Supporting Information

Copper-Catalyzed *gem*-Difluoroolefination of Diazo Compounds with $TMSCF_3$ via C–F Bond Cleavage

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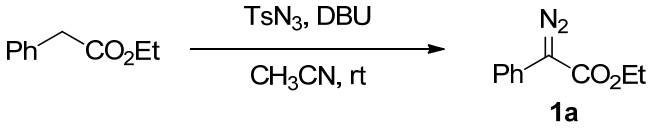
1. General Information.

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. The solvent NMP (*N*-methyl-2-pyrrolidone) and CH_2Cl_2 were distilled from CaH_2 and kept over activated 4Å MS; 1,4-dioxane, THF (Tetrahydrofuran), and toluene were distilled over sodium before being used. CuI and CuCl were purified according to reported procudures.[1] ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz or 300 MHz NMR spectrometer. ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of the residual solvent peak: $CHCl_3$ in $CDCl_3$: δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. For the isolated compounds, ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Data for ^1H, ^{13}C and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). Coupling constants are reported in hertz (Hz). Mass spactra were obtained on a mass spectrometer in the EI mode. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI mode.

2. Preparation of α–Diazo Ester 1a:[2]

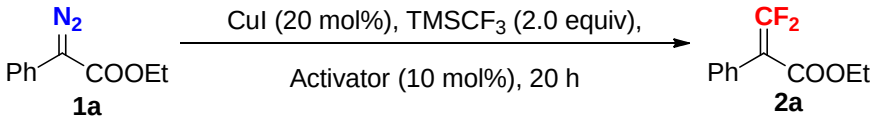


1a

At room temperature, a solution of 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) (2.28 g, 15 mmol) in anhydrous CH_3CN (20 mL) was added dropwise to a solution of ethyl phenyl acetate (1.64 g, 10 mmol) and *p*-toluenesulfonyl azide (TsN_3) (2.37 g, 12 mmol) in anhydrous CH_3CN (30 mL). Then the reaction mixture was stirred at room temperature for 15 hours. After water (20 mL) was added, the resulting mixture was extracted with diethyl ether (3 × 40 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous $MgSO_4$.

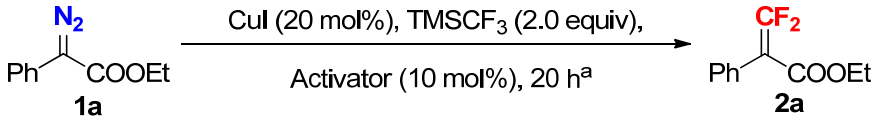
After the removal of the solvent under reduced pressure, the residual was purified by a silica gel column chromatography with petroleum ether (PE)/ethyl acetate (EA) (30:1) as the eluent to give **1a** as a red oil (1.73 g, 91% yield).

3. Typical experimental procedure for the investigation of Cu-catalyzed *gem*-difluoroolefination of compound 1a:



In a glovebox, to an oven-dried 10-mL vial equipped with a stir bar and a Teflon-lined screw cap were added CuI (19 mg, 0.1 mmol) and activator (e.g. CsF (7.6 mg, 0.05 mmol)). Then the vial was sealed and brought to the bench. Under N_2 atmosphere, $TMSCF_3$ (142 mg, 1.0 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**) (95 mg, 0.5 mmol) in solvent (if mixed solvents were used, e.g. NMP/1,4-dioxane (10:1), first added NMP (0.5 mL), then 1,4-dioxane (5 mL)) were added via syringe. Then the vial was sealed again. The resulting mixture was stirred over 20 hours. The reaction was monitored by ^{19}F NMR with $PhCF_3$ as an internal standard (or monitored by GC-MS) and results are summarized in Table S1.

Table S1: Cu-catalyzed *gem*-Difluoroolefination of compound 1a.

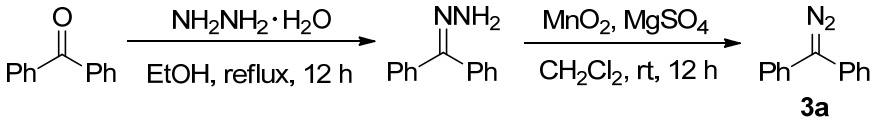


Entry	Activator	Solvent	Temp (°C)	Yield (%)[b]
1	CsF	NMP	rt	0
2	CsF	NMP	40	7
3	CsF	NMP	60	3

4	CsF	NMP	80	0
5	KF	NMP	rt	0
6	*t*BuOK	NMP	rt	0
7	CsF	DCM/NMP (4:1)	rt	7
8	CsF	THF/NMP (4:1)	rt	0
9	CsF	1,4-dioxane/NMP (4:1)	rt	31
10	CsF	1,4-dioxane/NMP (10:1)	rt	33
11	CsF	1,4-dioxane	rt	30
12	CsF	1,4-dioxane/NMP (10:1)	rt	33[c]
13	CsF	1,4-dioxane/NMP (10:1)	rt	2[d]
14	CsF	1,4-dioxane/NMP (10:1)	40	0[e]

[a] All reactions were carried out as followed: 0.1 mmol CuI, 0.05 mmol Activator, 1.0 mmol $TMSCF_3$ and 0.5 mmol **1a**, about 5 mL solvent were used. [b] Yields were determined by ^{19}F NMR with $PhCF_3$ as an internal standard. [c] 4 equivalents of $TMSCF_3$ were used. [d] 20 mol% CsF was used. [e] 40 mol% CsF was used.

4. Typical experimental procedure for preparation of diaryldiazomethanes 3 (Taking 3a for example):[3]



3a

Step 1. Preparation of benzophenone hydrazone:[3a,c]

Hydrazine monohydrate (80% purity, 18.2 mL, 300 mmol) was added to benzophenone (5.46 g, 30 mmol) in ethanol (60 mL). Then HOAc (0.5 mL) was added and the mixture was heated to reflux for 20 hours. After cooling to room temperature, benzophenone hydrazone precipitated as white needle-shaped crystals. Filtration of the crude mixture gave pure benzophenone hydrazone (4.7 g, 80%) as a white solid.

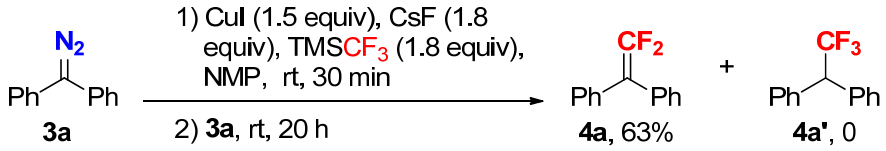
(*Note: When unsymmetrical ketones were used, an inseparable mixture of two isomers of ketone hydrazone was obtained, which was used in the next step without further purification.*)

Step 2. Preparation of diphenyldiazomethane:[3b,c]

A mixture of benzophenone hydrazone (4.5 g, 23 mmol), anhydrous $MgSO_4$ (2 g), and 60 mL CH_2Cl_2 was cooled to 0 °C. To this rapidly stirring mixture was added activated MnO_2 [4] (7.0 g, 80.5 mmol) in one portion. The reaction mixture was warmed to room temperature and kept stirring for 8 hours, then the solid was filtered off and washed with CH_2Cl_2. After removal of the solvent under reduced pressure, the residual was purified by silica gel with PE/Et_3N (20:1) as eluent to give **3a** as a purple oil or solid (3.8 g, 85% yield), which was fast used in next reaction**.**

(*Note: The silica gel must be pretreated with Et_3N and PE (Et_3N / PE = 1:10. Compounds* ***3a-3x*** *could be purified by pretreated silica gel,* ***3y*** *was used without chromatography purification. Et_3N, which was poisonous to Cu-catalyst, must be removed before used in next reaction. The purity of compounds* ***3a-3y*** *were determined by ^1H NMR, which was generally 85%~100%. The impurity was identified as Ar^1–N=N–Ar^2, which was also confirmed by GC-MS.*)

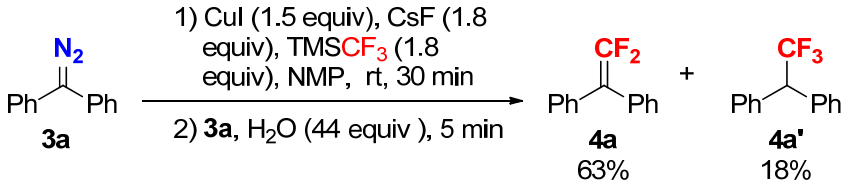
5. Typical experimental procedure for reaction of compound 3a with pre-generated $CuCF_3$ (eq 2(a)):[5]



In a glovebox, to an oven-dried 25-mL Schlenk tube equipped with a stir bar were added CuI (143 mg, 0.75 mmol) and CsF (137 mg, 0.9 mmol). Then the Schlenk tube was sealed with a septum and brought to the bench. $TMSCF_3$ (128 mg, 0.9 mmol) in NMP (3 mL) was added via syringe. After stirring at room temperature for 30 minutes, diphenyldiazomethane (**3a**) (97 mg, 0.5 mmol) in NMP (3 mL) was added. The reaction mixture was stirred at room

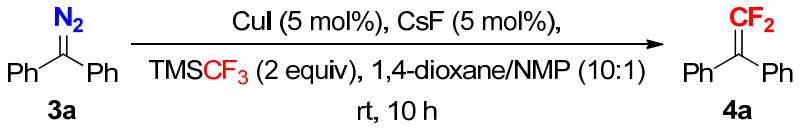
temperature for 20 hours. After the addition of $PhCF_3$ (42 mg) as an internal standard, the reaction was monitored by ^{19}F NMR.

6. Typical experimental procedure for reaction of compound 3a with pre-generated $CuCF_3$ with H_2O as promoter (eq 2(b)):[5]



In a glovebox, to an oven-dried 25-mL Schlenk tube equipped with a stir bar were added CuI (143 mg, 0.75 mmol) and CsF (137 mg, 0.9 mmol). Then the Schlenk tube was sealed with a septum and brought to the bench. $TMSCF_3$ (128 mg, 0.9 mmol) in NMP (3 mL) was added via syringe. After stirring at room temperature for 30 minutes, diphenyldiazomethane (**3a**) (97 mg, 0.5 mmol) in NMP (3 mL) was added, then H_2O (0.4 mL, 22 mmol) was added. After the addition of H_2O, the color of reaction mixture was changed from purple to light yellow during 5 minutes, which indicated that **3a** was exhausted. Then $PhCF_3$ (44 mg) was added as an internal standard, the reaction was monitored by ^{19}F NMR.

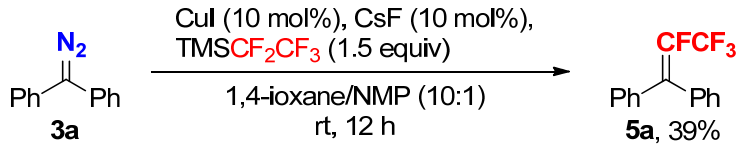
7. Typical experimental procedures for preparation of 2,2-diaryl-1,1-difluoroalkenes 4 (Taking 4a for example):



In a glovebox, to an oven-dried 10-mL vial equipped with a stir bar and a Teflon-lined screw cap were added CuI (9.5 mg, 0.05 mmol) and CsF (7.6 mg, 0.05 mmol)). Then the vial

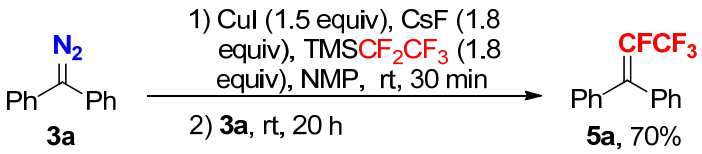
was sealed and brought to the bench. Under N_2 atmosphere, $TMSCF_3$ (142 mg, 1.0 mmol) in NMP (0.5 mL) was added, then diphenyldiazomethane (**3a**) (194 mg, 1.0 mmol) in 1,4-dioxane (5 mL) was added. Then the vial was sealed again. The resulting mixture was stirred for 10 hours at room temperature. After addition of H_2O (15 mL), the mixture was extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with H_2O (2 × 20 mL), then brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residual was purified by chromatography on silica gel with petroleum ether as eluent to afford **4a** (163 mg, 75% yield) as a colorless oil.

8. Typical experimental procedure for reaction of compound 3a with $TMSCF_2CF_3$ with CuI as catalyst (eq 3):



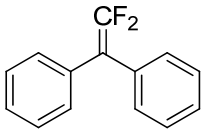
In a glovebox, to an oven-dried 10-mL vial equipped with a stir bar and a Teflon-lined screw cap were added CuI (9.5 mg, 0.05 mmol) and CsF (7.6 mg, 0.05 mmol)). Then the vial was sealed and brought to the bench. Under N_2 atmosphere, $TMSCF_2CF_3$ (144 mg, 0.75 mmol) in NMP (0.5 mL) was added, then diphenyldiazomethane (**3a**) (97 mg, 0.5 mmol) in 1,4-dioxane (5 mL) was added. Then the vial was sealed again. The resulting mixture was stirred for 12 hours at room temperature. After addition of H_2O (15 mL), the mixture was extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with H_2O (2 × 20 mL), then brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residual was purified by chromatography on silica gel with petroleum ether as eluent to afford **5a** (52 mg, 39% yield) as a colorless oil.

9. Typical experimental procedure for reaction of compound 3a with pre-generated $CuCF_2CF_3$ (eq 4):[5]



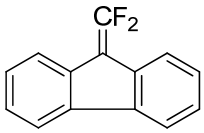
In a glovebox, to an oven-dried 25-mL Schlenk tube equipped with a stir bar were added CuI (143 mg, 0.75 mmol) and CsF (137 mg, 0.9 mmol). Then the Schlenk tube was sealed with a septum and brought to the bench. $TMSCF_2CF_3$ (173 mg, 0.9 mmol) in NMP (3 mL) was added via syringe. After stirring at room temperature for 30 minutes, diphenyldiazomethane (**3a**) (97 mg, 0.5 mmol) in NMP (3 mL) was added. The reaction mixture was stirred at room temperature for 20 hours. After the addition of $PhCF_3$ (50 mg) as an internal standard, the reaction was monitored by ^{19}F NMR.

(2,2-Difluoroethene-1,1-diyl)dibenzene (4a):[6]



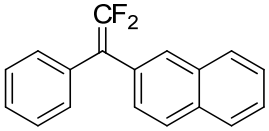
Colorless oil. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ 7.39–7.28 (m, 9H); ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ –87.82 (s, 2F); MS (EI, *m/z*): 216 (M^+, 100.00), 165 (84.69).

9-(Difluoromethylene)-9H-fluorene (4b):[7]



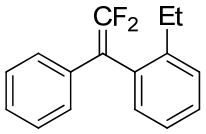
Yellow Solid. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 7.76 (d, *J* = 6.7 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.40–7.32 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ –75.24 (s, 2F); MS (EI, *m/z*): 214 (M^+, 100.00), 163 (13.78).

2-(2,2-Difluoro-1-phenylvinyl)naphthalene (4c):



White solid. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 7.86–7.77 (m, 4H), 7.51–7.47 (m, 2H), 7.40–7.32 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ –87.32 (d, *J* = 31.4 Hz, 1F), –87.54 (d, *J* = 31.4 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 154.2 (t, *J* = 293.7 Hz), 134.6 (t, *J* = 3.0 Hz), 133.5, 132.8, 131.9 (t, *J* = 3.9 Hz), 129.9 (t, *J* = 3.4 Hz), 129.2 (t, *J* = 3.0 Hz), 128.7, 128.3, 128.2, 127.9, 127.8, 127.5 (t, *J* = 3.0 Hz), 126.6, 126.5, 96.7 (t, *J* = 18.3 Hz); IR (film): 3058, 1706, 1445, 1251, 1238, 993, 818, 760, 698 cm^{-1}; MS (EI, *m/z*): 266 (M^+, 100.00), 215 (56.49); HRMS (EI): exact mass calcd for $C_{18}H_{14}F_2$ (M^+): 266.0907, found: 266.0905.

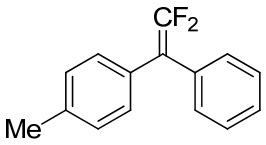
1-(2,2-Difluoro-1-phenylvinyl)-2-ethylbenzene (4d):



Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.37–7.18 (m, 9H), 2.47 (q, *J* = 7.7 Hz, 2H), 1.06 (t, *J* = 7.7 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3/CFCl_3$): δ –83.31 (d, *J* = 32.0 Hz, 1F), –88.50 (d, *J* = 32.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 153.6 (dd, *J* = 298.3 Hz, *J* = 287.2 Hz), 143.7 (d, *J* = 3.1 Hz), 134.2 (m), 132.4 (d, *J* = 4.8 Hz), 131.3 (t, *J* = 3.0 Hz), 129.0, 128.8, 128.5, 128.3 (dd, *J* = 5.3 Hz, *J* = 3.0 Hz), 127.2, 126.1, 94.8 (dd, *J* = 21.0 Hz, *J* = 14.6 Hz), 26.2, 14.9; IR (film): 3061, 2969, 2875, 1709, 1446, 1247, 985, 761 cm^{-1}; MS (EI, *m/z*):

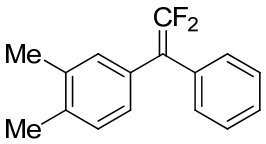
244 (M^+, 45.45), 178 (100.00); HRMS (EI): exact mass calcd for $C_{16}H_{14}F_2$ (M^+): 244.1064, found: 244.1067.

1-(2,2-Difluoro-1-phenylvinyl)-4-methylbenzene (4e):[8]



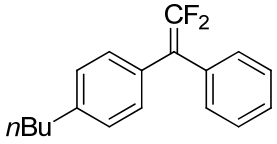
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.37–7.23 (m, 5H), 7.15 (s, 4H), 2.35 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3/CFCl_3$): δ –88.09 (d, J = 33.9 Hz, 1F), –88.30 (d, J = 34.1 Hz, 1F); MS (EI, *m/z*): 230 (M^+, 100.00), 215 (33.02).

4-(2,2-Difluoro-1-phenylvinyl)-1,2-dimethylbenzene (4f):



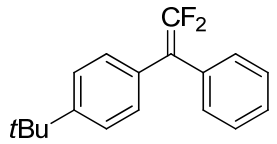
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.36–7.23 (m, 5H), 7.11 (d, J = 7.6 Hz, 1H), 7.03, (s, 1H), 6.99 (d, J = 7.9 Hz, 1H), 2.26 (s, 3H), 2.23 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3/CFCl_3$): δ –88.05 (d, J = 34.2 Hz, 1F), –88.53 (d, J = 34.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 153.7 (t, J = 292.1 Hz), 136.6, 136.1, 134.6 (t, J = 3.8 Hz), 131.8 (t, J = 3.1 Hz), 130.8 (t, J = 3.1 Hz), 129.7, 129.6 (t, J = 3.4 Hz), 128.4, 127.1 (t, J = 3.0 Hz), 96.1 (t, J = 18.4 Hz), 19.8, 19.5; IR (film): 3059, 2922, 1708, 1446, 1247, 984, 761 cm^{-1}; MS (EI, *m/z*): 244 (M^+, 100.00), 229 (39.48), 178 (20.74); HRMS (EI): exact mass calcd for $C_{16}H_{14}F_2$ (M^+): 244.1064, found: 244.1063.

1-Butyl-4-(2,2-difluoro-1-phenylvinyl)benzene (4g):



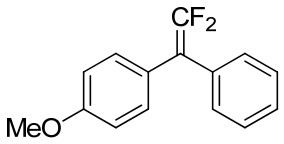
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.37–7.23 (m, 5H), 7.16 (s, 4H), 2.61 (t, J = 7.9 Hz, 2H), 1.61 (m, 2H), 1.38 (m, 2H), 0.93 (t, J = 7.1 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –88.16 (s, 2F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 153.7 (t, J = 293.5 Hz), 142.3, 134.5, 131.5, 129.6 (t, J = 3.1 Hz), 129.4 (t, J = 3.1 Hz), 128.4, 128.3, 127.5, 126.8 (d, J = 10.7 Hz), 96.1 (t, J = 18.4 Hz), 35.3, 33.5, 22.4, 13.9; IR (film): 3058, 2958, 2931, 2859, 1706, 1514, 1446, 1244, 988, 762, 698 cm^{-1}; MS (EI, *m/z*): 272 (M^+, 53.66), 229 (100.00); HRMS (EI): exact mass calcd for $C_{18}H_{18}F_2$ (M^+): 272.1377, found: 272.1378.

1-(*tert*-Butyl)-4-(2,2-difluoro-1-phenylvinyl)benzene (4h):



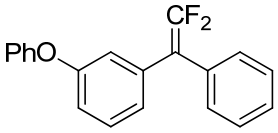
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.37–7.23 (m, 7H), 7.18 (d, J = 8.4 Hz, 2H), 1.32 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –87.94 (d, J = 34.1 Hz, 1F), –88.14 (d, J = 34.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 153.9 (t, J = 293.6 Hz), 150.6, 134.6 (t, J = 3.0 Hz), 131.4 (t, J = 2.8 Hz), 129.9 (t, J = 3.0 Hz), 129.3 (t, J = 3.8 Hz), 128.5, 127.6, 125.5, 96.2 (t, J = 18.4 Hz), 34.7, 31.4; IR (film): 3059, 2965, 1707, 1517, 1446, 1246, 989, 835, 763, 698 cm^{-1}; MS (EI, *m/z*): 272 (M^+, 38.81), 257 (100.00); HRMS (EI): exact mass calcd for $C_{18}H_{18}F_2$ (M^+): 272.1377, found: 272.1380.

1-(2,2-Difluoro-1-phenylvinyl)-4-methoxybenzene (4i):[9]



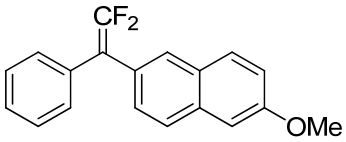
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.36–7.22 (m, 5H), 7.18 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –88.63 (d, J = 35.0 Hz, 1F), –88.83 (d, J = 35.0 Hz, 1F); MS (EI, *m/z*): 246 (M^+, 100.00), 183 (39.70).

1-(2,2-Difluoro-1-phenylvinyl)-3-phenoxybenzene (4j):



White solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.37–7.23 (m, 8H), 7.09 (t, J = 7.4 Hz, 1H), 7.01–6.97 (m, 4H), 6.92 (d, J = 8.1 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –86.841 (d, J = 30.9 Hz, 1F), –87.02 (d, J = 31.1 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 157.2, 157.0, 153.8 (t, J = 293.8 Hz), 136.1 (m), 133.9 (t, J = 3.2 Hz), 129.8, 129.62, 129.58, 129.54, 128.4, 127.7, 124.5 (t, J = 3.5 Hz), 123.3, 120.3 (t, J = 4.0 Hz), 118.8, 117.9, 95.9 (t, J = 18.1 Hz); IR (film): 3063, 1706, 1489, 1253, 1002, 756, 696 cm^{-1}; MS (EI, *m/z*): 308 (M^+, 100.00), 165 (37.02); HRMS (EI): exact mass calcd for $C_{20}H_{14}OF_2$ (M^+): 308.1013, found: 308.1017.

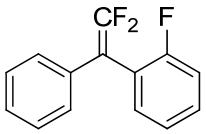
2-(2,2-Difluoro-1-phenylvinyl)-6-methoxynaphthalene (4k):



White solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.72–7.65 (m, 3H), 7.39–7.24 (m, 6H), 7.16–7.12 (m, 2H), 3.92 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –87.79 (d, J = 33.0 Hz, 1F), –87.96 (d, J = 33.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 158.3, 154.1 (t, J =

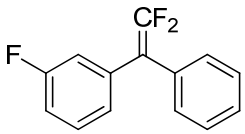
292.7 Hz), 134.7 (t, J = 2.9 Hz), 134.0, 129.9 (t, J = 3.9 Hz), 129.7, 129.5 (t, J = 3.0 Hz), 128.9 (m), 128.6, 127.9 (t, J = 3.1 Hz), 127.7, 127.1, 119.4, 105.7, 96.6 (t, J = 18.4 Hz), 55.3; IR (film): 3061, 2967, 1716, 1486, 1244, 1221, 1003, 856, 765, 696 cm^{-1}; MS (EI, *m/z*): 296 (M^+, 100.00), 202 (19.94); HRMS (EI): exact mass calcd for $C_{19}H_{14}OF_2$ (M^+): 296.1013, found: 296.1019.

1-(2,2-Difluoro-1-phenylvinyl)-2-fluorobenzene (4m):



Colorless oil. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ 7.37–7.10 (m, 9H); ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ –83.31 (dd, J = 27.3 Hz, J = 13.6 Hz, 1F), –87.50 (d, J = 25.8 Hz, 1F), –113.3 (s, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 160.5 (d, J = 251.2 Hz), 153.7 (dd, J = 296.2 Hz, J = 291.9 Hz), 133.6 (t, J = 14.2 Hz), 132.3 (q, J = 1.6 Hz), 130.2, 130.1, 128.7 (t, J = 3.8 Hz), 128.5, 127.5, 124.2 (d, J = 3.9 Hz), 116.1, 115.9, 90.5 (dd, J = 20.6 Hz, J = 19.0 Hz); IR (film): 3062, 3037, 1717, 1493, 1448, 1255, 988, 758 cm^{-1}; MS (EI, *m/z*): 234 (M^+, 100.00), 183 (64.45), 165 (53.89); HRMS (EI): exact mass calcd for $C_{14}H_9F_3$ (M^+): 234.0656, found: 234.0654.

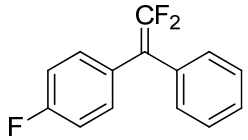
1-(2,2-Difluoro-1-phenylvinyl)-3-fluorobenzene (4n):



Colorless oil. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 7.44–7.23 (m, 6H), 7.06–6.96 (m, 3H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –86.41 (d, J = 29.9 Hz, 1F), –86.63 (d, J = 29.9 Hz, 1F), –112.88~–112.97 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 162.68 (d, J = 245.6 Hz),

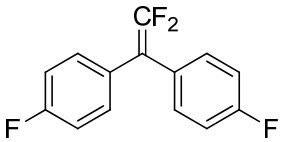
153.9 (dd, J = 294.8 Hz, J = 293.2 Hz), 136.4 (m), 133.6 (t, J = 3.0 Hz), 129.8 (d, J = 8.4 Hz), 129.6 (t, J = 3.0 Hz), 128.5, 127.8, 125.2 (q, J = 3.0 Hz), 116.6 (t, J = 3.9 Hz), 116.4 (t, J = 3.9 Hz), 114.6, 114.4, 95.4 (t, J = 17.5 Hz); IR (film): 3063, 1708, 1586, 1488, 1255, 1001, 836, 696 cm^{-1}; MS (EI, *m/z*): 234 (M^+, 100.00), 183 (84.15); HRMS (EI): exact mass calcd for $C_{14}H_9F_3$ (M^+): 234.0656, found: 234.0653.

1-(2,2-Difluoro-1-phenylvinyl)-4-fluorobenzene (4o):[9]



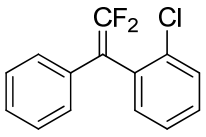
Colorless oil. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ 7.36–7.21 (m, 7H), 7.03 (t, J = 8.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ –87.90 (s, 1F), –87.92 (s, 1F), –114.21 (m, 1F); MS (EI, *m/z*): 234 (M^+, 100.00), 183 (91.20).

4,4'-(2,2-Difluoroethene-1,1-diyl)bis(fluorobenzene) (4p):[10]



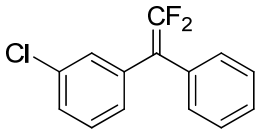
Colorless oil. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ 7.24–7.18 (m, 4H), 7.06–7.01 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$): δ –87.97 (s, 2F), –113.92 (m, 2F); MS (EI, *m/z*): 252 (M^+, 76.59), 201 (100.00).

1-Chloro-2-(2,2-difluoro-1-phenylvinyl)benzene (4q):



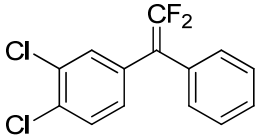
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 7.49–7.46 (m, 1H), 7.35–7.31 (m, 5H), 7.28–7.23 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ –82.61 (d, J = 27.3 Hz, 1F), –88.37 (d, J = 28.7 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 153.9 (dd, J = 297.6 Hz, J = 289.1 Hz), 135.1 (m), 133.3 (dd, J = 5.3 Hz, J = 3.0 Hz), 132.8 (dd, J = 5.3 Hz, J = 2.3 Hz), 132.5 (dd, J = 3.0 Hz, J = 1.5 Hz), 130.1, 129.8, 128.6, 128.4 (dd, J = 5.4 Hz, J = 3.0 Hz), 127.5, 127.1, 94.0 (dd, J = 22.1 Hz, J = 18.3 Hz); IR (film): 3060, 1716, 1497, 1249, 985, 757 cm^{-1}; MS (EI, *m/z*): 250 (M^+, 61.93), 165 (100.00); HRMS (EI): exact mass calcd for $C_{14}H_9F_2Cl$ (M^+): 250.0361, found: 250.0365.

1-Chloro-3-(2,2-difluoro-1-phenylvinyl)benzene (4r):



Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.39–7.23 (m, 8H), 7.16–7.12 (m, 1H), 7.28–7.23 (m, 3H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –86.41 (d, J = 28.6 Hz, 1F), –86.59 (d, J = 30.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 153.9 (t, J = 294.7 Hz), 136.1 (t, J = 3.1 Hz), 134.3, 133.5 (t, J = 3.2 Hz), 129.61, 129.56, 129.53, 128.5, 127.8, 127.7, 95.5 (m); IR (film): 3064, 1709, 1493, 1248, 996, 787, 695 cm^{-1}; MS (EI, *m/z*): 250 (M^+, 100.00), 165 (84.77); HRMS (EI): exact mass calcd for $C_{14}H_9F_2Cl$ (M^+): 250.0361, found: 250.0363.

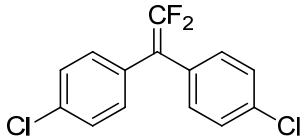
1,2-Dichloro-4-(2,2-difluoro-1-phenylvinyl)benzene (4s):



White solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.42–7.32 (m, 5H), 7.23 (d, J = 8.9 Hz, 2H), 7.10 (d, J = 8.4 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –85.71 (d, J = 27.9 Hz, 1F),

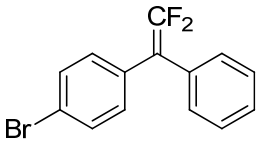
–86.07 (d, J = 27.8 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 153.9 (t, J = 294.6 Hz), 134.4 (t, J = 3.8 Hz), 133.2 (t, J = 3.0 Hz), 132.7, 131.8, 131.4 (t, J = 3.1 Hz), 130.4, 129.6 (t, J = 2.9 Hz), 128.9 (t, J = 3.8 Hz), 128.7, 128.1, 95.0 (dd, J = 19.8 Hz, J = 17.5 Hz); IR (film): 3062, 1708, 1474, 1246, 996, 760, 698 cm^{-1}; MS (EI, *m/z*): 284 (M^+, 92.47), 214 (100.00); HRMS (EI): exact mass calcd for $C_{14}H_8F_2Cl_2$ (M^+): 283.9971, found: 283.9972.

4,4'-(2,2-Difluoroethene-1,1-diyl)bis(chlorobenzene) (4t):[10]



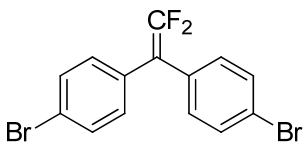
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 7.32 (d, J = 8.2 Hz, 4H), 7.16 (d, J = 8.3 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ –86.41 (s, 2F); MS (EI, *m/z*): 284 (M^+, 100.00), 214 (97.48).

1-Bromo-4-(2,2-difluoro-1-phenylvinyl)benzene (4u):[8]



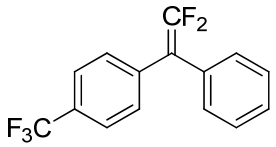
White solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.46 (d, J = 8.5 Hz, 2H), 7.38–7.22 (m, 5H), 7.12 (d, J = 8.3 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –86.75 (d, J = 31.0 Hz, 1F), –87.03 (d, J = 30.9 Hz, 1F); MS (EI, *m/z*): 294 (M^+, 25.66), 296 ([M+2]$^+$, 24.67), 84 (100.00).

4,4'-(2,2-Difluoroethene-1,1-diyl)bis(bromobenzene) (4v):[10]



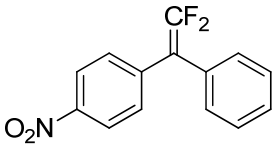
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 7.47 (d, J = 8.2 Hz, 4H), 7.10 (d, J = 8.2 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ –86.14 (s, 2F); MS (EI, *m/z*): 372 (M^+, 26.93), 374 ($[M+2]^+$, 55.58), 376 ($[M+4]^+$, 33.58), 214 (100.00).

1-(2,2-Difluoro-1-phenylvinyl)-4-(trifluoromethyl)benzene (4w):[8]



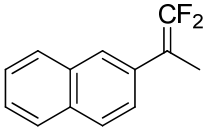
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.60 (d, J = 8.3 Hz, 2H),7.39–7.29 (m, 5H), 7.26–7.22 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ –62.65 (s, 3F), –85.63 (d, J = 28.9 Hz, 1F), –88.36 (d, J = 28.9 Hz, 1F); MS (EI, *m/z*): 284 (M^+, 100.00), 165 (46.21).

1-(2,2-Difluoro-1-phenylvinyl)-4-nitrobenzene (4x):[8]



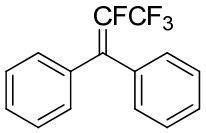
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 8.18 (d, J = 8.6 Hz, 2H), 7.44–7.33 (m, 5H), 7.23 (d, J = 7.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ –83.53 (d, J = 23.8 Hz, 1F), –84.81 (d, J = 23.2 Hz, 1F); MS (EI, *m/z*): 261 (M^+, 100.00), 165 (56.48), 214 (49.73).

2-(1,1-Difluoroprop-1-en-2-yl)naphthalene (4y):[11]



White solid. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ 7.82−7.78 (m, 4H), 7.51−7.45 (m, 3H), 2.07 (t, J = 3.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$/$CFCl_3$): δ −89.72 (dq, J = 43.5 Hz, J = 2.9 Hz, 1F), −90.37 (d, J = 42.3 Hz, 1F); MS (EI, *m/z*): 204 (M^+, 100.00), 128 (55.66).

(Perfluoroprop-1-ene-1,1-diyl)dibenzene (5a):[12]



Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.42−7.27 (m, 10H); ^{19}F NMR (282 MHz, $CDCl_3$/$CFCl_3$): δ −64.3 (d, J = 9.6 Hz, 3F), −128.8 (d, J = 9.5 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 142.0 (dq, J = 36.7 Hz, J = 261.7 Hz), 135.2, 134.43, 134.39, 129.6, 129.5, 129.0, 128.7, 128.3, 119.4 (qd, J = 273.3 Hz, J = 42.1 Hz); IR (film): 3061, 3030, 1667, 1447, 1345, 1194, 1137, 1099, 762, 699 cm^{-1}; MS (EI, *m/z*): 266 (M^+, 100.00), 196 (72.03); HRMS (EI): exact mass calcd for $C_{15}H_{10}F_4$ (M^+): 266.0719, found:266.0722.

10. References

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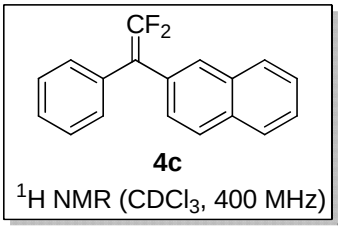
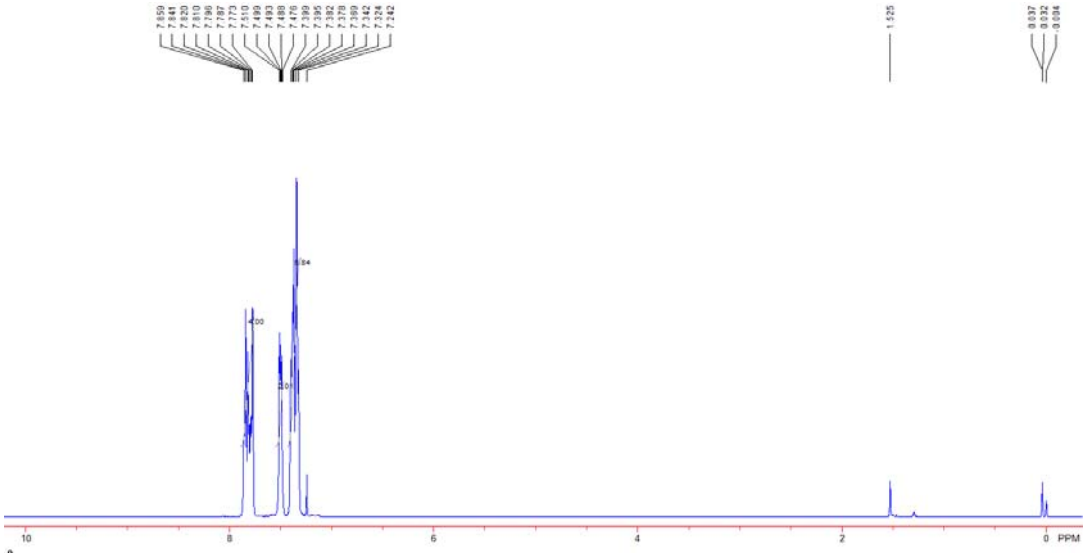
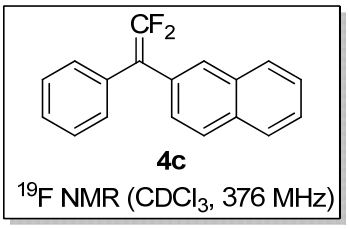
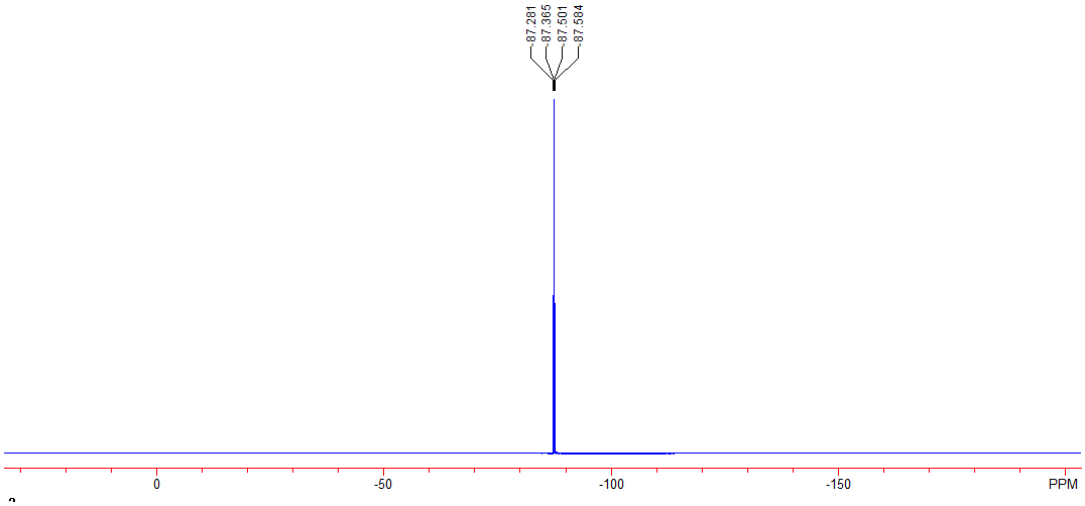
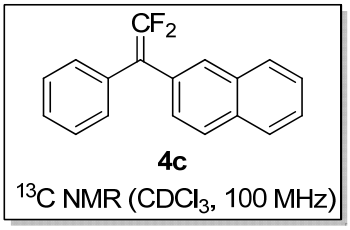
11. ^{1}H, ^{19}F and ^{13}C NMR Spectra of New Products.

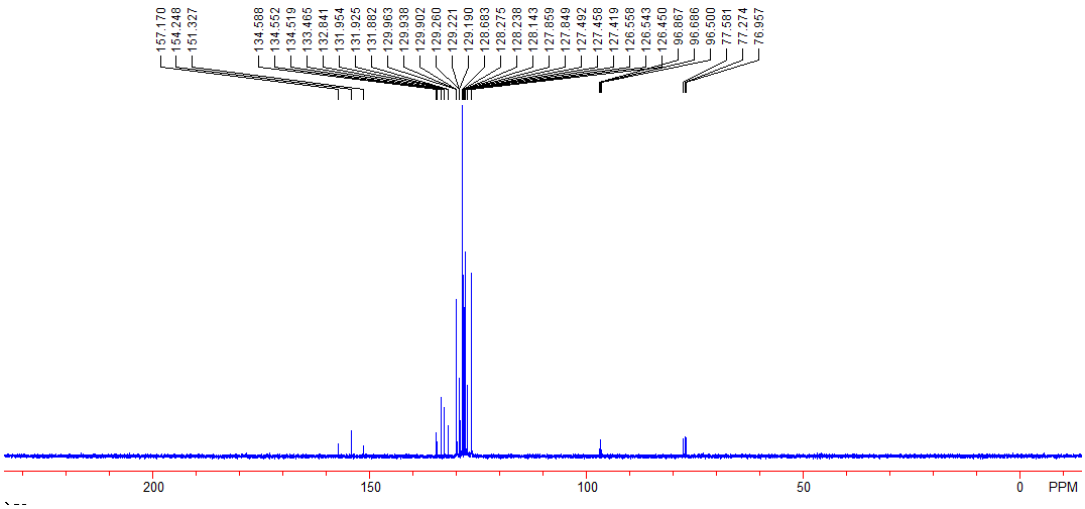









CF2
4c
13C NMR (CDCl3, 100 MHz)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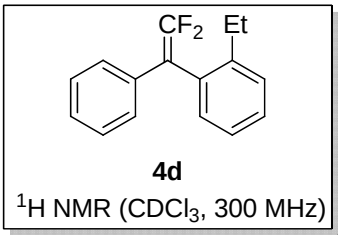
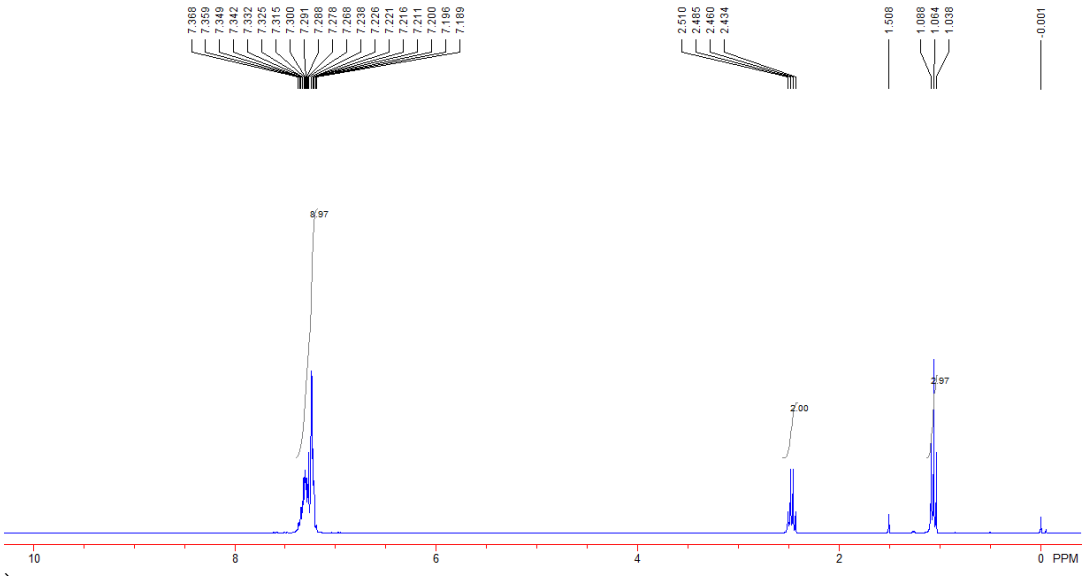
154.248
151.327
134.588
134.552
134.519
133.465
132.841
131.954
131.925
131.882
129.963
129.938
129.902
129.260
129.221
129.190
128.683
128.275
128.238
128.143
127.859
127.849
127.492
127.458
127.419
126.558
126.543
126.450
96.867
96.686
96.500
77.581
77.274
76.957
200
150
100
50
0
PPM


CF2
Et
4d
1H NMR (CDCl3, 300 MHz)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7.359
7.349
7.342
7.332
7.325
7.315
7.300
7.291
7.288
7.278
7.268
7.238
7.226
7.221
7.216
7.211
7.200
7.196
7.189
2.510
2.465
2.460
2.434
1.508
1.088
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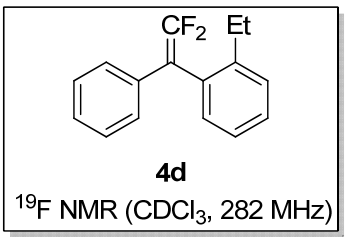
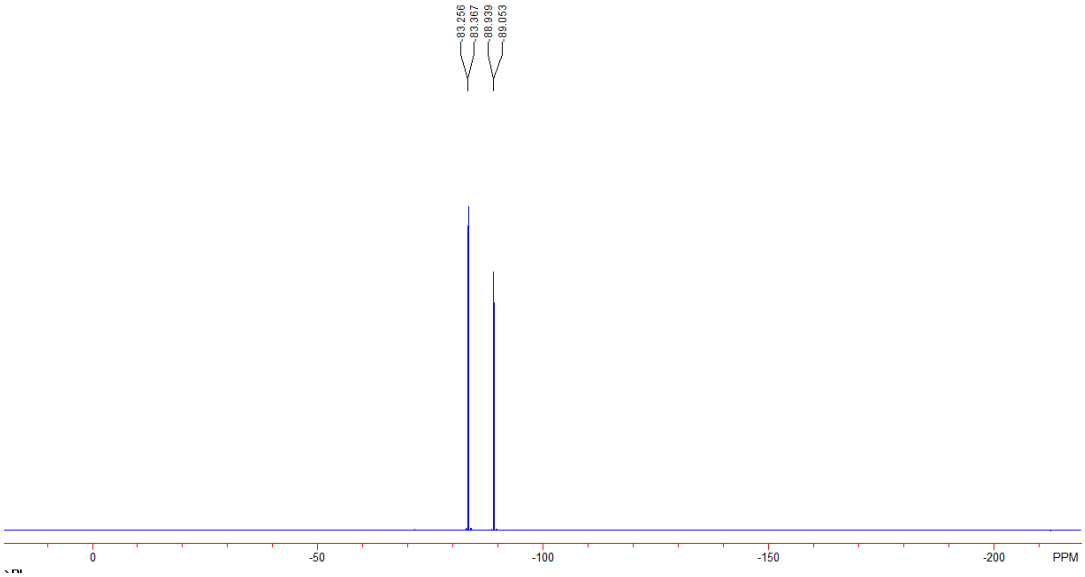
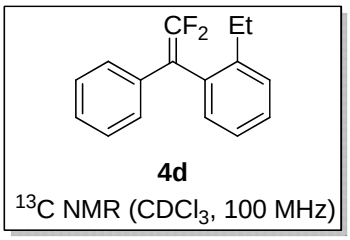
1.038
0.001
8.97
2.00
2.97
10
8
6
4
2
0
PPM



4d

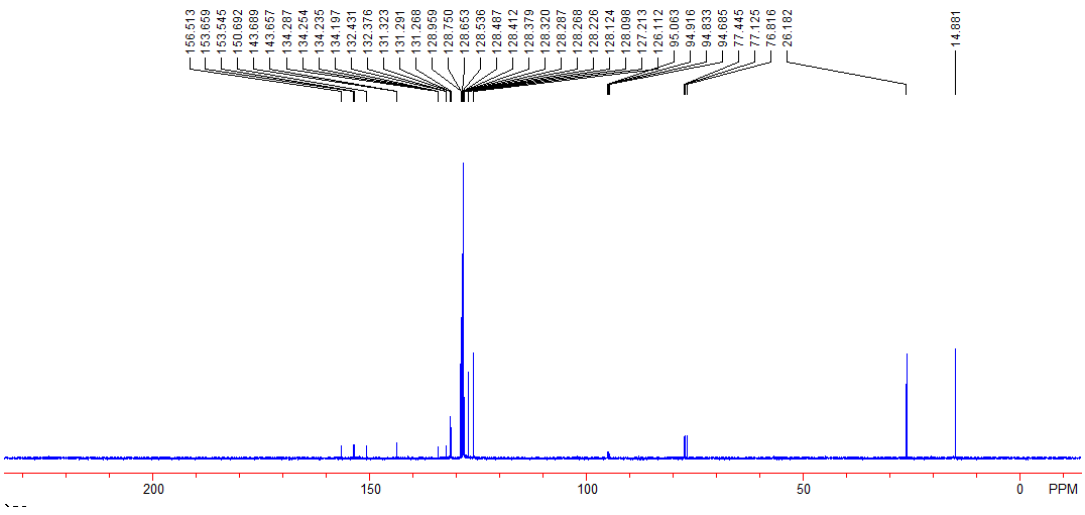
^{19}F NMR ($CDCl_3$, 282 MHz)

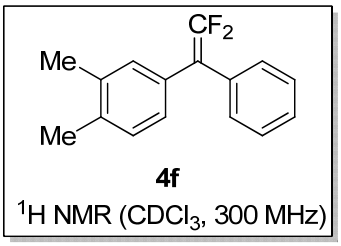




4d

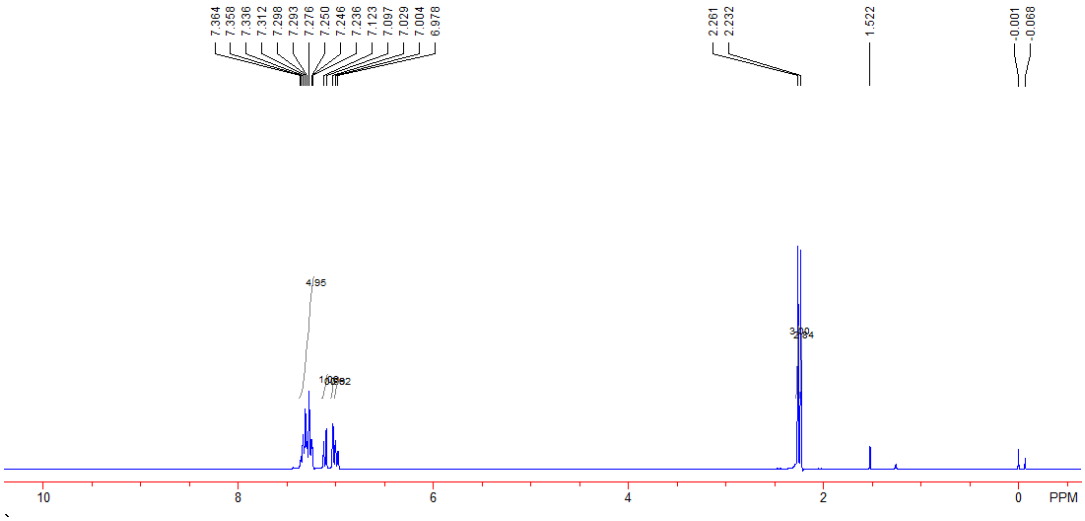
^{13}C NMR ($CDCl_3$, 100 MHz)

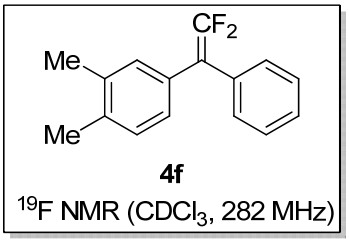




4f

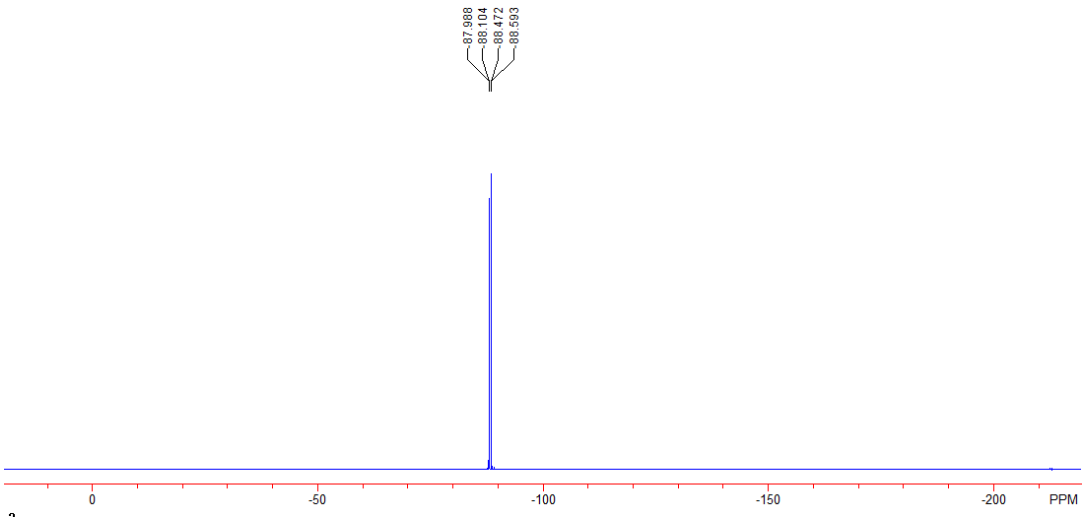
^{1}H NMR ($CDCl_3$, 300 MHz)

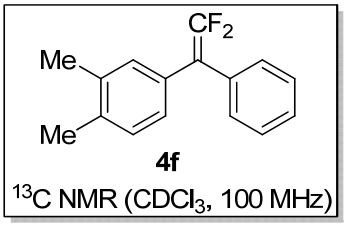




4f

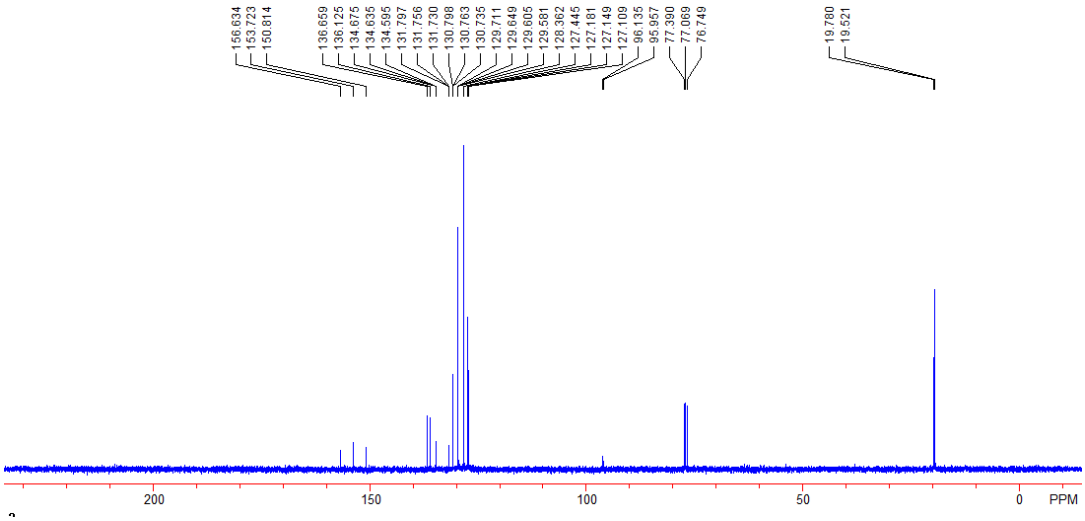
^{19}F NMR ($CDCl_3$, 282 MHz)

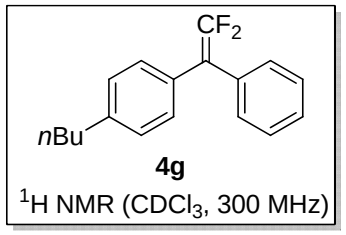




4f

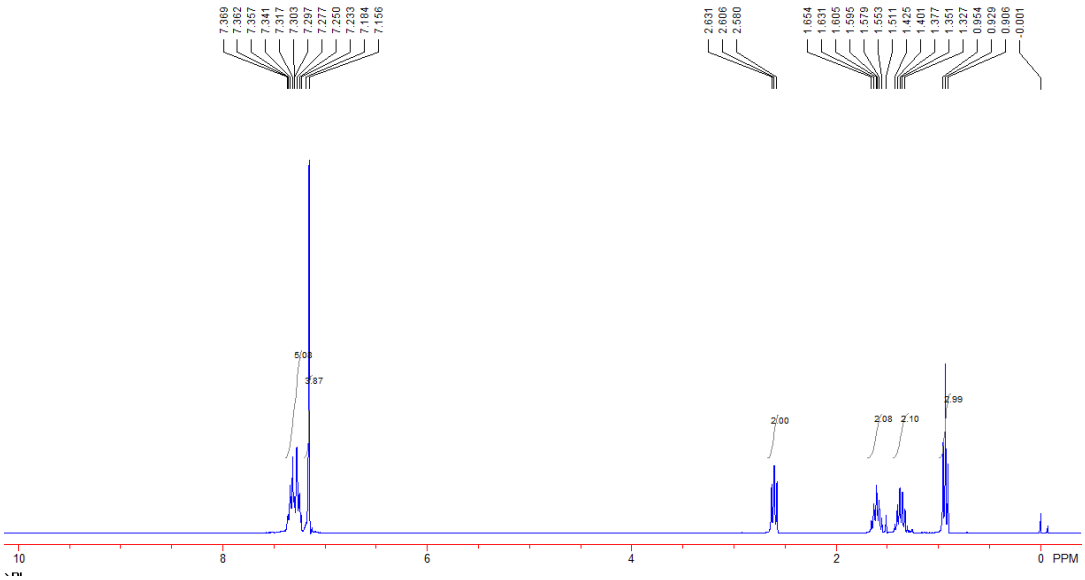
^{13}C NMR ($CDCl_3$, 100 MHz)

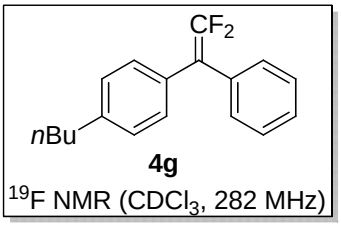




4g

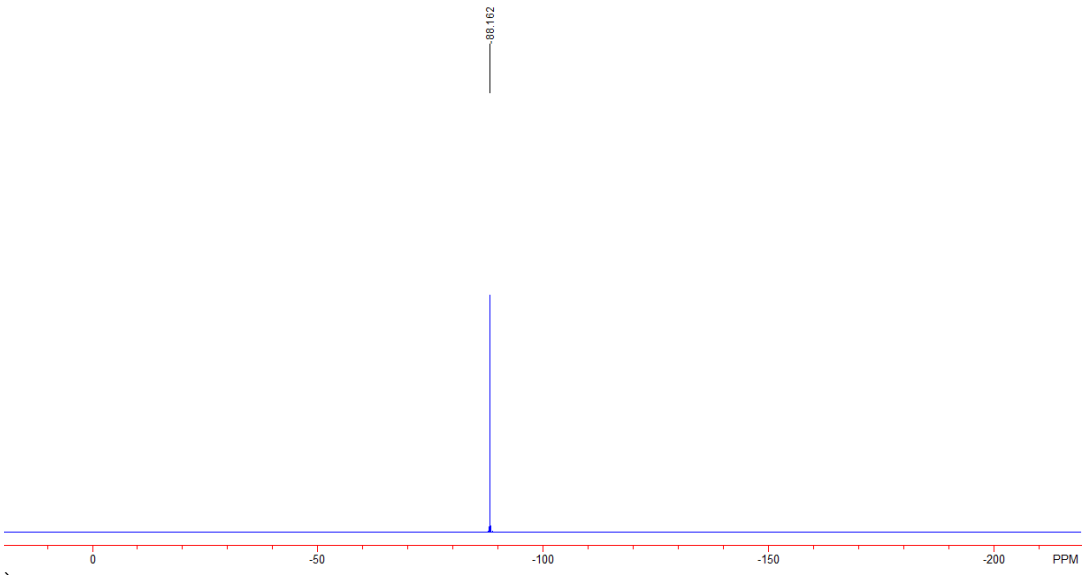
^{1}H NMR ($CDCl_3$, 300 MHz)

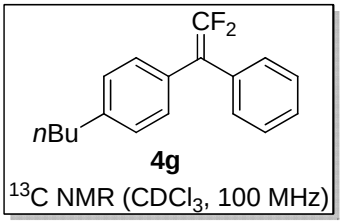




4g

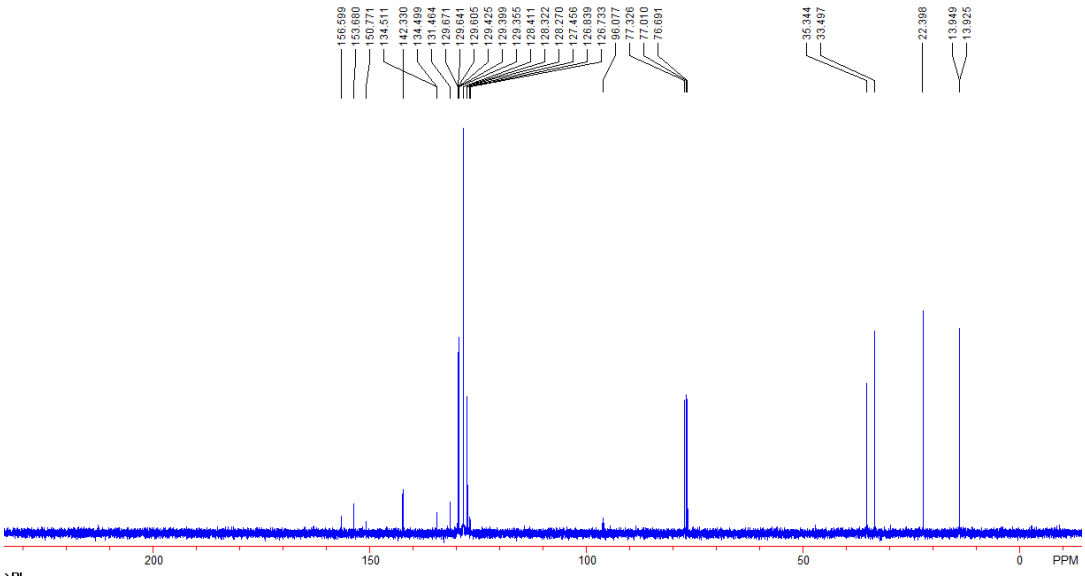
^{19}F NMR ($CDCl_3$, 282 MHz)

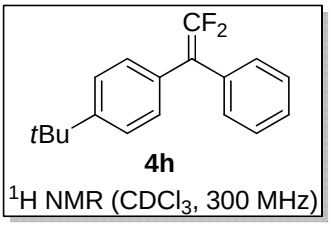




4g

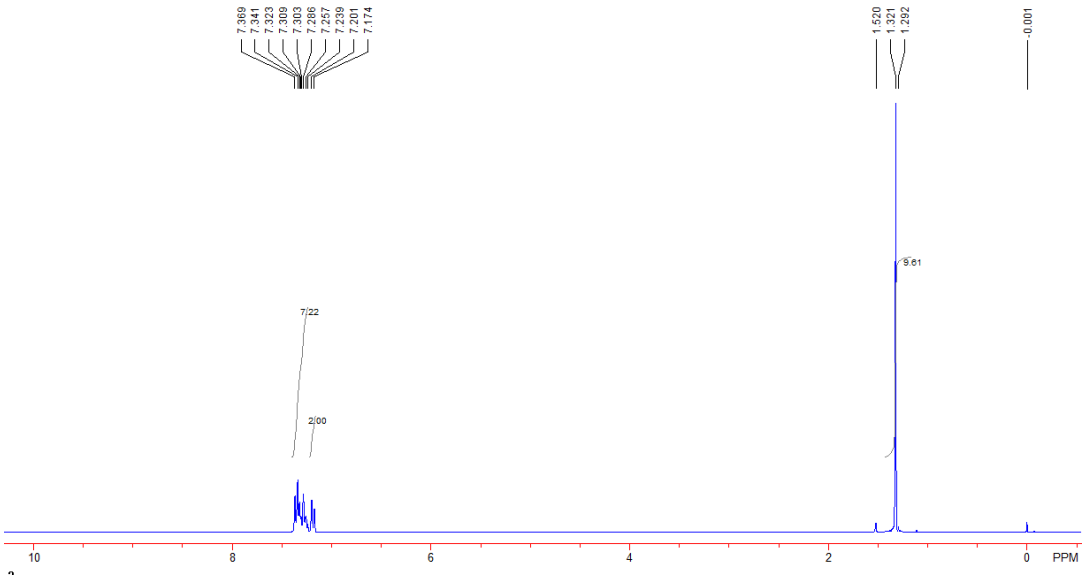
^{13}C NMR ($CDCl_3$, 100 MHz)

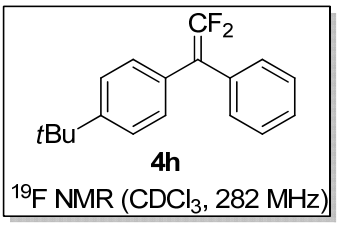




4h

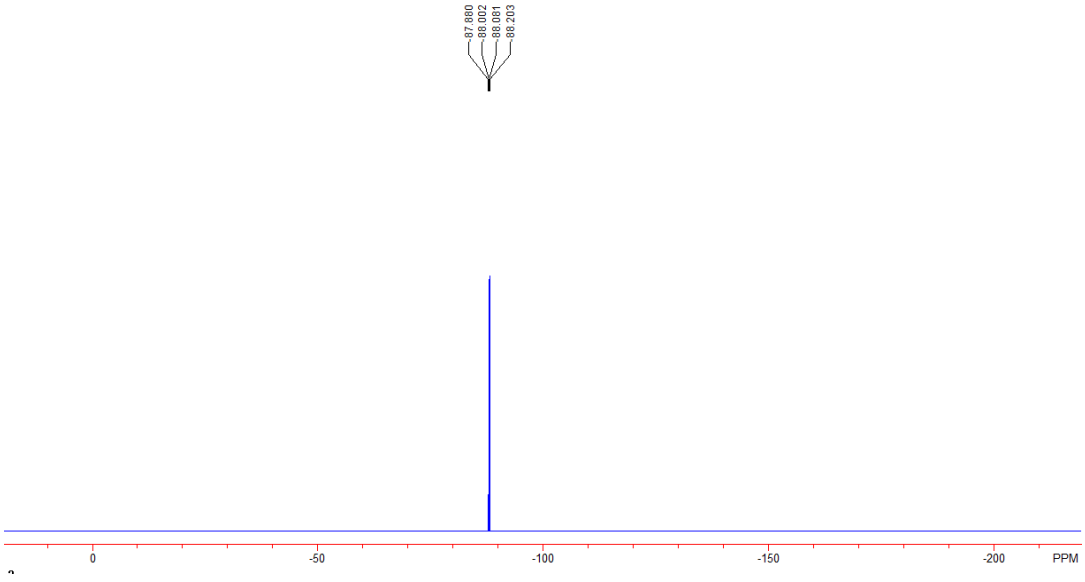
^{1}H NMR ($CDCl_3$, 300 MHz)

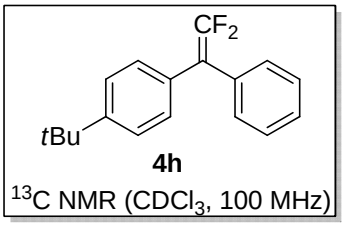




4h

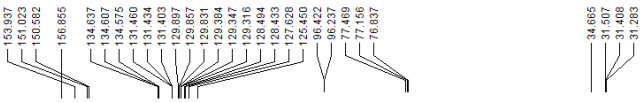
^{19}F NMR ($CDCl_3$, 282 MHz)

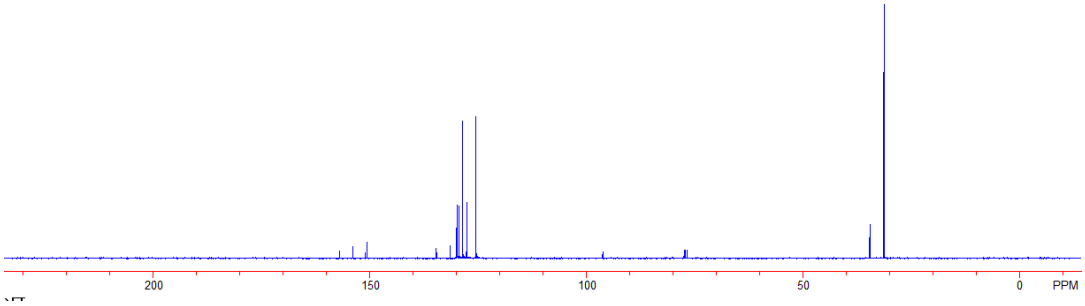


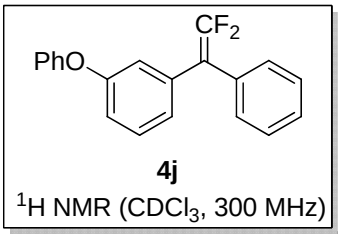


4h

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

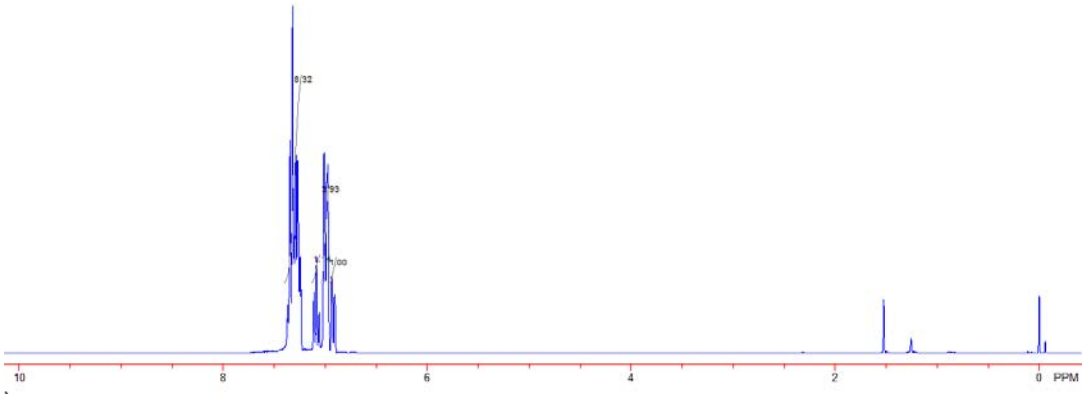


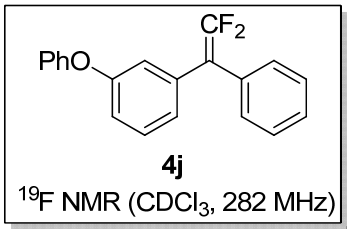




4j

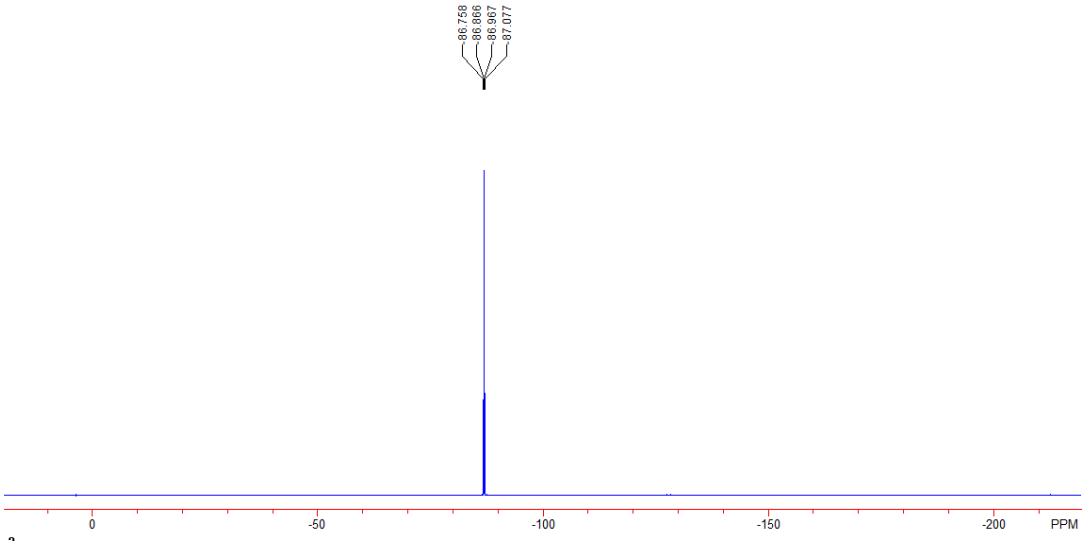
^{1}H NMR ($CDCl_3$, 300 MHz)

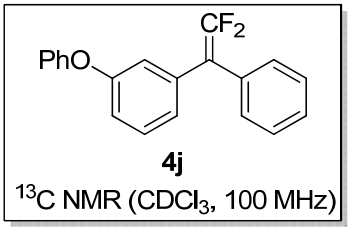




4j

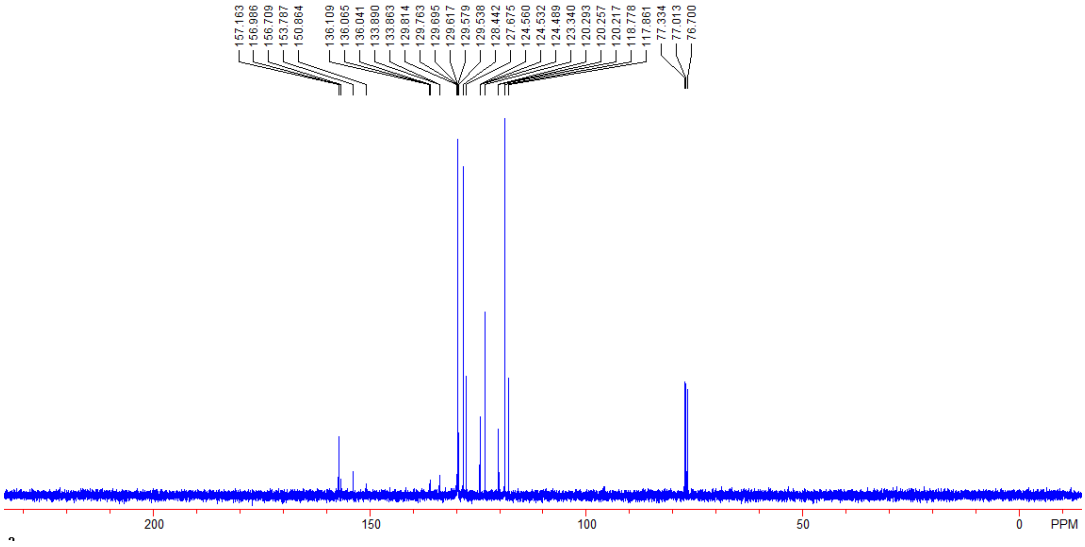
^{19}F NMR ($CDCl_3$, 282 MHz)

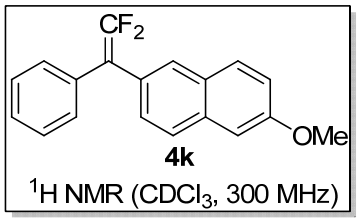


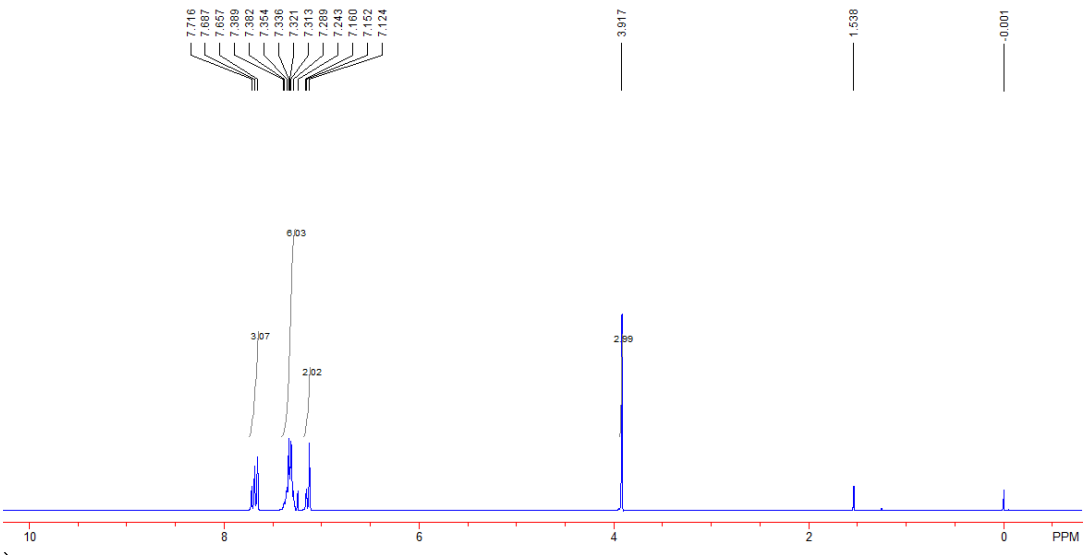


4j

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




CF2
OMe
4k
1H NMR (CDCl3, 300 MHz)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7.289
7.243
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7.152
7.124
3.917
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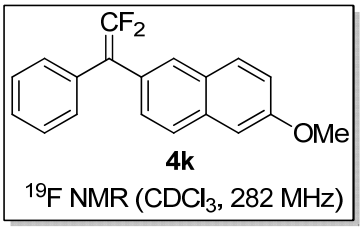
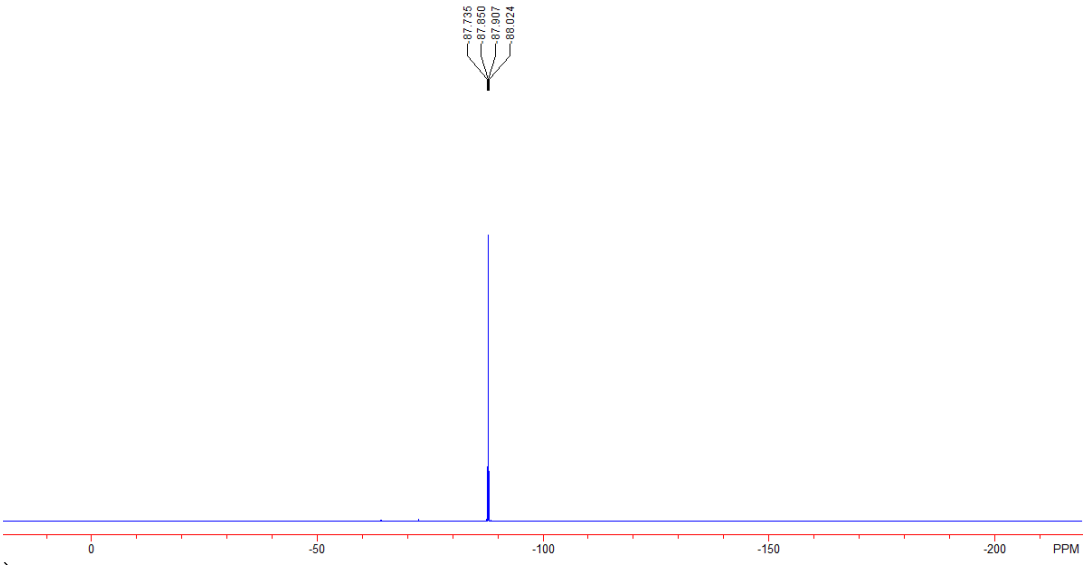
6.03
3.07
2.02
2.99
10
8
6
4
2
0
PPM


CF2
OMe
4k
19F NMR (CDCl3, 282 MHz)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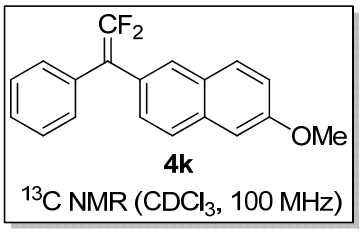
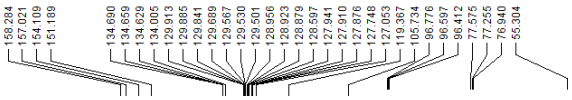
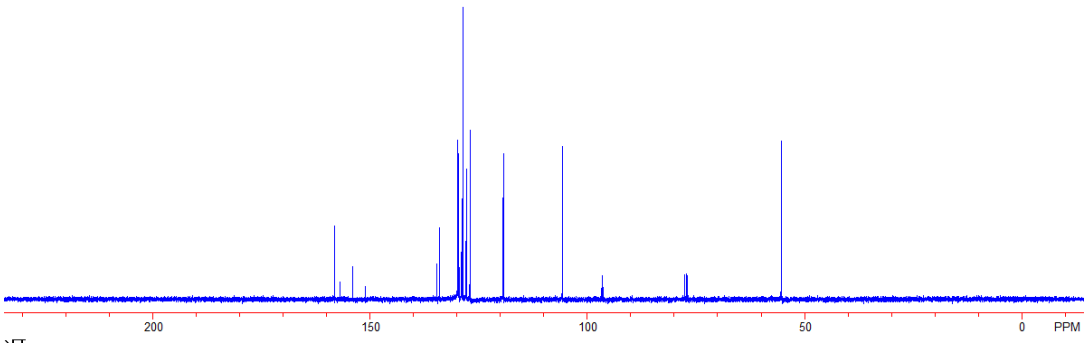
-87.907
-88.024
0
-50
-100
-150
-200
PPM

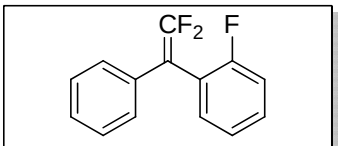


4k

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

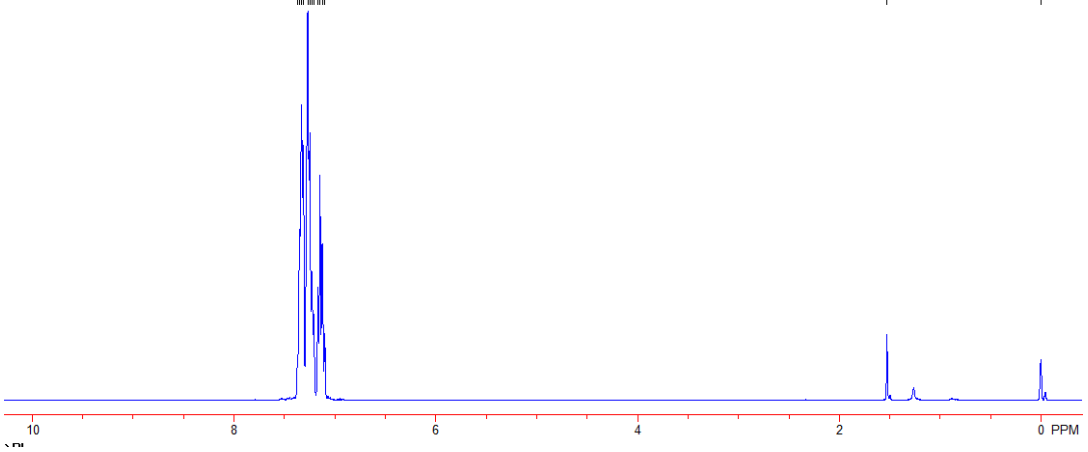


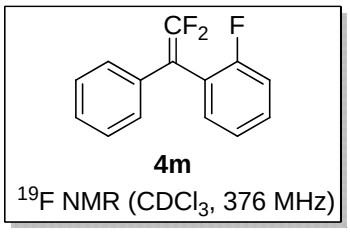




4m

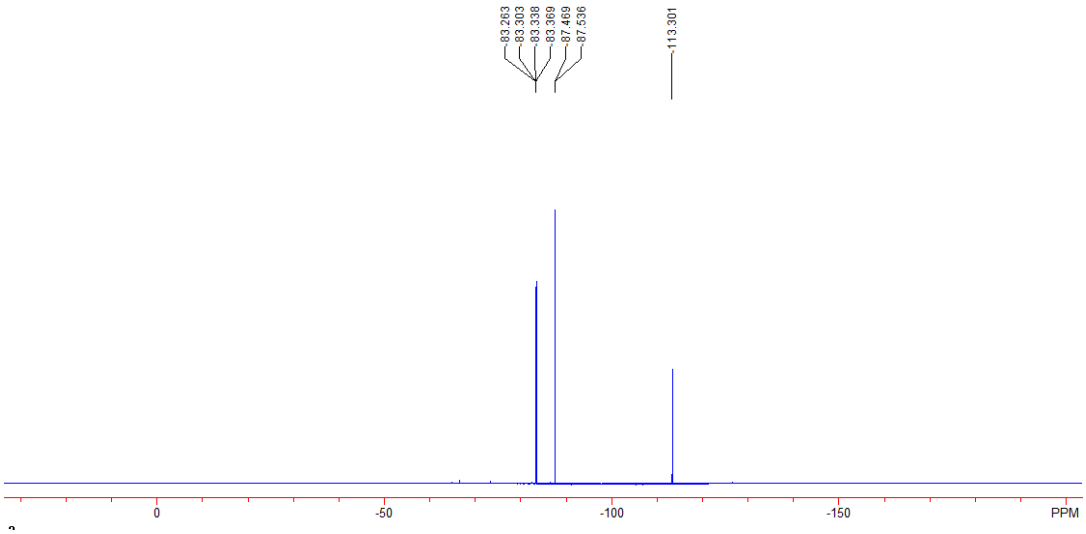
^{1}H NMR ($CDCl_3$, 400 MHz)

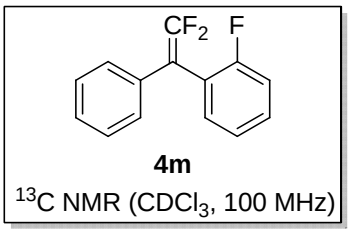




4m

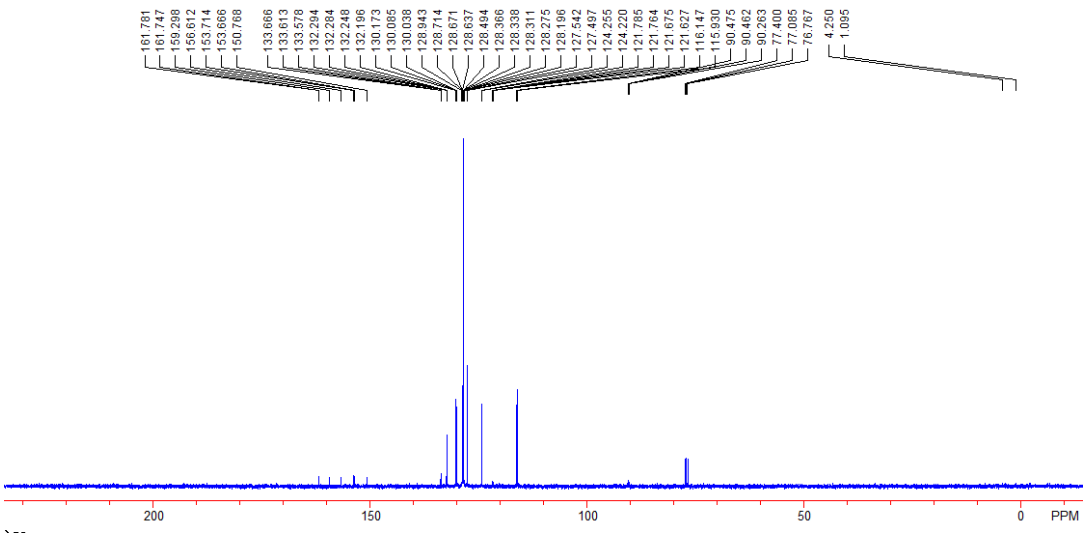
^{19}F NMR ($CDCl_3$, 376 MHz)

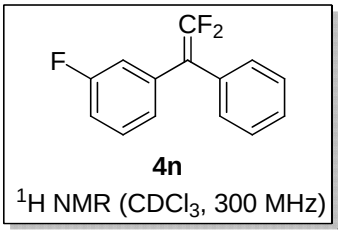




4m

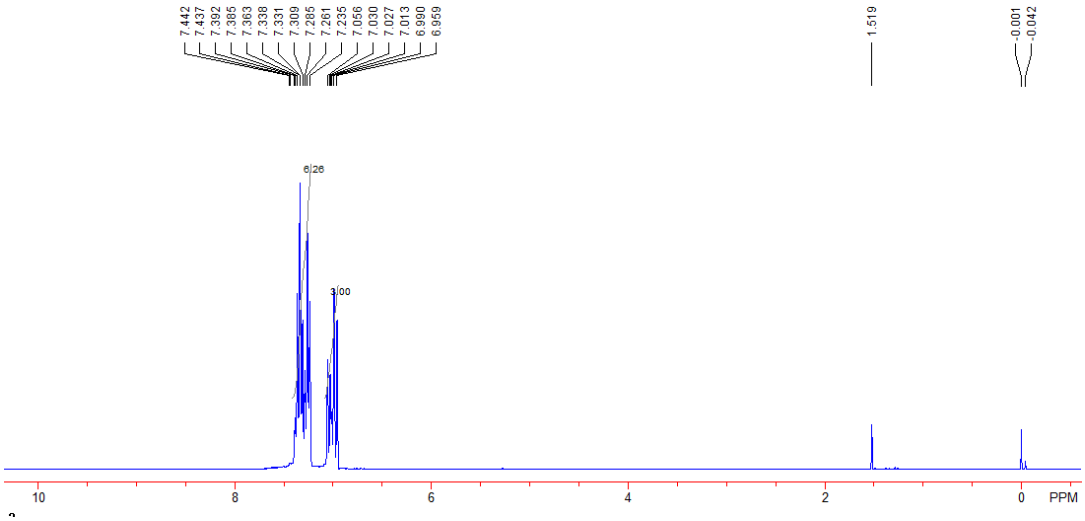
^{13}C NMR ($CDCl_3$, 100 MHz)

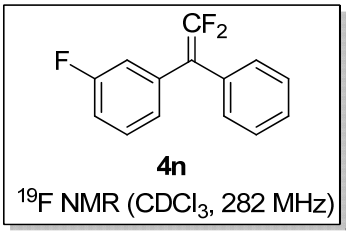




4n

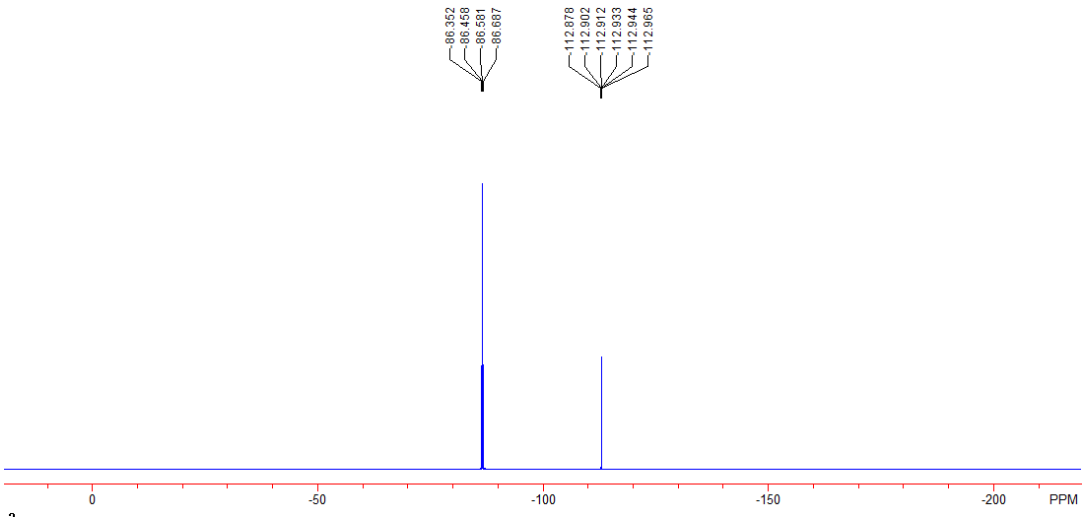
^{1}H NMR ($CDCl_3$, 300 MHz)

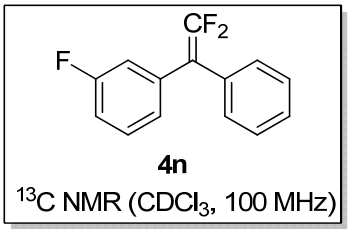




4n

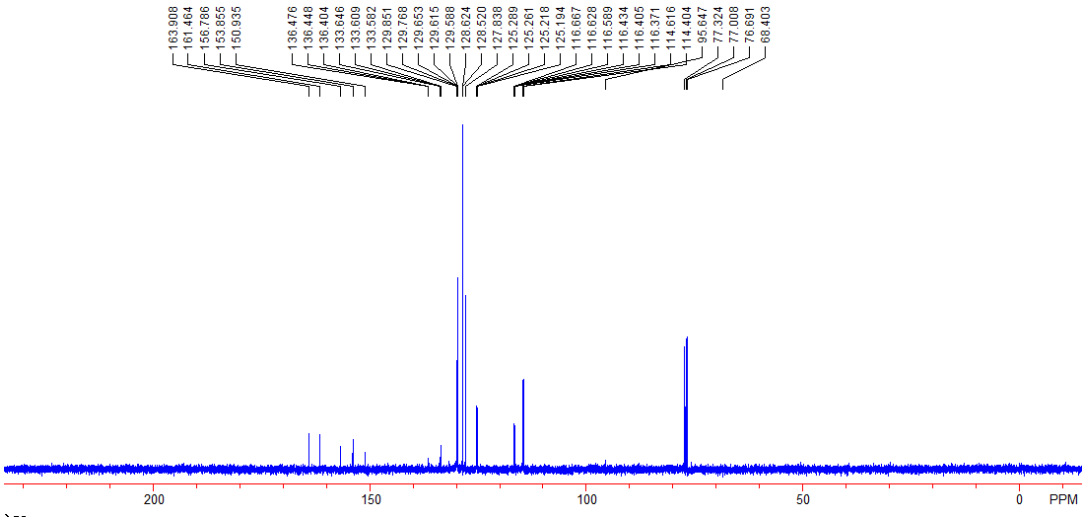
^{19}F NMR ($CDCl_3$, 282 MHz)

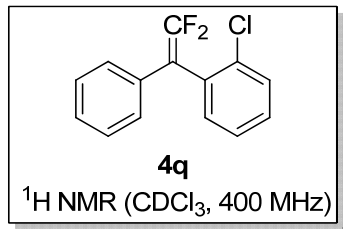




4n

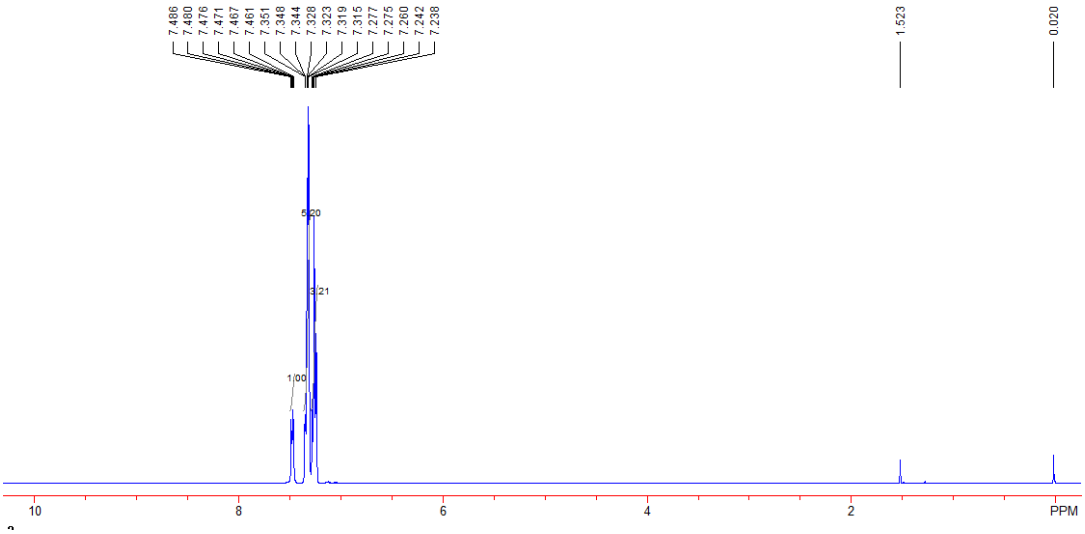
^{13}C NMR ($CDCl_3$, 100 MHz)

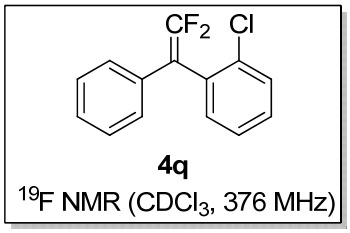


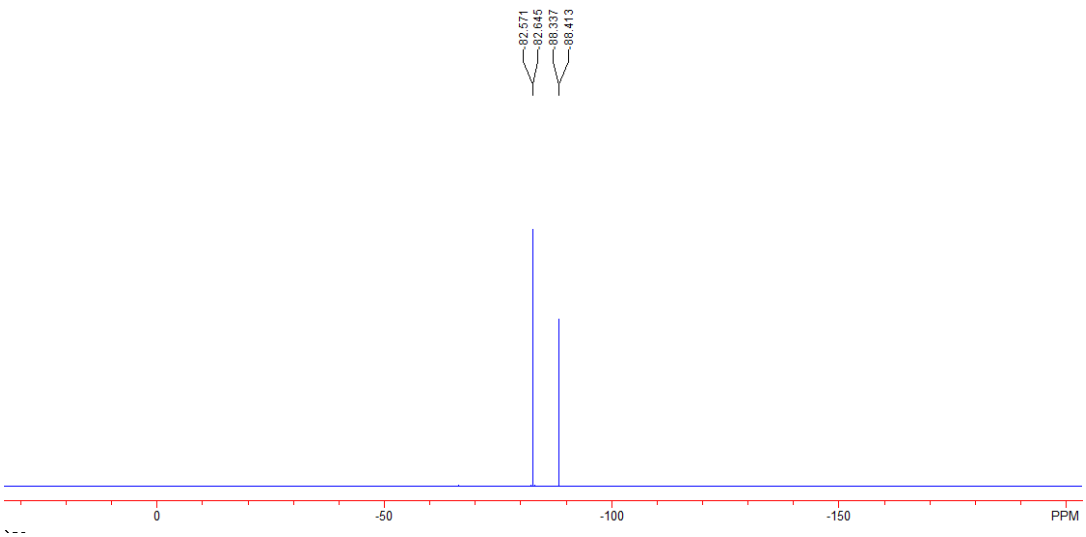


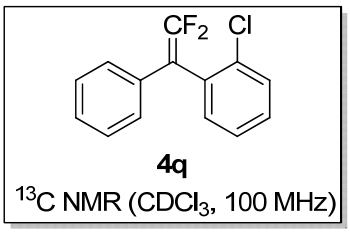
4q

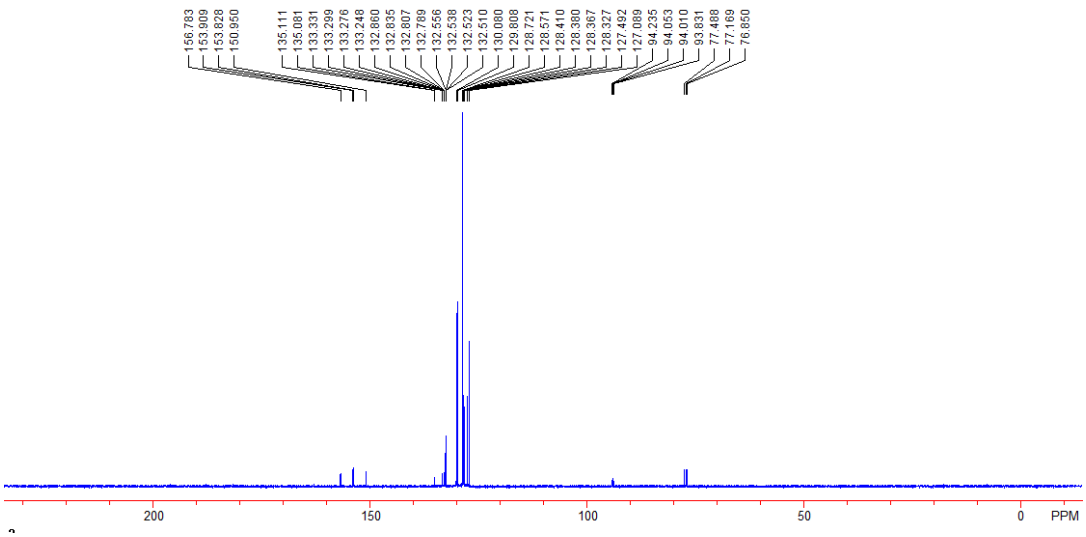
^{1}H NMR ($CDCl_3$, 400 MHz)

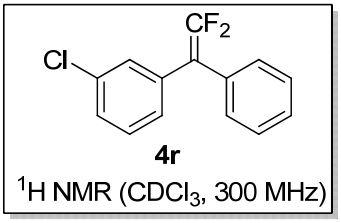



CF2 Cl
4q
19F NMR (CDCl3, 376 MHz)


82.571
82.645
88.337
88.413
0
-50
-100
-150
PPM

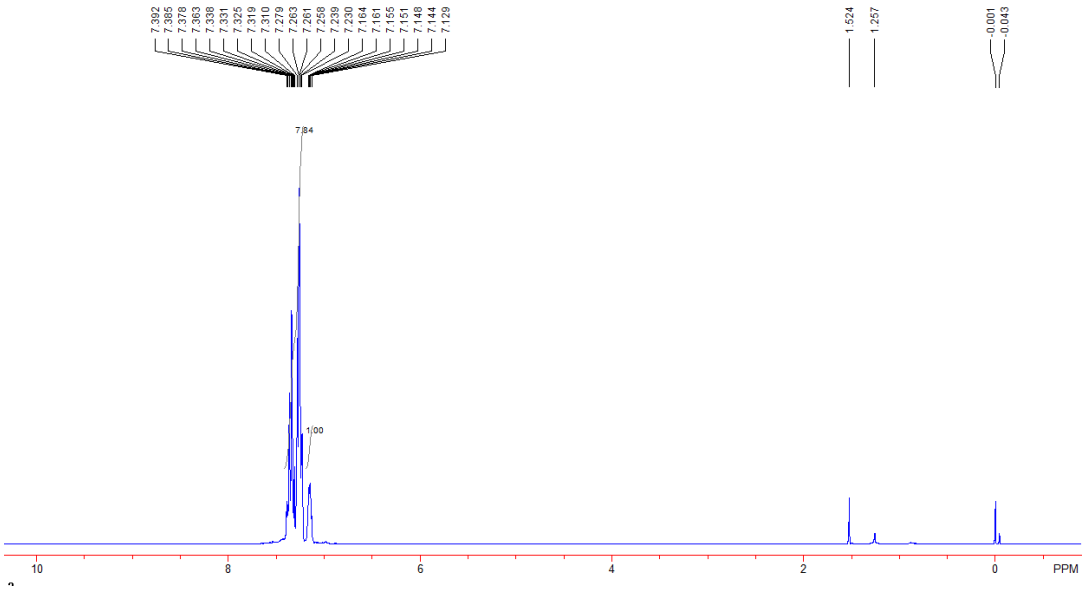

CF2 Cl
4q
13C NMR (CDCl3, 100 MHz)

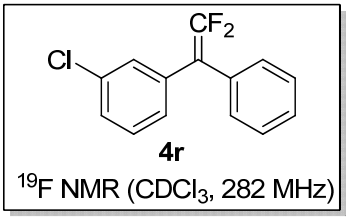

156.783
153.909
153.828
150.950
135.111
135.081
133.331
133.299
133.276
133.248
132.860
132.835
132.807
132.789
132.556
132.538
132.523
132.510
130.080
129.808
128.721
128.571
128.410
128.380
128.367
128.327
127.492
127.089
94.235
94.053
94.010
93.831
77.488
77.169
76.850
200
150
100
50
0
PPM



4r

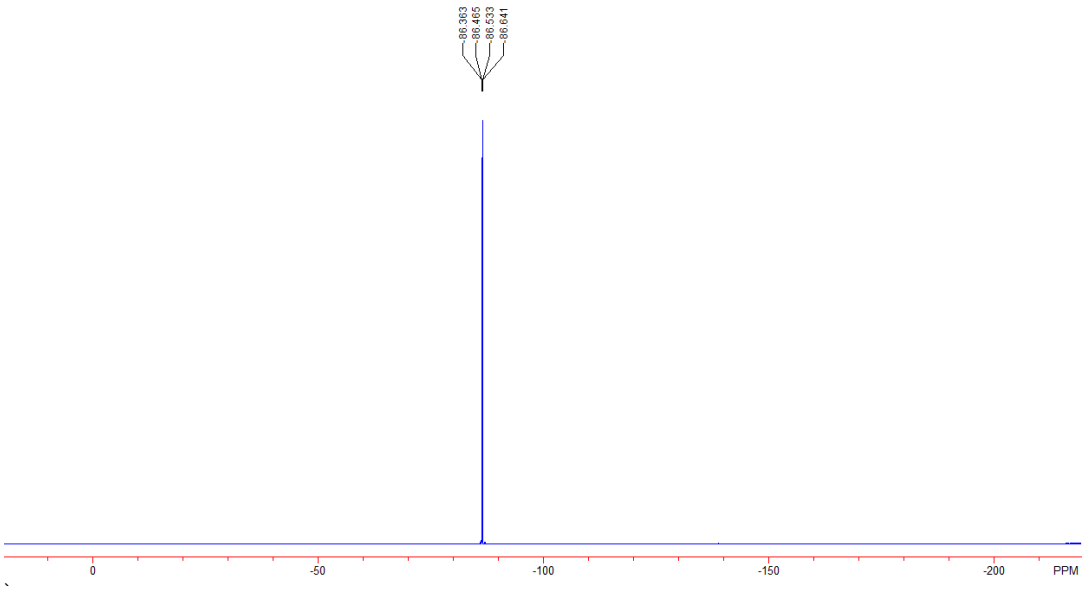
^{1}H NMR ($CDCl_3$, 300 MHz)

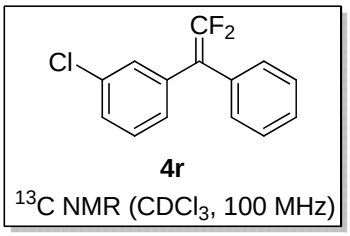




4r

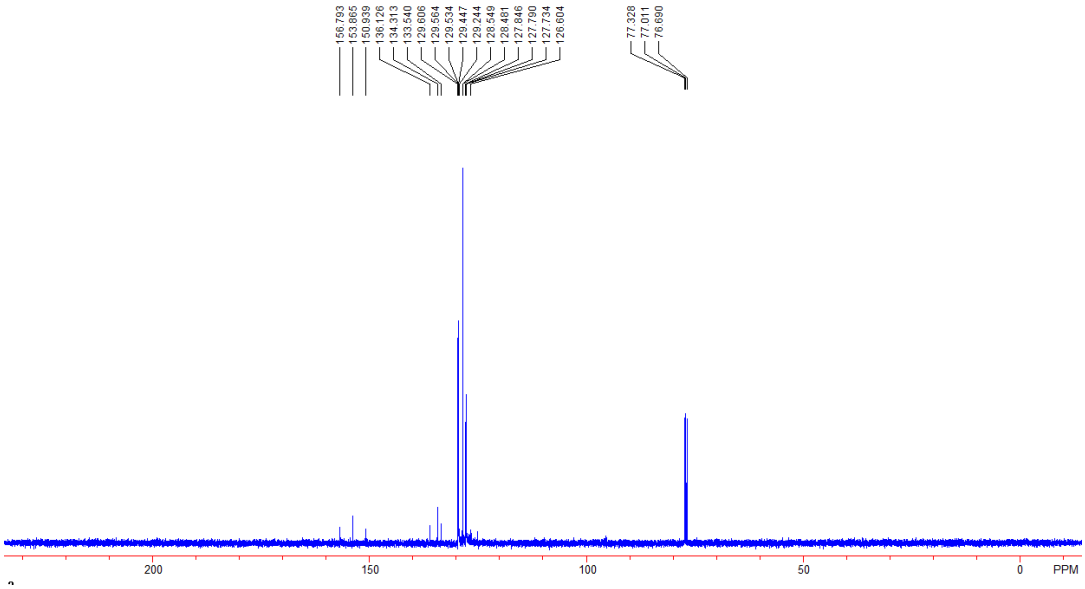
^{19}F NMR ($CDCl_3$, 282 MHz)

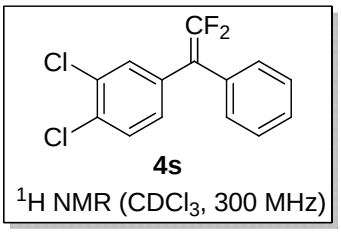




4r

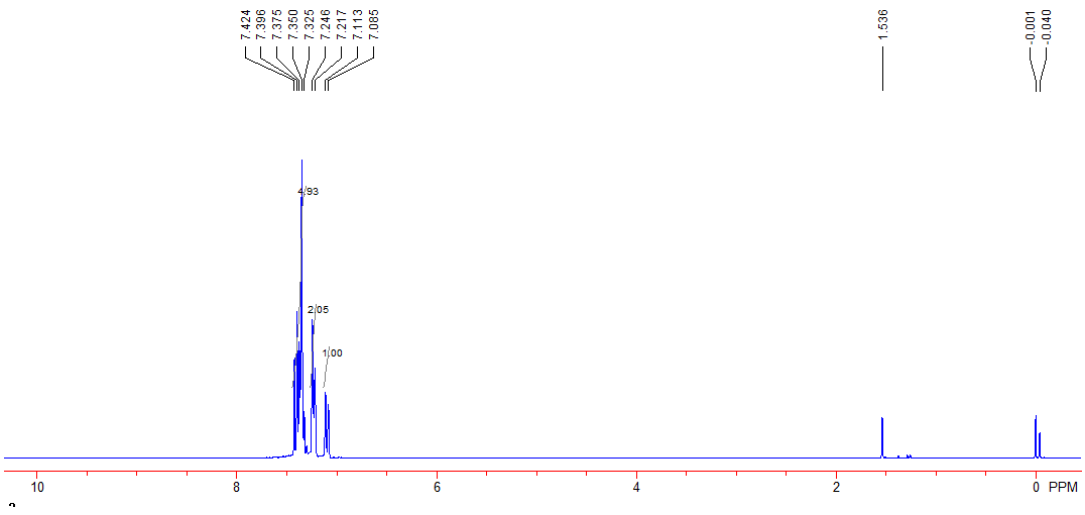
^{13}C NMR ($CDCl_3$, 100 MHz)

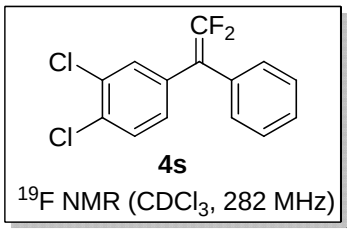




4s

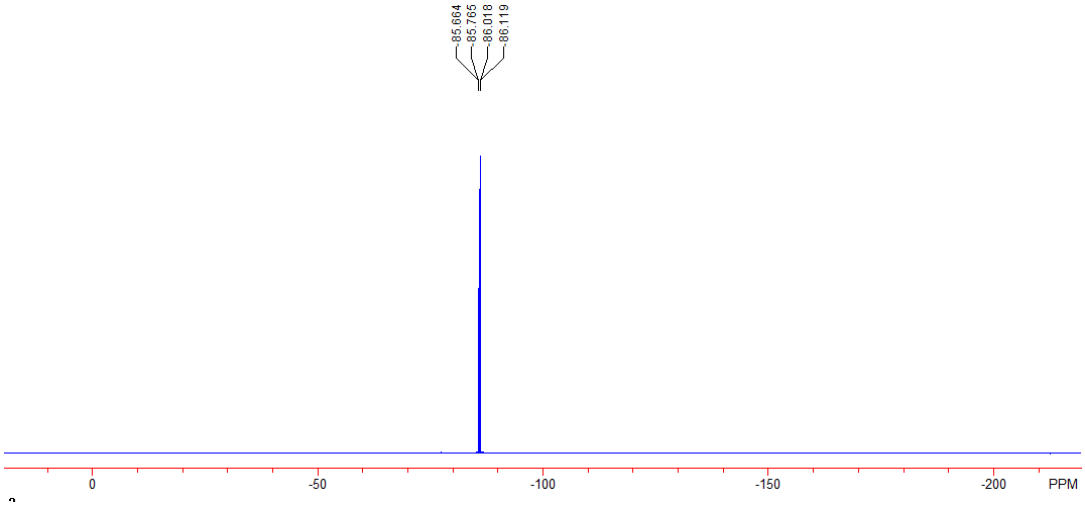
^{1}H NMR ($CDCl_3$, 300 MHz)

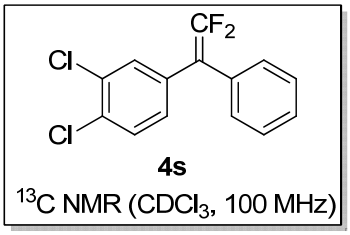




4s

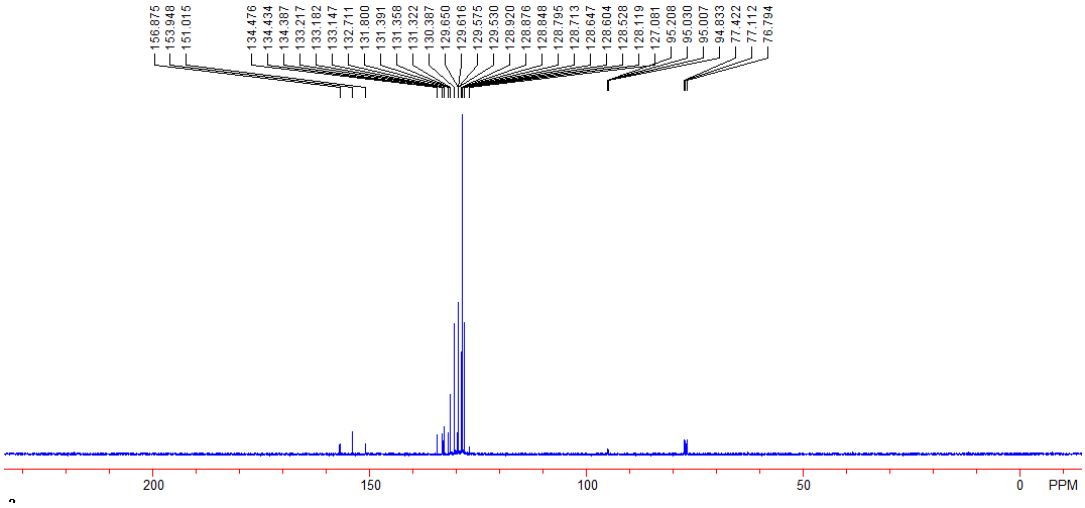
^{19}F NMR ($CDCl_3$, 282 MHz)

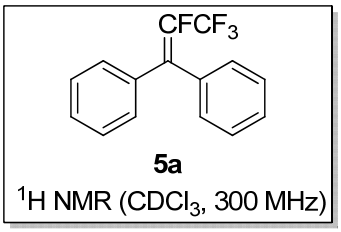




4s

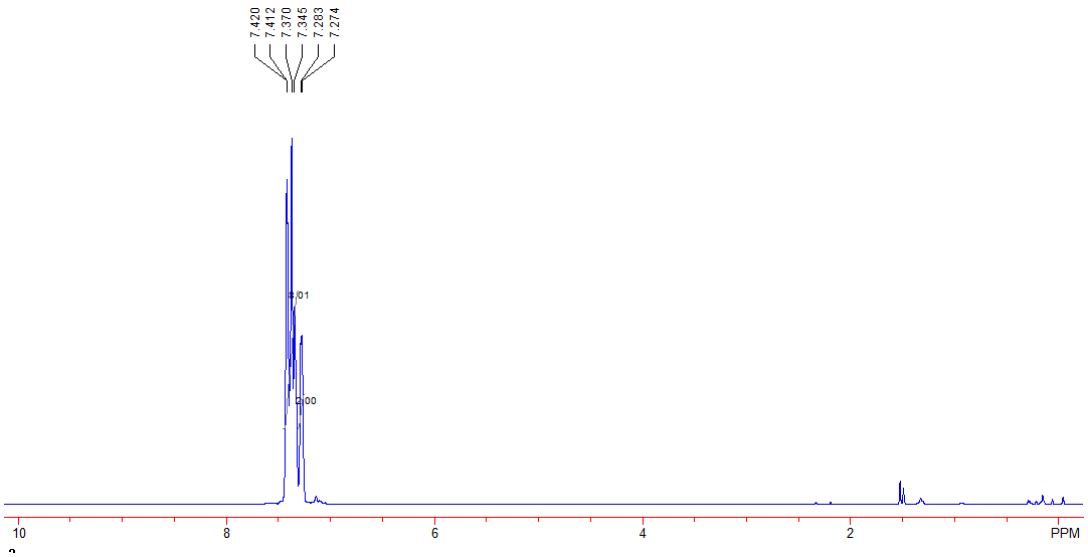
^{13}C NMR ($CDCl_3$, 100 MHz)

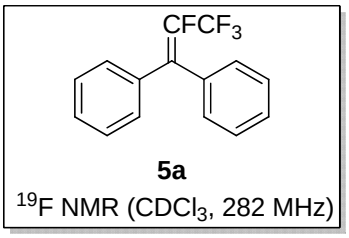




5a

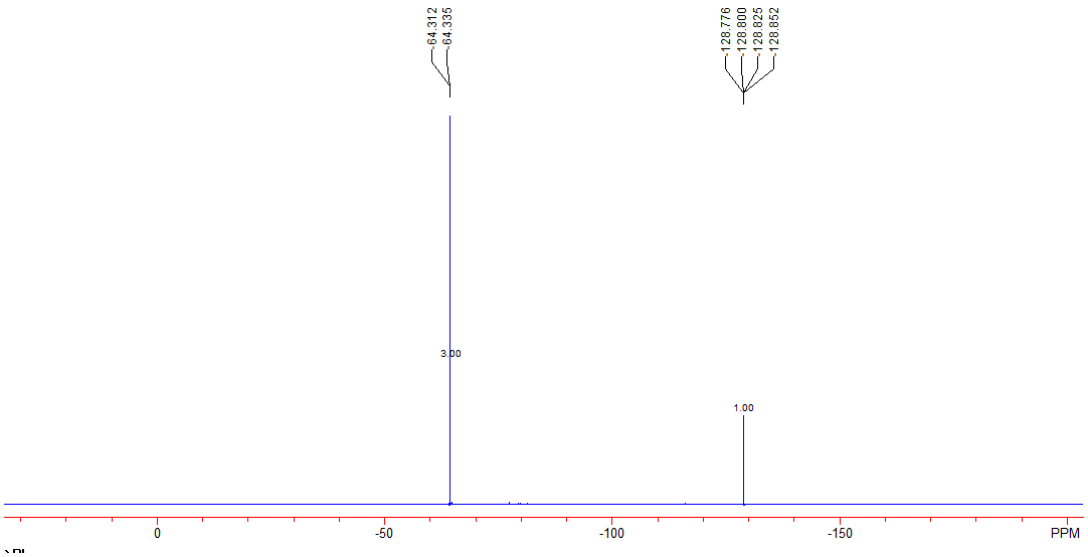
^{1}H NMR ($CDCl_3$, 300 MHz)

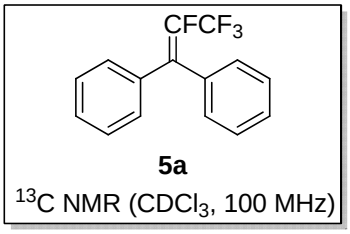




5a

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





5a

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