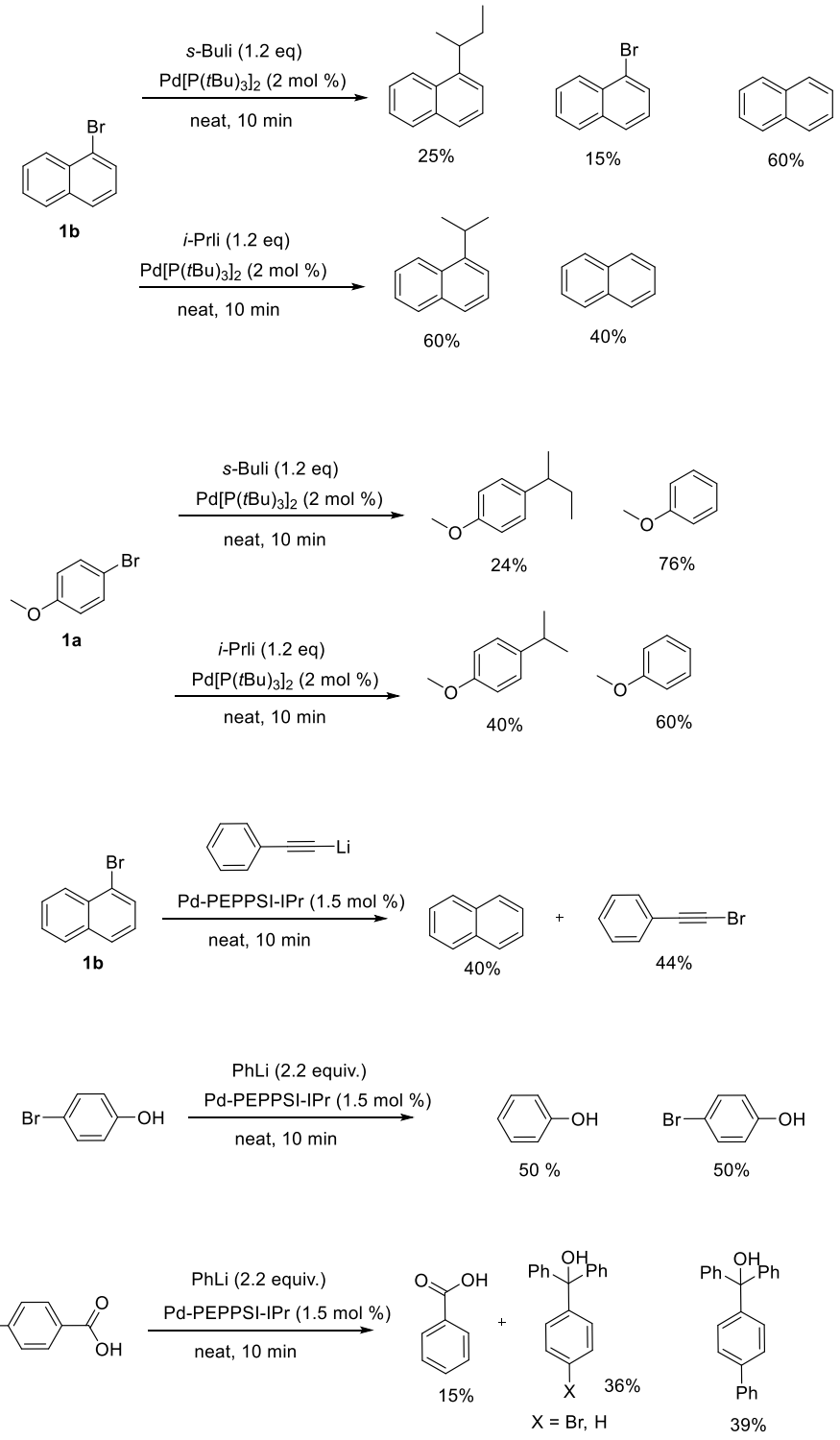
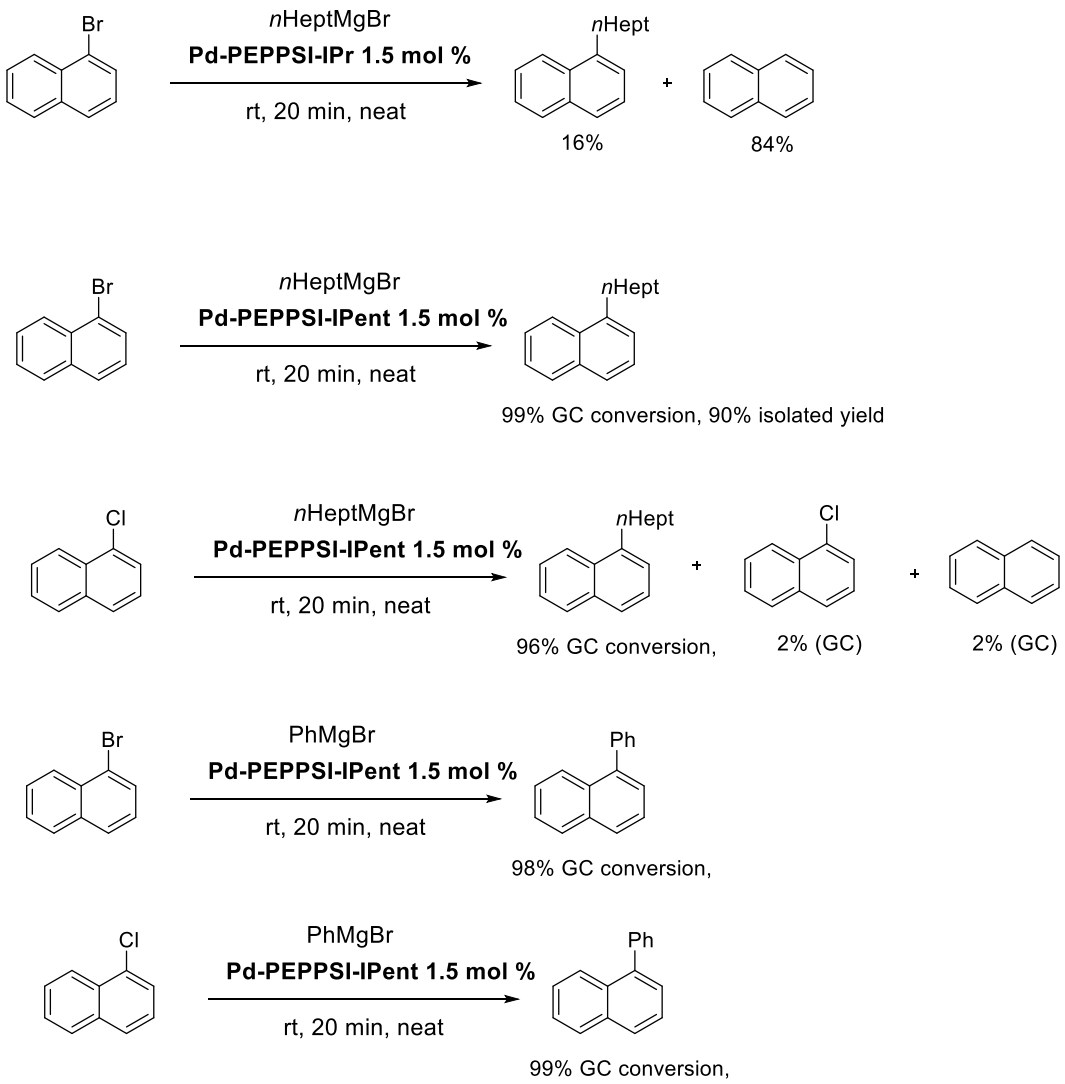
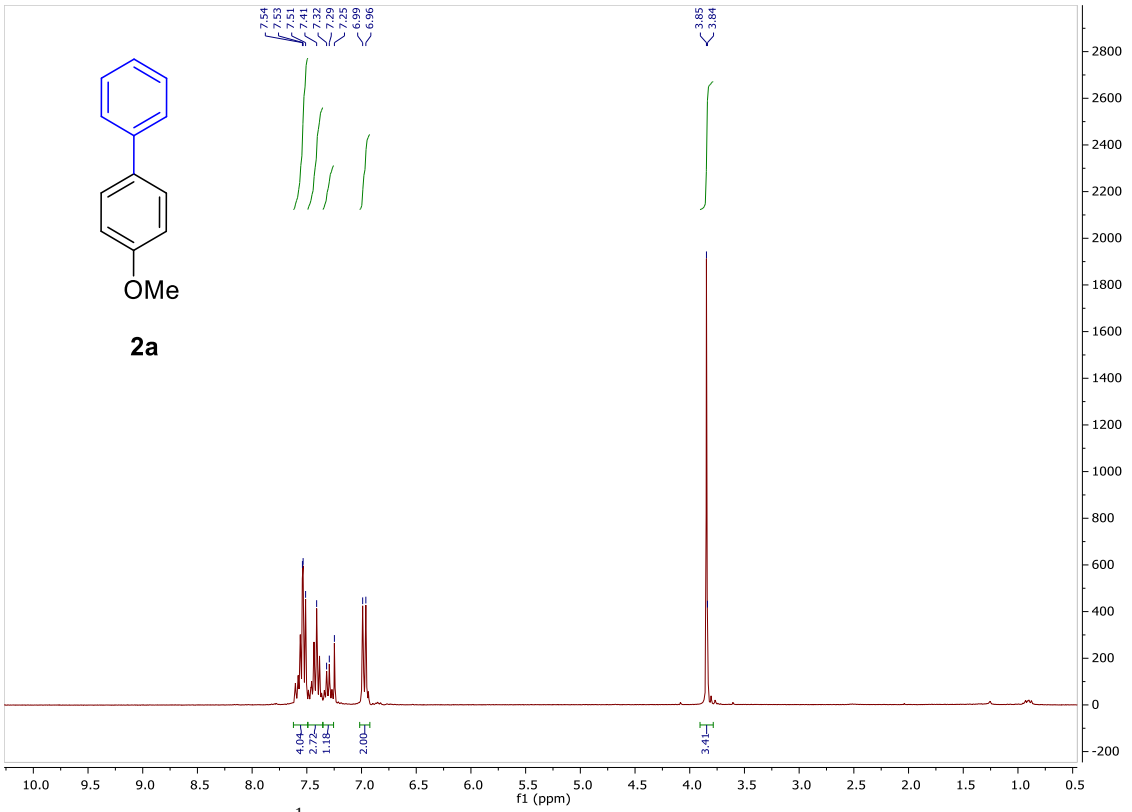
Supplementary Figures



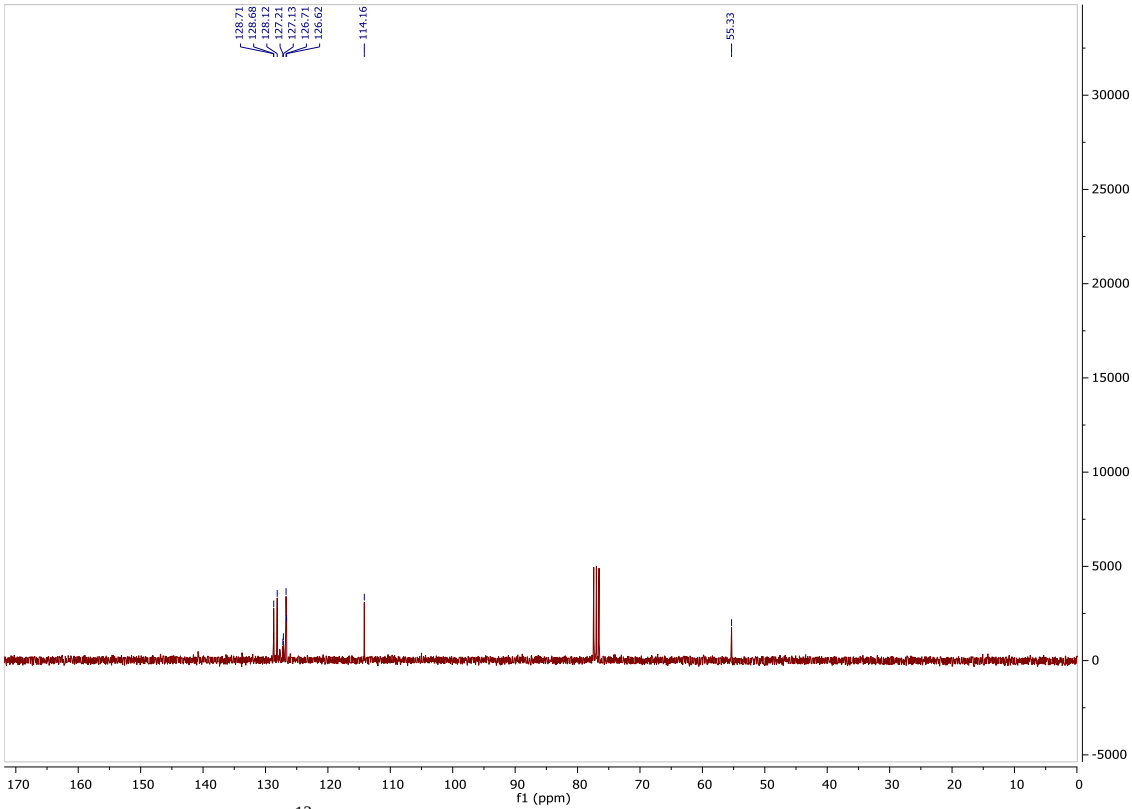
Supplementary Figure 1. Limitations of the method



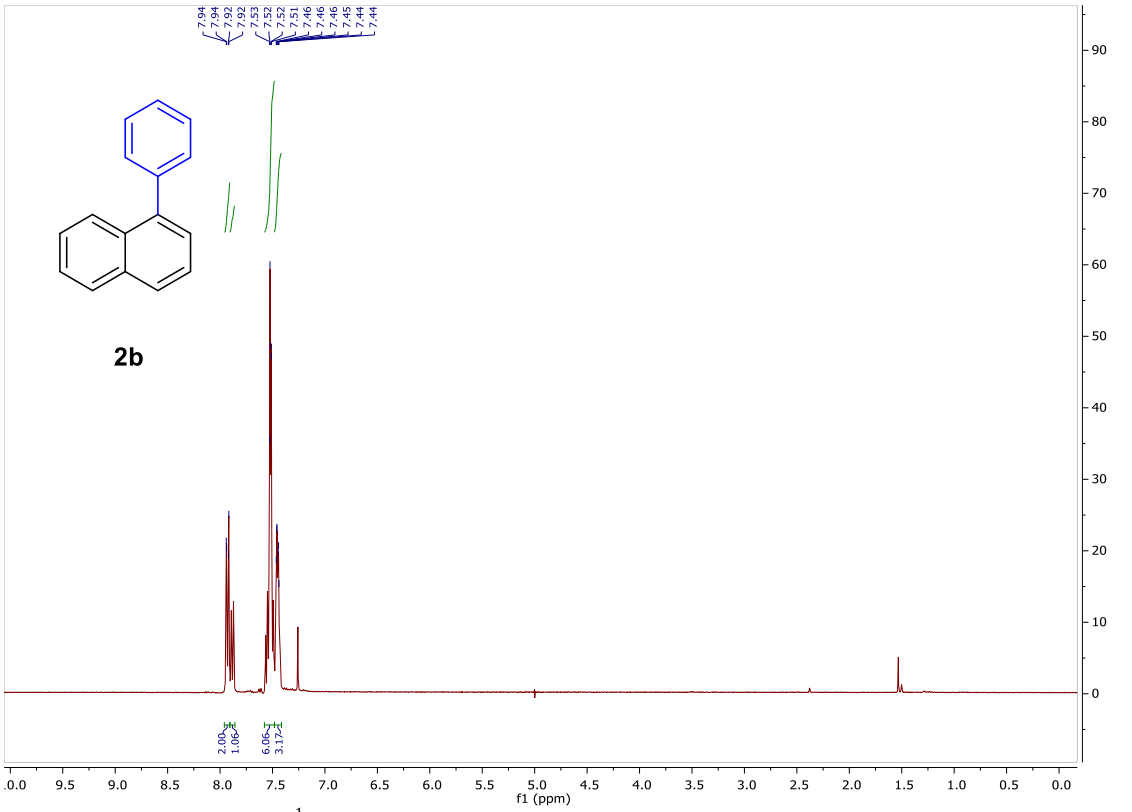
Supplementary Figure 2. Pd-catalysed cross-coupling of *n*-heptMgBr and PhMgBr with 1-chloro- and 1-bromonaphthalene under neat conditions. Conditions: The corresponding commercially available Grignard reagent (1,2 eq) was added over a mixture of substrate (1 mmol) and Pd-PEPPSI-*i*Pent (1.5 mol %, 12.5 mg) at room temperature for 10 min. After the addition was completed, the mixture was stirred for 10 min at room temperature followed by subsequent quenching with a saturated solution of aqueous NH_4Cl (1 mL). The mixture was extracted with Et_2O and the organic phases were combined and dried with anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the crude product that was then filtered over a silica gel plug.



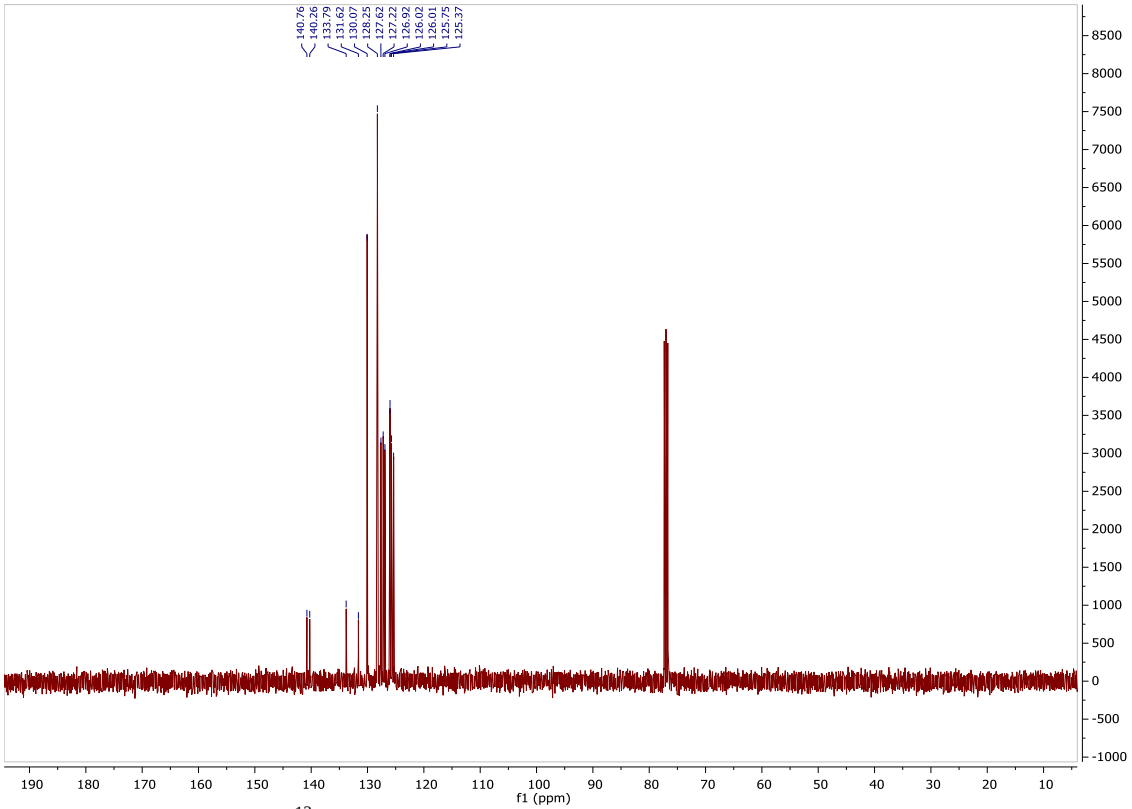
Supplementary Figure 3. ^{1}H NMR spectra of **2a**



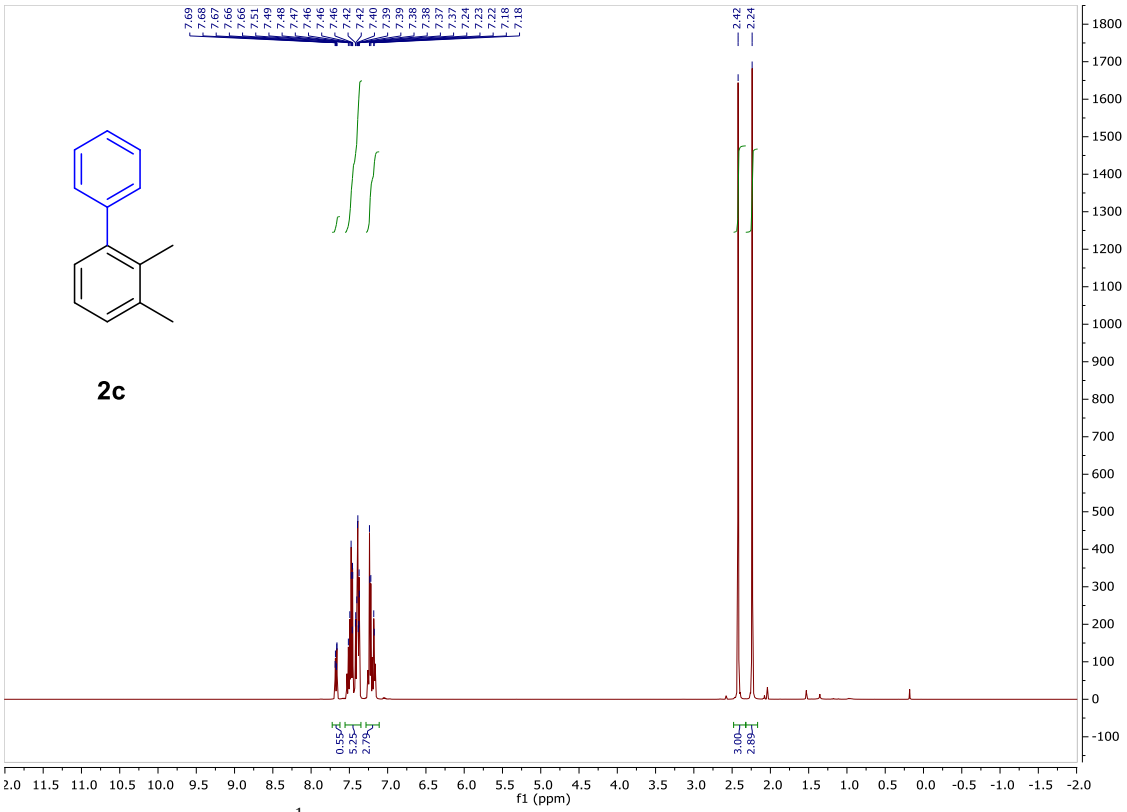
Supplementary Figure 4. ^{13}C NMR spectra of **2a**



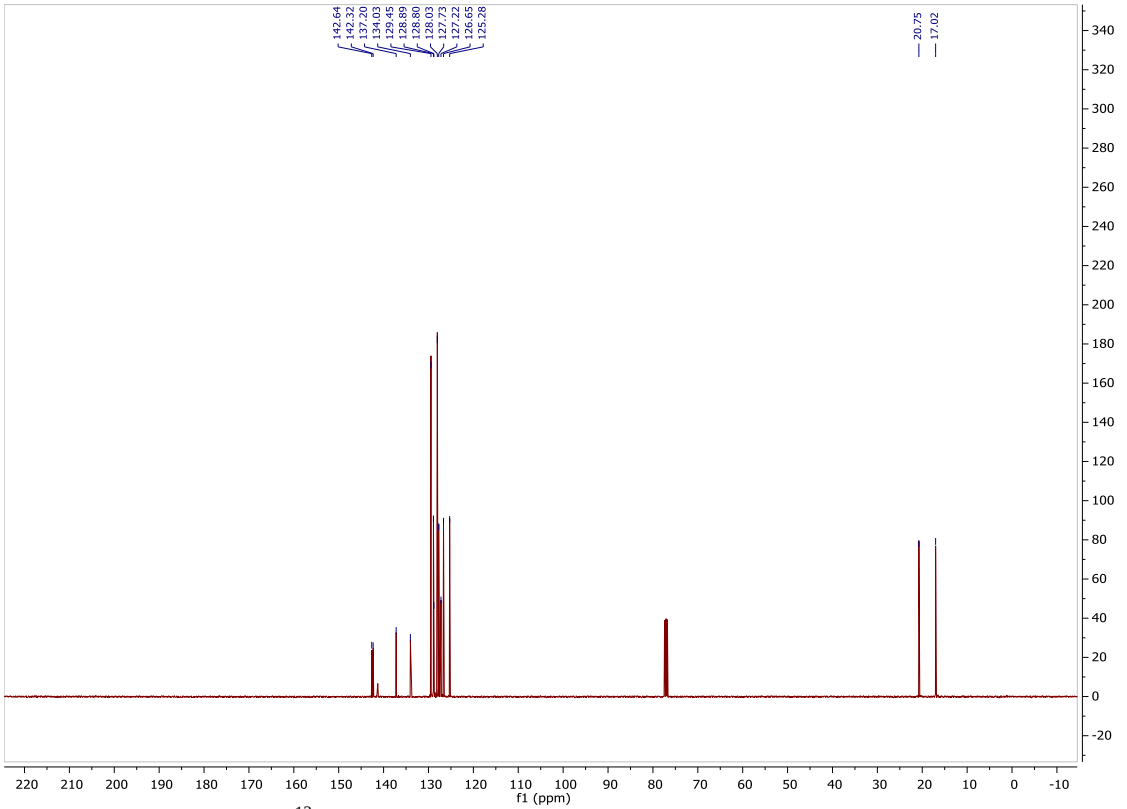
Supplementary Figure 5. ^{1}H NMR spectra of **2b**



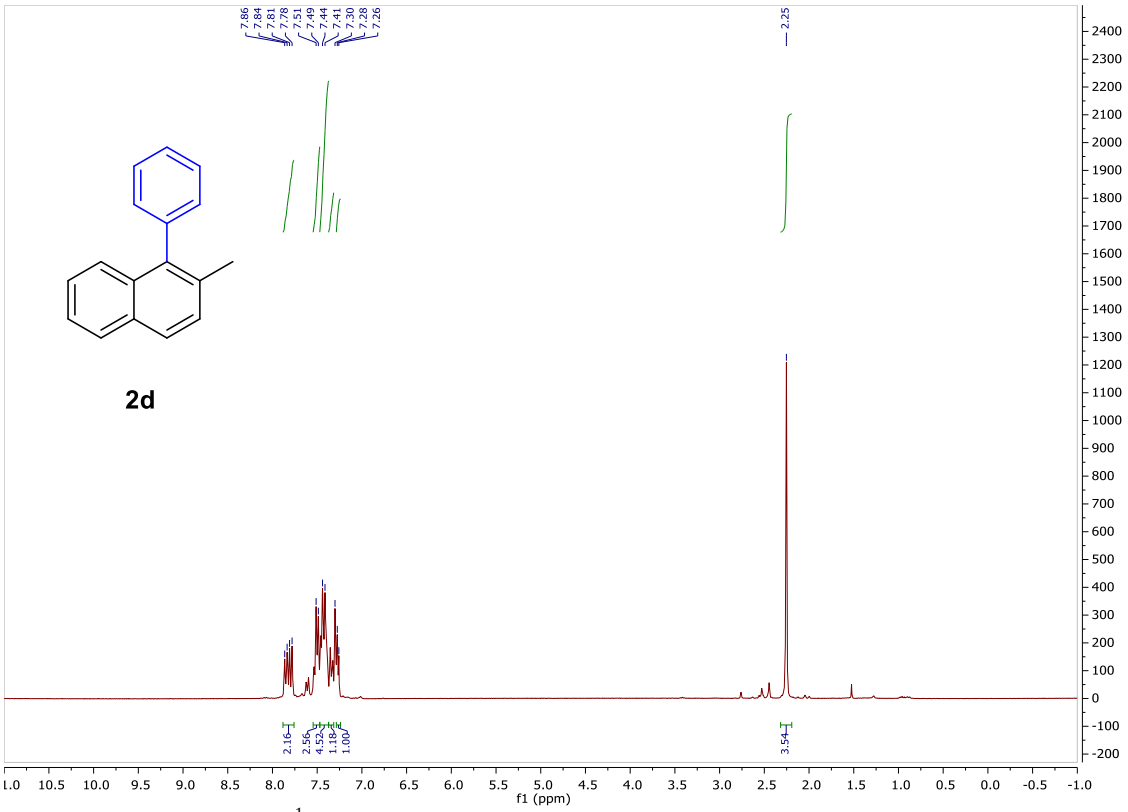
Supplementary Figure 6. ^{13}C NMR spectra of **2b**



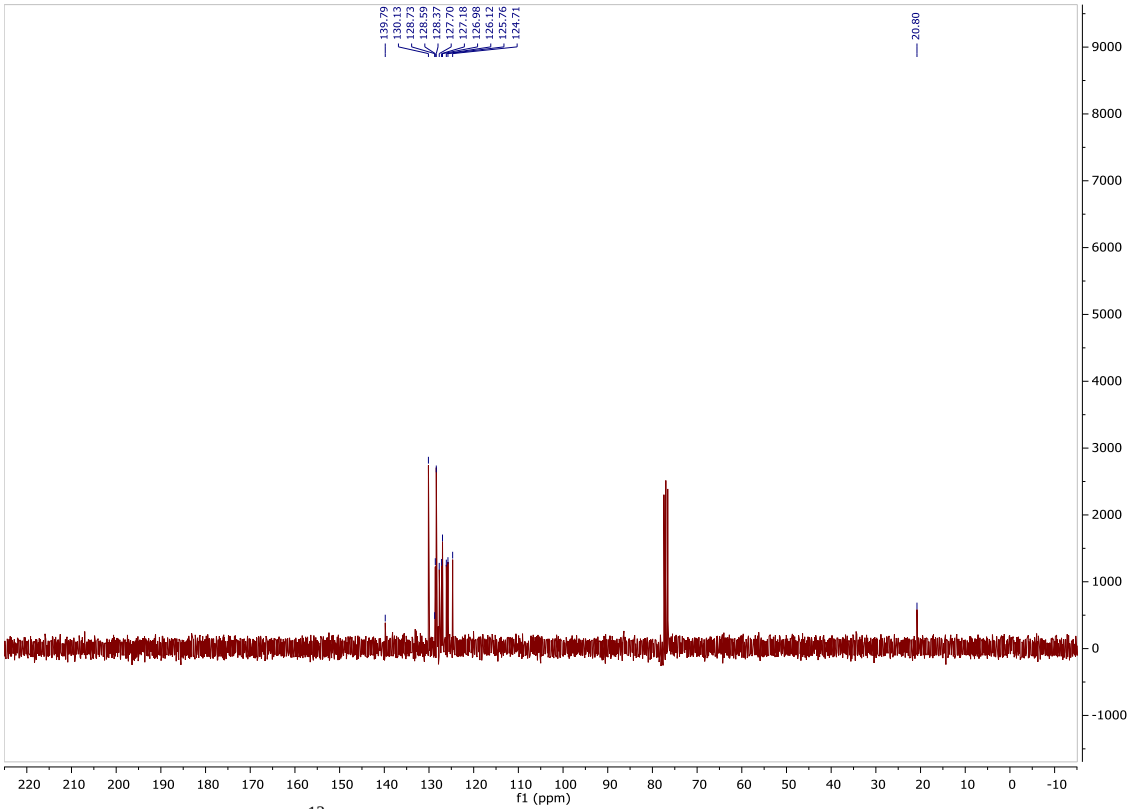
Supplementary Figure 7. ^{1}H NMR spectra of **2c**



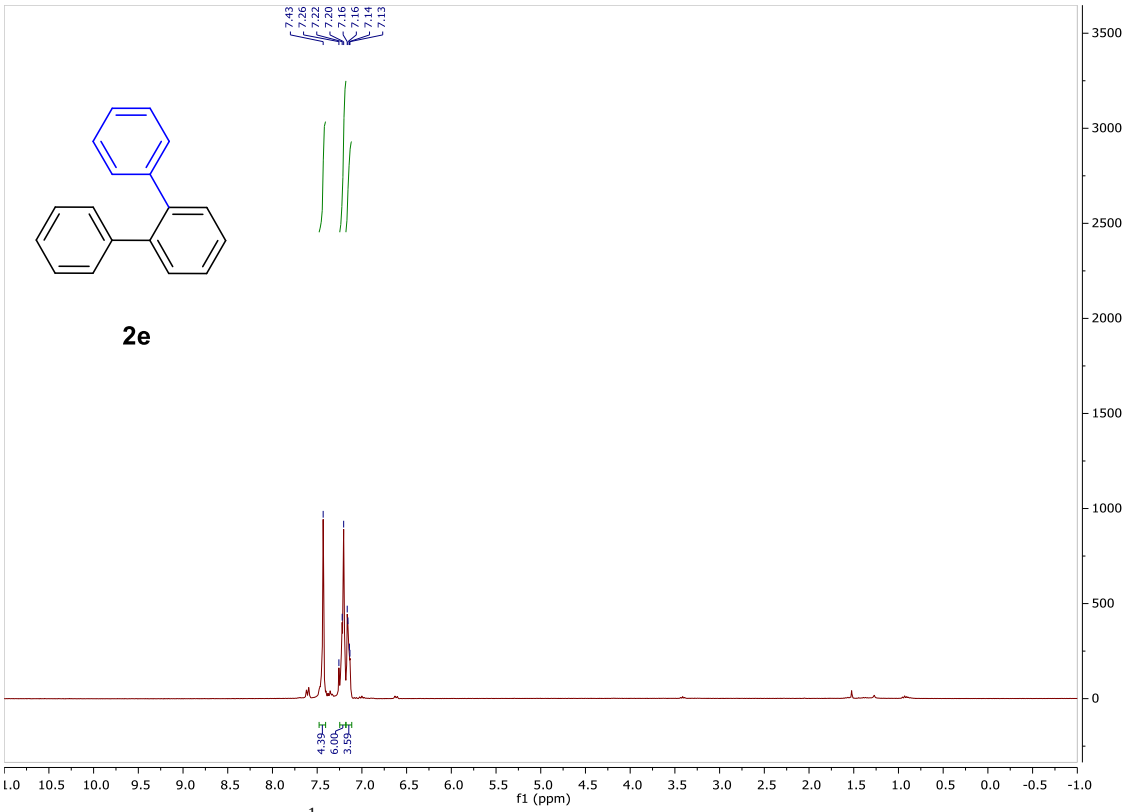
Supplementary Figure 8. ^{13}C NMR spectra of **2c**



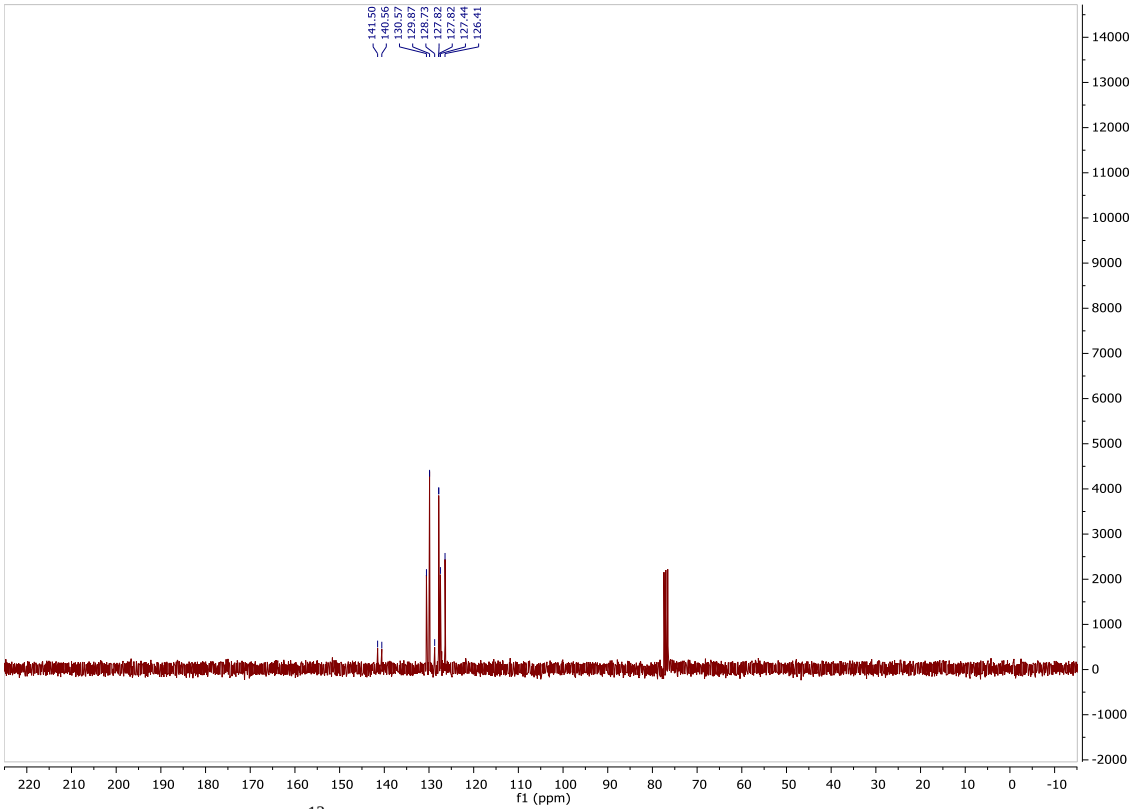
Supplementary Figure 9. ^{1}H NMR spectra of **2d**



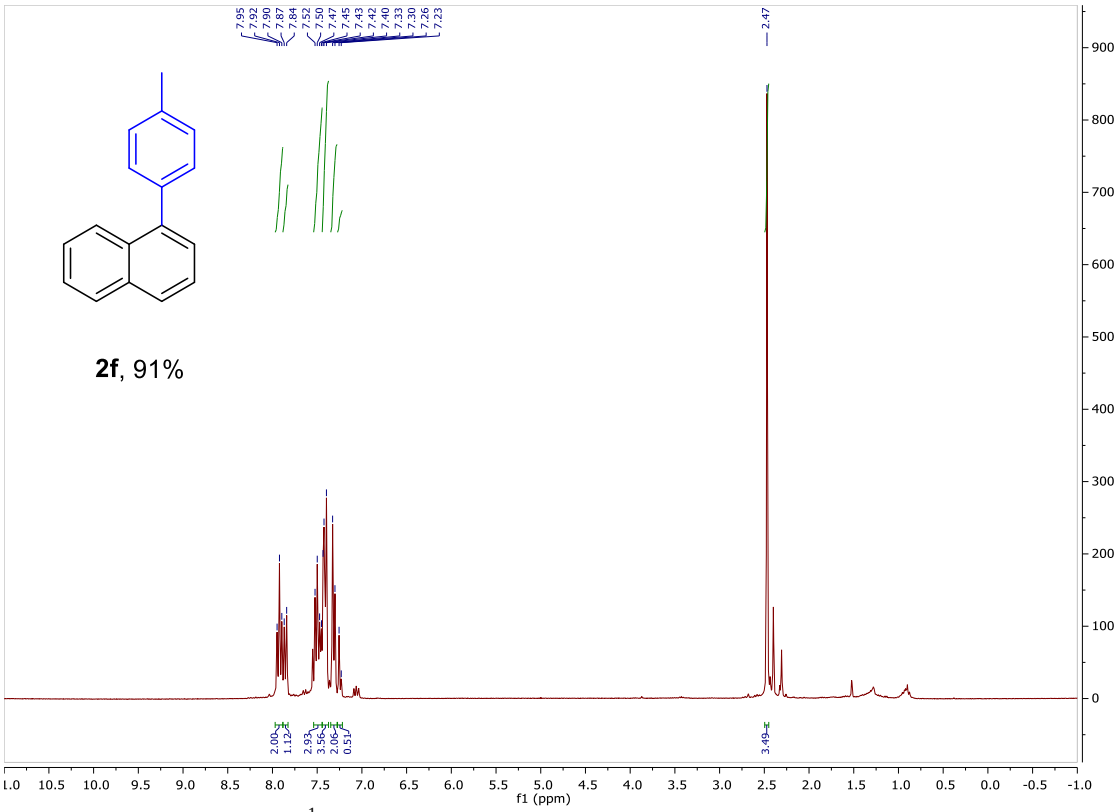
Supplementary Figure 10. ^{13}C NMR spectra of **2d**



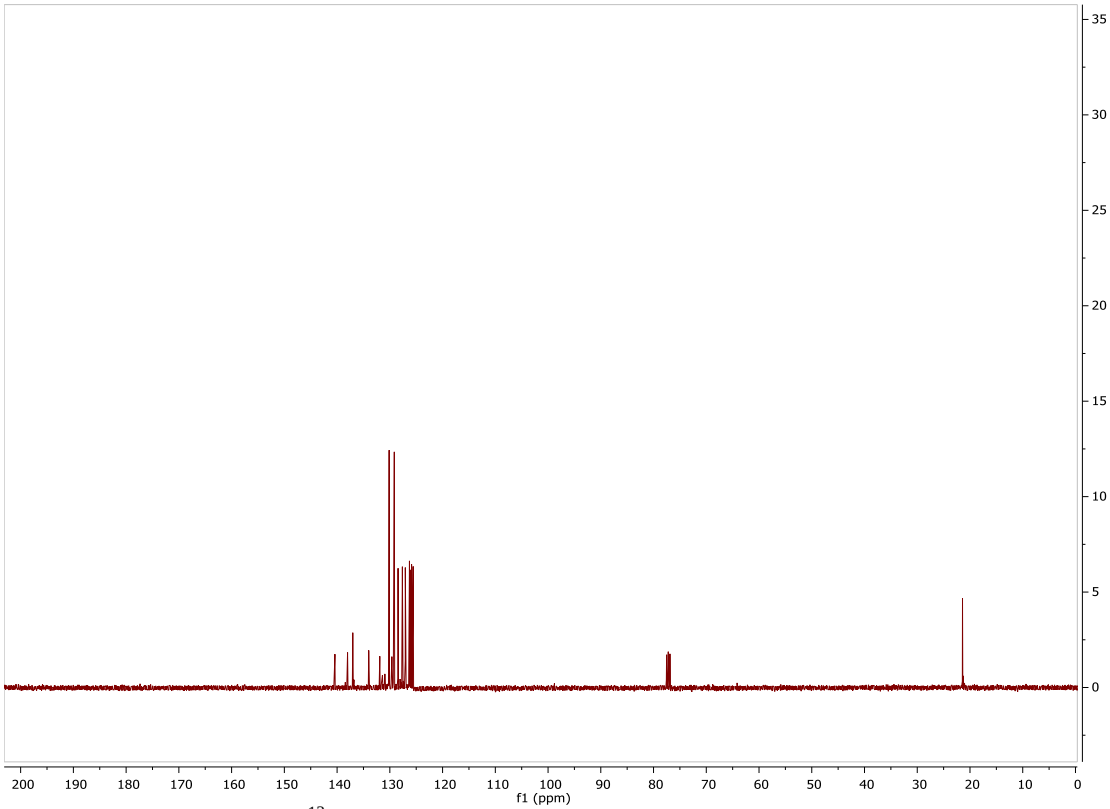
Supplementary Figure 11. ^{1}H NMR spectra of **2e**



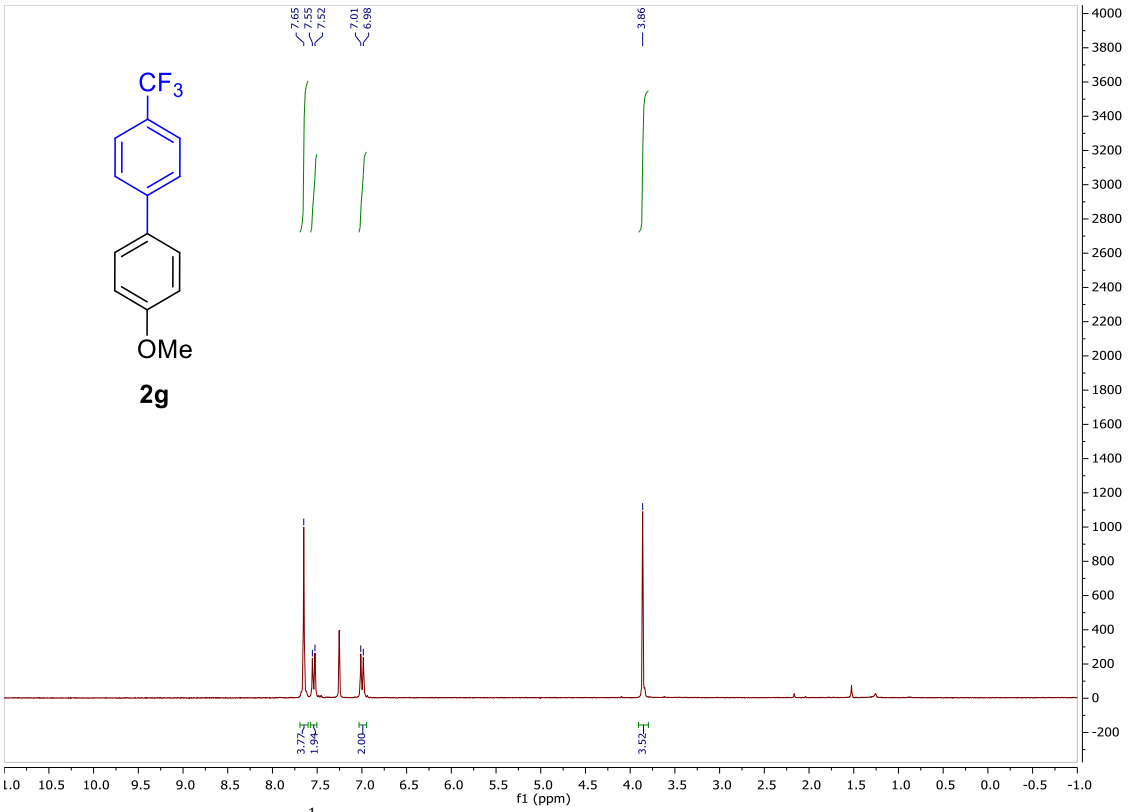
Supplementary Figure 12. ^{13}C NMR spectra of **2e**



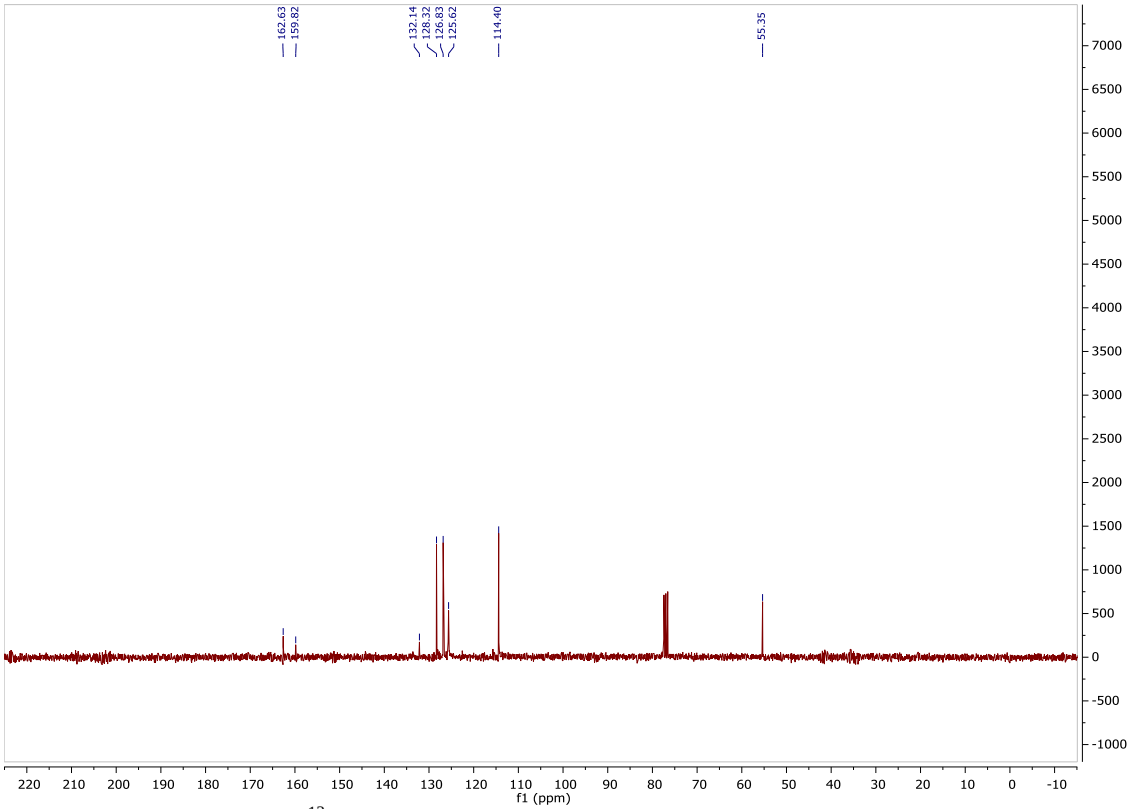
Supplementary Figure 13. ^{1}H NMR spectra of **2f**



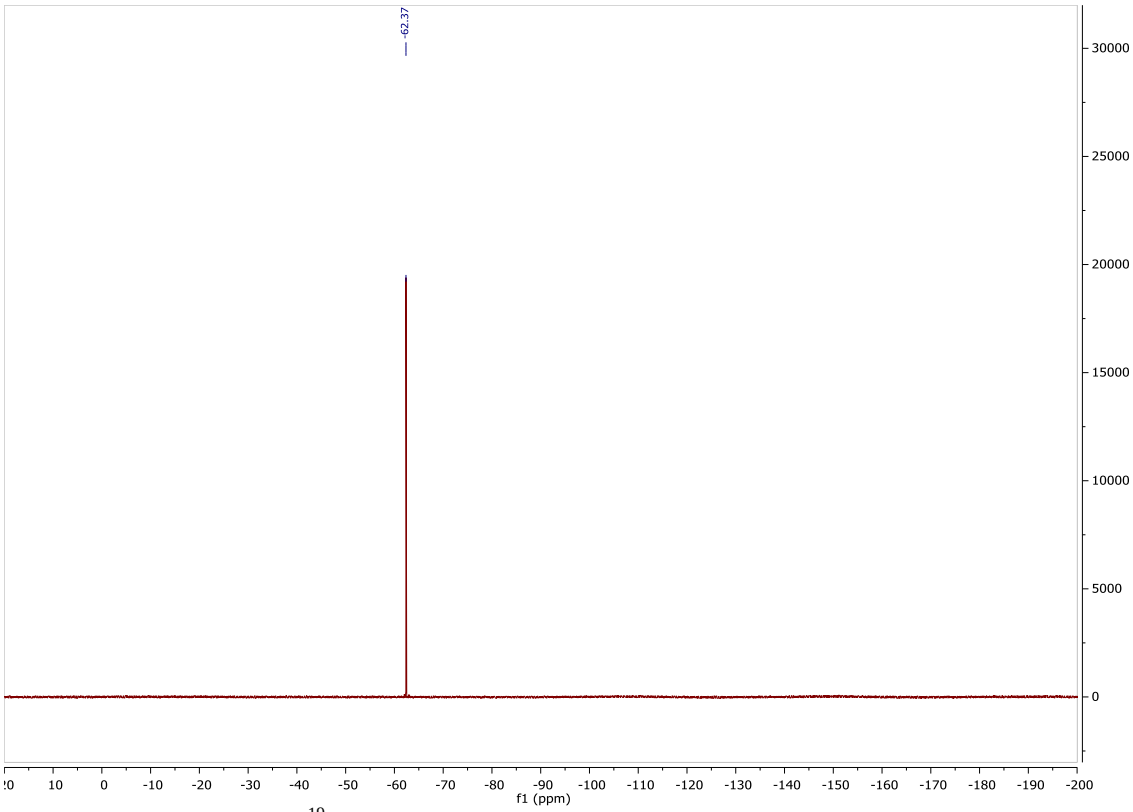
Supplementary Figure 14. ^{13}C NMR spectra of **2f**



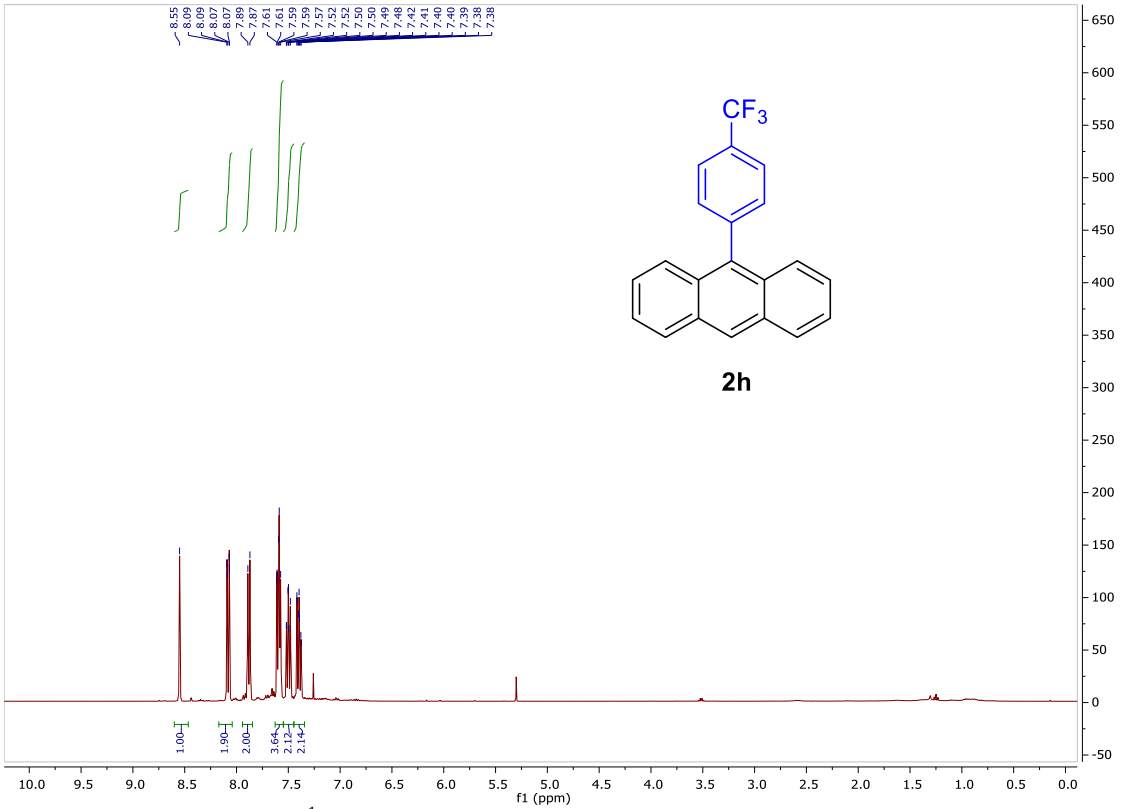
Supplementary Figure 15. ^{1}H NMR spectra of **2g**



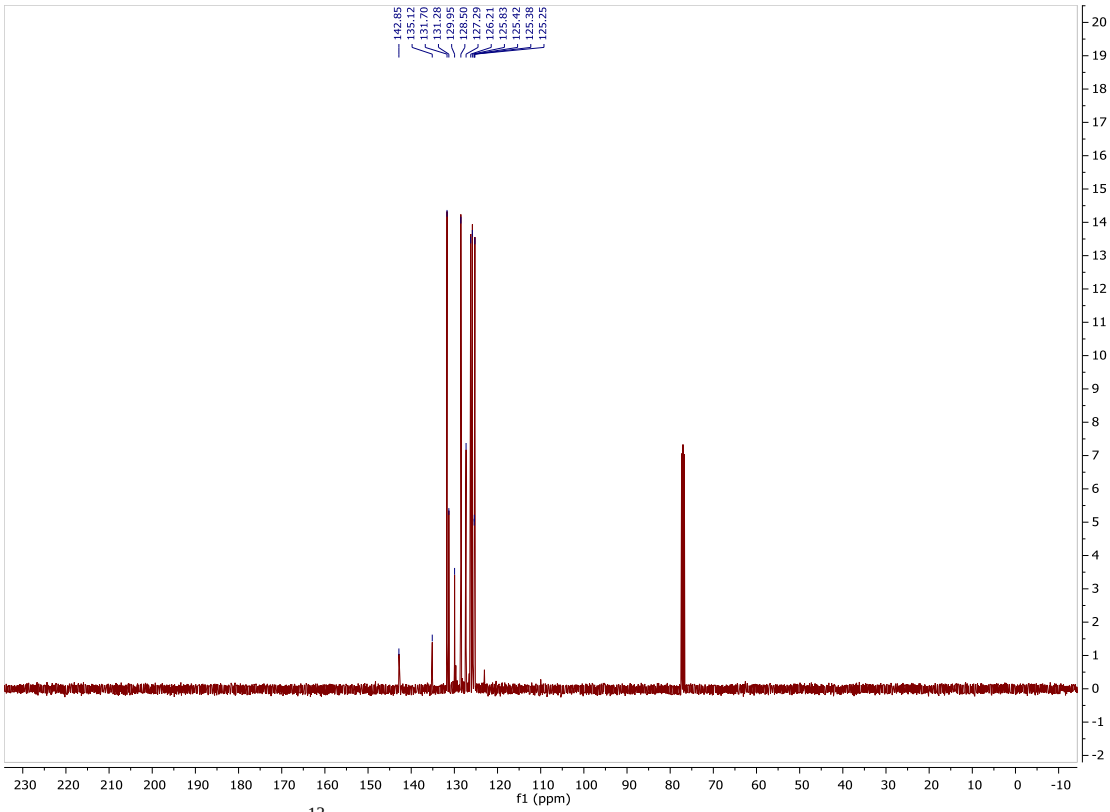
Supplementary Figure 16. ^{13}C NMR spectra of **2g**



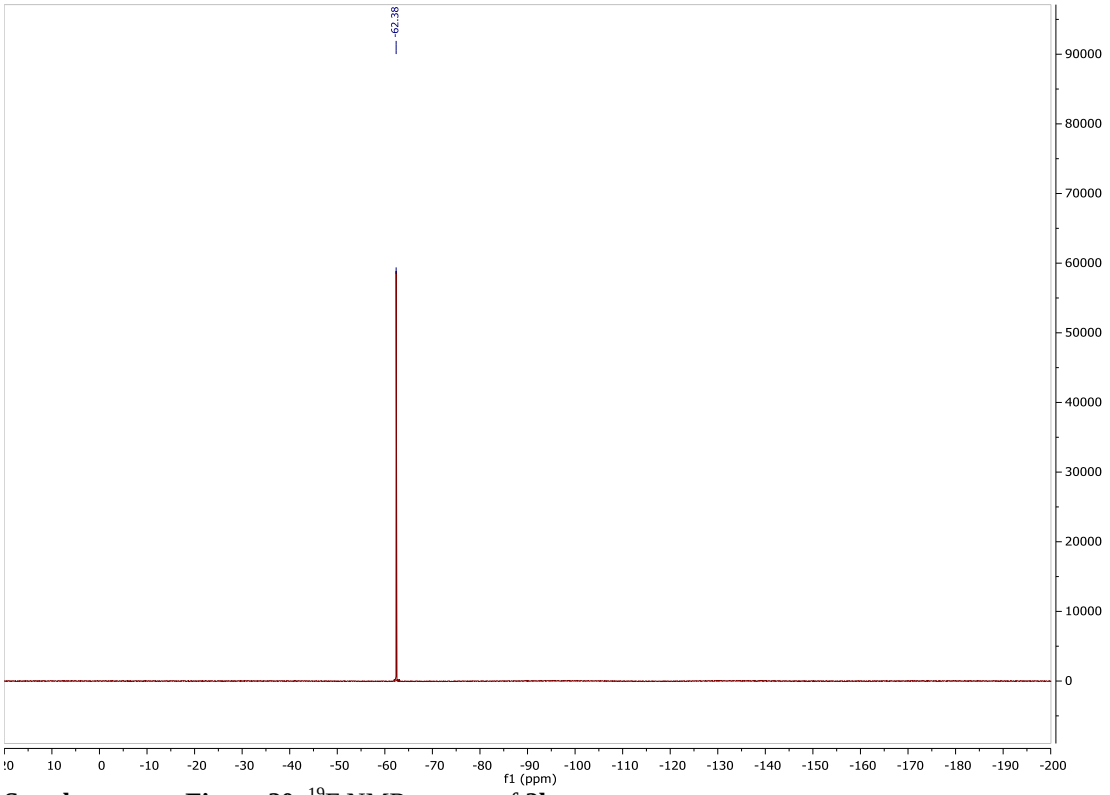
Supplementary Figure 17. ^{19}F NMR spectra of **2g**



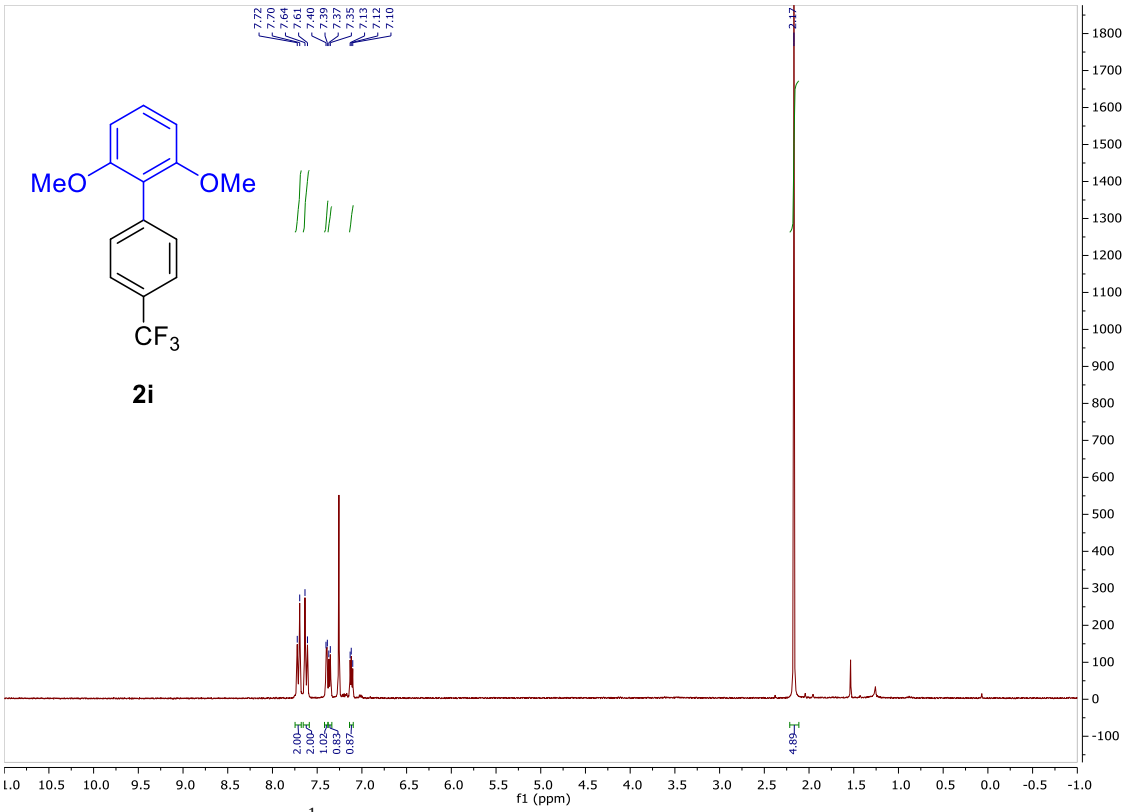
Supplementary Figure 18. ^{1}H NMR spectra of **2h**



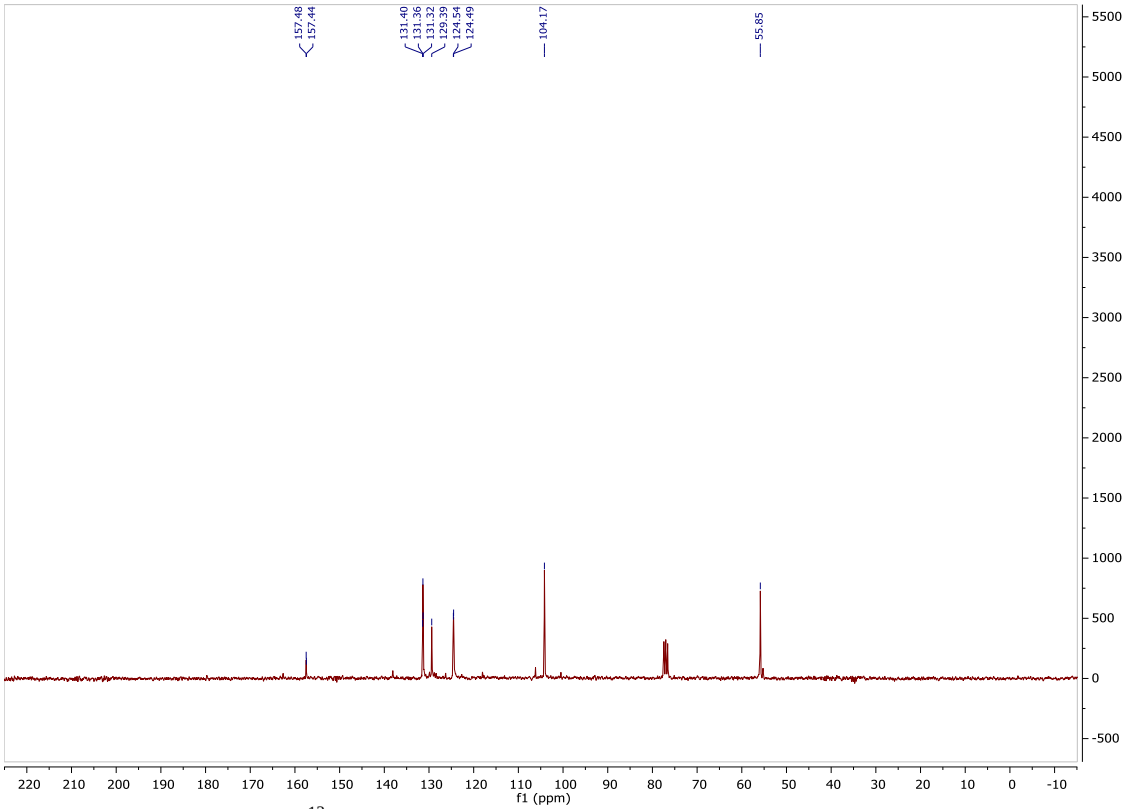
Supplementary Figure 19. ^{13}C NMR spectra of **2h**



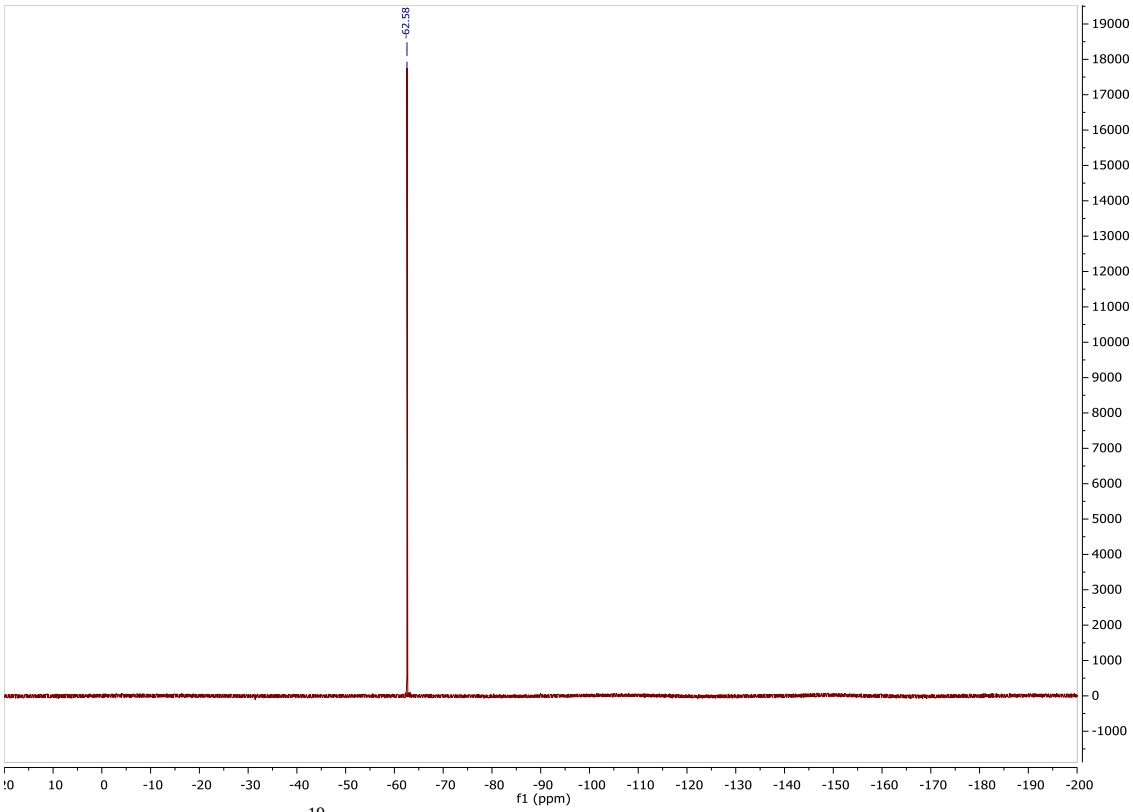
Supplementary Figure 20. ^{19}F NMR spectra of **2h**



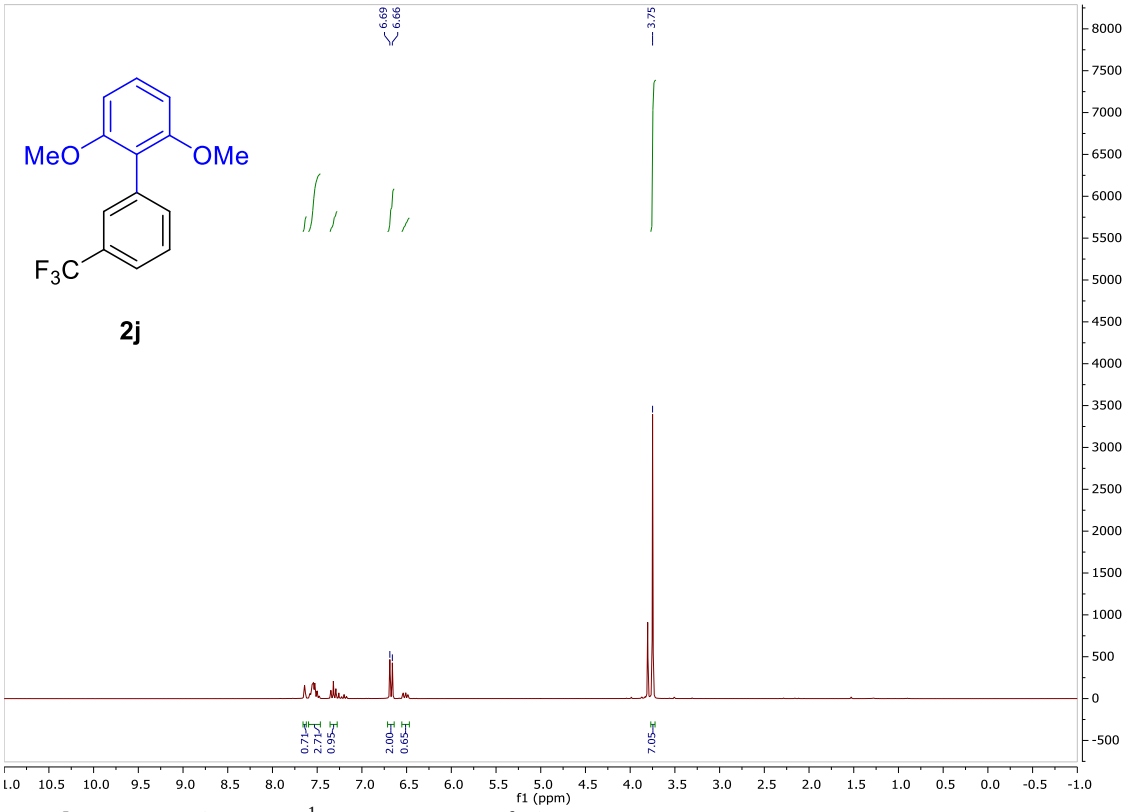
Supplementary Figure 21. ^{1}H NMR spectra of **2i**



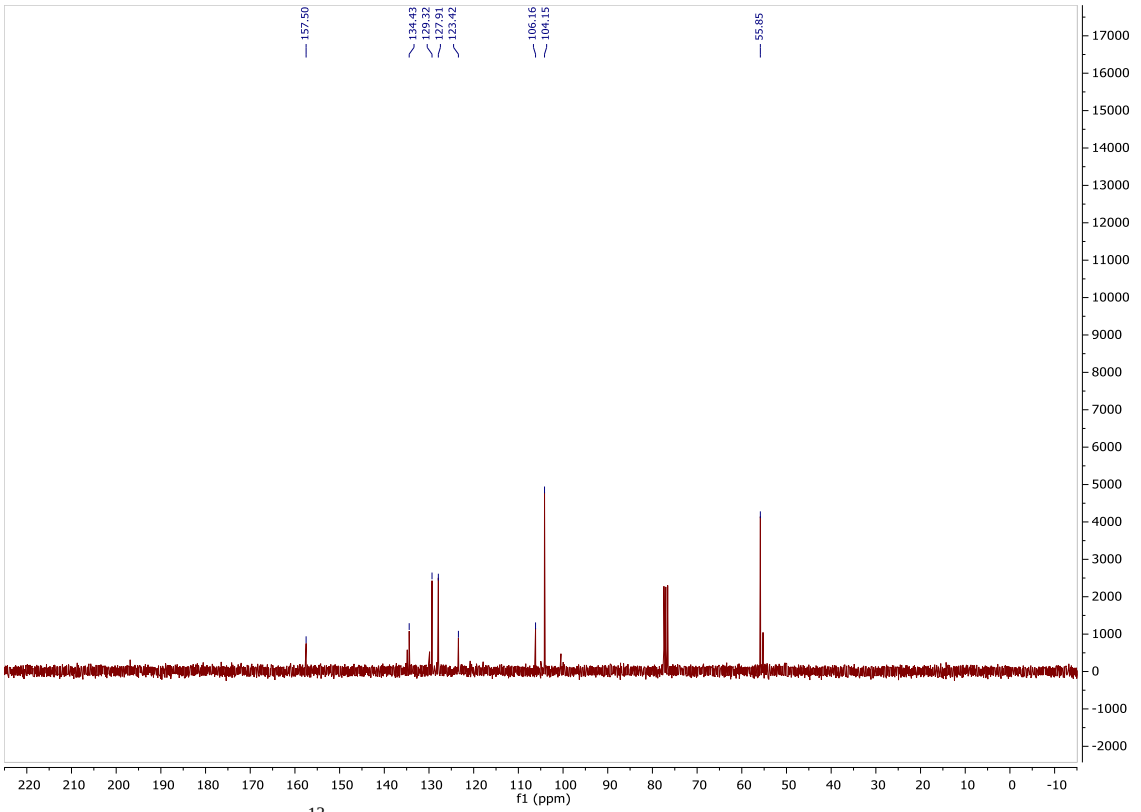
Supplementary Figure 22. ^{13}C NMR spectra of **2i**



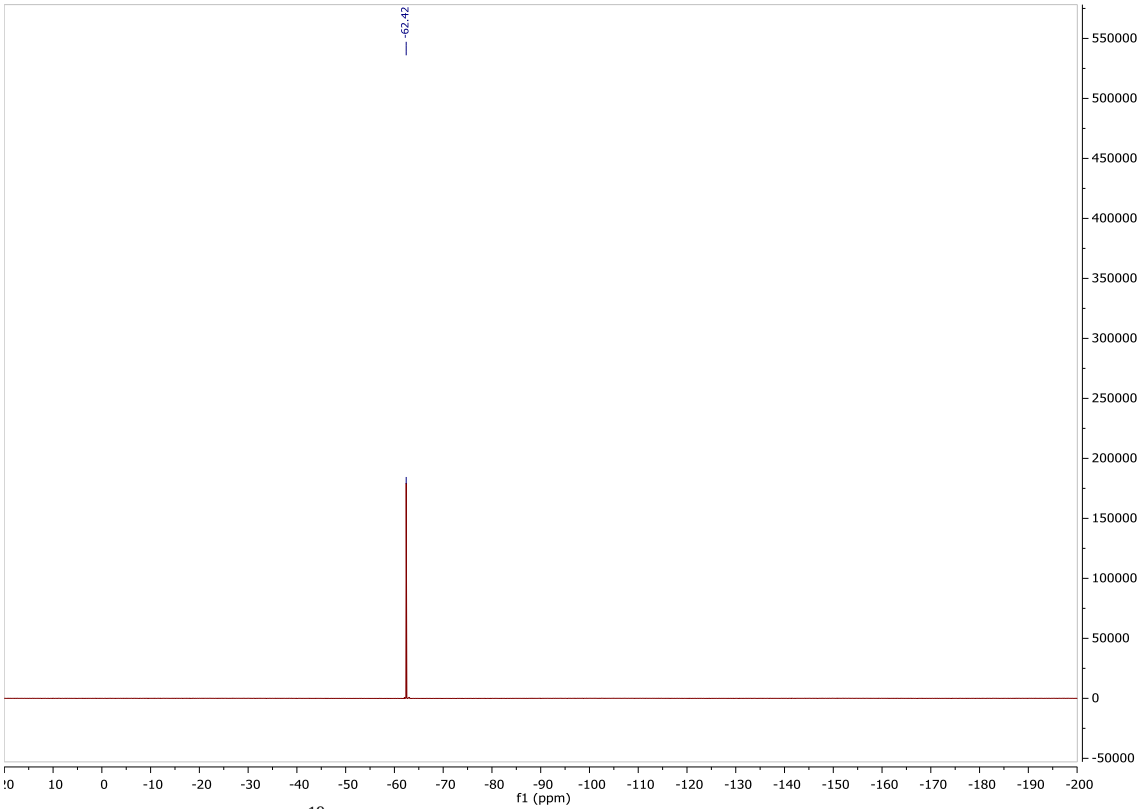
Supplementary Figure 23. ^{19}F NMR spectra of **2i**



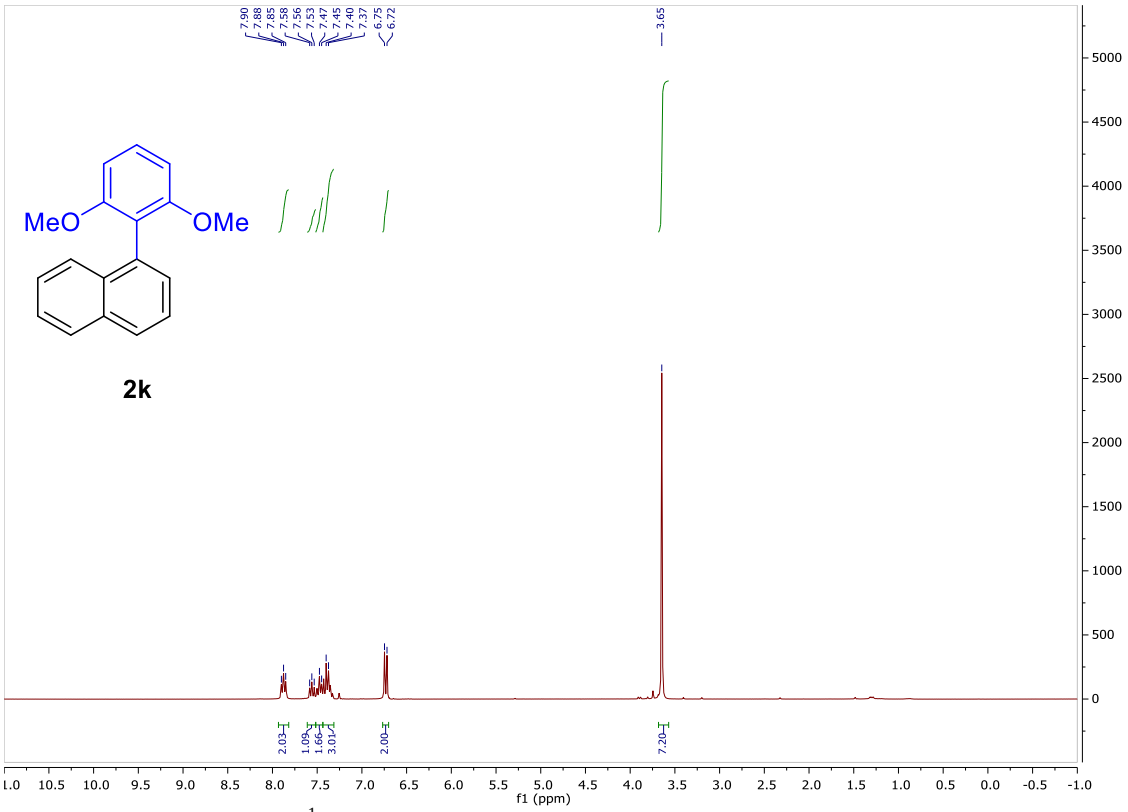
Supplementary Figure 24. ^{1}H NMR spectra of **2j**



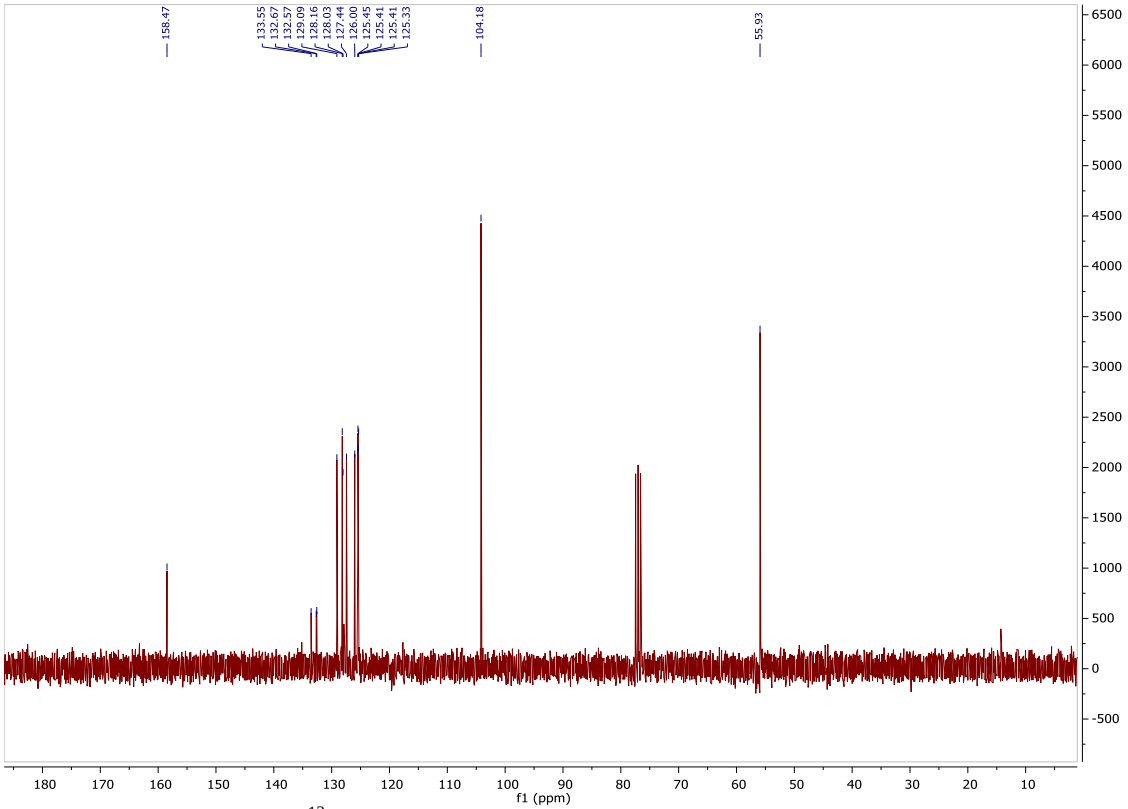
Supplementary Figure 25. ^{13}C NMR spectra of **2j**



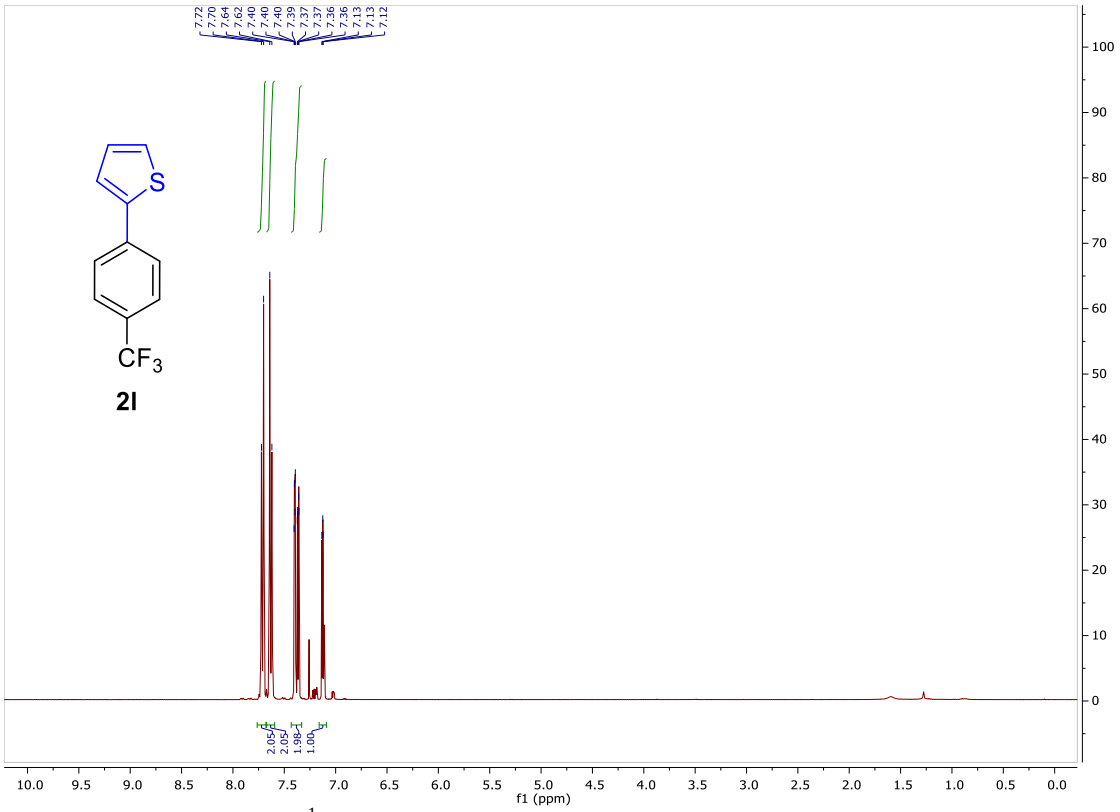
Supplementary Figure 26. ^{19}F NMR spectra of **2j**



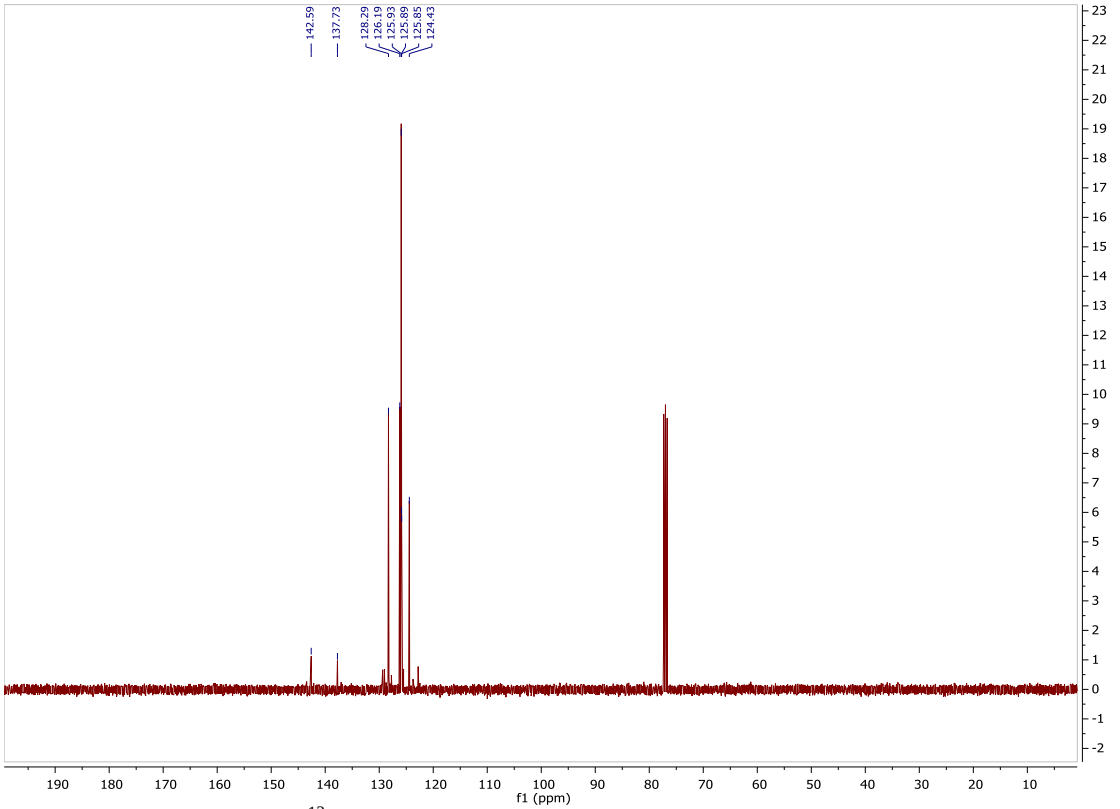
Supplementary Figure 27. ^{1}H NMR spectra of **2k**



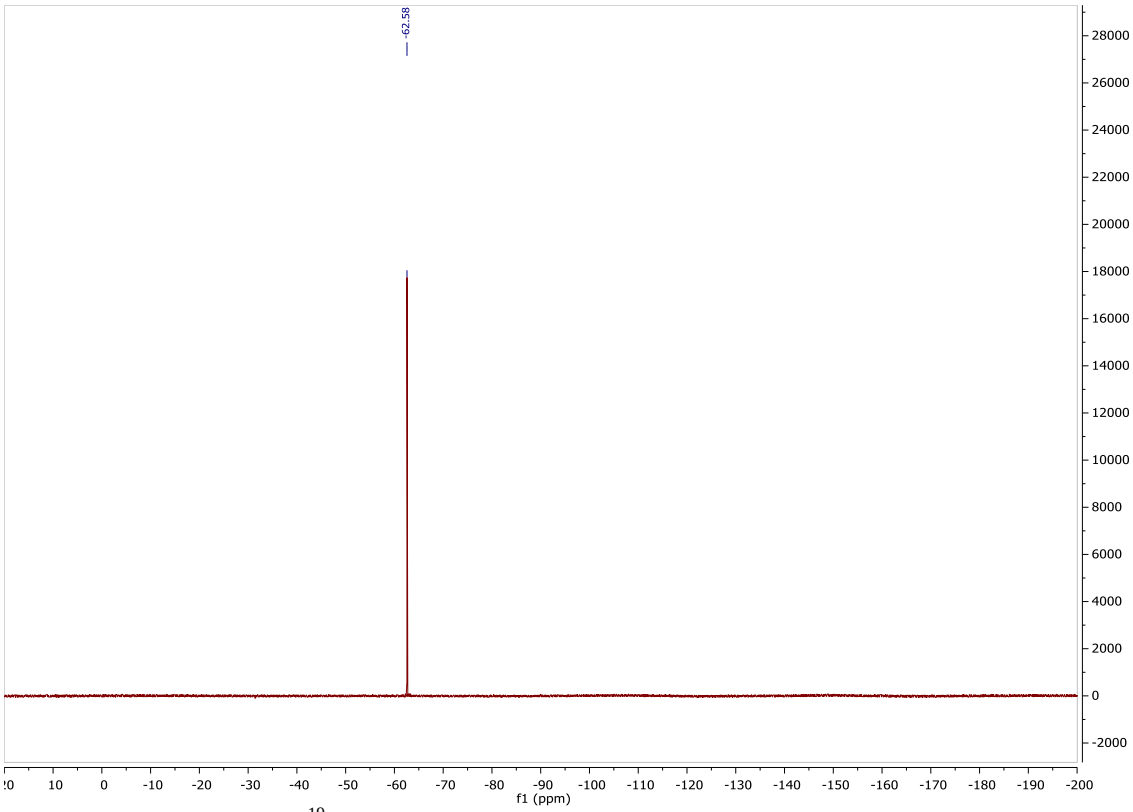
Supplementary Figure 28. ^{13}C NMR spectra of **2k**



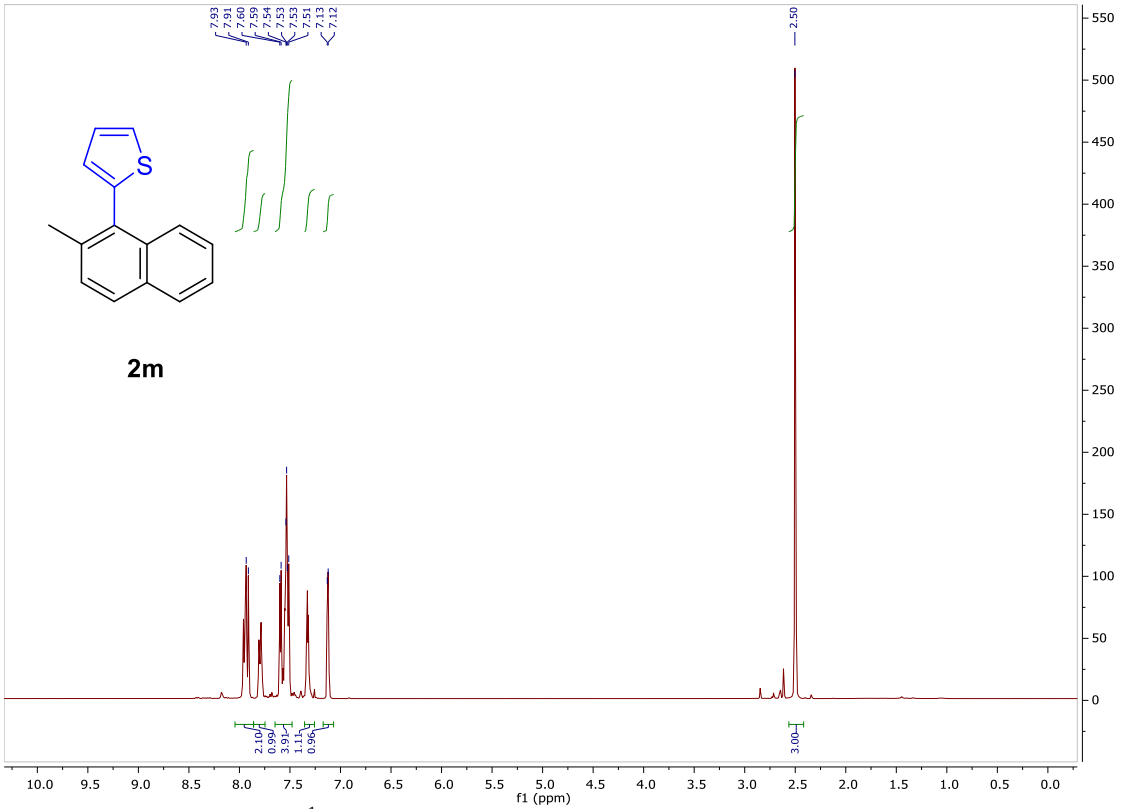
Supplementary Figure 29. ^{1}H NMR spectra of **2l**



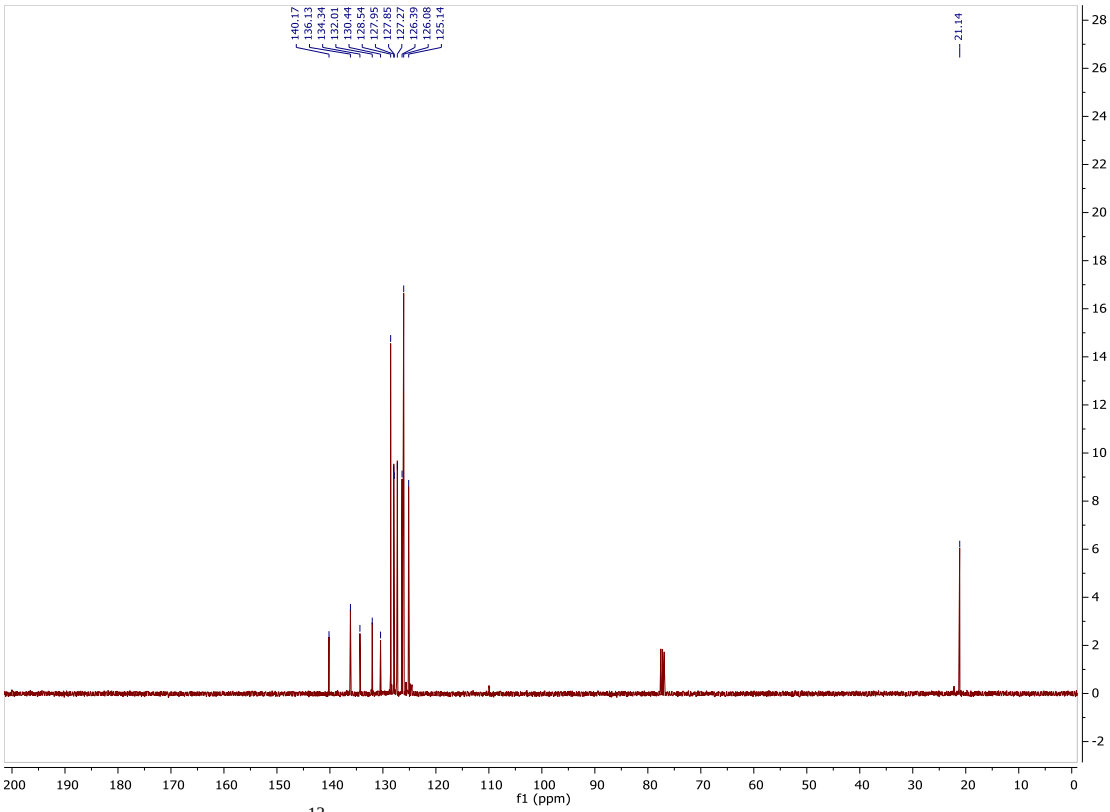
Supplementary Figure 30. ^{13}C NMR spectra of **2l**



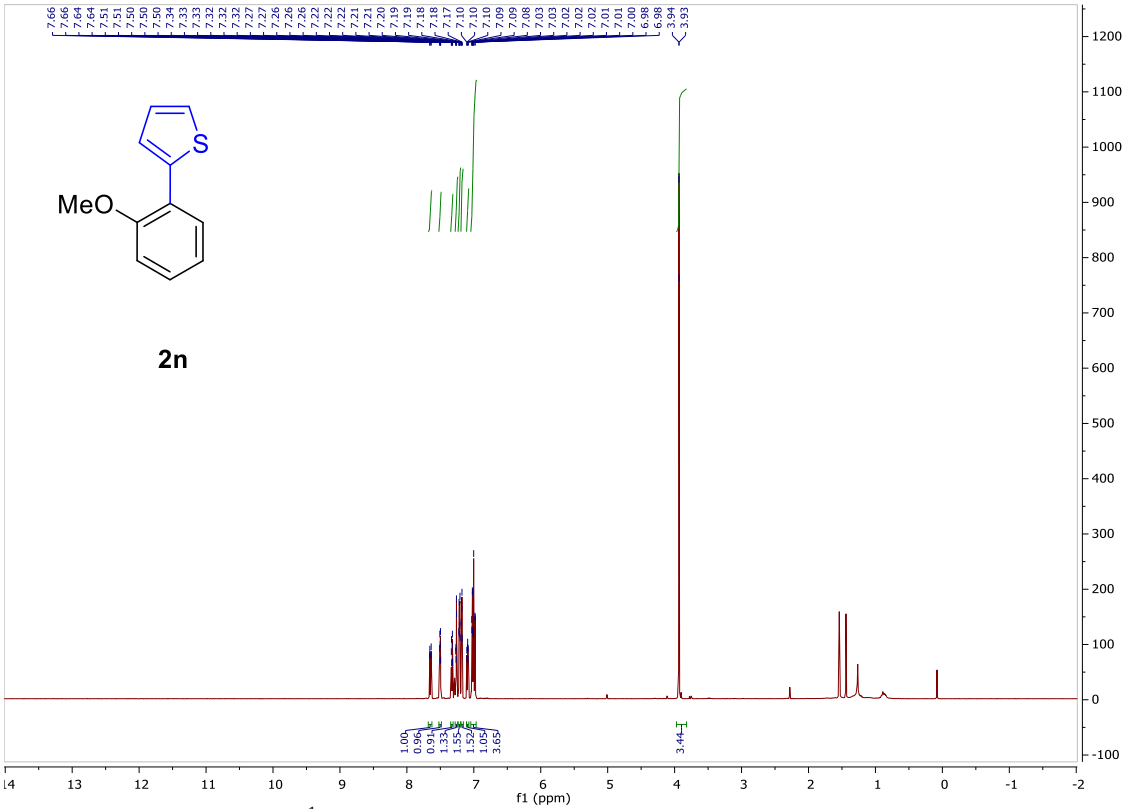
Supplementary Figure 31. ^{19}F NMR spectra of **2l**



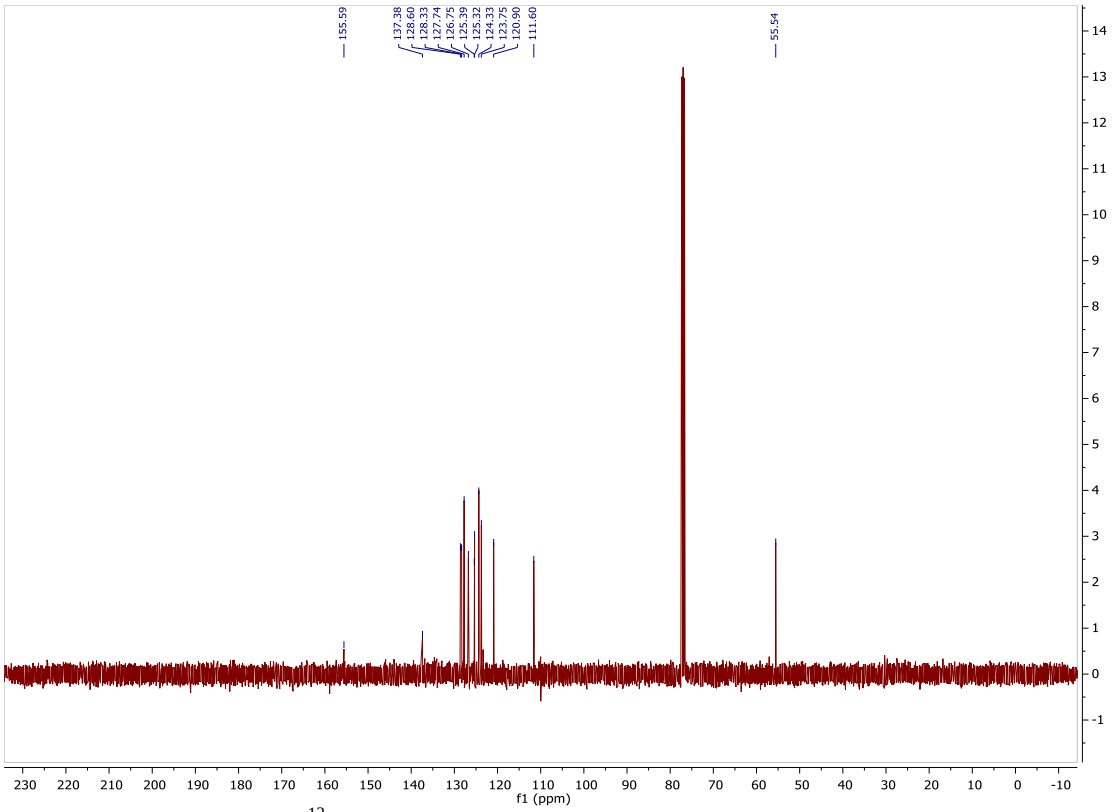
Supplementary Figure 32. ^{1}H NMR spectra of **2m**



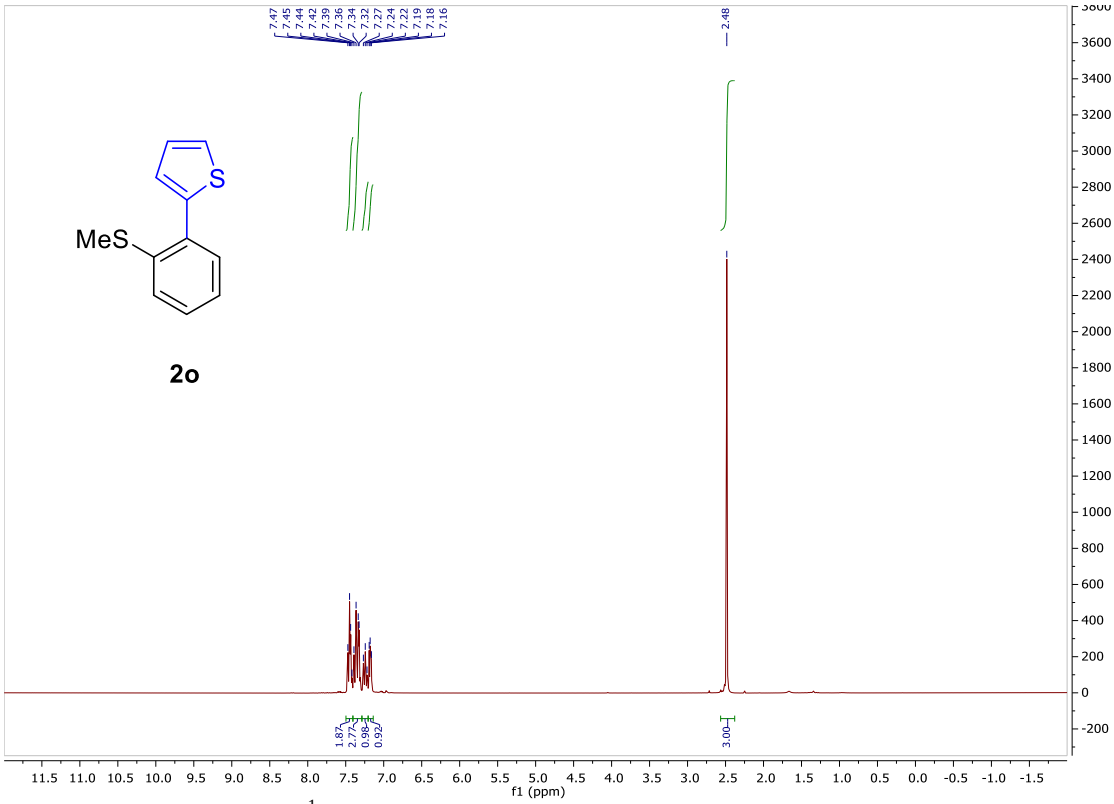
Supplementary Figure 33. ^{13}C NMR spectra of **2m**



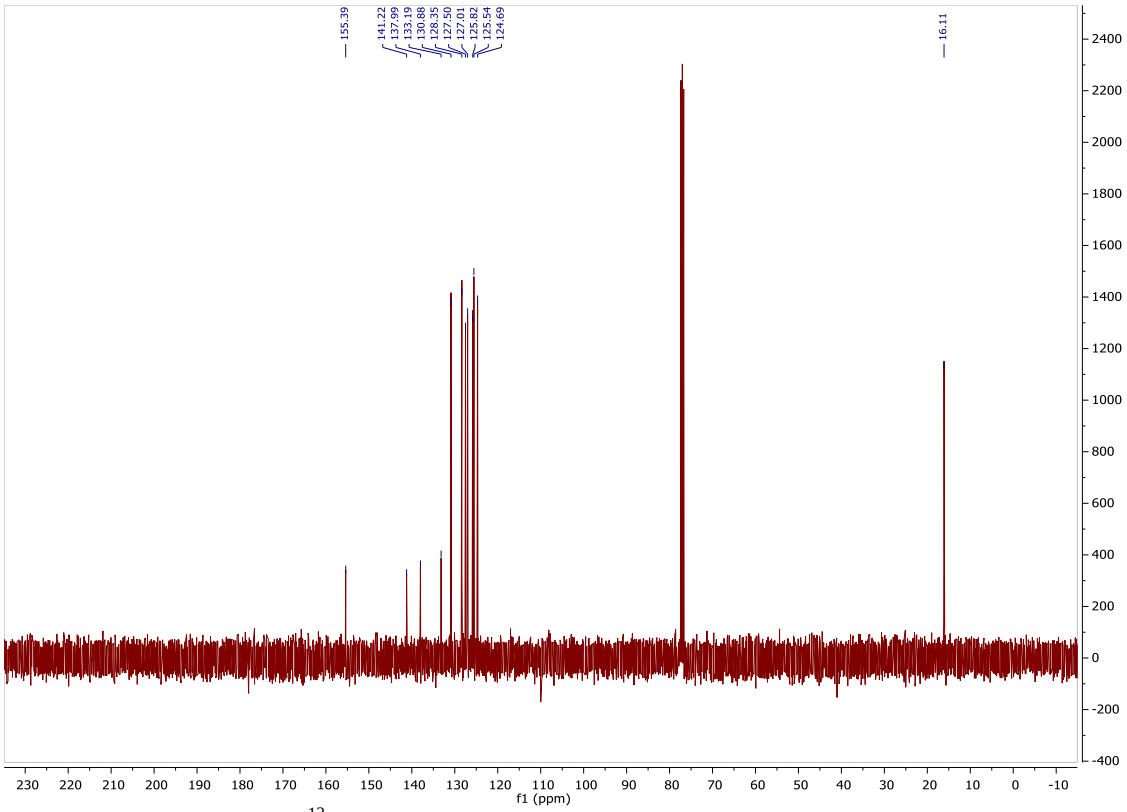
Supplementary Figure 34. ^{1}H NMR spectra of **2n**



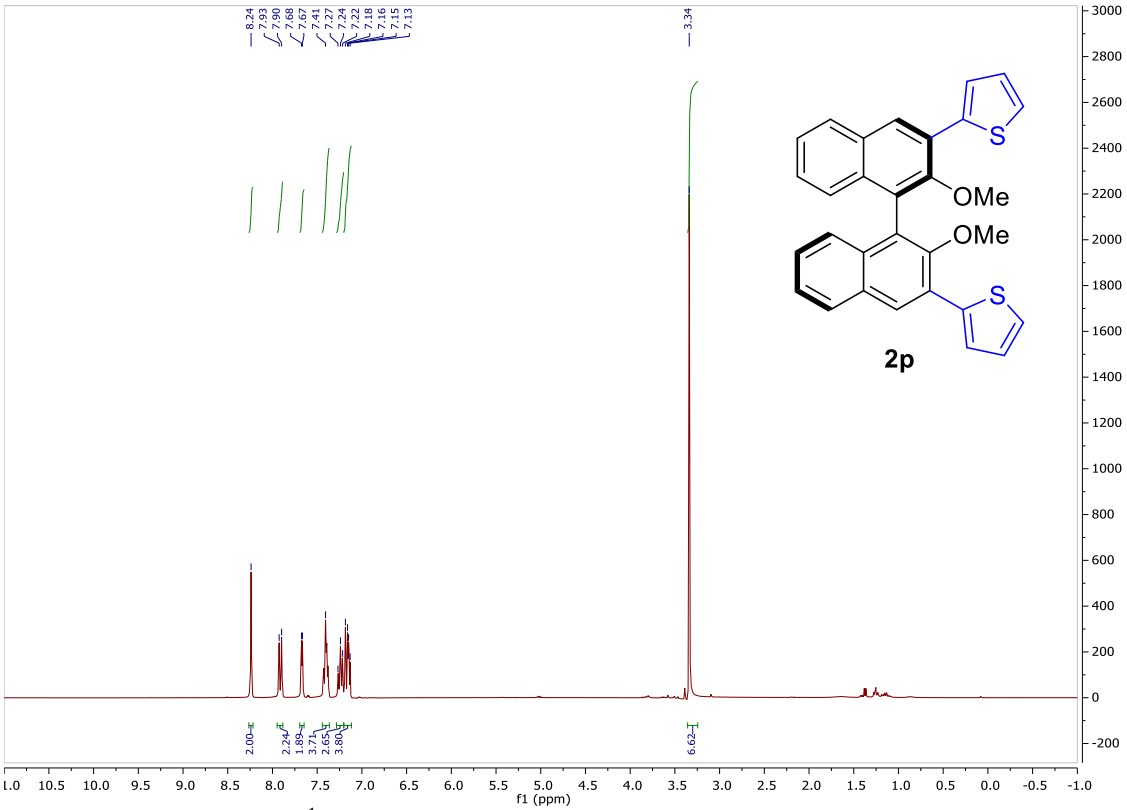
Supplementary Figure 35. ^{13}C NMR spectra of **2n**



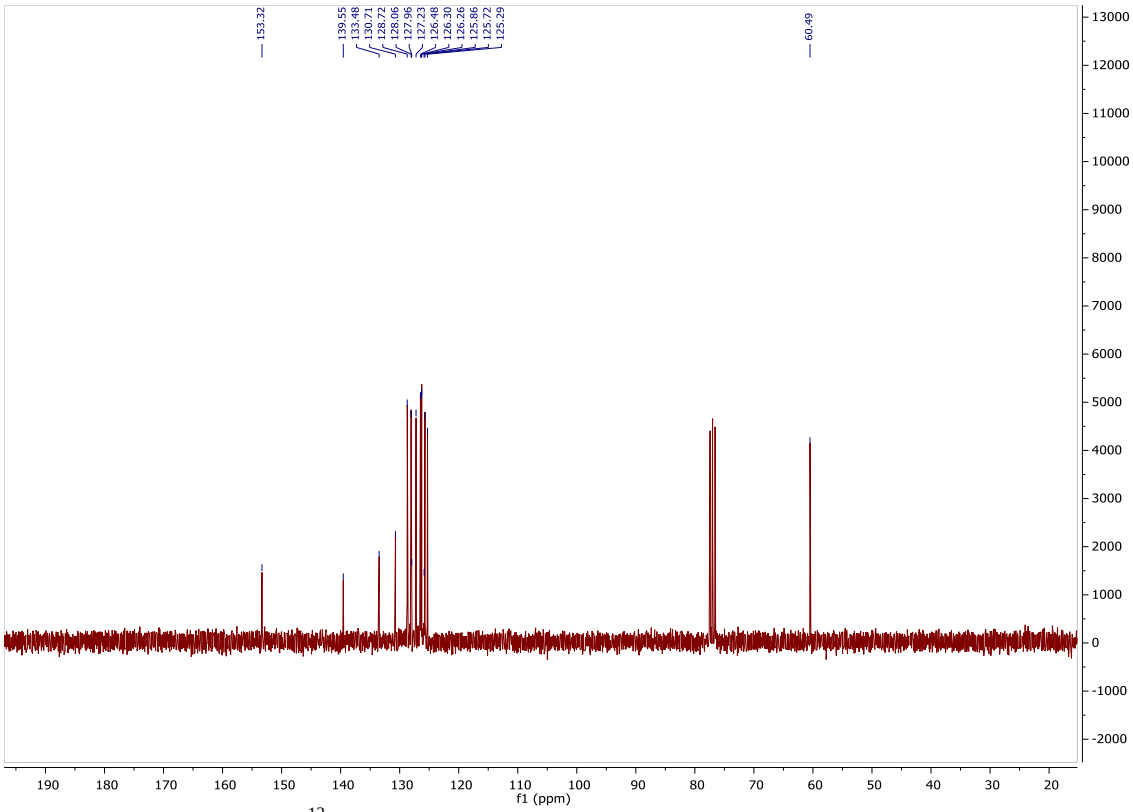
Supplementary Figure 36. ^{1}H NMR spectra of **2o**



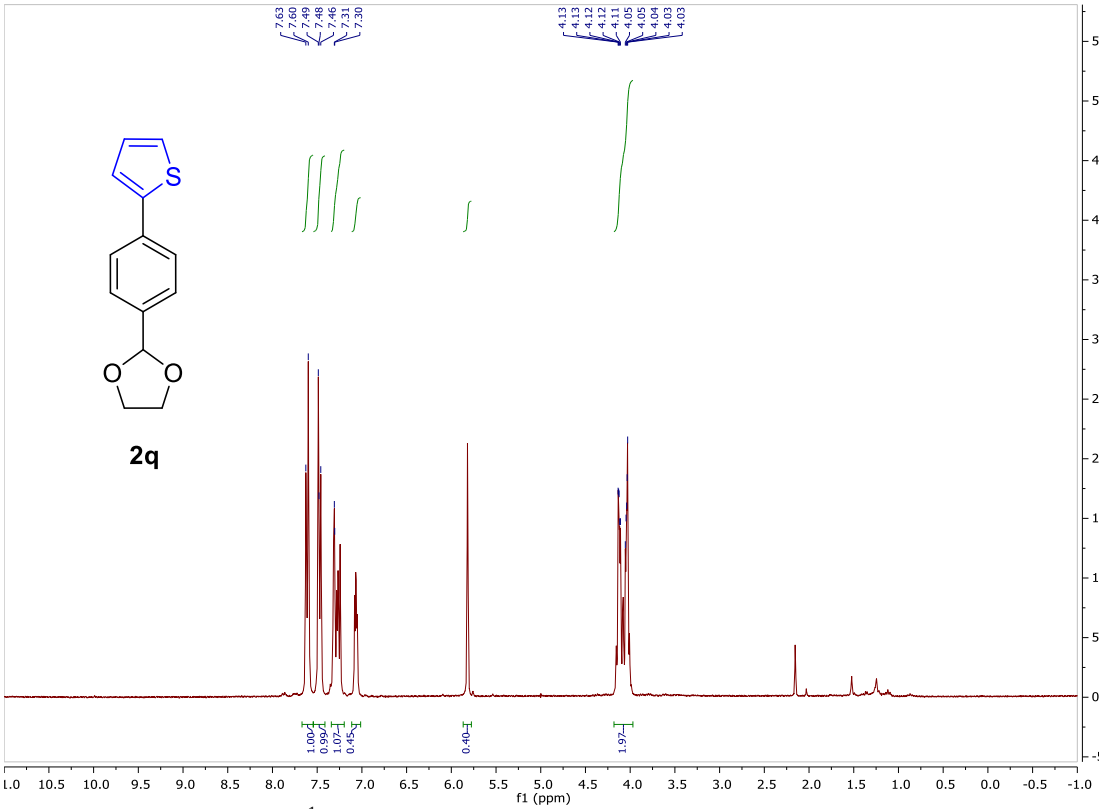
Supplementary Figure 37. ^{13}C NMR spectra of **2o**



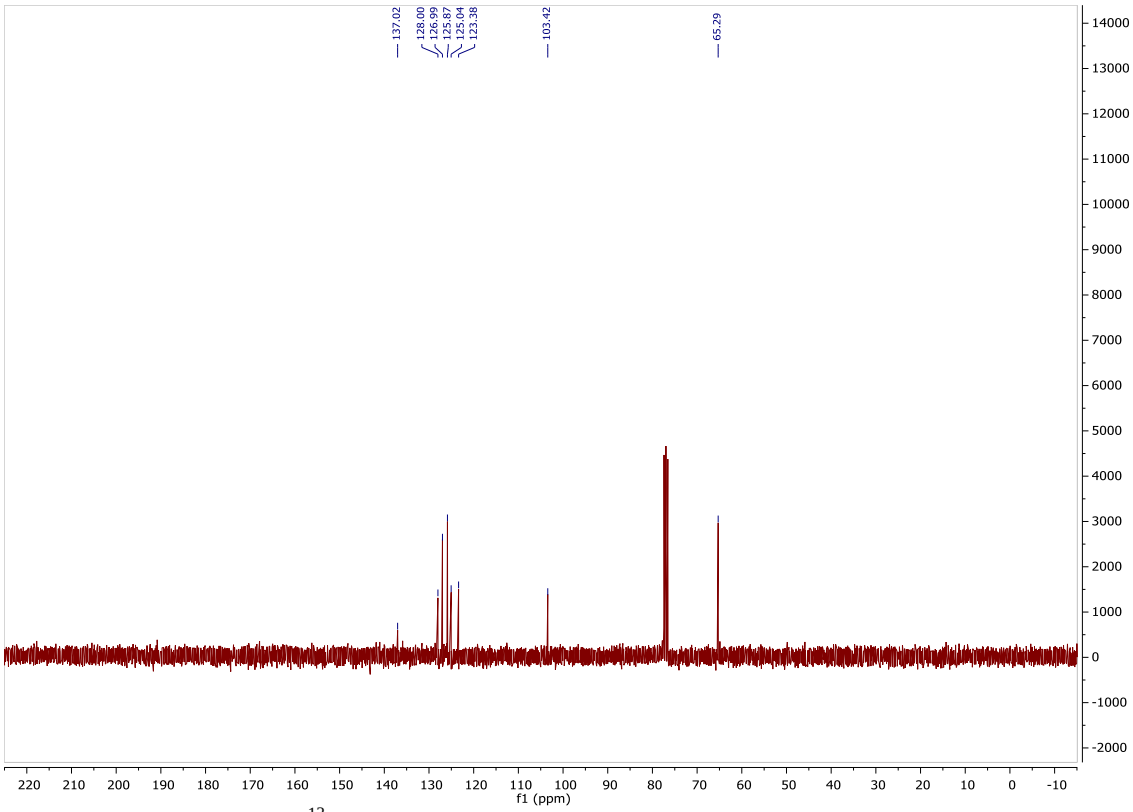
Supplementary Figure 38. ^{1}H NMR spectra of **2p**



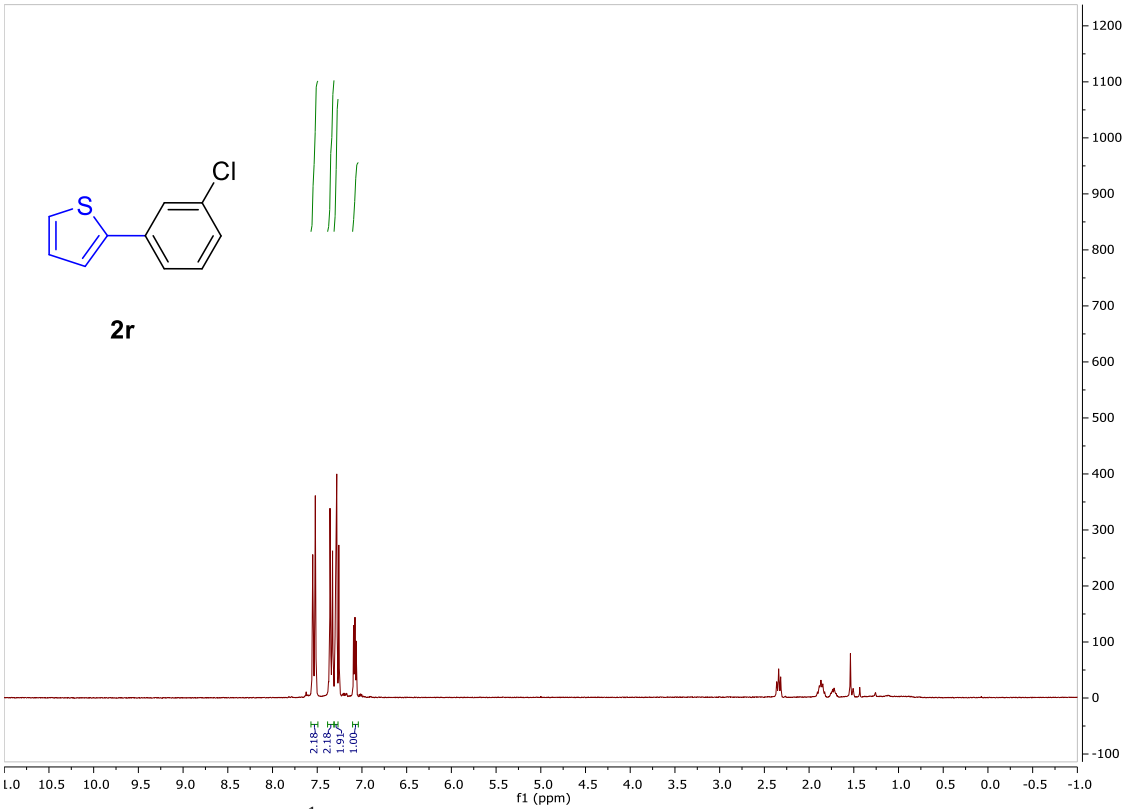
Supplementary Figure 39. ^{13}C NMR spectra of **2p**



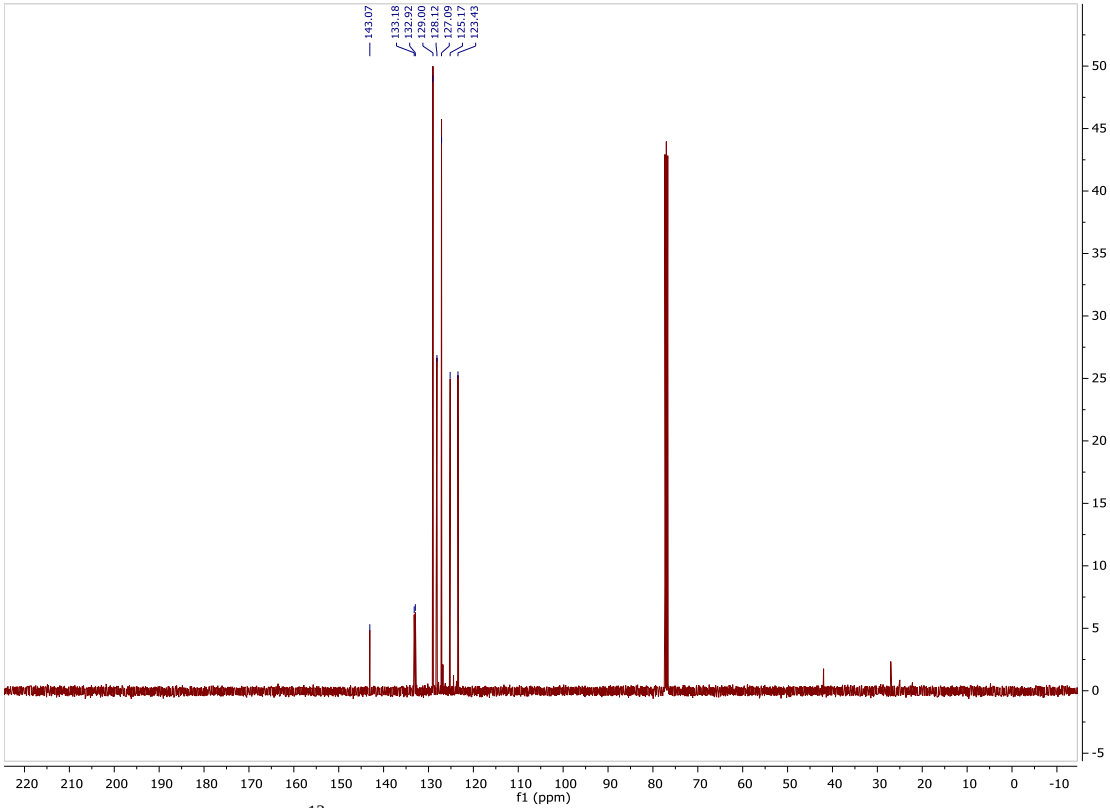
Supplementary Figure 40. ^{1}H NMR spectra of **2q**



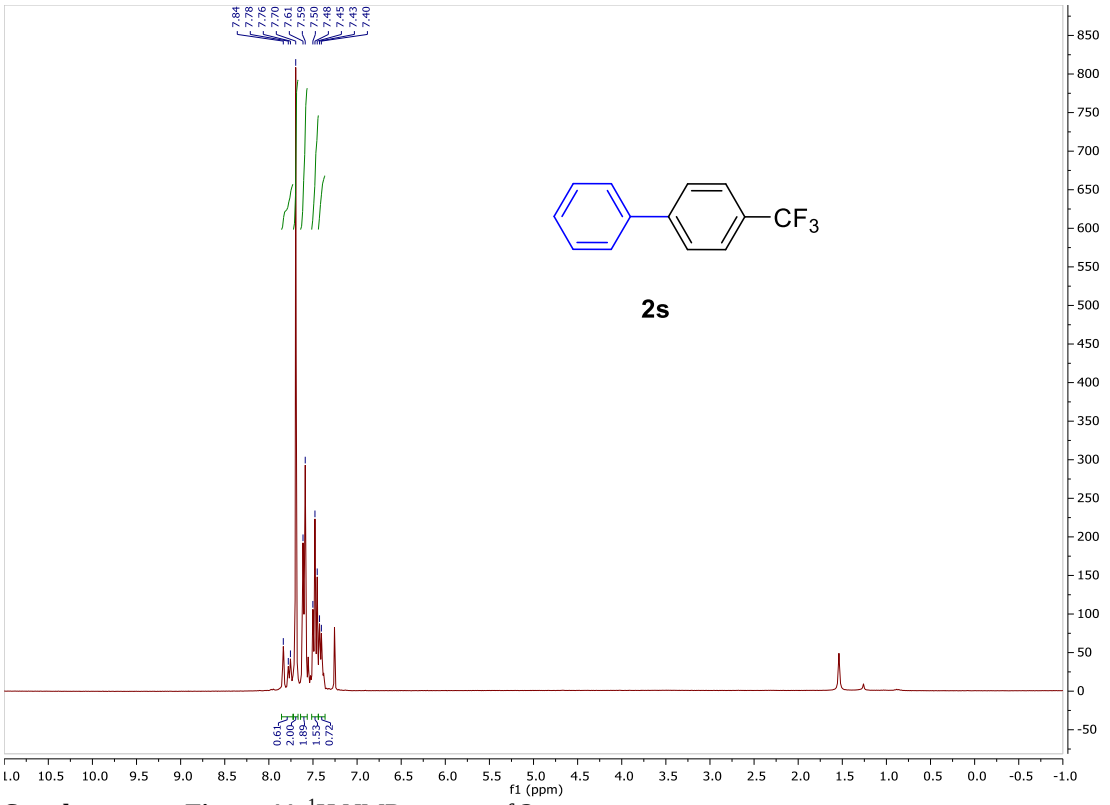
Supplementary Figure 41. ^{13}C NMR spectra of **2q**



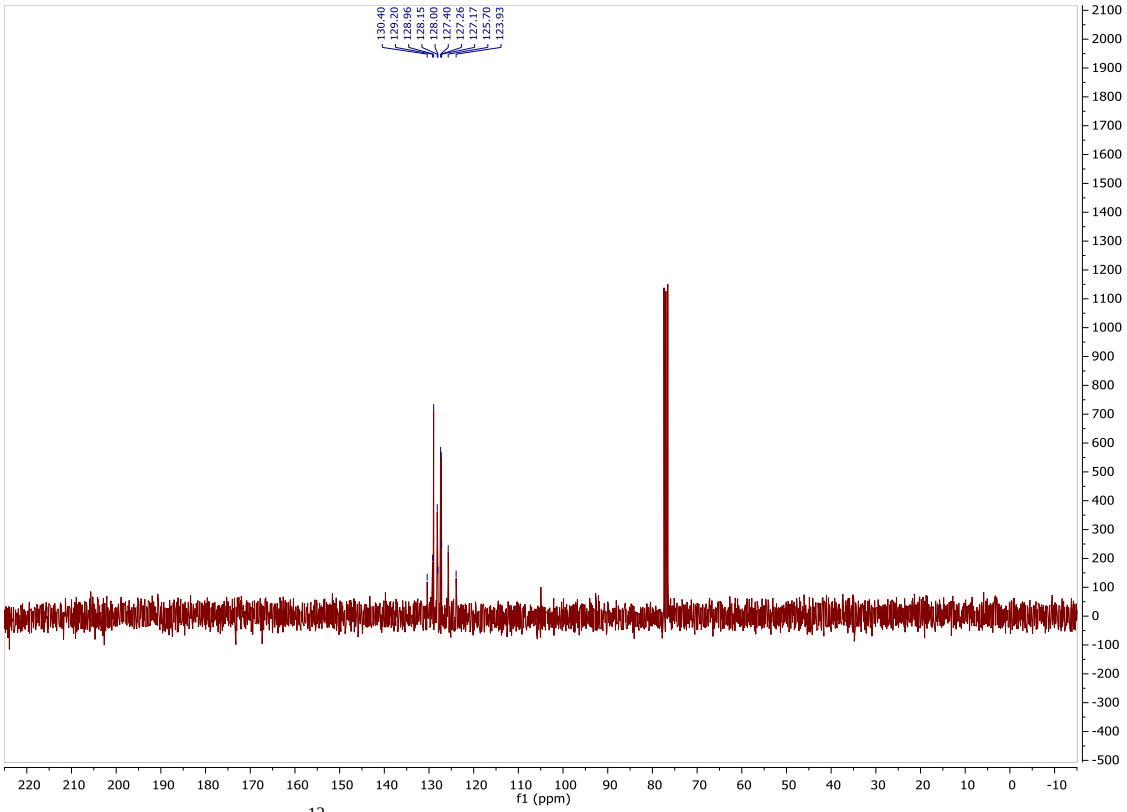
Supplementary Figure 42. ^{1}H NMR spectra of **2r**



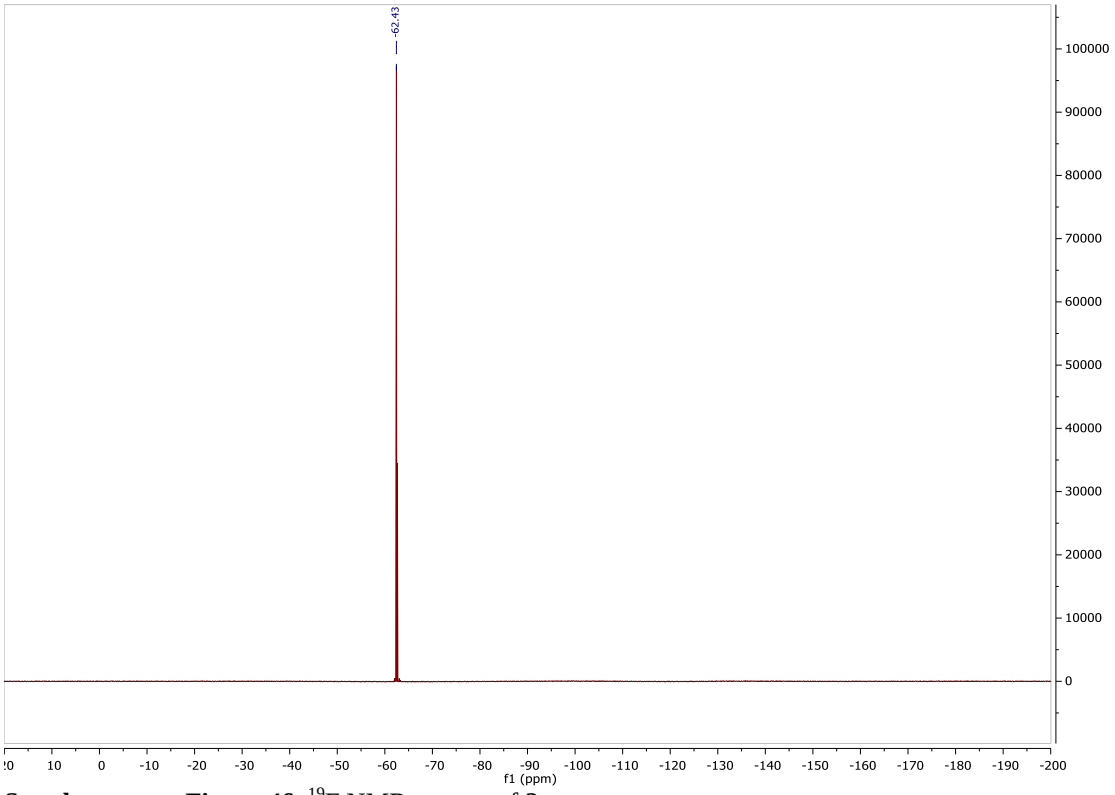
Supplementary Figure 43. ^{13}C NMR spectra of **2r**



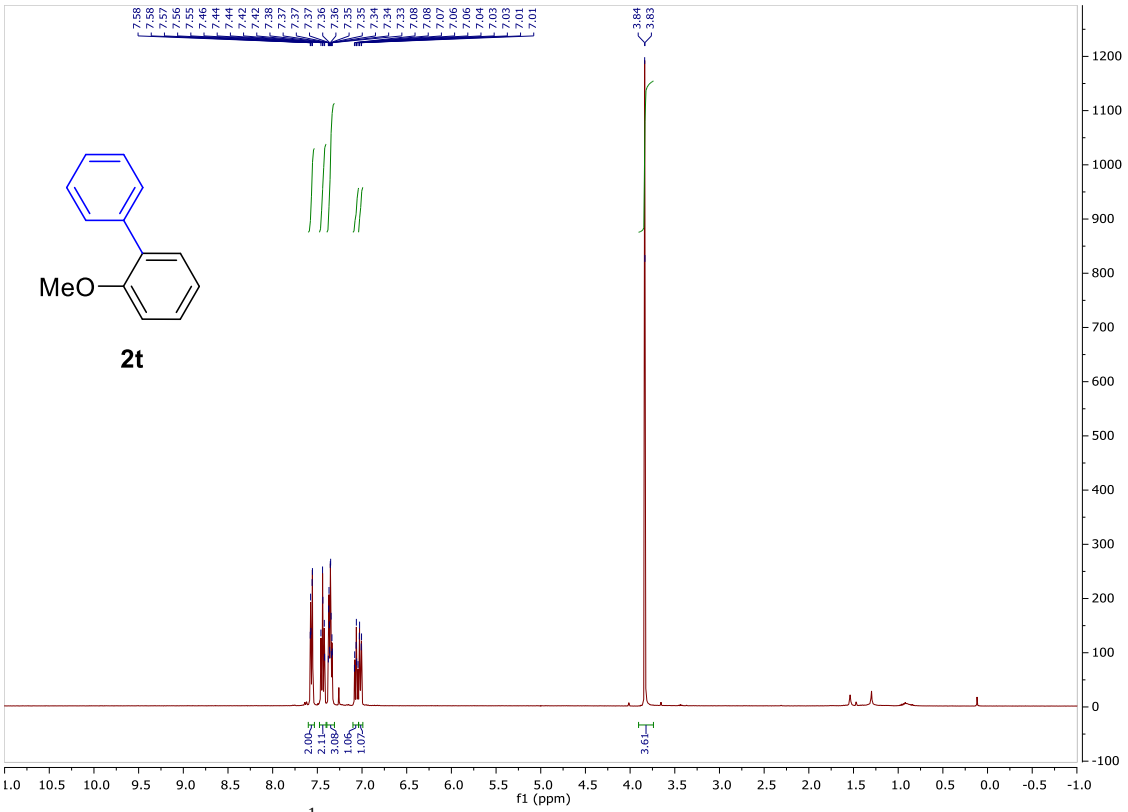
Supplementary Figure 44. ^{1}H NMR spectra of **2s**



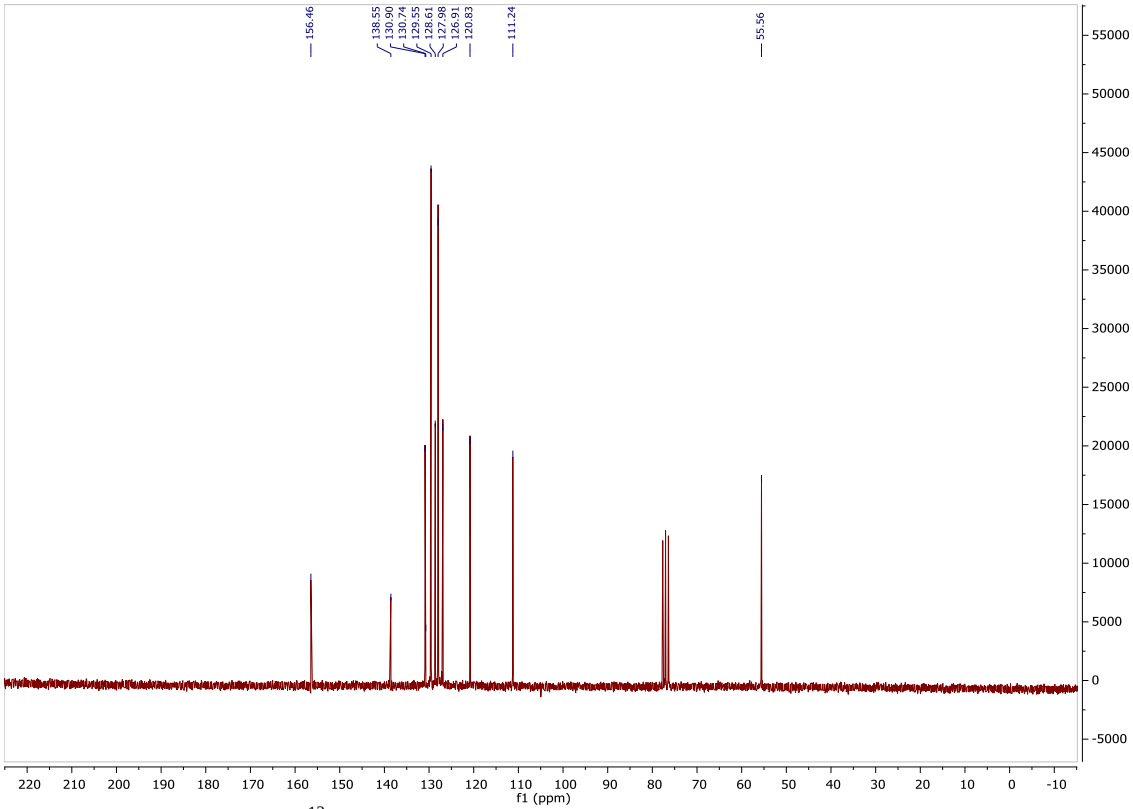
Supplementary Figure 45. ^{13}C NMR spectra of **2s**



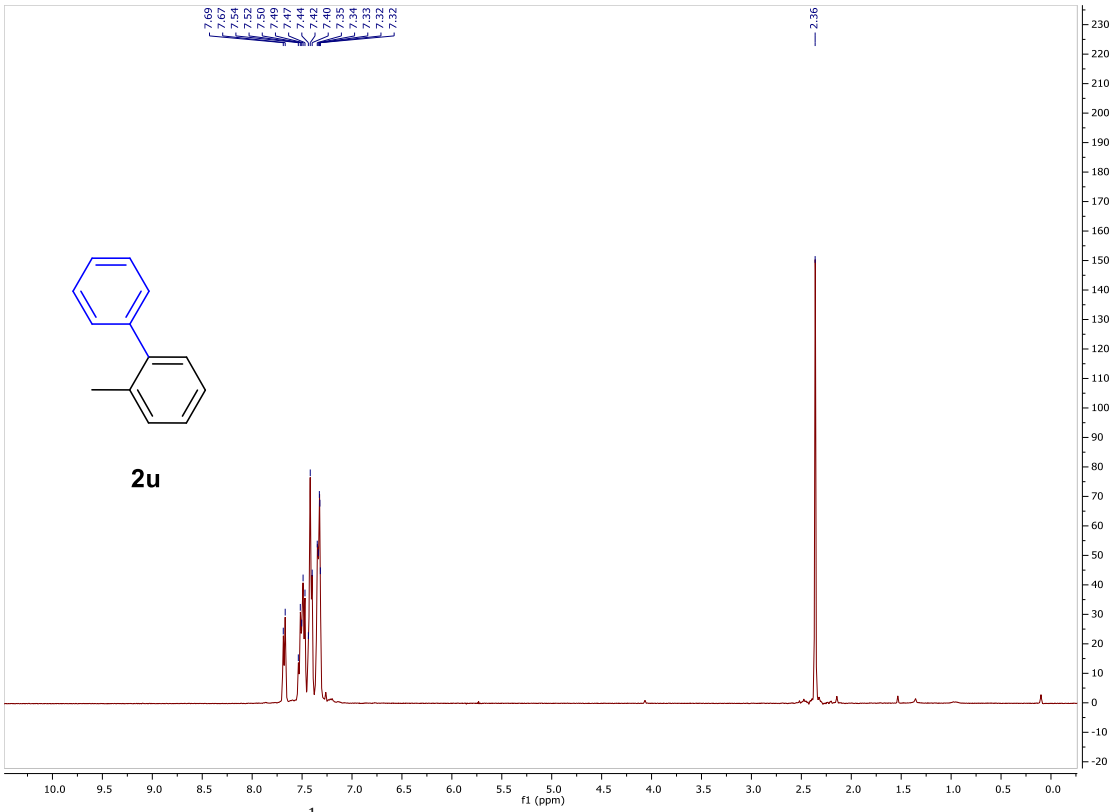
Supplementary Figure 46. ^{19}F NMR spectra of **2s**



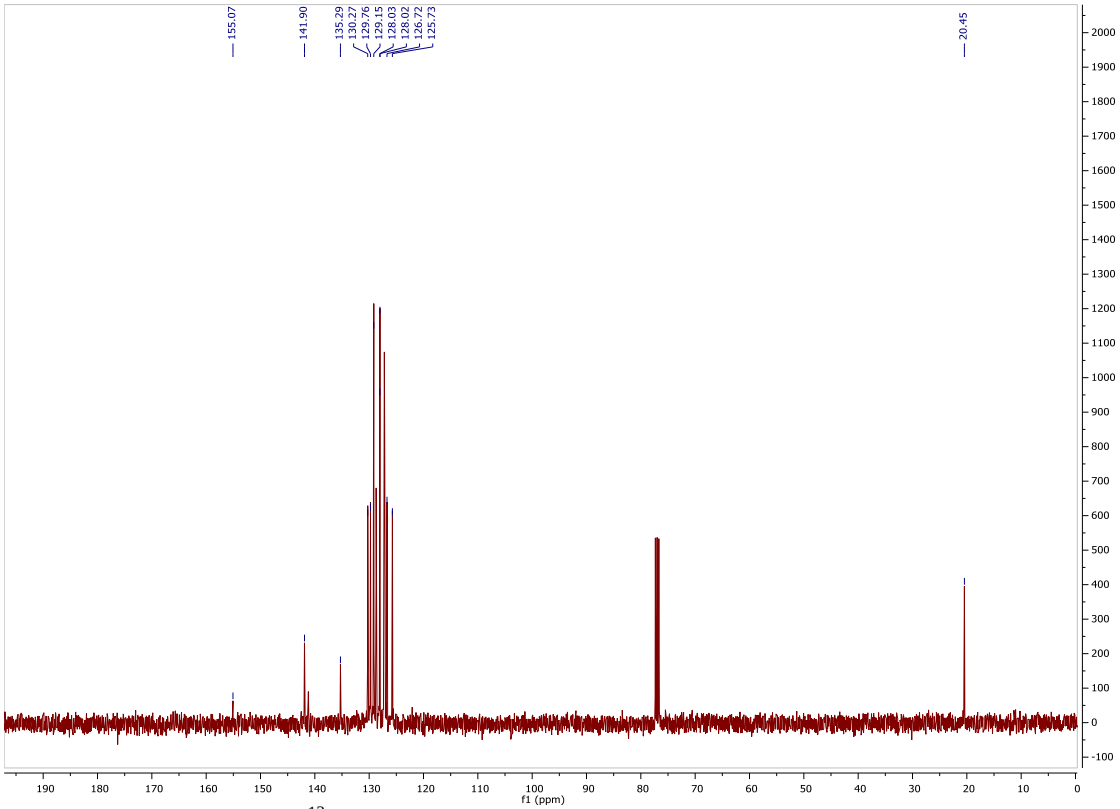
Supplementary Figure 47. ^{1}H NMR spectra of **2t**



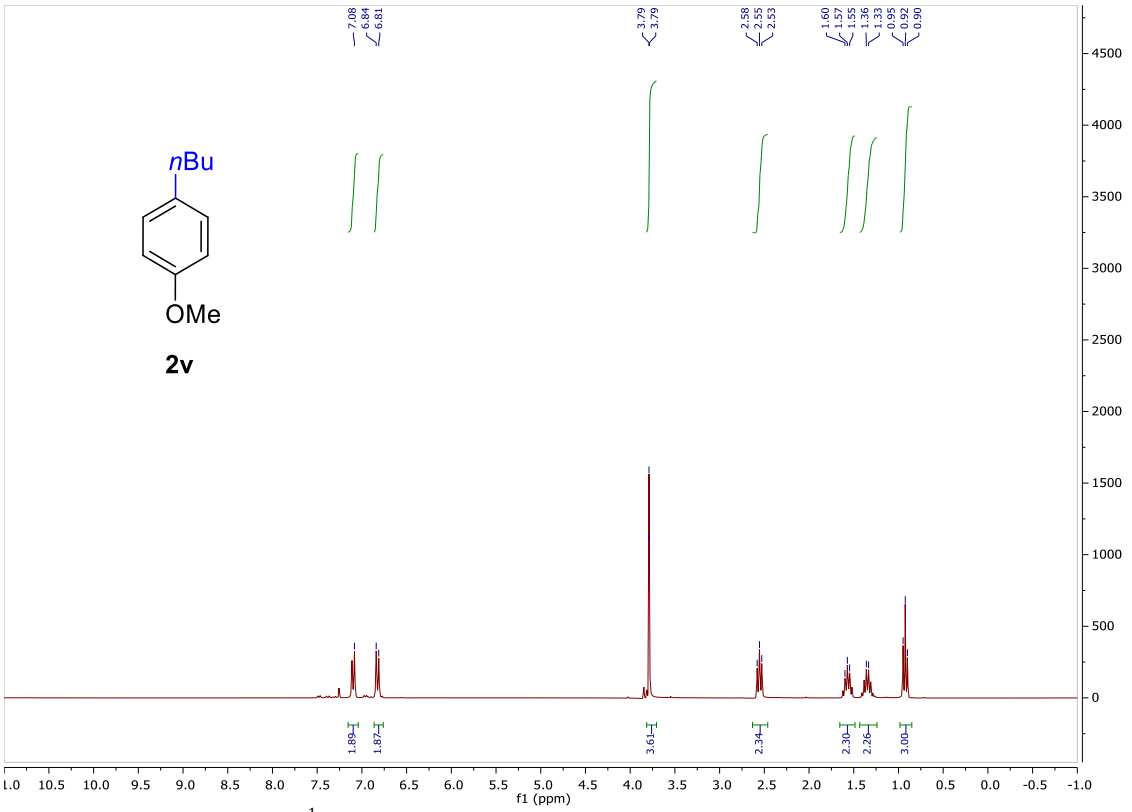
Supplementary Figure 48. ^{13}C NMR spectra of **2t**



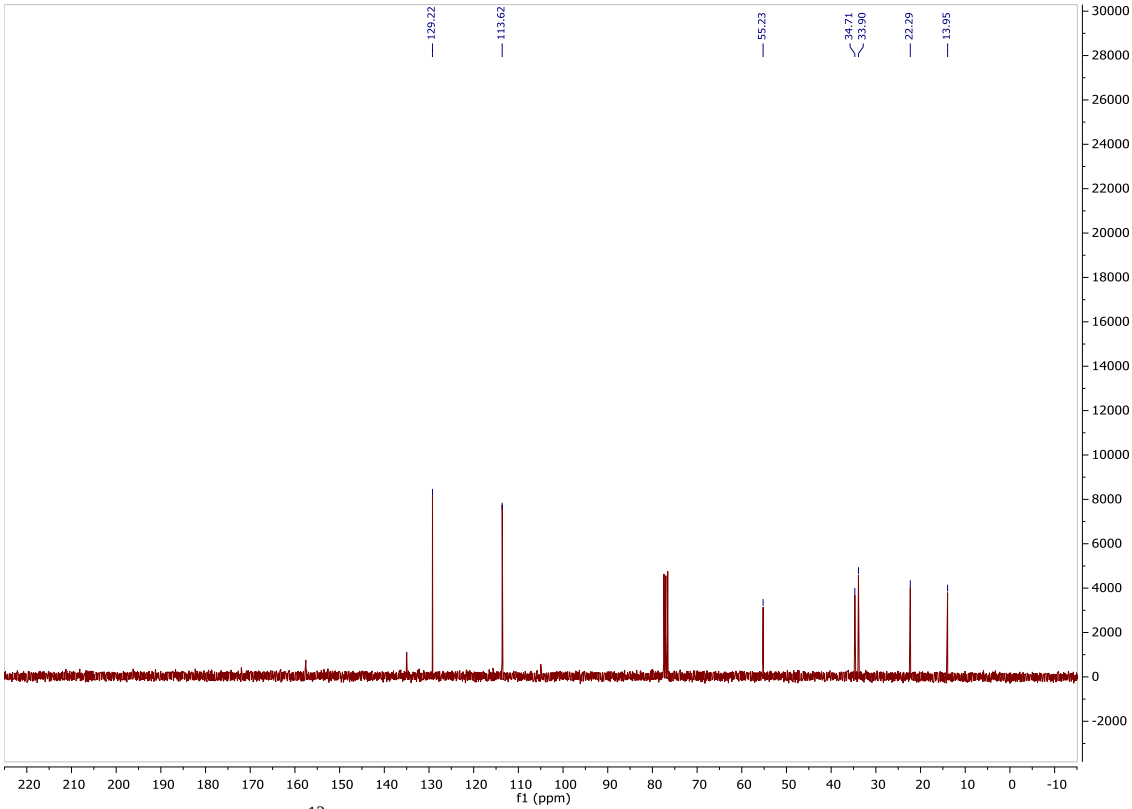
Supplementary Figure 49. ^{1}H NMR spectra of **2u**



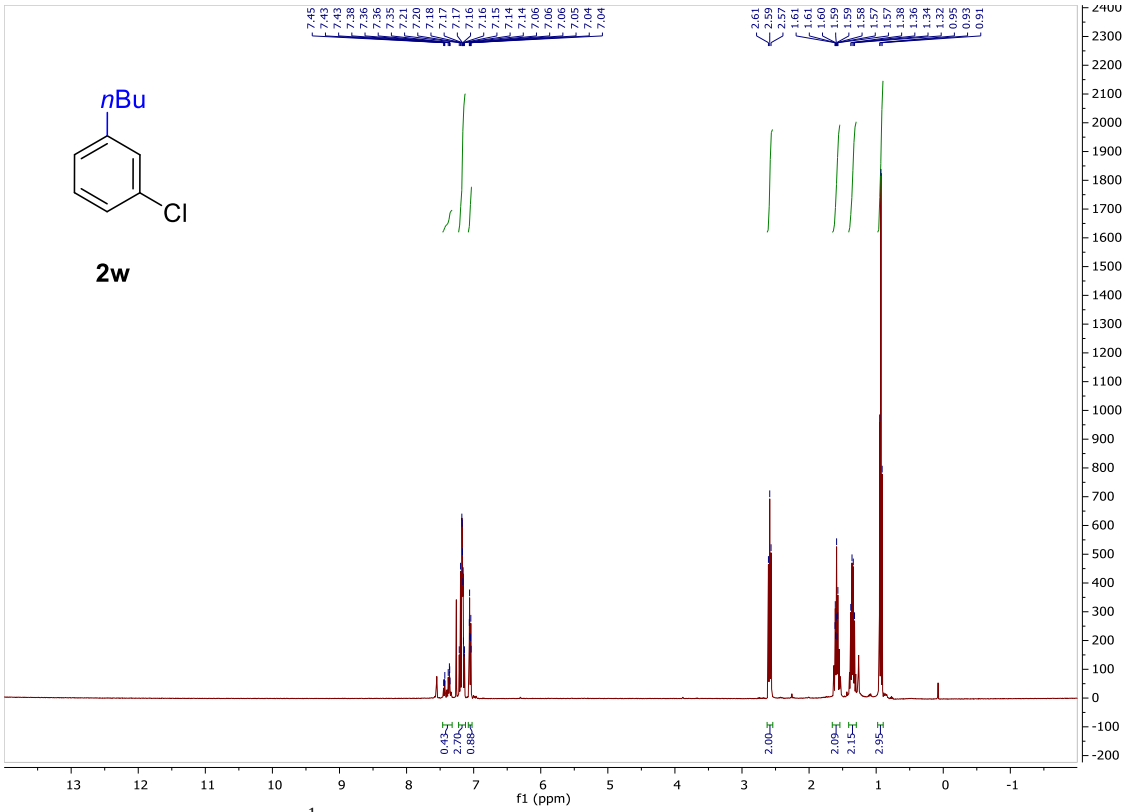
Supplementary Figure 50. ^{13}C NMR spectra of **2u**



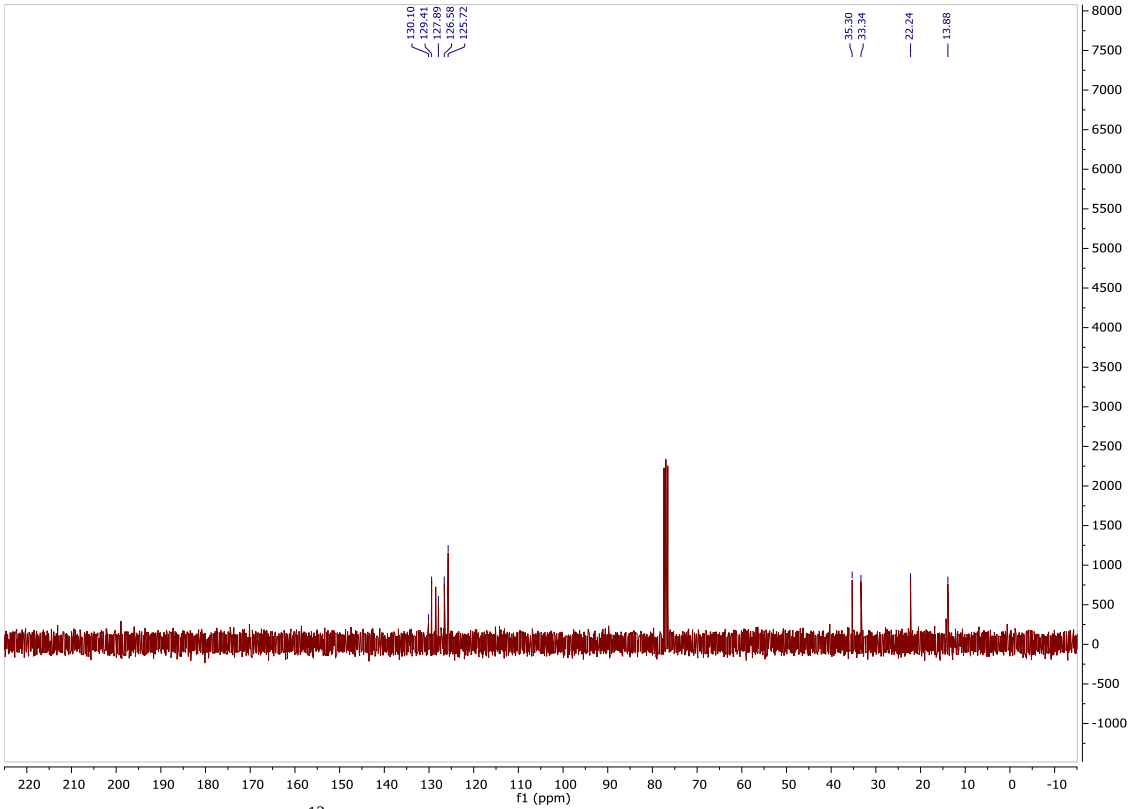
Supplementary Figure 51. ^{1}H NMR spectra of **2v**



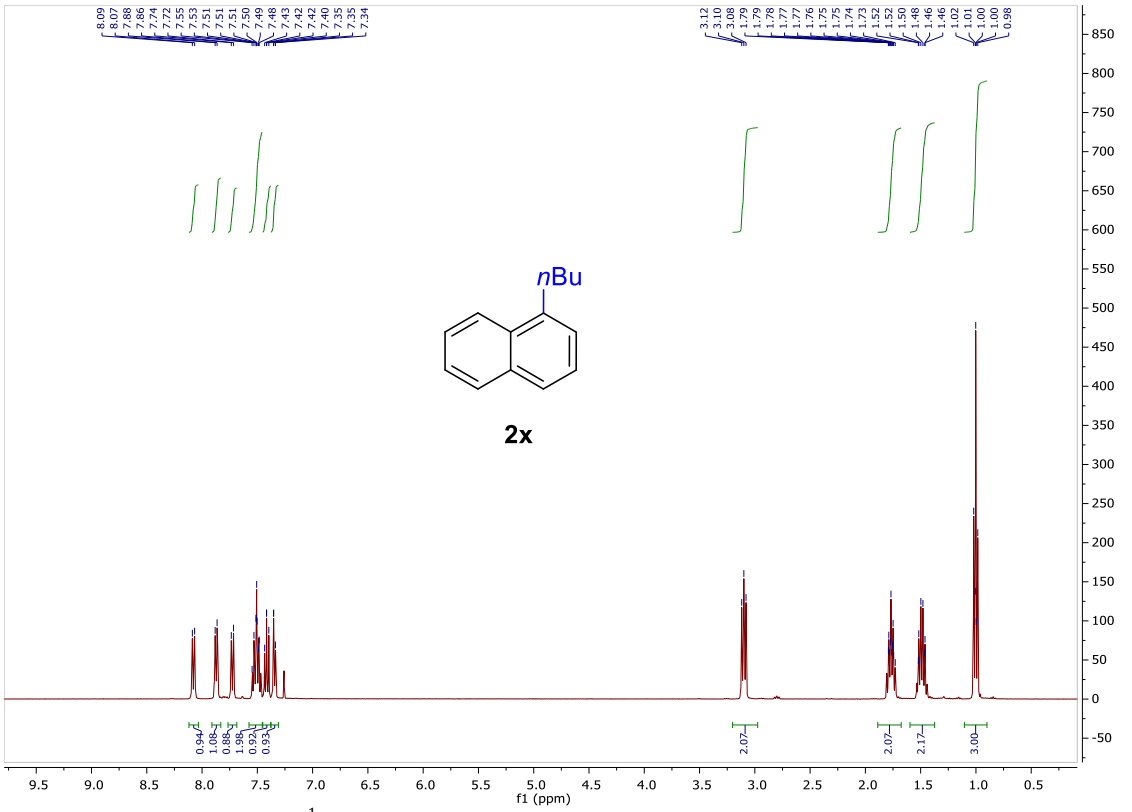
Supplementary Figure 52. ^{13}C NMR spectra of **2v**



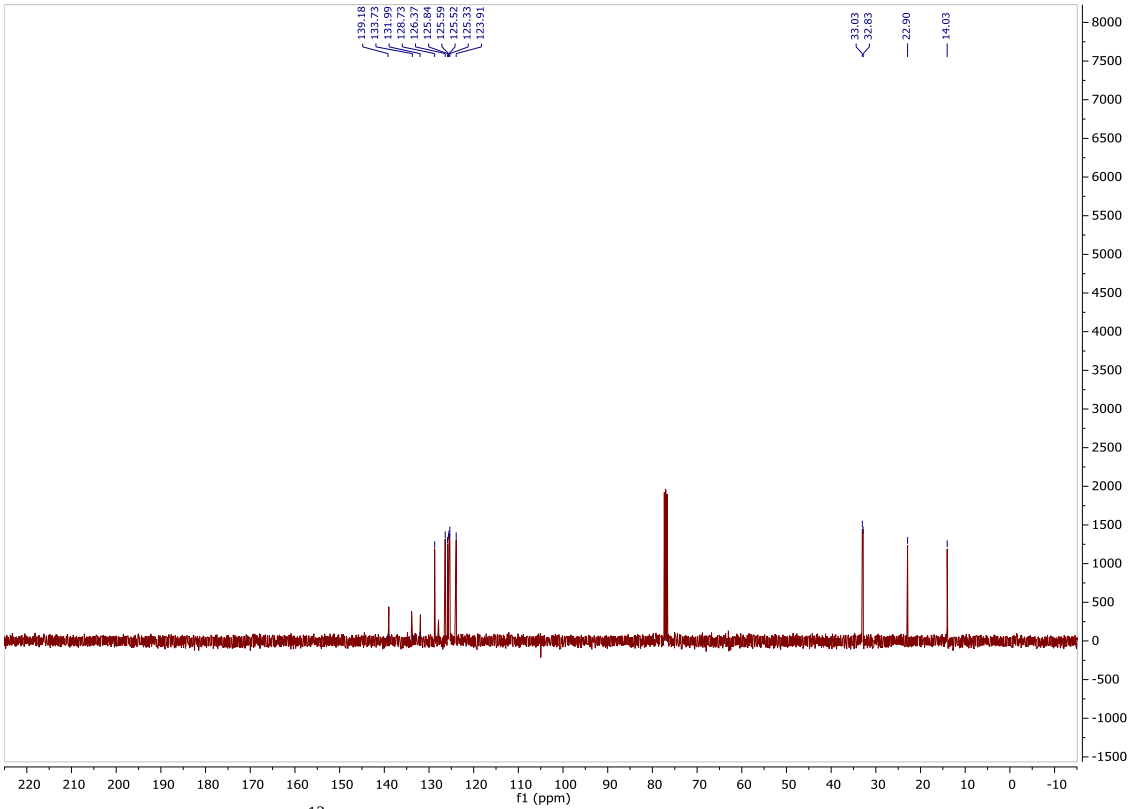
Supplementary Figure 53. ^{1}H NMR spectra of **2w**



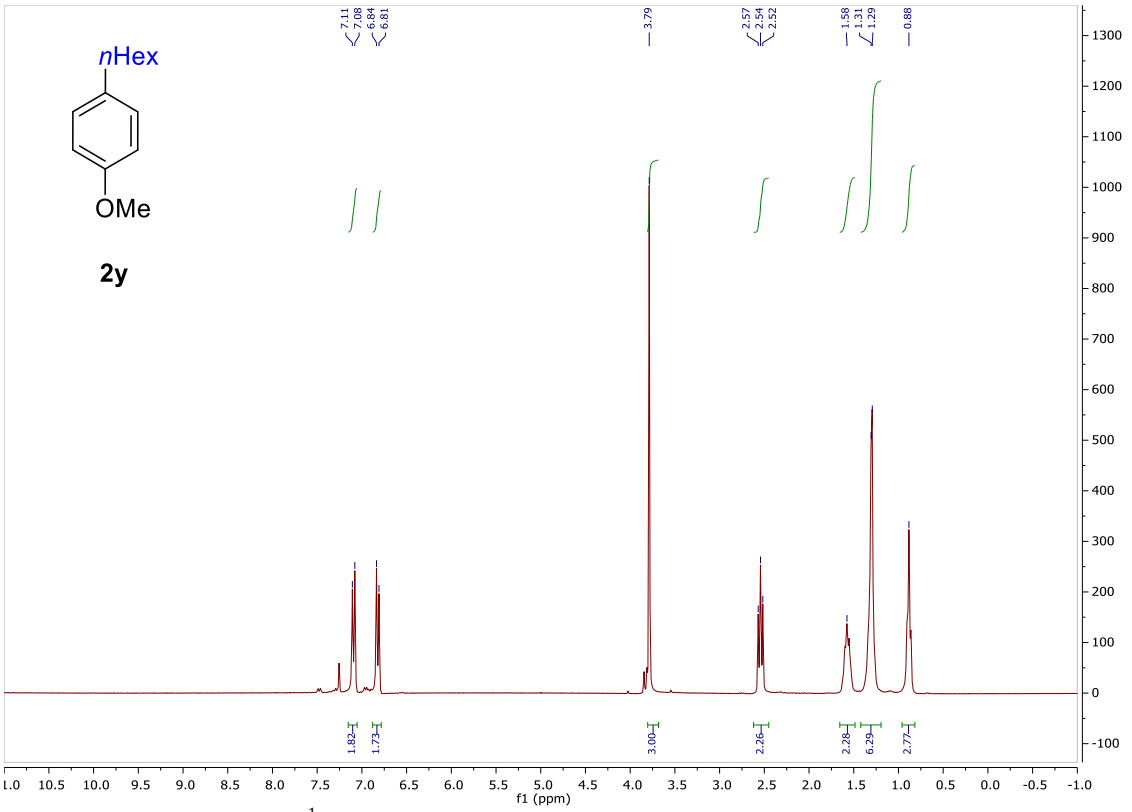
Supplementary Figure 54. ^{13}C NMR spectra of **2w**



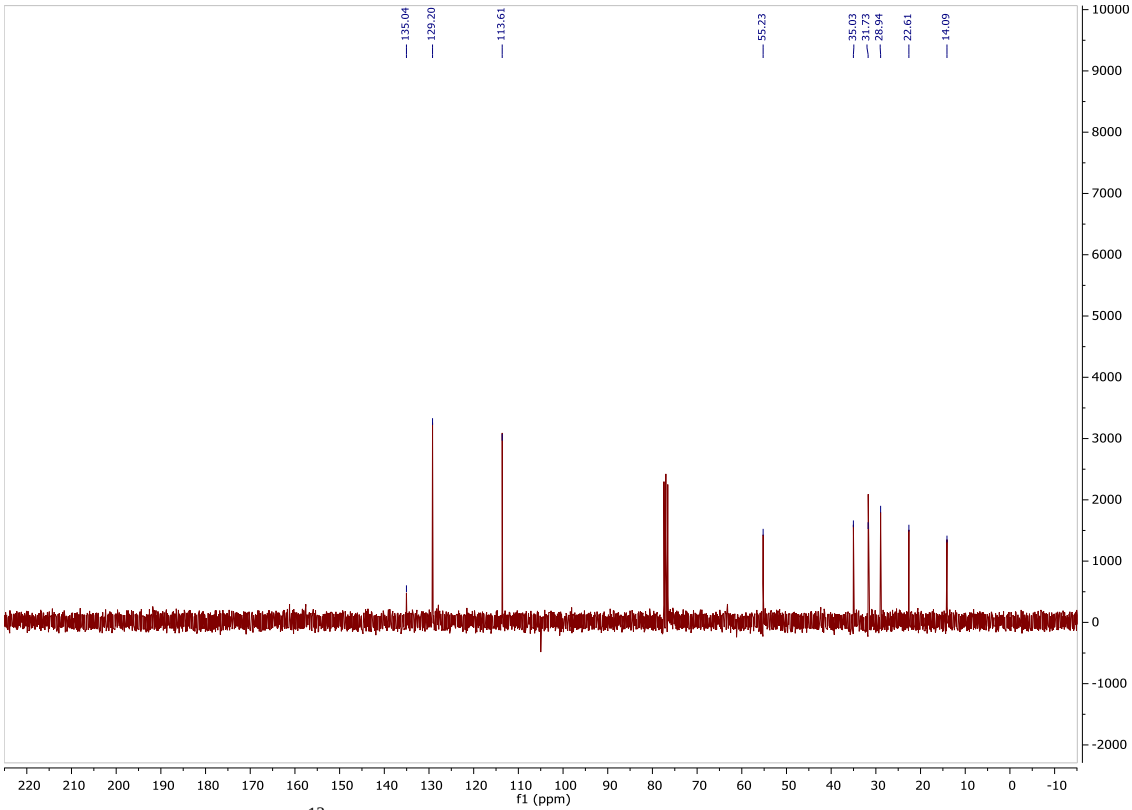
Supplementary Figure 55. ^{1}H NMR spectra of **2x**



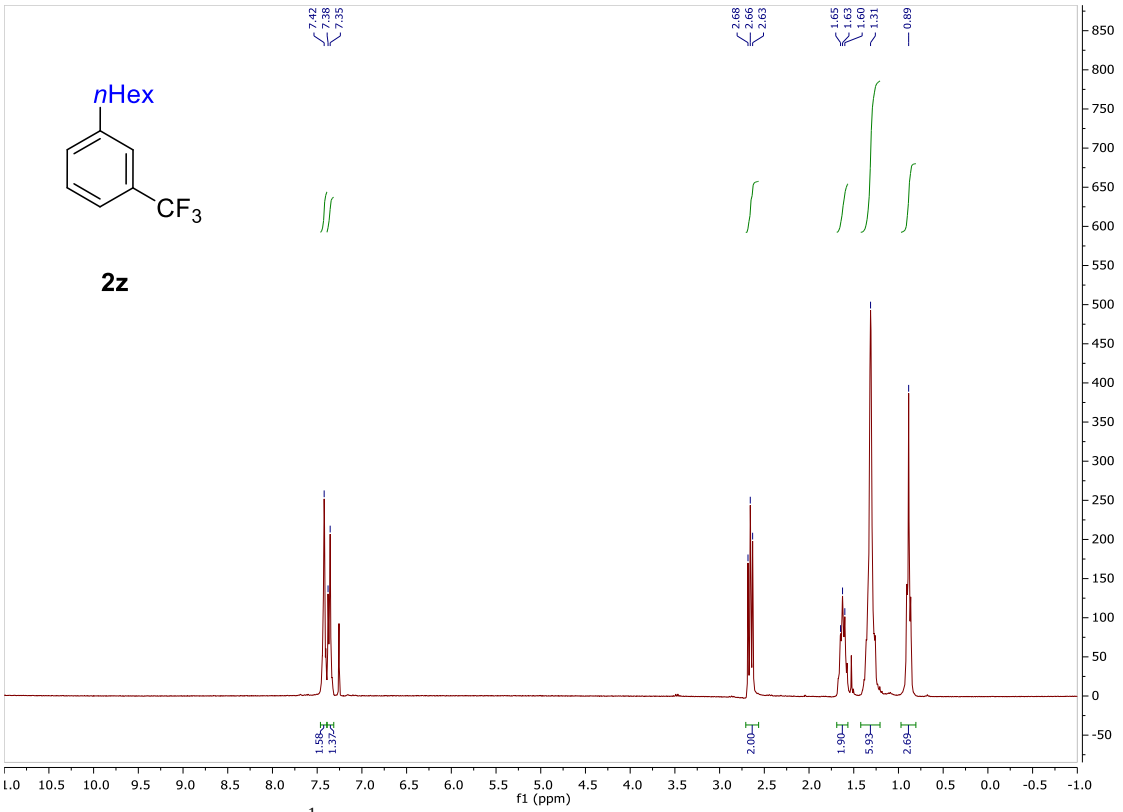
Supplementary Figure 56. ^{13}C NMR spectra of **2x**



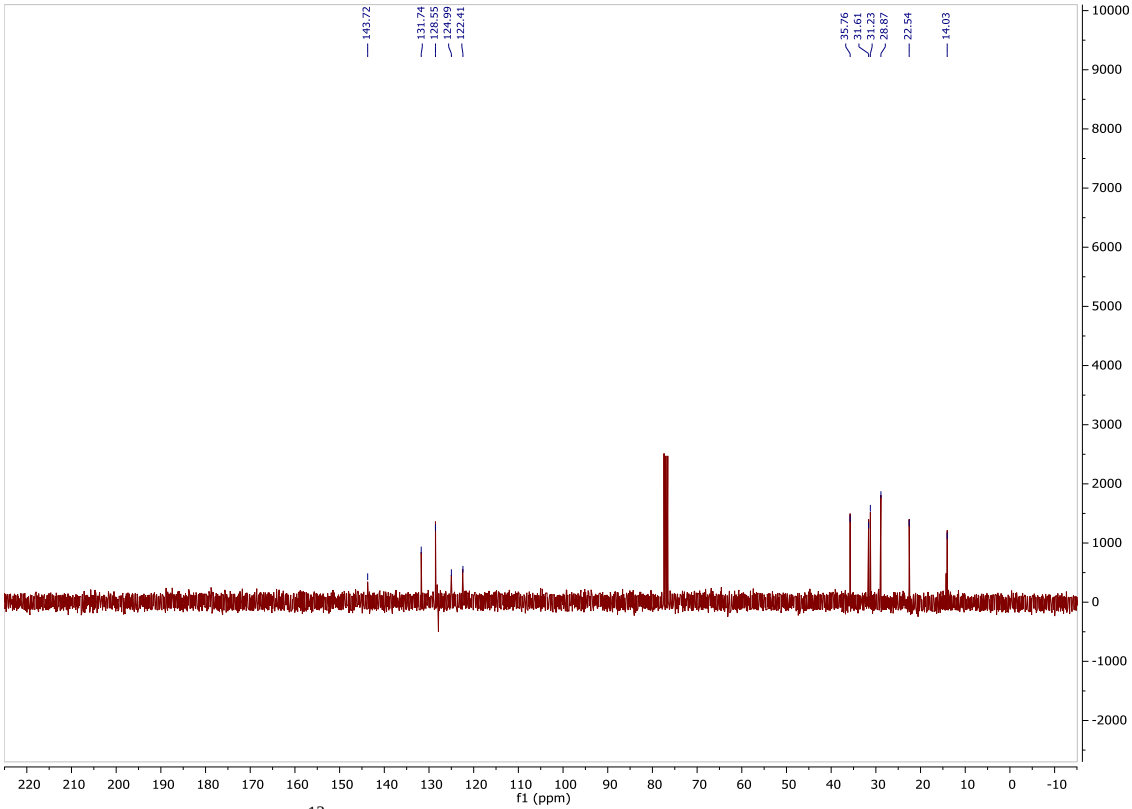
Supplementary Figure 57. ^{1}H NMR spectra of **2y**



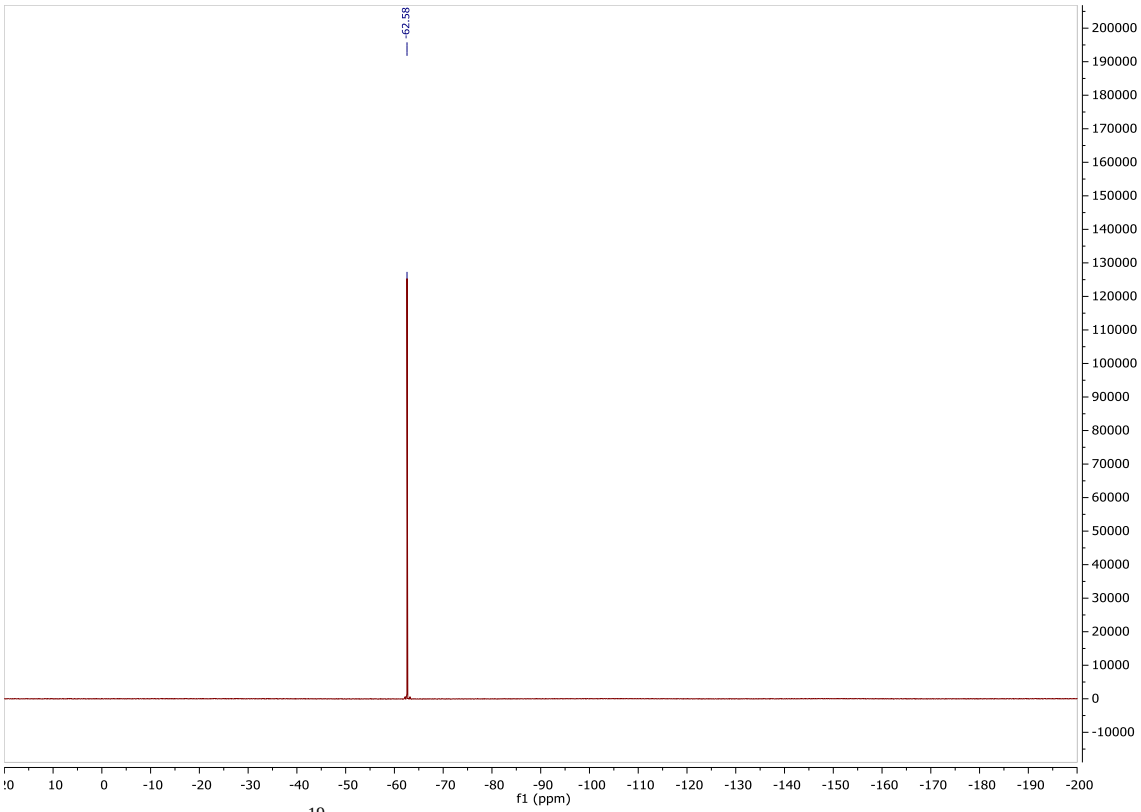
Supplementary Figure 58. ^{13}C NMR spectra of **2y**



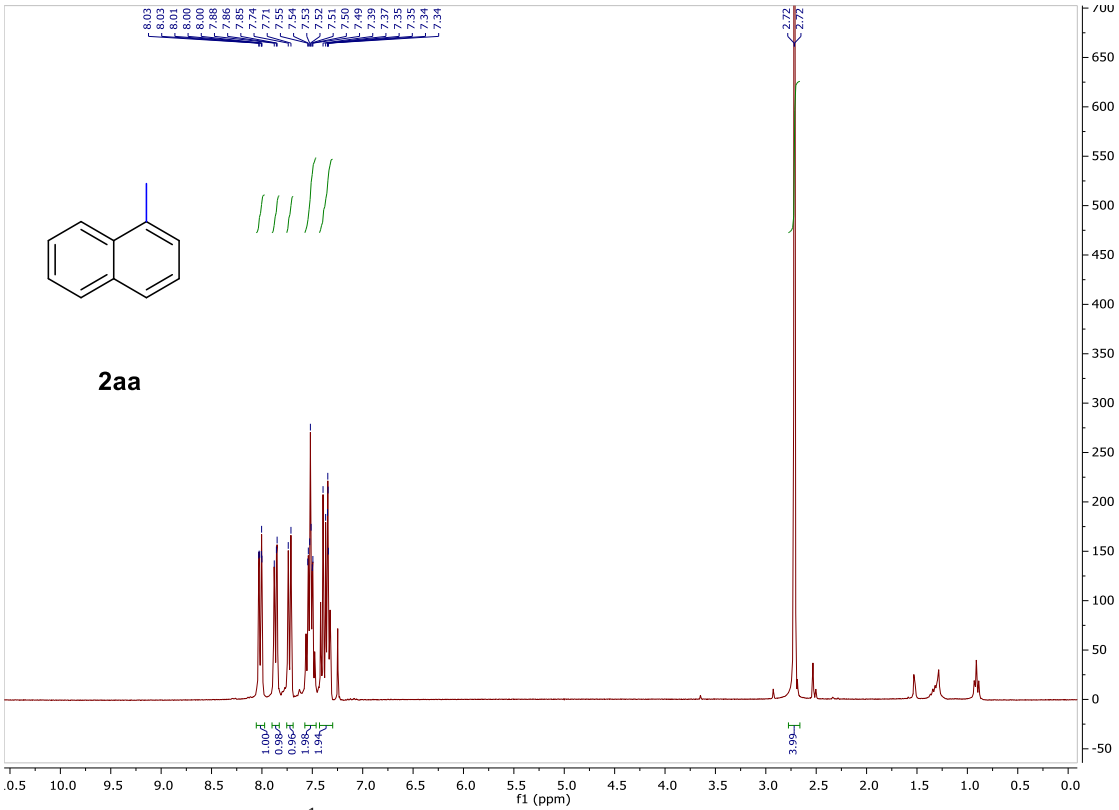
Supplementary Figure 59. ^{1}H NMR spectra of **2z**



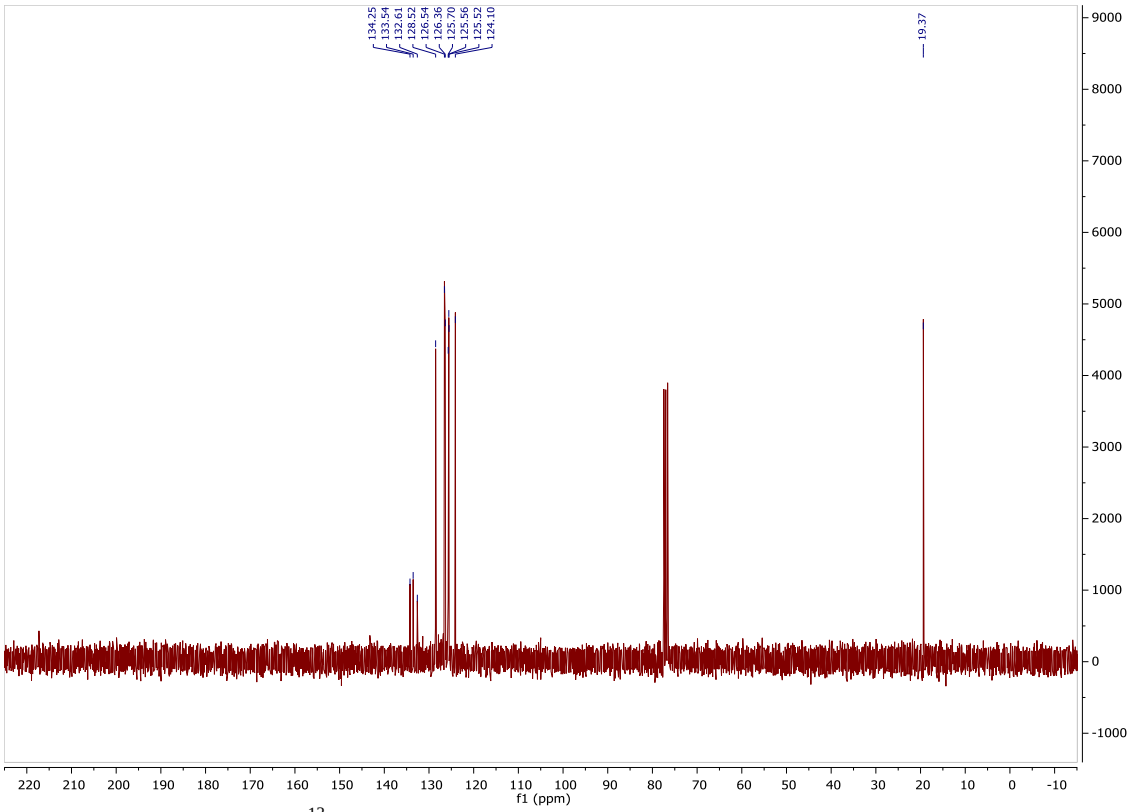
Supplementary Figure 60. ^{13}C NMR spectra of **2z**



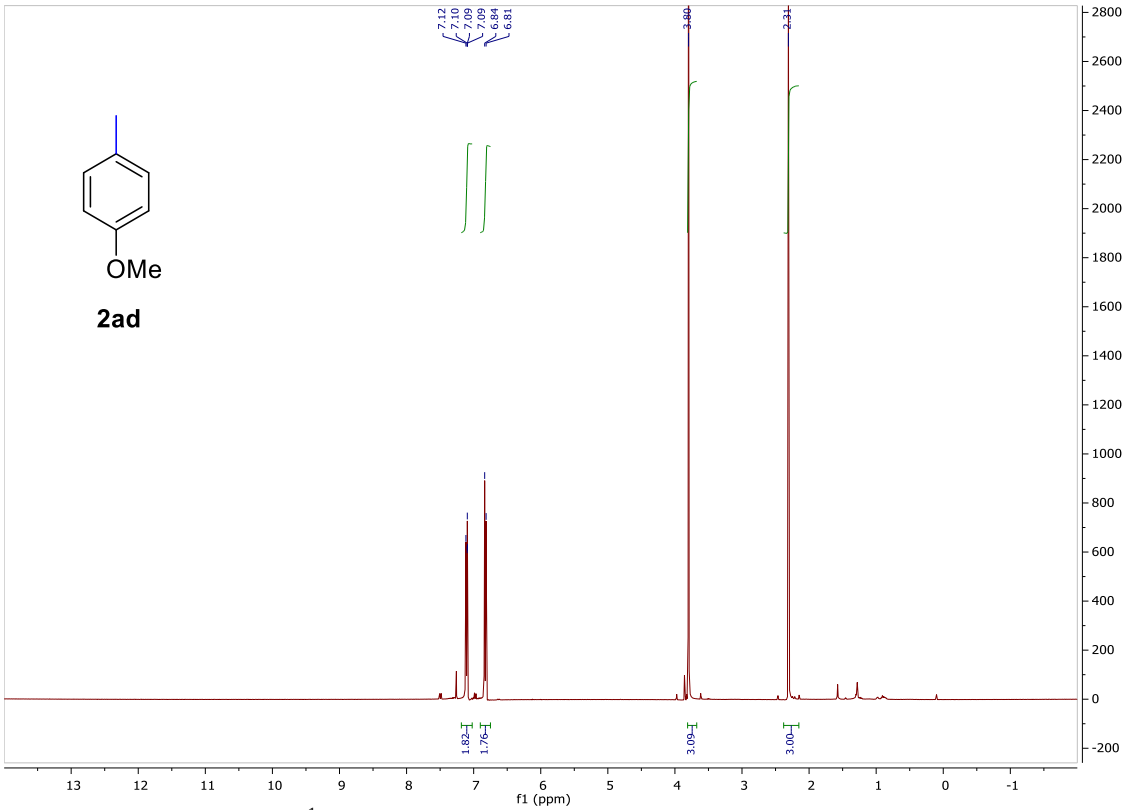
Supplementary Figure 61. ^{19}F NMR spectra of **2z**



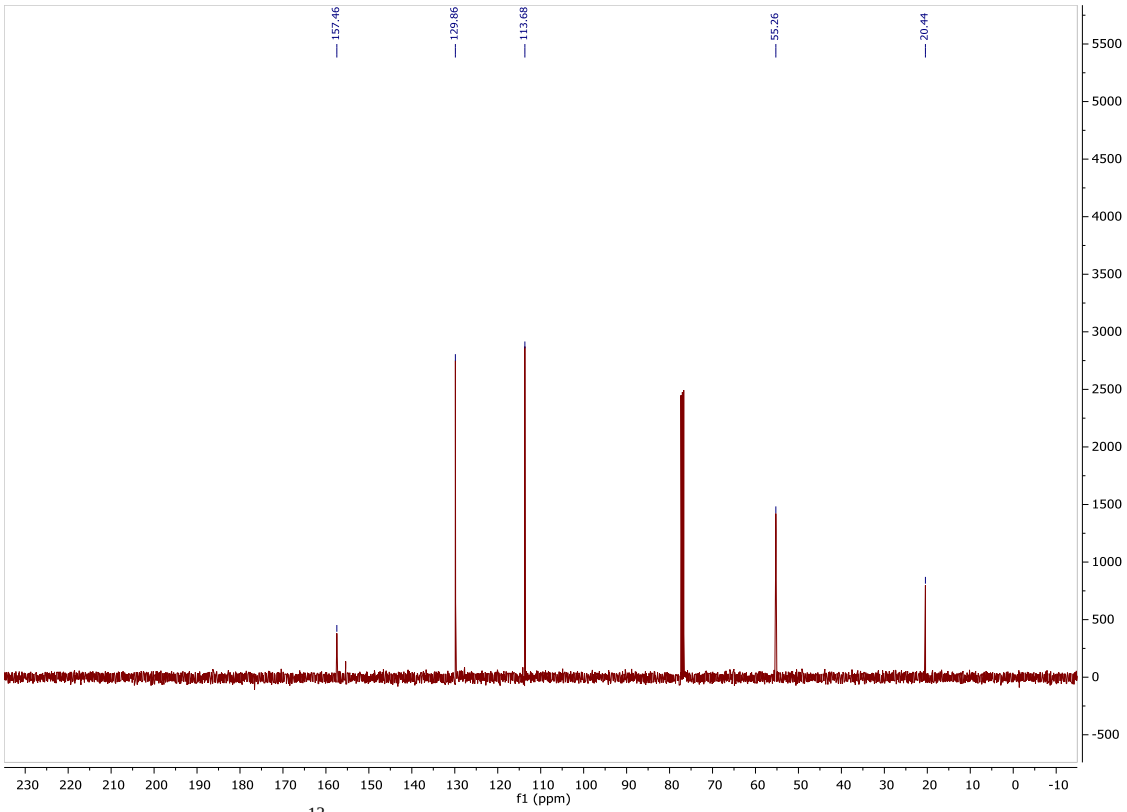
Supplementary Figure 62. ^{1}H NMR spectra of **2aa**



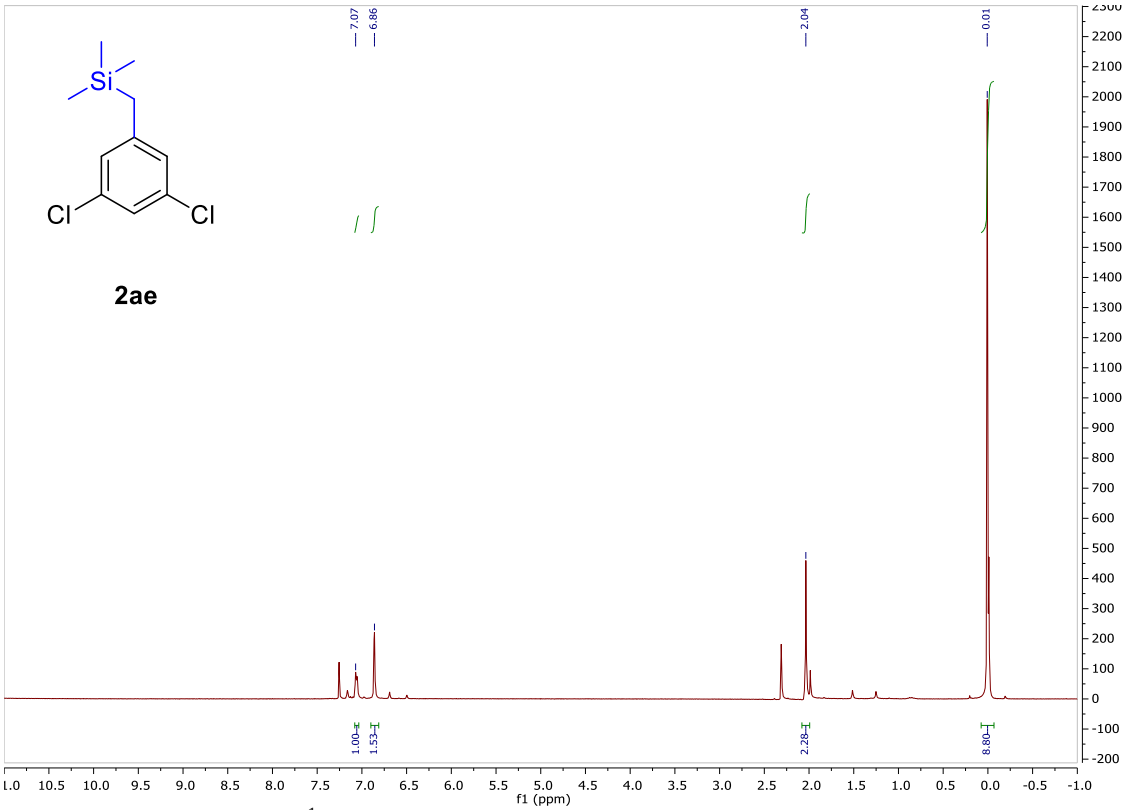
Supplementary Figure 63. ^{13}C NMR spectra of **2aa**



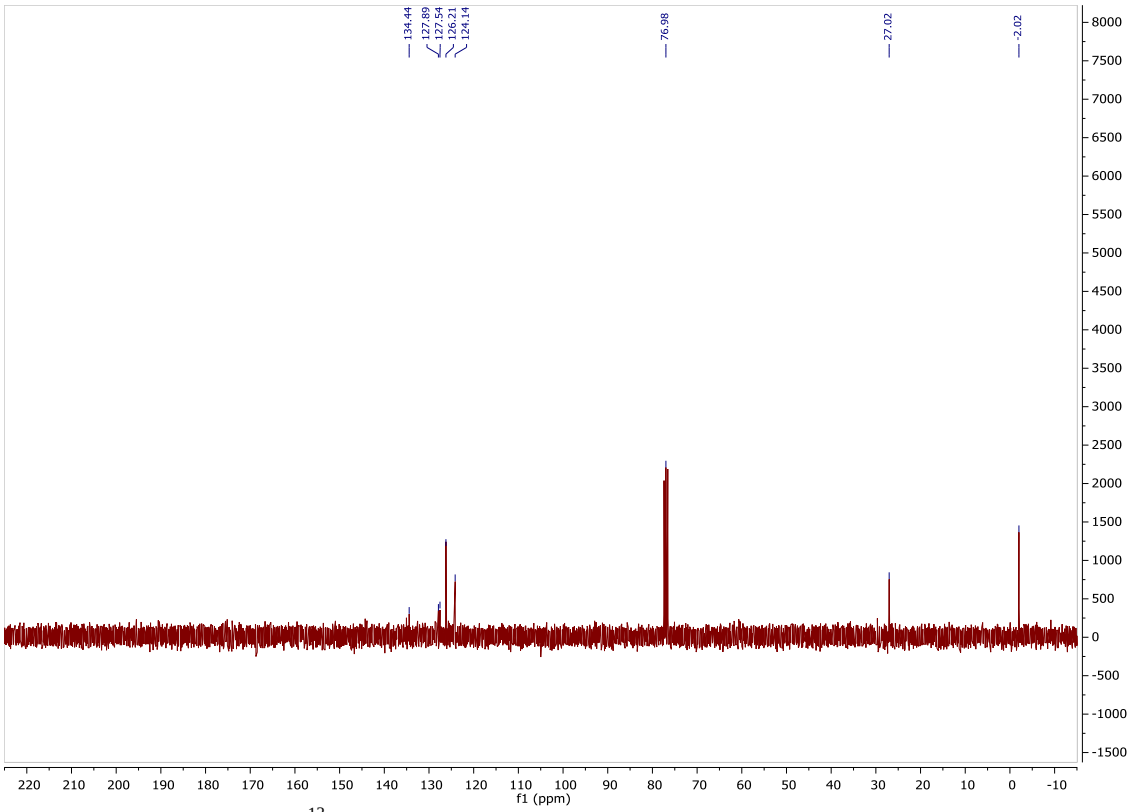
Supplementary Figure 64. ^{1}H NMR spectra of **2ad**



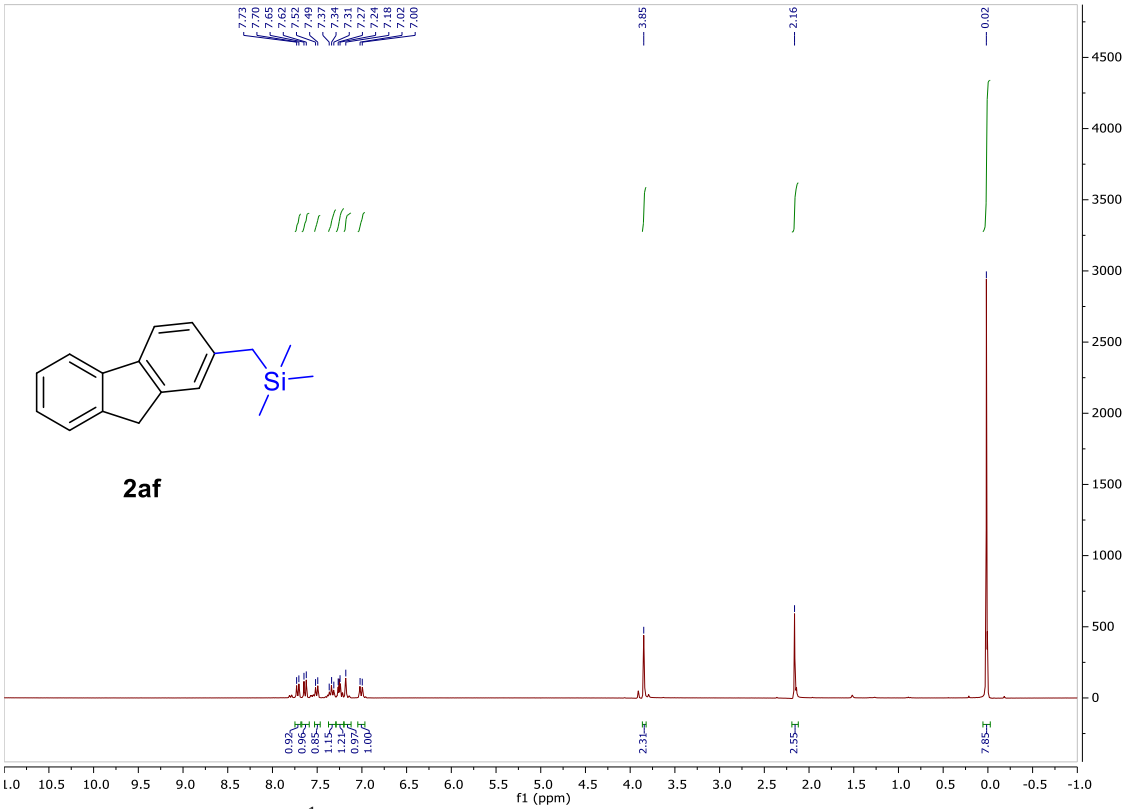
Supplementary Figure 65. ^{13}C NMR spectra of **2ad**



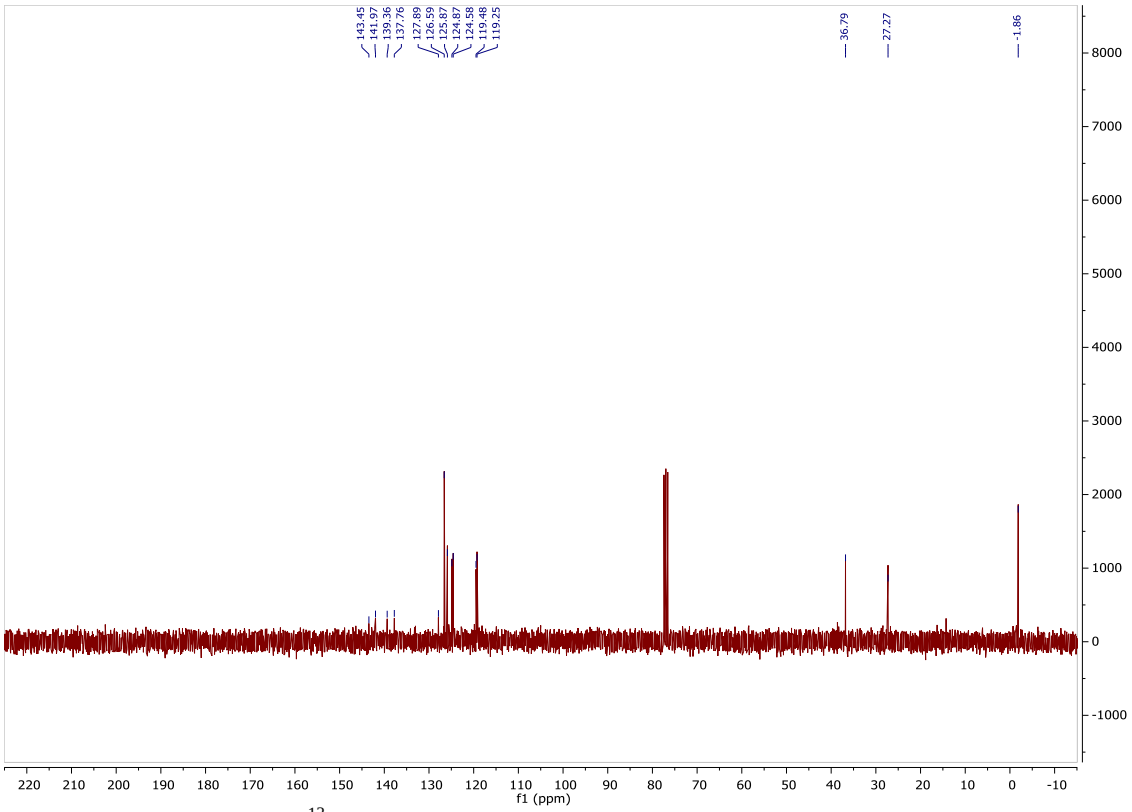
Supplementary Figure 66. ^{1}H NMR spectra of **2ae**



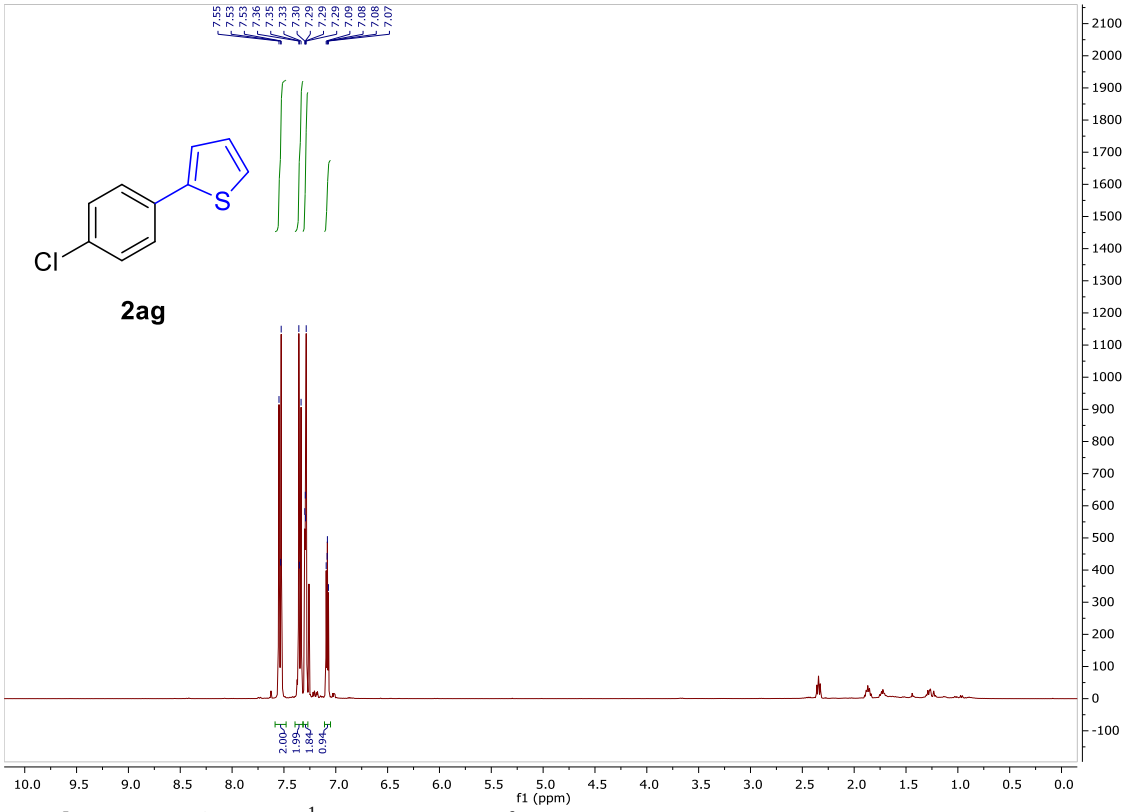
Supplementary Figure 67. ^{13}C NMR spectra of **2ae**



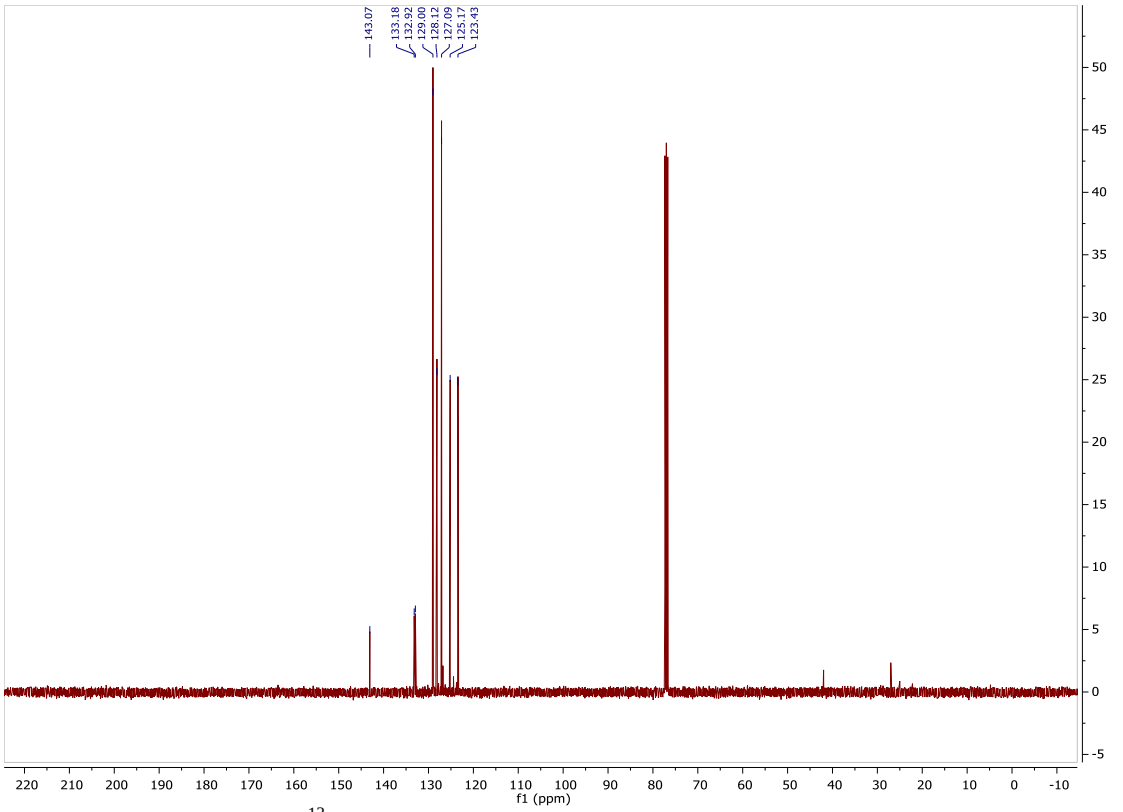
Supplementary Figure 68. ^{1}H NMR spectra of **2af**



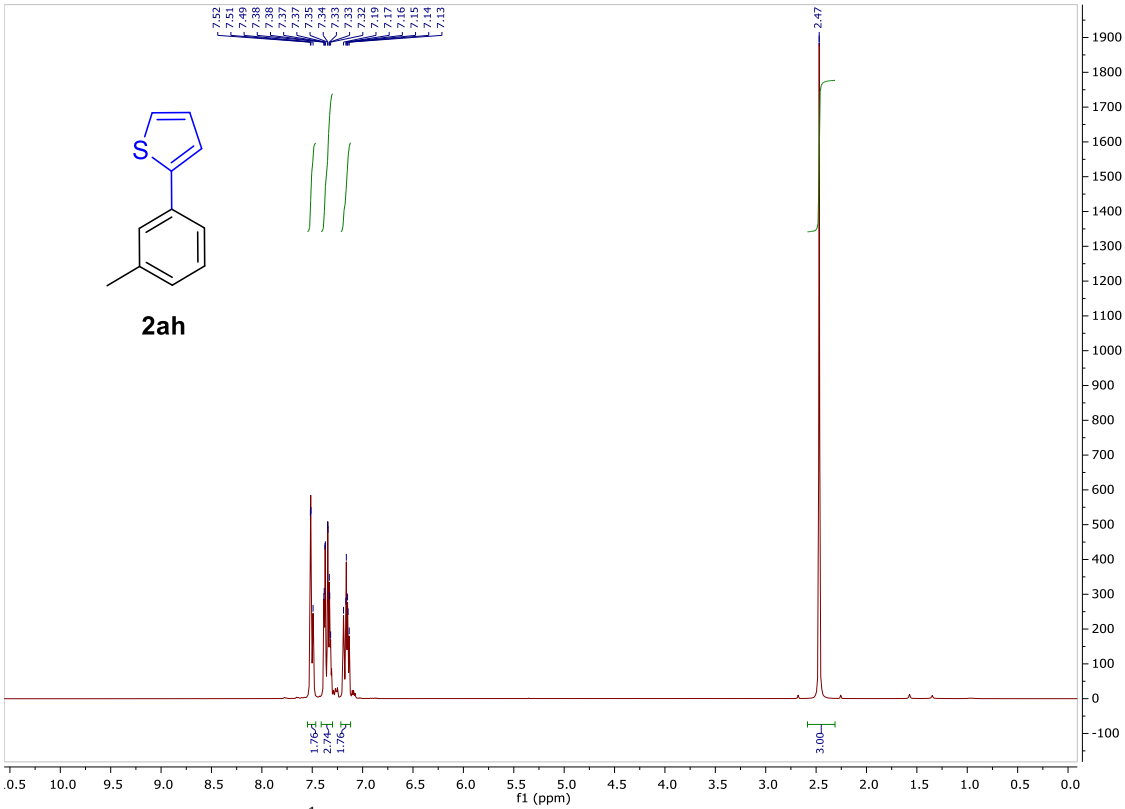
Supplementary Figure 69. ^{13}C NMR spectra of **2af**



Supplementary Figure 70. ^{1}H NMR spectra of **2ag**

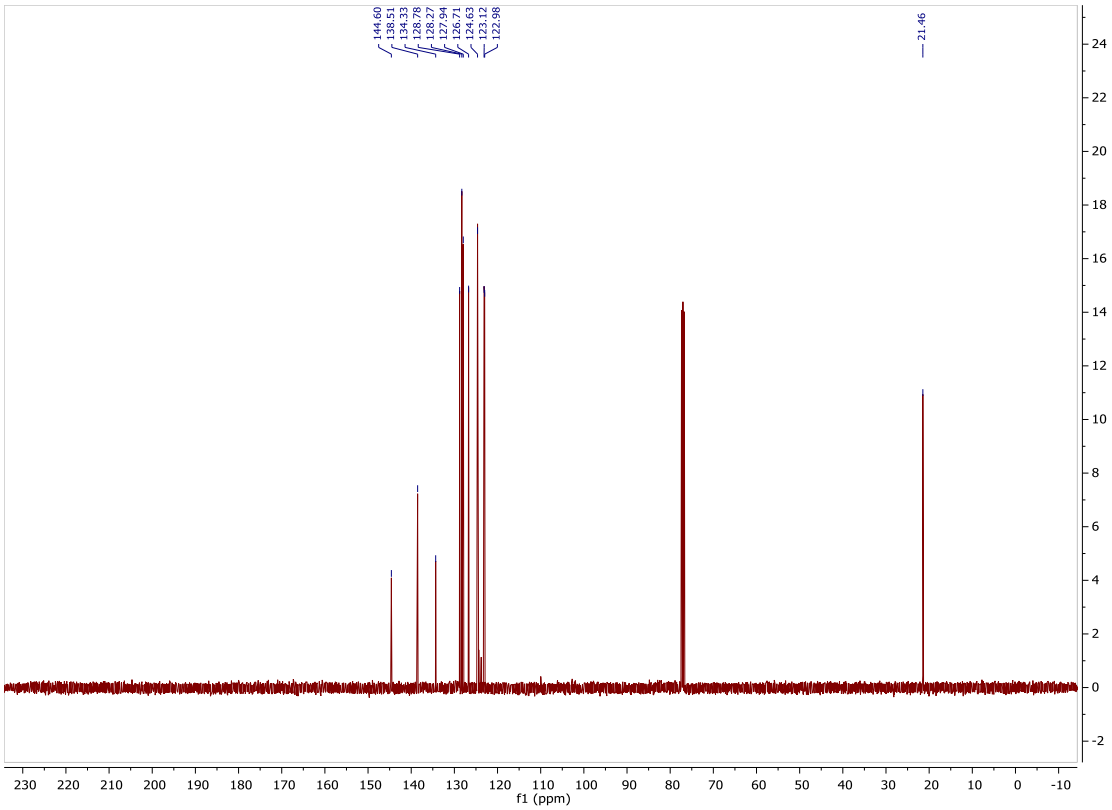


Supplementary Figure 71. ^{13}C NMR spectra of **2ag**



2ah

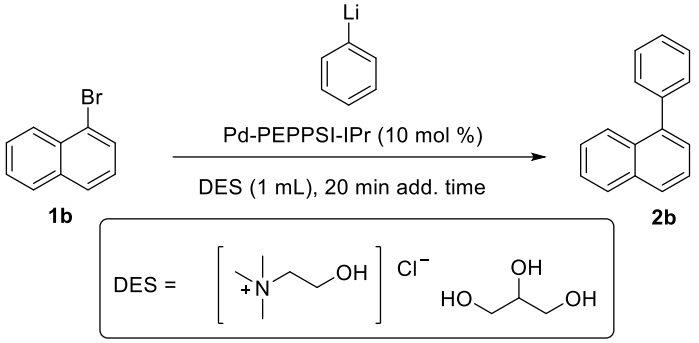
Supplementary Figure 72. ^{1}H NMR spectra of **2ah**



Supplementary Figure 73. ^{13}C NMR spectra of **2ah**

Supplementary Tables

Supplementary Table 1. Pd-catalysed cross-coupling reaction of organolithium compounds and organic halides employing deep eutectic solvents (DES). Conditions: Commercial available PhLi (1.8 M in nBu$_2$O) was added to a mixture of **1b** (0.3 mmol, 56 mg) and Pd-PEPPSI-iPr (10 mol %) in 1 mL of DES. Conversion determined by GC analysis.



entry	PhLi (equiv.)	Magnetic stirring speed	Reaction time after addition	Conversion
1	2 eq	1200 rpm	5 min	30%
2	10 eq	1200 rpm	5 min	53%
3	2 eq	300 rpm	2 hours	28%

Supplementary Notes:

Supplementary Note 1: The transformations described here have been performed under N_2 atmosphere. However, we have repeated the synthesis (e.g. compound **2m**) keeping the Schlenk flask open to the air and a similar selectivity (>99%) and isolated yield (95%) was obtained.

Supplementary Note 2: The authors have not experienced significant problems of exothermicity in comparison to usual couplings (or other catalytic reactions). The synthesis of **2aa** was performed on 6 mmol scale (1.25 g), with a small increase of temperature of 4 °C (from 25 °C to 28 °C) upon addition of the organolithium reagents.

Supplementary Note 3: The authors have performed a cross coupling of 1-bromonaphthalene and dry MeLi, by removing the solvent under vacuum of a commercial organolithium reagent, and subsequent transferring to a glove box. The cross coupling works although, with strongly reduced selectivity in which **2aa** was formed up to 15%. We do explicitly warn for the pyrophoric nature of dry organolithium species.

Supplementary Note 4: The authors have performed a cross coupling of 1-bromonaphthalene and phenyl lithium under conditions given in general procedure A, however using 1 eq of the lithium species, rather than 1,2. Compound **2b** was obtained in similar conversion and yield.

Supplementary Note 5: We did not experience any problem with salt formation (for instance on stirring the reaction mixture) under any of the conditions we used.

Supplementary Note 6: Experimental procedure and calculation of the E-factor for the synthesis of **2ag**, including aqueous work-up: The reaction mixture was quenched with 1 mL of water, extracted with 1 mL of AcOEt and the organic phase was dried with anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the crude product that was then filtered over a silica gel plug to afford the pure product. Yield 97%. The E factor including the water used for the work-up is 15.4. The E factor reported in literature for the Suzuki coupling is 84.

Supplementary Methods:

General

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and cerium/molybdenum or potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ^{1}H- and ^{13}C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. All reactions were carried out under a nitrogen atmosphere. THF and Et_2O were dried and distilled over sodium. $Pd[P(t\text{-}Bu)_3]_2$, was purchased from Strem, $Pd_2(dba)_3$, XPhos, Pd-PEPPSI-*i*Pr and Pd-PEPPSI-*i*Pent were purchased from Aldrich and used without further purification. *n*-BuLi (1.6 M solution in hexane) was purchased from Acros. PhLi (1.8 M solution in dibutylether), MeLi (1.6 M in diethylether), $TMSCH_2Li$ (1.0 M in pentane), *n*-HexLi (2.3 M in hexane), 2-thienylLi (1.0 M in THF/hexane), and the compounds used as precursor for the preparation of lithium reagents, namely 1-bromo-2,6-dimethoxy-benzene, 1-bromo-4-methylbenzene and 1-bromo-4-(trifluoromethyl)benzene were purchased from Aldrich. All the bromides were commercially available and were purchased from Aldrich, TCI Europe N.V. and Acros Organics. *p*-tolyllithium, (4-(trifluoromethyl)phenyl)lithium and (2,6-dimethoxyphenyl)lithium were prepared according to described procedures.[1,2,3,4] E factors were calculated according to the procedure reported by Lipshutz et.al..[5]

General Procedure A for the Cross-Coupling with (Hetero)aryllithium Reagents

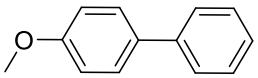
The corresponding commercially available or homemade (hetero)aryllithium reagent was added over a mixture of substrate (1 mmol) and Pd-PEPPSI-*i*Pr (1.5 mol %, 10.5 mg) at room temperature for 10 min. After the addition was completed a saturated solution of aqueous NH_4Cl was added and the mixture was extracted with AcOEt or Et_2O. The organic phases were combined and dried with anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the crude product that was then filtered over a silica gel plug.

General Procedure B for the Cross-Coupling with Alkyllithium Reagents

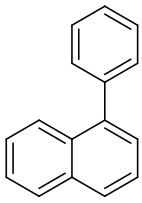
The corresponding commercially available alkyllithium reagent was added over a mixture of substrate (1 mmol) and $Pd[P(t\text{-}Bu)_3]_2$ (2 mol%, 10 mg) at room temperature for 10 min. After the addition was completed a saturated solution of aqueous NH_4Cl was added and the mixture was extracted with AcOEt or Et_2O. The organic phases were combined and dried with anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the crude product that was then filtered over a silica gel plug.

General Procedure C for Reactions Carried out in 120 mmol Scale

Commercially available *n*-BuLi (100 mL, 1.6 M solution in hexane) was added via cannula over a mixture of substrate (120 mmol, 27 g) and $Pd[P(t\text{-}Bu)_3]_2$ (0.4 mol%, 250 mg) at room temperature for 30 min, keeping the temperature between 20-25 °C with the use of an additional water bath. After the addition was completed water was slowly added and the mixture was extracted with AcOEt or Et_2O. The organic phase were combined and dried with anhydrous Na_2SO_4 and solvent was removed under reduced pressure affording the final product in reagent grade quality.

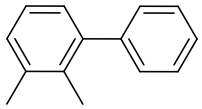


4-Methoxybiphenyl (2a):[3]
CAS Registry Number: 613-37-6.
Synthesized using catalytic system A with 1-bromo-4-methoxybenzene (1 mmol, 187 mg) and 798 μL of PhLi.
Catalytic system A: Reaction carried out at room temperature. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/ Et_2O 100:1), 155 mg, 84% yield.

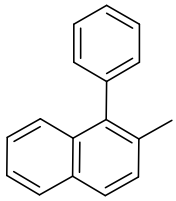


1-Phenylnaphthalene (2b):[6,3]
CAS Registry Number: 605-02-7

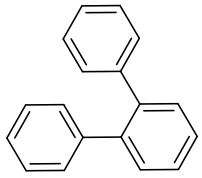
Synthesized using catalytic system A with 1-bromonaphthalene (1 mmol, 207 mg) and 798 µL of PhLi.
Catalytic system A: Reaction carried out at room temperature. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/Et_2O 100:1), 178 mg, 87% yield.



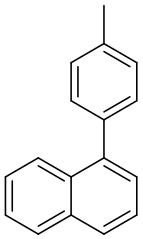
2,3-Dimethyl-1,1'-biphenyl (2c):[7]
CAS Registry Number: 3864-18-4
Synthesized using catalytic system A 1-bromo-2,3-dimethylbenzene (1 mmol, 185 mg) and 798 µL of PhLi.
Catalytic system A: Reaction carried out at room temperature. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/Et_2O 100:1), 159 mg, 87% yield.



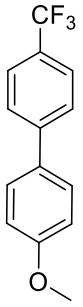
2-Methyl-1-phenylnaphthalene (2d):[8]
CAS Registry Number: 29304-63-0
Synthesized using catalytic system A with 1-bromo-2-methylnaphthalene (1 mmol, 221 mg) and 798 µL of PhLi. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/ Et_2O 100:1), 196 mg, 90% yield.



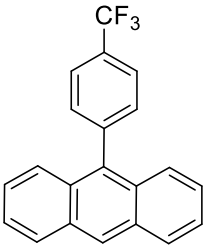
1,1':2',1"-Terphenyl (2e):[9]
CAS Registry Number: 84-15-1
Synthesized using catalytic system A with 2-bromo-1:1'-biphenyl (1 mmol, 233 mg) and 798 µL of PhLi. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane/ Et_2O 100:1), 225 mg, 98% yield.



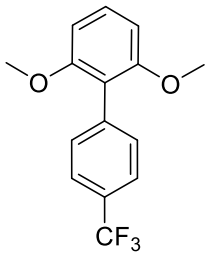
1-(*p*-Tolyl)naphthalene (2f):[6]
CAS Registry Number: 27331-34-6
Synthesized using catalytic system A with 1-bromonaphthalene (1 mmol, 207 mg) and 2394 µL of *p*-tolyllithium (0.6 M solution in diethylether).
White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/ Et_2O 100:1), 198 mg, 91% yield.



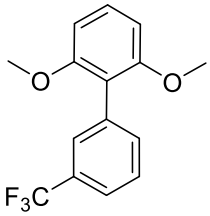
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenylphenyl (2g):[8]
CAS Registry Number: 10355-12-1
Synthesized using catalytic system A with 1-bromo-4-methoxybenzene (1 mmol, 187 mg) and 2394 µL of *p*-trifluoromethylphenyllithium (0.6 M solution in diethylether). Off white solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/ Et_2O 100:1), 229 mg, 91% yield.



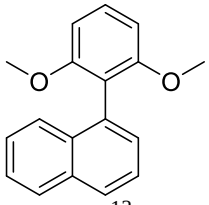
9-(4-(Trifluoromethyl)phenyl)anthracene (2h):[10]
CAS Registry Number: 386-23-2
Synthesized using catalytic system A with 9-bromoanthracene (1 mmol, 257 mg) and 2394 µL of *p*-trifluoromethylphenyllithium (0.6 M solution in diethylether). Yellow solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/ Et_2O 100:1), 305 mg, 92% yield.



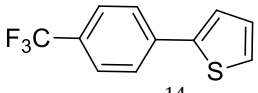
2,6-Dimethoxy-4'-(trifluoromethyl)-1,1'-biphenylphenyl (2i):[11]
CAS Registry Number: 603112-21-6
Synthesized using catalytic system A with 1-bromo-4-(trifluoromethyl)benzene (1 mmol, 225 mg) and 2394 µL of 2,3-dimethoxy-phenyllithium (0.6 M solution in diethylether). White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/ Et_2O 100:1), 274 mg, 97% yield.



2,6-Dimethoxy-3'-(trifluoromethyl)-1,1'-biphenylphenyl (2j):[12]
CAS Registry Number: 603112-20-5
Synthesized using catalytic system A with 1-bromo-3-(trifluoromethyl)benzene (1 mmol, 225 mg) and 2394 µL of 2,3-dimethoxy-phenyllithium (0.6 M solution in diethylether). White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane/ Et_2O 100:1), 237 mg, 84% yield.

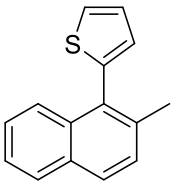


1-(2,6-Dimethoxyphenyl)naphthalene (2k):[13]
CAS Registry Number: 173300-93-1
Synthesized using catalytic system A with 1-bromonaphthalene (1 mmol, 207 mg) and 2394 µL of of 2,3-dimethoxy-phenyllithium (0.6 M solution in diethylether). White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 222 mg, 84% yield.

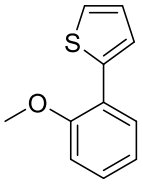


2-(4-(Trifluoromethyl)phenyl)thiophene (2l):[14]
CAS Registry Number: 115933-15-8.

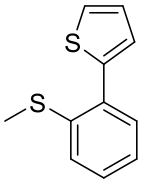
Synthesized using catalytic systems B with 1-bromo-4-(trifluoromethyl)benzene (1 mmol, 225 mg) and 1200 µL of 2-thienyllithium. White solid obtained after column chromatography (SiO_2, *n*-pentane/ EtOAc 100:1), 219 mg, 96% yield.



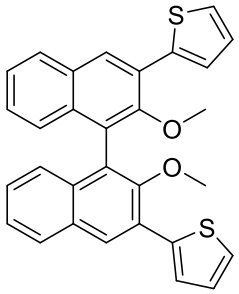
1-(2-Methylnaphthalen-1-yl)thiophene (2m):[15]
CAS Registry Number: 1064187-66-1
Synthesized using catalytic system B with 2-methyl-1-bromonaphthalene (1 mmol, 221 mg) and 1200 µL of 2-thienyllithium. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 220 mg, 98% yield.



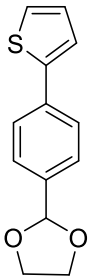
2-(2-Methoxyphenyl)thiophene (2n):[16]
CAS Registry Number: 17595-92-5
Synthesized using catalytic system B with 1-bromo-2-methoxybenzene (1 mmol, 187 mg) and 1200 µL of 2-thienyllithium. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 165 mg, 87% yield.



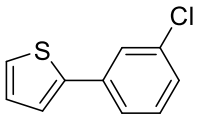
2-(2-(Methylthio)phenyl)thiophene (2o):
Synthesized using catalytic system B with (2-bromophenyl)(methyl)sulfane (1 mmol, 202 mg) and 1200 µL of 2-thienyllithium.Yellow oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), 88% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (q, *J* = 5.9, 5.1 Hz, 2H), 7.41 – 7.29 (m, 3H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.20 – 7.14 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.29, 138.07 , 133.24 , 130.95 , 128.43 , 127.58 , 127.09 , 125.90 , 125.61 , 124.76 , 16.17. HRMS (APCI+, *m/z*): calculated for $C_{11}H_{11}S_2$ [$M+H^+$]: 207.03022; found: 207.03149.



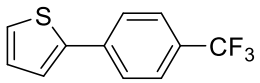
2,2'-(2,2'-Dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)dithiophene (2p):
Synthesized using catalytic system B with 3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthalene (1 mmol, 472 mg) and 2400 µL of 2-thienyllithium. Yellow solid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 3.5 Hz, 2H), 7.40 (q, *J* = 4.9, 4.3 Hz, 4H), 7.24 (t, *J* = 7.1 Hz, 3H), 7.16 (dd, *J* = 9.7, 6.1 Hz, 4H), 3.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.32, 139.55, 133.48, 130.71, 128.72, 128.06, 127.96, 127.23, 126.48, 126.31, 126.26, 125.86, 125.72, 125.29, 60.49. HRMS (APCI+, *m/z*): calculated for $C_{30}H_{23}O_2S_2$ [$M+H^+$]: 479.11395; found: 479.11182.



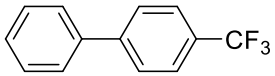
2-(4-(Thiophen-2-yl)phenyl)-1,3-dioxolane (2q):[16]
CAS Registry Number: 81707-47-3
Synthesized using catalytic system B with 2-bromo-4-phenyl)-1,3-dioxolane (1 mmol, 229 mg) and 1200 µL of 2-thienyllithium. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 197 mg, 85% yield.



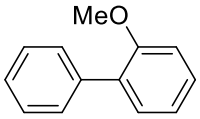
2-(3-Chlorophenyl)thiophene (2r):[17]
CAS Registry Number: 59156-10-4
Synthesized using catalytic system B with 1-bromo-3-chlorobenzene (1 mmol, 191 mg) and 1200 µL of 2-thienyllithium. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 169 mg, 87% yield.



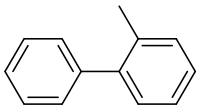
2-(4-(Trifluoromethyl)phenyl)thiophene (2l):[3]
CAS Registry Number: 115933-15-8
Synthesized using catalytic system B with 1-chloro-4-(trifluoromethyl)benzene (1 mmol, 180 mg) and 1200 µL of 2-thienyllithium. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 198 mg, 87% yield.



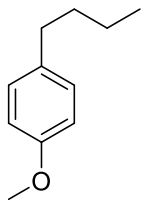
4-(Trifluoromethyl)-1,1'-biphenyl (2s):[18]
CAS Registry Number: 398-36-7
Synthesized using catalytic system A with 1-chloro-4-(trifluoromethyl)benzene (1 mmol, 180 mg) and 798 µL of PhLi. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 187 mg, 84% yield.



2-(Methoxy)-1,1'-biphenyl (2t):[19]
CAS Registry Number: 86-26-0
Synthesized using catalytic system A with 1-chloro-2-methoxybenzene (1 mmol, 142 mg) and 798 µL of PhLi. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 155 mg, 86% yield.

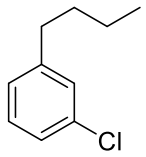


2-(Methyl)-1,1'-biphenyl (2u):[20]
CAS Registry Number: 643-58-3
Synthesized using catalytic system A with 2-chloro-toluene (1 mmol, 126 mg) and 798 µL of PhLi. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 141 mg, 84% yield.

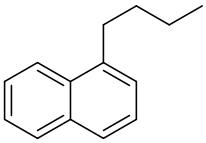


1-Butyl-4-methoxybenzene (2v).[13]
CAS Registry Number: 18272-84-9

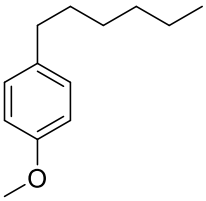
Synthesized using catalytic systems C with 1-bromo-4-methoxybenzene (1 mmol, 187 mg) and 750 µL of *n*-butyllithium. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 135 mg, 82% yield.



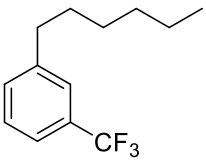
1-Butyl-3-chlorobenzene (2w).[21]
CAS Registry Number: 15499-28-2
Synthesized using catalytic systems C with 1-bromo-3-chlorobenzene (1 mmol, 191 mg) and 750 µL of *n*-butyllithium. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 144 mg, 85% yield.



1-Butylnaphthalene (2x).[22]
CAS Registry Number: 1634-09-9.
Synthesized using catalytic systems C with 1-bromo-naphthalene (1 mmol, 207 mg) and 750 µL of *n*-butyllithium. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 173 mg, 94% yield.

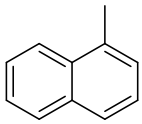


1-Hexyl-4-methoxybenzene (2y).[22]
CAS Registry Number: 81693-80-3.
Synthesized using catalytic systems C with 1-bromo-4-methoxybenzene (1 mmol, 187 mg) and 520 µL of *n*-hexyllithium. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 157 mg, 82% yield.

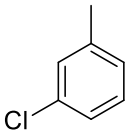


1-Hexyl-3-(trifluoromethyl)benzene (2z).

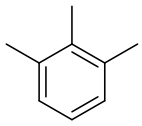
Synthesized using catalytic systems C with 1-bromo-3-(trifluoromethyl)benzene (1 mmol, 225 mg) and 520 µL of *n*-hexyllithium. Colorless oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.32 (m, 4H), 2,66 (t, *J* = 7.8 Hz, 2H), 1.63 (m, 2H), 1.34 (m, 6H), (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.44, 143.72, 131.74, 128.55, 124.99, 122.40, 35.76, 31.61, 31.23, 28.87, 22.54, 14.03. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. HRMS (APCI+, *m/z*): calculated for $C_{13}H_{18}F_3$ [$M+H^+$]: 231.13606; found: 231.13713.



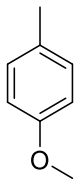
1-Methyl-naphthalene (2aa).[23]
CAS Registry Number: 90-12-0.
Synthesized using catalytic systems C with 1-bromonaphthalene (1 mmol, 207 mg) and 750 µL of methyllithium. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 122 mg, 86% yield.



1-Chloro-3-methylbenzene (2ab).[24]
CAS Registry Number: 108-41-8.
Synthesized using catalytic systems C with 1-bromo-3-chlorobenzene (1 mmol, 191 mg) and 750 µL of methyllithium. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 106 mg, 84% yield.

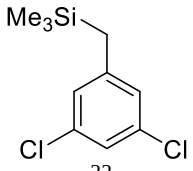


1,2,3-trimethylbenzene (2ac).
CAS Registry Number: 526-73-8.
Synthesized using catalytic systems C with 1,3-dimethyl-2-bromobenzene (1 mmol, 185 mg) and 750 µL of methyllithium. Selectivity based upon GC-results.

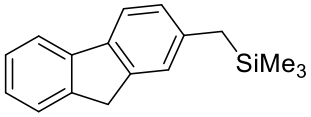


1-Methoxy-4-methylbenzene (2ad).[25]
CAS Registry Number: 104-93-8.

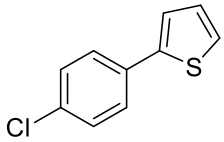
Synthesized using catalytic systems C with 1-bromo-4-methoxybenzene (1 mmol, 187 mg) and 750 µL of methyllithium. Colorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 101 mg, 83% yield.



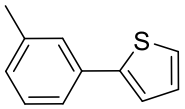
(3,5-Dichlorobenzyl)trimethylsilane (2ae).[22]
CAS Registry Number: 69380-94-5.
Synthesized using catalytic systems C with 1-bromo-3,5-dichlorobenzene (1 mmol, 225 mg) and 1200 µL of (trimethylsilyl)methyllithium. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 196 mg, 84% yield.



((9*H*-Fluoren-2-yl)methyl)trimethylsilane (2af).[26]
CAS Registry Number: 1694669-89-0
Synthesized using catalytic systems C with 2-bromo-9*H*-fluorene (1 mmol, 245 mg) and 1200 µL of (trimethylsilyl)methyllithium. White solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 214 mg, 85% yield.



2-(4-chlorophenyl)thiophene (2ag).[27]
CAS Registry Number: 40133-23-1
Synthesized using catalytic systems B with 1-bromo-4-chlorobenzene (1 mmol, 191 mg) and 1200 µL of 2-thienyllithium. Off white solid obtained after filtration over a silica plug (SiO_2, *n*-pentane), 189 mg, 97% yield.



2-(*m*-tolyl)thiophene (2ah).[28]
CAS Registry Number: 85553-43-1
Synthesized using catalytic systems B with 1-bromo-3-methylbenzene (1 mmol, 171 mg) and 1200 µL of 2-thienyllithium. Collorless oil obtained after filtration over a silica plug (SiO_2, *n*-pentane), 146 mg, 84% yield.

Supplementary References

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