



Supporting Information

for

Radical cation Diels–Alder reactions of arylidene cycloalkanes

Kaii Nakayama, Hidehiro Kamiya and Yohei Okada

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General remarks, photocatalyst analyzation data, synthesis procedure, additional control studies, electrochemical measurements, and characterization data, including copies of ^1H and ^{13}C NMR spectra

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1. General remarks

All reagents and solvents were purchased from commercial sources and used without further purification. TiO₂ used in this work was AEROXIDE® TiO₂ P 25. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel plates, with detection by UV absorption (254 nm) and by heating the plates after dipping them in a solution of 12 M molybdo(VI) phosphoric acid *n*-hydrate in 95% ethanol. Silica gel (particle size 40–50 μm, normal or reversed phase) was used for column chromatography. ¹H NMR spectra were collected on a 500 or 300 MHz NMR spectrometer using the deuterated solvent as an internal deuterium reference. Chemical shift data are given in δ units calibrated with residual protic solvent. The multiplicity of a signal is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. ¹³C NMR spectra were collected at 125 MHz with proton decoupling using the deuterated solvent as an internal carbon reference. Chemical shift data are given in δ units calibrated with residual solvent. High-resolution mass spectra (HRMS) were collected by electrospray ionization (ESI)- or direct analysis in real time (DART)-time-of-flight (TOF) spectrometers.

2. TiO₂ analysis

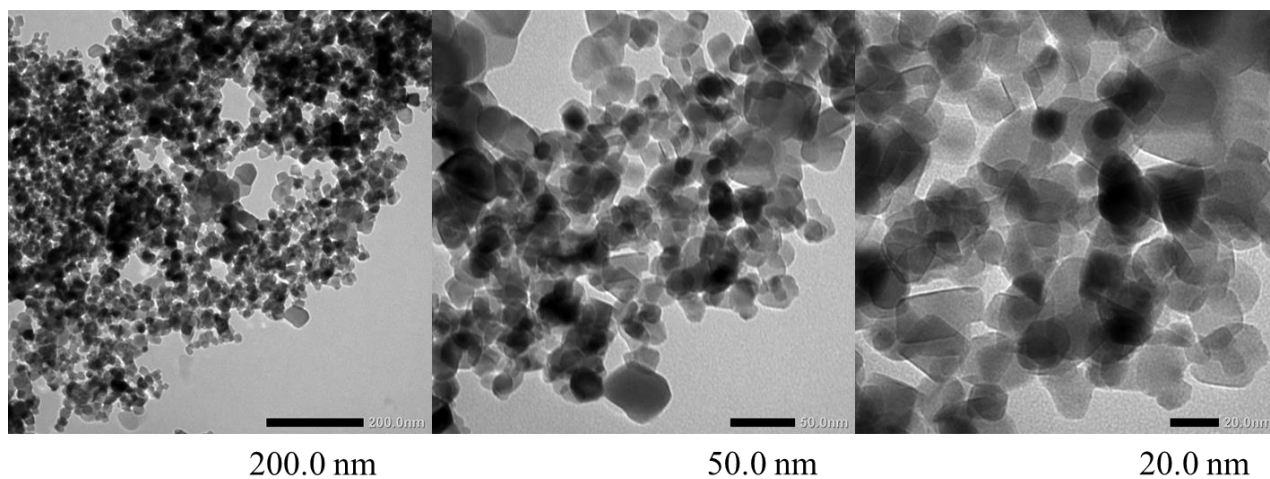


Figure S1. TEM images of TiO₂ used in this work.

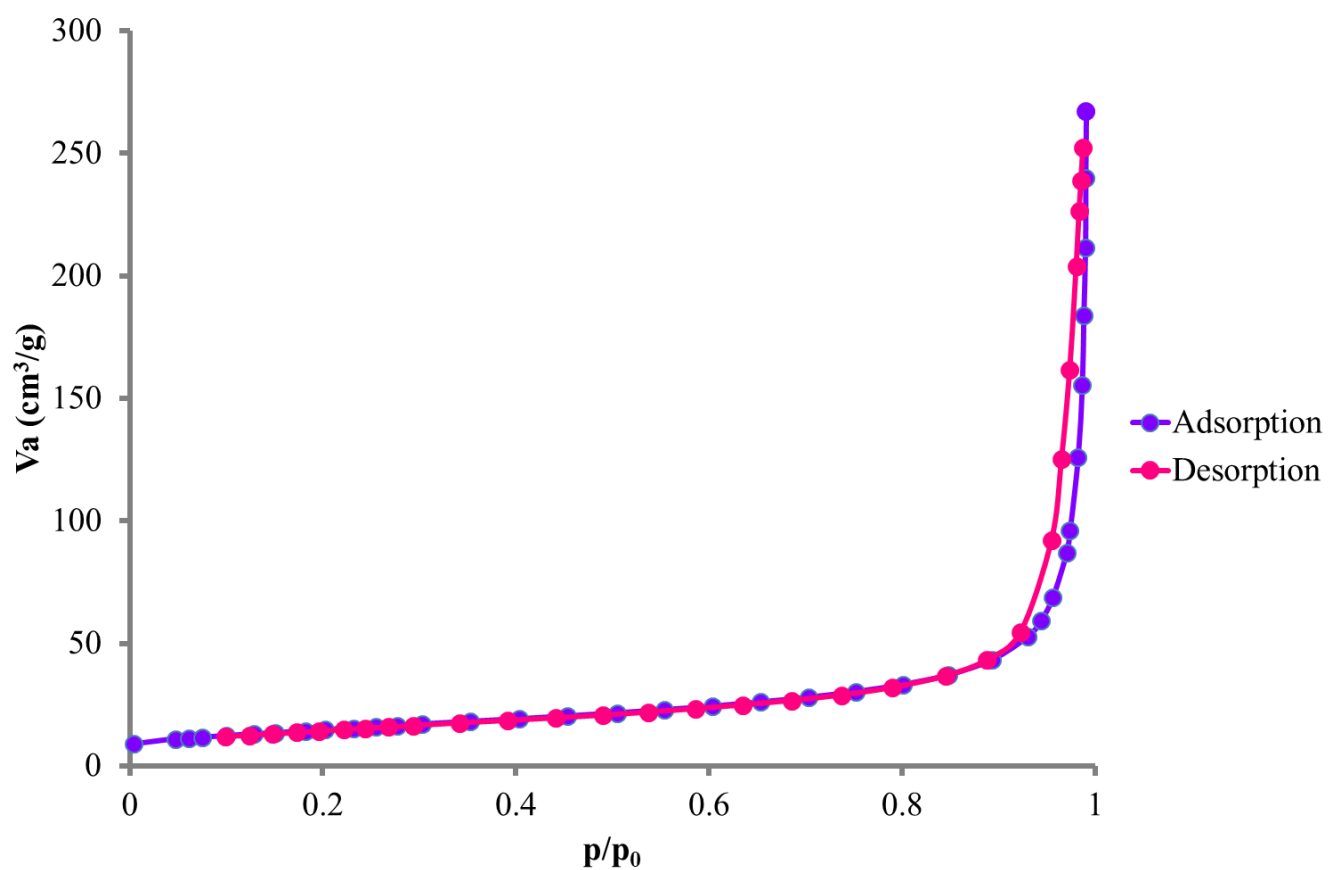
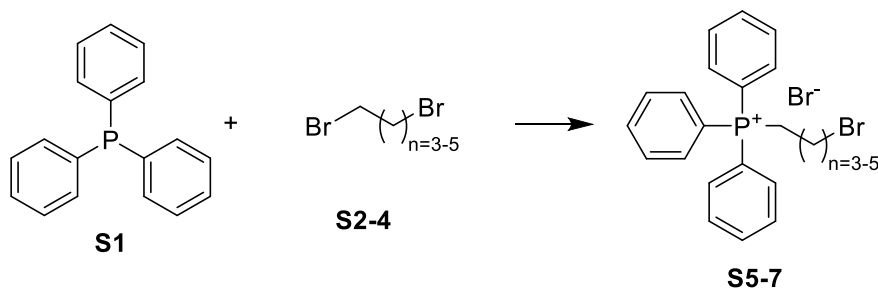
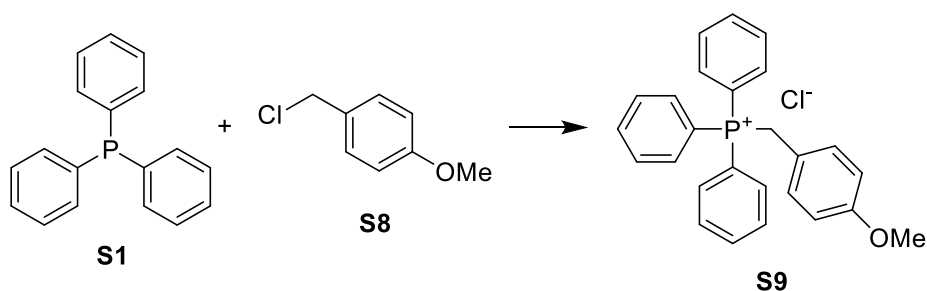


Figure S2. Adsorption isotherm of TiO₂ used in this work.

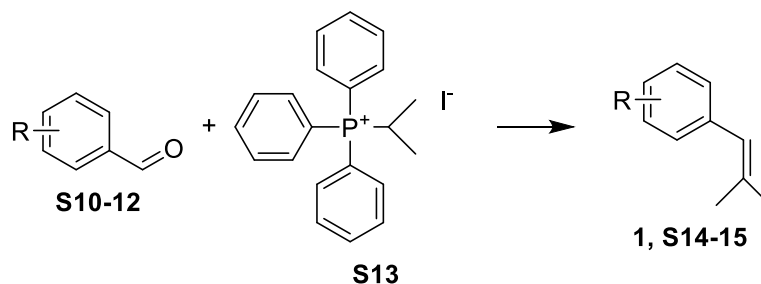
3. Synthetic procedure



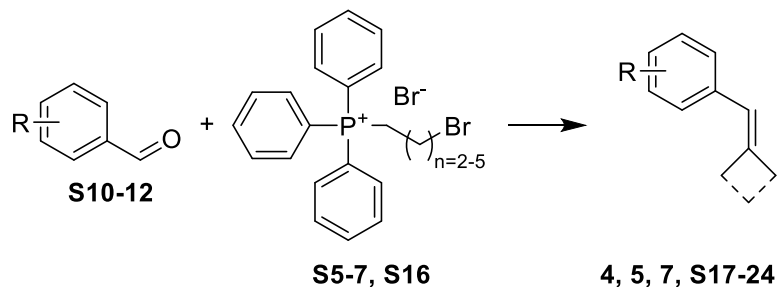
*General procedure for the synthesis of Wittig reagents (S5-7).*¹ The mixture of triphenylphosphine (**S1**, 1.3 g, 5 mmol) and respective dibromo alkane (**S2-4**, 25 mmol) was stirred at 90 °C for 5.5 h. After that, the resulting reaction mixture was cooled to rt, washed with toluene, and dried *in vacuo*. The mixture was sonicated with diethyl ether for 1 h and filtration gave the title compound quantitatively as a white solid.



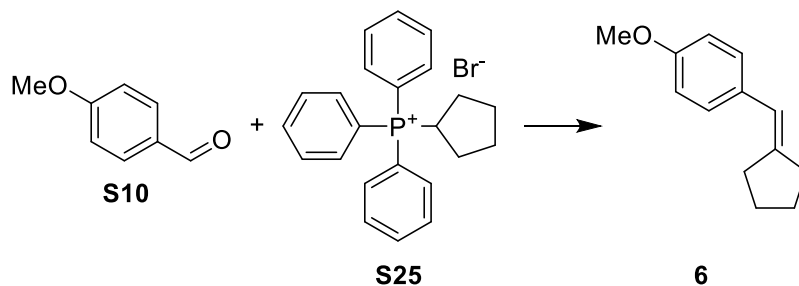
Synthesis of p-methoxybenzyl triphenyl phosphonium chloride (S9). To a solution of the triphenylphosphine (**S1**, 5.2 g, 20.0 mmol) in toluene (50 mL) stirred at rt was added *p*-methoxybenzyl chloride (**S8**, 1.7 g, 20.0 mmol). The resulting reaction mixture was stirred at 110 °C for 12 h and washed with toluene; filtration gave the title compound in 66% yield (5.5 g, 13.2 mmol) as a white solid.



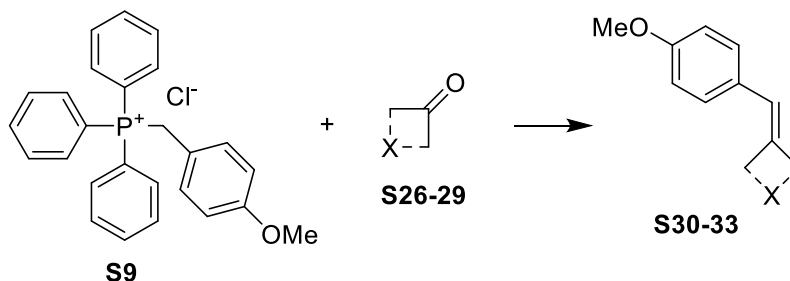
*General procedure for the synthesis of β -dimethyl arylidenes (**1, S14-15**).²* To a solution of the Wittig reagent (**S13**, 4.3 g, 10.0 mmol) in THF (50 mL) stirred at rt was added KO t -Bu (1.1 g, 10.0 mmol). The resulting reaction mixture was stirred at rt for 30 min, respective aldehyde (**S10-12**, 5.0 mmol) was added, and the reaction mixture was stirred at rt for 12 h. Hydrogen peroxide (2 mL) was added, diluted with water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane only) gave the titled compound.



*General procedure for the synthesis of β -cycloalkyl arylidenes (**4, 5, 7, S17-24**).³* To a solution of the Wittig reagent (**S5-7, S16**, 7.5 mmol) in THF (50 mL) stirred at rt was added KO t -Bu (1.7 g, 15.0 mmol). The resulting reaction mixture was stirred at 70 °C for 1 h, then the respective aldehyde (**S10-12**, 5.0 mmol) was added, and the reaction mixture was stirred at 70 °C for 3 h. After the reaction mixture was cooled to rt and stirred for 1 h, hydrogen peroxide (2 mL) was added, diluted with water, and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane only or hexane/ethyl acetate 20:1) gave the title compound.

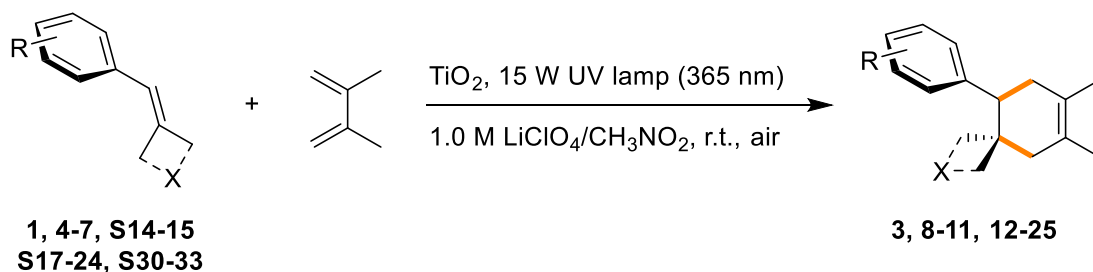


*Synthesis of p-methoxy- β -cyclopentyl arylidene (6).*⁴ To a solution of the cyclopentyltriphenylphosphonium bromide (**S25**, 5.0 mmol) in THF (25 mL) stirred at 0 °C was added *n*-butyl lithium (1.6 M in hexanes, 6.3 mmol). The resulting reaction mixture was stirred at 0 °C for 1 h, *p*-anisaldehyde (**S10**, 5.0 mmol) was added, and the reaction mixture was stirred at 0 °C for 16 h. *n*-Pentane was added to precipitate triphenylphosphine oxide, and the mixture was filtered and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate 20:1) gave the title compound.



*General procedure for the synthesis of β -heterocyclic arylidenes (S30-33).*⁵ To a solution of the Wittig reagent (**S9**, 2.1 g, 5.0 mmol) and KO^t-Bu (561 mg, 5.0 mmol) in THF (50 mL) stirred at 0 °C was added the respective cyclic ketone (**S26-29**, 6.0 mmol). The resulting reaction mixture was stirred at 0 °C for 2 h, hydrogen peroxide (2 mL) was added, the mixture diluted with water and extracted with EtOAc. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate 10:1) gave the title compound.

- (1) K. J. Deane; R. L. Summers; A. M. Lehane; R. E. Martin; R. A. Barrow, *ACS Med. Chem. Lett.*, **2014**, *5*, 576–581.
- (2) G. Occhialini; V. Palani; A. E. Wendlandt, *J. Am. Chem. Soc.* **2022**, *144*, 145–152.
- (3) Z. An; Y. Liu; Y. Sun; R. Yan, *Chem. Asian J.* **2020**, *15*, 3812–3815.
- (4) D. Toryn; S. Grebies; D. Mowpriya; N. Maximilian; S. L. Malte; G. Christian; R. J. Bart; G. Frank, *Angew. Chem. Int. Ed.* **2021**, *60*, 8537–8541.
- (5) P. R. D. Murray; W. M. M. Bussink; G. H. M. Davies, F. W. Mei; A. H. Antropow; J. T. Edwards; L. A. D’Agostino; J. M. Ellis; L. G. Hamann; F. R.-Michailidis; R. R. Knowles, *J. Am. Chem. Soc.* **2021**, *143*, 4055–4063.



General procedure for the TiO_2 photocatalytic reactions. To a solution of LiClO_4 (1.0 M, 426 mg) in CH_3NO_2 (4 mL) with TiO_2 (100 mg) stirred at rt were added the respective arylidene (0.20 mmol) and 2,3-dimethyl-1,3-butadiene (113 μL , 1.0 mmol). The resulting reaction mixture was irradiated by a 15 W UV lamp (365 nm) at rt under air, diluted with water, and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated in vacuo. Yields reported in the manuscript were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. Reversed phase silica gel column chromatography (acetonitrile only) and normal phase silica gel column chromatography (hexane only or hexane/ethyl acetate 20:1) gave the target compounds.

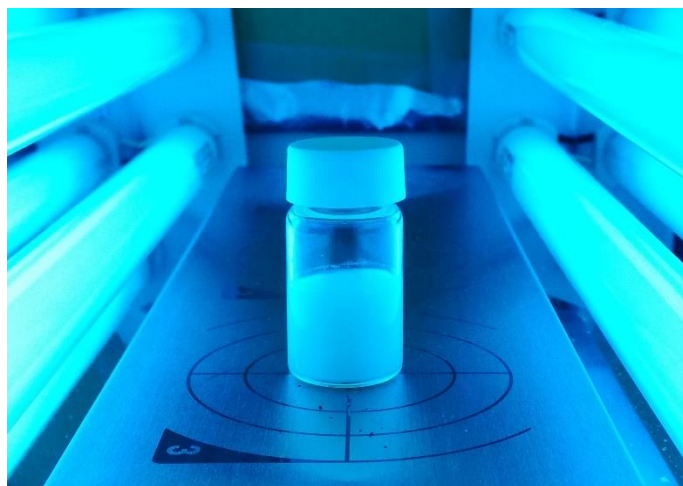
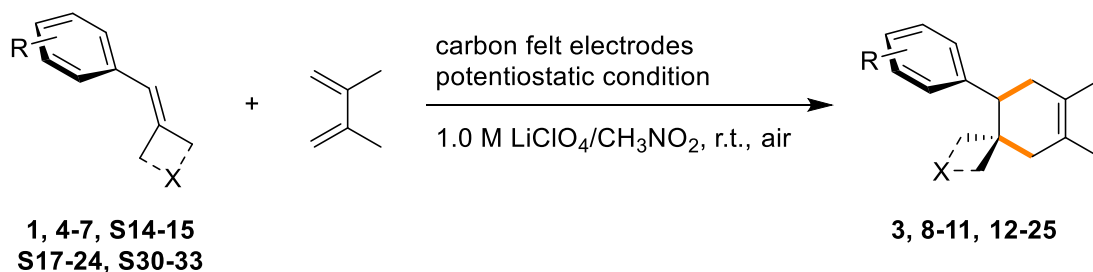


Figure S3. Setup of TiO_2 photocatalytic reactions.



General procedure for the electrolytic reactions. To a solution of LiClO₄ (1.0 M, 426 mg) in CH₃NO₂ (4 mL) stirred at rt were added the respective arylidene (0.20 mmol) and 2,3-dimethyl-1,3-butadiene (113 μ L, 1.0 mmol). The resulting reaction mixture was electrolyzed with carbon felt electrodes (1 cm $\times$ 1 cm) at rt under air, diluted with water, and extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo. Yields reported in the manuscript were determined by ¹H NMR analysis using CH₂Br₂ as an internal standard. Reversed phase silica gel column chromatography (acetonitrile only) and normal phase silica gel column chromatography (hexane only or hexane/ethyl acetate 20:1) gave the target compounds.

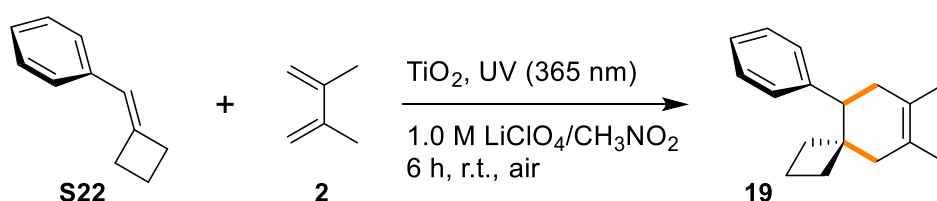


Figure S4. Setup of electrolytic reactions.

4. Additional optimization of the reaction conditions

To a solution of LiClO₄ in the solvent (4 mL) with TiO₂ (100 mg) stirred at rt were added the β -cyclobutylstyrene (**S22**, 0.20 mmol, 29.4 μ L) and 2,3-dimethyl-1,3-butadiene (**2**). The resulting reaction mixture was irradiated by a 15 W UV lamp (365 nm) or electrolyzed with carbon felt electrodes (1 cm $\times$ 1 cm) at rt under air, diluted with water, and extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo. Yields reported in the manuscript were determined by ¹H NMR analysis using CH₂Br₂ as an internal standard.

Table S1. Optimization of the conditions for radical cation Diels–Alder reaction using arylidene **S22**.

		
entry	conditions ^a	yield (%) ^b
1		55% (0%)
2	no LiClO ₄	0% (28%)
3	no light	0% (trace)
4	no TiO ₂	0% (26%)
5	2 eq of diene	34% (0%)
6	10 eq of diene	47% (trace)
7	CH ₃ CN solvent	13% (17%)
8	under O ₂	33% (trace)
9	under Ar	9% (16%)
10	reaction for 4 h	50% (6%)
11	CF (+) CF (-), constant voltage (1.5 V, 0.5 F/mol)	3% (24%)
12	CF (+) CF (-), constant voltage (1.5 V, 1 F/mol)	7% (5%)

^aUnless otherwise stated, reactions were carried out on a 0.2 mmol scale of β -cyclobutylstyrene (**S22**) with 5 eq of 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg TiO₂ in 4 mL of CH₃NO₂ using 15 W UV lamp. ^bDetermined by ¹H NMR analysis using CH₂Br₂ as an internal standard. Recovered starting material is reported in parentheses.

5. Electrochemical measurements

Cyclic voltammograms were recorded using 2 mM of arylidenes in 4 mL of CH_3NO_2 . LiClO_4 (1.0 M) was used as the supporting electrolyte, a glassy carbon (GC) disk was used as the working electrode, and a Pt wire was used as the counter electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan rate is 50 mV/s.

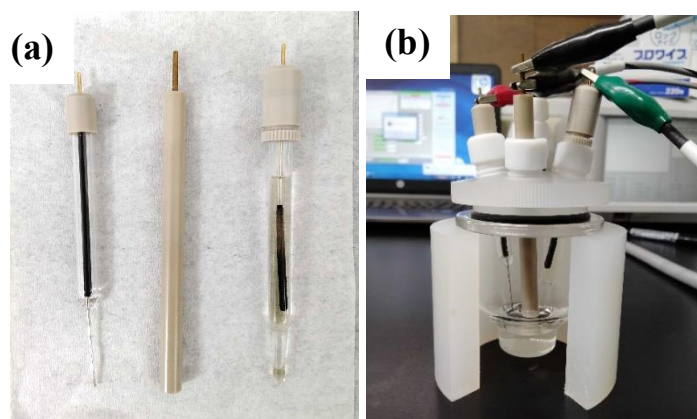


Figure S5. (a) Photograph of used electrodes in this electrochemical measurements, from left: Pt wire, GC disk, and Ag/AgCl electrode, (b) setup of cyclic voltammetry measurements.

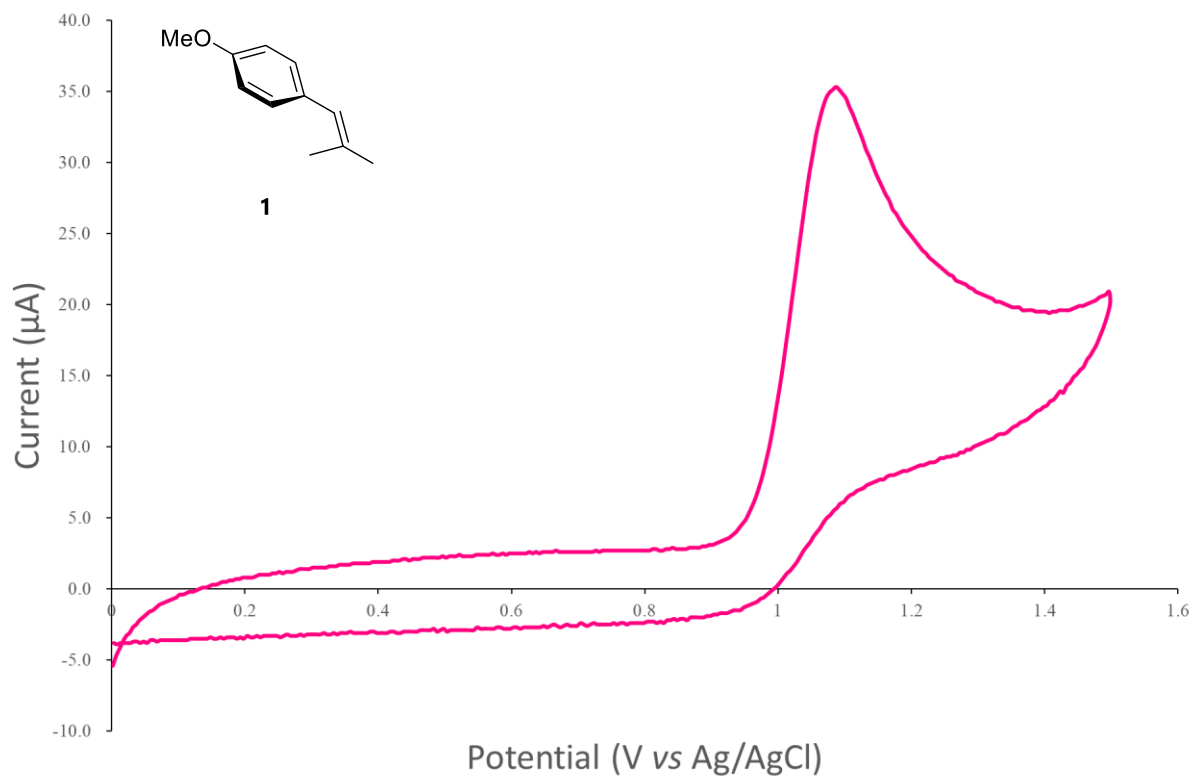


Figure S6. Cyclic voltammogram of the arylidene (**1**).

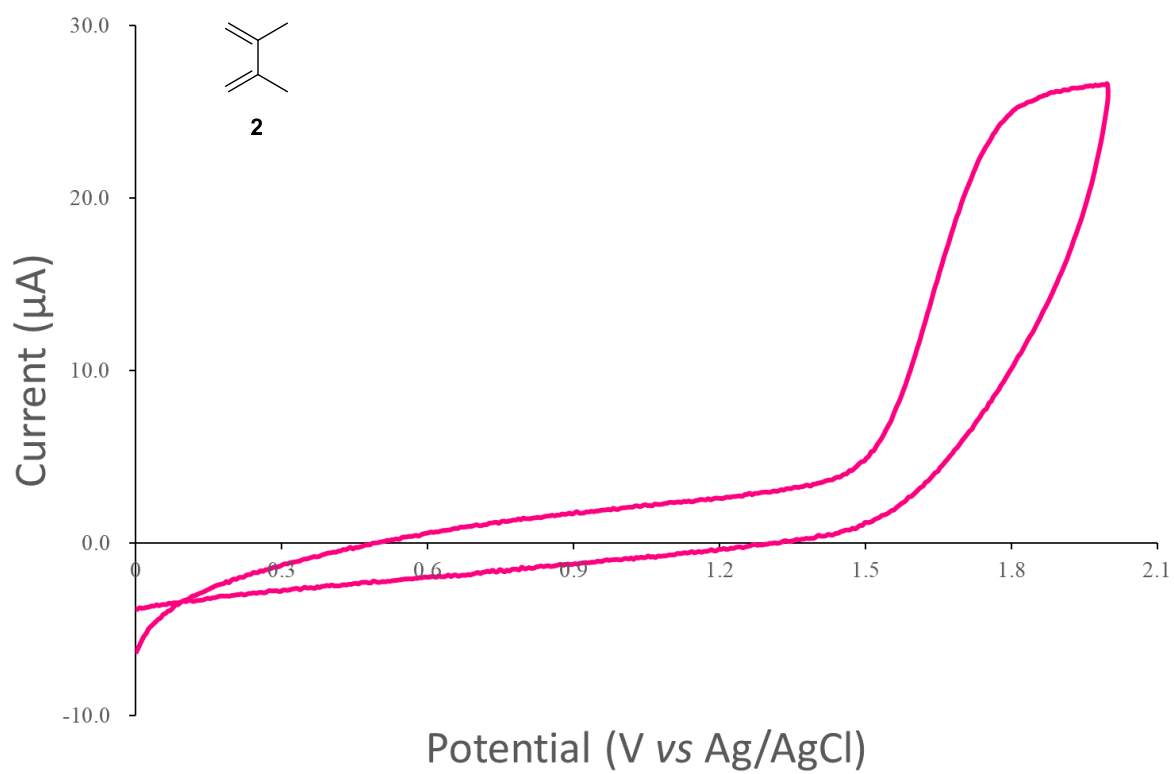


Figure S7. Cyclic voltammogram of the 2,3-dimethyl-1,3-butadiene (**2**).

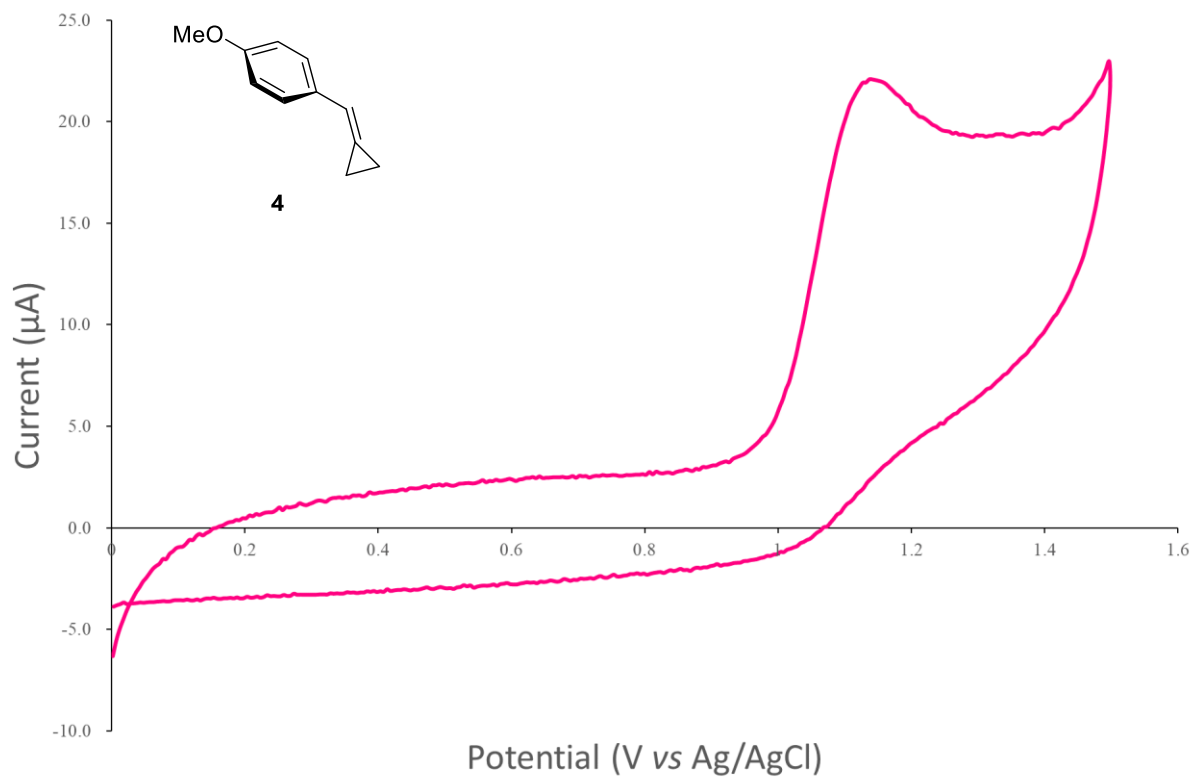


Figure S8. Cyclic voltammogram of the arylidene **4**.

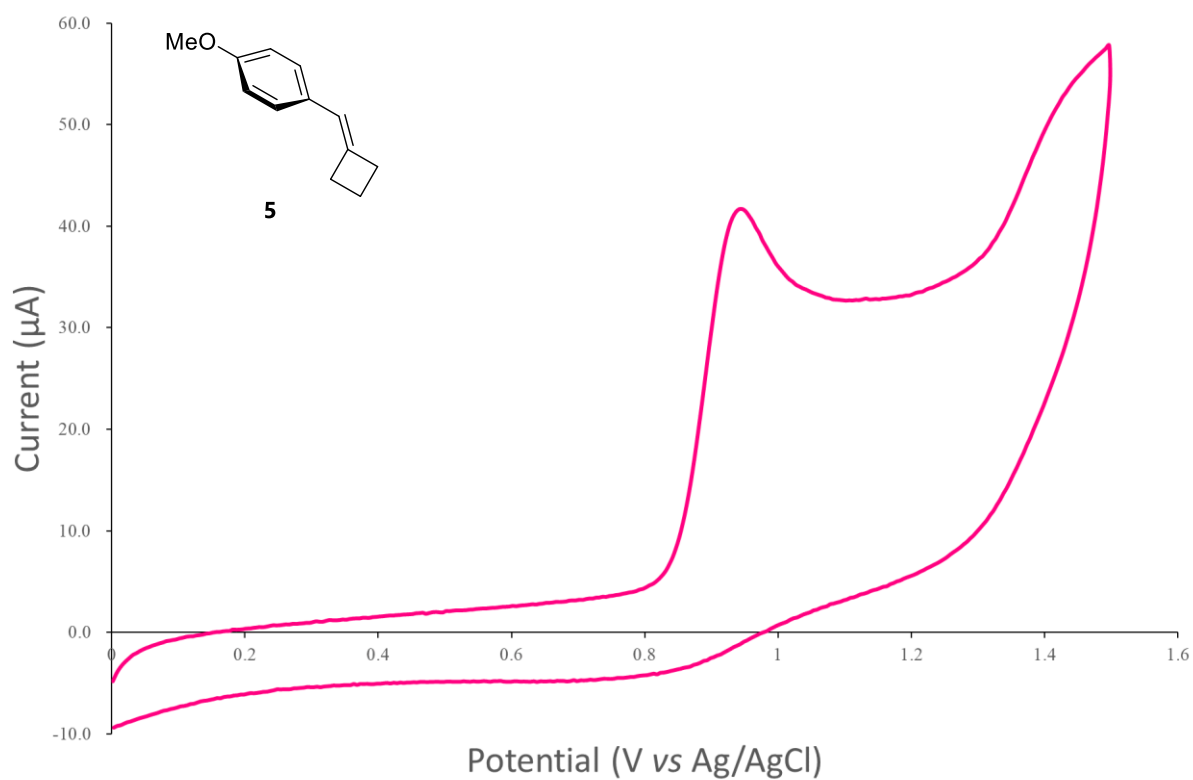


Figure S9. Cyclic voltammogram of the arylidene **5**.

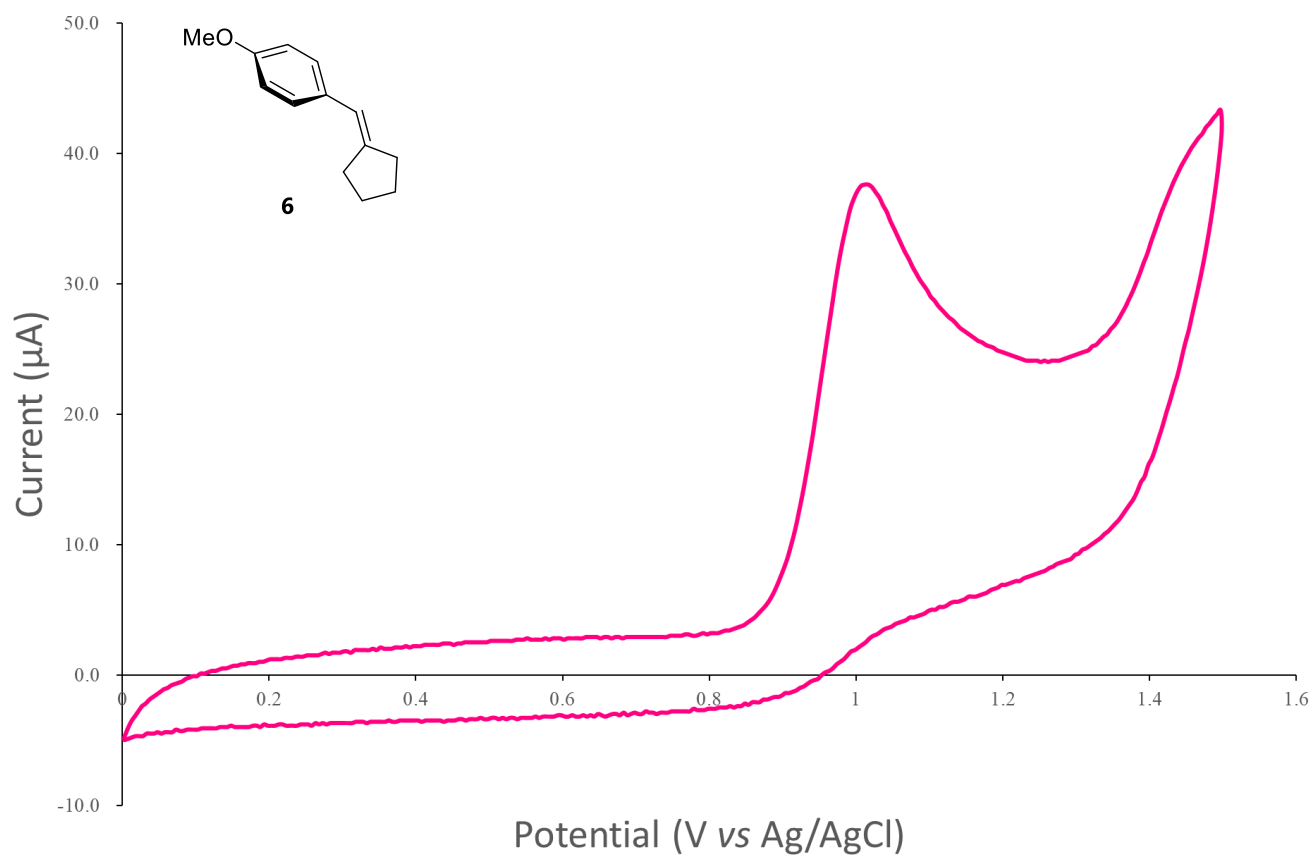


Figure S10. Cyclic voltammogram of the arylidene **6**.

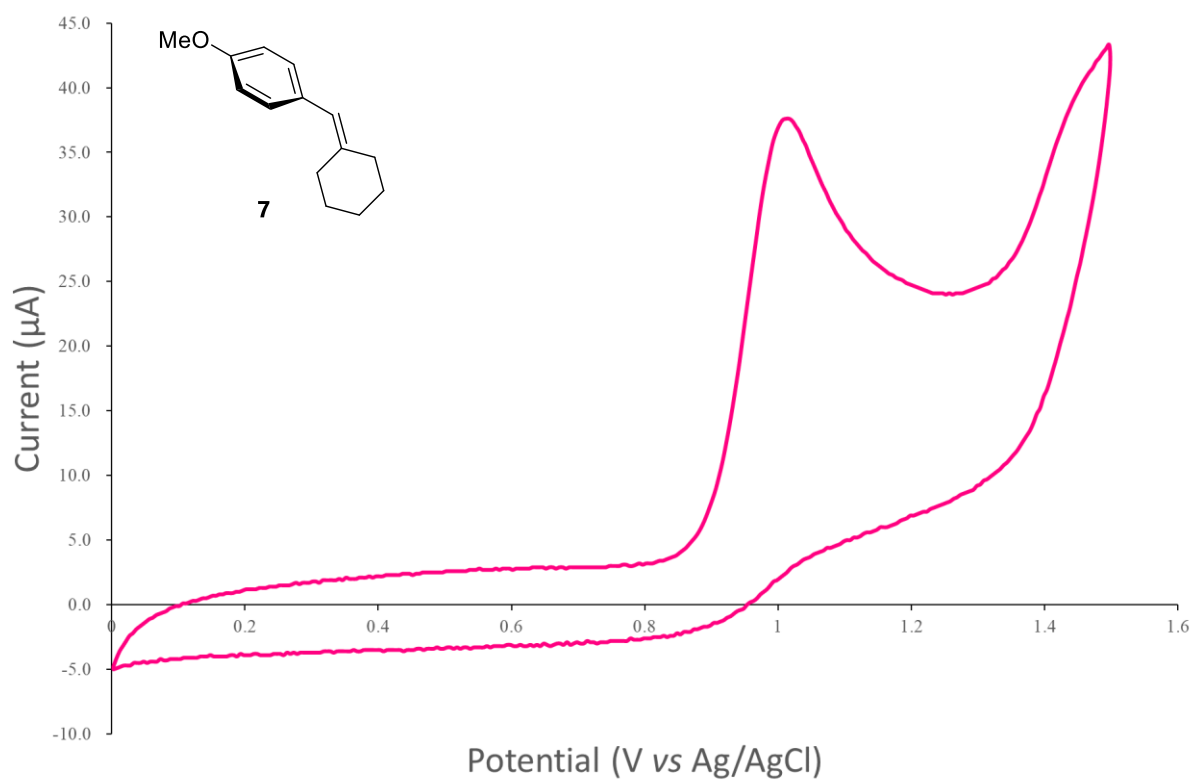


Figure S11. Cyclic voltammogram of the arylidene **7**.

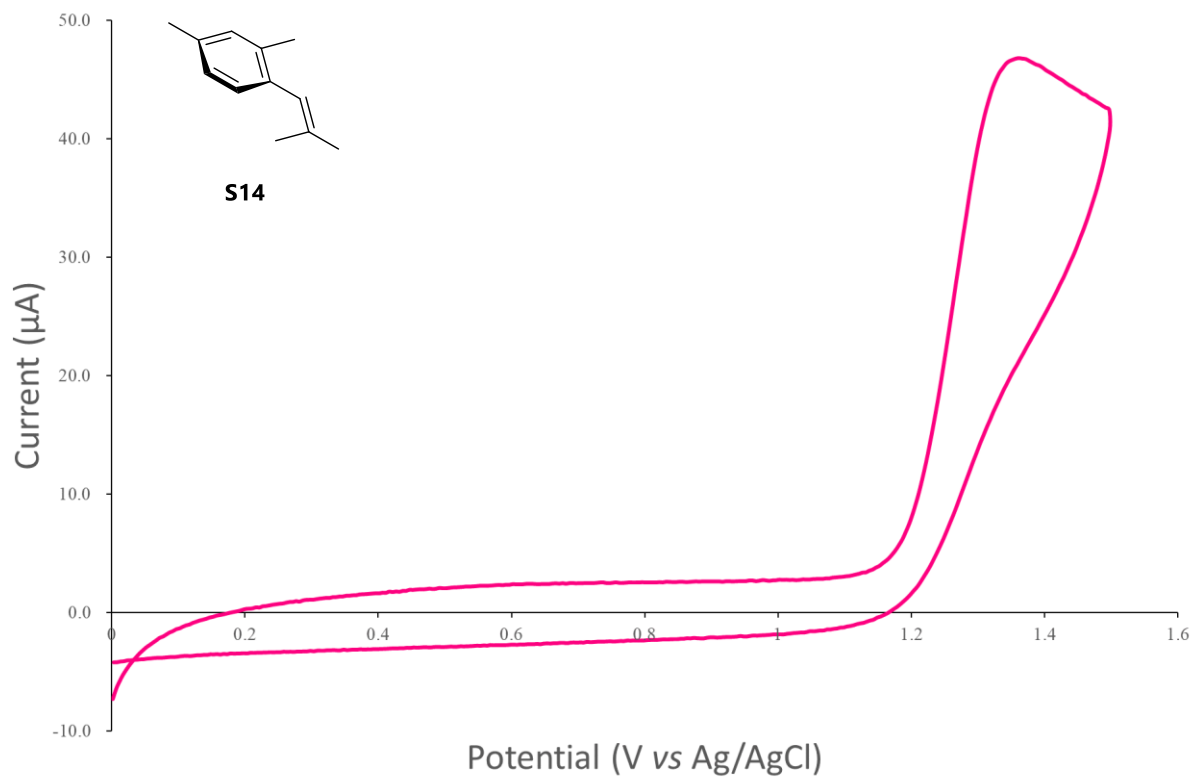


Figure S12. Cyclic voltammogram of the arylidene **S14**.

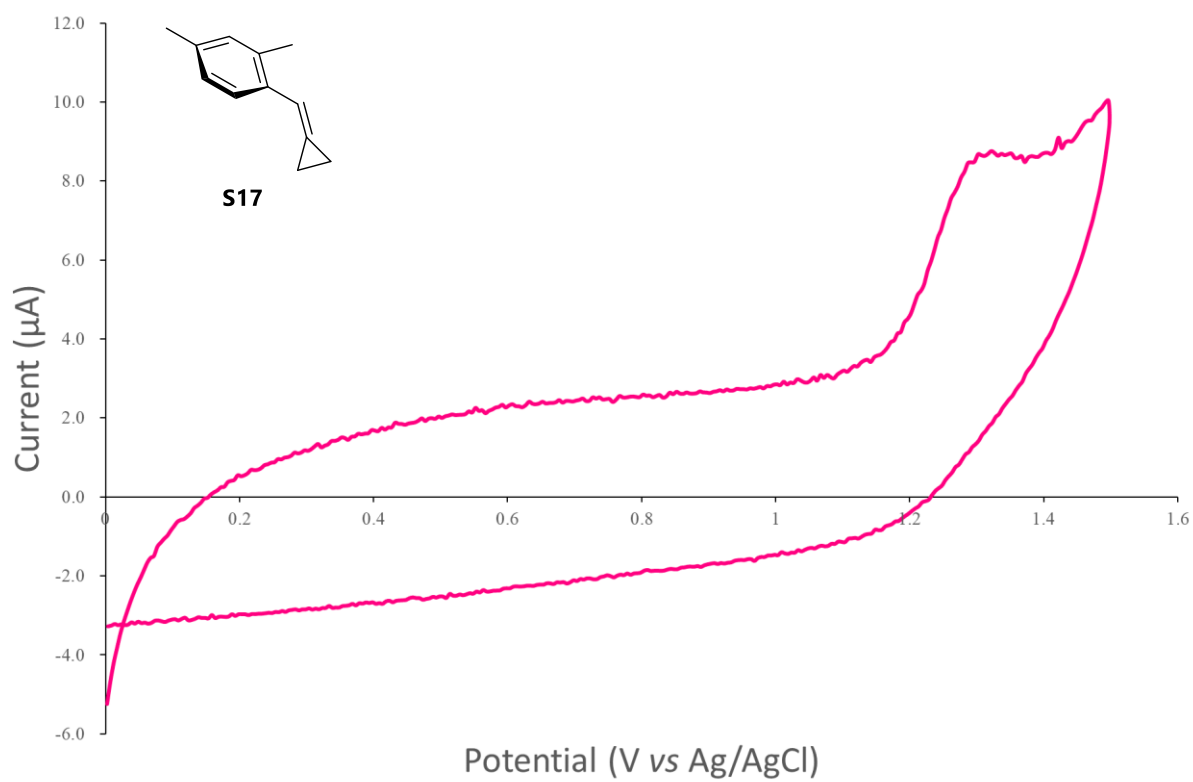


Figure S13. Cyclic voltammogram of the arylidene **S17**.

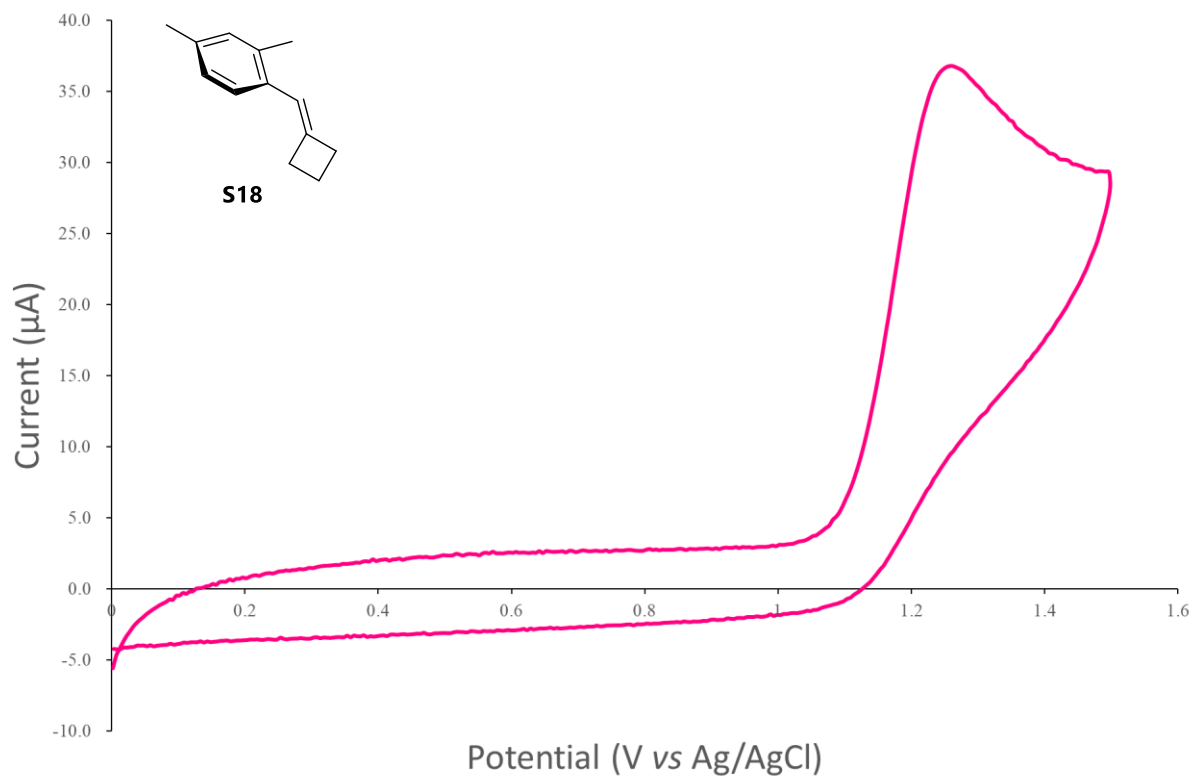


Figure S14. Cyclic voltammogram of the arylidene **S18**.

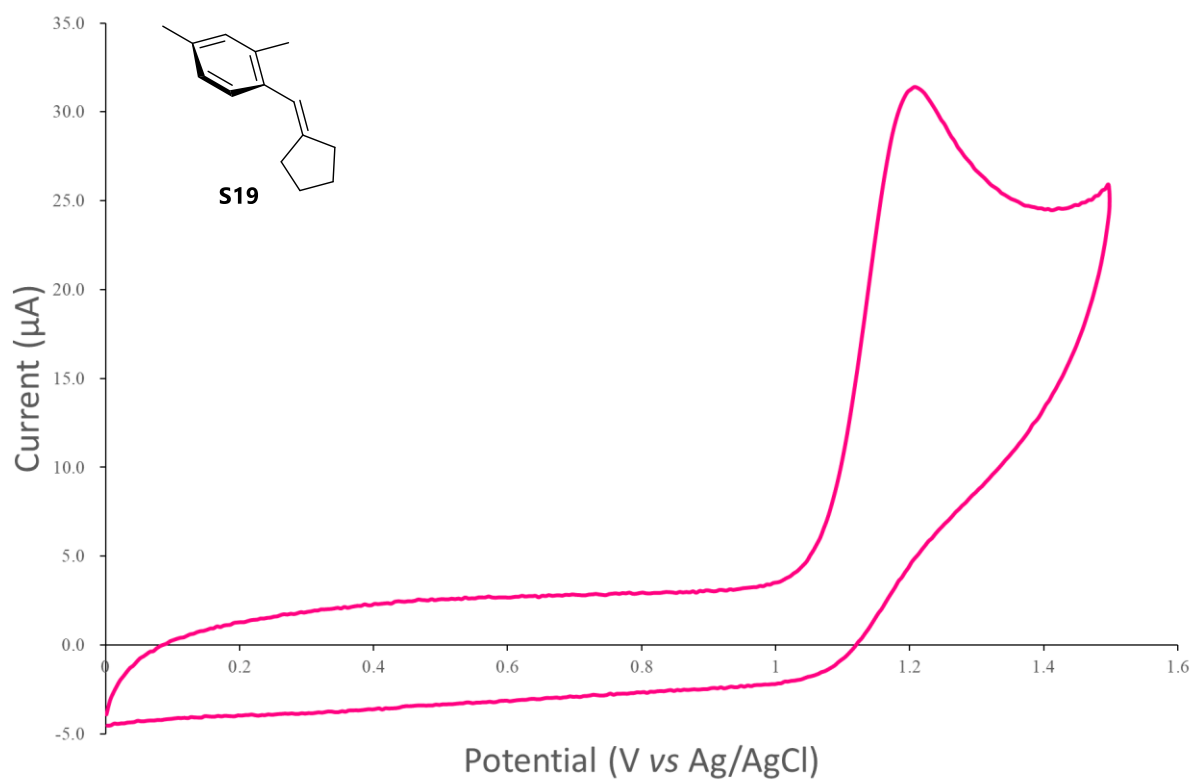


Figure S15. Cyclic voltammogram of the arylidene **S19**.

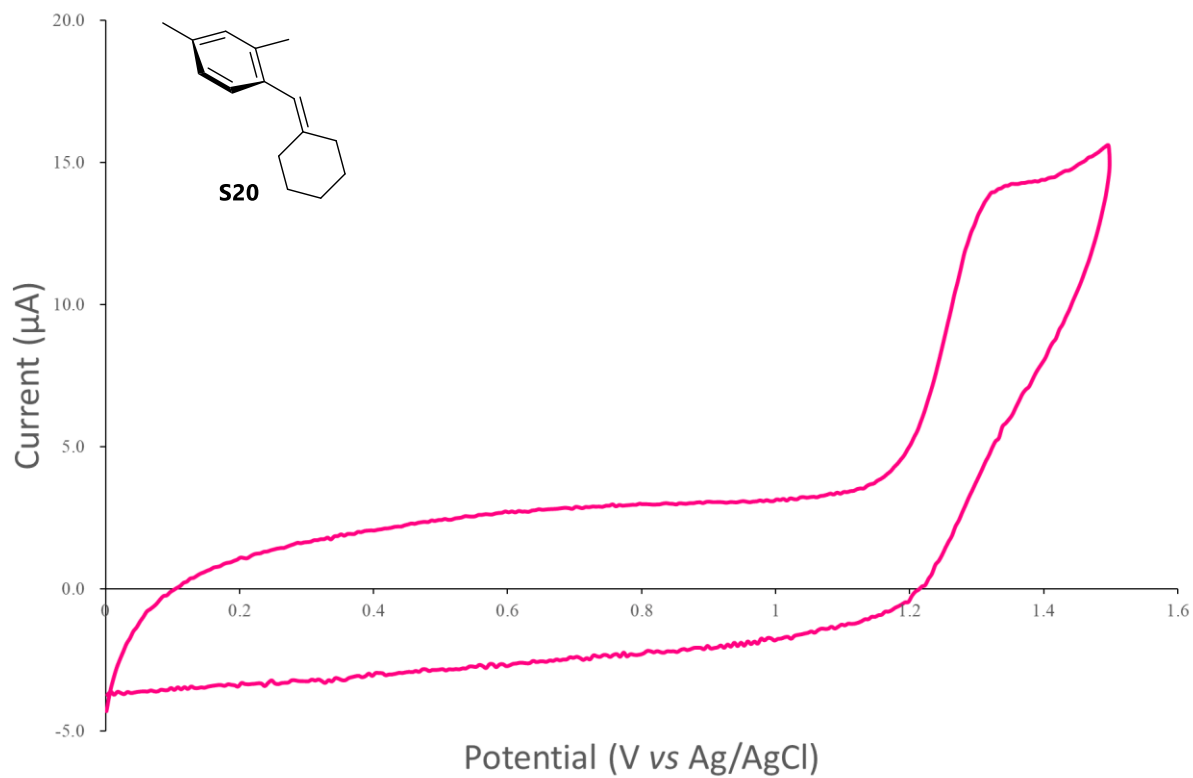


Figure S16. Cyclic voltammogram of the arylidene **S20**.

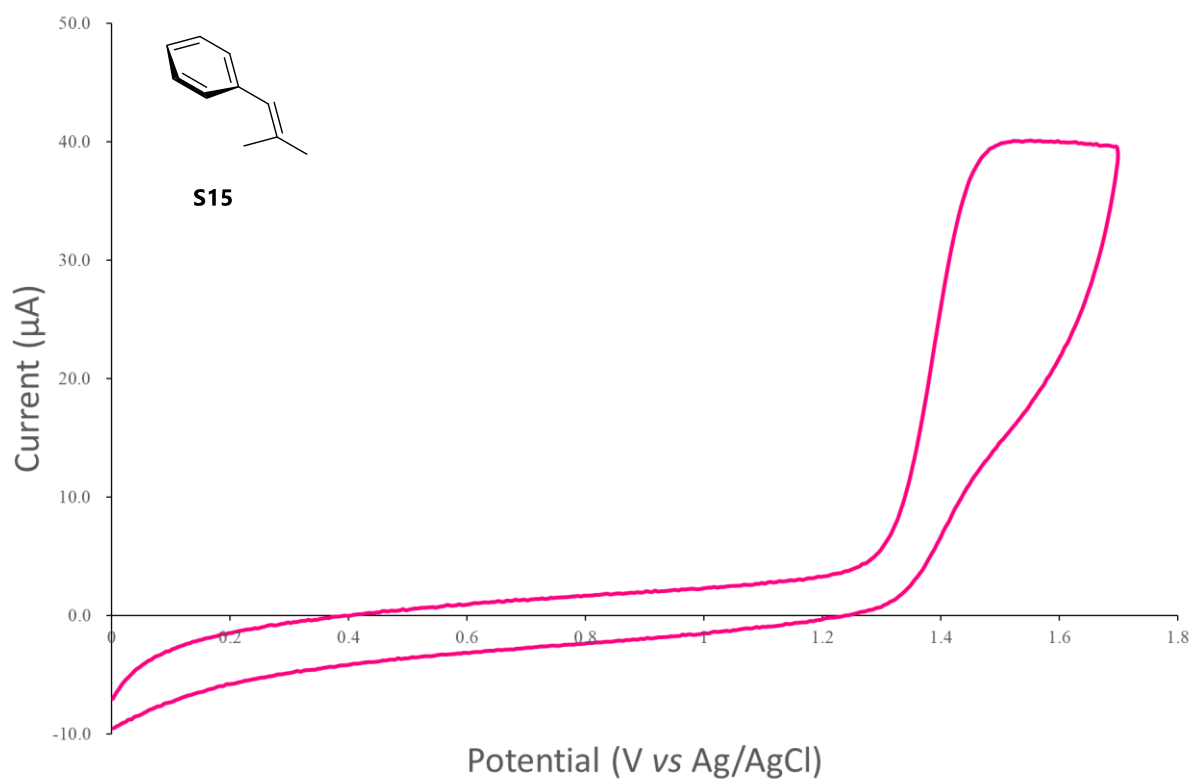


Figure S17. Cyclic voltammogram of the arylidene **S15**.

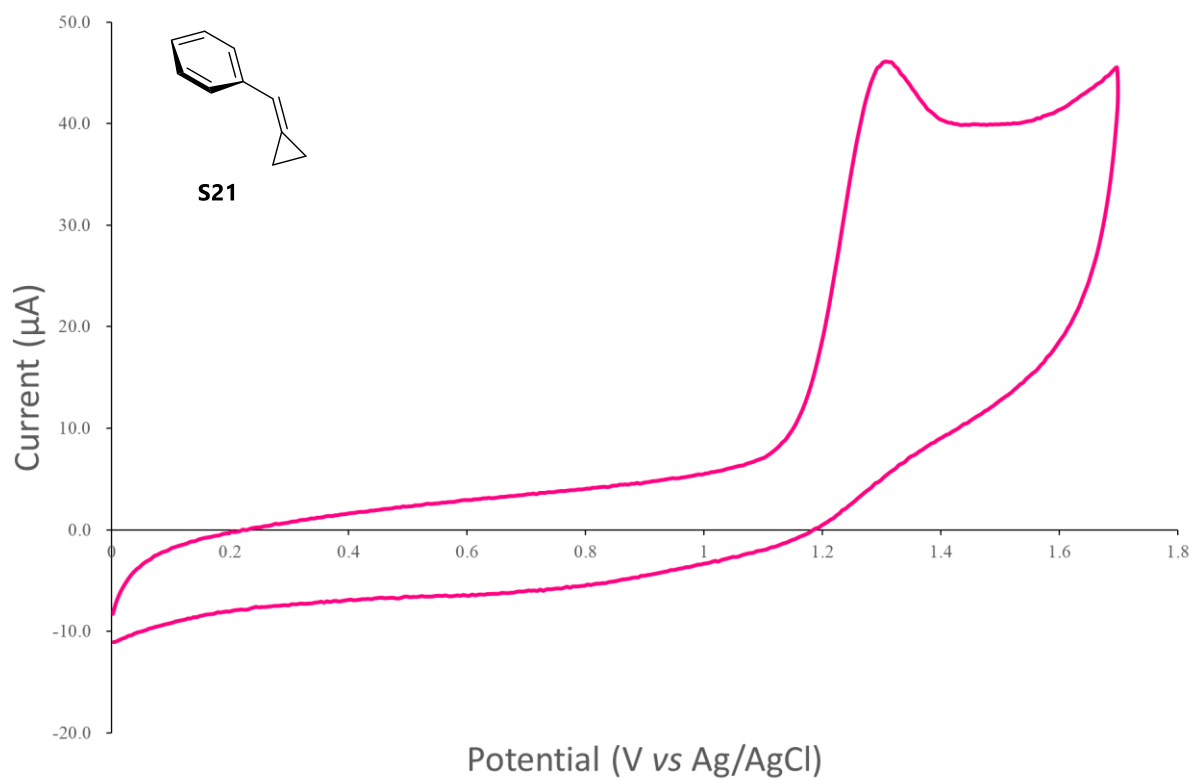


Figure S18. Cyclic voltammogram of the arylidene **S21**.

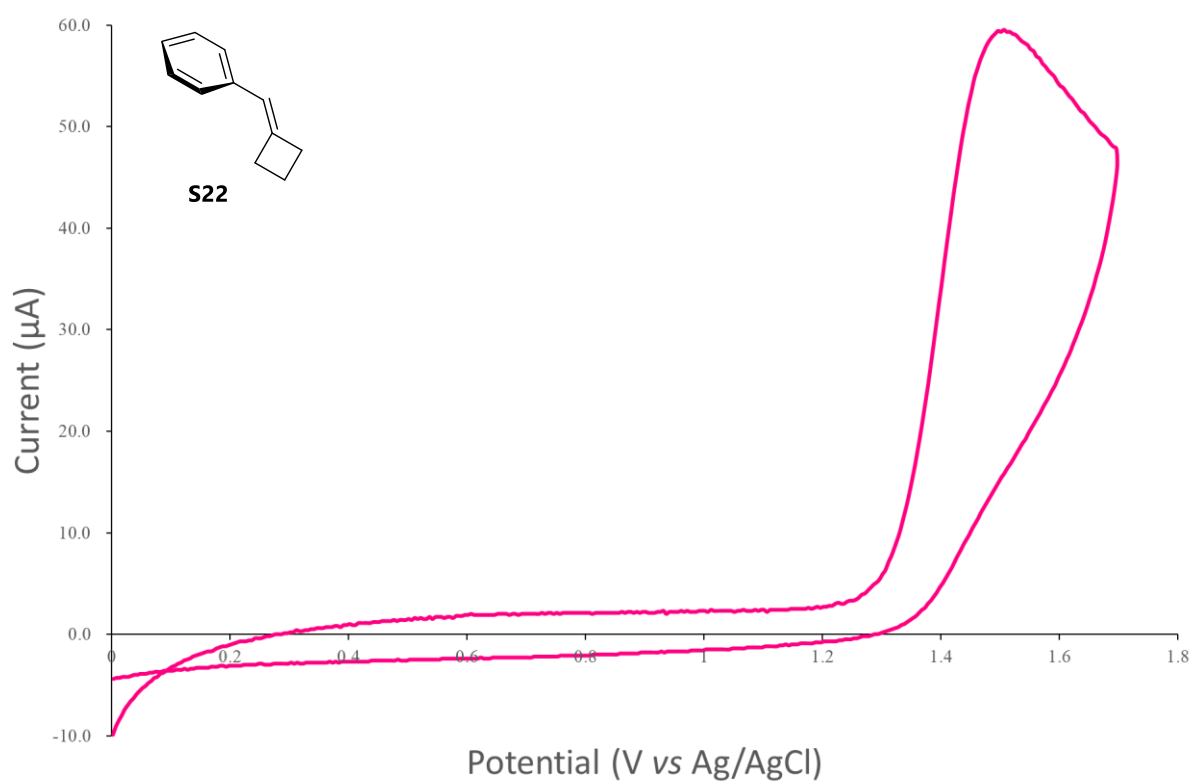


Figure S19. Cyclic voltammogram of the arylidene **S22**.

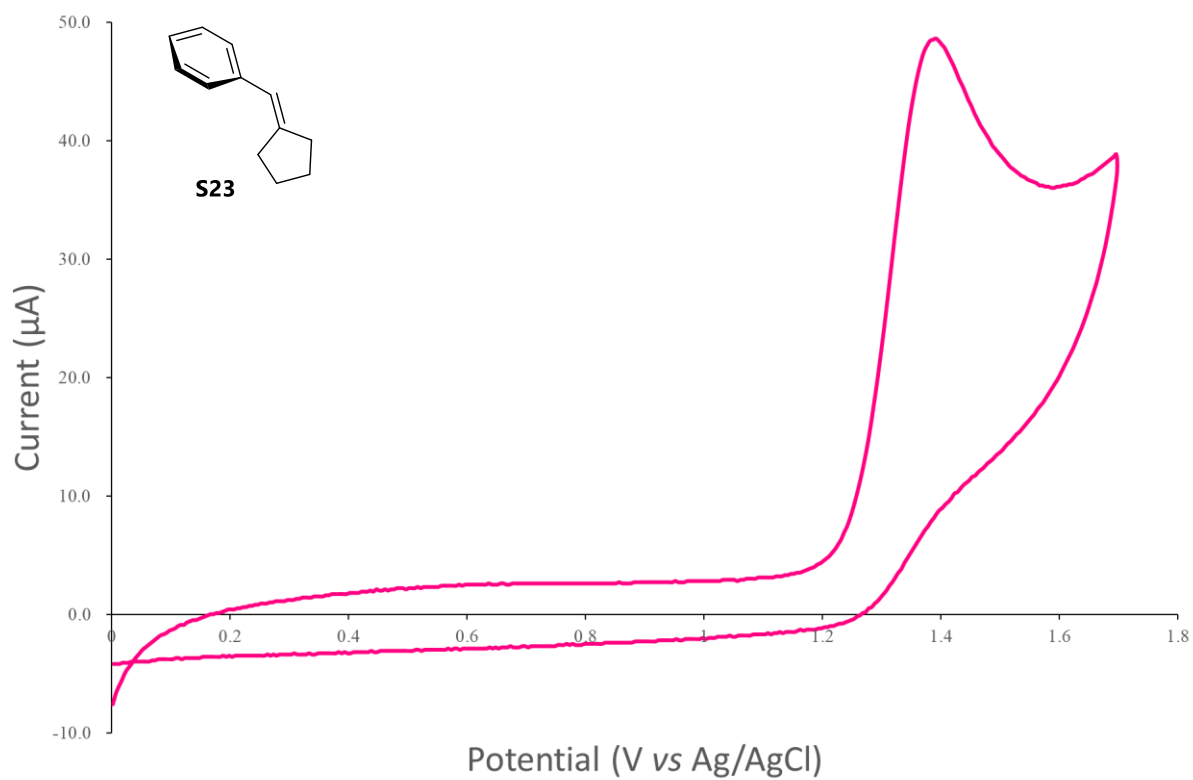


Figure S20. Cyclic voltammogram of the arylidene **S23**.

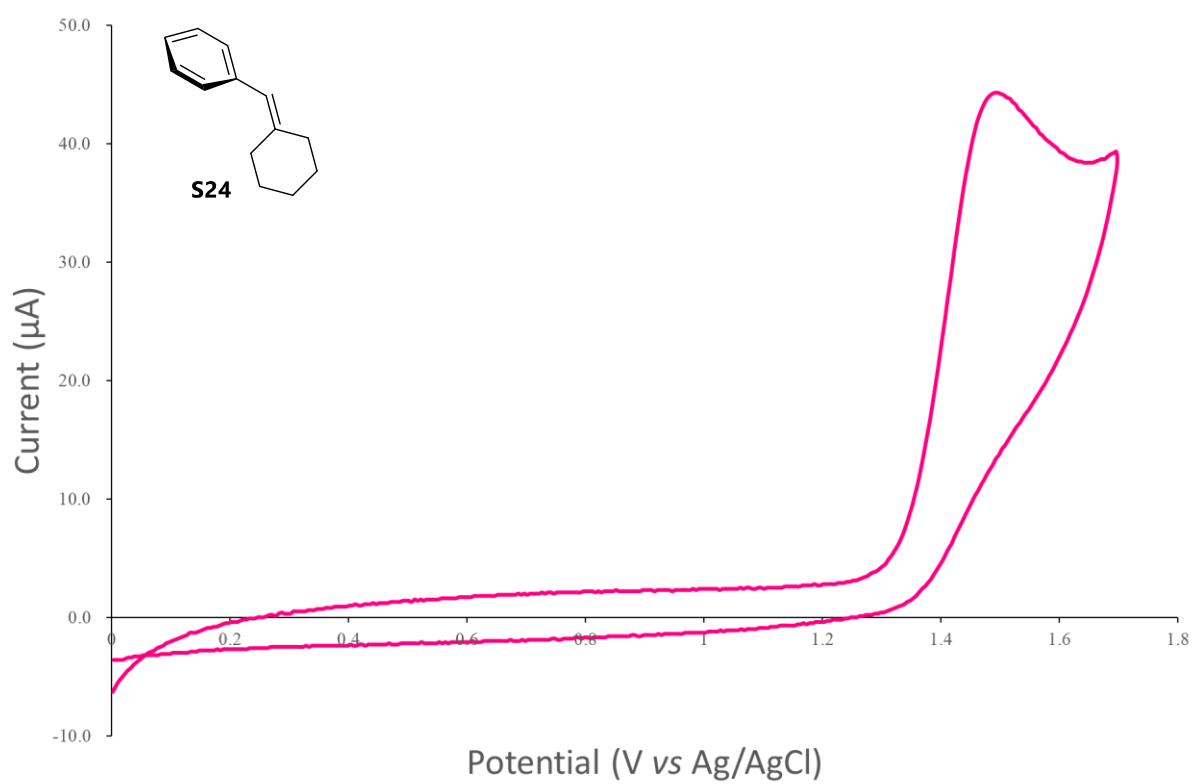


Figure S21. Cyclic voltammogram of the arylidene **S24**.

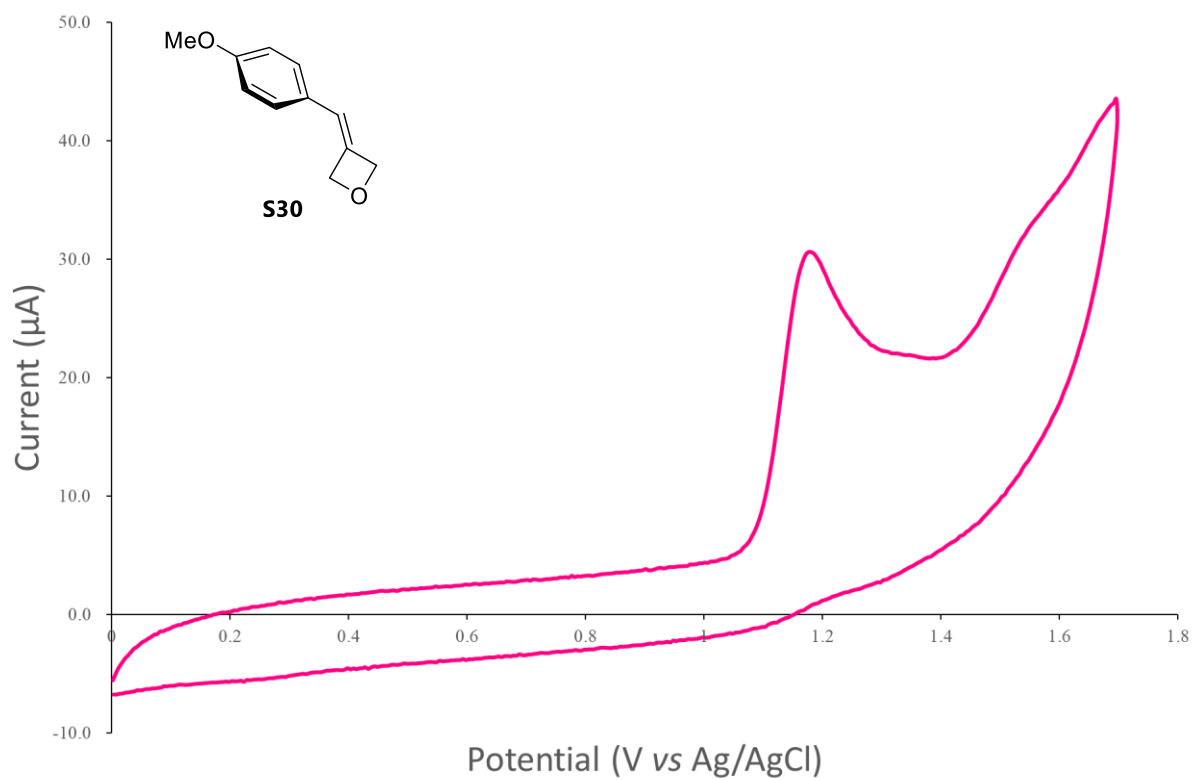


Figure S22. Cyclic voltammogram of the arylidene **S30**.

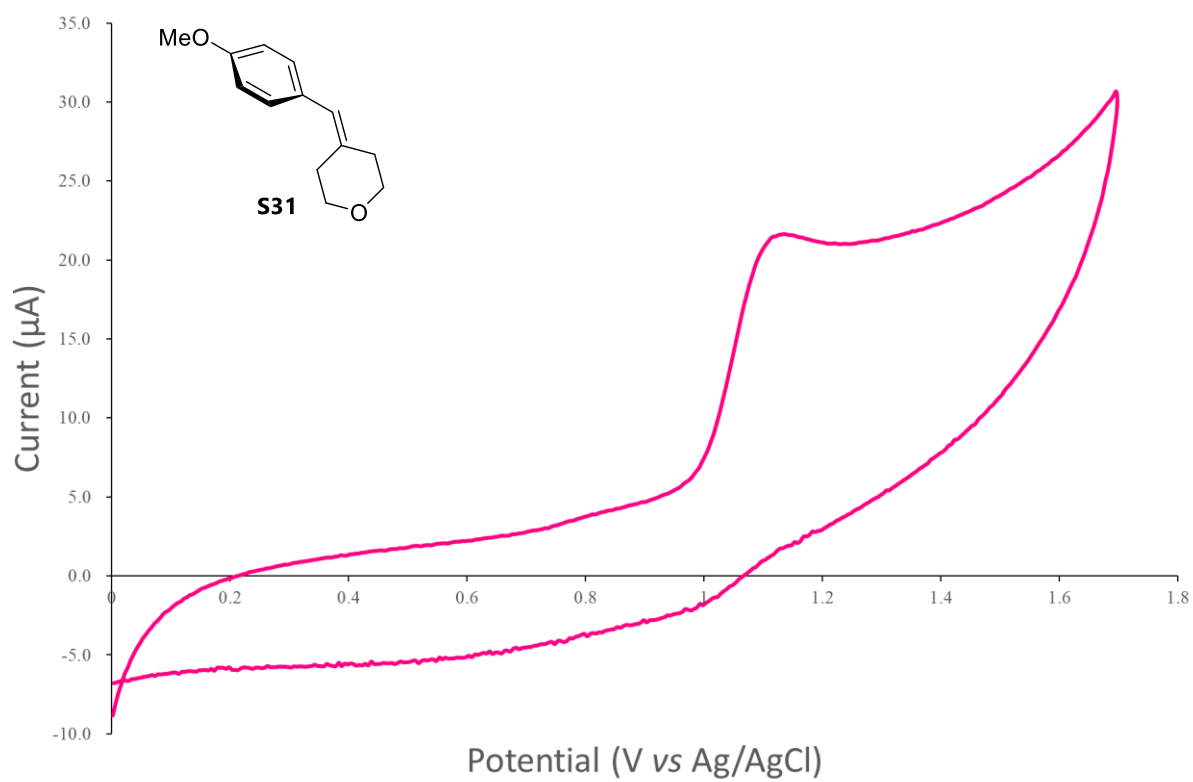


Figure S23. Cyclic voltammogram of the arylidene **S31**.

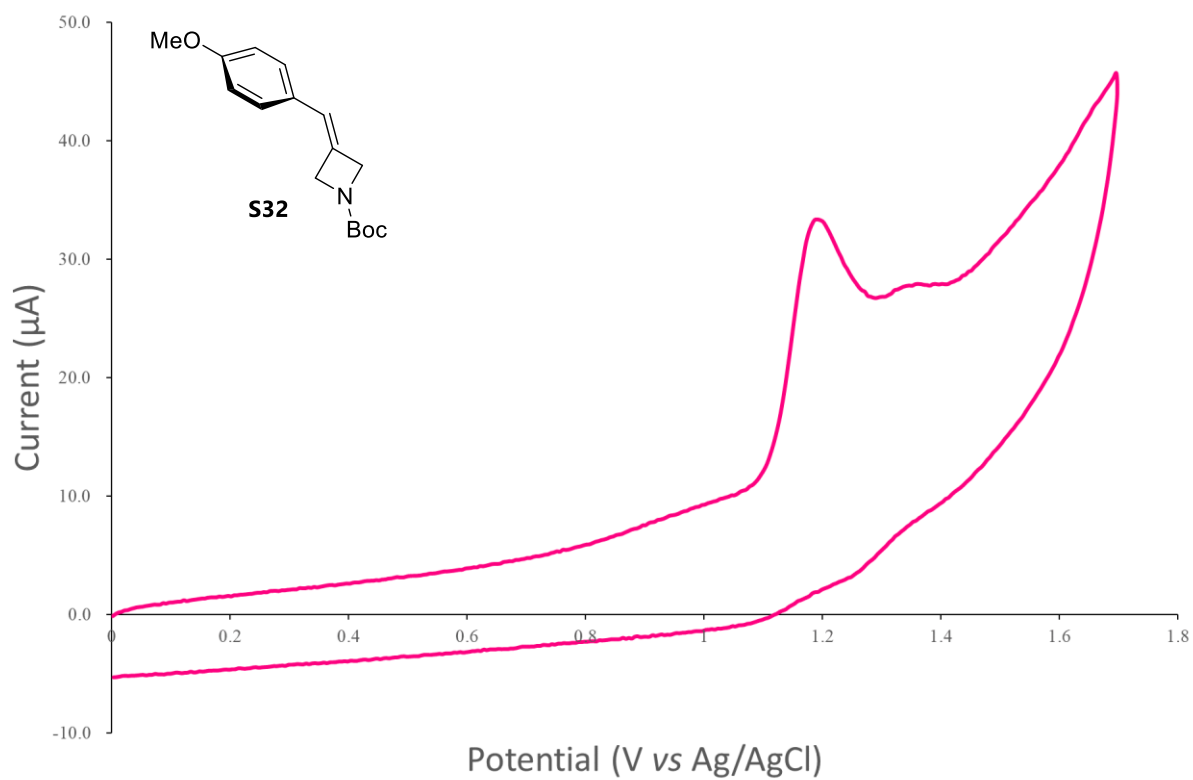


Figure S24. Cyclic voltammogram of the arylidene **S32**.

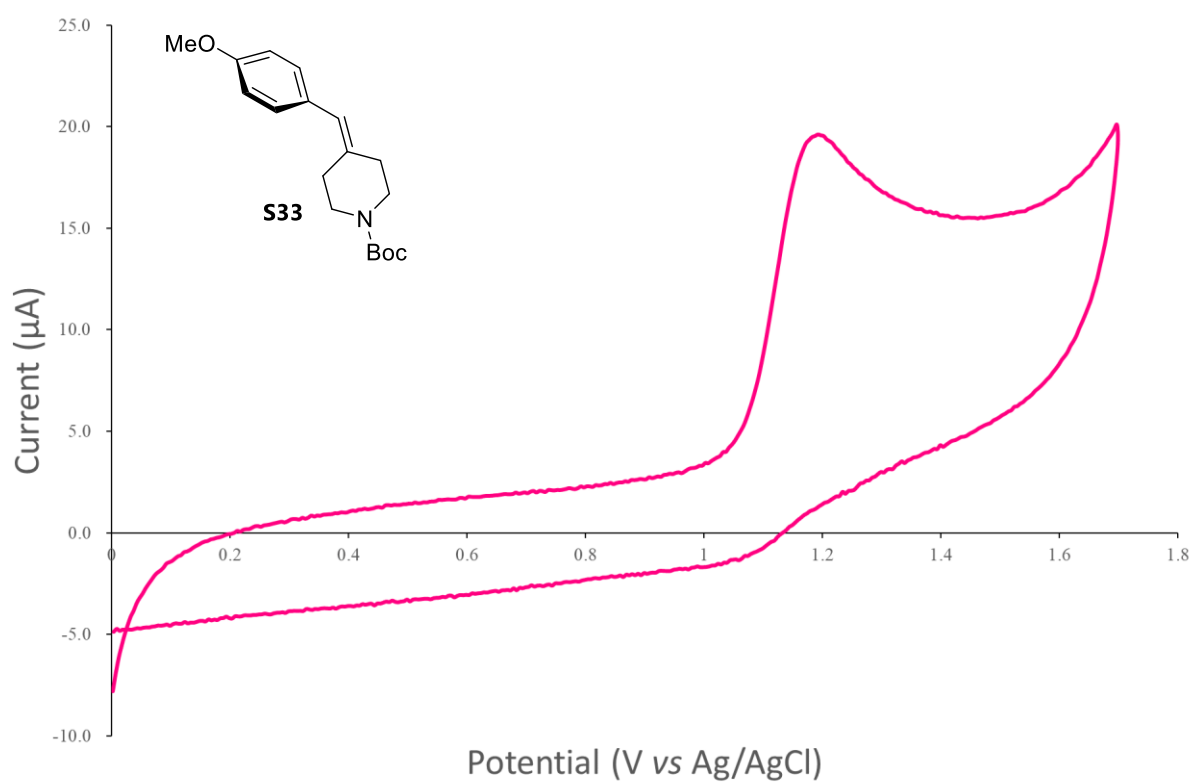
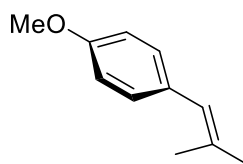


Figure S25. Cyclic voltammogram of the arylidene **S33**.

6. Characterization data, and copies of ^1H and ^{13}C NMR spectra

*1-Methoxy-4-(2-methylprop-1-en-1-yl)benzene (1).*¹ Colorless oil.

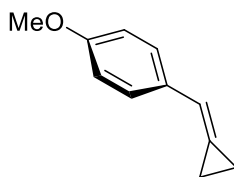


1

Product yield; 56% (458 mg, 2.8 mmol).

^1H NMR (CDCl_3 , 500 MHz) δ 7.16 (2H, d, $J = 8.6$ Hz), 6.86 (2H, d, $J = 8.6$ Hz), 6.21 (1H, s), 3.80 (3H, s), 1.88 (3H, s), 1.84 (3H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 157.9, 134.0, 131.5, 130.0, 124.8, 113.7, 55.3, 27.0, 19.5; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{15}\text{O}$ 163.1117, found 163.1132.

1-(Cyclopropylidenemethyl)-4-methoxybenzene (4). Yellow oil.

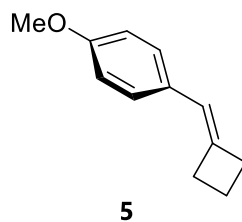


4

Product yield; 79% (633 mg, 3.9 mmol).

^1H NMR (CDCl_3 , 500 MHz) δ 7.47 (2H, d, $J = 8.6$ Hz), 6.87 (2H, d, $J = 8.6$ Hz), 6.69 (1H, m), 3.82 (3H, s), 1.38 (2H, dt, $J = 7.5, 1.7$ Hz), 1.15 (2H, dt, $J = 7.5, 1.7$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 158.8, 131.5, 127.9, 122.0, 117.8, 114.2, 55.5, 4.3, 0.8; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{13}\text{O}$ 161.0961, found 161.0977.

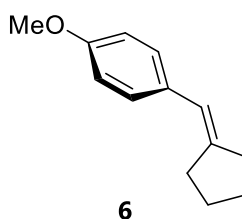
*1-(Cyclobutylidenemethyl)-4-methoxybenzene (5).*² *White solid.*



Product yield; 64% (560 mg, 3.2 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 8.14 (2H, d, J = 8.6 Hz), 6.84 (2H, d, J = 8.6 Hz), 6.02 (1H, quint, J = 2.3 Hz), 3.80 (3H, s), 3.01 (2H, t, J = 7.5 Hz), 2.86 (2H, t, J = 7.5 Hz), 2.10 (2H, quint, J = 8.0 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 157.9, 142.4, 131.2, 128.4, 120.4, 114.0, 55.5, 32.8, 32.7, 18.6; HRMS [M + H]⁺ calculated for C₁₂H₁₅O 175.1117, found 175.1140.

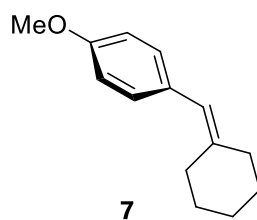
*1-(Cyclopentylidenemethyl)-4-methoxybenzene (6).*¹ *Colorless oil.*



Product yield; 25% (181 mg, 1.0 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.24 (2H, d, J = 8.6 Hz), 6.86 (2H, d, J = 8.6 Hz), 6.30 (1H, s), 3.81 (3H, s), 2.52 (2H, t, J = 6.9 Hz), 2.46 (2H, t, J = 6.9 Hz), 1.77 (2H, quint, J = 6.9 Hz), 1.65 (2H, quint, J = 6.9 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 157.7, 144.9, 132.0, 129.2, 120.3, 113.8, 55.4, 36.1, 31.2, 27.5, 26.0; HRMS [M + H]⁺ calculated for C₁₃H₁₇O 189.1274, found 189.1298.

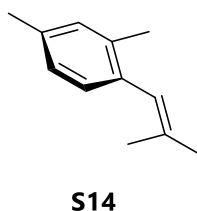
*1-(Cyclohexylidenemethyl)-4-methoxybenzene (7).*¹ Colorless oil.



Product yield; 98% (989 mg, 4.9 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.13 (2H, d, J = 8.6 Hz), 6.85 (2H, d, J = 8.6 Hz), 6.16 (1H, s), 3.80 (3H, s), 2.36 (2H, t, J = 5.7 Hz), 2.24 (2H, t, J = 5.7 Hz), 1.61 (4H, m), 1.54 (2H, quint, J = 5.2 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 157.9, 142.4, 131.2, 130.2, 121.6, 113.7, 55.4, 37.8, 29.6, 28.9, 28.1, 27.0; HRMS [M + H]⁺ calculated for C₁₄H₁₉ 203.1430, found 203.1444.

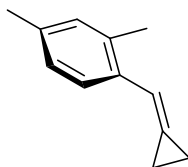
2,4-Dimethyl-1-(2-methylprop-1-en-1-yl)benzene (S14). Colorless oil.



Product yield; 55% (441 mg, 2.8 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.02 (1H, d, J = 7.5 Hz), 6.99 (1H, s), 6.96 (1H, d, J = 7.5 Hz), 6.18 (1H, s), 2.30 (3H, s), 2.20 (3H, s), 1.90 (3H, s), 1.70 (3H, s); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 136.4, 135.9, 135.2, 134.8, 130.7, 129.6, 126.2, 124.2, 26.4, 21.3, 20.1, 19.5; HRMS [M + H]⁺ calculated for C₁₂H₁₇ 161.1325, found 161.1332.

1-(Cyclopropylidenemethyl)-2,4-dimethylbenzene (S17). Yellow oil.

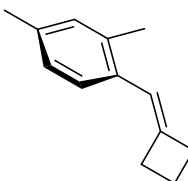


S17

Product yield; 34% (266 mg, 1.7 mmol).

^1H NMR (CDCl_3 , 500 MHz) δ 7.64 (1H, d, $J = 7.5$ Hz), 6.98 (1H, d, $J = 9.2$ Hz), 6.97 (1H, s), 6.92 (1H, d, $J = 1.7$ Hz), 2.36 (3H, s), 2.30 (3H, s), 1.38 (2H, m), 1.16 (2H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 136.5, 135.0, 134.0, 131.3, 126.9, 126.1, 124.1, 115.6, 21.3, 19.9, 4.3, 1.1; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{12}\text{H}_{15}$ 159.1168, found 159.1153.

1-(Cyclobutylidenemethyl)-2,4-dimethylbenzene (S18). Colorless oil.

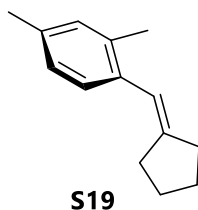


S18

Product yield; 61% (609 mg, 3.5 mmol).

^1H NMR (CDCl_3 , 500 MHz) δ 7.11 (1H, d, $J = 8.0$ Hz), 6.96 (1H, s), 6.95 (1H, d, $J = 8.0$ Hz), 6.19 (1H, s), 2.95 (2H, t, $J = 7.5$ Hz), 2.87 (2H, t, $J = 7.5$ Hz), 2.29 (3H, s), 2.27 (3H, s), 2.07 (2H, quint, $J = 7.5$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 136.5, 135.0, 134.0, 131.3, 126.9, 126.1, 124.0, 115.6, 21.3, 19.9, 4.3, 1.1; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{17}$ 173.1325, found 173.1347.

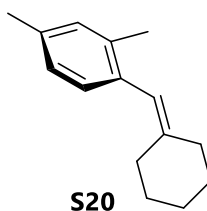
1-(Cyclopentylidenemethyl)-2,4-dimethylbenzene (S19). Colorless oil.



Product yield; 11% (107 mg, 0.57 mmol).

^1H NMR (CDCl_3 , 500 MHz) δ 7.19 (1H, d, $J = 7.5$ Hz), 6.97 (1H, s), 6.96 (1H, d, $J = 7.5$ Hz), 6.36 (1H, s), 2.47 (2H, t, $J = 6.9$ Hz), 2.40 (2H, t, $J = 6.9$ Hz), 2.30 (3H, s), 2.25 (3H, s), 1.69 (4H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 146.4, 135.9, 135.7, 135.2, 130.9, 128.2, 126.3, 118.8, 35.2, 31.0, 27.1, 25.9, 21.3, 20.2; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{14}\text{H}_{19}$ 187.1481, found 187.1489.

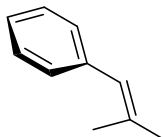
1-(Cyclohexylidenemethyl)-2,4-dimethylbenzene (S20). Colorless oil.



Product yield; 20% (200 mg, 1 mmol).

^1H NMR (CDCl_3 , 500 MHz) δ 6.99 (2H, d, $J = 3.4$ Hz), 6.94 (1H, d, $J = 8.0$ Hz), 6.11 (1H, s), 2.30 (3H, s), 2.26 (2H, t, $J = 5.7$ Hz), 2.20 (3H, s), 2.17 (2H, t, $J = 5.7$ Hz), 1.64 (2H, m), 1.58 (2H, m), 1.50 (2H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 142.9, 136.6, 136.0, 134.9, 130.7, 129.7, 126.1, 121.0, 37.6, 29.9, 29.1, 28.3, 27.1, 21.3, 20.2; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{21}$ 201.1638, found 201.1646.

(2-Methylprop-1-en-1-yl)benzene (**S15**).³ Colorless oil.

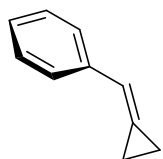


S15

Product yield; 97% (638 mg, 4.8 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.31 (2H, t, J = 8.0 Hz), 7.22 (2H, d, J = 6.9 Hz), 7.18 (1H, t, J = 7.5 Hz), 6.27 (1H, s), 1.91 (3H, s), 1.86 (3H, s); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 138.9, 135.7, 129.0, 128.3, 126.0, 125.4, 27.1, 19.7; HRMS [M + H]⁺ calculated for C₁₀H₁₃ 133.1012, found 133.1036.

(Cyclopropylidenemethyl)benzene (**S21**). Yellow oil.

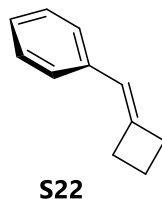


S21

Product yield; 42% (273 mg, 2.1 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.54 (2H, d, J = 7.5 Hz), 7.33 (2H, t, J = 7.5 Hz), 7.21 (1H, t, J = 7.5 Hz), 6.76 (1H, t, J = 1.7 Hz), 1.43 (2H, dt, J = 8.0, 2.3 Hz), 1.18 (2H, dt, J = 8.0, 1.7 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 138.5, 128.7, 126.9, 126.9, 124.5, 118.5, 4.5, 0.8; HRMS [M + H]⁺ calculated for C₁₀H₁₁ 131.0855, found 131.0864.

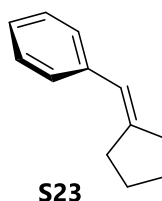
(Cyclobutylidenemethyl)benzene (**S22**).⁴ Colorless oil.



Product yield; 75% (539 mg, 3.7 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.29 (2H, t, J = 7.5 Hz), 7.20 (2H, d, J = 7.5 Hz), 7.14 (1H, t, J = 7.5 Hz), 6.07 (1H, t, J = 2.3 Hz), 3.05 (2H, t, J = 8.0 Hz), 2.88 (2H, t, J = 8.0 Hz), 2.11 (2H, quint, J = 8.0 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 145.0, 138.3, 128.6, 127.3, 126.0, 121.1, 33.0, 32.9, 18.6; HRMS [M + H]⁺ calculated for C₁₁H₁₃ 145.1012, found 145.1013.

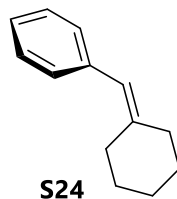
(Cyclopentylidenemethyl)benzene (**S23**).⁴ Colorless oil.



Product yield; 9% (74 mg, 0.47 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.31 (2H, d, J = 4.0 Hz), 7.30 (2H, s), 7.15 (1H, m), 6.36 (1H, t, J = 2.3 Hz), 2.55 (2H, t, J = 6.9 Hz), 2.49 (2H, t, J = 6.9 Hz), 1.78 (2H, quint, J = 6.9 Hz), 1.66 (2H, quint, J = 6.9 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 147.4, 139.1, 128.4, 128.2, 125.9, 121.1, 36.2, 31.4, 27.5, 25.9; HRMS [M + H]⁺ calculated for C₁₂H₁₅ 159.1168, found 159.1138.

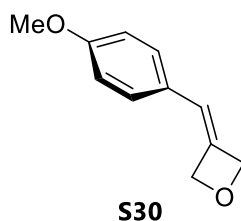
(Cyclohexylidenemethyl)benzene (**S24**).⁴ Colorless oil.



Product yield; 36% (312 mg, 1.8 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.30 (2H, t, J = 7.5 Hz), 7.20 (2H, d, J = 7.5 Hz), 7.18 (1H, t, J = 7.5 Hz), 6.23 (1H, s), 2.37 (2H, t, J = 5.7 Hz), 2.26 (2H, t, J = 5.7 Hz), 1.63 (4H, m), 1.55 (2H, m); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 143.7, 138.7, 129.2, 128.3, 126.0, 122.2, 37.9, 29.7, 28.9, 28.1, 27.0; HRMS [M + H]⁺ calculated for C₁₃H₁₇ 173.1325, found 173.1334.

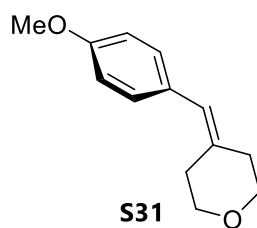
3-(4-Methoxybenzylidene)oxetane (**S30**).² Yellow solid.



Product yield; 25% (225 mg, 1.3 mmol).

¹H NMR (CDCl₃, 300 MHz) δ 6.94 (2H, d, J = 8.9 Hz), 6.87 (2H, d, J = 8.9 Hz), 6.04 (1H, t, J = 2.4 Hz), 5.55 (2H, q, J = 2.8 Hz), 5.38 (2H, q, J = 2.8 Hz), 3.81 (3H, s); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 158.7, 134.5, 129.1, 128.5, 119.2, 114.4, 80.6, 80.4, 55.5; HRMS [M + H]⁺ calculated for C₁₁H₁₃O₂ 177.0910, found 177.0920.

4-(4-Methoxybenzylidene)tetrahydro-2H-pyran (**S31**).¹ Yellow solid.



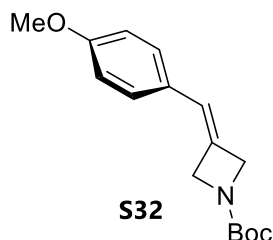
Product yield; 18% (184 mg, 0.90 mmol).

¹H NMR (CDCl₃, 300 MHz) δ 7.14 (2H, d, J = 8.6 Hz), 6.86 (2H, d, J = 8.6 Hz), 6.27 (1H, s), 3.81 (3H, s), 3.78 (2H, t, J = 5.9 Hz), 3.66 (2H, t, J = 5.9 Hz), 2.53 (2H, dt, J = 5.9, 1.4 Hz), 2.38 (2H, dt, J = 5.9, 1.4 Hz);

¹³C{¹H} NMR (125 MHz, CDCl₃) δ 158.2, 136.5, 130.2, 130.1, 123.5, 113.8, 69.7, 68.7, 55.4, 37.4, 30.8;

HRMS [M + H]⁺ calculated for C₁₃H₁₇O₂ 205.1223, found 205.1230.

tert-Butyl 3-(4-methoxybenzylidene)azetidine-1-carboxylate (**S32**).² Yellow solid.



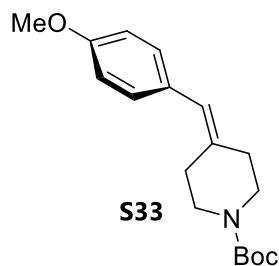
Product yield; 43% (597 mg, 2.2 mmol).

¹H NMR (CDCl₃, 300 MHz) δ 7.05 (2H, d, J = 8.9 Hz), 6.88 (2H, d, J = 8.9 Hz), 6.20 (1H, t, J = 2.1 Hz), 4.81 (2H, q, J = 2.8 Hz), 4.62 (2H, q, J = 2.8 Hz), 3.81 (3H, s), 1.48 (9H, s); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ

158.8, 156.6, 129.2, 128.6, 128.1, 121.9, 114.4, 80.0, 55.5, 28.7; HRMS [M + H]⁺ calculated for C₁₆H₂₂NO₃

276.1594, found 276.1611.

tert-Butyl 4-(4-methoxybenzylidene)piperidine-1-carboxylate (**S33**).⁵ White solid.

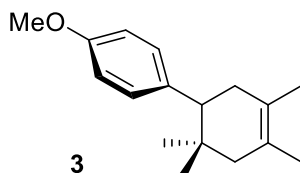


Product yield; 26% (402 mg, 1.3 mmol).

¹H NMR (CDCl₃, 500 MHz) δ 7.12 (2H, d, J = 8.6 Hz), 6.86 (2H, d, J = 8.6 Hz), 6.30 (1H, s), 3.80 (3H, s), 3.50 (2H, t, J = 5.2 Hz), 3.40 (2H, t, J = 5.2 Hz), 2.45 (2H, t, J = 5.2 Hz), 2.31 (2H, t, J = 5.2 Hz), 1.48 (9H, s); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 158.3, 155.1, 137.3, 130.3, 124.2, 113.9, 79.8, 55.5, 36.4, 29.4, 28.7;

HRMS [M + H]⁺ calculated for C₁₈H₂₆NO₃ 304.1907, found 304.1887.

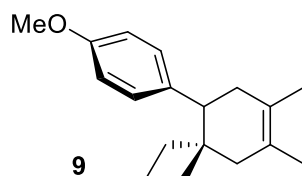
4'-Methoxy-2,2,4,5-tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**3**). Colorless oil.



¹H NMR (CDCl₃, 500 MHz) δ 7.11 (2H, d, J = 8.6 Hz), 6.81 (2H, d, J = 8.6 Hz), 3.79 (3H, s), 2.58 (1H, dd, J = 9.7, 5.7 Hz), 2.31 (1H, dd, J = 17.2, 10.3 Hz), 2.12 (1H, dd, J = 17.2, 3.4 Hz), 1.94 (1H, d, J = 17.2 Hz), 1.72 (1H, d, J = 17.8 Hz), 1.65 (3H, s), 1.64 (3H, s), 0.78 (3H, s), 0.77 (3H, s); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 158.1, 136.2, 130.1, 124.8, 124.6, 113.3, 55.5, 49.5, 47.6, 36.6, 33.4, 29.8, 22.6, 19.4, 18.9; HRMS

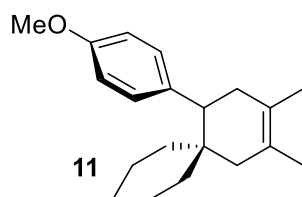
[M + H]⁺ calculated for C₁₇H₂₅O 245.1900, found 245.1928.

9-(4-Methoxyphenyl)-6,7-dimethylspiro[3.5]non-6-ene (**9**). Yellow oil.



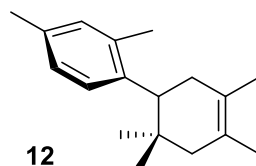
^1H NMR (CDCl_3 , 500 MHz) δ 7.11 (2H, d, $J = 8.6$ Hz), 6.81 (2H, d, $J = 8.6$ Hz), 3.79 (3H, s), 2.78 (1H, t, $J = 5.7$ Hz), 2.33 (1H, dd, $J = 18.3, 2.9$ Hz), 2.12 (1H, dd, $J = 17.8, 2.3$ Hz), 2.01 (3H, m), 1.81 (2H, m), 1.66 (6H, m), 1.62 (2H, m), 1.41 (1H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 158.1, 136.4, 129.5, 125.2, 124.7, 113.4, 55.4, 47.7, 42.8, 42.2, 35.0, 32.8, 29.8, 19.6, 19.0, 15.3; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{25}\text{O}$ 257.1900, found 257.1899.

5-(4-Methoxyphenyl)-2,3-dimethylspiro[5.5]undec-2-ene (**11**). Colorless oil.



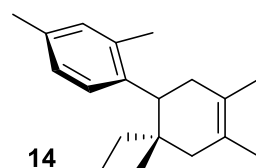
^1H NMR (CDCl_3 , 500 MHz) δ 7.09 (2H, d, $J = 8.0$ Hz), 6.79 (2H, d, $J = 8.0$ Hz), 3.79 (3H, s), 2.63 (1H, t, $J = 5.7$ Hz), 2.27 (1H, dd, $J = 17.8, 3.4$ Hz), 2.15 (1H, dd, $J = 17.2, 4.6$ Hz), 1.98 (1H, d, $J = 17.8$ Hz), 1.78 (1H, d, $J = 17.2$ Hz), 1.68 (3H, s), 1.65 (3H, s), 1.46 (5H, m), 1.31 (1H, m), 1.13 (4H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 158.0, 136.7, 130.2, 130.1, 124.6, 113.2, 55.4, 39.4, 36.9, 36.0, 35.5, 32.4, 30.0, 26.8, 22.2, 22.1, 19.8, 18.9; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{29}\text{O}$ 285.2213, found 285.2220.

2,2,2',4,4',5-Hexamethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (**12**). Colorless oil.



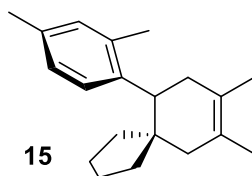
^1H NMR (CDCl_3 , 500 MHz) δ 7.16 (1H, d, $J = 8.6$ Hz), 6.96 (1H, s), 6.95 (1H, d, $J = 6.9$ Hz), 3.01 (1H, dd, $J = 9.7, 5.7$ Hz), 2.31 (3H, s), 2.28 (3H, s), 2.26 (1H, m), 2.05 (1H, dd, $J = 19.5, 4.6$ Hz), 2.01 (1H, d, $J = 17.2$ Hz), 1.77 (1H, d, $J = 16.6$ Hz), 1.65 (3H, s), 1.64 (3H, s), 0.86 (3H, s), 0.80 (3H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 139.9, 136.9, 135.2, 131.2, 127.5, 126.5, 125.1, 124.8, 48.5, 43.1, 37.5, 34.3, 28.9, 22.6, 21.2, 21.2, 19.5, 18.9; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{27}$ 243.2107, found 243.2104.

9-(2,4-Dimethylphenyl)-6,7-dimethylspiro[3.5]non-6-ene (**14**). Colorless oil.



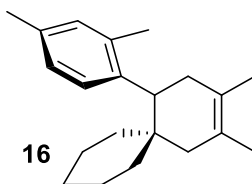
^1H NMR (CDCl_3 , 500 MHz) δ 7.17 (1H, d, $J = 7.5$ Hz), 7.00 (1H, d, $J = 8.6$ Hz), 6.99 (1H, s), 3.07 (1H, dd, $J = 9.7, 5.2$ Hz), 2.32 (2H, m), 2.30 (3H, s), 2.23 (3H, m), 2.21 (1H, m), 1.95 (2H, m), 1.80 (1H, m), 1.68 (3H, s), 1.64 (3H, s), 1.62 (1H, m), 1.53 (1H, m), 1.46 (2H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 139.2, 137.3, 135.3, 131.2, 127.0, 126.8, 126.3, 124.5, 46.1, 42.9, 41.8, 35.2, 31.2, 26.9, 21.2, 20.9, 19.4, 19.1, 15.9; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{27}$ 255.2107, found 255.2114.

10-(2,4-Dimethylphenyl)-7,8-dimethylspiro[4.5]dec-7-ene (**15**). Colorless oil.



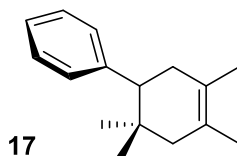
^1H NMR (CDCl_3 , 500 MHz) δ 7.17 (1H, d, J = 8.0 Hz), 6.96 (1H, s), 6.95 (1H, d, J = 8.0 Hz), 3.10 (1H, dd, J = 8.6, 4.3 Hz), 2.29 (3H, s), 2.28 (3H, s), 2.27 (1H, m), 2.12 (1H, dd, J = 17.2, 4.0 Hz), 1.97 (1H, d, J = 16.0 Hz), 1.89 (1H, d, J = 17.8 Hz), 1.65 (6H, s), 1.55 (3H, m), 1.40 (3H, m), 1.24 (2H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 140.1, 137.1, 135.2, 131.1, 127.3, 126.7, 126.1, 125.0, 46.4, 45.0, 41.8, 37.9, 37.7, 31.9, 24.5, 23.9, 21.1, 19.6, 19.0; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{29}$ 269.2264, found 269.2247.

5-(2,4-Dimethylphenyl)-2,3-dimethylspiro[5.5]undec-2-ene (**16**). Colorless oil.



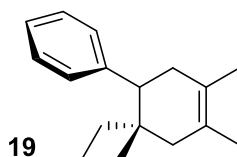
^1H NMR (CDCl_3 , 500 MHz) δ 7.15 (1H, d, J = 8.6 Hz), 6.96 (1H, s), 6.95 (1H, d, J = 6.9 Hz), 2.99 (1H, dd, J = 8.6, 6.3 Hz), 2.31 (3H, s), 2.28 (3H, s), 2.22 (1H, m), 2.20 (1H, d, J = 16.6 Hz), 2.08 (1H, dd, J = 17.8, 4.6 Hz), 1.90 (1H, d, J = 17.8 Hz), 1.69 (3H, s), 1.63 (3H, s), 1.55 (1H, m), 1.45 (2H, m), 1.40 (3H, m), 1.31 (1H, tt, J = 13.2, 3.4 Hz), 1.26 (1H, m), 0.98 (2H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 139.8, 137.2, 135.1, 131.1, 128.0, 126.5, 125.3, 124.4, 44.6, 39.6, 36.8, 36.6, 30.0, 29.4, 26.6, 22.1, 22.1, 21.5, 21.2, 19.7, 18.9; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{31}$ 283.2420, found 283.2420.

2,2,4,5-Tetramethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (17). Colorless oil.



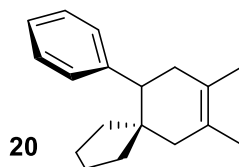
^1H NMR (CDCl_3 , 500 MHz) δ 7.25 (2H, d, $J = 7.5$ Hz), 7.19 (3H, m), 2.63 (1H, dd, $J = 9.7, 5.7$ Hz), 2.36 (1H, m), 2.14 (1H, dd, $J = 16.6, 4.0$ Hz), 1.96 (1H, d, $J = 17.2$ Hz), 1.74 (1H, d, $J = 16.6$ Hz), 1.66 (3H, s), 1.65 (3H, s), 0.80 (3H, s), 0.79 (3H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 144.2, 129.3, 127.9, 126.3, 124.8, 124.6, 50.4, 47.6, 36.4, 33.3, 29.8, 22.6, 19.4, 18.9; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{23}$ 215.1794, found 215.1783.

6,7-Dimethyl-9-phenylspiro[3.5]non-6-ene (19). Colorless oil.



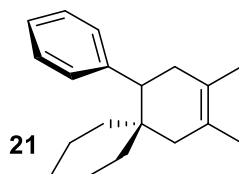
^1H NMR (CDCl_3 , 500 MHz) δ 7.26 (2H, m), 7.19 (3H, m), 2.84 (1H, t, $J = 5.7$ Hz), 2.35 (1H, d, $J = 16.6$ Hz), 2.16 (1H, d, $J = 15.5$ Hz), 2.04 (3H, m), 1.83 (2H, m), 1.67 (3H, s), 1.66 (1H, m), 1.66 (3H, s), 1.62 (1H, m), 1.41 (1H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 144.3, 128.7, 128.1, 126.2, 125.2, 124.8, 48.5, 42.7, 42.1, 34.8, 33.0, 29.9, 19.6, 19.0, 15.3; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}$ 227.1794, found 227.1780.

7,8-Dimethyl-10-phenylspiro[4.5]dec-7-ene (**20**). Colorless oil.



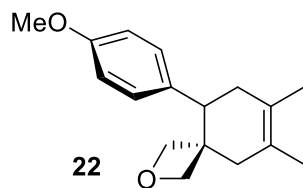
^1H NMR (CDCl_3 , 500 MHz) δ 6.30 (2H, t, $J = 6.3$ Hz), 7.19 (1H, s), 7.18 (2H, d, $J = 7.5$ Hz), 2.70 (1H, t, $J = 5.7$ Hz), 2.35 (1H, m), 2.22 (1H, m), 1.81 (2H, q, $J = 16.6$ Hz), 1.68 (3H, s), 1.66 (3H, s), 1.53 (4H, m), 1.41 (3H, m), 1.07 (1H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 145.4, 129.0, 128.0, 126.1, 125.3, 125.2, 48.8, 45.7, 42.6, 38.3, 37.0, 35.1, 24.4, 24.1, 19.7, 19.0; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{25}$ 241.1951, found 241.1964.

2,3-Dimethyl-5-phenylspiro[5.5]undec-2-ene (**21**). Colorless oil.



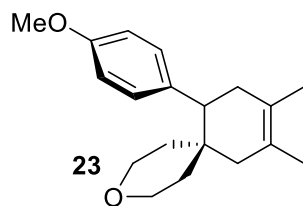
^1H NMR (CDCl_3 , 500 MHz) δ 7.24 (2H, m), 7.18 (3H, m), 2.68 (1H, t, $J = 5.7$ Hz), 2.30 (1H, dd, $J = 17.8$, 4.0 Hz), 2.20 (1H, dd, $J = 17.8$, 5.2 Hz), 2.00 (1H, d, $J = 17.2$ Hz), 1.80 (1H, d, $J = 17.8$ Hz), 1.69 (3H, s), 1.66 (3H, s), 1.46 (5H, m), 1.33 (1H, m), 1.13 (4H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 144.7, 129.4, 127.9, 126.2, 124.6, 124.6, 49.9, 39.3, 37.0, 35.8, 35.5, 32.5, 26.8, 22.2, 22.1, 19.8, 18.9; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{27}$ 255.2107, found 255.2116.

9-(4-Methoxyphenyl)-6,7-dimethyl-2-oxaspiro[3.5]non-6-ene (**22**). Colorless oil.



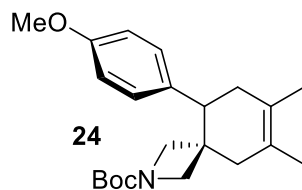
^1H NMR (CDCl_3 , 500 MHz) δ 7.11 (2H, d, $J = 8.6$ Hz), 6.82 (2H, d, $J = 8.6$ Hz), 4.69 (1H, d, $J = 5.7$ Hz), 4.47 (1H, d, $J = 5.7$ Hz), 4.31 (1H, d, $J = 5.7$ Hz), 4.11 (1H, d, $J = 5.7$ Hz), 3.78 (3H, s), 3.23 (1H, dt, $J = 3.2$ 2.9 Hz), 2.42 (1H, m), 2.33 (1H, d, $J = 17.2$ Hz), 2.18 (1H, d, $J = 19.5$ Hz), 2.14 (1H, d, $J = 21.2$ Hz), 1.69 (3H, s), 1.67 (3H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 158.5, 135.1, 129.2, 125.8, 124.1, 113.9, 83.2, 80.2, 55.4, 44.6, 42.8, 39.9, 35.0, 19.5, 19.0; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{O}_2$ 259.1693, found 259.1670.

11-(4-Methoxyphenyl)-8,9-dimethyl-3-oxaspiro[5.5]undec-8-ene (**23**). Colorless oil.



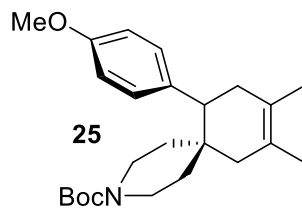
^1H NMR (CDCl_3 , 500 MHz) δ 7.07 (2H, d, $J = 8.6$ Hz), 6.80 (2H, d, $J = 8.6$ Hz), 3.78 (3H, s), 3.72 (2H, m), 3.61 (1H, dt, $J = 11.5, 2.9$ Hz), 3.52 (1H, dt, $J = 11.5, 2.9$ Hz), 2.64 (1H, t, $J = 5.7$ Hz), 2.36 (1H, dd, $J = 17.8, 5.2$ Hz), 2.15 (1H, m), 1.99 (2H, m), 1.70 (3H, s), 1.67 (3H, s), 1.49 (2H, m), 1.43 (1H, ddt, $J = 14.3, 2.9, 2.3$ Hz), 1.04 (1H, ddt, $J = 13.2, 2.9, 2.3$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 158.3, 135.8, 130.1, 125.0, 124.1, 113.5, 64.1, 55.5, 48.9, 37.7, 36.5, 35.4, 33.9, 33.5, 30.0, 19.8, 18.9; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{27}\text{O}_2$ 287.2006, found 287.2034.

tert-Butyl 9-(4-methoxyphenyl)-6,7-dimethyl-2-azaspiro[3.5]non-6-ene-2-carboxylate (**24**). Yellow oil.



^1H NMR (CDCl_3 , 500 MHz) δ 7.11 (2H, d, $J = 8.6$ Hz), 6.82 (2H, d, $J = 8.6$ Hz), 3.88 (1H, d, $J = 8.6$ Hz), 3.78 (3H, s), 3.66 (1H, d, $J = 8.0$ Hz), 3.52 (1H, d, $J = 8.0$ Hz), 3.28 (1H, d, $J = 8.6$ Hz), 2.99 (1H, dt, $J = 4.0$, 2.3 Hz), 2.43 (1H, dd, $J = 16.6$, 3.4 Hz), 2.15 (3H, m), 1.67 (6H, s), 1.41 (9H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 158.5, 156.9, 134.9, 129.4, 125.9, 124.1, 113.9, 79.4, 55.5, 45.0, 40.7, 37.5, 35.3, 28.7, 19.5, 19.0; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{32}\text{NO}_3$ 358.2377, found 385.2348.

tert-Butyl 11-(4-methoxyphenyl)-8,9-dimethyl-3-azaspiro[5.5]undec-8-ene-3-carboxylate (**25**). White solid.



^1H NMR (CDCl_3 , 500 MHz) δ 7.06 (2H, d, $J = 8.6$ Hz), 6.80 (2H, d, $J = 8.6$ Hz), 3.79 (3H, s), 3.72 (2H, m), 3.01 (1H, dt, $J = 13.8$, 2.3 Hz), 2.91 (1H, t, $J = 9.7$ Hz), 2.63 (1H, t, $J = 5.7$ Hz), 2.33 (1H, d, $J = 16.0$ Hz), 2.16 (1H, d, $J = 16.6$ Hz), 1.98 (1H, d, $J = 16.6$ Hz), 1.87 (1H, d, $J = 17.2$ Hz), 1.69 (3H, s), 1.67 (3H, s), 1.42 (9H, s), 1.32 (3H, m), 1.13 (1H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 158.3, 155.3, 130.1, 125.0, 124.0, 113.5, 79.4, 55.5, 48.5, 37.6, 35.7, 34.2, 30.0, 28.7, 19.8, 18.9; HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{36}\text{NO}_3$ 386.2690, found 386.2668.

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