Supplementary Information

Stereodivergent Atom Transfer Radical Addition of α-Functionalized Alkyl Iodides to Alkynes: A Strategy for Selective Synthesis of Both *E*- and *Z*-Iodoalkenes

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1. General information

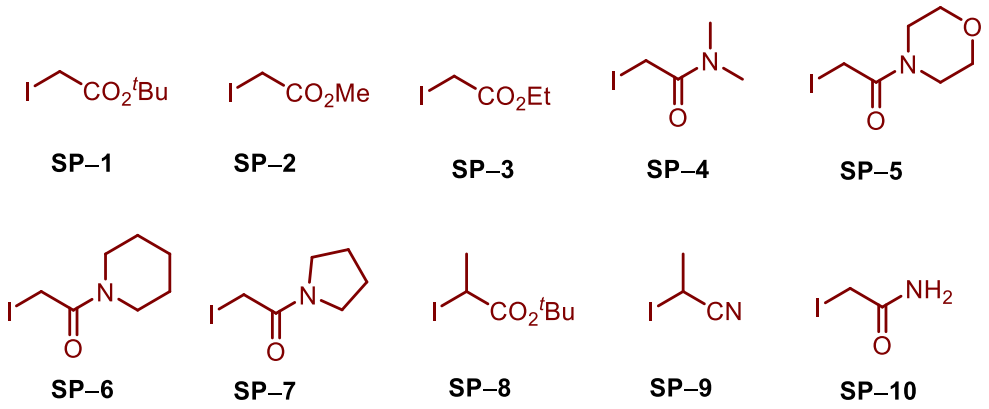
Unless otherwise noted, all commercially available materials were used without further purification. All reactions were performed in glassware under argon.

NMR–spectra were recorded on Bruker AvanceIII–400MHz and Ascend^{TM} 500MHz in solvents as indicated. Chemical shifts ($_{\delta}$) are given in ppm relative to tetramethylsilane ($\delta = 0$). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm). The following abbreviations were used to describe peak splitting patterns: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets). Coupling constants (*J*) were reported in hertz unit (Hz).

High–resolution mass spectra (HRMS) were recorded on a Bruker VPEXII spectrometer with EI and ESI mode unless otherwise stated. Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished by UV light (254 nm), or $KMnO_4$ staining solutions followed by heating, also by Gas chromatograph-Mass spectrometer analysis (GC-MS) on Agilent Technologies 5977A MSD. Flash column chromatography was performed using silica gel (200–300 mesh).

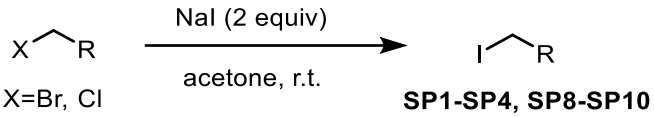
No attempts were made to optimize yields for substrate synthesis.

2. Preparation of the starting materials



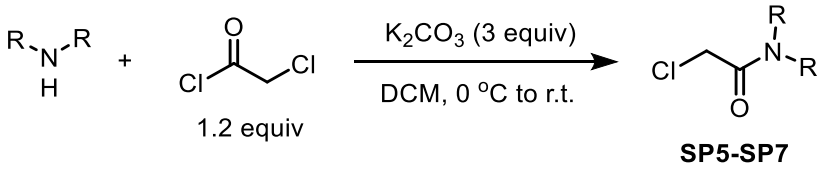
Supplementary Figure 1. List of α-iodides

2.1 Preparation of α-iodides SP1-SP4, SP8-SP9 (general procedure A)



According to the reported literature[1], in a glove box, a 100 mL round-bottom flask equipped with a stirring bar was charged with halide (1.0 equiv.), NaI (2.0 equiv.) and acetone (0.25 M). The flask was sealed and stirring for 3 h. After that, the suspension was filtered through a pad of celites. The filtrate was concentrated under reduced pressure and redissolved in ethyl acetate. The mixture was washed with water (2 × 30 mL) and brine (1 × 30 mL) and the filtrate was dried with sodium sulfate then concentrated under reduced pressure to give α-iodides **SP1-SP3**, **SP8-SP10**.

2.2 Preparation of α-iodides SP5-SP7



According to the reported literature[2], a 100 mL round-bottom flask equipped with a stirring bar was charged with K_2CO_3 (3.0 equiv.), amine (1.0 equiv.) and dry DCM (0.25 M). Then α-chloroacetyl chloride (1.2 equiv.) was added dropwise to the reaction mixture under nitrogen atmosphere at 0 °C. The reaction mixture was then warmed up to room temperature and stirred over 16 hours. After completion, the mixture was filtered and concentrated in vacuo to obtain a crude product. The residue was purified by flash chromatography (eluent = petroleum ether/ ethyl acetate, v/v) to obtain the chloramide. Then follow the **general procedure A** to obtain the α-iodides **SP5-SP7**.

3. Characterization of the starting materials

***tert*-butyl 2-iodoacetate (SP-1)**

Following the **general procedure A**, **SP-1** was obtained as a pale-yellow oil (4.44 g, 9.20 mmol, 92%). The spectroscopic properties of this compound were consistent with the data reported in the literature[5].

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 2H), 1.46 (s, 9H).

methyl 2-iodoacetate (SP-2)

Following the **general procedure A**, **SP-2** was obtained as a pale-yellow oil (810 mg, 4.05 mmol, 81%). The spectroscopic properties of this compound were consistent with the data reported in the literature[6].

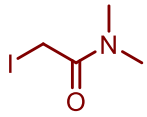
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.69 (s, 2H).

ethyl 2-iodoacetate (SP-3)

Following the **general procedure A**, **SP-3** was obtained as a pale-yellow oil (909 mg, 4.25 mmol, 85%). The spectroscopic properties of this compound were consistent with the data reported in the literature[7].

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, J = 7.2 Hz, 2H), 3.68 (s, 2H), 1.28 (t, J = 7.1 Hz, 3H).

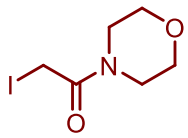
2-iodo-*N*,*N*-dimethylacetamide (SP-4)



Following the **general procedure A**, **SP-4** was obtained as a pale-yellow oil (680 mg, 3.20 mmol, 64%). The spectroscopic properties of this compound were consistent with the data reported in the literature[11].

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 2H), 3.04 (s, 3H), 2.95 (s, 3H).

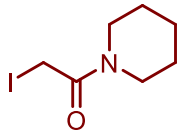
2-iodo-1-morpholinoethan-1-one (SP-5)



Following the **general procedure B**, **SP-5** was obtained as a white solid (918 mg, 3.60 mmol, 72%). The spectroscopic properties of this compound were consistent with the data reported in the literature[12].

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (d, J = 4.6 Hz, 2H), 3.69 – 3.64 (m, 4H), 3.61 (dd, J = 5.7, 3.6 Hz, 2H), 3.48 – 3.36 (m, 2H).

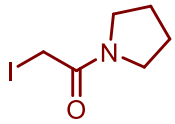
2-iodo-1-(piperidin-1-yl)ethan-1-one (SP-6)



Following the **general procedure B**, **SP-6** was obtained as a white solid (964 mg, 3.81 mmol, 76%). The spectroscopic properties of this compound were consistent with the data reported in the literature[13].

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 2H), 3.58 – 3.49 (m, 2H), 3.37 (ddd, *J* = 5.5, 3.3, 1.6 Hz, 2H), 1.64 (dt, *J* = 6.1, 2.9 Hz, 4H), 1.53 (tt, *J* = 7.9, 2.6 Hz, 2H).

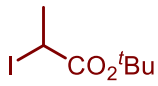
2-iodo-1-(pyrrolidin-1-yl)ethan-1-one (SP-7)



Following the **general procedure B**, **SP-7** was obtained as a white solid (964 mg, 3.81 mmol, 76%). The spectroscopic properties of this compound were consistent with the data reported in the literature[14].

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 2H), 3.46 (q, *J* = 6.3 Hz, 4H), 2.01 (dd, *J* = 13.3, 6.5 Hz, 2H), 1.89 (q, *J* = 6.6 Hz, 2H).

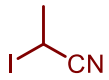
***tert*-butyl 2-iodopropanoate (SP-8)**



Following the **general procedure B**, **SP-8** was obtained as a pale-yellow oil (1.19 g, 4.65 mmol, 93%). The spectroscopic properties of this compound were consistent with the data reported in the literature[15].

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39 (q, *J* = 7.0 Hz, 1H), 1.90 (d, *J* = 7.0 Hz, 3H), 1.46 (s, 9H).

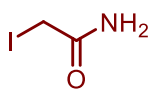
2-iodopropanenitrile (SP-9)



Following the **general procedure A**, **SP-9** was obtained as a pale-yellow oil (706 mg, 3.90 mmol, 78%). The spectroscopic properties of this compound were consistent with the data reported in the literature[16].

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (q, *J* = 7.2 Hz, 1H), 2.13 (d, *J* = 7.2 Hz, 3H).

2-iodoacetamide (SP-10)



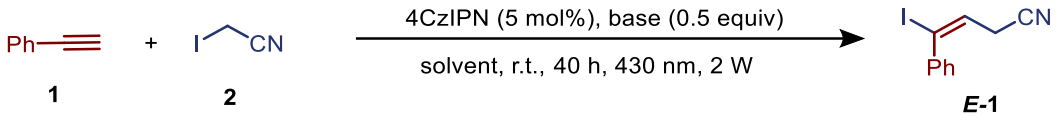
Following the **general procedure A, SP-10** was obtained as a pale-yellow oil (814 mg, 4.40 mmol, 88%). The spectroscopic properties of this compound were consistent with the data reported in the literature[8].

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 – 5.76 (m, 1H), 5.76 – 5.52 (m, 1H), 3.70 (s, 2H).

4. Reaction optimization for ATRA reaction

4.1 Reaction optimization for the synthesis of *E* isomer

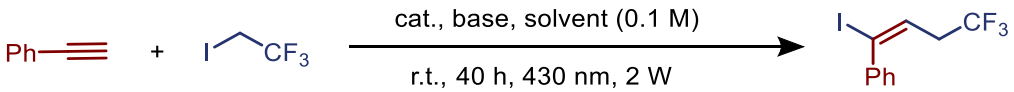
Supplementary Table 1. Reaction optimization for PC-catalyzed ATRA reaction of iodinated allylic nitrile



1 **2** ***E*-1**

entry	base	solvent	NMR yield	*E:Z*
1	PMP	DCM (0.1 M)	63%	69:31
2	PMP	DCE (0.1 M)	70%	73:27
3	PMP	toluene (0.1 M)	21%	93:7
4	PMP	MeCN (0.1 M)	45%	74:26
5	PMP	DCM (0.5 M)	37%	84:16
6	PMP	DCE (0.5 M)	34%	85:15
7	PMP	toluene (0.5 M)	38%	82:18
8	PMP	MeCN (0.5 M)	34%	76:24
9	$KHCO_3$	toluene (0.1 M)	61%	95:5
10	**K_3PO_4**	**toluene (0.1 M)**	**90%**	**96:4**
11	Cs_2CO_3	toluene (0.1 M)	85%	95:5
12	DIPEA	toluene (0.1 M)	37%	83:17
13	TEA	toluene (0.1 M)	30%	84:16
14	TMEDA	toluene (0.1 M)	21%	92:8

Supplementary Table 2. Reaction optimization for PC-catalyzed ATRA reaction of iodinated allylic trifluoromethane

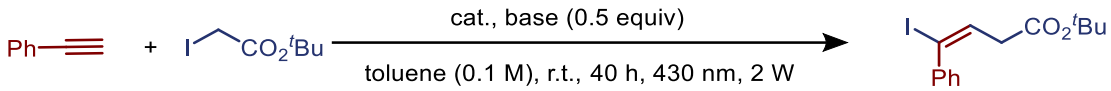


1 **3** ***E*-15**

entry	PC	base	solvent	NMR yield	*E:Z*
1	4CzIPN (5 mol%)	PMP (0.5 equiv)	CyH	-	-
2	4CzIPN (5 mol%)	PMP (0.5 equiv)	MeCN	66%	47:53
3	4CzIPN (5 mol%)	DIPEA (0.5 equiv)	MeCN	30%	47:53
4	4CzIPN (5 mol%)	TMEDA (0.5 equiv)	MeCN	46%	47:53
5	4CzIPN (5 mol%)	PMP (1.0 equiv)	MeCN	64%	44:56
6	4CzIPN (5 mol%)	PMP (1.0 equiv)	toluene	51%	52:48
7	4CzIPN (5 mol%)	PMP (1.0 equiv)	DCE	78%	50:50
8	**$Ir[dF(CF_3)ppy]_2(dtppby)PF_6$ (2 mol%)**	**PMP (1.0 equiv)**	**DCE**	**70%**	**93:7**
9	$Ir(ppy)_3$ (2 mol%)	PMP (1.0 equiv)	DCE	46%	79:21
10	$Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%)	PMP (1.0 equiv)	DCE	76%	49:51
11[a]	TX (5 mol%)	PMP (1.0 equiv)	DCE	39%	79:21

[a]405 nm 2 W light was used

Supplementary Table 3. Reaction optimization for PC-catalyzed ATRA reaction of iodinated allylic *tert*-butyl carboxylate

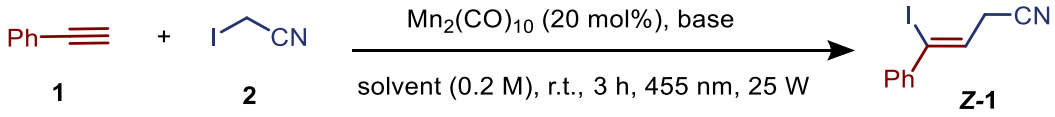


1 **4** ***E*-31**

entry	PC	base	NMR yield	*E:Z*
1	4CzIPN (5 mol%)	PMP	75%	89:11
2	4CzIPN (5 mol%)	K_3PO_4	49%	93:7
3	Ir[dF(CF_3)ppy]$_2$(dtppby)PF_6 (2 mol%)	PMP	75%	68:34
4	Ir[dF(Me)ppy]$_2$(dtppby)PF_6 (2 mol%)	PMP	69%	76:24
5	**Ir(dFppy)$_3$ (2 mol%)**	**PMP**	**66%**	**91:9**

4.2 Reaction optimization for the synthesis of *Z* isomer

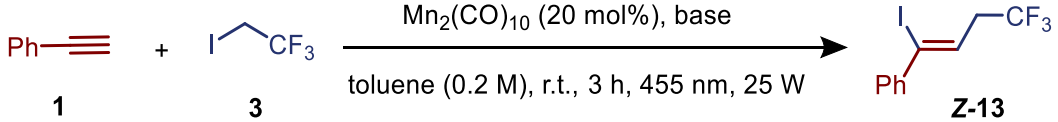
Supplementary Table 4. Reaction optimization for manganese-catalyzed ATRA reaction of iodinated allylic nitrile



1 **2** ***Z*-1**

entry	base	solvent	NMR yield	*E:Z*
1	$KHCO_3$	toluene	43%	21:79
2	K_2CO_3	toluene	40%	30:70
3	Cs_2CO_3	toluene	60%	34:66
4	PMP	toluene	-	-
5	K_3PO_4	toluene	77%	26:74
6	Et_3N	toluene	N. D.	N. D.
7	K_3PO_4	cyclohexane	39%	34:66
8	K_3PO_4	DCM	48%	31:69
9	K_3PO_4	PhCl	47%	22:78
10	K_2HPO_4	toluene	54%	34:66
11	$NaHCO_3$	toluene	49%	26:74
12	Na_3PO_4	toluene	62%	22:78
13	Na_2HPO_4	toluene	40%	34:66
14	**Na_2CO_3**	**toluene**	**78%**	**10:90**
15	-	toluen	38%	20:80

Supplementary Table 5. Reaction optimization for manganese-catalyzed ATRA reaction of iodinated allylic trifluoromethane

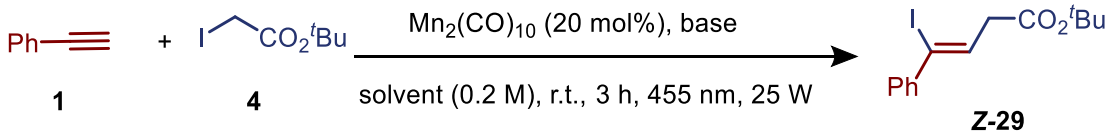


1 **3** ***Z*-13**

entry	base	NMR yield	*E:Z*
1	$KHCO_3$	45%	16:84
2	K_3PO_4	33% (*Z*)	/

3	Na_2CO_3	36% (*Z*)	/
4	**Na_3PO_4**	**73%**	**11:89**
5	$NaHCO_3$	49% (*Z*)	-
6	PMP	-	-
7	Cs_2CO_3	47% (*Z*)	-
8	K_2HPO_4	42% (*Z*)	-
9	-	27% (*Z*)	

Supplementary Table 6. Reaction optimization for manganese-catalyzed ATRA reaction of iodinated allylic *tert*-butyl carboxylate



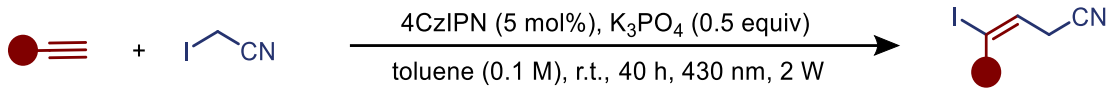
1 **4** ***Z*-29**

entry	base	solvent	NMR yield	*E:Z*
1	K_3PO_4	toluene	24% (*Z*)	-
2	Na_2CO_3	toluene	21% (*Z*)	-
3	PMP	toluene	-	-
4	Na_3PO_4	toluene	25%	26:74
5	$NaHCO_3$	toluene	21% (*Z*)	-
6	Cs_2CO_3	toluene	33%	12:88
7	K_2HPO_4	toluene	34% (*Z*)	-
8	Cs_2CO_3	cyclohexnae	-	-
9	Cs_2CO_3	MeCN	-	-
10	Cs_2CO_3	$PhCF_3$	-	-
11	Cs_2CO_3	PhCl	23% (*Z*)	-
12	$KHCO_3$	toluene	20% (*Z*)	-
13	NaOAc	toluene	10% (*Z*)	-
14	K_2CO_3	toluene	24% (*Z*)	-
15	Na_2HPO_4	toluene	21% (*Z*)	-
16[a]	**Cs_2CO_3**	**toluene**	**67%**	**12:88**
17	-	toluene	22% (*Z*)	-

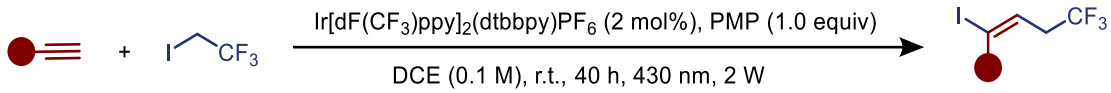
[a]1-ethynyl-4-methoxybenzene was used

5. General procedure for the synthesis of product

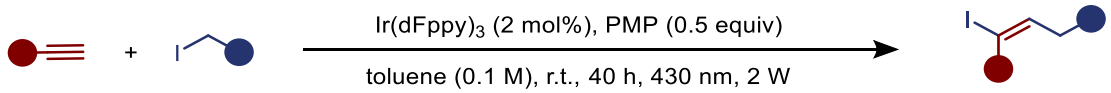
5.1 General procedure C for the synthesis of *E* isomer



A 15 mL tube was flame-dried and equipped with a magnetic stir bar. 4CzIPN (0.01 mmol, 5 mol%, 7.9 mg), K_3PO_4 (0.1 mmol, 0.5 equiv) and alkyne (0.2 mmol, 1.0 equiv) (when solid) were added into the tube which was then brought into the glove box. In the glove box, toluene (0.1 M, 2 mL), alkyne (0.2 mmol, 1.0 equiv) (when liquid) and iodoacetonitrile (0.4 mmol, 2.0 equiv) were added in order. Then the tube was carried out of the glove box and the mixture was stirred at room temperature under 430 nm irradiation for 40 h until the starting material was completely consumed. After completion, the solvent was removed and internal standard (CH_2Br_2) was added to aid in determining the NMR yield. The crude residue was purified by flash column chromatography.

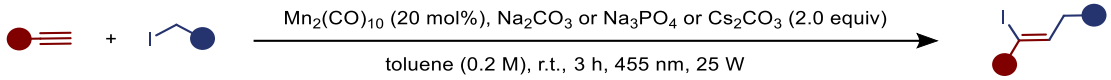


A 15 mL tube was flame-dried and equipped with a magnetic stir bar. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.004mmol, 2 mol%, 4.5 mg) and alkyne (0.2 mmol, 1.0 equiv) (when solid) were added into the tube which was then brought into the glove box. In the glove box, DCE (0.1 M, 2 mL), alkyne (0.2 mmol, 1.0 equiv) (when liquid), α-iodotrifluoromethane (0.6 mmol, 3.0 equiv) and PMP (0.2 mmol, 1.0 equiv) were added in order. Then the tube was carried out of the glove box and the mixture was stirred at room temperature under 430 nm irradiation for 40 h until the starting material was completely consumed. After completion, the solvent was removed and internal standard (CH_2Br_2) was added to aid in determining the NMR yield. The crude residue was purified by flash column chromatography.



A 15 mL tube was flame-dried and equipped with a magnetic stir bar. $Ir(dFppy)_3$ (0.004mmol, 2 mol%, 3.0 mg) and alkyne (0.2 mmol, 1.0 equiv) (when solid) were added into the tube which was then brought into the glove box. In the glove box, toluene (0.1 M, 2 mL), alkyne (0.2 mmol, 1.0 equiv) (when liquid), α-iodo ester (0.6 mmol, 3.0 equiv) and PMP (0.1 mmol, 0.5 equiv) were added in order. Then the tube was carried out of the glove box and the mixture was stirred at room temperature under 430 nm irradiation for 40 h until the starting material was completely consumed. After completion, the solvent was removed and internal standard (CH_2Br_2) was added to aid in determining the NMR yield. The crude residue was purified by flash column chromatography.

5.2 General procedure D for the synthesis of *Z* isomer

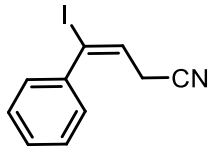


A 15 mL tube was flame-dried and equipped with a magnetic stir bar. Alkyne (0.4 mmol, 2.0 equiv) (when solid) and base (0.4 mmol, 2.0 equiv) were added into the tube which was then brought into the glove box. In the glove box, $Mn_2(CO)_{10}$ (0.04 mmol, 20 mol%, 15.6 mg), toluene (0.2 M, 1 mL), alkyne (0.4 mmol, 2.0 equiv) (when liquid), α-iodide (0.2 mmol, 1.0 equiv) were added in this order. Then the tube was carried out of the glove box and the mixture was stirred at room temperature under 455 nm irradiation for 3 h until the starting material was completely consumed. After completion, the crude mixture was filtered through a pad of celite, removed the solvent and internal standard (CH_2Br_2) was added to aid in determining the NMR yield. The crude residue was purified by flash column chromatography.

6. Characterization of the products

6.1 Characterization of the *E* isomers

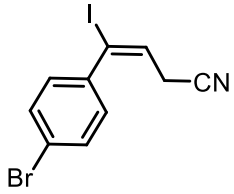
(*E*)-4-iodo-4-phenylbut-3-enenitrile (*E*-1)



Following the **general procedure C**, the product ***E*-1** was obtained in 90% NMR yield (96:4 ***E:Z***) and 82% isolated yield (97:3 ***E:Z***). The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.39 – 7.28 (m, 3H), 7.26 – 7.22 (m, 2H), 6.44 (t, *J* = 7.5 Hz, 1H), 2.96 (d, *J* = 7.5 Hz, 2H). *Z*-isomer (minor) 5.99 (t, *J* = 6.5 Hz, 1H), 3.37 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.1, 129.3, 128.9, 128.7, 128.1, 116.4, 101.9, 20.0.

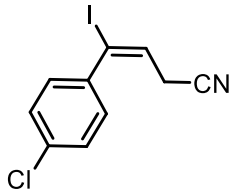
(*E*)-4-(4-bromophenyl)-4-iodobut-3-enenitrile (*E*-2)



Following the **general procedure C**, the product ***E*-2** was obtained in 66% NMR yield (95:5 ***E:Z***) and 58% isolated yield (98:2 ***E:Z***).The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.52 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.48 (t, *J* = 7.5 Hz, 1H), 2.96 (d, *J* = 7.5 Hz, 2H). *Z*-isomer (minor) 6.02 (t, *J* = 6.5 Hz, 1H), 3.37 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.0, 132.2, 129.7, 129.4, 123.5, 116.2, 100.2, 20.1.

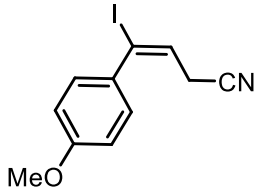
(*E*)-4-(4-chlorophenyl)-4-iodobut-3-enenitrile (*E*-3)



Following the **general procedure C**, the product ***E*-3** was obtained in 56% NMR yield (96:4 ***E:Z***) and 50% isolated yield (> 20:1 ***E:Z***). The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.36 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.47 (t, *J* = 7.5 Hz, 1H), 2.97 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.6, 135.3, 129.5, 129.4, 129.2, 116.2, 100.2, 20.1.

(*E*)-4-iodo-4-(4-methoxyphenyl)but-3-enenitrile (*E*-4)

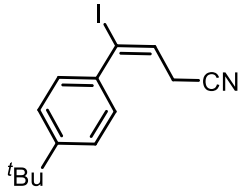


Following the **general procedure C**, the product ***E*-4** was obtained in 50% NMR yield (94:6 ***E:Z***) and 49% isolated yield (95:5 ***E:Z***). The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.22 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.41 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H), 2.99 (d, *J* = 7.5 Hz, 2H). *Z*-isomer (minor) 7.31 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.93 – 5.88 (m, 1H), 3.84 (s, 3H), 3.11 (d, *J* = 7.7 Hz, 2H). **^{13}C NMR (101**

MHz, $CDCl_3$) δ 160.1, 132.4, 129.7, 128.2, 116.6, 114.2, 102.3, 55.5, 20.1.

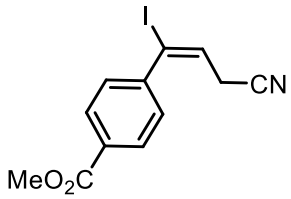
(*E*)-4-(4-(tert-butyl)phenyl)-4-iodobut-3-enenitrile (*E*-5)



Following the **general procedure C**, the product ***E*-5** was obtained in 64% NMR yield (97:3 ***E:Z***) and 58% isolated yield (98:2 ***E:Z***).The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.39 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.44 (t, *J* = 7.5 Hz, 1H), 3.01 (d, *J* = 7.6 Hz, 2H), 1.33 (s, 9H). *Z*-isomer (minor) 5.99 (t, *J* = 6.5 Hz, 1H), 3.39 (d, *J* = 6.6 Hz, 2H), 1.29 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.5, 137.1, 128.4, 128.0, 125.8, 116.6, 102.4, 34.9, 31.3, 20.1.

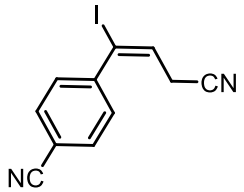
methyl (*E*)-4-(3-cyano-1-iodoprop-1-en-1-yl) benzoate (*E*-6)



Following the **general procedure C**, the product ***E*-6** was obtained in 62% NMR yield (95:5 ***E:Z***) and 51% isolated yield (98:2 ***E:Z***). The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 8.04 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.51 (t, *J* = 7.5 Hz, 1H), 3.93 (s, 3H), 2.96 (d, *J* = 7.5 Hz, 2H). *Z*-isomer (minor) 6.11 (t, *J* = 6.5 Hz, 1H), 3.40 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.2, 144.4, 130.8, 130.2, 129.7, 128.2, 116.1, 100.0, 52.5, 20.1.

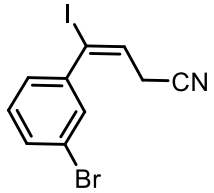
(*E*)-4-(3-cyano-1-iodoprop-1-en-1-yl) benzonitrile (*E*-7)



Following the **general procedure C**, the product ***E*-7** was obtained in 57% NMR yield (93:7 ***E:Z***) and 50% isolated yield (96:4 ***E:Z***).The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.70 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.55 (t, *J* = 7.6 Hz, 1H), 2.96 (d, *J* = 7.6 Hz, 2H). *Z*-isomer (minor) 7.65 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 6.14 (t, *J* = 6.5 Hz, 1H), 3.41 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.5, 132.8, 130.4, 129.0, 118.0, 115.8, 113.2, 98.6, 20.1.

(*E*)-4-(3-bromophenyl)-4-iodobut-3-enenitrile (*E*-8)

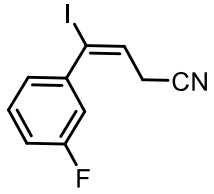


Following the **general procedure C**, the product ***E*-8** was obtained in 51% NMR yield (95:5 ***E:Z***) and 49% isolated yield (95:5 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.47 (ddd, *J* = 7.9, 2.0, 1.2 Hz, 1H), 7.41 (t, *J* = 1.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.20 (dt, *J* = 7.7, 1.4 Hz, 1H), 6.48 (t, *J* = 7.5 Hz, 1H), 2.99 (d, *J* = 7.4 Hz, 2H). *Z*-isomer (minor) 6.05 (t, *J* = 6.5 Hz, 1H), 3.39 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.9, 132.3, 130.9, 130.4, 129.7, 126.6, 122.7, 116.0, 99.1, 20.0. **EI-MS**:

calculated for [$C_{10}H_7BrNI$], 346.88011; Found 346.88017.

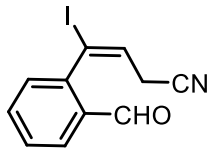
(*E*)-4-(3-fluorophenyl)-4-iodobut-3-enenitrile (*E*-9)



Following the **general procedure C**, the product ***E*-9** was obtained in 79% NMR yield (95:5 ***E:Z***) and 70% isolated yield (98:2 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.36 (td, *J* = 8.1, 5.8 Hz, 1H), 7.08 – 7.01 (m, 2H), 7.01 – 6.95 (m, 1H), 6.48 (t, *J* = 7.5 Hz, 1H), 2.99 (d, *J* = 7.5 Hz, 2H). *Z*-isomer (minor) 6.06 (t, *J* = 6.5 Hz, 0H), 3.39 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.5 (d, *J* = 248.8 Hz), 142.0 (d, *J* = 7.8 Hz), 130.6 (d, *J* = 8.5 Hz), 129.6, 123.7 (d, *J* = 3.0 Hz), 116.4 (d, *J* = 21.2 Hz), 116.2, 115.4 (d, *J* = 22.7 Hz), 99.6 (d, *J* = 2.3 Hz), 20.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.09 (td, *J* = 8.9, 5.8 Hz). **EI-MS**: calculated for [$C_{10}H_7FNI$], 286.96017; Found 286.96032.

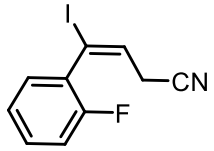
(*E*)-4-(2-formylphenyl)-4-iodobut-3-enenitrile (*E*-10)



Following the **general procedure C**, the product ***E*-10** was obtained in 51% NMR yield (75:25 ***E:Z***) and 45% isolated yield (70:30 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 10.27 (s, 1H), 7.94 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.65 (td, *J* = 7.6, 1.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 2.84 (dd, *J* = 7.4, 2.7 Hz, 2H). *Z*-isomer (minor) 7.92 – 7.88 (m, 1H), 7.62 – 7.56 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 5.89 (t, *J* = 6.5 Hz, 1H), 3.44 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 190.3, 142.4, 134.7, 133.8, 131.4, 130.1, 130.0, 129.0, 115.6, 96.0, 20.1. **ESI-MS**: calculated for $C_{11}H_{18}INONa$ [M + Na]+, 319.9543; Found 319.9547.

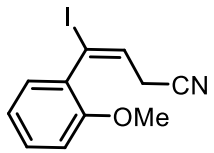
(*E*)-4-(2-fluorophenyl)-4-iodobut-3-enenitrile (*E*-11*)*



Following the general **procedure C**, the product ***E*-11** was obtained in 45% NMR yield (92:8 ***E:Z***) and 30% isolated yield (> 20:1 ***E:Z***). The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (500 MHz, $CDCl_3$) δ *E*-isomer (major) 7.39 – 7.32 (m, 1H), 7.28 (td, *J* = 7.6, 1.9 Hz, 1H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.08 (ddd, *J* = 9.5, 8.3, 1.1 Hz, 1H), 6.58 (t, *J* = 7.2 Hz, 1H), 2.93 (d, *J* = 7.3 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.8 (d, *J* = 250.0 Hz), 131.8, 131.5 (d, *J* = 8.4 Hz), 130.8 (d, *J* = 2.3 Hz), 127.5 (d, *J* = 15.4 Hz), 124.9 (d, *J* = 3.7 Hz), 116.4 (d, *J* = 21.4 Hz), 116.0, 92.0, 20.3 (d, *J* = 2.8 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -112.73 (dt, *J* = 9.9, 5.9 Hz).

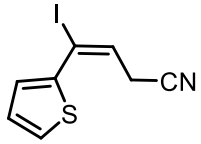
(*E*)-4-iodo-4-(2-methoxyphenyl)but-3-enenitrile (*E*-12)



Following the general **procedure C**, the product ***E*-12** was obtained in 71% NMR yield (95:5 ***E:Z***) and 63% isolated yield (97:3 ***E:Z***).The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.40 – 7.29 (m, 1H), 7.20 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.46 (t, *J* = 7.3 Hz, 1H), 3.88 (s, 3H), 2.85 (d, *J* = 7.2 Hz, 2H). *Z*-isomer (minor) 5.84 (t, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 3.37 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.1, 130.8, 130.1, 128.2, 120.9, 116.5, 111.4, 96.5, 55.6, 20.1.

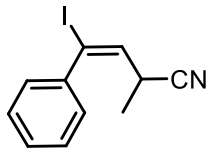
(*E*)-4-iodo-4-(thiophen-2-yl)but-3-enenitrile (*E*-13)



Following the general **procedure C**, the product ***E*-13** was obtained in 24% NMR yield (72:28 ***E:Z***) and 13% isolated yield (> 20:1 ***E:Z***). The spectroscopic properties of this compound were consistent with the data reported in the literature[9].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.45 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.17 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.48 (t, *J* = 7.4 Hz, 1H), 3.25 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.9, 129.9, 129.4, 128.0, 127.5, 116.4, 91.9, 20.6.

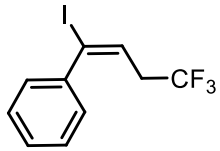
(*E*)-4-iodo-2-methyl-4-phenylbut-3-enenitrile (*E*-14)



Following the general **procedure C**, the product ***E*-14** was obtained in 17% NMR yield (95:5 ***E:Z***) and 15% isolated yield (95:5 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.44 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 6.40 (d, *J* = 9.9 Hz, 1H), 3.25 (dq, *J* = 9.9, 7.1 Hz, 1H), 1.36 (d, *J* = 7.1 Hz, 3H). *Z*-isomer (minor) δ 5.91 (d, *J* = 8.8 Hz, 1H), 1.27 (d, *J* = 11.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.5, 136.4, 129.3, 128.9, 128.0, 120.1, 100.6, 27.7, 18.8. **EI-MS**: calculated for [$C_{11}H_{10}NI$], 282.98524; Found 282.98558.

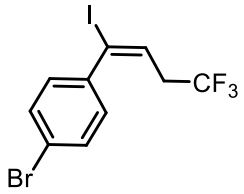
(*E*)-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-15)



Following the general **procedure C**, the product ***E*-15** was obtained in 70% NMR yield (93:7 ***E:Z***) and 61% isolated yield (92:8 ***E:Z***). The spectroscopic properties of this compound were consistent with the data reported in the literature[10].

^{1}H NMR (500 MHz, $CDCl_3$) δ *E*-isomer (major) 7.38 – 7.34 (m, 2H), 7.33 – 7.30 (m, 1H), 7.29 – 7.27 (m, 2H), 6.49 (t, *J* = 7.6 Hz, 1H), 2.74 (qd, *J* = 10.5, 7.6 Hz, 2H). *Z*-isomer (minor) 7.54 (d, *J* = 8.7 Hz, 1H), 7.47 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.13 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.98 (t, *J* = 6.6 Hz, 1H), 3.17 (qd, *J* = 10.7, 6.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.9, 130.1 (q, *J* = 3.4 Hz), 128.9, 128.7, 128.3, 125.0 (q, *J* = 277.0 Hz), 102.0, 36.5 (q, *J* = 30.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.22 (t, *J* = 10.8 Hz). *E*-isomer (major) -65.76 (t, *J* = 10.5 Hz).

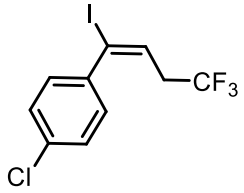
(*E*)-1-bromo-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-16)



Following the general **procedure C**, the product ***E*-16** was obtained in 70% NMR yield (91:9 ***E:Z***) and 64% isolated yield (93:7 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.50 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.50 (t, *J* = 7.6 Hz, 1H), 2.72 (qd, *J* = 10.4, 7.6 Hz, 2H). *Z*-isomer (minor) 7.46 (dd, *J* = 8.6, 2.3 Hz, 2H), 7.32 (dd, *J* = 10.2, 8.5 Hz, 2H), 5.98 (t, *J* = 6.6 Hz, 1H), 3.15 (qd, *J* = 10.6, 7.1 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.8, 132.0, 130.8 (q, *J* = 3.7 Hz), 129.9, 124.8 (q, *J* = 277.0 Hz), 123.1, 36.5 (q, *J* = 30.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.15 (t, *J* = 10.8 Hz). *E*-isomer (major) -65.67 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{10}H_7BrF_3I$], 389.87224; Found 389.87230.

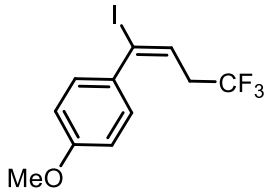
(*E*)-1-chloro-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene *(E*-17)



Following the general **procedure C**, the product ***E*-17** was obtained in 60% NMR yield (93:7 ***E:Z***) and 56% isolated yield (93:7 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major): 7.34 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.50 (t, *J* = 7.6 Hz, 1H), 2.72 (qd, *J* = 10.4, 7.6 Hz, 2H). *Z*-isomer (minor) 7.43 – 7.36 (m, 2H), 7.30 (dd, *J* = 8.6, 3.1 Hz, 2H), 5.97 (t, *J* = 6.6 Hz, 1H), 3.32 – 3.08 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.3, 134.9, 130.8 (q, *J* = 3.7 Hz), 129.6, 129.0, 124.9 (q, *J* = 277.0 Hz), 100.3, 36.5 (q, *J* = 30.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.17 (t, *J* = 10.8 Hz). *E*-isomer (major) -65.69 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{10}H_7ClF_3I$], 345.92276; Found 345.92265.

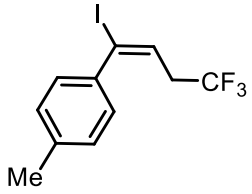
(*E*)-1-methoxy-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-18)



Following the general **procedure C**, the product ***E*-18** was obtained in 62% NMR yield (91:9 ***E:Z***) and 59% isolated yield (92:8 ***E:Z***).The spectroscopic properties of this compound were consistent with the data reported in the literature[10].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.21 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.44 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 2.75 (qd, *J* = 10.5, 7.5 Hz, 2H). *Z*-isomer (minor) 7.41 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 2H), 5.88 (t, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 3.15 (qd, *J* = 10.7, 6.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.8, 133.3, 129.8, 129.7 (q, *J* = 3.5 Hz), 125.0 (q, *J* = 277.3 Hz), 114.0, 102.4, 55.5, 36.4 (q, *J* = 30.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.26 (t, *J* = 10.6 Hz). *E*-isomer (major) -65.75 (t, *J* = 10.5 Hz).

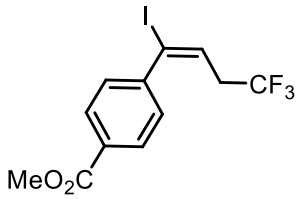
(*E*)-1-methyl-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-19*)*



Following the general **procedure C**, the product ***E*-19** was obtained in 63% NMR yield (93:7 ***E:Z***) and 55% isolated yield (93:7 ***E:Z***). The spectroscopic properties of this compound were consistent with the data reported in the literature[10].

^{1}H NMR (500 MHz, $CDCl_3$) δ *E*-isomer (major):7.16 (s, 4H), 6.46 (t, *J* = 7.6 Hz, 1H), 2.75 (qd, *J* = 10.5, 7.6 Hz, 2H), 2.36 (s, 3H). *Z*-isomer (minor) 7.41 – 7.31 (m, 4H), 5.94 (t, *J* = 6.6 Hz, 1H), 3.16 (qd, *J* = 10.7, 6.6 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.0, 138.1, 129.8 (q, *J* = 3.7 Hz), 129.4, 128.2, 125.0 (q, *J* = 277.2 Hz), 102.4, 36.4 (q, *J* = 30.1 Hz), 21.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.24 (t, *J* = 10.6 Hz). *E*-isomer (major) -65.77 (t, *J* = 10.5 Hz).

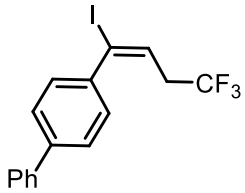
methyl (*E*)-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzoate (*E*-20)



Following the general **procedure C**, the product ***E*-20** was obtained in 31% NMR yield (88:12 ***E:Z***) and 20% isolated yield (89:11 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 8.03 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.53 (t, *J* = 7.6 Hz, 1H), 3.93 (s, 3H), 2.71 (qd, *J* = 10.4, 7.6 Hz, 2H). *Z*-isomer (minor) 7.99 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 6.07 (t, *J* = 6.6 Hz, 1H), 3.92 (s, 3H), 3.37 – 3.14 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 145.2, 131.9, 130.9 (q, *J* = 3.3 Hz), 130.0, 128.3, 124.8 (q, *J* = 276.6 Hz), 100.1, 52.5, 36.5 (q, *J* = 30.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.11 (t, *J* = 10.6 Hz). *E*-isomer (major) -65.71 (t, *J* = 10.3 Hz). **EI-MS**: calculated for [$C_{12}H_{10}O_2F_3I$], 369.96721; Found 369.96689.

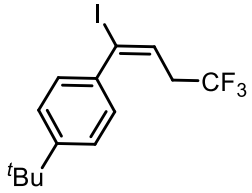
(*E*)-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl)-1,1'-biphenyl (*E*-21)



Following the **general procedure C**, the product ***E*-21** was obtained in 27% NMR yield (77:23 ***E:Z***) and 20% isolated yield (78:22 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.62 – 7.56 (m, 5H), 7.50 – 7.45 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.52 (t, *J* = 7.5 Hz, 1H), 2.81 (qd, *J* = 10.5, 7.5 Hz, 2H). *Z*-isomer (minor) 7.55 (s, 5H), 7.44 (s, 2H), 7.39 (dd, *J* = 7.9, 1.8 Hz, 2H), 6.04 (t, *J* = 6.6 Hz, 1H), 3.20 (qd, *J* = 10.6, 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.8, 140.2, 139.7, 130.2 (q, *J* = 3.5 Hz), 129.0, 128.8, 127.9, 127.4, 127.2, 125.0 (q, *J* = 277.2 Hz), 101.8, 36.6 (q, *J* = 30.5 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.15 (t, *J* = 10.6 Hz). *E*-isomer (major) -65.65 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{16}H_{12}F_3I$], 387.99303; Found 387.99327.

(*E*)-1-(tert-butyl)-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-22)

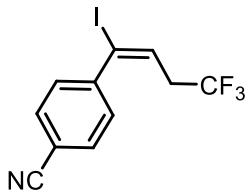


Following the **general procedure C**, the product ***E*-22** was obtained in 66% NMR yield (93:7 ***E:Z***) and 61% isolated yield (90:10 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.37 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.47 (t, *J* = 7.5 Hz, 1H), 2.78 (qd, *J* = 10.6, 7.5 Hz, 2H), 1.33 (s, 9H). *Z*-isomer (minor) 7.43 – 7.39 (m, 2H), 7.33 (d, *J* = 2.5 Hz, 2H), 5.96 (t, *J* = 6.6 Hz, 1H), 3.17 (qd, *J* = 10.7, 6.6 Hz, 2H), 1.35 (s, 9H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 152.1, 137.8, 129.7 (q, *J* = 3.5 Hz), 128.1, 125.6, 125.1 (q, *J* = 277.3 Hz), 102.5, 36.5 (q, *J* = 30.1 Hz), 34.9, 31.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.24 (t, *J* = 10.6 Hz). *E*-isomer (major) -65.71 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{14}H_{16}F_3I$], 368.02433; Found 368.02412.

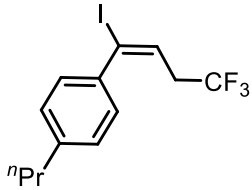
(*E*)-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzonitrile (*E*-23)



Following the general **procedure C**, the product ***E*-23** was obtained in 30% NMR yield (83:17 ***E:Z***) and 28% isolated yield (86:14 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.67 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.56 (t, *J* = 7.7 Hz, 1H), 2.70 (qd, *J* = 10.3, 7.7 Hz, 2H). *Z*-isomer (minor) 7.63 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 6.09 (t, *J* = 6.6 Hz, 1H), 3.18 (qd, *J* = 10.6, 6.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.3, 132.6, 131.7 (q, *J* = 3.3 Hz), 129.1, 125.0 (q, *J* = 277.3 Hz), 118.2, 112.8, 98.7, 36.6 (q, *J* = 30.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.06. *E*-isomer (major) -65.61. **EI-MS**: calculated for [$C_{11}H_7NF_3I$], 336.95698; Found 336.95680.

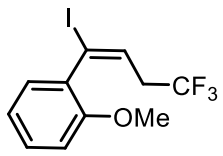
(*E*)-1-propyl-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-24)



Following the general **procedure C**, the product ***E*-24** was obtained in 43% NMR yield (98:2 ***E:Z***) and 48% isolated yield (93:7 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.21 – 7.10 (m, 4H), 6.46 (t, *J* = 7.5 Hz, 1H), 2.76 (qd, *J* = 10.5, 7.5 Hz, 2H), 2.61 – 2.55 (m, 2H), 1.73 – 1.52 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). *Z*-isomer (minor) 7.44 – 7.33 (m, 4H), 5.95 (t, *J* = 6.6 Hz, 1H), 3.16 (qd, *J* = 10.7, 6.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.7, 138.2, 129.7 (q, *J* = 3.2 Hz), 128.7, 128.2, 125.1 (q, *J* = 277.2 Hz), 102.5, 37.9, 36.5 (q, *J* = 30.1 Hz), 24.4, 14.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.24 (t, *J* = 10.7 Hz). *E*-isomer (major) -65.75 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{13}H_{14}F_3I$], 354.00868; Found 354.00865.

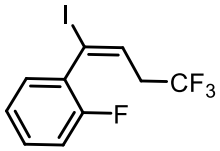
(*E*)-1-methoxy-2-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-25)



Following the general **procedure C**, the product ***E*-25** was obtained in 61% NMR yield (89:11 ***E:Z***) and 52% isolated yield (91:9 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.36 – 7.27 (m, 1H), 7.16 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.00 – 6.92 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.50 (t, *J* = 7.3 Hz, 1H), 3.87 (s, 3H), 2.63 (qd, *J* = 10.7, 7.3 Hz, 2H). *Z*-isomer (minor) 5.81 (t, *J* = 6.5 Hz, 1H), 3.84 (s, 3H), 3.15 (qd, *J* = 10.7, 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.6, 131.4 (q, *J* = 3.3 Hz), 130.5, 129.8, 125.1 (q, *J* = 277.2 Hz), 120.8, 111.5, 96.9, 55.7, 36.6 (q, *J* = 30.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.22 (t, *J* = 10.8 Hz). *E*-isomer (major) -65.70 (t, *J* = 10.8 Hz). **EI-MS**: calculated for [$C_{11}H_{10}OF_3I$], 341.97229; Found 341.97293.

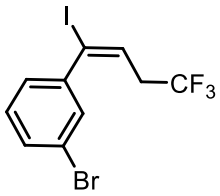
(*E*)-1-fluoro-2-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-26)



Following the general **procedure C**, the product ***E*-26** was obtained in 54% NMR yield (91:9 ***E:Z***) and 52% isolated yield (92:8 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.33 (dddd, *J* = 8.2, 7.1, 5.2, 1.9 Hz, 1H), 7.23 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.17 (td, *J* = 7.5, 1.1 Hz, 1H), 7.07 (ddd, *J* = 9.5, 8.3, 1.1 Hz, 1H), 6.60 (t, *J* = 7.4 Hz, 1H), 2.68 (qd, *J* = 10.5, 7.3 Hz, 2H). *Z*-isomer (minor) 5.97 (t, *J* = 6.6 Hz, 1H), 3.16 (qd, *J* = 10.6, 6.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1 (d, *J* = 249.8 Hz), 133.1 (q, *J* = 3.6 Hz), 131.1 (d, *J* = 8.1 Hz), 130.6 (d, *J* = 2.4 Hz), 128.3 (d, *J* = 15.3 Hz), 124.9 (q, *J* = 276.9 Hz), 124.6 (d, *J* = 3.8 Hz), 116.3 (d, *J* = 21.5 Hz), 92.2, 36.7 (q, *J* = 30.7 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.17 (t, *J* = 10.7 Hz), -113.8 (ddd, *J* = 10.2, 7.4, 5.2 Hz). *E*-isomer (major) -65.66 – -65.80 (m), -112.8 – -113.0 (m). **EI-MS**: calculated for [$C_{10}H_7F_4I$], 329.95231; Found 329.95274.

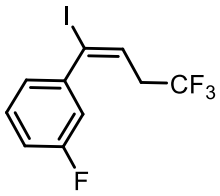
(*E*)-1-bromo-3-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-27)



Following the general **procedure C**, the product ***E*-27** was obtained in 52% NMR yield (93:7 ***E:Z***) and 48% isolated yield (94:6 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.25 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.21 (t, *J* = 1.9 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.30 (t, *J* = 7.6 Hz, 1H), 2.53 (qd, *J* = 10.4, 7.6 Hz, 2H). *Z*-isomer (minor) 7.30 – 7.28 (m, 1H), 7.17 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.02 (s, 1H), 7.01 (s, 1H), 5.80 (t, *J* = 6.5 Hz, 1H), 2.95 (qd, *J* = 10.6, 6.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.6, 134.6, 131.9, 131.0 (q, *J* = 3.5 Hz), 130.2, 126.7, 124.7 (q, *J* = 277.0 Hz), 122.5, 99.2, 36.4 (q, *J* = 30.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.10 (t, *J* = 10.6 Hz). *E*-isomer (major) -65.65 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{10}H_7BrF_3I$], 389.87224; Found 389.87234.

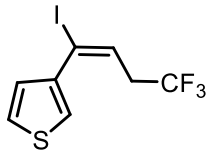
(*E*)-1-fluoro-3-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*E*-28)



Following the general **procedure C**, the product ***E*-28** was obtained in 62% NMR yield (93:7 ***E:Z***) and 58% isolated yield (93:7 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.34 (td, *J* = 8.0, 5.8 Hz, 1H), 7.08 – 7.00 (m, 2H), 7.00 – 6.93 (m, 1H), 6.50 (t, *J* = 7.6 Hz, 1H), 2.74 (qd, *J* = 10.4, 7.6 Hz, 2H). *Z*-isomer (minor) 6.03 (t, *J* = 6.6 Hz, 1H), 3.16 (qd, *J* = 10.6, 6.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.3 (d, *J* = 248.2 Hz), 142.7 (d, *J* = 8.0 Hz), 130.8 (q, *J* = 3.0 Hz), 130.3 (d, *J* = 8.4 Hz), 124.9 (q, *J* = 277.1 Hz), 123.8 (d, *J* = 3.1 Hz), 115.9 (d, *J* = 21.0 Hz), 115.4 (d, *J* = 22.6 Hz), 99.6, 36.4 (q, *J* = 30.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -65.15 (t, *J* = 10.8 Hz). *E*-isomer (major) -65.68 (t, *J* = 10.5 Hz), -111.67 (td, *J* = 8.8, 5.8 Hz). **EI-MS**: calculated for [$C_{10}H_7F_4I$], 329.95231; Found 329.95277.

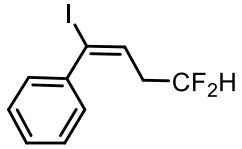
(*E*)-3-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) thiophene (*E*-29)



Following the general **procedure C**, the product ***E*-29** was obtained in 59% NMR yield (82:18 ***E:Z***) and 55% isolated yield (83:17 ***E:Z***).The spectroscopic properties of this compound were consistent with the data reported in the literature[10].

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.34 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.27 (d, *J* = 1.3 Hz, 1H), 7.08 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.47 (t, *J* = 7.6 Hz, 1H), 2.86 (qd, *J* = 10.5, 7.6 Hz, 2H). *Z*-isomer (minor) 7.45 (dd, *J* = 3.1, 1.4 Hz, 1H), 7.37 (dd, *J* = 5.1, 3.1 Hz, 1H), 6.10 (t, *J* = 6.7 Hz, 1H), 3.16 (qd, *J* = 10.6, 6.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.7, 130.5 (q, *J* = 3.5 Hz), 128.5, 126.2, 125.0 (q, *J* = 277.1 Hz), 124.4, 95.5, 36.8 (q, *J* = 30.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -65.13 – -65.24 (m), -65.62 (t, *J* = 10.5 Hz).

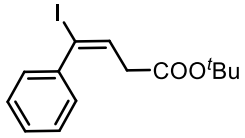
(*E*)-(4,4-difluoro-1-iodobut-1-en-1-yl) benzene (*E*-30)



Following the general **procedure C**, the product ***E*-30** was obtained in 56% NMR yield (85:15 ***E:Z***) and 52% isolated yield (90:10 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.40 – 7.27 (m, 5H), 6.50 (t, *J* = 7.6 Hz, 1H), 5.77 (tt, *J* = 56.3, 4.2 Hz, 1H), 2.52 (tdd, *J* = 17.3, 7.6, 4.2 Hz, 2H). *Z*-isomer (minor) 7.51 – 7.41 (m, 5H), 5.99 (t, *J* = 5.6 Hz, 1H), 3.07 – 2.83 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 132.1 (t, *J* = 6.4 Hz), 128.6, 128.5, 128.3, 114.9 (t, *J* = 241.3 Hz), 100.3, 36.7 (t, *J* = 22.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (minor) -115.21 (dt, *J* = 56.3, 17.3 Hz). *E*-isomer (major) -115.93 (dt, *J* = 56.4, 17.4 Hz). **EI-MS**: calculated for [$C_{10}H_9F_2I$], 293.97115; Found 293.97148.

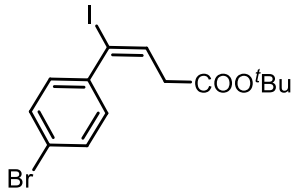
***tert*-butyl (*E*)-4-iodo-4-phenylbut-3-enoate (*E*-31)**



Following the general **procedure C**, the product ***E*-31** was obtained in 66% NMR yield (91:9 ***E:Z***) and 58% isolated yield (92:8 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.25 – 7.16 (m, 5H), 6.55 (t, *J* = 7.5 Hz, 1H), 2.83 (dd, *J* = 7.5, 2H), 1.36 (s, 9H). *Z*-isomer (minor) 7.40 – 7.36 (m, 5H), 6.12 (t, *J* = 6.4 Hz, 1H), 3.20 (d, *J* = 6.3 Hz, 2H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.4, 141.3, 134.8, 128.7, 128.5, 128.4, 97.9, 81.4, 38.4, 28.2. **ESI-MS**: calculated for $C_{14}H_{17}IO_2Na$ $[M + Na]^+$, 367.0165; Found 367.0171.

***tert*-butyl (*E*)-4-(4-bromophenyl)-4-iodobut-3-enoate (*E*-32)**

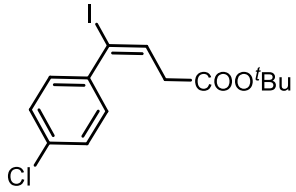


Following the **general procedure C**, the product ***E*-32** was obtained in 64% NMR yield (89:11 ***E:Z***) and 59% isolated yield (88:12 ***E:Z***).

^{1}H NMR (500 MHz, $CDCl_3$) δ *E*-isomer (major) 7.46 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.64 (t, *J* = 7.6 Hz, 1H), 2.88 (d, *J* = 7.5 Hz, 2H), 1.44 (s, 9H). *Z*-isomer (minor) 7.43 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.21 (t, *J* = 6.3 Hz, 1H), 3.26 (d, *J* = 6.4 Hz, 2H), 1.48 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.2, 140.3, 135.5, 131.0, 122.6, 96.2, 81.6, 38.5, 28.2. **ESI-MS**: calculated for

$C_{14}H_{16}BrIO_2Na$ [M + Na]$^+$, 444.9271; Found 444.9264.

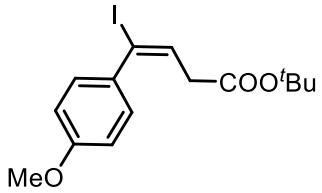
***tert*-butyl (*E*)-4-(4-chlorophenyl)-4-iodobut-3-enoate (*E*-33)**



Following the general **procedure C**, the product ***E*-33** was obtained in 59% NMR yield (90:10 ***E:Z***) and 50% isolated yield (89:11 ***E:Z***).

^{1}H NMR (500 MHz, $CDCl_3$) δ *E*-isomer (major) 7.30 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.64 (t, *J* = 7.7 Hz, 1H), 2.88 (d, *J* = 7.6 Hz, 2H), 1.4 (s, 9H). *Z*-isomer (minor) 7.41 (d, *J* = 8.6 Hz, 2H), 7.28 (s, 2H),6.20 (t, *J* = 6.3 Hz, 1H), 3.27 (d, *J* = 6.4 Hz, 2H), 1.46 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.2, 139.8, 135.5, 130.1, 128.7, 96.2, 81.5, 38.5, 28.2. **ESI-MS**: calculated for $C_{14}H_{16}ClIO_2Na$ [M + Na]$^+$, 400.9776; Found 400.9768.

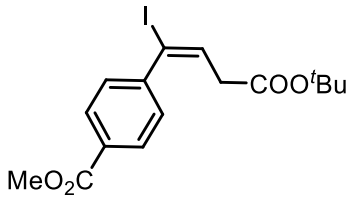
***tert*-butyl (*E*)-4-(4-methoxyphenyl)-4-iodobut-3-enoate (*E*-34)**



*F*ollowing the general **procedure C**, the product ***E*-34** was obtained in 61% NMR yield (89:11 ***E:Z***) and 52% isolated yield (85:15 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.24 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.6 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 2.91 (d, *J* = 7.5 Hz, 2H), 1.44 (s, 9H). *Z*-isomer (minor) 7.42 (d, *J* = 8.8 Hz, 2H), 6.81 (s, 2H), 6.59 (t, *J* = 7.5 Hz, 1H), 6.10 (t, *J* = 6.4 Hz, 1H), 3.26 (d, *J* = 6.3 Hz, 2H), 1.48 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.6, 159.5, 134.3, 130.2, 113.7, 98.4, 81.3, 55.5, 38.5, 28.2. **ESI-MS**: calculated for $C_{15}H_{19}IO_3Na$ [M + Na]$^+$, 397.0271; Found 397.0270.

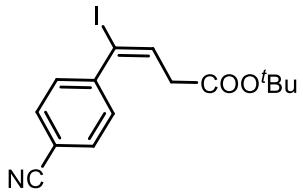
methyl (*E*)-4-(4-(*tert*-butoxy)-1-iodo-4-oxobut-1-en-1-yl) benzoate (*E*-35)



Following the general **procedure C**, the product ***E*-35** was obtained in 62% NMR yield (85:15 ***E:Z***) and 55% isolated yield (89:11 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 8.00 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 6.68 (t, *J* = 7.6 Hz, 1H), 3.92 (s, 3H), 2.88 (d, *J* = 7.7 Hz, 2H), 1.43 (s, 9H). *Z*-isomer (minor) 7.96 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 6.33 (t, *J* = 6.3 Hz, 1H), 3.29 (d, *J* = 6.4 Hz, 2H), 1.49 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.1, 166.6, 145.7, 135.8, 130.1, 129.8, 128.8, 96.1, 81.6, 52.4, 38.5, 28.2. **ESI-MS**: calculated for $C_{16}H_{19}IO_4Na$ [M + Na]$^+$, 425.0220; Found 425.0222.

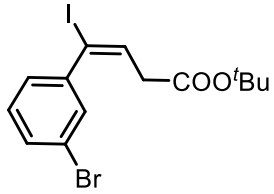
***tert*-butyl (*E*)-4-(4-cyanophenyl)-4-iodobut-3-enoate (*E*-36)**



Following the general **procedure C**, the product ***E*-36** was obtained in 50% NMR yield (80:20 ***E:Z***) and 34% isolated yield (93:7 ***E:Z***).

^{1}H NMR (400 MHz, CDCl$_3$) δ *E*-isomer (major) 7.66 – 7.60 (m, 2H), 7.44 – 7.38 (m, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 2.86 (d, *J* = 7.7 Hz, 2H), 1.44 (s, 9H). *Z*-isomer (minor) 7.59 (d, *J* = 3.9 Hz, 2H), 7.53 – 7.47 (m, 2H), 6.35 (t, 1H), 3.29 (d, *J* = 6.3 Hz, 2H), 1.48 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 168.7, 145.6, 136.4, 132.2, 129.4, 118.3, 112.2, 94.5, 81.7, 38.4, 28.0. **ESI-MS**: calculated for $C_{15}H_{16}NIO_2Na$ $[M + Na]^+$, 392.0118; Found 392.0134.

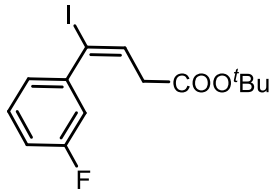
***tert*-butyl (*E*)-4-(3-bromophenyl)-4-iodobut-3-enoate (*E*-37)**



Following the general **procedure C**, the product ***E*-37** was obtained in 53% NMR yield (91:9 ***E:Z***) and 49% isolated yield (92:8 ***E:Z***).

^{1}H NMR (400 MHz, CDCl$_3$) δ *E*-isomer (major) 7.45 – 7.43 (m, 1H), 7.41 (dt, *J* = 6.6, 2.2 Hz, 1H), 7.22 – 7.19 (m, 2H), 6.65 (t, *J* = 7.6 Hz, 1H), 2.89 (d, *J* = 7.6 Hz, 2H), 1.45 (s, 9H). *Z*-isomer (minor) 7.62 (t, *J* = 1.9 Hz, 1H), 7.23 (d, *J* = 1.6 Hz, 1H), 7.19 – 7.17 (m, 1H), 6.24 (t, *J* = 6.3 Hz, 1H), 3.27 (d, *J* = 6.3 Hz, 2H), 1.49 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.0, 143.1, 135.7, 131.5, 131.4, 129.9, 127.3, 122.1, 95.3, 81.5, 38.4, 28.1. **ESI-MS**: calculated for $C_{14}H_{26}BrIO_2Na$ $[M + Na]^+$, 444.9271; Found 444.9268.

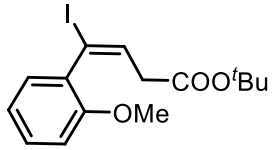
***tert*-butyl (*E*)-4-(3-fluorophenyl)-4-iodobut-3-enoate (*E*-38)**



Following the general **procedure C**, the product ***E*-38** was obtained in 70% NMR yield (88:12 ***E:Z***) and 68% isolated yield (90:10 ***E:Z***).

^{1}H NMR (400 MHz, CDCl$_3$) δ *E*-isomer (major) 7.34 – 7.27 (m, 1H), 7.09 – 7.04 (m, 1H), 7.03 – 6.94 (m, 2H), 6.65 (t, *J* = 7.6 Hz, 1H), 2.90 (d, *J* = 7.6 Hz, 2H), 1.44 (s, 9H). *Z*-isomer (minor) 6.26 (t, *J* = 6.4 Hz, 1H), 3.28 (d, *J* = 6.4 Hz, 2H), 1.46 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 169.2, 162.3 (d, *J* = 247.5 Hz), 143.3 (d, *J* = 8.0 Hz), 135.6, 130.0 (d, *J* = 8.5 Hz), 124.5 (d, *J* = 3.0 Hz), 115.9 (d, *J* = 22.3 Hz), 115.6 (d, *J* = 21.0 Hz), 95.7 (d, *J* = 2.4 Hz), 81.6, 38.5, 28.2. **^{19}F NMR (376 MHz, CDCl$_3$)** δ *E*-isomer (major) -112.40 (td, *J* = 9.1, 5.8 Hz). *Z*-isomer (minor) -113.22 – -113.37 (m). **ESI-MS**: calculated for $C_{14}H_{16}FIO_2Na$ $[M + Na]^+$, 385.0071; Found 385.0070.

***tert*-butyl (*E*)-4-iodo-4-(2-methoxyphenyl) but-3-enoate (*E*-39)**

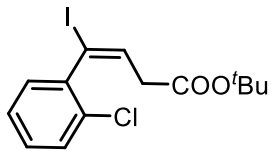


Following the general **procedure C**, the product ***E*-39** was obtained in 63% NMR yield (84:16 ***E:Z***) and 52% isolated yield (85:15 ***E:Z***).

^{1}H NMR (400 MHz, CDCl$_3$) δ *E*-isomer (major) 7.31 – 7.27 (m, 1H), 7.18 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.66 (t, *J* = 7.3 Hz, 1H),

3.86 (s, 3H), 2.78 (d, J = 7.3 Hz, 2H), 1.43 (s, 9H). *Z*-isomer (minor) 5.99 (t, J = 6.3 Hz, 1H), 3.26 (d, J = 6.4 Hz, 2H), 1.48 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 169.5, 155.7, 136.2, 130.3, 130.1, 120.6, 111.4, 92.5, 81.1, 55.7, 38.4, 28.2. **ESI-MS**: calculated for $C_{15}H_{19}IO_3Na$ $[M + Na]^+$, 397. 0271; Found 397.0271.

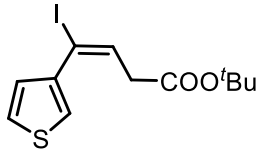
***tert*-butyl (*E*)-4-(2-chlorophenyl)-4-iodobut-3-enoate (*E*-40)**



Following the general **procedure C**, the product ***E*-40** was obtained in 71% NMR yield (61:39 ***E:Z***) and 58% isolated yield (63:47 ***E:Z***).

^{1}H NMR (400 MHz, CDCl$_3$) δ *E*-isomer (major) 7.46 (m, 1H), 7.40 – 7.30 (m, 3H), 6.82 (dd, J = 7.9, 6.7 Hz, 1H), 2.97 – 2.70 (m, 2H), 1.53 (s, 9H). *Z*-isomer (minor) 7.46 (m, 1H), 7.40 – 7.30 (m, 3H), 6.10 (t, J = 6.4 Hz, 1H), 3.37 (d, J = 6.4 Hz, 2H), 1.59 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 168.9, 137.0, 134.4, 132.1, 130.1, 130.0, 129.7, 127.0, 100.3, 81.3, 38.2, 28.0. **ESI-MS**: calculated for $C_{14}H_{16}ClIO_2Na$ $[M + Na]^+$, 400.9776; Found 400.9774.

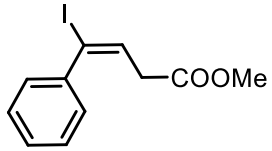
***tert*-butyl (*E*)-4-iodo-4-(thiophen-3-yl) but-3-enoate (*E*-41)**



Following the general **procedure C**, the product ***E*-41** was obtained in 51% NMR yield (74:26 ***E:Z***) and 48% isolated yield (76:24 ***E:Z***).

^{1}H NMR (400 MHz, CDCl$_3$) δ *E*-isomer (major) 7.35 – 7.27 (m, 3H), 6.61 (t, J = 7.6 Hz, 1H), 3.03 (d, J = 7.6 Hz, 2H), 1.46 (s, 9H). *Z*-isomer (minor) 7.40 (dd, J = 3.1, 1.4 Hz, 1H), 7.12 (dd, J = 5.0, 1.4 Hz, 2H), 6.33 (t, J = 6.4 Hz, 1H), 3.28 (d, J = 6.4 Hz, 2H), 1.48 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 169.5, 141.2, 135.0, 129.0, 125.5, 124.5, 91.7, 81.5, 38.9, 28.2. **ESI-MS**: calculated for $C_{12}H_{15}SIO_2Na$ $[M + Na]^+$, 372.9730; Found 372.9734.

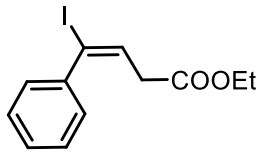
methyl (*E*)-4-iodo-4-phenylbut-3-enoate (*E*-42)



Following the general **procedure C**, the product ***E*-42** was obtained in 68% NMR yield (92:8 ***E:Z***) and 59% isolated yield (92:8 ***E:Z***).

^{1}H NMR (500 MHz, CDCl$_3$) δ *E*-isomer (major) 7.30 (dd, J = 8.1, 6.7 Hz, 3H), 7.25 – 7.21 (m, 2H), 6.62 (t, J = 7.5 Hz, 1H), 3.66 (s, 3H), 2.98 (d, J = 7.5 Hz, 2H). *Z*-isomer (minor) 7.47 – 7.42 (m, 2H), 7.18 – 7.06 (m, 3H), 6.19 (t, J = 6.4 Hz, 1H), 3.72 (s, 3H), 3.36 (d, J = 6.4 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 170.6, 141.1, 133.9, 128.6, 98.6, 52.2, 37.0. **ESI-MS**: calculated for $C_{11}H_{11}IO_2Na$ $[M + Na]^+$, 324.9696; Found 324.9694.

ethyl (*E*)-4-iodo-4-phenylbut-3-enoate (*E*-43)

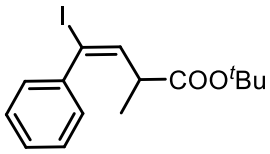


Following the general **procedure C**, the product ***E*-43** was obtained in 61% NMR yield (91:9 ***E:Z***) and 59% isolated yield (91:9 ***E:Z***).

^{1}H NMR (400 MHz, CDCl$_3$) δ *E*-isomer (major) 7.37 – 7.27 (m, 5H), 6.65 (t, J = 7.5 Hz, 1H), 4.14 (q,

J = 7.1 Hz, 2H), 2.99 (d, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). *Z*-isomer (minor) 7.55 – 7.44 (m, 5H), 6.23 (t, *J* = 6.4 Hz, 1H), 4.20 (q, *J* = 7.7 Hz, 2H), 3.37 (d, *J* = 6.4 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.2, 141.2, 134.1, 128.7, 128.6, 128.5, 98.4, 61.1, 37.3, 14.3. **ESI-MS**: calculated for $C_{12}H_{13}IO_2Na$ $[M + Na]^+$, 338.9852; Found 338.9857.

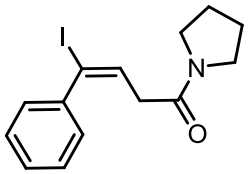
tert-butyl(*E*)-4-iodo-2-methyl-4-phenylbut-3-enoate (*E*-44)



Following the general **procedure C**, the product ***E*-44** was obtained in 10% NMR yield (82:18 ***E:Z***) and 14% isolated yield (80:20 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.35 – 7.28 (m, 5H), 6.48 (d, *J* = 10.4 Hz, 1H), 3.02 (dq, *J* = 10.3, 7.0 Hz, 1H), 1.45 (s, 9H), 1.16 (d, *J* = 7.0 Hz, 3H). *Z*-isomer (minor) 7.56 – 7.41 (m, 5H), 6.01 (d, *J* = 8.7 Hz, 1H), 3.48 – 3.38 (m, 1H), 1.48 (s, 9H), 1.33 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.6, 141.7, 128.6, 128.4, 128.4, 96.8, 81.1, 43.6, 28.2, 17.8. **ESI-MS**: calculated for $C_{15}H_{19}IO_2Na$ $[M + Na]^+$, 381.0322; Found 381.0324.

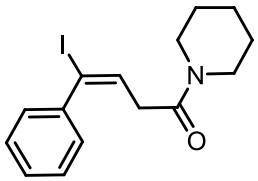
(*E*)-4-iodo-4-phenyl-1-(pyrrolidin-1-yl) but-3-en-1-one (*E*-45)



Following the general **procedure C**, the product ***E*-45** was obtained in 58% NMR yield (95:5 ***E:Z***) and 51% isolated yield (92:8 ***E:Z***).

^{1}H NMR (500 MHz, $CDCl_3$) δ *E*-isomer (major) 7.29 – 7.24 (m, 4H), 7.24 – 7.21 (m, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 3.37 (t, *J* = 6.8 Hz, 2H), 3.10 (t, *J* = 6.7 Hz, 2H), 2.92 (d, *J* = 7.3 Hz, 2H), 1.87 – 1.70 (m, 4H). *Z*-isomer (minor) 7.46 – 7.40 (m, 1H), 7.20 (m, *J* = 2.7 Hz, 1H), 6.31 (t, *J* = 6.1 Hz, 1H), 3.46 (dt, *J* = 14.3, 6.9 Hz, 4H), 3.28 (d, *J* = 6.2 Hz, 2H), 1.96 – 1.89 (m, 4H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.9, 141.6, 135.6, 128.7, 128.4, 97.2, 46.6, 46.0, 37.8, 26.1, 24.4. **ESI-MS**: calculated for $C_{14}H_{16}INONa$ $[M + Na]^+$, 364.0169; Found 364.0173.

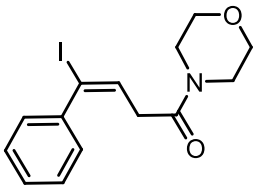
(*E*)-4-iodo-4-phenyl-1-(piperidin-1-yl)but-3-en-1-one (*E*-46)



Following the general **procedure C**, the product ***E*-46** was obtained in 64% NMR yield (93:7 ***E:Z***) and 60% isolated yield (91:9 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.29 (dt, *J* = 6.9, 1.3 Hz, 2H), 7.24 – 7.18 (m, 3H), 6.64 (t, *J* = 7.3 Hz, 1H), 3.45 (s, 2H), 3.09 (s, 2H), 2.98 (d, *J* = 7.3 Hz, 2H), 1.54 (td, *J* = 6.6, 3.4 Hz, 2H), 1.47 – 1.37 (m, 4H). *Z*-isomer (minor) 7.45 – 7.40 (m, 2H), 6.26 (t, *J* = 6.1 Hz, 1H), 3.32 (d, *J* = 6.1 Hz, 2H) 1.28 (s, 2H), 1.21 (d, *J* = 11.1 Hz, 4H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.8, 141.4, 135.8, 128.7, 128.5, 128.5, 97.1, 43.0, 36.6, 24.5. **ESI-MS**: calculated for $C_{15}H_{18}INONa$ $[M + Na]^+$, 378.0325; Found 378.0325.

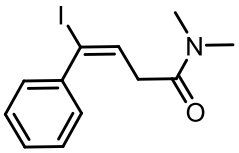
(*E*)-4-iodo-1-morpholino-4-phenylbut-3-en-1-one (*E*-47)



Following the general **procedure C**, the product ***E*-47** was obtained in 66% NMR yield (97:3 ***E:Z***) and 63% isolated yield (91:9 ***E:Z***).

^{1}H NMR (500 MHz, $CDCl_3$) δ *E*-isomer (major) 7.36 – 7.27 (m, 5H), 6.68 (t, *J* = 7.3 Hz, 1H), 3.64 (t, *J* = 4.7 Hz, 2H), 3.61 – 3.52 (m, 4H), 3.19 (t, *J* = 4.8 Hz, 2H), 3.02 (d, *J* = 7.3 Hz, 2H). *Z*-isomer (minor) 7.57 – 7.42 (m, 5H), 6.31 (t, *J* = 6.2 Hz, 1H), 3.69 (dd, *J* = 8.9, 4.9 Hz, 4H), 3.37 (d, *J* = 6.2 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.1, 141.3, 135.2, 128.6, 128.6, 97.5, 66.9, 66.6, 46.1, 42.2, 36.2. **ESI-MS**: calculated for $C_{14}H_{16}INO_2Na$ $[M + Na]^+$, 380.0118; Found 380.0121.

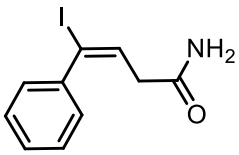
(*E*)-4-iodo-N,N-dimethyl-4-phenylbut-3-enamide (*E*-48)



Following the general **procedure C**, the product ***E*-48** was obtained in 69% NMR yield (93:7 ***E:Z***) and 60% isolated yield (91:9 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.36 – 7.28 (m, 5H), 6.69 (t, *J* = 7.3 Hz, 1H), 3.02 (d, *J* = 7.3 Hz, 2H), 2.91 (s, 3H), 2.80 (s, 3H). *Z*-isomer (minor) 7.56 – 7.45 (m, 5H), 6.33 (t, *J* = 6.1 Hz, 1H), 3.38 (d, *J* = 6.1 Hz, 2H), 3.08 (s, 3H), 2.98 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 141.5, 135.6, 128.7, 128.5, 97.2, 36.4. **ESI-MS**: calculated for $C_{12}H_{14}INONa$ $[M + Na]^+$, 338.0012; Found 338.0015.

(*E*)-4-iodo-4-phenylbut-3-enamide (*E*-49)

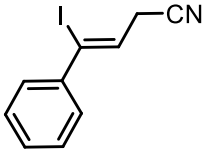


Following the general **procedure C**, the product ***E*-49** was obtained in 20% NMR yield with (75:25 ***E:Z***) and 17% isolated yield (86:14 ***E:Z***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *E*-isomer (major) 7.38 – 7.27 (m, 5H), 6.68 (t, *J* = 7.6 Hz, 1H), 5.51 (d, *J* = 66.9 Hz, 2H), 2.92 (d, *J* = 7.6 Hz, 2H). *Z*-isomer (minor) 7.51 – 7.44 (m, 5H), 6.22 (t, *J* = 6.8 Hz, 1H), 3.32 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 141.1, 134.6, 128.7, 128.6, 128.5, 99.3, 38.7. **ESI-MS**: calculated for $C_{10}H_{10}INONa$ $[M + Na]^+$, 309.9699; Found 309.9701.

6.2 Characterization of the *Z* isomers

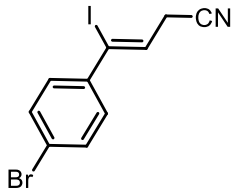
(*Z*) -4-iodo-4-phenylbut-3-enenitrile (*Z*-1)



Following the general **procedure D**, the product ***Z*-1** was obtained in 78% NMR yield (90:10 ***Z:E***) and 70% isolated yield (88:12 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.46 (d, *J* = 3.7 Hz, 2H), 7.33 (dd, *J* = 5.1, 2.1 Hz, 3H), 6.01 (t, *J* = 6.5 Hz, 1H), 3.40 (d, *J* = 6.5 Hz, 2H). *E*-isomer (minor) 7.41 – 7.35 (m, 3H), 7.28 (s, 2H), 6.46 (t, *J* = 7.5 Hz, 1H), 2.99 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.8, 129.4, 128.6, 128.5, 125.9, 116.8, 111.7, 26.6. **EI-MS**: calculated for $[C_{10}H_8NI]$, 268.97014; Found 268.97017.

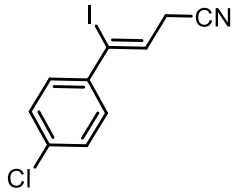
(*Z*)-4-(4-bromophenyl)-4-iodobut-3-enenitrile (*Z*-2)



Following the general **procedure D**, the product ***Z*-2** was obtained in 40% NMR yield (87:13 ***Z*:*E***) and 38% isolated yield (87:13 ***Z*:*E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.50 – 7.45 (m, 2H), 7.35 – 7.29 (m, 2H), 6.02 (t, *J* = 6.5 Hz, 1H), 3.38 (d, *J* = 6.5 Hz, 2H). *E*-isomer (minor) 7.52 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.18 – 7.11 (m, 2H), 6.48 (t, *J* = 7.5 Hz, 1H), 2.97 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.8, 131.8, 130.0, 126.6, 123.7, 116.6, 110.1, 26.6. **EI-MS**: calculated for [$C_{10}H_7NIBr$], 346.88066; Found 346.88068.

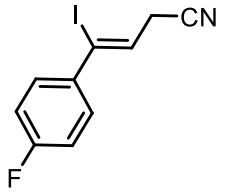
(*Z*)-4-(4-chlorophenyl)-4-iodobut-3-enenitrile (*Z*-3)



Following the general **procedure D**, the product ***Z*-3** was obtained in 49% NMR yield (89:11 ***Z*:*E***) and 41% isolated yield (89:11 ***Z*:*E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.41 – 7.36 (m, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 6.01 (t, *J* = 6.5 Hz, 1H), 3.38 (d, *J* = 6.5 Hz, 2H). *E*-isomer (minor) 7.36 – 7.34 (m, 2H), 7.25 – 7.19 (m, 2H), 6.48 (t, *J* = 7.5 Hz, 1H), 2.97 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.2, 135.3, 129.6, 128.7, 126.4, 116.5, 109.9, 26.5. **EI-MS**: calculated for [$C_{10}H_7NICl$], 302.93117; Found 302.93116.

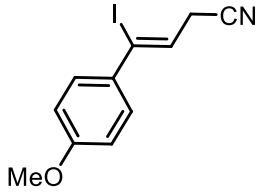
(*Z*)-4-(4-fluorophenyl)-4-iodobut-3-enenitrile (*Z*-4)



Following the general **procedure D**, the product ***Z*-4** was obtained in 72% NMR yield (88:12 ***Z*:*E***) and 68% isolated yield (87:13 ***Z*:*E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.43 (dd, *J* = 8.9, 5.2 Hz, 2H), 7.06 – 6.98 (m, 2H), 5.97 (t, *J* = 6.5 Hz, 1H), 3.38 (d, *J* = 6.5 Hz, 2H). *E*-isomer (minor) 7.19 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.09 (dd, *J* = 8.6, 1.8 Hz, 2H), 6.47 (t, *J* = 7.5 Hz, 1H), 2.97 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.1 (d, *J* = 250.1 Hz), 137.9 (d, *J* = 3.3 Hz), 130.2 (d, *J* = 8.4 Hz), 126.0, 116.6, 115.4 (d, *J* = 21.9 Hz), 110.0, 26.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ *E*-isomer (minor) -110.9 (ddd, *J* = 13.6, 8.3, 5.1 Hz). *Z*-isomer (major) -111.8 (ddd, *J* = 13.6, 8.6, 5.1 Hz). **EI-MS**: calculated for [$C_{10}H_7NIF$], 286.96072; Found 286.96075.

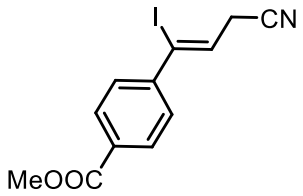
(*Z*)-4-iodo-4-(4-methoxyphenyl)but-3-enenitrile (*Z*-5)



Following the general **procedure D**, the product ***Z*-5** was obtained in 37% NMR yield (89:11 ***Z*:*E***) and 36% isolated yield (88:12 ***Z*:*E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.44 – 7.35 (m, 2H), 6.88 – 6.82 (m, 2H), 5.91 (t, *J* = 6.5 Hz, 1H), 3.83 (s, 3H), 3.38 (d, *J* = 6.5 Hz, 2H), *E*-isomer (minor) 7.22 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.41 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 2.99 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.4, 134.3, 129.8, 124.1, 116.9, 113.7, 111.6, 55.5, 26.6. **EI-MS**: calculated for [$C_{11}H_{10}NIO$], 298.98071; Found 298.98073.

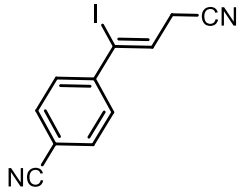
methyl (*Z*)-4-(3-cyano-1-iodoprop-1-en-1-yl) benzoate (*Z*-6)



Following the general **procedure D**, the product ***Z*-6** was obtained in 48% NMR yield (76:24 ***Z*:*E***) and 42% isolated yield (76:24 ***Z*:*E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 8.03 – 7.96 (m, 2H), 7.55 – 7.49 (m, 2H), 6.12 (t, *J* = 6.5 Hz, 1H), 3.93 (s, 3H), 3.41 (d, *J* = 6.5 Hz, 2H). *E*-isomer (minor) 8.05 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H),, 6.51 (t, *J* = 7.5 Hz, 1H), 3.94 (s, 3H), 2.97 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 145.8, 130.2, 129.9, 128.6, 128.2, 110.1, 52.5, 26.6, 20.1. **EI-MS**: calculated for [$C_{12}H_{10}NIO_2$], 326.97562; Found 326.97566.

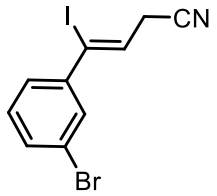
(*Z*)- 4-(3-cyano-1-iodoprop-1-en-1-yl) benzonitrile (*Z*-7)



Following the general **procedure D**, the product ***Z*-7** was obtained in 59% NMR yield (66:34 ***Z*:*E***) and 50% isolated yield (68:32 ***Z*:*E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.67 – 7.62 (m, 2H), 7.58 – 7.54 (m, 2H), 6.14 (t, *J* = 6.5 Hz, 1H), 3.41 (d, *J* = 6.6 Hz, 2H). *E*-isomer (minor) 7.72 – 7.68 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.55 (t, *J* = 7.6 Hz, 1H), 2.96 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.9, 132.9, 132.5, 130.4, 129.3, 129.0, 118.2, 113.1, 26.6. **EI-MS**: calculated for [$C_{11}H_7N_2I$], 293.96539; Found 293.96544.

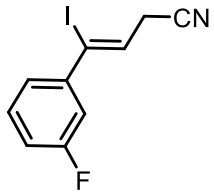
(*Z*)-4-(3-bromophenyl)-4-iodobut-3-enenitrile (*Z*-8)



Following the general **procedure D**, the product ***Z*-8** was obtained in 15% NMR yield (78:22 ***Z*:*E***) and 11% isolated yield (78:22 ***Z*:*E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.48 – 7.43 (m, 2H), 7.38 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.35 (s, 1H), 6.05 (t, *J* = 6.5 Hz, 1H), 3.39 (d, *J* = 6.6 Hz, 2H). *E*-isomer (minor) 6.48 (t, *J* = 7.5 Hz, 1H), 2.98 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.6, 133.3, 132.3, 131.3, 130.2, 130.0, 127.1, 120.3, 109.1, 26.4. **EI-MS**: calculated for [$C_{10}H_7BrNI$], 346.88011; Found 346.88015.

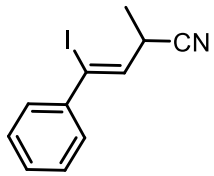
(*Z*)-4-(3-fluorophenyl)-4-iodobut-3-enenitrile (*Z*-9)



Following the general **procedure D**, the product ***Z*-9** was obtained in 44% NMR yield (84:16 ***Z:E***) and 40% isolated yield (85:15 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.34 – 7.21 (m, 2H), 7.16 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.10 (dt, *J* = 9.8, 2.2 Hz, 1H), 5.99 (t, *J* = 6.5 Hz, 1H), 3.32 (d, *J* = 6.5 Hz, 2H). *E*-isomer (minor) 7.01 – 6.92 (m, 4H), 6.41 (t, *J* = 7.5 Hz, 1H), 2.92 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.5 (d, *J* = 247.5 Hz), 130.2 (d, *J* = 8.5 Hz), 127.1, 124.1 (d, *J* = 2.9 Hz), 116.4 (d, *J* = 21.1 Hz), 115.9 (d, *J* = 23.2 Hz), 26.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ *E*-isomer (minor) -111.10 (td, *J* = 8.9, 6.0 Hz). *Z*-isomer (major) -112.42 – -112.58 (m). **EI-MS**: calculated for [$C_{10}H_7FNI$], 286.96017; Found 286.96028.

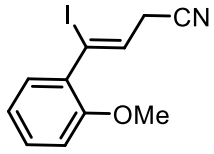
(*Z*)-4-iodo-2-methyl-4-phenylbut-3-enenitrile (*Z*-10)



Following the general **procedure D**, the product ***Z*-10** was obtained in 24% NMR yield (90:10 ***Z:E***) and 19% isolated yield (91:9 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.40 – 7.34 (m, 2H), 7.26 (dd, *J* = 5.2, 2.1 Hz, 3H), 5.84 (d, *J* = 8.6 Hz, 1H), 3.67 (dq, *J* = 8.6, 7.1 Hz, 1H), 1.45 (d, *J* = 7.2 Hz, 3H). *E*-isomer (minor) 7.31 (s, 2H), 7.23 (s, 3H), 6.33 (d, *J* = 10.0 Hz, 1H), 3.24 – 3.07 (m, 1H), 1.28 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.7, 132.8, 129.3, 128.5, 128.5, 120.2, 109.4, 34.1, 18.0. **EI-MS**: calculated for [$C_{11}H_{10}NI$], 282.98524; Found 282.98558.

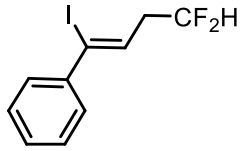
(*Z*)-4-iodo-4-(2-methoxyphenyl) but-3-enenitrile (*Z*-11)



Following the general **procedure D**, the product ***Z*-11** was obtained in 41% NMR yield (45:55 ***Z:E***) and 18% isolated yield (> 20:1 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer 7.34 – 7.27 (m, 1H), 7.18 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.90 – 6.85 (m, 1H), 5.84 (t, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 3.37 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.2, 130.6, 130.2, 127.7, 120.5, 111.4, 55.7, 26.2. **EI-MS**: calculated for [$C_{11}H_{10}NIO$], 298. 98071; Found 298.98073.

(Z)-(4,4-difluoro-1-iodobut-1-en-1-yl)benzene (*Z*-12)

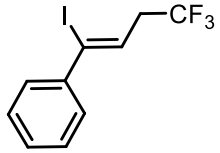


Following the general **procedure D**, the product ***Z*-12** was obtained in 72% NMR yield (85:15 ***Z:E***) and 68% isolated yield (94:6 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.49 – 7.44 (m, 2H), 7.36 – 7.27 (m, 3H), 6.10 -5.82(t, t, t, *J* = 4.3, 4.4, 4.3Hz, 1H), 5.98 (t, *J* = 6.8 Hz, 1H), 2.91 (tdd, *J* = 17.4, 6.7, 4.3 Hz, 2H). *E*-isomer (minor) 6.50 (t, *J* = 7.6 Hz, 1H), 2.52 (tdd, *J* = 17.3, 7.6, 4.2 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 128.9, 128.6, 128.5, 128.5, 115.4 (t, *J* = 241.2 Hz), 110.3, 42.9 (t, *J* = 22.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (major) -115.22 (dt, *J* = 56.0, 17.2 Hz), *E*-isomer (minor) -115.93 (dt, *J* = 56.5, 17.5 Hz). **EI-MS:** calculated for [$C_{10}H_9F_2I$], 293.97115; Found

293.97151.

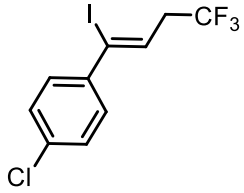
(*Z*)-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*Z*-13)



Following the general **procedure D**, the product ***Z*-13** was obtained in 73% NMR yield (89:11 ***Z:E***) and 65% isolated yield (90:10 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.52 – 7.42 (m, 2H), 7.37 – 7.29 (m, 3H), 5.98 (t, *J* = 6.6 Hz, 1H), 3.17 (qd, *J* = 10.7, 6.6 Hz, 2H). *E*-isomer (minor) 6.48 (t, *J* = 7.6 Hz, 1H), 2.85 – 2.60 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.6, 129.2, 128.6, 128.5, 126.7 (q, *J* = 275.5 Hz), 126.6 (q, *J* = 3.3 Hz), 111.2, 42.8 (q, *J* = 29.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (major) -65.21 (t, *J* = 10.5 Hz). *E*-isomer (minor) -65.75 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{10}H_8F_3I$], 311.96228; Found 311.96231.

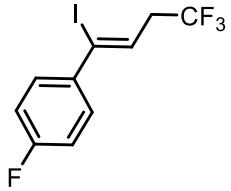
(*Z*)-1-chloro-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*Z*-14)



Following the general **procedure D**, the product ***Z*-14** was obtained in 42% NMR yield (93:7 ***Z:E***) and 40% isolated yield (93:7 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.44 – 7.37 (m, 2H), 7.32 – 7.28 (m, 2H), 5.97 (t, *J* = 6.6 Hz, 1H), 3.15 (qd, *J* = 10.6, 6.6 Hz, 2H). *E*-isomer (minor) 7.37 – 7.33 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.49 (t, *J* = 7.6 Hz, 1H), 2.72 (qd, *J* = 10.5, 7.6 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.0, 135.1, 129.8, 128.7, 128.2 (q, *J* = 274.4 Hz), 127.2 (q, *J* = 3.6 Hz), 109.5, 42.8 (q, *J* = 30.6 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (major) -65.17 (t, *J* = 10.7 Hz). *E*-isomer (minor) -65.68 (t, *J* = 10.4 Hz). **EI-MS**: calculated for [$C_{10}H_7ClF_3I$], 345.92276; Found 345.92269.

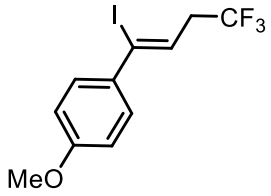
(*Z*)-1-fluoro-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*Z*-15)



Following the general **procedure D**, the product ***Z*-15** was obtained in 35% NMR yield (89:11 ***Z:E***) and 34% isolated yield (89:11 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.49 – 7.41 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.92 (t, *J* = 6.6 Hz, 1H), 3.15 (qd, *J* = 10.6, 6.6 Hz, 2H). *E*-isomer (minor) 6.56 – 6.42 (m, 1H), 2.72 (dd, *J* = 10.3, 7.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.1 (d, *J* = 249.4 Hz), 138.8, 130.3 (d, *J* = 8.2 Hz), 126.8 (q, *J* = 2.8 Hz), 126.8 (q, *J* = 277.2 Hz), 115.4 (d, *J* = 21.8 Hz), 109.6, 42.8 (q, *J* = 29.8 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (major) -65.21 (t, *J* = 10.7 Hz), -112.42 (ddd, *J* = 13.7, 8.4, 5.3 Hz). *E*-isomer (minor) -65.71 (t, *J* = 10.3 Hz). **EI-MS**: calculated for [$C_{10}H_7F_4I$], 329.95231; Found 329.95270.

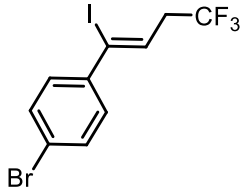
(*Z*)-1-methoxy-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*Z*-16)



Following the general **procedure D**, the product ***Z*-16** was obtained in 49% NMR yield (88:12 ***Z:E***) and 45% isolated yield (89:11 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.41 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.88 (t, *J* = 6.6 Hz, 1H), 3.82 (s, 3H), 3.15 (qd, *J* = 10.7, 6.6 Hz, 2H). *E*-isomer (minor) 7.22 – 7.11 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.44 (t, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 2.83 – 2.68 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.1, 135.0, 129.8, 128.3 (q, *J* = 274.5 Hz), 124.9 (q, *J* = 3.8 Hz), 113.6, 111.0, 55.4, 42.7 (q, *J* = 29.9 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -65.26 (t, *J* = 10.8 Hz), -65.74 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{11}H_{10}OF_3I$], 341.97229; Found 341.97294.

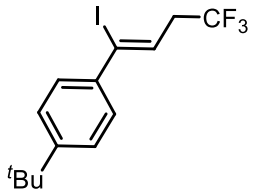
(*Z*)-1-bromo-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*Z*-17)



Following the general **procedure D**, the product ***Z*-17** was obtained in 52% NMR yield (91:9 ***Z:E***) and 48% isolated yield (91:9 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.46 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 5.97 (t, *J* = 6.6 Hz, 1H), 3.15 (qd, *J* = 10.6, 6.6 Hz, 2H). *E*-isomer (minor) 7.50 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.49 (t, *J* = 7.7 Hz, 1H), 2.79 – 2.65 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.5, 131.6, 130.1, 128.5 (q, *J* = 274.7 Hz), 127.3 (q, *J* = 3.5 Hz), 123.3, 42.8 (q, *J* = 29.8 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (major) -65.15 (t, *J* = 10.6 Hz). *E*-isomer (minor) -65.66 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{10}H_7BrF_3I$], 389.87224; Found 389.87234.

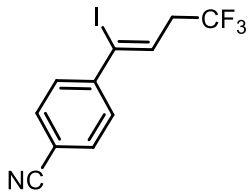
(*Z*)-1-(tert-butyl)-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzene (*Z*-18)



Following the general **procedure D**, the product ***Z*-18** was obtained in 37% NMR yield (93:7 ***Z:E***) and 33% isolated yield (93:7 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.43 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 5.96 (t, *J* = 6.6 Hz, 1H), 3.16 (qd, *J* = 10.6, 6.5 Hz, 2H), 1.33 (s, 9H). *E*-isomer (minor) 7.38 (s, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.46 (t, *J* = 7.5 Hz, 1H), 2.84 – 2.70 (m, 2H), 1.33 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.4, 139.7, 128.3, 125.9 (q, *J* = 277.7 Hz), 125.9 (q, *J* = 3.7 Hz), 125.4, 111.4, 42.8 (q, *J* = 29.8 Hz), 34.8, 31.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (major) -65.25 (t, *J* = 10.7 Hz). *E*-isomer (minor) -65.72 (t, *J* = 10.5 Hz). **EI-MS**: calculated for [$C_{14}H_{16}F_3I$], 368.02433; Found 368.02422.

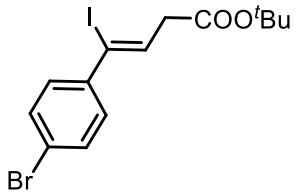
(*Z*)-4-(4,4,4-trifluoro-1-iodobut-1-en-1-yl) benzonitrile (*Z*-19)



Following the general **procedure D**, the product ***Z*-19** was obtained in 42% NMR yield (85:15 ***Z:E***) and 39% isolated yield (83:17 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.63 (d, *J* = 8.5 Hz, 2H), 7.59 – 7.54 (m, 2H), 76.09 (t, *J* = 6.6 Hz, 1H), 3.18 (qd, *J* = 10.6, 6.6 Hz, 2H). *E*-isomer (minor) 7.67 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.56 (t, *J* = 7.7 Hz, 1H), 2.78 – 2.61 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.6, 132.4, 129.5 (q, *J* = 3.9 Hz), 125.6 (q, *J* = 277.6 Hz), 129.3, 118.3, 112.8, 108.3, 42.9 (q, *J* = 30.0 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ *Z*-isomer (major) -65.04 (t, *J* = 10.6 Hz). *E*-isomer (minor) -65.59 (t, *J* = 10.3 Hz). **EI-MS**: calculated for [$C_{11}H_7NF_3I$], 336.95698; Found 336.95689.

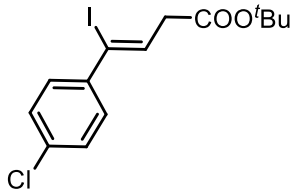
tert-butyl (*Z*)-4-(4-bromophenyl)-4-iodobut-3-enoate (*Z*-20)



Following the general **procedure D**, the product ***Z*-20** was obtained in 38% NMR yield (94:6 ***Z:E***) and 39% isolated yield (> 20:1 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.43 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.21 (t, *J* = 6.3 Hz, 1H), 3.26 (d, *J* = 6.3 Hz, 2H), 1.48 (s, 9H). *E*-isomer (minor) 2.88 (d, *J* = 7.5 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 141.8, 132.2, 131.4, 130.2, 122.7, 105.9, 81.6, 44.3, 28.3. **ESI-MS**: calculated for $C_{14}H_{16}BrIO_2Na$ $[M + Na]^+$, 444.9271; Found 444.9266.

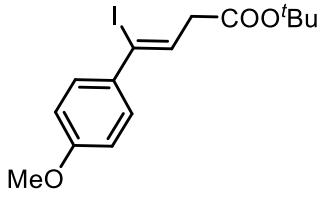
tert-butyl (*Z*)-4-(4-chlorophenyl)-4-iodobut-3-enoate (*Z*-21)



Following the general **procedure D**, the product ***Z*-21** was obtained in 30% NMR yield (94:6 ***Z:E***) and 27% isolated yield (> 20:1 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.41 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.20 (t, *J* = 6.3 Hz, 1H), 3.27 (d, *J* = 6.3 Hz, 2H), 1.48 (s, 9H). *E*-isomer (minor) 2.88 (d, *J* = 7.6 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.8, 141.4, 132.2, 129.9, 128.5, 105.9, 81.6, 44.3, 28.3. **ESI-MS**: calculated for $C_{14}H_{16}ClIO_2Na$ $[M + Na]^+$, 400.9776; Found 400.9764.

tert-butyl (*Z*)-4-iodo-4-(4-methoxyphenyl) but-3-enoate (*Z*-22)

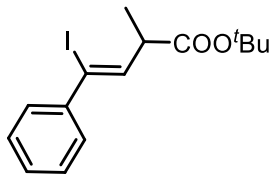


Following the general **procedure D**, the product ***Z*-22** was obtained in 67% NMR yield (88:12 ***Z:E***) and 66% isolated yield (87:13 ***Z:E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.42 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.10

(t, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 3.27 (d, *J* = 6.4 Hz, 2H), 1.48 (s, 9H). *E*-isomer (minor) 7.23 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.58 (t, *J* = 7.6 Hz, 1H), 2.91 (d, *J* = 7.5 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.1, 159.9, 135.6, 129.9, 122.5, 113.6, 107.5, 81.4, 55.5, 44.4, 28.3. **ESI-MS**: calculated for $C_{15}H_{19}IO_3Na$ $[M + Na]^+$, 397.0271; Found 397.0274.

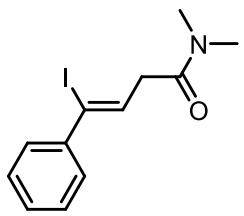
tert-butyl (*Z*)-4-iodo-2-methyl-4-phenylbut-3-enoate (*Z*-23)



Following the general **procedure D**, the product ***Z*-23** was obtained in 38% NMR yield (90:10 ***Z*:*E***) and 39% isolated yield (89:11 ***Z*:*E***).

^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.46 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.26 (m, 2H), 6.01 (d, *J* = 8.7 Hz, 1H), 3.54 – 3.30 (m, 1H), 1.48 (s, 9H), 1.33 (d, *J* = 7.1 Hz, 3H). *E*-isomer (minor) 6.52 (d, *J* = 11.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.1, 143.0, 137.9, 128.8, 128.6, 128.3, 105.9, 81.2, 49.5, 28.2, 17.3. **ESI-MS**: calculated for $C_{15}H_{19}IO_2Na$ $[M + Na]^+$, 381.0322; Found 381.0327.

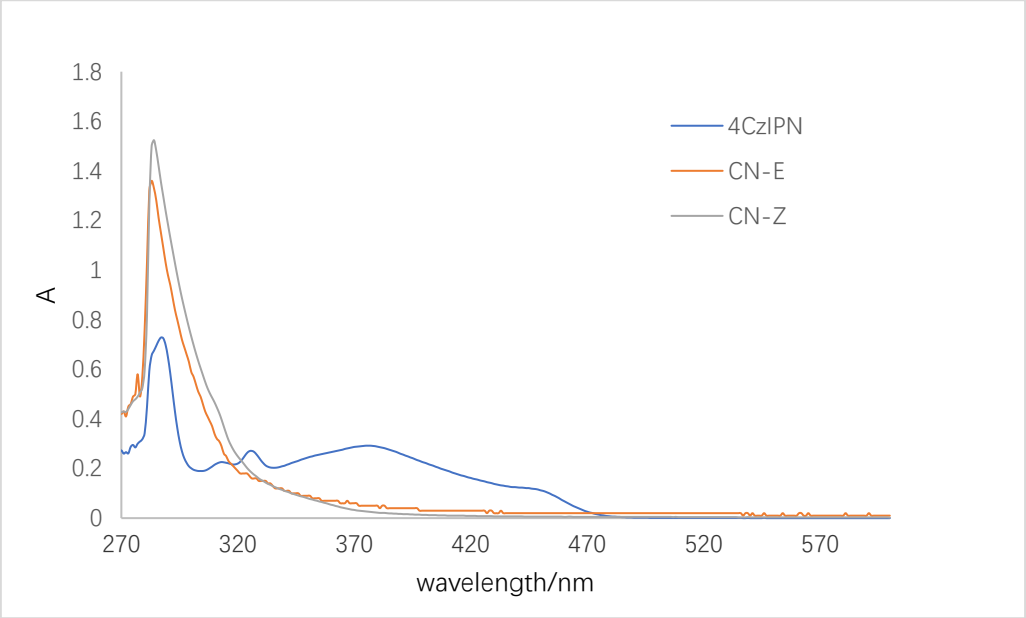
(Z)-4-iodo-N,N-dimethyl-4-phenylbut-3-enamide (*Z*-24)



Following the general **procedure D**, the product ***Z*-24** was obtained in 36% NMR yield (87:13 ***Z*:*E***) and 39% isolated yield (85:15 ***Z*:*E***).

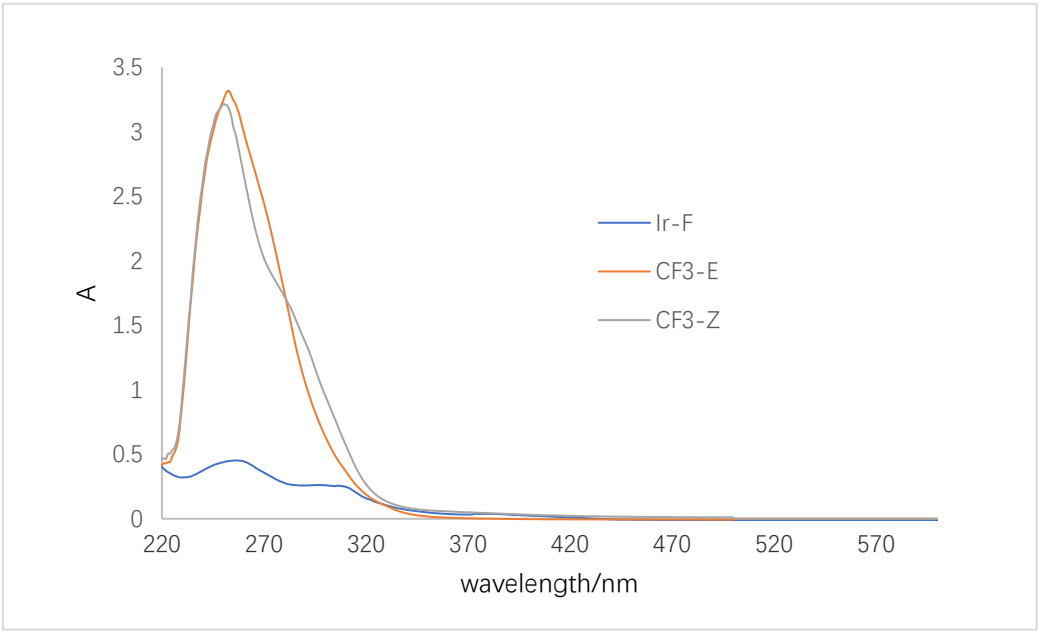
^{1}H NMR (400 MHz, $CDCl_3$) δ *Z*-isomer (major) 7.52 – 7.45 (m, 2H), 7.33 – 7.27 (m, 3H), 6.33 (t, *J* = 6.2 Hz, 1H), 3.38 (d, *J* = 6.2 Hz, 2H), 3.09 (s, 3H), 2.99 (s, 3H). *E*-isomer (minor) 6.70 (t, *J* = 7.3 Hz, 1H), 3.03 (d, *J* = 7.3 Hz, 2H), 2.91 (s, 3H), 2.80 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.0, 142.7, 135.7, 132.6, 128.8, 128.6, 128.3, 107.3, 43.0, 37.6, 35.8. **ESI-MS**: calculated for $C_{12}H_{14}INONa$ $[M + Na]^+$, 338.0012; Found 338.0016.

7. UV-spectra of representative E-isomers, Z-isomers and the photocatalysts



Supplementary Figure 2. UV of iodinated allylic nitrile product

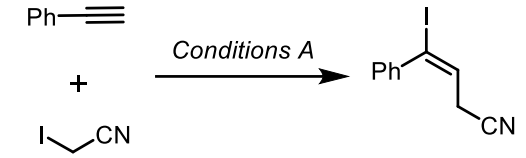
According to $E_{00} = hc/\lambda_{tail}$, E_{00}(4CzIPN) = 57.6 kcal/mol, E_{00}(*E*-1) = 67 kcal/mol, E_{00}(*Z*-1) = 53.5 kcal/mol



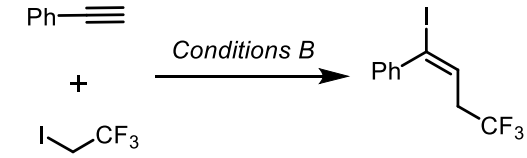
Supplementary Figure 3. UV of iodinated allylic trifluoromethane product

According to $E_{00} = hc/\lambda_{tail}$, E_{00}(Ir-F) = 62 kcal/mol, E_{00}(*E*-15)= 65.8 kcal/mol, E_{00}(*Z*-13) = 59 kcal/mol

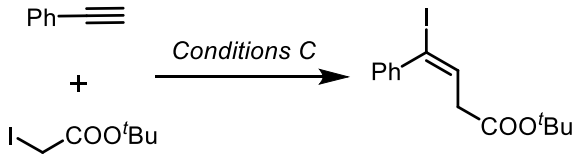
8. The time-course experiments for the synthesis of E isomers



time	yield/%	*E*:*Z*
0.5 h	11	>20:1
1 h	17	92:8



time	yield/%	*E*:*Z*
0.5 h	54	58:42
1 h	48	67:33
2 h	62	77:23
4 h	72	85:15

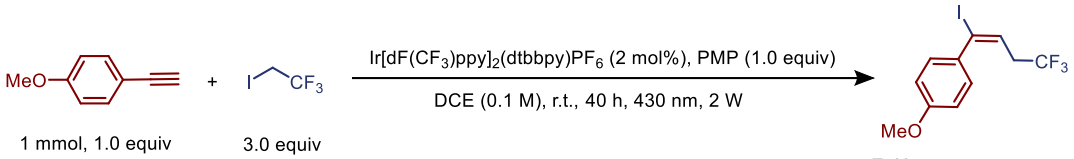


time	yield/%	*E*:*Z*
15 min	3	57:43
30 min	26	78:22
1 h	35	80:20
2 h	56	87:13

Supplementary Figure 4. The time-course experiments

9. Scale-up reactions and derivatization of the products

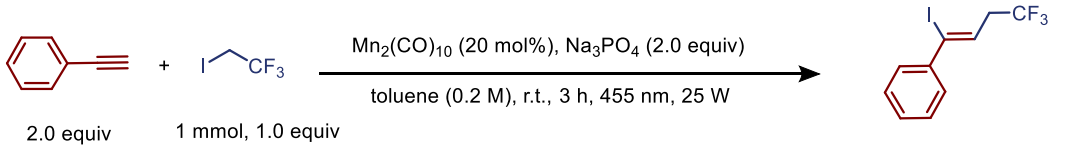
9.1 Scale-up reactions



1 mmol, 1.0 equiv　　3.0 equiv

E-18, 77% yield, *E*:*Z*=90:10

A 30 mL tube was flame-dried and equipped with a magnetic stir bar. Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.02mmol, 2 mol%, 22.5 mg) was added into the tube which was then brought into the glove box. In the glove box, DCE (0.1 M, 10 mL), 1-ethynyl-4-methoxybenzene (1 mmol, 1.0 equiv, 130 μL), α-iodotrifluoroethane (3 mmol, 3.0 equiv) and PMP (1 mmol, 1.0 equiv) were added in order. Then the tube was carried out of the glove box and the mixture was stirred at room temperature under 430 nm irradiation for 40 h until the starting material was completely consumed. After completion, the mixture was purified by flash column chromatography (eluent = petroleum ether) to afford ***E*-18** as a pale-yellow, transparent oil (263 mg, 0.77 mmol, 77%, *E*:*Z* = 90:10).

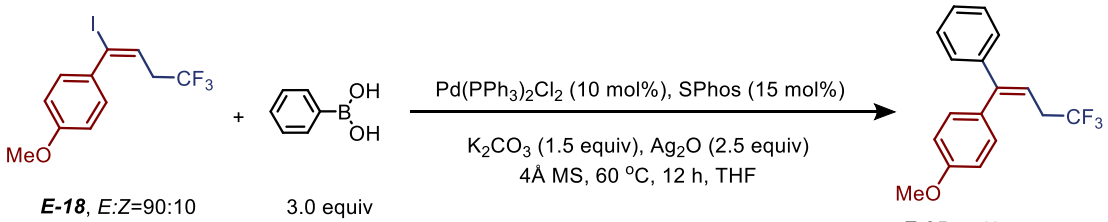


2.0 equiv　　1 mmol, 1.0 equiv

Z-13, 41% yield, *Z*:*E*=90:10

A 30 mL tube was flame-dried and equipped with a magnetic stir bar. Na_3PO_4 (2 mmol, 2.0 equiv) was added into the tube which was then brought into the glove box. In the glove box, $Mn_2(CO)_{10}$ (0.2 mmol, 20 mol%, 78 mg), toluene (0.2 M, 5 mL), Phenylacetylene (2 mmol, 2.0 equiv, 220 μL), α-iodotrifluoroethane (1 mmol, 1.0 equiv) were added in this order. Then the tube was carried out of the glove box and the mixture was stirred at room temperature under 455 nm irradiation for 3 h until the starting material was completely consumed. After completion, the mixture was purified by flash column chromatography (eluent = petroleum ether) to afford ***Z*-13** as a pale-yellow, transparent oil (128 mg, 0.41 mmol, 41%, *Z*:*E* = 90:10).

9.2 Suzuki-Miyaura coupling reaction

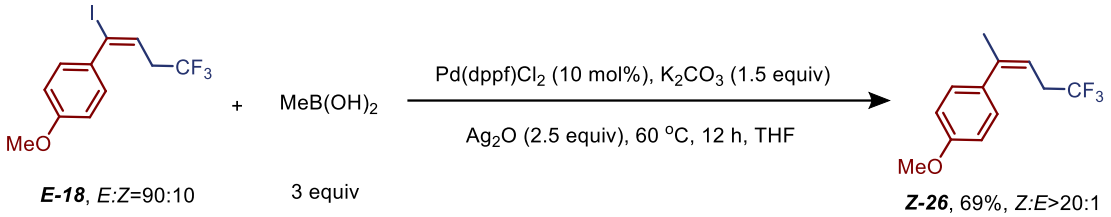


E-18, *E*:*Z*=90:10　　3.0 equiv

Z-25, 68%, *Z*:*E*=94:6

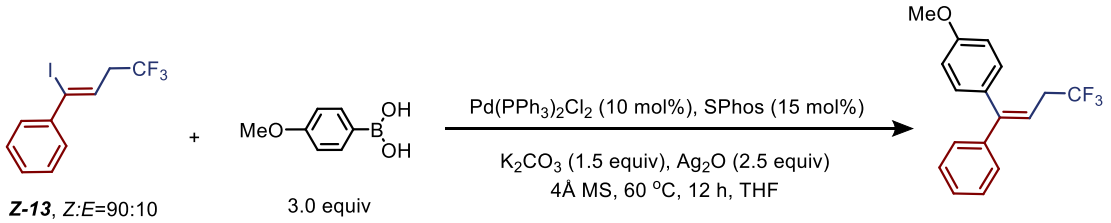
The reaction was performed by modifying a known procedure[3]. A flame-dried 15 mL Schlenk

tube was charged with ***E*-18** (68 mg, 0.2 mmol, 1.0 equiv, *E:Z*= 90:10), $PhB(OH)_2$ (74 mg, 0.6 mmol, 3.0 equiv) and K_2CO_3 (41 mg, 0.3 mmol, 1.5 equiv), then the tube was brought into the glove box. In the glove box, $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol, 10 mol%), Sphos (12 mg, 0.03 mmol, 15 mol%), Ag_2O (116 mg, 0.5 mmol, 2.5 equiv), 4ÅMS and anhydrous THF (0.1 M, 2 mL) was added in order. Then the tube was carried out of the glove box and heated to 60 ℃ for 12 h. After completion, the crude mixture was filtered through a pad of celite, then concentrated and purified by flash column chromatography (eluent = petroleum ether) to afford ***Z*-25** as a pale, transparent oil (40 mg, 0.14 mmol, 68%, *Z:E* = 94:6).



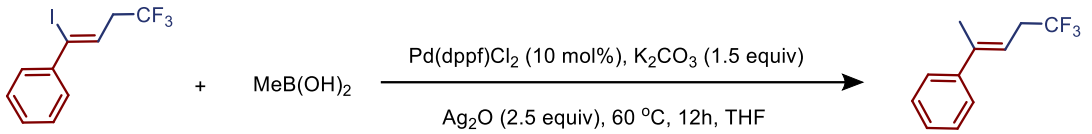
***E*-18**, *E*:*Z*=90:10 　　3 equiv 　　***Z*-26**, 69%, *Z*:*E*>20:1

The reaction was performed by modifying a known procedure[3]. A flame-dried 15 mL Schlenk tube was charged with ***E*-18** (34 mg, 0.1 mmol, 1 equiv, *E:Z*= 90:10), $MeB(OH)_2$ (18 mg, 0.3 mmol, 3 equiv) and K_2CO_3 (21 mg, 0.15 mmol, 1.5 equiv), then the tube was brought into the glove box. In the glove box, $Pd(dppf)_2Cl_2$ (7 mg, 0.01 mmol, 10 mol%), Ag_2O (58 mg, 0.25 mmol, 2.5 equiv) and anhydrous THF (0.1 M, 1 mL) was added in order. Then the tube was carried out of the glove box and heated to 60 ℃ for 12 h. After completion, the crude mixture was filtered through a pad of celite, then concentrated and purified by flash column chromatography (eluent = petroleum ether) to afford ***Z*-26** as a pale, transparent oil (16 mg, 0.069 mmol, 69%, *Z:E* > 20:1).



***Z*-13**, *Z*:*E*=90:10 　　3.0 equiv 　　***Z*-25**, 86%, *Z*:*E*=93:7

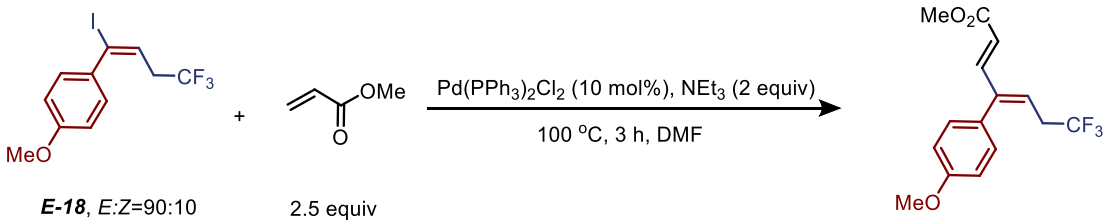
The reaction was performed by modifying a known procedure[3]. A flame-dried 15 mL Schlenk tube was charged with ***Z*-13** (31 mg, 0.1 mmol, 1.0 equiv, *Z:E*= 90:10), (4-methoxyphenyl)boronic acid (46 mg, 0.3 mmol, 3.0 equiv) and K_2CO_3 (21 mg, 0.15 mmol, 1.5 equiv), then the tube was brought into the glove box. In the glove box, $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol, 10 mol%), Sphos (6 mg, 0.015 mmol, 15 mol%), Ag_2O (58 mg, 0.25 mmol, 2.5 equiv), 4ÅMS and anhydrous THF (0.1 M, 1 mL) was added in order. Then the tube was carried out of the glove box and heated to 60 ℃ for 12 h. After completion, the crude mixture was filtered through a pad of celite, then concentrated and purified by flash column chromatography (eluent = petroleum ether) to afford ***Z*-25** as a pale, transparent oil (25 mg, 0.086 mmol, 86%, *Z:E* = 93:7).



Z-13, *Z:E*=90:10 3.0 equiv ***E-52***, 40%, *E:Z*>20:1

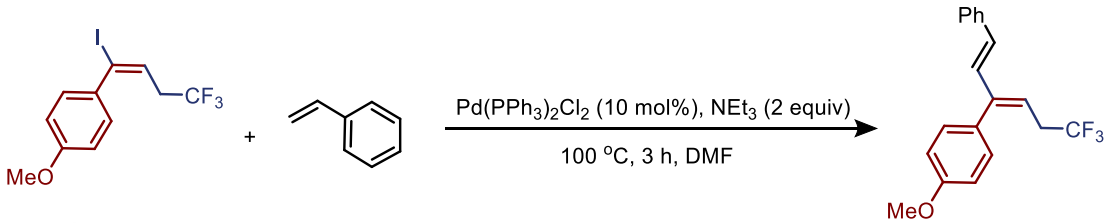
The reaction was performed by modifying a known procedure[3]. A flame-dried 15 mL Schlenk tube was charged with ***Z*-13** (31 mg, 0.1 mmol, 1.0 equiv, *Z:E*= 90:10), $MeB(OH)_2$ (18 mg, 0.3 mmol, 3.0 equiv) and K_2CO_3 (21 mg, 0.15 mmol, 1.5 equiv), then the tube was brought into the glove box. In the glove box, Pd(dppf) Cl_2 (7 mg, 0.01 mmol, 10 mol%), Ag_2O (58 mg, 0.25 mmol, 2.5 equiv) and anhydrous THF (0.1 M, 1 mL) was added in order. Then the tube was carried out of the glove box and heated to 60 °C for 12 h. After completion, the crude mixture was filtered through a pad of celite, then concentrated and purified by flash column chromatography (eluent = petroleum ether) to afford ***E*-52** as a pale, transparent oil (7 mg, 0.04 mmol, 40%, *E:Z* > 20:1).

9.3 Mizoroki-Heck coupling reaction



E-18, *E:Z*=90:10 2.5 equiv ***Z-27***, 63%, *Z:E*=82:18

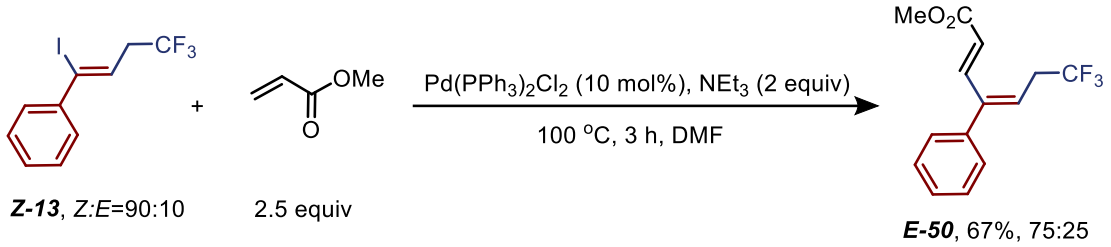
The reaction was performed by modifying a known procedure[4]. A flame-dried 15 mL Schlenk tube was charged with ***E*-18** (34 mg, 0.1 mmol, 1 equiv, *E:Z*= 90:10) and methyl acrylate (22 mg, 0.25 mmol, 2.5 equiv), then the tube was brought into the glove box. In the glove box, $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol, 10 mol%), NEt_3 (20 mg, 0.2 mmol, 2.0 equiv) and anhydrous DMF (0.1 M, 1 mL) was added in order. Then the tube was carried out of the glove box and heated to 100 °C for 3 h. After completion, the crude mixture was filtered through a pad of celite, then concentrated and purified by flash column chromatography (eluent = petroleum ether) to afford ***Z*-27** as a pale, transparent oil (19 mg, 0.063 mmol, 63%, *Z:E*=82:18).



E-18, *E:Z*=90:10 2.5 equiv ***Z-28***, 65%, *Z:E*=90:10

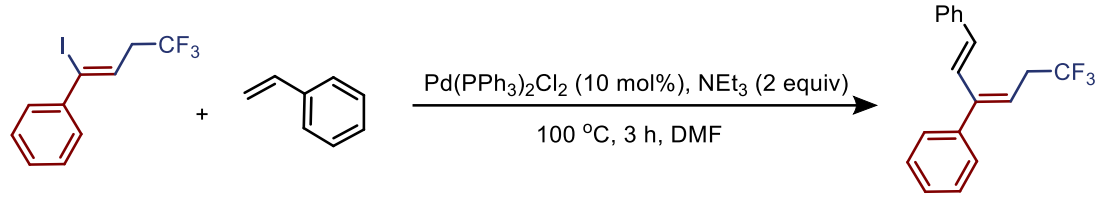
The reaction was performed by modifying a known procedure[4]. A flame-dried 15 mL Schlenk tube was charged with ***E*-18** (34 mg, 0.1 mmol, 1 equiv, *E:Z*= 90:10) and styrene (26 mg, 0.25 mmol, 2.5 equiv), then the tube was brought into the glove box. In the glove box, $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol, 10 mol%), NEt_3 (20 mg, 0.2 mmol, 2.0 equiv) and anhydrous DMF (0.1 M, 1 mL) was added

in order. Then the tube was carried out of the glove box and heated to 100 ℃ for 3 h. After completion, the crude mixture was filtered through a pad of celite, then concentrated and purified by flash column chromatography (eluent = petroleum ether/ ethyl acetate 50:1 v/v) to afford ***Z*-28** as a pale, transparent oil (21 mg, 0.065 mmol, 65%, *Z:E*=90:10).



***Z*-13**, *Z:E*=90:10 2.5 equiv ***E*-50**, 67%, 75:25

The reaction was performed by modifying a known procedure[4]. A flame-dried 15 mL Schlenk tube was charged with ***Z*-13** (31 mg, 0.1 mmol, 1 equiv, *Z:E*= 90:10) and methyl acrylate (22 mg, 0.25 mmol, 2.5 equiv), then the tube was brought into the glove box. In the glove box, $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol, 10 mol%), NEt_3 (20 mg, 0.2 mmol, 2.0 equiv) and anhydrous DMF (0.1 M, 1 mL) was added in order. Then the tube was carried out of the glove box and heated to 100 ℃ for 3 h. After completion, the crude mixture was filtered through a pad of celite, then concentrated and purified by flash column chromatography (eluent = petroleum ether) to afford ***E*-50** as a pale, transparent oil (18 mg, 0.067 mmol, 67%, *E:Z*=75:25).

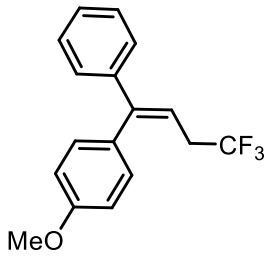


***Z*-13**, *Z:E*=90:10 2.5 equiv ***E*-51**, 45%, >20:1

The reaction was performed by modifying a known procedure[4]. A flame-dried 15 mL Schlenk tube was charged with ***Z*-13** (31 mg, 0.1 mmol, 1.0 equiv, *Z:E*= 90:10) and styrene (26 mg, 0.25 mmol, 2.5 equiv), then the tube was brought into the glove box. In the glove box, $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol, 10 mol%), NEt_3 (20 mg, 0.2 mmol, 2.0 equiv) and anhydrous DMF (0.1 M, 1 mL) was added in order. Then the tube was carried out of the glove box and heated to 100 ℃ for 3 h. After completion, the crude mixture was filtered through a pad of celite, then concentrated and purified by flash column chromatography (eluent = petroleum ether) to afford ***E*-51** as a pale, transparent oil (18 mg, 0.045 mmol, 45%, *E:Z* > 20:1).

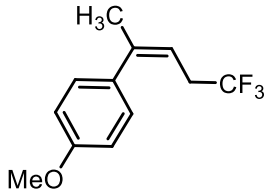
10. Characterization of the derivatization products

(*Z*)-1-methoxy-4-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) benzene (*Z*-25)



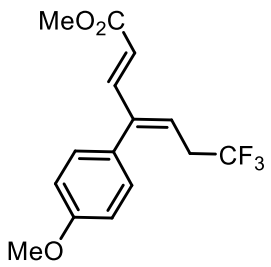
^{1}H NMR (400 MHz, CDCl$_3$) δ *Z*-isomer (major) 7.31 – 7.18 (m, 5H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.00 (t, *J* = 7.4 Hz, 1H), 3.83 (s, 3H), 2.92 (qd, *J* = 10.8, 7.4 Hz, 2H). *E*-isomer (minor) 7.16 (d, *J* = 9.0 Hz, 2H), 6.84 – 6.76 (m, 2H), 5.95 (d, *J* = 7.5 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.2, 147.5, 142.0, 131.1, 130.9, 128.4, 127.9, 127.6, 126.4 (q, *J* = 276.2 Hz), 115.9 (q, *J* = 3.2 Hz), 114.1, 55.4, 35.0 (q, *J* = 29.4 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ *Z*-isomer (major) -65.67 (t, *J* = 10.8 Hz). *E*-isomer (minor) -65.75 (t, *J* = 10.8 Hz). **ESI-MS**: calculated for $C_{17}H_{15}F_3OK$ $[M + K]^+$, 331.0707; Found 331.0722.

(*Z*)-1-methoxy-4-(5,5,5-trifluoropent-2-en-2-yl) benzene (*Z*-26)



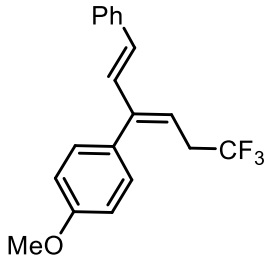
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.45 (td, *J* = 7.3, 1.6 Hz, 1H), 3.82 (s, 3H), 2.82 – 2.71 (m, 2H), 2.07 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.9, 143.3, 133.0, 128.9, 127.1, 126.4 (d, *J* = 276.6 Hz), 114.3 (q, *J* = 3.4 Hz), 114.0, 55.4, 34.3 (q, *J* = 29.2 Hz), 26.1. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -66.10 (t, *J* = 10.9 Hz). **ESI-MS**: calculated for $C_{12}H_{14}F_3O$ $[M + H]^+$, 231.0991; Found 231.0977.

methyl (*2E,4Z*)-7,7,7-trifluoro-4-(4-methoxyphenyl)hepta-2,4-dienoate (*Z*-27)



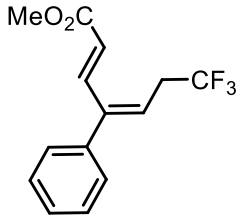
^{1}H NMR (400 MHz, CDCl$_3$) δ *Z*-isomer (major) 7.51 (d, *J* = 15.6 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.04 (t, *J* = 7.5 Hz, 1H), 5.51 (d, *J* = 15.6 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.83 (qd, *J* = 10.6, 7.4 Hz, 2H). *E*-isomer (minor) 7.71 (d, *J* = 15.6 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.87 (d, *J* = 15.6 Hz, 1H), 5.78 (t, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.29 – 3.09 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 167.5, 159.5, 147.5, 145.0, 127.4 (q, *J* = 9.1 Hz), 127.1, 125.8 (q, *J* = 277.4 Hz), 121.6, 114.4, 55.4, 51.8, 34.7 (q, *J* = 30.3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ *Z*-isomer (major) -65.42 (t, *J* = 10.7 Hz). *E*-isomer (minor) -65.67 (t, *J* = 10.5 Hz). **ESI-MS**: calculated for $C_{15}H_{15}F_3O_3Na$ $[M + Na]^+$, 323.0866; Found 323.0867.

1-methoxy-4-((*1E,3Z*)-6,6,6-trifluoro-1-phenylhexa-1,3-dien-3-yl) benzene (*Z*-28)



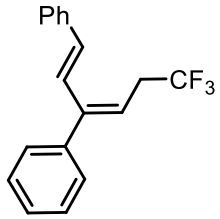
^{1}H NMR (400 MHz, CDCl$_3$) δ *Z*-isomer (major) 7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 3H), 7.11 (d, *J* = 16.1 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 5.53 (t, *J* = 7.5 Hz, 1H), 3.85 (s, 3H), 3.28 – 3.13 (m, 2H). *E*-isomer (minor) 5.87 – 5.70 (m, 1H), 3.87 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 159.4, 144.6, 137.1, 135.1, 133.4, 130.1, 128.8, 127.7(q, *J* = 257.2 Hz), 128.3, 126.8, 124.5, 117.7 (q, *J* = 2.4 Hz), 113.8, 55.5, 33.5 (q, *J* = 29.9 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ *Z*-isomer (major) -65.71 (t, *J* = 10.8 Hz). *E*-isomer (minor) -65.78 (t, *J* = 10.8 Hz). **ESI-MS**: calculated for $C_{19}H_{18}F_3O$ $[M + H]^+$, 319.1304; Found 319.1308.

methyl (*2E,4E*)-7,7,7-trifluoro-4-phenylhepta-2,4-dienoate (*E*-50)



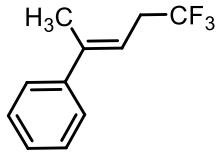
^{1}H NMR (400 MHz, CDCl$_3$) δ *E*-isomer (major) 7.53 (d, *J* = 15.6 Hz, 1H), 7.42 (t, *J* = 7.1 Hz, 2H), 7.36 (d, *J* = 6.8 Hz, 1H), 7.14 – 7.04 (m, 2H), 6.07 (t, *J* = 7.5 Hz, 1H), 5.48 (d, *J* = 15.6 Hz, 1H), 3.72 (s, 3H), 2.81 (qd, *J* = 10.6, 7.3 Hz, 2H). *Z*-isomer (minor) 7.72 (d, *J* = 15.6 Hz, 1H), 7.25 – 7.20 (m, 3H), 5.86 (s, 0H), 5.85 – 5.77 (m, 1H), 3.76 (s, 1H), 3.32 – 3.16 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 167.4, 147.1, 135.1, 129.1, 129.0, 128.7, 128.6, 128.3, 127.4 (q, *J* = 3.1 Hz), 125.7 (q, *J* = 277.0 Hz), 121.8, 51.8, 34.7 (q, *J* = 29.8 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ *Z*-isomer (minor) -65.44 (t, *J* = 10.6 Hz). *E*-isomer (major) -65.64 (t, *J* = 10.5 Hz). **ESI-MS**: calculated for $C_{14}H_{13}F_3O_2Na$ $[M + Na]^+$, 271.0940; Found 271.0957.

((*1E,3E*)-6,6,6-trifluorohexa-1,3-diene-1,3-diyl) dibenzene (*E*-51)



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.29 (m, 10H), 7.13 (d, *J* = 16.0 Hz, 1H), 6.49 (d, *J* = 16.1 Hz, 1H), 5.56 (t, *J* = 7.5 Hz, 1H), 3.23 (qd, *J* = 10.7, 7.5 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 145.1, 141.0, 137.0, 135.2, 129.0, 127.9, 126.9, 126.3 (q, *J* = 275.9 Hz), 124.2, 118.4 (q, *J* = 3.9 Hz), 33.5 (q, *J* = 29.6 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ *Z*-isomer (minor) -65.37 (t, *J* = 10.8 Hz). *E*-isomer (major) -65.75 (t, *J* = 10.6 Hz). **EI-MS**: calculated for $[C_{18}H_{15}F_3]$, 288.11204; Found 288.11249.

(*E*)-(5,5,5-trifluoropent-2-en-2-yl) benzene (*E*-52)



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 5.73 (td, *J* = 7.4, 1.6 Hz, 1H), 3.02 (qd, *J* = 10.8, 7.2 Hz, 2H), 2.09 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 142.9, 141.6, 128.5, 127.7, 126.5 (d, *J* = 276.6 Hz), 126.0, 115.2 (q, *J* = 3.4 Hz), 33.8 (q, *J* = 29.7 Hz), 16.5. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -65.94 (t, *J* = 10.9 Hz).

11. Reference

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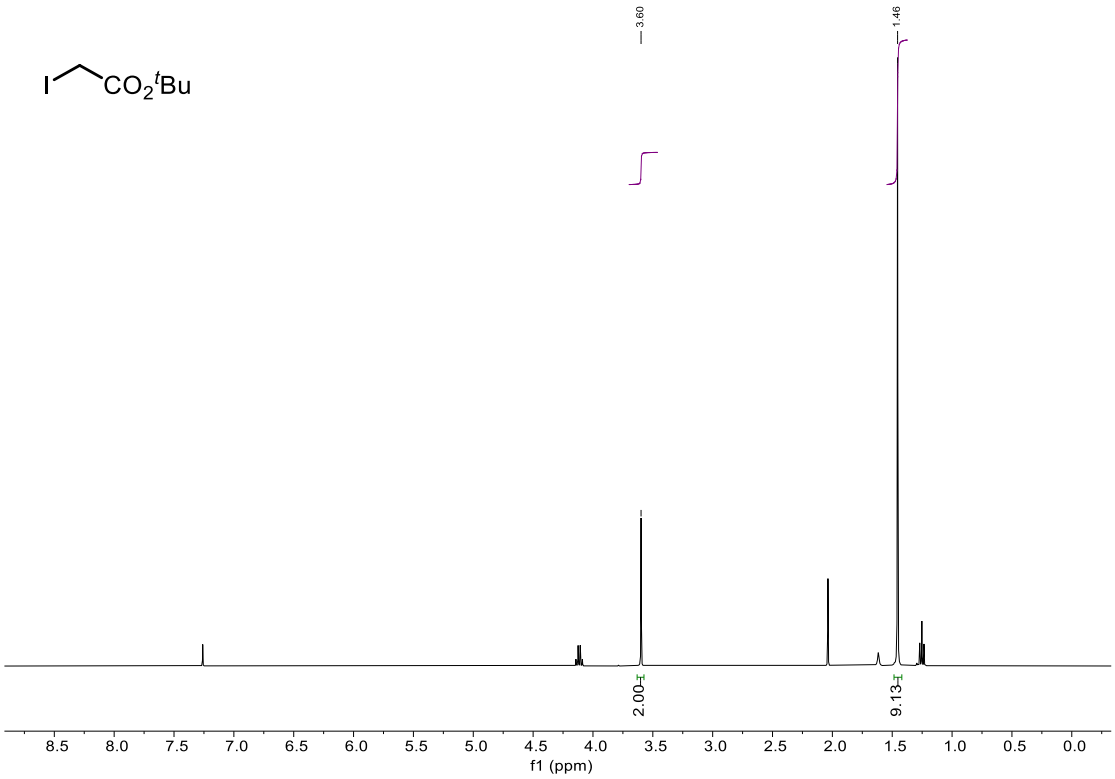
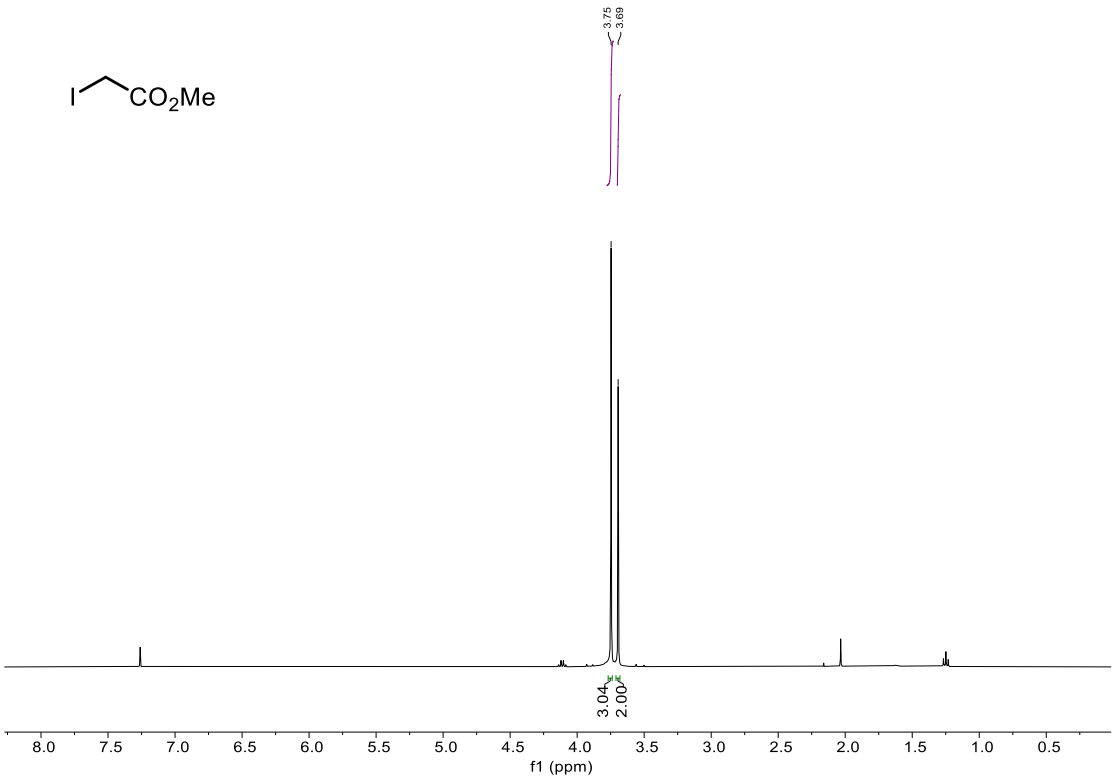
12. NMR spectra of the starting materials and products

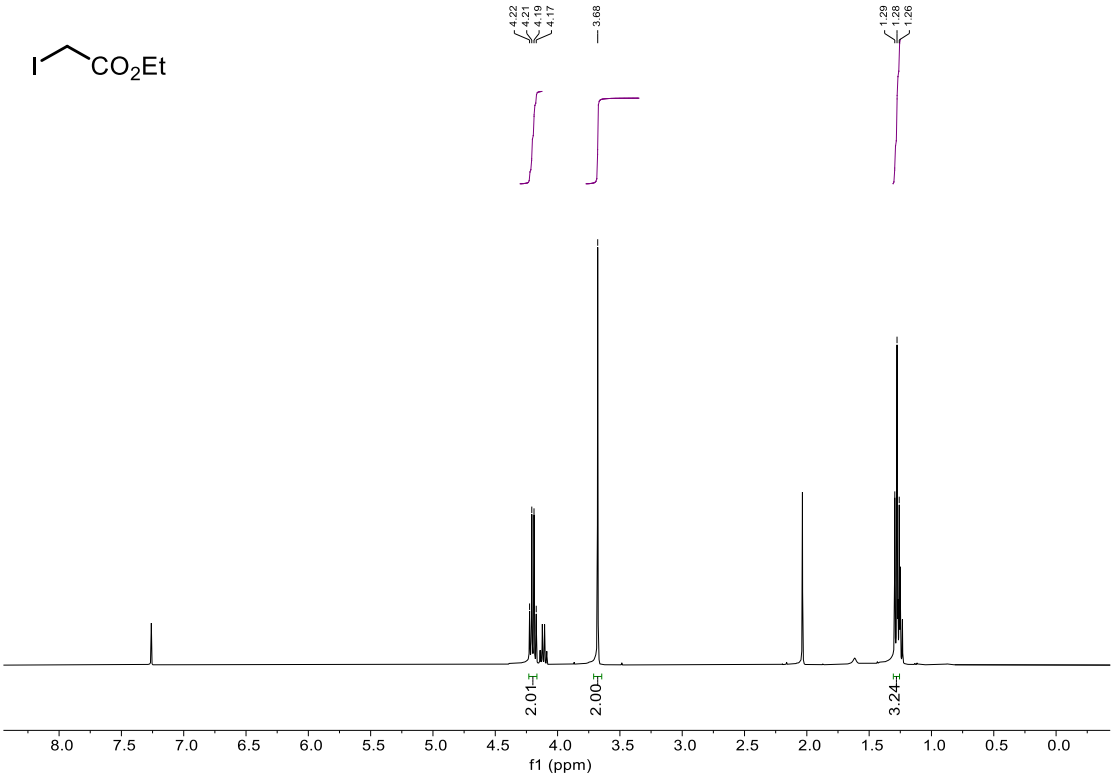
^{1}H NMR (400 MHz, CDCl3) of SP-1



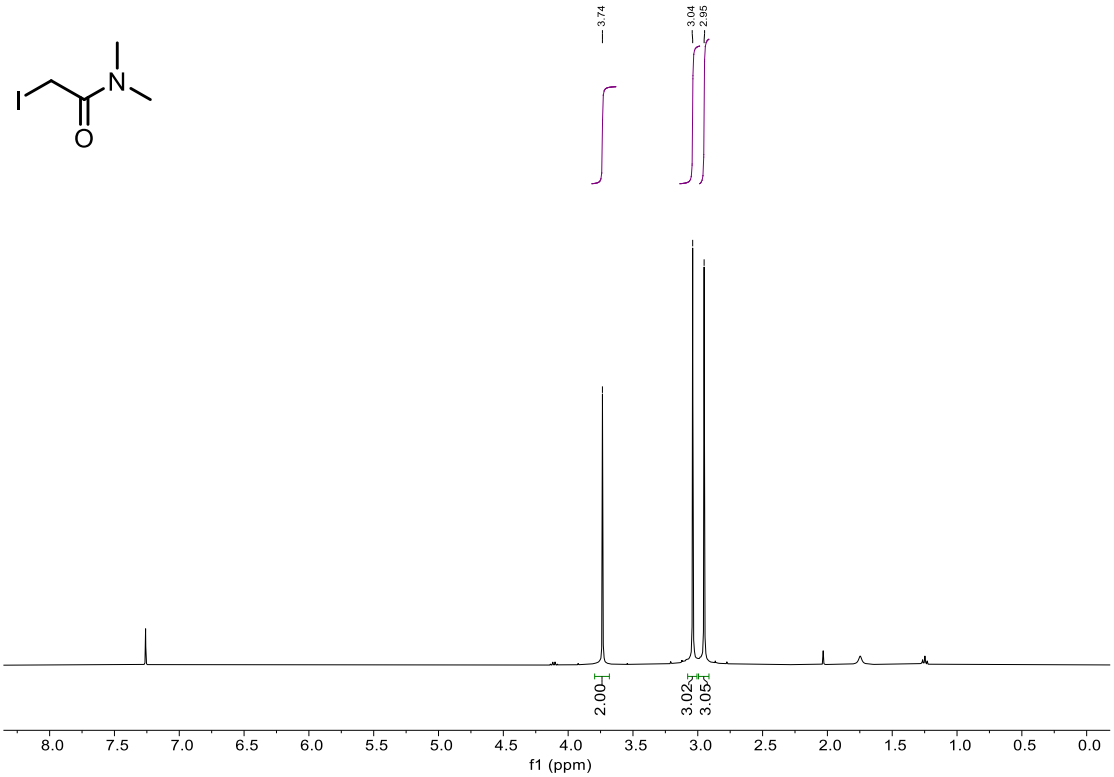
^{1}H NMR (400 MHz, CDCl3) of SP-2



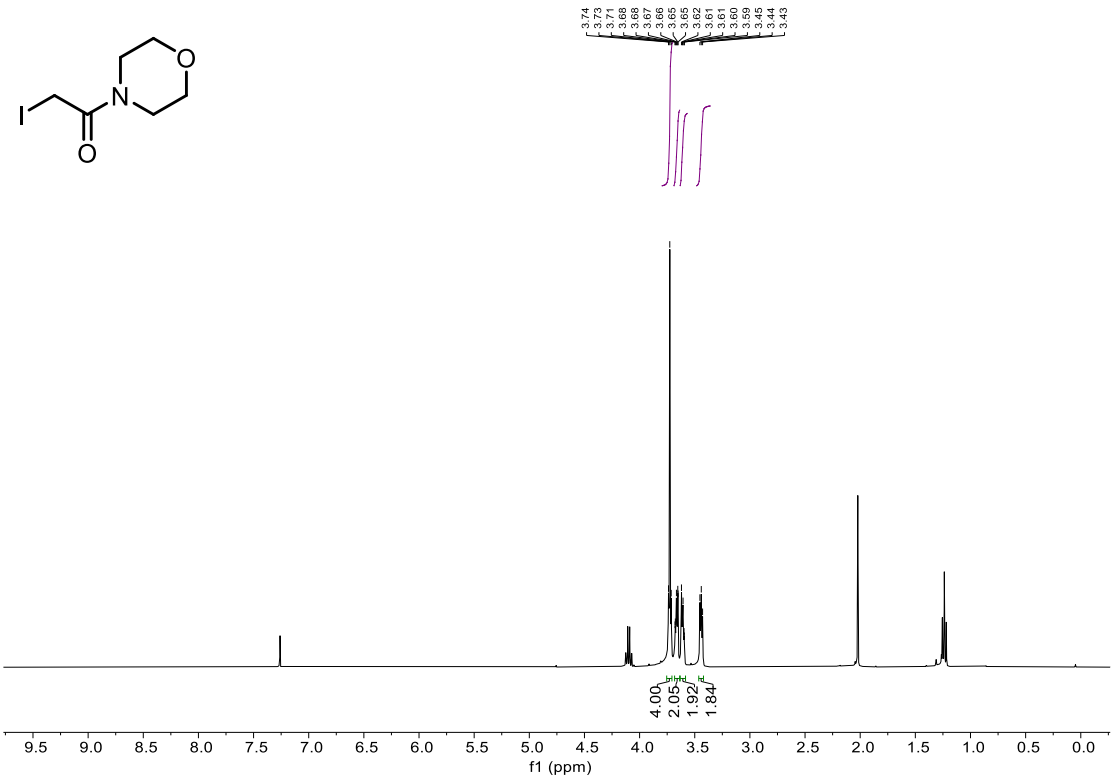
^{1}H NMR (400 MHz, CDCl3) of SP-3



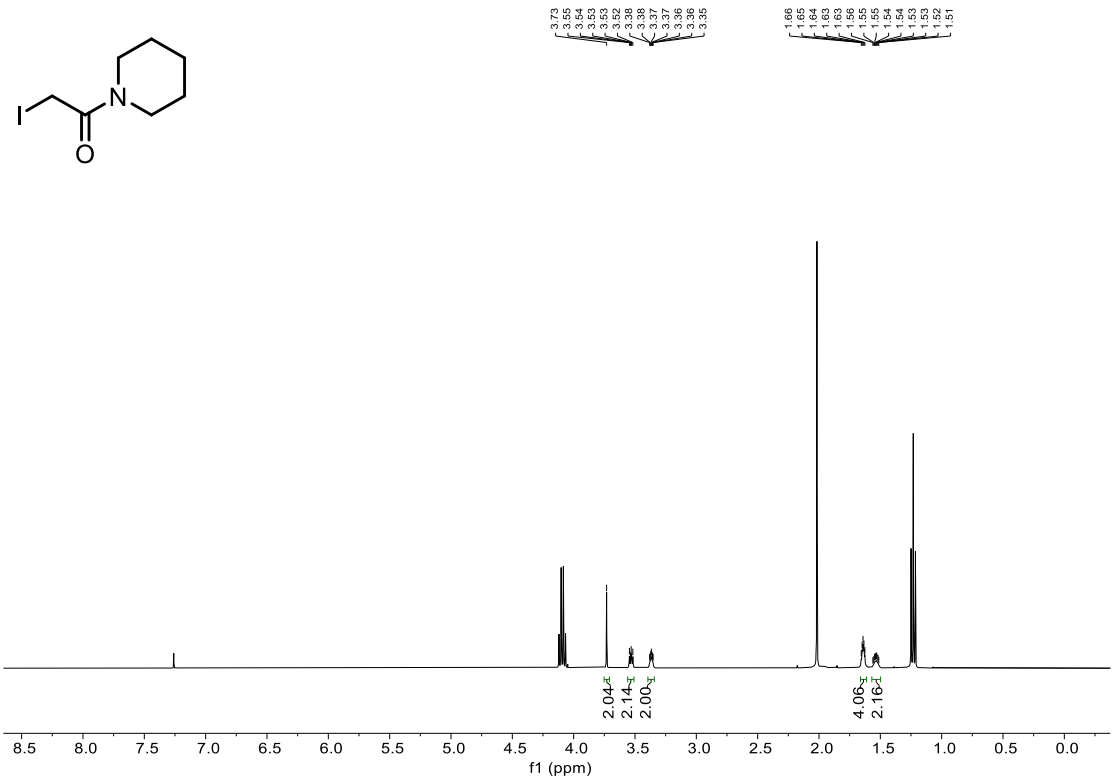
^{1}H NMR (400 MHz, CDCl3) of SP-4



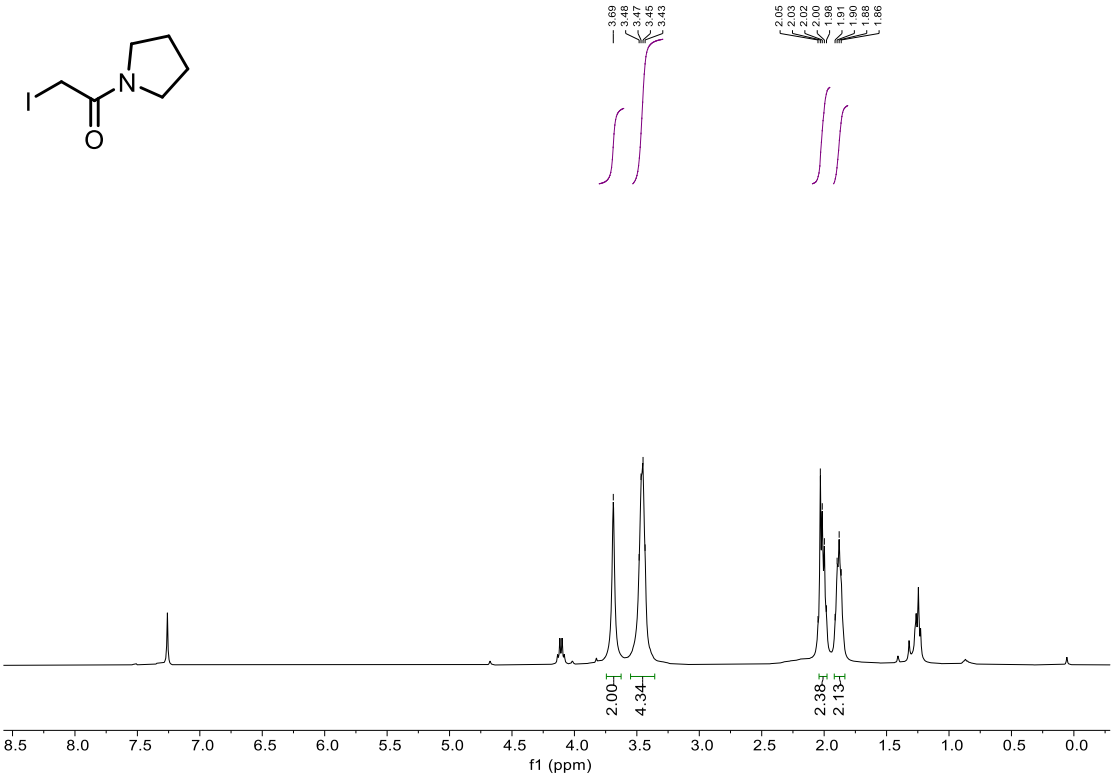
^{1}H NMR (400 MHz, CDCl3) of SP-5



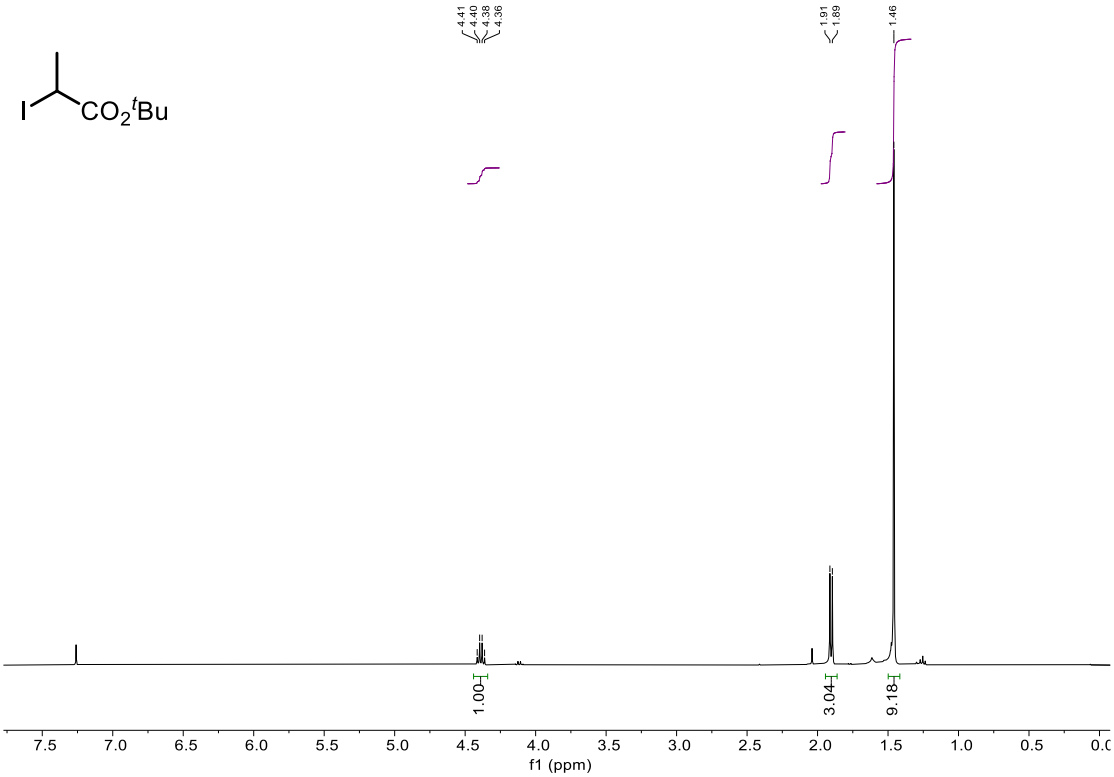
^{1}H NMR (400 MHz, CDCl3) of SP-6



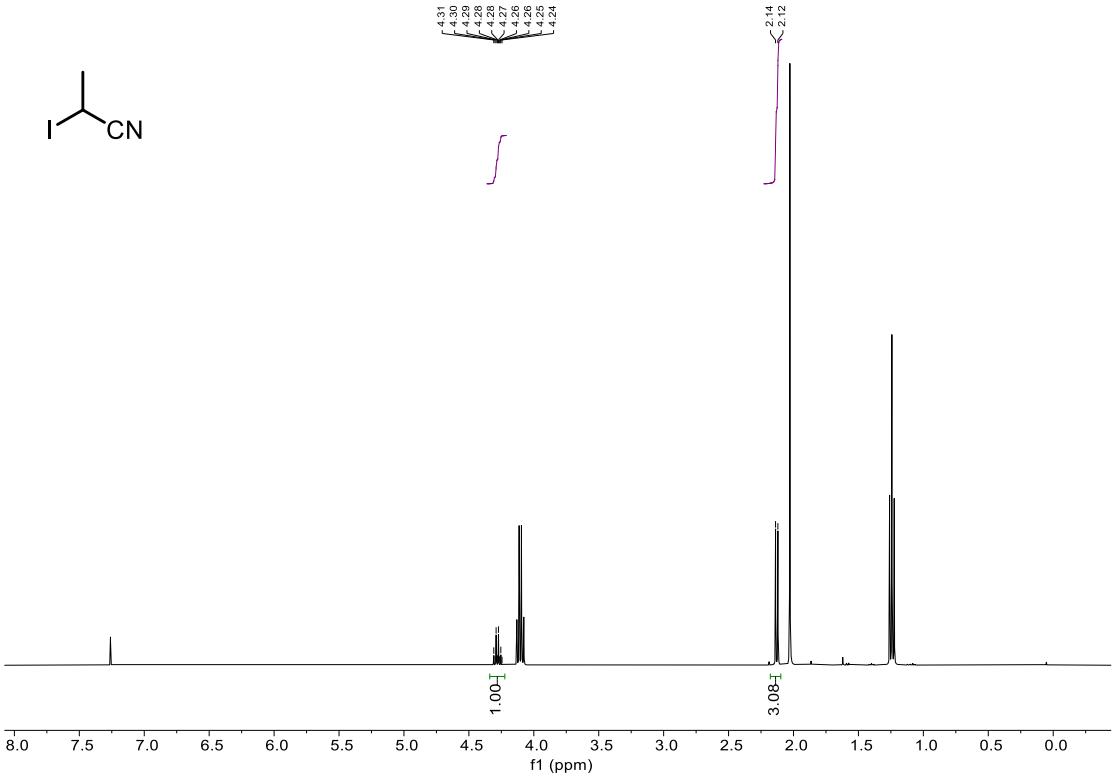
^{1}H NMR (400 MHz, CDCl3) of SP-7



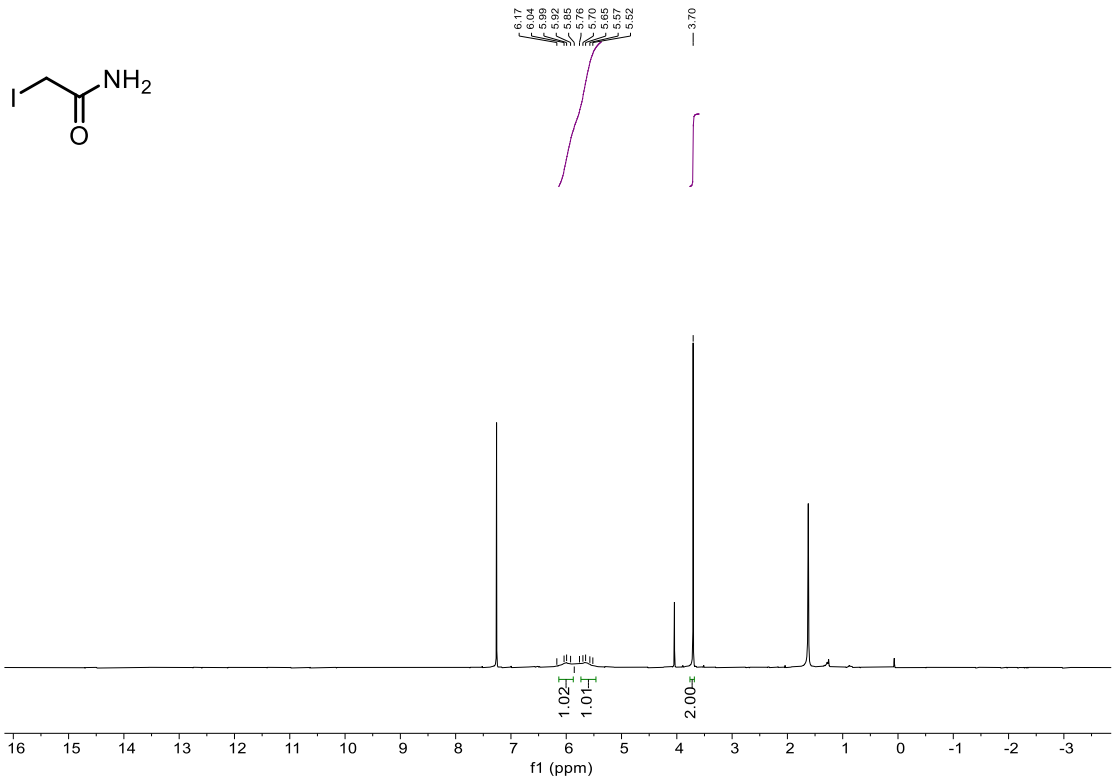
^{1}H NMR (400 MHz, CDCl3) of SP-8



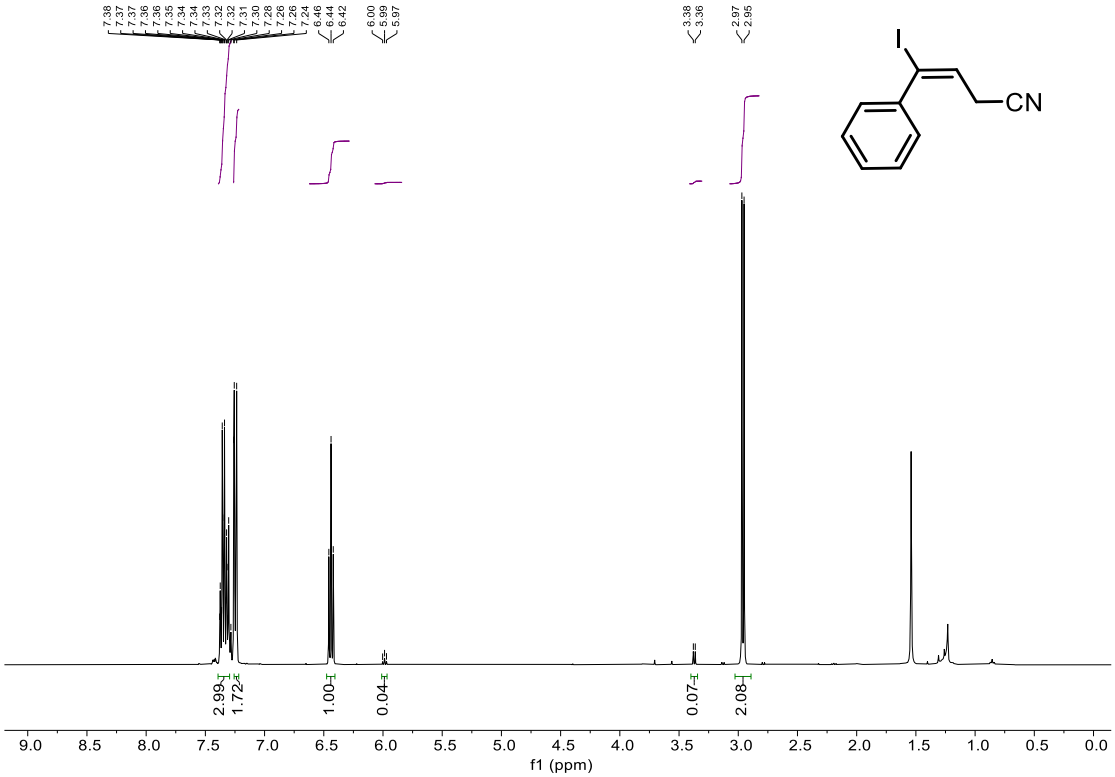
^{1}H NMR (400 MHz, CDCl3) of SP-9



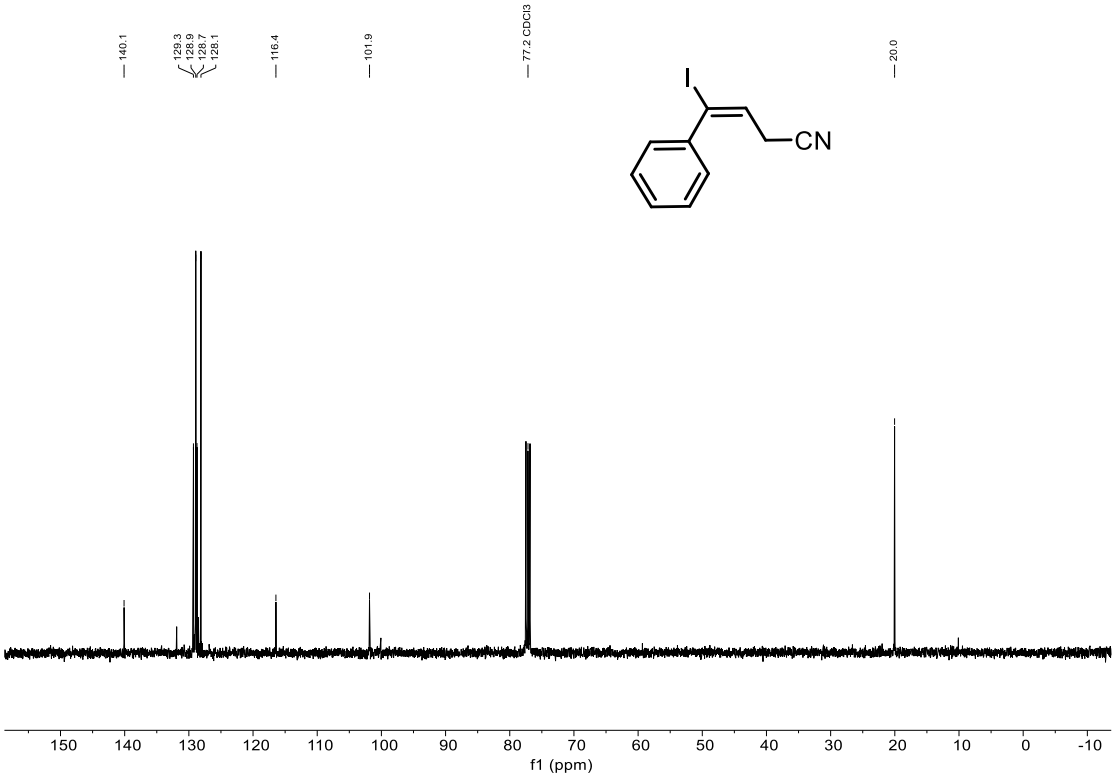
^{1}H NMR (400 MHz, CDCl3) of SP-10



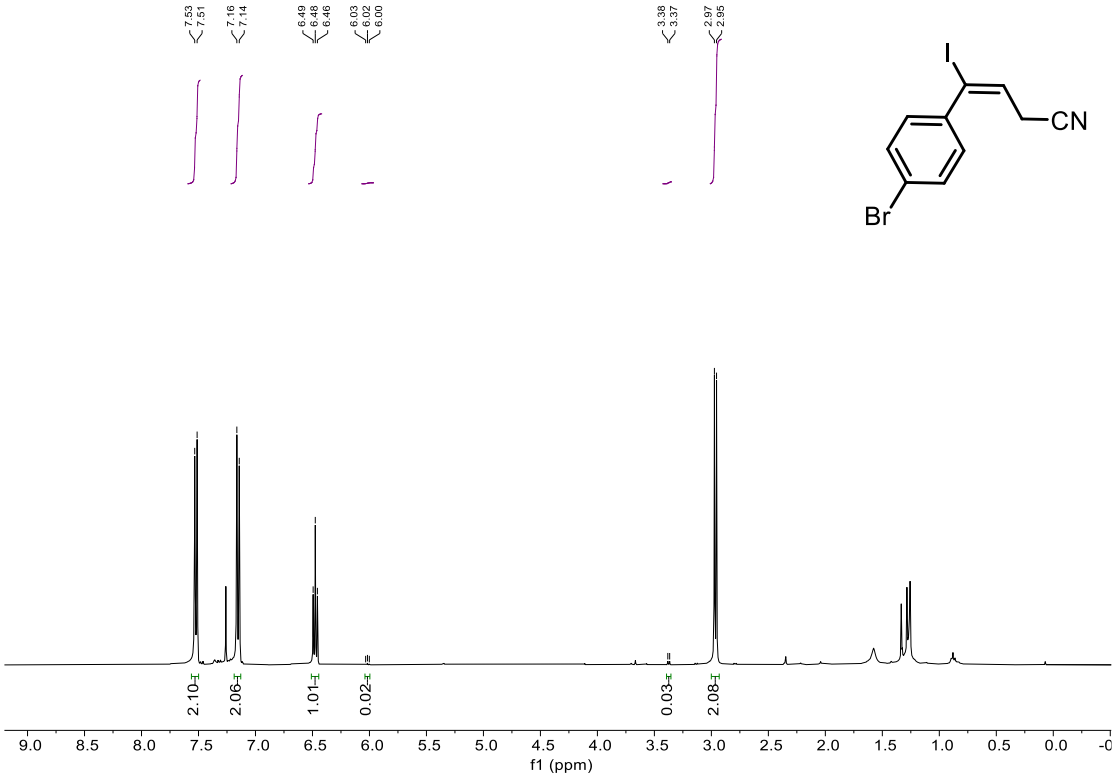
^{1}H NMR (400 MHz, CDCl3) of *E-1*



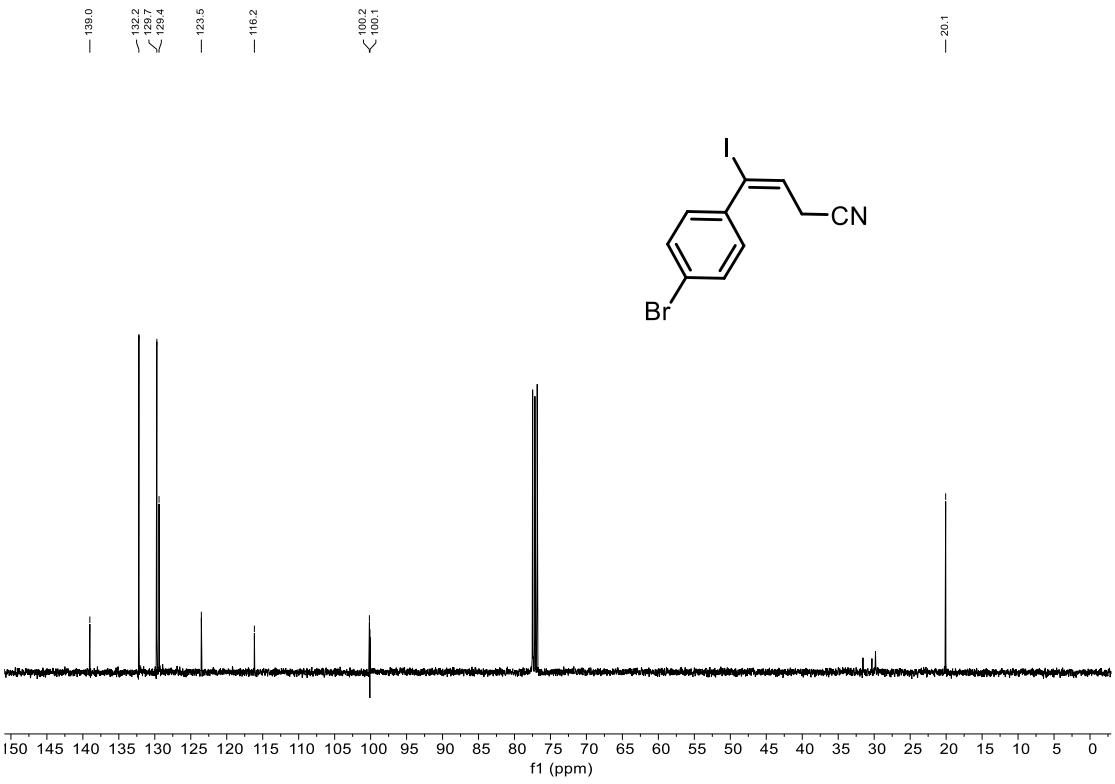
^{13}C NMR (101 MHz, $CDCl_3$) of *E-1*



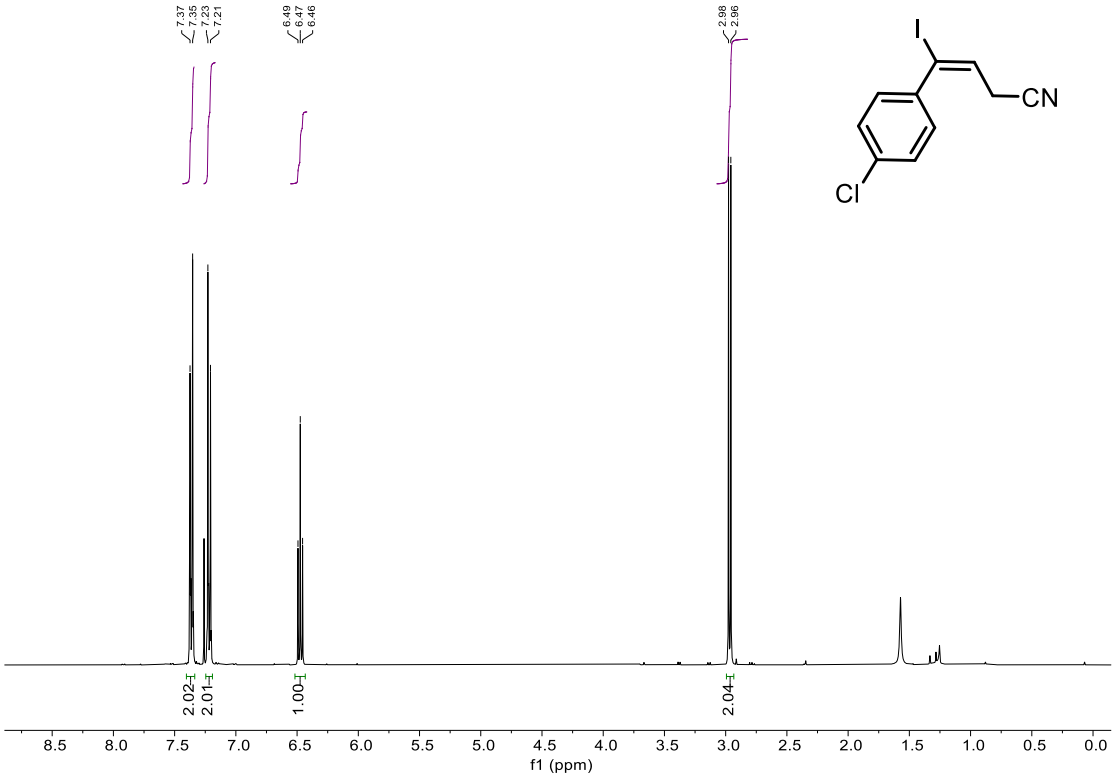
^{1}H NMR (400 MHz, CDCl3) of *E-2*



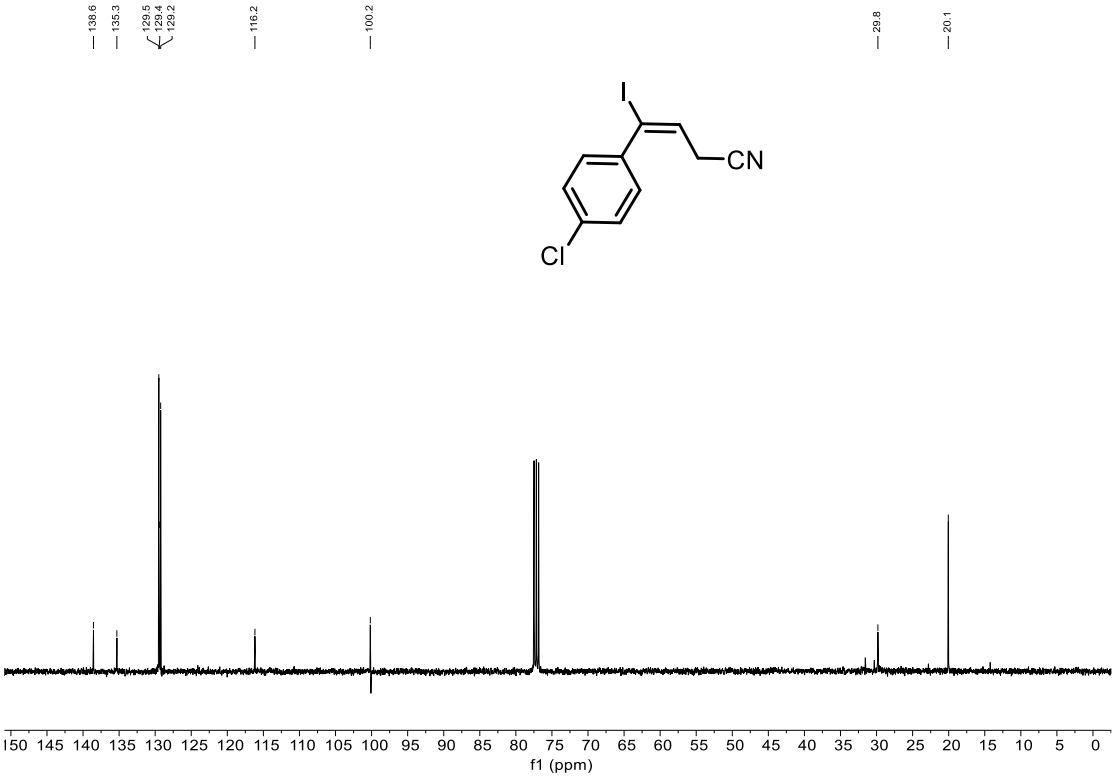
^{13}C NMR (101 MHz, $CDCl_3$) of *E-2*



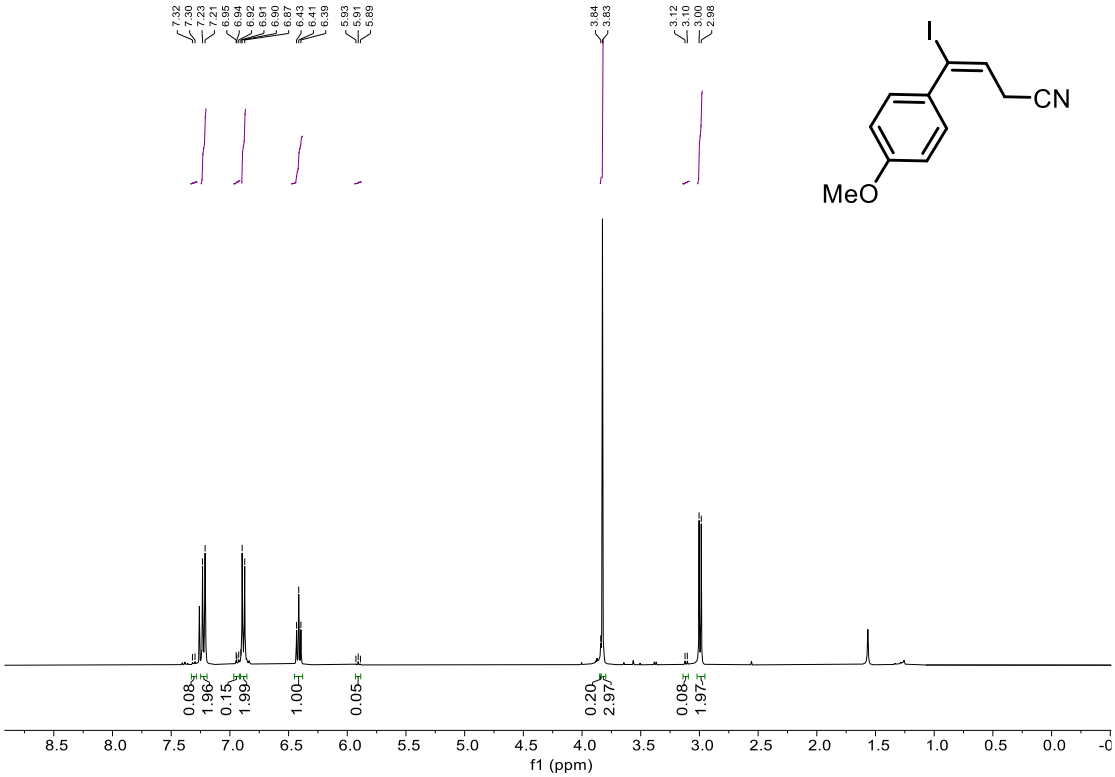
^{1}H NMR (400 MHz, CDCl3) of *E-3*



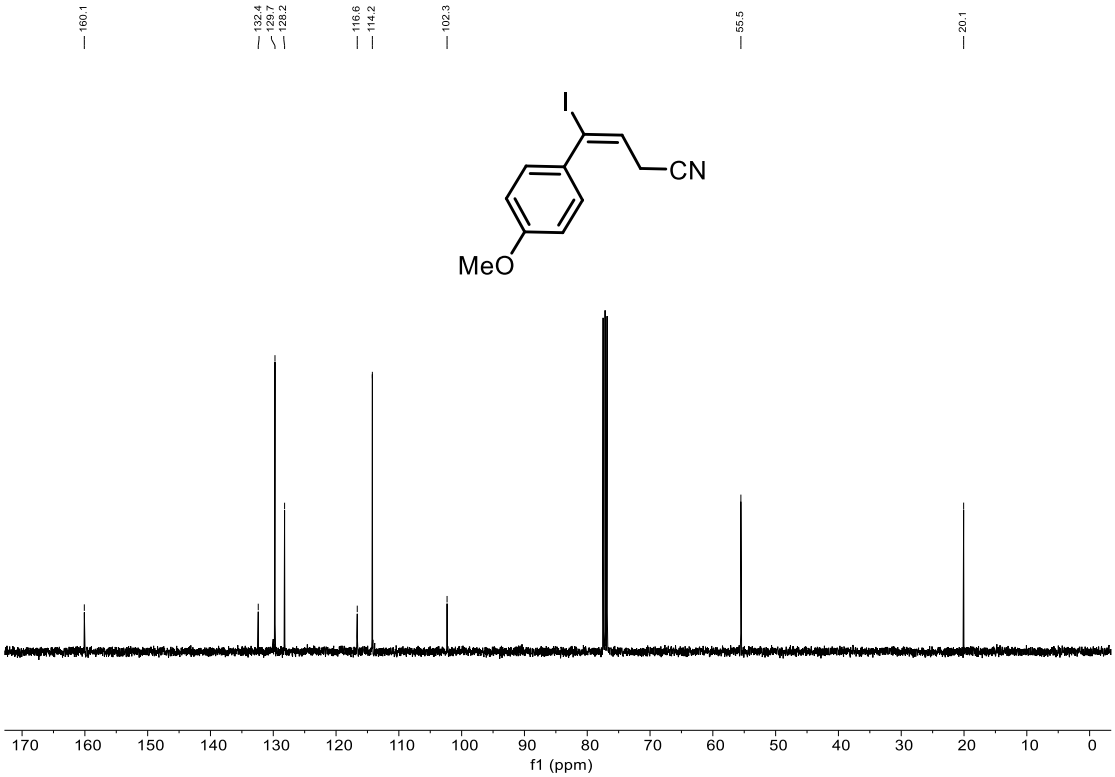
^{13}C NMR (101 MHz, $CDCl_3$) of *E-3*



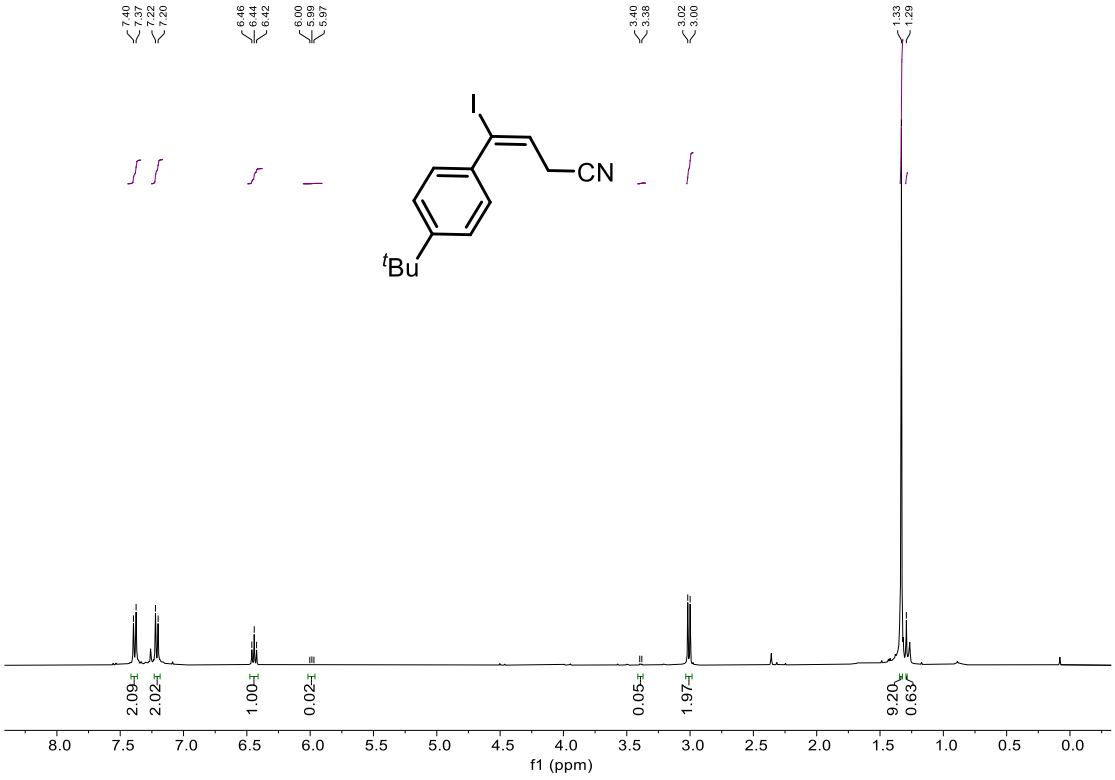
^{1}H NMR (400 MHz, CDCl3) of *E-4*



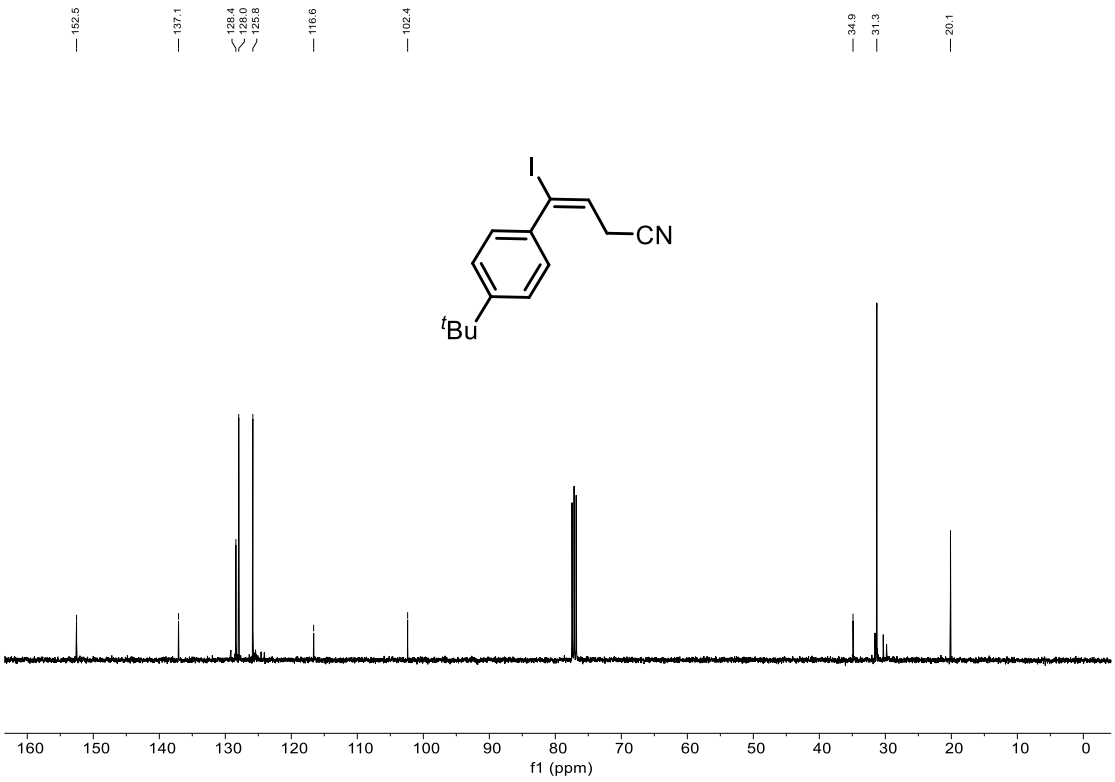
^{13}C NMR (101 MHz, $CDCl_3$) of *E-4*



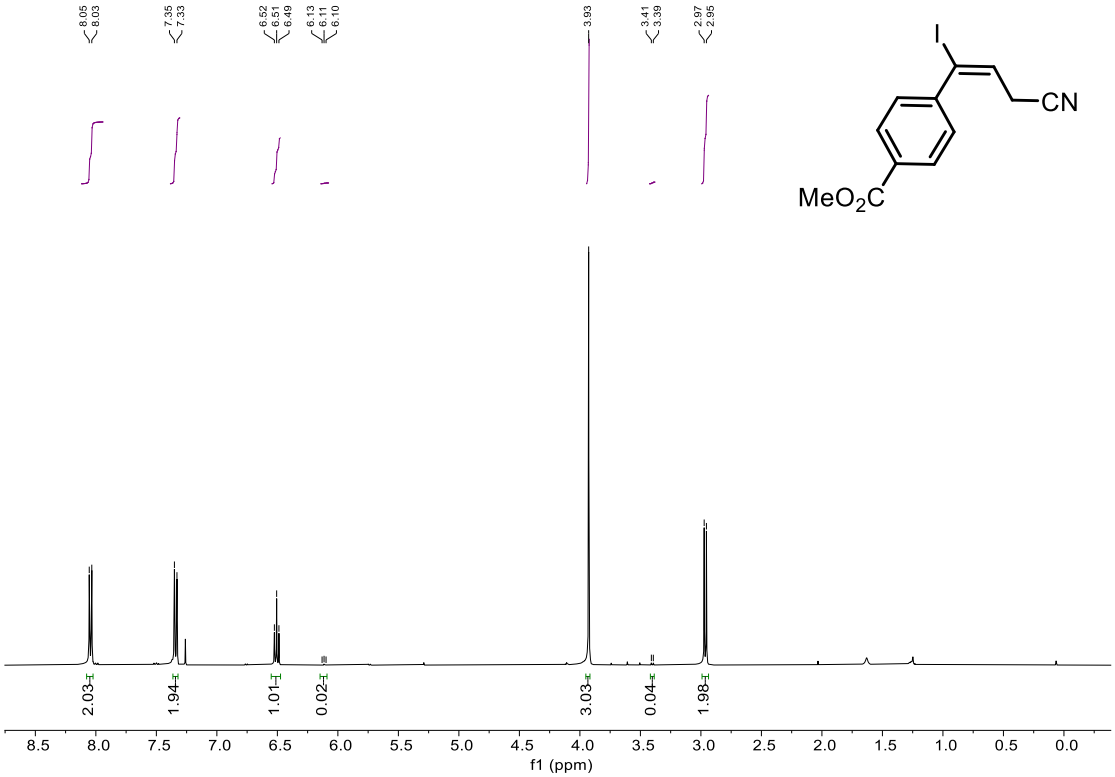
^{1}H NMR (400 MHz, CDCl3) of *E-5*



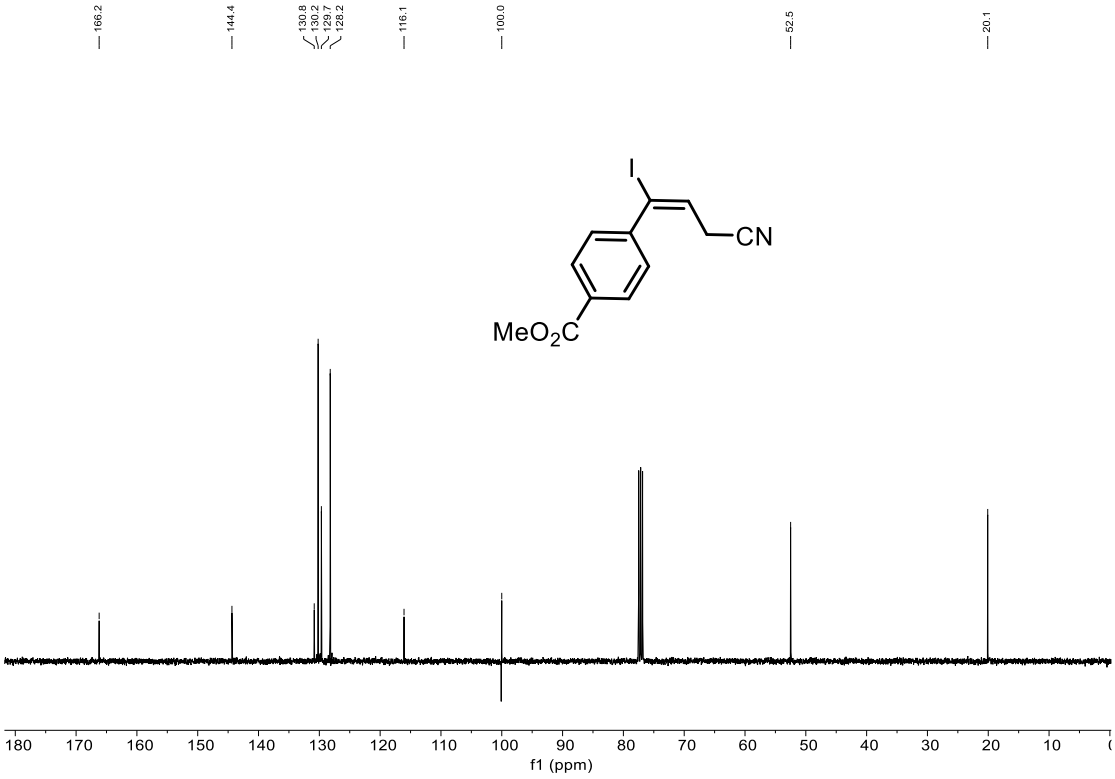
^{13}C NMR (101 MHz, CDCl$_3$) of *E-5*



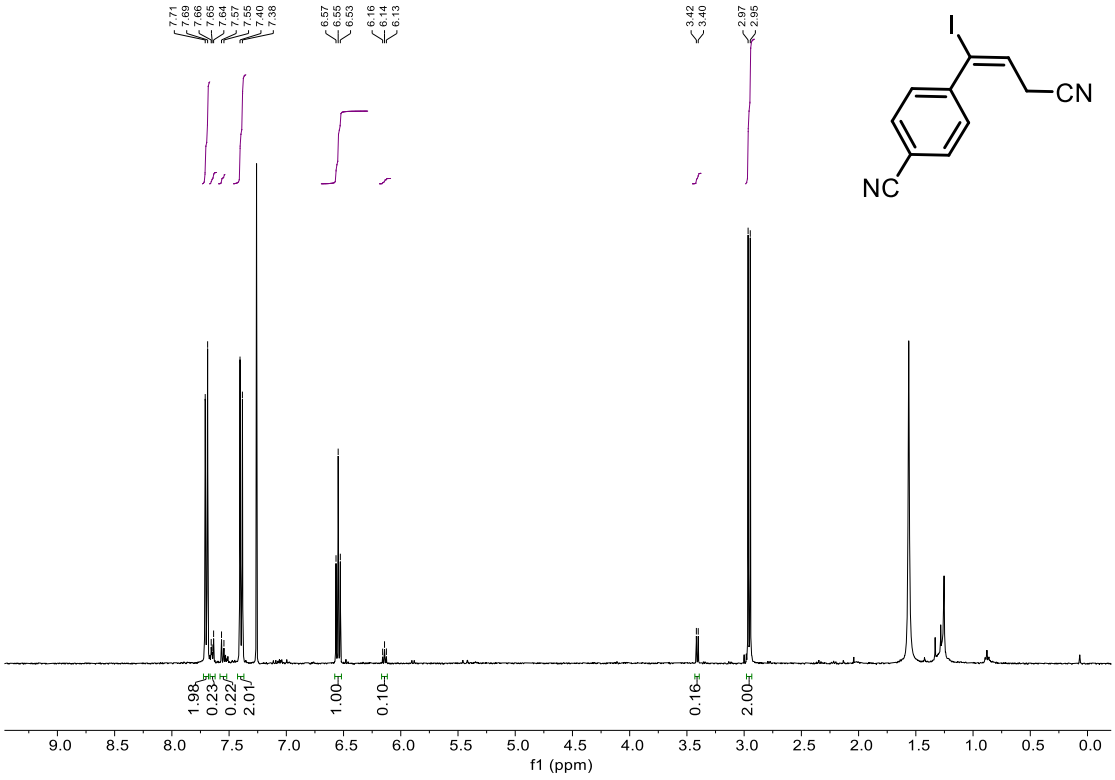
^{1}H NMR (400 MHz, CDCl3) of *E-6*



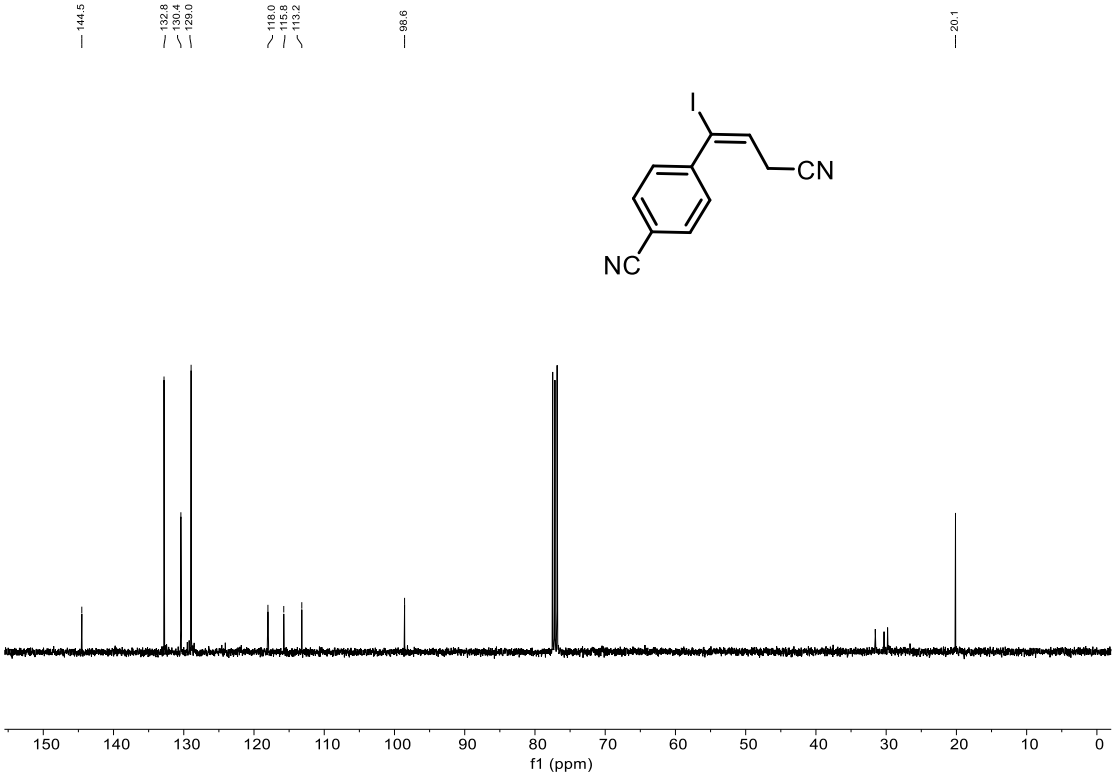
^{13}C NMR (101 MHz, CDCl$_3$) of *E-6*



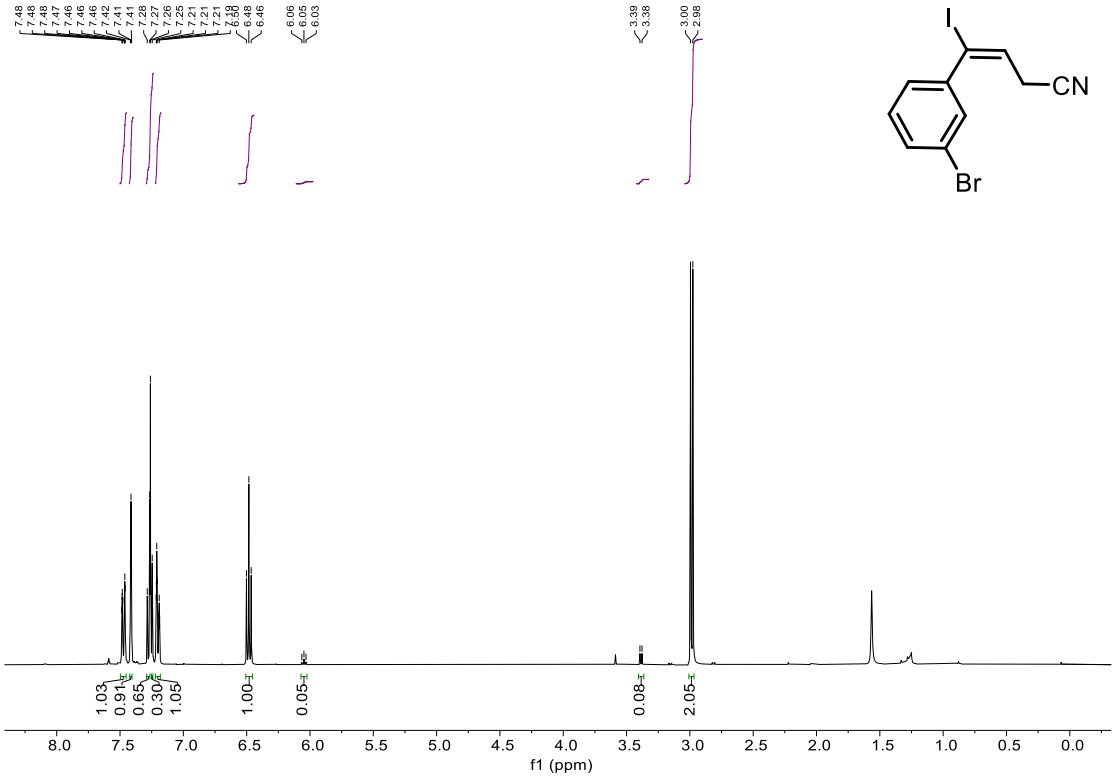
^{1}H NMR (400 MHz, CDCl3) of *E-7*



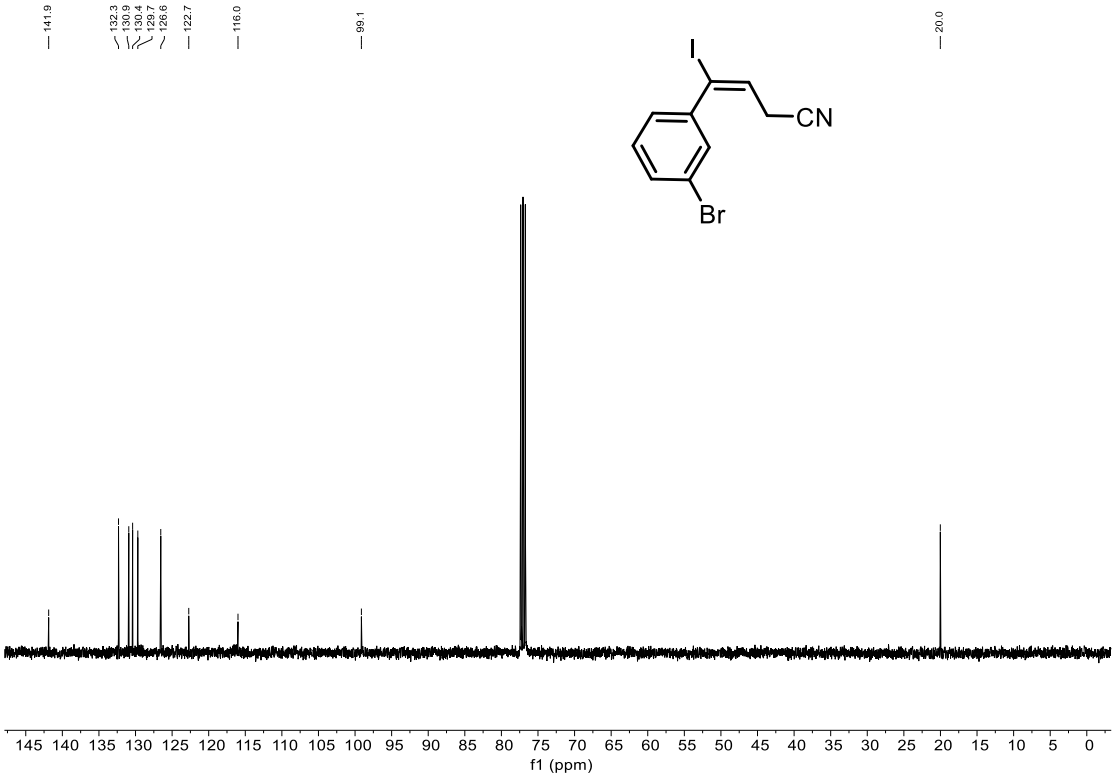
^{13}C NMR (101 MHz, $CDCl_3$) of *E-7*



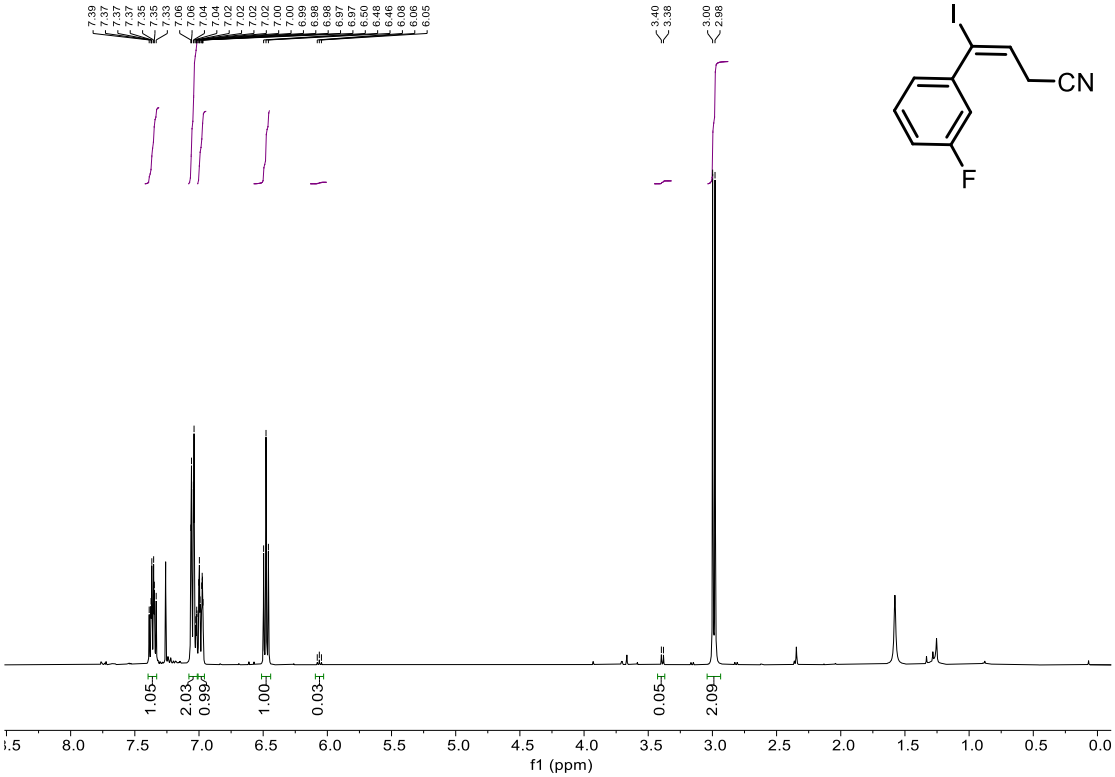
^{1}H NMR (400 MHz, CDCl3) of *E-8*



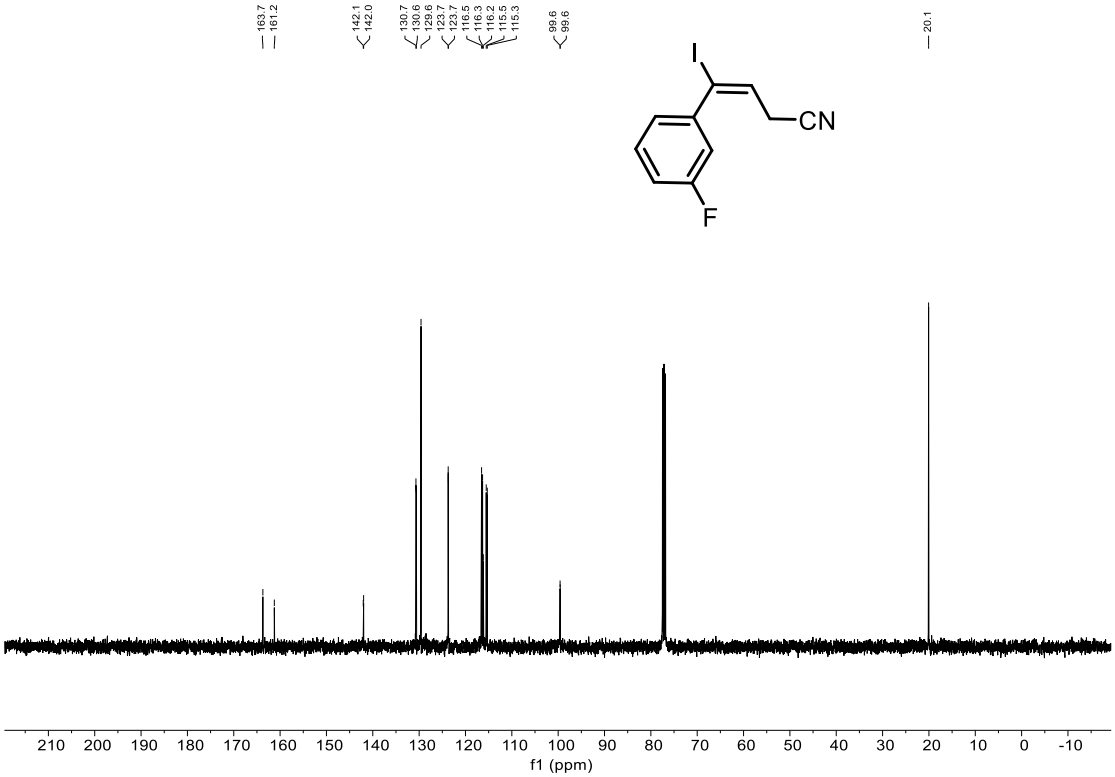
^{13}C NMR (101 MHz, $CDCl_3$) of *E-8*



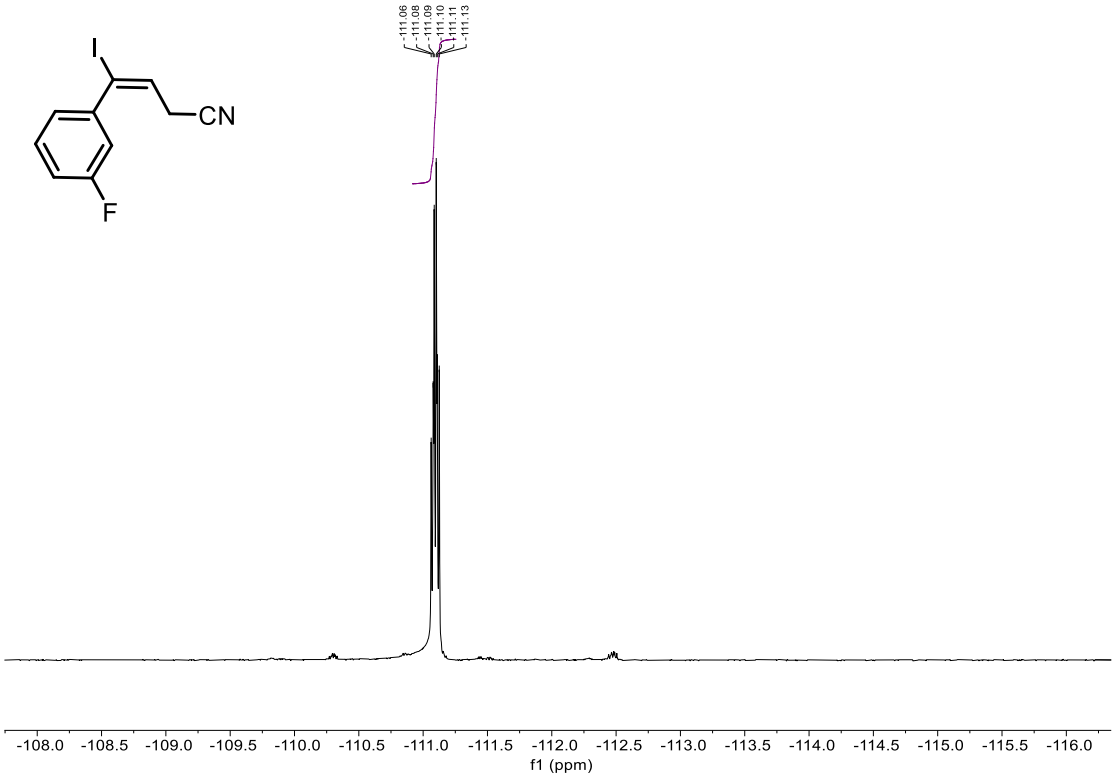
^{1}H NMR (400 MHz, CDCl3) of *E-9*



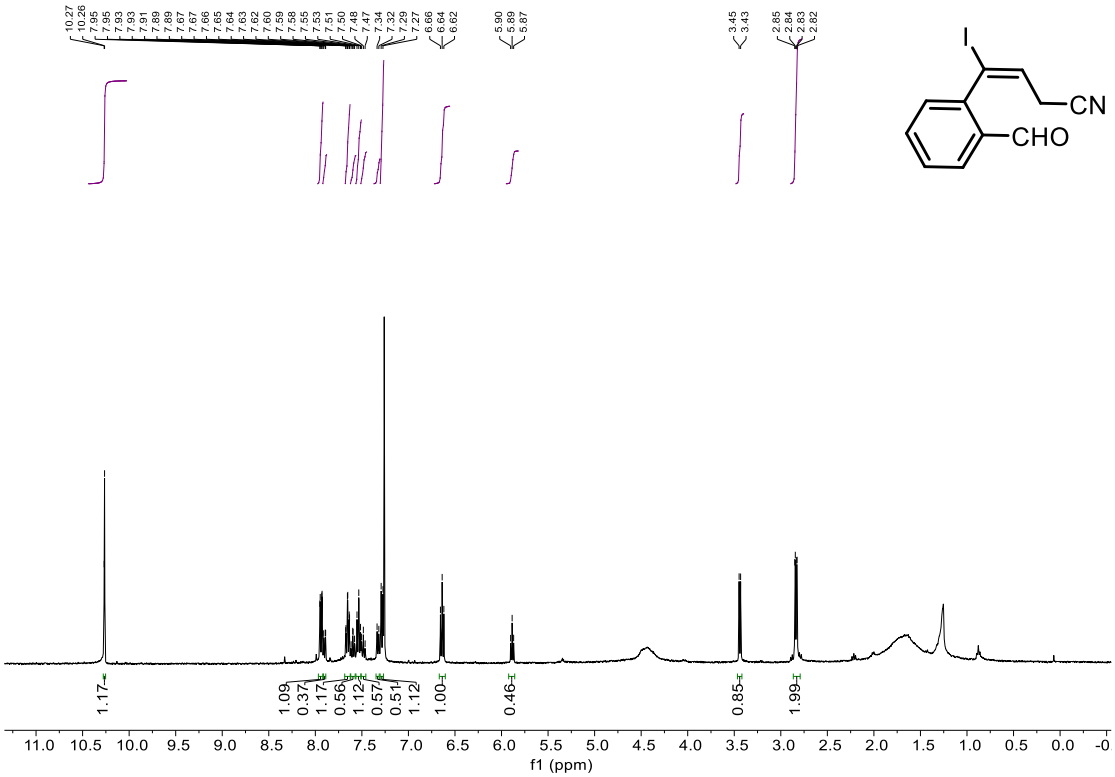
^{13}C NMR (101 MHz, $CDCl_3$) of *E-9*



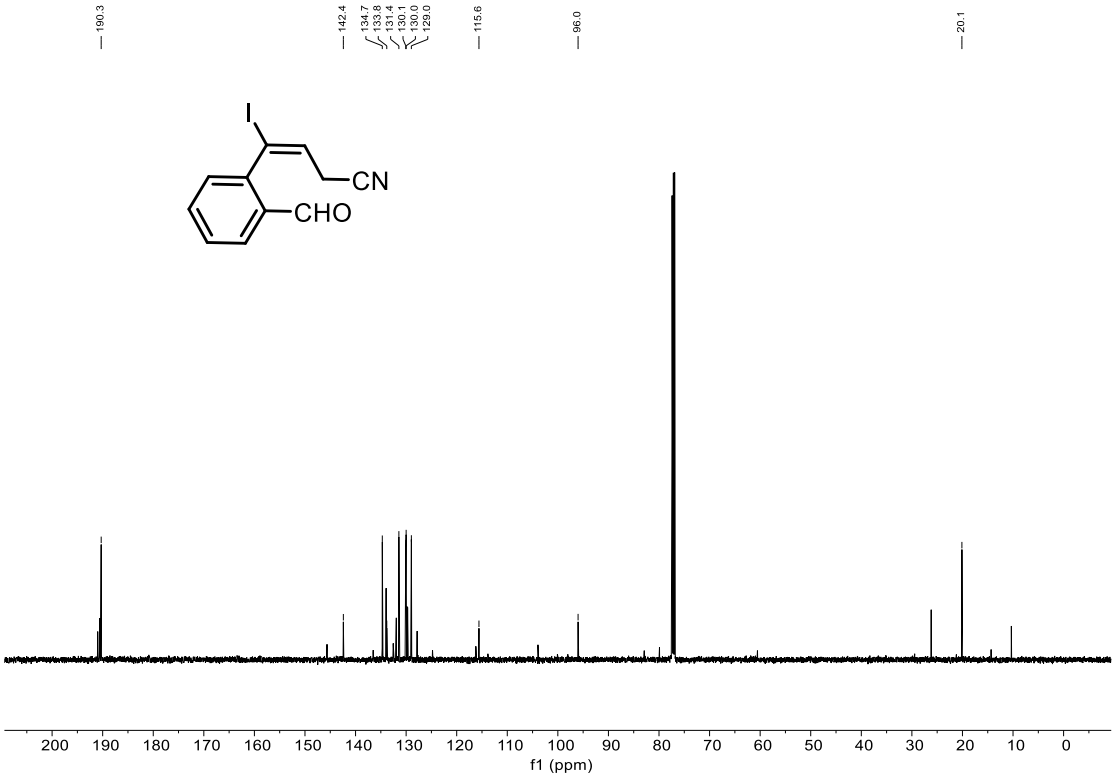
^{19}F NMR (376 MHz, CDCl3) of *E-9*



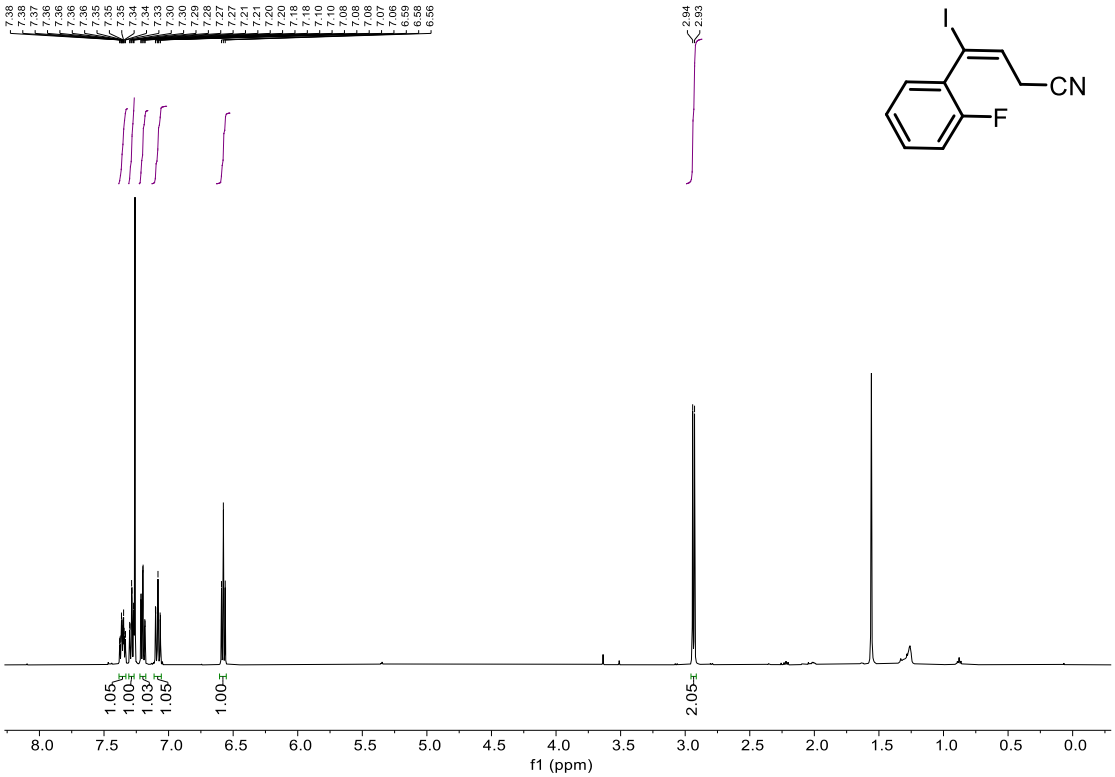
^{1}H NMR (400 MHz, CDCl3) of *E-10*



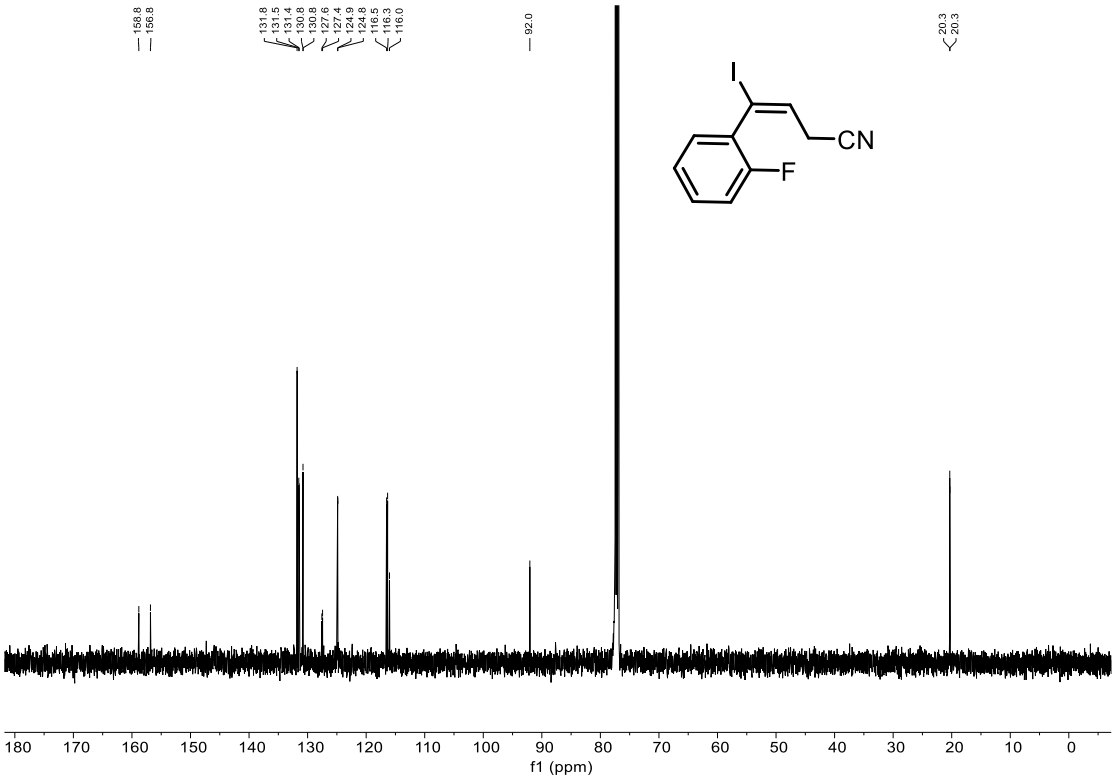
^{13}C NMR (126 MHz, $CDCl_3$) of *E-10*



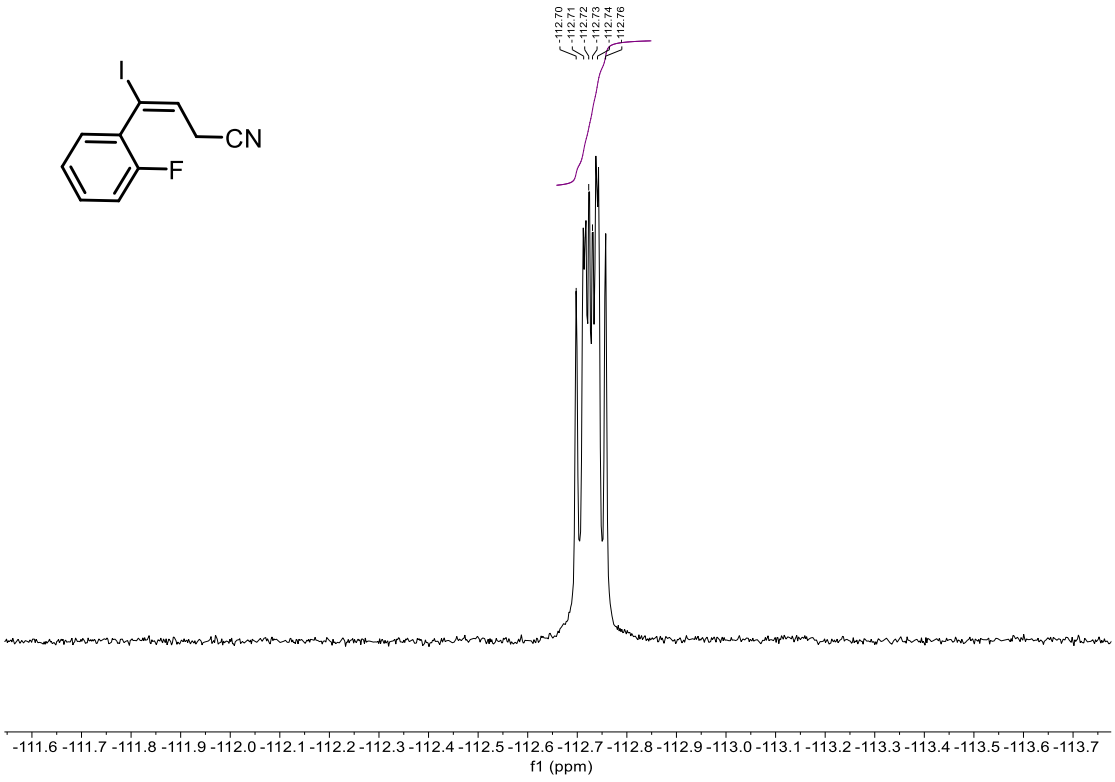
^{1}H NMR (500 MHz, CDCl3) of *E-11*



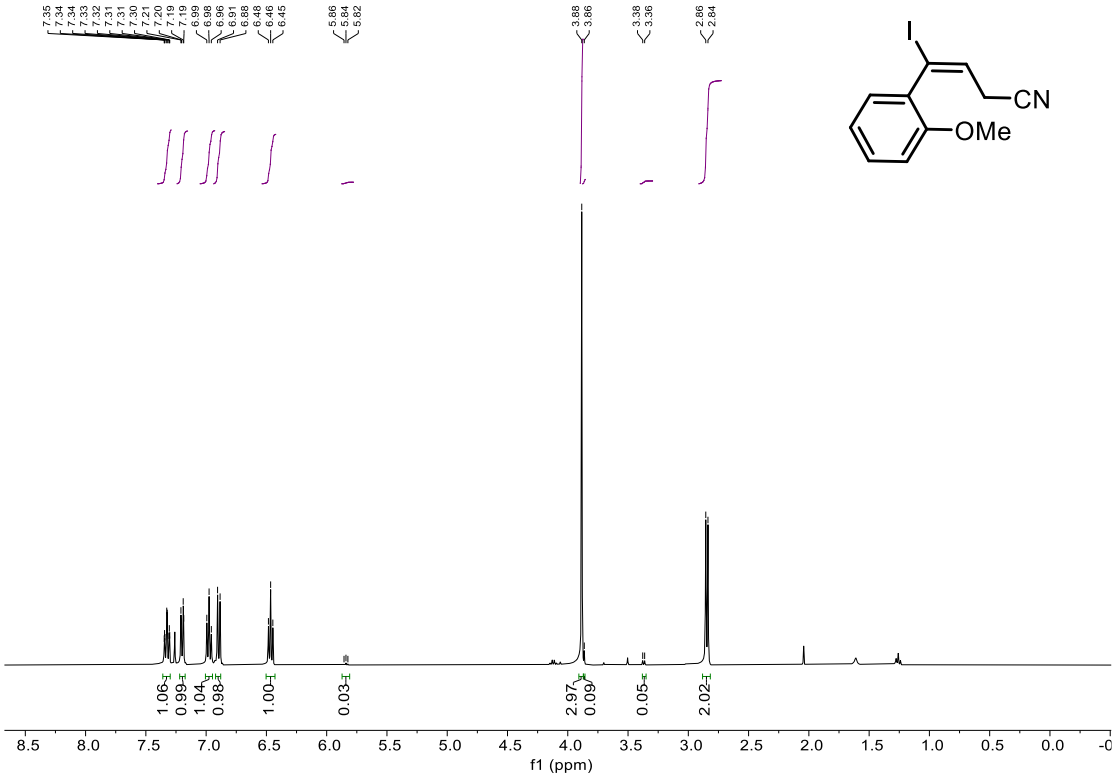
^{13}C NMR (126 MHz, $CDCl_3$) of *E-11*



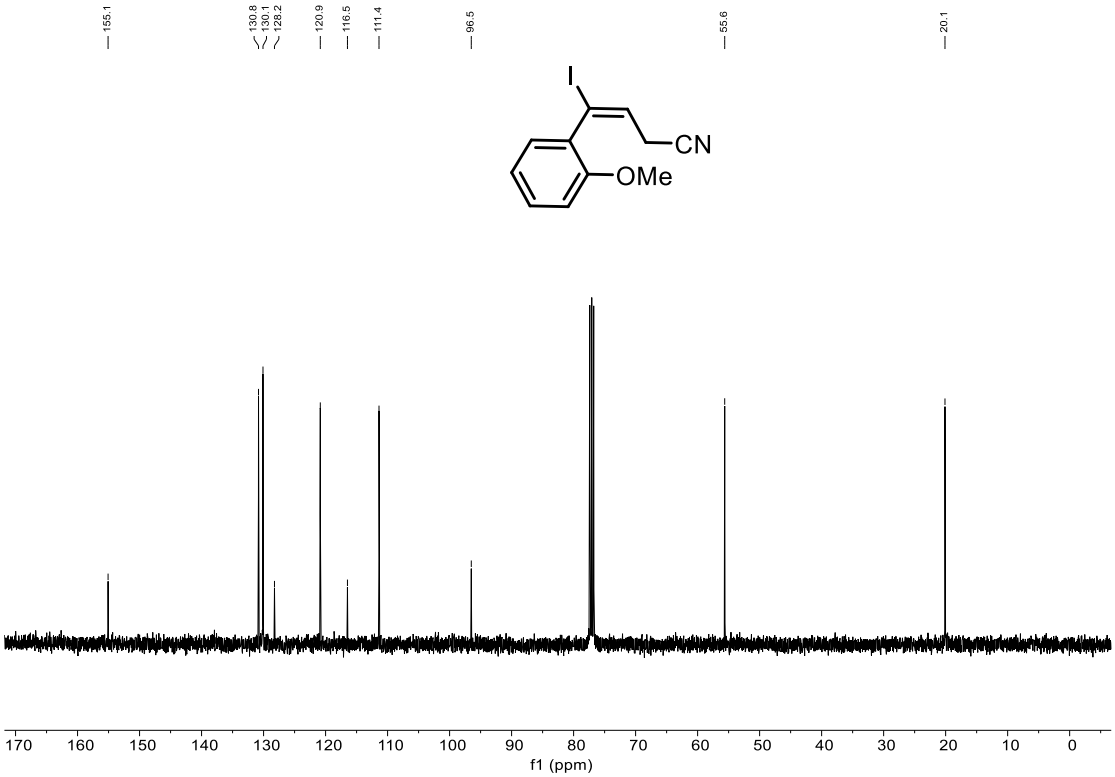
^{19}F NMR (376 MHz, CDCl3) of *E-11*



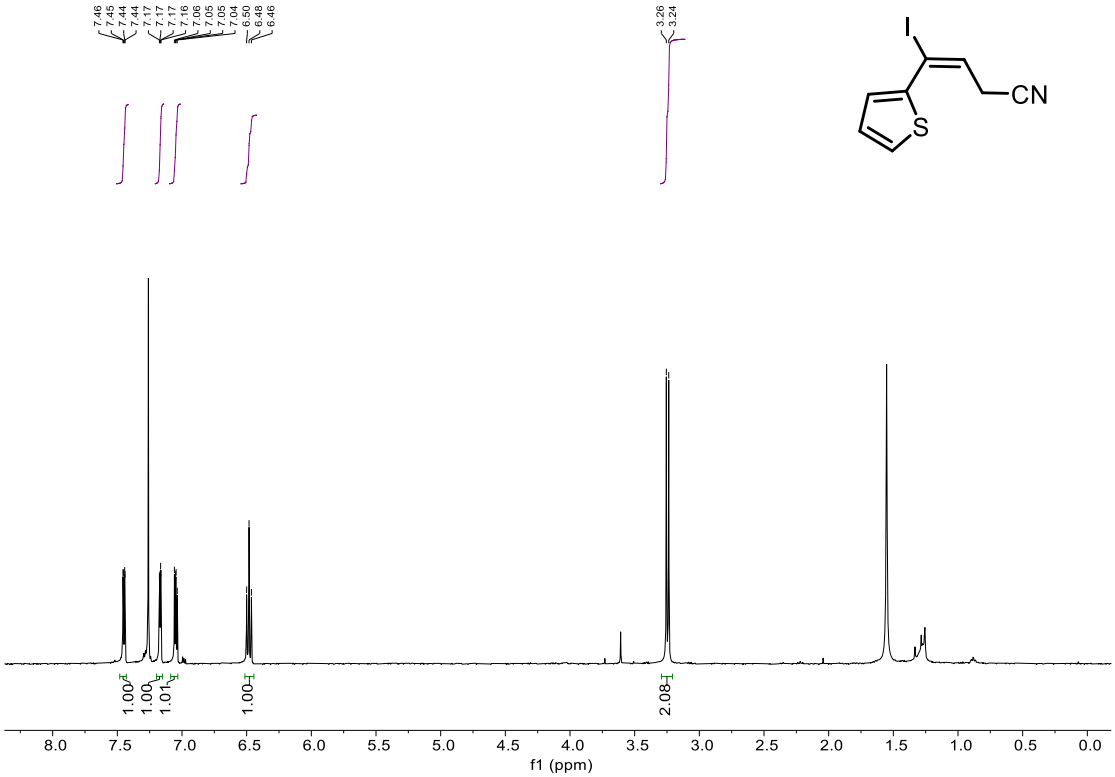
^{1}H NMR (400 MHz, CDCl3) of *E-12*



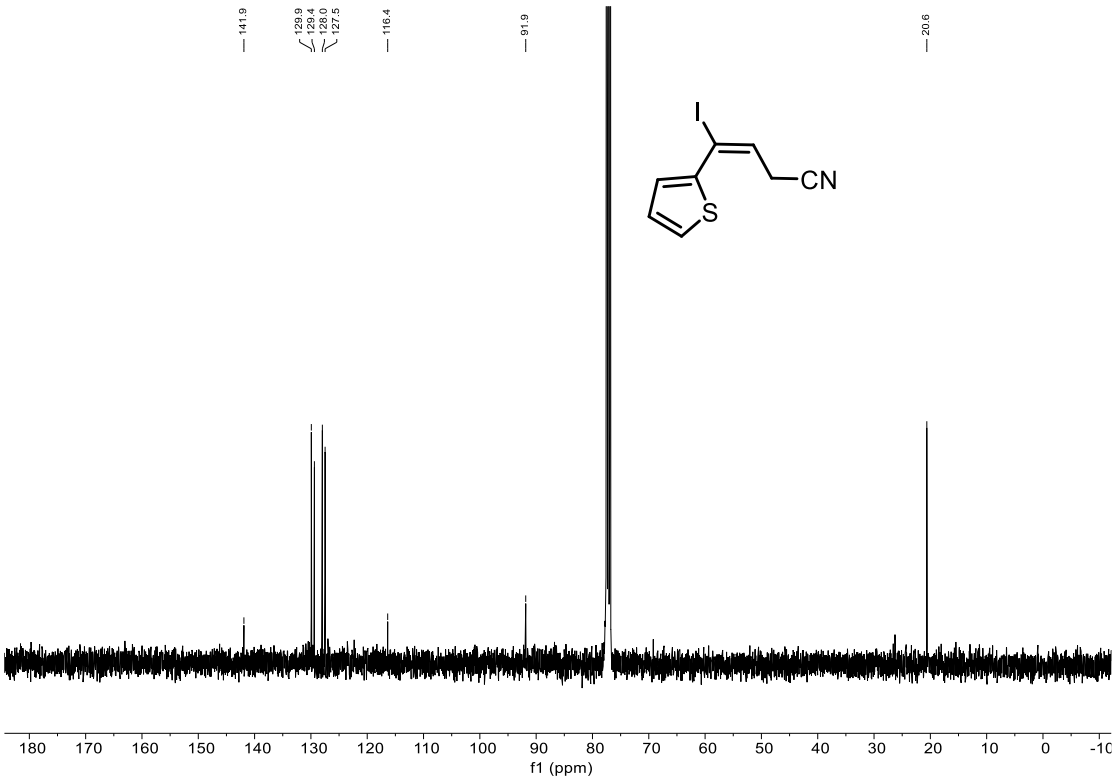
^{13}C NMR (101 MHz, $CDCl_3$) of *E-12*



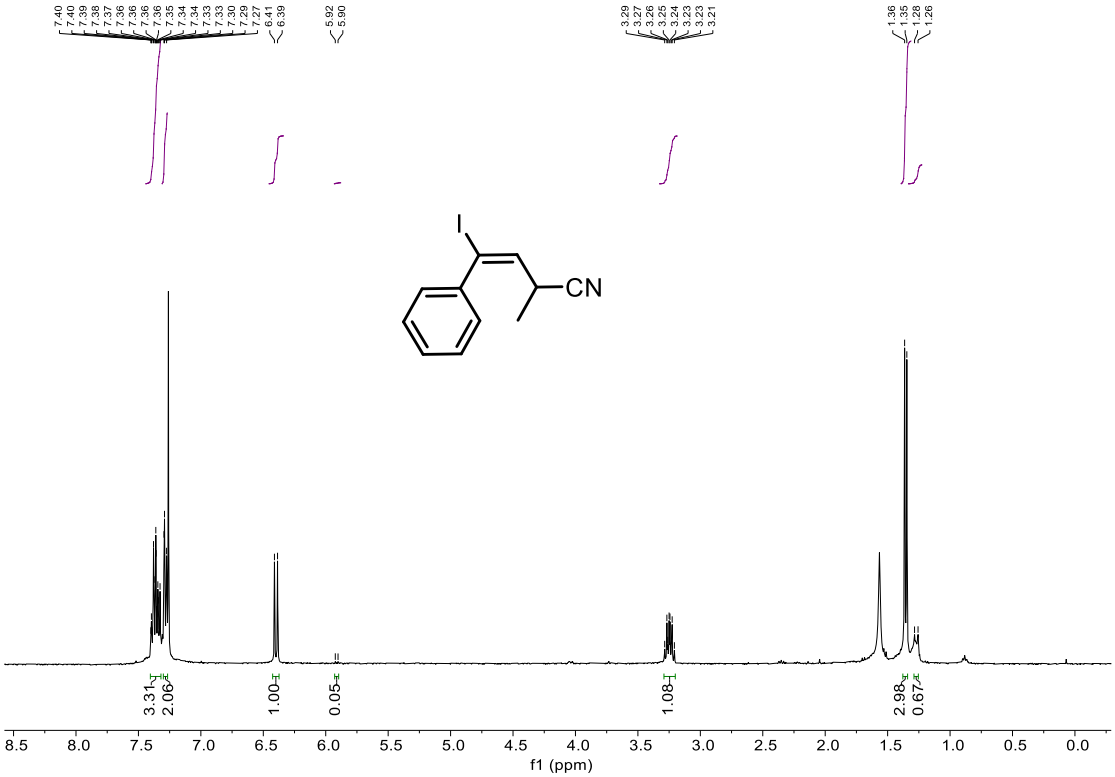
^{1}H NMR (400 MHz, CDCl3) of *E-13*



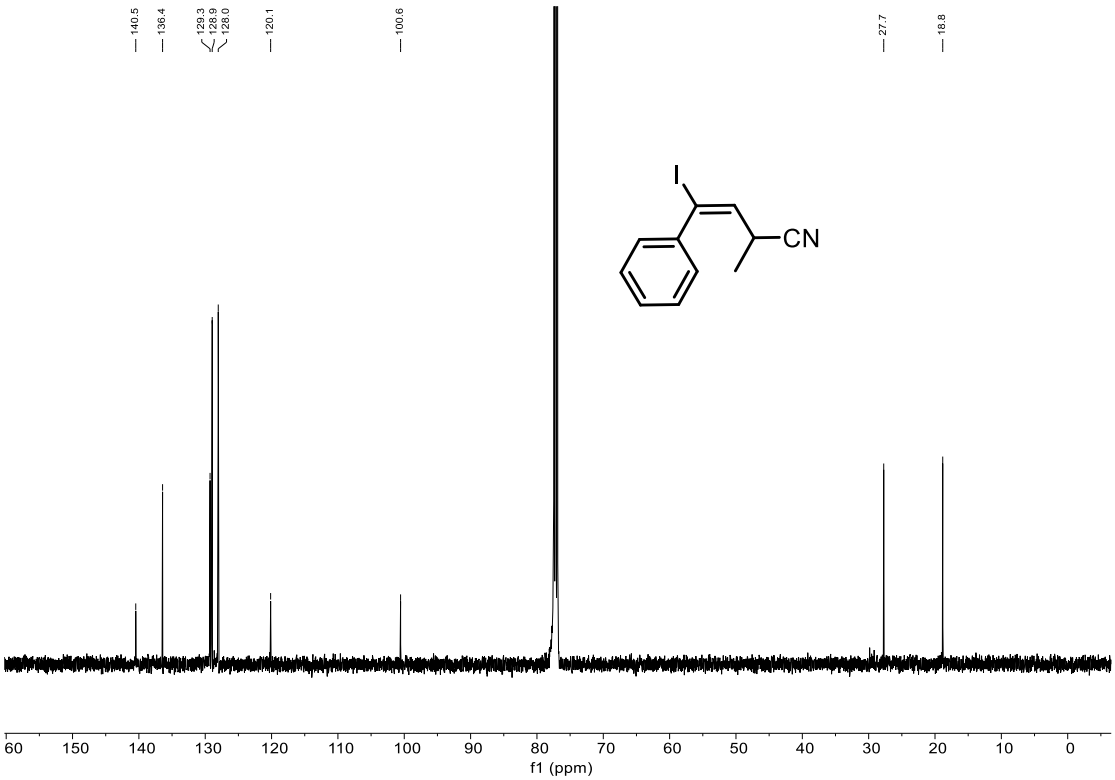
^{13}C NMR (126 MHz, CDCl$_3$) of *E-13*



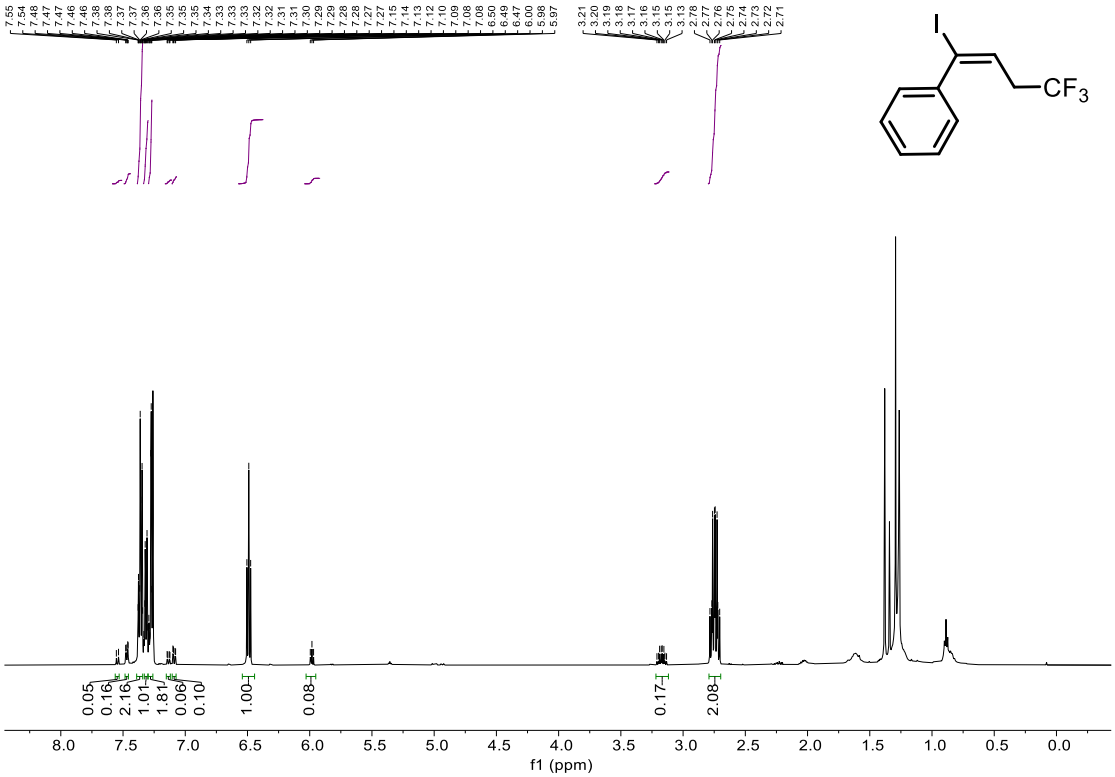
^{1}H NMR (400 MHz, CDCl3) of *E-14*



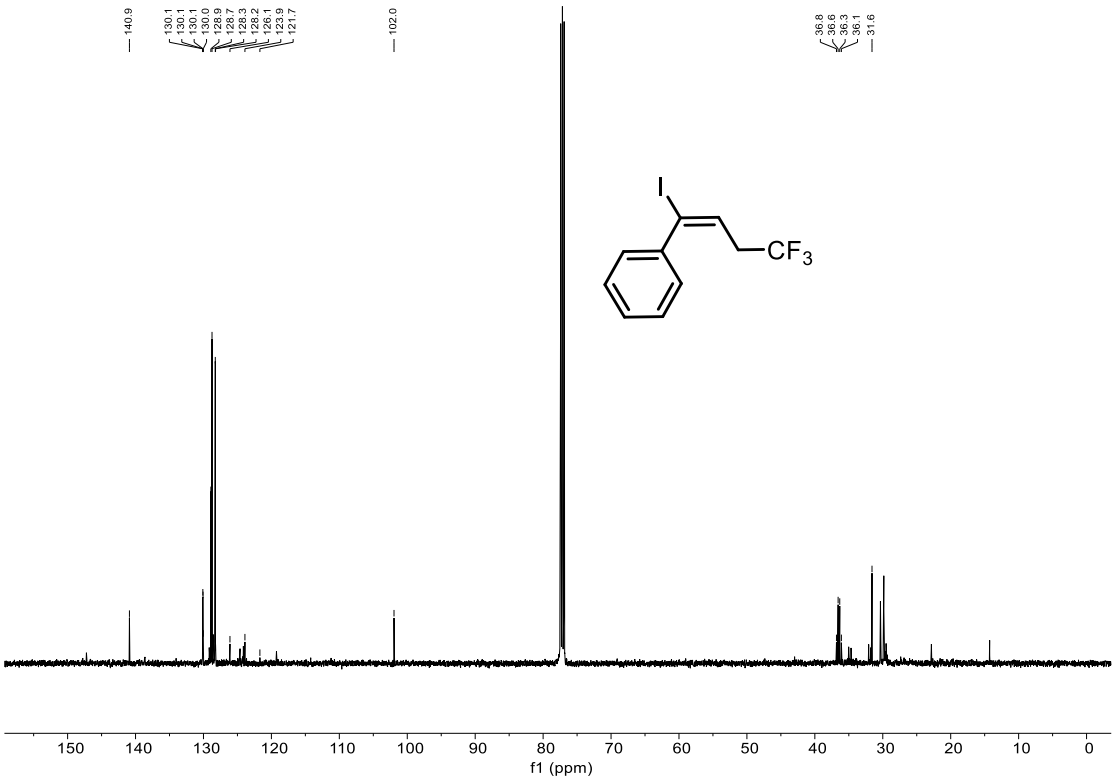
^{13}C NMR (126 MHz, $CDCl_3$) of *E-14*



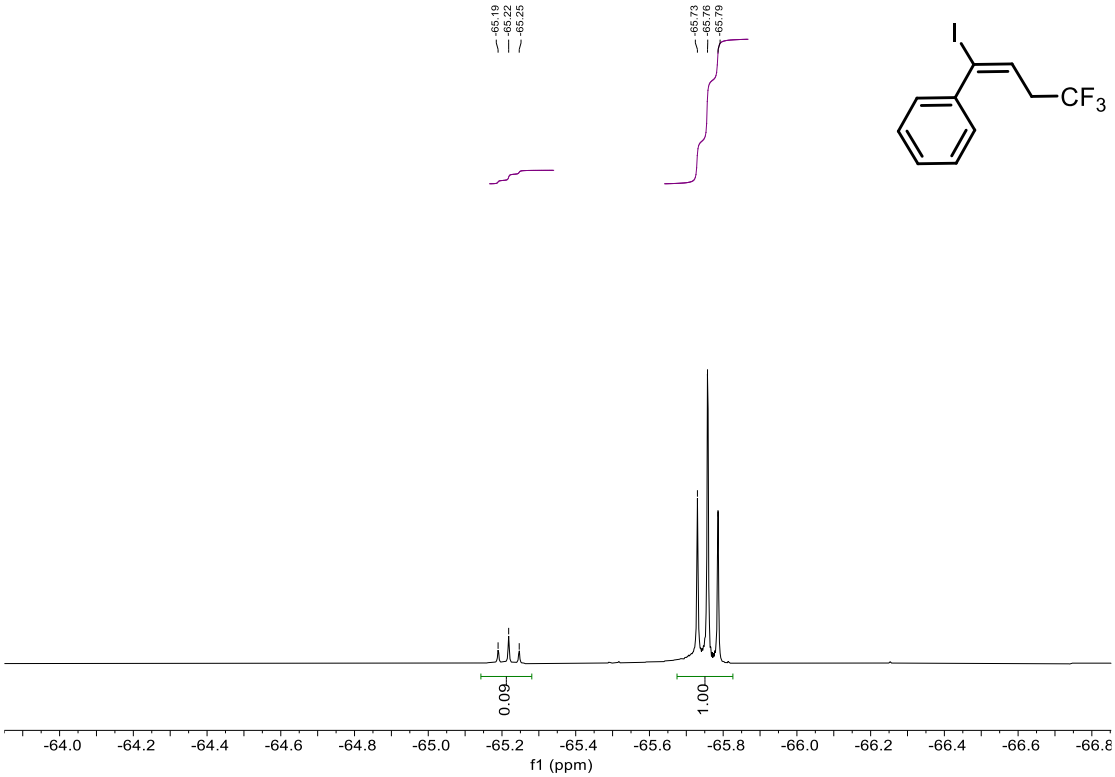
^{1}H NMR (500 MHz, CDCl3) of *E-15*



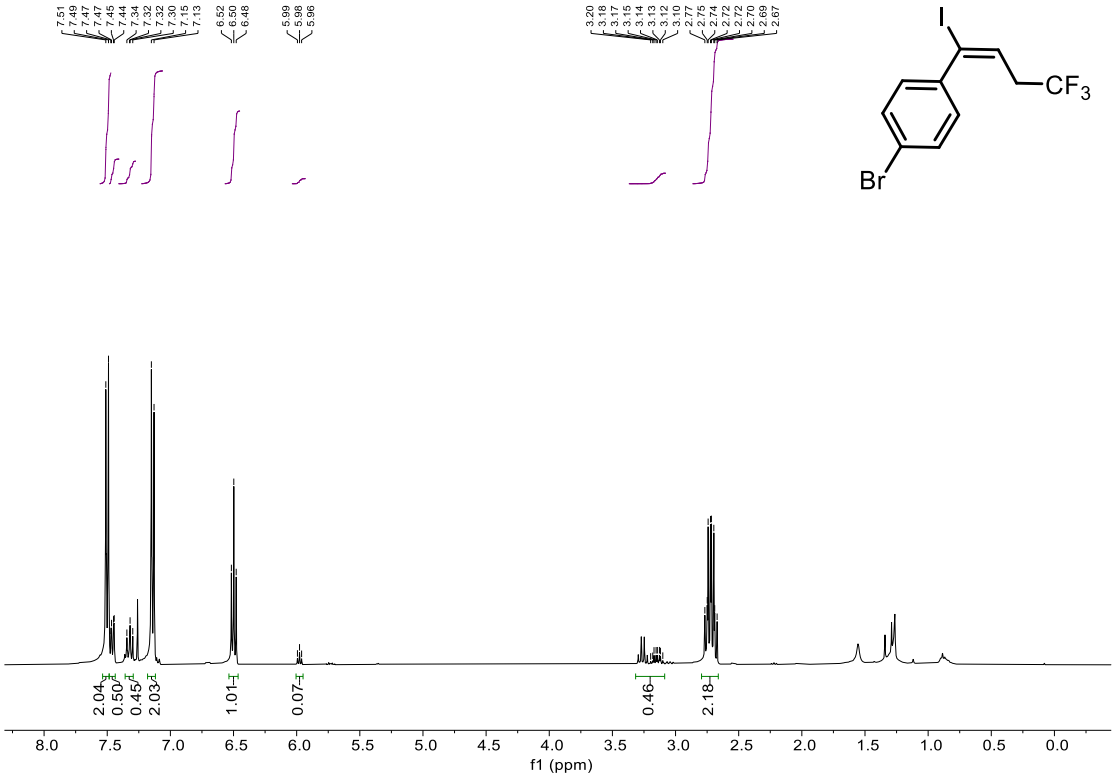
^{13}C NMR (126 MHz, CDCl$_3$) of *E-15*



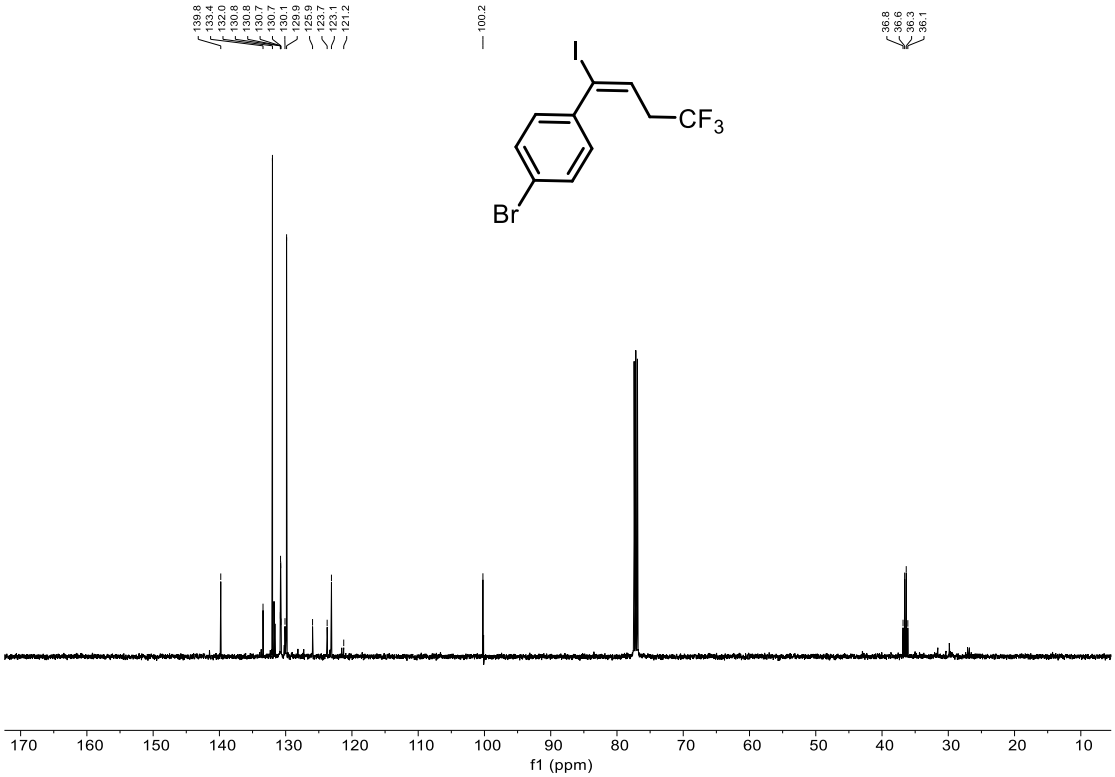
^{19}F NMR (376 MHz, $CDCl_3$) of *E-15*



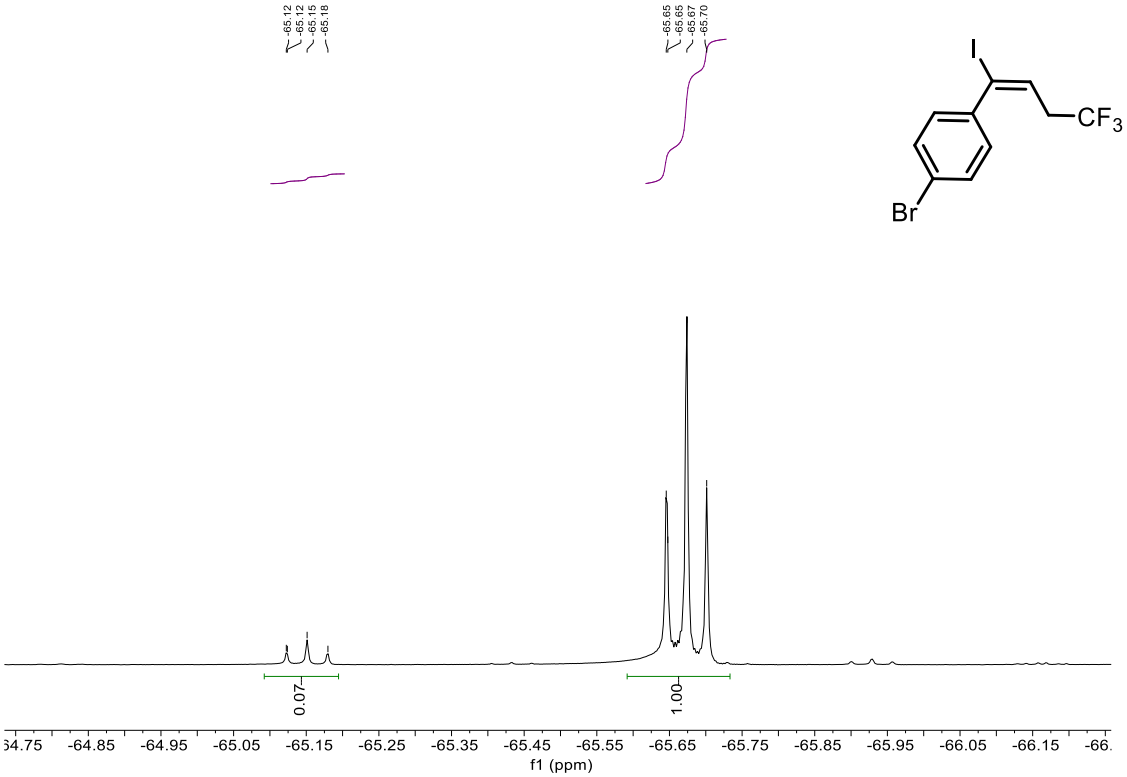
^{1}H NMR (400 MHz, CDCl3) of *E-16*



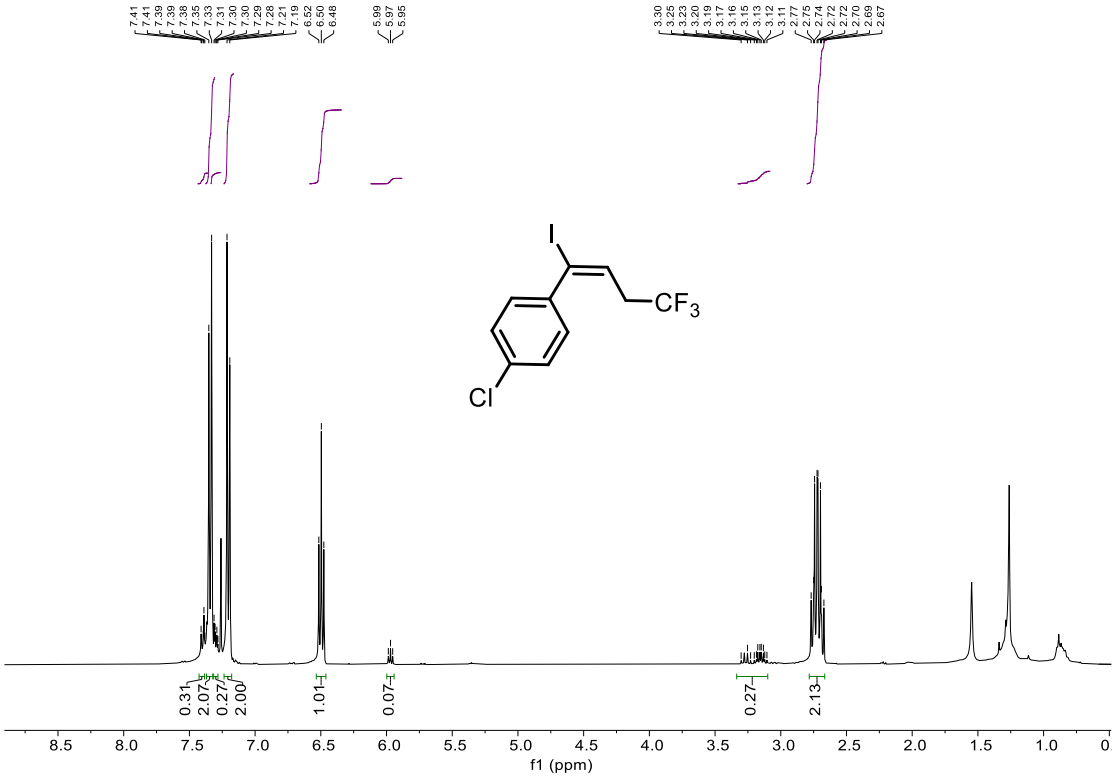
^{13}C NMR (126 MHz, $CDCl_3$) of *E-16*



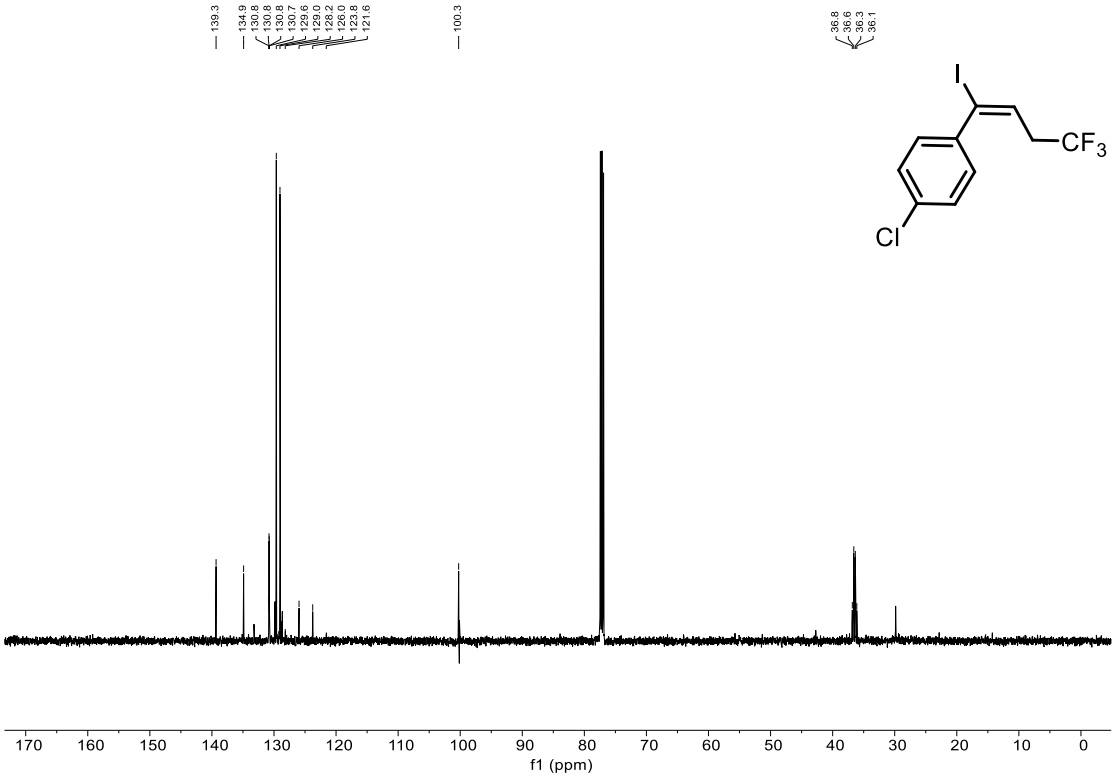
^{19}F NMR (376 MHz, $CDCl_3$) of *E-16*



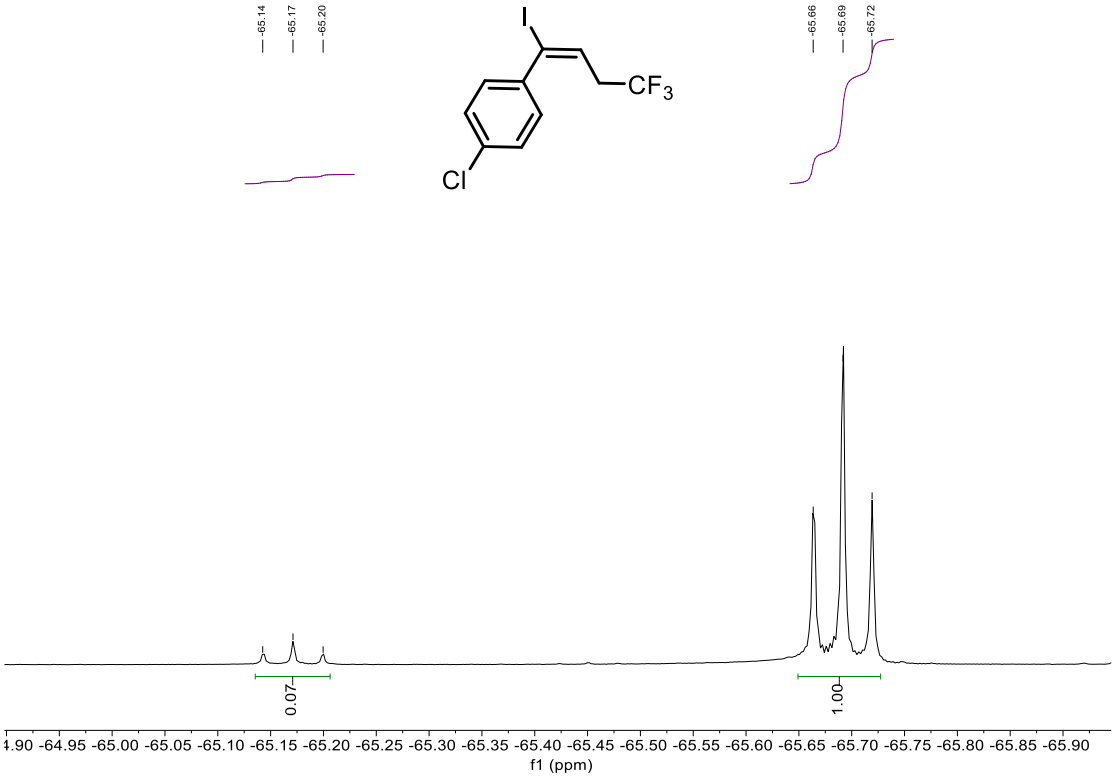
^{1}H NMR (400 MHz, CDCl3) of *E-17*



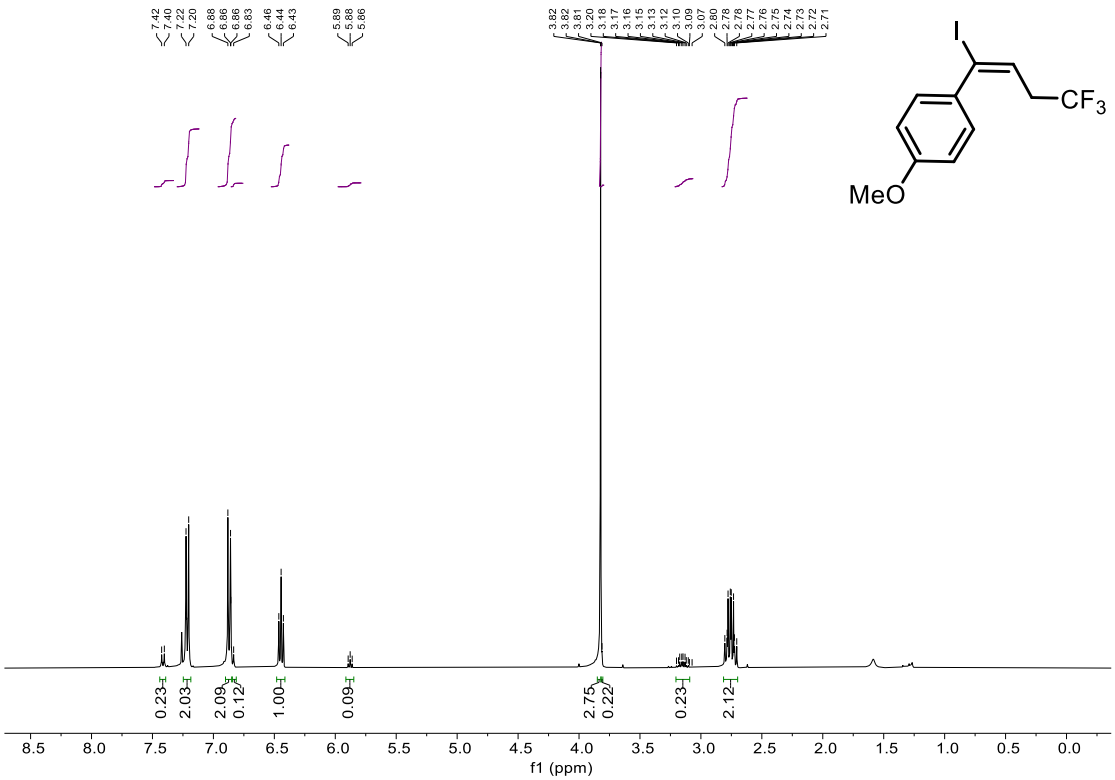
^{13}C NMR (126 MHz, $CDCl_3$) of *E-17*



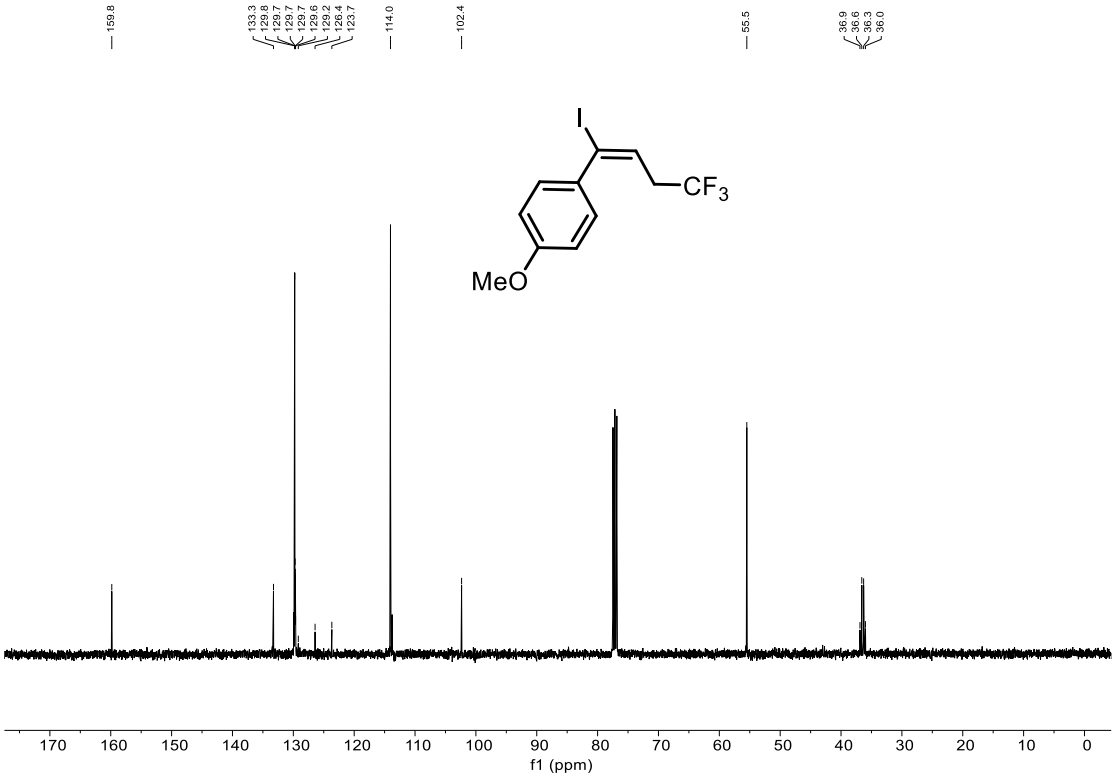
^{19}F NMR (376 MHz, $CDCl_3$) of *E-17*



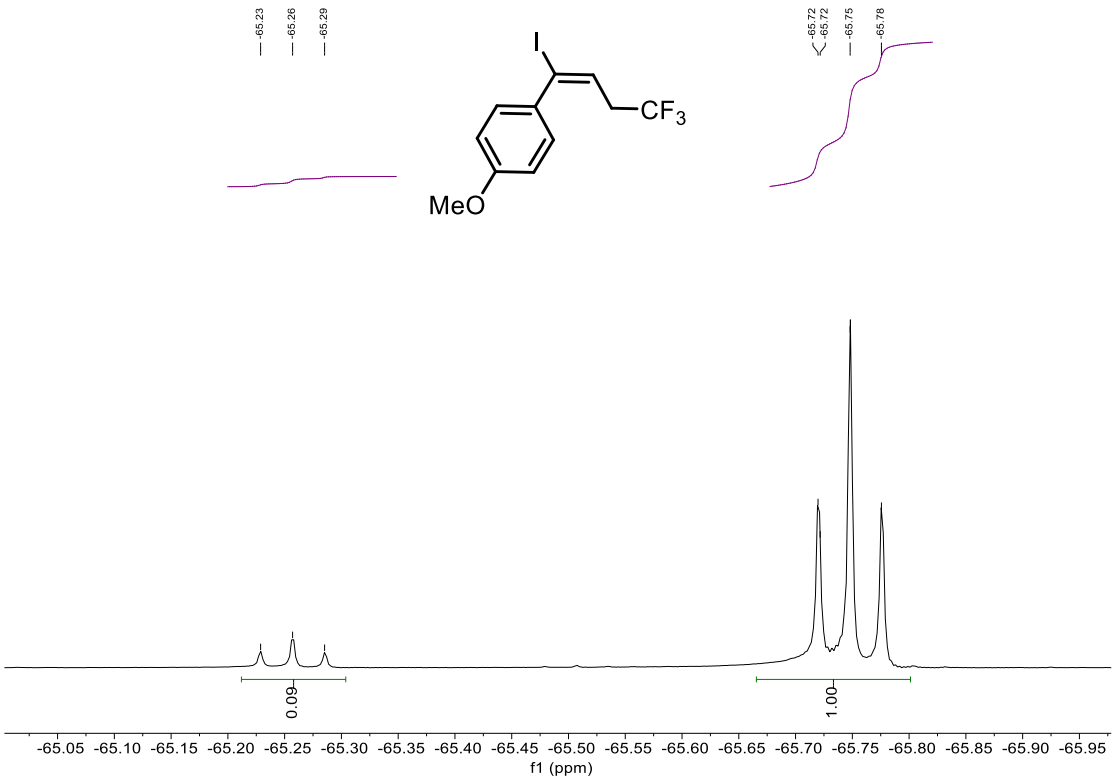
^{1}H NMR (400 MHz, CDCl3) of *E-18*



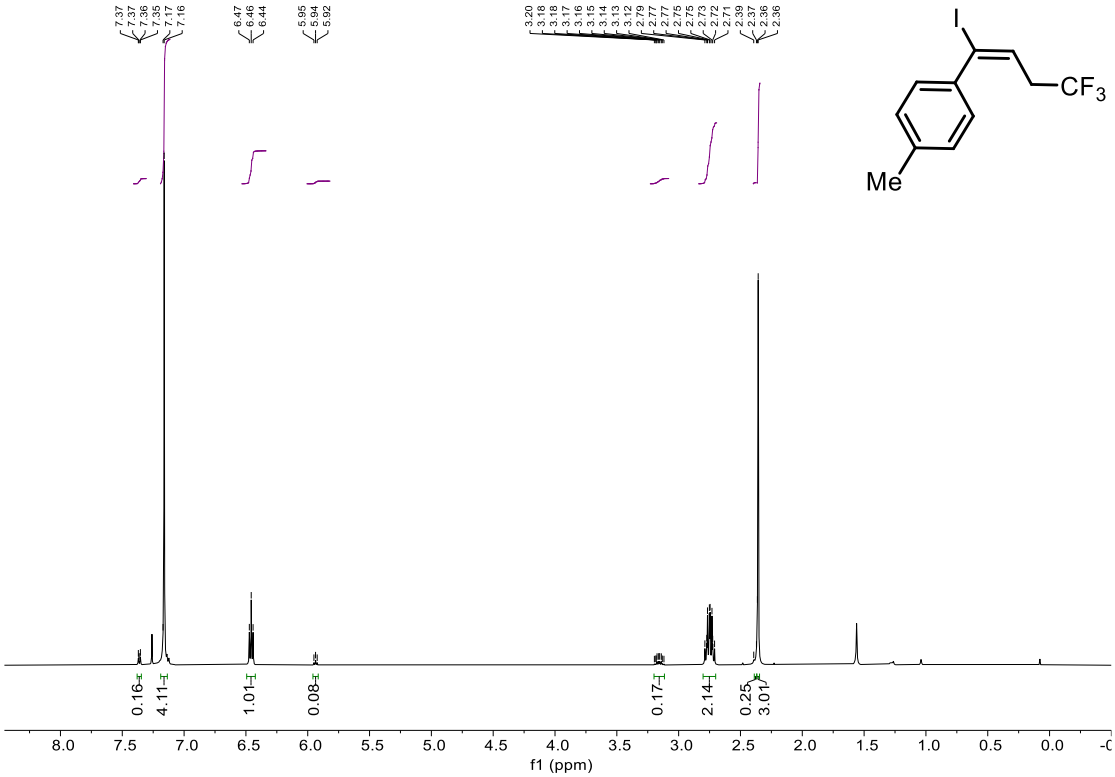
^{13}C NMR (101 MHz, $CDCl_3$) of *E-18*



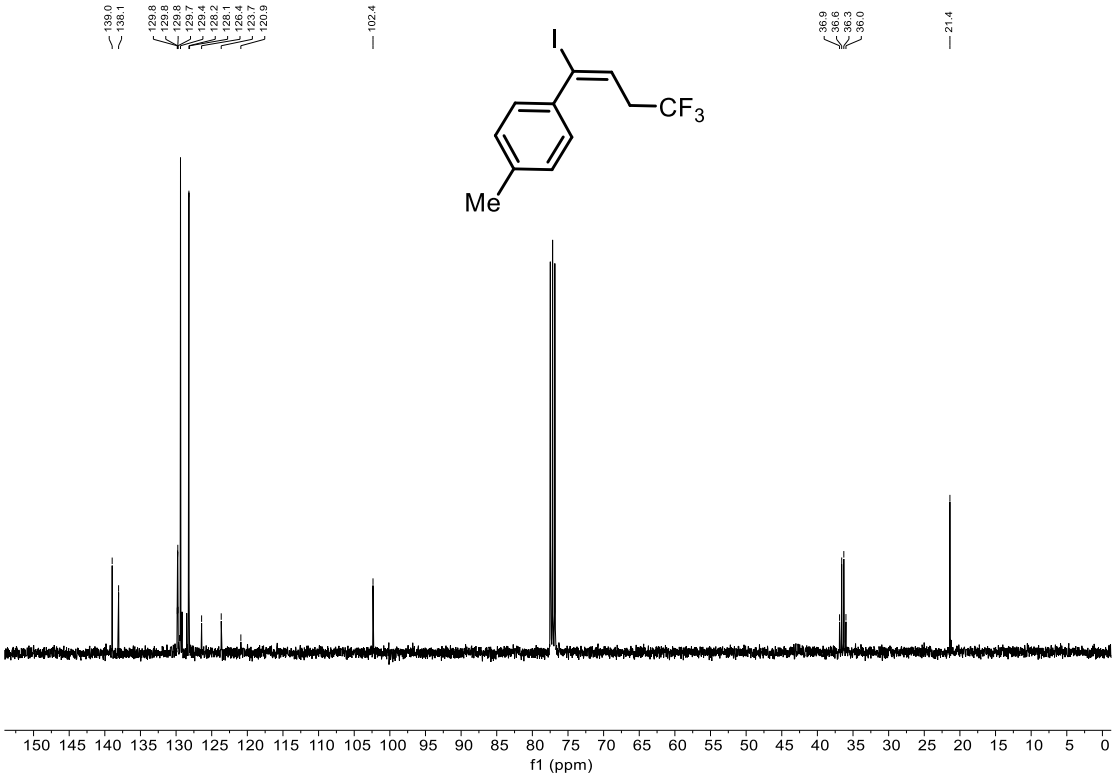
^{19}F NMR (376 MHz, $CDCl_3$) of *E-18*



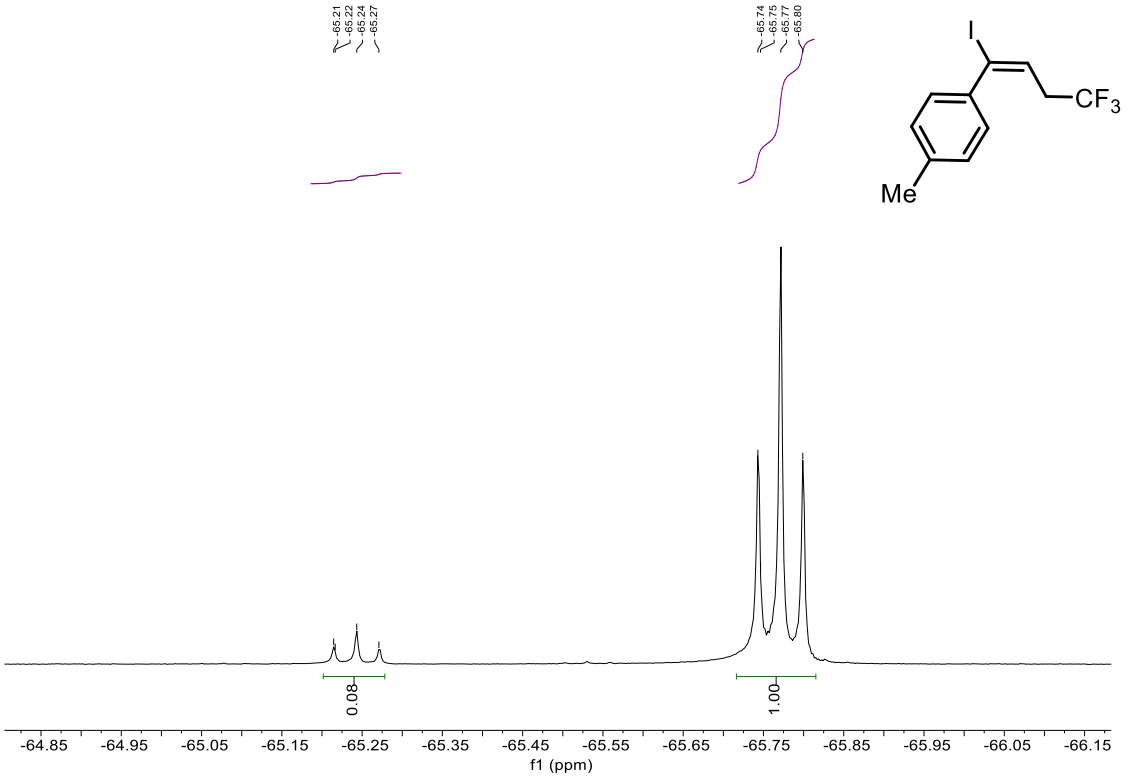
^{1}H NMR (500 MHz, CDCl3) of *E-19*



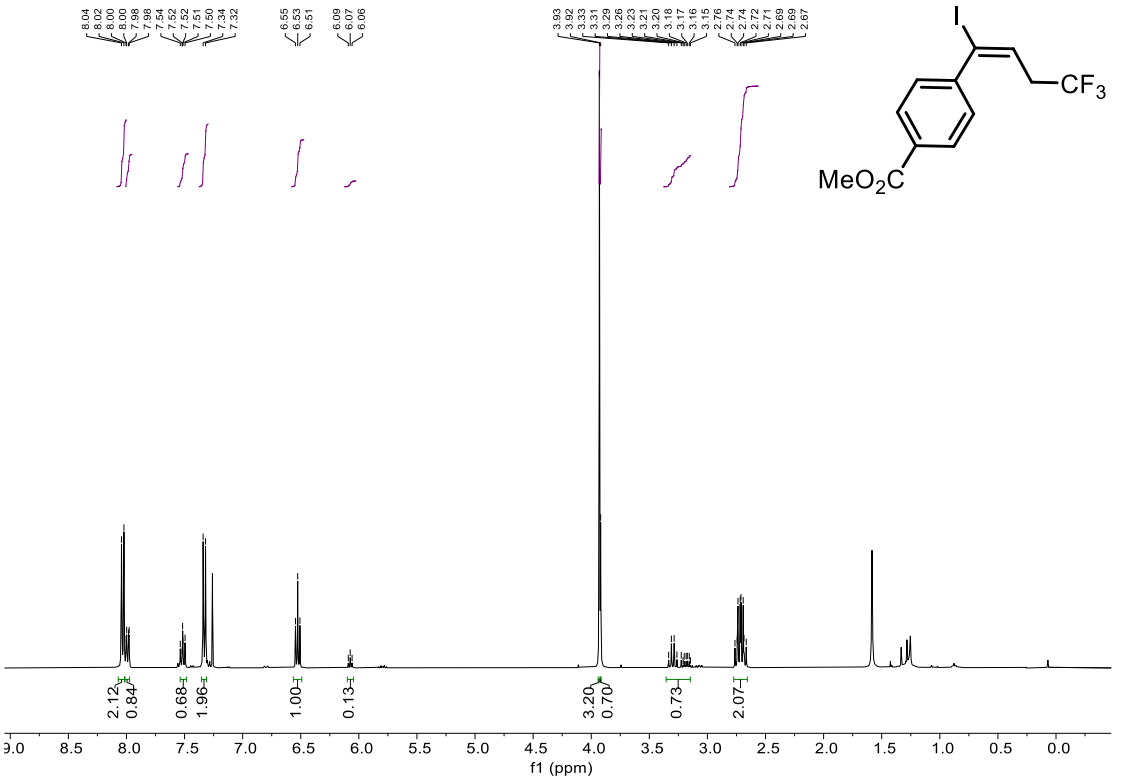
^{13}C NMR (101 MHz, CDCl$_3$) of *E-19*



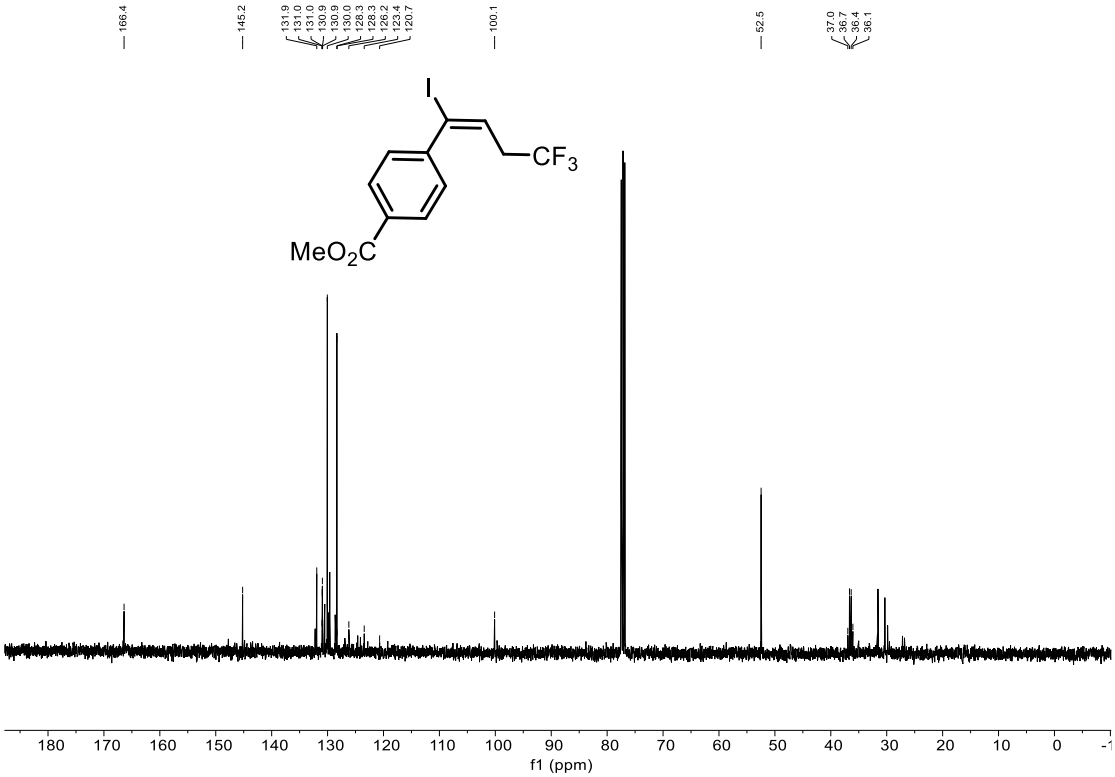
^{19}F NMR (376 MHz, $CDCl_3$) of *E-19*



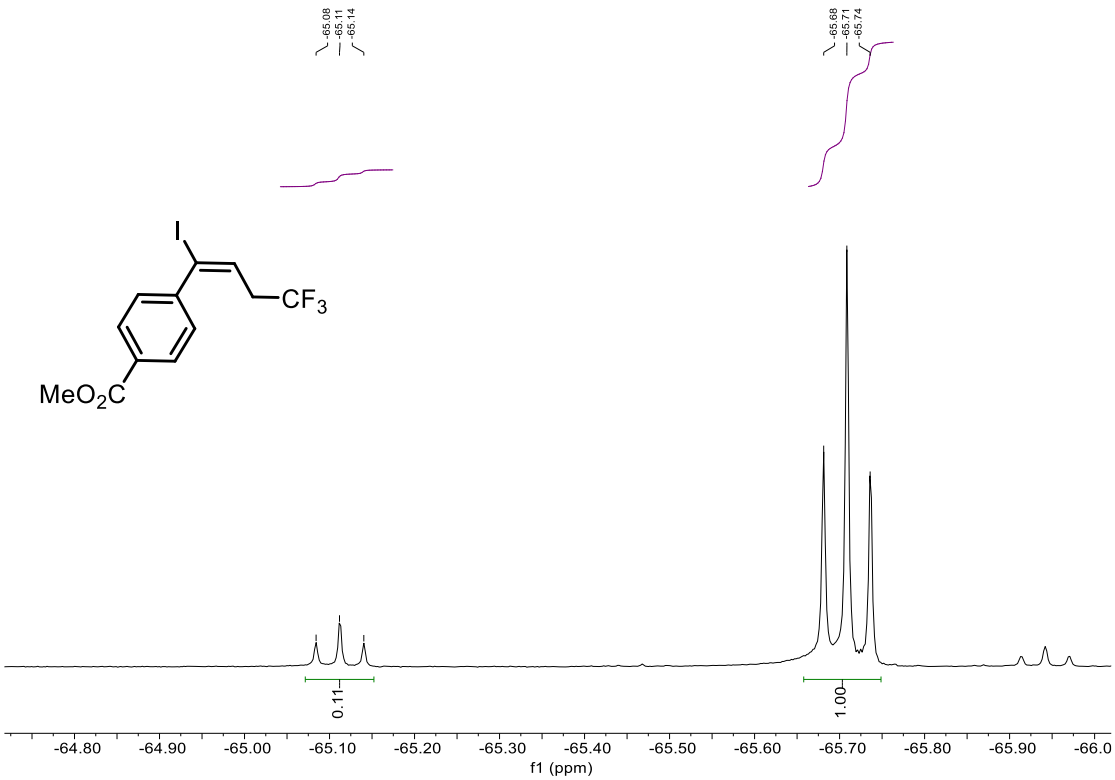
^{1}H NMR (400 MHz, CDCl3) of *E-20*



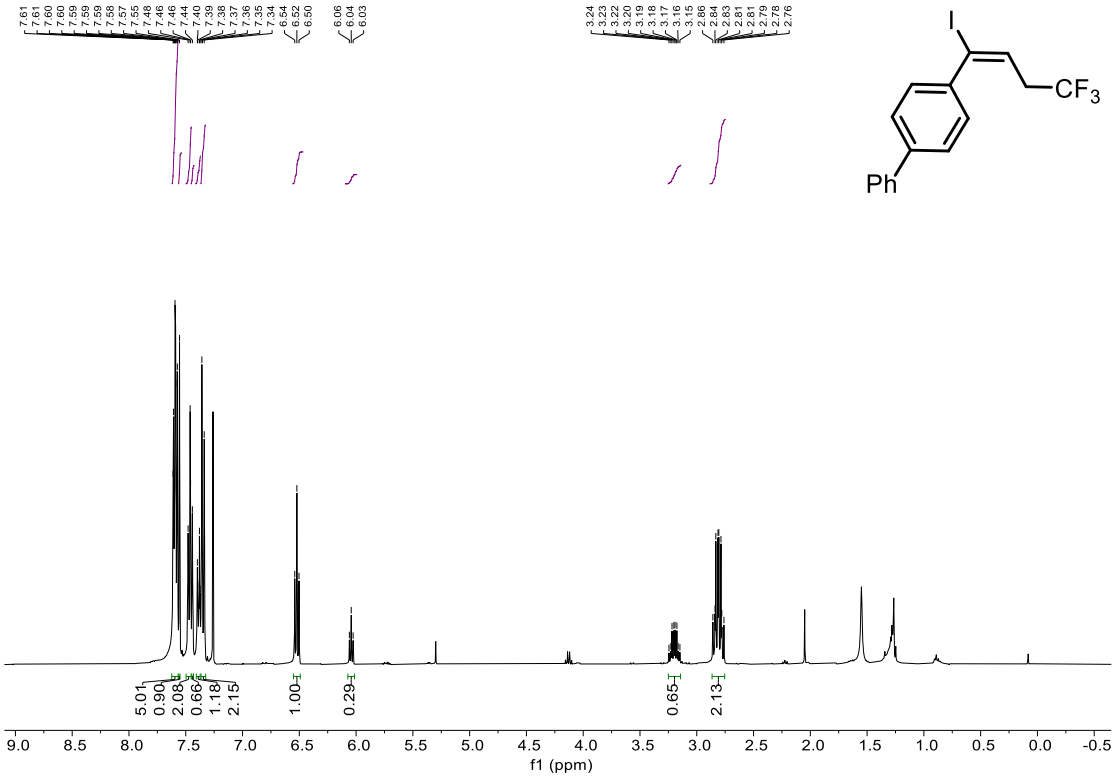
^{13}C NMR (101 MHz, $CDCl_3$) of *E-20*



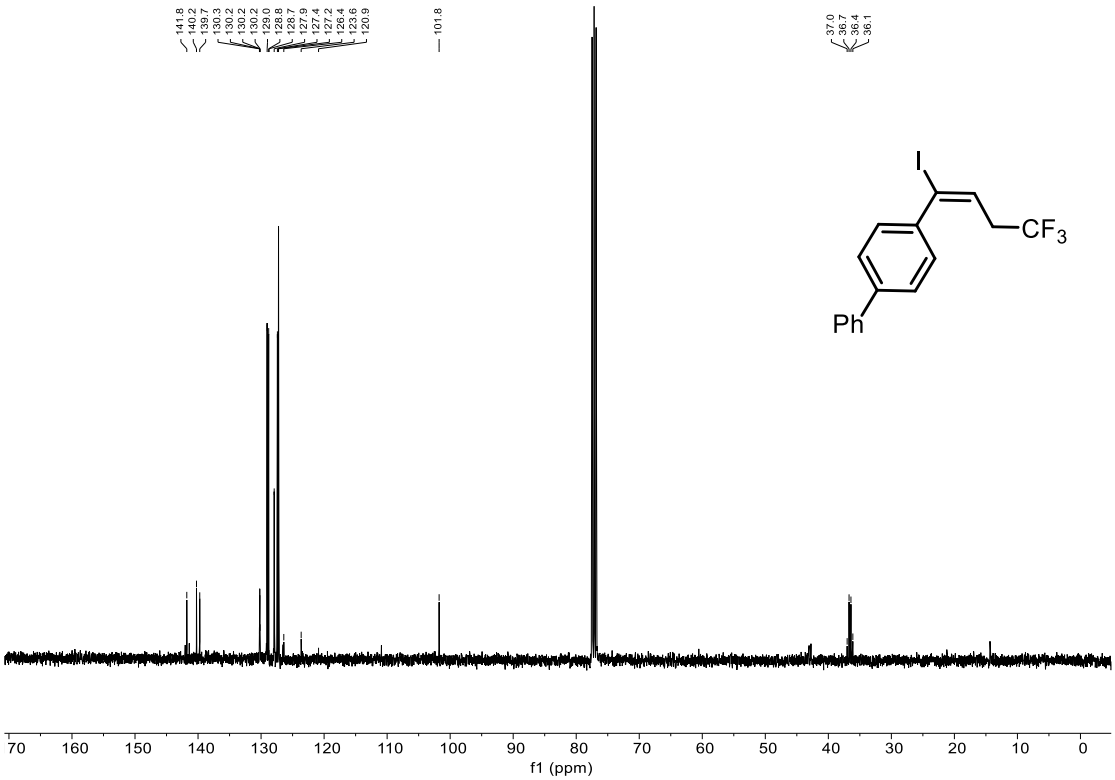
^{19}F NMR (376 MHz, $CDCl_3$) of *E-20*



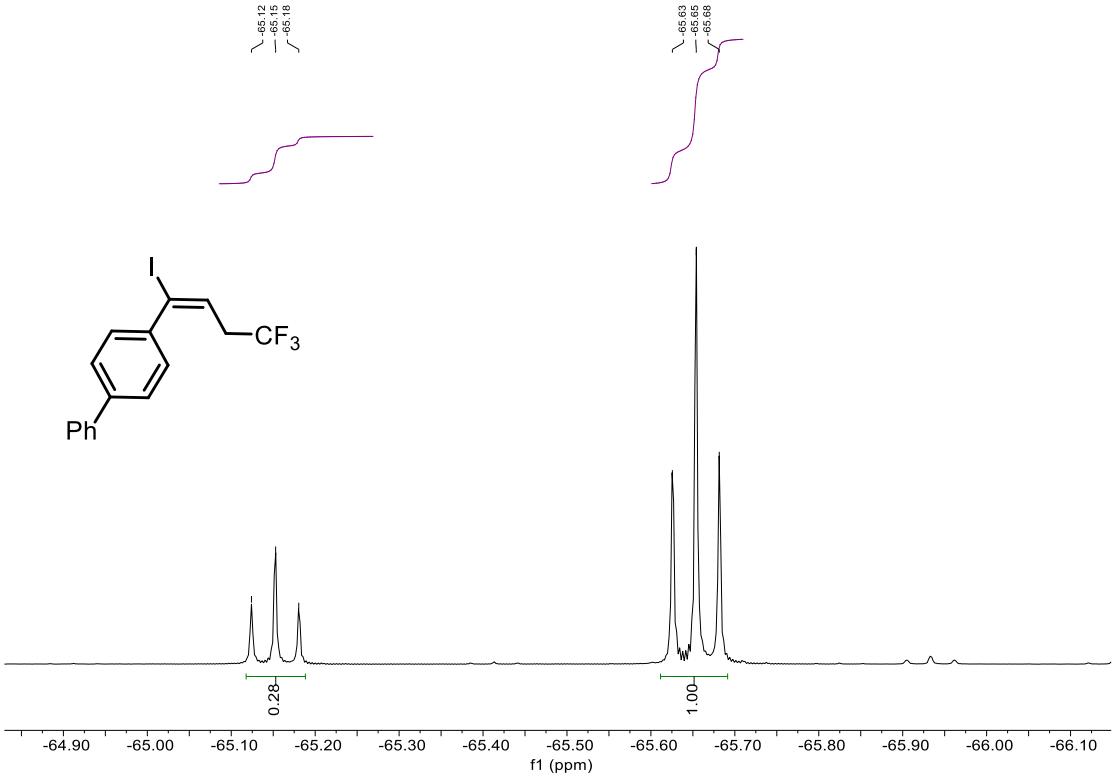
^{1}H NMR (400 MHz, CDCl3) of *E-21*



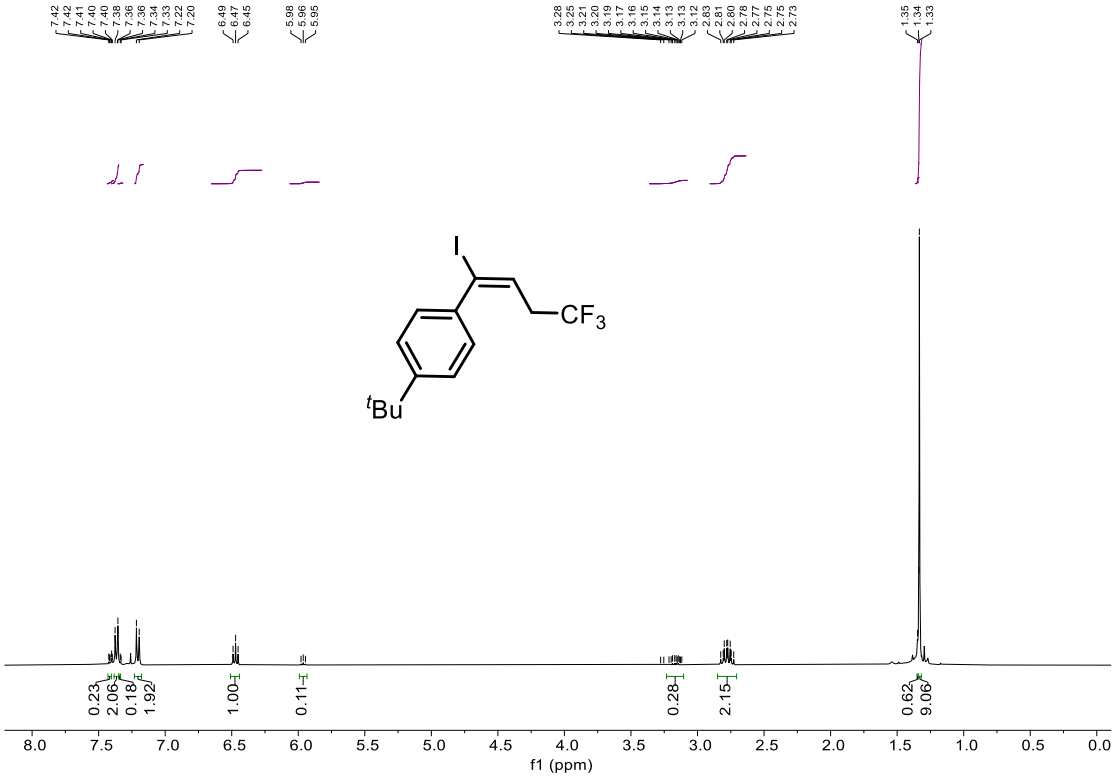
^{13}C NMR (101 MHz, $CDCl_3$) of *E-21*



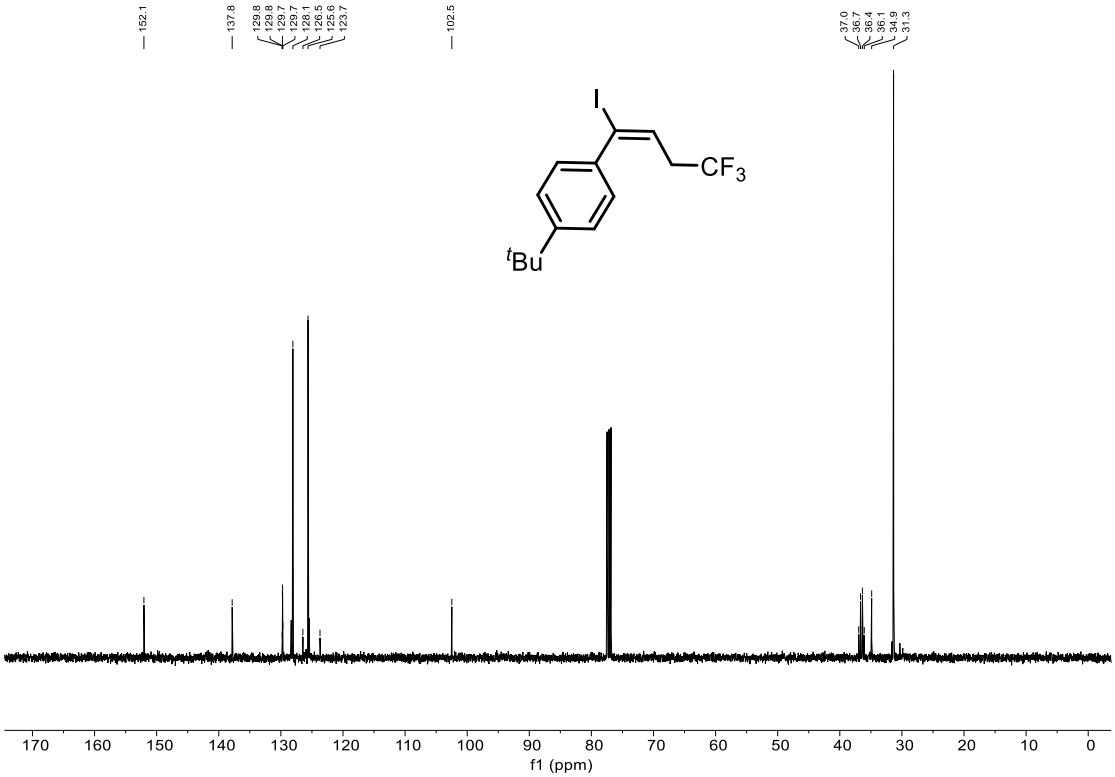
^{19}F NMR (376 MHz, $CDCl_3$) of *E-21*



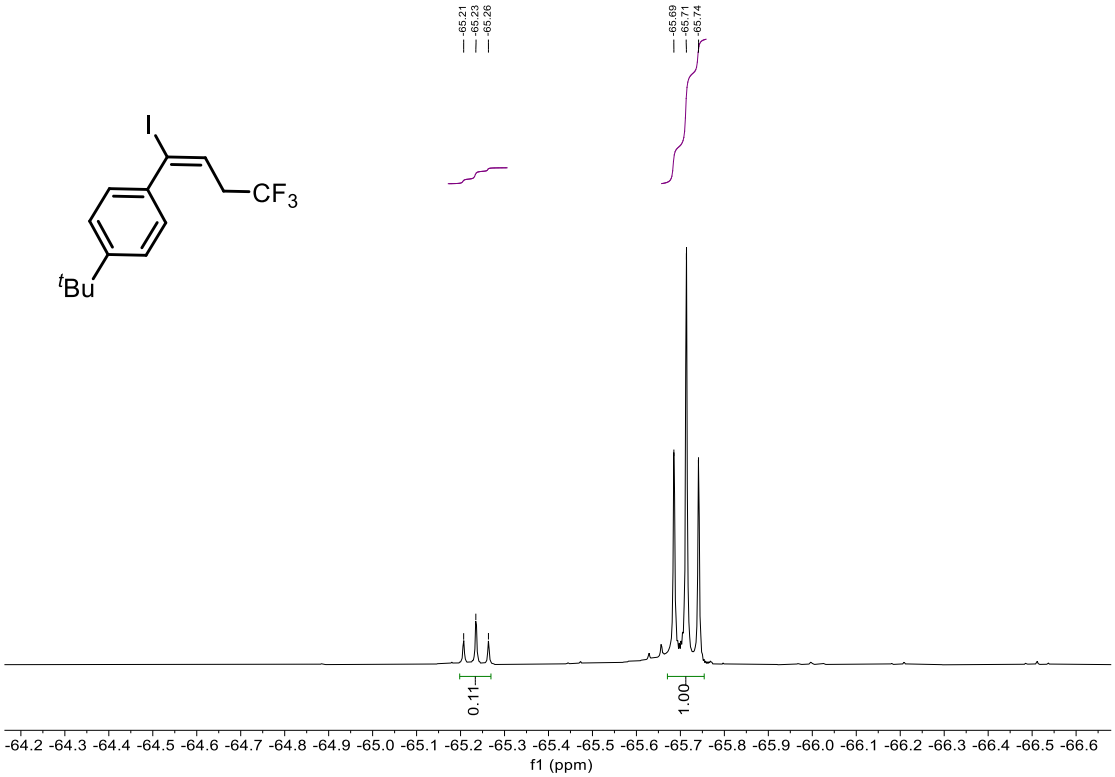
^{1}H NMR (400 MHz, CDCl3) of *E-22*



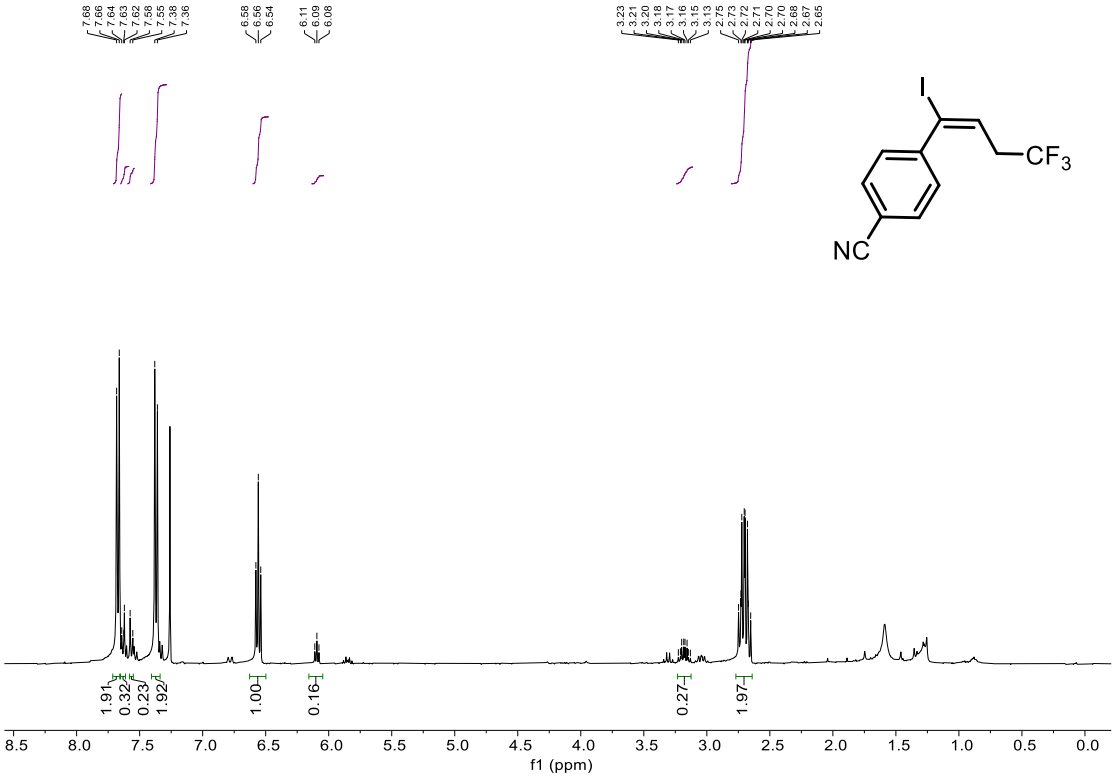
^{13}C NMR (101 MHz, $CDCl_3$) of *E-22*



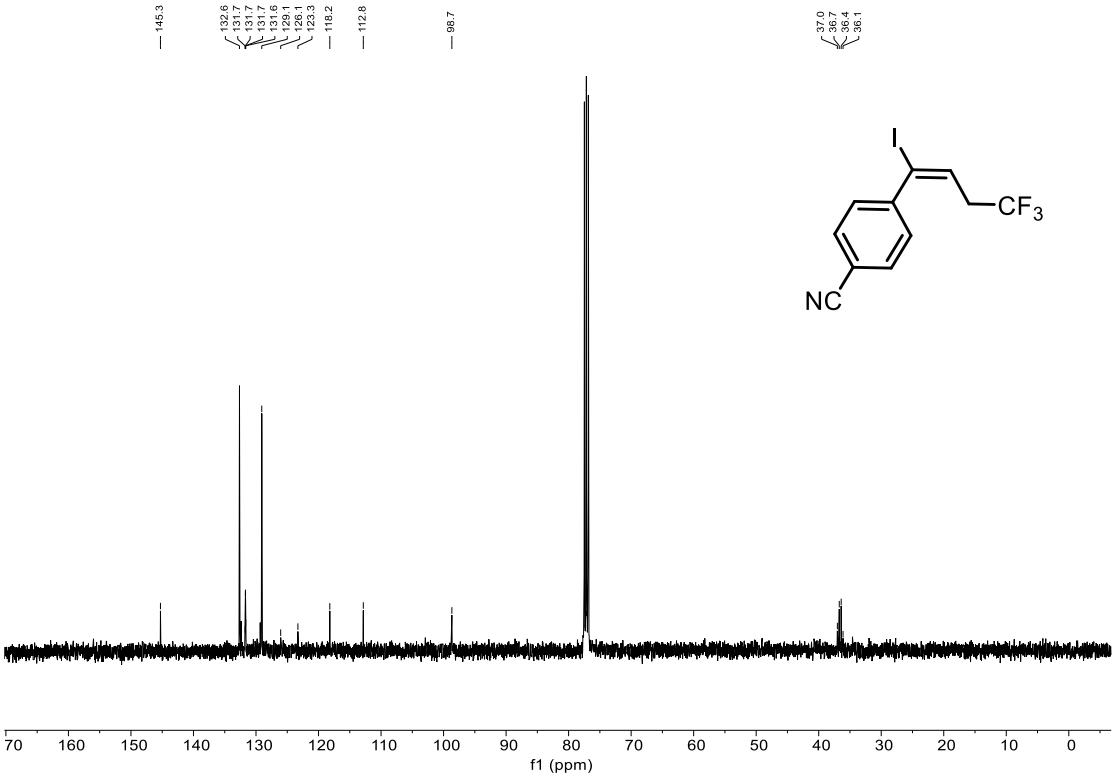
^{19}F NMR (376 MHz, $CDCl_3$) of *E-22*



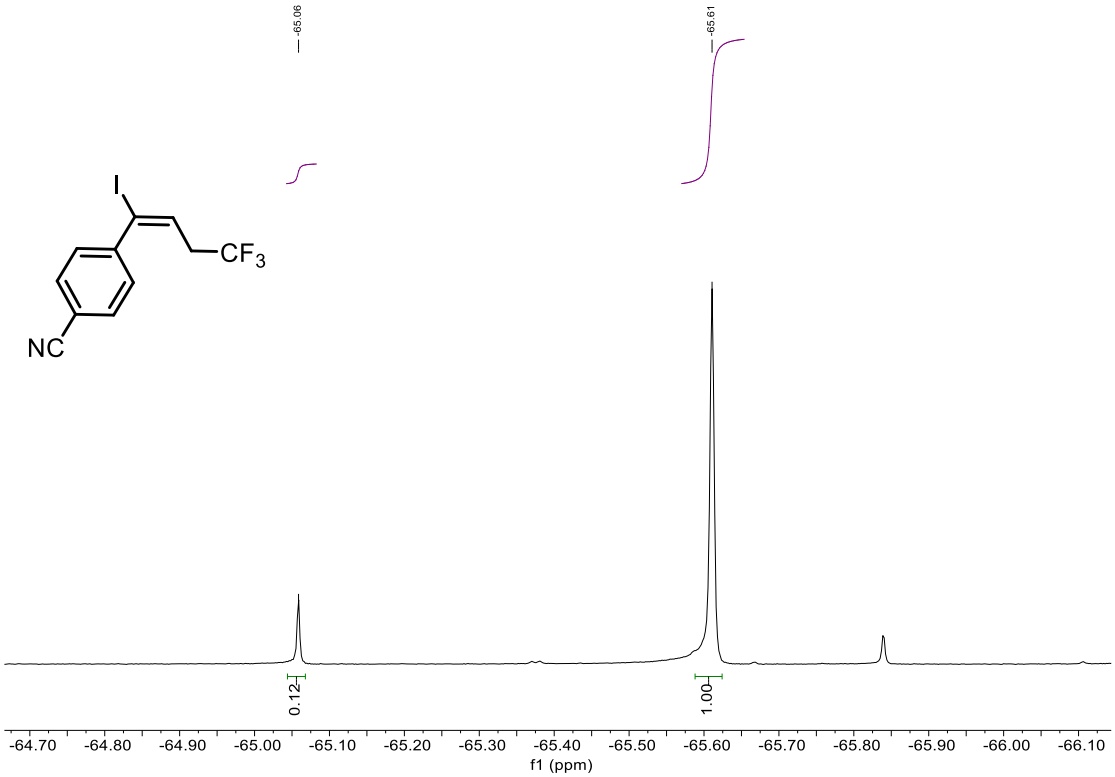
^{1}H NMR (400 MHz, CDCl3) of *E-23*



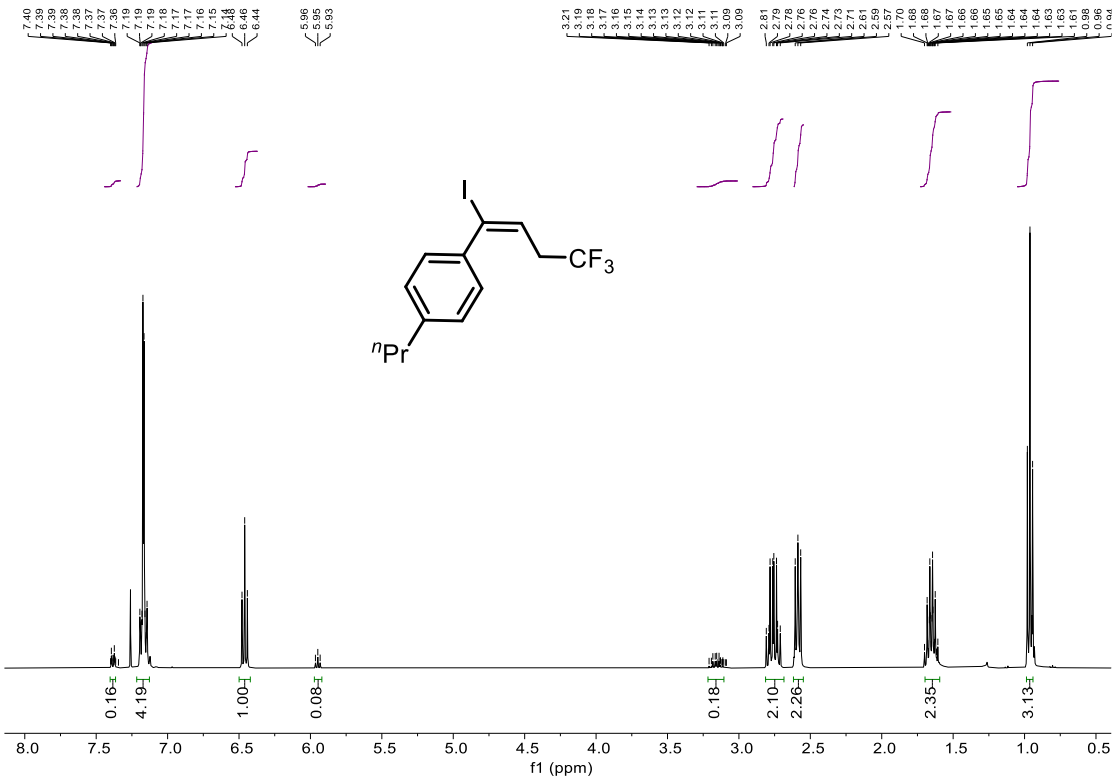
^{13}C NMR (101 MHz, CDCl$_3$) of *E-23*



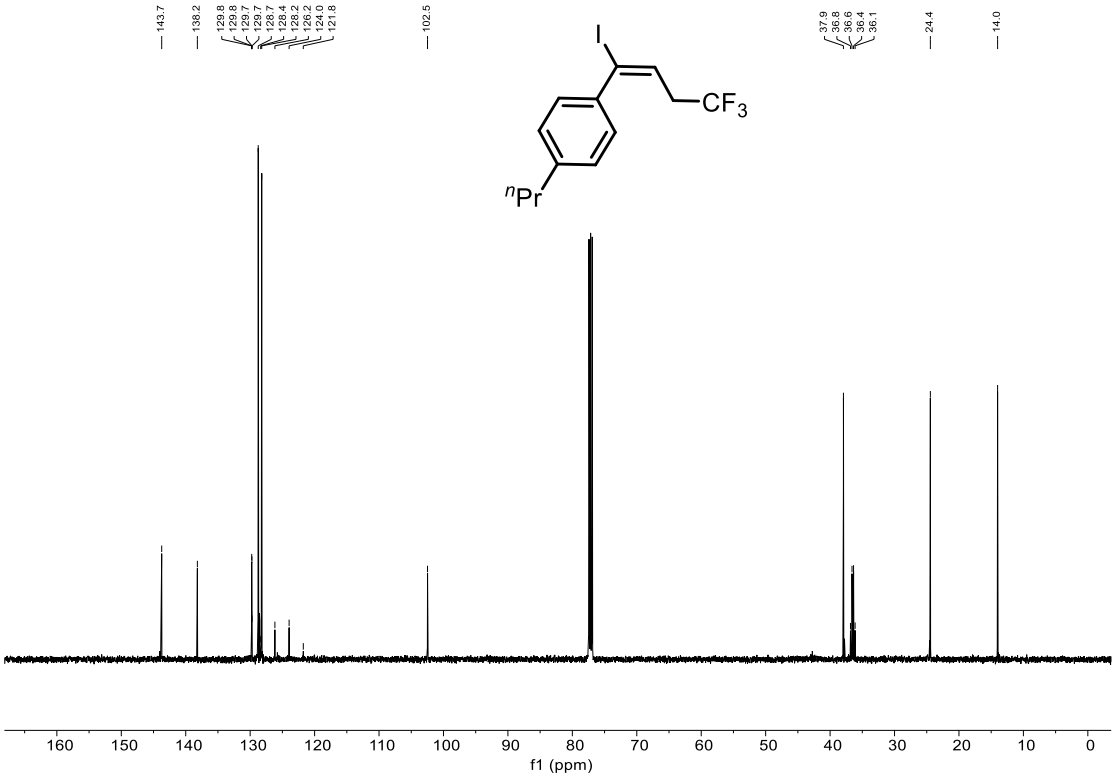
^{19}F NMR (376 MHz, $CDCl_3$) of *E-23*



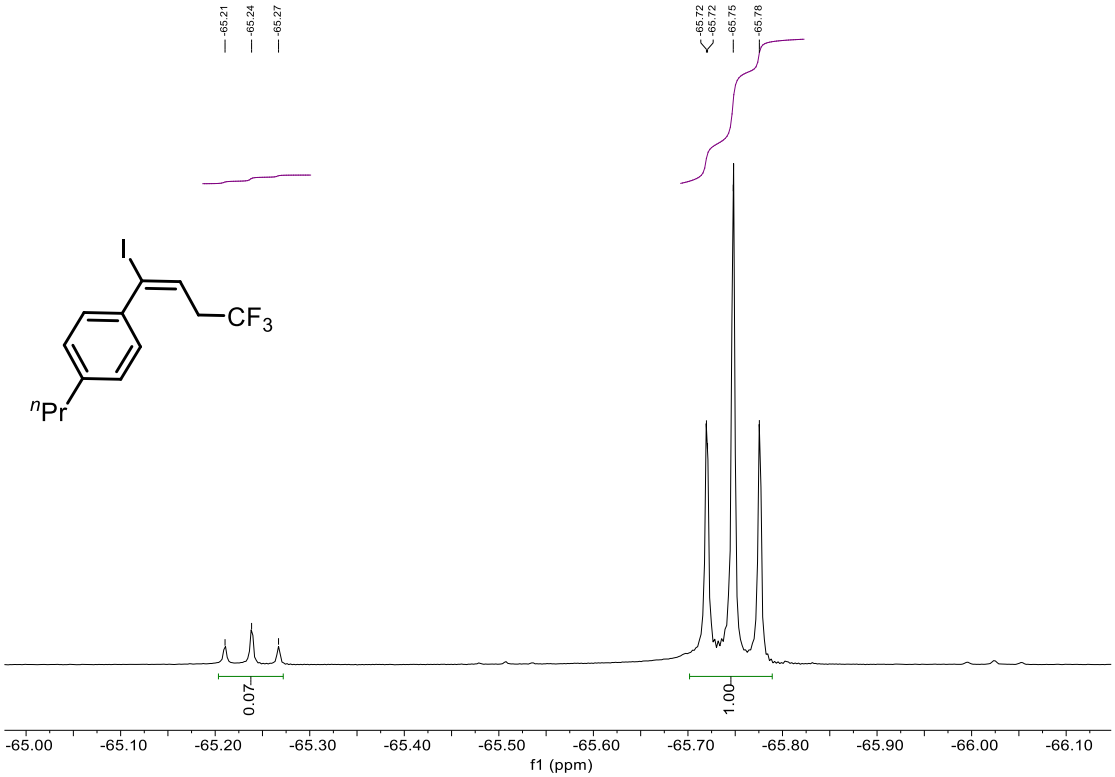
^{1}H NMR (400 MHz, CDCl3) of *E-24*



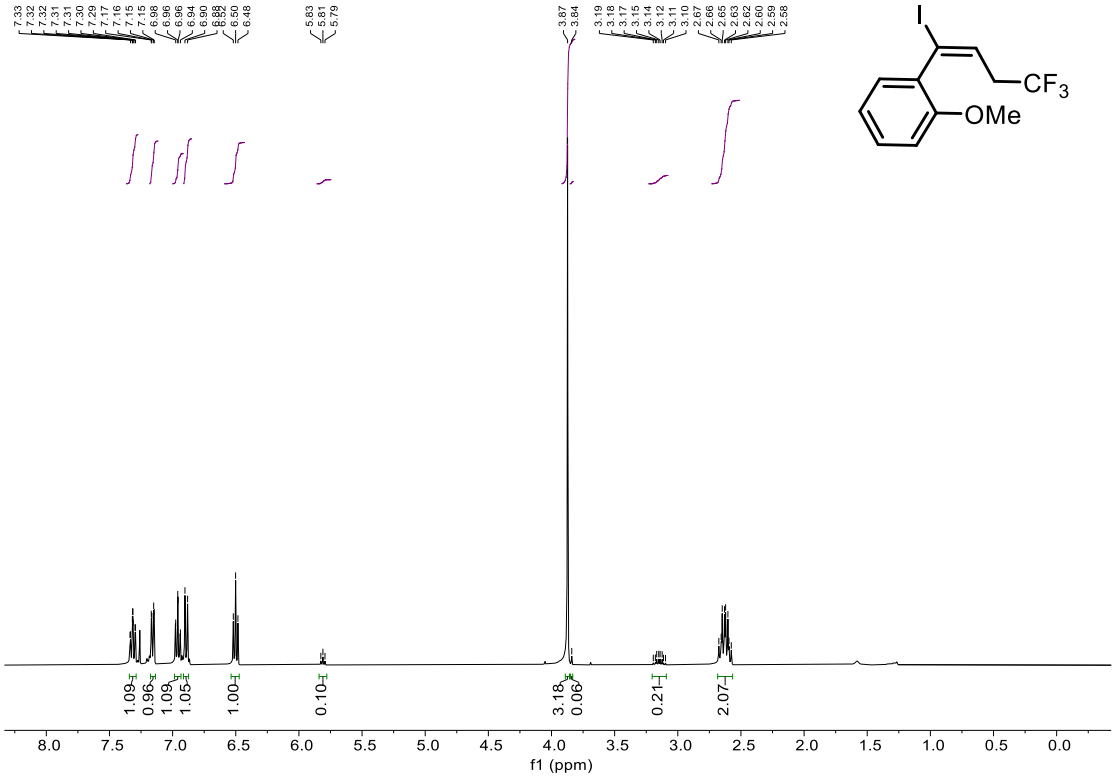
^{13}C NMR (126 MHz, $CDCl_3$) of *E-24*



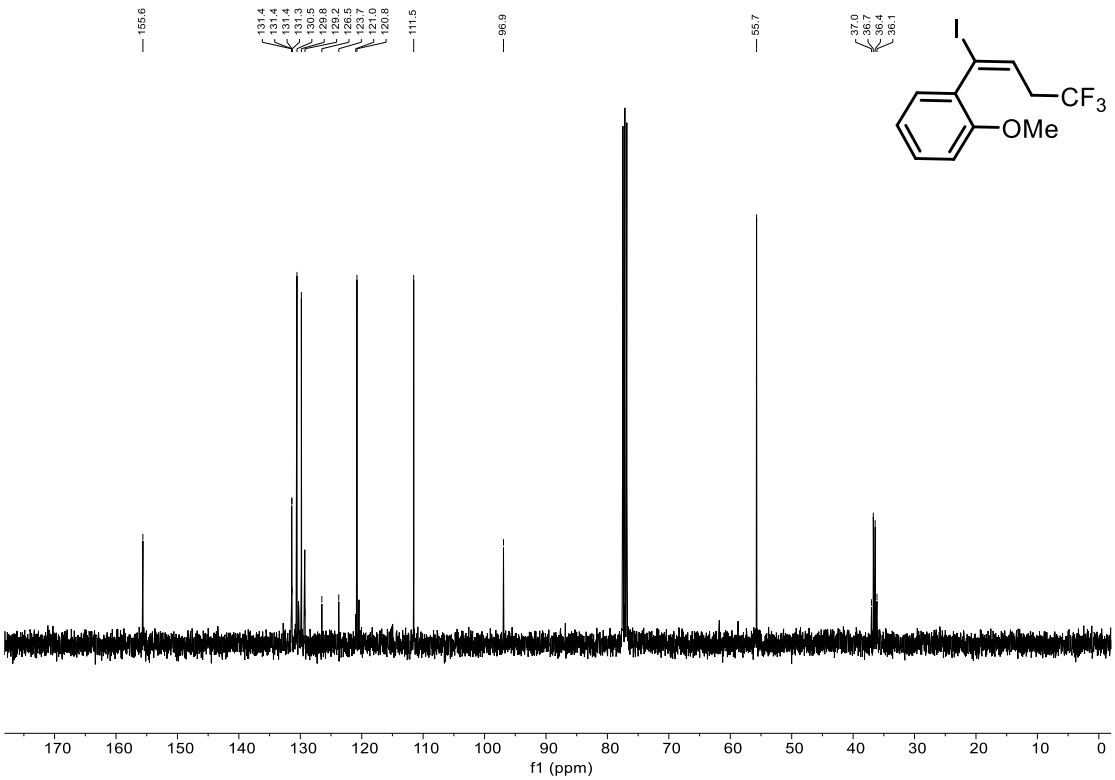
^{19}F NMR (376 MHz, $CDCl_3$) of *E-24*



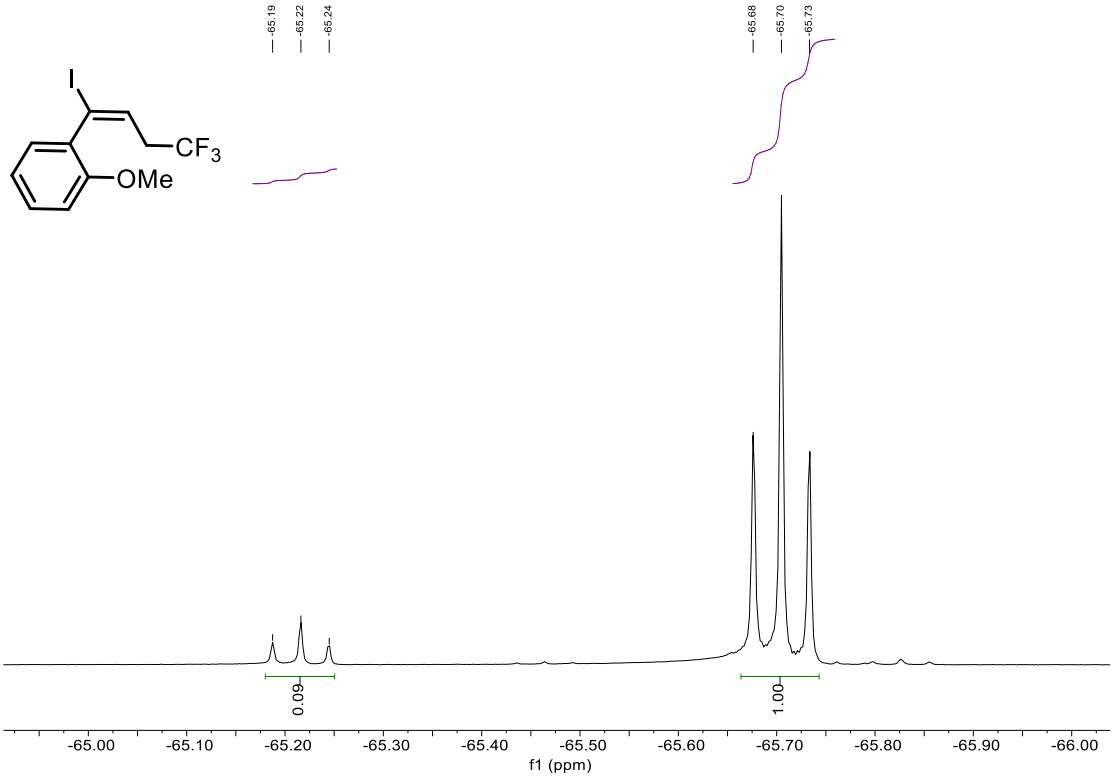
^{1}H NMR (400 MHz, CDCl3) of *E-25*



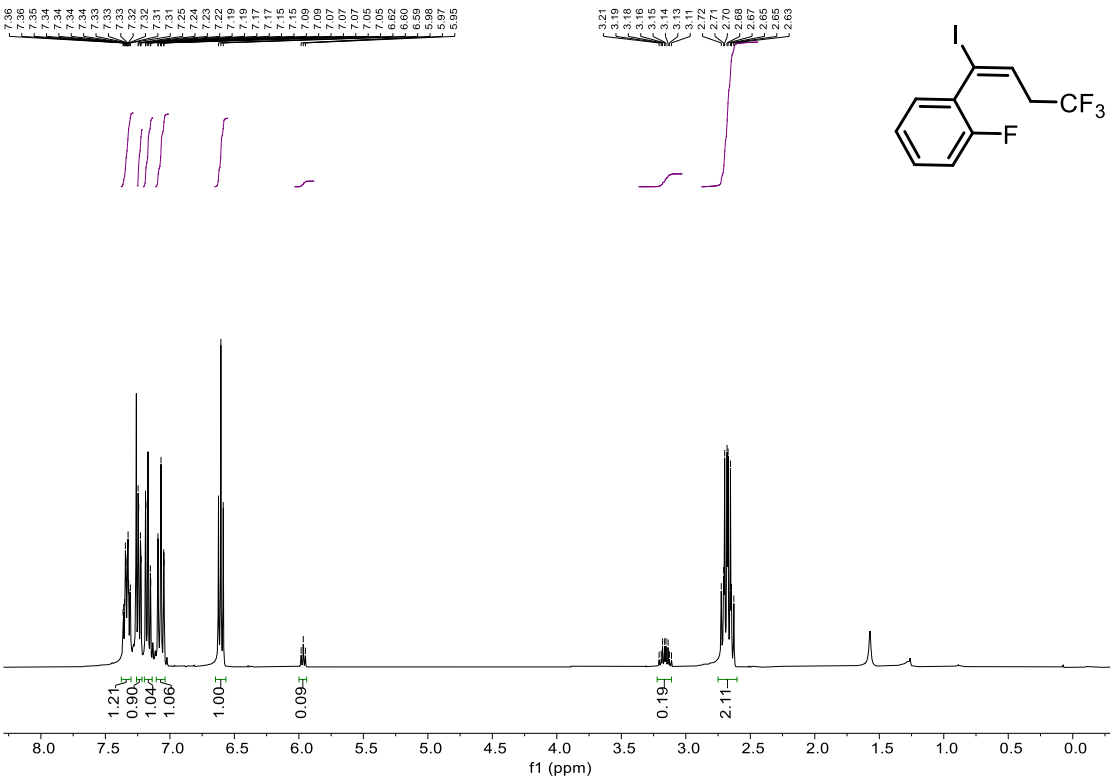
^{13}C NMR (101 MHz, CDCl$_3$) of *E-25*



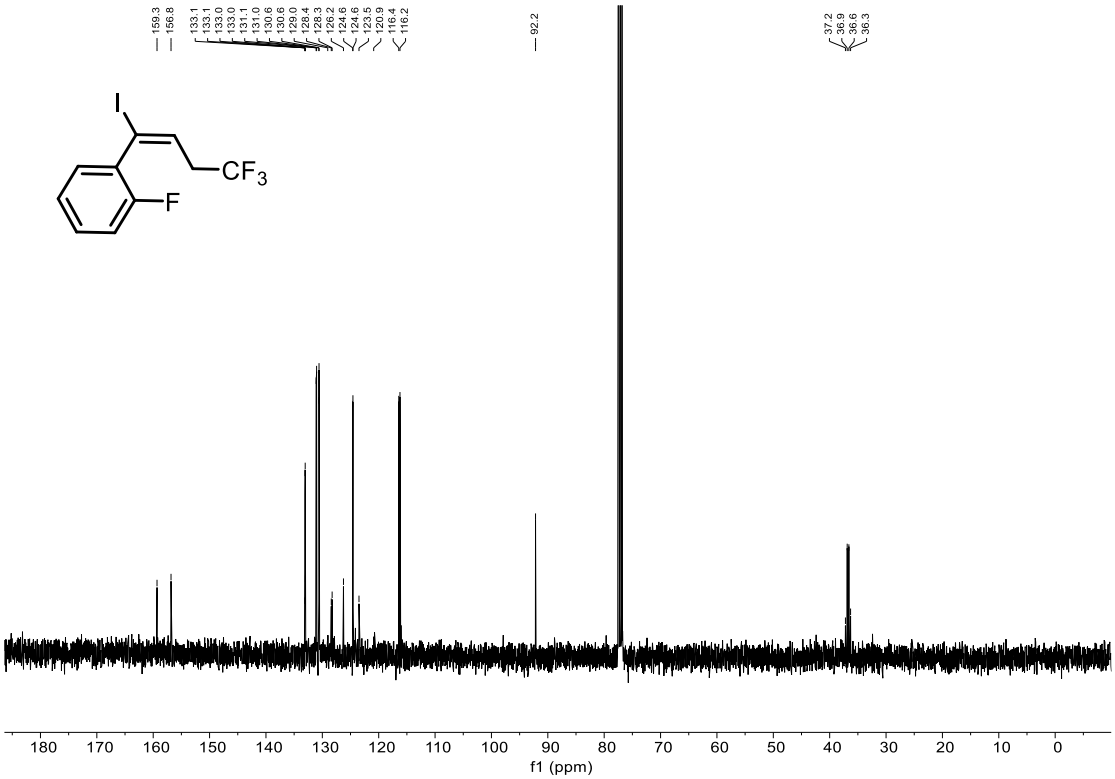
^{19}F NMR (376 MHz, $CDCl_3$) of *E-25*



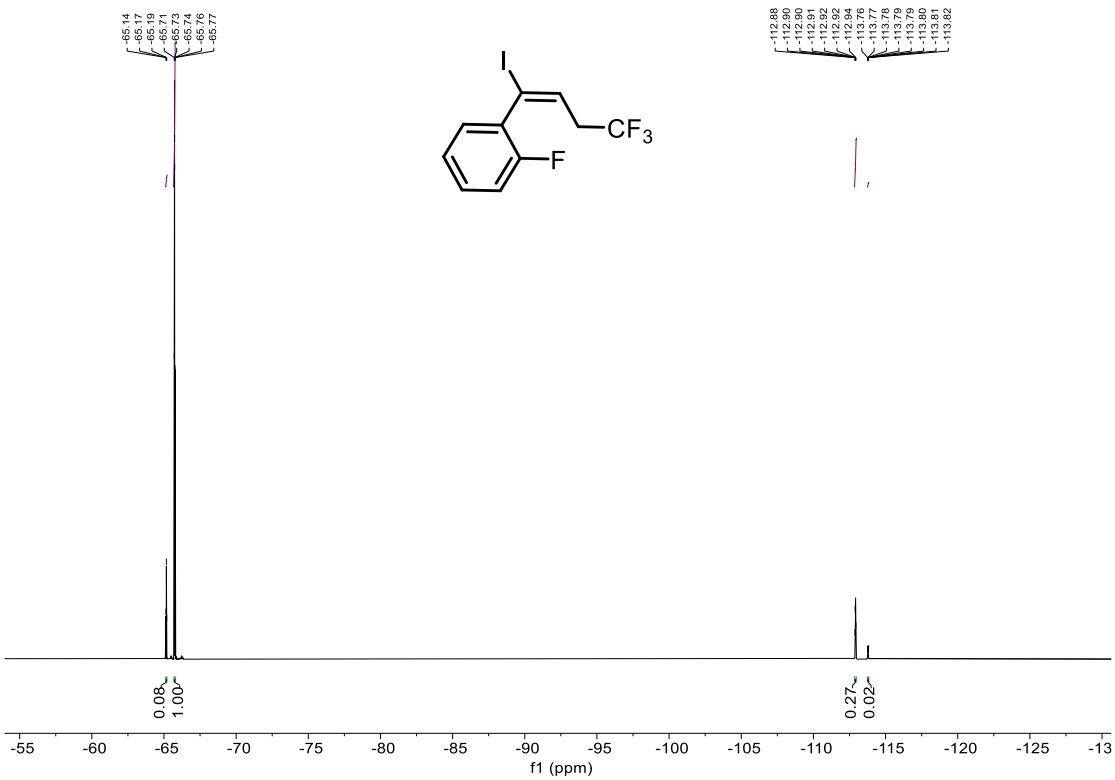
^{1}H NMR (400 MHz, CDCl3) of *E-26*



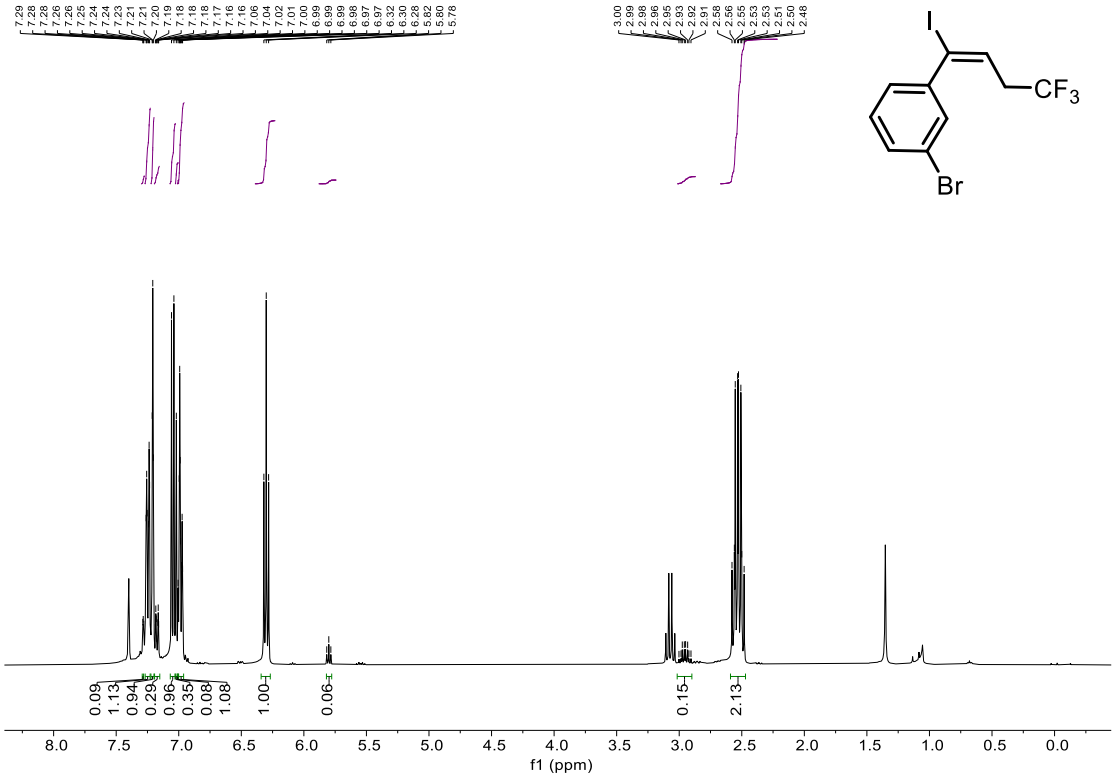
^{13}C NMR (101 MHz, $CDCl_3$) of *E-26*



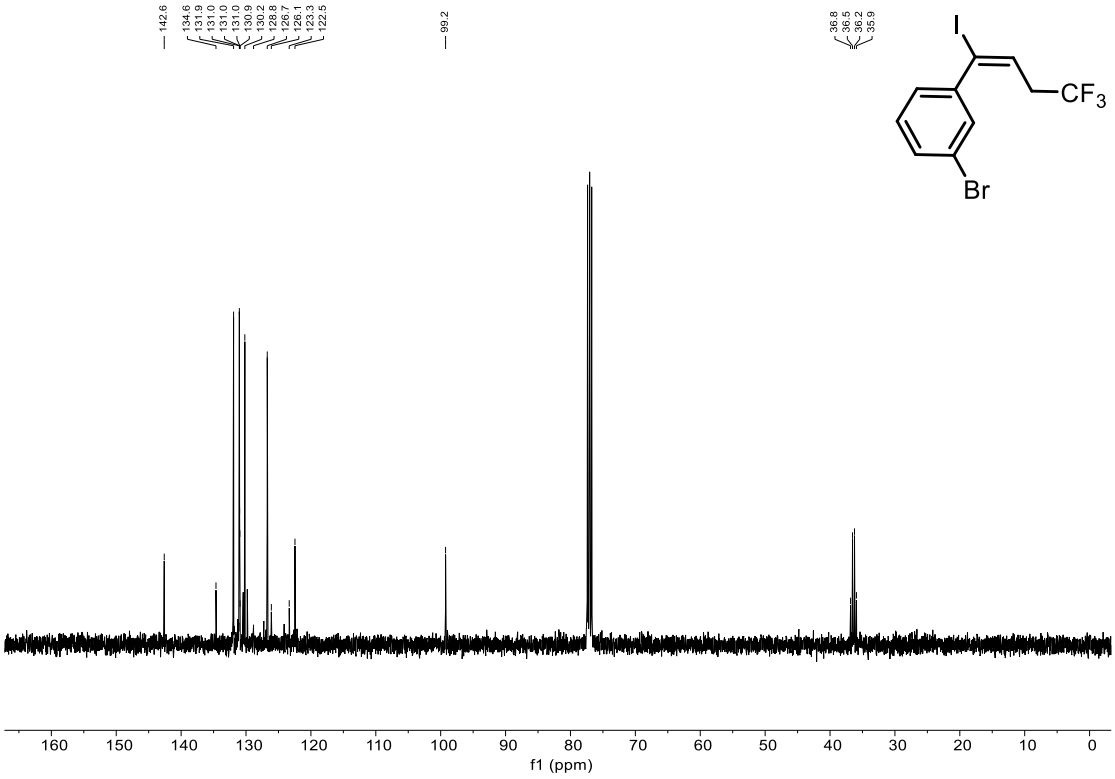
^{19}F NMR (376 MHz, $CDCl_3$) of *E-26*



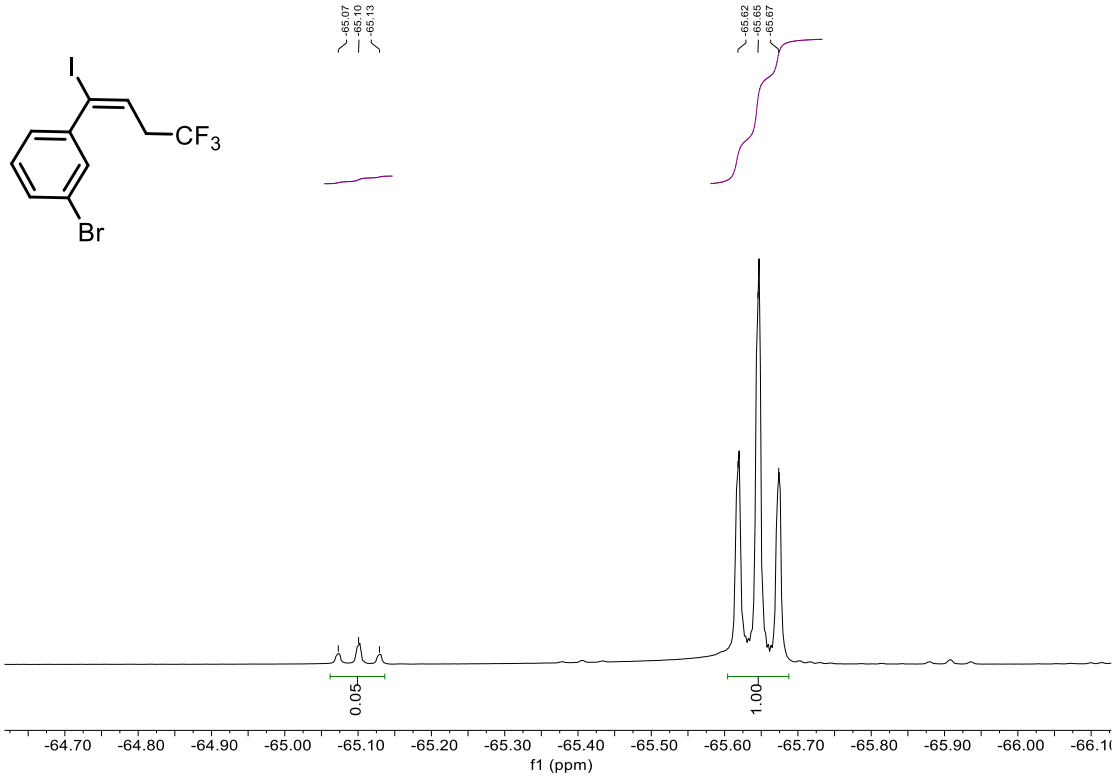
^{1}H NMR (400 MHz, CDCl3) of *E-27*



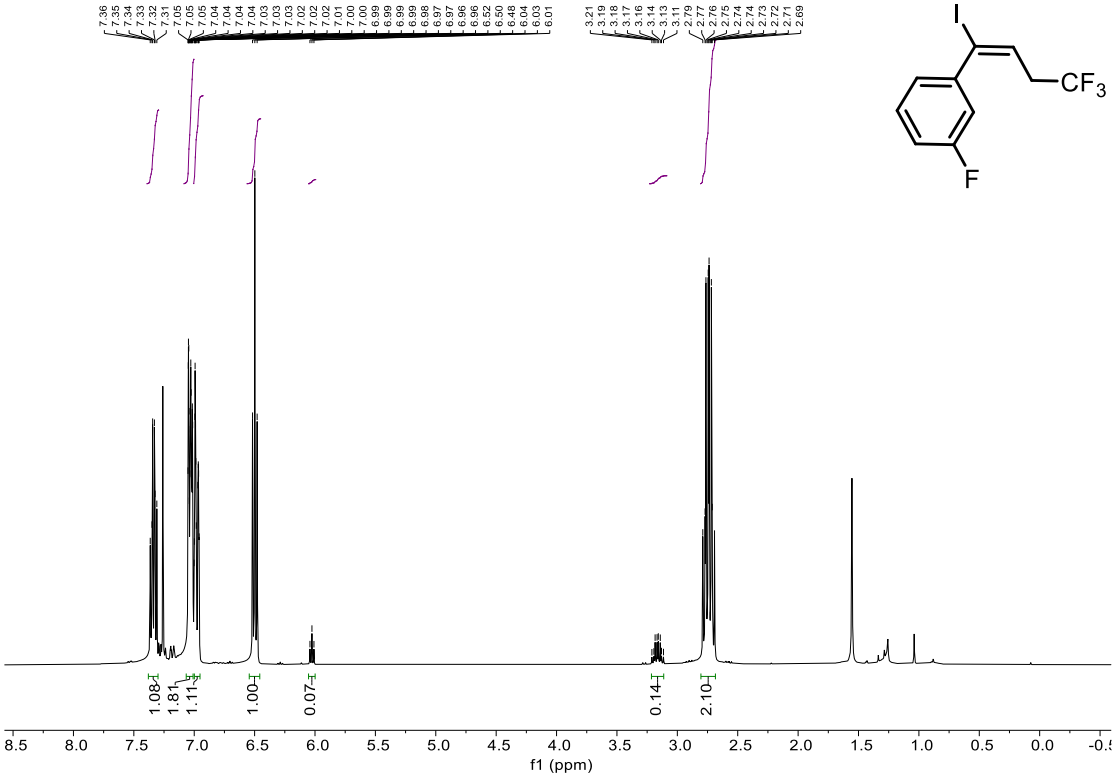
^{13}C NMR (101 MHz, $CDCl_3$) of *E-27*



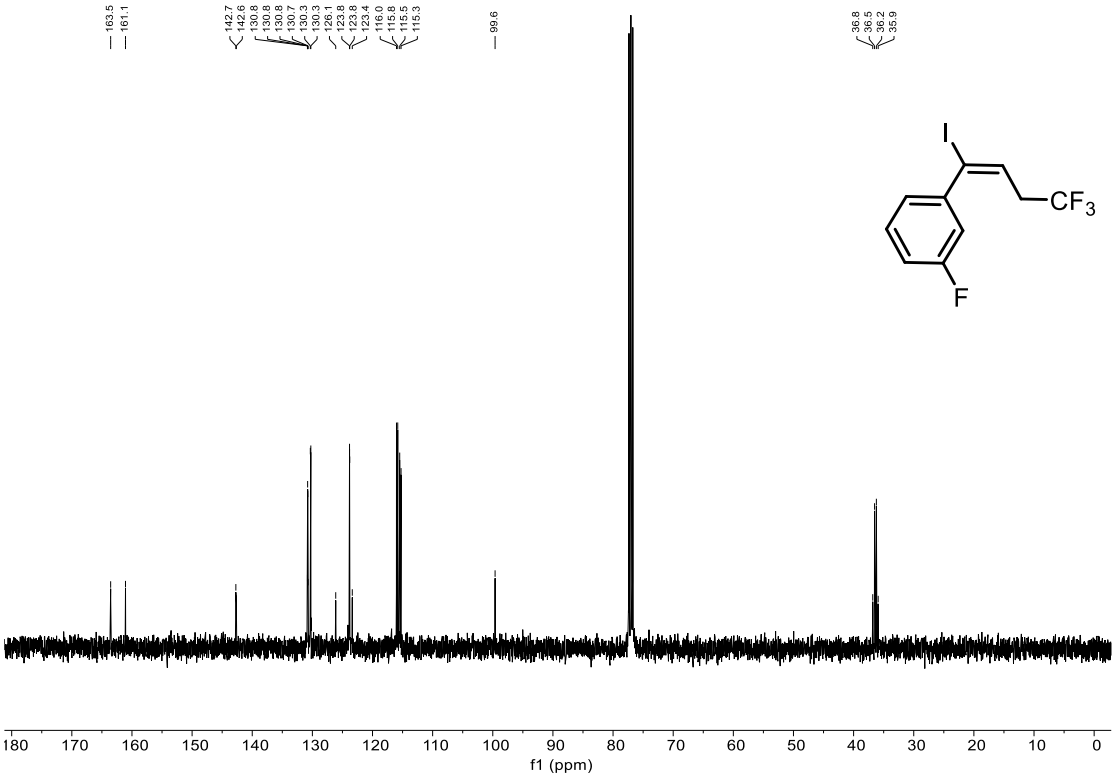
^{19}F NMR (376 MHz, $CDCl_3$) of *E-27*



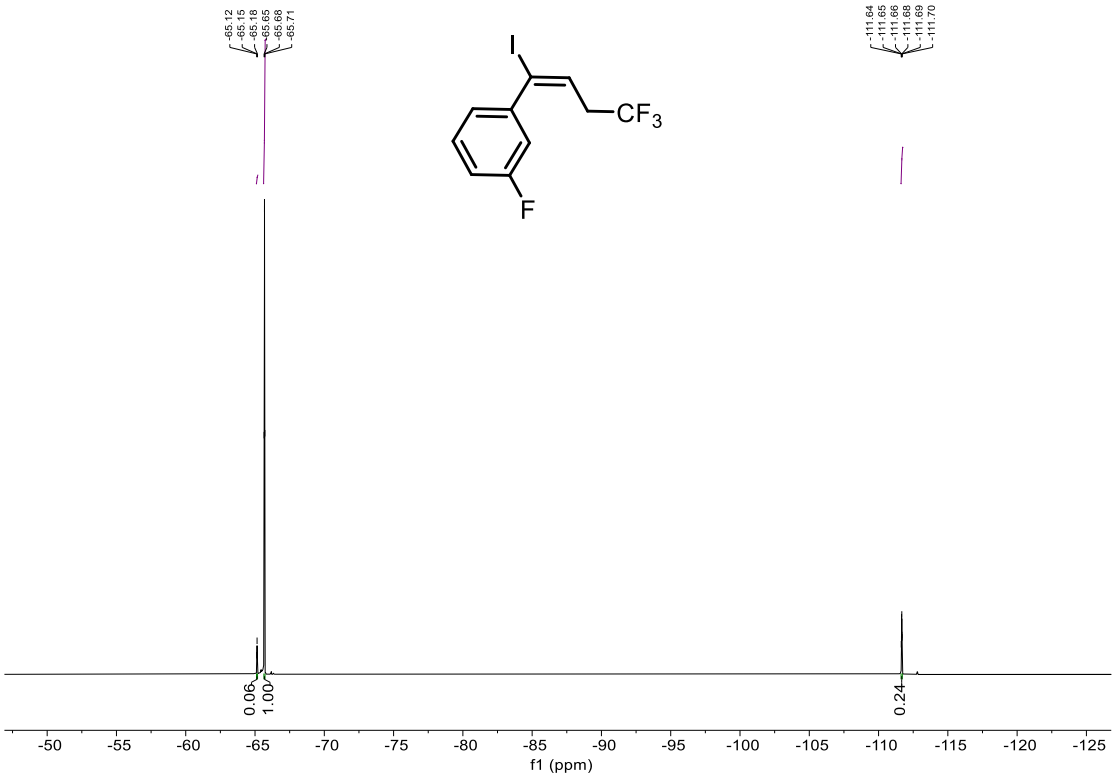
^{1}H NMR (400 MHz, CDCl3) of *E-28*



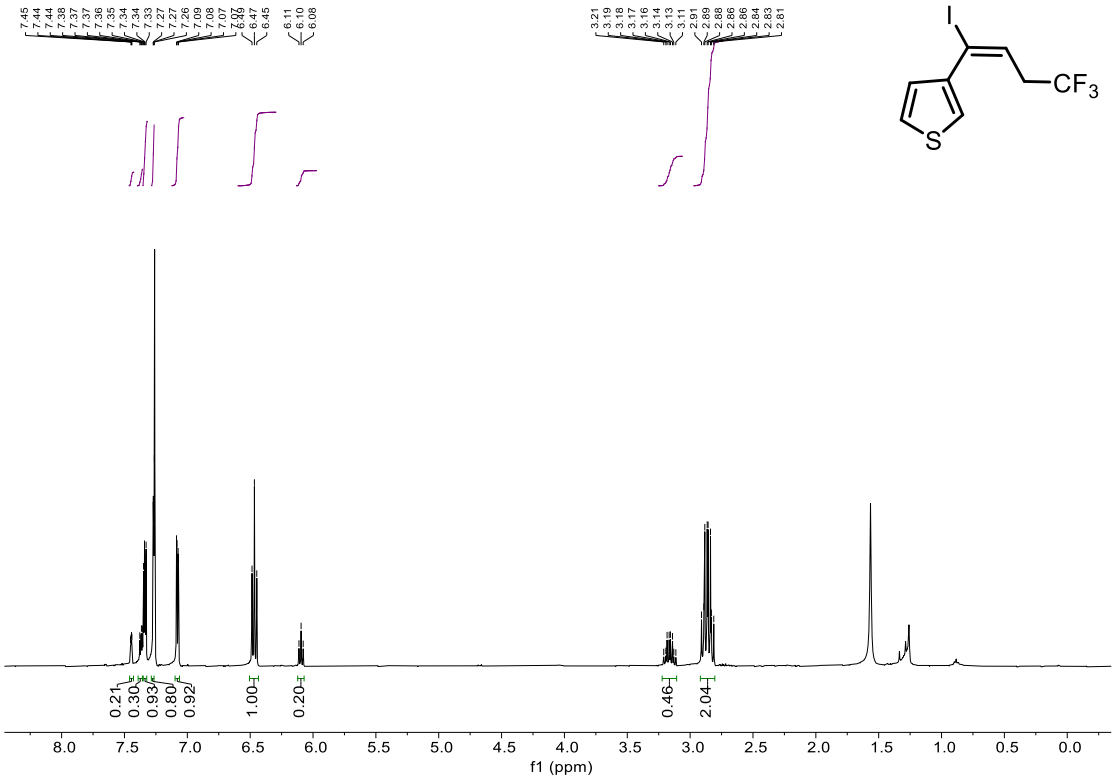
^{13}C NMR (101 MHz, $CDCl_3$) of *E-28*



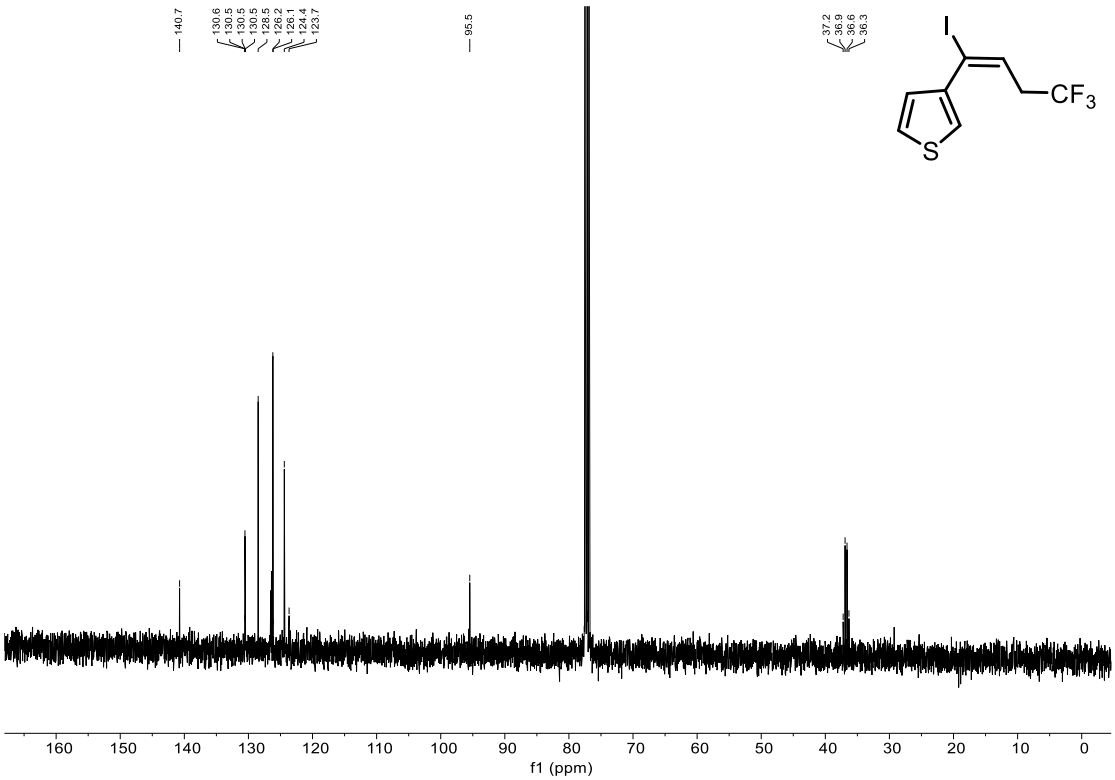
^{19}F NMR (376 MHz, $CDCl_3$) of *E-28*



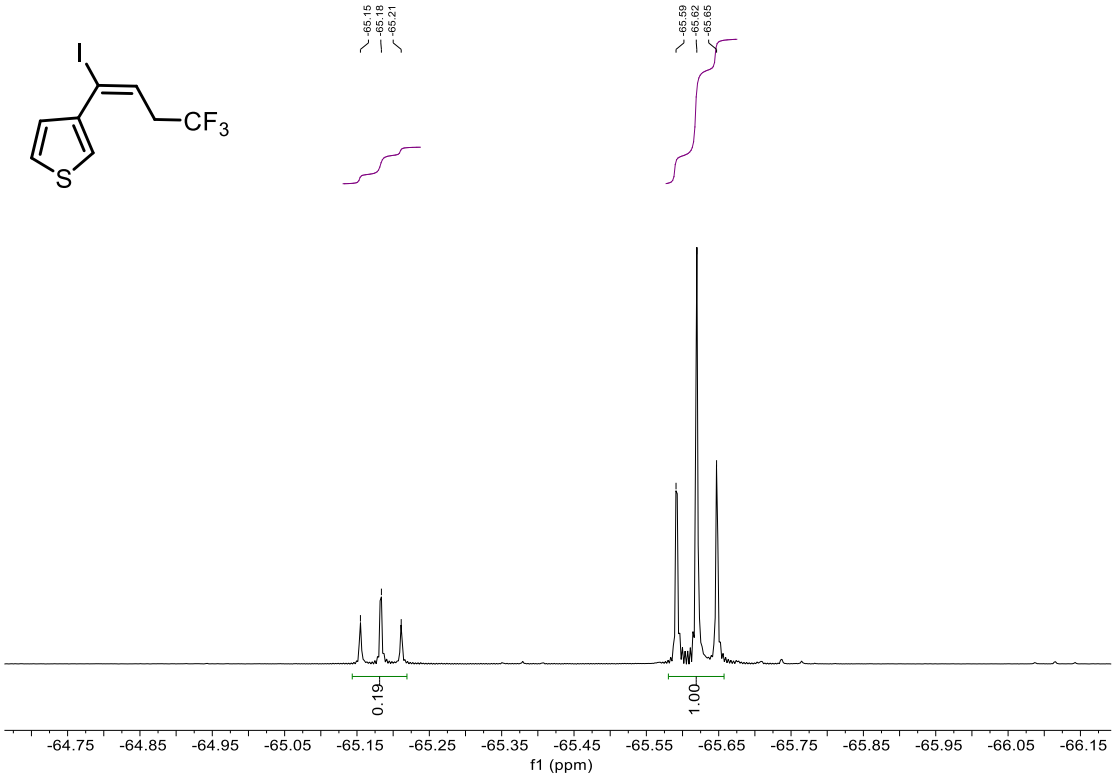
^{1}H NMR (400 MHz, CDCl3) of *E-29*



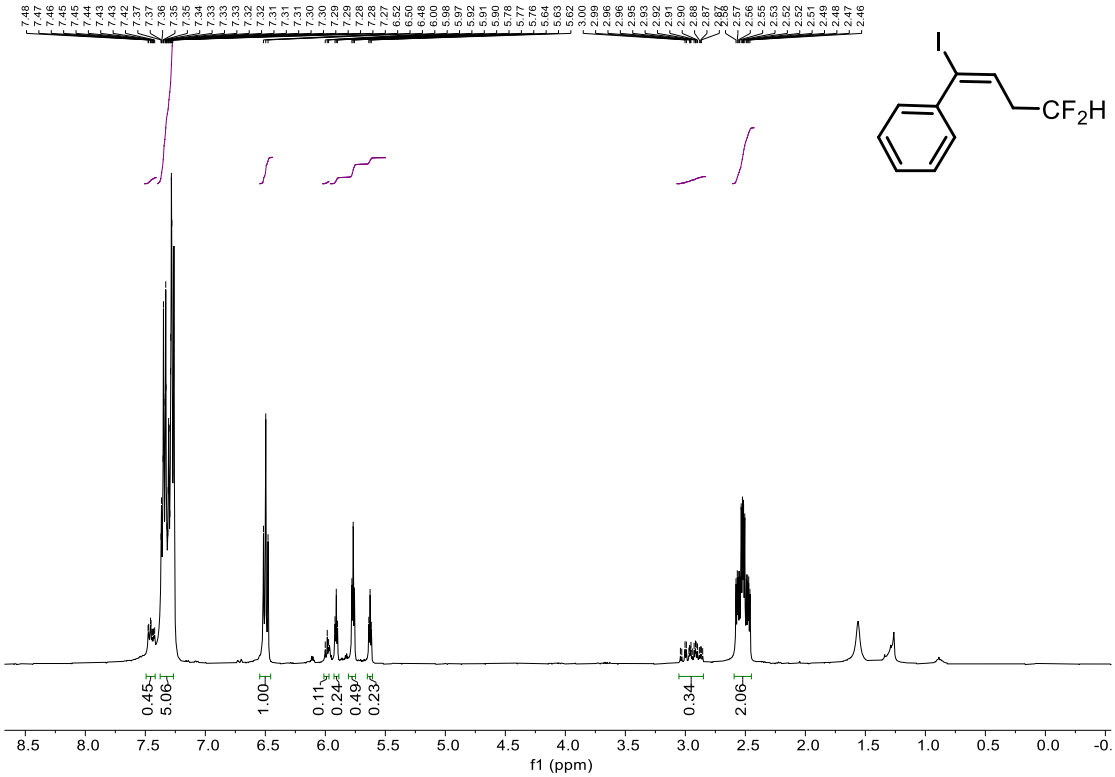
^{13}C NMR (101 MHz, CDCl$_3$) of *E-29*



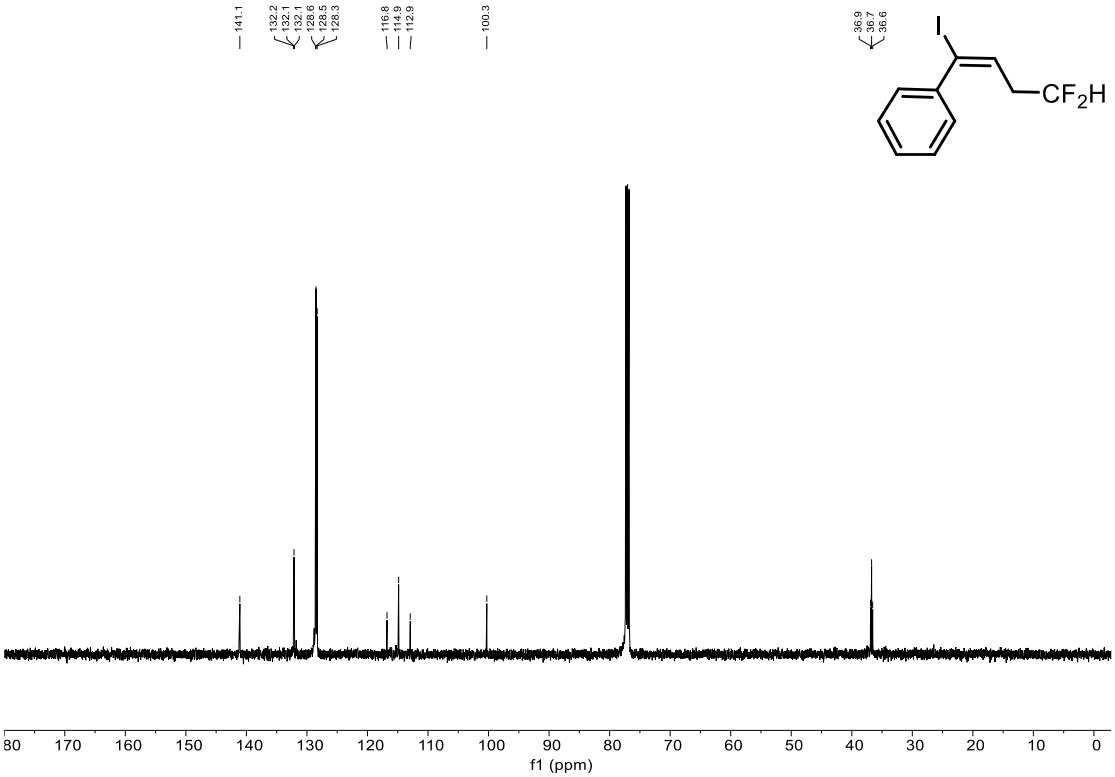
^{19}F NMR (376 MHz, $CDCl_3$) of *E-29*



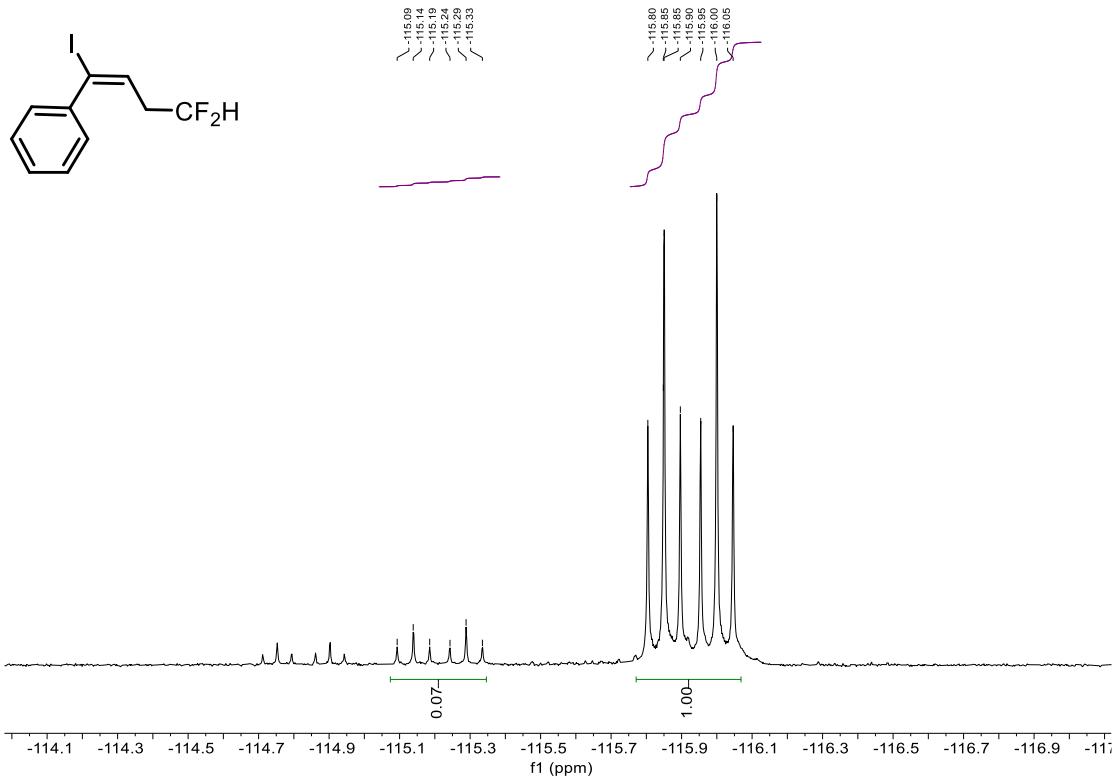
^{1}H NMR (400 MHz, CDCl3) of *E-30*



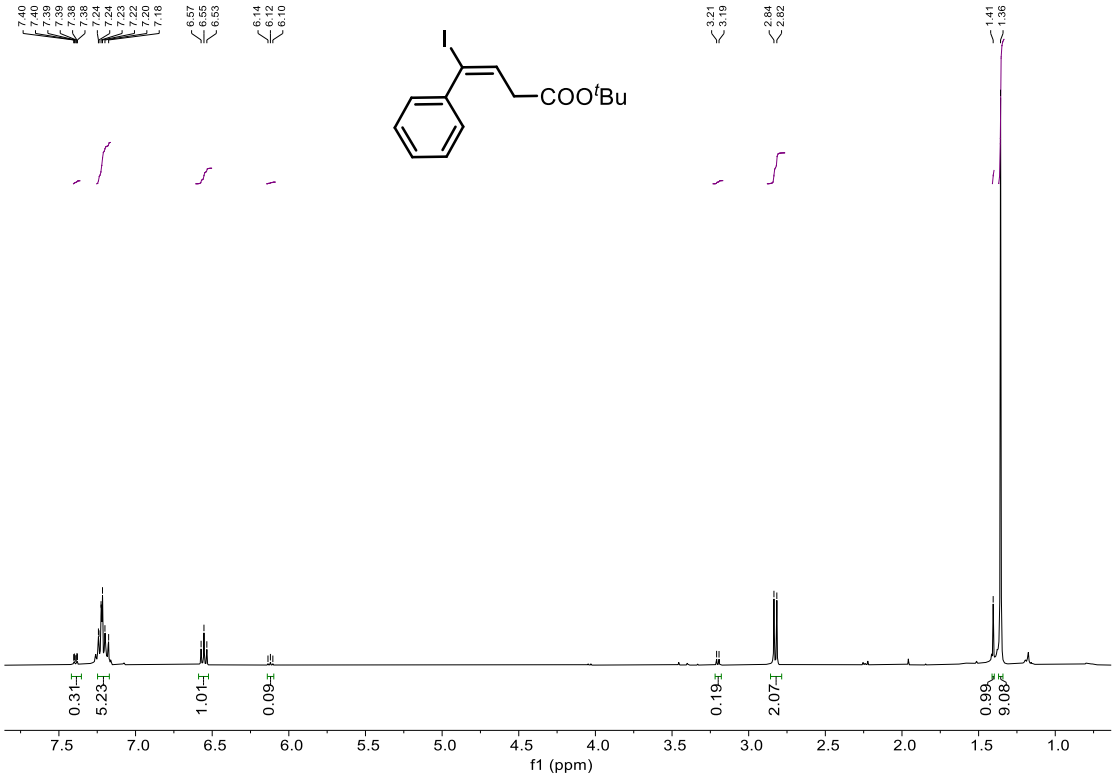
^{13}C NMR (126 MHz, $CDCl_3$) of *E-30*



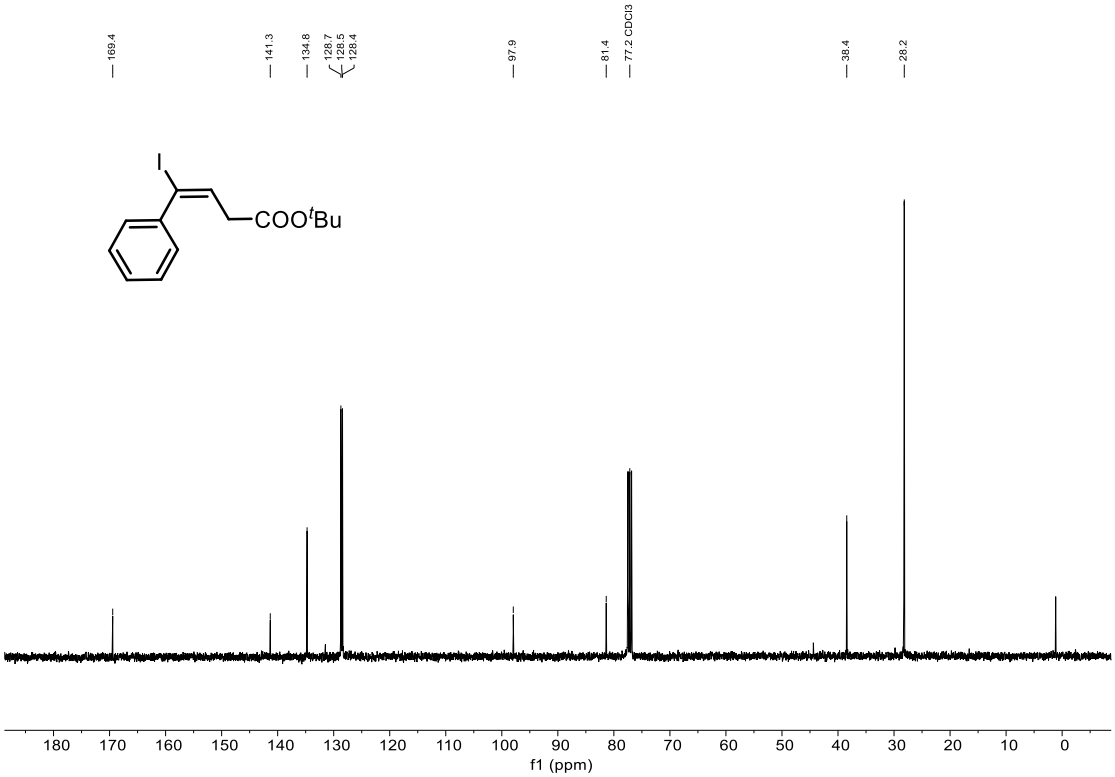
^{19}F NMR (376 MHz, $CDCl_3$) of *E-30*



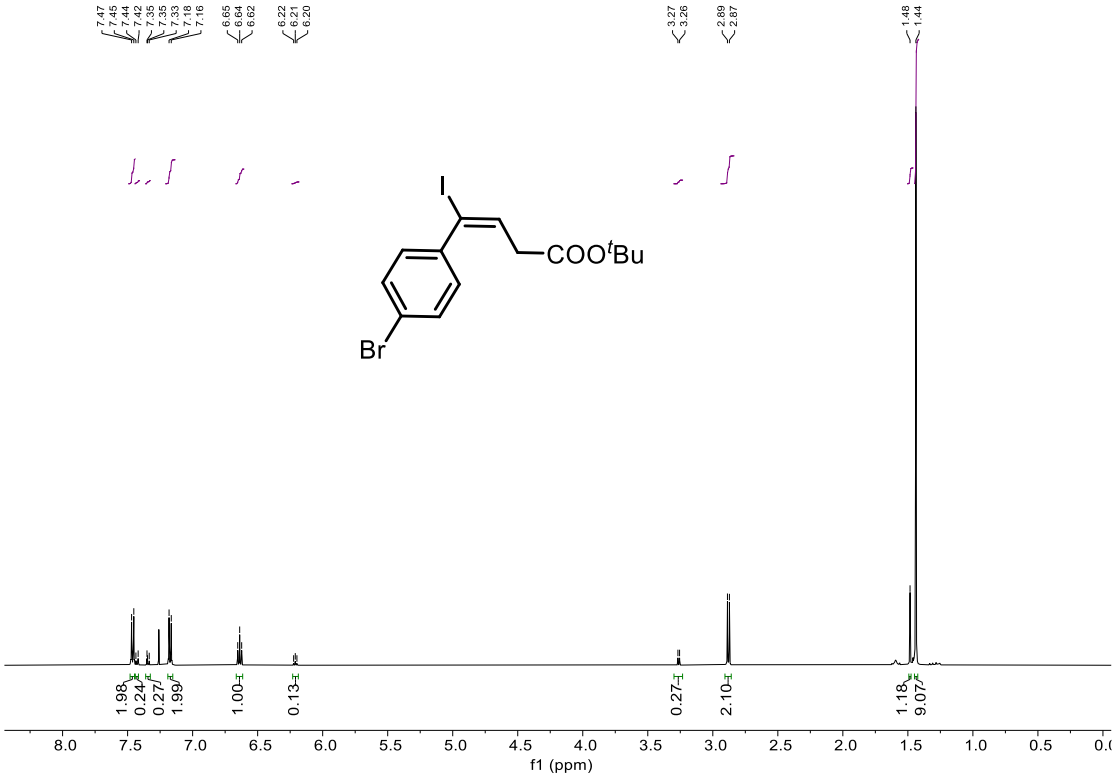
^{1}H NMR (400 MHz, CDCl3) of *E-31*



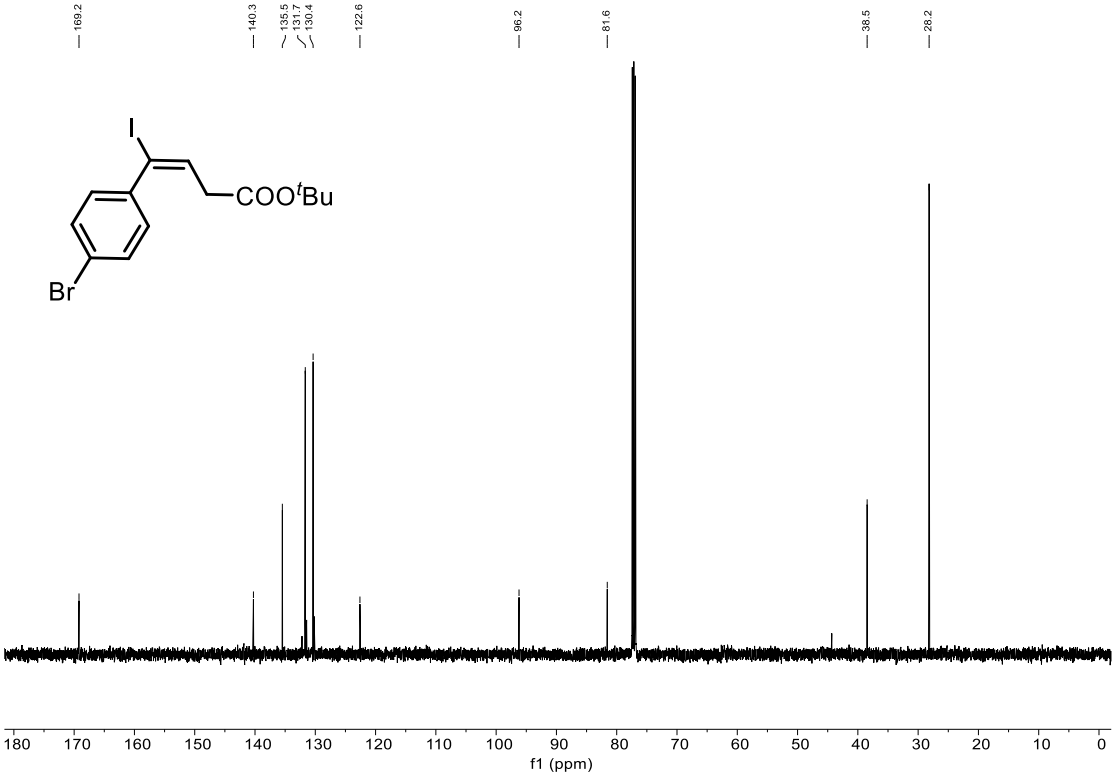
^{13}C NMR (101 MHz, CDCl$_3$) of *E-31*



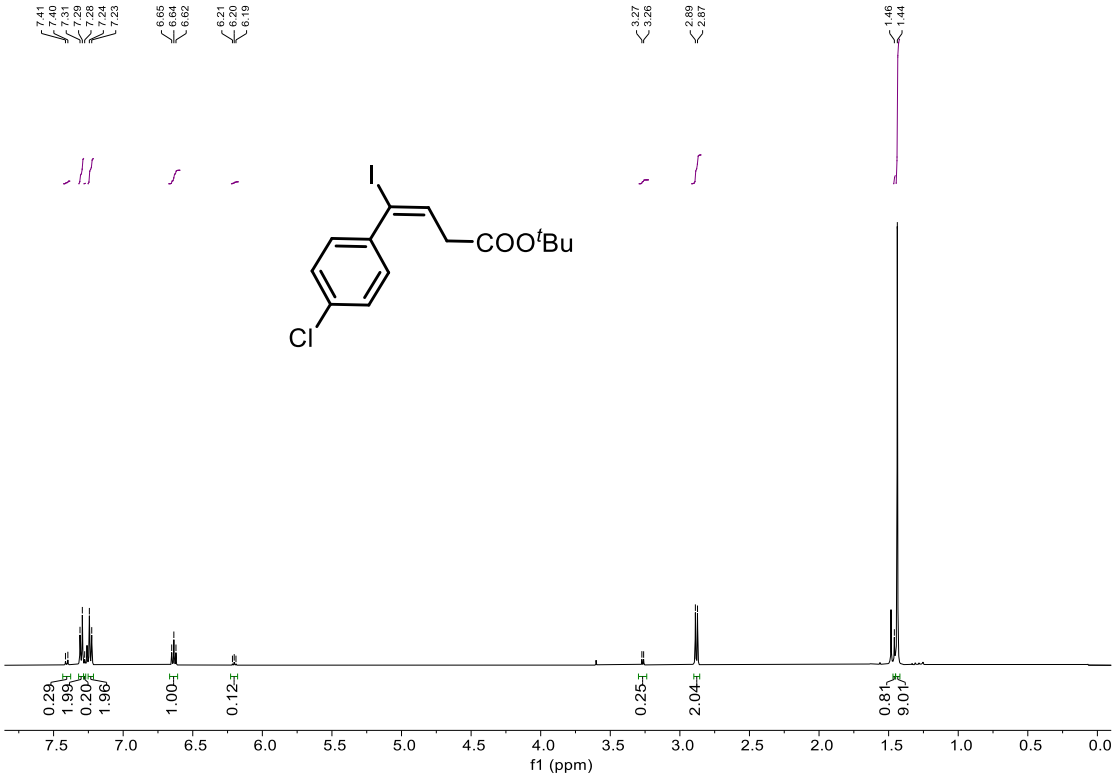
^{1}H NMR (500 MHz, CDCl3) of *E-32*



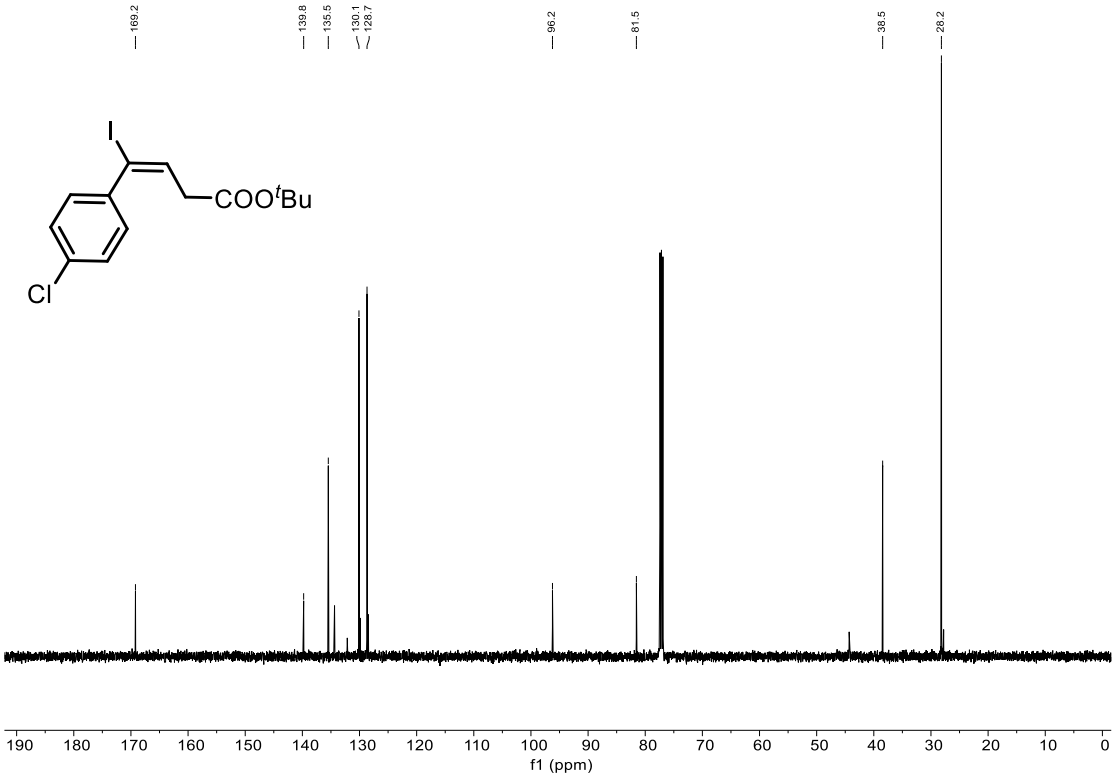
^{13}C NMR (126 MHz, CDCl$_3$) of *E-32*



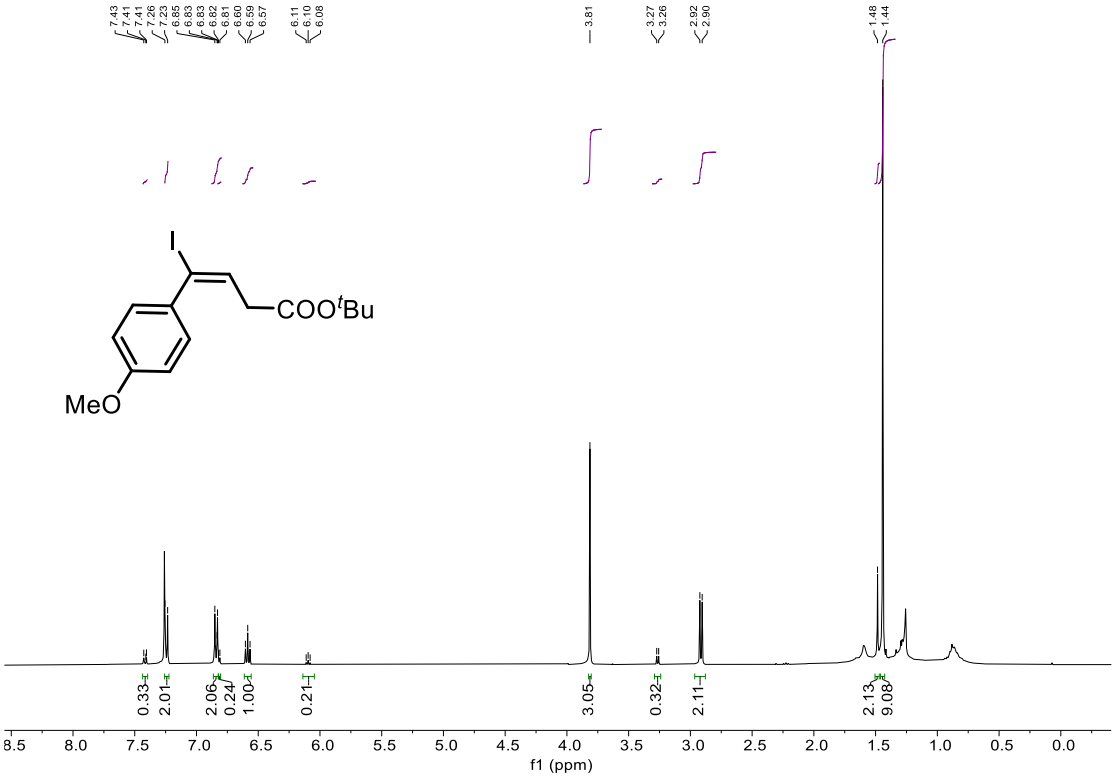
^{1}H NMR (500 MHz, CDCl3) of *E-33*



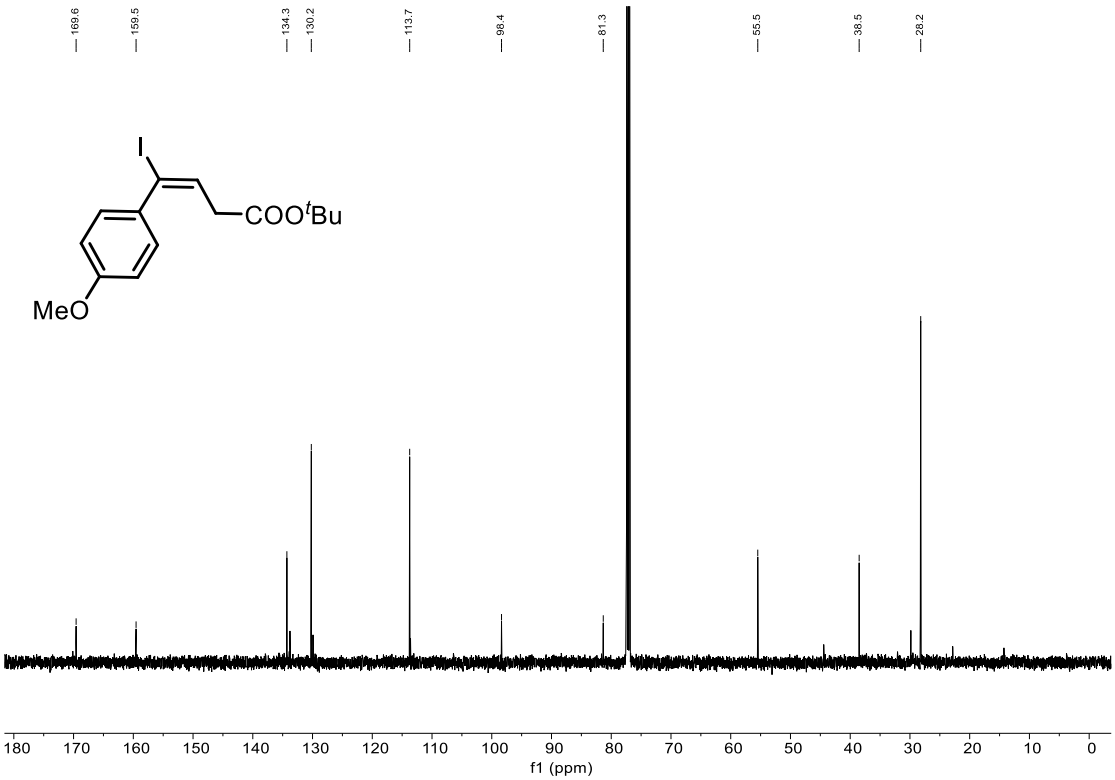
^{13}C NMR (126 MHz, CDCl$_3$) of *E-33*



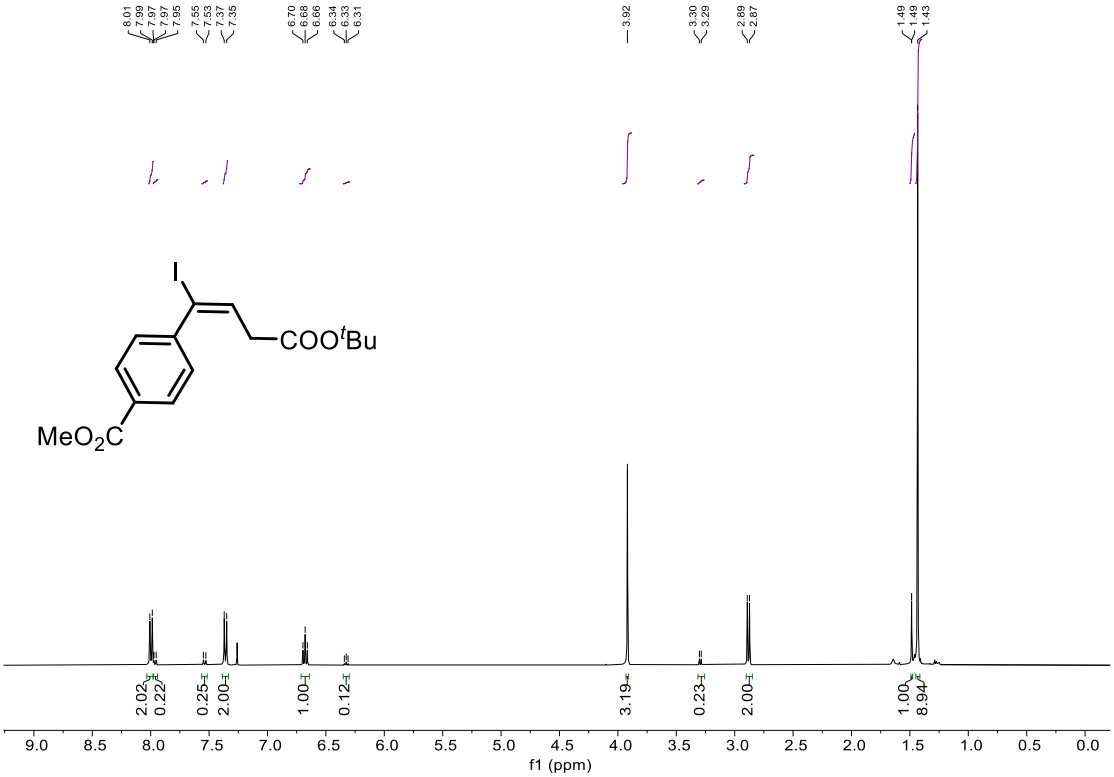
^{1}H NMR (400 MHz, CDCl3) of *E-34*



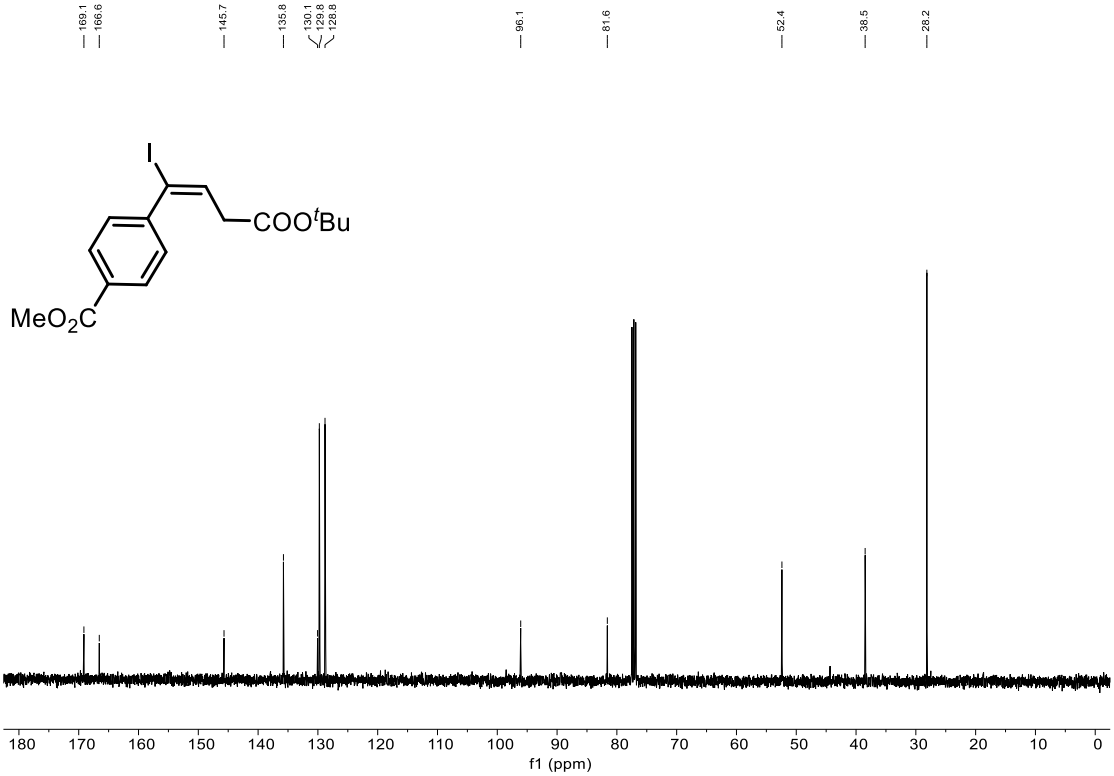
^{13}C NMR (126 MHz, CDCl$_3$) of *E-34*



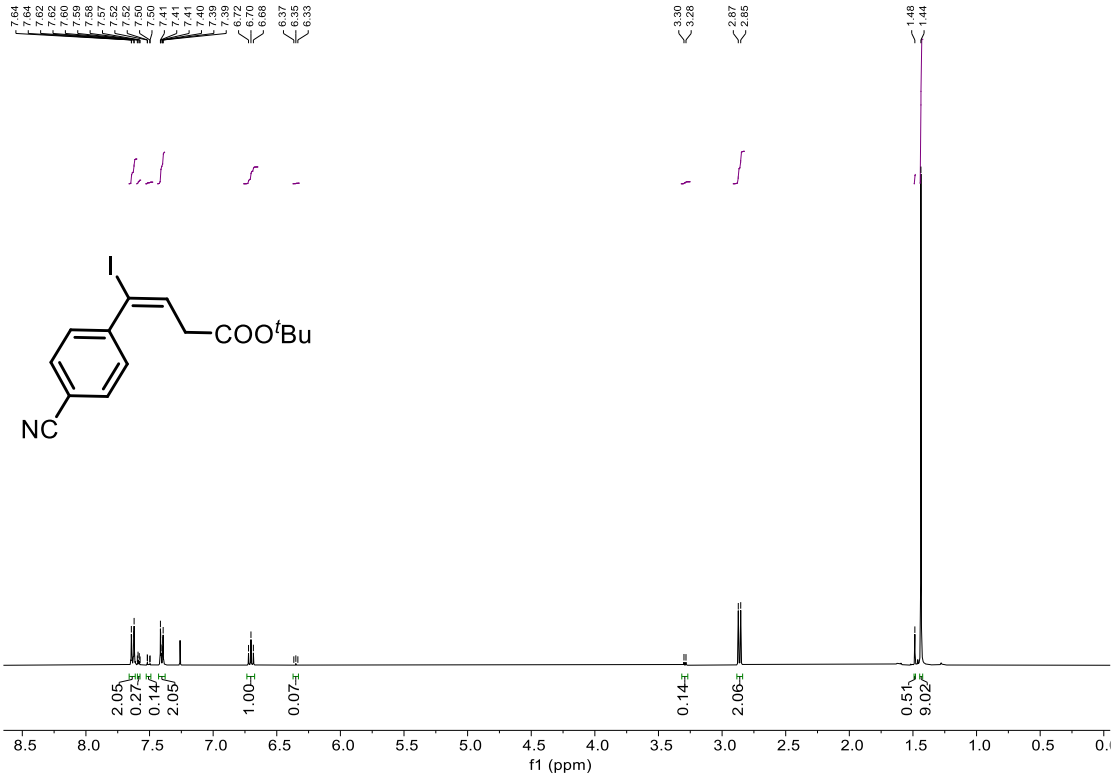
^{1}H NMR (400 MHz, CDCl3) of *E-35*



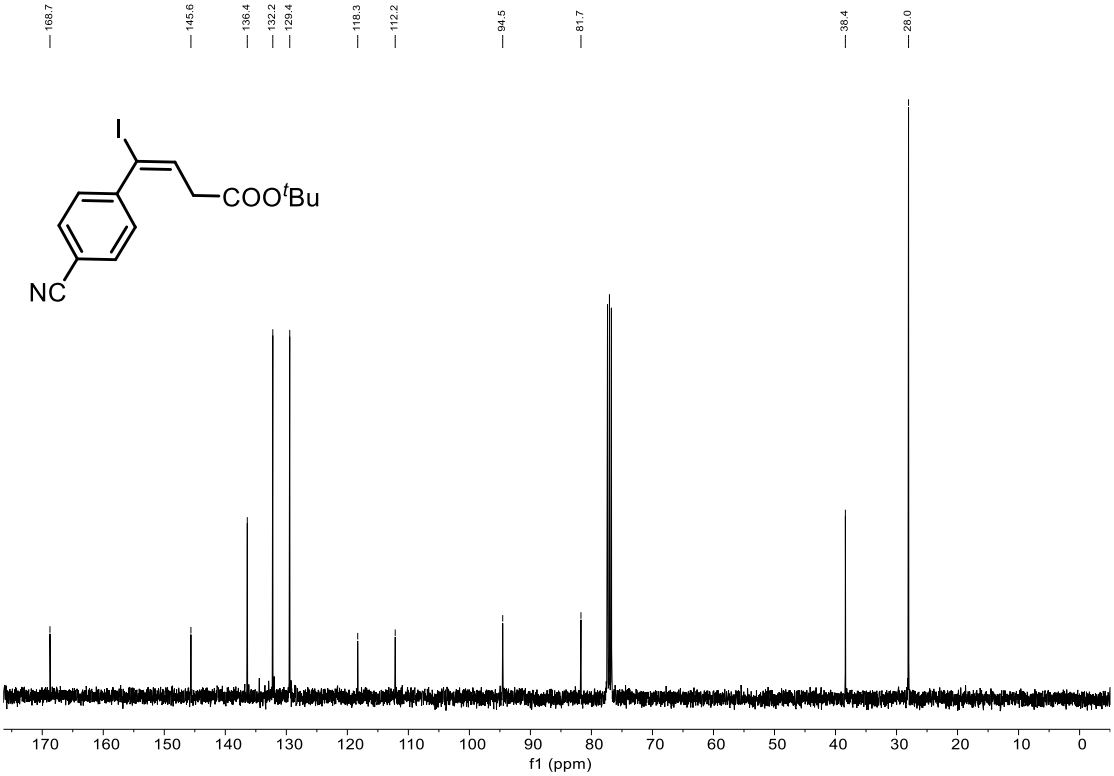
^{13}C NMR (101 MHz, CDCl$_3$) of *E-35*



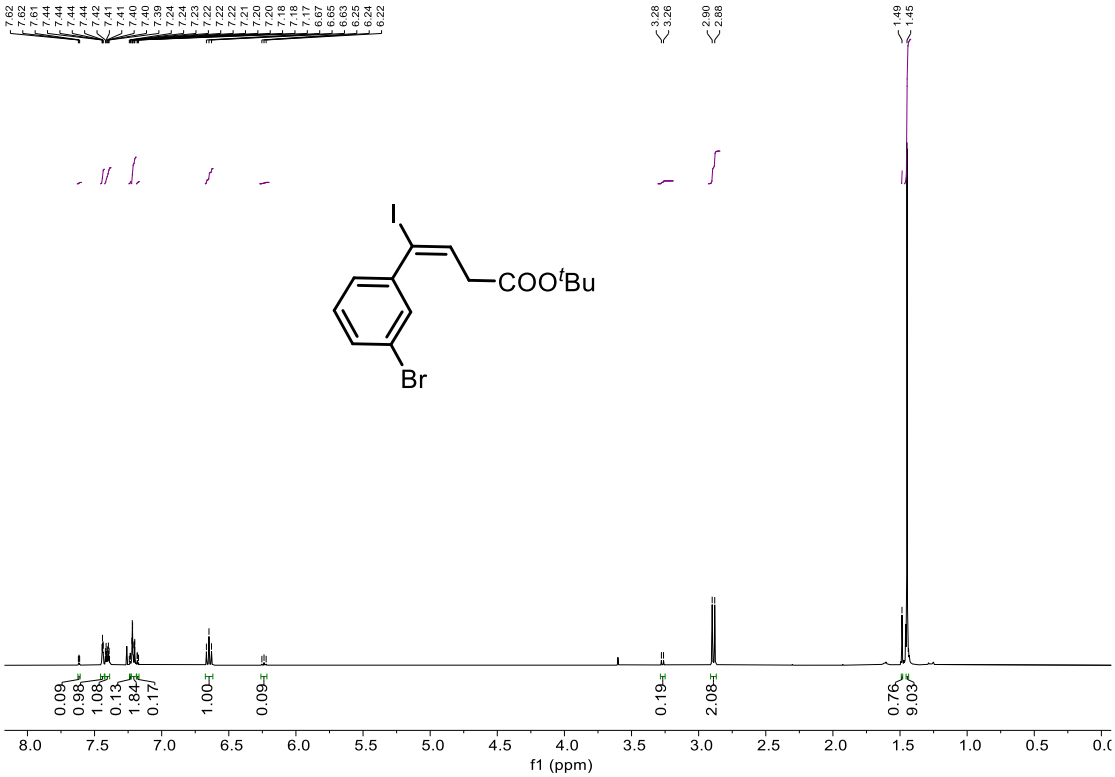
^{1}H NMR (400 MHz, CDCl3) of *E-36*



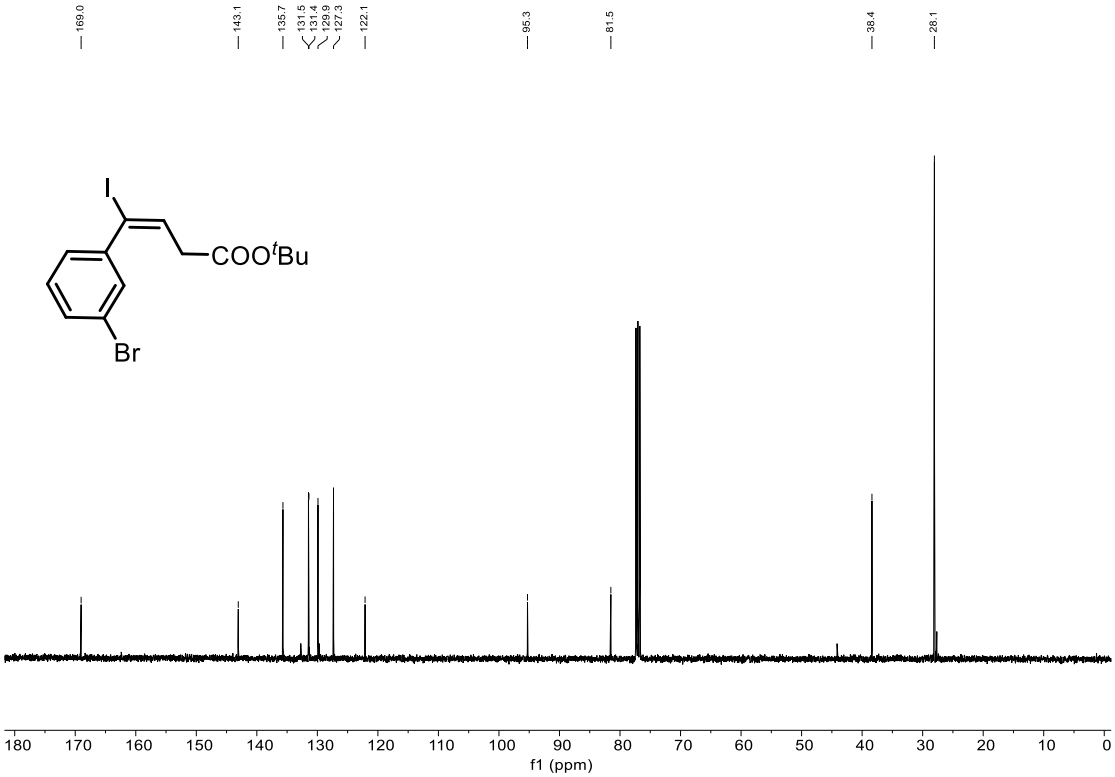
^{13}C NMR (101 MHz, CDCl$_3$) of *E-36*



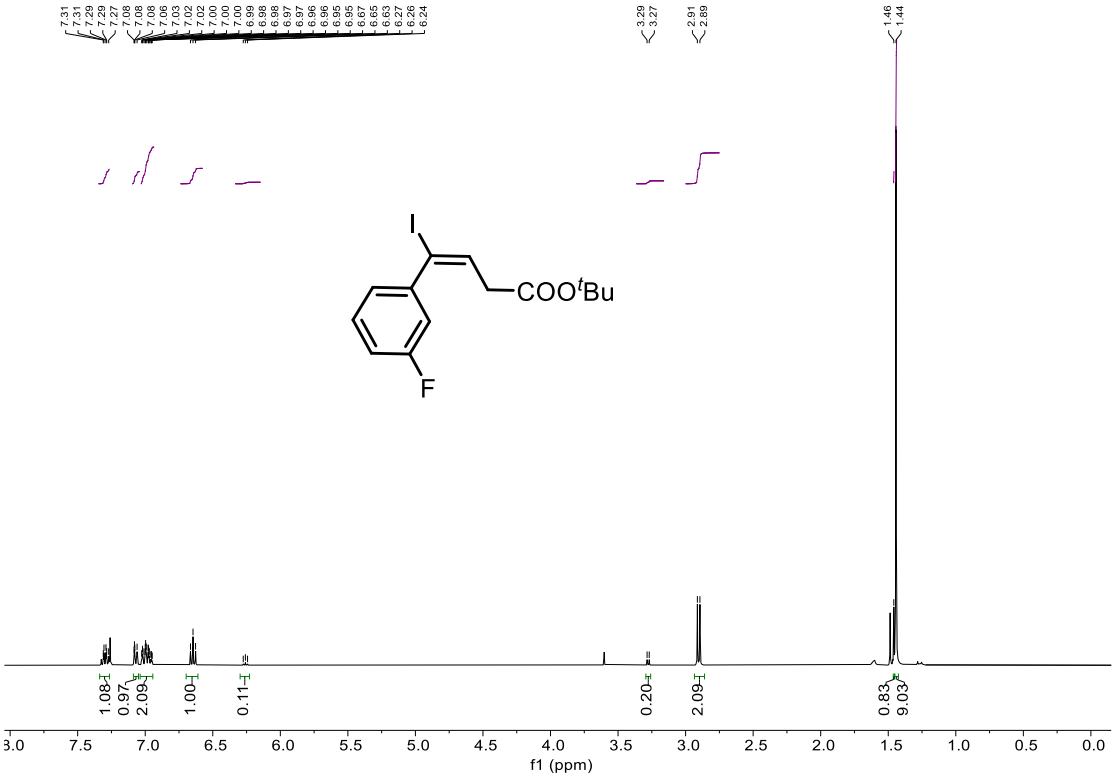
^{1}H NMR (400 MHz, CDCl3) of *E-37*



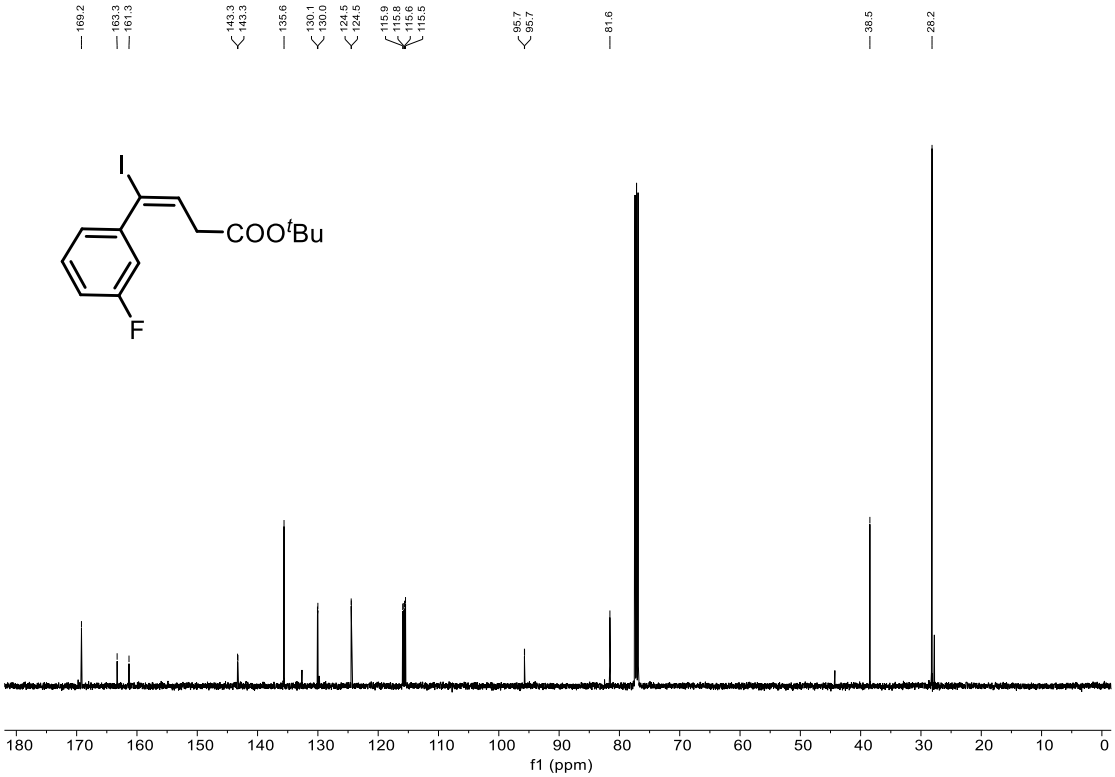
^{13}C NMR (101 MHz, $CDCl_3$) of *E-37*



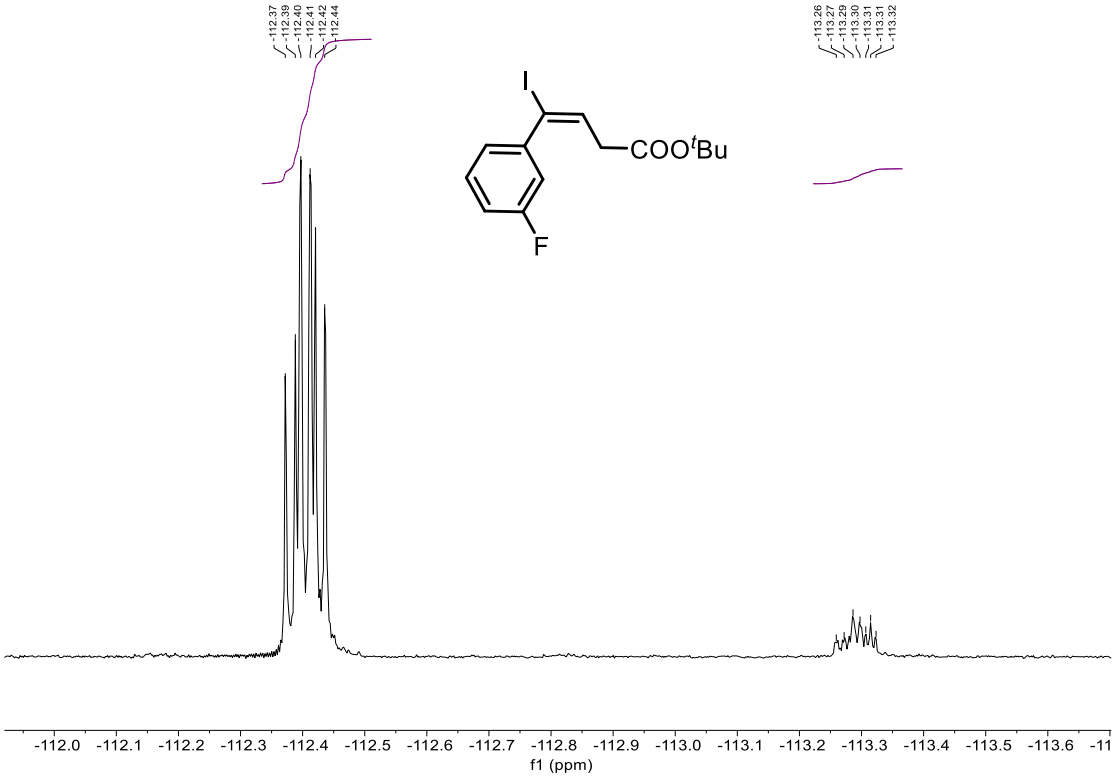
^{1}H NMR (400 MHz, CDCl3) of *E-38*



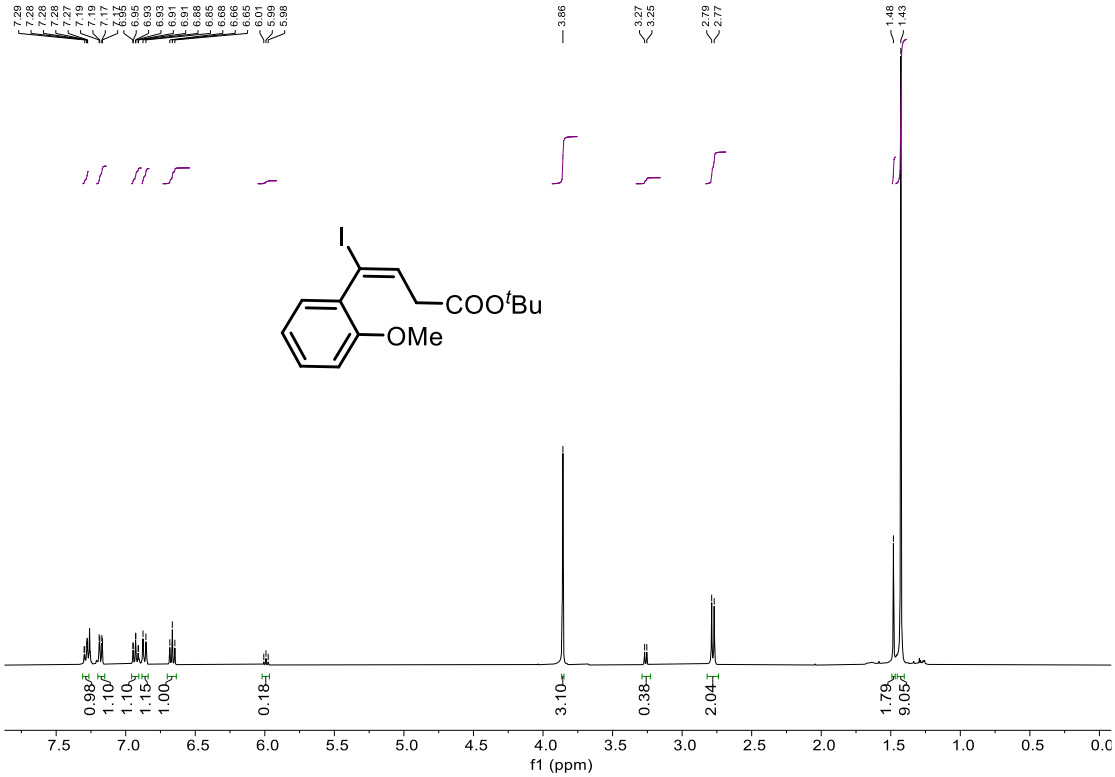
^{13}C NMR (126 MHz, $CDCl_3$) of *E-38*



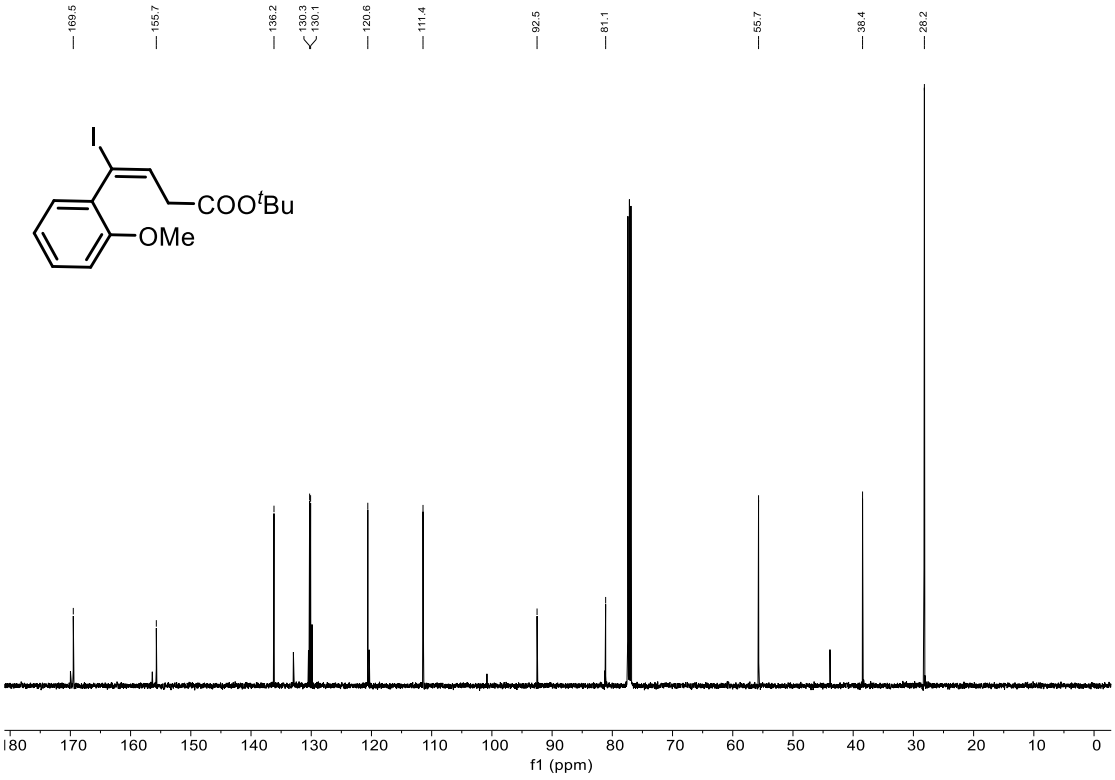
^{19}F NMR (376 MHz, $CDCl_3$) of *E-38*



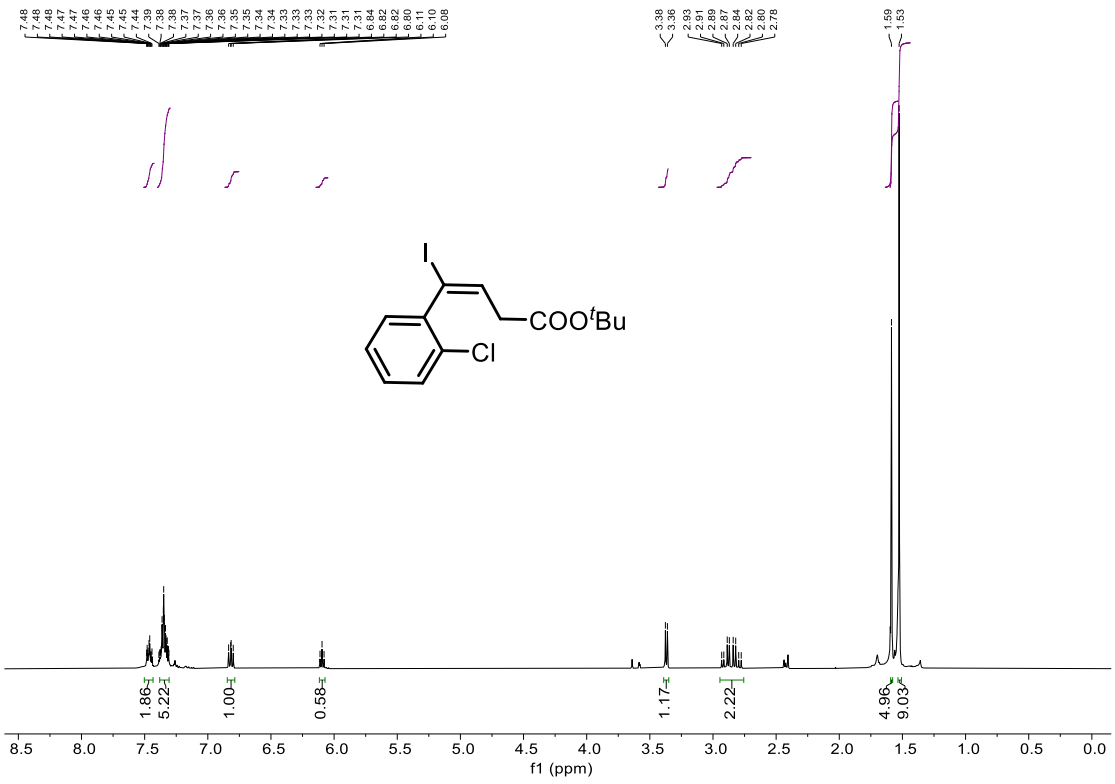
^{1}H NMR (400 MHz, CDCl3) of *E-39*



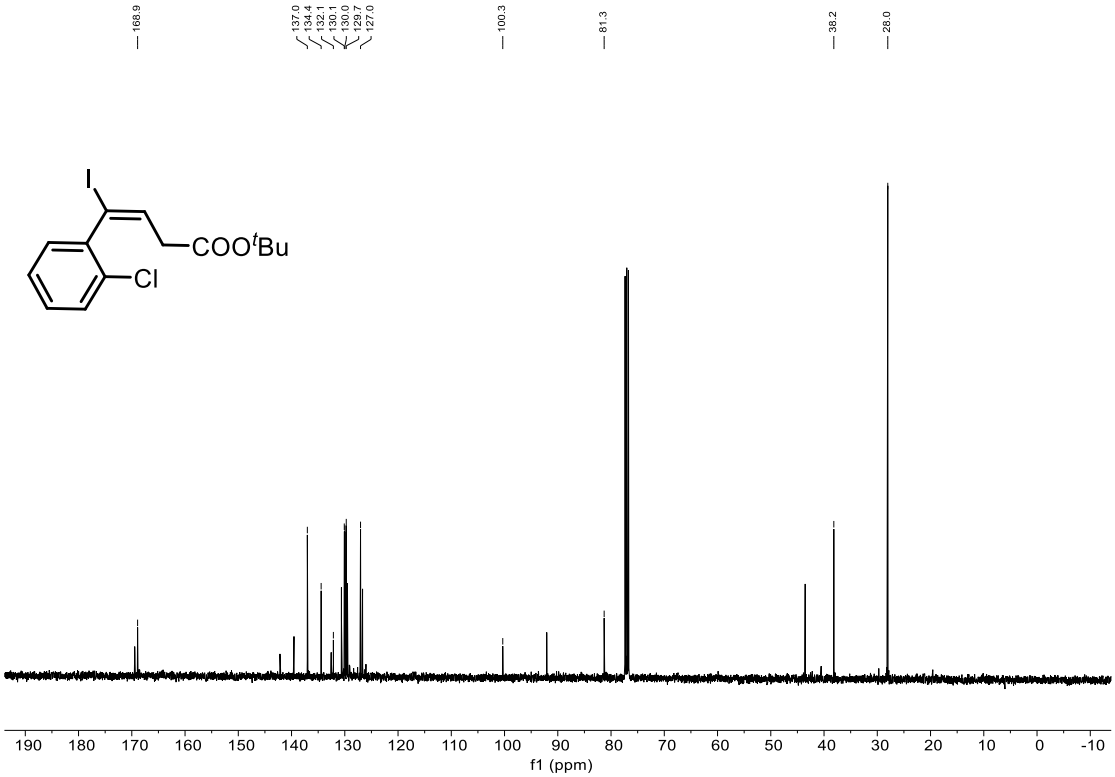
^{13}C NMR (126 MHz, $CDCl_3$) of *E-39*



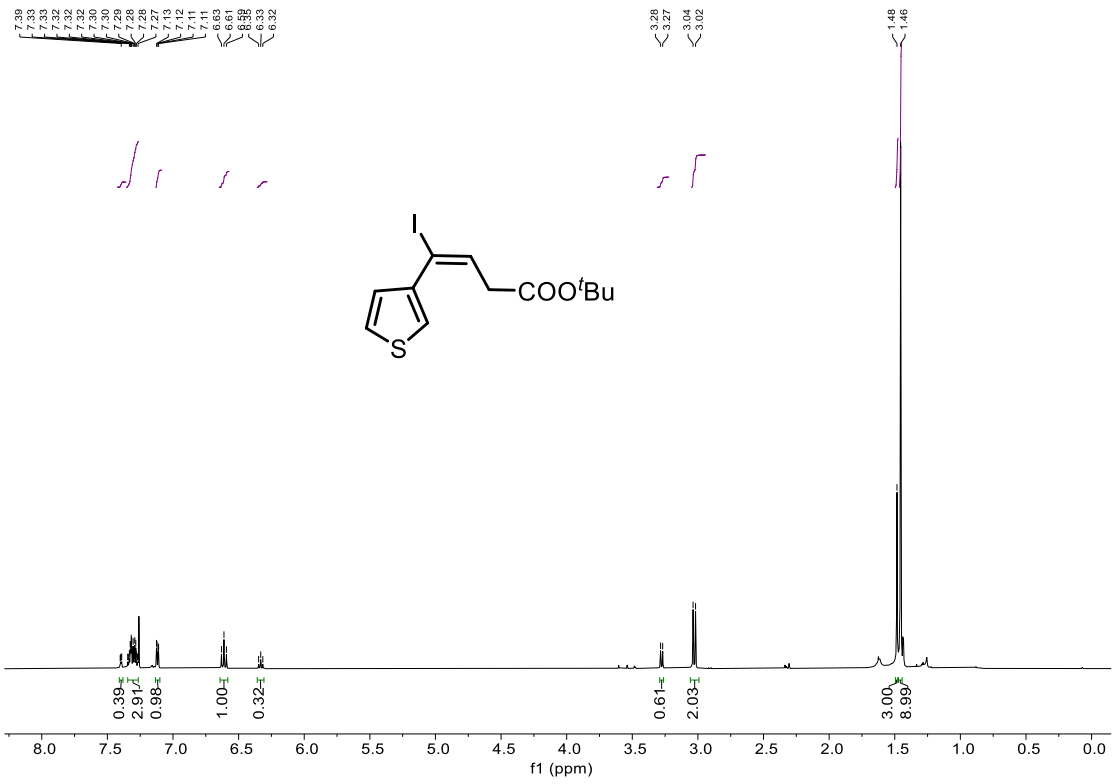
^{1}H NMR (400 MHz, CDCl3) of *E-40*



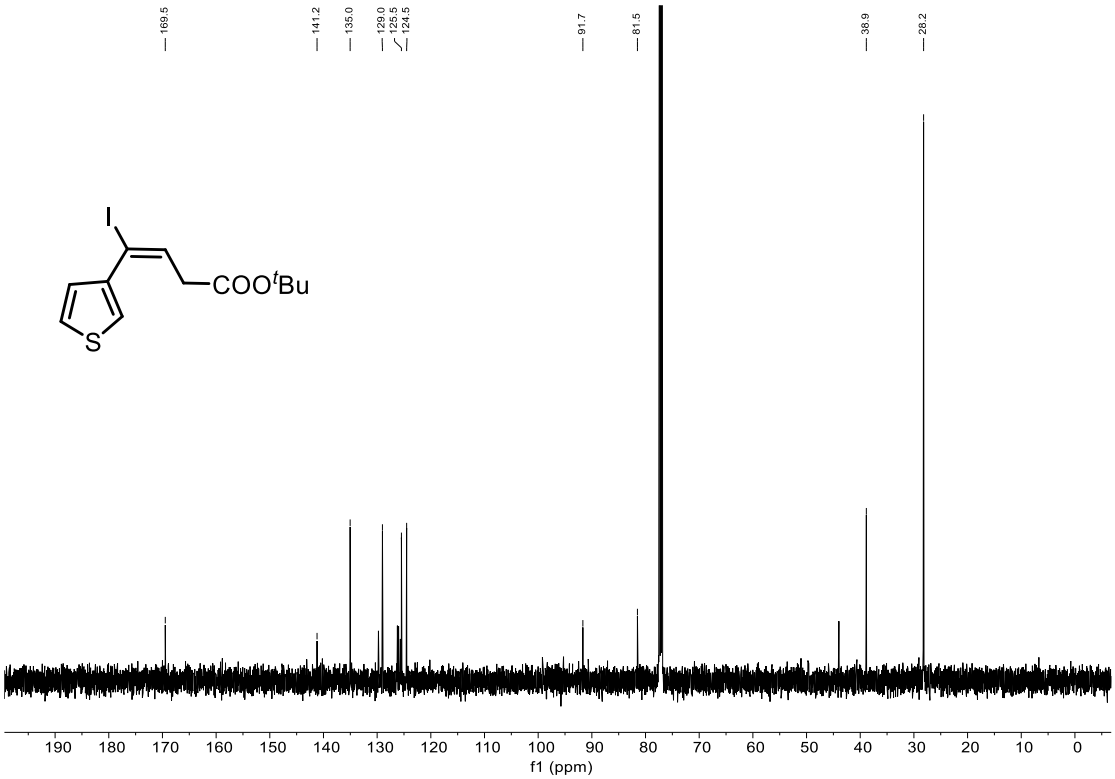
^{13}C NMR (101 MHz, $CDCl_3$) of *E-40*



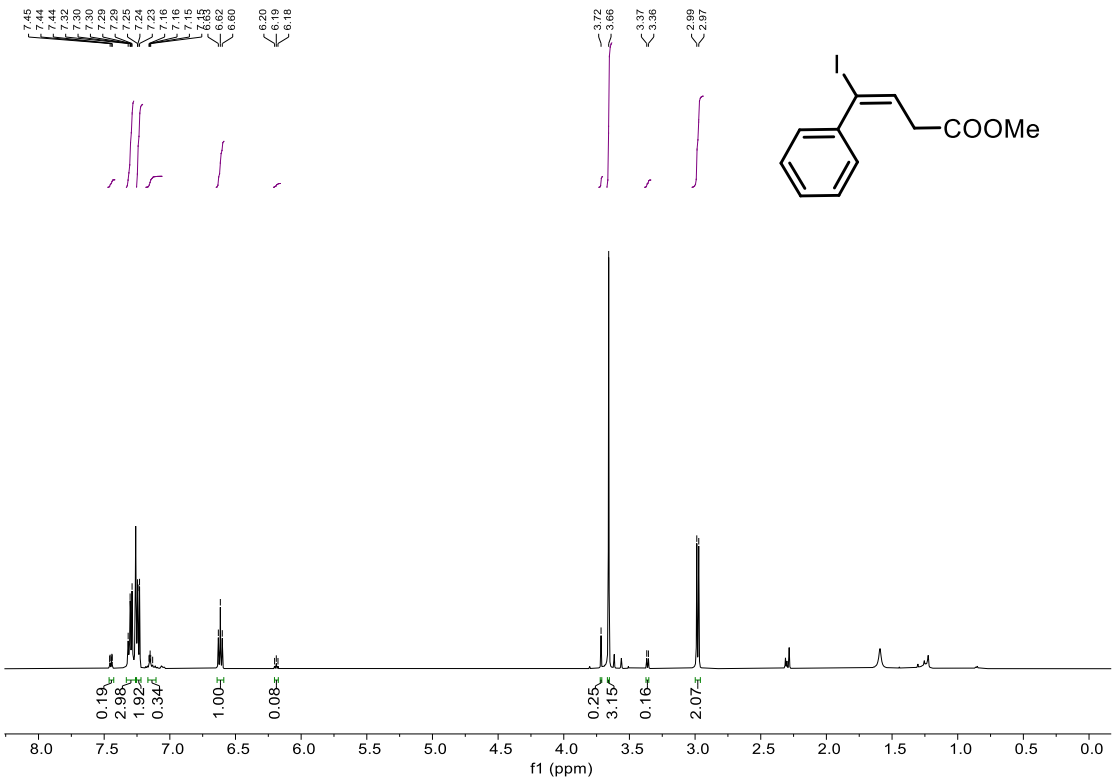
^{1}H NMR (400 MHz, CDCl3) of *E-41*



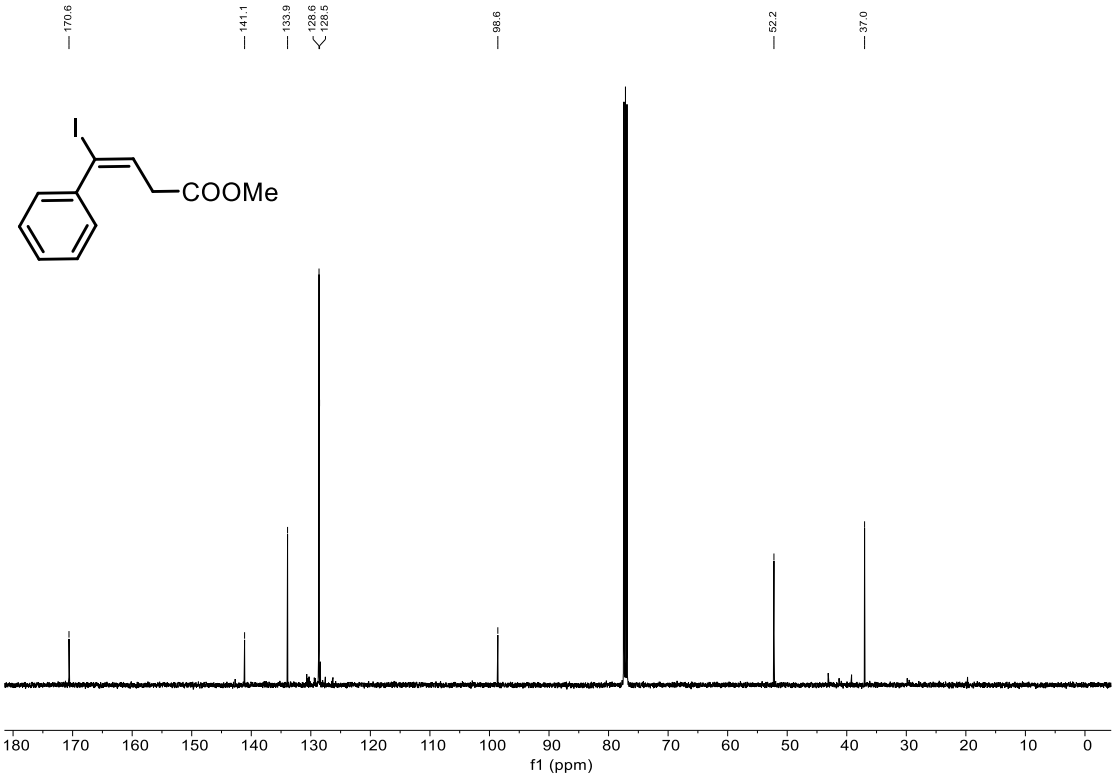
^{13}C NMR (126 MHz, $CDCl_3$) of *E-41*



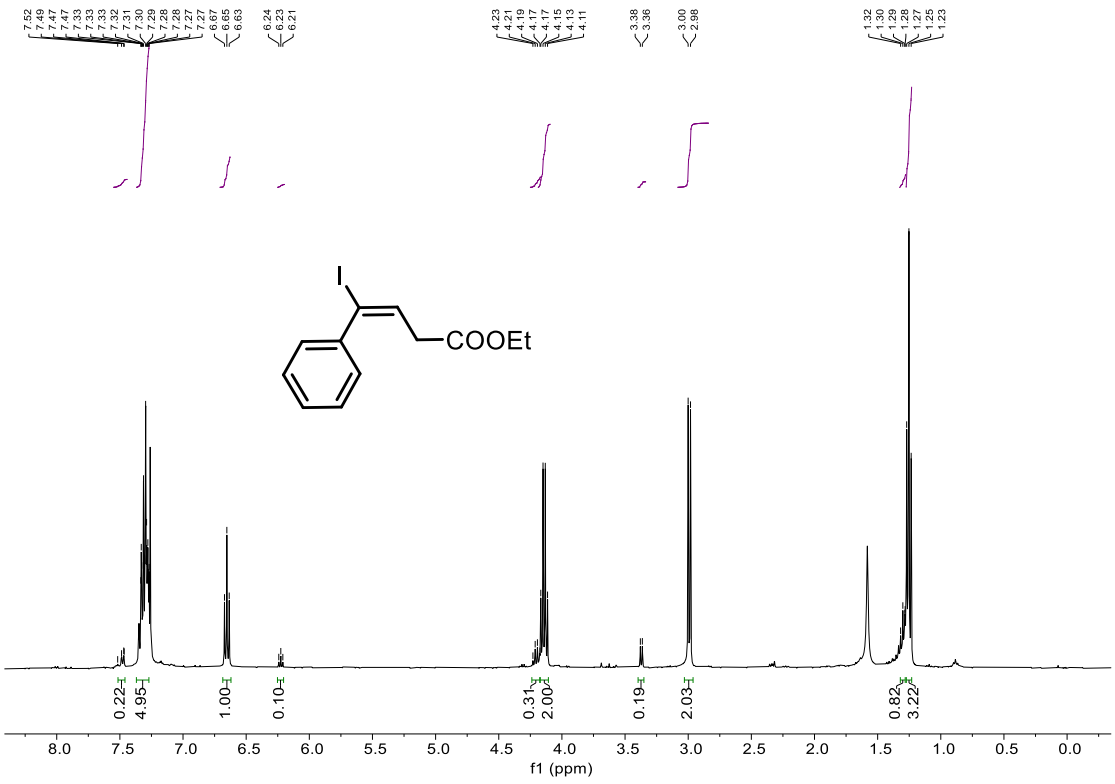
^{1}H NMR (500 MHz, CDCl3) of *E-42*



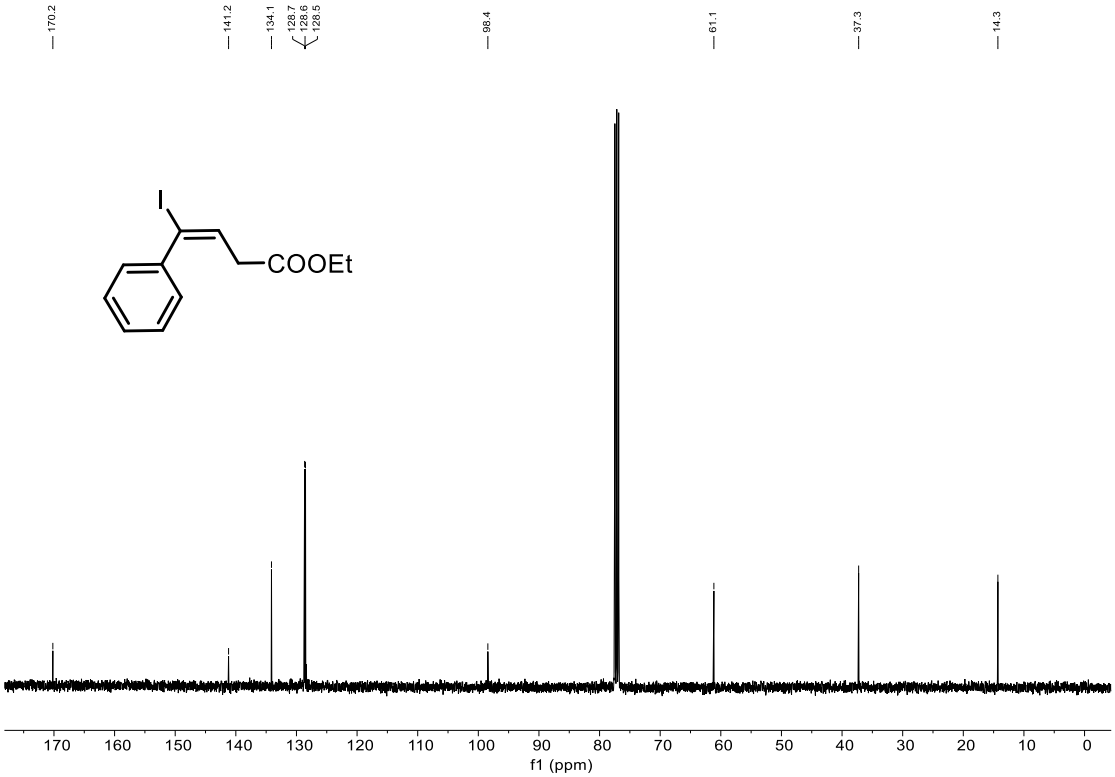
^{13}C NMR (126 MHz, $CDCl_3$) of *E-42*



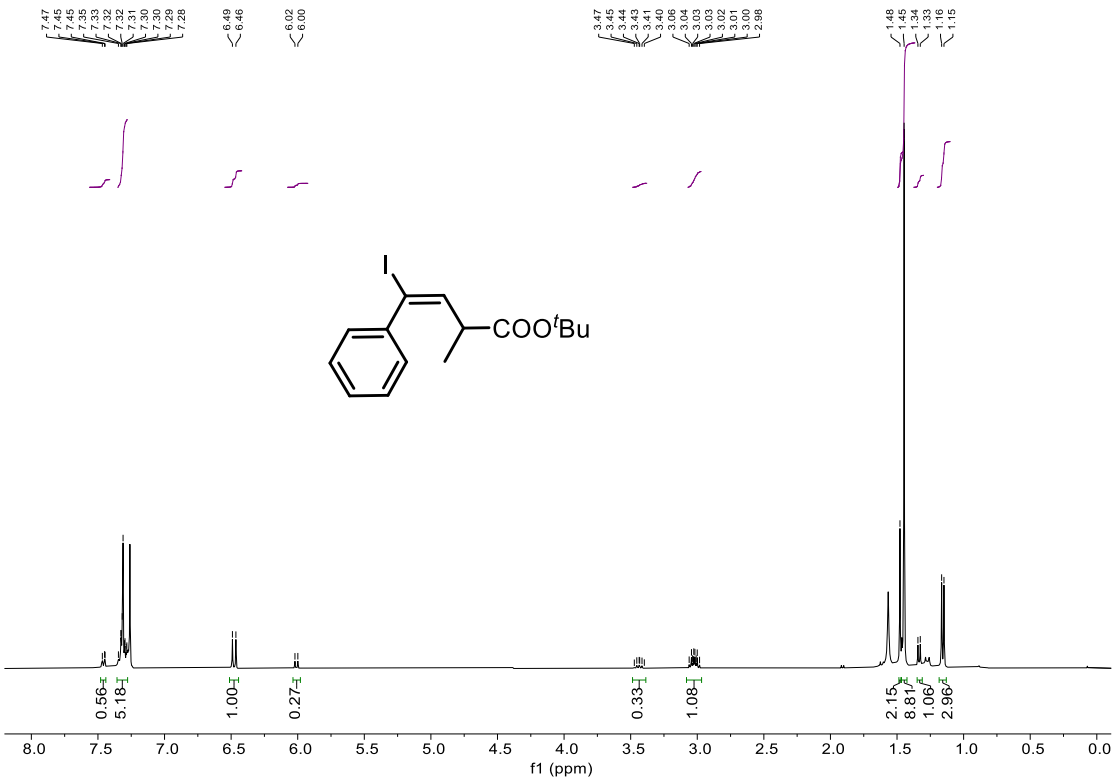
^{1}H NMR (400 MHz, CDCl3) of *E-43*



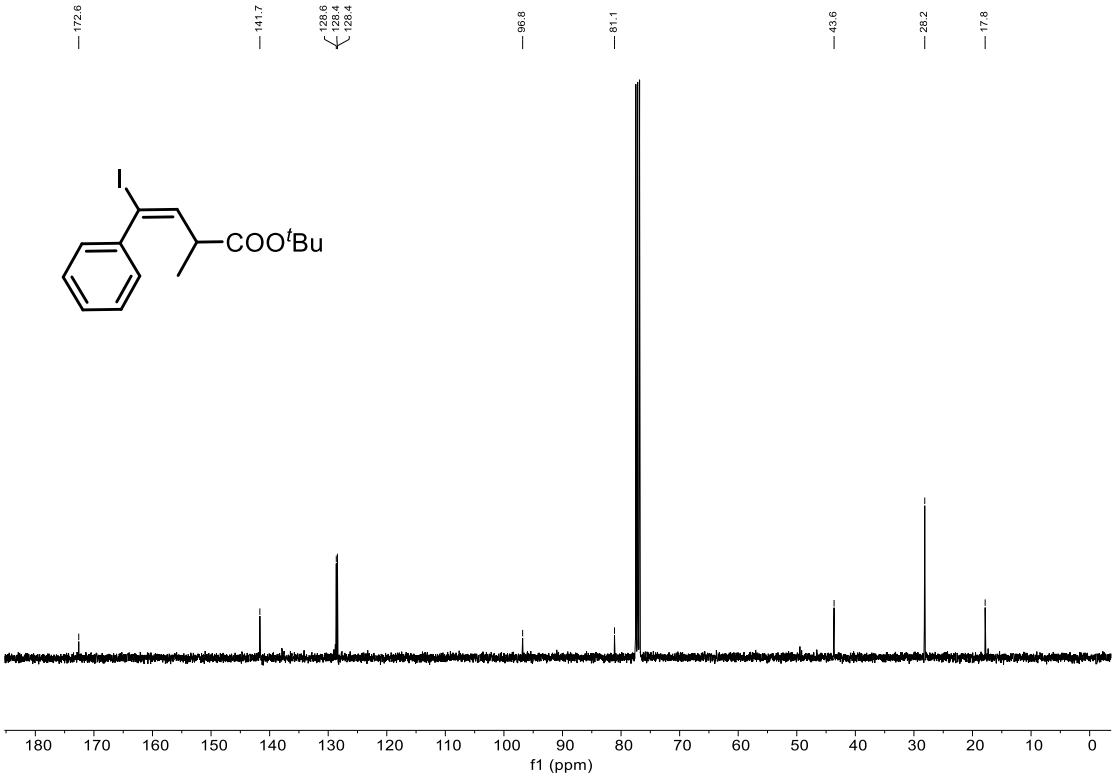
^{13}C NMR (101 MHz, $CDCl_3$) of *E-43*



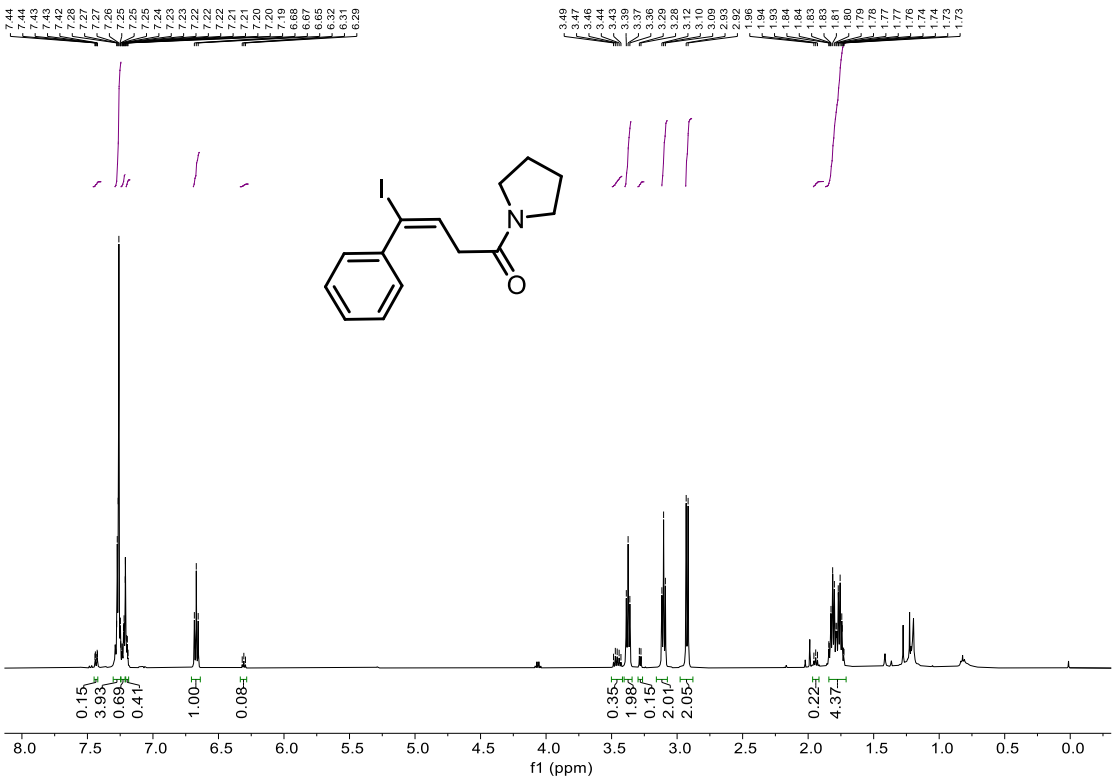
^{1}H NMR (400 MHz, CDCl3) of *E-44*



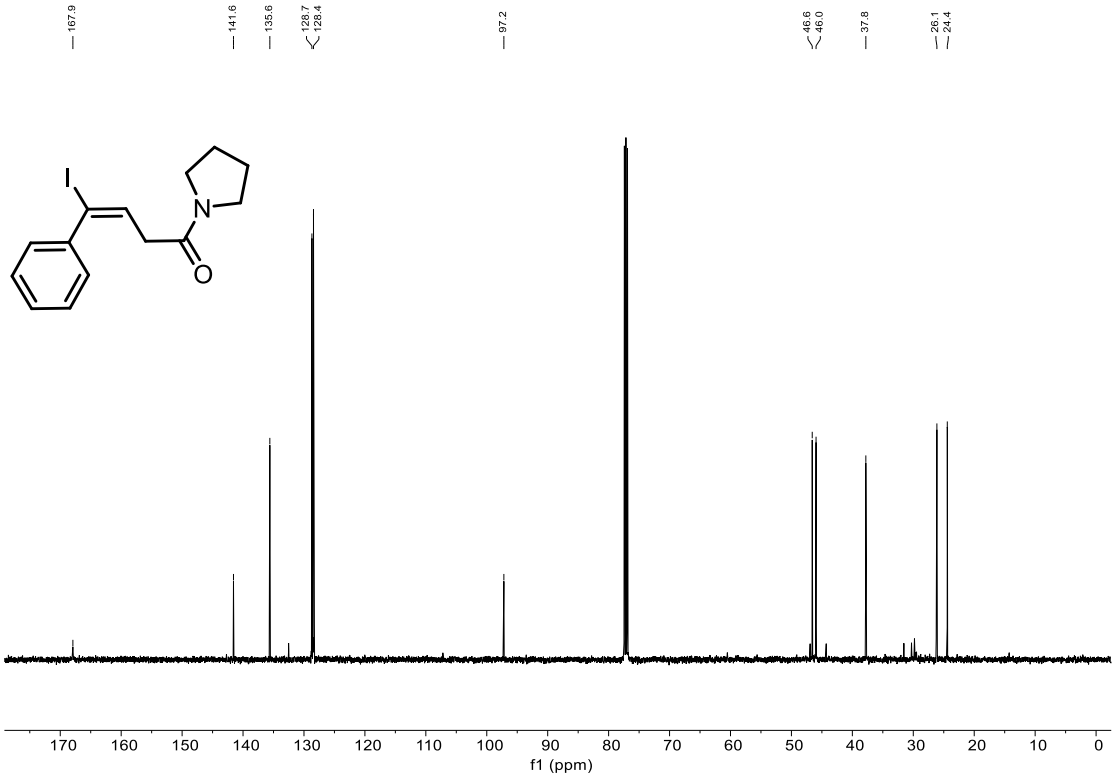
^{13}C NMR (101 MHz, $CDCl_3$) of *E-44*



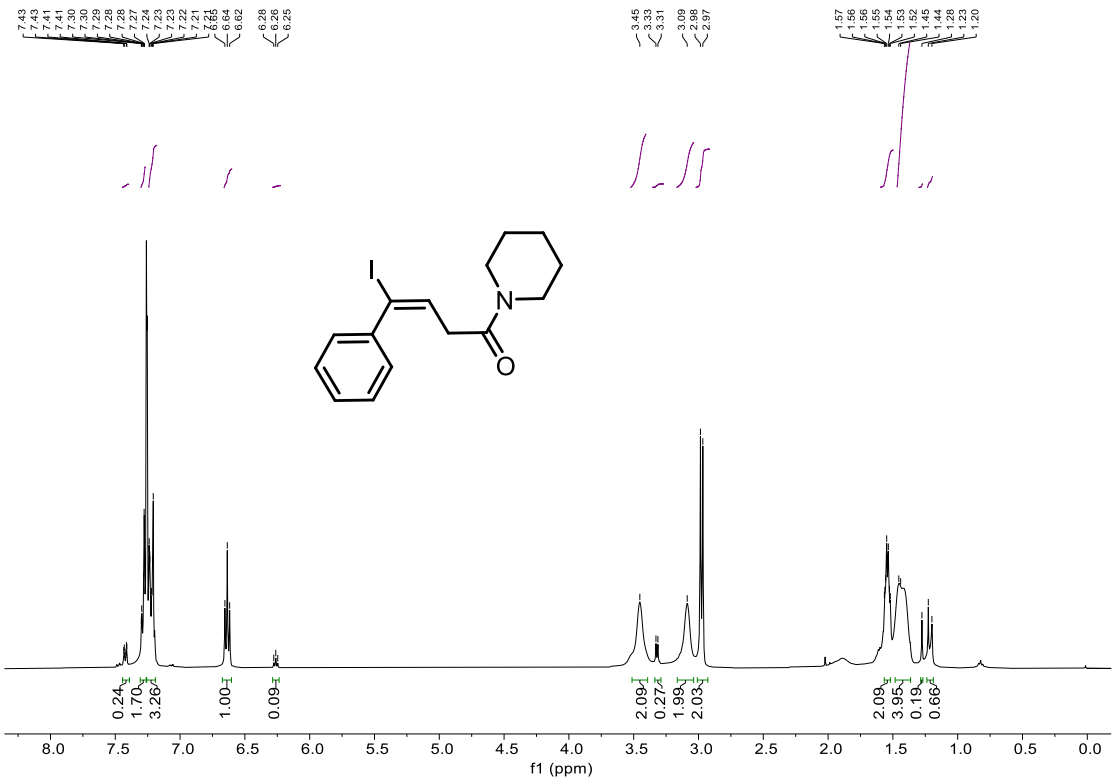
^{1}H NMR (500 MHz, CDCl3) of *E-45*



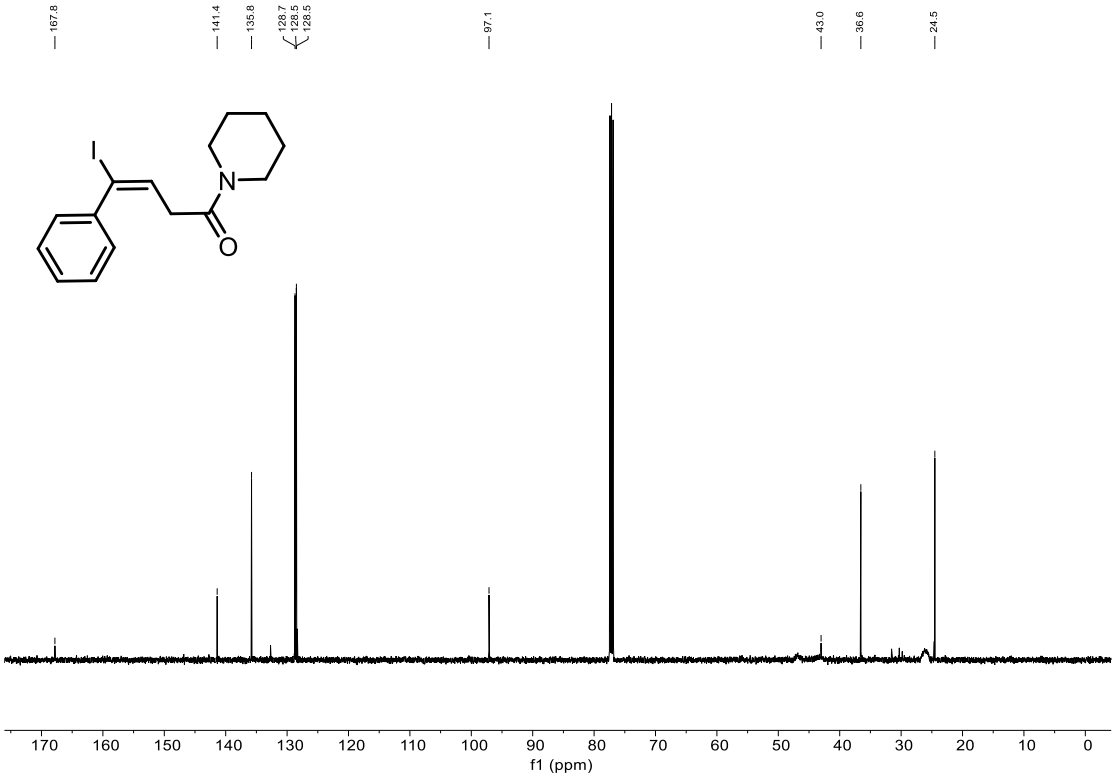
^{13}C NMR (126 MHz, $CDCl_3$) of *E-45*



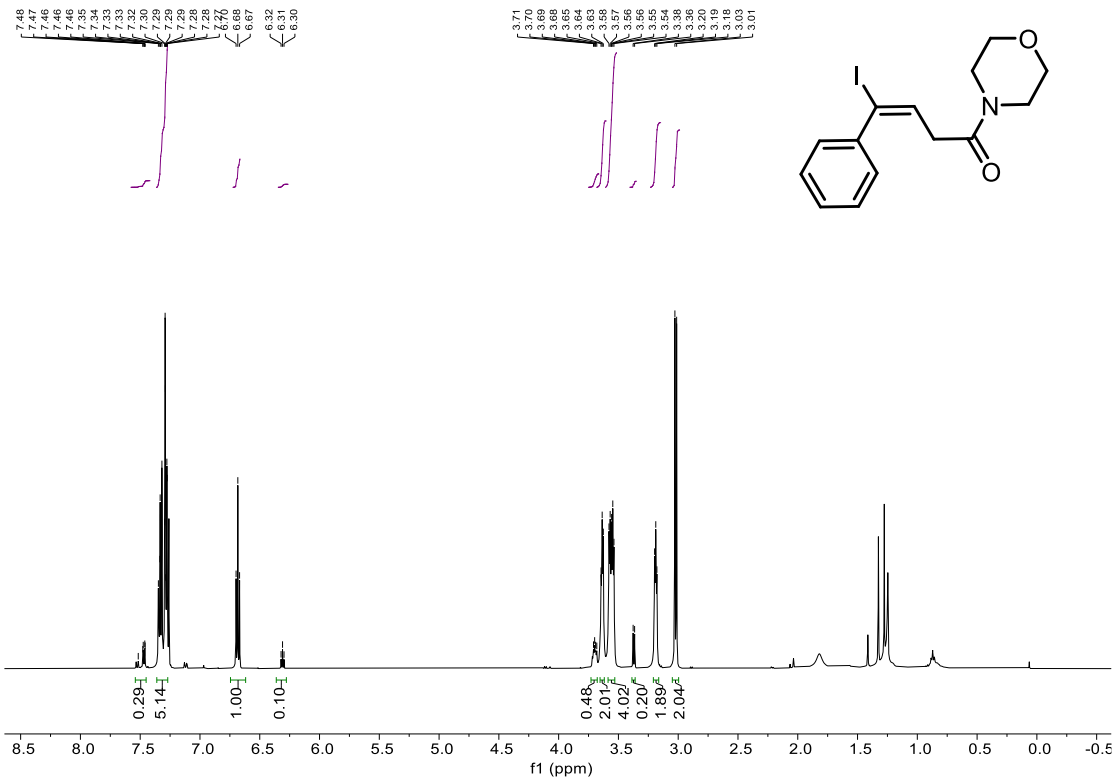
^{1}H NMR (400 MHz, CDCl3) of *E-46*



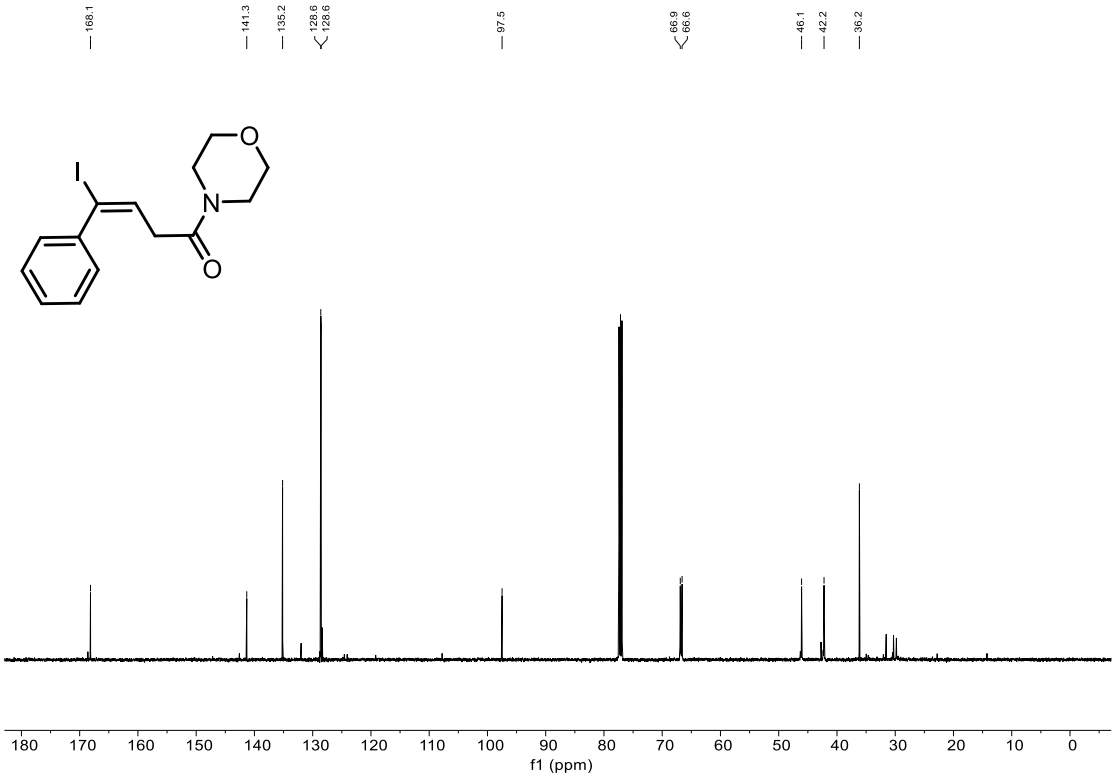
^{13}C NMR (126 MHz, $CDCl_3$) of *E-46*



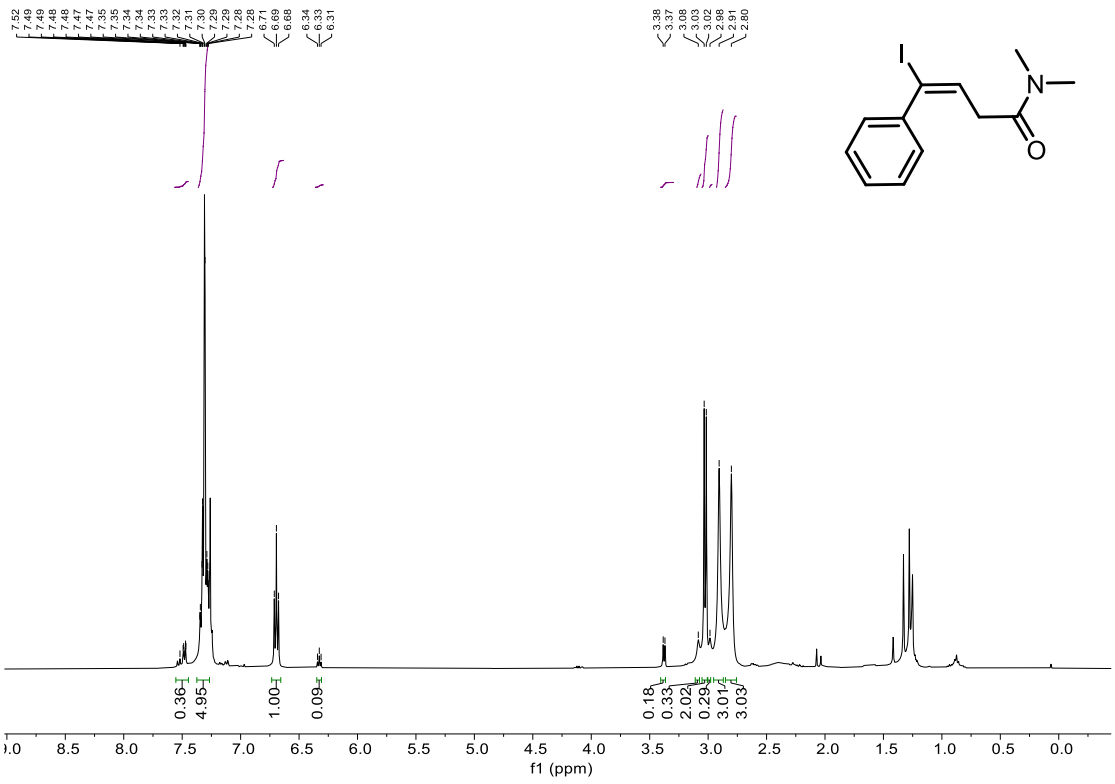
^{1}H NMR (500 MHz, CDCl3) of *E-47*



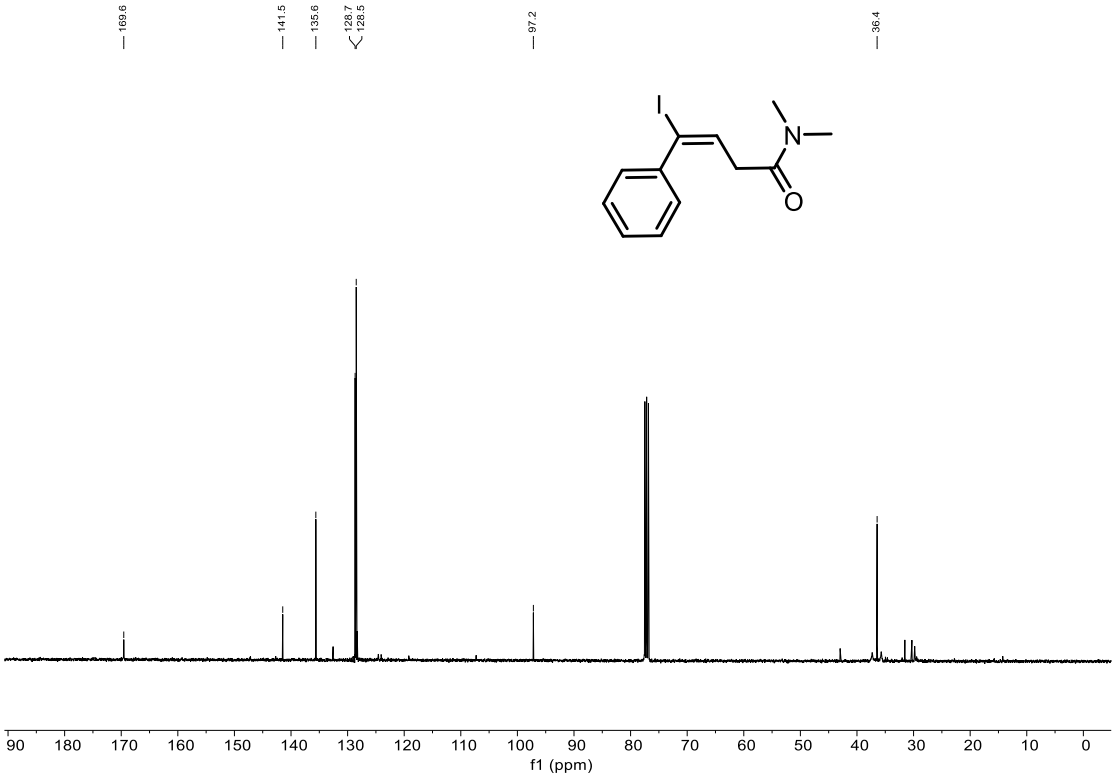
^{13}C NMR (126 MHz, $CDCl_3$) of *E-47*



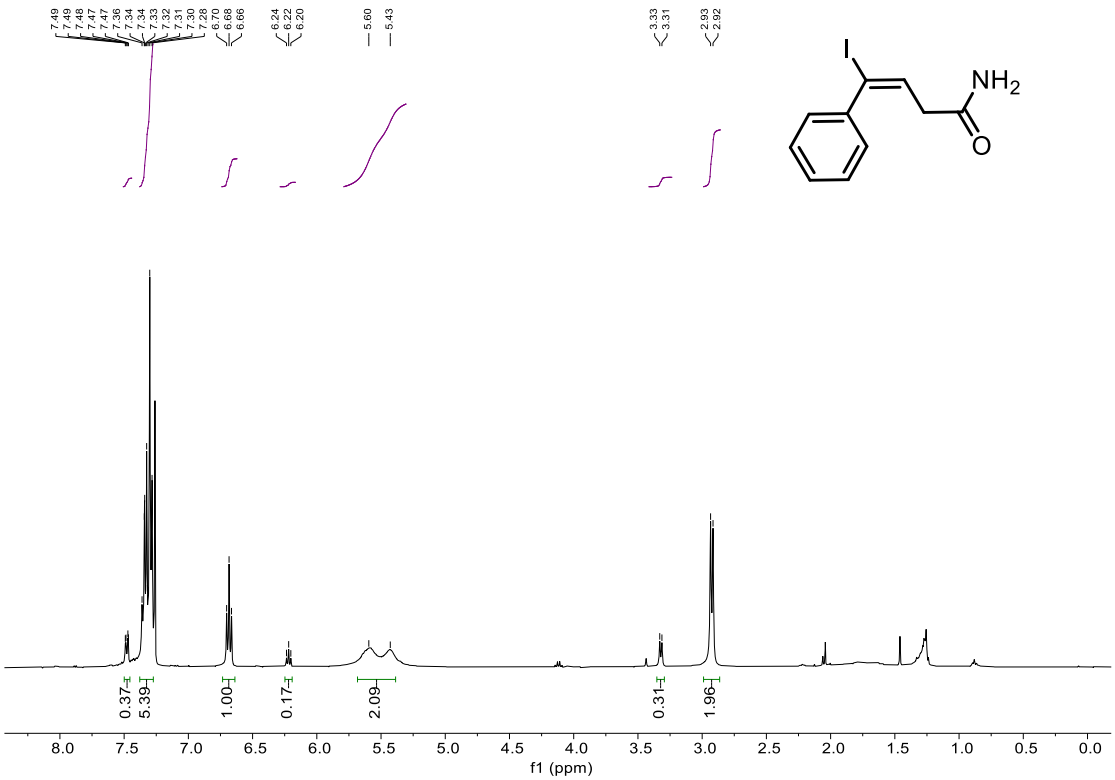
^{1}H NMR (400 MHz, CDCl3) of *E-48*



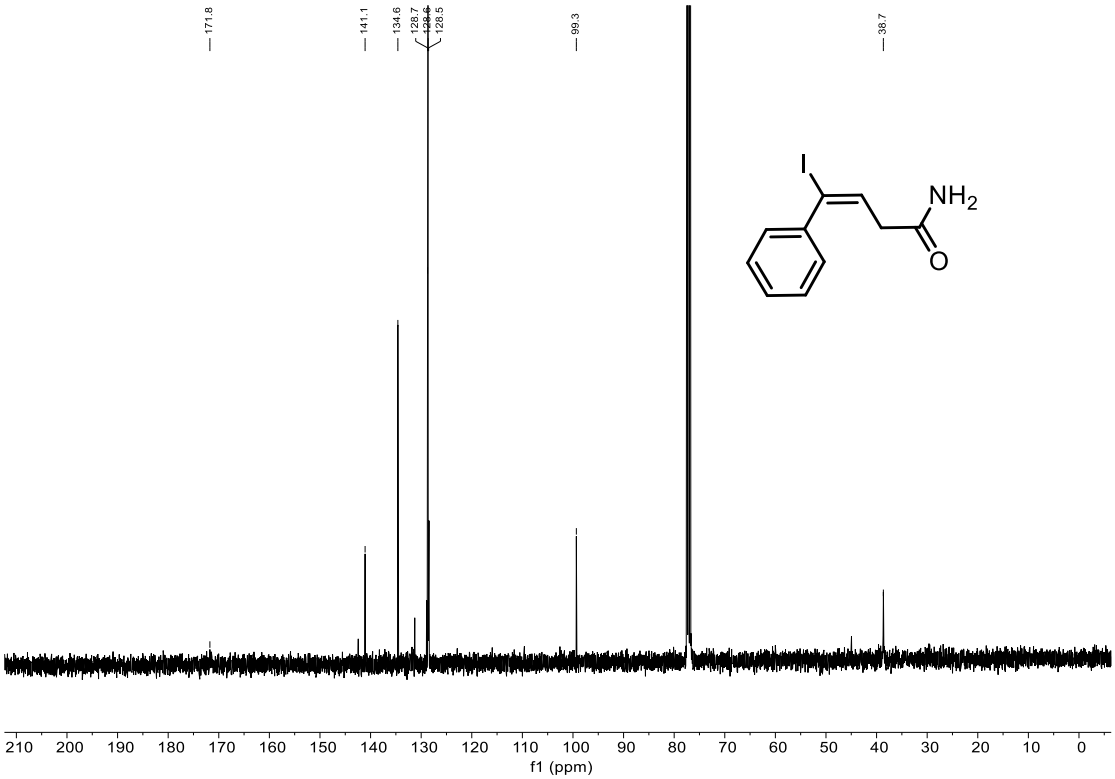
^{13}C NMR (101 MHz, $CDCl_3$) of *E-48*



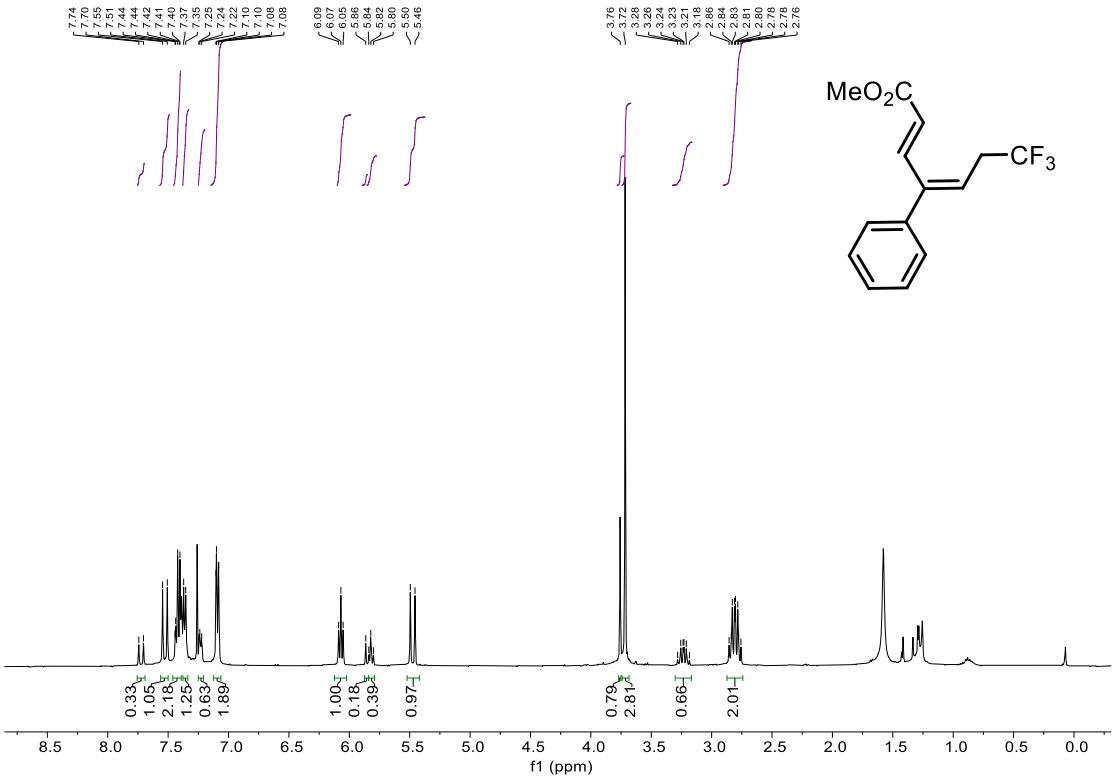
^{1}H NMR (400 MHz, CDCl3) of *E-49*



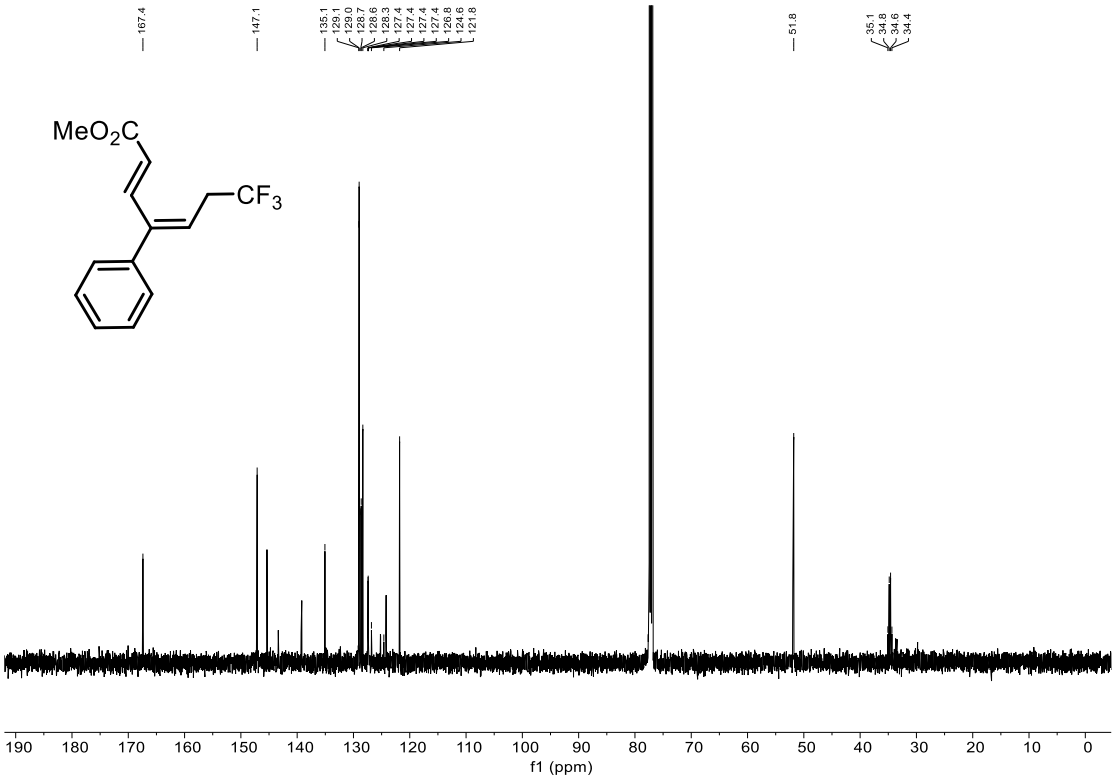
^{13}C NMR (101 MHz, $CDCl_3$) of *E-49*



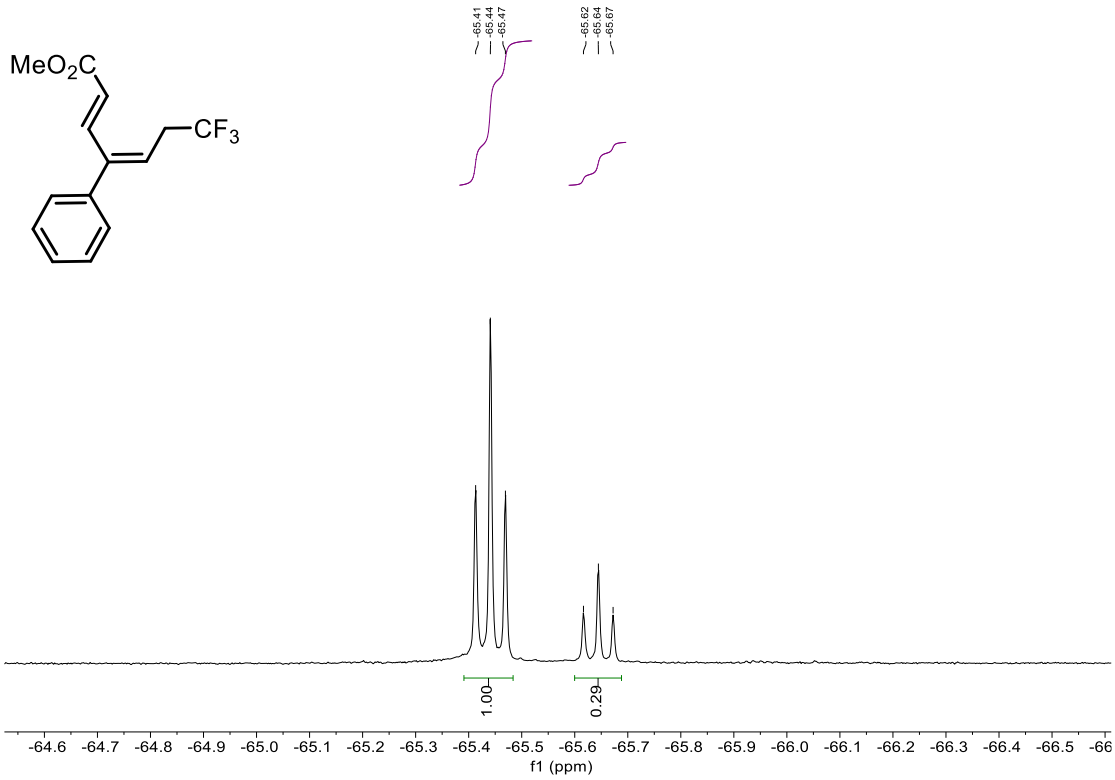
^{1}H NMR (400 MHz, CDCl3) of *E-50*



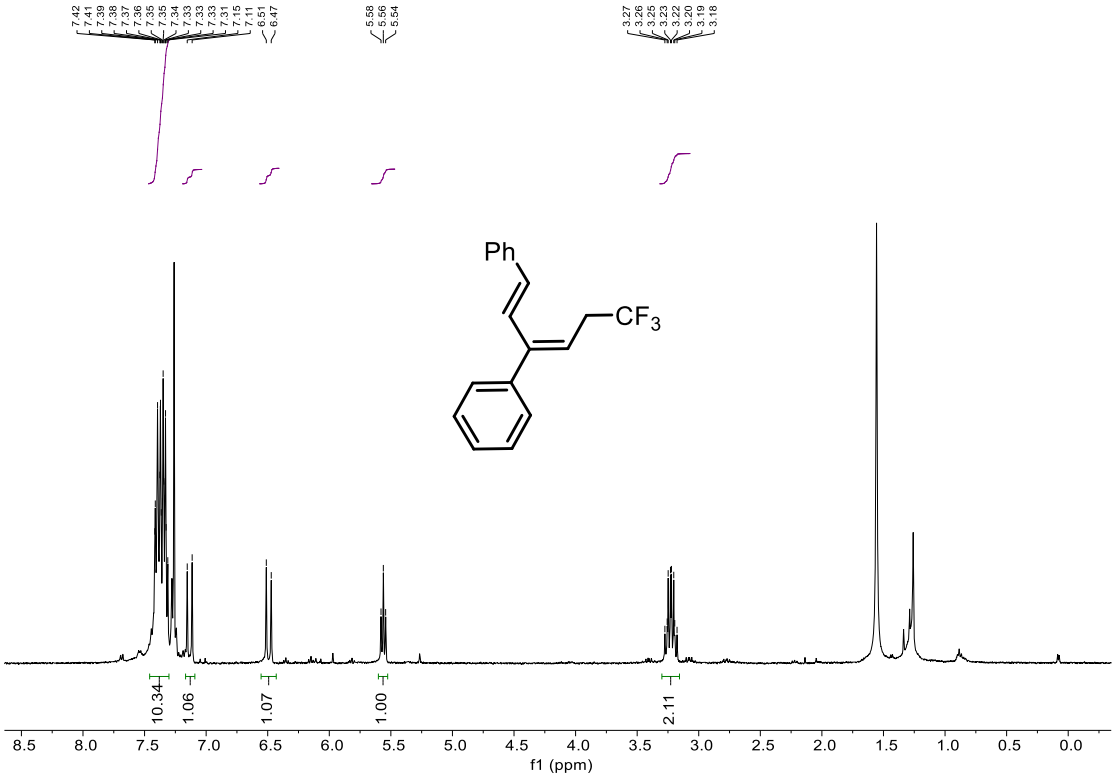
^{13}C NMR (126 MHz, $CDCl_3$) of *E-50*



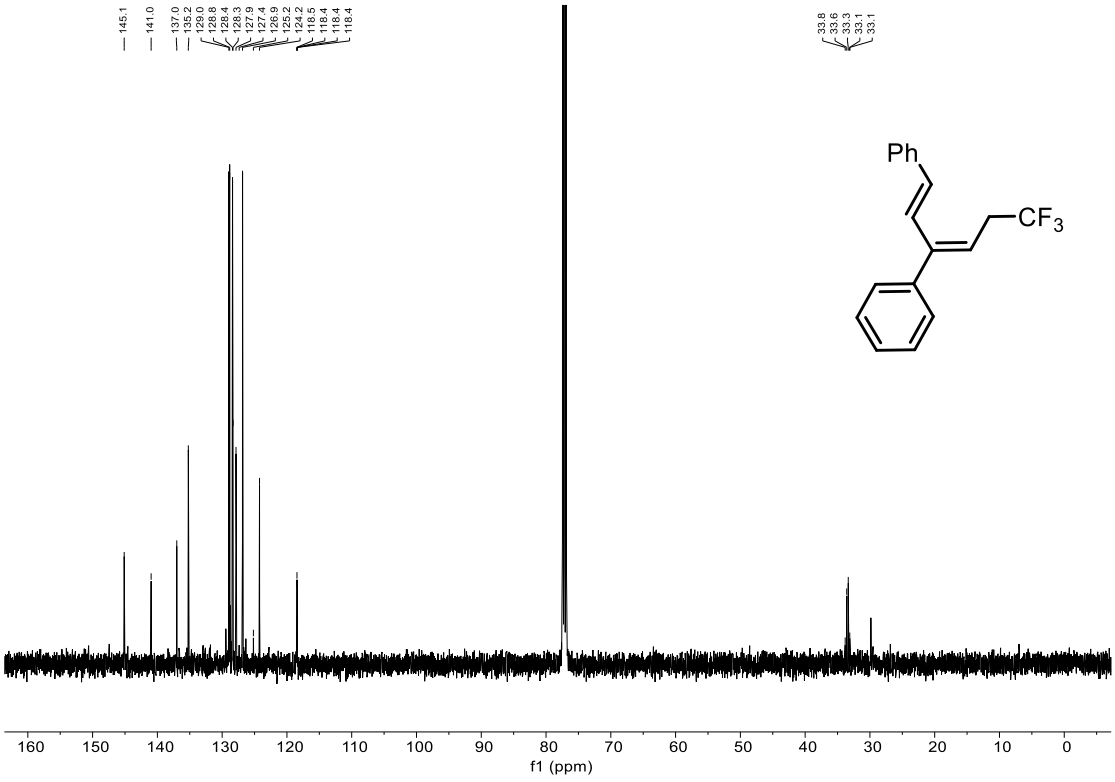
^{19}F NMR (376 MHz, $CDCl_3$) of *E-50*



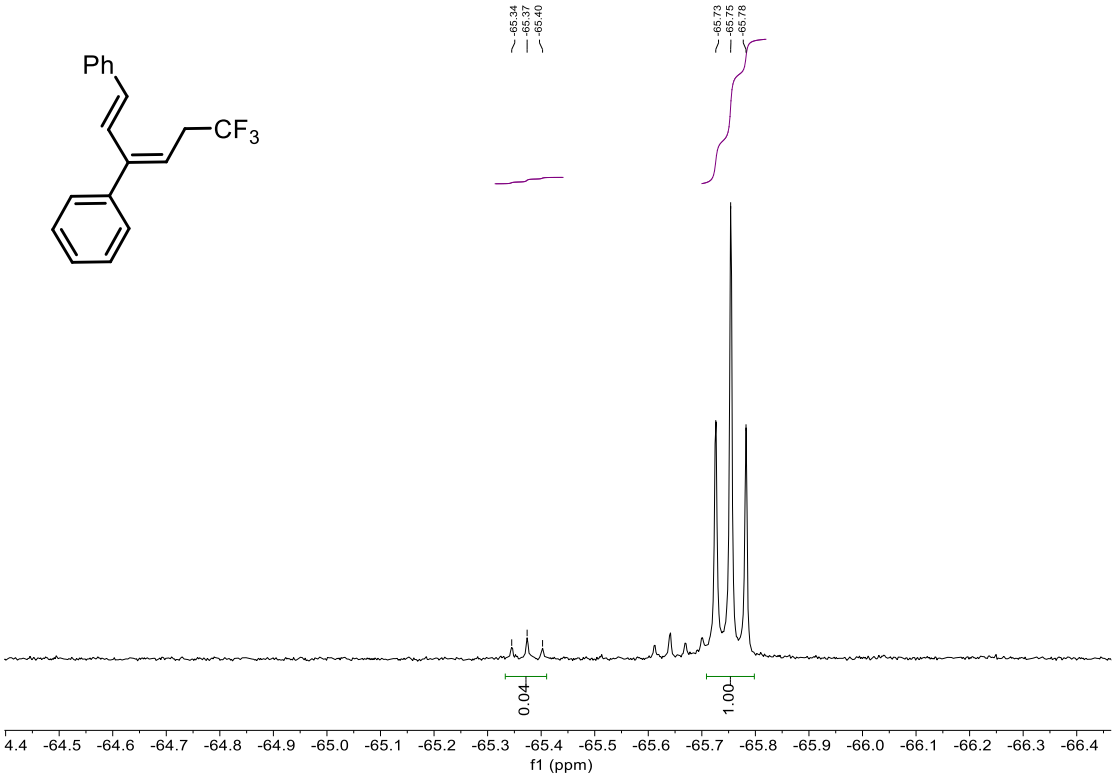
^{1}H NMR (400 MHz, CDCl3) of *E-51*



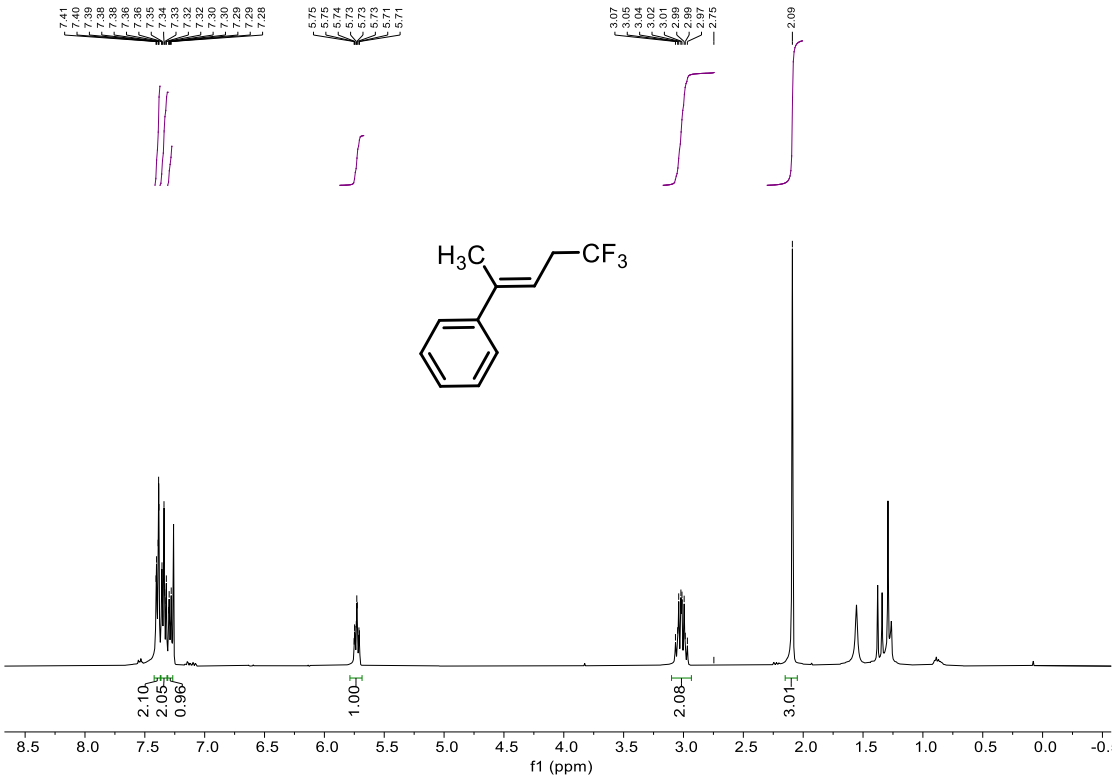
^{13}C NMR (126 MHz, $CDCl_3$) of *E-51*



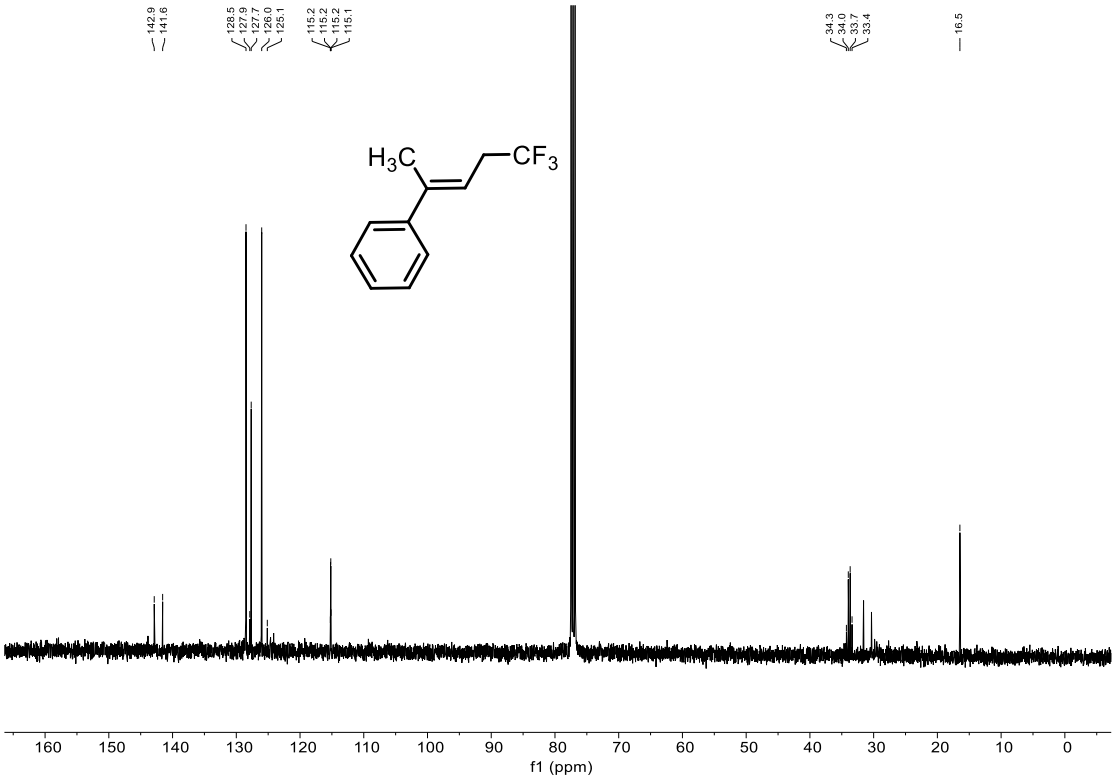
^{19}F NMR (376 MHz, $CDCl_3$) of *E-51*



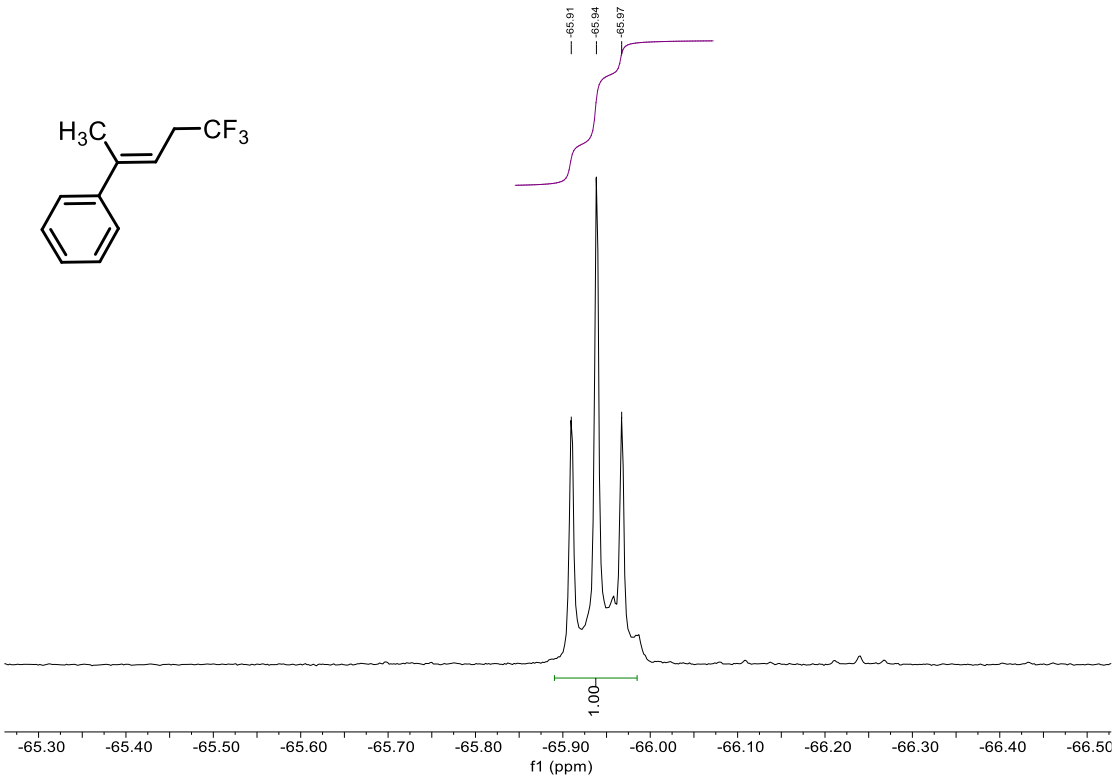
^{1}H NMR (400 MHz, CDCl3) of *E-52*



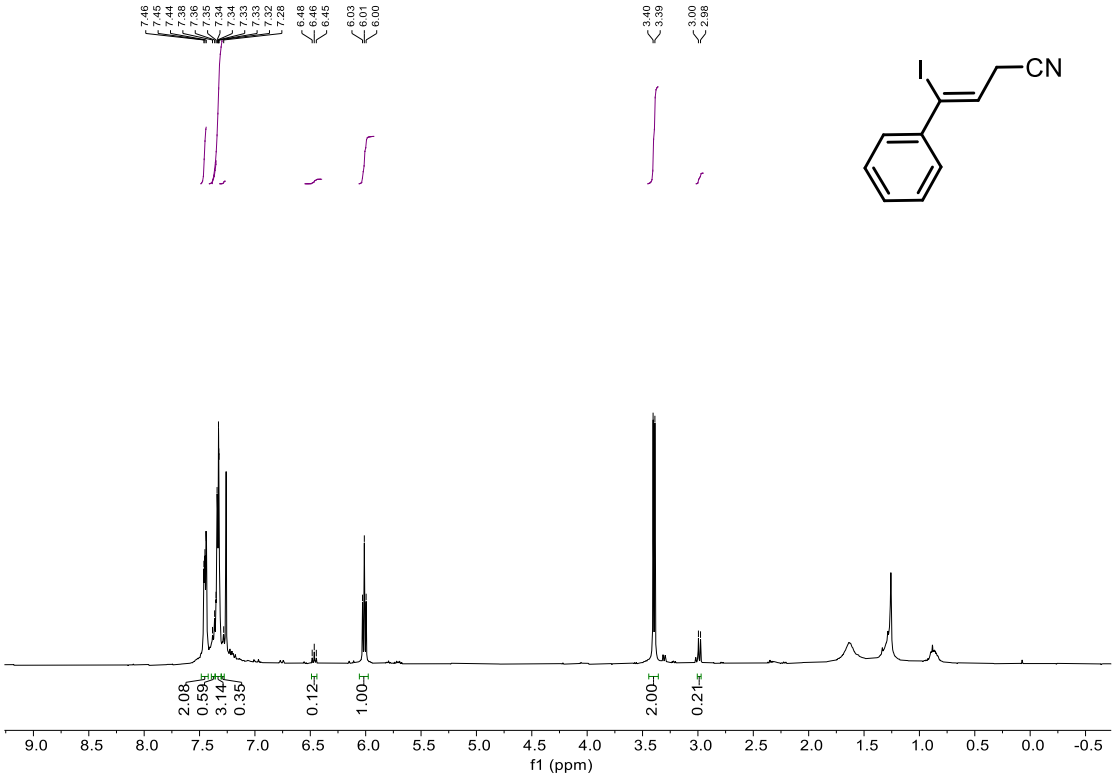
^{13}C NMR (101 MHz, $CDCl_3$) of *E-52*



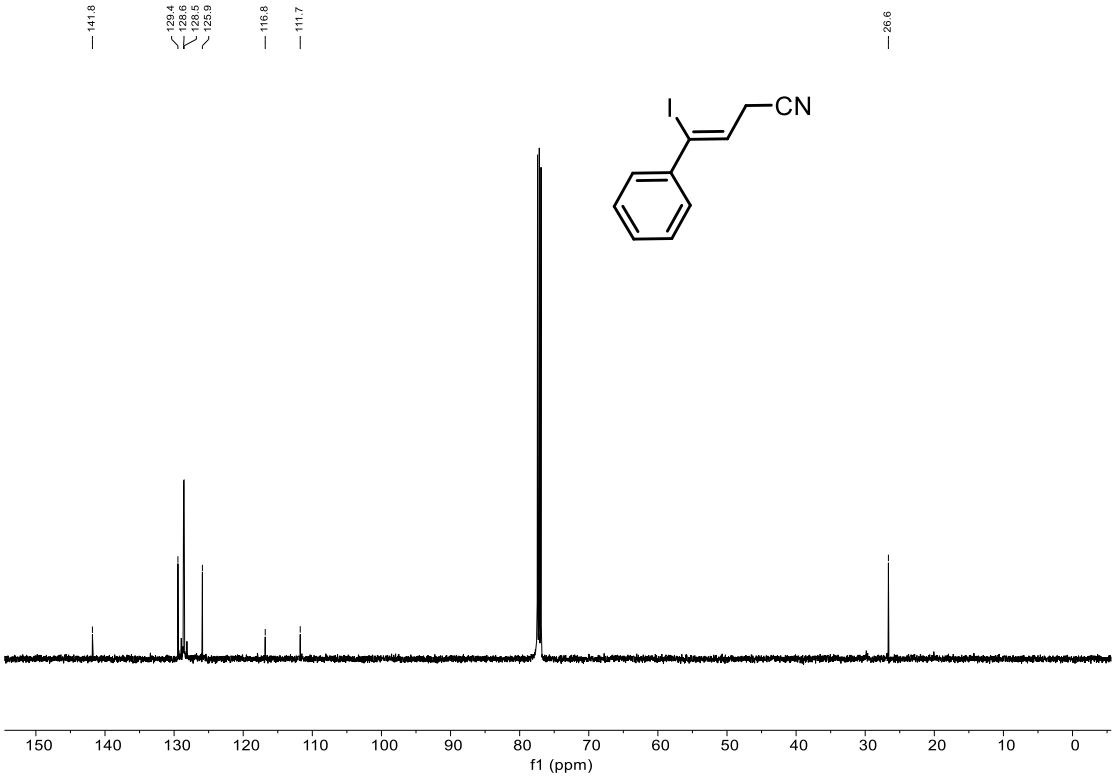
^{19}F NMR (376 MHz, $CDCl_3$) of *E-52*



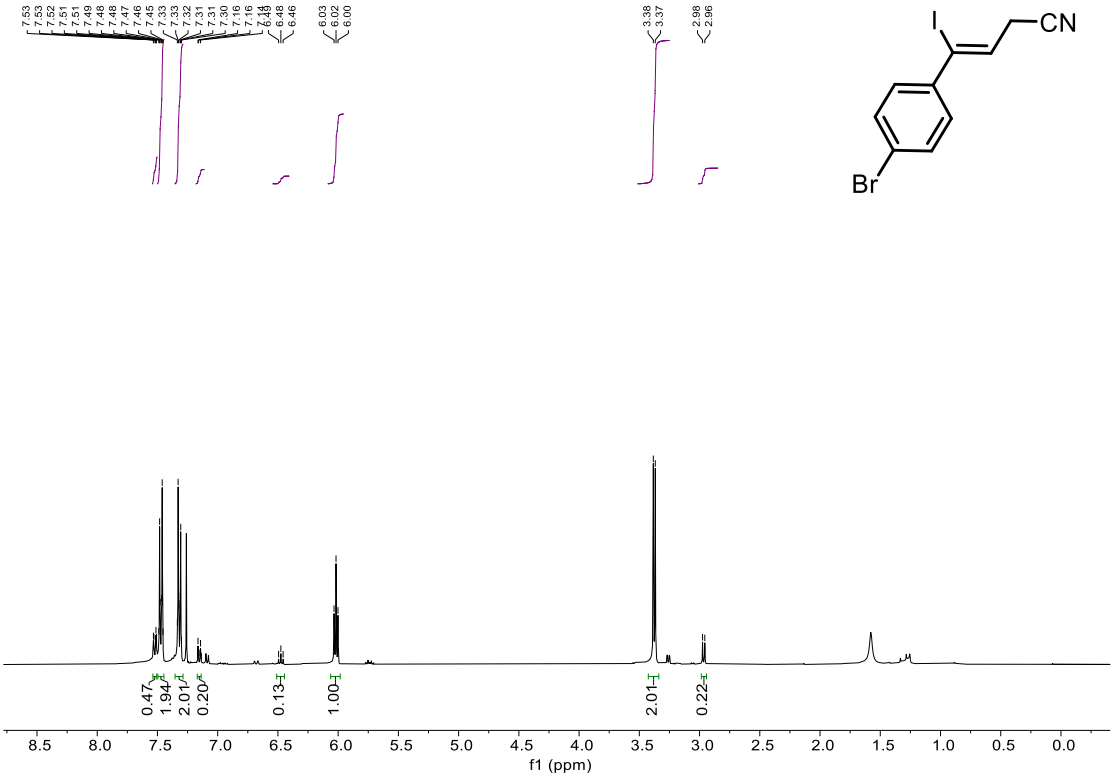
^{1}H NMR (400 MHz, CDCl3) of *Z-1*



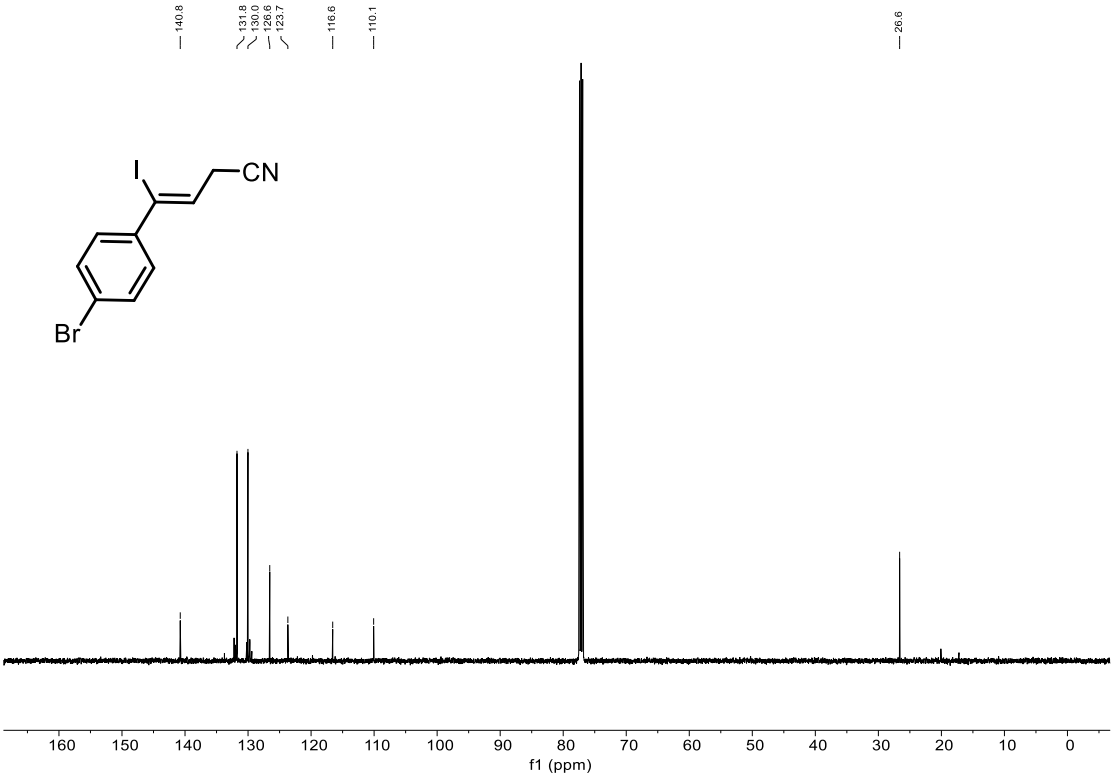
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-1*



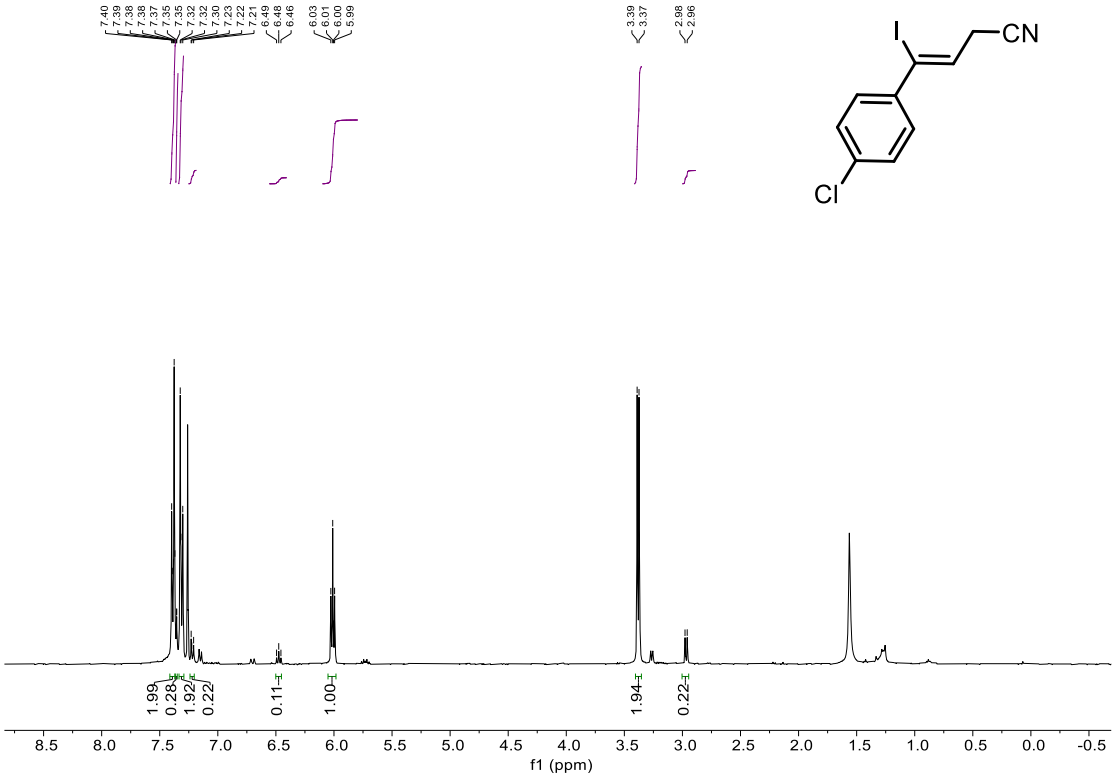
^{1}H NMR (400 MHz, CDCl3) of *Z-2*



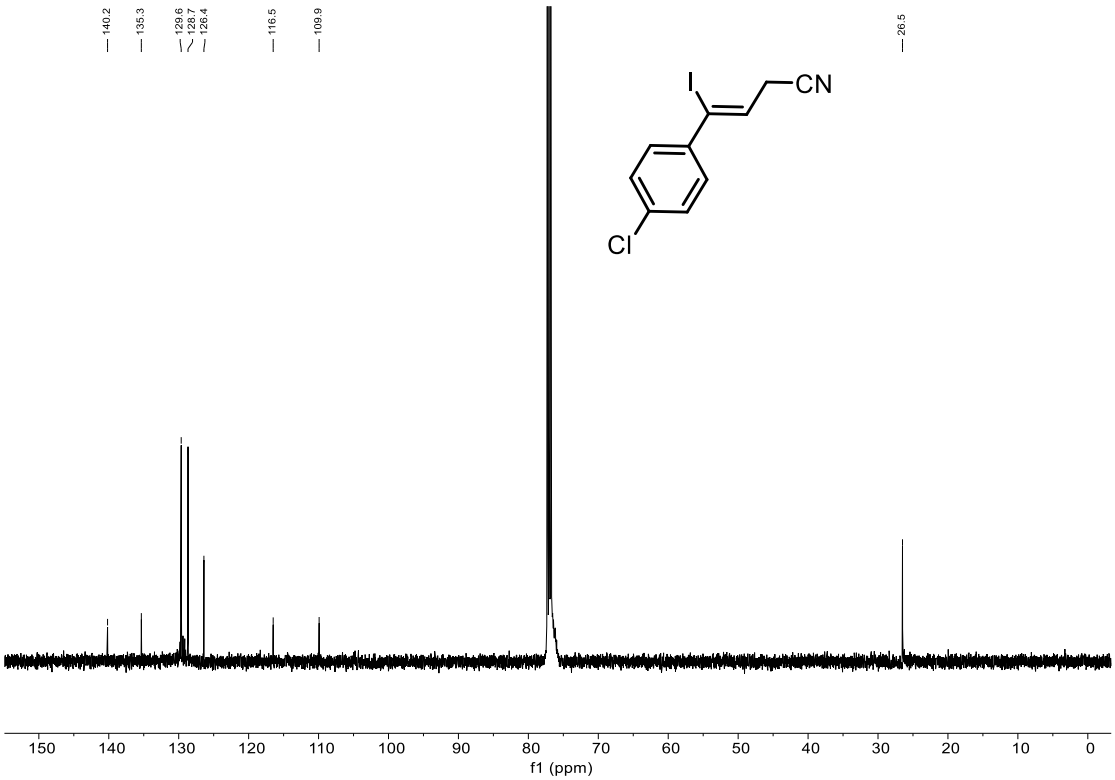
^{13}C NMR (126 MHz, CDCl$_3$) of *Z-2*



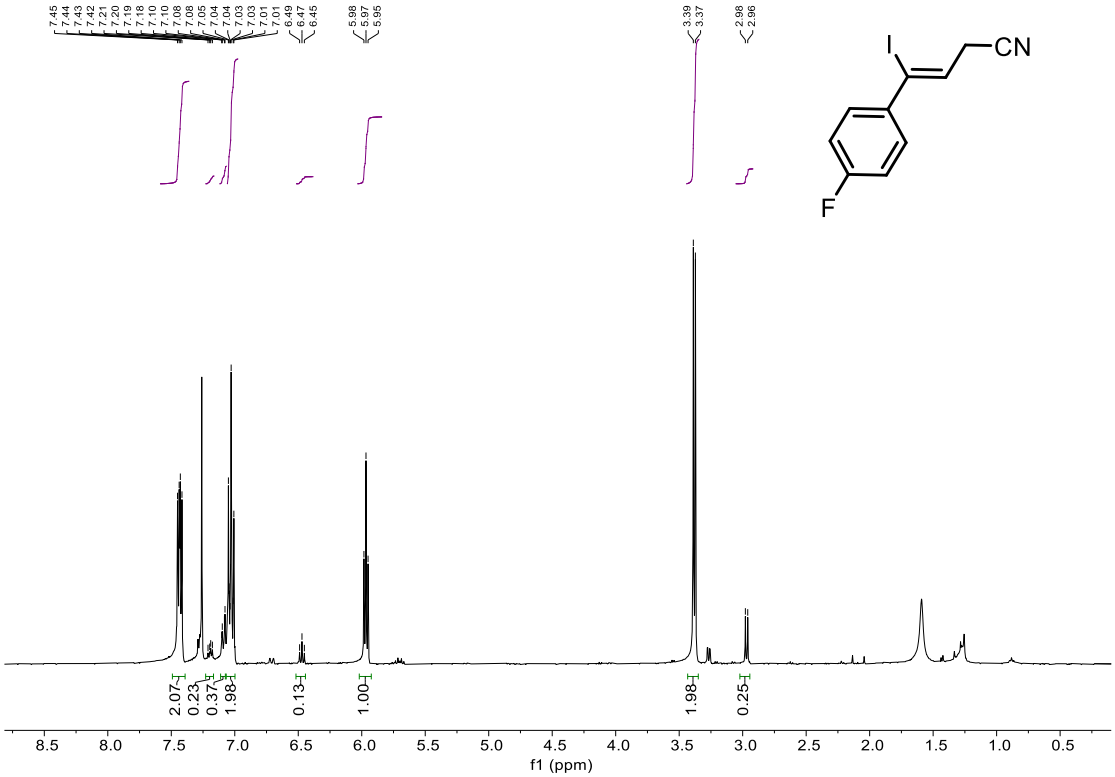
^{1}H NMR (400 MHz, CDCl3) of *Z-3*



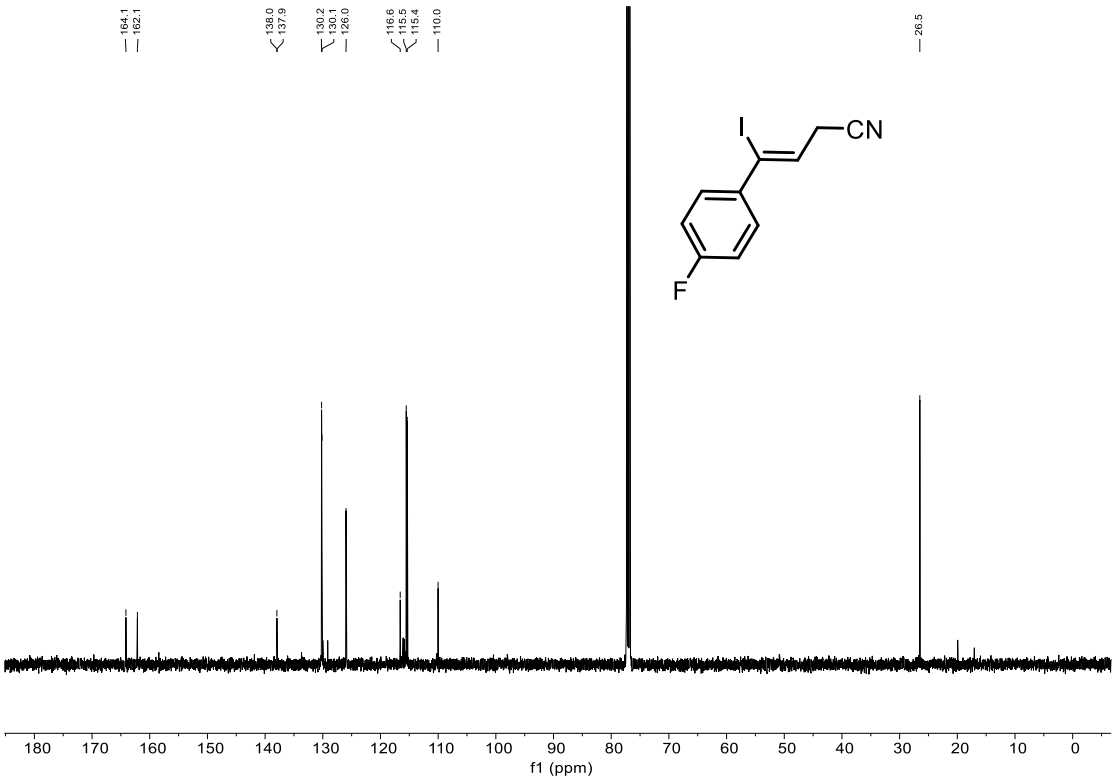
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-3*



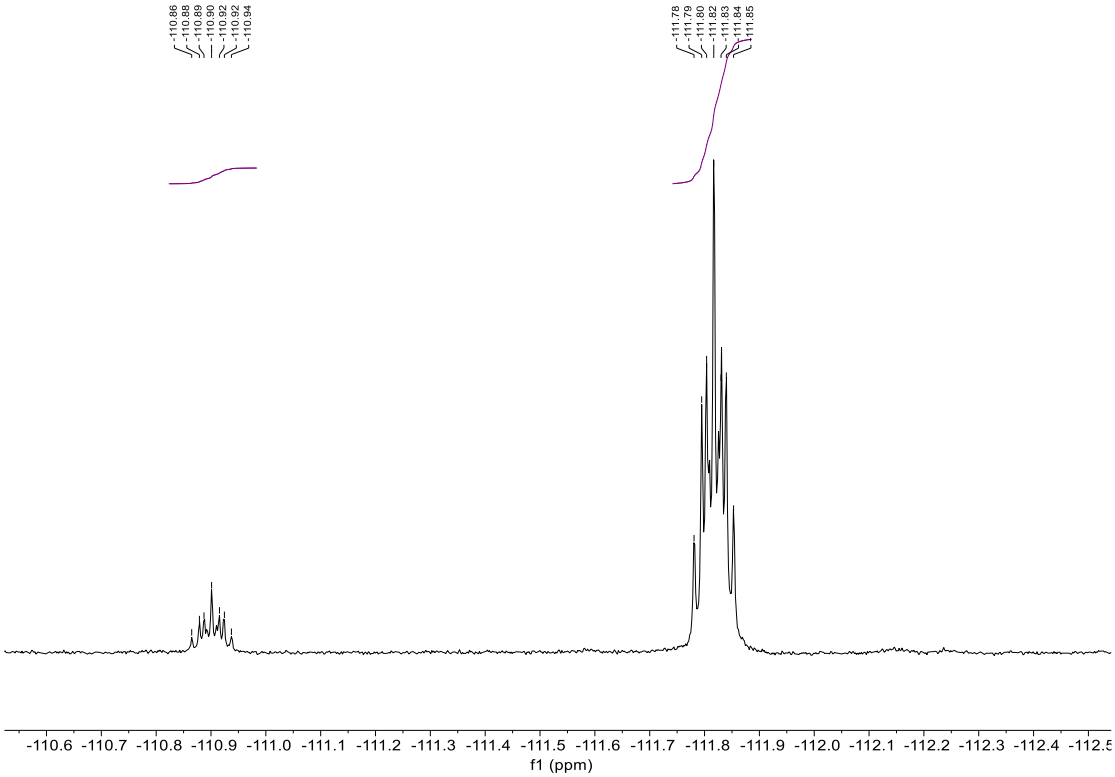
^{1}H NMR (400 MHz, CDCl3) of *Z-4*



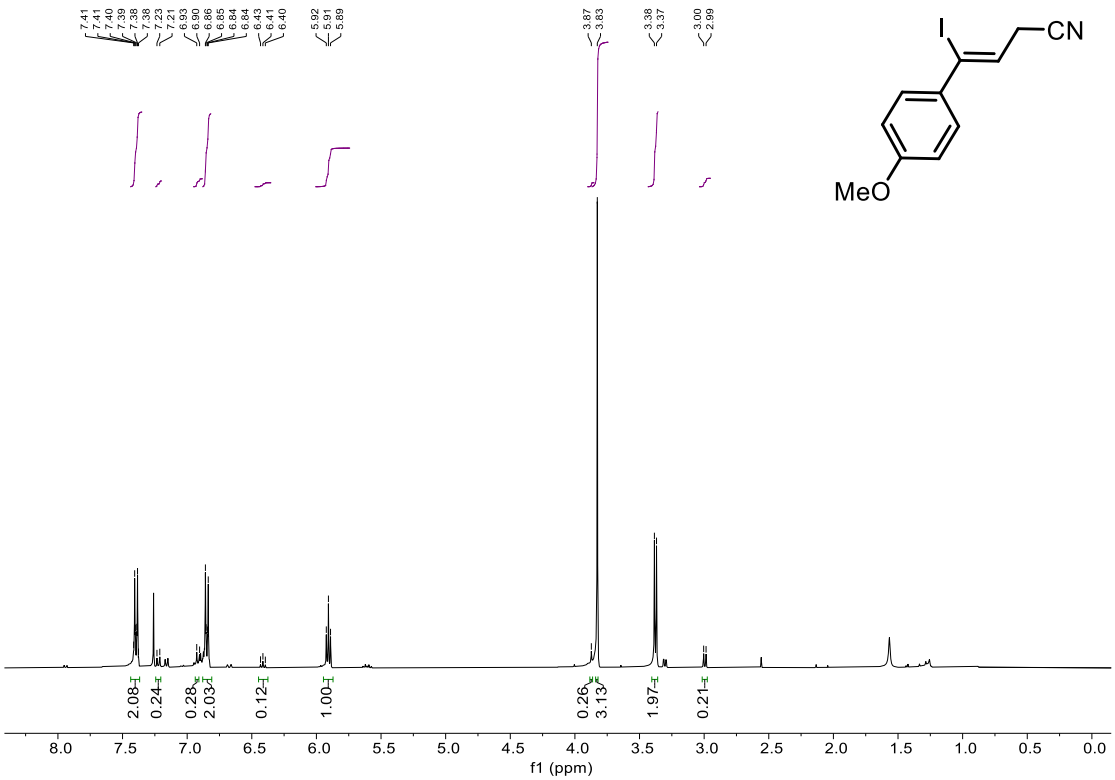
^{13}C NMR (126 MHz, CDCl$_3$) of *Z-4*



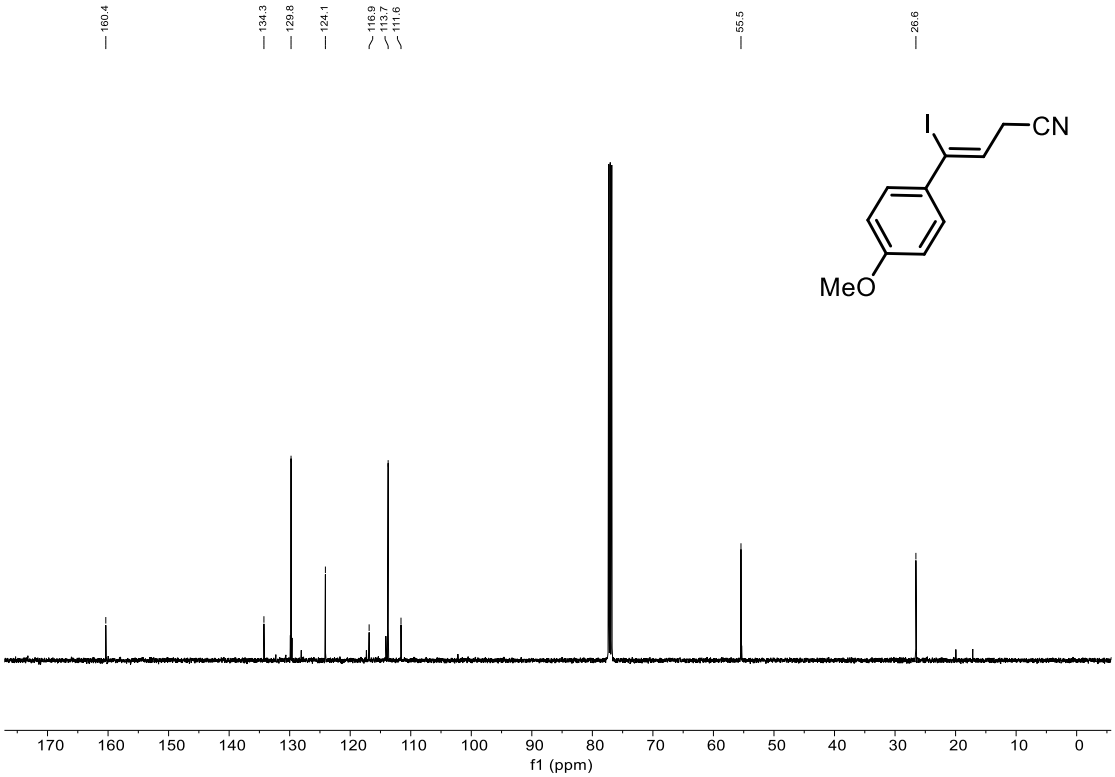
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-4*



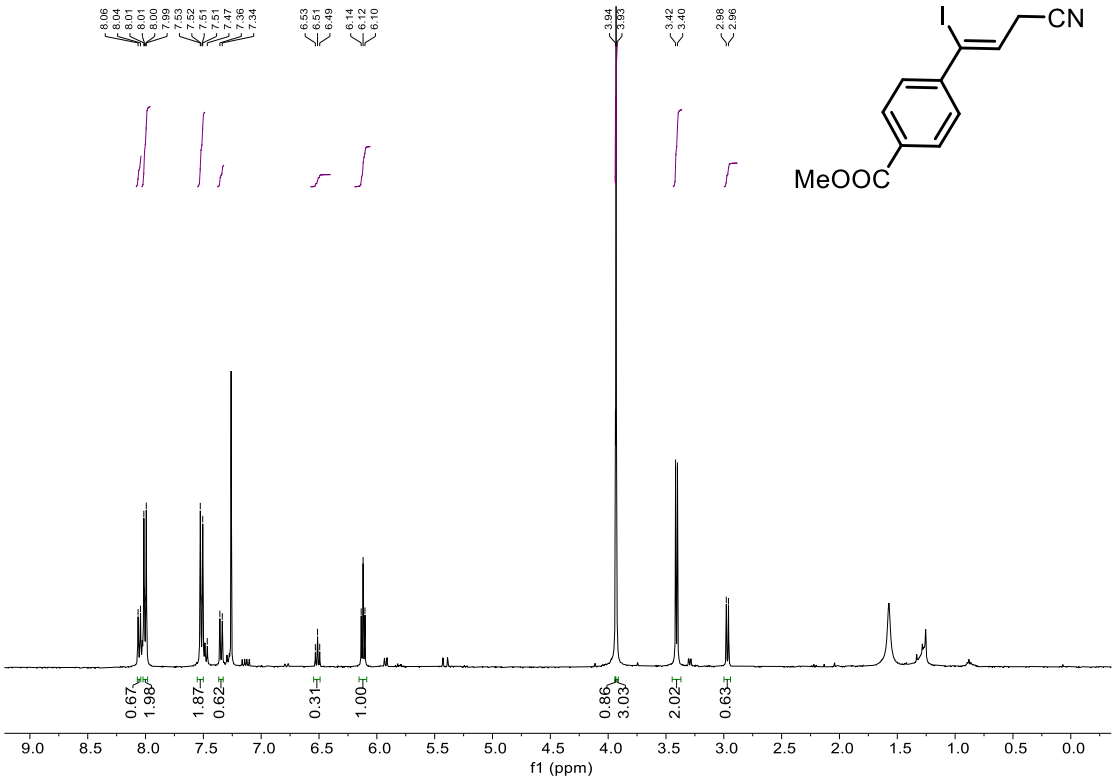
^{1}H NMR (400 MHz, CDCl3) of *Z-5*



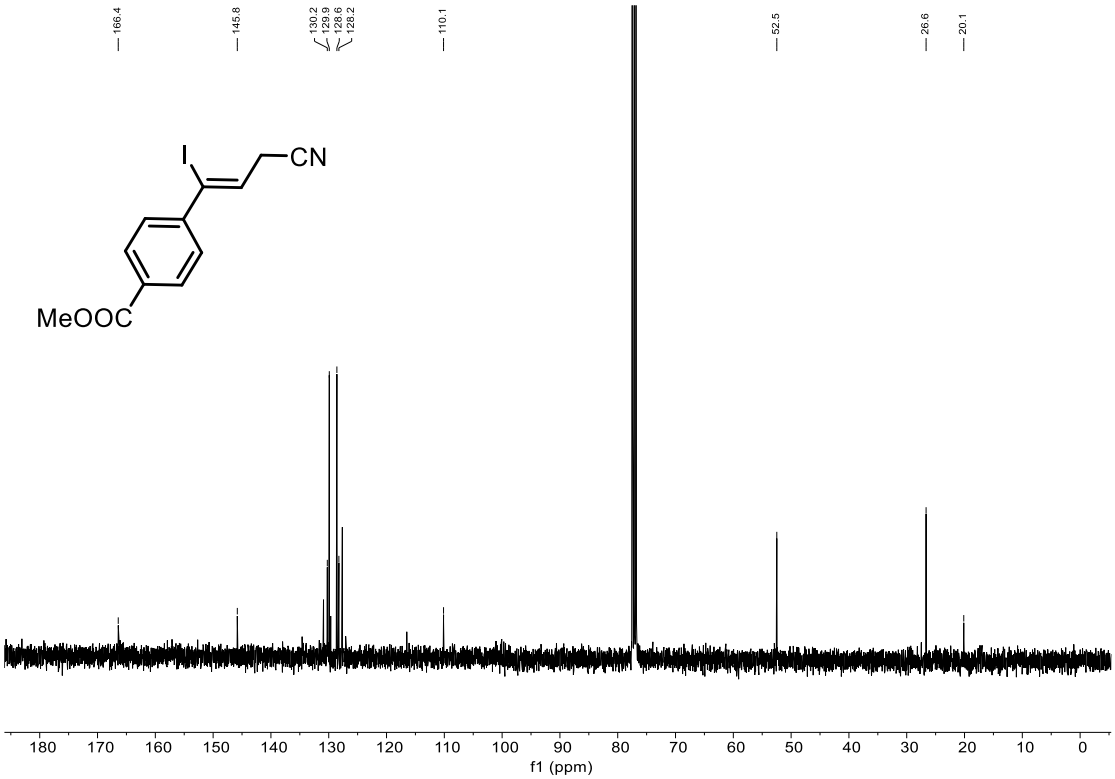
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-5*



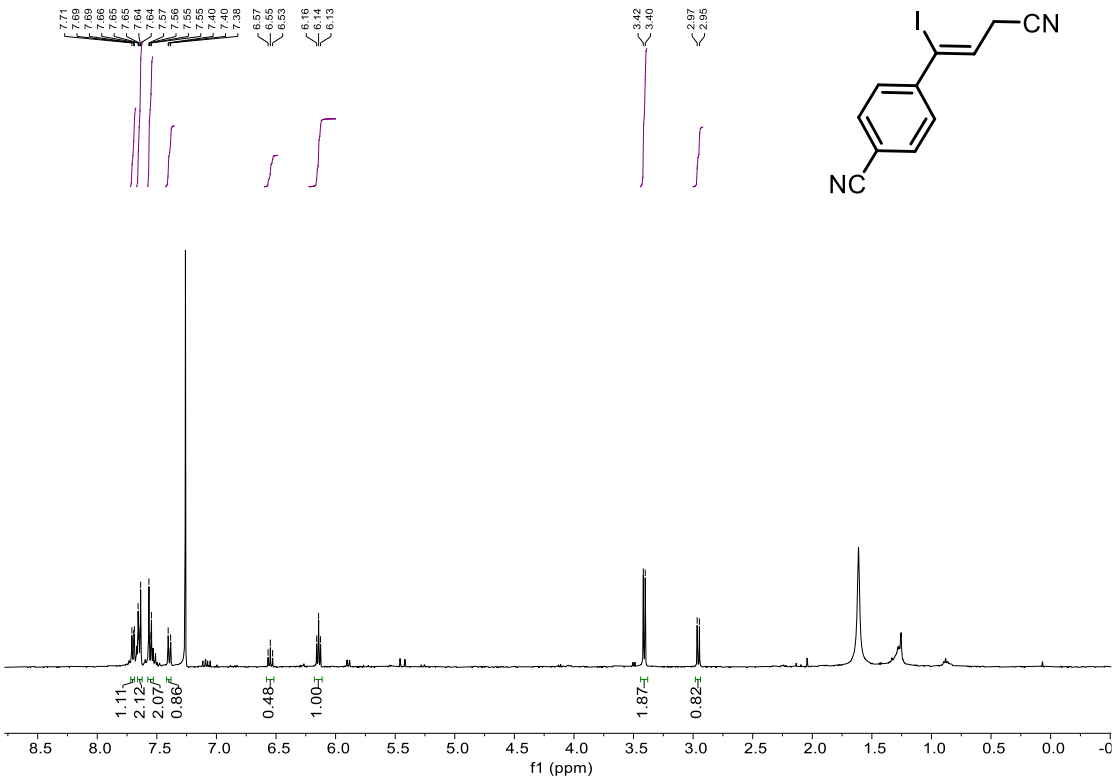
^{1}H NMR (400 MHz, CDCl3) of *Z-6*



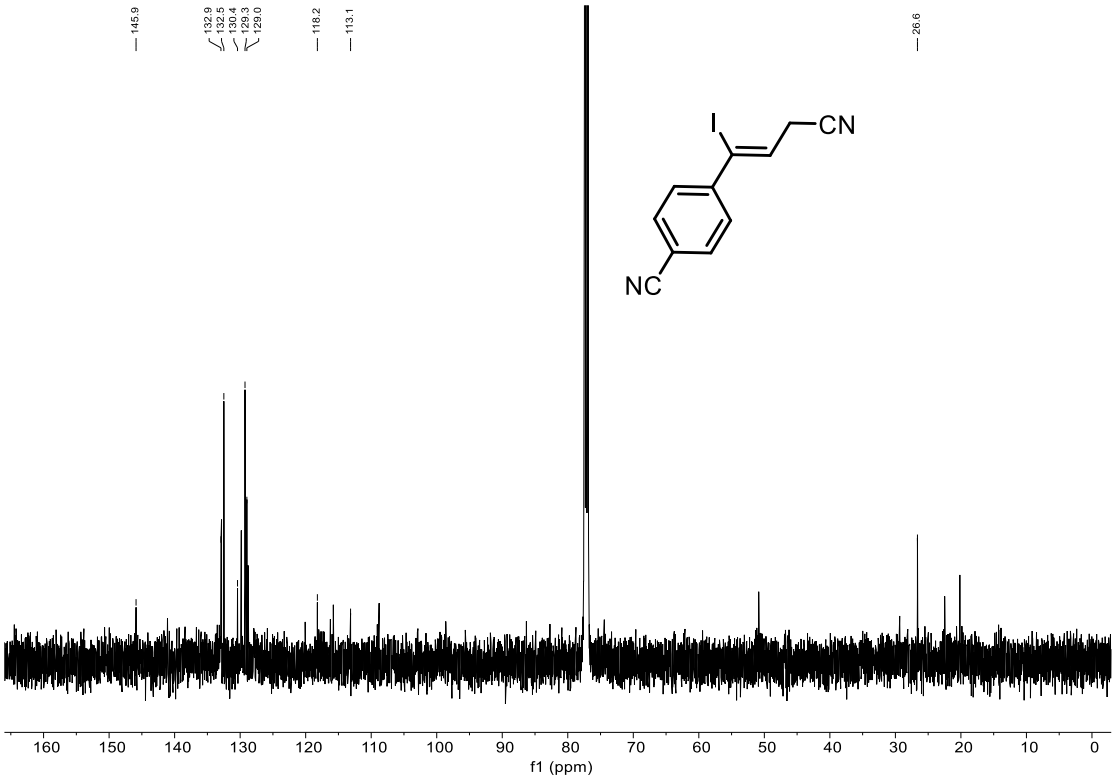
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-6*



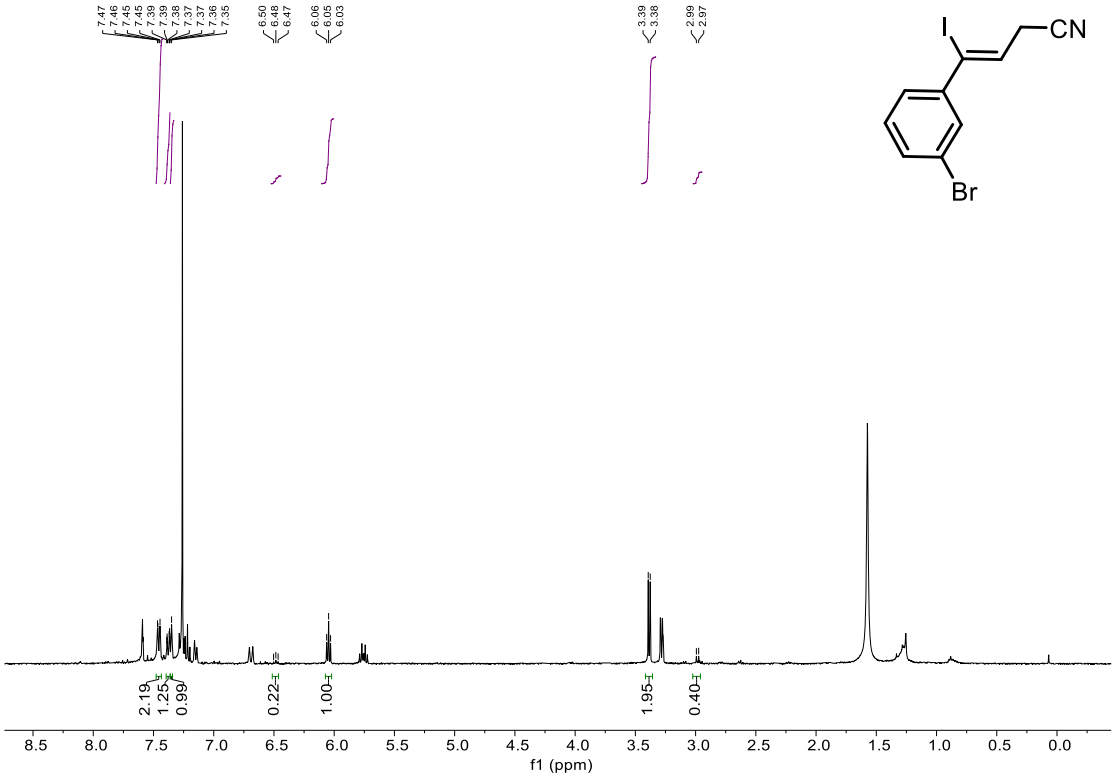
^{1}H NMR (400 MHz, CDCl3) of *Z-7*



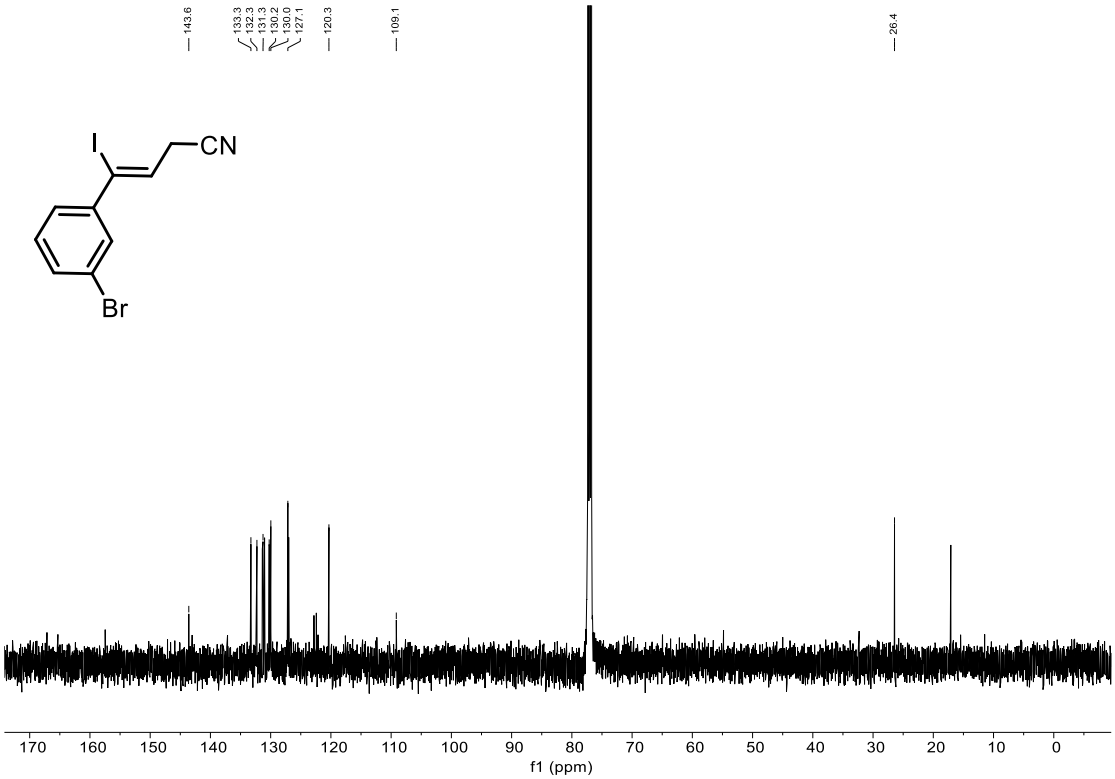
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-7*



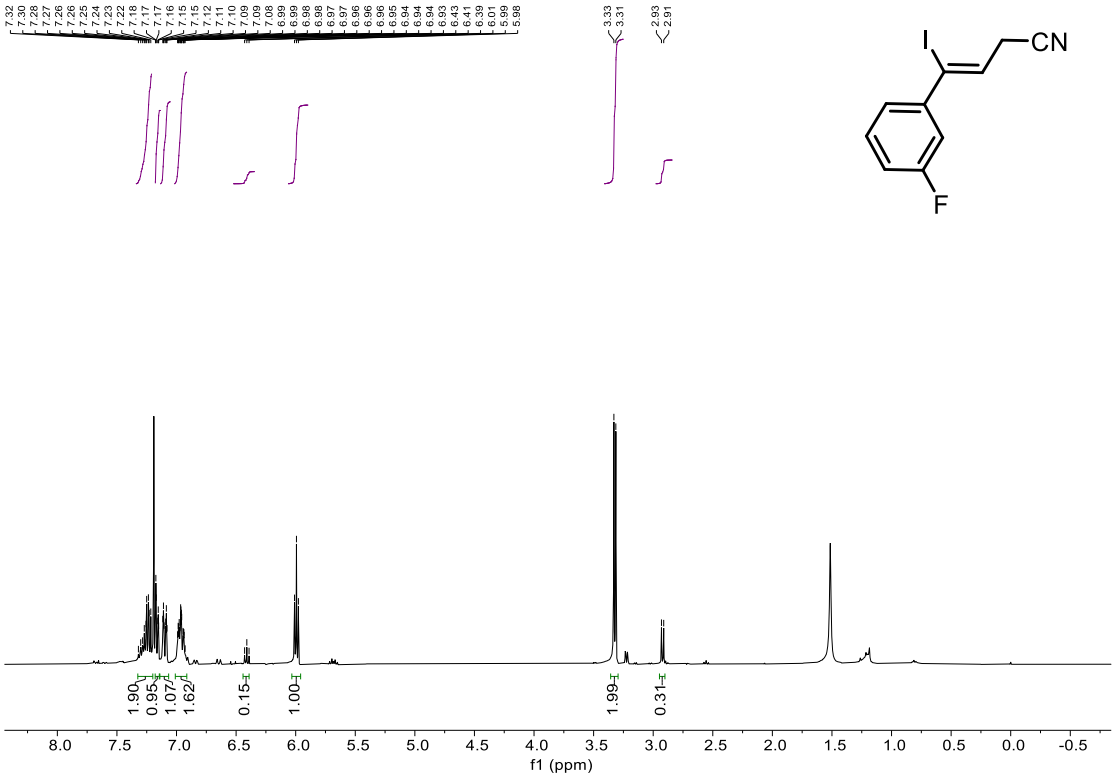
^{1}H NMR (400 MHz, CDCl3) of *Z-8*



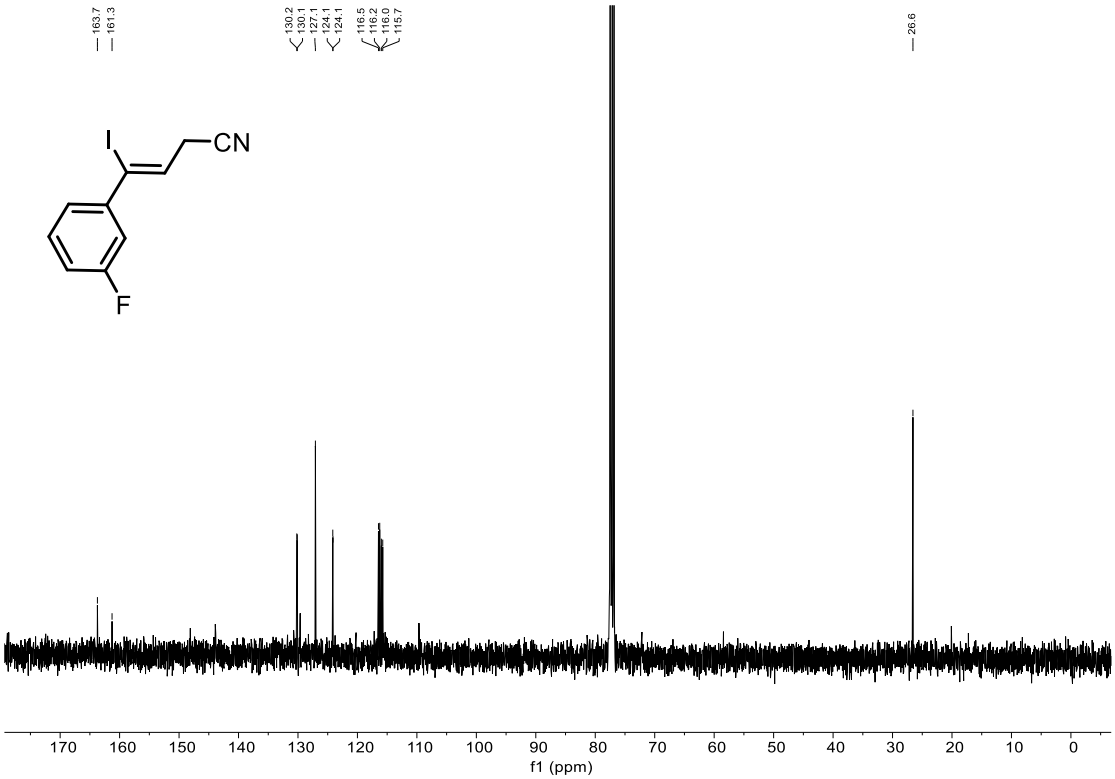
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-8*



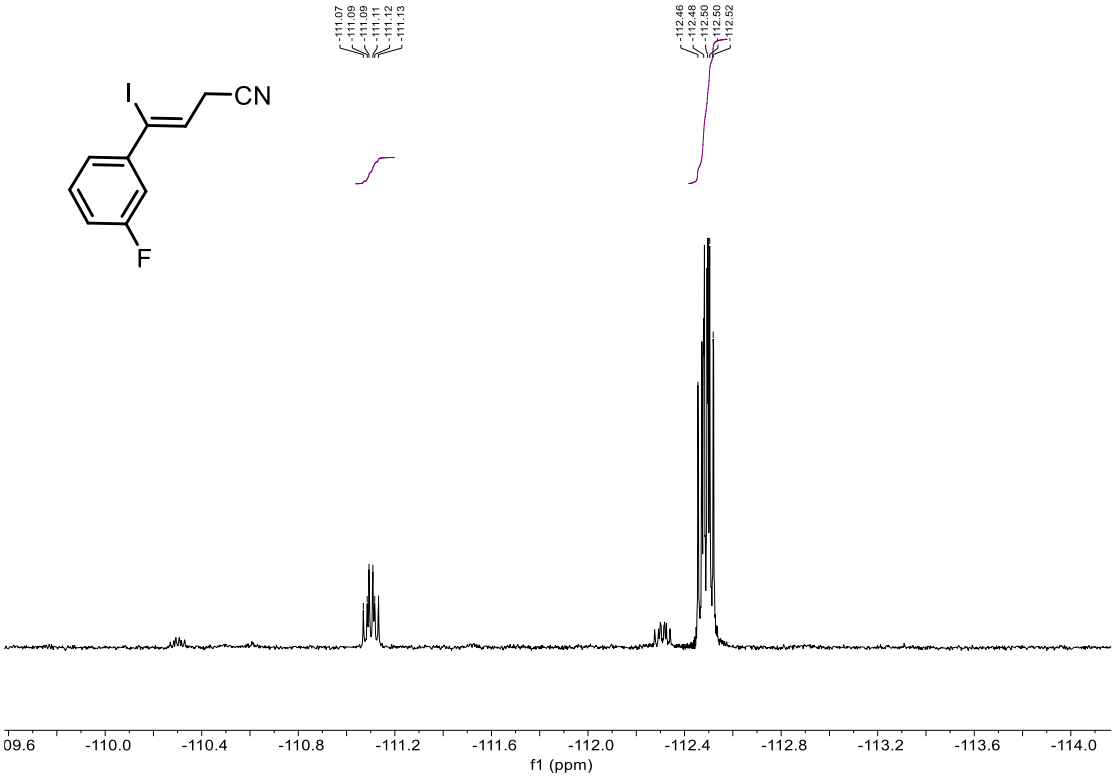
^{1}H NMR (400 MHz, CDCl3) of *Z-9*



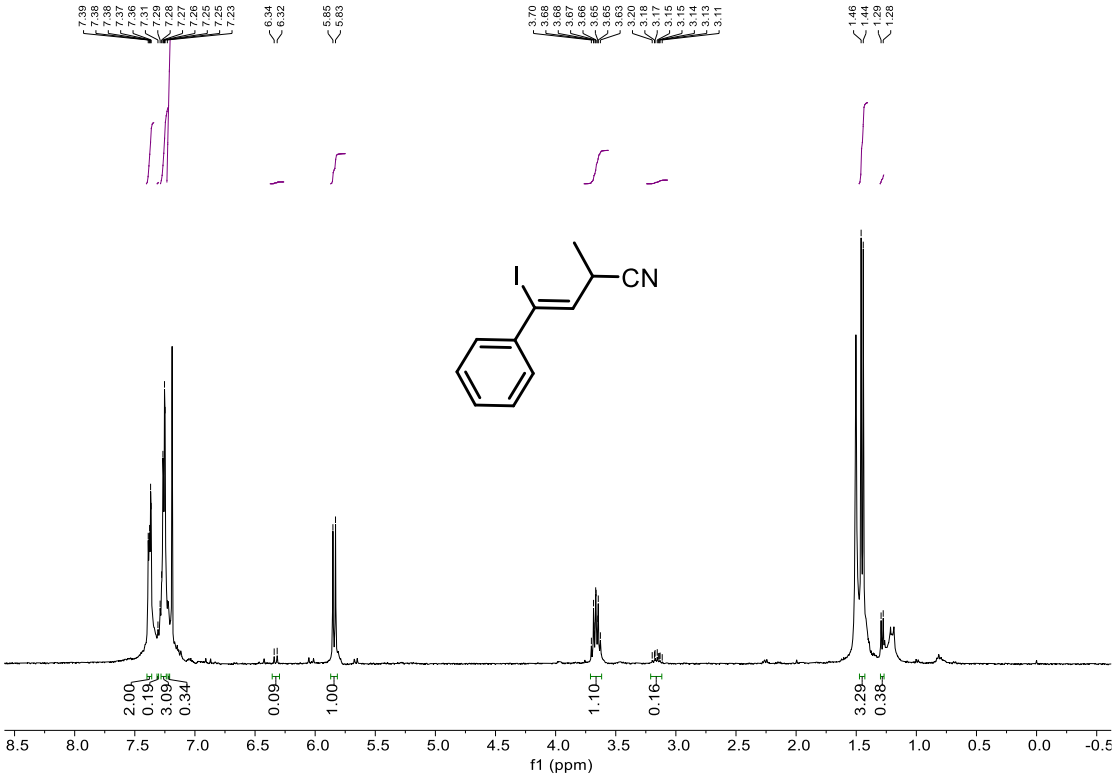
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-9*



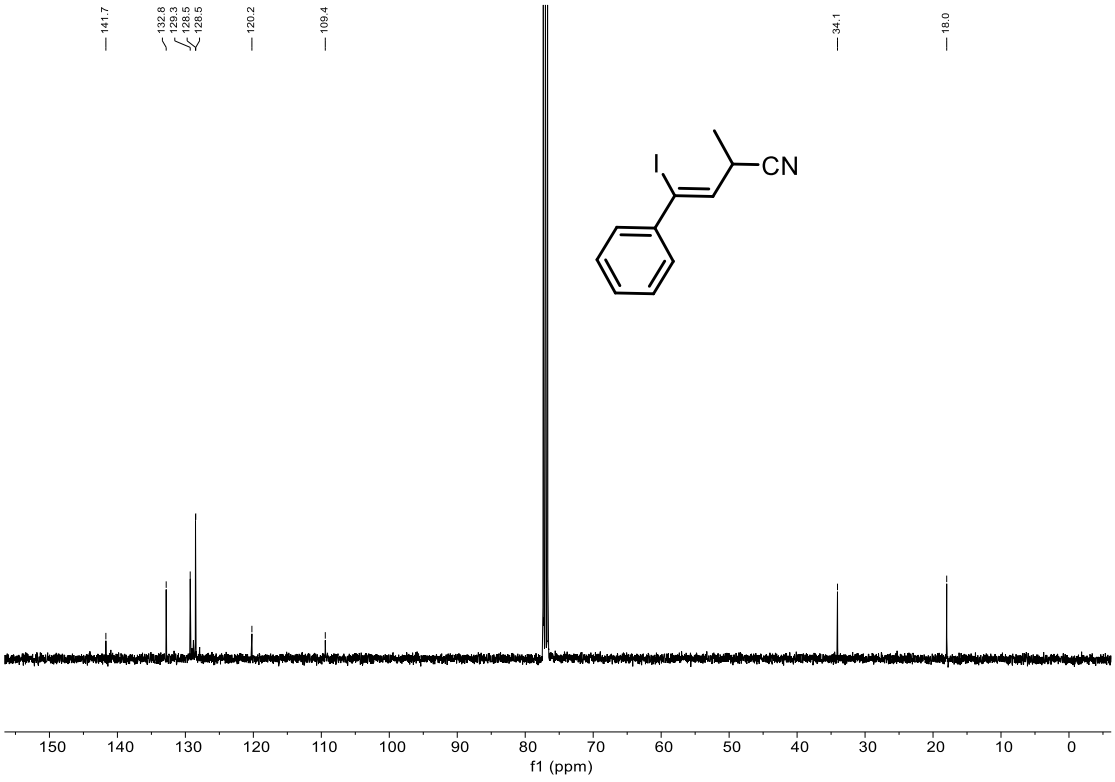
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-9*



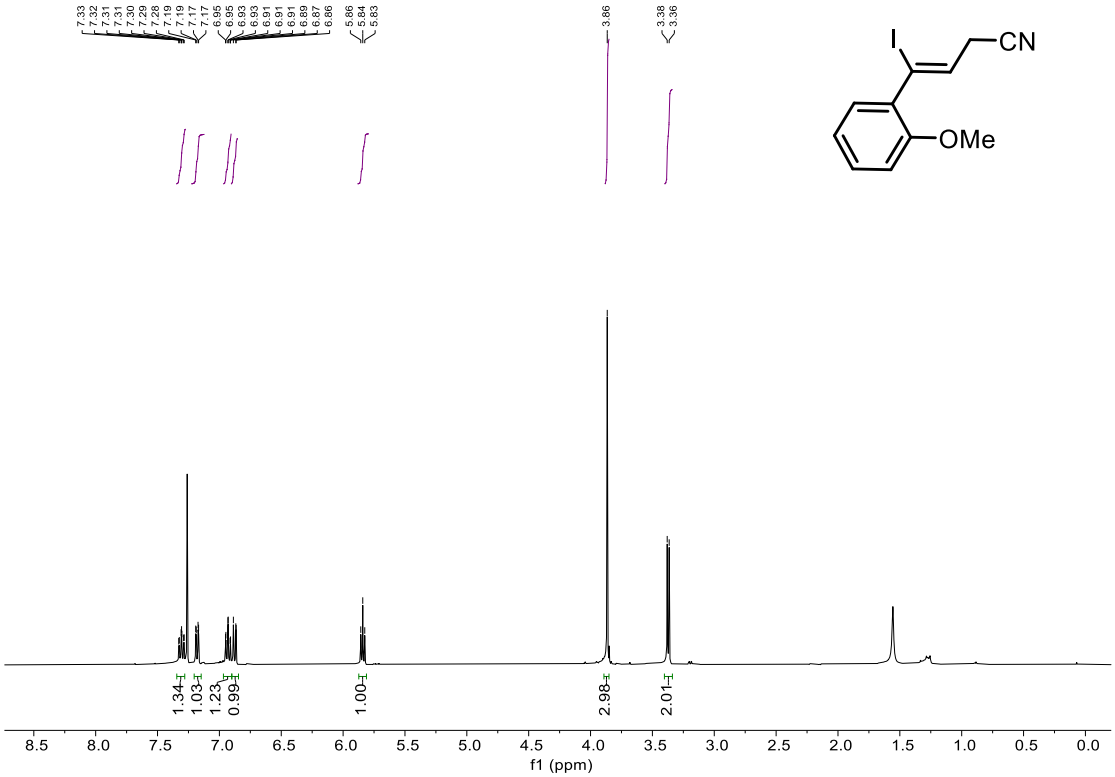
^{1}H NMR (400 MHz, CDCl3) of *Z-10*



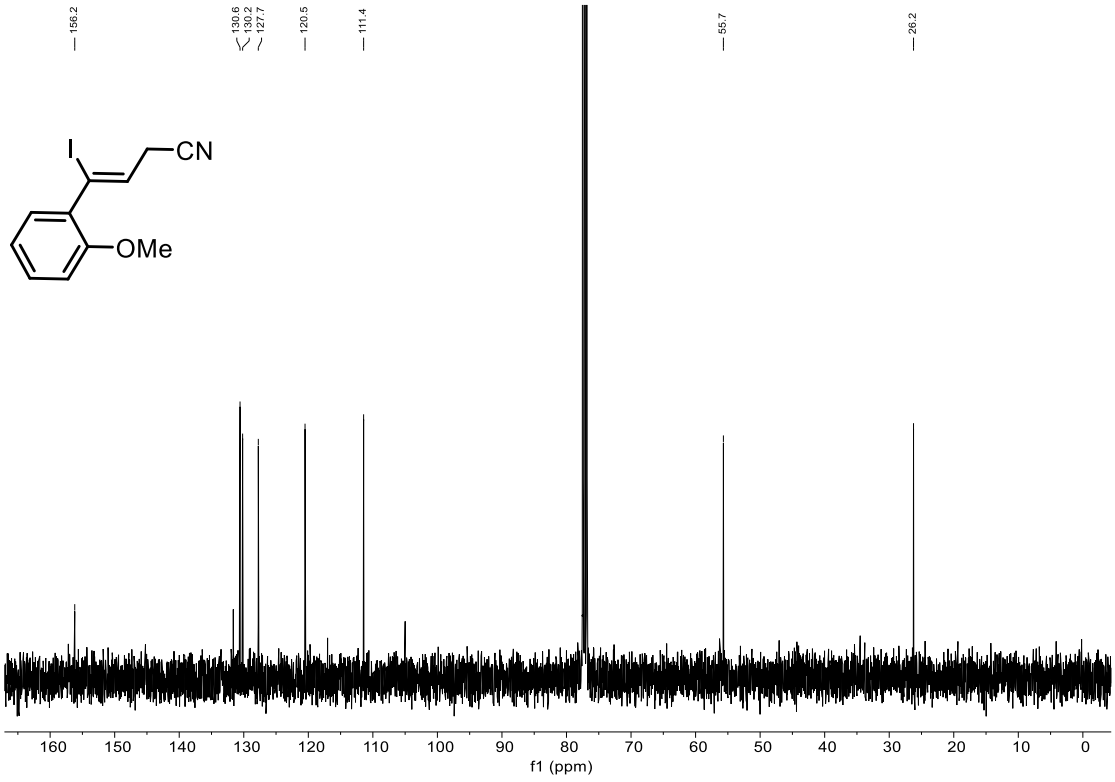
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-10*



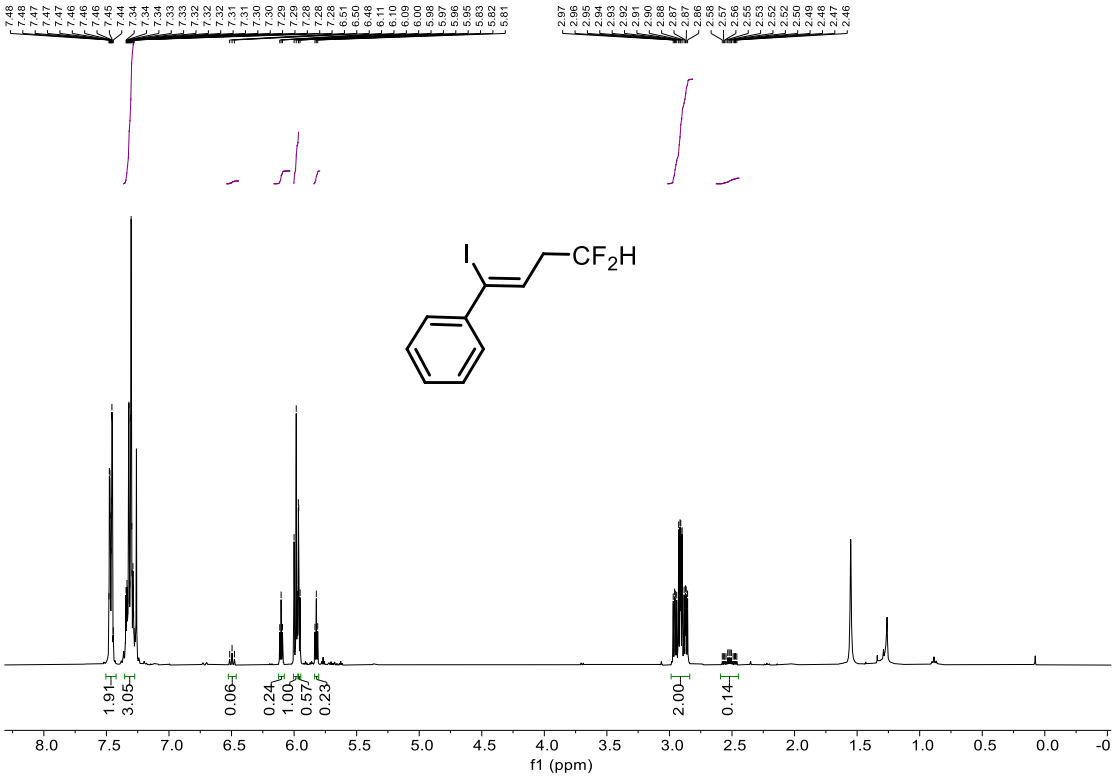
^{1}H NMR (400 MHz, CDCl3) of *Z-11*



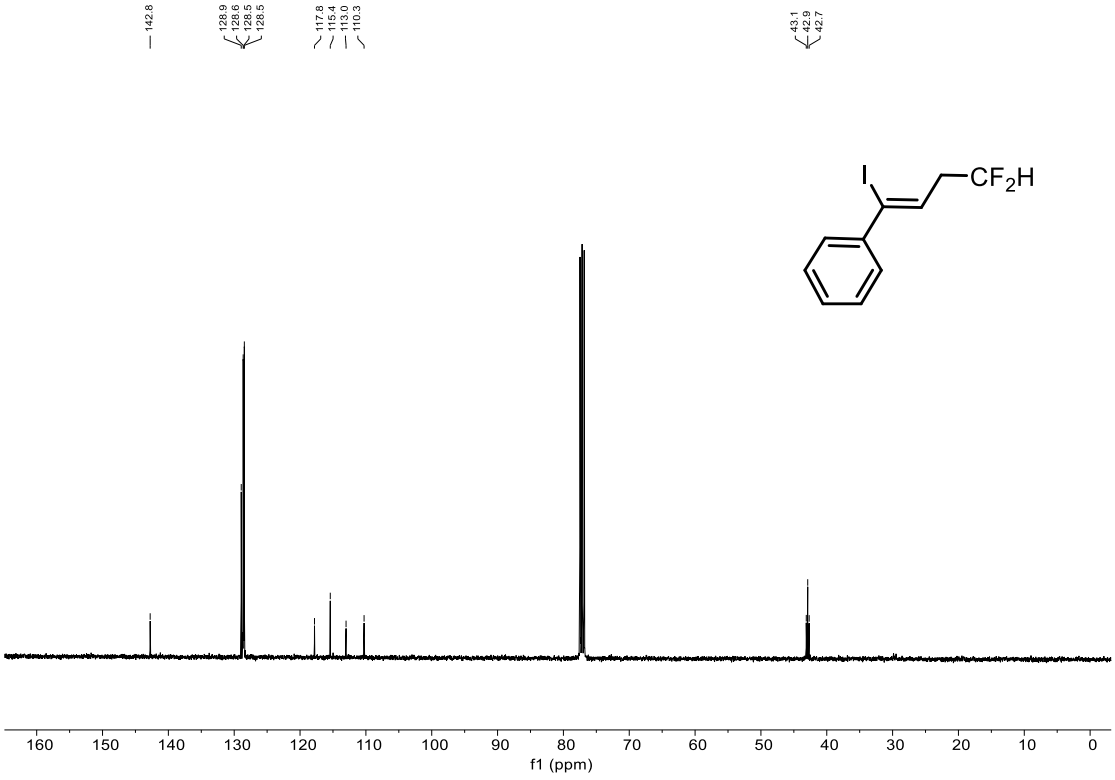
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-11*



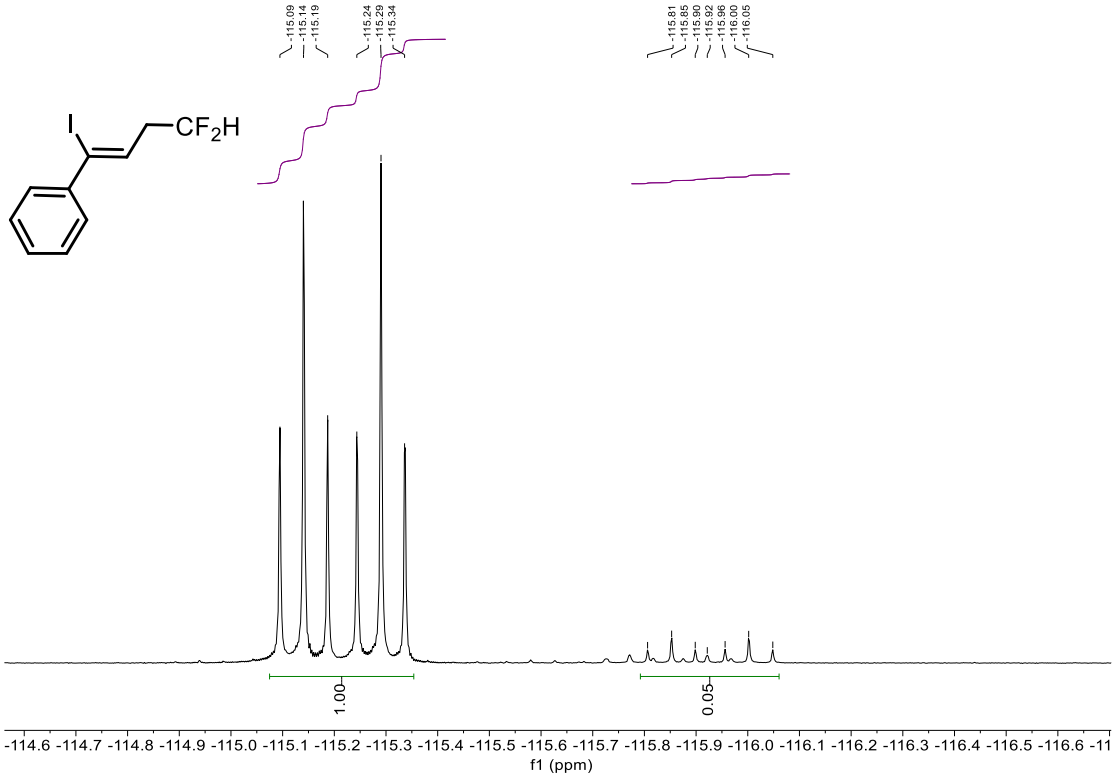
^{1}H NMR (400 MHz, CDCl3) of *Z-12*



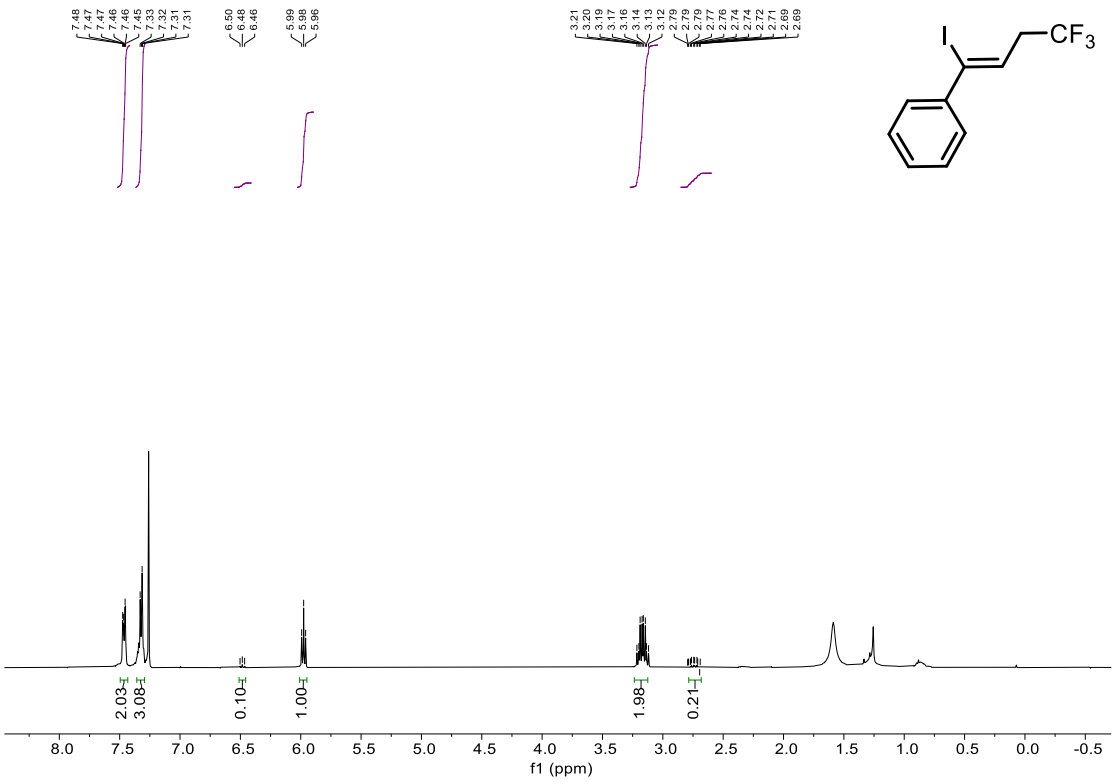
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-12*



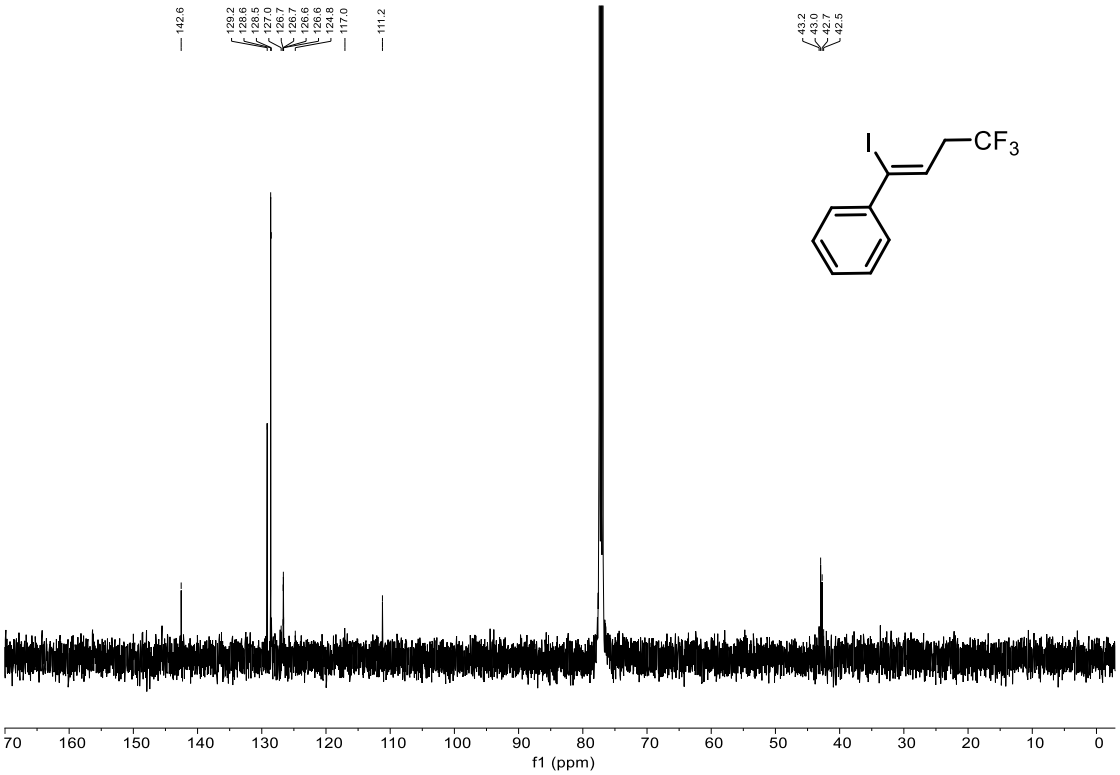
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-12*



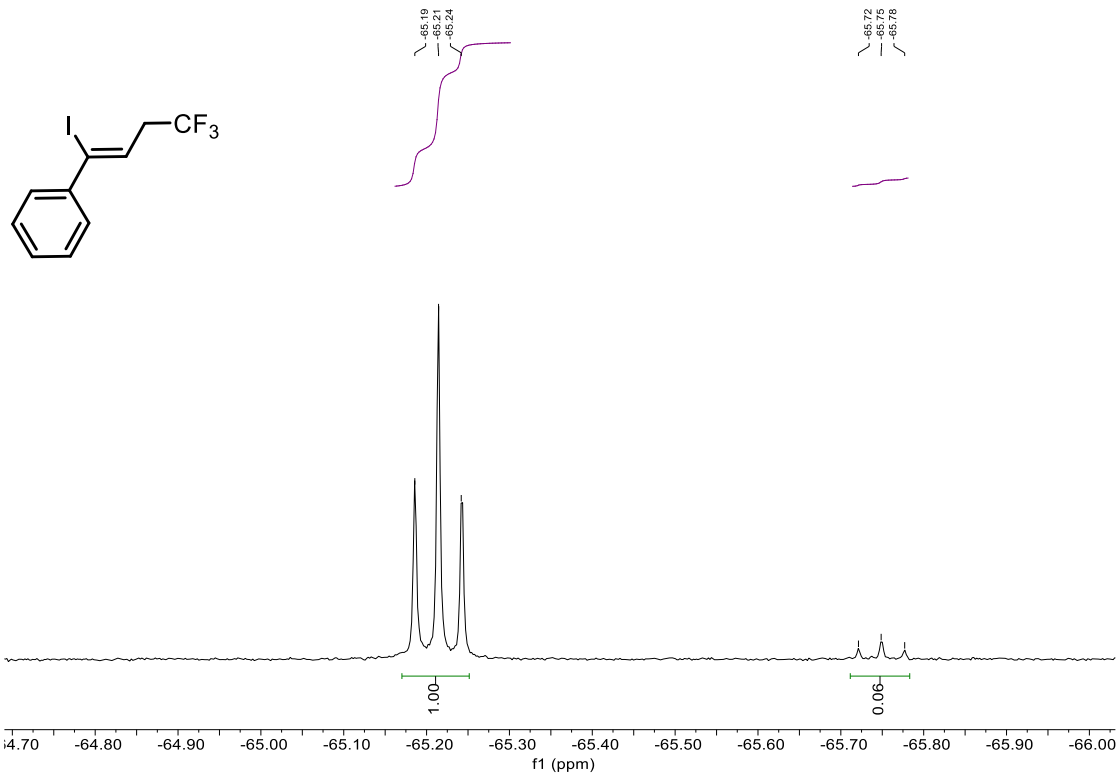
^{1}H NMR (400 MHz, CDCl3) of *Z-13*



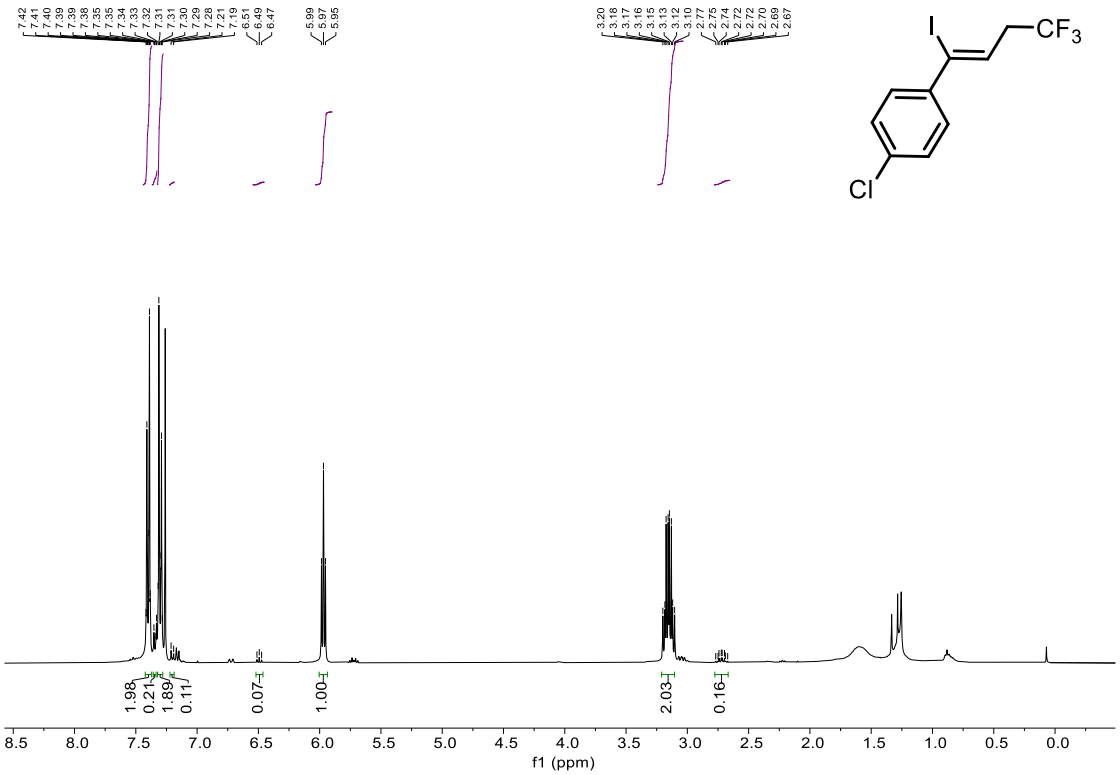
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-13*



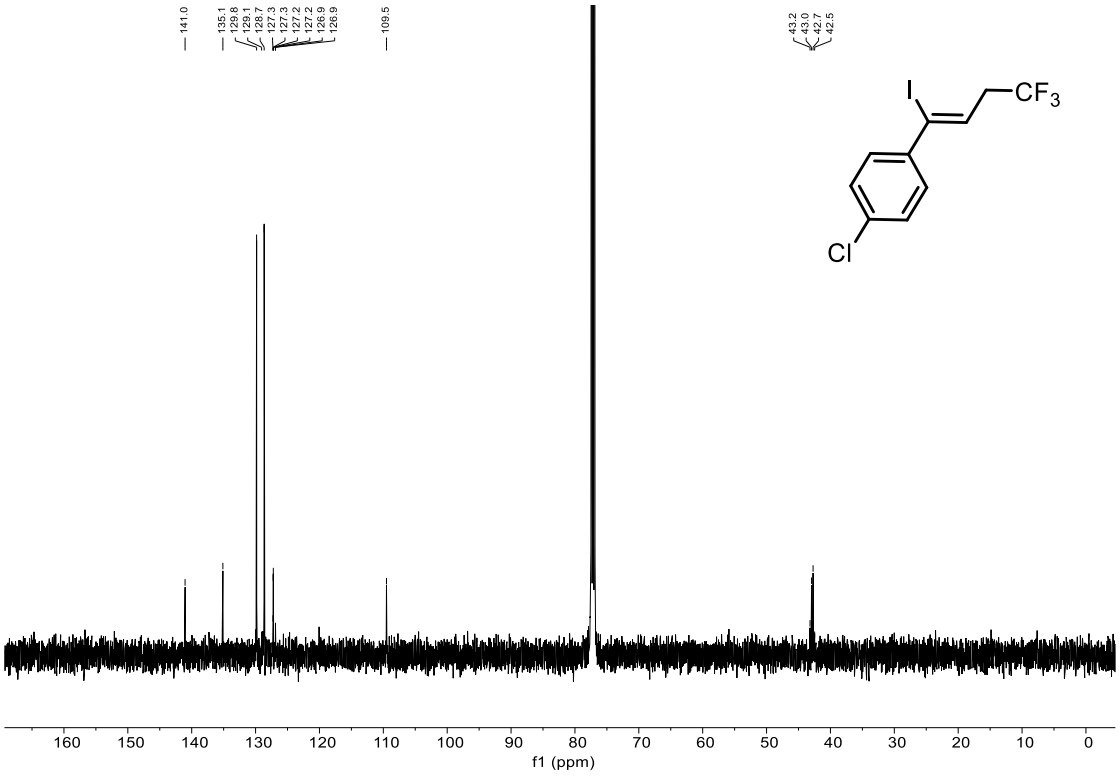
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-13*



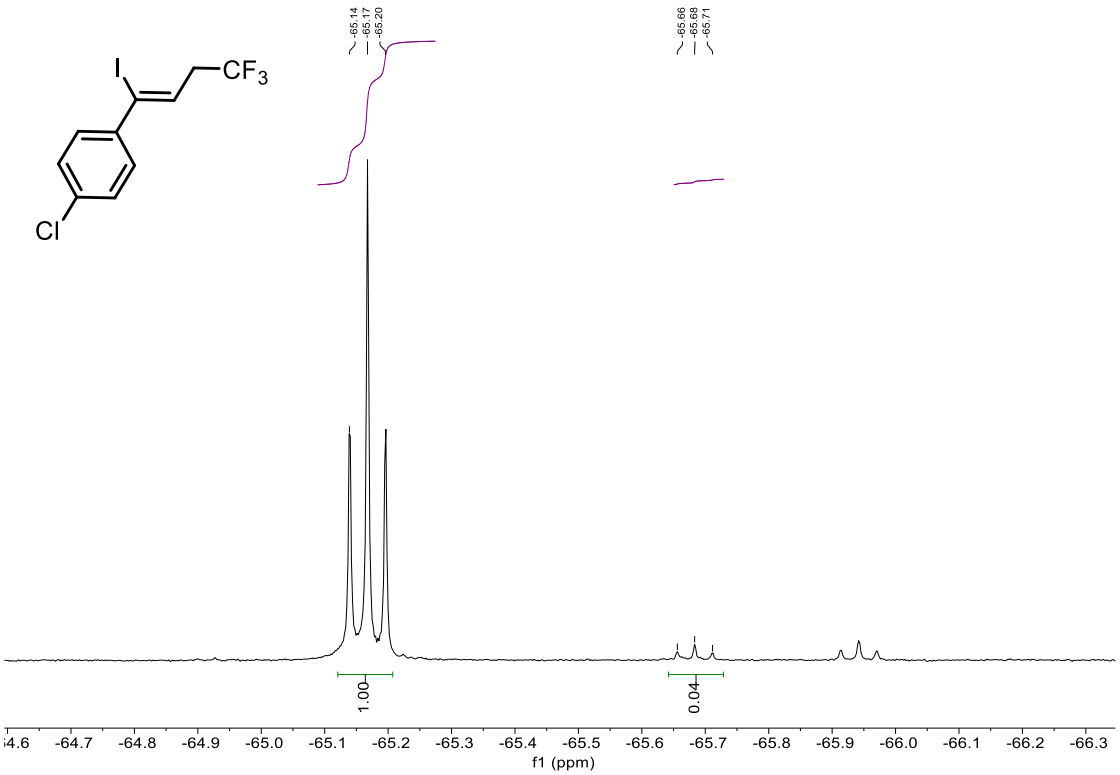
^{1}H NMR (400 MHz, CDCl3) of *Z-14*



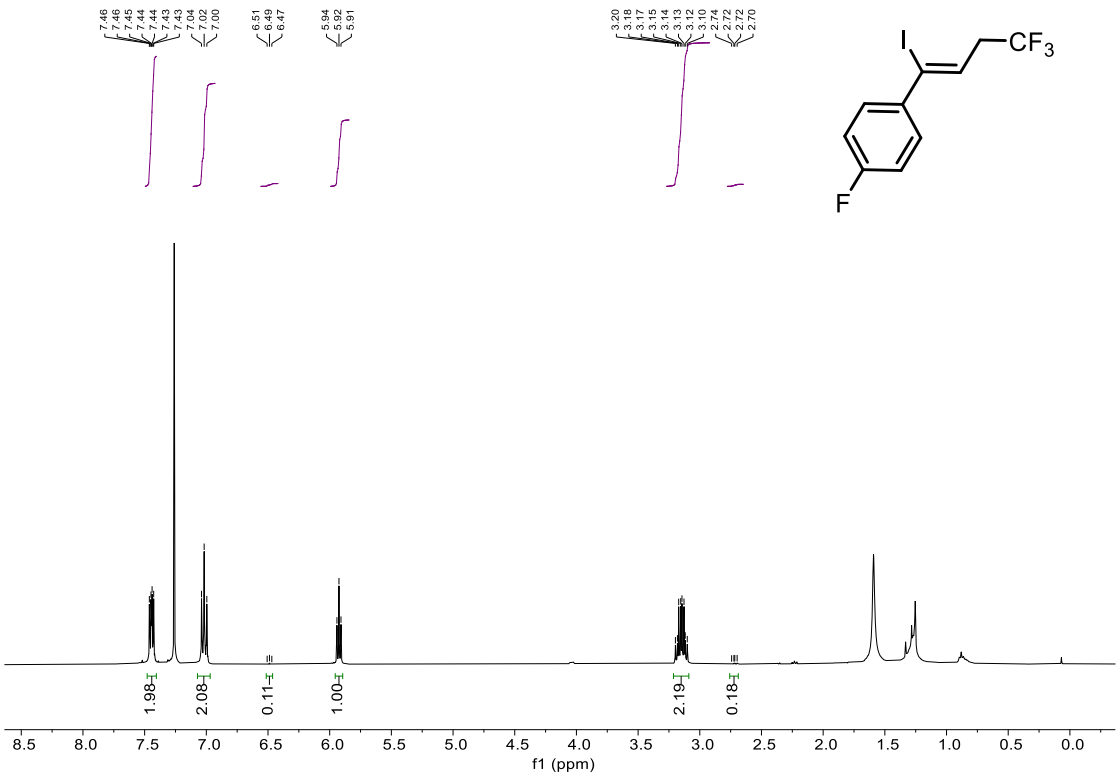
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-14*



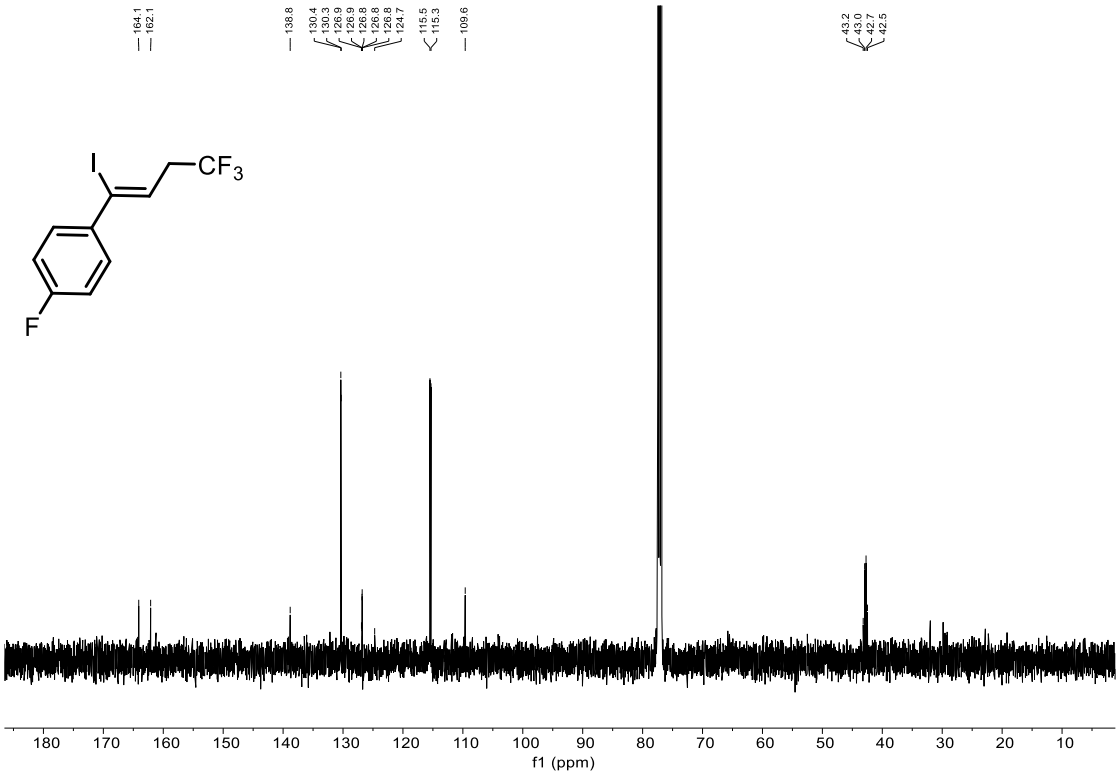
^{19}F NMR (376 MHz, CDCl$_3$) of *Z-14*



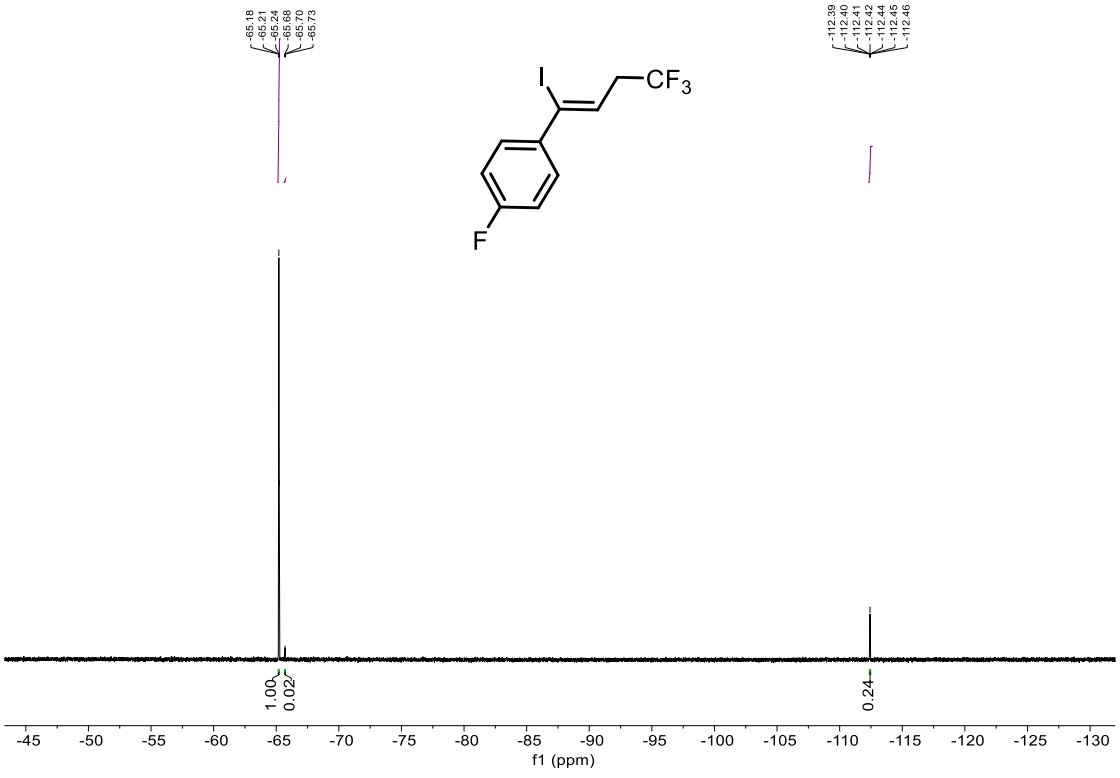
^{1}H NMR (400 MHz, CDCl3) of *Z-15*



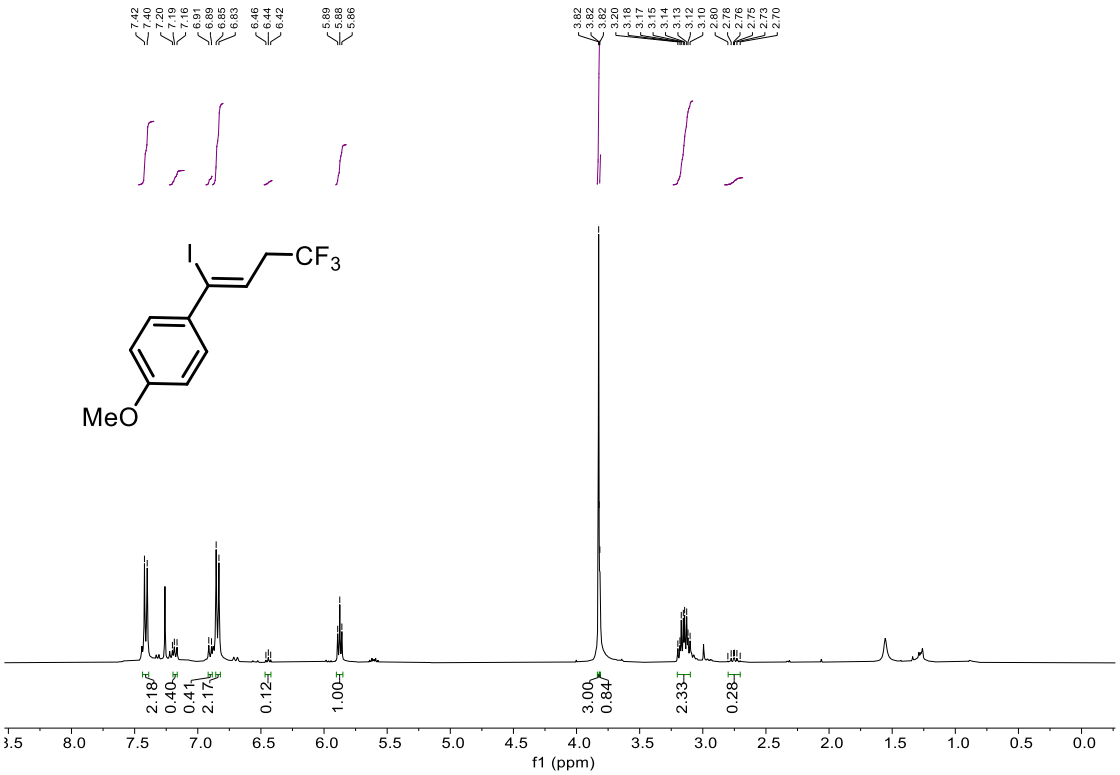
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-15*



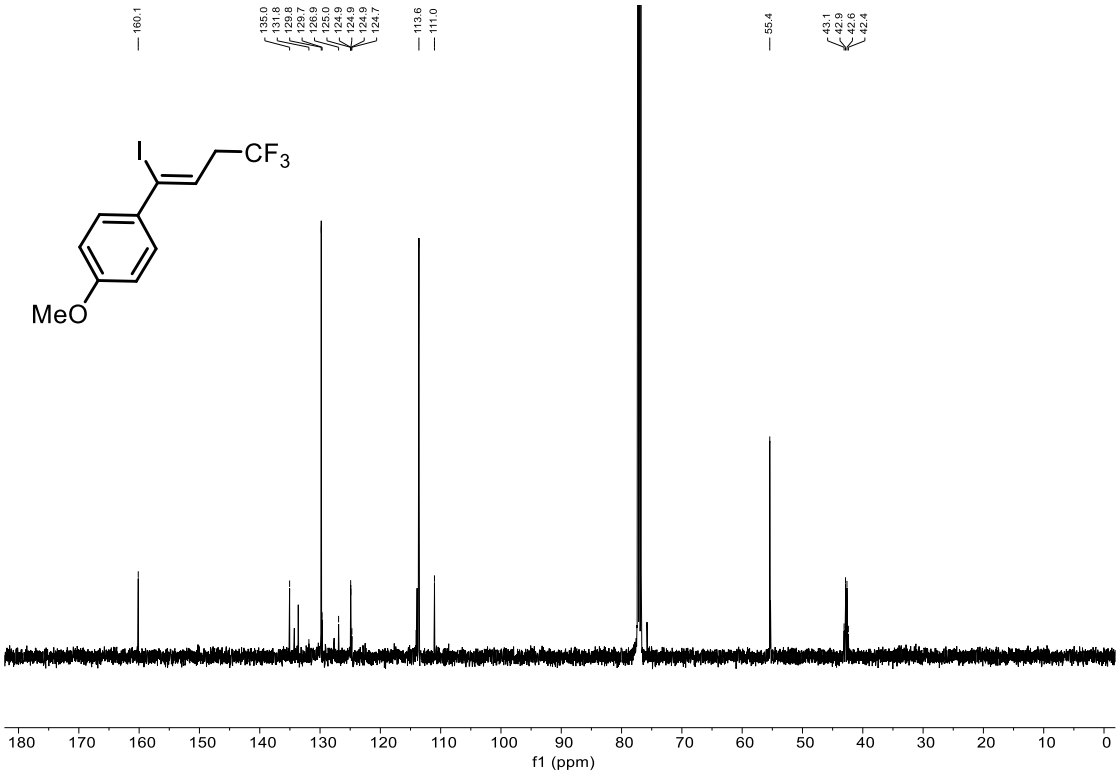
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-15*



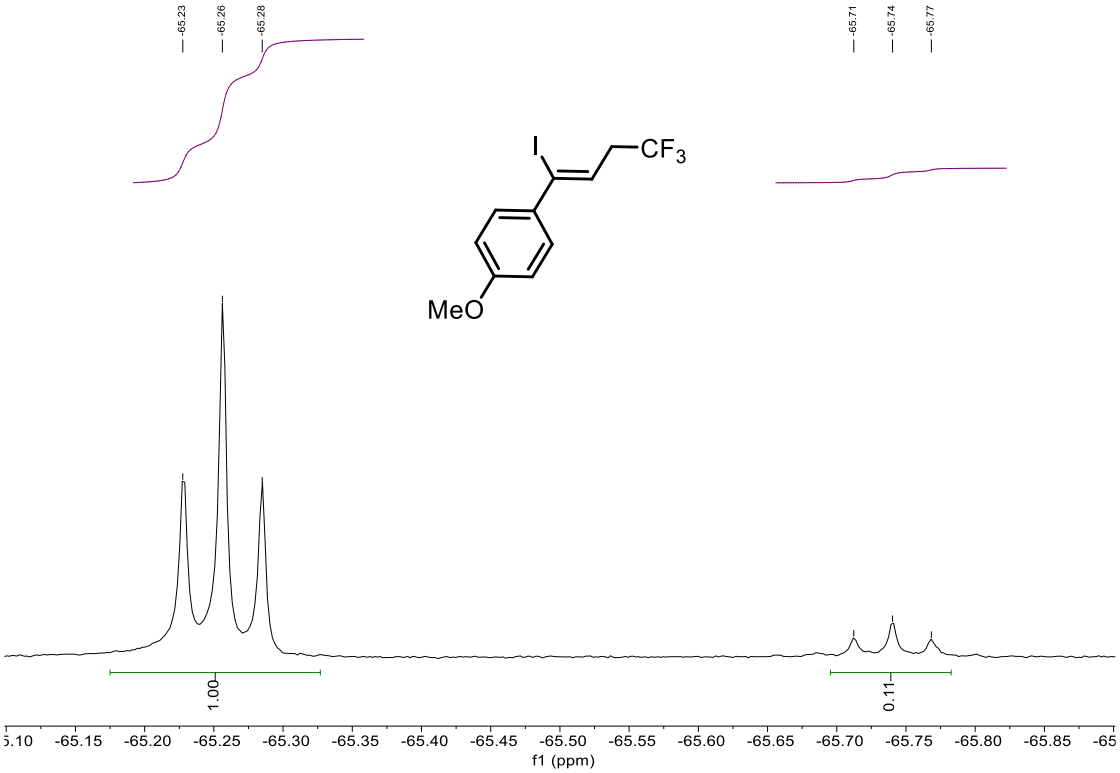
^{1}H NMR (400 MHz, CDCl3) of *Z-16*



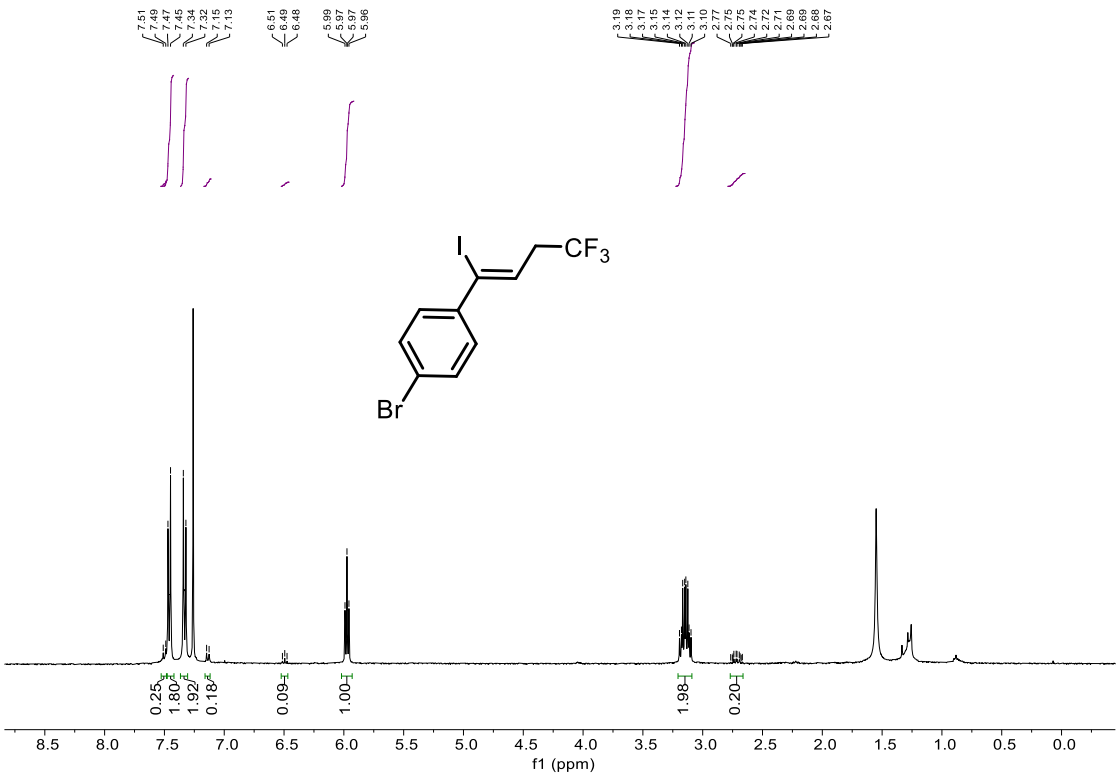
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-16*



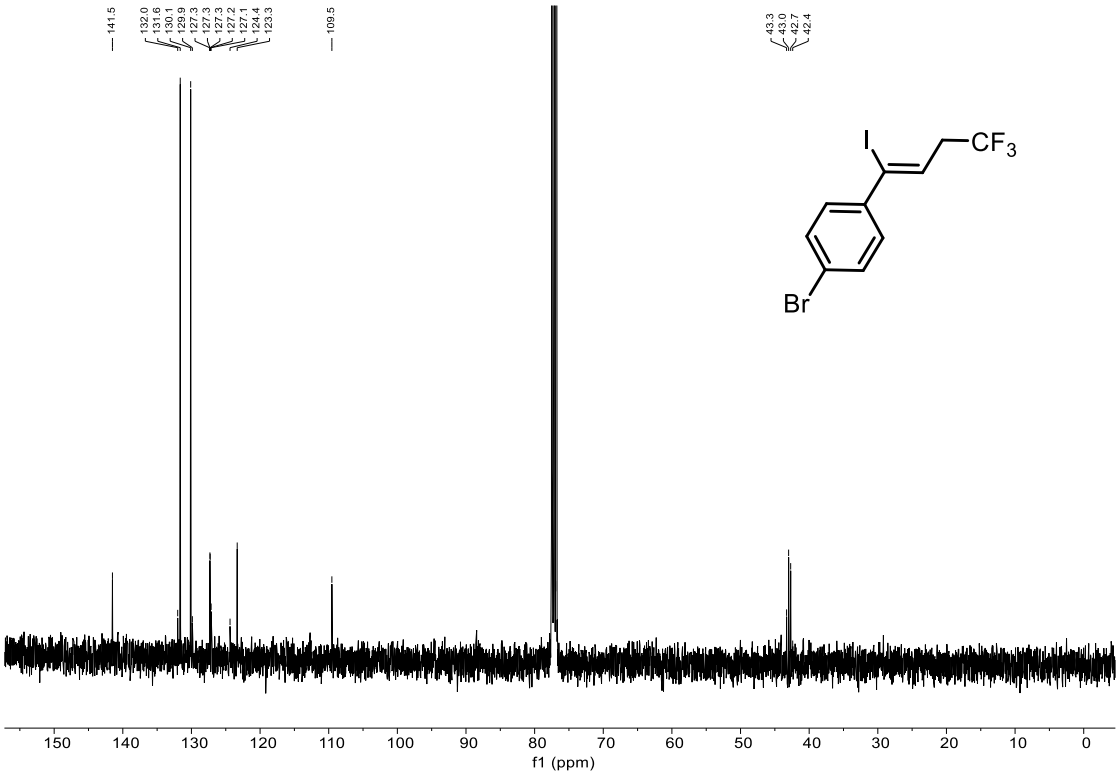
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-16*



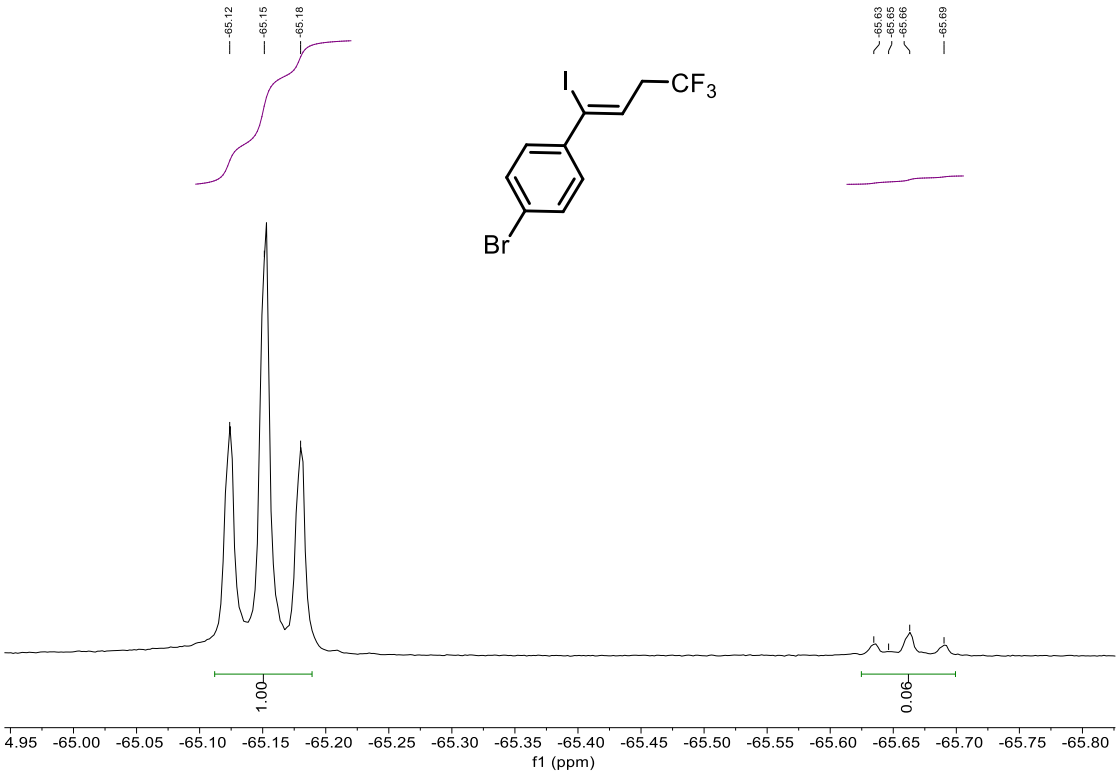
^{1}H NMR (400 MHz, CDCl3) of *Z-17*



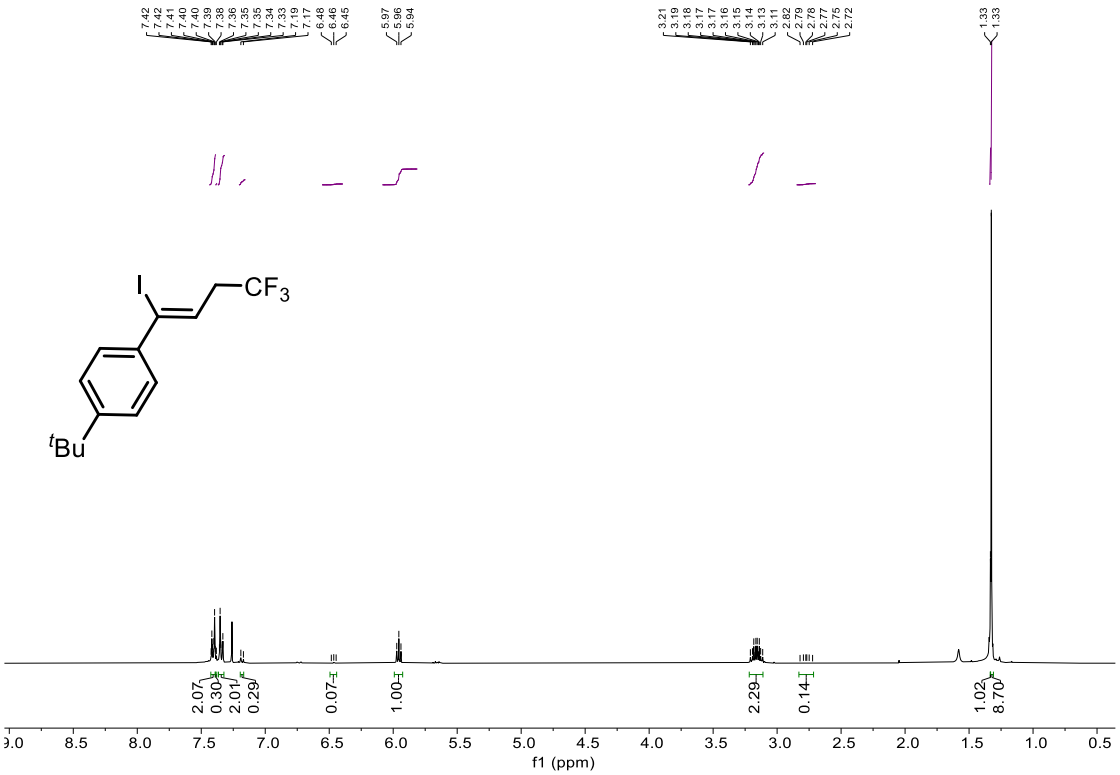
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-17*



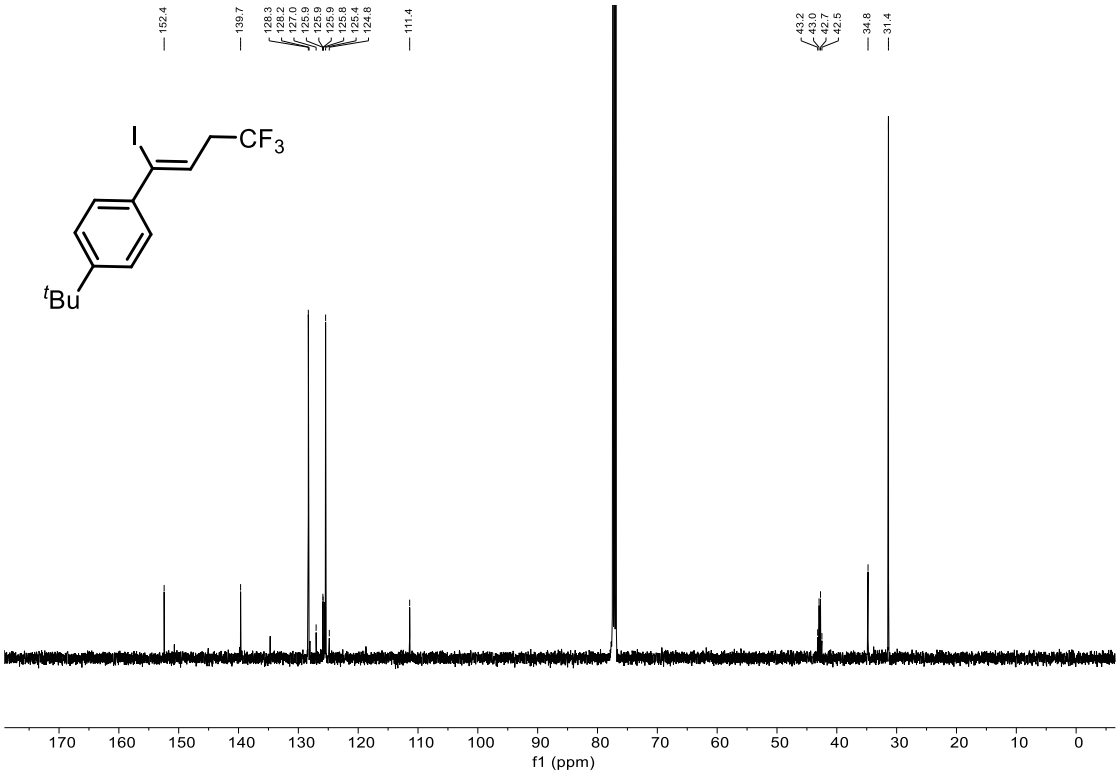
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-17*



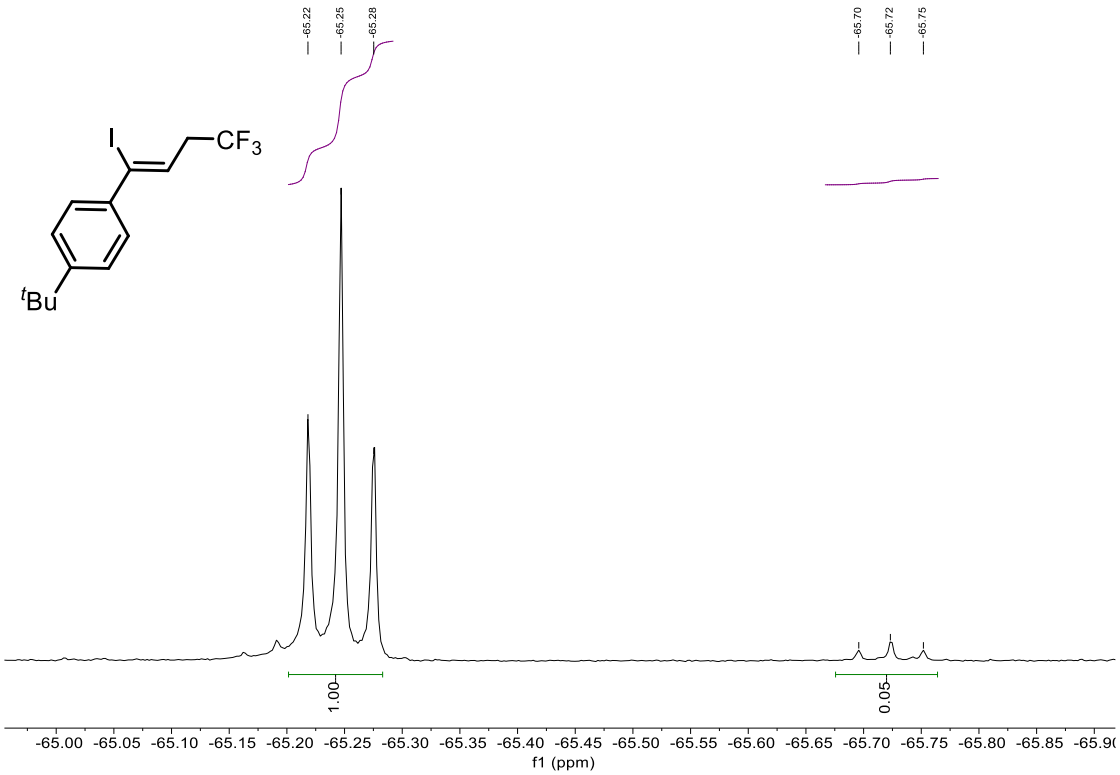
^{1}H NMR (400 MHz, CDCl3) of *Z-18*



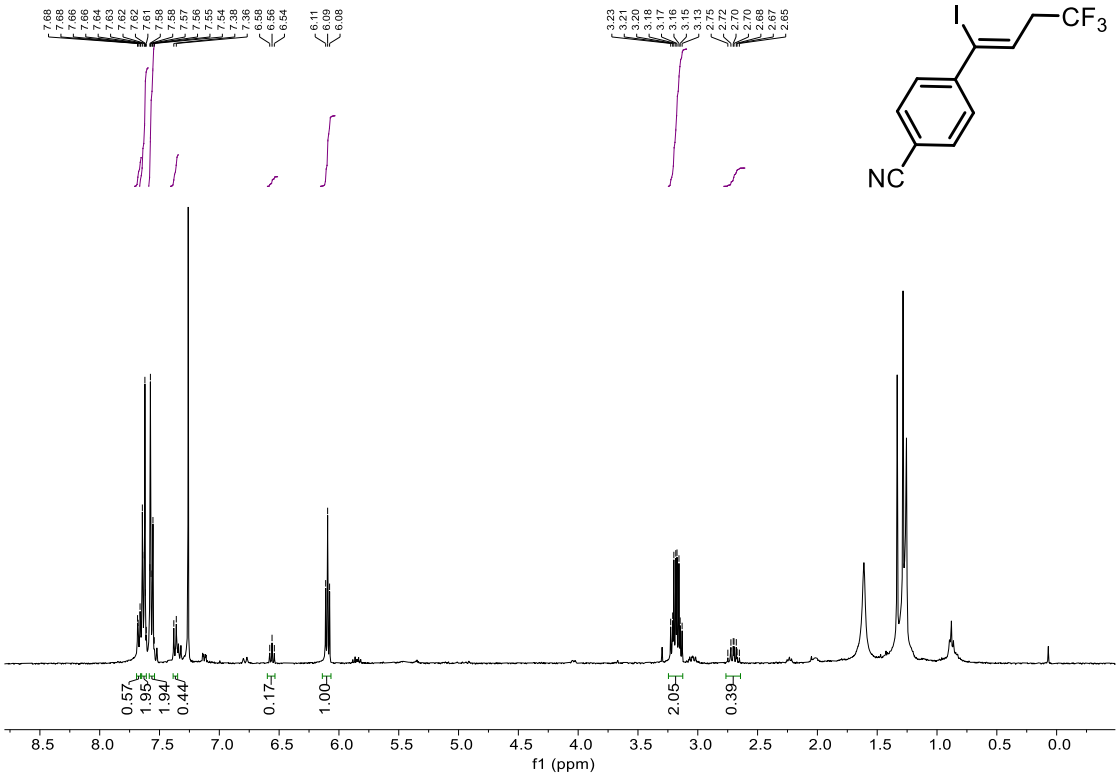
^{13}C NMR (126 MHz, $CDCl_3$) of *Z-18*



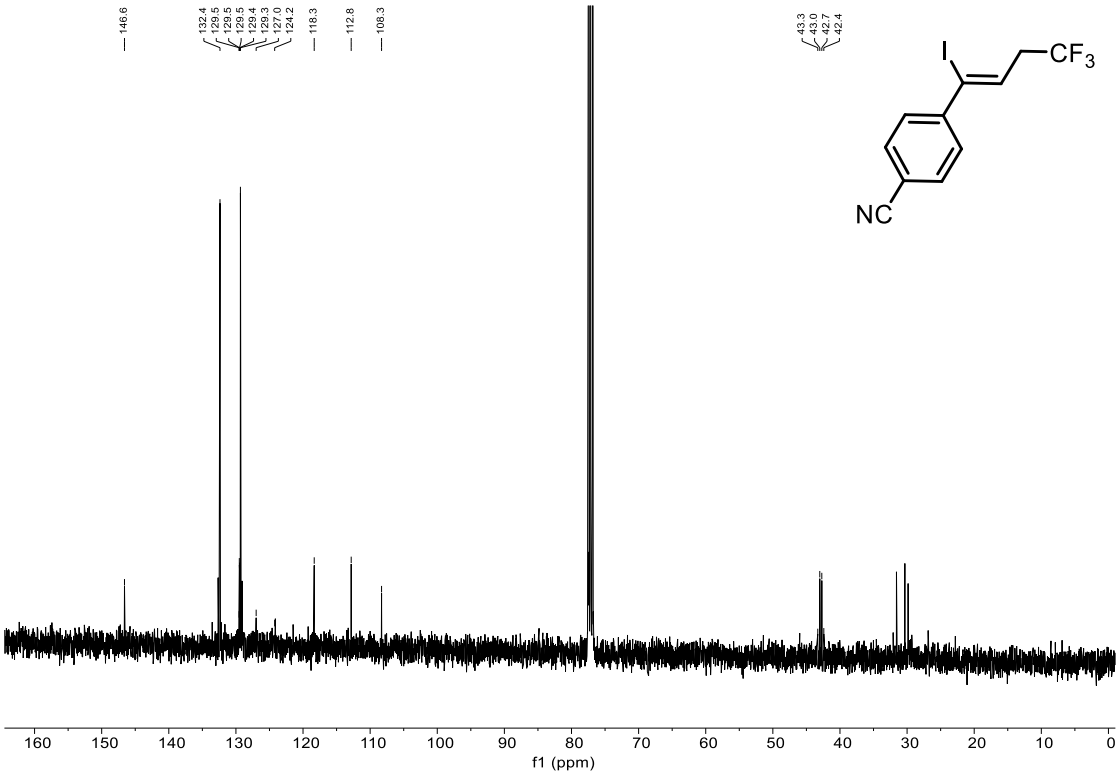
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-18*



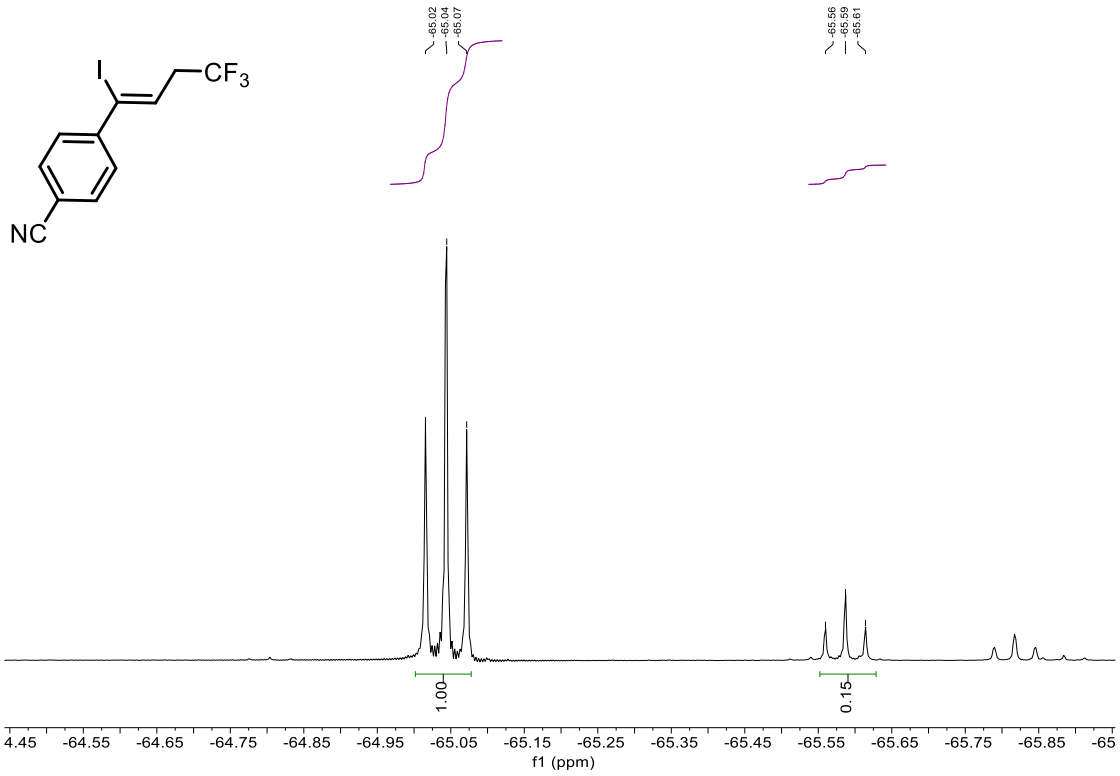
^{1}H NMR (400 MHz, CDCl3) of *Z-19*



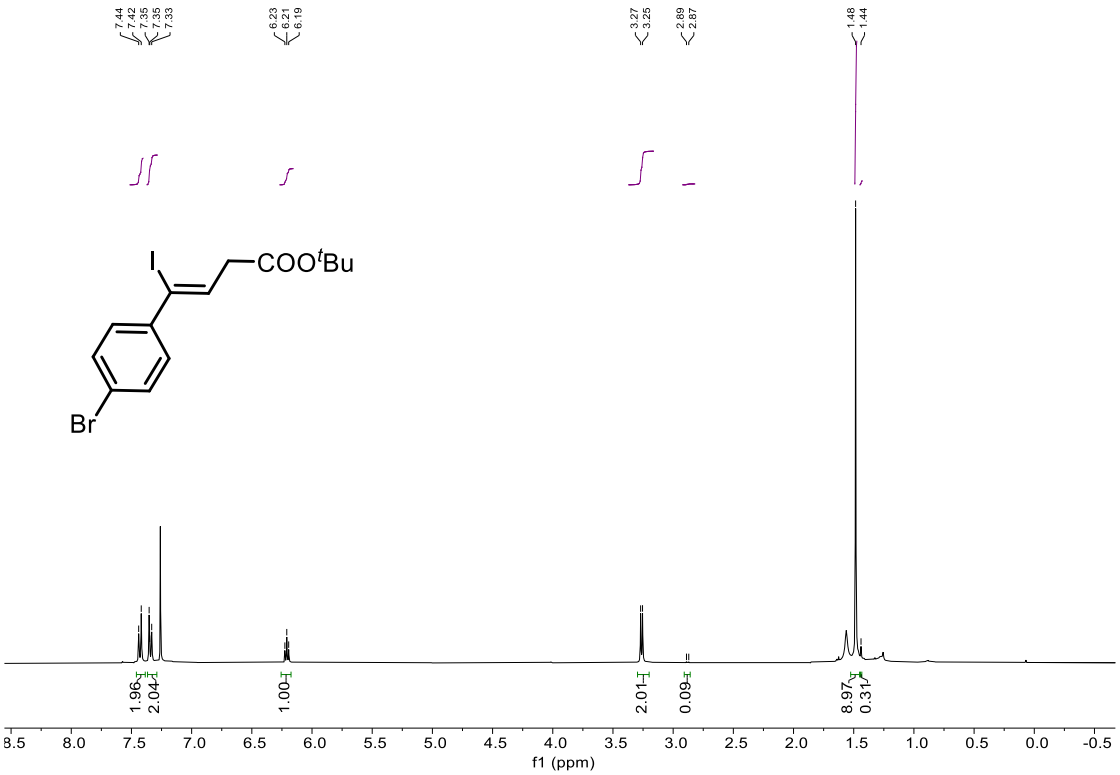
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-19*



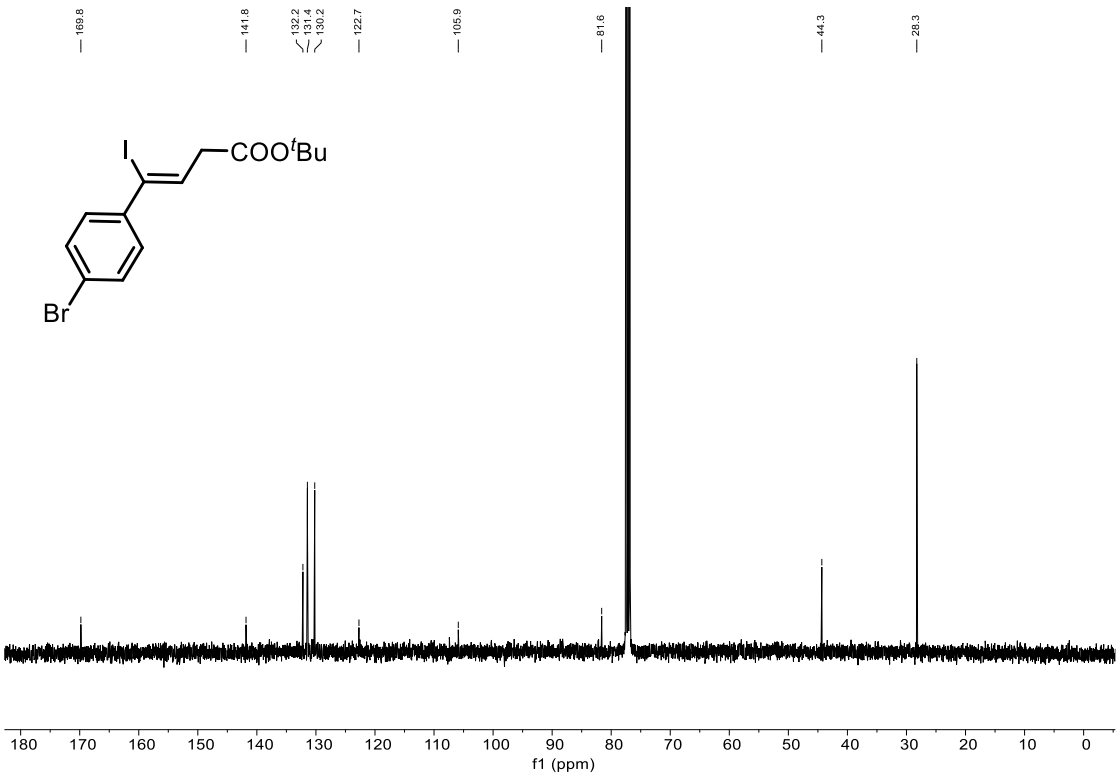
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-19*



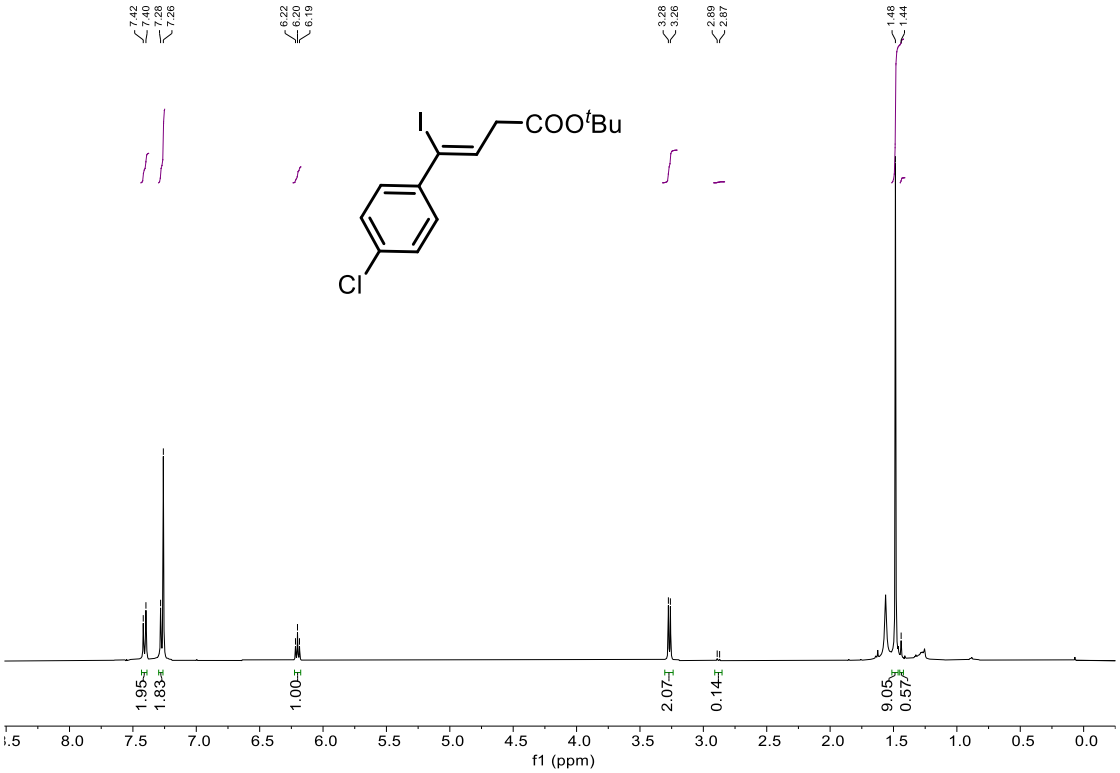
^{1}H NMR (400 MHz, CDCl3) of *Z-20*



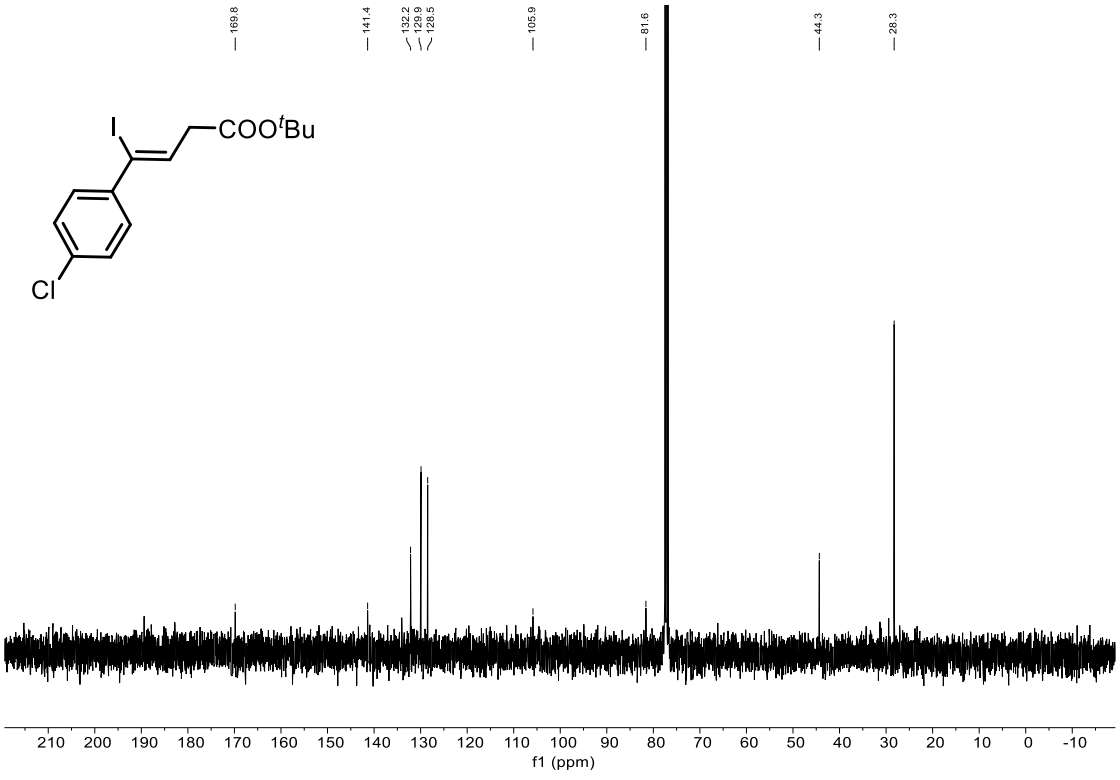
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-20*



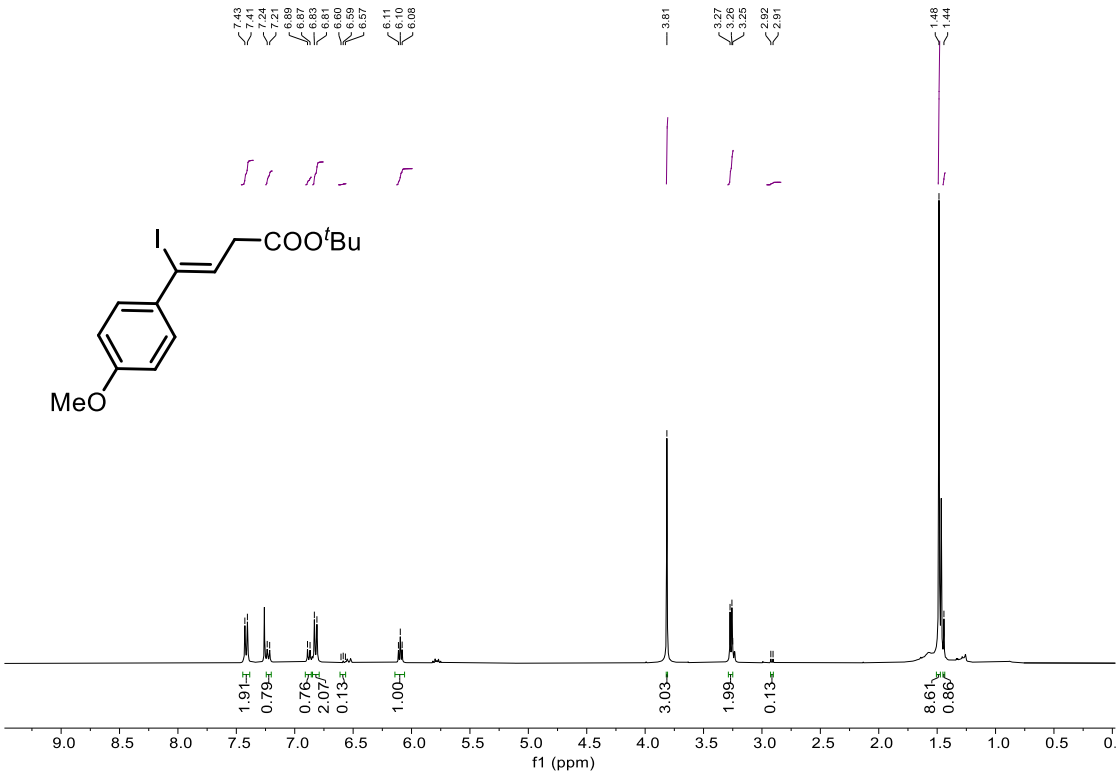
^{1}H NMR (400 MHz, CDCl3) of *Z-21*



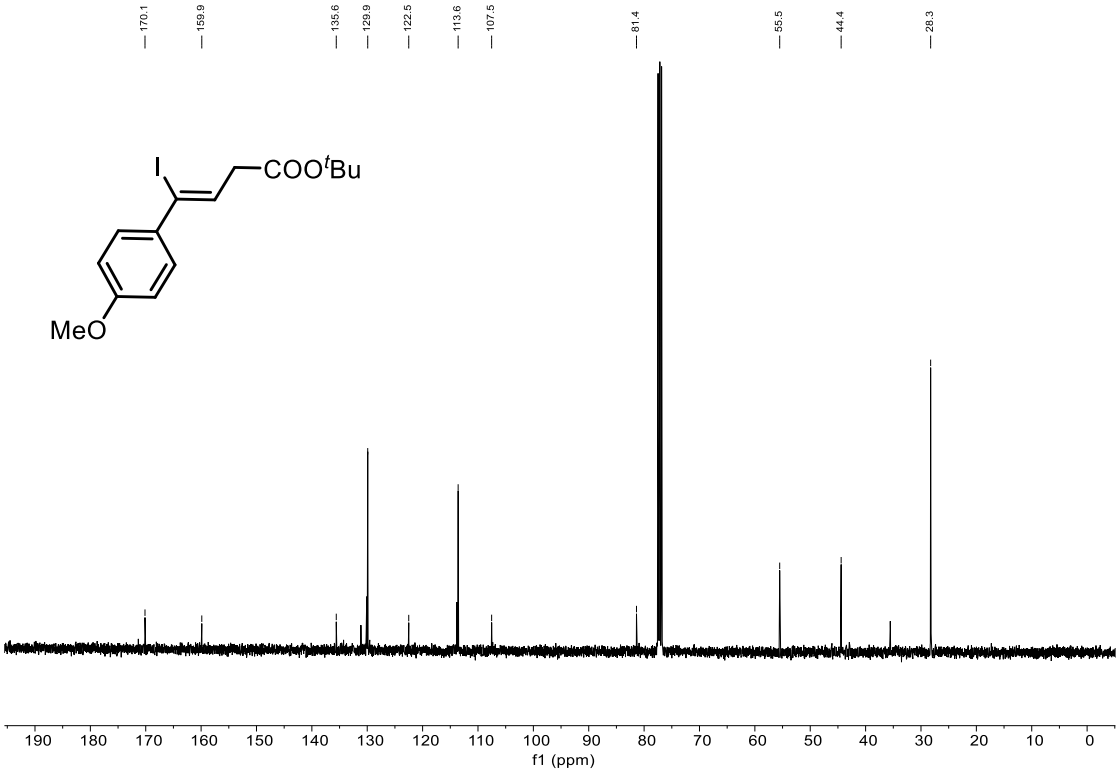
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-21*



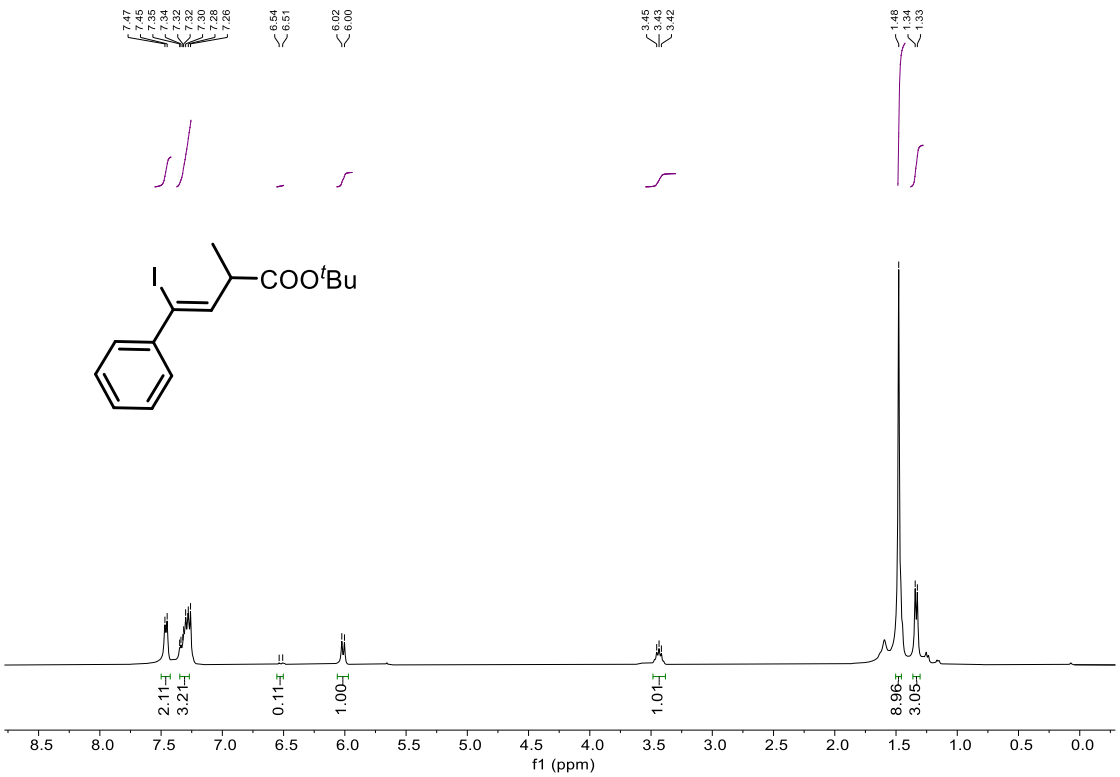
^{1}H NMR (400 MHz, CDCl3) of *Z-22*



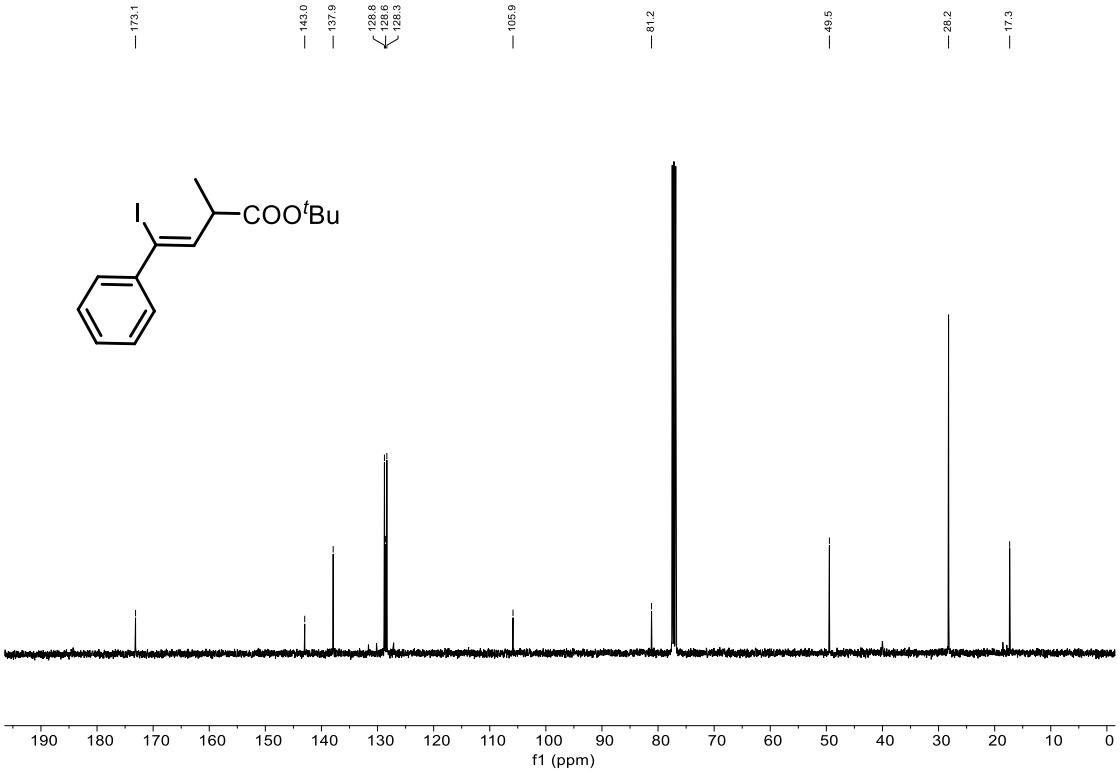
^{13}C NMR (101 MHz, CDCl$_3$) of *Z-22*



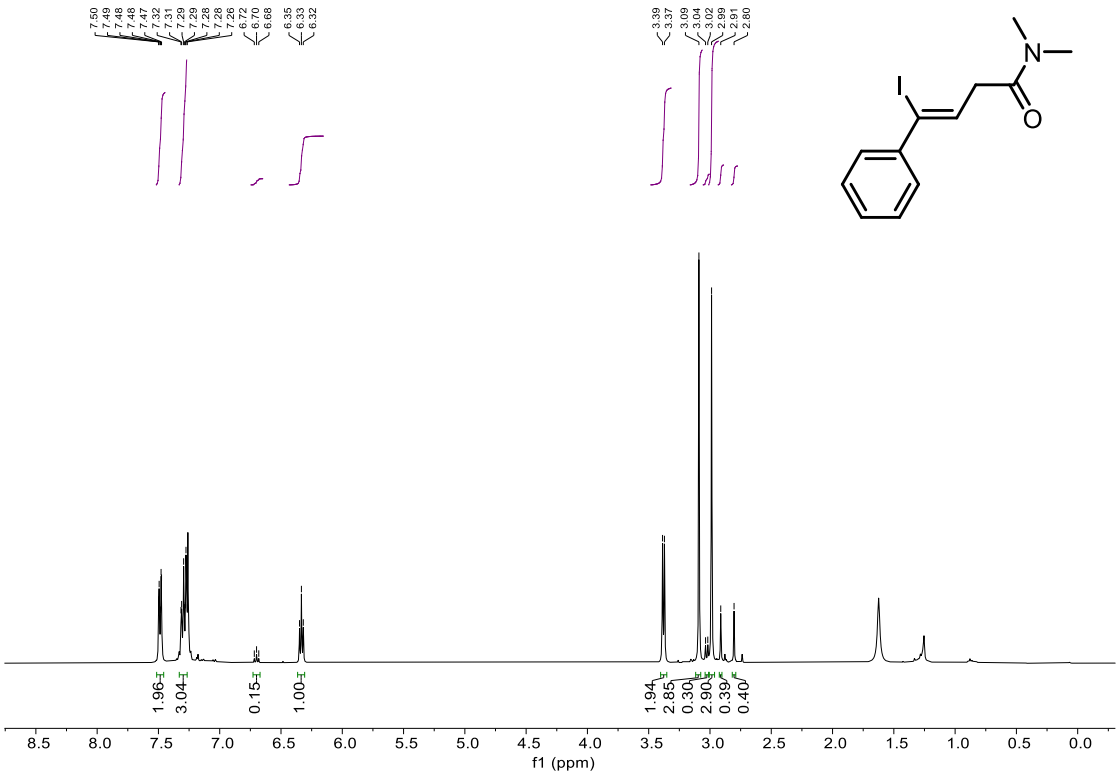
^{1}H NMR (400 MHz, CDCl3) of *Z-23*



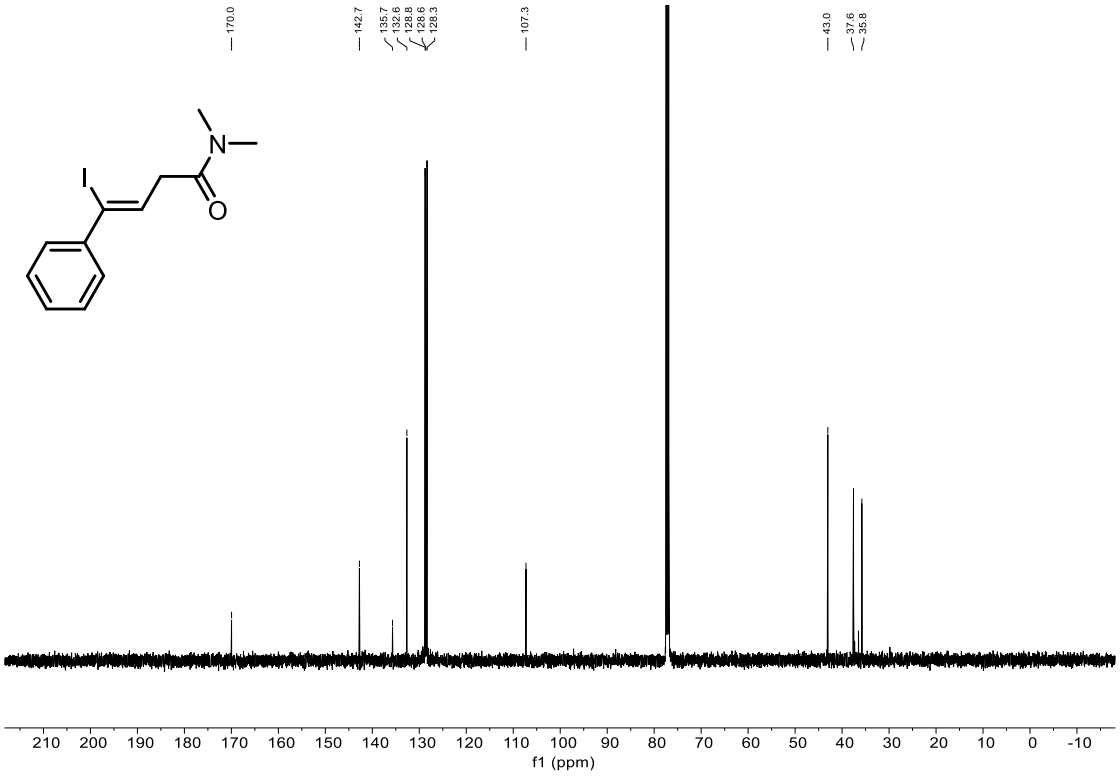
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-23*



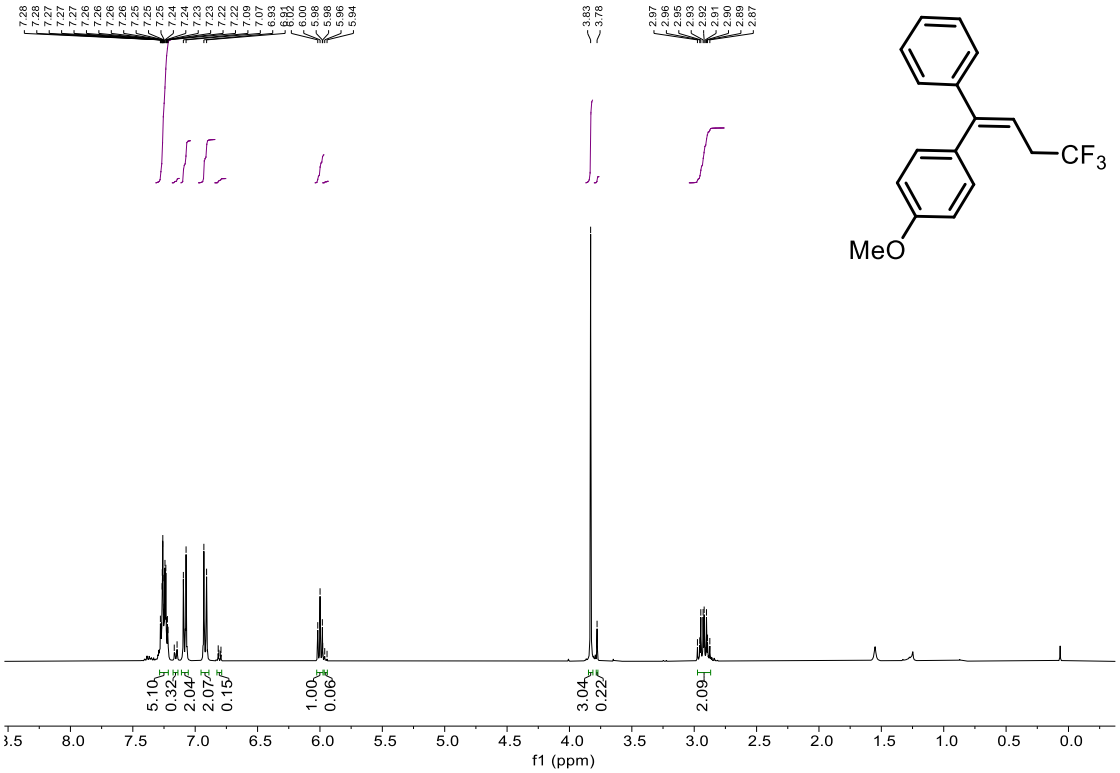
^{1}H NMR (400 MHz, CDCl3) of *Z-24*



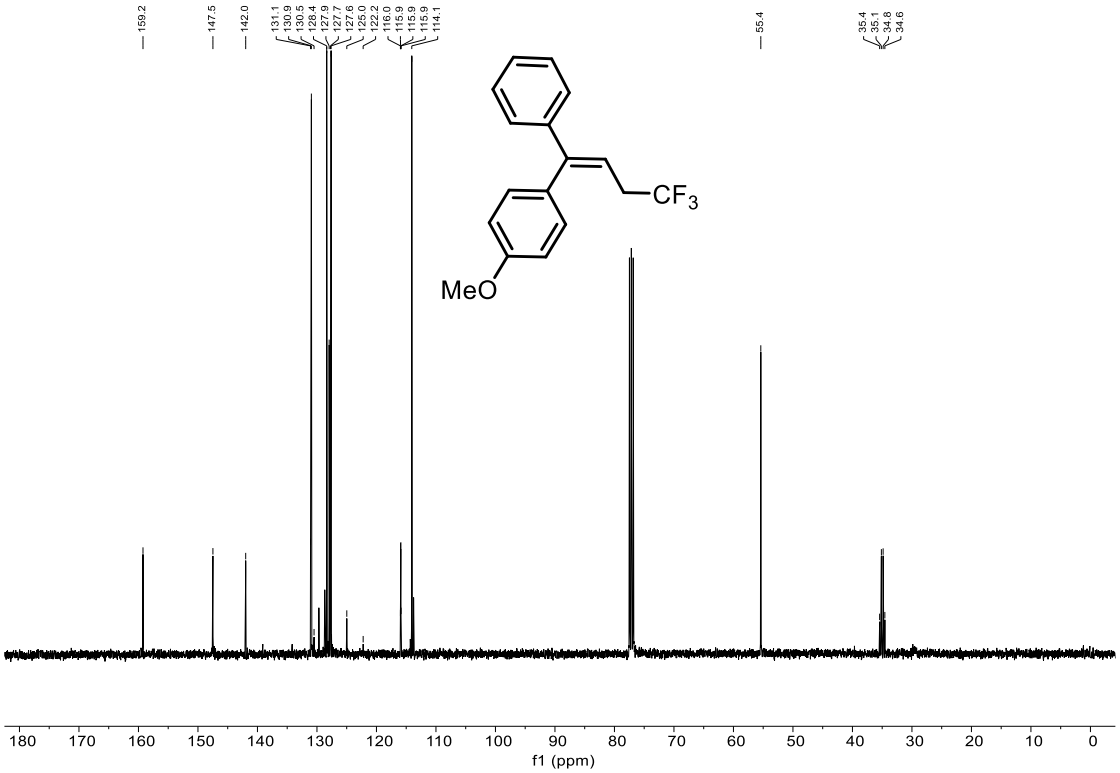
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-24*



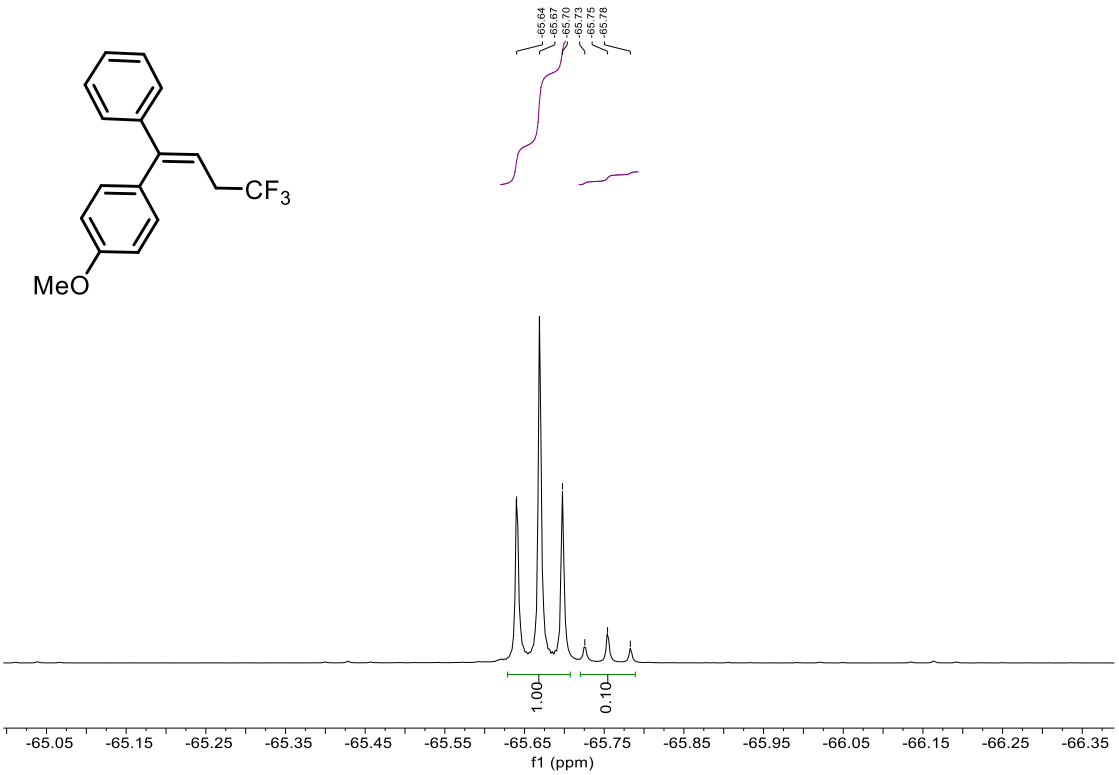
^{1}H NMR (400 MHz, CDCl3) of *Z-25*



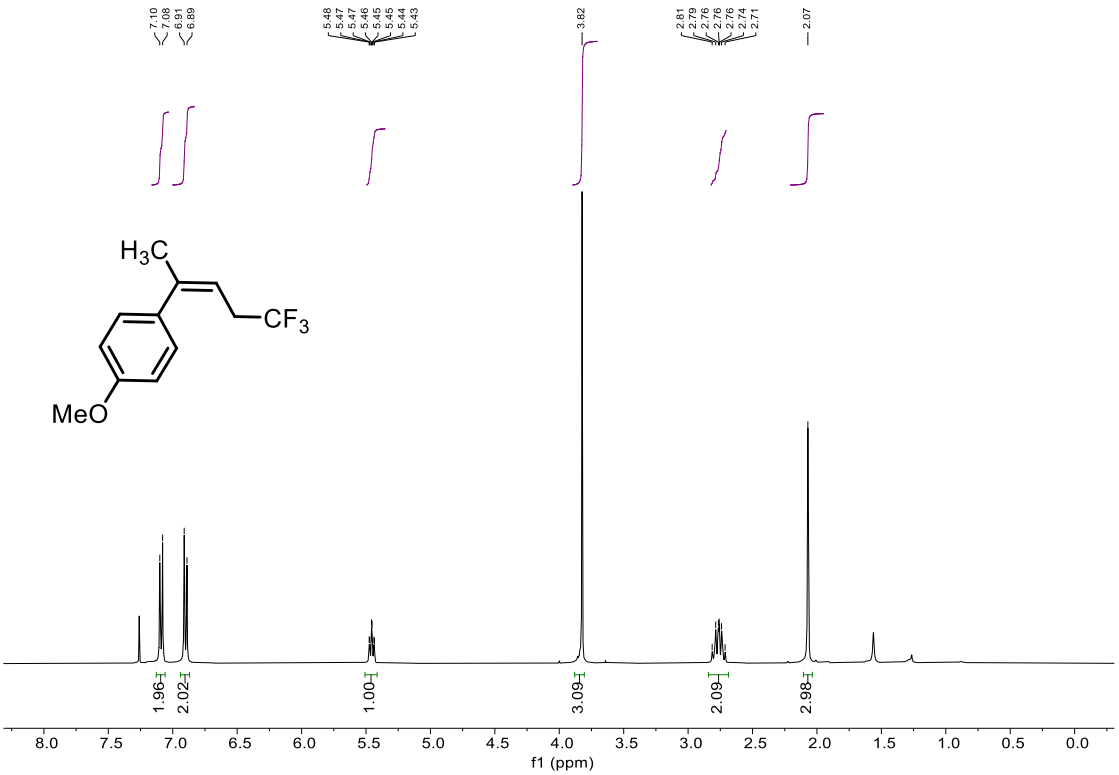
^{13}C NMR (101 MHz, CDCl$_3$) of *Z-25*



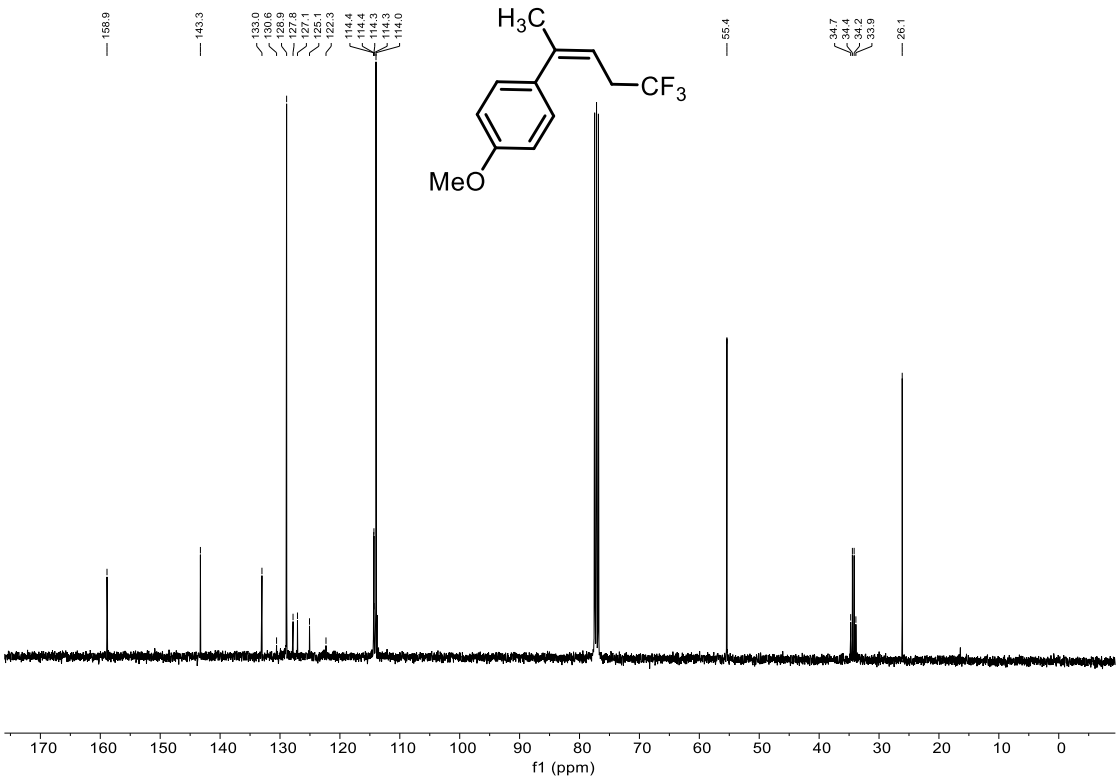
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-25*



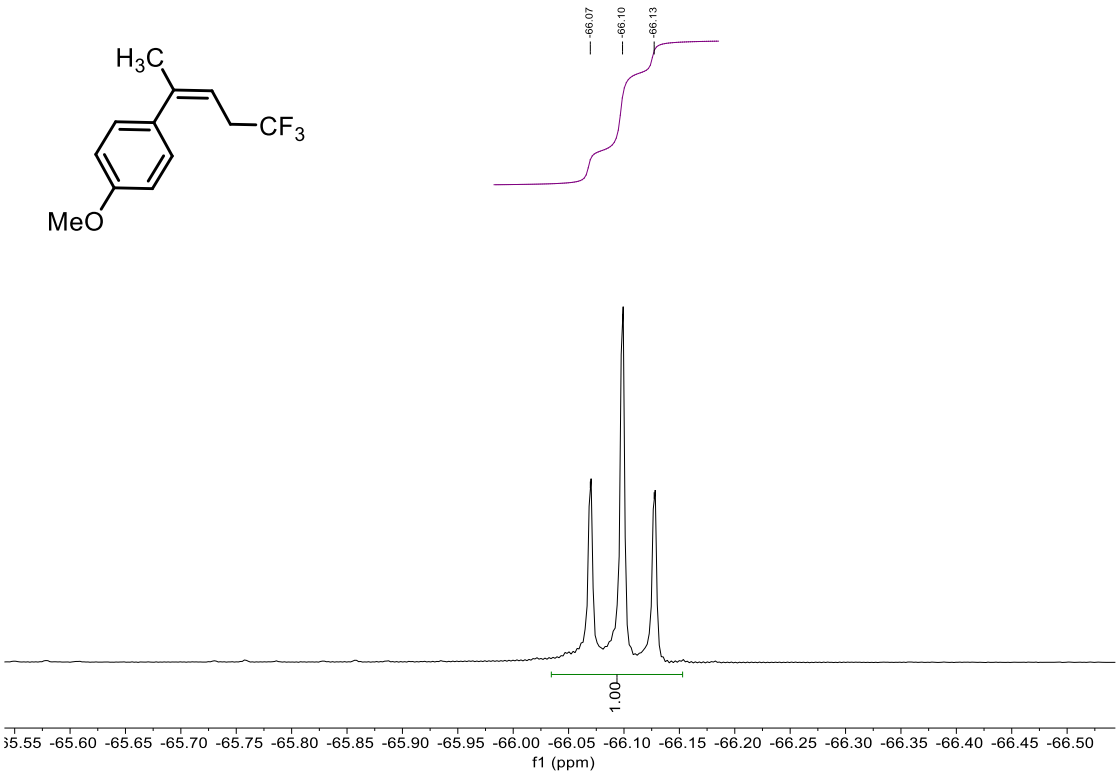
^{1}H NMR (400 MHz, CDCl3) of *Z-26*



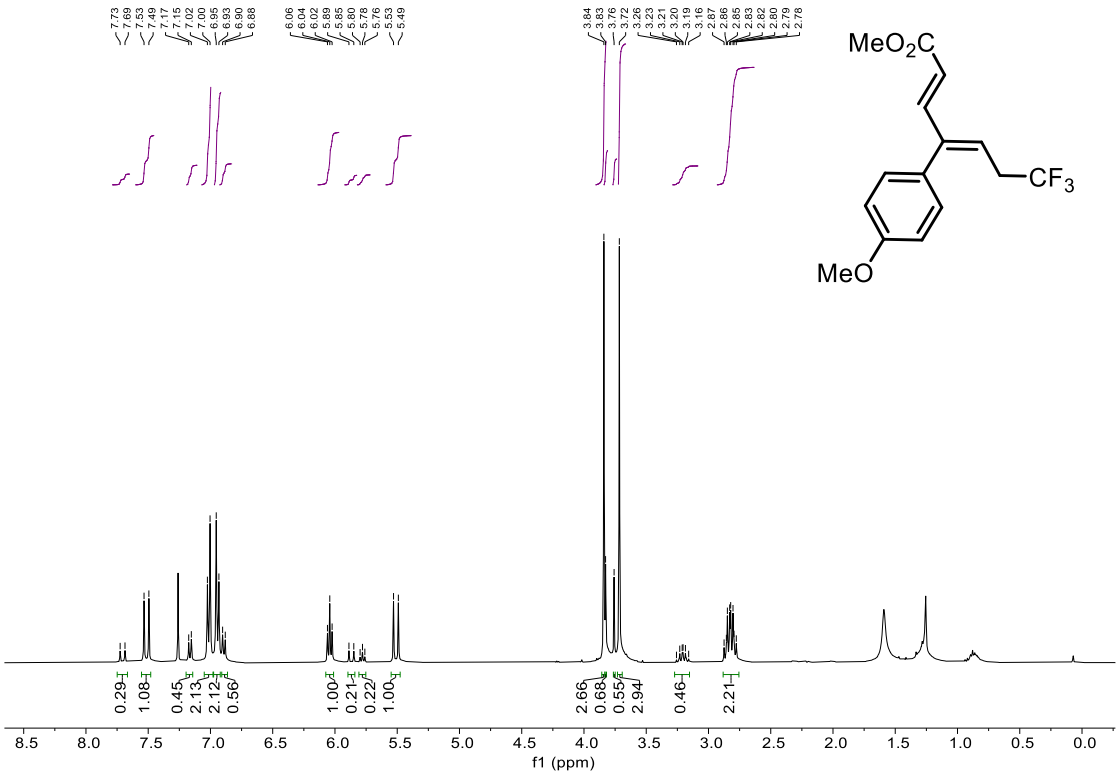
^{13}C NMR (101 MHz, $CDCl_3$) of *Z-26*



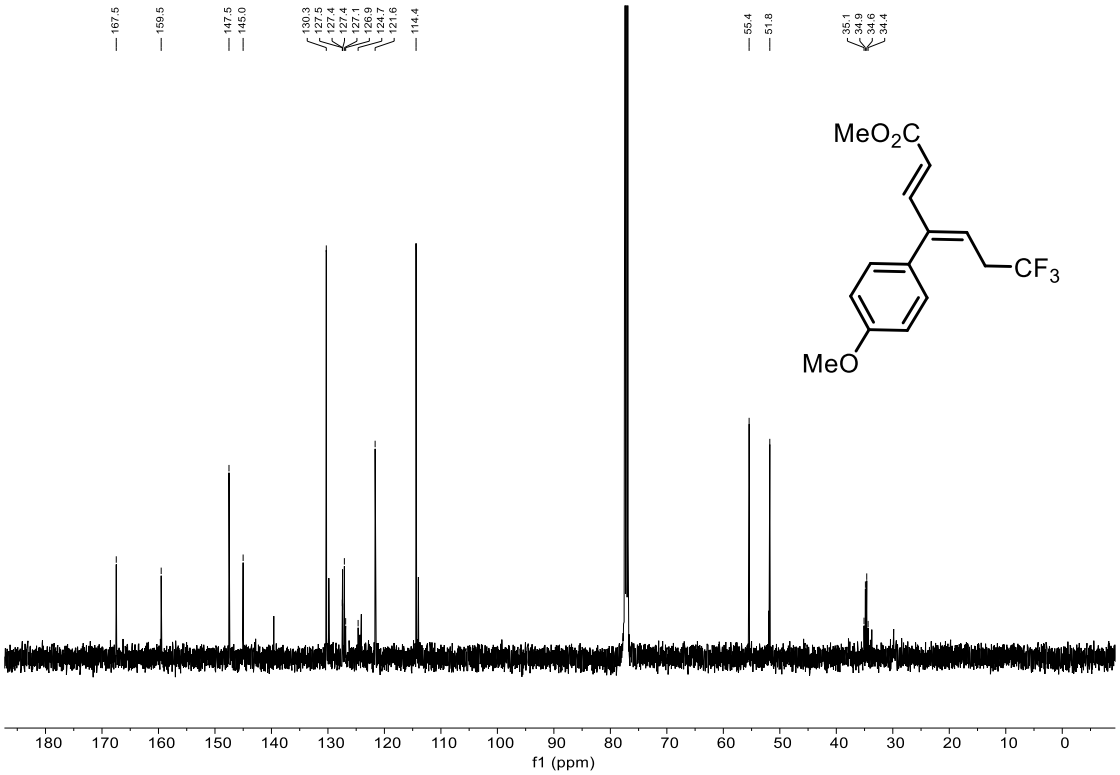
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-26*



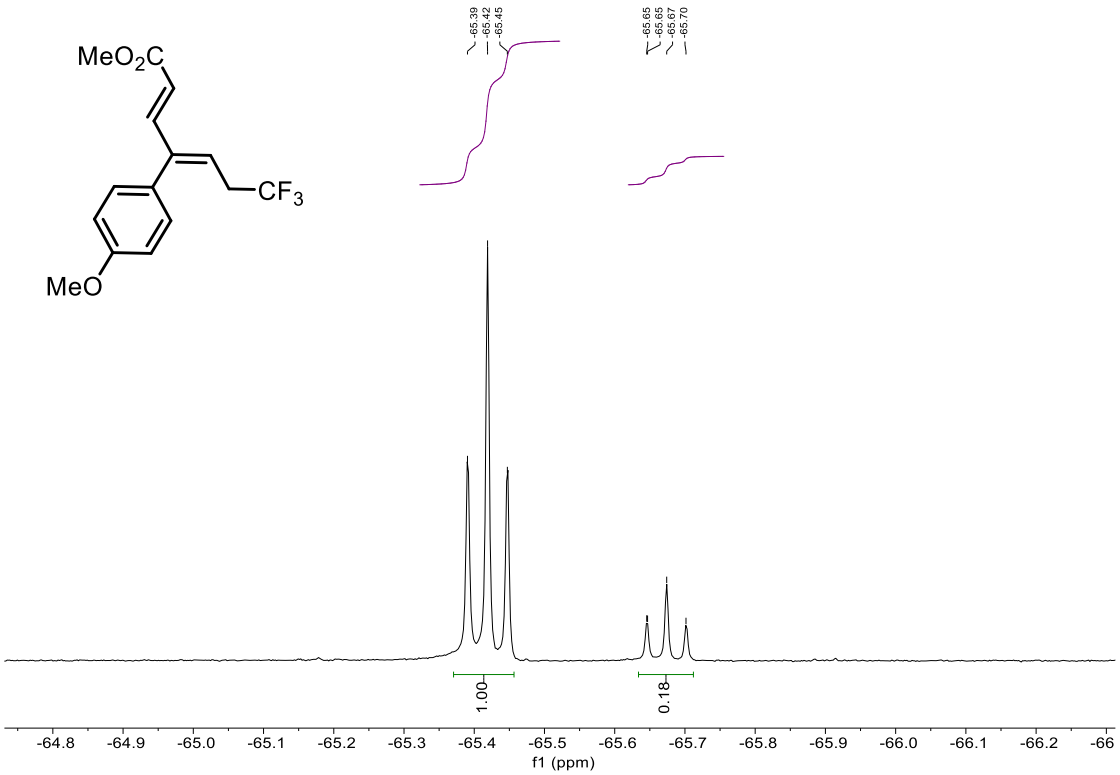
^{1}H NMR (400 MHz, CDCl3) of *Z-27*



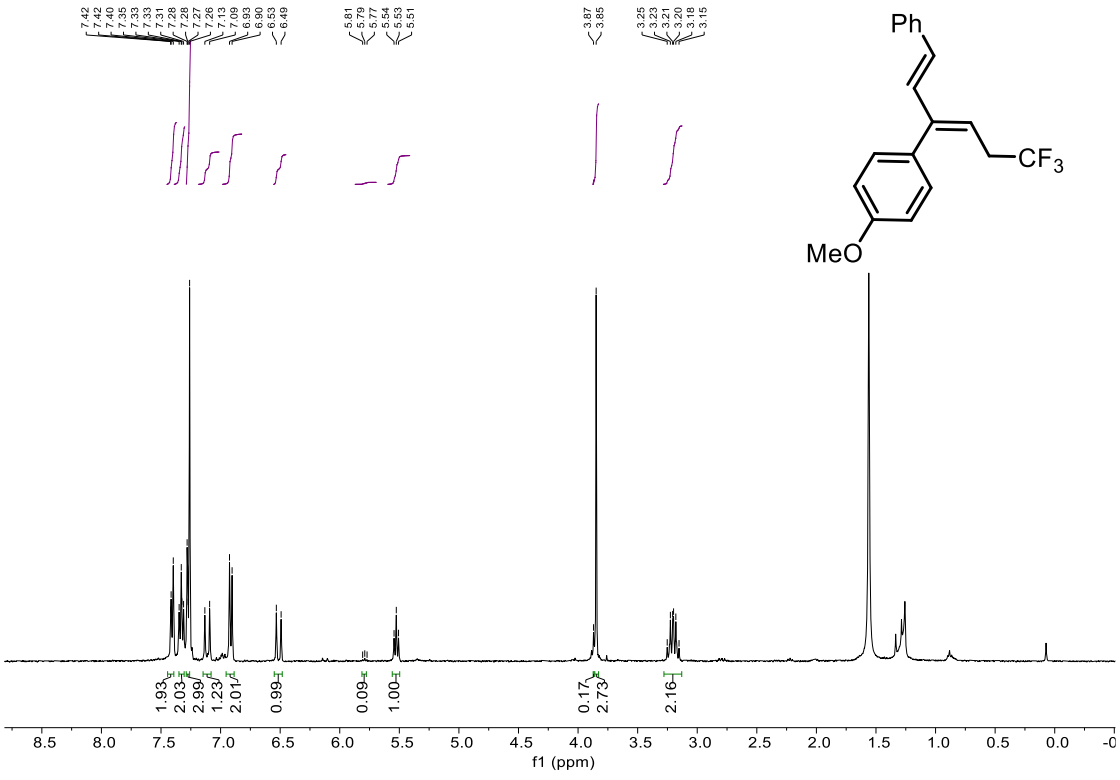
^{13}C NMR (126 MHz, CDCl$_3$) of *Z-27*



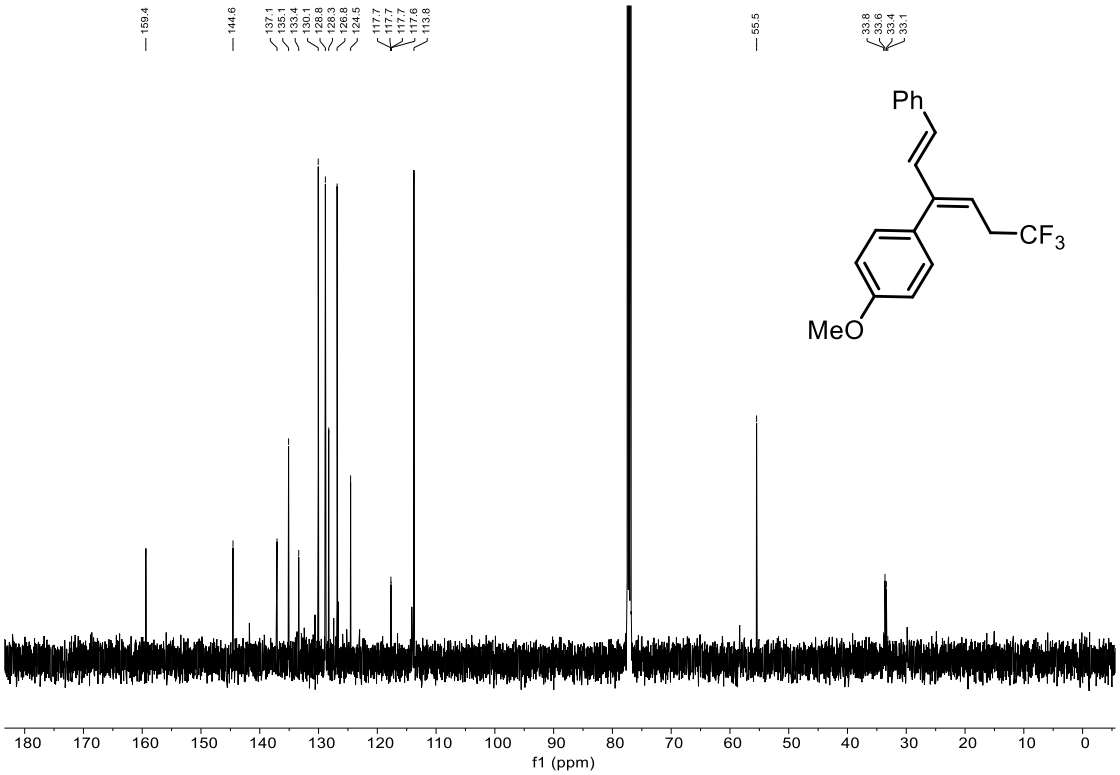
^{19}F NMR (376 MHz, $CDCl_3$) of *Z-27*



^{1}H NMR (400 MHz, CDCl3) of *Z-28*



^{13}C NMR (126 MHz, $CDCl_3$) of *Z-28*



^{19}F NMR (376 MHz, $CDCl_3$) of *Z-28*