Supporting Information

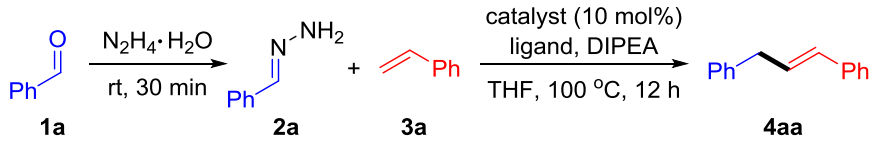
Direct Dehydrogenative Alkyl Heck-Couplings of Vinylarenes with Umpolung Aldehydes Catalyzed by Nickel

Lv et al

Supplementary Notes

^{1}H NMR spectra were recorded on Bruker 400 or 500 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal solvent signal (7.28 ppm in $CDCl_3$). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at 100 or 125 MHz and referenced to the internal solvent signal (central peak is 77.0 ppm in $CDCl_3$). $CDCl_3$ was used as the NMR solvent. Flash column chromatography was performed over silica gel 200-300. The reagent $Ni(cod)_2$ were weighed and handled in a glovebox. All reagents were purchased from Alfa, Acros, Aldrich, and TCI and used without further purification. The HRMS measurements were recorded on a TOF analyzer using an ESI or APCI source in the positive mode. [**Warning**: hydrazine monohydrate is potentially hazardous and should be performed with appropriate personal protection].

Supplementary Table 1 Optimization of the reaction conditions



1a **2a** **3a** **4aa**

entry	catalyst	ligand	base	**4aa** (%)
1	$Ni(cod)_2$	PEt_3	DIPEA	N.D.
2	$Ni(cod)_2$	PBu_3	DIPEA	N.D.
3	$Ni(cod)_2$	dppf	DIPEA	N.D.
4	$Ni(cod)_2$	dmpe	DIPEA	N.D.
5	$Ni(cod)_2$	dppp	DIPEA	N.D.
6	$Ni(cod)_2$	Ruphos	DIPEA	trace
7	$Ni(cod)_2$	Davephos	DIPEA	N.D.
8	$Ni(cod)_2$	DPEphos	DIPEA	trace
9	$Ni(cod)_2$	X-phos	DIPEA	trace
10	$Ni(cod)_2$	Xanphos	DIPEA	N.D.
11	$Ni(cod)_2$	*rac*-BINAP	DIPEA	N.D.
12	$Ni(cod)_2$	cataCXium A	DIPEA	N.D.
13	$Ni(cod)_2$	SIPr·HCl	DIPEA	trace
14	$Ni(cod)_2$	IPr·HCl	DIPEA	trace
15	$Ni(cod)_2$	IPr·HCl	DIPEA	trace
16	$Ni(cod)_2$	bipy	DIPEA	trace
17	$Ni(cod)_2$	1,10-phenanthroline	DIPEA	N.D.
18	$Ni(cod)_2$	triphos	DIPEA	N.D.
19	$Ni(cod)_2$	dcype	^tBuOK	N.D.
20	$Ni(cod)_2$	dcype	K_3PO_4	N.D.
21	$Ni(cod)_2$	dcype	Cs_2CO_3	N.D.
22	$Ni(cod)_2$	dcype	DABCO	44 (79:21)
23	$Ni(cod)_2$	dcype	Et_3N	62 (77:23)
24	$Ni(cod)_2$	dcype	DBU	42 (82:18)
25	$NiCl_2$	dcype	DIPEA	trace
26	$NiBr_2$·diglyme	dcype	DIPEA	trace
27	$Ni(acac)_2$	dcype	DIPEA	10 (78:22)
28	$Pd(OAc)_2$	dcype	DIPEA	N.D.
29	$CuCl_2$	dcype	DIPEA	N.D.
30	$CoCl_2$	dcype	DIPEA	N.D.

Reaction conditions: **3a** (0.2 mmol), **1a** (0.6 mmol), N_2H_4•H_2O (0.72 mmol), $Ni(cod)_2$ (10 mol%), ligand (20 mol% for monodentate, 10 mol% for bidentate), base (0.4 mmol), THF (1.0 mL), 100 ^oC, 12 h under N_2 unless other noted. NMR yields were determined by ^1H NMR using mesitylene as an internal standard and based on **3a**. The *E*:Z ratio was determined by ^1H NMR analysis of the crude mixture. N.D.= not detected.

Supplementary Methods

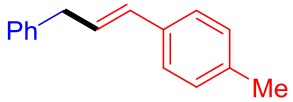
Experimental procedures

In situ preparation of hydrazone solution **2**: a mixture of aldehydes **1** (0.6 mmol, 3.0 equiv) and hydrazine monohydrate (36 μL, 0.72 mmol, 64–65 wt%, 3.6 equiv) in THF (0.6 mL) solution was stirred for 30 min at room temperature in air. Before use, a small amount of anhydrous Na_2SO_4 and 4Å MS was added.

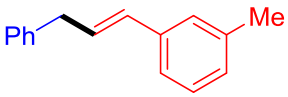
In a glovebox, a flame-dried reaction tube (10 cm^3) equipped with a magnetic stir bar was charged with $Ni(cod)_2$ (5.6 mg, 10 mol%), dcype (8.5 mg, 10 mol%) and THF (0.4 mL) before being sealed with a rubber septum. The reaction mixture was stirred at room temperature for 30 min. Then vinylarene **3** (0.2 mmol, 1.0 equiv), hydrazone solution **2** (0.6 mmol in 0.6 mL THF), DIPEA (0.4 mmol, 67 μL) and NaI (0.1 mmol, 15 mg) was added sequentially. After that, the reaction mixture was sealed with aluminum cap, moved out of glovebox, and stirred at 100 ℃ for 12 hour. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica by EtOAc (3.0 mL). The crude mixture was analyzed by GC-MS. The solvent was evaporated *in vacuo* to give the crude products. NMR yields were determined by ^1H NMR using mesitylene as an internal standard. The residue was purified by preparative TLC (ethyl acetate/petroleum ether) to give the pure product.

Data analyst

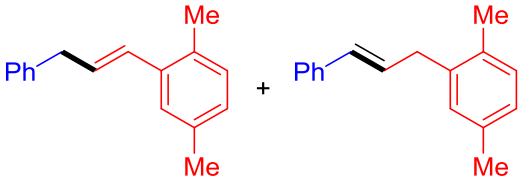
(*E*)-Prop-1-ene-1,3-diyldibenzene (4aa). (34 mg, 87%). Isolated by preparative TLC (hexane, R_f = 0.7); ^1H NMR (500 MHz, $CDCl_3$) δ 7.43-7.23 (m, 10H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.45-6.38 (m, 1H), 3.61 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 137.5, 131.1, 129.3, 128.7, 128.5, 127.1, 126.2, 126.1, 39.4; EI-MS (m/z): 194.2. The spectroscopic data for this product match the literature data.[1]



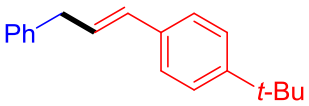
(*E*)-1-Methyl-4-(3-phenylprop-1-en-1-yl)benzene (4ab). (37 mg, 89%). Isolated by preparative TLC (hexane, R_f = 0.6); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.13 (m, 9H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.40-6.32 (m, 1H), 3.58 (d, *J* = 6.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 136.8, 134.7, 130.9, 129.2, 128.7, 128.5, 128.2, 126.1, 126.0, 39.4, 21.2; EI-MS (m/z): 208.1. The spectroscopic data for this product match the literature data.[2]



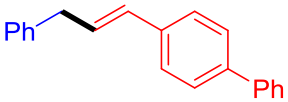
(*E*)-1-Methyl-3-(3-phenylprop-1-en-1-yl)benzene (4ac). (41 mg, 84%). Isolated by preparative TLC (hexane, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.31 (m, 3H), 7.27-7.05 (m, 6H), 6.46 (d, J = 15.6 Hz, 1H), 6.42-6.35 (m, 1H), 3.58 (d, J = 6.6 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 138.1, 137.4, 131.1, 129.0, 128.6, 128.5, 128.4, 127.9, 126.8, 126.1, 123.3, 39.4, 21.4; EI-MS (m/z): 208.1. The spectroscopic data for this product match the literature data.[2]



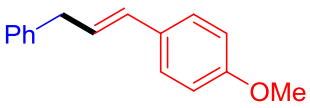
(*E*)-1,4-Dimethyl-2-(3-phenylprop-1-en-1-yl)benzene + 2-cinnamyl-1,4-dimethylbenzene (4ad). (combined 39.1 mg, 88%, 57:43). Isolated by preparative TLC (hexane, R_f = 0.5); **Major and minor**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.22 (m, 6H), 7.11-7.05 (m, 1H), 7.01-6.97 (m, 1H), 6.69 (d, J = 15.6 Hz, 0.4H), 6.44-6.22 (m, 1.6H), 3.61 (d, J = 6.8 Hz, 1H), 3.53 (d, J = 5.3 Hz, 1H), 2.34 (s, 3.1H), 2.33 (s, 2.9H); **Major and minor**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 138.0, 137.6, 136.3, 135.5, 135.3, 133.2, 132.0, 130.8, 130.2, 130.1, 130.2, 129.1, 128.7, 128.5, 127.8, 127.1, 127.2, 126.2, 126.1, 39.7, 36.9, 21.0, 19.4, 19.0; EI-MS (m/z): 222.1. The spectroscopic data for this product match the literature data.[3]



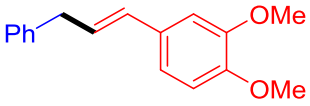
(*E*)-1-(*Tert*-butyl)-4-(3-phenylprop-1-en-1-yl)benzene (4ae). (44.5 mg, 89%). Isolated by preparative TLC (hexane, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.23 (m, 9H), 6.49 (d, J = 15.8 Hz, 1H), 6.43-6.34 (m, 1H), 3.59 (d, J = 7.4 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 140.4, 134.7, 130.9, 128.7, 128.5, 128.4, 126.2, 125.9, 125.5, 39.4, 34.5, 31.3; EI-MS (m/z): 250.2. The spectroscopic data for this product match the literature data.[2]



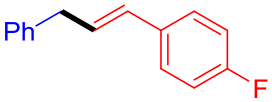
(*E*)-4-(3-Phenylprop-1-en-1-yl)-1,1'-biphenyl (4af). (43.8 mg, 81%). Isolated by preparative TLC (hexane, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.58 (m, 5H), 7.49-7.46 (m, 3H), 7.40-7.35 (m, 4H), 7.33-7.30 (m, 2H), 6.55 (d, J = 15.8 Hz, 1H), 6.49-6.43 (m, 1H), 3.63 (d, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 140.2, 139.9, 136.6, 130.7, 129.5, 128.8, 128.7, 128.6, 127.3, 126.9, 126.6, 126.3, 39.5; EI-MS (m/z): 270.2. The spectroscopic data for this product match the literature data.[2]



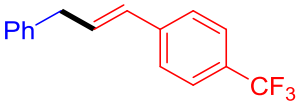
(*E*)-1-Methoxy-4-(3-phenylprop-1-en-1-yl)benzene (4ag). (38.5 mg, 86%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.24 (m, 7H), 6.88 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 15.6 Hz, 1H), 6.29-6.24 (m, 1H), 3.84 (s, 3H), 3.58 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 140.5, 130.5, 130.4, 128.7, 128.6, 127.3, 127.1, 126.2, 113.9, 55.4, 39.4; EI-MS (m/z): 224.1. The spectroscopic data for this product match the literature data.[2]



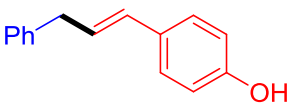
(*E*)-1,2-Dimethoxy-4-(3-phenylprop-1-en-1-yl)benzene (4ah). (44.2 mg, 87%). Isolated by preparative TLC (hexane: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.26 (m, 6H), 6.96-6.80 (m, 2H), 6.44 (d, J = 15.7 Hz, 1H), 6.30-6.24 (m, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.58 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 148.5, 140.4, 130.9, 130.7, 128.7, 128.5, 127.4, 126.2, 119.2, 111.2, 108.6, 56.0, 55.8, 39.4; EI-MS (m/z): 254.1. The spectroscopic data for this product match the literature data.[2]



(*E*)-1-Fluoro-4-(3-phenylprop-1-en-1-yl)benzene (4ai). (40.7 mg, 96%). Isolated by preparative TLC (hexane, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.33 (m, 4H), 7.30-7.24 (m, 3H), 7.06-7.01 (m, 2H), 6.46 (d, J = 15.8 Hz, 1H), 6.32 (dt, J = 15.8, 6.7 Hz, 1H), 3.59 (d, J = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$ = 244.6 Hz), 140.0, 133.6 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.8, 129.0, 128.6, 128.5, 127.5 (d, $J_{C\text{-}F}$ = 7.8 Hz), 126.2, 115.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 39.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.3; EI-MS (m/z): 212.1. The spectroscopic data for this product match the literature data.[2]

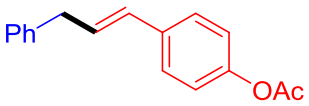


(*E*)-1-(3-Phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzene (4aj). (41.4 mg, 79%). Isolated by preparative TLC (hexane, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.39-7.25 (m, 5H), 6.52-6.46 (m, 2H), 3.60 (d, J = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 139.6, 132.1, 129.8, 128.9 (q, $J_{C\text{-}F}$ = 32.4 Hz), 128.7, 128.6, 126.4, 126.3, 125.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.3 (q, $J_{C\text{-}F}$ = 271.8 Hz), 39.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.5; EI-MS (m/z): 262.1. The spectroscopic data for this product match the literature data.[2]

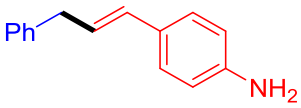


(*E*)-4-(3-phenylprop-1-en-1-yl)phenol (4ak). (29 mg, 69%). Isolated by preparative TLC (hexane: ethyl acetate = 3:1, R_f = 0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 3H), 7.29-7.25 (m, 3H), 6.83-6.78 (m, 3H), 6.43 (d, J = 15.8 Hz, 1H), 6.24 (dt, J = 15.8, 6.8 Hz, 1H), 4.88 (br, 1H), 3.56 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$)

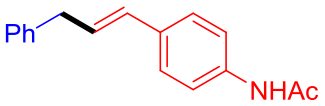
δ 154.7, 140.5, 130.4, 129.8, 128.7, 128.5, 127.5, 127.2, 126.1, 115.4, 39.3; EI-MS (m/z): 210.1. The spectroscopic data for this product match the literature data.[4]



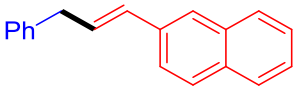
(*E*)-4-(3-Phenylprop-1-en-1-yl)phenyl acetate (4al). (32.3 mg, 64%). Isolated by preparative TLC (hexane:ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.36-7.24 (m, 5H), 7.06-7.04 (m, 2H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.40-6.31 (m, 1H), 3.57 (d, *J* = 6.7 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 149.7, 140.1, 135.3, 130.1, 129.6, 129.5, 128.7, 128.5, 127.0, 126.1, 121.6, 39.3, 21.1; EI-MS (m/z): 252.1. The spectroscopic data for this product match the literature data.[5]



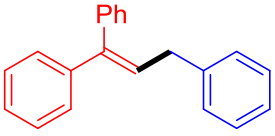
(*E*)-4-(3-Phenylprop-1-en-1-yl)aniline (4am). (31 mg, 74%). Isolated by preparative TLC (hexane:ethyl acetate = 3:1, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.22 (m, 5H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.19 (dt, *J* = 15.6, 6.8 Hz, 1H), 3.67 (br, 2H), 3.55 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 140.7, 130.8, 128.7, 128.5, 128.3, 127.2, 126.0, 125.6, 115.2, 39.4; EI-MS (m/z): 209.1. The spectroscopic data for this product match the literature data.[6]



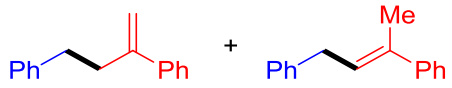
(*E*)-*N*-(4-(3-Phenylprop-1-en-1-yl)phenyl)acetamide (4an). (46.7 mg, 93%). Isolated by preparative TLC (dichloromethane: methanol = 30:1, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 (br, 1H), 7.38-7.30 (m, 4H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.25-7.20 (m, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.38-6.28 (m, 1H), 3.56 (d, *J* = 6.8 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 140.2, 136.9, 133.7, 130.4, 129.2, 128.7, 128.5, 126.7, 126.2, 119.9, 39.3, 24.6; EI-MS (m/z): 251.1. The spectroscopic data for this product match the literature data.[6]



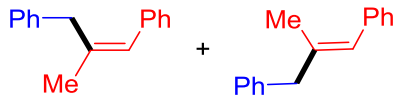
(*E*)-2-(3-Phenylprop-1-en-1-yl)naphthalene (4ao). (41 mg, 84%). Isolated by preparative TLC (hexane, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.79 (m, 3H), 7.74 (s, 1H), 7.62 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.50-7.25 (m, 7H), 6.66 (d, *J* = 15.7 Hz, 1H), 6.57-6.50 (m, 1H), 3.65 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 135.0, 133.7, 132.8, 131.2, 129.8, 128.8, 128.6, 128.2, 127.9, 127.7, 126.3, 126.2, 125.8, 125.6, 123.6, 39.5; EI-MS (m/z): 244.1. The spectroscopic data for this product match the literature data.[2]



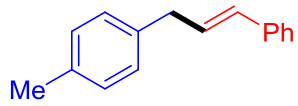
Prop-1-ene-1,1,3-triyltribenzene (4ap). (25.9 mg, 48%). Isolated by preparative TLC (hexane, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.38-7.22 (m, 13H), 6.30 (t, J = 7.6 Hz, 1H), 3.51 (d, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 142.4, 141.0, 139.8, 129.9, 128.5, 128.4, 128.3, 128.1, 127.8, 127.4, 127.2, 127.1, 126.0, 35.9; EI-MS (m/z): 270.1. The spectroscopic data for this product match the literature data.[7]



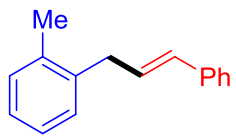
But-3-ene-1,3-diyldibenzene (4aq) and (*E*)-But-2-ene-1,3-diyldibenzene (4aq'). (combined 26.6 mg, 64%, 60:40). Isolated by preparative TLC (hexane, R_f = 0.7); **Major (4aq)**: ^{1}H NMR (500 MHz, $CDCl_3$) 7.52-7.23 (m, 10H), 5.36 (d, J = 0.9 Hz, 1H), 5.13 (d, J = 0.9 Hz, 1H), 2.91-2.81 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 141.9, 141.0, 128.4, 128.3, 127.4, 126.1, 125.8, 112.7, 37.2, 34.7. **Minor (4aq')**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.25 (m, 10H), 6.04 (tq, J = 7.4, 1.3 Hz, 1H), 3.64 (d, J = 7.4 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 141.1, 135.7, 128.4, 128.3, 126.7, 126.6, 125.9, 125.7, 34.9, 16.0; EI-MS (m/z): 208.1. The spectroscopic data for this product match the literature data.[6]



(*Z*)-(2-Methylprop-1-ene-1,3-diyl)dibenzene (4ar) and (*E*)-(2-Methylprop-1-ene-1,3-diyl)dibenzene (4ar'). (combined 14.6 mg, 35%, 67:33). Isolated by preparative TLC (hexane, R_f = 0.7); **Major**: ^{1}H NMR (500 MHz, $CDCl_3$) 7.35-7.30 (m, 6H), 7.25-7.21 (m, 4H), 6.55 (s, 1H), 3.64 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 138.2, 137.0, 128.6, 128.5, 128.4, 128.2, 127.4, 126.3, 126.0, 38.5, 24.0; **Minor**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.30 (m, 6H), 7.25-7.21 (m, 4H), 6.41 (s, 1H), 3.51 (s, 2H), 1.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 138.4, 138.1, 129.0, 128.9, 128.3, 128.0, 126.8, 126.2, 126.1, 47.1, 17.6; EI-MS (m/z): 208.1. The spectroscopic data for this product match the literature data.[8]

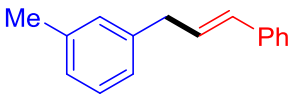


1-Cinnamyl-4-fluorobenzene (4ba). (38.3 mg, 92%). Isolated by preparative TLC (hexane, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.13 (m, 9H), 6.48 (d, J = 15.8 Hz, 1H), 6.38 (dt, J = 15.8, 6.7 Hz, 1H), 3.55 (d, J = 6.7 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 137.1, 135.7, 130.8, 129.5, 129.2, 128.5, 127.0, 126.1, 38.9, 21.0; EI-MS (m/z): 208.1. The spectroscopic data for this product match the literature data.[9]

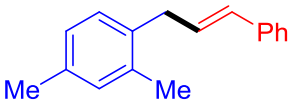


1-Cinnamyl-2-methylbenzene (4bb). (37.0 mg, 89%). Isolated by preparative TLC (hexane, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24-7.19 (m, 5H), 6.44-6.34 (m, 2H), 3.57 (d, J = 5.1 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.5, 136.4, 131.0, 130.2, 129.2, 128.8,

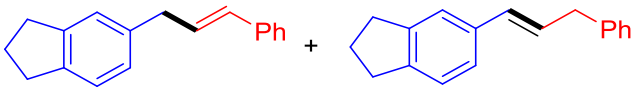
128.7, 127.0, 126.4, 126.1, 126.0, 36.8, 19.4; EI-MS (m/z): 208.1. The spectroscopic data for this product match the literature data.[9]



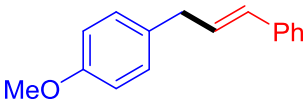
1-Cinnamyl-3-methylbenzene (4bc). (39.1 mg, 94%). Isolated by preparative TLC (hexane, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, J = 7.6 Hz, 1.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 3H), 7.10-7.06 (m, 2H), 6.50 (d, J = 15.8 Hz, 1H), 6.39 (dt, J = 16.0 Hz, 6.8 Hz, 1H), 3.56 (d, J = 6.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 138.1, 137.1, 131.0, 129.4, 129.3, 128.5, 128.4, 127.1, 126.9, 126.1, 125.7, 39.3, 21.4; EI-MS (m/z): 208.1. The spectroscopic data for this product match the literature data.[9]



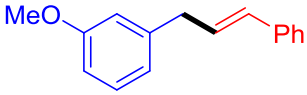
1-Cinnamyl-2,4-dimethylbenzene (4bd). (39.1 mg, 88%). Isolated by preparative TLC (hexane, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.24-7.20 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.03-6.99 (m, 2H), 6.43-6.36 (m, 2H), 3.53 (d, J = 5.2 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 136.2, 135.8, 135.1, 131.0, 130.7, 129.2, 128.8, 128.4, 127.0, 126.7, 126.0, 36.5, 20.9, 19.3; EI-MS (m/z): 222.1. The spectroscopic data for this product match the literature data.[10]



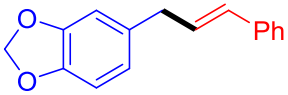
5-Cinnamyl-2,3-dihydro-1H-indene (4be) and . (*E*)-5-(3-phenylprop-1-en-1-yl)-2,3-dihydro-1H-indene (4be') (combined 40.3 mg, 86%, 71:29). Isolated by preparative TLC (hexane, R_f = 0.7); **Major and minor**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.29 (m, 4H), 7.25-7.16 (m, 4H), 6.50 (d, J = 15.8 Hz, 1H), 6.39 (dt, J = 15.8, 6.6 Hz, 1H), 3.56 (d, J = 6.6 Hz, 2H), 2.94-2.90 (m, 4H), 2.13-2.09 (m, 2H); **Major and minor:** ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 144.6, 143.4, 142.1, 140.5, 138.0, 137.6, 135.6, 131.4, 130.7, 129.8, 128.7, 128.5, 127.0, 126.5, 126.1, 124.8, 124.3, 122.0, 121.9, 39.4, 39.3, 32.8, 32.7, 32.6, 32.5, 25.6, 25.5; EI-MS (m/z): 234.1. The spectroscopic data for this product match the literature data.[10]



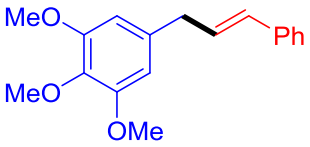
1-Cinnamyl-4-methoxybenzene (4bf). (36.7 mg, 82%). Isolated by preparative TLC (hexane: ethyl acetate = 40:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.25-7.19 (m, 3H), 6.90 (d, J = 7.2 Hz, 2H), 6.47 (d, J = 15.8 Hz, 1H), 6.41-6.35 (m, 1H), 3.84 (s, 3H), 3.53 (d, J = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 137.6, 132.2, 130.8, 129.7, 129.6, 128.5, 127.2, 126.1, 113.9, 55.3, 38.5; EI-MS (m/z): 224.1. The spectroscopic data for this product match the literature data.[9]



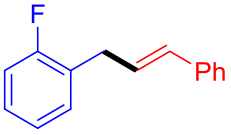
1-Cinnamyl-3-methoxybenzene (4bg). (36.3 mg, 81%). Isolated by preparative TLC (hexane: ethyl acetate =60:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.24 (m, 6H), 7.01-6.81 (m, 3H), 6.50 (d, J = 15.8 Hz, 1H), 6.40 (dt, J = 15.8, 6.8 Hz, 1H), 3.84 (s, 3H), 3.57 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 141.8, 137.5, 131.2, 129.5, 129.1, 128.5, 127.2, 126.2, 121.1, 114.4, 111.6, 55.2, 39.4; EI-MS (m/z): 224.1. The spectroscopic data for this product match the literature data.[11]



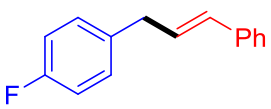
5-Cinnamylbenzo[d][1,3]dioxole (4bh). (34.3 mg, 72%). Isolated by preparative TLC (hexane: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.27-7.22 (m, 1H), 6.82-6.71 (m, 3H), 6.47 (d, J = 15.8 Hz, 1H), 6.35 (dt, J = 15.8, 6.7 Hz, 1H), 5.96 (s, 2H), 3.49 (d, J = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 145.9, 137.4, 133.9, 131.0, 129.3, 128.5, 127.1, 126.1, 121.4, 109.2, 108.2, 100.8, 39.0; EI-MS (m/z): 238.1. The spectroscopic data for this product match the literature data.[12]



5-Cinnamyl-1,2,3-trimethoxybenzene (4bi). (44.3 mg, 78%). Isolated by preparative TLC (hexane: ethyl acetate = 8:1, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.34-7.31 (m, 2H), 7.25-7.21 (m, 1H), 6.50 (d, J = 15.6 Hz, 1H), 6.49 (m, 2H), 6.41-6.34 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.52 (d, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 137.4, 136.4, 135.9, 131.2, 129.0, 128.6, 127.2, 126.2, 105.6, 60.9, 56.1, 39.7; EI-MS (m/z): 284.1. The spectroscopic data for this product match the literature data.[13]

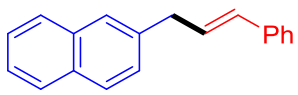


1-Cinnamyl-2-fluorobenzene (4bj). (39.4 mg, 93%). Isolated by preparative TLC (hexane, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.22 (m, 7H), 7.15-7.04 (m, 2H), 6.51 (d, J = 15.8 Hz, 1H), 6.39 (dt, J = 15.8, 6.6 Hz, 1H), 3.62 (d, J = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (d, $J_{C\text{-}F}$ = 244.2 Hz), 137.3, 131.4, 130.6 (d, $J_{C\text{-}F}$ = 4.8 Hz), 128.5, 127.9 (d, $J_{C\text{-}F}$ = 8.4 Hz), 127.6, 127.2, 127.1 (d, $J_{C\text{-}F}$ = 16.7 Hz), 126.1, 32.2 (d, $J_{C\text{-}F}$ = 3.3 Hz), 124.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.5 Hz), 32.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ -118.4; EI-MS (m/z): 212.1. The spectroscopic data for this product match the literature data.[14]

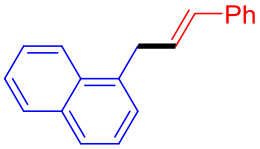


1-Cinnamyl-4-fluorobenzene (4bk). (40.7 mg, 96%). Isolated by preparative TLC (hexane, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.22 (m, 7H), 7.06-7.01 (m, 2H), 6.48 (d, J = 15.6 Hz, 1H), 6.36 (dt, J = 15.6, 6.8 Hz,

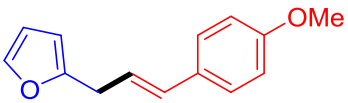
1H), 3.56 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5 (d, $J_{C\text{-}F}$ = 243.3 Hz), 137.4, 135.8 (d, $J_{C\text{-}F}$ = 3.9 Hz), 131.3, 130.0 (d, $J_{C\text{-}F}$ = 7.7 Hz), 129.0, 128.6, 127.3, 126.2, 115.3 (d, $J_{C\text{-}F}$ = 21.0 Hz), 38.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -117.2; EI-MS (m/z): 212.1. The spectroscopic data for this product match the literature data.[1]



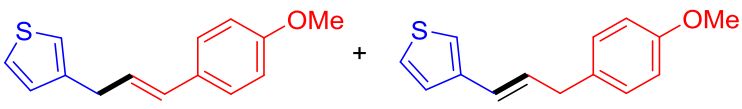
2-Cinnamylnaphthalene (4bl). (37.1 mg, 76%). Isolated by preparative TLC (hexane, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.84 (m, 3H), 7.72 (s, 1H), 7.50-7.45 (m, 2H), 7.42-7.40 (m, 3H), 7.32 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 15.8 Hz, 1H), 6.47 (dt, J = 15.8, 6.2 Hz, 1H), 3.75 (d, J = 6.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 137.5, 133.7, 132.2, 131.3, 129.1, 128.5, 128.0, 127.6, 127.5, 127.4, 127.1, 126.7, 126.2, 126.0, 125.3, 39.5; EI-MS (m/z): 244.1. The spectroscopic data for this product match the literature data.[12]



1-Cinnamylnaphthalene (4bm). (31.7 mg, 65%). Isolated by preparative TLC (hexane, R_f = 0.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19-8.13 (m, 1H), 7.93-7.88 (m, 1H), 7.82-7.79 (m, 1H), 7.58-7.22 (m, 9H), 6.59-6.41 (m, 2H), 4.05 (d, J = 4.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 136.3, 133.9, 132.1, 131.3, 128.9, 128.7, 128.5, 127.1, 126.4, 126.1, 125.9, 125.6, 125.5, 124.0, 36.5; EI-MS (m/z): 244.1. The spectroscopic data for this product match the literature data.[14]

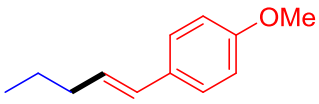


(*E*)-2-(3-(4-Methoxyphenyl)allyl)furan (4bn). (29.1 mg, 68%). Isolated by preparative TLC (hexane: ethyl acetate = 60:1, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, J = 0.8, 1.8 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 15.7 Hz, 1H), 6.33 (dd, J = 1.9, 3.1 Hz, 1H), 6.19 (dt, J = 15.7, 6.8 Hz, 1H), 6.09 (dd, J = 0.8, 3.1 Hz, 1H), 3.83 (s, 3H), 3.56 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 154.2, 141.3, 131.4, 130.1, 127.3, 123.4, 113.9, 110.3, 105.5, 55.3, 31.8; EI-MS (m/z): 214.1. The spectroscopic data for this product match the literature data.[15]

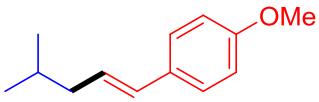


(*E*)-3-(3-(4-Methoxyphenyl)allyl)thiophene (4bn) and (*E*)-3-(3-(4-Methoxyphenyl)prop-1-en-1-yl) thiophene (4bn'). (combined 17.5 mg, 38%, 40:60). Isolated by preparative TLC (hexane: ethyl acetate = 60:1, R_f = 0.5); **Major and minor**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.31 (m, 1H), 7.31-7.29 (m, 1H), 7.27-7.26 (m, 1H), 7.04-7.02 (m, 1H), 7.02-6.99 (m, 1H), 6.91-6.90 (m, 1H), 6.88-6.86 (m, 1H), 6.54 (d, J =11.4 Hz, 0.6H), 6.43 (d, J =15.8 Hz, 0.4H), 6.25 (dt, J =15.8, 6.8 Hz, 0.4H), 5.83 (dt, J =11.4, 7.4 Hz, 0.6H), 3.84 (s, 1.8 H), 3.83 (s, 1.2 H), 3.68 (d, J = 7.4 Hz, 1.2H), 3.56 (d, J = 6.8 Hz, 0.8H); **Major and minor**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9,

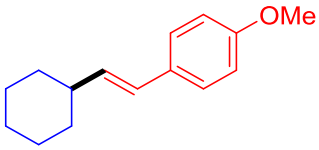
158.5, 141.1, 140.9, 130.4, 130.3, 129.9, 129.8, 129.5, 128.5, 128.4, 128.2, 127.2, 126.4, 125.6, 125.5, 120.8, 120.4, 114.0, 113.7, 55.3, 33.8, 29.5; EI-MS (m/z): 230.1. The spectroscopic data for this product match the literature data.[15,16]



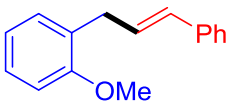
(*E*)-1-Methoxy-4-(pent-1-en-1-yl)benzene (4bp). (14.8 mg, 42%). Isolated by preparative TLC (hexane: ethyl acetate = 150:1, R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.34 (d, *J* =15.8 Hz, 1H), 6.10 (dt, *J* =15.8, 6.8 Hz, 1H), 3.82 (s, 3H), 2.19 (ddd, *J* =15.8, 7.0, 1.3 Hz, 2H), 1.50 (dq, *J* =14.5, 7.2 Hz, 2H), 0.97 (t, *J* =7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 130.8, 129.2, 128.9, 127.0, 113.9, 55.3, 35.1, 22.7, 13.7; EI-MS (m/z): 176.1. The spectroscopic data for this product match the literature data.[16]



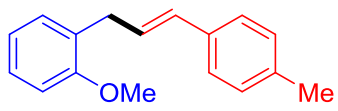
(*E*)-1-Methoxy-4-(4-methylpent-1-en-1-yl)benzene (4bq). (14.8 mg, 39%). Isolated by preparative TLC (hexane: ethyl acetate =100:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.10 (dt, *J* = 15.7, 7.2 Hz, 1H), 3.83 (s, 3H), 2.10 (td, *J* = 7.2, 1.3 Hz, 2H), 1.77-1.69 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 130.8, 130.1, 127.7, 127.0, 113.9, 55.3, 42.4, 28.7, 22.4; EI-MS (m/z): 190.1. The spectroscopic data for this product match the literature data.[17]



(*E*)-1-(2-Cyclohexylvinyl)-4-methoxybenzene (4br). (17.3 mg, 40%). Isolated by preparative TLC (hexane: ethyl acetate =80:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.06 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.82 (s, 3H), 2.15-2.09 (m, 1H), 1.85-1.68 (m, 5H), 1.36-1.18 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 134.8, 130.9, 127.0, 126.5, 113.9, 55.3, 41.1, 33.1, 26.2, 26.1; EI-MS (m/z): 216.2. The spectroscopic data for this product match the literature data.[18]



1-Cinnamyl-2-methoxybenzene (4ca). (41.2 mg, 92%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.33-7.30 (m, 2H), 7.27-7.21 (m, 3H), 6.95 (td, *J* = 7.4, 1.0 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.45-6.40 (m, 1H), 3.89 (s, 3H), 3.58 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 137.8, 130.7, 130.0, 128.9, 128.7, 128.5, 127.4, 126.9, 126.1, 120.6, 110.4, 55.4, 33.4; EI-MS (m/z): 224.1. The spectroscopic data for this product match the literature data.[19]



(*E*)-1-Methoxy-2-(3-(p-tolyl)allyl)benzene (4cb). (40.5 mg, 85%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.26-7.17 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 6.47 (d, J = 15.8 Hz, 1H), 6.43-6.36 (m, 1H), 3.90 (s, 3H), 3.59 (d, J = 6.5 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 136.6, 135.0, 130.6, 129.9, 129.2, 127.9, 127.4, 126.0, 120.6, 110.4, 55.4, 33.4, 21.2; HRMS (ESI) calcd for $C_{17}H_{19}O$ [M + H^+], 239.1430; found: 239.1426.

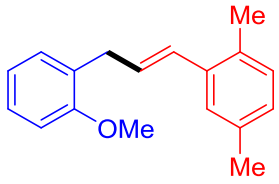
(*E*)-1-Methoxy-2-(3-(m-tolyl)allyl)benzene (4cc). (37.2 mg, 78%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.20 (m, 5H), 7.06-7.04 (m, 1H), 6.95 (td, J = 7.4, 1.0 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.45 (d, J = 15.8 Hz, 1H), 6.44-6.37 (m, 1H), 3.89 (s, 3H), 3.58 (d, J = 5.6 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 138.0, 137.7, 130.8, 129.9, 128.8, 128.7, 128.4, 127.7, 127.4, 126.8, 123.3, 120.6, 110.4, 55.4, 33.4, 21.4; HRMS (ESI) calcd for $C_{17}H_{19}O$ [M + H^+], 239.1430; found: 239.1431.

(*E*)-1-(3-(4-Fluorophenyl)allyl)-2-methoxybenzene (4cd). (46.5 mg, 83%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.34 (m, 4H), 7.27-7.24 (m, 2H), 6.96 (td, J = 7.4, 1.0 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.48 (d, J = 15.8 Hz, 1H), 6.43-6.37 (m, 1H), 3.89 (s, 3H), 3.59 (d, J = 6.7 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 149.9, 135.1, 130.5, 129.8, 128.9, 128.1, 127.4, 125.8, 125.4, 120.5, 110.4, 55.4, 34.5, 33.4, 31.4; HRMS (ESI) calcd for $C_{20}H_{25}O$ [M + H^+], 281.1900; found: 281.1902.

(*E*)-1-Methoxy-2-(3-(4-methoxyphenyl)allyl)benzene (4ce).[17] (41.7 mg, 82%). Isolated by preparative TLC (hexane: ethyl acetate = 40:1, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.8 Hz, 2H), 7.26-7.20 (m, 2H), 6.94 (td, J = 7.4, 1.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.41 (d, J = 15.8 Hz, 1H),

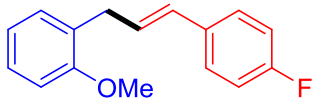
6.30-6.25 (m, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.55 (d, J = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 157.3, 130.7, 130.1, 129.8, 129.6, 129.0, 127.3, 127.2, 126.7, 120.5, 113.9, 110.4, 55.4, 55.3, 33.3; EI-MS (m/z): 254.1.

(*E*)-1,2-Dimethoxy-4-(3-(2-methoxyphenyl)prop-1-en-1-yl)benzene (4cf). (51.7 mg, 91%). Isolated by preparative TLC (hexane: ethyl acetate = 8:1, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 7.00-6.89 (m, 4H), 6.84-6.81 (m, 1H), 6.41 (d, J = 15.8 Hz, 1H), 6.30-6.25 (m, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.57 (d, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 149.0, 148.3, 131.0, 130.3, 129.9, 128.9, 127.4, 127.0, 120.5, 119.0, 111.1, 110.4, 108.7, 55.9, 55.8, 55.4, 33.3; HRMS (ESI) calcd for $C_{18}H_{21}O_3$ [M + H^+], 285.1485; found: 285.1481.

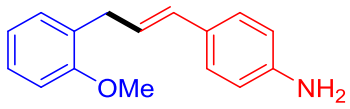


(*E*)-2-(3-(2-Methoxyphenyl)prop-1-en-1-yl)-1,4-dimethylbenzene (4cg). (43.9 mg, 87%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.05 (m, 4H), 7.03-6.89 (m, 3H), 6.68 (d, J = 15.8 Hz, 1H), 6.39-6.25 (m, 1H), 3.90 (s, 3H), 3.61 (d, J = 6.8 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 136.7, 135.3, 132.0, 130.1, 129.8, 129.7, 128.9, 128.8, 127.6, 127.4, 126.2, 120.6, 110.3, 55.4, 33.7, 21.0, 19.4; HRMS (ESI) calcd for $C_{18}H_{21}O$ [M + H^+], 253.1587; found: 253.1590.

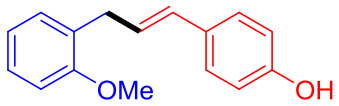
(*E*)-4-(3-(2-Methoxyphenyl)prop-1-en-1-yl)-1,1'-biphenyl (4ch). (49.2 mg, 82%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.59-7.55 (m, 2H), 7.48-7.45 (m, 4H), 7.38-7.34 (m, 1H), 7.28-7.22 (m, 2H), 6.96 (td, J = 7.4, 1.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.52 (d, J = 15.8 Hz, 1H), 6.49-6.39 (m, 1H), 3.90 (s, 3H), 3.60 (d, J = 5.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 140.9, 139.7, 136.9, 130.2, 129.9, 129.2, 128.8, 127.5, 127.2, 126.9, 126.5, 120.6, 110.4, 55.4, 33.5; HRMS (ESI) calcd for $C_{22}H_{21}O$ [M + H^+], 301.1587; found: 301.1585.



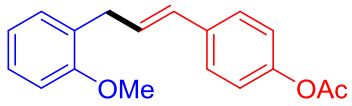
(*E*)-1-(3-(4-Fluorophenyl)allyl)-2-methoxybenzene (4ci). (39.7 mg, 81%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.28-7.22 (m, 2H), 7.05-6.98 (m, 2H), 6.96 (td, *J* = 7.4, 1.0 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.39-6.31 (m, 1H), 3.89 (s, 3H), 3.57 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$ = 245.8 Hz), 157.3, 134.0 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.9, 129.5, 128.7, 128.6, 127.6 (d, $J_{C\text{-}F}$ = 7.6 Hz), 127.5, 120.6, 115.3 (d, $J_{C\text{-}F}$ = 21.8 Hz), 110.4, 55.4, 33.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.7; HRMS (ESI) calcd for $C_{16}H_{16}FO$ [M + H^+], 243.1180; found: 243.1182.



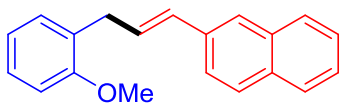
(*E*)-4-(3-(2-methoxyphenyl)prop-1-en-1-yl)aniline (4cj). (36.8 mg, 77%). Isolated by preparative TLC (hexane: ethyl acetate = 2:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.19 (m, 4H), 6.94 (td, *J* = 7.4, 1.0 Hz, 1H), 6.91 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.25-6.19 (m, 1H), 3.88 (s, 3H), 3.65 (br, 2H), 3.54 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 145.4, 130.5, 129.8, 129.2, 128.7, 127.3, 127.2, 125.2, 120.5, 115.2, 110.4, 55.4, 33.3; HRMS (ESI) calcd for $C_{16}H_{18}NO$ [M + H^+], 240.1383; found: 240.1385.



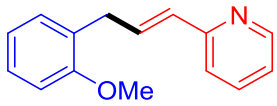
(*E*)-4-(3-(2-Methoxyphenyl)prop-1-en-1-yl)phenol (4ck). (25.5 mg, 53%). Isolated by preparative TLC (hexane: ethyl acetate = 5:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.25 (m, 2H), 7.23-7.21 (m, 2H), 6.95-6.88 (m, 2H), 6.80-6.76 (m, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.28-6.22 (m, 1H), 4.85 (br, 1H), 3.87 (s, 3H), 3.54 (d, *J* = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 154.6, 130.8, 130.0, 129.8, 128.9, 127.4, 127.3, 126.8, 120.5, 115.3, 110.4, 55.4, 33.3; HRMS (ESI) calcd for $C_{16}H_{17}O_2$ [M + H^+], 241.1223; found: 241.1225.



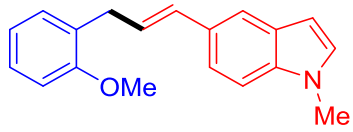
(*E*)-4-(3-(2-Methoxyphenyl)prop-1-en-1-yl)phenyl acetate (4cl). (21.4 mg, 38%). Isolated by preparative TLC (hexane: ethyl acetate = 10:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.24 (td, *J* = 7.8, 1.7 Hz, 1H), 7.21 (td, *J* = 7.4, 1.7 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.94 (td, *J* = 7.4, 1.0 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.38-6.33 (m, 1H), 3.87 (s, 3H), 3.55 (d, *J* = 6.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 157.3, 149.5, 135.6, 129.8, 129.7, 129.3, 128.6, 127.5, 127.0, 121.5, 120.6, 110.4, 55.4, 33.4, 21.1; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ [M + H^+], 283.1329; found: 283.1333.



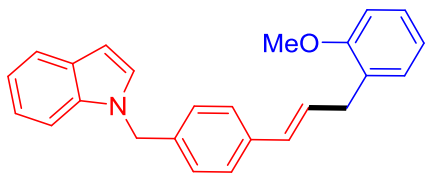
(*E*)-2-(3-(2-methoxyphenyl)prop-1-en-1-yl)naphthalene (4cm). (41.2 mg, 75%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.82 (m, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.74 (s, 1H), 7.65 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.51-7.44 (m, 2H), 7.30-7.27 (m, 2H), 6.99 (td, *J* = 7.6, 1.0 Hz, 1H), 6.95 (dd, *J* = 8.6, 1.0 Hz, 1H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.61-6.55 (m, 1H), 3.92 (s, 3H), 3.67 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 135.3, 133.7, 132.7, 130.8, 130.0, 129.5, 128.7, 128.0, 127.9, 127.7, 127.5, 126.1, 125.6, 125.5, 123.7, 120.6, 110.5, 55.5, 33.6; HRMS (ESI) calcd for $C_{20}H_{19}O$ [M + H^+], 275.1430; found: 275.1428.



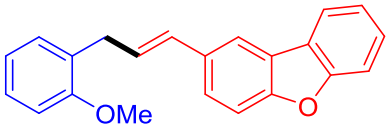
(*E*)-2-(3-(2-methoxyphenyl)prop-1-en-1-yl)pyridine (4cn). (37.2 mg, 83%). Isolated by preparative TLC (hexane: ethyl acetate = 5:1, R_f = 0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.2 Hz, 1H), 7.60 (td, *J* = 7.8, 1.8 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.25-7.21 (m, 2H), 7.11-7.08 (m, 1H), 6.95-6.87 (m, 3H), 6.54 (dt, *J* = 15.8, 1.4 Hz, 1H), 3.87 (s, 3H), 3.62 (dd, *J* = 6.8, 0.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 156.1, 149.3, 136.4, 134.0, 130.6, 130.1, 128.0, 127.6, 121.6, 121.0, 120.6, 110.4, 55.4, 33.4; HRMS (APCI) calcd for $C_{15}H_{16}ON$ [M + H+], 226.1226; found: 226.1229.



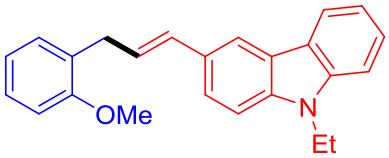
(*E*)-5-(3-(2-Methoxyphenyl)prop-1-en-1-yl)-1-methyl-1H-indole (4co). (39.4 mg, 71%). Isolated by preparative TLC (hexane: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.37 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.30-7.24 (m, 3H), 7.04 (d, *J* = 3.0 Hz, 1H), 6.97 (td, *J* = 7.4, 0.9 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.48 (dd, *J* = 3.0, 0.6 Hz, 1H), 6.38 (dt, *J* =15.8, 6.8 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.62 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 136.2, 131.9, 129.9, 129.5, 129.4, 129.1, 128.7, 127.3, 125.8, 120.6, 120.0, 118.9, 110.4, 109.2, 101.1, 55.5, 33.4, 32.9; HRMS (APCI) calcd for $C_{19}H_{20}ON$ [M + H^+], 278.1539; found: 278.1548.



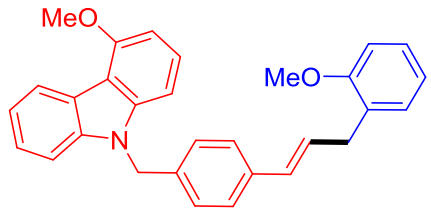
(*E*)-1-(4-(3-(2-methoxyphenyl)prop-1-en-1-yl)benzyl)-1H-indole (4cp). (57.1 mg, 81%). Isolated by preparative TLC (hexane: ethyl acetate = 10:1, R_f = 0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 1H), 7.40-7.38 (m, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.32-7.26 (m, 3H), 7.23-7.18 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.00 (td, *J* = 7.4, 1.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.65-6.63 (m, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.46-6.38 (m, 1H), 5.33 (s, 2H), 3.91 (s, 3H), 3.62 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 137.3, 136.1, 130.2, 129.9, 129.3, 129.1, 128.8, 128.6, 128.3, 127.5, 127.1, 126.5, 121.7, 121.0, 120.6, 119.6, 110.5, 109.8, 101.7, 55.4, 49.9, 33.5; HRMS (APCI) calcd for $C_{25}H_{24}ON$ [M + H^+], 354.1852; found: 354.1856.



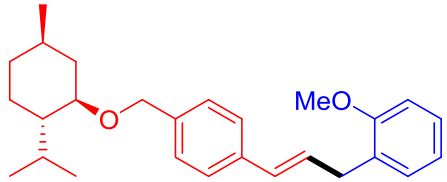
(*E*)-2-(3-(2-Methoxyphenyl)prop-1-en-1-yl)dibenzo[b,d]furan (4cq). (39.4 mg, 92%). Isolated by preparative TLC (hexane: ethyl acetate =60:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.96 (m, 2H), 7.61-7.59 (m, 1H), 7.56-7.47 (m, 3H), 7.41-7.36 (m, 1H), 7.30-7.26 (m, 2H), 7.01-6.92 (m, 2H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.51-6.46 (m, 1H), 3.92 (s, 3H), 3.65 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 156.6, 155.5, 133.0, 130.5, 130.0, 128.8, 128.3, 127.5, 127.1, 125.6, 124.5, 124.3, 122.7, 120.7, 120.6, 118.0, 111.7, 111.5, 110.5, 55.5, 33.5; HRMS (APCI) calcd for $C_{22}H_{19}O_2$ [M + H^+], 315.1380; found: 315.1382.



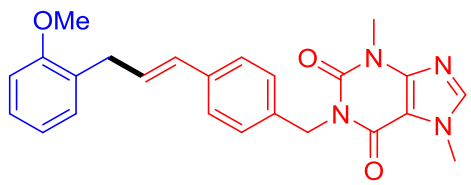
(*E*)-9-Ethyl-3-(3-(2-methoxyphenyl)prop-1-en-1-yl)-9H-carbazole (4cr). (46.4 mg, 68%). Isolated by preparative TLC (hexane: ethyl acetate = 10:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.57 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.27-7.24 (m, 2H), 6.98 (td, *J* = 7.4, 0.9 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 15.8 Hz, 1H), 6.45 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 3.65 (d, *J* = 6.8 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 140.3, 139.3, 131.4, 129.9, 129.2, 129.1, 127.3, 126.1, 125.6, 124.1, 123.1, 123.0, 120.6, 120.5, 118.8, 118.1, 110.4, 108.5, 108.4, 55.5, 37.6, 33.5, 13.8; HRMS (APCI) calcd for $C_{24}H_{24}ON$ [M + H^+], 342.1852; found: 342.1862.



(*E*)-4-methoxy-9-(4-(3-(2-methoxyphenyl)prop-1-en-1-yl)benzyl)-9H-carbazole (4cs). (76.2 mg, 88%). Isolated by preparative TLC (hexane: ethyl acetate = 10:1, R_f = 0.6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.6 Hz, 1H), 7.47-7.38 (m, 3H), 7.36-7.32 (m, 1H), 7.30-7.26 (m, 3H), 7.24-7.11 (m, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.96 (td, *J* = 7.4, 0.9 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.40-6.33 (m, 1H), 5.49 (s, 2H), 4.15 (s, 3H), 3.88 (s, 3H), 3.57 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 156.4, 142.2, 139.9, 137.1, 135.9, 130.2, 129.9, 129.1, 128.6, 127.5, 126.7, 126.6, 126.5, 124.9, 123.2, 122.5, 120.6, 119.5, 112.2, 110.4, 108.4, 102.0, 100.4, 55.5, 55.4, 46.6, 33.4; HRMS (APCI) calcd for $C_{30}H_{28}O_2N$ [M + H^+], 434.2115; found: 434.2110.

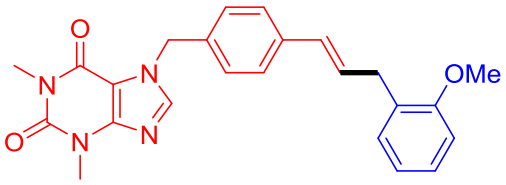


1-((*E*)-3-(4-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)allyl)-2-methoxybenzene (6). (0.1 mmol scale, 31 mg, 79%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.27-7.22 (m, 2H), 6.94 (t, *J* = 7.1 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.40 (td, *J* = 15.8, 6.0 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 3.88 (s, 3H), 3.57 (d, *J* = 6.2 Hz, 2H), 3.23-3.16 (m, 1H), 2.35-2.30 (m, 1H), 2.25-2.20 (m, 1H), 1.70-1.63 (m, 2H), 1.42-1.29 (m, 2H), 1.03-0.85 (m, 9H), 0.74 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 137.8, 137.0, 130.5, 129.9, 128.7, 128.1, 128.0, 127.4, 126.0, 120.6, 110.4, 78.6, 70.2, 55.4, 48.4, 40.3, 34.6, 33.4, 31.6, 25.5, 23.3, 22.4, 21.1, 16.1; HRMS (ESI) calcd for $C_{46}H_{67}O_3$ [M + H^+], 415.2608; found: 415.2603.

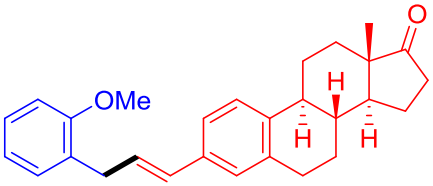


(*E*)-1-(4-(3-(2-Methoxyphenyl)prop-1-en-1-yl)benzyl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione (8). (0.1 mmol scale, 38.3 mg, 92%). Isolated by preparative TLC (dichloromethane: methanol = 1:10, R_f = 0.3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.24-7.17 (m, 2H),

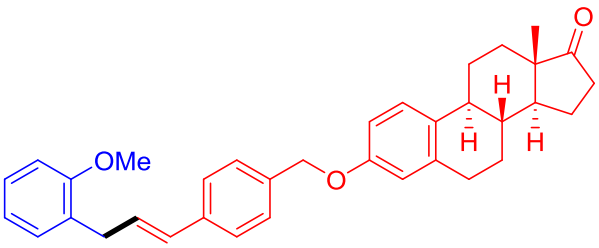
6.93-6.86 (m, 2H), 6.41 (d, J = 15.8 Hz, 1H), 6.35 (td, J = 15.8, 6.4 Hz, 1H), 5.17 (s, 2H), 3.99 (s, 3H), 3.85 (s, 3H), 3.59 (s, 3H), 3.53 (d, J = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 155.3, 151.6, 148.9, 141.5, 137.2, 136.0, 130.4, 129.8, 129.1, 129.0, 128.7, 127.4, 126.1, 120.5, 110.3, 107.7, 55.4, 44.2, 33.6, 33.4, 29.8; HRMS (ESI) calcd for $C_{24}H_{25}O_3N_4$ [M + H^+], 417.1921; found: 417.1920.



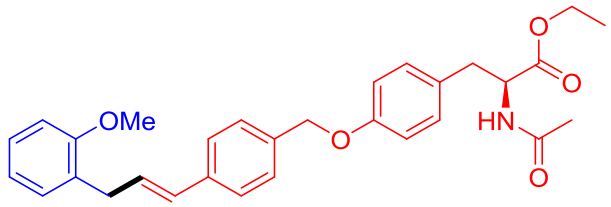
(*E*)-7-(4-(3-(2-methoxyphenyl)prop-1-en-1-yl)benzyl)-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (10). (37.2 mg, 88%). Isolated by preparative TLC (dichloromethane: methanol = 1:10, R_f = 0.4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.23-7.17 (m, 2H), 6.94-6.88 (m, 2H), 6.40 (s, 2H), 5.50-5.47 (m, 2H), 3.86 (m, 3H), 3.60 (s, 3H), 3.55 (s, 2H), 3.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 155.3, 151.7, 148.9, 140.8, 138.3, 133.6, 130.1, 129.8, 129.7, 128.4, 128.2, 127.5, 126.9, 126.7, 120.5, 110.4, 55.4, 50.1, 33.4, 29.8, 28.0; HRMS (APCI) calcd for $C_{24}H_{25}O_3N_4$ [M + H^+], 417.1921; found: 417.1916.



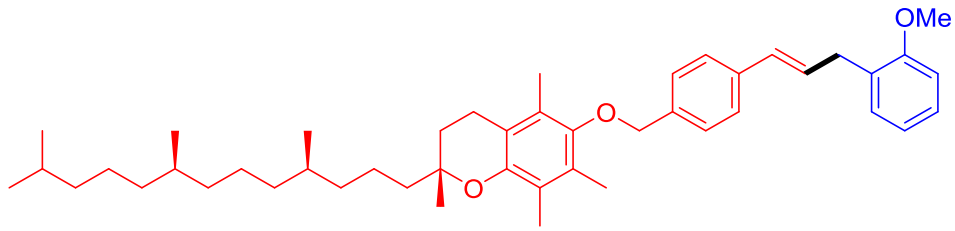
(8R,9S,13S,14S)-3-((*E*)-3-(2-Methoxyphenyl)prop-1-en-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (12). (0.1 mmol scale, 36.4 mg, 91%). Isolated by preparative TLC (hexane: ethyl acetate =5:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.19 (m, 4H), 7.13 (s, 1H), 6.96-6.90 (m, 2H), 6.44-6.34 (m, 2H), 3.88 (s, 3H), 3.57 (d, J = 6.2 Hz, 2H), 2.94-2.91 (m, 2H), 2.57-2.51 (m, 1H), 2.46-2.43 (m, 1H), 2.33-2.30 (m, 1H), 2.21-2.14 (m, 1H), 2.11-1.98 (m, 3H), 1.70-1.57 (m, 3H), 1.55-1.45 (m, 3H), 0.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.9, 157.3, 138.6, 136.5, 135.4, 130.4, 129.8, 128.8, 128.3, 127.4, 126.7, 125.5, 123.6, 120.5, 110.4, 55.4, 50.5, 48.0, 44.4, 38.2, 35.9, 33.4, 31.6, 29.4, 26.6, 25.8, 21.6, 13.9; HRMS (APCI) calcd for $C_{28}H_{33}O_2$ [M + H^+], 401.2475; found: 401.2484.



(8R,9S,13S,14S)-3-((4-((*E*)-3-(2-Methoxyphenyl)prop-1-en-1-yl)benzyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (14). (0.1 mmol scale, 38.5 mg, 76%). Isolated by preparative TLC (hexane: ethyl acetate =5:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.35 (m, 4H), 7.26-7.21 (m, 3H), 6.96-6.89 (m, 2H), 6.84-6.74 (m, 2H), 6.48-6.38 (m, 2H), 5.04 (s, 2H), 3.88 (s, 3H), 3.57 (d, *J* = 5.7 Hz, 2H), 2.94-2.90 (m, 2H), 2.56-2.50 (m, 1H), 2.44-2.40 (m, 1H), 2.30-2.26 (m, 1H), 2.21-2.13 (m, 1H), 2.11-1.97 (m, 3H), 1.69-1.61 (m, 3H), 1.55-1.46 (m, 3H), 0.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 221.0, 157.3, 156.9, 137.8, 137.5, 135.8, 132.3, 130.3, 129.9, 129.2, 128.6, 127.6, 127.5, 126.3, 126.2, 120.6, 115.0, 112.5, 110.4, 69.8, 55.4, 50.4, 48.0, 44.0, 38.4, 35.9, 33.4, 31.6, 29.7, 26.6, 25.9, 21.6, 13.9; HRMS (APCI) calcd for $C_{35}H_{39}O_3$ [M + H^+], 507.2907; found: 507.2894.

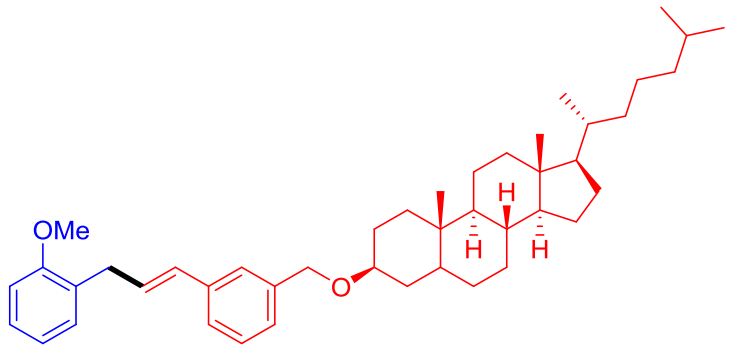


Ethyl (*S*,*E*)-2-acetamido-3-(4-((4-(3-(2-methoxyphenyl)prop-1-en-1-yl)benzyl)oxy)phenyl)propanoate (16). (0.1 mmol scale, 30.2 mg, 62%). Isolated by preparative TLC (hexane: ethyl acetate = 1:1, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.26-7.20 (m, 2H), 7.05-7.02 (m, 2H), 6.95-6.89 (m, 4H), 6.48-6.38 (m, 2H), 5.94 (d, *J* = 7.4 Hz, 1H), 5.02 (s, 2H), 4.87-4.82 (m, 1H), 4.22-4.17 (m, 2H), 3.87 (s, 3H), 3.57 (d, *J* = 5.6 Hz, 2H), 3.12-3.05 (m, 2H), 2.01 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 169.6, 157.9, 157.3, 137.6, 135.5, 130.3, 130.2, 129.9, 129.3, 129.0, 128.6, 128.1, 127.7, 127.5, 126.3, 120.6, 115.0, 110.4, 69.9, 61.5, 55.4, 53.3, 37.1, 33.4, 23.2, 14.2; HRMS (APCI) calcd for $C_{30}H_{34}O_5N$ [M + H^+], 488.2432; found: 488.2437.



(R)-6-((4-((*E*)-3-(2-Methoxyphenyl)prop-1-en-1-yl)benzyl)oxy)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (18). (0.1 mmol scale, 55.3 mg, 83%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.29-7.26 (m, 2H), 6.98 (td, *J* = 7.6, 0.8 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.46 (td, *J* = 15.8, 6.0 Hz, 1H), 4.73 (s, 2H), 3.91 (s, 3H), 3.62 (d, *J* = 6.0 Hz, 2H), 2.65 (t, *J* = 6.6 Hz, 2H), 2.27 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H),

1.92-1.80 (m, 2H), 1.66-1.55 (m, 3H), 1.52-1.44 (m, 4H), 1.38-1.28 (m, 11H), 1.23-1.11 (m, 6H), 0.95-1.91 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 148.2, 147.9, 137.4, 136.7, 130.5, 129.9, 129.0, 128.7, 127.9, 127.5, 126.2, 126.0, 122.9, 120.6, 117.6, 110.4, 74.8, 74.6, 55.4, 40.1, 39.4, 37.5, 37.4, 33.5, 32.8, 32.7, 31.4, 28.0, 24.9, 24.5, 24.0, 22.8, 22.7, 21.1, 20.7, 19.8, 19.7, 13.0, 12.1, 11.9; HRMS (APCI) calcd for $C_{46}H_{67}O_3$ [M + H^+], 667.5085; found: 667.5104.



(3S,8R,9S,10S,13R,14S,17R)-3-((3-((*E*)-3-(2-Methoxyphenyl)prop-1-en-1-yl)benzyl)oxy)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene (20). (0.1 mmol scale, 53 mg, 85%). Isolated by preparative TLC (hexane: ethyl acetate = 50:1, R_f = 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.26-7.21 (m, 2H), 6.94 (td, *J* = 7.4, 1.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.39 (td, *J* = 15.8, 6.2 Hz, 1H), 4.57-4.51 (m, 2H), 3.88 (s, 3H), 3.56 (d, *J* = 6.2 Hz, 2H), 3.36-3.30 (m, 1H), 2.00-1.97 (m, 1H), 1.92-1.90 (m, 1H), 1.85-1.81 (m, 1H), 1.76-1.66 (m, 3H), 1.59-1.45 (m, 4H), 1.39-1.25 (m, 10H), 1.20-0.96 (m, 10H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 2.2 Hz, 3H), 0.89 (d, *J* = 2.2 Hz, 3H), 0.83 (s, 3H), 0.68 (s, 3H), 0.65-0.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 137.9, 137.0, 130.5, 129.9, 128.7, 127.7, 127.4, 126.0, 120.5, 110.4, 77.8, 69.5, 56.5, 56.3, 55.4, 54.5, 44.9, 42.6, 40.1, 39.5, 37.0, 36.2, 35.8, 35.5, 34.9, 33.4, 32.2, 28.9, 28.3, 28.0, 24.2, 23.9, 22.8, 22.6, 21.3, 18.7, 12.3, 12.1; HRMS (APCI) calcd for $C_{44}H_{65}O_2$ [M + H^+], 625.4979; found: 625.4982.

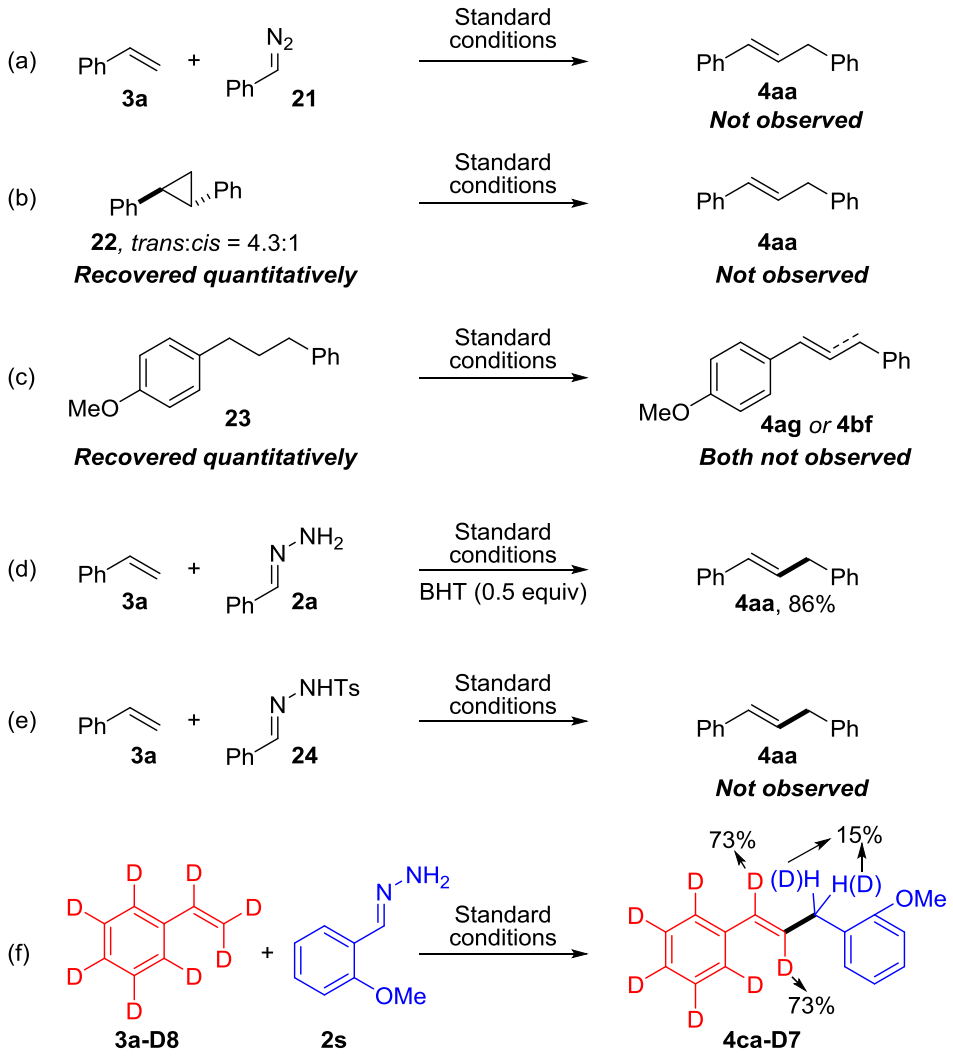
Mechanistic study

The phenyldiazomethane **21** was prepared following a literature procedure.[20] To a solution of benzaldehyde **1a** (0.6 mmol) in THF (2.0 mL) was added hydrazine monohydrate (36 μL, 0.72 mmol, 64–65 wt%). The resulting mixture was stirred for 30 min at room temperature and then cooled to 0 ^{o}C. Activated MnO_2 (2.4 mmol) and $MgSO_4$ (2.4 mmol) were added. The reaction mixture was stirred for 2 h at 0 ^{o}C and 1 h at room temperature, then filtered through celite and used immediately without further purification. When phenyldiazomethane was used instead of benzaldehyde hydrazone under the standard conditions, the desired product **4aa** was not observed (see Supplementary Figure 1a). This result excluded the participation of carbene or diazo compound species.

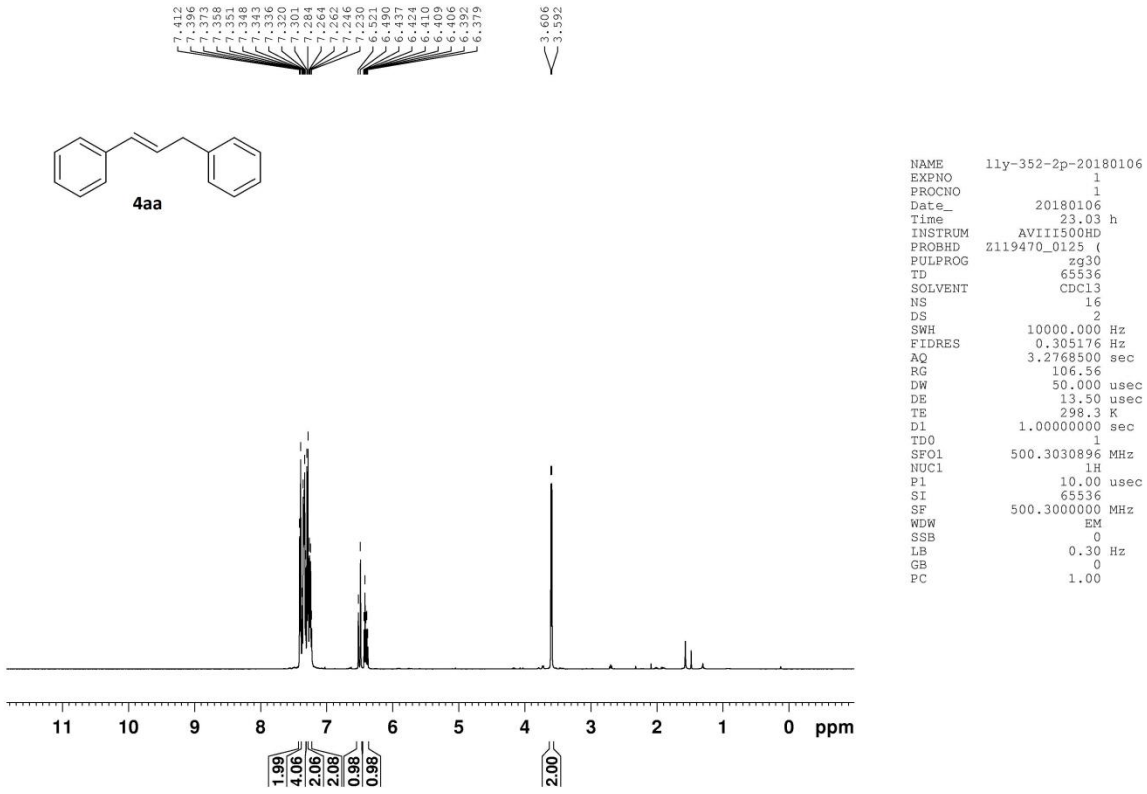
The 1,2-diphenylcyclopropane **22** was prepared following a literature procedure.[21] A dry Schlenk was charged with styrene (2.0 mmol), K_2CO_3 (1.5 mmol), *N*-Tosyl phenylhydrazone (1.0 mmol) and dioxane (5.0 mL) under nitrogen atmosphere. The reaction mixture was heated at 110 ^oC, stirred and refluxed for 6 h. After the mixture was cooled to room temperature, diluted with dichloromethane (10.0 mL) and filtered through celite. The solvent was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel with hexane to give the product **22** (*trans*:*cis* = 4.3:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.31 (m, 4H), 7.23-7.20 (m, 2H), 7.18-7.16 (m, 4H), 7.13-7.10 (m, 0.92H), 7.08-7.05 (m, 0.46H), 6.98-6.96 (m, 0.92H), 2.51 (dd, *J* = 8.6, 6.4 Hz, 0.46H), 2.20 (dd, *J* = 7.4, 6.0 Hz, 2H), 1.50-1.46 (m, 2.46H). The spectroscopic data for this substrate match the literature data.[21] When 1,2-diphenylcyclopropane **22** was used instead of benzaldehyde hydrazone and styrene under the standard conditions, the desired product **4aa** was not observed (see Supplementary Figure 1b). This result ruled out the pathway that ring opening of cyclopropane to give the desired product.

The 1-methoxy-4-(3-phenylpropyl)benzene **23** was prepared following a literature procedure.[22] In a glovebox, a flame-dried reaction tube equipped with a magnetic stir bar was charged with $Ni(cod)_2$ (11.2 mg, 10 mol%), PMe_3 (17 μL, 40 mol%) and 1,4-dioxane (2.0 mL) before being sealed with a rubber septum and taken out of the glove box. The reaction mixture was stirred at room temperature for 30 min. Then 4-methoxyphenyl triflate (0.2 mmol), (3-bromopropyl)benzene (0.6 mmol), hydrazine solution (1 M in THF, 0.4 mmol, 400 μL) and K_3PO_4 (1.2 mmol) were added sequentially. After that, the reaction mixture was sealed with aluminum cap, moved out of glovebox and stirred at 110 ℃ for 12 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica and washed with EtOAc (5.0 mL). The solvent was evaporated *in vacuo* to give the crude product. The residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether) to give the pure substrate **23**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.23-7.20 (m, 3H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.00-1.94 (m, 2H). The spectroscopic data for this product match the literature data.[22] When **23** was used under the standard conditions, the desired product **4aa** was not observed (see Supplementary Figure 1c). This result ruled out the hydrazone addition to the vinylarene and followed by dehydrogenation pathway.

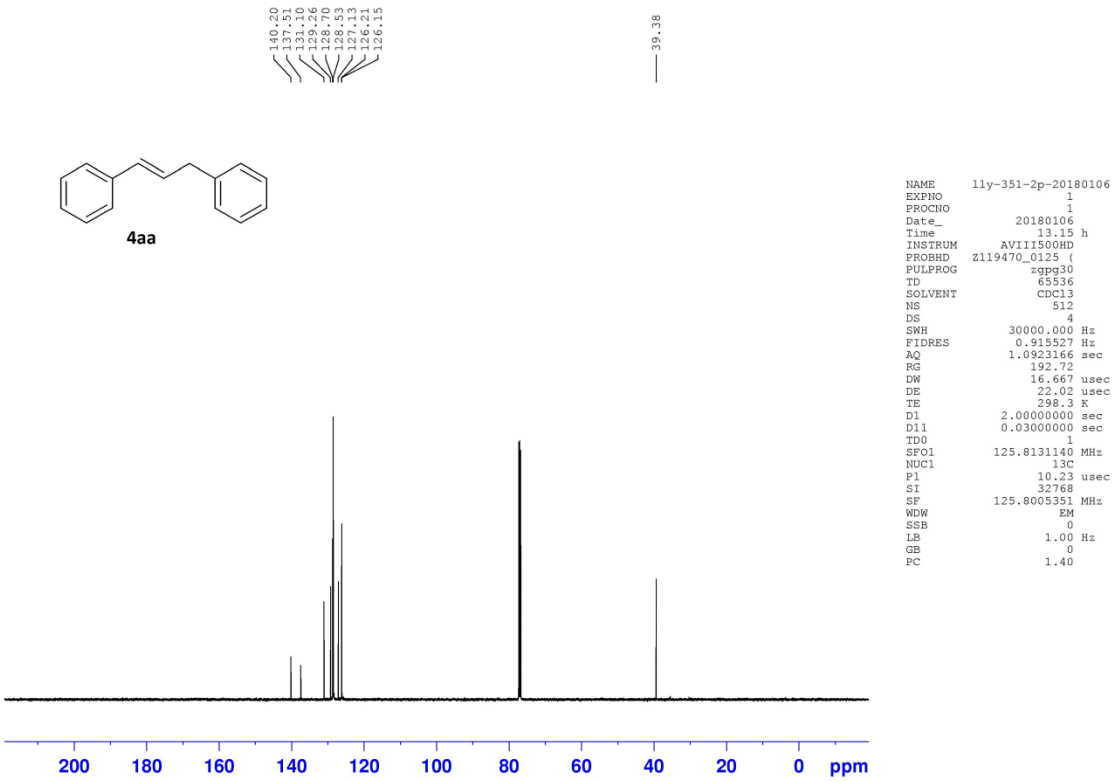
When deuterated styrene (**3a**-D8) was reacted with hydrazone under the optimized conditions, the H/D exchanges both in the double bond moiety (73% D) and benzylic position (15% D) were observed in the corresponding product **4a**-D7. ^1H NMR (500 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2H), 6.95 (td, *J* = 7.4, 1.0 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.50-6.46 (m, 0.27H), 6.44-6.37 (m, 0.27H), 3.89 (s, 3H), 3.59-3.58 (m, 1.7H); EI-MS (m/z): 231.2. This outcome revealed that there were iterative Ni-(H)D species addition/elimination steps during the reaction process (see Supplementary Figure 1f)



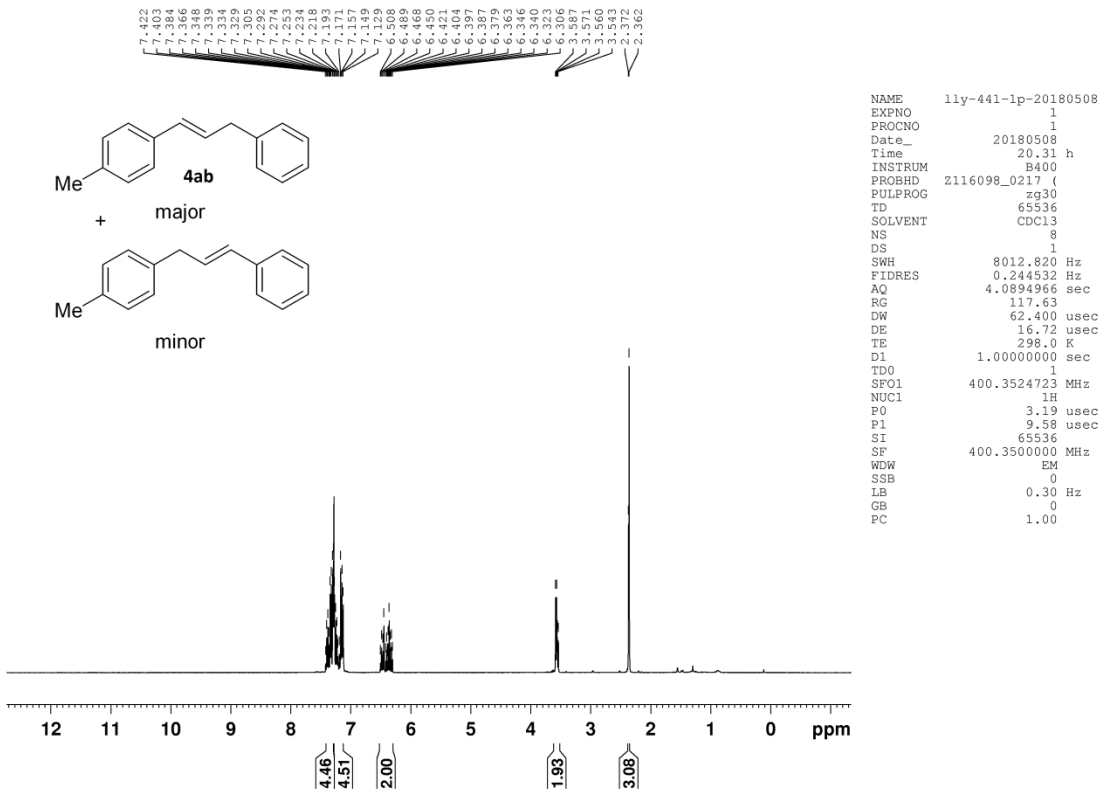
Supplementary Figure 1 Mechanistic studies. **a** Reaction of styrene with phenyldiazomethane did not give the desired product; **b** Reaction of 1,2-diphenylcyclopropane under the standard conditions did not give the desired product; **c** Reaction of 1-methoxy-4-(3-phenylpropyl)benzene under the standard conditions did not give the desired product; **d** Radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol (BHT) added and the reaction was almost unaffected; **e** *N*-Ts hydrazone used instead of simple hydrazone did not give the desired product; **f** H/D exchanges occurred in the isotope experiment



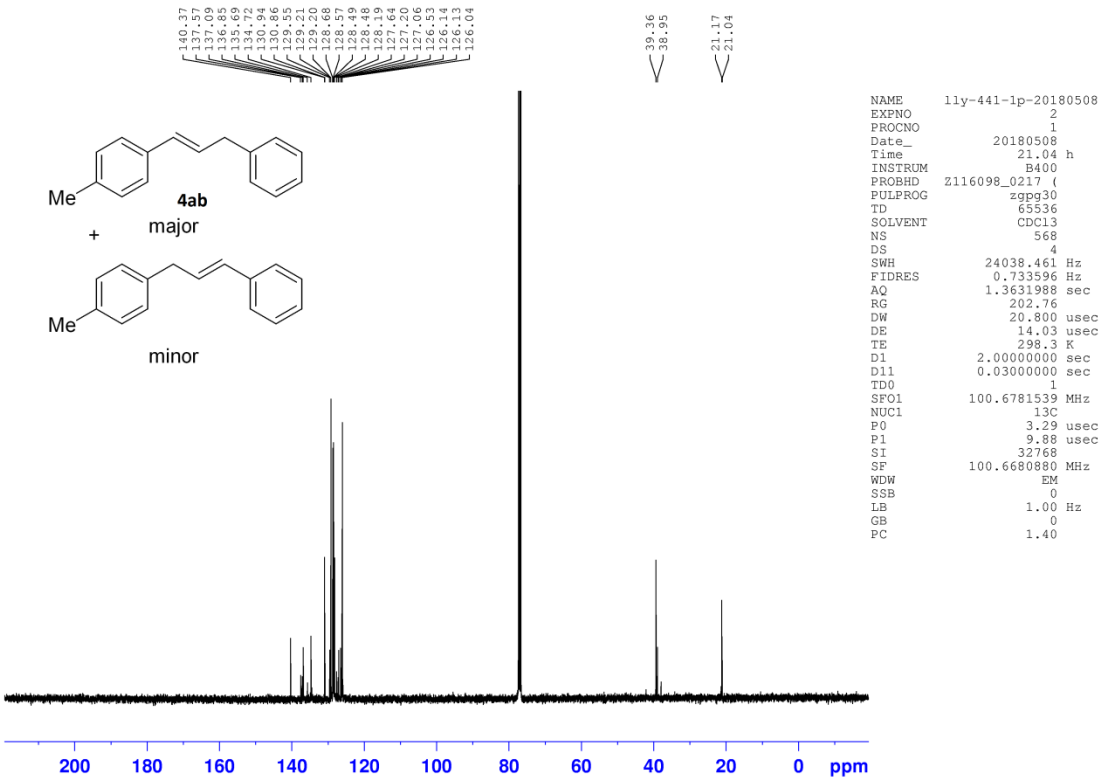
Supplementary Figure 2. ^{1}H NMR spectra for compound **4aa**



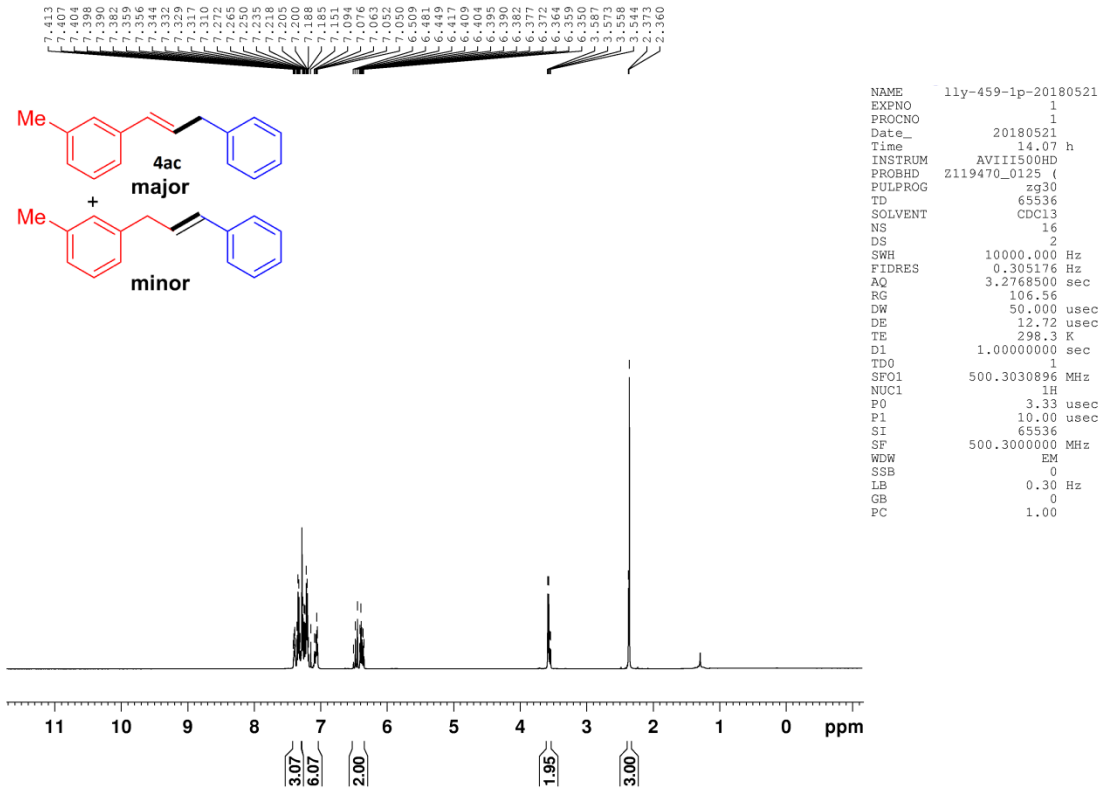
Supplementary Figure 3. ^{13}C NMR spectra for compound **4aa**



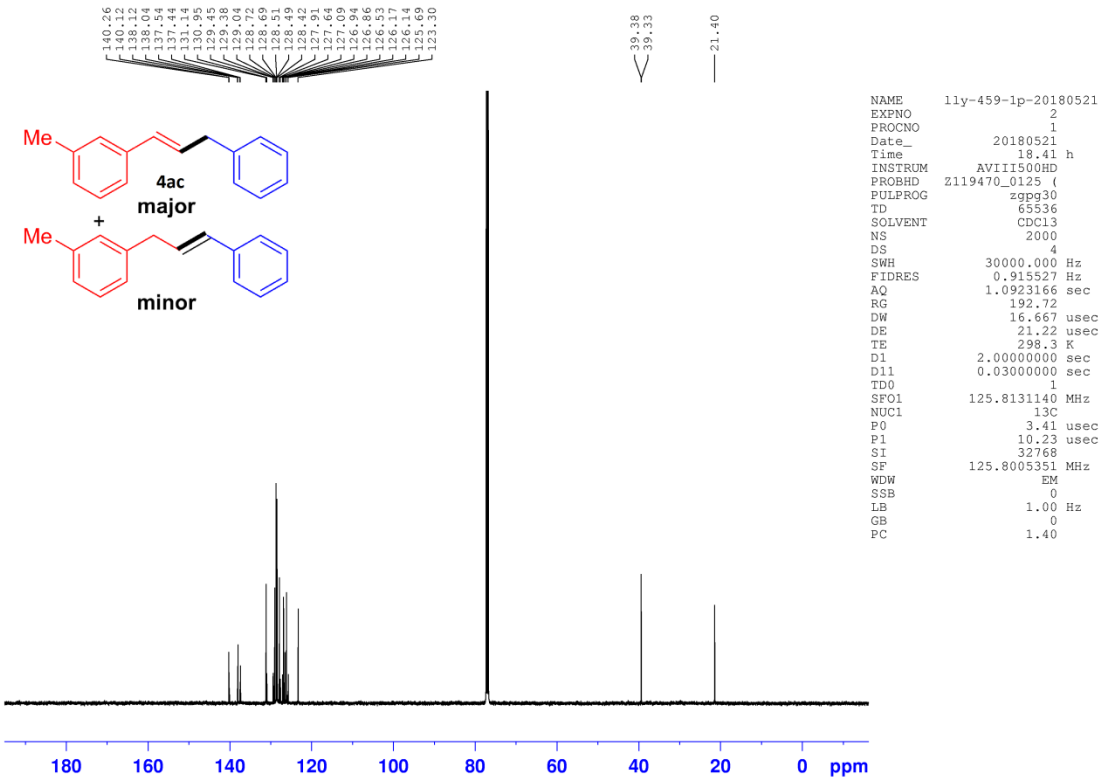
Supplementary Figure 4. ^{1}H NMR spectra for compound **4ab**



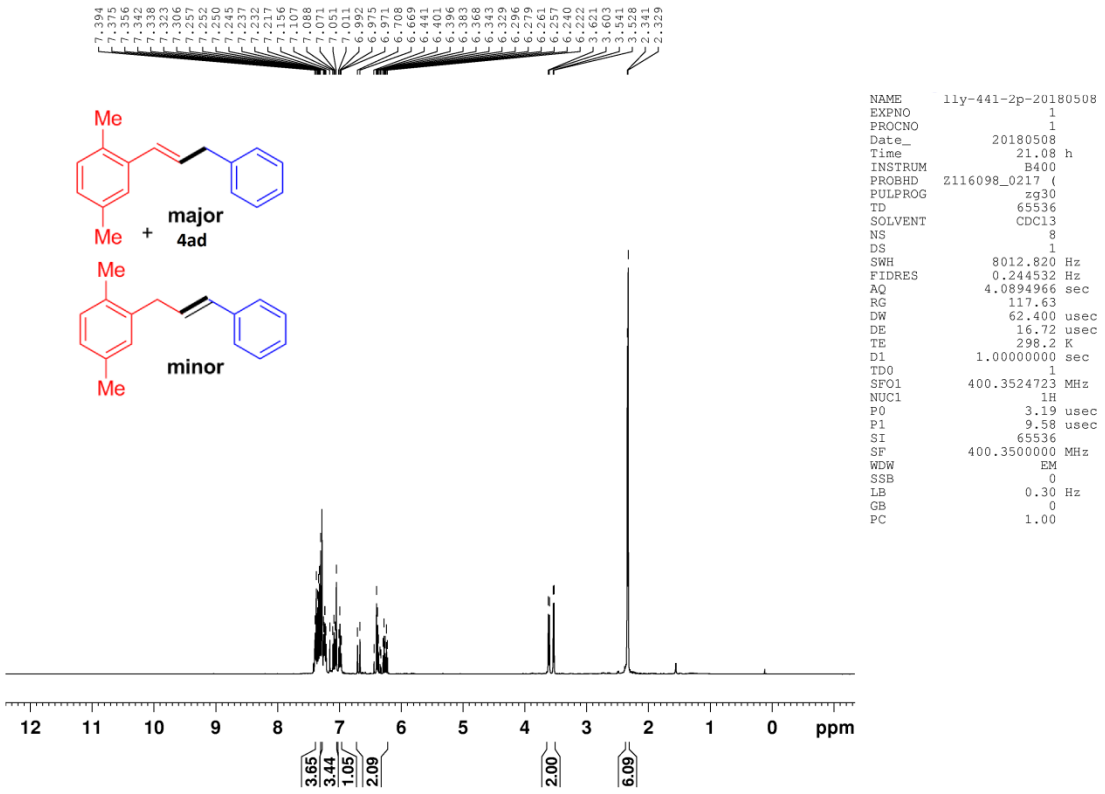
Supplementary Figure 5. ^{13}C NMR spectra for compound **4ab**



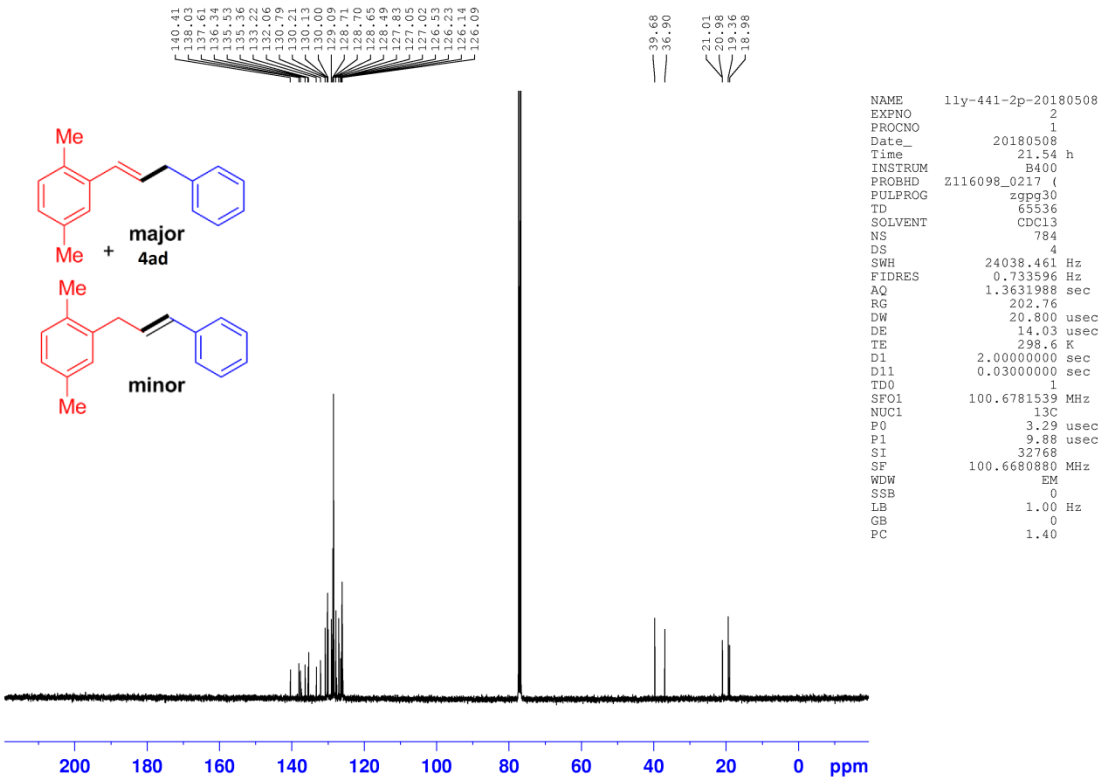
Supplementary Figure 6. ^{1}H NMR spectra for compound **4ac**



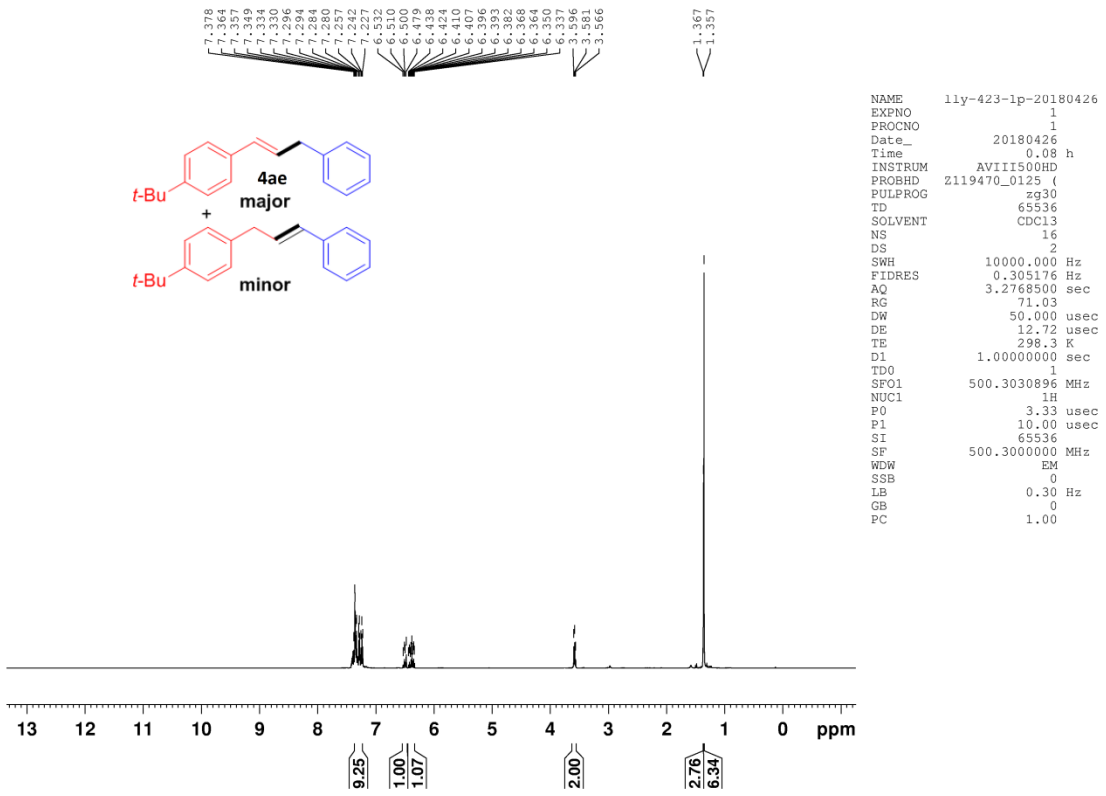
Supplementary Figure 7. ^{13}C NMR spectra for compound **4ac**



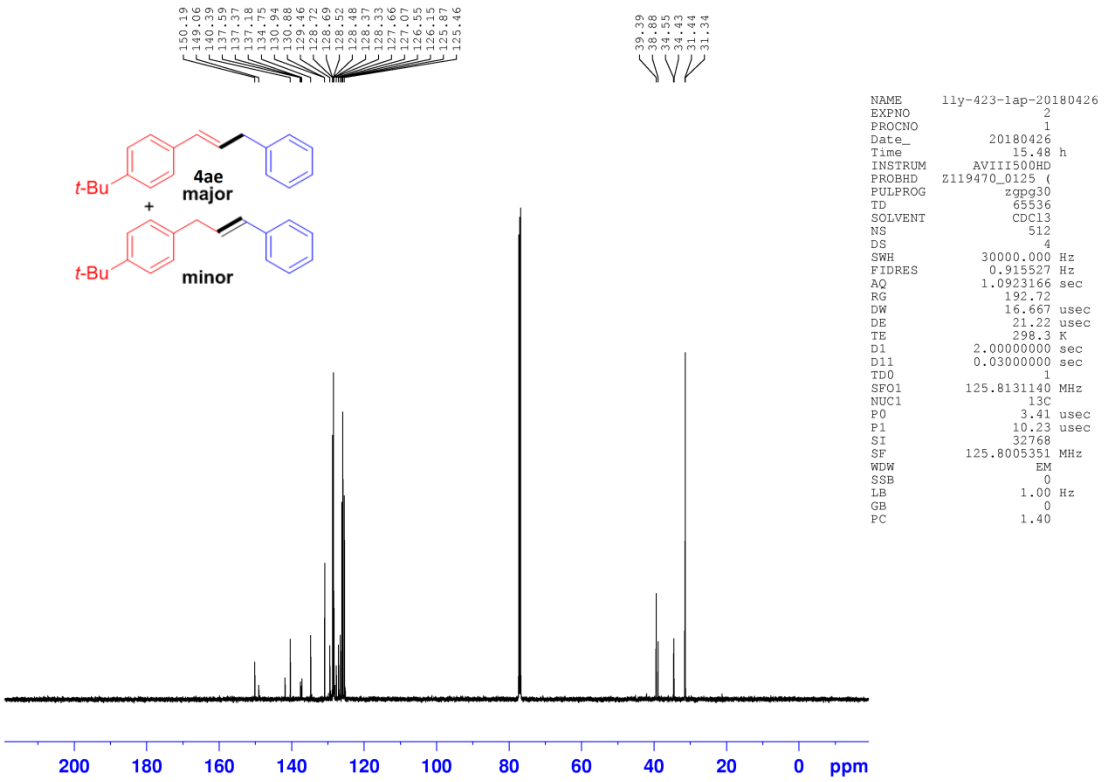
Supplementary Figure 8. ^{1}H NMR spectra for compound **4ad**



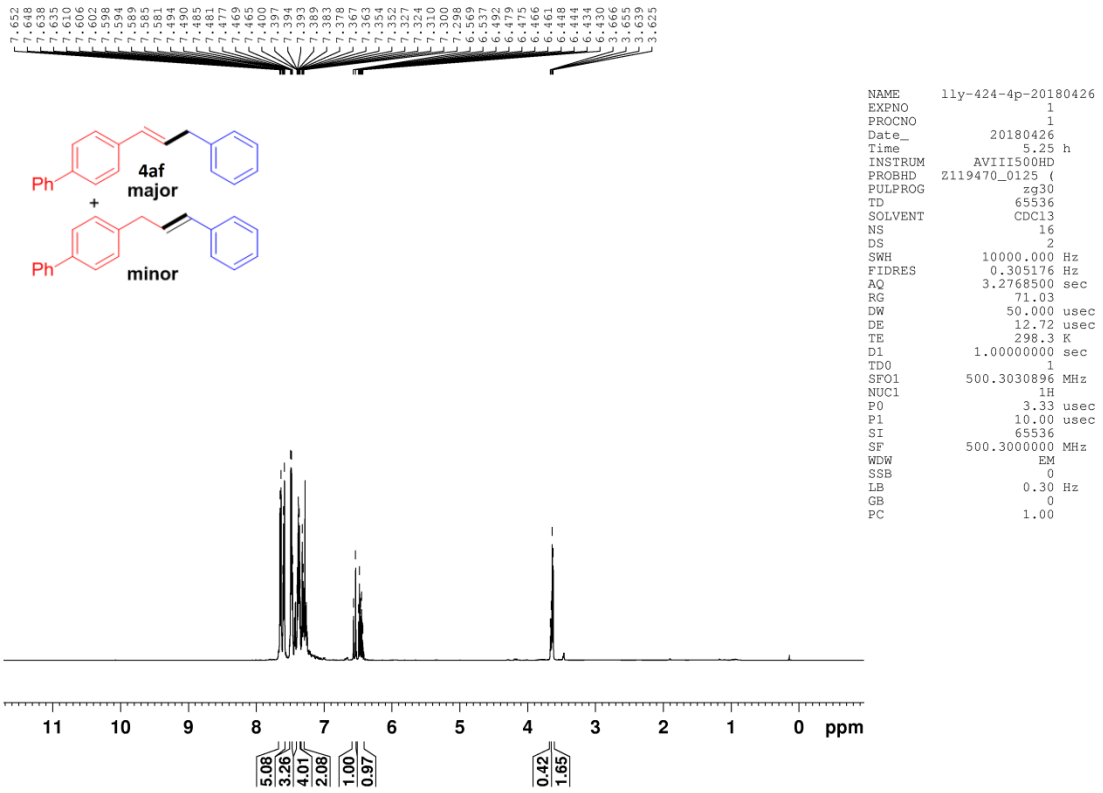
Supplementary Figure 9. ^{13}C NMR spectra for compound **4ad**



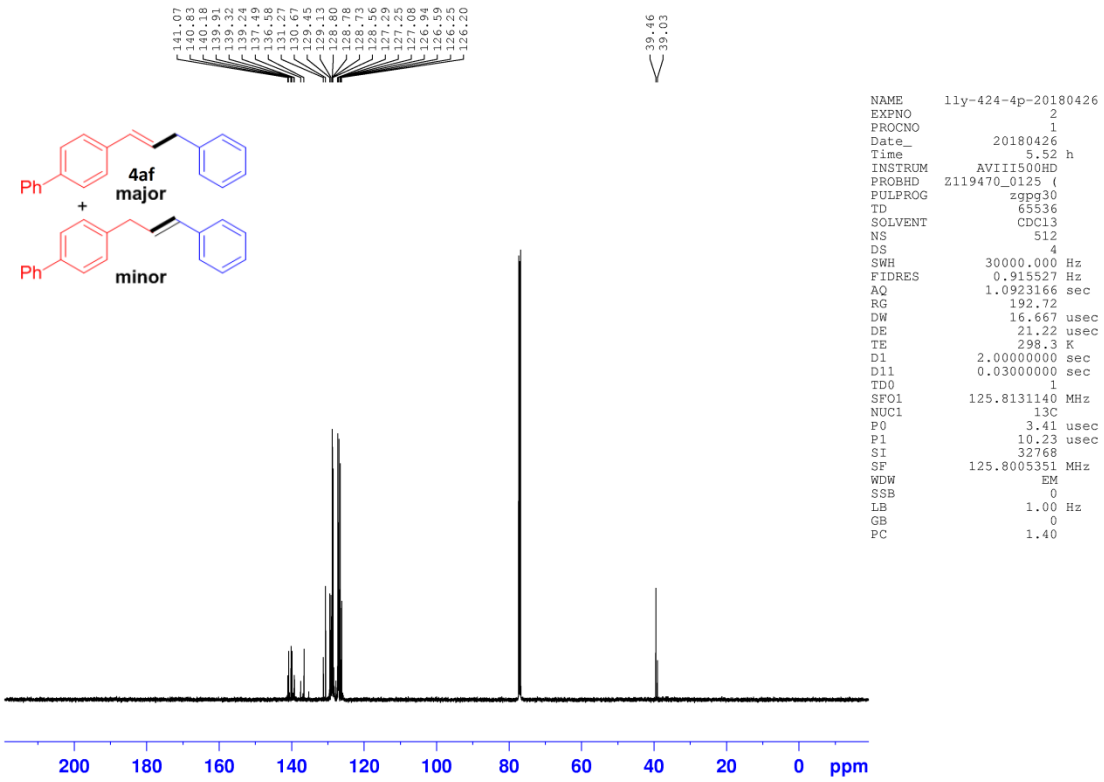
Supplementary Figure 10. ^{1}H NMR spectra for compound **4ae**



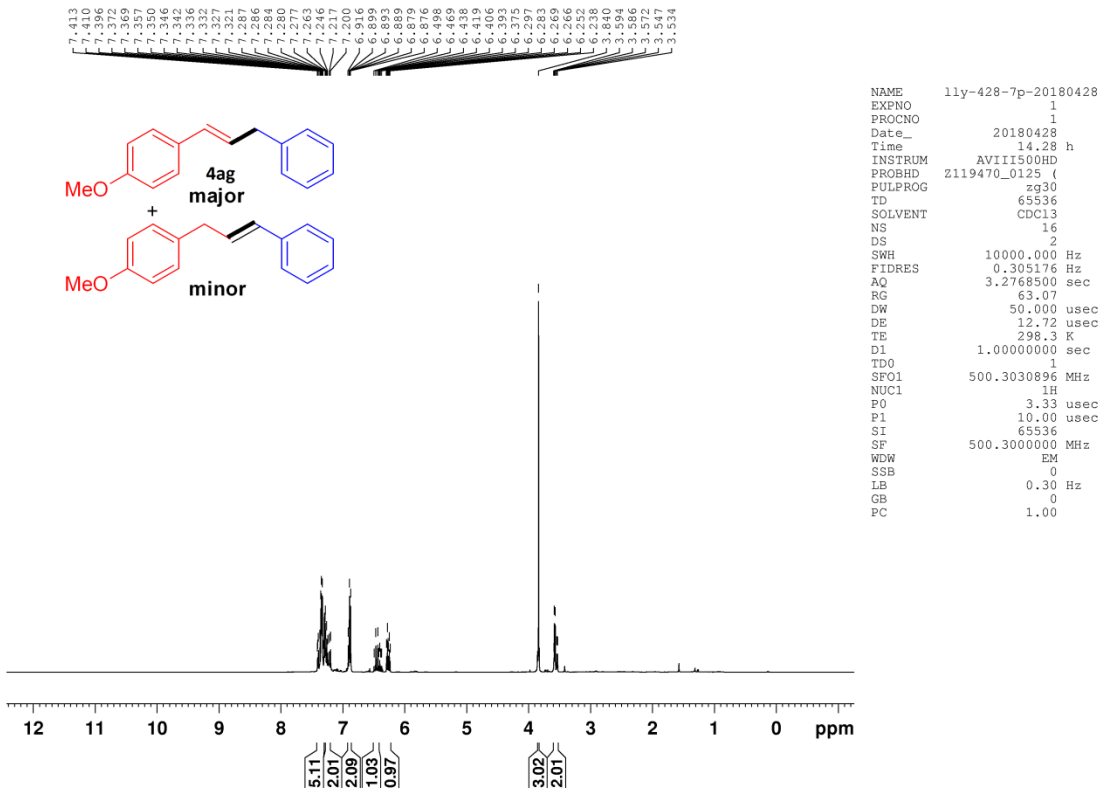
Supplementary Figure 11. ^{13}C NMR spectra for compound **4ae**



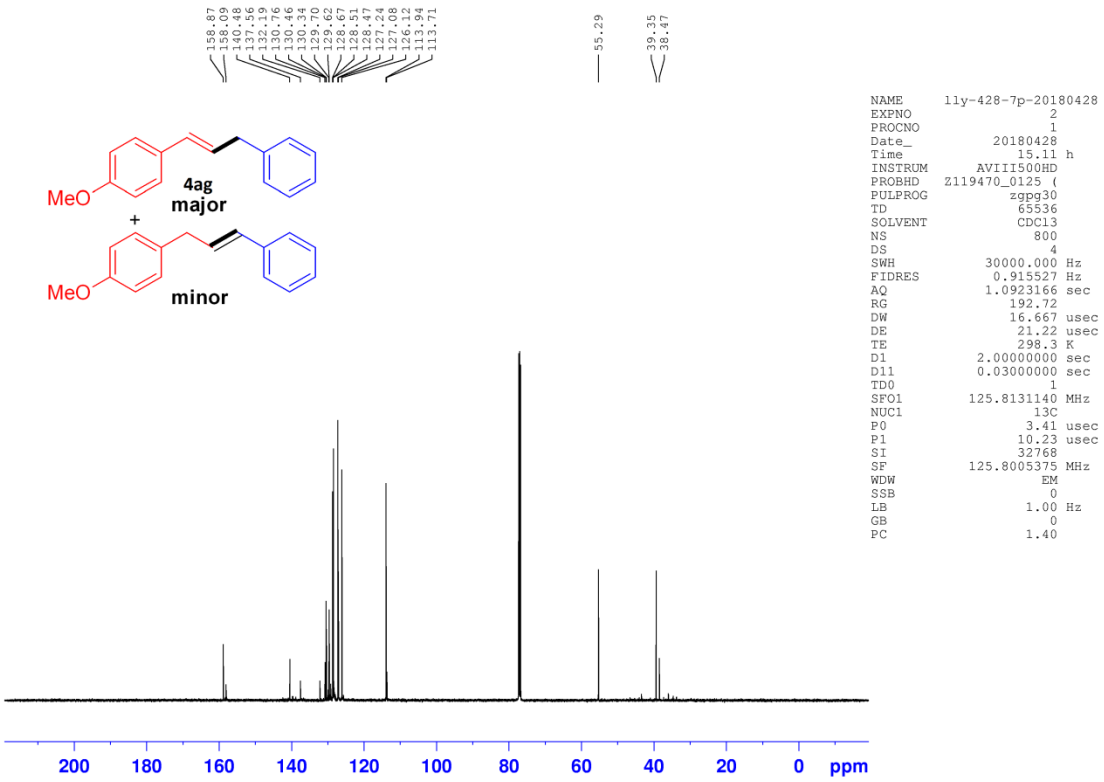
Supplementary Figure 12. ^{1}H NMR spectra for compound **4af**



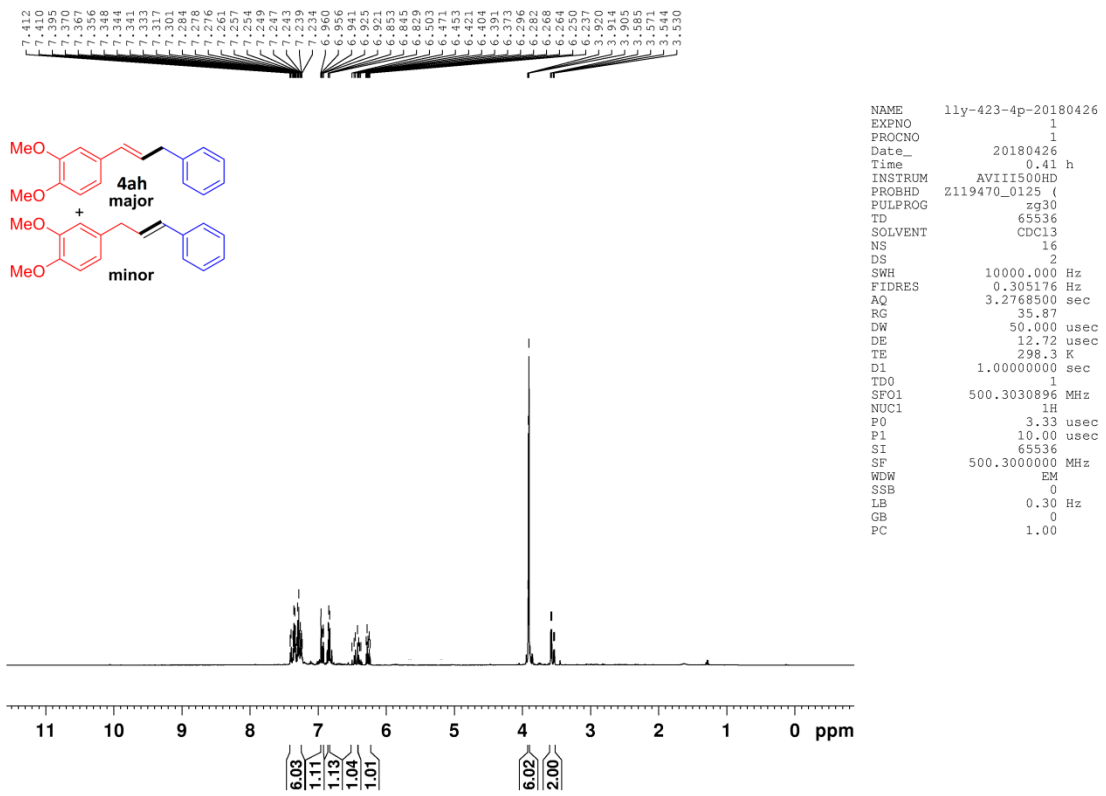
Supplementary Figure 13. ^{13}C NMR spectra for compound **4af**



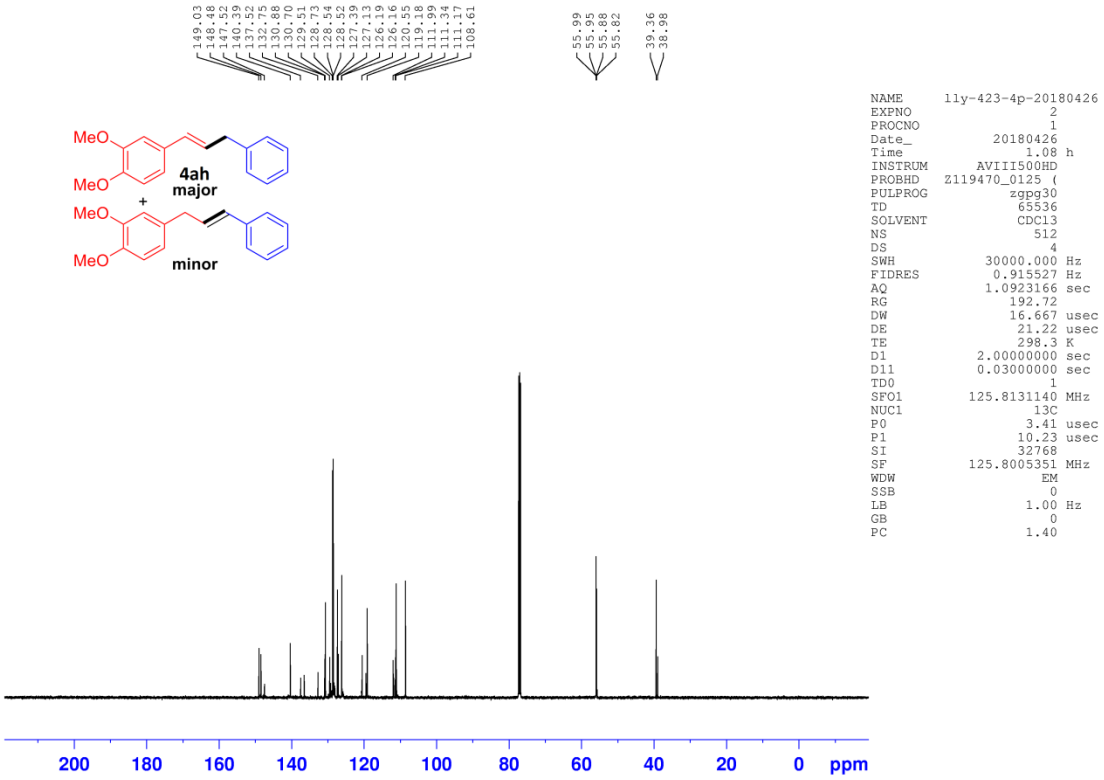
Supplementary Figure 14. ^{1}H NMR spectra for compound **4ag**



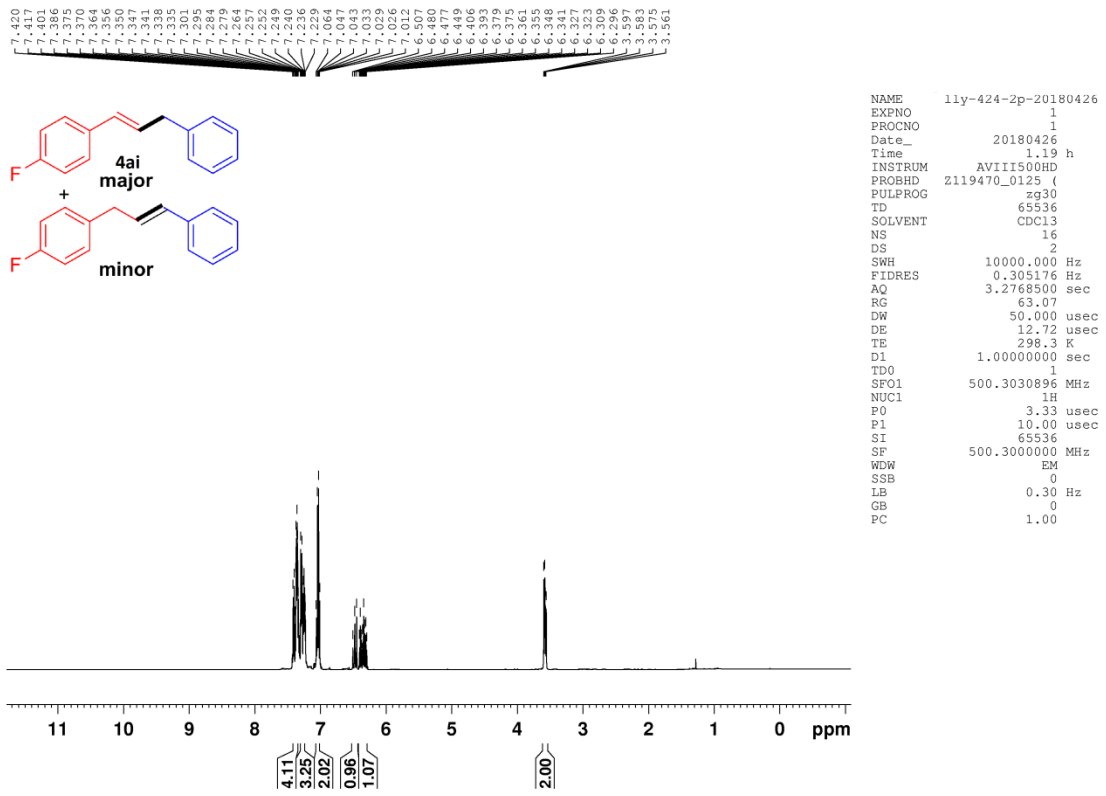
Supplementary Figure 15. ^{13}C NMR spectra for compound **4ag**



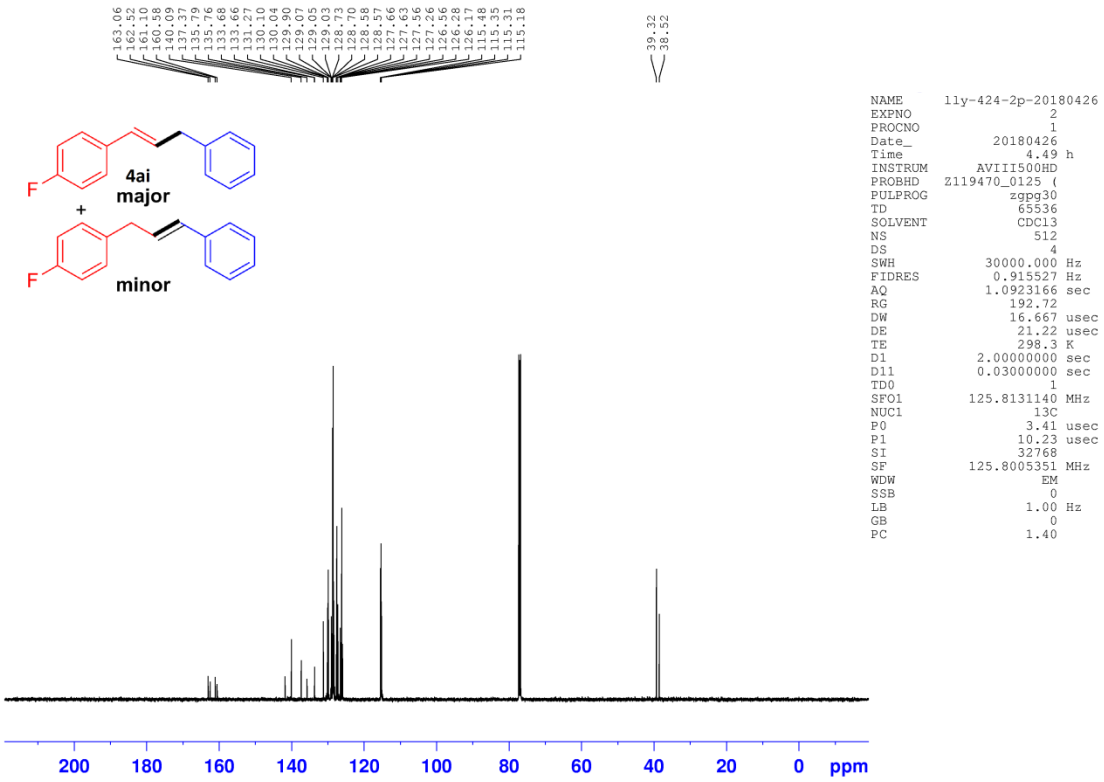
Supplementary Figure 16. ^{1}H NMR spectra for compound **4ah**



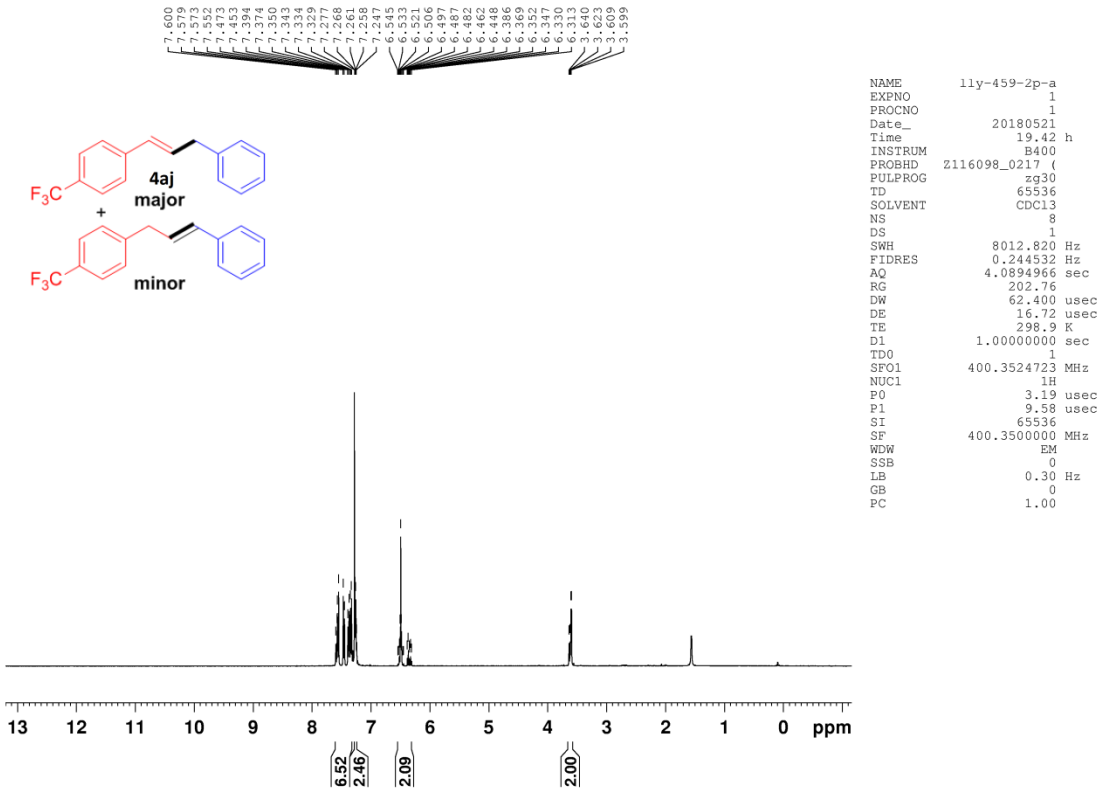
Supplementary Figure 17. ^{13}C NMR spectra for compound **4ah**



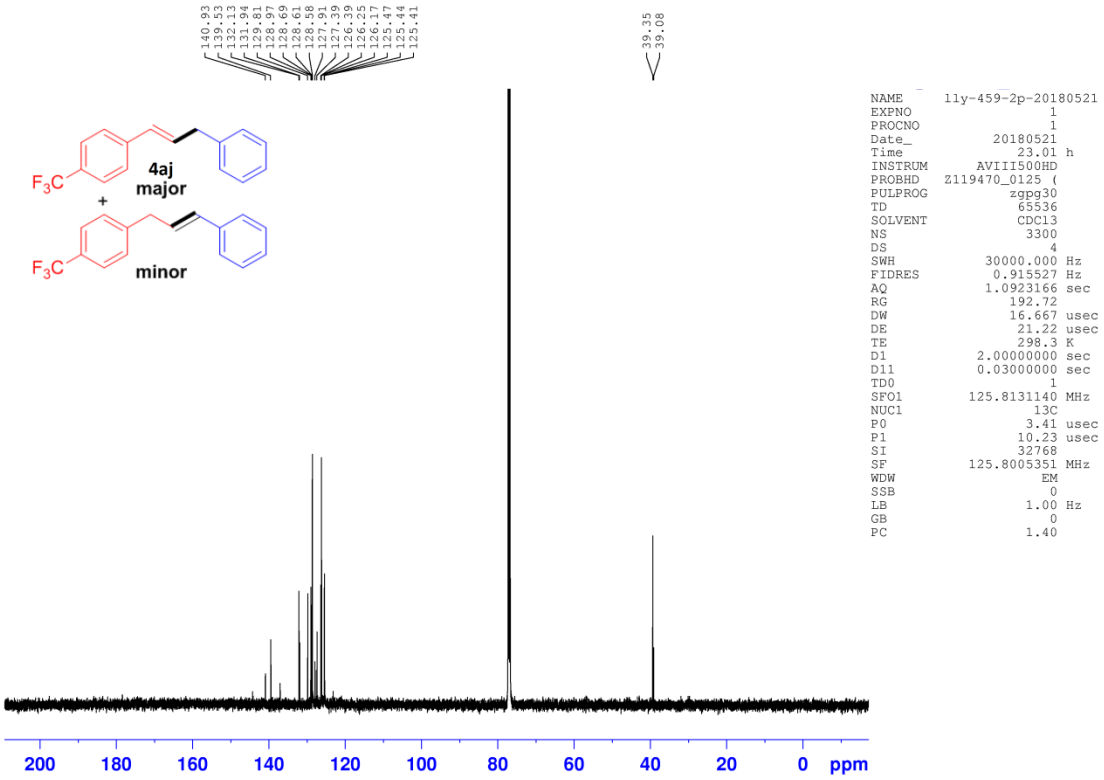
Supplementary Figure 18. ^{1}H NMR spectra for compound **4ai**



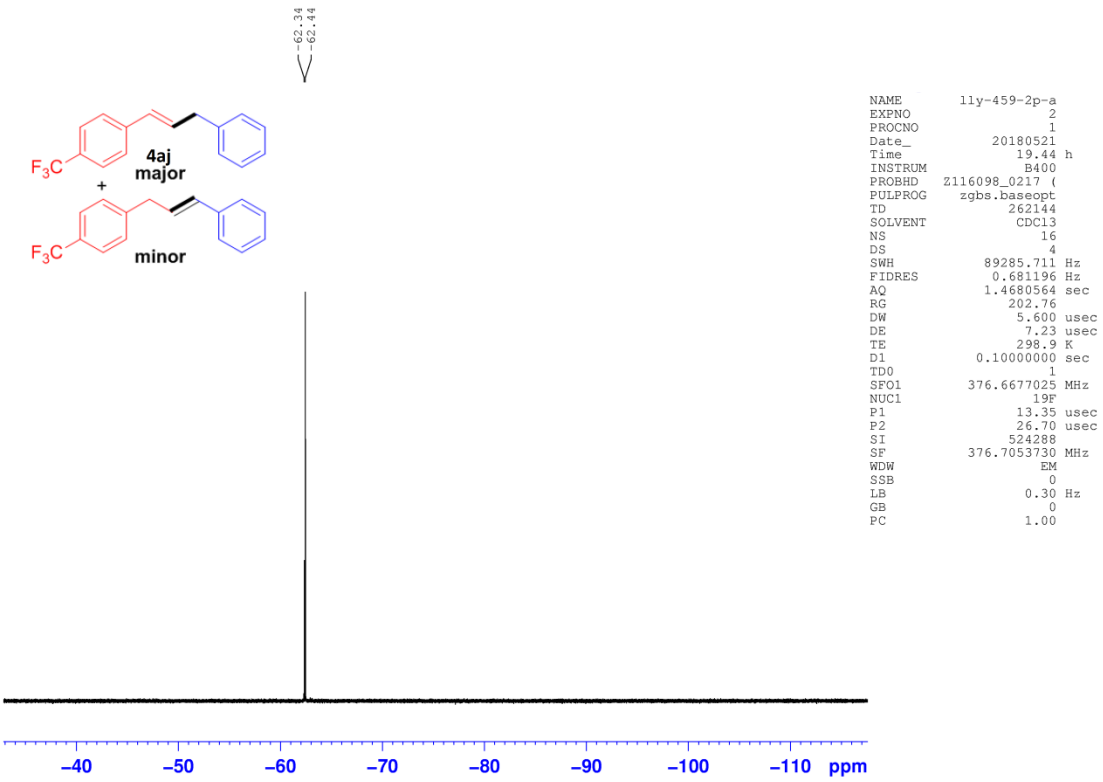
Supplementary Figure 19. ^{13}C NMR spectra for compound **4ai**



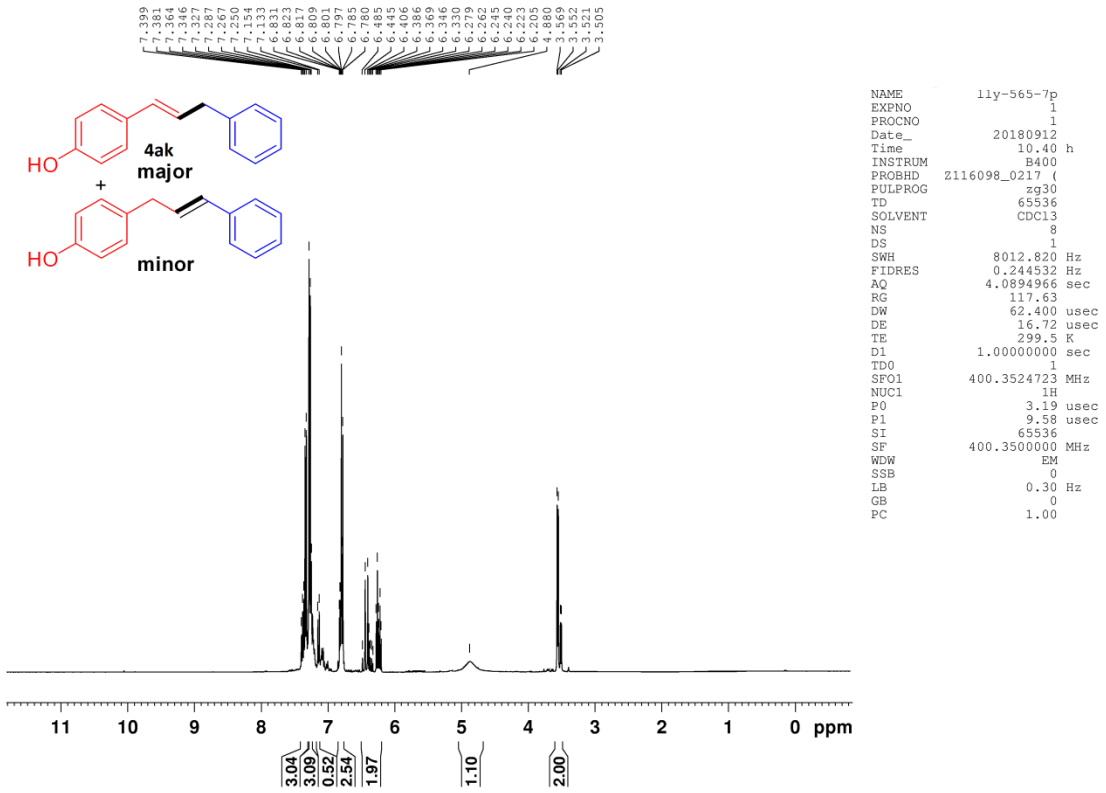
Supplementary Figure 20. ^{1}H NMR spectra for compound **4aj**



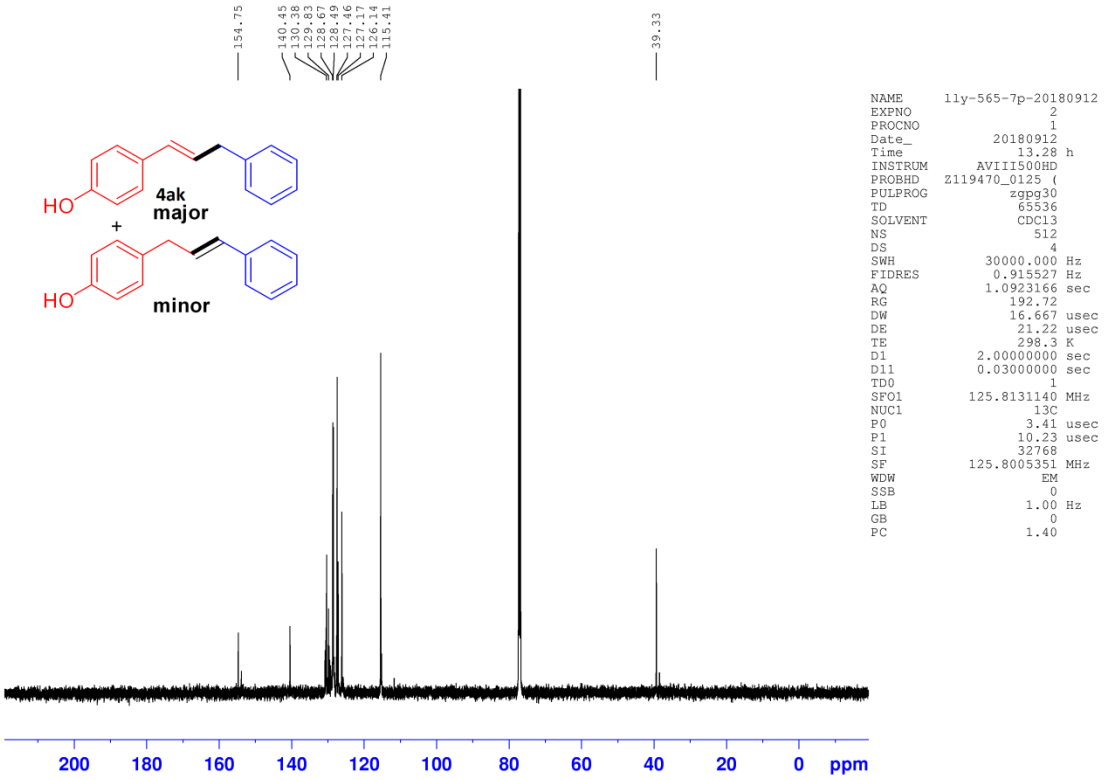
Supplementary Figure 21. ^{13}C NMR spectra for compound **4aj**



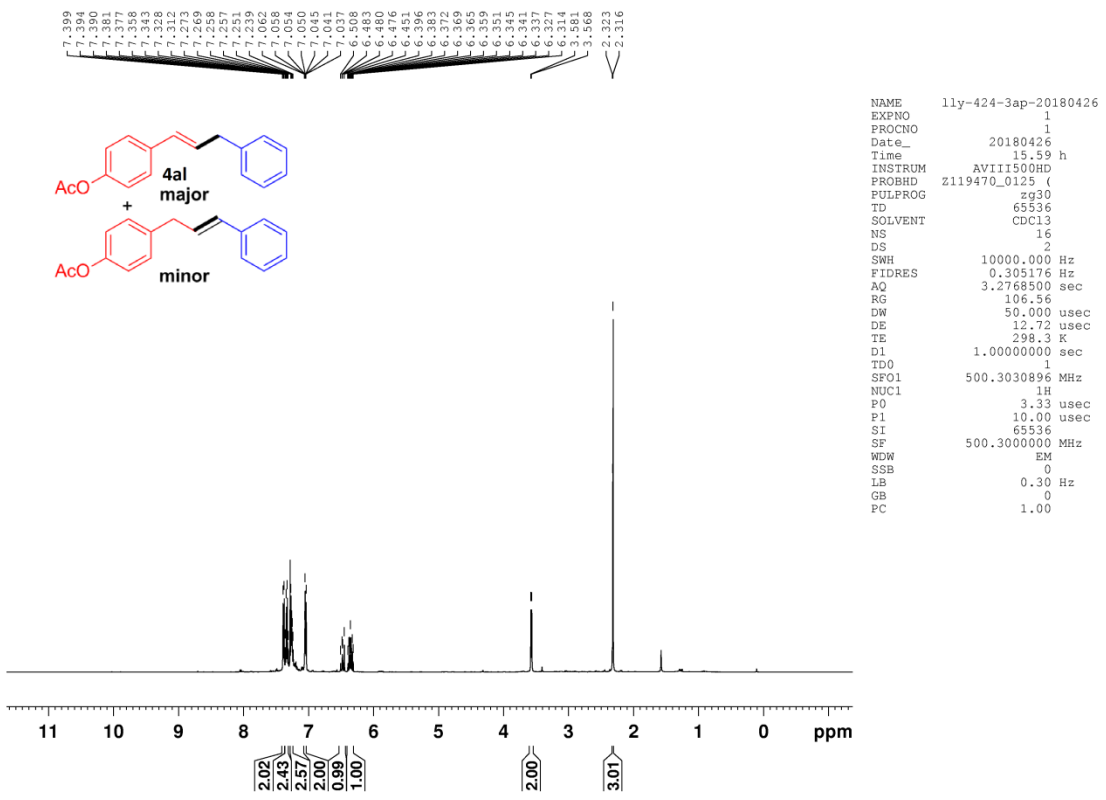
Supplementary Figure 22. ^{19}F NMR spectra for compound **4aj**



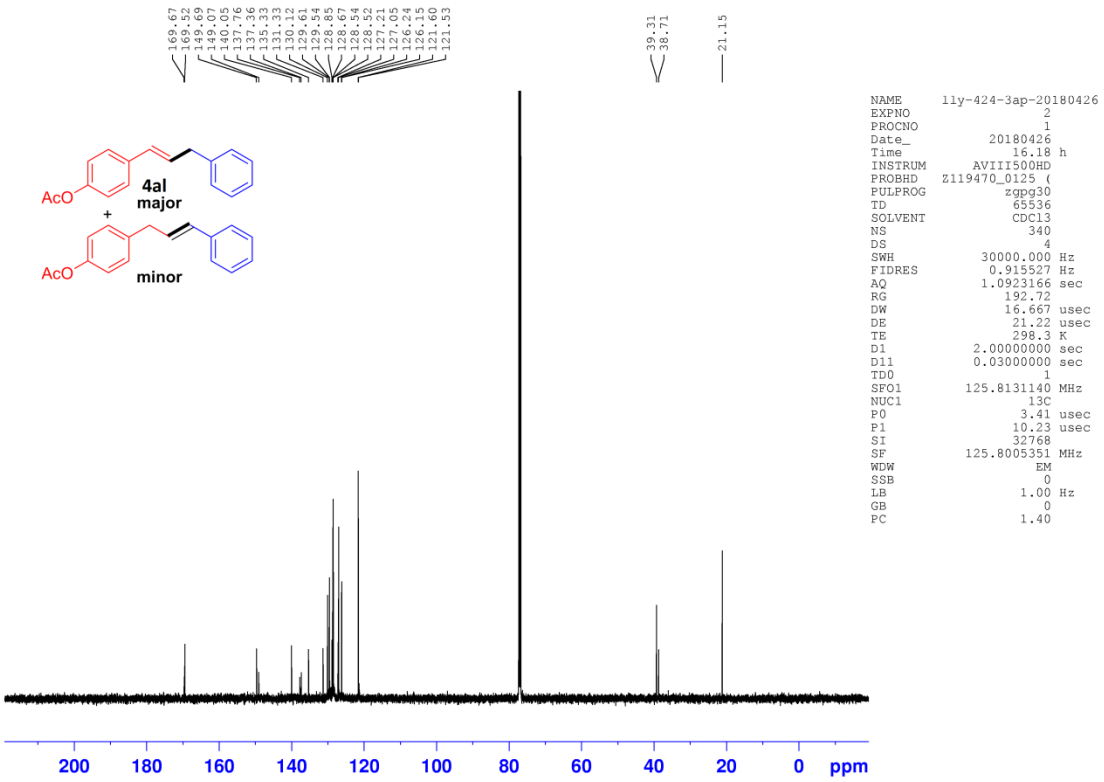
Supplementary Figure 23. ^{1}H NMR spectra for compound **4ak**



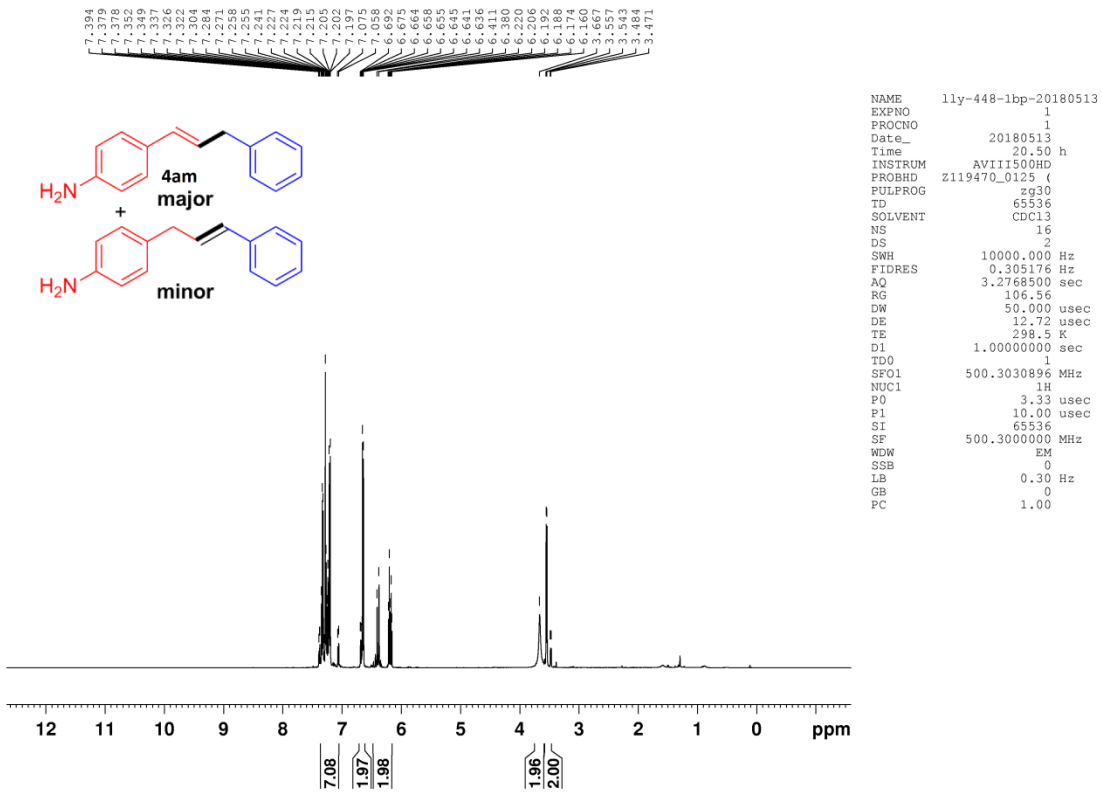
Supplementary Figure 24. ^{13}C NMR spectra for compound **4ak**



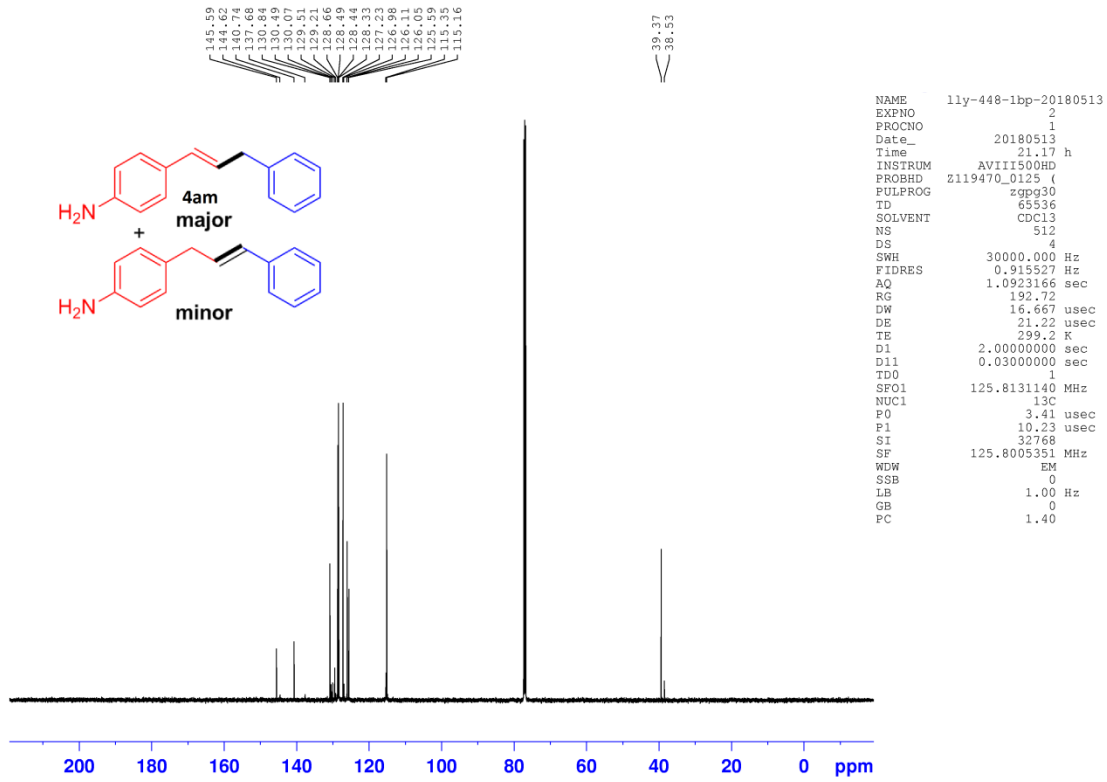
Supplementary Figure 25. ^{1}H NMR spectra for compound **4al**



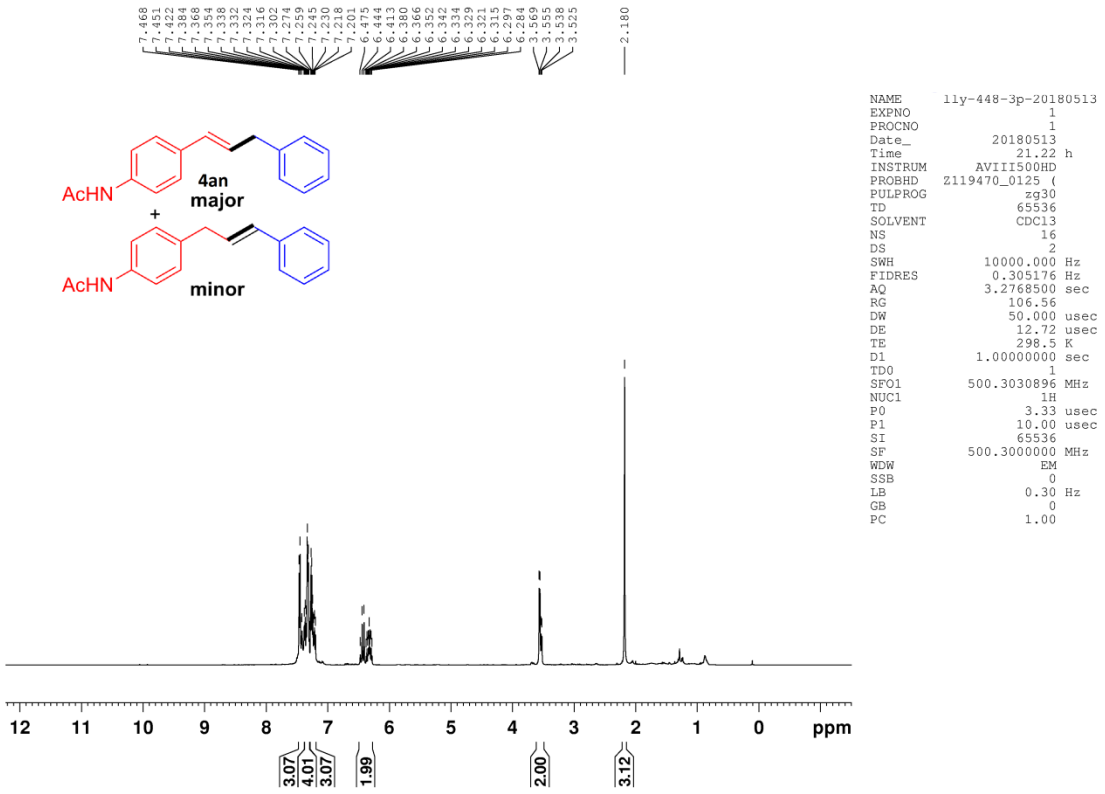
Supplementary Figure 26. ^{13}C NMR spectra for compound **4al**



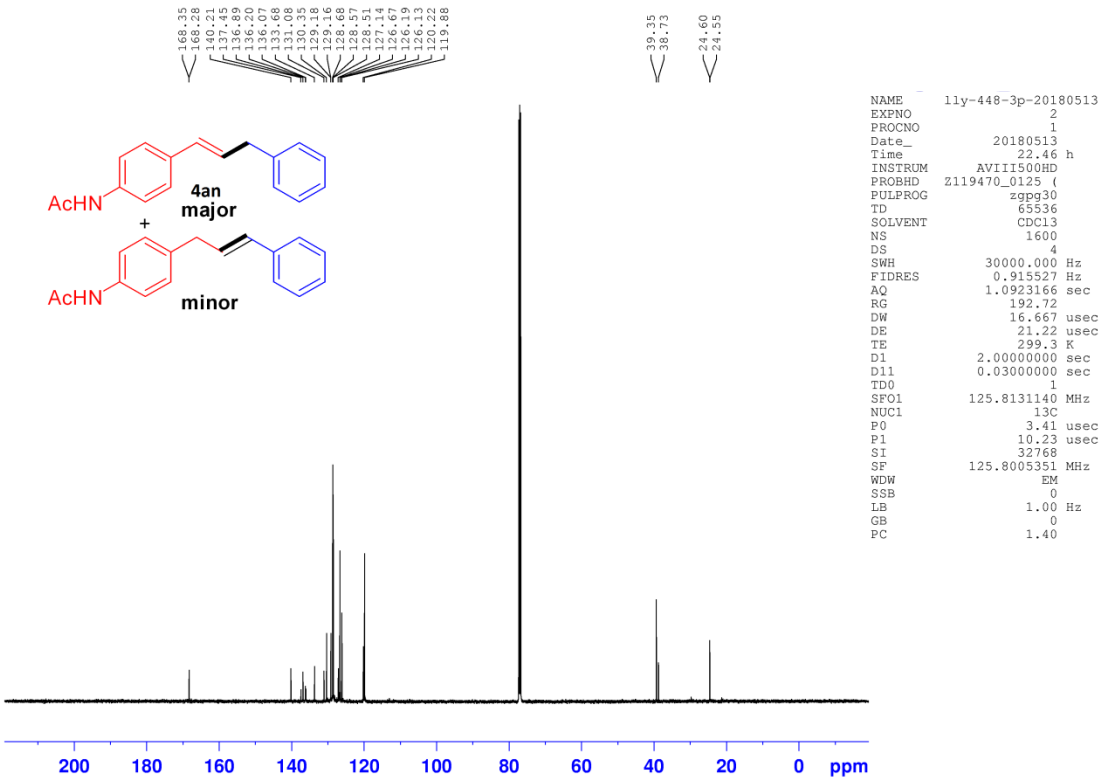
Supplementary Figure 27. ^{1}H NMR spectra for compound **4am**



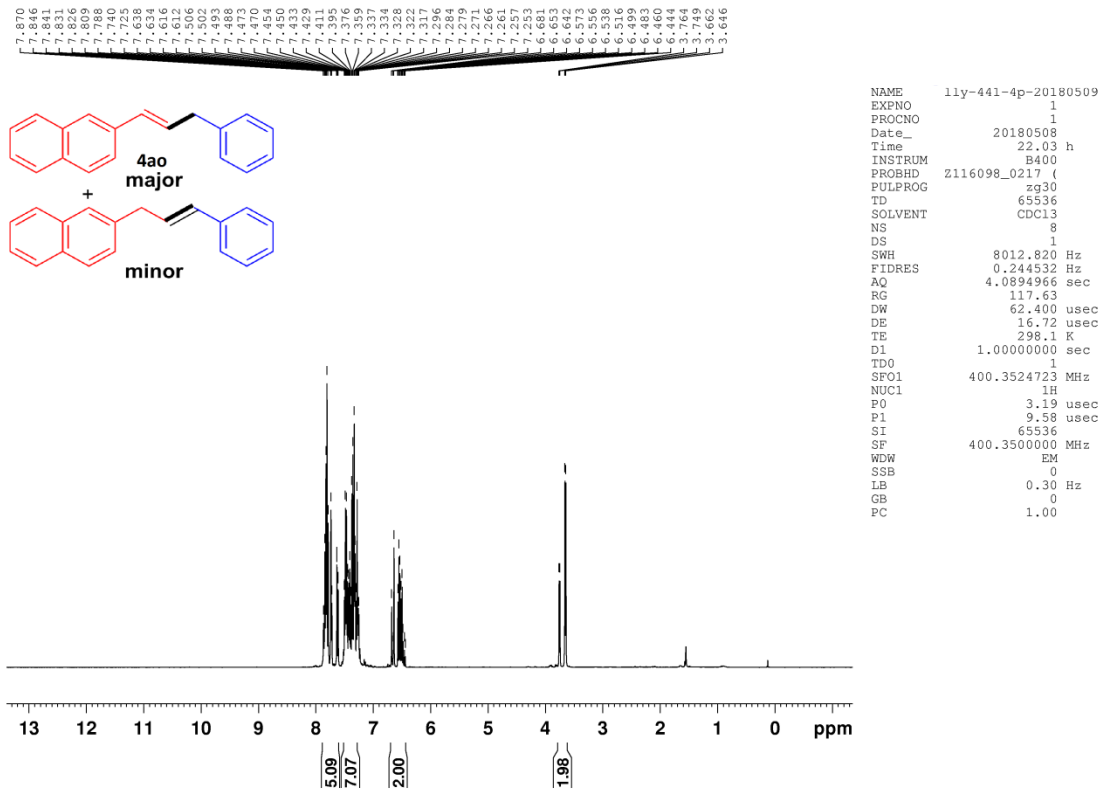
Supplementary Figure 28. ^{13}C NMR spectra for compound **4am**



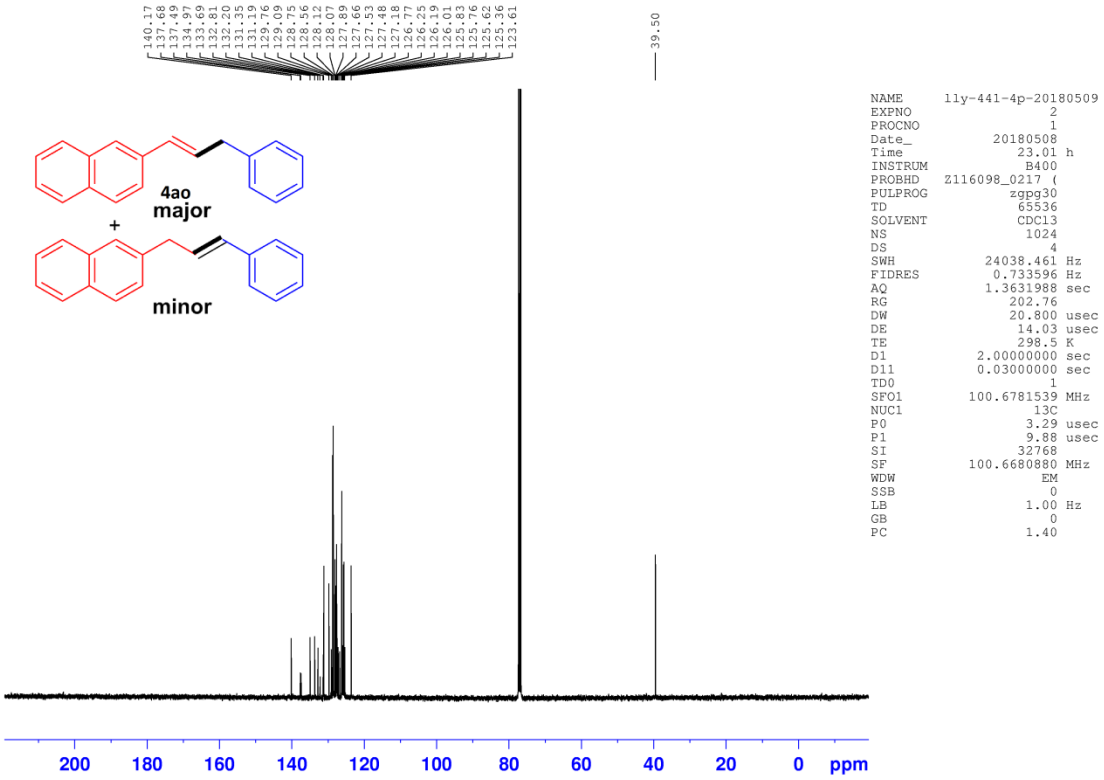
Supplementary Figure 29. ^{1}H NMR spectra for compound **4an**



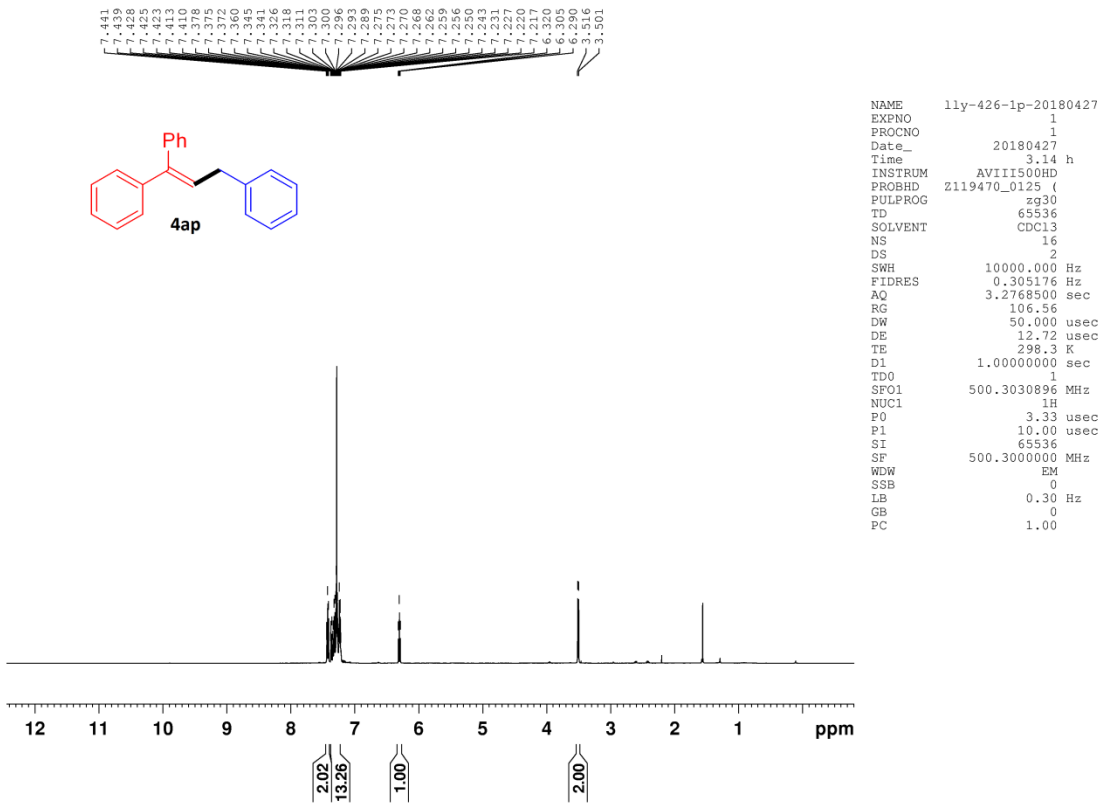
Supplementary Figure 30. ^{13}C NMR spectra for compound **4an**



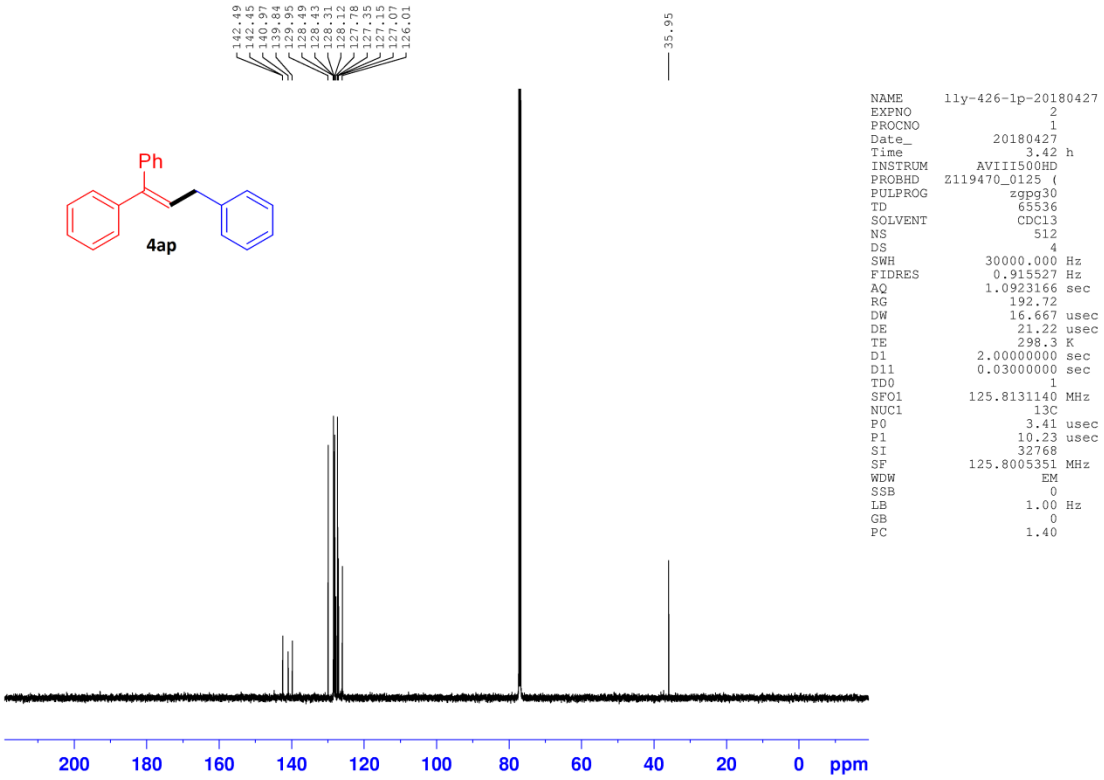
Supplementary Figure 31. ^{1}H NMR spectra for compound **4ao**



Supplementary Figure 32. ^{13}C NMR spectra for compound **4ao**



Supplementary Figure 33. ^{13}C NMR spectra for compound **4ap**



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DE	21.22 usec
TE	298.3 K
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TD0	1
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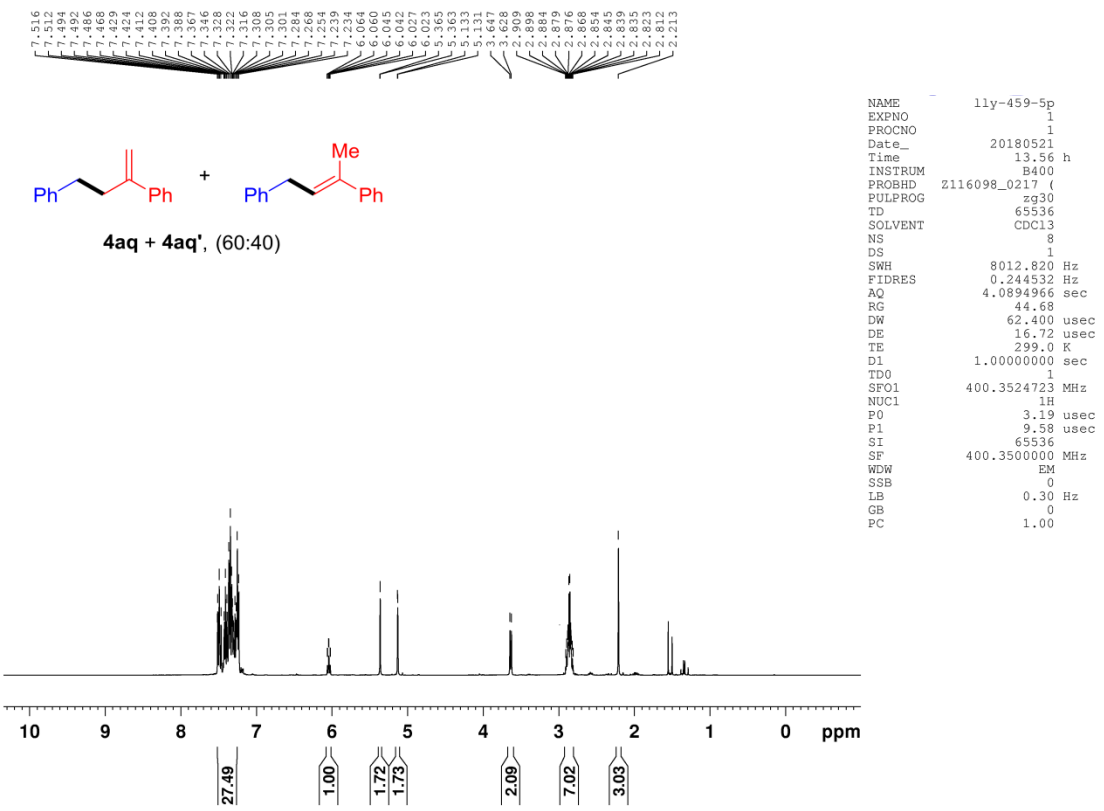
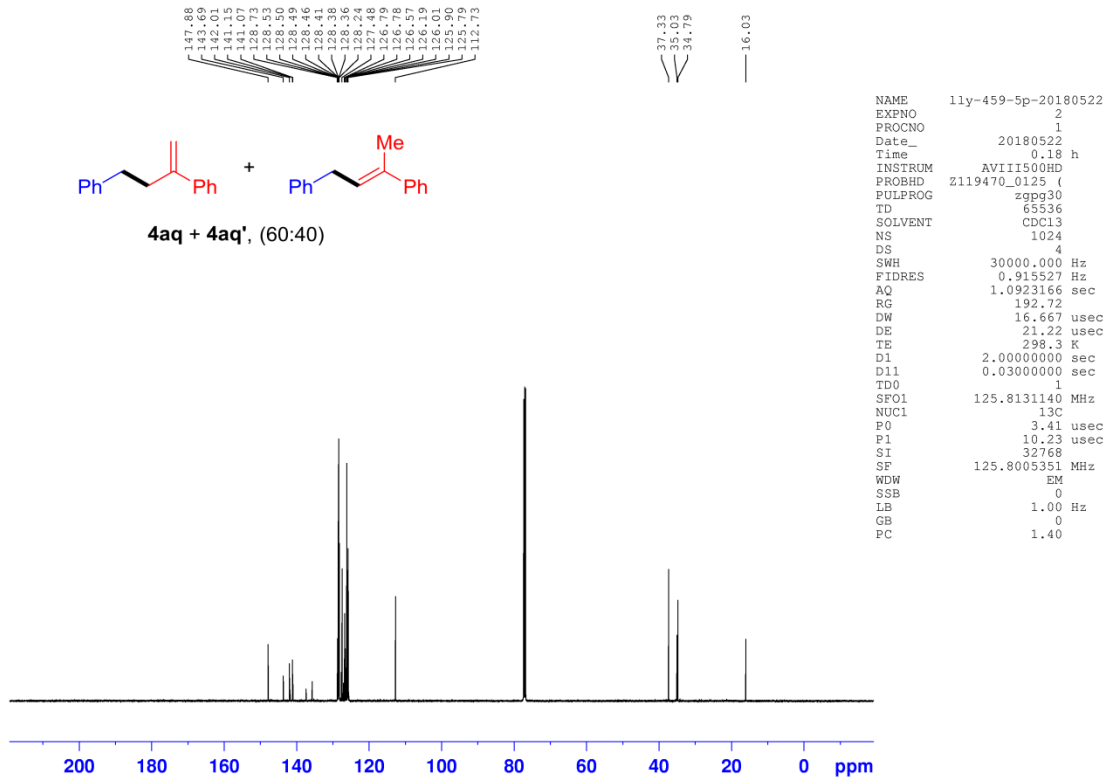
LB	1.00 Hz
GB	0
PC	1.40

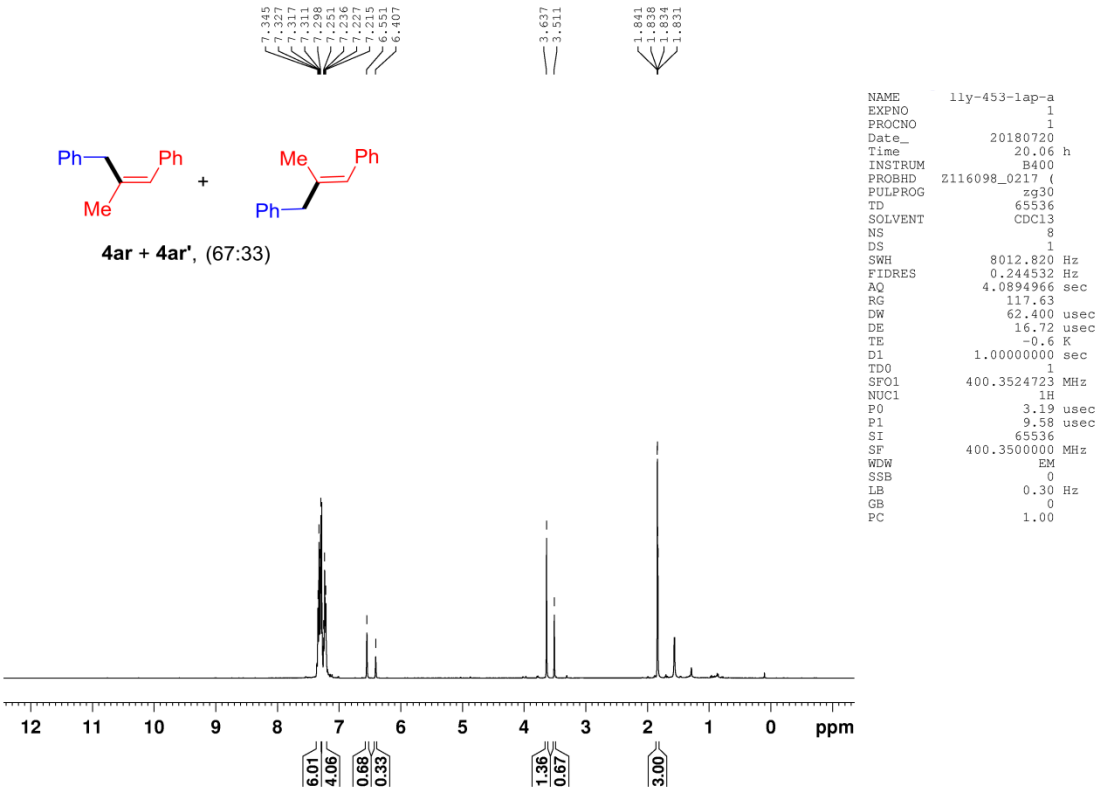
Supplementary Figure 34. ^{13}C NMR spectra for compound **4ap**



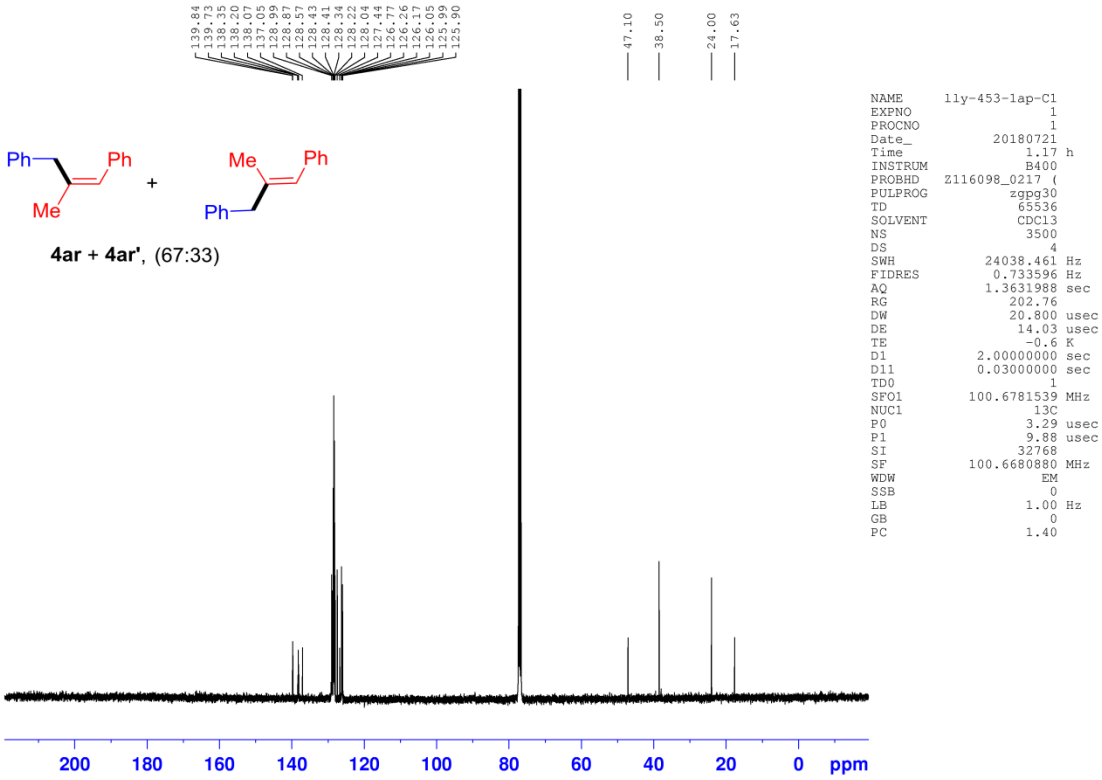
Supplementary Figure 35. ^{1}H NMR spectra for compound **4aq** and **4aq'**



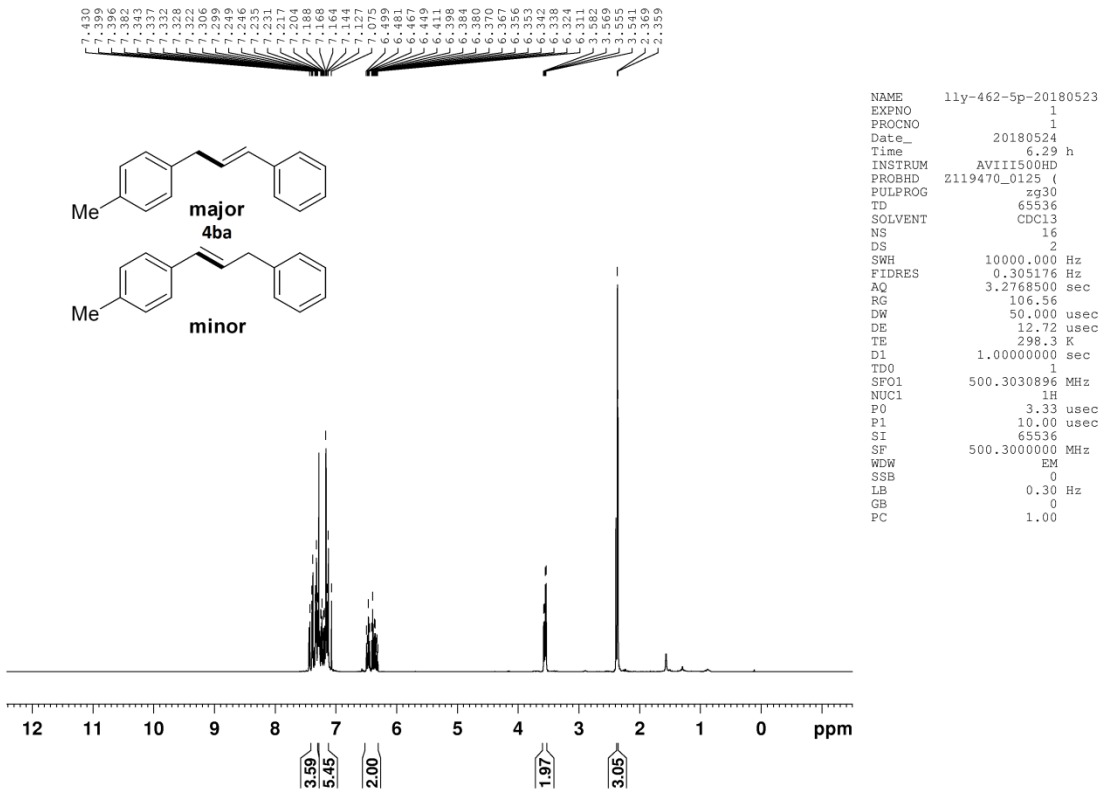
Supplementary Figure 36. ^{13}C NMR spectra for compound **4aq** and **4aq'**



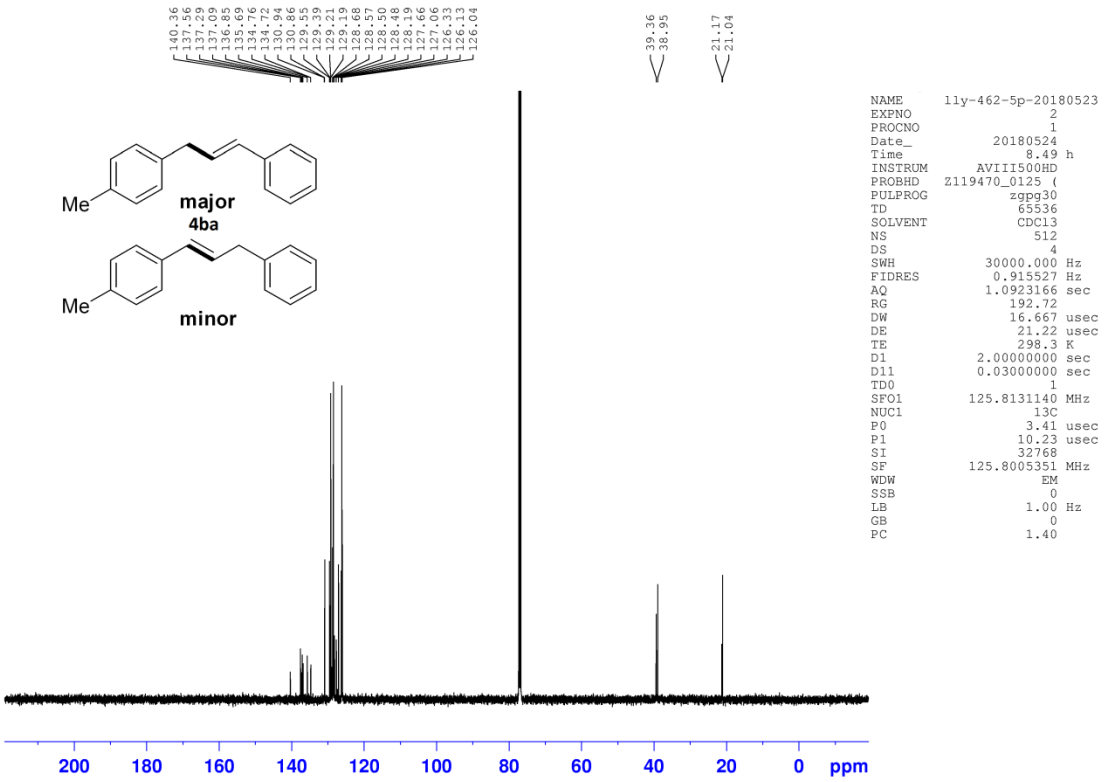
Supplementary Figure 37. ^{1}H NMR spectra for compound **4ar** and **4ar'**



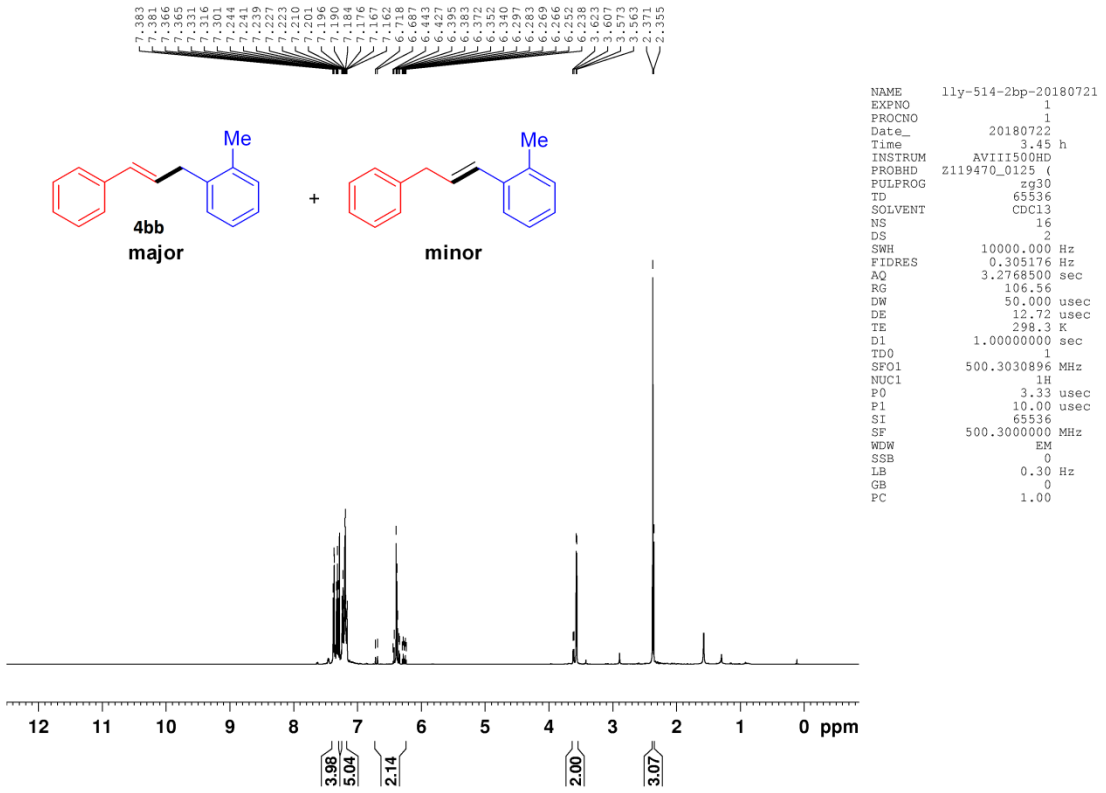
Supplementary Figure 38. ^{13}C NMR spectra for compound **4ar** and **4ar'**



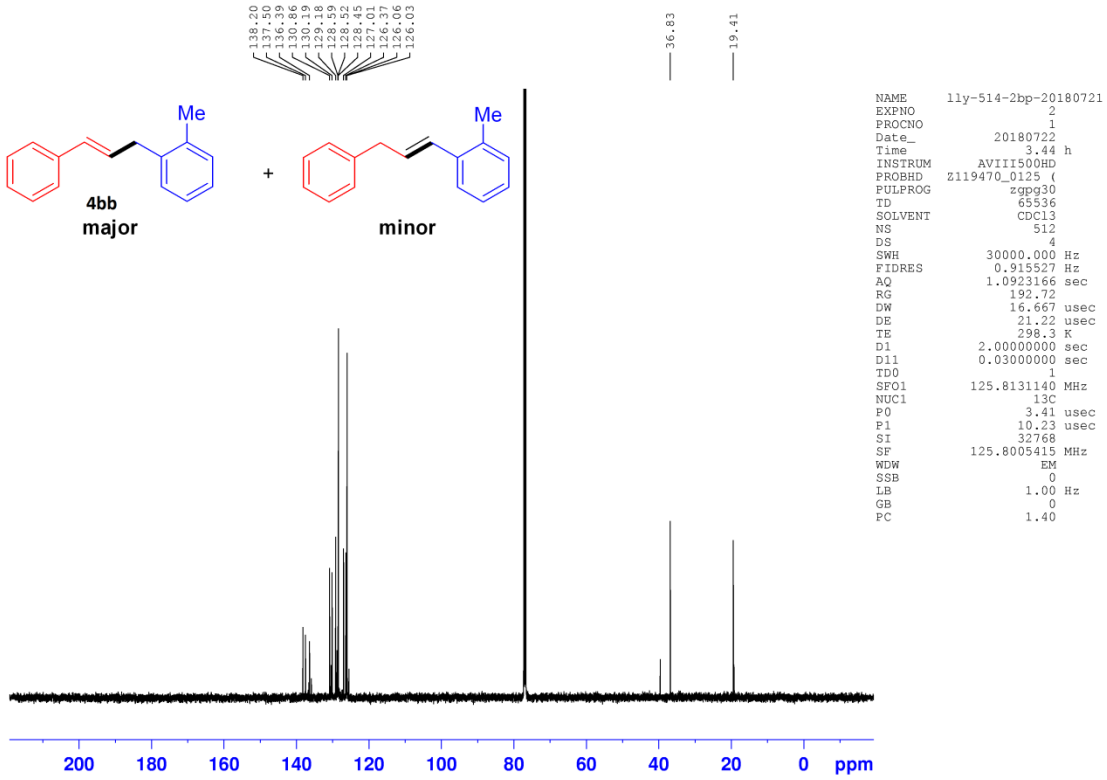
Supplementary Figure 39. ^{1}H NMR spectra for compound **4ba**



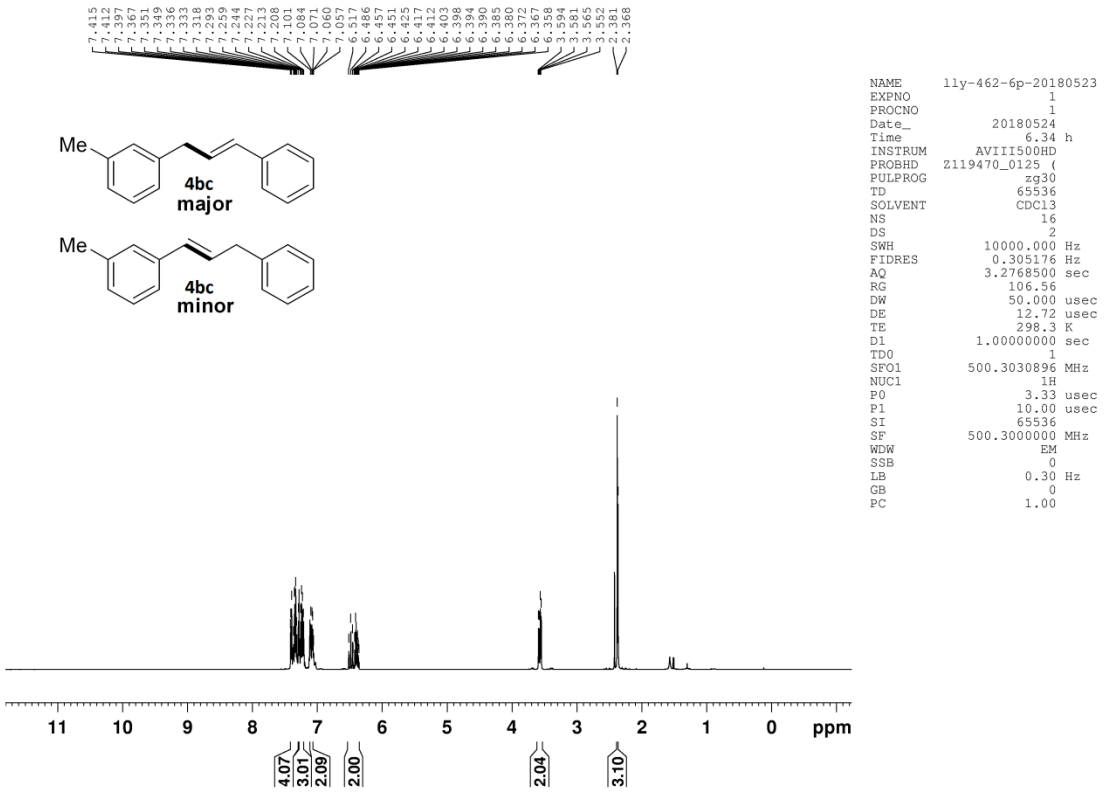
Supplementary Figure 40. ^{13}C NMR spectra for compound **4ba**



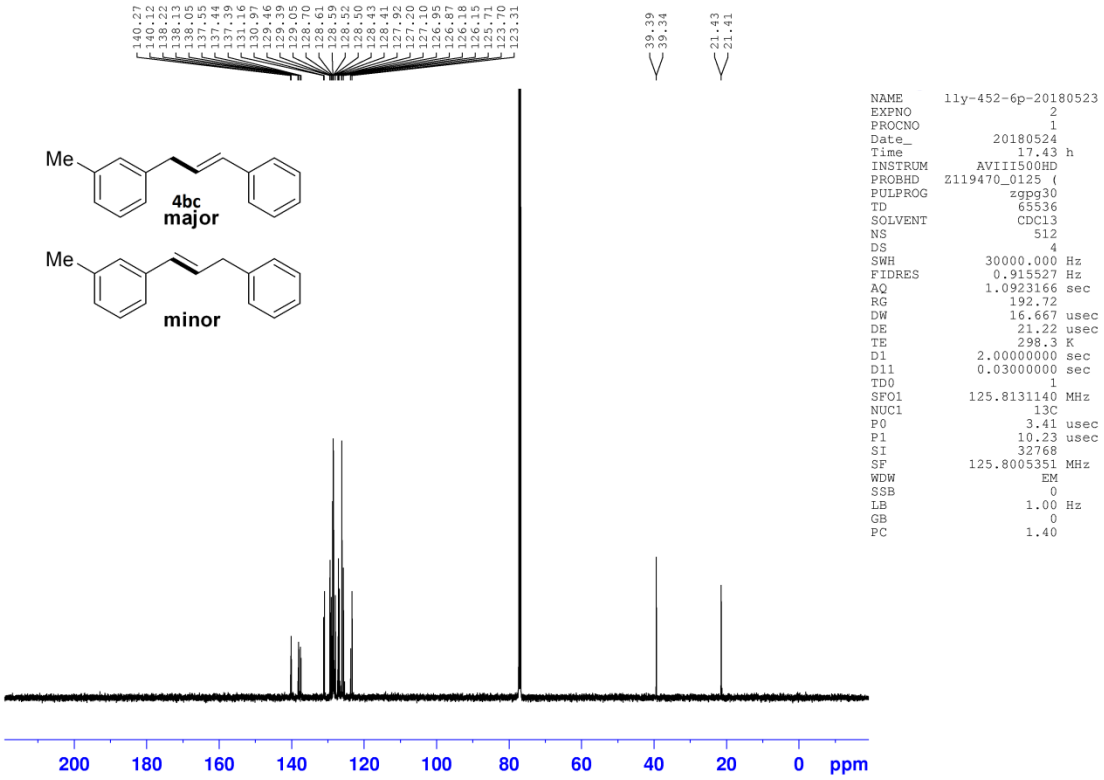
Supplementary Figure 41. ^{1}H NMR spectra for compound **4bb**



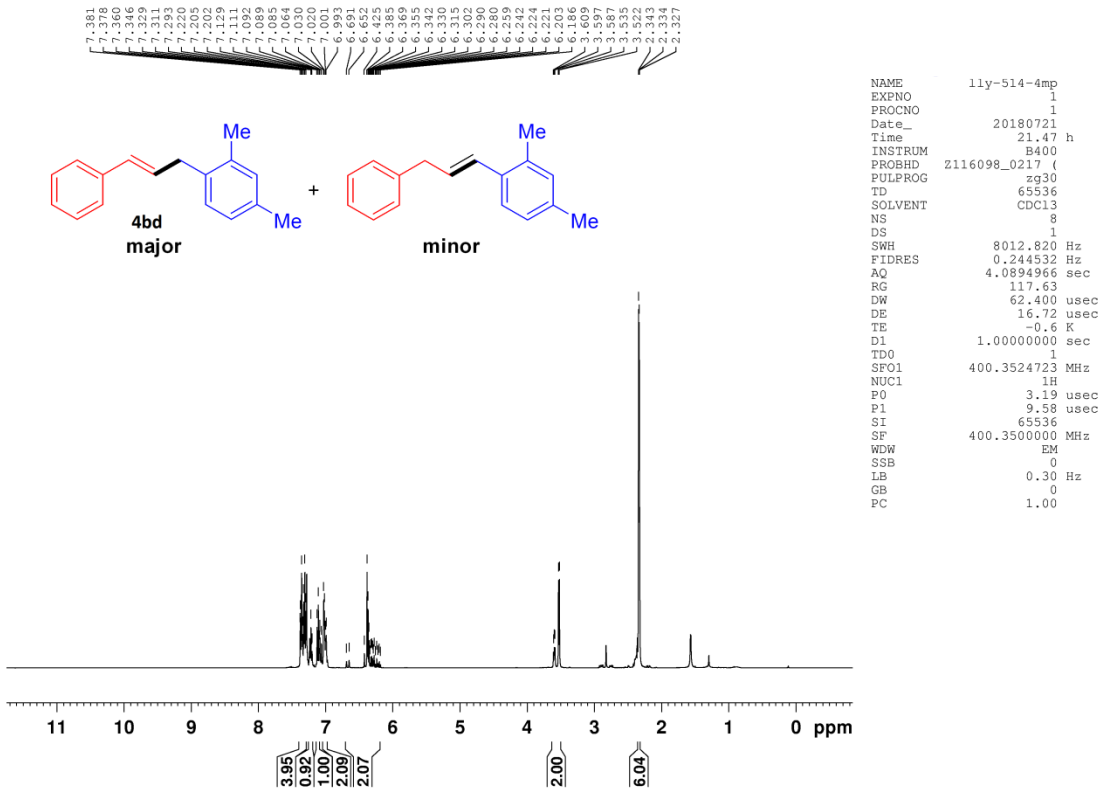
Supplementary Figure 42. ^{13}C NMR spectra for compound **4bb**



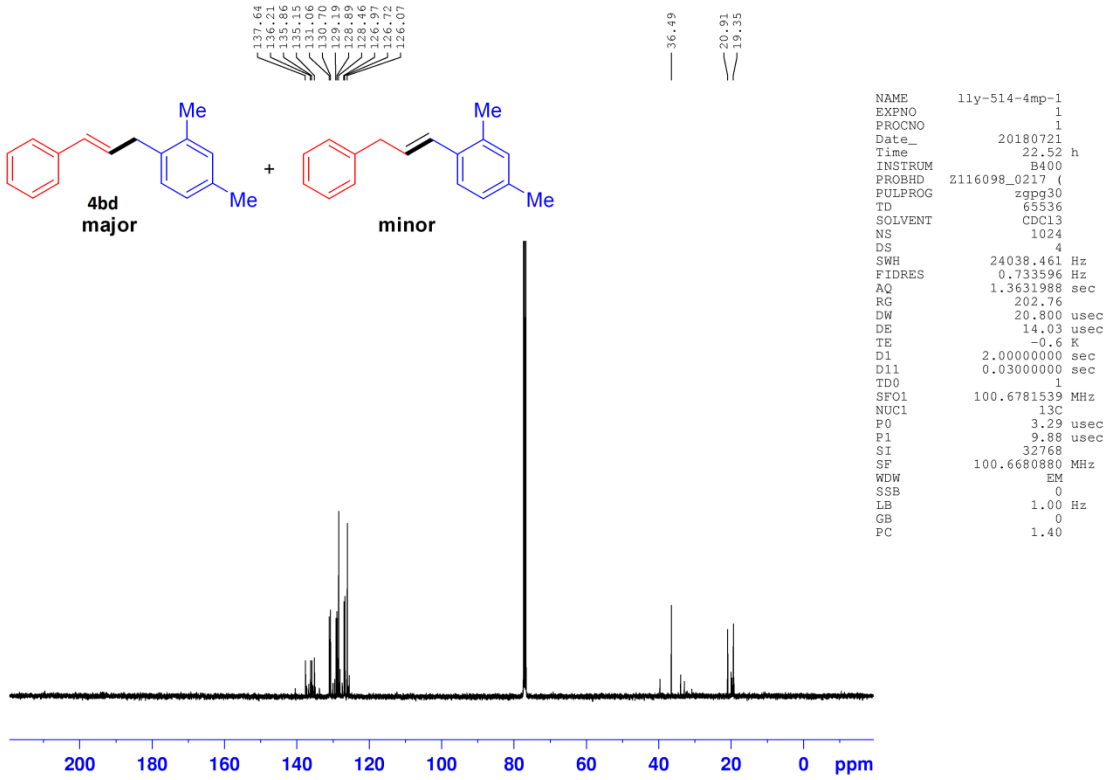
Supplementary Figure 43. ^{1}H NMR spectra for compound **4bc**



Supplementary Figure 44. ^{13}C NMR spectra for compound **4bc**



Supplementary Figure 45. ^{1}H NMR spectra for compound **4bd**

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PROCNO                  1
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PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              1.3631988 sec
RG                 202.76
DW                 20.800 usec
DE                 14.03 usec
TE                  -0.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1
SFO1         100.6781539 MHz
NUC1                 13C
P0                  3.29 usec
P1                  9.88 usec
SI                 32768
SF           100.6680880 MHz
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SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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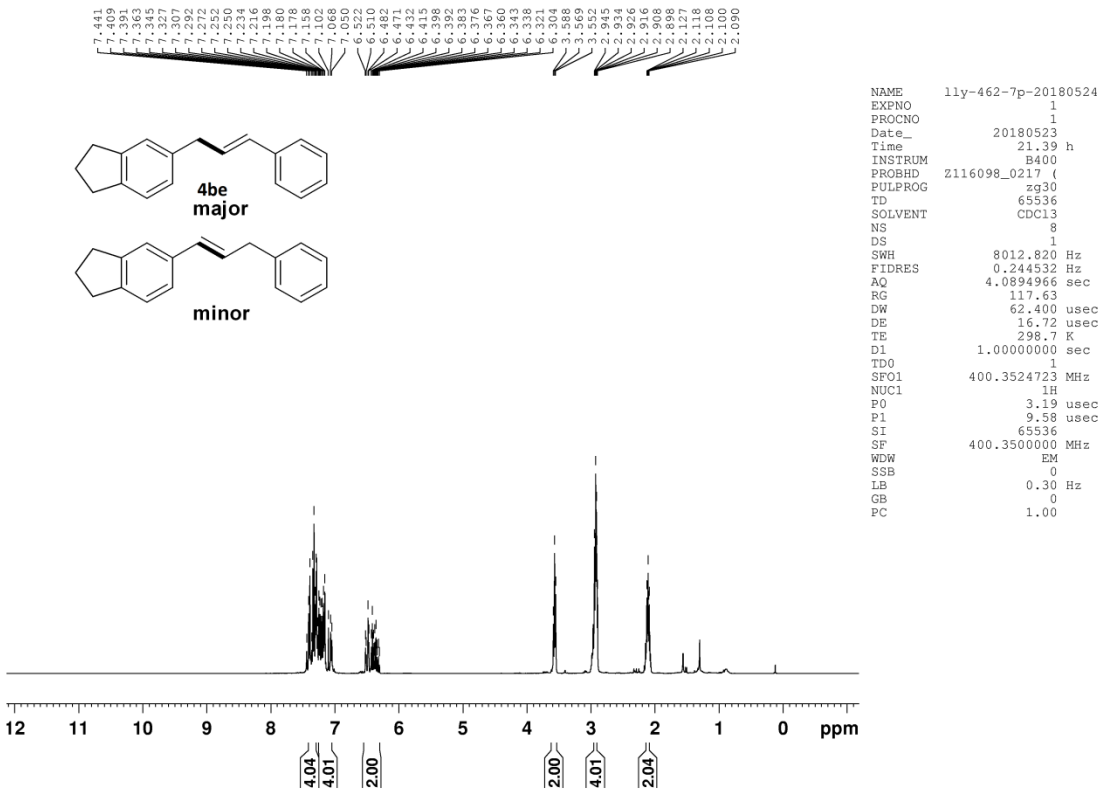
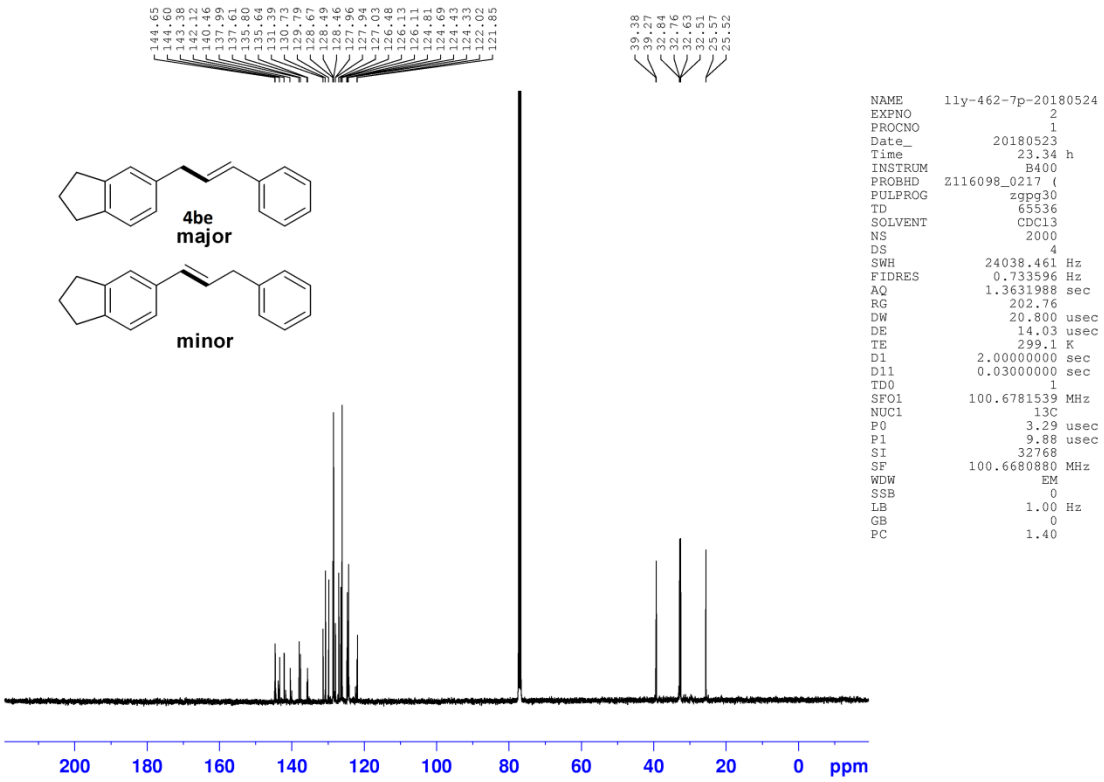
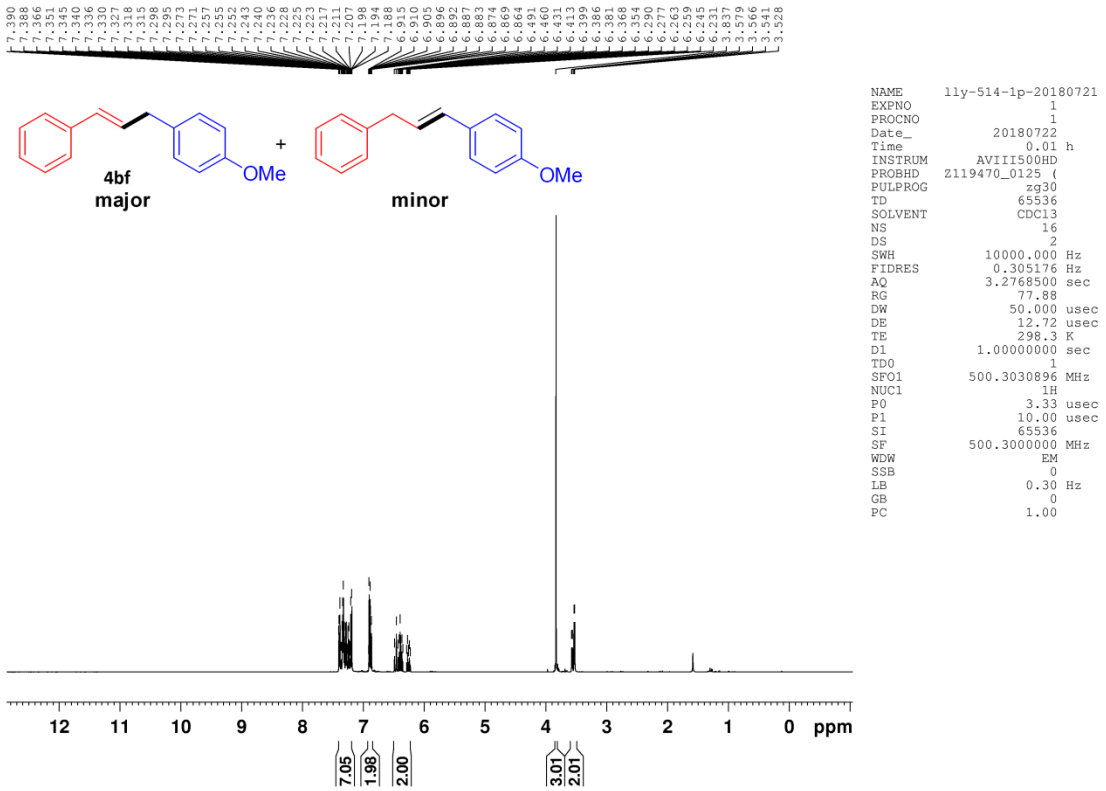
Supplementary Figure 46. ^{13}C NMR spectra for compound **4bd**



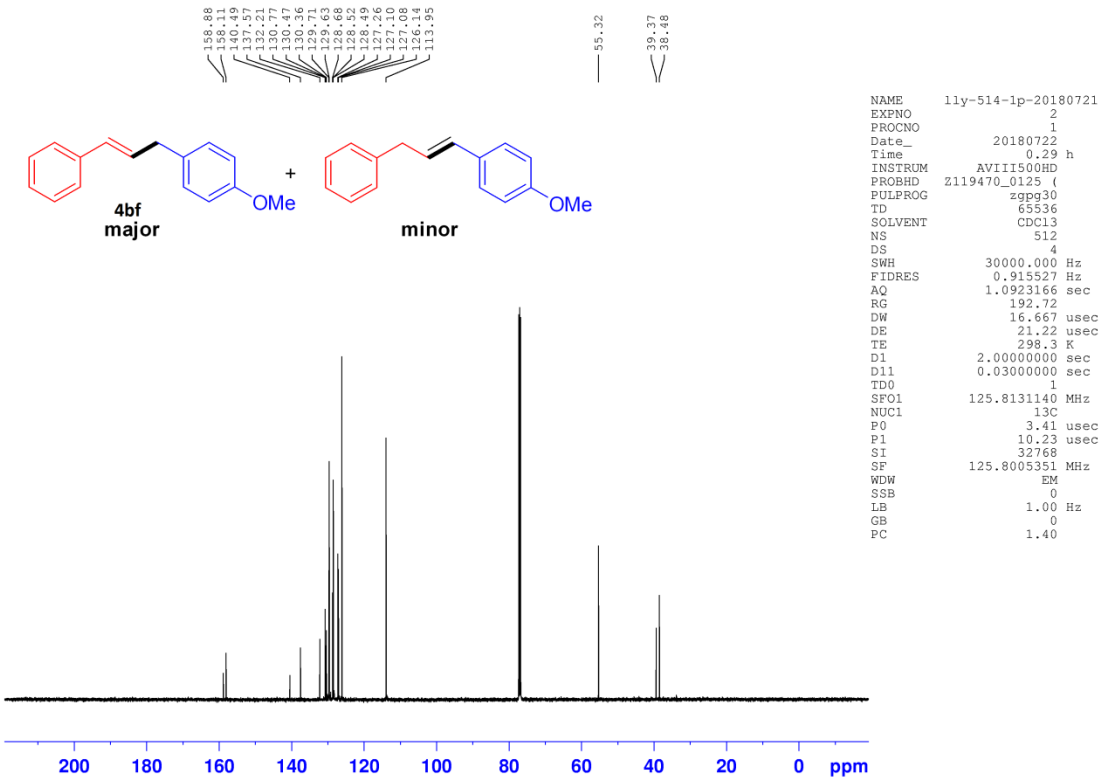
Supplementary Figure 47. ^{1}H NMR spectra for compound **4be**



Supplementary Figure 48. ^{13}C NMR spectra for compound **4be**



Supplementary Figure 49. ^{1}H NMR spectra for compound **4bf**



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PROCNO	1
Date_	20180722
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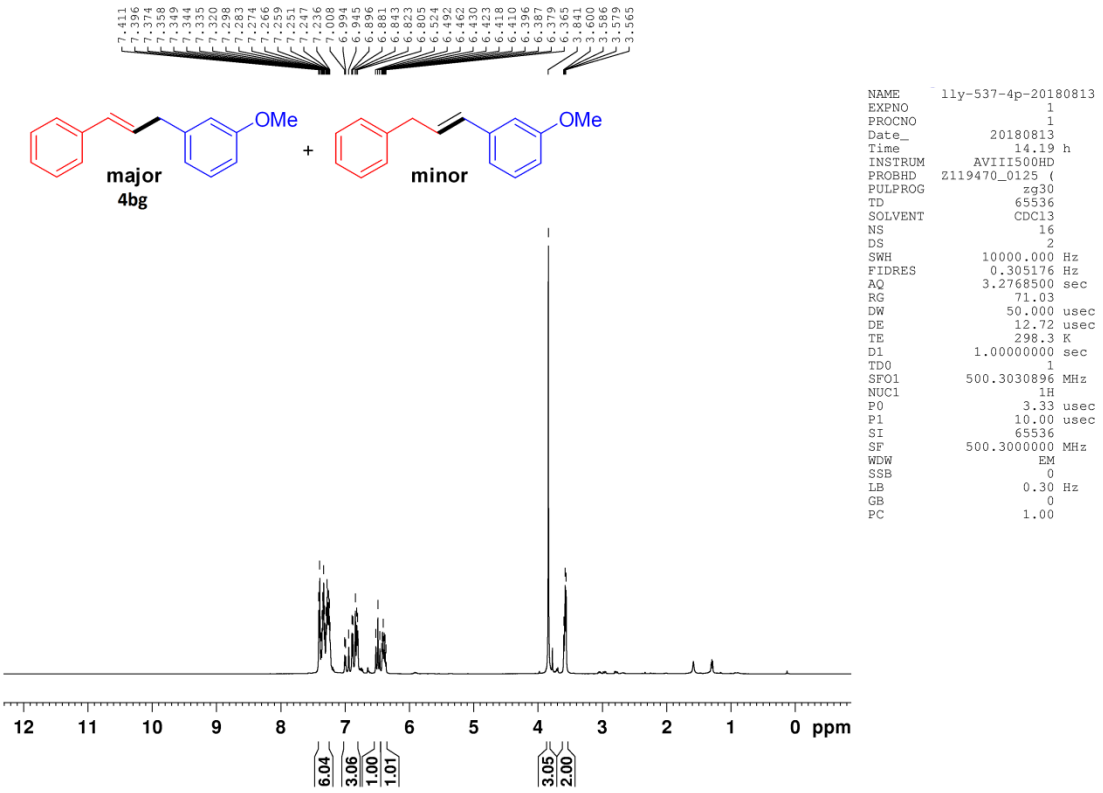
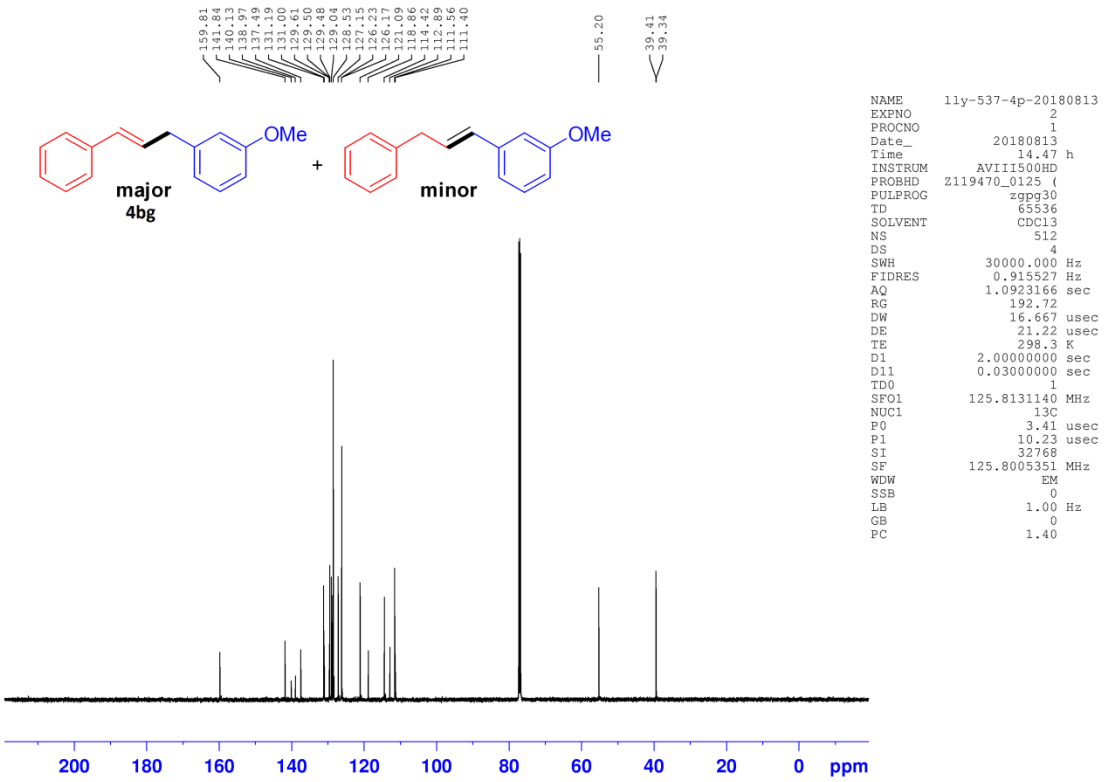
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

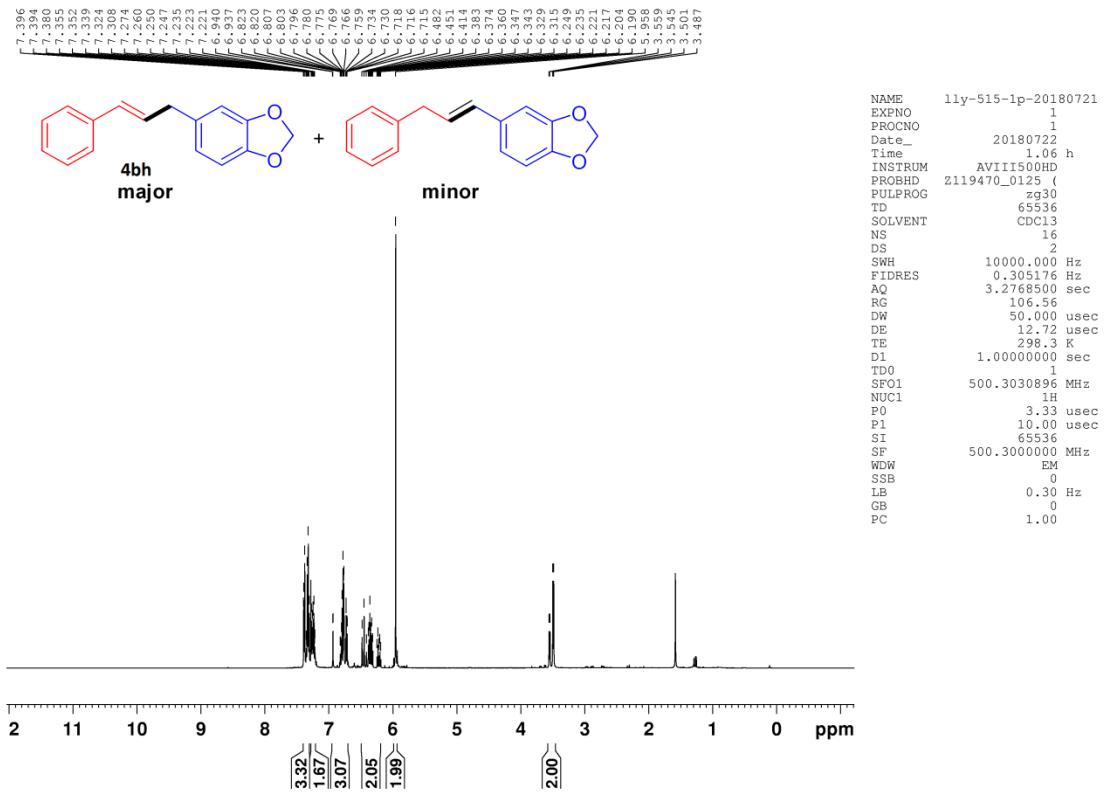
Supplementary Figure 50. ^{13}C NMR spectra for compound **4bf**



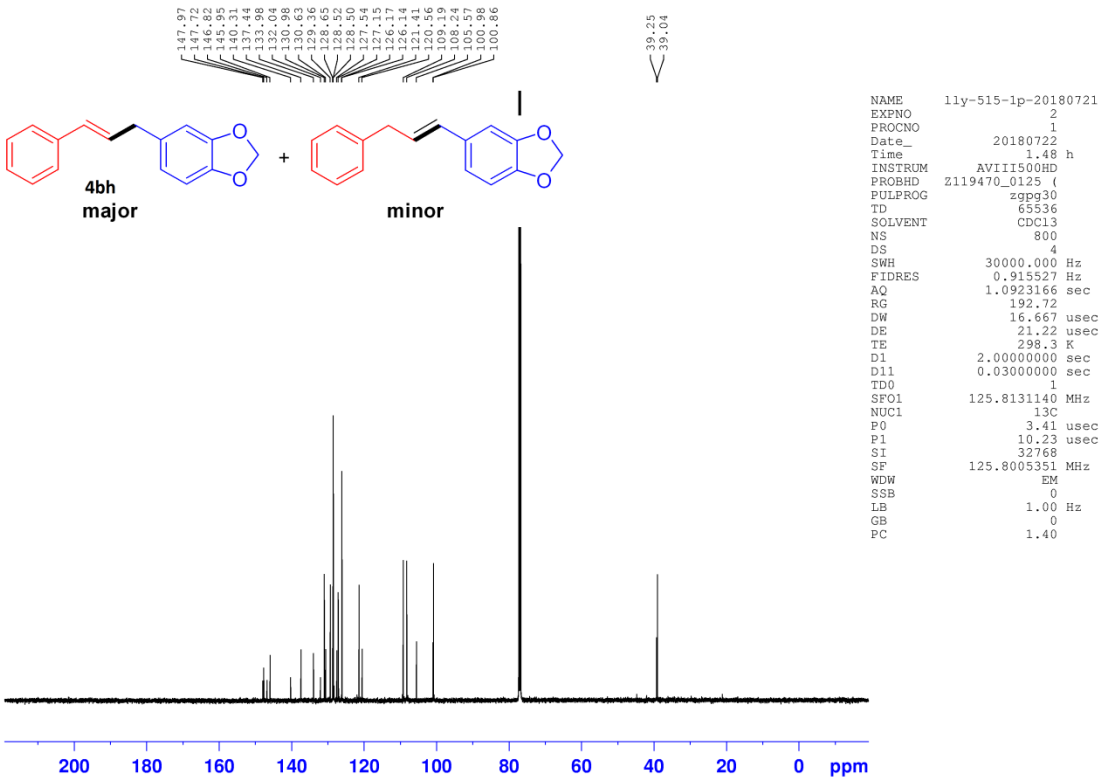
Supplementary Figure 51. ^{1}H NMR spectra for compound **4bg**



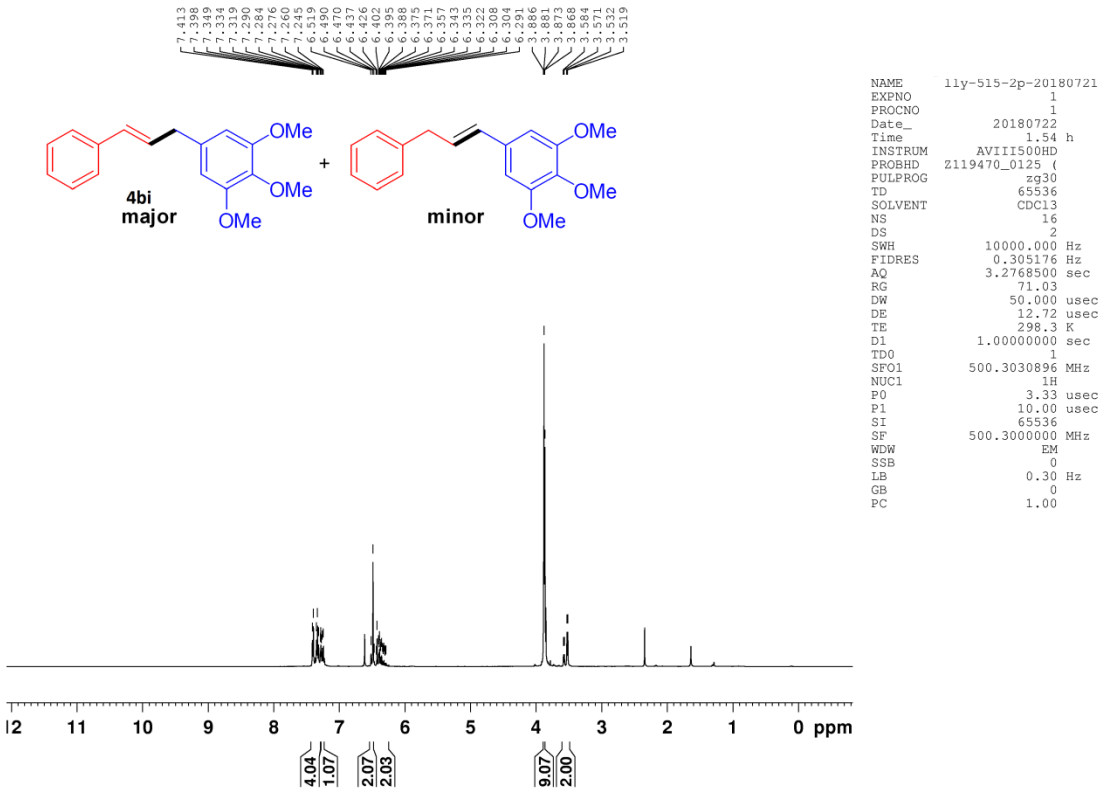
Supplementary Figure 52. ^{13}C NMR spectra for compound **4bg**



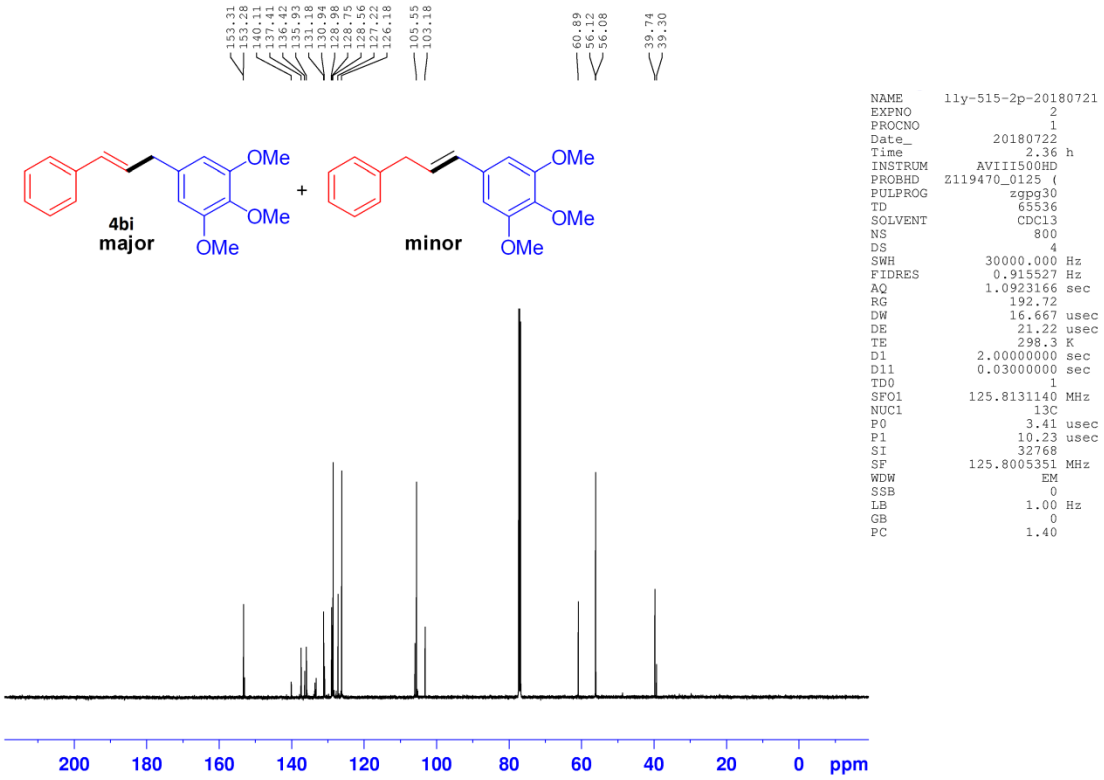
Supplementary Figure 53. ^{1}H NMR spectra for compound **4bh**



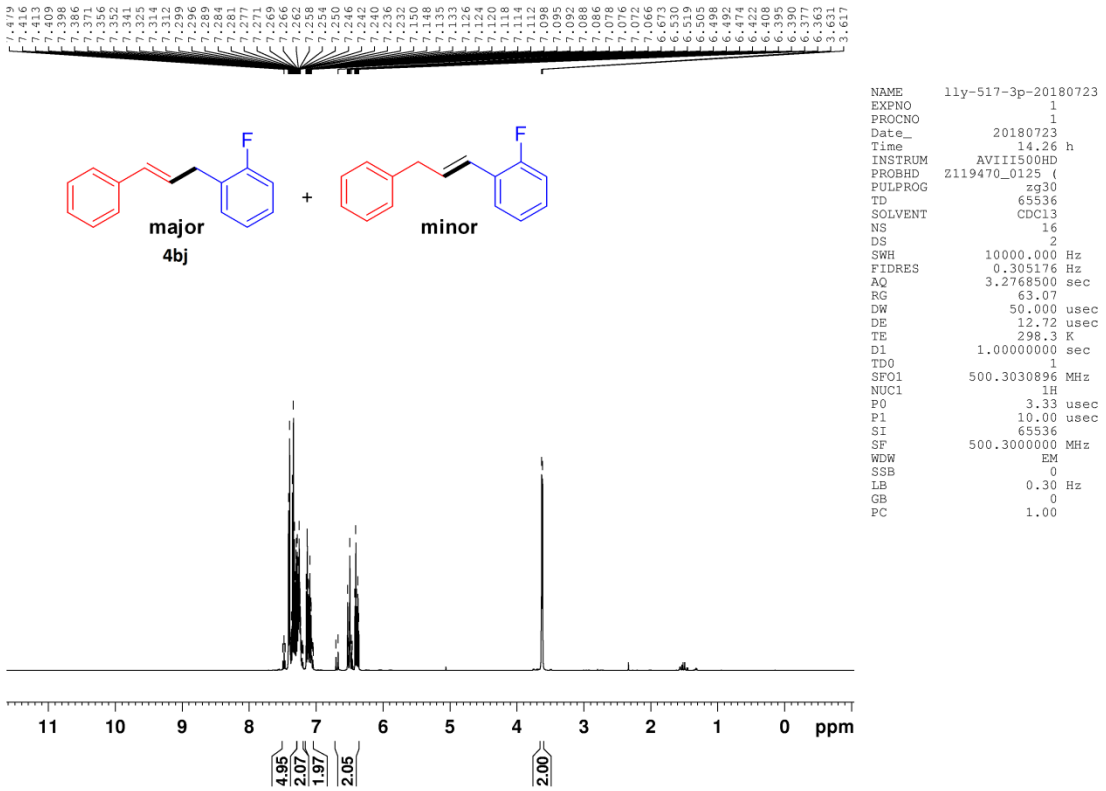
Supplementary Figure 54. ^{13}C NMR spectra for compound **4bh**



Supplementary Figure 55. ^{1}H NMR spectra for compound **4bi**



Supplementary Figure 56. ^{13}C NMR spectra for compound **4bi**



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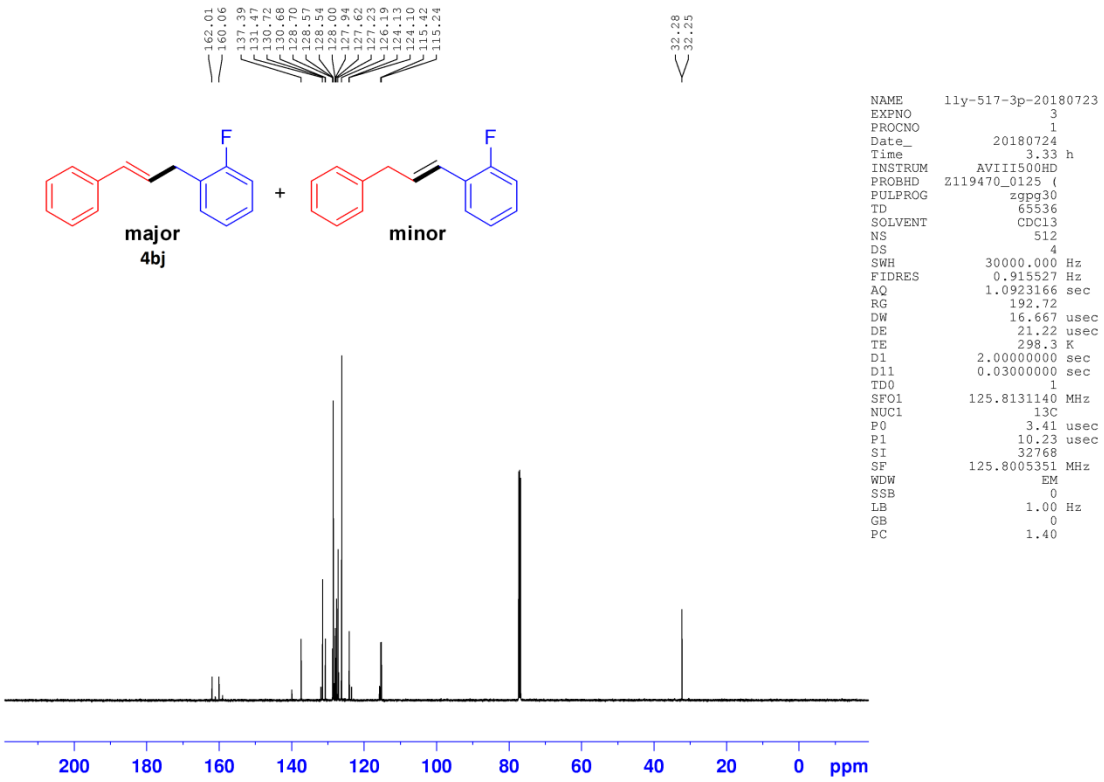
PROBHD	Z119470_0125 (
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10000.000 Hz
FIDRES	0.305176 Hz
AQ	3.2768500 sec
RG	63.07
DW	50.000 usec
DE	12.72 usec
TE	298.3 K
D1	1.00000000 sec
TD0	1
SFO1	500.3030896 MHz
NUC1	1H
P0	3.33 usec
P1	10.00 usec
SI	65536
SF	500.3000000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Supplementary Figure 57. ^{1}H NMR spectra for compound **4bj**



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PROCNO	1
Date_	20180724
Time	3.33 h
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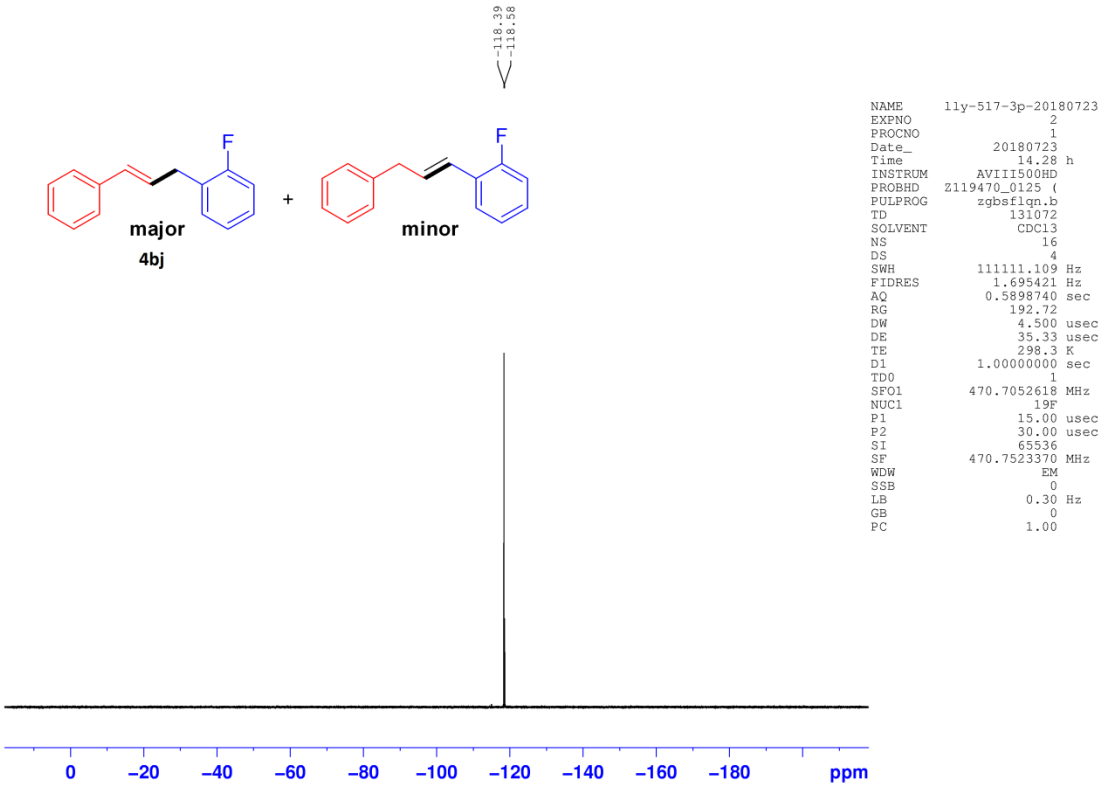
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Supplementary Figure 58. ^{13}C NMR spectra for compound **4bj**

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PROCNO                         1
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PULPROG               zgbsflqn.b
TD                         131072
SOLVENT                    CDCl3
NS                             16
DS                              4
SWH                   111111.109 Hz
FIDRES                  1.695421 Hz
AQ                      0.5898740 sec
RG                        192.72
DW                         4.500 usec
DE                        35.33 usec
TE                        298.3 K
D1                    1.00000000 sec
TD0                             1
SFO1                470.7052618 MHz
NUC1                        19F
P1                        15.00 usec
P2                        30.00 usec
SI                         65536
SF                  470.7523370 MHz
WDW                           EM
SSB                            0
LB                        0.30 Hz
GB                             0
PC                        1.00
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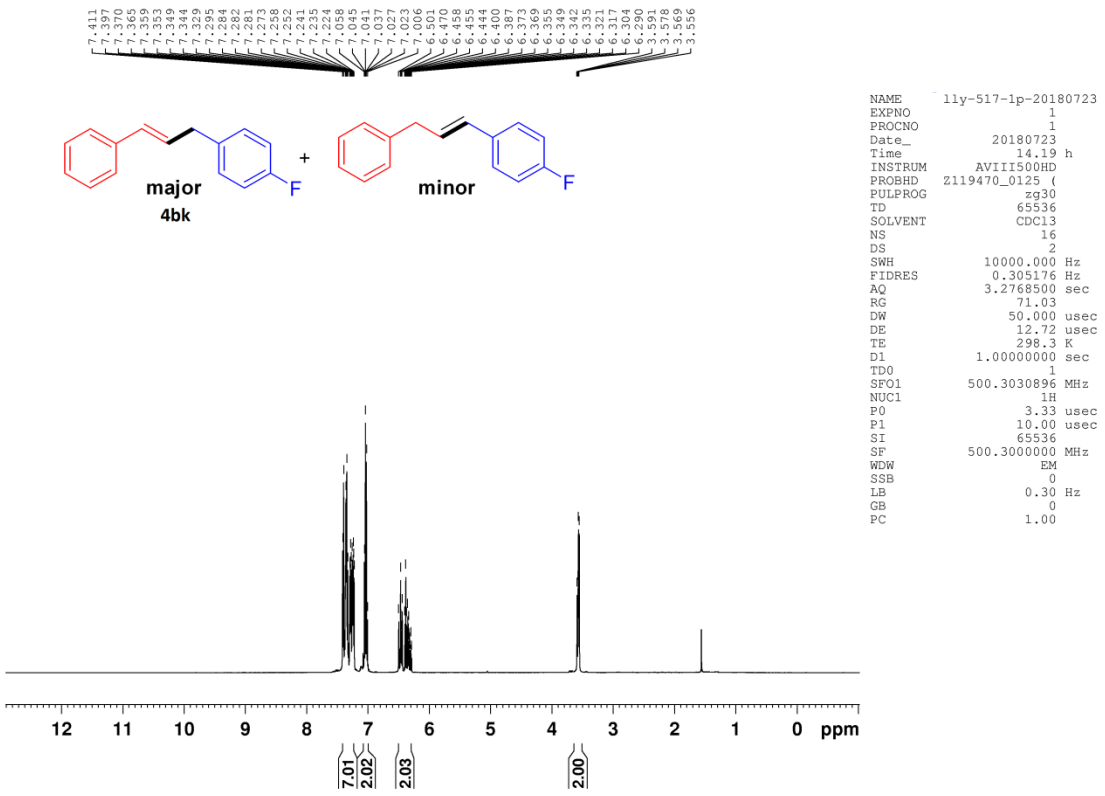
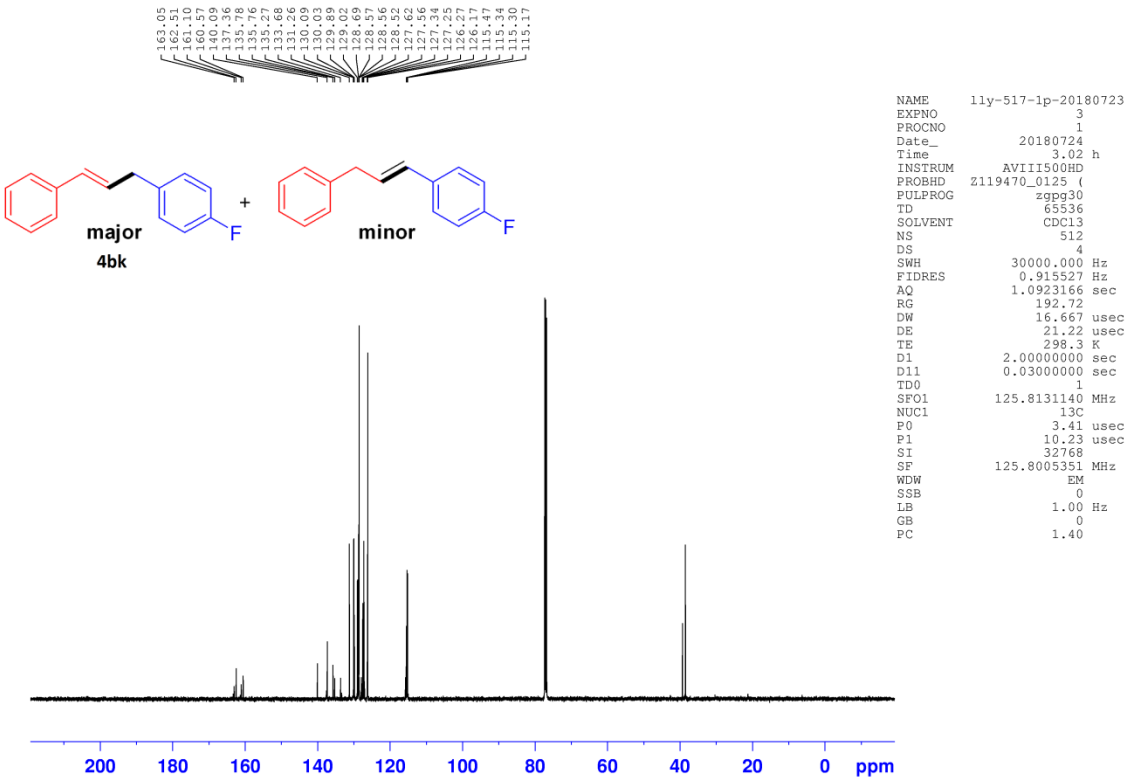
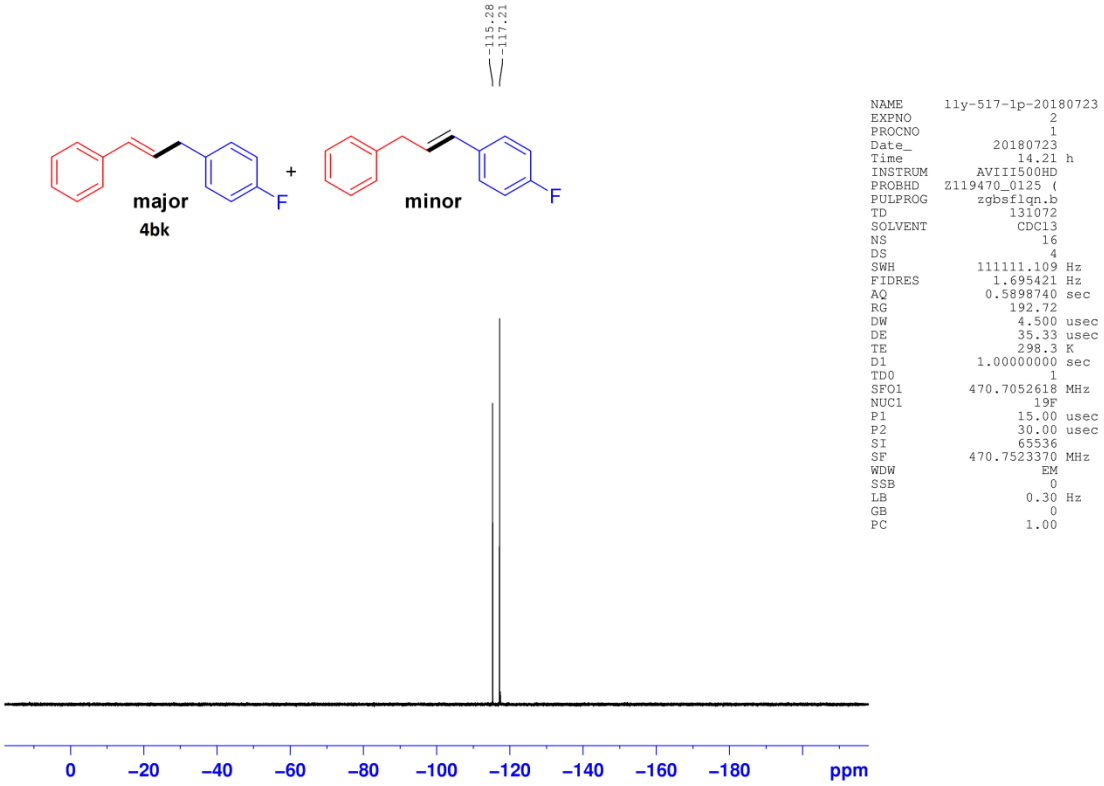
Supplementary Figure 59. ^{19}F NMR spectra for compound **4bj**



Supplementary Figure 60. ^{1}H NMR spectra for compound **4bk**



Supplementary Figure 61. ^{13}C NMR spectra for compound **4bk**

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PROCNO                        1
Date_                  20180723
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PULPROG              zgbsflqn.b
TD                       131072
SOLVENT                  CDCl3
NS                           16
DS                            4
SWH                 111111.109 Hz
FIDRES                1.695421 Hz
AQ                    0.5898740 sec
RG                       192.72
DW                        4.500 usec
DE                       35.33 usec
TE                       298.3 K
D1                  1.00000000 sec
TD0                           1
SFO1                470.7052618 MHz
NUC1                         19F
P1                       15.00 usec
P2                       30.00 usec
SI                       65536
SF                  470.7523370 MHz
WDW                          EM
SSB                           0
LB                        0.30 Hz
GB                            0
PC                        1.00
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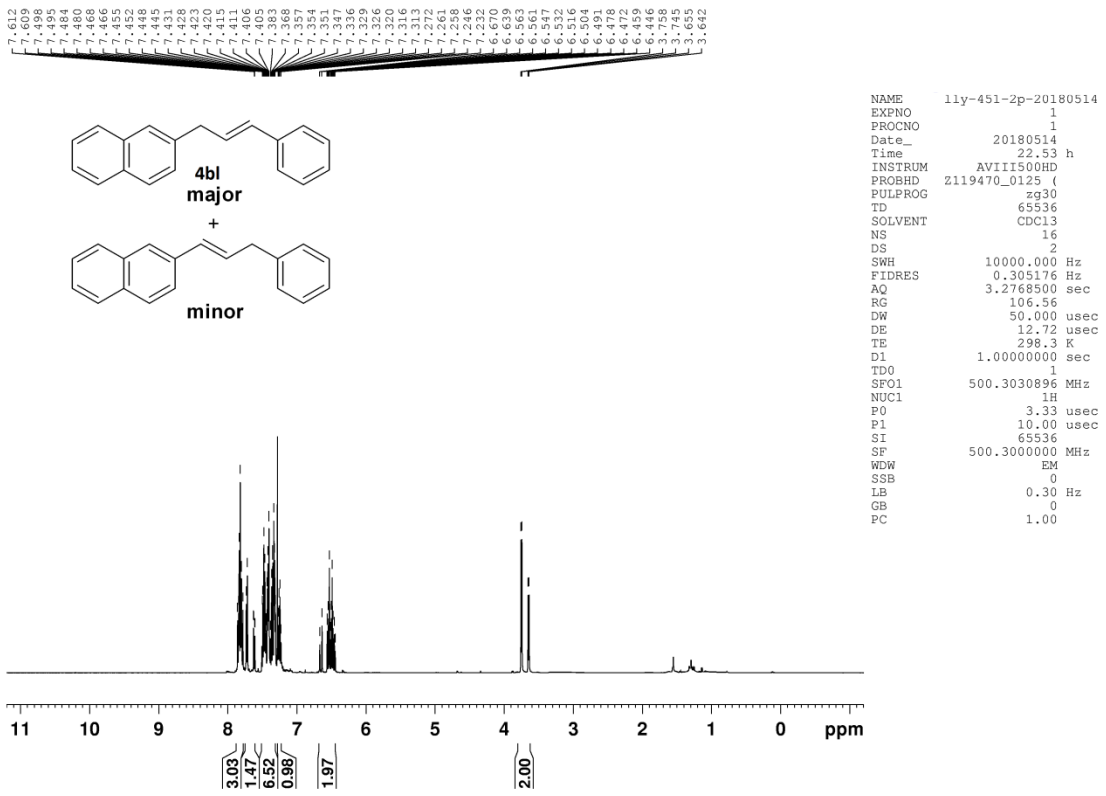
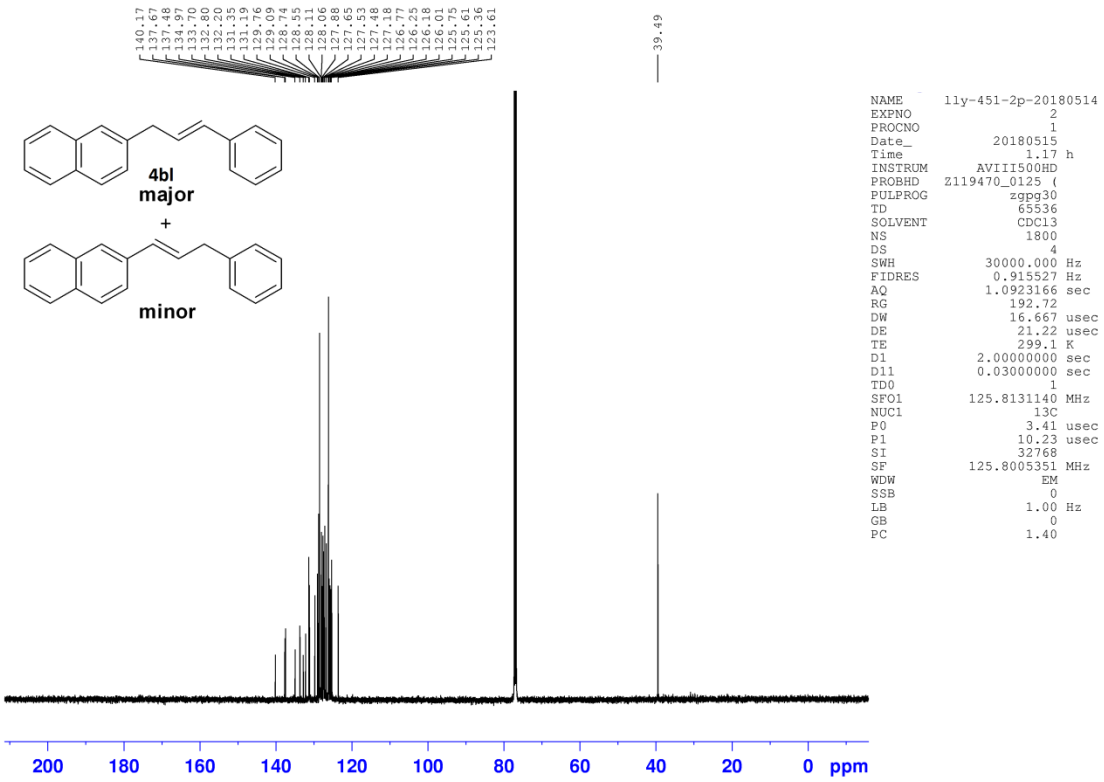
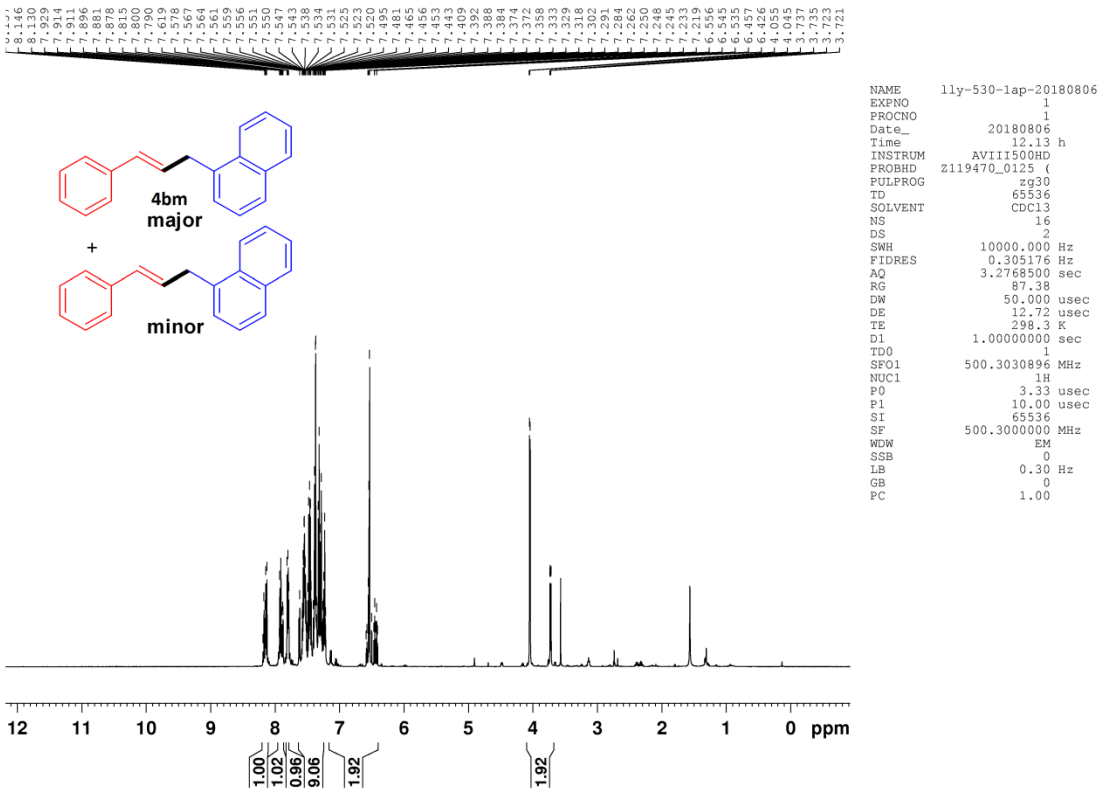
Supplementary Figure 62. ^{19}F NMR spectra for compound **4bk**



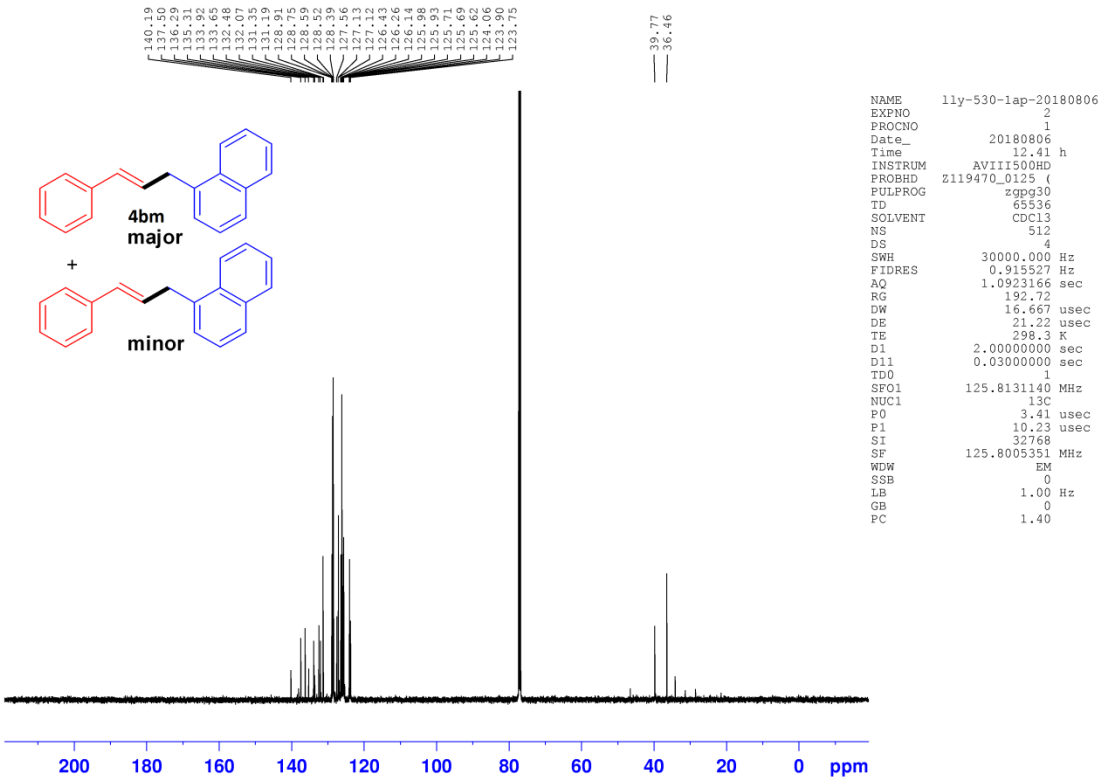
Supplementary Figure 63. ^{1}H NMR spectra for compound **4bl**



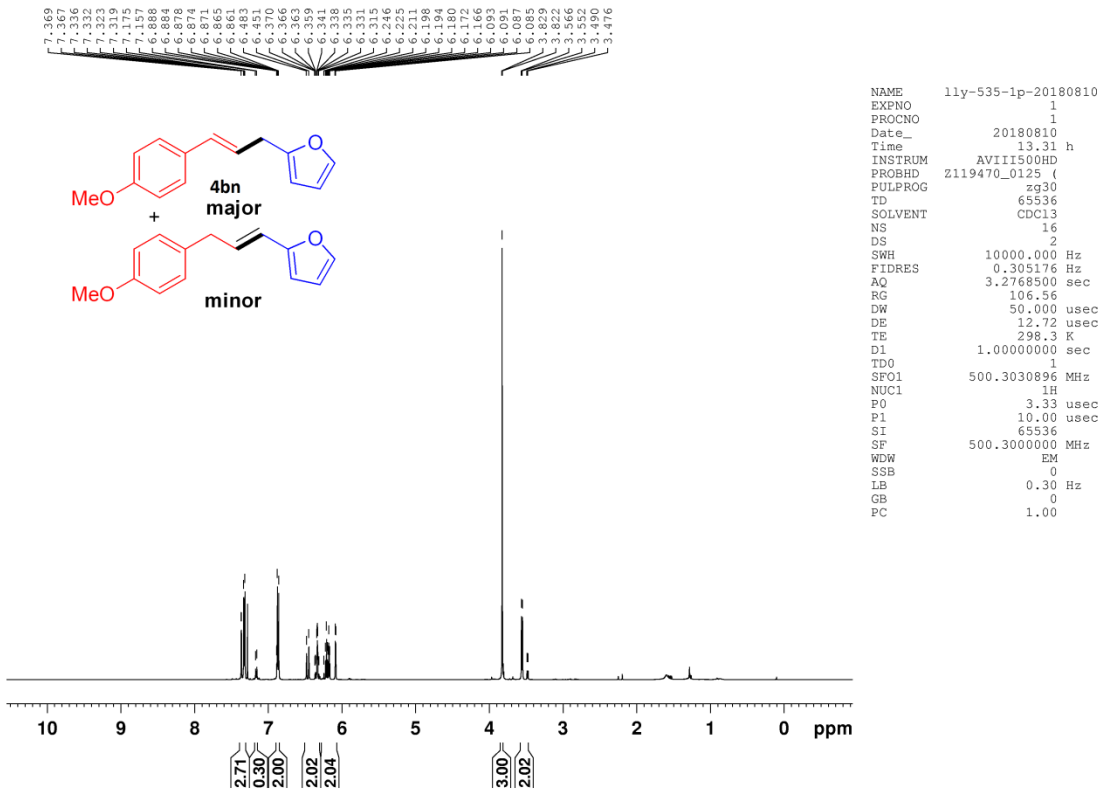
Supplementary Figure 64. ^{13}C NMR spectra for compound **4bl**



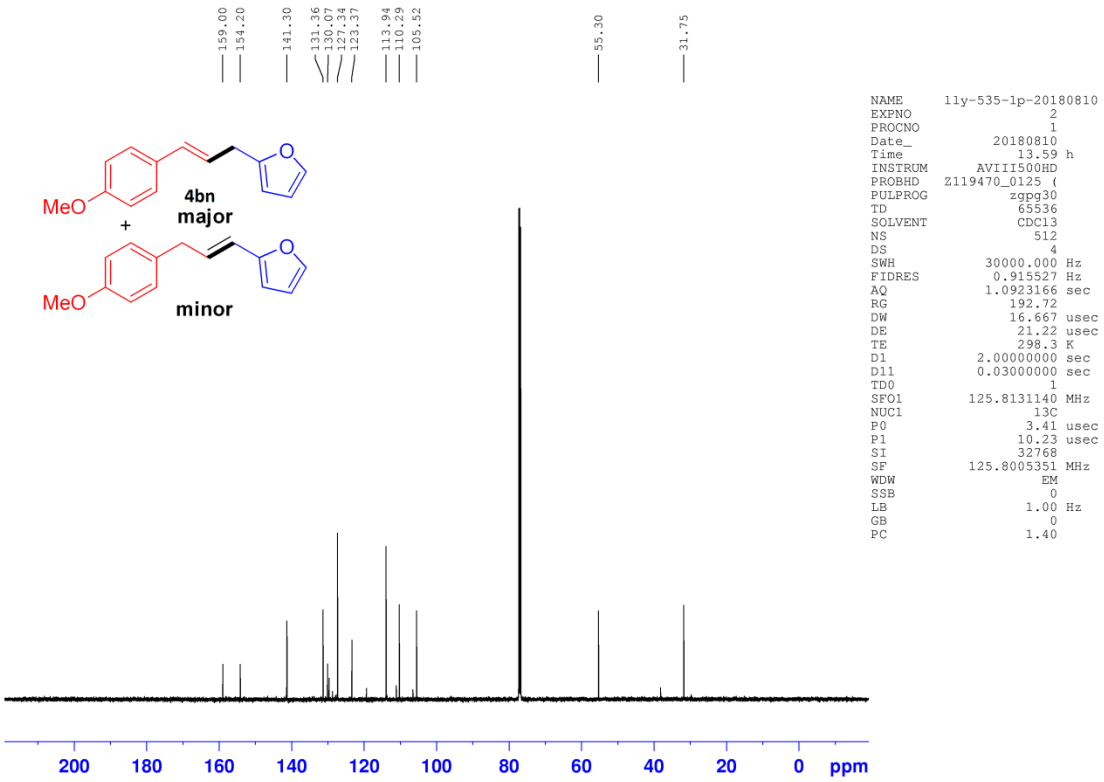
Supplementary Figure 65. ^{1}H NMR spectra for compound **4bm**



Supplementary Figure 66. ^{13}C NMR spectra for compound **4bm**



Supplementary Figure 67. ^{1}H NMR spectra for compound **4bn**



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PROCNO	1
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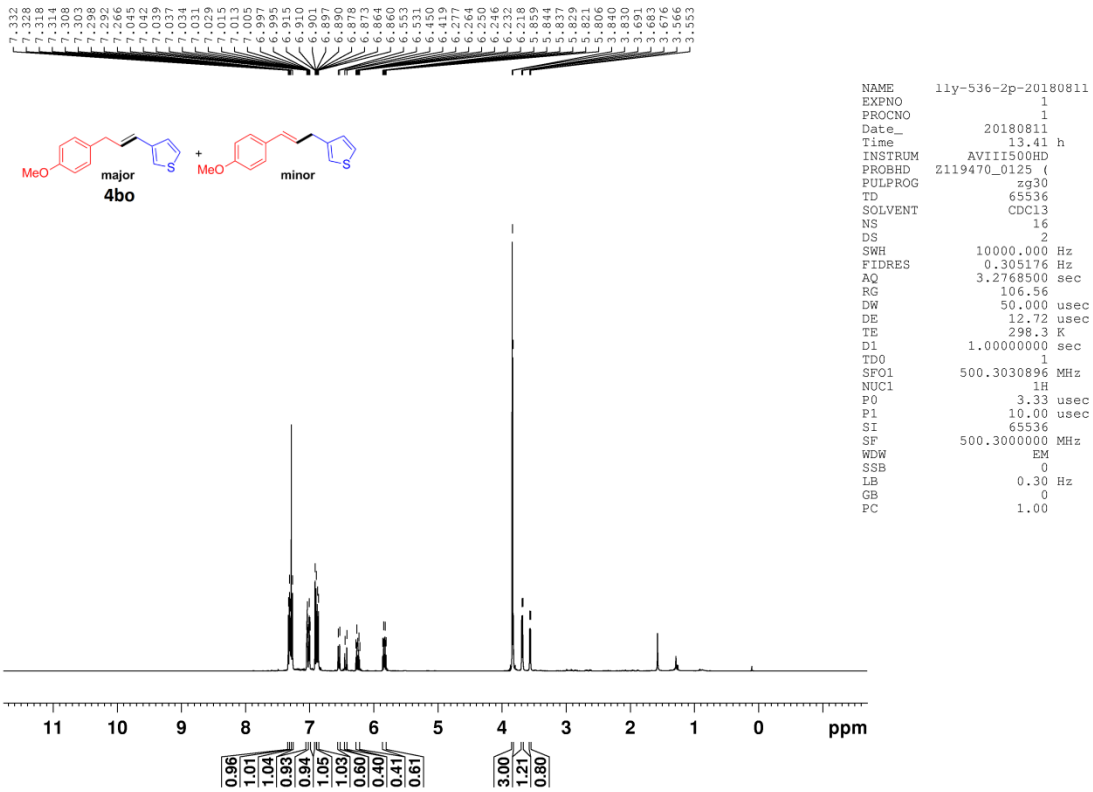
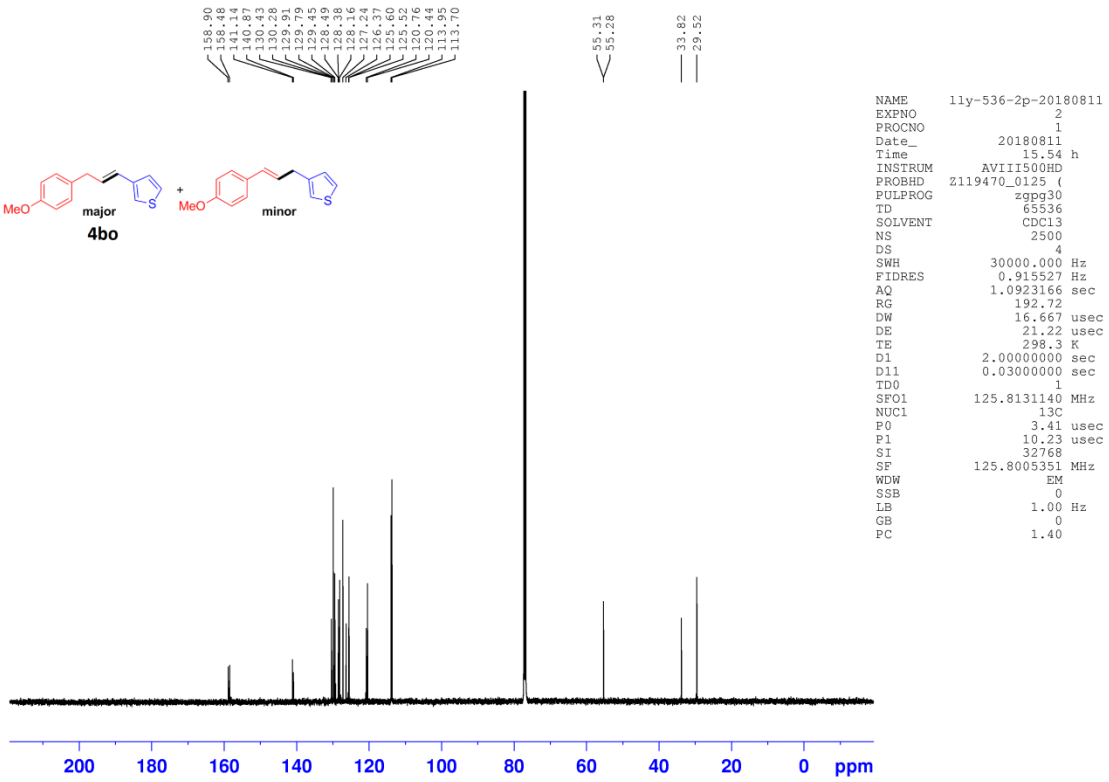
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

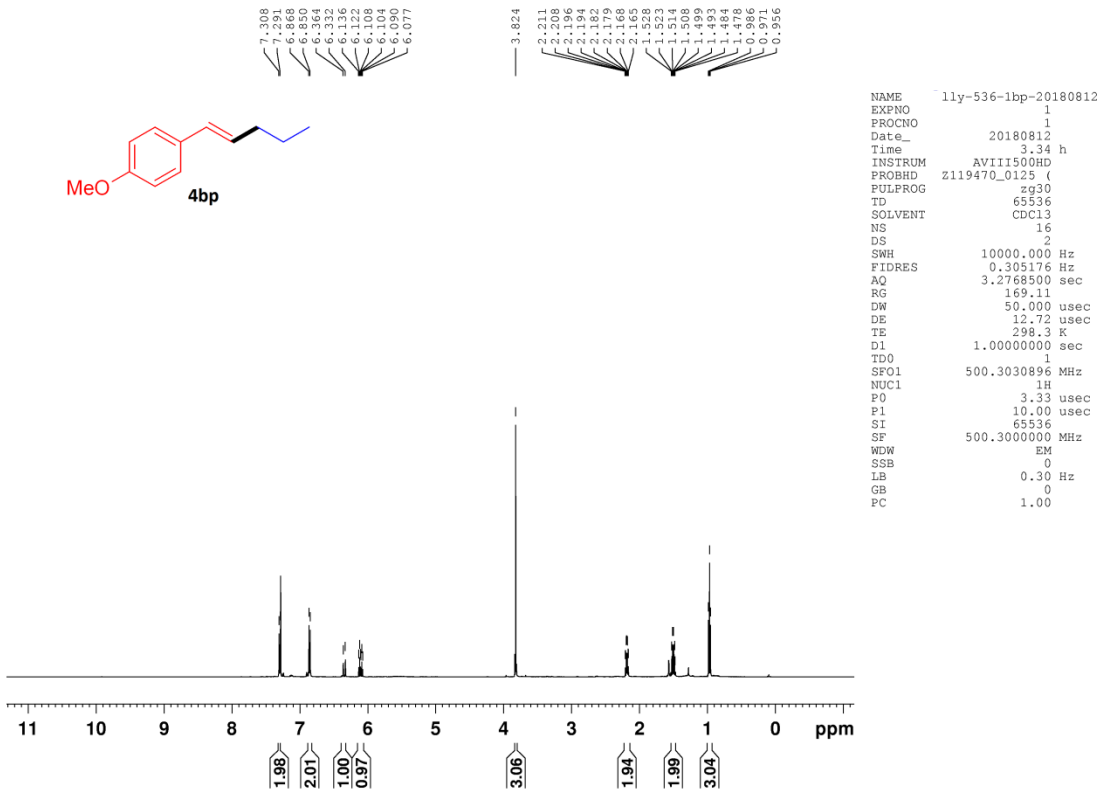
Supplementary Figure 68. ^{13}C NMR spectra for compound **4bn**



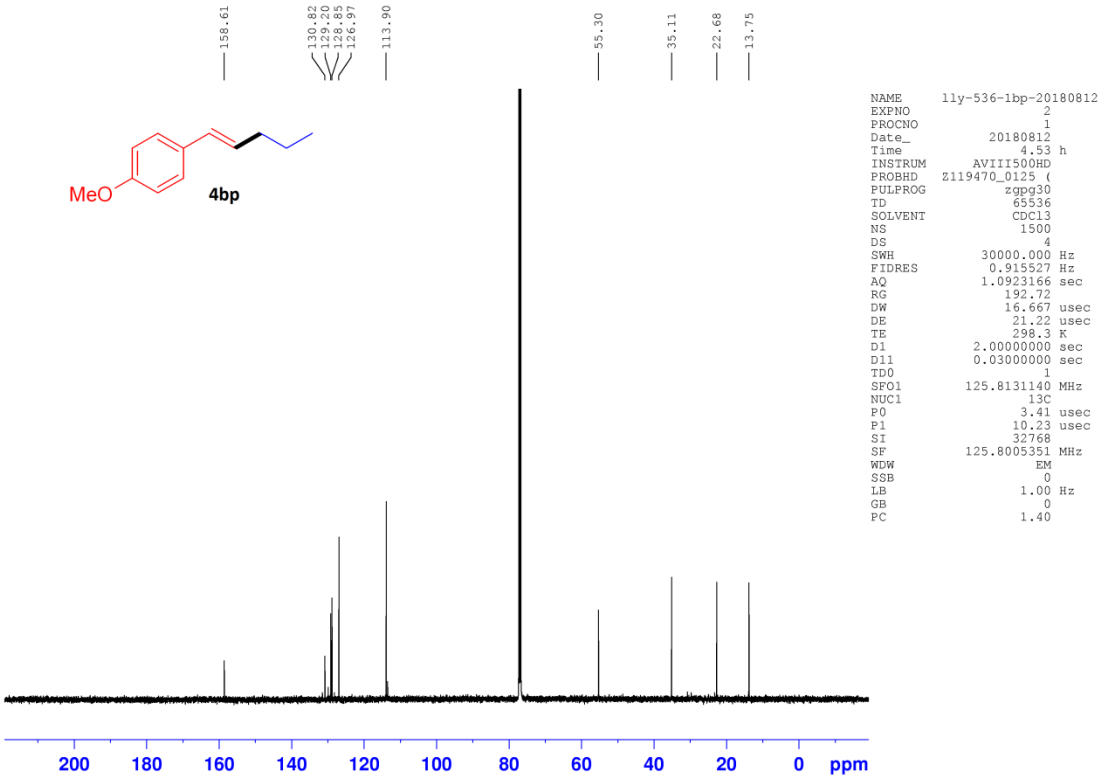
Supplementary Figure 69. ^{1}H NMR spectra for compound **4bo**



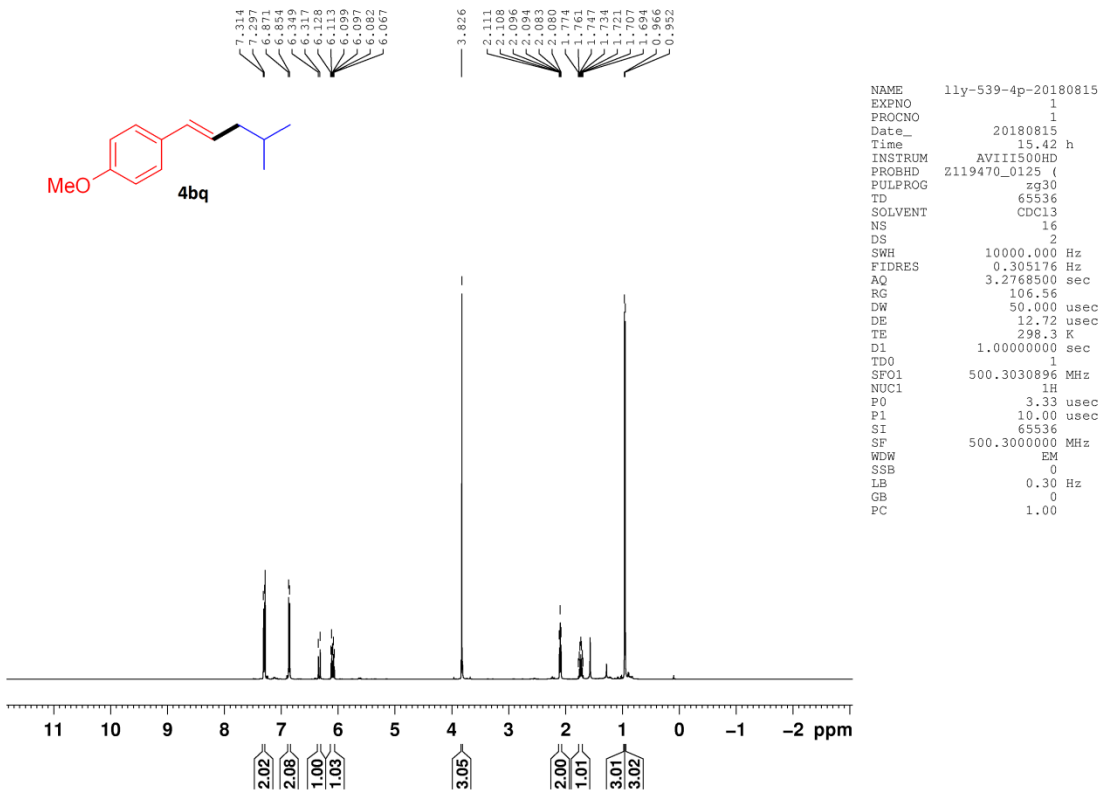
Supplementary Figure 70. ^{13}C NMR spectra for compound **4bo**



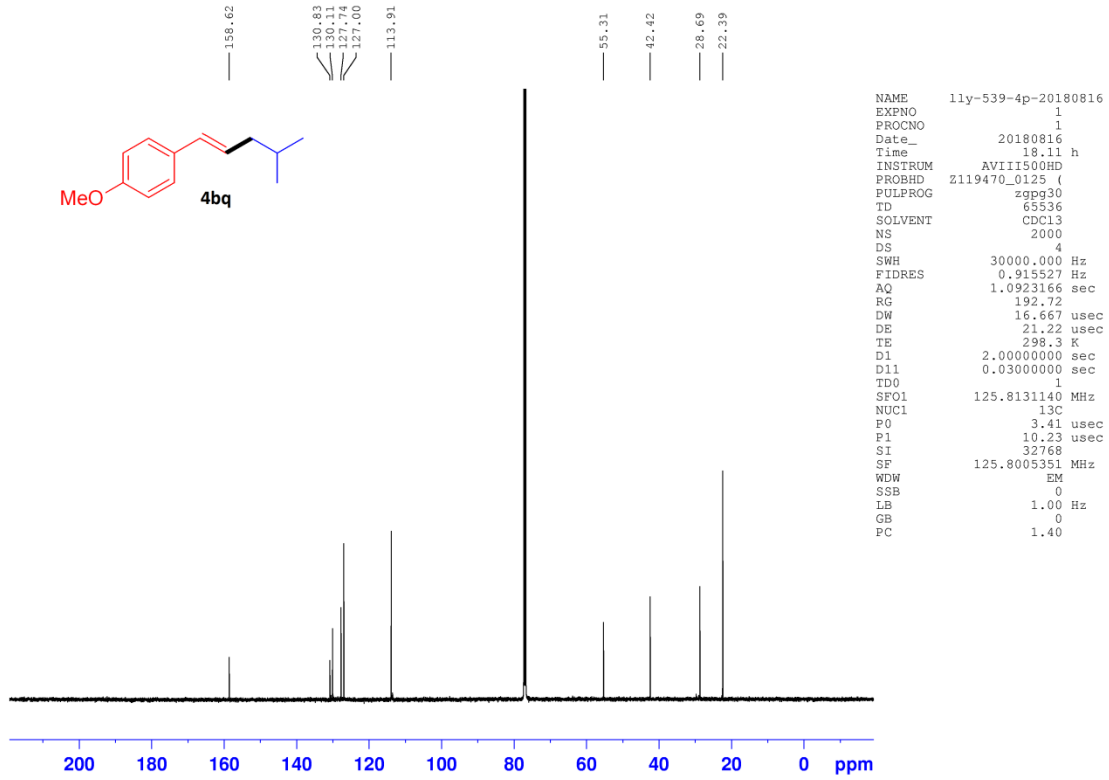
Supplementary Figure 71. ^{1}H NMR spectra for compound **4bp**



Supplementary Figure 72. ^{13}C NMR spectra for compound **4bp**



Supplementary Figure 73. ^{1}H NMR spectra for compound **4bq**



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PROCNO	1
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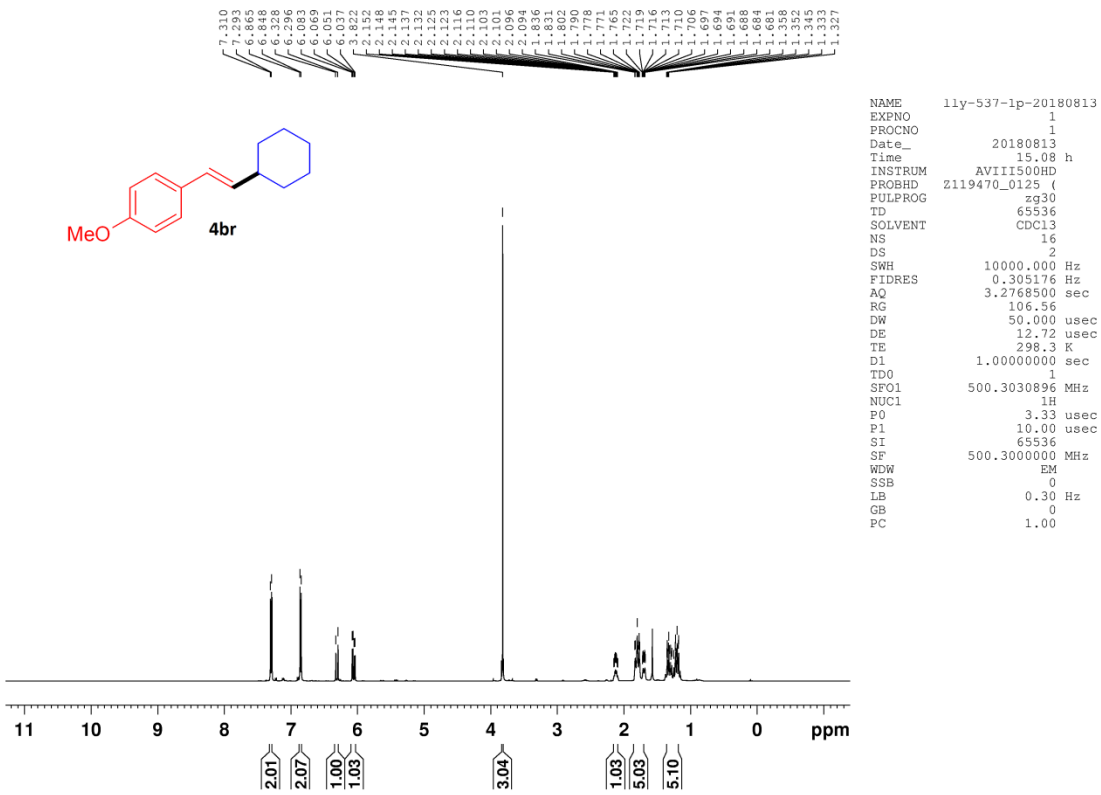
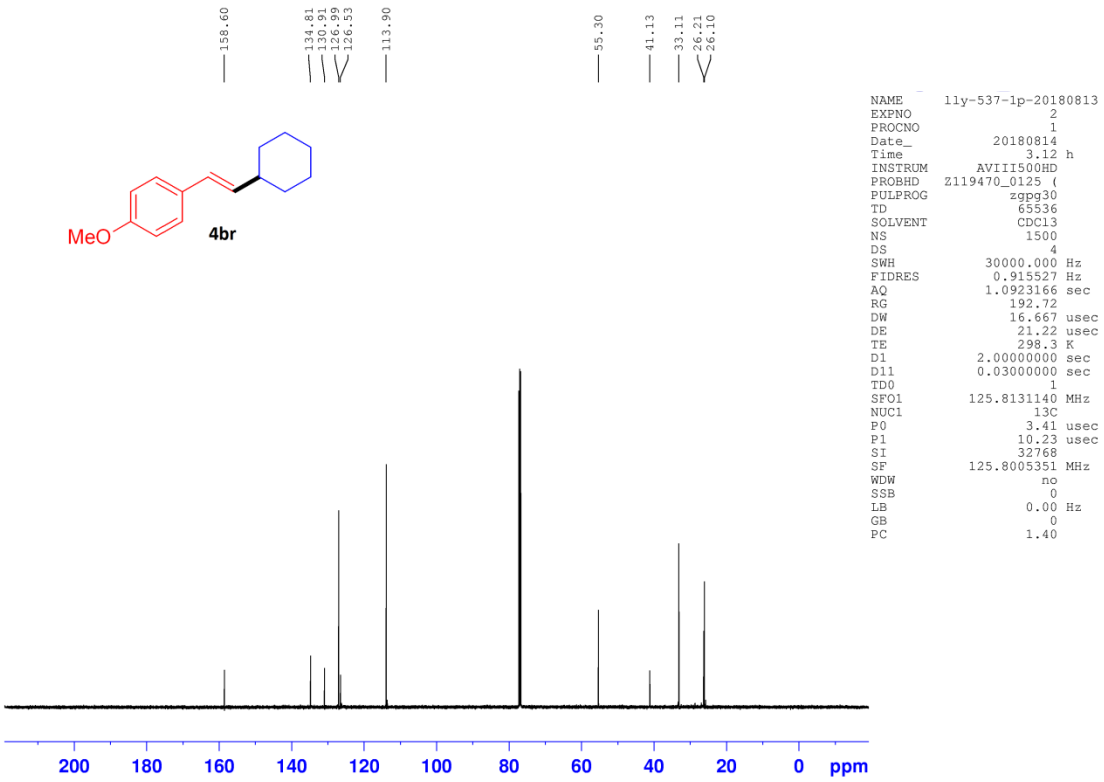
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2000
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Supplementary Figure 74. ^{13}C NMR spectra for compound **4bq**



Supplementary Figure 75. ^{1}H NMR spectra for compound **4br**



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PROCNO	1
Date_	20180814
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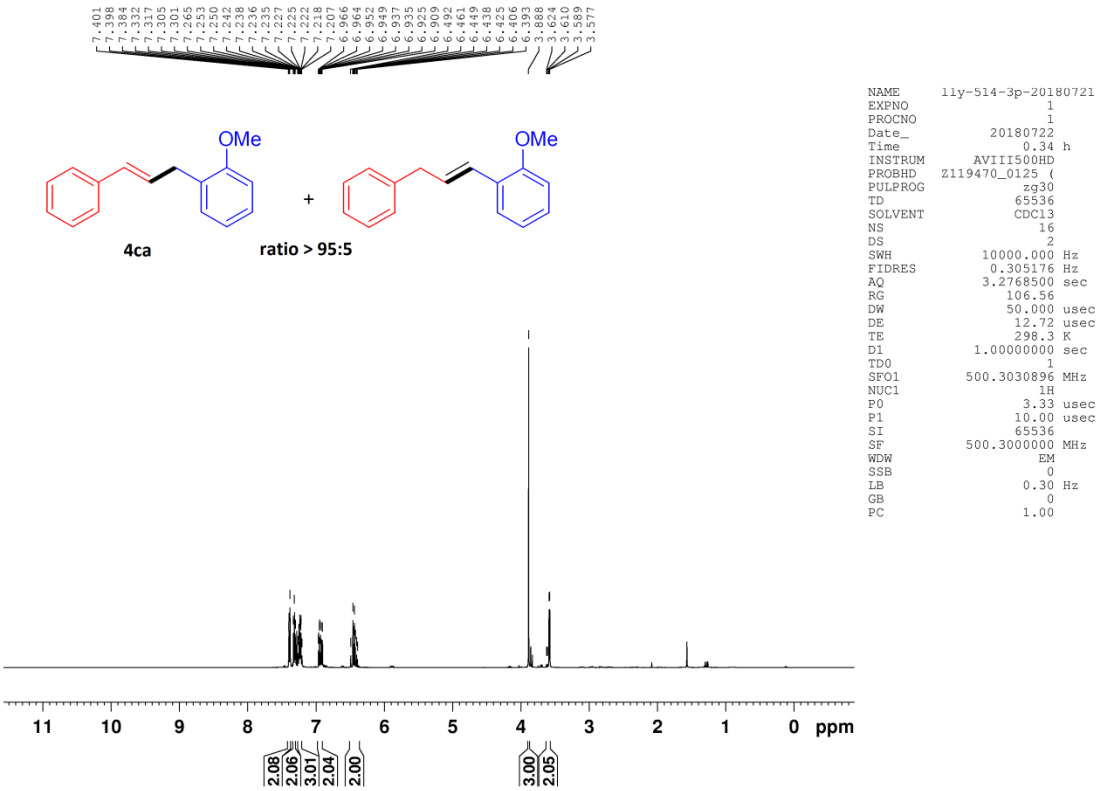
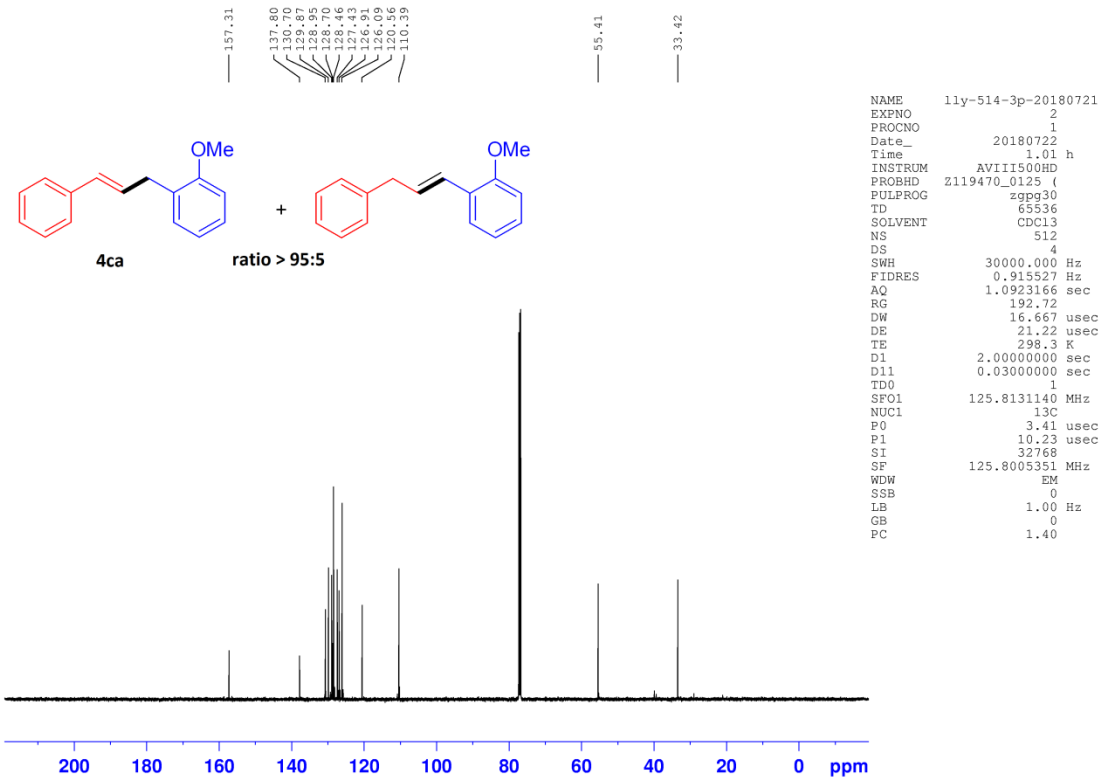
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1500
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

Supplementary Figure 76. ^{13}C NMR spectra for compound **4br**



Supplementary Figure 77. ^{1}H NMR spectra for compound **4ca**

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NAME          lly-514-3p-20180721
EXPNO                          2
PROCNO                         1
Date_                   20180722
Time                       1.01 h
INSTRUM              AVIII500HD
PROBHD           Z119470_0125 (
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          512
DS                            4
SWH                   30000.000 Hz
FIDRES                0.915527 Hz
AQ                    1.0923166 sec
RG                       192.72
DW                       16.667 usec
DE                       21.22 usec
TE                       298.3 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1
SFO1                125.8131140 MHz
NUC1                        13C
P0                        3.41 usec
P1                       10.23 usec
SI                        32768
SF                  125.8005351 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                        1.40
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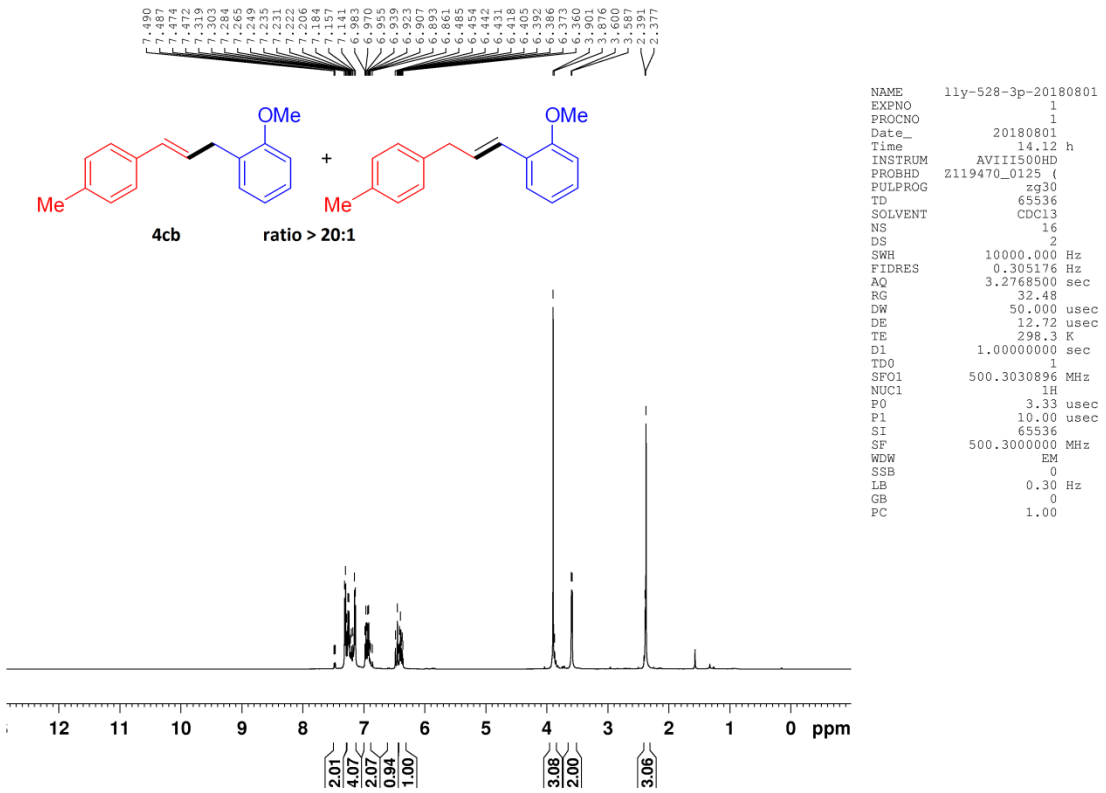
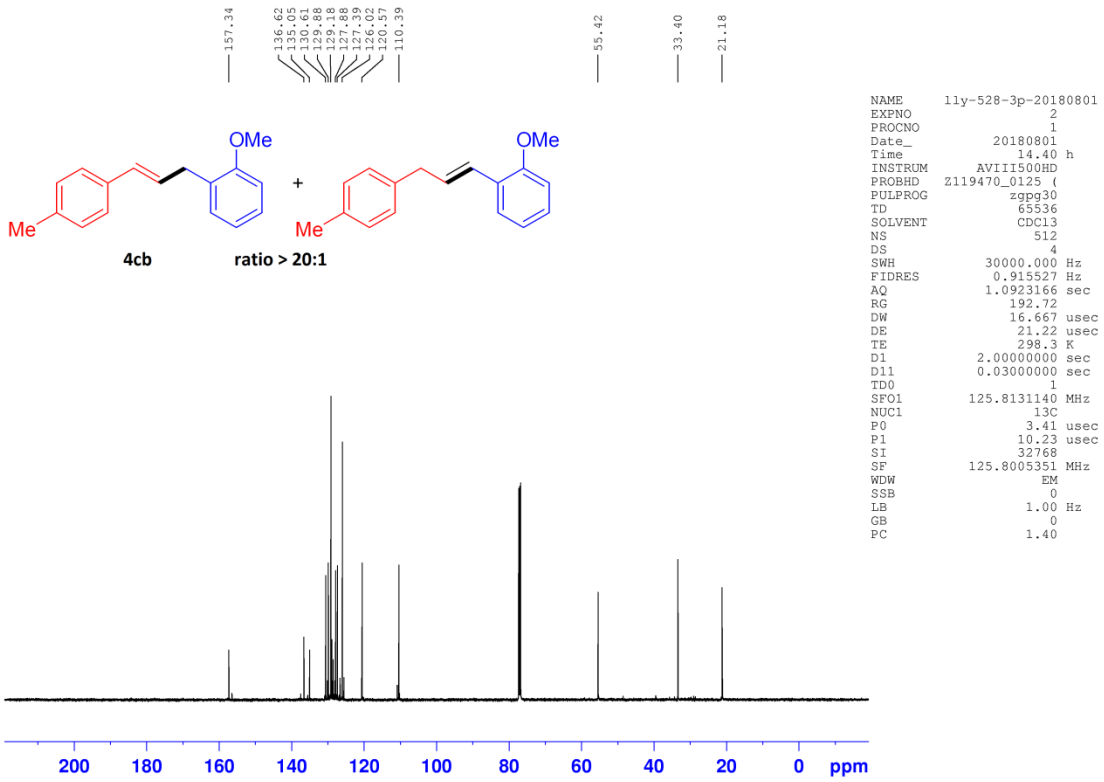
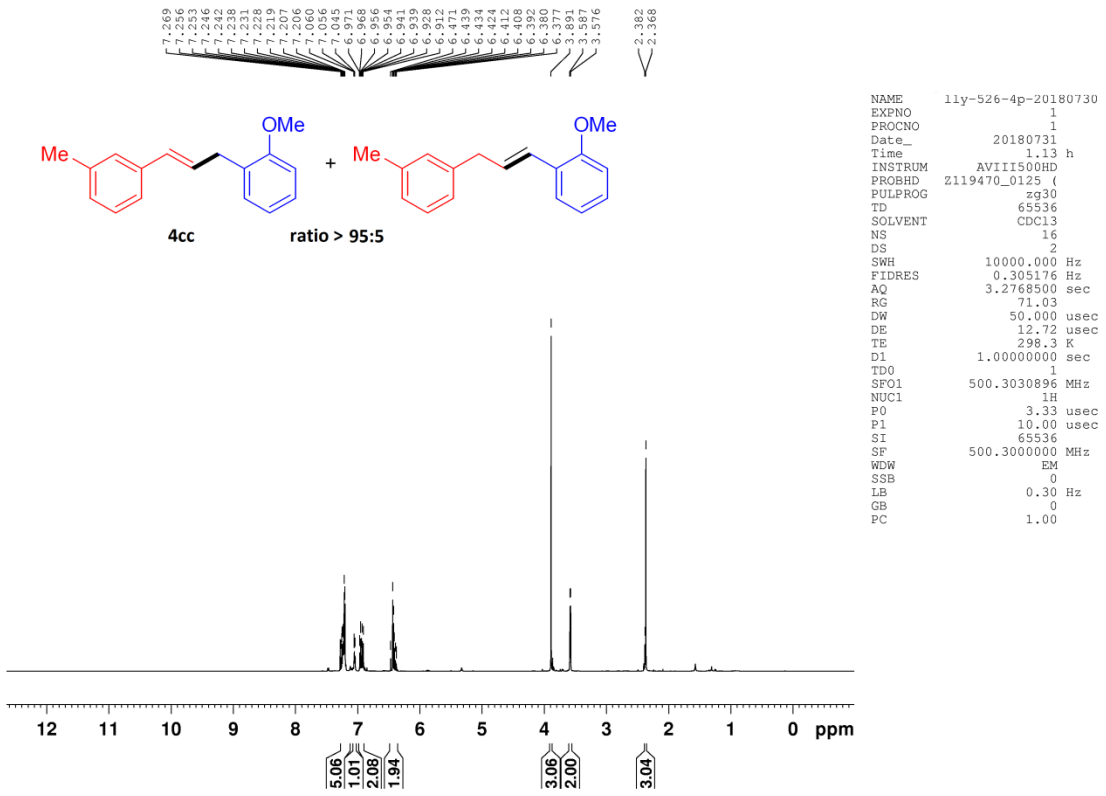
Supplementary Figure 78. ^{13}C NMR spectra for compound **4ca**



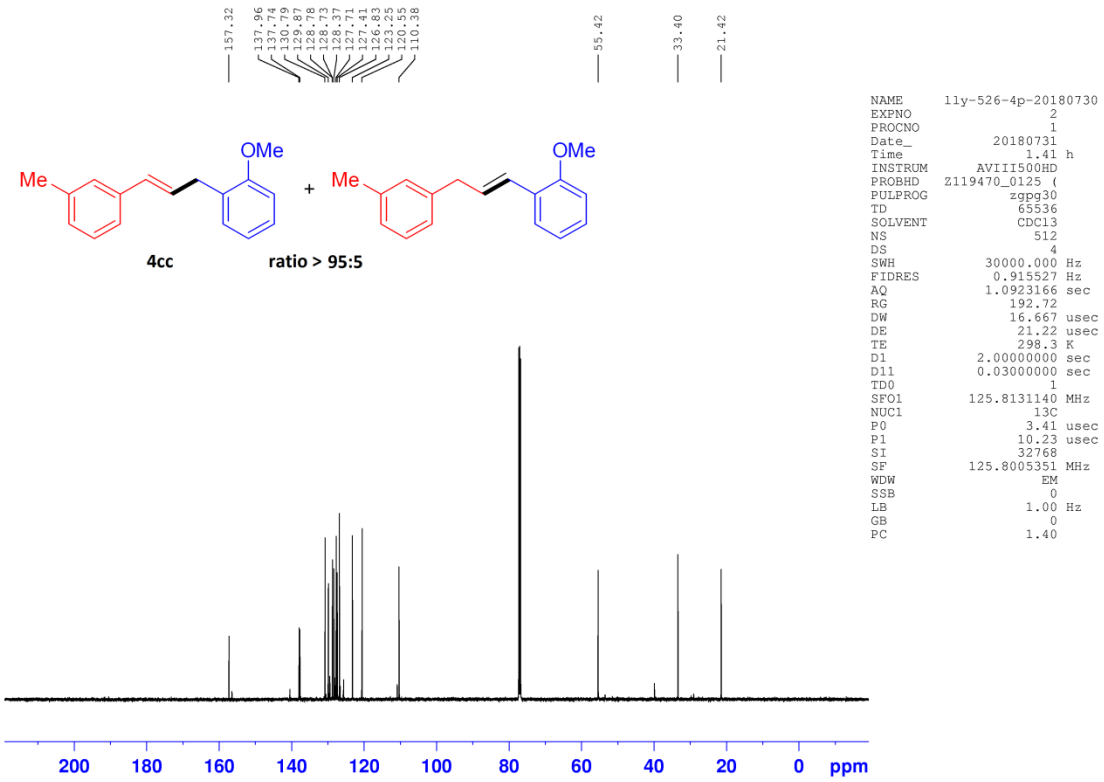
Supplementary Figure 79. ^{1}H NMR spectra for compound **4cb**



Supplementary Figure 80. ^{13}C NMR spectra for compound **4ca**



Supplementary Figure 81. ^{1}H NMR spectra for compound **4cc**

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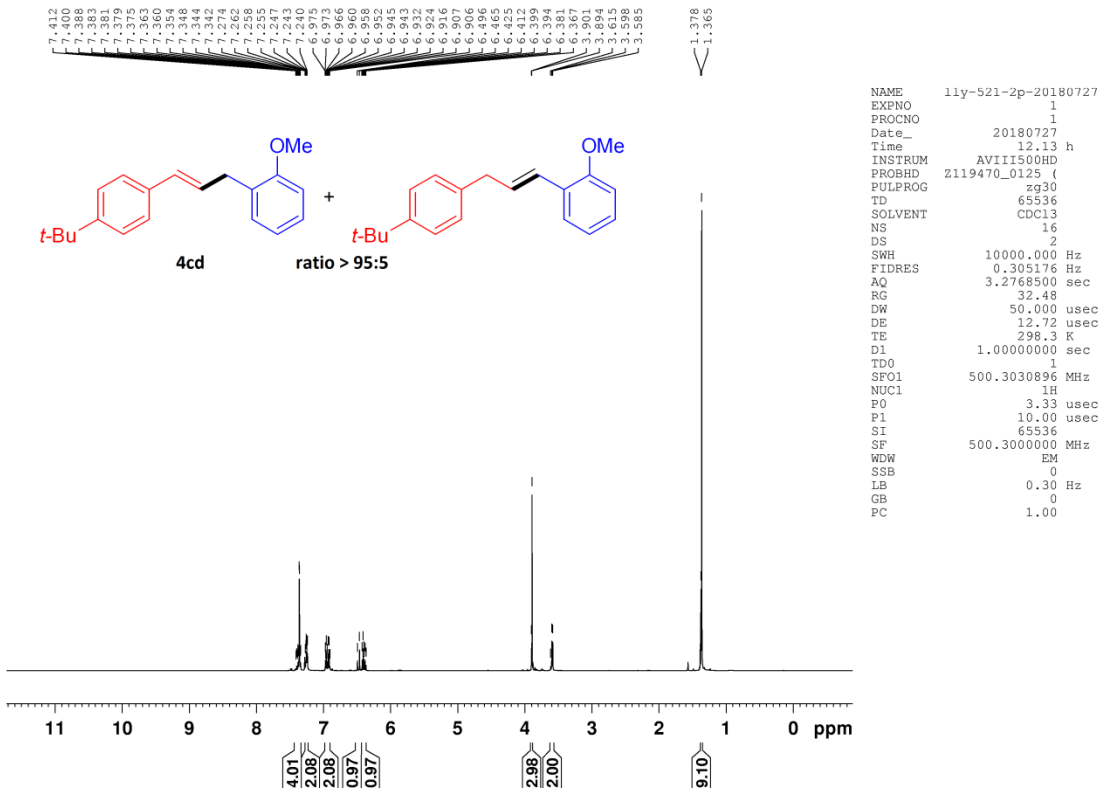
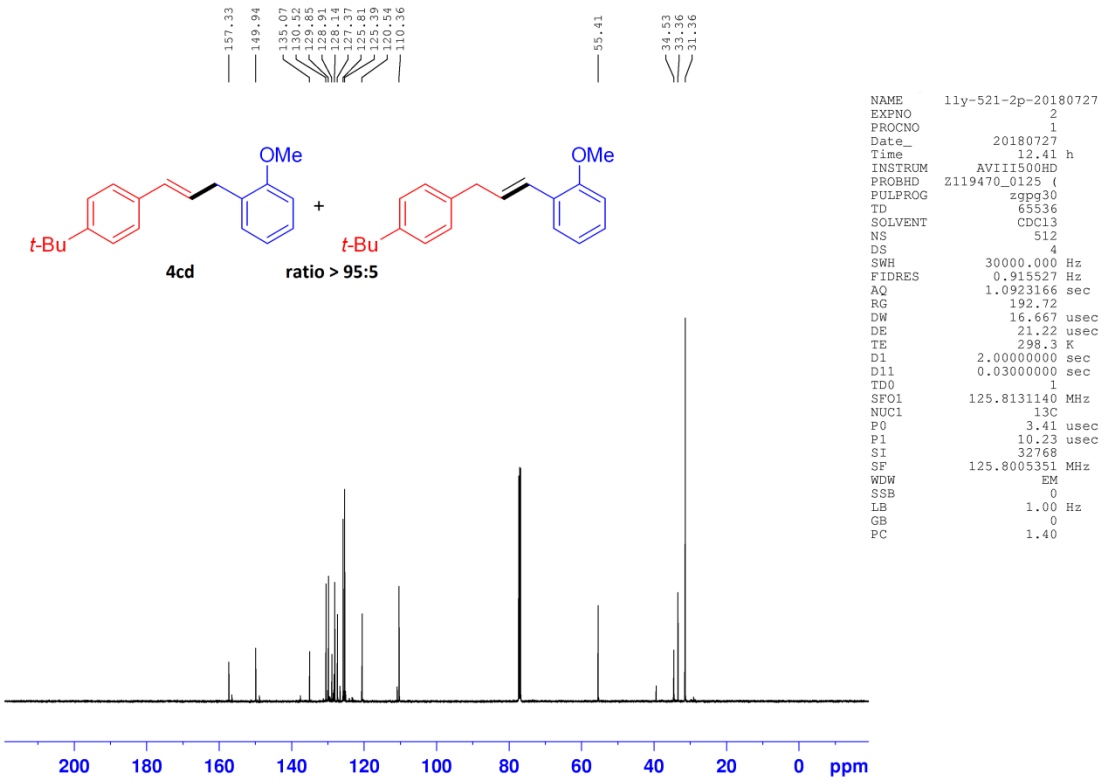
EXPNO                          2
PROCNO                         1
Date_                   20180731
Time                        1.41 h
INSTRUM              AVIII500HD
PROBHD          Z119470_0125 (
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         512
DS                           4
SWH                  30000.000 Hz
FIDRES               0.915527 Hz
AQ                   1.0923166 sec
RG                      192.72
DW                      16.667 usec
DE                      21.22 usec
TE                      298.3 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1
SFO1               125.8131140 MHz
NUC1                        13C
P0                       3.41 usec
P1                      10.23 usec
SI                       32768
SF                 125.8005351 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

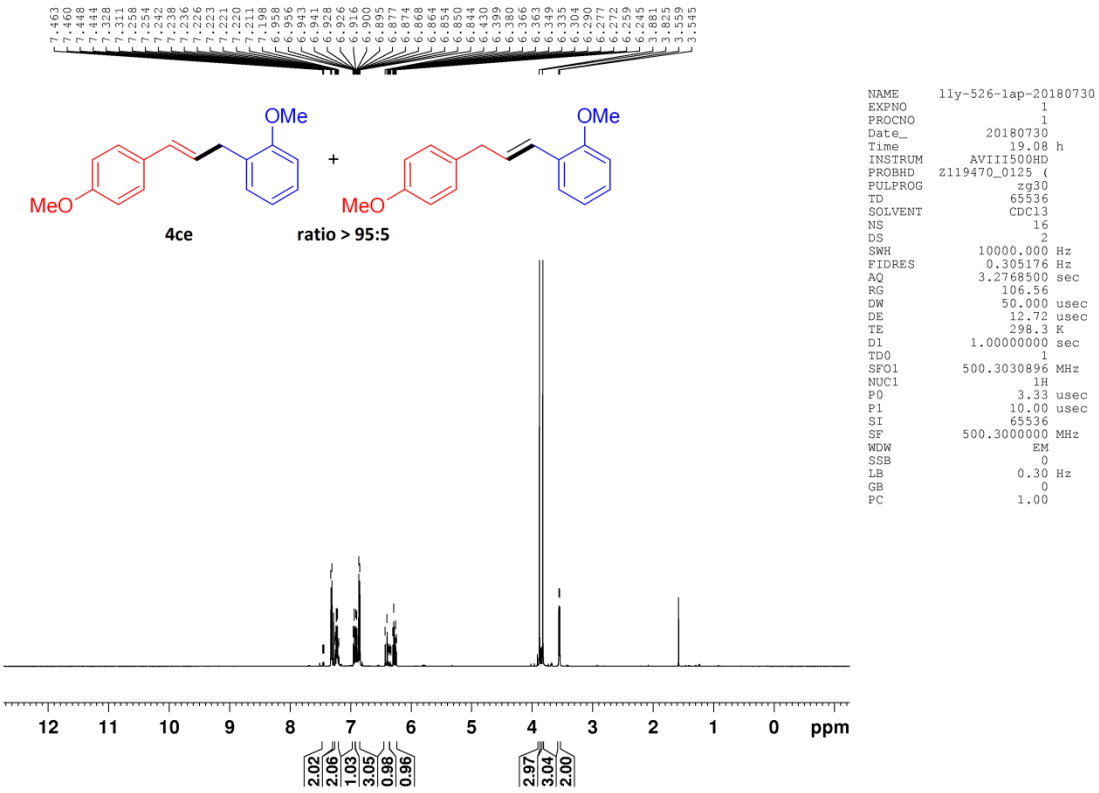
Supplementary Figure 82. ^{13}C NMR spectra for compound **4cc**



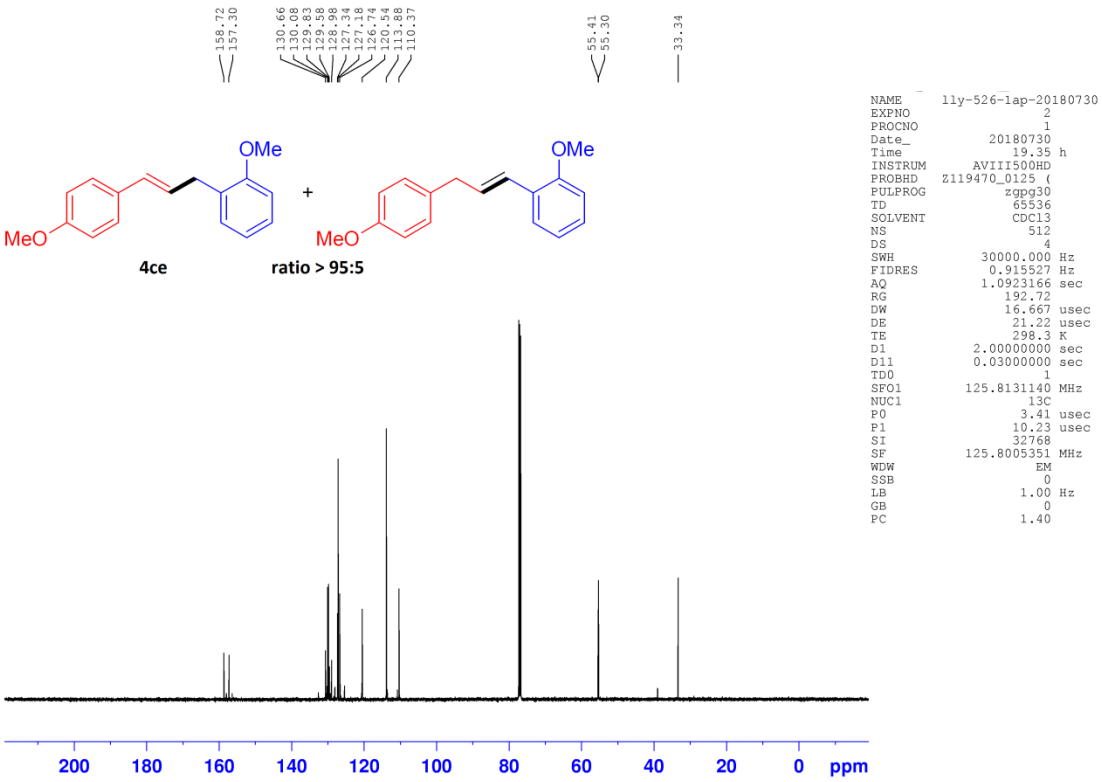
Supplementary Figure 83. ^{1}H NMR spectra for compound **4cd**



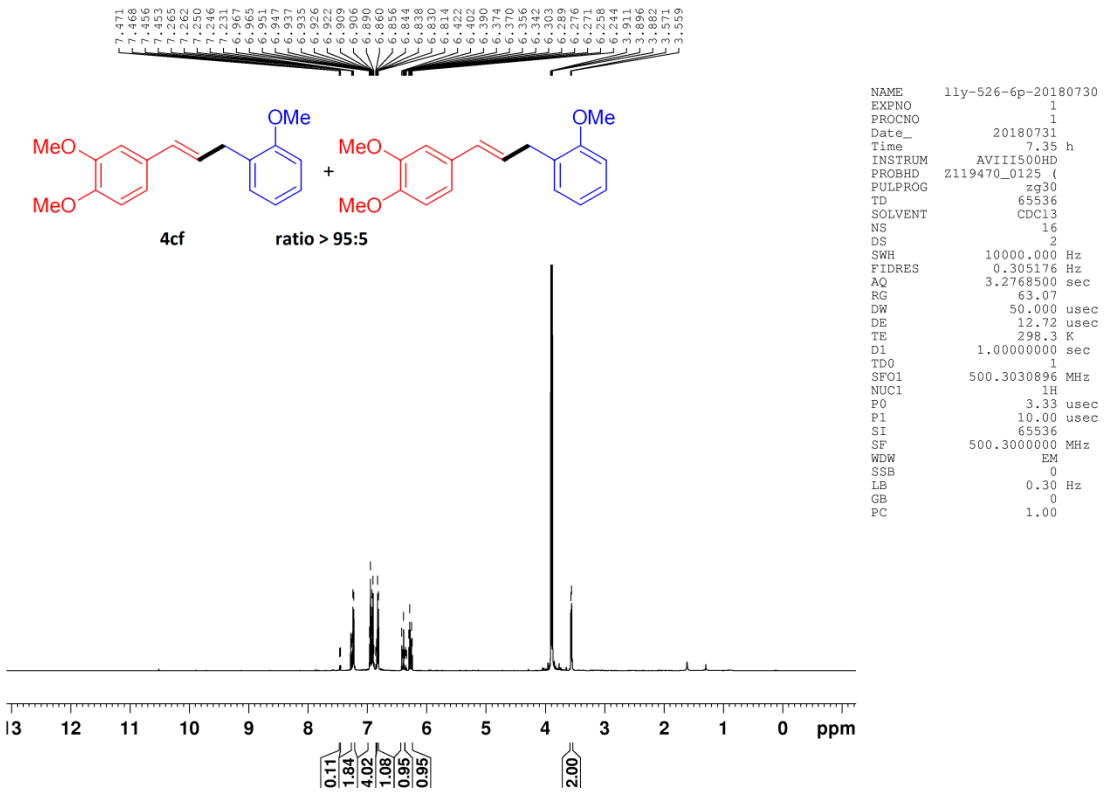
Supplementary Figure 84. ^{13}C NMR spectra for compound **4cd**



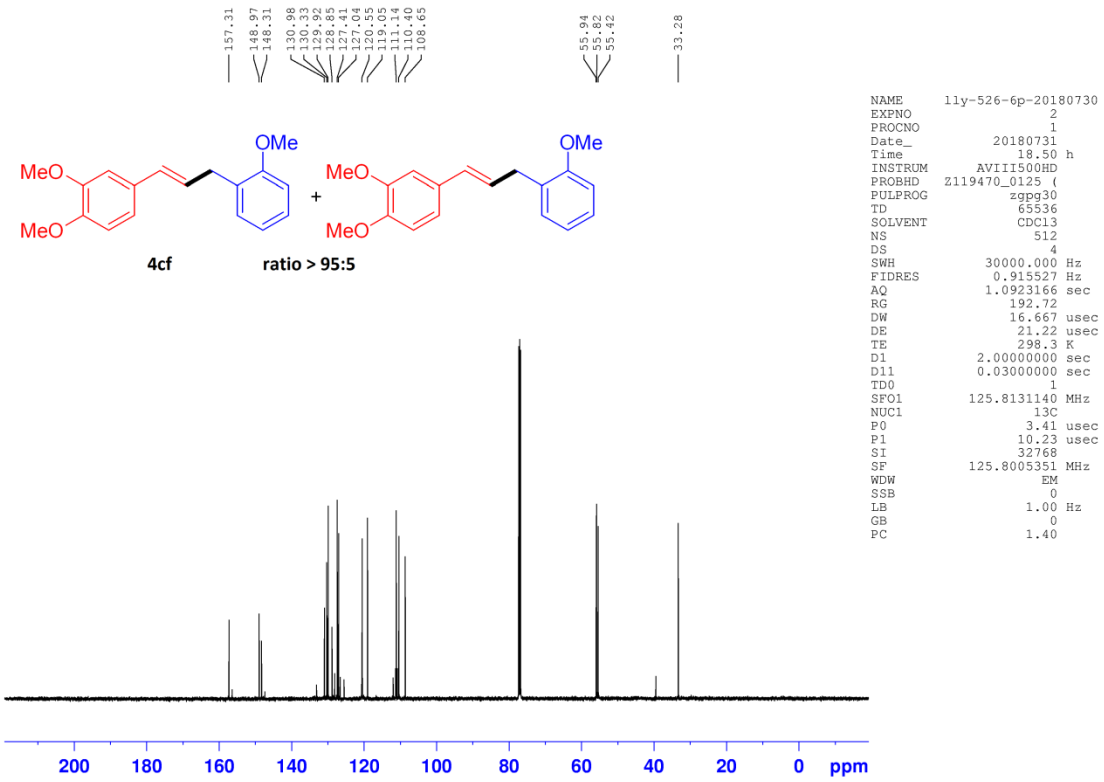
Supplementary Figure 85. ^{1}H NMR spectra for compound **4ce**



Supplementary Figure 86. ^{13}C NMR spectra for compound **4ce**

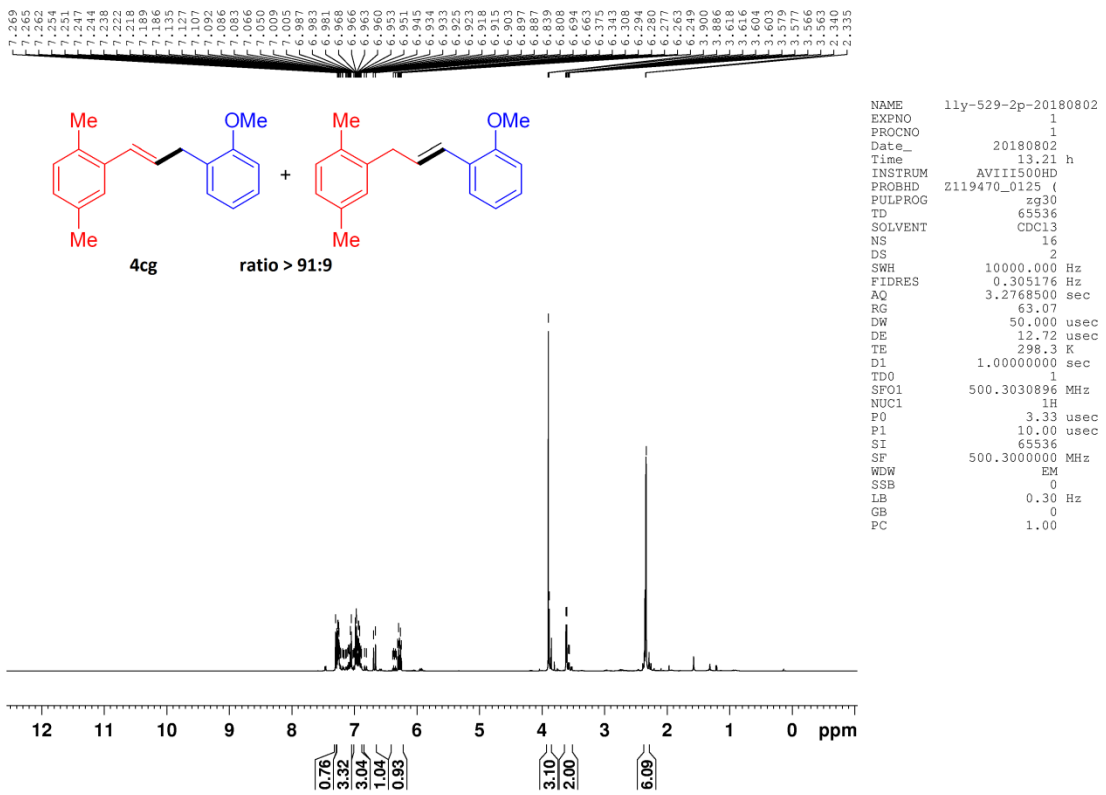


Supplementary Figure 87. ^{1}H NMR spectra for compound **4cf**

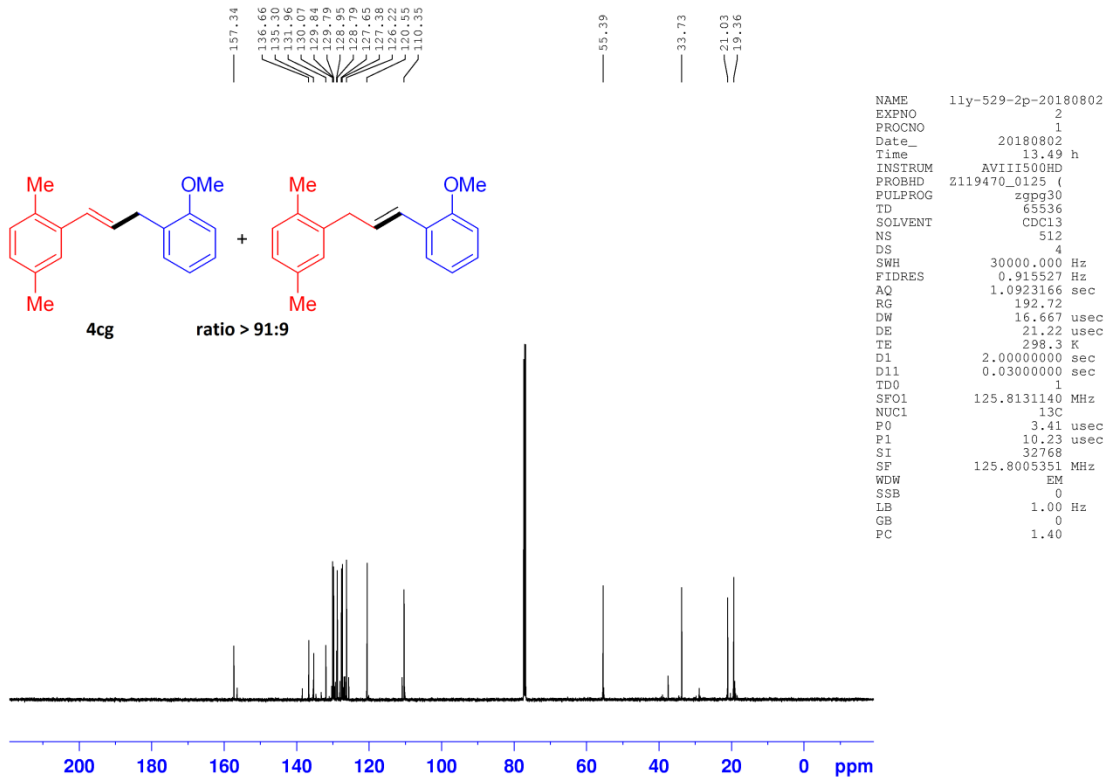


NAME	lly-526-6p-20180730
EXPNO	2
PROCNO	1
Date_	20180731
Time	18.50 h
INSTRUM	AVIII500HD
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

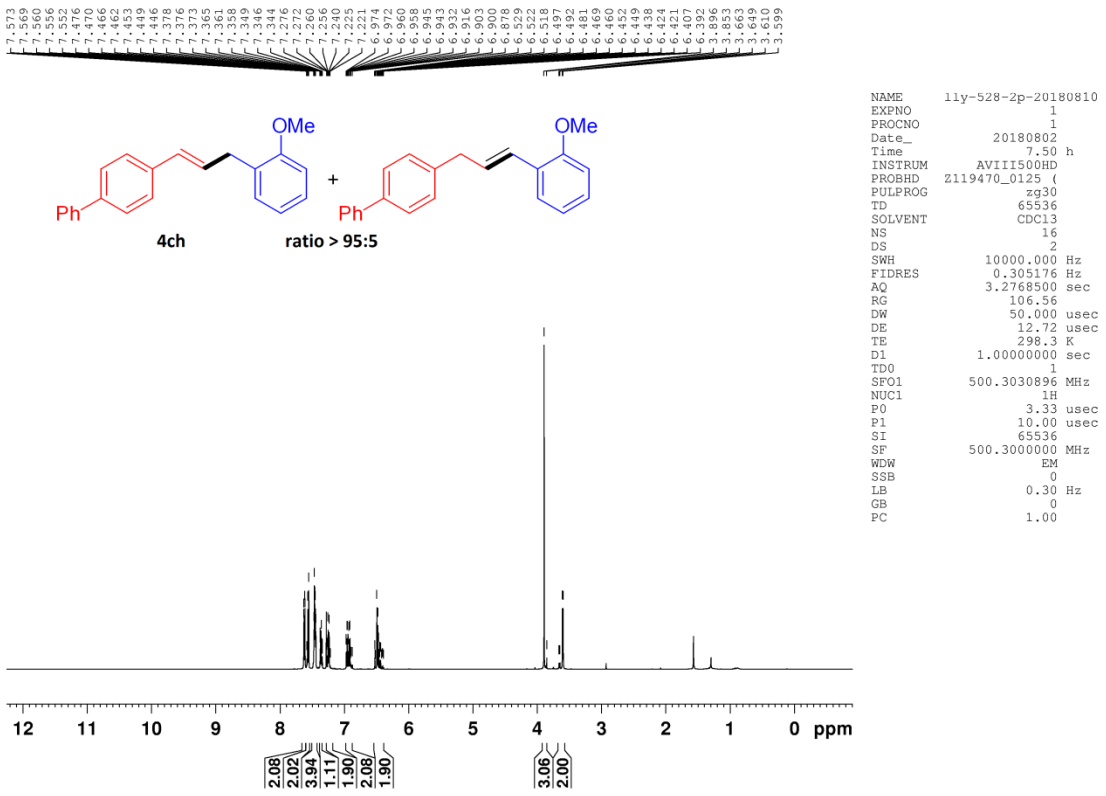
Supplementary Figure 88. ^{13}C NMR spectra for compound **4cf**



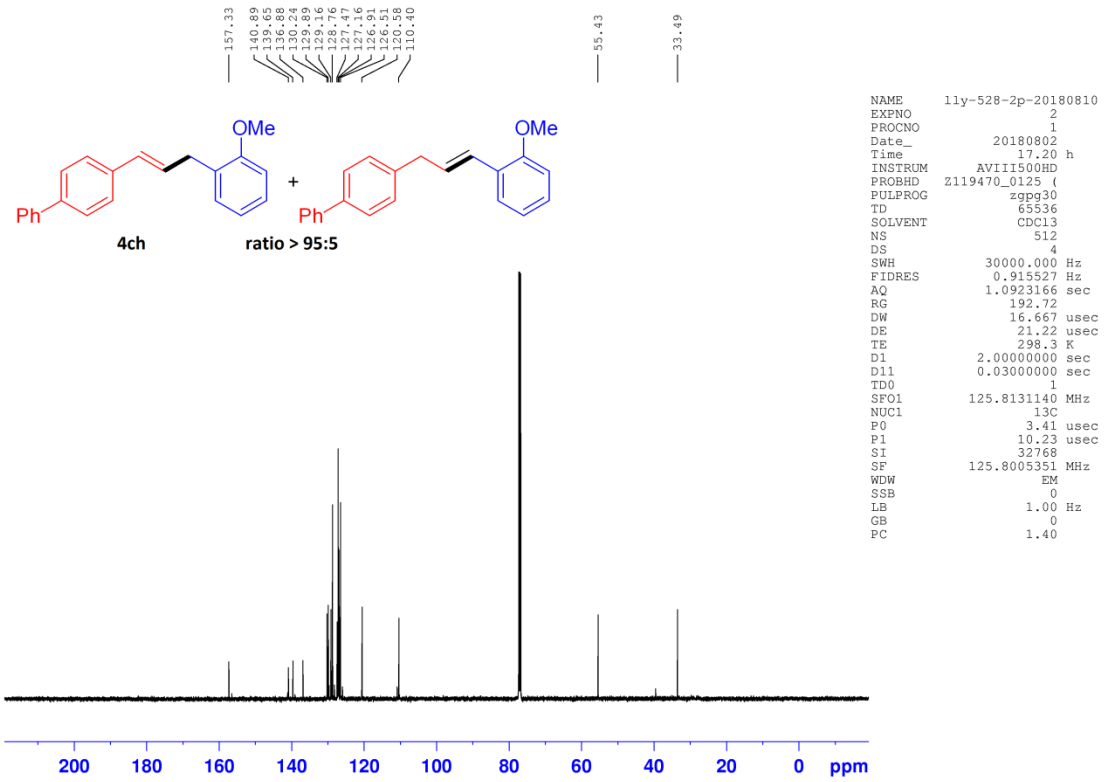
Supplementary Figure 89. ^{1}H NMR spectra for compound **4cg**



Supplementary Figure 90. ^{13}C NMR spectra for compound **4cg**



Supplementary Figure 91. ^{1}H NMR spectra for compound **4ch**

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NAME        lly-528-2p-20180810
EXPNO                         2
PROCNO                        1
Date_                  20180802
Time                      17.20 h
INSTRUM              AVIII500HD
PROBHD          Z119470_0125 (
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         512
DS                           4
SWH                  30000.000 Hz
FIDRES               0.915527 Hz
AQ                   1.0923166 sec
RG                      192.72
DW                      16.667 usec
DE                      21.22 usec
TE                      298.3 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1
SFO1               125.8131140 MHz
NUC1                        13C
P0                       3.41 usec
P1                      10.23 usec
SI                       32768
SF                 125.8005351 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```
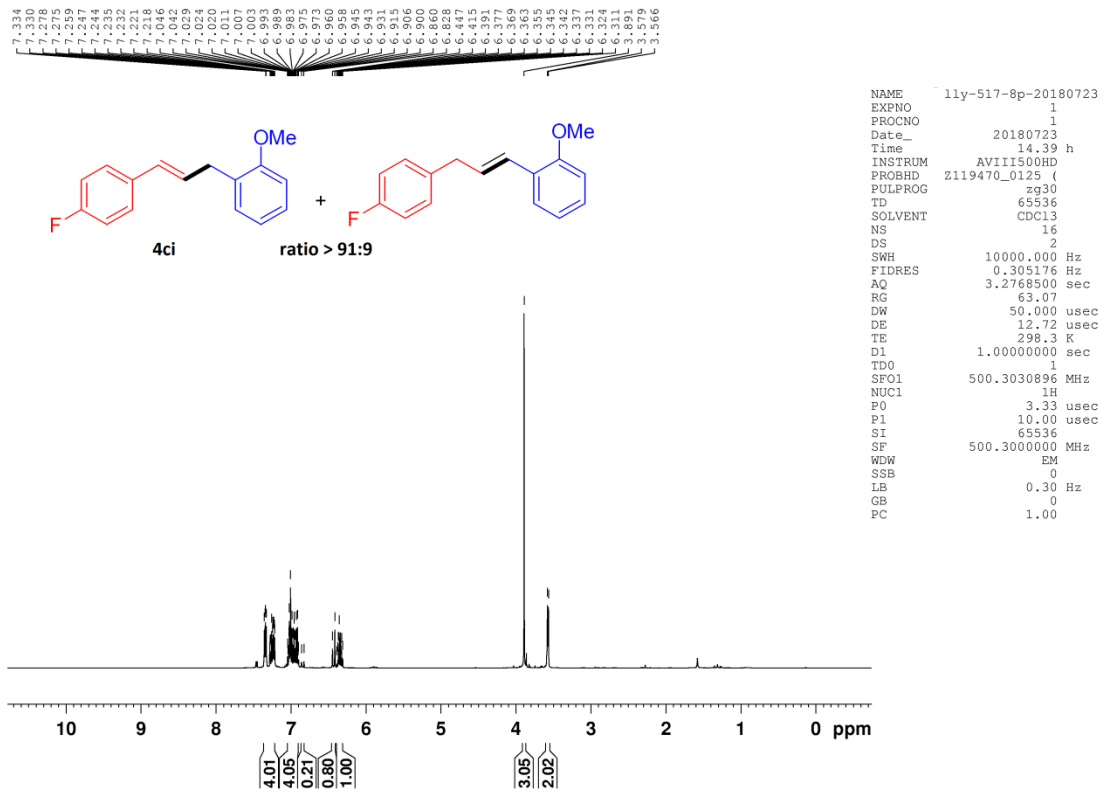
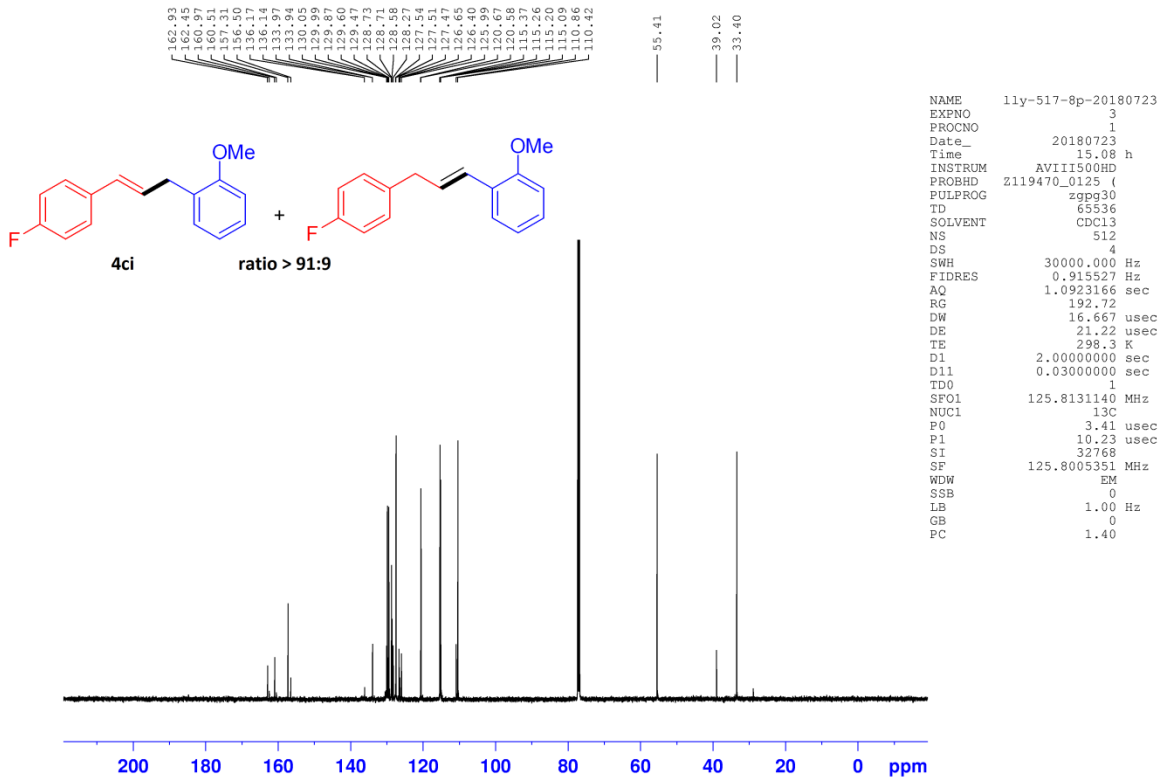

Supplementary Figure 92. ^{13}C NMR spectra for compound **4ch**

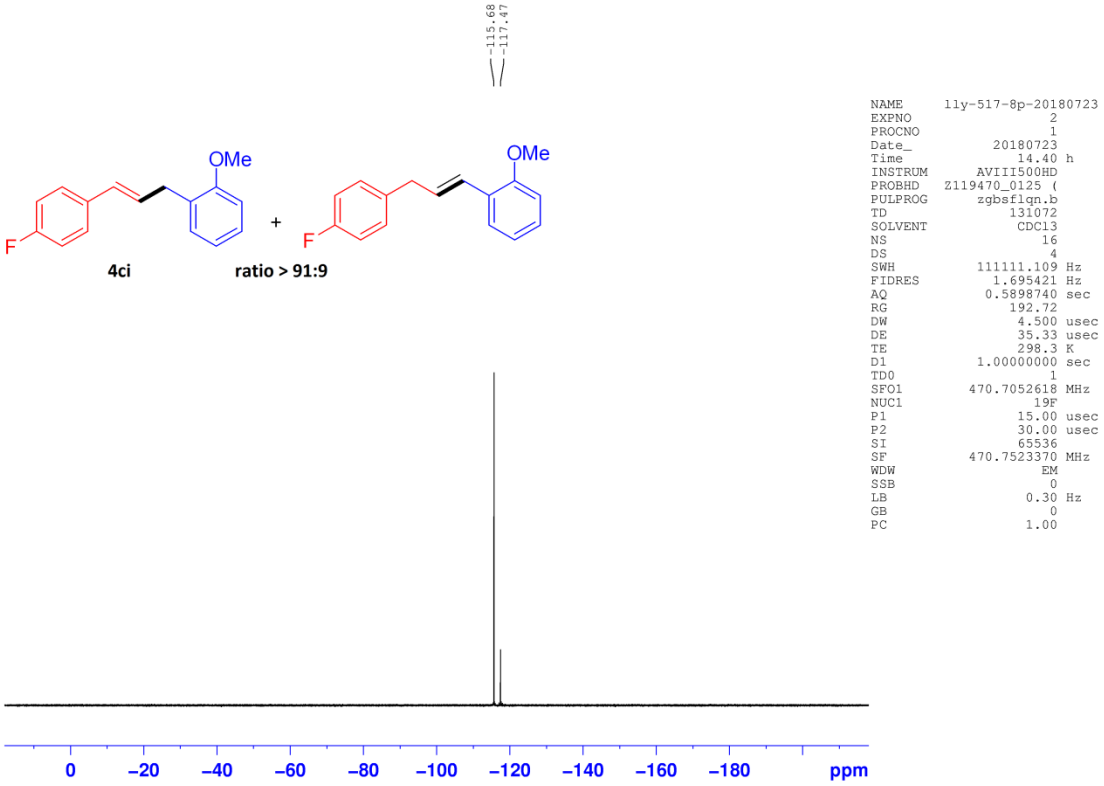


Supplementary Figure 93. ^{1}H NMR spectra for compound **4ci**



NAME	lly-517-8p-20180723
EXPNO	3
PROCNO	1
Date_	20180723
Time	15.08 h
INSTRUM	AVIII500HD
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Supplementary Figure 94. ^{13}C NMR spectra for compound **4ci**

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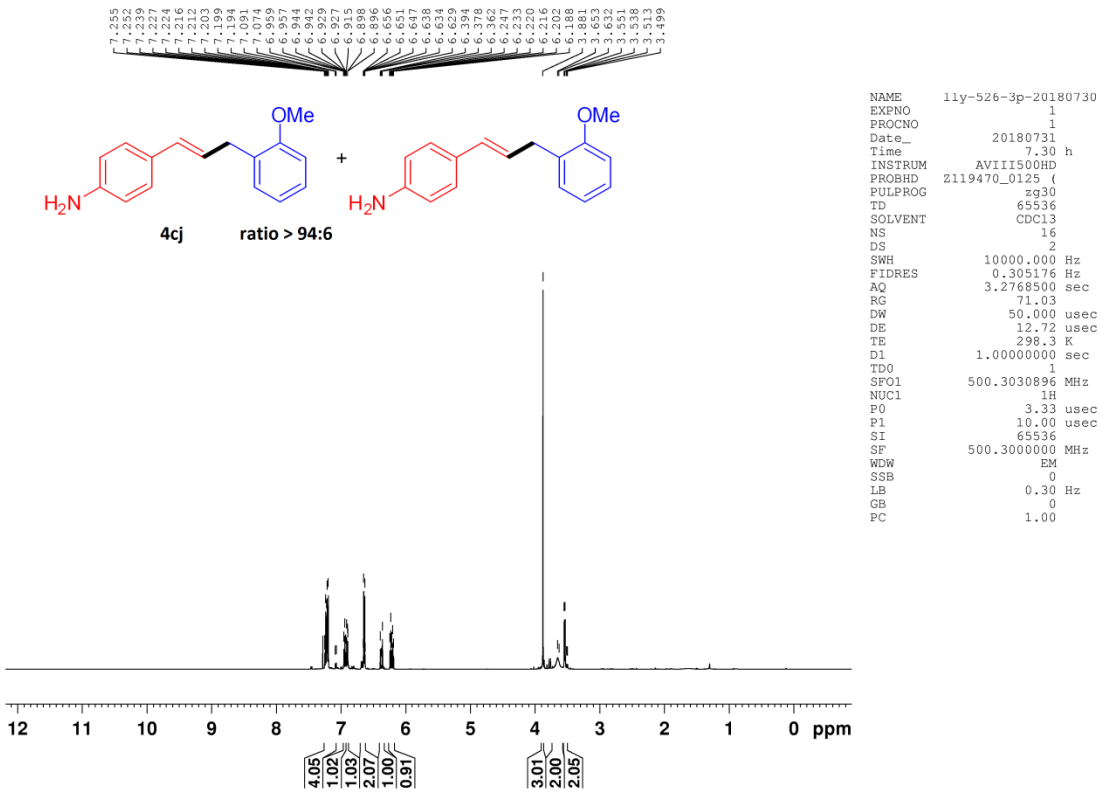
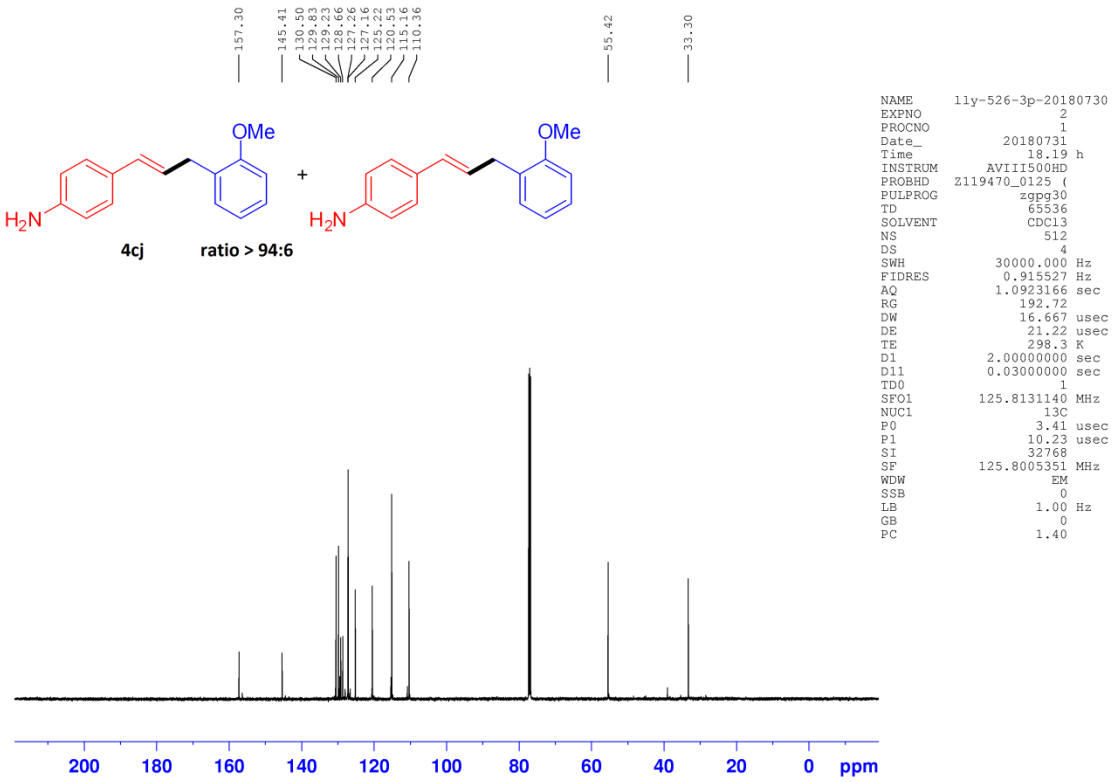
NAME        lly-517-8p-20180723
EXPNO                         2
PROCNO                        1
Date_                  20180723
Time                      14.40 h
INSTRUM              AVIII500HD
PROBHD          Z119470_0125 (
PULPROG              zgbsflqn.b
TD                       131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 111111.109 Hz
FIDRES                1.695421 Hz
AQ                    0.5898740 sec
RG                       192.72
DW                        4.500 usec
DE                       35.33 usec
TE                       298.3 K
D1                  1.00000000 sec
TD0                           1
SFO1                470.7052618 MHz
NUC1                         19F
P1                       15.00 usec
P2                       30.00 usec
SI                       65536
SF                  470.7523370 MHz
WDW                          EM
SSB                           0
LB                        0.30 Hz
GB                            0
PC                        1.00
```

Supplementary Figure 95. ^{19}F NMR spectra for compound **4ci**



Supplementary Figure 96. ^{1}H NMR spectra for compound **4cj**

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NAME        lly-526-3p-20180730
EXPNO                         2
PROCNO                        1
Date_                  20180731
Time                      18.19 h
INSTRUM             AVIII500HD
PROBHD          Z119470_0125 (
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         512
DS                           4
SWH                  30000.000 Hz
FIDRES               0.915527 Hz
AQ                   1.0923166 sec
RG                      192.72
DW                      16.667 usec
DE                      21.22 usec
TE                      298.3 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1
SFO1               125.8131140 MHz
NUC1                        13C
P0                       3.41 usec
P1                      10.23 usec
SI                       32768
SF                 125.8005351 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```
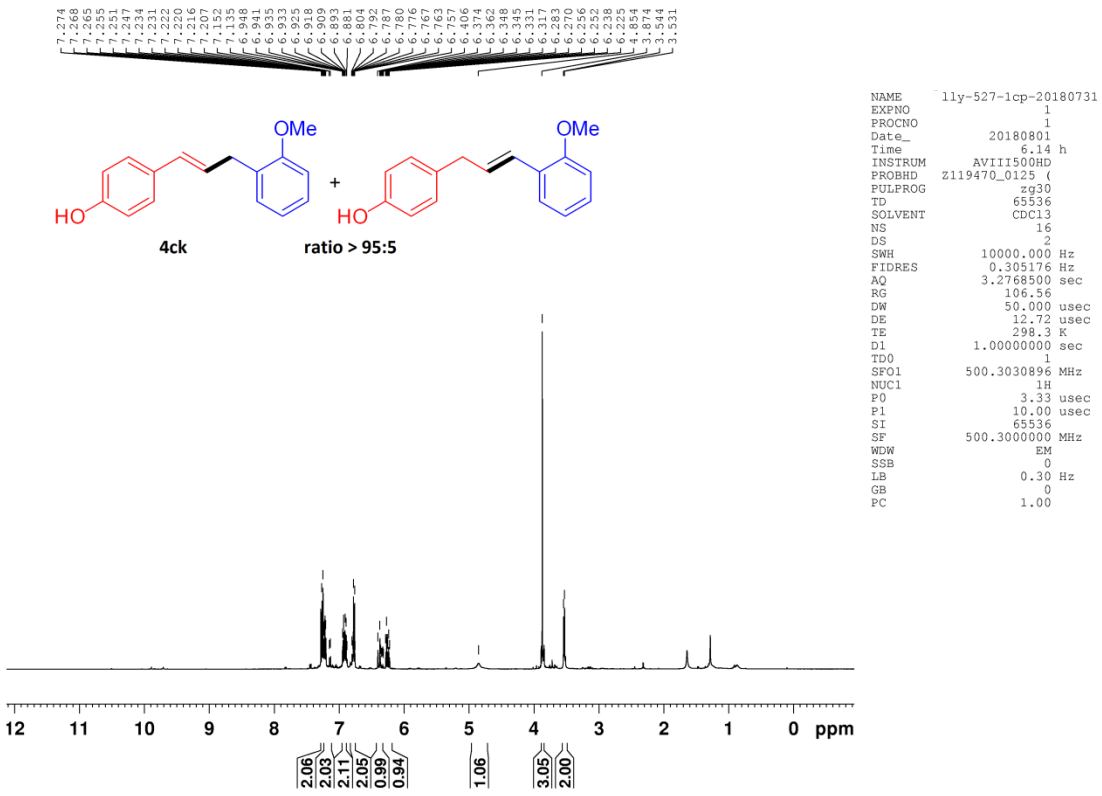
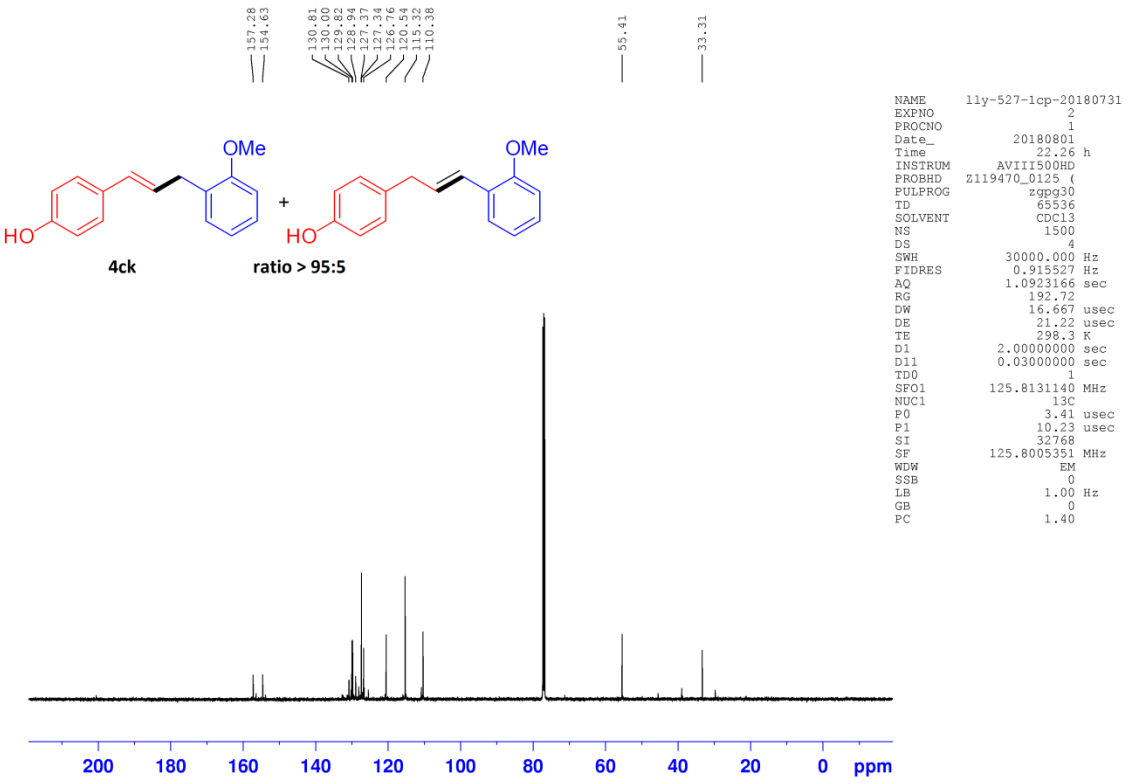

Supplementary Figure 97. ^{13}C NMR spectra for compound **4cj**

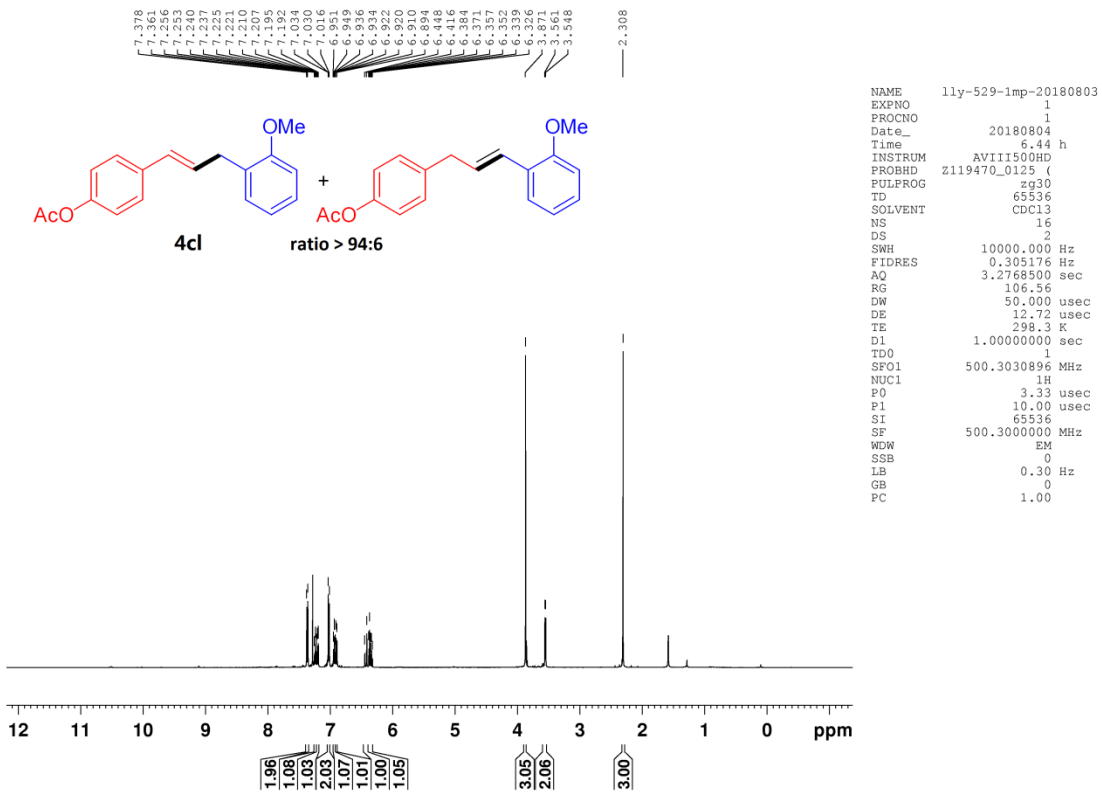


Supplementary Figure 98. ^{1}H NMR spectra for compound **4ck**

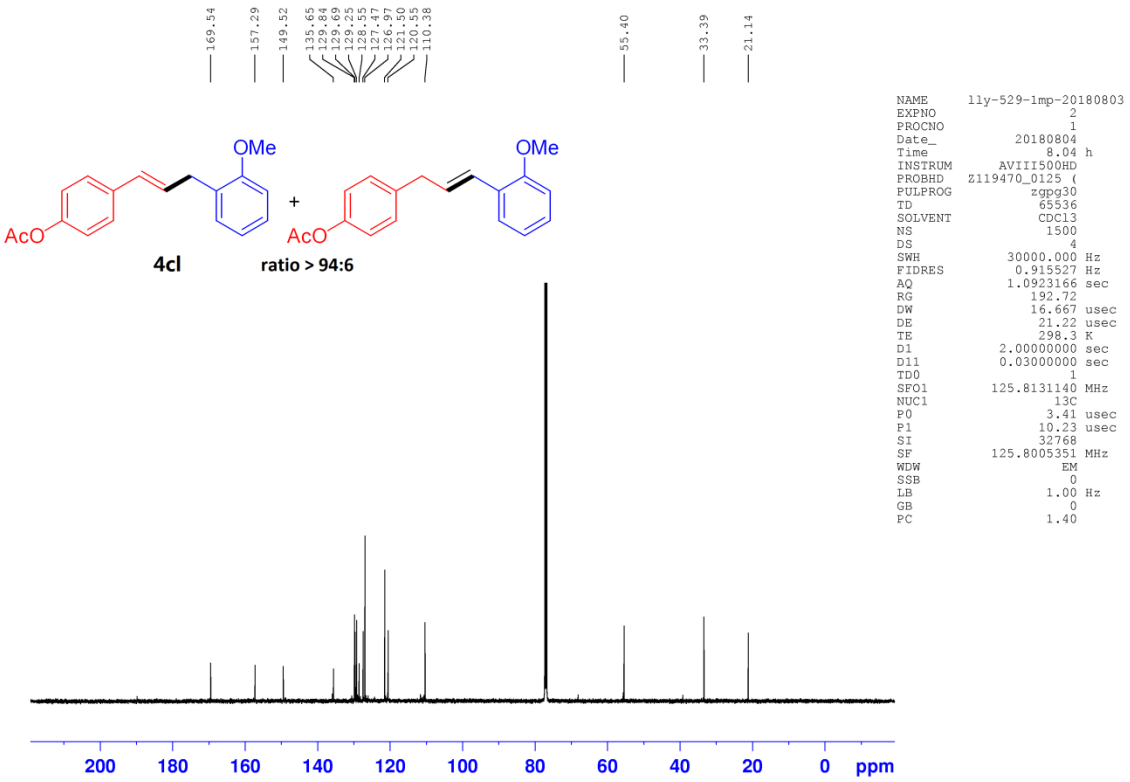


NAME	lly-527-1cp-20180731
EXPNO	2
PROCNO	1
Date_	20180801
Time	22.26 h
INSTRUM	AVIII500HD
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1500
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

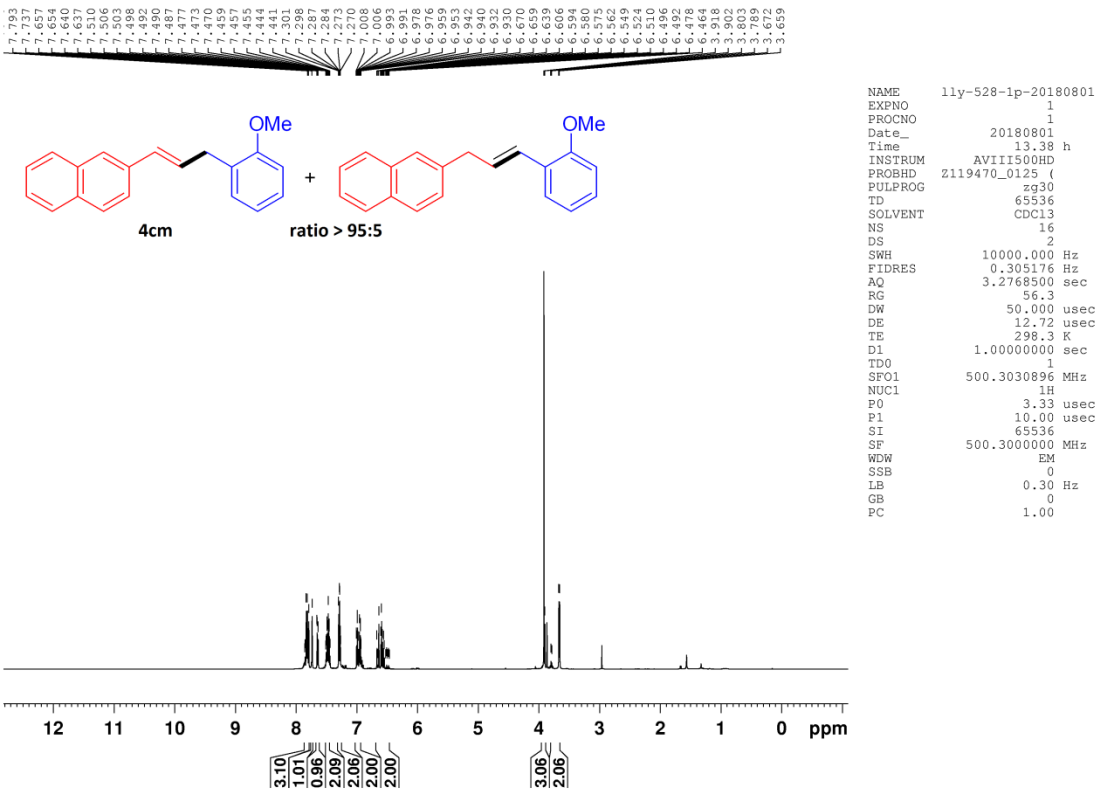
Supplementary Figure 99. ^{13}C NMR spectra for compound **4ck**



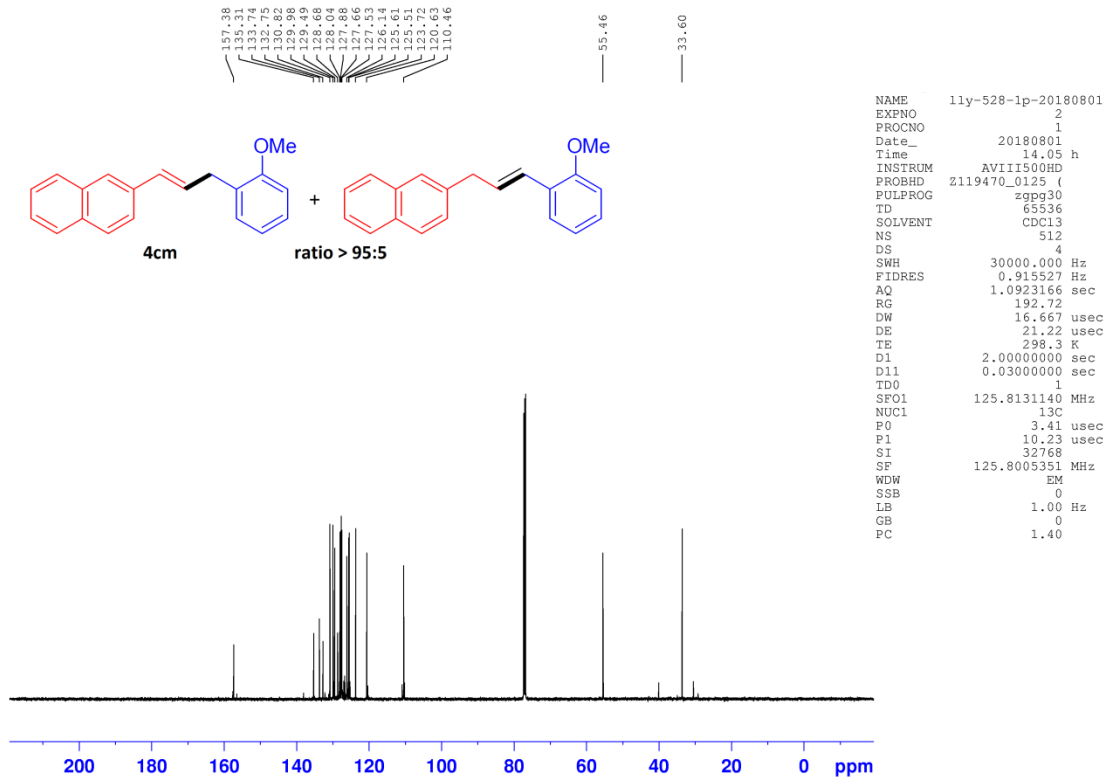
Supplementary Figure 100. ^{1}H NMR spectra for compound **4cl**



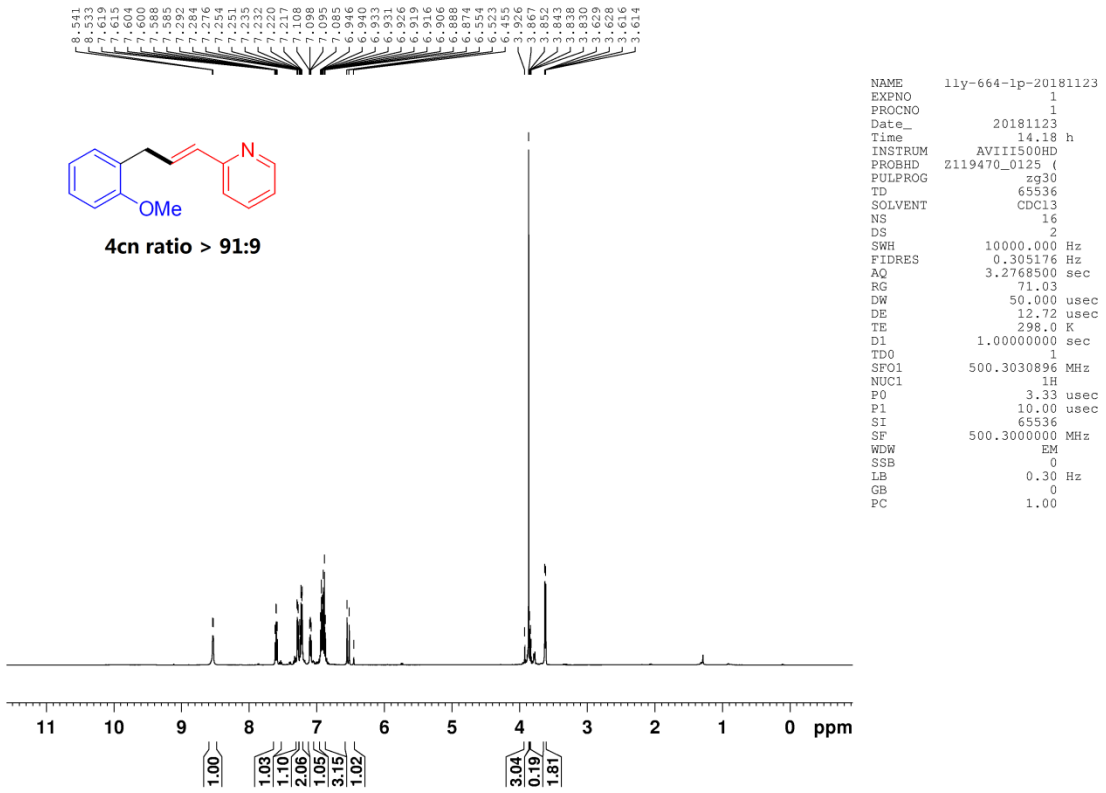
Supplementary Figure 101. ^{13}C NMR spectra for compound **4cl**



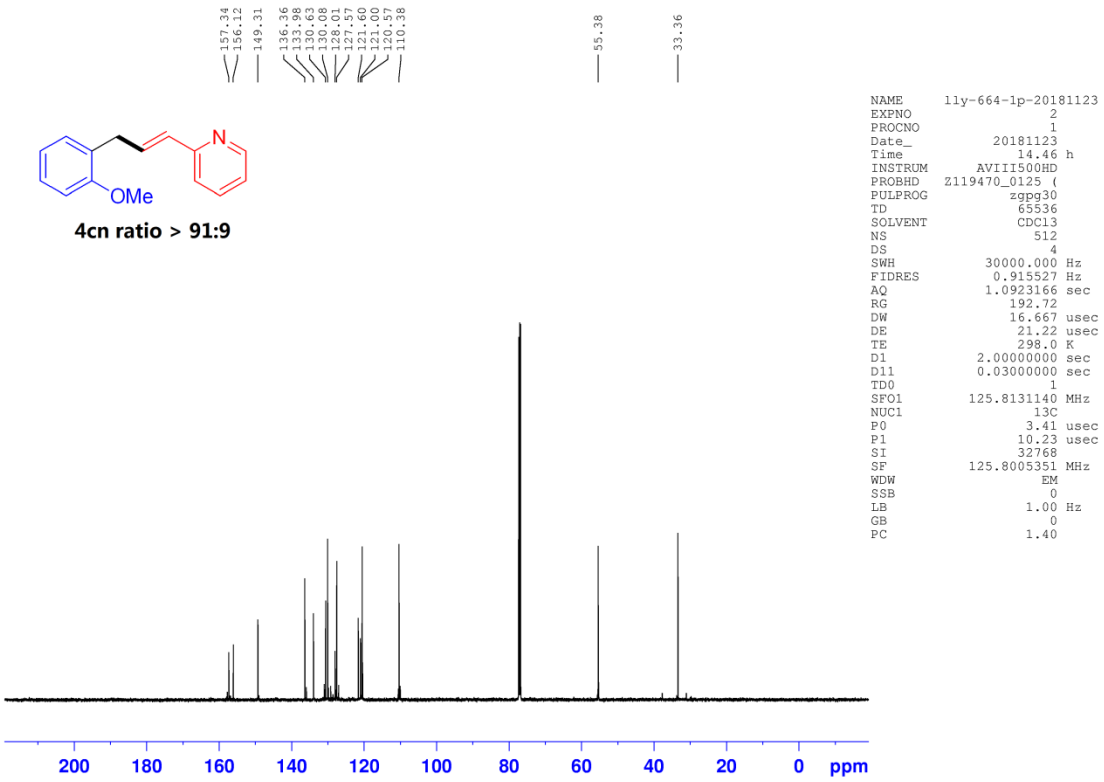
Supplementary Figure 102. ^{1}H NMR spectra for compound **4cm**



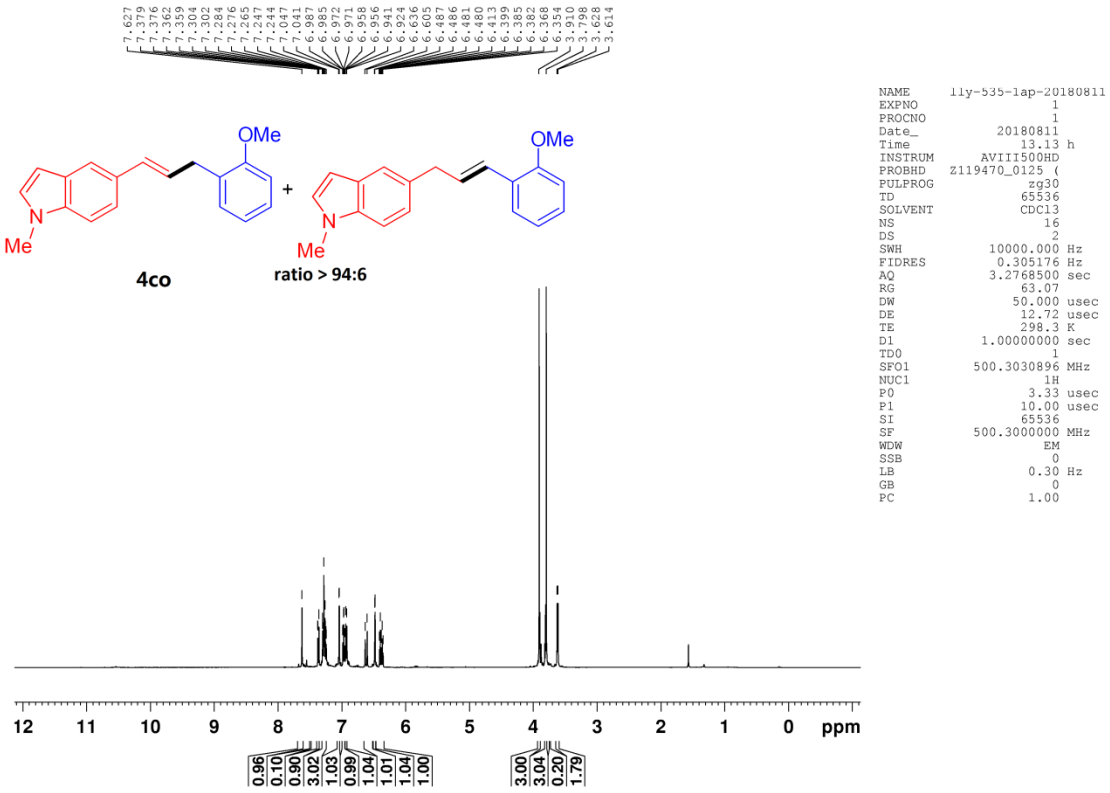
Supplementary Figure 103. ^{13}C NMR spectra for compound **4cm**



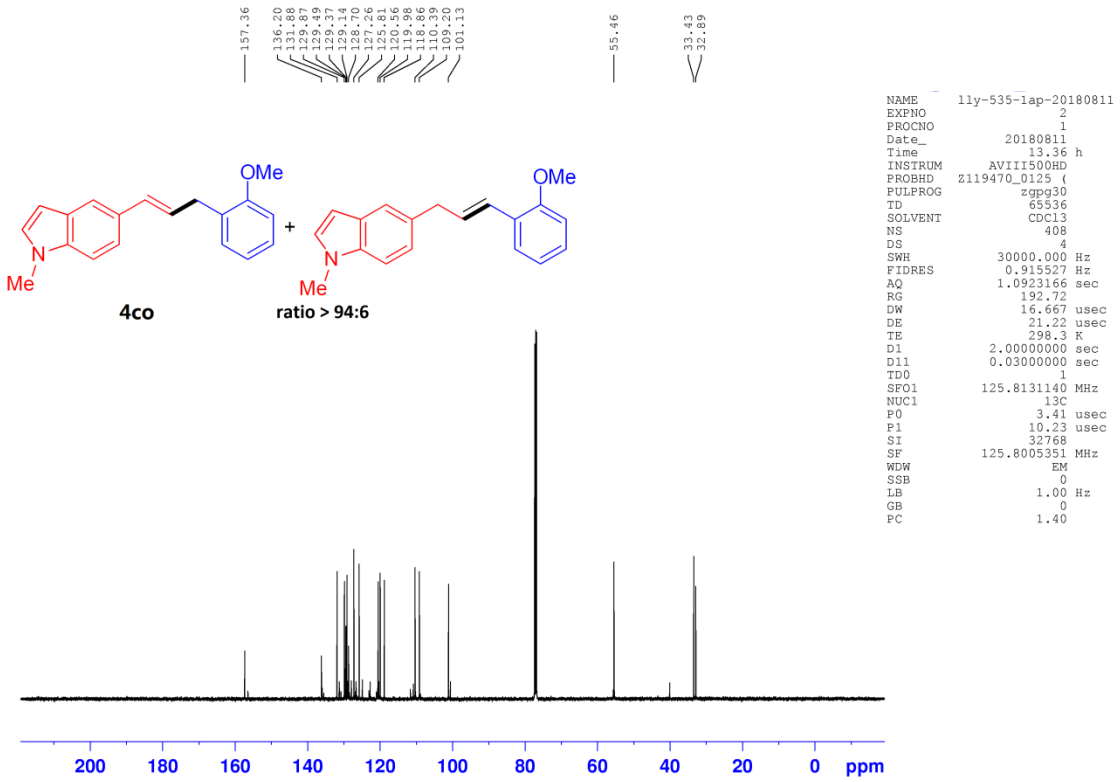
Supplementary Figure 104. ^{1}H NMR spectra for compound **4cn**



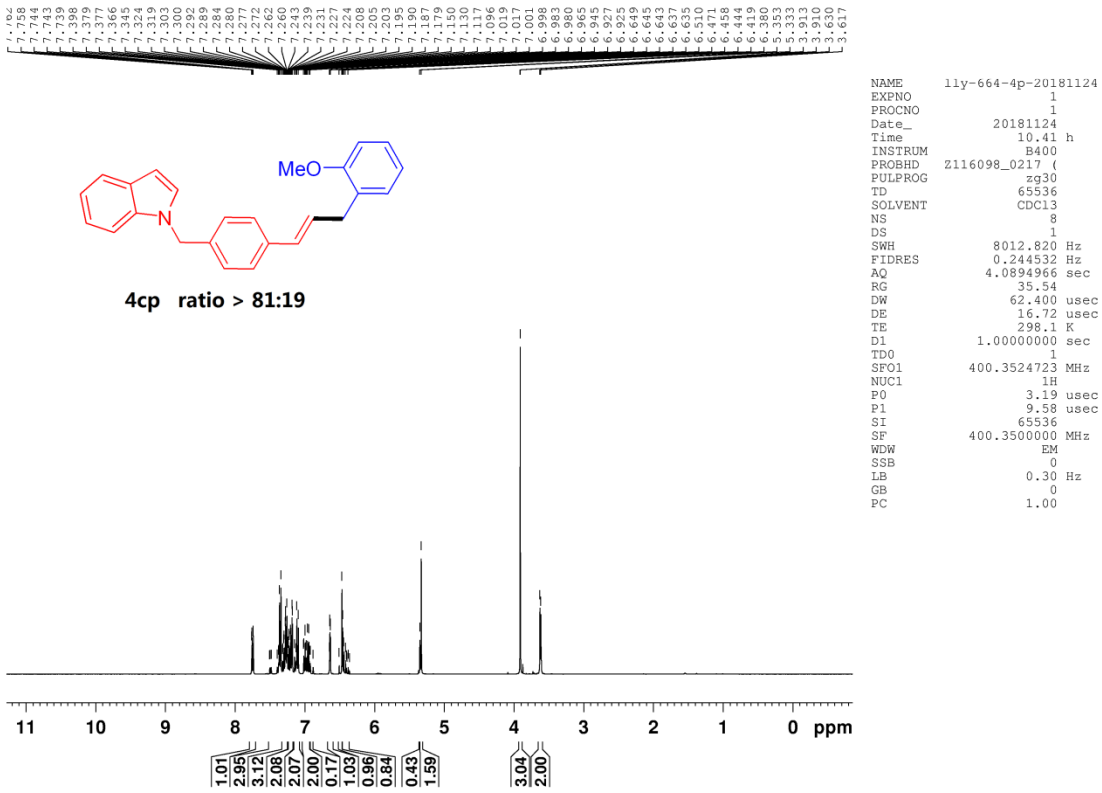
Supplementary Figure 105. ^{13}C NMR spectra for compound **4cn**



Supplementary Figure 106. ^{1}H NMR spectra for compound **4co**

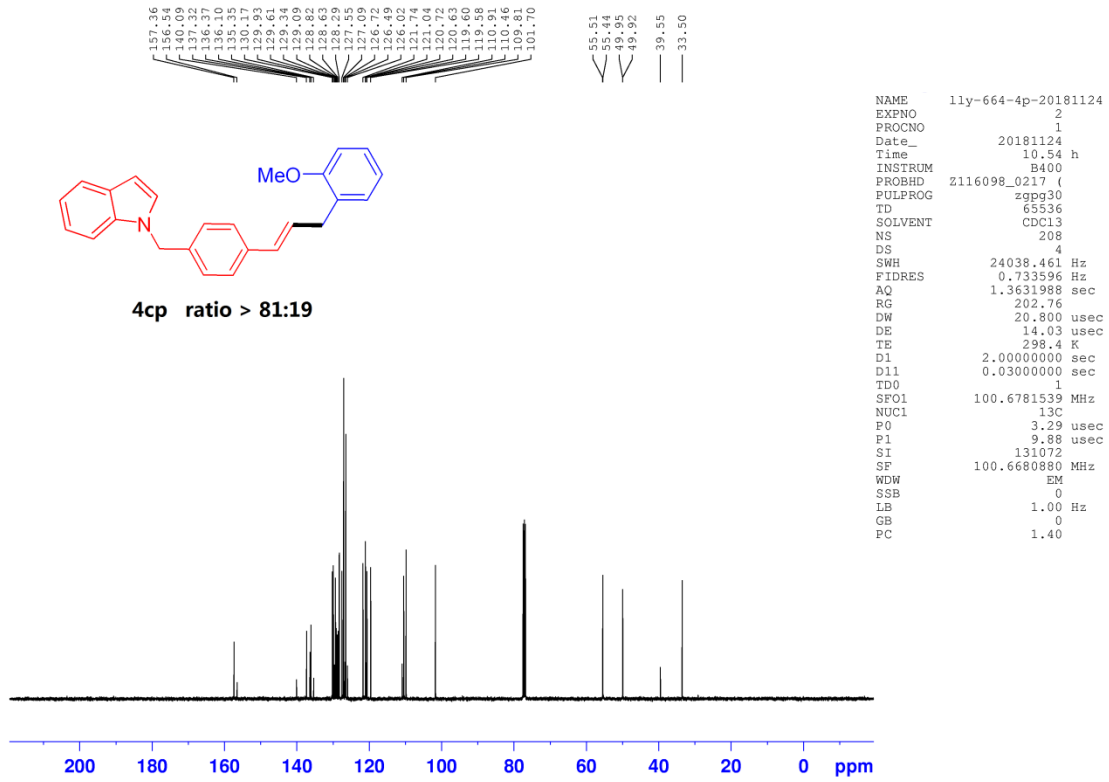


Supplementary Figure 107. ^{13}C NMR spectra for compound **4co**

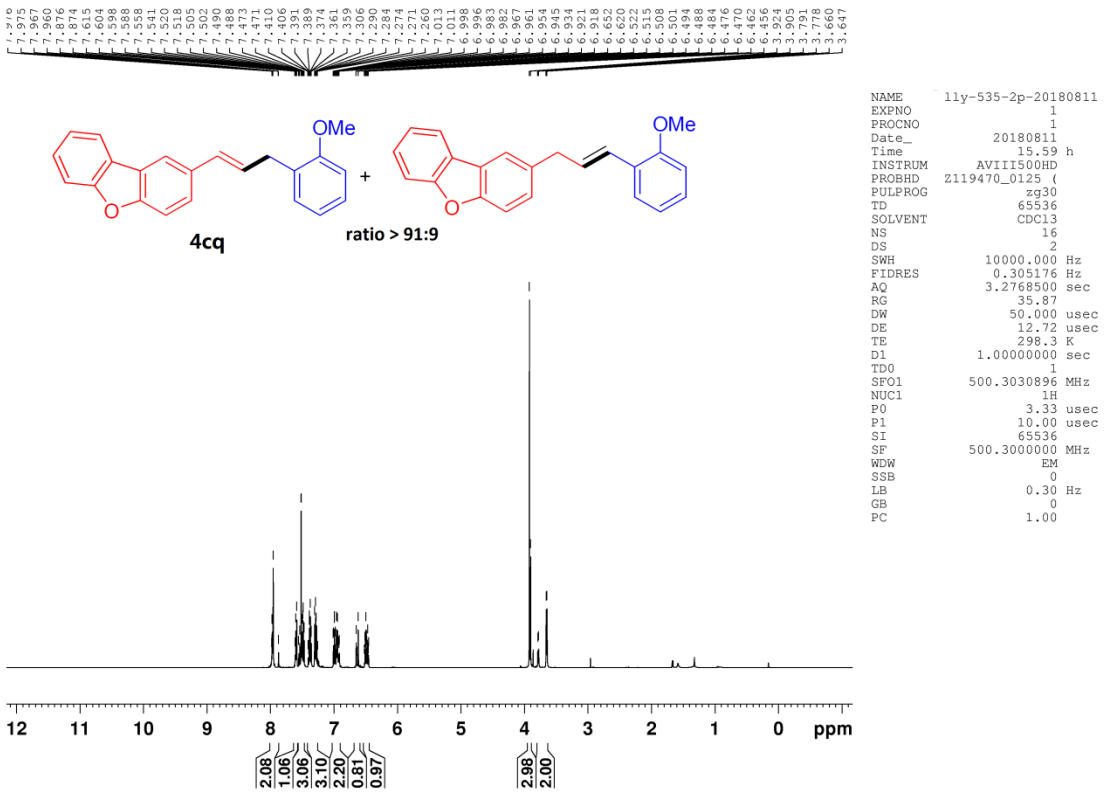


NAME	11y-664-4p-20181124
EXPNO	1
PROCNO	1
Date_	20181124
Time	10.41 h
INSTRUM	B400
PROBHD	Z116098_0217 (
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	1
SWH	8012.820 Hz
FIDRES	0.244532 Hz
AQ	4.0894966 sec
RG	35.54
DW	62.400 usec
DE	16.72 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1
SFO1	400.3524723 MHz
NUC1	1H
P0	3.19 usec
P1	9.58 usec
SI	65536
SF	400.3500000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Supplementary Figure 108. ^{1}H NMR spectra for compound **4cp**

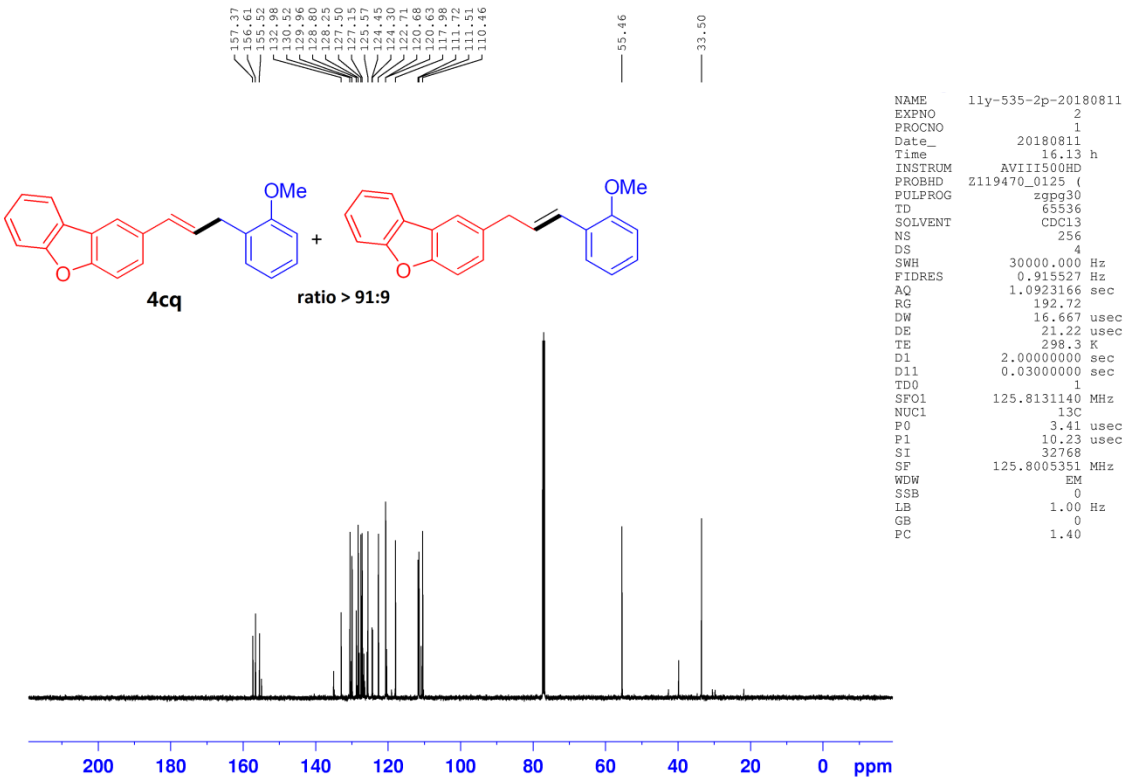


Supplementary Figure 109. ^{13}C NMR spectra for compound **4cp**

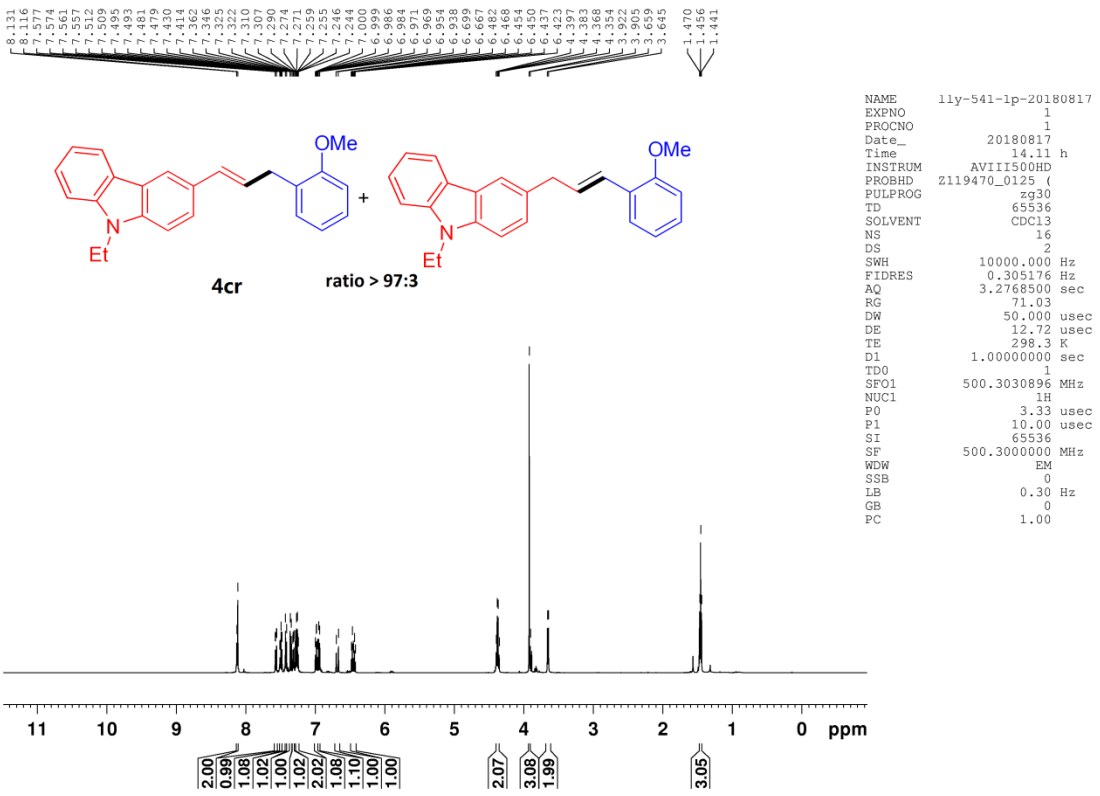


NAME	lly-535-2p-20180811
EXPNO	1
PROCNO	1
Date_	20180811
Time	15.59 h
INSTRUM	AVIII500HD
PROBHD	Z119470_0125 (
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10000.000 Hz
FIDRES	0.305176 Hz
AQ	3.2768500 sec
RG	35.87
DW	50.000 usec
DE	12.72 usec
TE	298.3 K
D1	1.00000000 sec
TD0	1
SFO1	500.3030896 MHz
NUC1	1H
P0	3.33 usec
P1	10.00 usec
SI	65536
SF	500.3000000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

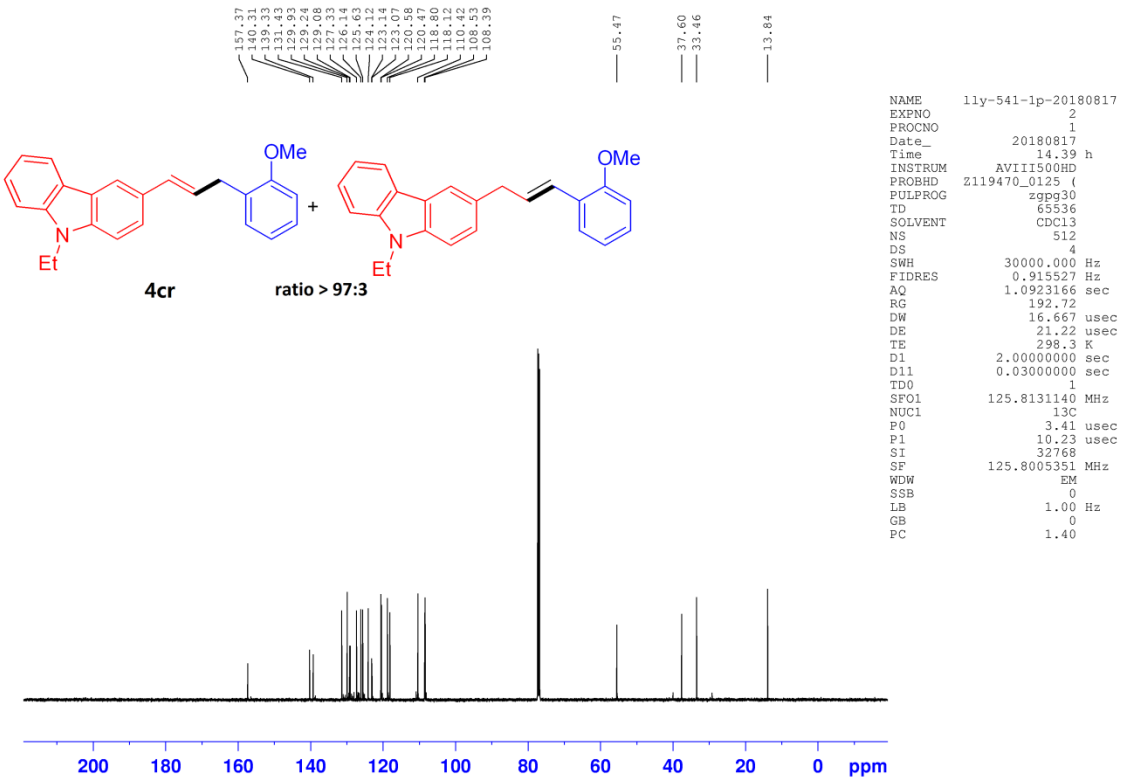
Supplementary Figure 110. ^{1}H NMR spectra for compound **4cq**



Supplementary Figure 111. ^{13}C NMR spectra for compound **4cq**

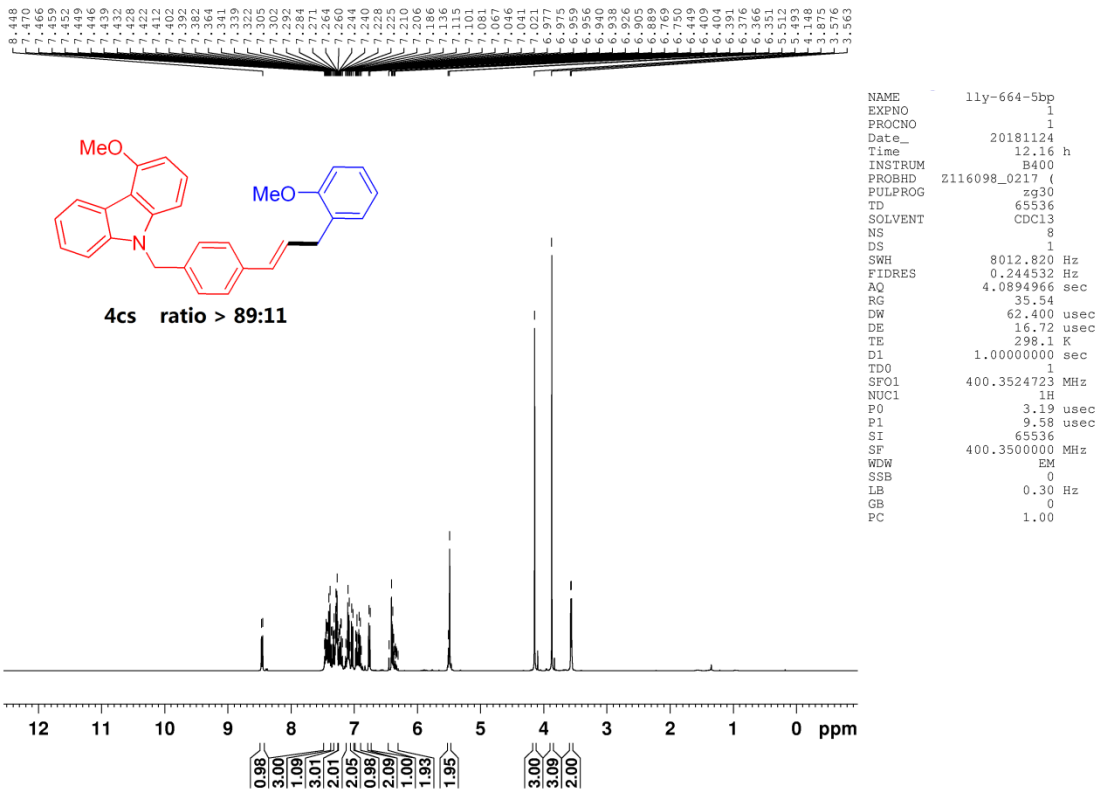


Supplementary Figure 112. ^{1}H NMR spectra for compound **4cr**



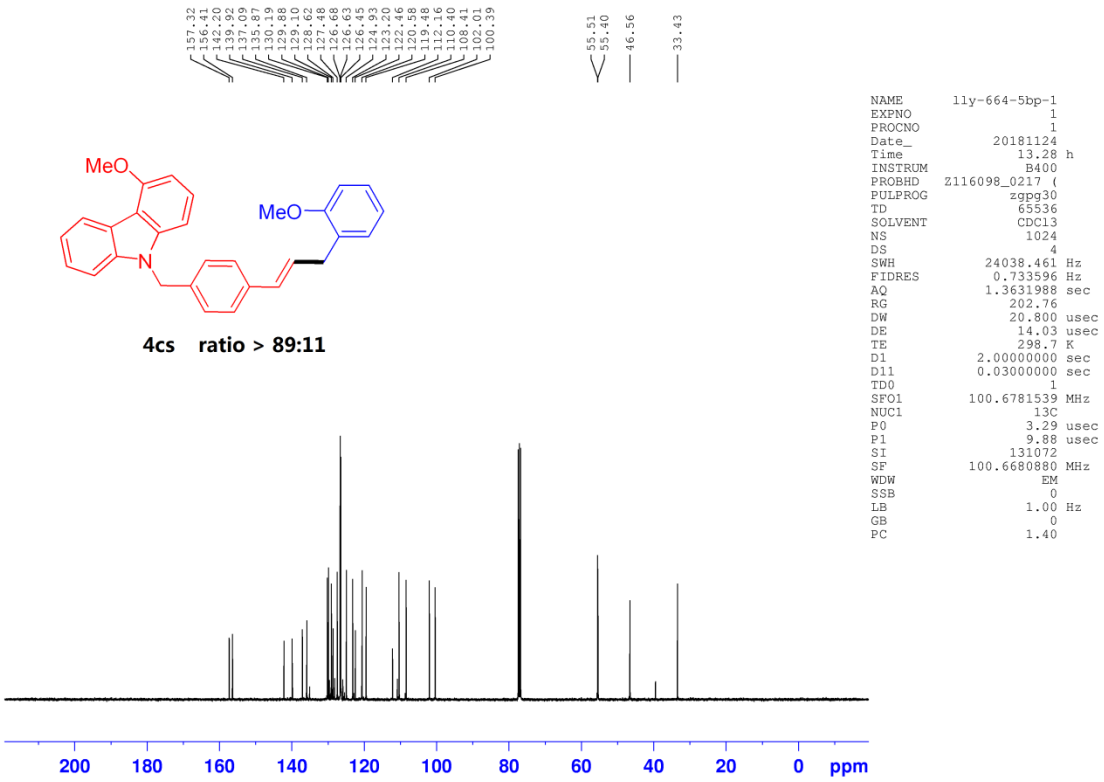
NAME	lly-541-1p-20180817
EXPNO	2
PROCNO	1
Date_	20180817
Time	14.39 h
INSTRUM	AVIII500HD
PROBHD	Z119470_0125 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	30000.000 Hz
FIDRES	0.915527 Hz
AQ	1.0923166 sec
RG	192.72
DW	16.667 usec
DE	21.22 usec
TE	298.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	125.8131140 MHz
NUC1	13C
P0	3.41 usec
P1	10.23 usec
SI	32768
SF	125.8005351 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Supplementary Figure 113. ^{1}H NMR spectra for compound **4cr**



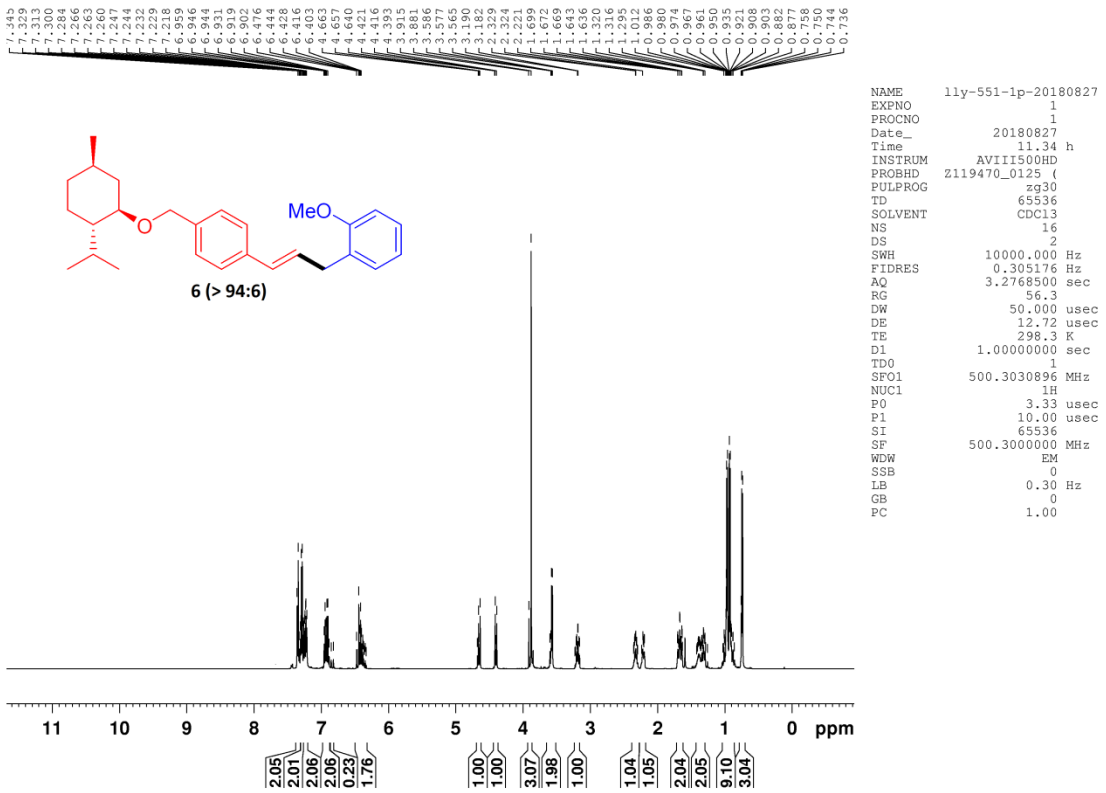
NAME	lly-664-5bp
EXPNO	1
PROCNO	1
Date_	20181124
Time	12.16 h
INSTRUM	B400
PROBHD	Z116098_0217 (
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	1
SWH	8012.820 Hz
FIDRES	0.244532 Hz
AQ	4.0894966 sec
RG	35.54
DW	62.400 usec
DE	16.72 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1
SFO1	400.3524723 MHz
NUC1	1H
P0	3.19 usec
P1	9.58 usec
SI	65536
SF	400.3500000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Supplementary Figure 114. ^{1}H NMR spectra for compound **4cs**

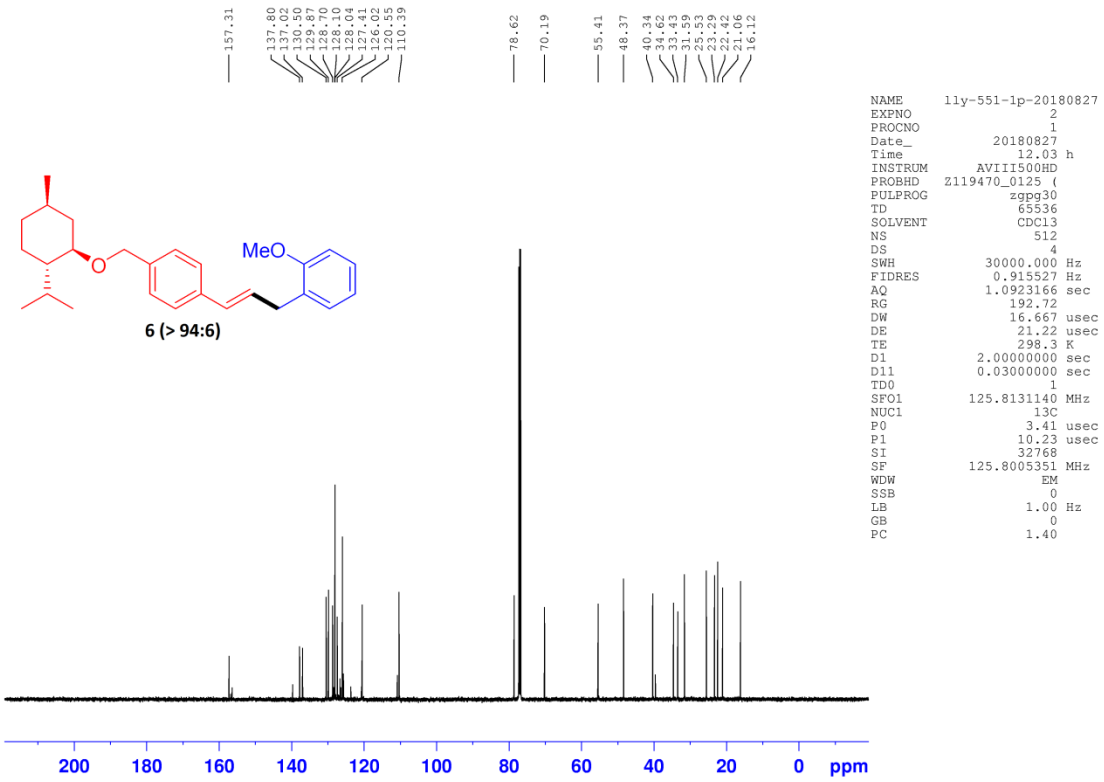


NAME	lly-664-5bp-1
EXPNO	1
PROCNO	1
Date_	20181124
Time	13.28 h
INSTRUM	B400
PROBHD	Z116098_0217 (
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.733596 Hz
AQ	1.3631988 sec
RG	202.76
DW	20.800 usec
DE	14.03 usec
TE	298.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
SFO1	100.6781539 MHz
NUC1	13C
P0	3.29 usec
P1	9.88 usec
SI	131072
SF	100.6680880 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

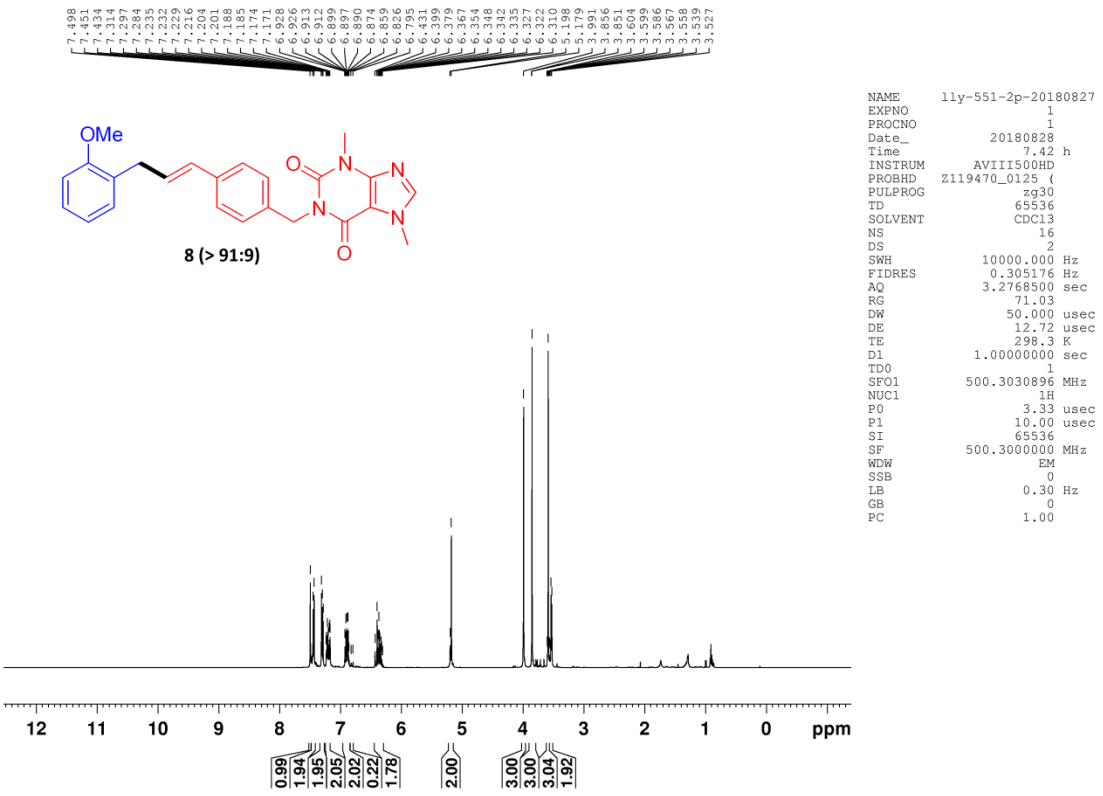
Supplementary Figure 115. ^{13}C NMR spectra for compound **4cs**



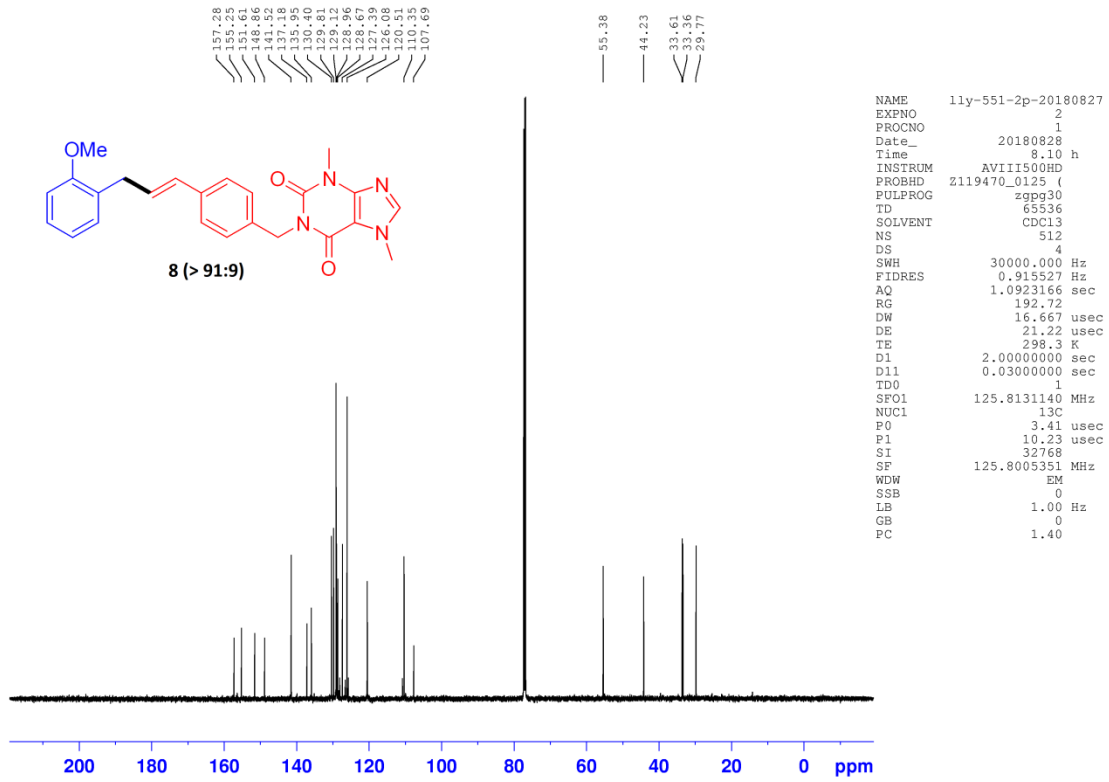
Supplementary Figure 116. ^{1}H NMR spectra for compound **6**



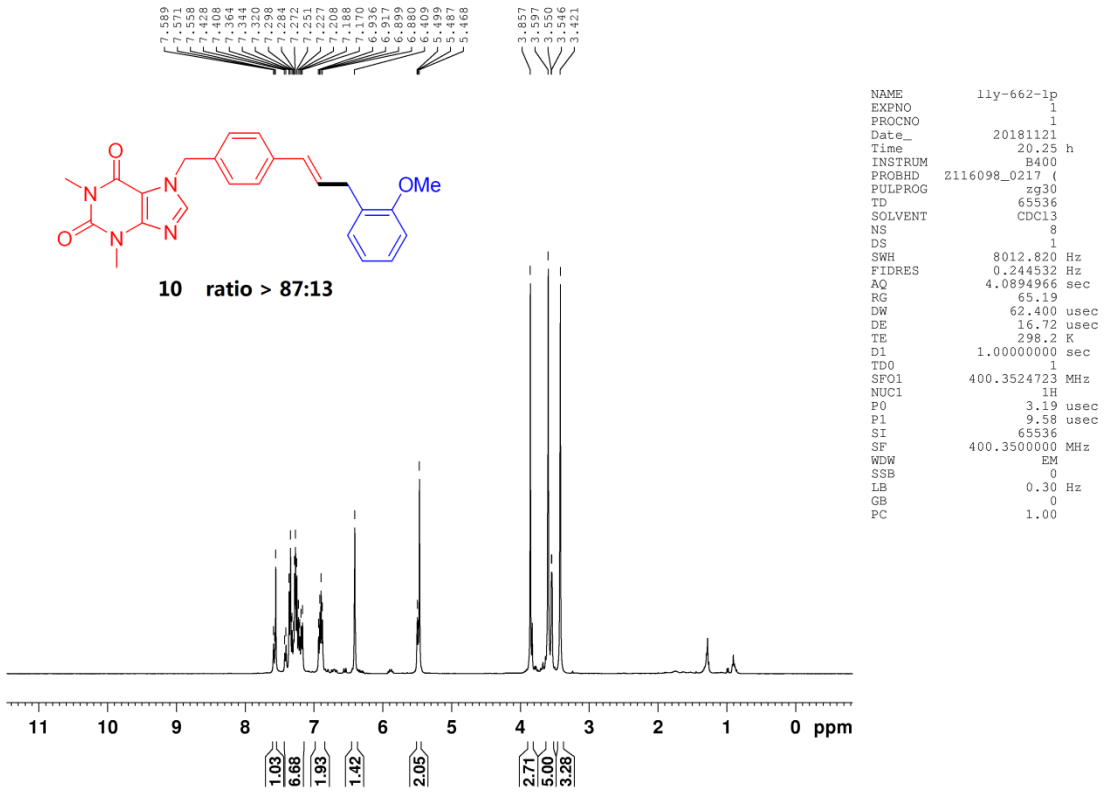
Supplementary Figure 117. ^{13}C NMR spectra for compound **6**



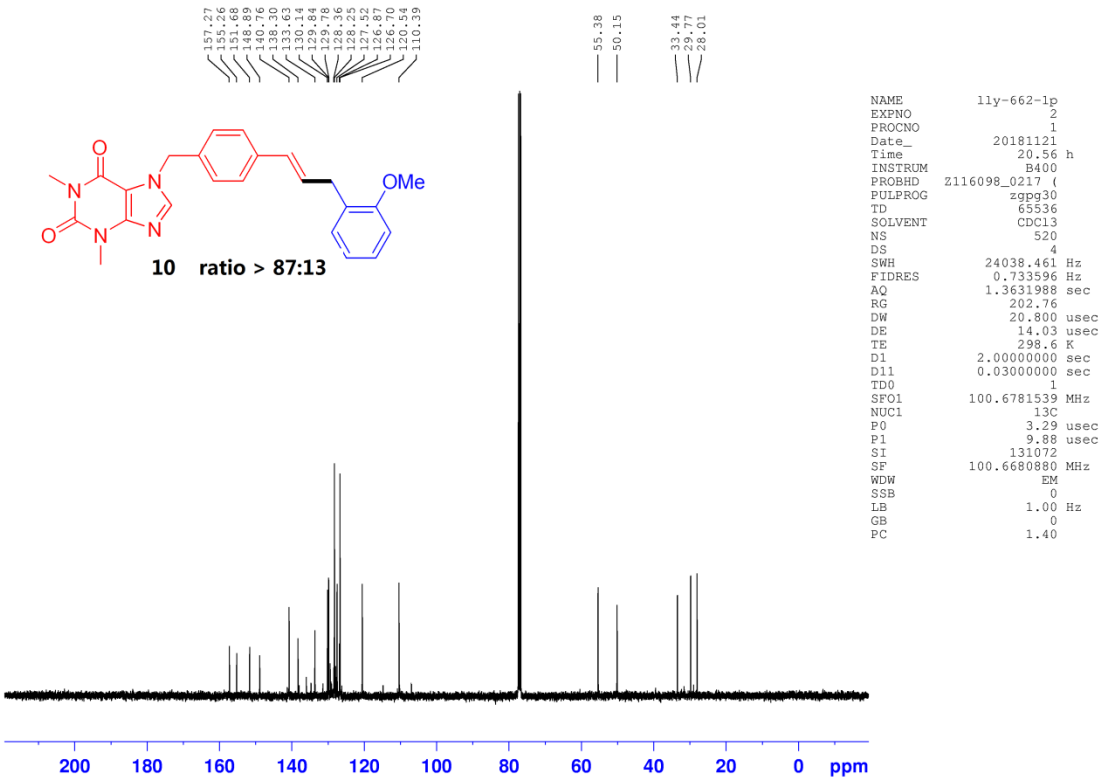
Supplementary Figure 118. ^{1}H NMR spectra for compound **8**



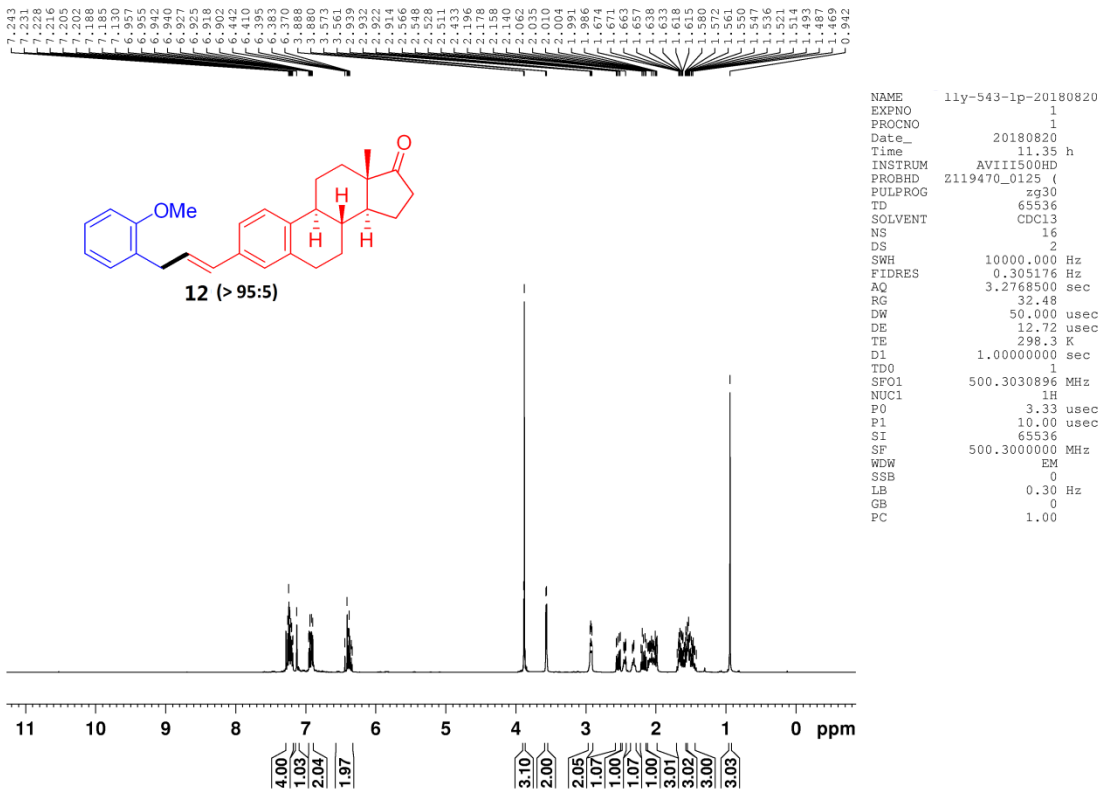
Supplementary Figure 119. ^{13}C NMR spectra for compound **8**



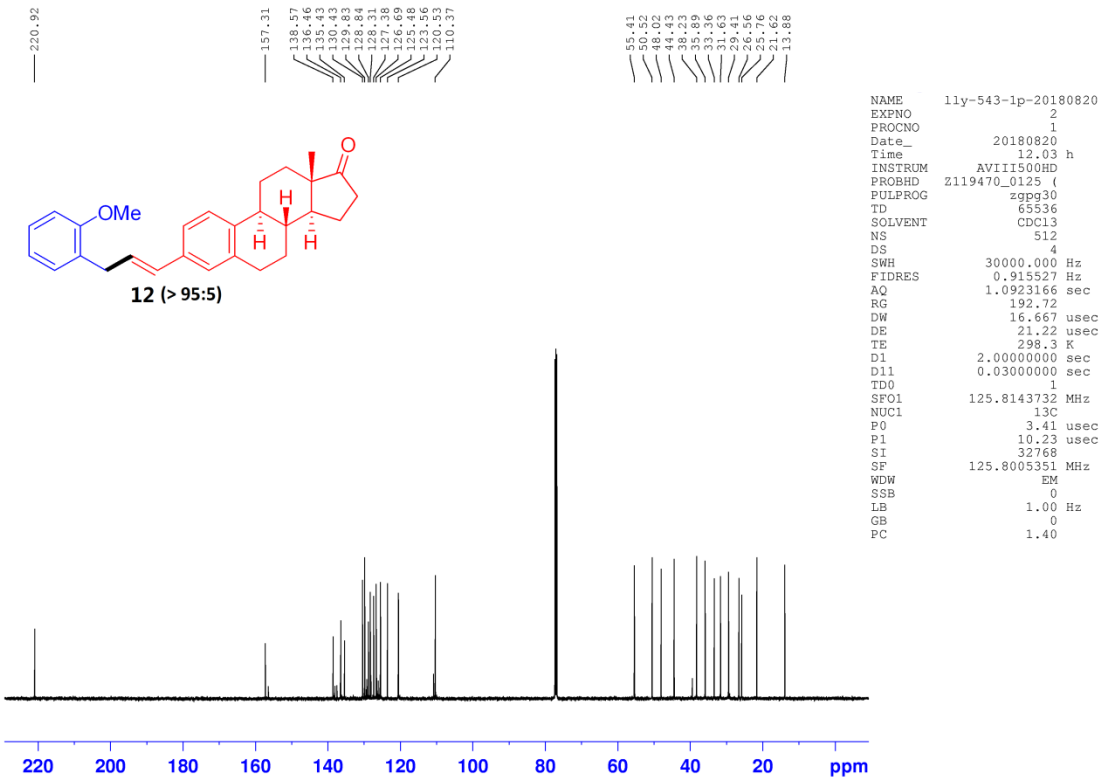
Supplementary Figure 120. ^{1}H NMR spectra for compound **10**



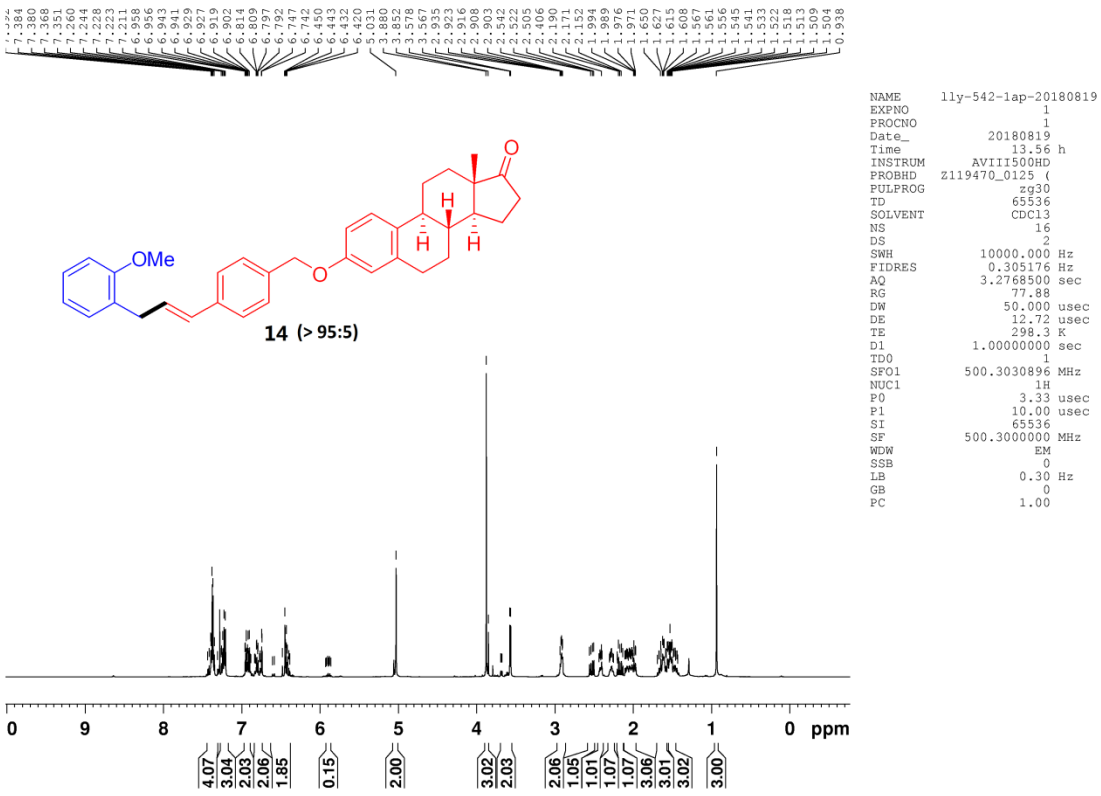
Supplementary Figure 121. ^{13}C NMR spectra for compound **10**



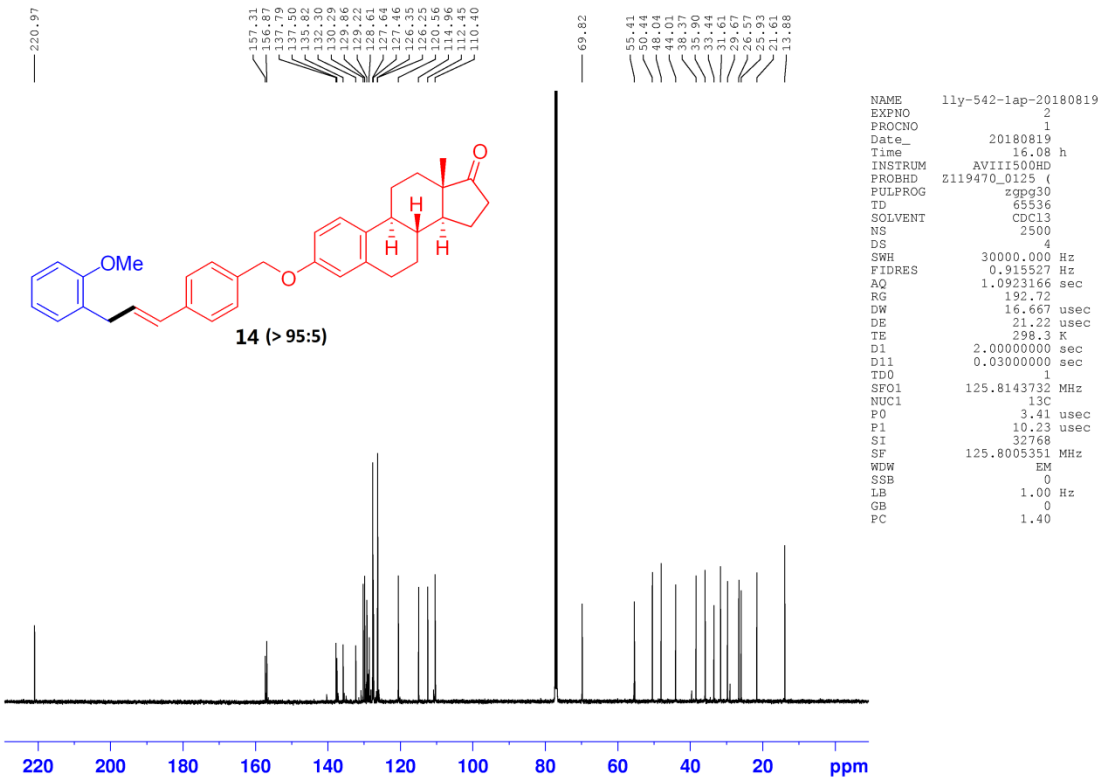
Supplementary Figure 122. ^{1}H NMR spectra for compound **12**



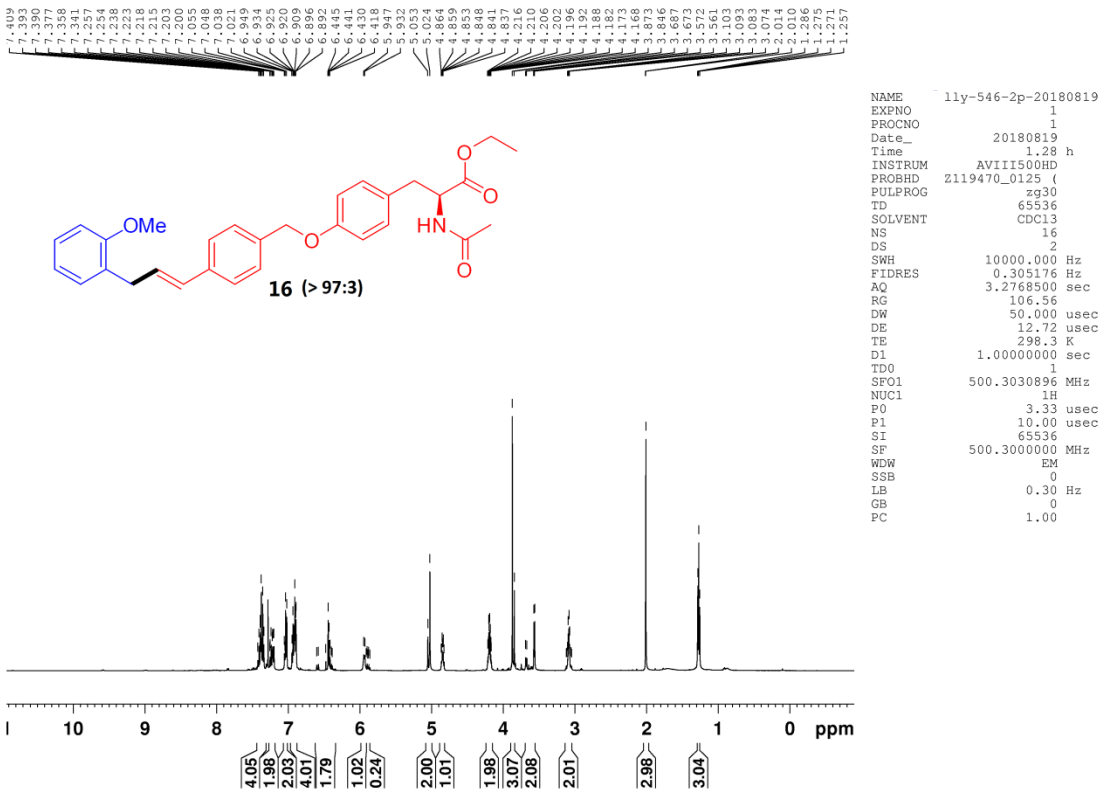
Supplementary Figure 123. ^{13}C NMR spectra for compound **12**



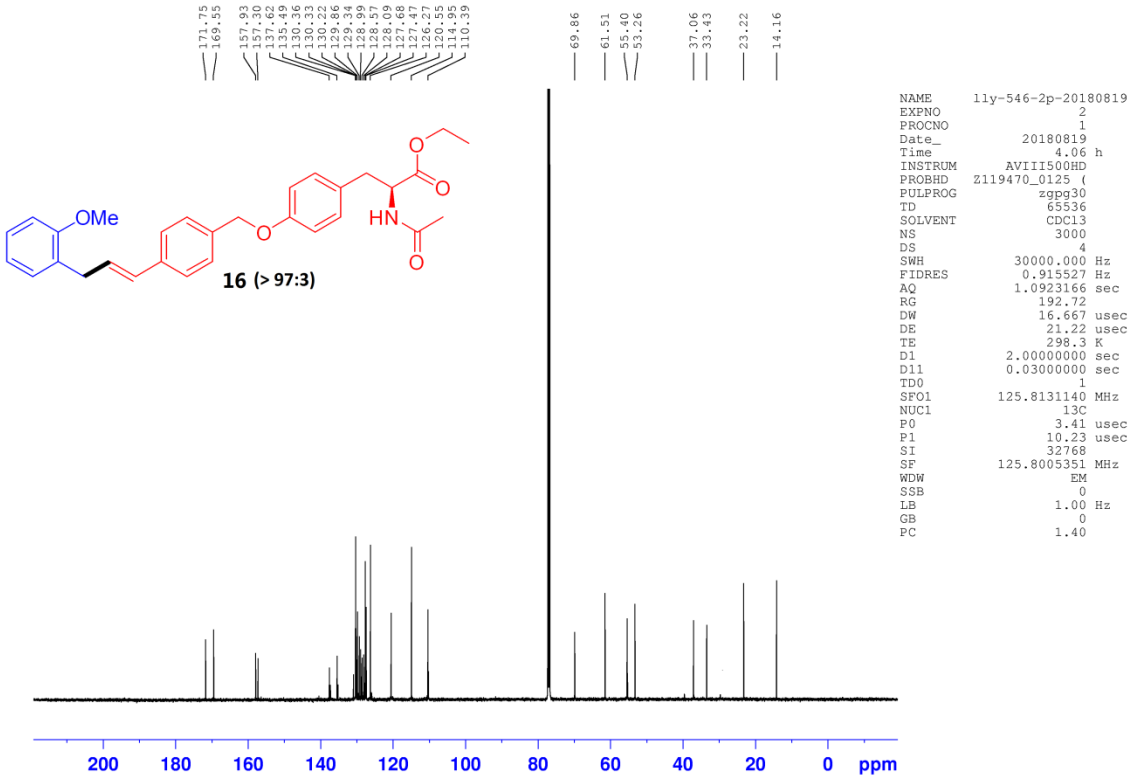
Supplementary Figure 124. ^{1}H NMR spectra for compound **14**



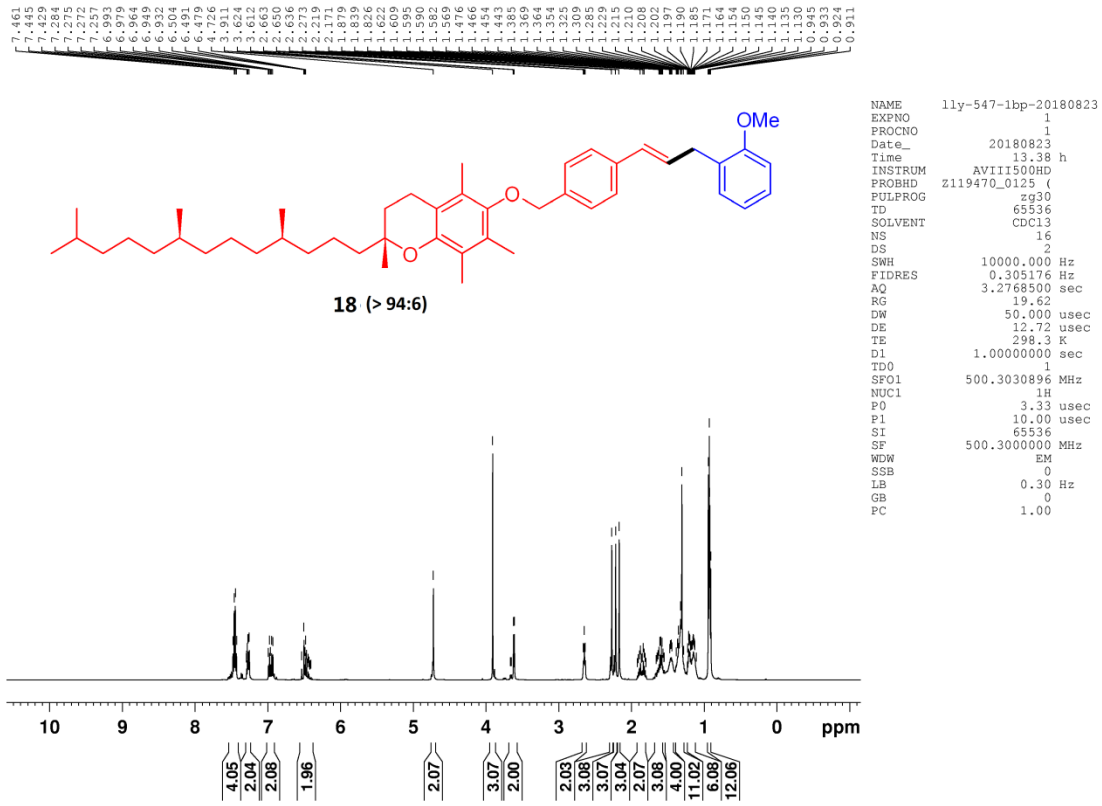
Supplementary Figure 125. ^{13}C NMR spectra for compound **14**



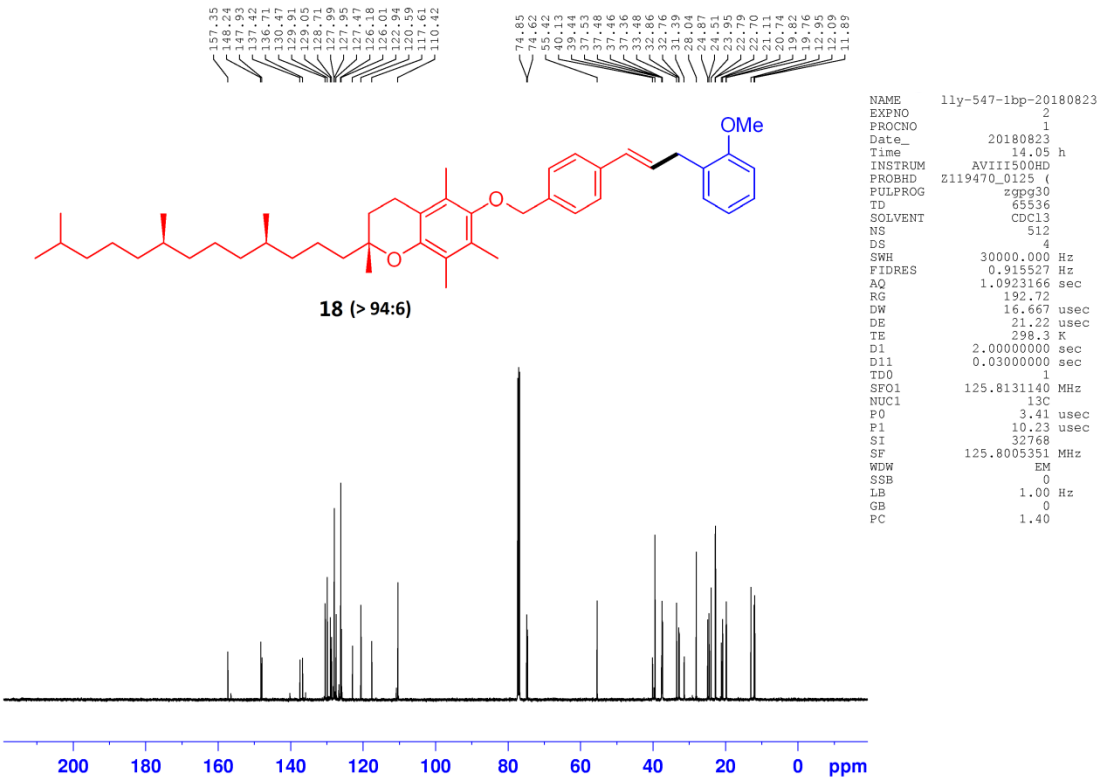
Supplementary Figure 126. ^{1}H NMR spectra for compound **16**



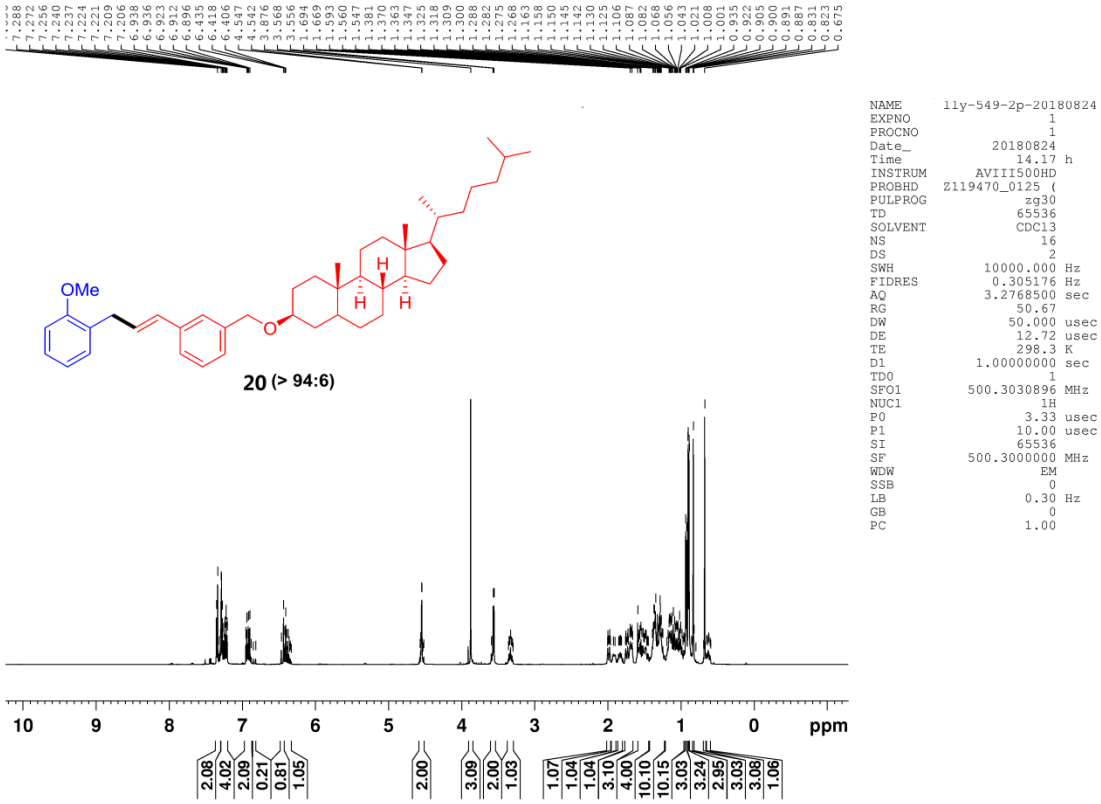
Supplementary Figure 127. ^{13}C NMR spectra for compound **16**



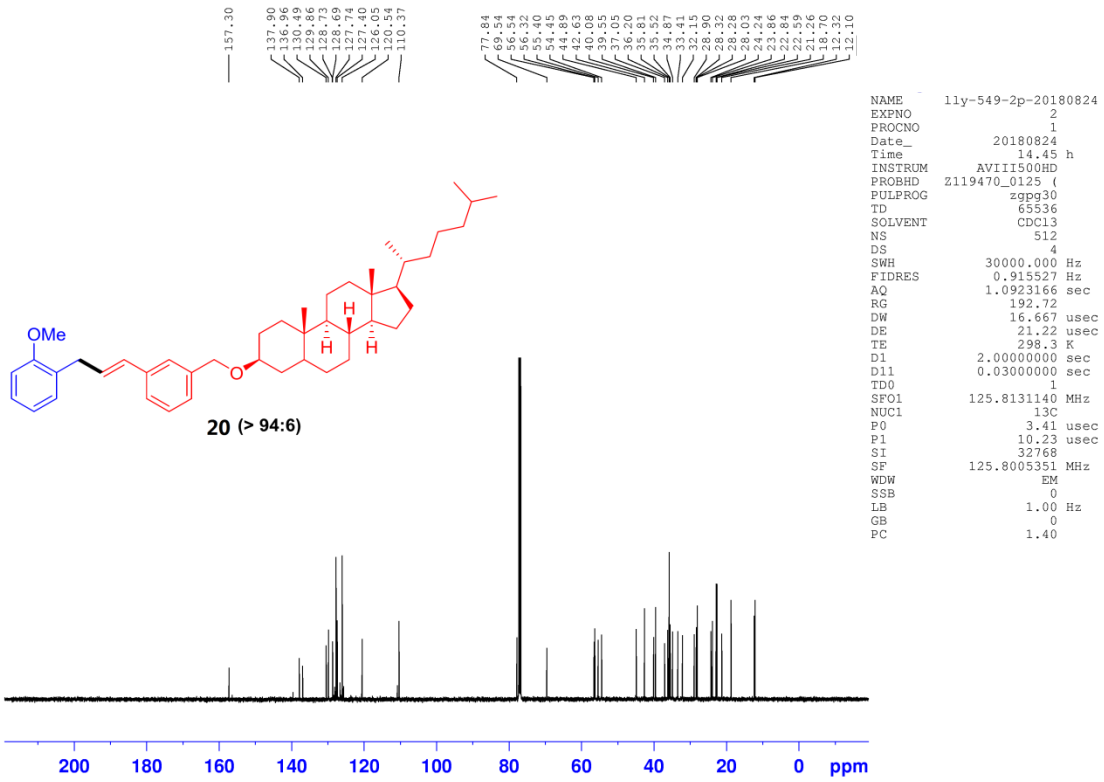
Supplementary Figure 128. ^{1}H NMR spectra for compound **18**



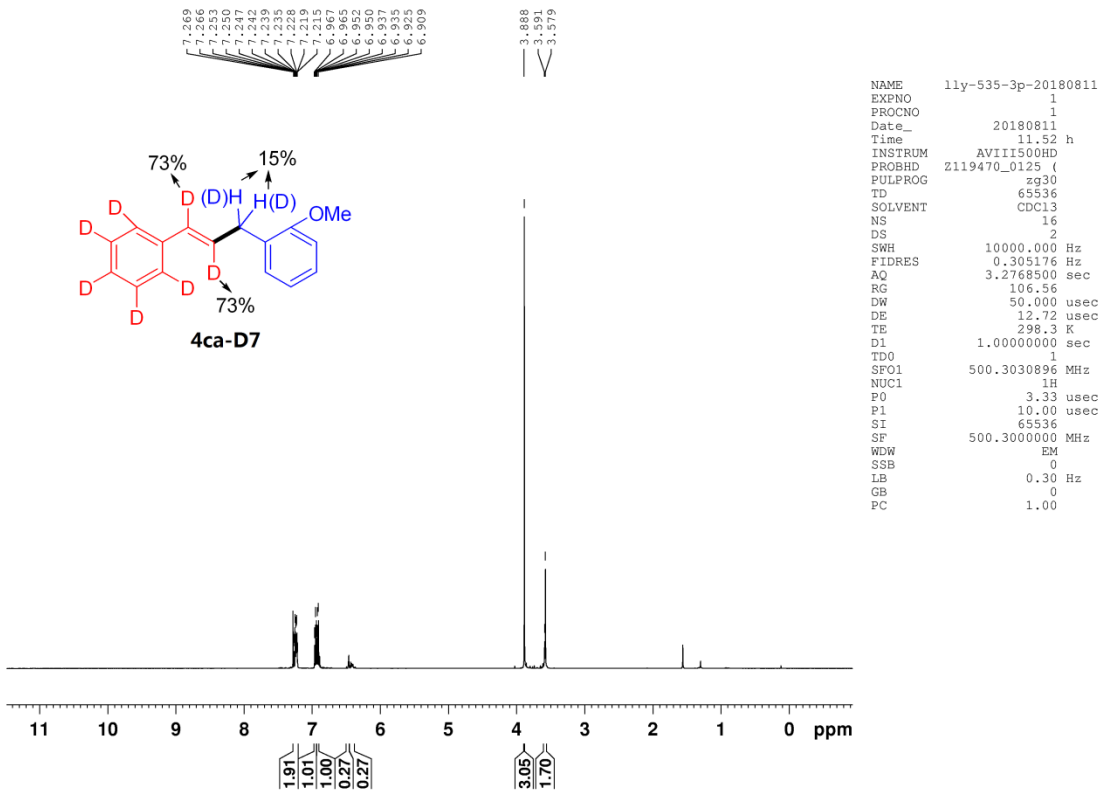
Supplementary Figure 129. ^{13}C NMR spectra for compound **18**



Supplementary Figure 130. ^{1}H NMR spectra for compound **20**



Supplementary Figure 131. ^{13}C NMR spectra for compound **20**



Supplementary Figure 132. ^{1}H NMR spectra for compound **4ca-D7**

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