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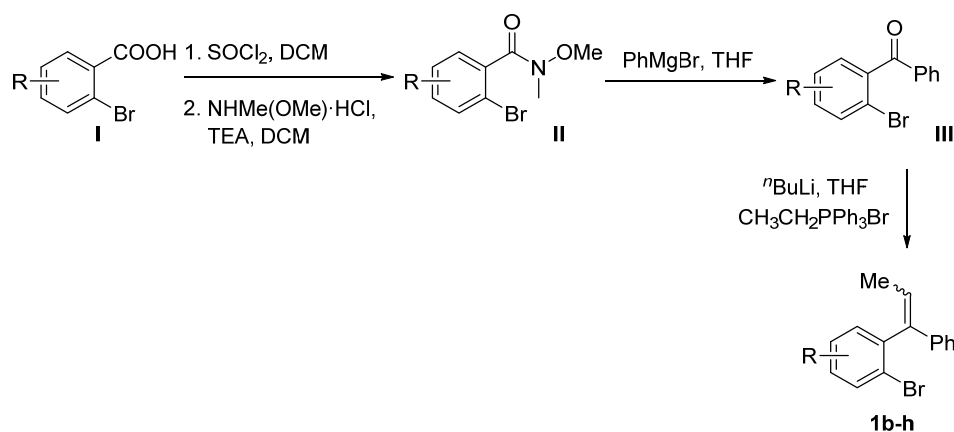
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## 1. General Information

All commercially available chemical resources were used as received, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) supplied by Yantai Jiangyou Silicon Material Company (China). Visualization was accomplished with UV light or basic aqueous potassium permanganate (KMnO<sub>4</sub>). Chromatography was achieved using forced flow (flash chromatography) of the indicated solvent system on 230-400 mesh silica gel (Silicycle flash F60) unless otherwise noted. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Varian mercury-400 and Bruker AM-400 spectrometers. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR spectra are expressed in parts per million (ppm, δ scale) downfield from SiMe<sub>4</sub> relative to the residual <sup>1</sup>H and <sup>13</sup>C signals of the solvent and TMS (TMS : δ 0.000 ppm (<sup>1</sup>H NMR); CDCl<sub>3</sub>: 77.06 ppm (<sup>13</sup>C NMR)), and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet. High-resolution mass spectra (HRMS) were acquired through the National Center for Organic Mass Spectrometry in Shanghai, Shanghai Institute of Organic Chemistry (CAS) and determined on a Waters Micromass GCT Premier spectrometer. The 1,1,2-trisubstituted alkenes **1a,1q**,<sup>1,2</sup> symmetrical alkynes **2a-h**,<sup>3</sup> were prepared according to the literatures. The alkynes **2i-k** were purchased and used directly from commercial sources.

## 2. Procedures for the synthesis 1b-1r

Typical procedure for the synthesis of substrate **1b-1r**:



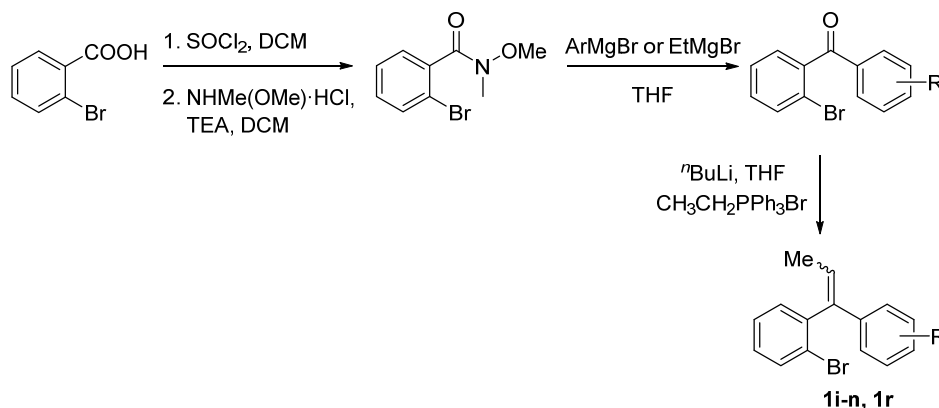
To a suspension of **I** (14.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added SOCl<sub>2</sub> (5.4 mL, 74.3 mmol) portionwise at r.t. under Ar. Then it was heated to reflux and allowed to stir at this temperature for further 3 hours. The yellowish solution was cooled to r.t. and the solvent was removed under vacuo. To the mixture of NHMe(OMe)·HCl (2.19 g, 22.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added TEA (6.2 mL, 44.6 mmol) dropwise, followed by the solution of acyl chloride in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at 0 °C under Ar. Then the mixture was stirred at r.t. overnight. The solid was dissolved by H<sub>2</sub>O and diluted by CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The residue was purified by flash chromatography on silica gel.

To a solution of **II** (3.9 mmol) in THF (10 mL) was added phenylmagnesium bromide (5.8 mmol) dropwise at 0 °C under Ar. Then the mixture was allowed to stir at 0 °C for 3 hours. Sat.NH<sub>4</sub>Cl (aq) was added to quench the reaction and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under

vacuo. The residue was purified by flash chromatography on silica gel.

To the stirred mixture of triphenyl phosphonium salt (1.39 g, 3.74 mmol) in THF (10 mL) was added <sup>n</sup>BuLi (1.5 mL, 2.5 N in hexane, 3.74 mmol) dropwise at 0 °C under Ar. After stirring for 1 hour, a solution of **III** (2.9 mmol) in THF (5 mL) was added to the yellowish mixture dropwise at the same temperature. Then it was allowed to stir at r.t. overnight. H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> were added to the orange mixture above. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The residue was purified by flash chromatography on silica gel.

Typical procedure for the synthesis of substrate **1i-1n**, **1r**:

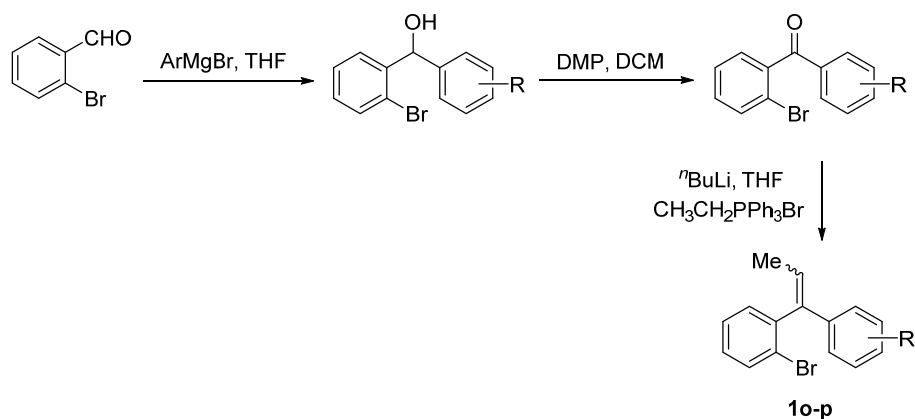


To a suspension of 2-bromobenzoic acid (70 g, 0.35 mol) in CH<sub>2</sub>Cl<sub>2</sub> (500 mL) was added SOCl<sub>2</sub> (127 mL, 1.75 mol) portionwise at r.t. under Ar. Then it was heated to reflux and allowed to stir at this temperature for further 3 hours. The yellowish solution was cooled to r.t. and the solvent was removed under vacuo. To the mixture of NHMe(OMe)·HCl (52 g, 0.525 mol) in CH<sub>2</sub>Cl<sub>2</sub> (200 mL) was added TEA (146 mL, 1.05 mol) dropwise, followed by the solution of 2-bromobenzoyl chloride above in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at 0 °C under Ar. Then the mixture was stirred at r.t. overnight. The solid was dissolved by H<sub>2</sub>O and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The residue was purified by flash chromatography on silica gel to afford 2-bromo-N-methoxy-N-methylbenzamide.

To a solution of 2-bromo-N-methoxy-N-methylbenzamide (952 mg, 3.9 mmol) in THF (10 mL) was added arylmagnesium bromide (5.8 mmol) dropwise at 0 °C under Ar. Then the mixture was allowed to stir at 0 °C for 3 hours. Sat.NH<sub>4</sub>Cl (aq) was added to quench the reaction and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The residue was purified by flash chromatography on silica gel to afford aryl ketone.

To the stirred mixture of triphenyl phosphonium salt (1.39 g, 3.74 mmol) in THF (10 mL) was added <sup>n</sup>BuLi (1.5 mL, 2.5 N in hexane, 3.74 mmol) dropwise at 0 °C under Ar. After 1 hour stirring at 0 °C, a solution of aryl ketone (2.9 mmol) in THF (5 mL) was added to the yellowish mixture dropwise at the same temperature. Then it was allowed to stir at r.t. overnight. H<sub>2</sub>O was added to quench the reaction and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The residue was purified by flash chromatography on silica gel.

Typical procedure for the synthesis of substrate **1o-1p**:

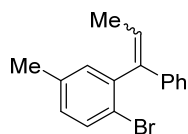


To a solution of 2-bromobenzaldehyde (8.4 mL, 72 mmol) in THF (200 mL) was added arylmagnesium bromide (108 mmol) dropwise at 0 °C under Ar. Then the mixture was allowed to stir at 0 °C for 3 hours. Sat.NH<sub>4</sub>Cl (aq) was added to quench the reaction and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The residue was purified by flash chromatography on silica gel.

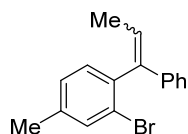
Dess-Martin Periodinane (14.3 g, 33.7 mmol) was added to the solution of arylalcohol (22.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) portionwise at 0 °C. Then the mixture was stirred at r.t. for 2 hours. The white solid was filtered through a celite pad and the filter cake was washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined filtrates were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The residue was purified by flash chromatography on silica gel.

To a stirred mixture of triphenyl phosphonium salt (1.39 g, 3.74 mmol) in THF (10 mL) was added <sup>t</sup>BuLi (1.5 mL, 2.5 N in hexane, 3.74 mmol) dropwise at 0 °C under Ar. After 1 hour, a solution of aryl ketone (2.9 mmol) in THF (5 mL) was added to the yellowish mixture dropwise at the same temperature. Then it was allowed to stir at r.t. overnight. H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> were added to the orange mixture above. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo. The residue was purified by flash chromatography on silica gel.

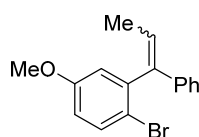
#### Characterization data of Compounds **1b-r**



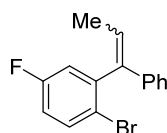
**1-Bromo-4-methyl-2-(1-phenylprop-1-en-1-yl)benzene (1b)** colorless oil  $R_f = 0.50$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 (d,  $J = 8.0$  Hz, 0.7H), 7.39 (d,  $J = 8.0$  Hz, 0.3H), 7.32-7.19 (m, 5H), 7.09-6.67 (m, 1.7H), 6.91 (d,  $J = 8.0$  Hz, 0.3H), 6.31 (q,  $J = 7.2$  Hz, 0.7H), 5.82 (q,  $J = 7.2$  Hz, 0.3H), 2.30 (s, 2.1H), 2.28 (s, 0.9H), 1.90 (d,  $J = 7.2$  Hz, 0.9H), 1.62 (d,  $J = 7.2$  Hz, 2.1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.58, 141.71, 141.23, 140.62, 140.38, 139.14, 137.30, 136.89, 132.69, 132.55, 132.48, 132.22, 129.68, 129.57, 129.24, 128.26, 127.82, 127.72, 126.82, 126.70, 126.19, 125.11, 120.90, 120.25, 20.94, 20.87, 15.55, 15.39 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for C<sub>16</sub>H<sub>15</sub>Br<sup>+</sup> 286.0357, found 286.0359.



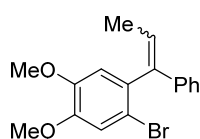
**2-Bromo-4-methyl-1-(1-phenylprop-1-en-1-yl)benzene (1c)** colorless oil  $R_f = 0.52$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (s, 0.7H), 7.35 (s, 0.3H), 7.31-7.13 (m, 6H), 7.06-7.04 (m, 1H), 6.31 (q,  $J = 7.2$  Hz, 0.7H), 5.82 (q,  $J = 7.2$  Hz, 0.3H), 2.36 (s, 2H), 2.30 (s, 1H), 1.90 (d,  $J = 7.2$  Hz, 0.9H), 1.62 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.00, 141.49, 141.11, 140.75, 139.29, 138.77, 138.47, 137.57, 133.44, 133.32, 131.49, 131.39, 129.68, 128.29, 128.25, 127.89, 127.81, 127.69, 126.78, 126.67, 126.17, 125.26, 124.03, 123.34, 20.86, 20.72, 15.55, 15.42 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{16}\text{H}_{15}\text{Br}^+$  286.0357, found 286.0363.



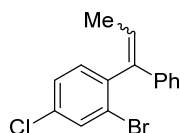
**1-Bromo-4-methoxy-2-(1-phenylprop-1-en-1-yl)benzene (1d)** colorless oil  $R_f = 0.15$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.8$  Hz, 0.7H), 7.40 (d,  $J = 8.8$  Hz, 0.3H), 7.33-7.18 (m, 5H), 6.84-6.67 (m, 2H), 6.32 (q,  $J = 7.2$  Hz, 0.7H), 5.85 (q,  $J = 7.2$  Hz, 0.3H), 3.78 (s, 3H), 1.91 (d,  $J = 7.2$  Hz, 0.9H), 1.64 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.96, 158.64, 145.74, 141.69, 141.57, 141.17, 140.24, 138.84, 133.52, 133.48, 129.68, 128.30, 127.87, 127.85, 126.90, 126.79, 126.13, 125.16, 117.41, 116.80, 114.78, 114.70, 114.19, 114.13, 55.51, 15.53, 15.38 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{16}\text{H}_{15}\text{BrO}^+$  302.0306, found 302.0301.



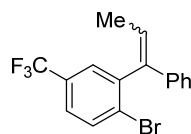
**1-Bromo-4-fluoro-2-(1-phenylprop-1-en-1-yl)benzene (1e)** colorless oil  $R_f = 0.35$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61-7.57 (m, 0.7H), 7.48-7.44 (m, 0.3H), 7.34-7.18 (m, 5H), 7.02-6.99 (m, 0.3H), 6.95-6.91 (m, 1.4H), 6.87-6.83 (m, 0.3H), 6.33 (q,  $J = 7.2$  Hz, 0.7H), 5.86 (q,  $J = 7.2$  Hz, 0.3H), 1.91 (d,  $J = 7.2$  Hz, 0.9H), 1.63 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.93 (d,  $J = 246.0$  Hz), 161.78 (d,  $J = 246.0$  Hz), 146.58 (d,  $J = 7.5$  Hz), 142.63 (d,  $J = 7.5$  Hz), 140.92, 140.47, 139.84, 138.40, 134.14 (d,  $J = 8.2$  Hz), 134.12 (d,  $J = 8.2$  Hz), 129.64, 128.68, 128.38, 127.96, 127.10, 127.01, 126.12, 125.74, 118.68 (d,  $J = 22.3$  Hz), 118.58 (d,  $J = 3.2$  Hz), 118.56 (d,  $J = 22.3$  Hz), 117.80 (d,  $J = 3.2$  Hz), 115.99 (d,  $J = 22.3$  Hz), 115.52 (d,  $J = 22.3$  Hz), 15.50, 15.37 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.02, -115.71 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{12}\text{BrF}^+$  290.0106, found 290.0104.



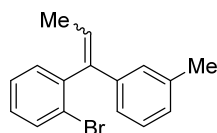
**1-Bromo-4,5-dimethoxy-2-(1-phenylprop-1-en-1-yl)benzene (1f)** colorless oil  $R_f = 0.10$  (silica, petroleum ether, UV detection); major : minor = 1.5 : 1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 -7.20 (m, 5H), 7.11 (s, 0.6H), 7.00 (s, 0.4H), 6.77 (s, 0.4H), 6.65 (s, 0.6H), 6.33 (q,  $J = 7.2$  Hz, 0.6H), 5.84 (q,  $J = 7.2$  Hz, 0.4H), 3.91 (s, 1.8H), 3.86 (s, 1.2H), 3.84 (s, 1.2H), 3.82 (s, 1.8H), 1.91 (d,  $J = 7.2$  Hz, 1.2H), 1.64 (d,  $J = 7.2$  Hz, 1.8H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.61, 148.47, 148.45, 147.97, 141.46, 140.98, 140.51, 139.21, 137.19, 132.57, 129.60, 128.29, 127.84, 126.86, 126.73, 126.09, 125.42, 115.63, 115.39, 114.38, 114.30, 113.72, 113.62, 56.16, 56.10, 15.57, 15.43 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{Br}^+$  332.0412, found 332.0411.



**2-Bromo-4-chloro-1-(1-phenylprop-1-en-1-yl)benzene (1g)** colorless oil  $R_f = 0.31$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (s, 0.7H), 7.54 (s, 0.3H), 7.35-7.10 (m, 7H), 6.34 (q,  $J = 7.2$  Hz, 0.7H), 5.84 (q,  $J = 7.2$  Hz, 0.3H), 1.91 (d,  $J = 7.2$  Hz, 0.9H), 1.62 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.44, 140.68, 140.28, 140.11, 139.27, 134.61, 133.63, 133.28, 132.61, 132.44, 132.42, 131.47, 129.63, 128.53, 128.37, 127.95, 127.80, 127.34, 127.06, 126.96, 126.12, 125.85, 124.76, 123.99, 15.55, 15.43 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{12}\text{ClBr}^+$  305.9802, found 305.9811.

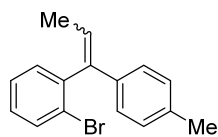


**1-Bromo-2-(1-phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzene (1h)** colorless oil  $R_f = 0.53$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.8$  Hz, 0.7H), 7.64 (d,  $J = 8.8$  Hz, 0.3H), 7.54 (s, 0.3H), 7.46-7.45 (m, 1.3H), 7.38-7.23 (m, 3.4H), 7.20-7.16 (m, 2H), 6.38 (q,  $J = 7.2$  Hz, 0.7H), 5.88 (q,  $J = 7.2$  Hz, 0.3H), 1.94 (d,  $J = 7.2$  Hz, 0.9H), 1.64 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.69, 141.72, 140.85, 140.25, 139.74, 138.15, 133.66, 133.62, 130.07 (q,  $J = 32.9$  Hz), 129.67, 129.66 (q,  $J = 32.9$  Hz), 129.18, 128.47, 128.40, 128.37, 128.33, 128.04, 127.71, 127.24, 127.14, 126.31, 126.14, 125.46 (q,  $J = 3.6$  Hz), 125.05 (q,  $J = 3.6$  Hz), 123.91 (q,  $J = 271.0$  Hz), 123.86 (q,  $J = 271.0$  Hz), 15.53, 15.42 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.40 ppm; HRMS (DART)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{12}\text{BrF}_3^+$  340.0074, found 340.0067.

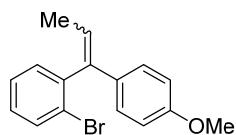


**1-Bromo-2-(1-(m-tolyl)prop-1-en-1-yl)benzene (1i)** colorless oil  $R_f = 0.45$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.0$  Hz, 0.7H), 7.52 (d,  $J = 8.0$  Hz, 0.3H), 7.35-7.08 (m, 4H), 7.03-6.96 (m, 3H), 6.31 (q,  $J = 7.2$  Hz, 0.7H), 5.81 (q,  $J = 7.2$  Hz, 0.3H), 2.31 (s, 0.9H), 2.29 (s, 2.1H), 1.90 (d,  $J = 7.2$  Hz, 0.9H), 1.60 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.01, 141.69, 141.30, 140.82, 140.48, 138.99, 137.75, 137.35, 132.99, 132.88, 131.74, 131.71, 130.19, 128.63, 128.30, 128.17, 127.85,

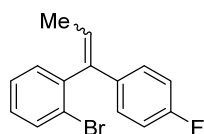
127.70, 127.54, 127.39, 127.05, 126.90, 126.78, 125.09, 124.32, 123.63, 123.45, 21.58, 21.54, 15.49, 15.43 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for  $C_{16}H_{15}Br^+$  286.0357, found 286.0359.



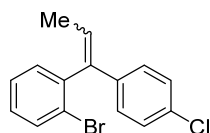
**1-Bromo-2-(1-(*p*-tolyl)prop-1-en-1-yl)benzene (1j)** colorless oil  $R_f = 0.42$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.64 (d,  $J = 8.0$  Hz, 0.7H), 7.51 (d,  $J = 8.0$  Hz, 0.3H), 7.35-7.32 (m, 0.7H), 7.28-7.24 (m, 1H), 7.20-7.16 (m, 1.3H), 7.11-7.05 (m, 4H), 6.29 (q,  $J = 7.2$  Hz, 0.7H), 5.80 (q,  $J = 7.2$  Hz, 0.3H), 2.33 (s, 0.9H), 2.30 (s, 2.1H), 1.91 (d,  $J = 7.2$  Hz, 0.9H), 1.60 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  145.09, 141.56, 141.04, 140.86, 137.67, 136.56, 136.38, 136.11, 132.96, 132.87, 131.74, 131.68, 129.55, 129.01, 128.61, 128.57, 128.30, 127.40, 127.05, 126.01, 124.30, 124.24, 123.65, 21.27, 21.11, 15.44, 15.41 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for  $C_{16}H_{15}Br^+$  286.0357, found 286.0353.



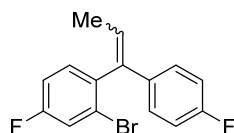
**1-Bromo-2-(1-(4-methoxyphenyl)prop-1-en-1-yl)benzene (1k)** colorless oil  $R_f = 0.21$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.64 (d,  $J = 8.0$  Hz, 0.7H), 7.52 (d,  $J = 8.0$  Hz, 0.3H), 7.34-7.32 (m, 0.7H), 7.27-7.25 (m, 1H), 7.21-7.16 (m, 1.3H), 7.13-7.11 (m, 2H), 6.86-6.79 (m, 2H), 6.22 (q,  $J = 7.2$  Hz, 0.7H), 5.77 (q,  $J = 7.2$  Hz, 0.3H), 3.80 (s, 0.9H), 3.77 (s, 2.1H), 1.91 (d,  $J = 7.2$  Hz, 0.9H), 1.59 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  158.68, 158.32, 145.18, 141.27, 140.97, 140.68, 133.30, 133.01, 132.92, 131.74, 131.68, 131.58, 130.84, 128.62, 128.30, 127.43, 127.26, 127.07, 126.95, 124.29, 123.69, 123.31, 113.70, 113.27, 55.28, 55.23, 15.41, 15.40 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for  $C_{16}H_{15}OBr^+$  302.0306, found 302.0308.



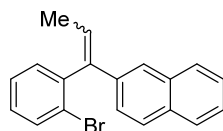
**1-Bromo-2-(1-(4-fluorophenyl)prop-1-en-1-yl)benzene (1l)** colorless oil  $R_f = 0.38$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.64 (d,  $J = 8.0$  Hz, 0.7H), 7.52 (d,  $J = 8.0$  Hz, 0.3H), 7.37-7.09 (m, 5H), 7.01-6.92 (m, 2H), 6.25 (q,  $J = 7.2$  Hz, 0.7H), 5.83 (q,  $J = 7.2$  Hz, 0.3H), 1.89 (d,  $J = 7.2$  Hz, 0.9H), 1.61 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  161.98 (d,  $J = 245.0$  Hz), 161.61 (d,  $J = 245.0$  Hz), 144.70, 140.82, 140.51, 140.33, 136.73 (d,  $J = 3.2$  Hz), 135.01 (d,  $J = 3.2$  Hz), 133.10, 133.04, 131.72, 131.64, 131.34, 131.26, 128.85, 128.55, 128.01, 127.78, 127.70, 127.52, 127.18, 125.14, 124.23, 123.60, 115.10 (d,  $J = 21.4$  Hz), 114.79 (d,  $J = 21.4$  Hz), 15.49, 15.34 ppm;  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -115.4, -116.0 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for  $C_{15}H_{12}BrF^+$  290.0106, found 290.0107.



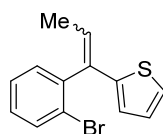
**1-Bromo-2-(1-(4-chlorophenyl)prop-1-en-1-yl)benzene (1m)** colorless oil  $R_f = 0.36$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8$  Hz, 0.7H), 7.52 (d,  $J = 8$  Hz, 0.3H), 7.37-7.25 (m, 2H), 7.23-7.10 (m, 5H), 6.31 (q,  $J = 7.2$  Hz, 0.7H), 5.85 (q,  $J = 7.2$  Hz, 0.3H), 1.90 (d,  $J = 7.2$  Hz, 0.9H), 1.61 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.41, 140.73, 140.27, 140.17, 139.00, 137.47, 133.09, 133.04, 132.62, 132.53, 131.76, 131.64, 131.02, 128.94, 128.64, 128.50, 128.42, 128.08, 127.55, 127.43, 127.21, 125.89, 124.23, 123.60, 15.56, 15.39 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{12}\text{BrCl}^+$  305.9811, found 305.9804.



**2-Bromo-4-fluoro-1-(1-(4-fluorophenyl)prop-1-en-1-yl)benzene (1n)** colorless oil  $R_f = 0.39$  (silica, petroleum ether, UV detection); major : minor = 2.3 : 1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.39 (m, 0.7H), 7.28-7.26 (m, 0.3H), 7.23-7.21 (m, 0.3H), 7.16-7.06 (m, 3.4H), 7.02-6.92 (m, 2.3H), 6.26 (q,  $J = 7.2$  Hz, 0.7H), 5.82 (q,  $J = 7.2$  Hz, 0.3H), 1.89 (d,  $J = 7.2$  Hz, 0.9H), 1.60 (d,  $J = 7.2$  Hz, 2.1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.01 (d,  $J = 245.0$  Hz), 161.65 (d,  $J = 245.0$  Hz), 161.59 (d,  $J = 249.0$  Hz), 161.43 (d,  $J = 249.0$  Hz), 140.85 (d,  $J = 3.5$  Hz), 136.58 (d,  $J = 3.5$  Hz), 136.47 (d,  $J = 3.6$  Hz), 134.82 (d,  $J = 3.6$  Hz), 139.85, 139.42, 132.43 (d,  $J = 8.2$  Hz), 131.23 (d,  $J = 8.2$  Hz), 128.47, 127.72, 127.64, 125.77, 124.33 (d,  $J = 9.5$  Hz), 123.65 (d,  $J = 9.5$  Hz), 120.24 (d,  $J = 24.1$  Hz), 120.19 (d,  $J = 24.1$  Hz), 115.17 (d,  $J = 21.2$  Hz), 114.87 (d,  $J = 21.2$  Hz), 114.85 (d,  $J = 20.8$  Hz), 114.28 (d,  $J = 20.8$  Hz), 15.51, 15.38 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.14, -113.79, -115.17, -115.81 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{11}\text{BrF}_2^+$  308.0012, found 308.0015.



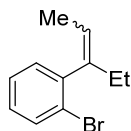
**1-Bromo-2-(1-(*m*-tolyl)prop-1-en-1-yl)benzene (1o)** colorless oil  $R_f = 0.79$  (silica, petroleum ether, UV detection); major : minor = 1.5 : 1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81-7.63 (m, 4H), 7.54-7.52 (m, 1H), 7.44-7.32 (m, 4H), 7.29-7.20 (m, 1.6H), 7.13-7.09 (m, 0.4H), 6.48 (q,  $J = 7.2$  Hz, 0.6H), 5.93 (q,  $J = 7.2$  Hz, 0.4H), 1.96 (d,  $J = 7.2$  Hz, 1.2H), 1.66 (d,  $J = 7.2$  Hz, 1.8H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.83, 141.70, 141.25, 140.64, 137.80, 136.64, 133.46, 133.14, 133.08, 133.01, 132.52, 132.30, 131.89, 131.81, 128.81, 128.54, 128.49, 128.44, 128.20, 128.05, 128.03, 127.86, 127.63, 127.51, 127.27, 127.14, 126.02, 125.95, 125.85, 125.64, 125.24, 124.41, 124.24, 123.72, 15.65, 15.52 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_{15}\text{Br}^+$  322.0357, found 322.0369.



**2-(1-(2-Bromophenyl)prop-1-en-1-yl)thiophene (1p)** colorless oil  $R_f = 0.76$  (silica, petroleum ether, UV detection); major : minor = 1.5 : 1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8$  Hz, 0.4H), 7.56 (d,  $J = 8$  Hz, 0.6H), 7.36-7.28 (m, 2H), 7.23-7.09 (m, 2H), 6.98-6.96 (m, 0.6H), 6.87-

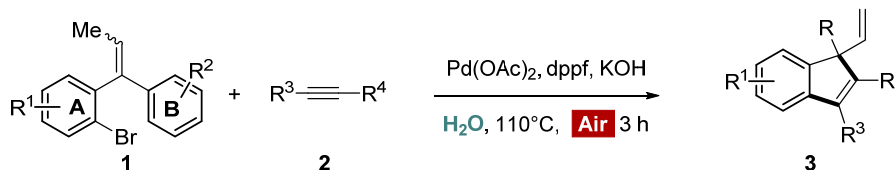


6.85 (m, 0.4H), 6.75 (d,  $J = 7.2$  Hz, 0.6H), 6.44 (d,  $J = 7.2$  Hz, 0.4H), 6.30 (q,  $J = 7.2$  Hz, 0.4H), 5.72 (q,  $J = 7.2$  Hz, 0.6H), 2.10 (d,  $J = 7.2$  Hz, 1.8H), 1.58 (d,  $J = 7.2$  Hz, 1.2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.44, 144.50, 141.73, 139.81, 135.75, 135.41, 132.92, 132.85, 131.41, 131.34, 129.05, 128.76, 127.46, 127.37, 127.24, 127.21, 127.19, 126.59, 125.36, 124.17, 124.09, 123.92, 123.54, 15.71, 15.02 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{13}\text{H}_{11}\text{BrS}^+$  277.9765, found 277.9767.



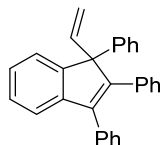
**1-Bromo-2-(pent-2-en-3-yl)benzene (1r)** colorless oil  $R_f = 0.85$  (silica, petroleum ether, UV detection); major : minor = 4 : 1;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 8.0$  Hz, 0.8H), 7.53 (d,  $J = 8.0$  Hz, 0.2H), 7.29-7.21 (m, 1H), 7.13-7.05 (m, 2H), 5.58 (q,  $J = 6.8$  Hz, 0.8H), 5.37 (q,  $J = 6.8$  Hz, 0.2H), 2.48-2.43 (m, 0.4H), 2.33-2.27 (m, 1.6H), 1.77 (d,  $J = 6.8$  Hz, 0.6H), 1.40 (d,  $J = 6.8$  Hz, 2.4H), 0.99 (t,  $J = 7.6$  Hz, 2.4H), 0.89 (t,  $J = 7.6$  Hz, 0.6H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.11, 143.11, 142.66, 142.27, 132.59, 132.56, 131.06, 130.61, 128.04, 127.91, 127.09, 126.87, 124.38, 123.21, 121.40, 30.95, 23.91, 14.50, 13.47, 12.50 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{11}\text{H}_{13}\text{Br}^+$  224.0201, found 224.0208.

### 3. General procedure for the double Heck reaction of alkenes and alkynes



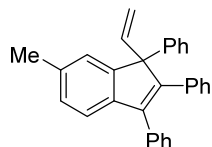
To the suspension of alkene **1** (0.30 mmol), alkyne **2** (0.36 mmol),  $\text{Pd}(\text{OAc})_2$  (3.4 mg, 0.015 mmol), dppf (16.6 mg, 0.03 mmol) and KOH (33.6 mg, 0.60 mmol) in a sealed tube was added  $\text{H}_2\text{O}$  (1.5 mL). The mixture was stirred at room temperature for 5 min and then reacted at 110 °C for further 3 h. After being cooled down to room temperature,  $\text{H}_2\text{O}$  was removed and the residue was purified by flash chromatography on silica gel.

#### Characterization data of Compounds 3aa-ra, 3ac-ai, 3aj+3aj', 3ak+3ak'

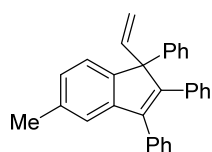


**1,2,3-Triphenyl-1-vinyl-1H-indene (3aa)** colorless oil (102 mg, 92% yield);  $R_f = 0.31$  (silica, petroleum ether, UV detection);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.33 (m, 7H), 7.31-7.25 (m, 3H), 7.23-7.21 (m, 1H), 7.20-7.01 (m, 6H), 6.89 (d,  $J = 7.2$  Hz, 2H), 6.42 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.20 (d,  $J = 17.2$  Hz, 1H), 5.15 (d,  $J = 10.4$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.65, 148.43, 143.85, 142.29, 140.42, 138.16, 135.65, 135.43, 129.84, 129.68, 128.72, 128.56,

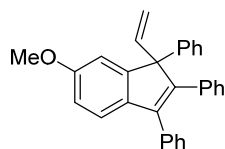
127.70, 127.40, 126.98, 126.94, 126.84, 126.77, 125.95, 124.99, 121.37, 115.25, 66.38 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for  $C_{29}H_{22}^+$  370.1715, found 370.1722.



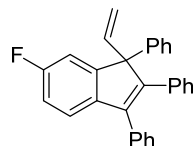
**6-Methyl-1,2,3-triphenyl-1-vinyl-1H-indene (3ba)** colorless oil (94 mg, 82% yield);  $R_f$  = 0.19 (silica, petroleum ether, UV detection);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40-7.33 (m, 6H), 7.30-7.23 (m, 5H), 7.06-6.99 (m, 4H), 6.91-6.86 (m, 3H), 6.42 (dd,  $J$  = 17.2, 10.4 Hz, 1H), 5.20 (d,  $J$  = 17.2 Hz, 1H), 5.20 (d,  $J$  = 10.4 Hz, 1H), 2.32 (s, 3H) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  150.92, 147.45, 142.57, 141.24, 140.37, 138.36, 135.80, 135.78, 135.65, 129.83, 129.66, 128.70, 128.52, 127.66, 127.62, 127.32, 127.04, 126.77, 126.68, 125.70, 121.07, 115.16, 66.16, 21.65 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for  $C_{30}H_{24}^+$  384.1878, found 384.1876.



**5-Methyl-1,2,3-triphenyl-1-vinyl-1H-indene (3ca)** colorless oil (96 mg, 84% yield);  $R_f$  = 0.44 (silica, petroleum ether, UV detection);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40-7.32 (m, 7H), 7.29-7.21 (m, 3H), 7.15 (s, 1H), 7.06-6.96 (m, 5H), 6.89-6.87 (m, 2H), 6.41 (dd,  $J$  = 17.2, 10.4 Hz, 1H), 5.20 (d,  $J$  = 17.2 Hz, 1H), 5.14 (d,  $J$  = 10.4 Hz, 1H), 2.34 (s, 3H) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  148.67, 147.96, 144.00, 142.57, 140.48, 138.37, 136.54, 135.74, 135.60, 129.85, 129.71, 128.69, 128.57, 127.67, 127.35, 126.96, 126.87, 126.81, 126.67, 124.66, 122.01, 115.13, 66.04, 21.58 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for  $C_{30}H_{24}^+$  384.1878, found 384.1877.

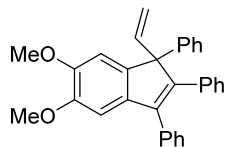


**6-Methoxy-1,2,3-triphenyl-1-vinyl-1H-indene (3da)** colorless oil (103 mg, 86% yield);  $R_f$  = 0.60 (silica, petroleum ether / ethyl acetate = 20:1 v/v, UV detection);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40-7.31 (m, 6H), 7.30-7.22 (m, 5H), 7.05-6.99 (m, 3H), 6.88-6.86 (m, 2H), 6.79 (dd,  $J$  = 8.4, 2.4 Hz, 1H), 6.66 (d,  $J$  = 2.4 Hz, 1H), 6.41 (dd,  $J$  = 17.2, 10.4 Hz, 1H), 5.21 (d,  $J$  = 17.2 Hz, 1H), 5.16 (d,  $J$  = 10.4 Hz, 1H), 3.74 (s, 3H) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  158.51, 152.43, 146.49, 142.56, 140.01, 138.32, 136.83, 135.81, 135.68, 129.78, 129.64, 128.74, 128.54, 127.66, 127.34, 126.98, 126.75, 126.67, 121.93, 115.28, 112.05, 111.51, 66.20, 55.54 ppm; HRMS (EI)  $m/z$ :  $[M]^+$  calcd for  $C_{30}H_{24}O^+$  400.1827, found 400.1819.

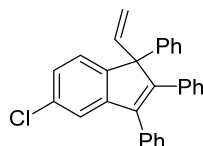


**6-Fluoro-1,2,3-triphenyl-1-vinyl-1H-indene (3ea)** colorless oil (90 mg, 77% yield);  $R_f$  = 0.31 (silica, petroleum ether, UV detection);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.39-7.32 (m, 7H), 7.30-7.26 (m, 4H), 7.10-7.01 (m, 3H), 7.96-7.91 (m, 1H), 6.88-6.86 (m, 2H), 6.80 (dd,  $J$  = 8.4, 2.4 Hz, 1H), 6.39 (dd,  $J$  = 17.6, 10.4 Hz, 1H), 5.20 (d,  $J$  = 17.6 Hz, 1H), 5.17 (d,  $J$  = 10.4 Hz, 1H) ppm;

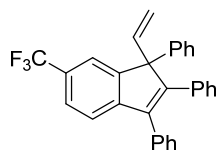
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.72 (d,  $J = 244.0$  Hz), 152.70 (d,  $J = 8.0$  Hz), 148.17 (d,  $J = 4.0$  Hz), 141.76, 139.71, 139.54, 137.76, 135.40, 135.21, 129.74, 129.60, 128.87, 128.65, 127.76, 127.56, 127.05, 127.02, 126.89, 122.21 (d,  $J = 8.0$  Hz), 115.50, 113.79 (d,  $J = 23.0$  Hz), 112.60 (d,  $J = 23.0$  Hz), 66.27 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.90 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{29}\text{H}_{21}\text{F}^+$  388.1627, found 388.1626.



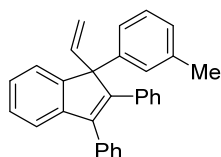
**5,6-Dimethoxy-1,2,3-triphenyl-1-vinyl-1H-indene (3fa)** colorless oil (99 mg, 77% yield);  $R_f = 0.20$  (silica, petroleum ether / ethyl acetate = 20:1 v/v, UV detection);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.35 (m, 4H), 7.33-7.23 (m, 6H), 7.06-6.99 (m, 3H), 6.89-6.83 (m, 3H), 6.64 (s, 1H), 6.42 (dd,  $J = 17.2, 10.8$  Hz, 1H), 5.21-5.13 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.47, 147.99, 147.58, 143.35, 142.55, 140.07, 138.69, 136.37, 135.80, 135.67, 129.73, 129.59, 128.72, 128.64, 127.65, 127.38, 126.94, 126.70, 126.67, 115.06, 108.59, 104.69, 66.21, 56.32, 56.15 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{31}\text{H}_{26}\text{O}_2^+$  430.1933, found 430.1929.



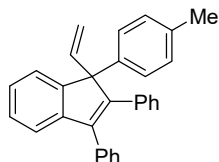
**5-Chloro-1,2,3-triphenyl-1-vinyl-1H-indene (3ga)** colorless oil (98 mg, 81% yield);  $R_f = 0.41$  (silica, petroleum ether, UV detection);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.37 (m, 4H), 7.33-7.29 (m, 6H), 7.27-7.26 (m, 1H), 7.16-7.13 (m, 1H), 7.11-7.07 (m, 1H), 7.05-6.99 (m, 3H), 6.87 (d,  $J = 6.8$  Hz, 2H), 6.39 (dd,  $J = 17.6, 10.4$  Hz, 1H), 5.17 (d,  $J = 17.6$  Hz, 1H), 5.16 (d,  $J = 10.4$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.13, 148.93, 145.77, 141.62, 139.53, 137.74, 135.19, 134.78, 132.96, 129.79, 129.55, 128.85, 128.75, 127.79, 127.71, 127.27, 127.04, 126.89, 125.94, 125.87, 121.53, 115.50, 66.10 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{29}\text{H}_{21}\text{Cl}^+$  404.1332, found 404.1340.



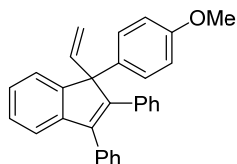
**1,2,3-Triphenyl-6-(trifluoromethyl)-1-vinyl-1H-indene (3ha)** white solid (115 mg, 88% yield);  $R_f = 0.19$  (silica, petroleum ether, UV detection);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.51 (m, 1H), 7.44-7.24 (m, 12H), 7.12-7.02 (m, 3H), 6.89-6.88 (m, 2H), 6.42 (dd,  $J = 16.8, 10.8$  Hz, 1H), 5.19-5.14 (m, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.38, 151.03, 147.45, 140.91, 139.52, 137.41, 135.00, 134.71, 129.81, 129.57, 128.98, 128.77, 127.84, 127.83 (q,  $J = 31.8$  Hz) 127.78, 127.47, 127.26, 126.95, 124.60 (q,  $J = 270.7$  Hz), 124.42 (q,  $J = 3.8$  Hz), 121.64 (q,  $J = 3.8$  Hz), 121.42, 115.72, 66.55 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.41 ppm; HRMS (DART)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{30}\text{H}_{22}\text{F}_3^+$  439.1668, found 439.1665.



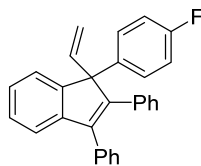
**2,3-Diphenyl-1-(*m*-tolyl)-1-vinyl-1*H*-indene (3ia)** colorless oil (72 mg, 63% yield);  $R_f = 0.34$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.31 (m, 6H), 7.26-7.22(m, 1H), 7.19-7.14 (m, 4H), 7.10-7.01 (m, 5H), 6.91-6.89 (m, 2H), 6.40 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.17 (d,  $J = 17.2$  Hz, 1H), 5.13 (d,  $J = 10.4$  Hz, 1H), 2.30 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.67, 148.43, 143.86, 142.16, 140.33, 138.39, 138.21, 135.73, 135.53, 129.90, 129.71, 128.56, 127.69, 127.60, 127.57, 127.38, 126.90, 126.77, 125.91, 124.97, 124.03, 121.33, 115.04, 66.34, 21.74 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{30}\text{H}_{24}^+$  384.1878, found 384.1882.



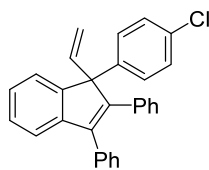
**2,3-Diphenyl-1-(*p*-tolyl)-1-vinyl-1*H*-indene (3ja)** colorless oil (100 mg, 87% yield);  $R_f = 0.25$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.29 (m, 6H), 7.23-7.15 (m, 4H), 7.09-7.01 (m, 6H), 6.92-6.90 (m, 2H), 6.41 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.18 (d,  $J = 17.2$  Hz, 1H), 5.13 (d,  $J = 10.4$  Hz, 1H), 2.32 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.83, 148.48, 143.81, 140.28, 139.13, 138.36, 136.28, 135.75, 135.51, 129.86, 129.70, 129.45, 128.54, 127.68, 127.36, 126.89, 126.85, 126.75, 125.93, 124.89, 121.30, 115.06, 66.10, 21.14 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{30}\text{H}_{24}^+$  384.1878, found 384.1870.



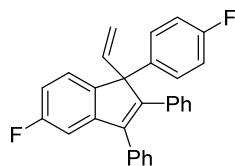
**1-(4-Methoxyphenyl)-2,3-diphenyl-1-vinyl-1*H*-indene (3ka)** colorless oil (111 mg, 93% yield);  $R_f = 0.52$  (silica, petroleum ether / ethyl acetate = 20:1 v/v, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.28 (m, 6H), 7.25-7.22 (m, 3H), 7.19-7.16 (m, 1H), 7.10-7.01 (m, 4H), 6.90 (d,  $J = 6.8$  Hz, 2H), 6.82 (d,  $J = 8.4$  Hz, 2H), 6.39 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.19 (d,  $J = 17.2$  Hz, 1H), 5.12 (d,  $J = 10.4$  Hz, 1H), 3.78 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.40, 150.89, 148.61, 143.75, 140.13, 138.42, 135.76, 135.46, 133.98, 129.86, 129.68, 128.52, 128.11, 127.69, 127.35, 126.91, 126.76, 125.92, 124.88, 121.31, 115.04, 114.06, 65.81, 55.23 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{30}\text{H}_{24}\text{O}^+$  400.1827, found 400.1825.



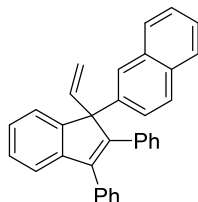
**1-(4-Fluorophenyl)-2,3-diphenyl-1-vinyl-1*H*-indene (3la)** colorless oil (101 mg, 87% yield);  $R_f = 0.38$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.32 (m, 6H), 7.30-7.25 (m, 3H), 7.21-7.18 (m, 1H), 7.09-7.02 (m, 4H), 6.96 (t,  $J = 8.4$  Hz, 2H), 6.89-6.87 (m, 2H), 6.39 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.20 (d,  $J = 17.2$  Hz, 1H), 5.15 (d,  $J = 10.4$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.79 (d,  $J = 242.0$  Hz), 150.47, 148.35, 143.75, 138.02, 137.89 (d,  $J = 3.0$  Hz), 135.38 (d,  $J = 28.0$  Hz), 129.80, 129.64, 128.68, 128.61, 128.57, 127.77, 127.48, 127.03 (d,  $J = 6.0$  Hz), 126.05, 124.91, 121.49, 115.62, 115.49, 115.41, 65.82 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.25 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{29}\text{H}_{21}\text{F}^+$  388.1627, found 388.1617.



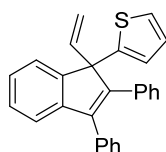
**1-(4-Chlorophenyl)-2,3-diphenyl-1-vinyl-1H-indene (3ma)** colorless oil (96 mg, 79% yield);  $R_f = 0.54$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.28 (m, 6H), 7.26-7.23 (m, 5H), 7.21-7.18 (m, 1H), 7.10-7.03 (m, 4H), 6.89 (d,  $J = 6.8$  Hz, 2H), 6.38 (dd,  $J = 17.6, 10.8$  Hz, 1H), 5.23-5.15 (m, 2H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) 150.19, 148.15, 143.79, 140.97, 140.68, 137.72, 135.41, 135.18, 132.56, 129.79, 129.63, 128.86, 128.59, 128.48, 127.82, 127.52, 127.11, 127.08, 126.10, 124.92, 121.54, 115.71, 65.89 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{29}\text{H}_{21}\text{Cl}^+$  404.1332, found 404.1335.



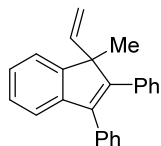
**5-Fluoro-1-(4-fluorophenyl)-2,3-diphenyl-1-vinyl-1H-indene (3na)** colorless oil (105 mg, 86% yield);  $R_f = 0.52$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.31 (m, 5H), 7.28-7.24 (m, 2H), 7.13-7.09 (m, 1H), 7.07-7.03 (m, 3H), 6.99-6.95 (m, 3H), 6.91-6.86 (m, 3H), 6.36 (dd,  $J = 17.4, 10.4$  Hz, 1H), 5.19 (d,  $J = 17.4$  Hz, 1H), 5.17 (d,  $J = 10.4$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.60 (d,  $J = 242.0$  Hz), 161.87 (d,  $J = 244.0$  Hz), 150.34, 145.85 (d,  $J = 9.0$  Hz), 145.78, 139.69 (d,  $J = 2.0$  Hz), 137.85, 137.51 (d,  $J = 4.0$  Hz), 135.17, 134.67, 129.72, 129.48, 128.72, 128.60, 128.52, 127.85, 127.55 (d,  $J = 39.0$  Hz), 125.80 (d,  $J = 8.0$  Hz), 115.73, 115.56 (d,  $J = 8.0$  Hz), 112.71 (d,  $J = 23.0$  Hz), 108.63 (d,  $J = 24.0$  Hz), 65.34 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.72, -115.93 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{29}\text{H}_{20}\text{F}_2^+$  406.1533, found 406.1527.



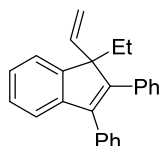
**2-(2,3-Diphenyl-1-vinyl-1H-inden-1-yl)naphthalene (3oa)** colorless oil (98 mg, 78% yield);  $R_f = 0.45$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (s, 1H), 7.85 (d,  $J = 7.6$  Hz, 1H), 7.79 (d,  $J = 7.6$  Hz, 1H), 7.67 (d,  $J = 8.4$  Hz, 1H), 7.51-7.43 (m, 4H), 7.41-7.32 (m, 4H), 7.28-7.24 (m, 1H), 7.20-7.14 (m, 2H), 7.09-7.03 (m, 2H), 6.98 (t,  $J = 7.2$  Hz, 2H), 6.88 (d,  $J = 7.2$  Hz, 2H), 6.54 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.28-5.21 (m, 2H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) 150.25, 148.40, 144.03, 140.73, 140.07, 137.95, 135.66, 135.41, 133.78, 132.53, 129.78, 129.73, 128.59, 128.51, 127.95, 127.78, 127.60, 127.47, 127.01, 126.99, 126.06, 126.00, 125.85, 125.73, 125.30, 125.28, 121.45, 115.48, 66.49 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{33}\text{H}_{24}^+$  420.1878, found 420.1869.



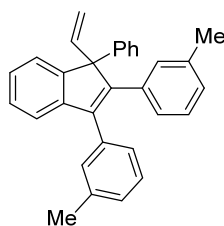
**2-(2,3-Diphenyl-1-vinyl-1*H*-inden-1-yl)thiophene (3pa)** colorless oil (91 mg, 81% yield);  $R_f = 0.29$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.32 (m, 5H), 7.30-7.23 (m, 4H), 7.14-7.07 (m, 4H), 7.02-7.00 (m, 2H), 6.95-6.94 (m, 1H), 6.92-6.90 (m, 1H), 6.41 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.27 (d,  $J = 17.2$  Hz, 1H), 5.18 (d,  $J = 10.4$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) 150.04, 148.32, 146.07, 143.25, 139.95, 138.26, 135.39, 135.11, 130.04, 129.62, 128.50, 127.71, 127.45, 127.35, 127.10, 126.65, 126.08, 125.20, 124.75, 124.18, 121.43, 115.54, 63.70 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{27}\text{H}_{20}\text{S}^+$  376.1286, found 376.1295.



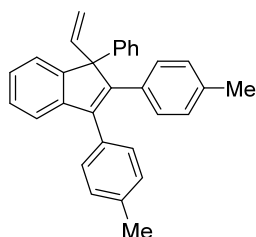
**1-Methyl-2,3-diphenyl-1-vinyl-1*H*-indene (3qa)** white solid (65 mg, 71% yield);  $R_f = 0.44$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.30 (m, 6H), 7.27-7.21 (m, 5H), 7.18-7.16 (m, 3H), 5.82 (dd,  $J = 17.6, 10.4$  Hz, 1H), 5.34 (d,  $J = 17.6$  Hz, 1H), 5.25 (d,  $J = 10.4$  Hz, 1H), 1.48 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.92, 150.19, 143.61, 141.50, 139.31, 136.11, 135.26, 129.72, 129.60, 128.35, 127.74, 127.17, 126.96, 126.94, 125.78, 122.98, 120.73, 113.67, 57.84, 19.54 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{24}\text{H}_{20}^+$  308.1565, found 308.1577.



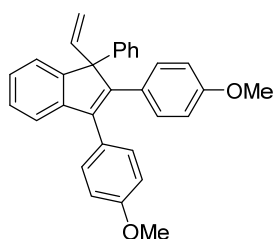
**1-Ethyl-2,3-diphenyl-1-vinyl-1*H*-indene (3ra)** colorless oil (71 mg, 74% yield);  $R_f = 0.31$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.30 (m, 5H), 7.28-7.23 (m, 6H), 7.19-7.16 (m, 3H), 5.89 (dd,  $J = 17.6, 10.4$  Hz, 1H), 5.32 (d,  $J = 17.6$  Hz, 1H), 5.22 (d,  $J = 10.4$  Hz, 1H), 2.22-2.13 (m, 1H), 2.00-1.91 (m, 1H), 0.48 (t,  $J = 7.2$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.86, 147.62, 144.86, 141.97, 141.18, 136.22, 135.42, 129.66, 129.61, 128.37, 127.80, 127.16, 126.90, 126.83, 125.70, 123.04, 120.55, 113.50, 62.25, 25.64, 7.77 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{25}\text{H}_{22}^+$  322.1722, found 322.1717.



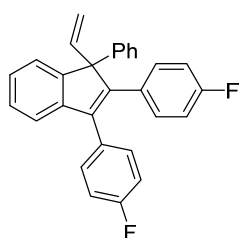
**1-Phenyl-2,3-di-*p*-tolyl-1-vinyl-1*H*-indene (3ac)** colorless oil (92 mg, 77% yield);  $R_f = 0.19$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.32 (m, 3H), 7.29-7.22 (m, 6H), 7.18-7.07 (m, 4H), 6.93-6.87 (m, 2H), 6.71-6.69 (m, 2H), 6.44 (dd,  $J = 17.2, 10.8$  Hz, 1H), 5.19 (d,  $J = 17.2$  Hz, 1H), 5.14 (d,  $J = 10.8$  Hz, 1H), 2.33 (s, 3H), 2.05 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.65, 148.29, 144.11, 142.48, 140.37, 138.36, 138.00, 136.89, 135.49, 130.54, 130.12, 128.65, 128.40, 128.09, 127.62, 127.47, 126.99, 126.94, 126.77, 126.69, 125.81, 124.92, 121.38, 115.10, 66.31, 21.53, 21.44 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{31}\text{H}_{26}^+$  398.2035, found 398.2022



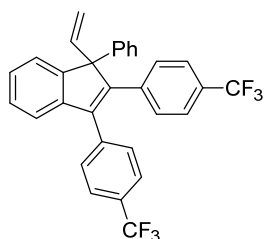
**1-Phenyl-2,3-di-*p*-tolyl-1-vinyl-1*H*-indene (3ad)** colorless oil (87 mg, 73% yield);  $R_f = 0.23$  (silica, petroleum ether, UV detection);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.29 (m, 6H), 7.25-7.13 (m, 6H), 7.08-7.06 (m, 1H), 6.85-6.79 (m, 4H), 6.42 (dd,  $J = 17.6, 10.4$  Hz, 1H), 5.18 (d,  $J = 17.6$  Hz, 1H), 5.12 (d,  $J = 10.4$  Hz, 1H), 2.37 (s, 3H), 2.20 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.59, 147.86, 144.11, 142.60, 139.87, 138.38, 136.95, 136.51, 132.72, 132.60, 129.66, 129.52, 129.31, 128.69, 128.46, 126.92, 126.75, 126.67, 125.70, 124.87, 121.26, 115.11, 66.22, 21.42, 21.20 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{31}\text{H}_{26}^+$  398.2035, found 398.2041.



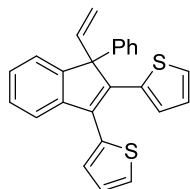
**2,3-Bis(4-methoxyphenyl)-1-phenyl-1-vinyl-1*H*-indene (3ae)** colorless oil (94 mg, 73% yield);  $R_f = 0.36$  (silica, petroleum ether / ethyl acetate = 20:1 v/v, UV detection);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.33 (m, 5H), 7.29-7.21 (m, 4H), 7.16-7.12 (m, 1H), 7.07-7.06 (m, 1H), 6.92 (d,  $J = 8.8$  Hz, 2H), 6.85 (d,  $J = 8.8$  Hz, 2H), 6.58 (d,  $J = 8.8$  Hz, 2H), 6.42 (dd,  $J = 17.6, 10.4$  Hz, 1H), 5.18 (d,  $J = 17.6$  Hz, 1H), 5.13 (d,  $J = 10.4$  Hz, 1H), 3.84 (s, 3H), 3.69 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.79, 158.29, 150.55, 147.34, 144.20, 142.68, 138.96, 138.51, 131.00, 130.88, 128.71, 128.17, 127.95, 126.92, 126.76, 126.68, 125.60, 124.85, 121.09, 115.09, 114.07, 113.18, 66.17, 55.26, 55.05 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{31}\text{H}_{26}\text{O}_2^+$  430.1933, found 430.1940.



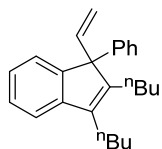
**2,3-Bis(4-fluorophenyl)-1-phenyl-1-vinyl-1*H*-indene (3af)** colorless oil (96 mg, 79% yield);  $R_f = 0.41$  (silica, petroleum ether, UV detection);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.29 (m, 5H), 7.28-7.17 (m, 5H), 7.10-7.04 (m, 3H), 6.85-6.81 (m, 2H), 6.76-6.72 (m, 2H), 6.37 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.18 (d,  $J = 17.2$  Hz, 1H), 5.16 (d,  $J = 10.4$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.17 (d,  $J = 246.0$  Hz), 161.76 (d,  $J = 246.0$  Hz), 150.54, 147.79, 143.50, 141.83, 139.47, 137.88, 131.53, 131.45 (d,  $J = 8.0$  Hz), 131.33 (d,  $J = 8.0$  Hz), 130.07, 130.04, 128.81, 126.99, 126.96, 126.19, 125.07, 121.17, 115.73 (d,  $J = 22.0$  Hz), 115.45, 114.87 (d,  $J = 22.0$  Hz), 66.39 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.13, -114.48 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{29}\text{H}_{20}\text{F}_2^+$  406.1533, found 406.1527.



**1-Phenyl-2,3-bis(4-(trifluoromethyl)phenyl)-1-vinyl-1H-indene (3ag)** colorless oil (100 mg, 66% yield);  $R_f = 0.47$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 8.0$  Hz, 2H), 7.50 (d,  $J = 8.0$  Hz, 2H), 7.33-7.24 (m, 9H), 7.25-7.22 (m, 1H), 7.13 (d,  $J = 7.2$  Hz, 1H), 6.95 (d,  $J = 7.2$  Hz, 2H), 6.37 (dd,  $J = 17.2, 10.8$  Hz, 1H), 5.21-5.17 (m, 2H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.69, 148.34, 142.78, 141.27, 140.60, 138.93, 138.69, 137.31, 130.52, 130.38, 130.06, 129.96, 129.93, 129.73, 129.65, 129.54, 129.41, 129.33, 128.98, 128.84, 128.72, 128.34, 128.21, 127.66, 127.64, 127.22, 126.95, 126.85, 125.78 (q,  $J = 3.8$  Hz), 124.91 (q,  $J = 3.8$  Hz), 124.13 (q,  $J = 271$  Hz), 124.04 (q,  $J = 271$  Hz), 121.43, 115.90, 66.66 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.56, -62.75 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{31}\text{H}_{20}\text{F}_6^+$  506.1469, found 506.1461.

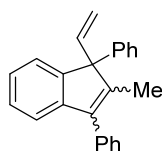


**2,2'-(1-Phenyl-1-vinyl-1H-indene-2,3-diyl)dithiophene (3ah)** colorless oil (64 mg, 56% yield);  $R_f = 0.48$  (silica, petroleum ether / ethyl acetate = 20:1 v/v, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (dd,  $J = 4.8$  Hz, 1.2 Hz, 2H), 7.35-7.14 (m, 9H), 7.11-7.027 (m, 2H), 6.79-6.77 (m, 1H), 6.67-6.66 (m, 1H), 6.59 (dd,  $J = 17.2, 10.4$  Hz, 1H), 5.18 (d,  $J = 10.4$  Hz, 1H), 5.12 (d,  $J = 17.2$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.74, 144.56, 143.77, 141.83, 138.35, 136.98, 135.37, 132.71, 128.79, 128.41, 128.32, 127.68, 127.21, 127.05, 127.01, 126.96, 126.45, 126.34, 126.17, 124.55, 121.38, 115.90, 66.47 ppm; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{25}\text{H}_{18}\text{S}_2^+$  382.0850, found 382.0840.

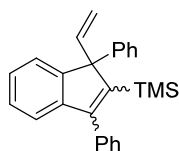


**2,3-Dibutyl-1-phenyl-1-vinyl-1H-indene (3ai)** colorless oil (83 mg, 84% yield);  $R_f = 0.38$  (silica, petroleum ether, UV detection);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.16 (m, 5H), 7.13-7.11 (m, 2H), 7.08-7.02 (m, 2H), 6.42 (dd,  $J = 17.6, 10.4$  Hz, 1H), 5.06 (d,  $J = 10.4$  Hz, 1H), 5.01 (d,  $J = 17.6$  Hz, 1H), 2.55 (t, 7.6 Hz, 2H), 2.30-2.17 (m, 2H), 1.67-1.59 (m, 2H), 1.49-1.41 (m, 2H), 1.29-1.22 (m, 4H), 0.97 (t, 7.2 Hz, 3H), 0.78 (t, 7.2 Hz, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.24, 148.88, 145.03, 142.46, 139.14, 137.95, 128.29, 127.28, 126.57, 126.49, 124.55, 124.06, 119.16, 113.63, 66.00, 32.02, 31.17, 26.87, 25.62, 23.36, 23.19, 14.14, 13.81 ppm; HRMS (DART)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{31}^+$  331.2420, found 331.2418.





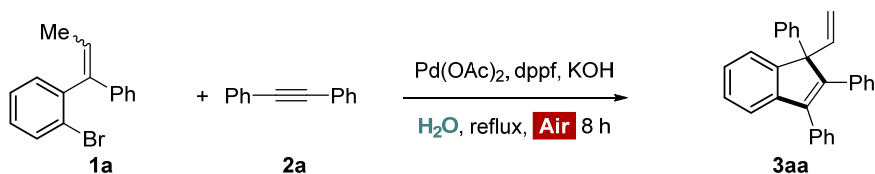
**2-Methyl-1,3-diphenyl-1-vinyl-1H-indene** and **3-methyl-1,2-diphenyl-1-vinyl-1H-indene (3aj + 3aj')** colorless oil (75 mg, 81% yield);  $R_f = 0.19$  (silica, petroleum ether, UV detection); major : minor = 5.3 : 1,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.46 (m, 0.64H), 7.41-7.39 (m, 1H), 7.32-7.11 (m, 10H), 7.05-7.01 (m, 2.36H), 6.46 (dd,  $J = 17.2, 10.4$  Hz, 0.16H), 6.34 (dd,  $J = 17.2, 10.4$  Hz, 0.84H), 5.19-5.16 (m, 0.16H), 5.12-5.06 (m, 1.84H), 2.22 (s, 2.52H), 1.87 (s, 0.48H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.26, 150.19, 147.71, 146.66, 145.04, 144.33, 142.19, 142.11, 138.65, 138.57, 138.44, 136.28, 135.20, 135.08, 129.41, 129.30, 128.59, 128.45, 127.93, 127.29, 127.18, 126.99, 126.89, 126.75, 126.70, 126.59, 125.70, 124.91, 124.62, 124.41, 120.20, 119.96, 114.72, 114.50, 66.38, 65.90, 12.20, 11.97 ppm; HRMS (DART)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}^+$  309.1638, found 309.1635.



**(1,3-Diphenyl-1-vinyl-1H-inden-2-yl)trimethylsilane** and **(1,2-diphenyl-1-vinyl-1H-inden-3-yl)tri-methylsilane (3ak + 3ak')** colorless oil (68 mg, 62% yield);  $R_f = 0.24$  (silica, petroleum ether, UV detection); major : minor = 1.7 : 1,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 7.6$  Hz, 0.37H), 7.47-7.38 (m, 3.26H), 7.29-7.00 (m, 9H), 6.93 (d,  $J = 6.8$  Hz, 0.63H), 6.83 (d,  $J = 7.6$  Hz, 0.74H), 6.71 (dd,  $J = 16.8, 10.4$  Hz, 0.63H), 6.23 (dd,  $J = 16.8, 10.4$  Hz, 0.37H), 5.13-5.06 (m, 2H), 0.06 (s, 3.33H), -0.23 (s, 5.67H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.67, 154.20, 152.94, 151.28, 150.54, 147.75, 145.60, 142.56, 141.00, 138.45, 138.38, 138.33, 137.74, 137.39, 129.95, 129.38, 128.44, 128.26, 128.16, 127.56, 127.43, 127.39, 127.30, 126.73, 126.68, 126.62, 126.57, 126.55, 125.95, 125.38, 124.96, 124.29, 123.07, 121.05, 114.80, 113.82, 69.24, 69.09, 1.00, 0.30 ppm; HRMS (FI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{26}\text{H}_{26}\text{Si}^+$  366.1804, found 366.1803.

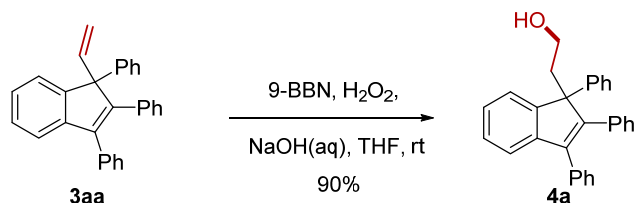
#### 4. Studies on the synthetic utility:

##### Gram-scale reaction:

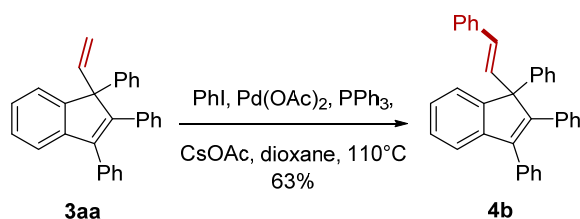


To the mixture of alkene **1a** (10 g, 36.8 mmol), alkyne **2a** (7.85 g, 44.1 mmol),  $\text{Pd}(\text{OAc})_2$  (413 mg, 1.84 mmol), dppf (2.04 g, 3.68 mmol) and KOH (4.1 g, 73.6 mmol) was added  $\text{H}_2\text{O}$  (180 mL). The mixture was stirred at room temperature for 5 min and then reacted at reflux for further 8 h. After being cooled down to room temperature,  $\text{H}_2\text{O}$  was removed and the residue was purified by flash chromatography on silica gel to afford 11.035 g **3aa** (81%).

## Transformation of Products:

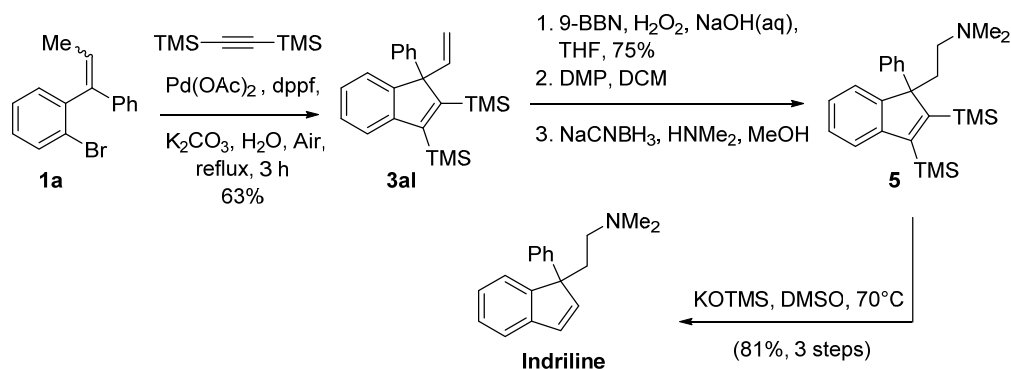


**2-(1,2,3-Triphenyl-1H-inden-1-yl)ethan-1-ol (4a)** To a solution of **3aa** (74 mg, 0.2 mmol) in THF (1 mL) was added 9-Borabicyclo[3.3.1]nonane (0.8 mL, 0.5 M in THF, 0.4 mmol) in THF dropwise at 0 °C. The resulting mixture was warmed to room temperature and allowed to stir at this temperature for 5 h. Then 3N NaOH (aq) was added to the mixture followed by 30% H<sub>2</sub>O<sub>2</sub> (0.3 mL) at 0 °C. After stirring at room temperature 1 h, CH<sub>2</sub>Cl<sub>2</sub> was added. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuo and the residue was purified by flash chromatography on silica gel to afford **4a** as a colorless oil (70 mg, 90% yield). *R*<sub>f</sub> = 0.36 (silica, petroleum ether / ethyl acetate = 20:1 v/v, UV detection); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37-7.31 (m, 6H), 7.29-7.24 (m, 6H), 7.20-7.06 (m, 3H), 7.03-7.00 (m, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 3.49-3.42 (m, 1H), 3.25-3.19 (m, 1H), 2.85-2.79 (m, 1H), 2.58-2.51 (m, 1H), 0.95 (br, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.39, 148.99, 143.98, 142.46, 141.23, 135.19, 135.12, 129.55, 129.42, 128.79, 128.61, 127.89, 127.50, 127.15, 127.06, 126.76, 126.46, 126.31, 123.00, 120.98, 60.63, 59.24, 36.37 ppm; HRMS (EI) *m/z*: [M]<sup>+</sup> calcd for C<sub>29</sub>H<sub>24</sub>O<sup>+</sup> 388.1827, found 388.1833.



**(E)-1,2,3-Triphenyl-1-styryl-1H-indene (4b)** To a solution of **3aa** (74 mg, 0.2 mmol), Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol), PPh<sub>3</sub> (10.5 mmol, 0.04 mmol) and CsOAc (77 mg, 0.4 mmol) in dioxane (1 mL) was added PhI (45 μL, 0.4 mmol) under Ar. The mixture was stirred at room temperature for 5 min and then reacted at 110 °C for further 3 h. The solvent was removed under vacuo and the residue was purified by flash chromatography on silica gel to afford **4b** as a colorless oil (56 mg, 63% yield). *R*<sub>f</sub> = 0.34 (silica, petroleum ether, UV detection); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.34 (m, 7H), 7.32-7.23 (m, 10H), 7.20-7.17 (m, 2H), 7.11-7.03 (m, 3H), 6.94-6.93 (m, 2H), 6.81 (d, *J* = 16.4 Hz, 1H), 6.54 (d, *J* = 16.4 Hz, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.93, 148.72, 143.92, 142.56, 140.43, 137.39, 135.66, 135.34, 130.39, 129.91, 129.68, 129.65, 128.74, 128.54, 128.52, 127.77, 127.41, 127.14, 127.01, 126.96, 126.85, 126.50, 126.12, 125.08, 121.45, 65.83 ppm; HRMS (EI) *m/z*: [M]<sup>+</sup> calcd for C<sub>35</sub>H<sub>26</sub><sup>+</sup> 446.2035, found 446.2033.

## Synthesis of the Indriline:



**(1-Phenyl-1-vinyl-1H-indene-2,3-diyl)bis(trimethylsilane) (3al)** To the mixture of alkene **1a** (81.6 mg, 0.30 mmol), 1,2-Bis(trimethylsilyl)ethyne (61.2 mg, 0.36 mmol), Pd(OAc)<sub>2</sub> (3.4 mg, 0.015 mmol), dppf (16.6 mg, 0.03 mmol) and K<sub>2</sub>CO<sub>3</sub> (82.8 mg, 0.60 mmol) was added H<sub>2</sub>O (1.5 mL). in a sealed tube was added H<sub>2</sub>O (1.5 mL). The mixture was stirred at room temperature for 5 min and then reacted at 80 °C for further 3 h. After being cooled down to room temperature, H<sub>2</sub>O was removed and the residue was purified by flash chromatography on silica gel to afford **3al** as a colorless oil (68 mg, 63% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.23-7.12 (m, 6H), 7.06-7.03 (m, 1H), 6.92-6.91 (m, 1H), 6.73 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.01 (d, *J* = 10.8 Hz, 1H), 4.93 (dd, *J* = 17.2 Hz, 1H), 0.48 (s, 9H), 0.06 (s, 9H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.47, 153.62, 152.28, 147.90, 142.85, 138.16, 128.49, 126.39, 126.31, 126.11, 125.13, 124.35, 123.26, 114.00, 72.23, 2.81, 2.25 ppm; HRMS (FI) *m/z*: [M]<sup>+</sup> calcd for C<sub>23</sub>H<sub>30</sub>Si<sub>2</sub><sup>+</sup> 362.1886, found 362.1881.

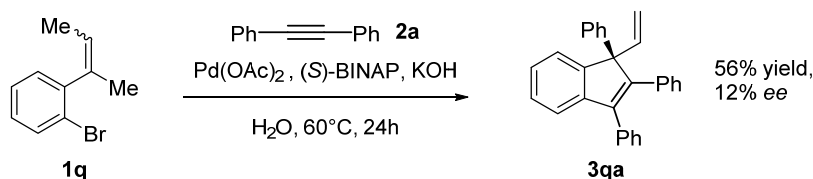
**Indriline: (N,N-dimethyl-2-(1-phenyl-1H-inden-1-yl)ethan-1-amine)** To a solution of **3al** (72 mg, 0.2 mmol) in THF (1 mL) was added 9-Borabicyclo[3.3.1]nonane (0.8 mL, 0.5 M in THF, 0.4 mmol) in THF dropwise at 0 °C. The resulting mixture was warmed to room temperature and allowed to stir at this temperature for 5 h. Then 3N NaOH (aq) was added to the mixture followed by 30% H<sub>2</sub>O<sub>2</sub> (0.3 mL) at 0 °C. After stirring at room temperature 1 h, CH<sub>2</sub>Cl<sub>2</sub> was added. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuo to afford crude product as a colorless oil. (57 mg, 75% yield).

Dess-Martin Periodinane (50 mg, 0.12 mmol) was added to the solution of the crude alcohol (30 mg, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) at 0 °C. Then the mixture was stirred at r.t. for 2 hours. The white solid was filtered through a celite pad and the filter cake was washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined filtrates were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuo to afford the crude aldehyde. The crude was used for the next step without further purification.

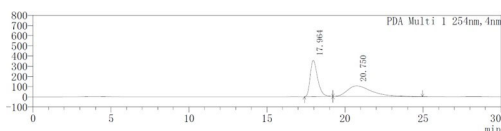
To a solution of crude aldehyde and HNMe<sub>2</sub> (40 μL, 0.08 mmol, 2 M in THF) in methanol (1 mL) was added NaCNBH<sub>3</sub> (6 mg, 0.10 mmol) at room temperature and allowed to stir at this temperature for 3 h. After removing the solvent, the residue was dissolved with DMSO (1 mL) and KOTMS (20 mg, 0.16 mmol) was added. Then the mixture was heated to 70 °C and allowed to stir at this temperature for 4 h. After being cooled down to room temperature, solvent was removed and the residue was purified by flash chromatography on silica gel to afford **Indriline** as a

colorless oil (17 mg, 81% yield, 3 steps)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.30 (m, 3H), 7.27-7.24 (m, 4H), 7.20-7.14 (m, 2H), 6.81 (d,  $J = 5.2$  Hz, 1H), 6.54 (d,  $J = 5.2$  Hz, 1H), 2.61-2.55 (m, 1H), 2.38-2.24 (m, 2H), 2.20 (s, 6H), 1.94-1.86 (m, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) 150.77, 143.97, 143.40, 141.86, 130.43, 128.59, 127.01, 126.70, 126.24, 125.68, 123.10, 121.62, 59.74, 55.21, 45.26, 34.19 ppm; HRMS (FI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_{21}\text{N}^+$  263.1674, found 263.1669.

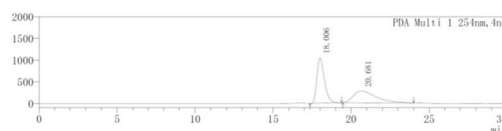
### Preliminary enantioselective studies



To the suspension of alkene **1q** (0.20 mmol), alkyne **2a** (0.24 mmol),  $\text{Pd}(\text{OAc})_2$  (2.3 mg, 0.01 mmol), (*S*)-BINAP (12.4 mg, 0.02 mmol) and KOH (33.6 mg, 0.60 mmol) in a sealed tube was added  $\text{H}_2\text{O}$  (1.5 mL). The mixture was stirred at room temperature for 5 min and then reacted at  $60^\circ\text{C}$  for further 24 h. After being cooled down to room temperature,  $\text{H}_2\text{O}$  was removed and the residue was purified by flash chromatography on silica gel. HPLC analysis: Chiracel OJ-H + Chiracel OJ-H column (the two columns were connected to each other in this order); detected at 254 nm,  $30^\circ\text{C}$ ; 1% *i*-PrOH in *n*-Hexane; flow = 0.5 mL/min; Retention time:  $t$  (major) = 18.0 min,  $t$  (minor) = 20.7 min.

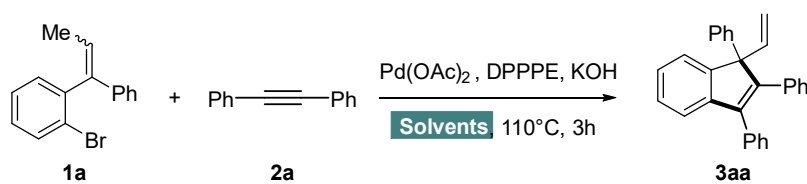


Entry	Retention time	Area%
1	17.964	50.958
2	20.750	49.042



Entry	Retention time	Area%
1	18.006	55.710
2	20.681	44.290

## 5. Control experiments

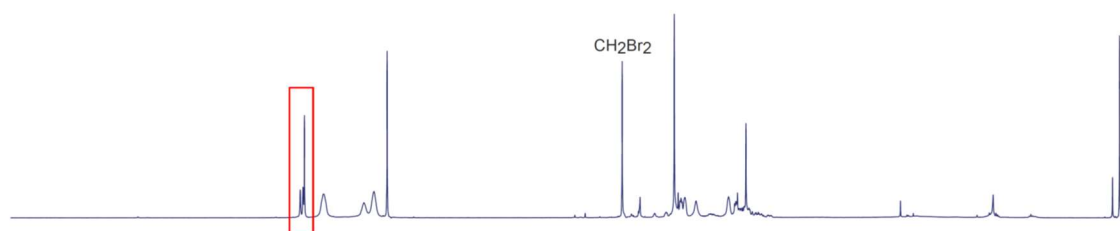


Entry	Solvent	Atmosphere	Yield (%)
1	dioxane	Ar	47
2	dioxane	Air	4
3	dioxane	O <sub>2</sub>	0
4	H <sub>2</sub> O	Ar	87
5	H <sub>2</sub> O	Air	82
6	H <sub>2</sub> O	O <sub>2</sub>	63

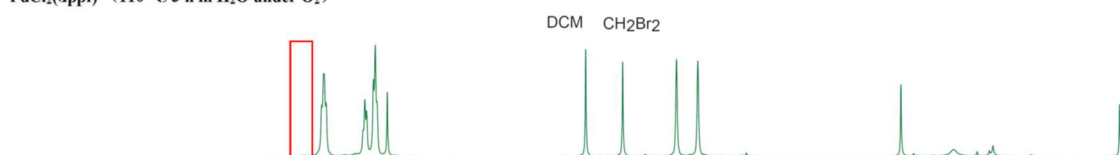
Reaction condition: **1a** (0.20 mmol, 1.0 equiv), **2a** (1.2 equiv), Pd(OAc)<sub>2</sub> (0.05 equiv), DPPPE (0.1 equiv), KOH (0.40 mmol, 2.0 equiv), H<sub>2</sub>O (1mL). Yields determined by NMR analysis using CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

## 6. Stability of catalyst under O<sub>2</sub>

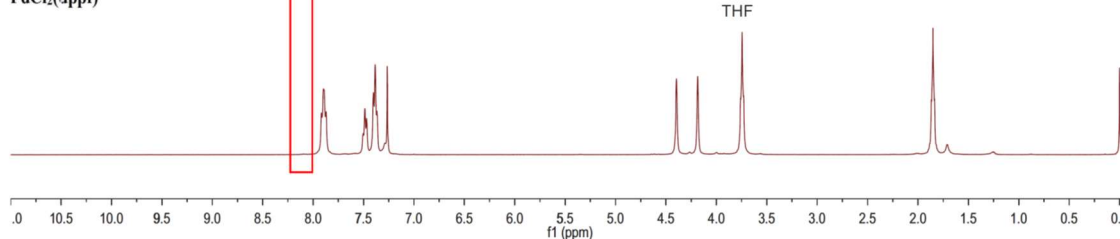
PdCl<sub>2</sub>(dppf) (110 °C 3 h in dioxane under O<sub>2</sub>)



PdCl<sub>2</sub>(dppf) (110 °C 3 h in H<sub>2</sub>O under O<sub>2</sub>)



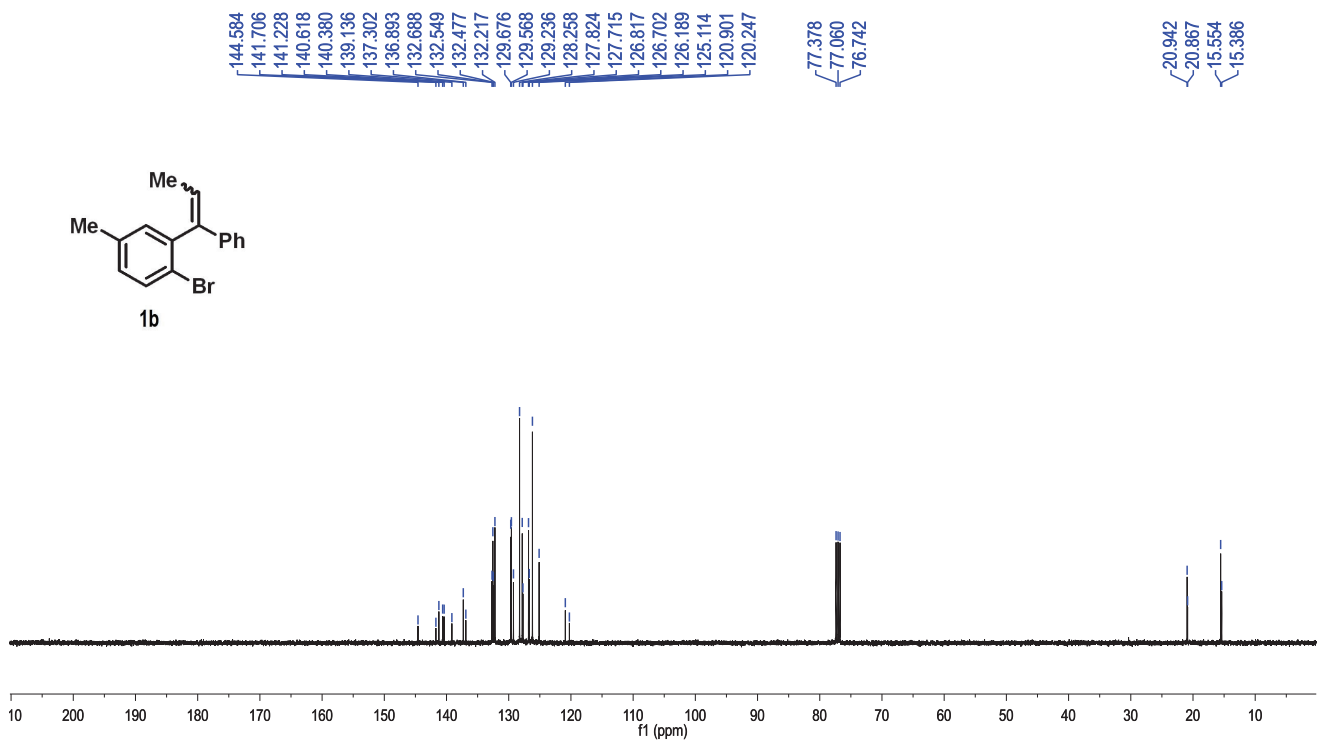
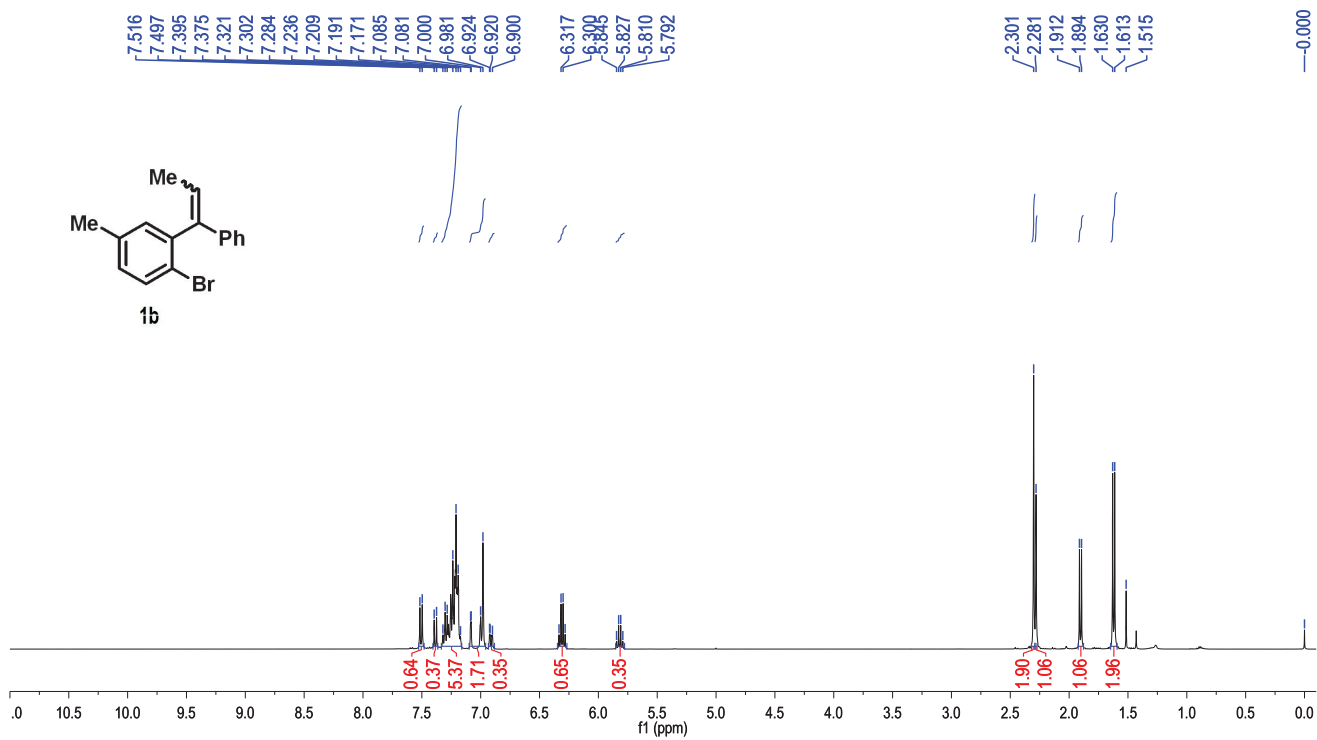
PdCl<sub>2</sub>(dppf)

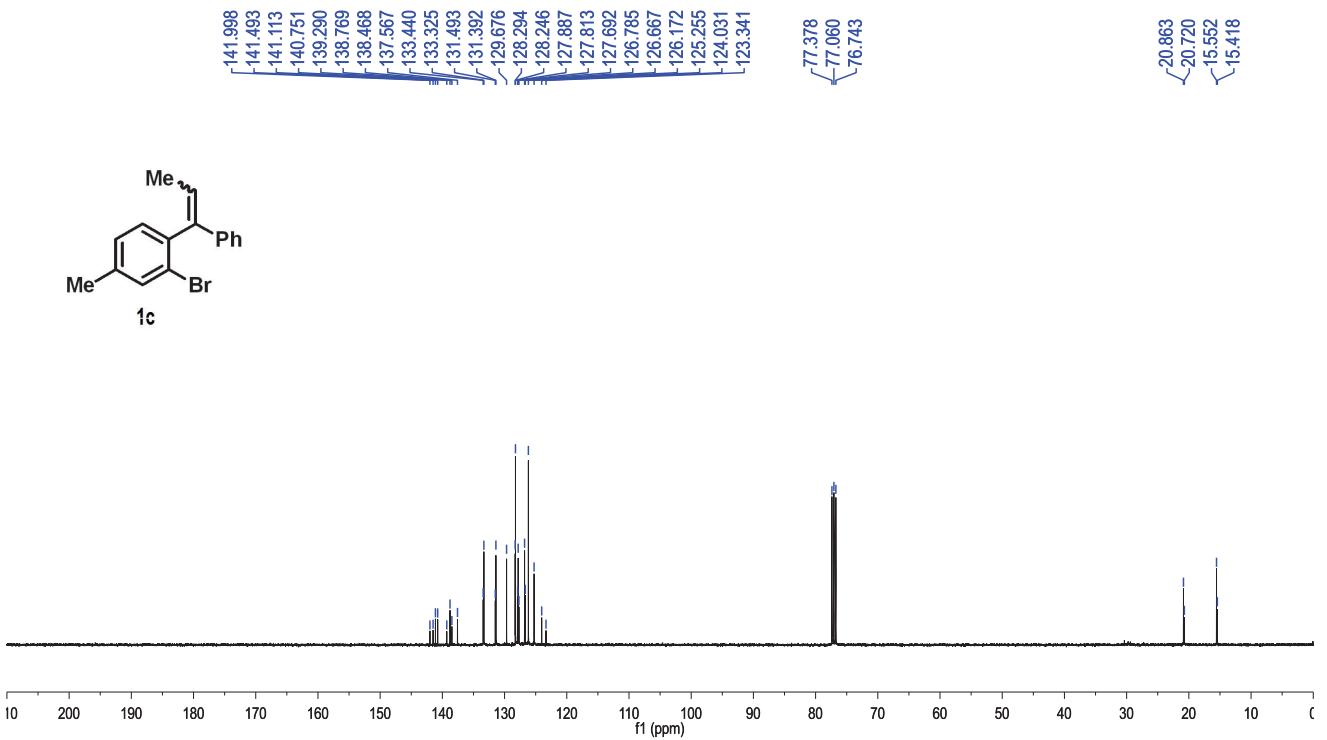
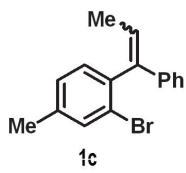
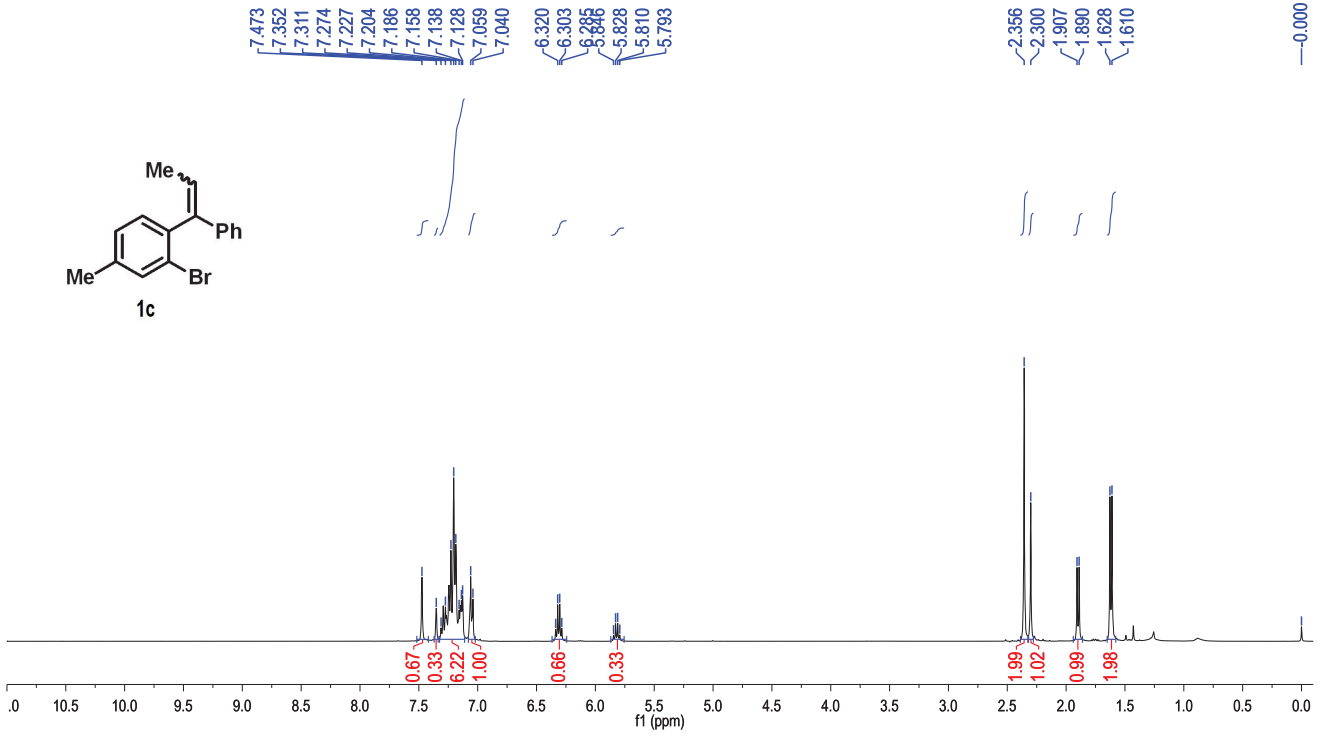
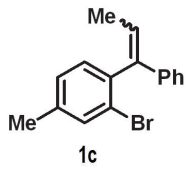


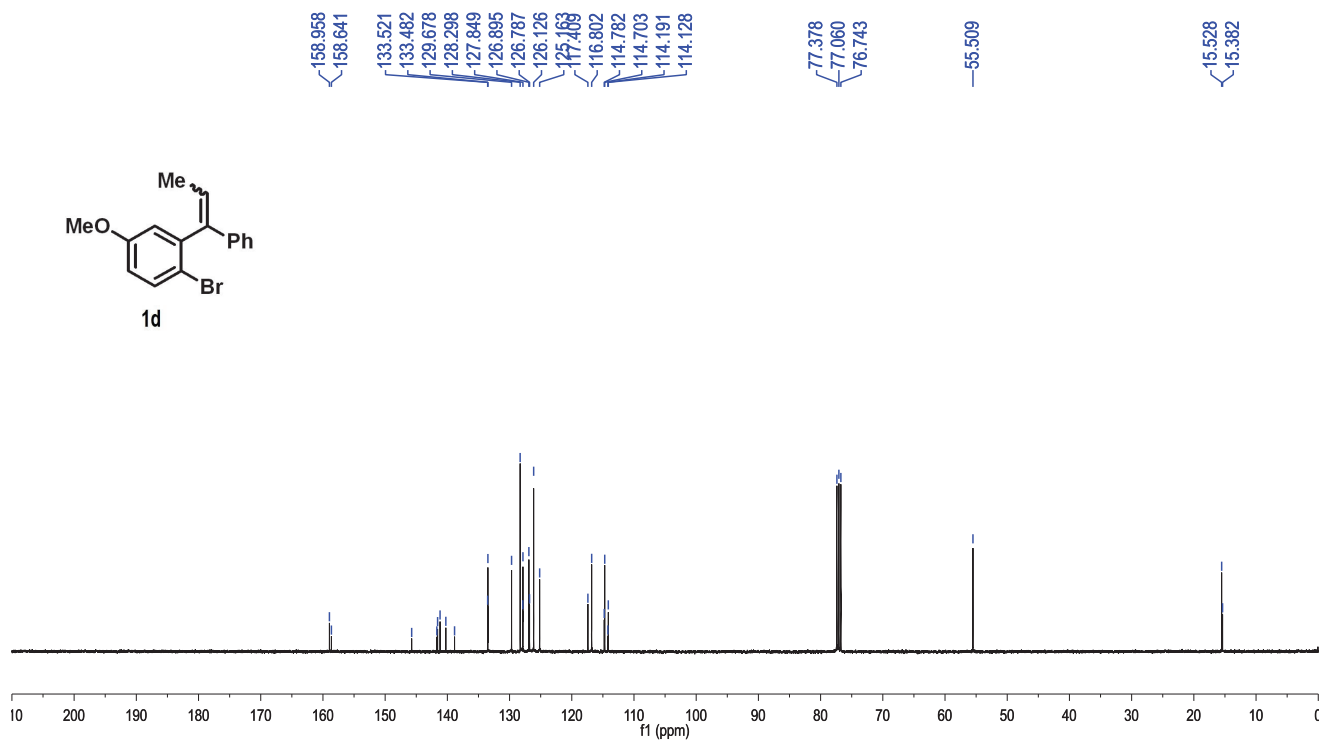
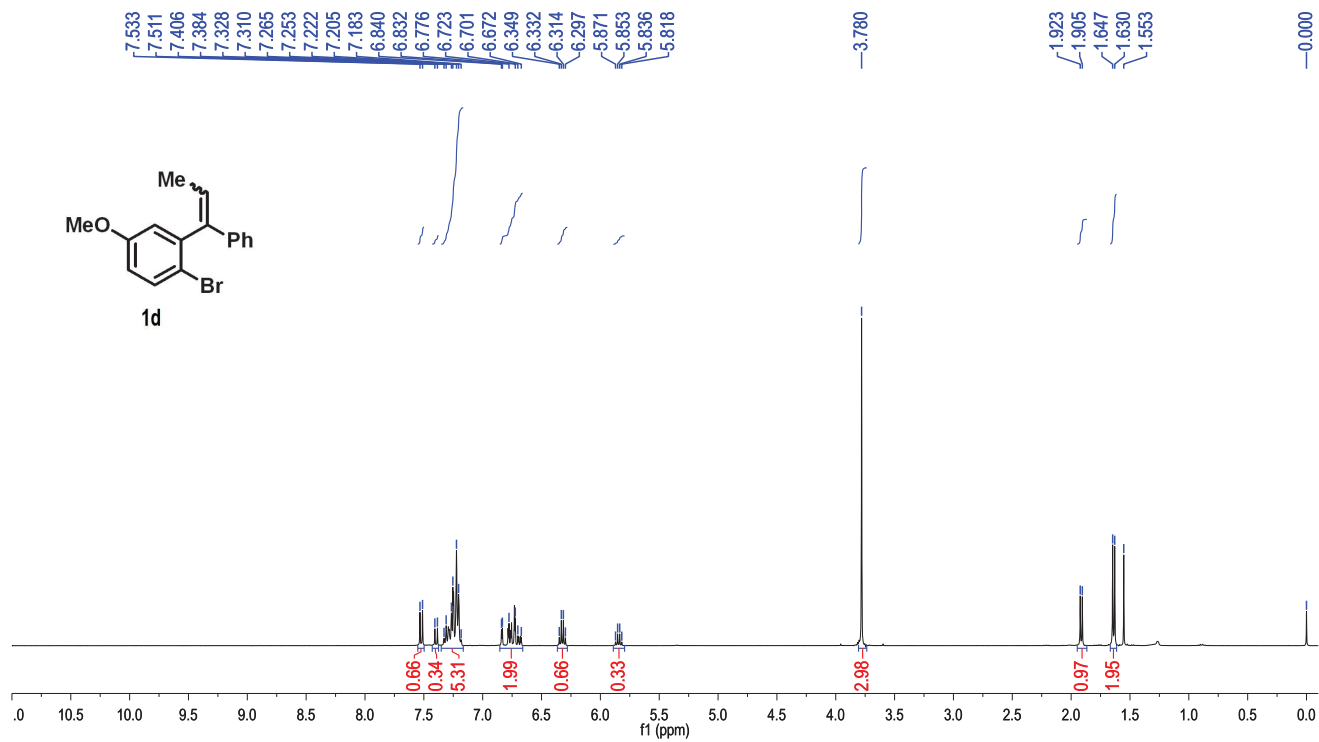
Reaction condition: PdCl<sub>2</sub>(dppf) (0.20 mmol) Yields determined by NMR analysis using CH<sub>2</sub>Br<sub>2</sub> as an internal standard

## 7. References

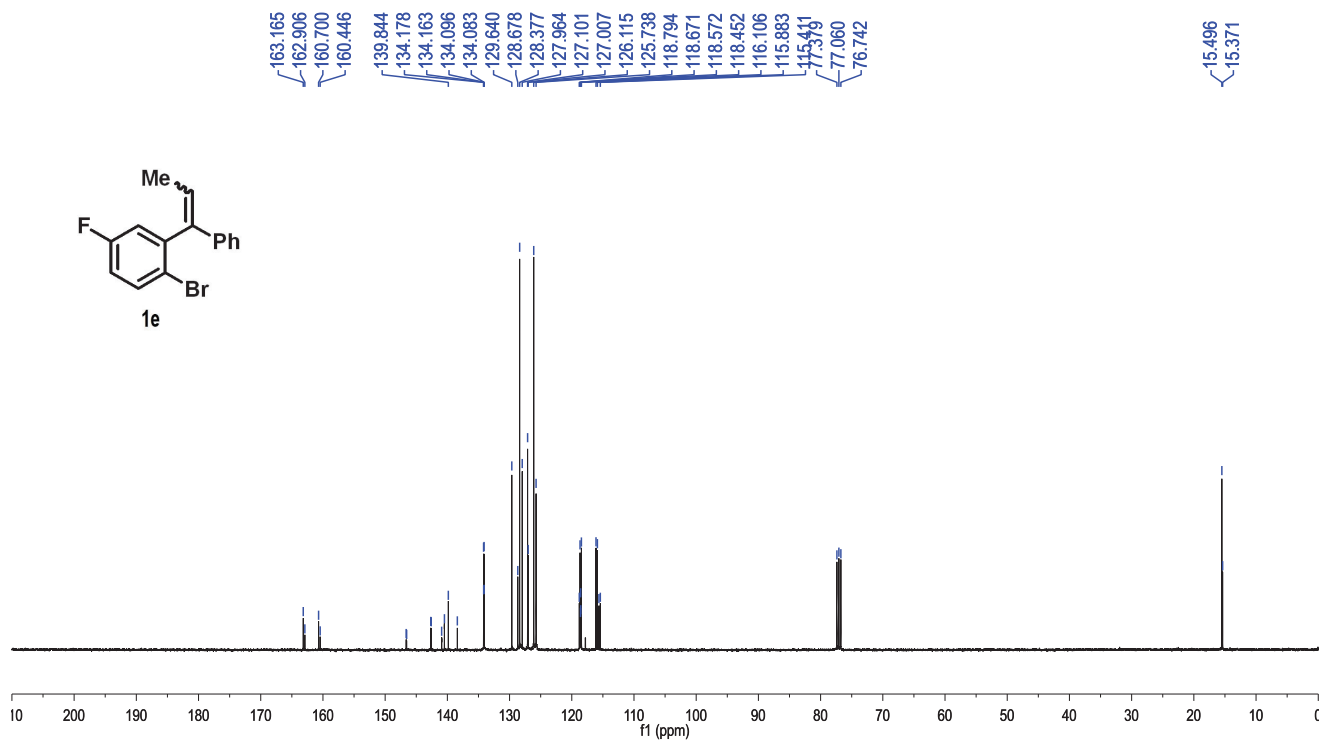
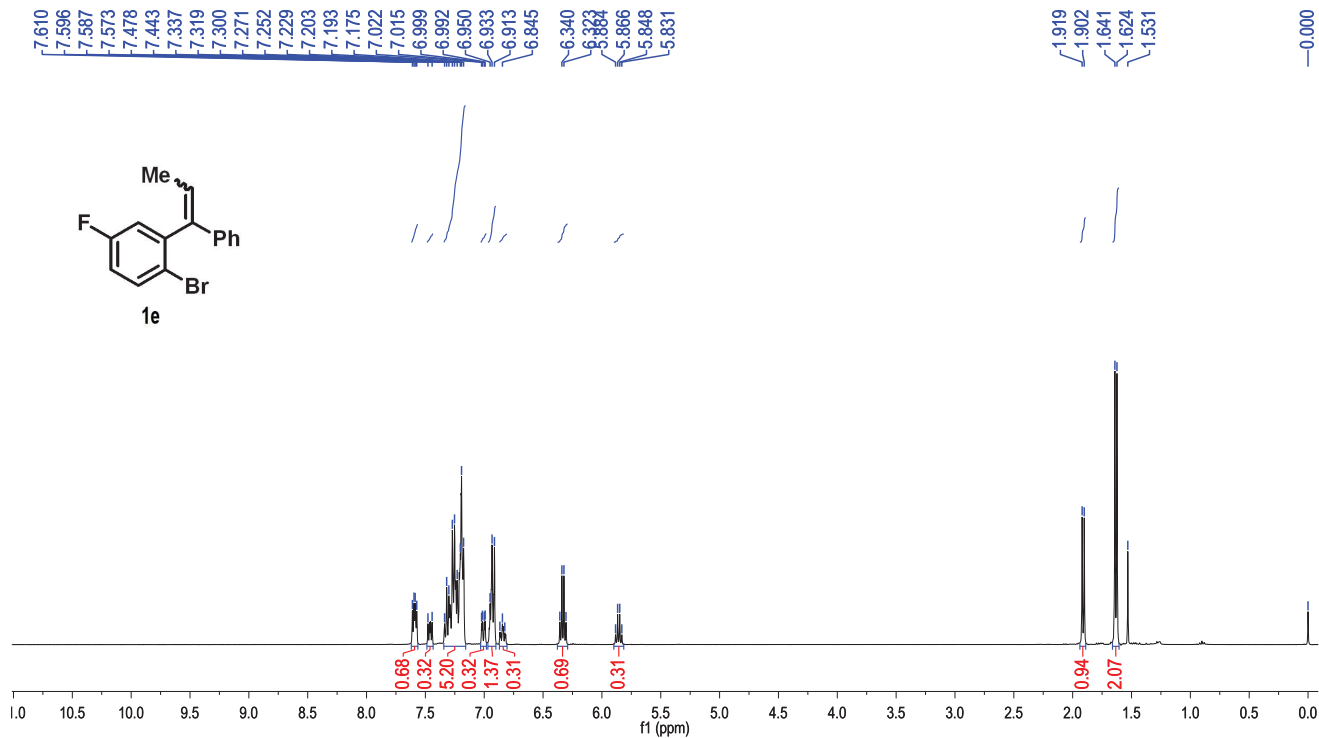
- [1] S. Nicolai, S. Erard, D. F. González, J. Waser, *Org. Lett.* **2010**, *12*, 384;
- [2] S. Maity, N. Zheng, *Angew. Chem. Int. Ed.*, **2012**, *51*, 9562-9566;
- [3] D. Wei, T.-J. Hu, C.-G. Feng, G.-Q. Lin, *Chin. J. Chem.* **2018**, *36*, 743.

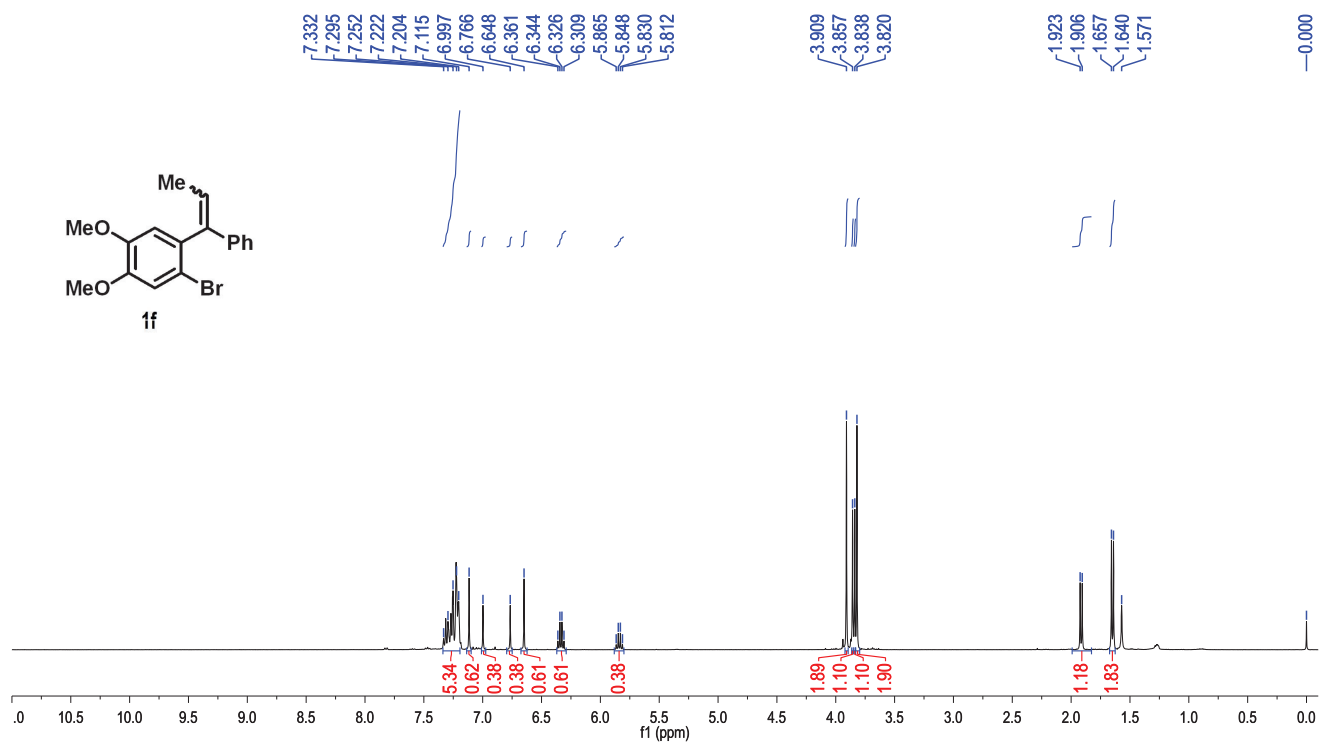
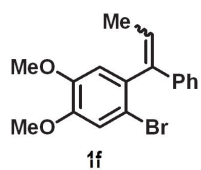
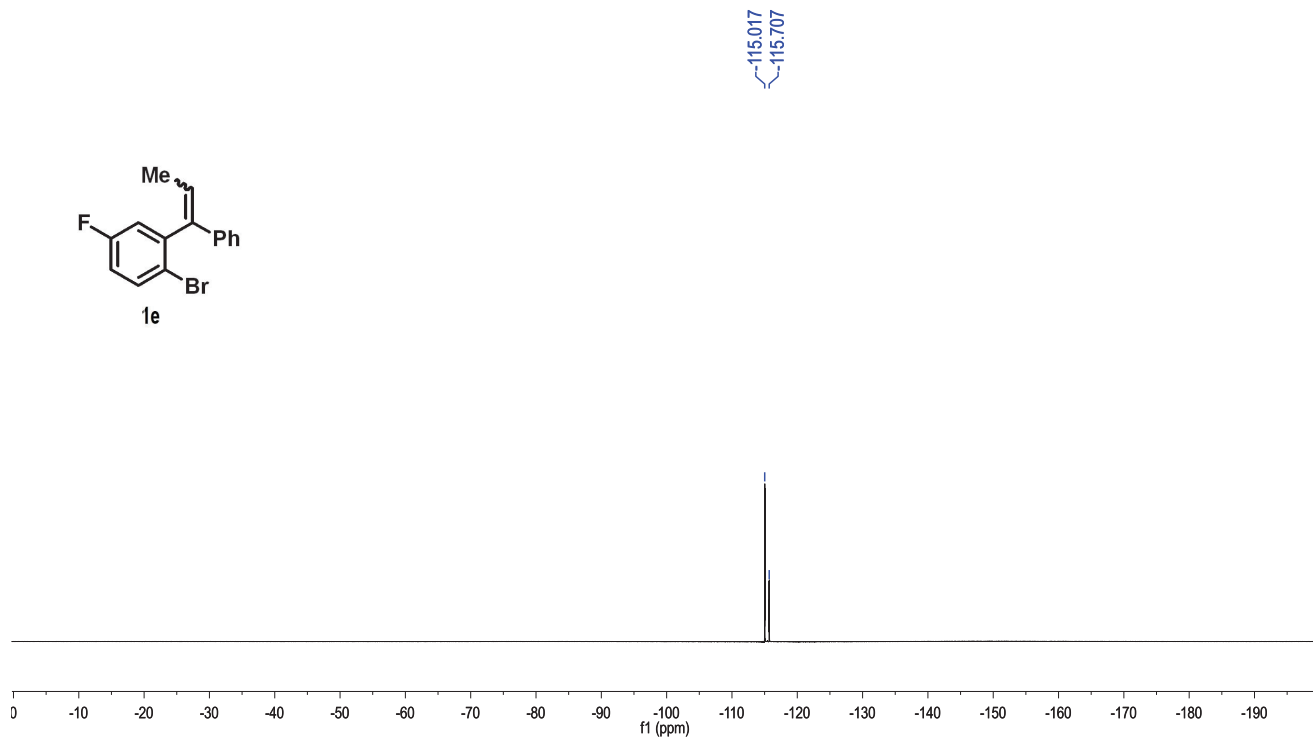


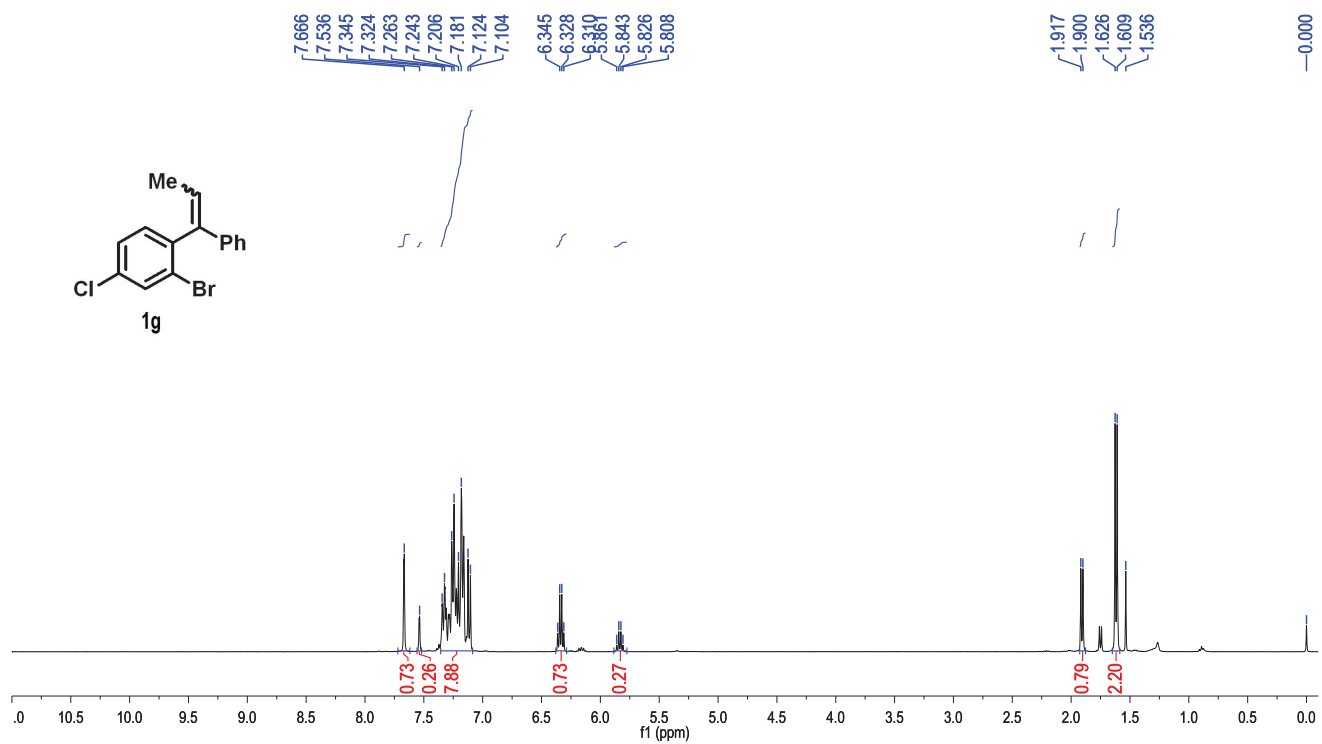
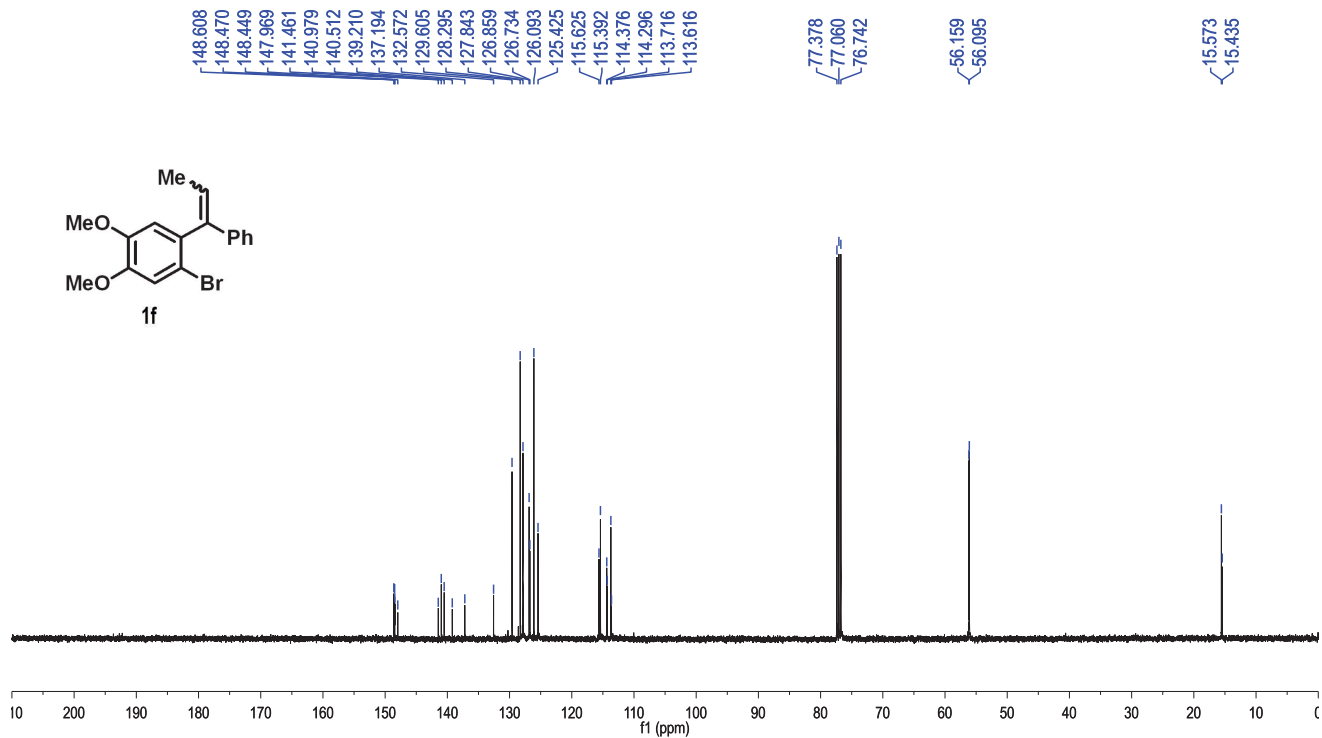


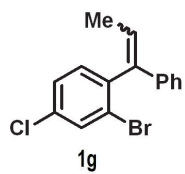








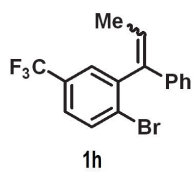
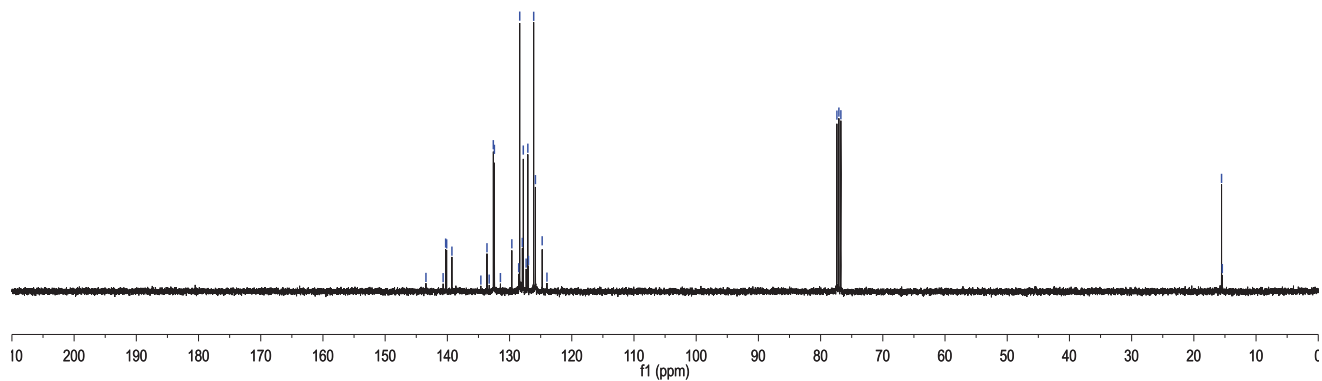




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