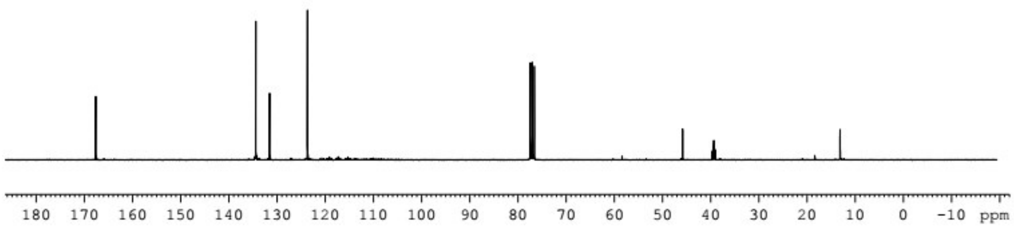


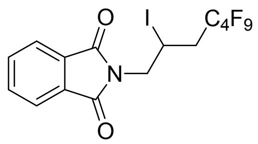
4p, ^{1}H NMR (300 MHz, $CDCl_3$)



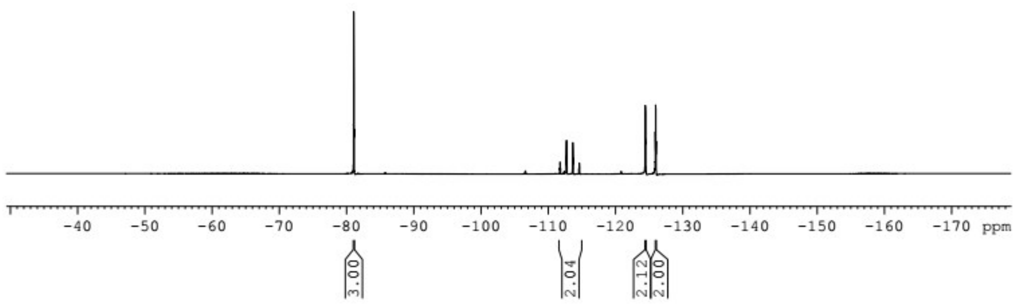


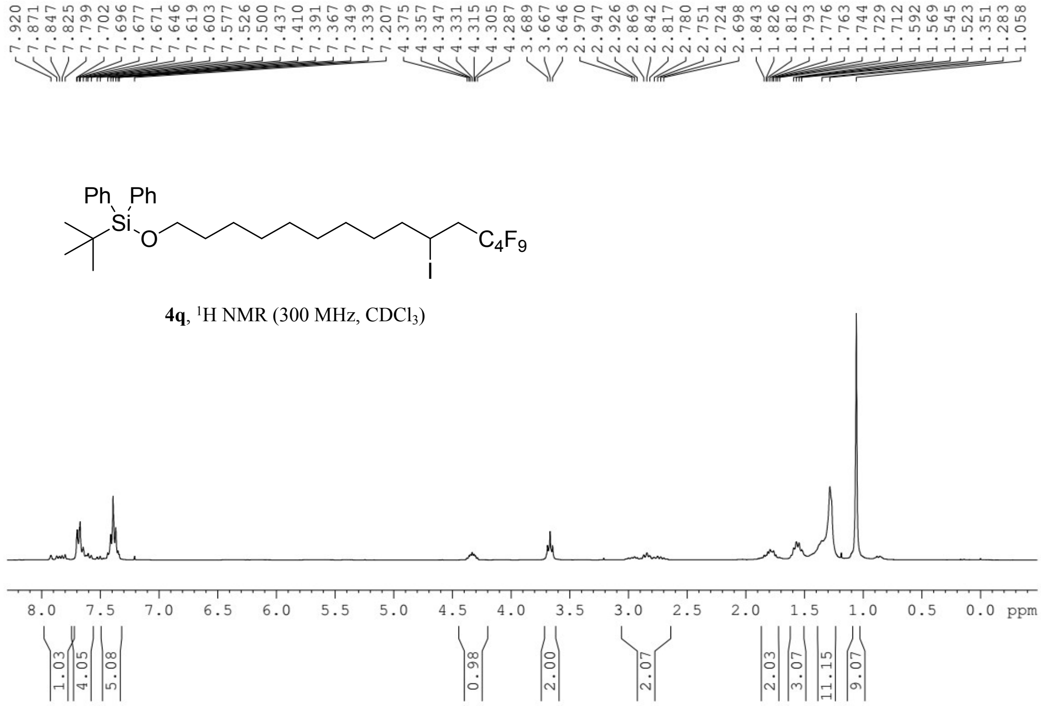
4p, ^{13}C NMR (75 MHz, $CDCl_3$)



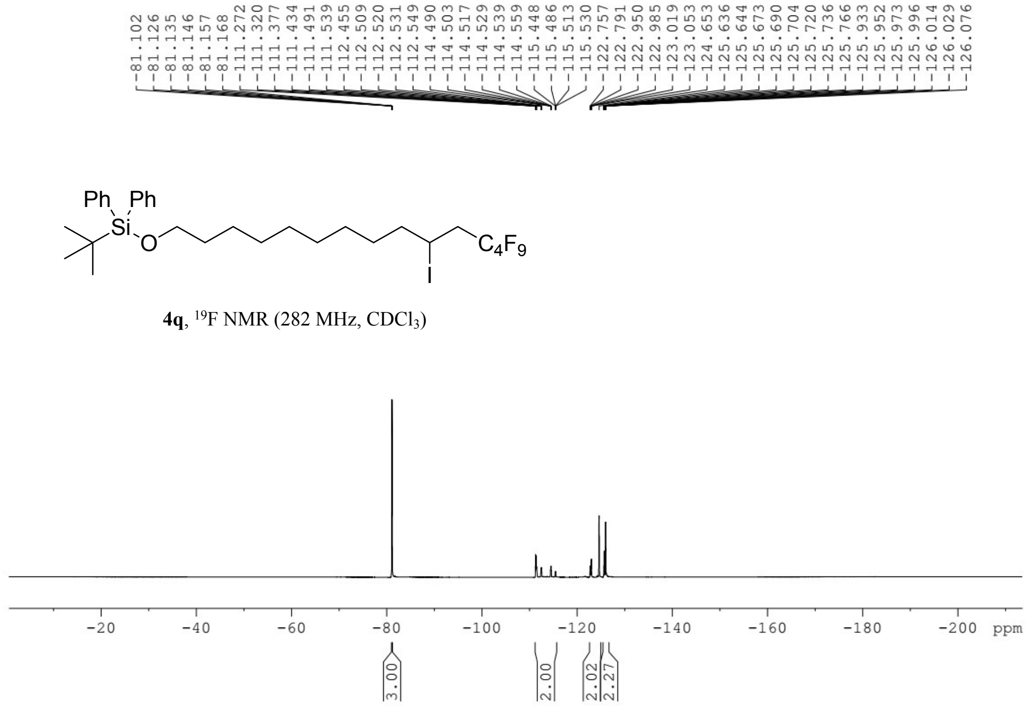


4p, ^{19}F NMR (282 MHz, $CDCl_3$)

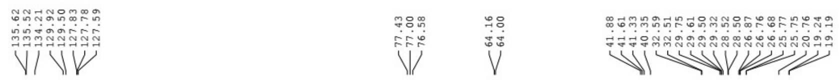


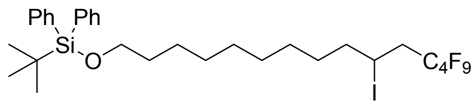


4q, ^{1}H NMR (300 MHz, $CDCl_3$)

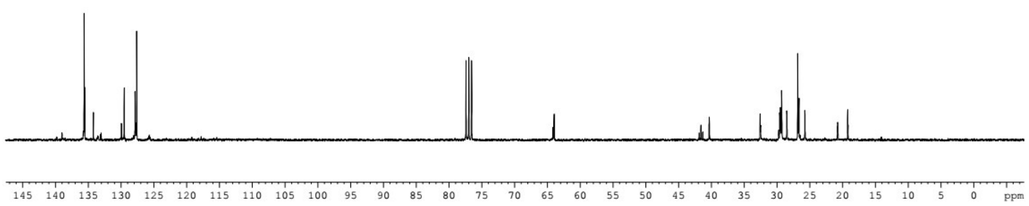


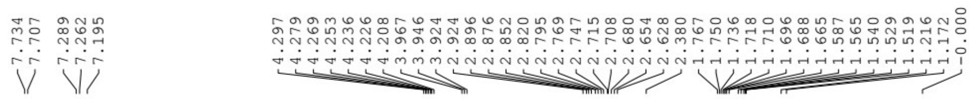
4q, ^{19}F NMR (282 MHz, $CDCl_3$)

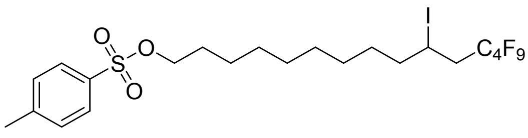




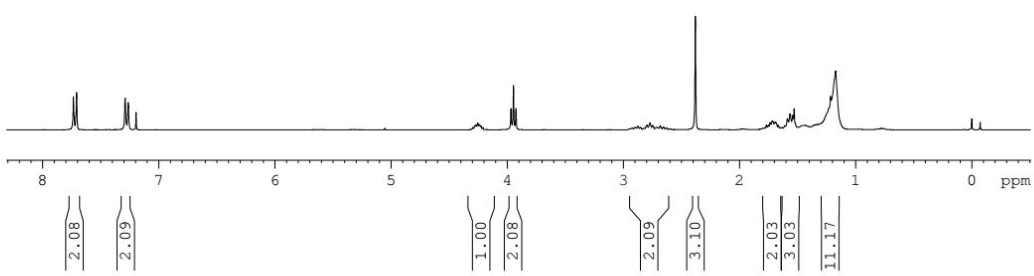
4q, ^{13}C NMR (75 MHz, $CDCl_3$)

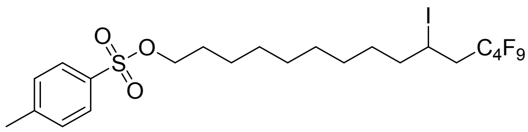




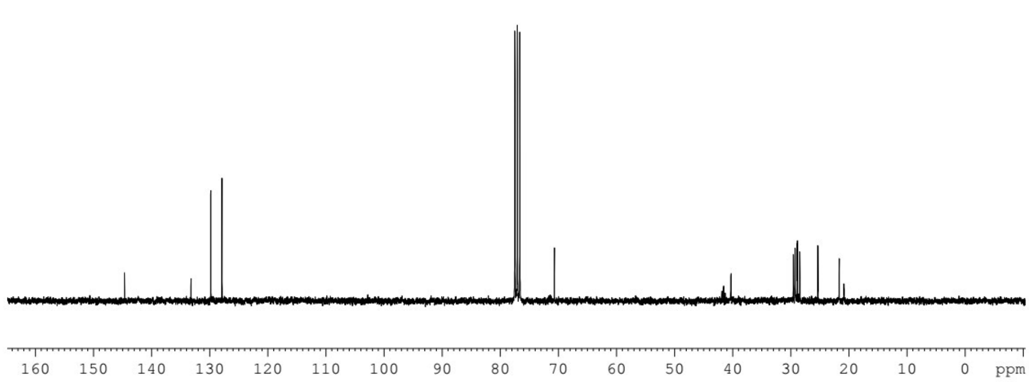


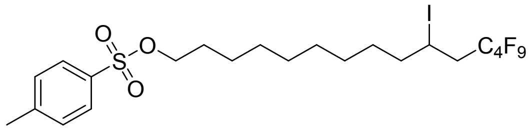
4r, ^{1}H NMR (300 MHz, $CDCl_3$)



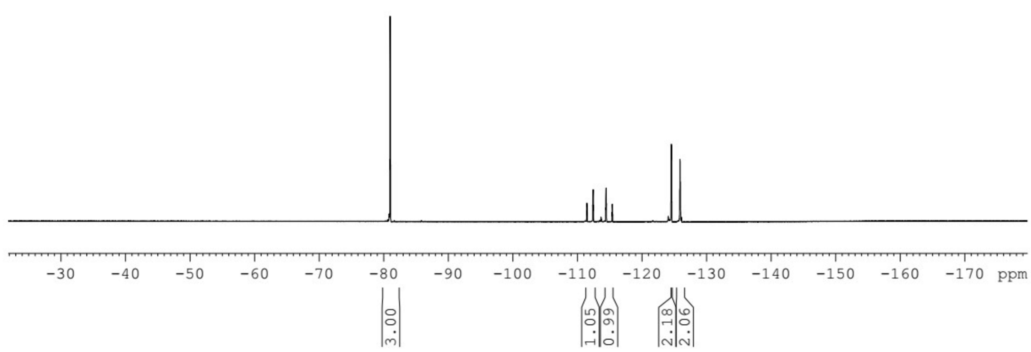


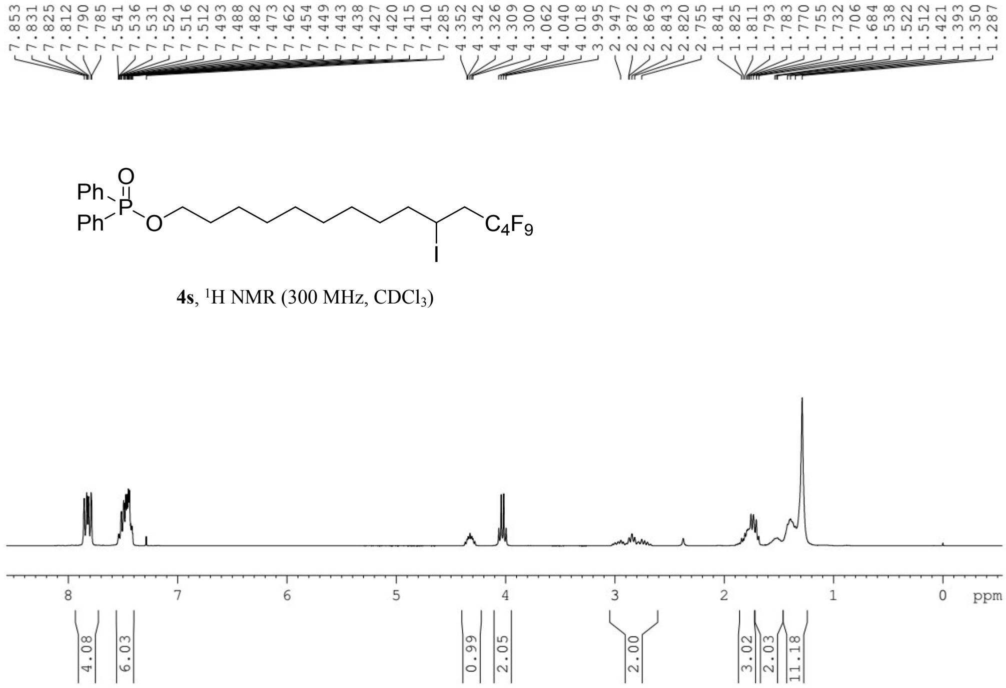
4r, ^{13}C NMR (75 MHz, $CDCl_3$)



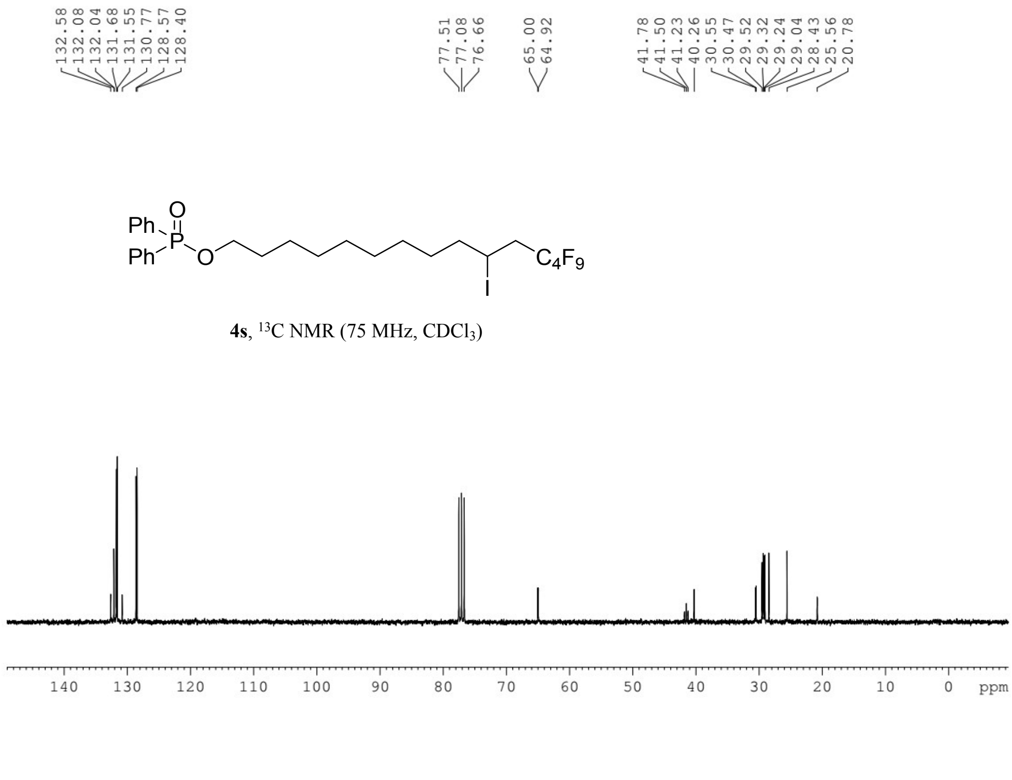


4r, ^{19}F NMR (282 MHz, $CDCl_3$)

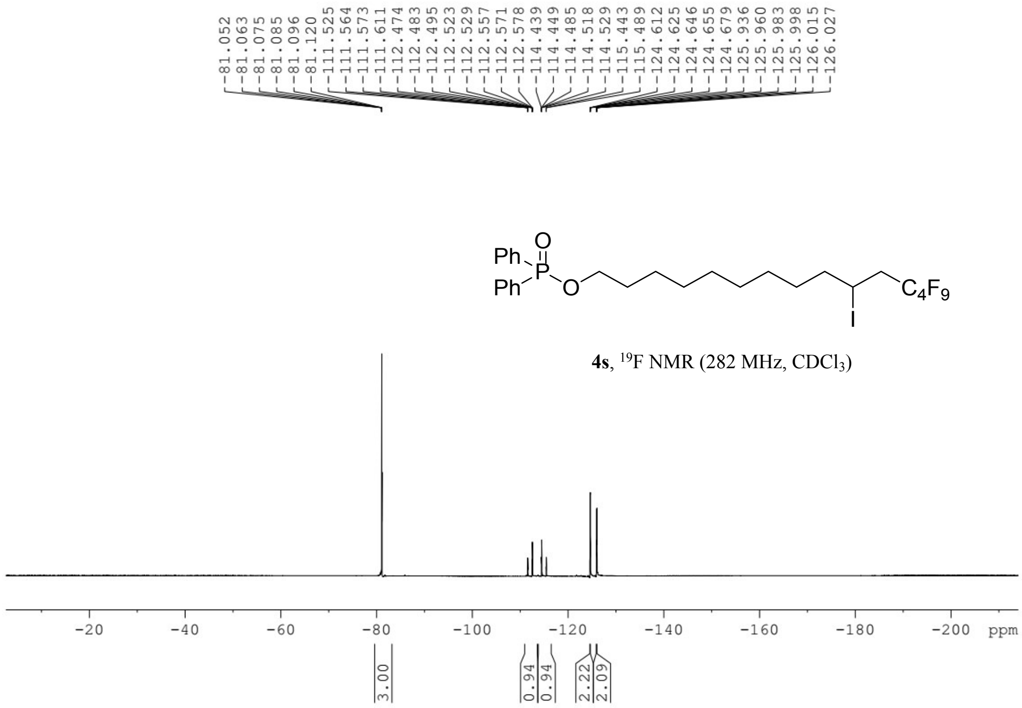




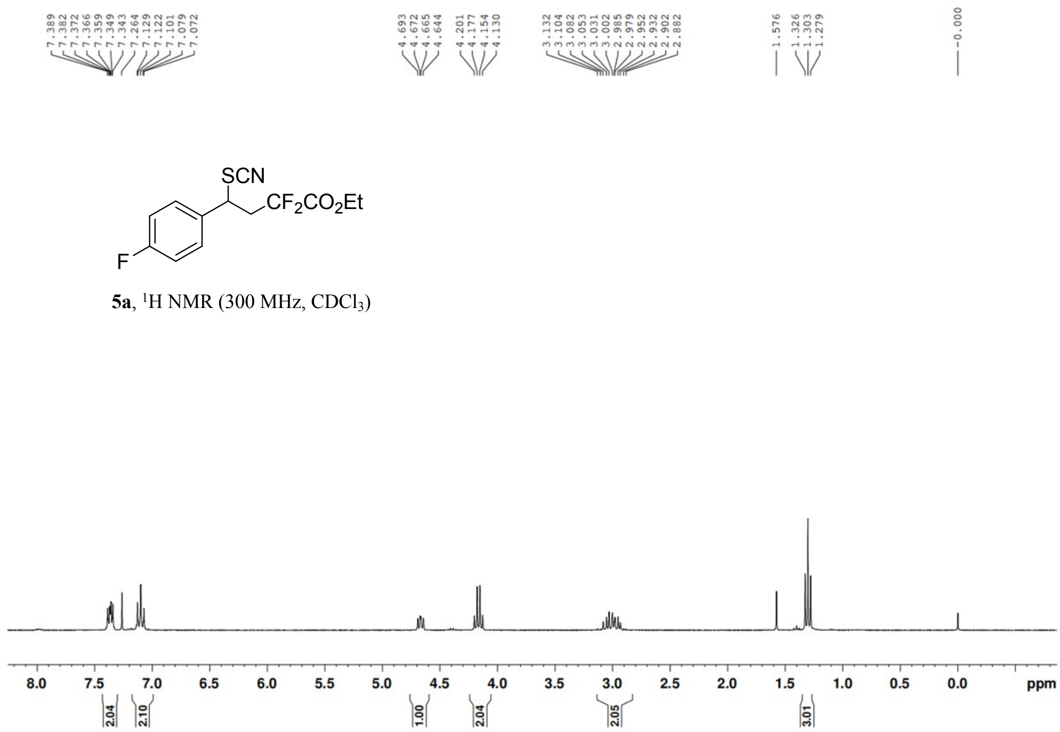
4s, ^{1}H NMR (300 MHz, $CDCl_3$)



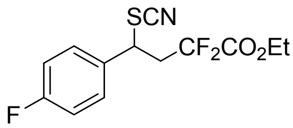
4s, ^{13}C NMR (75 MHz, $CDCl_3$)



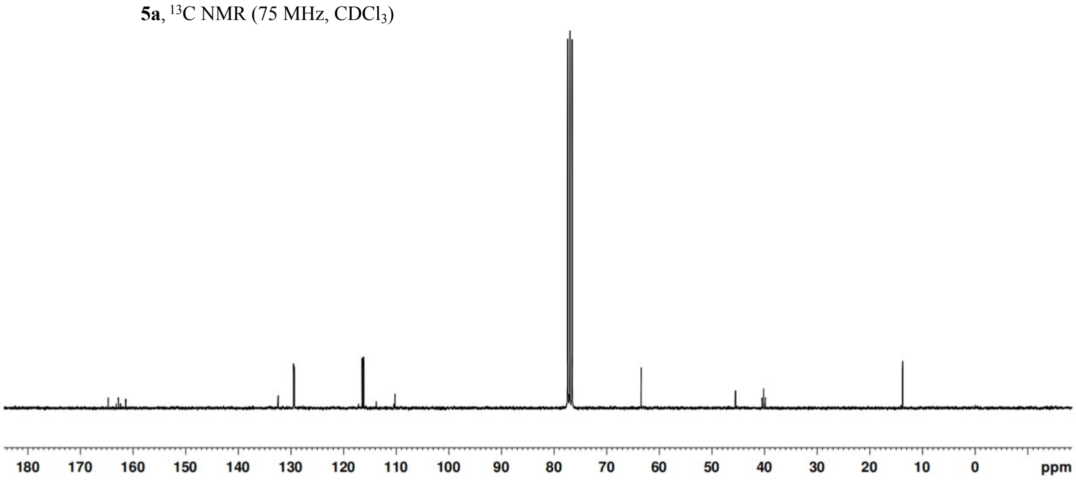
4s, ^{19}F NMR (282 MHz, $CDCl_3$)

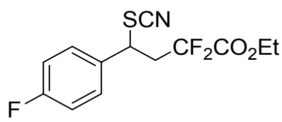


5a, ^{1}H NMR (300 MHz, $CDCl_3$)

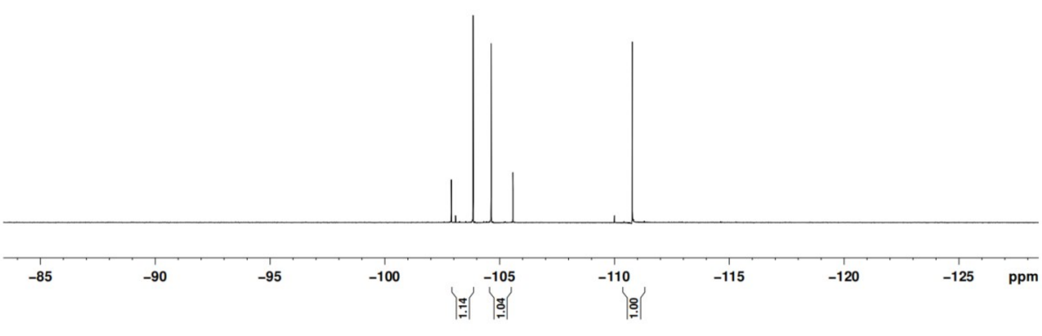


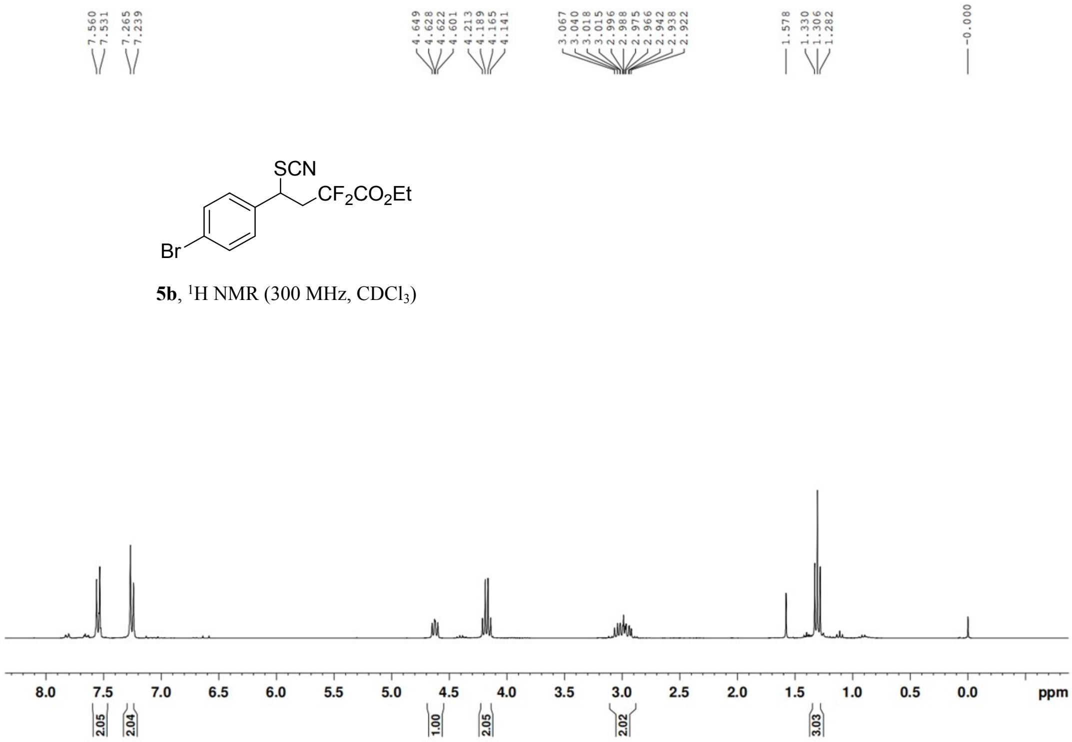
5a, ^{13}C NMR (75 MHz, $CDCl_3$)



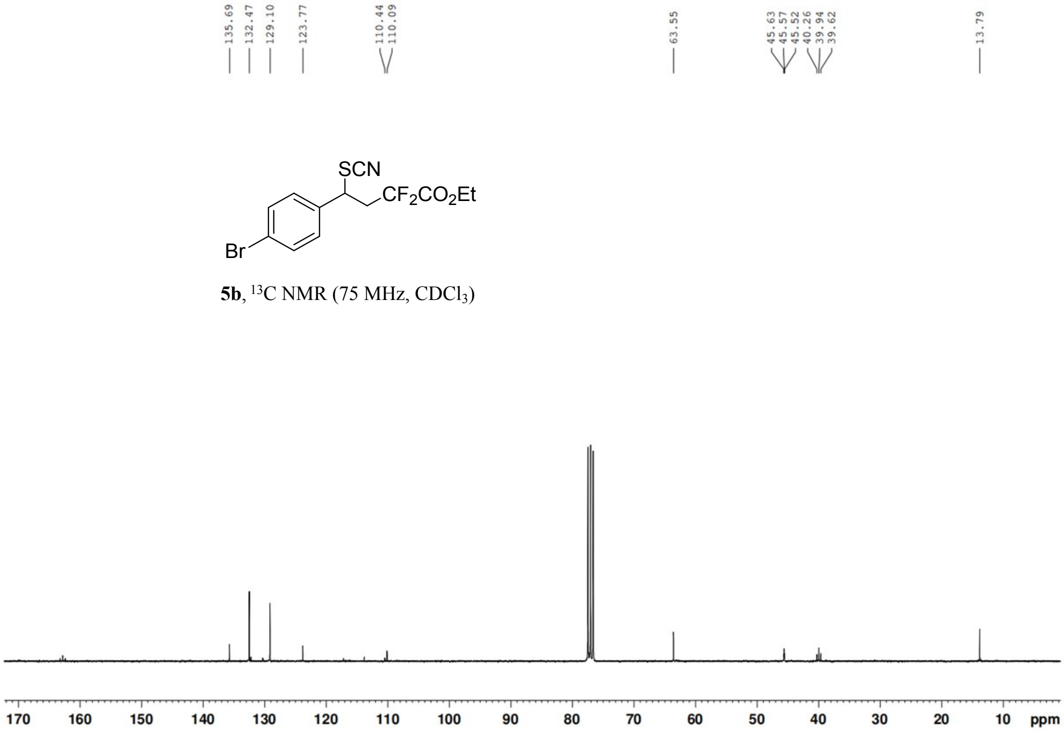


5a, ^{19}F NMR (282 MHz, $CDCl_3$)

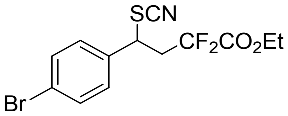




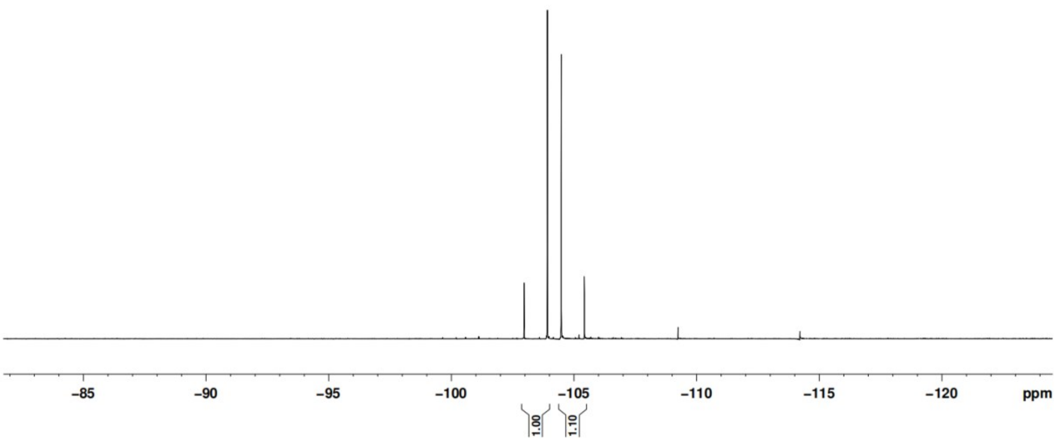
5b, ^{1}H NMR (300 MHz, $CDCl_3$)

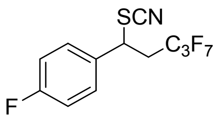


5b, ^{13}C NMR (75 MHz, $CDCl_3$)

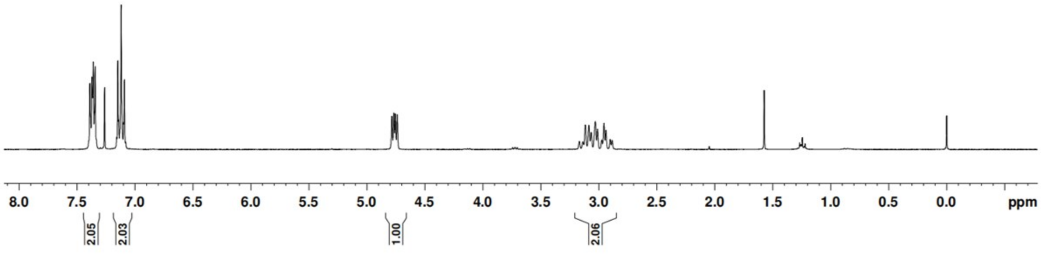


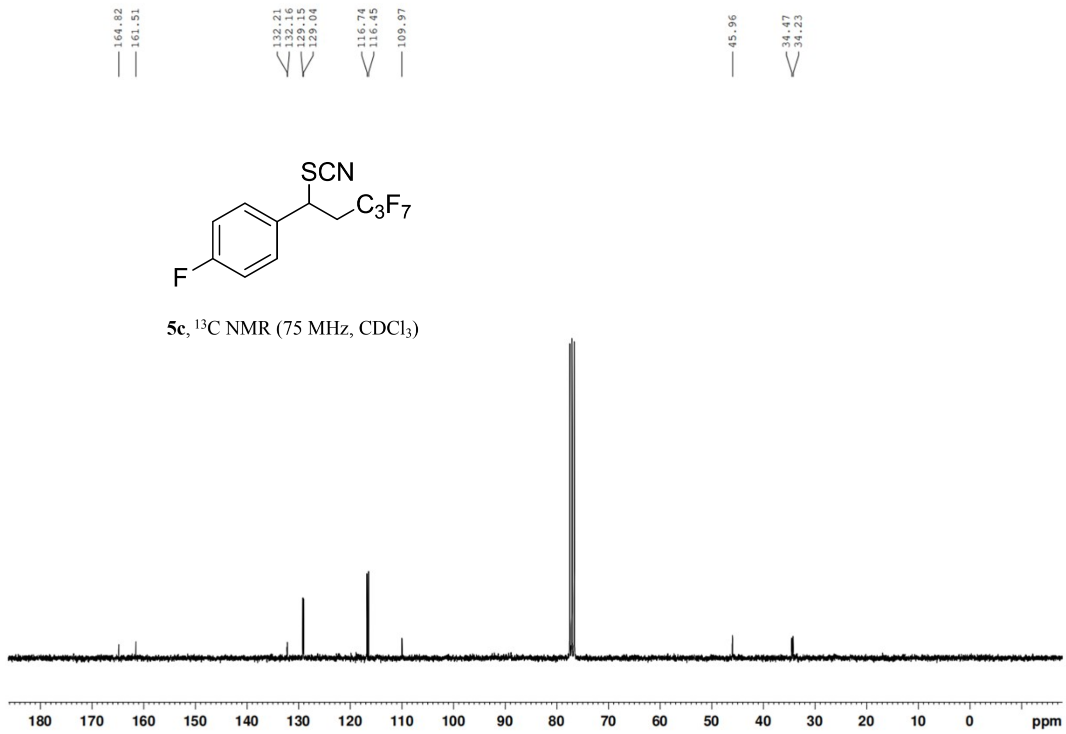
5b, ^{19}F NMR (282 MHz, $CDCl_3$)



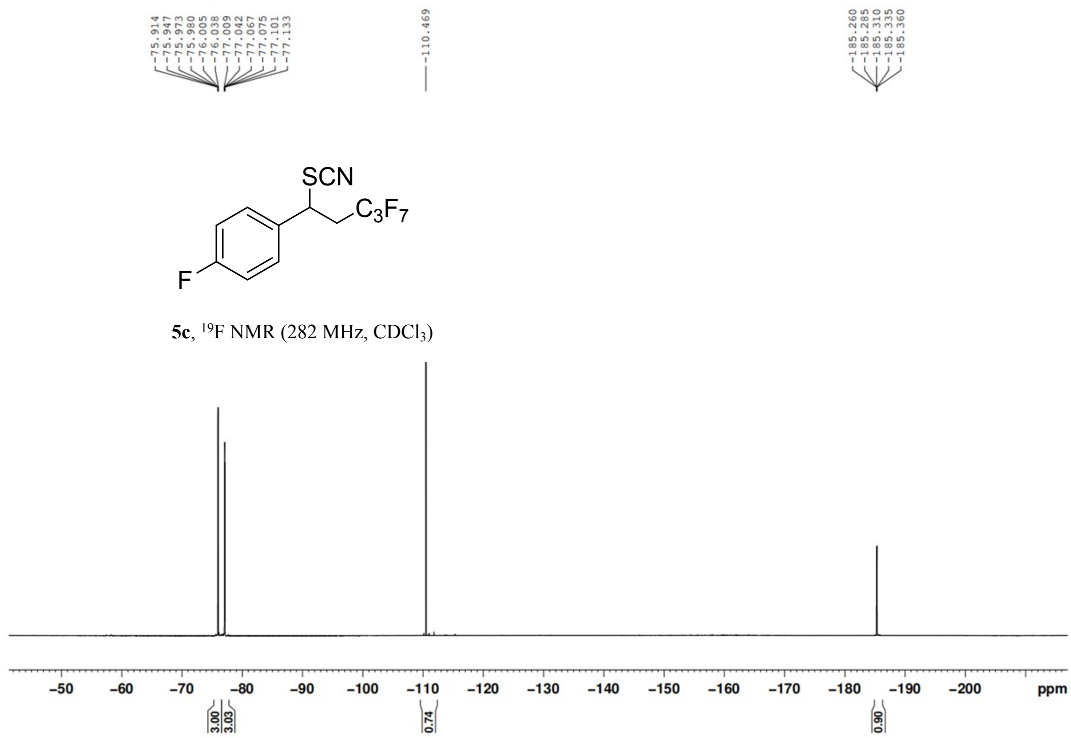


5c, ^{1}H NMR (300 MHz, $CDCl_3$)

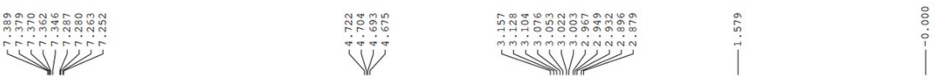


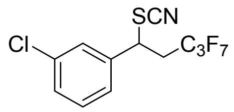


5c, ^{13}C NMR (75 MHz, $CDCl_3$)

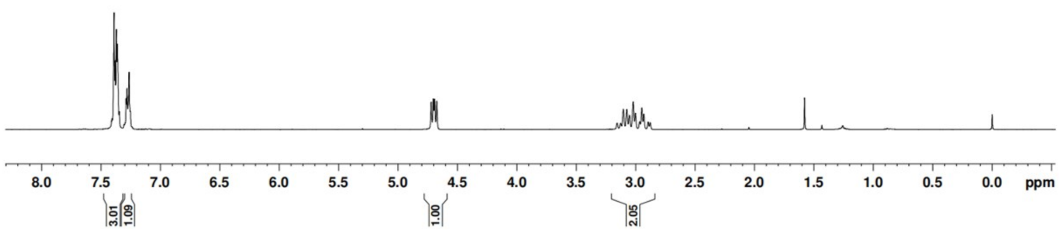


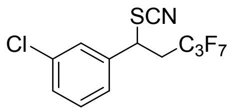
5c, ^{19}F NMR (282 MHz, $CDCl_3$)



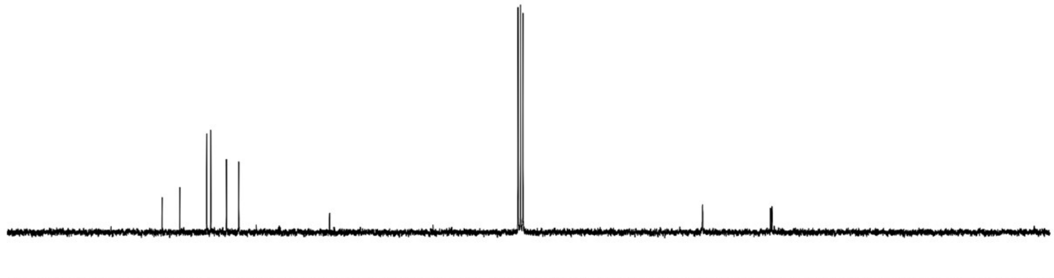


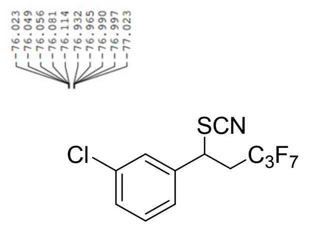
5d, ^{1}H NMR (300 MHz, $CDCl_3$)



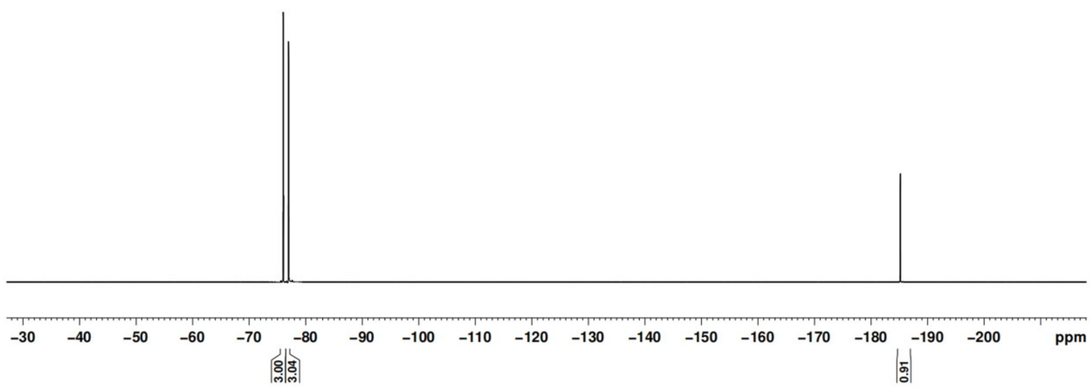


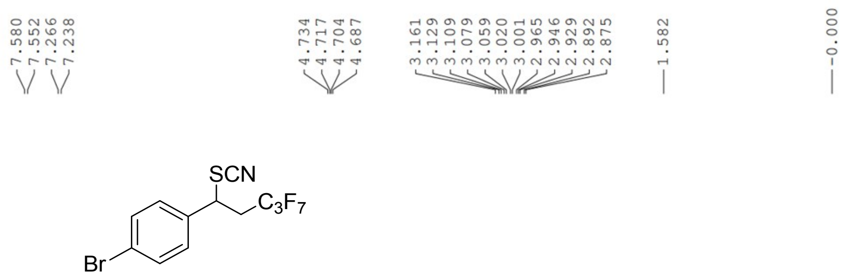
5d, ^{13}C NMR (75 MHz, $CDCl_3$)



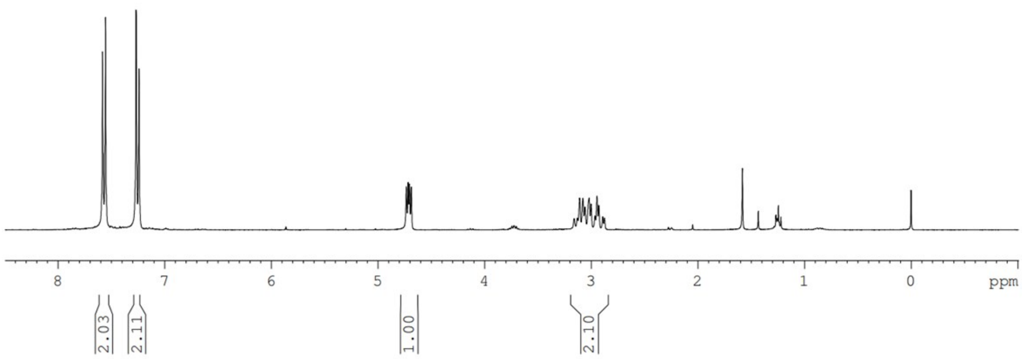


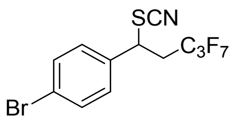
5d, ^{19}F NMR (282 MHz, $CDCl_3$)



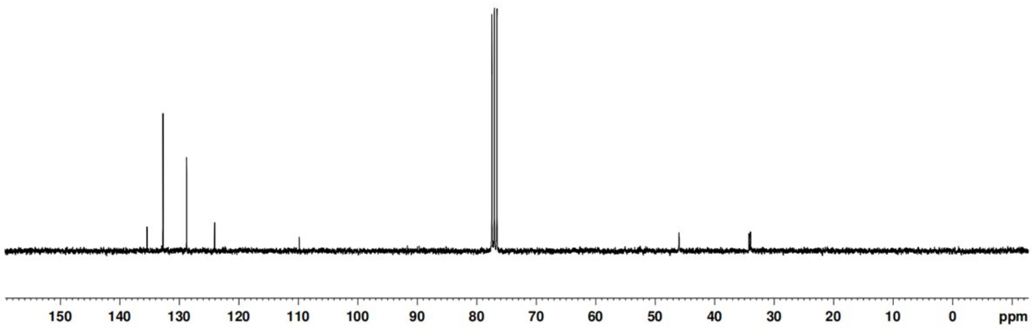


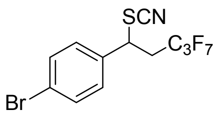
5e, ^{1}H NMR (300 MHz, $CDCl_3$)



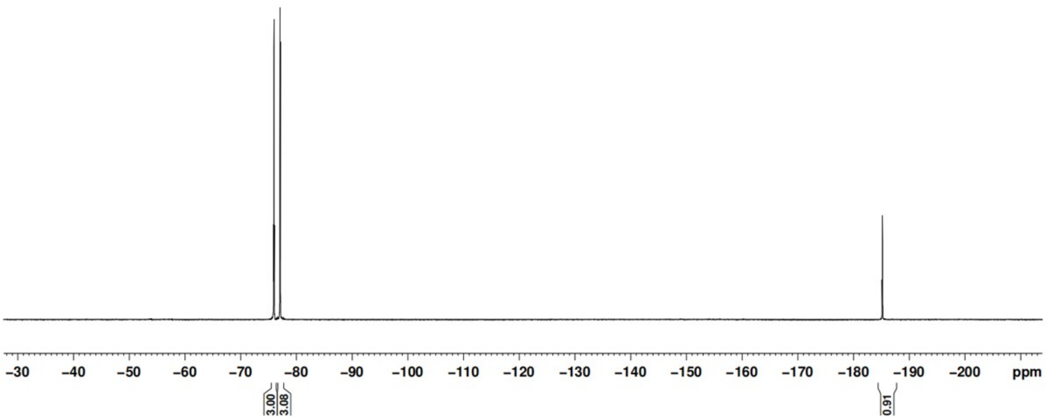


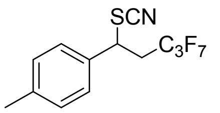
5e, ^{13}C NMR (75 MHz, CDCl$_3$)



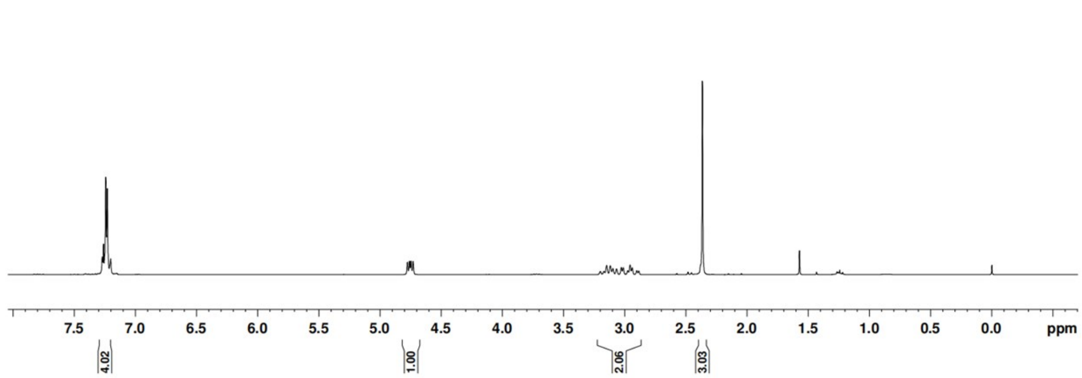


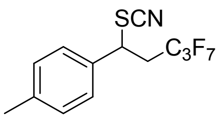
5e, ^{19}F NMR (282 MHz, CDCl$_3$)



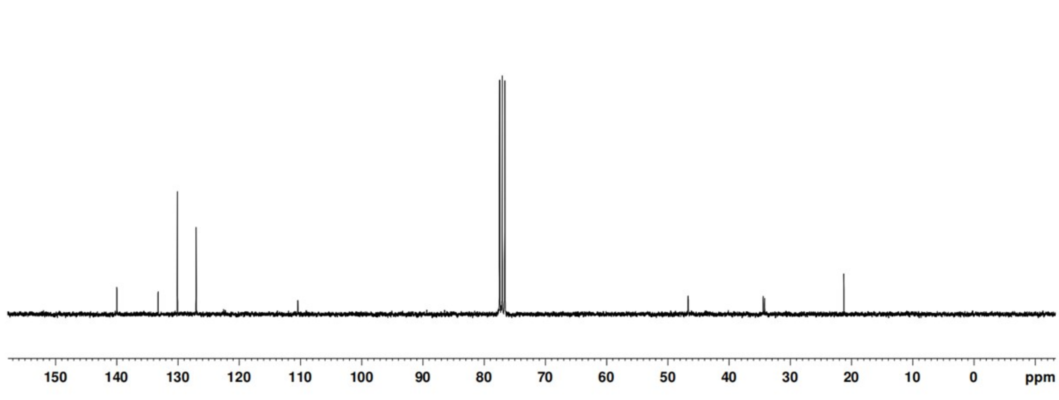


5f, ¹H NMR (300 MHz, $CDCl_3$)

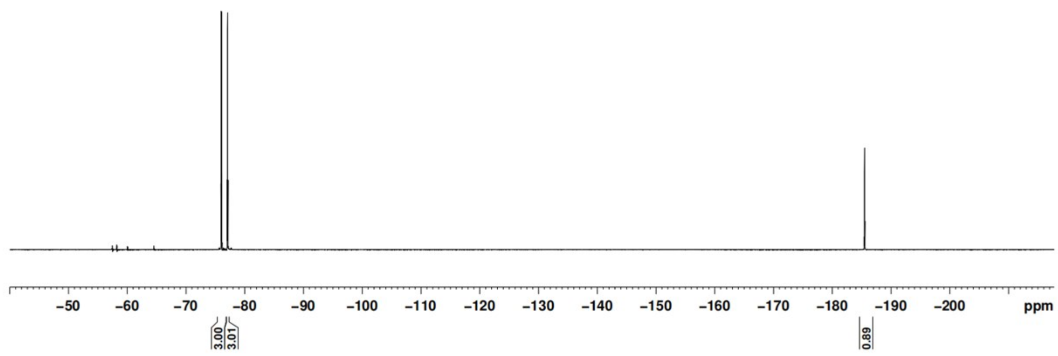


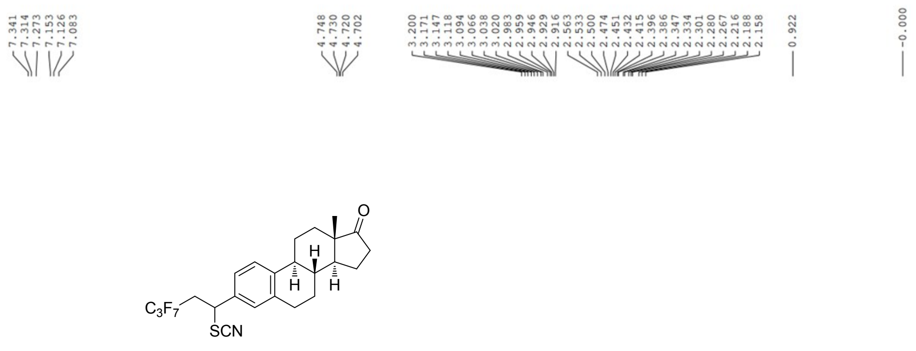


5f, ¹³C NMR (75 MHz, $CDCl_3$)

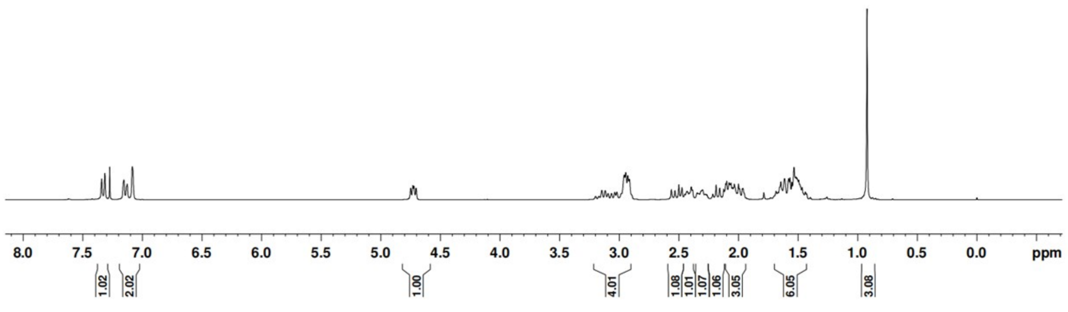


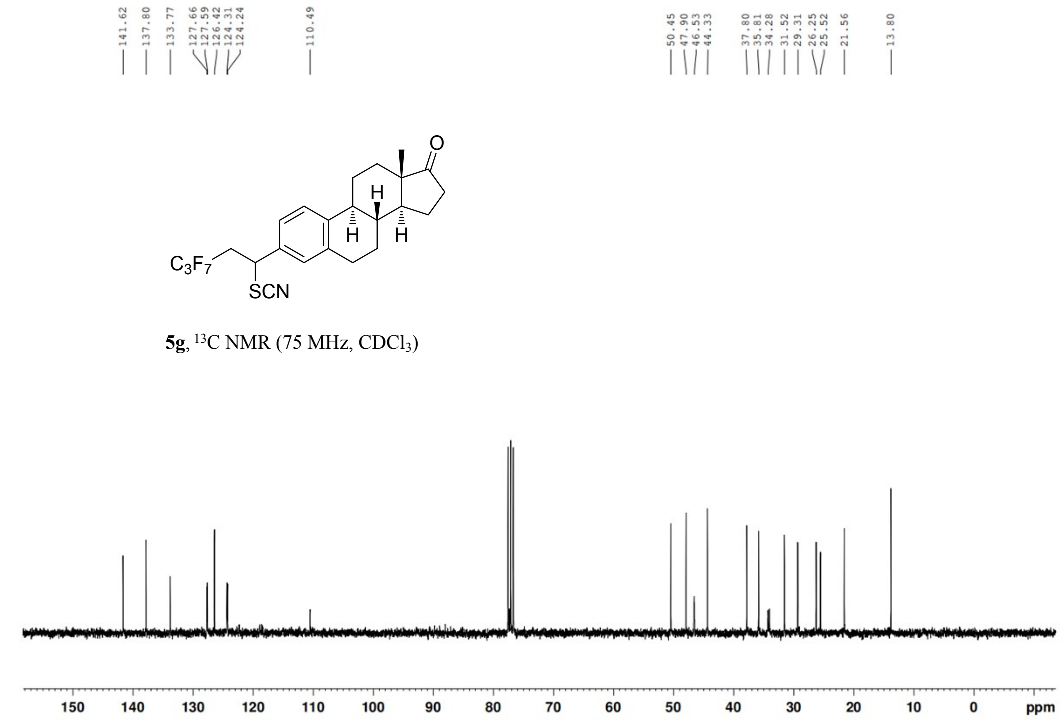
5f, ^{19}F NMR (282 MHz, $CDCl_3$)



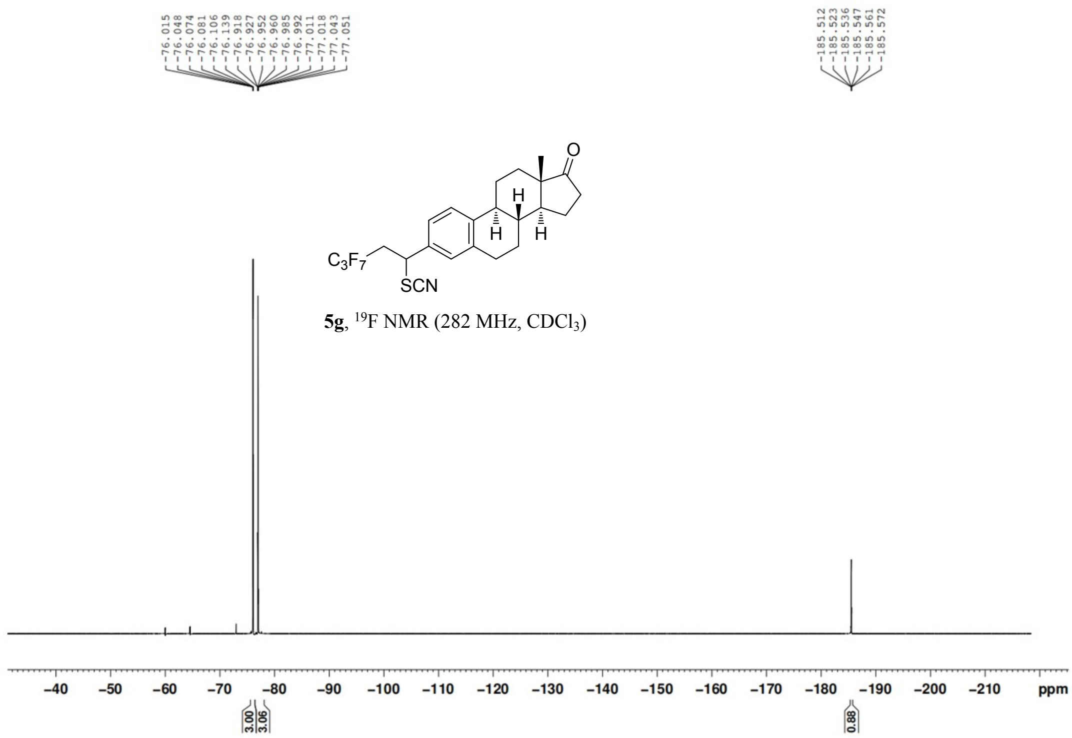


5g, ^{1}H NMR (300 MHz, $CDCl_3$)

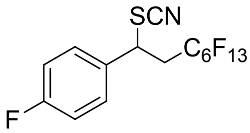




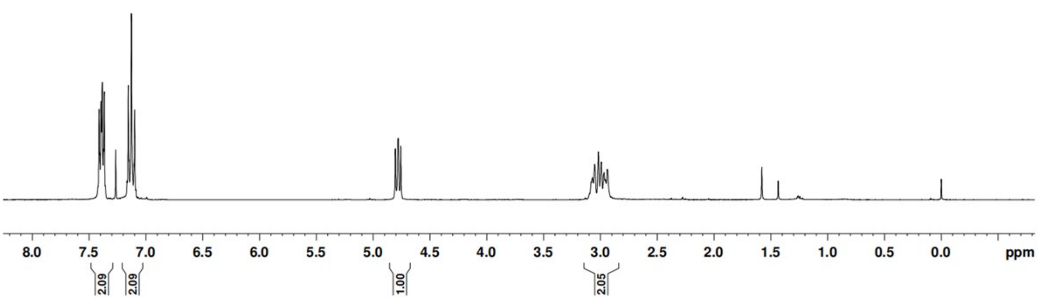
5g, ^{13}C NMR (75 MHz, $CDCl_3$)

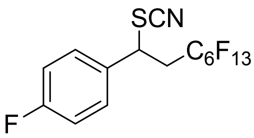


5g, ^{19}F NMR (282 MHz, $CDCl_3$)

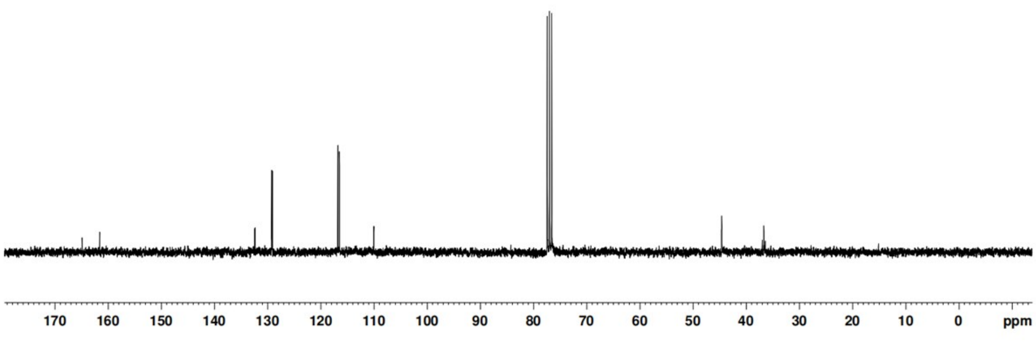


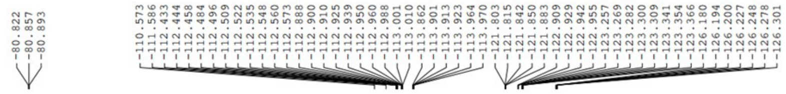
5h, ^{1}H NMR (300 MHz, $CDCl_3$)

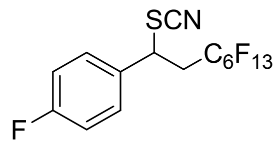




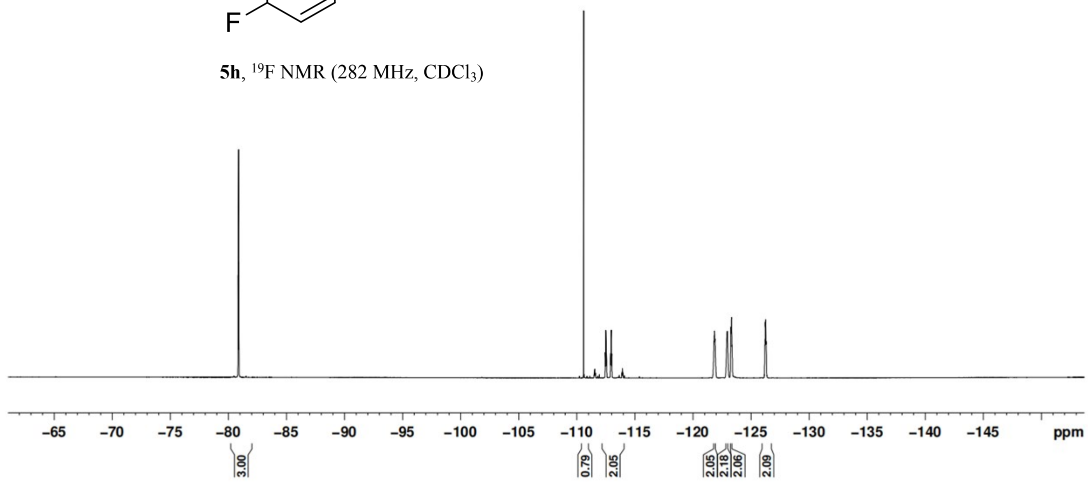
5h, ^{13}C NMR (75 MHz, $CDCl_3$)

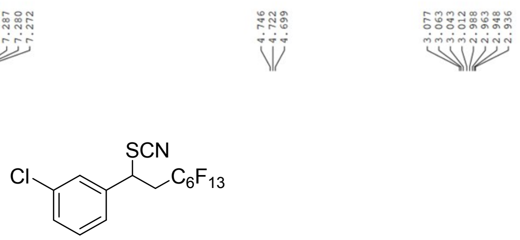




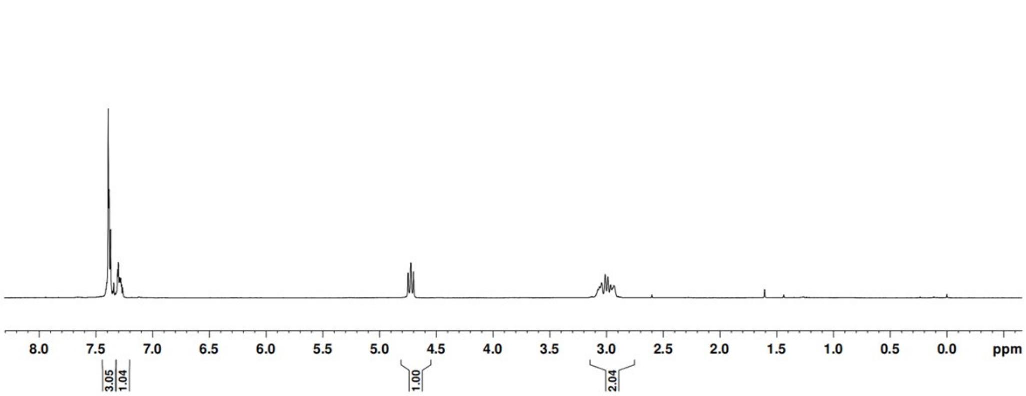


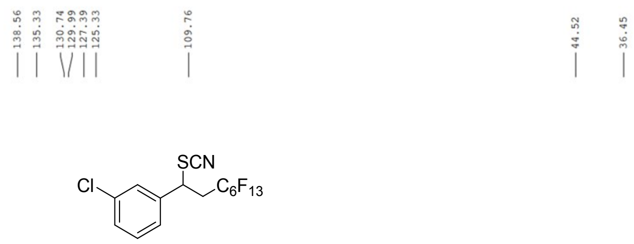
5h, ^{19}F NMR (282 MHz, $CDCl_3$)



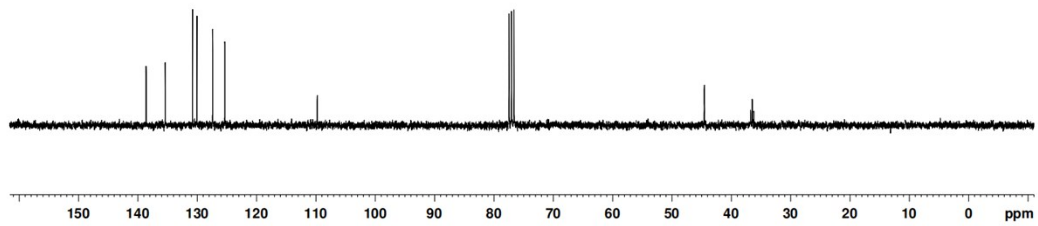


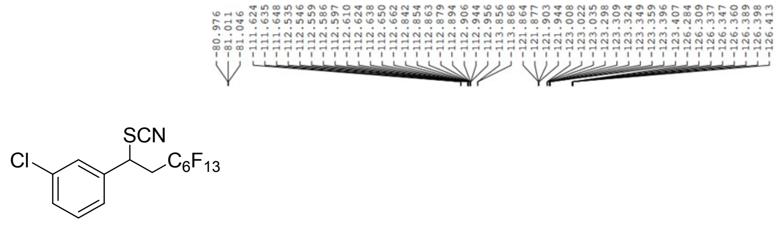
5i, ^{1}H NMR (300 MHz, $CDCl_3$)



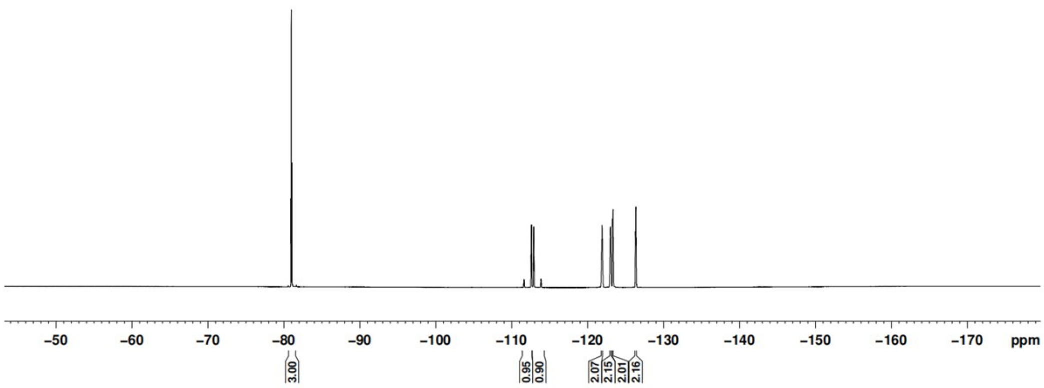


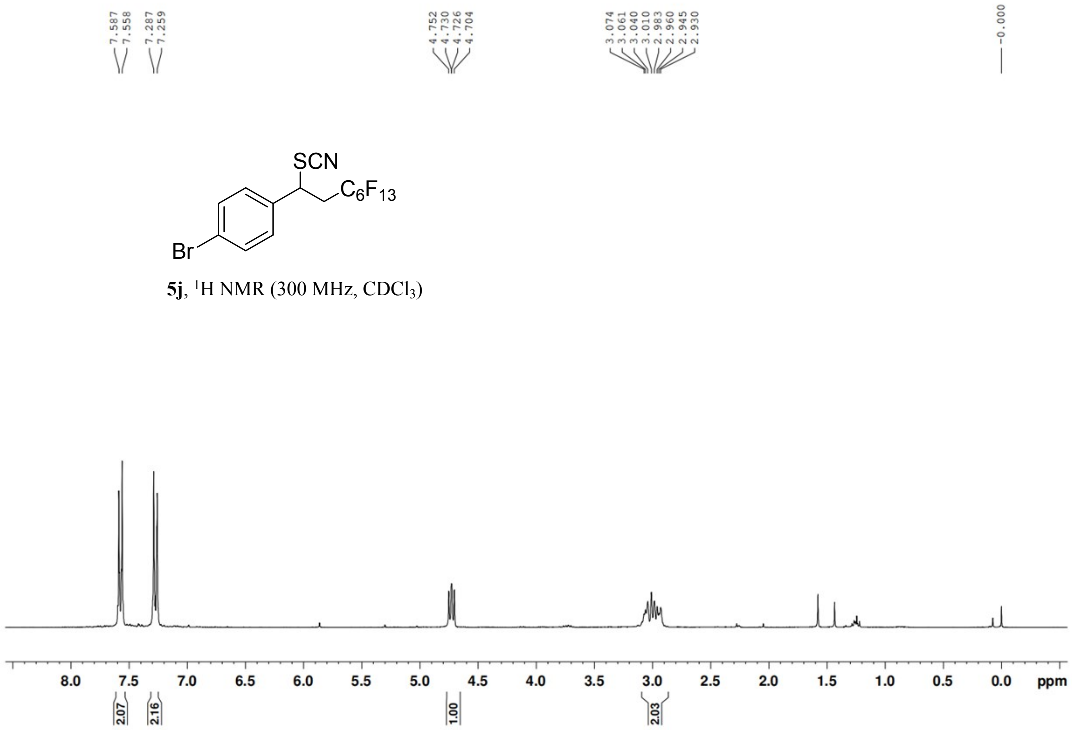
5i, ^{13}C NMR (75 MHz, $CDCl_3$)



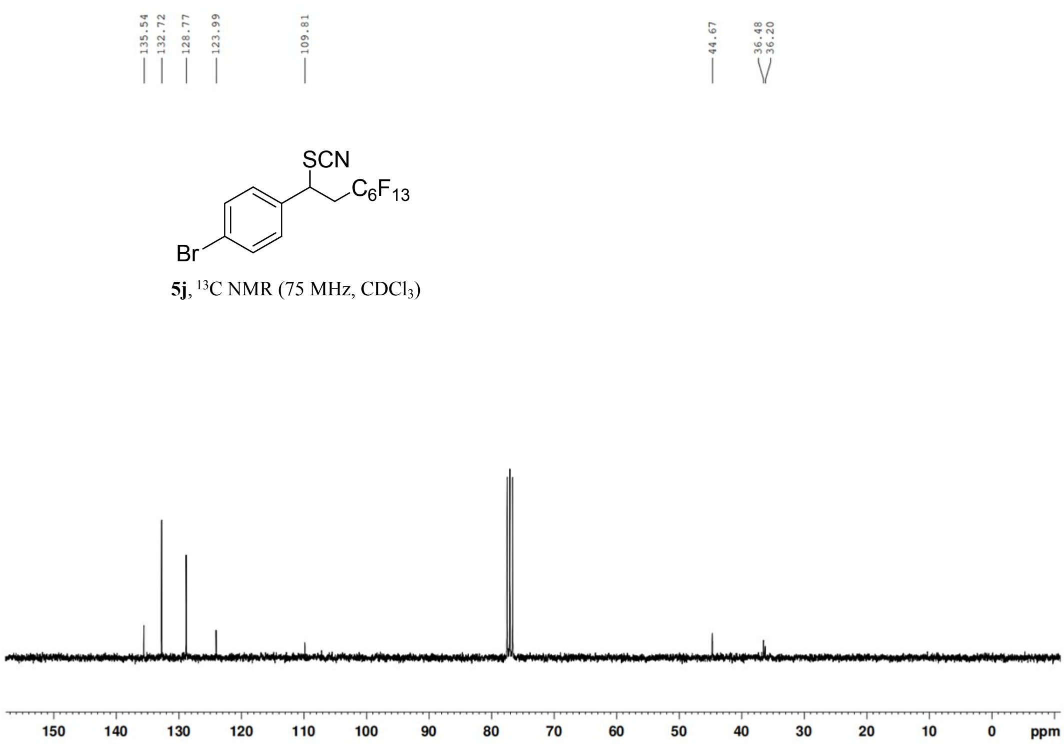


5i, ^{19}F NMR (282 MHz, $CDCl_3$)

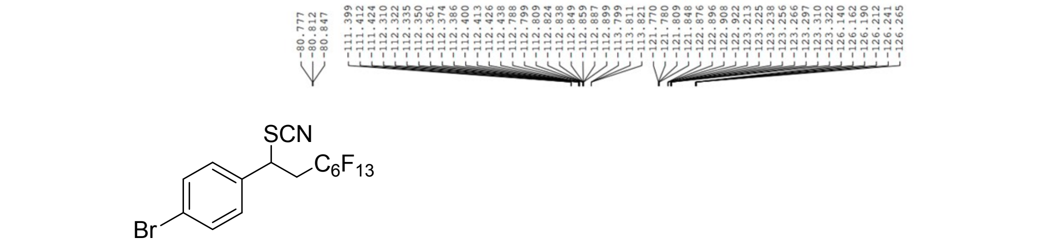




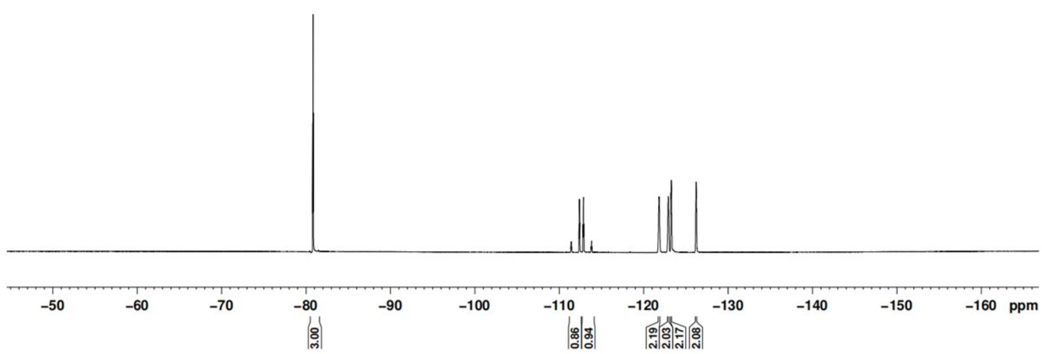
5j, ^{1}H NMR (300 MHz, $CDCl_3$)



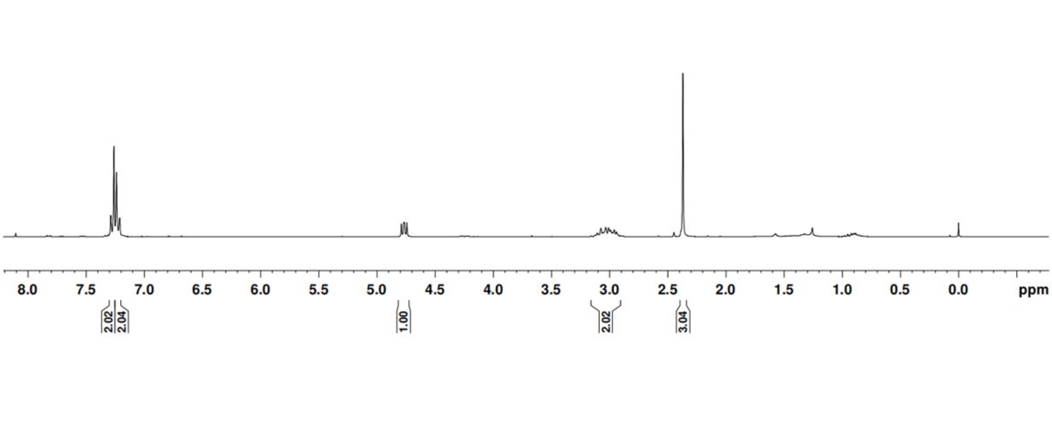
5j, ^{13}C NMR (75 MHz, $CDCl_3$)

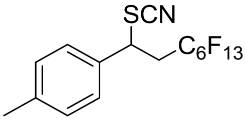


5j, ^{19}F NMR (282 MHz, $CDCl_3$)

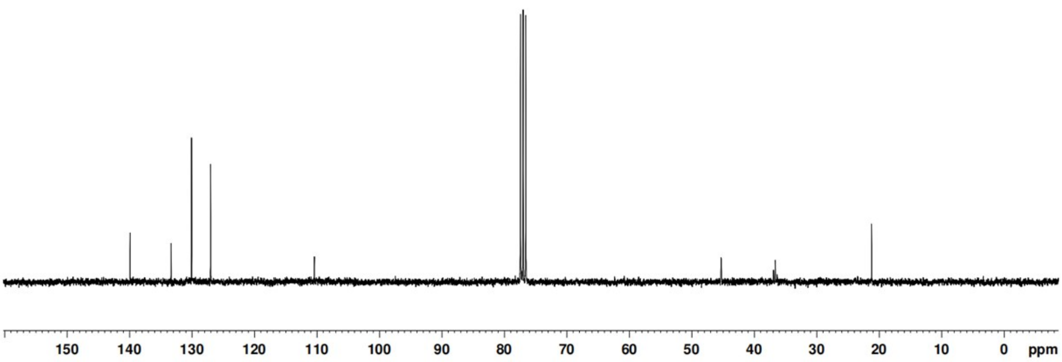


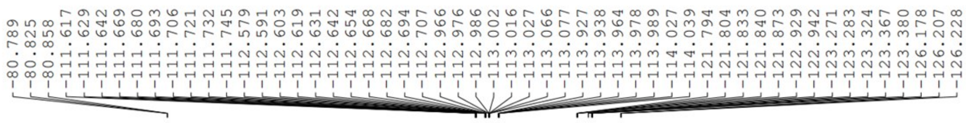
5k, ^{1}H NMR (300 MHz, $CDCl_3$)

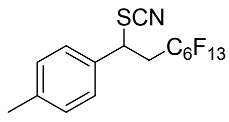




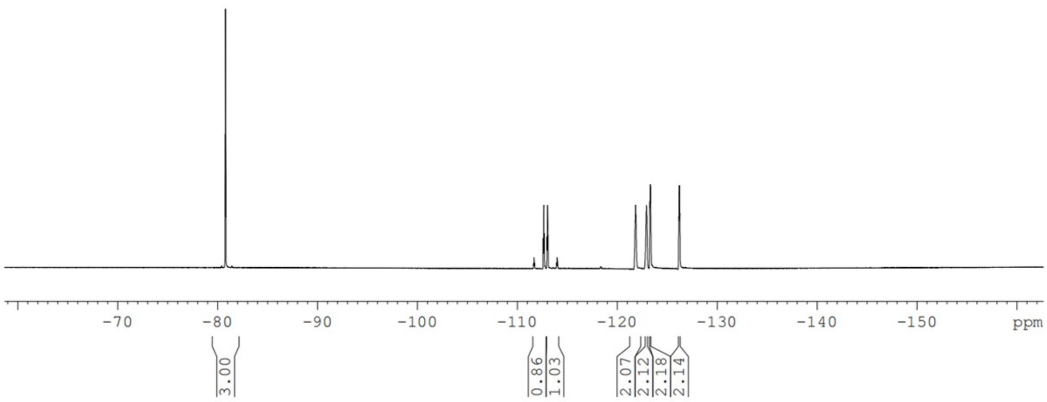
5k, [13]C NMR (75 MHz, $CDCl_3$)

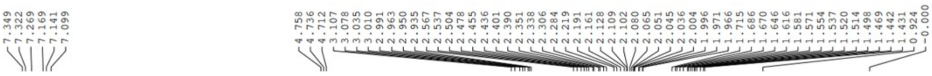


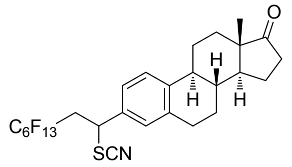




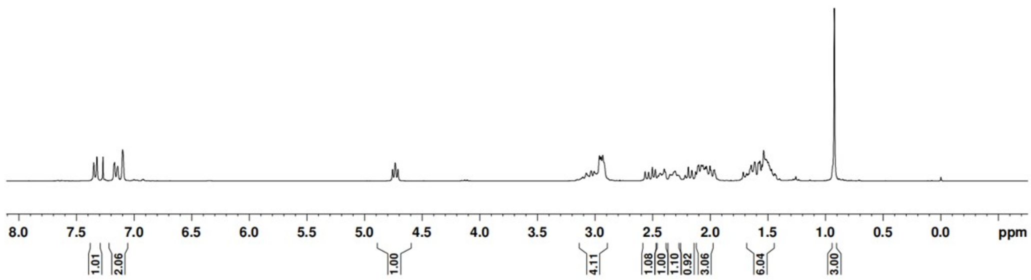
5k, [19]F NMR (282 MHz, $CDCl_3$)

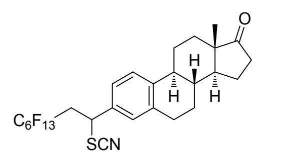




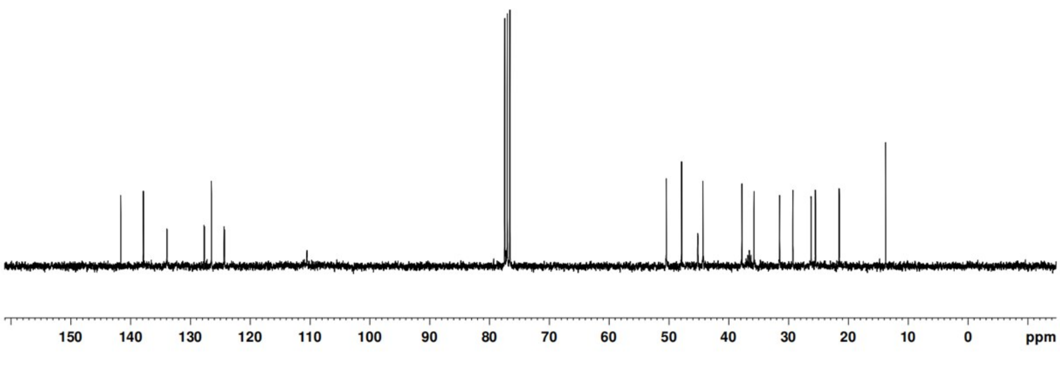


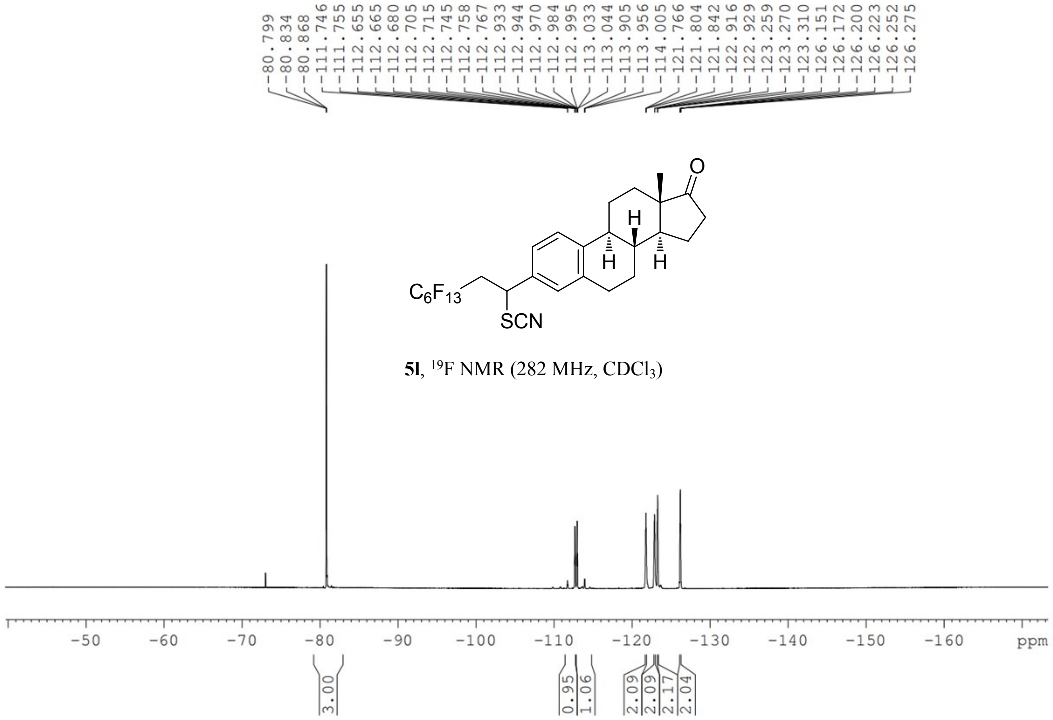
5l, ¹H NMR (300 MHz, $CDCl_3$)



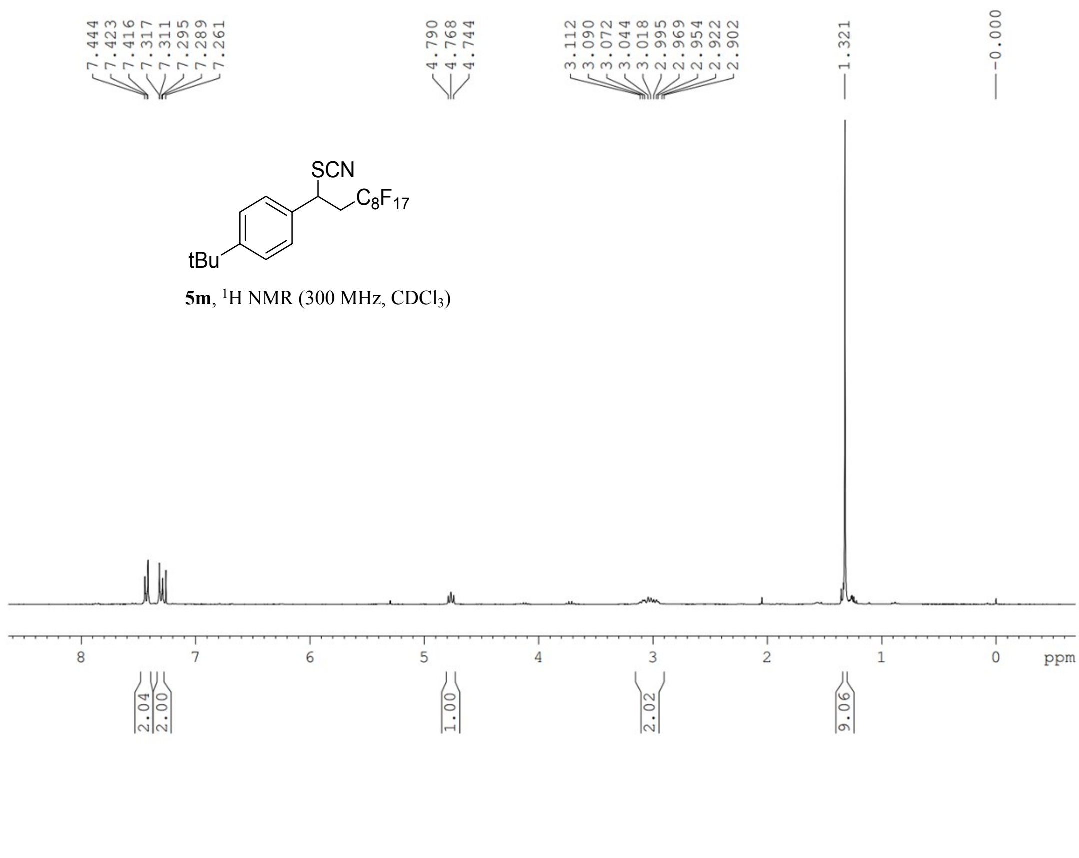


5l, ¹³C NMR (75 MHz, $CDCl_3$)

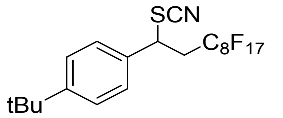




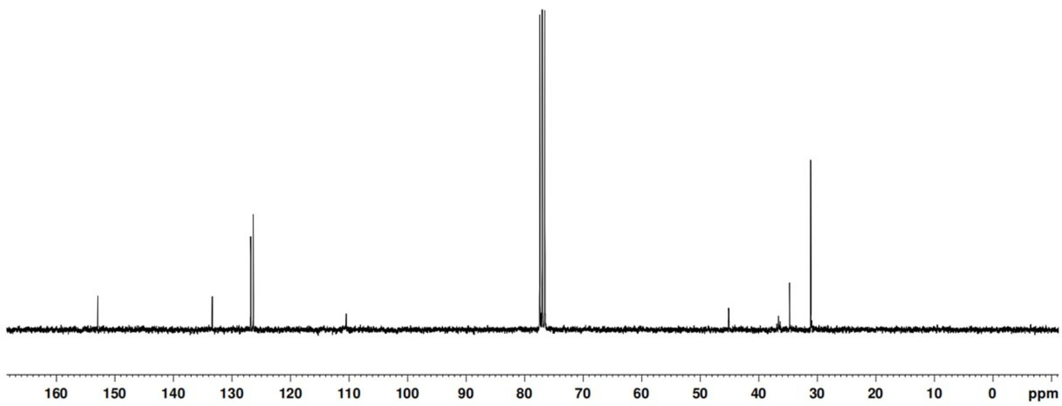
5l, ^{19}F NMR (282 MHz, $CDCl_3$)

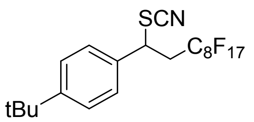


5m, ^{1}H NMR (300 MHz, $CDCl_3$)

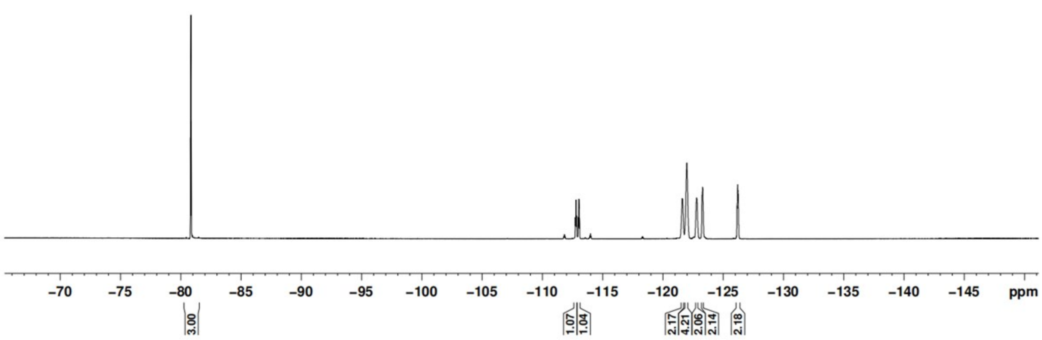


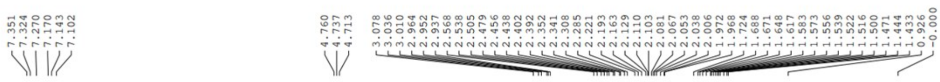
5m, ^{13}C NMR (75 MHz, $CDCl_3$)

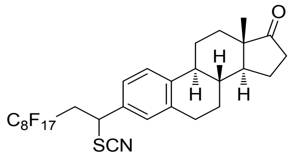




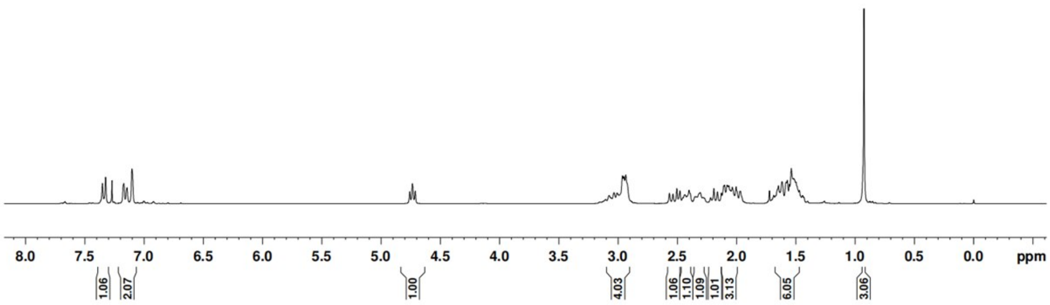
5m, ^{19}F NMR (282 MHz, $CDCl_3$)

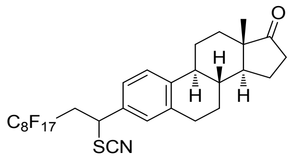




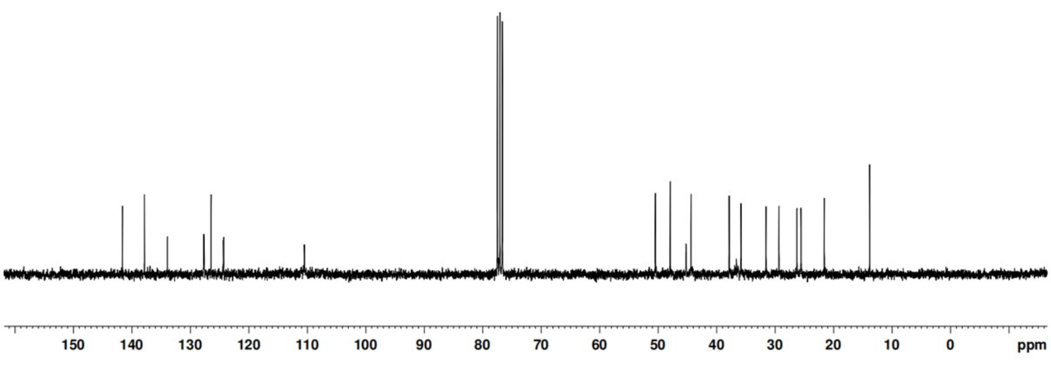


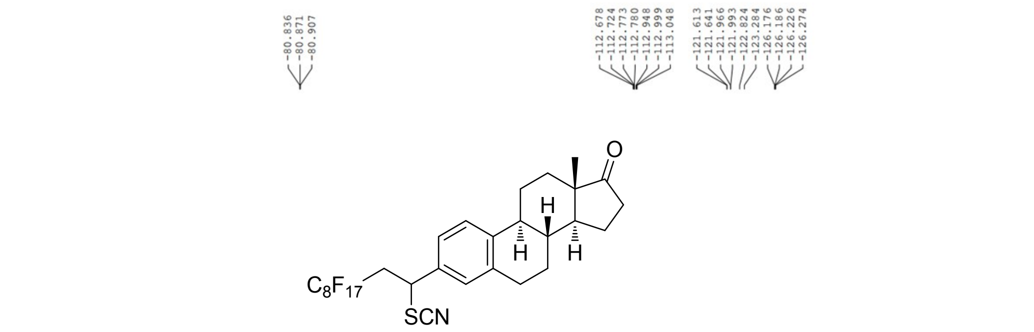
5n, ^{1}H NMR (300 MHz, $CDCl_3$)



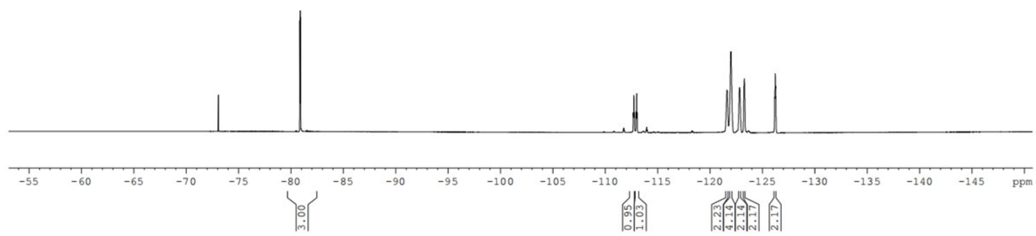


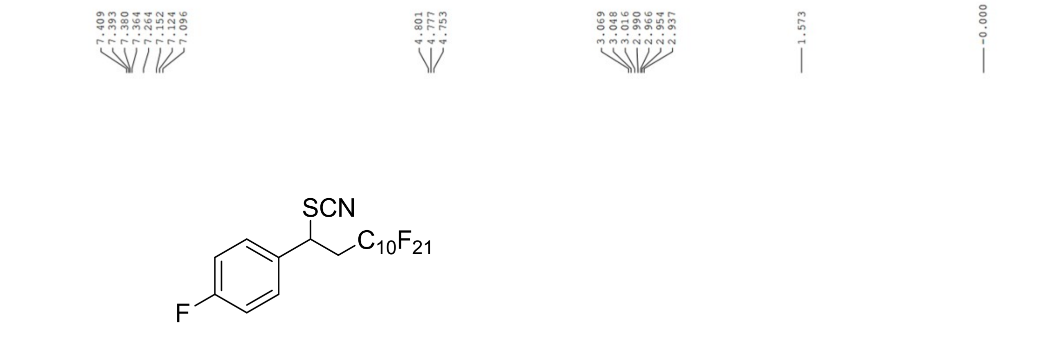
5n, ^{13}C NMR (75 MHz, $CDCl_3$)



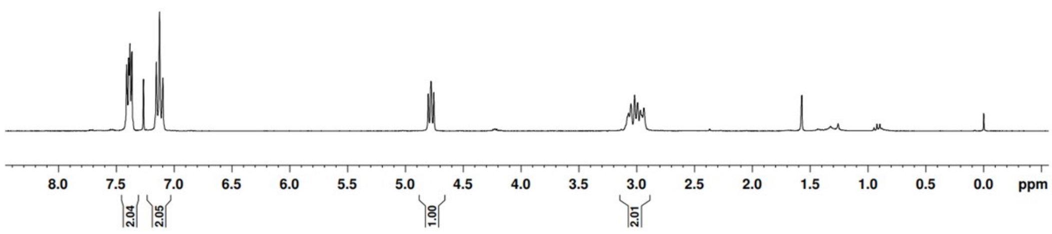


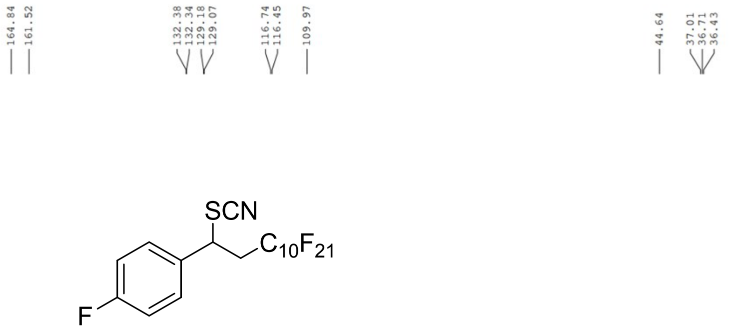
5n, ^{19}F NMR (282 MHz, $CDCl_3$)



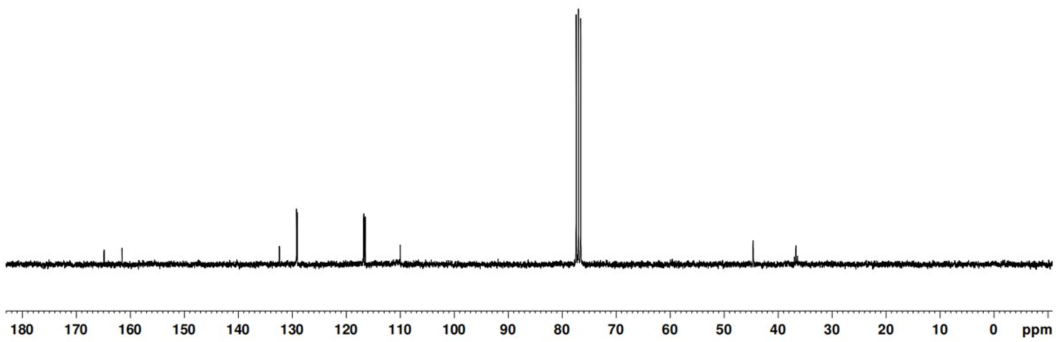


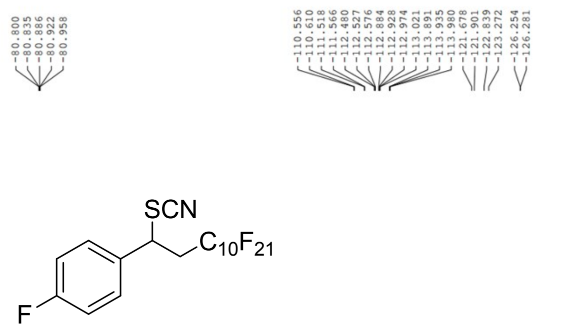
5o, ^{1}H NMR (300 MHz, $CDCl_3$)



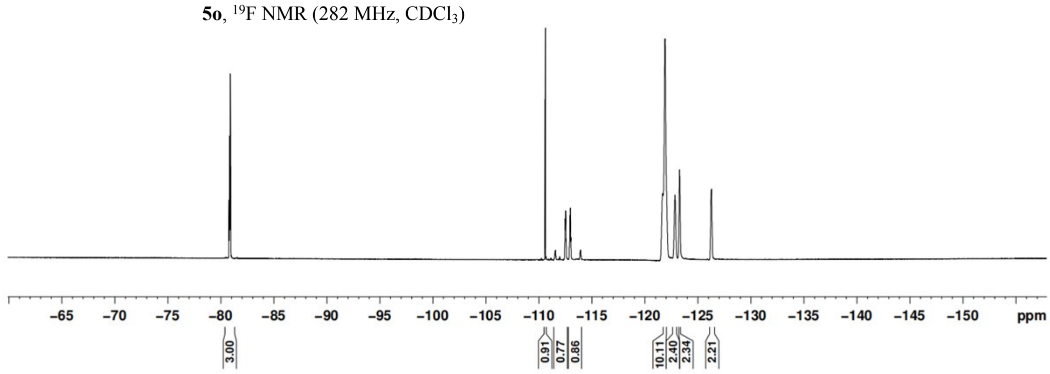


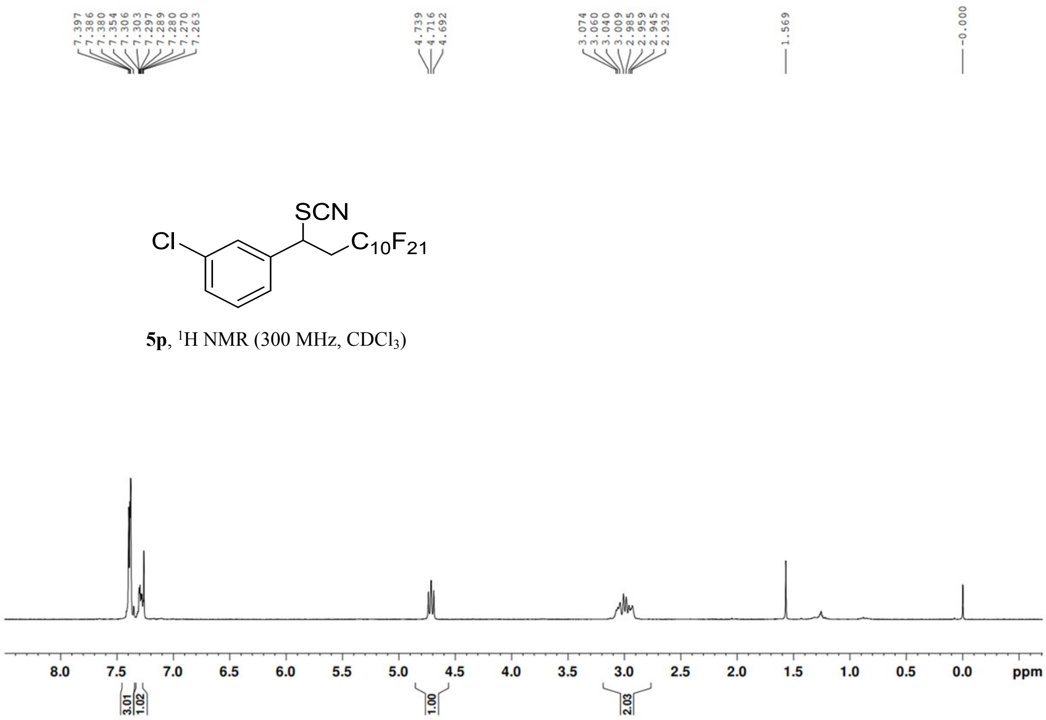
5o, ^{13}C NMR (75 MHz, $CDCl_3$)



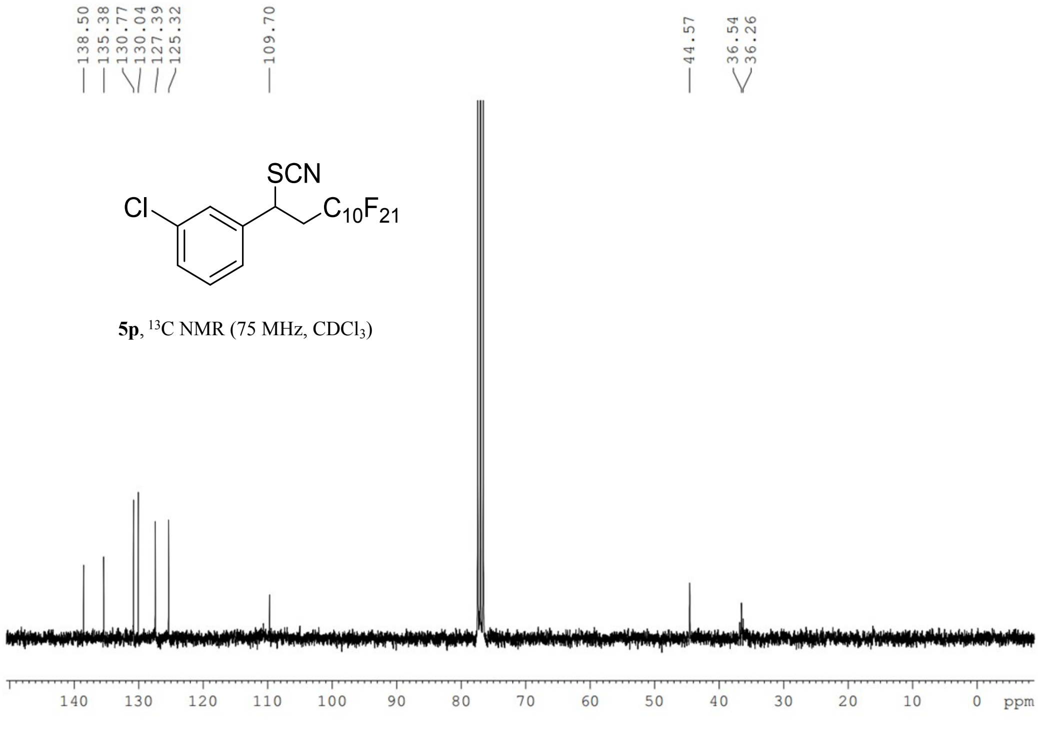


5o, ^{19}F NMR (282 MHz, $CDCl_3$)

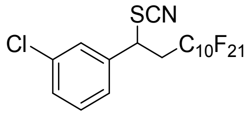




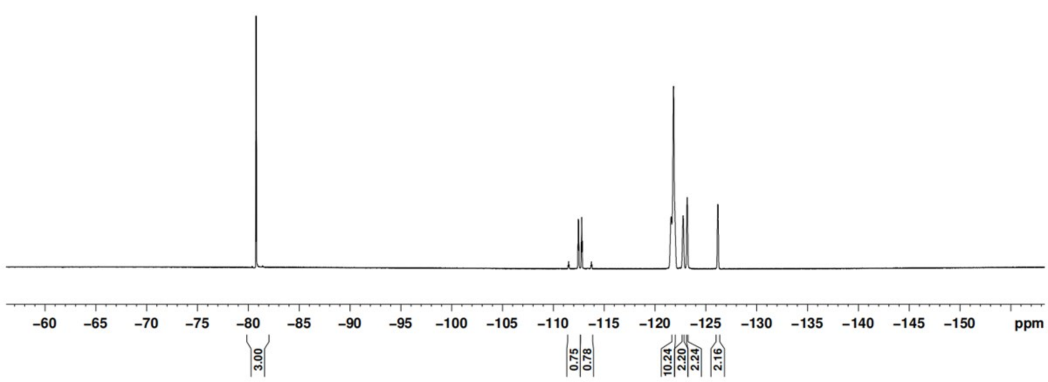
5p, ^{1}H NMR (300 MHz, $CDCl_3$)

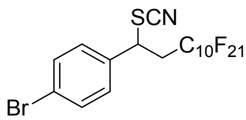


5p, ^{13}C NMR (75 MHz, $CDCl_3$)

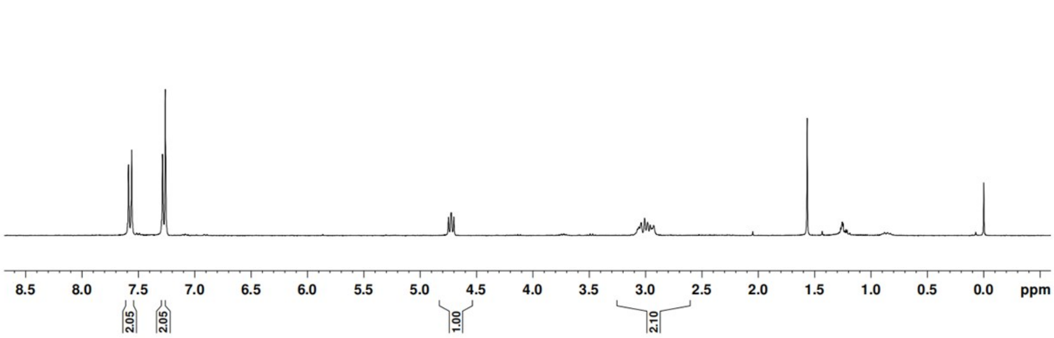


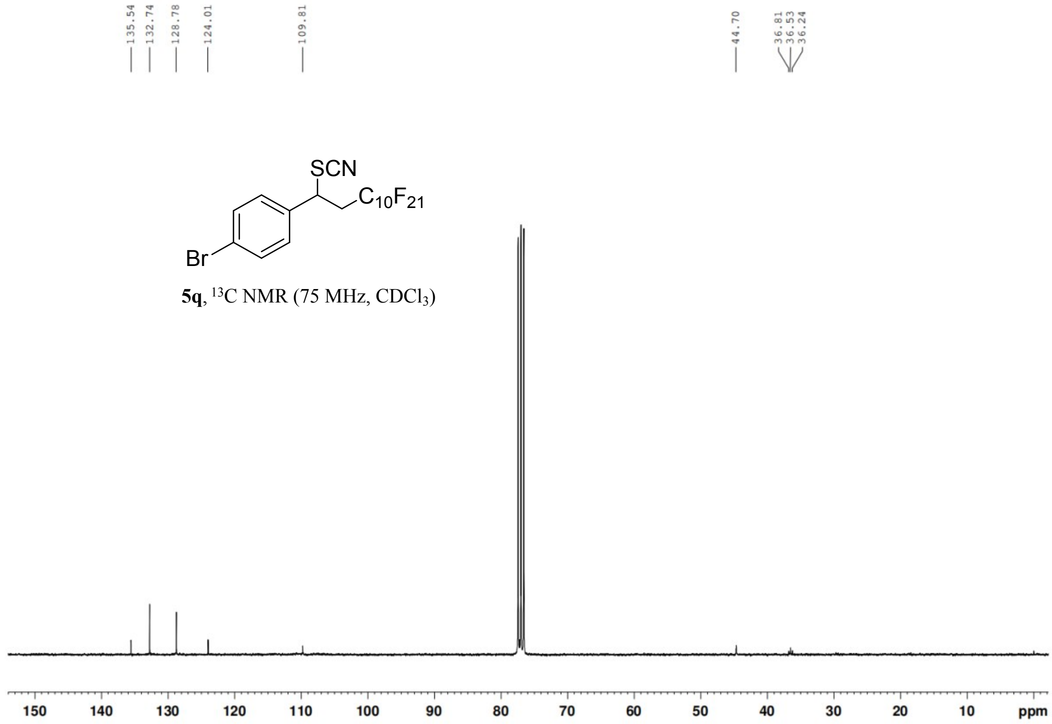
5p, ^{19}F NMR (282 MHz, $CDCl_3$)



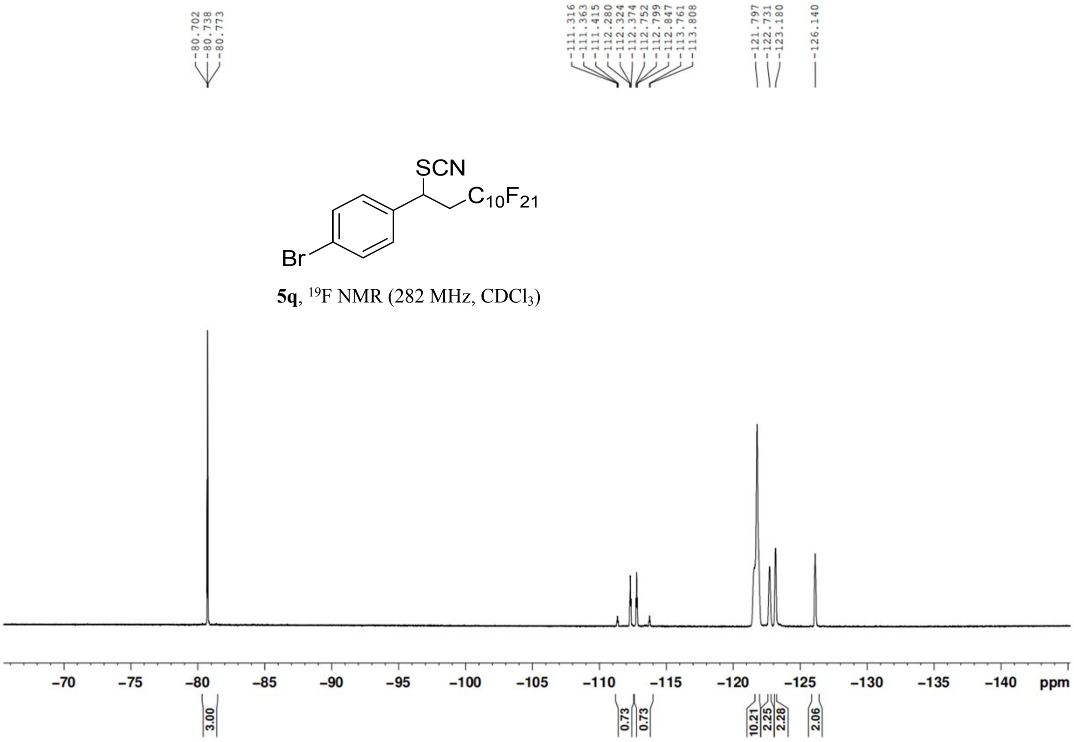


5q, ^{1}H NMR (300 MHz, $CDCl_3$)

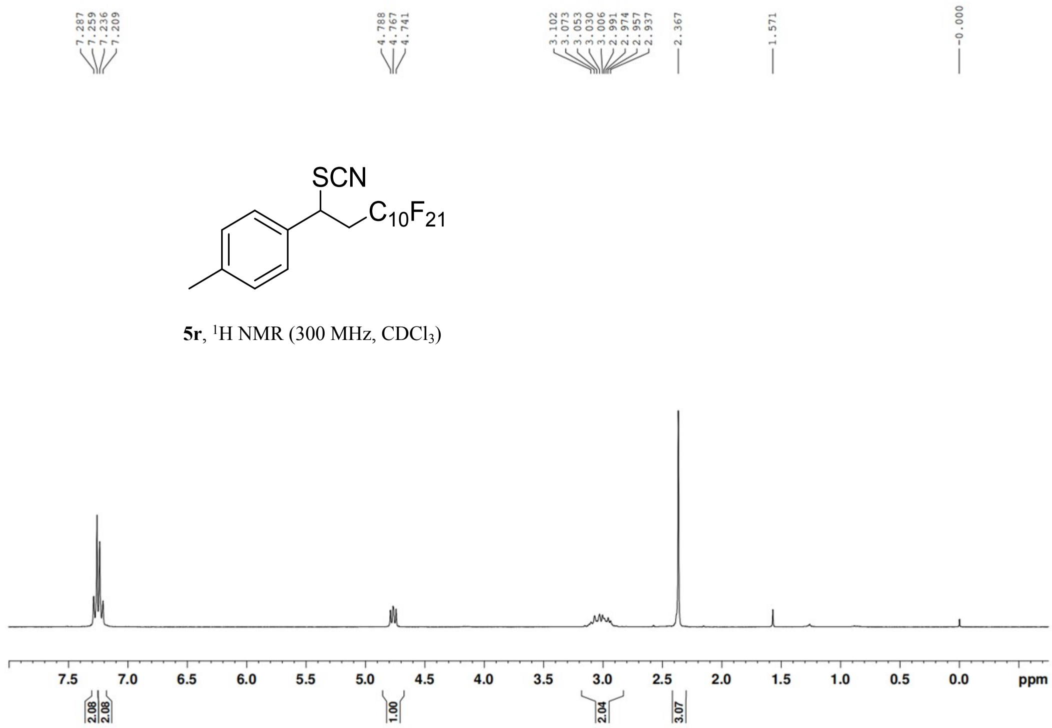




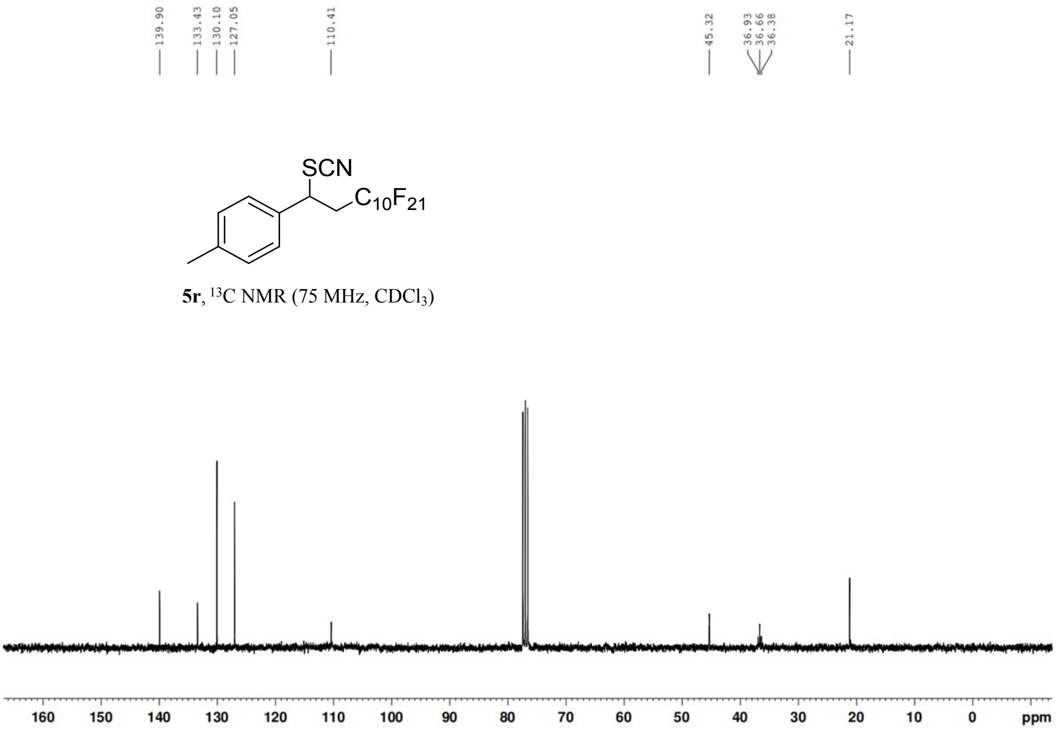
5q, ^{13}C NMR (75 MHz, $CDCl_3$)



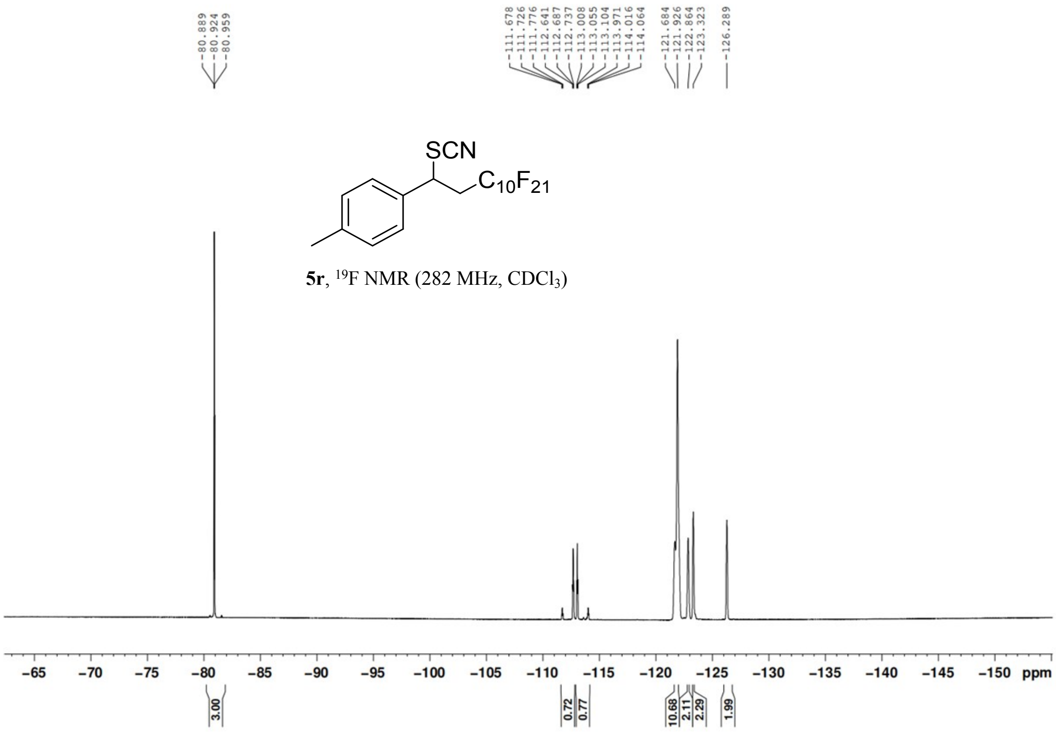
5q, ^{19}F NMR (282 MHz, $CDCl_3$)



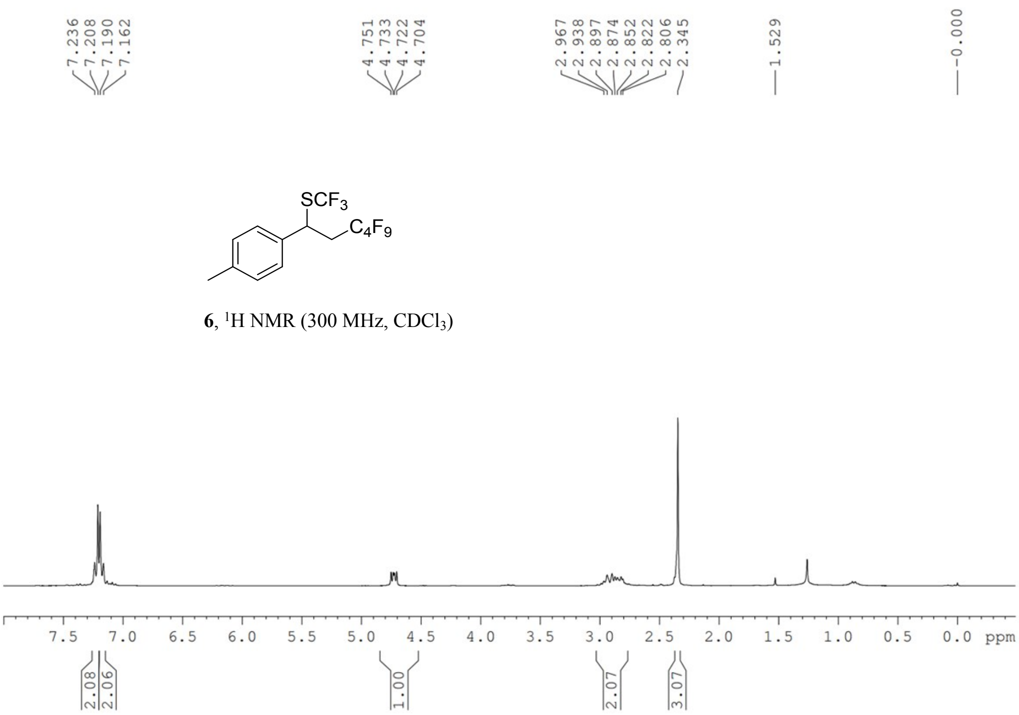
5r, ^{1}H NMR (300 MHz, $CDCl_3$)



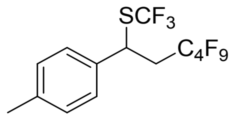
5r, ^{13}C NMR (75 MHz, $CDCl_3$)



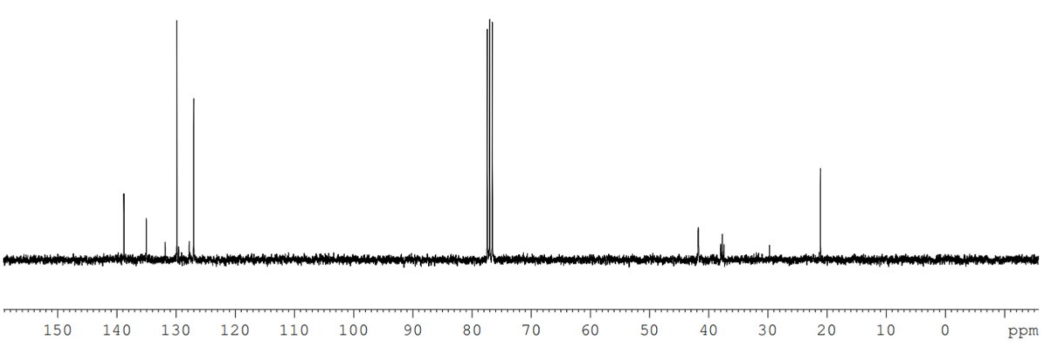
5r, ^{19}F NMR (282 MHz, $CDCl_3$)

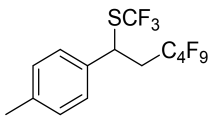


6, ^{1}H NMR (300 MHz, $CDCl_3$)

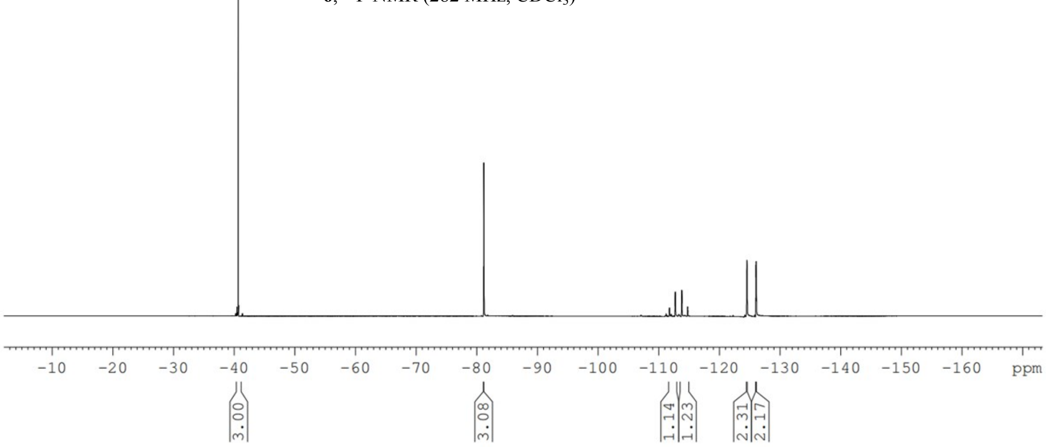


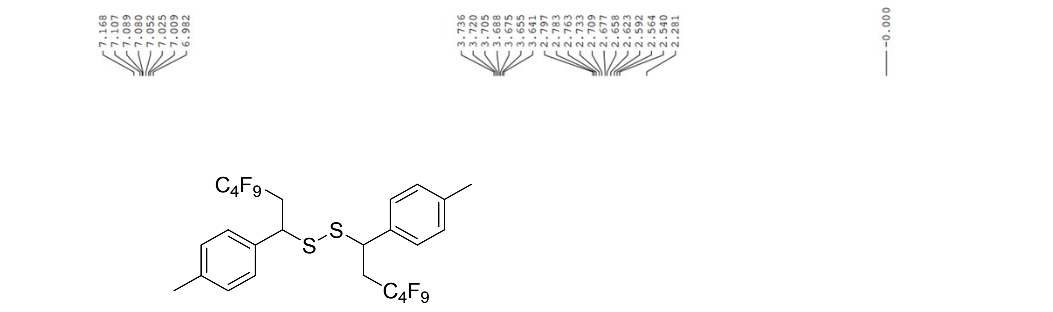
6, ^{13}C NMR (75 MHz, $CDCl_3$)



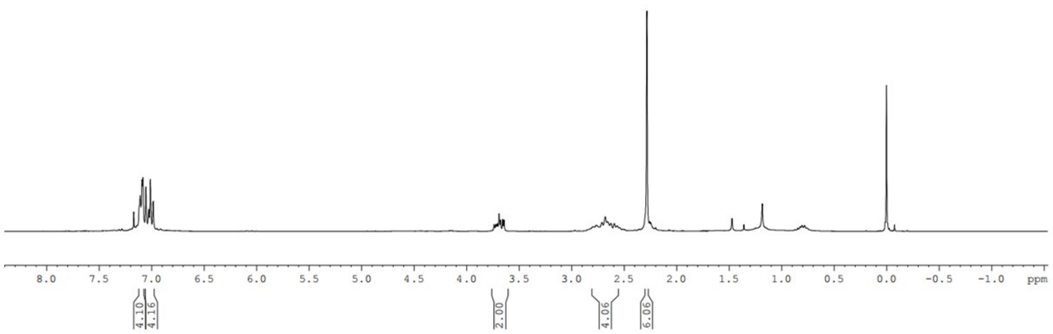


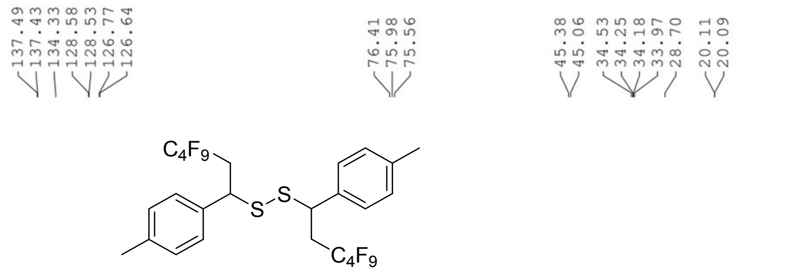
6, ^{19}F NMR (282 MHz, $CDCl_3$)



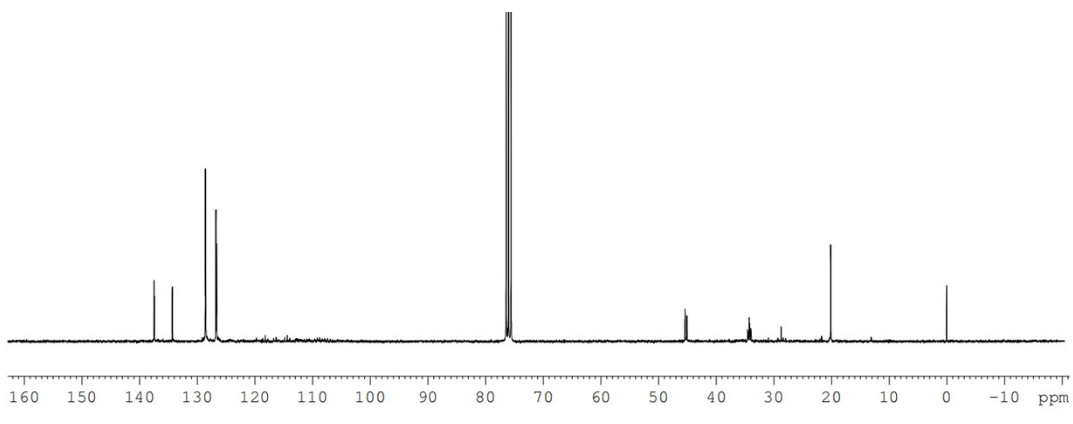


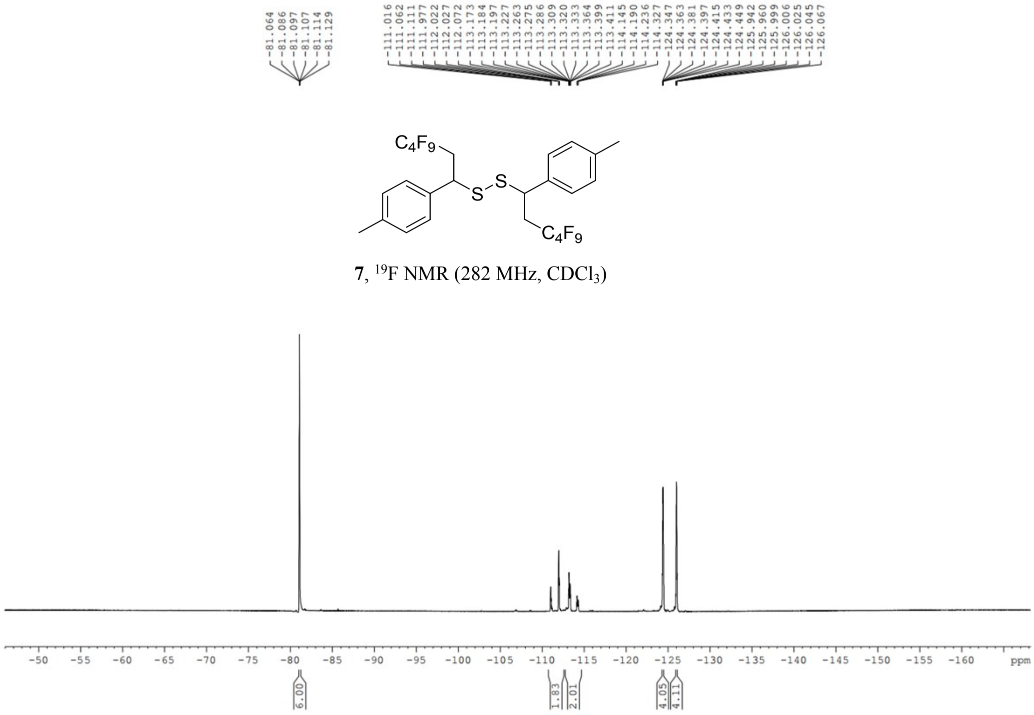
7, ^{1}H NMR (300 MHz, $CDCl_3$)



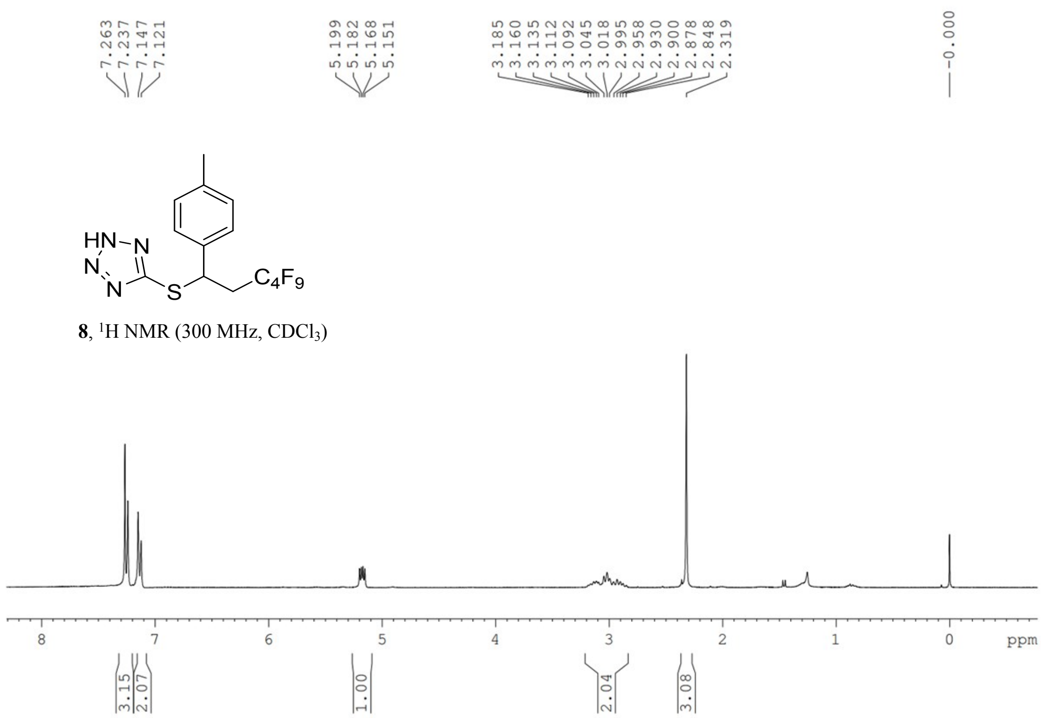


7, ^{13}C NMR (75 MHz, $CDCl_3$)

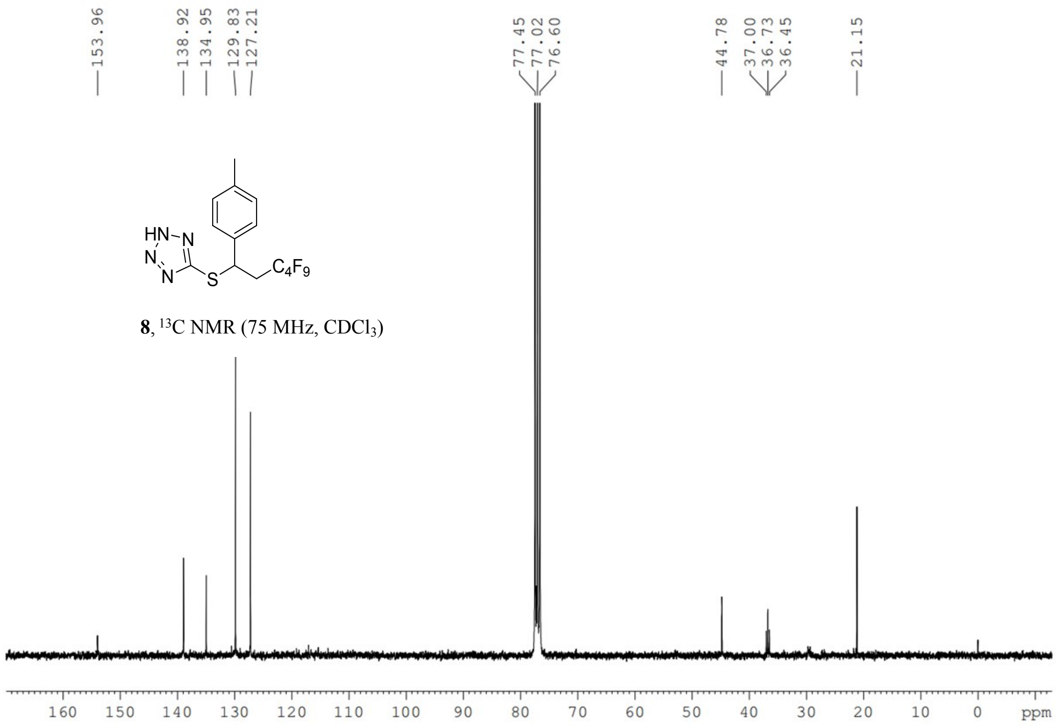




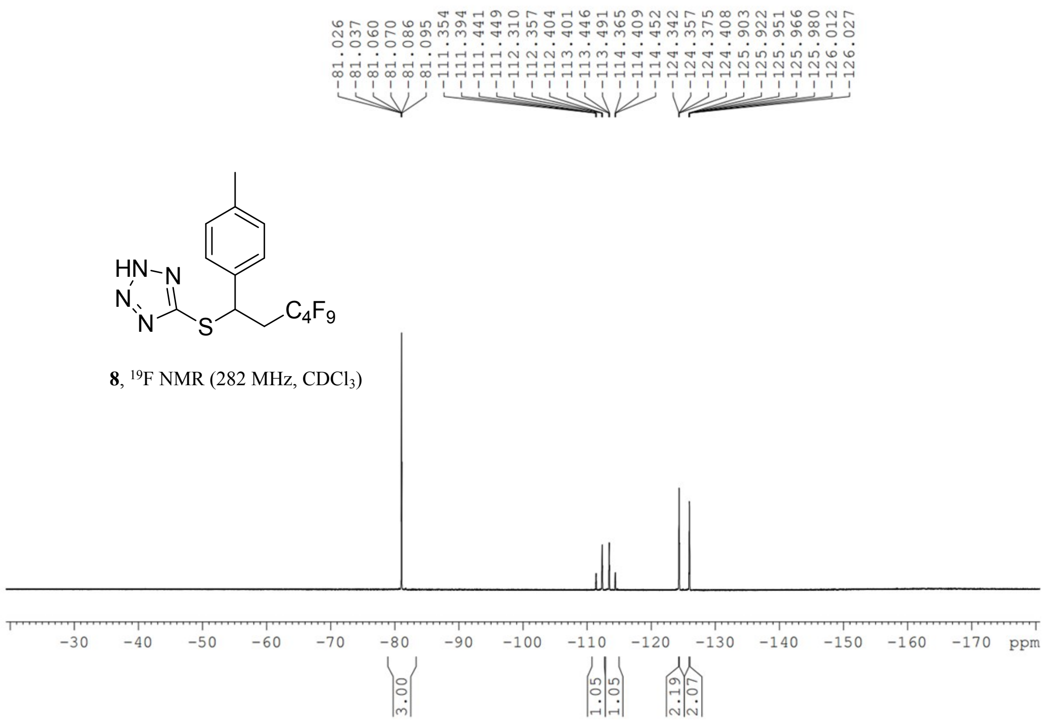
7, ^{19}F NMR (282 MHz, $CDCl_3$)



8, ^{1}H NMR (300 MHz, $CDCl_3$)



8, ^{13}C NMR (75 MHz, $CDCl_3$)



8, ^{19}F NMR (282 MHz, $CDCl_3$)