Boronic acid–mediated ring-opening and Ni-catalyzed arylation of 1-arylcyclopropyl tosylates

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Supporting Information 1: Experimental Data

Table of Contents

A. General Information

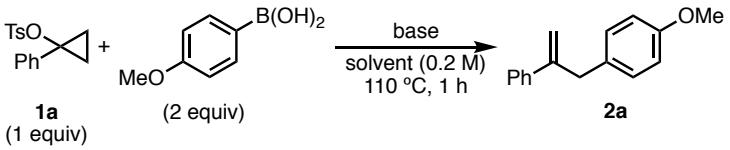
Unless otherwise noted, all reactions were set up on the benchtop and run under an atmosphere of Ar or N_2 using flame-dried glassware and anhydrous solvents. PhMe was purchased as HPLC-grade (inhibitor-free) from Caledon or Sigma–Aldrich, and was dried using a PureSolv MD 5 solvent purification system and used without further manipulation. All other commercial reagents were used as received. Compounds were purified by flash column chromatography using SiliCycle SilicaFlash P60 silica gel. The 8-mL threaded culture tubes used for reactions were purchased from Fisher (catalogue no. 14-957-76A) and were sealed using size 19 rubber septa and electrical tape.

1-Arylcyclopropyl tosylates are known to be sensitive to Lewis acids and silica,[1] so these products were purified by flash column chromatography buffered with 1% NEt_3.

GC-MS data was obtained on a Shimadzu GCMS-QP2010 SE; yields represent peak areas calibrated against each compound's response factor relative to *n*-dodecane internal standard. ^1H and ^{13}C NMR spectra were recorded on Varian MercuryPlus 400 MHz, Agilent DD2 500 MHz, or Bruker AvanceIII 400 MHz spectrometers. TLC samples were run on EMD Millipore TLC Silica gel 60 F_{254} plates and were visualized by UV or by staining with standard $KMnO_4$ or vanillin stains.

B. Optimization Tables

Table S1. Evaluation of base and solvent

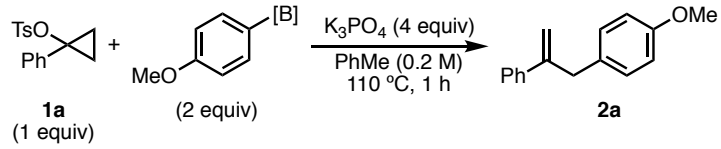


1a (1 equiv) (2 equiv) **2a**

Entry	Base (equiv)	Solvent	Yield (%)	r.r.
1	K_3PO_4 (4)	PhMe	92	8.9:1
2	K_3PO_4 (3)	PhMe	92	8.3:1
3	K_3PO_4 (2.5)	PhMe	86	7.5:1
4	K_3PO_4 (2)	PhMe	83	6.5:1
5	K_3PO_4 (1.2)	PhMe	54	6.9:1
6	K_2CO_3 (4)	PhMe	81	5.7:1
7	K_2CO_3 (1.2)	PhMe	36	6.0:1
8	KO*t*-Bu (4)	PhMe	<5	–
9	KO*t*-Bu (1.2)	PhMe	35	7.5:1
10	LiO*t*-Bu (4)	PhMe	14	8.7:1
11	Cs_2CO_3 (4)	PhMe	38	13:1
12	NaOH (1.2)	PhMe	<5	–
13	NaOMe (1.2)	PhMe	20	15:1
14	NaOAc (1.2)	PhMe	<5	–
15	$NaHCO_3$ (1.2)	PhMe	<5	–
16	NEt_3 (1.2)	PhMe	<5	–
17	TBAF•xH_2O (1.2)	PhMe	<5	–
18	none	PhMe	<5	–
19	K_3PO_4 (4)	1,4-dioxane	38	>20:1
20	K_3PO_4 (4)	$PhCF_3$	93	9.5:1
21	K_3PO_4 (4)	DMF	<5	–
22	K_3PO_4 (4)	*n*-BuOH	<5	–

Yields determined by GC-MS using *n*-dodecane as internal standard.

Table S2. Evaluation of arylboron reagent

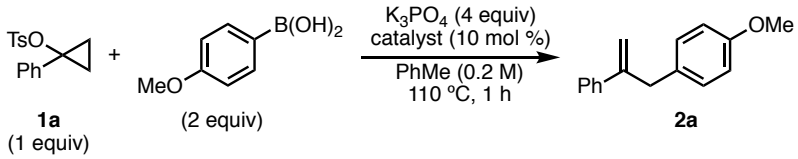


1a (1 equiv) (2 equiv) **2a**

Entry	Ar[B]	Yield (%)	r.r.
1	$ArB(OH)_2$	92	8.9:1
2	ArBnep	<5	–
3	Bpin	<5	–
4	$(ArBO)_3$ (0.67 equiv)	33	7.6:1
5	BF_3K	<5	–

Yields determined by GC-MS using *n*-dodecane as internal standard.

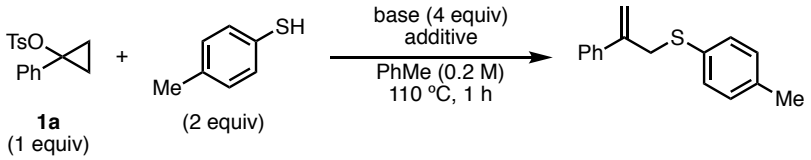
Table S3. Evaluation of catalyst



Entry	Catalyst	Yield (%)	r.r.
1	none	92	8.9:1
2	$NiCl_2(PPh_3)_2$	97	20:1
3	$NiCl_2(PCy_3)_2$	82	>20:1
4	$NiCl_2$(dppe)	84	>20:1
5	$NiCl_2$(bpy)	71	>20:1
6	$PdCl_2(PPh_3)_2$	22	–

Yields determined by GC-MS using *n*-dodecane as internal standard.

Table S4. Evaluation of ring-opening functionalization with other nucleophiles



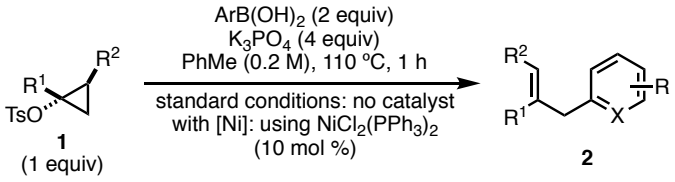
Entry	Base	Additive (equiv)	Relative GC-MS Area (%)
1	K_3PO_4	$PhB(OH)_2$ (2)	89
2	K_3PO_4	$PhB(OH)_2$ (1)	92
3	K_3PO_4	$PhB(OH)_2$ (0.4)	89
4	K_3PO_4	$PhB(OH)_2$ (0.1)	25
5	K_3PO_4	none	18
6	none	$NiCl_2(PPh_3)_2$ (0.1)	33
7	K_2HPO_4	none	16

Areas are uncalibrated compared to *n*-dodecane as an internal standard.

C. Preparation of Allyl Products

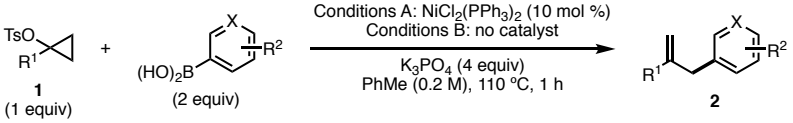
C.1. Preparation of arylated products

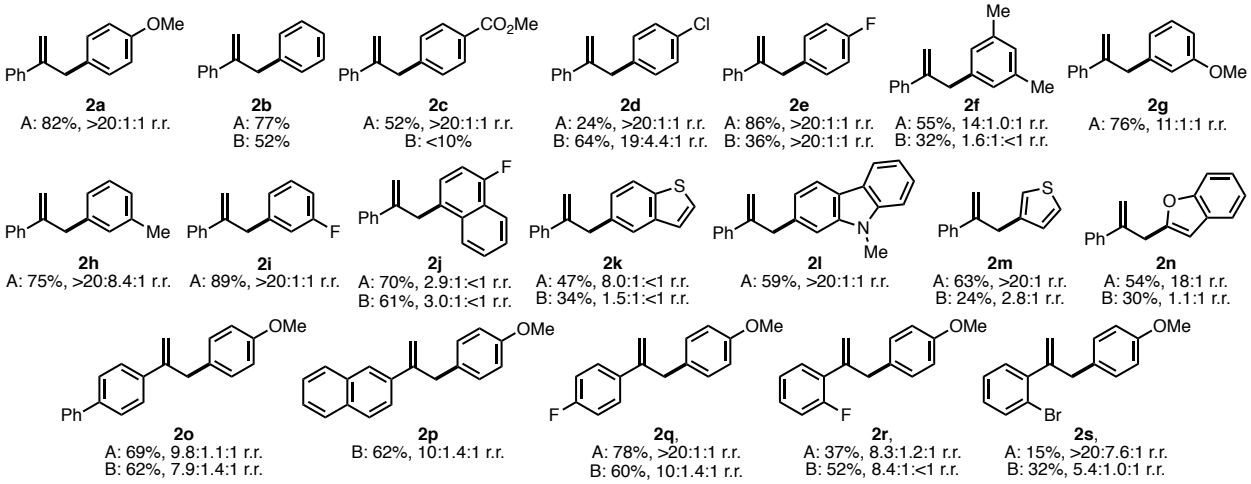
General Procedure A: Ring-opening Arylation of 1-Arylcyclopropyl Tosylates

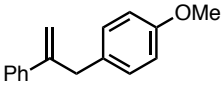


Representative procedure on 0.20-mmol scale: An 8-mL threaded culture tube with a stir bar was fitted with a size 19 septum and was flame-dried under vacuum and cooled under N_2. To this tube was added cyclopropyl tosylate substrate (0.20 mmol, 1.0 equiv), arylboronic acid (0.40 mmol, 2.0 equiv), potassium phosphate (0.17 g, 0.80 mmol, 4.0 equiv), and, for reactions using Ni, $NiCl_2(PPh_3)_2$ (13 mg, 0.020 mmol, 10 mol %). (For cyclopropyl tosylate substrates that were oils, they were later added with PhMe as 0.20 M stock solutions, 1.0 mL, 0.20 mmol, 1.0 equiv.) The tube was sealed and evacuated and backfilled with N_2 (×3), and PhMe (1.0 mL, 0.20 M) was added. The reaction was stirred at r.t. for 1 min, then was placed into an oil bath pre-heated at 110 °C and was stirred at this temperature for 1 h. The reaction was removed from the bath, cooled to r.t., and quenched with sat. aq. NH_4Cl. The solution was extracted with Et_2O or EtOAc (×3), and the organic fractions were combined and filtered over a pipette plug of $MgSO_4$ and Celite. The crude solution was analyzed by GC-MS to determine regioisomer ratios. The solution was concentrated and the residue was purified by flash column chromatography to yield the desired product.

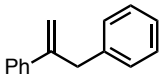
Table S5: Scope of the Reaction in the Presence and Absence of Ni Catalyst



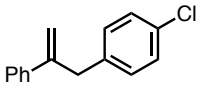




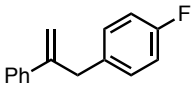
1-Methoxy-4-(2-phenylallyl)benzene (2a): Prepared according to General Procedure A on 0.30-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield the product as a colourless oil (55 mg, 0.246 mmol, 82%). Analytical data (major regioisomer):[2] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.50–7.43 (m, 2H), 7.36–7.24 (m, 3H), 7.21–7.14 (m, 2H), 6.89–6.81 (m, 2H), 5.50 (app d, J = 1.4 Hz, 1H), 5.04 (app dd, J = 2.8, 1.4 Hz, 1H), 3.84–3.78 (m, 5H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 158.1, 147.5, 141.0, 131.7, 130.0, 128.4, 127.5, 126.3, 114.4, 113.9, 55.4, 40.9 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.79.



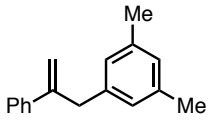
Prop-2-ene-1,2-diyldibenzene (2b): Prepared on 0.20-mmol scale without Ni and on 0.30-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–30% PhMe/hexanes) to yield the product as a colourless oil (no Ni: 20 mg, 0.103 mmol, 52%; with Ni: 45 mg, 0.232 mmol, 77%). Analytical data:[3] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.50–7.43 (m, 2H), 7.35–7.15 (m, 8H), 5.55–5.49 (m, 1H), 5.06–5.01 (m, 1H), 3.88–3.83 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 147.1, 141.0, 139.7, 129.1, 128.5, 128.4, 127.6, 126.3, 126.2, 114.7, 41.8 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.68.



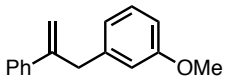
1-Chloro-4-(2-phenylallyl)benzene (2d): Prepared on 0.20-mmol scale without Ni and on 0.20-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–20% PhMe/hexanes) to yield the product as a colourless oil, which was an inseparable mixture of regioisomers (no Ni: 29 mg, 0.127 mmol, 64%, 19:4.4:1 r.r.; with Ni: 11 mg, 0.048 mmol, 24%, >20:1:1 r.r.). Analytical data (major regioisomer):[4] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.44–7.39 (m, 2H), 7.32–7.27 (m, 2H), 7.27–7.21 (m, 3H), 7.18–7.13 (m, 2H), 5.51–5.49 (m, 1H), 5.06–5.02 (m, 1H), 3.83–3.79 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 146.5, 140.4, 138.0, 131.9, 130.2, 128.5, 128.3, 127.6, 126.1, 114.8, 41.0 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.81.



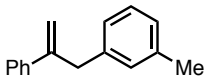
1-Fluoro-4-(2-phenylallyl)benzene (2e): Prepared on 0.20-mmol scale without Ni and on 0.30-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a colourless oil (no Ni: 15 mg, 0.071 mmol, 36%, >20:1:1 r.r.; with Ni: 55 mg, 0.259 mmol, 86%, >20:1:1 r.r.). Analytical data (major regioisomer):[5] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.48–7.41 (m, 2H), 7.36–7.25 (m, 3H), 7.24–7.17 (m, 2H), 7.03–6.95 (m, 2H), 5.54–5.50 (m, 1H), 5.05 (td, J = 1.3, 1.4 Hz, 1H), 3.88–3.79 (m, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −117.3 ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 162.8, 160.4, 147.1, 140.7, 135.2, 135.2, 130.5, 130.4, 128.4, 127.7, 126.3, 115.4, 115.2, 114.8, 41.0 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.71.



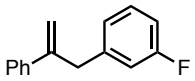
1,3-Dimethyl-5-(2-phenylallyl)benzene (2f): Prepared on 0.20-mmol scale without Ni and on 0.30-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–30% PhMe/hexanes) to yield the product as a colourless oil (no Ni: 14 mg, 0.063 mmol, 32%, 1.6:1:<1 r.r.; with Ni: 37 mg, 0.166 mmol, 55%, 14:1.0:1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.47–7.42 (m, 2H), 7.33–7.27 (m, 2H), 7.26–7.21 (m, 1H), 6.88–6.85 (m, 2H), 6.84–6.81 (m, 1H), 5.51–5.49 (m, 1H), 5.01 (td, J = 1.4, 1.4 Hz, 1H), 3.76 (dd, J = 0.7, 0.7 Hz, 2H), 2.30–2.25 (m, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 147.1, 141.1, 139.5, 137.9, 128.4, 127.9, 127.5, 126.9, 126.2, 114.6, 41.6, 21.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{19}$ (M+H): 223.1481; found: 223.1464; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.76.



1-Methoxy-3-(2-phenylallyl)benzene (2g): Prepared on 0.10-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a colourless oil (17 mg, 0.076 mmol, 76%, 11:1:1 r.r.). The chemical shifts and splitting patterns were consistent with a related compound, 1-allyl-3-methoxybenzene.[6] Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.47–7.41 (m, 2H), 7.33–7.15 (m, 4H), 6.86–6.82 (m, 1H), 6.80–6.78 (m, 1H), 6.75–6.71 (m, 1H), 5.52–5.49 (m, 1H), 5.07–5.04 (m, 1H), 3.82 (d, J = 1.3 Hz, 2H), 3.77 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 159.8, 146.8, 141.3, 140.9, 129.4, 128.4, 127.6, 126.3, 121.5, 114.8, 114.8, 111.6, 55.2, 41.8 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.71.

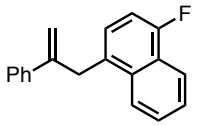


1-Methyl-3-(2-phenylallyl)benzene (2h): Prepared on 0.20-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–6% PhMe/hexanes) to yield the product as a colourless oil (17 mg, 0.15 mmol, 75%, >20:8.4:1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.47–7.42 (m, 2H), 7.33–7.27 (m, 2H), 7.25–7.21 (m, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.08–6.99 (m, 3H), 5.51 (d, J = 1.3 Hz, 1H), 5.03 (q, J = 1.4 Hz, 1H), 3.81 (d, J = 1.2 Hz, 2H), 2.32 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 146.9, 140.9, 139.4, 137.9, 129.7, 128.2, 128.2, 127.4, 126.8, 126.1, 125.9, 114.5, 41.5, 21.4 ppm; **HRMS** *m/z* (DART): found for $C_{17}H_{17}$ (M+H): 209.1325; found: 209.1325; **R_f** (9:1 hexanes/PhMe; UV/Vanillin): 0.62.

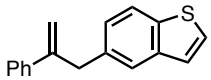


1-Fluoro-3-(2-phenylallyl)benzene (2i): Prepared on 0.20-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–6% PhMe/hexanes) to yield the product as a colourless oil (38 mg, 0.18 mmol, 89%, >20:1:1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.43–7.39 (m, 2H), 7.29 (tt, J = 6.6, 1.0 Hz, 2H), 7.26–7.18 (m, 2H), 7.01 (ddq, J = 7.6, 1.5, 0.8 Hz, 1H), 6.93 (dt, J = 10.0, 1.9 Hz, 1H), 6.92–6.83 (m, 1H), 5.52 (dd, J = 1.2, 0.6 Hz, 1H), 5.05 (q, J = 1.3 Hz, 1H), 3.85–3.82

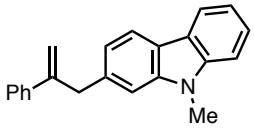
(m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ_C 162.0, 146.6, 142.1, 140.4, 129.7, 128.3, 127.6, 126.1, 124.5, 115.8, 115.0, 113.1, 41.4 ppm; **^{19}F NMR** (377 MHz, $CDCl_3$, 298 K): δ_F -113.69 – -113.82 (m) ppm; **HRMS** *m/z* (DART): found for $C_{14}H_{15}F$ (M+H): 213.1074; found: 213.1070; $\mathbf{R_f}$ (9:1 hexanes/PhMe; UV/Vanillin): 0.62.



1-Fluoro-4-(2-phenylallyl)naphthalene (2j): Prepared on 0.20-mmol scale without Ni and on 0.30-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–20% PhMe/hexanes) to yield the product as a colourless oil, which was an inseparable mixture of regioisomers (no Ni: 32 mg, 0.122 mmol, 61%, 3.0:1:<1 r.r.; with Ni: 55 mg, 0.120 mmol, 70%, 2.0:1:<1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 8.20–8.11 (m, 1H), 8.03–7.94 (m, 1H), 7.59–7.50 (m, 4H), 7.42–7.23 (m, 4H), 7.07 (dd, *J* = 10.4, 7.8 Hz, 1H), 5.54–5.49 (m, 1H), 4.81–4.74 (m, 1H), 4.21 (dd, *J* = 1.0, 0.89 Hz, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −125.2 ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 146.4, 141.2, 134.0, 133.8, 133.4, 131.4, 128.9, 128.7, 128.6, 128.6, 127.8, 127.0, 127.0, 126.0, 126.0, 124.5, 124.4, 121.3, 121.3, 115.0, 109.1, 108.9, 38.6 ppm; **HRMS** *m/z* (DART): found for $C_{19}H_{16}F$ (M+H): 263.1231; found: 263.1231; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.71.

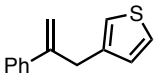


5-(2-Phenylallyl)benzothiophene (2k): Prepared on 0.20-mmol scale in the absence of Ni and on 0.30-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a white solid (no Ni: 17 mg, 0.068 mmol, 34%, 1.5:1:<1 r.r.; with Ni: 35 mg, 0.140 mmol, 47%, 8.0:1:<1 r.r.). The NMR chemical shifts and splitting patterns were consistent with a related compound, 5-allylbenzothiophene.[7] Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.79 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.70–7.68 (m, 1H), 7.49–7.45 (m, 2H), 7.41 (d, *J* = 5.4 Hz, 1H), 7.32–7.21 (m, 5H), 5.54 (d, *J* = 1.4 Hz, 1H), 5.08 (dt, *J* = 1.4, 1.4 Hz, 1H), 3.97 (dd, *J* = 1.0, 1.0 Hz, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 147.2, 140.9, 140.1, 137.8, 135.8, 128.4, 127.6, 126.6, 126.3, 125.8, 123.8, 123.8, 122.4, 114.8, 41.7 ppm; **HRMS** *m/z* (DART): calcd for $C_{17}H_{15}S$ (M+H): 251.0889; found: 251.0901; $\mathbf{R_f}$ (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.70.

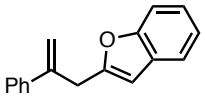


9-Methyl-2-(2-phenylallyl)-9*H*-carbazole (2l): Prepared on 0.30-mmol using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a colourless oil, which was an inseparable mixture of regioisomers (53 mg, 0.178 mmol, 59%, >20:1:1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 8.05 (dt, *J* = 7.7, 1.1 Hz, 1H), 8.00 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.52–7.49 (m, 2H), 7.47–7.43 (m, 1H), 7.39–7.35 (m, 1H), 7.32–7.27 (m, 2H), 7.27–7.19 (m, 3H), 7.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.55 (d, *J* = 1.5 Hz, 1H), 5.10 (dt, *J* = 1.5, 1.4 Hz, 1H),

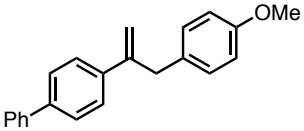
4.07–4.07 (m, 2H), 3.80 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 147.4, 141.4, 141.1, 141.0, 137.5, 128.2, 127.4, 126.2, 125.3, 122.7, 121.1, 120.3, 120.1, 120.0, 118.8, 114.6, 108.6, 108.3, 42.4, 29.0 ppm; **HRMS** *m/z* (DART): found for $C_{22}H_{20}N$ (M+H): 298.1590; found: 298.1591; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.54.



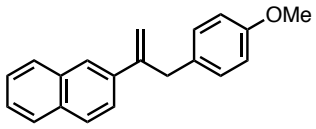
3-(2-Phenylallyl)thiophene (2m): Prepared on 0.20-mmol scale in the absence of Ni and on 0.30-mmol scale using $NiCl_2(PPh_3)_2$. The crude residue was purified by flash column chromatography (gradient of 0–30% PhMe/hexanes) to yield the product as a colourless oil (no Ni: 9.4 mg, 0.047 mmol, 24%, 2.8:1 r.r.; with Ni: 38 mg, 0.190 mmol, 63%, >20:1 r.r.). Analytical data (major regioisomer):[4] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.48–7.43 (m, 2H), 7.37–7.21 (m, 4H), 6.99–6.93 (m, 2H), 5.52–5.47 (m, 1H), 5.11–5.07 (m, 1H), 3.87–3.83 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 146.7, 140.9, 140.2, 128.7, 128.4, 127.6, 126.2, 125.4, 121.6, 114.3, 36.4 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.75.



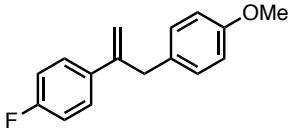
2-(2-Phenylallyl)benzofuran (2n): Prepared on 0.30-mmol scale using $NiCl_2(PPh_3)_2$, and on 0.20-mmol scale without Ni. The crude residue was purified by flash column chromatography (gradient of 0–40% PhMe/hexanes) to yield the product as a white solid (no Ni: 14 mg, 0.060 mmol, 30%, 1.1:1 r.r.; with Ni: 38 mg, 0.162 mmol, 54%, 18:1 r.r.). Analytical data (major regioisomer):[4] **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.51–7.47 (m, 2H), 7.47–7.41 (m, 2H), 7.35–7.30 (m, 2H), 7.29–7.24 (m, 1H), 7.24–7.14 (m, 2H), 6.42–6.39 (m, 1H), 5.58–5.56 (m, 1H), 5.24–5.21 (m, 1H), 3.99 (dd, J = 1.2, 1.2 Hz, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 156.9, 154.9, 143.5, 140.2, 129.0, 128.5, 127.9, 126.1, 123.5, 122.6, 120.5, 115.5, 111.0, 103.9, 34.9 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.74.



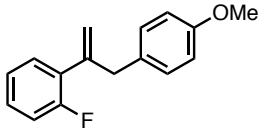
4-(3-(4-Methoxyphenyl)prop-1-en-2-yl)-1,1'-biphenyl (2o): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–90% PhMe/hexanes) to yield the product as a white solid, which was an inseparable mixture of isomers (with Ni: 41 mg, 0.136 mmol, 69%, 9.8:1.2:1 r.r.; no Ni: 37 mg, 0.123 mmol, 62%, 7.9:1.4:1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.61–7.56 (m, 2H), 7.55–7.50 (m, 4H), 7.46–7.40 (m, 2H), 7.36–7.31 (m, 1H), 7.20–7.15 (m, 2H), 6.87–6.80 (m, 2H), 5.55 (d, J = 1.4 Hz, 1H), 5.05 (td, J = 1.4, 1.4 Hz, 1H), 3.84–3.81 (m, 2H), 3.78 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.1, 146.9, 140.8, 140.3, 139.8, 131.6, 130.0, 128.9, 127.4, 127.1, 127.1, 126.7, 114.5, 114.0, 55.4, 40.8 ppm; **HRMS** *m/z* (DART): calcd for $C_{22}H_{21}O$ (M+H): 301.1587; found: 301.1591; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.48.



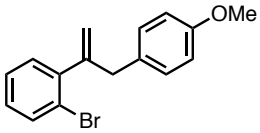
2-(3-(4-Methoxyphenyl)prop-1-en-2-yl)naphthalene (2p): The product was prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 30–80% PhMe/hexanes) to yield the product as a white solid (no Ni: 34 mg, 0.124 mmol, 62%, 10:1.4:1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.88–7.85 (m, 1H), 7.82–7.76 (m, 3H), 7.66–7.61 (m, 1H), 7.45–7.41 (m, 2H), 7.22–7.17 (m, 2H), 6.86–6.80 (m, 2H), 5.65–5.62 (m, 1H), 5.13 (td, J = 1.5, 1.4 Hz, 1H), 3.93–3.90 (m, 2H), 3.77 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.0, 147.2, 138.1, 133.3, 132.8, 131.5, 129.9, 128.2, 127.8, 127.5, 126.1, 125.8, 124.9, 124.6, 114.9, 113.8, 55.2, 40.8 ppm; **HRMS** *m/z* (DART): calcd for $C_{20}H_{19}O$ (M+H): 275.1430; found: 275.1434; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.52.



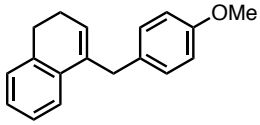
1-Fluoro-4-(3-(4-methoxyphenyl)prop-1-en-2-yl)benzene (2q): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–70% PhMe/hexanes) to yield the product as a colourless oil, which was an inseparable mixture of isomers (with Ni: 38 mg, 0.157 mmol, 79%, >20:1:1 r.r.; no Ni: 29 mg, 0.120 mmol, 60%, 10:1.4:1 r.r.). Analytical data (major regioisomer):[8] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.43–7.35 (m, 2H), 7.16–7.10 (m, 2H), 7.02–6.93 (m, 2H), 6.86–6.79 (m, 2H), 5.42 (d, J = 1.2 Hz, 1H), 5.02 (d, J = 1.4 Hz, 1H), 3.78 (s, 3H), 3.77–3.74 (m, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −115.2 ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 163.6, 161.2, 158.2, 146.5, 137.1, 131.4, 130.0, 128.0, 127.9, 115.3, 115.1, 114.3, 114.3, 114.0, 55.3, 41.1 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{16}OF$: 243.1180; found: 243.1176; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.51.



1-Fluoro-2-(3-(4-methoxyphenyl)prop-1-en-2-yl)benzene (2r): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–70% PhMe/hexanes) to yield the product as a colourless oil (with Ni: 18 mg, 0.074 mmol, 37%, 8.3:1.2:1 r.r.; no Ni: 25 mg, 0.103 mmol, 52%, 8.4:1:<1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.23–7.15 (m, 2H), 7.13–7.07 (m, 2H), 7.06–6.97 (m, 2H), 6.82–6.76 (m, 2H), 5.29–5.27 (m, 1H), 5.19–5.16 (m, 1H), 3.81–3.73 (m, 5H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 161.2, 158.8, 158.2, 144.6, 131.4, 130.3, 130.3, 130.1, 128.9, 128.8, 124.0, 124.0, 117.5, 117.5, 115.9, 115.7, 113.8, 55.3, 42.1, 42.0 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{16}OF$ (M+H): 243.1180; found: 243.1185; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.56.

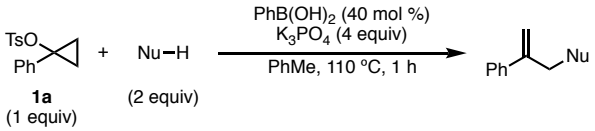


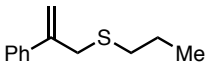
1-Bromo-2-(3-(4-methoxyphenyl)prop-1-en-2-yl)benzene (2s): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–70% PhMe/hexanes) to yield the product as a colourless oil, which was an inseparable mixture of regioisomers (with Ni: 9.1 mg, 0.030 mmol, 15%, >20:7.6:1 r.r.; no Ni: 19 mg, 0.063 mmol, 32%, 5.4:1.0:1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.58–7.53 (m, 1H), 7.21–7.16 (m, 1H), 7.12–7.07 (m, 3H), 7.02–6.98 (m, 1H), 6.84–6.79 (m, 2H), 5.11–5.09 (m, 1H), 5.02–5.00 (m, 1H), 3.79 (s, 3H), 3.68–3.65 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.2, 150.1, 143.7, 132.8, 130.9, 130.7, 130.5, 128.6, 127.1, 122.1, 116.4, 113.8, 55.3, 42.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{16}H_{16}OBr$: 303.0379; found: 303.0387; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.54.



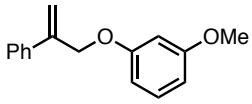
4-(4-Methoxybenzyl)-1,2-dihydronaphthalene (2t): Prepared on 0.20-mmol scale. The crude residue was purified by flash column chromatography (gradient of 20–70% PhMe/hexanes) to yield the product as a white solid (no Ni: 25 mg, 0.100 mmol, 50%, 7.9:1:<1 r.r.). Analytical data (major regioisomer): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.24–7.06 (m, 6H), 6.87–6.79 (m, 2H), 5.80–5.76 (m, 1H), 3.78 (s, 3H), 3.75–3.71 (m, 2H), 2.78 (td, *J* = 8.2, 1.0 Hz, 2H), 2.35–2.27 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 158.0, 136.8, 135.8, 135.1, 132.1, 129.8, 127.6, 127.4, 126.8, 126.4, 123.3, 113.9, 55.4, 38.3, 28.5, 23.4 ppm; **HRMS** *m/z* (DART): calcd for $C_{18}H_{19}O$ (M+H): 251.1430; found: 251.1438; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.52.

C.2. Preparation of allyl products from other nucleophiles

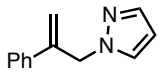




(2-Phenylallyl)(propyl)sulfane (4a): Prepared on 0.20-mmol scale using phenylboronic acid as catalyst (10 mg, 0.080 mmol, 40 mol %) and propanethiol (37 μL, 0.40 mmol, 2.0 equiv) as nucleophile. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc/hexanes) to yield the product as a colourless oil (22 mg, 0.114, 57%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.53–7.46 (m, 2H), 7.38–7.33 (m, 2H), 7.32–7.28 (m, 1H), 5.46–5.44 (m, 1H), 5.23–5.21 (m, 1H), 3.62–3.58 (m, 2H), 2.49–2.44 (m, 2H), 1.65–1.56 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 143.9, 139.6, 128.4, 127.9, 126.4, 114.9, 36.6, 33.6, 22.6, 13.7 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.77.



1-Methoxy-3-((2-phenylallyl)oxy)benzene (4b): Prepared on 0.20-mmol scale using phenylboronic acid as catalyst (10 mg, 0.080 mmol, 40 mol %) and 3-methoxyphenol (55 mg, 0.40 mmol, 2.0 equiv) as nucleophile. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc/hexanes) to yield the product as a colourless oil (19 mg, 0.079 mmol, 40%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.52–7.46 (m, 2H), 7.39–7.27 (m, 3H), 7.22–7.17 (m, 1H), 6.61–6.51 (m, 3H), 5.64–5.61 (m, 1H), 5.49–5.46 (m, 1H), 4.91–4.87 (m, 2H), 3.79 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 161.0, 160.0, 143.1, 138.5, 130.0, 128.6, 128.2, 126.2, 115.1, 107.1, 106.8, 101.6, 70.0, 55.4 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.64.

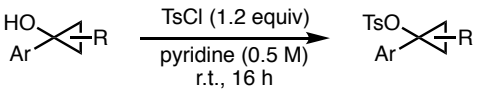


1-(2-Phenylallyl)-1*H*-pyrazole (4c): Prepared on 0.20-mmol scale using phenylboronic acid as catalyst (10 mg, 0.080 mmol, 40 mol %) and pyrazole (27 mg, 0.40 mmol, 2.0 equiv) as nucleophile. The crude residue was purified by flash column chromatography (0–50% EtOAc/hexanes) to yield the product as a colourless oil (14 mg, 0.076, 38%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.52 (dd, J = 1.9, 0.7 Hz, 1H), 7.41–7.37 (m, 3H), 7.34–7.27 (m, 3H), 6.24 (dd, J = 2.1, 2.1 Hz, 1H), 5.56 (td, J = 1.6, 0.9 Hz, 1H), 5.19–5.17 (m, 2H), 5.05–5.02 (m, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 143.6, 139.5, 138.3, 129.5, 128.7, 128.3, 126.1, 115.8, 106.0, 56.1 ppm; **R_f** (9:1 hexanes/EtOAc; UV/$KMnO_4$): 0.19.

D. Preparation of Cyclopropyl Tosylate Starting Materials

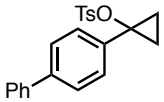
Cyclopropanol intermediates were prepared as previously described[9] or according to literature procedures.[10]

General Procedure B: Synthesis of Cyclopropyl Tosylates

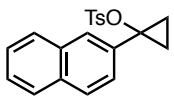


To an appropriate-sized flask with a stir bar were sequentially added cyclopropanol (1.0 equiv), tosyl chloride (1.2 equiv), and pyridine (0.50 M), and the solution was stirred for 16 h. Then, while stirring, the reaction was quenched with H_2O until the solution became heterogeneous. The solution was extracted with EtOAc (×1) and the layers were separated. The organic layer was washed with H_2O (×1) and brine (×1), washed over $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography on silica buffered with NEt_3 (1%) to yield the desired product.

1-Phenylcyclopropyl 4-methylbenzenesulfonate (1a): Prepared on 28-mmol scale. The crude material was reprecipitated (pyridine/H_2O) and the solid was washed with hexanes (×3) and dried under high vacuum to yield the product as an off-white solid (4.4 g, 15 mmol, 44%). Analytical data:[11] **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.52–7.44 (m, 2H), 7.33–7.26 (m, 2H), 7.22–7.15 (m, 3H), 7.13–7.07 (m, 2H), 2.36 (s, 3H), 1.66–1.56 (m, 2H), 1.18–1.11 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 144.2, 137.8, 135.2, 129.4, 128.2, 128.2, 128.2, 127.8, 67.2, 21.7, 13.7 ppm; **R_f** (5% EtOAc/hexanes; UV): 0.40.

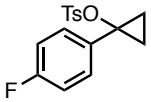


1-([1,1'-Biphenyl]-4-yl)cyclopropyl 4-methylbenzenesulfonate (S1): Prepared on 1.8-mmol scale. The crude material was purified by flash column chromatography (99:0:1–79:20:1 hexanes/EtOAc/NEt_3) to yield the product as a white solid (0.36 g, 0.99 mmol, 55%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.54–7.47 (m, 4H), 7.47–7.41 (m, 2H), 7.40–7.32 (m, 5H), 7.11–7.06 (m, 2H), 2.31 (s, 3H), 1.71–1.60 (m, 2H), 1.24–1.14 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 144.2, 141.2, 140.7, 136.6, 135.2, 129.4, 128.9, 128.7, 127.9, 127.6, 127.2, 126.9, 67.1, 21.7, 13.7 ppm; **R_f** (9:1 hexanes/EtOAc; UV/vanillin): 0.28.

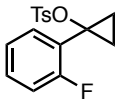


1-(Naphthalen-2-yl)cyclopropyl 4-methylbenzenesulfonate (S2): Prepared on 0.50-mmol scale. The crude residue was purified by flash column chromatography (99:0:1–69:30:1 hexanes/EtOAc/NEt_3), and the fractions containing product were collected and concentrated, and the solid was washed with Et_2O to yield the product as a white solid (0.12 g, 0.36 mmol, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.77–7.72 (m, 1H), 7.71–7.66 (m, 1H), 7.64–7.58 (m,

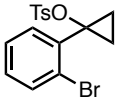
2H), 7.48–7.43 (m, 2H), 7.43–7.37 (m, 3H), 7.89–7.85 (m, 2H), 2.14 (s, 3H), 1.74–1.68 (m, 2H), 1.28–1.22 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 144.2, 134.9, 134.7, 133.1, 132.8, 129.2, 128.2, 128.1, 127.8, 127.6, 127.3, 126.5, 126.3, 126.1, 67.5, 21.4, 13.6 ppm; **R_f** (9:1 hexanes/EtOAc; UV/vanillin): 0.31.



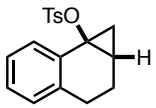
1-(4-Fluorophenyl)cyclopropyl 4-methylbenzenesulfonate (S3): Prepared on 2.5-mmol scale. The crude residue was purified by flash column chromatography (99:0:1–69:30:1 hexanes/EtOAc/NEt_3) to yield the product as a colourless oil (0.26 g, 0.85 mmol, 34%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.49–7.43 (m, 2H), 7.33–7.24 (m, 2H), 7.16–7.09 (m, 2H), 6.90–6.81 (m, 2H), 2.37 (s, 3H), 1.65–1.54 (m, 2H), 1.15–1.05 (m, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −113.2 ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ_C 163.7, 161.3, 144.3, 135.1, 130.5, 130.4, 129.3, 127.6, 115.1, 114.9, 66.5, 21.5, 13.4 ppm; **R_f** (9:1 hexanes/EtOAc; UV/vanillin): 0.26.



1-(2-Fluorophenyl)cyclopropyl 4-methylbenzenesulfonate (S4): Prepared on 2.5-mmol scale. The crude residue was purified by flash column chromatography (99:0:1–69:30:1 hexanes/EtOAc/NEt_3) to yield the product as a white solid (0.27 g, 0.88 mmol, 35%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ_H 7.48–7.36 (m, 3H), 7.23–7.15 (m, 1H), 7.10–7.05 (m, 2H), 7.00 (td, J = 7.5, 1.2 Hz, 1H), 6.76 (ddd, J = 9.5, 7.2, 1.5 Hz, 1H), 2.34 (s, 3H), 1.64–1.58 (m, 2H), 1.16–1.10 (m, 2H) ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, 298 K): δ_F −113.3 ppm; **R_f** (9:1 hexanes/EtOAc; UV/vanillin): 0.27.



1-(2-Bromophenyl)cyclopropyl 4-methylbenzenesulfonate (S5): Prepared on 5.4-mmol scale. The crude residue was purified by flash column chromatography (99:0:1–59:40:1 hexanes/EtOAc/NEt_3) and the fractions containing product were combined and concentrated, and the solid was washed with Et_2O to yield the product as a white solid (0.24 g, 0.65 mmol, 12%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.47 (dd, J = 7.7, 1.8 Hz, 1H), 7.42–7.37 (m, 2H), 7.28 (dd, J = 8.0, 1.3 Hz, 1H), 7.19 (td, J = 7.5, 1.3 Hz, 1H), 7.07–7.01 (m, 3H), 2.32 (s, 3H), 1.71–1.66 (m, 2H), 1.19–1.13 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 143.9, 135.4, 134.8, 133.1, 133.1, 130.4, 129.1, 127.6, 126.9, 126.8, 67.0, 21.7, 13.8 ppm; **R_f** (9:1 hexanes/EtOAc; UV/vanillin): 0.29.



(*trans*)-1,1a,2,3-Tetrahydro-7b*H*-cyclopropanaphthalen-7b-yl 4-methylbenzenesulfonate (1b): Prepared on 1.2-mmol scale. The crude residue was purified by flash column chromatography (99:0:1–79:20:1 hexanes/EtOAc/NEt_3) to yield the product as a white solid

(0.26 g, 0.83 mmol, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ_H 7.77–7.71 (m, 2H), 7.49–7.44 (m, 1H), 7.30–7.24 (m, 2H), 7.14–7.07 (m, 2H), 7.05–7.00 (m, 1H), 2.70 (ddd, J = 15.7, 5.0, 2.7 Hz, 1H), 2.43 (s, 3H), 2.37–2.27 (m, 2H), 2.02–1.89 (m, 2H), 1.48 (dd, J = 10.6, 6.5 Hz, 1H), 1.05 (ddd, J = 7.2, 6.5, 0.7 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K): δ_C 144.7, 136.1, 135.6, 132.5, 129.8, 128.4, 127.8, 126.4, 126.3, 125.3, 64.2, 25.8, 22.2, 21.8, 18.6, 16.7 ppm; **R_f** (9:1 hexanes/EtOAc; UV/vanillin): 0.33.

E. References

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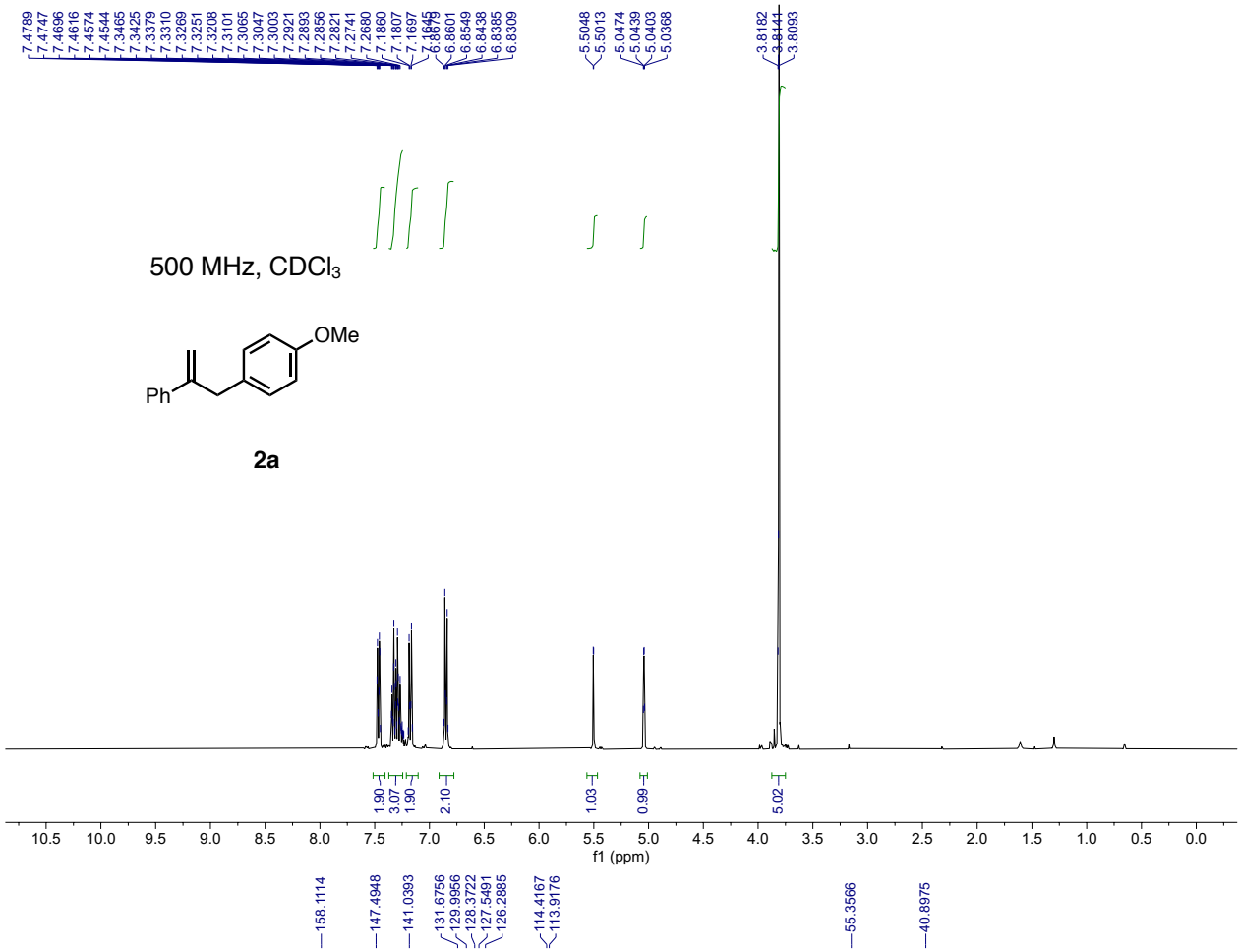
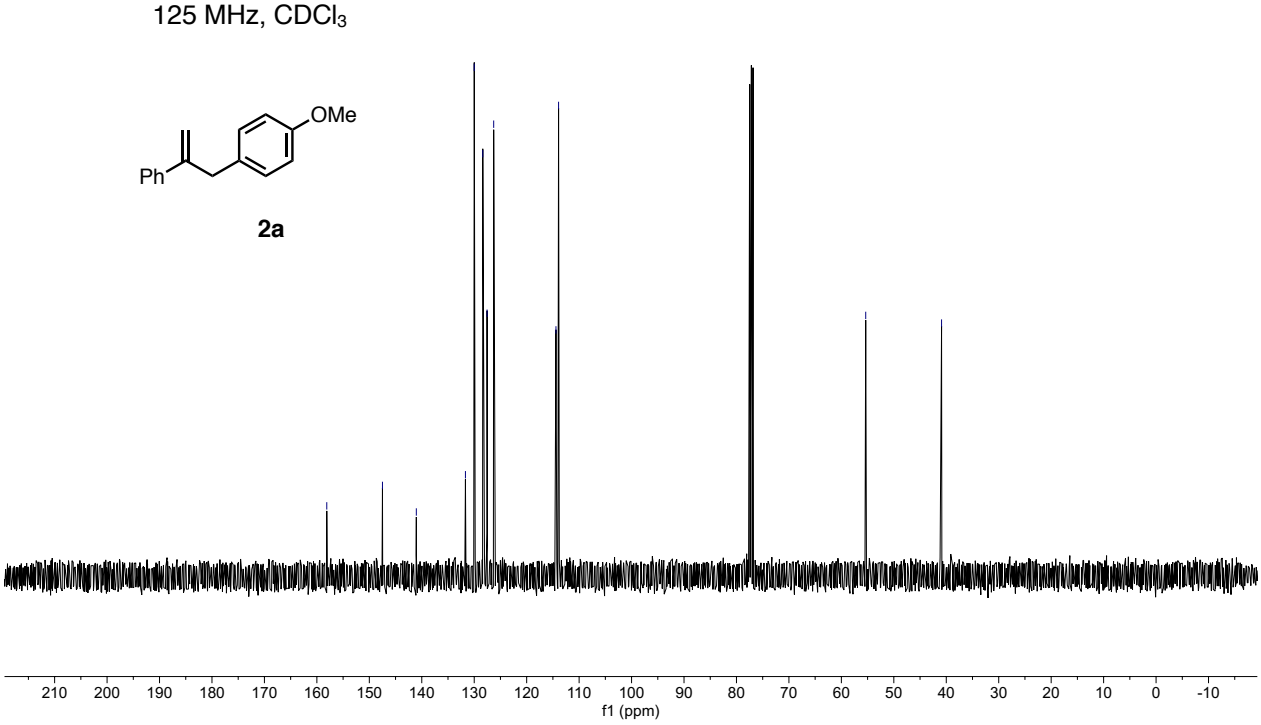
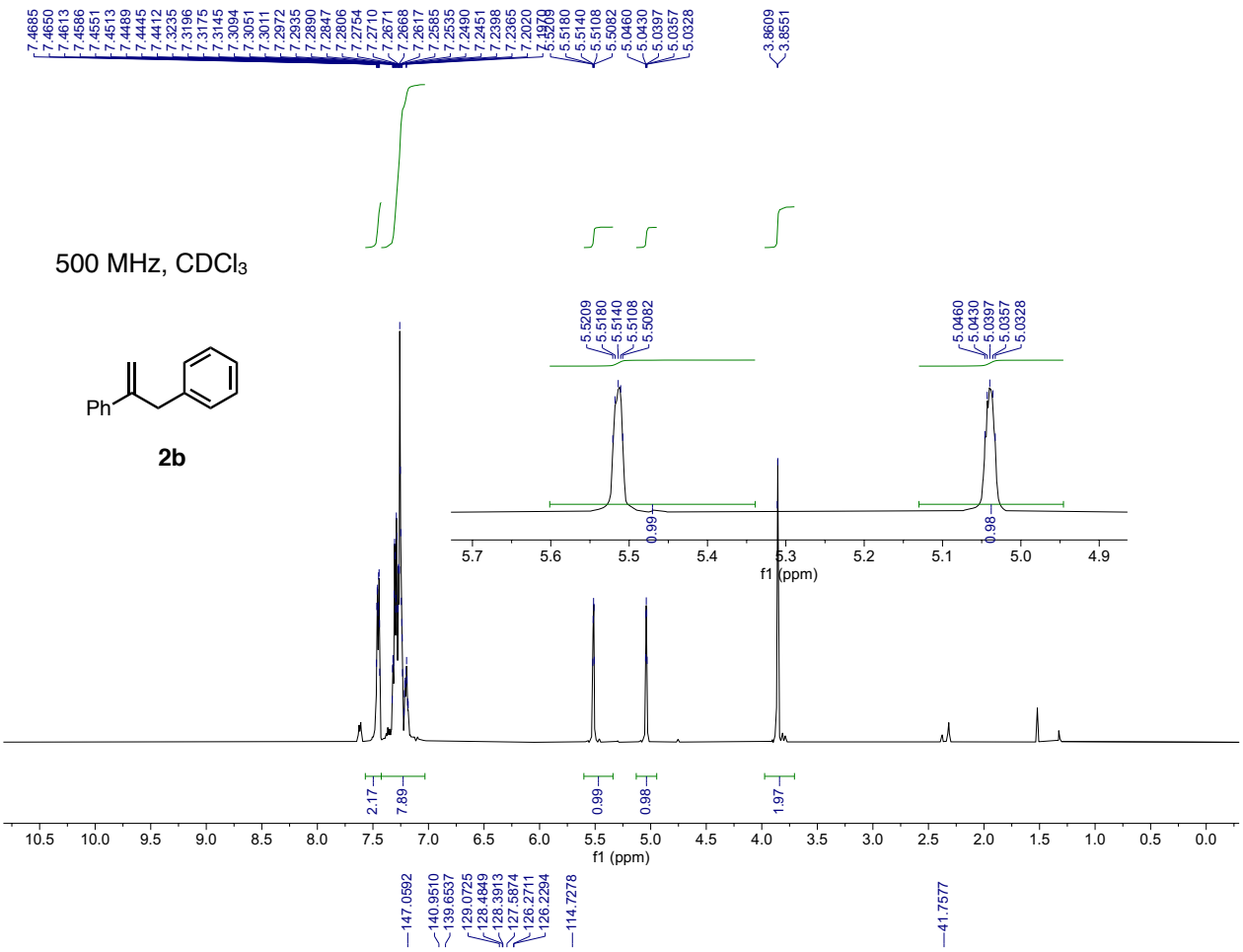
F. NMR Spectra



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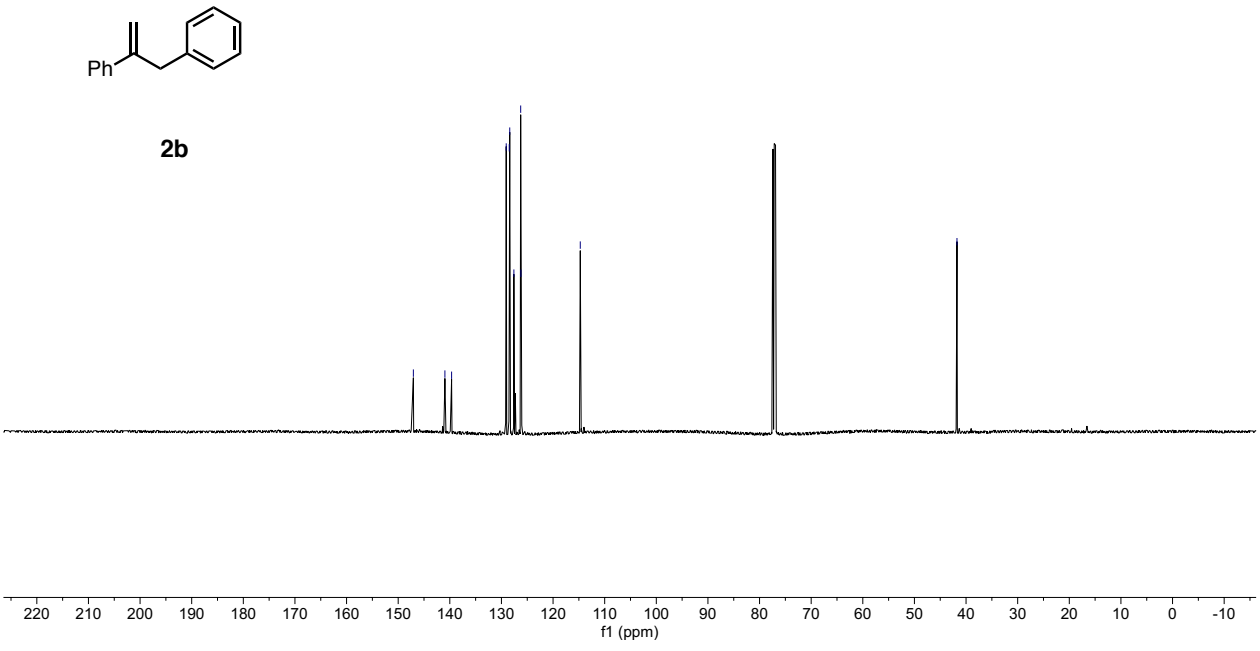
2b
f1 (ppm)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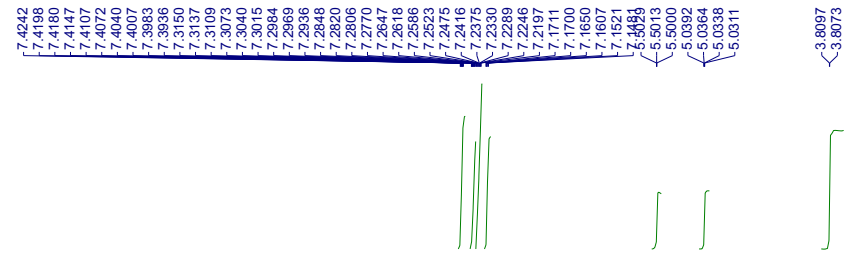
f1 (ppm)



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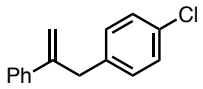
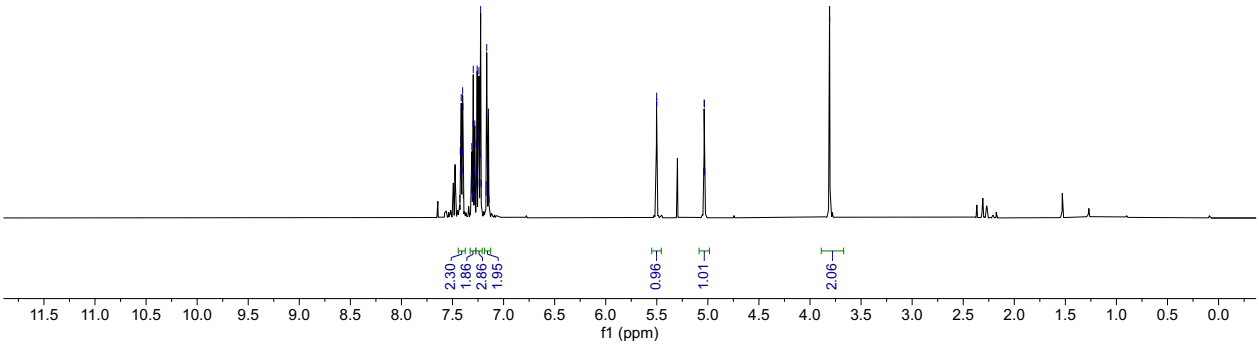


2d



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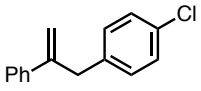

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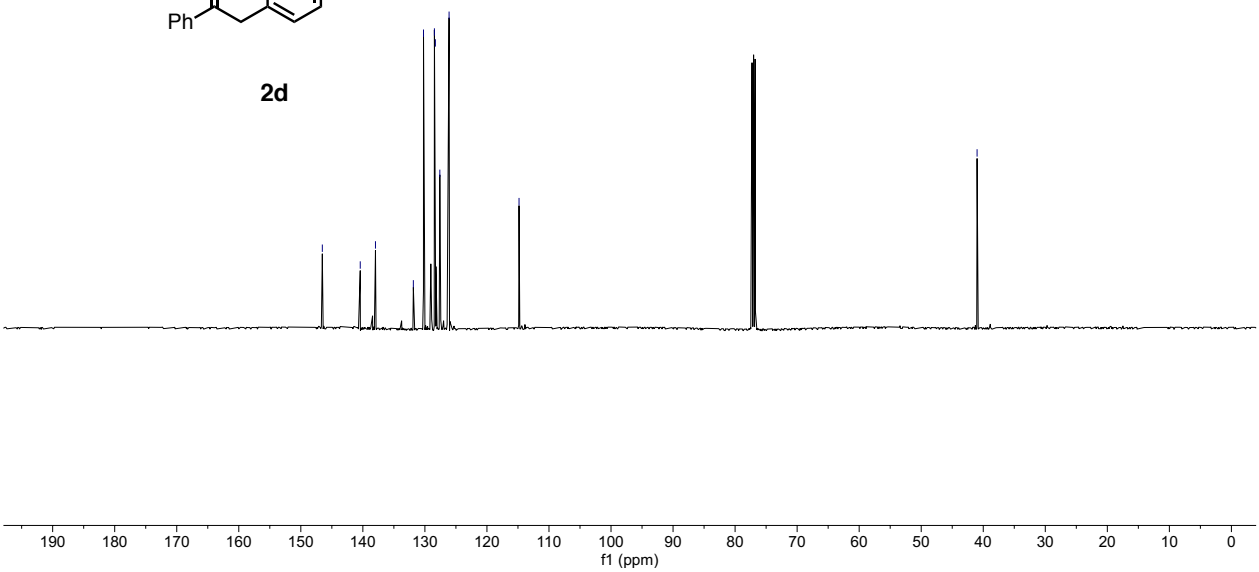

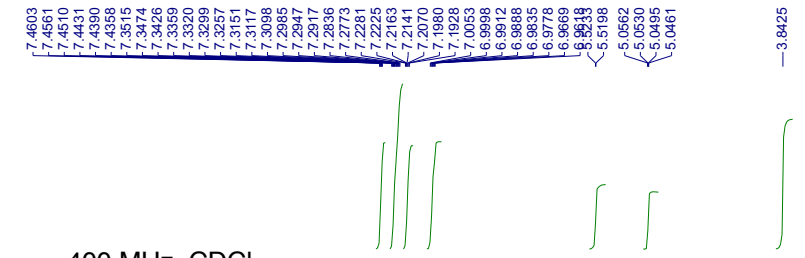

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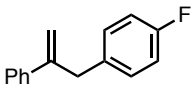
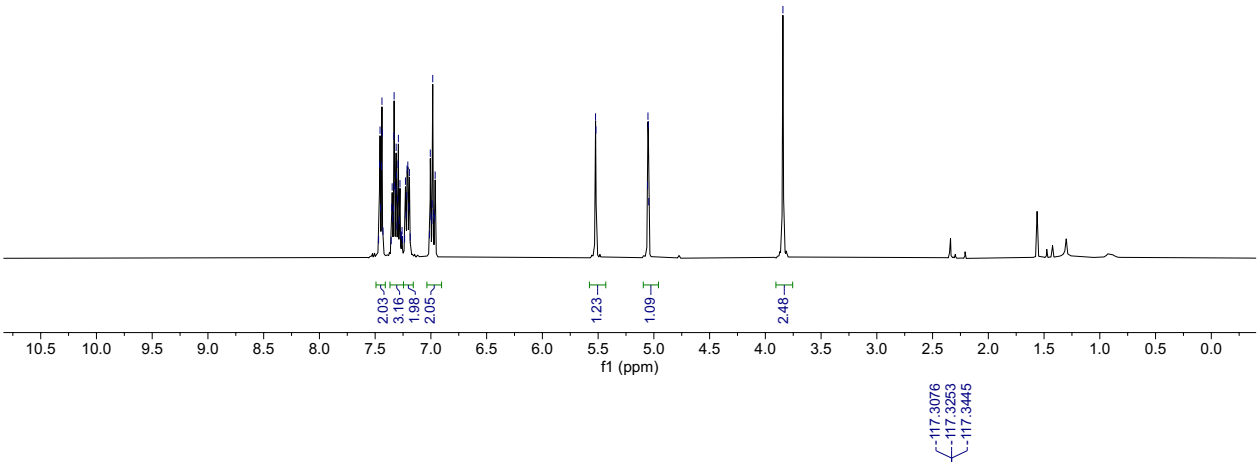


2e



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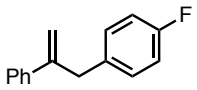

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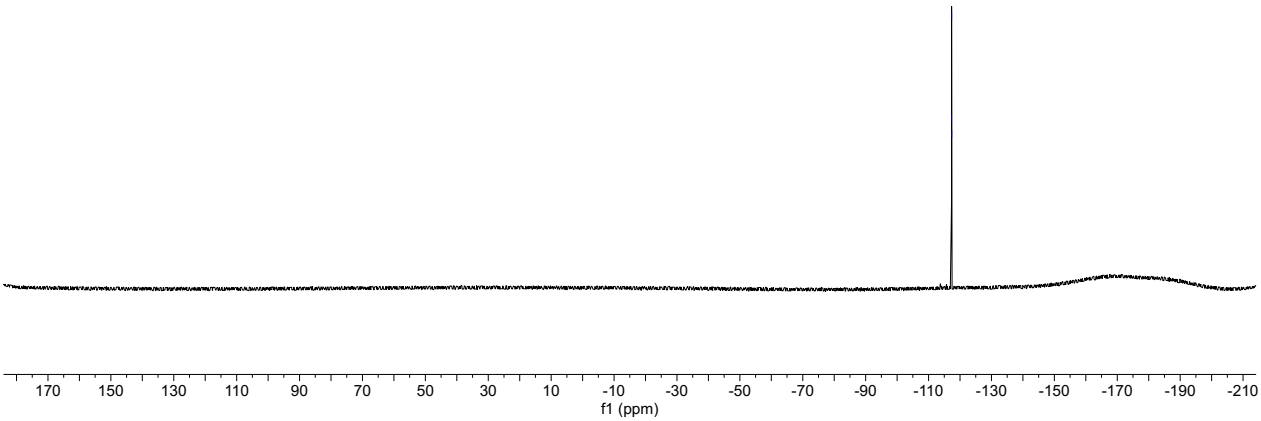

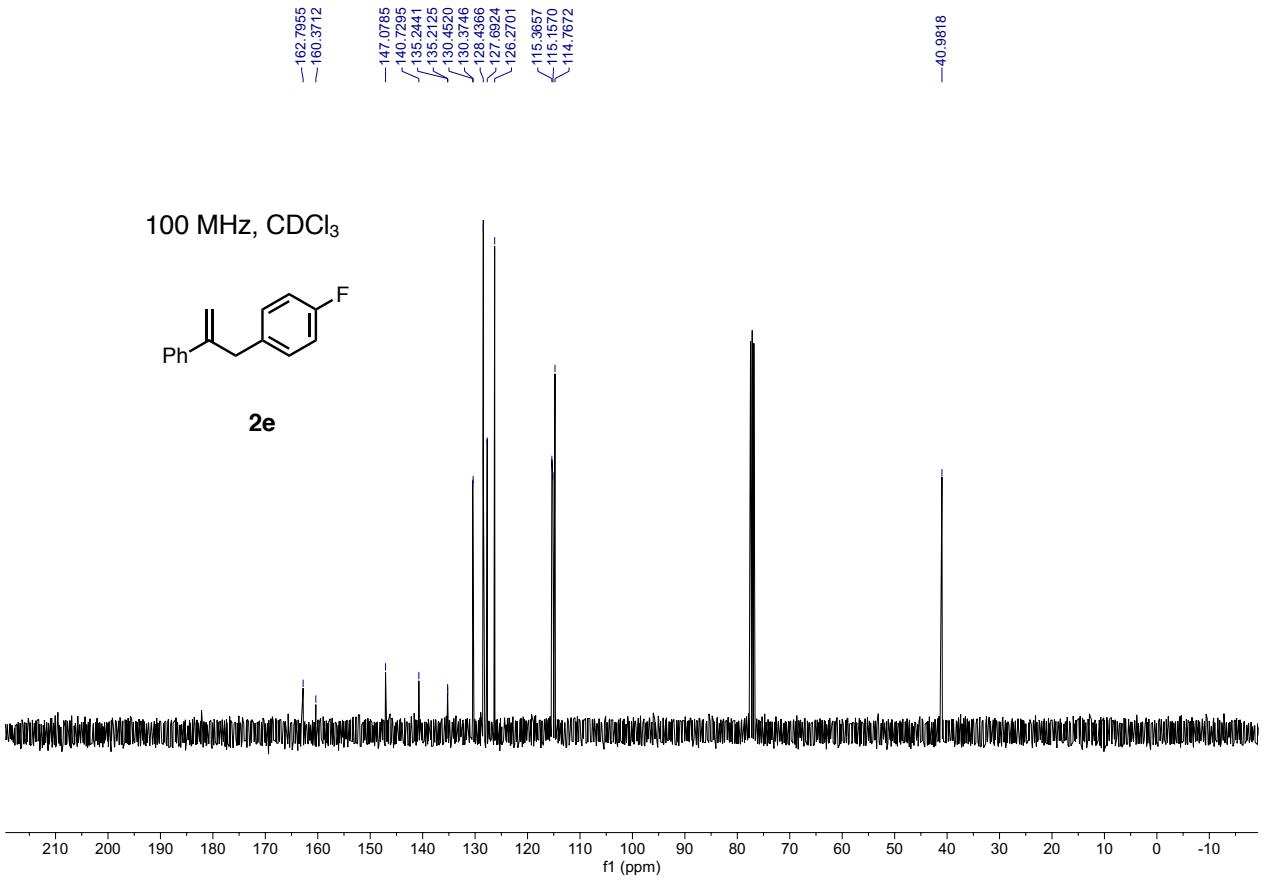
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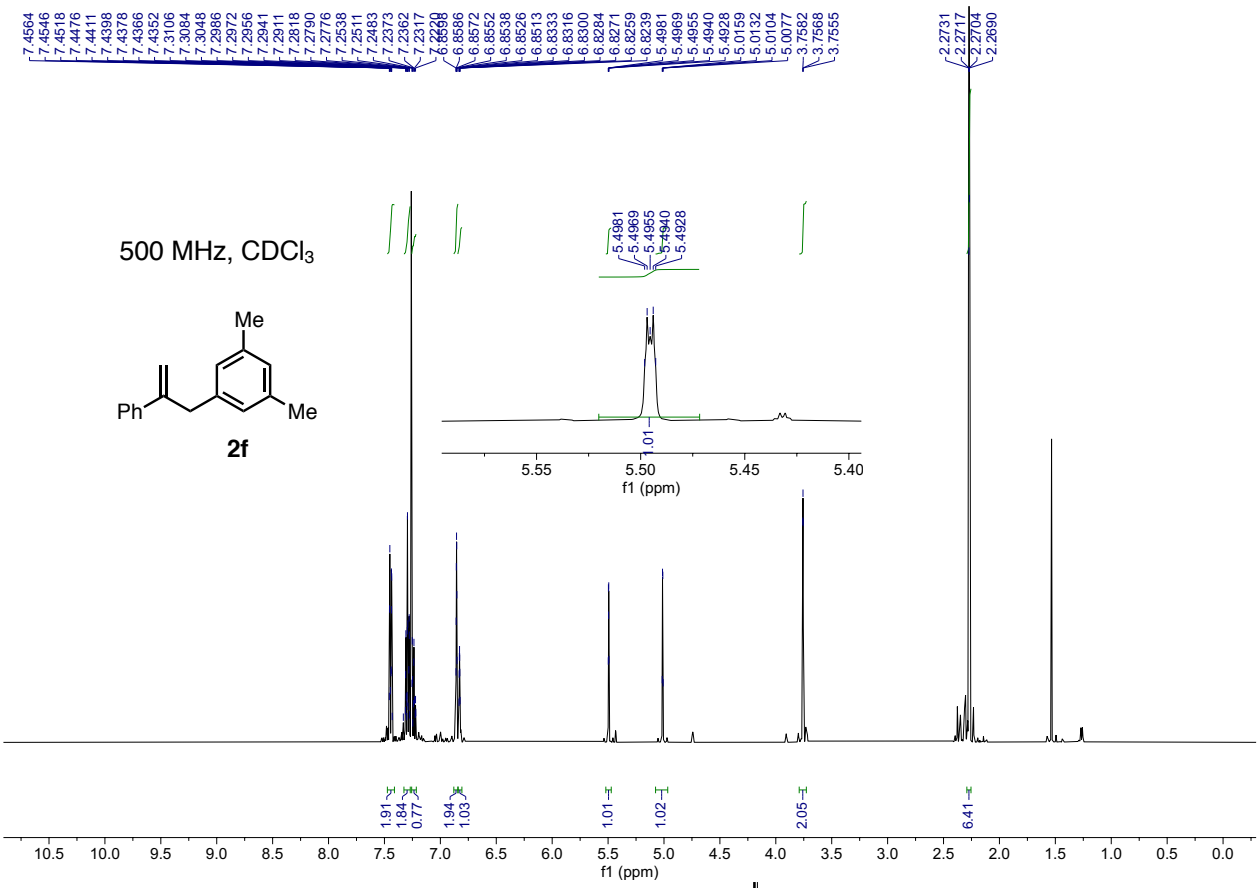
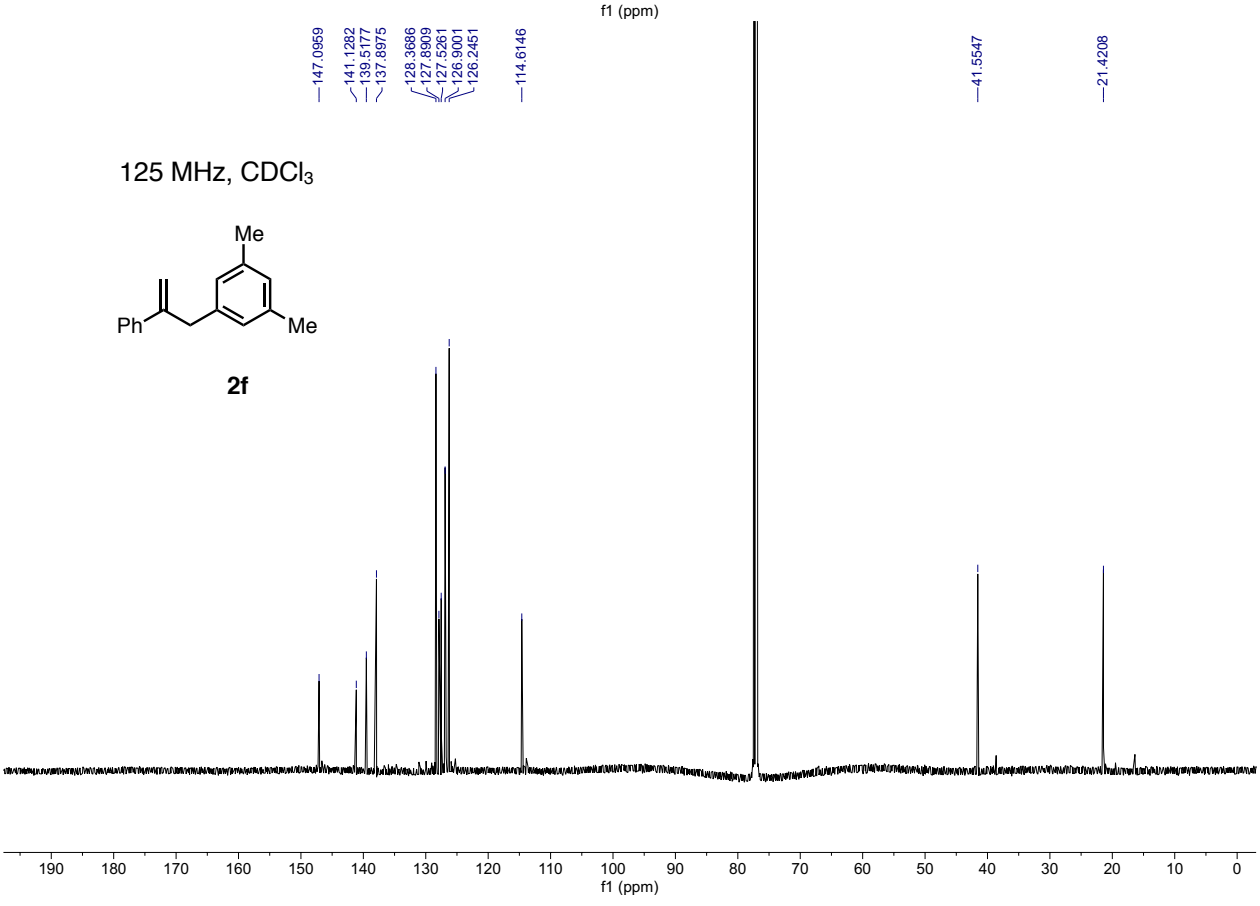
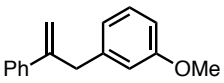
127.6924
126.2701
115.3657
115.1570
114.7672
40.9818
100 MHz, CDCl3
F
Ph
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


500 MHz, CDCl3
Me
Ph
Me
2f
f1 (ppm)

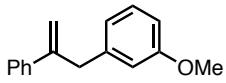

125 MHz, CDCl3
Me
Ph
Me
2f
f1 (ppm)

500 MHz, $CDCl_3$



2g

125 MHz, $CDCl_3$



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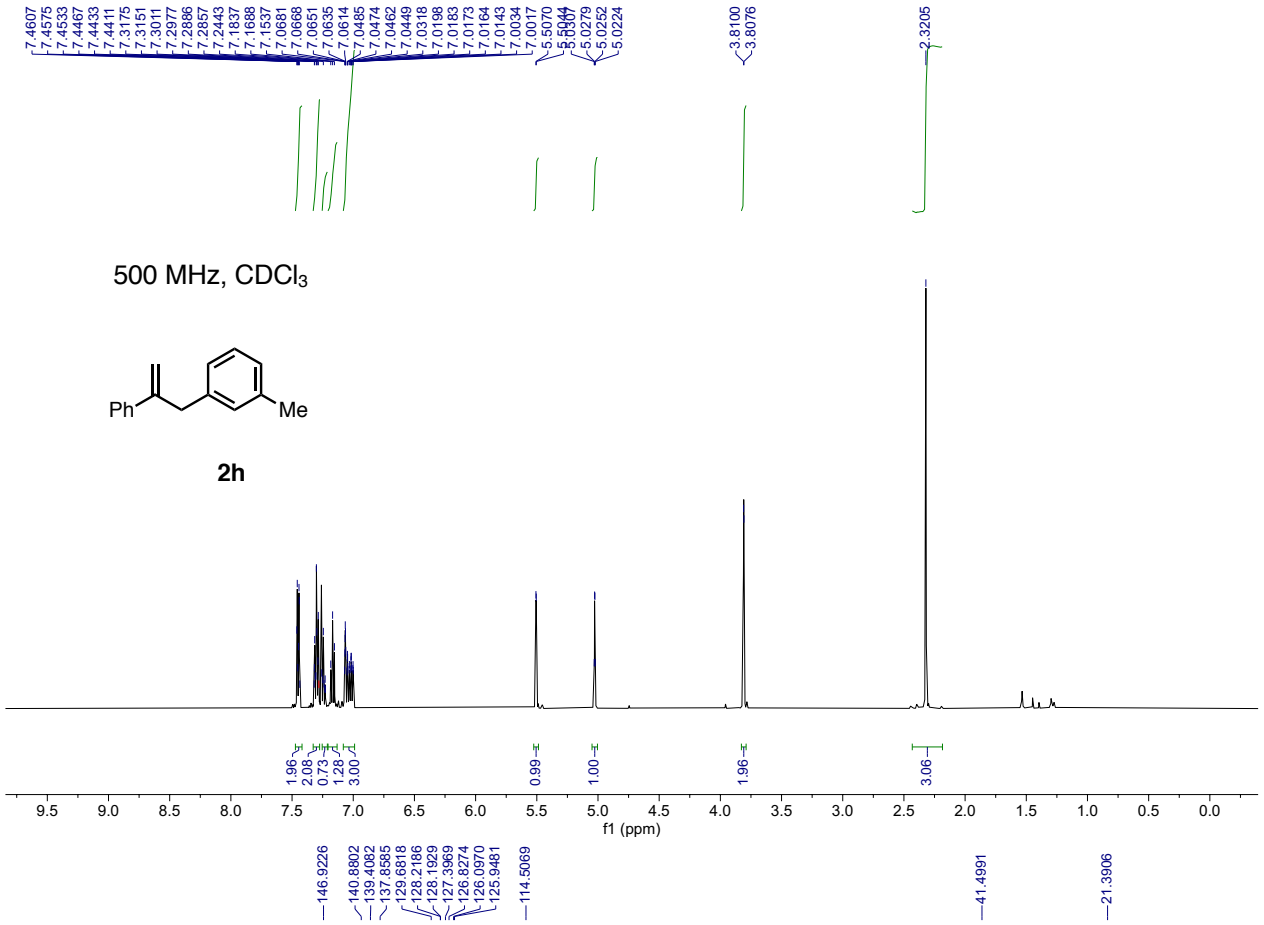
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5.0252
5.0224
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2.3205
500 MHz, CDCl3
Ph
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2h
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0.73
1.28
3.00
0.99
1.00
1.96
3.06
f1 (ppm)
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139.4082
137.8585
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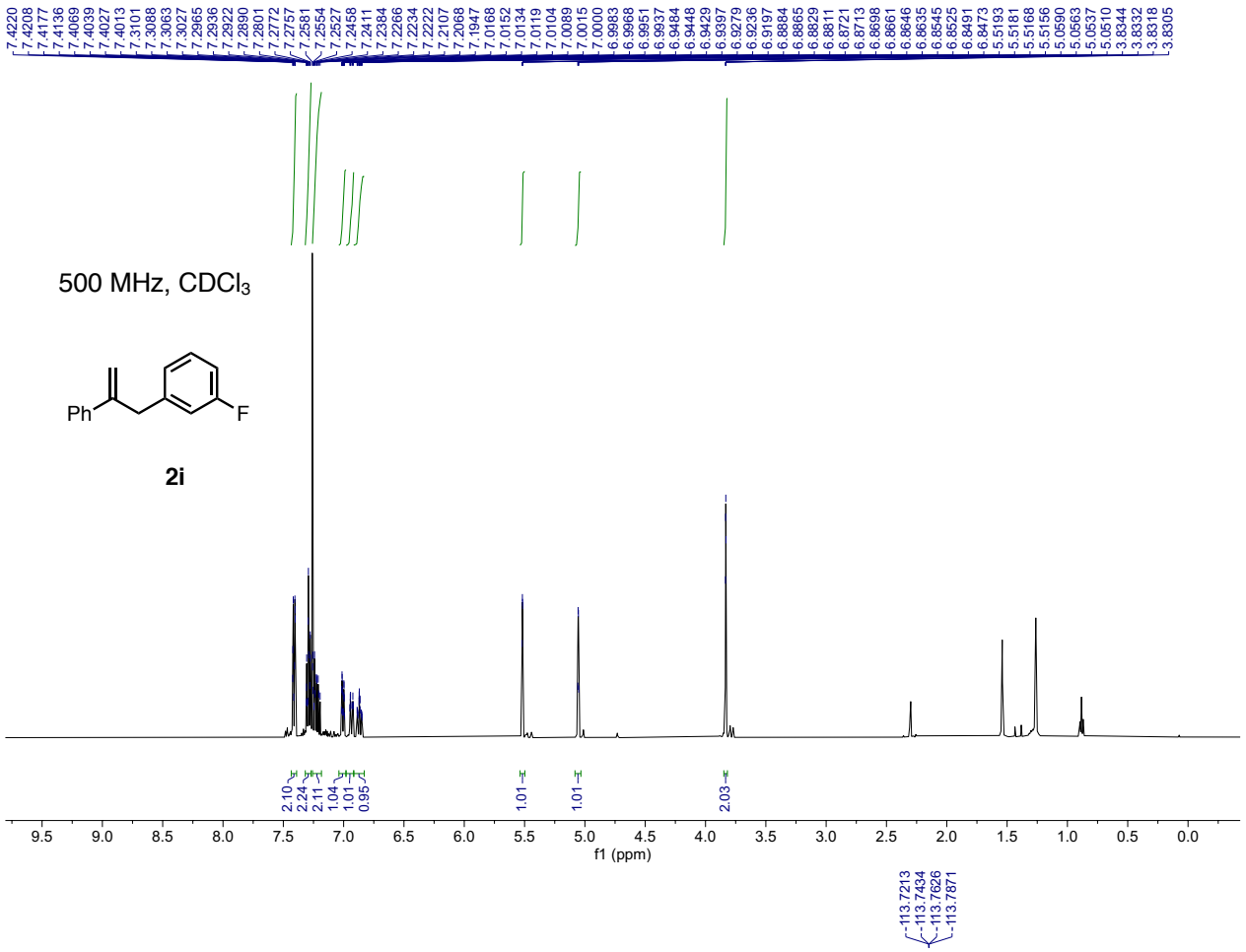
125 MHz, CDCl3
Ph
Me
2h
f1 (ppm)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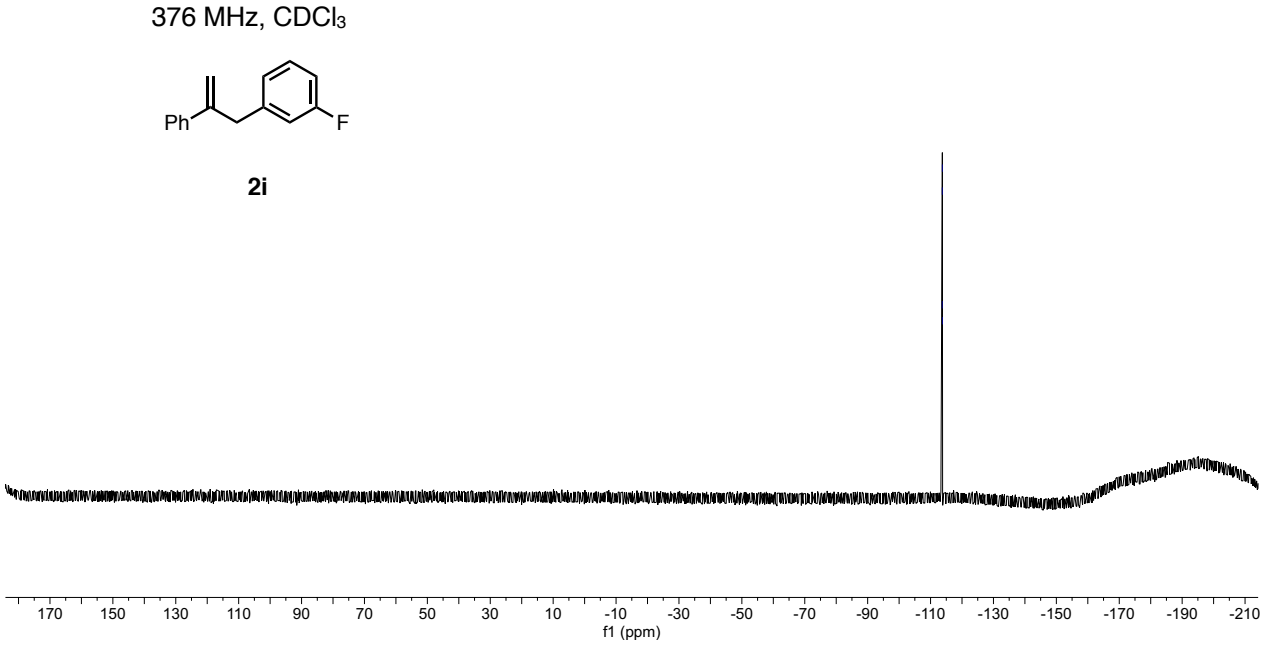
Ph
F
2i
f1 (ppm)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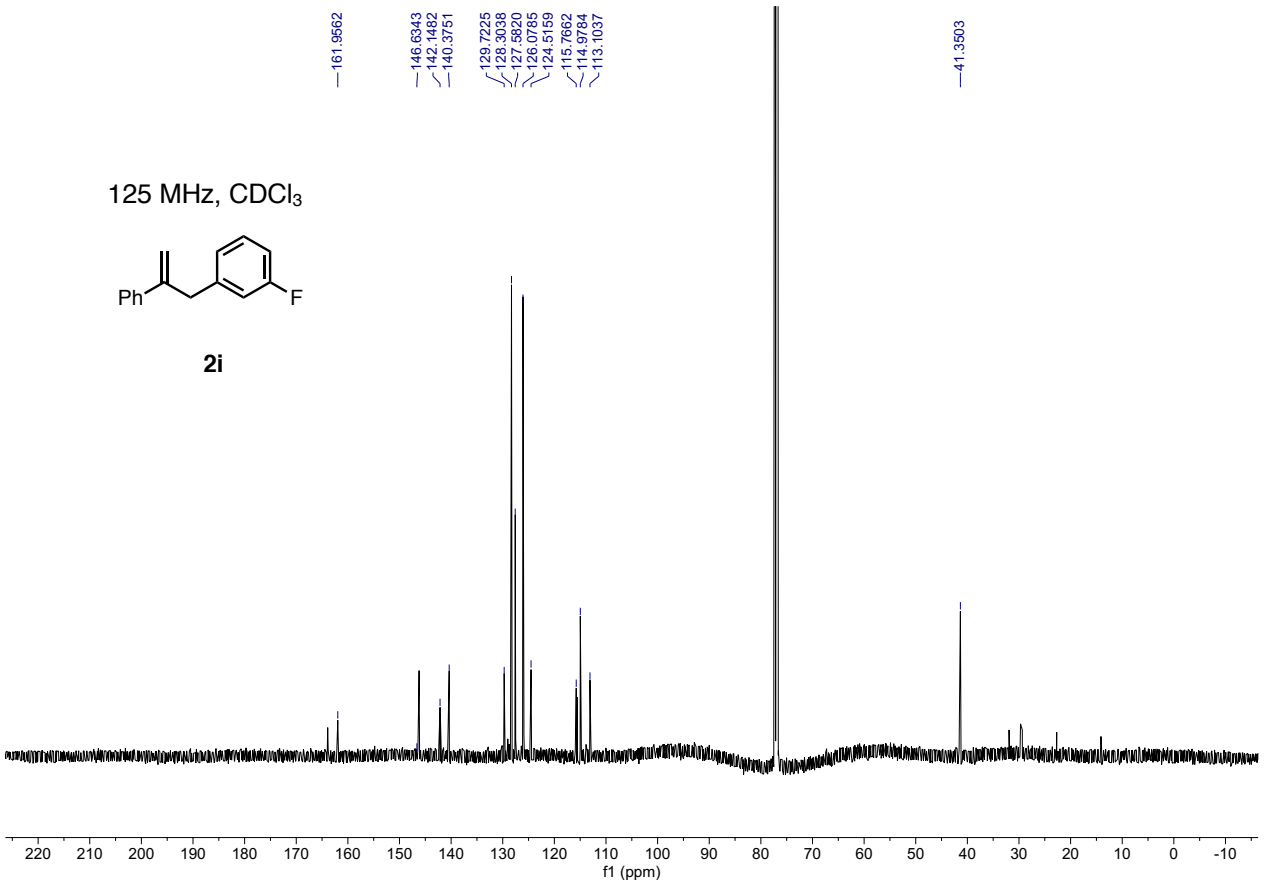
Ph
F
2i
f1 (ppm)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125 MHz, CDCl3
Ph
F
2i
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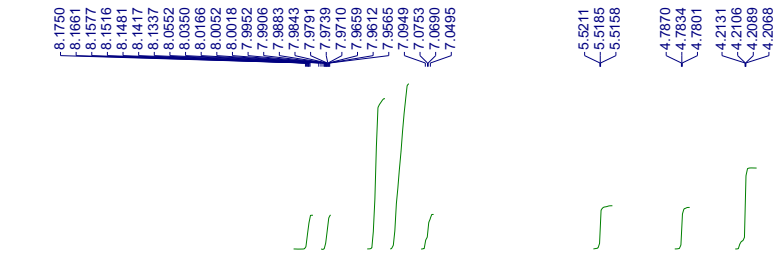
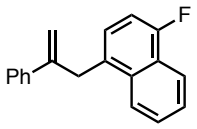
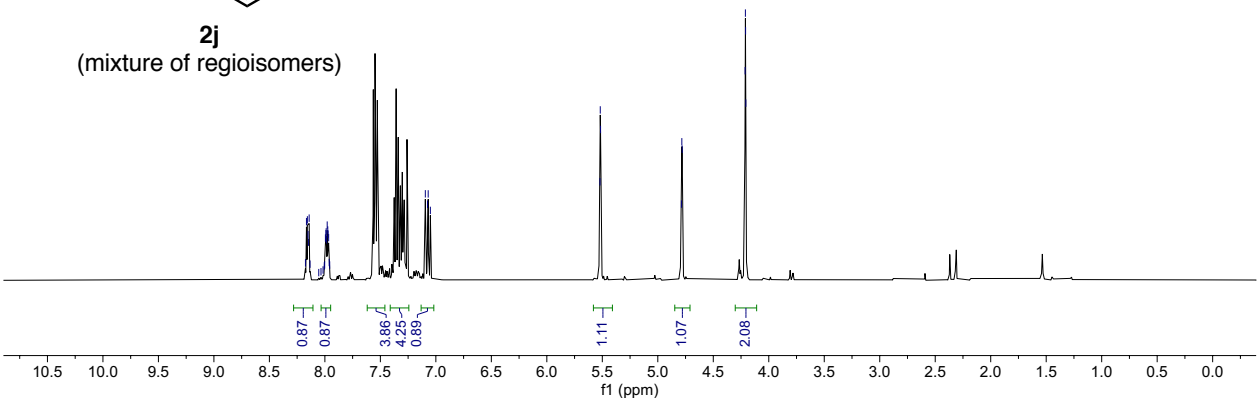
f1 (ppm)



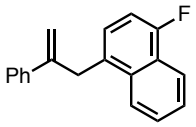
400 MHz, $CDCl_3$



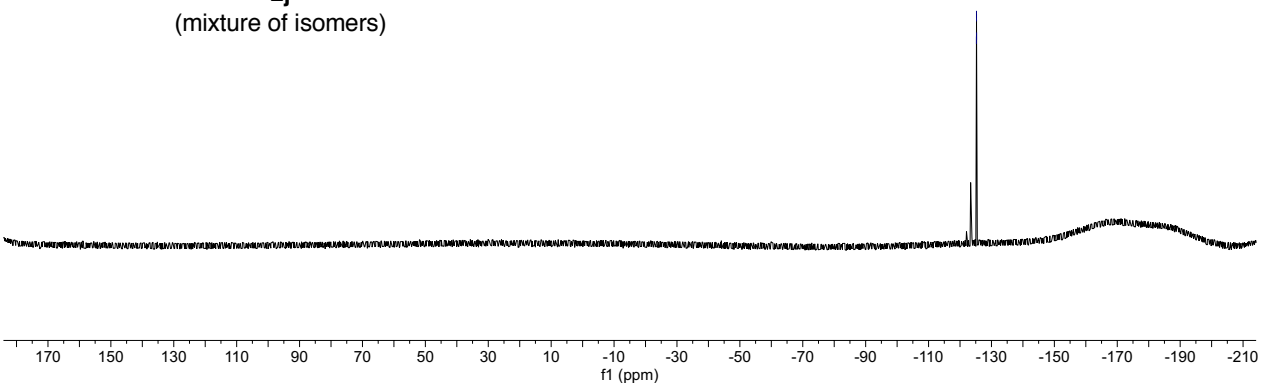
2j
(mixture of regioisomers)

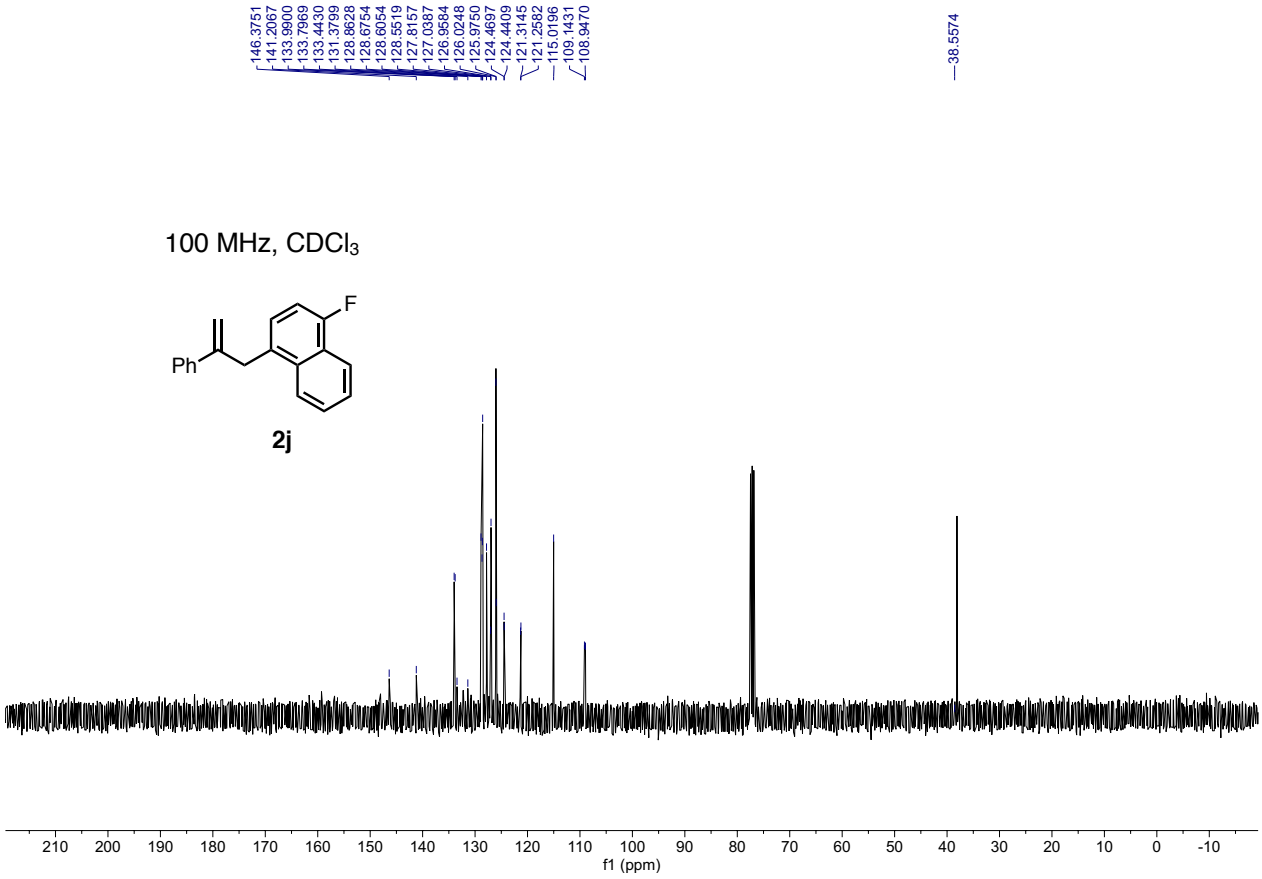


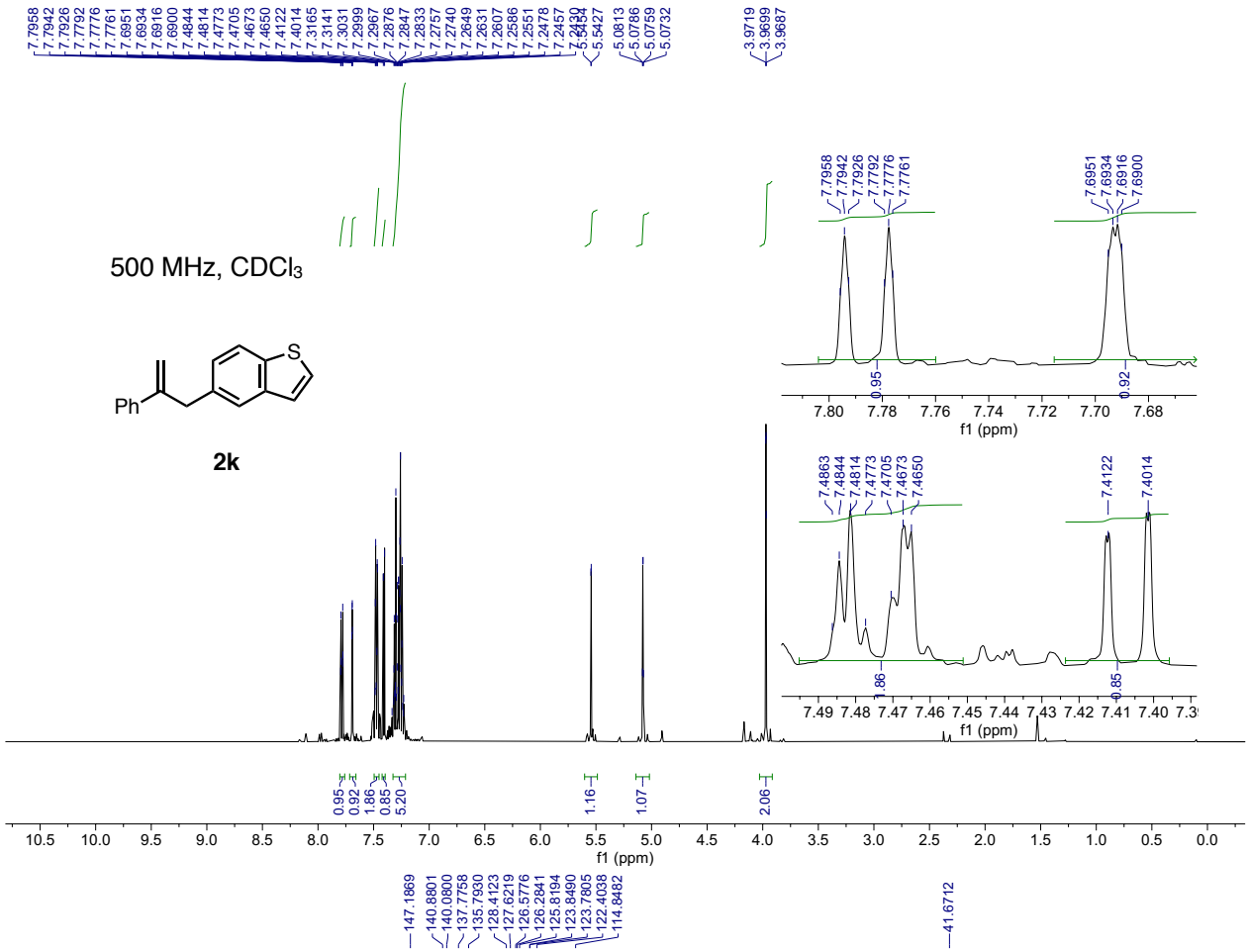
376 MHz, $CDCl_3$

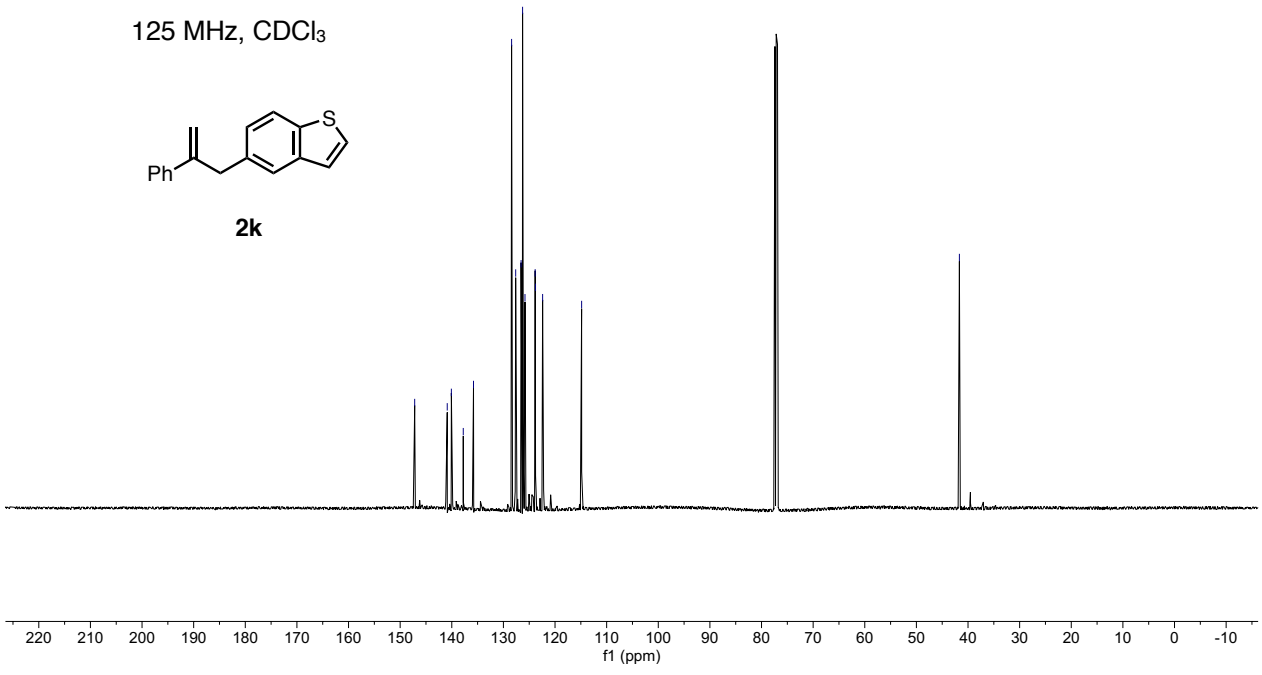


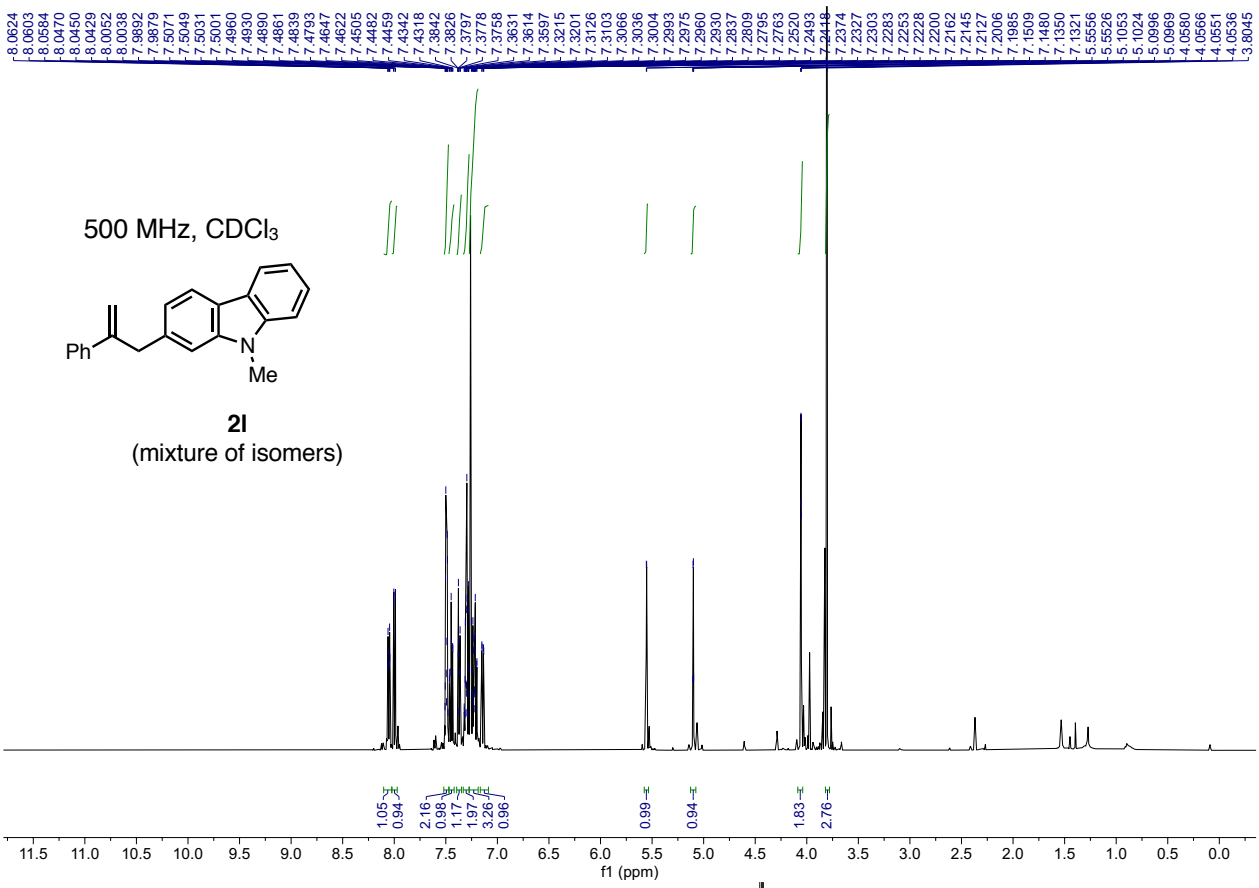
2j
(mixture of isomers)

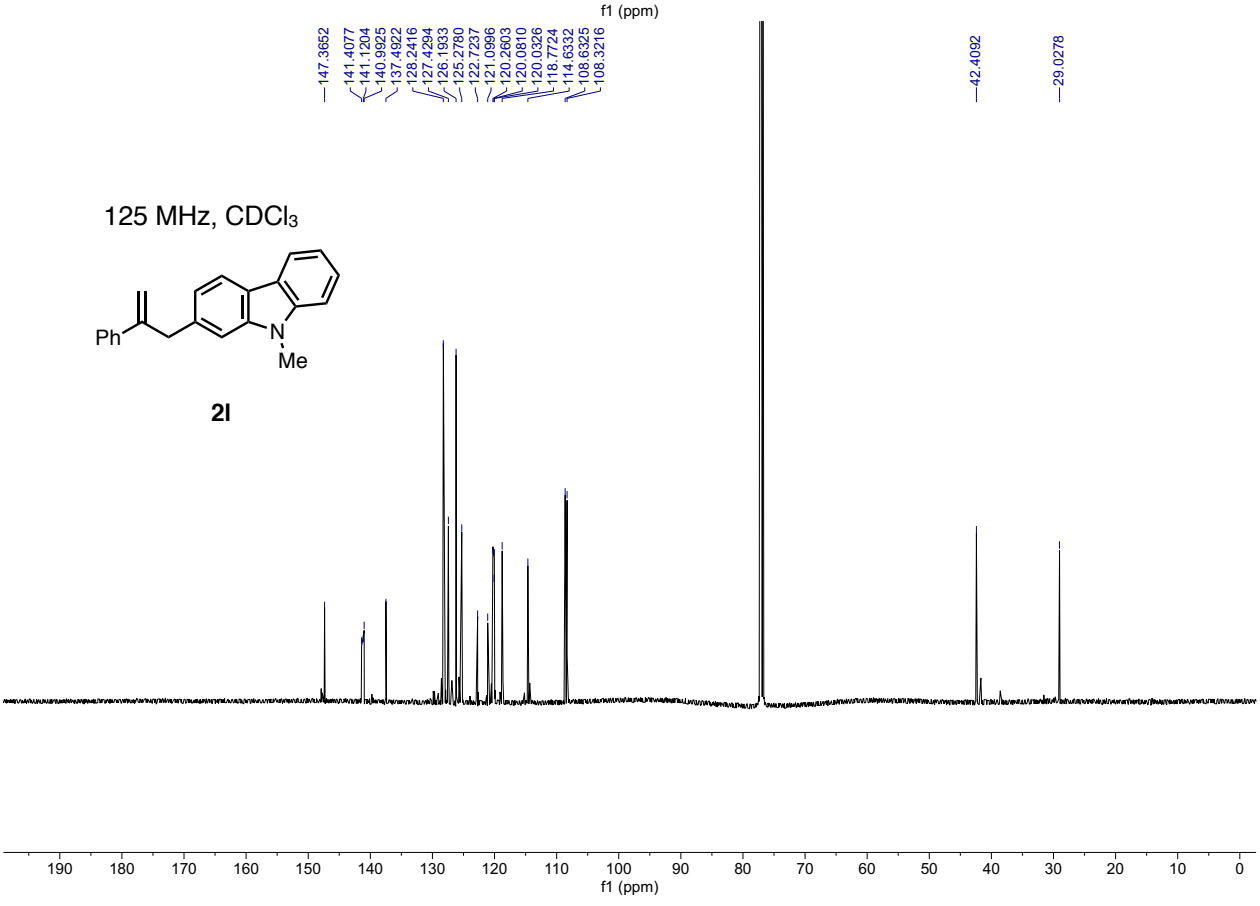


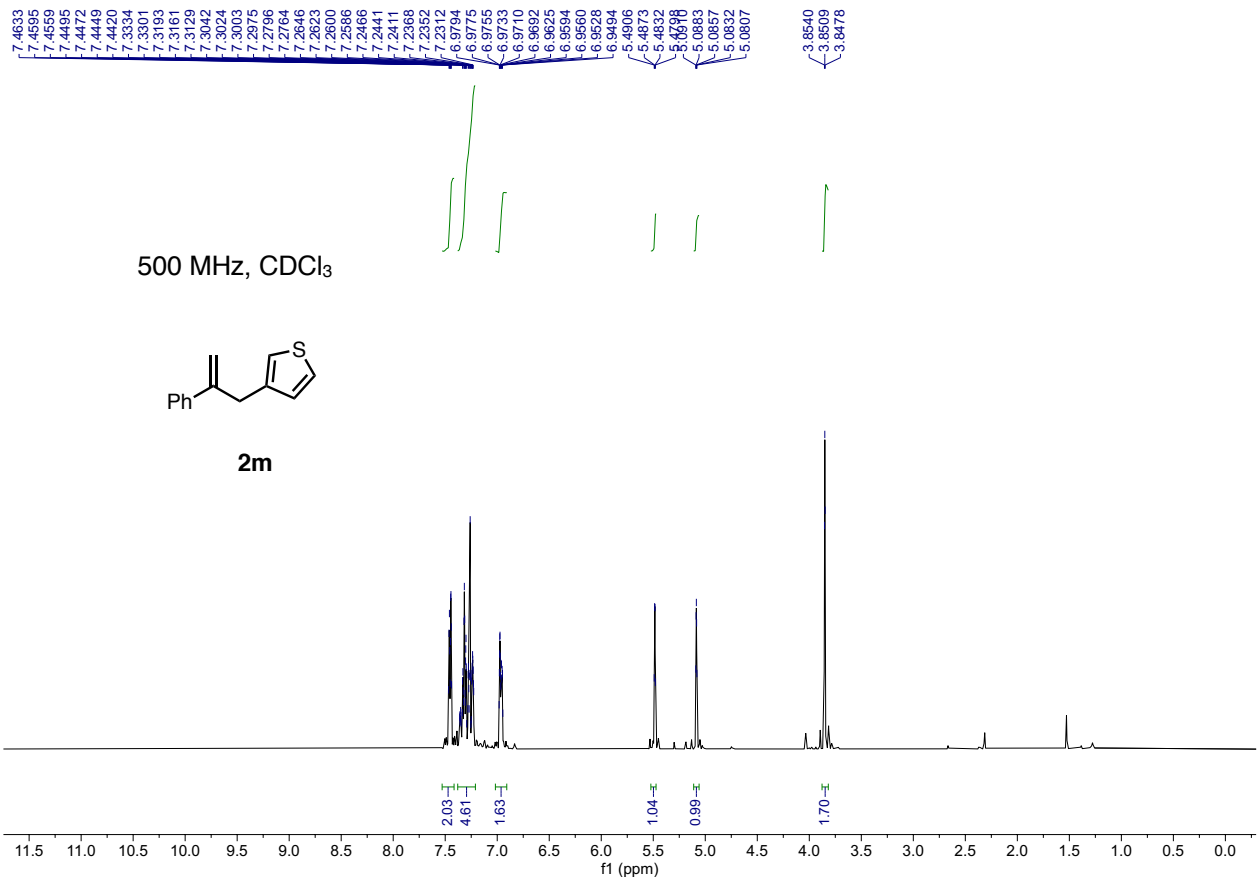

146.3751
141.2067
133.9900
133.7969
133.4430
131.3799
128.8628
128.6754
128.6054
128.5519
127.8157
127.0387
126.9584
126.0248
125.9750
124.4697
124.4409
121.3145
121.2582
115.0196
109.1431
108.9470
38.5574
100 MHz, CDCl3
F
Ph
2j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

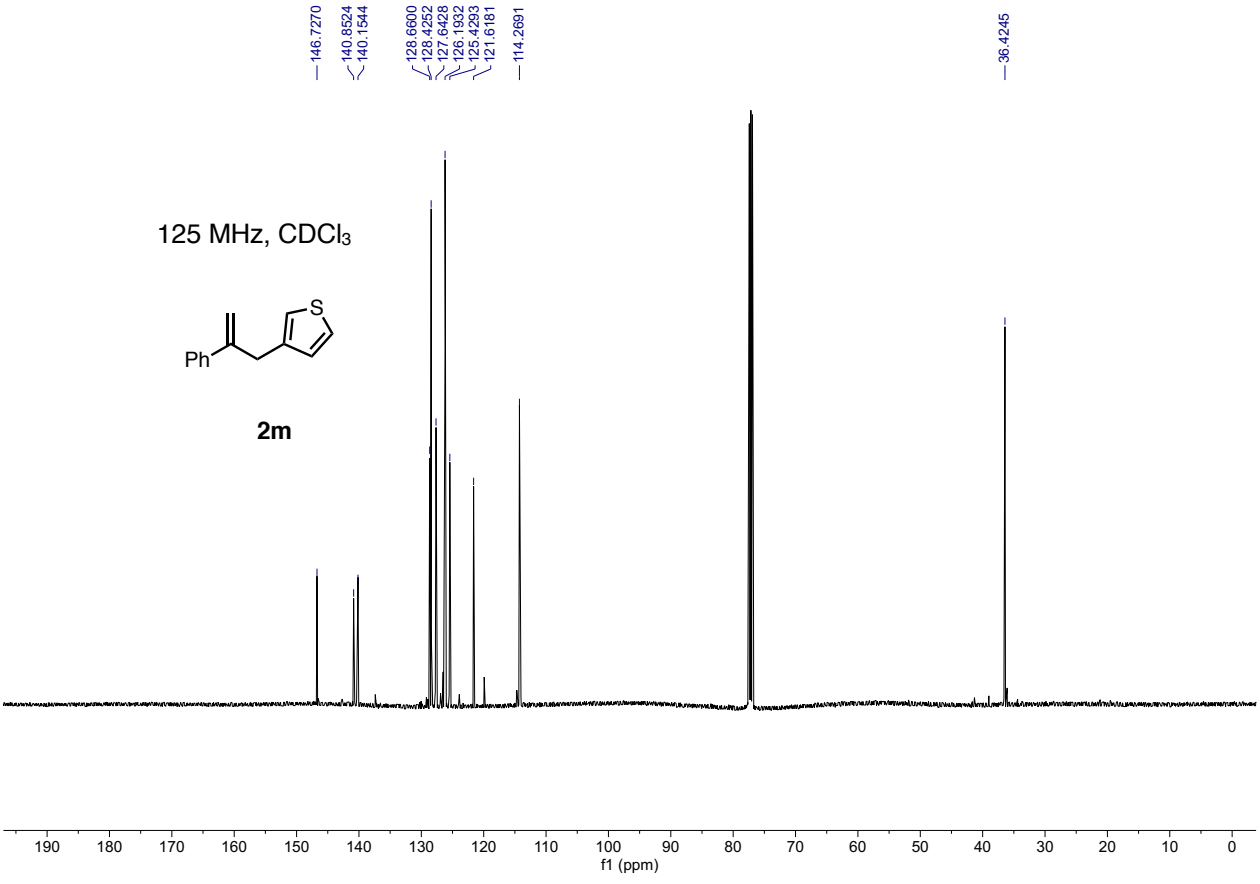

500 MHz, CDCl3
Ph
S
2k
f1 (ppm)

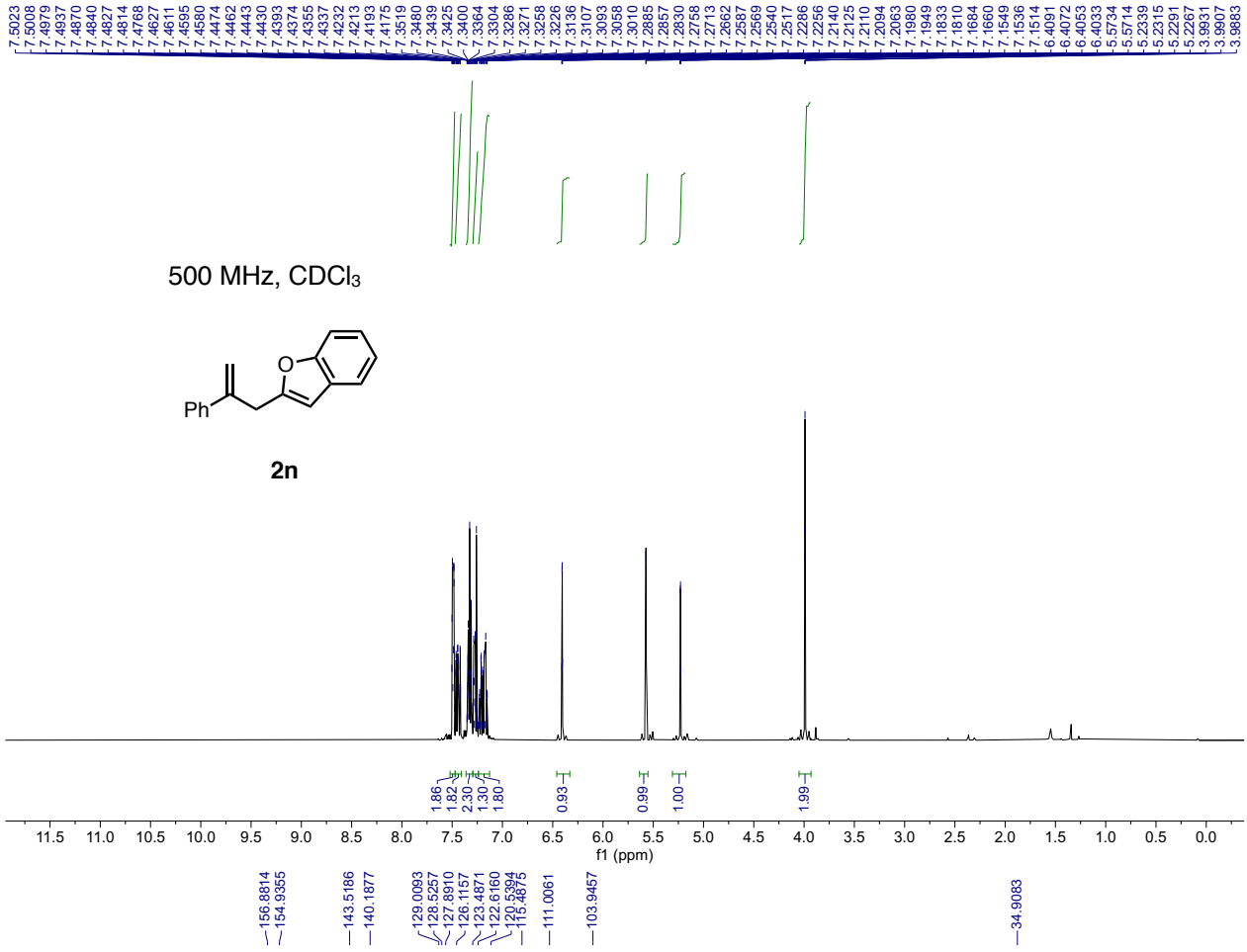

125 MHz, CDCl3
Ph
S
2k
f1 (ppm)

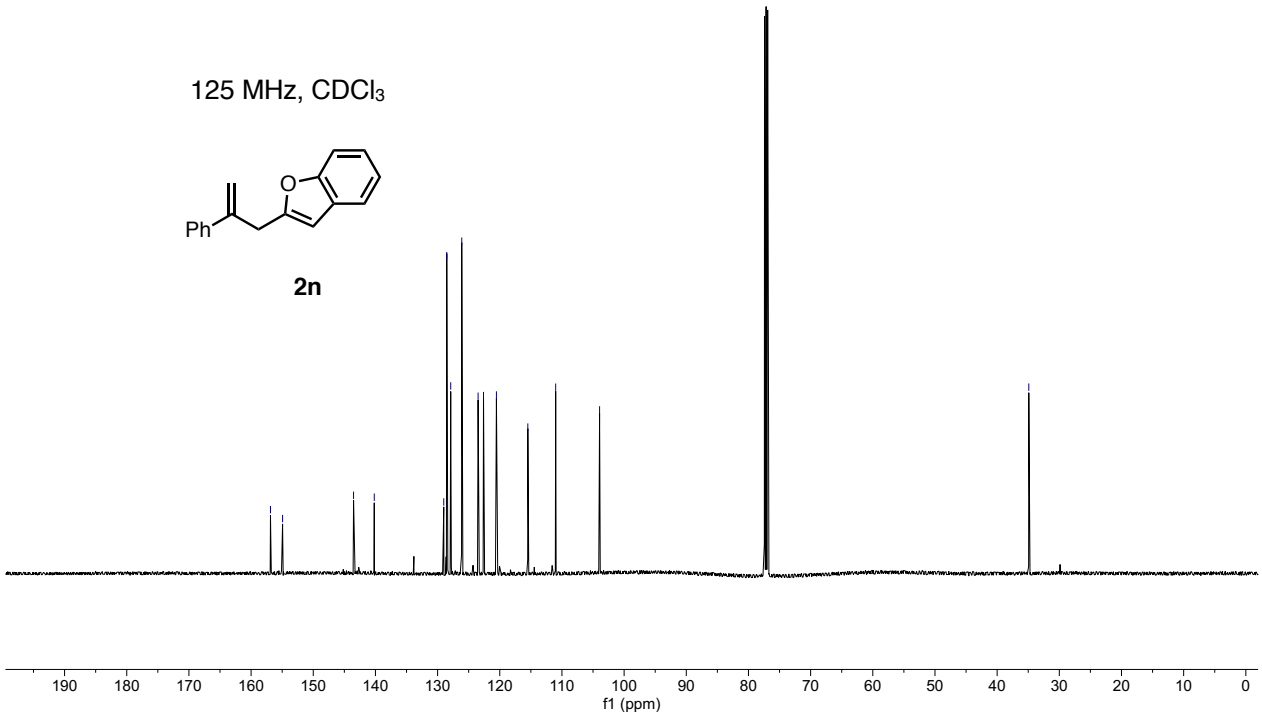

500 MHz, CDCl3
Ph
N
Me
2l
(mixture of isomers)
f1 (ppm)

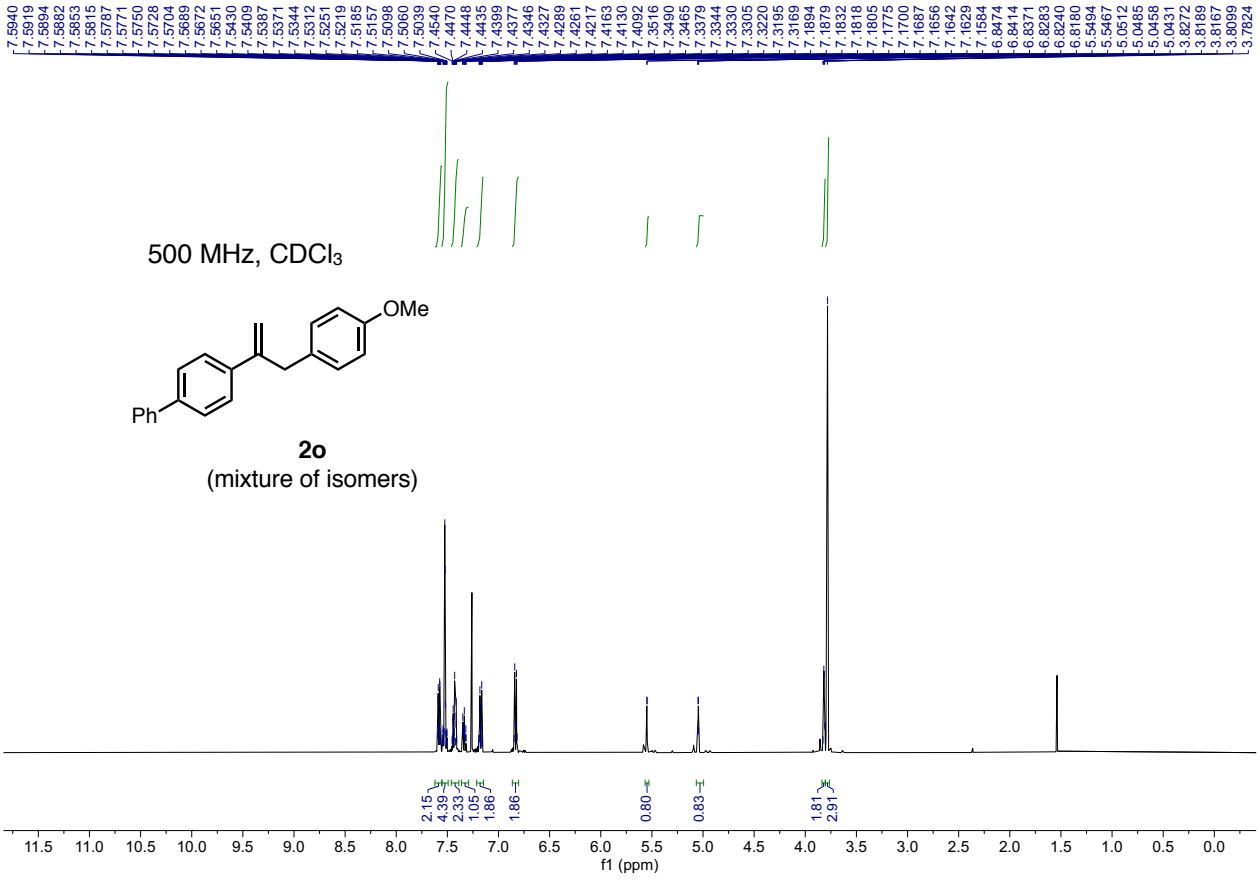

125 MHz, CDCl3
Ph
N
Me
2l
f1 (ppm)

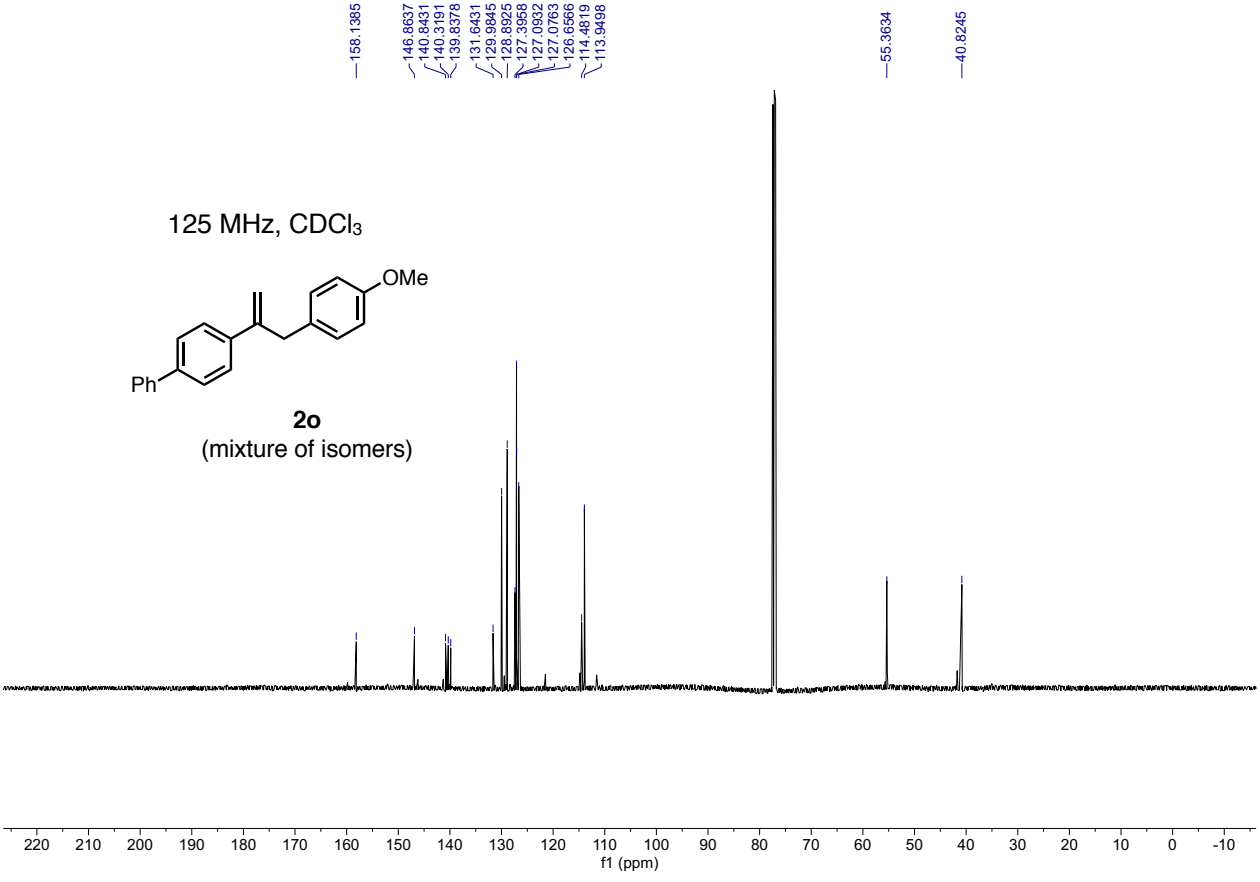

7.4633
7.4595
7.4559
7.4495
7.4472
7.4449
7.4420
7.3334
7.3301
7.3193
7.3161
7.3129
7.3042
7.3024
7.3003
7.2975
7.2796
7.2764
7.2646
7.2623
7.2600
7.2586
7.2466
7.2441
7.2411
7.2368
7.2352
7.2312
6.9794
6.9775
6.9755
6.9733
6.9710
6.9692
6.9625
6.9594
6.9560
6.9528
6.9494
5.4906
5.4873
5.4832
5.0883
5.0857
5.0832
5.0807
3.8540
3.8509
3.8478
500 MHz, CDCl3
S
Ph
2m
2.03
4.61
1.63
1.04
0.99
1.70
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

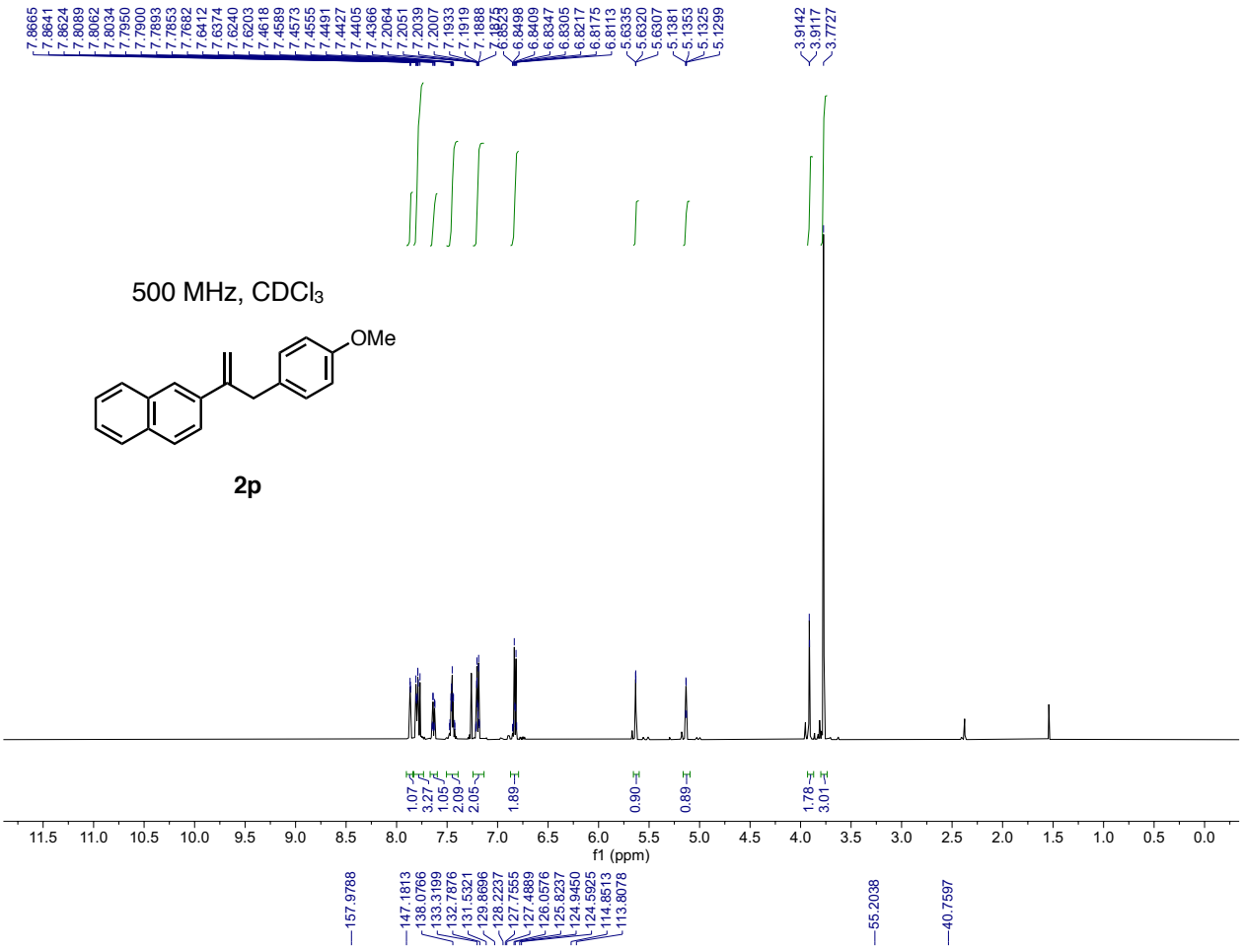

146.7270
140.8524
140.1544
128.6600
128.4252
127.6428
126.1932
125.4293
121.6181
114.2691
36.4245
125 MHz, CDCl3
S
Ph
2m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

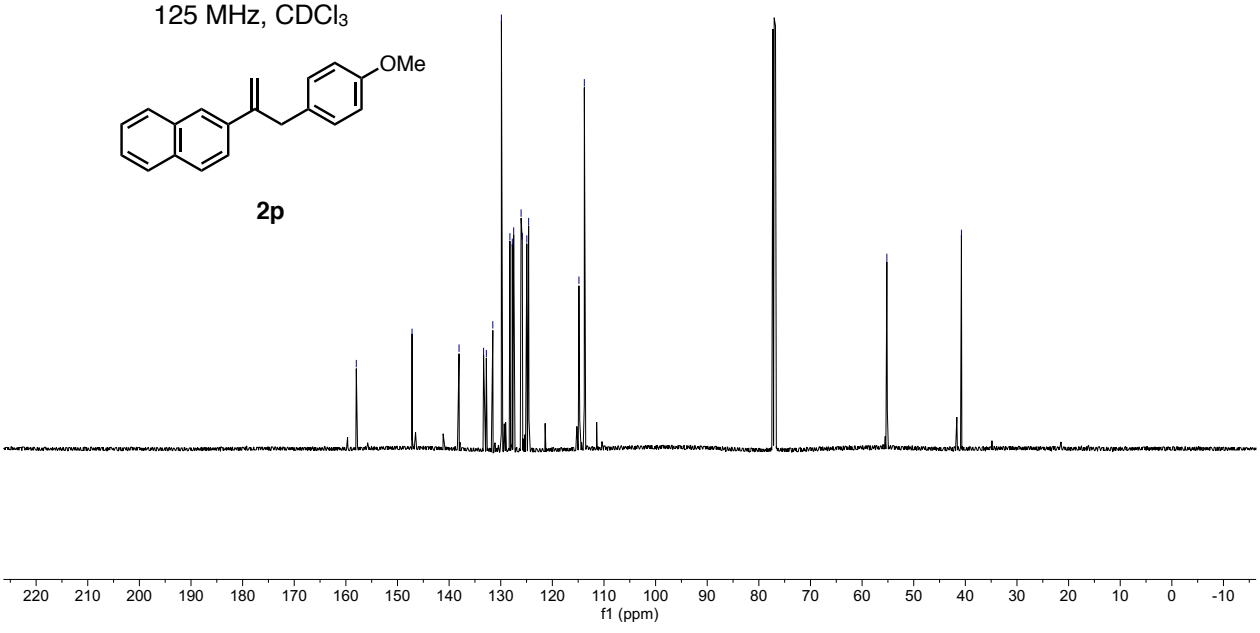

500 MHz, CDCl3
Ph
O
2n
f1 (ppm)

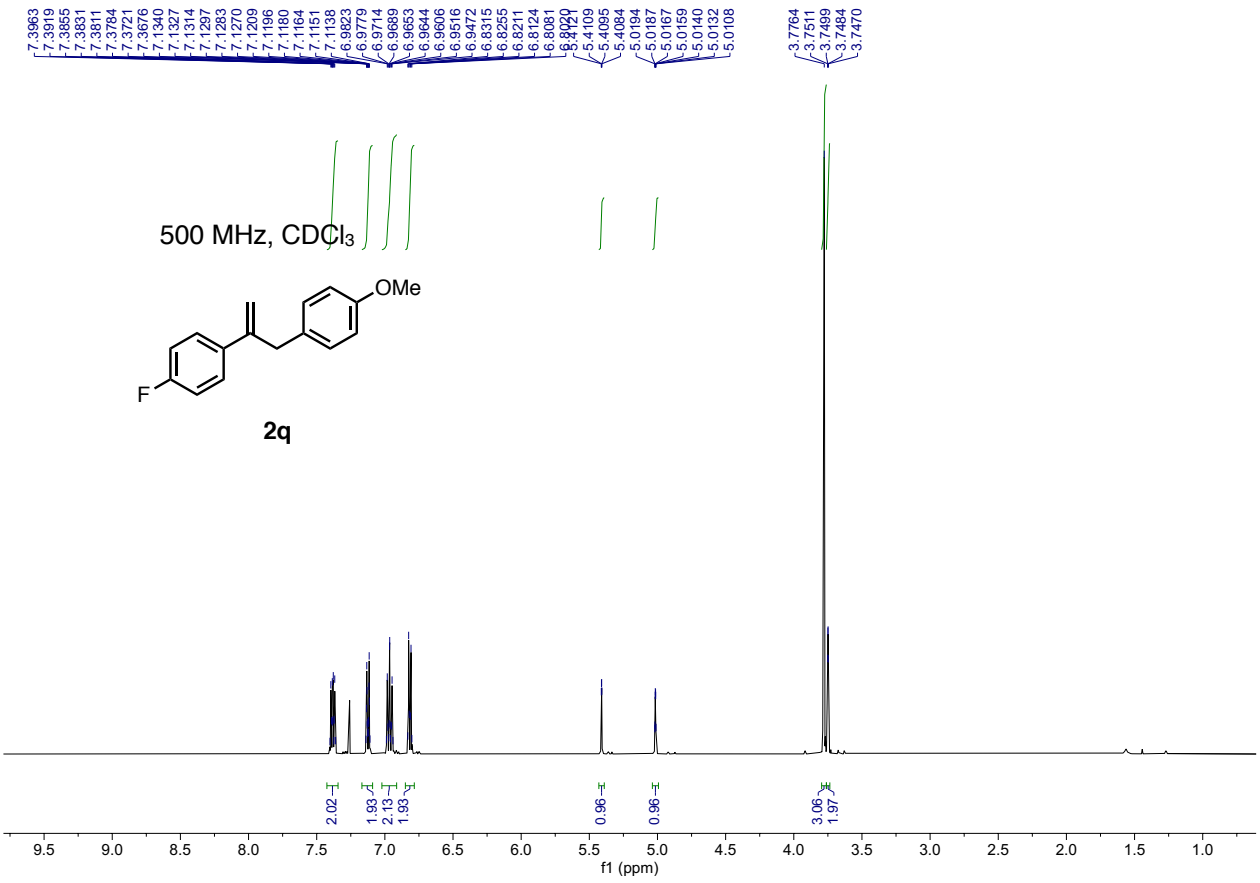

125 MHz, CDCl3
Ph
O
2n
f1 (ppm)

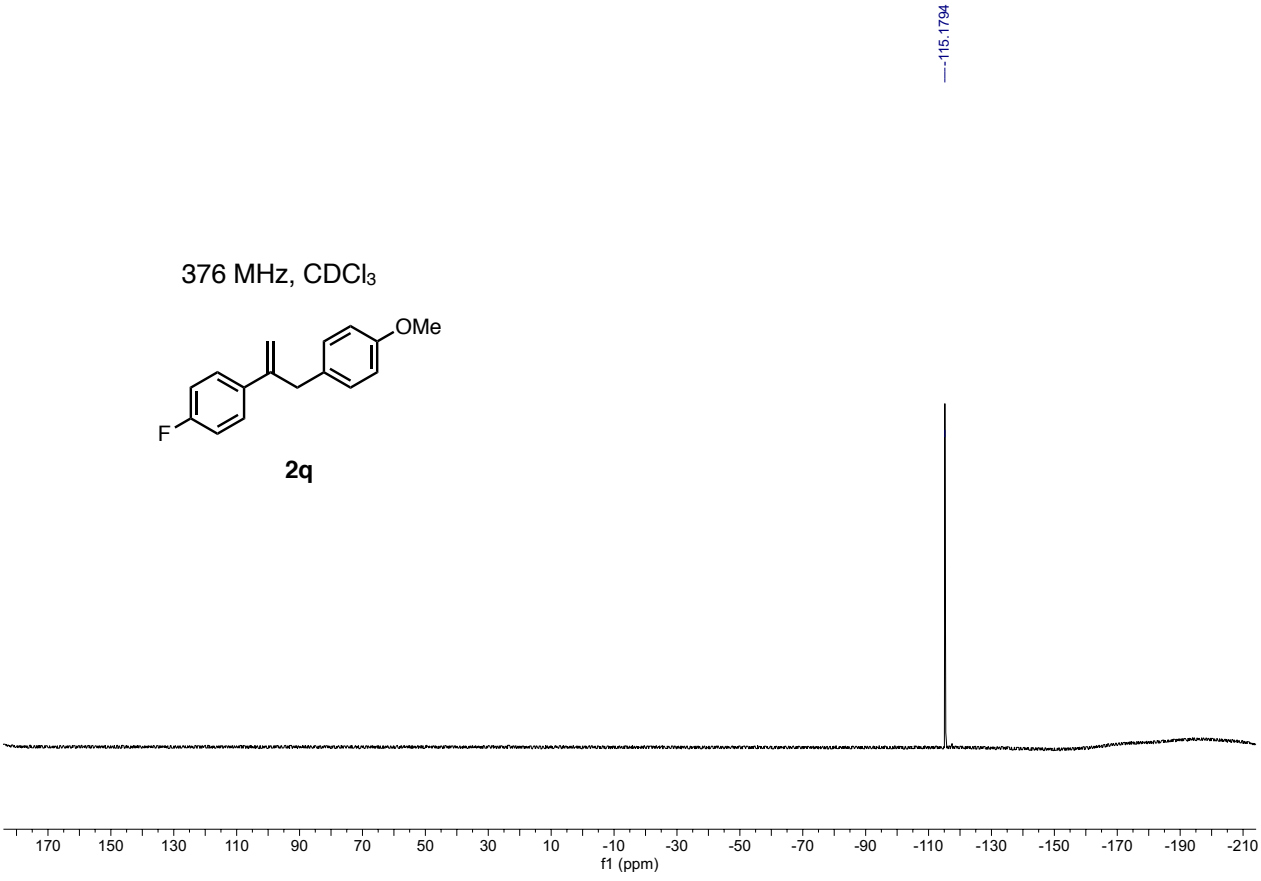

500 MHz, CDCl3
OMe
Ph
2o
(mixture of isomers)
f1 (ppm)

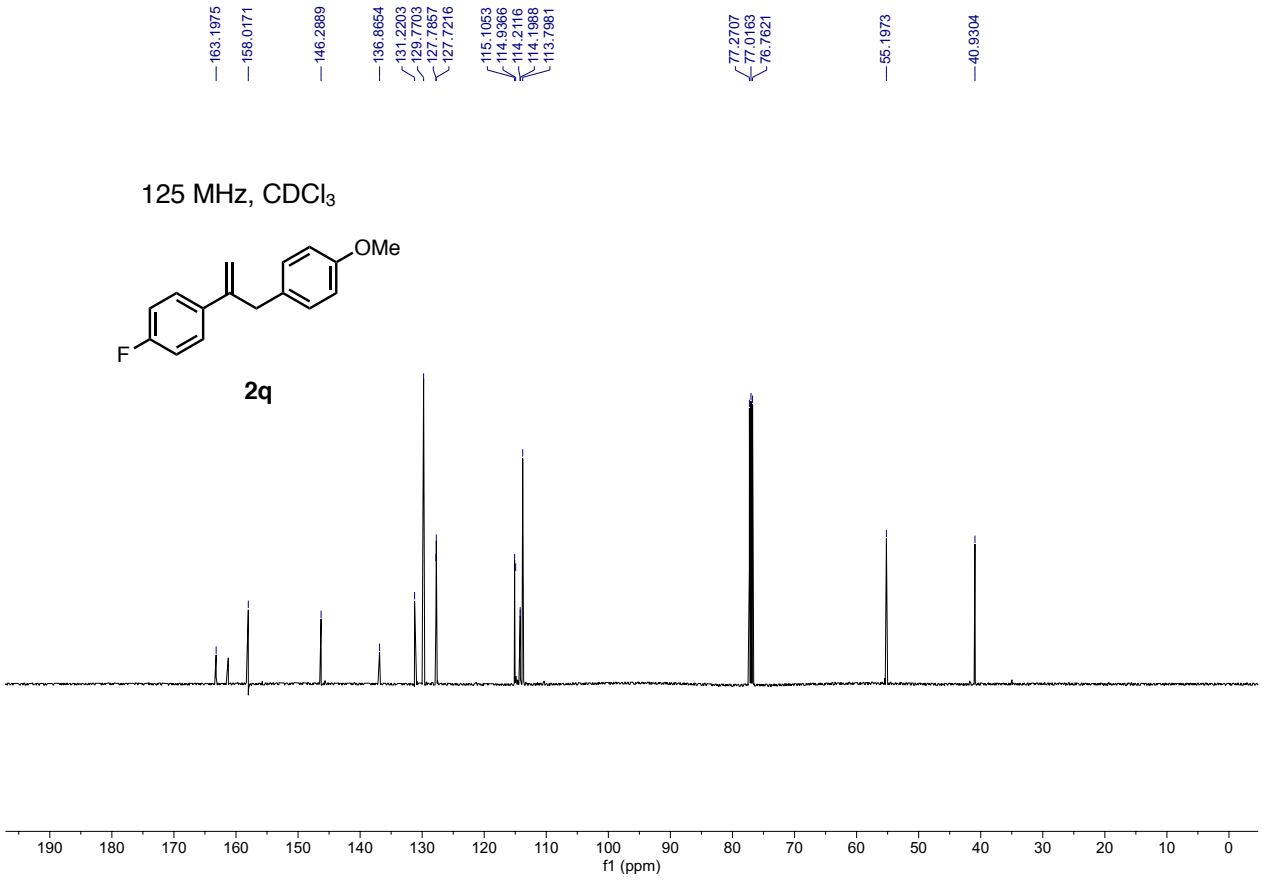

125 MHz, CDCl3
OMe
Ph
2o
(mixture of isomers)
f1 (ppm)

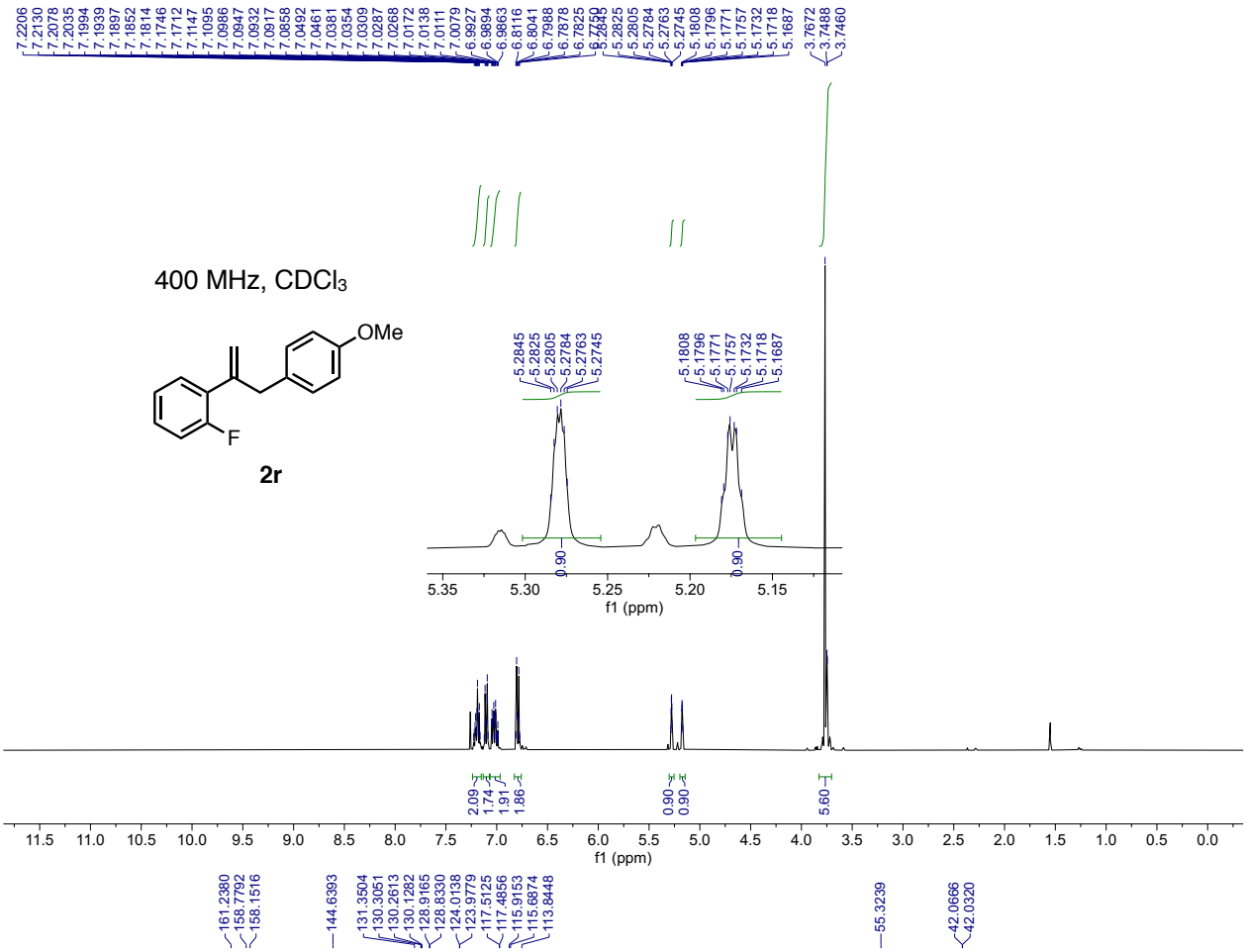

7.8665
7.8641
7.8624
7.8089
7.8062
7.8034
7.7950
7.7900
7.7893
7.7853
7.7682
7.6412
7.6374
7.6240
7.6203
7.4618
7.4589
7.4573
7.4555
7.4491
7.4427
7.4405
7.4366
7.2064
7.2051
7.2039
7.2007
7.1933
7.1919
7.1888
6.8498
6.8409
6.8347
6.8305
6.8217
6.8175
6.8113
5.6335
5.6320
5.6307
5.1381
5.1353
5.1325
5.1299
3.9142
3.9117
3.7727
500 MHz, CDCl3
OMe
2p
1.07
3.27
1.05
2.09
2.05
1.89
0.90
0.89
1.78
3.01
f1 (ppm)
157.9788
147.1813
138.0766
133.3199
132.7876
131.5321
129.8696
128.2237
127.7555
127.4889
126.0576
125.8237
124.9450
124.5925
114.8513
113.8078
55.2038
40.7597

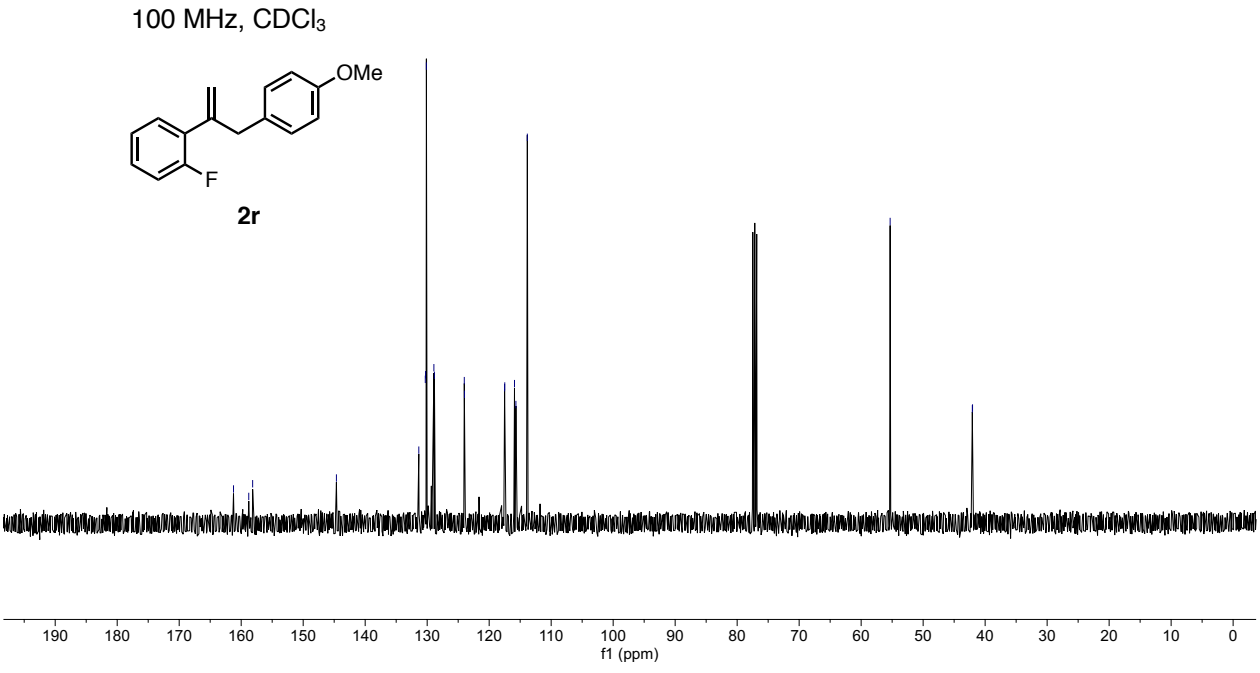

125 MHz, CDCl3
OMe
2p
f1 (ppm)


7.3963
7.3919
7.3855
7.3831
7.3811
7.3784
7.3721
7.3676
7.1340
7.1327
7.1314
7.1297
7.1283
7.1270
7.1209
7.1196
7.1180
7.1164
7.1151
7.1138
6.9823
6.9779
6.9714
6.9689
6.9653
6.9644
6.9606
6.9516
6.9472
6.8315
6.8255
6.8211
6.8124
6.8081
6.8020
6.8021
5.4109
5.4095
5.4084
5.0194
5.0187
5.0167
5.0159
5.0140
5.0132
5.0108
3.7764
3.7511
3.7499
3.7484
3.7470
500 MHz, CDCl3
OMe
F
2q
2.02
1.93
2.13
1.93
0.96
0.96
3.06
1.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

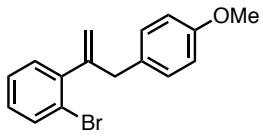

-115.1794
376 MHz, CDCl3
OMe
F
2q
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


163.1975
158.0171
146.2889
136.8654
131.2203
129.7703
127.7857
127.7216
115.1053
114.9366
114.2116
114.1988
113.7981
77.2707
77.0163
76.7621
55.1973
40.9304
125 MHz, CDCl3
OMe
F
2q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


400 MHz, CDCl3
OMe
F
2r
f1 (ppm)

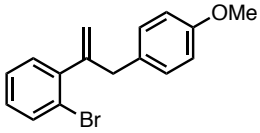

100 MHz, CDCl3
OMe
F
2r
f1 (ppm)

500 MHz, $CDCl_3$

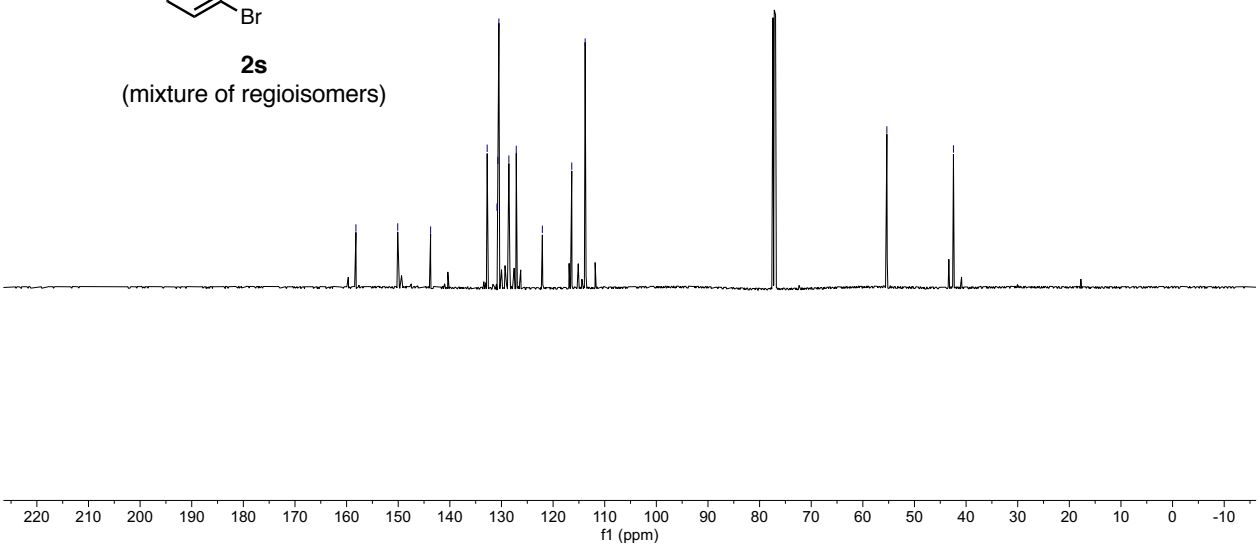


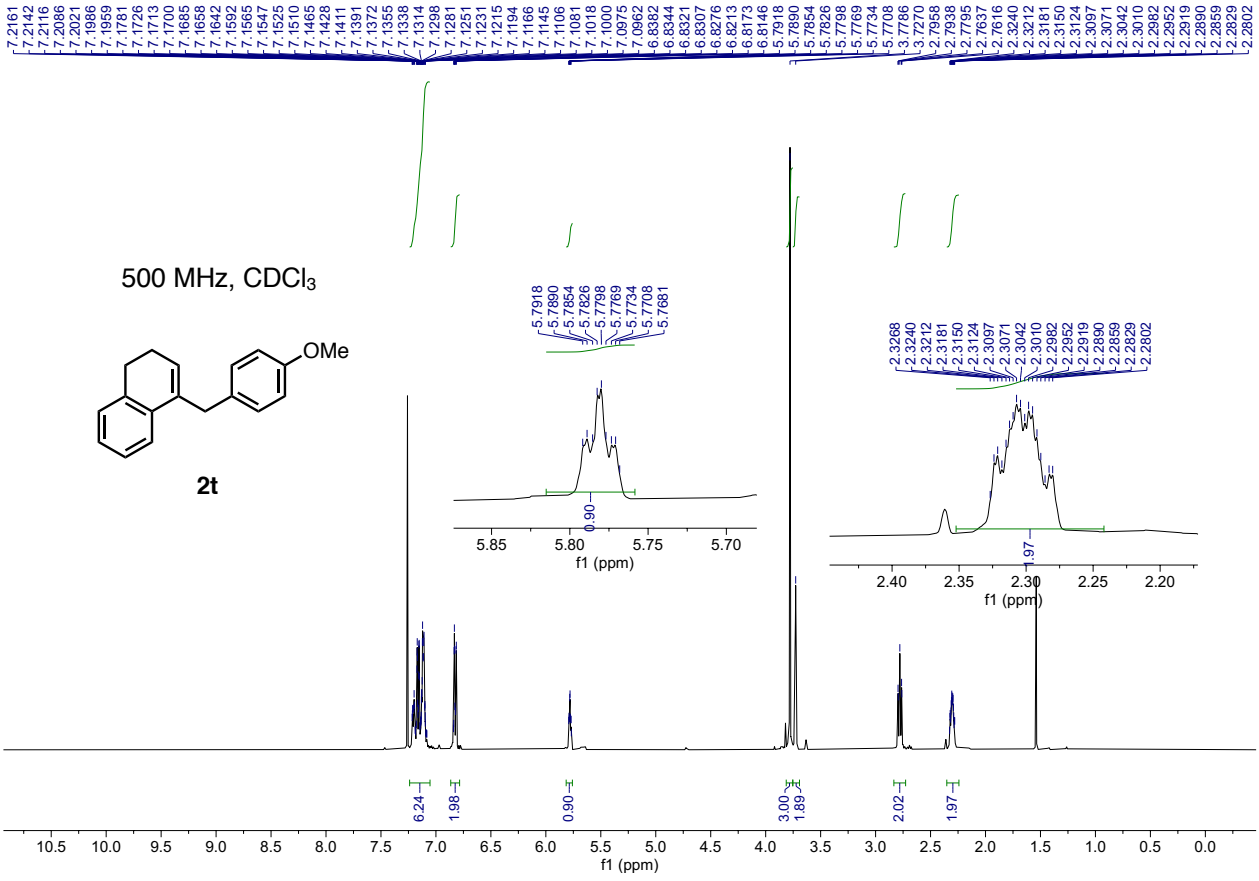
2s
(mixture of regioisomers)

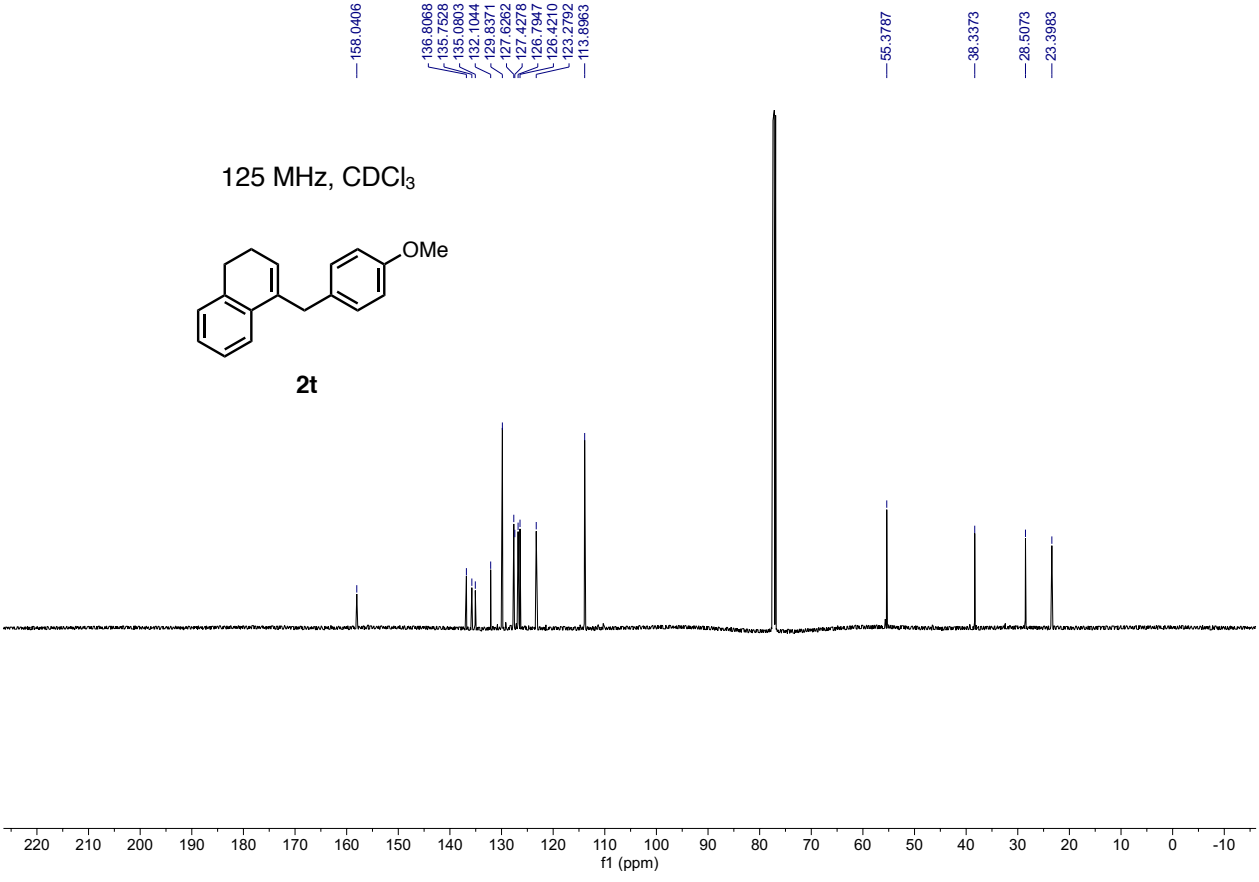
125 MHz, $CDCl_3$

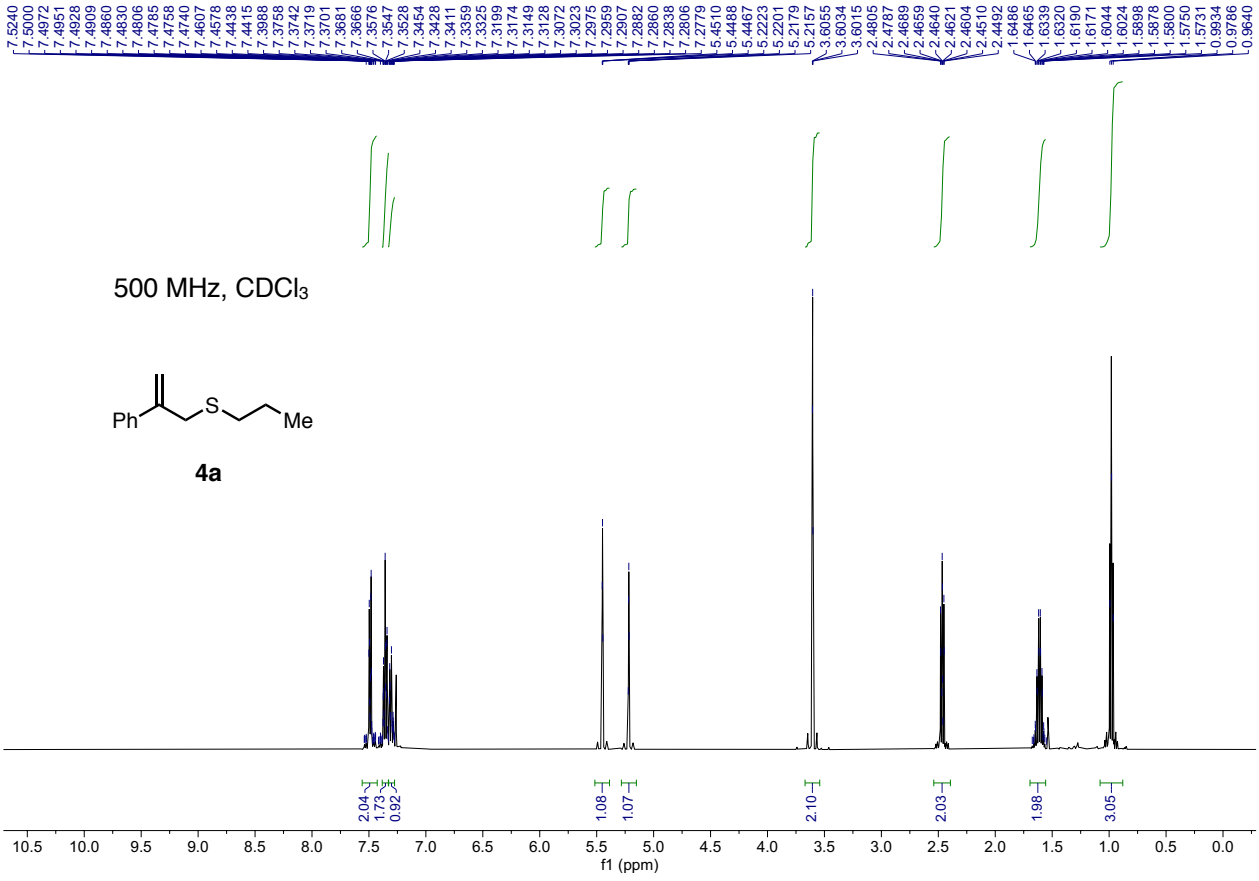


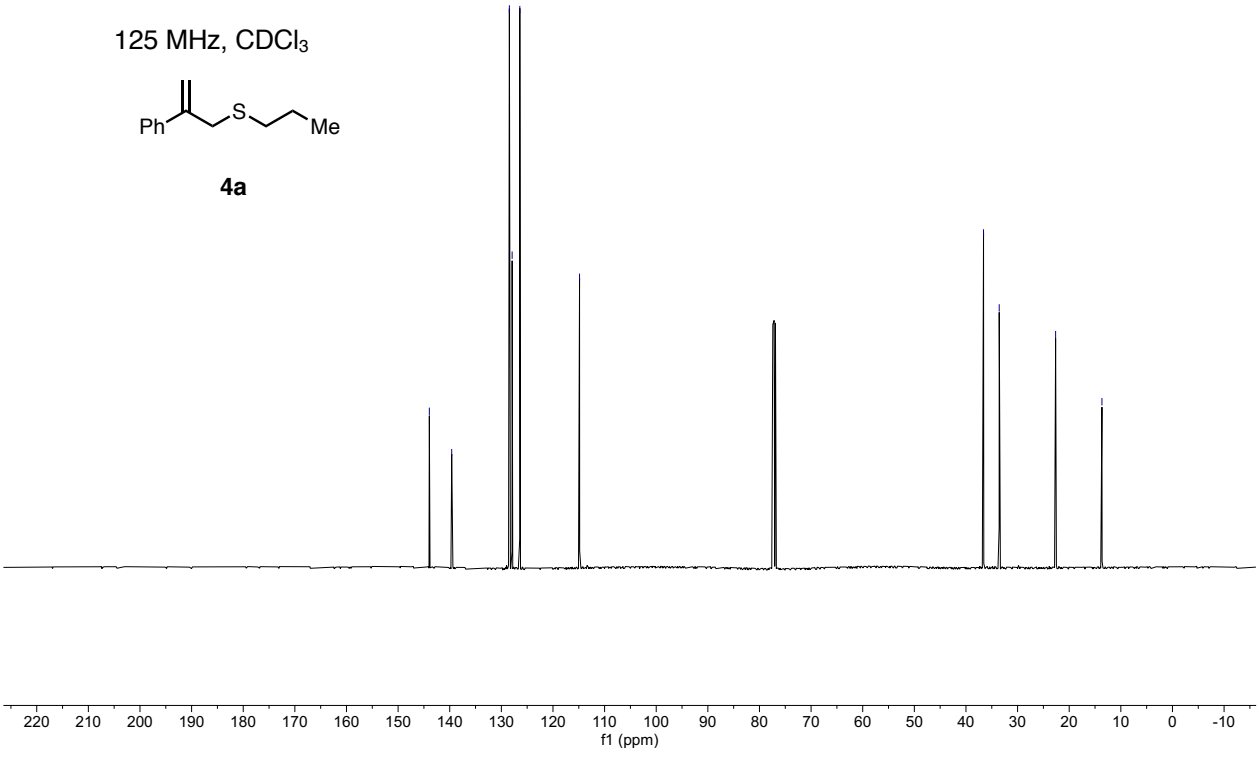
2s
(mixture of regioisomers)

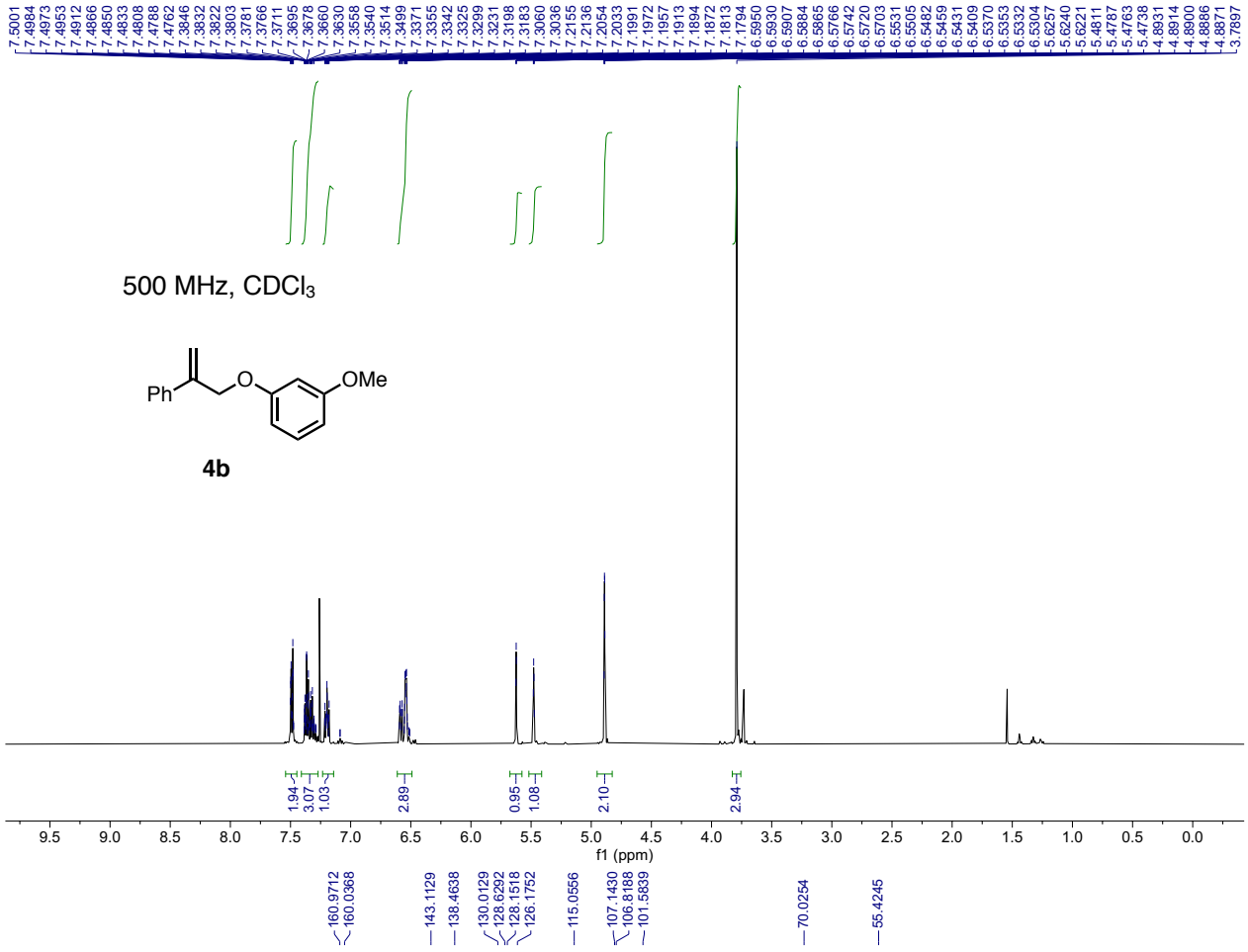


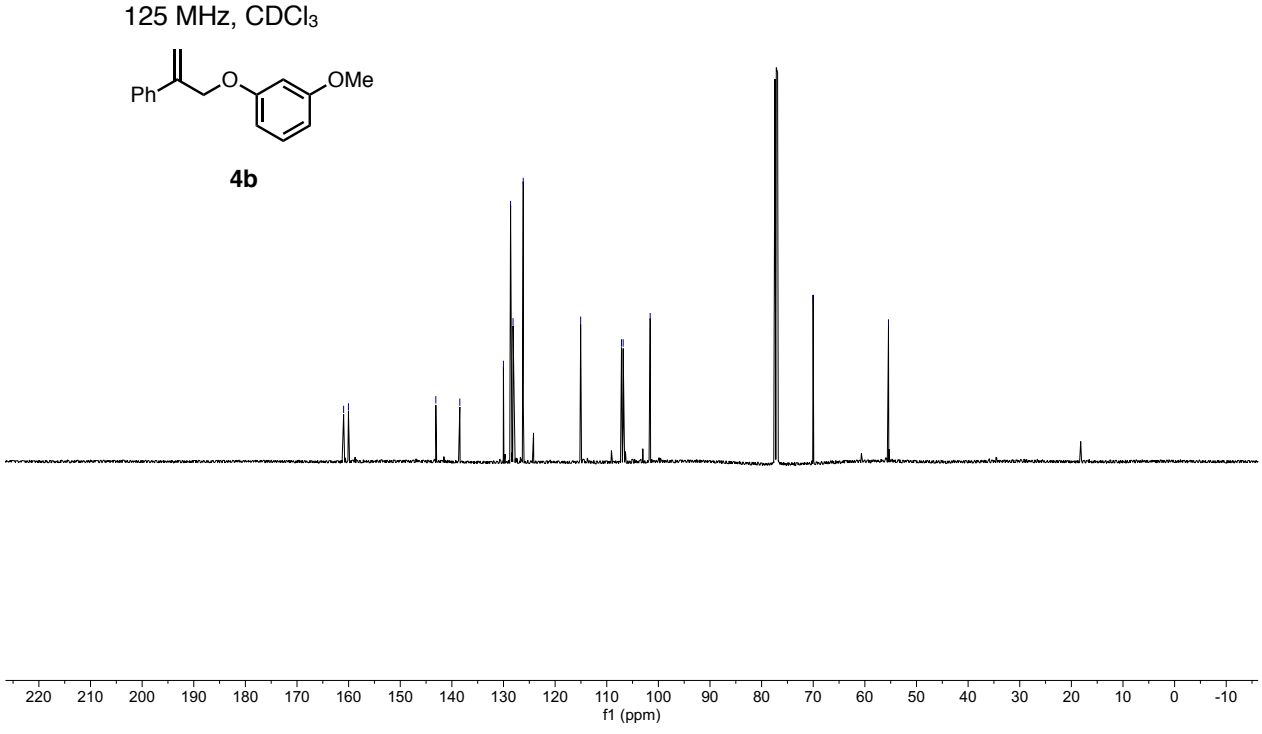

500 MHz, CDCl3
OMe
2t
f1 (ppm)

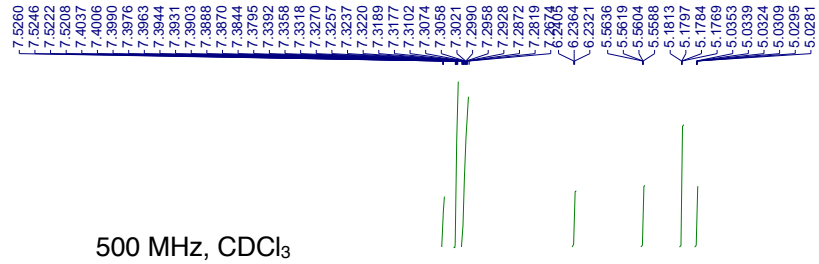

125 MHz, CDCl3
OMe
2t
f1 (ppm)


500 MHz, CDCl3
Ph
S
Me
4a
f1 (ppm)

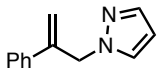

125 MHz, CDCl3
Ph
S
Me
4a
f1 (ppm)


500 MHz, CDCl3
Ph
O
OMe
4b
f1 (ppm)

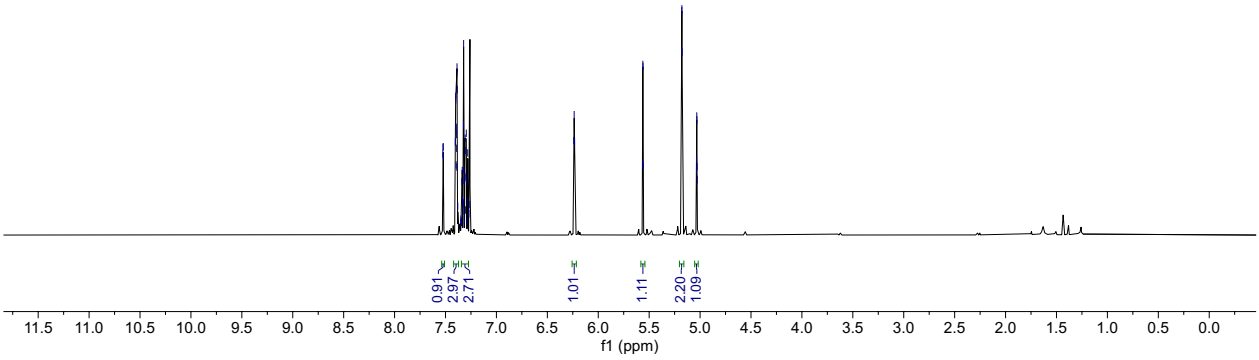

125 MHz, CDCl3
Ph
O
OMe
4b
f1 (ppm)

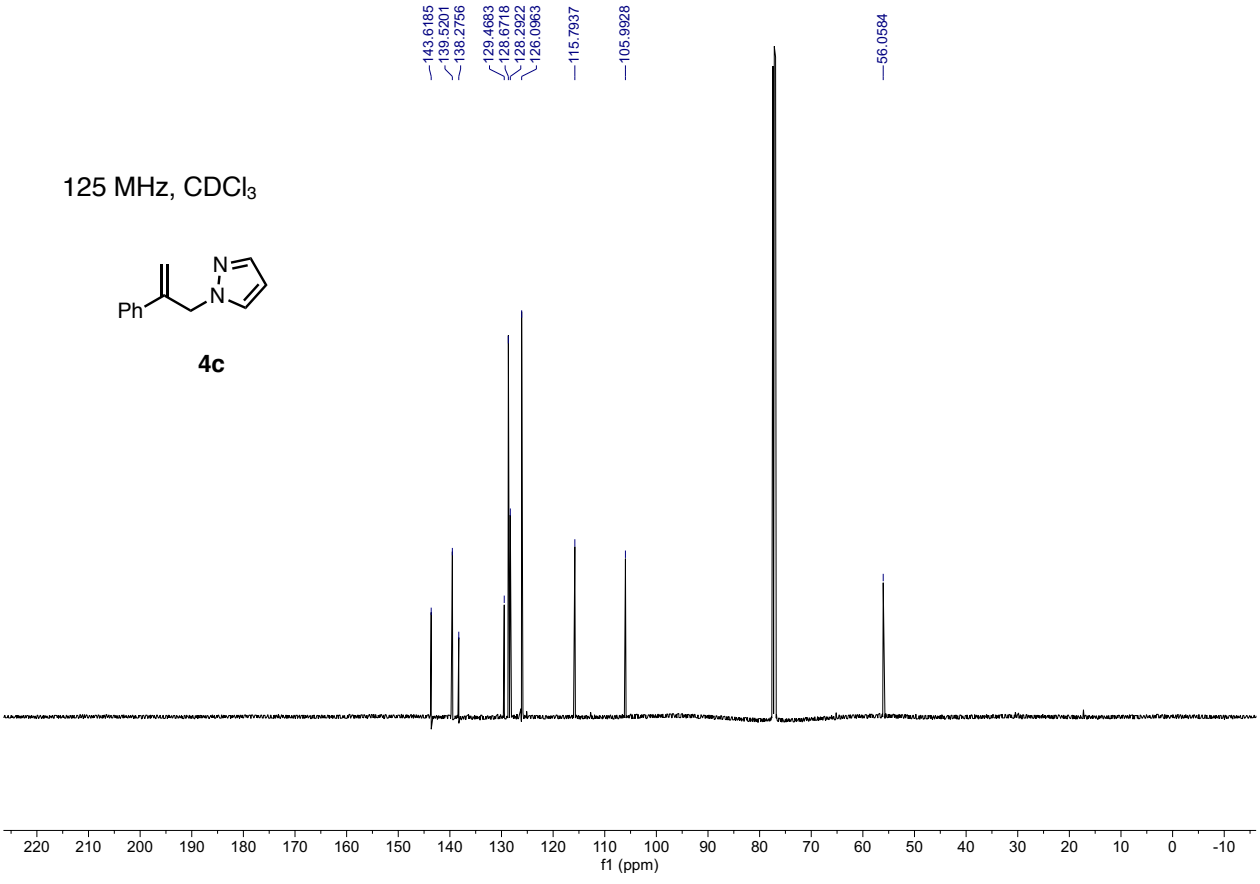


500 MHz, $CDCl_3$



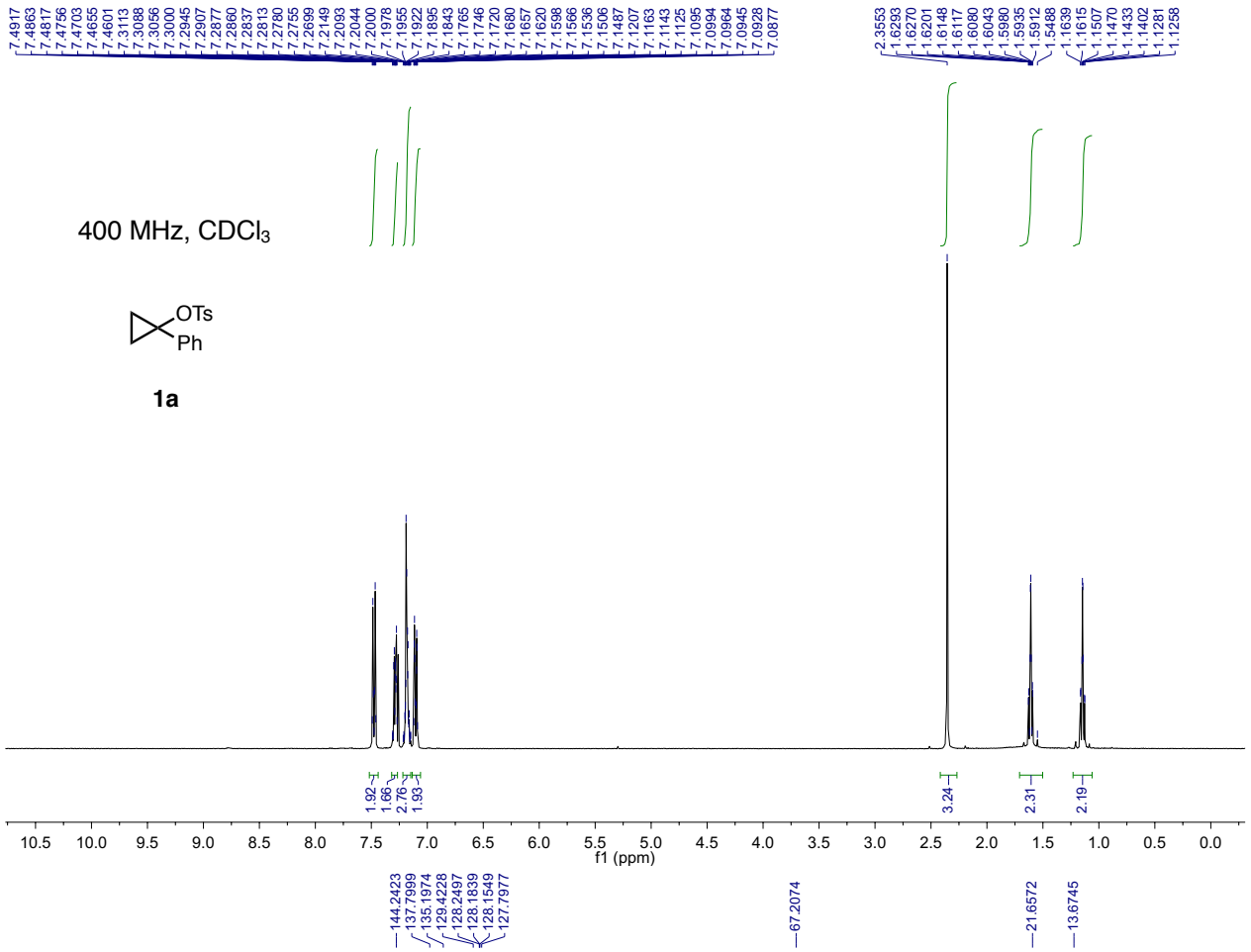
4c

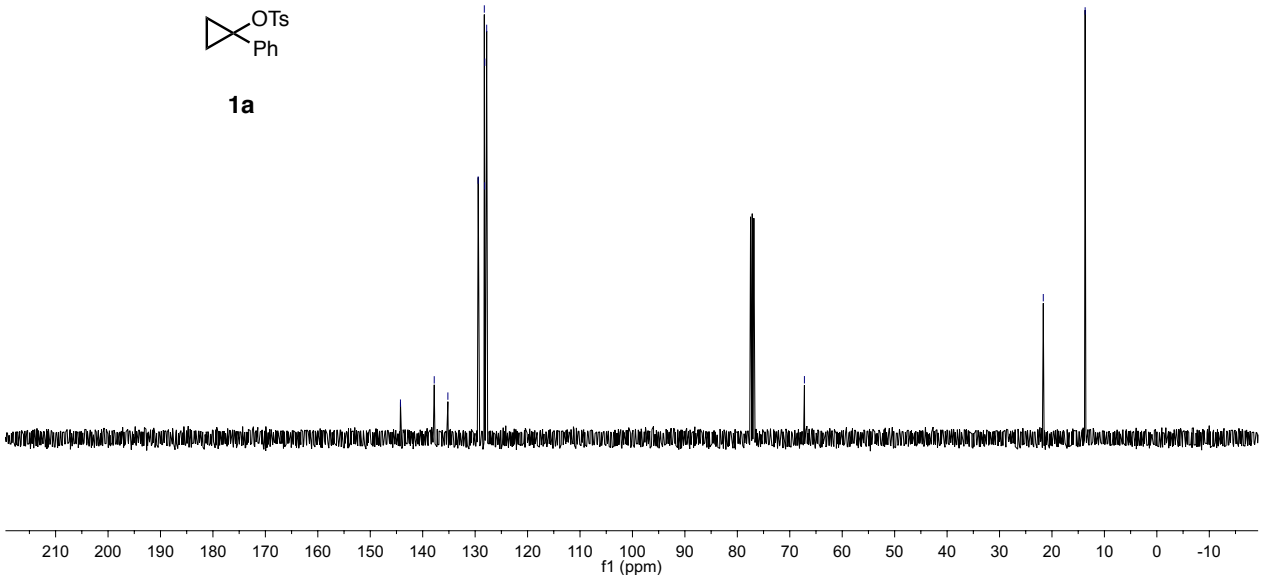


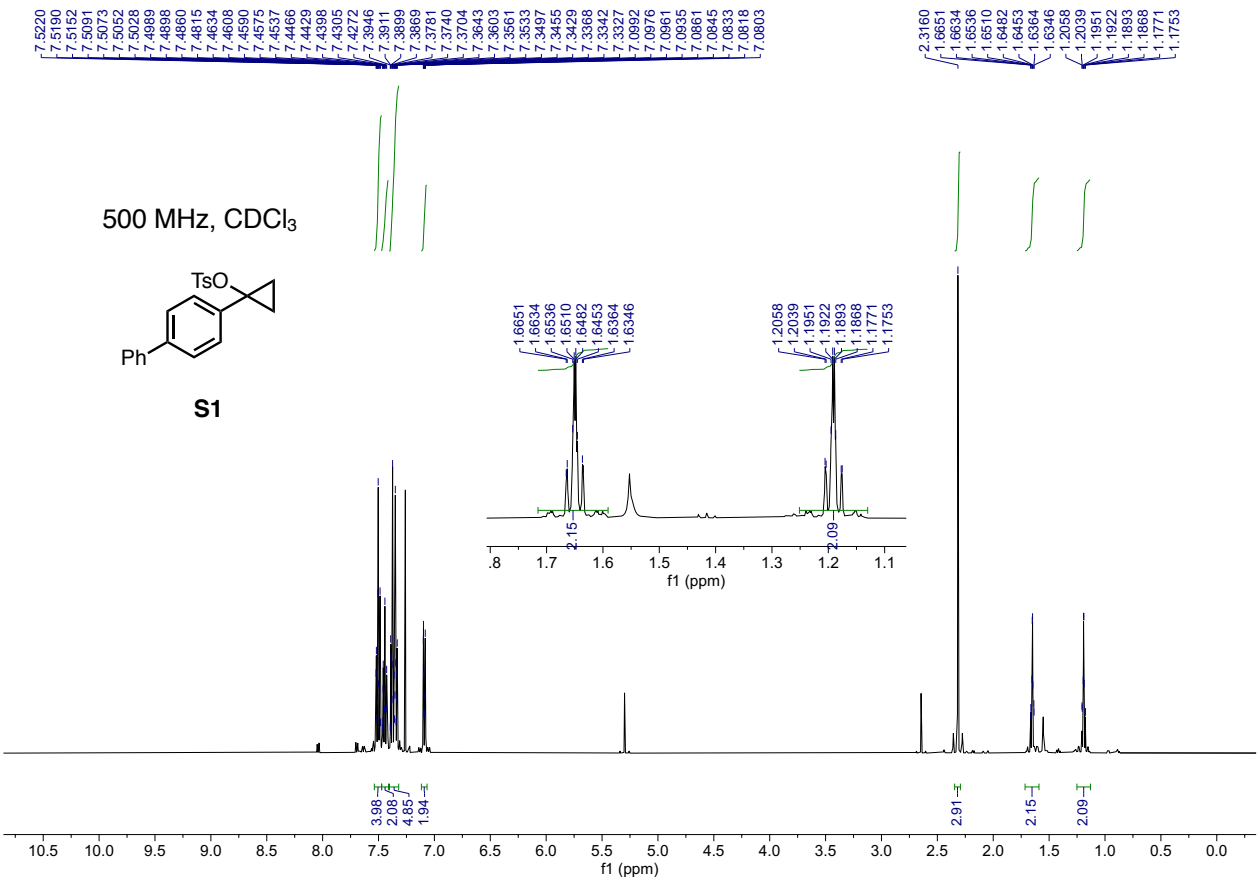


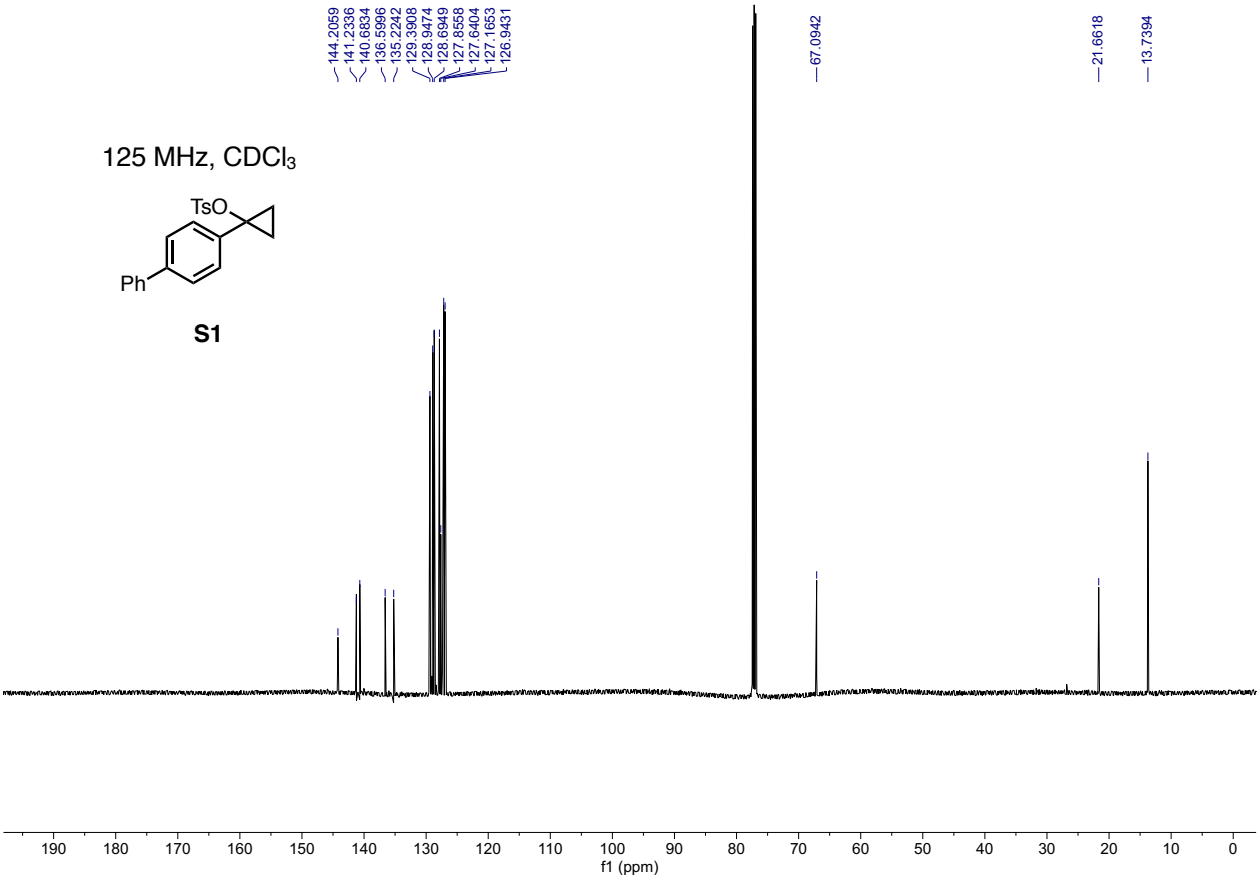
125 MHz, $CDCl_3$

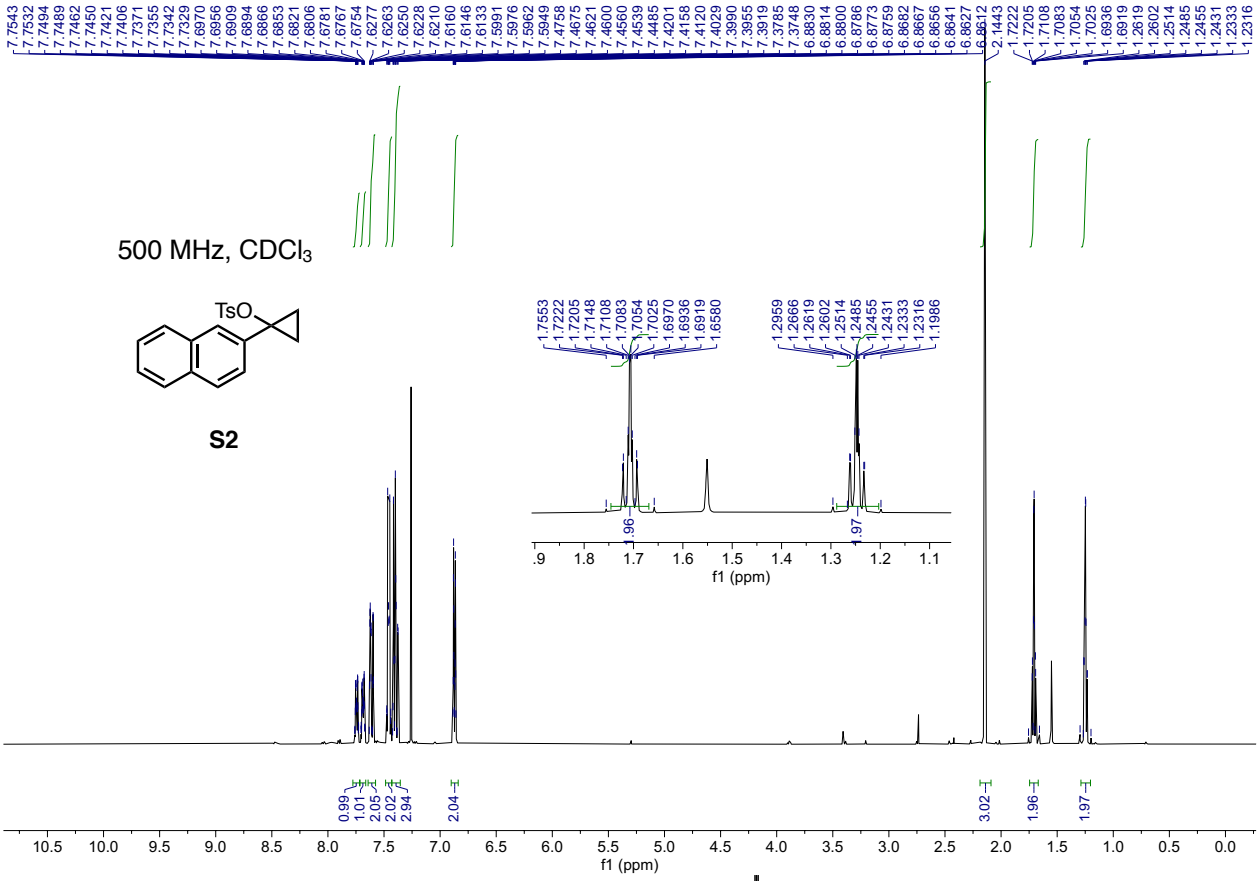
4c

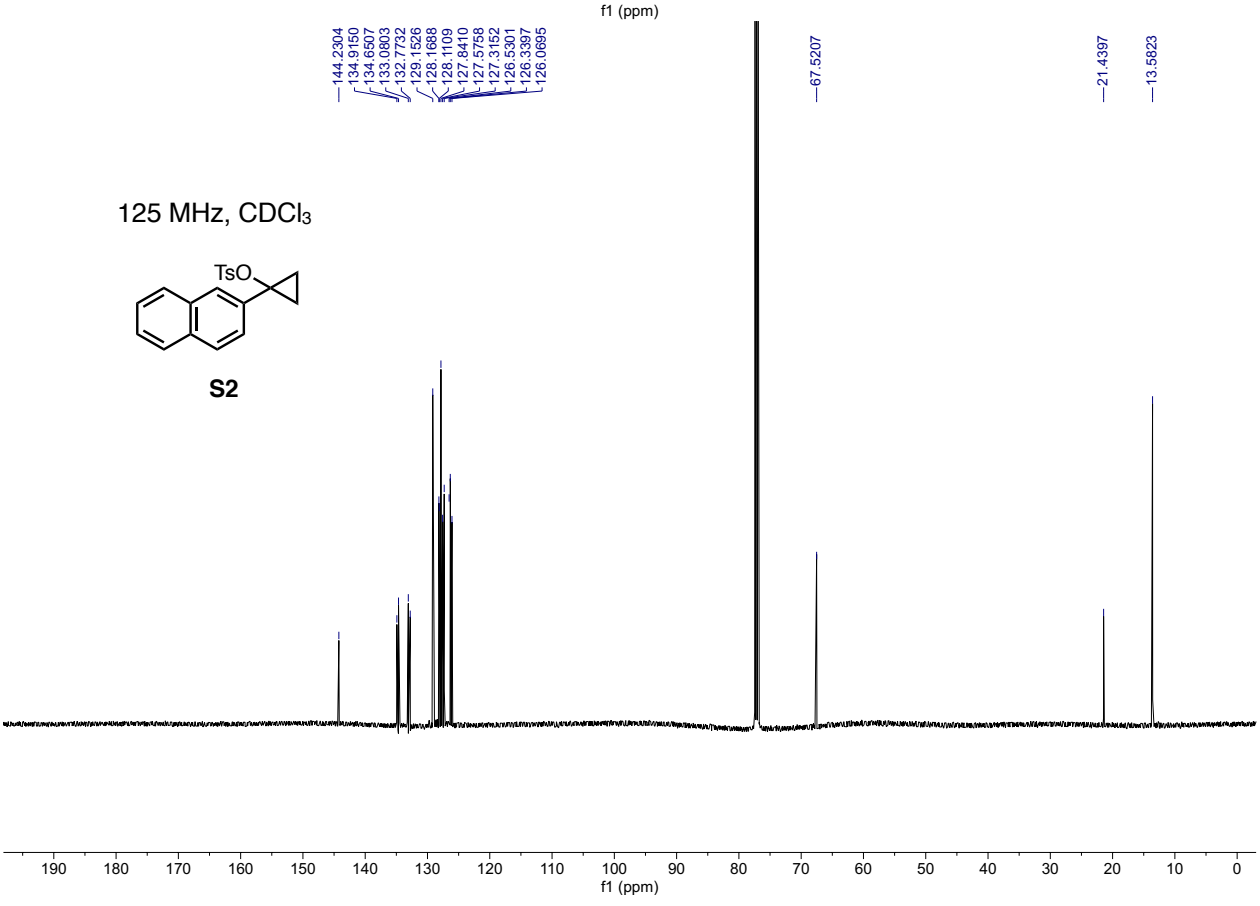

400 MHz, CDCl3
OTs
Ph
1a
f1 (ppm)

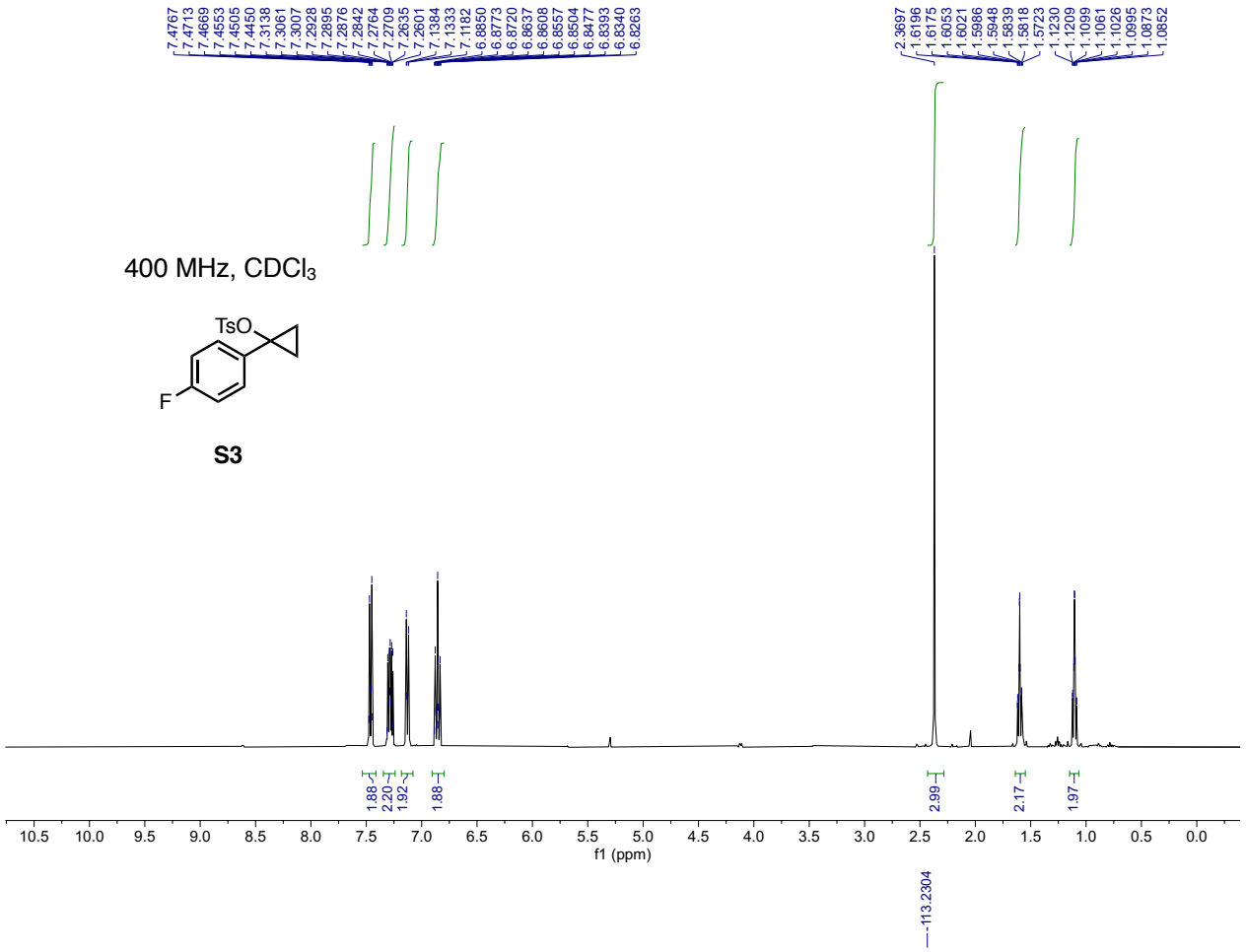

100 MHz, CDCl3
OTs
Ph
1a
f1 (ppm)

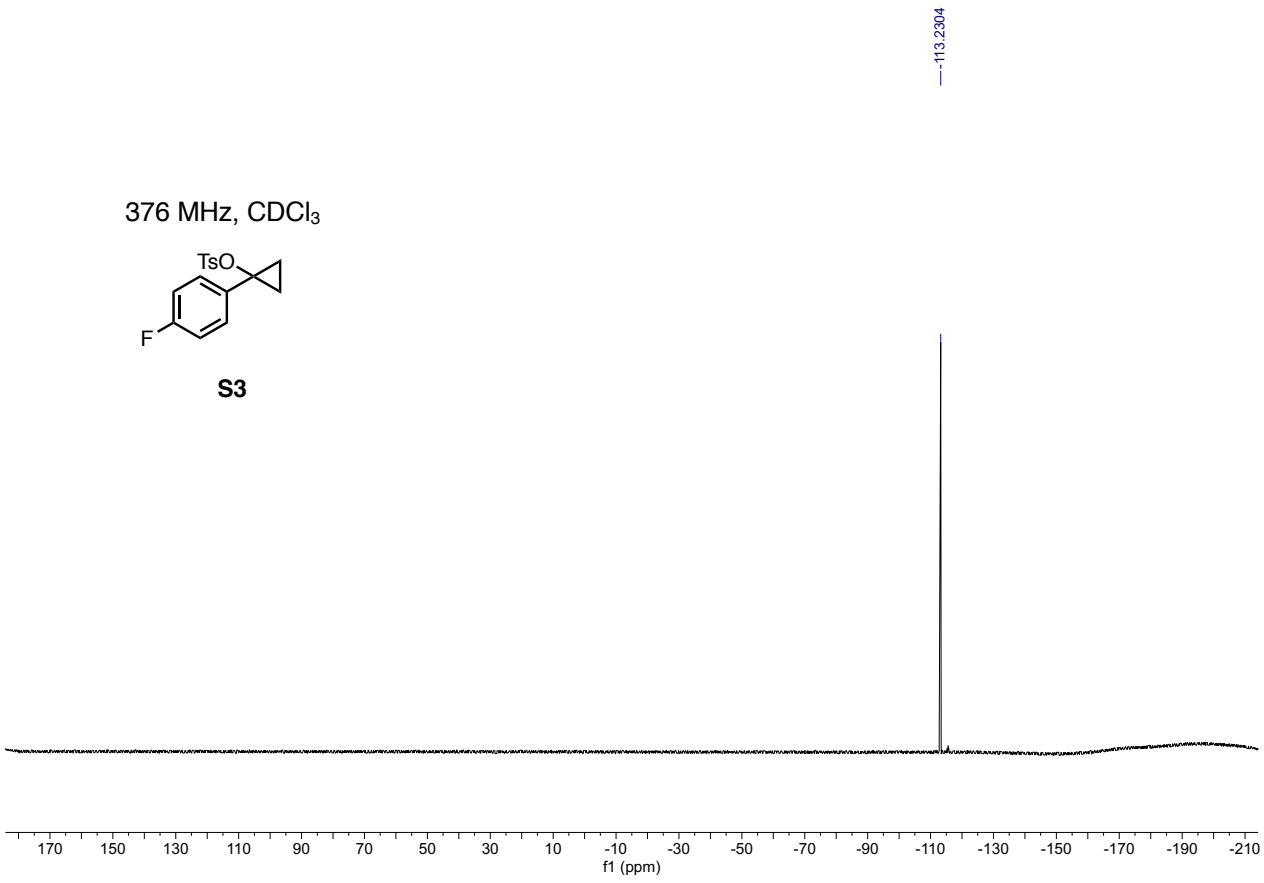

500 MHz, CDCl3
TsO
Ph
S1
f1 (ppm)

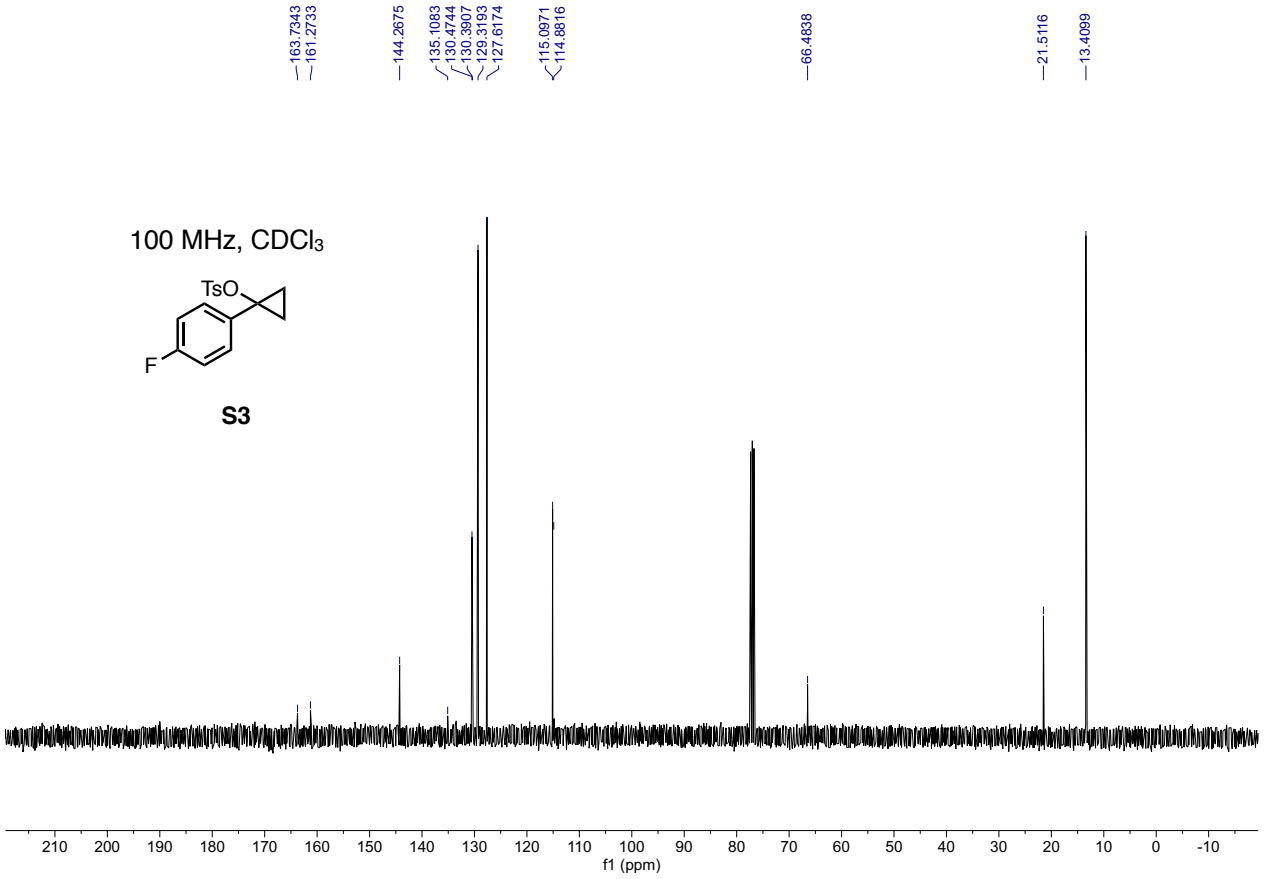

125 MHz, CDCl3
TsO
Ph
S1
f1 (ppm)

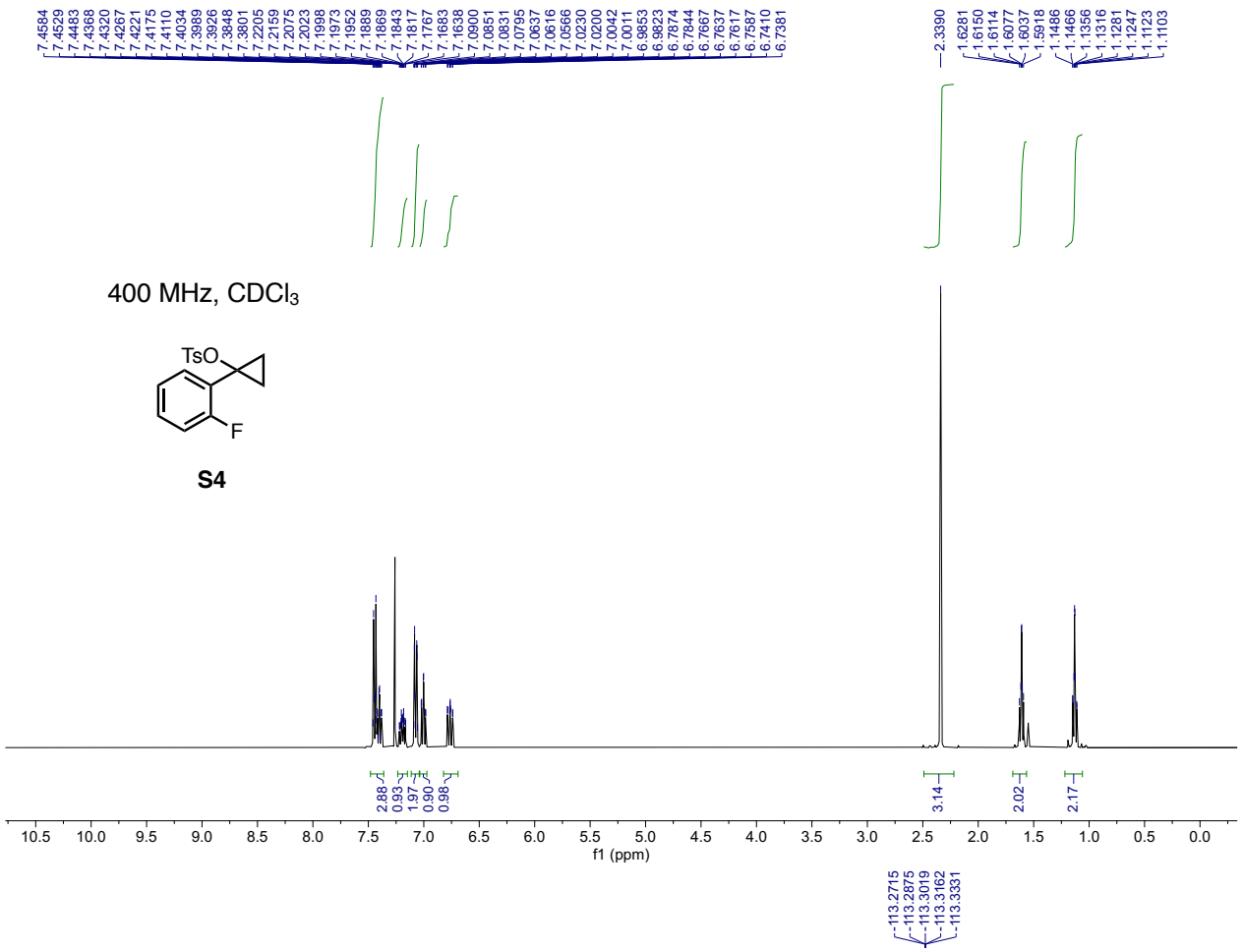

500 MHz, CDCl3
TsO
S2
f1 (ppm)

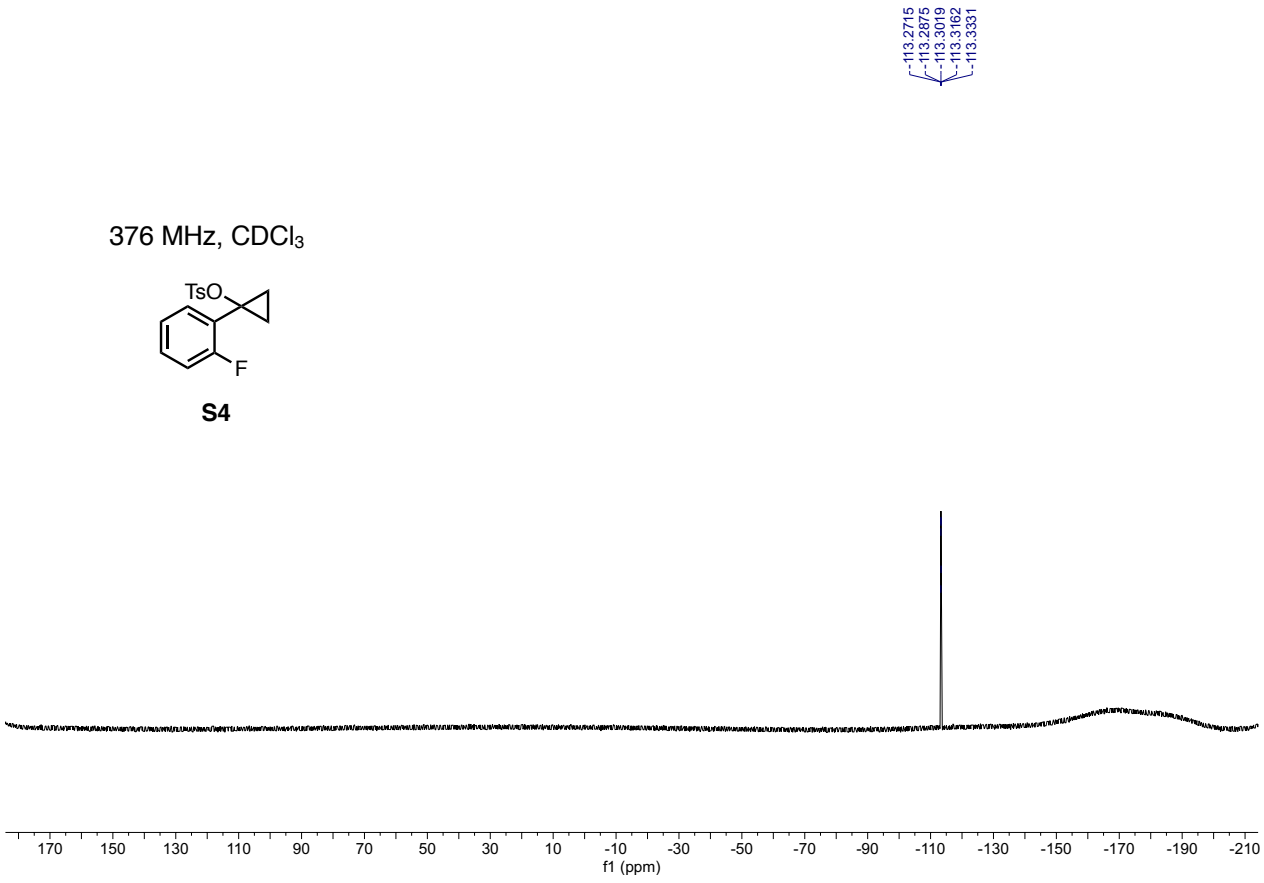

125 MHz, CDCl3
TsO
S2
f1 (ppm)

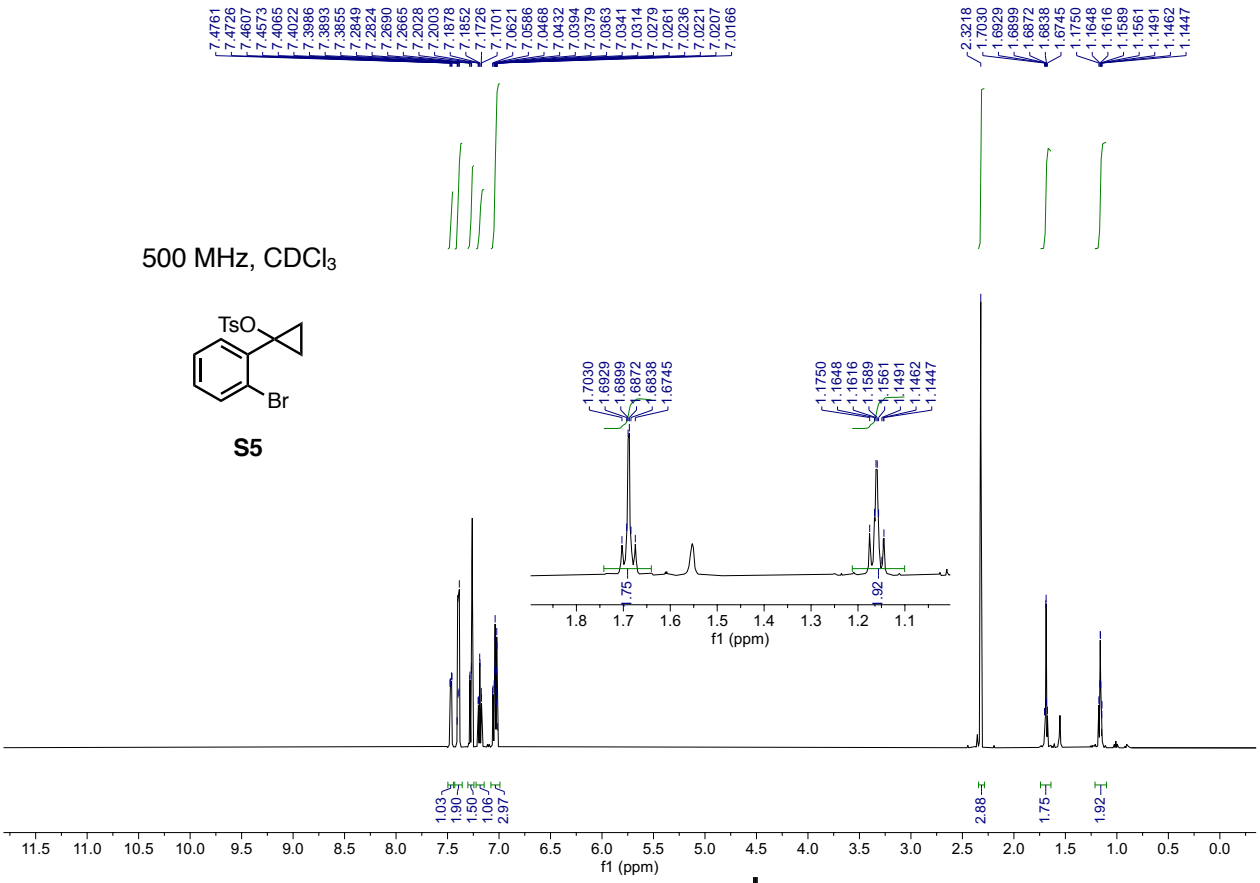

7.4767
7.4713
7.4669
7.4553
7.4505
7.4450
7.3138
7.3061
7.3007
7.2928
7.2895
7.2876
7.2842
7.2764
7.2709
7.2635
7.2601
7.1384
7.1333
7.1182
6.8850
6.8773
6.8720
6.8637
6.8608
6.8557
6.8504
6.8477
6.8393
6.8340
6.8263
2.3697
1.6196
1.6175
1.6053
1.6021
1.5986
1.5948
1.5839
1.5818
1.5723
1.1230
1.1209
1.1099
1.1061
1.1026
1.0995
1.0873
1.0852
400 MHz, CDCl3
TsO
F
S3
1.88
2.20
1.92
1.88
2.99
2.17
1.97
f1 (ppm)

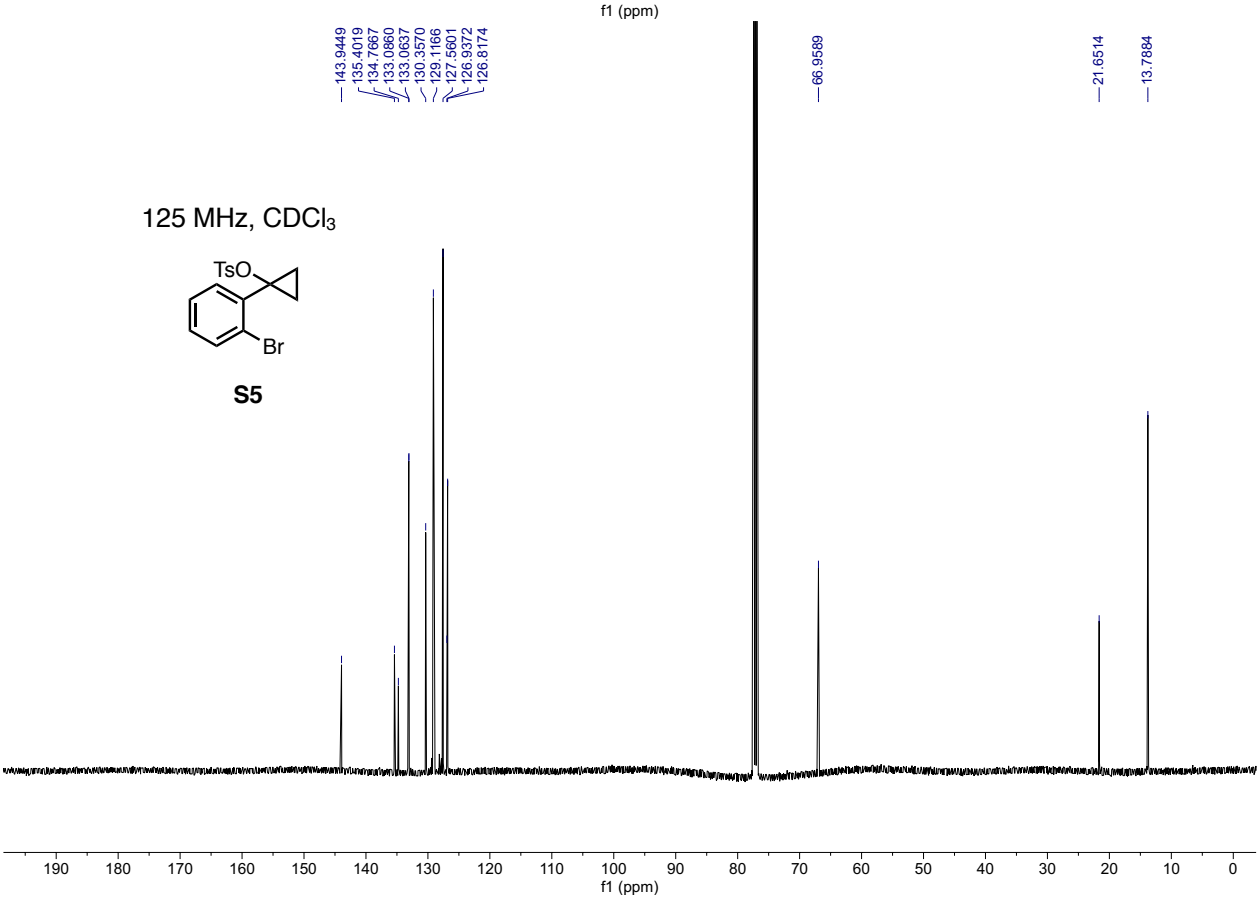

-113.2304
376 MHz, CDCl3
TsO
F
S3
f1 (ppm)

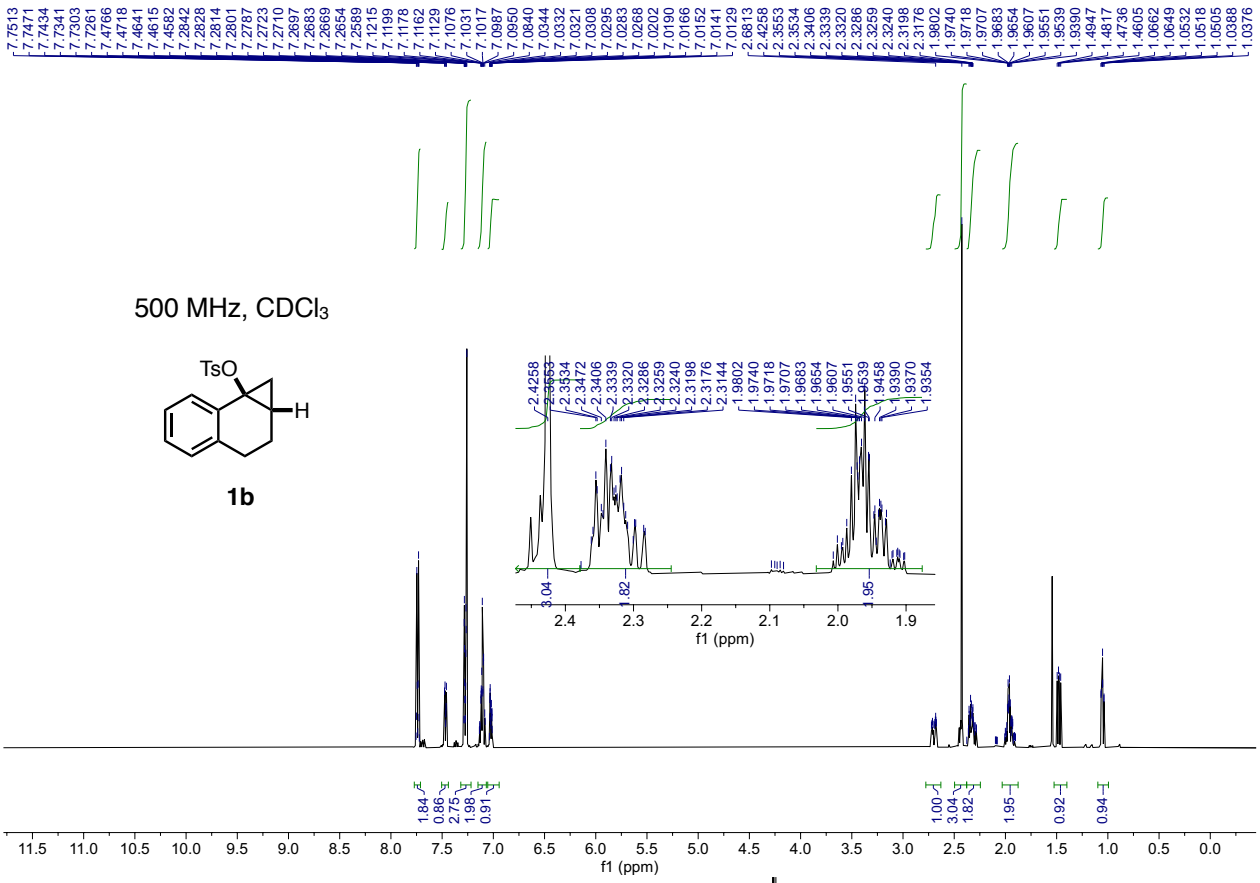

163.7343
161.2733
144.2675
135.1083
130.4744
130.3907
129.3193
127.6174
115.0971
114.8816
66.4838
21.5116
13.4099
100 MHz, CDCl3
TsO
F
S3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

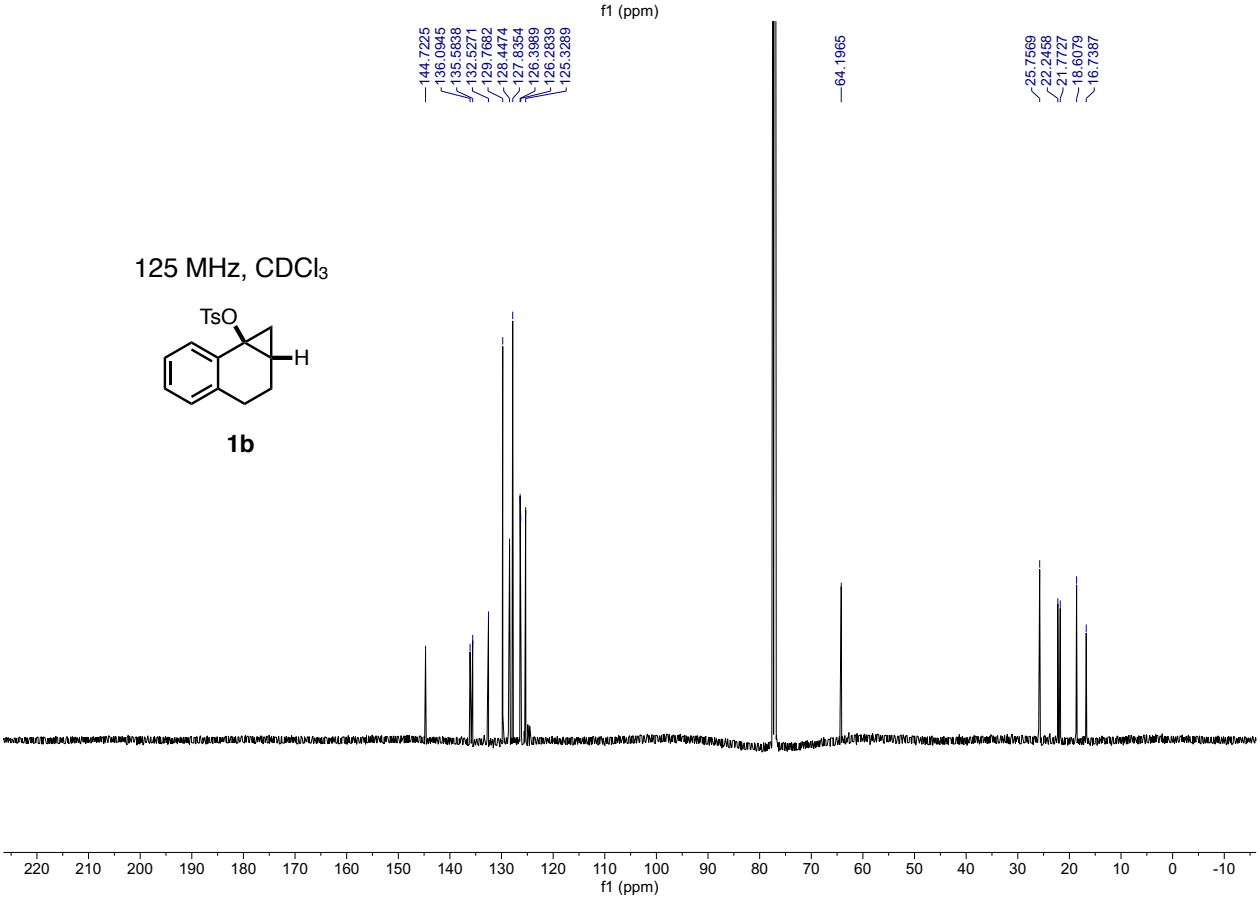

7.4584
7.4529
7.4483
7.4368
7.4320
7.4267
7.4221
7.4175
7.4110
7.4034
7.3989
7.3926
7.3848
7.3801
7.2205
7.2159
7.2075
7.2023
7.1998
7.1973
7.1952
7.1889
7.1869
7.1843
7.1817
7.1767
7.1683
7.1638
7.0900
7.0851
7.0831
7.0795
7.0637
7.0616
7.0566
7.0230
7.0200
7.0042
7.0011
6.9853
6.9823
6.7874
6.7844
6.7667
6.7637
6.7617
6.7587
6.7410
6.7381
2.3390
1.6281
1.6150
1.6114
1.6077
1.6037
1.5918
1.1486
1.1466
1.1356
1.1316
1.1281
1.1247
1.1123
1.1103
400 MHz, CDCl3
TsO
F
S4
2.88
0.93
1.97
0.90
0.98
3.14
2.02
2.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


376 MHz, CDCl3
TsO
F
S4
-113.2715
-113.2875
-113.3019
-113.3162
-113.3331
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


500 MHz, CDCl3
TsO
Br
S5
f1 (ppm)


125 MHz, CDCl3
TsO
Br
S5
f1 (ppm)


500 MHz, CDCl3
TsO
H
1b
f1 (ppm)


125 MHz, CDCl3
TsO
H
1b
f1 (ppm)