Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoredox Suzuki Coupling Using Alkyl Boronic Acids and Esters

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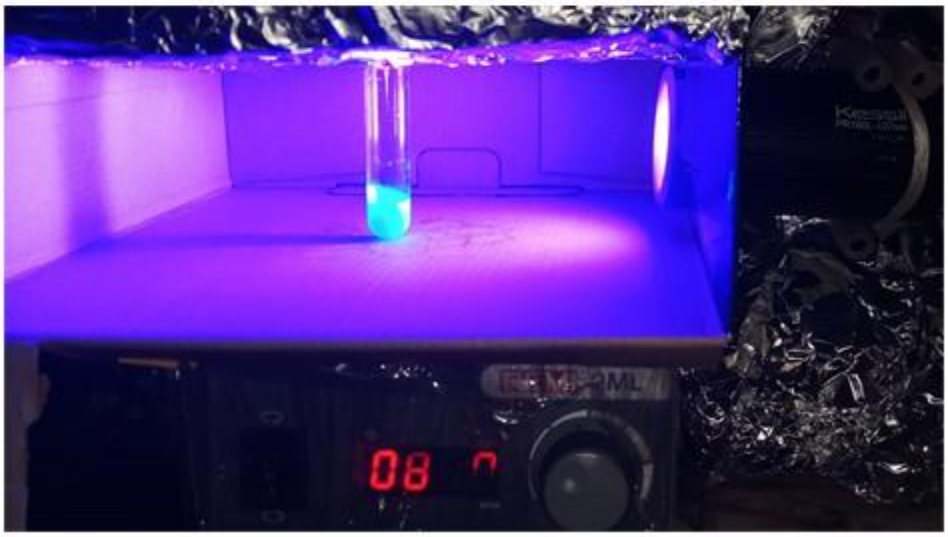
1(a). General Information:

General Methods: All the solvents were distilled prior to use. Dry solvents were prepared according to the standard procedures. All other reagents were used as received from either Aldrich or Lancaster chemical companies. Reactions requiring inert atmosphere were carried out

under argon atmosphere. Infrared (IR) spectra were recorded on a JASCO 4100 FT-IR spectrometer. ^{1}H NMR spectra were measured on Bruker AVANCE 400 MHz and 500 MHz spectrometers. Chemical shifts were reported in ppm relative to solvent signals. ^{13}C NMR spectra were recorded on Bruker 100 MHz and 125 MHz spectrometers with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. The high-resolution mass spectra (HRMS) were performed on Micromass QTOF micro mass spectrometer equipped with a Harvard apparatus syringe pump. X-ray crystallographic data were recorded using Bruker-AXS Kappa CCD-Diffractometer with graphite monochromator $Mo_{K\alpha}$ radiation (λ=0.7107 A). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares techniques against *F2* (SHELXL-97). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program. For thin layer chromatography (TLC) analysis throughout this work, E-merck precoated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used. Acme (India) silica gel (100-200 mesh) was used for column chromatography.

For the experimental Set-up of this photo-catalytic reactions were set up in a light bath which is described below. Description of light: Blue Kessil LED, PR160L-427nm; S/N:L4M4G20258 KSPR160-427; 19V-40W; Taiwan. Here the reaction was set up on the table lamp stand, which is fixed on a Cardboard Rectangle Corrugated Paper Box. The reaction was set-up top of a magnetic stirrer. A lid which rest on the top was fashioned from cardboard and holes were made such that reaction tubes (18 x 150 mm, 27 ml borosilicate tube) were held firmly in the cardboard lid which was placed on the top of bath. All the reactions were performed at room temperature.

Outside picture of our reaction set-up

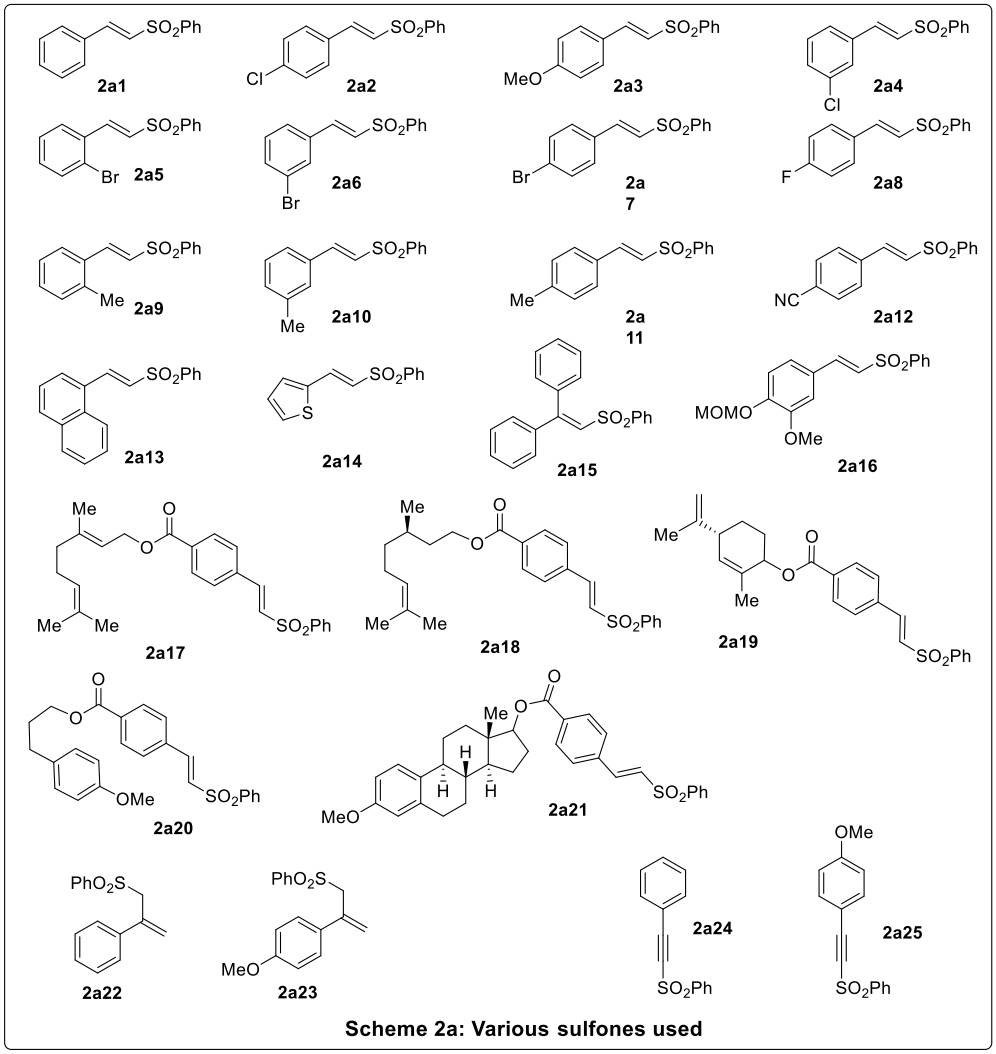


Open image our photocatalytic reaction

2. Synthesis of starting materials:

2(a). Synthesis of sulfones and boronic esters:

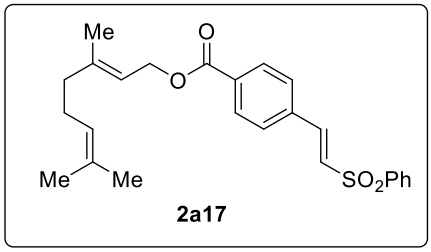
We have purchased most of the boronic acids. The boronate esters and the sulfones were synthesized by following the references as given bellow.



Scheme 2a: Various sulfones used

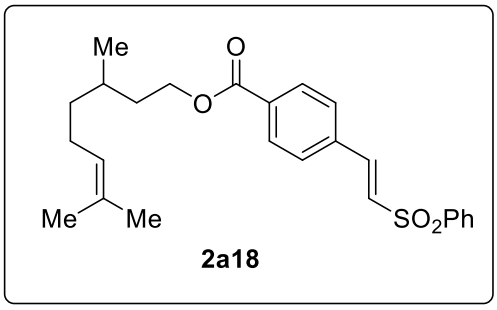
Compound 2a1, 2a3, 2a6, 2a7, 2a11, 2a14, 2a16 were synthesized by following ref 1. Compound 2a2, 2a8, 2a9, 2a10 were synthesized by following ref 2. Compound 2a4, 2a12, 2a13, 2a5, 2a15, 2a22, 2a23, 2a24, 2a25 were synthesized by following ref 3. Compound 2a17 to 2a21 were synthesized as by the following ref 4. Experimental data have been given in SI, section 2(a). For

all cases,4-vinyl benzoic acid was taken 10 mmol and the mentioned yield was the overall yield after two steps. The spectral data have been given in SI, section 11(a).



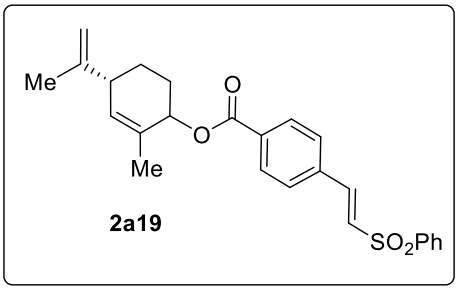
2a17

(*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-((*E*)-2-(phenylsulfonyl)vinyl)benzoate ($C_{25}H_{28}O_4S$) (2a17): Here Geraniol used for coupling. The product purified by silica gel chromatography (20% EtOAc/hexane), colourless gummy, yield 67%. IR (Neat) cm^{-1} : 3050, 2980, 2939, 2858, 1703, 1610, 1567, 1447, 1313, 1276, 1146, 1090, 1084, 968, 928, 830, 760, 683. ^1H NMR (400 MHz, CDCl3) δ 8.06 (d, *J* = 6.0 Hz, 2H), 7.97 (d, *J* = 5.7 Hz, 2H), 7.76 – 7.62 (m, 2H), 7.56 (dd, *J* = 14.5, 7.8 Hz, 3H), 7.27 (d, *J* = 5.5 Hz, 1H), 6.96 (dd, *J* = 15.4, 5.5 Hz, 1H), 5.46 (d, *J* = 5.6 Hz, 1H), 5.10 (s, 1H), 4.86 (d, *J* = 6.1 Hz, 2H), 2.10 (s, 4H), 1.77 (d, *J* = 5.5 Hz, 3H), 1.68 (d, *J* = 4.8 Hz, 3H), 1.60 (dd, *J* = 8.1, 5.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 165.75, 142.82, 141.04, 140.42, 136.46, 133.67, 132.73, 131.90, 130.30, 129.78, 129.50, 128.47, 127.87, 123.77, 118.20, 62.30, 39.60, 26.35, 25.72, 17.75, 16.63. $[M+H]^+$ calculated for $C_{25}H_{28}O_4S$ is 425.1781 and found 425.1751.



2a18

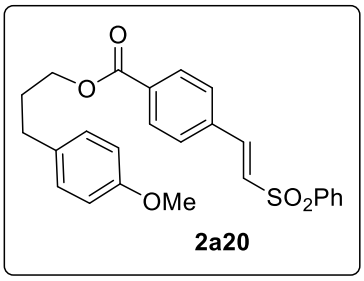
3,7-dimethyloct-6-en-1-yl (*E*)-4-(2-(phenylsulfonyl)vinyl)benzoate ($C_{25}H_{30}O_4S$) (2a18): Here Citronellol (CAS: 106-22-9) used for coupling. The product purified by silica gel chromatography (20% EtOAc/hexane), colourless gummy, yield 70%. IR (Neat) cm^{-1} : 3058, 2959, 2910, 2852, 1706, 1609, 1565, 1447, 1311, 1267, 1140, 1113, 1078, 969, 832, 752, 683. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 31.4, 8.0 Hz, 4H), 7.79 – 7.50 (m, 6H), 6.95 (d, *J* = 15.4 Hz, 1H), 5.10 (d, *J* = 6.1 Hz, 1H), 4.38 – 4.34 (m, 2H), 2.03 (brs, 2H), 1.81 (dd, *J* = 12.8, 4.9 Hz, 2H), 1.67 (s, 4H), 1.62 (d, *J* = 13.8 Hz, 3H), 1.51 – 1.36 (m, 1H), 1.33 – 1.19 (m, 1H), 0.97 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.70, 140.97, 140.38, 136.46, 133.63, 132.63, 131.36, 130.19, 129.79, 129.45, 128.46, 127.81, 124.54, 63.91, 36.96, 35.47, 29.58, 25.72, 25.40, 19.53, 17.68. $[M+H]^+$ calculated for $C_{25}H_{30}O_4S$ is 427.1938 and found 427.1914.



2a19

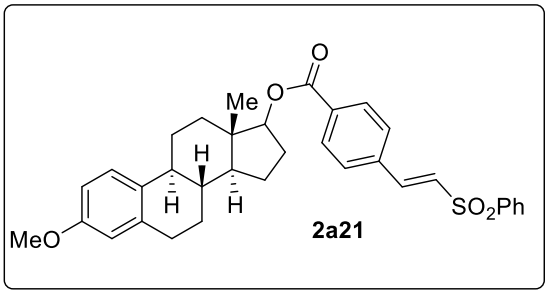
(4*R*)-2-methyl-4-(prop-1-en-2-yl)cyclohex-2-en-1-yl 4-((*E*)-2-(phenylsulfonyl)vinyl)benzoate ($C_{25}H_{26}O_4S$)

(2a19): Here Carveol used for coupling. The product purified by silica gel chromatography (20% EtOAc/hexane), colourless gummy, yield 71%. IR (Neat) cm^{-1} : 3060, 2961, 2922, 2856, 1711, 1610, 1447, 1314, 1070, 1194, 1138, 1084, 1016, 965, 810, 747, 686. ^{1}H NMR (400 MHz,) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.49 – 7.44 (m, 3H), 7.29 – 7.21 (m, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 15.4 Hz, 1H), 5.58 (brs, 2H), 4.64 (brs, 2H), 2.31 – 2.18 (m, 2H), 2.07 – 2.03 (m, 1H), 1.63 – 1.59 (m, 6H), 1.53 (t, *J* = 11.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.60, 148.25, 141.06, 140.47, 137.61, 136.61, 133.74, 132.85, 130.37, 129.56, 128.56, 127.94, 127.57, 126.46, 109.60, 74.47, 40.35, 34.10, 30.90, 20.63, 19.09. $[M+H]^+$ calculated for $C_{25}H_{26}O_4S$ is 423.1625 and found 423.1604.



2a20

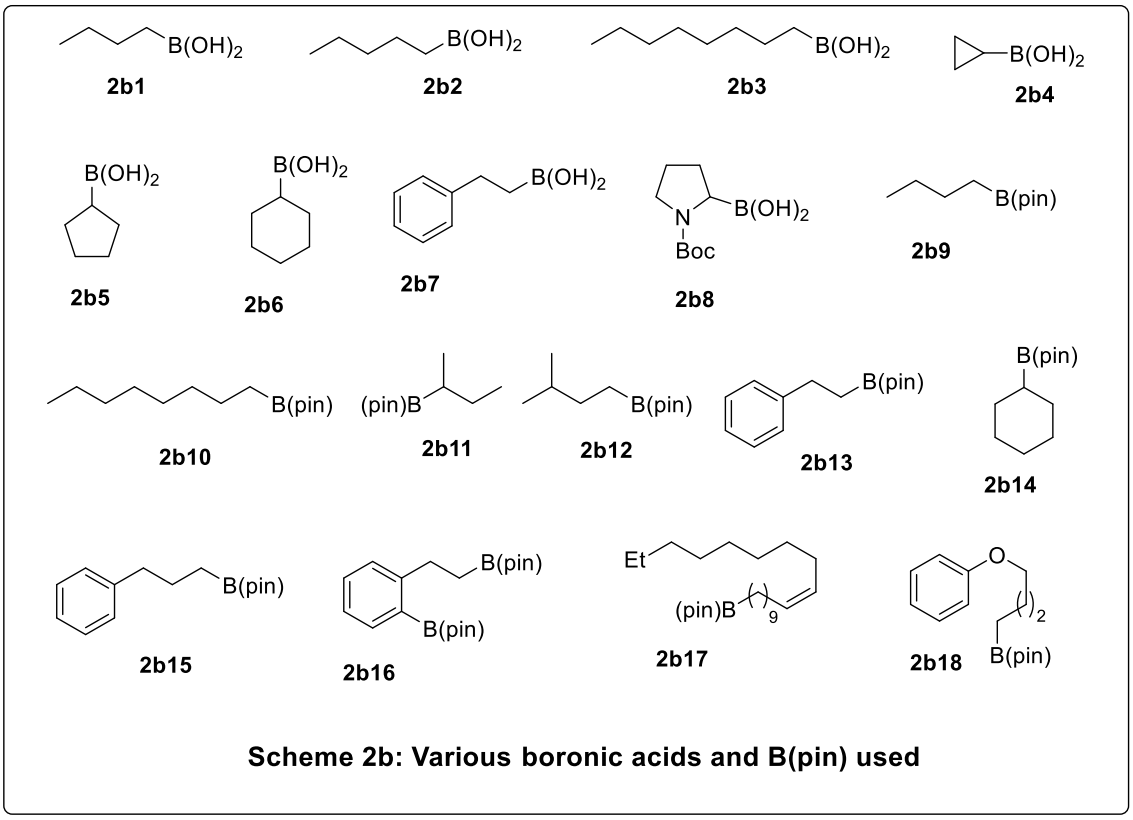
3-(4-methoxyphenyl)propyl (*E*)-4-(2-(phenylsulfonyl)vinyl)benzoate ($C_{25}H_{24}O_5S$) (2a20): It was synthesized from Estragole. First hydroboration followed by H_2O_2/NaOH oxidation were performed to get the corresponding alcohol which was further engaged for coupling without purification.[ref-4] After the coupling and sulfonation as by ref(2)4, the product purified by silica gel chromatography (20% EtOAc/hexane), colourless gummy, yield 72%. IR (Neat) cm^{-1} : 3052, 2964, 2932, 2851, 1708, 1610, 1531, 1447, 1310, 1278, 1251, 1154, 1102, 1085, 1032, 961, 826, 752, 689. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.79 – 7.73 (m, 2H), 7.51 (d, *J* = 15.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.36 (dd, *J* = 14.4, 8.0 Hz, 4H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 15.4 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 3.57 (s, 3H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.93 – 1.74 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.73, 158.10, 141.04, 140.44, 136.57, 133.72, 133.18, 132.59, 130.30, 129.87, 129.54, 129.40, 128.52, 127.90, 114.05, 64.80, 55.35, 31.48, 30.50. $[M+H]^+$ calculated for $C_{25}H_{24}O_5S$ is 437.1417 and found 437.1401.



2a21

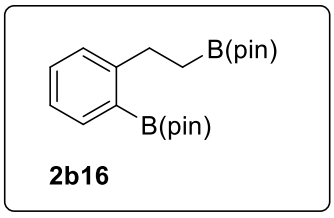
(8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl 4-((*E*)-2-(phenylsulfonyl)vinyl)benzoate ($C_{34}H_{36}O_5S$) (2a21): It was synthesized from Estrone. First phenolic methylation was done by refluxing

acetone (as solvent, 1 mL/mmol of estrone), dimethyl sulfate (1 equiv) and K_2CO_3 (1.1 equiv) for 3 h. Then reaction mixture was filtered and solvent was removed. Next the crude reaction mixture was dissolved in cold dry MeOH and 1.5 equiv $NaBH_4$ were added sequentially. Allowed to stir for 1 h at rt. MeOH was removed by rotavap. Workup was done by EA/water (3 X 10 ml). Organic layer was concentrated and went for the coupling without purification. After the coupling and sulfonation as by ref-4, the product purified by silica gel chromatography (20% EtOAc/hexane), colourless gummy, yield 55%. IR (Neat) cm^{-1} : 3057, 2956, 2919, 2862, 2840, 1704, 1610, 1495, 1447, 1297, 1278, 1245, 1138, 1083, 1037, 979, 816, 750, 685. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 15.3 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.57 (dd, *J* = 15.0, 7.8 Hz, 3H), 7.26 (s, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 15.4 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.64 (s, 1H), 4.93 (t, *J* = 8.4 Hz, 1H), 3.78 (s, 3H), 2.86 (s, 2H), 2.31 (d, *J* = 9.7 Hz, 2H), 2.23 (d, *J* = 8.5 Hz, 1H), 1.95 (d, *J* = 10.1 Hz, 2H), 1.75 (d, *J* = 38.8 Hz, 3H), 1.49 (t, *J* = 9.7 Hz, 3H), 1.44 – 1.33 (m, 2H), 0.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.76, 157.71, 141.15, 140.52, 138.04, 136.55, 133.77, 133.04, 132.59, 130.34, 129.84, 129.60, 128.57, 127.98, 126.49, 114.03, 111.70, 83.88, 55.38, 50.02, 43.98, 43.59, 38.82, 37.21, 29.94, 27.93, 27.43, 26.40, 23.56, 12.54. $[M+NH_4]^+$ calculated for $C_{34}H_{36}O_5S$ is 574.2622 and found 574.2599.



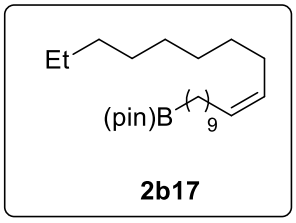
Scheme 2b: Various boronic acids and B(pin) used

Here compounds 2b1 to 2b8 were purchased from sigma Aldrich. Compounds 2b9 to 2b15 and 2b18 were synthesized by following the ref 5.



4,4,5,5-tetramethyl-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)-1,3,2-dioxaborolane ($C_{20}H_{32}B_2O_4$) (2b16): This compound was synthesized starting from 2-bromo styrene. In a 10 mL oven-dried reaction vessel 4-cyanopyridine (10.4 mg, 0.1 mmol), $NaBH_4$ (9.5 mg, 0.25 mmol), $B_2(pin)_2$ (253.9 mg, 1 mmol) are taken, sealed with a septum, and degassed by vacuum evacuation and nitrogen backfilling (three times). Then olefin (0.5 mmol) was added and MeOH (0.4 mL) was added. The reaction mixture was then stirred at 100 ^oC for 5 hours. Then the reaction mixture was cooled to room temperature, brine (10 mL) was then added and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography using 10% EtOAc/Hexane with 69% of yield and went for the next step. A flask charged with $PdCl_2(dppf)$ (0.03 mmol), KOAc (3.0 mmol), and $B_2(pin)_2$ (1.1

mmol) was flushed with nitrogen. dioxane (6 mL) and the first step product (1.0 mmol) were then added. After being stirred at 110 °C for an appropriate period, the product was extracted with benzene, washed with water, and dried over anhydrous magnesium sulfate. The final product 2b16 was purified by silica gel chromatography (10% EtOAc/hexane), colourless gummy liquid, overall yield 58%. IR (Neat) cm^{-1} : 3072, 3016, 2960, 2931, 1600, 1487, 1442, 1374, 1348, 1313, 1216, 1143, 964, 861. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.3 Hz, 1H), 7.30 (td, *J* = 7.6, 1.0 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 3.03 – 2.95 (m, 2H), 1.33 (s, 12H), 1.21 (s, 12H), 1.09 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.87, 135.98, 130.80, 128.67, 124.82, 83.37, 82.90, 30.03, 24.93, 24.90.



2b17

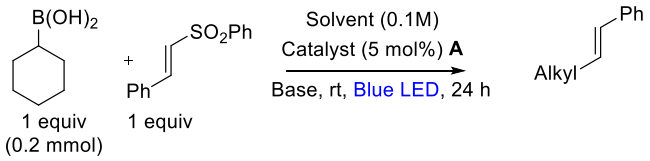
(Z)-4,4,5,5-tetramethyl-2-(nonadec-10-en-1-yl)-1,3,2-dioxaborolane ($C_{25}H_{49}BO_2$) (2b17): This compound was synthesized starting from Oleic acid. Here first $LiAlH_4$ (2 equiv) was added to a round bottom flask containing Oleic acid (1 equiv, 0.5 g), 10 mL dry THF at 0 ^{o}C and stirred for 6 h at rt. Then the reaction mixture was quenched by water and work-up was performed with EtOAc (3 × 5 mL). Organic layer is collected, concentrated and the corresponding alcohol (2b18-A) was isolated with 90% yield. Then went for next step. Then to a round bottom flask containing triphenyl phosphine (1.1 equiv, 2 g) and DCM (15 mL); CBr_4 (1.1 equiv) was added at 0 ^{o}C portion wise. Then after 10 minutes 2b18-A (1 equiv), was added at 0 ^{o}C and stirred for 2 h at rt. Then the reaction mixture was diluted with hexane and filtered through celite pad. The celite pad was washed with EtOAc (3 × 5 mL). The combined organic layer was concentrated to avail the corresponding bromide (2b18-B) with 91% yield. Next for the borylation, we follow dehalogenetive borylation [ref-6] leads to the final product. The final product was purified by silica gel chromatography (10% EtOAc/hexane), colourless gummy liquid, overall yield 52%. IR (Neat) cm^{-1} : 3011, 2924, 2854, 1640, 1466, 1372, 1317, 1215, 1144, 967, 847. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.20 (m, 2H), 1.96 (s, 4H), 1.20 (d, *J* = 8.1 Hz, 39H), 0.85 (dt, *J* = 13.7, 6.9 Hz, 3H), 0.74 – 0.67 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.03, 129.98, 82.91, 32.55, 32.05, 29.92, 29.66, 29.61, 29.52, 29.45, 27.37, 27.34, 24.94, 24.13, 22.81, 14.21.

3. Optimization, general procedure and the scope for the *E*-olefin from boronic acid:

3(a): Optimization:

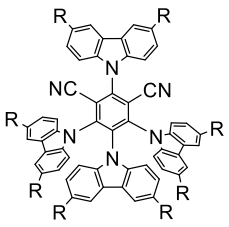
We have initiated our studies using cyclohexyl boronic acid, phenyl vinyl sulfone and 4CzIPN as a photocatalyst. We hypothesized that activation of boronic acid with a Lewis base will lower the oxidation potential of boronic acid, which will be suitable for generation of alkyl radical using organophotocatalyst. Gratifyingly, we observed formation of olefin product by using DMAP as a Lewis base using an equal ratio of methanol and acetone as a solvent. The stereoselectivity was improved using *iso*-propanol as a solvent in comparison to methanol and other solvent combinations screened. A further effort with variation of reaction time and solvents did not improve the yield and stereoselectivity. Polar aprotic solvents can also act as a Lewis acid to activate the organoboron compounds. Based on that hypothesis, we have screened several polar aprotic solvents. We observed variable yield and stereoselectivity using different polar aprotic solvents. Superior yield and stereoselectivity was observed by using DMA as a solvent. In our recently published paper, we also observed that DMA plays a crucial role to attain high *E*-selectivity. Hence keeping DMA as optimal solvent, we engaged various organic and inorganic bases as an external activator, but none of them succeeded to improve the outcome. We also have screened other catalysts for this reaction based on their redox potential and triplet energy transfer. However, we did not observe any improvement using these modified catalysts (Table 1, entry 25-28). By increasing the amount of boronic acid in compare to the sulfone improved the yield by keeping high stereoselectivity.

Table 1. Optimization for *E*-selective Vinylation

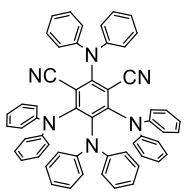


Entry	Solvent	Catalyst (X)	Base (equiv)	*dr* (**E**/**Z**)	Time	Yield [a](%)
1	Acetone:MeOH (1:1)	Ir-cat	DMAP(0.4)	68:32	24 h	54
2	Acetone:MeOH (1:1)	A	DMAP(0.4)	72:28	24 h	58
3	Acetone	A	DMAP(0.4)	69:31	24 h	33
4	MeOH	A	DMAP(0.4)	40:60	24 h	60
5	^{i}PrOH	A	DMAP(0.4)	89:11	24 h	56
6	^{i}PrOH:MeOH (1:1)	A	DMAP(0.4)	85:15	24 h	55
7	DME	A	--	92:08	24 h	22
8	ACN	A	--	30:70	24 h	20
9	DMA	A	--	97:03	24 h	74
10	NMP	A	--	86:14	24 h	13
11	DMF	A	--	70:30	24 h	45
12	DMSO	A	--	100:0	24 h	39
13	HMPA	A	--	91:09	24 h	41
14	Benzene	A	--	--	24 h	--
15	Toluene	A	--	--	24 h	--
16	Dioxane	A	--	60:40	24 h	23
17	Acetone	A	--	69:31	24 h	33
18	MeOH	A	--	55:45	24 h	65
19	iPrOH	A	--	82:18	24 h	62
20	DMA	A	PPh_3 (1.0)	91:09	24 h	31
21	DMA	A	DMAP (1.0)	90:10	24 h	64
22	DMA	A	NaO^{t}Bu (1.0)	97:03	24 h	42
23	DMA	A	Cs_2CO_3 (1.0)	86:14	24 h	58
24	DMA	A	K_3PO_4 (1.0)	97:03	24 h	56
25	DMA	B	--	--	24 h	--
26	DMA	C	--	60:40	24 h	28
27	DMA	D	--	--	24 h	--
28	DMA	E	--	--	24 h	--
29[b]	DMA	A	--	100:0	24 h	88
30[c]	DMA	A	--	99:01	24 h	78
31[b]	DMA	A	--	92:08	36 h	62

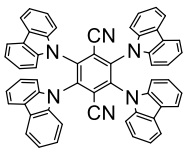
0.1 M solvent w.r.t boronic acid; [a]Isolated yield; [b]2 equivalent of boronic acid used; [c]3 equivalent of boronic acid used



R = H (**Cat-A**)
OMe (**Cat-B**), Cl (**Cat-C**)



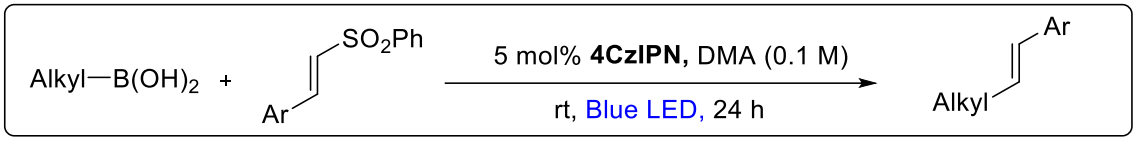
Cat-D



Cat-E

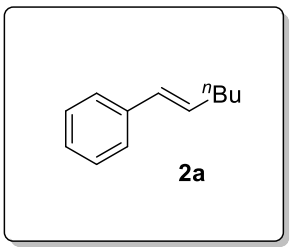
Ir-Cat. : Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6

3(b): General procedure (3B):

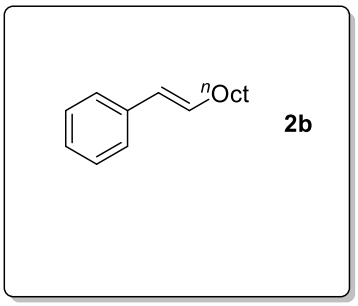


To a dry 20 mL vial equipped with a magnetic stir bar was added 4CzIPN (5 mol%), alkyl boronic acid (2 equiv) and sulfone (1 equiv). The vial was sealed and then DMA (0.1 M w.r.t boronic acid) was added to the vial and the resulting mixture was degassed by freeze-pump-thaw under nitrogen (three times). Then, the vial was placed in a photo reactor and irradiated with Blue LED at rt for 24 h. After that the reaction mixture was diluted with H_2O (4 mL) and workup by using Et_2O (3 X 5 mL). Purification by flash column chromatography or preparative TLC afforded the (*E*)-alkene.

3(c): Scope for the *E*-olefin from boronic acid:

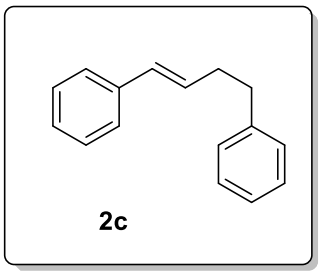


(*E*)-hex-1-en-1-ylbenzene ($C_{12}H_{16}$) (2a):[ref-7] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (20 mg) 60% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.7, 6.8 Hz, 1H), 2.23 (q, *J* = 7.1 Hz, 2H), 1.53 – 1.44 (m, 2H), 1.39 (dt, *J* = 14.2, 7.1 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 138.09, 131.34, 129.82, 128.60, 126.87, 126.03, 32.87, 31.67, 22.42, 14.11.

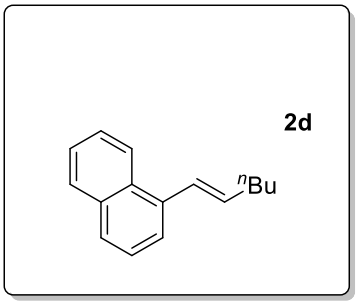


(*E*)-dec-1-en-1-ylbenzene ($C_{16}H_{24}$) (2b):[ref-8] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (32 mg) 75% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.35 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* =

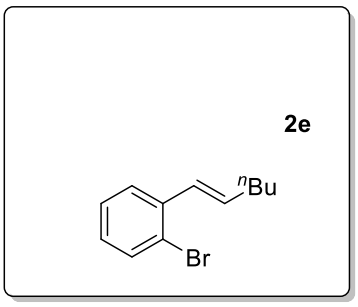
15.7, 6.9 Hz, 1H), 2.21 (td, *J* = 7.8, 1.0 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.39 – 1.27 (m, 10H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 138.20, 131.42, 129.90, 128.61, 126.88, 126.08, 33.20, 32.06, 29.65, 29.57, 29.44, 29.41, 22.82, 14.22.



(*E*)-but-1-ene-1,4-diyldibenzene ($C_{16}H_{16}$) (2c):[ref-9] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (30 mg) 71% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.38 – 7.16 (m, 10H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.80 (t, *J* = 7.8 Hz, 2H), 2.54 (dd, *J* = 14.8, 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 141.93, 137.96, 130.60, 130.14, 128.63, 128.51, 127.08, 126.17, 126.04, 36.05, 34.97.

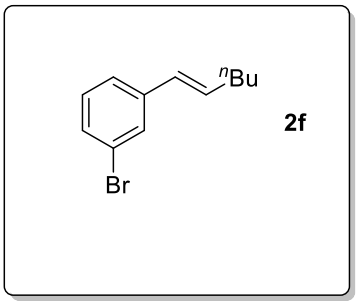


(*E*)-1-(hex-1-en-1-yl)naphthalene ($C_{16}H_{18}$) (2d):[ref-10] Synthesized using general procedure **4A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (30 mg) 72% (*E*:*Z* = 92:08). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.41 (m, 1H), 7.11 (d, *J* = 15.6 Hz, 1H), 6.24 (dt, *J* = 15.5, 6.9 Hz, 1H), 2.39 – 2.30 (m, 2H), 1.55 (d, *J* = 8.0 Hz, 2H), 1.44 (dt, *J* = 14.4, 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.01, 134.68, 133.84, 131.36, 128.60, 127.33, 127.09, 125.90, 125.81, 125.75, 124.15, 123.67, 33.28, 31.76, 22.47, 14.12.

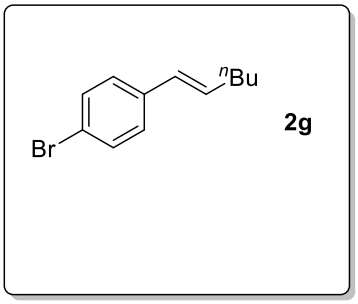


(*E*)-1-bromo-2-(hex-1-en-1-yl)benzene ($C_{12}H_{15}Br$) (2e):[ref-11] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (33 mg) 70% (*E*:*Z* =

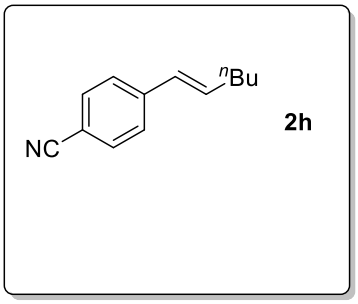
82:18). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 2H), 7.30 – 7.23 (m, 1H), 7.05 (dd, *J* = 12.0, 7.6 Hz, 1H), 6.76 – 6.65 (m, 1H), 6.17 (ddd, *J* = 14.6, 12.1, 5.7 Hz, 1H), 2.32 – 2.21 (m, 2H), 1.52 – 1.44 (m, 2H), 1.40 (d, *J* = 4.9 Hz, 2H), 0.94 (dd, *J* = 12.0, 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.94, 134.27, 132.67, 130.72, 128.52, 128.26, 126.92, 124.19, 31.96, 28.21, 22.45, 14.03.



(*E*)-1-bromo-3-(hex-1-en-1-yl)benzene ($C_{12}H_{15}Br$) (2f):[ref-12] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (29 mg) 61% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz,) δ 7.51 (s, 1H), 7.28 (dd, *J* = 15.6, 10.8 Hz, 2H), 7.17 (s, 1H), 6.35 – 6.22 (m, 2H), 2.23 (d, *J* = 5.9 Hz, 2H), 1.46 (d, *J* = 6.3 Hz, 2H), 1.42 – 1.33 (m, 2H), 0.95 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.29, 133.07, 130.10, 129.71, 128.89, 128.50, 124.73, 122.84, 32.81, 31.50, 22.39, 14.08.

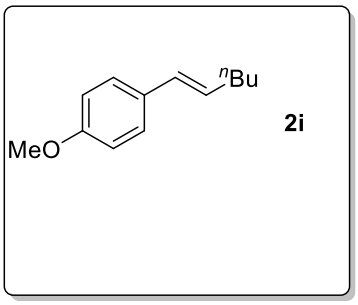


(*E*)-1-bromo-4-(hex-1-en-1-yl)benzene ($C_{12}H_{15}Br$) (2g):[ref-13] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (26 mg) 58% (*E*:*Z* = 98:02). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.26 – 6.16 (m, 1H), 2.20 (dd, *J* = 13.6, 6.6 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.36 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.09, 132.28, 131.67, 128.77, 127.61, 120.50, 32.84, 31.55, 22.41, 14.07.

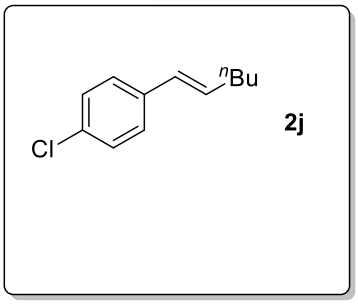


(*E*)-4-(hex-1-en-1-yl)benzonitrile ($C_{13}H_{15}N$) (2h):[ref-12] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (22 mg) 60% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H),

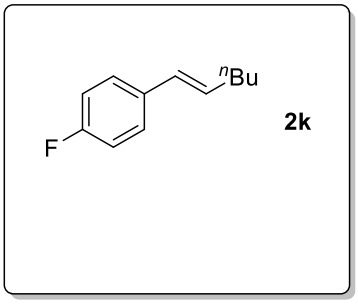
7.40 (d, *J* = 8.1 Hz, 2H), 6.38 (d, *J* = 3.1 Hz, 2H), 2.25 (q, *J* = 7.1, 6.2 Hz, 2H), 1.46 (q, *J* = 7.4 Hz, 2H), 1.38 (q, *J* = 6.8 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.65, 135.74, 132.49, 128.62, 126.53, 119.26, 110.17, 32.93, 31.34, 22.41, 14.02.



(*E*)-1-(hex-1-en-1-yl)-4-methoxybenzene ($C_{13}H_{18}O$) (2i):[ref-12] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (25 mg) 69% (*E*:*Z* = 91:09:). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.80 (s, 3H), 2.18 (q, *J* = 6.8 Hz, 2H), 1.47 – 1.35 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.84, 131.09, 130.08, 129.24, 127.13, 114.12, 55.46, 32.82, 31.85, 22.41, 14.08.

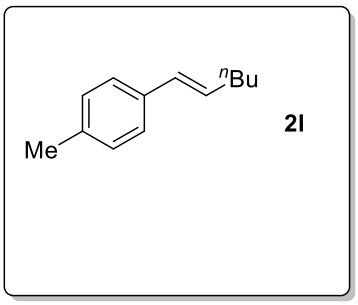


(*E*)-1-chloro-4-(hex-1-en-1-yl)benzene ($C_{12}H_{15}Cl$) (2j):[ref-14] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (25 mg) 66% (*E*:*Z* = 92:08:). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 4H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.19 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.20 (td, *J* = 8.1, 1.3 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.37 (dq, *J* = 14.0, 6.9 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.68, 132.46, 132.14, 128.74, 127.27, 32.82, 31.60, 22.41, 14.05.

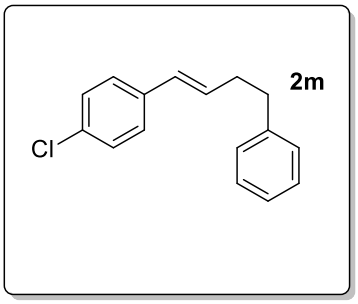


(*E*)-1-fluoro-4-(hex-1-en-1-yl)benzene ($C_{12}H_{15}F$) (2k):[ref-14] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5%

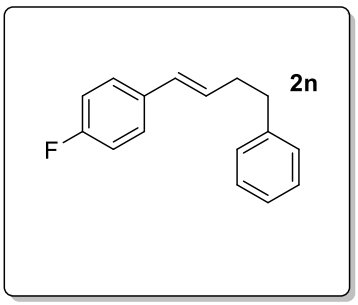
EtOAc/hexane), colourless liquid, yield (20 mg) 58% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (ddd, *J* = 13.1, 7.3, 5.3 Hz, 2H), 6.91 – 6.84 (m, 2H), 6.25 (d, *J* = 15.8 Hz, 1H), 6.04 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.11 (td, *J* = 7.8, 1.2 Hz, 2H), 1.40 – 1.32 (m, 2H), 1.27 (dt, *J* = 14.0, 7.0 Hz, 2H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.05 (d, *J* = 245.7 Hz, C-F coupling), 134.32, 131.11 (d, *J* = 2.5 Hz), 128.74, 127.45 (d, *J* = 7.5 Hz), 115.42 (d, *J* = 21.4 Hz), 32.78, 31.69, 22.41, 14.06.



(*E*)-1-(hex-1-en-1-yl)-4-methylbenzene ($C_{13}H_{18}$) (2l):[ref-14] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (21 mg) 61% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8 Hz, 2H), 7.09 (d, *J* = 8 Hz, 2H), 6.36 – 6.32 (m, 1H), 6.20 – 6.13 (m, 1H), 2.32 (s, 3H), 2.22 – 2.17 (m, 2H), 1.44 – 1.37 (m, 2H), 1.37 (brs, 2H), 0.93 – 0.90 (t, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 135.4, 130.3, 129.7, 129.3, 125.9, 32.8, 31.7, 22.4, 21.2, 14.0.

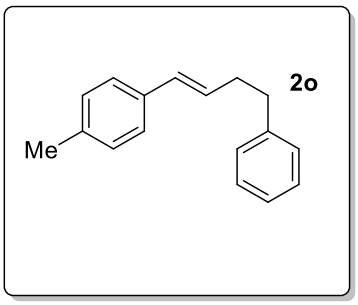


(*E*)-1-chloro-4-(4-phenylbut-1-en-1-yl)benzene ($C_{16}H_{15}Cl$) (2m):[ref-41] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (33 mg) 68% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz,) δ 7.32 – 7.25 (m, 4H), 7.23 – 7.10 (m, 5H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.84 – 2.72 (m, 2H), 2.52 (dd, *J* = 14.7, 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.75, 136.43, 132.69, 130.87, 129.45, 128.77, 128.61, 128.54, 127.36, 126.11, 35.92, 34.91.

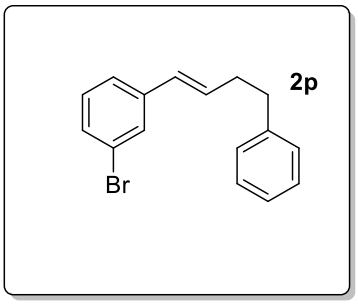


(*E*)-1-fluoro-4-(4-phenylbut-1-en-1-yl)benzene ($C_{16}H_{15}F$) (2n):[ref-17] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (30 mg) 66% (*E*:*Z* =

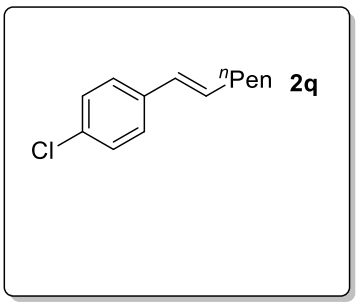
100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.20 (ddd, *J* = 21.9, 10.8, 5.6 Hz, 3H), 7.03 – 6.94 (m, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.83 – 2.75 (m, 2H), 2.57 – 2.48 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.23 (d, *J* = 229 Hz), 141.84, 134.08, 129.89, 129.43, 128.62, 128.53, 127.56 (d, *J* = 3.6 Hz), 126.08, 115.47 (d, *J* = 21 Hz) 36.02, 34.88..



(*E*)-1-methyl-4-(4-phenylbut-1-en-1-yl)benzene ($C_{17}H_{18}$) (2o):[ref-17] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (33 mg) 74% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz,) δ 7.35 – 7.29 (m, 3H), 7.26 – 7.23 (m, 4H), 7.13 (t, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.5, 6.8 Hz, 1H), 2.85 – 2.78 (m, 2H), 2.56 – 2.51 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.02, 136.80, 135.17, 130.41, 129.33, 129.11, 128.64, 128.49, 126.06, 126.00, 36.12, 34.98, 21.26.

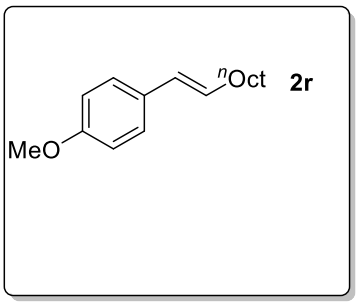


(*E*)-1-bromo-3-(4-phenylbut-1-en-1-yl)benzene ($C_{16}H_{15}Br$) (2p):[ref-18] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (41 mg) 72% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.30 (t, *J* = 9.3 Hz, 2H), 7.26 (s, 1H), 7.24 – 7.16 (m, 4H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.29 – 6.20 (m, 1H), 2.79 (t, *J* = 7.7 Hz, 2H), 2.53 (dd, *J* = 14.4, 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.68, 140.12, 131.82, 130.12, 129.95, 129.29, 129.06, 128.60, 128.56, 126.13, 124.83, 122.89, 35.85, 34.88.

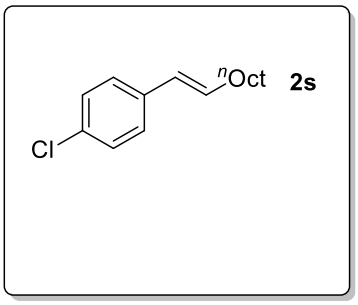


(*E*)-1-chloro-4-(hept-1-en-1-yl)benzene ($C_{13}H_{17}Cl$) (2q):[ref-15] Synthesized using general procedure **3B** (with 0.2 mmol of

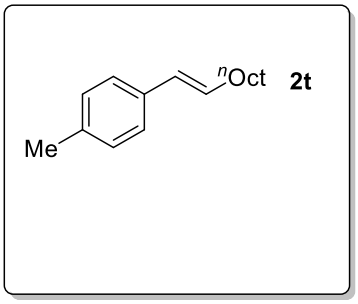
sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 67% (*E:Z* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.3 Hz, 4H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.25 – 6.12 (m, 1H), 2.17 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.44 (d, *J* = 6.6 Hz, 2H), 1.35 – 1.29 (m, 4H), 0.88 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.69, 132.46, 132.19, 128.74, 127.27, 33.12, 31.59, 29.12, 22.69, 14.16.



(*E*)-1-(dec-1-en-1-yl)-4-methoxybenzene ($C_{17}H_{26}O$) (2r):[ref-19] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (35 mg) 72% (*E*:*Z* = 90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 6.88 – 6.78 (m, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.80 (s, 3H), 2.24 – 2.10 (m, 2H), 1.44 (dd, *J* = 14.6, 7.0 Hz, 2H), 1.29 (dd, *J* = 21.2, 7.9 Hz, 10H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.82, 131.08, 129.31, 129.20, 127.13, 114.11, 55.46, 33.17, 32.06, 29.70, 29.66, 29.44, 29.41, 22.82, 14.23.

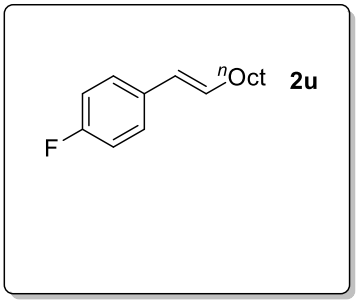


(*E*)-1-chloro-4-(dec-1-en-1-yl)benzene ($C_{16}H_{23}Cl$) (2s):[ref-19] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (35 mg) 70% (*E*:*Z* = 97:03). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 4.9 Hz, 4H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.20 (td, *J* = 8.0, 1.1 Hz, 2H), 1.46 (dd, *J* = 14.6, 7.1 Hz, 2H), 1.36 – 1.28 (m, 10H), 0.90 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.69, 132.45, 132.19, 128.73, 127.27, 33.16, 32.04, 29.63, 29.46, 29.42, 29.40, 22.82, 14.22.

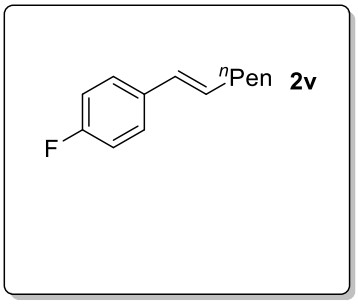


(*E*)-1-(dec-1-en-1-yl)-4-methylbenzene ($C_{17}H_{26}$) (2t):[ref-19] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5%

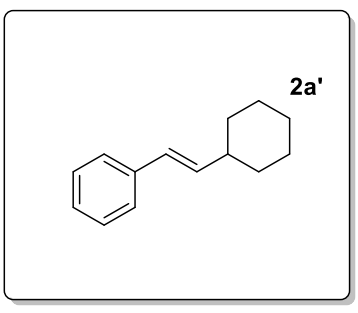
EtOAc/hexane), colourless liquid, yield (33 mg) 73% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.7, 6.8 Hz, 1H), 2.33 (d, *J* = 8.9 Hz, 3H), 2.18 (q, *J* = 6.7 Hz, 2H), 1.44 (dd, *J* = 13.8, 6.6 Hz, 2H), 1.26 (d, *J* = 6.5 Hz, 10H), 0.89 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.55, 135.32, 130.39, 129.62, 129.30, 125.93, 33.19, 32.04, 29.65, 29.60, 29.44, 29.39, 22.83, 21.26, 14.26.



(*E*)-1-(dec-1-en-1-yl)-4-fluorobenzene ($C_{16}H_{23}F$) (2u):[ref-20] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colorless liquid, yield (32 mg) 69% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 6.97 (dd, *J* = 12.1, 5.3 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.7, 6.9 Hz, 1H), 2.18 (dt, *J* = 7.7, 4.0 Hz, 2H), 1.46 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.35 – 1.26 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.05 (d, *J* = 245 Hz), 134.34 (d, *J* = 2.5 Hz), 131.18 (d, *J* = 1.2 Hz), 128.72, 127.45 (d, *J* = 7.5 Hz), 115.42 (d, *J* = 21 Hz), 33.13, 32.05, 29.64, 29.55, 29.43, 29.40, 22.82, 14.22.

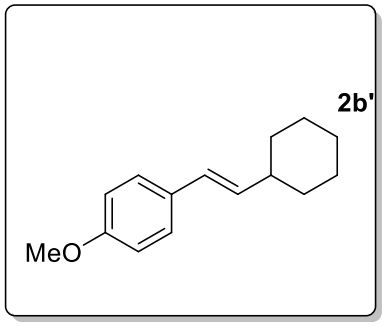


(*E*)-1-fluoro-4-(hept-1-en-1-yl)benzene ($C_{13}H_{17}F$) (2v):[ref-16] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (26 mg) 68% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.18 – 6.09 (m, 1H), 2.19 (q, *J* = 7.1 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.37 – 1.29 (m, 4H), 0.90 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.06 (d, *J* = 245 Hz), 134.33 (d, *J* = 3.7 Hz), 131.16 (d, *J* = 1.2 Hz), 128.73, 127.45 (d, *J* = 7.5 Hz), 115.42 (d, *J* = 21 Hz), 33.09, 31.60, 29.21, 22.70, 14.16.

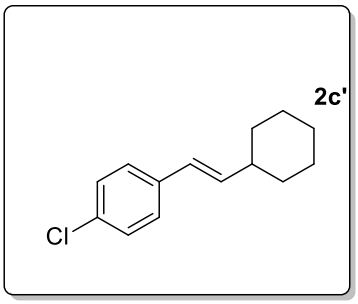


(*E*)-(2-cyclohexylvinyl)benzene ($C_{14}H_{18}$) (2a'):[ref-21] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless

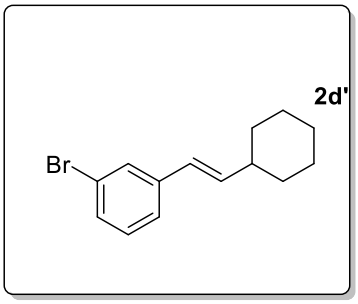
liquid, yield (31 mg) 84% (*E*:*Z* = 100:0). We also have performed the gran scale synthesis using 3 mmol of cyclohexyl boronic acid and 72% yield observed. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.26 (dd, *J* = 16.1, 8.5 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.19 – 2.03 (m, 1H), 1.77 (ddd, *J* = 12.4, 11.2, 8.4 Hz, 4H), 1.69 – 1.61 (m, 1H), 1.36 – 1.27 (m, 2H), 1.22 – 1.12 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.30, 137.00, 128.59, 127.47, 126.87, 126.12, 41.30, 33.16, 26.37, 26.22.



(*E*)-1-(2-cyclohexylvinyl)-4-methoxybenzene ($C_{15}H_{20}O$) (2b'):[ref-21] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 66% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.8, 1.9 Hz, 2H), 6.87 – 6.73 (m, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.79 (s, 3H), 2.10 (dtd, *J* = 10.4, 7.2, 3.4 Hz, 1H), 1.84 – 1.70 (m, 4H), 1.67 (ddd, *J* = 9.3, 3.3, 1.7 Hz, 1H), 1.36 – 1.25 (m, 2H), 1.23 – 1.10 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.81, 134.97, 131.14, 127.16, 126.75, 114.10, 55.46, 41.26, 33.28, 26.38, 26.25.

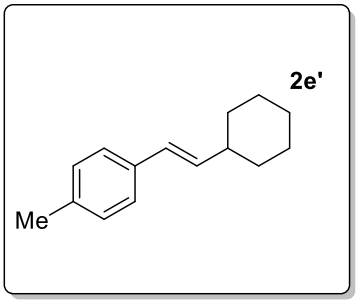


(*E*)-1-chloro-4-(2-cyclohexylvinyl)benzene ($C_{14}H_{17}Cl$) (2c'):[ref-21] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (33 mg) 76% (*E*:*Z* = 100:0). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 4H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.11 (dd, *J* = 7.2, 3.8 Hz, 1H), 1.81 – 1.71 (m, 4H), 1.67 (ddd, *J* = 13.0, 4.1, 2.5 Hz, 1H), 1.38 – 1.27 (m, 2H), 1.17 (dd, *J* = 17.5, 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.73, 136.80, 132.42, 128.72, 127.32, 126.32, 41.27, 33.06, 26.32, 26.17.

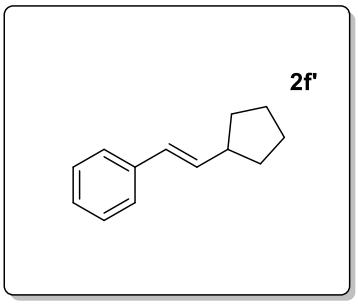


(*E*)-1-bromo-3-(2-cyclohexylvinyl)benzene ($C_{14}H_{17}Br$) (2d'):[ref-22] Synthesized using general procedure **3B** (with 0.2 mmol of

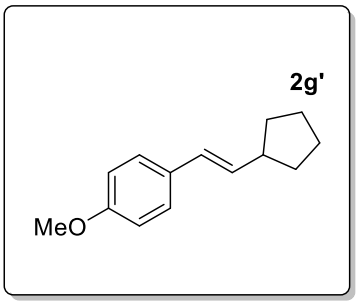
sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (31 mg) 61% (*E*:*Z* = 91:09). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.26 (d, *J* = 16.1 Hz, 1H), 6.17 (dd, *J* = 16.0, 6.7 Hz, 1H), 2.16 – 2.07 (m, 1H), 1.86 – 1.73 (m, 4H), 1.68 (d, *J* = 12.9 Hz, 1H), 1.35 – 1.29 (m, 2H), 1.15 (dd, *J* = 17.9, 8.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.54, 138.66, 130.08, 129.72, 128.98, 126.18, 124.84, 122.87, 41.27, 33.01, 26.30, 26.15.



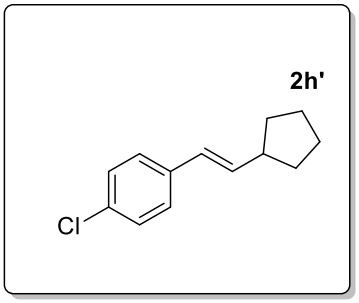
(*E*)-1-(2-cyclohexylvinyl)-4-methylbenzene ($C_{15}H_{20}$) (2e'):[ref-21] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (25 mg) 64% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz,) δ 7.32 – 7.23 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.36 (d, *J* = 11.6 Hz, 3H), 2.16 – 2.06 (m, 1H), 1.87 – 1.75 (m, 4H), 1.70 (d, *J* = 13.0 Hz, 1H), 1.40 – 1.33 (m, 2H), 1.23 (dd, *J* = 10.3, 8.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.53, 136.01, 135.42, 129.29, 127.15, 125.96, 41.28, 33.16, 26.34, 26.22, 21.26.



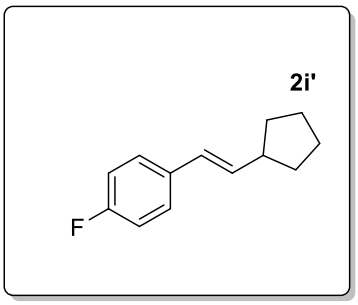
(*E*)-(2-cyclopentylvinyl)benzene ($C_{13}H_{16}$) (2f'):[ref-23] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (27 mg) 80% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.27 (dd, *J* = 14.8, 7.1 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 15.8, 7.7 Hz, 1H), 2.58 (dt, *J* = 15.9, 8.0 Hz, 1H), 1.92 – 1.78 (m, 2H), 1.77 – 1.66 (m, 2H), 1.65 – 1.56 (m, 2H), 1.39 (tt, *J* = 16.2, 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.06, 135.85, 128.59, 127.96, 126.84, 126.04, 43.97, 33.36, 25.37.



(*E*)-1-(2-cyclopentylvinyl)-4-methoxybenzene ($C_{14}H_{18}O$) (2g'):[ref-25] Synthesized using general procedure **3B** (with mmol of sulfone, purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 71% (*E*:*Z* = 86:14). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.32 (t, *J* = 11.1 Hz, 1H), 6.08 (dd, *J* = 15.8, 7.8 Hz, 1H), 3.82 (s, 3H), 2.65 – 2.47 (m, 1H), 1.86 (dd, *J* = 11.9, 6.1 Hz, 2H), 1.71 (d, *J* = 6.8 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.40 (dd, *J* = 15.6, 11.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.69, 137.13, 133.73, 127.30, 127.10, 114.02, 55.42, 43.97, 33.44, 25.35.

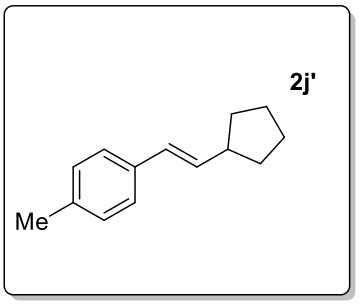


(*E*)-1-chloro-4-(2-cyclopentylvinyl)benzene ($C_{13}H_{15}Cl$) (2h'):[ref-25] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 68% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz,) δ 7.42 – 7.18 (m, 4H), 6.33 (t, *J* = 11.5 Hz, 1H), 6.20 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.60 (dt, *J* = 15.9, 8.0 Hz, 1H), 1.96 – 1.81 (m, 2H), 1.73 (dd, *J* = 7.4, 3.6 Hz, 2H), 1.67 – 1.61 (m, 2H), 1.45 – 1.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.56, 132.32, 128.69, 127.25, 126.83, 43.94, 33.30, 25.36.

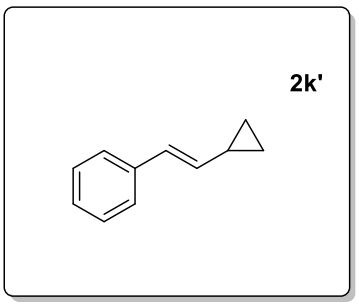


(*E*)-1-(2-cyclopentylvinyl)-4-fluorobenzene ($C_{13}H_{15}F$) (2i'):[ref-24] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (26 mg) 69% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.11 (dd, *J* = 15.8, 7.8 Hz, 1H), 2.57 (dd, *J* = 16.2, 8.1 Hz, 1H), 1.85 (dd, *J* = 16.6, 10.7 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.60 (dd, *J* = 13.4, 9.1 Hz, 2H), 1.45 – 1.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.96 (d, *J*

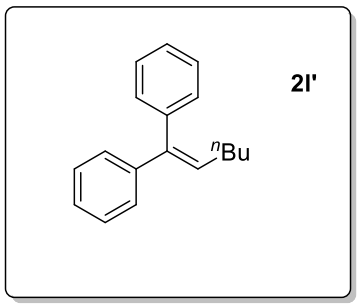
= 245 Hz), 135.56 (d, *J* = 2.5 Hz), 134.20 (d, *J* = 3.03 Hz), 127.43 (d, *J* = 7.0 Hz), 126.82, 115.41 (d, *J* = 22 Hz), 43.92, 33.35, 25.36.



(*E*)-1-(2-cyclopentylvinyl)-4-methylbenzene ($C_{14}H_{18}$) (2j'):[ref-24] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (27 mg) 73% (*E*:*Z* = 91:09). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.17 (dd, *J* = 15.8, 7.8 Hz, 1H), 2.61 (dd, *J* = 16.1, 8.0 Hz, 1H), 2.36 (d, *J* = 10.1 Hz, 3H), 1.87 (dd, *J* = 11.6, 6.4 Hz, 2H), 1.79 – 1.68 (m, 2H), 1.62 (dd, *J* = 14.3, 9.9 Hz, 2H), 1.46 – 1.37 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.51, 135.40, 134.85, 129.30, 127.87, 125.99, 43.91, 33.41, 25.40, 21.24.

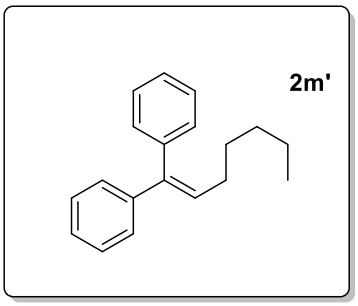


(*E*)-(2-cyclopropylvinyl)benzene ($C_{11}H_{12}$) (2k'):[ref-26] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (14 mg) 49% (*E*:*Z* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.03 (m, 5H), 6.40 (d, *J* = 16.1 Hz, 1H), 5.66 (dd, *J* = 15.3, 8.9 Hz, 1H), 1.17 – 1.12 (m, 1H), 0.76 (d, *J* = 6.9 Hz, 2H), 0.45 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.03, 135.00, 128.62, 127.59, 126.69, 126.50, 125.74, 14.61, 7.36.

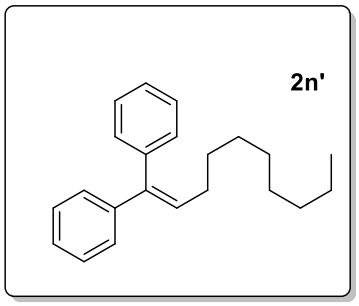


hex-1-ene-1,1-diyldibenzene ($C_{18}H_{20}$) (2l'):[ref-37] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (38 mg) 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 10.1, 4.5 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.26 – 7.18 (m, 5H), 7.18 – 7.14 (m, 2H), 6.08 (t, *J* = 7.5 Hz, 1H), 2.11 (dd, *J* =

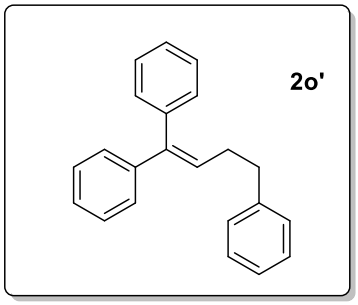
14.8, 7.4 Hz, 2H), 1.48 – 1.37 (m, 2H), 1.35 – 1.27 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.12, 141.66, 140.56, 130.44, 130.11, 128.25, 128.20, 127.36, 126.94, 126.86, 32.33, 29.62, 22.50, 14.08.



Hept-1-ene-1,1-diyldibenzene ($C_{19}H_{22}$) (2m'):[ref-35] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (35 mg) 71%. ^{1}H NMR (400 MHz, CDCl3) δ 7.41 – 7.12 (m, 9H), 6.08 (d, J = 7.0 Hz, 1H), 2.09 (d, J = 5.5 Hz, 2H), 1.43 (s, 2H), 1.26 (s, 4H), 0.86 (d, J = 2.2 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 143.06, 141.49, 140.48, 130.52, 130.09, 128.19, 127.33, 126.92, 126.85, 31.64, 29.88, 29.80, 22.68, 14.18.

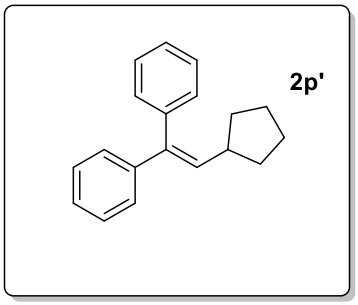


dec-1-ene-1,1-diyldibenzene ($C_{22}H_{28}$) (2n'):[ref-36] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (42 mg) 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.12 (m, 10H), 6.08 (d, *J* = 7.5 Hz, 1H), 2.10 (s, 2H), 1.41 (s, 2H), 1.24 (s, 9H), 0.87 (d, *J* = 7.1 Hz, 4H). 13C NMR (126 MHz, CDCl3) δ 143.12, 141.63, 140.56, 130.50, 130.12, 128.25, 128.20, 127.36, 126.94, 126.86, 32.03, 30.11, 29.90, 29.59, 29.44, 29.39, 22.80, 14.21.



But-1-ene-1,1,4-triyltribenzene ($C_{22}H_{20}$) (2o'):[ref-38] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (38 mg) 68%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.26 (tt, *J* = 19.1, 9.4 Hz, 6H), 7.17 (dd, *J* = 13.8, 7.0 Hz, 3H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 7.0 Hz, 2H),

6.11 (t, *J* = 7.3 Hz, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.43 (dd, *J* = 15.0, 7.5 Hz, 2H). 13C NMR (126 MHz, CDCl3) δ 142.85, 142.49, 141.85, 140.28, 129.97, 128.95, 128.68, 128.44, 128.29, 128.22, 127.37, 127.05, 127.02, 125.99, 36.34, 31.75.



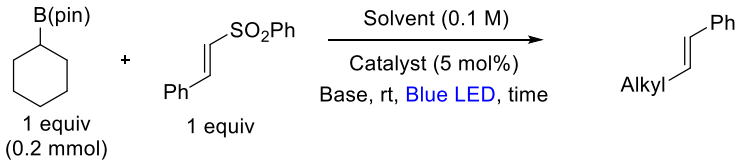
(2-cyclopentylethene-1,1-diyl)dibenzene ($C_{19}H_{20}$) (2p'):[ref-34] Synthesized using general procedure **3B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (37 mg) 74% . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 3H), 7.21 (tt, *J* = 10.6, 4.0 Hz, 7H), 5.96 (dd, *J* = 9.9, 5.8 Hz, 1H), 2.59 – 2.44 (m, 1H), 1.77 (s, 2H), 1.67 (d, *J* = 2.4 Hz, 2H), 1.53 – 1.44 (m, 2H), 1.43 – 1.32 (m, 2H). 13C NMR (101 MHz, $CDCl_3$) δ 143.00, 140.72, 140.05, 135.60, 130.14, 128.19, 127.37, 126.91, 126.82, 40.56, 34.36, 25.74.

4. Optimization, general procedure and the scope for the *E*-olefin from boronate ester:

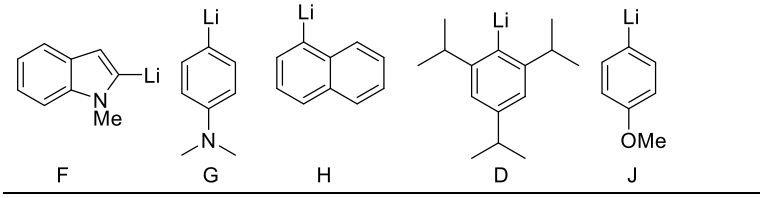
4(a): Optimization:

Further, we focused on the deborylative vinylation starting from boronate esters. Boronic esters are suitable precursors for various APIs and pharmaceutical intermediate synthesis as they are widely available commercially. Among the boronate esters, activated pinacolate ester is well explored as the SET oxidative radical precursor. Therefore we applied our previous condition but resulted in poor yield which indicates that the DMA alone is insufficient to activate the B(pin) and requires an external activator. Further, based on the Ley group work, we employed Acetone/MeOH condition which result in moderate yield and poor selectivity. However, the

Table 2. Optimization for *E*-selective Vinylation



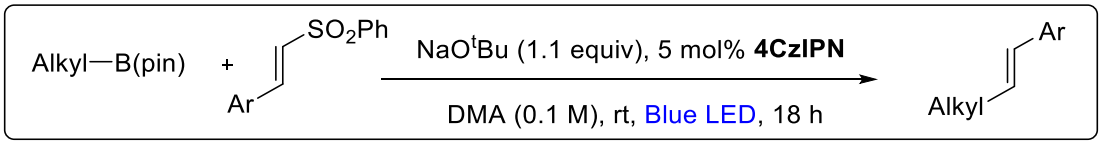
Entry	Solvent	Catalyst	Base/Activator (equiv)	Time (h)	*dr* (**E**/**Z**)	Yield [b](%)
1	DMA	A	--	12	98:02	10
2	Acetone:MeOH (1:1)	Ir-Cat	DMAP (0.4)	12	65:35	18
3	Acetone:MeOH (1:1)	A	DMAP (0.4)	12	70:30	26
4	Acetone	A	DMAP (0.4)	12	72:28	21
5	MeOH	A	DMAP (0.4)	12	75:25	25
6	DMA	A	PhLi (1.1)	12	91:09	35
7	ACN	A	PhLi (1.1)	12	92:08	24
8	MeOH	A	PhLi (1.1)	12	95:05	29
9	THF	A	PhLi (1.1)	12	40:60	19
10	DMF	A	PhLi (1.1)	12	92:08	32
11	dioxane	A	PhLi (1.1)	12	62:38	22
12	DMSO	A	PhLi (1.1)	12	90:10	16
13	DMA	A	PhLi (1.1)	12	91:09	30
14	DMA	--	F (1.1)	12	100:0	10
15	DMA	A	G (1.1)	12	99:01	19
16	DMA	A	H (1.1)	12	99:01	13
17	DMA	A	I (1.1)	12	12:88	9
18	DMA	A	J (1.1)	12	80:20	16
19	DMA	A	DMAP(1.1)	12	99:01	30
20	DMA	A	PPh_3 (1.1)	12	99:01	11
21	DMA	A	K_3PO_4 (1.1)	12	98:02	20
22	DMA	A	NaOMe (1.1)	12	92:08	38
23	DMA	A	NaO^{t}Bu (1.1)	12	97:03	52
24	DMA	A	Cs_2CO_3 (1.1)	12	94:06	26
25	DMA	A	NaO^{t}Bu (1.1)	6	100:0	39
26	DMA	A	NaO^{t}Bu (1.1)	18	99:01	72
27	DMA	A	NaO^{t}Bu (1.1)	24	99:01	50
28	DMA	A	NaO^{t}Bu (1.1)	18	100:0	48
19	DMA	B	NaO^{t}Bu (1.1)	12	--	--
30	DMA	C	NaO^{t}Bu (1.1)	12	100:0	12
31	DMA	D	NaO^{t}Bu (1.1)	12	--	--
32	DMA	E	NaO^{t}Bu (1.1)	12	--	--



0.1 M solvent w.r.t boronate ester. For the experiments from entry 2 to entry 14, the boronate complex made in Et_2O.

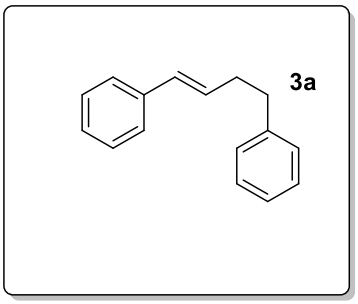
Aggarwal group also performed the deborylative radical initiation using phenyl lithium as activator. Hence in our reaction, we prepared boronate complex using PhLi and further screamed several solvents. Among them, DMA was found to be better yielding with an excellent *E*/*Z* ratio. Next to improve yield we have also screened other organo-lithium but none of them succeeded. Further we move to various organic and inorganic bases. Among them NaO^{t}Bu found to be best yielding. However, after the several alteration of various parameters such as catalyst, concentration, time etc, a combination of 1 equivalent each of boronate ester, sulfone, base, 5 mole% 4CzIPN in DMA (0.1 M) under blue light irradiation found to be optimal resulting the 72% as the isolated yield (*E*/*Z* = 99/01).

4(b): General procedure (4B):



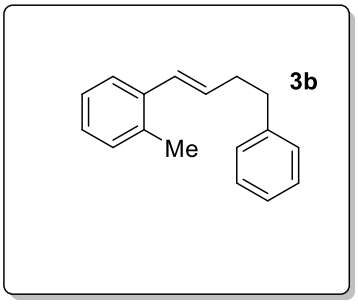
To a dry 20 mL vial equipped with a magnetic stir bar was added 4CzIPN (5 mol%), alkyl boronate ester (1 equiv), NaO^{t}Bu (1.1 equiv) and sulfone (1 equiv). The vial was sealed and then DMA (0.1 M w.r.t boronic acid) was added to the vial and the resulting mixture was degassed by freeze-pump-thaw under nitrogen (three times). Then, the vial was placed in a photo reactor and irradiated with Blue LED at rt for 18 h. After that the reaction mixture was diluted with H_2O and workup by using Et_2O. Purification by flash column chromatography or preparative TLC afforded the (*E*)-alkene.

4(c): Scope for the *E*-olefin from boronic acid:

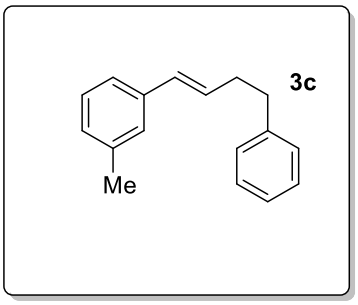


(*E*)-but-1-ene-1,4-diyldibenzene ($C_{16}H_{16}$) (3a):[ref-42] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 69% (*E*:*Z* = 95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.13 (m, 10H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.28 – 6.11 (m, 1H), 2.82 – 2.66 (m, 2H), 2.47 (dd, *J* = 14.9, 7.2 Hz,

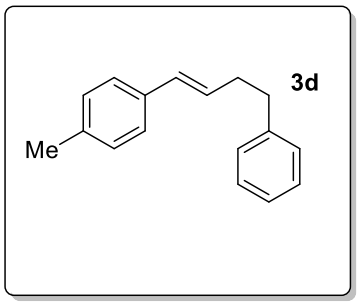
2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 141.92, 137.93, 130.57, 130.13, 128.63, 128.51, 127.08, 126.16, 126.04, , 36.04, 34.98.



(*E*)-1-methyl-2-(4-phenylbut-1-en-1-yl)benzene ($C_{17}H_{18}$) (3b):[ref-17] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (27 mg) 61% (*E*:*Z* = 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 6.96 (m, 15H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.38 (d, *J* = 11.3 Hz, 0.5H), 6.20 – 5.95 (m, 1H), 5.79 – 5.56 (m, 0.5H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 1H), 2.49 (dd, *J* = 14.5, 7.5 Hz, 2H), 2.44 – 2.37 (m, 1H), 2.21 (s, 3H), 2.13 (s, 1.5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.92, 137.09, 136.84, 135.16, 131.76, 131.43, 130.27, 129.89, 129.09, 128.87, 128.68, 128.61, 128.48, 128.41, 127.03, 126.97, 126.14, 126.01, 125.97, 125.73, 125.44, 36.11, 35.20, 19.89.

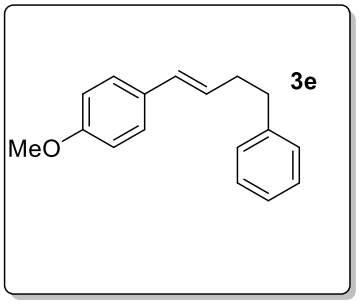


(*E*)-1-methyl-3-(4-phenylbut-1-en-1-yl)benzene ($C_{17}H_{18}$) (3c):[ref-17] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 65% (*E*:*Z* = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.07 (m, 9H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.08 (m, 1H), 2.79 – 2.65 (m, 2H), 2.45 (dd, *J* = 14.9, 7.1 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.97, 138.14, 137.87, 130.64, 129.92, 128.62, 128.54, 128.50, 127.88, 126.91, 126.02, 123.31, 36.07, 34.99, 21.53.

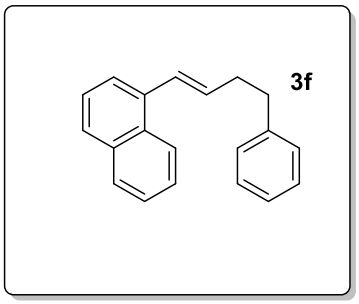


(*E*)-1-methyl-4-(4-phenylbut-1-en-1-yl)benzene ($C_{17}H_{18}$) (3d):[ref-17] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (30 mg) 67% (*E*:*Z* =

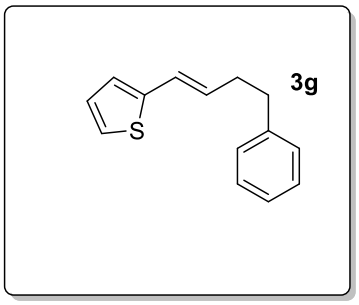
80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.10 (m, 9H), 6.31 (d, *J* = 15.6 Hz, 1H), 6.24 – 6.03 (m, 1H), 2.81 – 2.66 (m, 2H), 2.52 – 2.40 (m, 2H), 2.25 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.01, 136.78, 135.16, 131.27, 130.40, 129.33, 129.10, 128.63, 128.49, 126.05, 36.12, 34.99, 21.26.



(*E*)-1-methoxy-4-(4-phenylbut-1-en-1-yl)benzene ($C_{17}H_{18}O$) (3e):[ref-27] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 60% (*E*:*Z* = 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 7H), 6.77 (t, *J* = 6.9 Hz, 2H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.05 (dd, *J* = 14.7, 7.8 Hz, 1H), 3.72 (d, *J* = 2.0 Hz, 3H), 2.84 – 2.65 (m, 2H), 2.51 – 2.35 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.95, 142.04, 129.90, 128.62, 128.48, 127.98, 127.23, 125.99, 114.11, 113.77, 55.44, 36.20, 34.98.

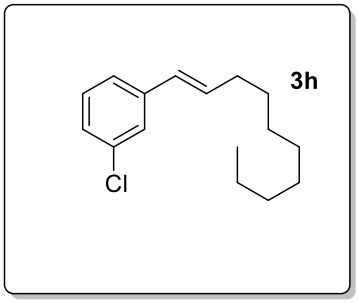


(*E*)-1-(4-phenylbut-1-en-1-yl)naphthalene ($C_{20}H_{18}$) (3f):[ref-28] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (35 mg) 69% (*E*:*Z* = 95:05). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 1H), 7.79 – 7.69 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.39 (p, *J* = 6.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.14 (t, *J* = 7.1 Hz, 1H), 7.02 (d, *J* = 15.6 Hz, 1H), 6.17 (dt, *J* = 15.3, 6.9 Hz, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.58 (dd, *J* = 14.7, 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.88, 135.79, 133.76, 133.34, 131.32, 128.74, 128.56, 128.54, 128.01, 127.48, 126.06, 125.92, 125.78, 124.17, 123.77, 36.04, 35.32.

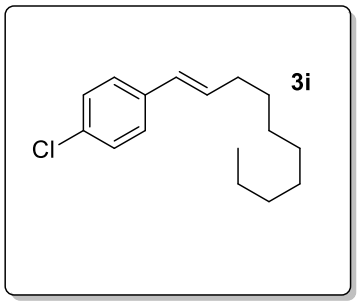


(*E*)-2-(4-phenylbut-1-en-1-yl)thiophene ($C_{14}H_{14}S$) (3g):[ref-29] Synthesized using general procedure **4B** (with 0.2 mmol of

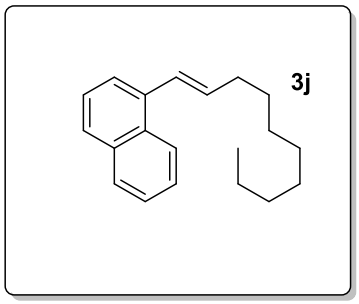
sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (29 mg) 68% (*E*:*Z* = 84:16). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.16 (m, 5H), 7.04 (d, *J* = 4.9 Hz, 1H), 6.88 (ddd, *J* = 28.7, 18.1, 4.0 Hz, 2H), 6.64 – 6.40 (m, 1H), 6.22 – 5.96 (m, 1H), 2.73 (dd, *J* = 14.4, 7.0 Hz, 2H), 2.56 – 2.31 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.09, 141.78, 130.11, 128.60, 128.53, 127.36, 126.08, 124.52, 123.80, 123.40, 35.91, 34.81.



(*E*)-1-chloro-3-(dec-1-en-1-yl)benzene ($C_{16}H_{23}Cl$) (3h):[ref-40] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (35 mg) 70% (*E*:*Z* = 96:04). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.18 (s, 1H), 7.12 (s, 1H), 7.08 (dd, *J* = 6.5, 2.2 Hz, 1H), 6.24 (d, *J* = 15.9 Hz, 1H), 6.20 – 6.11 (m, 1H), 2.13 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.38 (dd, *J* = 14.4, 7.0 Hz, 2H), 1.27 – 1.19 (m, 10H), 0.81 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.09, 134.60, 133.08, 129.80, 128.67, 126.82, 126.01, 124.31, 33.14, 32.04, 29.62, 29.42, 29.40, 29.38, 22.82, 14.22.

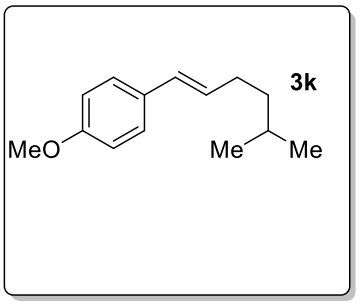


(*E*)-1-chloro-4-(dec-1-en-1-yl)benzene ($C_{16}H_{23}Cl$) (3i):[ref-19] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (36 mg) 72% (*E*:*Z* = 97:03). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 4.5 Hz, 4H), 6.25 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.7, 6.8 Hz, 1H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.39 (dt, *J* = 14.6, 7.2 Hz, 2H), 1.27 – 1.19 (m, 10H), 0.82 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.67, 132.44, 132.19, 128.73, 128.71, 127.27, 33.16, 32.04, 29.63, 29.45, 29.42, 29.40, 22.82, 14.22.

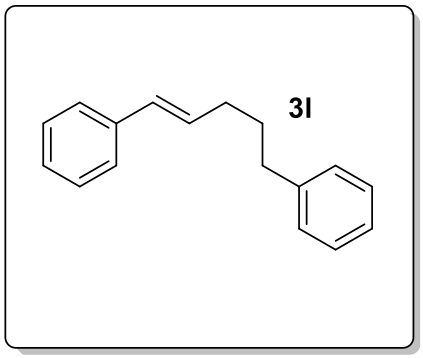


(*E*)-1-(dec-1-en-1-yl)naphthalene ($C_{20}H_{26}$) (3j):[ref-20] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5%

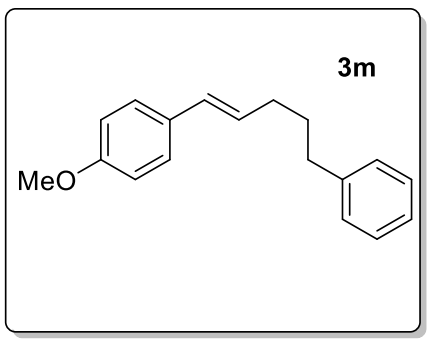
EtOAc/hexane), colourless liquid, yield (35 mg) 67% (*E*:*Z* = 95:05). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.37 (m, 4H), 7.12 (d, *J* = 15.4 Hz, 1H), 6.32 – 6.15 (m, 1H), 2.35 – 2.33 (m, 2H), 1.56 - 1.54 (m, 2H), 1.41 – 1.31 (m, 10H), 0.91 -0.90 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.01, 134.73, 133.83, 131.36, 128.60, 127.32, 127.08, 125.89, 125.81, 125.74, 124.16, 123.66, 33.60, 32.07, 29.67, 29.60, 29.48, 29.43, 22.84, 14.24.



(*E*)-1-methoxy-4-(5-methylhex-1-en-1-yl)benzene ($C_{14}H_{20}O$) (3k):[ref-30] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (25 mg) 62% (*E*:*Z* = 97:03). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.27 (d, *J* = 15.8 Hz, 1H), 6.19 – 5.91 (m, 1H), 3.74 (s, 3H), 2.13 (dd, *J* = 14.4, 6.7 Hz, 2H), 1.54 (dd, *J* = 13.4, 6.7 Hz, 1H), 1.28 (dd, *J* = 15.2, 7.0 Hz, 2H), 0.85 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.83, 131.08, 129.39, 129.08, 127.12, 114.11, 55.46, 38.88, 31.00, 27.71, 22.67.

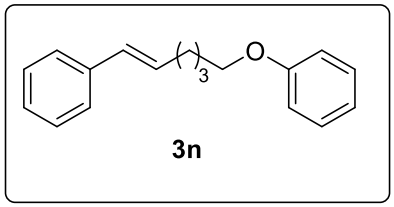


(2-cyclopentylethene-1,1-diyl)dibenzene ($C_{19}H_{20}$) (3l):[ref-31] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (31 mg) 71% (*E*:*Z* = 95:05). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 -7.12 (m, 10H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.18 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.18 (d, *J* = 6.7 Hz, 2H), 1.83 – 1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.54, 137.96, 130.70, 130.37, 128.62, 128.45, 128.38, 127.00, 126.08, 125.87, 35.54, 32.68, 31.17.

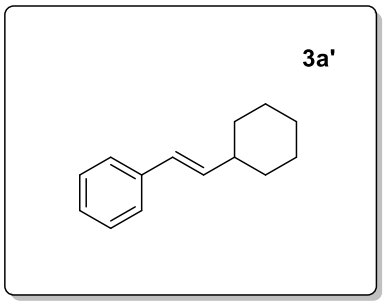


(2-cyclopentylethene-1,1-diyl)dibenzene ($C_{19}H_{20}$) (3m):[ref-32] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (34 mg)

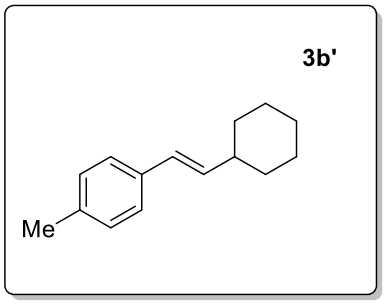
68% (*E*:*Z* = 92:08). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 5H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.26 (d, *J* = 15.8 Hz, 1H), 6.02 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.73 (s, 3H), 2.68 – 2.51 (m, 2H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.79 – 1.65 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.91, 142.61, 130.91, 129.76, 128.63, 128.56, 128.44, 127.17, 125.85, 114.13, 55.46, 35.57, 32.66, 31.30.



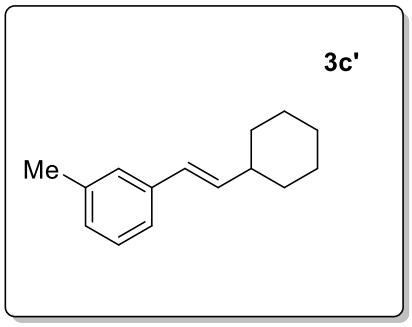
(*E*)-(6-phenoxyhex-1-en-1-yl)benzene ($C_{18}H_{20}O$) (3n): Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (36 mg) 73% (*E*:*Z* = 98:02). IR (Neat) cm^{-1} : 3029, 2954, 2913, 2851, 1710, 1602, 1451, 1368, 1262, 1167, 1101, 1017, 964. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.94 (dd, *J* = 15.0, 7.8 Hz, 3H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.30 – 6.20 (m, 1H), 4.00 (t, *J* = 6.4 Hz, 2H), 2.31 (q, *J* = 7.2 Hz, 2H), 1.87 (dd, *J* = 14.3, 7.4 Hz, 2H), 1.72 – 1.63 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.25, 137.94, 130.62, 130.42, 129.56, 128.63, 127.02, 126.10, 120.68, 114.69, 67.80, 32.83, 28.98, 25.98. $[M+H]^+$ calculated for $C_{27}H_{34}O_2$ is 252.1514 and found 252.1512.



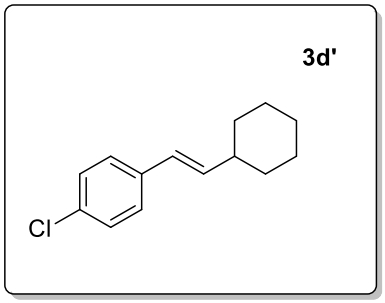
(*E*)-(2-cyclohexylvinyl)benzene ($C_{14}H_{18}$) (3a'):[ref-21] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (27 mg) 72% (*E*:*Z* = 99:01). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.26 (dd, *J* = 16.1, 8.5 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.19 – 2.03 (m, 1H), 1.77 (ddd, *J* = 12.4, 11.2, 8.4 Hz, 4H), 1.69 – 1.61 (m, 1H), 1.36 – 1.27 (m, 2H), 1.22 – 1.12 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.30, 137.00, 128.59, 127.47, 126.87, 126.12, 41.30, 33.16, 26.37, 26.22.



(*E*)-1-(2-cyclohexylvinyl)-4-methylbenzene ($C_{15}H_{20}$) (3b'):[ref-21] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (29 mg) 73% (*E*:*Z* = 80:20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 2H), 7.07 (q, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.23 (d, *J* = 16.0 Hz, 1H), 6.04 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.24 (s, 3H), 2.09 – 1.99 (m, 1H), 1.69 (dd, *J* = 25.7, 8.7 Hz, 4H), 1.30 – 1.19 (m, 2H), 1.17 – 1.04 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.53, 136.01, 129.29, 128.68, 127.24, 126.00, 41.27, 33.20, 26.38, 26.24, 21.24.

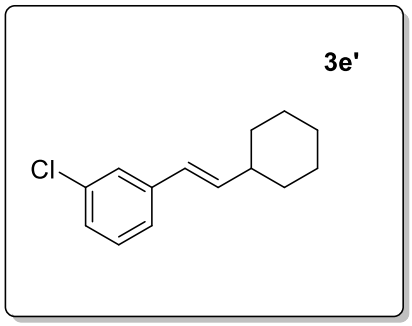


(*E*)-1-(2-cyclohexylvinyl)-3-methylbenzene ($C_{15}H_{20}$) (3c'):[ref-39] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (27 mg) 69% (*E*:*Z* = 93:07). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 3H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.34 (s, 3H), 2.12 (d, *J* = 4.0 Hz, 1H), 1.79 (t, *J* = 15.4 Hz, 4H), 1.69 (d, *J* = 12.8 Hz, 1H), 1.38 – 1.28 (m, 2H), 1.25 – 1.10 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.22, 137.10, 135.82, 127.51, 126.67, 126.49, 125.81, 122.29, 40.31, 32.17, 25.37, 25.22, 20.53.

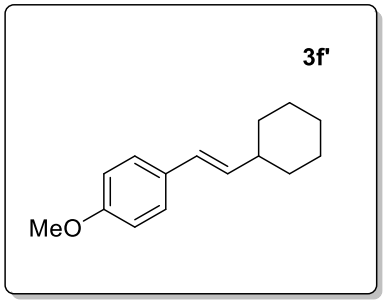


(*E*)-1-chloro-4-(2-cyclohexylvinyl)benzene ($C_{14}H_{17}Cl$) (3d'):[ref-21] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (29 mg) 66% (*E*:*Z* = 88:12). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 4H), 6.21 (d, *J* = 16.0 Hz, 1H), 6.07 (dd, *J* = 15.9, 6.8 Hz, 1H), 2.10 – 2.01

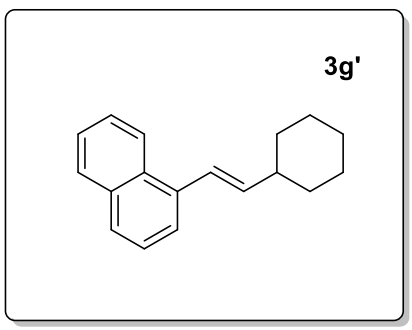
(m, 1H), 1.71 (t, *J* = 13.9 Hz, 4H), 1.61 (d, *J* = 12.6 Hz, 1H), 1.29 – 1.19 (m, 2H), 1.11 (dt, *J* = 22.0, 11.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.72, 136.79, 132.42, 128.71, 127.31, 126.31, 41.27, 33.05, 26.31, 26.17.



(*E*)-1-chloro-3-(2-cyclohexylvinyl)benzene ($C_{14}H_{17}Cl$) (3e'):[ref-21] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 64% (*E*:*Z* = 79:21). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.22 (dd, *J* = 15.4, 4.4 Hz, 2H), 7.17 – 7.09 (m, 1H), 6.27 (t, *J* = 11.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 6.7 Hz, 1H), 2.19 – 2.06 (m, 1H), 1.78 (dd, *J* = 18.5, 8.0 Hz, 3H), 1.69 (d, *J* = 17.1 Hz, 2H), 1.30 (dd, *J* = 20.3, 7.7 Hz, 2H), 1.23 – 1.16 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.21, 138.58, 134.58, 129.78, 126.80, 126.27, 126.03, 124.38, 41.27, 33.00, 26.30, 26.15.

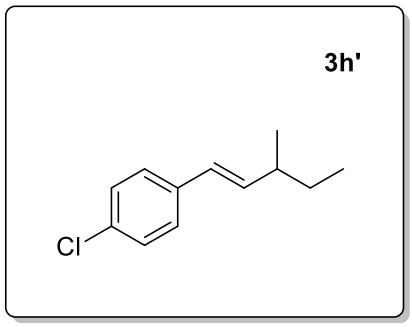


(*E*)-1-(2-cyclohexylvinyl)-4-methoxybenzene ($C_{15}H_{20}O$) (3f'):[ref-21] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (26 mg) 61% (*E*:*Z* = 93:07). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.8, 1.9 Hz, 2H), 6.86 – 6.79 (m, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.79 (s, 3H), 2.10 (dtd, *J* = 10.4, 7.2, 3.4 Hz, 1H), 1.85 – 1.71 (m, 4H), 1.67 (ddd, *J* = 9.3, 3.3, 1.7 Hz, 1H), 1.38 – 1.26 (m, 2H), 1.24 – 1.10 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.82, 134.97, 131.14, 127.16, 126.76, 114.10, 55.45, 41.26, 33.28, 26.38, 26.25.



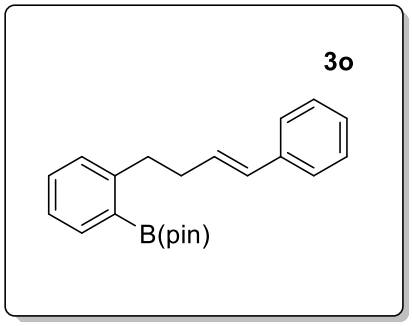
(*E*)-1-(2-cyclohexylvinyl)naphthalene ($C_{18}H_{20}$) (3g'):[ref-22] Synthesized using general procedure **4B** (with 0.2 mmol of

sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (33 mg) 70% (*E*:*Z* = 88:12). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 15.7 Hz, 1H), 6.20 (dd, *J* = 15.7, 6.9 Hz, 1H), 2.31 – 2.24 (m, 1H), 1.91 (d, *J* = 12.8 Hz, 2H), 1.88 – 1.77 (m, 2H), 1.72 (d, *J* = 12.7 Hz, 1H), 1.43 – 1.33 (m, 2H), 1.26 (dd, *J* = 15.7, 9.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.37, 136.11, 133.83, 131.43, 128.60, 127.29, 125.86, 125.80, 125.73, 124.59, 124.14, 123.60, 41.69, 33.24, 26.40, 26.24.

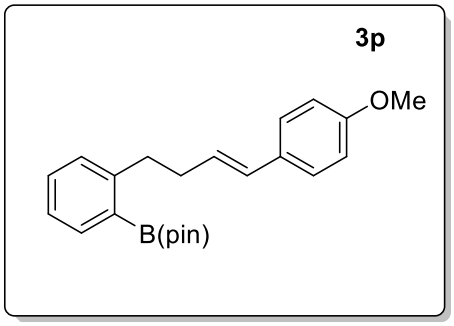


(*E*)-1-chloro-4-(3-methylpent-1-en-1-yl)benzene ($C_{12}H_{15}Cl$) (3h'):[ref-33] Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (26 mg) 68% (*E*:*Z* = 81:19). ^{1}H NMR (500 MHz,) δ 7.19 (d, *J* = 8.2 Hz, 4H), 6.24 (d, *J* = 15.9 Hz, 1H), 6.18 – 6.04 (m, 1H), 2.02 (t, *J* = 6.9 Hz, 2H), 1.66 (dt, *J* = 13.2, 6.6 Hz, 1H), 0.87 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.63, 132.49, 130.82, 129.83, 128.74, 127.30, 42.52, 29.85, 28.71, 22.51.

4(d): Chemoselective transformation:



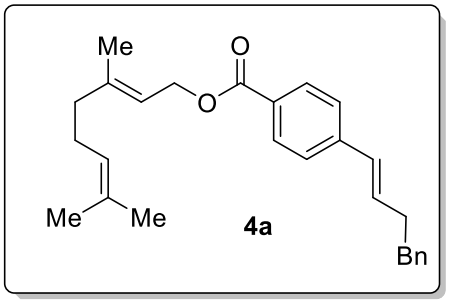
(*E*)-4,4,5,5-tetramethyl-2-(2-(4-phenylbut-3-en-1-yl)phenyl)-1,3,2-dioxaborolane ($C_{22}H_{27}BO_2$) (b18): Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (48 mg) 72% (*E*:*Z* = 91:09). IR (Neat) cm^{-1} : 3051, 2928, 2842, 1735, 1602, 1464, 1307, 1248, 1174, 1115, 1025. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.9 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.17 (m, 3H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.7, 6.8 Hz, 1H), 3.13 – 2.98 (m, 2H), 2.48 (dd, *J* = 15.2, 7.2 Hz, 2H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.02, 138.23, 136.33, 131.04, 130.97, 130.06, 129.43, 128.59, 126.90, 126.13, 125.32, 83.62, 36.80, 36.06, 25.07. $[M+K]^+$ calculated for $C_{22}H_{27}BO_2$ is 373.1736 and found 373.1681.



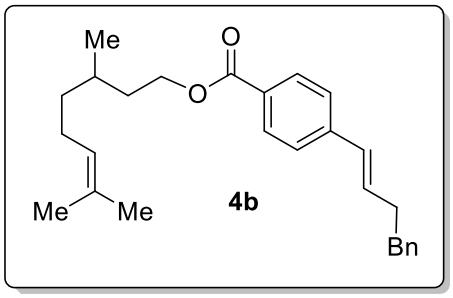
(E)-2-(2-(4-(4-methoxyphenyl)but-3-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ($C_{23}H_{29}BO_3$) (3p): Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (49 mg) 67% (*E*:*Z* = 93:07). IR (Neat) cm^{-1}: 3051, 2928, 2842, 1735, 1602, 1464, 1307, 1248, 1174, 1115, 1025. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.24 (m, 1H), 7.20 (s, 2H), 7.16 – 7.08 (m, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.27 (d, *J* = 15.6 Hz, 1H), 6.22 – 5.91 (m, 1H), 3.72 (s, 3H), 3.10 –

2.88 (m, 2H), 2.36 (d, *J* = 7.0 Hz, 2H), 1.26 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.86, 149.13, 136.29, 131.02, 129.44, 129.40, 128.85, 128.33, 128.17, 127.20, 125.28, 114.11, 83.62, 55.46, 36.80, 36.22, 25.07. $[M+Na]^+$ calculated for $C_{23}H_{29}BO_3$ is 387.2102 and found 387.2004.

5. Scope for the bioactive molecules functionalization:

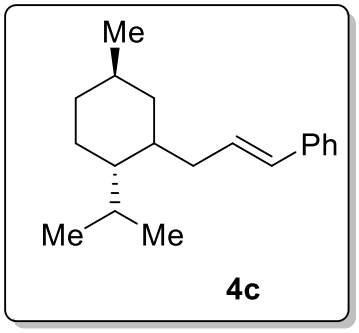


(*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-((E)-4-phenylbut-1-en-1-yl)benzoate ($C_{27}H_{32}O_2$) (4a): Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (50 mg) 65% (*E*:*Z* = 92:08). IR (Neat) cm^{-1}: 3050, 2966, 2920, 2864, 1710, 1600, 1441, 1368, 1251, 1167, 1113, 1010, 957. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 14.7, 8.9 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.17 (m, 6H), 6.48 – 6.36 (m, 1H), 5.47 (t, *J* = 6.4 Hz, 1H), 5.09 (d, *J* = 6.1 Hz, 1H), 4.83 (d, *J* = 6.8 Hz, 2H), 2.86 – 2.72 (m, 2H), 2.71 – 2.50 (m, 2H), 2.10 (d, *J* = 11.7 Hz, 4H), 1.76 (s, 3H), 1.68 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.67, 142.37, 142.27, 141.64, 132.92, 131.97, 130.06, 129.91, 129.64, 128.59, 128.55, 126.14, 125.93, 123.94, 118.69, 61.94, 39.71, 35.78, 35.05, 26.49, 25.80, 17.84, 16.70. $[M+H]^+$ calculated for $C_{27}H_{32}O_2$ is 389.2475 and found 389.2454.

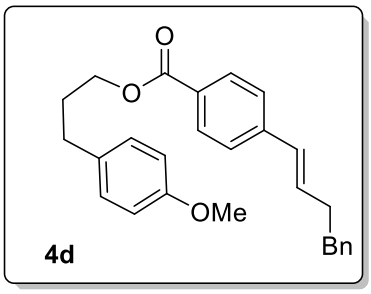


3,7-dimethyloct-6-en-1-yl (E)-4-(4-phenylbut-1-en-1-yl)benzoate ($C_{27}H_{34}O_2$) (4b): Synthesized using general procedure **4B** (Here we used the racemic Citronellol CAS: 106-22-9)(with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (51 mg) 66% (*E*:*Z* = 93:07). IR (Neat) cm^{-1} : 3027, 2956, 2923, 2854, 1714, 1606, 1453, 1378, 1261, 1177, 1103, 1017, 967. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 11.6 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.40 (dd, *J* = 12.2, 6.3 Hz, 1H), 5.10 (s, 1H), 4.34 (d, *J* = 3.3 Hz, 2H), 2.79 (dd, *J* = 18.1, 10.4 Hz, 2H), 2.56 (dd, *J* = 14.1, 7.0 Hz, 2H), 2.00 (d, *J* = 8.3 Hz, 2H), 1.83 – 1.75 (m, 1H), 1.67 (s, 3H), 1.56 (s, 3H), 1.45 – 1.35 (m, 2H), 1.25 – 1.15 (m, 2H), 0.96 (s, 3H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 166.72, 142.25, 141.62, 132.95, 131.53, 129.99, 129.86, 128.95, 128.59, 128.55, 126.13, 125.94, 124.73, 63.55, 37.15, 35.78, 35.68, 35.08, 29.73, 25.86, 25.56, 19.67, 17.82. $[M+H]^+$ calculated for $C_{27}H_{34}O_2$ is 391.2632 and found 391.2644.

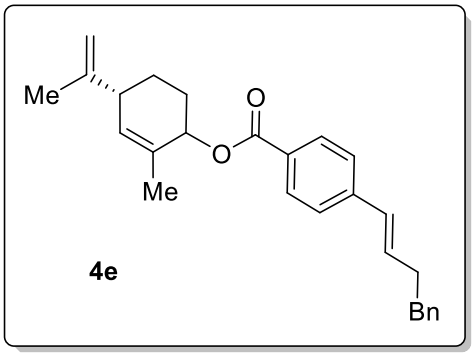


(±)-((*E*)-3-((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)prop-1-en-1-yl)benzene ($C_{19}H_{28}$) (4c): Synthesized using general procedure **4B** (Here we used racemic Menthol CAS: 89-78-1) (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (40 mg) 78% (*E*:*Z* = 94:06). IR (Neat) cm^{-1} : 3022, 2964, 2922, 2878, 2853, 1608, 1498, 1454, 1382, 1319, 1283, 1250, 1153, 1108, 1018, 963. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 4H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.29 (d, *J* = 15.6 Hz, 1H), 6.23 – 5.90 (m, 1H), 2.26 – 1.74 (m, 3H), 1.62 (dd, *J* = 34.3, 20.2 Hz, 2H), 1.39 – 1.23 (m, 3H), 0.89 – 0.58 (m, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.24, 131.19, 129.66, 128.62, 126.88, 126.10, 46.69, 41.74, 39.66, 36.73, 35.55, 33.04, 26.73, 24.58, 22.86, 21.72, 15.46. $[M+H]^+$ calculated for $C_{19}H_{28}$ is 257.2264 and found 257.2297.

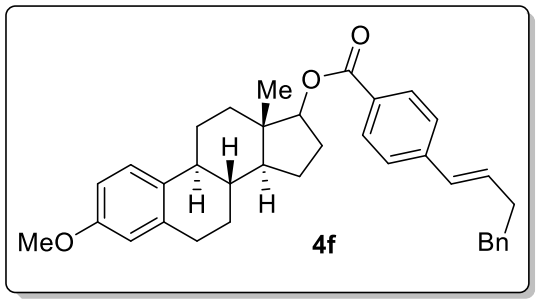


3-(4-methoxyphenyl)propyl (*E*)-4-(4-phenylbut-1-en-1-yl)benzoate ($C_{27}H_{28}O_3$) (4d): Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (59 mg) 71% (*E*:*Z* = 93:07). IR (Neat) cm^{-1} : 3027, 2956, 2931, 2856, 1712, 1607, 1512, 1454, 1270, 1251, 1177, 1105, 1035, 968. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 3H), 7.13 (d, *J* = 8.1 Hz, 3H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.41 (dd, *J* = 11.9, 6.0 Hz, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.85 – 2.75 (m, 2H), 2.75 – 2.64 (m, 3H), 2.56 (dd, *J* = 14.0, 6.9 Hz, 1H), 2.10 – 2.02 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.62, 158.13, 142.37, 141.63, 134.04, 133.45, 133.02, 130.03, 129.89, 129.49, 128.60, 128.56,

126.15, 125.98, 114.09, 64.31, 55.42, 35.78, 35.04, 31.56, 30.70. $[M+H]^+$ calculated for $C_{27}H_{28}O_3$ is 401.2111 and found 401.2093.

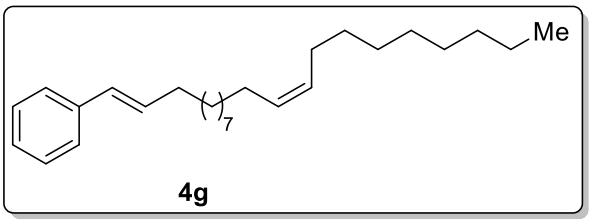


(4*R*)-2-methyl-4-(prop-1-en-2-yl)cyclohex-2-en-1-yl 4-((*E*)-4-phenylbut-1-en-1-yl)benzoate ($C_{27}H_{30}O_2$) (4e): Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (51 mg) 66% (*E*:*Z* = 88:12), $[\alpha]_D^{25}$ -120 (c 0.33, DCM). IR (Neat) cm^{-1} : 3026, 2975, 2923, 2854, 1711, 1606, 1495, 1453, 1269, 1177, 1102, 1016, 967. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 1H), 7.49 – 7.37 (m, 2H), 7.32 – 7.24 (m, 4H), 7.25 – 7.07 (m, 3H), 6.50 – 6.34 (m, 1H), 5.67 (brs, 2H), 4.74 (brs, 2H), 2.86 – 2.76 (m, 1H), 2.66 – 2.53 (m, 2H), 2.44 – 2.28 (m, 2H), 2.17 – 2.03 (m, 2H), 1.80 – 1.61 (m, 7H), 1.28 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.45, 148.47, 142.40, 141.63, 134.04, 133.38, 133.03, 130.08, 129.89, 129.66, 128.60, 128.56, 126.09, 125.99, 109.53, 73.84, 40.46, 35.78, 35.06, 34.23, 30.99, 20.67, 19.14. $[M+H]^+$ calculated for $C_{27}H_{30}O_2$ is 387.2319 and found 387.2296..



(8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl 4-((*E*)-4-phenylbut-1-en-1-yl)benzoate ($C_{36}H_{40}O_3$) (4f): Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (64 mg) 62% (*E*:*Z* = 82:18), $[\alpha]_D^{25}$ +309 (c 0.07, DCM). IR (Neat) cm^{-1} : 3024, 2926, 2890, 2853, 1712, 1607, 1499, 1453, 1305, 1281, 1138, 1120, 1037, 981. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 7.6 Hz, 2H), 7.50 – 7.26 (m, 5H), 7.23 – 7.07 (m, 4H), 6.68 (dd, *J* = 29.5, 4.4 Hz, 2H), 6.50 – 6.37 (m, 1H), 4.92 (s, 1H), 3.78 (s, 3H), 2.90 – 2.76 (m, 3H), 2.61 (dd, *J* = 36.6, 8.0 Hz, 2H), 2.38 – 2.22 (m, 3H),

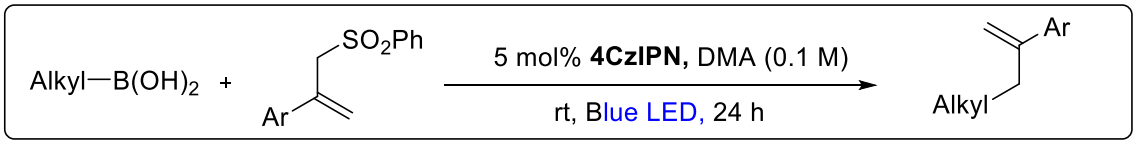
2.00 – 1.87 (m, 2H), 1.83 – 1.64 (m, 2H), 1.52 – 1.48 (m, 4H), 1.38 (brs, 2H), 1.26 (brs, 1H), 0.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.58, 157.69, 142.30, 141.64, 138.07, 134.00, 132.95, 132.72, 130.00, 129.59, 128.61, 128.56, 126.51, 126.14, 125.97, 114.02, 111.68, 83.30, 55.37, 50.06, 44.01, 43.55, 38.84, 37.22, 35.79, 35.05, 29.97, 27.97, 27.44, 26.43, 23.59, 12.52. $[M+H]^+$ calculated for $C_{36}H_{40}O_3$ is 521.3050 and found 521.3018.



((1*E*,12*Z*)-henicosa-1,12-dien-1-yl)benzene ($C_{27}H_{44}$) (4g): Synthesized using general procedure **4B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (53 mg) 70% (*E*:*Z* = 84:16). IR (Neat) cm^{-1} : 3022, 2963, 2931, 2853, 1601, 1464, 1349, 1273, 1178, 1072, 1027, 964. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.9 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.12 (dd, *J* = 14.4, 7.3 Hz, 1H), 6.40 – 6.26 (m, 1H), 6.21 – 6.07 (m, 1H), 5.37 – 5.19 (m, 2H), 2.14 – 2.10 (m, 1H), 1.94 (d, *J* = 5.5 Hz, 4H), 1.38 (dd, *J* = 14.5, 7.0 Hz, 2H), 1.30 – 1.18 (m, 23H), 0.81 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.20, 133.40, 131.40, 130.10, 128.61, 128.24, 126.89, 126.08, 33.19, 32.07, 30.14, 29.94, 29.93, 29.68, 29.66, 29.56, 29.49, 29.47, 29.44, 29.39, 28.79, 27.39, 22.83, 14.23. . $[M+K]^+$ calculated for $C_{27}H_{44}$ is 407.3075 and found 407.2942.

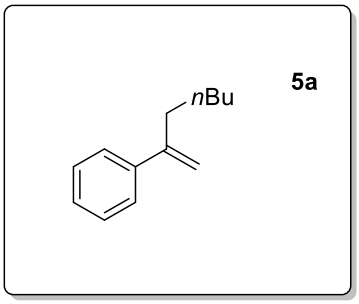
6. Scope for the allylation:

6(a): General procedure (6A):

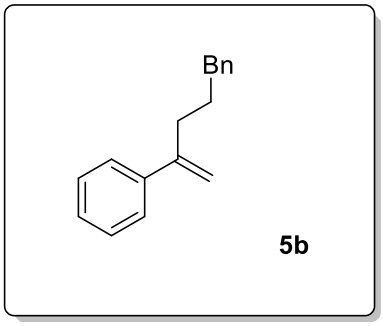


To a dry 20 mL vial equipped with a magnetic stir bar was added 4CzIPN (5 mol%), alkyl boronic acid (2 equiv) and sulfone (1 equiv). The vial was sealed and then DMA (0.1 M w.r.t boronic acid) was added to the vial and the resulting mixture was degassed by freeze-pump-thaw under nitrogen (three times). Then, the vial was placed in a photo reactor and irradiated with Blue LED at rt for 24 h. After that the reaction mixture was diluted with H_2O and workup by

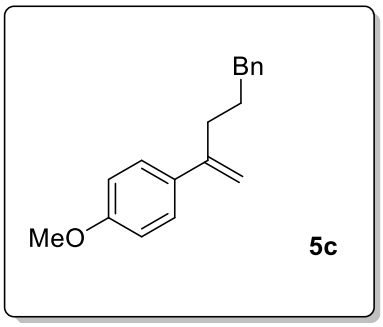
using Et_2O. Purification by flash column chromatography or preparative TLC afforded the allylated product.



Hept-1-en-2-ylbenzene ($C_{13}H_{18}$) (5a):[ref-43] Synthesized using general procedure **6A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (18 mg) 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.24 (dd, *J* = 9.9, 4.8 Hz, 2H), 7.21 – 7.15 (m, 1H), 5.18 (s, 1H), 4.97 (d, *J* = 1.2 Hz, 1H), 2.41 (t, *J* = 7.6 Hz, 2H), 1.36 (d, *J* = 7.7 Hz, 2H), 1.29 – 1.19 (m, 4H), 0.79 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.93, 141.62, 128.35, 127.36, 126.25, 112.13, 35.46, 31.72, 28.10, 22.64, 14.21.

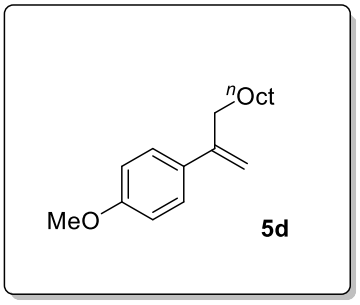


Pent-4-ene-1,4-diyldibenzene ($C_{17}H_{18}$) (5b):[ref-44] Synthesized using general procedure **6A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (30 mg) 69%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.3, 5.8 Hz, 2H), 7.31 (dd, *J* = 10.1, 4.8 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.15 (dd, *J* = 11.0, 7.2 Hz, 3H), 5.27 (s, 1H), 5.06 (d, *J* = 1.3 Hz, 1H), 2.68 – 2.60 (m, 2H), 2.54 (t, *J* = 7.3 Hz, 2H), 1.85 – 1.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.59, 142.48, 141.55, 128.61, 128.42, 128.41, 127.46, 126.32, 125.87, 112.55, 35.61, 35.06, 30.04.

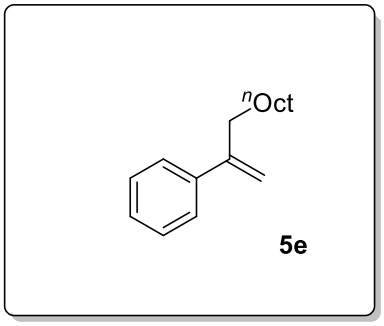


1-methoxy-4-(5-phenylpent-1-en-2-yl)benzene ($C_{18}H_{20}O$) (5c):[ref-44] Synthesized using general procedure **6A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (29 mg) 63%.^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34 – 7.23 (m, 4H), 7.15 (d, *J* = 6.9 Hz, 3H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.21 (s, 1H), 4.99 (s,

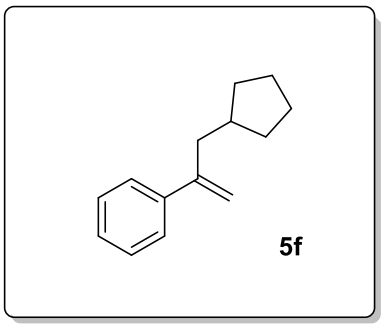
1H), 3.81 (d, *J* = 2.3 Hz, 3H), 2.64 (t, *J* = 7.1 Hz, 2H), 2.50 (d, *J* = 6.7 Hz, 2H), 1.83 – 1.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 159.14, 147.73, 142.51, 133.83, 128.61, 128.40, 127.33, 125.84, 113.76, 111.07, 55.42, 35.59, 35.04, 30.07.



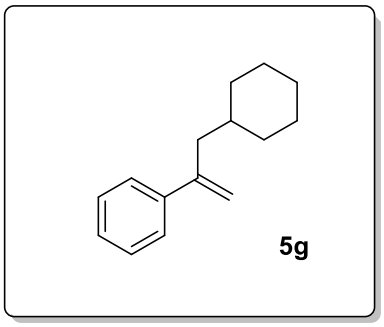
1-methoxy-4-(undec-1-en-2-yl)benzene ($C_{18}H_{28}O$) (5d): Synthesized using general procedure **6A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (37 mg) 72%. IR (Neat) cm^{-1} : 3025, 2970, 2921, 2864, 1600, 1491, 1463, 1261, 1170, 1100, 1011, 961. ^{1}H NMR (400 MHz,) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.89 – 6.84 (m, 2H), 5.18 (d, *J* = 1.3 Hz, 1H), 4.96 (d, *J* = 1.0 Hz, 1H), 3.81 (s, 3H), 2.51 – 2.40 (m, 2H), 1.45 – 1.39 (m, 2H), 1.26 (d, *J* = 11.5 Hz, 12H), 0.86 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.58, 136.94, 133.97, 127.46, 126.74, 113.72, 55.47, 32.07, 29.89, 29.72, 29.59, 29.47, 28.93, 22.83, 15.95, 14.23. $[M+H]^+$ calculated for $C_{18}H_{28}O$ is 261.2213 and found 261.2205.



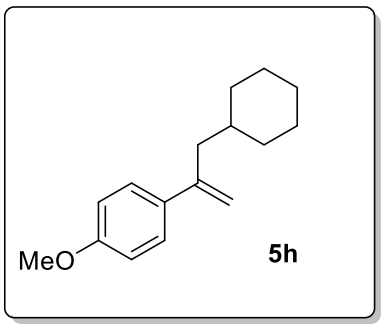
Undec-1-en-2-ylbenzene ($C_{17}H_{26}$) (5e):[ref-45] Synthesized using general procedure **6A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (35 mg) 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.19 (d, *J* = 2.2 Hz, 1H), 5.17 (s, 1H), 4.97 (s, 1H), 2.45 – 2.37 (m, 2H), 1.36 (s, 2H), 1.16 (s, 14H), 0.80 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.94, 141.62, 128.35, 127.36, 126.25, 112.13, 35.50, 32.03, 29.71, 29.60, 29.50, 29.45, 28.41, 22.82, 14.27.



(3-cyclopentylprop-1-en-2-yl)benzene ($C_{14}H_{18}$) (5f):[ref-46] Synthesized using general procedure **6A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (26 mg) 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.25 (dd, *J* = 9.4, 4.9 Hz, 2H), 7.21 – 7.16 (m, 1H), 5.15 (s, 1H), 4.97 (s, 1H), 2.43 (d, *J* = 7.3 Hz, 2H), 1.84 (dt, *J* = 15.1, 7.6 Hz, 1H), 1.67 – 1.56 (m, 2H), 1.53 – 1.47 (m, 2H), 1.43 – 1.33 (m, 2H), 1.07 (dd, *J* = 11.7, 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.59, 141.76, 128.32, 127.33, 126.40, 112.90, 42.13, 38.31, 32.56, 25.20.



(3-cyclohexylprop-1-en-2-yl)benzene ($C_{15}H_{20}$) (5g):[ref-47] Synthesized using general procedure **6A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (30 mg) 74%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.25 (ddd, *J* = 7.3, 3.9, 1.2 Hz, 1H), 5.25 (d, *J* = 1.8 Hz, 1H), 5.00 (s, 1H), 2.39 (d, *J* = 7.1 Hz, 2H), 1.70 – 1.59 (m, 5H), 1.38 – 1.30 (m, 1H), 1.14 – 1.10 (m, 3H), 0.91 – 0.85 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.42, 141.79, 128.35, 127.32, 126.42, 113.52, 43.81, 35.99, 33.43, 26.75, 26.37.

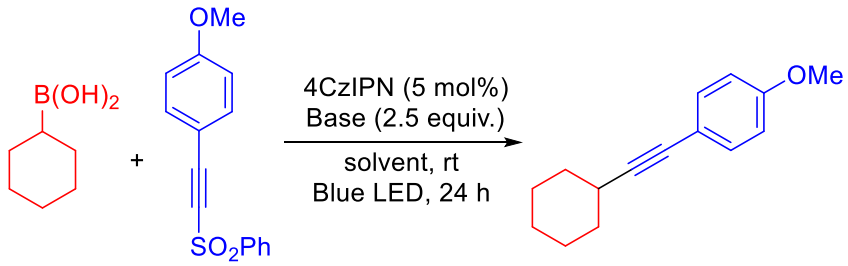


1-(3-cyclohexylprop-1-en-2-yl)-4-methoxybenzene ($C_{16}H_{22}O$) (5h):[ref-48] Synthesized using general procedure **6A** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (36 mg) 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 6.7 Hz, 2H), 6.88 (d, *J* = 6.8 Hz, 2H), 5.22 (s, 1H), 4.94 (s, 1H), 3.87 – 3.83 (m, 3H), 2.38 (d, *J* = 6.4 Hz, 2H), 1.76 – 1.63 (m, 5H), 1.34 (d, *J* = 3.6 Hz, 1H), 1.15 (s, 3H), 0.90 (d, *J* = 11.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.12, 146.66, 134.19, 127.47, 113.77, 112.02, 55.41, 43.87, 36.02, 33.44, 26.76, 26.39.

7. Scope for the alkynylation:

7(a): Optimization:

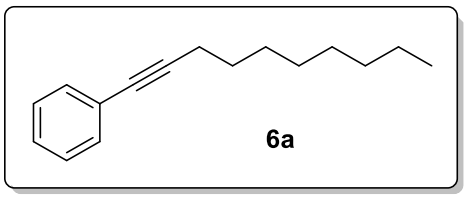
Table 3: Optimization for alkynylation:



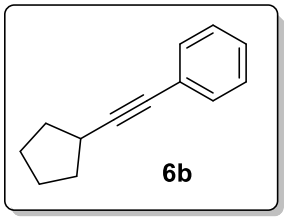
Entry	Addiitve	Solvent	Yield
1	none	Dioxane	--
2	none	DMA	12%
3	none	MeCN	--
4	none	Dioxane:MeCN (1:1)	--
5	NaOMe	DMF	9%
6	NaOMe	DMA	21%
7	NaOMe	Dioxane	66%
8	NaOMe	Dioxane, no 4CzIPN	n.r.

7(b) General Procedure (7B):

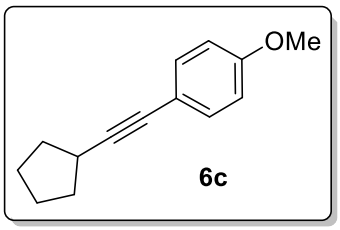
To a dry 20 mL vial equipped with a stir bar was added alkyl boronic acid (0.4 mmol, 2 equiv.), sodium methoxide (2.5 equiv.), alkynyl sulfone (1.0 equiv.) and 4CzIPN (5 mol%). The vial was sealed and then 1,4-dioxane (0.1 M) was added to the vial and the resulting mixture was degassed by freeze-pump-thaw under nitrogen (three times). Then, the vial was placed in a photo reactor and irradiated with Blue LED bulb (λ = 427 nm) for 24 h. After the complete consumption, the reaction mixture was diluted with H_2O and workup by using Et_2O. Purification by flash column chromatography or preparative TLC afforded the alkynylated product.



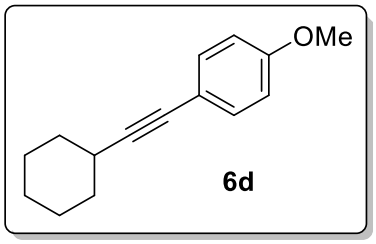
Dec-1-yn-1-ylbenzene ($C_{16}H_{22}$) (6a):[ref-49] Synthesized using general procedure **7B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (30 mg) 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.29 – 7.25 (m, 3H), 2.39 (t, *J* = 7.0 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.37 – 1.24 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.72, 128.31, 127.57, 124.37, 90.65, 80.76, 32.01, 29.36, 29.29, 29.10, 28.96, 22.81, 19.59, 14.21.



(cyclopentylethynyl)benzene ($C_{13}H_{14}$) (6b):[ref-50] Synthesized using general procedure **7B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (22 mg) 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 9.3 Hz, 2H), 7.28 – 7.24 (m, 3H), 2.82 (p, *J* = 7.4 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.78 -1.73 (m, 2H), 1.72 - 1.67 (m, 2H), 1.61 - 1.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.67, 128.28, 127.52, 124.28, 94.75, 80.17, 34.06, 30.92, 25.19.

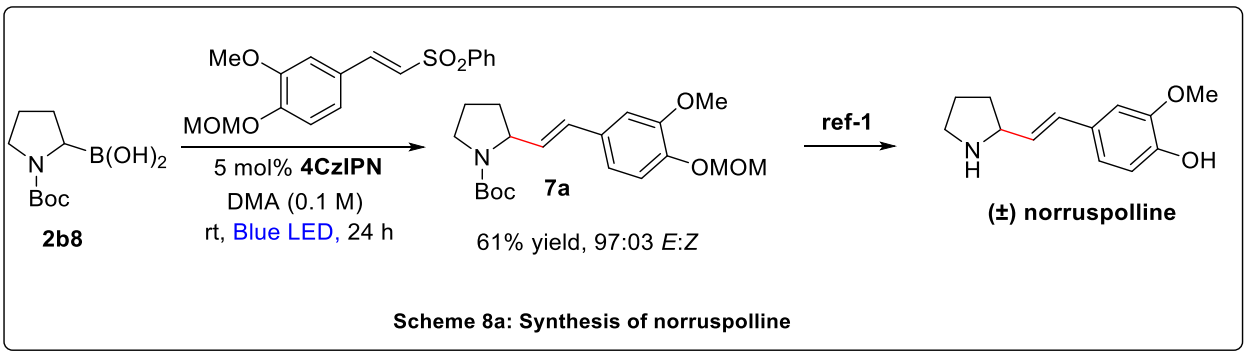


1-(cyclopentylethynyl)-4-methoxybenzene ($C_{14}H_{16}O$) (6c):[ref-51] Synthesized using general procedure **7B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (26 mg) 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.80 (p, *J* = 7.4 Hz, 1H), 1.99 - 1.97 (m, 2H), 1.76 - 1.73 (m, 2H), 1.72 – 1.62 (m, 2H), 1.21 - 1.17 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.05, 132.98, 116.45, 113.90, 93.07, 79.85, 55.39, 34.12, 30.95, 25.18.



1-(cyclohexylethynyl)-4-methoxybenzene ($C_{15}H_{18}O$) (6d): [ref-52] Synthesized using general procedure **7B** (with 0.2 mmol of sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.58 -2.53 (m, 1H), 1.87 - 1.85 (m, 2H), 1.75 - 1.73 (m, 2H), 1.34 - 1.33 (m, 3H), 1.20 - 1.17 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.06, 133.02, 116.43, 113.89, 93.00, 80.27, 55.40, 32.98, 29.83, 26.80, 26.09, 25.11, 24.69.

8. Drug molecule synthesis:[ref-1:]



Scheme 8a: Synthesis of norruspolline

Here **7a** has been prepared following the general procedure **3B**, using (*E*)-2-methoxy-1-(methoxymethoxy)-4-(2-(phenylsulfonyl)vinyl)benzene (1.00 equiv, 0.30 mmol), **2b8** (100 mg, 0.60 mmol, 2 equiv.). After 24 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure **3B**. Combined organic layers are concentrated and purification was performed by preparative TLC using 14:1 hexane: EtOAc provided the title compound **7a**

(58 mg, 61%, *E:Z* = 97:03) as a yellow liquid. IR (Neat) cm^{-1} : 3523, 3384, 3186, 3066, 2967, 2928, 2867, 1677, 1589, 1514, 1446, 1400, 1138, 1083, 1033, 961, 843. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.2 Hz, 1H), 6.92 – 6.78 (m, 2H), 6.33 – 6.29 (m, 1H), 5.97 (brs, 1H), 5.21 (s, 2H), 4.37 (brs, 1H), 3.89 (s, 3H), 3.50 - 3.45 (m, 5H), 2.08 (brs, 1H), 1.91 – 1.75 (brs, 3H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.81, 149.99, 146.15, 132.05, 129.57, 129.23, 119.45, 116.66, 109.61, 95.72, 79.31, 59.06, 56.30, 56.02, 46.46, 32.05, 31.76, 28.66, 23.24, 22.80. Further the (±) norruspolline can be synthesized from **7a** as described in ref-1**.**

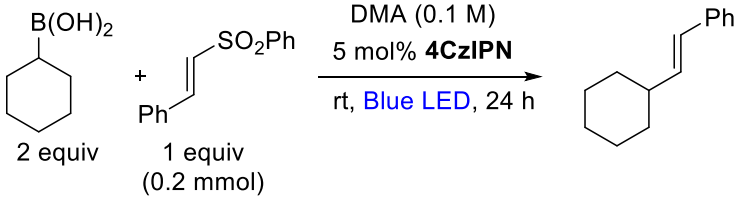
9. Experiments for the mechanistic investigation and other experiments

9(a). For boronic acid:

9(a)a: Control experiments:

Here to determine the role of each component, we carried out a control experiment. We found that, the role of each component such as boronic acid, vinyl sulfone, photocatalyst and light, is crucial and no product was observed in the absence of any of them.

Table 4: Control experiment for boronic acid

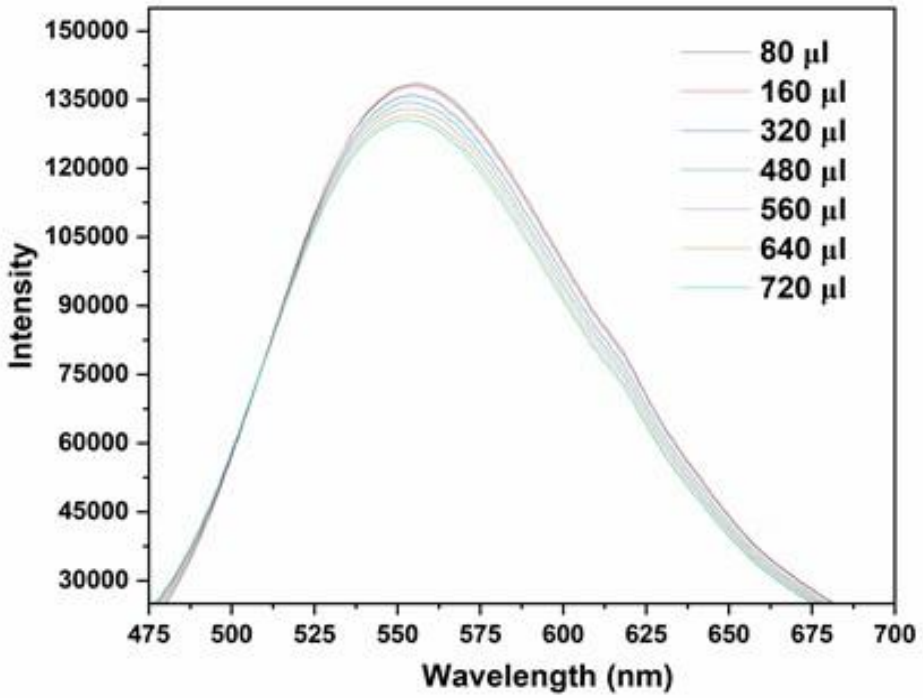


Entry	Light	Boronic acid	Sulfone	PC	*dr* (**E**/**Z**)	Yield [b](%)
1	No	Yes	Yes	Yes	--	--
2	Yes	Yes	Yes	No	--	--
3	Yes	No	Yes	Yes	--	--
4	Yes	Yes	No	Yes	--	--

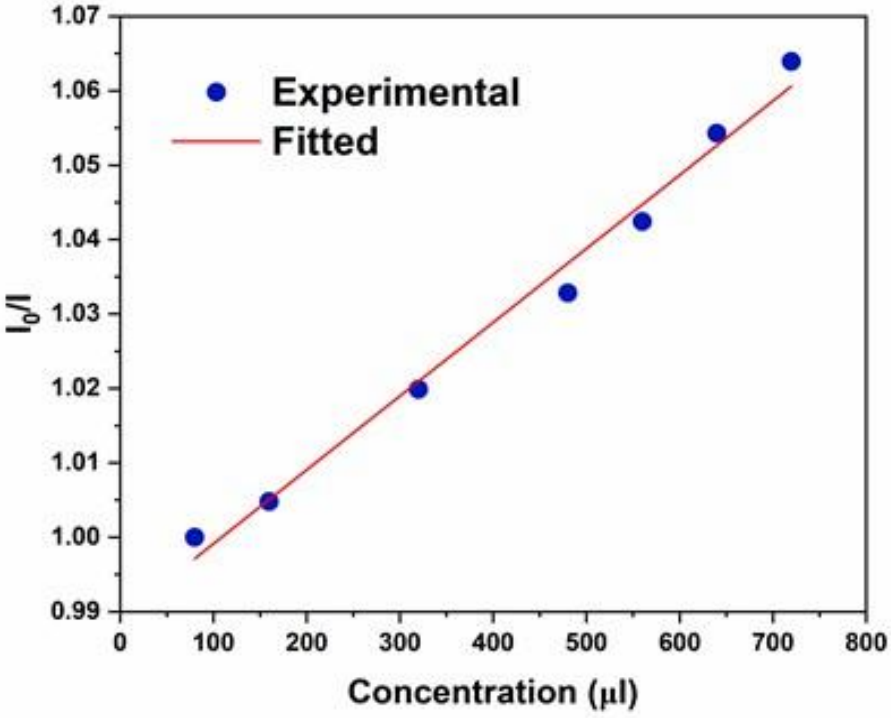
0.1 M solvent w.r.t boronic acid

9(a)b: Emission Quenching Experiments (Stern–Volmer Studies):

However, further to establish the fluorescence quenching ability of the DMA-activated boronic acid, we carried out the photo-luminescence experiment. The experiment was performed on a



a) Fluorescence quenching of 4CzIPN in the presence of variable concentrations of ["Butyl boronic acid + DMA]

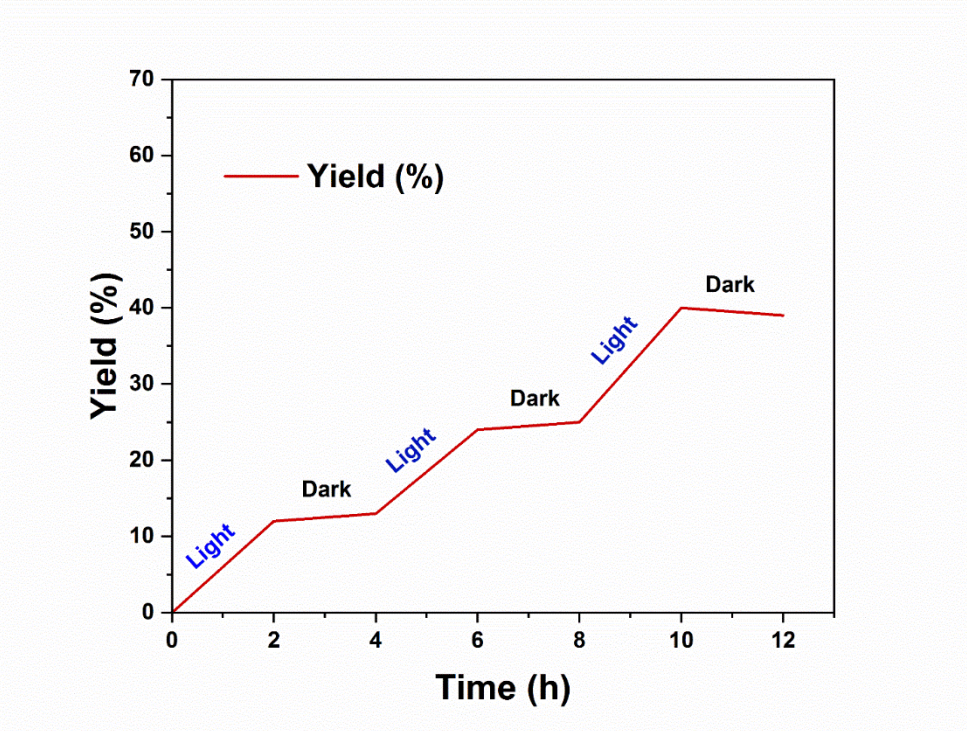


b) Stern-Volmer plot of 4CzIPN in the presence of variable concentrations of ["Butyl boronic acid + DMA]

fluorescence spectrophotometer (FLS 920, Edinburgh Instruments, Photonic division). We prepared 10^{-5} (M) solution of 4CzIPN in ACN, 10^{-4} (M) solution of *n*butyl boronic acid in DMA. Next, all the solutions were degassed and kept under nitrogen atmosphere. Further, an appropriate amount of quencher was added in a 1.0 cm quartz cuvette containing 2.5 ml of 10^{-5} (M)solution of 4CzIPN in ACN. The solutions were irradiated at 365 nm and emission was measured at 557 nm for calculation. The relative intensity I_0/I was calculated as a function of quencher concentration, where I is the intensity in the presence of the quencher, while I_0 is the luminescence intensity in the absence of the quencher. The Stern-Volmer experiment demonstrates that the mixture of boronic acid and DMA is able to quench the excited state of 4CzIPN, substantiating the hypothesis of the interaction between boronic acids and DMA leading to a redox-active substrate. [Ref(6)4]

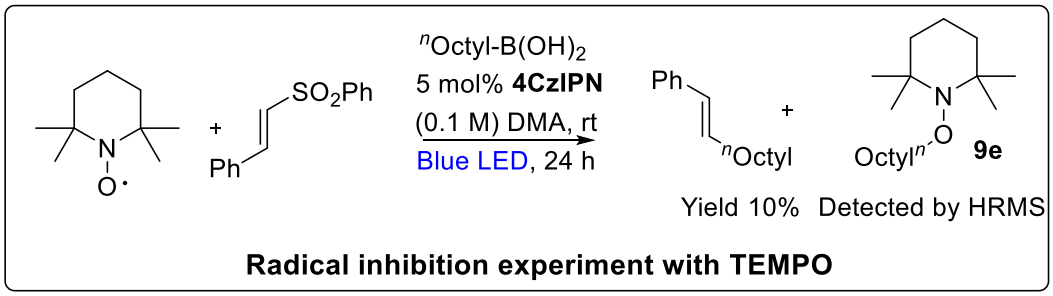
9(a)c: Light/dark experiment:

Six standard reactions were started according to general procedure **3B**. After 2 h, the Blue LED was turned off, and one vial was removed from the irradiation setup. The remaining five vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed, and the Blue LED was turned back on to irradiate the remaining four reactions. After an additional 2 h of irradiation, the Blue LED was turned off, and one vial was removed. The remaining three vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The remaining one vial were stirred in the absence of light for an additional 2 h and finally taken out for analysis. The work up was performed according to the general procedure **3B** The yield was determined by ^{1}H NMR spectroscopy using 3,4,5-tri methoxy benzaldehyde as the internal standard. After yield calculation, we found that, in the absence of light no product formation occurred. This result indicates that the light is crucial for this reaction.

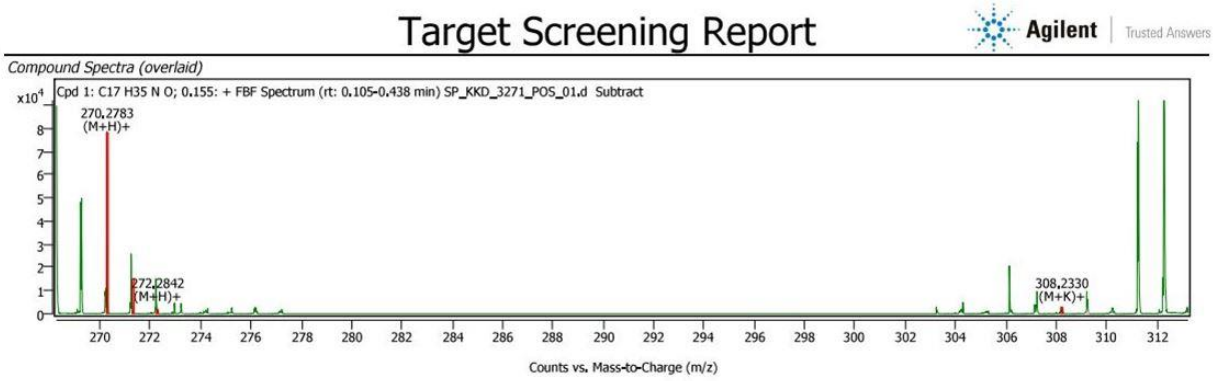


9(a)d: TEMPO trapping experiment:

Next to prove the radical pathway of vinylation we carried out the following reaction according to the general procedure **3B** along with the addition of 1 equivalent of a radical quencher (TEMPO) to the reaction mixture. An adduct (**9e**) between cyclohexane ring and TEMPO itself detected by HRMS $[M+H]^+$ calculated 269.2719 and found 269.2710. The vinylated product was isolated in 10% of yield. Hence these results support the radical based mechanism.



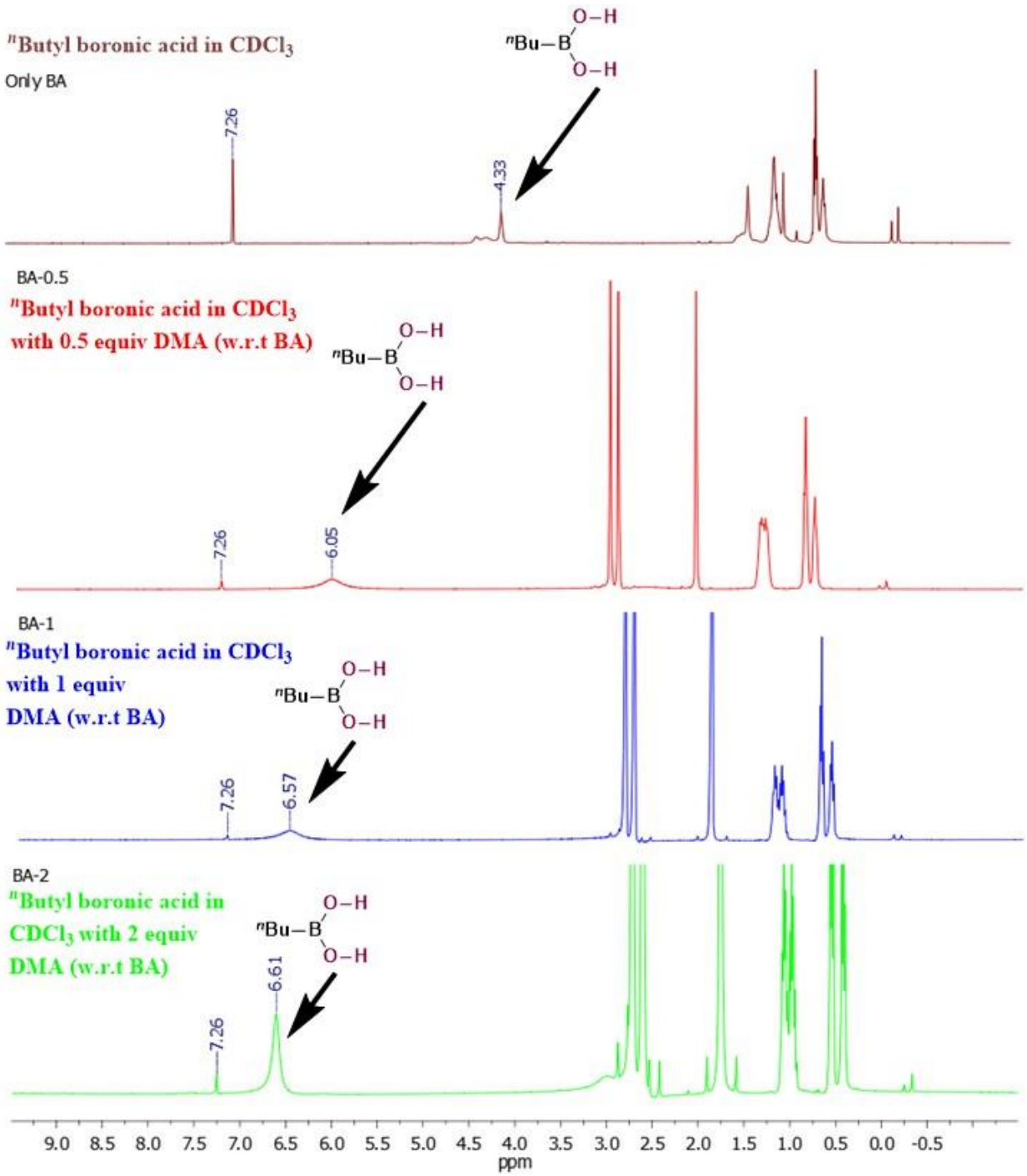
Radical inhibition experiment with TEMPO



HR-ESI mass spectra of 2,2,6,6-tetramethyl-1-(octyloxy)piperidine

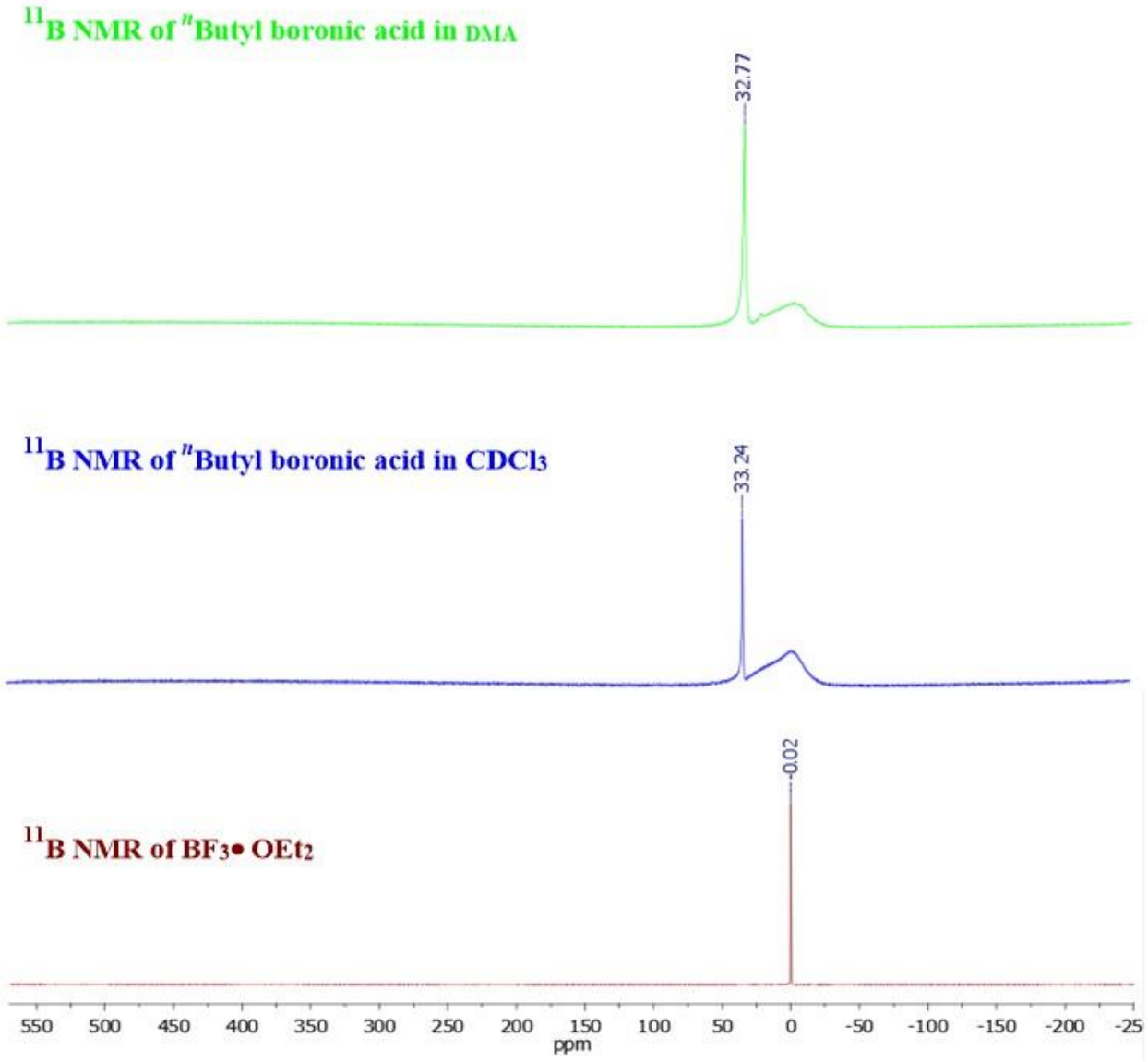
9(a)e: Proton (^{1}H) and boron (^{11}B) NMR experiment:

Next to demonstrate the interaction between boronic acids and DMA, ^{1}H-NMR and ^{11}B-NMR were recorded of following samples. First for the proton NMR, we have taken 30 mg of ^{n}butyl



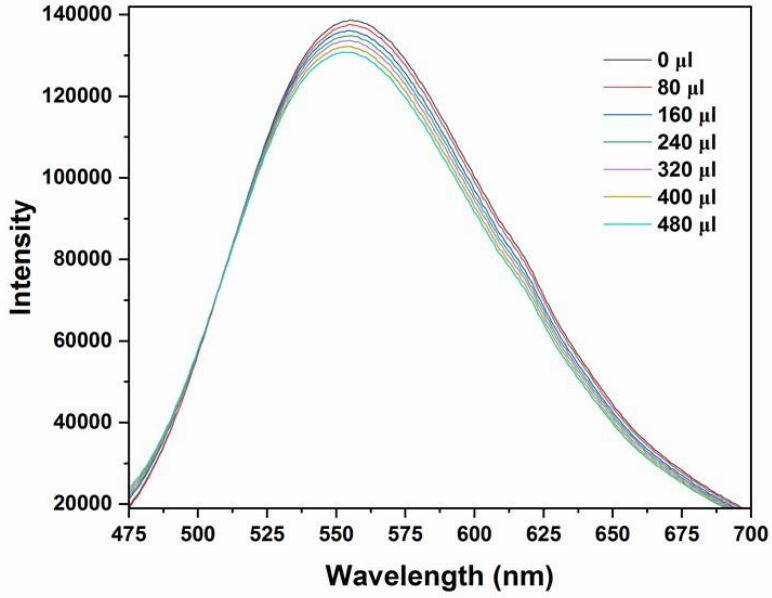
boronic acid in 0.7 mL $CDCl_3$. Then a proton NMR was recorded. Then to the NMR tube 0.5 equiv DMA (w.r.t boronic acid) added and properly mixed with it. Then a ^{1}H-NMR recorded. Here we observed a downfield shift of hydrogens (B-O-H) could be observed as a result of the formation of hydrogen bonds between boronic acid and DMA. However further with increasing concentrations of DMA we observed a downfield shift of hydrogens (B-O-H). We have also recorded the ^{11}B-NMR of the boronic acid in both $CDCl_3$ and DMA. Here $BF_3.Et_2O$ has taken as

the standard (0.00 ppm). In DMA case we found around 0.47 ppm shift towards the shielded region. Hence makes the boronic acid more oxidisable.

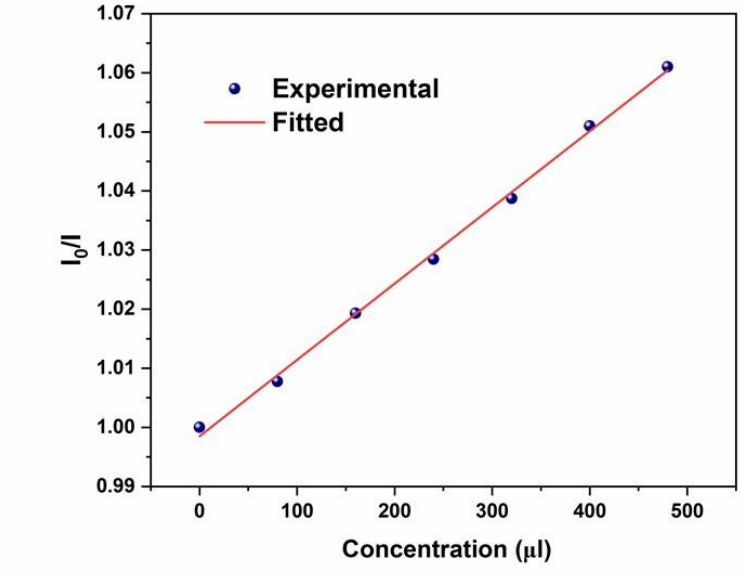


9(b). For boronate ester:

9(b)a: Emission Quenching Experiments (Stern–Volmer Studies):



a) Fluorescence quenching of 4CzIPN in the presence of variable concentrations of [^{n}Butyl B(pin) + NaO^{t}Bu + DMA]



b) Stern-Volmer plot of 4CzIPN in the presence of variable concentrations of [^{n}Butyl B(pin) + NaO^{t}Bu + DMA]

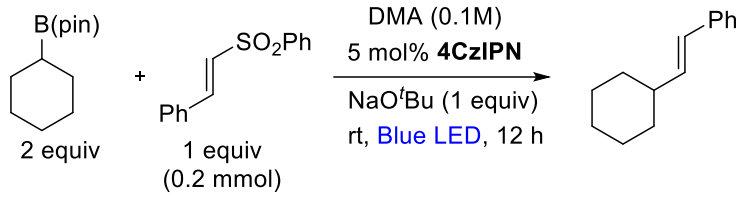
However,

further to establish the fluorescence quenching ability of the NaO^{t}Bu activated boronate ester, we carried out the photo-luminescence experiment. The experiment was performed on a fluorescence spectrophotometer (FLS 920, Edinburgh Instruments, Photonic division). We prepared 10^{-5} (M) solution of 4CzIPN in ACN and 10^{-4} (M) solution of [^{n}butyl-B(pin) (1 equiv) + NaO^{t}Bu (1 equiv)] in DMA. Next, all the solutions were degassed and kept under nitrogen atmosphere. Further, an appropriate amount of quencher was added in a 1.0 cm quartz cuvette equipped with 2.5 ml of 10^{-5} (M) solution of 4CzIPN in ACN. The solutions were irradiated at 365 nm and emission was measured at 557 nm. The relative intensity I_0/I was calculated as a function of quencher concentration, where I is the intensity in the presence of the quencher, while I_0 is the luminescence intensity in the absence of the quencher. The Stern-Volmer experiment demonstrates that the mixture of [^{n}butyl-B(pin) + NaO^{t}Bu + DMA] is able to quench the excited state of 4CzIPN.

9(b)b: Control experiments:

Here to determine the role of each component, we carried out a control experiment. We found that, the role of each component such as boronate ester, vinyl sulfone, photocatalyst and light is crucial, and no product was observed in absence of any of them. However, in the absence of base only 10% yield was isolated which indicate that DMA can promote for the deborylative vinylation but is inefficient resulting the poor yield.

Table 5: Control experiment for boronate ester



Entry	Light	Boronate ester	Base	Sulfone	PC	*dr* (**E**/**Z**)	Yield (%)
1	No	Yes	Yes	Yes	Yes	--	--
2	Yes	Yes	Yes	No	Yes	--	--
3	Yes	No	Yes	Yes	Yes	--	--
4	Yes	Yes	No	Yes	Yes	nd	10
5	Yes	Yes	Yes	Yes	No	--	--

0.1 M solvent w.r.t boronate ester

9(b)c: Cyclic voltammetry measurements:

The experiments were conducted using a cyclic potentiometer with a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode [referenced to SCE using ferrocene (Fc) as an internal standard (0.42 V vs. SCE)].[ref(9)1] In the standard procedure, in 10 ml of 10^{-3} (M) boronate ester (**2b13**) solution in ACN (**ACN-bpin-B**), 260 mg of $[N(Bu)_4]F.3H_2O$ electrolyte was added and total solution was degassed to make the stock solution. Next 5 ml of the stock solution was transferred to the reactor and it was sealed with a rubber septum and purged with nitrogen. Each measurement was conducted at 10 mV/s at room temperature under nitrogen atmosphere without stirring. The cyclic voltammogram was measured. Next we made another 10 ml of 10^{-3} (M) boronate ester (**2b13**) along with 1 equiv of NaO^{t}Bu (w.r.t boronate ester) solution in ACN (**ACN-bpin-base-C**), 260 mg of $[N(Bu)_4]F.3H_2O$ electrolyte was added

and total solution was degassed to make the stock solution. With this stock solution another cyclic voltammogram was measured. In the voltammogram, at ~ 0.75 V it is possible to observe a new local maximum, which is related to the species formed through the interaction between boronate ester and NaO^{t}Bu in the mixture. In our case the Nernst equation could not be employed as we are getting an irreversible cyclic voltammogram. Therefore to estimate the value of $E^0_{½}$ of the NaO^{t}Bu-boronate ester complex, the half peak potential $E_{p/2}$ (which corresponds to the potential at half the maximum of the local maximum current in the cyclic voltammogram) was calculated according to the following relation[ref-53].

$$f\ (E_{p/2}\ ) = \frac{C_{max}}{2}$$

Hence in the case of NaO^{t}Bu-boronate ester complex, the half peak potential value was found to be 0.48 V vs SCE. This species can therefore quench the excited state of 4CzIPN, as the value found lies in the redox window of the PC. However, we also further conducted this experiment using DMA as the solvent instead of ACN. Here also we found the same $E_{p/2}$ value but with higher peak intensity, which suggest the more reactivity of NaO^{t}Bu-boronate ester complex in DMA solution. Here **ACN-A** is correspond to only pure ACN with $[N(Bu)_4]F.3H_2O$ electrolyte. **DMA-D** is correspond to only pure DMA with $[N(Bu)_4]F.3H_2O$ electrolyte, **DMA-bpin-E** is correspond to 10^{-3} (M) boronate ester (**2b13**) solution with $[N(Bu)_4]F.3H_2O$ electrolyte and **DMA-bpin-base-F** is correspond to 10^{-3} (M) boronate ester (**2b13**) + 1 equiv of NaO^{t}Bu (w.r.t boronate ester) solution with $[N(Bu)_4]F.3H_2O$ electrolyte.

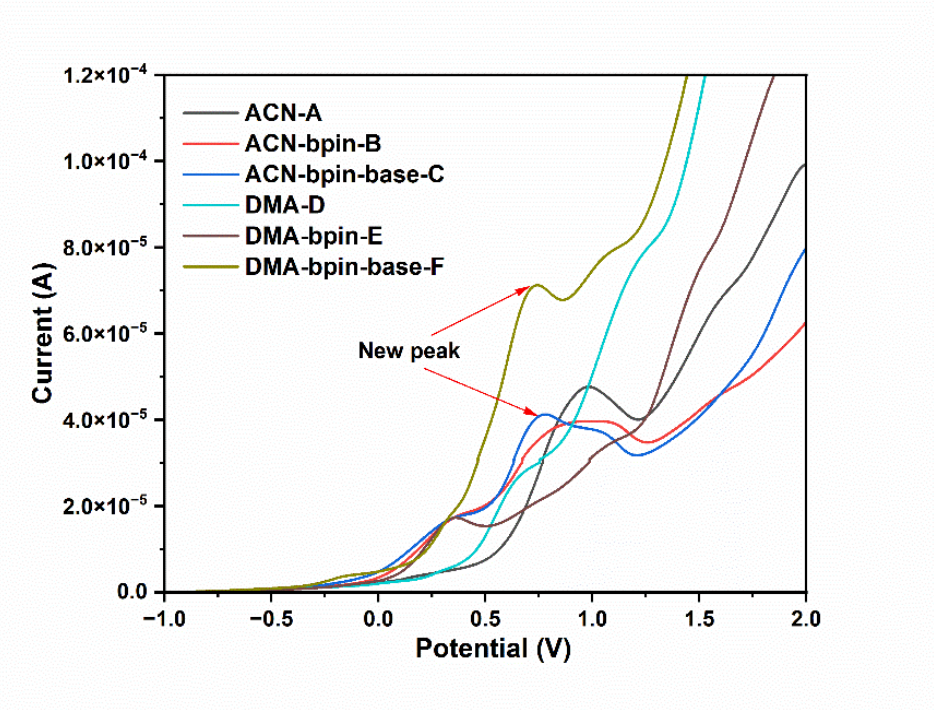
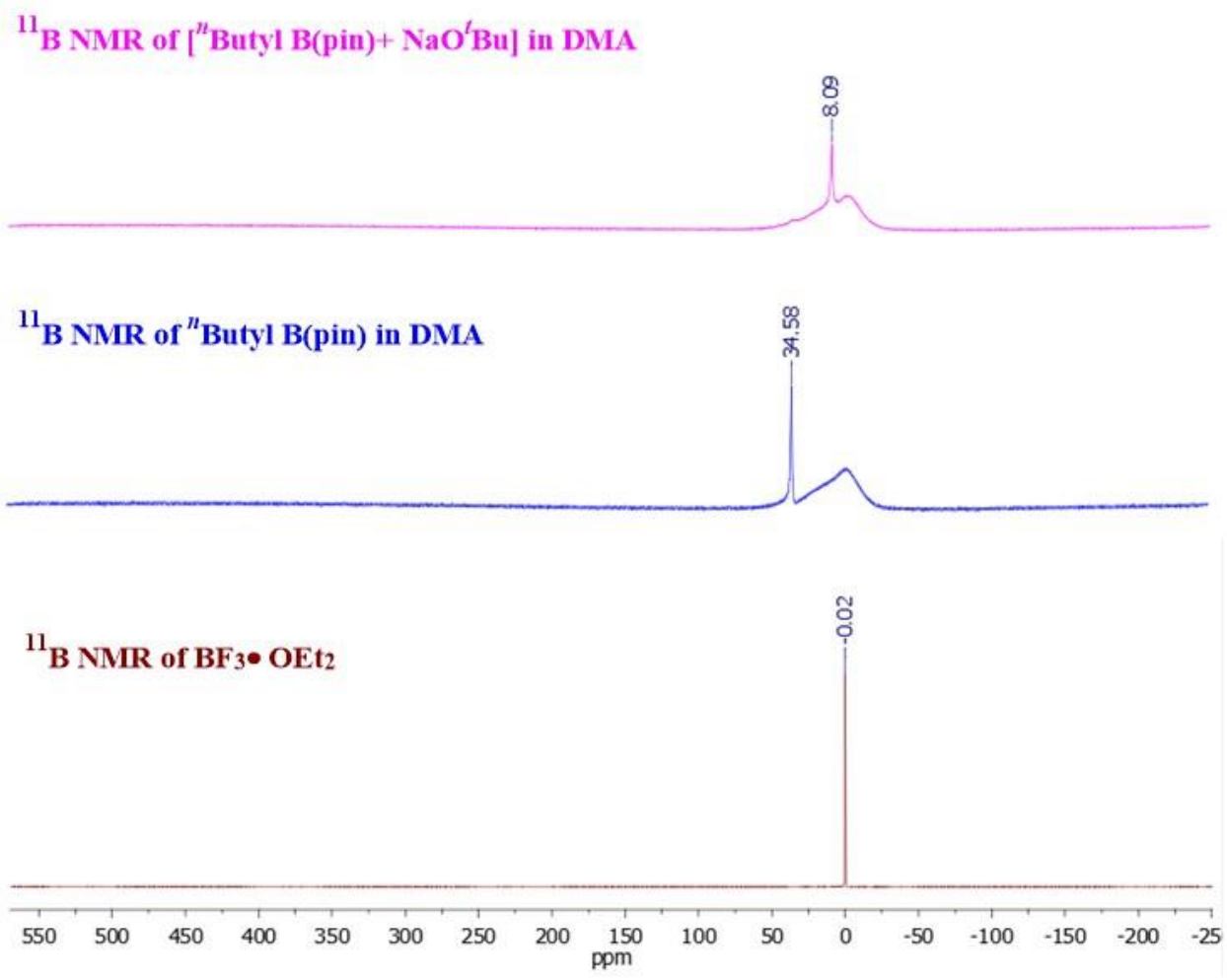


Figure S12: Cyclic voltammogram of NaO^{t}Bu + ^{n}butyl B(pin) complex in the presence of ACN and DMA

9(b)d: Boron (^{11}B) NMR experiment:

Next to demonstrate the effect of base, we recorded ^{11}B-NMR of the boronate ester in $CDCl_3$, DMA and NaO^{t}Bu/DMA mixture. Here $BF_3.Et_2O$ has taken as the standard (0.00 ppm). We have taken 30 mg of ^{n}butyl boronate pinacolate ester in 0.7 mL $CDCl_3$ and ^{11}B-NMR recorded. Then in another tube 30 mg of ^{n}butyl boronate pinacolate ester in 0.7 mL DMA and ^{11}B-NMR recorded but only 0.3 ppm up field shift observed. Further to this NMR tube 1 equiv of NaO^{t}Bu (w.r.t boronate ester) added and ^{11}B-NMR recorded. Surprisingly the previous peak disappear and a new peak appear in 8.09 ppm. This indicates the interaction between boronate ester and the NaO^{t}Bu and make the boronate complex **9b**.

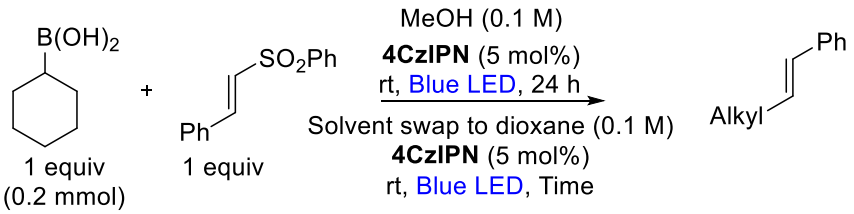


10. Optimization, general procedure and the scope for the *cis* olefin from boronic acid

10(a): Optimization:

However we have also developed one-pot *Z*-selective vinylation. In our initial approach (Table , entry) we observed that while screening the other solvents, few solvents such as MeOH, ACN promotes the *Z*-selectivity over *E*. In our previous paper we observed that solvent polarity plays a crucial role for the *Z*/*E* selectivity. With this combined hints and from the outcome of *trans* optimization, we initiated our optimization. We selected some solvents and screamed with other parameters. Here w.r.t MeOH, although the ACN results in better *cis* selectivity but ended up

Table 6. Optimization for *Z*-selective Vinylation



Entry	Solvent	Catalyst	Time (h)	*dr* (**E**/**Z**)	Yield [b](%)
1	MeOH	5	24	40:60	65
2	Dioxane	5	24	60:40	23
3	Toluene	5	24	--	--
4	ACN	5	24	30:70	20
5	ACN	5	48	nd	9
6	ACN	5	72	nd	--
7	MeOH	5	48	80:20	36
8	MeOH	5	72	--	10
9	Dioxane	5	48	40:60	25
10	Dioxane	5	72	20:80	27
11	DMA:diox (1:1)	5	72	90:10	32
12	ACN:DMA (1:1)	5	72	88:12	28
13	ACN:DMA:Diox (1:1:1)	5	72	70:30	16
14	ACN:DMA (10:1)	5	72	nd	10
15	Dioxane:DMA (10:1)	5	72	nd	11
16[a]	DMA then diox	5	72	89:11	49
17[b]	DMA then diox	5	72	80:20	46
18[c]	MeOH then diox	5	72	20:80	58
19[c]	MeOH then ACN	5	72	35:65	29
20[c]	MeOH then Toluene	5	72	50:50	32

0.1 M solvent w.r.t boronic acid. [a]reaction done for 24 h in DMA, then to it 0.1 M dioxane added and again for 72 h.[b]reaction done for 24 h in DMA, then to it 0.1 M dioxane, 5 mol% 4CzIPN added and again for 72 h. [c]reaction done for 24 h in MeOH, then to it 0.1 M corresponding solvent, 5 mol% 4CzIPN added and again for 72 h.

with poor yield. Whereas toluene fails and dioxane show moderate *E*/*Z* selectivity in 24 h. Further while optimizing reaction time, we found that at 72 h only the dioxane result the product in excellent *cis* selectivity. With this information in our hand, we focus on one-pot step wise

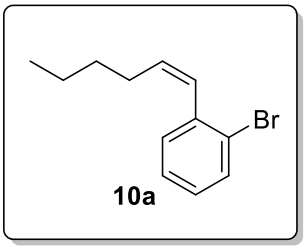
optimization. For that we utilized several mix solvent concepts such as table 6 entry 11 to 15, where we utilized several solvent mixtures with prescribed ratio. But none of them leads to good *cis* selectivity. Then the reaction was carried out for 24 h in DMA for better yield followed by dioxane 72 h in one pot. But failed to improve *cis* selectivity which indicate the presence of DMA might be opposing the selectivity reversal process. Therefor as our previous paper ref-1, considering the effect of solvent, we thought that the solvent swapping might help to improve *cis* selectivity. However, DMA being high boiling, after the product formation, removal of DMA resulted in a loss of product. On the other side MeOH being lower boiling and better *cis* selectivity over DMA, the reaction was carried out for 24 h in MeOH followed by solvent switching to dioxane and the reaction was stirred for 72 h which result in maximum yield and excellent *cis* selectivity (table 6; entry 18)

10(b): General procedure (10B):

To a dry 20 mL vial equipped with a magnetic stir bar was added 4CzIPN (5 mol%), alkyl boronic acid (2 equiv) and sulfone (1 equiv). The vial was sealed and then MeOH (0.1 M w.r.t boronic acid) was added to the vial and the resulting mixture was degassed by freeze-pump-thaw under nitrogen (three times). Then, the vial was placed in a photo reactor and irradiated with Blue LED at rt for 24 h. After that the solvent swap to dioxane (0.1 M) and additional 5 mol% 4CzIPN was added. Then the resulting mixture was degassed by freeze-pump-thaw under nitrogen (three times). Then, the vial was placed in a photo reactor and irradiated with Blue LED at rt for 72 h. After that the reaction mixture was diluted with H_2O and workup by using Et_2O. Purification by flash column chromatography or preparative TLC afforded the (*Z*)-alkene.

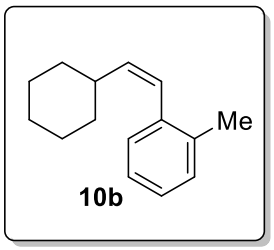
10(c): Scope for the *Z*-olefin:

(*Z*)-1-bromo-2-(hex-1-en-1-yl)benzene ($C_{12}H_{15}Br$) (10a):[ref-54] Synthesized using general procedure **10B** (with 0.2 mmol of corresponding sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (28 mg) 60% (*E*:*Z* = 05:95). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 1H), 7.27 - 7.25 (m, 2H), 7.12 – 7.06 (m, 1H), 6.44 (d, *J* = 11.5 Hz, 1H), 5.77 (dt, *J* = 11.5, 7.5 Hz, 1H), 2.20 - 2.15 (m, 2H),

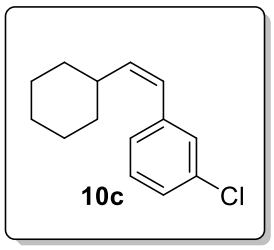


10a

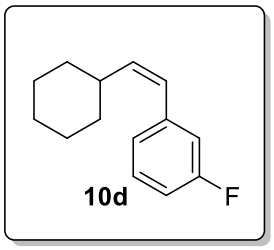
1.32 - 1.25 (m, 4H), 0.88 - 0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.86, 134.27, 132.64, 130.71, 128.47, 128.26, 126.91, 124.16, 29.85, 28.21, 22.45, 14.06.



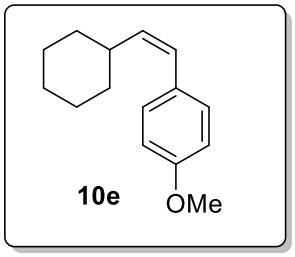
(*Z*)-1-(2-cyclohexylvinyl)-2-methylbenzene ($C_{15}H_{20}$) (10b):[ref-55] Synthesized using general procedure **10B** (with 0.2 mmol of corresponding sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (20 mg) 51% (*E*:*Z* = 08:92). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 4H), 6.32 (d, *J* = 11.6 Hz, 1H), 5.54 (t, *J* = 11.4 Hz, 1H), 2.36-2.31 (m, 1H), 2.26 (s, 3H), 1.69 – 1.62 (m, 5H), 1.24-1.13 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.85, 137.48, 136.31, 129.83, 129.00, 126.83, 126.19, 125.53, 36.94, 33.46, 26.19, 25.78, 20.12.



(*Z*)-1-chloro-3-(2-cyclohexylvinyl)benzene ($C_{14}H_{17}$) (10c):[ref-55] Synthesized using general procedure **10B** (with 0.2 mmol of corresponding sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (19 mg) 57% (*E*:*Z* = 06:94). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.25 (s, 1H), 7.22 (s, 1H), 7.21 – 7.17 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.24 (d, *J* = 11.8 Hz, 1H), 5.53 (t, *J* = 10.9 Hz, 1H), 2.51 (m, 1H), 1.76 – 1.66 (m, 5H), 1.28 – 1.16 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 140.38, 139.94, 134.19, 129.54, 128.77, 126.85, 126.63, 125.78, 124.38, 37.10, 33.30, 26.14, 25.74.



(*Z*)-1-(2-cyclohexylvinyl)-3-fluorobenzene ($C_{14}H_{17}F$) (10d):[ref-54] Synthesized using general procedure **10B** (with 0.2 mmol of corresponding sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (23 mg) 56% (*E*:*Z* = 15:85). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 1H), 7.10 – 7.01 (m, 1H), 6.98 – 6.85 (m, 2H), 6.27 (d, *J* = 11.9 Hz, 1H), 5.52 (t, *J* = 10.2 Hz, 1H), 2.60 – 2.49 (m, 1H), 1.78 – 1.65 (m, 5H), 1.29 – 1.16 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.92 (d, *J* = 244 Hz), 140.27 (d, *J* = 12.6 Hz), 138.41, 129.69 (d, *J* = 8.8 Hz), 125.97 (d, *J* = 2.5 Hz), 124.49 (d, *J* = 3.7), 115.42 (d, *J* = 21 Hz), 113.40 (d, *J* = 21.4 Hz), 37.11, 33.29, 26.15, 25.77.



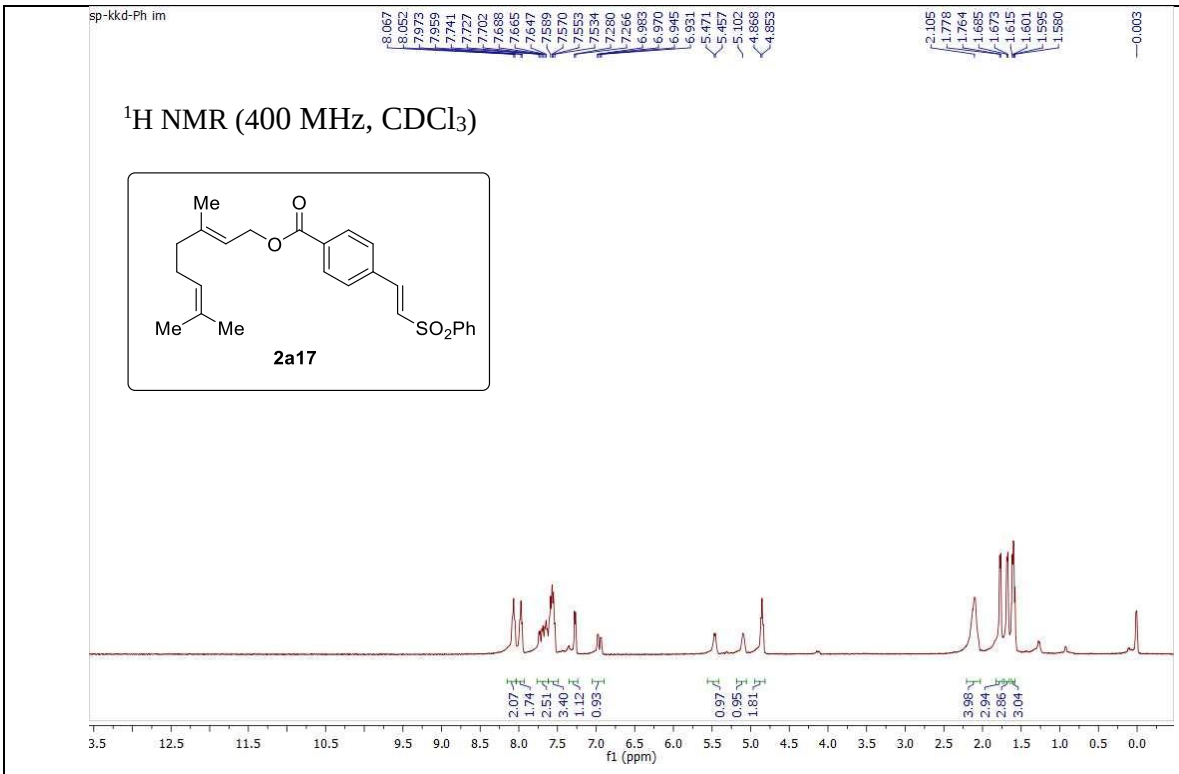
(*Z*)-1-(2-cyclohexylvinyl)-4-methoxybenzene ($C_{15}H_{20}O$) (10e):[ref-54] Synthesized using general procedure **10B** (with 0.2 mmol of corresponding sulfone), purified by silica gel chromatography (2 to 5% EtOAc/hexane), colourless liquid, yield (24 mg) 58% (*E*:*Z* = 12:88). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.24 (d, *J* = 11.7 Hz, 1H), 5.40 (t, *J* = 11.7 Hz, 1H), 3.82 (s, 3H), 2.57 (m, 1H), 1.78 – 1.66 (m, 5H), 1.30 – 1.20 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.40, 137.72, 130.83, 129.92, 126.47, 113.83, 55.42, 37.05, 33.49, 26.25, 25.91.

Reference:

Ref-1: *Chem. Sci.* **2022**, *13*, 9678-9684. Ref-2: *RSC Adv*. **2015**, *5*, 37013-37017. Ref-3: *RSC Adv.* **2016**, *6*, 59661-59676. Ref-5: *Org. Biomol. Chem.,* **2020**,*18,* 8939-8974. Ref-6: *Angew. Chem. Int. Ed*. **2012**, *51*, 528-532. Compound 2a: ref-7: *Chem. Eur. J.* **2010**, *16*, 9905-9909. Compound 2b: ref -8: *Angew. Chem. Int. Ed*. **2015**, *54*, 14518-14522. Compound 2c: ref-9: *J. Am. Chem. Soc*. **2011**, *133*, 9119-9123. Compound 2d: ref-10: In Organic Reactions, (Ed.). https://doi.org/10.1002/0471264180.or032.024. Compound 2e: ref-11: *Chin. J. Org. Chem*. **2012**, *32*, 1439-1444. Compound 2h, 2i: ref-12: *J. Am. Chem. Soc.* **1987**, *109*, 2393-2401. Compound 2g: ref-13: *Org. Lett*. **2021**, *23*, 9664-9668. Compound 2l, 2f, 2k, 2j: ref-14: *Chin. J. Chem.* **2022**, *40*, 2269-2275. Compound 2q: ref-15: *Chem. Commun.* **2011**, *47*, 2158-2160. Compound 2v: ref-16 *J. Am. Chem. Soc*. **2022**, *144*, 19115-19126. Compound 3b, 3c, 3d, 2o, 2n: ref-17: *Org. Lett*. **2020**, *22*, 7768-7772. Compound 2p: ref-18: *Adv. Synth. Catal*. **2009**, *351,* 859-864. Compound 2r, 2s, 3i, 2t: ref-19: *J. Organomet. Chem*. **2011**, *696*, 211-215. Compound 2u, 3j: ref-20: *J. Org. Chem*. **2002**, *67*, 8424-8429. Compound 2a', 3a', 2c', 3d', 2b', 3f', 2e', 3b', 3e': ref-21: *J. Am. Chem. Soc*. **2002**, *124*, 6514-6515. Compound 2d', 3g': ref-22: *Chem. Sci.* **2014**, *5*, 2379-2382. Compound 2f': ref-23: *Chem. Commun*. **2015**, *51*, 7546-7549. Compound 2i', 2j': ref-24: *Beilstein J. Org. Chem*. **2013**, *9*, 1718-1723. Compound 2g', 2h': ref-25: *Chem. Eur. J*. **2003**, *9*, 2123-2128. Compound 2k': ref-26: *Tetrahedron Lett*. **1992**, *33*, 3307-3310. Compound 3e: ref-27: *Org. Lett*. **2013**, *15*, 4258-4261. Compound 3f: ref-28: *Tetrahedron Lett.* **1998**, *39*, 6935-6938. Compound 3g: ref-29: *Angew. Chem. Int. Ed*. **2018**, *57*, 15143-15147. Compound 3k: ref-30: *J. Org. Chem*. **2018**, *83*, 13734-13742. Compound 3l: ref-31:. *Angew. Chem. Int. Ed.* **2020**, *59*, 6466-6472. Compound 3m: ref-32: *Eur. J. Org. Chem*. **2014**, *2014*, 6625-6629. Compound 3h': ref-33: *Org. Lett.* **2019**, *21*, 776-779. Compound 2p': ref-34: *Org. Biomol. Chem.* **2015**, *13*, 5880-5884. Compound 2m': ref-35: *J. Organomet. Chem.* **2013**, *724*, 129-134. Compound 2n': ref-36: *Chem. Commun*. **2019**, *55*, 107-110. Compound 2l': ref-37: *J. Am. Chem. Soc*. **1997**, *119*, 7406-7407. Compound 2o': ref-38: *Org. Lett*. **2013**, *15*, 3034-3037. Compound 3c': ref-39: *Chem. Commun*. **2015**, *51,* 7546-7549. Compound 3h: ref-40: *J. Org. Chem*. **2019**,

84, 13053-13064.Compound 2m: ref-41: *Adv. Synth. Catal*. **2019**, *361*, 2877-2884. Compound 3a: ref-42: *Chem. Lett*. **1978**, *7*, 413-416. Ref-43: *J. Org. Chem*. **2004**, *69*, 8971-8974. Ref-44: *J. Am. Chem. Soc*. **1979**, *101*, 7367-7373. Ref-45: *Org. Lett*. **2014**, *16*, 5486-5489. Ref-46: *ACS Catal*. **2021**, *11*, 10862-10870. Ref-47: *Tetrahedron Lett*. **1998**, *39*, 4163-4166. Ref-48: *Org. Lett*. **2014**, *16*, 5486-5489. Compound 6a: ref-49: *New J. Chem*. **2018**, *42*, 11465-11470. Compound 6b: ref-50: *Org. Lett*. **2017**, *19*, 2658–266. Compound 6c: ref-51: *Chem. Eur. J.* **2019**, *25*, 14532-14535. Compound 6d: ref-52: *ACS Catal*. **2022**, *12*, 13108–13115. Ref-53: *Synlett* **2015**, *27*, 714-723. Compound 10a, 10c and 10d ref-54: *J. Org. Chem*. **2020**, *85*, 15638-15644. Compound 10b ref-55: *J. Am. Chem. Soc*. **2015**, *137*, 4932-4935.

11. NMR spectra of compounds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Me
Me
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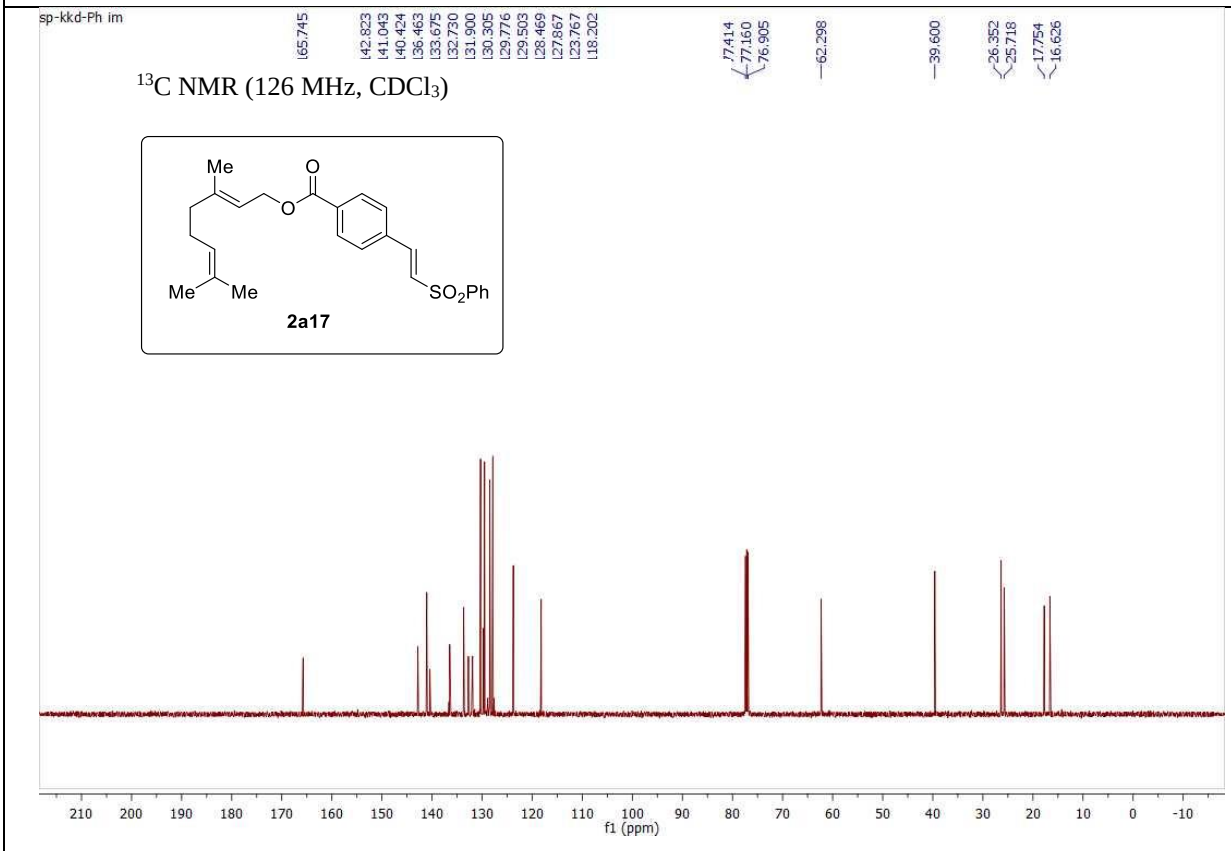
f1 (ppm)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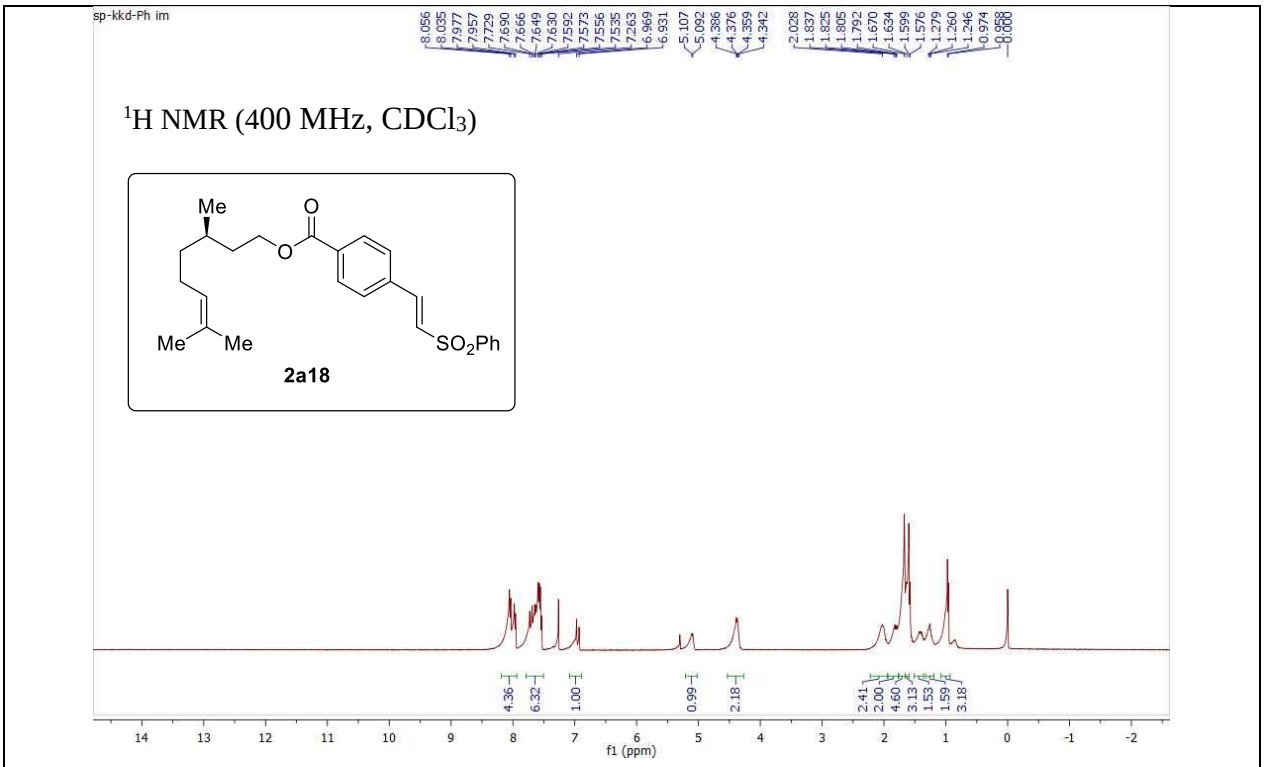
SO_2Ph
2a17
f1 (ppm)



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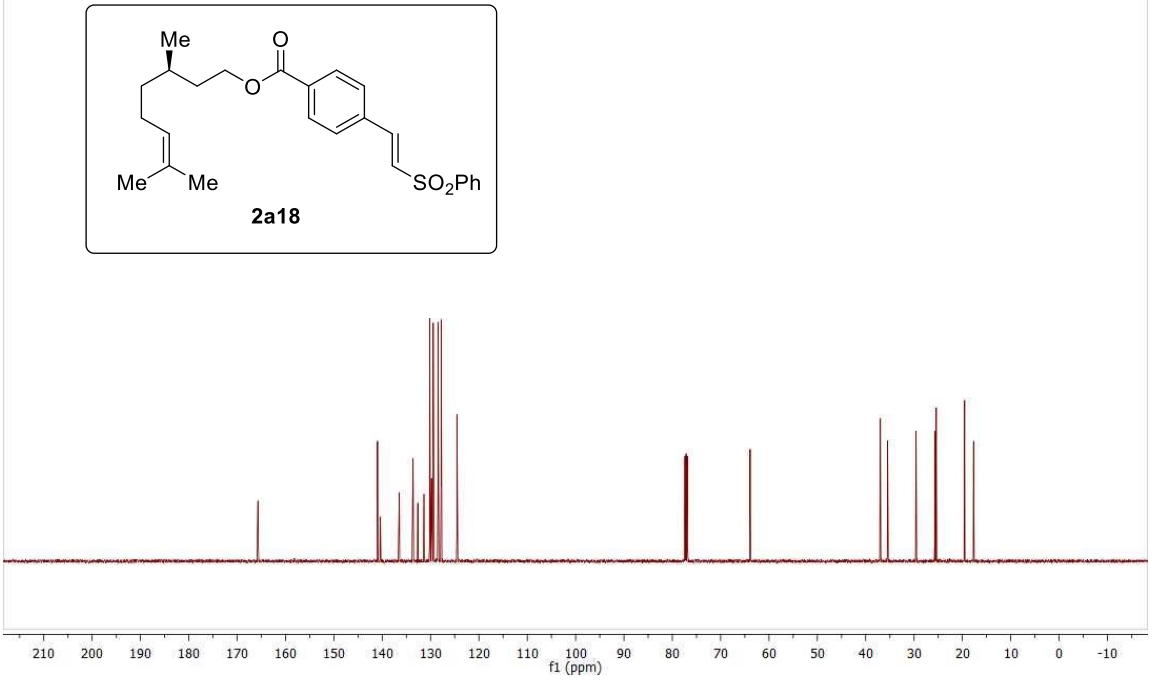

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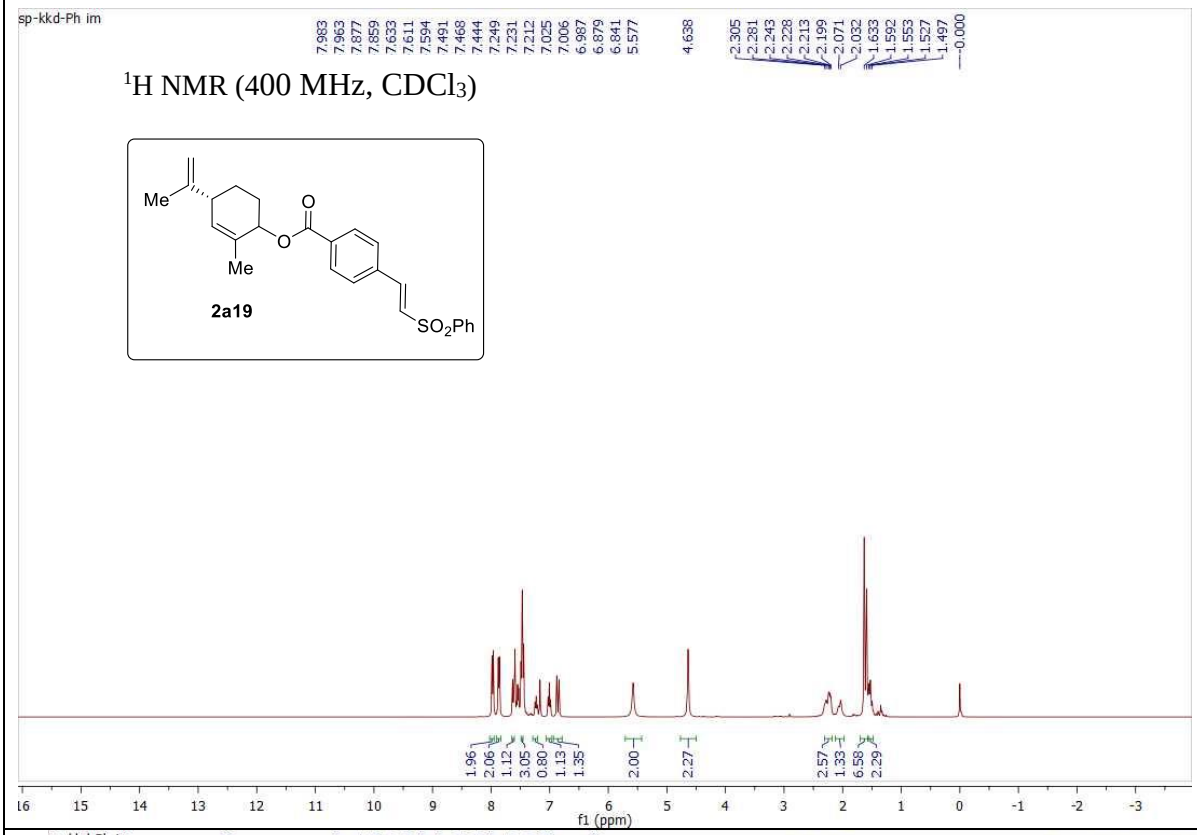
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2.305
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O
O
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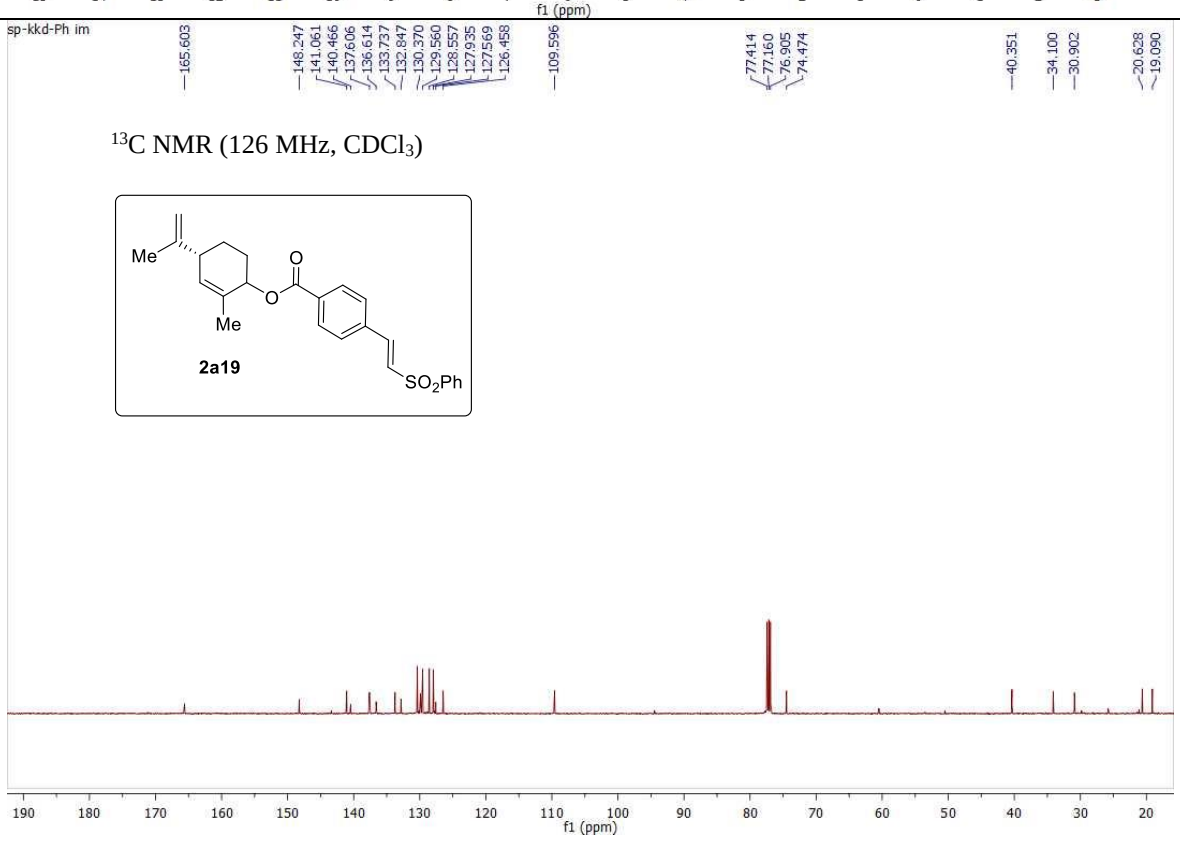
f1 (ppm)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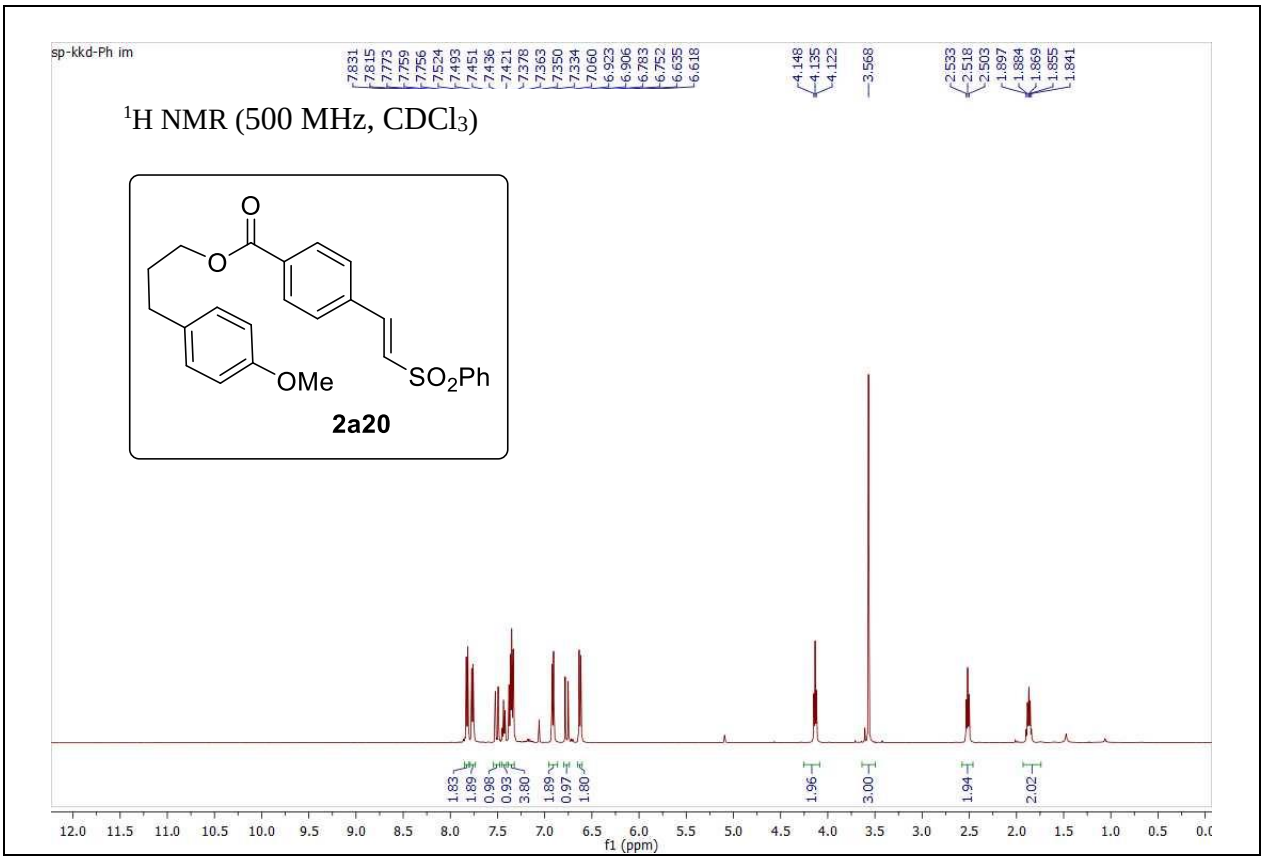
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O
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SO2Ph
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0.93
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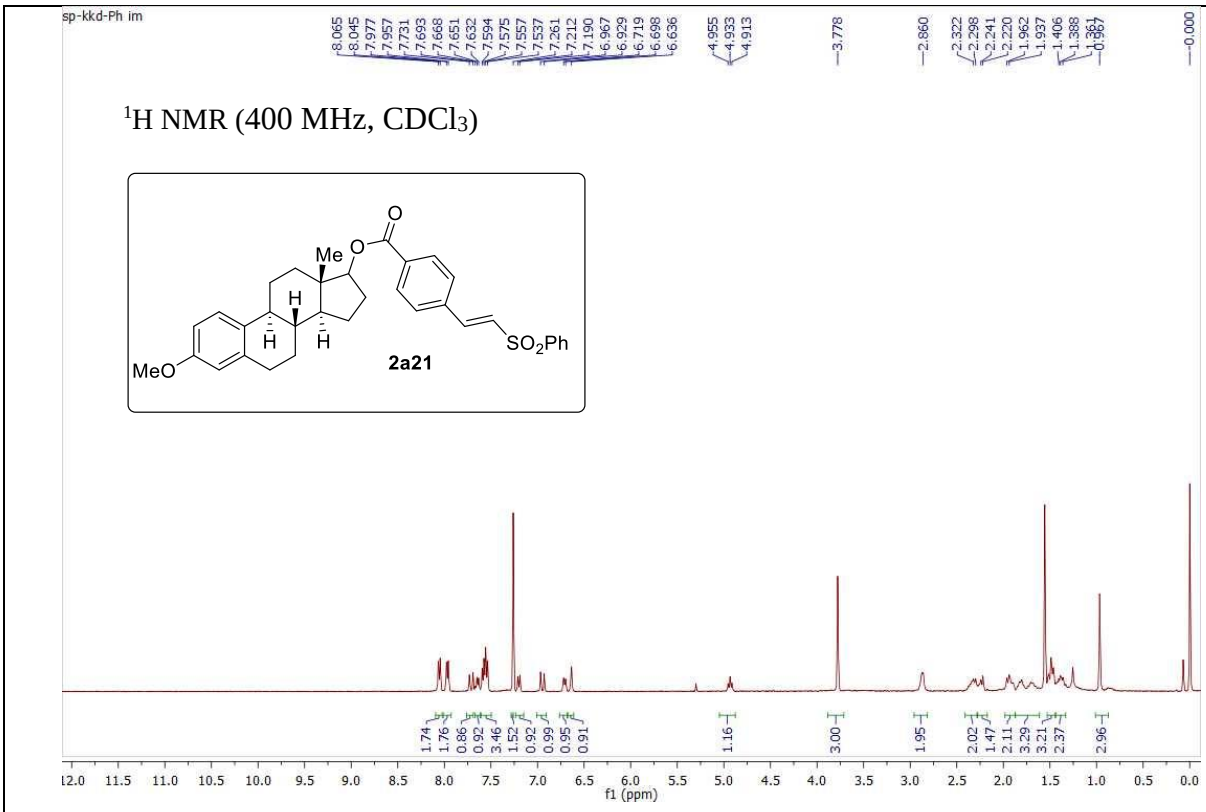
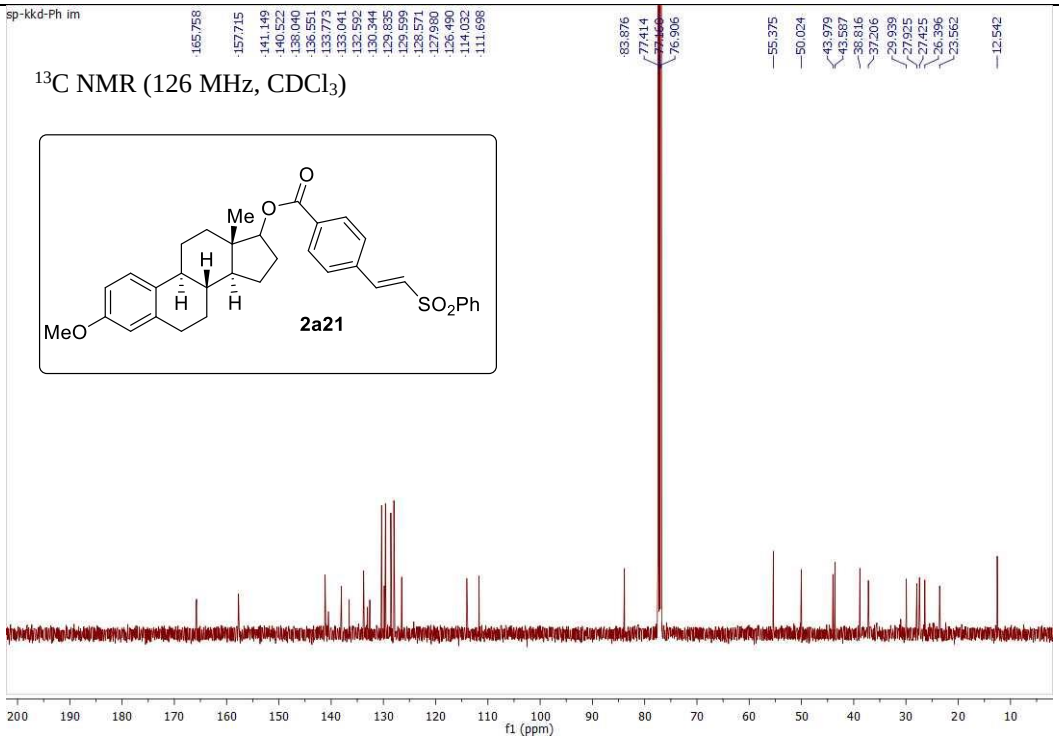
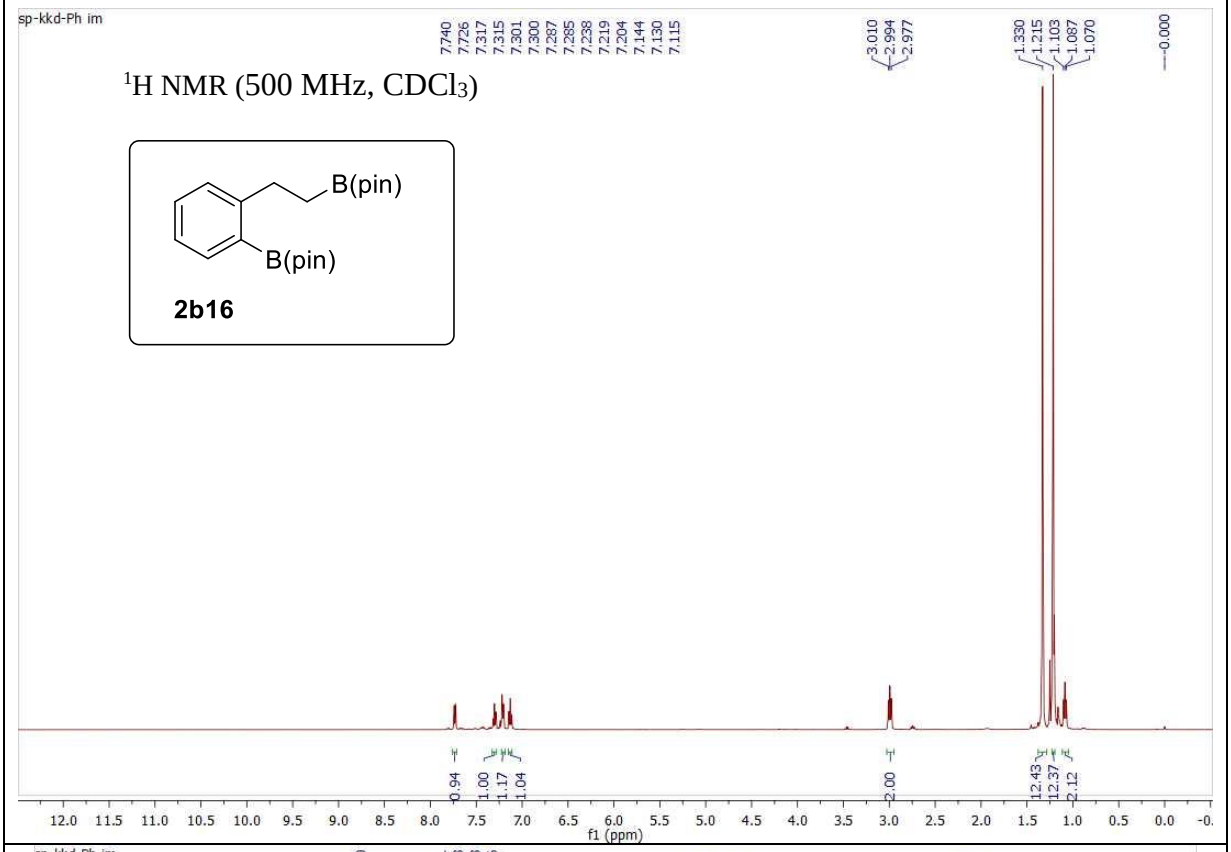
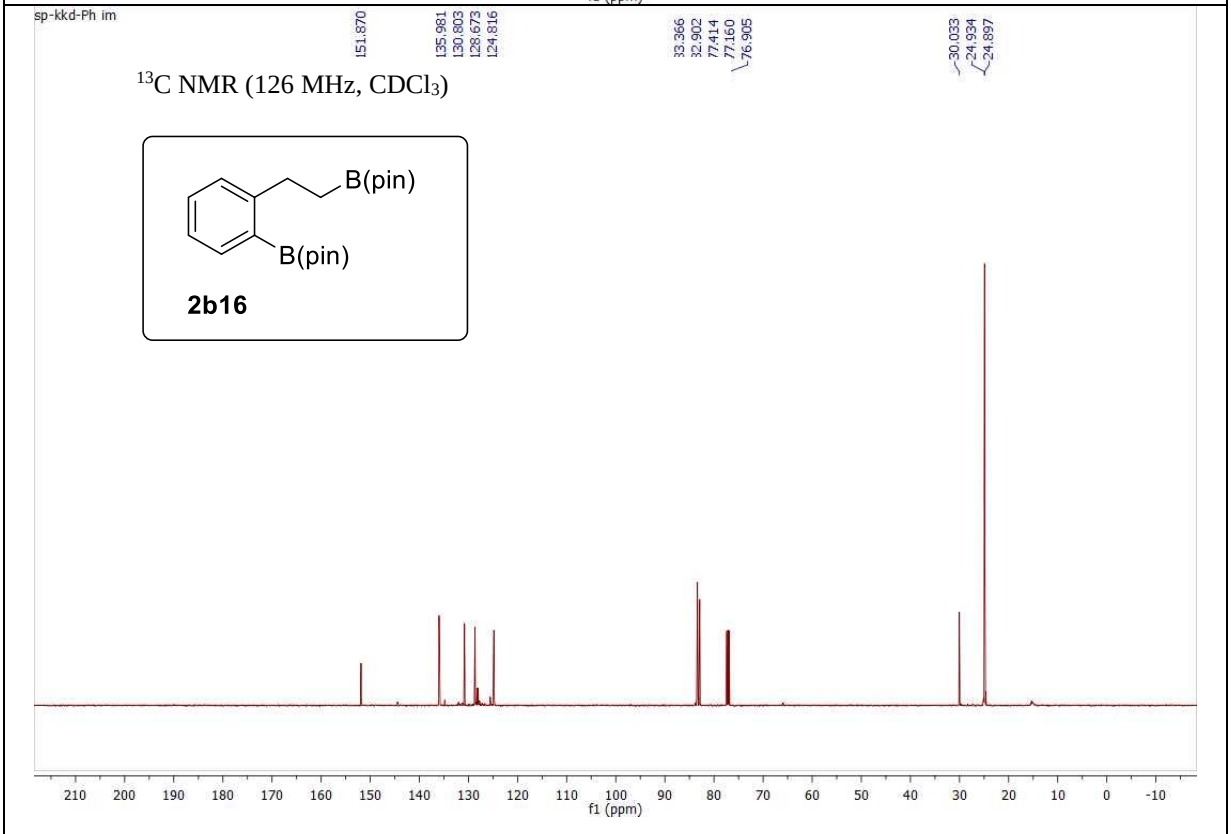
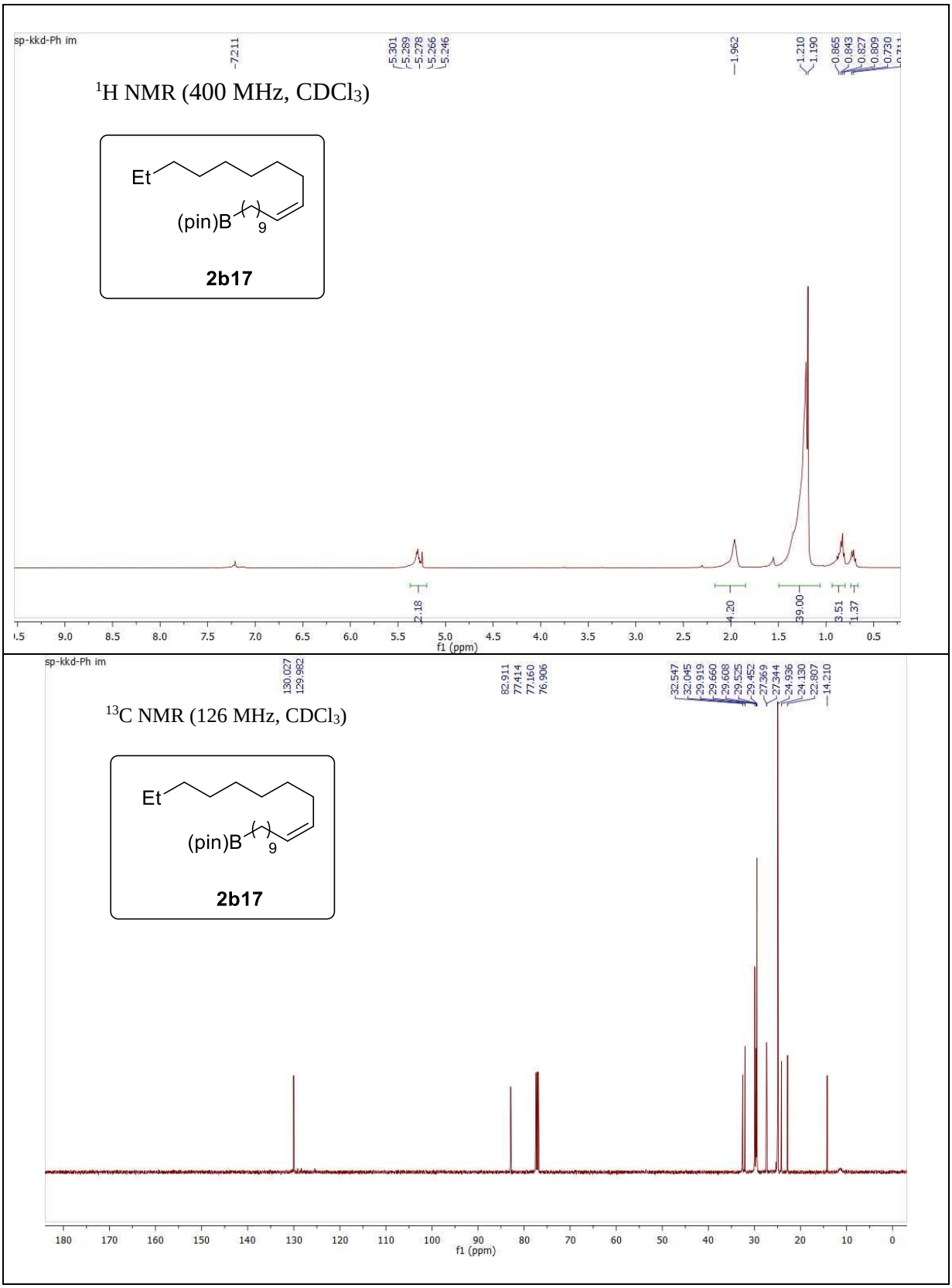
0.97
1.80
1.96
3.00
1.94
2.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

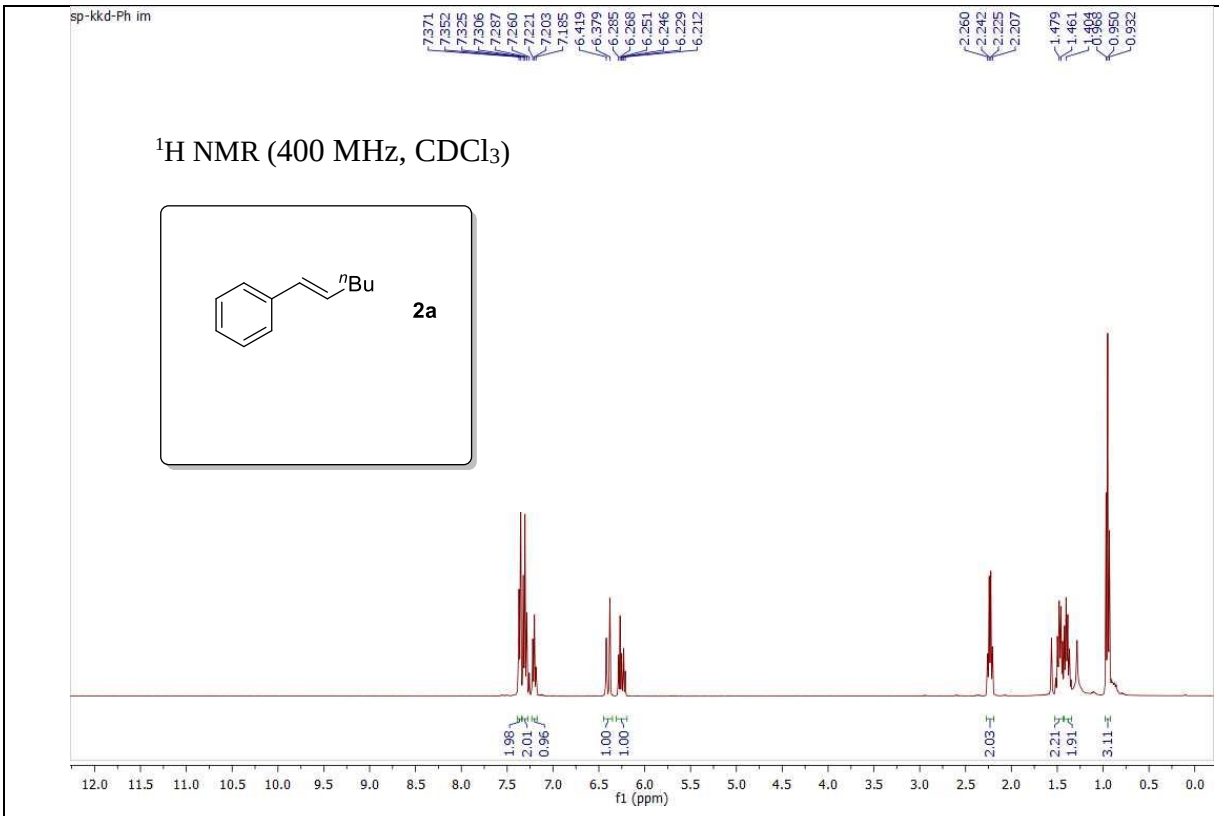

sp-kkd-Ph im
^{1}H NMR (400 MHz, $CDCl_3$)
Me
O
H
H
H
MeO
SO_2Ph
2a21
f1 (ppm)

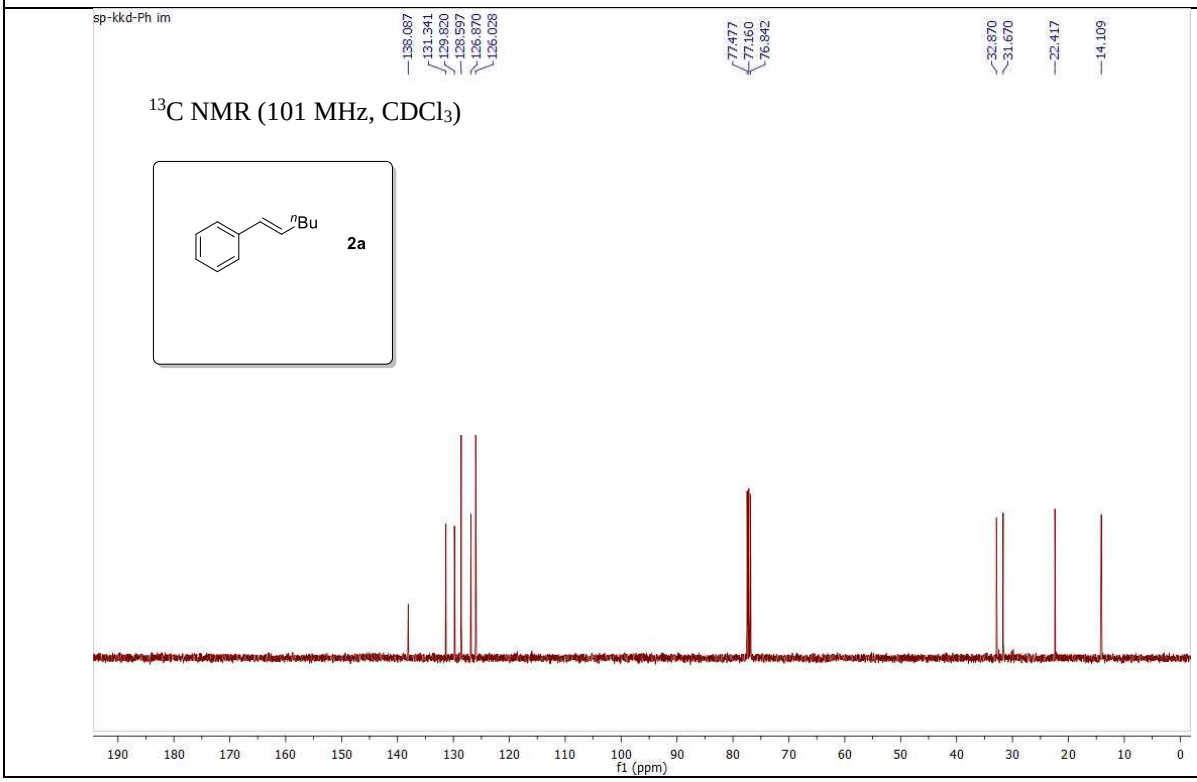

sp-kkd-Ph im
^{13}C NMR (126 MHz, $CDCl_3$)
Me
O
H
H
H
MeO
SO_2Ph
2a21
f1 (ppm)

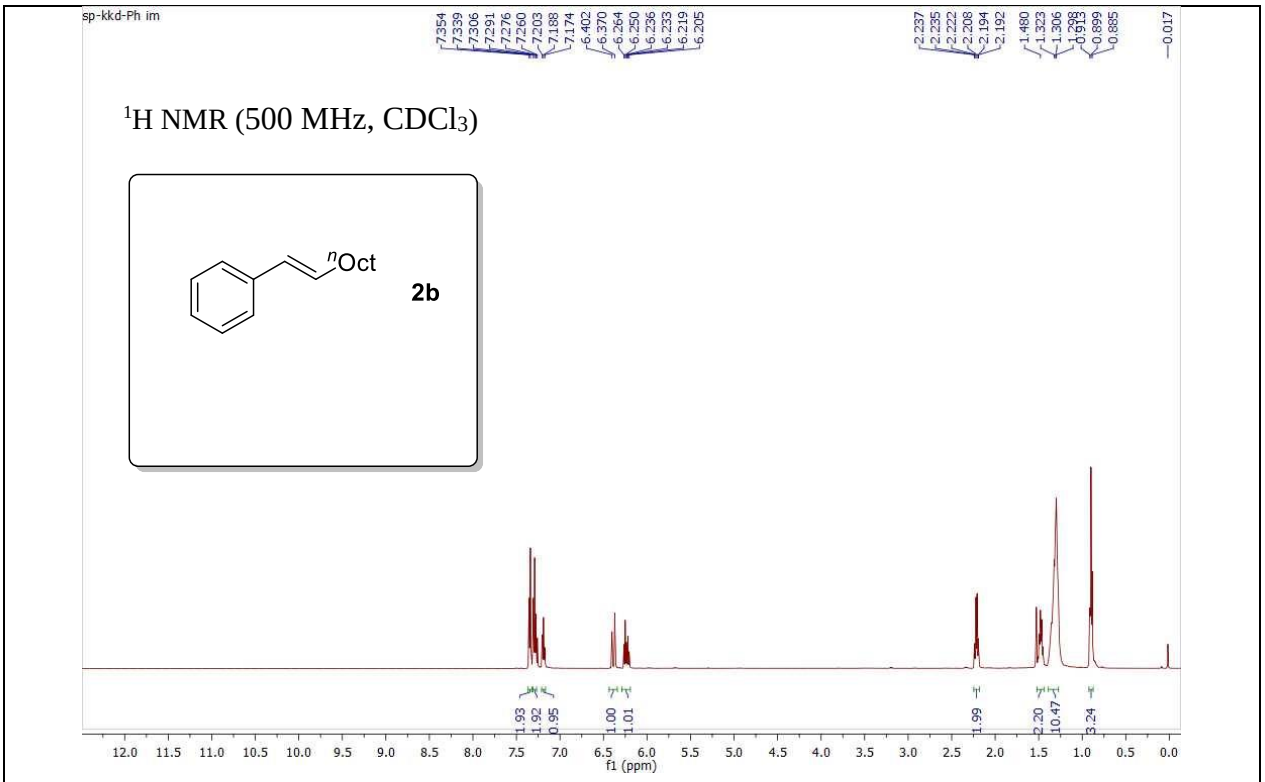

sp-kkd-Ph im
^{1}H NMR (500 MHz, $CDCl_3$)
B(pin)
B(pin)
2b16
f1 (ppm)


sp-kkd-Ph im
^{13}C NMR (126 MHz, $CDCl_3$)
B(pin)
B(pin)
2b16
f1 (ppm)

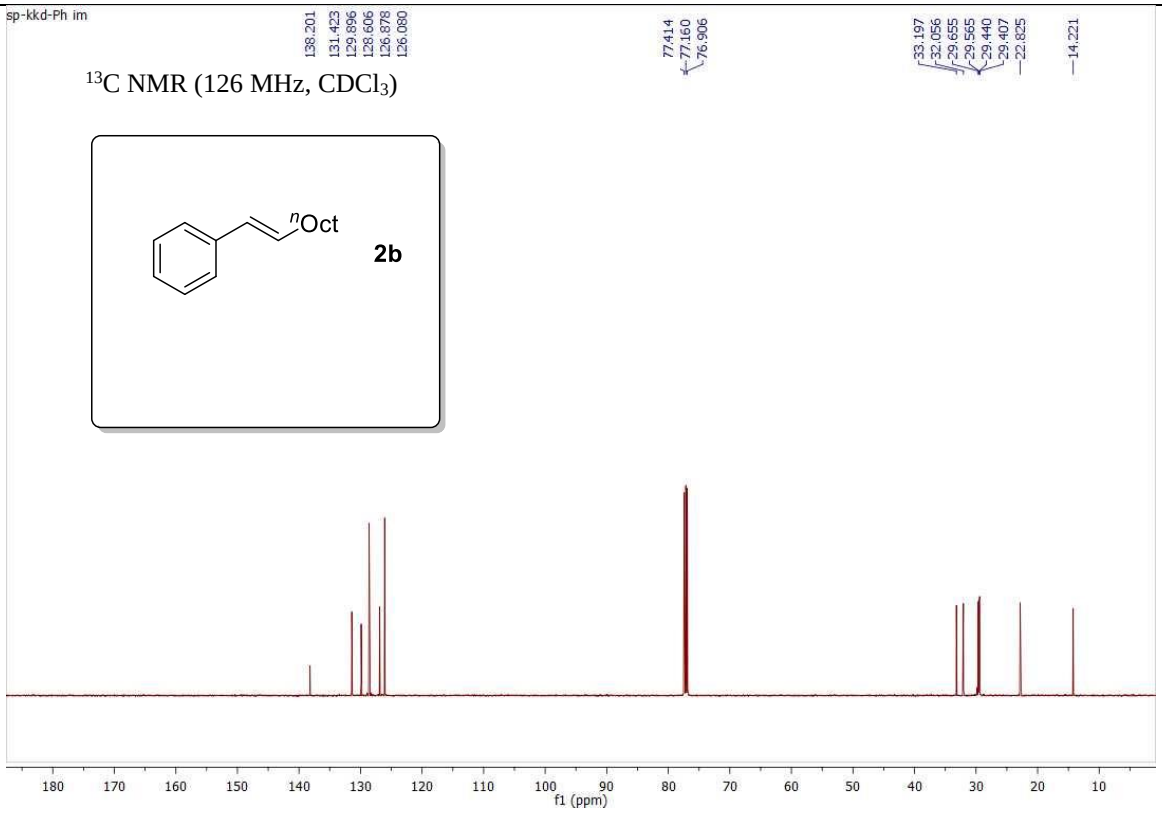

sp-kkd-Ph im
^{1}H NMR (400 MHz, $CDCl_3$)
Et
(pin)B
9
2b17
sp-kkd-Ph im
^{13}C NMR (126 MHz, $CDCl_3$)
Et
(pin)B
9
2b17
f1 (ppm)


sp-kkd-Ph im
7371
7352
7325
7306
7287
7260
7221
7203
7185
6419
6379
6285
6268
6251
6246
6229
6212
2260
2242
2225
2207
1479
1461
0950
0932
^{1}H NMR (400 MHz, $CDCl_3$)
^{n}Bu
2a
1.98
2.01
0.96
1.00
1.00
2.03
2.21
1.91
3.11
f1 (ppm)

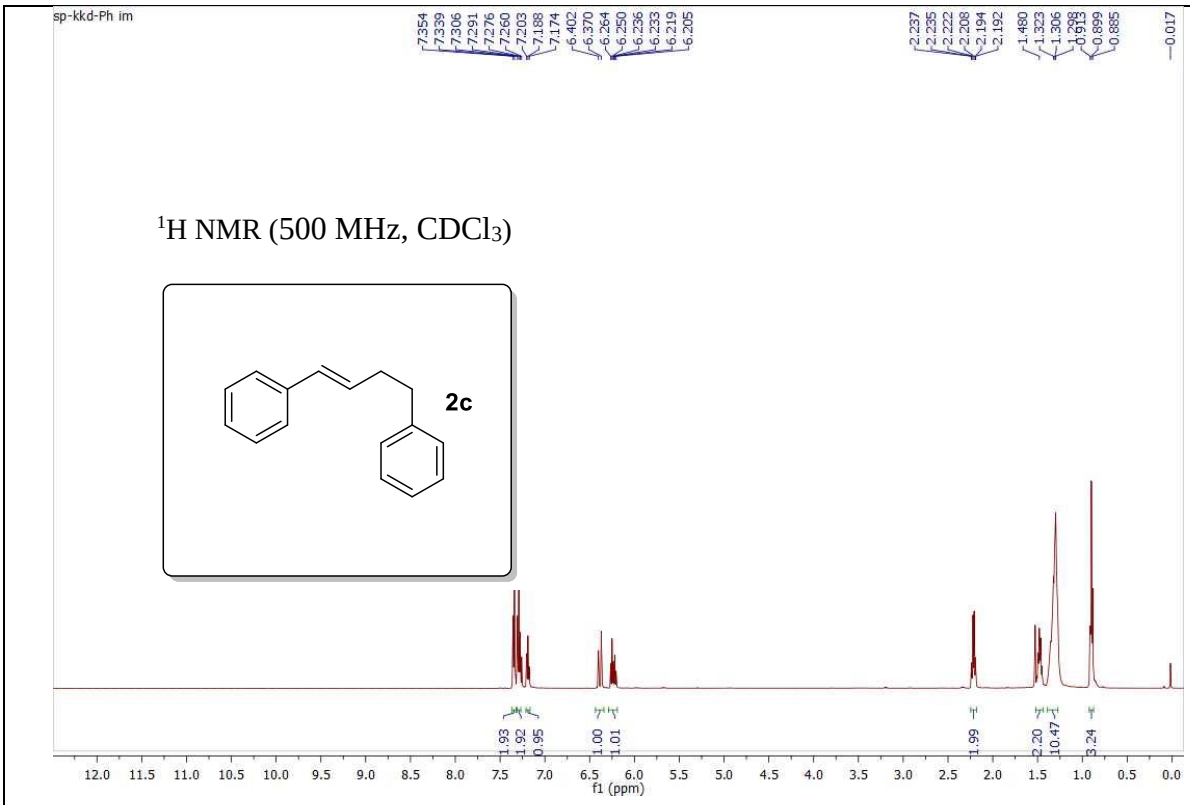

sp-kkd-Ph im
138.087
131.341
129.820
128.597
126.870
126.028
77.477
77.160
76.842
32.870
31.670
22.417
14.109
^{13}C NMR (101 MHz, $CDCl_3$)
^{n}Bu
2a
f1 (ppm)



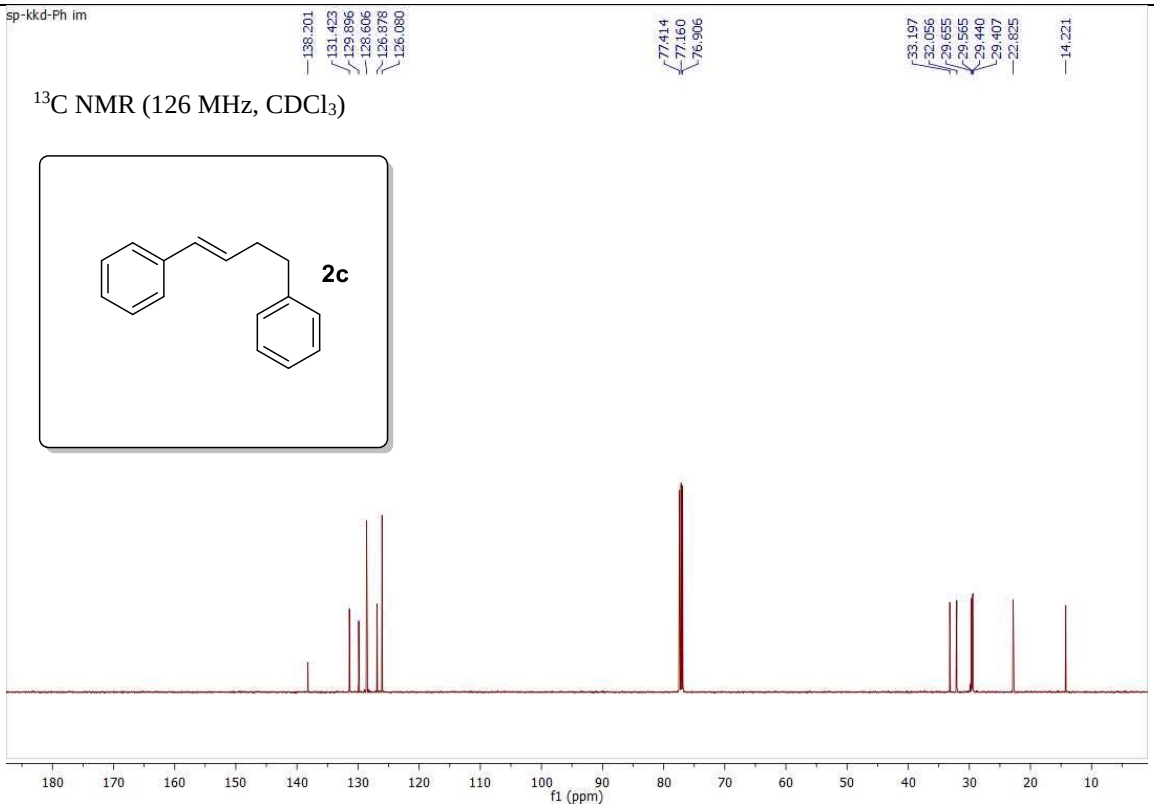
^{1}H NMR (500 MHz, $CDCl_3$)



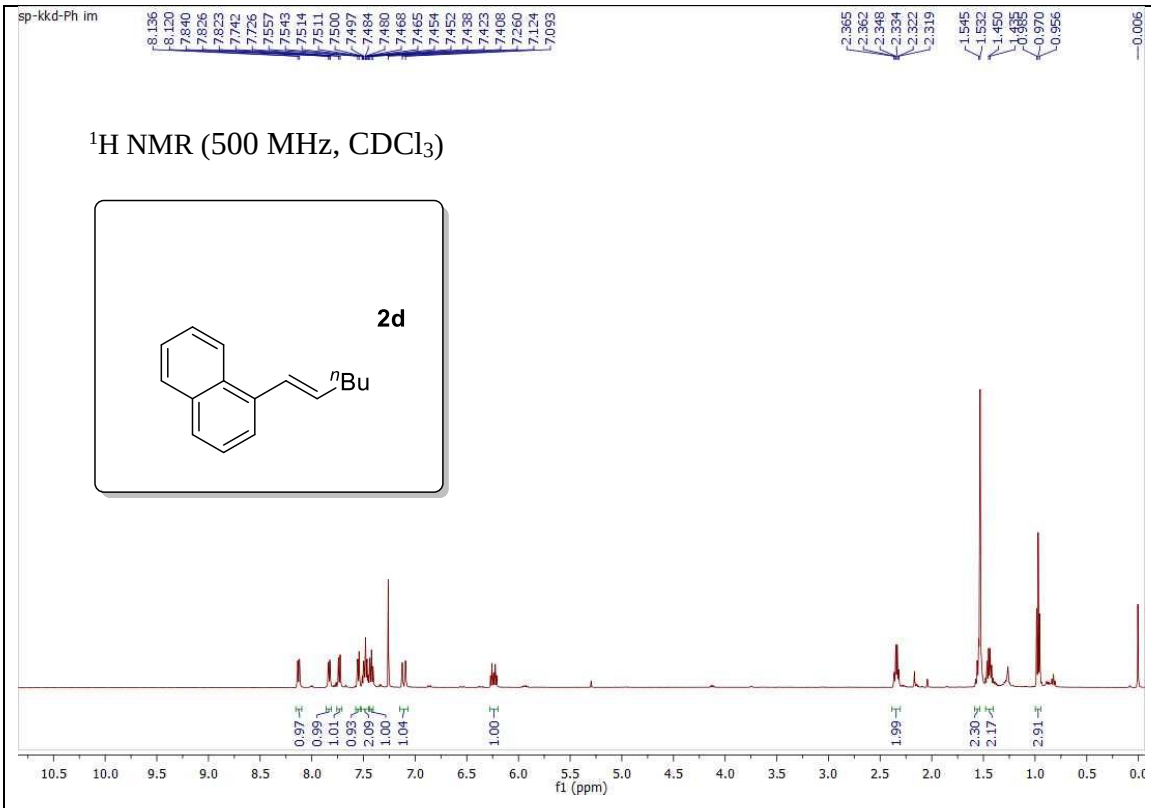
^{13}C NMR (126 MHz, $CDCl_3$)



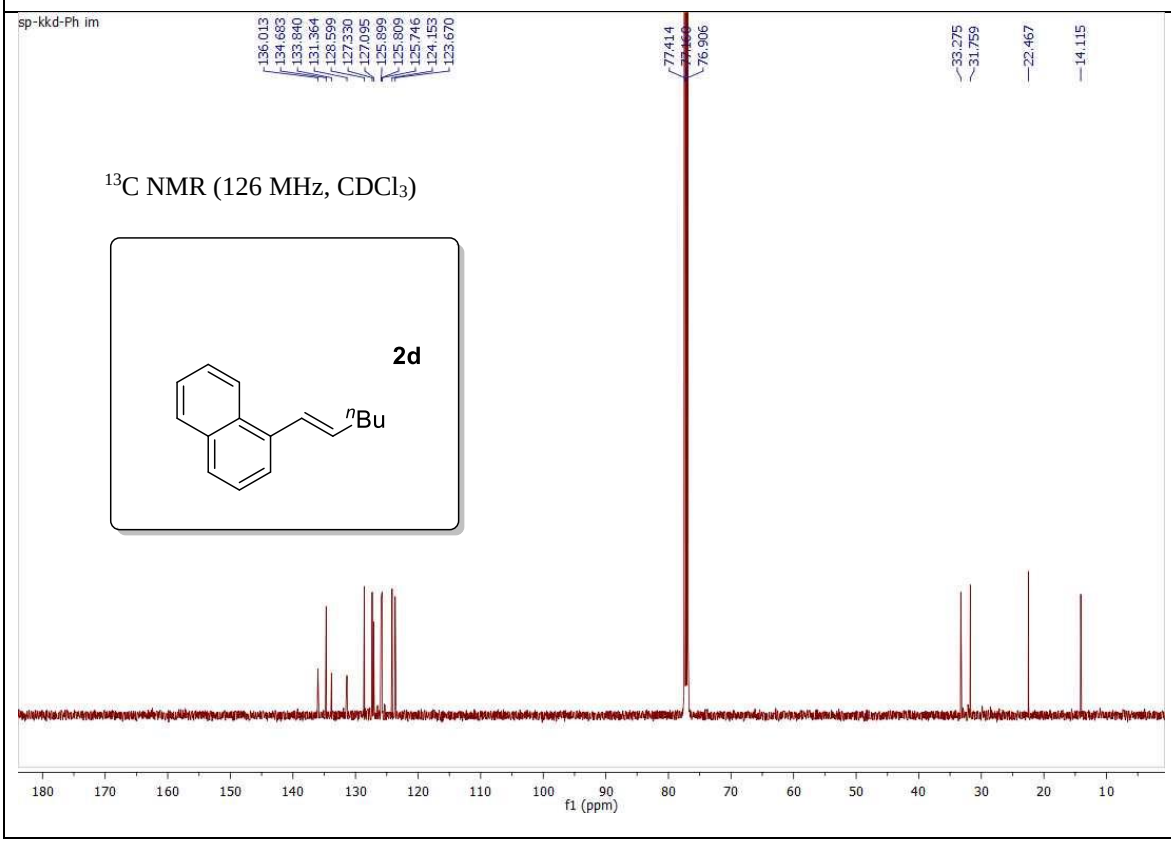
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

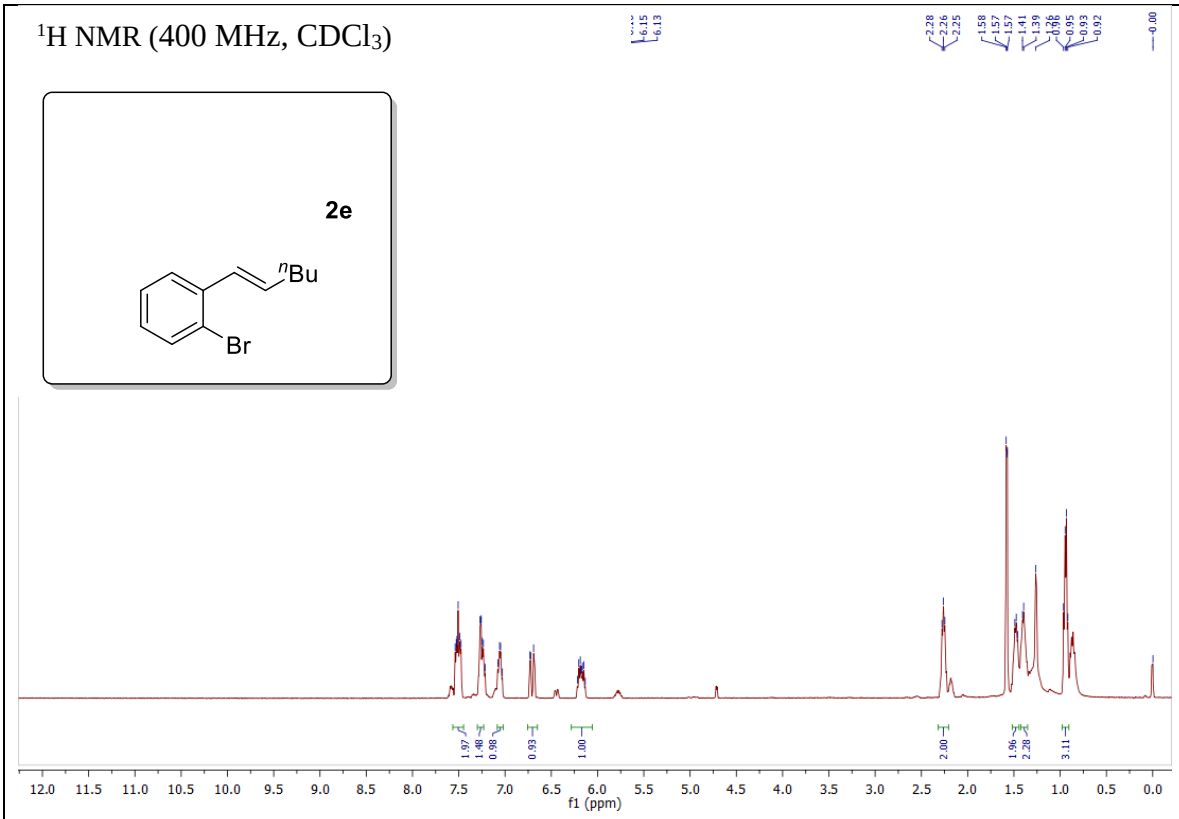


^{1}H NMR (500 MHz, $CDCl_3$)

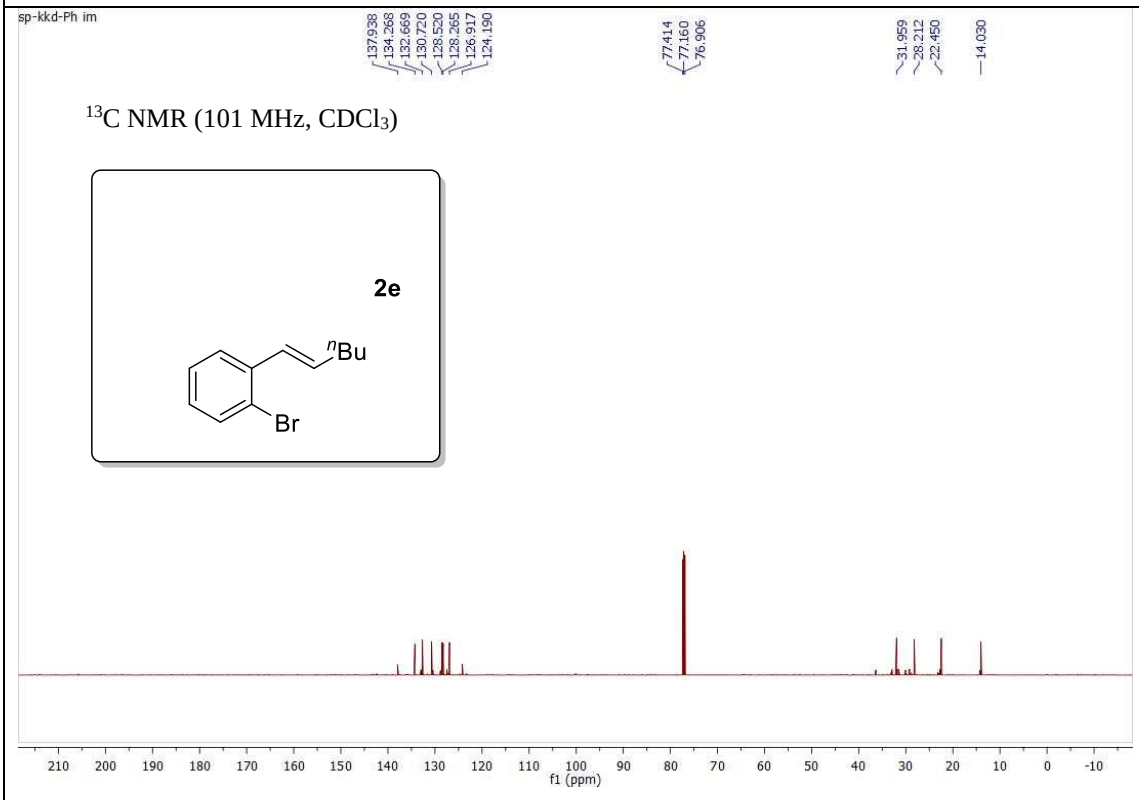


^{13}C NMR (126 MHz, $CDCl_3$)

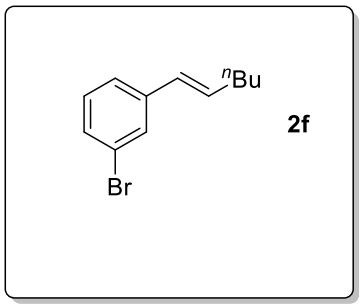
^{1}H NMR (400 MHz, $CDCl_3$)



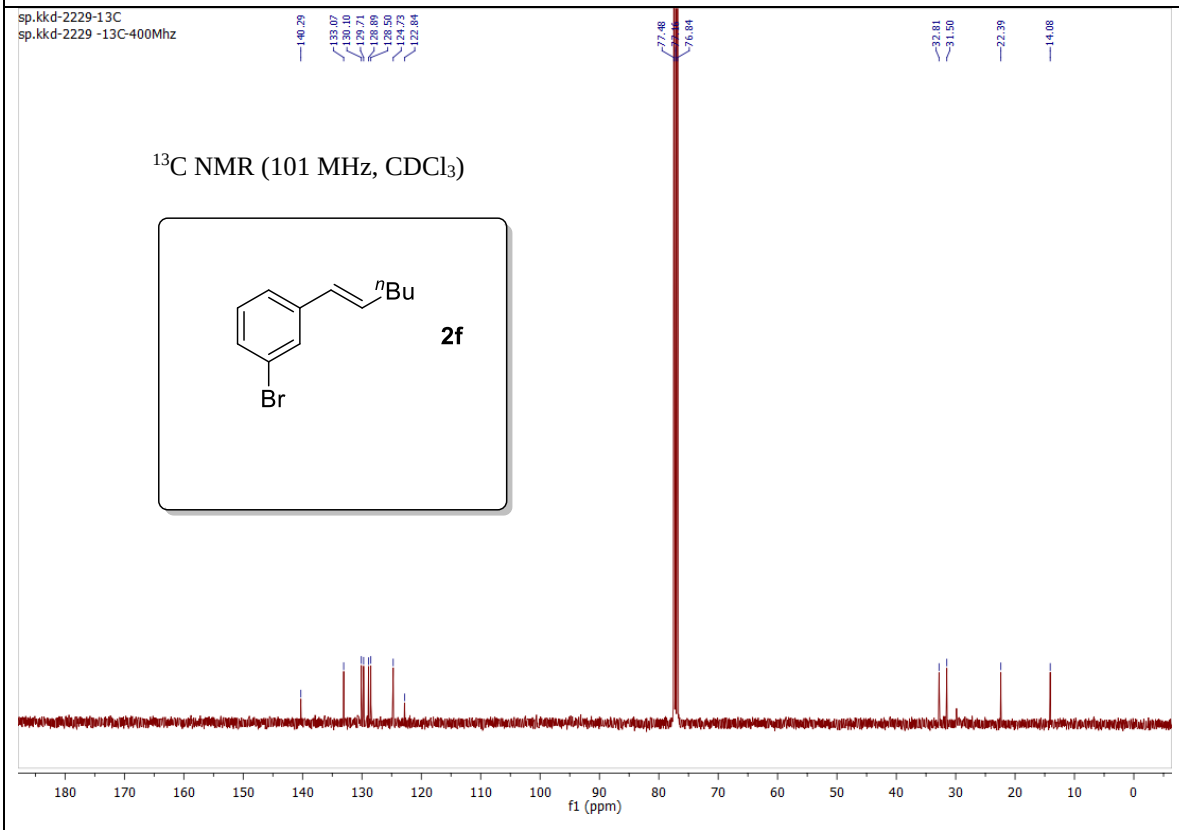
^{13}C NMR (101 MHz, $CDCl_3$)



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

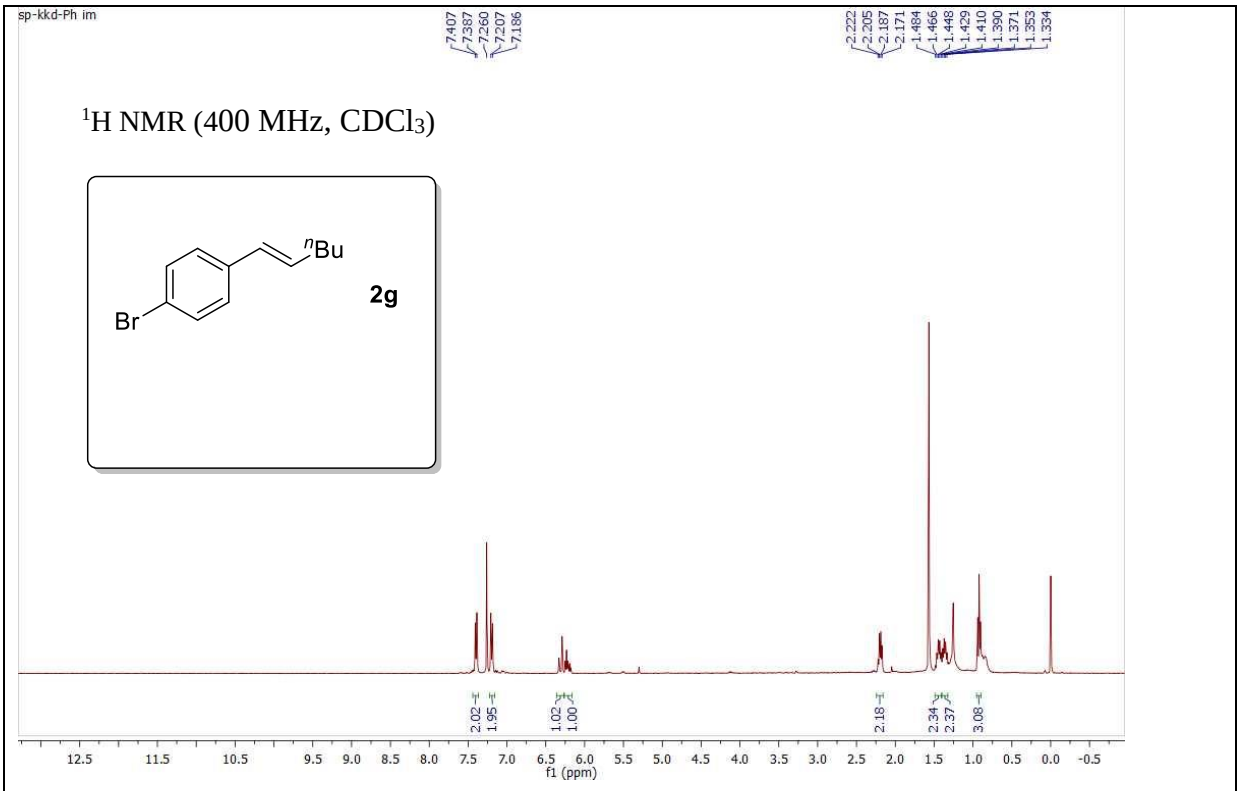


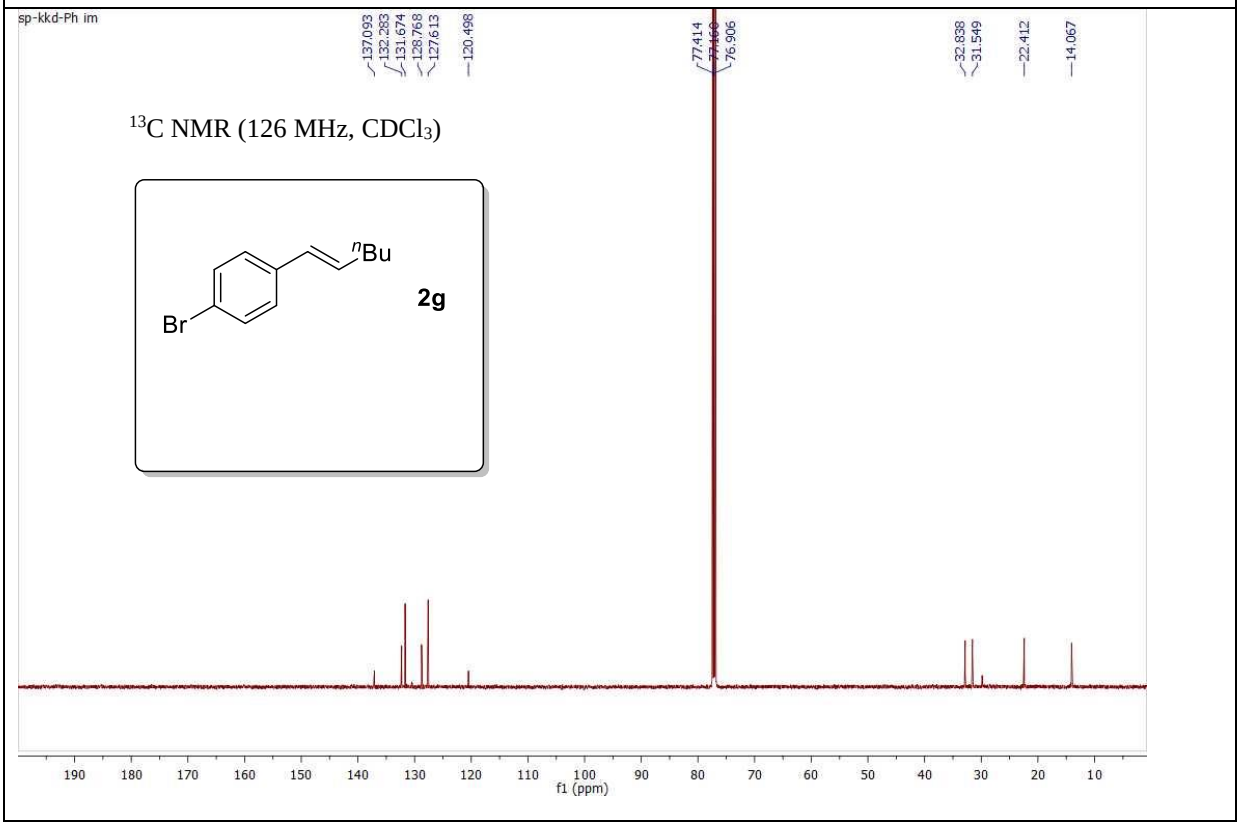
2f

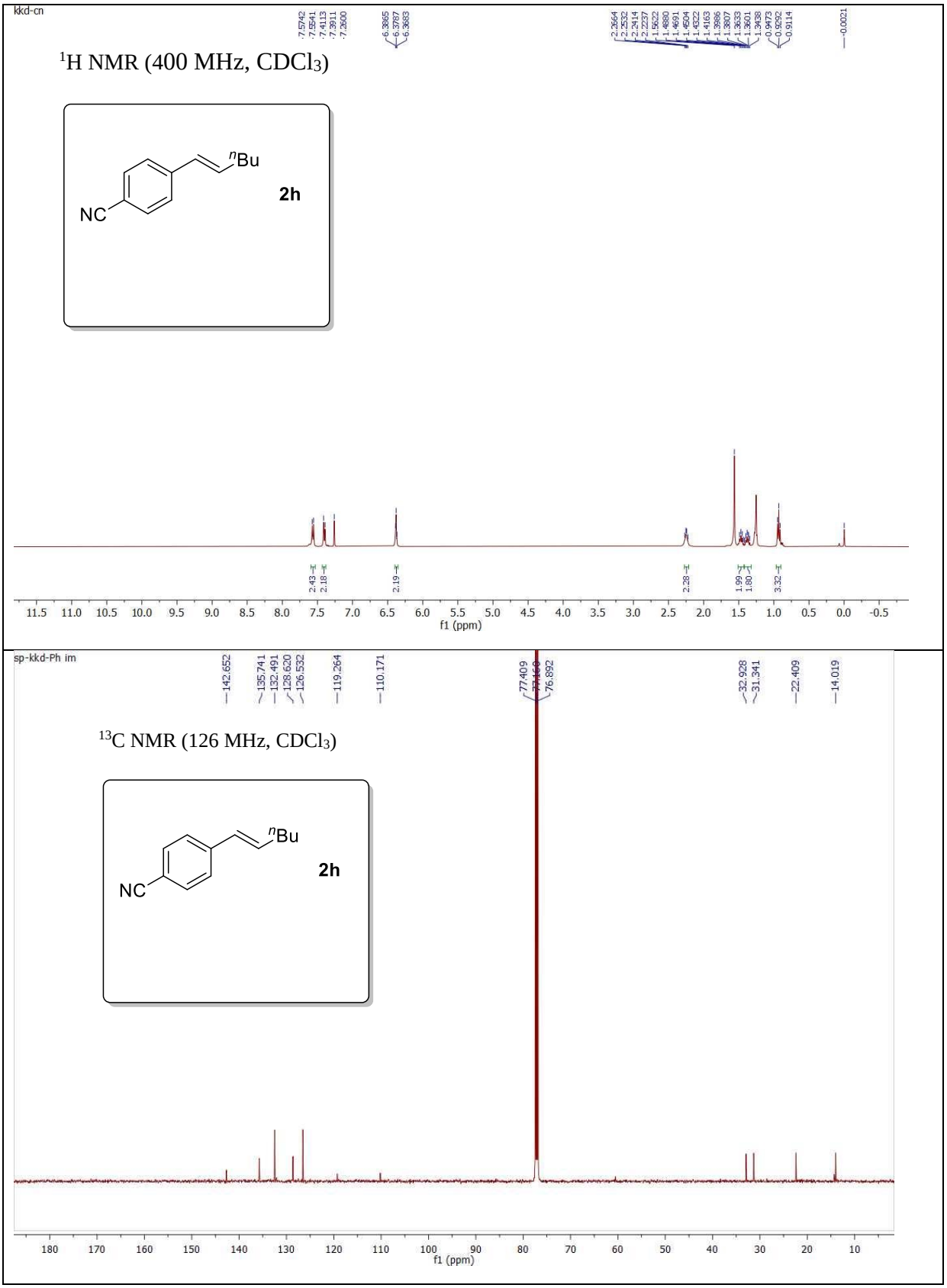


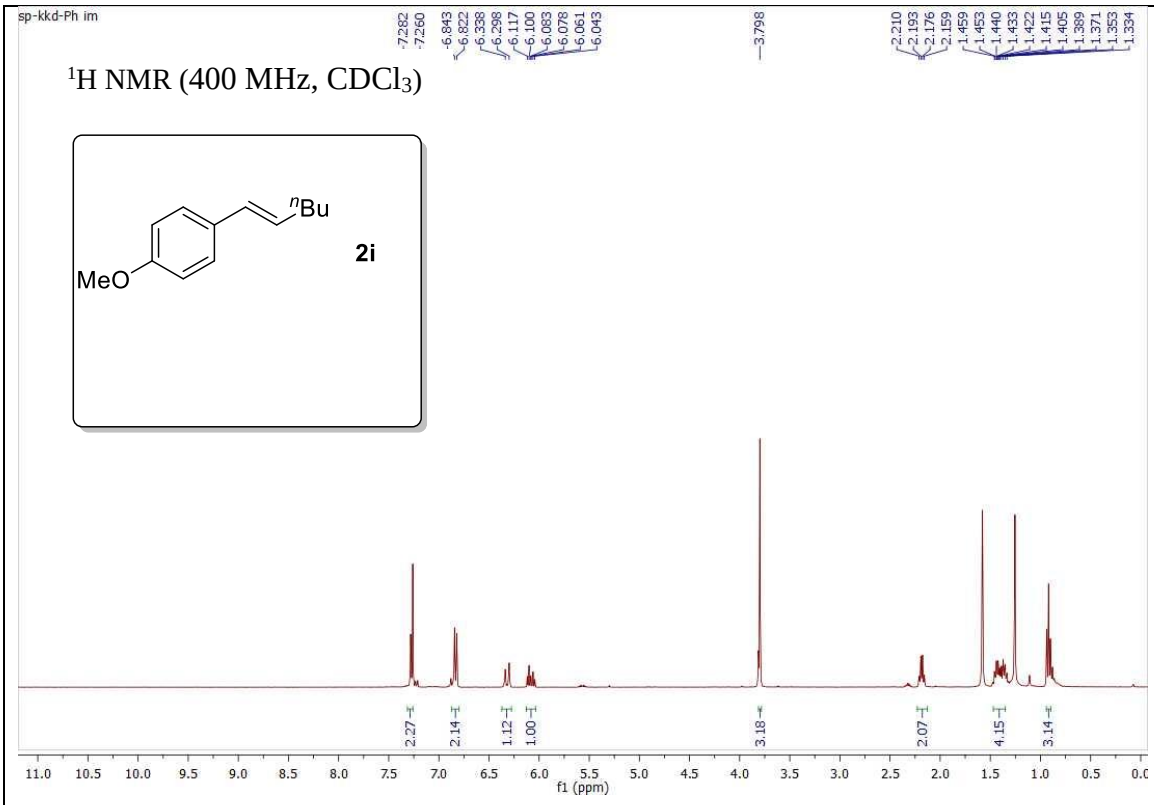
^{13}C NMR (101 MHz, $CDCl_3$)

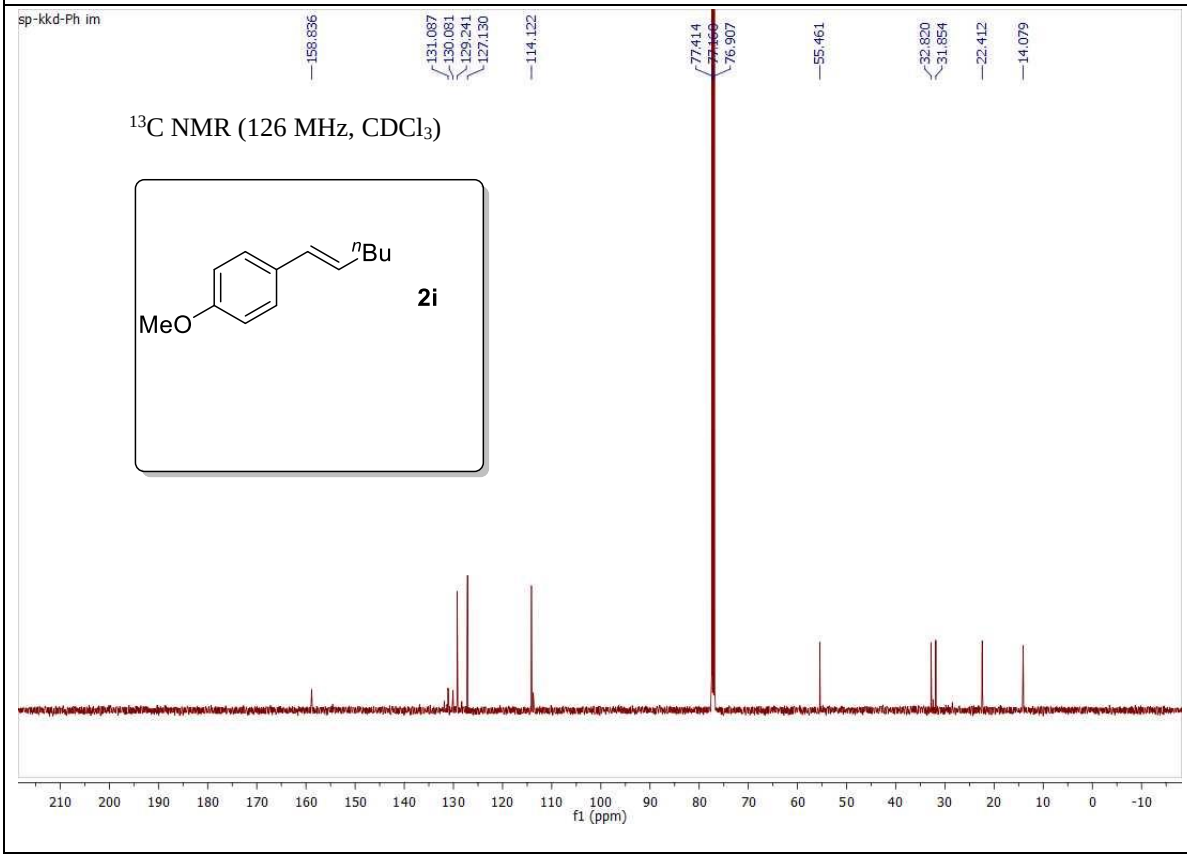
2f

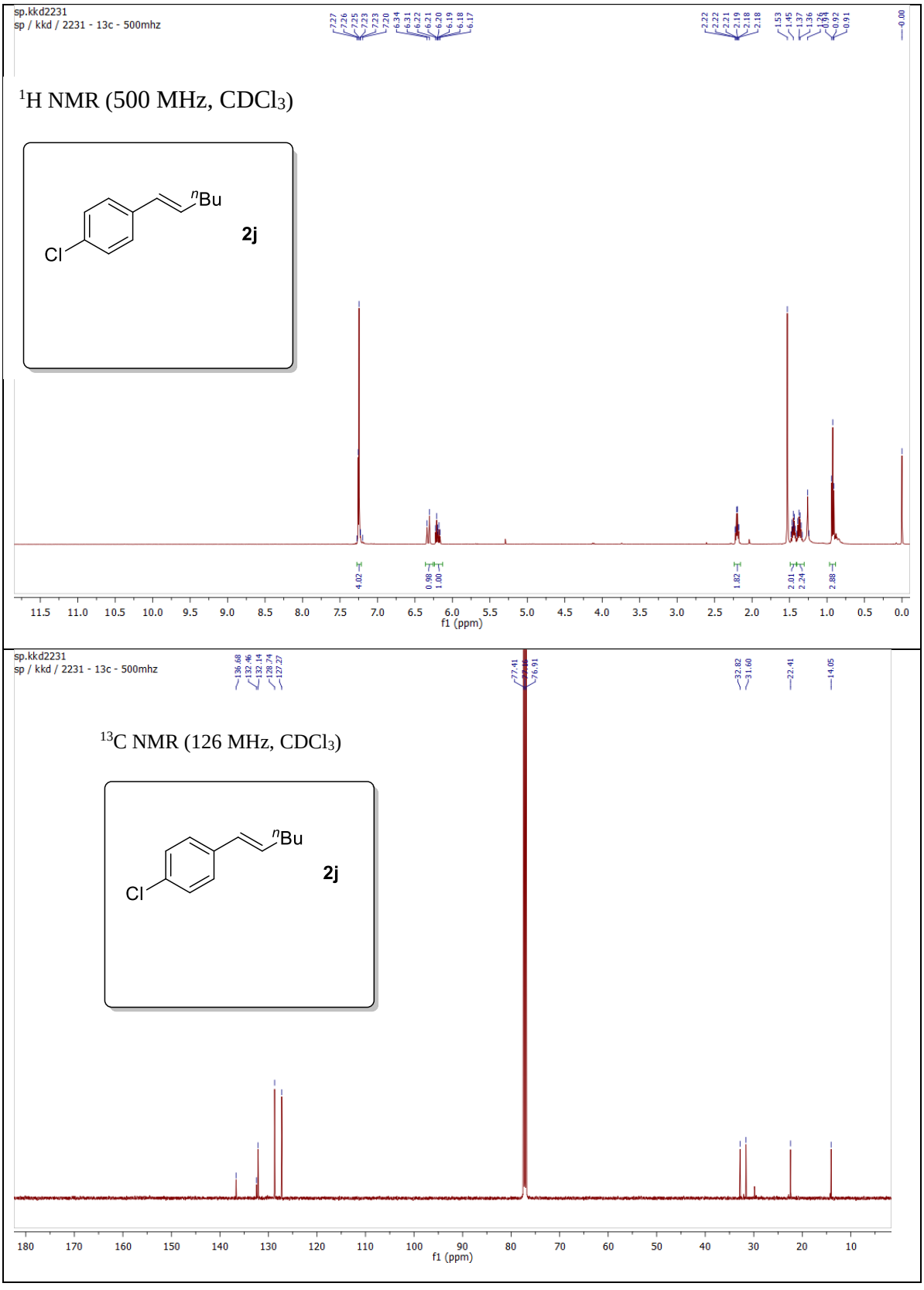

sp-kkd-Ph im
7.407
7.387
7.260
7.207
7.186
2.222
2.205
2.187
2.171
1.484
1.466
1.448
1.429
1.410
1.390
1.371
1.353
1.334
^{1}H NMR (400 MHz, $CDCl_3$)
^{n}Bu
Br
2g
2.02
1.95
1.02
1.00
2.18
2.34
2.37
3.08
f1 (ppm)

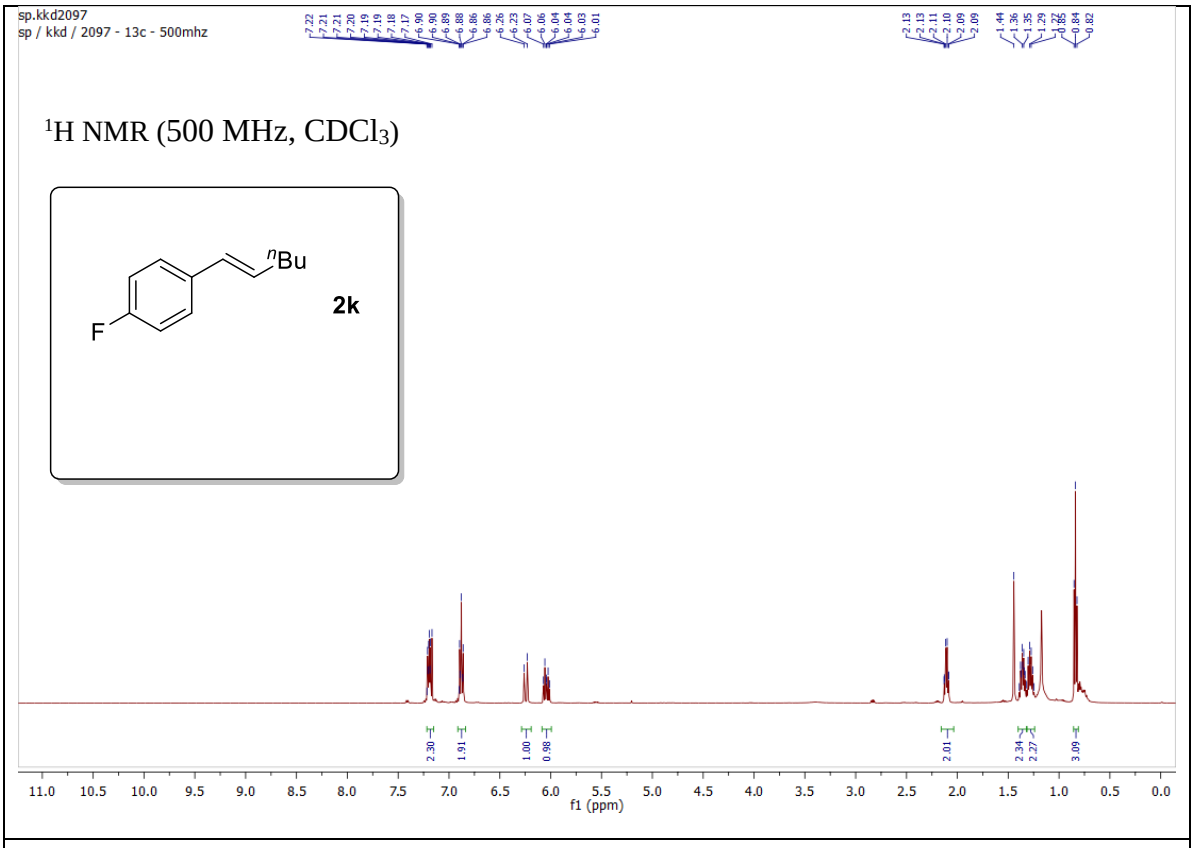

sp-kkd-Ph im
137.093
132.283
131.674
128.768
127.613
120.498
77.414
77.166
76.906
32.838
31.549
22.412
14.067
^{13}C NMR (126 MHz, $CDCl_3$)
^{n}Bu
Br
2g
f1 (ppm)

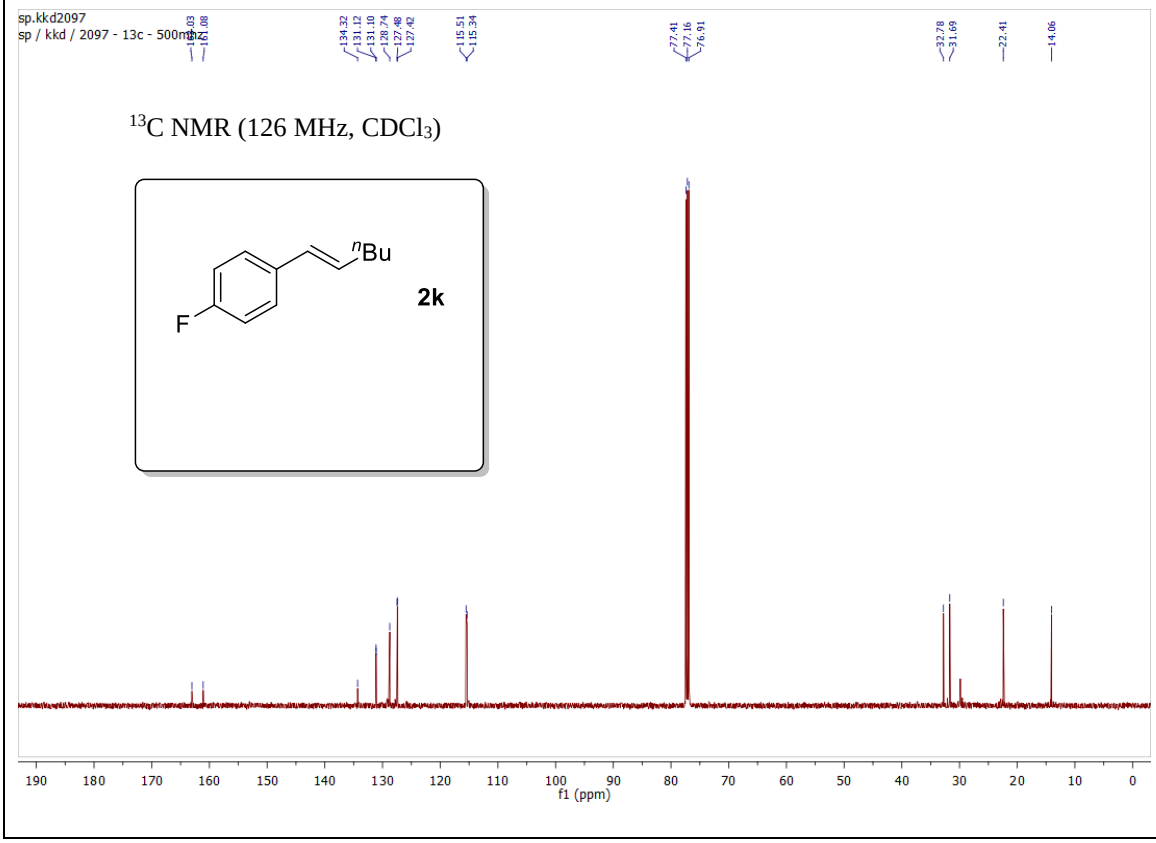

kkd-cn
^{1}H NMR (400 MHz, $CDCl_3$)
nBu
NC
2h
f1 (ppm)
sp-kkd-Ph im
^{13}C NMR (126 MHz, $CDCl_3$)
nBu
NC
2h
f1 (ppm)

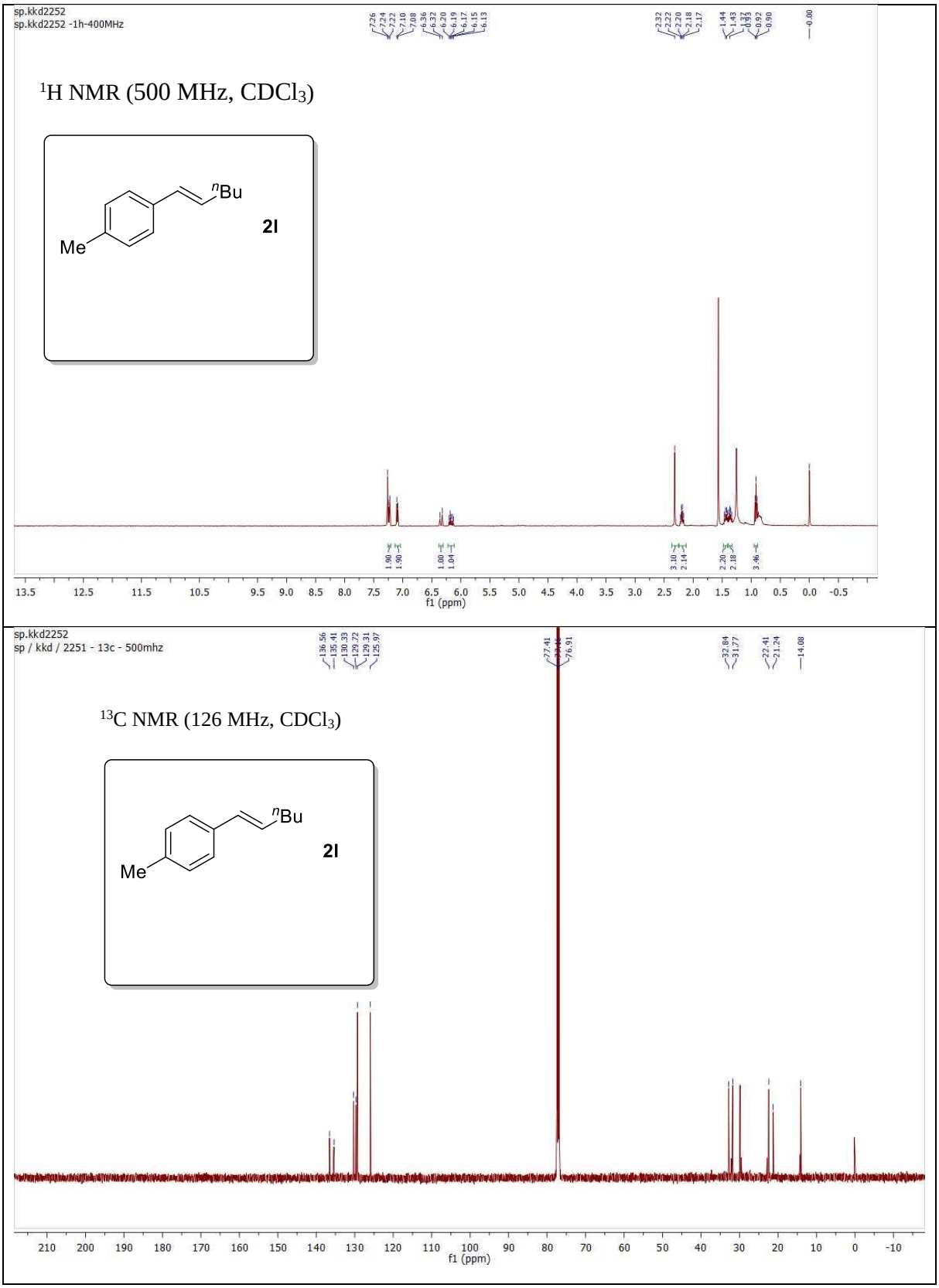

sp-kkd-Ph im
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
^{n}Bu
2i
f1 (ppm)


sp-kkd-Ph im
^{13}C NMR (126 MHz, $CDCl_3$)
MeO
^{n}Bu
2i
f1 (ppm)

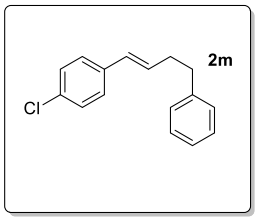

sp.kkd2231
sp / kkd / 2231 - 13c - 500mhz
^{1}H NMR (500 MHz, CDCl$_3$)
nBu
Cl
2j
f1 (ppm)
sp.kkd2231
sp / kkd / 2231 - 13c - 500mhz
^{13}C NMR (126 MHz, CDCl$_3$)
nBu
Cl
2j
f1 (ppm)

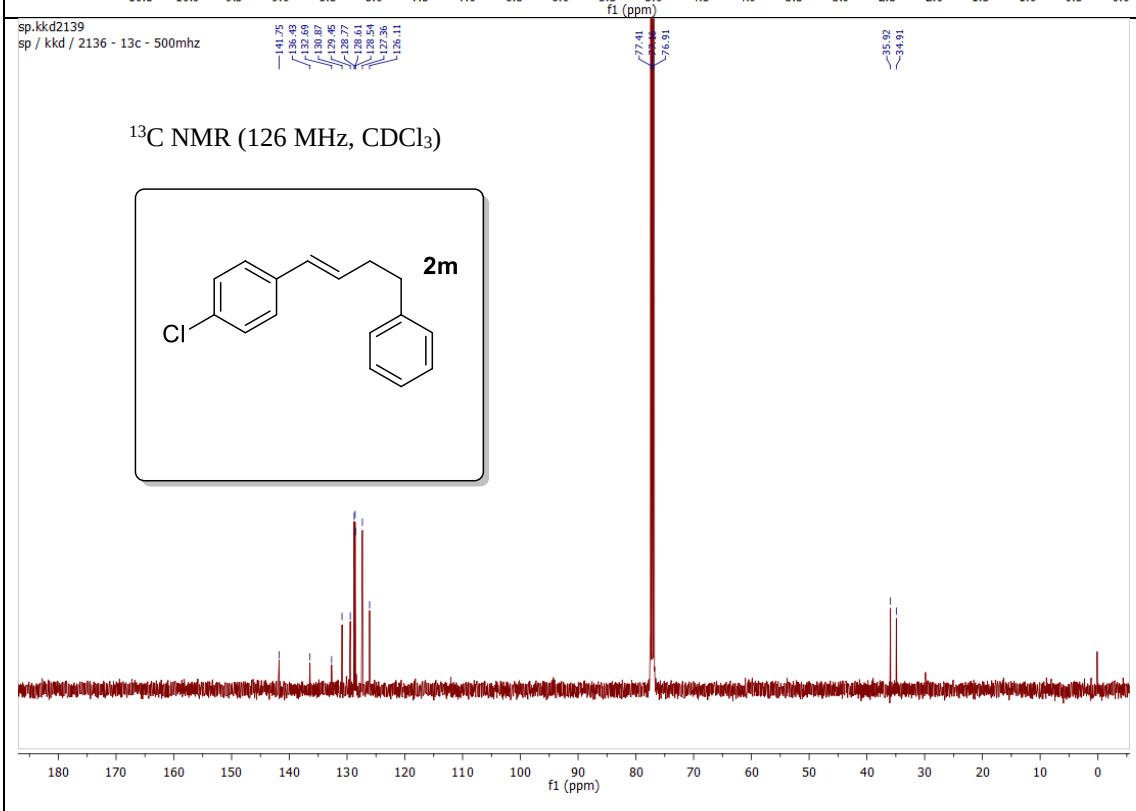

sp.kkd2097
sp / kkd / 2097 - 13c - 500mhz
^{1}H NMR (500 MHz, $CDCl_3$)
nBu
F
2k
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


sp.kkd2097
sp / kkd / 2097 - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
nBu
F
2k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


sp.kkd2252
sp.kkd2252 -1h-400MHz
7.26
7.24
7.22
7.10
7.08
6.36
6.32
6.20
6.19
6.17
6.15
6.13
2.32
2.22
2.20
2.18
2.17
1.44
1.43
1.37
0.93
0.92
0.90
0.00
1H NMR (500 MHz, CDCl3)
nBu
Me
2l
1.90
1.90
1.00
1.04
3.10
2.14
2.20
2.18
3.46
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
sp.kkd2252
sp / kkd / 2251 - 13c - 500mhz
136.56
135.41
130.33
129.72
129.31
125.97
77.41
77.16
76.91
32.84
31.77
22.41
21.24
14.08
13C NMR (126 MHz, CDCl3)
nBu
Me
2l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

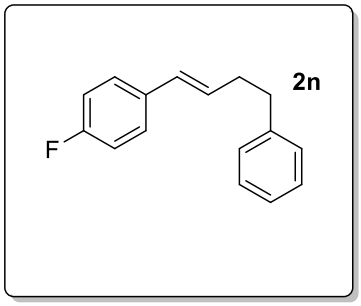
^{1}H NMR (500 MHz, $CDCl_3$)

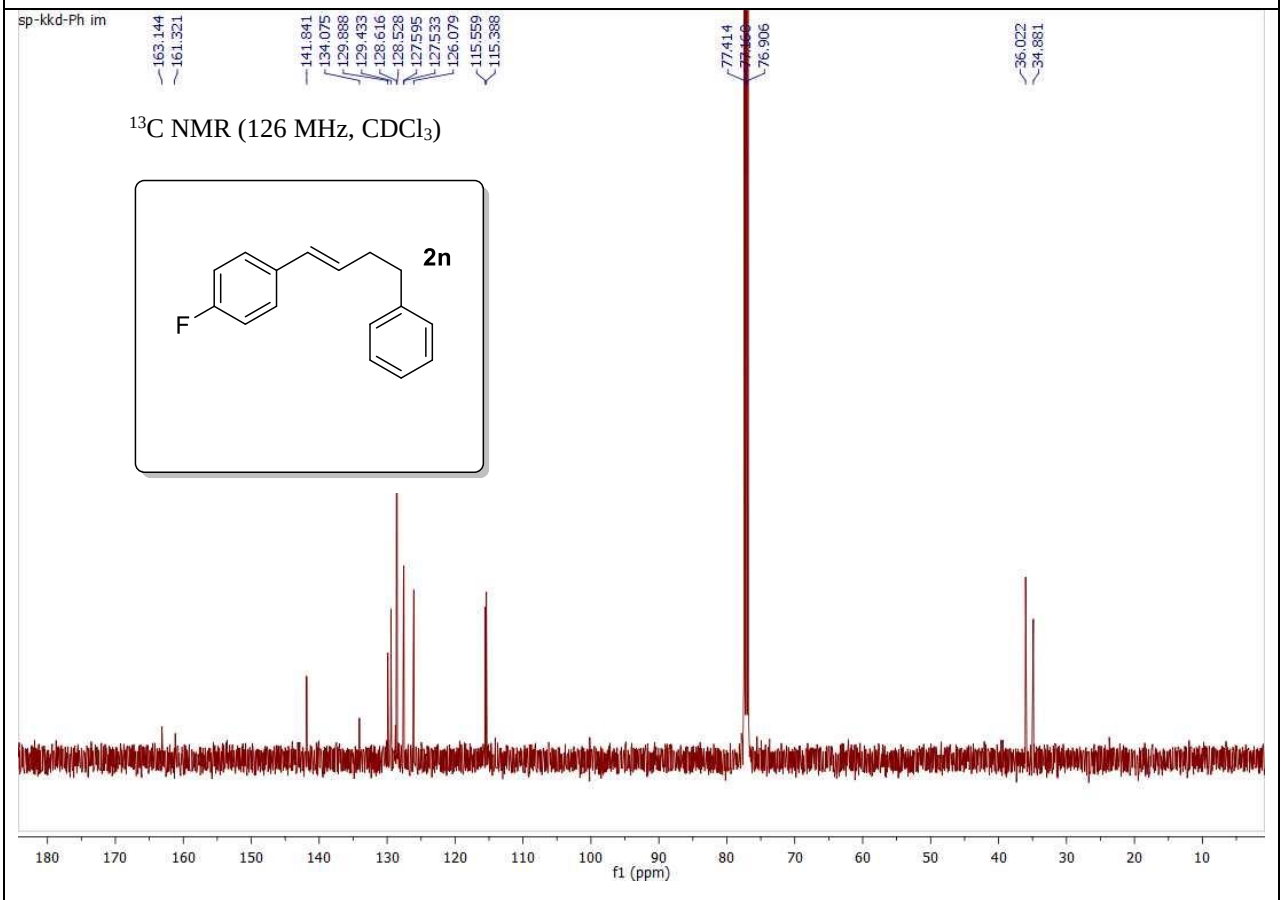




^{13}C NMR (126 MHz, $CDCl_3$)

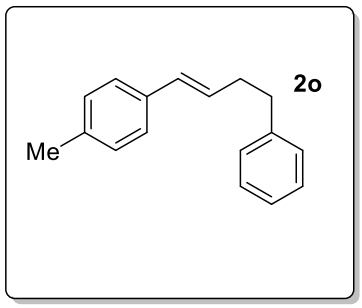
^{1}H NMR (500 MHz, $CDCl_3$)

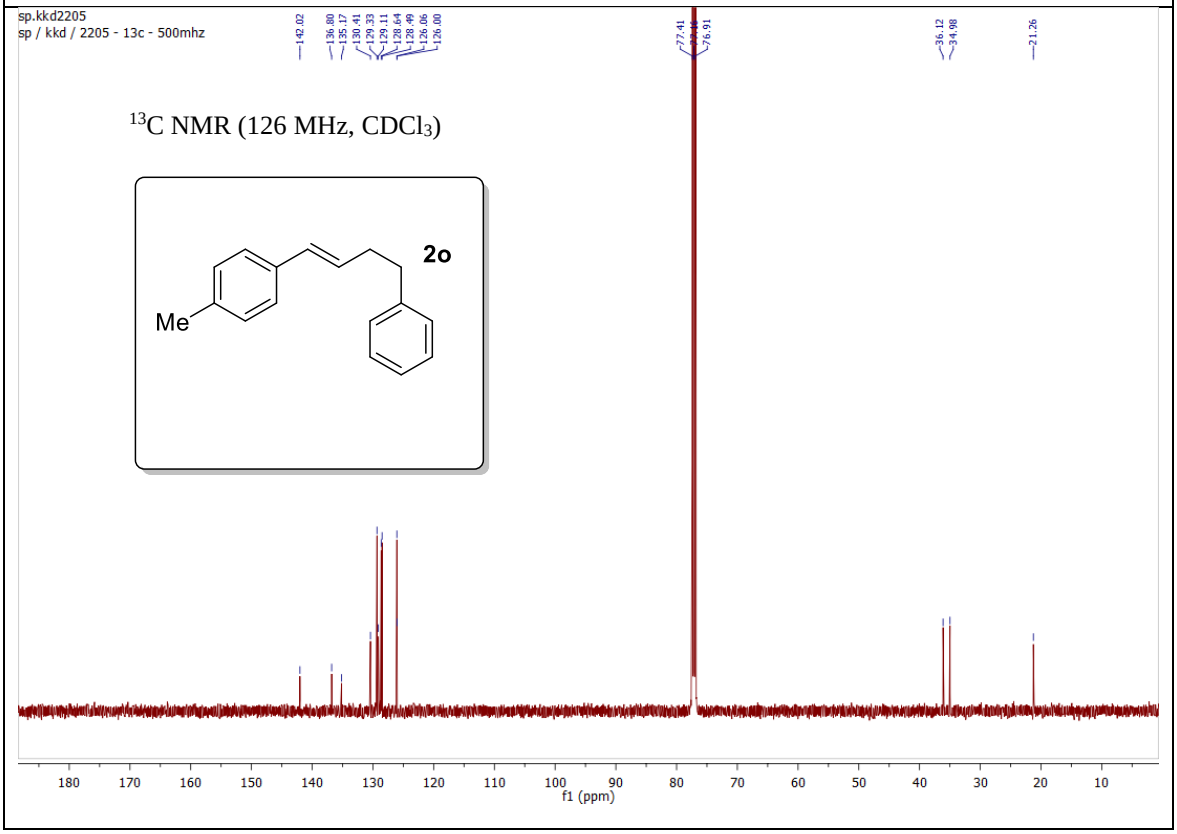




^{13}C NMR (126 MHz, $CDCl_3$)

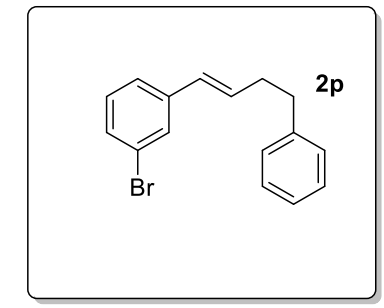
^{1}H NMR (400 MHz, $CDCl_3$)



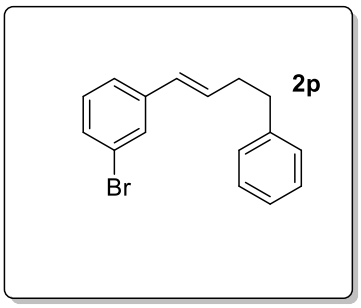


^{13}C NMR (126 MHz, $CDCl_3$)

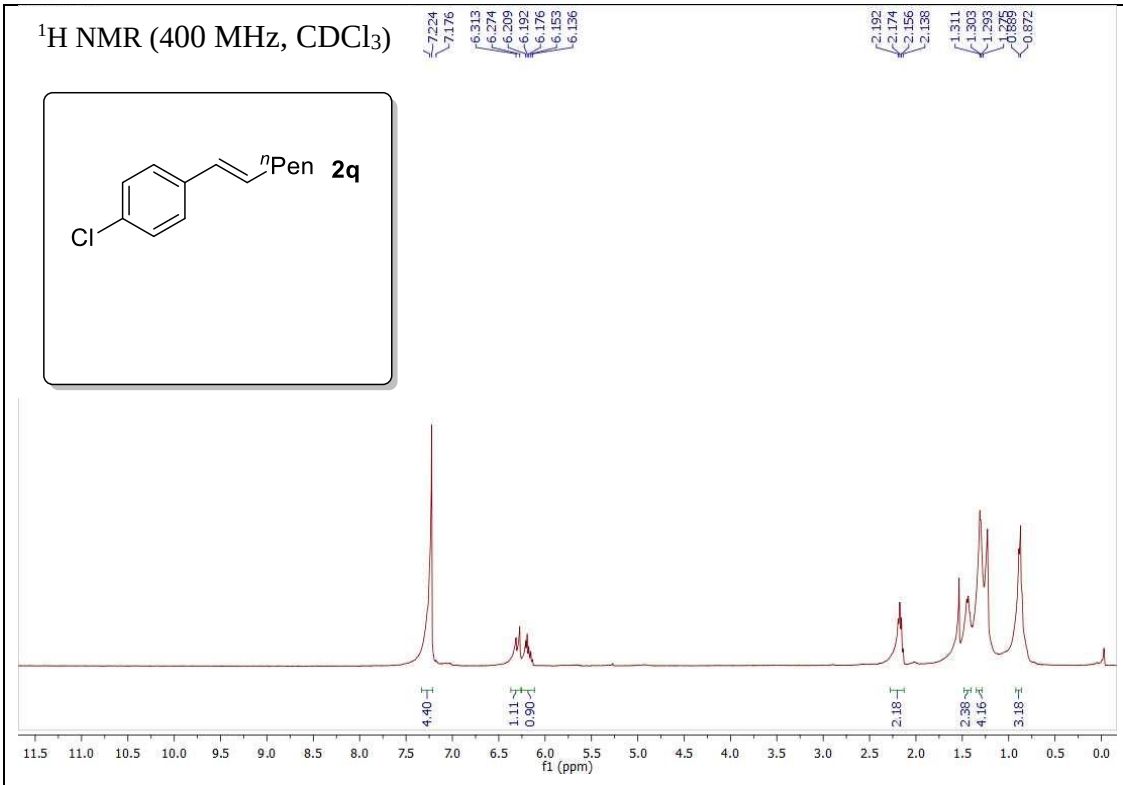
^{1}H NMR (500 MHz, $CDCl_3$)

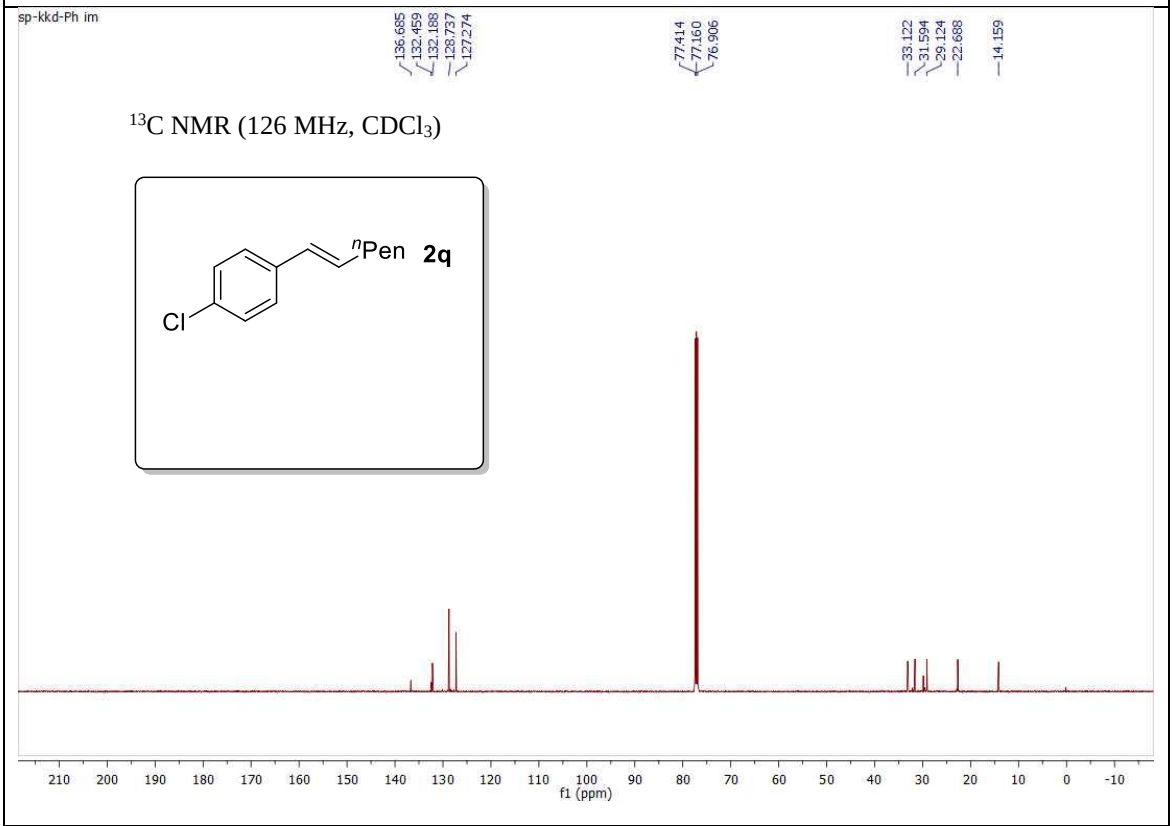


^{13}C NMR (126 MHz, $CDCl_3$)



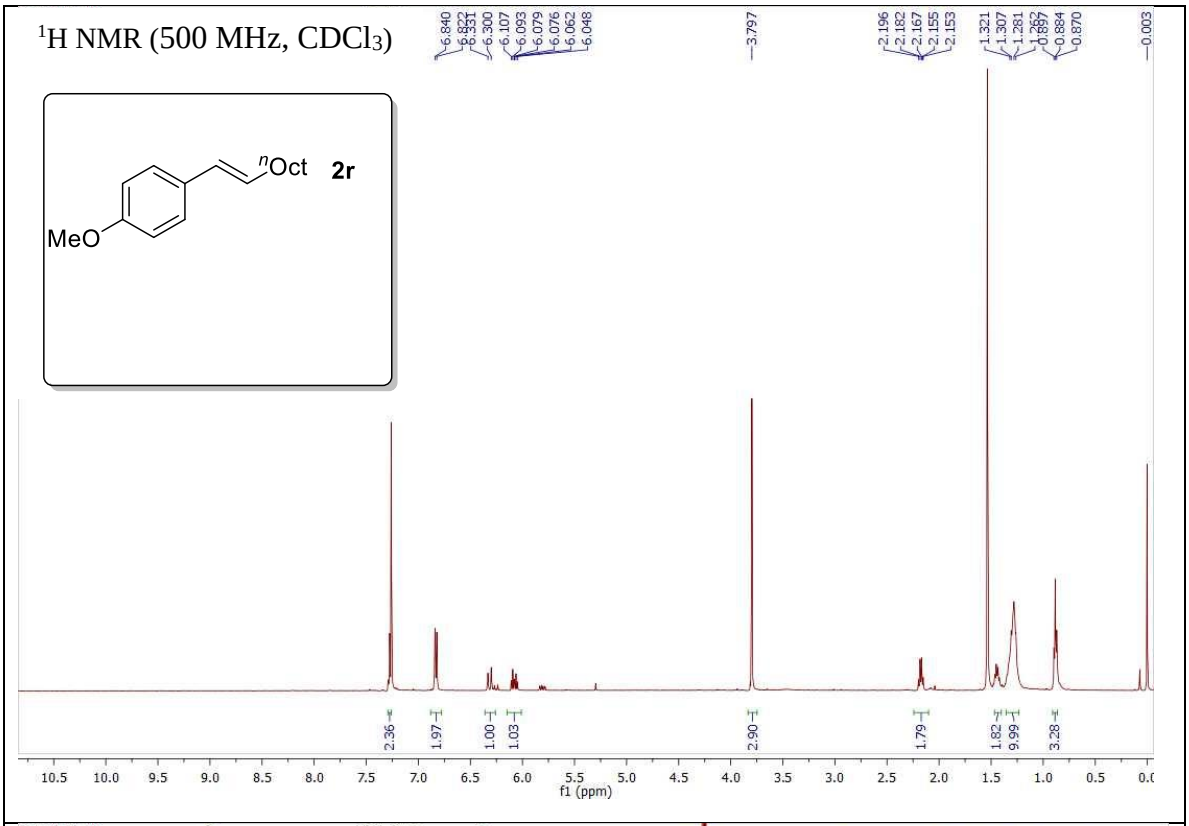
^{1}H NMR (400 MHz, $CDCl_3$)

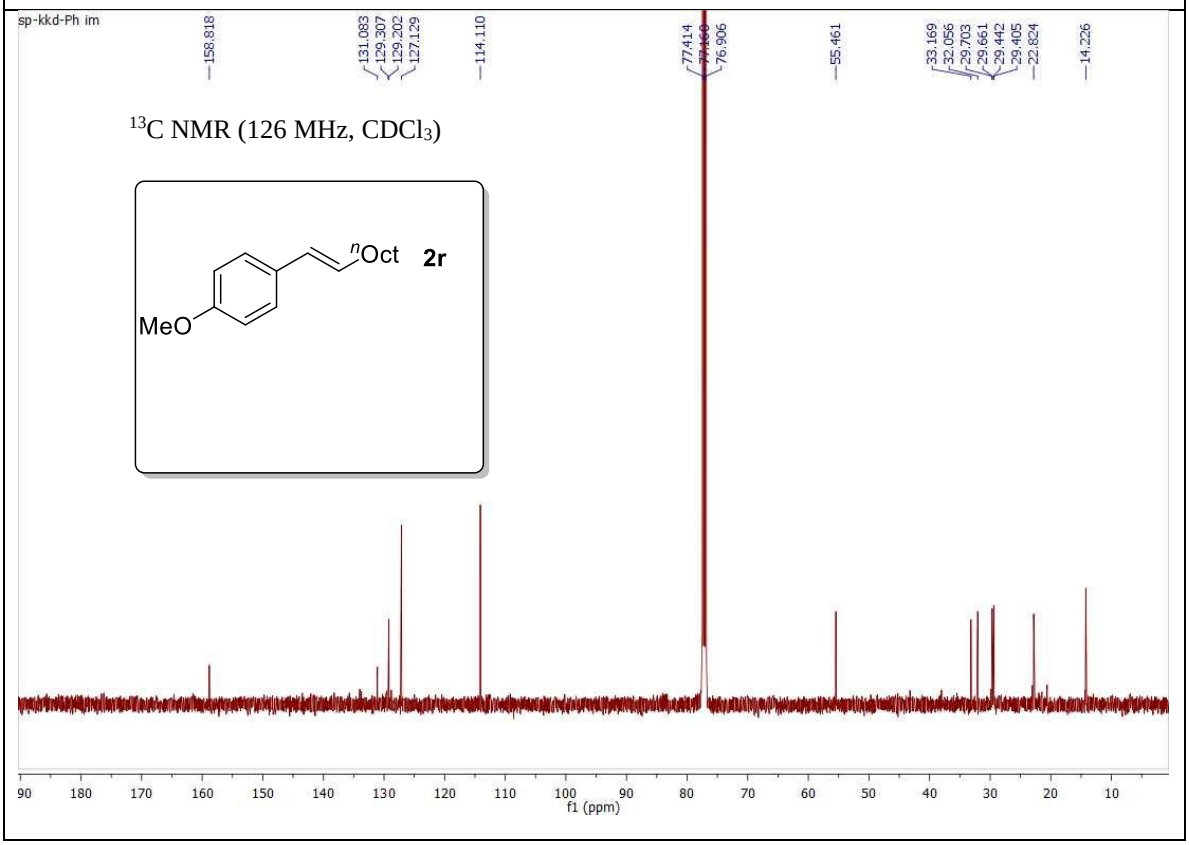




^{13}C NMR (126 MHz, $CDCl_3$)

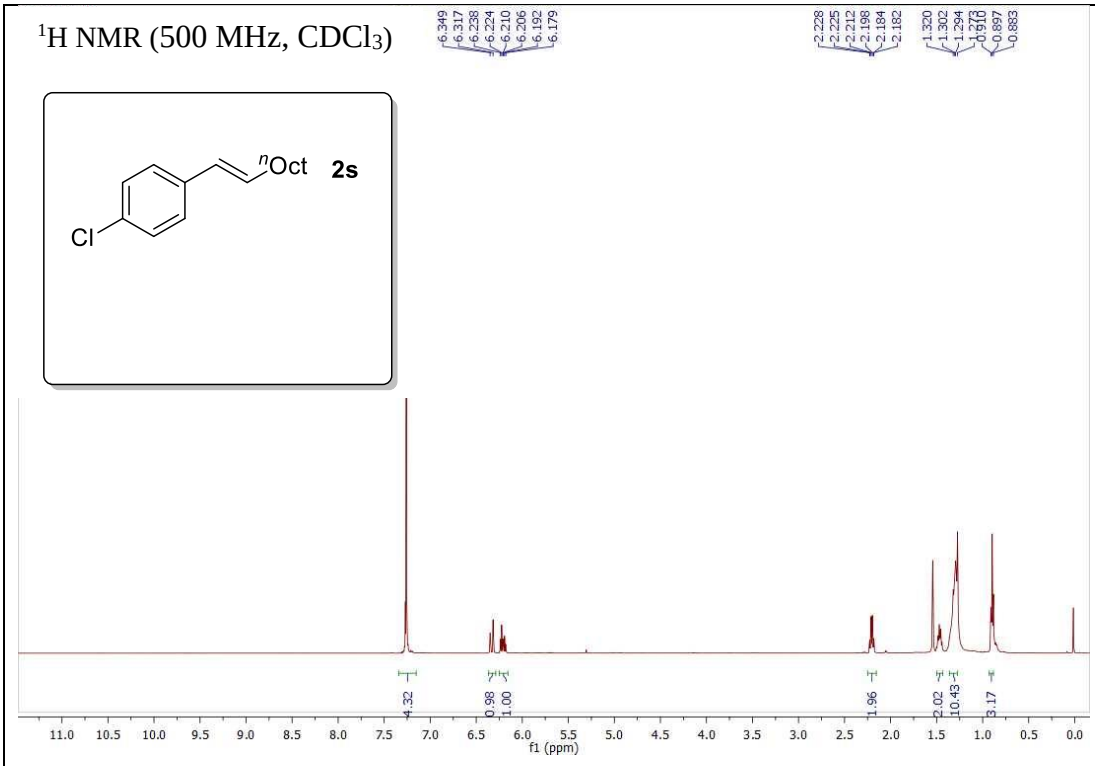
^{1}H NMR (500 MHz, $CDCl_3$)



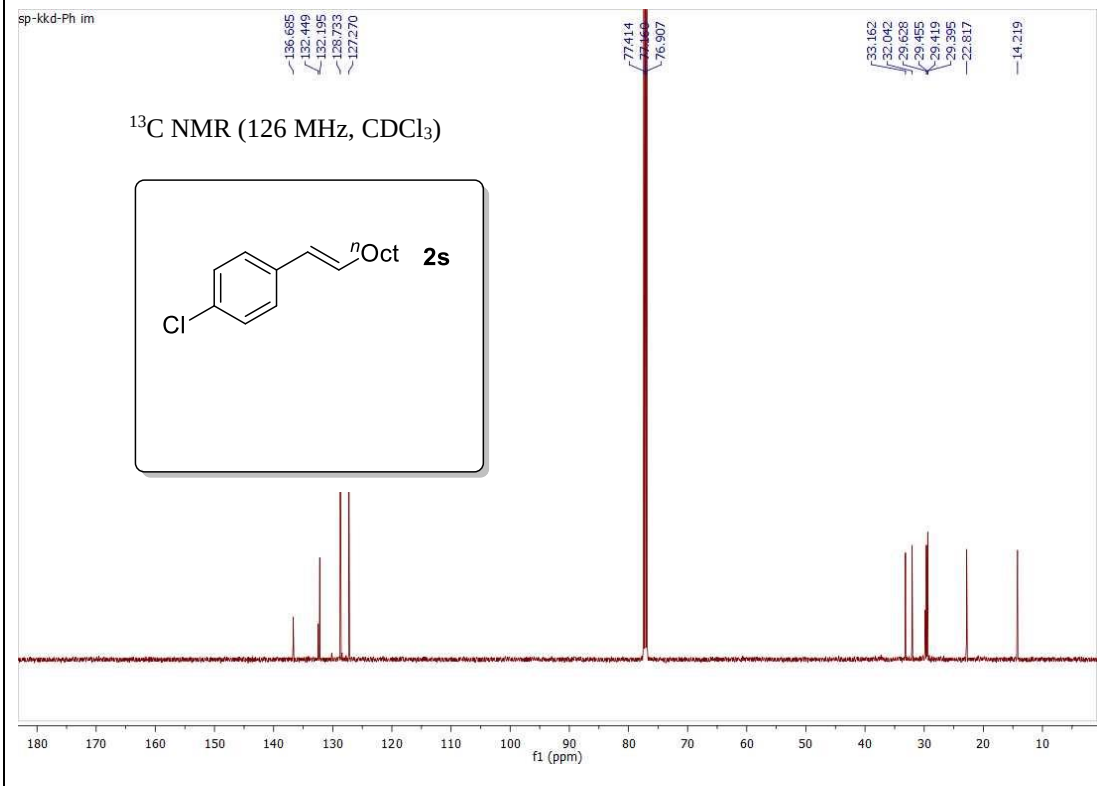


^{13}C NMR (126 MHz, $CDCl_3$)

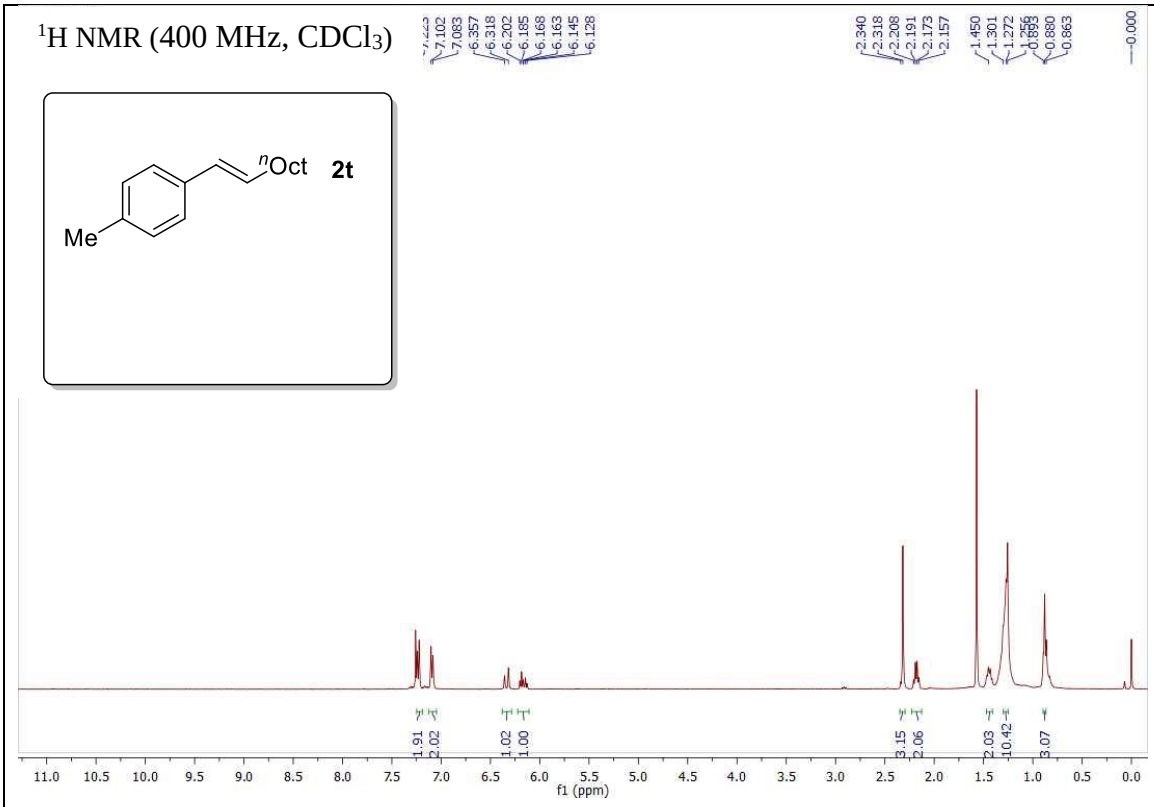
^{1}H NMR (500 MHz, $CDCl_3$)



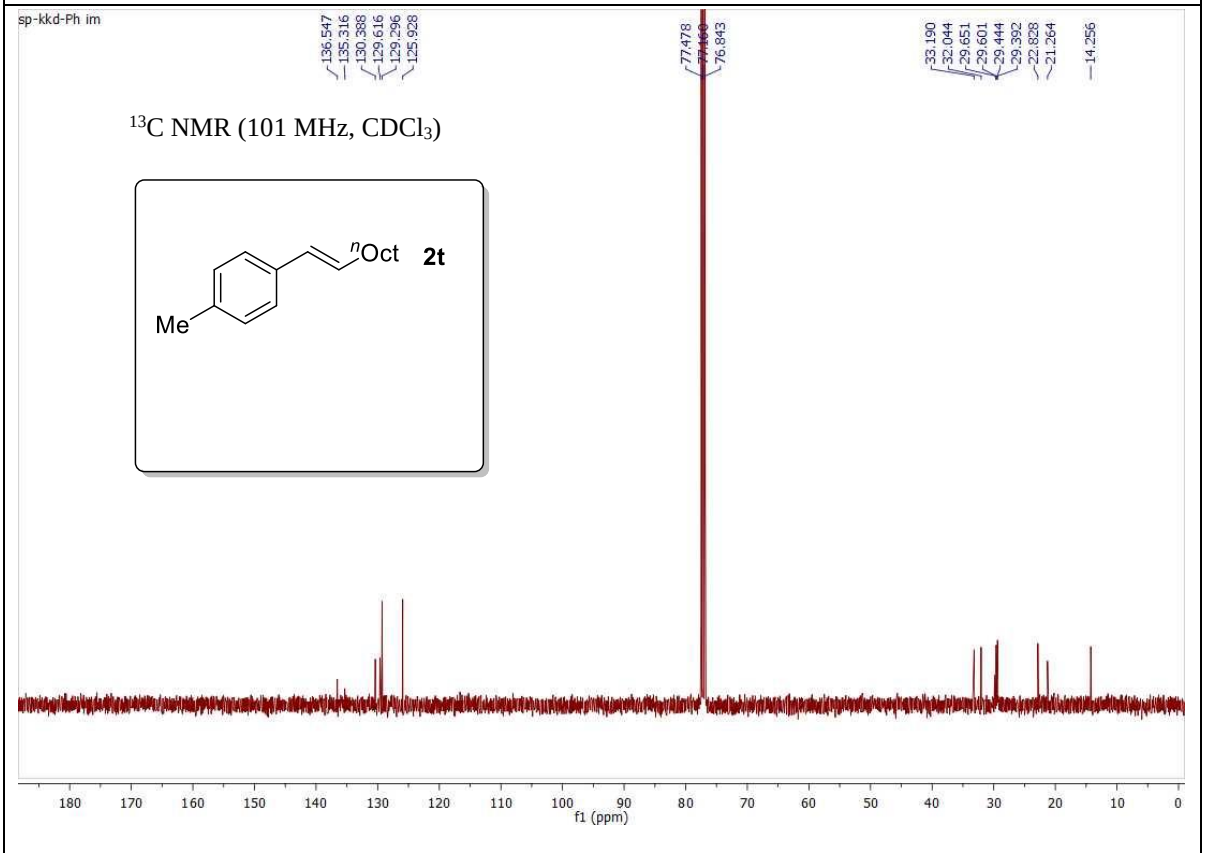
^{13}C NMR (126 MHz, $CDCl_3$)



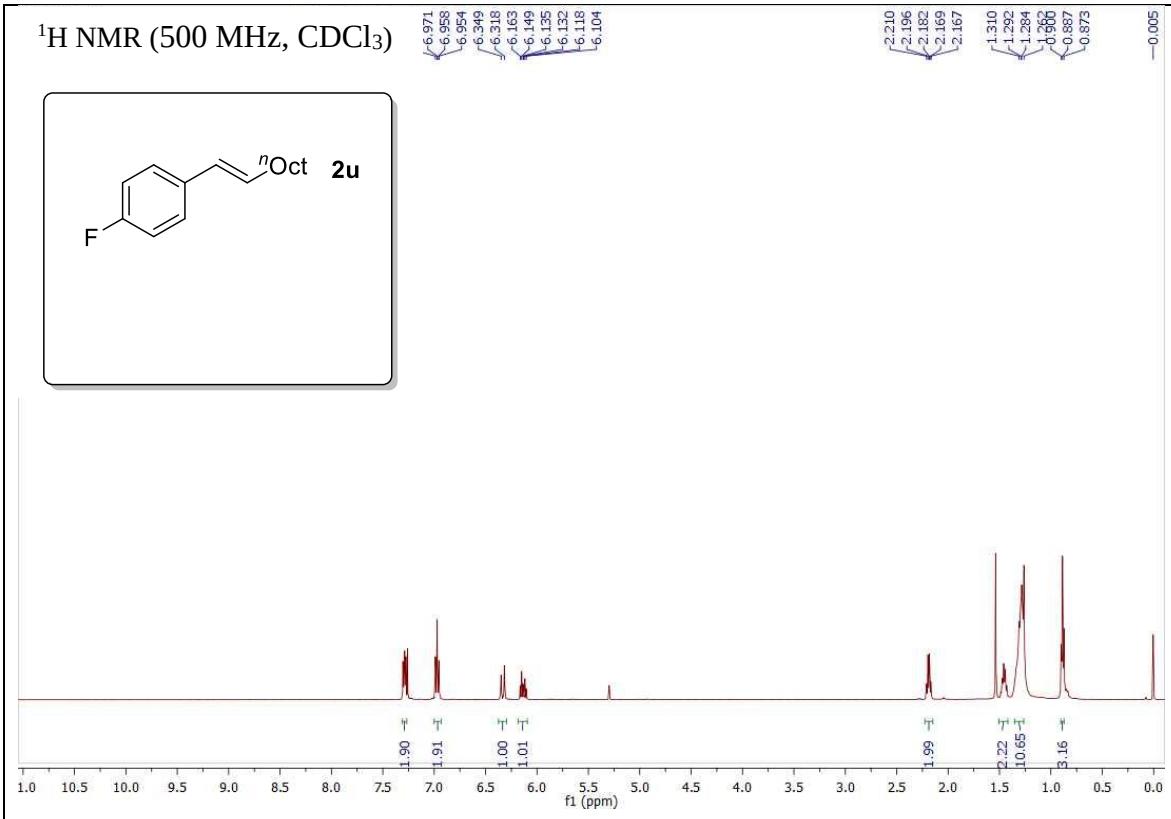
^{1}H NMR (400 MHz, $CDCl_3$)

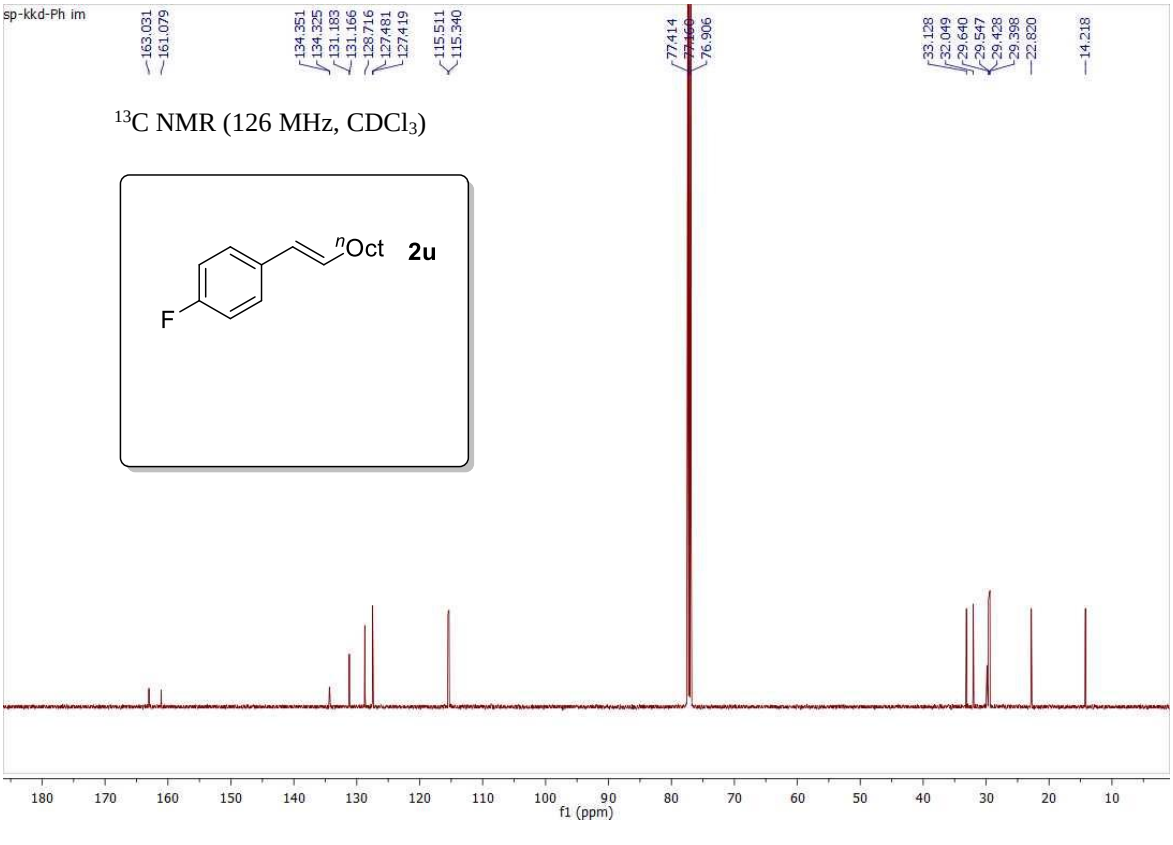


^{13}C NMR (101 MHz, $CDCl_3$)

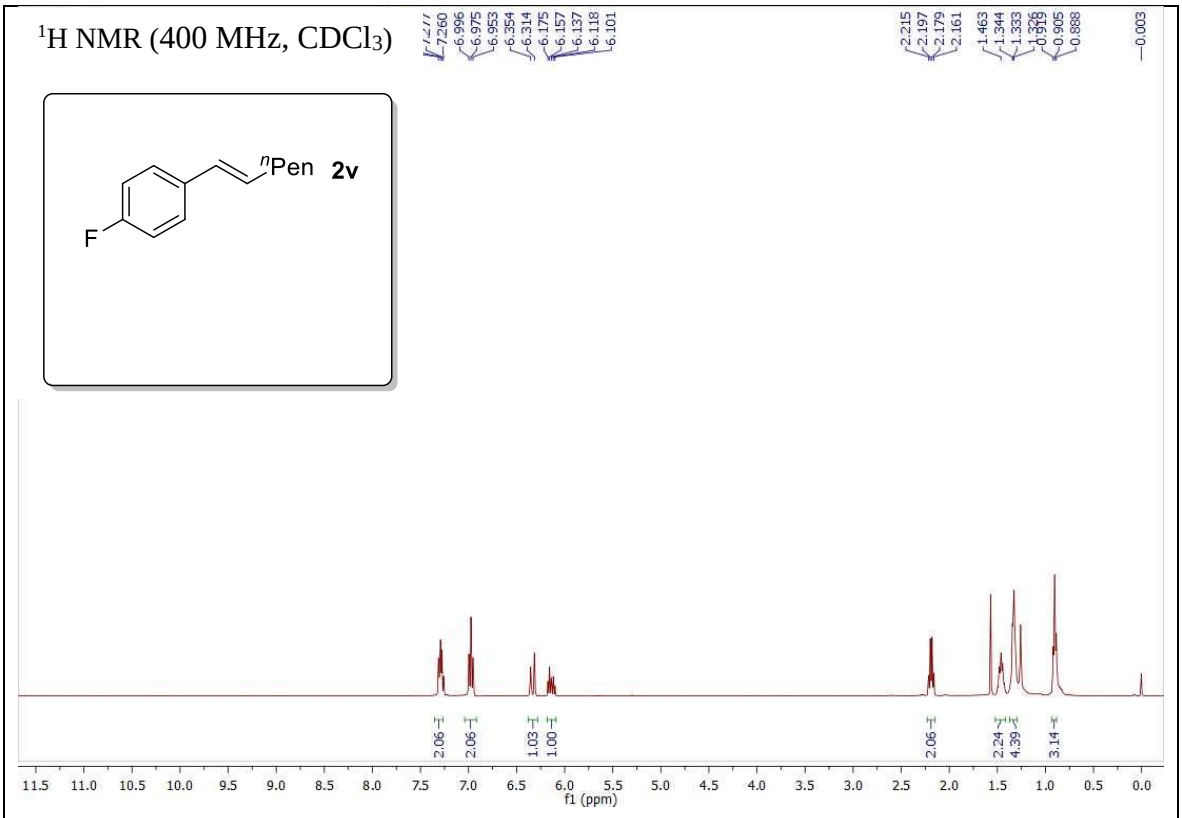


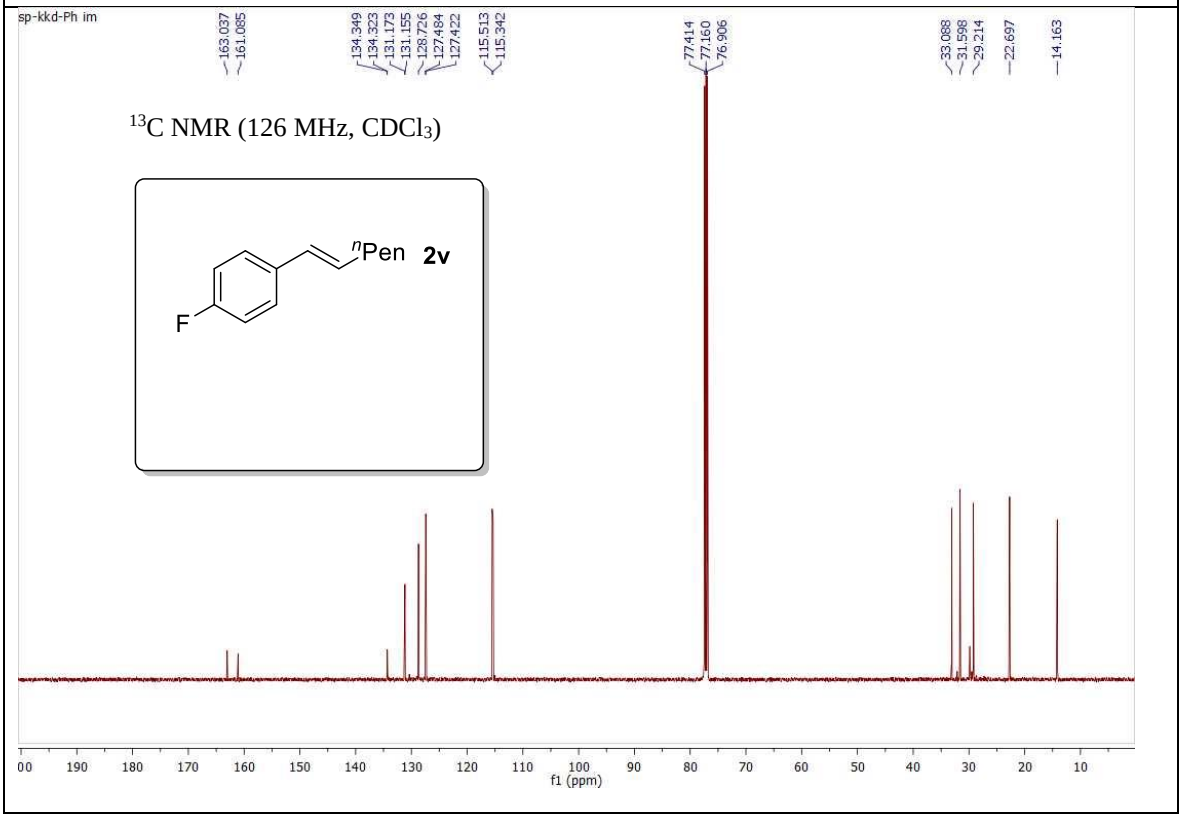
^{1}H NMR (500 MHz, $CDCl_3$)



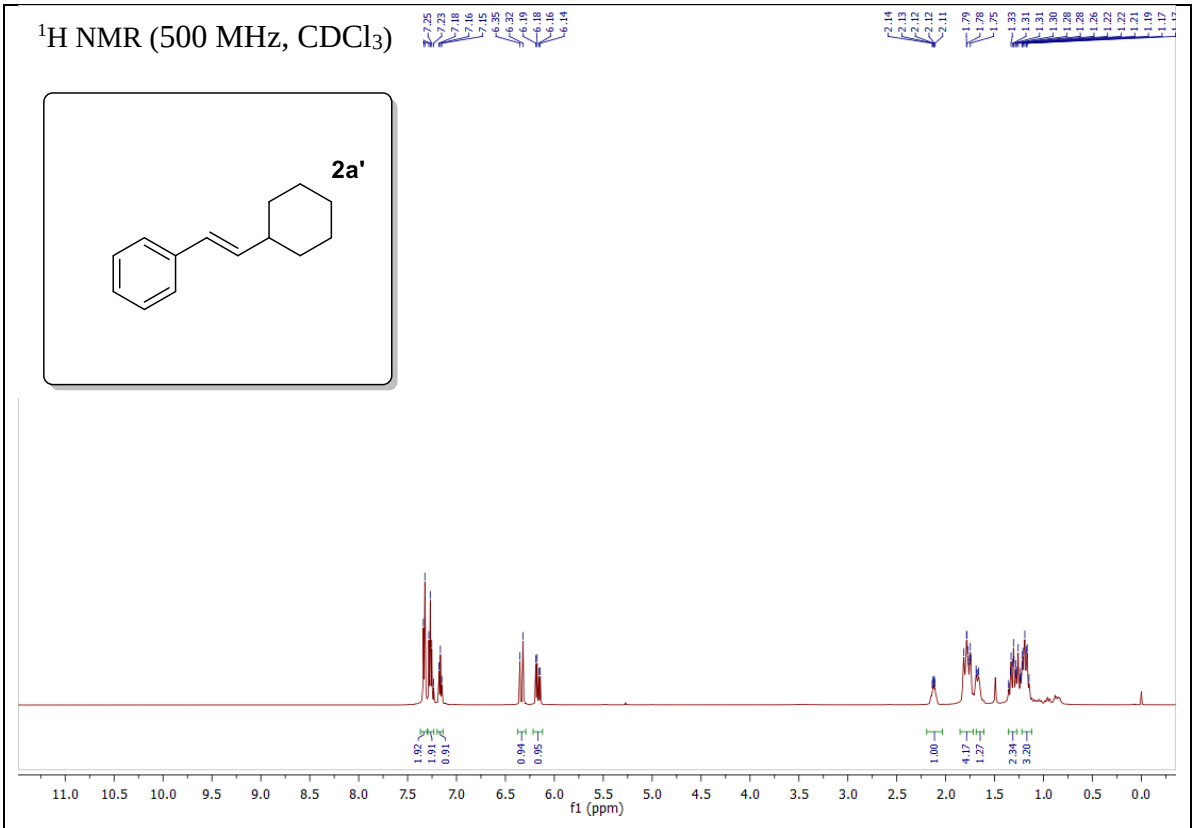


^{1}H NMR (400 MHz, $CDCl_3$)

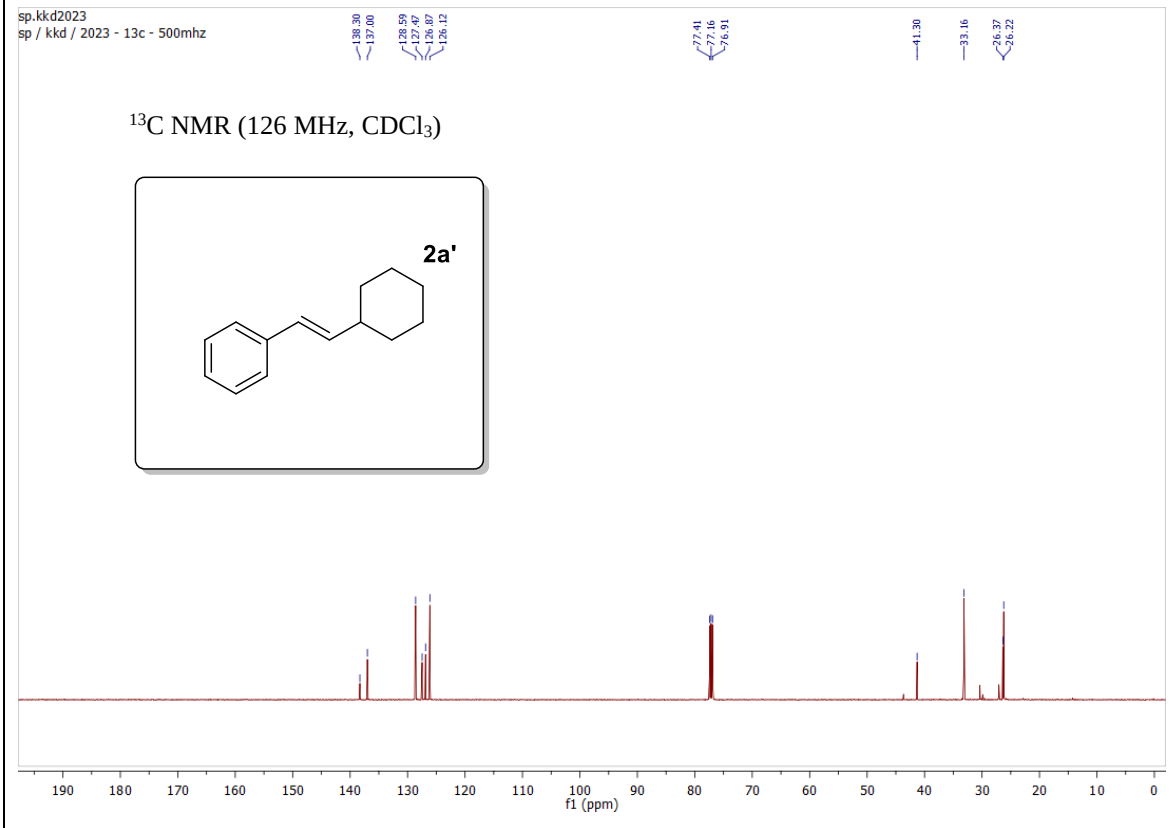




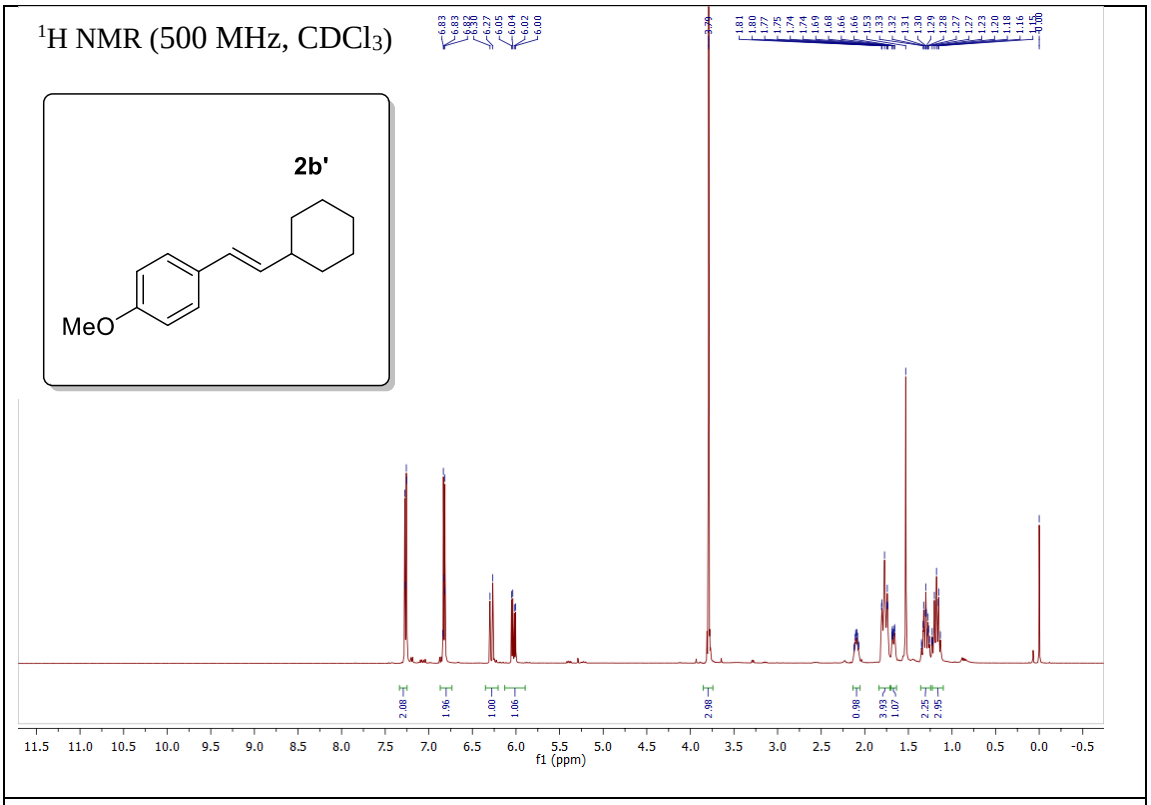
^{1}H NMR (500 MHz, $CDCl_3$)



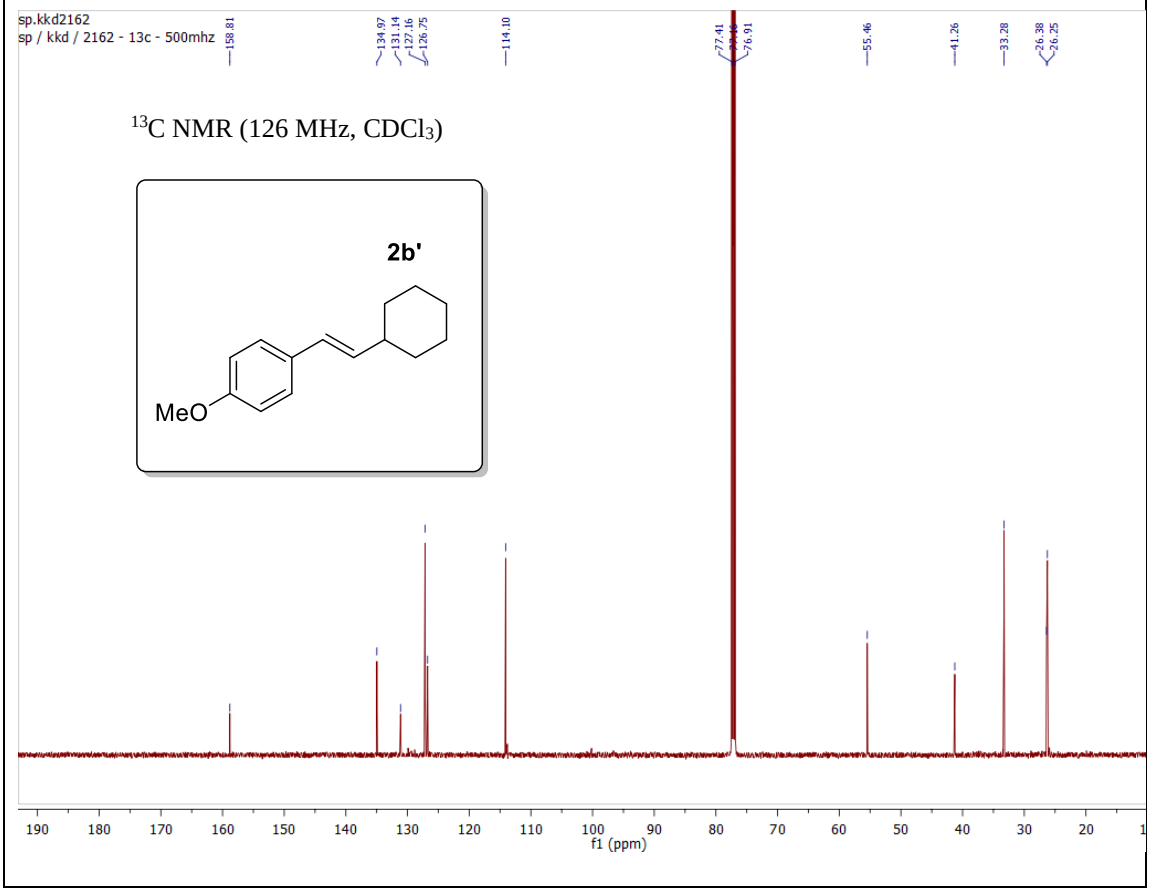
^{13}C NMR (126 MHz, $CDCl_3$)



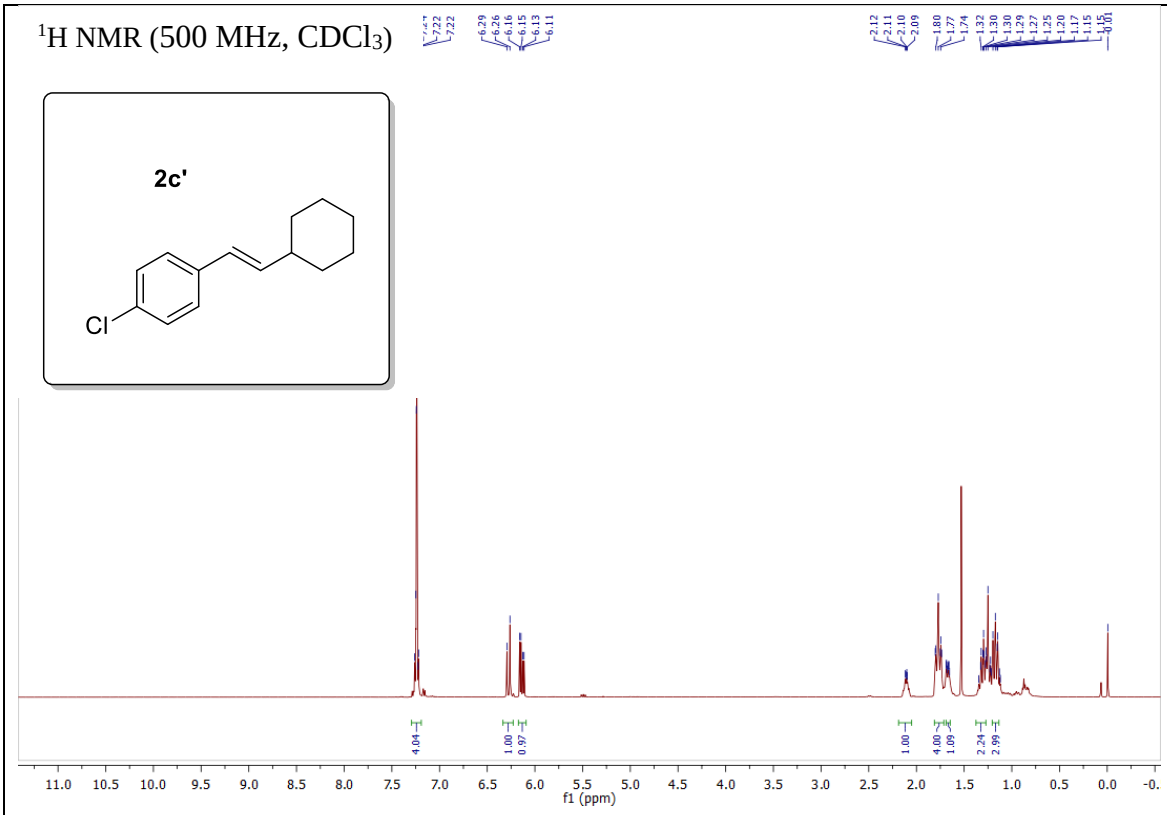
^{1}H NMR (500 MHz, $CDCl_3$)



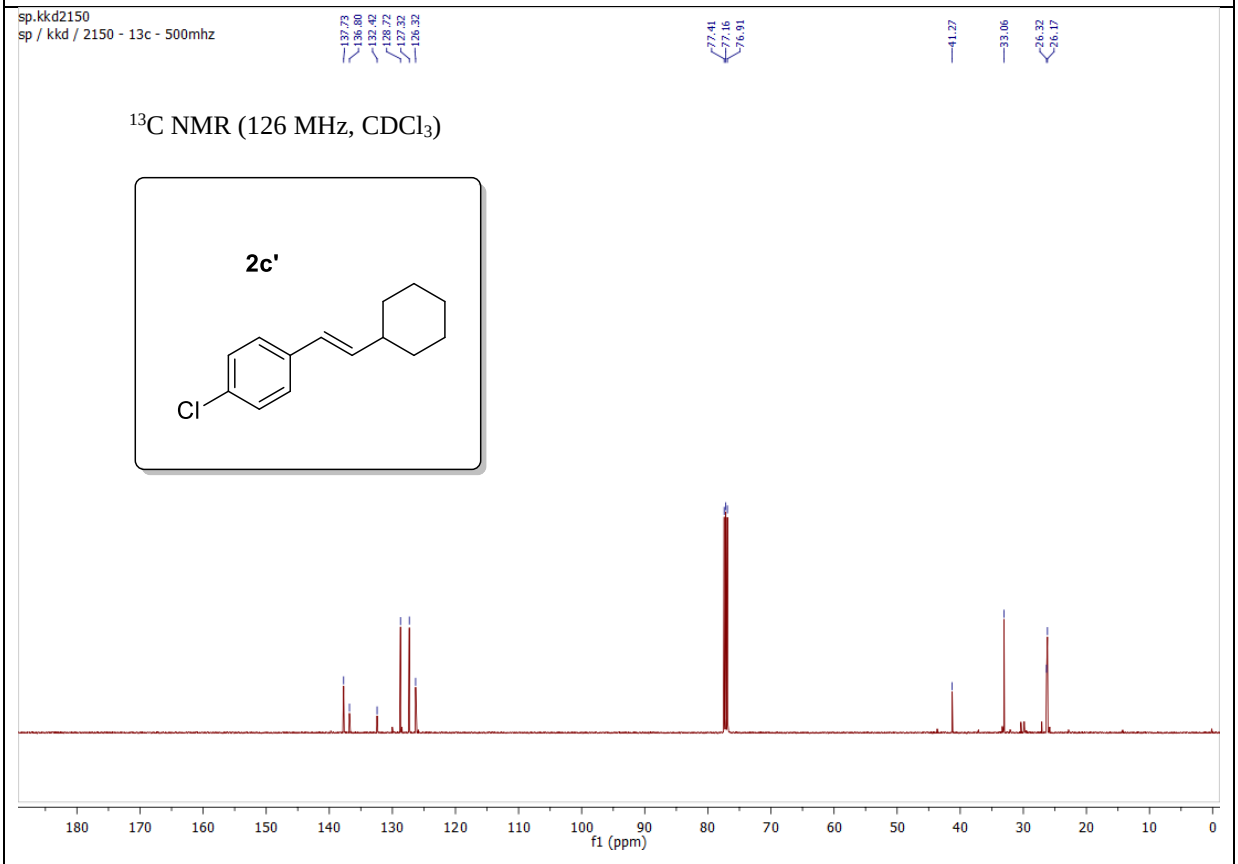
^{13}C NMR (126 MHz, $CDCl_3$)



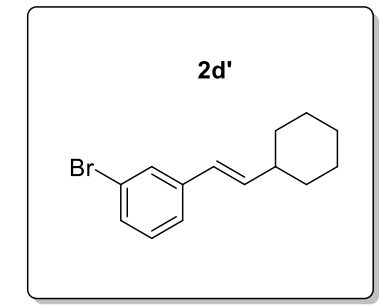
^{1}H NMR (500 MHz, $CDCl_3$)



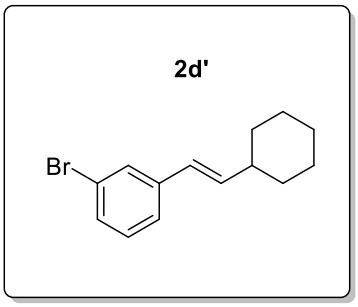
^{13}C NMR (126 MHz, $CDCl_3$)



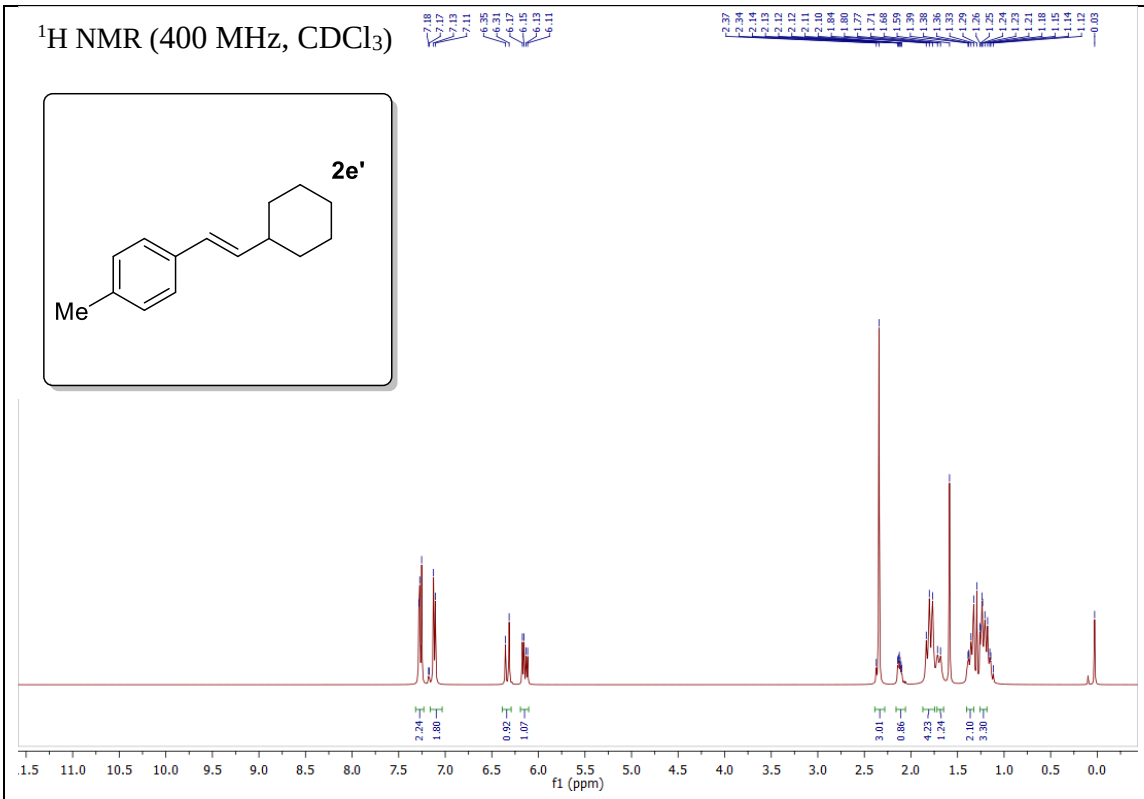
^{1}H NMR (500 MHz, $CDCl_3$)



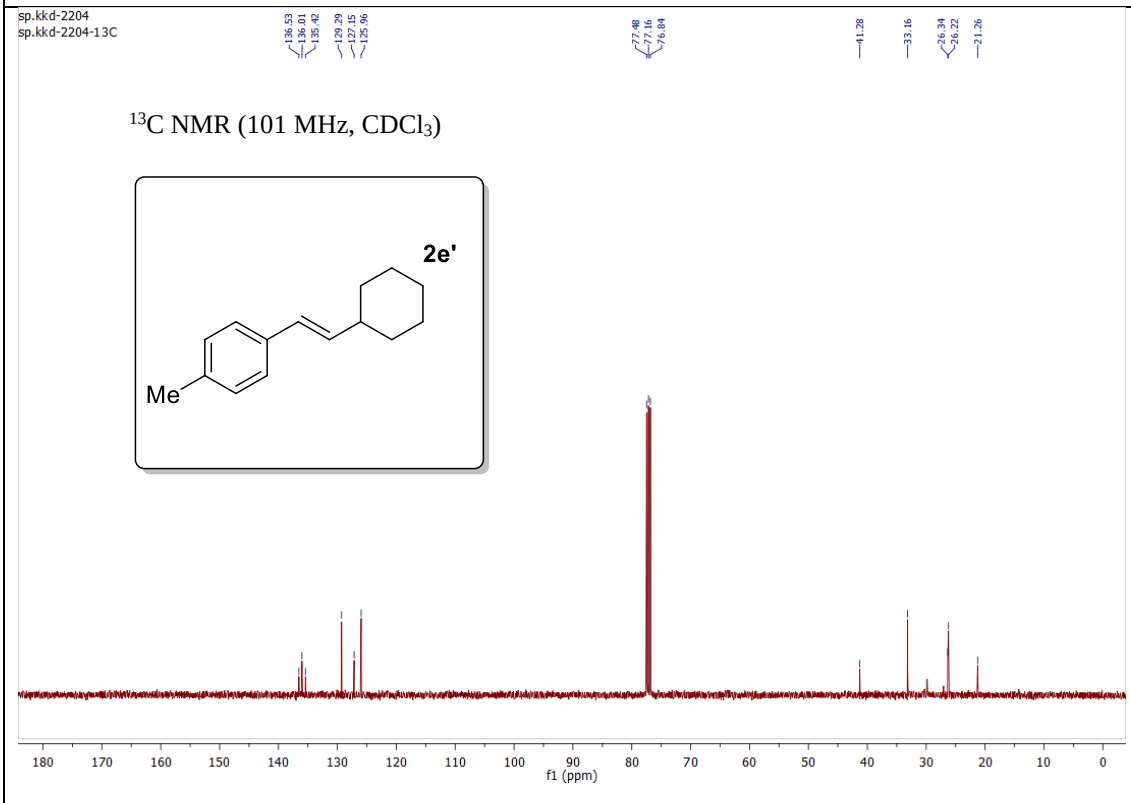
^{13}C NMR (126 MHz, $CDCl_3$)



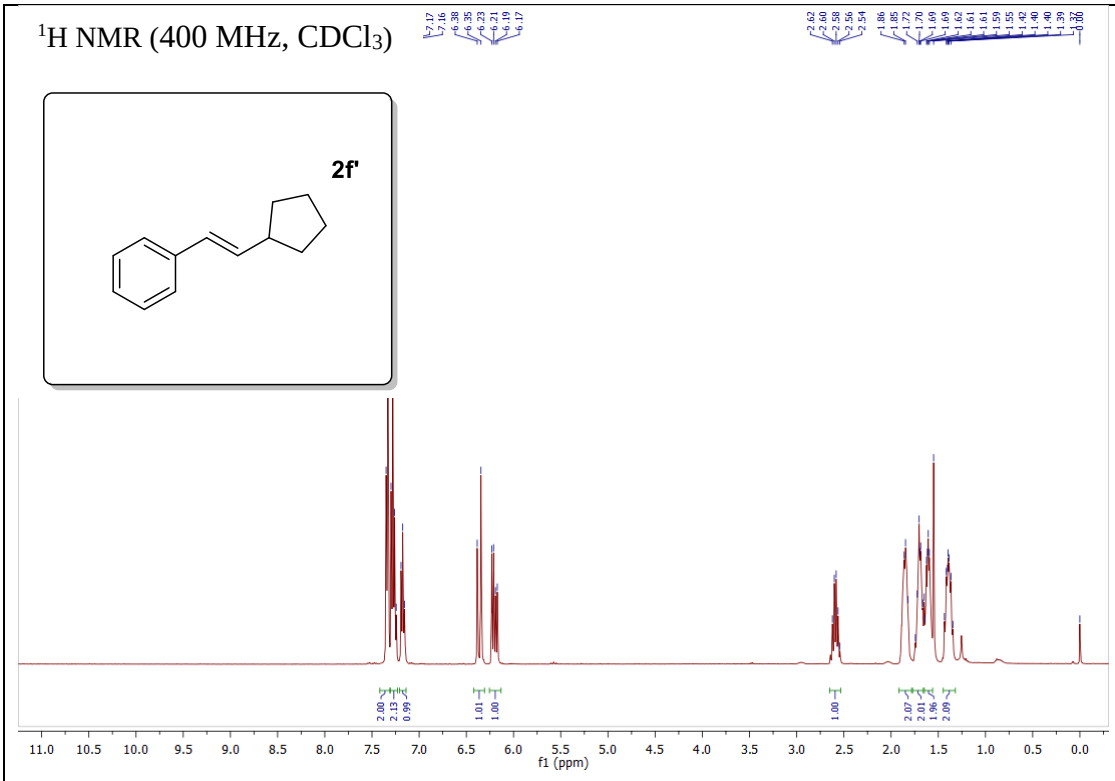
^{1}H NMR (400 MHz, $CDCl_3$)

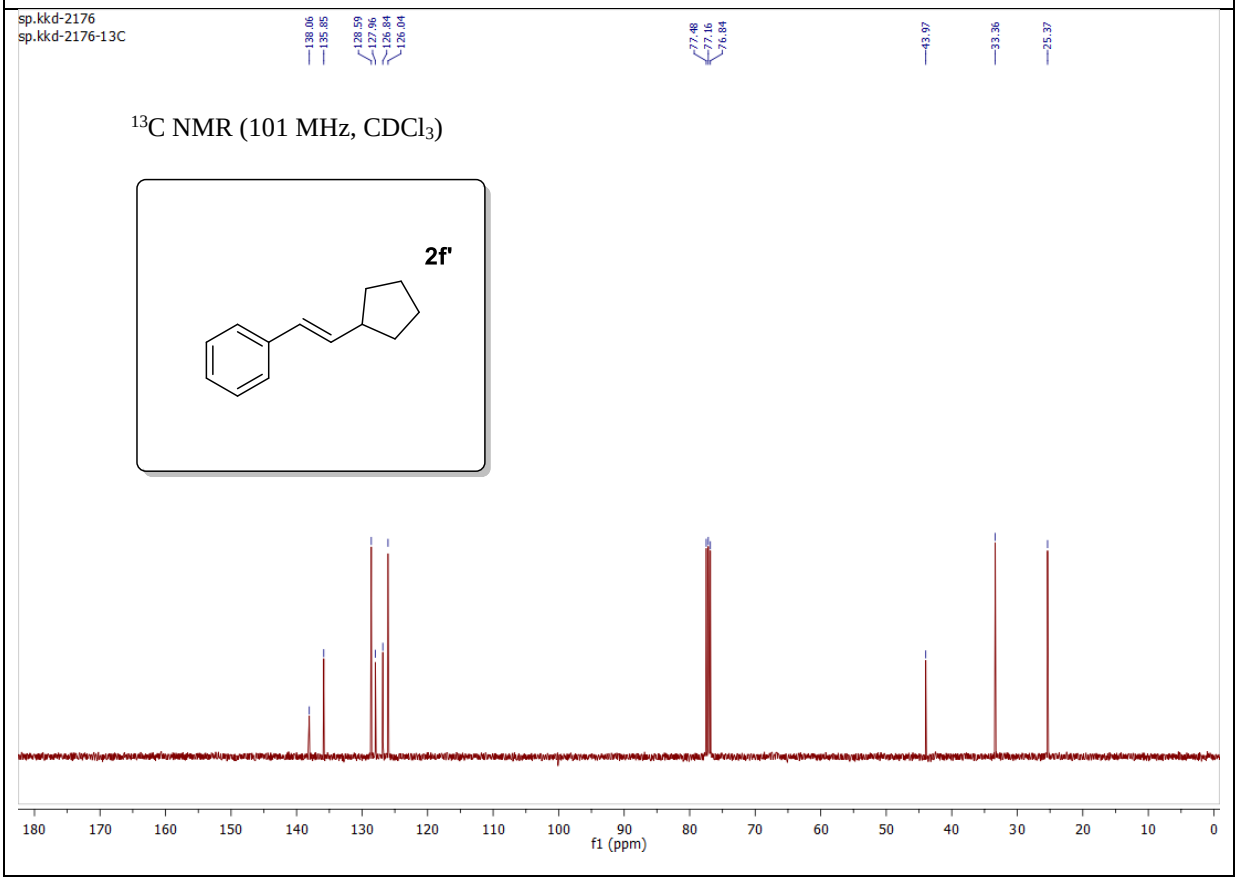


^{13}C NMR (101 MHz, $CDCl_3$)



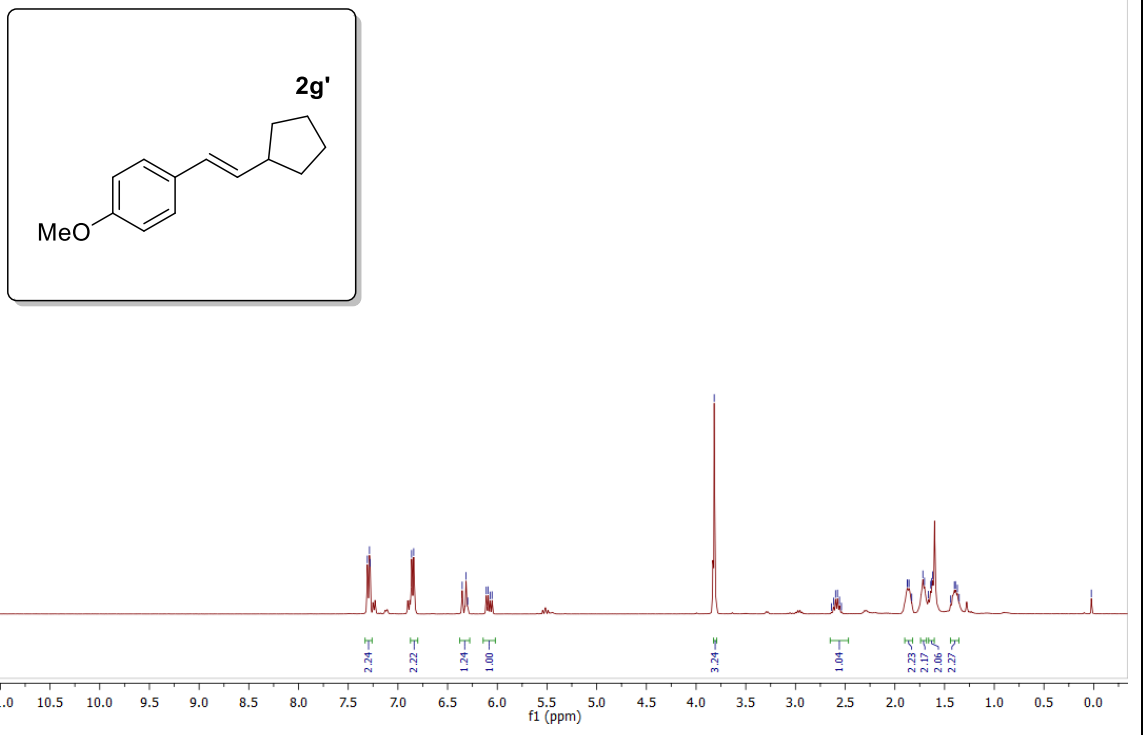
^{1}H NMR (400 MHz, $CDCl_3$)



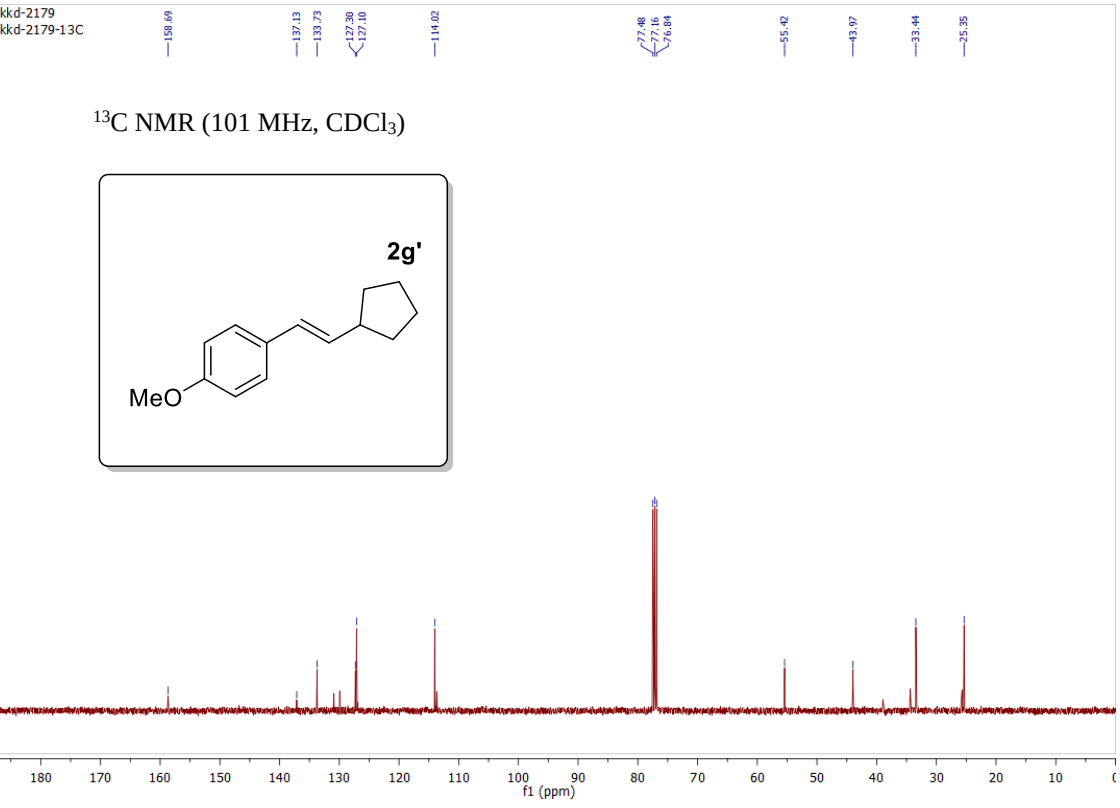


^{13}C NMR (101 MHz, $CDCl_3$)

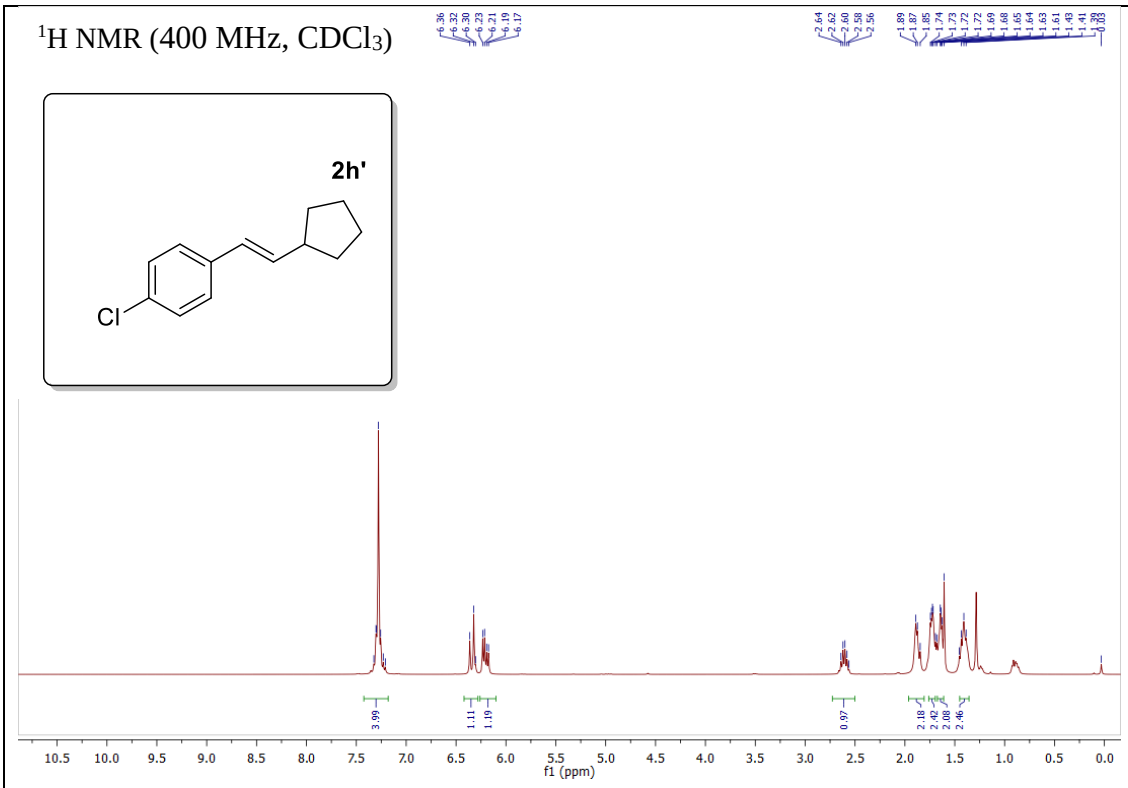
^{1}H NMR (400 MHz, $CDCl_3$)



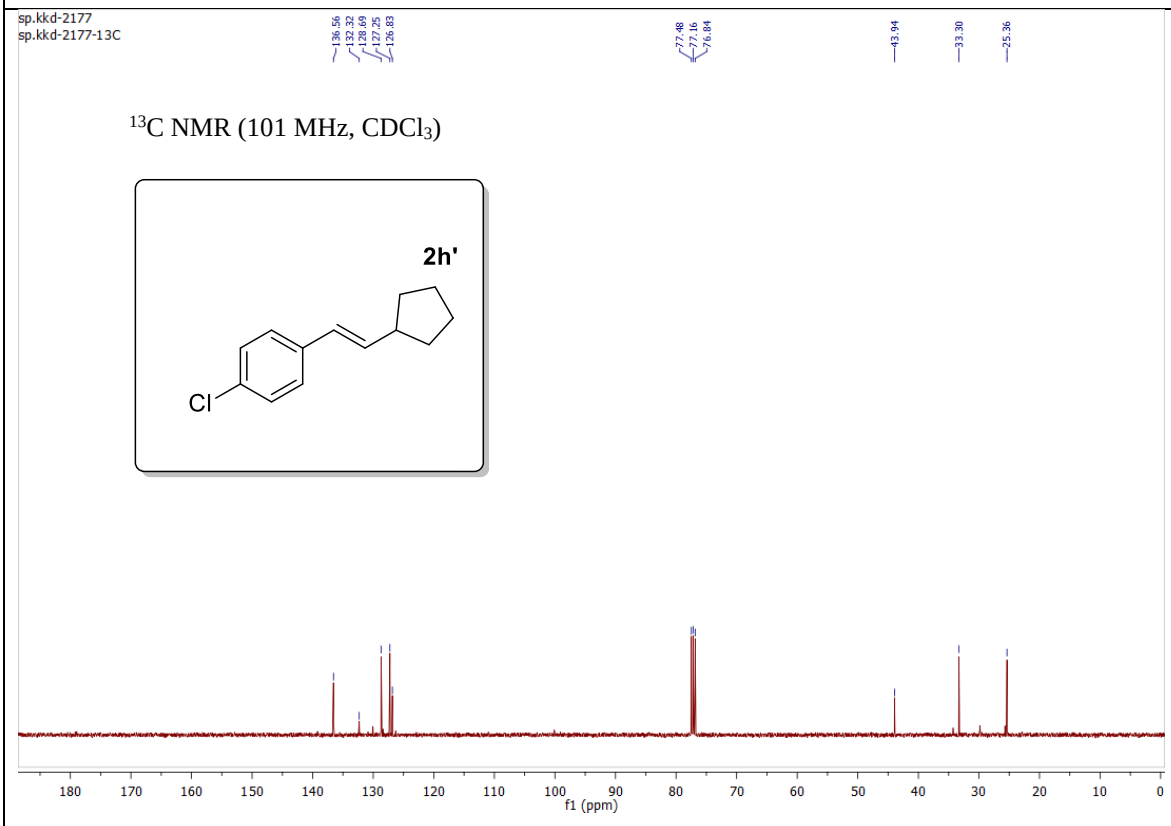
^{13}C NMR (101 MHz, $CDCl_3$)



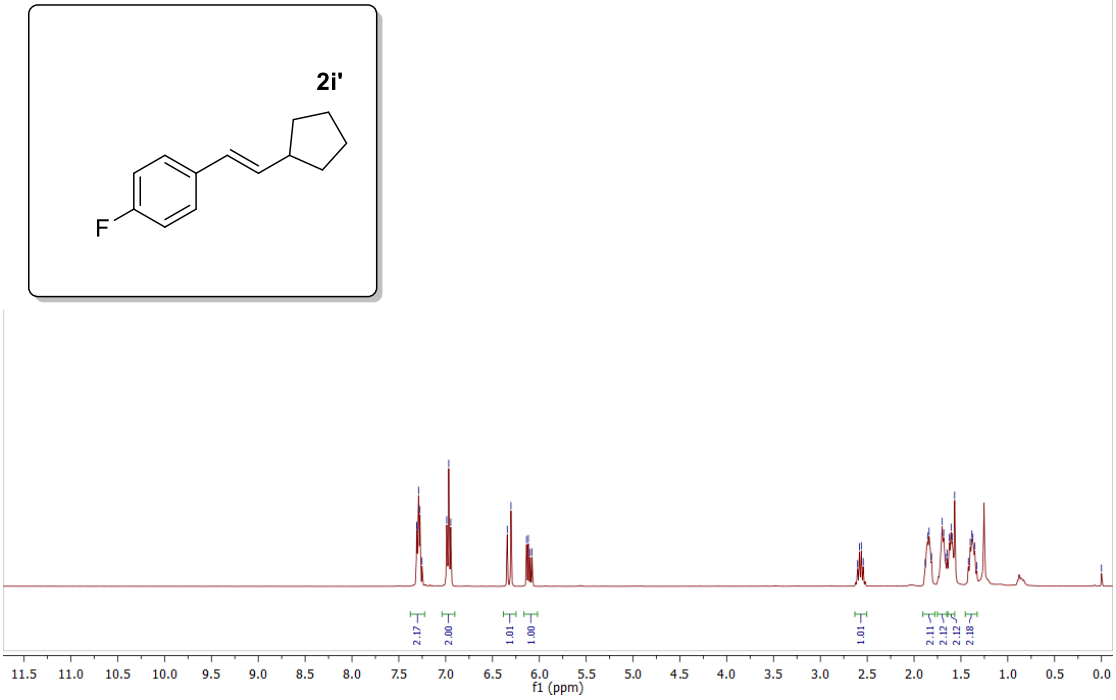
^{1}H NMR (400 MHz, $CDCl_3$)

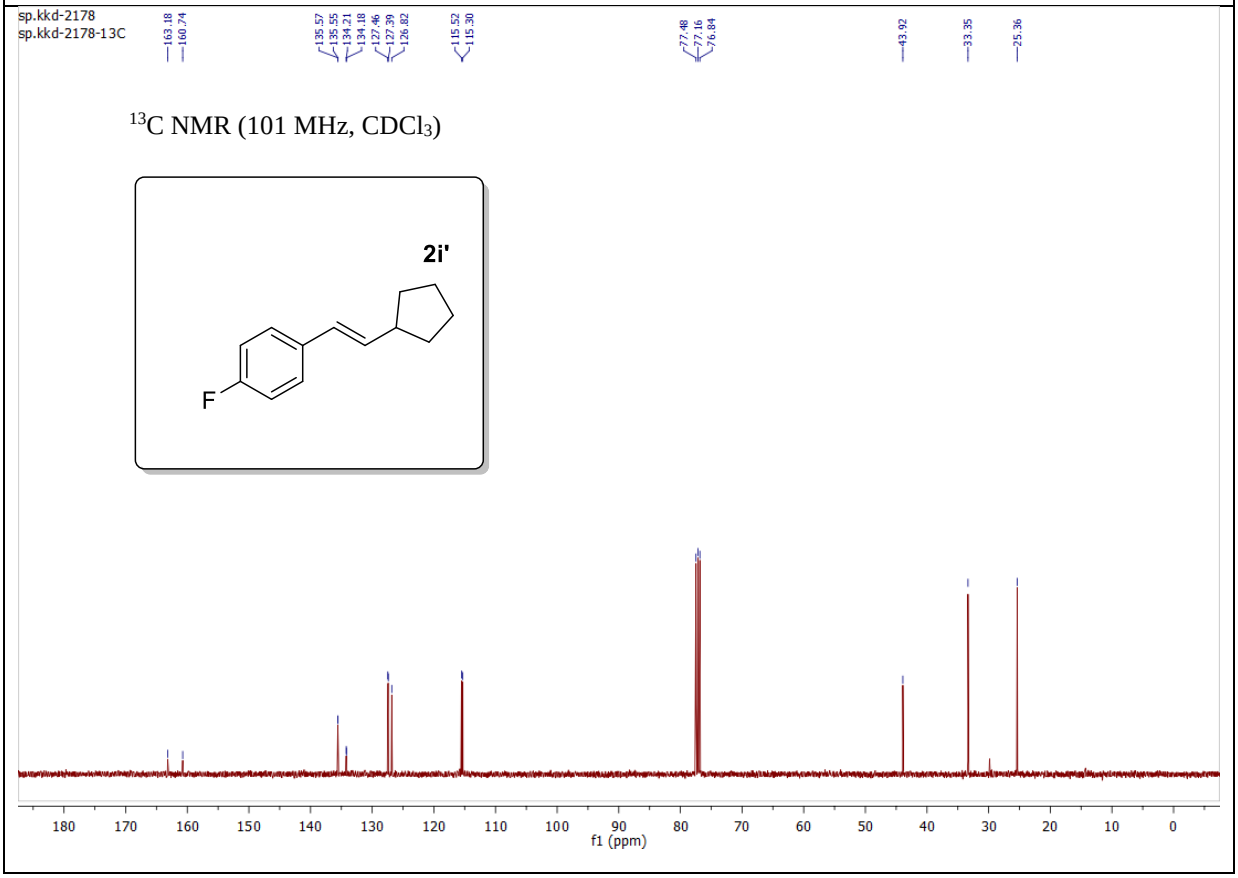


^{13}C NMR (101 MHz, $CDCl_3$)



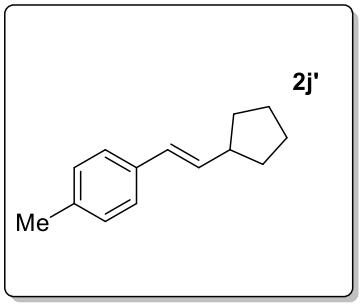
^{1}H NMR (400 MHz, $CDCl_3$)



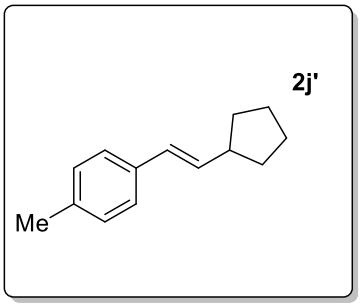


^{13}C NMR (101 MHz, $CDCl_3$)

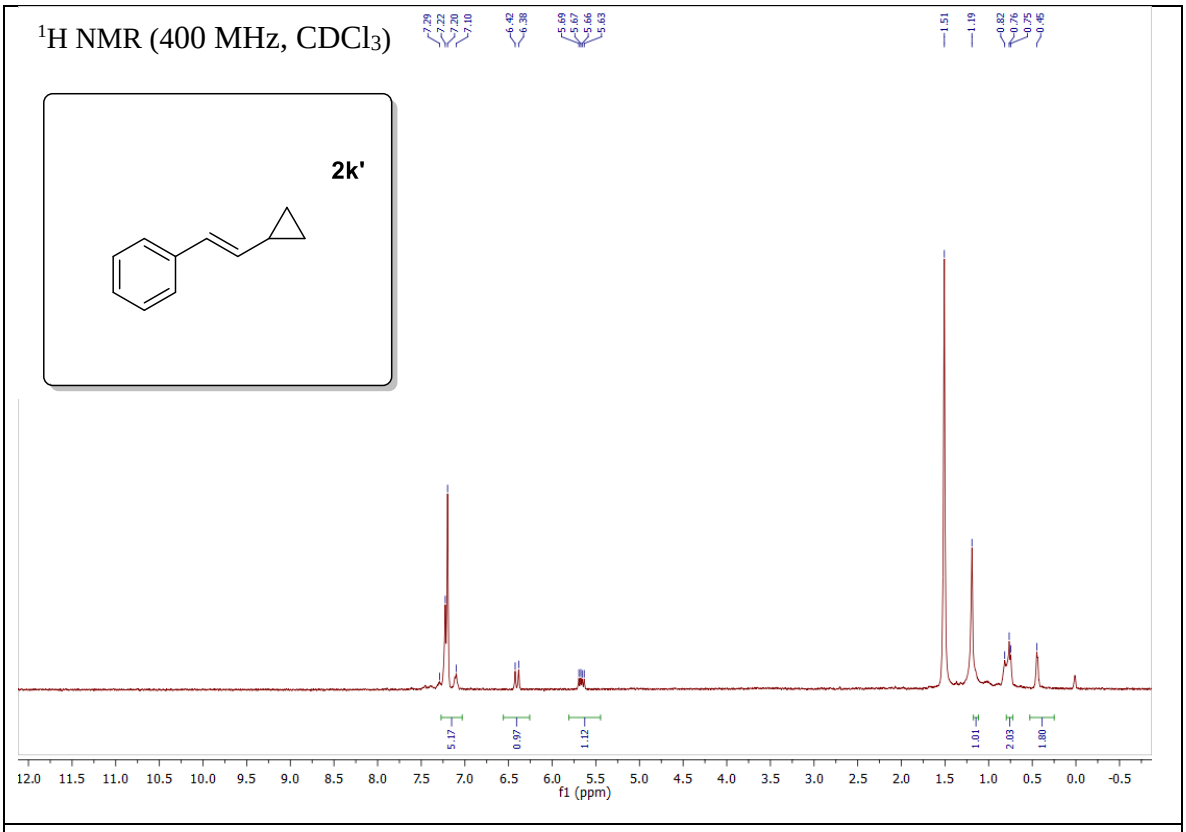
^{1}H NMR (400 MHz, $CDCl_3$)



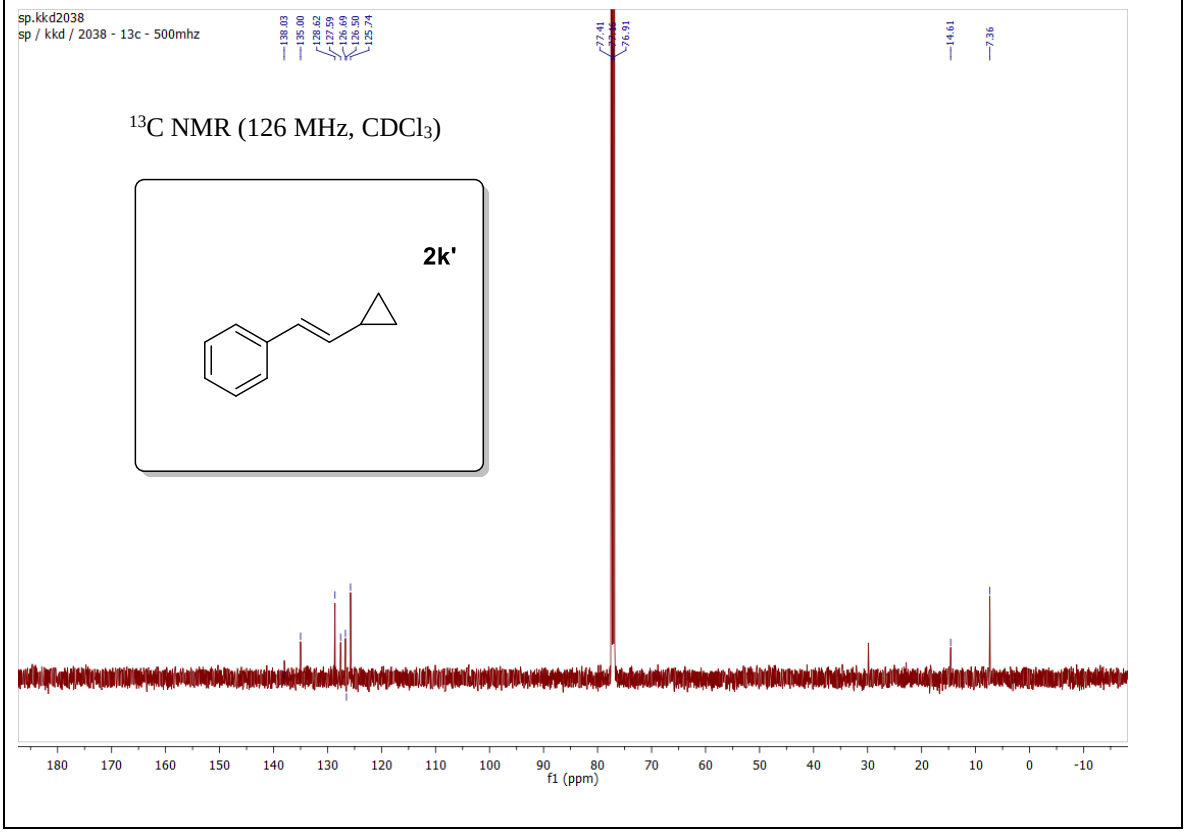
^{13}C NMR (126 MHz, $CDCl_3$)



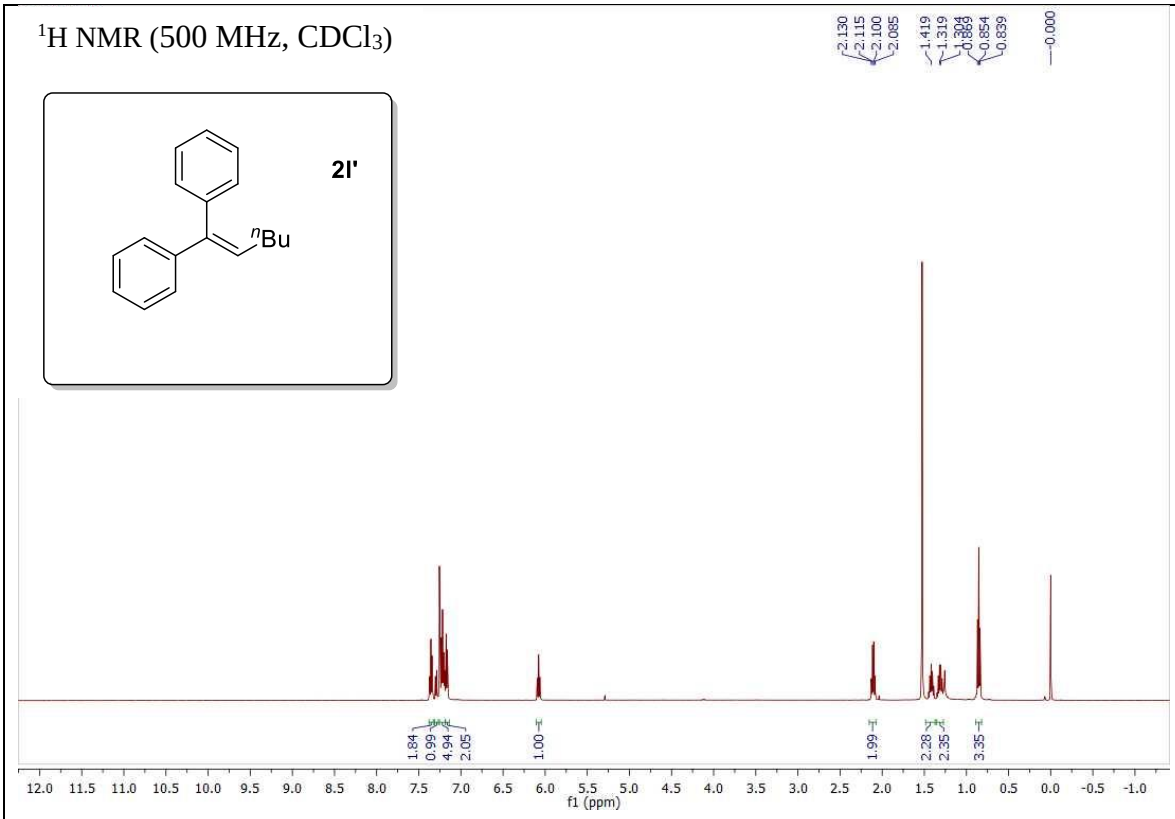
^{1}H NMR (400 MHz, $CDCl_3$)

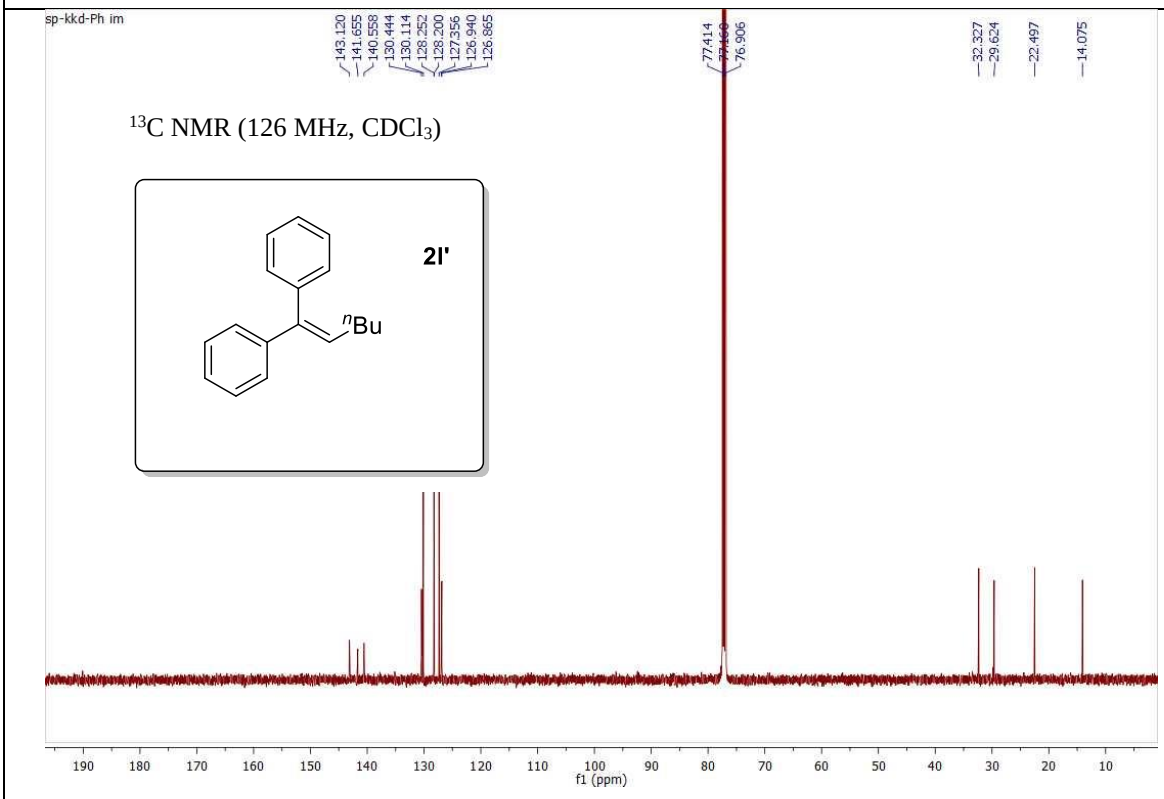


^{13}C NMR (126 MHz, $CDCl_3$)



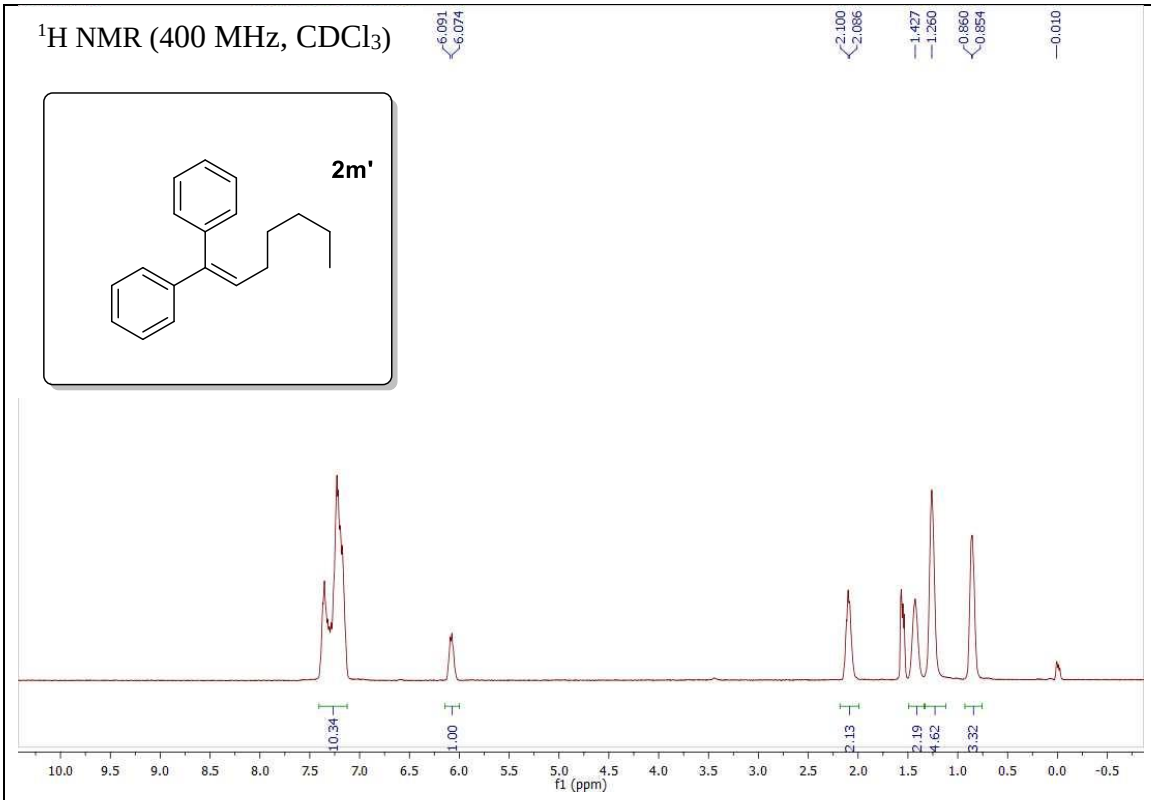
^{1}H NMR (500 MHz, $CDCl_3$)



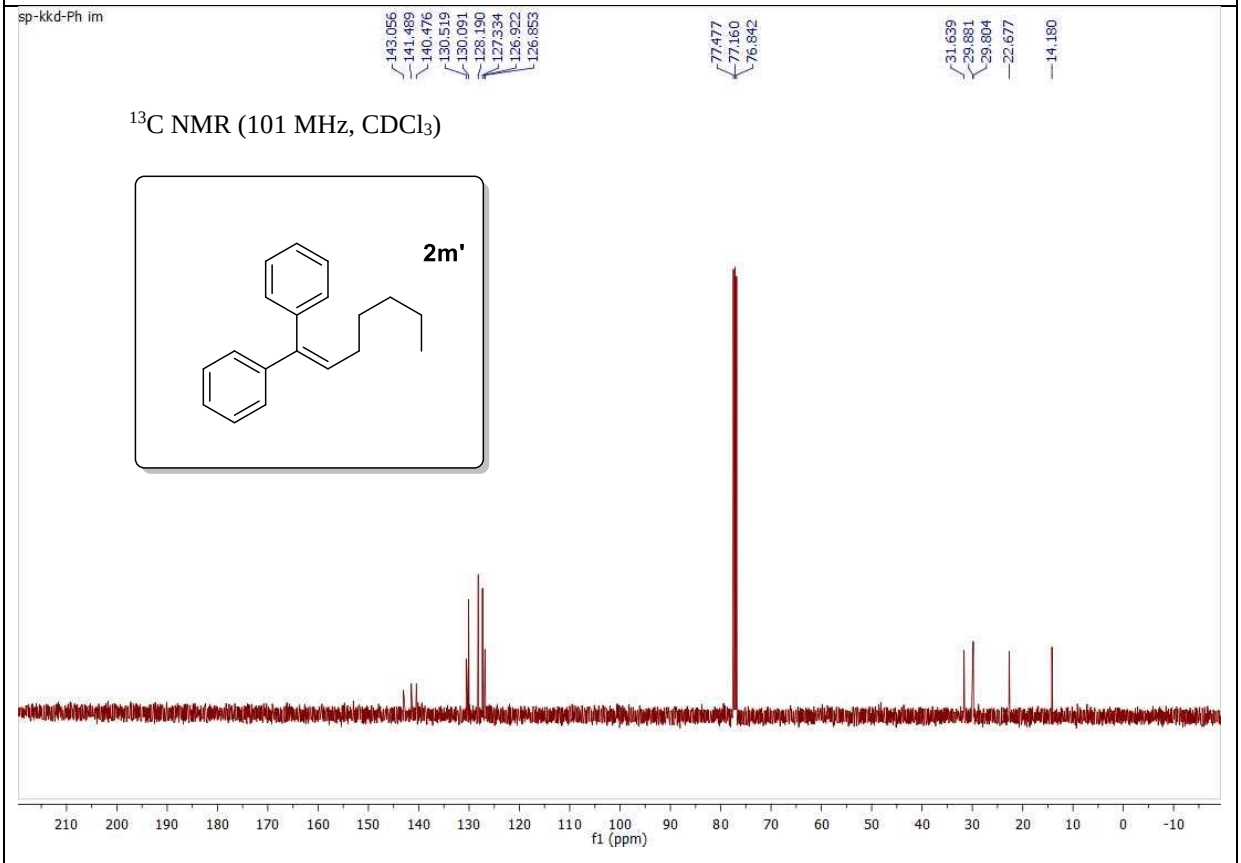


^{13}C NMR (126 MHz, $CDCl_3$)

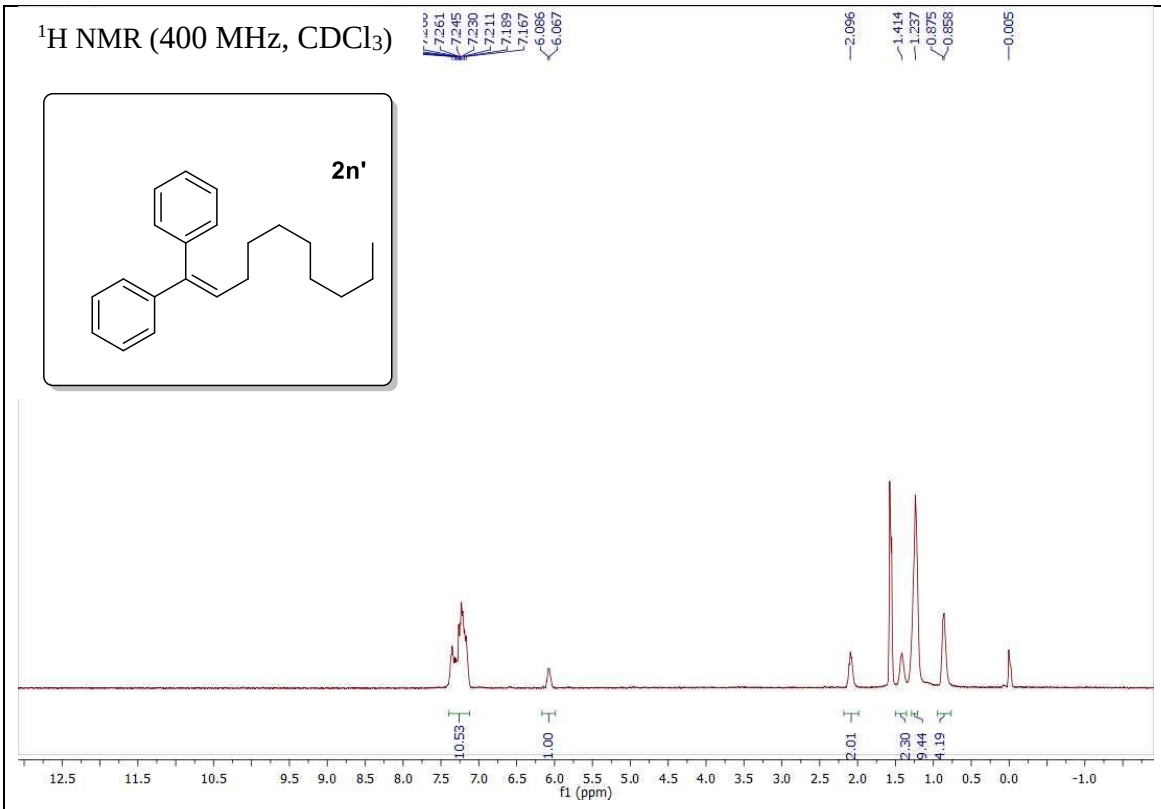
^{1}H NMR (400 MHz, $CDCl_3$)



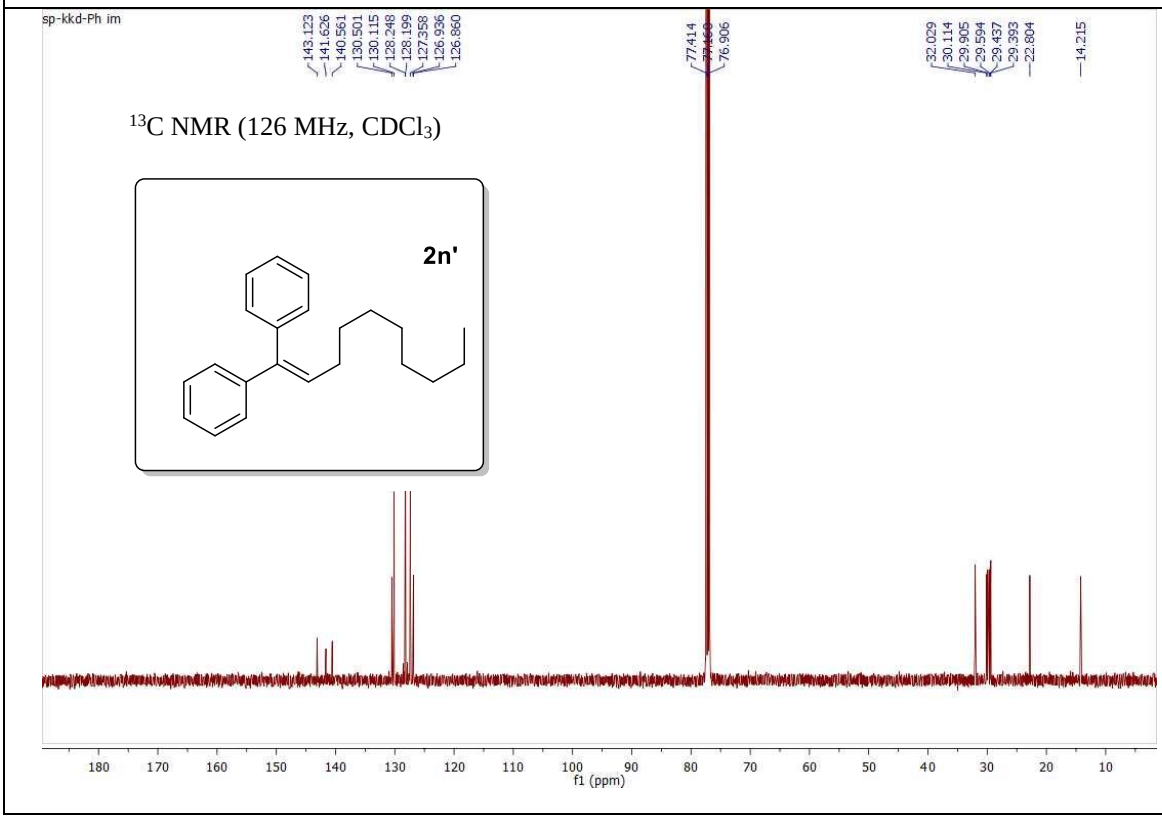
^{13}C NMR (101 MHz, $CDCl_3$)



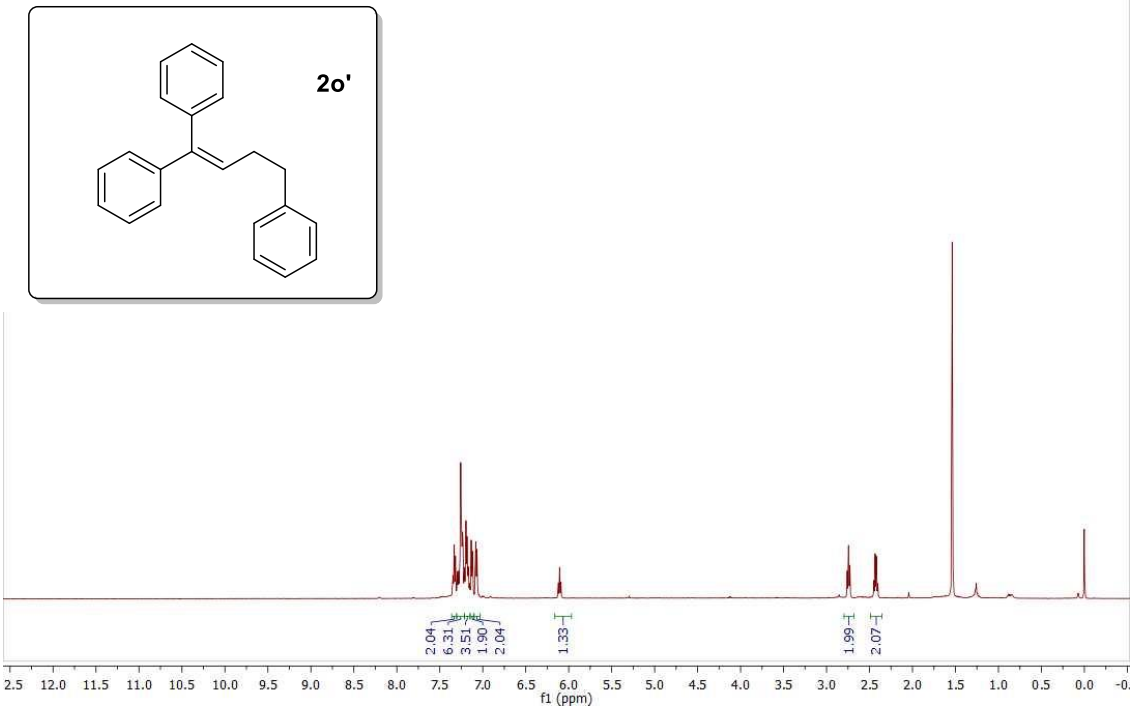
^{1}H NMR (400 MHz, $CDCl_3$)



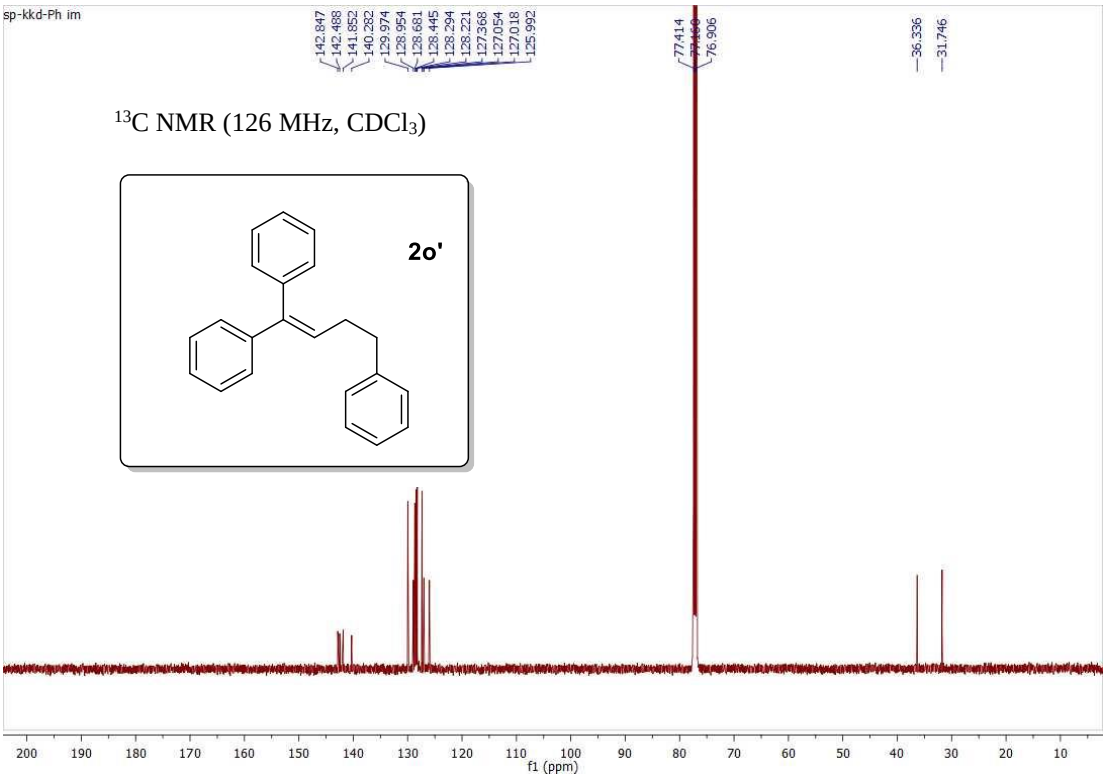
^{13}C NMR (126 MHz, $CDCl_3$)



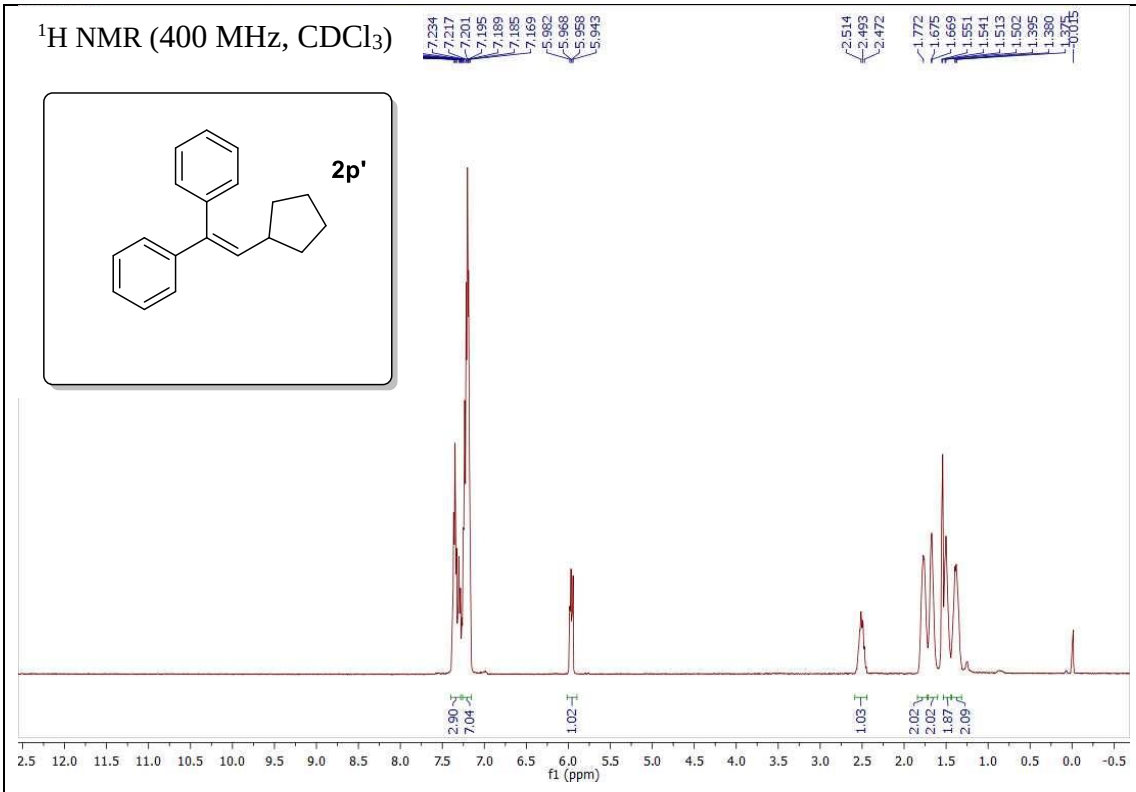
^{1}H NMR (500 MHz, $CDCl_3$)

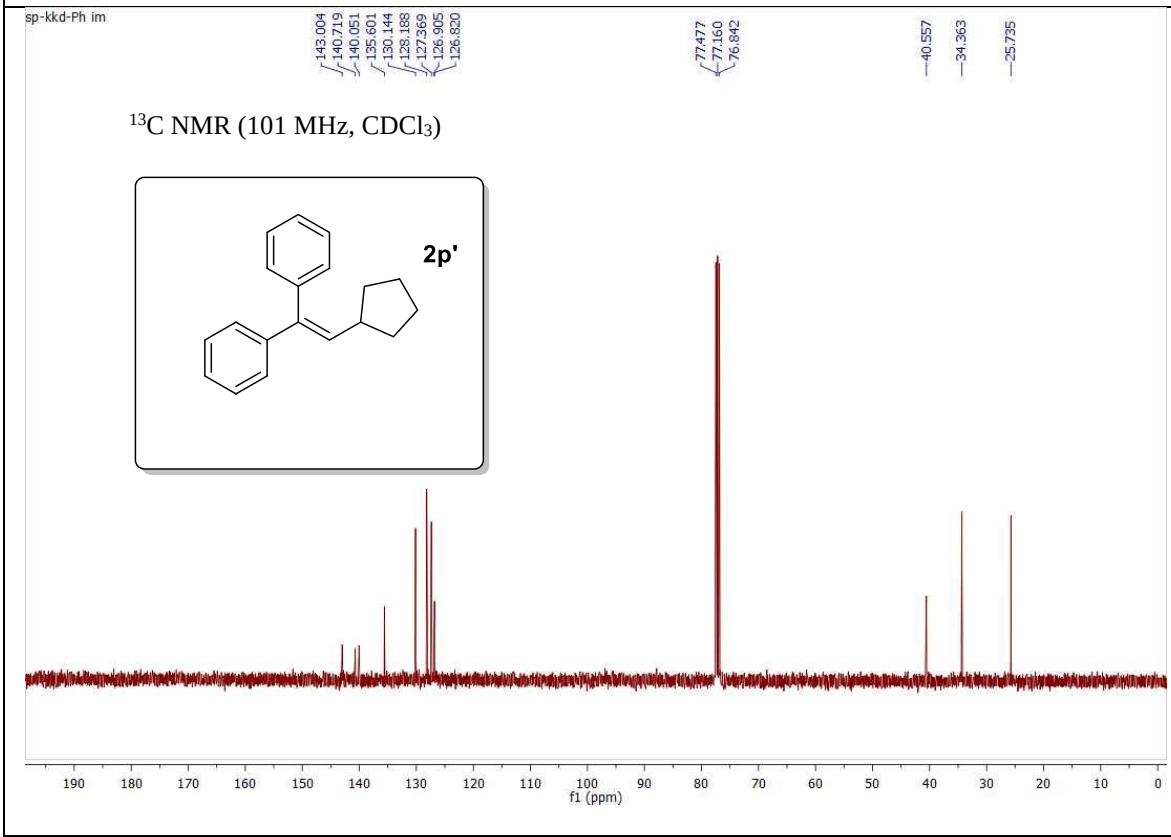


^{13}C NMR (126 MHz, $CDCl_3$)

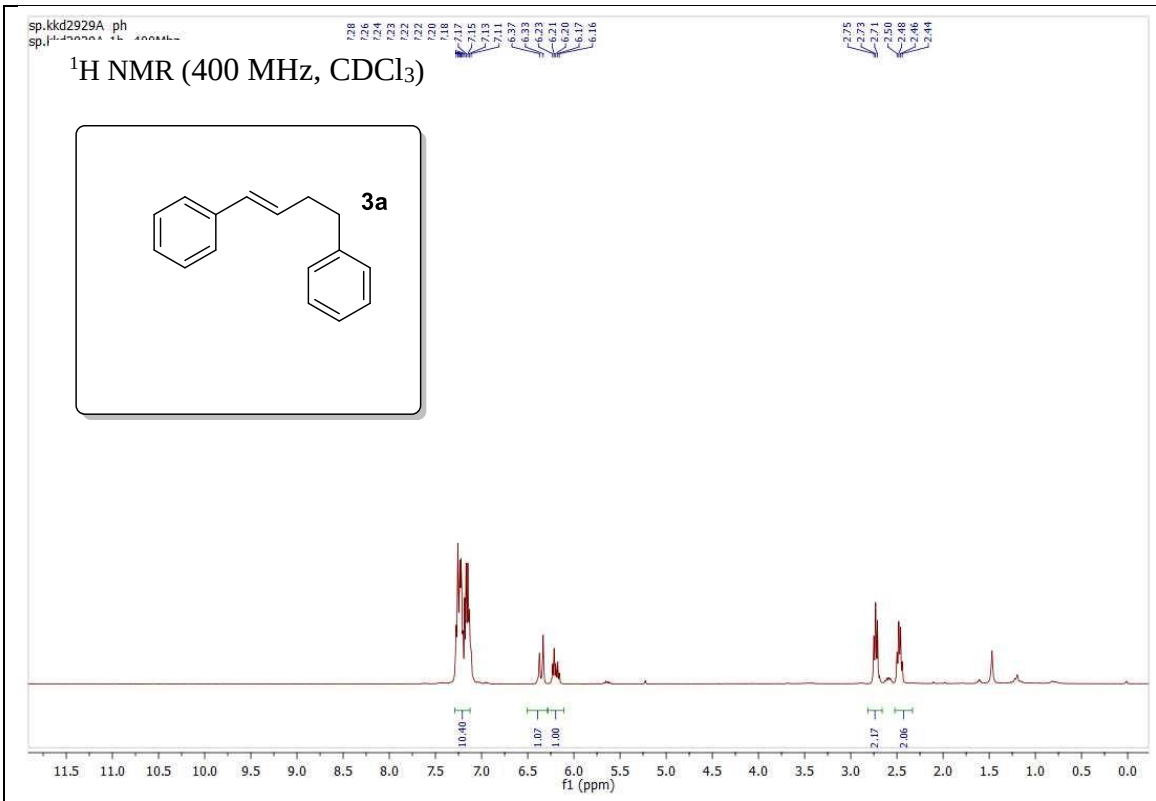


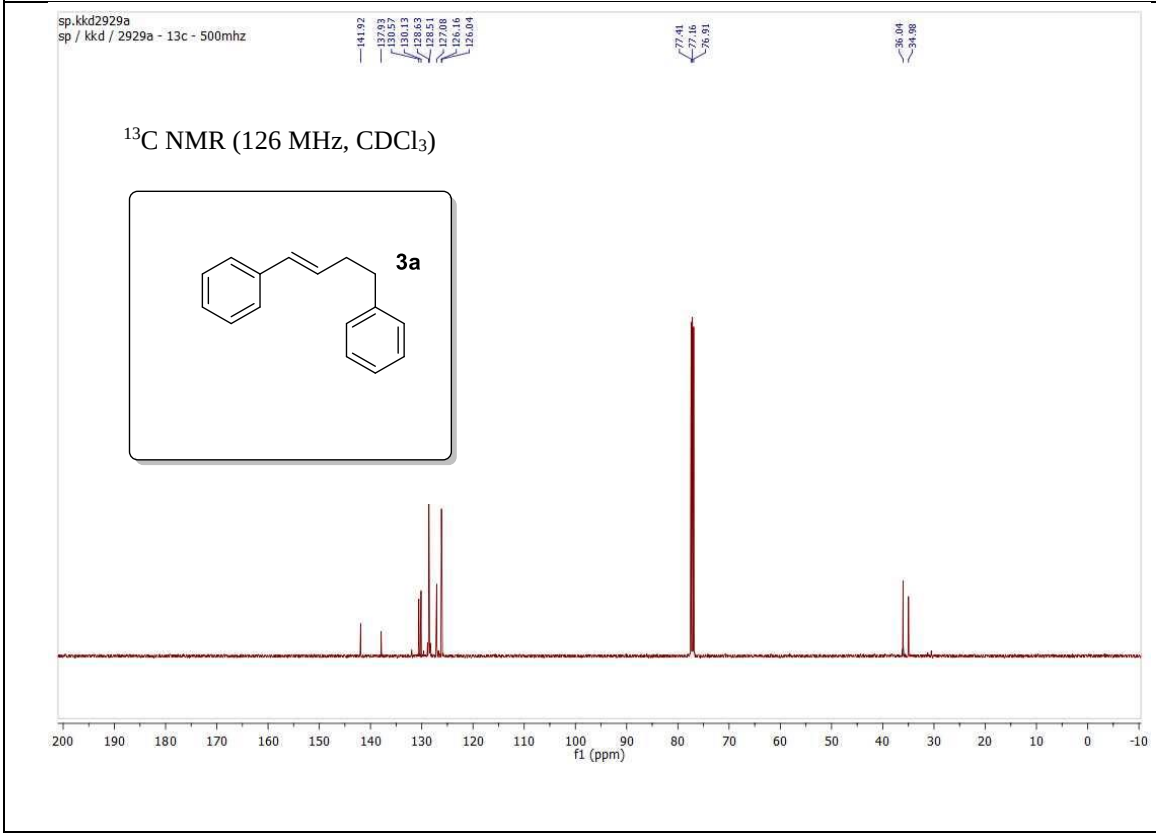
^{1}H NMR (400 MHz, $CDCl_3$)

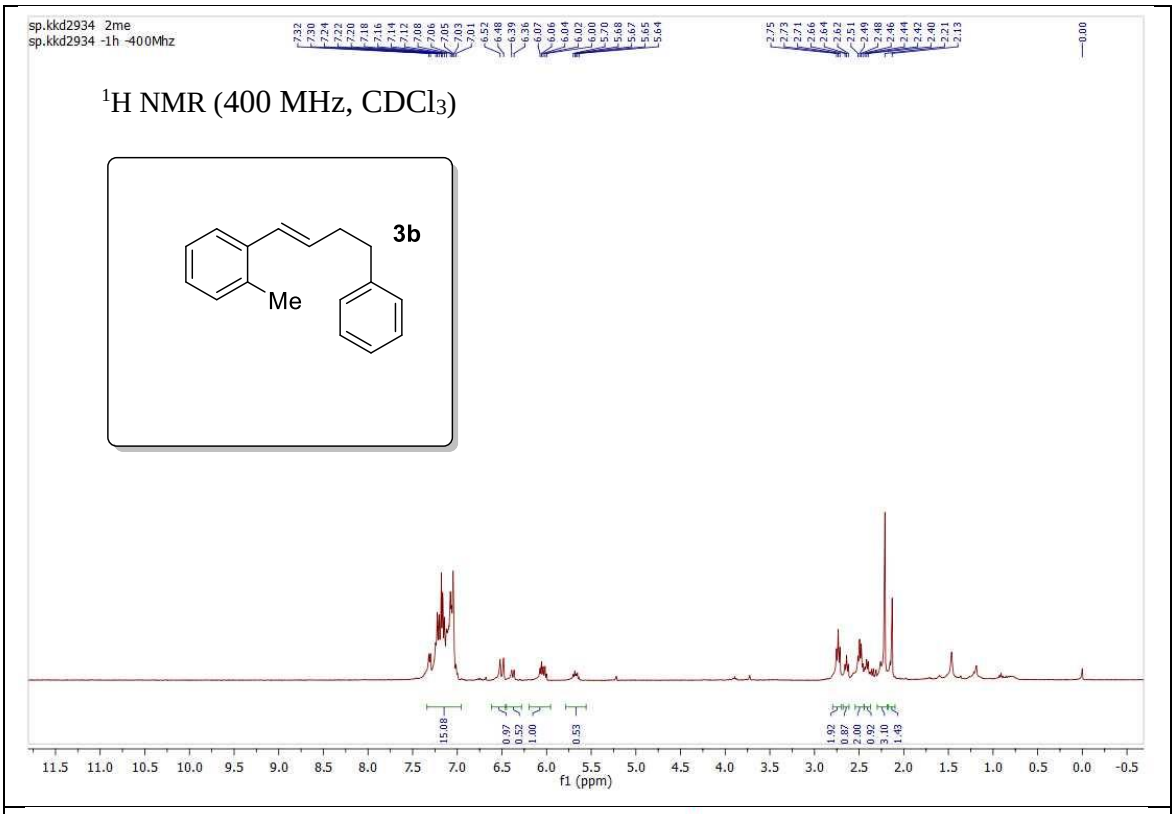


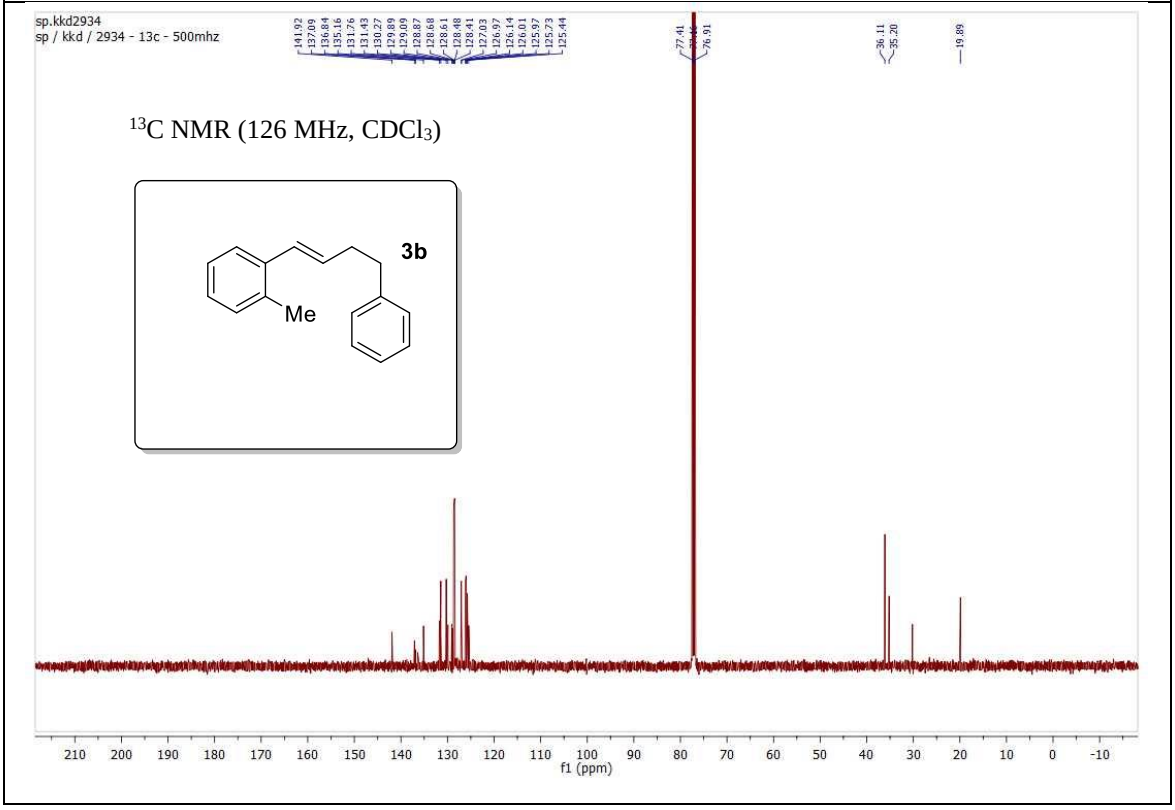


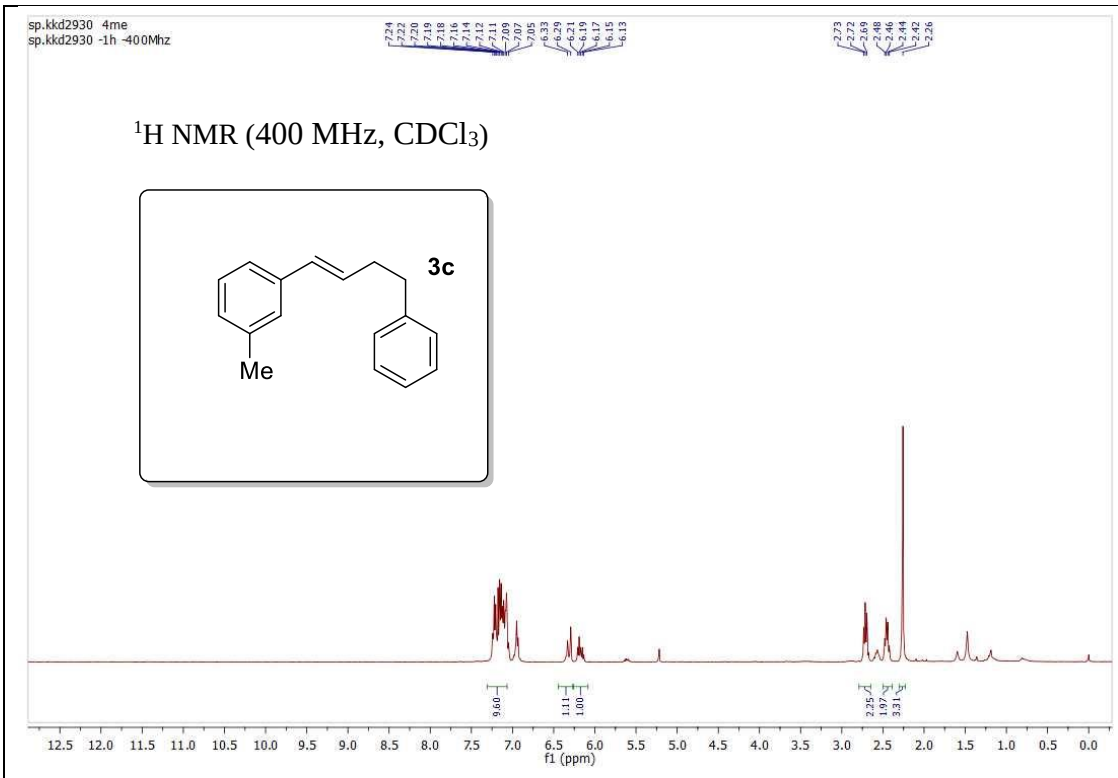
^{13}C NMR (101 MHz, $CDCl_3$)


sp.kkd2929A ph
^{1}H NMR (400 MHz, $CDCl_3$)
3a
10.40
1.07
1.00
2.17
2.06
f1 (ppm)

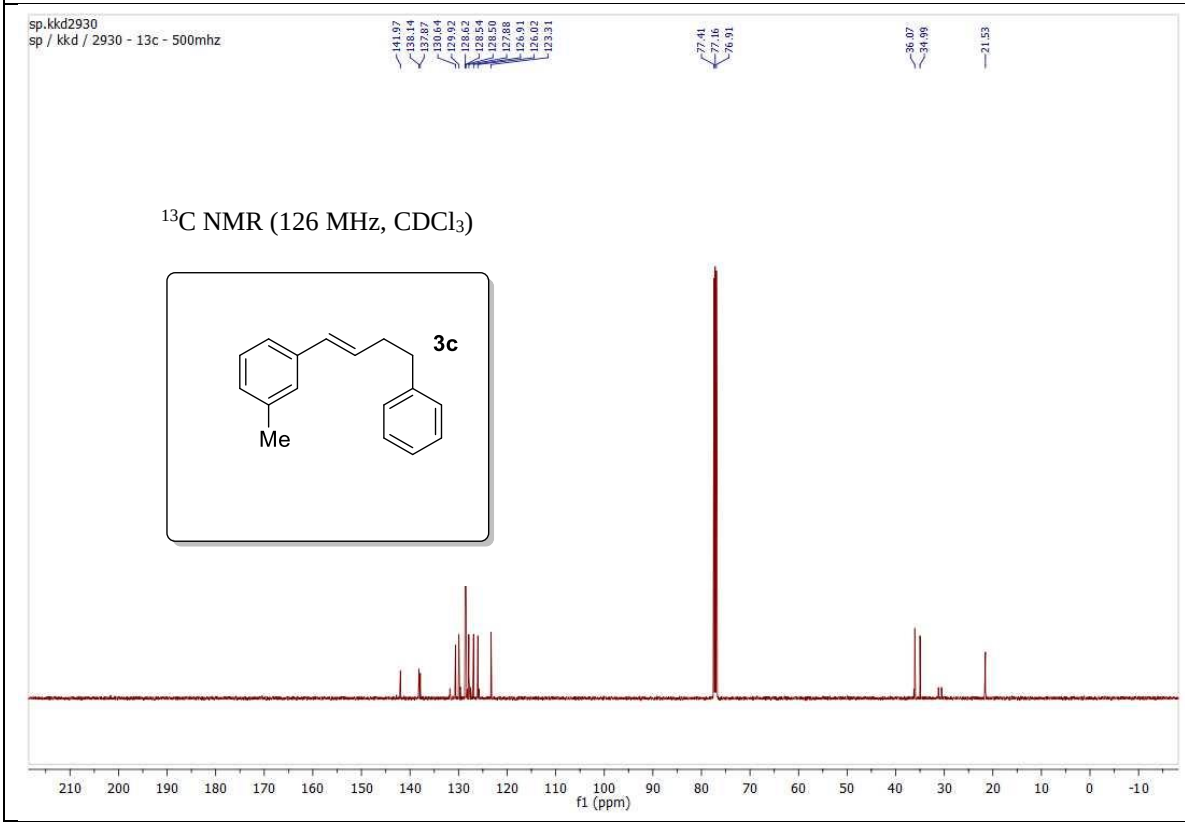

sp.kkd2929a
sp / kkd / 2929a - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3a
f1 (ppm)


sp.kkd2934 2me
sp.kkd2934 -1h -400Mhz
1H NMR (400 MHz, CDCl3)
3b
Me
15.08
0.97
0.52
1.00
0.53
1.92
0.87
2.00
0.92
3.10
1.48
f1 (ppm)

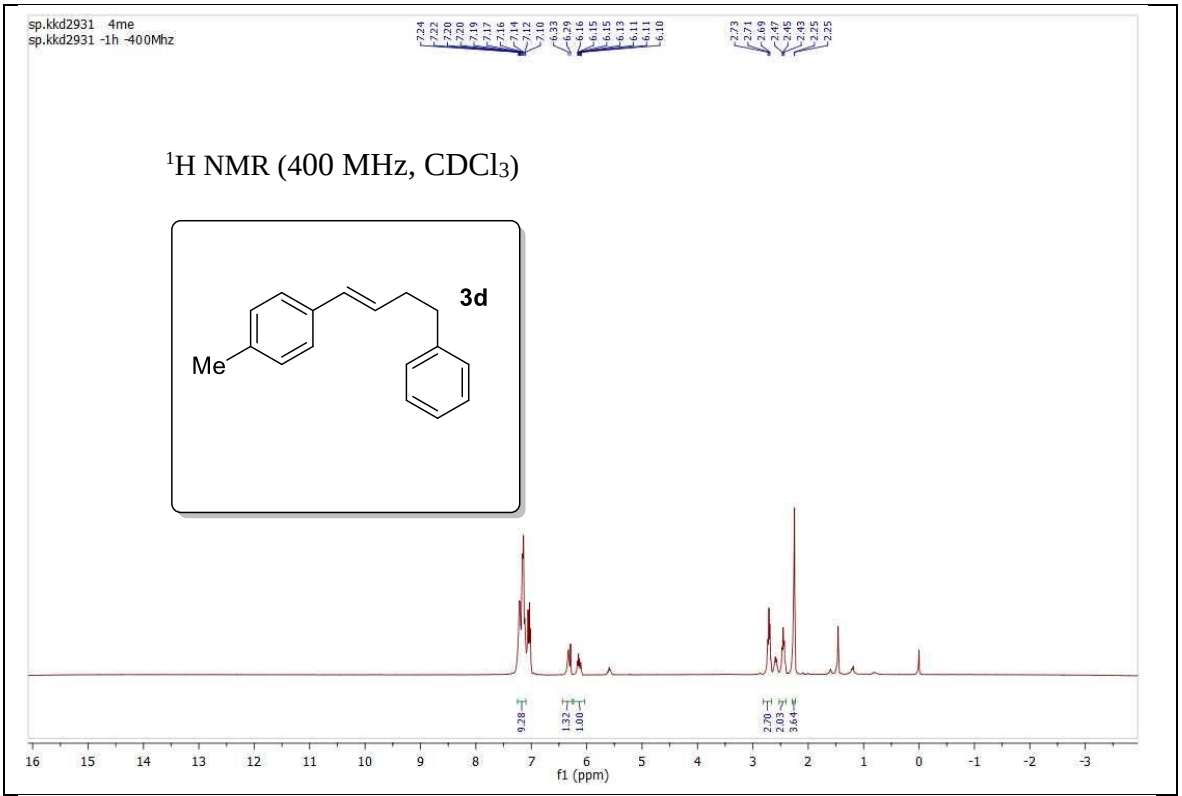

sp.kkd2934
sp / kkd / 2934 - 13c - 500mhz
13C NMR (126 MHz, CDCl3)
3b
Me
f1 (ppm)

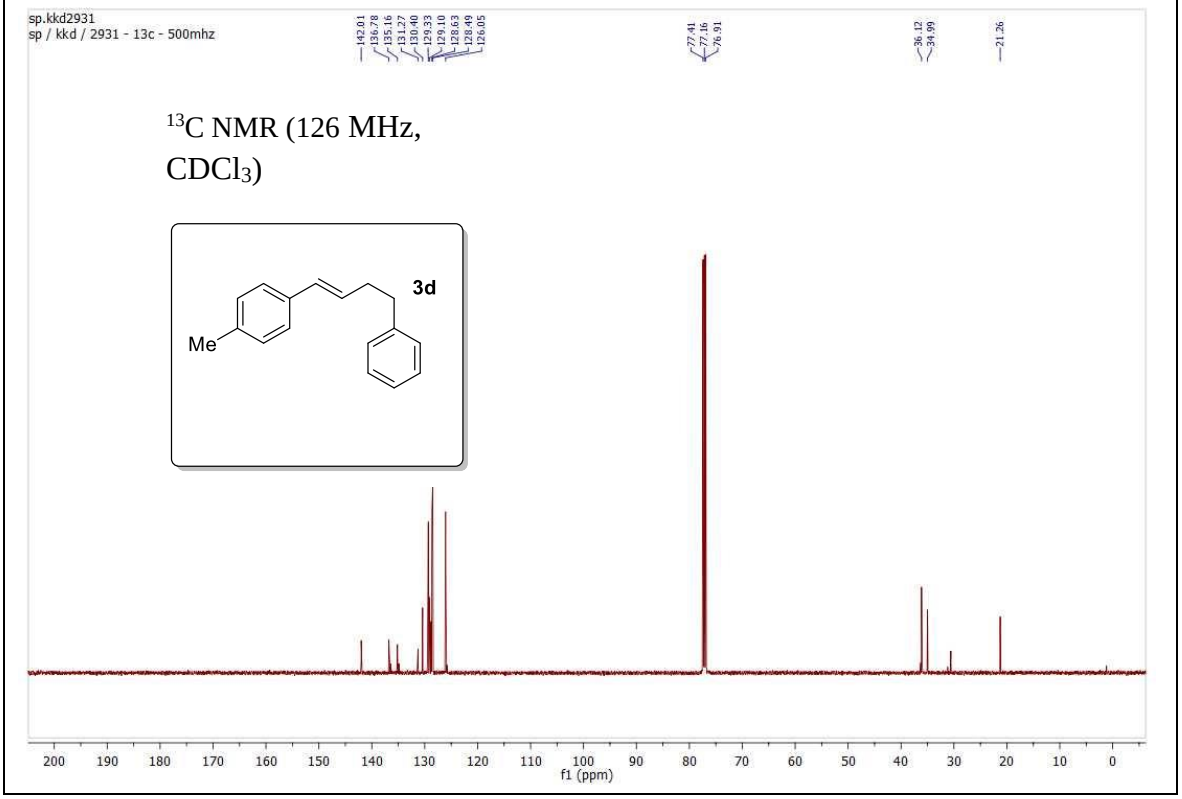


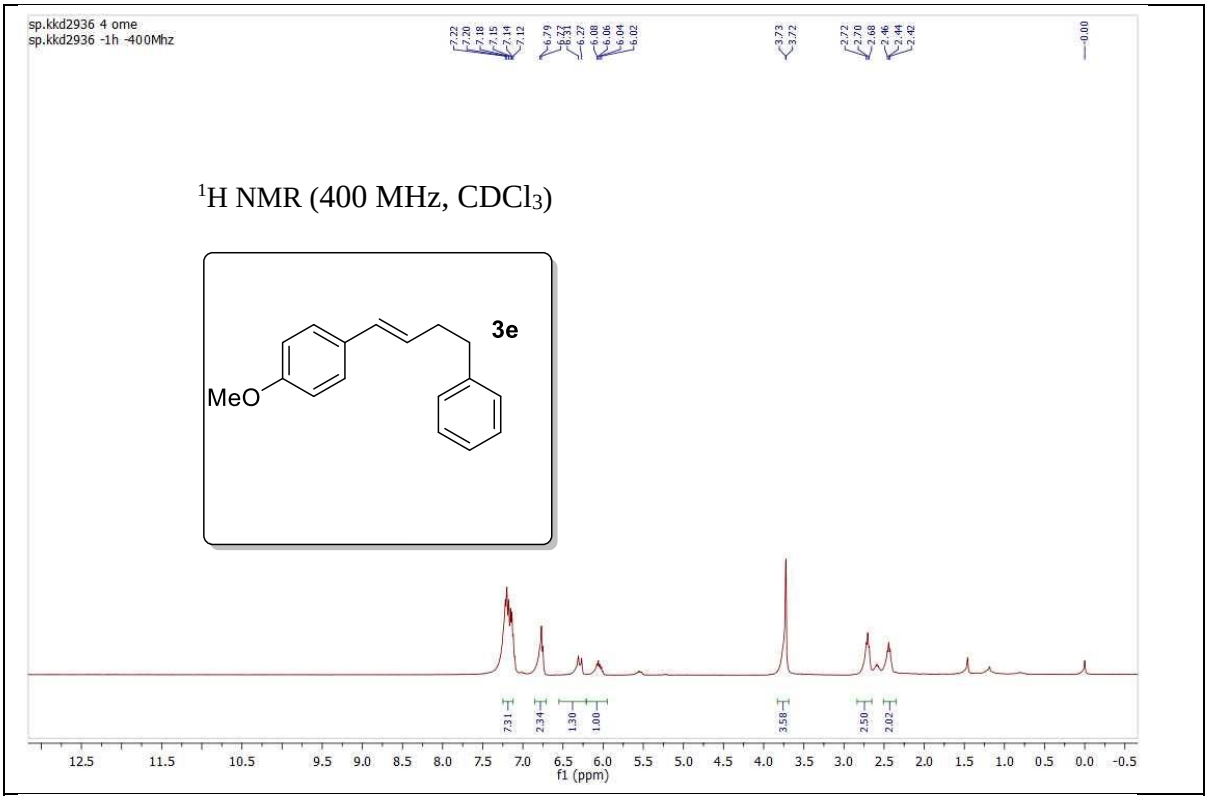
^{1}H NMR (400 MHz, $CDCl_3$)

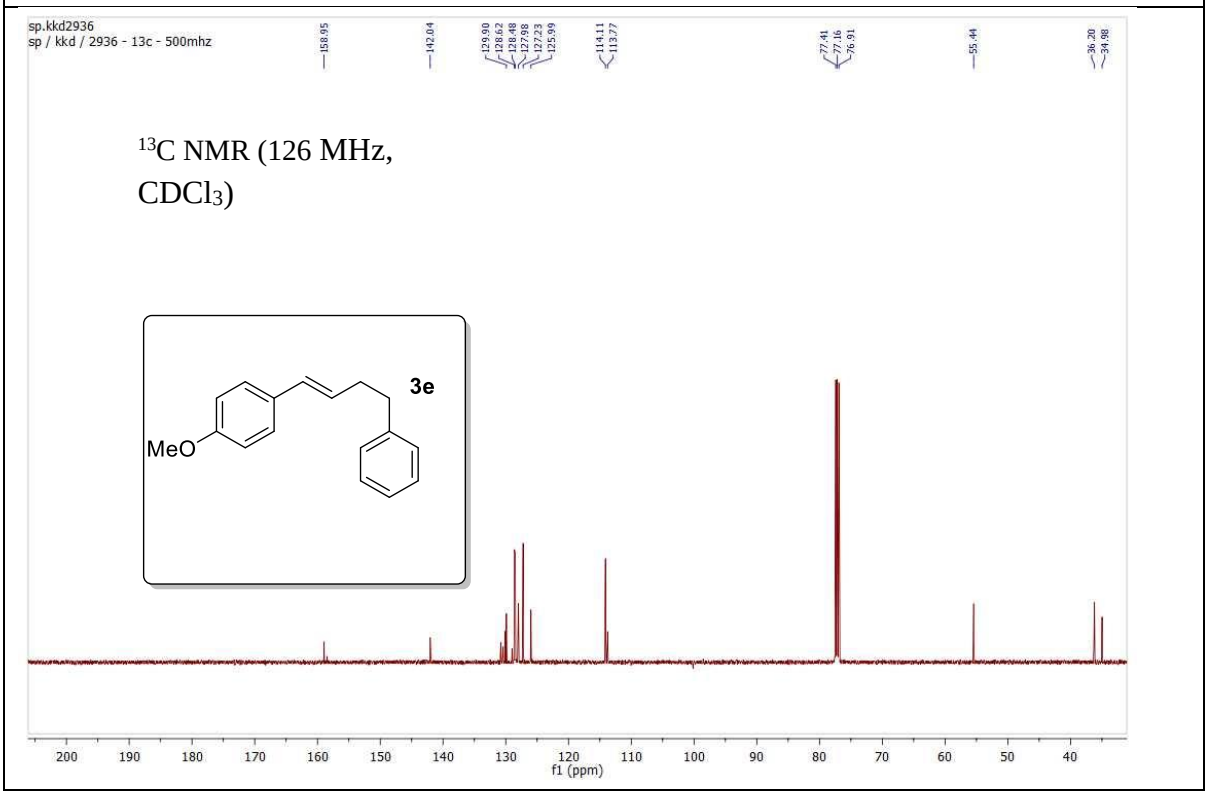


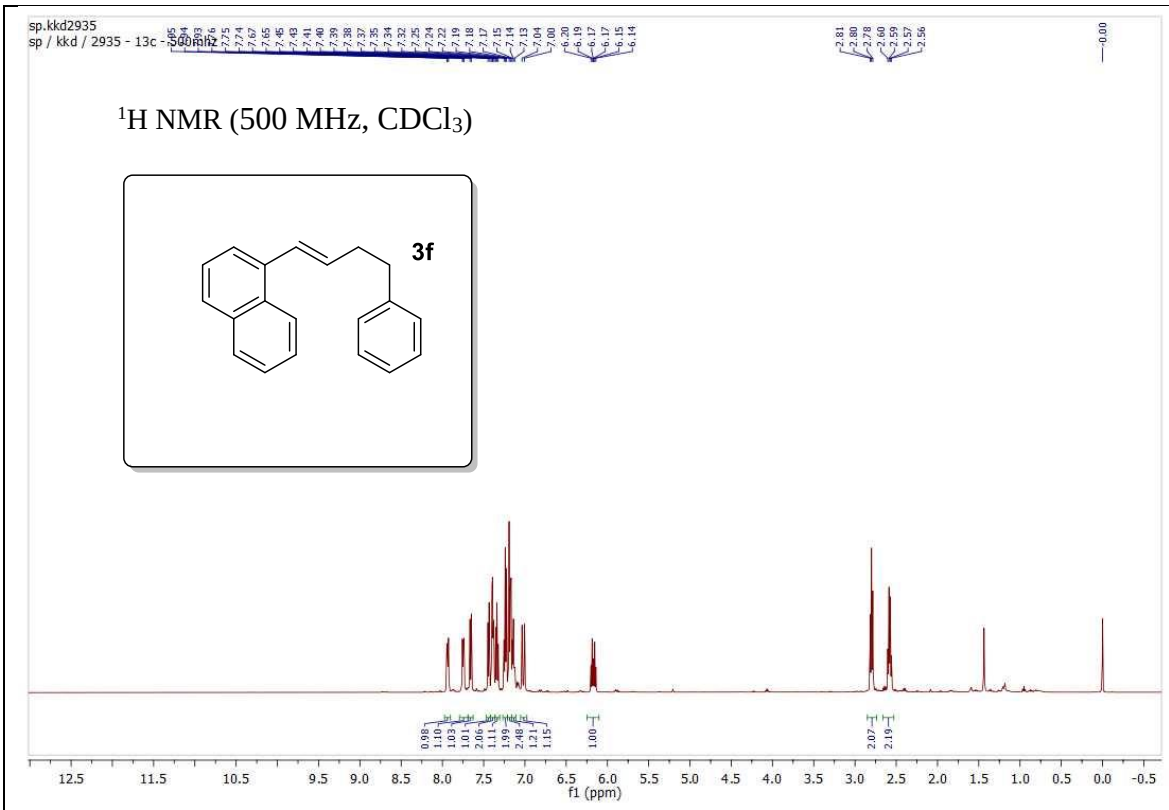
^{13}C NMR (126 MHz, $CDCl_3$)

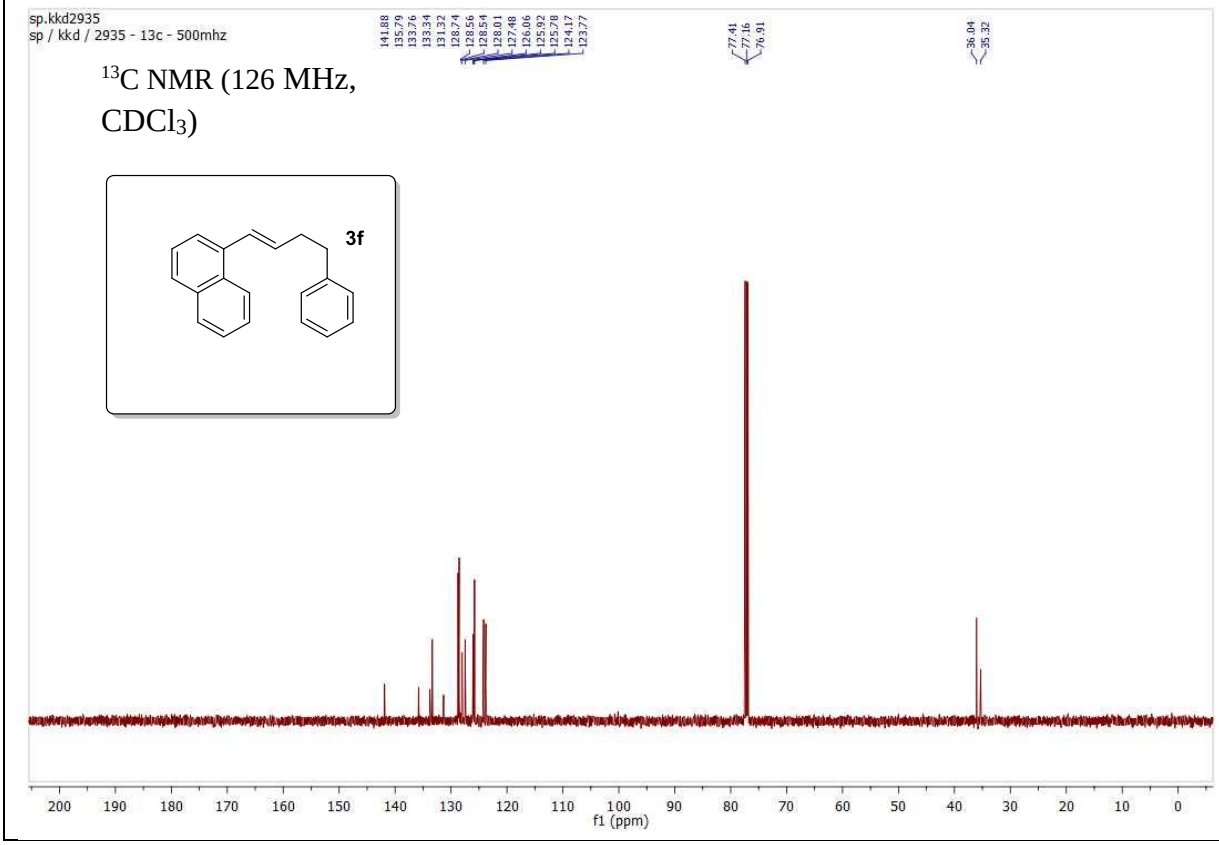

sp.kkd2931 4me
sp.kkd2931 -1h -400Mhz
^{1}H NMR (400 MHz, $CDCl_3$)
3d
Me
f1 (ppm)

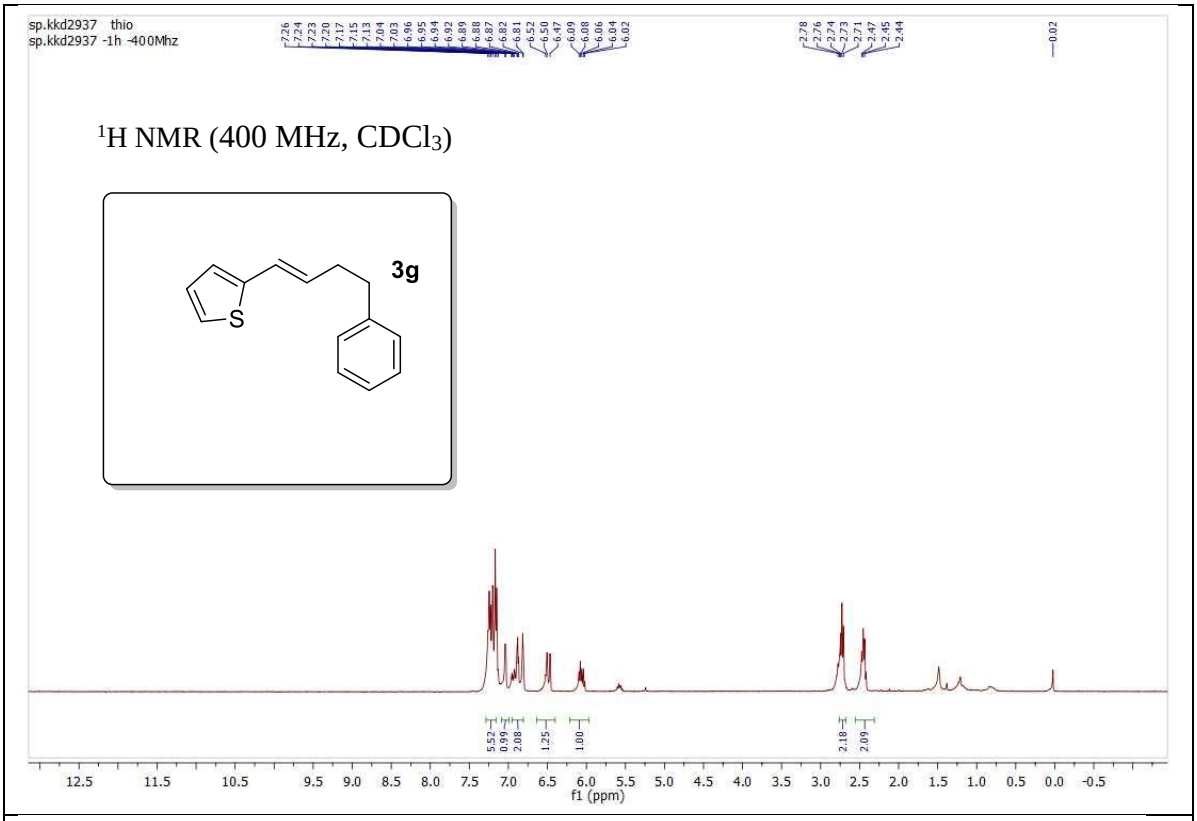

sp.kkd2931
sp / kkd / 2931 - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3d
Me
f1 (ppm)

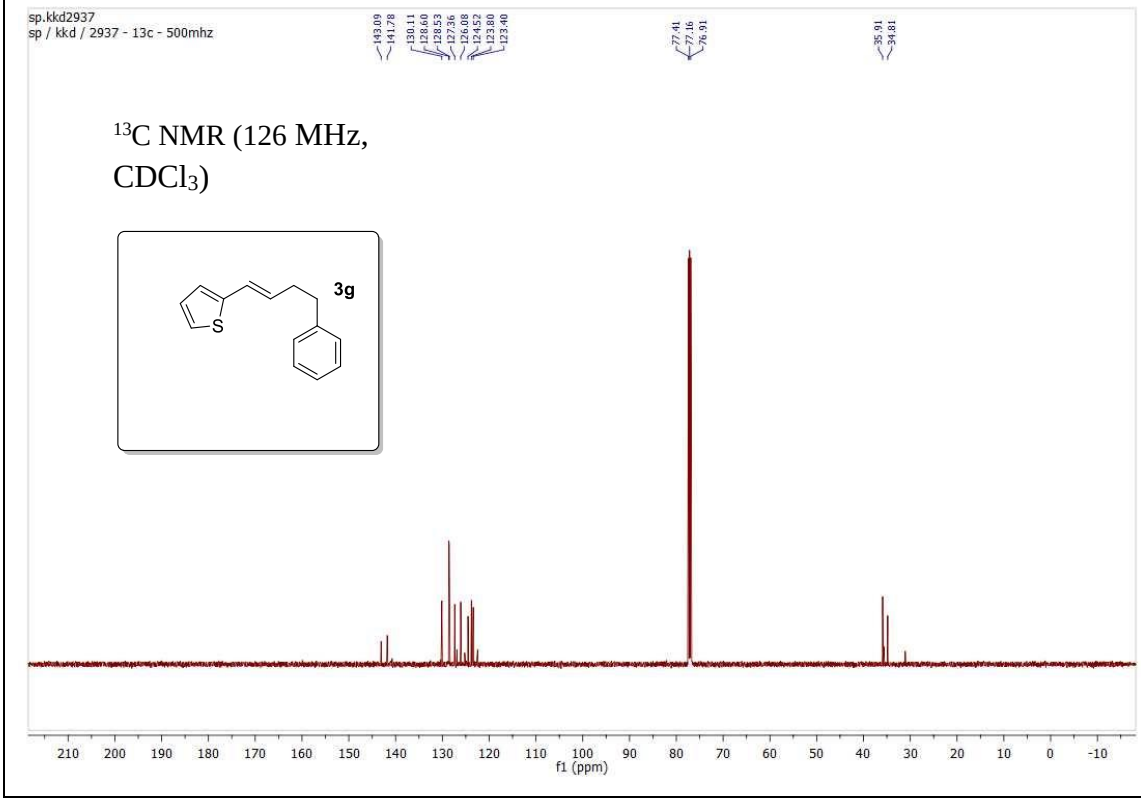

sp.kkd2936 4 ome
sp.kkd2936 -1h -400Mhz
^{1}H NMR (400 MHz, $CDCl_3$)
3e
MeO
f1 (ppm)

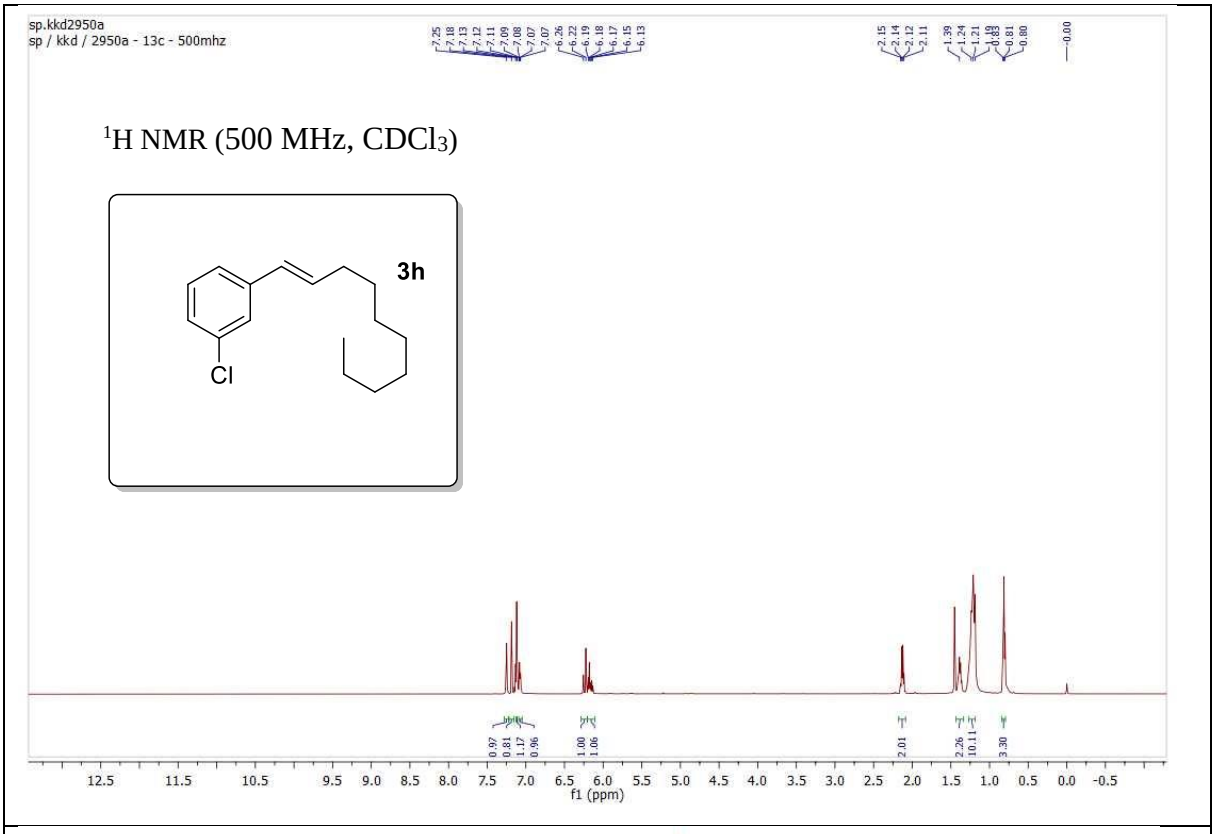

sp.kkd2936
sp / kkd / 2936 - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3e
MeO
f1 (ppm)

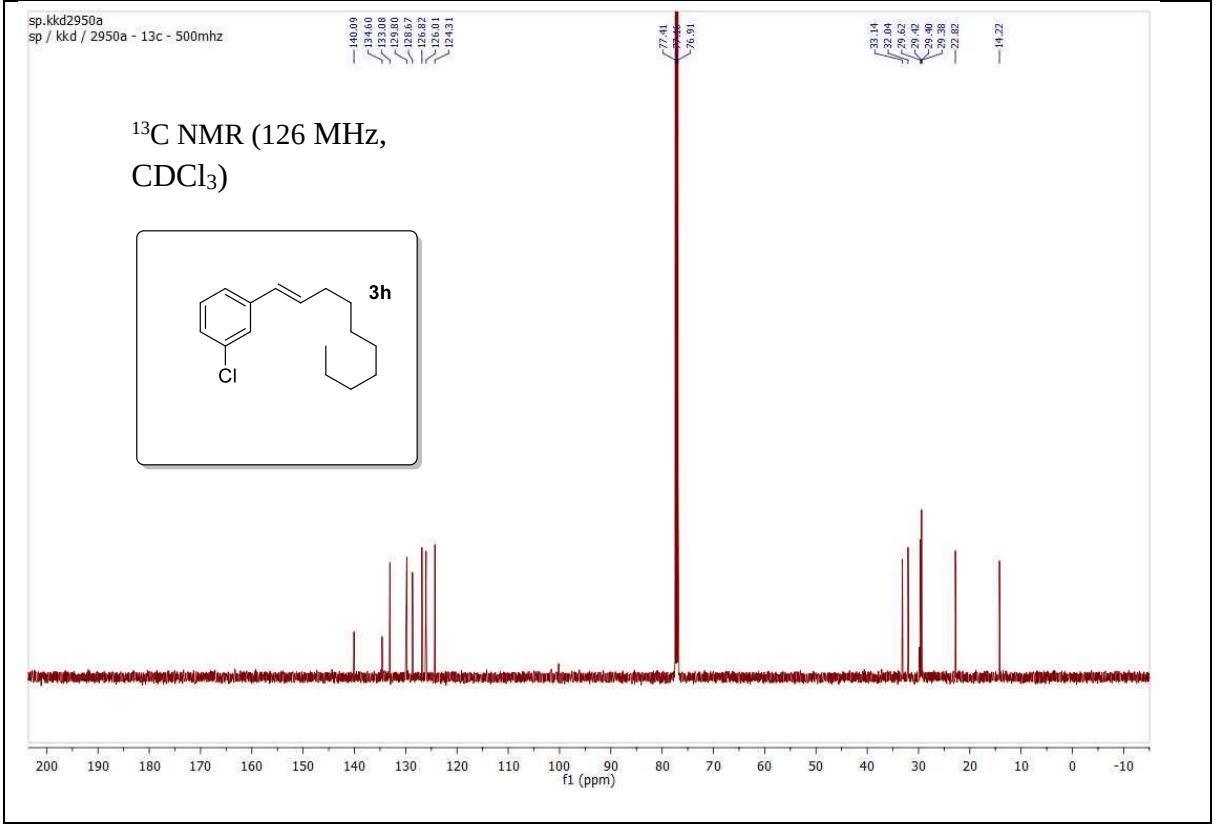

sp.kkd2935
sp / kkd / 2935 - 13c - 500mhz
^{1}H NMR (500 MHz, $CDCl_3$)
3f
f1 (ppm)

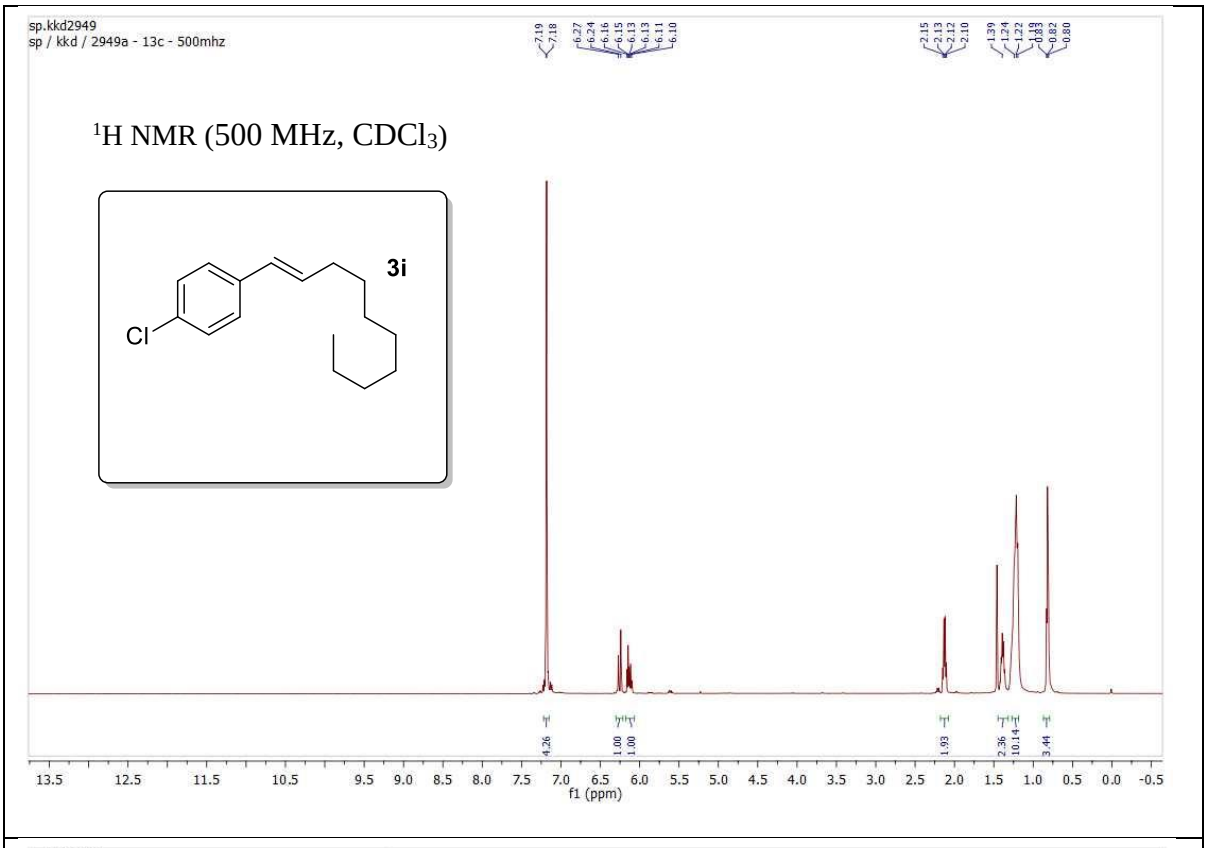

sp.kkd2935
sp / kkd / 2935 - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3f
f1 (ppm)

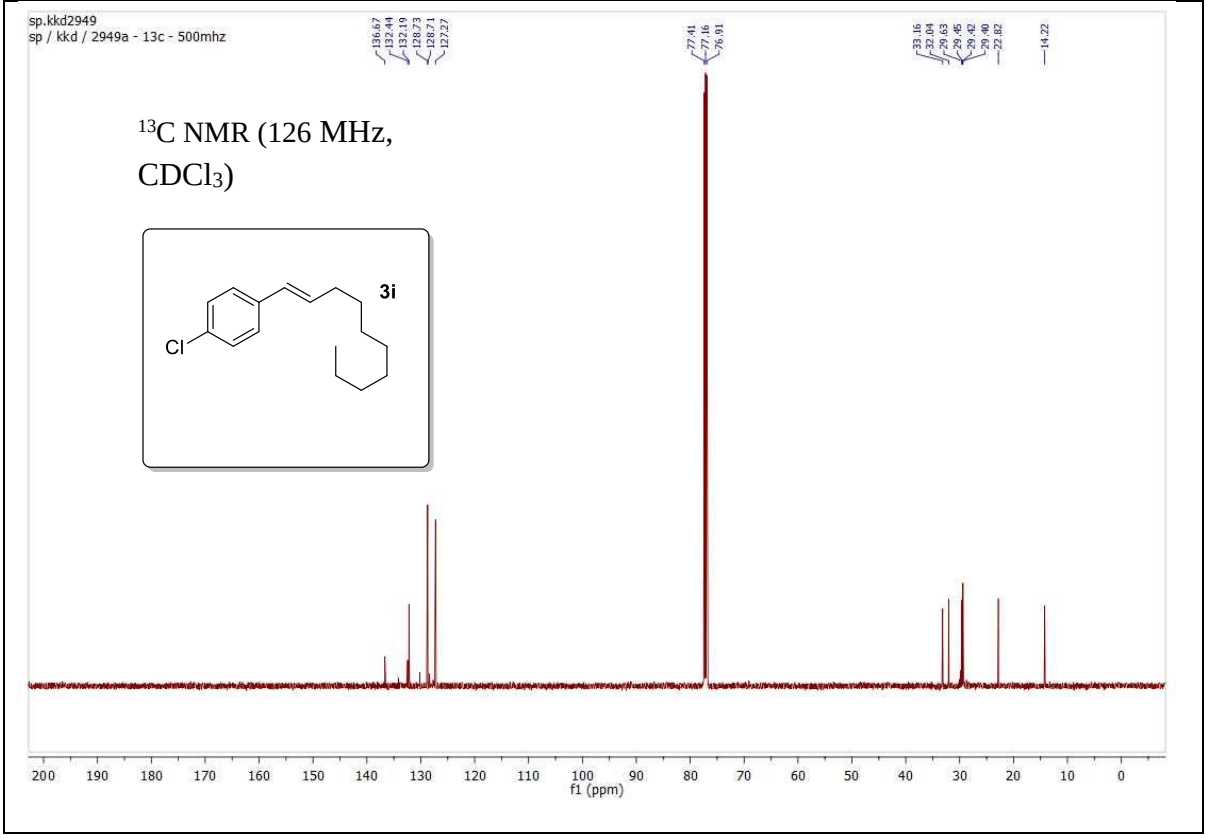

sp.kkd2937 thio
sp.kkd2937 -1h -400Mhz
^{1}H NMR (400 MHz, $CDCl_3$)
3g
S
5.52
0.99
2.08
1.25
1.00
2.18
2.09
f1 (ppm)

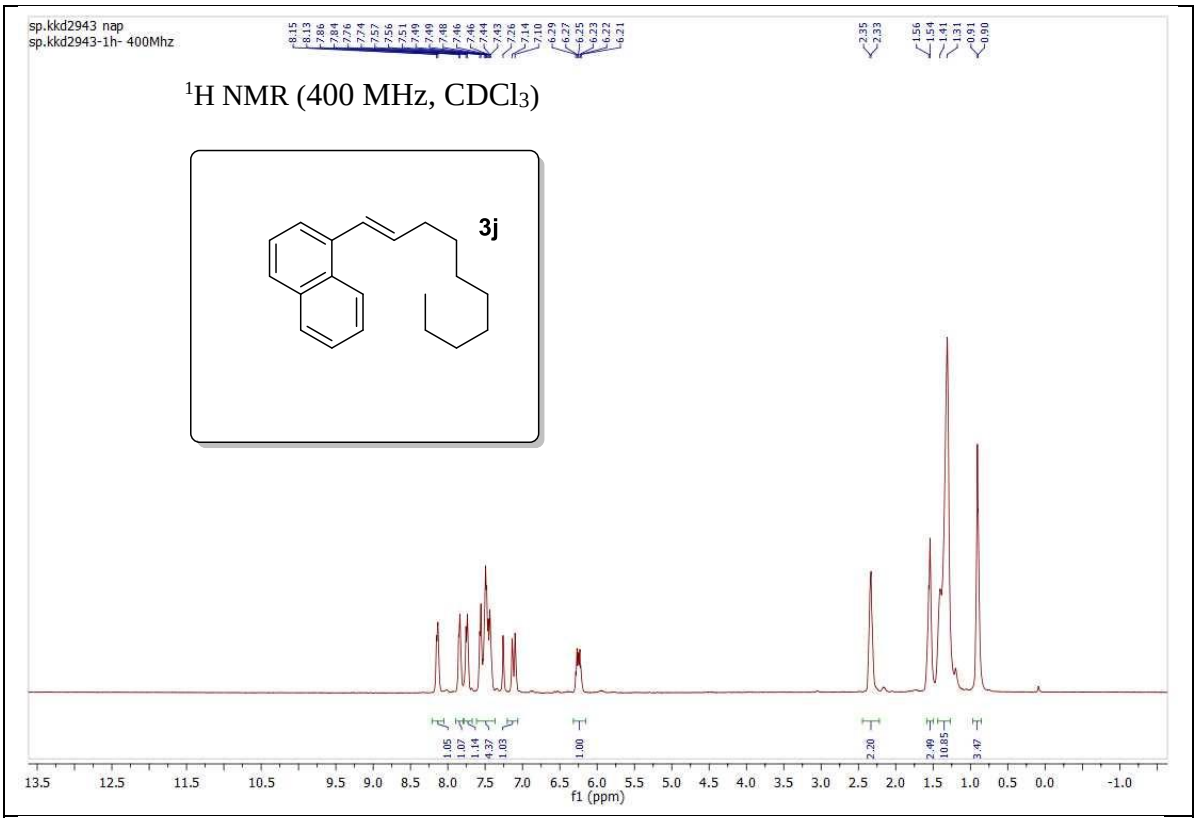

sp.kkd2937
sp / kkd / 2937 - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3g
S
f1 (ppm)


sp.kkd2950a
sp / kkd / 2950a - 13c - 500mhz
^{1}H NMR (500 MHz, $CDCl_3$)
3h
Cl
f1 (ppm)

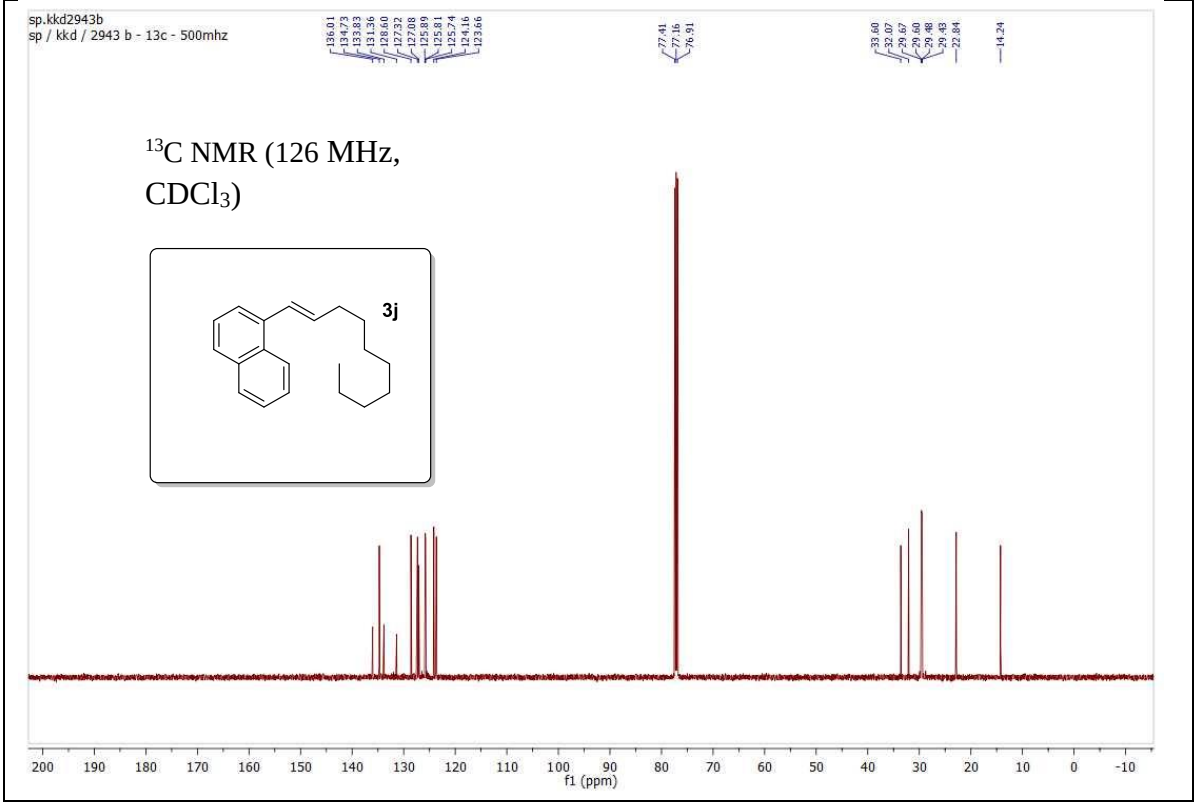

sp.kkd2950a
sp / kkd / 2950a - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3h
Cl
f1 (ppm)


sp.kkd2949
sp / kkd / 2949a - 13c - 500mhz
7.19
7.18
6.27
6.24
6.16
6.15
6.13
6.13
6.11
6.10
2.15
2.13
2.12
2.10
1.39
1.24
1.22
1.03
0.83
0.82
0.80
1H NMR (500 MHz, CDCl3)
3i
Cl
4.26
1.00
1.00
1.93
2.36
10.14
3.44
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

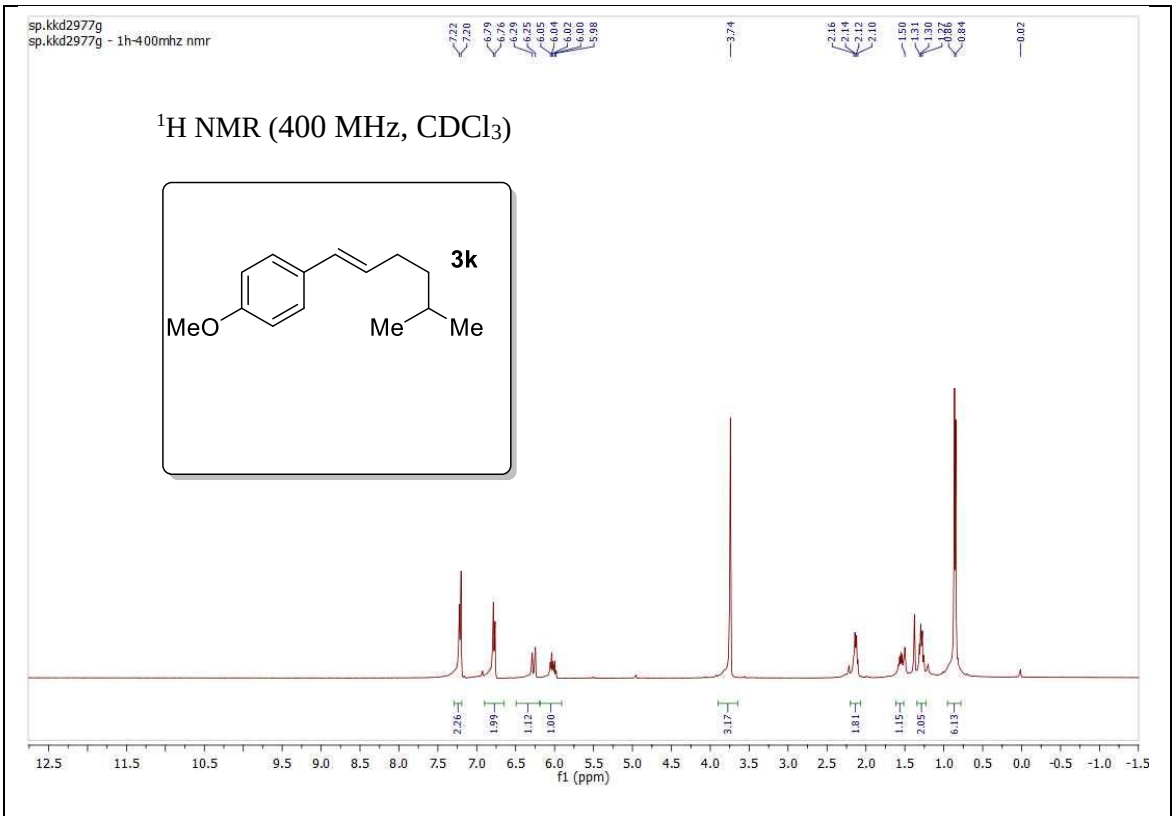

sp.kkd2949
sp / kkd / 2949a - 13c - 500mhz
136.67
132.44
132.19
128.73
128.71
127.27
77.41
77.16
76.91
33.16
32.04
29.63
29.45
29.42
29.40
22.82
14.22
13C NMR (126 MHz, CDCl3)
3i
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

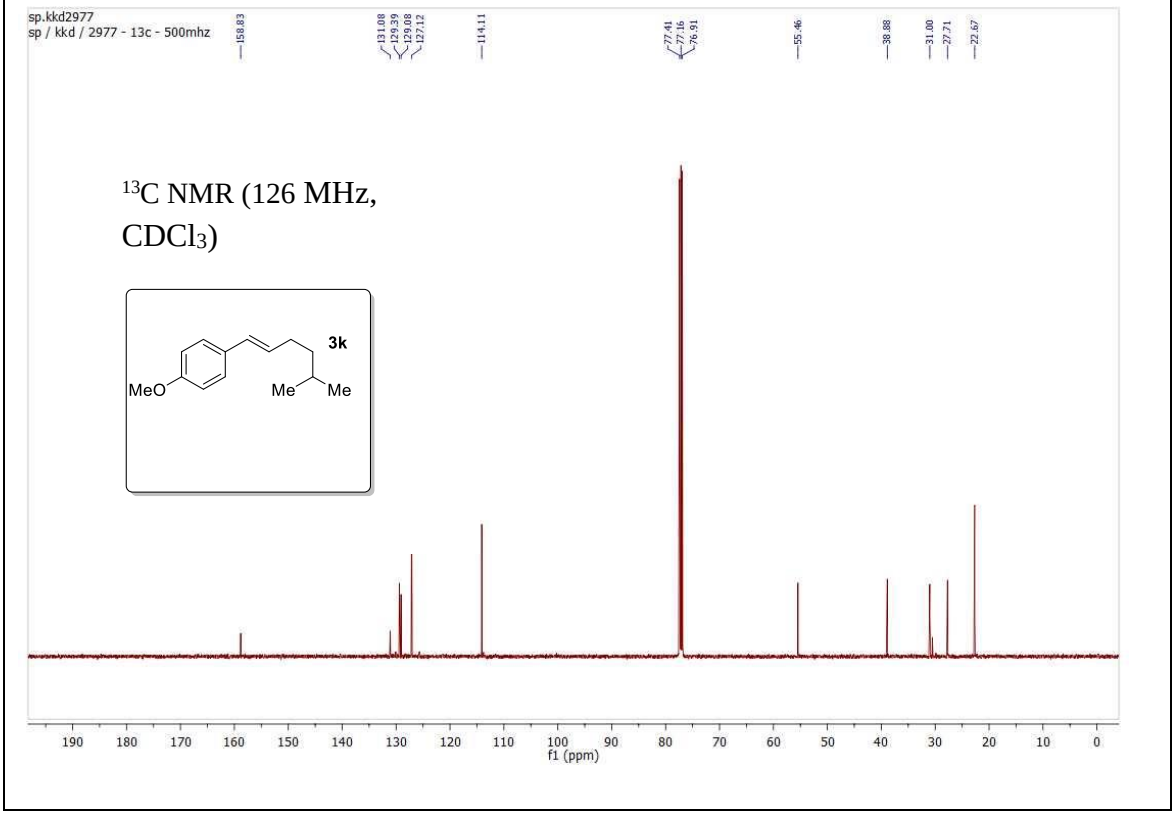


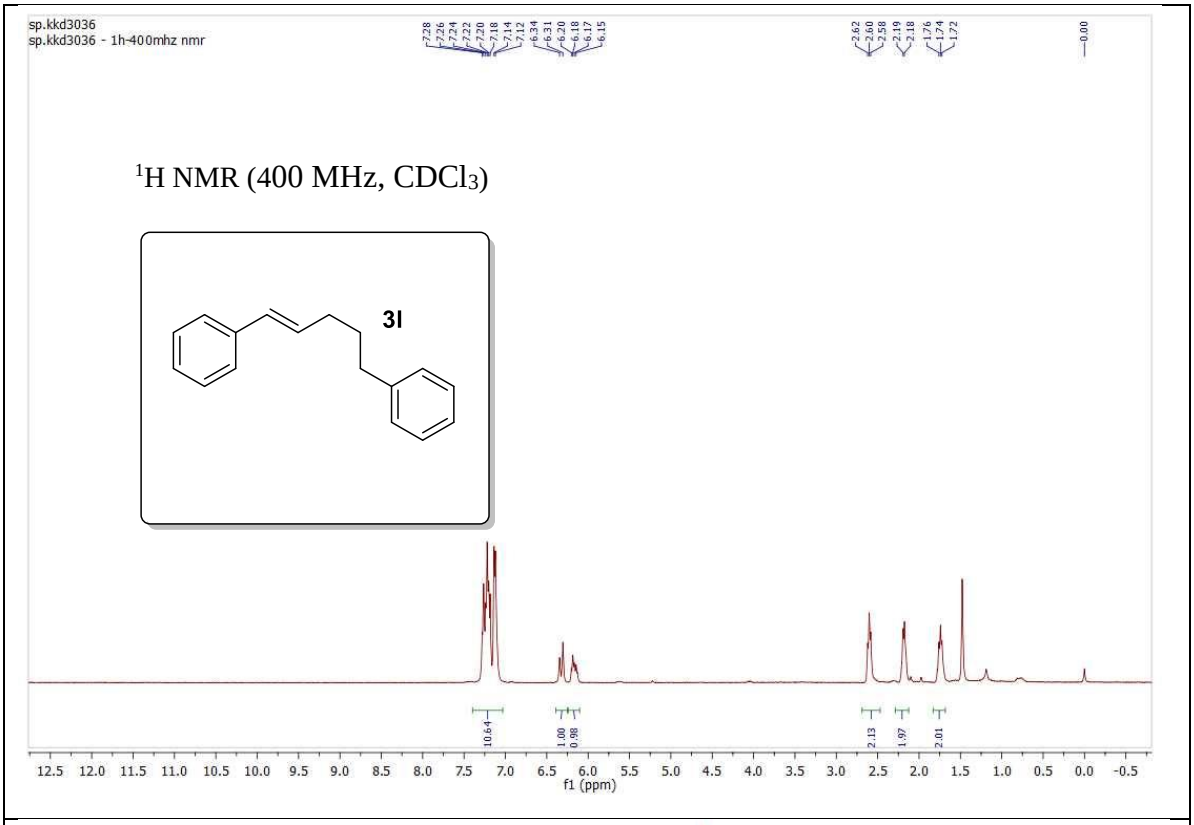
^{1}H NMR (400 MHz, $CDCl_3$)



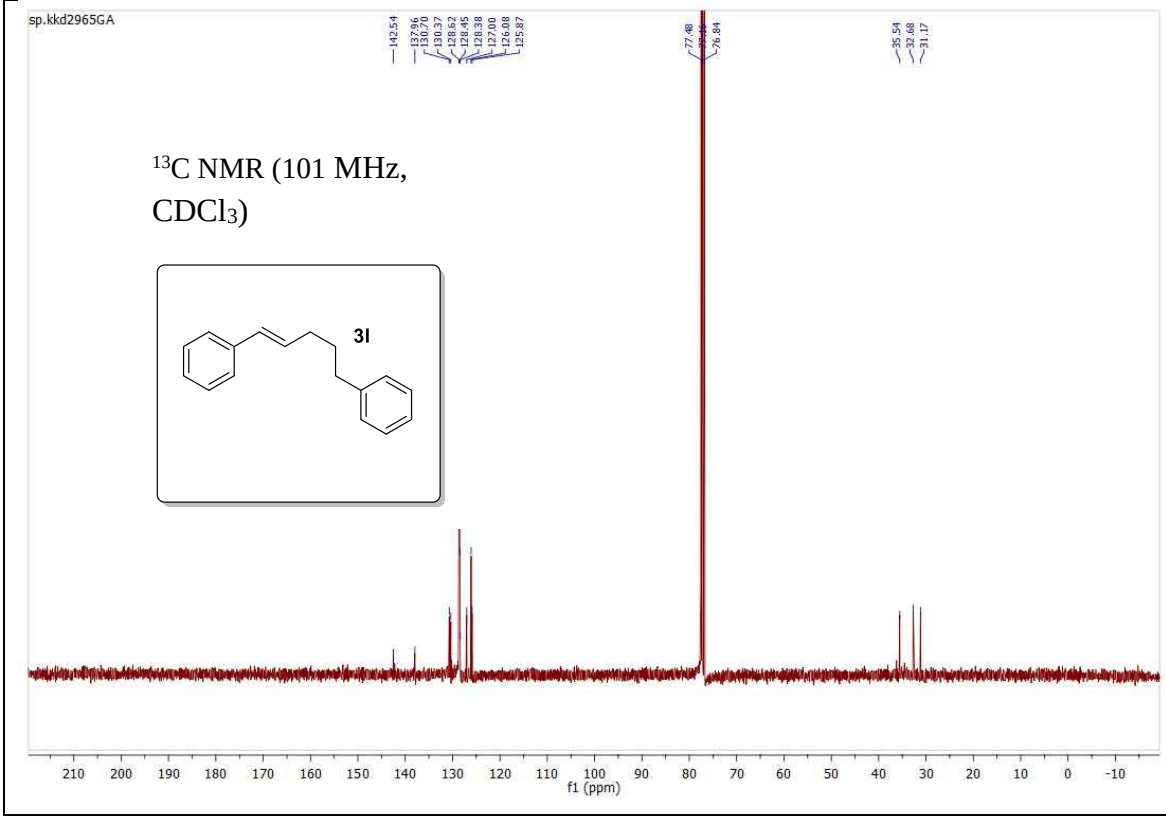
^{13}C NMR (126 MHz, $CDCl_3$)


sp.kkd2977g
sp.kkd2977g - 1h-400mhz nmr
7.22
7.20
6.79
6.76
6.29
6.25
6.05
6.04
6.02
6.00
5.98
3.74
2.16
2.14
2.12
2.10
1.50
1.31
1.30
1.27
0.86
0.84
0.02
1H NMR (400 MHz, CDCl3)
3k
MeO
Me
Me
2.26
1.99
1.12
1.00
3.17
1.81
1.15
2.05
6.13
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

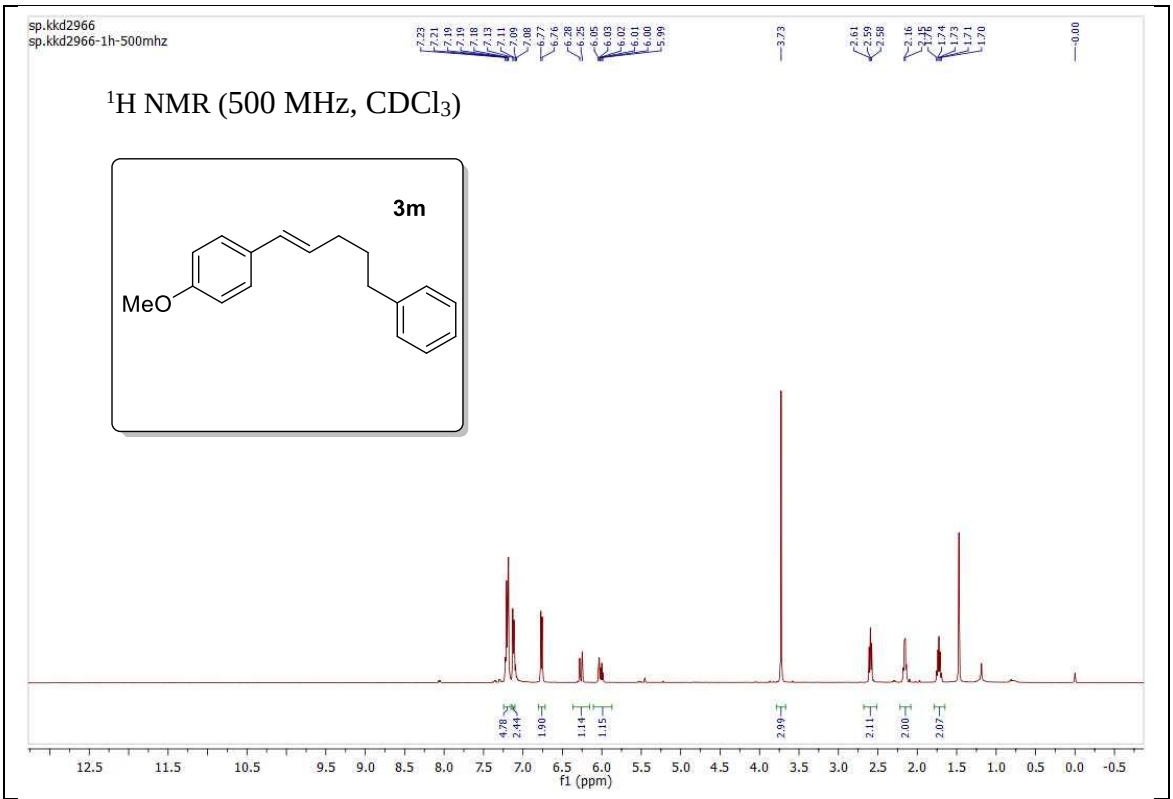

sp.kkd2977
sp / kkd / 2977 - 13c - 500mhz
158.83
131.08
129.39
129.08
127.12
114.11
77.41
77.16
76.91
55.46
38.88
31.00
27.71
22.67
13C NMR (126 MHz, CDCl3)
3k
MeO
Me
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



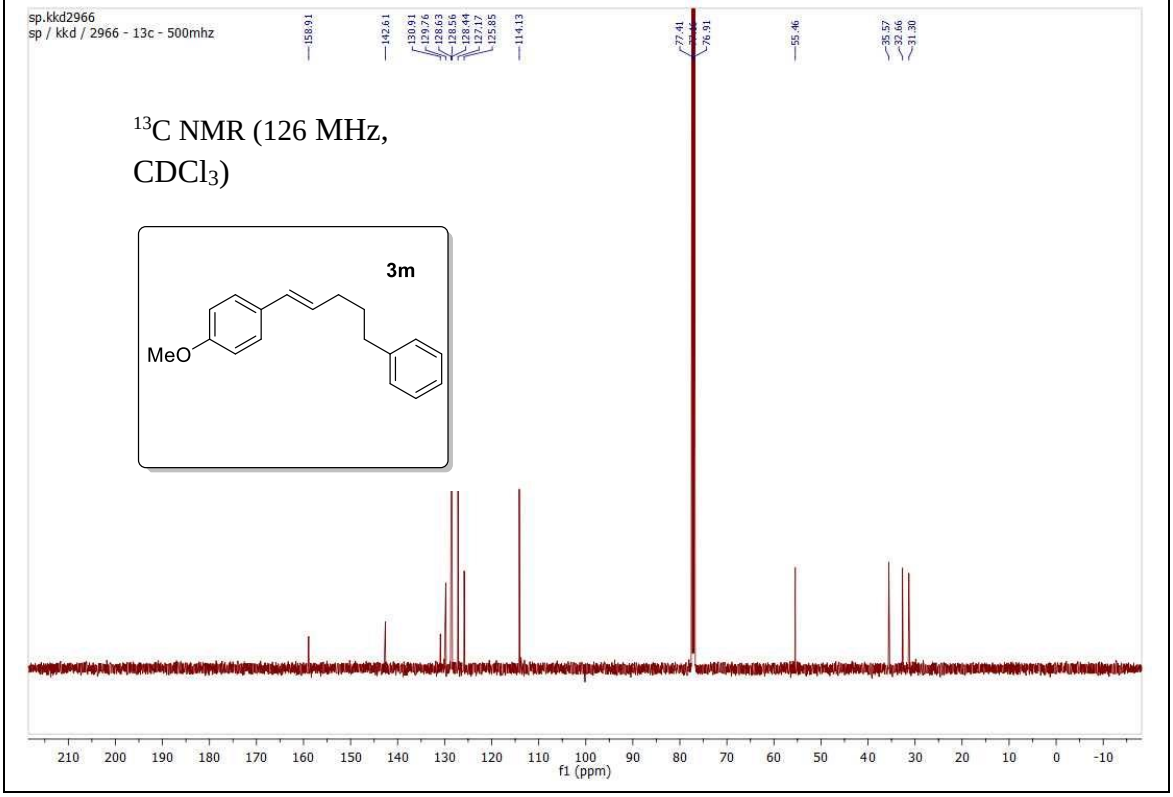
^{1}H NMR (400 MHz, $CDCl_3$)



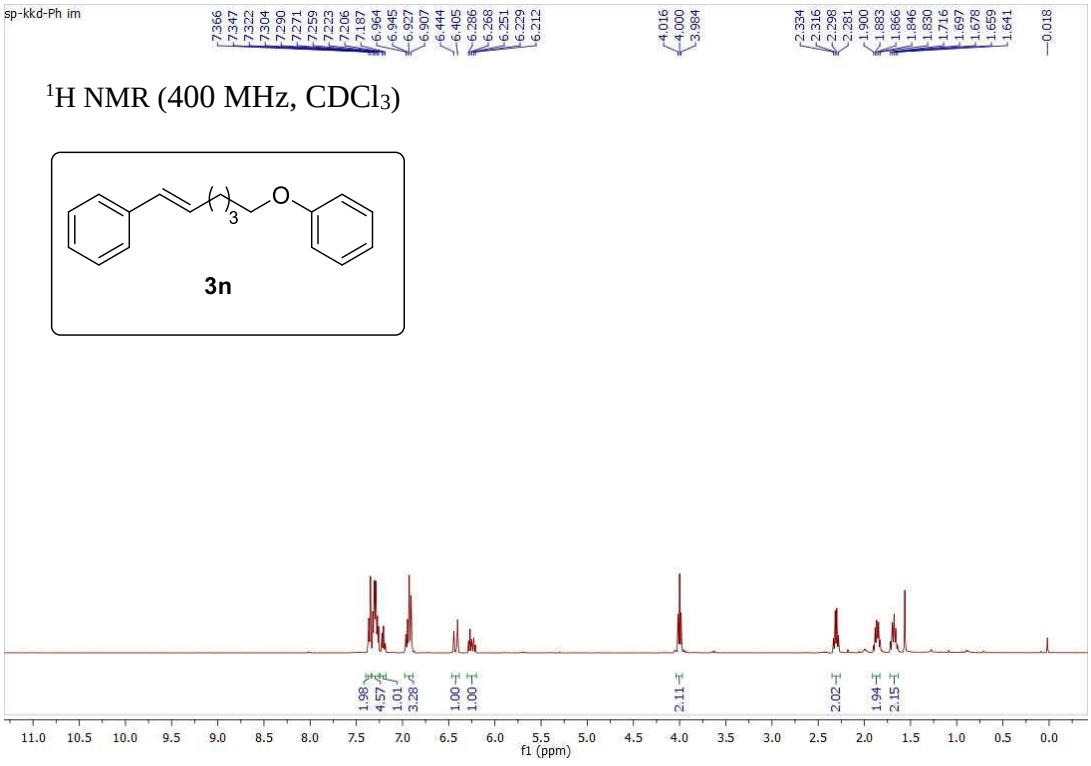
^{13}C NMR (101 MHz, $CDCl_3$)



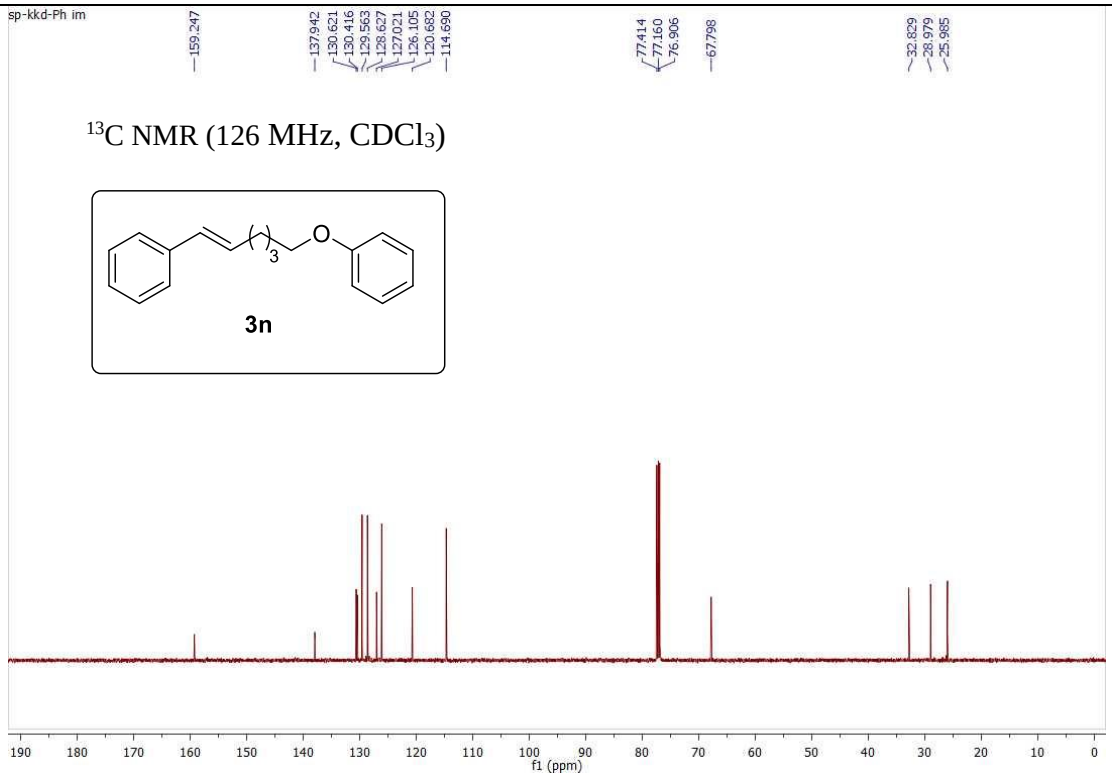
^{1}H NMR (500 MHz, $CDCl_3$)



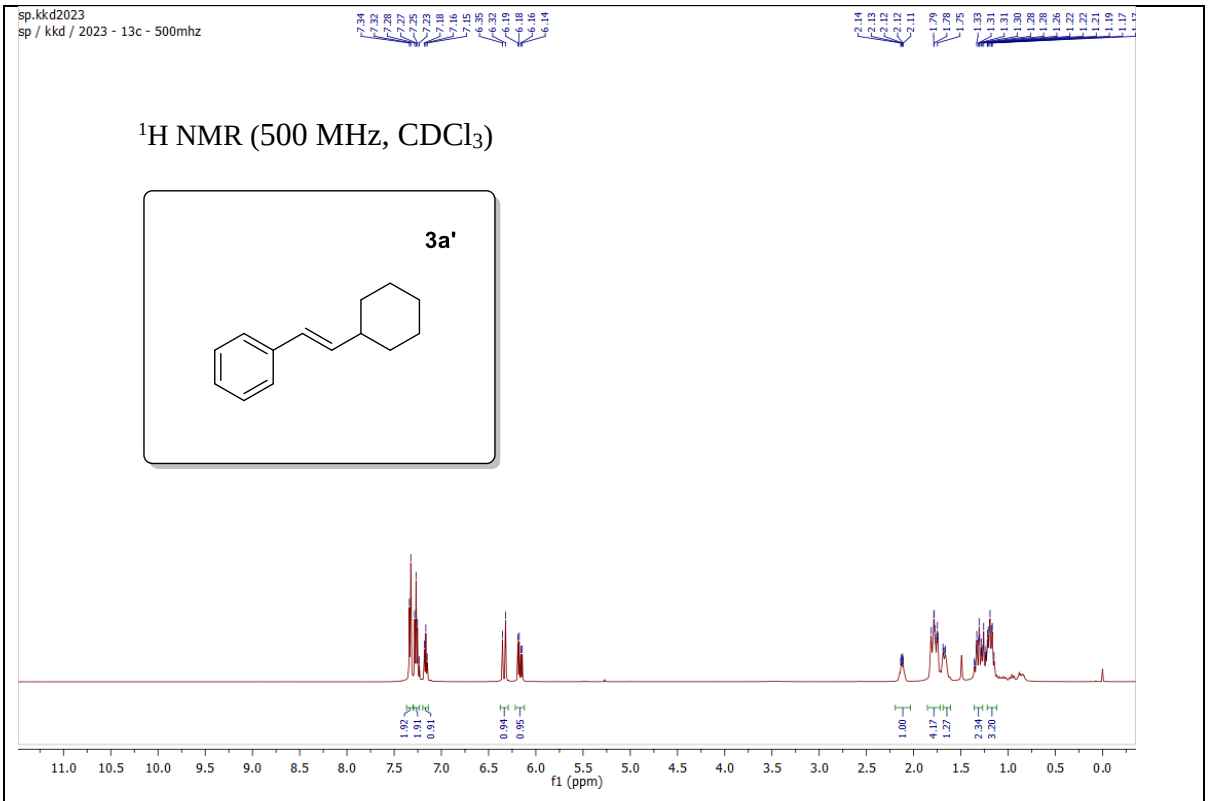
^{13}C NMR (126 MHz, $CDCl_3$)

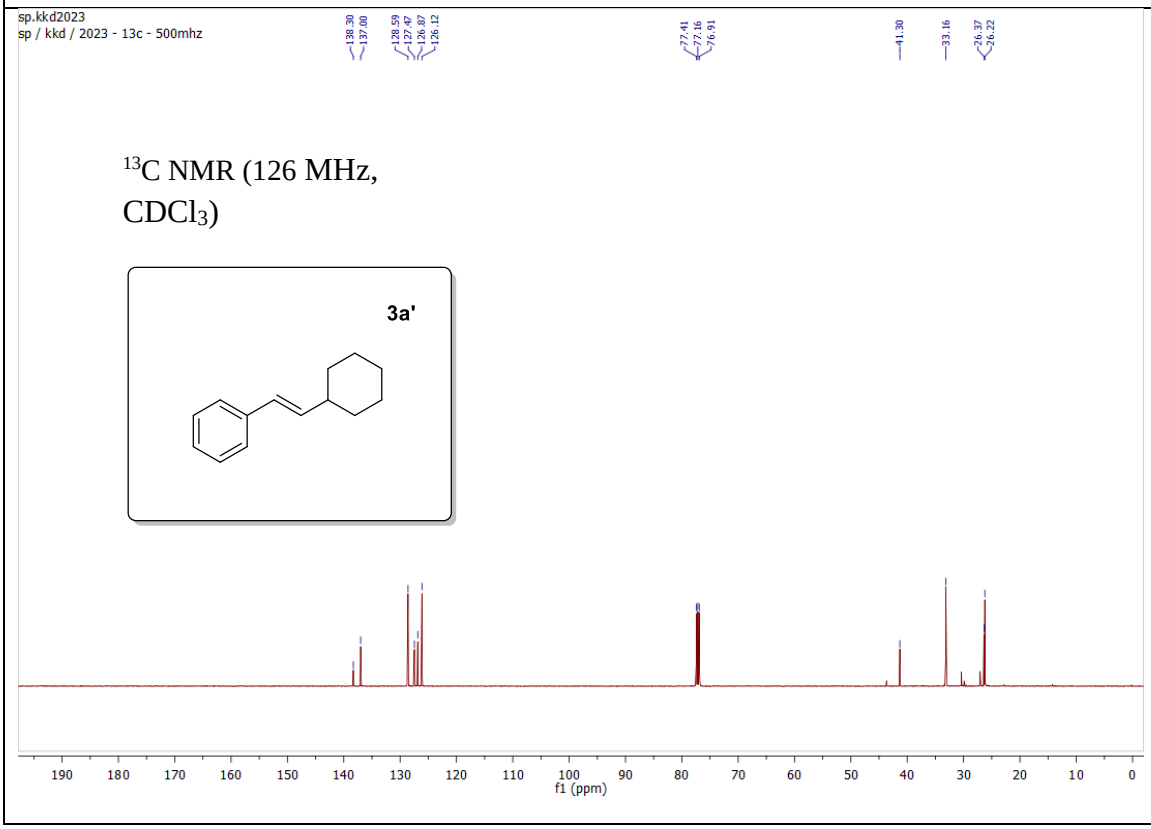


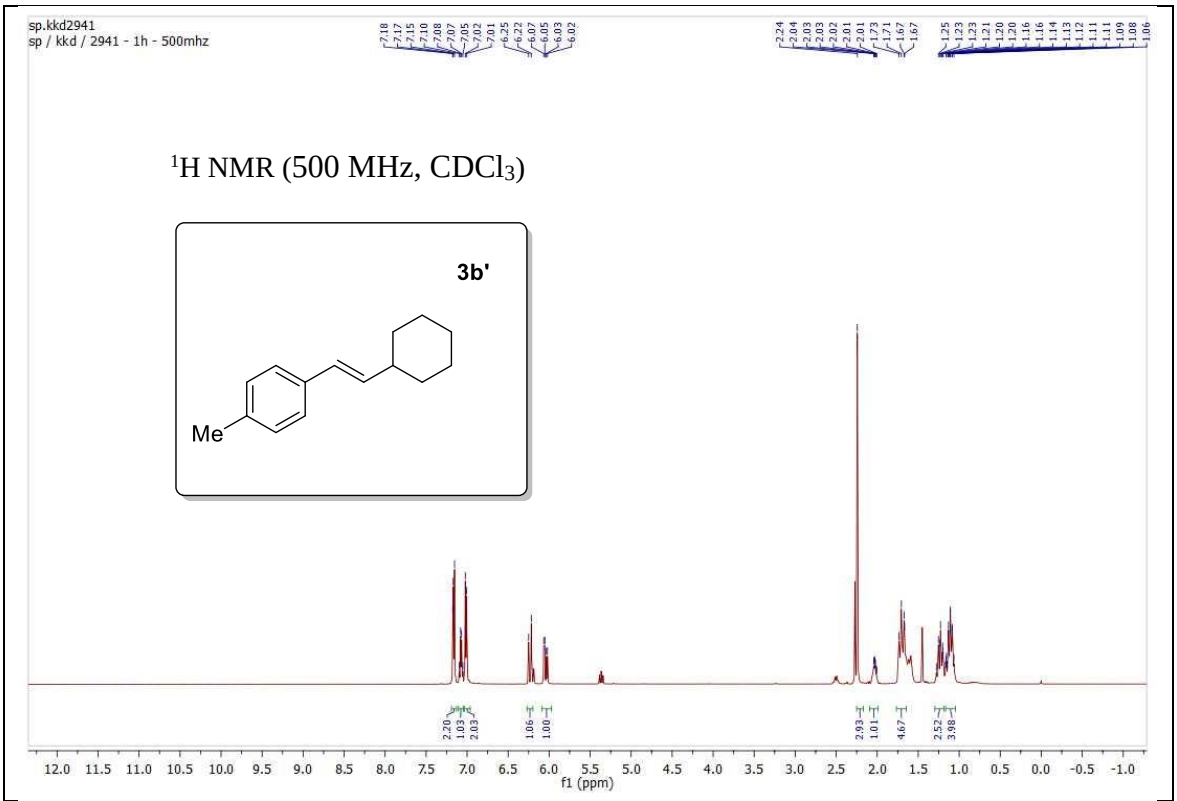
^{1}H NMR (400 MHz, $CDCl_3$)

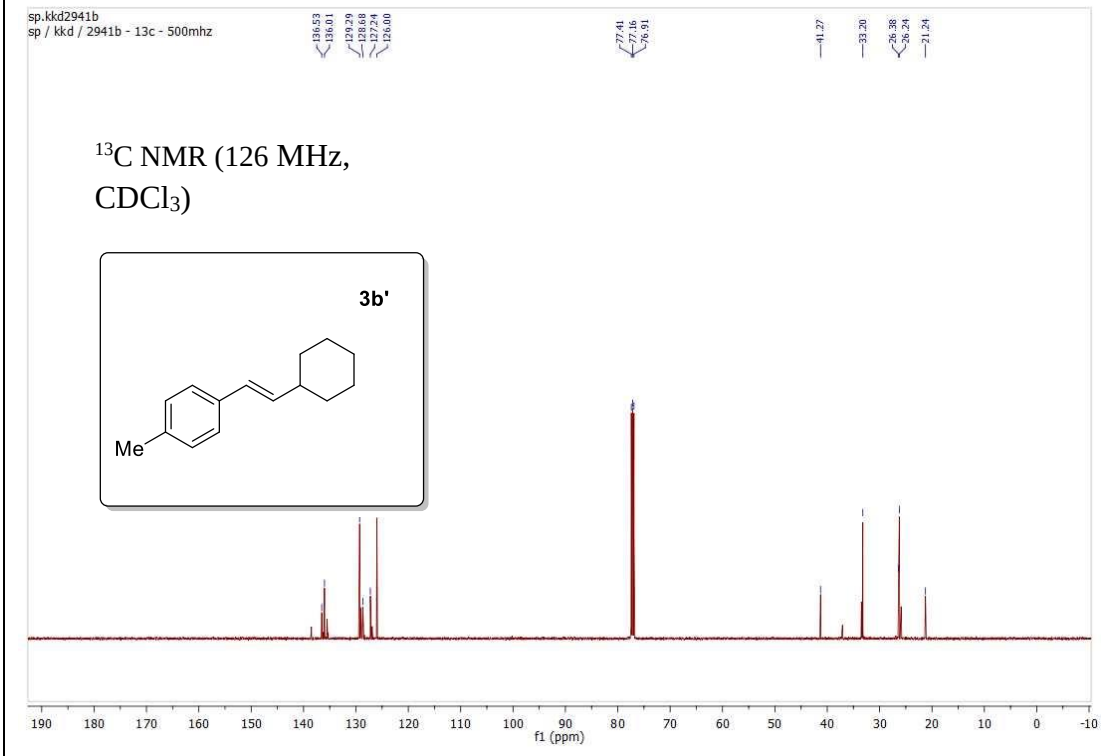


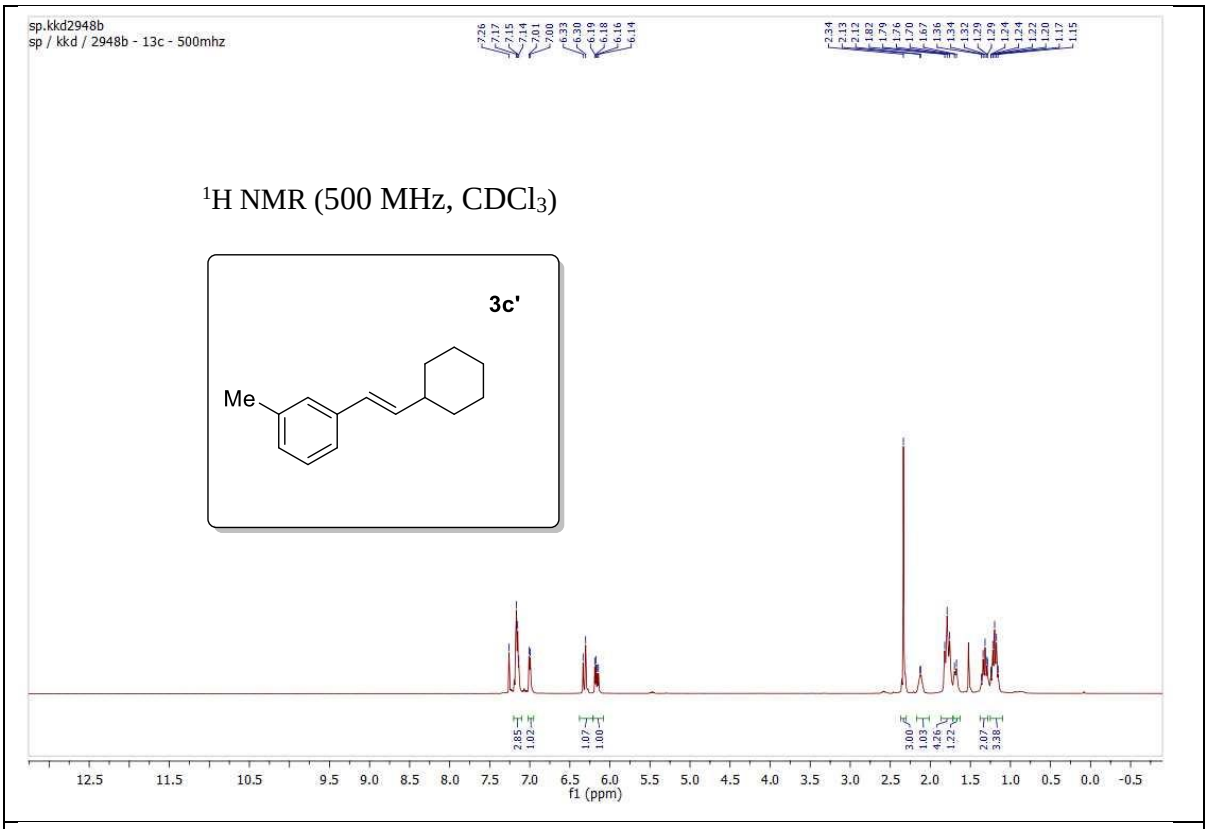
^{13}C NMR (126 MHz, $CDCl_3$)


sp.kkd2023
sp / kkd / 2023 - 13c - 500mhz
7.34
7.32
7.28
7.27
7.25
7.23
7.18
7.16
7.15
6.35
6.32
6.19
6.18
6.16
6.14
2.14
2.13
2.12
2.12
2.11
1.79
1.78
1.75
1.33
1.31
1.31
1.30
1.28
1.28
1.26
1.22
1.22
1.21
1.19
1.17
1H NMR (500 MHz, CDCl3)
3a'
1.92
1.91
0.91
0.94
0.95
1.00
4.17
1.27
2.34
3.20
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

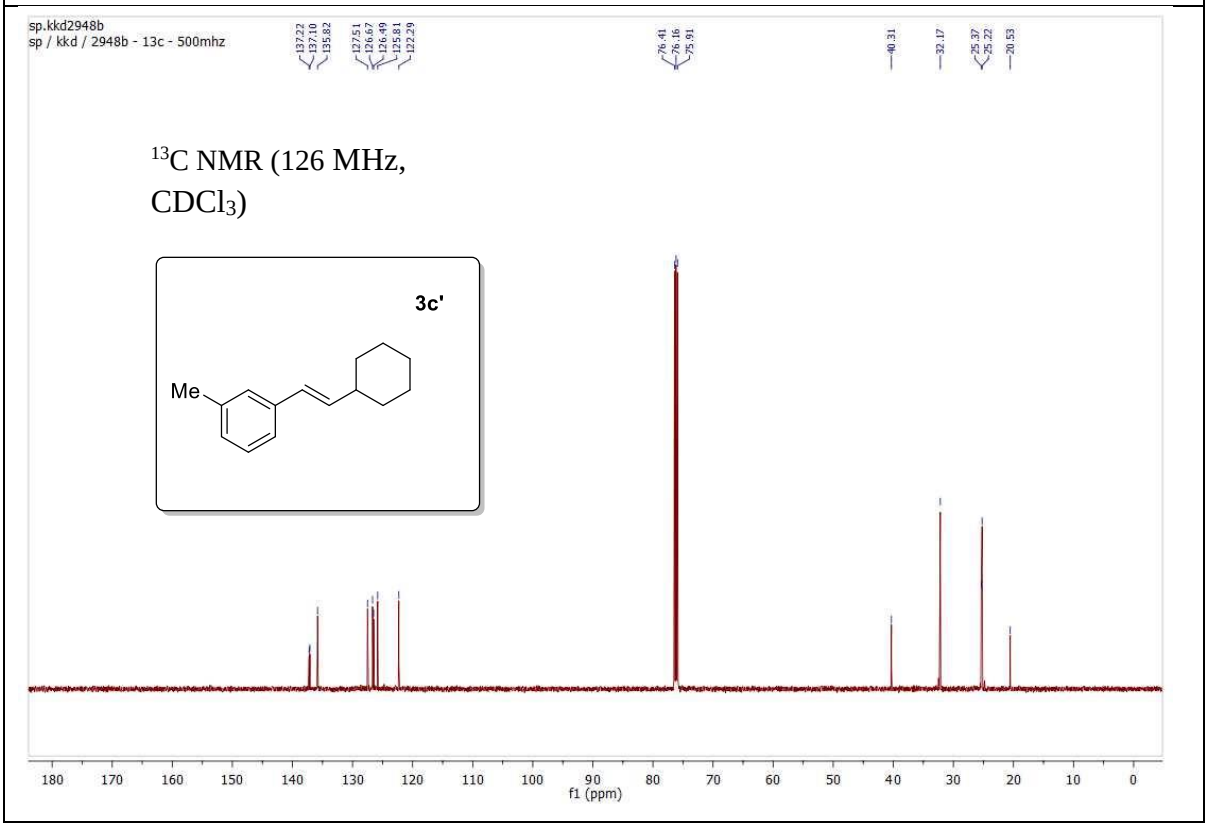

sp.kkd2023
sp / kkd / 2023 - 13c - 500mhz
138.30
137.00
128.59
127.47
126.87
126.12
77.41
77.16
76.91
41.30
33.16
26.37
26.22
13C NMR (126 MHz, CDCl3)
3a'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


sp.kkd2941
sp / kkd / 2941 - 1h - 500mhz
^{1}H NMR (500 MHz, $CDCl_3$)
3b'
Me
f1 (ppm)

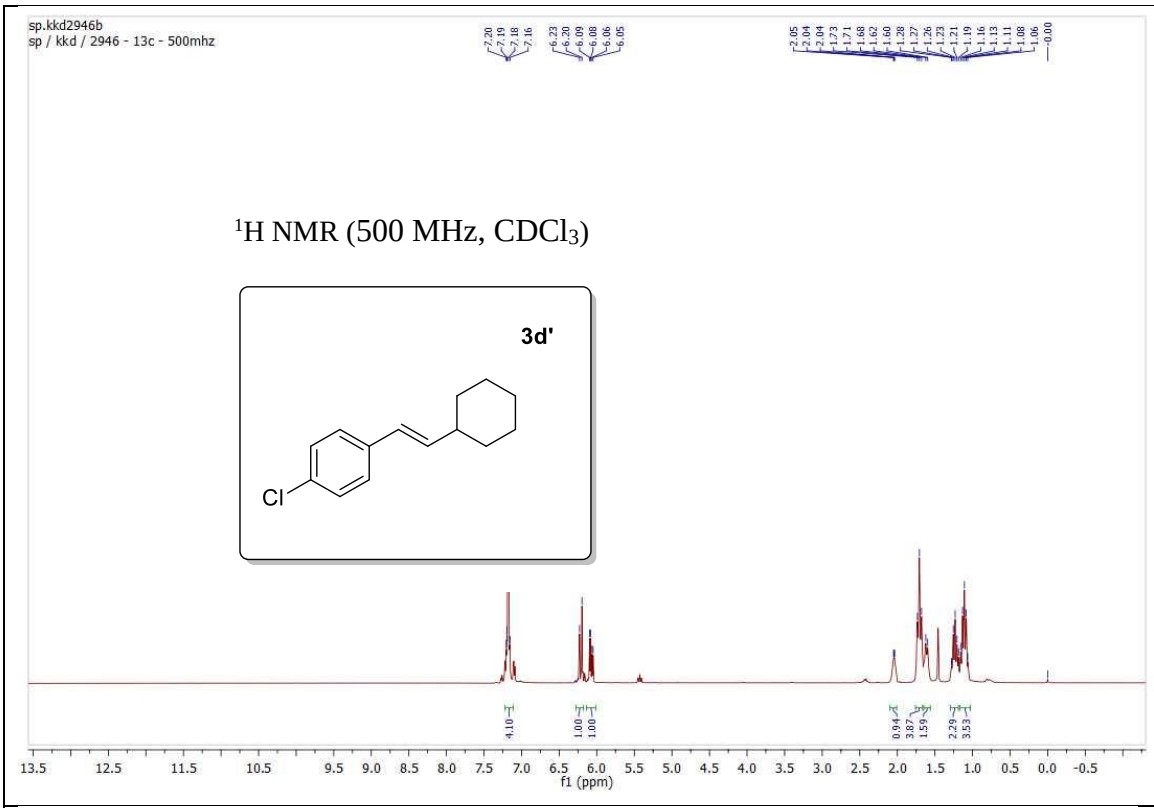

sp.kkd2941b
sp / kkd / 2941b - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3b'
Me
f1 (ppm)

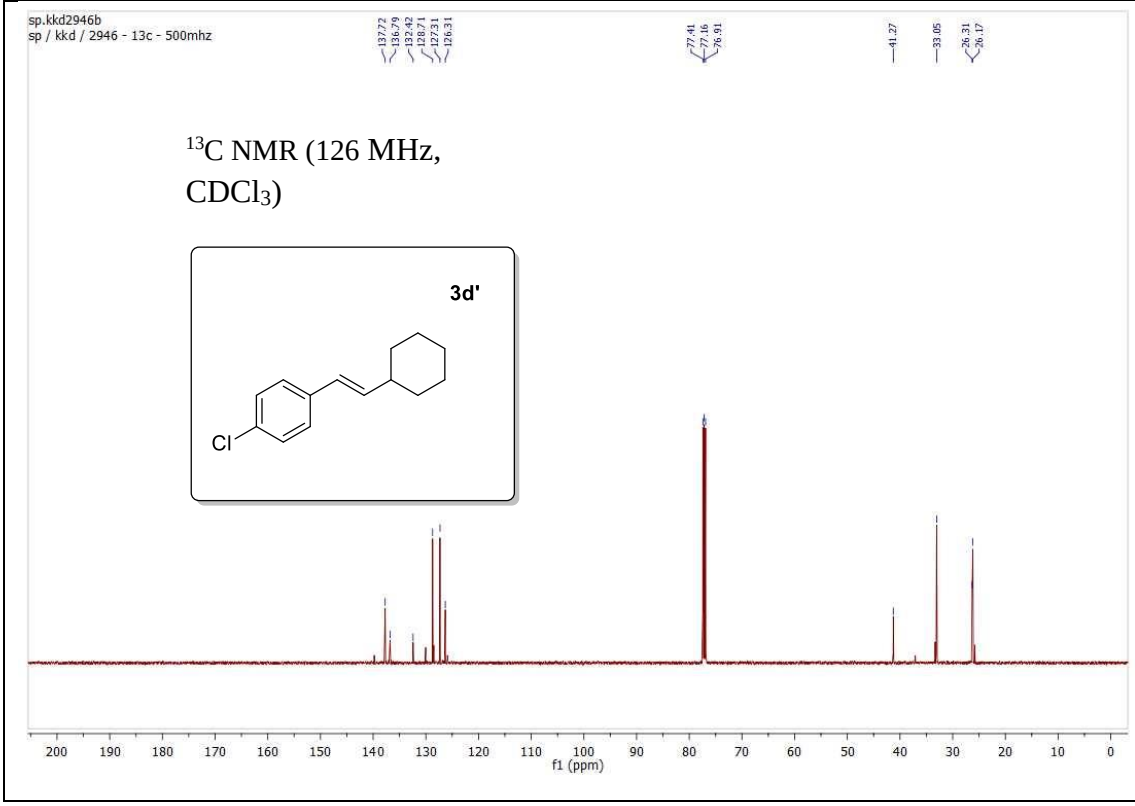


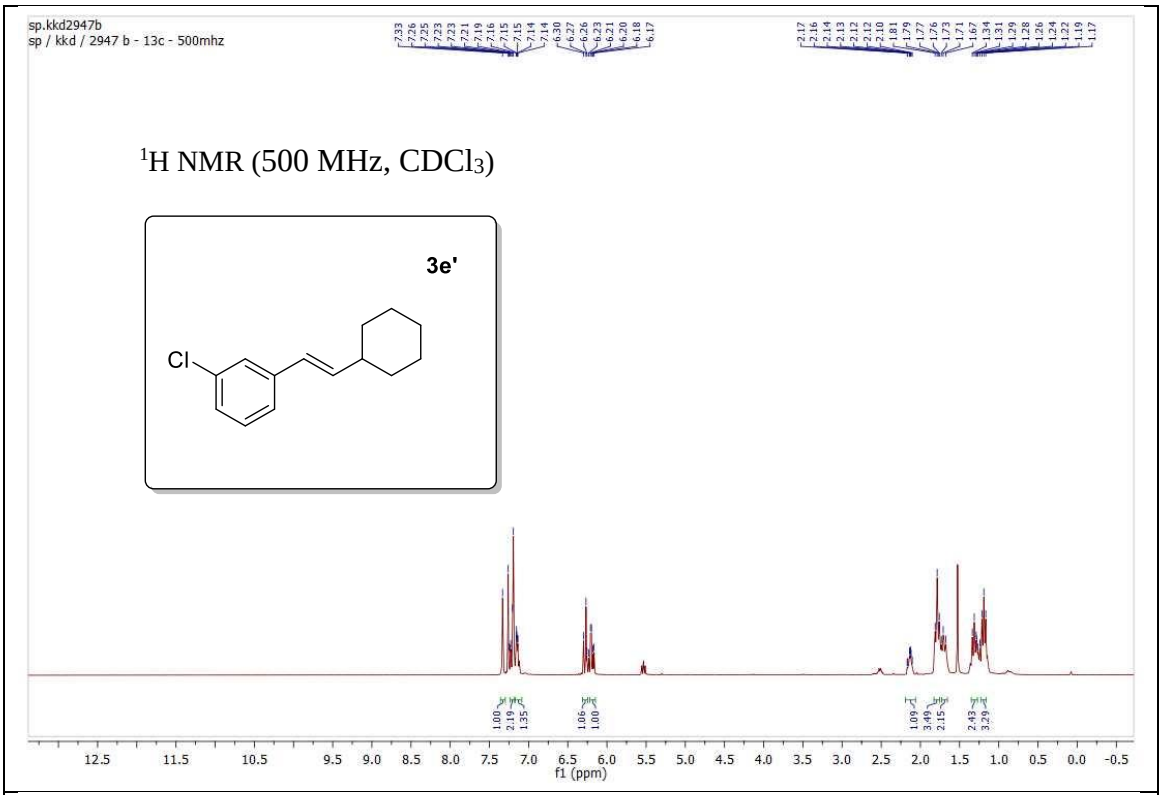
^{1}H NMR (500 MHz, $CDCl_3$)

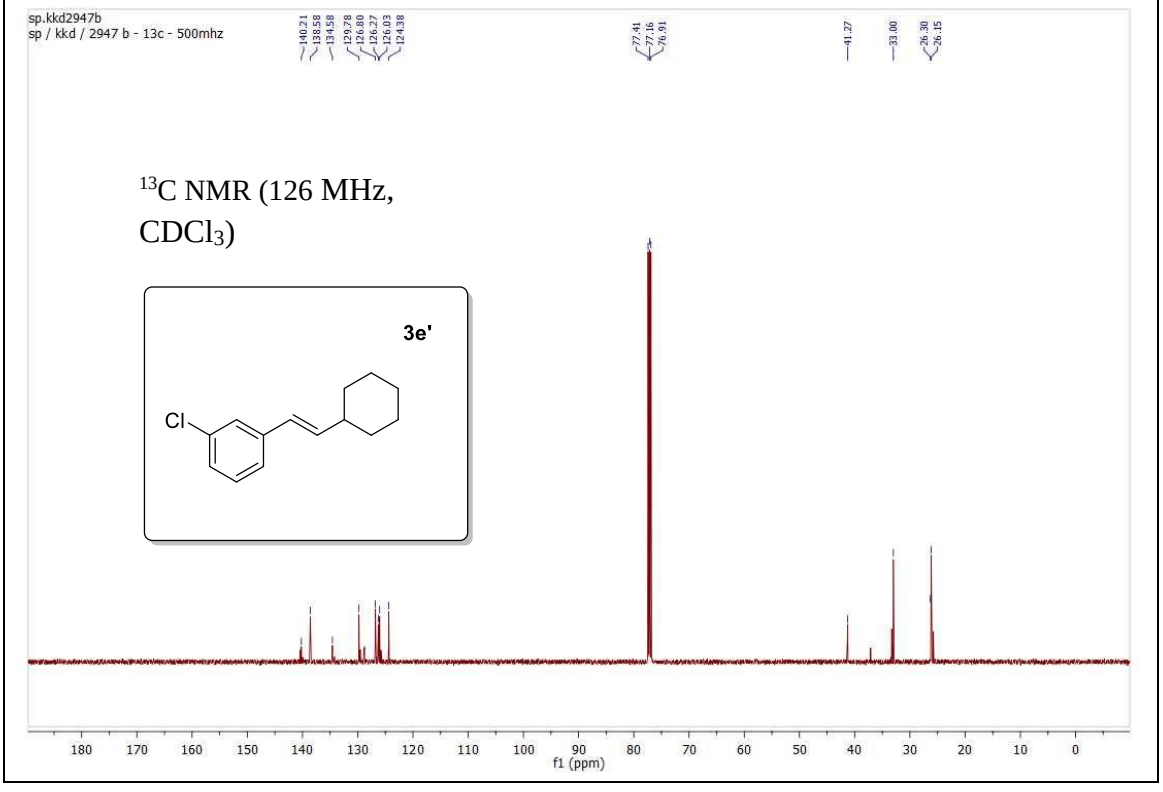


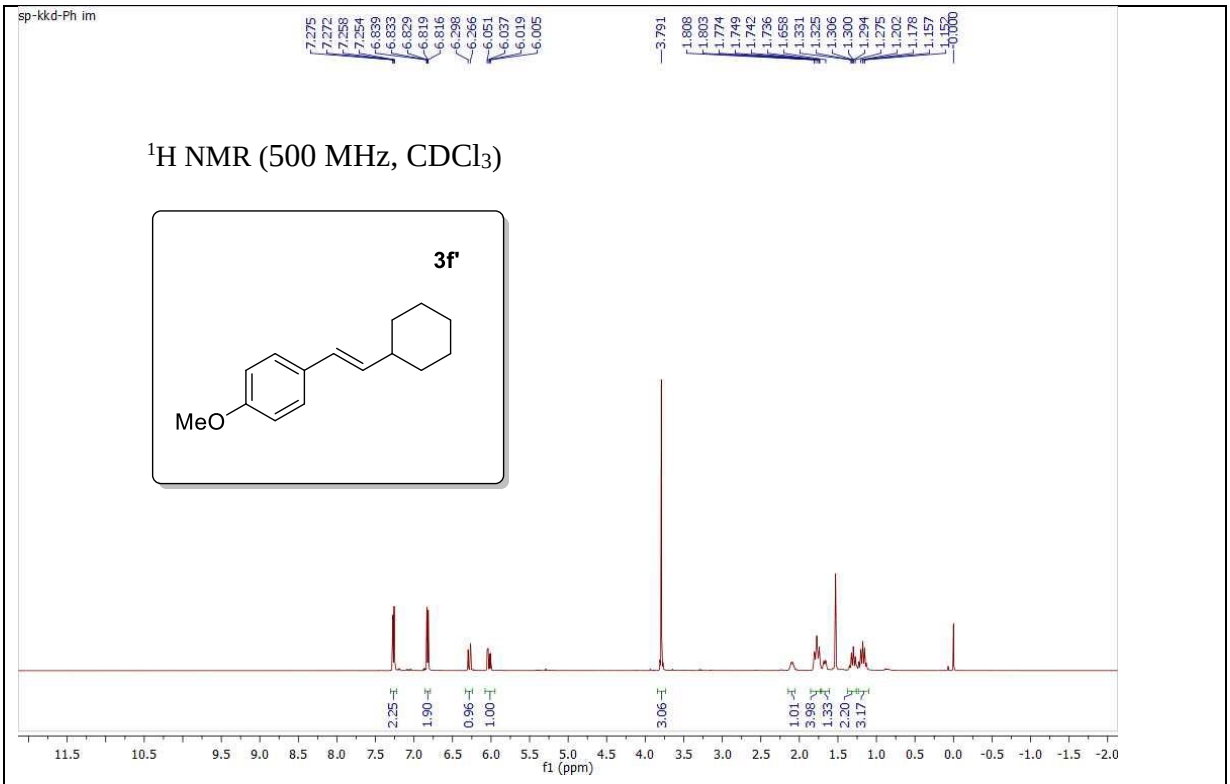
^{13}C NMR (126 MHz, $CDCl_3$)


sp.kkd2946b
sp / kkd / 2946 - 13c - 500mhz
^{1}H NMR (500 MHz, $CDCl_3$)
3d'
Cl
f1 (ppm)

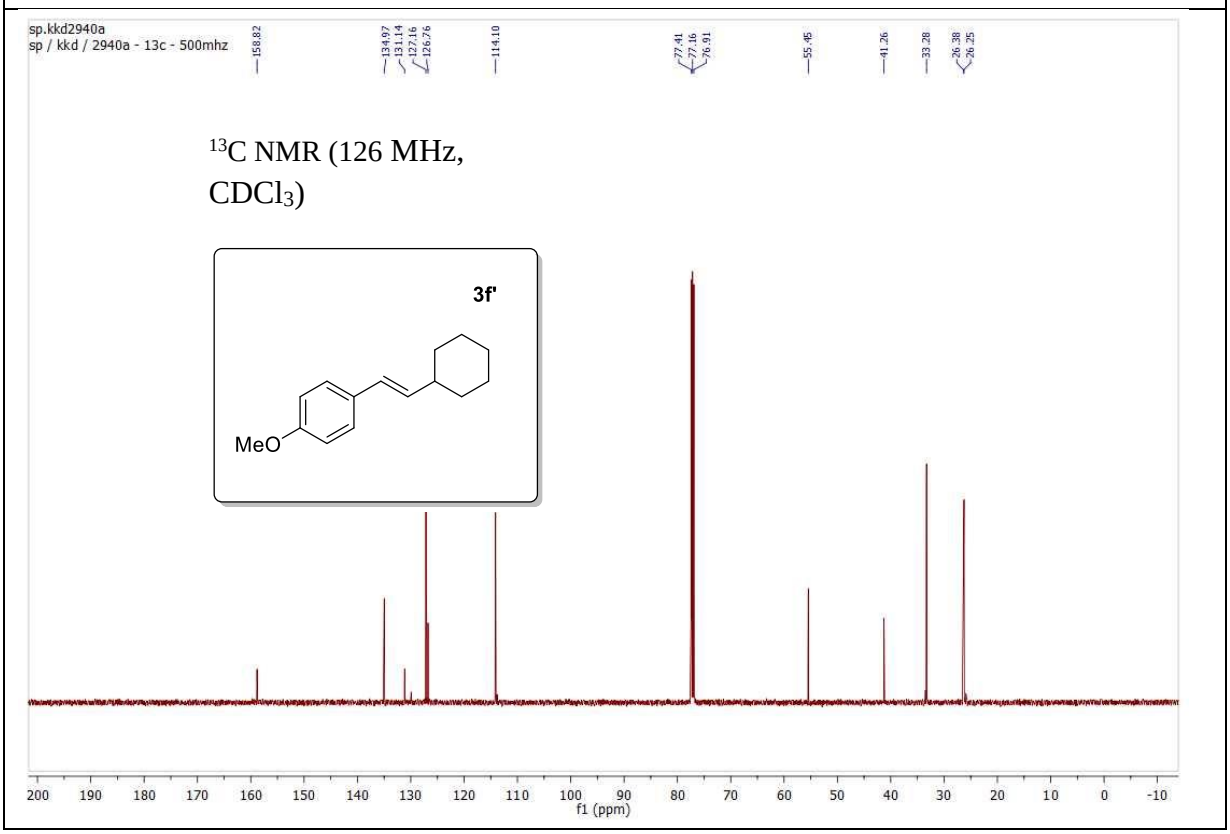

sp.kkd2946b
sp / kkd / 2946 - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3d'
Cl
f1 (ppm)


sp.kkd2947b
sp / kkd / 2947 b - 13c - 500mhz
^{1}H NMR (500 MHz, $CDCl_3$)
3e'
Cl
f1 (ppm)

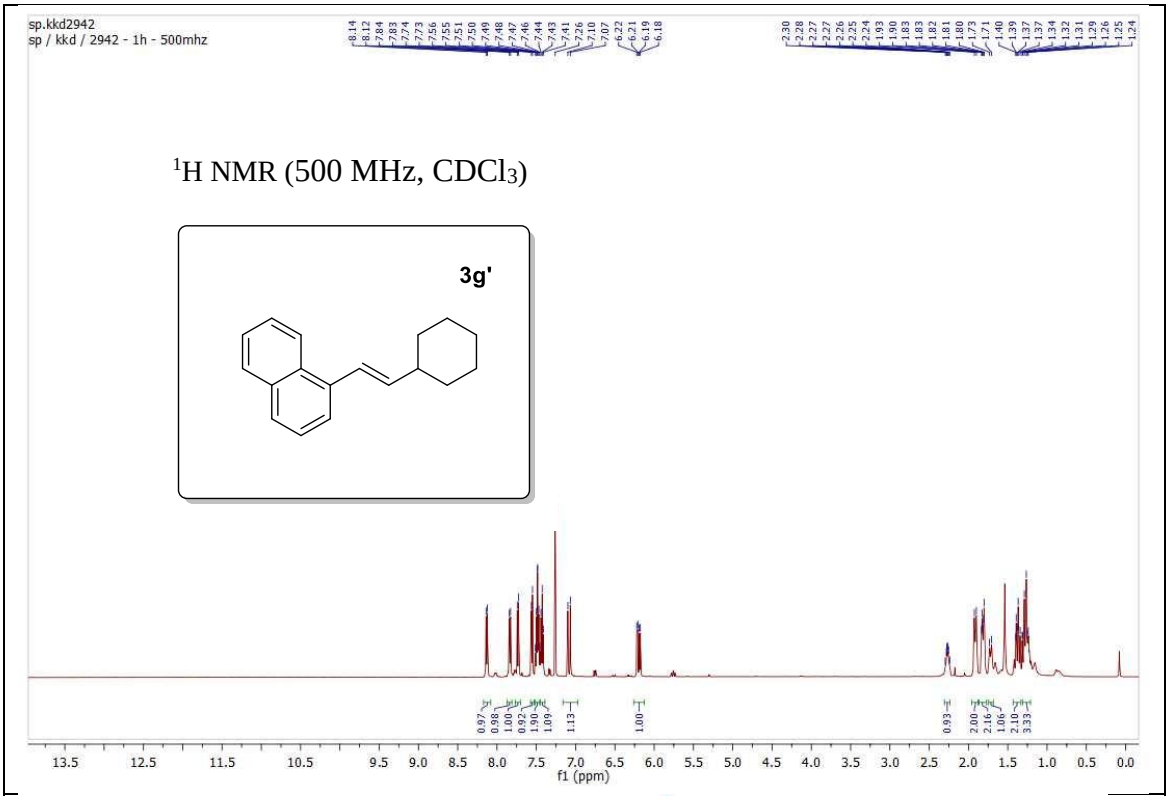

sp.kkd2947b
sp / kkd / 2947 b - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3e'
Cl
f1 (ppm)

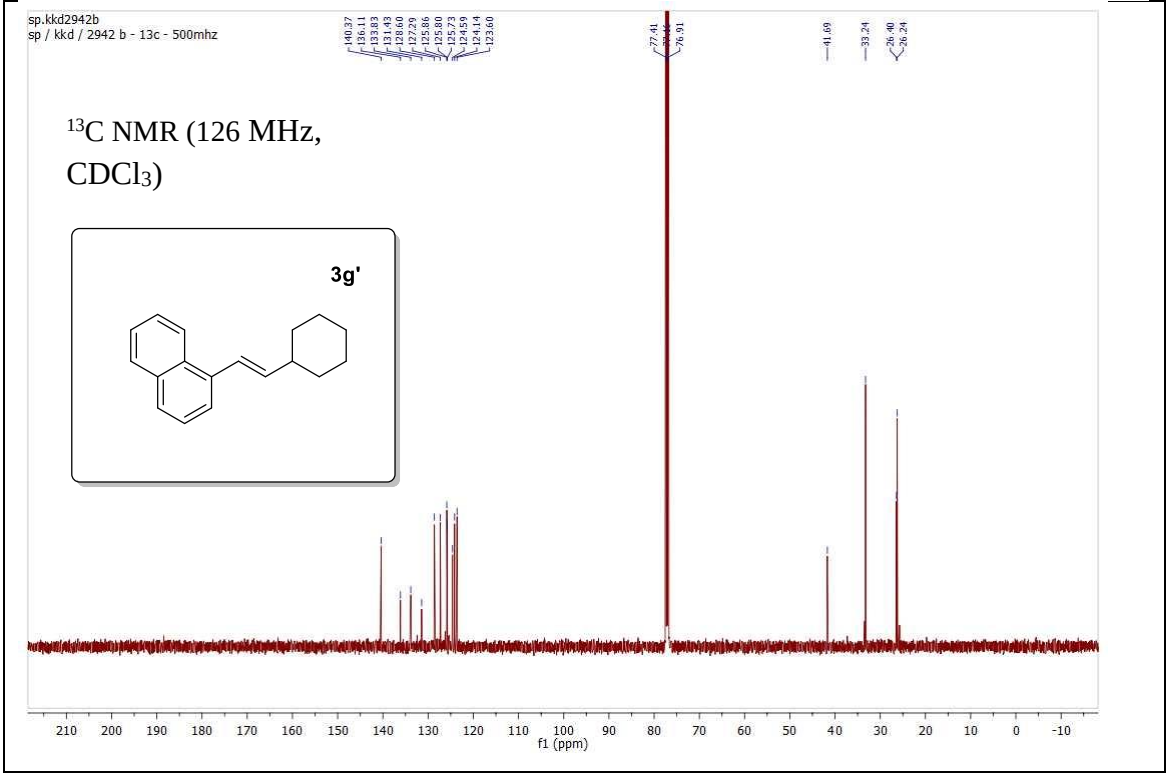


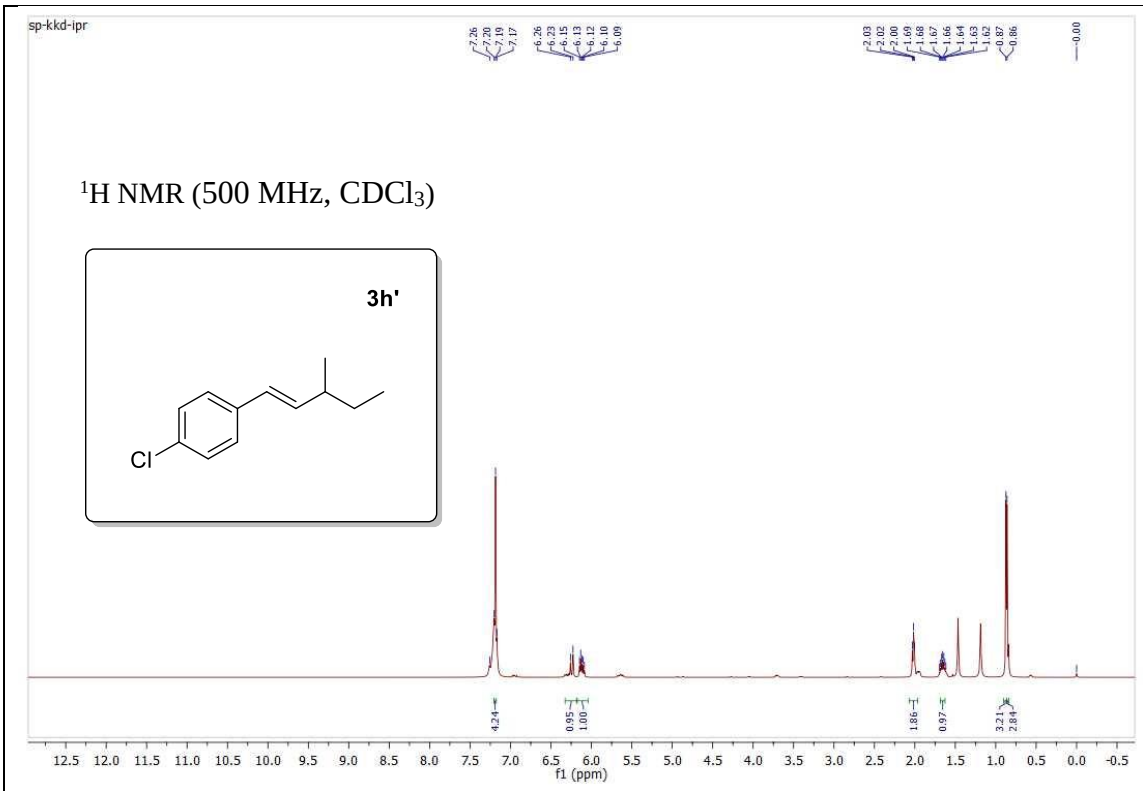
^{1}H NMR (500 MHz, $CDCl_3$)

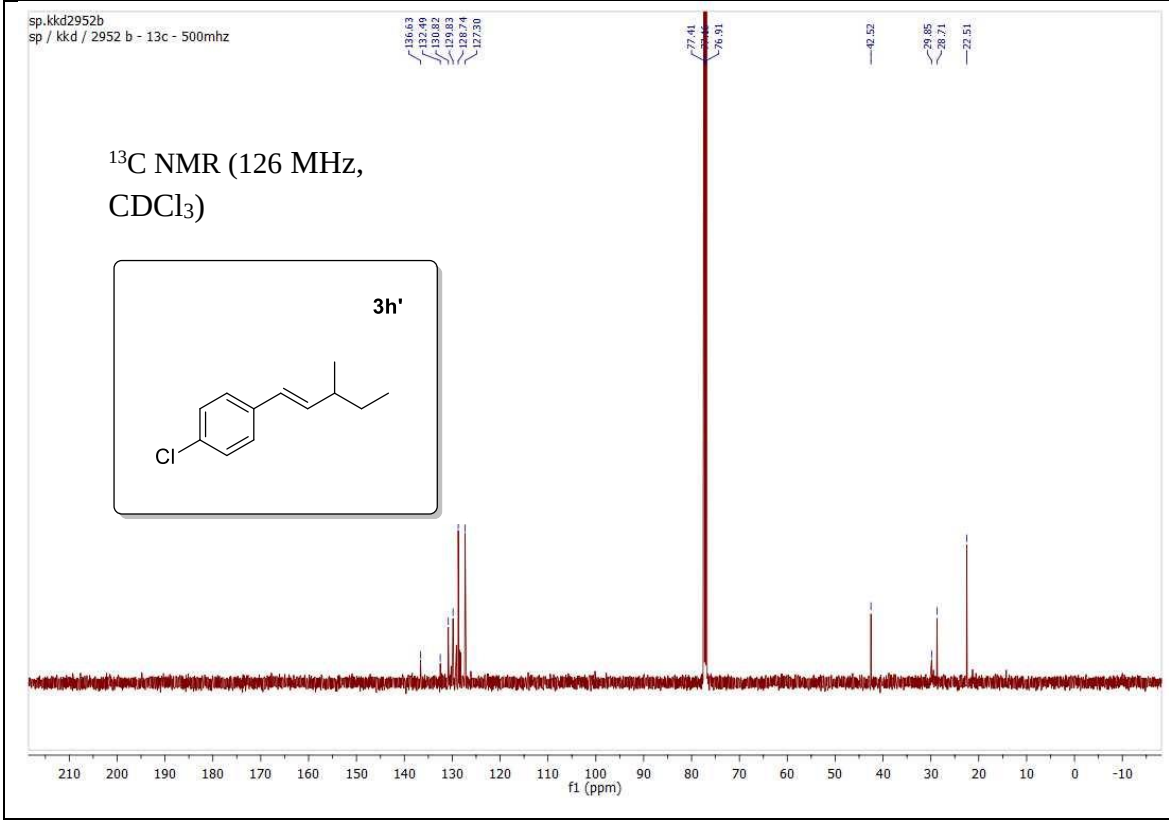


^{13}C NMR (126 MHz, $CDCl_3$)


sp.kkd2942
sp / kkd / 2942 - 1h - 500mhz
^{1}H NMR (500 MHz, $CDCl_3$)
3g'
f1 (ppm)

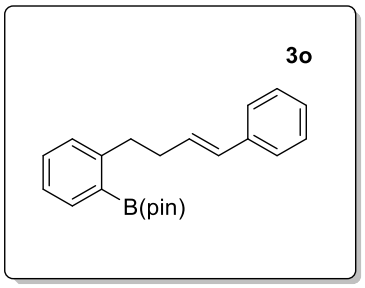

sp.kkd2942b
sp / kkd / 2942 b - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3g'
f1 (ppm)


sp-kkd-ipr
^{1}H NMR (500 MHz, $CDCl_3$)
3h'
Cl
f1 (ppm)


sp.kkd2952b
sp / kkd / 2952 b - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
3h'
Cl
f1 (ppm)

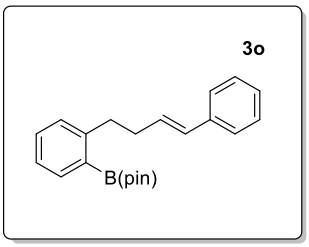
sp.kkd2958a
sp.kkd2958a-1h-500mhz

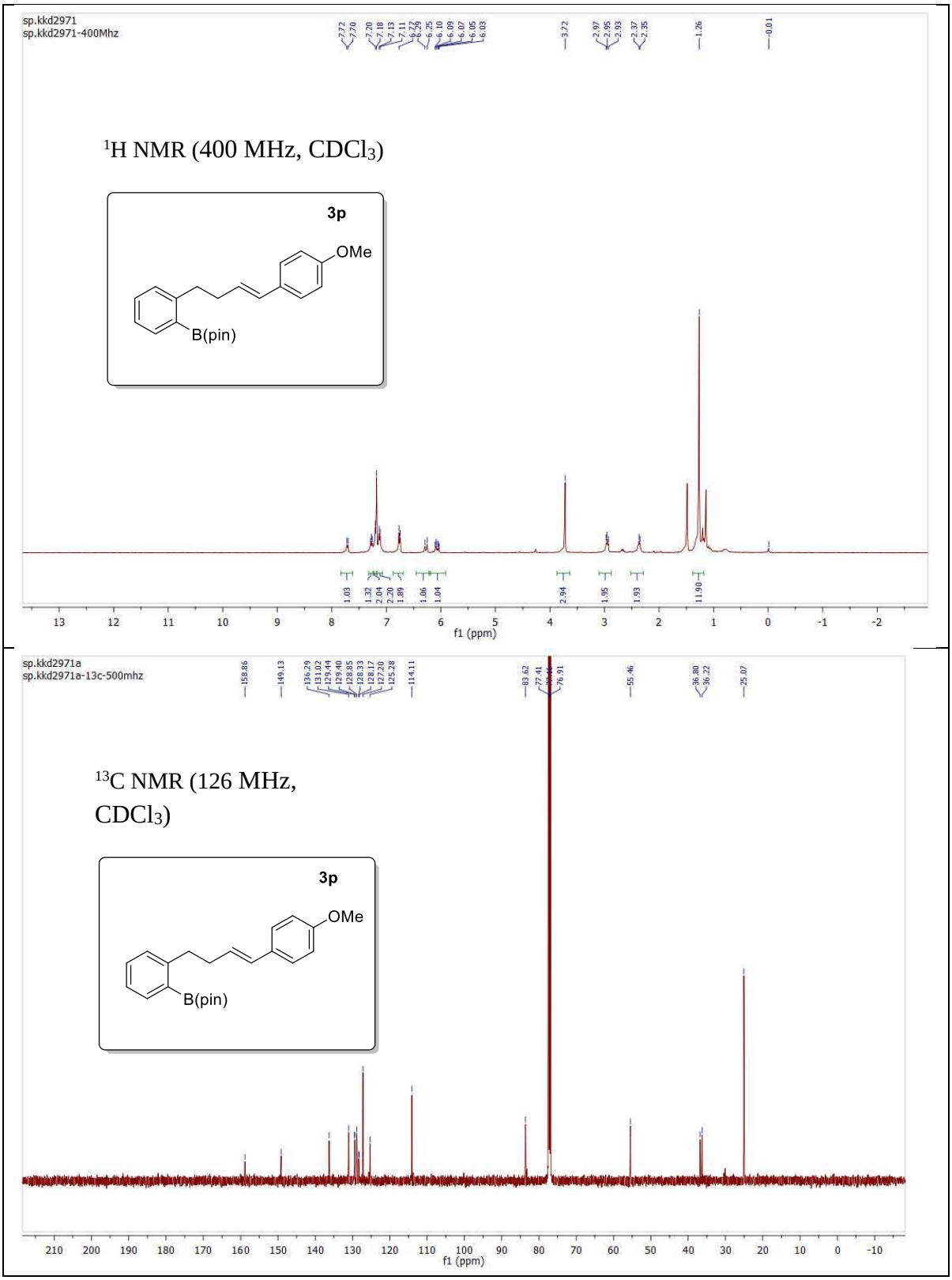
^{1}H NMR (500 MHz, $CDCl_3$)



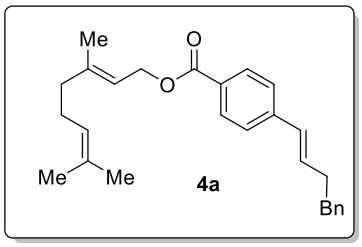
sp.kkd2958ba
sp.kkd2958ba-13c-500mhz

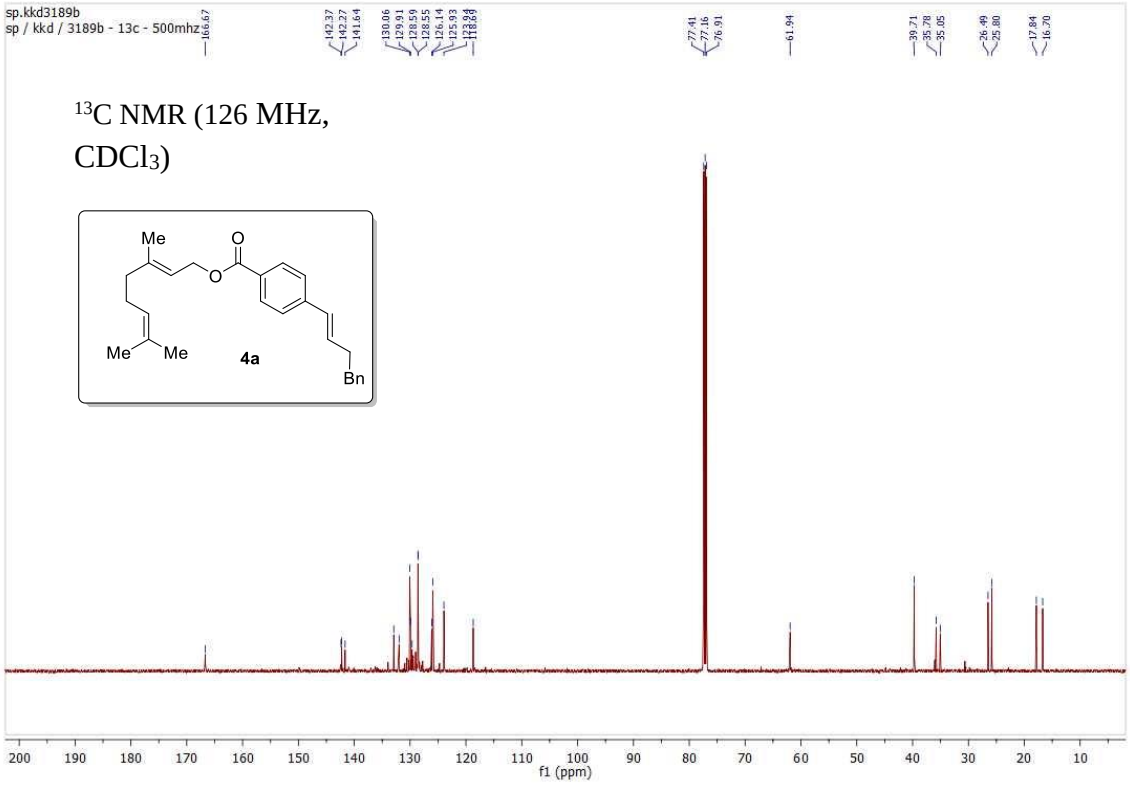
^{13}C NMR (126 MHz, $CDCl_3$)



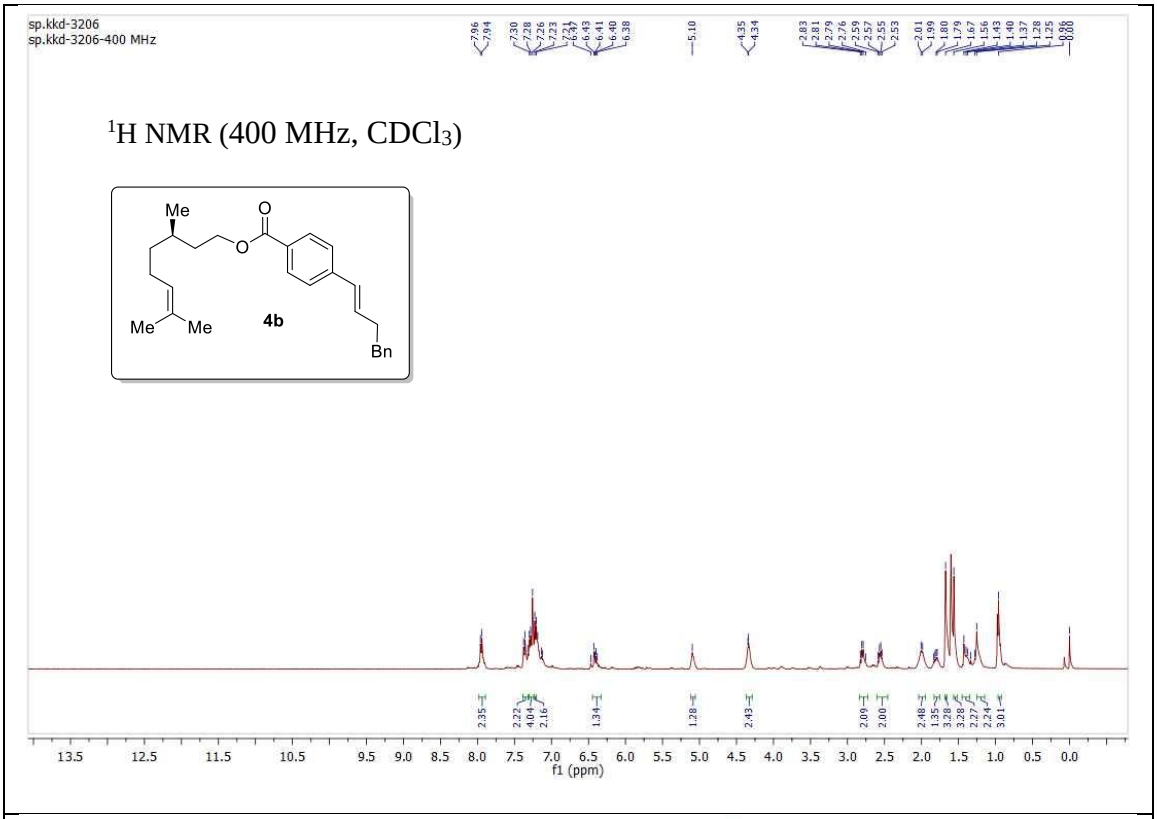

sp.kkd2971
sp.kkd2971-400Mhz
7.72
7.70
7.20
7.18
7.13
7.11
6.77
6.29
6.25
6.10
6.09
6.07
6.05
6.03
3.72
2.97
2.95
2.93
2.37
2.35
1.26
0.01
1H NMR (400 MHz, CDCl3)
3p
OMe
B(pin)
1.03
1.32
2.04
2.20
1.89
1.06
1.04
2.94
1.95
1.93
11.90
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
sp.kkd2971a
sp.kkd2971a-13c-500mhz
158.86
149.13
136.29
131.02
129.44
129.40
128.85
128.33
128.17
127.20
125.28
114.11
83.62
77.41
77.16
76.91
55.46
36.80
36.22
25.07
13C NMR (126 MHz,
CDCl3)
3p
OMe
B(pin)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

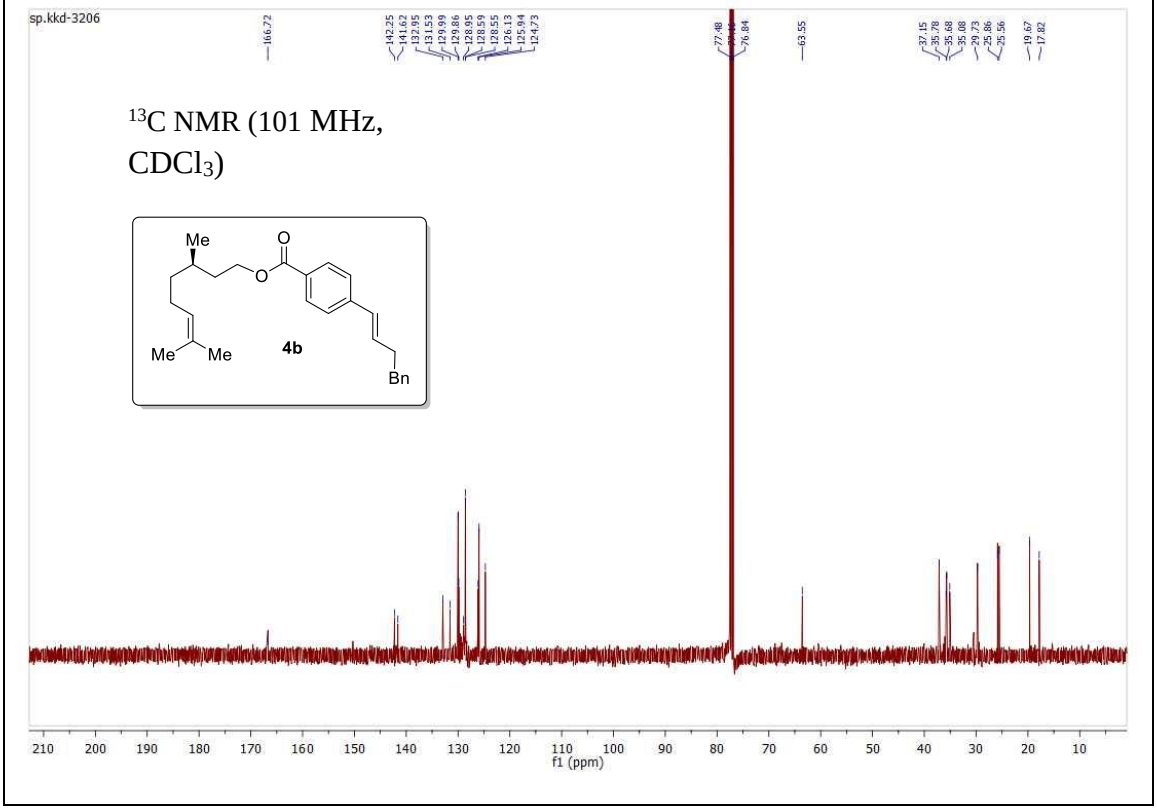
^{1}H NMR (400 MHz, $CDCl_3$)

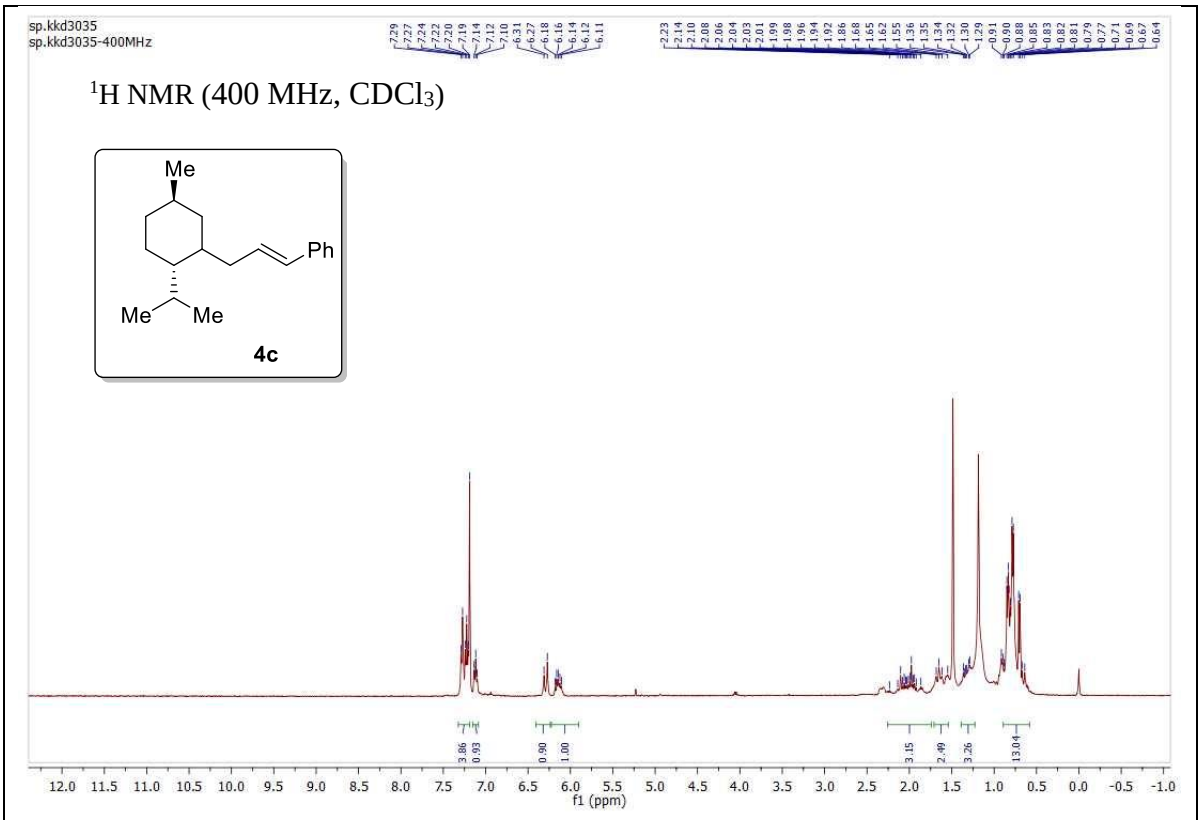




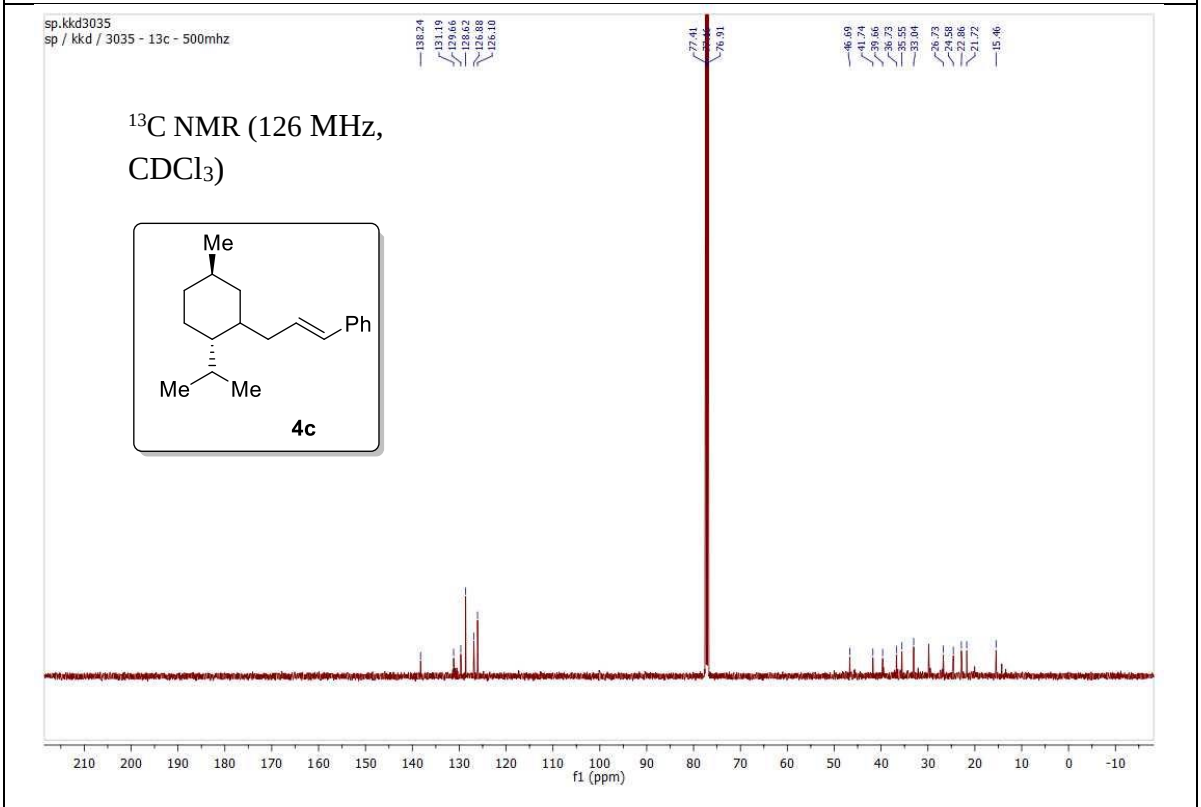
^{13}C NMR (126 MHz, $CDCl_3$)


sp.kkd-3206
sp.kkd-3206-400 MHz
1H NMR (400 MHz, CDCl3)
Me
O
O
Me
Me
4b
Bn
f1 (ppm)

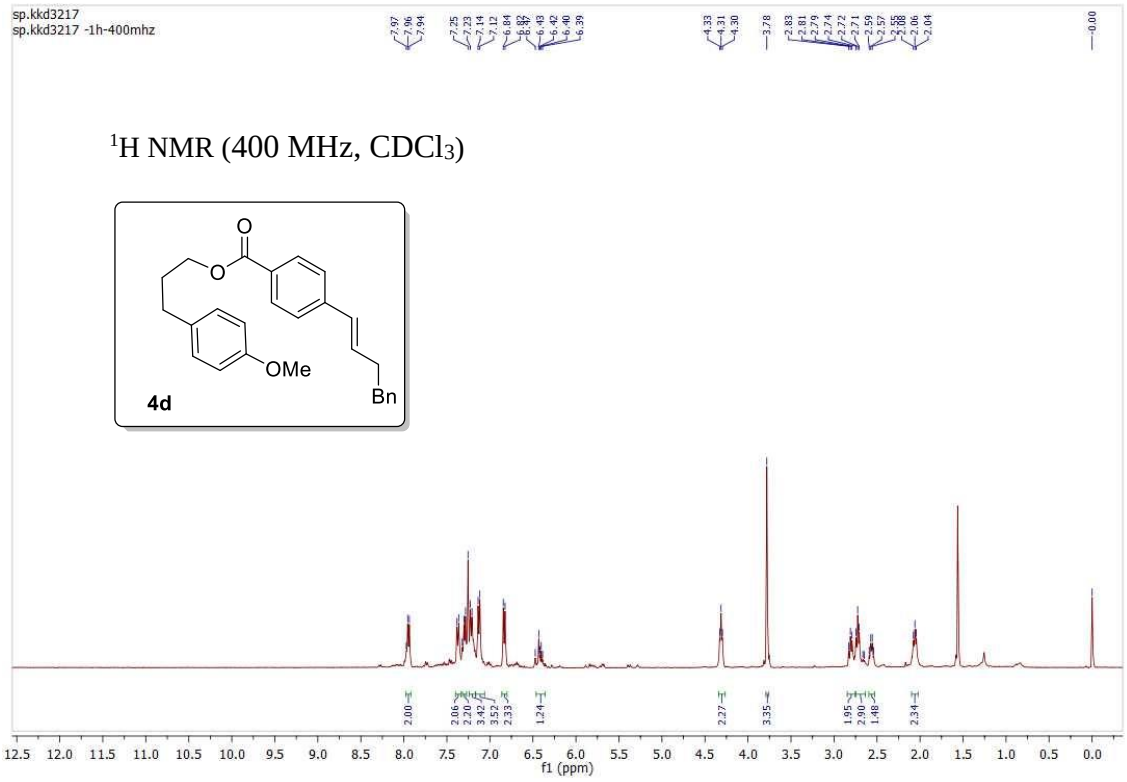

sp.kkd-3206
13C NMR (101 MHz, CDCl3)
Me
O
O
Me
Me
4b
Bn
f1 (ppm)

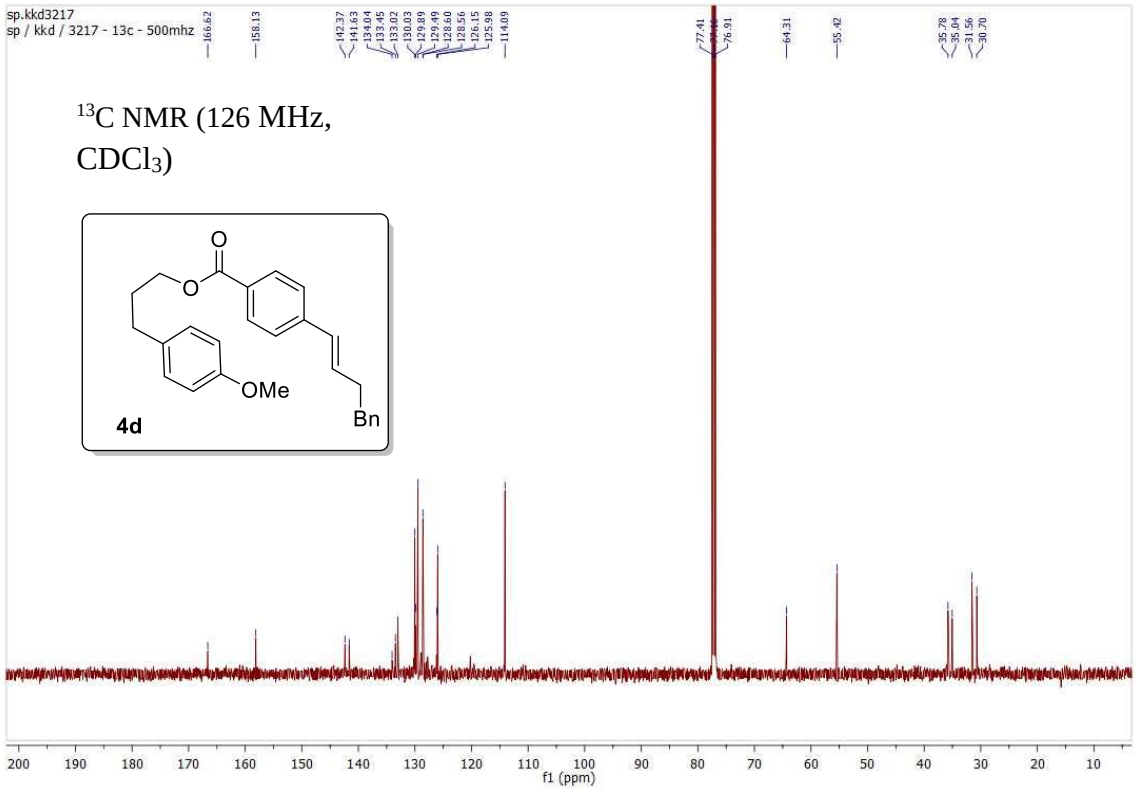


^{1}H NMR (400 MHz, $CDCl_3$)

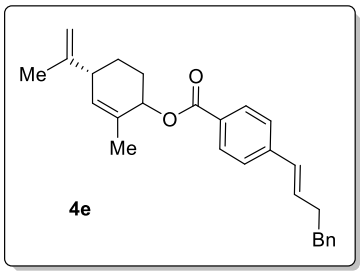


^{13}C NMR (126 MHz, $CDCl_3$)

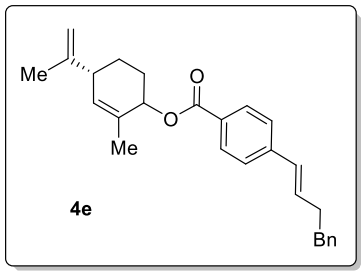

sp.kkd3217
sp.kkd3217 -1h-400mhz
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
OMe
Bn
4d
f1 (ppm)


sp.kkd3217
sp / kkd / 3217 - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
O
O
OMe
Bn
4d
f1 (ppm)

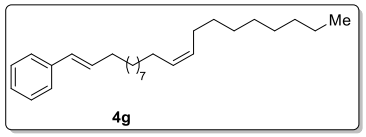
^{1}H NMR (400 MHz, $CDCl_3$)

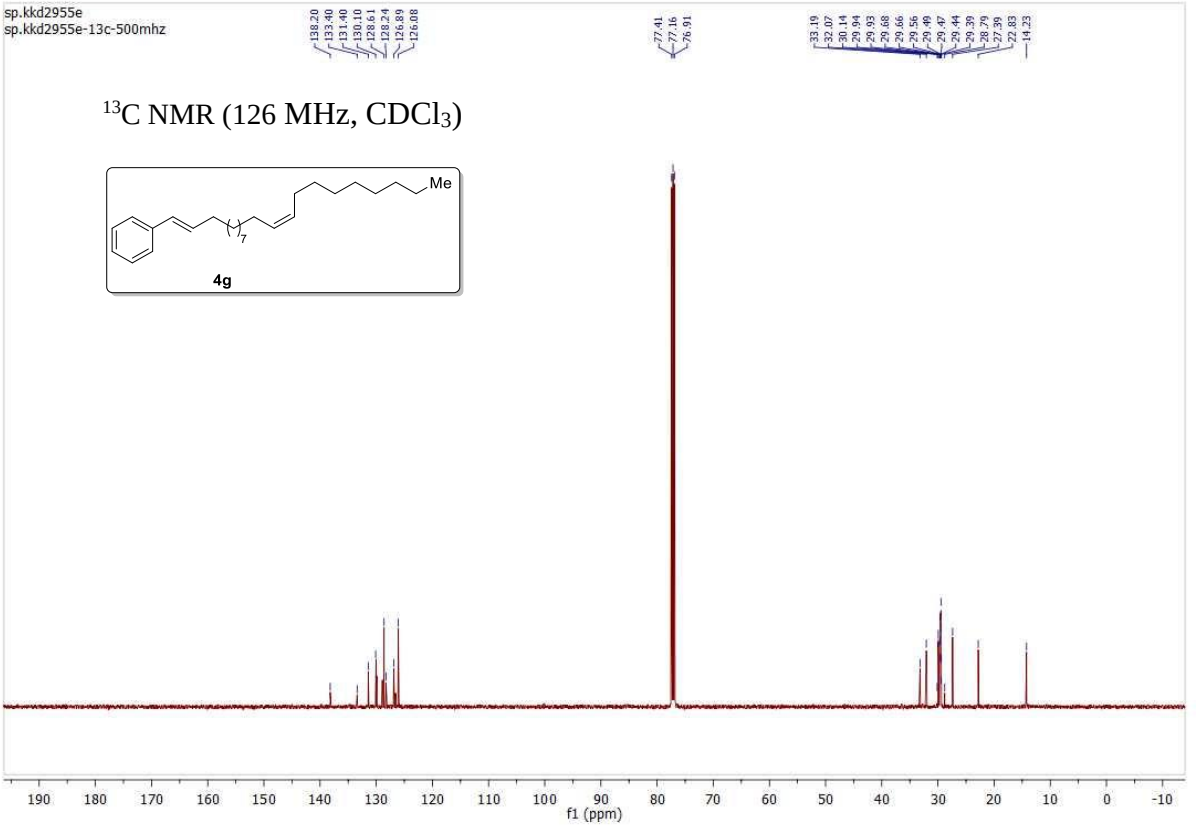


^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

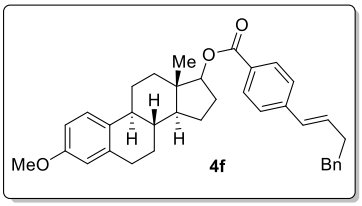


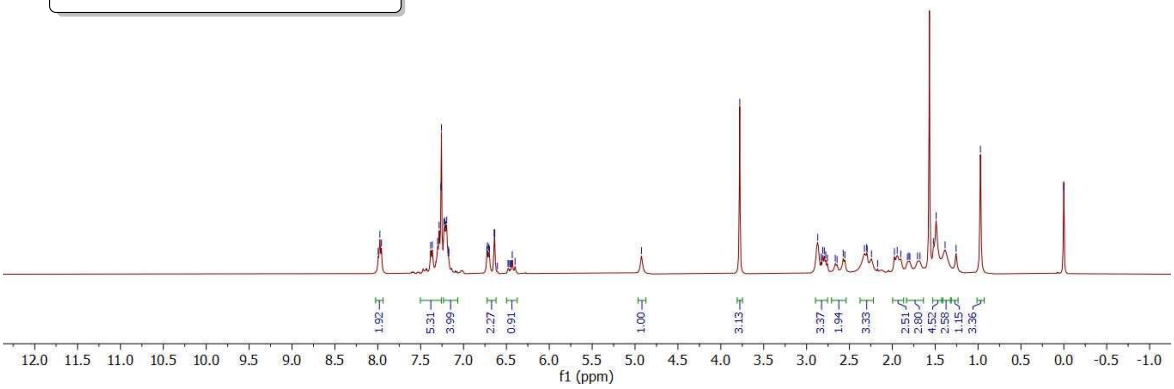


^{13}C NMR (126 MHz, $CDCl_3$)

kkd-estrone

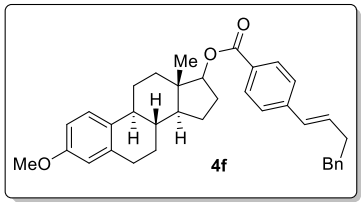
^{1}H NMR (400 MHz, $CDCl_3$)

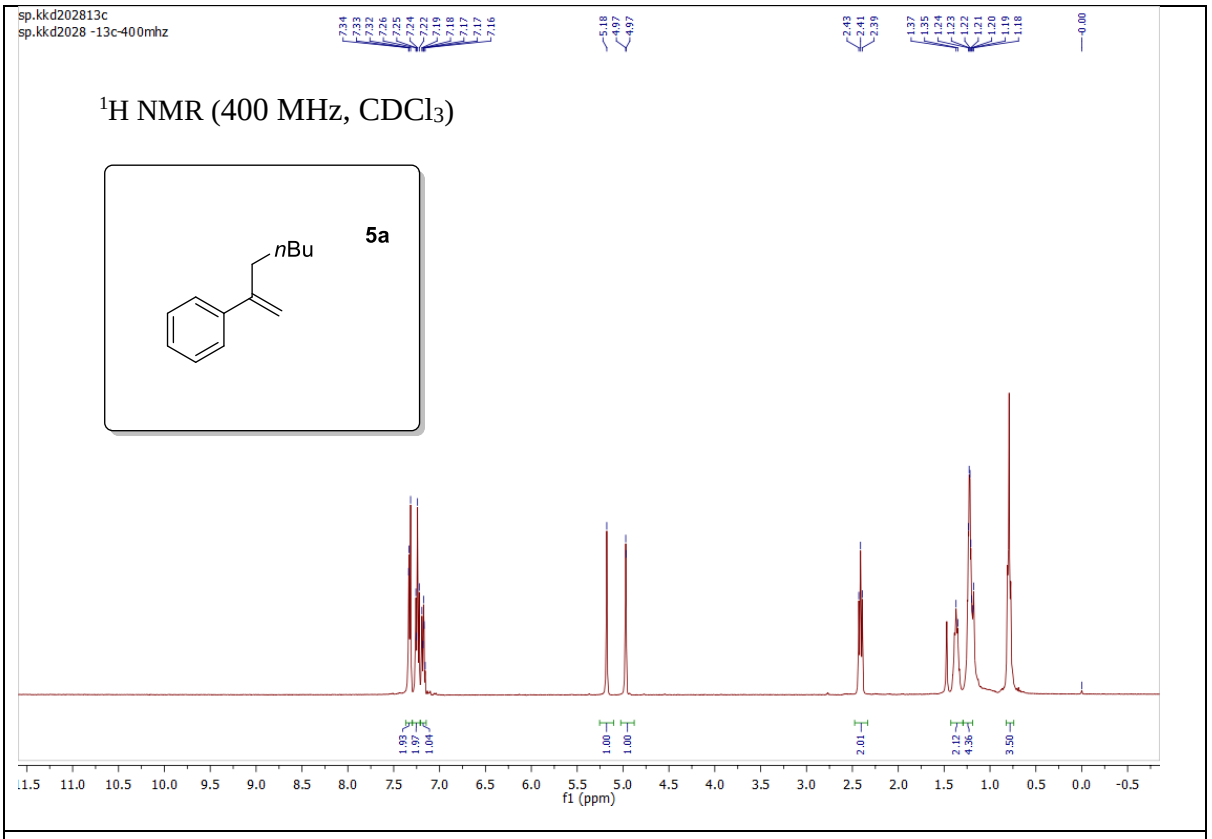


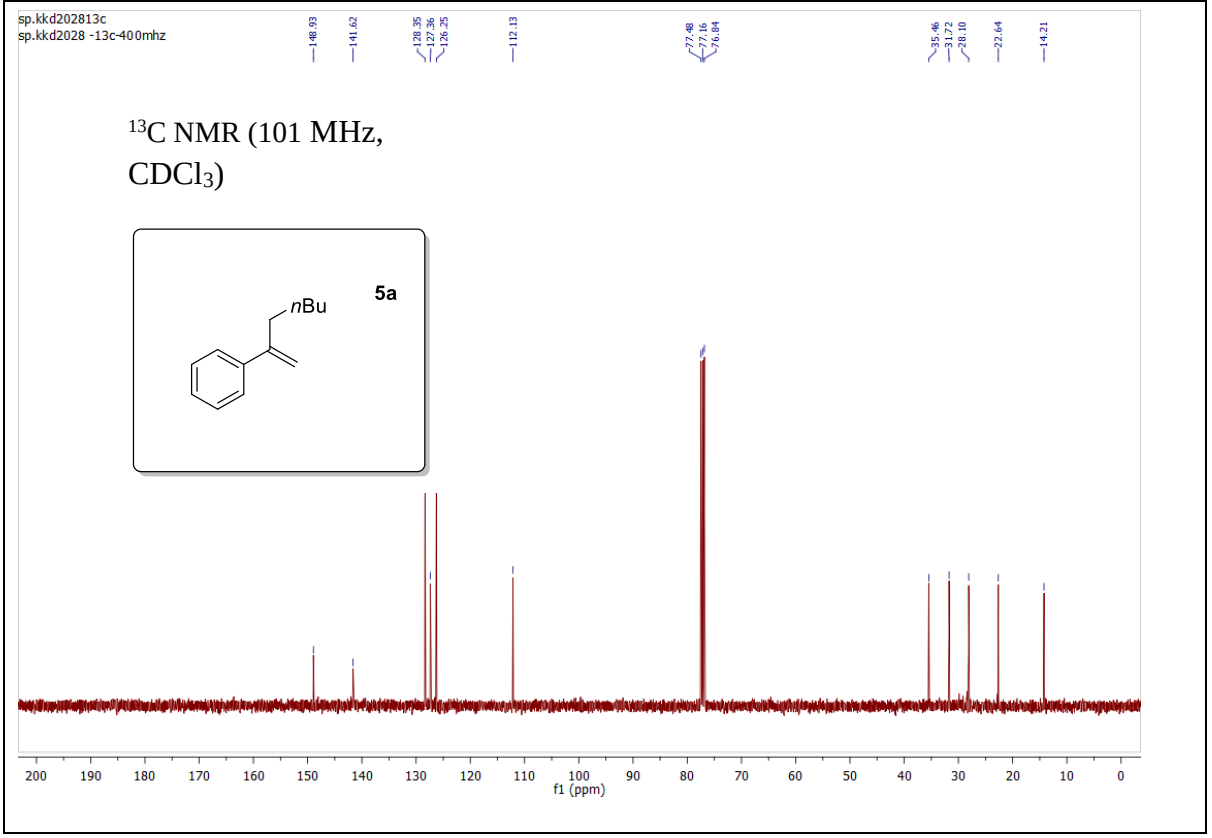


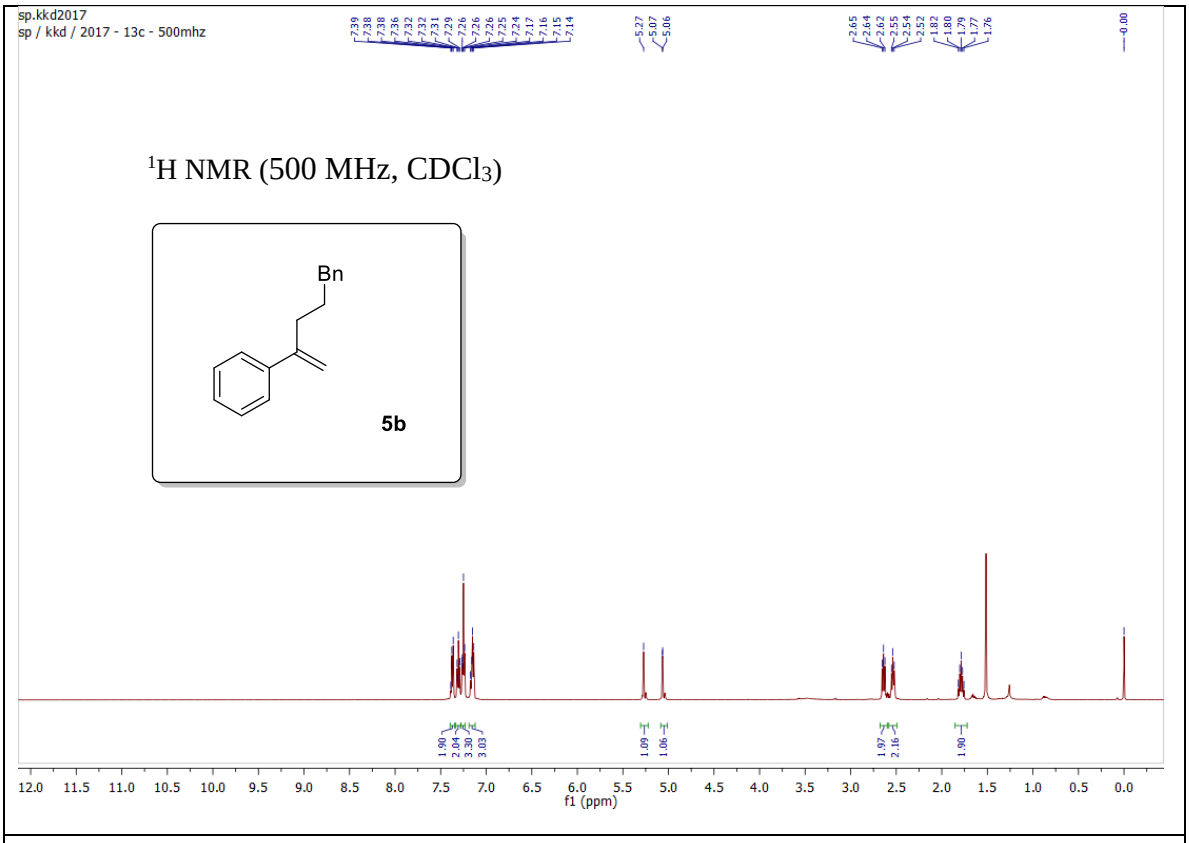
sp-kkd-Ph im

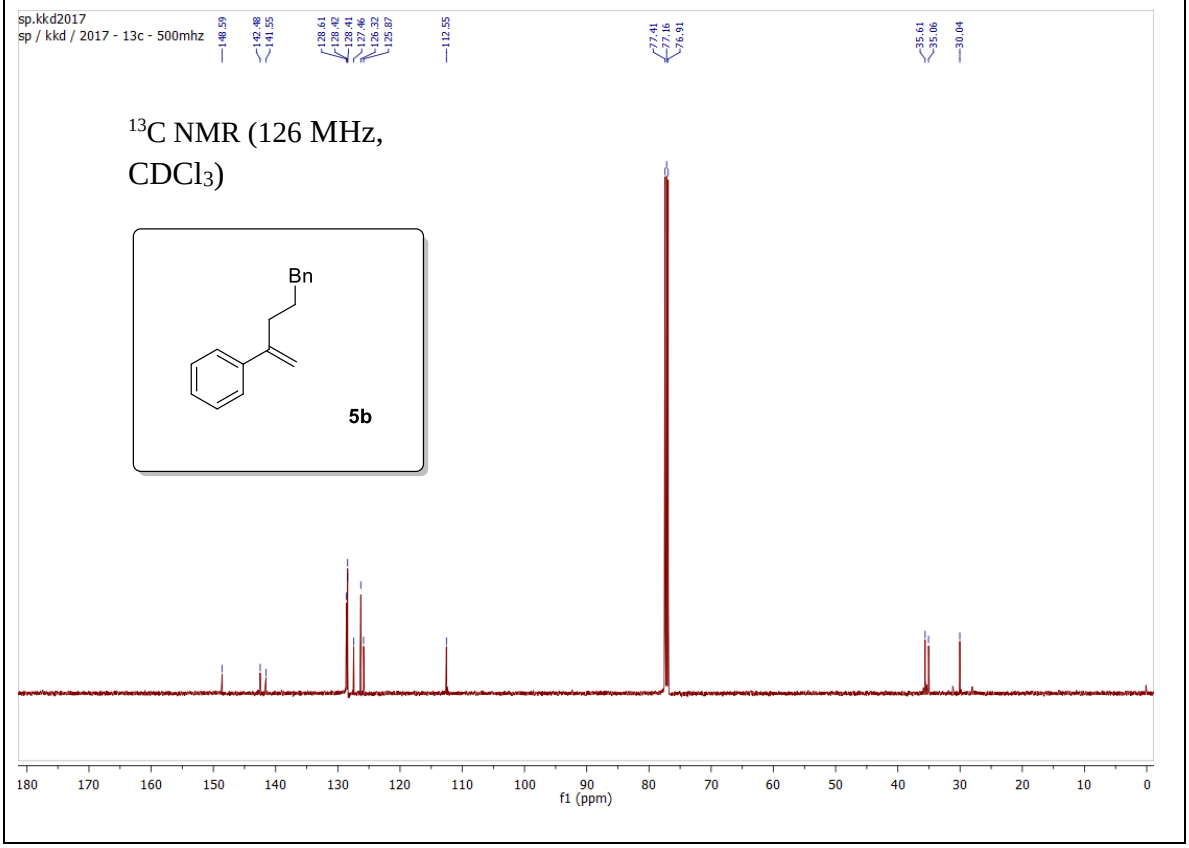
^{13}C NMR (126 MHz, $CDCl_3$)

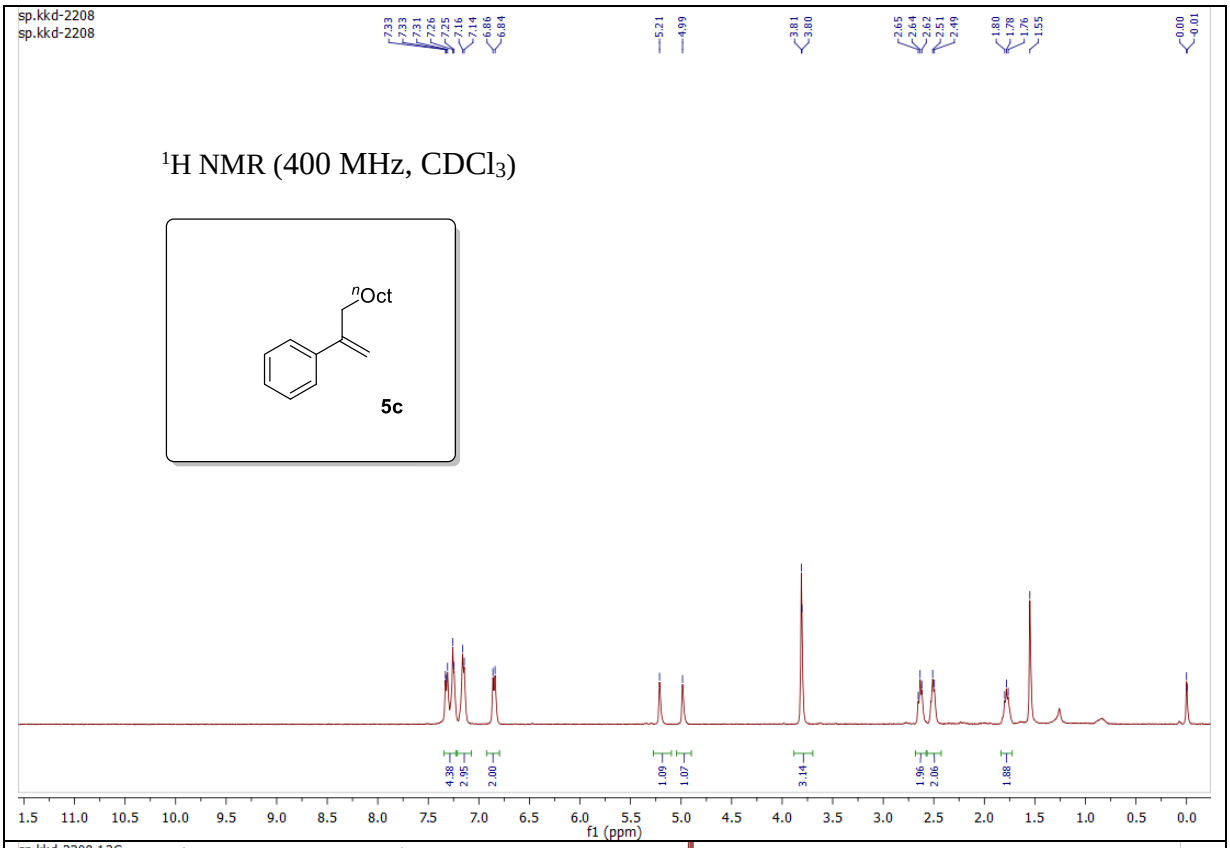


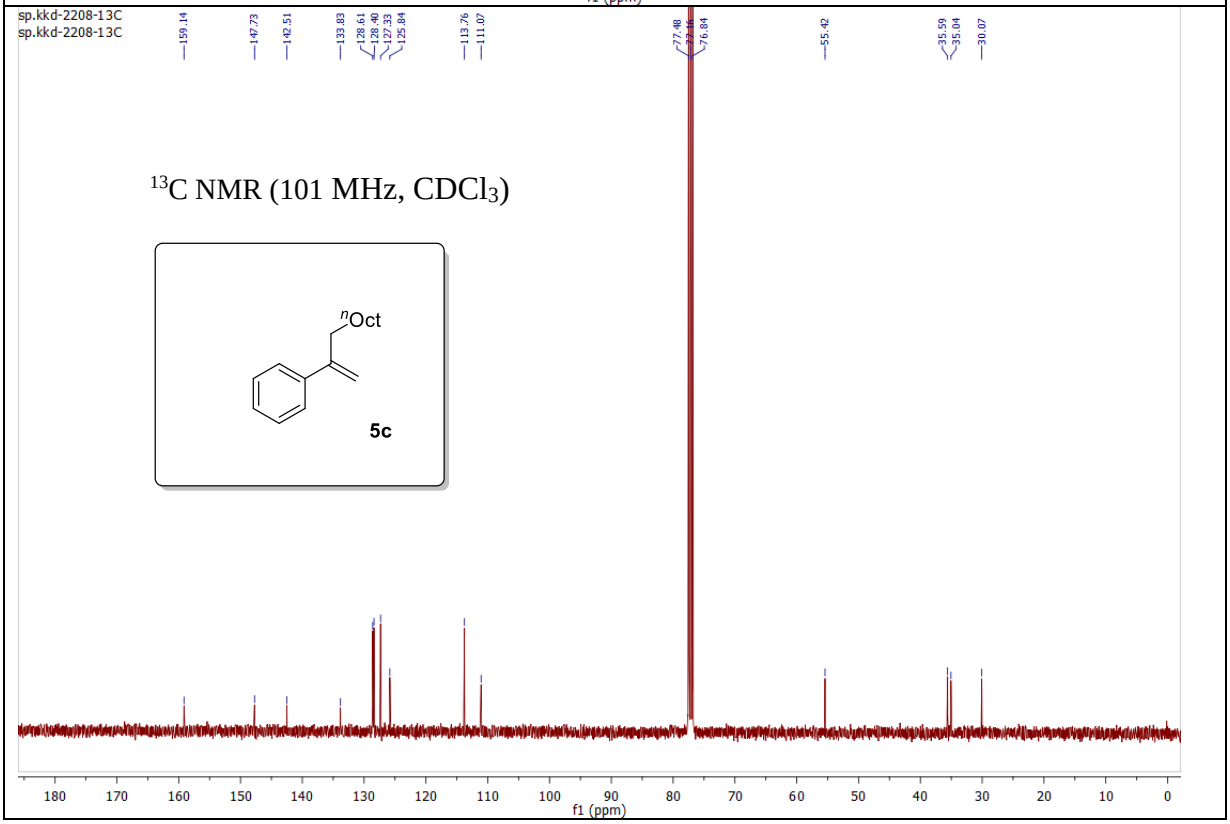

sp.kkd202813c
sp.kkd2028 -13c-400mhz
7.34
7.33
7.32
7.26
7.25
7.24
7.22
7.19
7.18
7.17
7.17
7.16
5.18
4.97
4.97
2.43
2.41
2.39
1.37
1.35
1.24
1.23
1.22
1.21
1.20
1.19
1.18
0.00
1H NMR (400 MHz, CDCl3)
5a
nBu
1.93
1.97
1.04
1.00
1.00
2.01
2.12
4.36
3.50
f1 (ppm)

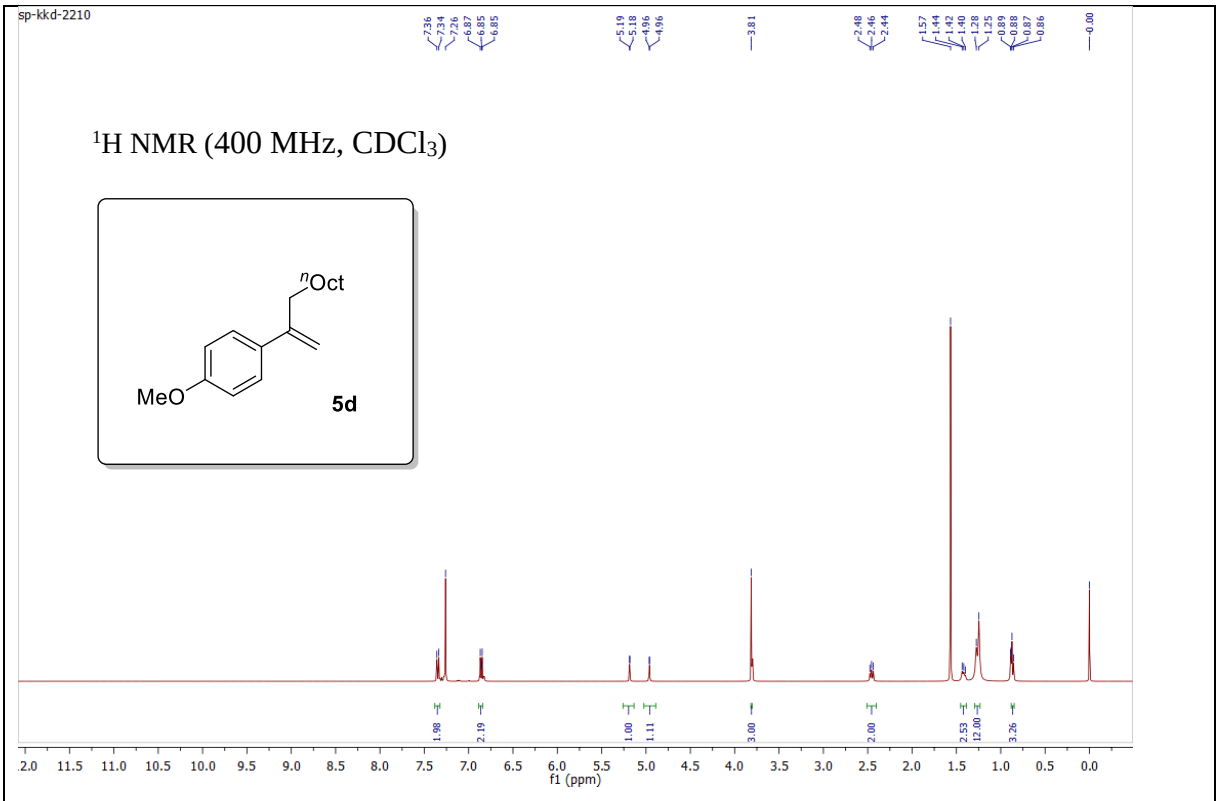

sp.kkd202813c
sp.kkd2028 -13c-400mhz
148.93
141.62
128.35
127.36
126.25
112.13
77.48
77.16
76.84
35.46
31.72
28.10
22.64
14.21
13C NMR (101 MHz, CDCl3)
5a
nBu
f1 (ppm)

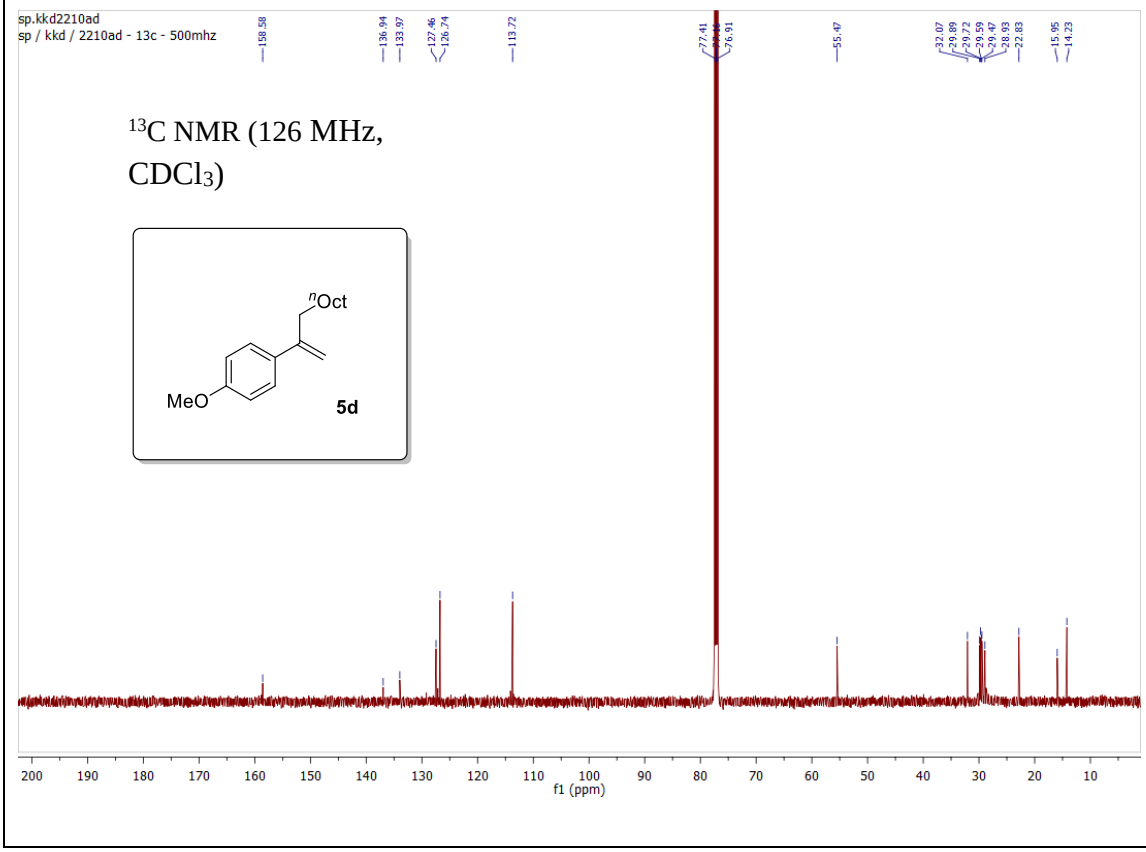

sp.kkd2017
sp / kkd / 2017 - 13c - 500mhz
7.39
7.38
7.38
7.36
7.32
7.31
7.29
7.26
7.26
7.26
7.25
7.24
7.17
7.16
7.15
7.14
5.27
5.07
5.06
2.65
2.64
2.62
2.55
2.54
2.52
1.82
1.80
1.79
1.77
1.76
0.00
1H NMR (500 MHz, CDCl3)
Bn
5b
1.90
2.04
3.30
3.03
1.09
1.06
1.97
2.16
1.90
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

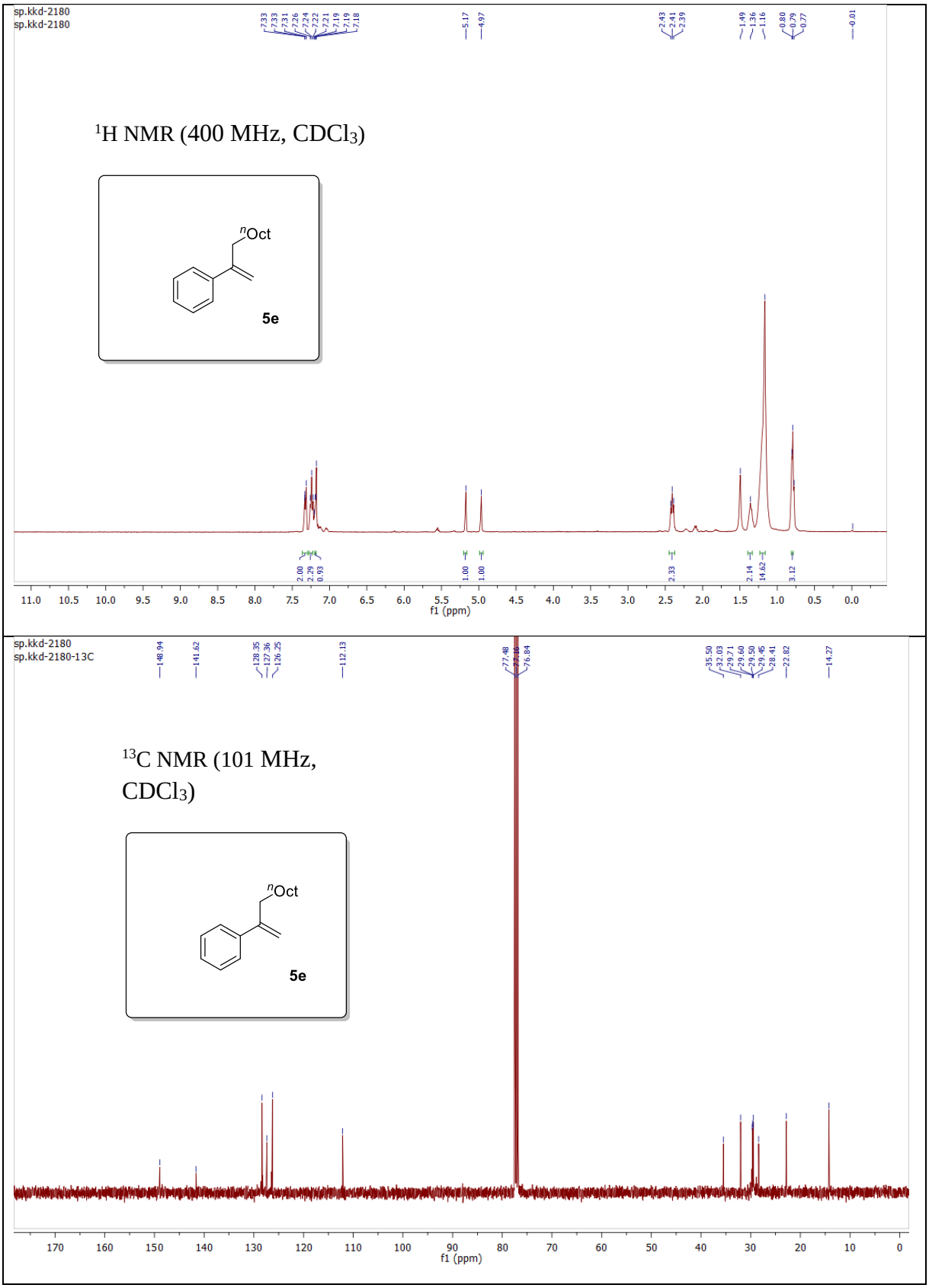

sp.kkd2017
sp / kkd / 2017 - 13c - 500mhz
148.59
142.48
141.55
128.61
128.42
128.41
127.46
126.32
125.87
112.55
77.41
77.16
76.91
35.61
35.06
30.04
13C NMR (126 MHz, CDCl3)
Bn
5b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


sp.kkd-2208
sp.kkd-2208
7.33
7.33
7.31
7.26
7.25
7.16
7.14
6.86
6.84
5.21
4.99
3.81
3.80
2.65
2.64
2.62
2.51
2.49
1.80
1.78
1.76
1.55
0.00
-0.01
^{1}H NMR (400 MHz, $CDCl_3$)
^{n}Oct
5c
4.38
2.95
2.00
1.09
1.07
3.14
1.96
2.06
1.88
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

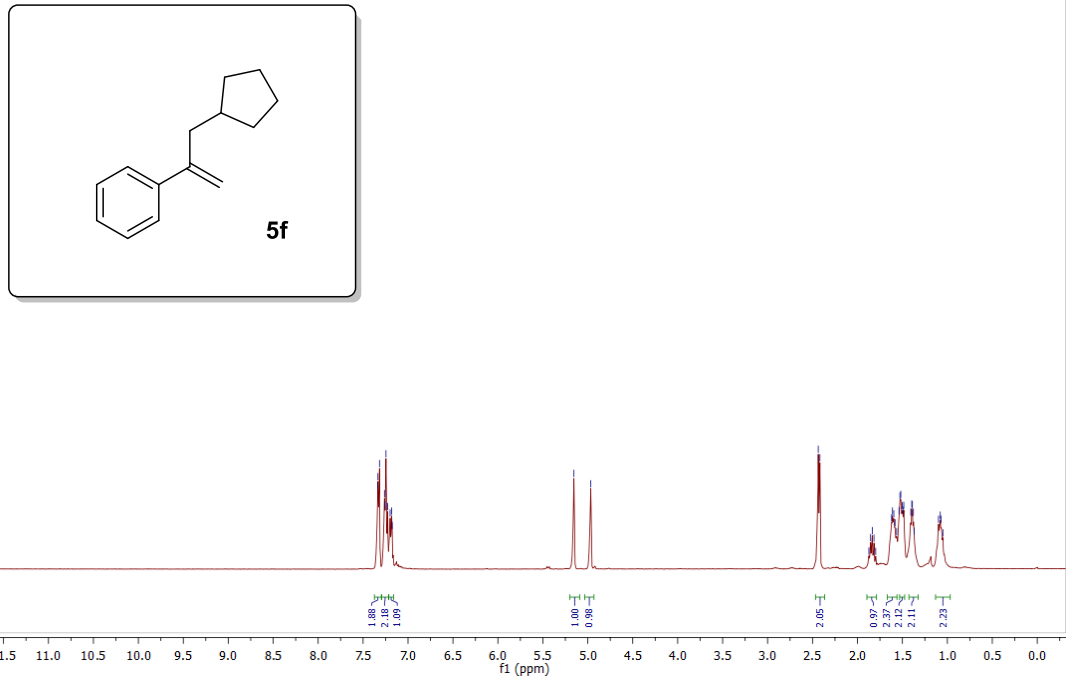

sp.kkd-2208-13C
sp.kkd-2208-13C
159.14
147.73
142.51
133.83
128.61
128.40
127.33
125.84
113.76
111.07
77.48
77.16
76.84
55.42
35.59
35.04
30.07
^{13}C NMR (101 MHz, $CDCl_3$)
^{n}Oct
5c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

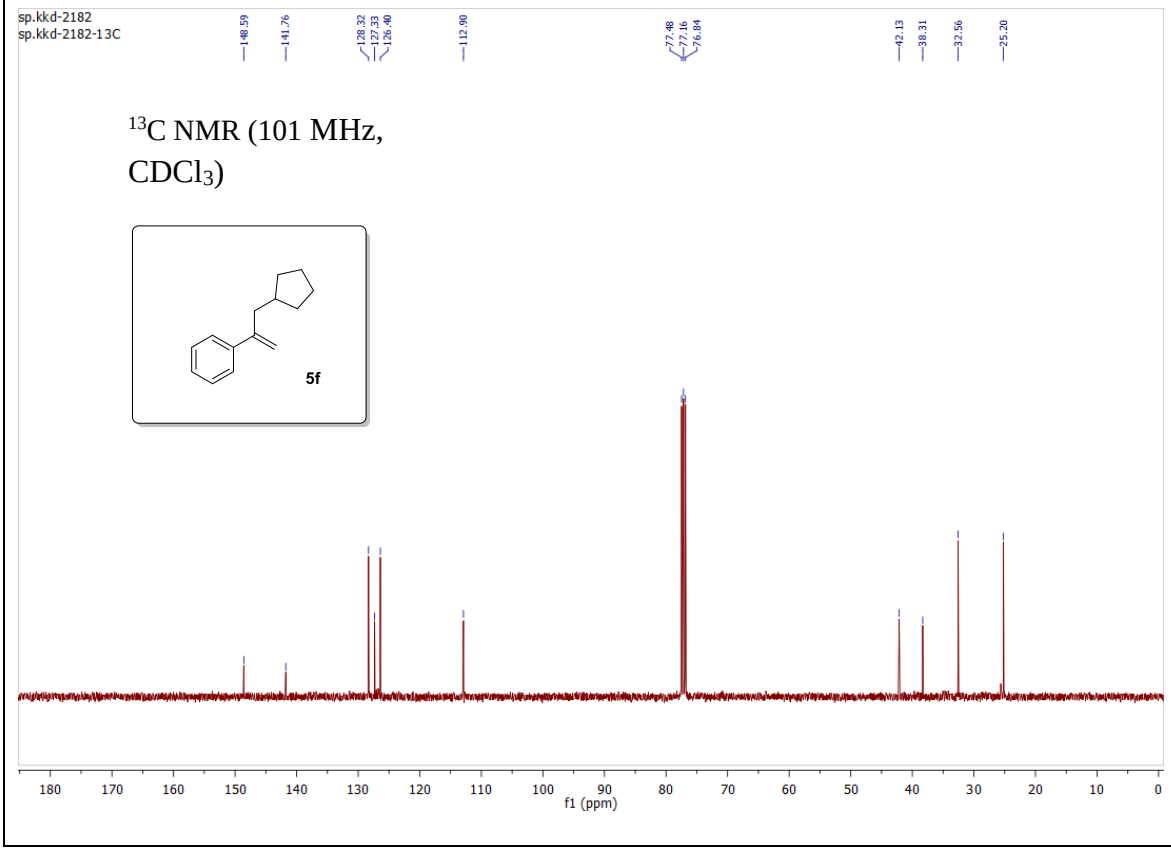

sp-kkd-2210
^{1}H NMR (400 MHz, $CDCl_3$)
^{n}Oct
MeO
5d
f1 (ppm)


sp.kkd2210ad
sp / kkd / 2210ad - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
^{n}Oct
MeO
5d
f1 (ppm)


sp.kkd-2180
sp.kkd-2180
7.33
7.33
7.31
7.26
7.24
7.22
7.21
7.19
7.18
5.17
4.97
2.43
2.41
2.39
1.49
1.36
1.16
0.80
0.79
0.77
-0.01
^{1}H NMR (400 MHz, $CDCl_3$)
nOct
5e
2.00
2.29
0.93
1.00
1.00
2.33
2.14
14.62
3.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
sp.kkd-2180
sp.kkd-2180-13C
148.94
141.62
128.35
127.36
126.25
112.13
77.48
77.16
76.84
35.50
32.03
29.71
29.60
29.50
29.45
28.41
22.82
14.27
^{13}C NMR (101 MHz, $CDCl_3$)
nOct
5e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

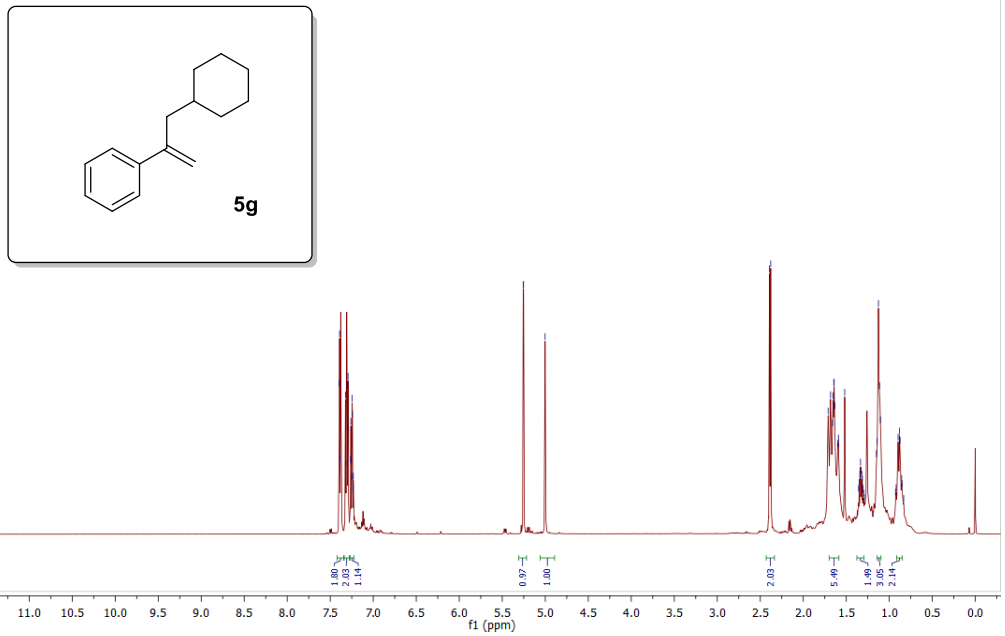
^{1}H NMR (400 MHz, $CDCl_3$)

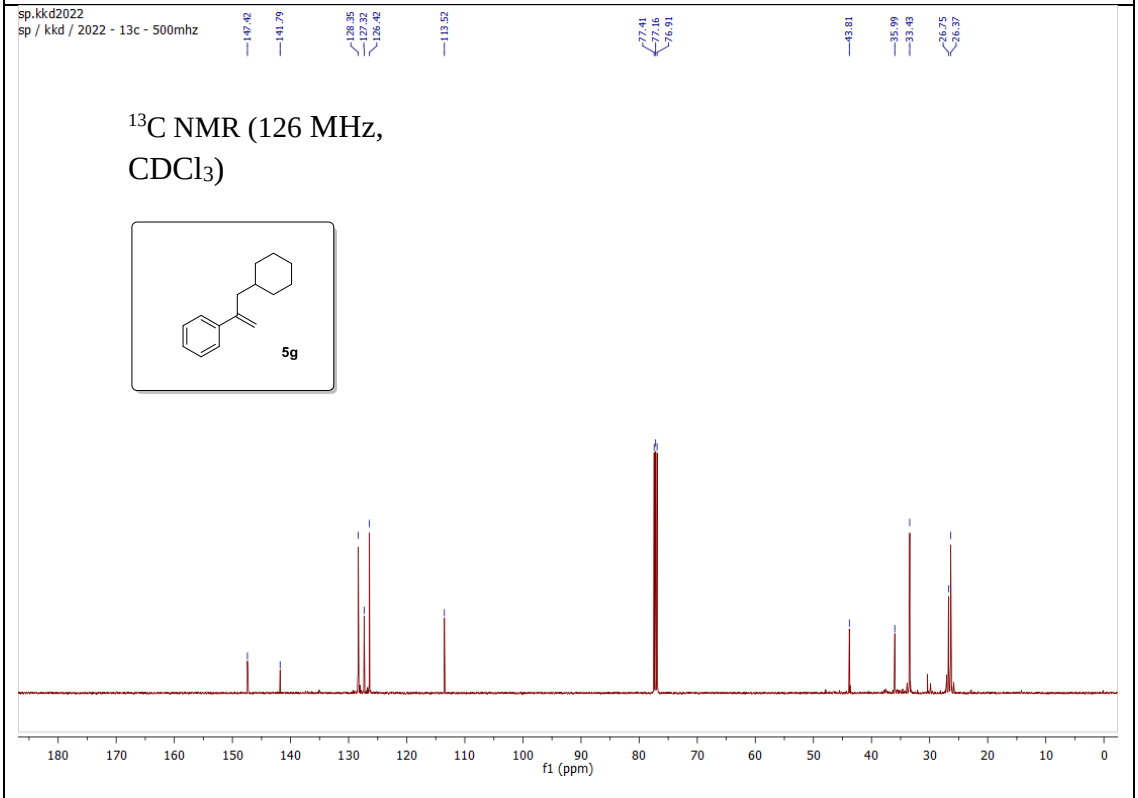




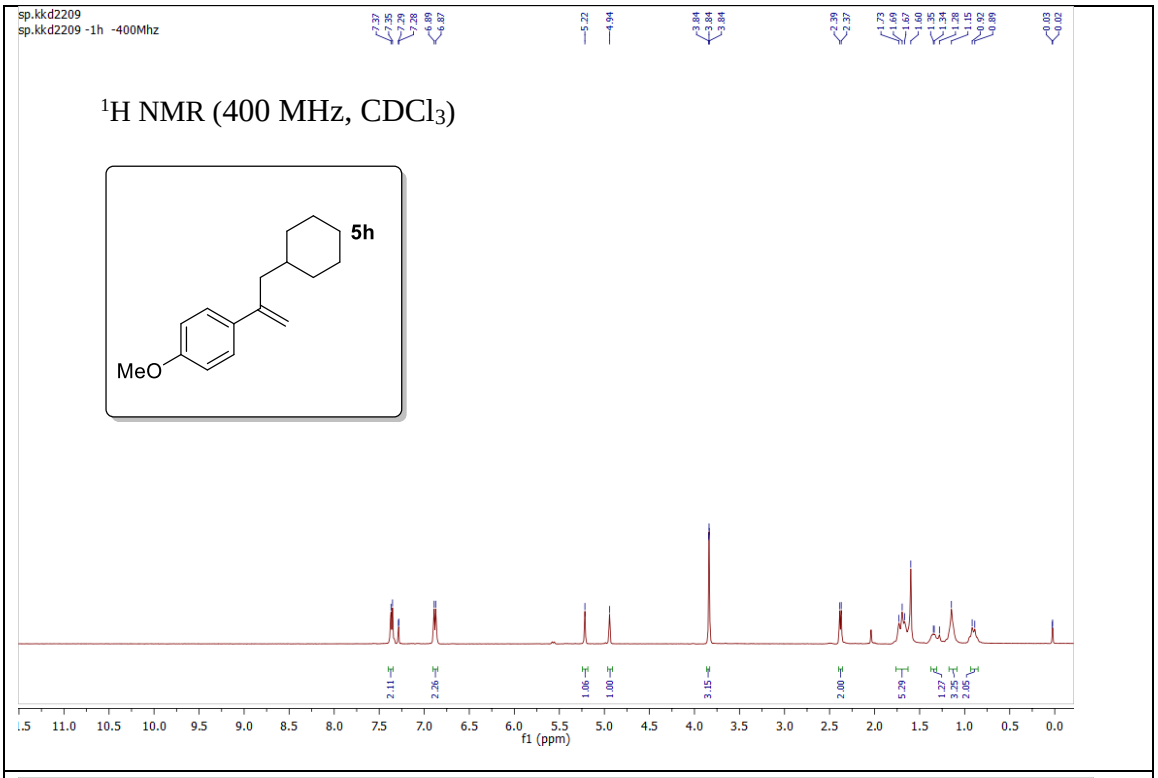
^{13}C NMR (101 MHz, $CDCl_3$)

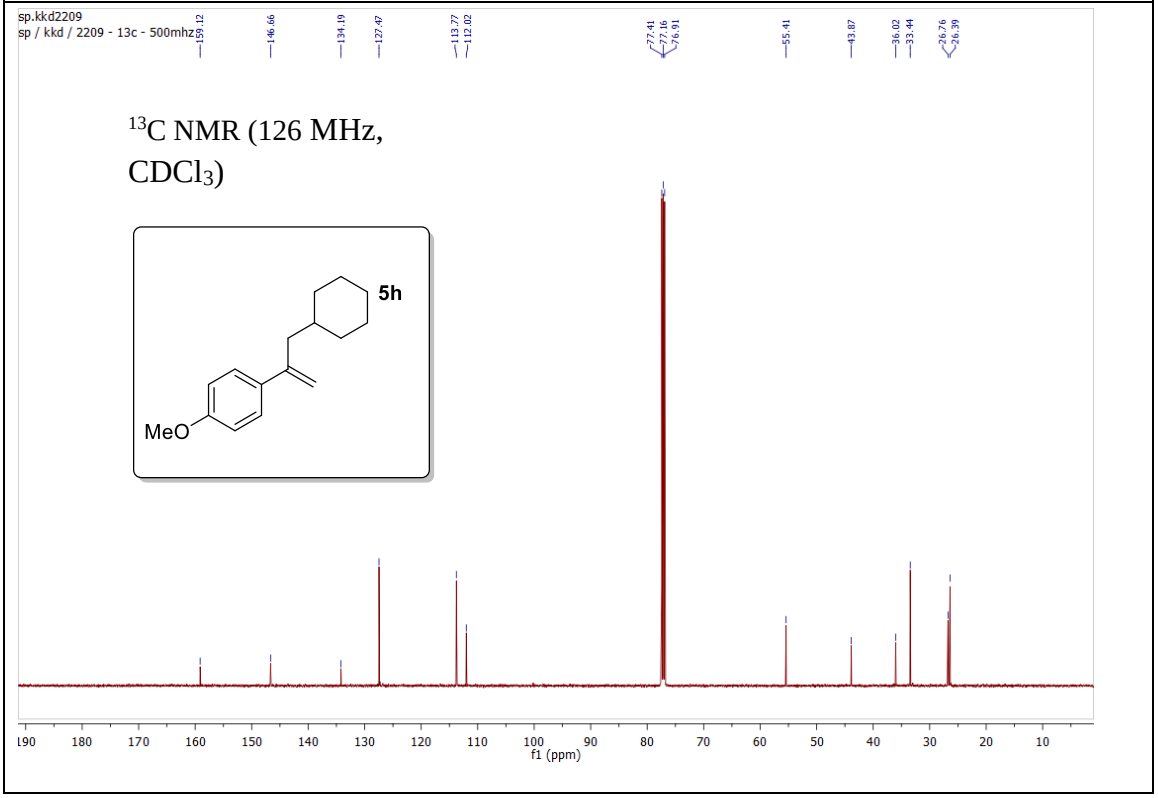
^{1}H NMR (500 MHz, $CDCl_3$)



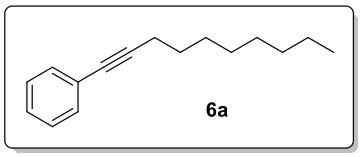


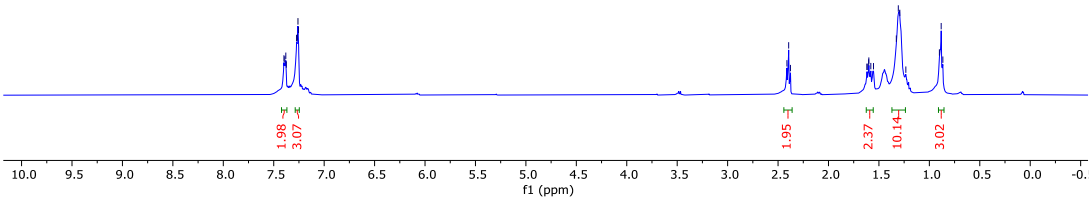
^{13}C NMR (126 MHz, $CDCl_3$)


sp.kkd2209
sp.kkd2209 -1h -400Mhz
^{1}H NMR (400 MHz, $CDCl_3$)
5h
MeO
f1 (ppm)

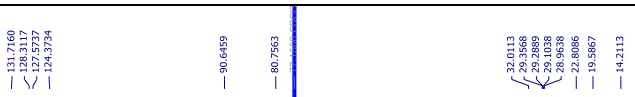

sp.kkd2209
sp / kkd / 2209 - 13c - 500mhz
^{13}C NMR (126 MHz, $CDCl_3$)
5h
MeO
f1 (ppm)

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

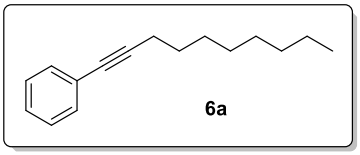


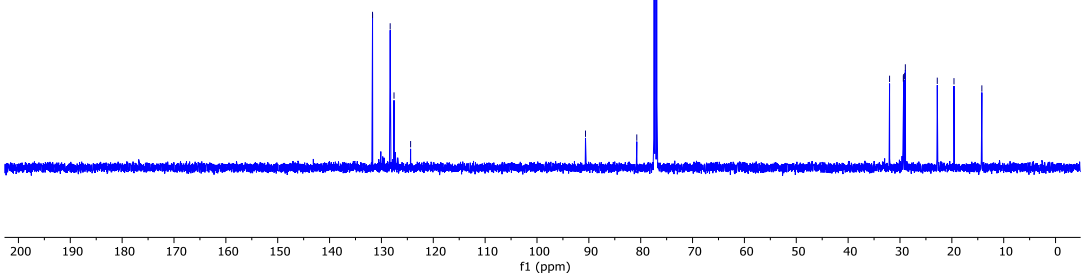


sp.som517.4.fid
sp / som / 517 - 13c - 500mhz

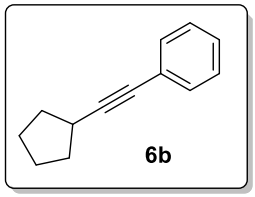


^{13}C NMR (126 MHz, $CDCl_3$)



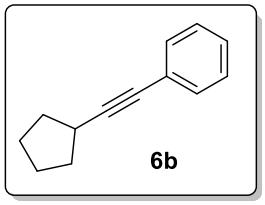


^{1}H NMR (400 MHz, $CDCl_3$)

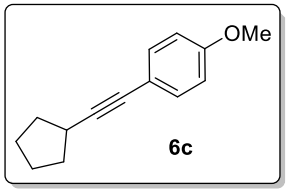


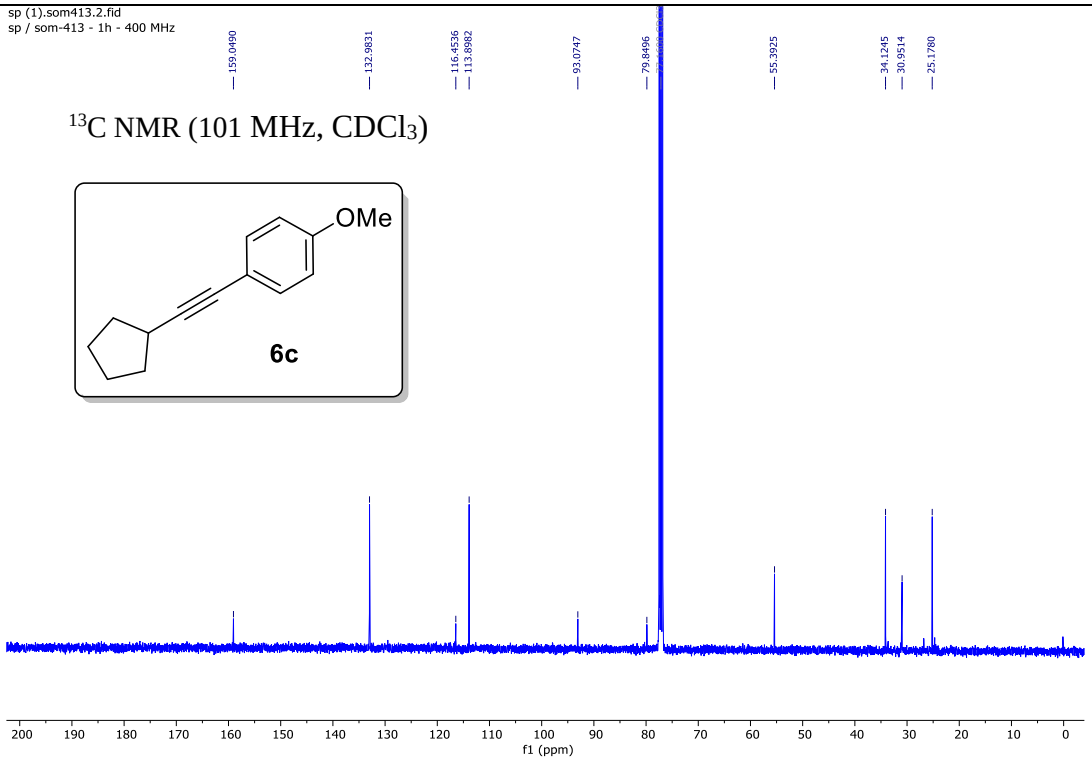
sp.som420.2.fid
sp.som420-1H 400 MHz

^{13}C NMR (101 MHz, $CDCl_3$)



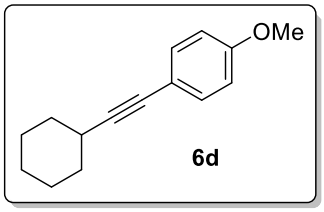
^{1}H NMR (400 MHz, $CDCl_3$)

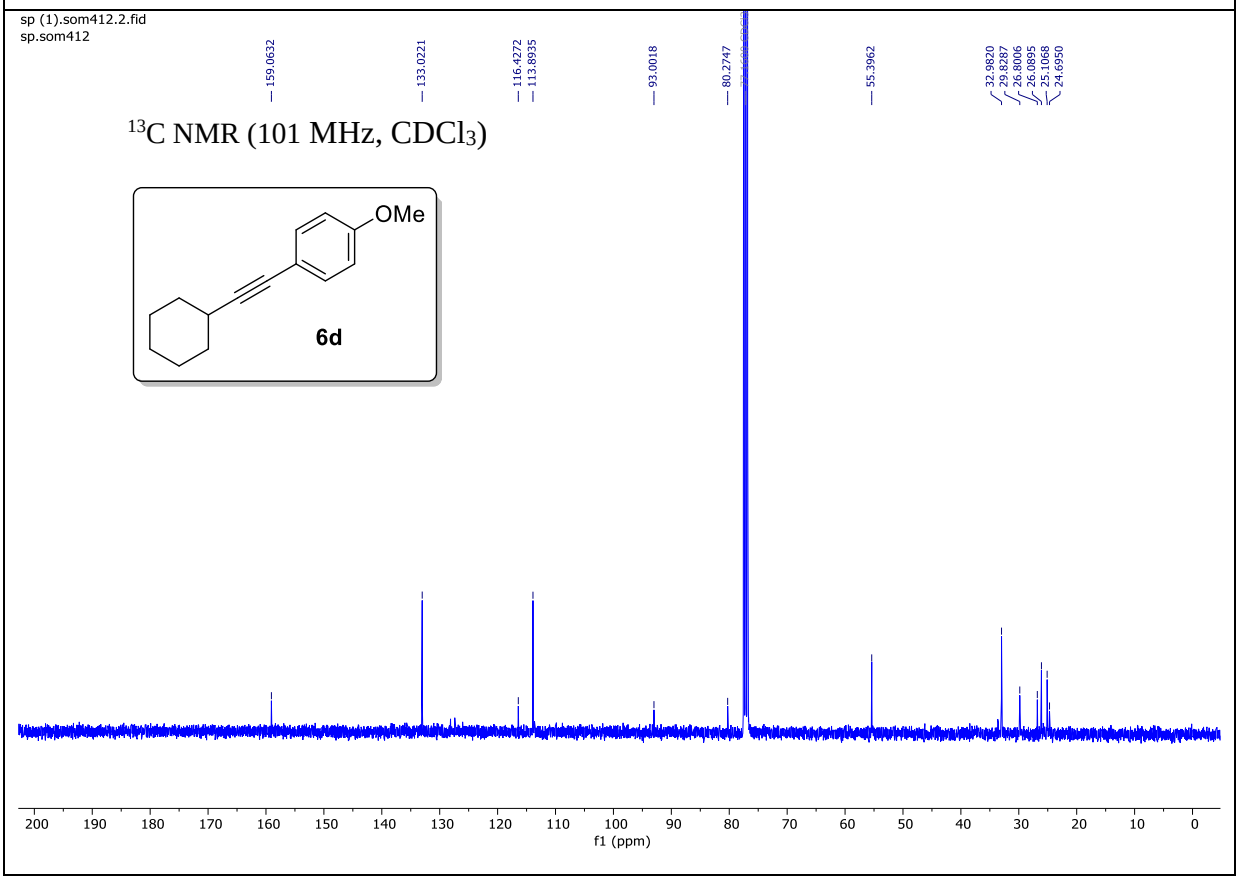




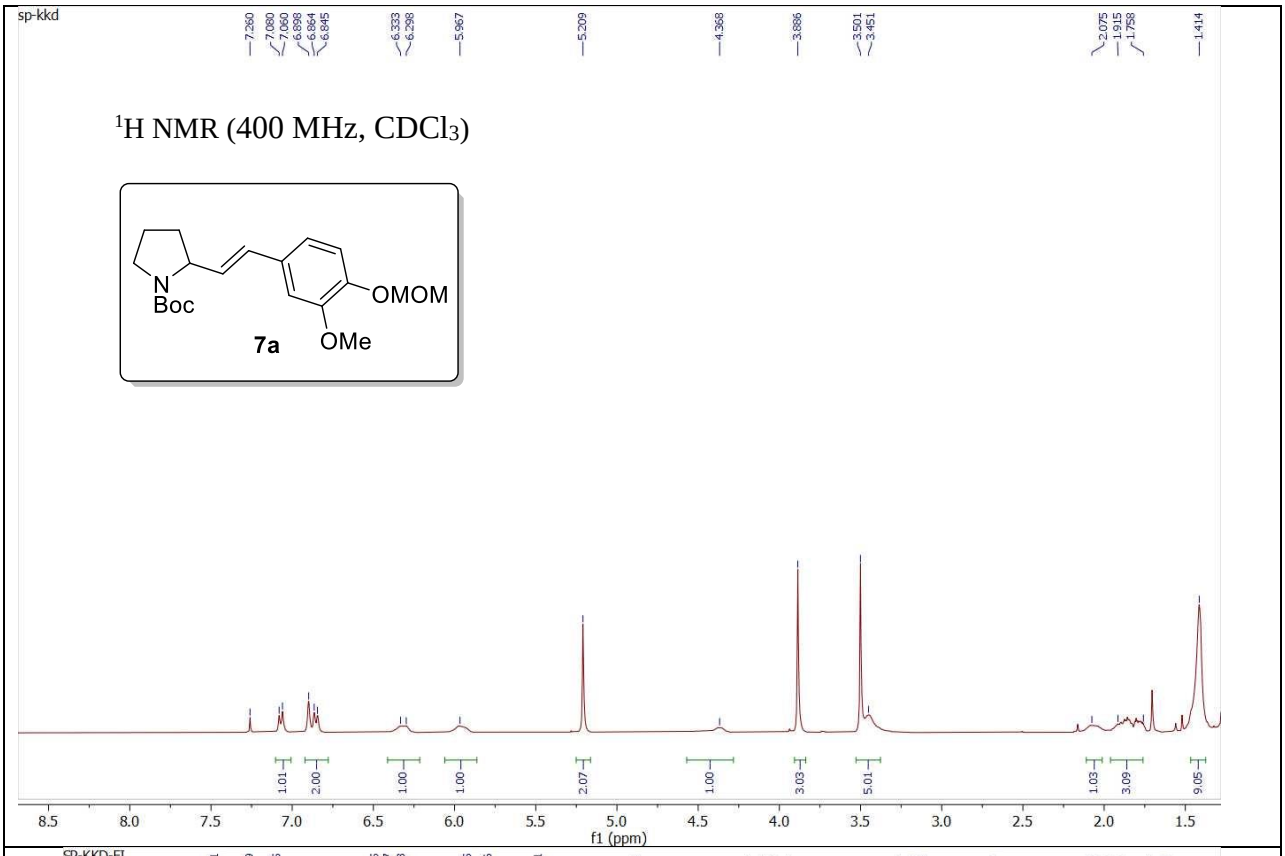
^{13}C NMR (101 MHz, $CDCl_3$)

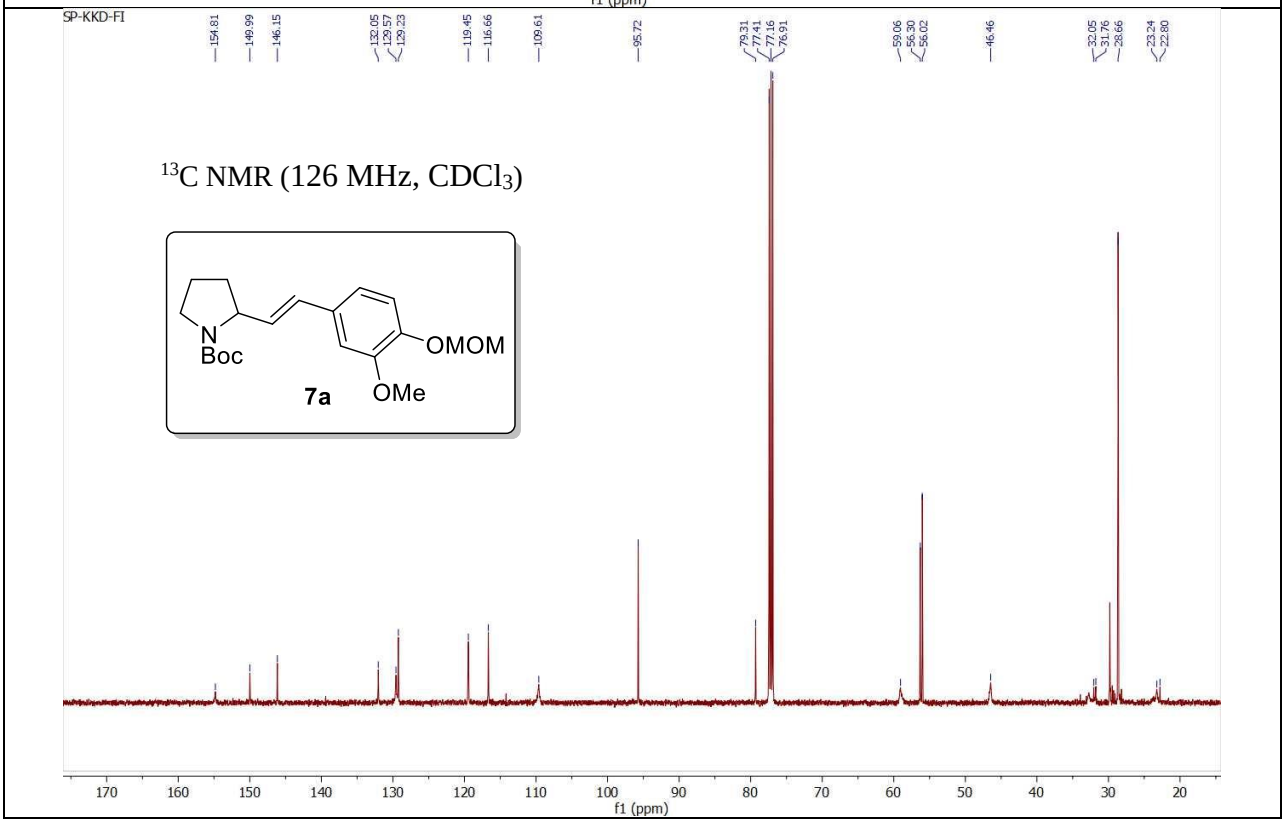
^{1}H NMR (400 MHz, $CDCl_3$)



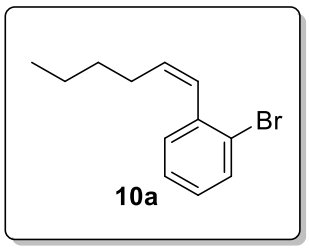


^{13}C NMR (101 MHz, $CDCl_3$)


sp-kkd
7.260
7.080
7.060
6.898
6.864
6.845
6.333
6.298
5.967
5.209
4.368
3.886
3.501
3.451
2.075
1.915
1.758
1.414
1H NMR (400 MHz, CDCl3)
N
Boc
OMOM
OMe
7a
1.01
2.00
1.00
1.00
2.07
1.00
3.03
5.01
1.03
3.09
9.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

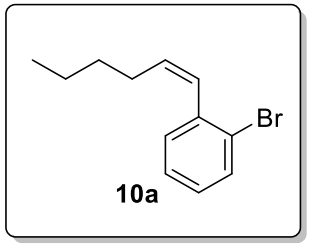

SP-KKD-FI
154.81
149.99
146.15
132.05
129.57
129.23
119.45
116.66
109.61
95.72
79.31
77.41
77.16
76.91
59.06
56.30
56.02
46.46
32.05
31.76
28.66
23.24
22.80
13C NMR (126 MHz, CDCl3)
N
Boc
OMOM
OMe
7a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

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

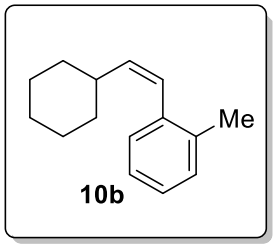


sp.som344.2.fid
sp.som344-13C-400 MHz

^{13}C NMR (101 MHz, $CDCl_3$)

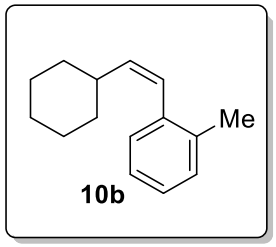


^{1}H NMR (400 MHz, $CDCl_3$)



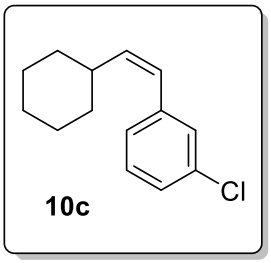
sp.som583.6.fid
sp / som / 583 - 13c - 500mhz

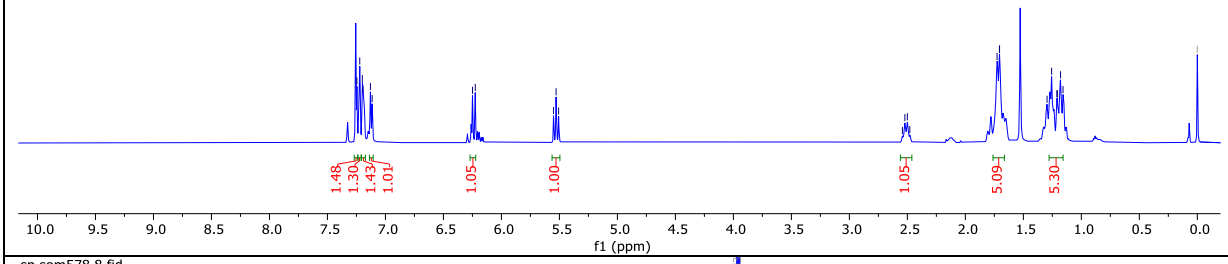
^{13}C NMR (126 MHz, $CDCl_3$)



sp.som578.9.fid
sp / som / 578 - 13c - 500mhz

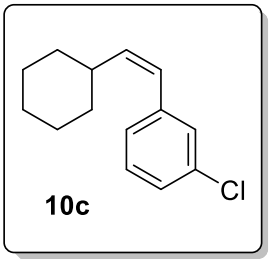
^{1}H NMR (500 MHz, $CDCl_3$)



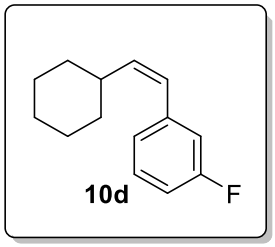


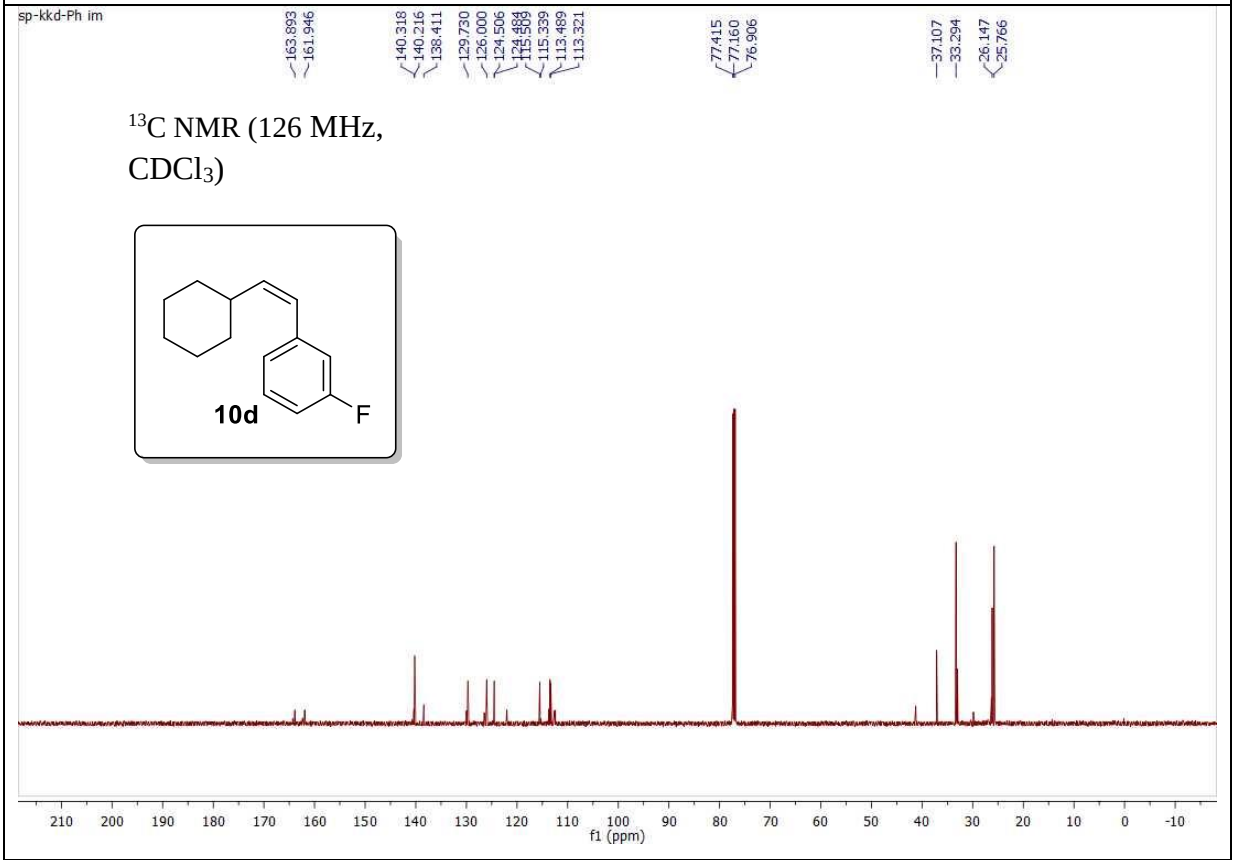
sp.som578.8.fid
sp / som / 578 - 13c - 500mhz

^{13}C NMR (126 MHz, $CDCl_3$)



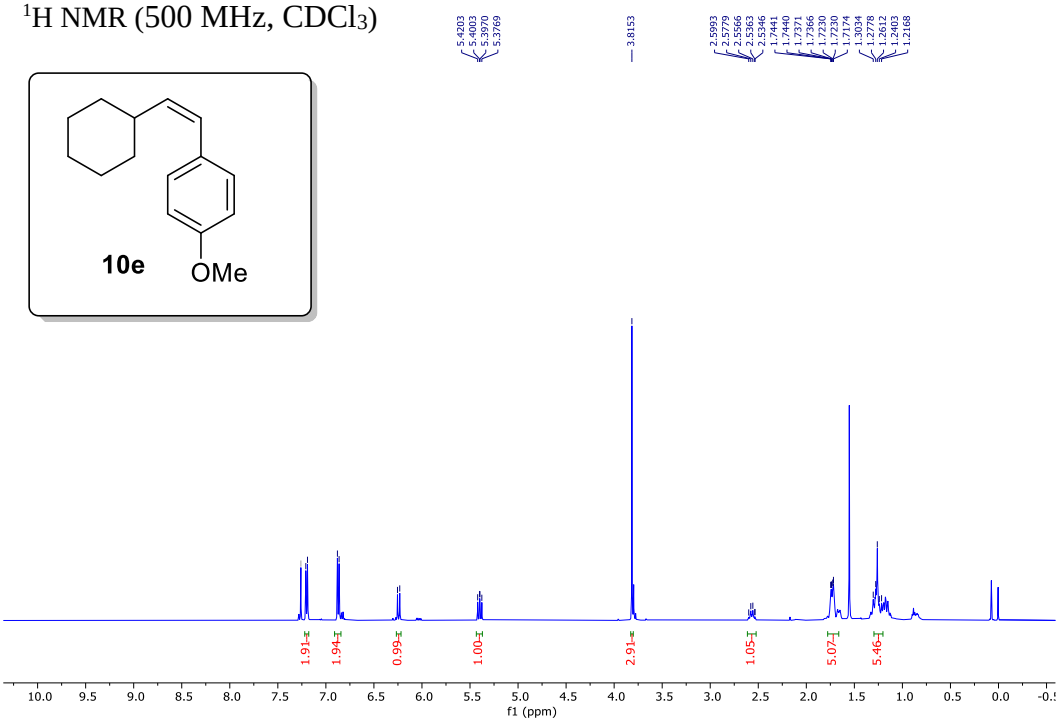
^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (126 MHz, $CDCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)



sp.som308.8.fid
sp / som / 308 - 1h - 500mhz

^{13}C NMR (126 MHz, $CDCl_3$)