Methyl viologen as a catalytic acceptor for electron donor-acceptor photoinduced cyclization reactions

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1. General Information

Reactions, which required oxygen-free conditions, were performed in prior to use oven-dried glassware under argon atmosphere using standard *Schlenk* technique. The used solvents for these reactions were either distilled freshly over commercially purchased extra-dry solvents from *Acros Organics*. The applied substrates were either synthesized or purchased from *Sigma Aldrich, Alfa Aesar, Acros, ABCR, TCI* or *BLDPharm* and were used without further purification. Trifluoroethanol was purchased from *ABCR* and was dried over molecular sieves (4A beads, 8-12 mesh obtained from BLDPharm). The purification of the product *via* flash column chromatography (FC) was performed on *Merck Geduran Si 60* (40-63 µm) or *VWR silica gel 60* (40-63 µm). The solvents were distilled prior to use. The reaction monitoring was performed on thin layer chromatography (TLC) purchased from *Merck silica gel 60 F254* – plates and detected using UV light or anisaldehyde stain (0.5% anisaldehyde, 10% glacial acetic acid, 85% methanol, 5% concentrated H_2SO_4)

^{1}H-NMR (300 MHz, 500 MHz and 600 MHz), ^{13}C-NMR (75 MHz, 126 MHz and 151 MHz) and 19F-NMR (282 MHz) were recorded on *Bruker Avance II 300, Agilent DD2 500* and *Agilent DD2 600* spectrometers at 299 K. The chemical shifts are stated in ppm and referenced to the solvent residual peak of CDCl3 (δ = 7.26 ppm). The multiplets are given as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). The mass spectra were measured on the *Thermo Fischer Scientific LTQ Orbitrap XL* and the peaks were displayed in *m/z*.

The UV-vis absorption spectra were measured using a *Jasco V-730* with a spectral bandwith of 1.0 nm and a scan rate of 1000 nm/min. The spectra were recorded in a range of 200-600m and glass cuvettes with an optical length of 1 mm and 1 cm were used. The fluorescence emission spectra were recorded on a *Jasco Spectrafluorometer FP-8500* with a spectral bandwidth of 5.0m and a scan rate of 1000 nm/min. The samples were measured in glass cuvettes with an optical length of 1 cm.

1.1 Photoreaction setup

The photoreactions were performed in a tailor-made photoreactor equipped with 3 W and 10 W green LEDs (emission maxima: 520 nm) supplied by *Avonec*. The water cooling of the reaction has been performed using a chiller purchased by *Huber* (*Huber minichiller 280*) and the temperature was set to 20°C. The photoreactions were performed in 10 mL headspace vials supplied by *Omnilab* (Headspacevial ND20, 10 ml, 46 x 22.5 mm, rounded bottom). The vials were placed in designated spots of the photoreactor and each reaction was irradiated by one LED from below, maintaining an equal distance to the light source for each reaction. To ensure comparable light intensity for each sample, illuminance in cd·sr·m^{-2} was measured three times for each LED 143 mm from the LEDs, using a *PeakTech 5030*. For the 3 W and 10 W LEDs illuminances of 8383 cd·sr·m^{-2}(spot A), 7850 cd·sr·m^{-2} (spot B), 9240 cd·sr·m^{-2} (spot C) and 52567 cd·sr·m^{-2}(spot D), 53367 cd·sr·m^{-2} (spot E), 52634 cd·sr·m^{-2} (spot F) were measured respectively.

Figure S1: Photoreaction setup

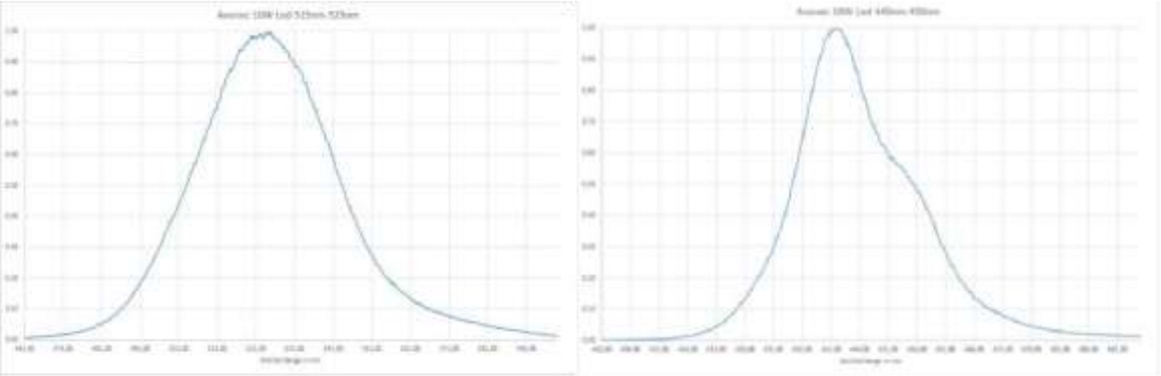
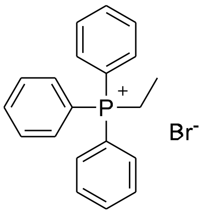


Figure S2: Emission spectrum of the irradiation source.

2. Substrates Synthesis

2.1 Synthesis of the Wittig reagent (S1)


S1

In accordance to a procedure of *Diver et al.*[1] a Schlenk tube was charged with triphenyl phosphine (26.20 g, 100.00 mmol, 1.00 eq.) and dissolved in toluene. Afterwards ethyl bromide (8.73 mL, 117.00 mmol, 1.17 eq.) were added and the solution was refluxed overnight. The formed residue was filtrated, washed with cold toluene and dried under vacuo. The white solid (32.00 g, 86.20 mmol, 86%) was used without further purification.

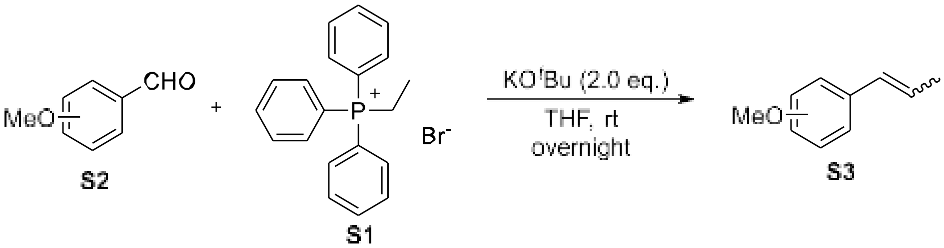
^{1}H-NMR (300 MHz, $CDCl_3$, 299 K): δ (ppm) = 7.76 – 7.52 (m, 15H), 3.63 (dq, J = 12.4, 7.5 Hz, 2H), 1.25 (dt, J = 20.0, 7.5 Hz, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$, 299 K): δ (ppm) = 134.9 (d, J = 3.1 Hz), 133.4 (d, J = 9.9 Hz), 130.3 (d, J = 12.5 Hz), 117.7 (d, J = 85.9 Hz), 16.9 (d, J = 51.7 Hz), 6.6 (d, J = 5.2 Hz).

^{31}P NMR (122 MHz, $CDCl_3$, 299 K): δ (ppm) = 26.0.

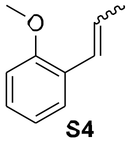
HRMS (ESI) *m/z*: $[M]^+$ calculated for $C_{20}H_{20}P^+$: 291.1297, found: 291.1292.

2.2 General procedure for the Wittig-Olefination of Methoxybenzaldehydes (GP1)



In accordance to a procedure of *Lautens et al.*[2] the triphenyl(propyl)phosphonium bromide (3.71 g, 10.00 mmol, 2.00 eq.) was dissolved in THF (30 mL) and at 0°C KO^{t}Bu (1.12 g, 10.00 mmol, 2.00 eq.) was added. After the addition the reaction solution turned in most cases yellow, indicating the ylide formation. After 30 min stirring, the methoxybenzaldehyde (5.00 mmol, 1.00 eq.) was added at 0°C and the reaction mixture was stirred overnight at rt. Afterwards THF was removed under vacuo and water and EtOAc were added. The organic phase was separated and the aqueous phase was washed once with EtOAc. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under vacuo. The product was purified via FC (Pentane: Et_2O).

1-Methoxy-2-(prop-1-en-1-yl)benzene (S4)



S4

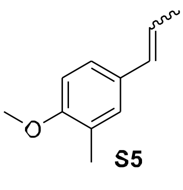
1-Methoxy-2-(prop-1-en-1-yl)benzene was synthesized according to the GP1 using 2-methoxybenzaldehyde (272.00 mg, 2.00 mmol, 1.00 eq.), ethyltriphenylphosphonium bromide (1.48 g, 4.00 mmol, 2.00 eq.), potassium *tert*-butoxide (448 mg, 4.00 mmol, 2.00 eq.) and THF (12 mL). The purification via FC (pentane : Et_2O = 95:5) gave the product (272 mg, 1.19 mmol, 59% d.r. = 4:1) as a clear liquid.

^{1}H NMR (300 MHz, Major isomer, $CDCl_3$) δ 7.32 – 7.14 (m, 2H), 7.03 – 6.82 (m, 2H), 6.57 (dd, *J* = 11.5, 1.9 Hz, 1H), 5.87 (dd, *J* = 11.6, 7.1 Hz, 1H), 3.85 (s, 3H), 1.85 (dd, *J* = 7.1, 1.9 Hz, 3H).

^{13}C NMR (76 MHz, Major isomer, $CDCl_3$) δ 157.1, 130.2, 128.0, 127.0, 125.3, 120.0, 110.4, 55.5, 14.7.

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_{13}O^+$: 149.0961, found: 149.0961

2-Methyl-1-methoxy-4-(prop-1-en-1-yl)benzene (S5)



S5

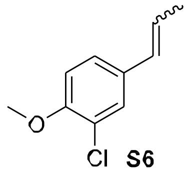
2-Methyl-1-methoxy-4-(prop-1-en-1-yl)benzene was synthesized according to the GP1 using 3-methyl-4-methoxybenzaldehyde (767.00 mg, 5.10 mmol, 1.00 eq.), ethyltriphenylphosphonium bromide (4.27 g, 11.50 mmol, 2.30 eq.), potassium *tert*-butoxide (1.29 g, 11.50 mmol, 2.30 eq.) and THF (30 mL). The purification via FC (pentane: Et_2O) = 95:5 gave the product (665.00 mg, 4.10 mmol, 82%, d.r. = 3:1) as a clear liquid.

^{1}H-NMR (400 MHz, Major isomer, $CDCl_3$, 299 K): δ (ppm) = δ 7.16 (dd, *J* = 6.8, 2.2 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.41 (dt, *J* = 11.7, 1.9 Hz, 1H), 5.86 – 5.68 (m, 1H), 3.87 (s, 3H), 2.28 (s, 3H), 1.95 (dd, *J* = 7.2, 1.9 Hz, 3H).

^{13}C NMR (100 MHz, Major isomer, $CDCl_3$) δ 156.5, 131.4, 130.0, 129.6, 127.4, 126.3, 124.9, 109.7, 55.4, 16.4, 14.7.

MS (EI) : *m/z* 162.0 (100) $[M]^+$; 147.0 (75) $[M-CH_3]^+$; 131.0 (20) $[M-OCH_3]^+$.

2-Chloro-1-methoxy-4-(prop-1-en-1-yl)benzene (S6)



S6

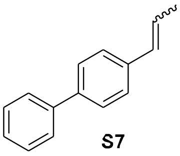
2-Chloro-1-methoxy-4-(prop-1-en-1-yl)benzene was synthesized according to the GP1 using 3-chloro-4-methoxybenzaldehyde (853.00 mg, 5.00 mmol, 1.00 eq.), ethyltriphenylphosphonium bromide (3.71 g, 10.00 mmol, 2.00 eq.), potassium *tert*-butoxide (1.12 g, 10.00 mmol, 2.00 eq.) and THF (30 mL). The purification via FC (pentane: Et_2O) = 95:5 gave the product (483.00 mg, 2.64 mmol, 53%, d.r. = 2:1) as a pale-yellow liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K): δ (ppm) = 7.34 (dd, J = 10.2, 2.2 Hz, 1H), 7.20 – 7.12 (m, 1H), 6.87 (dd, J = 14.8, 8.5 Hz, 1H), 6.36 – 6.24 (m, 1H), 6.11 (dq, J = 15.7, 6.5 Hz, 0.35H), 5.74 (dq, J = 11.6, 7.2 Hz, 0.65H), 3.90 (s, 2H), 3.89 (s, 1H), 1.87 (td, J = 7.0, 1.7 Hz, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$, 299 K): δ (ppm) = 153.5, 131.3, 130.6, 128.3, 128.3, 126.6, 122.1, 111.8, 56.3, 14.7.

MS (EI) : *m/z* 182.0 (100) $[M]^+$; 167.0 (45) $[M-CH_3]^+$; 157.0 (45) $[M-OCH_3]^+$.

4-(Prop-1-en-1-yl)-1,1'-biphenyl (S7)



S7

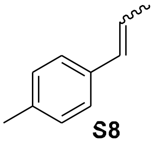
4-(Prop-1-en-1-yl)-1,1'-biphenyl was synthesized according to the GP1 using [1,1'-biphenyl]-4-carbaldehyde (364.00 mg, 2.00 mmol, 1.00 eq.), ethyltriphenylphosphonium bromide (1.48 g, 4.00 mmol, 2.00 eq.), potassium *tert*-butoxide (448.00 mg, 4.00 mmol, 2.00 eq.) and THF (12 mL). The purification via FC (pentane: Et_2O = 95:5) gave the product (253.00 mg, 1.30 mmol, d.r. = 3:2) as a white solid.

^{1}H NMR (300 MHz, Major isomer, $CDCl_3$) δ 7.67 – 7.52 (m, 4H), 7.51 – 7.33 (m, 5H), 6.56 – 6.40 (m, 1H), 6.31 (dq, *J* = 15.8, 6.4 Hz, 1H), 1.95 (ddd, *J* = 13.9, 6.8, 1.7 Hz, 3H).

^{13}C NMR (76 MHz, Major isomer, $CDCl_3$) δ 141.0, 139.6, 137.1, 130.7, 128.9, 127.3, 127.3, 127.1, 126.3, 126.0, 18.7.

MS (EI) : *m/z* 194.1 (100) $[M]^+$; 193.1 (40), $[M-H]^+$ 179.1 (40) $[M-CH_3]^+$.

1-Methyl-4-(prop-1-en-1-yl)benzene (S8)



S8

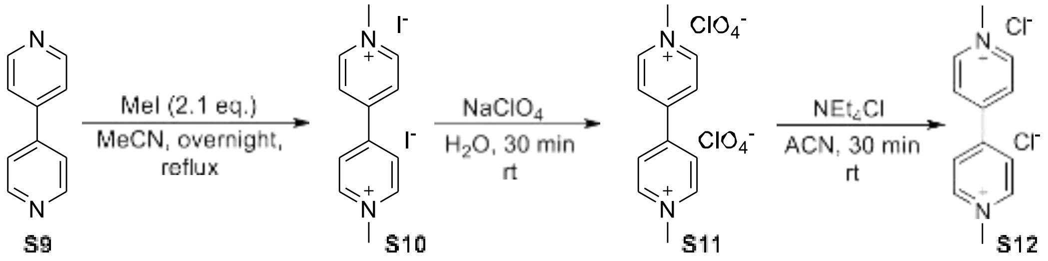
1-Methyl-4-(prop-1-en-1-yl)benzene was synthesized according to the GP1 using 4-methylbenzaldehyde (240.00 mg, 2.00 mmol, 1.00 eq.), ethyltriphenylphosphonium bromide (1.48 g, 4.00 mmol, 2.00 eq.), potassium *tert*-butoxide (448 mg, 4.00 mmol, 2.00 eq.) and THF (12 mL). The purification via FC (pentane : Et_2O = 95:5) gave the product (210.00 mg, 1.59 mmol, 79% d.r. = 4:1) as a clear liquid.

^{1}H NMR (300 MHz, Major isomer, $CDCl_3$) δ 7.28 – 7.10 (m, 4H), 6.42 (ddq, *J* = 13.5, 11.5, 1.8 Hz, 1H), 5.78 (dq, *J* = 11.6, 7.2 Hz, 1H), 2.36 (d, *J* = 7.8 Hz, 3H), 1.91 (ddd, *J* = 9.1, 6.9, 1.7 Hz, 3H).

^{13}C NMR (76 MHz, Major isomer, $CDCl_3$) δ 136.1, 134.8, 129.8, 128.9, 128.8, 126.1, 21.2, 14.7.

MS (EI) : *m/z* 132.1 (70) $[M]^+$; 117.1 (100) $[M-CH_3]^+$.

3. N,N-Dimethylbipyridinyl dichloride synthesis



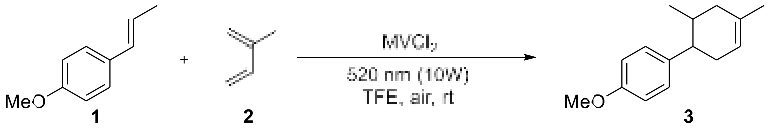
For the three-step synthesis of *N,N*-Dimethylbipyridinyl dichloride, 4,4´-bipyridine (4.69 g, 30.0 mmol, 1.00 eq.) was dissolved in acetonitrile (90 mL). After the addition of methyliodide (4.02 mL, 64.3 mmol, 2.14 eq.), the reaction was refluxed overnight. The reaction mixture was cooled to rt and then filtrated. The residue was washed with acetonitrile, dried under vacuo and used without further purification. The formed *N,N*-dimethylbipyridinyl diiodide was dissolved in dest. water (160 mL) and $NaClO_4$ * H_2O (10.5 g, 75.0 mmol, 2.50 eq.) was added. After 30 min, the formed residue was filtrated and washed with dest. water. The filtrate was concentrated and another portion of $NaClO_4$ * H_2O was added. The combined residues were dried under vacuo and were applied in the next step without further purification. In the last step $NEtCl_4$ was added to a MeCN (200 mL) solution of 1,1´-Dimethyl[4,4´-bipyridine]-1,1´diium dichlorate (8.31 g, 21.6 mmol, 1.00 equiv.). After 30 min stirring at room temperature, the mixture was filtrated and washed with MeCN. The product was obtained as an off-white solid (5.55 g, 21.6 mmol, 72% overall yield).

^{1}H-NMR (300 MHz, D_2O, 299 K): δ (ppm) = 9.06 (d, J = 6.4 Hz, 4H), 8.53 (d, J = 6.5 Hz, 4H), 4.51 (s, 6H).

^{13}C-NMR (76 MHz, D_2O, 299 K): δ (ppm) = 149.9, 146.3, 126.7, 48.4.

HRMS (ESI) *m/z*: [M]$^+$ calculated for $C_{12}H_{14}N_2^+$: 93.0573, found: 93.0572.

4. Optimization of the [4+2] cycloaddition

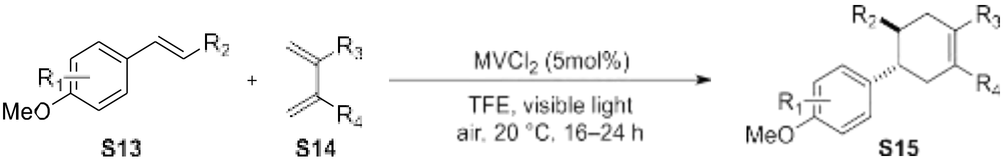


Entry	Diene	Methyl viologen	Solvent	Time	NMR yield
1	Isoprene (3.0 eq.)	100 mol%	TFE (2 mL)	24 h	60%
2	Isoprene (3.0 eq.)	50 mol%	TFE (2 mL)	24 h	56%
3	Isoprene (3.0 eq.)	20 mol%	TFE (2 mL)	24 h	65%
4	Isoprene (3.0 eq.)	10 mol%	TFE (2 mL)	24 h	59%
5	Isoprene (3.0 eq.)	5 mol%	TFE (2 mL)	24 h	60%
6	Isoprene (3.0 eq.)	5 mol%	TFE (1 mL)	24 h	64%
7	Isoprene (3.0 eq.)	5 mol%	TFE (1 mL)	24 h	66% (64%)
8	Isoprene (3.0 eq.)	5 mol%	TFE (1 mL)	18 h	58% (61%)
9	Isoprene (3.0 eq.)	5 mol%	TFE (1 mL)	16 h	66%
10[a]	Isoprene (3.0 eq.)	5 mol%	TFE (1 mL)	16 h	27%
11	Isoprene (3.0 eq.)	5 mol%	SDS (4w%) (1 mL)	16 h	1%
12	Isoprene (3.0 eq.)	5 mol%	H_2O (1 mL)	16 h	5%
13	Isoprene (3.0 eq.)	5 mol%	$MeNO_2$ (1 mL)	16 h	0%
14	Isoprene (3.0 eq.)	5 mol%	MeOH (1 mL)	16 h	0%
15	Isoprene (3.0 eq.)	5 mol%	DCE:TFE (4:1) (1 mL)	16 h	3%
16[b]	Isoprene (3.0 eq.)	5 mol%	HFIP (1 mL)	16 h	3%
17[b]	Isoprene (3.0 eq.)	5 mol%	TFE (1 mL)	16 h	0%
18[c]	Isoprene (3.0 eq.)	0 mol%	TFE (1 mL)	16 h	1%
19[d]	Isoprene (3.0 eq.)	5 mol%	TFE (1 mL)	16 h	14%

Reactions were performed with *trans*-Anethole (0.2 mmol), Methylviologen and Isoprene (3.0 eq.) in solvent under irradiation with a 520 nm LED (10W) for 16 h at rt. For the determination of the yield, Dibromomethane was used as internal standard. [a] 3W 520 nm LED, [b] dark$_2$. [c] without $MVCl_2$. [d] degassed solvent.

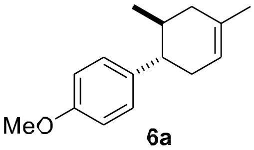
5. Synthesis and characterization data of the [4+2] cycloaddition product

5.1 General procedure for the [4+2] cycloaddition. (GP2)



In a 10 mL headspace vial, olefin (0.20 mmol, 1.00 eq.) was dissolved in molecular sieve dried 2,2,2-trifluoroethanol 1 mL), followed by addition of diene (0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.) under aerobic conditions. Then the headspace vial was sealed and irradiated with a green LED (520 nm, 10 W) for 16 h at 20°C. The reaction mixture was transferred to a separatory funnel and afterwards brine (75 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 25 mL and the combined organic layers were dried over anhydrous $MgSO_4$ Afterwards it was filtered, the filtrate was concentrated under vacuum and the product was purified via FC. Configuration was defined by comparing NMR data with known literature.[3]

4'-Methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6a)



6a

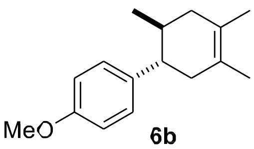
4'-Methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl was synthesized according to the GP2 using *trans*-anethole (29.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), isoprene (64 μL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light for 16 h. The purification via FC (pentane: Et_2O = 98:2) gave the product (31.00 mg, 0.14 mmol, 72%) as a clear liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 299 K): δ (ppm) = 7.13 – 7.04 (m, 2H), 6.89 – 6.80 (m, 2H), 5.44 (tt, J = 3.6, 1.8 Hz, 1H), 3.80 (s, 3H), 2.49 – 2.01 (m, 4H), 2.00 – 1.74 (m, 2H), 1.70 (q, J = 1.7 Hz, 3H), f0.71 (d, J = 6.2 Hz, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$, 299 K): δ (ppm) = 157.9, 138.3, 134.0, 128.6, 121.0, 113.8, 55.3, 47.1, 40.0, 35.4, 34.1, 23.5, 20.4.

MS (EI) : *m/z* 148.1 (100) $[M-C_5H_8]^+$; 216.1 (14) $[M]^+$; 201.1 (5) $[M-CH_3]^+$.

4'-Methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6b)



6b

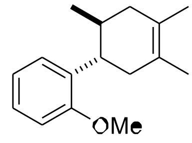
4'-Methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl was synthesized according to the GP2 using *trans*-anethole (29.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68 μL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light for 16 h. The purification via FC (pentane: Et_2O = 98:2) gave the product (38.50 mg, 0.17 mmol, 84%) as a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.04 (m, 2H), 6.96 – 6.76 (m, 2H), 3.81 (s, 3H), 2.35 (td, *J* = 10.2, 6.2 Hz, 1H), 2.26 – 2.01 (m, 3H), 1.87 (tdd, *J* = 11.0, 5.9, 2.6 Hz, 2H), 1.72 – 1.57 (m, 6H), 0.71 (d, *J* = 6.2 Hz, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$, 299 K): δ (ppm) = 157.9, 138.3, 128.6, 125.6, 125.4, 113.8, 55.3, 47.9, 42.0, 41.8, 34.4, 20.1, 18.8.

MS (EI) : *m/z* 148.1 (100) $[M-C_5H_8]^+$; 230.1 (15) $[M]^+$; 215.2 (5) $[M-CH_3]^+$.

2'-Methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6c)



6c

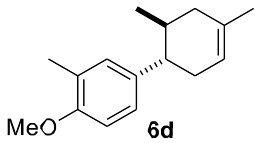
2'-Methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl was synthesized according to the GP2 using 1-methoxy-2-(prop-1-en-1-yl)benzene (d.r. = 3:1, 29.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68 μL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light for 72 h. The purification via FC (pentane: Et_2O = 95:5) gave the product (42.00 mg, 0.17mmol, 83% d.r. = 4:1) as a clear liquid.

^{1}H NMR (300 MHz, Major isomer, $CDCl_3$) δ 7.17 (dd, *J* = 8.0, 6.3 Hz, 2H), 6.98 – 6.90 (m, 1H), 6.88 (dd, *J* = 9.0, 6.8 Hz, 1H), 3.81 (s, 3H), 2.97 (td, *J* = 10.6, 5.7 Hz, 1H), 2.40 – 2.13 (m, 1H), 2.19 – 1.94 (m, 3H), 1.94 – 1.78 (m, 1H), 1.64 (d, *J* = 9.8 Hz, 6H), 0.72 (dd, *J* = 11.7, 6.5 Hz, 3H).

^{13}C NMR (76 MHz, Major isomer, $CDCl_3$) δ 157.6, 134.2, 127.9, 126.6, 125.8, 125.3 120.8, 110.7, 55.5, 41.7, 40.2, 33.1, 19.7, 18.9, 18.8.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{22}ONa^+$: 253.1563, found: 235.1562

4'-Methoxy-2,3',4-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6d)

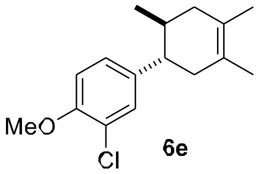


6d

4'-Methoxy-2,3',4-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl was synthesized according to the GP2 using 1-methoxy-2-methyl-4-(prop-1-en-1-yl)benzene (34.30 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), isoprene (64 µL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light for 16 h. The purification via FC (pentane: Et$_2$O = 95:5) gave the product (29.90 mg, 0.13 mmol, 65%, d.r. = 11:10) as a clear liquid.

^{1}H-NMR (300 MHz, Major isomer, CDCl$_3$): δ (ppm) = 6.96 (d, J = 7.8 Hz, 2H), 6.76 (d, J = 8.0 Hz, 1H), 5.52 – 5.25 (m, 1H), 3.82 (s, 3H), 2.34 – 2.03 (m, 7H), 1.99 – 1.74 (m, 2H), 1.70 (q, J = 1.6 Hz, 3H), 0.72 (d, J = 6.2 Hz, 3H).
^{13}C-NMR (76 MHz, Major isomer, CDCl$_3$): δ (ppm) = 156.1, 137.9, 133.9, 130.1, 126.3, 125.8, 121.1, 109.9, 55.5, 47.1, 40.0, 35.5, 34.0, 23.5, 20.5, 16.5.
MS (EI): *m/z* 162.0 (100) [M-C$_5$H$_8$]$^+$; 230.1 (11) [M]$^+$; 215.1 (5) [M-CH$_3$]$^+$.

3'-Chloro-4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6e)



6e

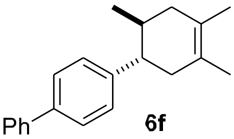
3'-Chloro-4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl was synthesized according to the GP2 using 2-chloro-1-methoxy-4-(prop-1-en-1-yl)benzene (d.r. = 2:1, 36.40 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68 µL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light for 16 h. The purification via FC (pentane: Et$_2$O = 95:5) gave the product (35.00 mg, 0.12 mmol, 61%, d.r. = 2:1) as a clear liquid.

^{1}H NMR (300 MHz, Major isomer, CDCl$_3$) δ 7.21 – 7.14 (m, 1H), 7.01 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 2.31 (td, *J* = 9.8, 6.5 Hz, 1H), 2.17 – 1.99 (m, 3H), 1.80 (s, 2H), 1.71 – 1.57 (m, 6H), 0.70 (dd, *J* = 6.3, 2.6 Hz, 3H).

^{13}C NMR (76 MHz, Major isomer, CDCl$_3$) δ 153.2, 139.5, 129.3, 126.9, 125.5, 125.3, 122.2, 112.1, 56.3, 47.8, 41.7, 41.6, 34.3, 20.0, 18.8, 18.7.

HRMS (ESI) m/z: [M+Na]$^+$ calculated for C$_{16}$H$_{21}$OClNa$^+$: 287.1173, found: 287.1173

2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1':4',1''-terphenyl (6f)


6f

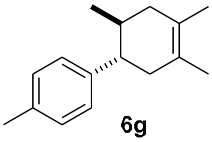
2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1':4',1''-terphenyl was synthesized according to the GP2 using 4-(prop-1-en-1-yl)-1,1'-biphenyl (d.r. = 4:3, 38.82 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68.00 μL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light for 16 h. The purification via FC (pentane: Et_2O) = 95:5 gave the product (35.00 mg, 0.12 mmol, 61%, d.r. = 4:3) as a clear liquid.

^{1}H NMR (300 MHz, Major isomer, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.57 – 7.48 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.30 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 2.44 (td, *J* = 10.3, 6.0 Hz, 1H), 2.33 – 2.05 (m, 3H), 2.03 – 1.79 (m, 2H), 1.65 (d, *J* = 8.0 Hz, 6H), 0.75 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (76 MHz, Major isomer, $CDCl_3$) δ 145.3, 141.2, 138.8, 128.8 128.2, 127.1, 127.1, 127.0, 125.5, 48.5, 41.8, 41.6, 34.1, 20.2, 18.9, 18.8.

MS (EI) : *m/z* 194.1 (100) $[M-C_6H_{10}]^+$; 276.2 (20) $[M]^+$.

2,4,4',5-Tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6g)


6g

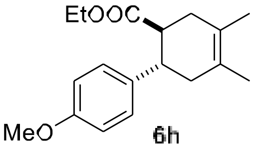
2,4,4',5-Tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl was synthesized according to the GP2 using 1-methyl-4-(prop-1-en-1-yl)benzene (*d.r.* = 4:1, 26.40 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68μL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 445 nm light for 16 h. The purification via FC (pentane: Et_2O = 95:5) gave the product (27.00 mg, 0.13 mmol, 64% d.r. = 4:1) as a clear liquid.

^{1}H NMR (300 MHz, Major isomer, $CDCl_3$) δ 7.19 – 6.92 (m, 4H), 2.33 (d, *J* = 1.0 Hz, 4H), 2.29 – 2.17 (m, 1H), 2.16 – 2.03 (m, 2H), 1.96 – 1.71 (m, 2H), 1.70 – 1.56 (m, 6H), 0.72 (dd, *J* = 6.5, 4.9 Hz, 3H).

^{13}C NMR (76 MHz, Major isomer, $CDCl_3$) δ 143.0, 135.2, 129.0, 128.6, 128.0, 127.5, 125.5, 125.3, 48.3, 41.8, 41.6, 34.0, 21.0, 20.0, 18.7, 18.6.

MS (EI): *m/z* 132.5 (100) $[M-C_6H_{10}]^+$; 214.2 (30) $[M]^+$.

4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (6h)



6h

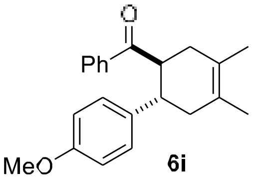
4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate was synthesized according to the GP2 using ethyl (*E*)-3-(4-methoxyphenyl)acrylate (41.20 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68.00 μL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 445 nm light for 24 h. The purification via FC (pentane: Et_2O = 95:5) gave the product (52.00 mg, 0.18 mmol, 90%) as a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.05 (m, 2H), 6.89 – 6.73 (m, 2H), 3.86 (qd, *J* = 7.1, 1.5 Hz, 2H), 3.77 (d, *J* = 1.3 Hz, 3H), 2.95 (ddd, *J* = 11.3, 9.4, 7.2 Hz, 1H), 2.78 (td, *J* = 11.1, 5.2 Hz, 1H), 2.50 – 2.34 (m, 1H), 2.27 – 2.13 (m, 3H), 1.66 (s, 6H), 0.94 (td, *J* = 7.1, 1.2 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 175.3, 158.2, 136.2, 128.5, 125.4, 123.8, 113.7, 60.0, 55.3, 47.2, 43.0, 40.4, 35.6, 18.8, 18.7, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{24}O_3Na^+$: 311.1617, found: 311.1618

4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (6i)



6i

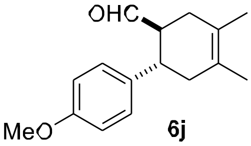
4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone was synthesized according to the GP2 using (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (47.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68 μL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 445 nm light for 24 h. The purification via FC (pentane: Et_2O= 95:5) gave the product (57.50 mg, 0.18 mmol, 90%) as a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.74 (m, 2H), 7.53 – 7.44 (m, 1H), 7.42 – 7.32 (m, 2H), 7.19 – 7.03 (m, 2H), 6.75 – 6.60 (m, 2H), 3.96 (td, *J* = 10.6, 5.5 Hz, 1H), 3.69 (s, 3H), 3.24 (ddd, *J* = 11.2, 9.4, 7.0 Hz, 1H), 2.29 (t, *J* = 10.2 Hz, 4H), 1.68 (s, 6H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 203.8, 157.8, 137.4, 136.8, 132.8, 128.5, 128.3, 128.1, 125.8, 124.2, 113.8, 55.2, 47.7, 42.2, 40.9, 37.1, 18.8, 18.7.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{24}O_2Na^+$: 343.1669, found: 343.1669

4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde (6j)


6j

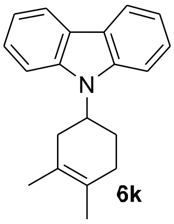
4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde was synthesized according to the GP2 using (*E*)-3-(4-methoxyphenyl)acrylaldehyde (32.40 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68 µL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 445 nm light for 24 h. The purification via FC (pentane: Et_2O = 95:5) gave the product (40.00 mg, 0.16 mmol, 82%) as a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.45 (d, *J* = 3.1 Hz, 1H), 7.21 – 7.02 (m, 2H), 6.94 – 6.76 (m, 2H), 3.78 (s, 3H), 3.03 (ddd, *J* = 10.5, 8.7, 6.5 Hz, 1H), 2.74 (dddd, *J* = 10.3, 8.9, 5.6, 3.1 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.22 (s, 2H), 2.06 (dd, *J* = 17.2, 5.5 Hz, 1H), 1.75 – 1.57 (m, 6H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 204.8, 158.3, 135.5, 128.4, 125.7, 123.4, 114.2, 55.3, 52.4, 40.7, 39.8, 31.2, 18.8.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{16}H_{20}O_2Na^+$: 267.1356, found: 267.1353

9-(3,4-Dimethylcyclohex-3-en-1-yl)-9H-carbazole (6k)


6k

9-(3,4-Dimethylcyclohex-3-en-1-yl)-9H-carbazole was synthesized according to the GP2 using 9-vinyl-9H-carbazole (38.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 2,3-dimethylbuta-1,3-diene (68 µL, 0.60 mmol, 3.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light for 24 h. The purification via FC (pentane: Et_2O = 90:10) gave the product (16.00 mg, 0.06 mmol, 29%) as a white solid.

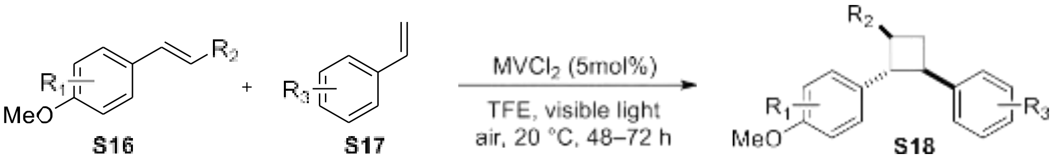
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 8.05 (m, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.43 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 2H), 7.26 – 7.18 (m, 2H), 4.80 (dddd, *J* = 12.9, 11.3, 5.9, 3.3 Hz, 1H), 3.04 (t, *J* = 14.4 Hz, 1H), 2.80 – 2.59 (m, 1H), 2.37 (d, *J* = 10.2 Hz, 1H), 2.23 (d, *J* = 17.2 Hz, 2H), 2.12 – 1.95 (m, 1H), 1.72 (d, *J* = 16.8 Hz, 6H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 139.8, 126.1, 125.4, 124.5, 123.4, 120.4, 118.6, 110.2, 52.5, 35.0, 32.7, 27.9, 19.2, 18.9.

HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{22}N^+$: 276.1747, found: 276.1747

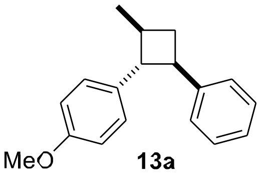
6. Synthesis and characterization data of the [2+2] cycloaddition product

6.1 General procedure for the [2+2] cycloaddition. (GP3)



In a 10 mL headspace vial, olefin **S16** (0.20 mmol, 1.00 eq.) was dissolved in dry TFE (dried over molecular sieve1 mL), followed by addition of olefin **S17** (0.40 mmol, 2.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.) under aerobic condition. Afterwards the headspace vial was sealed and irradiated with LED (10W) for 48 h or 72 h at 20°C. The reaction mixture was diluted with brine (75 mL) and extracted with dichloromethane (25 mL×3). The combined organic layers were dried over anhydrous sodium sulfate. The dried solution was filtered, the filtrate was concentrated under vacuum and the product was purified via FC.

1-Methoxy-4-(2-methyl-4-phenylcyclobutyl)benzene (13a)

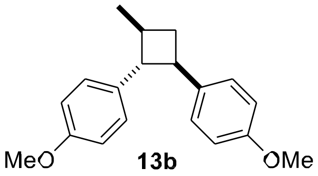


13a

1-Methoxy-4-(2-methyl-4-phenylcyclobutyl)benzene was synthesized according to the GP3 using *trans*-anethole (29.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), styrene (46 µL, 0.40 mmol, 2.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light (10 W) for 48 h. The purification via FC (pentane: Et_2O) = 90:10 gave the product (32.50 mg, 0.13 mmol, 65%) as a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.15 (m, 5H), 6.94 – 6.79 (m, 2H), 3.80 (s, 3H), 3.41 (td, *J* = 10.0, 7.9 Hz, 1H), 2.96 (t, *J* = 9.5 Hz, 1H), 2.53 (dt, *J* = 9.9, 7.8 Hz, 1H), 2.34 (tdd, *J* = 15.8, 7.6, 4.6 Hz, 1H), 1.71 (q, *J* = 10.0 Hz, 1H), 1.20 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (76 MHz, $CDCl_3$) δ 158.1, 144.7, 135.9, 128.3, 127.9, 126.7, 126.0, 113.8, 55.6, 55.3, 44.2, 35.6, 34.0, 20.6.
HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{20}ONa^+$: 275.1406, found: 275.1406

3-Methylcyclobutane-1,2-diyl)bis(methoxybenzene) (13b)



13b

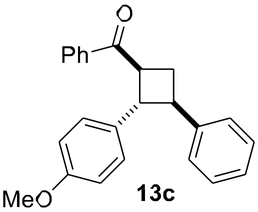
3-Methylcyclobutane-1,2-diyl)bis(methoxybenzene) was synthesized according to the GP3 using *trans*-anethole (29.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), 1-methoxy-4-vinylbenzene (53.2 µL, 0.40 mmol, 2.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm (10 W) light for 48 h. The purification via FC (pentane: Et_2O = 90:10) gave the product (27.00 mg, 0.10 mmol, 48%) as a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 7.04 (m, 4H), 6.92 – 6.77 (m, 4H), 3.79 (d, *J* = 3.7 Hz, 6H), 3.31 (td, *J* = 10.0, 7.9 Hz, 1H), 2.89 (t, *J* = 9.5 Hz, 1H), 2.58 – 2.41 (m, 1H), 2.41 – 2.22 (m, 1H), 1.65 (q, *J* = 10.0 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 158.1, 157.9, 136.9, 136.0, 127.8, 127.7, 113.8, 113.7, 55.9, 55.4, 43.7, 35.4, 34.3, 20.6.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{22}O_2Na^+$: 305.1512, found: 305.1510

2-(4-Methoxyphenyl)-3-phenylcyclobutyl)(phenyl)methanone (13c)



13c

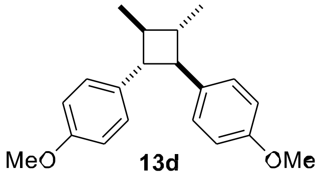
2-(4-Methoxyphenyl)-3-phenylcyclobutyl)(phenyl)methanone was synthesized according to the GP3 using (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (47.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), styrene (46 µL, 0.40 mmol, 2.00 eq.), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 445 nm light (10 W) for 72 h. The purification via FC (pentane: Et_2O) = 90:10 gave the product (25.50 mg, 0.07 mmol, 35%) as a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.56 – 7.47 (m, 1H), 7.43 – 7.35 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.15 (m, 5H), 6.87 – 6.78 (m, 2H), 4.02 – 3.87 (m, 2H), 3.77 (s, 3H), 3.76 – 3.63 (m, 1H), 2.79 – 2.65 (m, 1H), 2.54 – 2.38 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 200.04, 158.52, 143.57, 136.13, 134.75, 133.23, 128.69, 128.62, 128.54, 128.26, 126.90, 126.58, 114.06, 55.42, 49.53, 46.83, 43.13, 30.43.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{24}H_{22}O_2Na^+$: 365.1512, found: 365.1511

3,4-Dimethylcyclobutane-1,2-diyl)bis(methoxybenzene) (13d)



13d

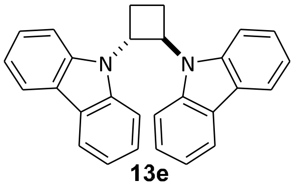
3,4-Dimethylcyclobutane-1,2-diyl)bis(methoxybenzene) was synthesized according to the GP3 using *trans*-anethole (29.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm light (10 W) for 48 h. The purification via FC (pentane: Et_2O = 90:10) gave the product (12.00 mg, 0.04 mmol, 20%) as a clear liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 – 7.08 (m, 4H), 6.88 – 6.77 (m, 4H), 3.78 (s, 6H), 2.85 – 2.73 (m, 2H), 1.91 – 1.76 (m, 2H), 1.21 – 1.14 (m, 6H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 157.94, 135.95, 127.76, 113.70, 55.28, 52.48, 43.23, 18.91.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{20}H_{24}O_2Na^+$: 319.1668, found: 319.1667

1,2-Di(9H-carbazol-9-yl)cyclobutane (13e)



13e

1,2-Di(9H-carbazol-9-yl)cyclobutane was synthesized according to the GP3 using 9-vinyl-9H-carbazole (38.60 mg, 0.20 mmol, 1.00 eq.), TFE (1 mL), and methyl viologen (2.60 mg, 0.01 mmol, 0.05 eq.). The mixture was irradiated with 520 nm (10 W) light for 48 h. The purification via FC (pentane: Et_2O = 90:10) gave the product (15.50 mg, 0.04 mmol, 40%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 – 7.97 (m, 4H), 7.57 (d, *J* = 8.3 Hz, 4H), 7.40 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 4H), 7.25 – 7.18 (m, 4H), 6.31 (td, *J* = 7.2, 2.3 Hz, 2H), 3.12 (qd, *J* = 6.6, 3.1 Hz, 2H), 2.75 (td, *J* = 9.8, 7.2 Hz, 2H).

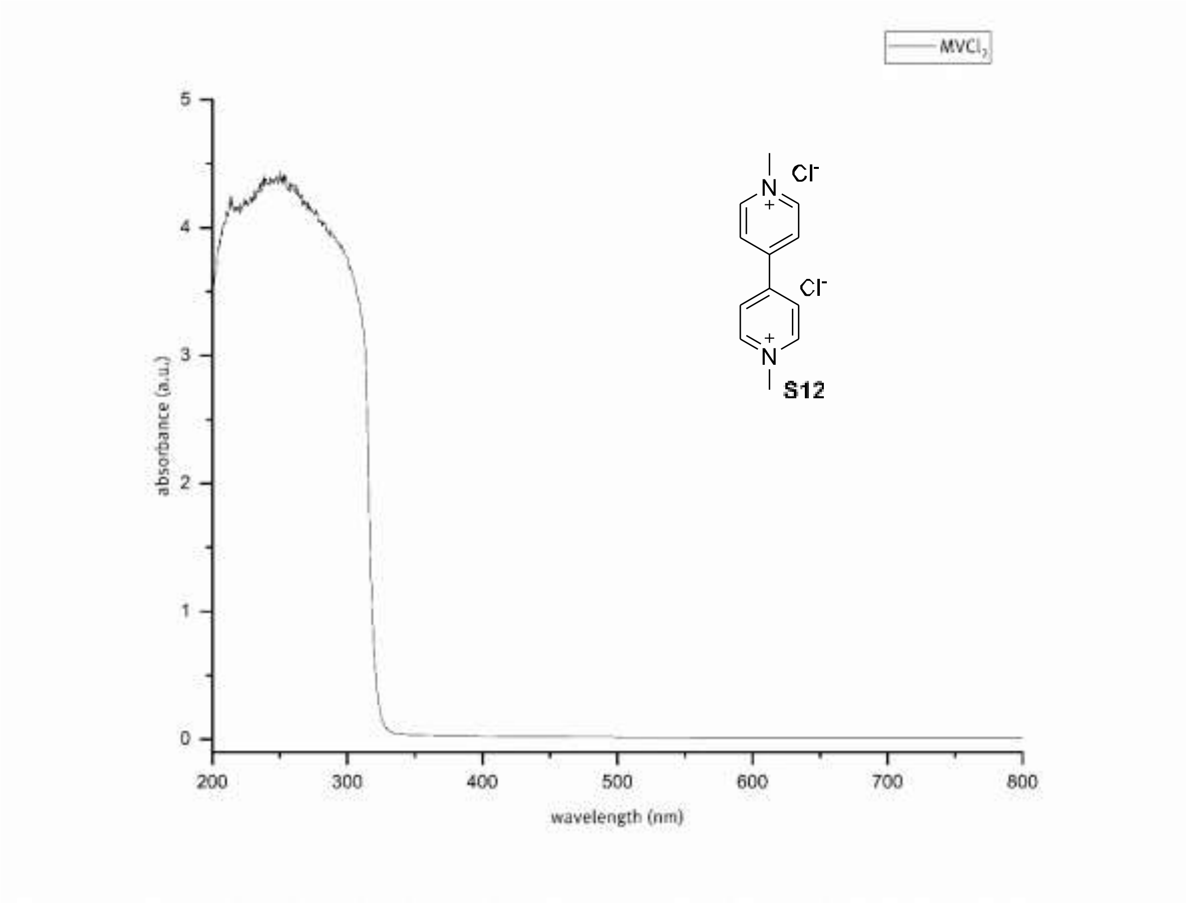
^{13}C NMR (76 MHz, $CDCl_3$) δ 140.06, 125.91, 123.70, 120.65, 119.48, 109.79, 54.55, 21.02.

HRMS (ESI) m/z: HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{22}N_2Na^+$: 409.1675, found: 409.1673

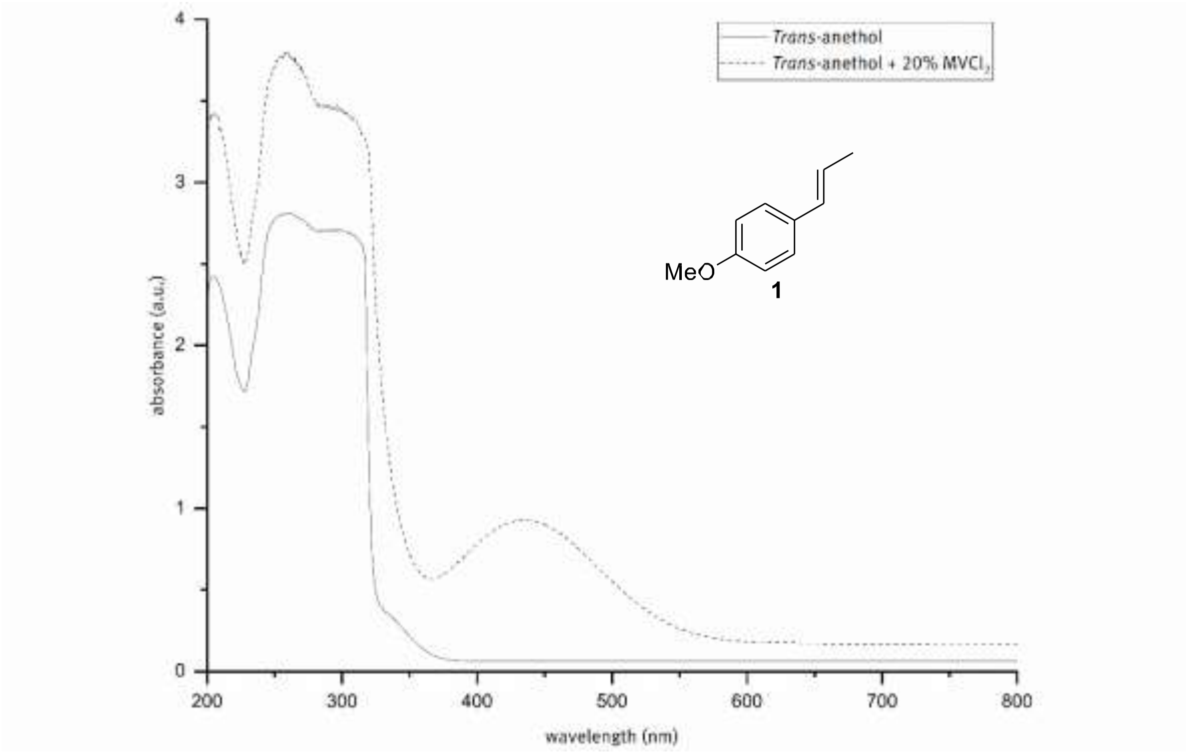
7. UV/Vis spectra

The desired molecule (0.40 mmol or 0.20 mmol) was dissolved in solvent (6 mL or respectively 3 mL) and another solution of $MVCl_2$ (103 mg, 0.40 mmol) in 4w% SDS solution or organic solution (6 mL) was prepared. A cuvette was charged with 1 mL of the solution of the analyzing compound and was diluted with another 1 mL 4w% SDS solution or organic solution. An UV/Vis spectrum at 25°C was recorded from this sample. Afterwards in another cuvette 1 mL of 4w% SDS solution or organic solution containing the analyzing compound, 0.80 mL of solvent and 0.20 mL of the $MVCl_2$ were added and the spectrum was recorded.

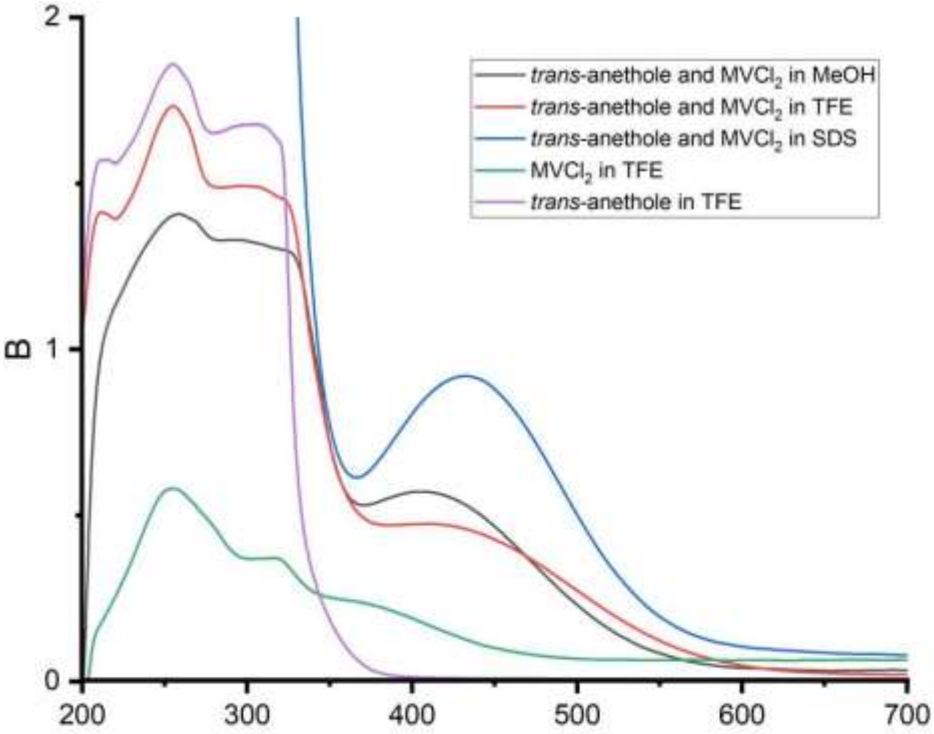
Methylviologen dichloride



Anethole



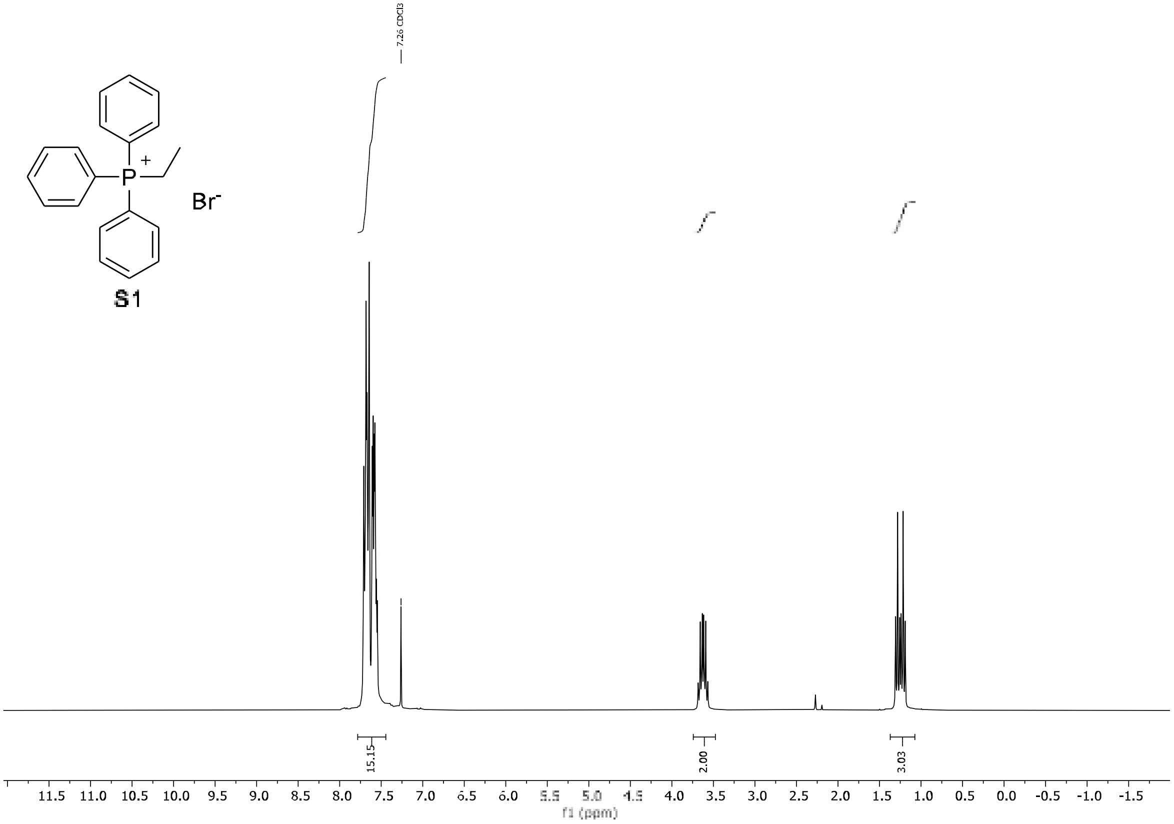
UV/Vis-measurement of only trans-anethole and trans-anethole/MVCl$_2$ in SDS. After the addition of MVCl$_2$ to trans-anethole, the solution turned from colorless to red.



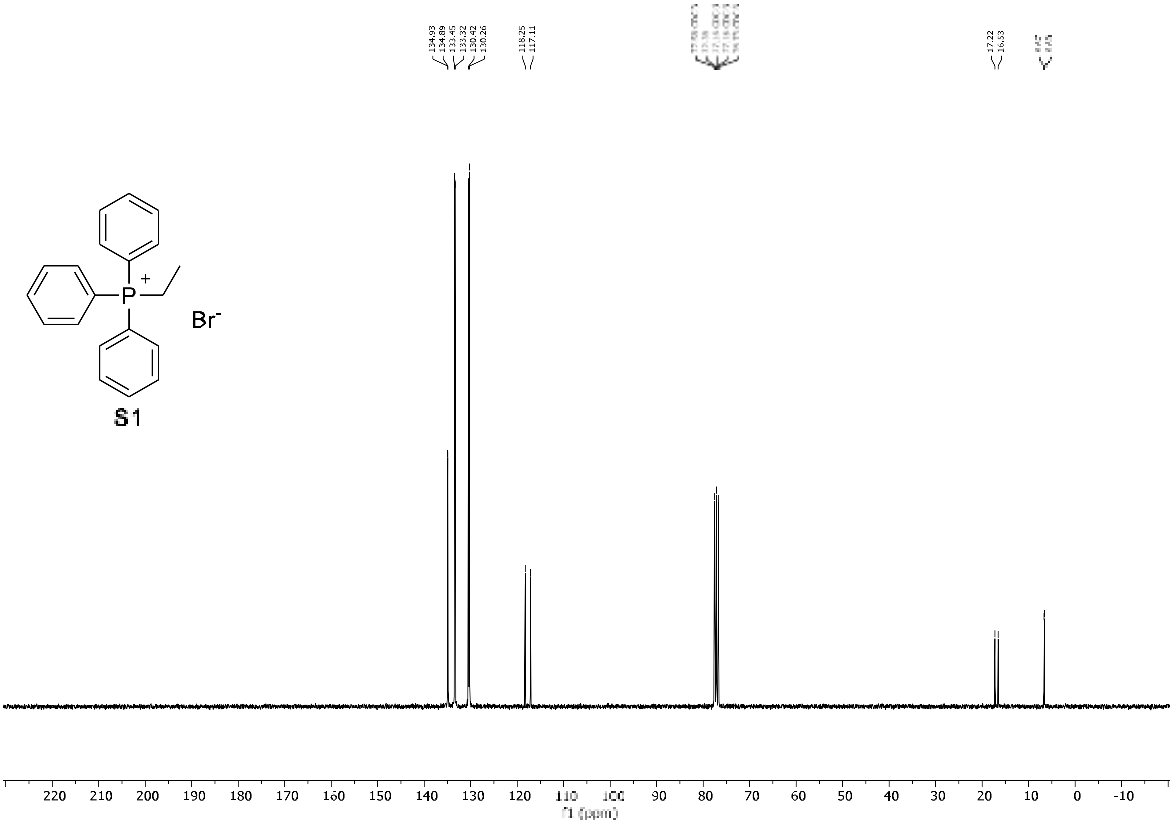
UV/Vis-measurements of trans-anethole/MVCl2 in different solvents.

8. NMR spectra

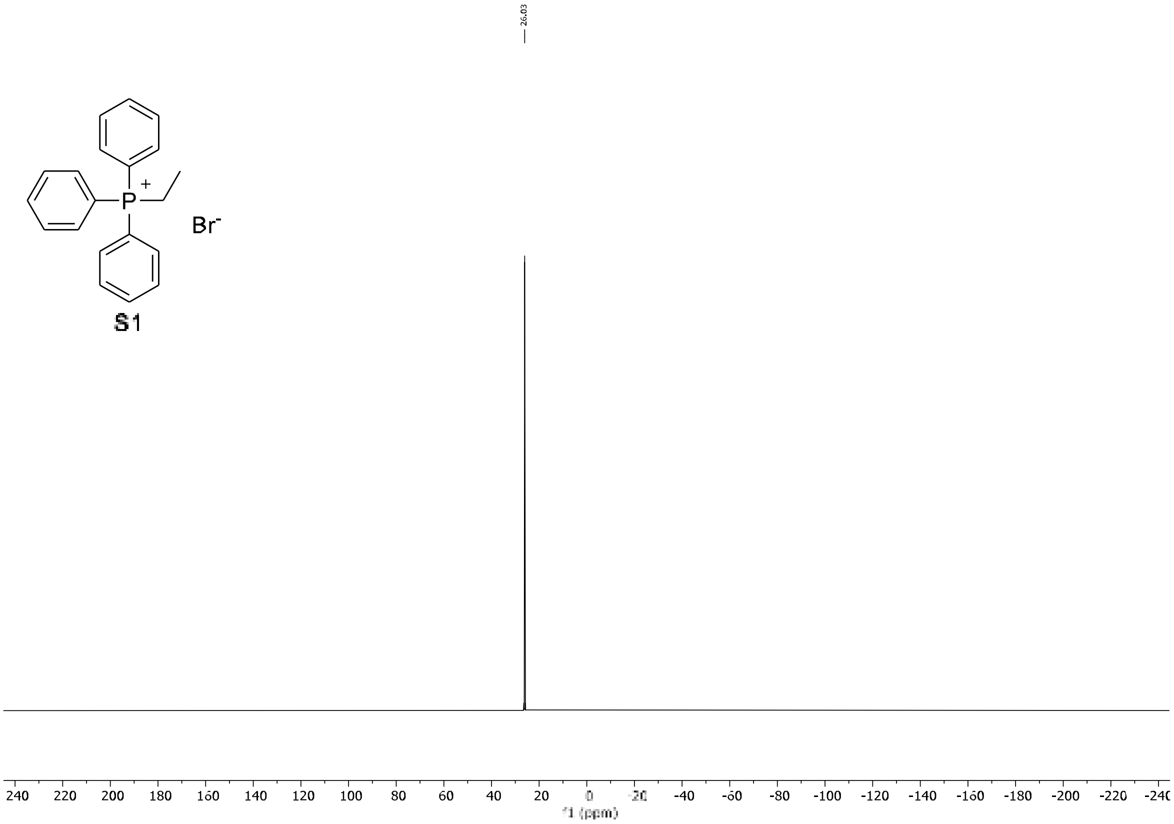
^{1}H-NMR of the Wittig reagent (S1)



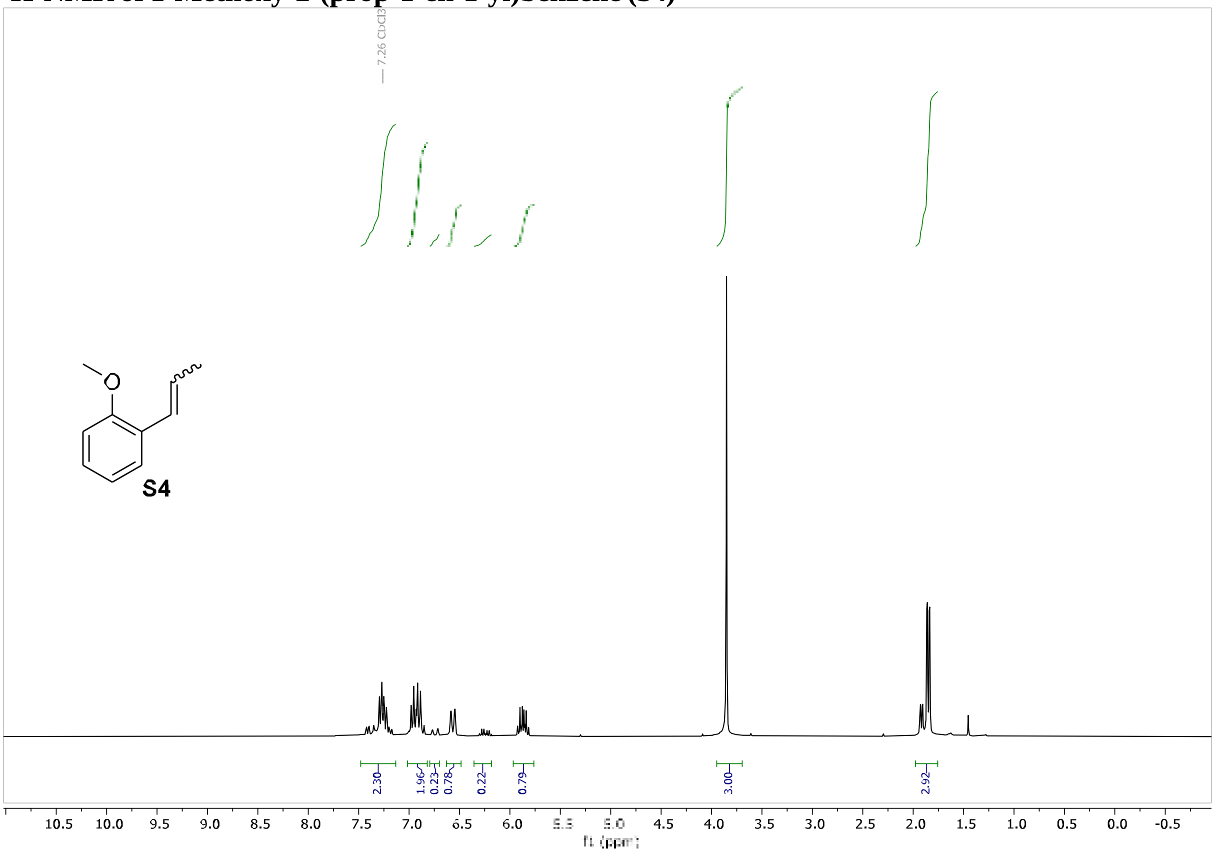
^{13}C-NMR of the Wittig reagent (S1)



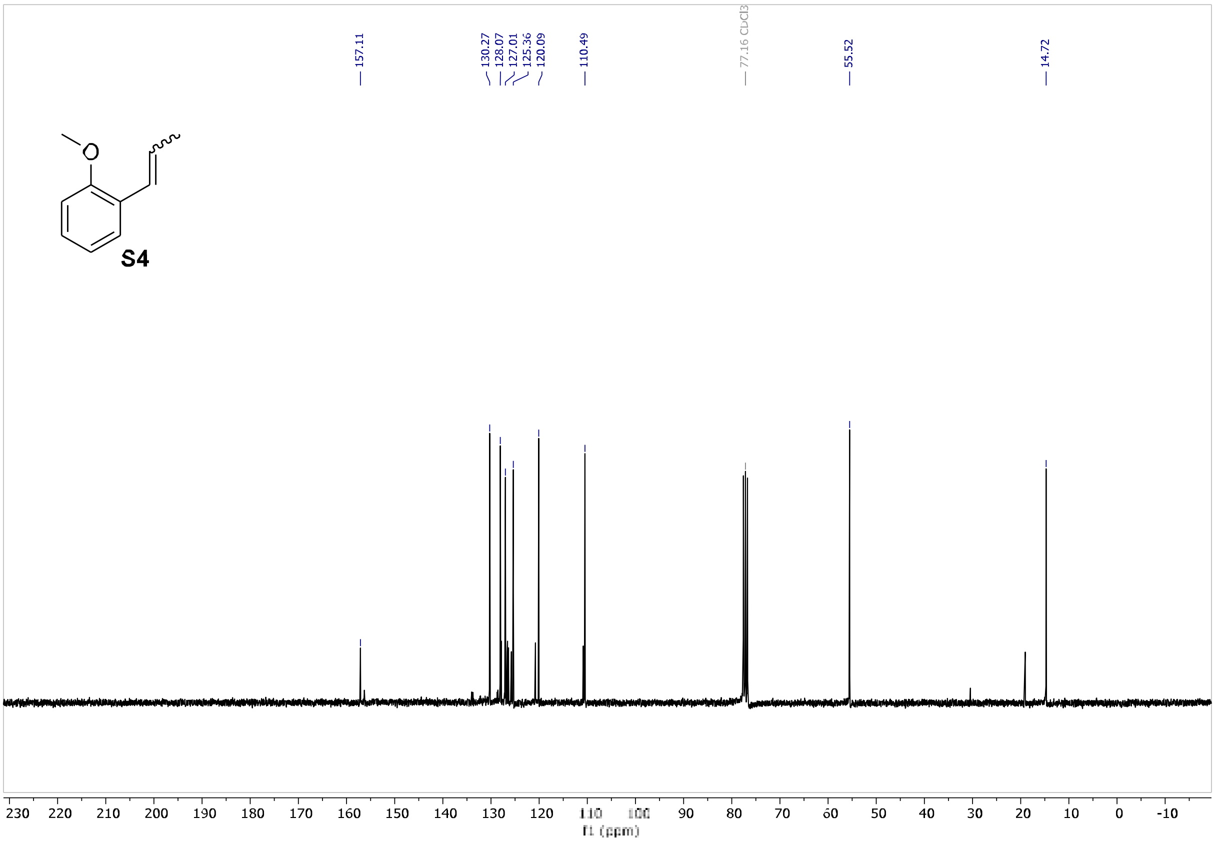
^{19}F-NMR of the Wittig reagent (S1)



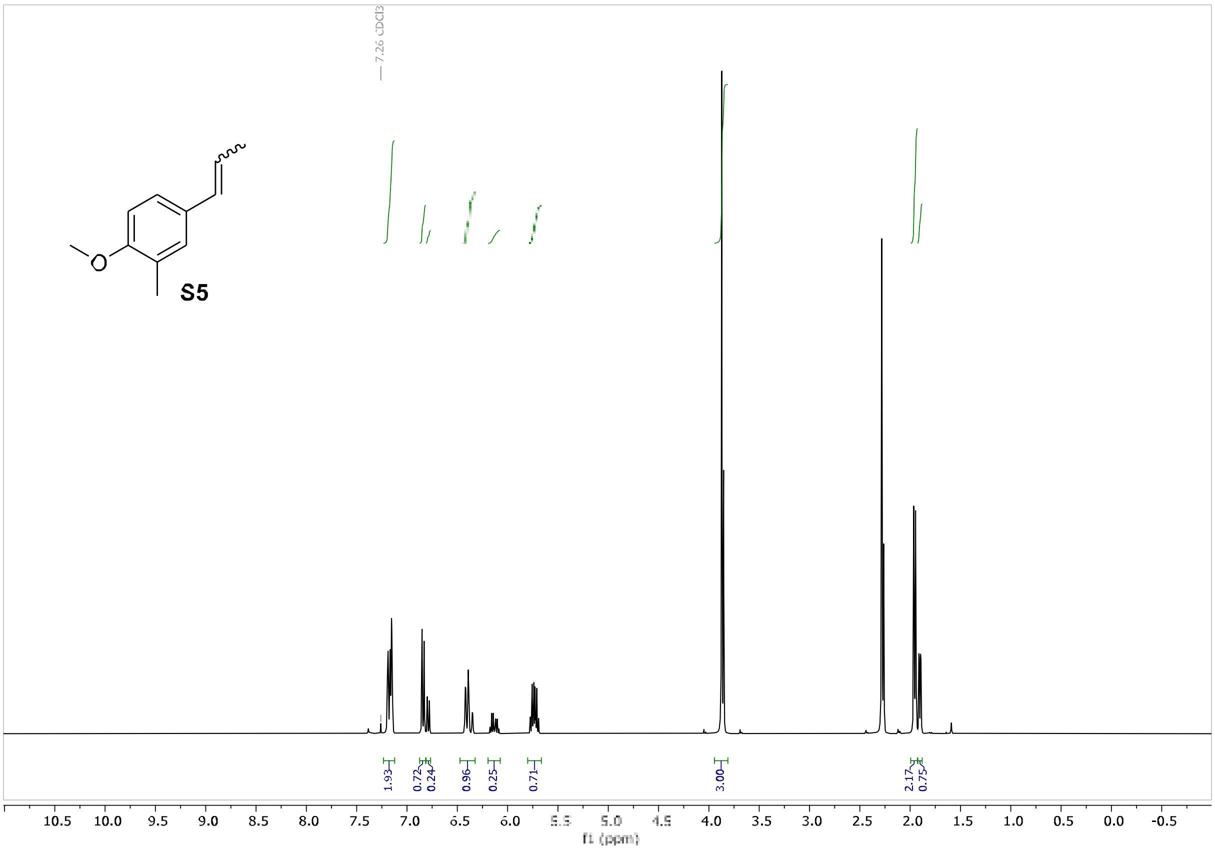
^{1}H-NMR of 1-Methoxy-2-(prop-1-en-1-yl)benzene (S4)



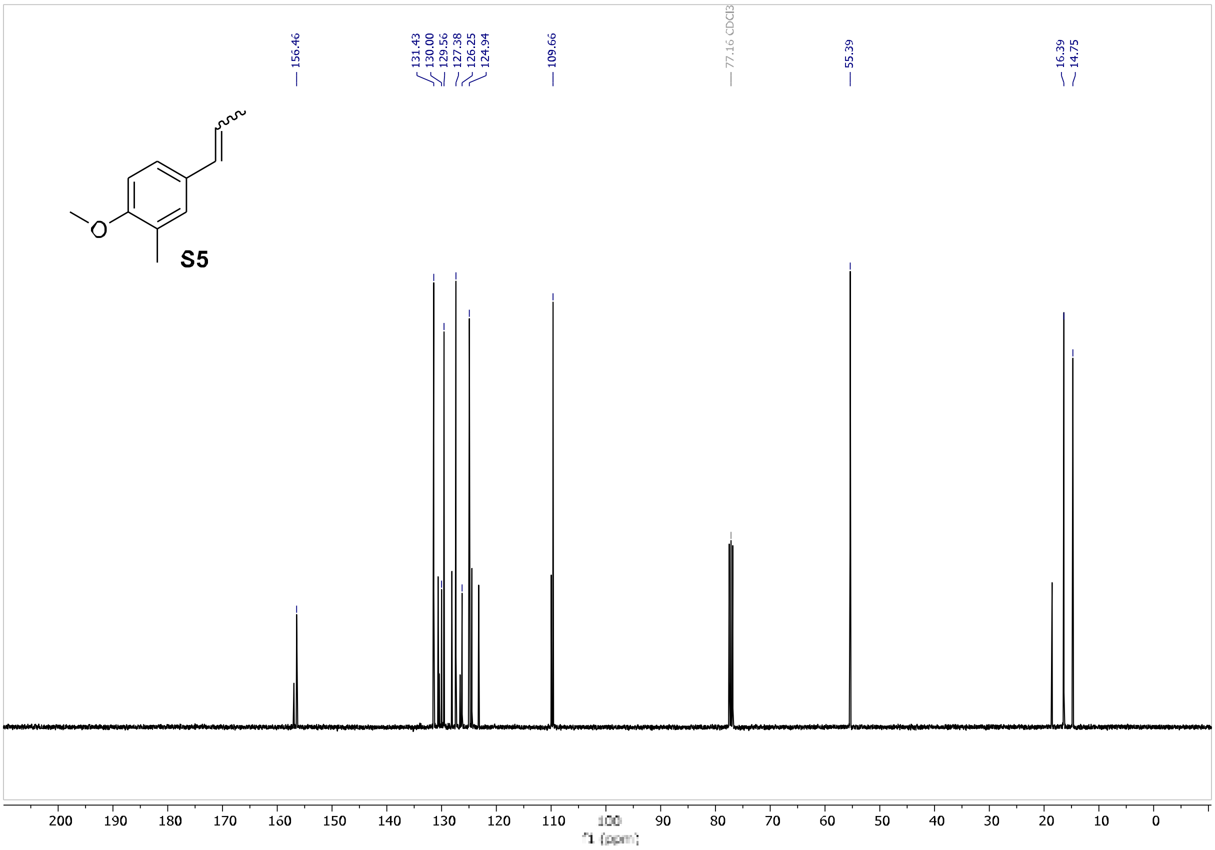
^{13}C-NMR of 1-Methoxy-2-(prop-1-en-1-yl)benzene (S4)



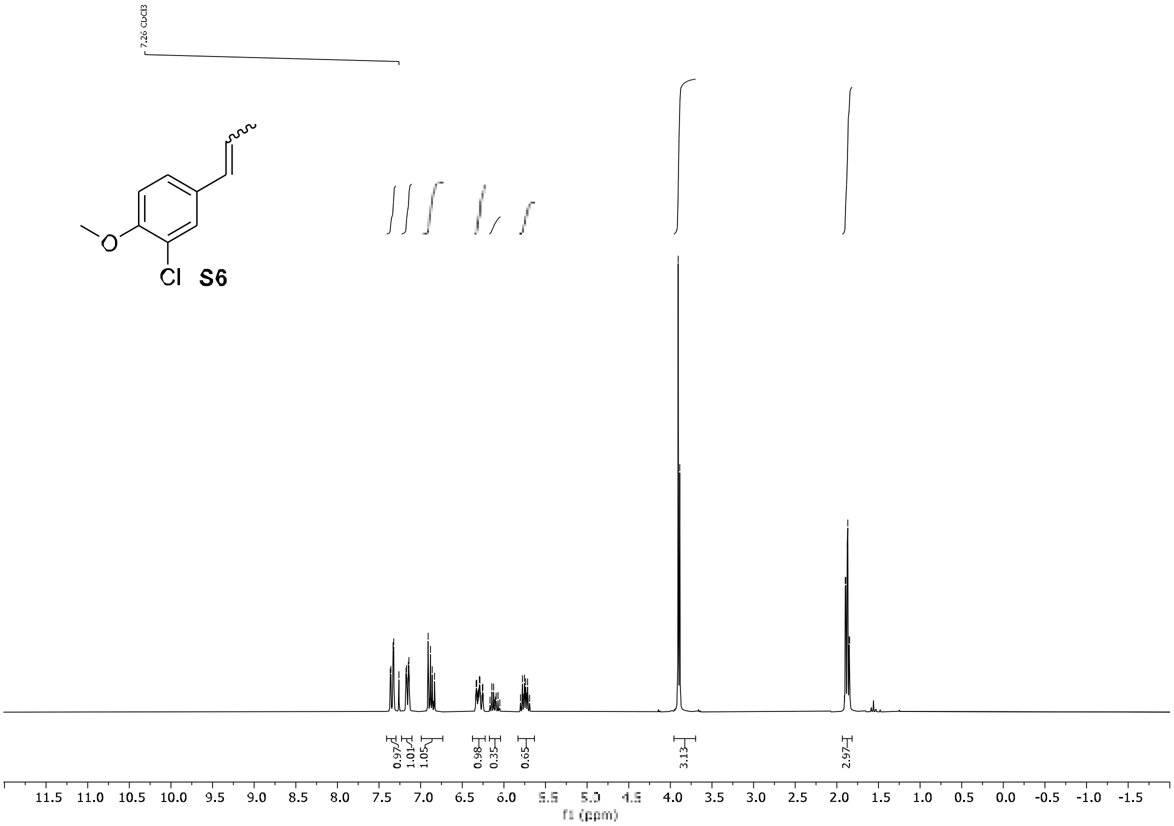
^{1}H-NMR of 2-Methyl-1-methoxy-4-(prop-1-en-1-yl)benzene (S5)



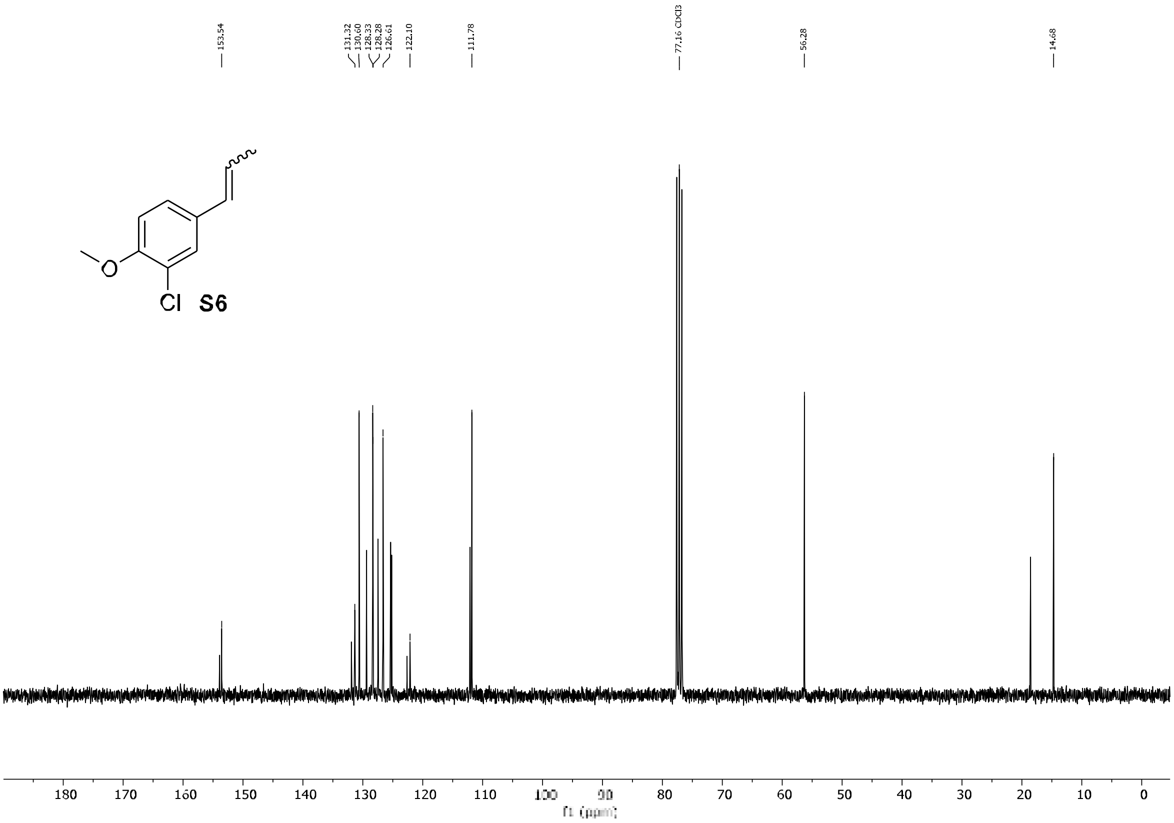
^{13}C-NMR of 2-Methyl-1-methoxy-4-(prop-1-en-1-yl)benzene (S5)



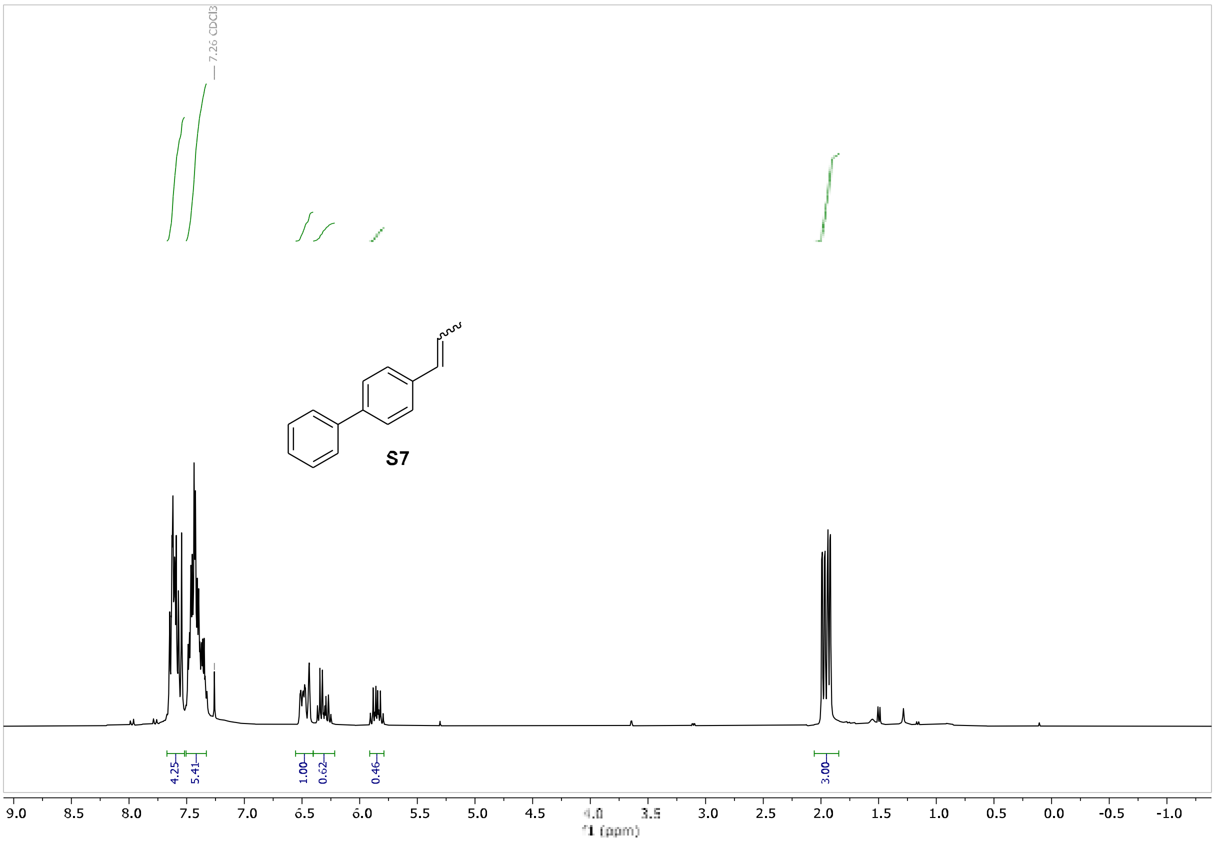
^{1}H-NMR of 2-Chloro-1-methoxy-4-(prop-1-en-1-yl)benzene (S6)



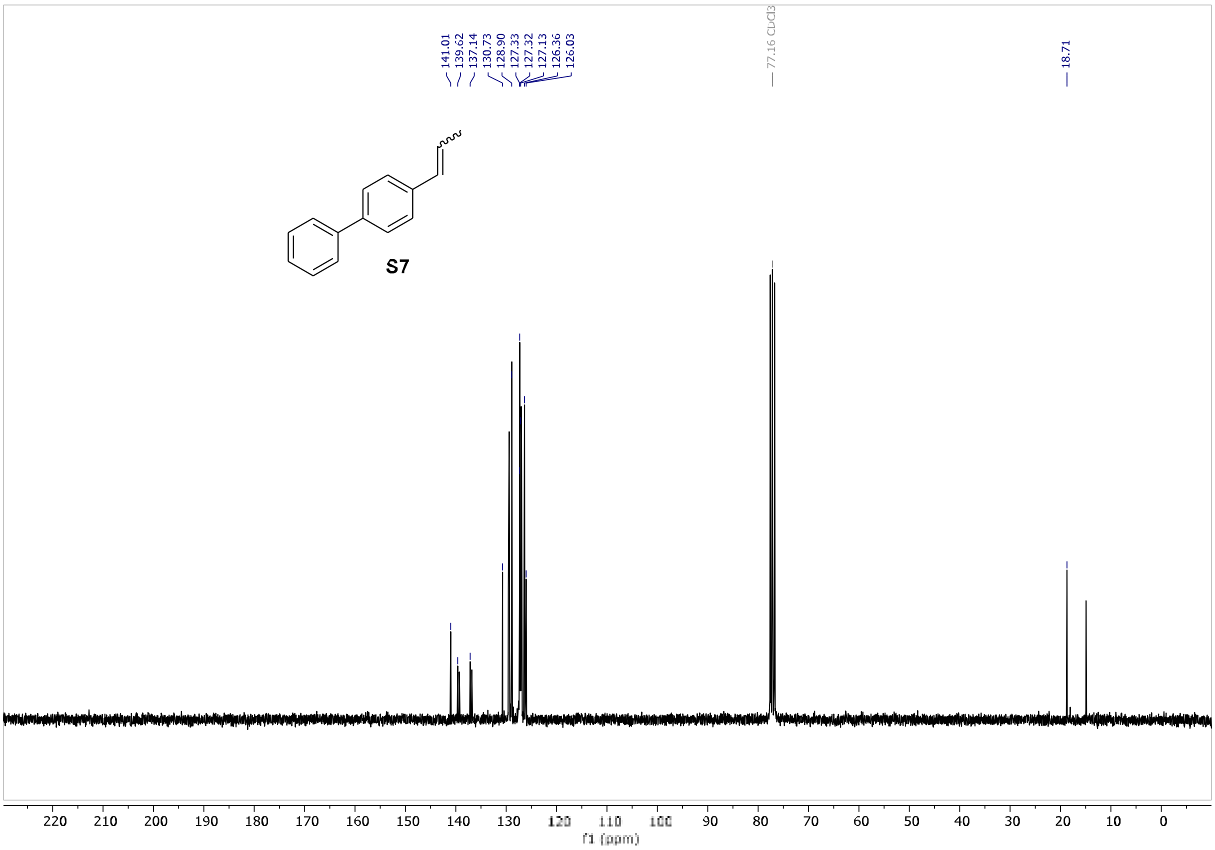
^{13}C-NMR of 2-Chloro-1-methoxy-4-(prop-1-en-1-yl)benzene (S6)



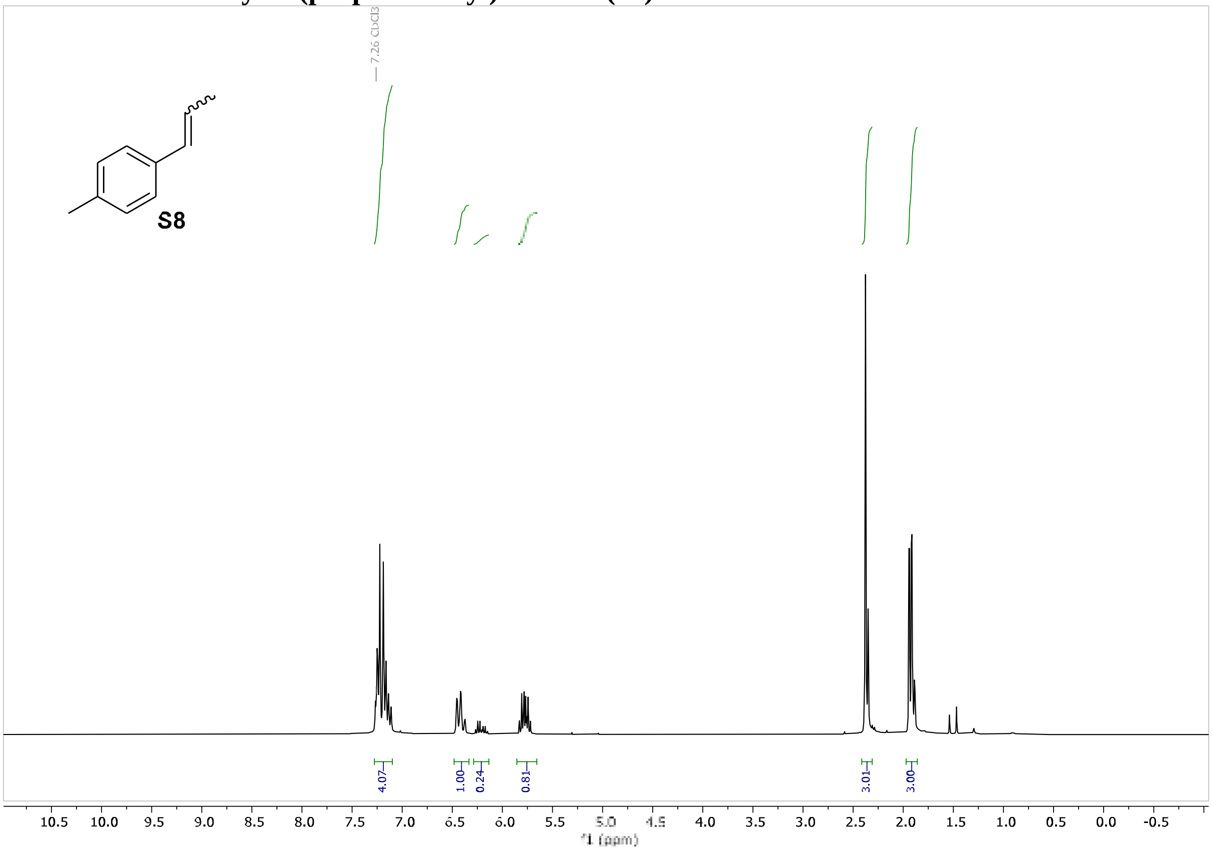
^{1}H-NMR of 4-(Prop-1-en-1-yl)-1,1'-biphenyl (S7)



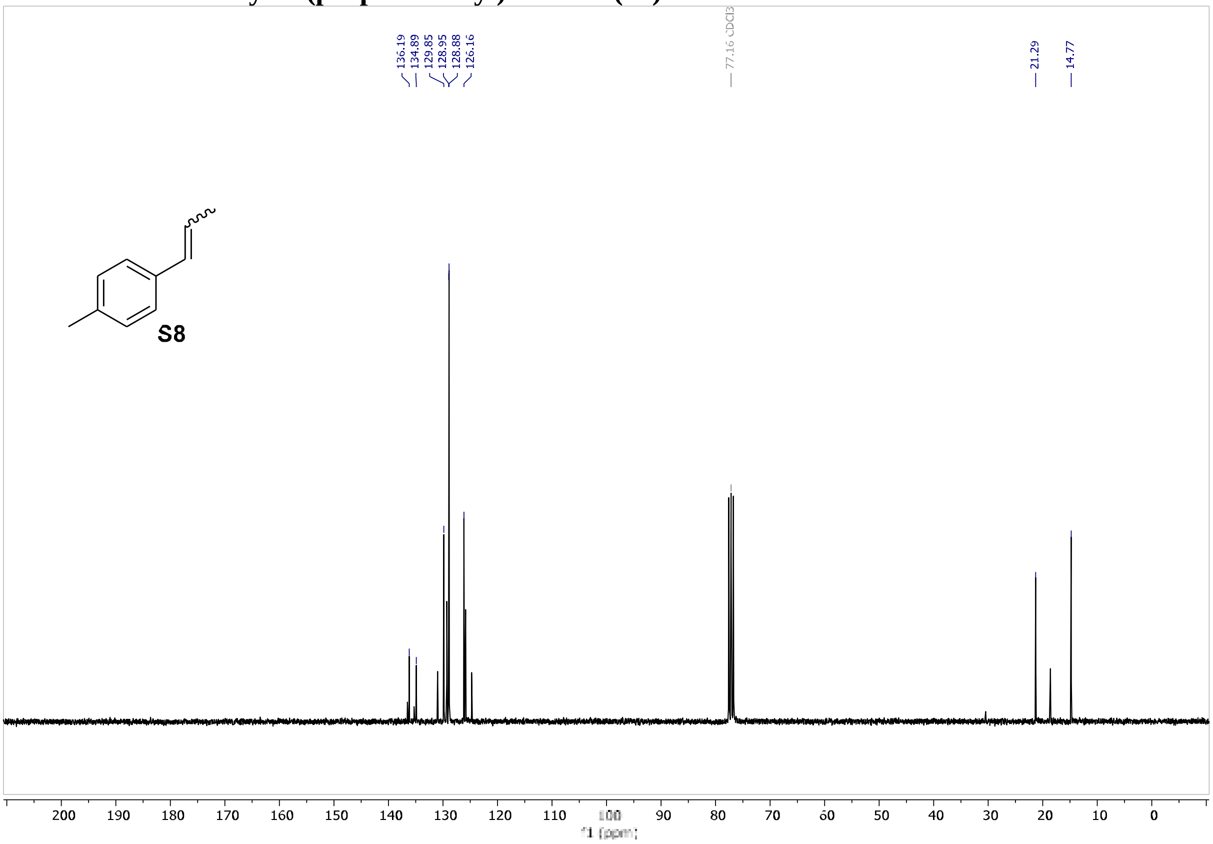
^{13}C-NMR of 4-(Prop-1-en-1-yl)-1,1'-biphenyl (S7)



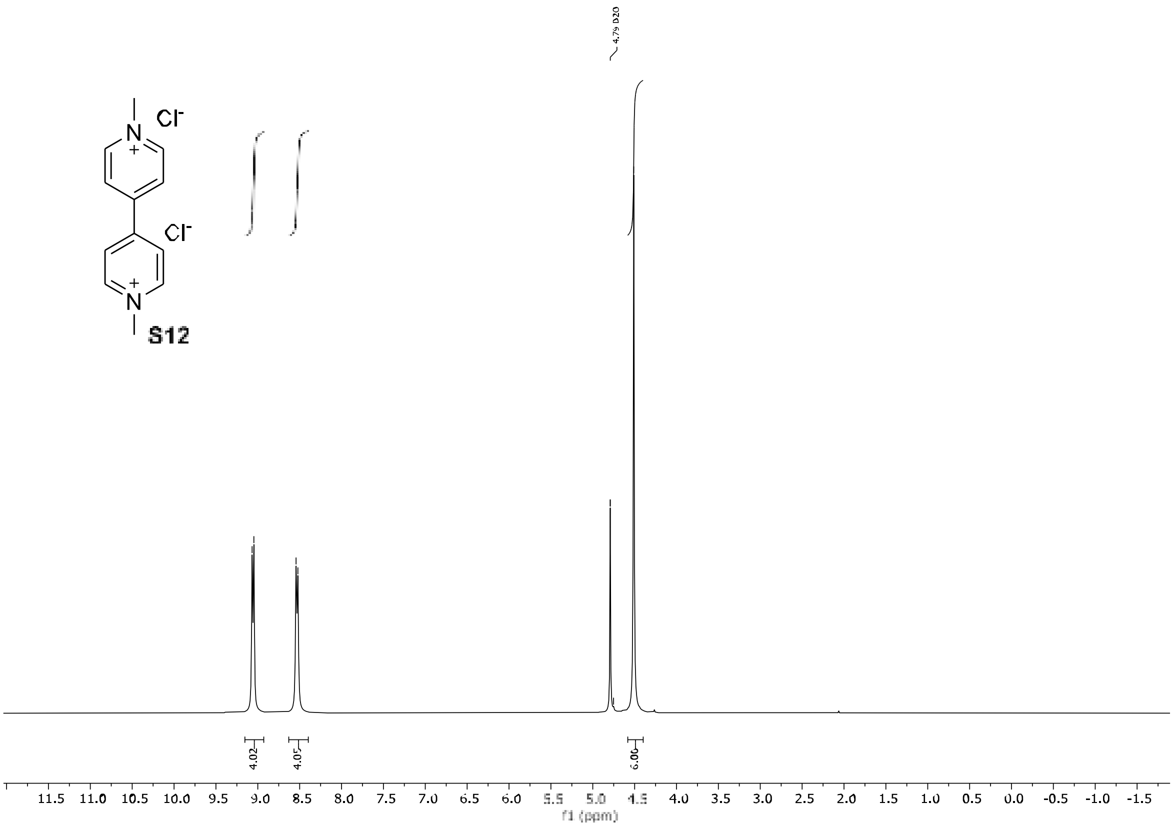
^{1}H-NMR of 1-Methyl-4-(prop-1-en-1-yl)benzene (S8)



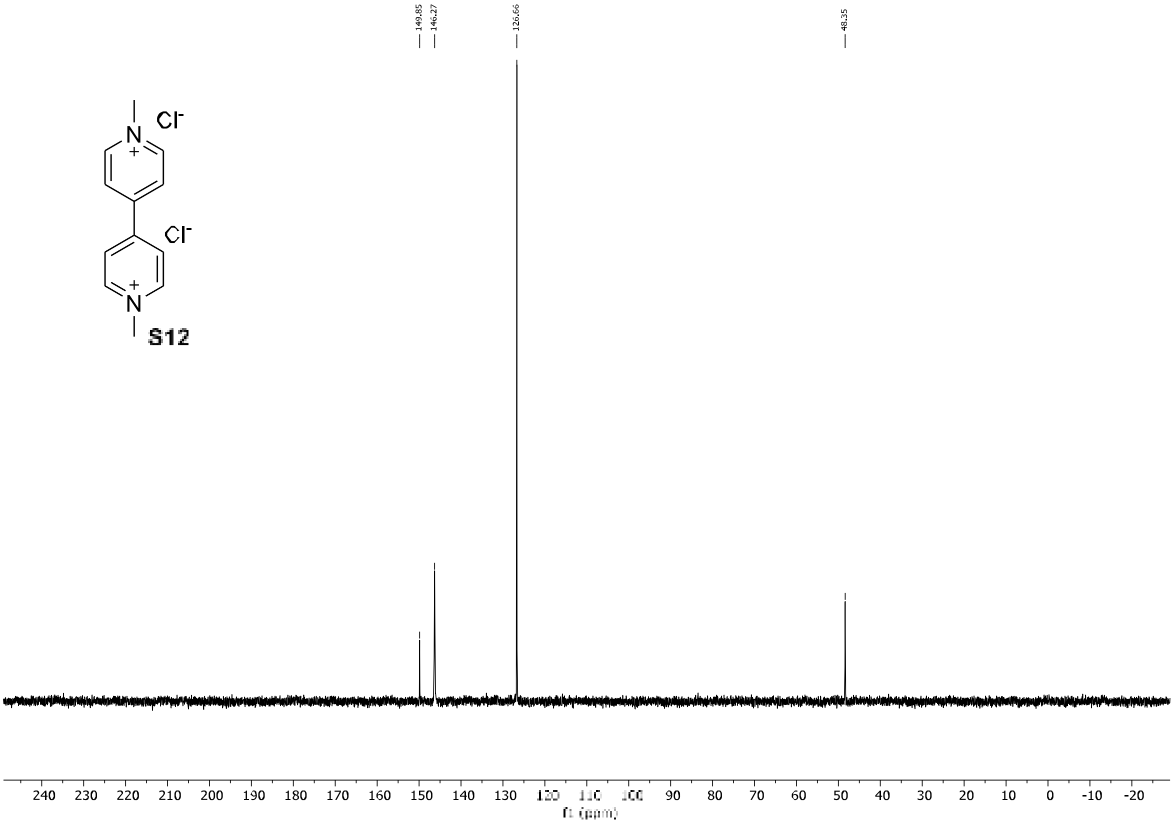
^{13}C-NMR of 1-Methyl-4-(prop-1-en-1-yl)benzene (S8)



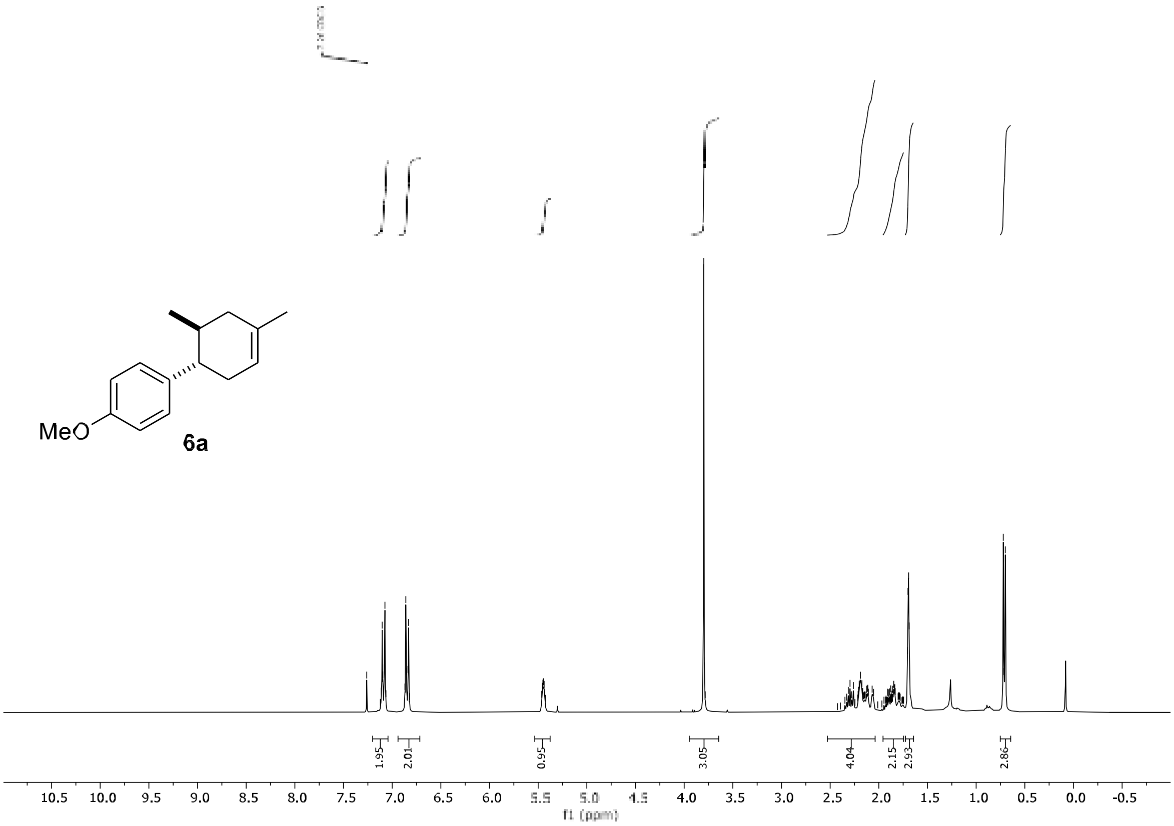
^{1}H-NMR of N,N-Dimethylbipyridinyl dichloride



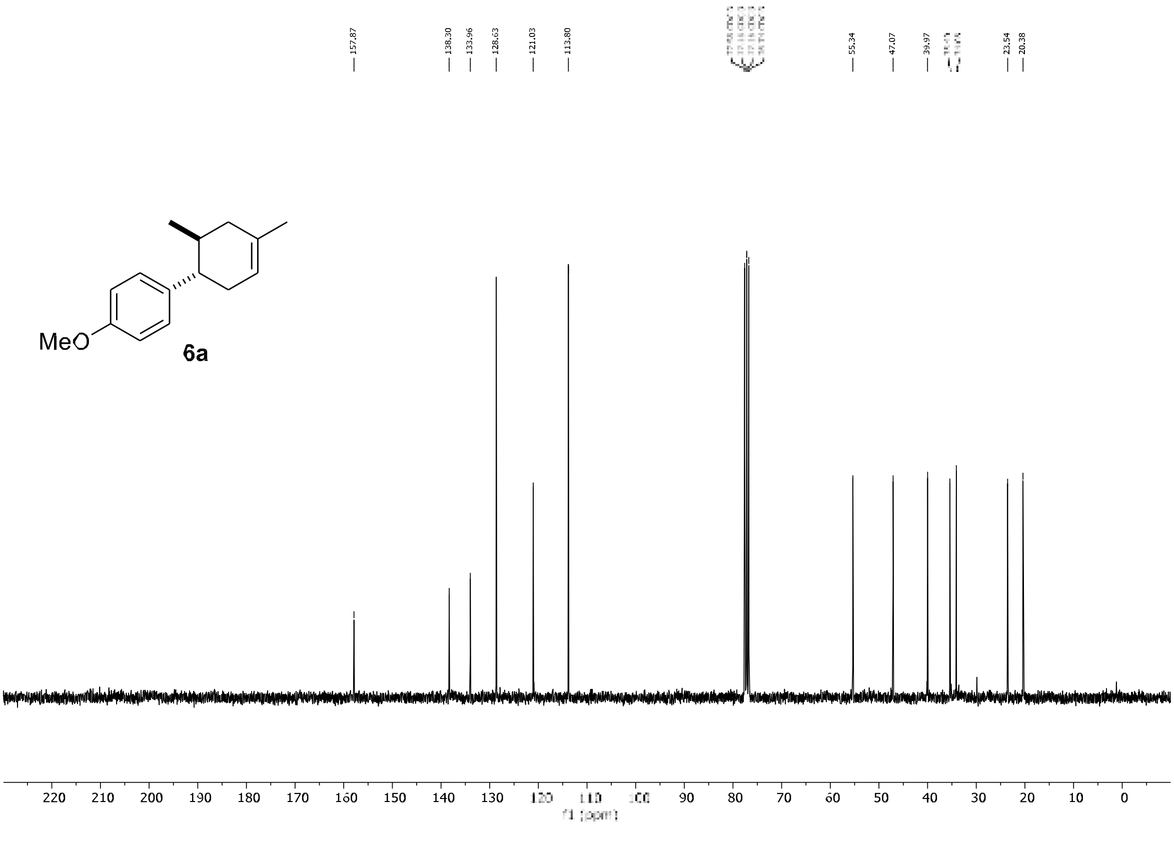
^{13}C-NMR of N,N-Dimethylbipyridinyl dichloride



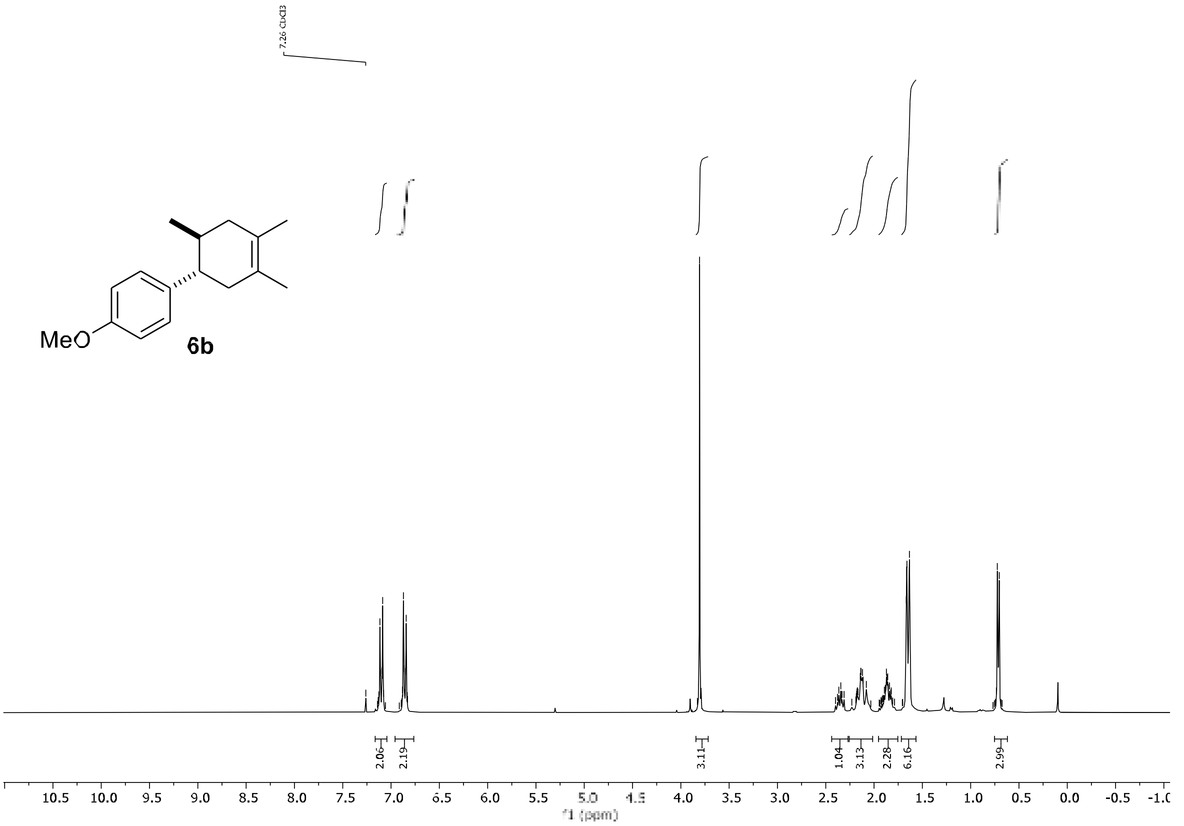
^{1}H-NMR of 4'-Methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6a)



^{13}C-NMR of 4'-Methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6a)

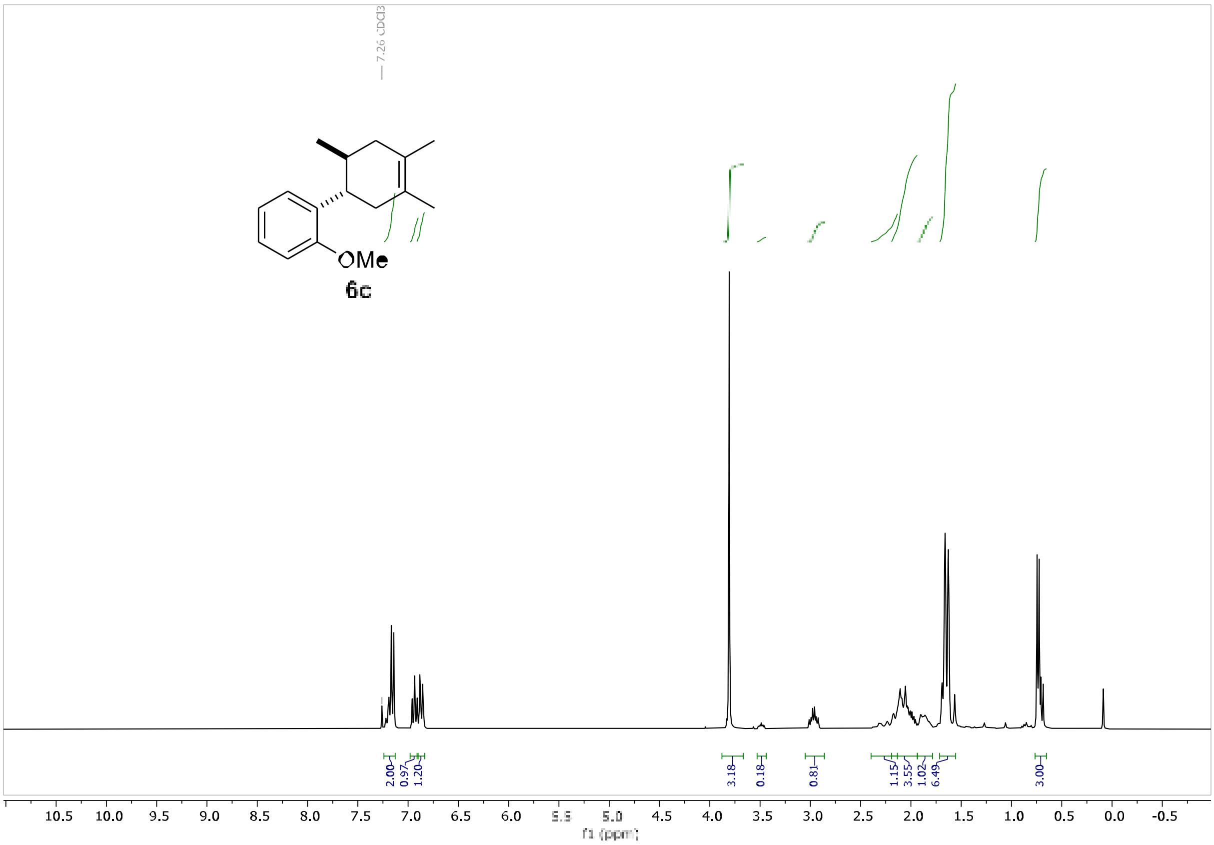


^{1}H-NMR of 4'-Methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6b)

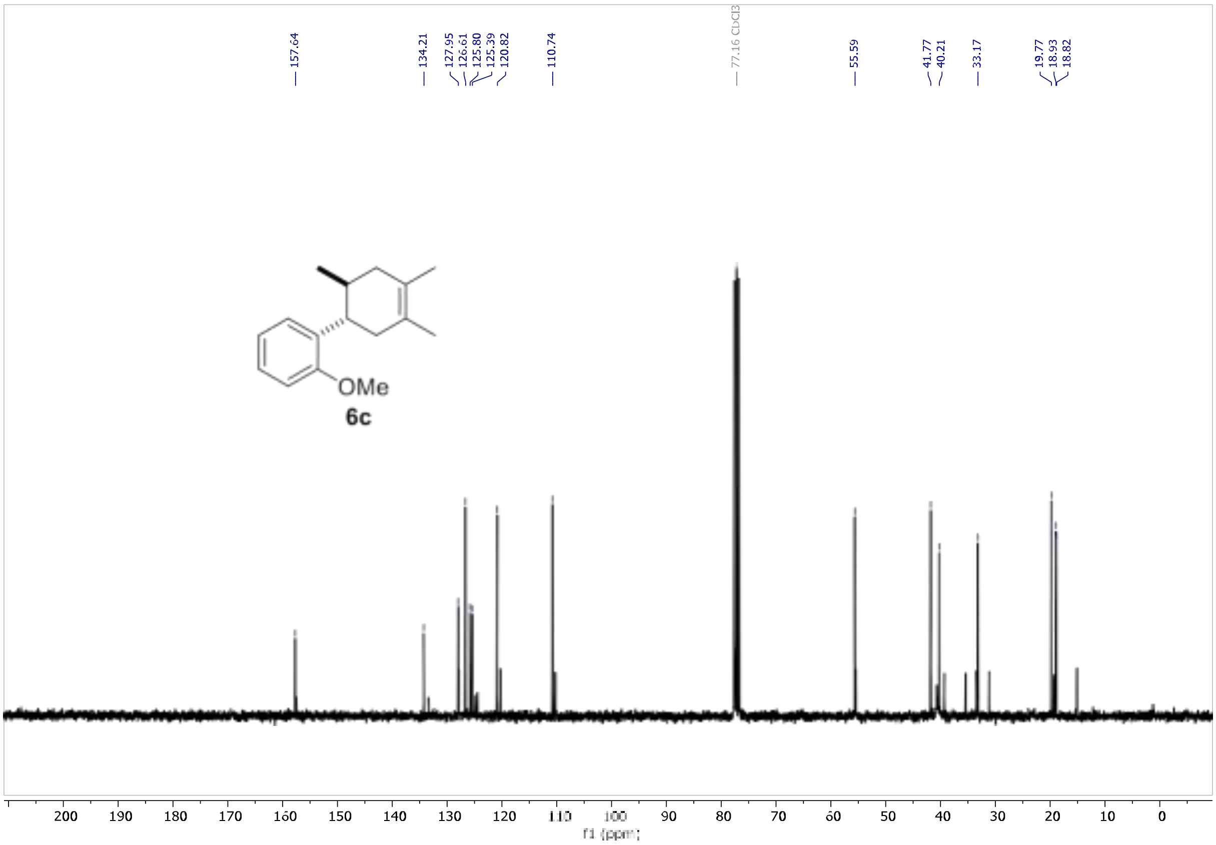


^{13}C-NMR of 4'-Methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6b)

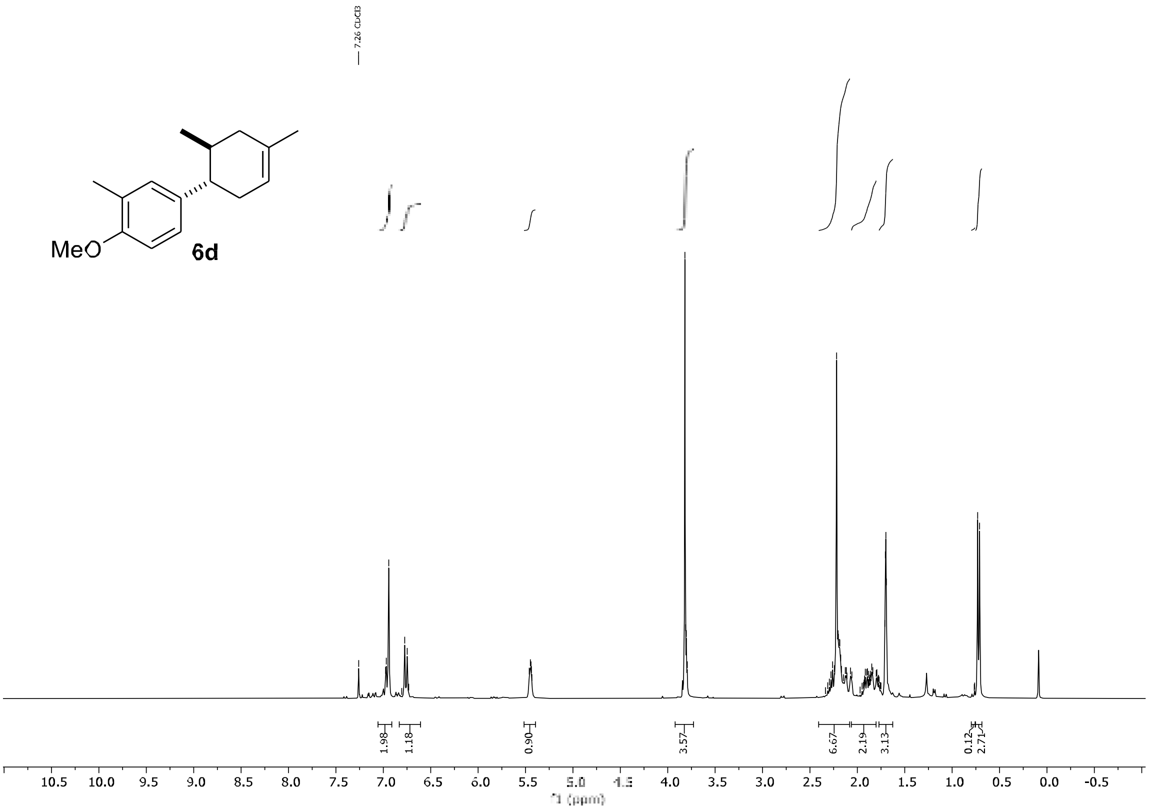
^{1}H-NMR of 2'-Methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6c)



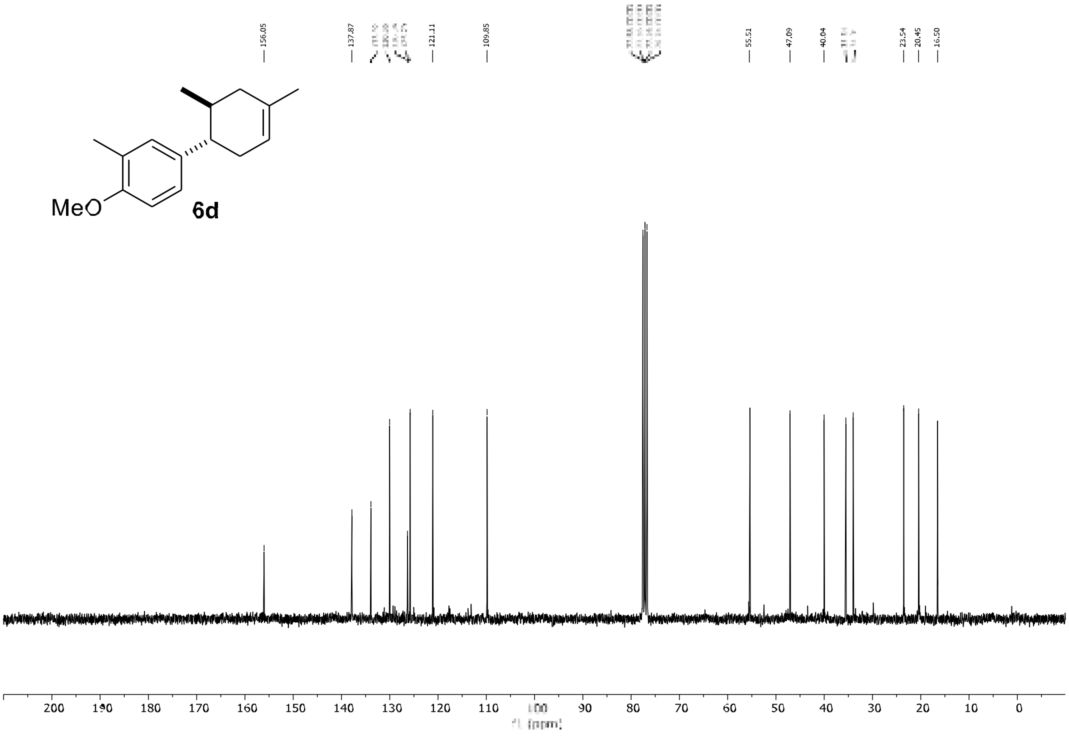
^{13}C-NMR of 2'-Methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6c)



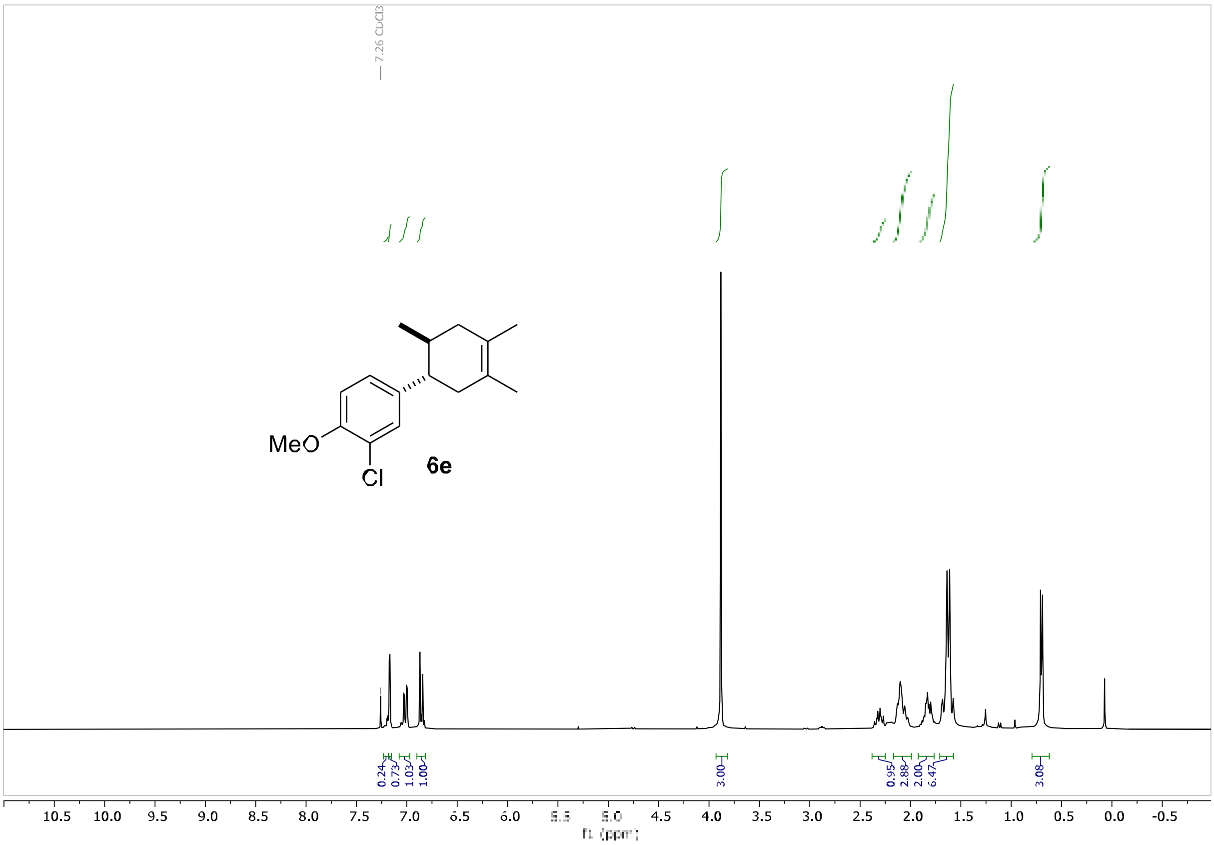
^{1}H-NMR of 4'-Methoxy-2,3',4-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6d)



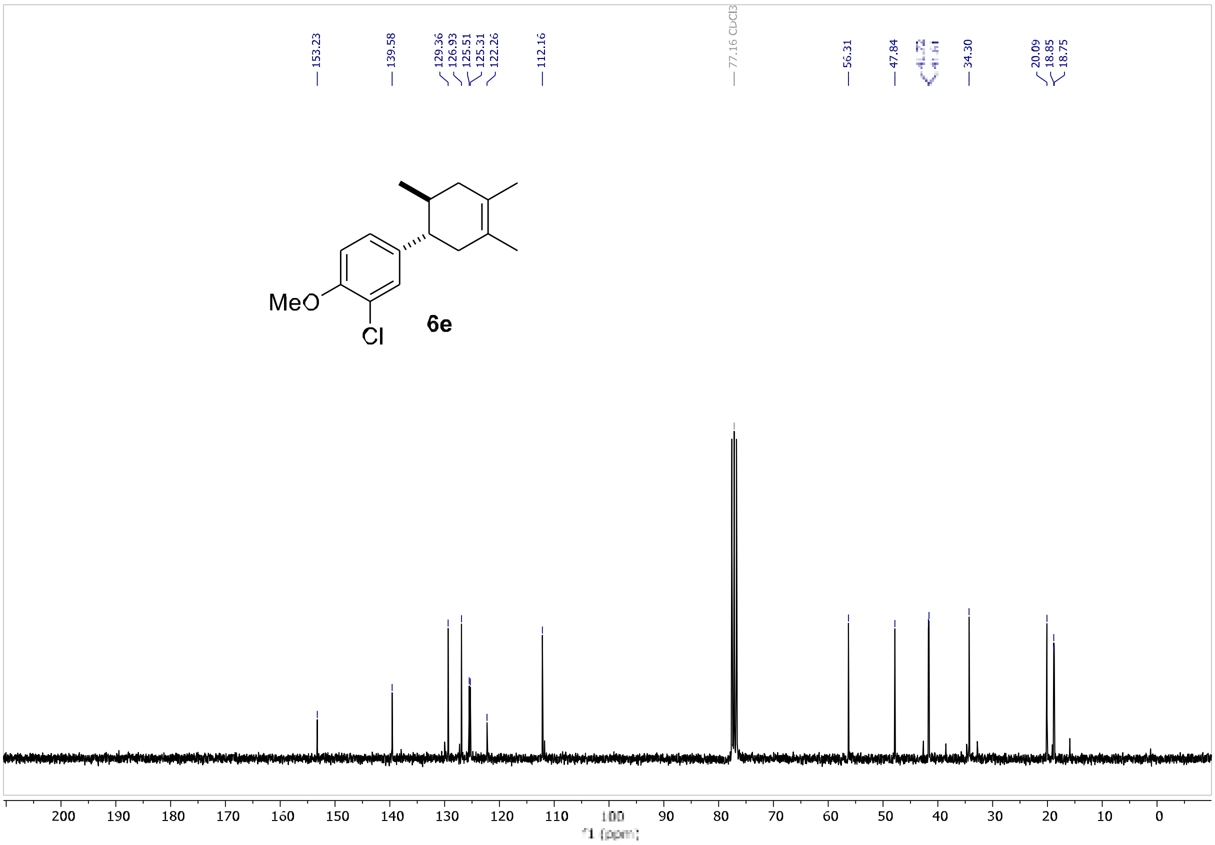
^{13}C-NMR of 4'-Methoxy-2,3',4-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6d)



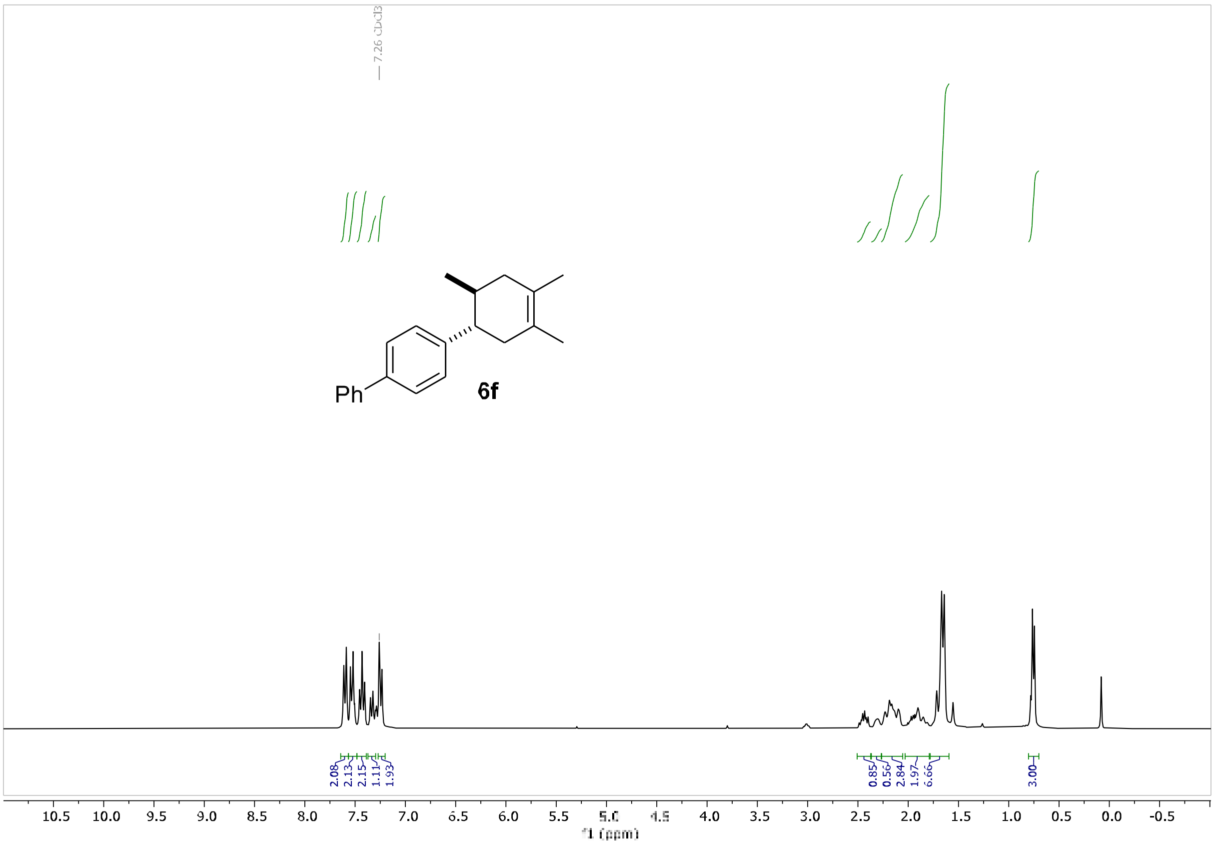
^{1}H-NMR of 3'-Chloro-4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6e)



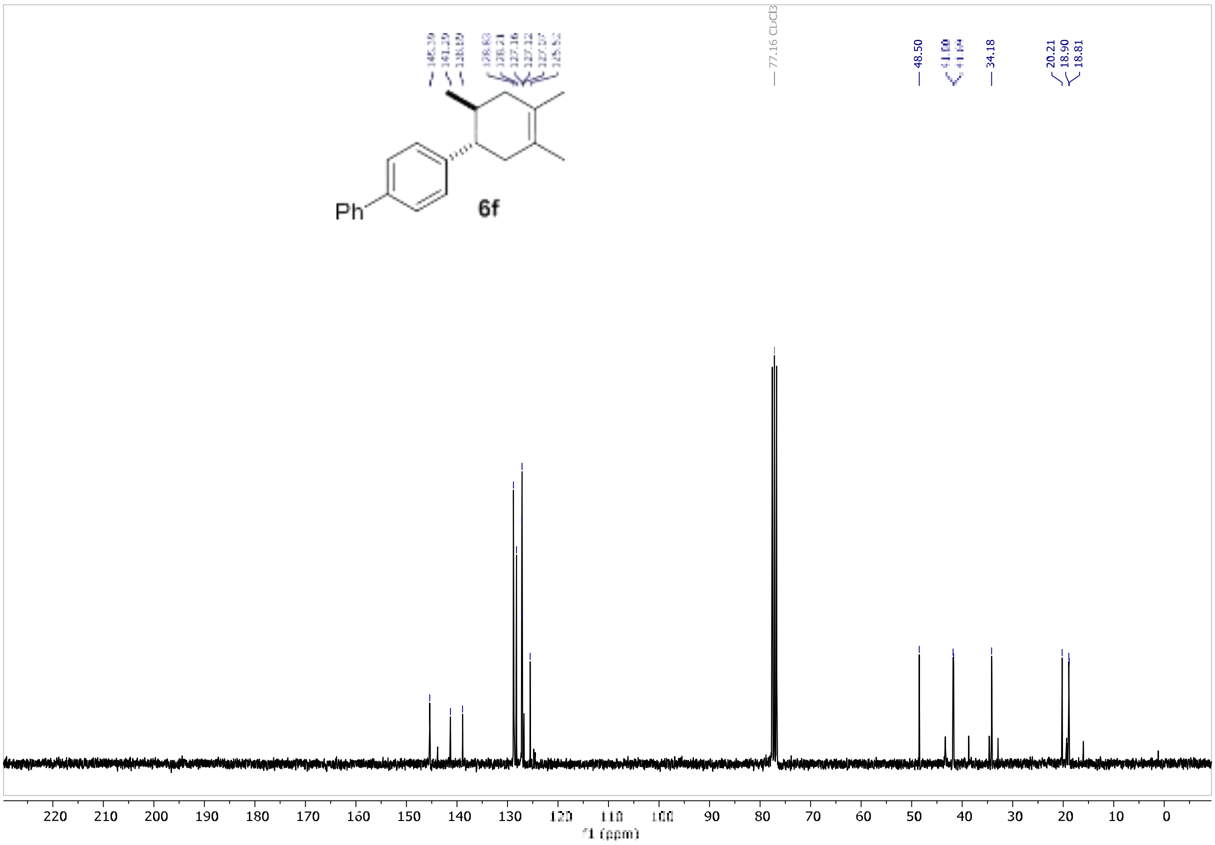
^{13}C-NMR of 3'-Chloro-4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6e)



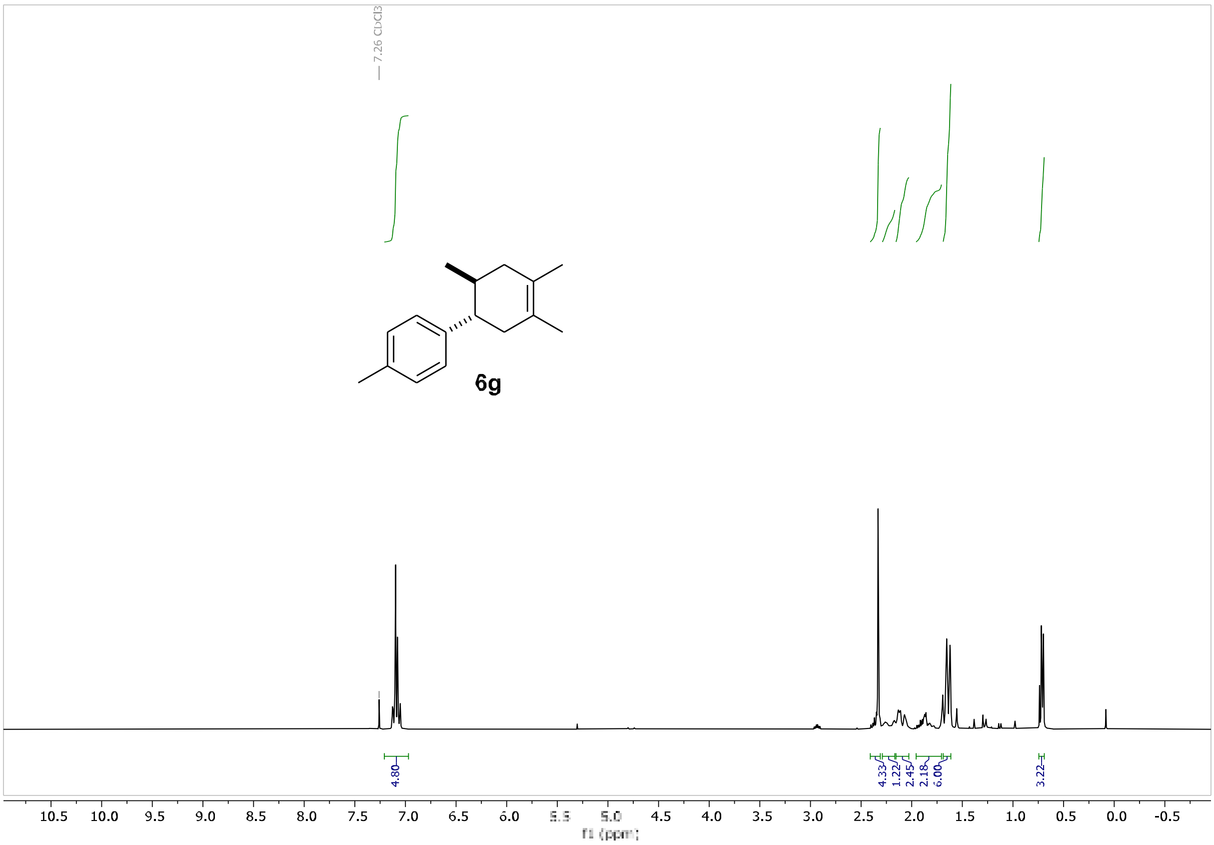
^{1}H-NMR of 2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1':4',1''-terphenyl (6f)



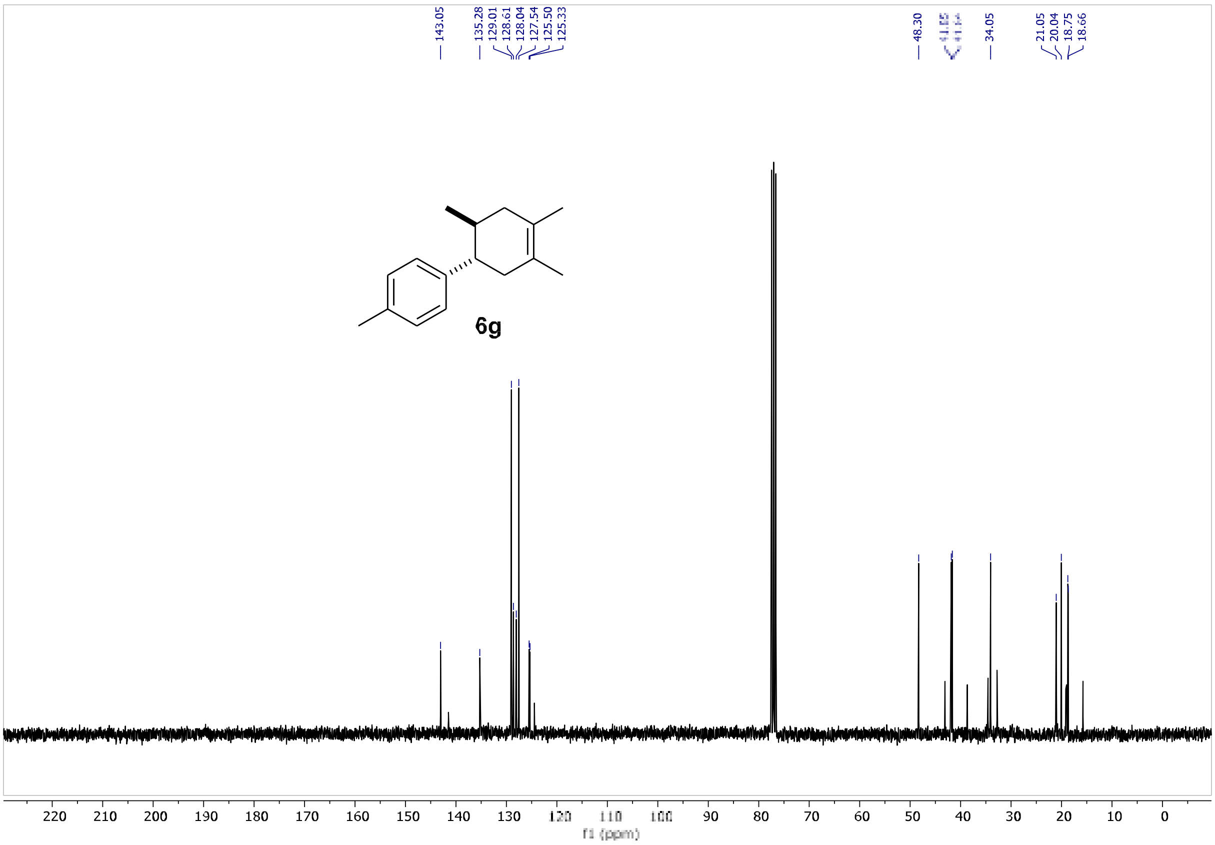
^{13}C-NMR of 2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1':4',1''-terphenyl (6f)



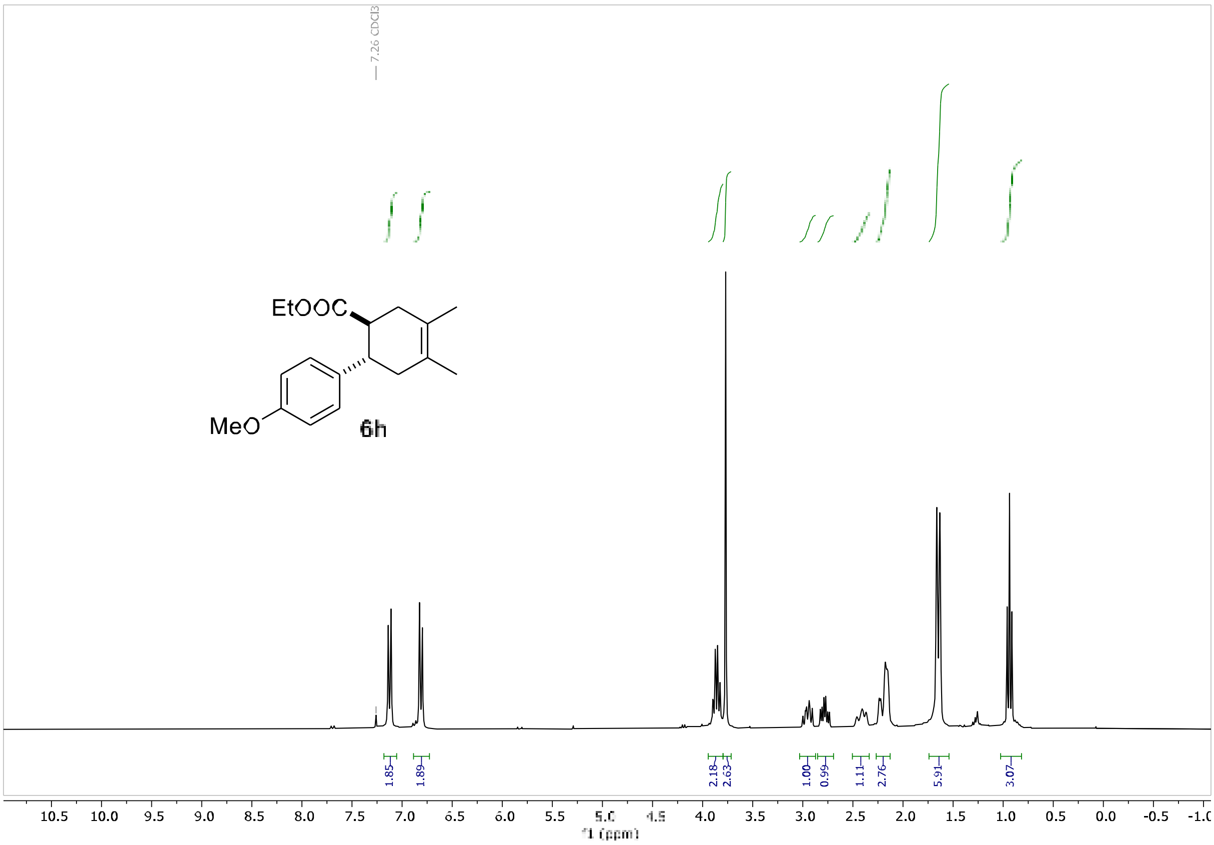
^{1}H-NMR of 2,4,4',5-Tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6g)



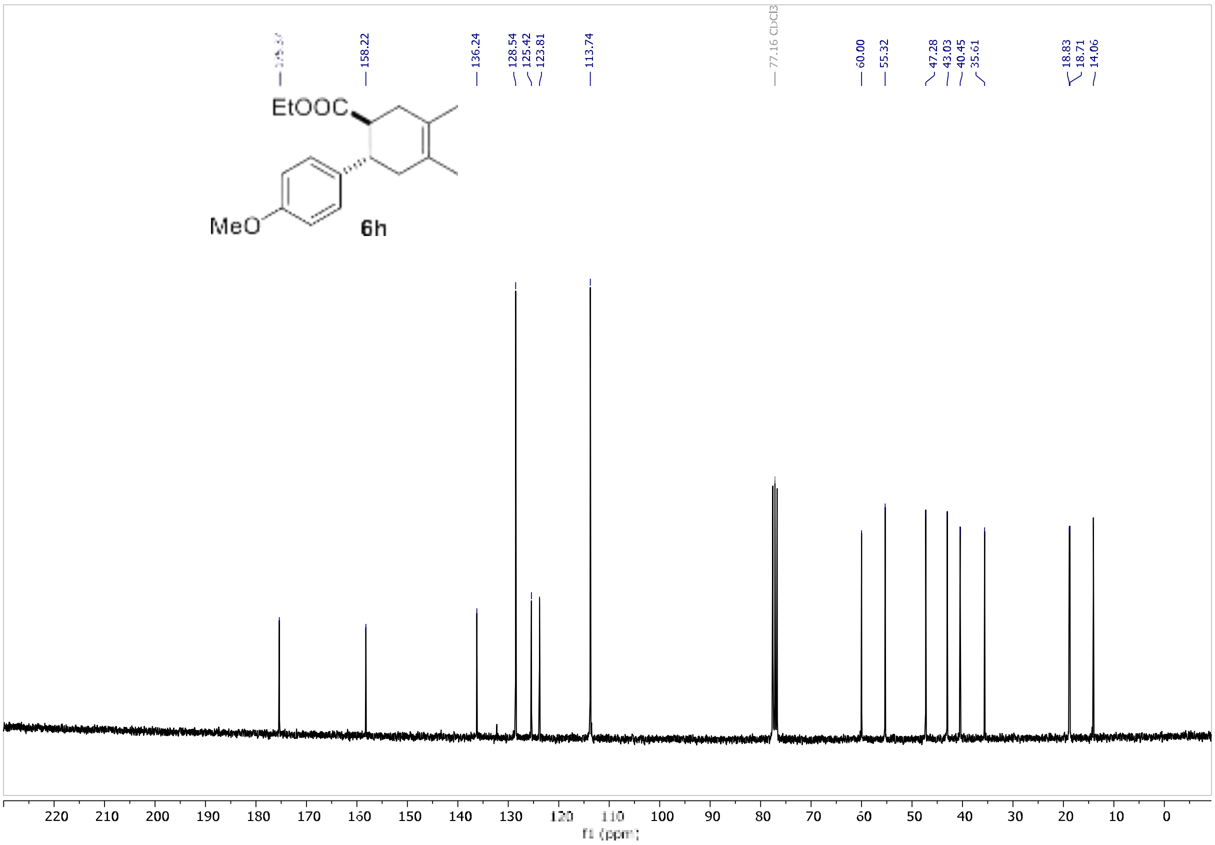
^{13}C-NMR of 2,4,4',5-Tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6g)



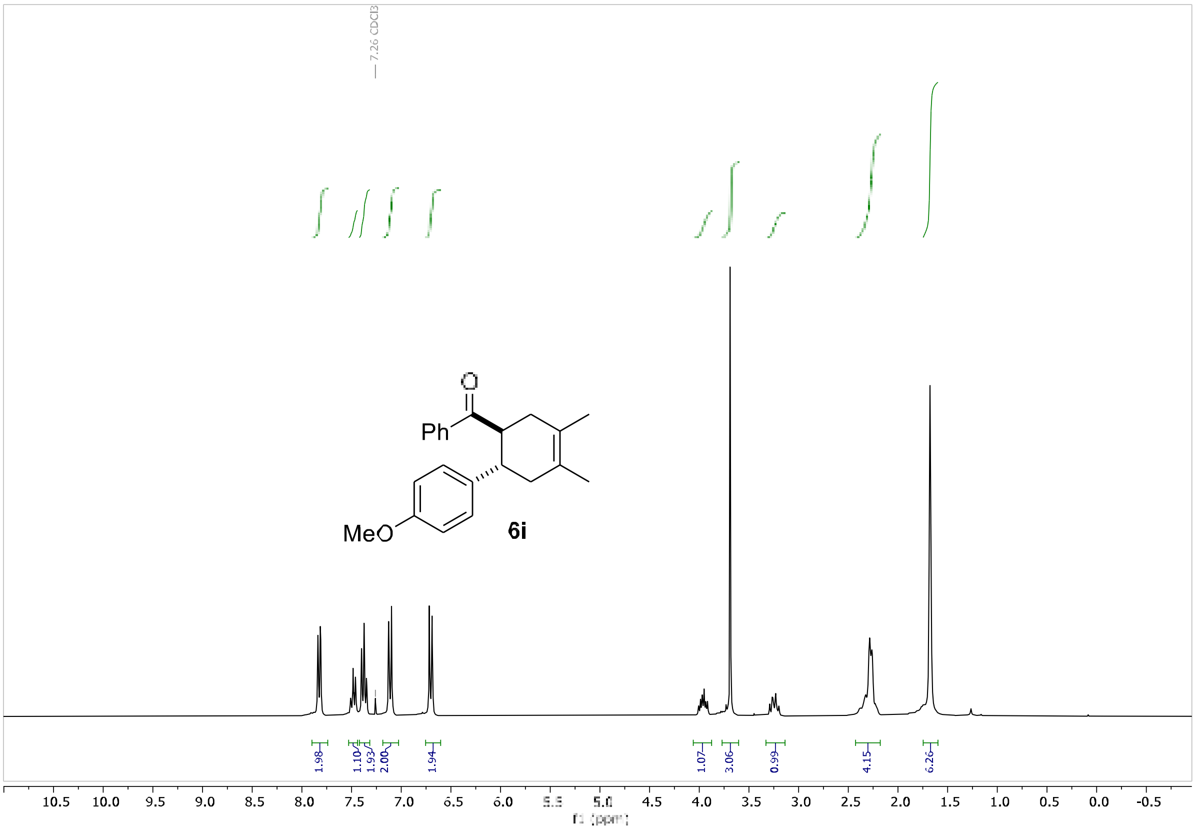
^{1}H-NMR of 4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (6h)



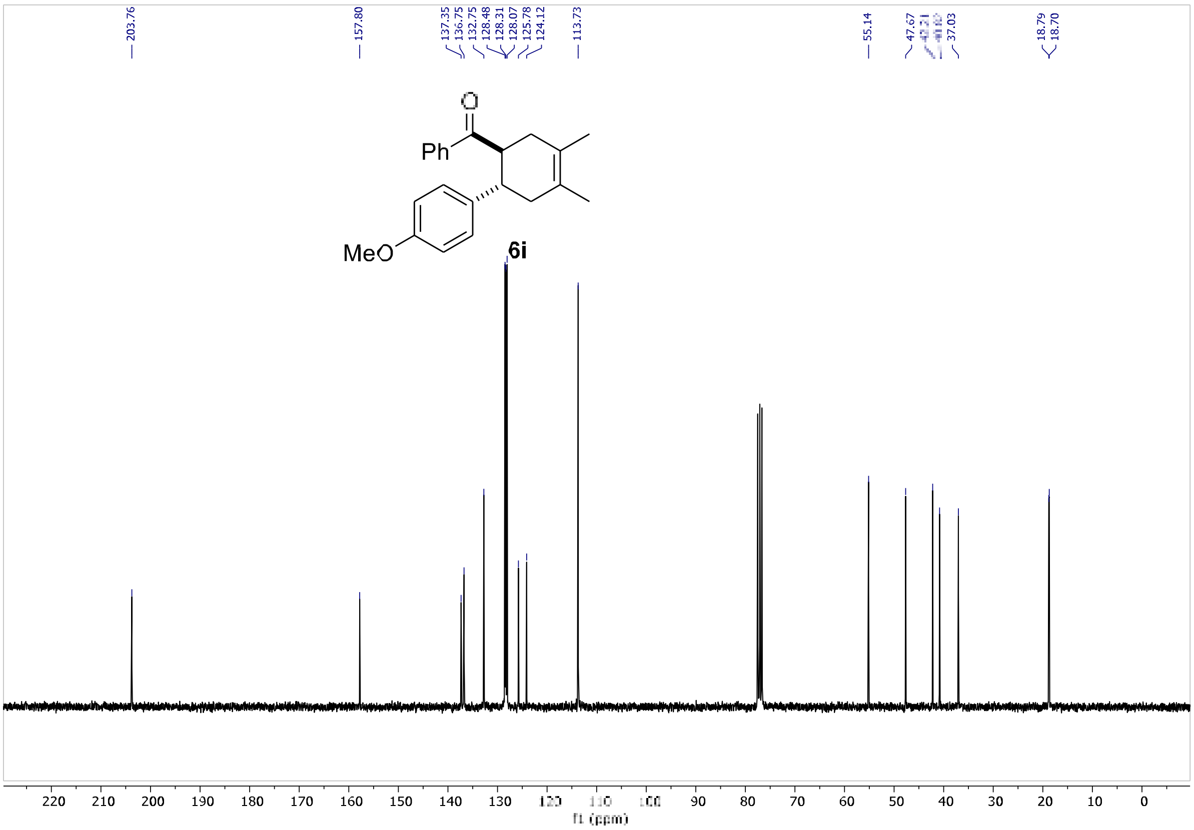
^{13}C-NMR of 4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (6h)



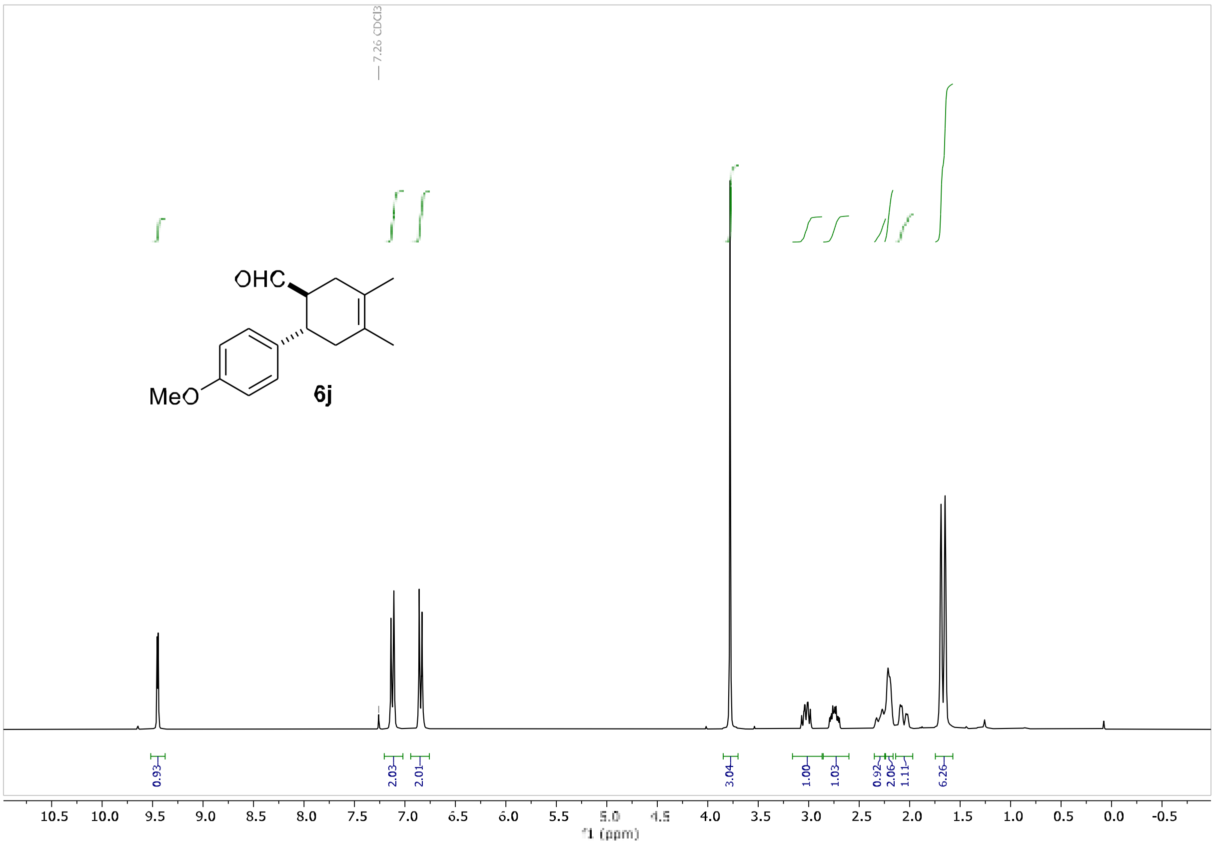
^{1}H-NMR of 4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (6i)



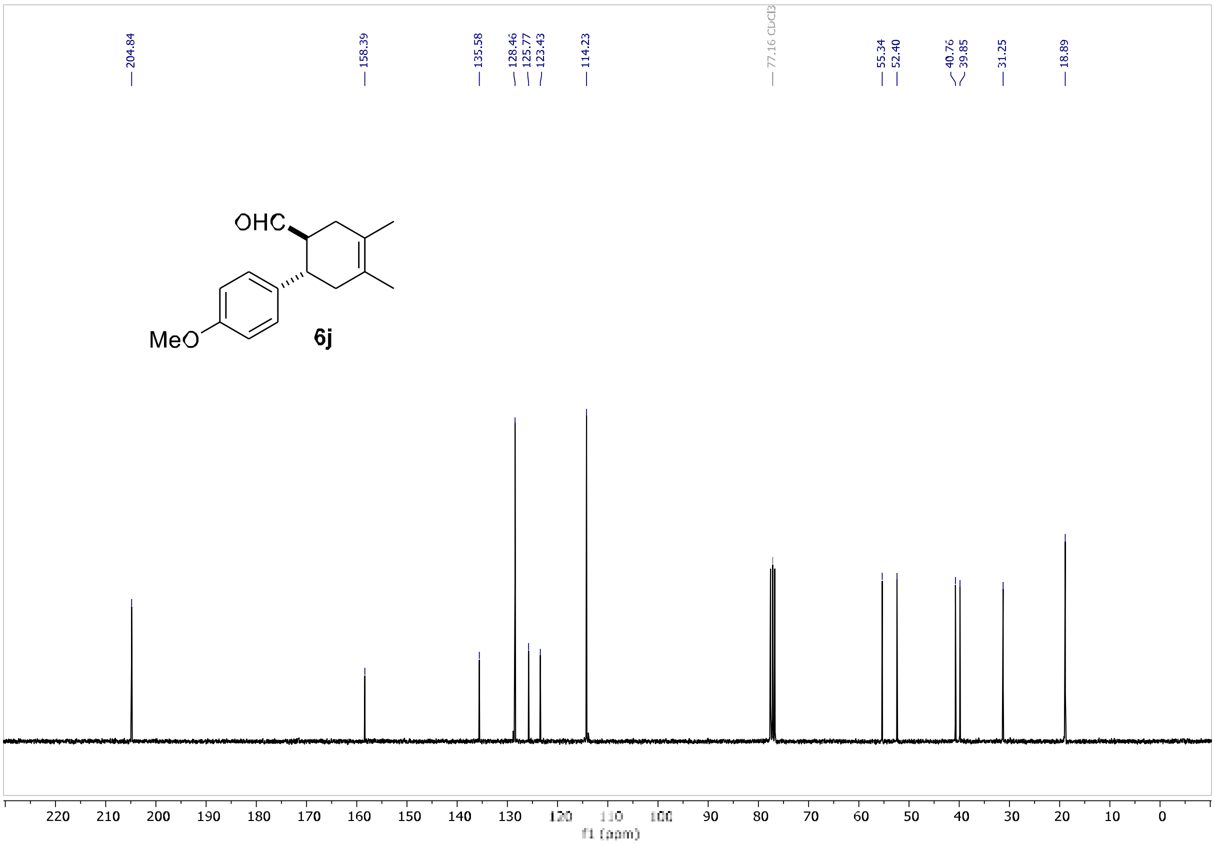
^{13}C-NMR of 4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-yl)(phenyl)methanone (6i)



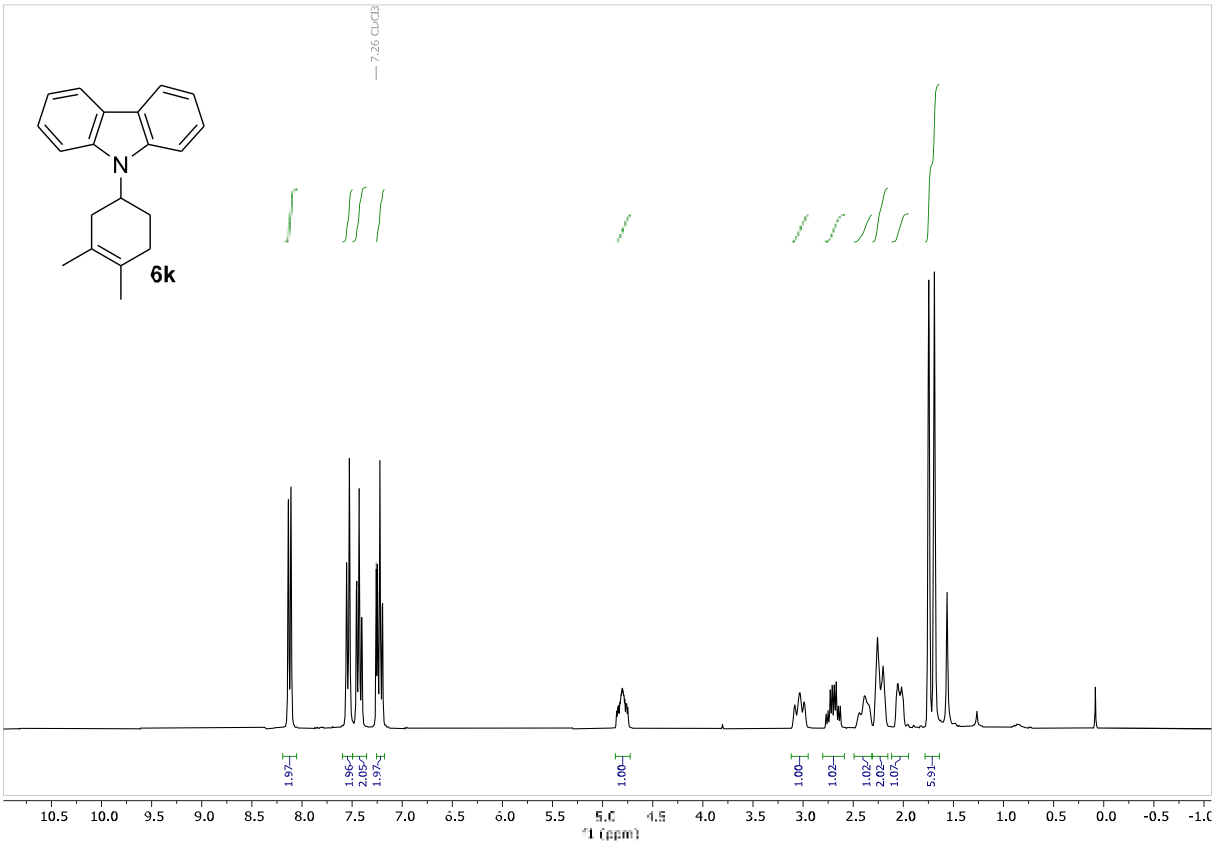
^{1}H-NMR of 4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde (6j)



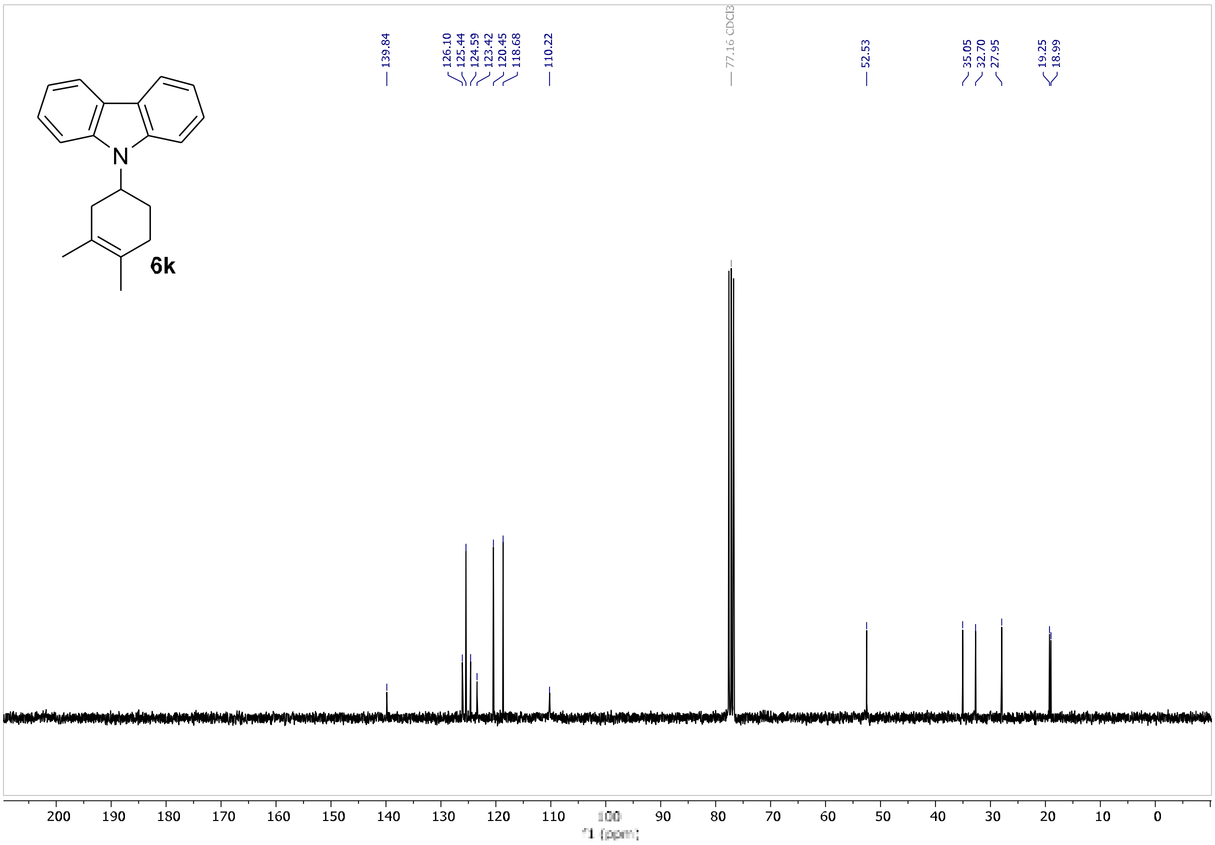
^{13}C-NMR of 4'-Methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde (6j)



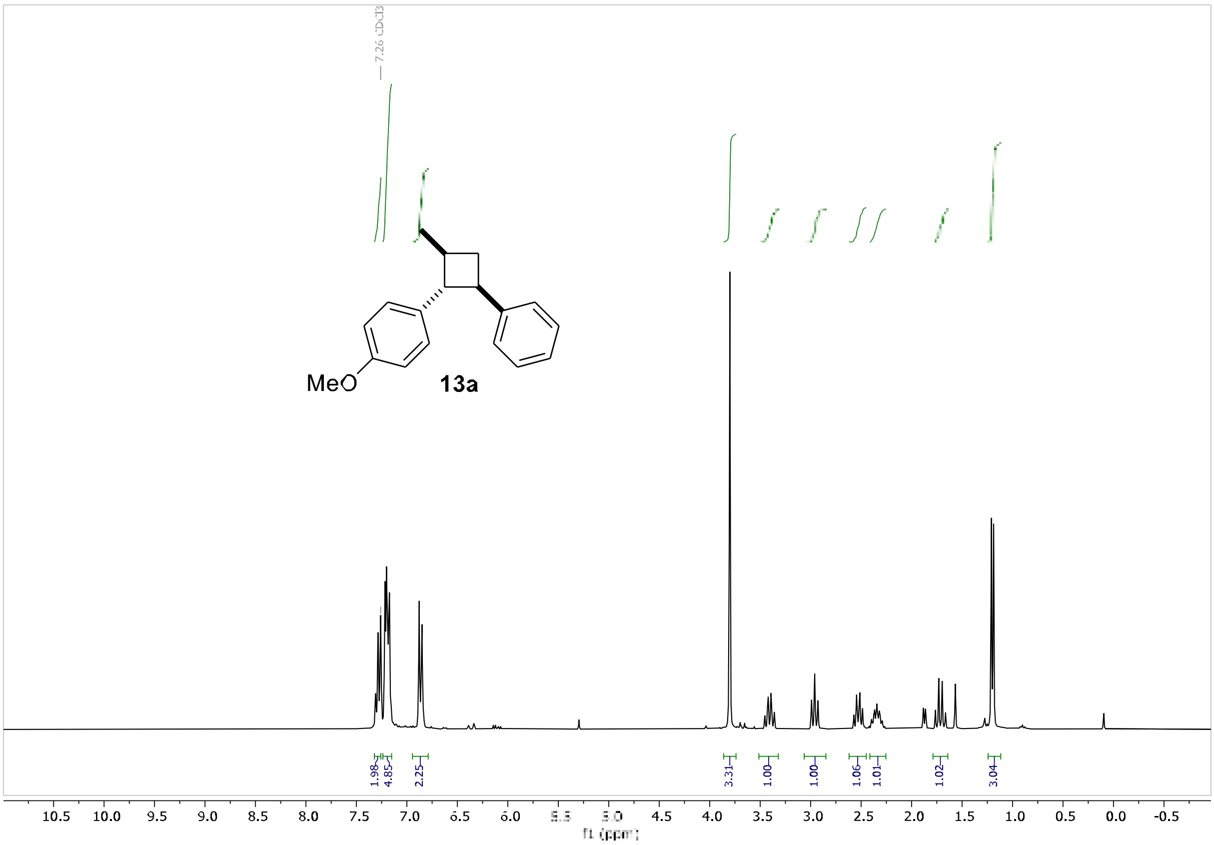
^{1}H-NMR of 9-(3,4-Dimethylcyclohex-3-en-1-yl)-9H-carbazole (6k)



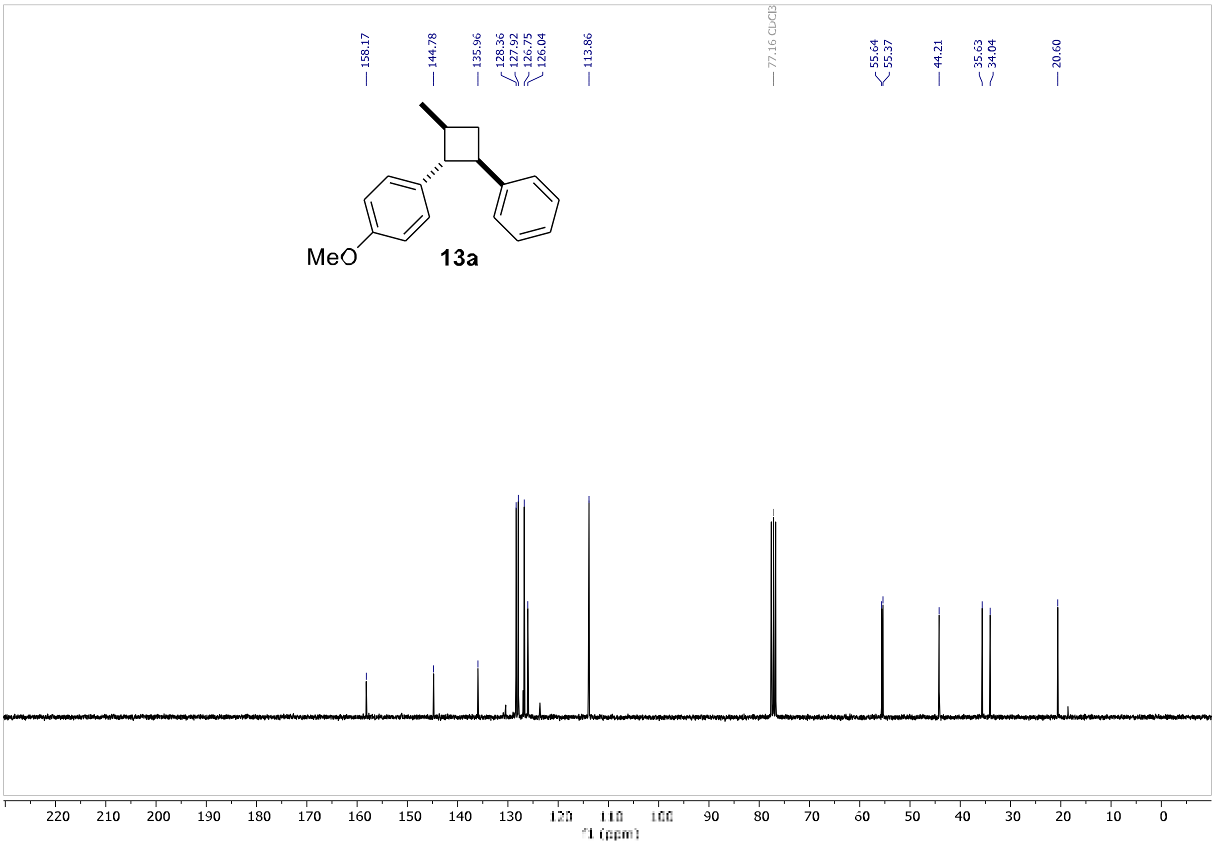
^{13}C-NMR of 9-(3,4-Dimethylcyclohex-3-en-1-yl)-9H-carbazole (6k)



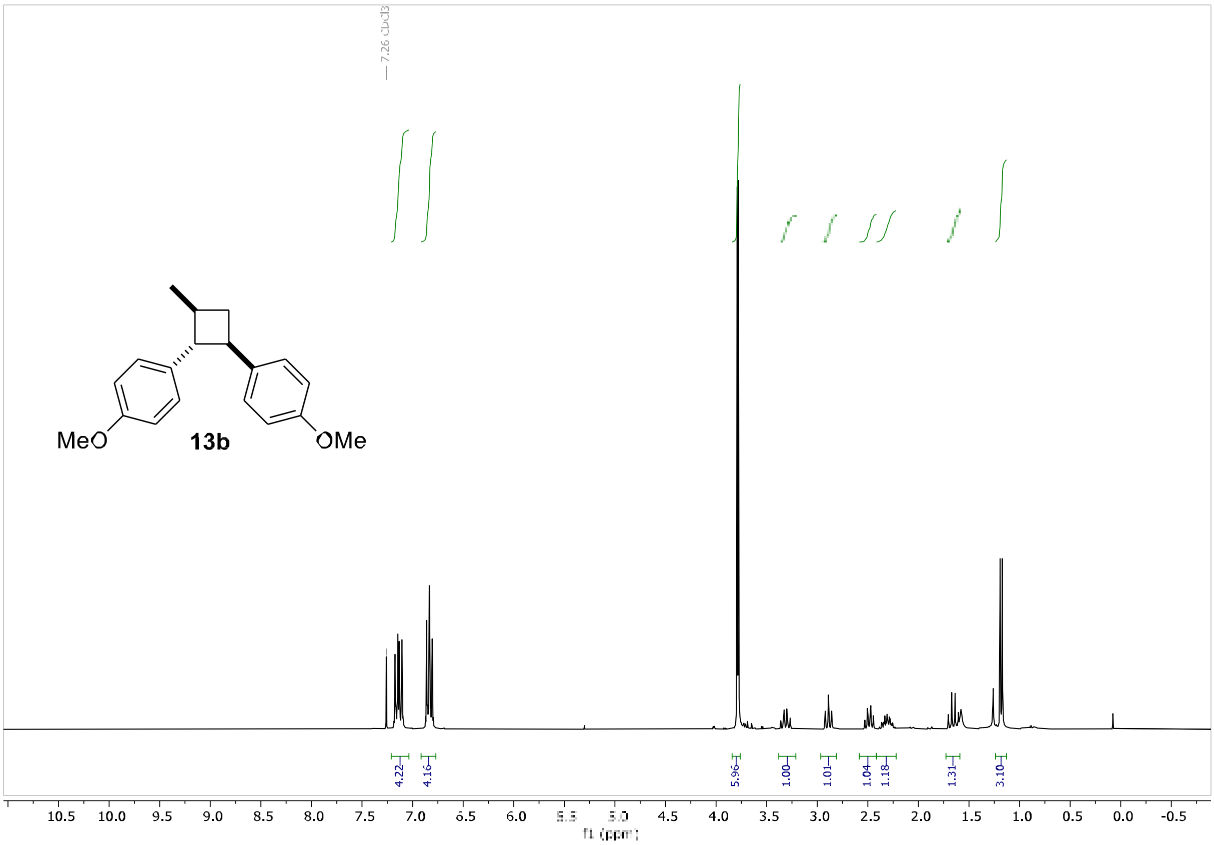
^{1}H-NMR of 1-Methoxy-4-(2-methyl-4-phenylcyclobutyl)benzene (13a)



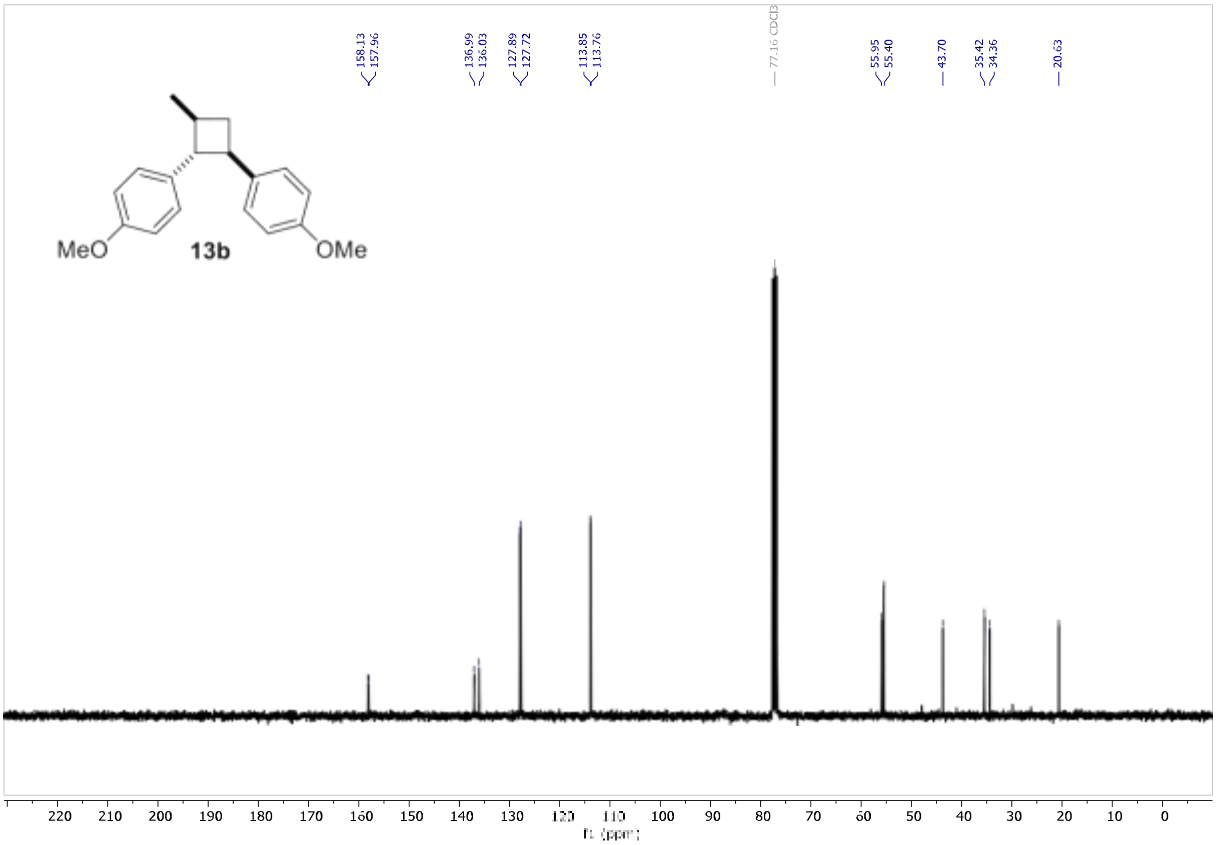
^{13}C-NMR of 1-Methoxy-4-(2-methyl-4-phenylcyclobutyl)benzene (13a)



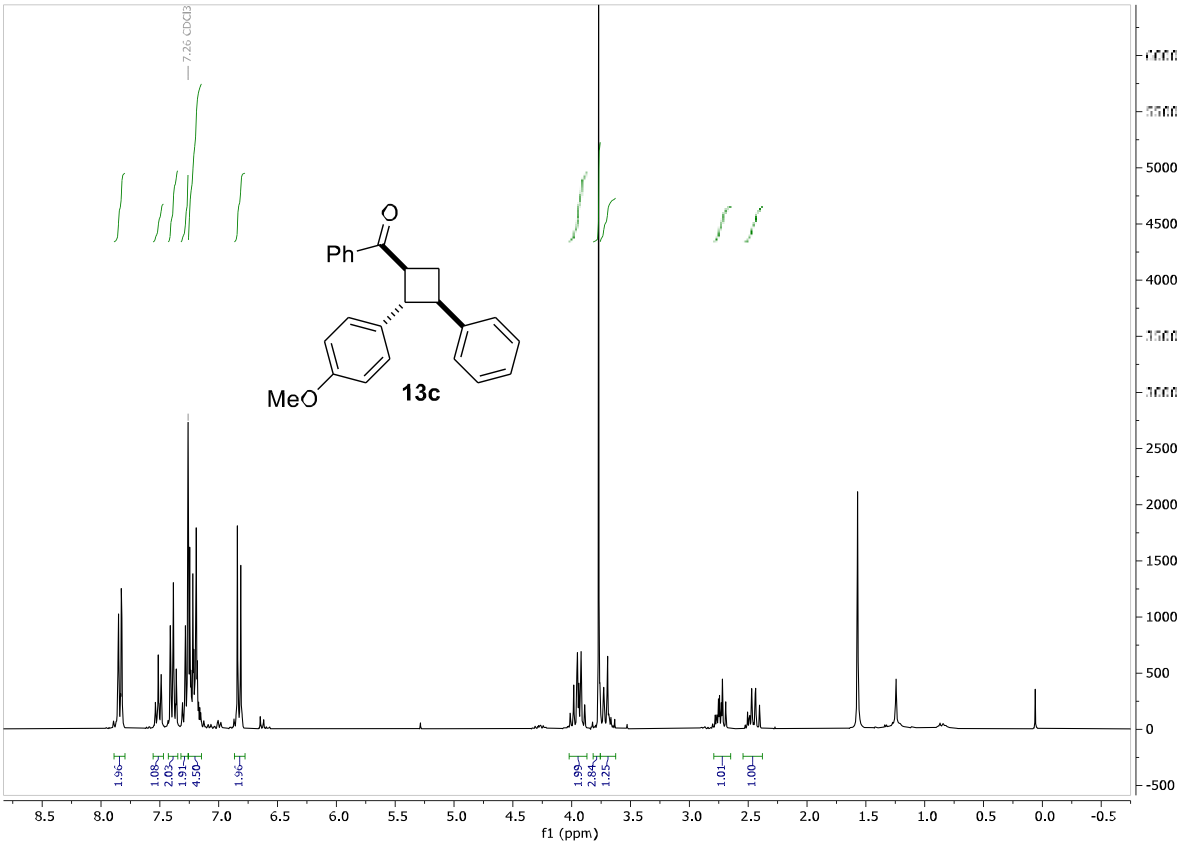
^{1}H-NMR of 3-Methylcyclobutane-1,2-diyl)bis(methoxybenzene) (13b)



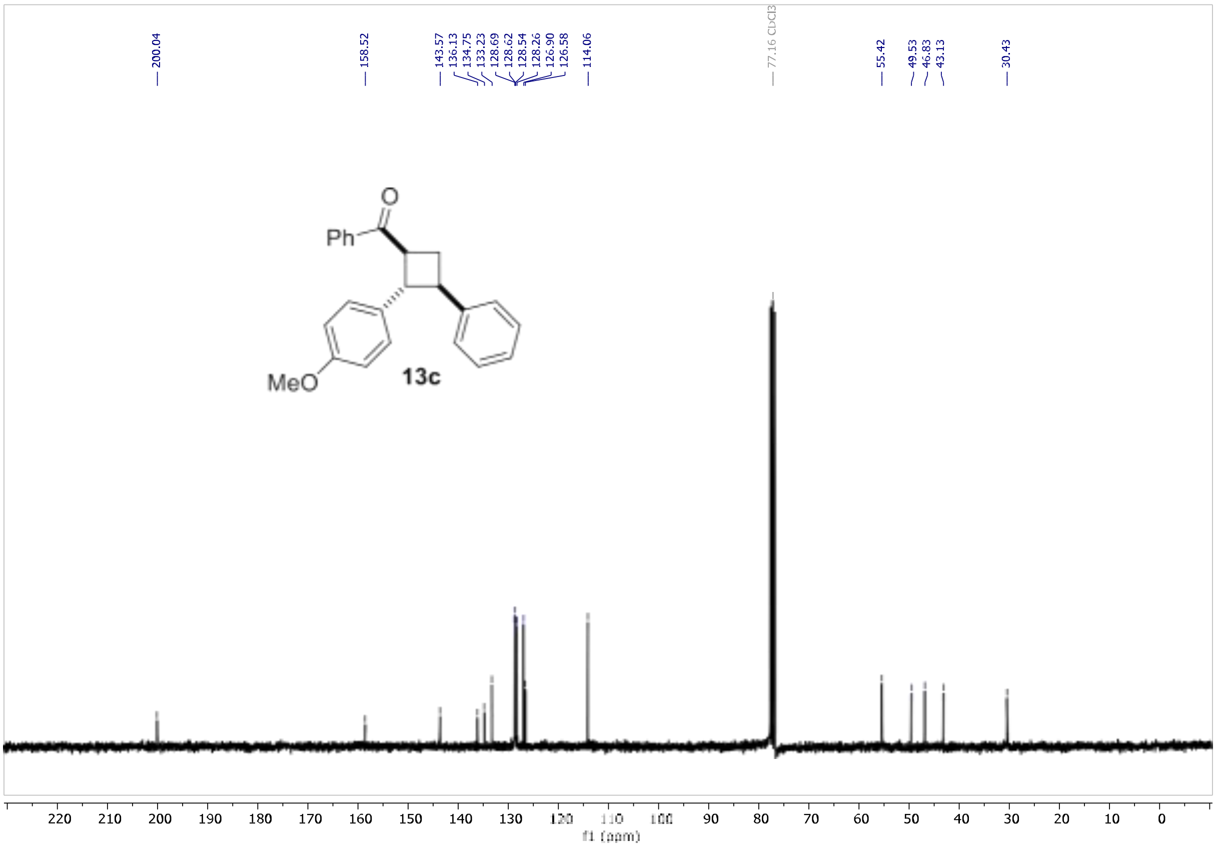
^{13}C-NMR of 3-Methylcyclobutane-1,2-diyl)bis(methoxybenzene) (13b)



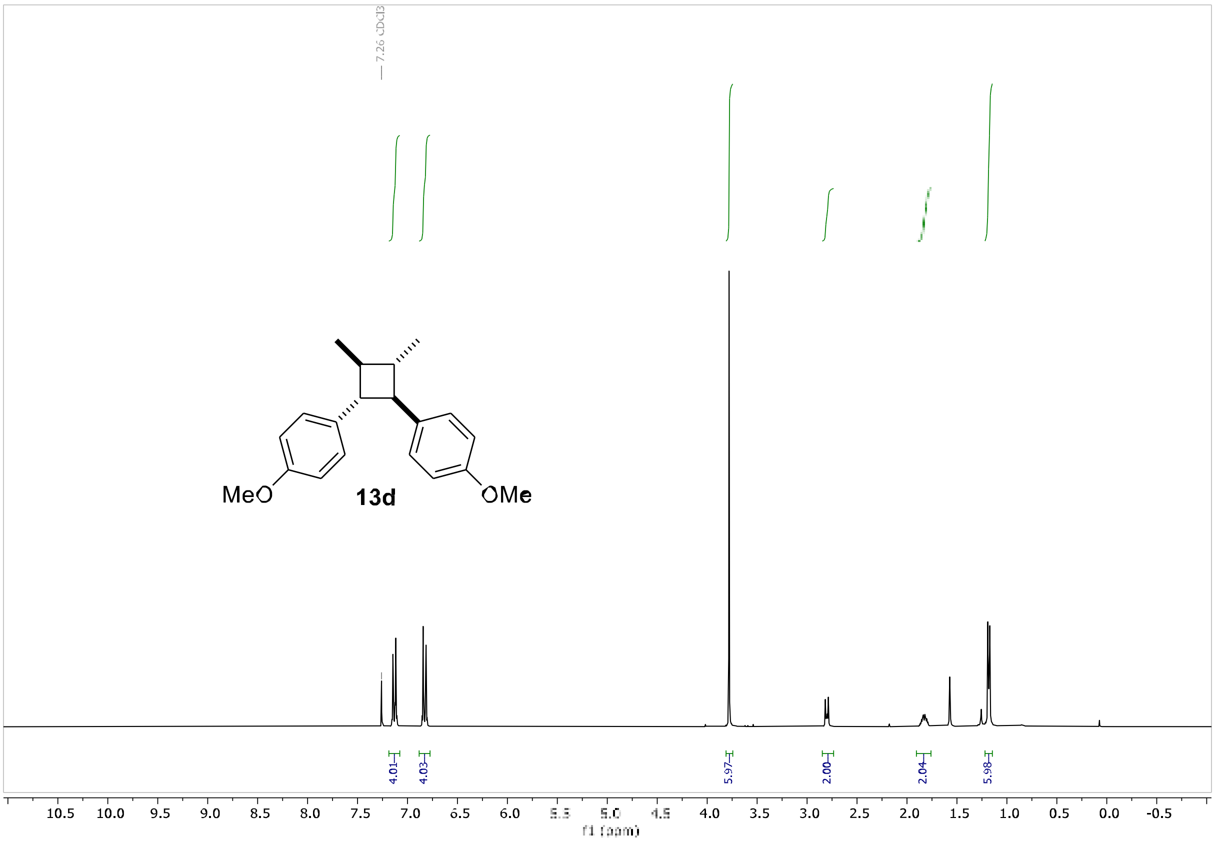
^{1}H-NMR of 2-(4-Methoxyphenyl)-3-phenylcyclobutyl)(phenyl)methanone (13c)



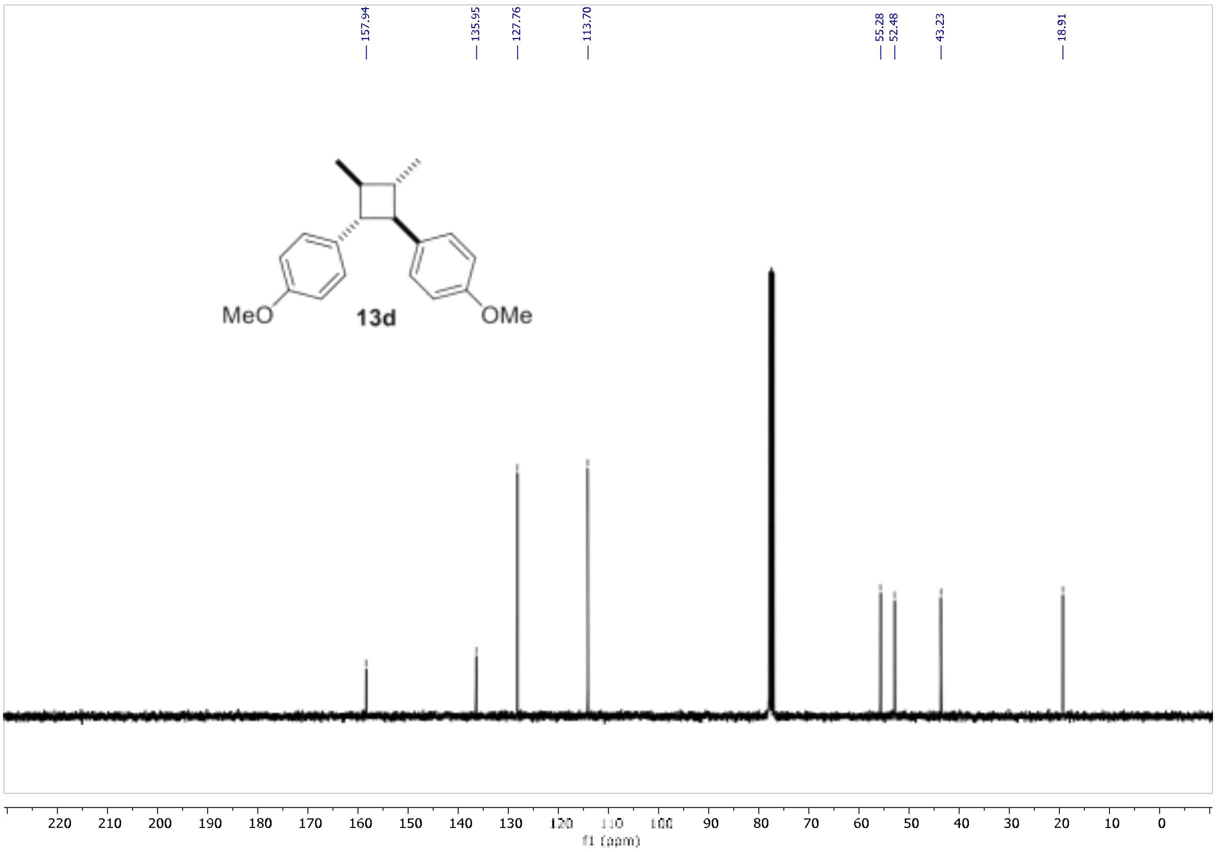
^{13}C-NMR of 2-(4-Methoxyphenyl)-3-phenylcyclobutyl)(phenyl)methanone (13c)



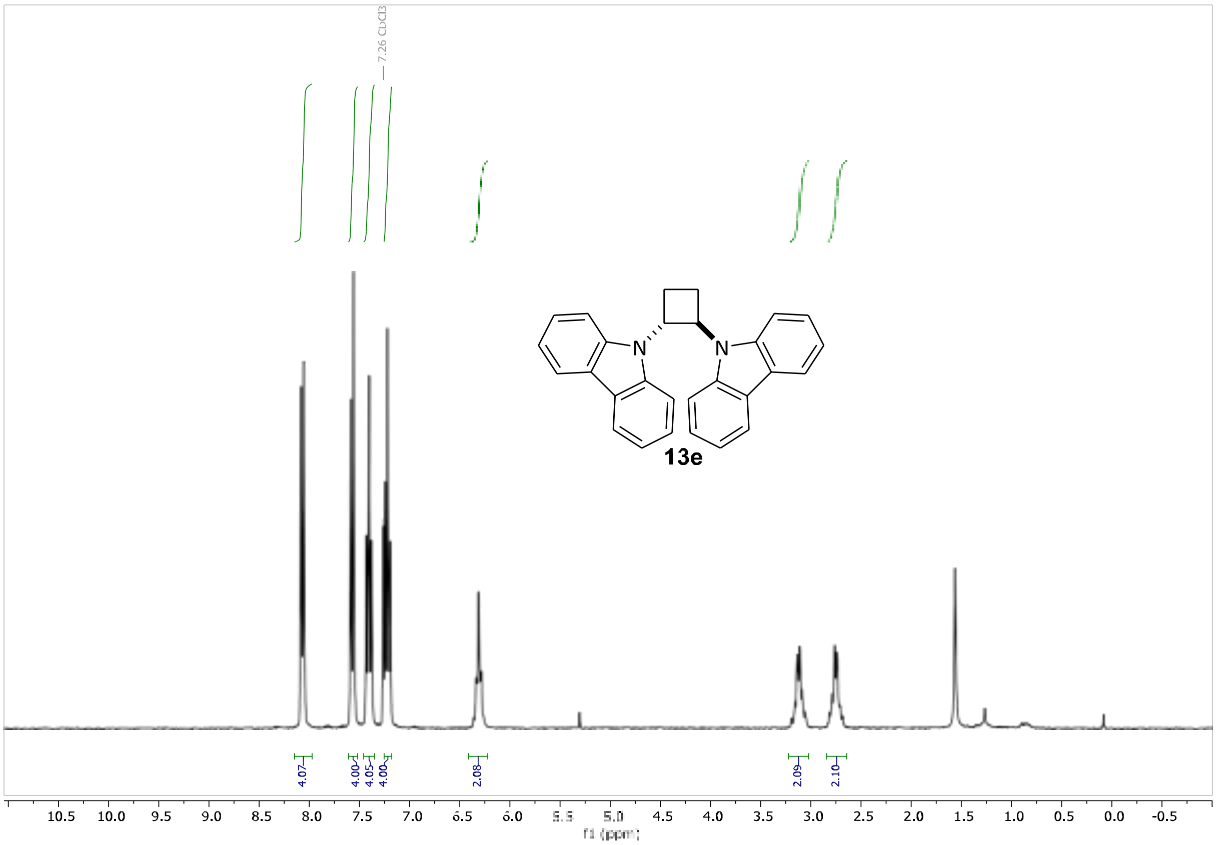
^{1}H-NMR of 3,4-Dimethylcyclobutane-1,2-diyl)bis(methoxybenzene) (13d)



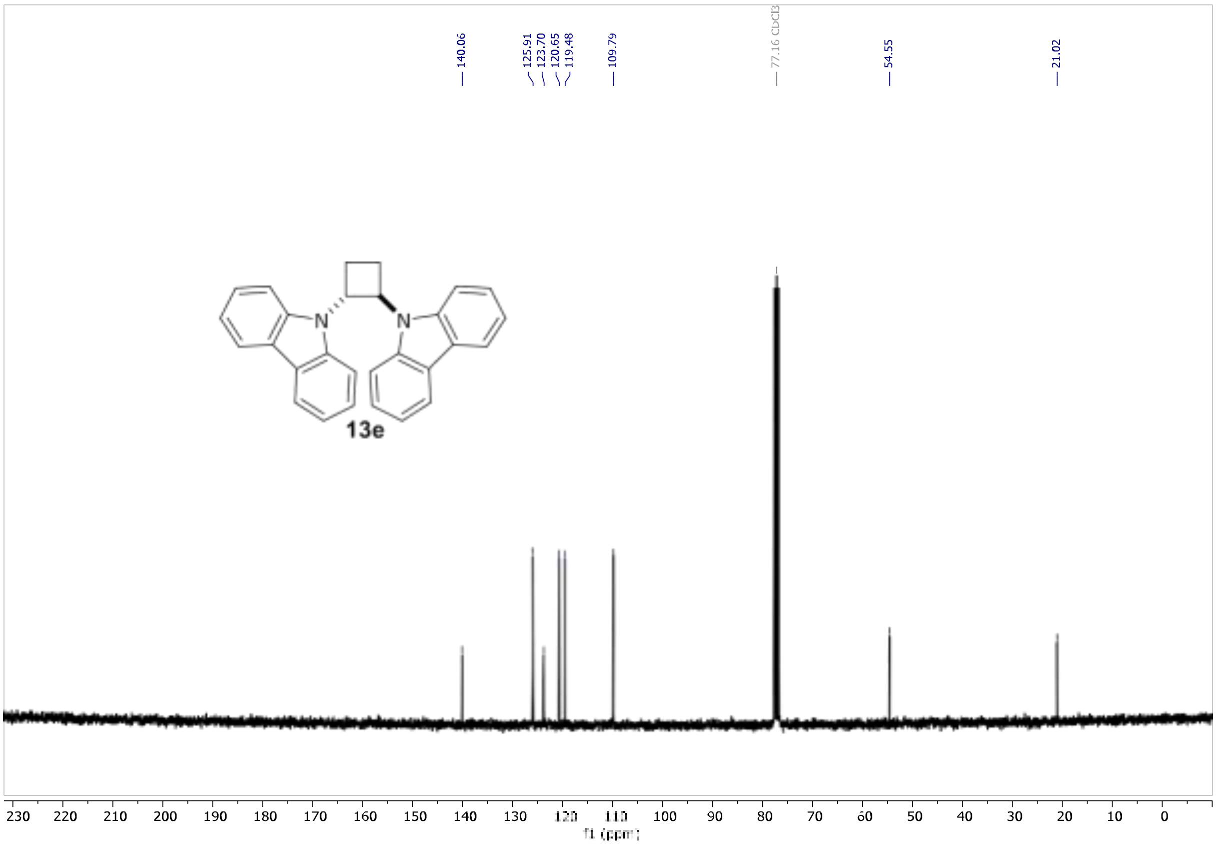
^{13}C-NMR of 3,4-Dimethylcyclobutane-1,2-diyl)bis(methoxybenzene) (13d)



^{1}H-NMR of 1,2-Di(9H-carbazol-9-yl)cyclobutane (13e)



^{13}C-NMR of 1,2-Di(9H-carbazol-9-yl)cyclobutane (13e)



9. Reference

[1] Z. R. Gregg, J. R. Griffiths, S. T. Diver, *Organometallics* **2018**, *37*, 1526–1533.
[2] R. J. Ross, R. Jeyaseelan, M. Lautens, *Org. Lett.* **2020**, *22*, 4838–4843.
[3] S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 19350–19353.