Supporting Information

Silver-Mediated Trifluoromethylation–Iodination of Arynes

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General Information

^{1}H NMR and ^{13}C NMR were obtained on a Bruker AM400 Spectrometer. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as internal reference. $CDCl_3$ was referenced to -77.00 ppm in ^{13}C and 7.26 ppm in ^{1}H NMR spectra. ^{19}F NMR spectra ($CFCl_3$ as external standard and low field is positive) were obtained on a Bruker AM300 spectrometer. ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), quartet (q), multiplet (m), and broad resonance (br).

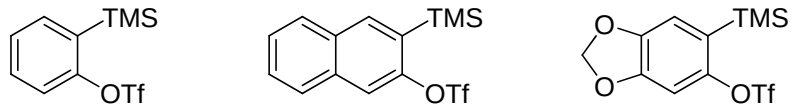
Materials and Methods

Silver fluoride (>99%) was obtained from Aldrich. Cesium fluoride (>99%) was obtained from Acros. 2,2,6,6-tetramethylpiperidine was obtained from TCI. Unless otherwise noted, all other reagents were purchased from commercial suppliers and used as received. MeCN was distilled from CaH_2. 1-iodophenylacetylene was prepared according to literature procedures[1]. All syntheses were conducted using standard Schlenk techniques or in an inert atmosphere glovebox unless otherwise stated.

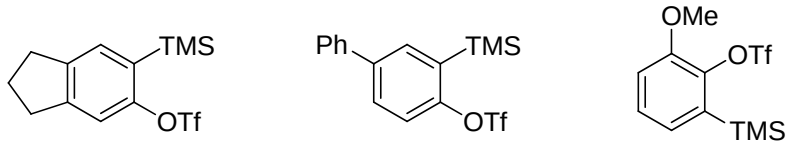
Experimental Details

Preparation of Aryne precursors

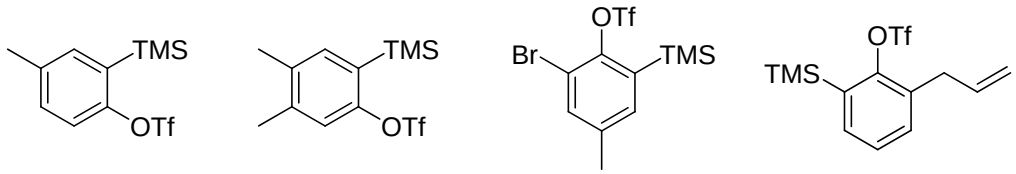
Aryne precursors **1a-i** were synthesized according to the literature procedures[2].



1a **1b** **1c**

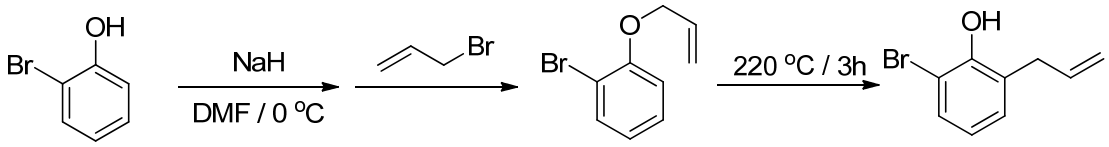


1d **1e** **1f**

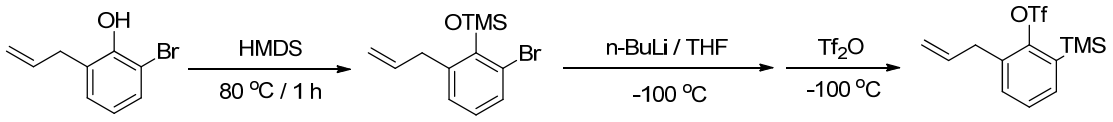


1g **1h** **1i** **1j**

Preparation of 2-allyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1j**):



To a dry 500 mL round bottom flask charged with NaH (4.8 g, 60 %, 120 mmol, 1.5 equiv) DMF (150 mL) was added, the mixture was cooled to 0 ^{o}C, then 2-bromophenol (13.84 g, 80 mmol, 1 equiv) in DMF (50 mL) was slowly added. The reaction was allowed to warm to room temperature and stirring was continued for additional 30 min. 3-bromoprop-1-ene was slowly added and the mixture was stirred at room temperature for 3 h. Then the reaction mixture was diluted with water (300 mL) and extracted with PE (3 * 200 mL). The organic phases were combined, washed with water (3 * 300 mL) and brine (300 mL), dried over $MgSO_4$ and evaporated. The residue was heated at 220 ^{o}C for 3 h, distilled under vacuum (2 Torr, 78 - 80 ^{o}C). The product (14.10 g, 83 %) was received as pale yellow oil.



1j

2-allyl-6-bromophenol (14.10 g, 66.2 mmol, 1 equiv) was introduced in a 500 mL round bottom flask and Hexamethyldisilazane (20.67 mL, 99.3 mmol, 1.5 equiv) was then added, the reaction mixture was heated at 80 ^{o}C for 1 h. After cooling down, excess HMDS was removed under vacuum. The residue was dissolved in THF (250 mL), cooled to -100 ^{o}C, then n-BuLi (2.5 M in hexane, 29.1 mL, 72.8 mmol, 1.1 equiv) was added dropwise and the mixture was stirred at -100 ^{o}C for 30 min. Then trifluoromethanesulfonic anhydride (22.41 g, 13.3 mL, 79.44 mmol, 1.2 equiv) was added dropwise at -100 ^{o}C, and the reaction was allowed to warm up to -40 ^{o}C. Saturated solution of $NaHCO_3$ (100 mL) was added and the reaction was continued to warm up to room temperature. After extracting the mixture with PE (3 * 200 mL), the organic phases were combined and washed with water (150 mL) and brine (150 mL), dried over $MgSO_4$ and evaporated. The desired product **1j** was isolated by column chromatography (hexane) as a colourless oil (14.58 g, 65 %).

Preparation of $CuCF_3$

$$CuI + TMSCF_3 + CsF \xrightarrow[\text{r. t. / 0.5h}]{\text{DMF}} \left[CuCF_3 \right]$$

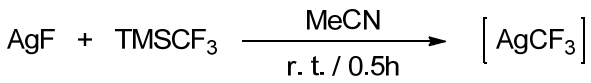
To an oven-dried 10 mL round-bottomed flask equipped with a stir bar was added CuI (38 mg, 0.2 mmol, 1 equiv), $TMSCF_3$ (28 mg, 0.2 mmol, 1 equiv), CsF (45 mg, 0.3 mmol, 1.5 equiv) and DMF 2 ml. After the mixture was stirred at r. t. for 30 min, a suspension ($CuCF_3$) was formed. This suspension was immediately used without further purification.

Preparation of $Zn(CF_3)_2$

$$ZnCl_2 + TMSCF_3 + CsF \xrightarrow[\text{r. t. / 0.5h}]{\text{DMF}} \left[Zn(CF_3)_2 \right]$$

To an oven-dried 10 mL round-bottomed flask equipped with a stir bar was added $ZnCl_2$ (13.6 mg, 0.1 mmol, 1 equiv), $TMSCF_3$ (28 mg, 0.2 mmol, 1 equiv), CsF (45 mg, 0.3 mmol, 1.5 equiv) and DMF 2 mL. After the mixture was stirred at r. t. for 30 min, a suspension $Zn(CF_3)_2$ was formed. This suspension was immediately used without further purification.

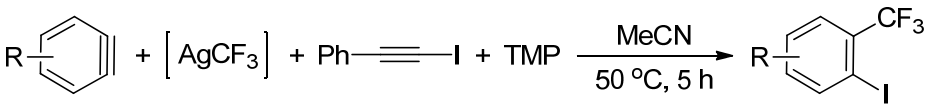
Preparation of $AgCF_3$



To an oven-dried 50 mL round-bottomed flask equipped with a stir bar was added AgF (191 mg, 1.5 mmol, 1 equiv), $TMSCF_3$ (213 mg, 1.5 mmol, 1 equiv) and MeCN 10 mL. After the mixture was stirred at r. t. for 30 min, a dark brown suspension ($AgCF_3$) was formed. This suspension was immediately used without further purification. **Since $AgCF_3$ is photosensitive, the preparation and use of $AgCF_3$ should be carried out in dark place.**

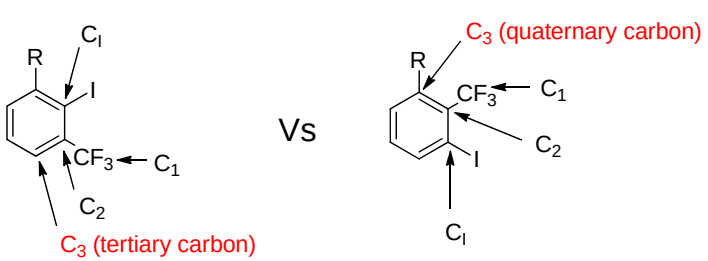
General Procedure for Silver Mediated Tandem Trifluoromethylation-Iodination of Arynes

Standard Procedure:



A solution of Aryne precursor (149 mg, 0.5 mmol, 1 equiv), 1-iodophenylacetylene (342 mg, 1.5 mmol, 3 equiv) and 2,2,6,6-tetramethylpiperidine (212 mg, 1.5 mmol, 3 equiv) in 10 mL of MeCN was added to a suspension of $AgCF_3$ (fleshly prepared, 1.5 mmol, 3 equiv) in 10 mL of MeCN. Then CsF (304mg, 2 mmol, 4 equiv) was added. The mixture was vigorously stirred at 50 ^{o}C for 5 h and then filtered through a layer of Celite. The filtrate was evaporated and the residue was purified by silica gel flash column chromatograph using hexanes as eluent.

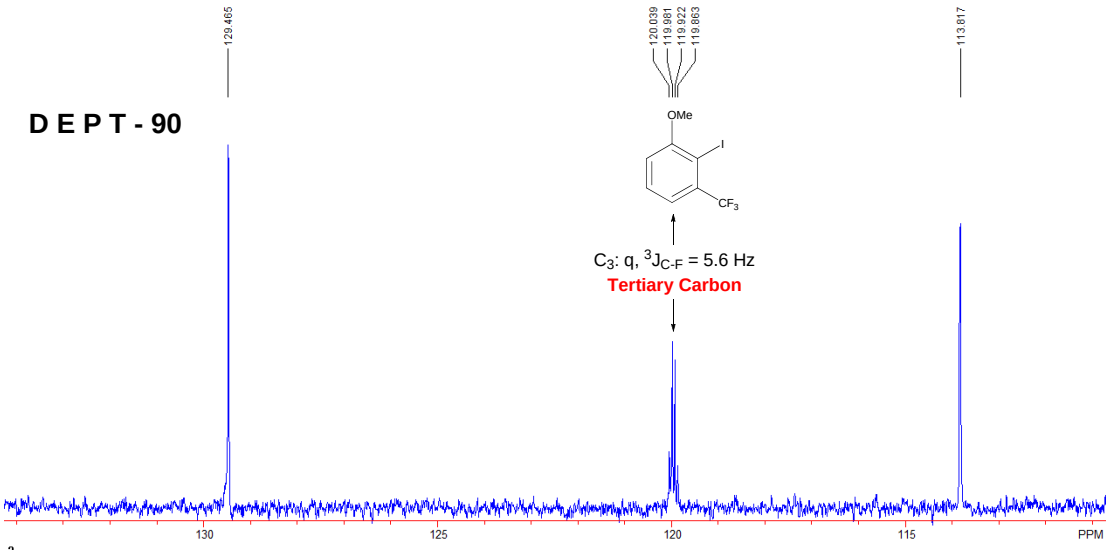
Identification of regioselective isomers

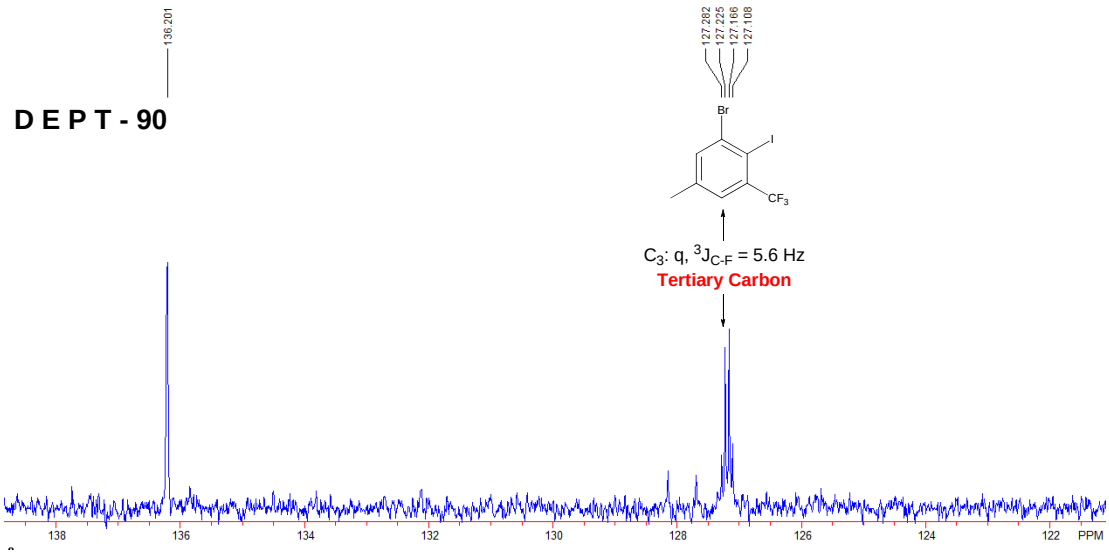


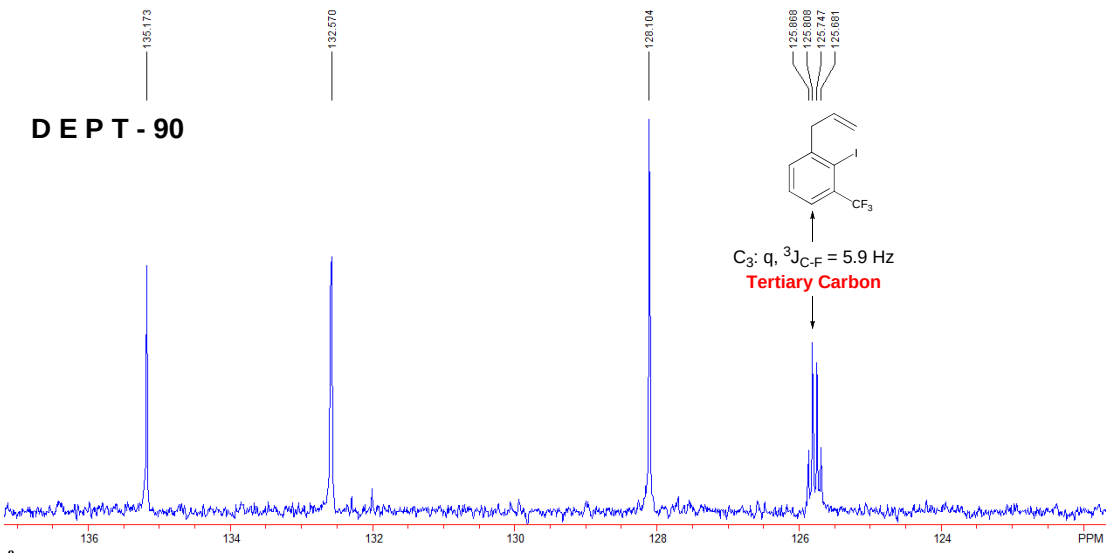
Typical feature of ^{13}C NMR

C_1: q, $^1J_{C\text{-}F}$ = ca. 272 Hz
C_2: q, $^2J_{C\text{-}F}$ = ca. 30 Hz
C_3: q, $^3J_{C\text{-}F}$ = ca. 6 Hz
C_I: ca. 90 ppm. $^3J_{C\text{-}F}$ = 0 Hz

^{13}C NMR (DEPT-90) was introduced to identify the substitution information of C_3, which may deduce the regioselectivity of reaction.

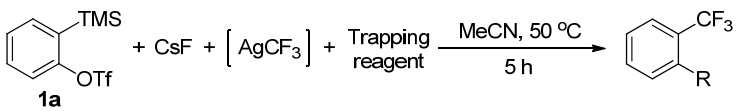






Optimiziation of Trifluoromethylation-Iodination of Benzyne Reaction

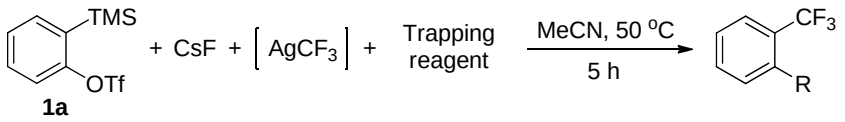
In order to take full advantage of benzyne, series of trapping reagents were tested for the reaction. The screening experiments are reported in Table S1 – S3.



Entry[a]	Trapping reagent	R	Yield (%)
1	$FeCl_3$	H	0
2	MnO_2	H	59
3	$CuCl_2$	H	0
4	$CuBr_2$	H	8
5	CuF_2	H	75
6	PhSSPh	H	74
7	PhSeSePh	H	14
8	PhTePh	H	0
9	$TMSCH_2I$	H	62
10	O_2	H	3
11	CO_2	H	4
12	CuCl (0.2 eqiv.) + Togni reagent	H	69
13	AuCl (0.2 eqiv.) + Togni reagent	H	0
14	$Pd(OAc)_2$	H	47

[a] Reaction condition: **1a** (0.1 mmol), CsF (0.4 mmol), $AgCF_3$ (fleshly prepared, 0.2 mmol), Additive (0.2 mmol), MeCN (4 mL). Determined by ^{19}F NMR with ^{-}OTf (a fragment of **1a**) as an internal standard.

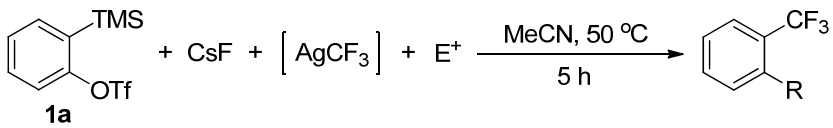
Table S1

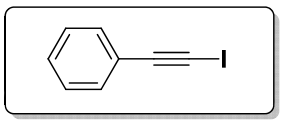
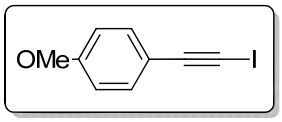
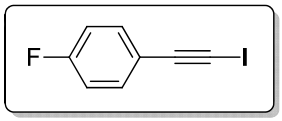


Entry[a]	Trapping reagent	R	Yield (%)
1	CH_3I	H	0
2	Togni reagent	H	17
3	Selectfluor	H	0
4	PhCHO	H	82
5	NFSI	H	5
6	I_2	H	0
7	NCS	Cl (H)	6 (31)
8	NBS	H	5
9	NIS	H	15
10	n-BuSnCl	H	20
11	$(n\text{-}Bu_3Sn)_2$	H	24
12	allyl chloride	H	0
13	allyl bromide	H	6
14	Ph—≡—Br	H	69
15	Ph—≡—I	I (H)	39 (47)

[a] Reaction condition: **1a** (0.1 mmol), CsF (0.4 mmol), $AgCF_3$ (fleshly prepared, 0.2 mmol), Electrophile (0.2 mmol), MeCN (4 mL). Determined by ^{19}F NMR with ^{-}OTf (a fragment of **1a**) as an internal standard.

Table S2



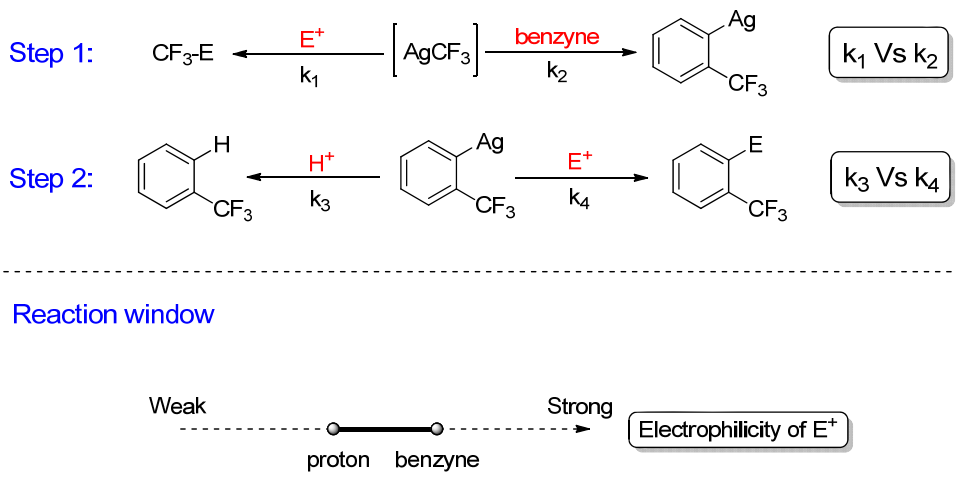
Entry[a]	E+	Equiv.	R = H (%)	R = I (%)
1		1	43	31
2		2	47	39
3		5	44	22
4		10	7	0
5		1	63	20
6		2	44	31
7		5	19	41
8		10	12	27
9		1	33	42
10		2	34	30
11		5	41	26

[a] Reaction condition: **1a** (0.1 mmol), CsF (0.4 mmol), $AgCF_3$ (fleshly prepared, 0.2 mmol), MeCN (4 mL). Determined by ^{19}F NMR with ^{-}OTf (a fragment of **1a**) as an internal standard.

Table S3

Summary of the results (Tables S1-S3):

To ensure the smooth trifluoromethylation of benzyne and to inhibit the protonation of the newly formed aryl silver species, the trapping of the aryl silver species should choose an electrophile of modest reactivity (such as 1-iodophenylacetylene), which is less reactive than benzyne ($k_1 < k_2$), but more reactive than proton ($k_4 > k_3$).



To improve the reaction effciency, a number of ligands were tested as additives. The screening experiments are reported in Tables S4 – S9.

Entry	Additive	Equiv.	R = H (%)	R = I (%)
1	MeOH	1	30	51
2	MeOH	2	33	35
3	MeOH	5	22	34
4	MeOH	10	20	56
5	MeOH	20	7	36
6	EtOH	1	43	38
7	EtOH	2	35	46
8	EtOH	5	26	43
9	EtOH	10	32	49
10	EtOH	20	13	53
11	i-PrOH	2	0	5
12	BuOH	2	32	47
13	t-BuOH	2	38	41
14	i-BuOH	2	37	41
15	PhOH	2	6	18
16	BnOH	2	36	45
17	Glycol	2	25	59
18	Glycerin	2	42	33
19	1,4-butanediol	2	23	44
20	1,3-butanediol	2	18	34
21	2,3-butanediol	2	12	28
22	1,2-propanediol	2	32	49
23	n-octyl alcohol	2	34	45
24	cetanol	2	40	49

[a] Reaction condition: **1a** (0.1 mmol), CsF (0.4 mmol), **2** (fleshly prepared, 0.2 mmol), **3** (0.2 mmol), MeCN (4 ml). The yield was determined by ^{19}F NMR with ^{-}OTf (a fragment of **1a**) as an internal standard.

Table S4

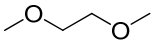
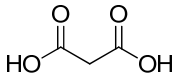
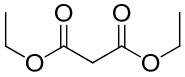
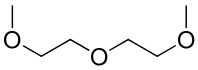
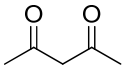
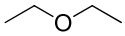
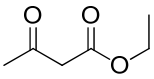
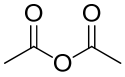
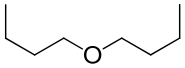
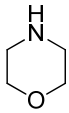
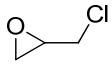
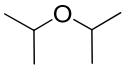
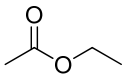
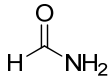
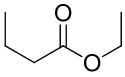
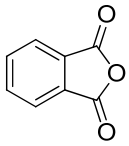
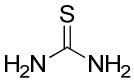
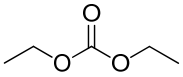
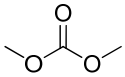
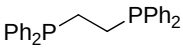
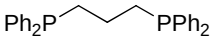
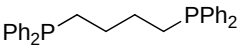
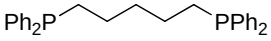
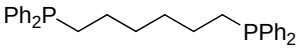
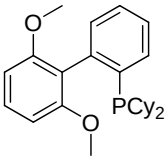
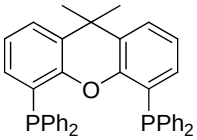
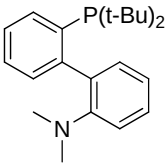
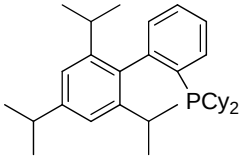
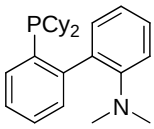
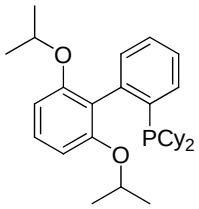
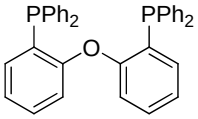
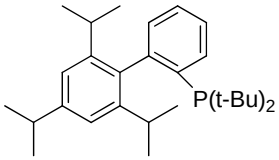
Additive (2 equiv)	R = H (%)	R = I (%)	Additive (2 equiv)	R = H (%)	R = I (%)
	0	4		0	0
PhSMe	0	16		0	44
	37	40		7	0
	39	38		2	3
	42	41		92	0
	37	40		39	39
	2	35		44	32
	40	39		43	32
	46	27		25	37
	40	36		73	11
	0	0		42	35
	41	37			

Table S5

Additive (2 equiv)	R = H (%)	R = I (%)	Additive (2 equiv)	R = H (%)	R = I (%)
MeONa	30	24	DMSO	43	34
EtONa	49	39	DMF	40	36
t-BuONa	11	42	DMA	46	37
t-BuOK	0	0	NMP	45	30
t-BuOLi	8	32	KSCN	0	0
HMPA	43	36	Na_2CO_3	42	38
K_2CO_3	41	39	$NaHCO_3$	35	27
Cs_2CO_3	34	43	$TESCF_3$	3	0
AcONa	48	38	R-BINOL	8	0

Table S6

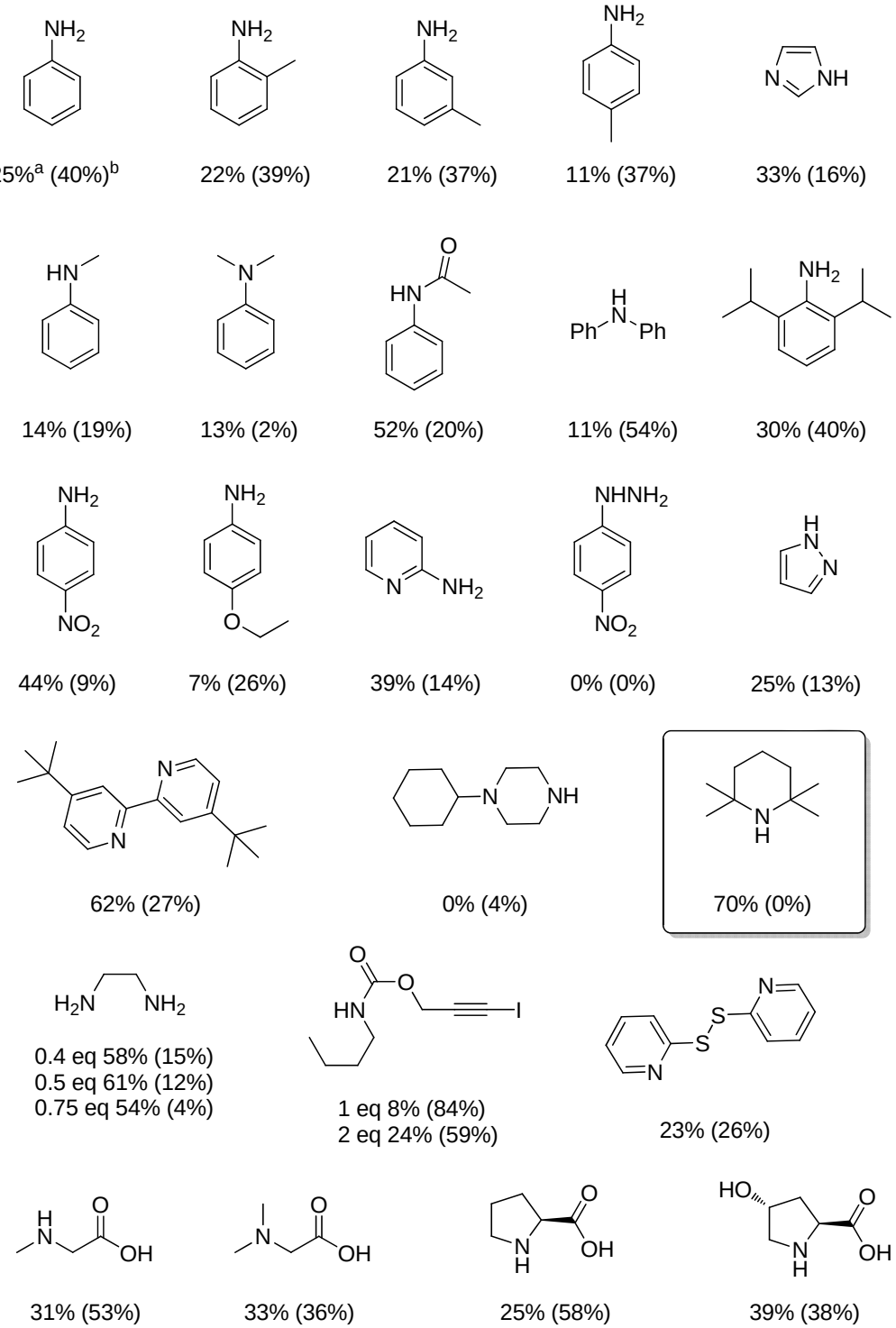
PPh_3			
0%[a] (0%)[b]	7% (4%)	4% (2%)	0% (0%)
			PBu_3
4% (8%)	4% (5%)	3% (12%)	6% (30%)
			
0% (0%)	0% (0%)	24% (6%)	
			
22% (0%)	0% (0%)	7% (0%)	
		R-BINAP	
0% (0%)	41% (5%)	8% (0%)	

Ligand: 2 equiv

[a] yield of desired product.

[b] yield of $PhCF_3$.

Table S7

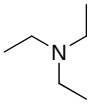
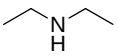
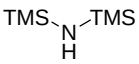
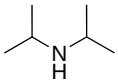
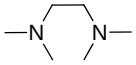
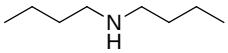
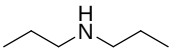
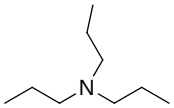
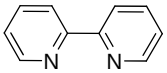
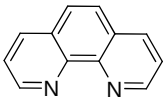
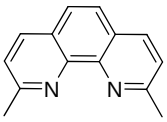
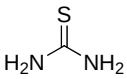
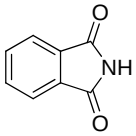
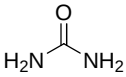
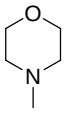
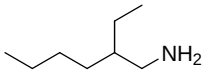
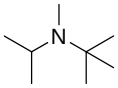
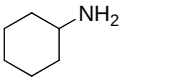
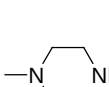
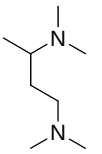
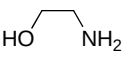
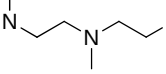
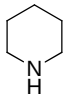
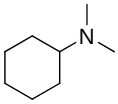
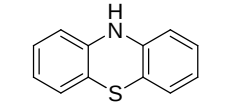


Ligand: 2 equiv

[a] yield of desired product.

[b] yield of $PhCF_3$.

Table S8

				
11%[a] (0%)[b]	54% (0%)	36% (0%)	56% (0%)	0% (0%)
				
47% (2%)	43% (9%)	6% (6%)	59% (2%)	
			$TsNH_2$	
54% (28%)	2eq 61% (4%) 1eq 58% (11%)	2eq 46% (2%) 1eq 56% (13%)	20% (42%)	
				
0% (0%)	12% (8%)	6% (0%)	40% (37%)	
				
9% (1%)	43% (5%)	5% (0%)	8% (40%)	
				
23% (0%)	17% (0%)	30% (0%)	3% (0%)	
				
21% (0%)	9% (0%)	0% (0%)	9% (0%)	
				
29% (2%)	6% (0%)	4% (8%)		

Ligand: 2 equiv

[a] yield of desired product.

[b] yield of $PhCF_3$.

Table S9

Since some diols and alkylamines were found to give much better results than other additives, we continued to test the effect of these ligands (Table S10).

Ethanediol (equiv)	R = I (%)	R = H (%)	Diisopropylamine (equiv)	R = I (%)	R = H (%)
1	55	27	1	50	3
3	48	37	3	53	0
5	46	36	5	32	0
10	31	39	10	13	0

Benzylamine (equiv)	R = I (%)	R = H (%)	n-$BuNH_2$ (equiv)	R = I (%)	R = H (%)
0.5	59	15	0.5	57	18
1	62	8	1	54	9
2	58	0	2	27	0
5	43	0	5	23	0

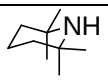
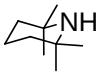
	R = I (%)	R = H (%)		R = I (%)	R = H (%)
1	59	13	3	69	0
1.5	72	0	5	46	0
2	71	0	10	34	0
2.5	73	0			

Table S10

Various solvents were tested for the reaction. The screening experiments are reported in Table S11.

Solvent	Yield	Solvent	Yield
PhCN	mess	C_6F_{14}	mess
PhCN + MeCN	mess	C_6F_{14} + MeCN	62%[a] (0%)[b]
BnCN	0% (0%)	n-hexane	no reaction
BnCN + MeCN	13% (5%)	n-hexane + MeCN	55% (0%)

[a] yield of desired product.
[b] yield of $PhCF_3$.

Polarity of solvent

Additional Solvent (Toluene)	R = I (%)	R = H (%)	Additional Solvent (THF)	R = I (%)	R = H (%)
0.1 ml	77	0	0.1 ml	79	3
0.5 ml	68	0	0.5 ml	76	7
1.0 ml	63	0	1.0 ml	68	9
2.0 ml	50	0	2.0 ml	53	23

Solvent = MeCN (4 ml) + Additional Solvent

Volume of MeCN

MeCN (ml)	R = I (%)	R = H (%)
4	68	13
6	48	31
8	44	34
10	37	39

Table S11

Different reaction temperatures were also screened, The screening experiments are reported in Table S12.

Temperature	R = I (%)	R = H (%)
20	67	0
40	72	0
60	74	0
80	62	13

Table S12

The screening experiments (variation of reactant ratio) are reported in Table S13.

Entry	AgF	$TMSCF_3$	1a	CsF	Ph—≡—I		R = I (%)	R = H (%)
1	2	4	1	4	2	2	0	0
2	1.5	3	1	4	2	2	0	0
3	1.5	2	1	4	2	2	19	2
4	1.5	1.5	1	4	2	2	30	9
5	2	2	1	4	1	2	43	27
6	2	2	1	4	1.5	2	68	8
7	2	2	1	4	2	2	73	0
8	2	2	1	4	2.5	2	66	0
9	2	1.8	1	4	2	2	68	0
10	2	2	1	4	2	2	73	0
11	3	2.6	1	4	2	2	76	9
12	3	3	1	4	2	2	77	10
13	1.5	1.5	1	4	1.5	1.5	50	20
14	2	2	1	4	2	2	75	0
15	2.5	2.5	1	4	2.5	2.5	70	0
16	3	3	1	4	3	3	82	0
17	4	4	1	4	4	4	76	0

Reaction condition: MeCN (4 mL), 50 °C, 5 h. The yield was determined by ^{19}F NMR with ^{-}OTf (a fragment of **1a**) as an internal standard.

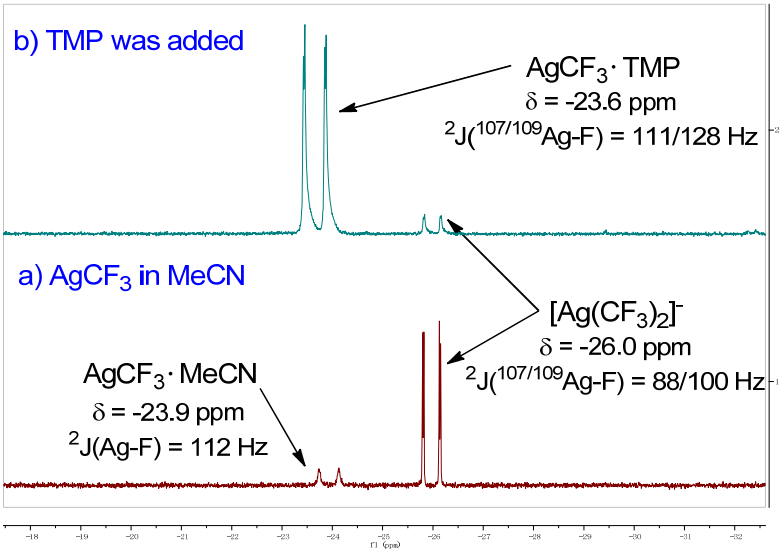
Table S13

Experiments for Mechanistic Investigations

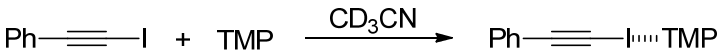
Coordination Between $AgCF_3$ and 2,2,6,6-tetramethylpiperidine (TMP)

$$AgCF_3 \cdot D \rightleftharpoons [Ag \cdot D_n]^+ + [Ag(CF_3)_2]^- \quad (5)$$

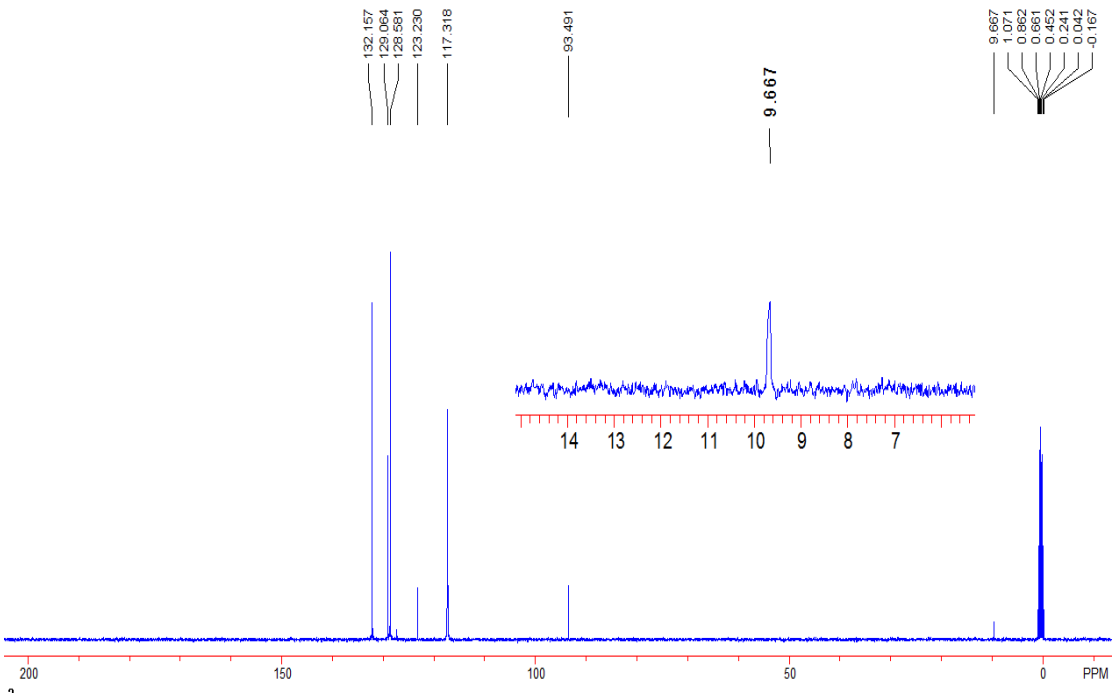
D = MeCN, TMP



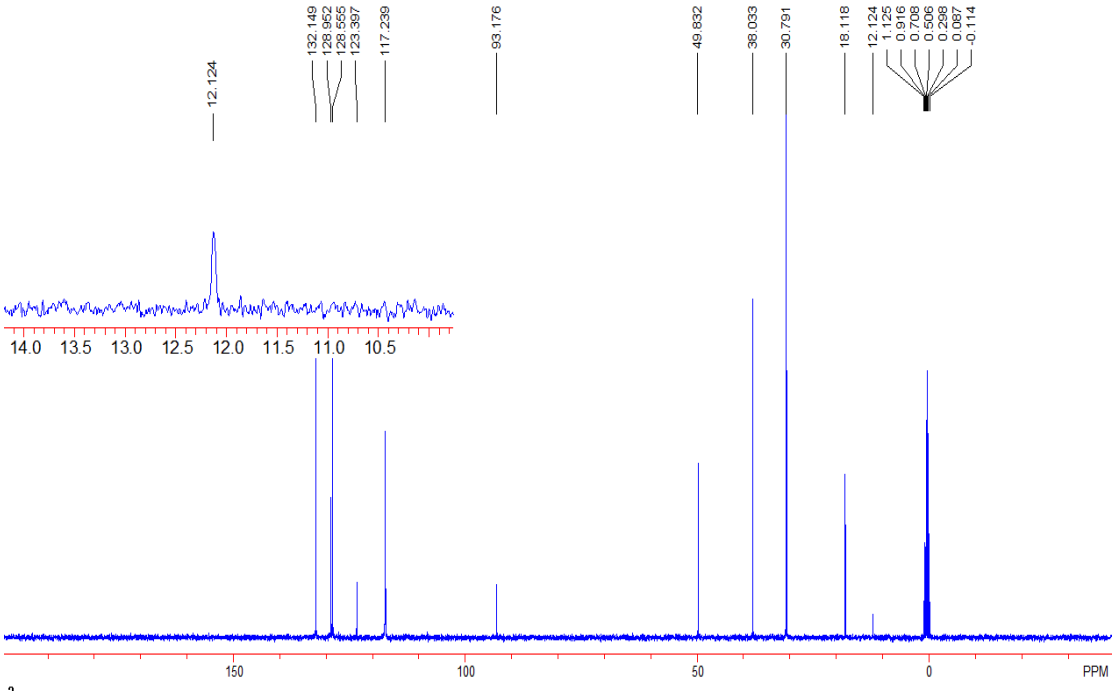
Halogen Bonding Between 1-iodophenylacetylene and 2,2,6,6-tetramethylpiperidine



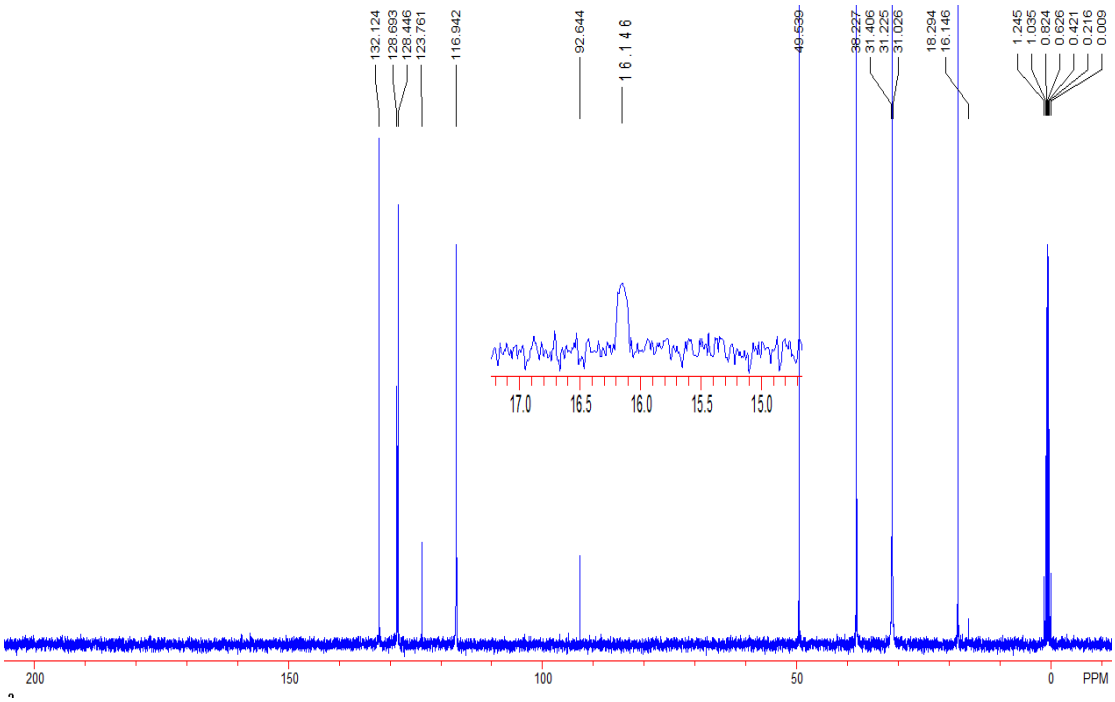
A: 1-iodophenylacetylene (0.188 mmol) in 0.5 mL CD_3CN

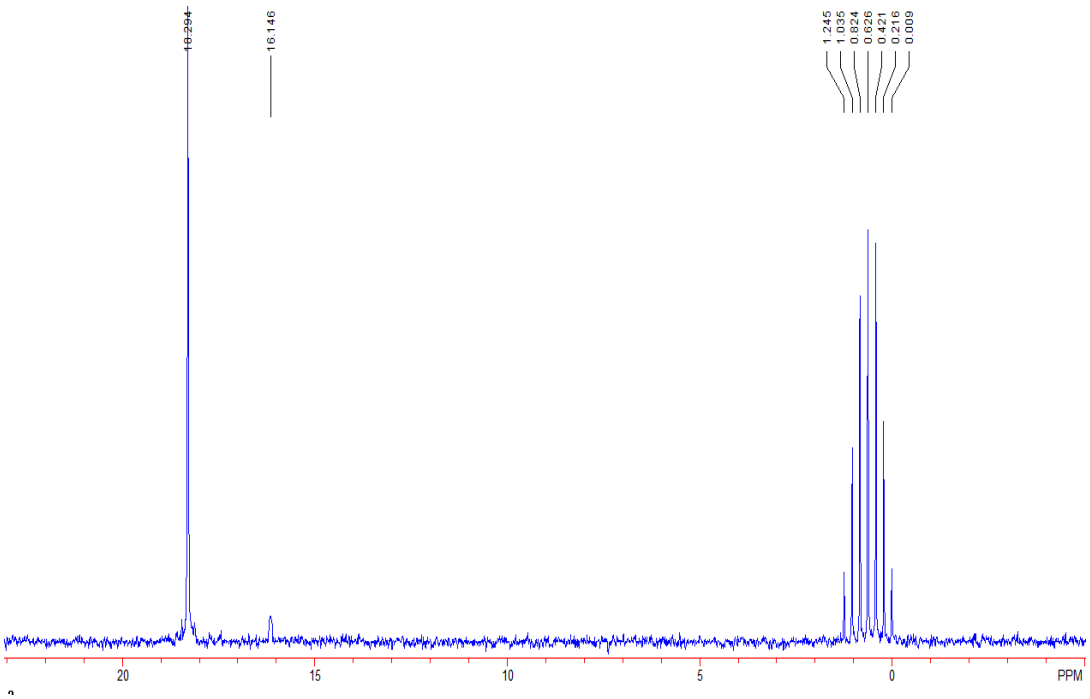


B: 1-iodophenylacetylene (0.188 mmol) and TMP (1 equiv) in 0.5 mL CD_3CN

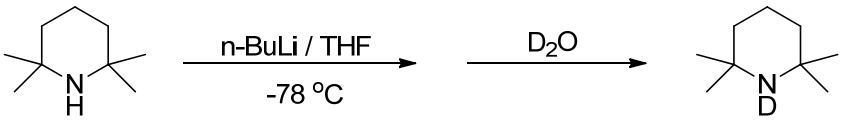


C: 1-iodophenylacetylene (0.188 mmol) and TMP (5 equiv) in 0.5 mL CD_3CN



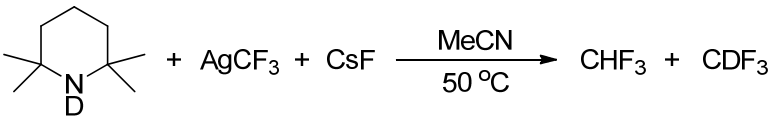


Preparation of Deuterated 2,2,6,6-tetramethylpiperidine (TMP)

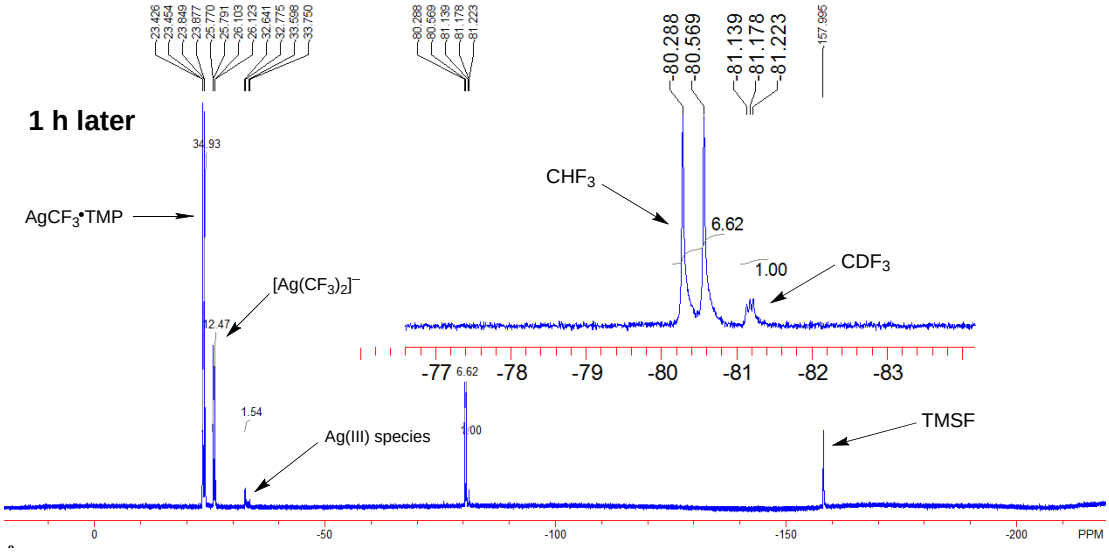


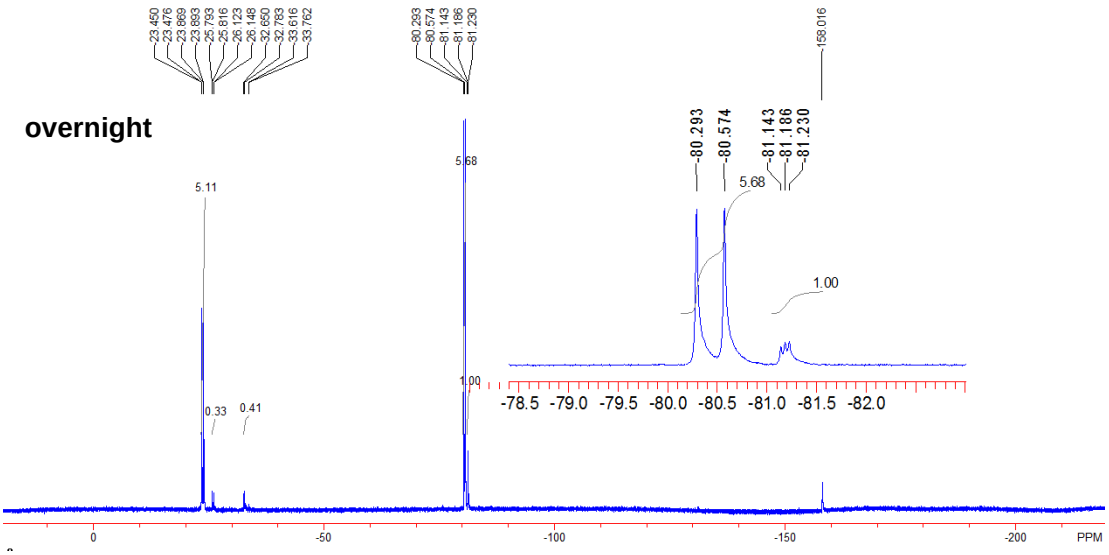
Under nitrogen, TMP (2.061 g, 14.6 mmol, 1 equiv) was added into a 100 mL round flask and dissolved in THF (50 mL). After cooling the solution to -78 °C, n-BuLi (5.85 mL, 2.5 M in THF, 14.6 mmol, 1 equiv) was added dropwise and the resulting mixture was stirred for 30 min. The reaction mixture was warmed up to room temperature and the solvent was evaporated. THF (25 mL) was added and the solution was again cooled to -78 °C, then D_2O (0.292 g, 14.6 mmol, 1 equiv) in THF (5 mL) was slowly added. The reaction was allowed to warm to room temperature. The solvent was evaporated and the residue was distilled. The product (1.24 g, 60 %) was received as a colourless oil.

Deprotonation of TMP by $AgCF_3$

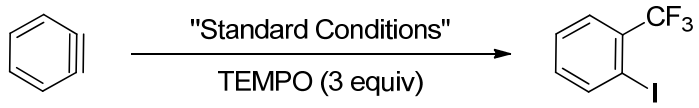


To a fleshly prepared $AgCF_3$ (0.2 mmol in 2 mL MeCN, 1 equiv) was added deuterated TMP (28 mg, 0.2 mmol, 1 equiv) and CsF (61 mg, 0.4 mmol, 4 equiv). The resulting mixture was shielded from light and stirred at room temperature. The reaction was monitored by ^{19}F NMR.



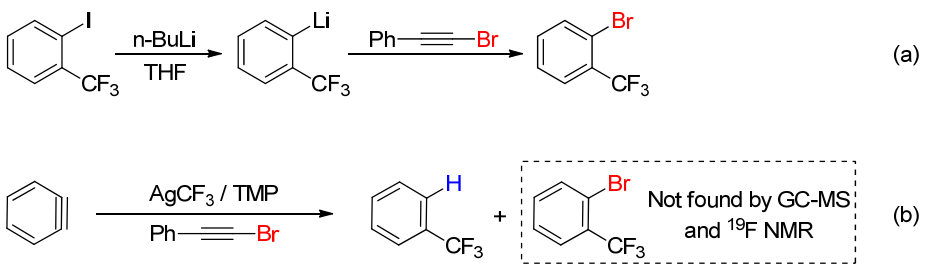


Add Radical Scavenger (TEMPO) to the Standard Conditions



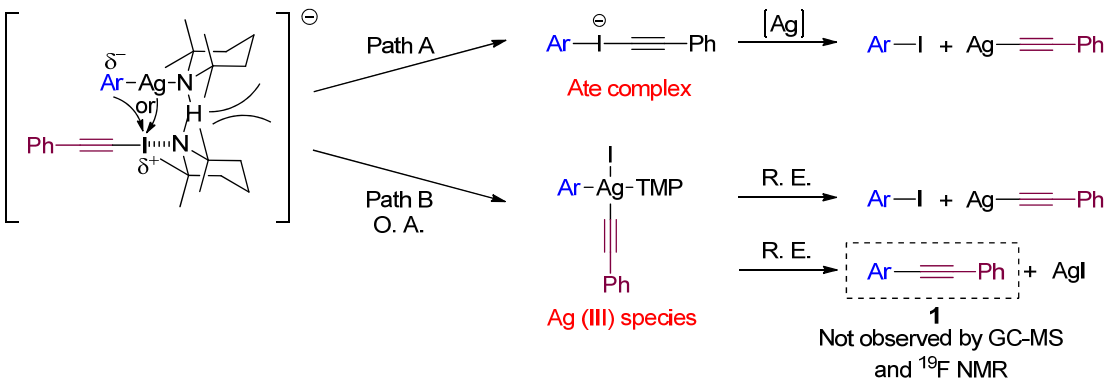
A solution of Aryne precursor (29.8 mg, 0.1 mmol, 1 equiv), 1-iodophenylacetylene (68.4 mg, 0.3 mmol, 3 equiv) and 2,2,6,6-tetramethylpiperidine (42.5 mg, 0.3 mmol, 3 equiv) in 2 mL of MeCN was added to a suspension of $AgCF_3$ (fleshly prepared, 0.3 mmol, 3 equiv) in 2 mL of MeCN. Then CsF (61 mg, 0.4 mmol, 4 equiv) and TEMPO (46.8 mg, 0.3 mmol, 3equiv) was added. The mixture was vigorously stirred at 50 ^{o}C for 5 h and then filtered through a layer of Celite. The filtrate was determined by ^{19}F NMR with $^{-}$OTf as an internal standard. ^{19}F NMR yield: 80 %.

To probe whether aryl anion is involved in the reaction condition



[*o*-(Trifluoromethyl)phenyl]lithium reacts smoothly with bromophenylacetylene to give the *o*-trifluoromethyl bromobenzene (eq a), in contrast, bromophenylacetylene is tolerated in trifluoromethylation of benzyne (eq b). These experiment phenomena suggest that there is no such a "naked" carbanion but arylsilver complex existing in our reaction system.

Discussion on the possibility of Ag (III) pathways



If Ag (III) species are formed during the reaction, there will be two reductive elimination pathways which offer different products. Since no alkynylation byproduct (compound **1)** was produced, the Ag (III) intermediate could be ruled out.

References

(1) Picard, J.; Lubin-Germain, N.; Uziel, J.; Augé, J. *Synthesis* **2006**, 6, 979.

(2) a) Pena, D.; Perez, D.; Guitian, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, 121, 5827.

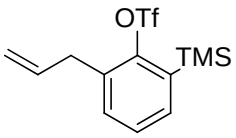
b) Pena, D.; Perez, D.; Guitian, E.; Castedo, L. *J. Org. Chem.* **2000**, 65, 6944.

c) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, 122, 7280.

d) Yoshida, H.; Sugiura, S.; Kunai, A. *Org. Lett.* **2002**, 4, 2767.

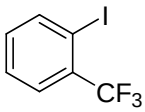
e) Pena, D.; Cobas, A.; Perez, D.; Guitian, E. *Synthesis*, **2002**, 10, 1454.

Analytical Data



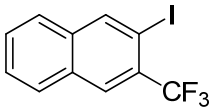
1j

2-allyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (1j): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, J = 6.8 Hz, J = 2.8 Hz, 1H), 7.35 - 7.29 (m, 2H), 5.94 - 5.84 (m, 1H), 5.16 - 5.10 (m, 1H), 3.50 (d, J = 6.8 Hz, 2H), 0.38 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.57 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.02, 135.26, 135.11, 135.10, 133.57, 132.66, 128.14, 118.66 (q, J = 316.3 Hz), 117.33, 34.33, 0.15. IR (neat): 3081.7, 2957.3, 1641.8, 1402.0, 1252.5, 1215.6, 1141.5, 1105.0, 1056.4, 995.2, 918.9, 879.3, 844.1, 773.9, 739.0, 691.2, 651.3, 628.9, 612.2, 590.4, 571.4, 527.5, 497.2, 439.7. HRMS (EI): Calcd for $C_{13}H_{17}F_3O_3SSi$, 338.0620; Found 338.0625.



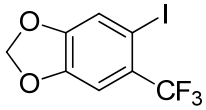
4a

1-iodo-2-(trifluoromethyl)benzene (4a): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.24 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.05, 133.65 (q, J_{C-F} = 30.5 Hz), 132.87, 127.95, 127.59 (q, J_{C-F} = 5.2 Hz), 122.82 (q, J_{C-F} = 272.0 Hz), 90.99. IR (neat): 3069.7, 2925.7, 1589.5, 1571.5, 1473.4, 1438.8, 1315.3, 1262.0, 1176.8, 1135.0, 1109.1, 1087.1, 1035.9, 1013.2, 954.1, 871.8, 763.3, 721.7, 676.3, 636.9, 595.1, 437.8. HRMS (EI): Calcd for $C_7H_4F_3I$, 271.9310; Found 271.9316.



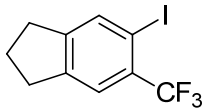
4b

2-iodo-3-(trifluoromethyl)naphthalene (4b): white solid, Mp 59-62 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.15 (s, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.60 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.44 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.63, 135.61, 131.05, 129.52 (q, J_{C-F} = 30.6 Hz), 129.08, 128.81, 128.09 (q, J_{C-F} = 6.4 Hz), 127.79, 126.62, 123,02 (q, J_{C-F} = 271.3 Hz), 84.92. IR (neat): 3057.1, 1625.9, 1589.6, 1497.5, 1455.7, 1432.0, 1325.9, 1292.3, 1232.4, 1199.1, 1158.1, 1116.6, 1082.8, 949.1, 901.8, 884.8, 873.8, 742.9, 633.4, 601.2, 569.1, 470.8. HRMS (EI): Calcd for $C_{11}H_6F_3I$, 321.9466; Found 321.9461.



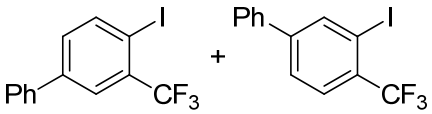
4c

5-iodo-6-(trifluoromethyl)benzo[d][1,3]dioxole (4c): white solid, Mp 74-76 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.12 (s, 1H), 6.06 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -61.59 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.71, 148.09, 127.22 (q, J_{C-F} = 31.5 Hz), 122.70 (q, J_{C-F} = 271.6 Hz), 121.33, 108.21 (q, J_{C-F} = 5.9 Hz), 102.58, 80.66. IR (neat): 3118.5, 3093.0, 3065.2, 2920.4, 1624.5, 1507.7, 1487.5, 1411.9, 1391.3, 1354.3, 1277.7, 1245.3, 1226.7, 1165.7, 1133.9, 1111.7, 1071.6, 1032.6, 931.1, 912.1, 882.7, 840.9, 691.9, 614.3, 581.4, 485.6, 440.5. HRMS (EI): Calcd for $C_8H_4F_3IO_2$, 315.9208; Found 315.9203.



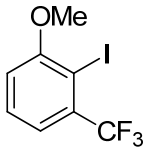
4d

5-iodo-6-(trifluoromethyl)-2,3-dihydro-1H-indene (4d): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.51 (s, 1H), 2.91 (m, 4H), 2.11 (quintet, J = 7.6 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.26 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.30, 144.71, 137.83, 131.18 (q, J_{C-F} = 30.4 Hz), 123.61 (q, J_{C-F} = 6.1 Hz), 123.19 (q, J_{C-F} = 270.8 Hz), 87.76, 32.42 (2 overlapping carbons), 25.35. IR (neat): 2955.7, 2847.0, 1605.3, 1561.2, 1476.0, 1436.0, 1393.6, 1324.5, 1288.7, 1206.7, 1153.3, 1128.1, 1086.0, 904.0, 881.6, 746.0, 663.9, 629.6, 469.7, 439.8. HRMS (EI): Calcd for $C_{10}H_8F_3I$, 311.9623; Found 311.9624.



4e (1:1)

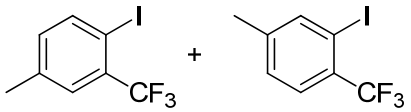
3-iodo-4-(trifluoromethyl)-1,1'-biphenyl and 4-iodo-3-(trifluoromethyl)-1,1'-biphenyl (4e, 1:1): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 4H), 7.47 – 7.36 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.73 (s, 3F), -63.08 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.97, 142.49, 141.47, 140.59, 138.76, 138.08, 134.07 (q, J_{C-F} = 30.7 Hz), 132.22 (q, J_{C-F} = 30.9 Hz), 131.32, 129.17, 129.13, 128.75, 128.46, 127.86 (q, J_{C-F} = 5.5 Hz), 127.29, 126.96, 126.51, 126.35 (q, J_{C-F} = 5.6 Hz), 123.01 (q, J_{C-F} = 272.5 Hz), 122.86 (q, J_{C-F} = 272.1 Hz), 91.48, 89.33. IR (neat): 3063.1, 3032.4, 1597.3, 1550.5, 1469.9, 1449.0, 1398.3, 1376.4, 1315.2, 1291.1, 1267.1, 1250.9, 1176.9, 1131.2, 1095.3, 1045.2, 1011.3, 899.5, 837.2, 761.3, 732.6, 696.7, 663.5, 441.7. HRMS (EI): Calcd for $C_{13}H_8F_3I$, 347.9623; Found 347.9619.



4f

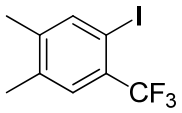
2-iodo-1-methoxy-3-(trifluoromethyl)benzene (4f): white solid, Mp 40-41 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, J = 8.2 Hz, 1H), 7.27 (d, J = 8.2 Hz, 1H), 6.98 (d, J = 8.2Hz, 1H), 3.93 (s, 3H). ^{19}F

NMR (282 MHz, $CDCl_3$): δ -62.54 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.19, 135.47 (q, J_{C-F} = 29.5 Hz), 129.45, 122.83 (q, J_{C-F} = 272.9 Hz), 119.96 (q, J_{C-F} = 5.9 Hz), 113.83, 85.00, 56.94. IR (neat): 2943.7, 2841.5, 1574.4, 1471.1, 1428.7, 1316.5, 1269.7, 1167.7, 1132.1, 1096.5, 1040.3, 1016.7, 859.4, 787.8, 752.4, 715.5, 677.5. HRMS (EI): Calcd for $C_8H_6F_3IO$, 301.9415; Found 301.9414.



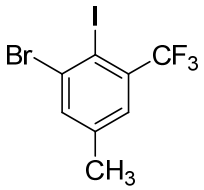
4g (1:1)

1-iodo-4-methyl-2-(trifluoromethyl)benzene and 2-iodo-4-methyl-1-(trifluoromethyl)benzene (4g, 1:1): colourless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.4 Hz, 1H), 7.86 (s, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.71 (s, 3F), -63.14 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.57, 142.53, 141.81, 138.31, 133.69, 133.39 (q, J_{C-F} = 30.5 Hz), 130.91 (q, J_{C-F} = 30.8 Hz), 128.59, 128.44 (q, J_{C-F} = 4.9 Hz), 127.33 (q, J_{C-F} = 5.2 Hz), 123.01 (q, J_{C-F} = 270.6 Hz), 122.83 (q, J_{C-F} = 272.8 Hz), 90.90, 86.73, 20.91, 20.67. IR (neat): 2926.6, 1602.9, 1567.8, 1471.6, 1384.2, 1312.8, 1265.4, 1207.6, 1173.7, 1131.3, 1092.9, 1019.8, 822.0, 742.7, 662.7, 596.6, 520.1, 445.3. HRMS (EI): Calcd for $C_8H_6F_3I$, 285.9466; Found 285.9465.



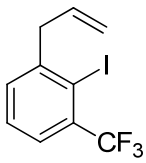
4h

1-iodo-4,5-dimethyl-2-(trifluoromethyl)benzene (4h): colourless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.38 (s, 1H), 2.24 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.63 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.69, 142.35, 136.86, 131.02 (q, J_{C-F} = 30.4 Hz), 128.66 (q, J_{C-F} = 5.6 Hz), 123.00 (q, J_{C-F} = 271.5 Hz), 87.07, 19.35, 19.10. IR (neat): 2970.4, 2923.1, 2859.2, 1596.8, 1557.0, 1488.2, 1448.2, 1388.5, 1370.2, 1298.1, 1229.7, 1159.8, 1147.9, 1119.2, 1105.3, 998.0, 909.2, 886.3, 874.0, 763.2, 740.2, 637.5, 560.9, 481.5, 445.3. HRMS (EI): Calcd for $C_9H_8F_3I$, 299.9623; Found 299.9619.



4i

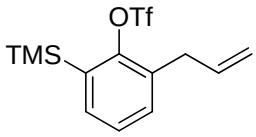
1-bromo-2-iodo-5-methyl-3-(trifluoromethyl)benzene (1i): colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.38 (s, 1H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.86 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.89, 136.20, 136.19 (q, J_{C-F} = 30.6 Hz), 133.88, 127.18 (q, J_{C-F} = 5.6 Hz), 122.30 (q, J_{C-F} = 272.6 Hz), 95.33, 20.66. IR (neat): 2925.8, 1423.4, 1397.0, 1308.2, 1191.0, 1157.9, 1136.0, 1113.3, 1011.2, 866.3, 792.3, 696.5, 532.5. HRMS (EI): Calcd for $C_8H_5BrF_3I$, 363.8571; Found 363.8573.



4j

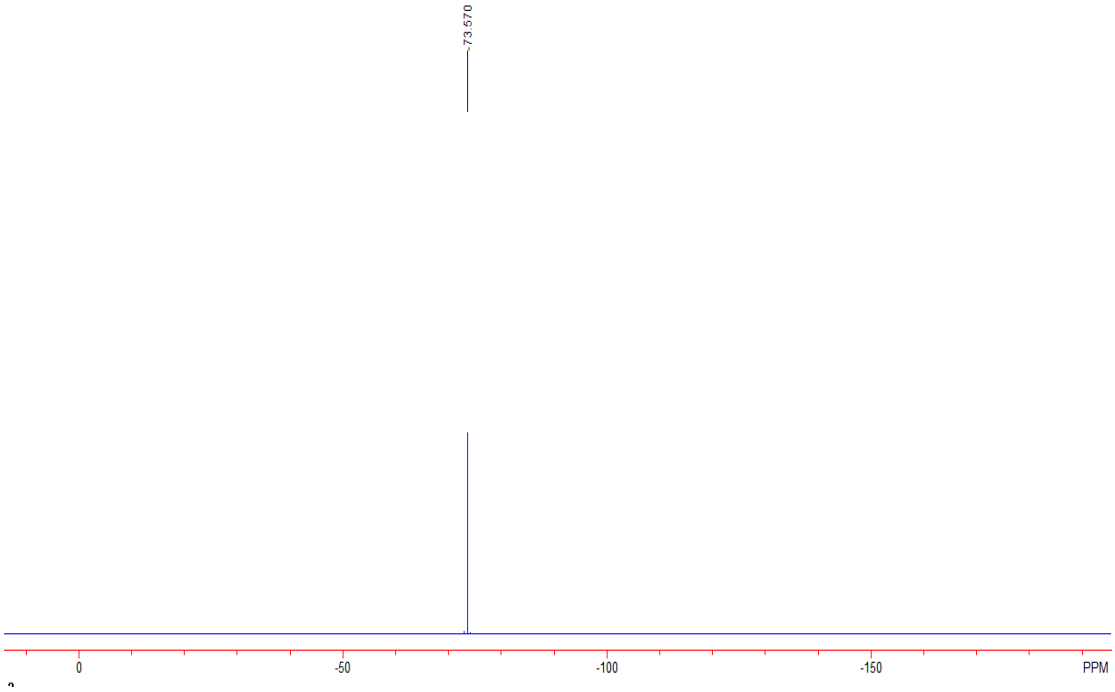
1-allyl-2-iodo-3-(trifluoromethyl)benzene (1j): colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (dd, J = 6.0 Hz, J = 3.6 Hz, 1H), 7.40 - 7.37 (m, 2H), 6.01 - 5.90 (m, 1H), 5.21 - 5.07 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.72 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.95, 135.17, 134.63 (q, J_{C-F} = 29.8 Hz), 132.58, 128.10, 125.78 (q, J_{C-F} = 5.9 Hz), 123.17 (q, J_{C-F} = 272.3 Hz), 117.38, 98.19, 46.22. IR (neat): 3082.1, 2981.6, 2921.4, 1639.0, 1578.3, 1459.5, 1437.6, 1418.9, 1316.3, 1249.8, 1164.0, 1135.0, 1092.1, 1012.0, 993.1, 921.2, 799.6, 762.8, 723.6, 679.2. HRMS (EI): Calcd for $C_{10}H_8F_3I$, 311.9623; Found 311.9622.

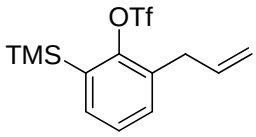
NMR Spectra of Product



1j

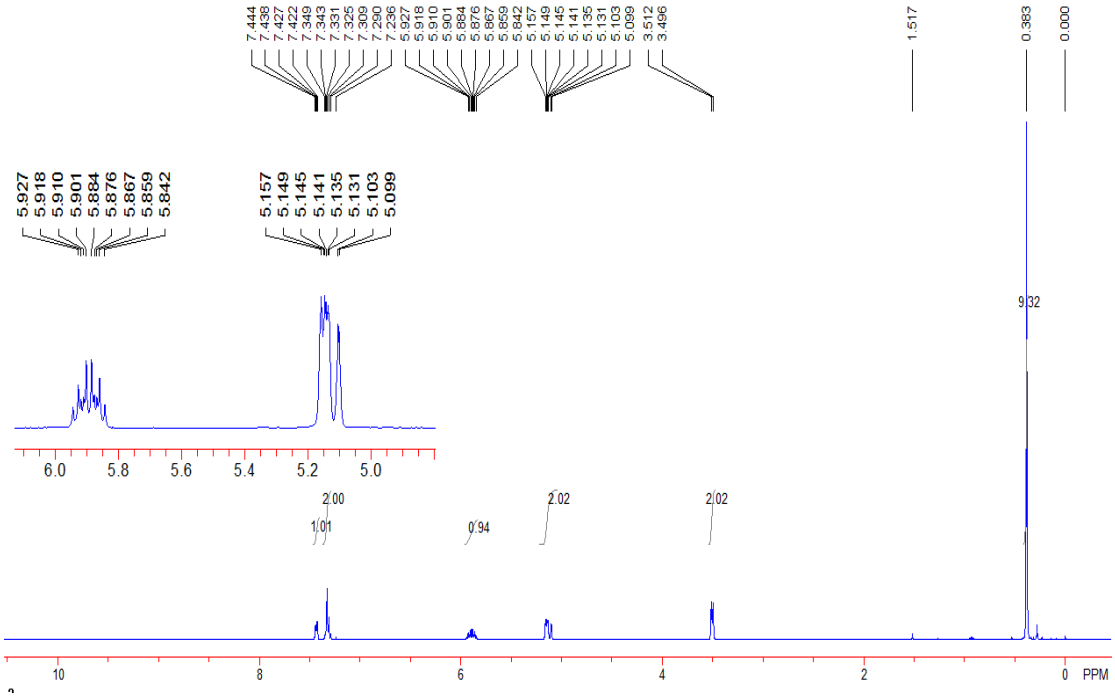
^{19}F NMR (376 MHz, $CDCl_3$)

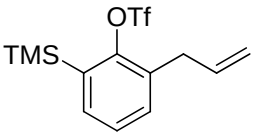




1j

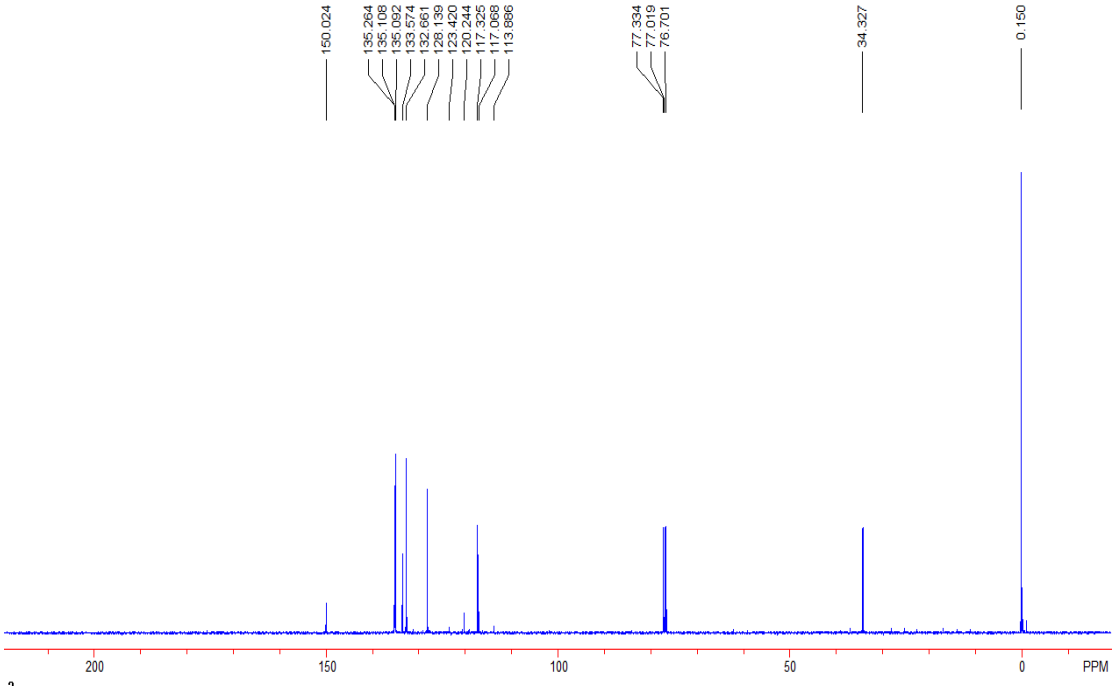
^{1}H NMR (400 MHz, $CDCl_3$)

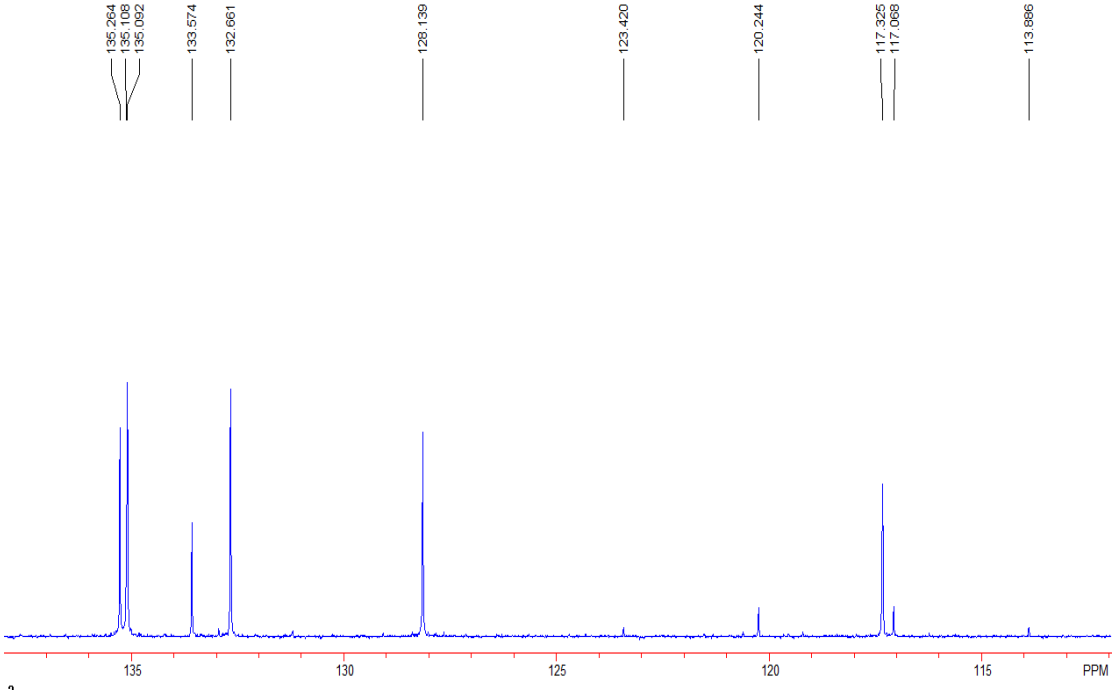


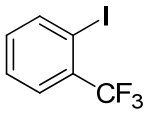


1j

^{13}C NMR (100 MHz, $CDCl_3$)

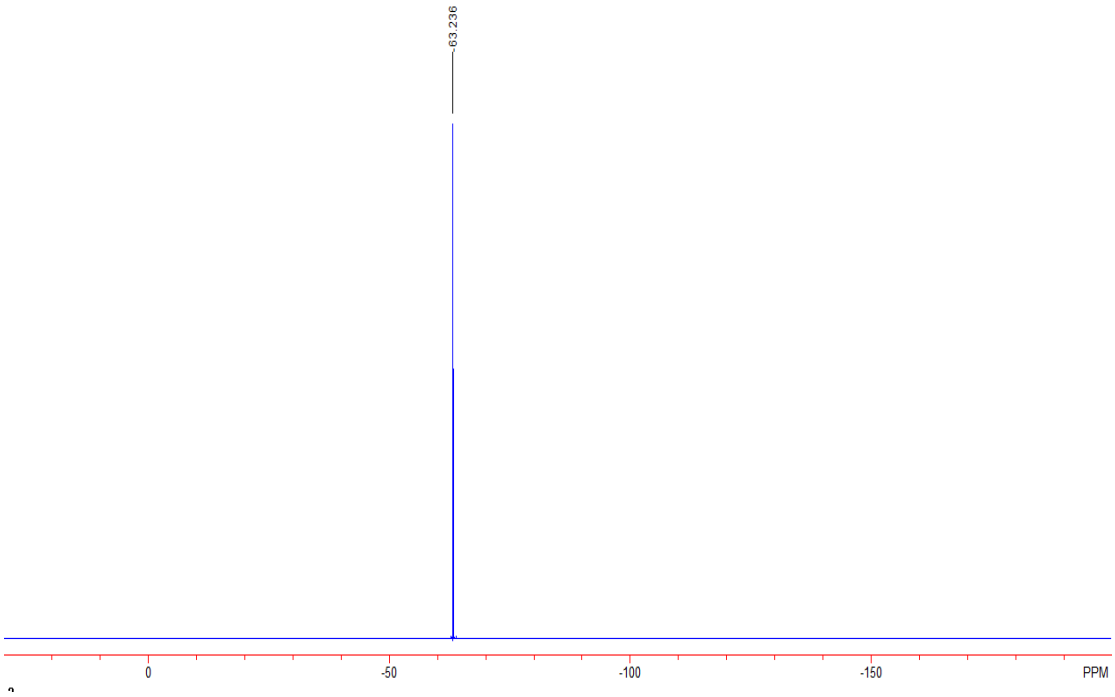


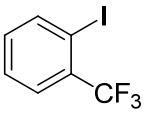




4a

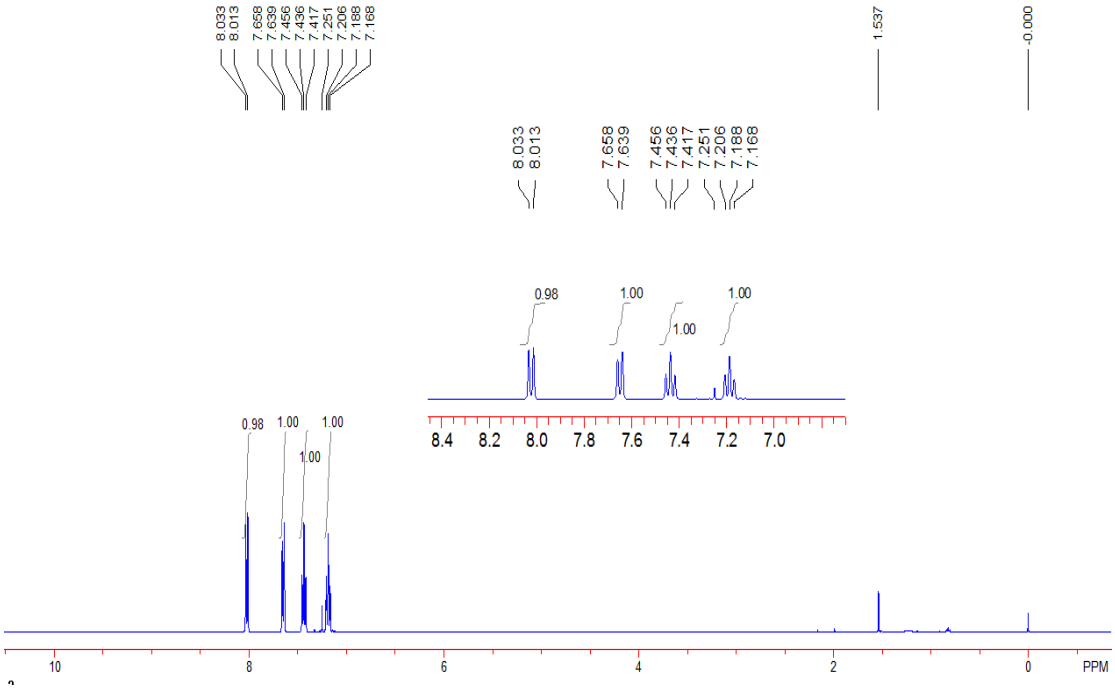
^{19}F NMR (282 MHz, $CDCl_3$)

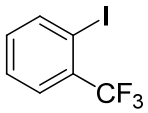




4a

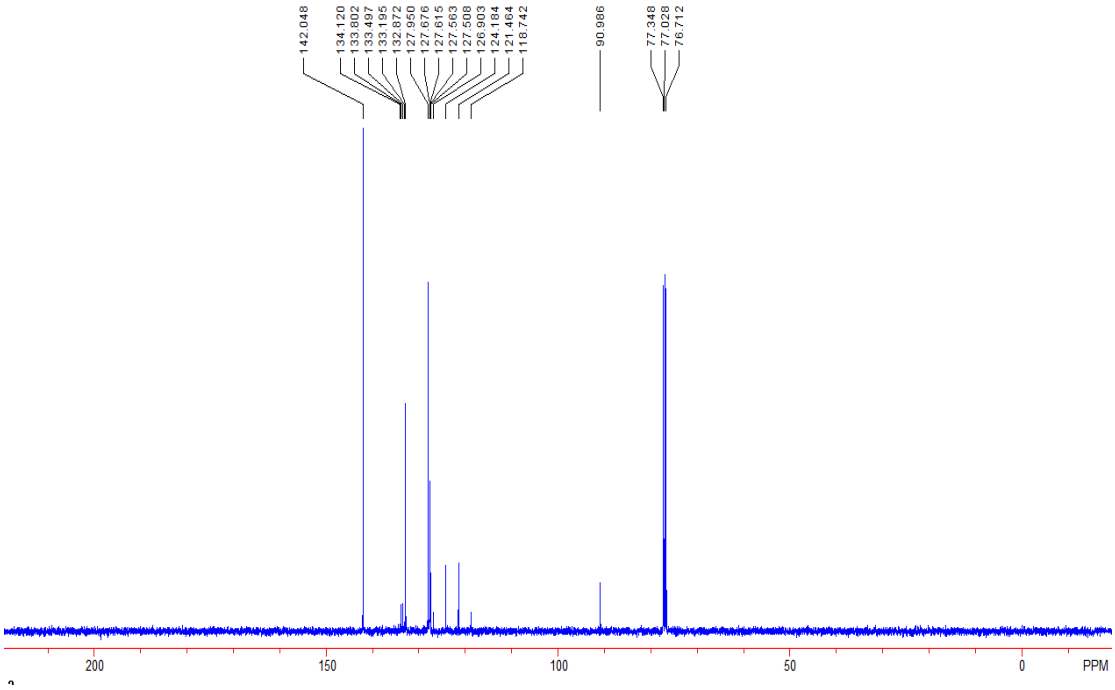
^{1}H NMR (400 MHz, $CDCl_3$)

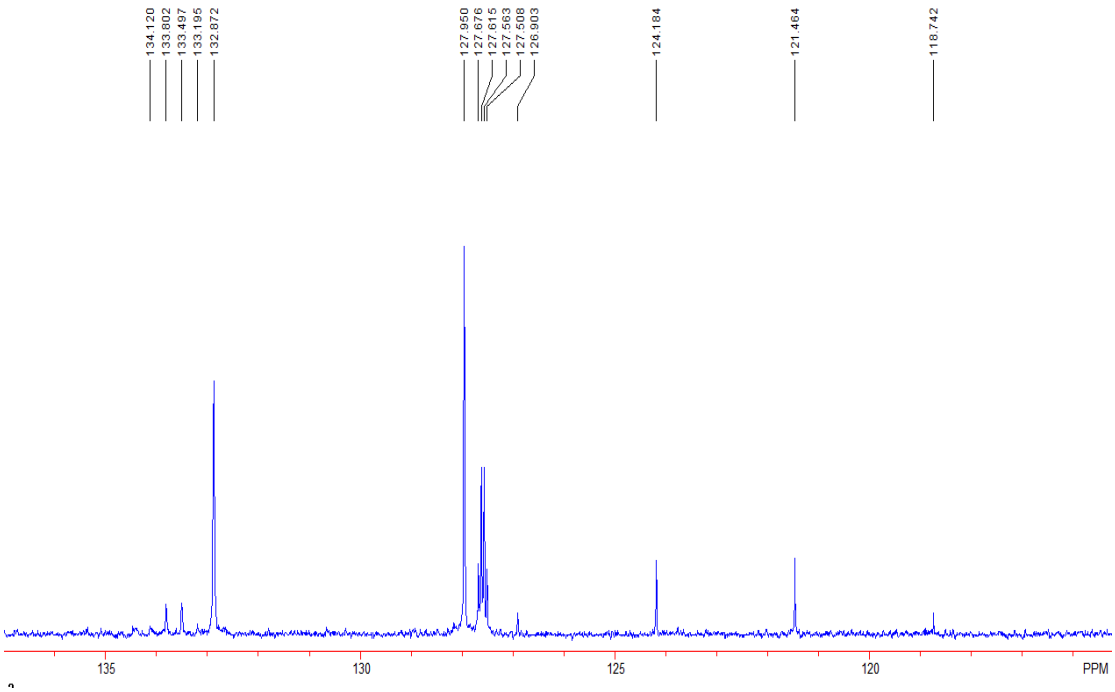


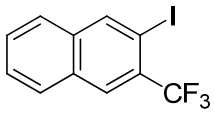


4a

^{13}C NMR (100 MHz, $CDCl_3$)

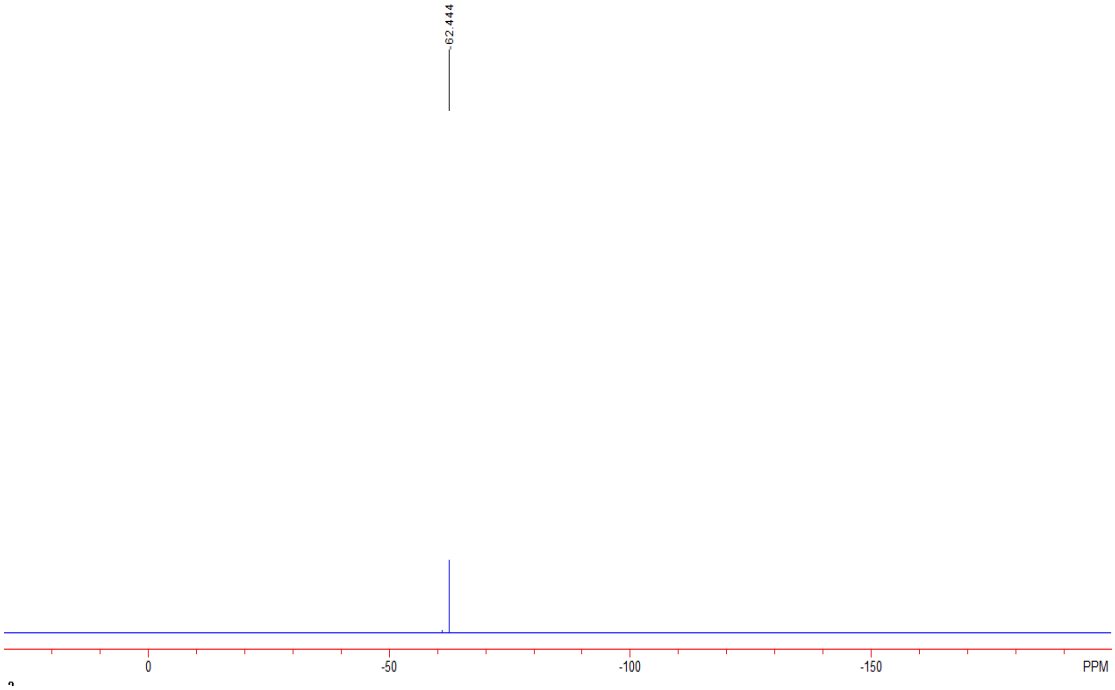


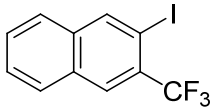




4b

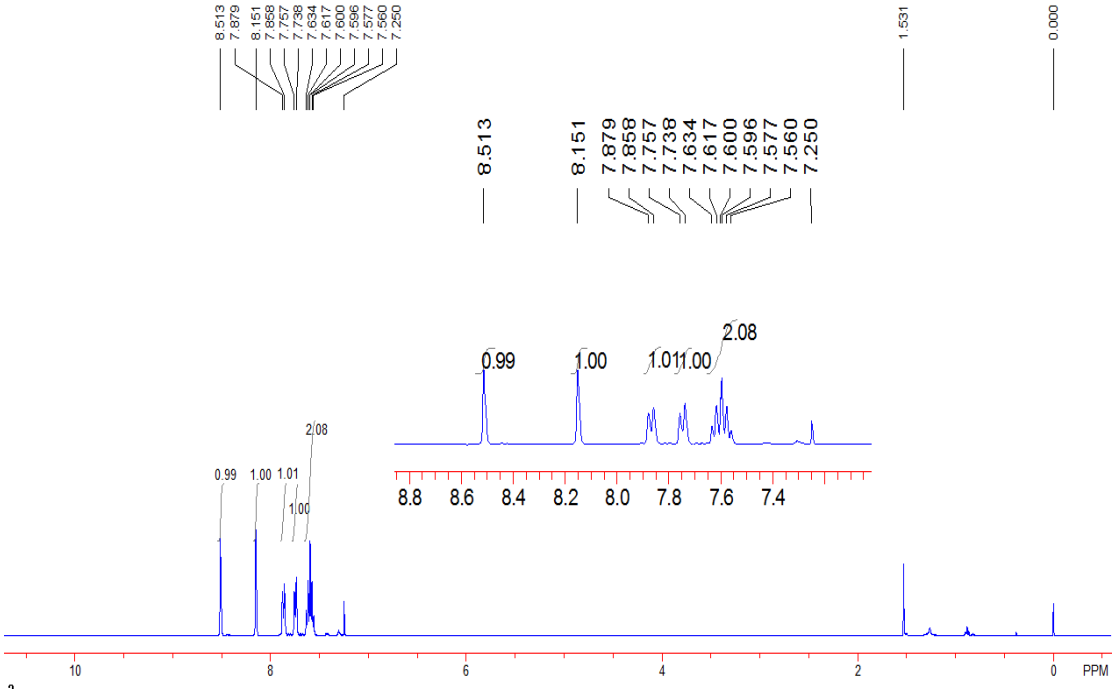
^{19}F NMR (282 MHz, $CDCl_3$)

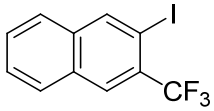




4b

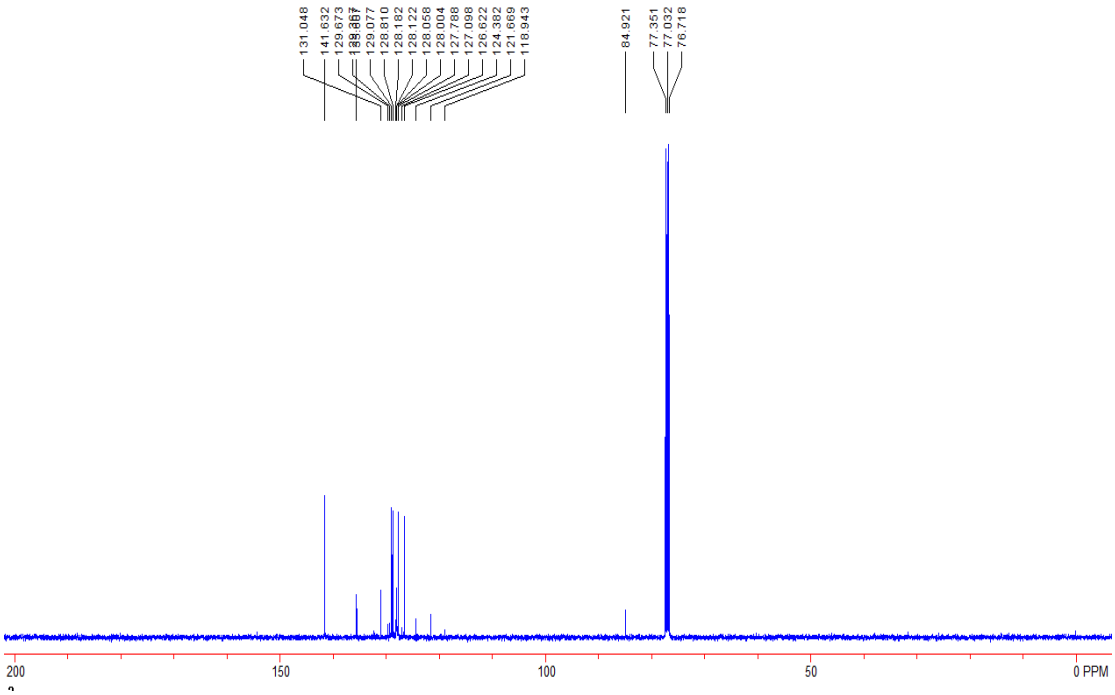
^{1}H NMR (400 MHz, $CDCl_3$)

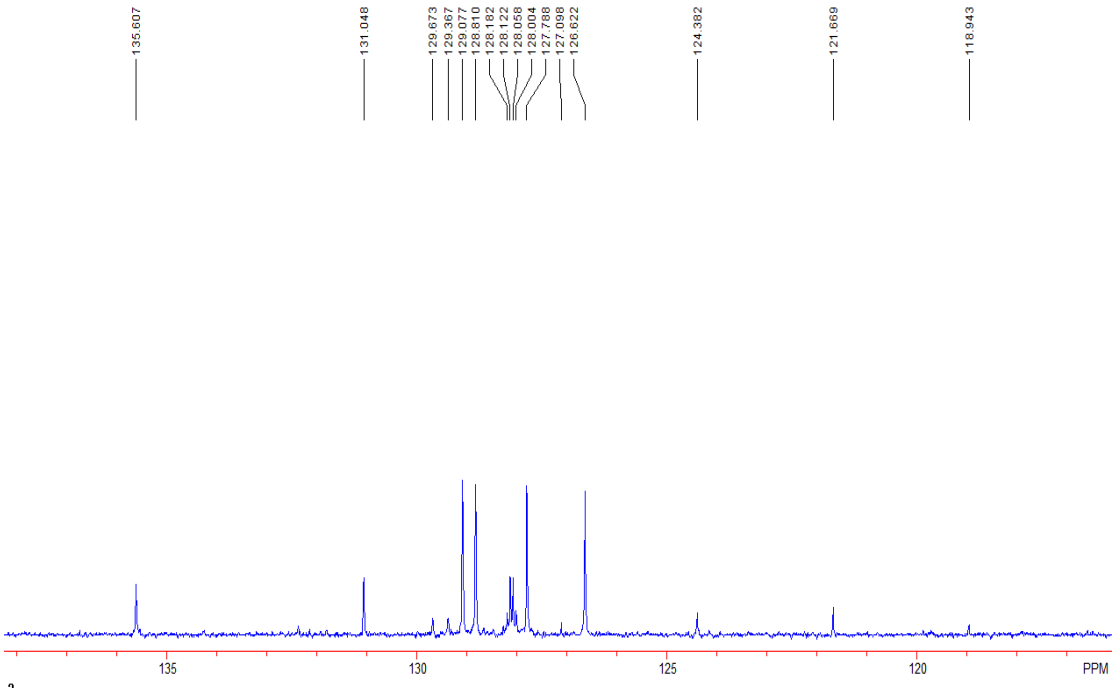


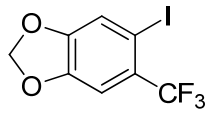


4b

^{13}C NMR (100 MHz, $CDCl_3$)

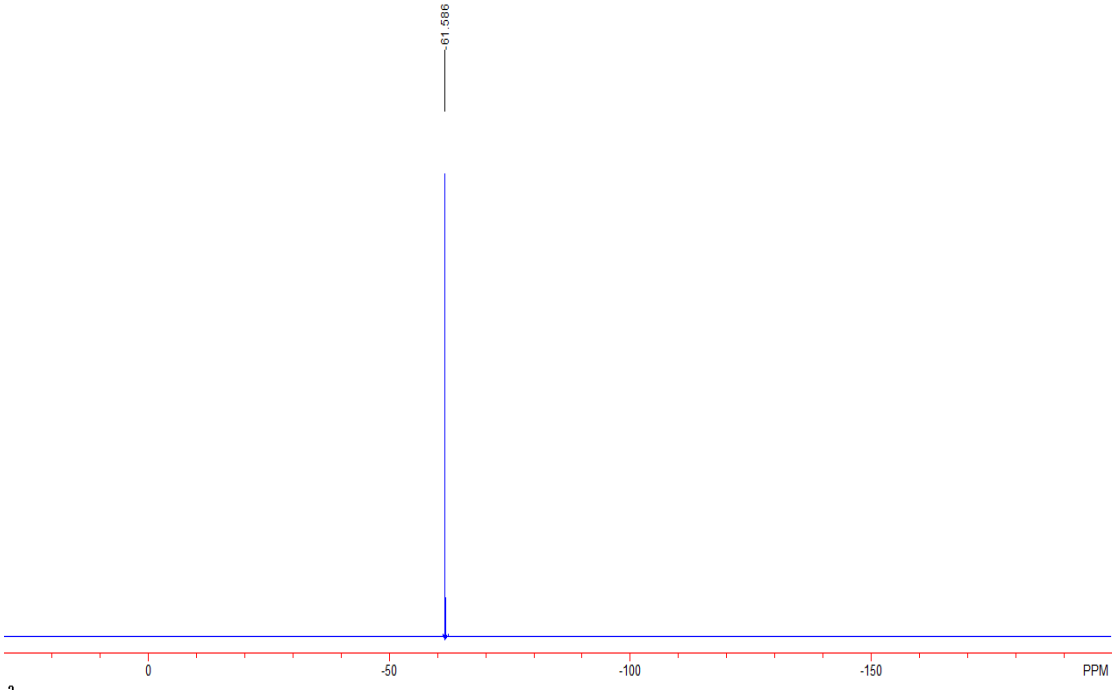


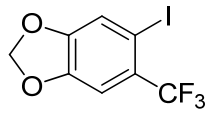




4c

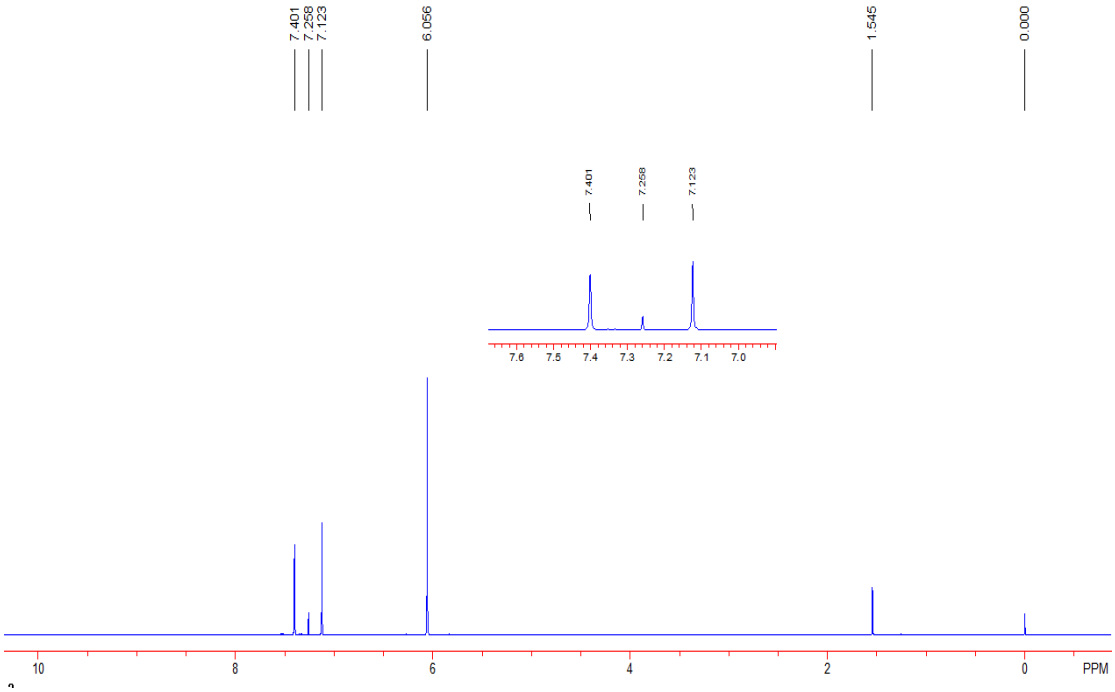
^{19}F NMR (282 MHz, $CDCl_3$)

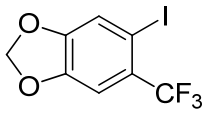




4c

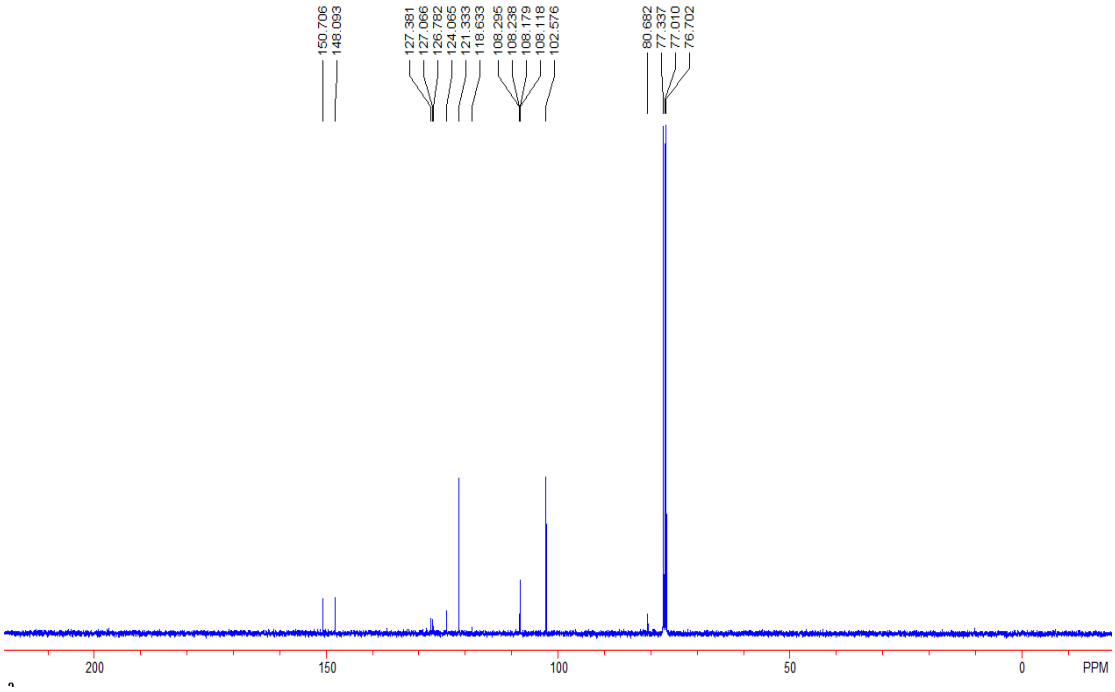
^{1}H NMR (400 MHz, $CDCl_3$)

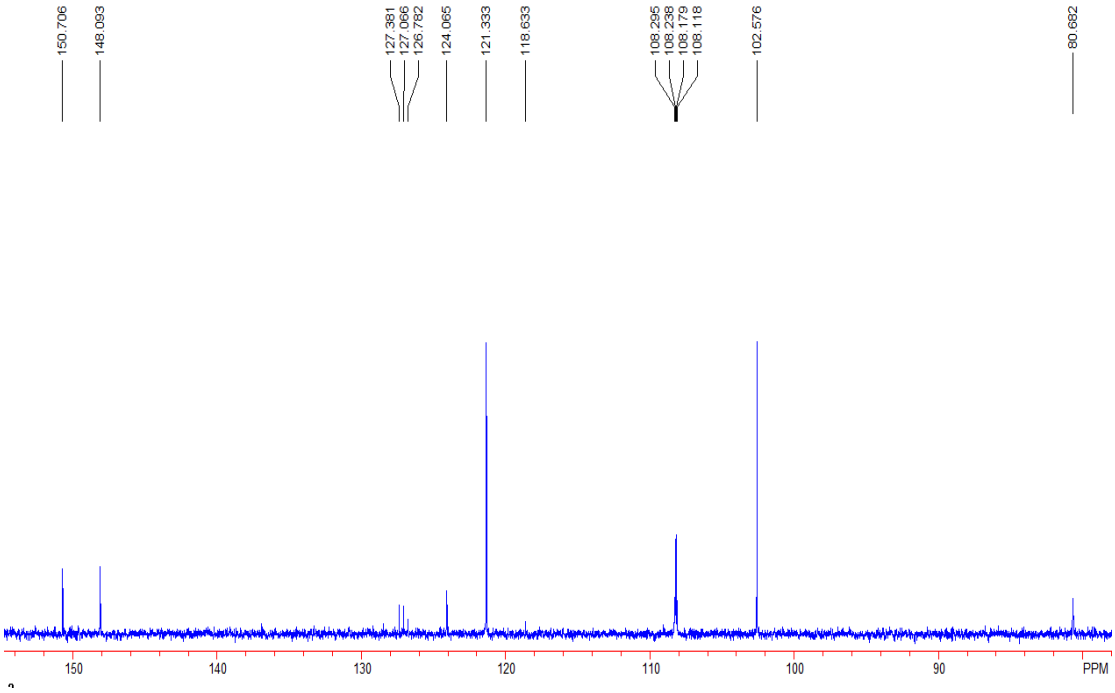


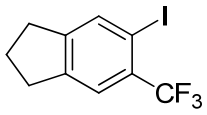


4c

^{13}C NMR (100 MHz, $CDCl_3$)

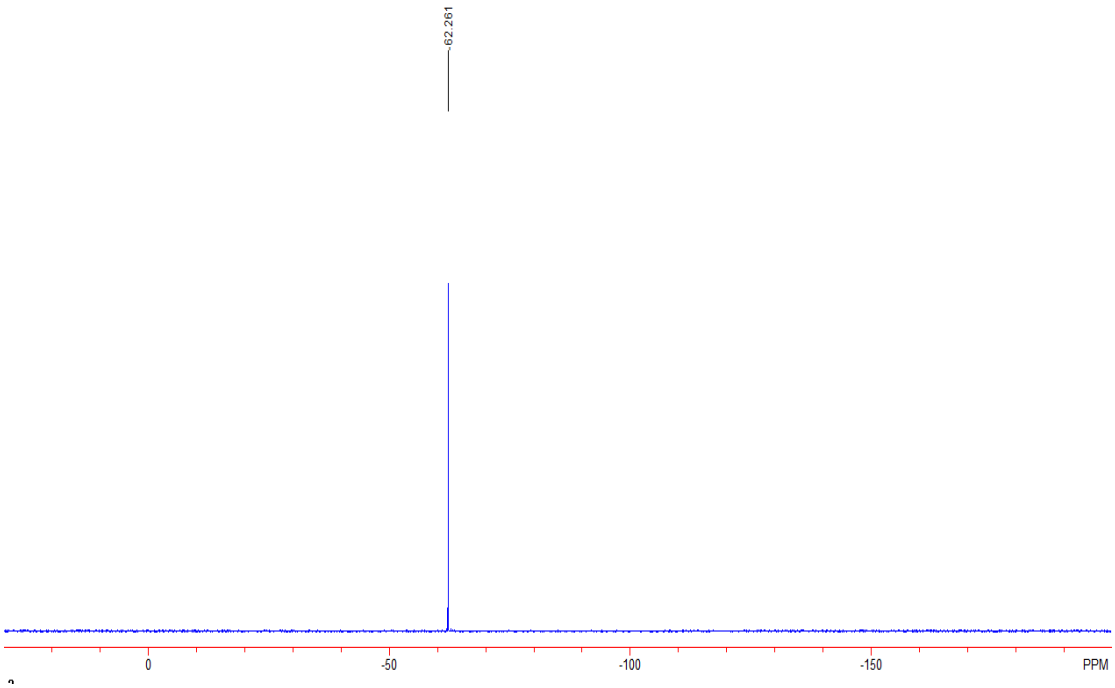


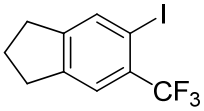




4d

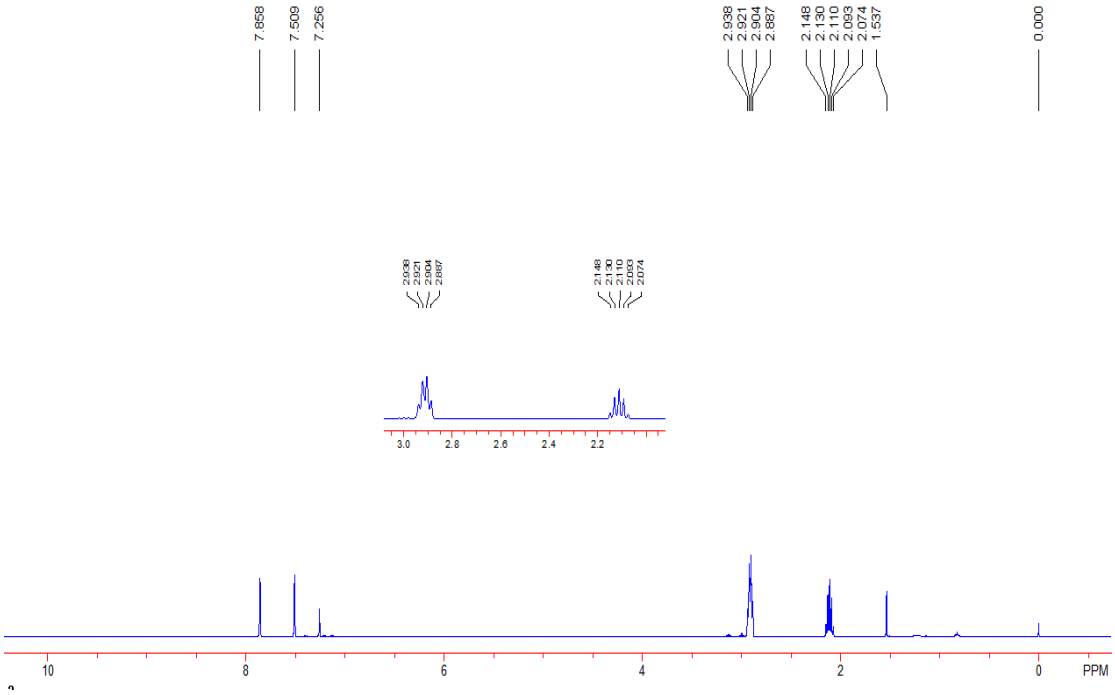
^{19}F NMR (282 MHz, $CDCl_3$)

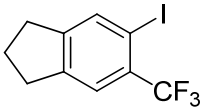




4d

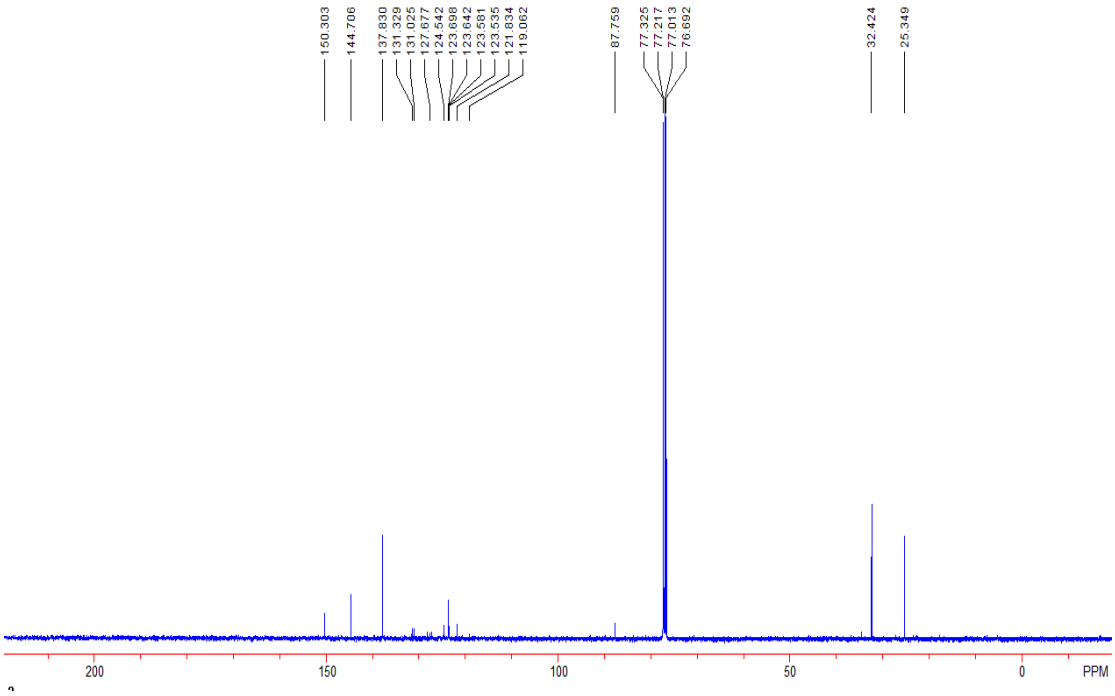
^{1}H NMR (400 MHz, $CDCl_3$)

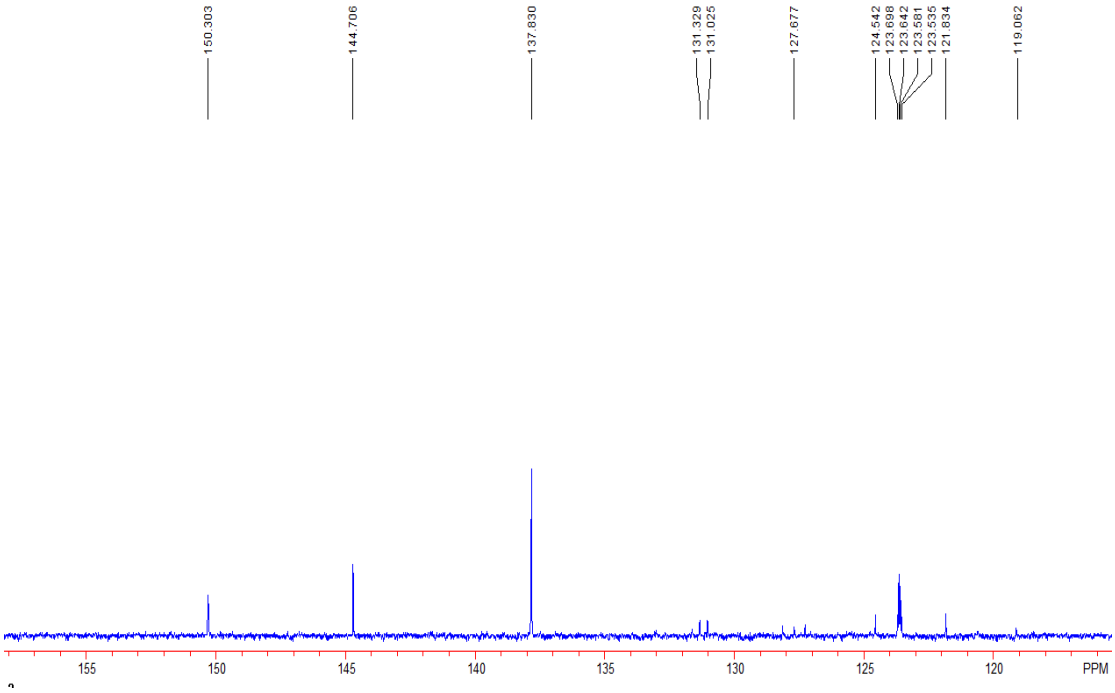


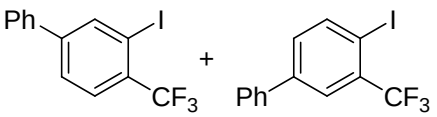


4d

^{13}C NMR (100 MHz, $CDCl_3$)

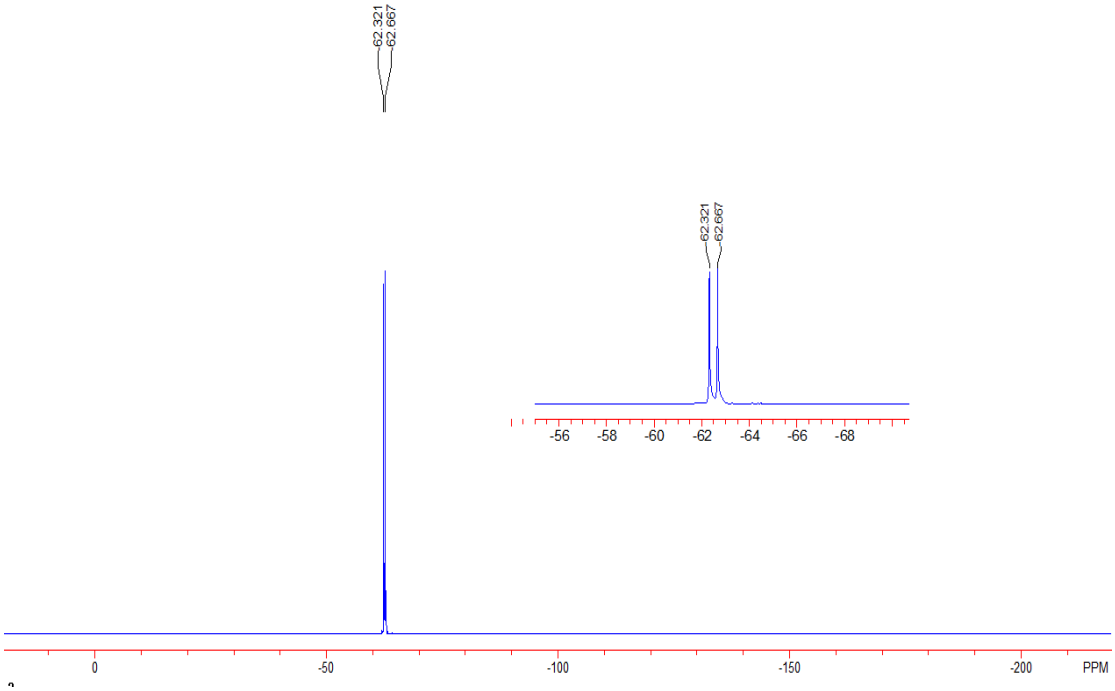


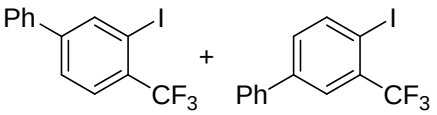




4e (1:1)

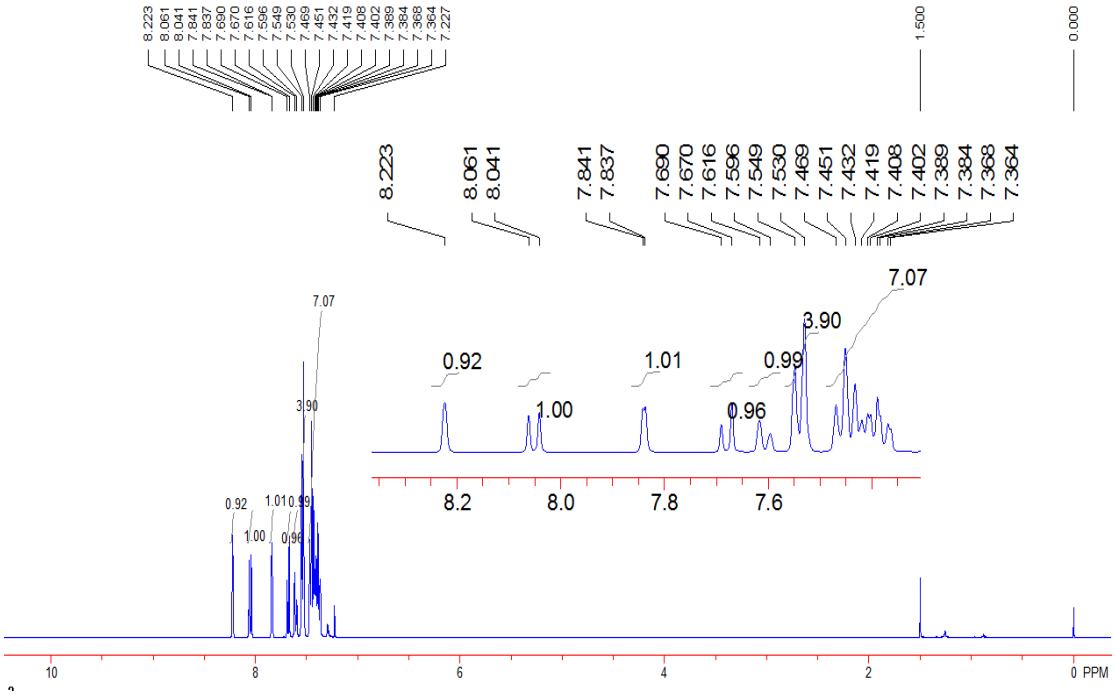
^{19}F NMR (282 MHz, $CDCl_3$)

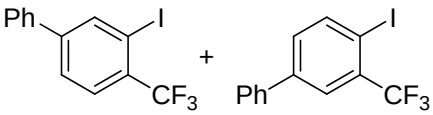




4e (1:1)

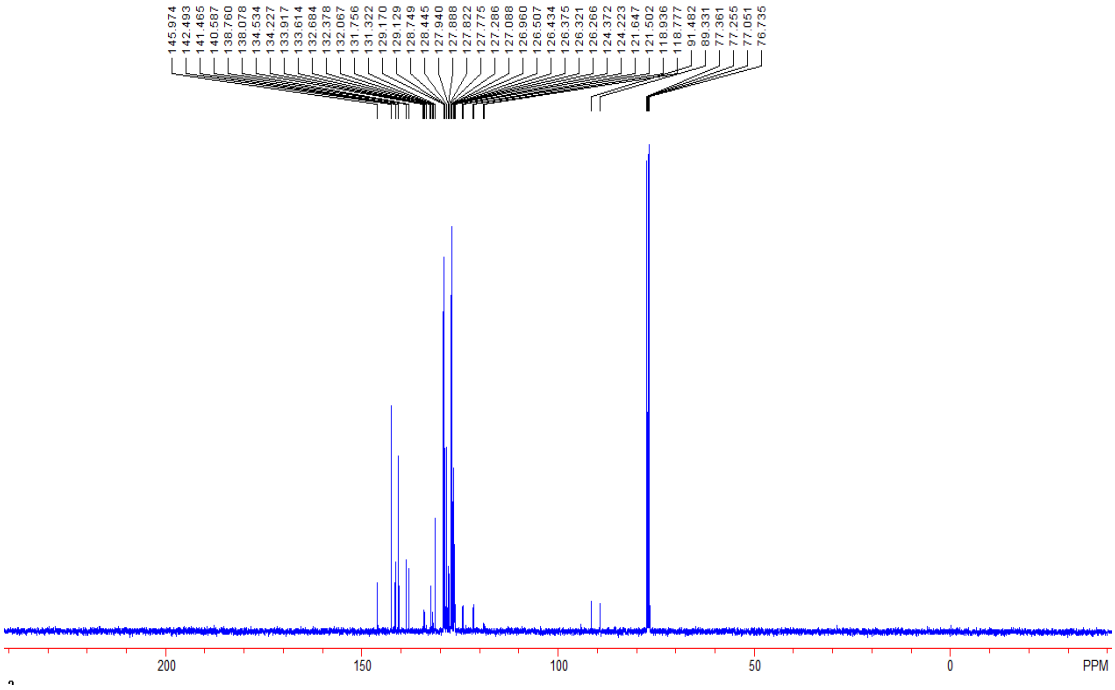
^{1}H NMR (400 MHz, $CDCl_3$)

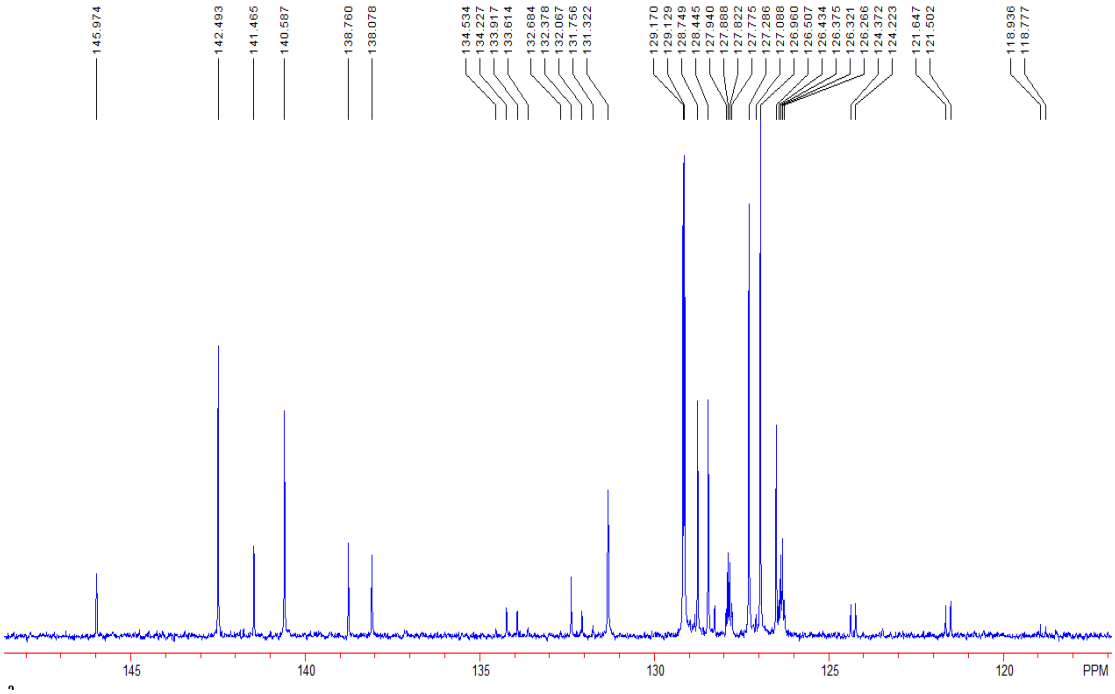


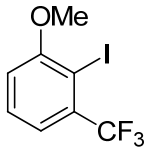


4e (1:1)

^{13}C NMR (100 MHz, $CDCl_3$)

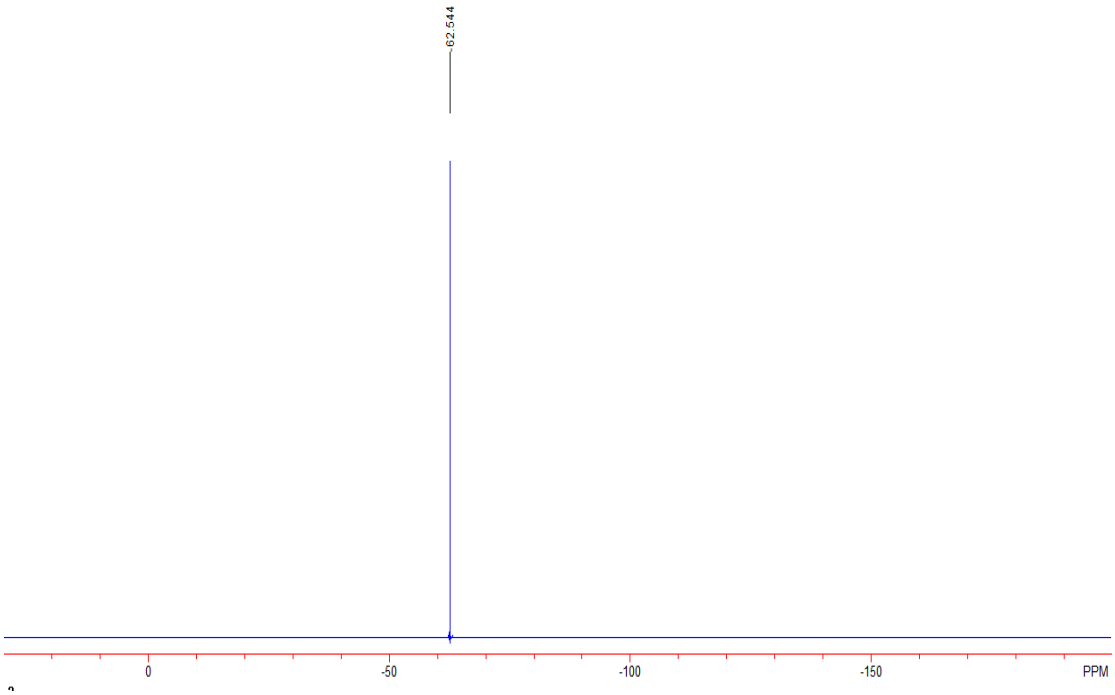


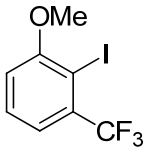




4f

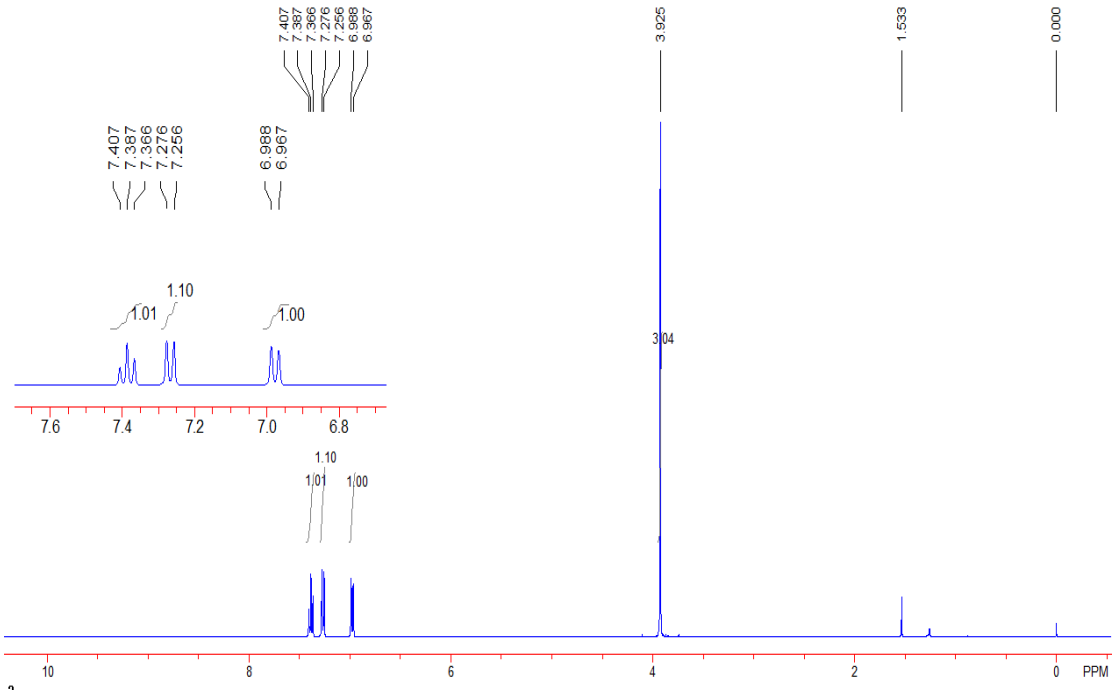
^{19}F NMR (282 MHz, $CDCl_3$)

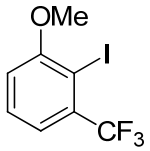




4f

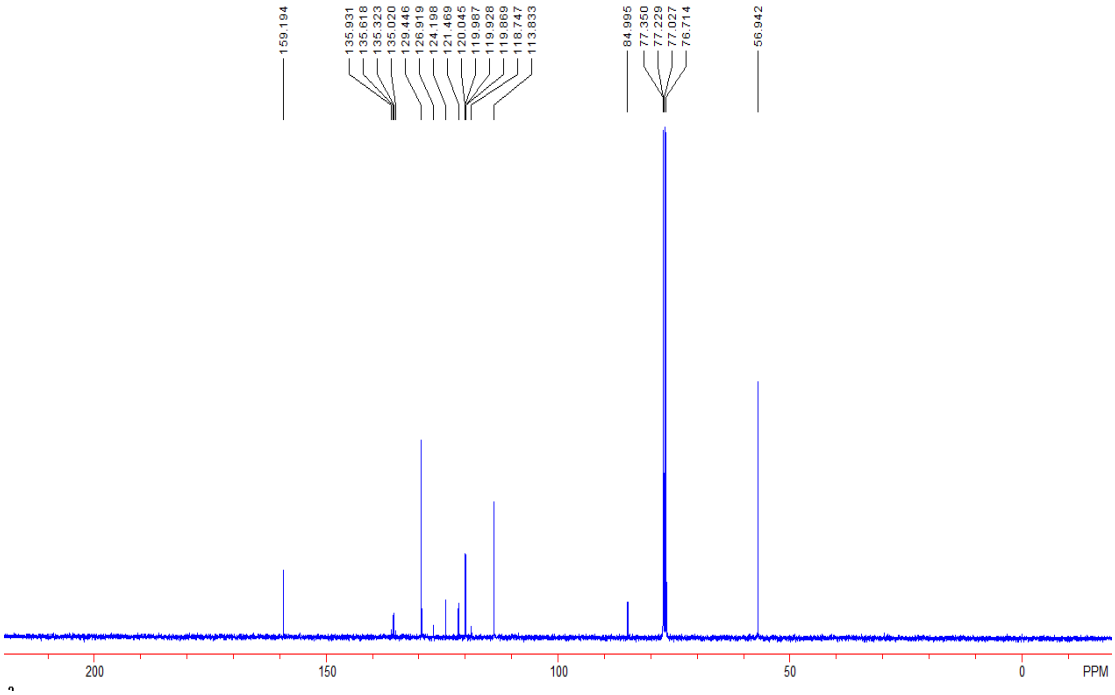
^{1}H NMR (400 MHz, $CDCl_3$)

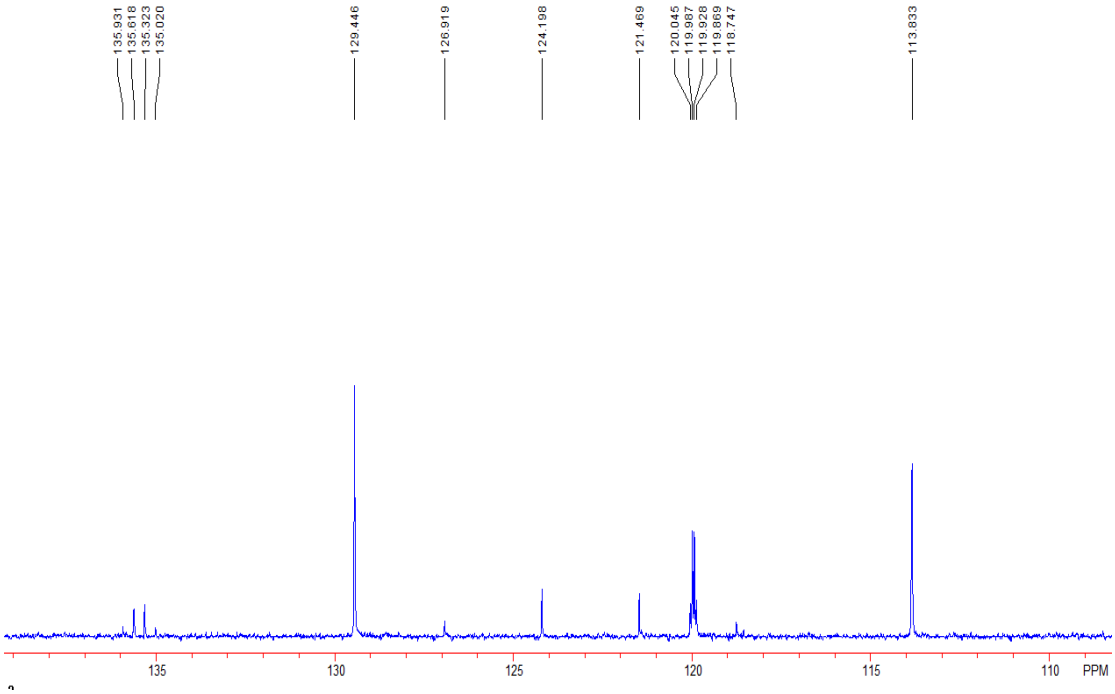


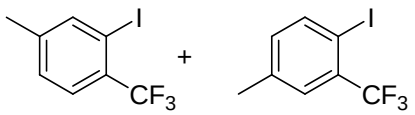


4f

^{13}C NMR (100 MHz, $CDCl_3$)

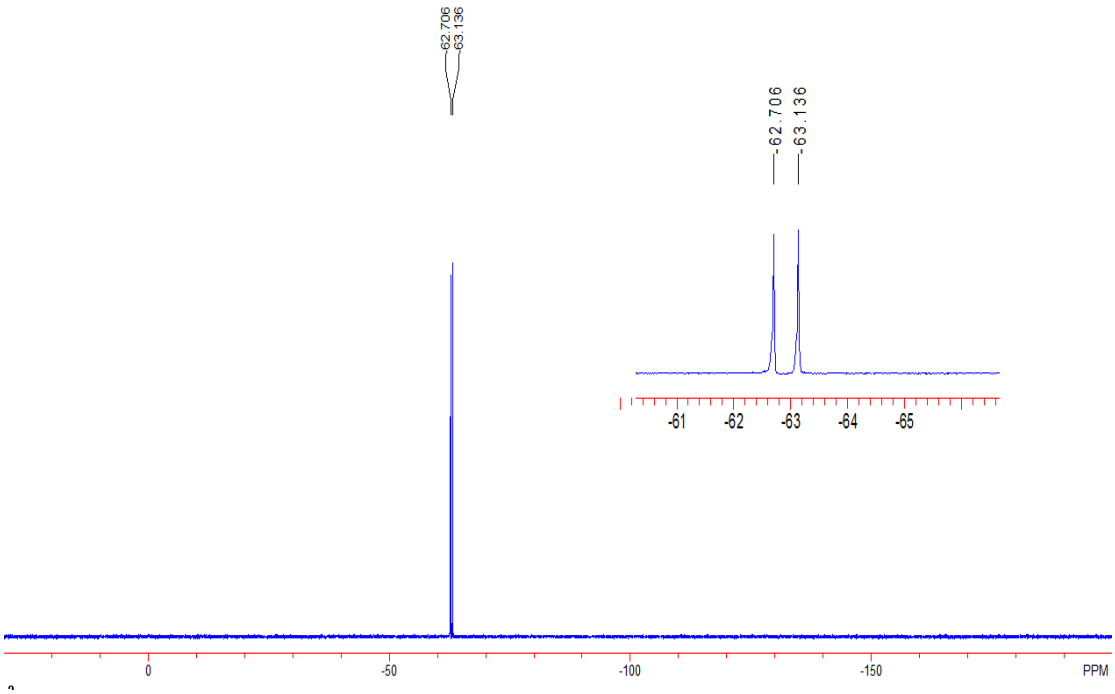


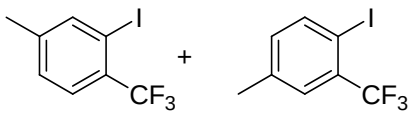




4g (1:1)

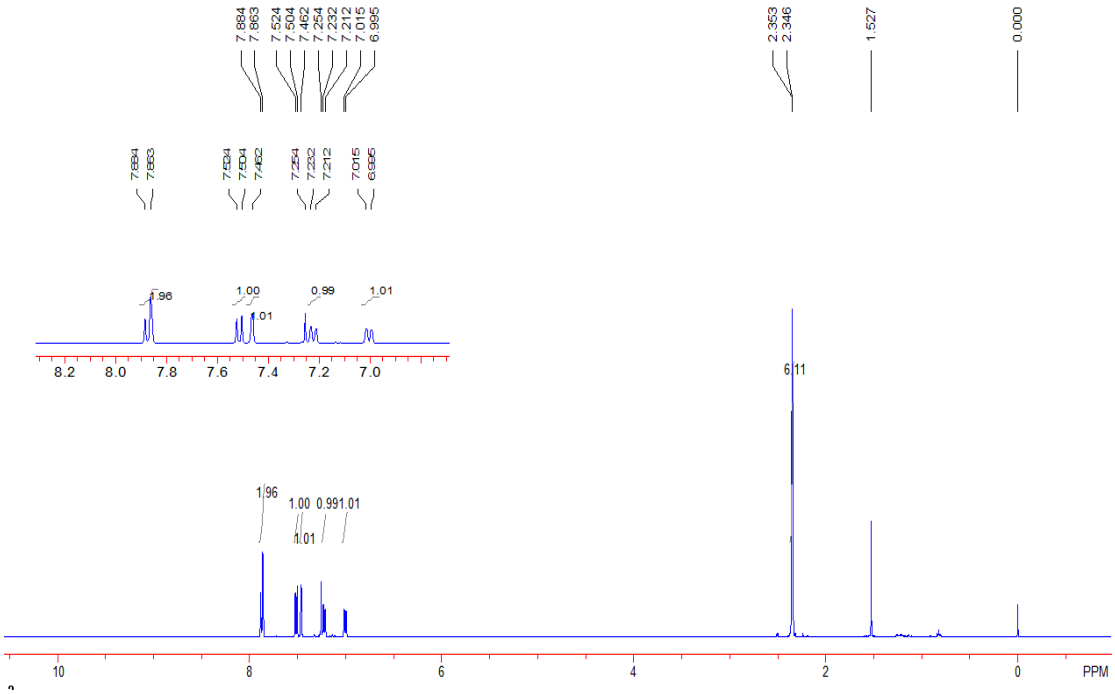
^{19}F NMR (282 MHz, $CDCl_3$)

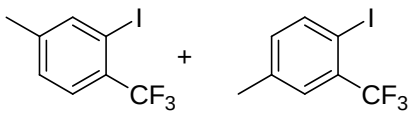




4g (1:1)

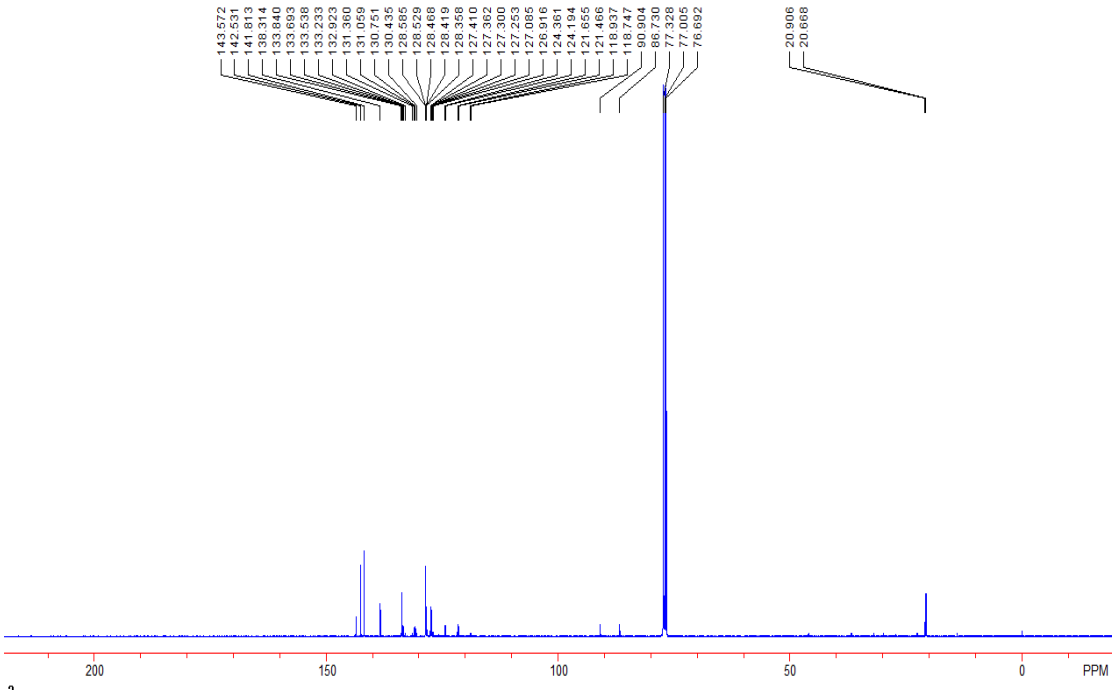
^{1}H NMR (400 MHz, $CDCl_3$)

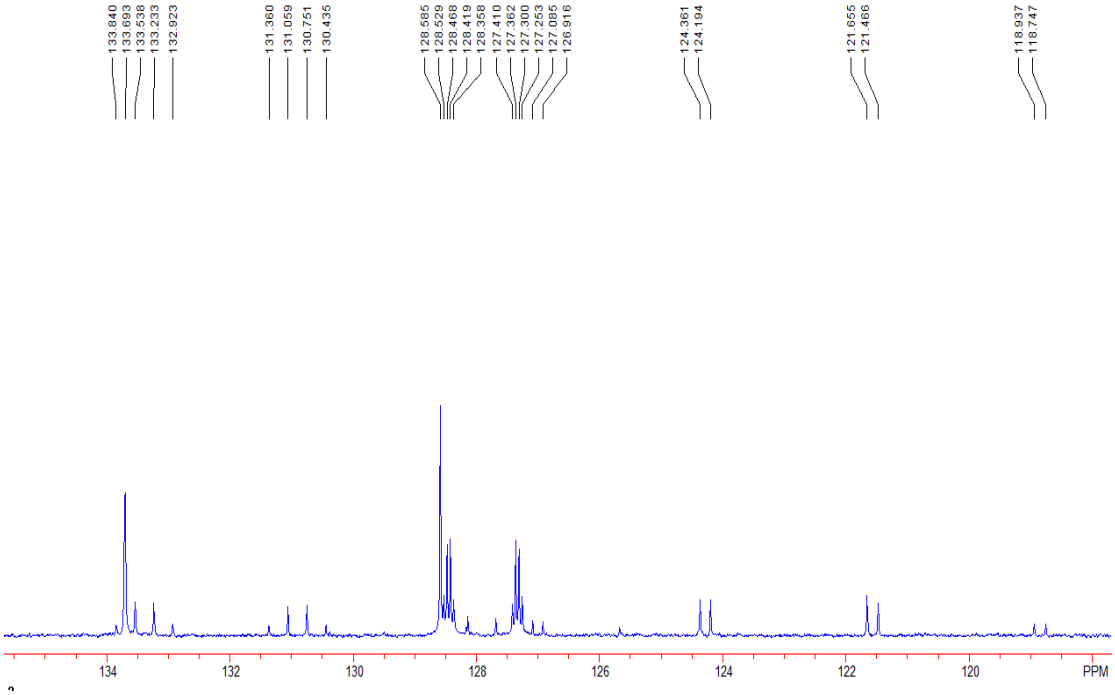


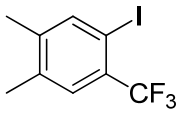


4g (1:1)

^{13}C NMR (100 MHz, $CDCl_3$)

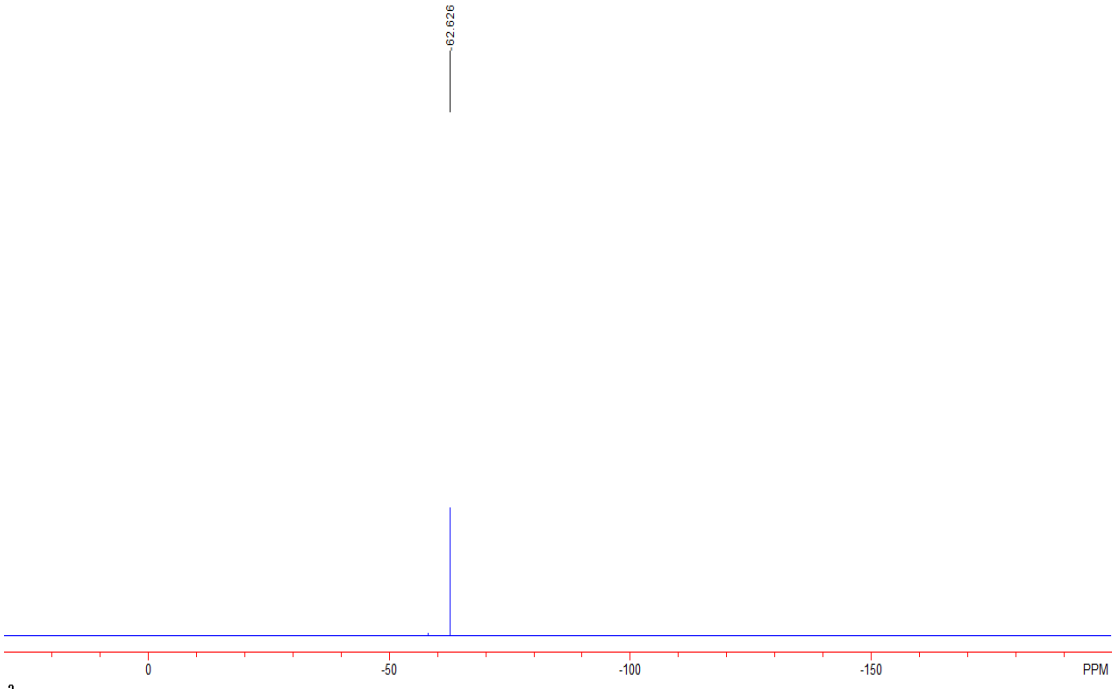


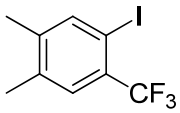




4h

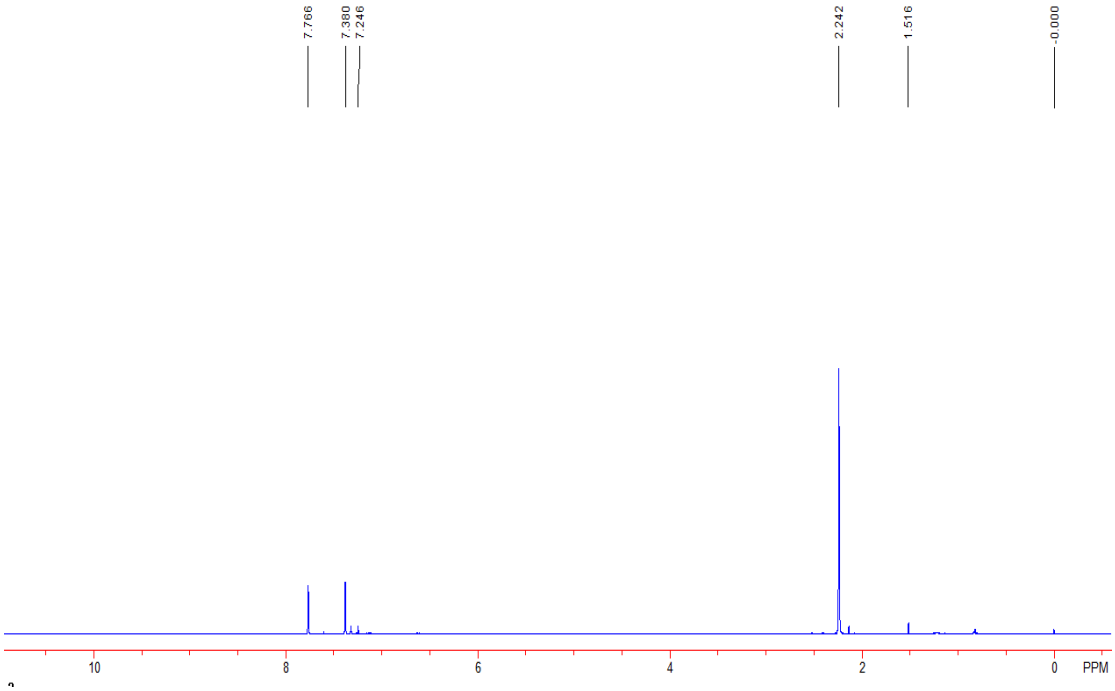
^{19}F NMR (282 MHz, $CDCl_3$)

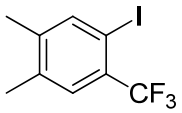




4h

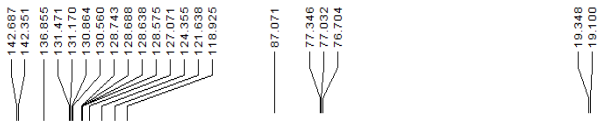
^{1}H NMR (400 MHz, $CDCl_3$)

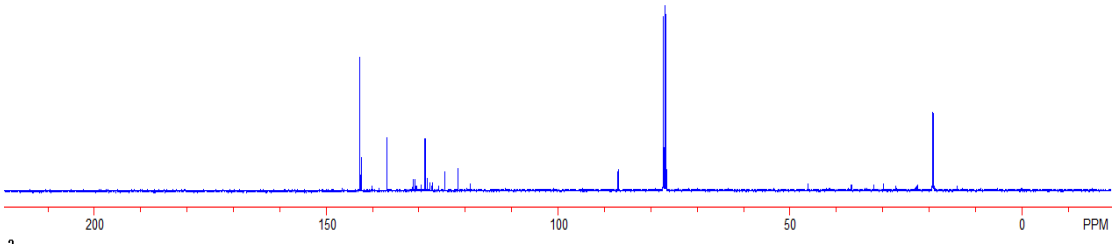


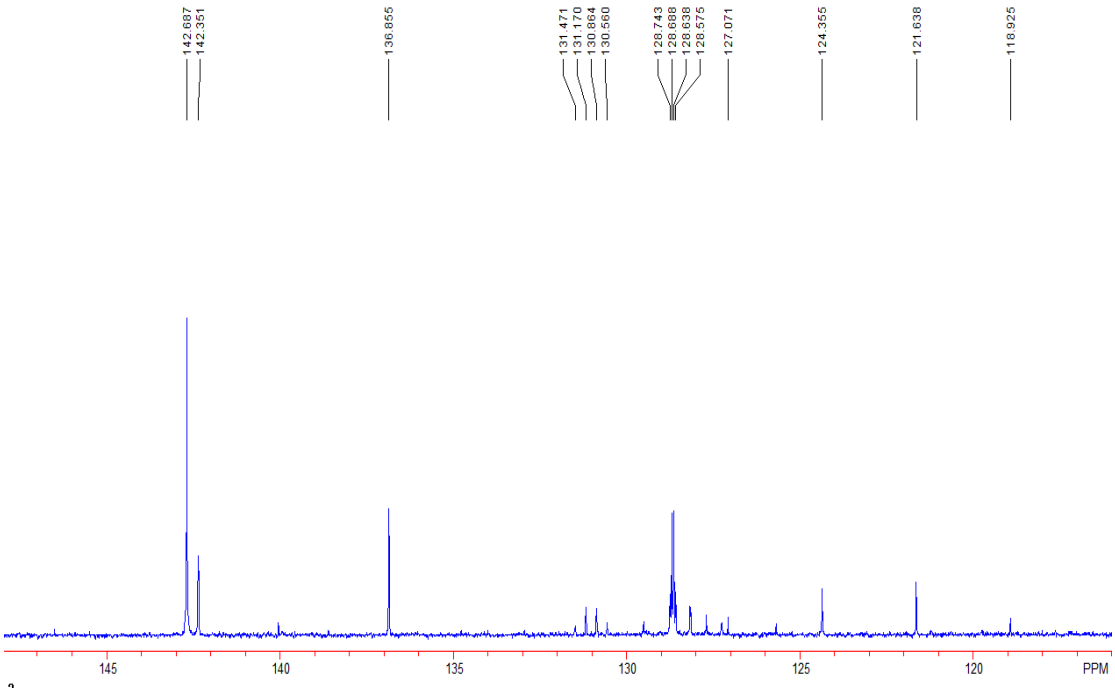


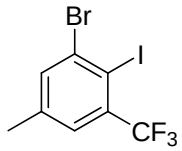
4h

^{13}C NMR (100 MHz, $CDCl_3$)



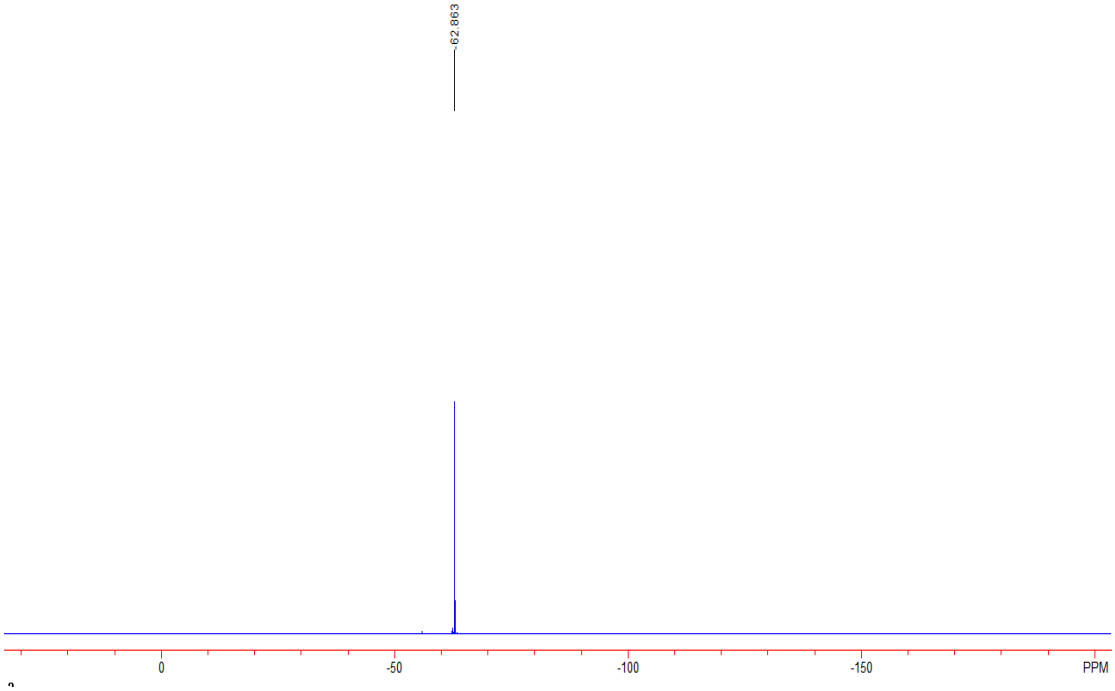


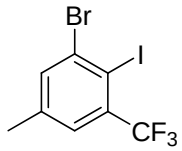




4i

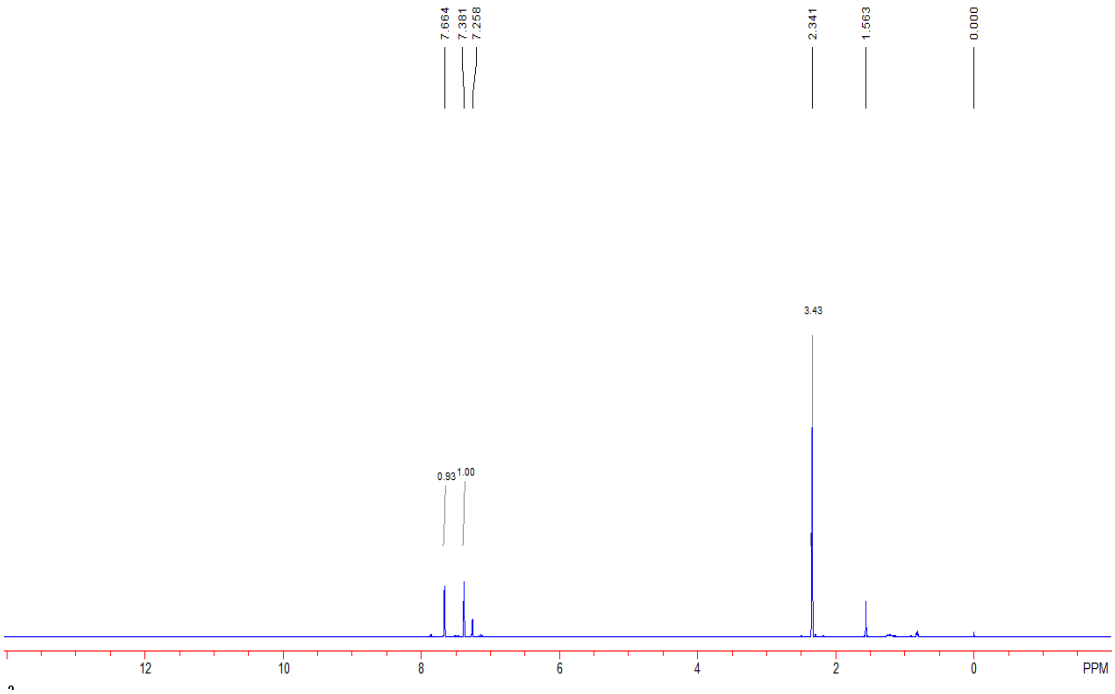
^{19}F NMR (376 MHz, $CDCl_3$)

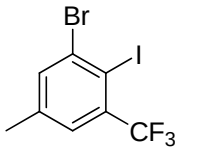




4i

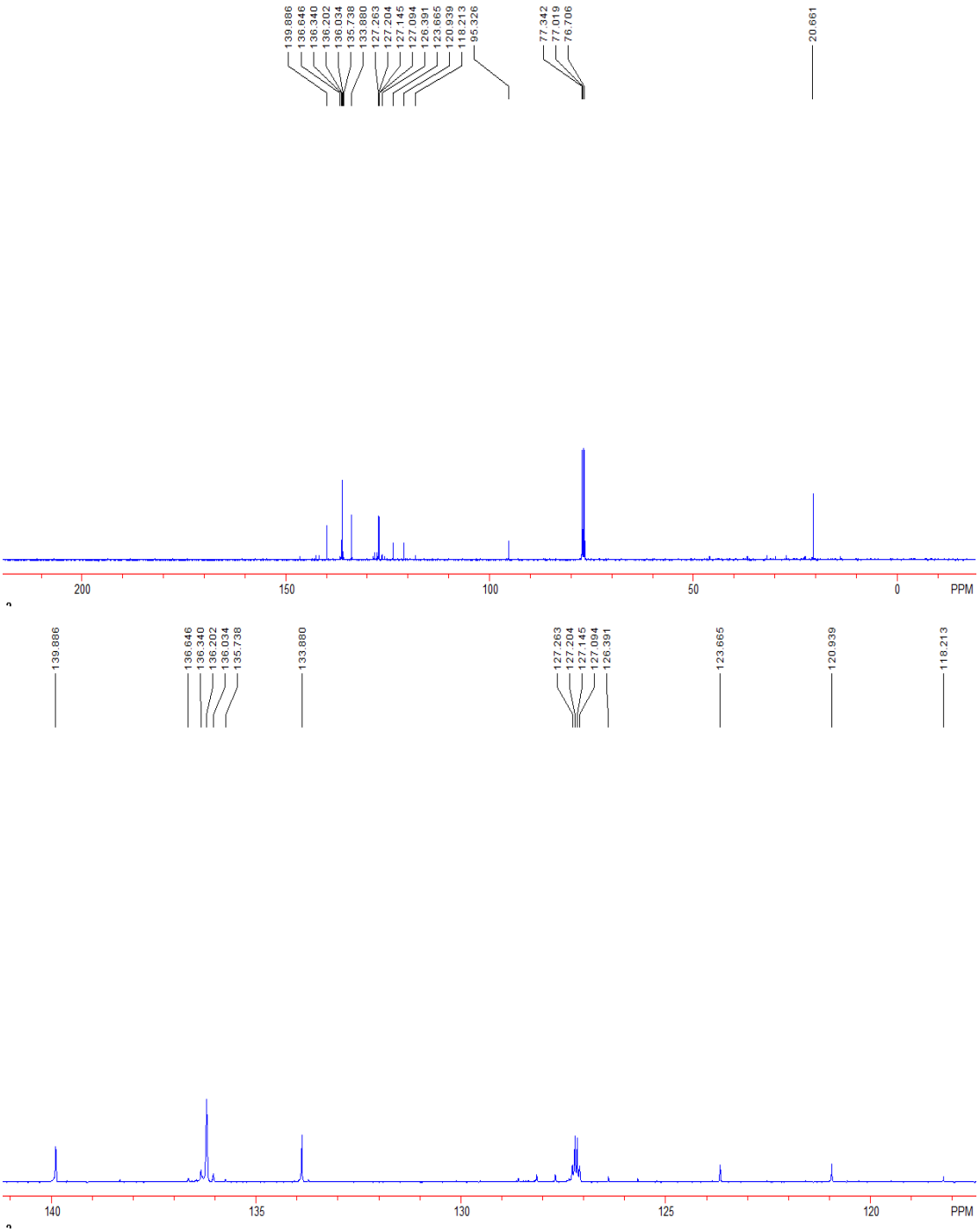
^{1}H NMR (400 MHz, $CDCl_3$)

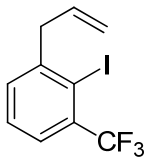




4i

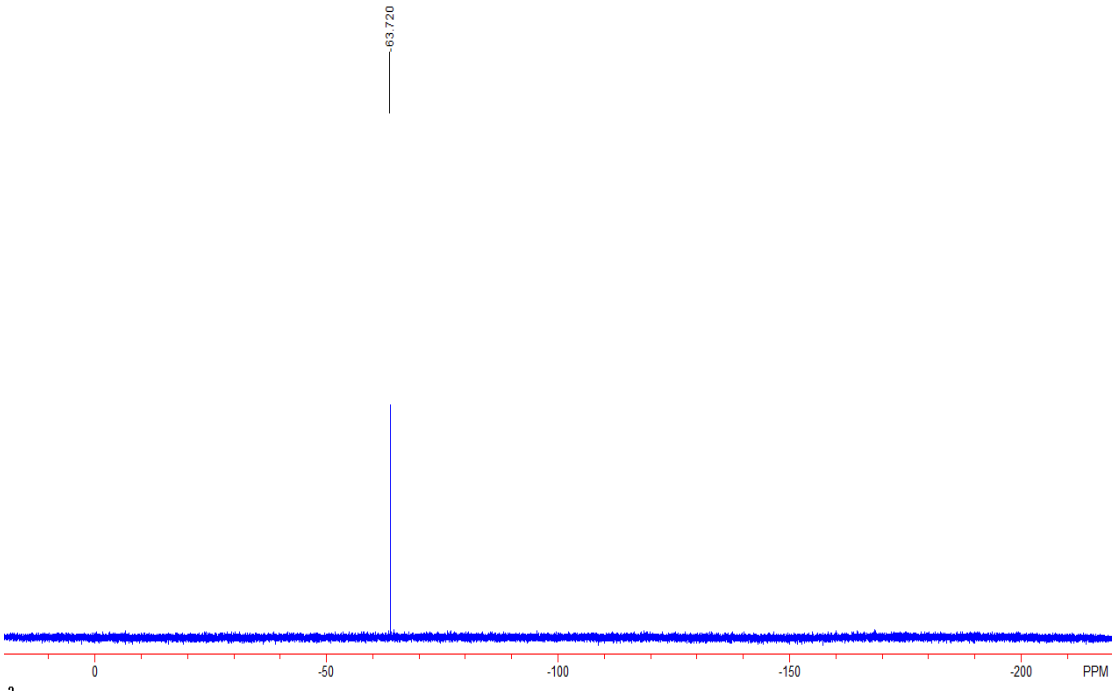
^{13}C NMR (100 MHz, $CDCl_3$)

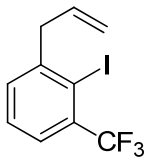




4j

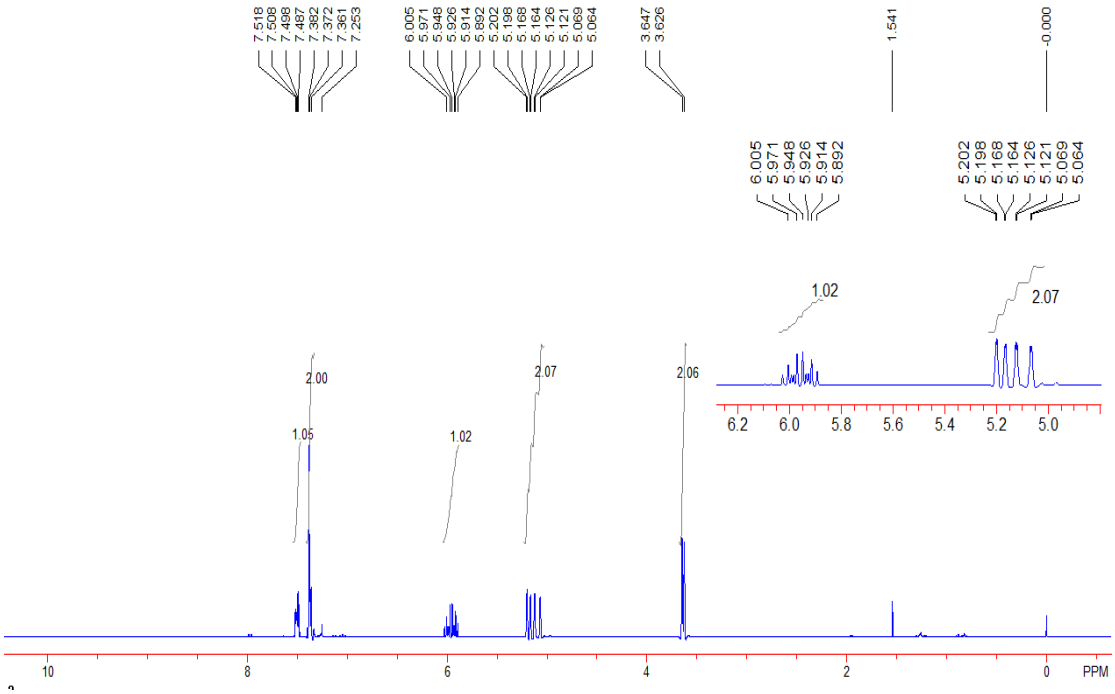
^{19}F NMR (282 MHz, $CDCl_3$)

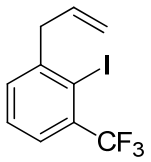


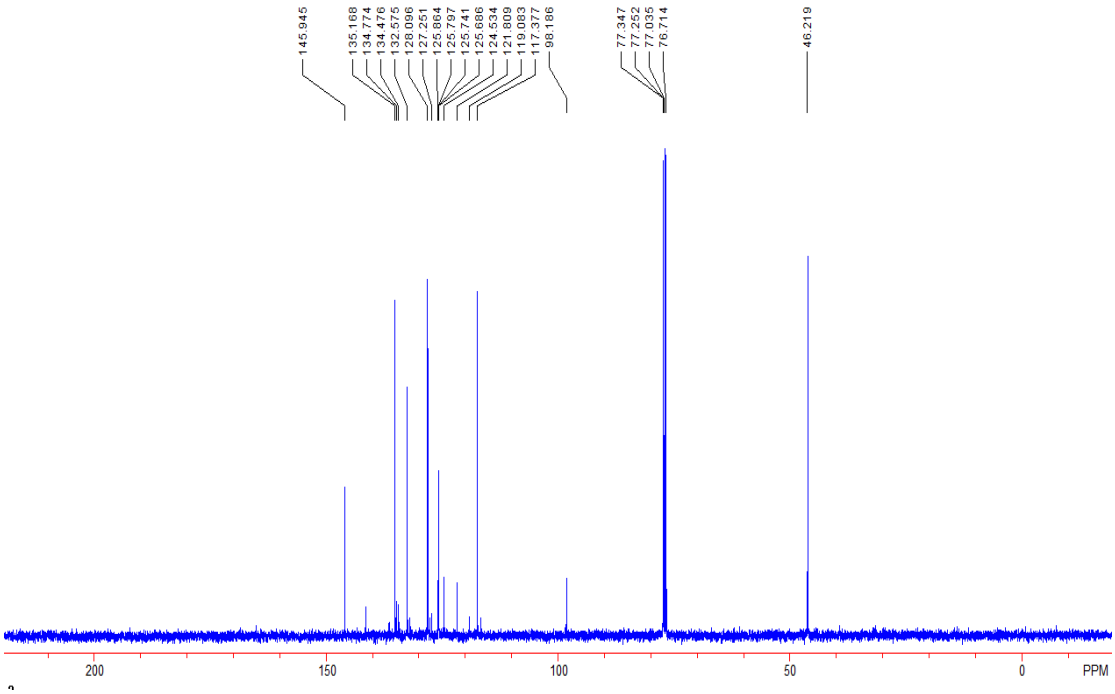


4j

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





4j

^{13}C NMR (100 MHz, $CDCl_3$)