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Supporting Information for

Palladium-Catalyzed Trisallylation of Azoles with Alkyne via sequential C(sp^2)-H and C(sp^3)-H Functionalization

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General methods and materials

Reactions were monitored by TLC analysis which was performed on aluminum plates pre-coated with silica gel (MERCK, 60 F-254), and visualized by UV fluorescence (λmax = 254 nm) and/or by staining with 1% w/v $KMnO_4$ in 0.5 M aqueous K_2CO_3. Products were purified by flash column chromatography which was performed using MACHEREY-NAGEL silica gel 60® (230-400 mesh).

NMR (Nuclear Magnetic Resonance) spectra were acquired on a VARIAN Mercury (300 MHz) or on a BRUKER Avance 400 spectrometer or on a Bruker 500 DRX NMR spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in ppm and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Chemical shifts for ^{13}C NMR spectra are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard and with complete proton decoupling.

HRMS (High Resolution Mass Spectra) was measured on a THERMO SCIENTIFIC Advantage and a THERMO SCIENTIFIC Exactive instrument equipped with an APCI source in the positive-ion mode.

Melting points for solids were measured on a BÜCHI Dr. Tottoli melting point apparatus and are given uncorrected.

Solvents: Toluene was freshly distilled over Sodium/Benzophenone and degassed with argon prior to use. 1,2-Dichloroethane (DCE) was freshly distilled over CaH_2 and collected under Argon. THF was freshly distilled over Na and collected under Argon. DMF was purchased from Acros and used as received. Solvents employed for

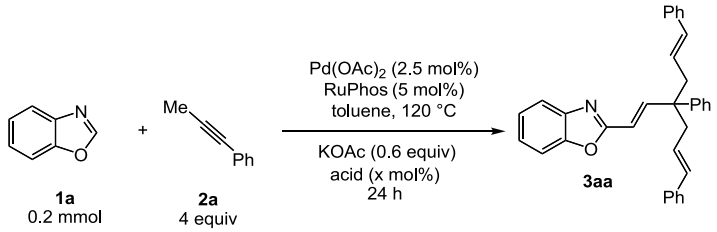
work-up and column chromatography were purified prior to use by evaporation on a rotary evaporator.

Substrates: benzoxazole (**1a**) and 1-phenyl-1-propyne (**2a**) were purchased from Sigma-Aldrich and used without further purification. Azoles (**1b**-**1k**) were synthesized according to literatures.[1] 2-allylbenzoxazole (**8b**) was prepared based on the literatures.[2]

Ligands and metal catalysts were purchased from Acros, Sigma-Aldrich, ABCR, Alfa Aesar and were used as received.

Optimization studies

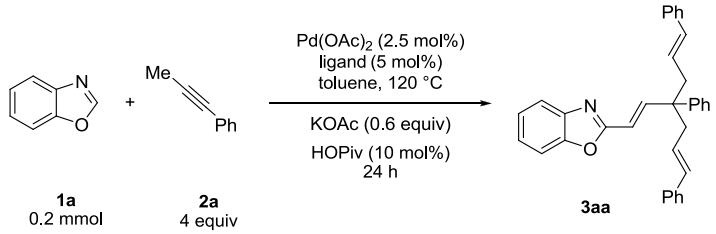
Table S1. Screening of acids



entry [a]	acid (x)	yield/%
1	HOAc (10)	41
2	PhCOOH (10)	65 (72)
3	Ph_3COOH (10)	54
4	**HOPiv (10)**	**74**
5	HOPiv (20)	74
6	HOPiv (60)	71

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol), **2a** (4 equiv.), $Pd(OAc)_2$ (2.5 mol%), RuPhos (5 mol%), KOAc (0.6 equiv), acid (10 mol%), toluene (0.2 mL), 24 h, 120 °C. NMR yield was determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Isolated yields are reported in parentheses.

Table S2. Screening of ligands

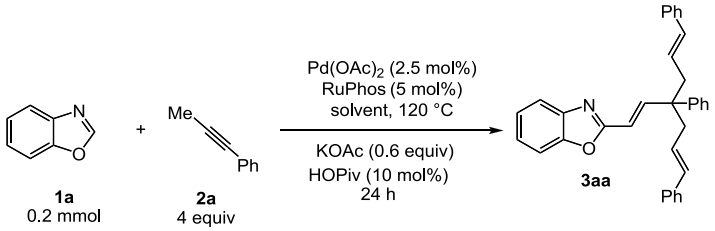


entry [a]	ligand	yield/%
1	XPhos	69
2	RuPhos	74
3	SPhos	64
4	PCy_3	14
5	PPh_3	32
6	JohnPhos	17

7	BrettPhos	0
8	dppe	0
9	dppp	10
10	dppb	15
11	dppf	21
12	DPEphos	24

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol), **2a** (4 equiv.), $Pd(OAc)_2$ (2.5 mol%), ligand (5 mol%), KOAc (0.6 equiv), HOPiv (10 mol%), toluene (0.2 mL), 24 h, 120 °C. NMR yield was determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

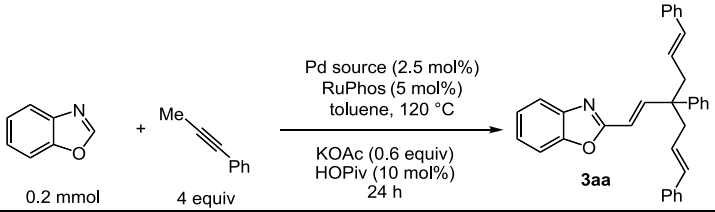
Table S3. Screening of Solvents



entry [a]	solvent	yield/%
1	toluene	74
2	DCE	0
3	DMSO	0
4	DMF	0
5	THF	47
6[b]	toluene	70

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol), **2a** (4 equiv.), $Pd(OAc)_2$ (2.5 mol%), RuPhos (5 mol%), KOAc (0.6 equiv), HOPiv (10 mol%), solvent (0.2 mL), 24 h, 120 °C. NMR yield was determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b]3 equivalents of alkyne was used.

Table S4. Screening of Pd sources

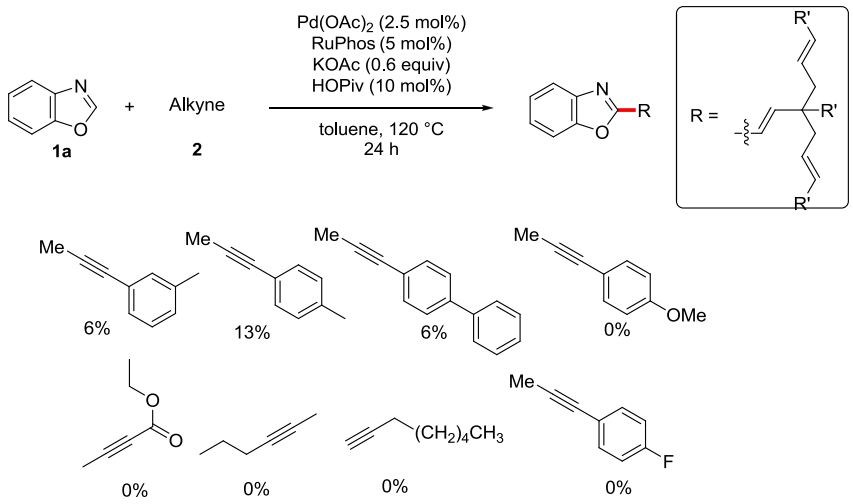


entry [a]	Pd source	Yield/%
1	$PdCl_2$	68

2	$Pd(TFA)_2$	58
3	$Pd(dba)_2$	51
4	$Pd(OAc)_2$	74
5[b]	$Pd(OAc)_2$	77 (81)

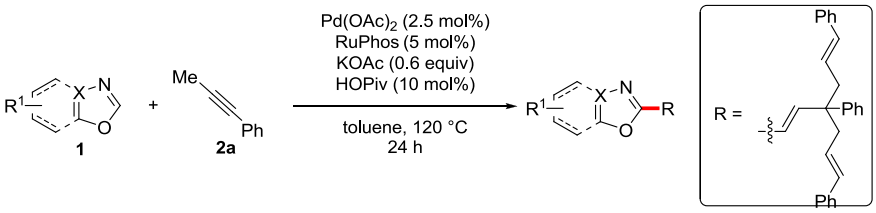
[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol), **2a** (4 equiv.), Pd source (2.5 mol%), RuPhos (5 mol%), KOAc (0.6 equiv), HOPiv (10 mol%), toluene (0.2 mL), 24 h, 120 °C. NMR yield was determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Isolated yields are reported in parentheses. [b]**1a** (0.4 mmol), **2a** (4 equiv.), Pd source (2.5 mol%), RuPhos (5 mol%), KOAc (0.6 equiv), HOPiv (10 mol%), toluene (0.8 mL, 0.5M), 24 h, 120 °C.

Unsuccessful alkynes:



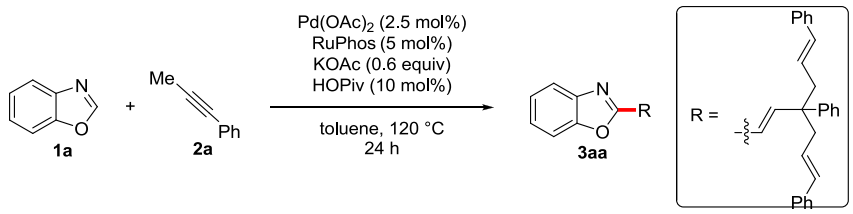
Experimental details and characterization data

Typical procedure for triallylation of azoles with alkyne



A 2 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 2.5 mol%), RuPhos (9.3 mg, 0.02 mmol, 5 mol%), KOAc (23.5 mg, 0.24 mmol, 0.6 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards HOPiv (4.8 M in toluene) (8.3 μL, 0.04 mmol, 10 mol%), azoles (0.4 mmol, 1.0 equiv), alkyne (1.6 mmol, 4.0 equiv) and 0.8 ml of freshly distilled toluene were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 120 ^{o}C for 24 hours. The mixture was cooled down to room temperature. After the solvents were removed under reduced pressure, the residue was purified with column chromatography on silica gel afford the corresponding product after drying in vacuo.

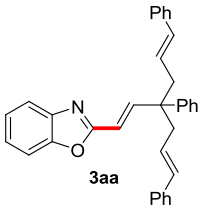
Gram scale reaction:



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk

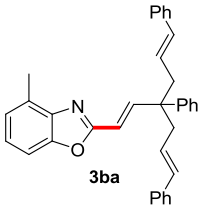
tube was charged with $Pd(OAc)_2$ (16.8 mg, 0.075 mmol, 2.5 mol%), RuPhos (70.0 mg, 0.15 mmol, 5 mol%), KOAc (176.6 mg, 1.8 mmol, 0.6 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards HOPiv (4.8 M in toluene) (62.5 μL, 0.3 mmol, 10 mol%), benzoxazole (**1a**) (357.7 mg, 3 mmol, 1.0 equiv), 1-phenyl-1-propyne (**2a**) (1.394 g, 12 mmol, 4.0 equiv) and 6 ml of freshly distilled toluene were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 120 ^{o}C for 31 hours. The mixture was cooled down to room temperature. After the solvents were removed under reduced pressure, the residue was purified with column chromatography on silica gel (toluene) afford the corresponding product (1.1416 g, 81% yield) after drying in vacuo.

Characterization for the allylated products 3



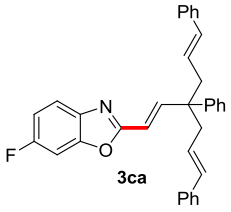
3aa

Yellow foam, 152.4 mg, 81% yield. ^{1}H NMR (400 MHz, C_6D_6) δ 7.73-7.66 (m, 1H), 7.38 (d, *J* = 16.4 Hz, 1H), 7.25-7.17 (m, 5H), 7.15 (d, *J* = 3.5 Hz, 3H), 7.10-6.92 (m, 10H), 6.69 (d, *J* = 16.4 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 2H), 6.09-5.97 (m, 2H), 2.65 (d, *J* = 7.2 Hz, 4H); ^{13}C NMR (101 MHz, C_6D_6) δ 162.6, 150.9, 149.5, 144.1, 143.1, 137.8, 134.1, 128.8, 128.7, 127.7, 127.4, 126.9, 126.5, 125.5, 125.1, 124.6, 120.5, 116.7, 110.5, 48.4, 41.3; HR-MS ($C_{34}H_{30}ON$; $[M+H]^+$, pos. ESI): calcd: 468.2322, found: 468.2323.



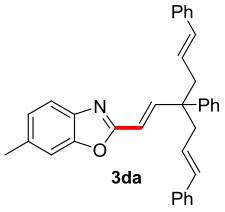
3ba

Yellow foam, 134.3 mg, 70% yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.38 (d, *J* = 16.5 Hz, 1H), 7.23-7.19 (m, 2H), 7.19-7.16 (m, 6H), 7.04-7.09 (m, 6H), 7.02-6.98 (m, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 16.5 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 2H), 6.07-5.98 (m, 2H), 2.66 (dd, *J* = 7.0, 1.0 Hz, 4H), 2.59 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 161.8, 150.6, 148.9, 144.2, 142.2, 137.8, 134.1, 130.9, 128.8, 128.5, 127.7, 127.4, 126.9, 126.5, 125.5, 125.1, 125.0, 116.8, 107.8, 48.3, 41.3, 16.5; HR-MS ($C_{35}H_{32}ON$; $[M+H]^+$, pos. ESI): calcd: 482.2478, found: 482.2476.



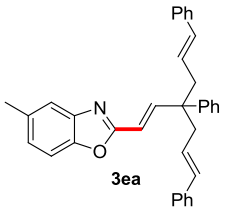
3ca

Yellow oil, 58.3 mg, 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 9.0, 5.0 Hz, 1H), 7.47-7.36 (m, 4H), 7.32-7.27 (m, 9H), 7.26 (s, 1H), 7.23-7.18 (m, 3H), 7.10 -7.04 (m, 1H), 6.58 (d, *J* = 16.5 Hz, 1H), 6.47 (d, *J* = 15.5 Hz, 2H), 6.09-5.97 (m, 2H), 2.91 (d, *J* = 6.5 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (d, *J* = 3.5 Hz), 160.8 (d, *J* = 244.7 Hz) 150.4 (d, *J* = 14.7 Hz), 149.8, 143.5, 138.4 (d, *J* = 1.6 Hz), 137.4, 133.8, 128.65, 128.60, 127.4, 127.3, 126.9, 126.2, 125.4, 120.2 (d, *J* = 10.1 Hz), 115.9, 112.4 (d, *J* = 24.6 Hz), 98.6 (d, *J* = 28.2 Hz), 48.4, 41.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.01 (m, 1F); HR-MS ($C_{34}H_{29}ONF$; $[M+H]^+$, pos. ESI): calcd: 486.2228, found: 486.2228.



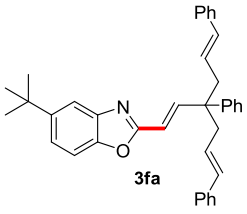
3da

Yellow oil, 145.2 mg, 75% yield. ^{1}H NMR (400 MHz, C_6D_6) δ 7.61 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 16.4 Hz, 1H), 7.24-7.15 (m, 7H), 7.11-7.01 (m, 6H), 7.01-6.96 (m, 3H), 6.83 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.70 (d, *J* = 16.4 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 2H), 6.08-5.94 (m, 2H), 2.65 (d, *J* = 7.2 Hz, 4H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 162.2, 151.3, 148.8, 144.2, 141.0, 137.9, 135.4, 134.1, 128.8, 128.7, 127.7, 127.4, 126.9, 126.5, 125.9, 125.6, 119.9, 116.9, 110.7, 48.2, 41.4, 21.5; HR-MS ($C_{35}H_{32}ON$; $[M+H]^+$, pos. ESI): calcd: 482.2478, found: 482.2477.



3ea

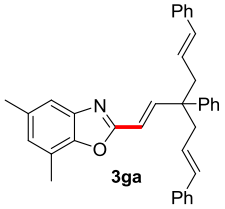
Yellow solid, 133.0 mg, 69% yield, m.p.= 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.46-7.38 (m, 5H), 7.35-7.28 (m, 10H), 7.27-7.21 (m, 2H), 7.16 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.64 (d, *J* = 16.4 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 2H), 6.14-6.02 (m, 2H), 2.95 (d, *J* = 7.2 Hz, 4H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 149.3, 148.7, 143.7, 142.3, 137.5, 134.3, 133.7, 128.6, 128.58, 127.5, 127.3, 126.9, 126.3, 126.2, 125.6, 119.9, 116.3, 109.8, 48.4, 41.2, 21.5; HR-MS ($C_{35}H_{32}ON$; $[M+H]^+$, pos. ESI): calcd: 482.2478, found: 482.2477.



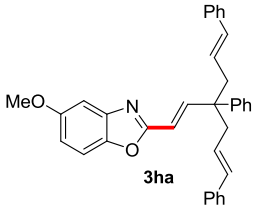
3fa

White solid, 184.6 mg, 88% yield, m.p.= 134-136 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.88 (d, *J* = 1.6 Hz, 1H), 7.40 (d, *J* = 16.4 Hz, 1H), 7.24-7.17 (m, 7H), 7.15-7.11 (m, 3H), 7.09-7.04 (m, 5H), 7.03-6.97 (m, 2H), 6.74 (d, *J* = 16.4 Hz, 1H), 6.36 (d, *J* = 15.6 Hz, 2H), 6.09-5.98 (m, 2H), 2.66 (d, *J* = 7.2 Hz, 4H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ 162.8, 149.04, 149.0, 144.2, 143.2, 137.9, 134.1, 128.8, 128.7,

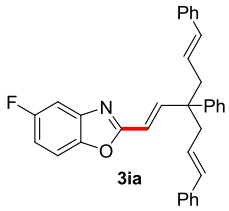
127.7, 127.4, 126.9, 126.5, 125.6, 123.0, 117.2, 116.9, 109.7, 48.4, 41.4, 34.8, 31.8; HR-MS ($C_{38}H_{38}ON$; $[M+H]^+$, pos. ESI): calcd: 524.2948, found: 524.2947.



Yellow solid, 119.2 mg, 60% yield, m.p.= 140-142 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.45-7.44 (m, 1H), 7.42 (d, *J* = 16.4 Hz, 1H), 7.23-7.20 (m, 2H), 7.19-7.16 (m, 4H), 7.14-7.13 (m, 1H), 7.10-6.97 (m, 8H), 6.72 (d, *J* = 16.4 Hz, 1H), 6.64 (dt, *J* = 1.6, 0.8 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 2H), 6.03 (dt, *J* = 15.6, 7.2 Hz, 2H), 2.70-2.59 (m, 4H), 2.21 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 162.5, 148.7, 148.4, 144.2, 143.0, 137.9, 134.2, 134.1, 128.82, 128.75, 127.7, 127.6, 127.4, 126.9, 126.5, 125.6, 120.2, 118.0, 117.0, 48.4, 41.2, 21.4, 15.1; HR-MS ($C_{36}H_{34}ON$; $[M+H]^+$, pos. ESI): calcd: 496.2635, found: 496.2639.

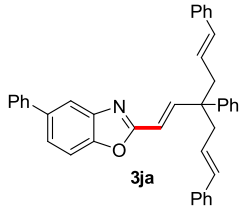


Yellow solid, 267.2 mg, 95% yield, m.p.= 136-138 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.38 (d, *J* = 16.4 Hz, 1H), 7.25-7.16 (m, 8H), 7.10-6.96 (m, 9H), 6.79 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.70 (d, *J* = 16.4 Hz, 1H), 6.36 (d, *J* = 15.6 Hz, 2H), 6.09-5.97 (m, 2H), 3.27 (s, 3H), 2.66 (d, *J* = 7.2 Hz, 4H); ^{13}C NMR (101 MHz, C_6D_6) δ 163.4, 157.9, 149.0, 145.5, 145.2, 144.0, 137.9, 134.1, 128.8, 128.7, 127.4, 126.9, 126.5, 125.6, 116.9, 114.3, 110.7, 103.3, 55.3, 48.4, 41.4; HR-MS ($C_{35}H_{32}O_2N$; $[M+H]^+$, pos. ESI): calcd: 498.2428, found: 498.2431.



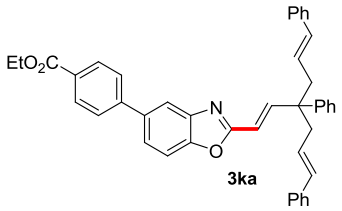
3ia

Yellow oil, 73.5 mg, 38% yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.35 (d, *J* = 16.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.15 (m, 7H), 7.09-7.05 (m, 5H), 7.04-6.97 (m, 3H), 6.80 (dd, *J* = 9.0, 4.5 Hz, 1H), 6.63 (dt, *J* = 9.5, 3.0 Hz, 1H), 6.61 (d, *J* = 16.5 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 2H), 6.06-5.96 (m, 2H), 2.63 (d, *J* = 7.0 Hz, 4H); ^{13}C NMR (126 MHz, C_6D_6) δ 164.3, 160.5 (d, *J* = 240.7 Hz), 150.2, 147.0 (d, *J* = 1.3 Hz), 143.9, 142.8 (d, *J* = 13.2 Hz), 137.7, 134.2, 128.83, 128.78, 127.6, 127.5, 127.0, 126.4, 125.3, 116.4, 112.6 (d, *J* = 26.3 Hz), 110.7 (d, *J* = 10.0 Hz), 106.7 (d, *J* = 25.5 Hz), 48.4, 41.3; ^{19}F NMR (471 MHz, C_6D_6) δ -177.86 (m, 1F); HR-MS ($C_{34}H_{29}ONF$; $[M+H]^+$, pos. ESI): calcd: 486.2228, found: 486.2231.

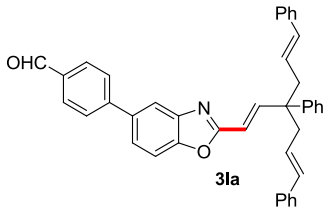


3ja

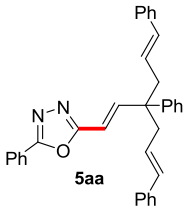
Yellow foam, 125.8 mg, 58% yield. ^{1}H NMR (400 MHz, C_6D_6) δ 8.05-7.96 (m, 1H), 7.48-7.40 (m, 3H), 7.28 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.25-7.19 (m, 6H), 7.16-7.14 (m, 5H), 7.13-7.10 (m, 1H), 7.09-7.05 (m, 5H), 7.02-6.98 (m, 2H), 6.73 (d, *J* = 16.4 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 2H), 6.10-5.98 (m, 2H), 2.68 (d, *J* = 7.2 Hz, 4H); ^{13}C NMR (101 MHz, C_6D_6) δ 163.2, 150.4, 150.0, 144.1, 143.8, 141.5, 138.7, 137.8, 134.2, 129.0, 128.8, 128.8, 128.5, 127.7, 127.5, 127.3, 127.0, 126.5, 125.5, 124.9, 119.1, 116.7, 110.5, 48.5, 41.4; HR-MS ($C_{40}H_{35}ON$; $[M+H]^+$, pos. ESI): calcd: 544.2635, found: 544.2637.



Yellow oil, 142.9 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19-8.10 (m, 2H), 7.94 (s, 1H), 7.71-7.68 (m, 2H), 7.63-7.51 (m, 2H), 7.49-7.38 (m, 4H), 7.38-7.33 (m, 1H), 7.33-7.25 (m, 9H), 7.25-7.18 (m, 2H), 6.65 (d, *J* = 16.5 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 2H), 6.12-5.99 (m, 2H), 4.43 (q, *J* = 7.0 Hz, 2H), 2.94 (d, *J* = 7.0 Hz, 4H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 163.3, 150.5, 150.2, 145.4, 143.5, 142.9, 137.4, 137.2, 133.8, 130.2, 129.3, 128.6, 128.59, 127.4, 127.34, 127.33, 126.9, 126.2, 125.4, 124.8, 118.6, 116.0, 110.7, 61.1, 48.5, 41.1, 14.4; HR-MS ($C_{43}H_{38}O_3N$; $[M+H]^+$, pos. ESI): calcd: 616.2846, found: 616.2840.

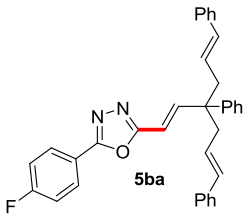


Yellow oil, 115.3 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.99-7.94 (m, 3H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.62-7.54 (m, 2H), 7.46-7.38 (m, 4H), 7.35 (d, *J* = 16.4 Hz, 1H), 7.33-7.26 (m, 9H), 7.23-7.18 (m, 2H), 6.64 (d, *J* = 16.4 Hz, 1H), 6.48 (d, *J* = 15.8 Hz, 2H), 6.11-5.98 (m, 2H), 2.93 (d, *J* = 7.2 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 163.5, 150.7, 150.5, 147.1, 143.5, 143.0, 137.5, 136.9, 135.3, 133.8, 130.4, 128.7, 128.6, 128.1, 127.5, 127.4, 127.0, 126.2, 125.4, 124.9, 118.8, 116.1, 110.8, 48.6, 41.2; HR-MS ($C_{41}H_{34}O_2N$; $[M+H]^+$, pos. ESI): calcd: 572.2584, found: 572.2586.



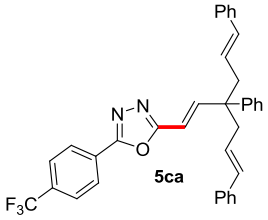
5aa

Yellow oil, 159.3 mg, 81% yield. ^{1}H NMR (400 MHz, Acetone) δ 8.11-8.01 (m, 2H), 7.62-7.49 (m, 5H), 7.43-7.39 (m, 2H), 7.35-7.22 (m, 10H), 7.19-7.15 (m, 2H), 6.70 (d, *J* = 16.4 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 2H), 6.26-6.12 (m, 2H), 3.03 (dd, *J* = 7.2, 0.8 Hz, 4H); ^{13}C NMR (101 MHz, Acetone) δ 164.7, 164.6, 150.0, 144.8, 138.5, 134.4, 132.5, 130.1, 129.4, 128.4, 128.0, 127.6, 127.5, 126.9, 126.5, 125.1, 113.1, 49.4, 41.7; HR-MS ($C_{35}H_{31}ON_2$; $[M+H]^+$, pos. ESI): calcd: 495.2431, found: 495.2432.



5ba

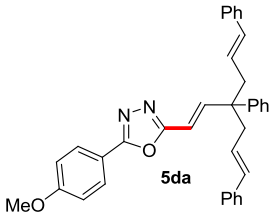
Yellow oil, 162.5 mg, 79% yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.70-7.59 (m, 2H), 7.25-7.16 (m, 8H), 7.13-7.06(m, 6H), 7.04-6.98 (m, 2H), 6.61-6.59 (m, 3H), 6.38 (d, *J* = 16.0 Hz, 2H), 6.08-5.94 (m, 2H), 2.73-2.59 (m, 4H); ^{13}C NMR (126 MHz, C_6D_6) δ 164.7 (d, *J* = 252.4 Hz), 163.9, 163.3, 148.6, 143.7, 137.7, 134.3, 129.3 (d, *J* = 8.8 Hz), 128.9, 128.5, 127.64, 127.58, 127.1, 126.5, 125.2, 120.8 (d, *J* = 3.3 Hz), 116.2 (d, *J* = 22.2 Hz), 112.7, 48.4, 41.2; ^{19}F NMR (471 MHz, C_6D_6) δ -107.67 (m, 1F); HR-MS ($C_{35}H_{30}ON_2F$; $[M+H]^+$, pos. ESI): calcd: 513.2337, found: 513.2335.



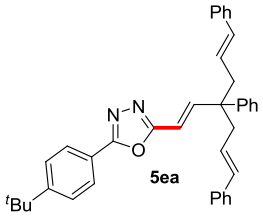
5ca

Yellow oil, 209.6 mg, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.49-7.39 (m, 4H), 7.36-7.31 (m, 1H), 7.31-7.28 (m, 7H), 7.28-7.16 (m, 4H), 6.68 (d, *J* = 16.5 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 2H), 6.10-5.95 (m, 2H), 2.93 (d, *J* = 7.0 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4,

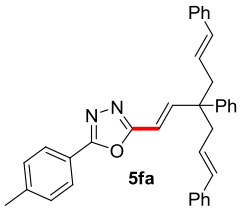
163.0, 150.1, 143.1, 137.3, 134.0, 133.6 (q, *J* = 32.9 Hz), 128.7, 128.6, 127.4, 127.39, 127.3, 127.1, 126.2, 126.1 (q, *J* = 3.9 Hz), 125.0, 123.6 (q, *J* = 273.2 Hz), 48.5, 14.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.05 (s, 3F); HR-MS ($C_{36}H_{30}ON_2F_3$; $[M+H]^+$, pos. ESI): calcd: 563.2305, found: 563.2302.



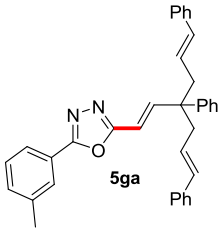
Yellow foam, 108 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.96 (m, 2H), 7.45-7.39 (m, 4H), 7.35-7.26 (m, 9H), 7.25-7.18 (m, 2H), 7.12 (d, *J* = 16.4 Hz, 1H), 7.03-6.95 (m, 2H), 6.65 (d, *J* = 16.4 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 2H), 6.09-5.96 (m, 2H), 3.88 (s, 3H), 2.92 (d, *J* = 7.2 Hz, 4H); ^{13}C NMR (101 MHz, C_6D_6) δ 164.1, 163.5, 162.4, 148.6, 143.4, 137.4, 133.9, 128.8, 128.7, 128.6, 127.4, 127.3, 127.0, 126.2, 125.2, 116.5, 114.5, 112.4, 55.5, 48.4, 41.0; HR-MS ($C_{36}H_{33}O_2N_2$; $[M+H]^+$, pos. ESI): calcd: 525.2537, found: 525.2535.



White solid, 144.7 mg, 66% yield, m.p.= 120-122 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.99-7.89 (m, 2H), 7.22-7.16 (m, 7H), 7.15-7.14 (m, 5H), 7.10-7.07 (m, 4H), 7.03-6.97 (m, 2H), 6.60 (d, *J* = 16.5 Hz, 1H), 6.37 (d, *J* = 15.5 Hz, 2H), 6.06-5.93 (m, 2H), 2.62 (d, *J* = 7.0 Hz, 3H), 1.10 (s, 7H); ^{13}C NMR (101 MHz, C_6D_6) δ 164.3, 163.8, 154.8, 148.3, 143.8, 137.8, 134.3, 128.85, 128.81, 127.7, 127.5, 127.07, 127.05, 126.5, 126.1, 125.3, 122.1, 112.9, 48.3, 41.2, 34.8, 31.0; HR-MS ($C_{39}H_{39}ON_2$; $[M+H]^+$, pos. ESI): calcd: 551.3057, found: 551.3058.

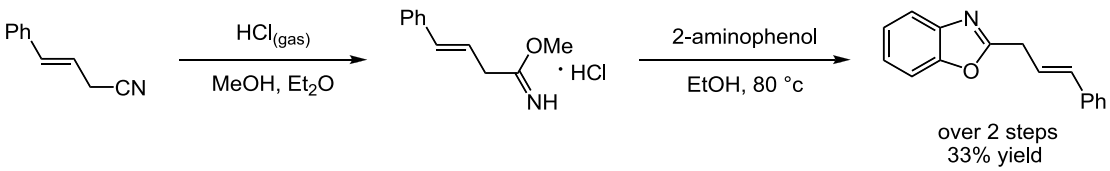


White foam, 133.6 mg, 66% yield. ^{1}H NMR (400 MHz, C_6D_6) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.34-7.29 (m, 7H), 7.28-7.26 (m, 2H), 7.22-7.16 (m, 5H), 7.14-7.09 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 16.8 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 2H), 6.18-6.06 (m, 2H), 2.76 (d, *J* = 7.2 Hz, 4H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 164.4, 163.8, 148.3, 143.9, 141.7, 137.8, 134.3, 129.8, 128.8, 128.5, 127.7, 127.5, 127.1, 127.05, 126.5, 125.4, 122.1, 112.9, 48.4, 41.2, 21.3; HR-MS ($C_{36}H_{33}ON_2$; $[M+H]^+$, pos. ESI): calcd: 509.2587, found: 509.2588.



Yellow oil, 151.8 mg, 75% yield. ^{1}H NMR (400 MHz, C_6D_6) δ 7.80-7.70 (m, 2H), 7.18-7.10 (m, 9H), 7.06-7.00 (m, 5H), 6.98-6.94 (m, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 16.6 Hz, 1H), 6.32 (d, *J* = 15.6 Hz, 2H), 6.04-5.90 (m, 2H), 2.60 (d, *J* = 7.2 Hz, 4H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 164.4, 163.9, 148.4, 143.8, 138.8, 137.8, 134.3, 132.2, 129.0, 128.8, 128.5, 127.69, 127.67, 127.1, 126.5, 125.4, 124.7, 124.4, 112.9, 48.4, 41.2, 21.0; HR-MS ($C_{36}H_{33}ON_2$; $[M+H]^+$, pos. ESI): calcd: 509.2587, found: 509.2584.

Synthesis of 2-cinnamybenzoxazole (8a)

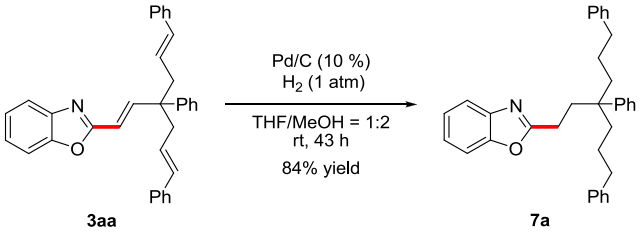


To a solution of (*E*)-4-phenylbut-3-enenitrile (1.4 g, 10 mmol) and methanol (0.64 g,

20 mmol) in ethyl ether (50 mL), dry HCl gas was introduced for 18 h at room temperature. The resulting light brown solid was filtrate and dried under the high vacuum. A mixture of the solid and 2-aminophenol (1.4 g, 13 mmol) in ethanol (20 mL) was heated at 80 °C for 2d. The mixture was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to afford **8a** in 33% yield (780 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.65 (m, 1H), 7.51-7.48 (m, 1H), 7.44-7.37 (m, 2H), 7.33-7.29 (m, 4H), 7.27-7.18 (m, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.46 (dt, *J* = 16.0, 7.2 Hz, 1H), 3.88 (dd, *J* = 7.2, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 151.1, 141.5, 136.8, 134.1, 128.6, 127.8, 126.5, 124.8, 124.3, 122.1, 119.9, 110.5, 32.6; HR-MS ($C_{16}H_{14}ON$; $[M+H]^+$, pos. ESI): calcd: 236.1070, found: 236.1067.

Derivatization of Allylated Benzoxazole 3aa

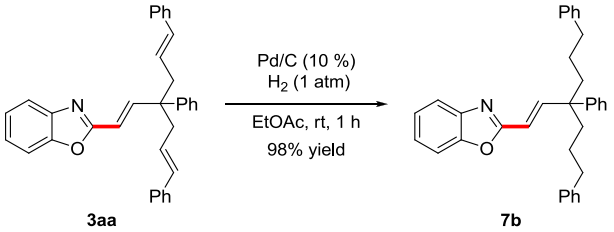
1 Synthesis of **7a**



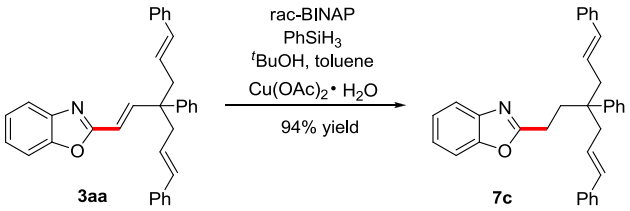
A solution of **3aa** (50 mg, 0.107 mmol) in MeOH (2 mL) and THF (1 mL) was hydrogenated on 10% Pd/C (5 mg, 10 mol %) under 1 atom of H_2 for 43 h. After removal of catalyst, the solvent was removed and the residue was purified by column chromatography on silica gel (cyclohexane/toluene = 1/1) to afford **7a** in 84% yield (42.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.58 (m, 1H), 7.45-7.38 (m, 1H), 7.29-7.19 (m, 10H), 7.18-7.11 (m, 3H), 7.08-7.05 (m, 4H), 2.55-2.50 (m, 6H), 2.28-2.17 (m, 2H), 1.73 (q, *J* = 8.0 Hz, 4H), 1.51-1.30 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 150.9, 146.1, 142.3, 141.5, 128.4, 128.3, 126.5, 125.9, 125.8, 124.5, 124.1, 119.6, 110.3, 43.1, 36.4, 36.3, 34.9, 25.3, 23.6; HR-MS

($C_{34}H_{36}ON$; $[M+H]^+$, pos. ESI): calcd: 474.2791, found: 474.2789.

2 Synthesis of **7b**

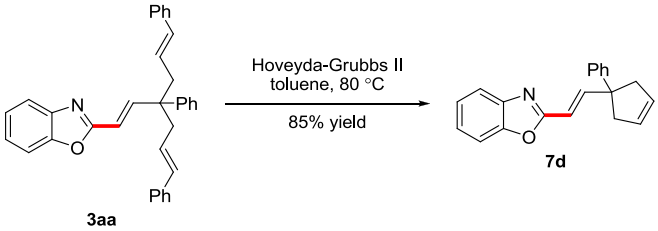


A solution of **3aa** (47.6 mg, 0.102 mmol) in EtOAc (2 mL) was hydrogenated on 10% Pd/C (4.7 mg, 10 mol %) under 1 atom of H_2 for 1 h. After removal of catalyst, the solvent was removed and the residue was purified by column chromatography on silica gel (cyclohexane/toluene = 1/1) to afford **7b** in 98% yield (47 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.65 (m, 1H), 7.52-7.44 (m, 1H), 7.36-7.28 (m, 5H), 7.28-7.22 (m, 6H), 7.121-7.16 (m, 3H), 7.13-7.10 (m, 4H), 6.45 (d, *J* = 16.8 Hz, 1H), 2.59 (t, *J* = 7.6 Hz, 4H), 2.07-1.85 (m, 4H), 1.56-1.38 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 150.6, 150.4, 144.5, 142.13, 142.1, 128.5, 128.4, 128.38, 127.3, 126.5, 125.9, 125.1, 124.5, 119.9, 115.5, 110.4, 48.0, 37.1, 36.4, 25.8; HR-MS ($C_{34}H_{34}ON$; $[M+H]^+$, pos. ESI): calcd: 472.2635, found: 472.2634.

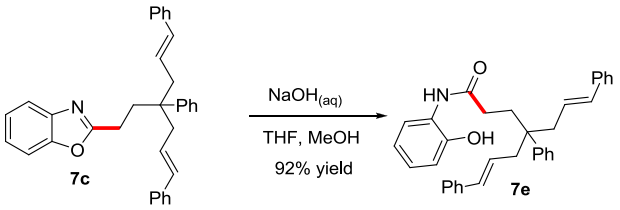


A solution of **3aa** (46.8 mg, 0.10 mmol), $Cu(OAc)_2$ H_2O (2.0 mg, 0.01 mmol), *rac*-BINAP (6.2 mg, 0.01 mmol), and *t*-BuOH (38 μL, 0.40 mmol) in toluene (1 mL) was stirred at 0 ℃ for 15 min. $PhSiH_3$ (49 μL, 0.40 mmol) was then added dropwise. The mixture was stirred at 0 ℃ for 2 h, then at room temperature for 24 h. The reaction was quenched carefully with silica gel (*ca.* 250 mg), and the resulting suspension was concentrated *in vacuo* and the residue was purified by column chromatography to give the reduced product 7c in 94% yield (44 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.61 (m, 1H), 7.50-7.44 (m, 2H), 7.44-7.37 (m,

3H), 7.33-7.25 (m, 11H), 7.25-7.17 (m, 2H), 6.48 (d, *J* = 15.6 Hz, 2H), 6.15-6.02 (m, 2H), 2.95-2.68 (m, 6H), 2.50-2.37 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 150.9, 144.9, 141.4, 137.6, 133.4, 128.6, 128.56, 127.2, 126.7, 126.4, 126.2, 125.9, 124.5, 124.1, 119.6, 110.3, 44.6, 41.0, 35.3, 23.7; HR-MS ($C_{34}H_{32}ON$; $[M+H]^+$, pos. ESI): calcd: 470.2478, found: 470.2480.



A 10-mL screw-top schlenk tube was charged with **3aa** (233.8 mg, 0.5 mmol), Hoveyda-Grubbs II catalyst (15.7 mg, 5 mol %), and toluene (5 mL) at rt. Then, the mixture was heated at 80 ℃ for 36 h. The reaction mixture was cooled to rt and purified by column chromatography on silica gel (petroleum ether/dichloromethane = 1:1) to give **7d** in 85% yield (136.4 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 1H), 7.45-7.42 (m, 1H), 7.41-7.31 (m, 4H), 7.31-7.27 (m, 3H), 7.27-7.23 (m, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 5.88-5.82 (m, 2H), 3.05-2.84 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 151.6, 150.4, 146.0, 142.1, 129.2, 128.7, 127.4, 126.6, 125.0, 124.4, 119.8, 114.0, 110.3, 53.6, 44.4; HR-MS ($C_{20}H_{18}ON$; $[M+H]^+$, pos. ESI): calcd: 288.1383, found: 288.1382.



To a solution of benzoxazole **7c** (47.2 mg, 0.1 mmol) in THF (1.0 mL) and MeOH (1.0 mL) was added 2 M aqueous NaOH solution (1.0 mL) and the reaction was heated at 70 ℃ for 18 h. After cooling to room temperature, the mixture was acidified with 10% aqueous HCl solution (10 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (20:1→5:1 petroleum ether

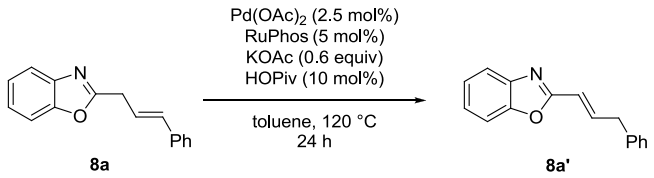
/EtOAc) gave the amide **7e** as a red oil (44.7 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.41 (d, *J* = 4.4 Hz, 4H), 7.33-7.26 (m, 9H), 7.24-7.15 (m, 3H), 7.10-7.06 (m, 1H), 7.01-6.94 (m, 1H), 6.82-6.71 (m, 2H), 6.46 (d, *J* = 16.0 Hz, 2H), 6.12-6.00 (m, 2H), 2.70 (qd, *J* = 14.8, 6.8 Hz, 4H), 2.25 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 148.7, 144.9, 137.4, 133.4, 128.8, 128.7, 128.6, 127.4, 127.2, 126.7, 126.5, 126.2, 125.9, 125.6, 122.0, 120.4, 119.9, 44.4, 41.1, 34.5, 32.0; HR-MS ($C_{34}H_{33}O_2NNa$; $[M+Na]^+$, pos. ESI): calcd: 510.2404, found: 510.2408.

Experimental details for mechanistic studies

Study of Olefin Isomerization

To gain insights into the regioselectivity of the products, isomerization studies were performed with **8a**. Under the standard reaction conditions, **8a** can isomerize to **8a'** with the ratio of 1.7:1. However, in the absence of $Pd(OAc)_2$ and Ruphos, only lower isomerization was observed. Isomerization studies indicated that isomer **8a'** was mainly formed via a palladium-catalyzed process.

Table S5. Olefin isomerization Experiments[a]



entry	variation from the condition above	ratio of **8a** to **8a'**[b]
1	none	1.7:1
2	no KOAc	1.6:1
3	no HOPiv	1.8:1
4	no $Pd(OAc)_2$, RuPhos	12.5:1

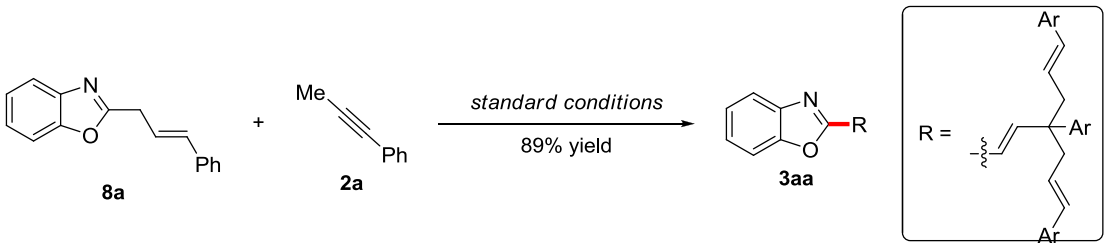
[a]Reaction conditions (unless otherwise specified): **8a** (0.1 mmol), $Pd(OAc)_2$ (2.5 mol %), RuPhos (5 mol %), KOAc (0.6 equiv), HOPiv (10 mol %), toluene (0.2 mL), 24 h, 120 °C. [b]determined by ^{1}H-NMR spectroscopy of the crude mixture.

A 2 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $Pd(OAc)_2$ (0.6 mg, 2.5 μmol, 2.5 mol%), RuPhos (2.3 mg, 5 μmol, 5 mol%), KOAc (5.9 mg, 0.06 mmol, 0.6 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards HOPiv (4.8 M in toluene) (2.1 μL, 0.01 mmol, 10 mol%), **8a** (0.1 mmol, 1.0 equiv) and 0.2 ml of freshly distilled toluene were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 120 ^{o}C for 24 hours. The mixture was cooled down to room temperature. After the solvents were removed

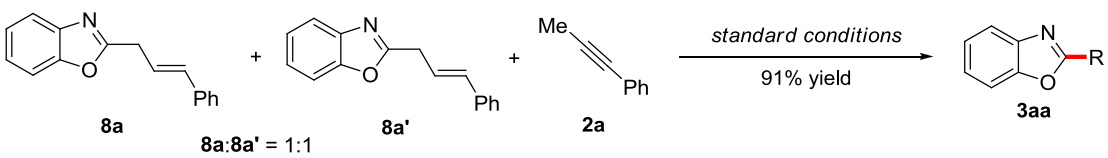
under reduced pressure, the ratio of **8a**/**8a'**was determined by ^{1}H NMR of this mixture.

The test of the reaction intermediates

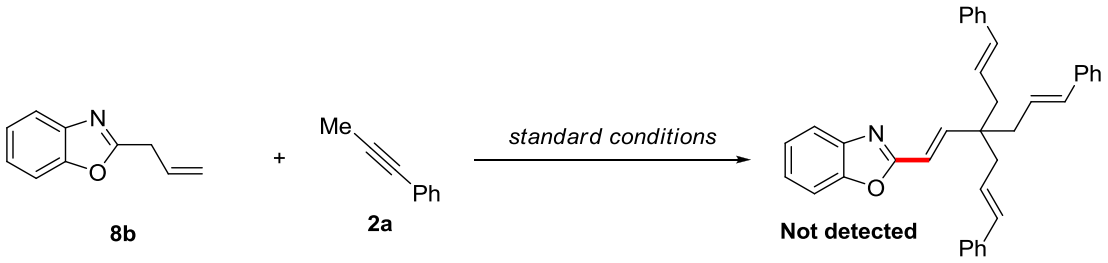
The reaction of 8a with alkyne



A 2 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $Pd(OAc)_2$ (0.6 mg, 2.5 μmol, 2.5 mol%), RuPhos (2.3 mg, 5 μmol, 5 mol%), KOAc (5.9 mg, 0.06 mmol, 0.6 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards HOPiv (4.8 M in toluene) (2.1 μL, 0.01 mmol, 10 mol%), **8a** (23.5 mg, 0.1 mmol, 1.0 equiv), **2a** (34.8 mg, 0.3 mmol, 3.0 equiv) and 0.2 ml of freshly distilled toluene were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 120 ^{o}C for 24 hours. The mixture was cooled down to room temperature. After the solvents were removed under reduced pressure, the crude mixture was measured by ^{1}H NMR. Then, the residue was purified with column chromatography on silica gel (toluene) afford **3aa** (41.8 mg, 89% yield) after drying in vacuo.

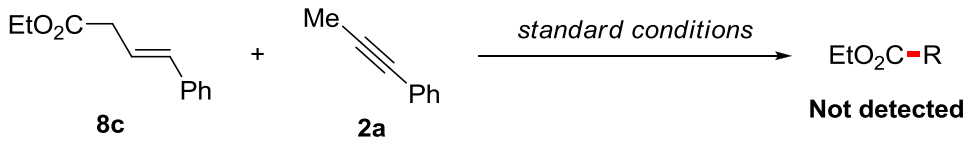


A 2 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $Pd(OAc)_2$ (0.6 mg, 2.5 μmol, 2.5 mol%), RuPhos (2.3 mg, 5 μmol, 5 mol%), KOAc (5.9 mg, 0.06 mmol, 0.6 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards HOPiv (4.8 M in toluene) (2.1 μL, 0.01 mmol, 10 mol%), a mixture of **8a** and **8a'** in 1:1 (23.5 mg, 0.1 mmol, 1.0 equiv), **2a** (34.8 mg, 0.3 mmol, 3.0 equiv) and 0.2 ml of freshly distilled toluene were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 120 ^{o}C for 24 hours. The mixture was cooled down to room temperature. After the solvents were removed under reduced pressure, the crude mixture was measured by ^{1}H NMR. Then, the residue was purified with column chromatography on silica gel (toluene) afford **3aa** (42.6 mg, 91% yield) after drying in vacuo.



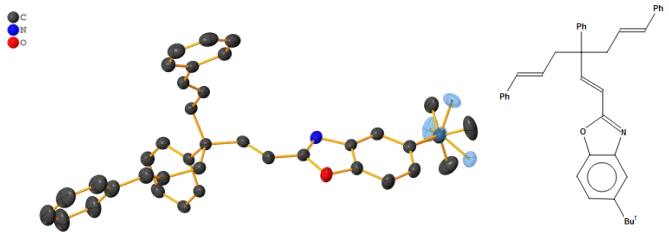
A 2 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $Pd(OAc)_2$ (0.6 mg, 2.5 μmol, 2.5 mol%), RuPhos (2.3 mg, 5 μmol, 5 mol%), KOAc (5.9 mg, 0.06 mmol, 0.6 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards HOPiv (4.8 M in toluene) (2.1 μL, 0.01 mmol, 10 mol%), **8b** (15.9 mg, 0.1 mmol, 1.0 equiv), **2a** (46.5 mg, 0.4 mmol, 4.0 equiv) and 0.2 ml of freshly distilled toluene were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 120 ^{o}C for 24 hours. The mixture was cooled down to room temperature. After the solvents were removed under reduced pressure, the crude mixture was

measured by ^{1}H NMR and no desired product could be detected.



A 2 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $Pd(OAc)_2$ (0.6 mg, 2.5 μmol, 2.5 mol%), RuPhos (2.3 mg, 5 μmol, 5 mol%), KOAc (5.9 mg, 0.06 mmol, 0.6 equiv). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards HOPiv (4.8 M in toluene) (2.1 μL, 0.01 mmol, 10 mol%), **8c** (19.0 mg, 0.1 mmol, 1.0 equiv), **2a** (46.5 mg, 0.4 mmol, 4.0 equiv) and 0.2 ml of freshly distilled toluene were added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was stirred at 120 ^{o}C for 24 hours. The mixture was cooled down to room temperature. After the solvents were removed under reduced pressure, the crude mixture was measured by ^{1}H NMR. No desired product could be detected.

X-Ray crystal structures of 3fa



Experimental. Single colourless block-shaped crystals of (**Breit_JZ_169_0m_a**) were recrystallised from hexane by slow evaporation. A suitable crystal (0.18×0.17×0.06) mm^3 was selected and mounted on a MITIGEN holder in perfluoroether oil on a Bruker SMART APEX2 area detector diffractometer. The crystal was kept at T = 100 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2018/1 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

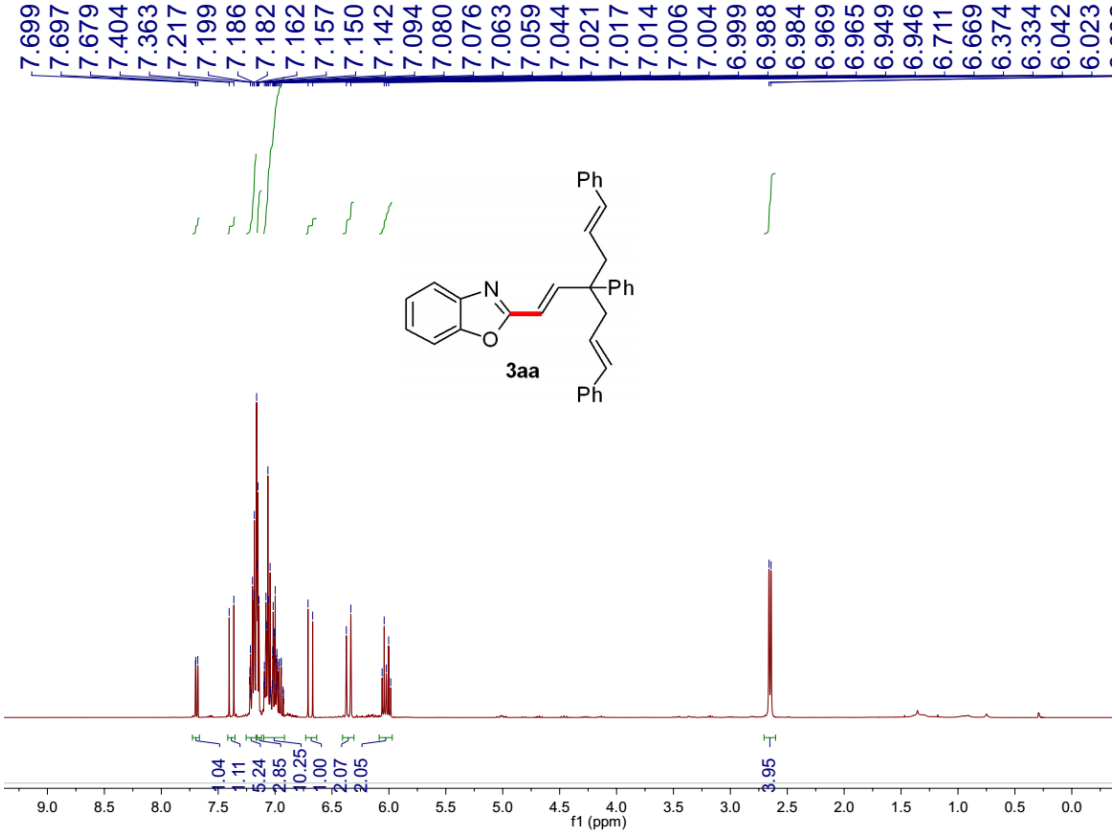
Compound	**Breit_JZ_169_0 m_a**
CCDC	1810746
Formula	$C_{38}H_{37}NO$
$D_{calc.}$/ g cm^{-3}	1.132
μ/mm^{-1}	0.067
Formula Weight	523.68
Colour	colourless
Shape	block
Size/mm^3	0.18×0.17×0.06
T/K	100
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	15.211(11)
b/Å	9.492(8)
c/Å	22.154(15)
α/°	90
β/°	106.112(11)
γ/°	90
V/Å^3	3073(4)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK_α
Θ_{min}/°	1.393
Θ_{max}/°	27.008
Measured Refl.	45257
Independent Refl.	6659
Reflections Used	4841
R_{int}	0.0415
Parameters	398
Restraints	535
Largest Peak	0.288
Deepest Hole	-0.230
GooF	1.017
wR_2 (all data)	0.1342
wR_2	0.1223
R_1 (all data)	0.0762
R_1	0.0520

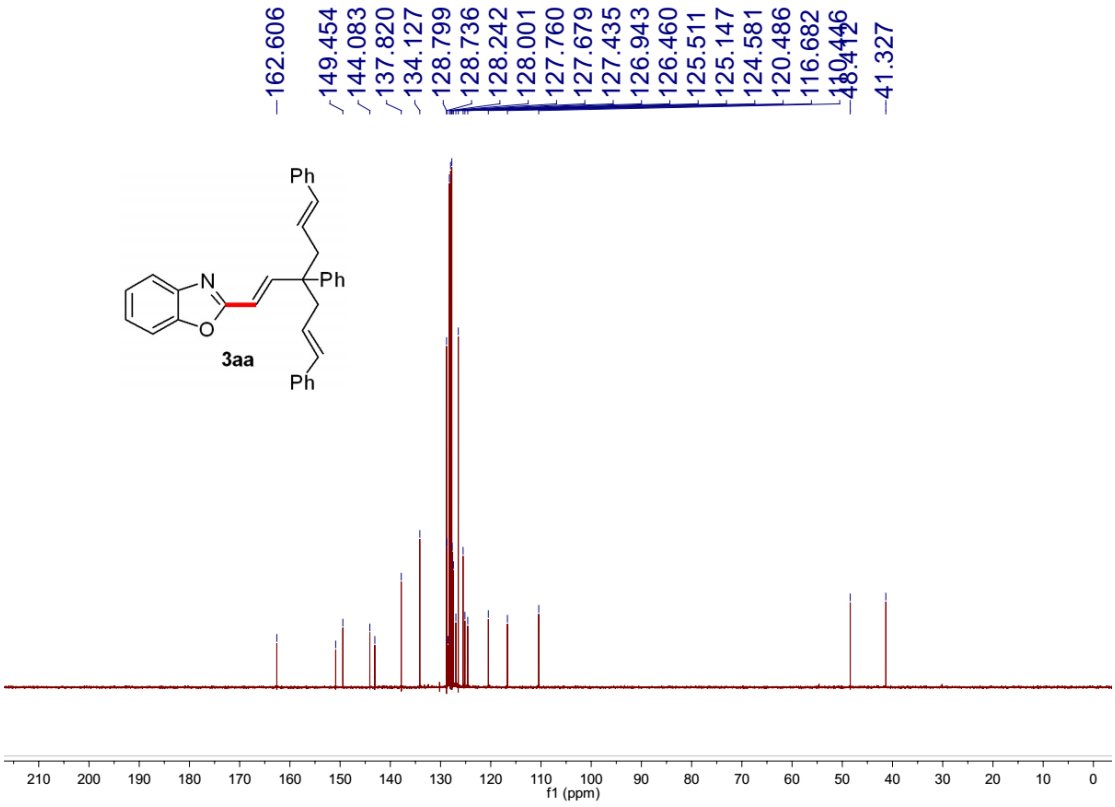
References

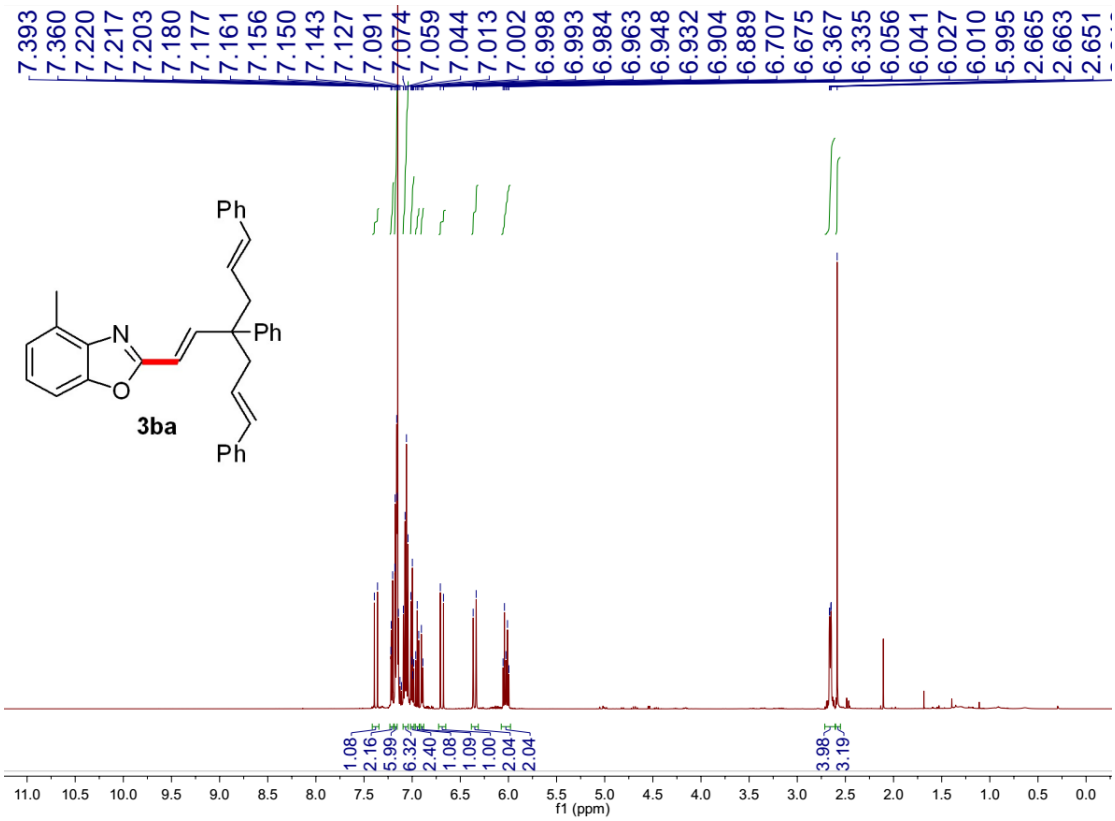
[1] (a) W. Xie, J. H. Yoon and S. Chang, *J. Am. Chem. Soc.*, 2016**, 138**, 12605; (b) D. Yu, L. Lu and Q. Shen, *Org. Lett*., 2013, **15**, 940; (c) Q. Liu, P. Wu, Y. Yang, Z. Zeng, J. Liu, H. Yi and A.-W. Lei, *Angew. Chem. Int. Ed*., 2012, **51**, 4666; (d) S. H. Cho, J. Y. K. S. Y. Lee and S. Chang, *Angew. Chem. Int. Ed*., 2009, **48**, 9127.

[2] F. Babudri, S. Florio and L. Ronzini, *Tetrahedron*, 1986, **42**, 3905.

Copies of NMR spectra



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7.044
7.013
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6.993
6.984
6.963
6.948
6.932
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6.707
6.675
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6.056
6.041
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6.010
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2.651
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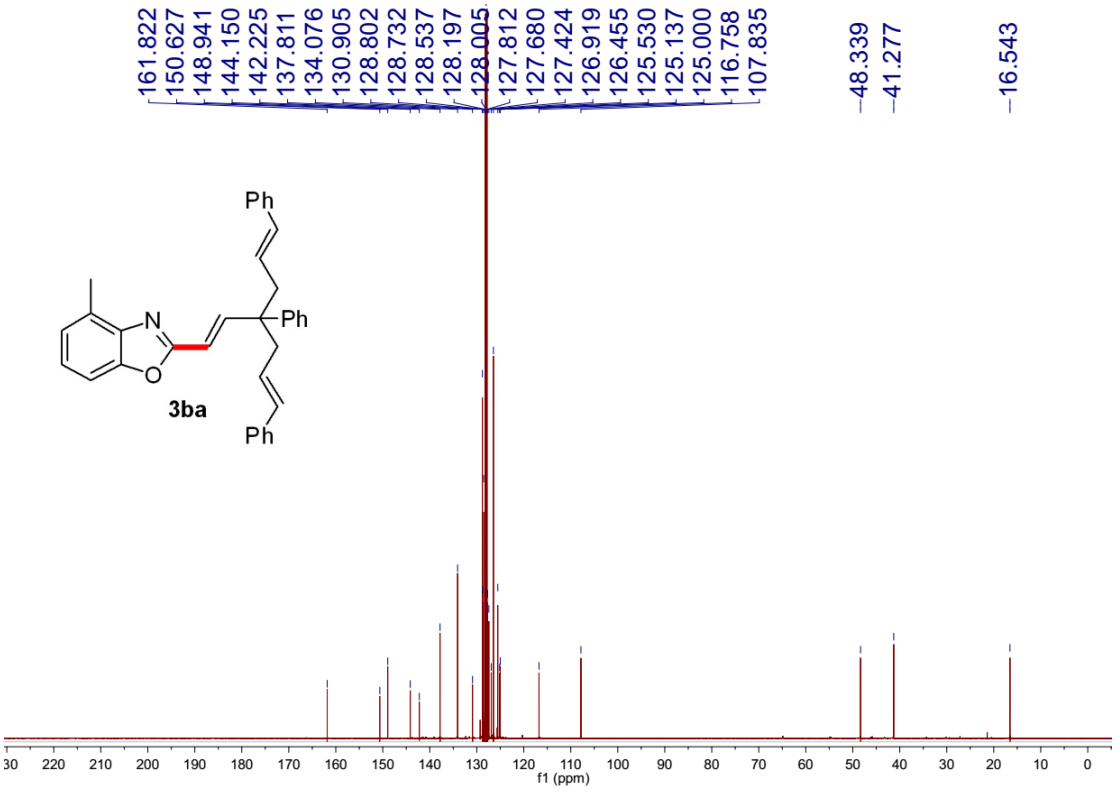
3.19
f1 (ppm)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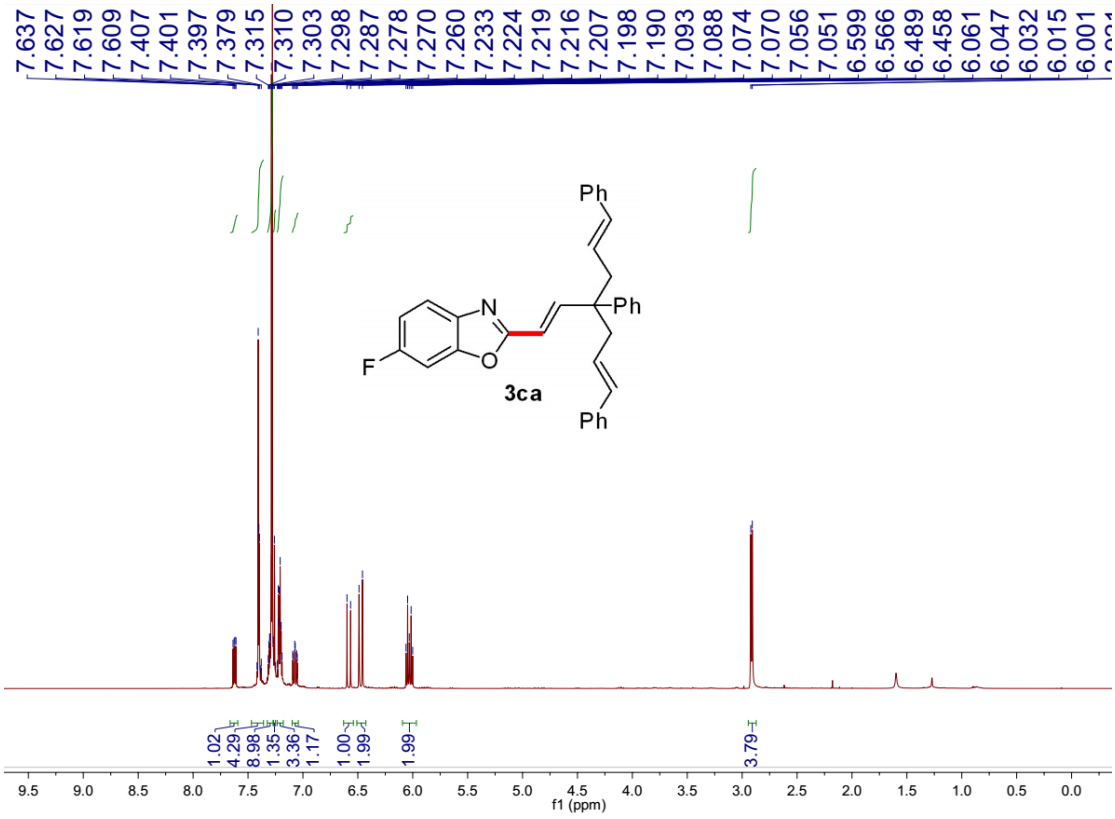
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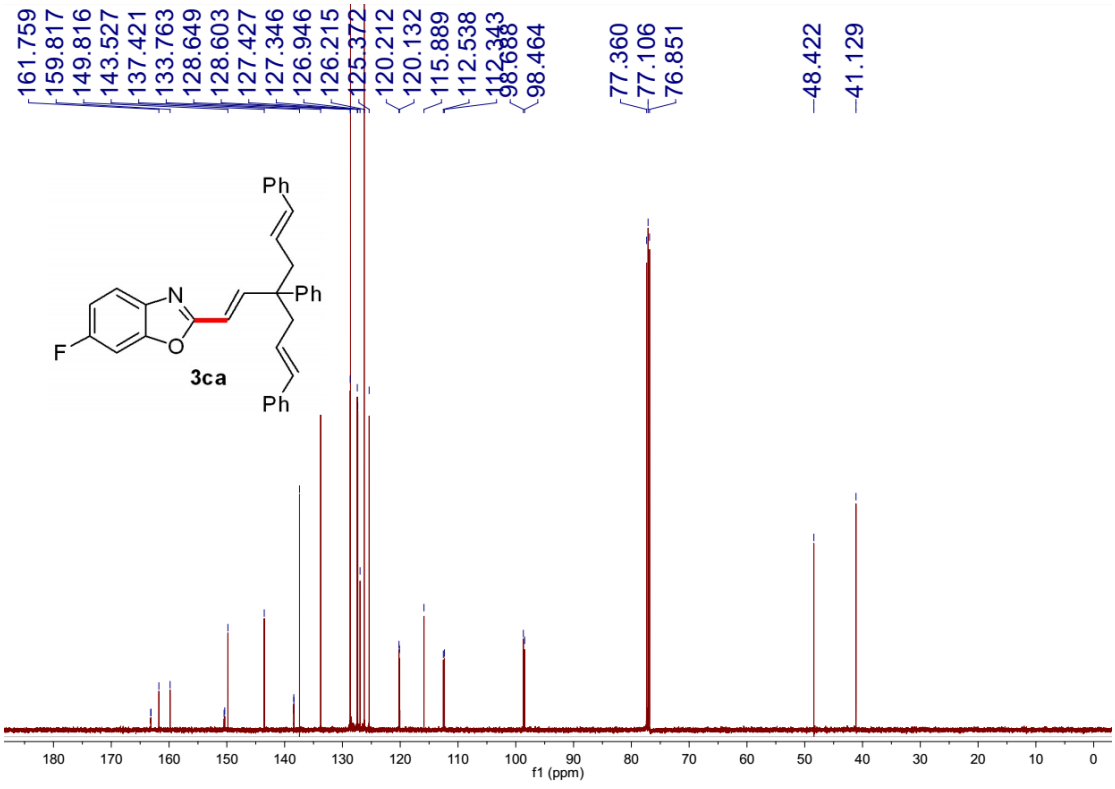
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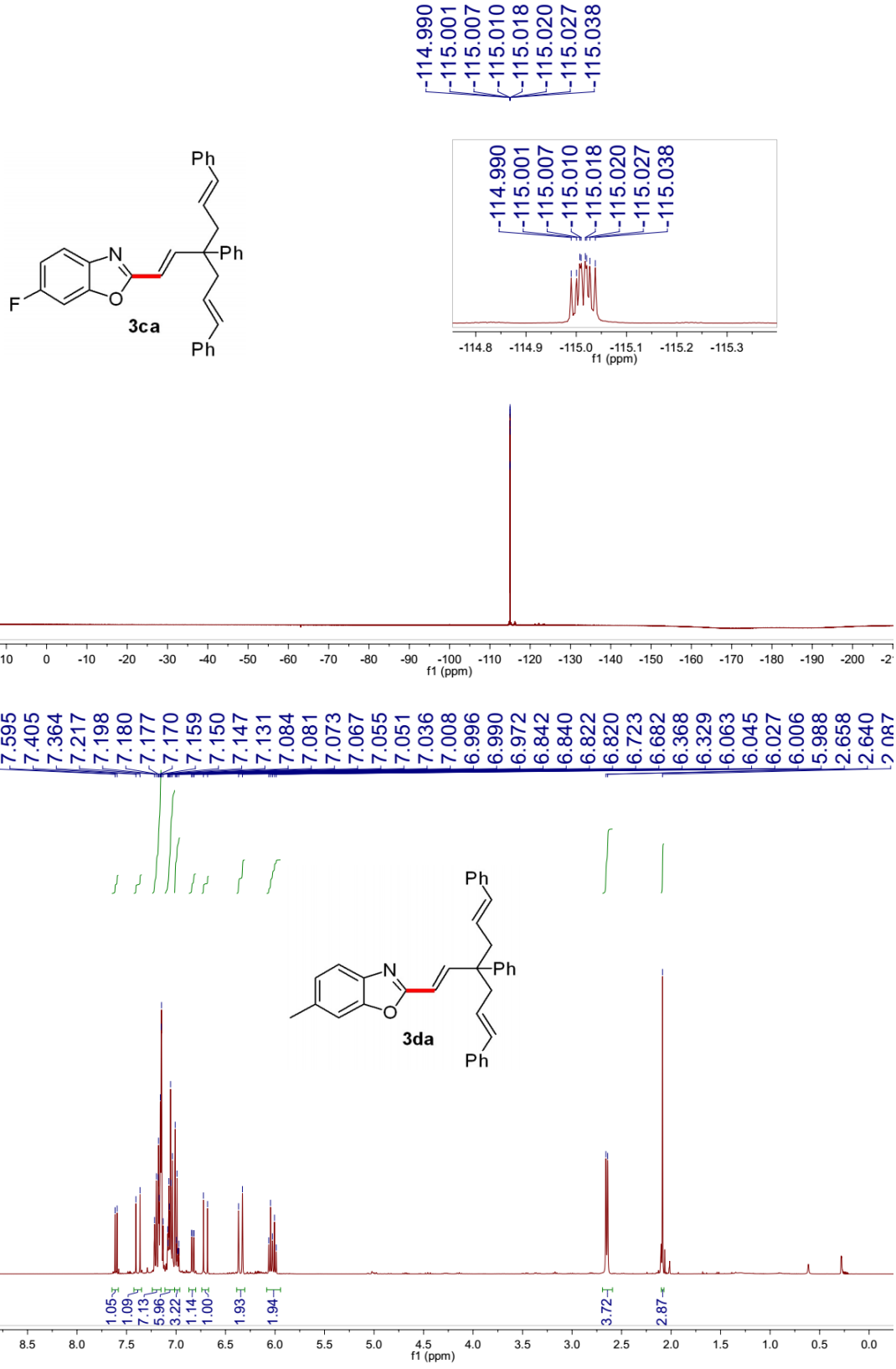
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f1 (ppm)
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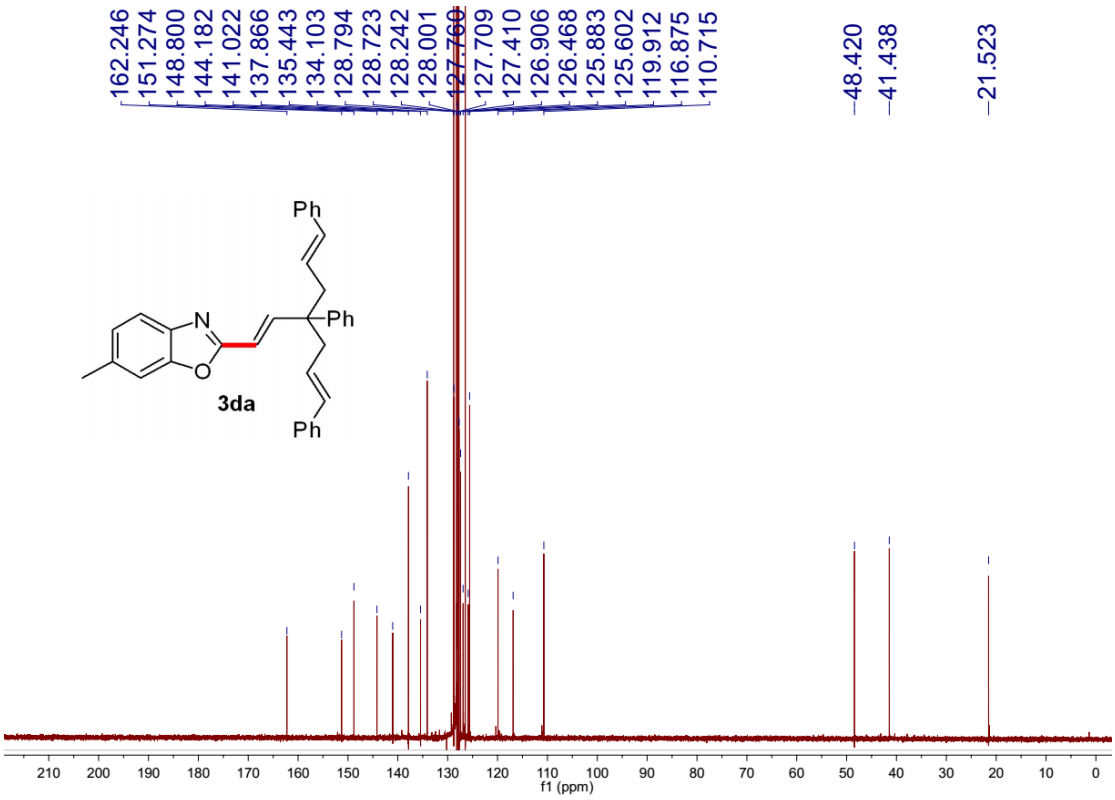
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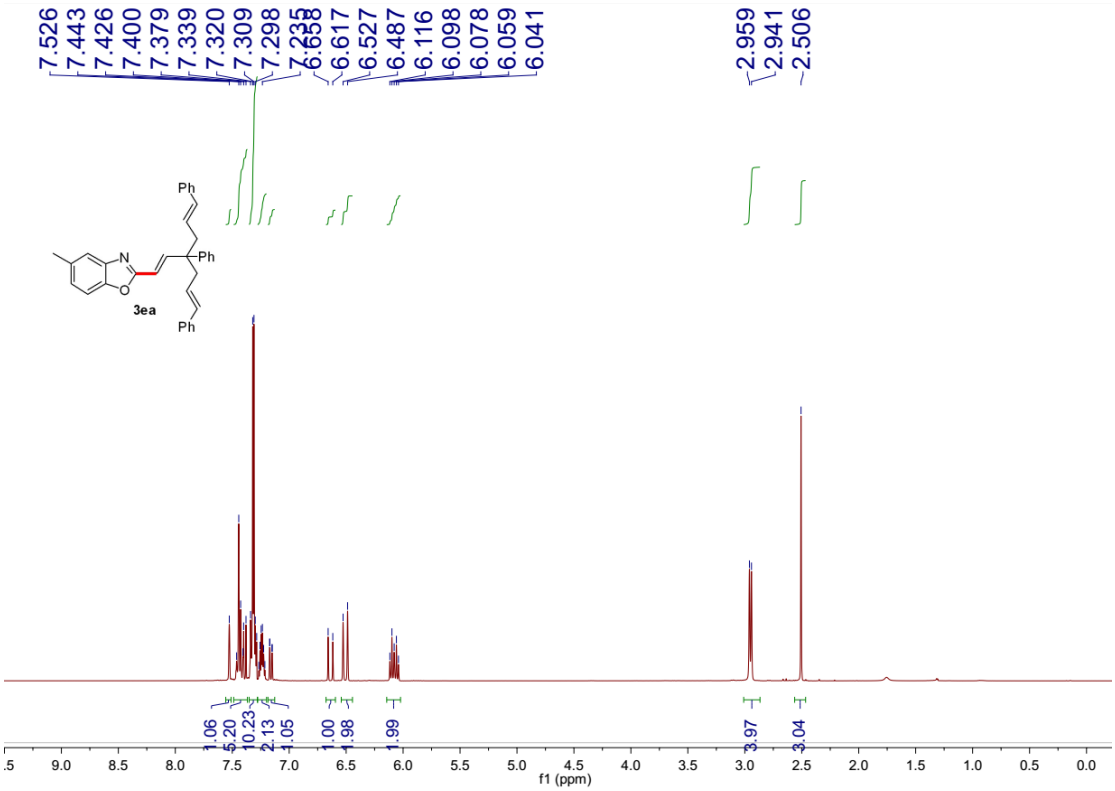
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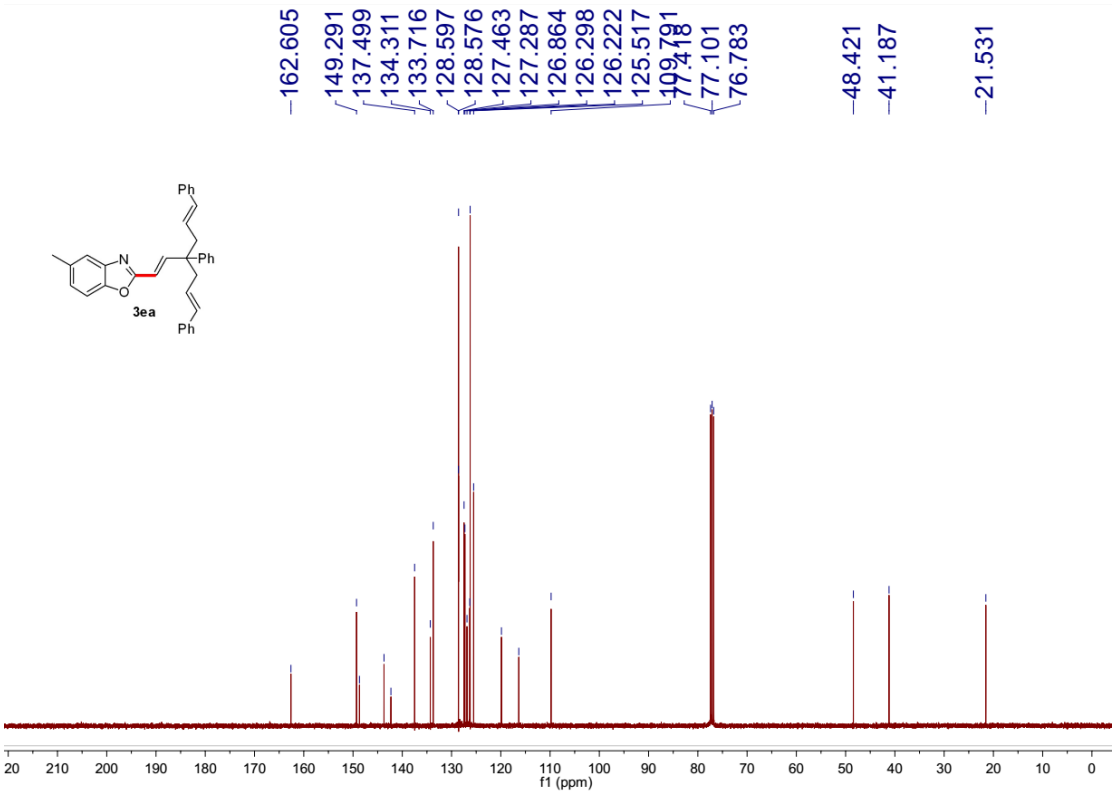
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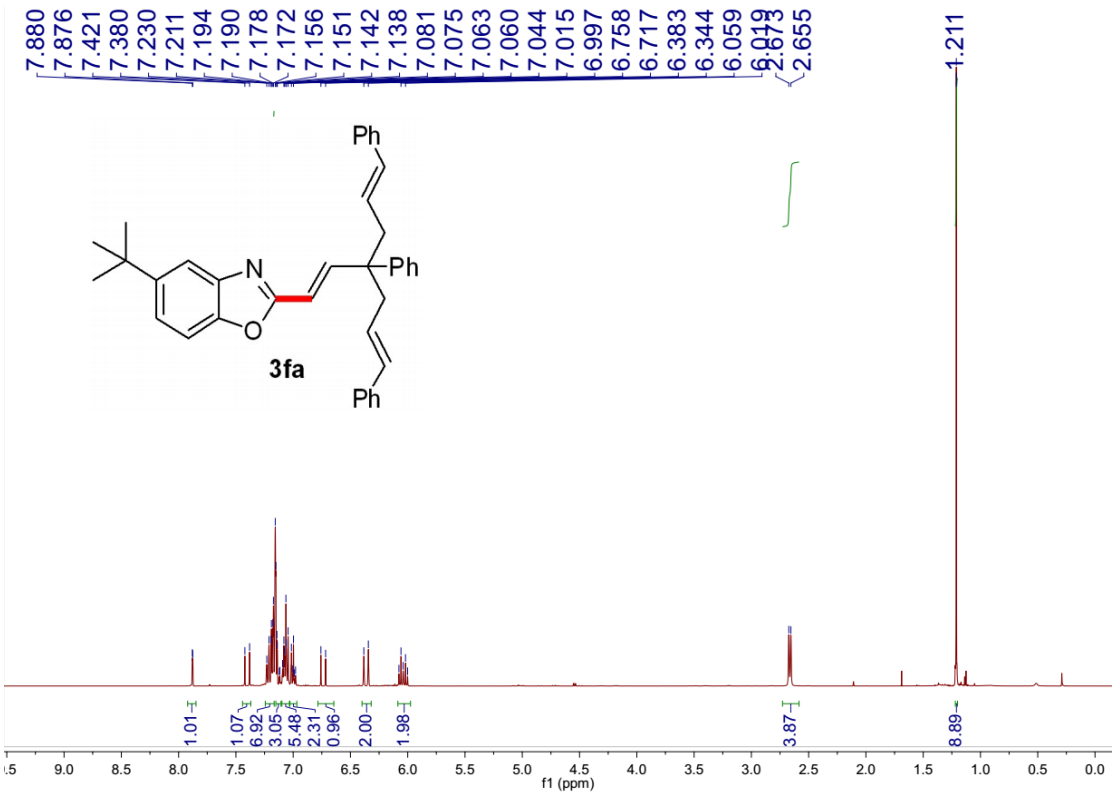
f1 (ppm)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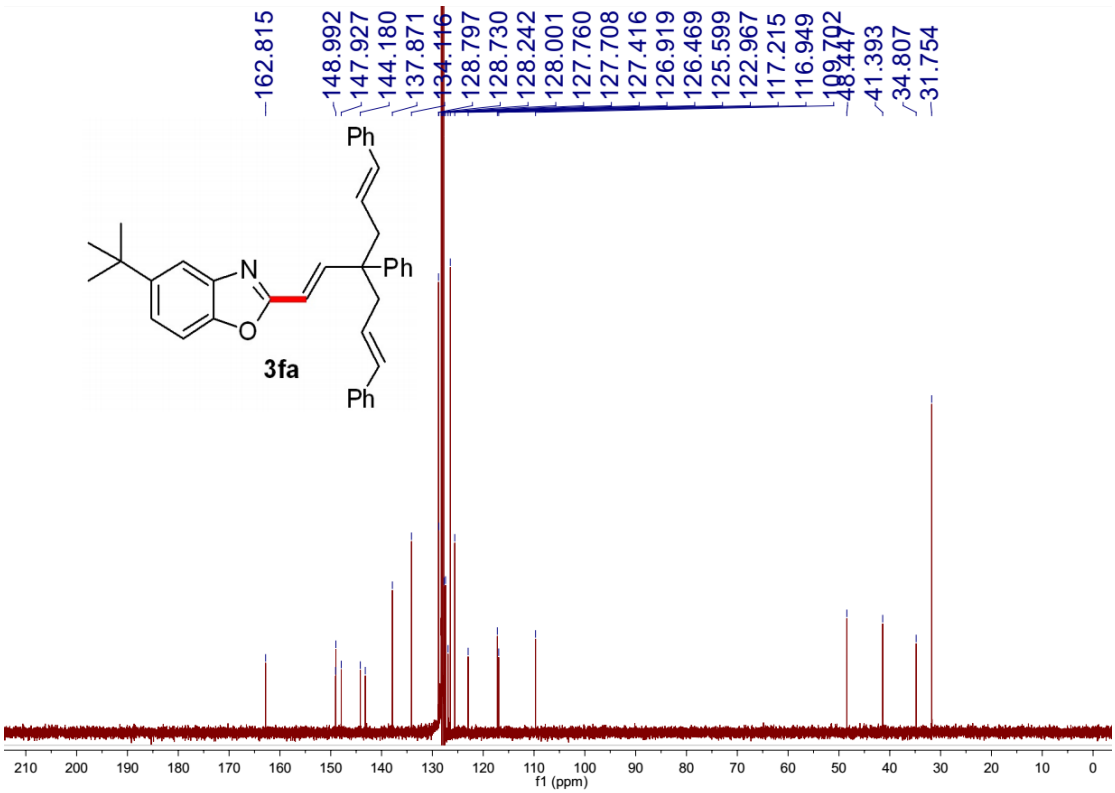
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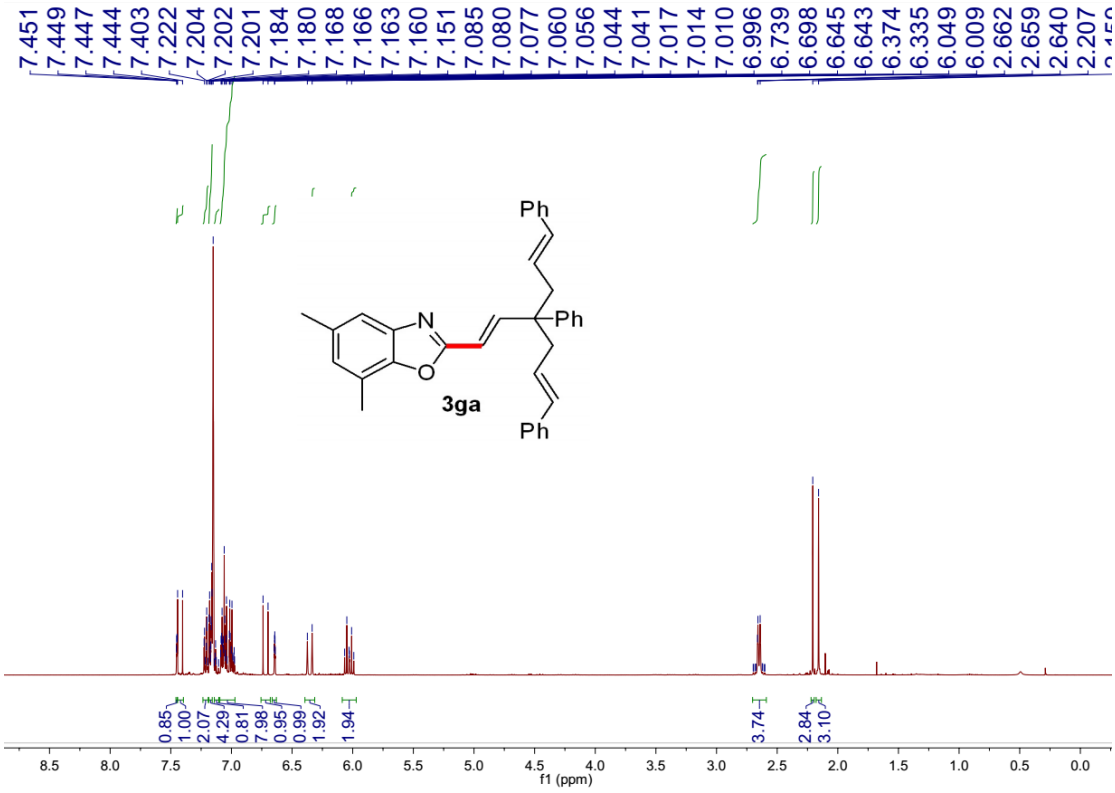
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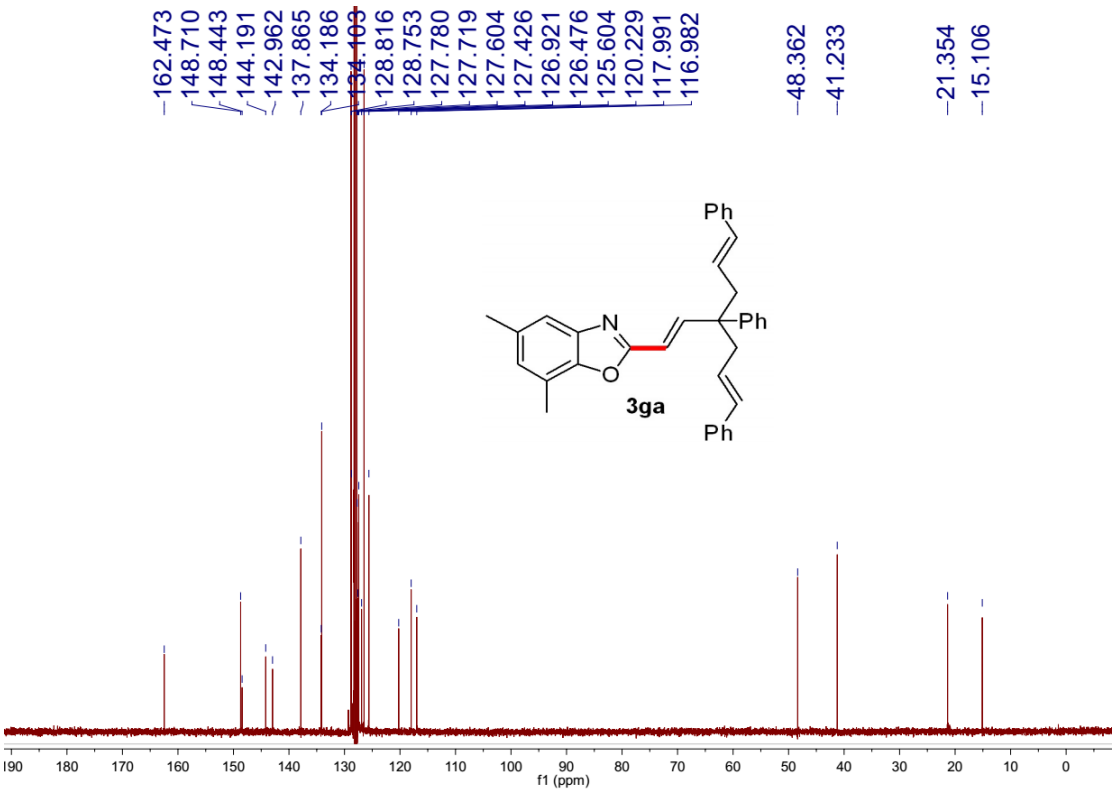
f1 (ppm)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148.710
148.443
144.191
142.962
137.865
134.186
134.103
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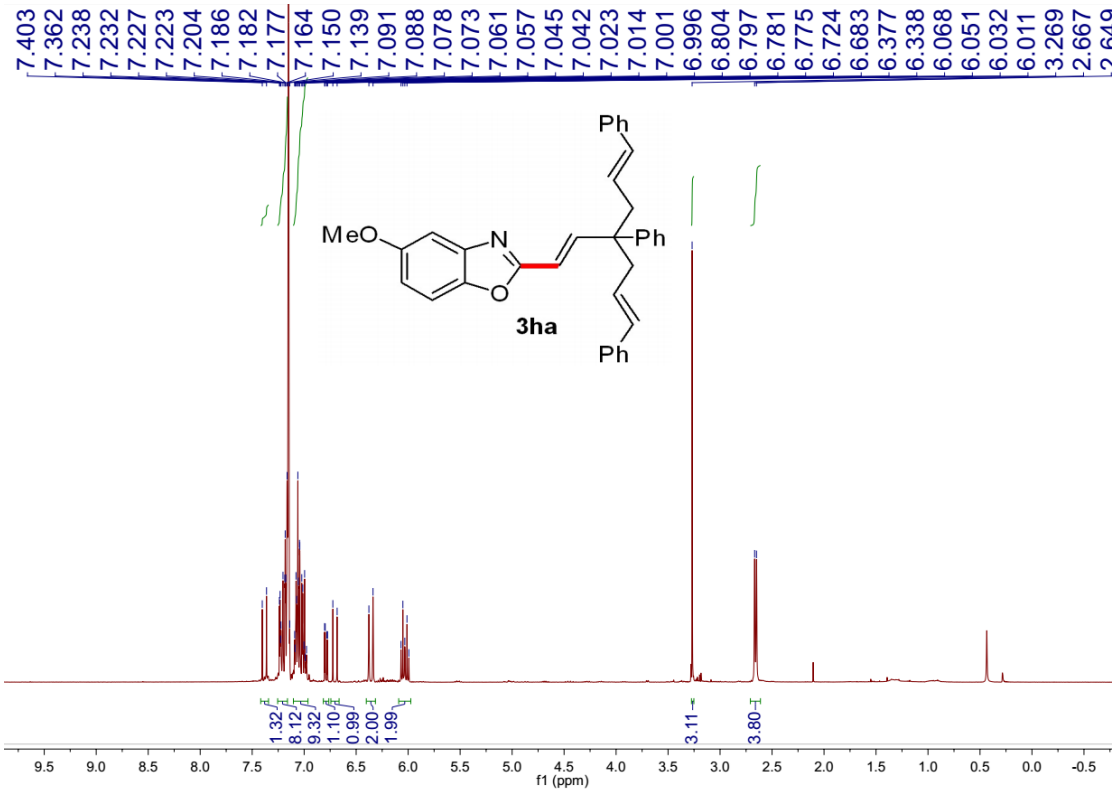
128.753
127.780
127.719
127.604
127.426
126.921
126.476
125.604
120.229
117.991
116.982
48.362
41.233
21.354
15.106
Ph
N
O
Ph
Ph
3ga
f1 (ppm)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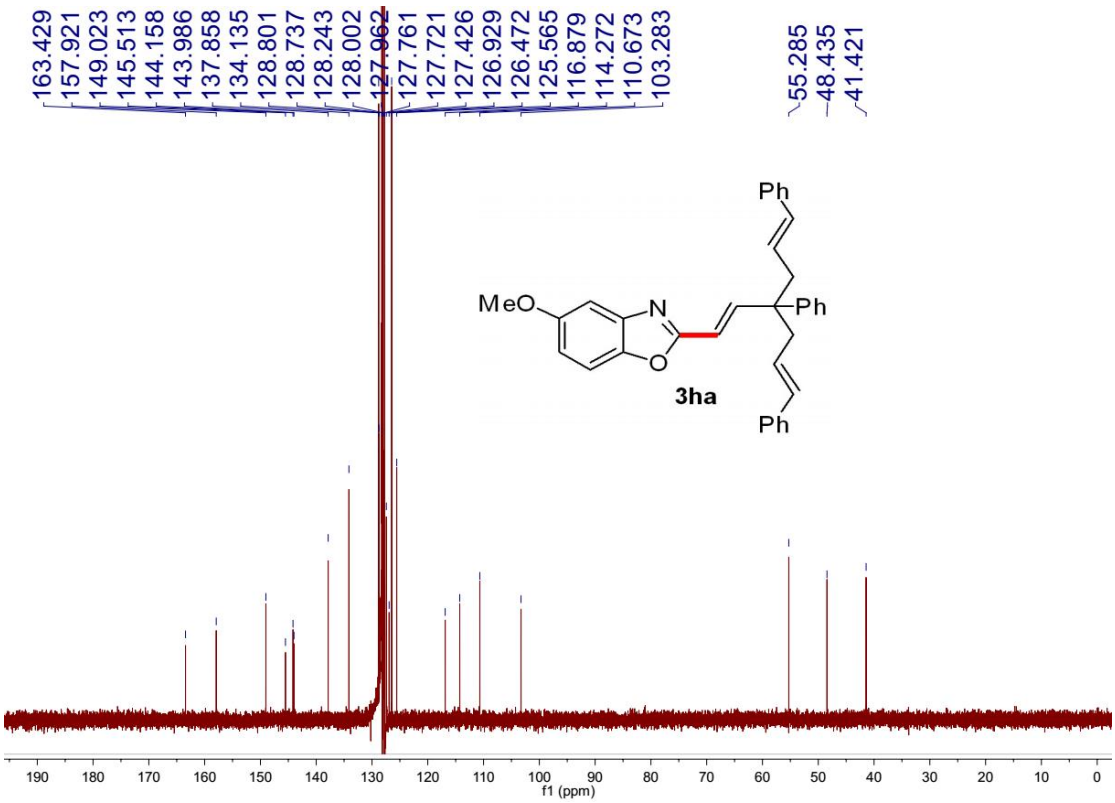
7.362
7.238
7.232
7.227
7.223
7.204
7.186
7.182
7.177
7.164
7.150
7.139
7.091
7.088
7.078
7.073
7.061
7.057
7.045
7.042
7.023
7.014
7.001
6.996
6.804
6.797
6.781
6.775
6.724
6.683
6.377
6.338
6.068
6.051
6.032
6.011
3.269
2.667
MeO
N
O
Ph
Ph
Ph
3ha
1.32
8.12
9.32
1.10
0.99
2.00
1.99
3.11
3.80
f1 (ppm)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134.135
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128.737
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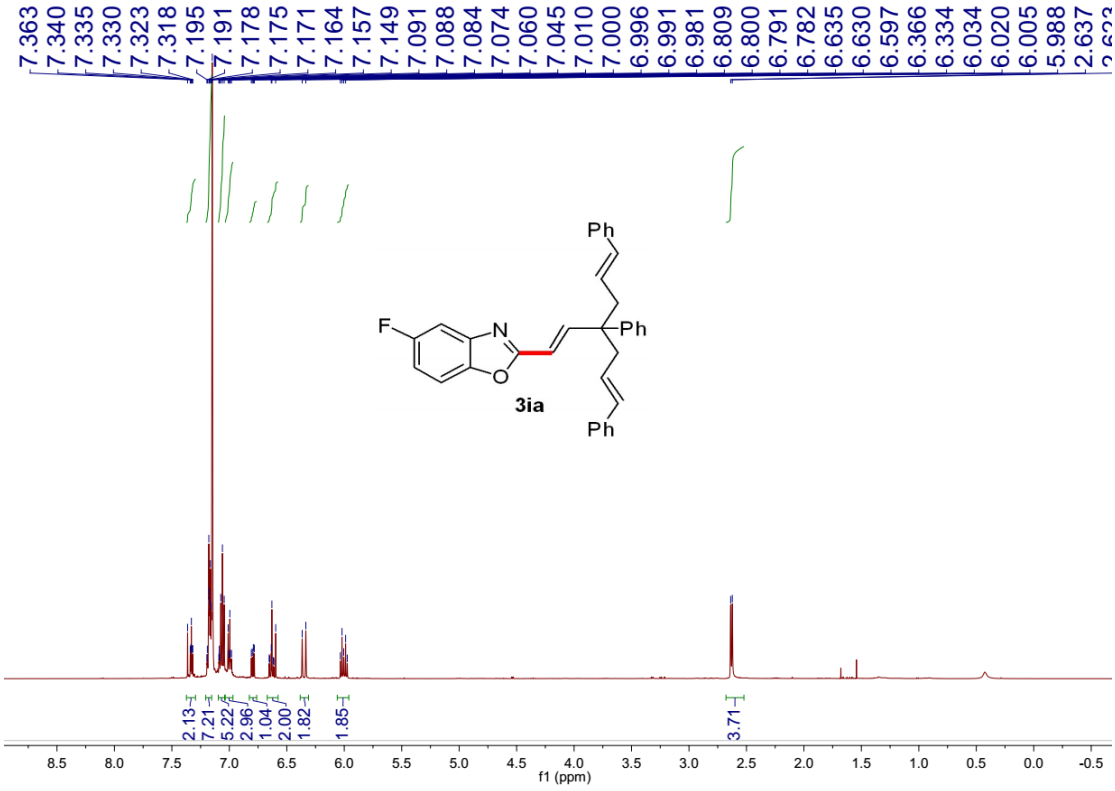
127.962
127.761
127.721
127.426
126.929
126.472
125.565
116.879
114.272
110.673
103.283
55.285
48.435
41.421
MeO
N
O
Ph
Ph
Ph
3ha
f1 (ppm)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7.330
7.323
7.318
7.195
7.191
7.178
7.175
7.171
7.164
7.157
7.149
7.091
7.088
7.084
7.074
7.060
7.045
7.010
7.000
6.996
6.991
6.981
6.809
6.800
6.791
6.782
6.635
6.630
6.597
6.366
6.334
6.034
6.020
6.005
5.988
2.637
F
N
O
Ph
Ph
Ph
3ia
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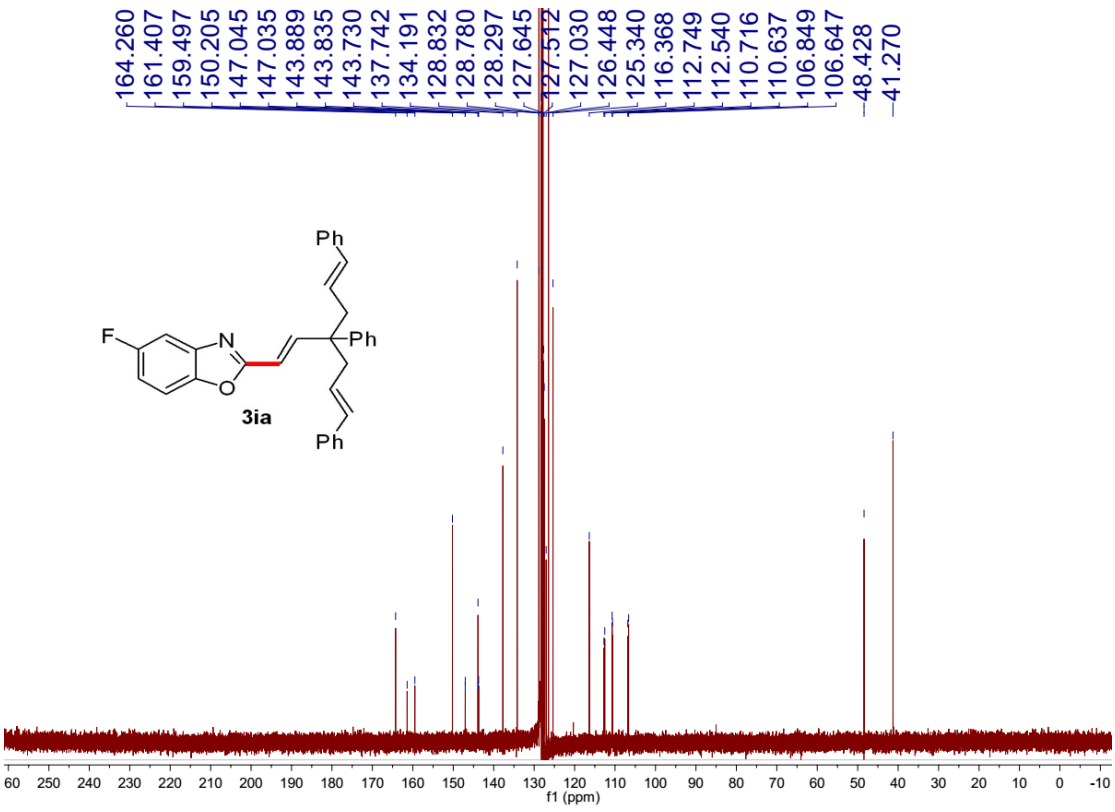
7.21
5.22
2.96
1.04
2.00
1.82
1.85
3.71
f1 (ppm)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161.407
159.497
150.205
147.045
147.035
143.889
143.835
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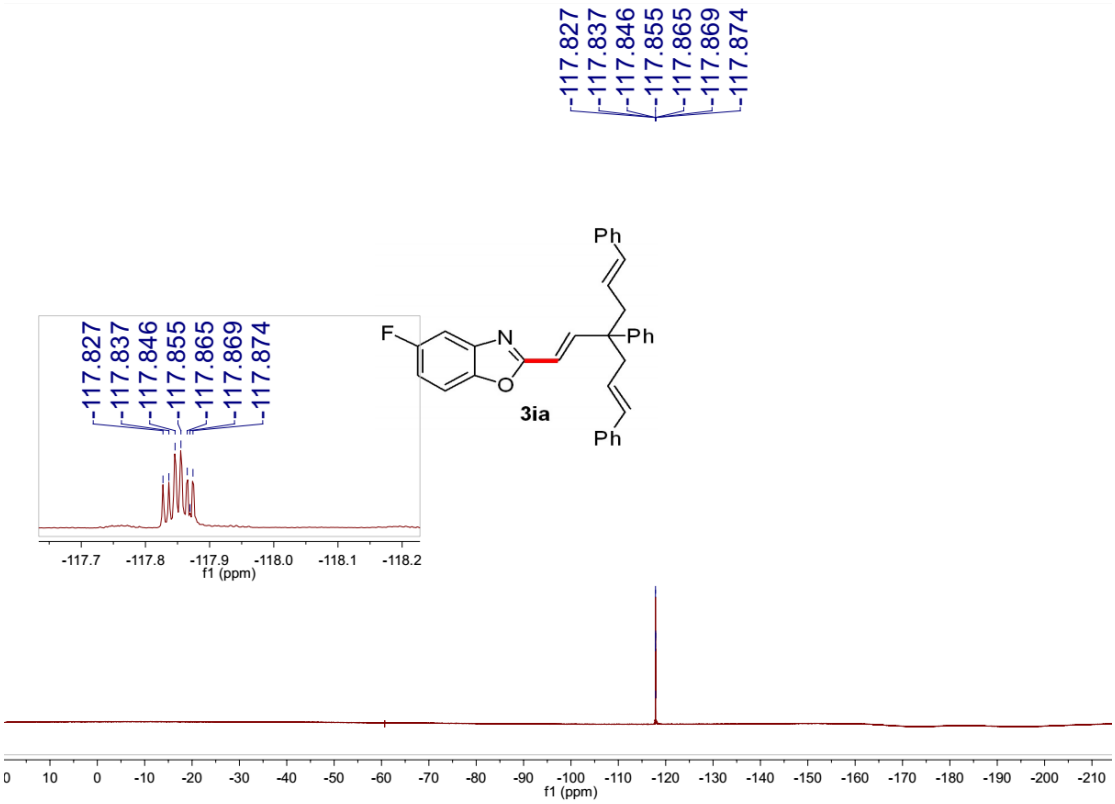
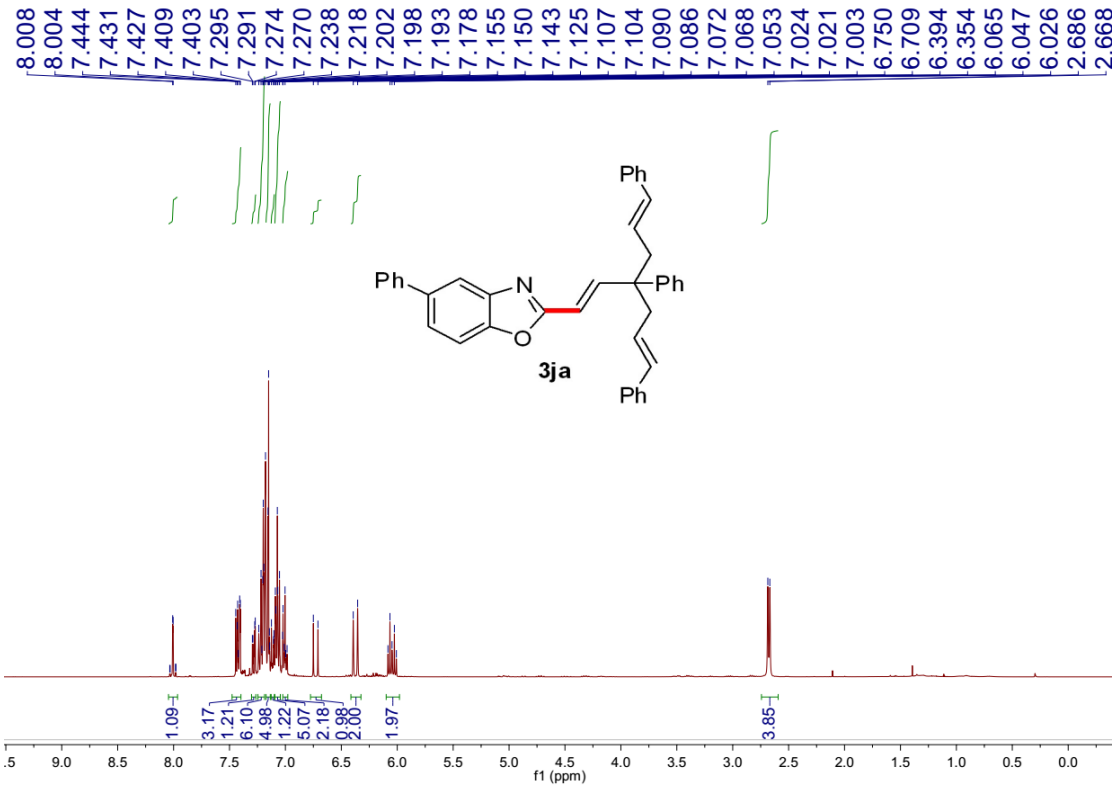
137.742
134.191
128.832
128.780
128.297
127.645
127.512
127.030
126.448
125.340
116.368
112.749
112.540
110.716
110.637
106.849
106.647
48.428
41.270
Ph
F
N
O
Ph
Ph
3ia
60 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


117.827
117.837
117.846
117.855
117.865
117.869
117.874
Ph
F
N
O
Ph
Ph
3ia
-117.7 -117.8 -117.9 -118.0 -118.1 -118.2
f1 (ppm)
0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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8.004
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7.431
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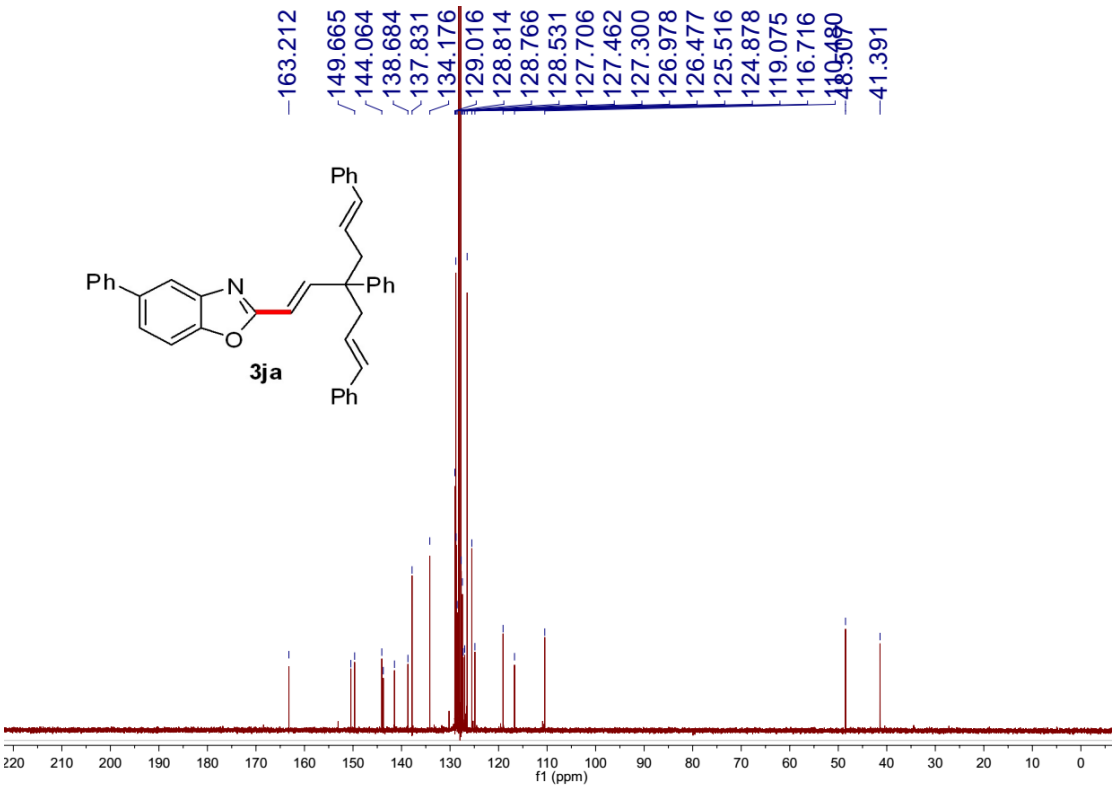
7.409
7.403
7.295
7.291
7.274
7.270
7.238
7.218
7.202
7.198
7.193
7.178
7.155
7.150
7.143
7.125
7.107
7.104
7.090
7.086
7.072
7.068
7.053
7.024
7.021
7.003
6.750
6.709
6.394
6.354
6.065
6.047
6.026
2.686
2.668
Ph
Ph
N
O
Ph
Ph
3ja
1.09
3.17
1.21
6.10
4.98
1.22
5.07
2.18
0.98
2.00
1.97
3.85
f1 (ppm)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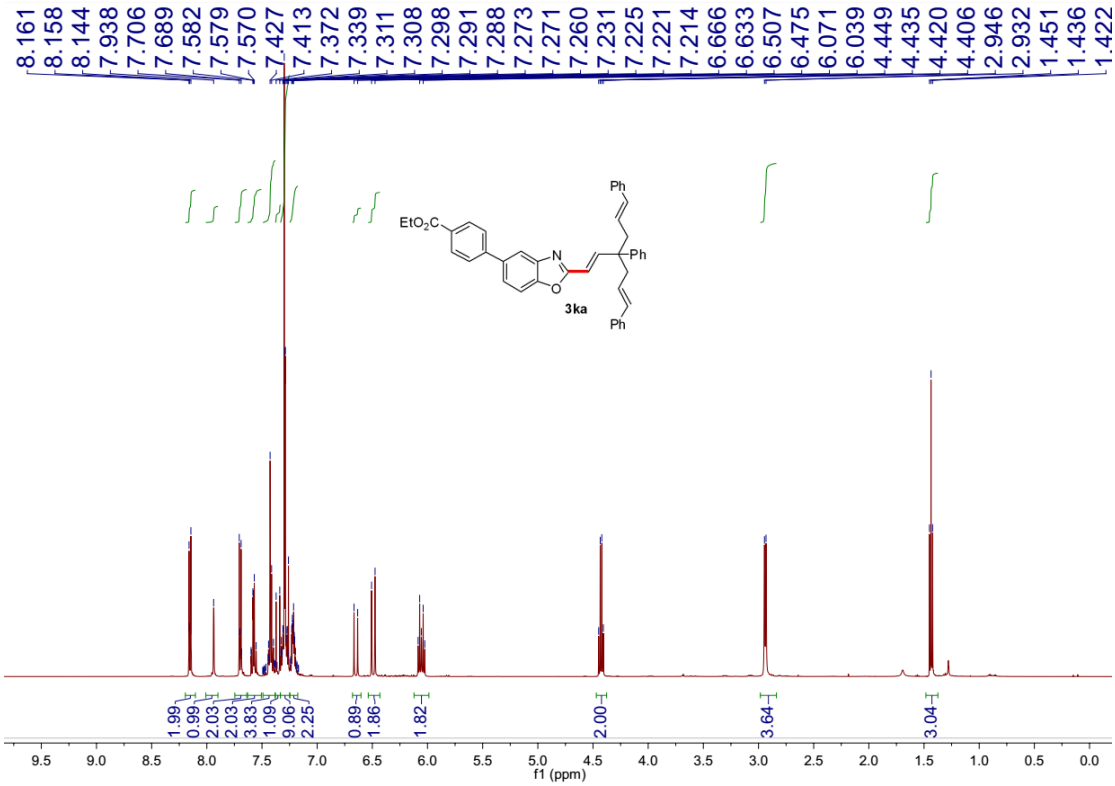
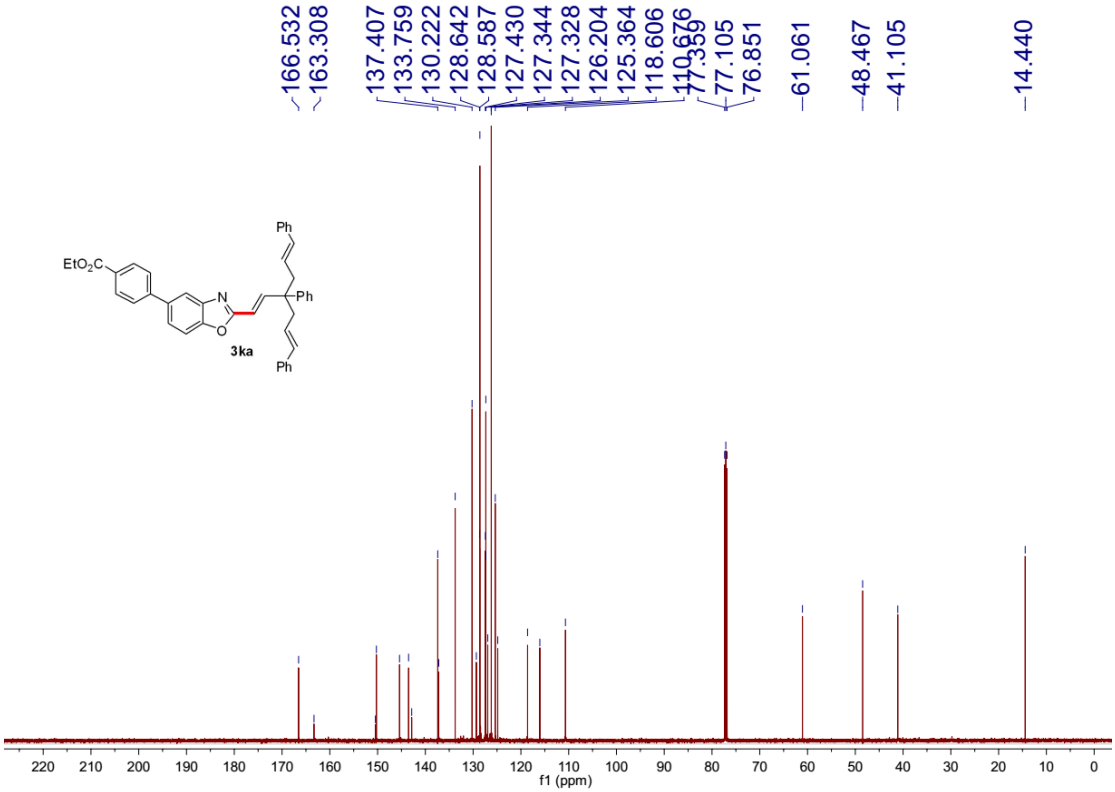
149.665
144.064
138.684
137.831
134.176
129.016
128.814
128.766
128.531
127.706
127.462
127.300
126.978
126.477
125.516
124.878
119.075
116.716
110.480
48.507
41.391
Ph
Ph
N
O
Ph
Ph
3ja
f1 (ppm)


8.161
8.158
8.144
7.938
7.706
7.689
7.582
7.579
7.570
7.427
7.413
7.372
7.339
7.311
7.308
7.298
7.291
7.288
7.273
7.271
7.260
7.231
7.225
7.221
7.214
6.666
6.633
6.507
6.475
6.071
6.039
4.449
4.435
4.420
4.406
2.946
2.932
1.451
1.436
1.422
Ph
EtO2C
N
O
Ph
3ka
Ph
1.99
0.99
2.03
2.03
3.83
1.09
9.06
2.25
0.89
1.86
1.82
2.00
3.64
3.04
f1 (ppm)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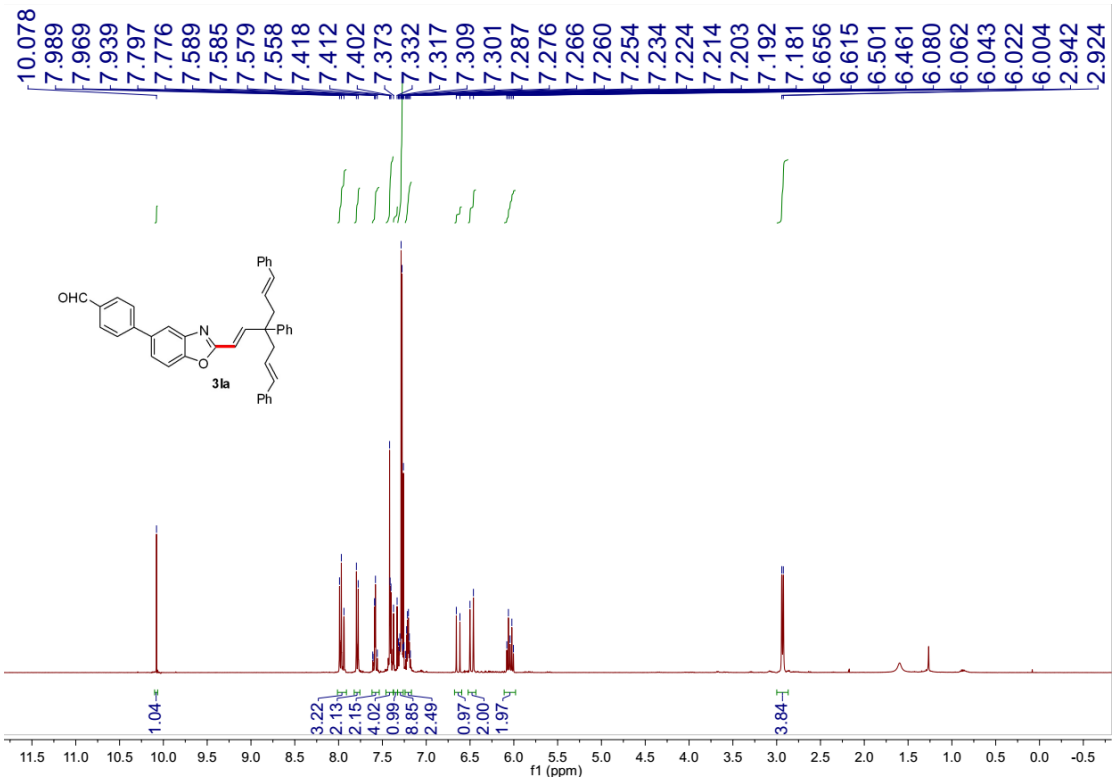
137.407
133.759
130.222
128.642
128.587
127.430
127.344
127.328
126.204
125.364
118.606
110.676
77.359
77.105
76.851
61.061
48.467
41.105
14.440
EtO2C
N
O
Ph
3ka
Ph
Ph
f1 (ppm)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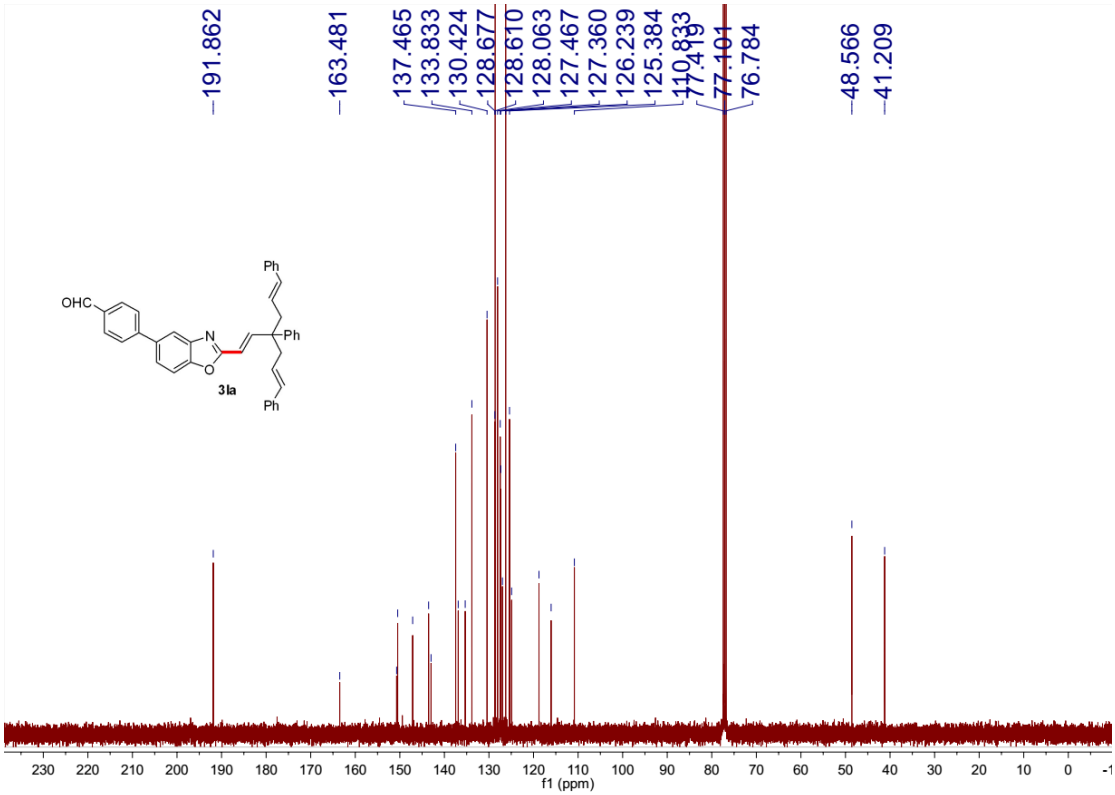
7.969
7.939
7.797
7.776
7.589
7.585
7.579
7.558
7.418
7.412
7.402
7.373
7.332
7.317
7.309
7.301
7.287
7.276
7.266
7.260
7.254
7.234
7.224
7.214
7.203
7.192
7.181
6.656
6.615
6.501
6.461
6.080
6.062
6.043
6.022
6.004
2.942
2.924
OHC
N
O
Ph
Ph
Ph
3la
1.04
3.22
2.13
2.15
4.02
0.99
8.85
2.49
0.97
2.00
1.97
3.84
f1 (ppm)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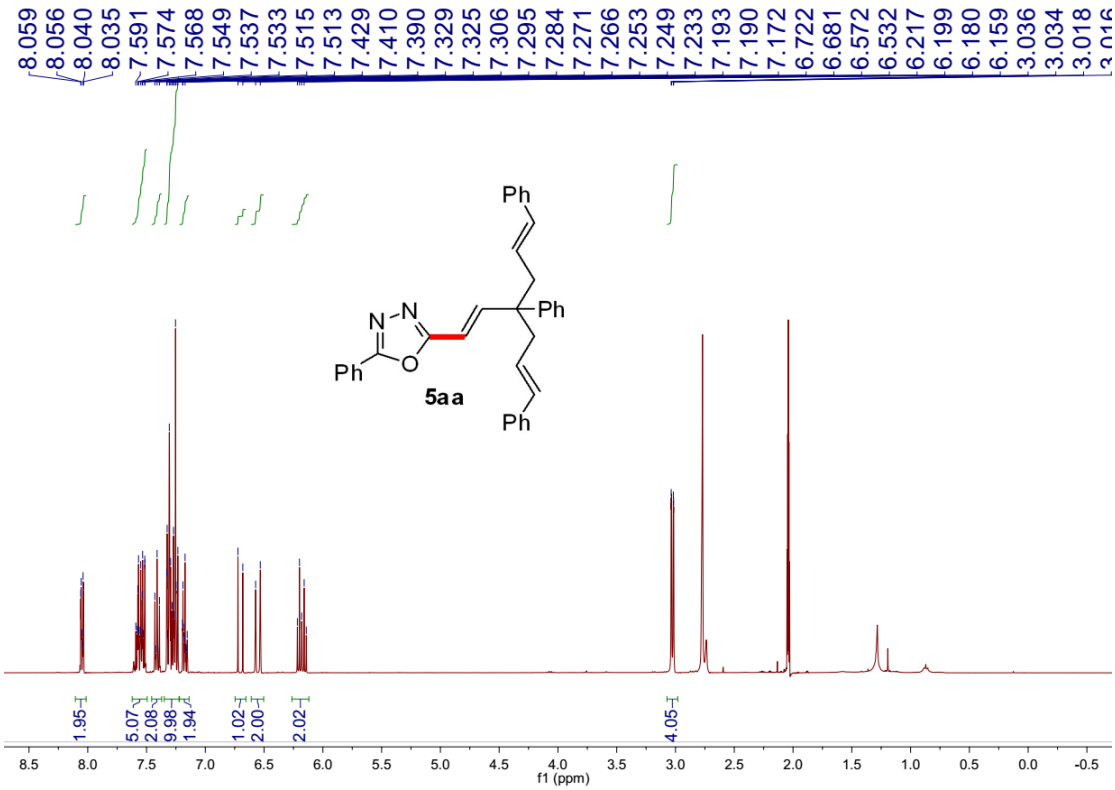
133.833
130.424
128.677
128.610
128.063
127.467
127.360
126.239
125.384
110.833
77.419
77.101
76.784
48.566
41.209
OHC
N
O
Ph
Ph
Ph
3la
f1 (ppm)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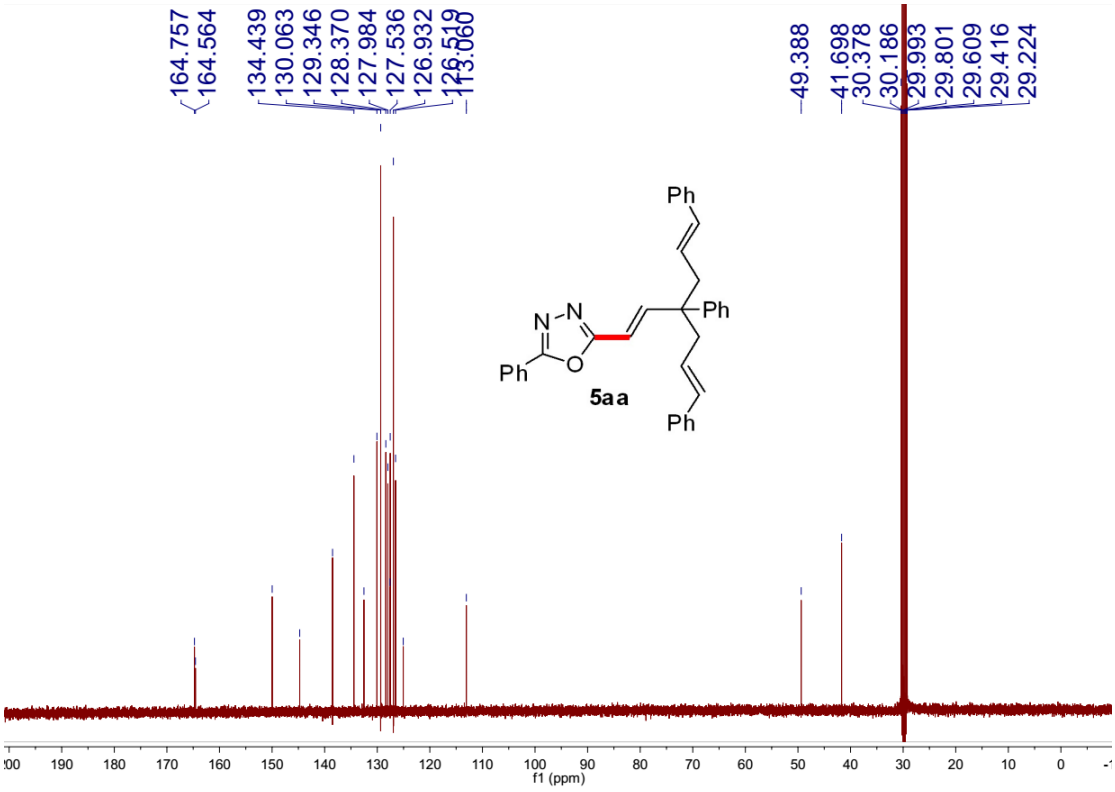
8.056
8.040
8.035
7.591
7.574
7.568
7.549
7.537
7.533
7.515
7.513
7.429
7.410
7.390
7.329
7.325
7.306
7.295
7.284
7.271
7.266
7.253
7.249
7.233
7.193
7.190
7.172
6.722
6.681
6.572
6.532
6.217
6.199
6.180
6.159
3.036
3.034
3.018
Ph
N
N
O
Ph
Ph
Ph
5aa
1.95
5.07
2.08
9.98
1.94
1.02
2.00
2.02
4.05
f1 (ppm)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164.564
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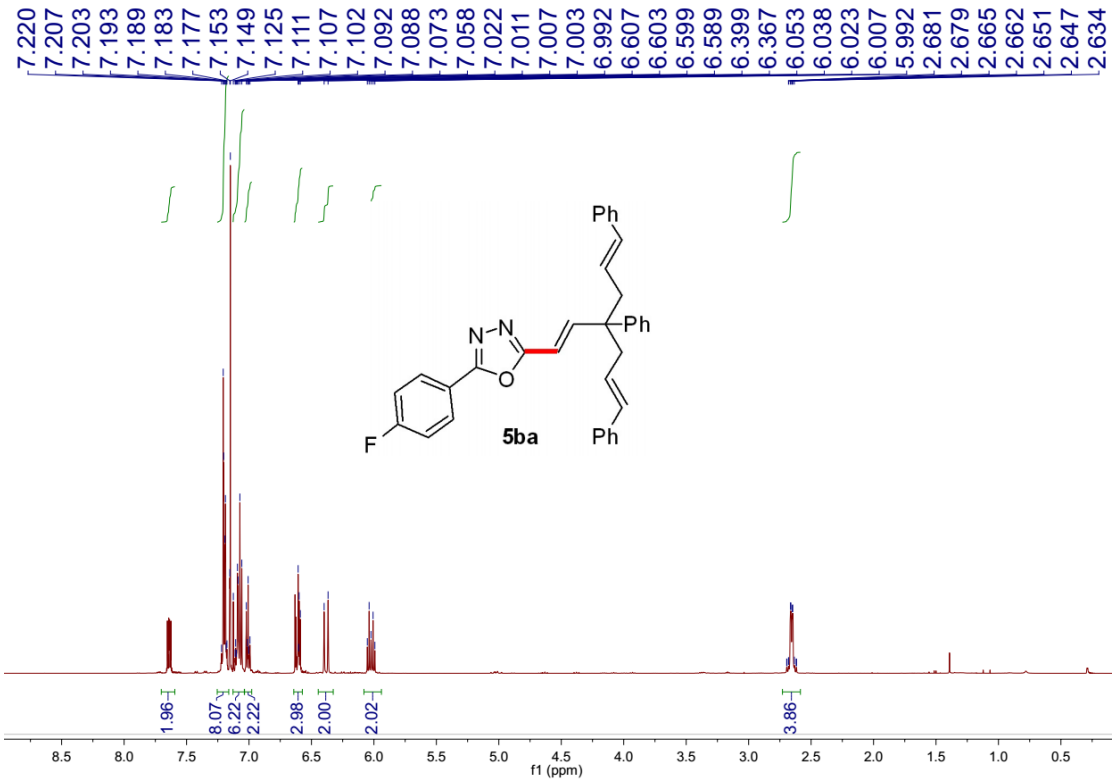
128.370
127.984
127.536
126.932
126.519
113.060
49.388
41.698
30.378
30.186
29.993
29.801
29.609
29.416
29.224
Ph
N
N
O
Ph
Ph
Ph
5aa
f1 (ppm)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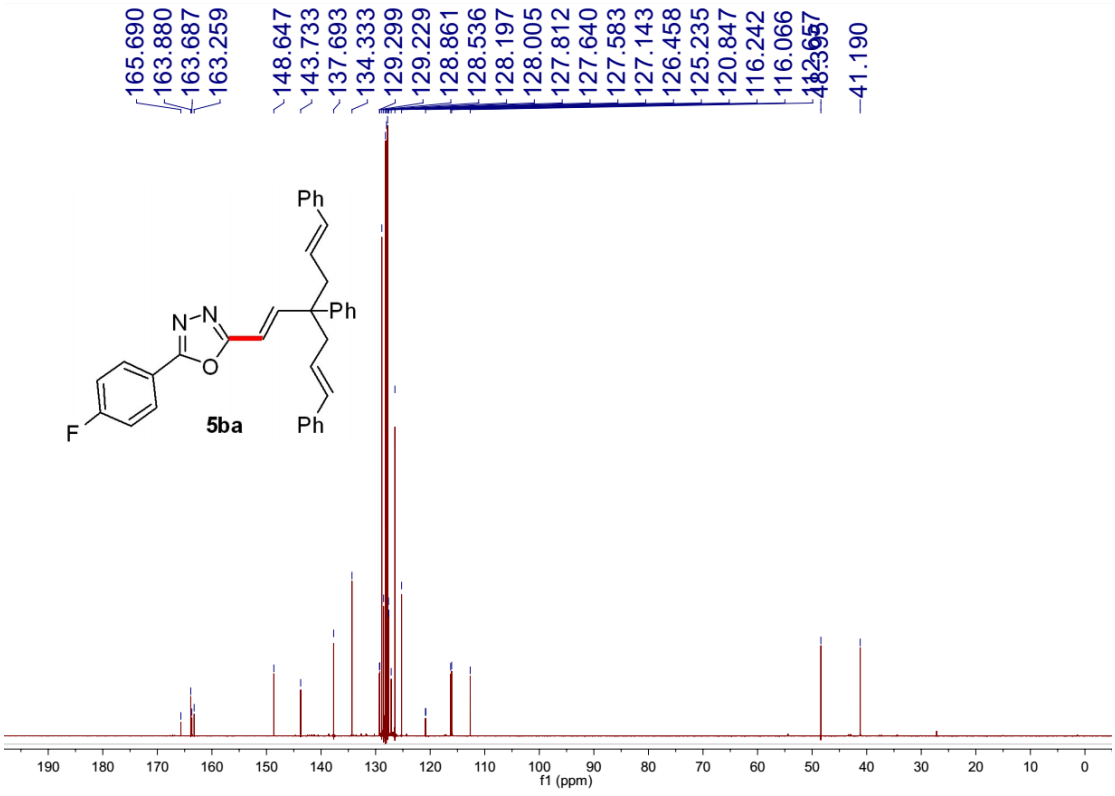
7.203
7.193
7.189
7.183
7.177
7.153
7.149
7.125
7.111
7.107
7.102
7.092
7.088
7.073
7.058
7.022
7.011
7.007
7.003
6.992
6.607
6.603
6.599
6.589
6.399
6.367
6.053
6.038
6.023
6.007
5.992
2.681
2.679
2.665
2.662
2.651
2.647
2.634
Ph
Ph
N
N
O
F
5ba
Ph
1.96
8.07
6.22
2.22
2.98
2.00
2.02
3.86
f1 (ppm)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163.259
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137.693
134.333
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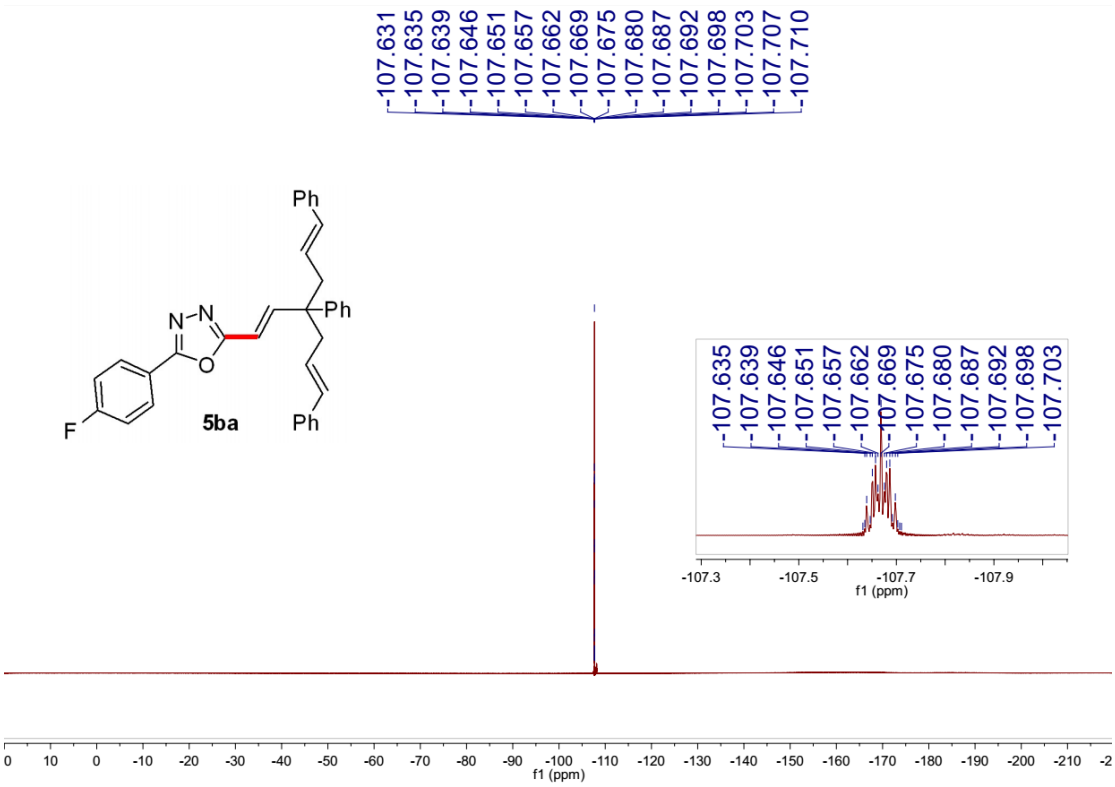
129.229
128.861
128.536
128.197
128.005
127.812
127.640
127.583
127.143
126.458
125.235
120.847
116.242
116.066
41.190
Ph
Ph
N
N
O
F
5ba
Ph
f1 (ppm)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-107.639
-107.646
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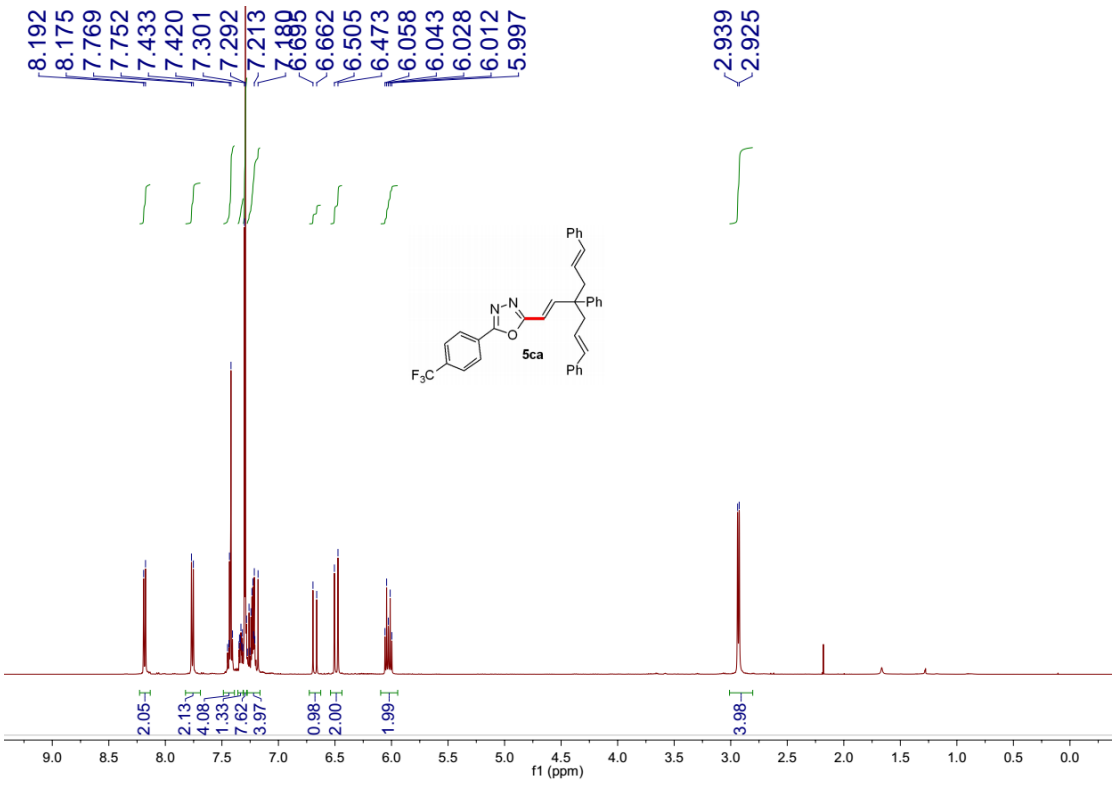
-107.657
-107.662
-107.669
-107.675
-107.680
-107.687
-107.692
-107.698
-107.703
-107.707
-107.710
Ph
N
N
O
Ph
F
5ba
Ph
-107.635
-107.639
-107.646
-107.651
-107.657
-107.662
-107.669
-107.675
-107.680
-107.687
-107.692
-107.698
-107.703
-107.3
-107.5
-107.7
-107.9
f1 (ppm)
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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8.175
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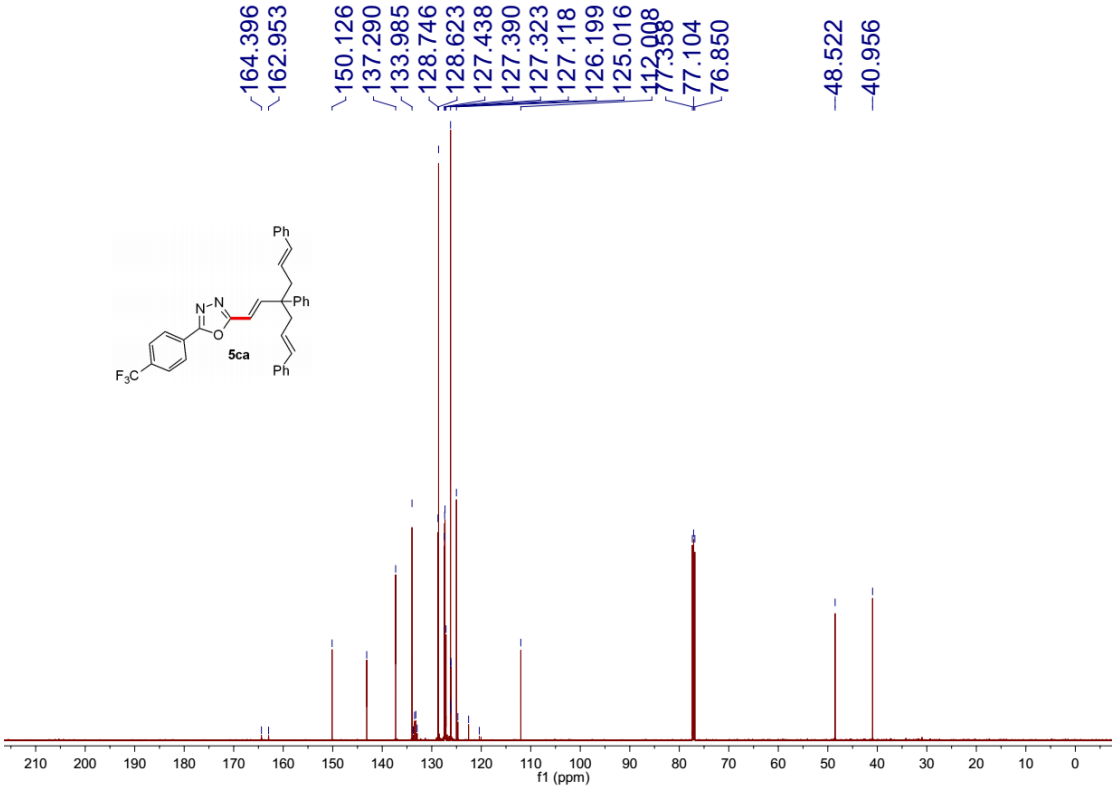
7.752
7.433
7.420
7.301
7.292
7.213
6.662
6.505
6.473
6.058
6.043
6.028
6.012
5.997
2.939
2.925
Ph
N
N
O
Ph
F3C
5ca
Ph
2.05
2.13
4.08
1.33
7.62
3.97
0.98
2.00
1.99
3.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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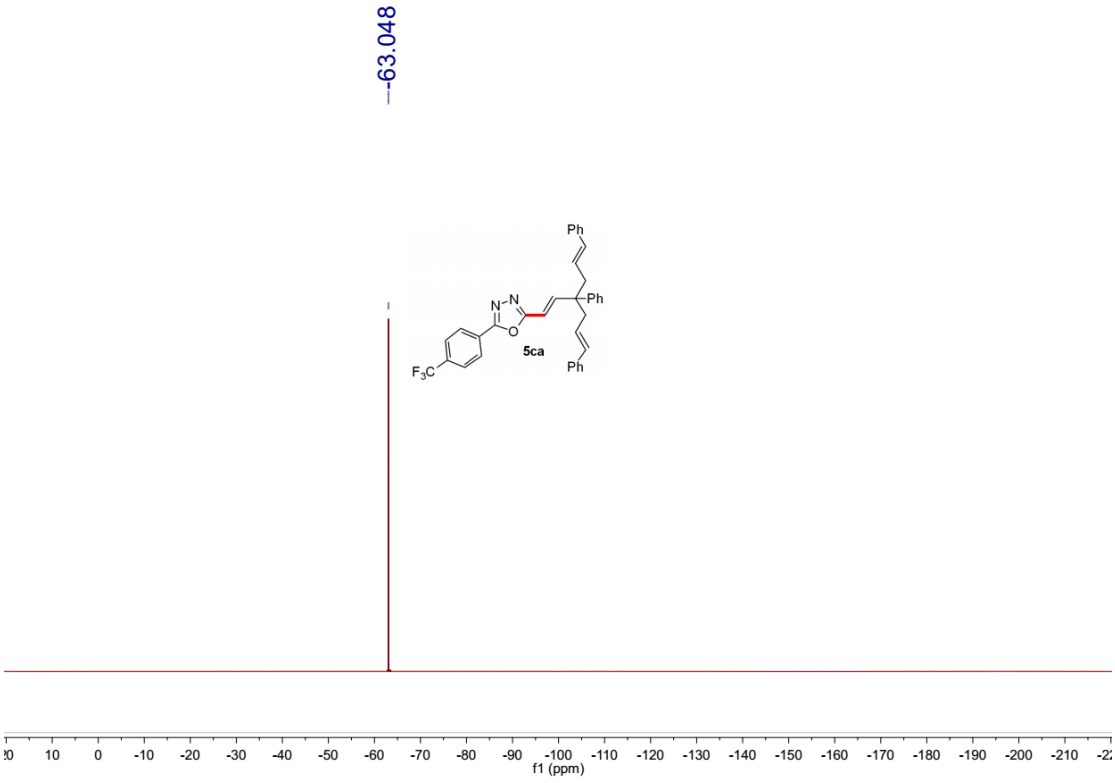
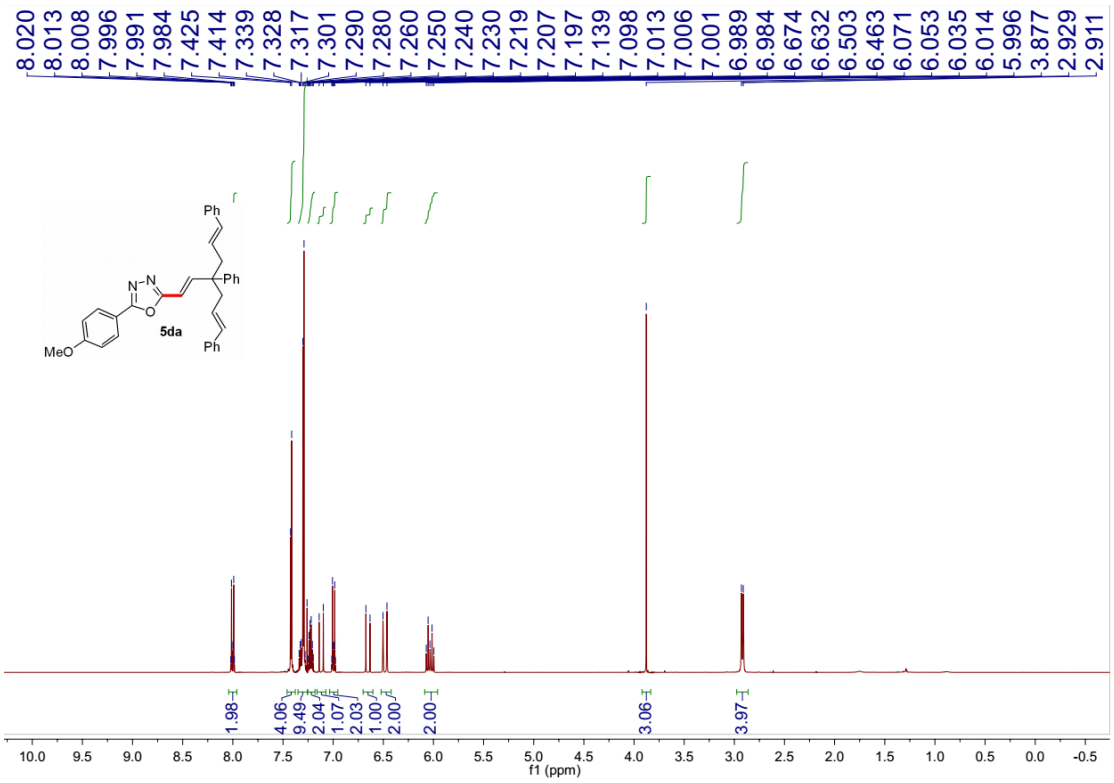
128.623
127.438
127.390
127.323
127.118
126.199
125.016
112.008
77.358
77.104
76.850
48.522
40.956
Ph
Ph
Ph
N
N
O
F3C
5ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.048
Ph
Ph
Ph
N
N
O
F3C
5ca
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.414
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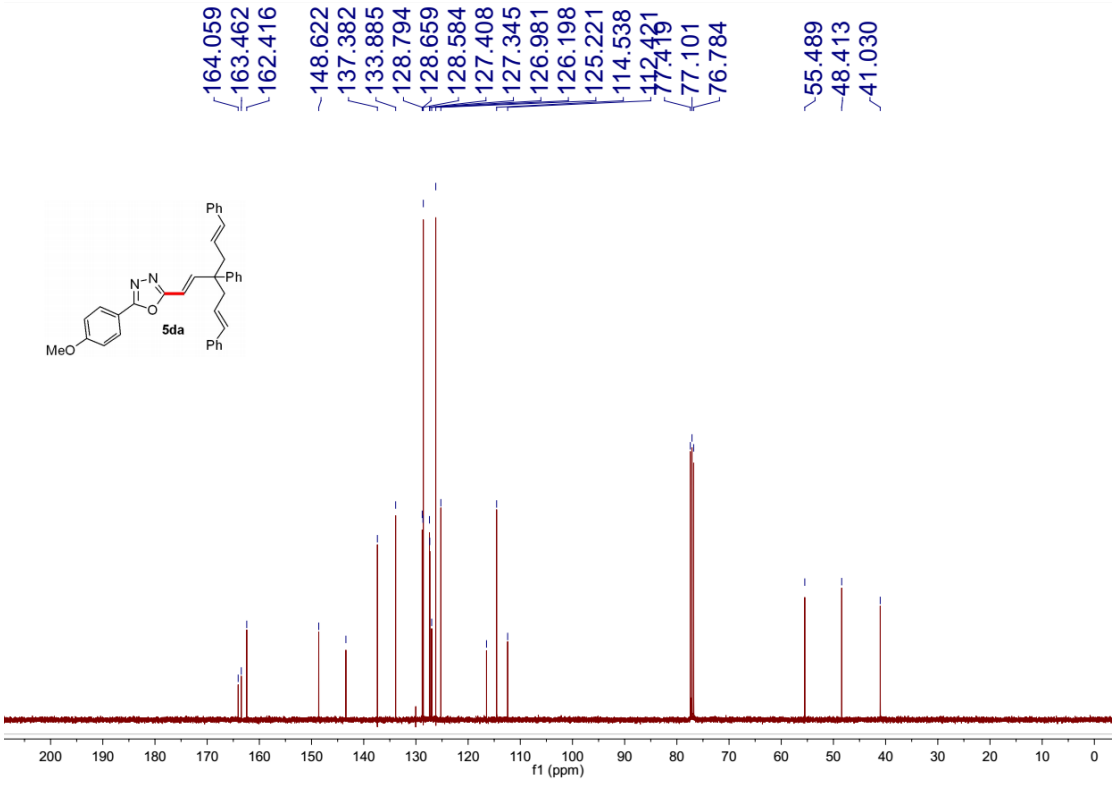
7.328
7.317
7.301
7.290
7.280
7.260
7.250
7.240
7.230
7.219
7.207
7.197
7.139
7.098
7.013
7.006
7.001
6.989
6.984
6.674
6.632
6.503
6.463
6.071
6.053
6.035
6.014
5.996
3.877
2.929
2.911
Ph
Ph
Ph
N
N
O
MeO
5da
1.98
4.06
9.49
2.04
1.07
2.03
1.00
2.00
2.00
3.06
3.97
f1 (ppm)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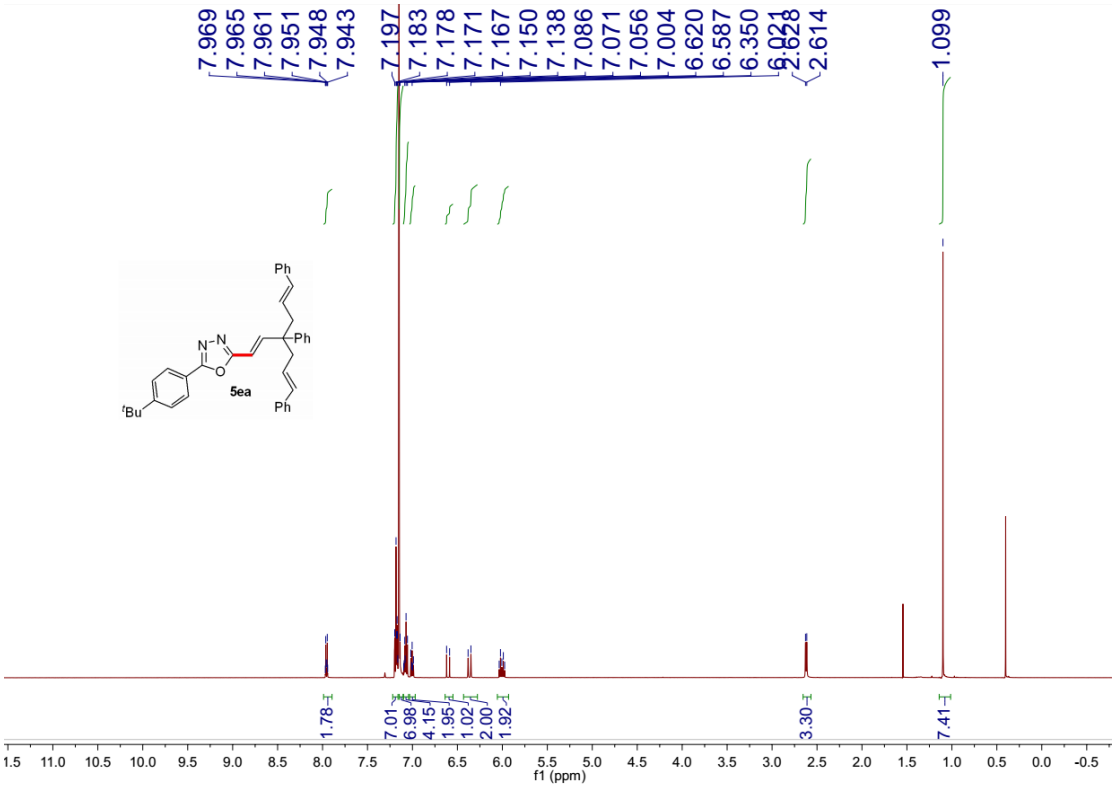
133.885
128.794
128.659
128.584
127.408
127.345
126.981
126.198
125.221
114.538
112.421
77.419
77.101
76.784
55.489
48.413
41.030
Ph
Ph
Ph
N
N
O
MeO
5da
f1 (ppm)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7.961
7.951
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7.197
7.183
7.178
7.171
7.167
7.150
7.138
7.086
7.071
7.056
7.004
6.620
6.587
6.350
6.021
2.628
2.614
1.099
Ph
Ph
Ph
N
N
O
5ea
tBu
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6.98
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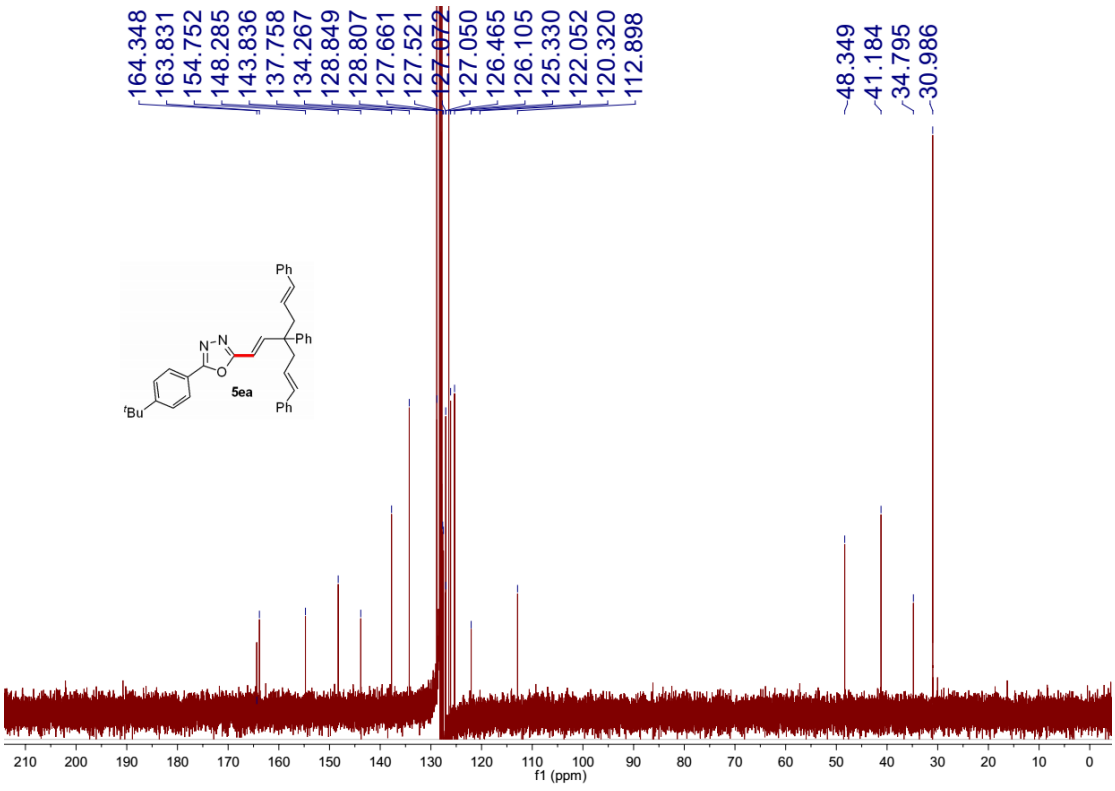
1.95
1.02
2.00
1.92
3.30
7.41
f1 (ppm)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143.836
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128.807
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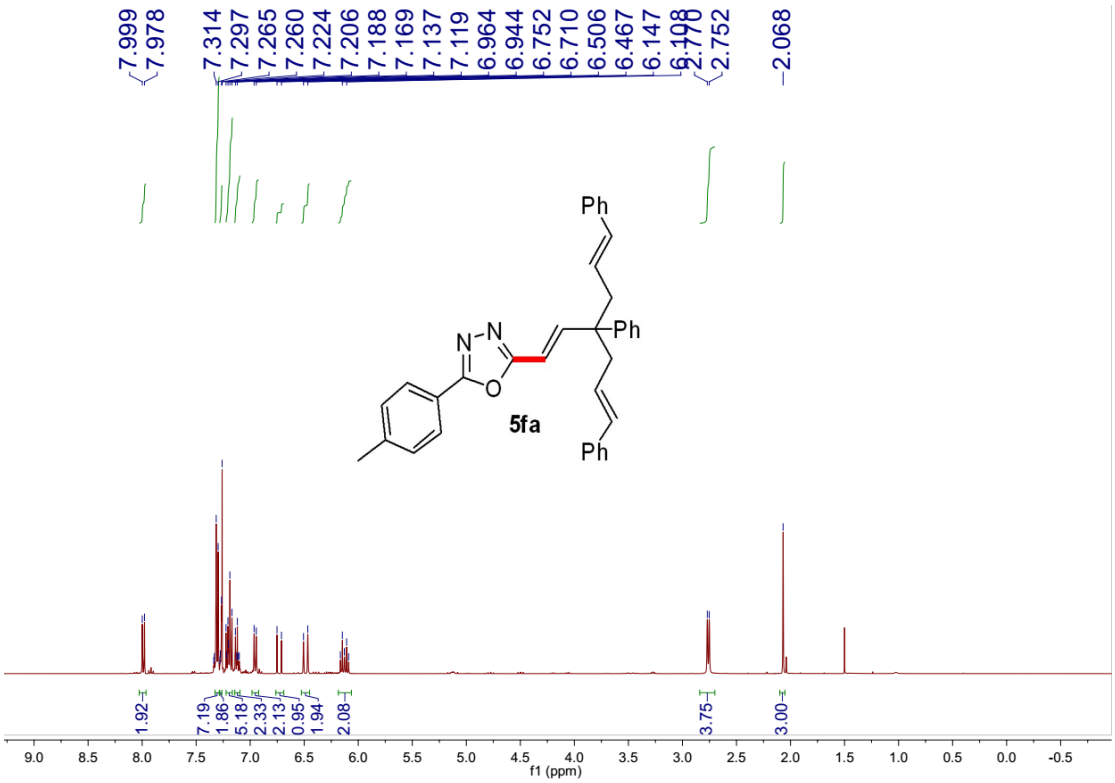
127.521
127.072
127.050
126.465
126.105
125.330
122.052
120.320
112.898
48.349
41.184
34.795
30.986
Ph
Ph
Ph
N
N
O
5ea
tBu
f1 (ppm)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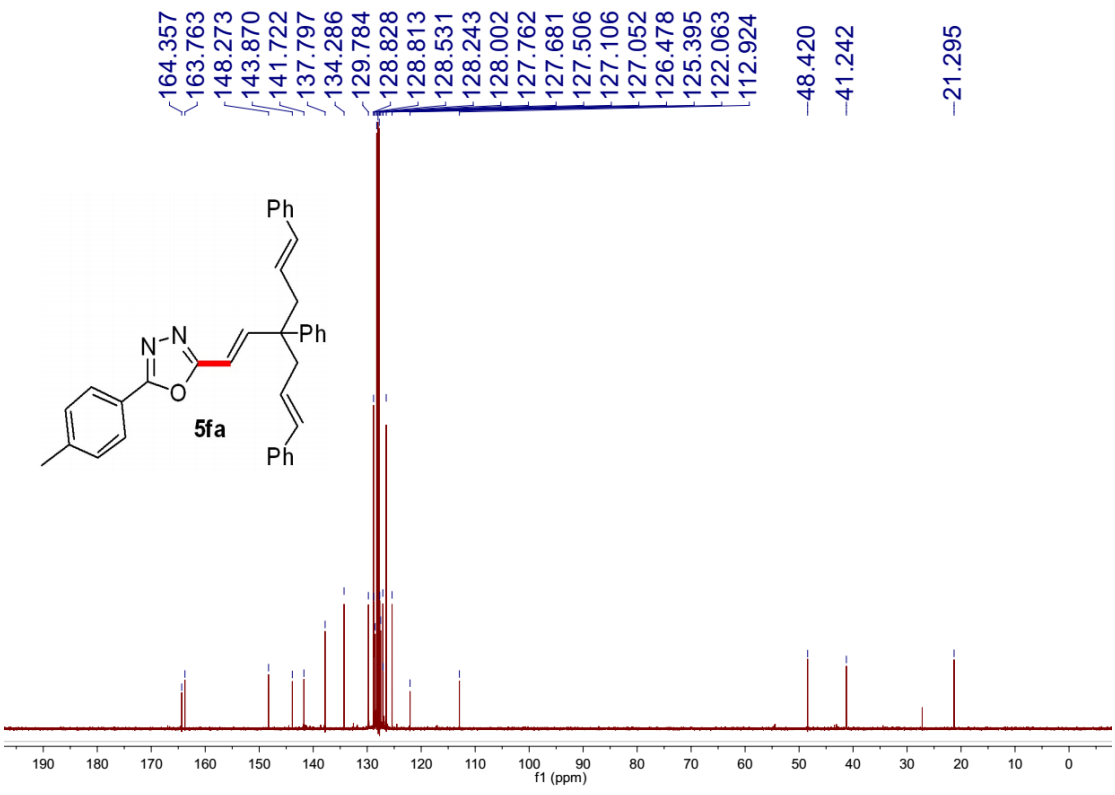
7.314
7.297
7.265
7.260
7.224
7.206
7.188
7.169
7.137
7.119
6.964
6.944
6.752
6.710
6.506
6.467
6.147
6.108
2.770
2.752
2.068
Ph
Ph
Ph
N
N
O
5fa
1.92
7.19
1.86
5.18
2.33
2.13
0.95
1.94
2.08
3.75
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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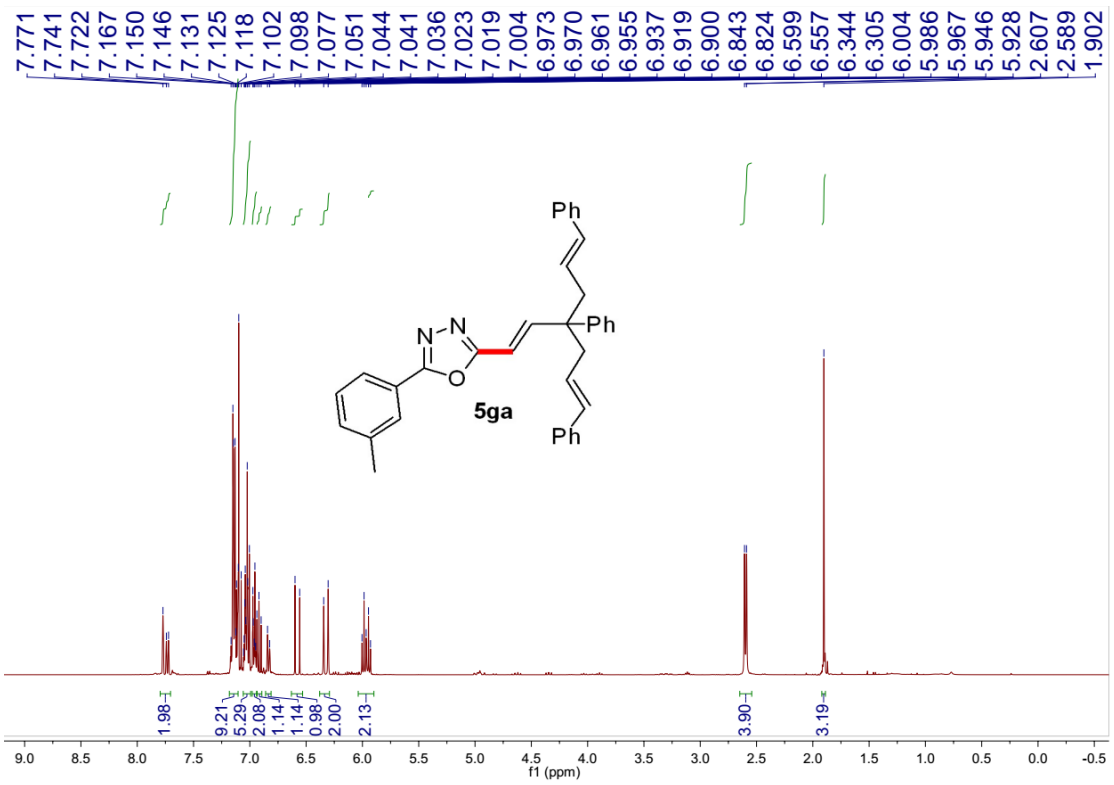
148.273
143.870
141.722
137.797
134.286
129.784
128.828
128.813
128.531
128.243
128.002
127.762
127.681
127.506
127.106
127.052
126.478
125.395
122.063
112.924
48.420
41.242
21.295
Ph
Ph
Ph
N
N
O
5fa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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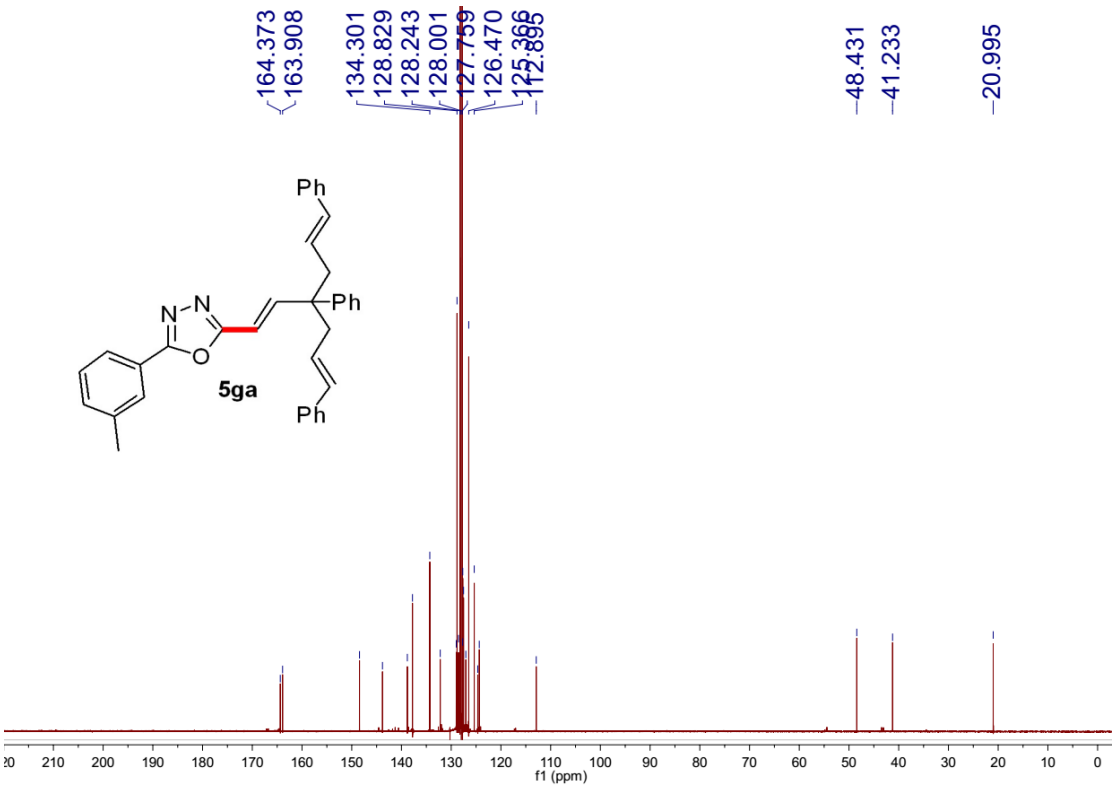
7.741
7.722
7.167
7.150
7.146
7.131
7.125
7.118
7.102
7.098
7.077
7.051
7.044
7.041
7.036
7.023
7.019
7.004
6.973
6.970
6.961
6.955
6.937
6.919
6.900
6.843
6.824
6.599
6.557
6.344
6.305
6.004
5.986
5.967
5.946
5.928
2.607
2.589
1.902
Ph
Ph
Ph
N
N
O
5ga
1.98
9.21
5.29
2.08
1.14
1.14
0.98
2.00
2.13
3.90
3.19
f1 (ppm)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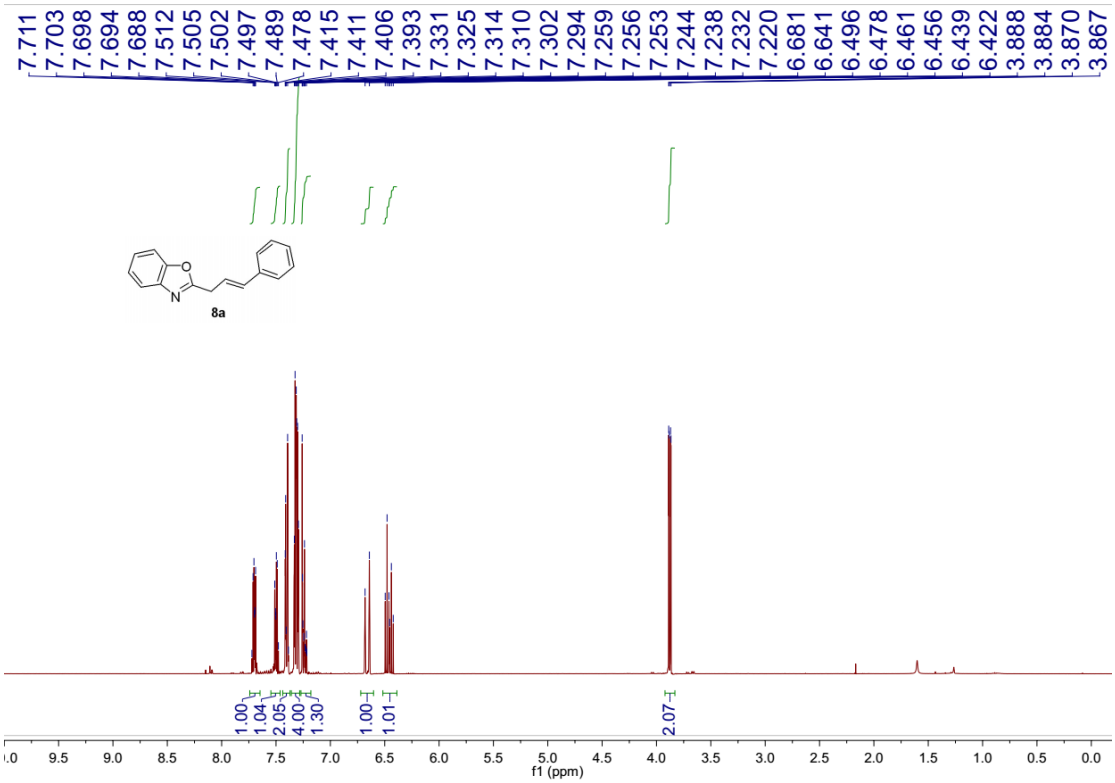
163.908
134.301
128.829
128.243
128.001
127.759
126.470
48.431
41.233
20.995
Ph
Ph
Ph
N
N
O
5ga
f1 (ppm)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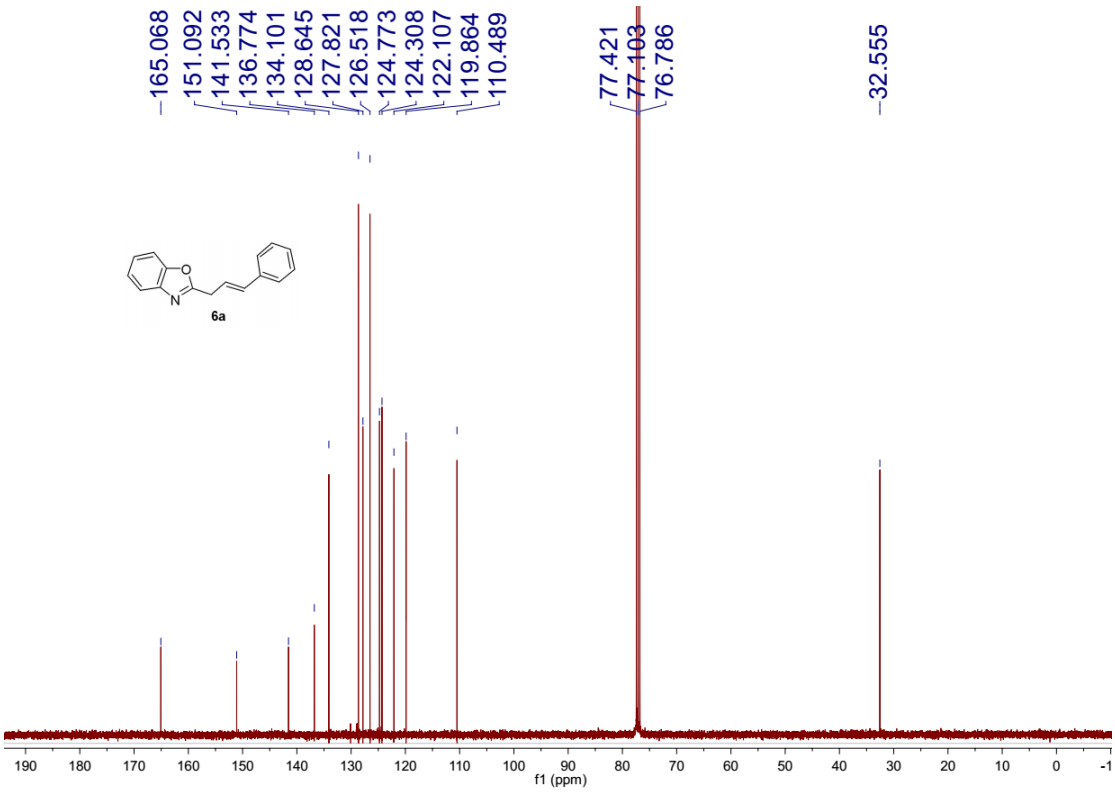
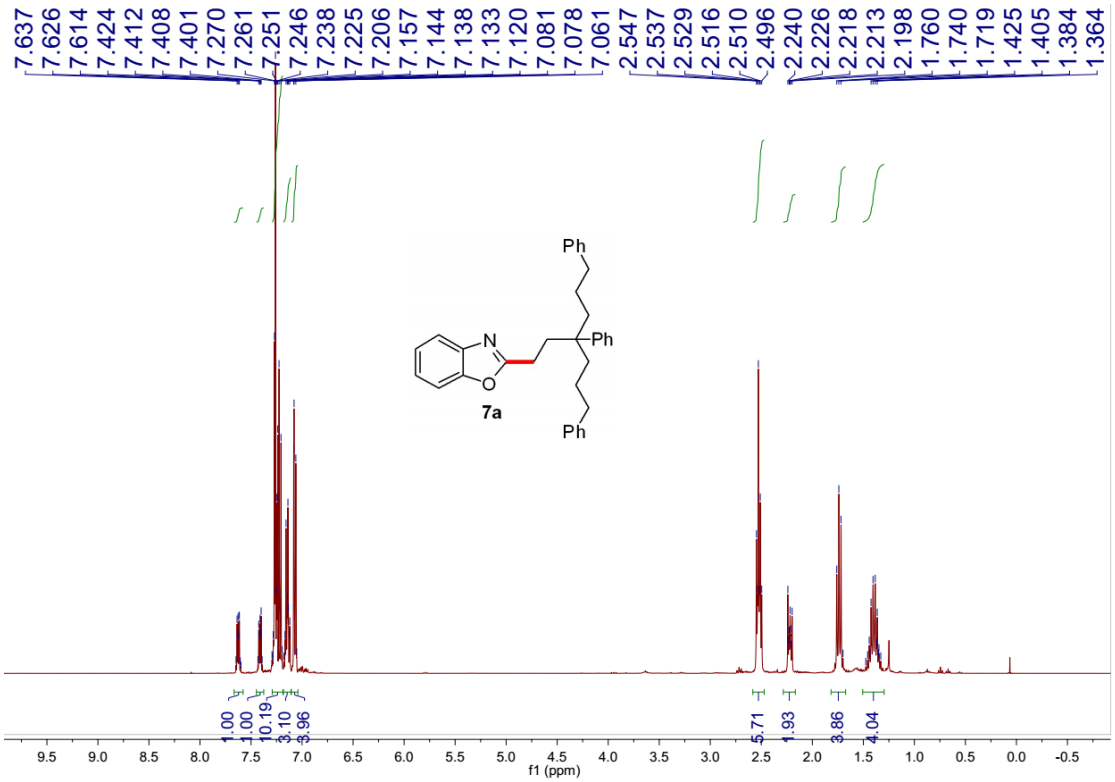
7.698
7.694
7.688
7.512
7.505
7.502
7.497
7.489
7.478
7.415
7.411
7.406
7.393
7.331
7.325
7.314
7.310
7.302
7.294
7.259
7.256
7.253
7.244
7.238
7.232
7.220
6.681
6.641
6.496
6.478
6.461
6.456
6.439
6.422
3.888
3.884
3.870
3.867
8a
1.00
1.04
2.05
4.00
1.30
1.00
1.01
2.07
f1 (ppm)


165.068
151.092
141.533
136.774
134.101
128.645
127.821
126.518
124.773
124.308
122.107
119.864
110.489
77.421
77.103
76.786
32.555
6a
f1 (ppm)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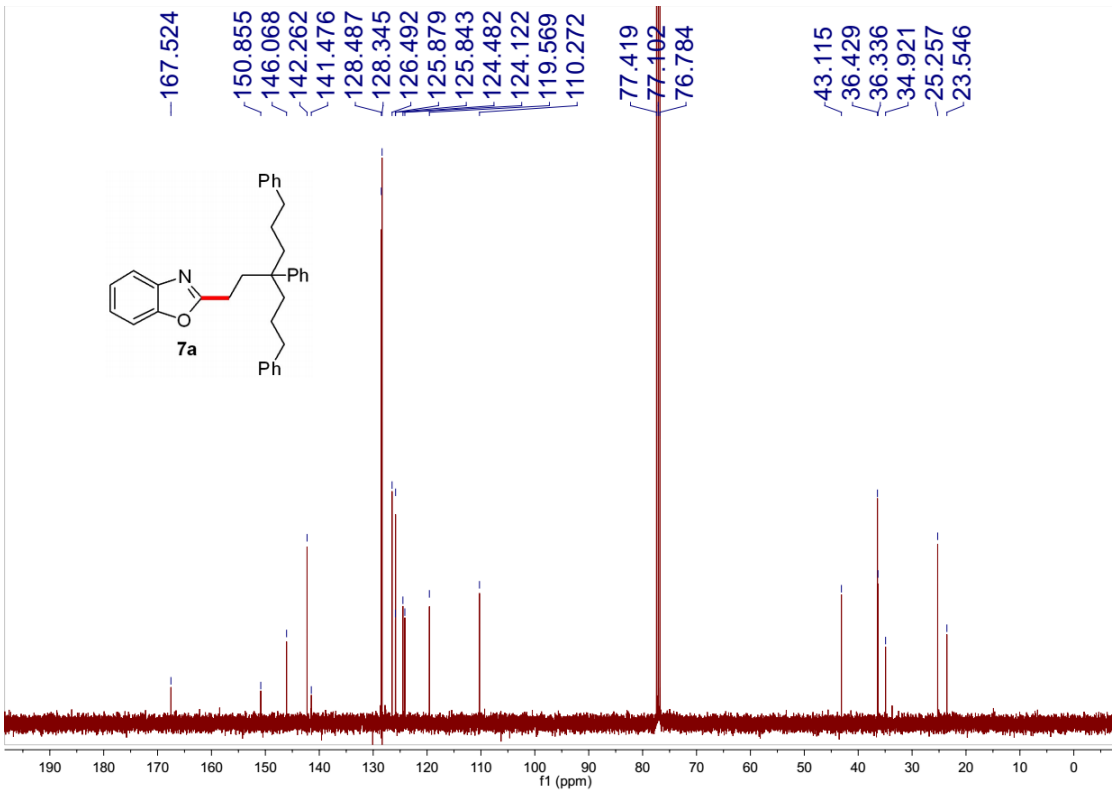
7.614
7.424
7.412
7.408
7.401
7.270
7.261
7.251
7.246
7.238
7.225
7.206
7.157
7.144
7.138
7.133
7.120
7.081
7.078
7.061
2.547
2.537
2.529
2.516
2.510
2.496
2.240
2.226
2.218
2.213
2.198
1.760
1.740
1.719
1.425
1.405
1.384
1.364
Ph
N
O
Ph
Ph
7a
1.00
1.00
10.19
3.10
3.96
5.71
1.93
3.86
4.04
f1 (ppm)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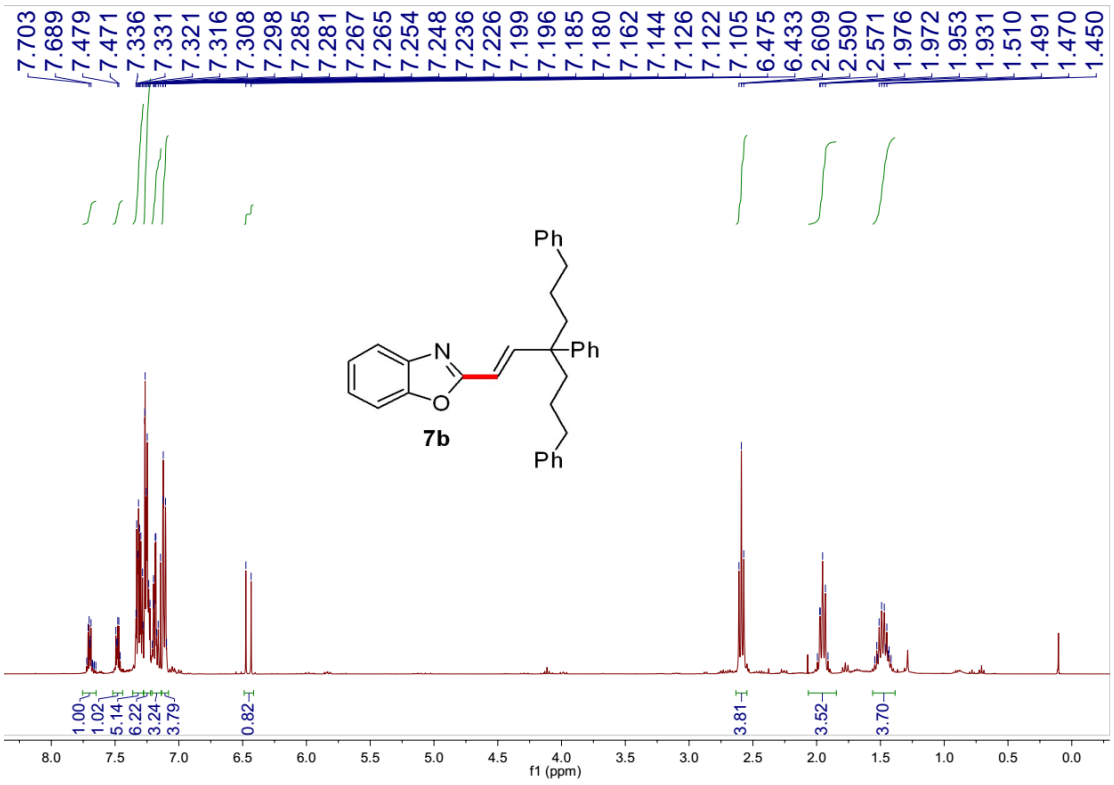
150.855
146.068
142.262
141.476
128.487
128.345
126.492
125.879
125.843
124.482
124.122
119.569
110.272
77.419
77.102
76.784
43.115
36.429
36.336
34.921
25.257
23.546
Ph
N
O
Ph
Ph
7a
f1 (ppm)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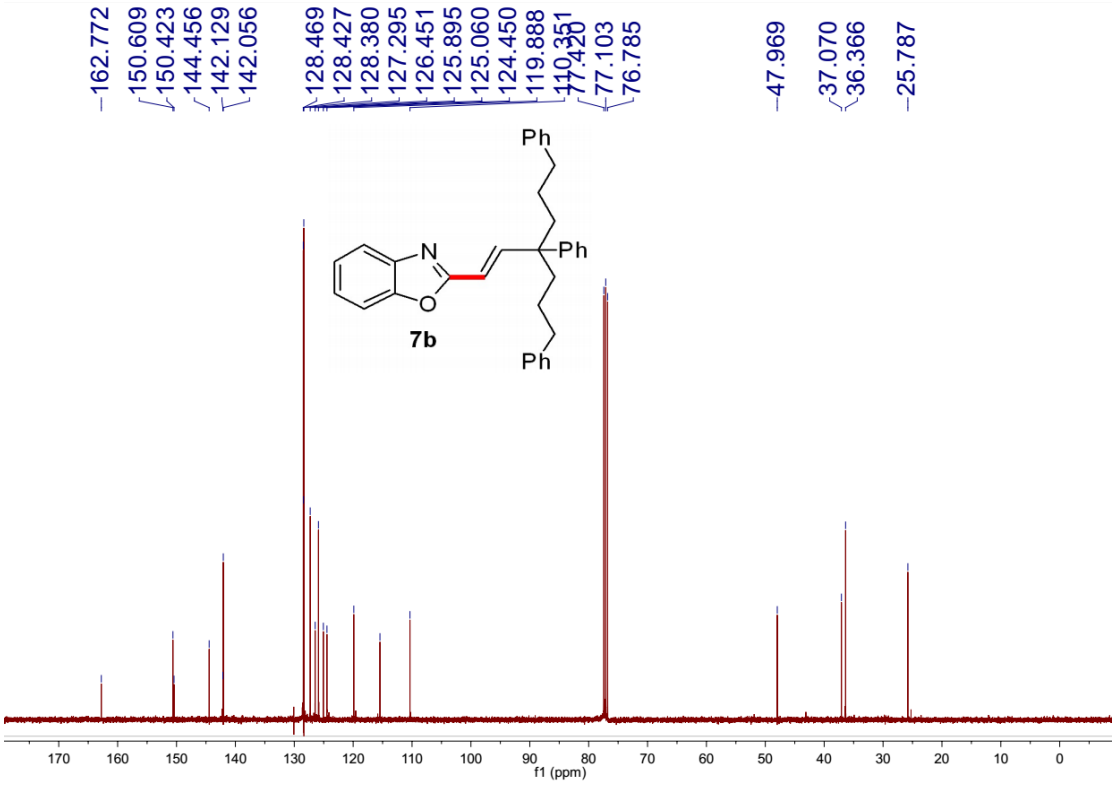
7.479
7.471
7.336
7.331
7.321
7.316
7.308
7.298
7.285
7.281
7.267
7.265
7.254
7.248
7.236
7.226
7.199
7.196
7.185
7.180
7.162
7.144
7.126
7.122
7.105
6.475
6.433
2.609
2.590
2.571
1.976
1.972
1.953
1.931
1.510
1.491
1.470
1.450
Ph
N
Ph
O
Ph
7b
1.00
1.02
5.14
6.22
3.24
3.79
0.82
3.81
3.52
3.70
f1 (ppm)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150.423
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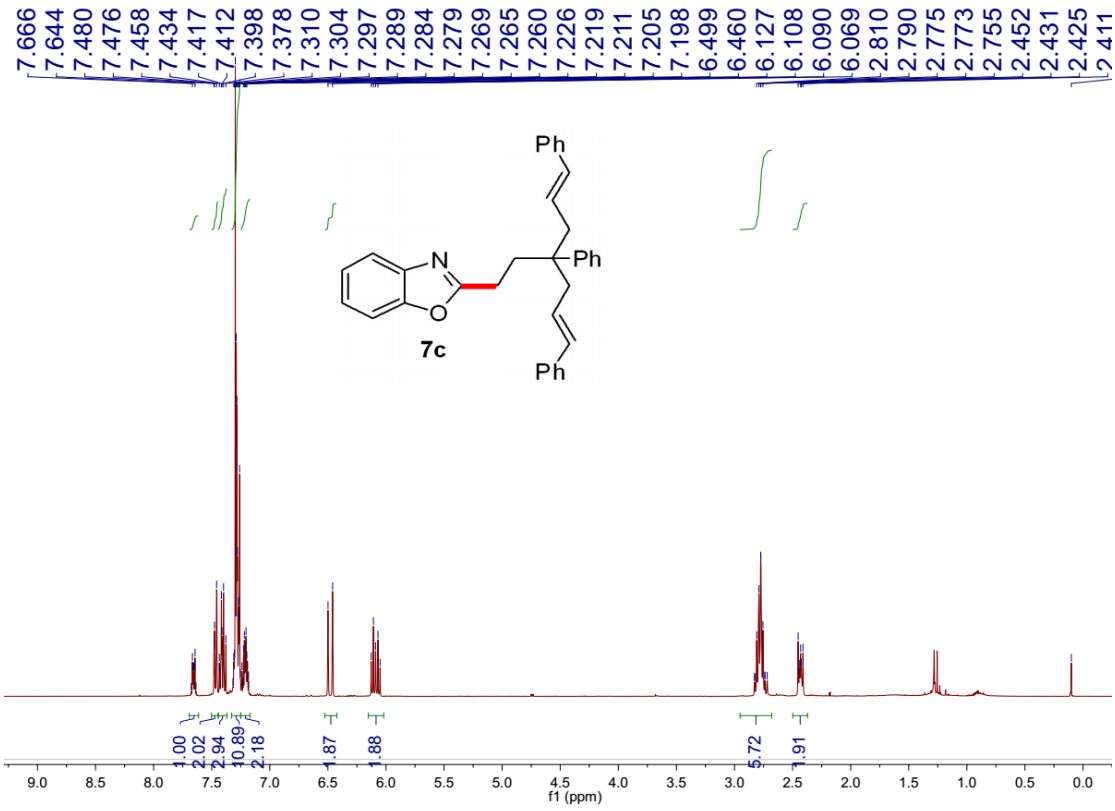
142.129
142.056
128.469
128.427
128.380
127.295
126.451
125.895
125.060
124.450
119.888
110.351
77.420
77.103
76.785
47.969
37.070
36.366
25.787
Ph
N
Ph
O
Ph
7b
f1 (ppm)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7.434
7.417
7.412
7.398
7.378
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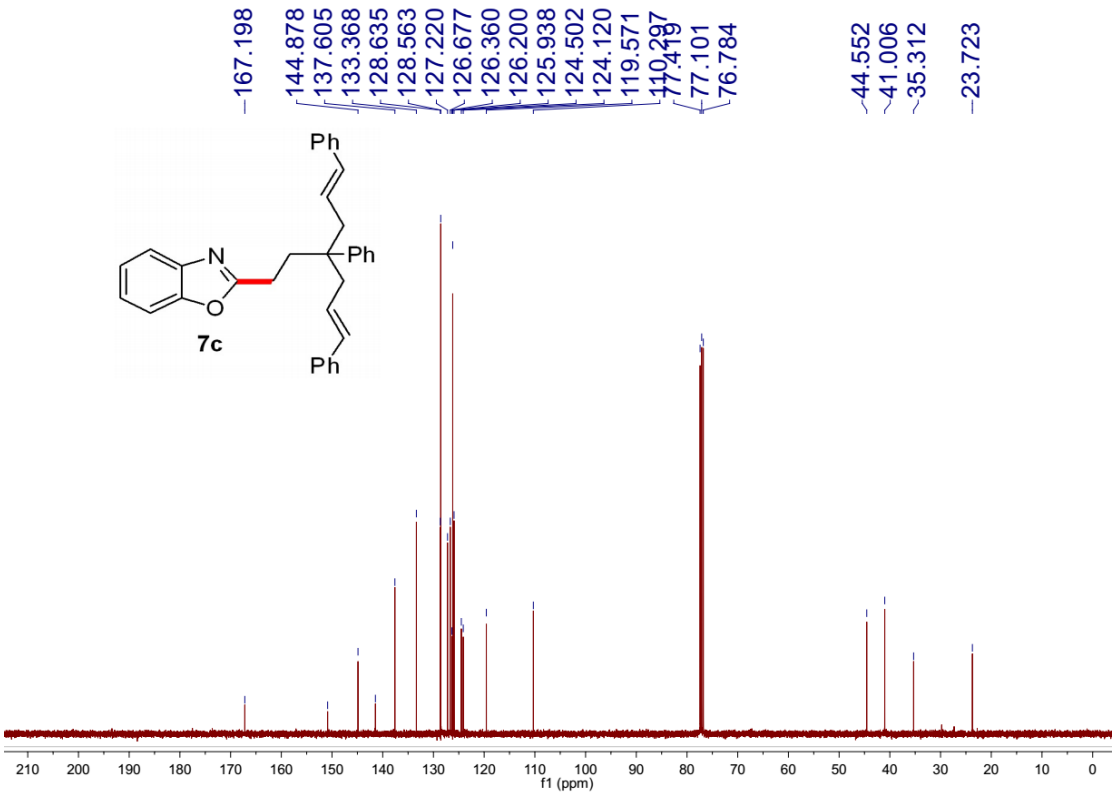
7.304
7.297
7.289
7.284
7.279
7.269
7.265
7.260
7.226
7.219
7.211
7.205
7.198
6.499
6.460
6.127
6.108
6.090
6.069
2.810
2.790
2.775
2.773
2.755
2.452
2.431
2.425
2.411
Ph
N
O
Ph
Ph
7c
1.00
2.02
2.94
10.89
2.18
1.87
1.88
5.72
1.91
f1 (ppm)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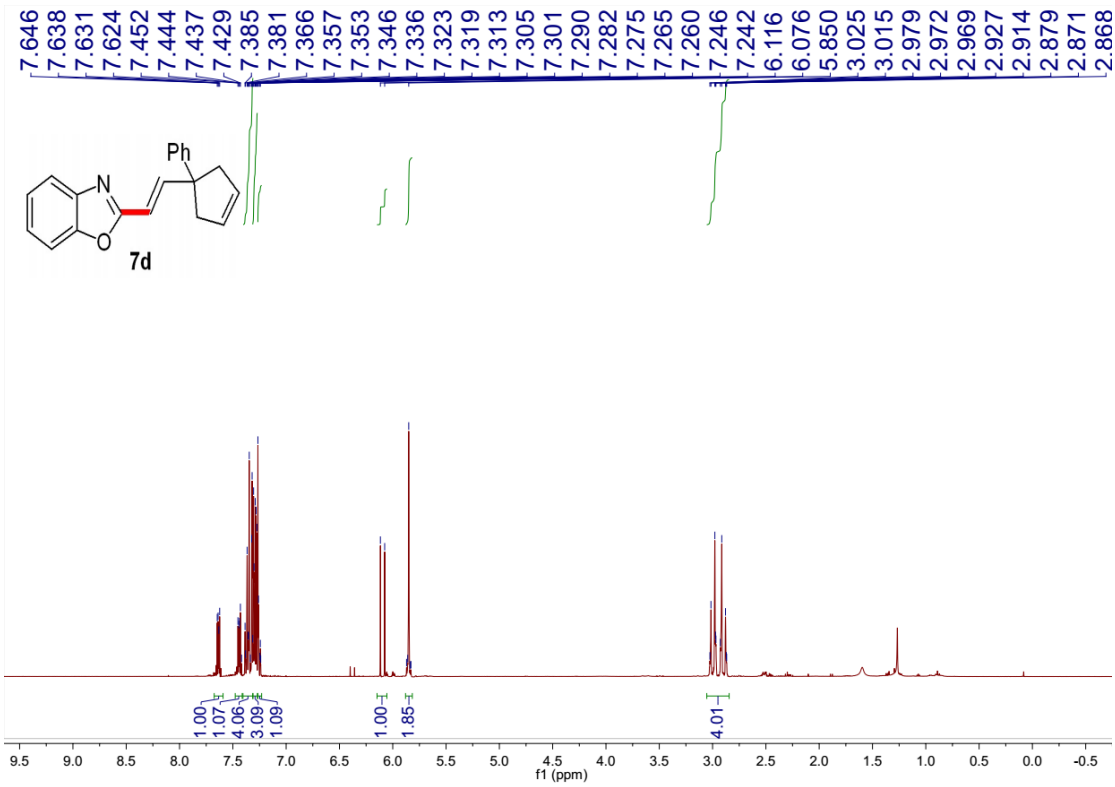
137.605
133.368
128.635
128.563
127.220
126.677
126.360
126.200
125.938
124.502
124.120
119.571
110.297
77.419
77.101
76.784
44.552
41.006
35.312
23.723
Ph
N
O
Ph
Ph
7c
f1 (ppm)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7.631
7.624
7.452
7.444
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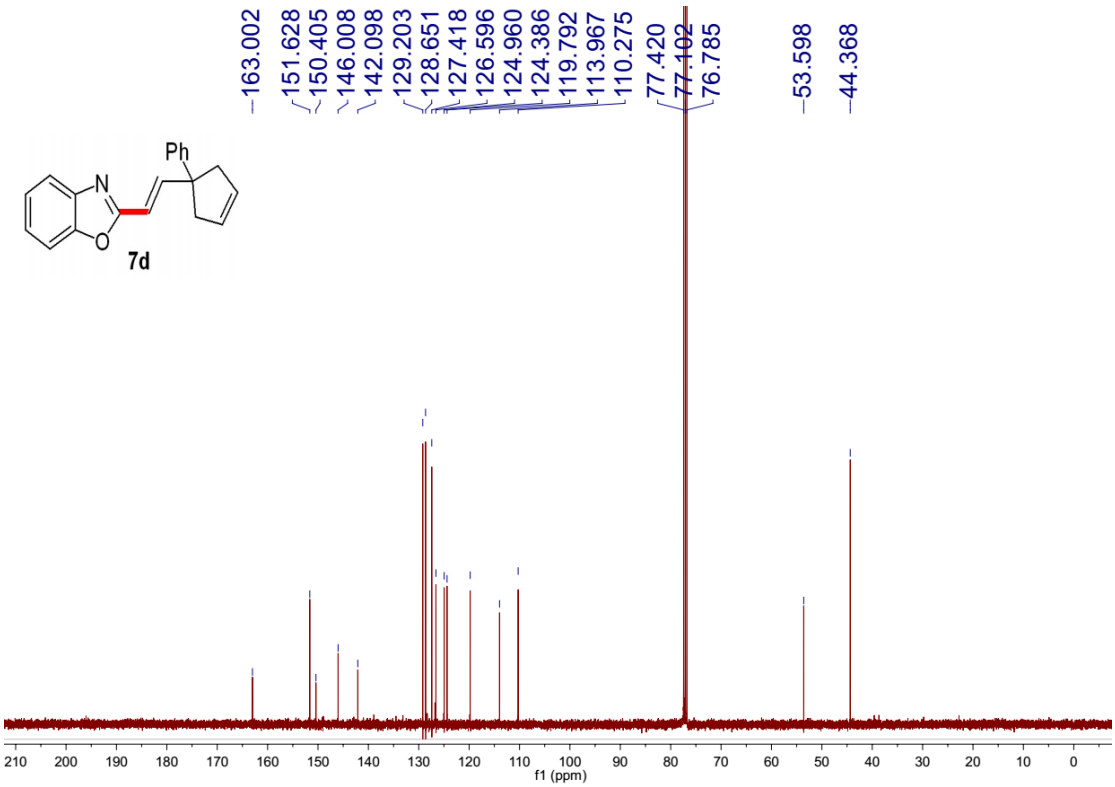
7.429
7.385
7.381
7.366
7.357
7.353
7.346
7.336
7.323
7.319
7.313
7.305
7.301
7.290
7.282
7.275
7.265
7.260
7.246
7.242
6.116
6.076
5.850
3.025
3.015
2.979
2.972
2.969
2.927
2.914
2.879
2.871
2.868
Ph
N
O
7d
1.00
1.07
4.06
3.09
1.09
1.00
1.85
4.01
f1 (ppm)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151.628
150.405
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142.098
129.203
128.651
127.418
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124.960
124.386
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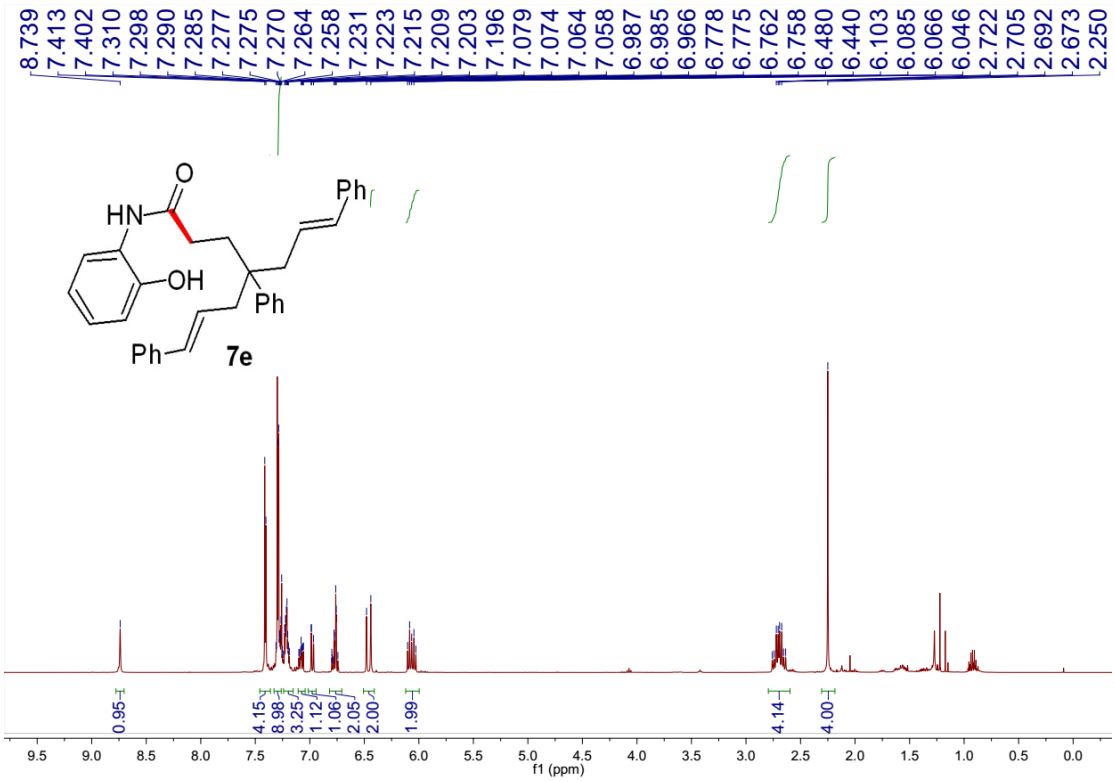
113.967
110.275
77.420
77.102
76.785
53.598
44.368
Ph
N
O
7d
f1 (ppm)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7.277
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7.270
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7.258
7.231
7.223
7.215
7.209
7.203
7.196
7.079
7.074
7.064
7.058
6.987
6.985
6.966
6.778
6.775
6.762
6.758
6.480
6.440
6.103
6.085
6.066
6.046
2.722
2.705
2.692
2.673
2.250
O
HN
OH
Ph
Ph
Ph
7e
0.95
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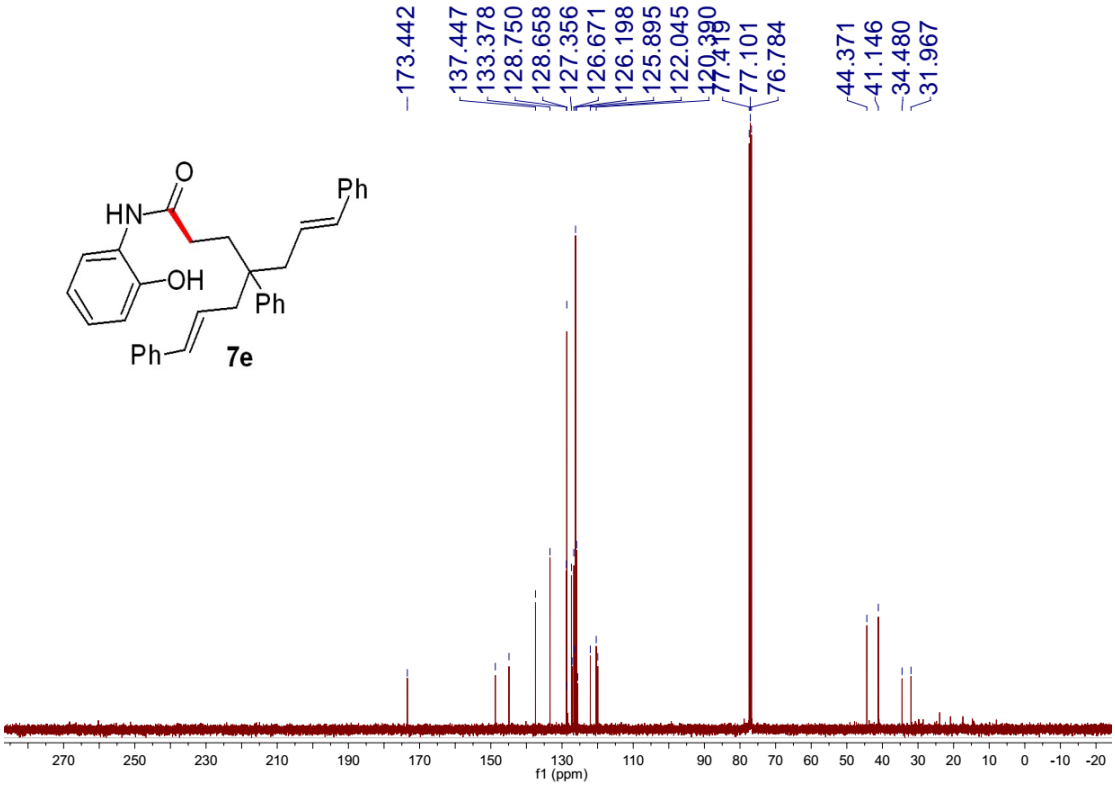
8.98
3.25
1.12
1.06
2.05
2.00
1.99
4.14
4.00
f1 (ppm)


173.442
137.447
133.378
128.750
128.658
127.356
126.671
126.198
125.895
122.045
120.390
77.419
77.101
76.784
44.371
41.146
34.480
31.967
O
HN
OH
Ph
Ph
Ph
7e
f1 (ppm)