

Supplementary Materials for

Electrochemical oxidation-induced etherification via C(sp³)-H/O-H cross-coupling

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Figs. S1 and S2

Table S1

Spectroscopic data

General information

All reactions were run under a dry nitrogen atmosphere on a Schlenk tube. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. All the solvents were purified according to the solvent handbook. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anode electrode is carbon rod electrodes (Φ 6mm) and the cathode electrode is platinum plate electrodes (15 mm \times 15 mm \times 0.3 mm) or nickel plate electrodes (15 mm \times 15 mm \times 1 mm). Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. All compounds were characterized by ^1H NMR, ^{13}C NMR. ^1H and ^{13}C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^1H), CDCl_3 (77.16 ppm for ^{13}C) and DMSO (2.50 ppm for ^1H , 39.52 ppm for ^{13}C), respectively.

Graphical guide for the set-up

As experimental set-up, a carbon rod electrode (Φ 6mm), nickel plate electrode (15 mm x 15 mm x 1 mm) a platinum plate electrode (15 mm \times 15 mm \times 0.3 mm), rubber plugs, an undivided three-necked bottle and a dual display potentiostat (DJS-292B) (made in China) were used.



A) current control synthesis



B) Assembly of electrochemical cell



C) Carbon rod anode and platinum plate cathode



D) Carbon rod anode and nickel plate cathode



E) Assembly of electrode



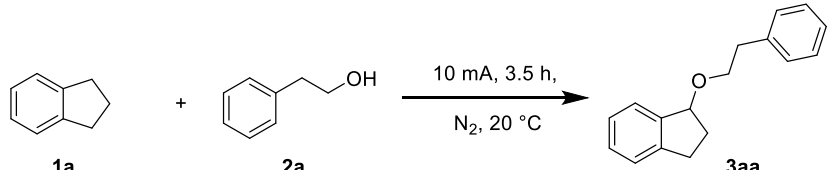
F) Assembly of electrode

Figure S1. Graphical guide for the set-up (Photo Credit: Huamin Wang, Wuhan University)

Experimental section

1) Impact of reaction parameters

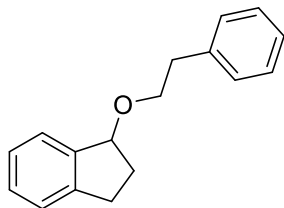
Table S1. Impact of reaction parameters ^[a]



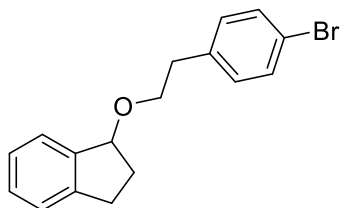
Entry	Ratio of 1a:2a	Solvents	Bases	Electrolyte	Electrodes	Isolated yield(% 3aa)
1	1:3	DCE	—	Bu ₄ NClO ₄	C(+) Pt(-)	27
2	1:3	DCE	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Pt(-)	50
3	1:3	DCE	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) C(-)	32
4	1:3	DCE	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	56
5 ^b	1:3	CH ₃ CN	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	31
6 ^c	1:3	DCE/THF	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	50
7	1:3	DCE/Et ₂ O	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	60
8 ^d	1:3	DCE/Et ₂ O	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	60
9 ^e	1:3	DCE/Et ₂ O	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	49
10	1:3	DCE/Et ₂ O	Na ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	24
11	1:3	DCE/Et ₂ O	NaOAc	Bu ₄ NClO ₄	C(+) Ni(-)	25
12	1:3	DCE/Et ₂ O	Cs ₂ CO ₃	Bu ₄ NBF ₄	C(+) Ni(-)	40
13	1:2	DCE/Et ₂ O	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	24
14	1:3	DCE/Et ₂ O	Cs ₂ CO ₃	Bu ₄ NClO ₄	—	n.d. ^f
15 ^g	1:3	DCE/Et ₂ O	Cs ₂ CO ₃	Bu ₄ NClO ₄	C(+) Ni(-)	50

^a Standard conditions: Carbon rod anode, nickel plate (15 mm x 15 mm x 1 mm) cathode, constant current = 10 mA, **1a** (0.5 mmol), **2a** (3 equiv.), ⁿBu₄NClO₄ (0.5 equiv.), Cs₂CO₃ (2 equiv.), 20°C, in DCE/Et₂O (6 mL/0.5 mL) under N₂ atmosphere for 3.5 h, and an undivided cell, isolated yields. ^bCH₃CN (6 mL). ^cDCE/THF (6 mL/0.5 mL). ^d DCE/Et₂O (6 mL/2 mL). ^e Cs₂CO₃ (1.5 equiv.). ^f“n.d.” means “not detected”.

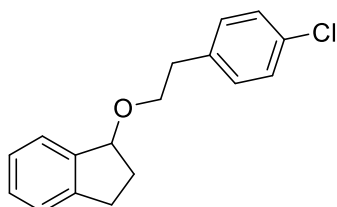
2) Procedure and analytical data of compounds.



1-Phenethoxy-2,3-dihydro-1H-indene (3aa): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.15 (m, 9H), 4.91 (dd, $J = 6.7, 4.2$ Hz, 1H), 3.73 (qd, $J = 9.2, 8.3, 5.3$ Hz, 2H), 3.10 – 3.00 (m, 1H), 2.91 (td, $J = 7.4, 2.8$ Hz, 2H), 2.78 (ddd, $J = 16.0, 8.4, 5.6$ Hz, 1H), 2.32 (ddt, $J = 12.5, 8.7, 6.1$ Hz, 1H), 2.05 (ddt, $J = 13.1, 8.6, 5.1$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.97, 142.92, 139.18, 129.10, 128.42, 128.38, 126.40, 126.27, 125.14, 124.97, 83.47, 69.77, 36.80, 32.48, 30.28. HRMS (ESI+) calculated for $\text{C}_{17}\text{H}_{18}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 261.1250; found: 261.1253.

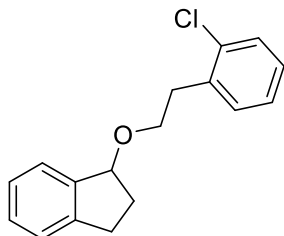


1-(4-Bromophenoxy)-2,3-dihydro-1H-indene (3ab): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.31 (d, $J = 7.2$ Hz, 1H), 7.24 (d, $J = 3.6$ Hz, 2H), 7.22 – 7.16 (m, 1H), 7.09 (d, $J = 8.3$ Hz, 2H), 4.89 (dd, $J = 6.6, 4.3$ Hz, 1H), 3.76 – 3.64 (m, 2H), 3.09 – 2.99 (m, 1H), 2.84 (t, $J = 7.1$ Hz, 2H), 2.81 – 2.73 (m, 1H), 2.35 – 2.25 (m, 1H), 2.07 – 1.97 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.94, 142.75, 138.32, 131.39, 130.85, 128.42, 126.39, 125.06, 124.99, 120.04, 83.48, 69.21, 36.12, 32.42, 30.26. HRMS (ESI+) calculated for $\text{C}_{17}\text{H}_{17}\text{BrNaO}^+$ ($\text{M}+\text{Na}$) $^+$: 339.0355; found: 339.0355.

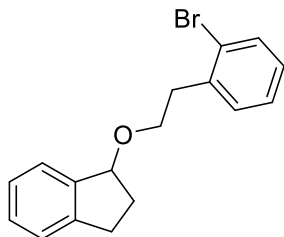


1-(4-Chlorophenoxy)-2,3-dihydro-1H-indene (3ac): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, $J = 7.2$ Hz, 1H), 7.27 – 7.17 (m, 5H), 7.15 (d, $J = 8.3$ Hz, 2H), 4.89 (dd, $J = 6.6, 4.4$ Hz, 1H), 3.80 – 3.64 (m, 2H), 3.04 (ddd, $J = 16.0, 8.4, 5.8$ Hz,

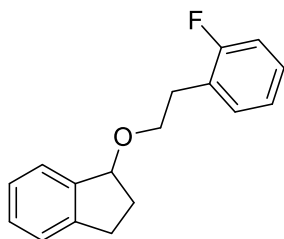
1H), 2.86 (t, $J = 7.0$ Hz, 2H), 2.78 (ddd, $J = 16.0, 8.5, 5.6$ Hz, 1H), 2.30 (ddt, $J = 12.8, 8.4, 6.2$ Hz, 1H), 2.07 – 1.97 (m, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 143.94, 142.77, 137.80, 131.96, 130.43, 128.44, 128.42, 126.39, 125.06, 124.98, 83.48, 69.30, 36.06, 32.42, 30.26. HRMS (ESI+) calculated for $\text{C}_{17}\text{H}_{17}\text{ClNaO}^+$ ($\text{M}+\text{Na}$) $^+$: 295.0860; found: 295.0863.



1-(2-Chlorophenoxy)-2,3-dihydro-1H-indene (3ad): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform- d) δ 7.36 – 7.29 (m, 2H), 7.29 – 7.08 (m, 6H), 4.91 (dd, $J = 6.7, 4.5$ Hz, 1H), 3.81 – 3.69 (m, 2H), 3.10 – 2.98 (m, 3H), 2.82 – 2.71 (m, 1H), 2.36 – 2.26 (m, 1H), 2.08 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 143.88, 142.87, 136.67, 134.21, 131.32, 129.45, 128.34, 127.77, 126.74, 126.38, 125.05, 124.92, 83.40, 67.62, 34.43, 32.46, 30.22. HRMS (EI+) calculated for $\text{C}_{17}\text{H}_{17}\text{ClO}$ (M^+): 272.0968; found: 272.0973.

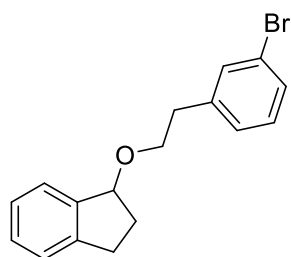


1-(2-Bromophenoxy)-2,3-dihydro-1H-indene (3ae): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform- d) δ 7.57 – 7.48 (m, 1H), 7.34 (d, $J = 7.1$ Hz, 1H), 7.29 – 7.16 (m, 5H), 7.05 (td, $J = 7.7, 1.8$ Hz, 1H), 4.93 (dd, $J = 6.7, 4.5$ Hz, 1H), 3.82 – 3.70 (m, 2H), 3.11 – 2.99 (m, 3H), 2.82 – 2.73 (m, 1H), 2.37 – 2.26 (m, 1H), 2.10 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 143.90, 142.88, 138.39, 132.80, 131.33, 128.37, 128.05, 127.41, 126.40, 125.08, 124.94, 124.75, 83.43, 67.71, 36.95, 32.48, 30.25. HRMS (ESI+) calculated for $\text{C}_{17}\text{H}_{17}\text{BrNaO}^+$ ($\text{M}+\text{Na}$) $^+$: 339.0355; found: 339.0354.

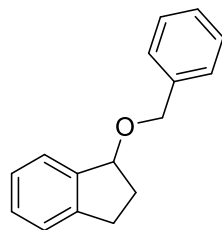


1-(2-Fluorophenoxy)-2,3-dihydro-1H-indene (3af): The synthesis procedure is the same as for

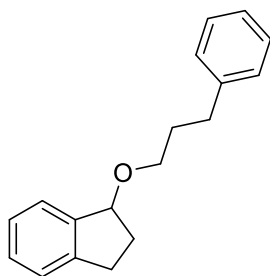
3a. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, $J = 6.4$ Hz, 1H), 7.28 – 7.11 (m, 5H), 7.02 (dt, $J = 18.0, 8.3$ Hz, 2H), 4.91 (s, 1H), 3.75 (qd, $J = 6.8, 2.5$ Hz, 2H), 3.04 (dt, $J = 14.0, 6.0$ Hz, 1H), 2.95 (t, $J = 6.1$ Hz, 2H), 2.77 (dt, $J = 14.4, 6.4$ Hz, 1H), 2.31 (dq, $J = 12.8, 6.2$ Hz, 1H), 2.09 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.36 (d, $J_{\text{CF}} = 245.8$ Hz), 143.91, 142.88, 131.48 (d, $J_{\text{CF}} = 4.8$ Hz), 128.35, 128.01 (d, $J_{\text{CF}} = 8.1$ Hz), 126.39, 125.97 (d, $J_{\text{CF}} = 15.9$ Hz), 125.00 (d, $J_{\text{CF}} = 13.6$ Hz), 123.97 (d, $J_{\text{CF}} = 3.6$ Hz), 115.23 (d, $J_{\text{CF}} = 22.3$ Hz), 83.41, 68.13, 32.46, 30.23, 29.99, 29.97. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -118.46. HRMS (ESI+) calculated for $\text{C}_{17}\text{H}_{17}\text{FNaO}^+$ ($\text{M}+\text{Na}$) $^+$: 279.1156; found: 279.1155.



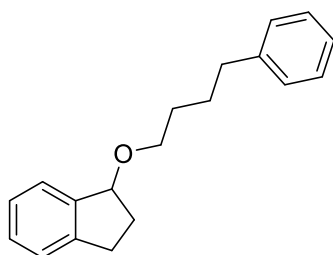
1-(3-Bromophenoxy)-2,3-dihydro-1H-indene (3ag): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.33 (dd, $J = 7.4, 3.3$ Hz, 2H), 7.25 – 7.11 (m, 5H), 4.89 (dd, $J = 6.6, 4.4$ Hz, 1H), 3.78 – 3.64 (m, 2H), 3.05 (ddd, $J = 14.5, 8.2, 5.9$ Hz, 1H), 2.85 (t, $J = 7.0$ Hz, 2H), 2.82 – 2.74 (m, 1H), 2.37 – 2.25 (m, 1H), 2.08 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.93, 142.73, 141.69, 132.10, 129.90, 129.33, 128.43, 127.77, 126.42, 125.09, 124.98, 122.39, 83.52, 69.12, 36.33, 32.39, 30.26. HRMS (ESI+) calculated for $\text{C}_{17}\text{H}_{17}\text{BrNaO}^+$ ($\text{M}+\text{Na}$) $^+$: 339.0355; found: 339.0352.



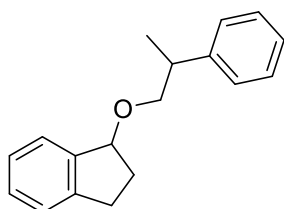
1-(Benzyloxy)-2,3-dihydro-1H-indene (3ah): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 3H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.30 – 7.16 (m, 4H), 5.01 (dd, $J = 6.6, 4.4$ Hz, 1H), 4.67 – 4.57 (m, 2H), 3.09 (ddd, $J = 14.9, 8.1, 6.0$ Hz, 1H), 2.86 – 2.74 (m, 1H), 2.34 (ddt, $J = 12.6, 8.4, 6.2$ Hz, 1H), 2.19 – 2.09 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.09, 142.91, 138.86, 128.46, 128.43, 127.81, 127.58, 126.39, 125.18, 124.98, 82.67, 70.56, 32.54, 30.31. HRMS (ESI+) calculated for $\text{C}_{16}\text{H}_{16}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 247.1093; found: 247.1095.



1-(3-Phenylpropoxy)-2,3-dihydro-1H-indene (3ai): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, J = 6.7 Hz, 1H), 7.29 – 7.13 (m, 8H), 4.88 (dd, J = 6.7, 4.5 Hz, 1H), 3.62 – 3.46 (m, 2H), 3.14 – 3.00 (m, 1H), 2.84 – 2.74 (m, 1H), 2.71 (t, J = 7.6 Hz, 2H), 2.32 (dddd, J = 12.4, 8.4, 6.7, 5.7 Hz, 1H), 2.05 (dddd, J = 13.1, 8.4, 5.7, 4.4 Hz, 1H), 1.96 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.91, 143.14, 142.14, 128.61, 128.39, 128.32, 126.38, 125.81, 125.11, 124.95, 83.31, 67.79, 32.58, 32.49, 31.71, 30.29. HRMS (ESI+) calculated for $\text{C}_{18}\text{H}_{20}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 275.1406; found: 275.1404.

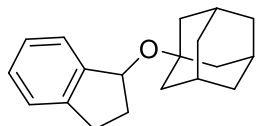


1-(4-Phenylbutoxy)-2,3-dihydro-1H-indene (3aj): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, J = 7.0 Hz, 1H), 7.34 – 7.08 (m, 8H), 4.89 (dd, J = 6.7, 4.4 Hz, 1H), 3.55 (td, J = 6.2, 2.9 Hz, 2H), 3.12 – 3.00 (m, 1H), 2.79 (ddd, J = 15.6, 8.3, 5.8 Hz, 1H), 2.62 (t, J = 7.3 Hz, 2H), 2.38 – 2.28 (m, 1H), 2.04 (ddt, J = 10.0, 8.5, 5.5 Hz, 1H), 1.76 – 1.60 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.95, 143.13, 142.66, 128.56, 128.38, 128.33, 126.39, 125.78, 125.13, 124.97, 83.29, 68.64, 35.89, 32.53, 30.30, 29.84, 28.33. HRMS (ESI+) calculated for $\text{C}_{19}\text{H}_{22}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 289.1563; found: 289.1562.

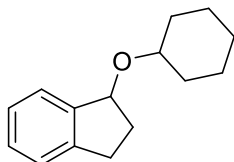


1-(2-Phenylpropoxy)-2,3-dihydro-1H-indene (3ak): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.14 (m, 9H), 4.89 (ddd, J = 11.1, 6.7, 4.8 Hz, 1H), 3.67

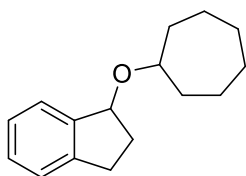
(ddd, $J = 14.9, 9.1, 5.9$ Hz, 1H), 3.54 (dt, $J = 14.2, 8.5$ Hz, 1H), 3.09 – 2.96 (m, 2H), 2.82 – 2.70 (m, 1H), 2.36 – 2.24 (m, 1H), 2.01 (dddd, $J = 19.1, 17.4, 8.6, 5.4$ Hz, 1H), 1.31 (dd, $J = 7.0, 2.7$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.68, 144.65, 143.82, 143.08, 143.05, 128.41, 128.40, 128.28, 127.53, 127.51, 126.39, 126.37, 125.09, 125.07, 124.90, 124.88, 83.54, 83.52, 74.65, 40.43, 40.29, 32.39, 32.36, 30.23, 18.57, 18.55. HRMS (ESI+) calculated for $\text{C}_{18}\text{H}_{20}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 275.1406; found: 275.1411.



(3s,5s,7s)-1-((2,3-Dihydro-1H-inden-1-yl)oxy)adamantane (3al): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.29 (m, 1H), 7.24 – 7.13 (m, 3H), 5.23 (t, $J = 7.1$ Hz, 1H), 2.99 (ddd, $J = 15.8, 9.1, 2.7$ Hz, 1H), 2.82 – 2.71 (m, 1H), 2.40 (dtd, $J = 12.9, 8.0, 3.0$ Hz, 1H), 2.20 (s, 3H), 1.98 – 1.81 (m, 7H), 1.67 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.02, 142.77, 127.65, 126.57, 124.79, 124.59, 74.00, 72.88, 43.06, 36.60, 36.44, 30.78, 30.12. HRMS (ESI+) calculated for $\text{C}_{19}\text{H}_{24}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 291.1719; found: 291.1721.

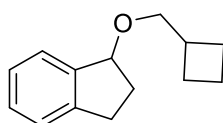


1-(Cyclohexyloxy)-2,3-dihydro-1H-indene (3am): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 1H), 7.26 – 7.16 (m, 3H), 5.03 (t, $J = 6.1$ Hz, 1H), 3.49 (tt, $J = 9.4, 3.8$ Hz, 1H), 3.03 (ddd, $J = 15.8, 8.6, 4.6$ Hz, 1H), 2.77 (dt, $J = 15.6, 7.6$ Hz, 1H), 2.38 (dddd, $J = 12.9, 8.3, 6.8, 4.6$ Hz, 1H), 1.98 (dddd, $J = 12.5, 8.7, 6.9, 5.4$ Hz, 3H), 1.77 (q, $J = 4.0, 3.3$ Hz, 2H), 1.60 – 1.51 (m, 1H), 1.43 – 1.18 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.03, 143.41, 128.00, 126.45, 124.81, 124.78, 80.67, 76.60, 33.87, 33.62, 32.77, 30.10, 25.94, 24.50, 24.46. HRMS (ESI+) calculated for $\text{C}_{15}\text{H}_{20}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 239.1406; found: 239.1414.



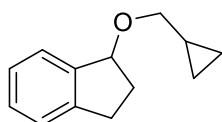
1-(Cycloheptyloxy)-2,3-dihydro-1H-indene (3an): The synthesis procedure is the same as for **3a**.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.32 (m, 1H), 7.24 – 7.13 (m, 3H), 4.97 (t, J = 6.1 Hz, 1H), 3.69 (tt, J = 8.2, 4.3 Hz, 1H), 3.03 (ddd, J = 15.8, 8.6, 4.6 Hz, 1H), 2.77 (dt, J = 15.6, 7.6 Hz, 1H), 2.38 (dddd, J = 12.8, 8.2, 6.7, 4.5 Hz, 1H), 2.03 – 1.90 (m, 3H), 1.76 – 1.62 (m, 4H), 1.61 – 1.51 (m, 4H), 1.41 (ddqd, J = 11.8, 5.9, 4.3, 2.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.12, 143.43, 128.01, 126.47, 124.82, 124.78, 81.00, 79.10, 35.33, 34.34, 33.75, 30.10, 28.56, 28.44, 23.19, 23.04. HRMS (ESI+) calculated for $\text{C}_{16}\text{H}_{22}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 253.1563; found: 253.1565.



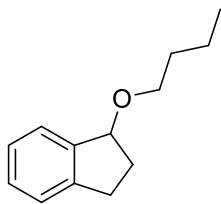
1-(4-Phenylbutoxy)-2,3-dihydro-1H-indene (3ao): The synthesis procedure is the same as for **3a**.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, J = 6.7 Hz, 1H), 7.29 – 7.16 (m, 3H), 4.91 (dd, J = 6.8, 4.6 Hz, 1H), 3.52 (d, J = 6.9 Hz, 2H), 3.05 (ddd, J = 16.0, 8.5, 5.4 Hz, 1H), 2.79 (ddd, J = 15.6, 8.4, 6.0 Hz, 1H), 2.59 (dq, J = 14.8, 7.4 Hz, 1H), 2.35 (dddd, J = 13.7, 8.4, 6.7, 5.5 Hz, 1H), 2.05 (dddd, J = 17.8, 8.7, 6.4, 3.9 Hz, 3H), 1.95 – 1.82 (m, 2H), 1.79 – 1.69 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.88, 143.21, 128.25, 126.37, 125.12, 124.90, 83.31, 73.44, 35.43, 32.46, 30.26, 25.32, 25.22, 18.75. HRMS (ESI+) calculated for $\text{C}_{14}\text{H}_{18}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 225.1250; found: 225.1247.

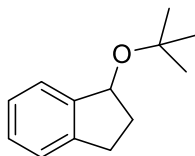


1-(Cyclopropylmethoxy)-2,3-dihydro-1H-indene (3ap): The synthesis procedure is the same as

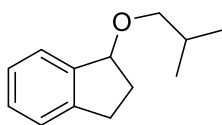
for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, J = 7.0 Hz, 1H), 7.32 – 7.11 (m, 3H), 4.94 (dd, J = 6.7, 4.5 Hz, 1H), 3.38 (qd, J = 10.0, 6.9 Hz, 2H), 3.07 (ddd, J = 14.8, 8.4, 5.7 Hz, 1H), 2.79 (ddd, J = 15.4, 8.3, 5.8 Hz, 1H), 2.33 (dq, J = 13.4, 6.2 Hz, 1H), 2.13 – 2.02 (m, 1H), 1.09 (tdt, J = 6.8, 5.2, 3.4 Hz, 1H), 0.65 – 0.43 (m, 2H), 0.22 (q, J = 4.9, 4.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.93, 143.03, 128.26, 126.32, 125.13, 124.88, 82.98, 73.46, 32.49, 30.26, 11.09, 3.32, 3.19. HRMS (ESI+) calculated for $\text{C}_{13}\text{H}_{16}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 211.1093; found: 211.1092.



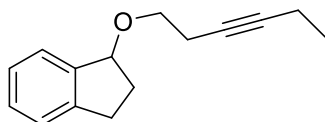
1-Butoxy-2,3-dihydro-1H-indene (3aq): ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, $J = 6.6$ Hz, 1H), 7.26 – 7.17 (m, 3H), 4.90 (dd, $J = 6.7, 4.5$ Hz, 1H), 3.59 – 3.49 (m, 2H), 3.06 (ddd, $J = 15.9, 8.5, 5.6$ Hz, 1H), 2.79 (ddd, $J = 15.8, 8.4, 5.8$ Hz, 1H), 2.34 (dddd, $J = 13.2, 8.5, 6.7, 5.6$ Hz, 1H), 2.05 (dddd, $J = 13.1, 8.5, 5.8, 4.5$ Hz, 1H), 1.65 – 1.55 (m, 2H), 1.45 – 1.35 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.89, 143.21, 128.26, 126.36, 125.10, 124.92, 83.23, 68.62, 32.53, 32.26, 30.27, 19.56, 14.08. HRMS (EI+) calculated for $\text{C}_{13}\text{H}_{18}\text{O}$ (M+): 190.1358; found: 190.1364.



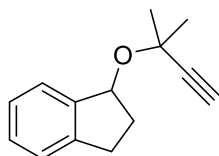
1-(Tert-butoxy)-2,3-dihydro-1H-indene (3ar): ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 1H), 7.23 – 7.16 (m, 3H), 5.07 (t, $J = 7.0$ Hz, 1H), 2.98 (ddd, $J = 15.8, 9.1, 2.9$ Hz, 1H), 2.76 (dt, $J = 16.1, 8.4$ Hz, 1H), 2.49 – 2.37 (m, 1H), 1.92 (dtd, $J = 12.9, 8.9, 6.9$ Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.95, 142.61, 127.67, 126.57, 124.65, 124.61, 75.98, 73.67, 36.28, 30.06, 28.93. HRMS (ESI+) calculated for $\text{C}_{13}\text{H}_{18}\text{NaO}^+$ (M+Na) $^+$: 213.1250; found: 213.1249.



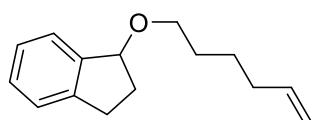
1-Isobutoxy-2,3-dihydro-1H-indene (3as): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, $J = 6.6$ Hz, 1H), 7.28 – 7.16 (m, 3H), 4.89 (dd, $J = 6.7, 4.8$ Hz, 1H), 3.37 – 3.23 (m, 2H), 3.05 (ddd, $J = 15.6, 8.5, 5.4$ Hz, 1H), 2.79 (ddd, $J = 15.5, 8.3, 6.1$ Hz, 1H), 2.40 – 2.28 (m, 1H), 2.10 – 1.99 (m, 1H), 1.88 (dp, $J = 13.4, 6.7$ Hz, 1H), 0.93 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.81, 143.32, 128.22, 126.36, 125.08, 124.90, 83.37, 75.83, 32.49, 30.24, 28.85, 19.67, 19.65. HRMS (EI+) calculated for $\text{C}_{13}\text{H}_{18}\text{O}$ (M+): 190.1358; found: 190.1362.



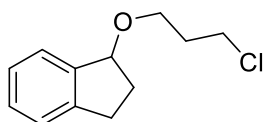
1-(Hex-3-yn-1-yloxy)-2,3-dihydro-1H-indene (3at): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, $J = 7.1$ Hz, 1H), 7.28 – 7.17 (m, 3H), 4.96 (dd, $J = 6.5$, 4.5 Hz, 1H), 3.62 (t, $J = 7.3$ Hz, 2H), 3.06 (ddd, $J = 14.6$, 8.3, 5.8 Hz, 1H), 2.81 (dd, $J = 8.5$, 5.8 Hz, 1H), 2.45 (tt, $J = 7.3$, 2.3 Hz, 2H), 2.39 – 2.28 (m, 1H), 2.16 (qq, $J = 7.7$, 2.6 Hz, 2H), 2.11 – 2.02 (m, 1H), 1.11 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.94, 142.72, 128.40, 126.40, 125.12, 124.93, 83.40, 82.85, 76.15, 67.40, 32.37, 30.23, 20.54, 14.30, 12.52. HRMS (ESI+) calculated for $\text{C}_{15}\text{H}_{18}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 237.1250; found: 237.1249.



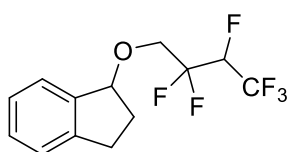
1-((2-Methylbut-3-yn-2-yl)oxy)-2,3-dihydro-1H-indene (3au): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 (td, $J = 4.4$, 2.1 Hz, 1H), 7.29 – 7.18 (m, 3H), 5.37 (t, $J = 6.8$ Hz, 1H), 3.01 (ddd, $J = 15.8$, 9.1, 3.4 Hz, 1H), 2.80 (dt, $J = 16.0$, 8.1 Hz, 1H), 2.61 – 2.38 (m, 2H), 2.07 – 1.95 (m, 1H), 1.60 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.27, 142.85, 127.98, 126.62, 125.06, 124.66, 87.55, 78.91, 71.95, 70.80, 35.26, 30.17, 30.14, 29.88. HRMS (EI+) calculated for $\text{C}_{14}\text{H}_{16}\text{O}$ (M^+): 200.1201; found: 200.1202.



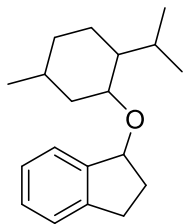
1-(Hex-5-en-1-yloxy)-2,3-dihydro-1H-indene (3av): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, $J = 6.8$ Hz, 1H), 7.29 – 7.16 (m, 3H), 5.81 (ddt, $J = 16.9$, 10.2, 6.7 Hz, 1H), 5.08 – 4.83 (m, 3H), 3.54 (tt, $J = 5.9$, 3.0 Hz, 2H), 3.05 (dd, $J = 8.5$, 5.9 Hz, 1H), 2.80 (ddd, $J = 15.5$, 8.2, 5.9 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.07 (q, $J = 7.3$ Hz, 3H), 1.62 (dt, $J = 14.7$, 6.5 Hz, 2H), 1.53 – 1.43 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.94, 143.18, 138.97, 128.32, 126.39, 125.12, 124.96, 114.60, 83.27, 68.67, 33.73, 32.54, 30.29, 29.66, 25.71. HRMS (ESI+) calculated for $\text{C}_{15}\text{H}_{20}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 239.1406; found: 239.1406.



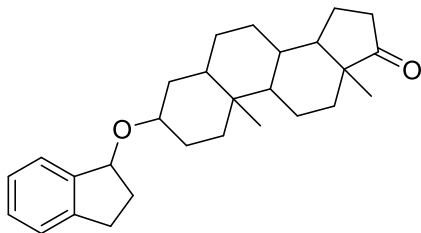
1-(3-Chloropropoxy)-2,3-dihydro-1H-indene (3aw): ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, $J = 7.0$ Hz, 1H), 7.30 – 7.15 (m, 3H), 4.91 (dd, $J = 6.7, 4.3$ Hz, 1H), 3.67 (dt, $J = 12.6, 6.1$ Hz, 4H), 3.12 – 2.99 (m, 1H), 2.86 – 2.74 (m, 1H), 2.34 (ddd, $J = 20.9, 8.5, 6.3$ Hz, 1H), 2.10 – 1.97 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.89, 142.82, 128.43, 126.42, 125.04, 124.97, 83.50, 64.95, 42.21, 33.04, 32.36, 30.24. HRMS (ESI+) calculated for $\text{C}_{12}\text{H}_{15}\text{ClNaO}^+$ ($\text{M}+\text{Na}$) $^+$: 233.0704; found: 233.0703.



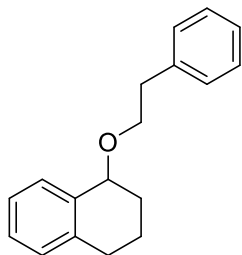
1-(2,2,3,4,4,4-Hexafluorobutoxy)-2,3-dihydro-1H-indene (3ax): HRMS (EI+) calculated for $\text{C}_{13}\text{H}_{12}\text{F}_6\text{O}$ (M^+): 298.0792; found: 298.0789. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, $J = 7.3$ Hz, 1H), 7.33 – 7.19 (m, 3H), 5.34 – 4.81 (m, 2H), 4.03 – 3.72 (m, 2H), 3.01-3.16 (m, 1H), 2.91-2.77 (m, 1H), 2.30-2.43 (m, 1H), 2.05-2.17 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.31, 144.27, 141.18, 141.17, 129.17, 126.72, 126.70, 125.26, 125.22, 125.19, 122.55, 122.29, 119.92, 119.89, 119.74, 119.69, 119.64(2), 119.63(5), 119.49, 117.44, 117.39, 117.19, 117.16, 116.94, 116.68, 114.95, 114.91, 114.71, 114.66, 85.21, 85.07, 85.06, 84.89, 84.82, 84.61, 84.52, 84.27, 84.17, 83.92, 83.82, 83.57, 83.28, 83.03, 82.93, 82.68, 82.59, 82.34, 82.24, 81.99, 81.89, 81.65, 66.56, 66.45, 66.30, 66.21, 66.11, 65.96, 65.86, 31.98, 31.87, 30.23, 30.22. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -73.95, -73.97, -73.98, -73.99, -74.00, -74.01, -74.02, -74.03, -74.05, -116.70, -116.72, -116.73, -116.75, -116.76, -116.77, -116.79, -116.80, -116.99, -117.00, -117.01, -117.03, -117.04, -117.06, -117.07, -117.09, -120.65, -120.67, -120.68, -120.70, -120.71, -120.72, -120.73, -120.75, -120.76, -120.78, -121.38, -121.40, -121.41, -121.43, -121.44, -121.45, -121.46, -121.47, -121.49, -121.51, -214.41, -214.43, -214.44, -214.45, -214.46, -214.47, -214.48, -214.49, -214.51, -214.52, -214.54, -214.55, -214.56, -214.57, -214.59.



1-((2-Isopropyl-5-methylcyclohexyl)oxy)-2,3-dihydro-1H-indene (3ay): ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 (q, $J = 4.3, 3.4$ Hz, 1H), 7.20 (d, $J = 1.5$ Hz, 3H), 4.97 (dt, $J = 24.6, 6.0$ Hz, 1H), 3.28 (dtd, $J = 18.9, 10.5, 4.2$ Hz, 1H), 3.08 – 2.97 (m, 1H), 2.76 (dtd, $J = 15.5, 7.7, 3.6$ Hz, 1H), 2.44 – 2.17 (m, 3H), 2.09 – 1.93 (m, 1H), 1.64 (dddq, $J = 15.6, 9.2, 6.1, 2.9$ Hz, 2H), 1.40 (dtp, $J = 15.3, 9.5, 3.2$ Hz, 1H), 1.25 (dddt, $J = 12.7, 10.0, 6.3, 3.1$ Hz, 1H), 1.05 – 0.84 (m, 9H), 0.75 (dd, $J = 38.8, 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.21, 143.93, 143.46, 143.41, 128.07, 127.99, 126.57, 126.29, 124.95, 124.89, 124.85, 124.76, 82.53, 80.97, 79.20, 78.11, 48.76, 48.24, 42.48, 41.61, 35.45, 34.65, 34.59, 33.39, 31.78, 30.31, 30.00, 25.33, 25.03, 23.13, 23.10, 22.60, 22.58, 21.33, 21.24, 15.94, 15.90. HRMS (ESI+) calculated for $\text{C}_{19}\text{H}_{28}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 295.2032; found: 295.2030.

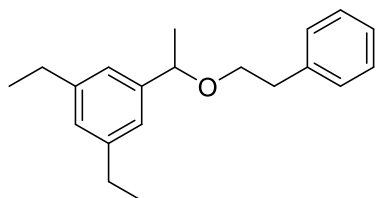


3-((2,3-dihydro-1H-inden-1-yl)oxy)-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (3az): ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 1H), 7.25 – 7.13 (m, 3H), 5.04 (ddd, $J = 7.5, 5.4, 2.9$ Hz, 1H), 3.49 (tdd, $J = 11.2, 5.6, 2.3$ Hz, 1H), 3.04 (ddd, $J = 15.8, 8.6, 4.8$ Hz, 1H), 2.77 (dt, $J = 15.5, 7.4$ Hz, 1H), 2.50 – 2.32 (m, 2H), 2.12 – 1.88 (m, 4H), 1.83 – 1.63 (m, 5H), 1.61 – 1.42 (m, 3H), 1.40 – 1.23 (m, 7H), 1.06 – 0.93 (m, 2H), 0.85 (d, $J = 6.1$ Hz, 6H), 0.70 (td, $J = 11.6, 3.8$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 221.49, 143.86, 143.83, 143.48, 143.44, 128.06, 126.44, 124.80, 80.96, 80.84, 77.57, 77.45, 54.59, 51.51, 47.89, 45.14, 45.08, 37.20, 37.15, 36.11, 36.02, 36.01, 35.93, 35.36, 35.12, 33.97, 33.86, 31.64, 31.03, 30.10, 29.79, 29.40, 28.77, 28.64, 28.61, 21.86, 20.57, 13.90, 12.39. HRMS (ESI+) calculated for $\text{C}_{28}\text{H}_{38}\text{NaO}_2^+$ ($\text{M}+\text{Na}$) $^+$: 429.2764; found: 429.2771.

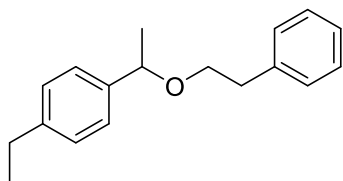


1-Phenethoxy-1,2,3,4-tetrahydronaphthalene (3ba): The synthesis procedure is the same as for **3a**.

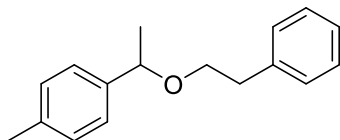
^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.36 – 7.02 (m, 9H), 4.37 (t, $J = 4.2$ Hz, 1H), 3.79 (dt, $J = 9.3, 7.0$ Hz, 1H), 3.66 (dt, $J = 9.3, 6.9$ Hz, 1H), 2.83 (t, $J = 6.9$ Hz, 2H), 2.76 – 2.58 (m, 2H), 1.81 (dd, $J = 9.3, 2.9$ Hz, 3H), 1.62 (ddt, $J = 11.7, 9.5, 6.4$ Hz, 1H). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) δ 139.23, 136.97, 136.87, 129.12, 128.88, 128.60, 128.17, 127.21, 126.00, 125.36, 74.63, 68.82, 36.08, 28.49, 27.66, 18.45. HRMS (ESI+) calculated for $\text{C}_{18}\text{H}_{20}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 275.1406; found: 275.1402.



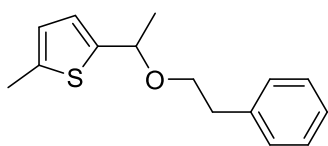
1,3-Diethyl-5-(1-phenethoxyethyl)benzene (3ca): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.26 – 7.20 (m, 2H), 7.17 (d, $J = 7.2$ Hz, 3H), 6.90 (d, $J = 7.0$ Hz, 3H), 4.35 (q, $J = 6.4$ Hz, 1H), 3.58 – 3.44 (m, 2H), 2.87 (td, $J = 7.3, 6.8, 2.9$ Hz, 2H), 2.59 (q, $J = 7.6$ Hz, 4H), 1.42 (d, $J = 6.5$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (101 MHz, $\text{Chloroform-}d$) δ 144.32, 144.04, 139.24, 129.04, 128.28, 126.58, 126.14, 123.01, 78.31, 69.62, 36.70, 28.92, 24.34, 15.71. HRMS (ESI+) calculated for $\text{C}_{20}\text{H}_{26}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 305.1876; found: 305.1875.



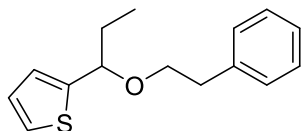
1-Ethyl-4-(1-phenethoxyethyl)benzene (3da): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.29 – 7.07 (m, 9H), 4.36 (q, $J = 6.5$ Hz, 1H), 3.60 – 3.39 (m, 2H), 2.98 – 2.75 (m, $J = 7.0$ Hz, 2H), 2.61 (q, $J = 7.6$ Hz, 2H), 1.41 (d, $J = 6.5$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (101 MHz, $\text{Chloroform-}d$) δ 143.33, 141.17, 139.11, 129.01, 128.30, 127.92, 126.20, 126.15, 78.01, 69.60, 36.67, 28.62, 24.24, 15.65. HRMS (ESI+) calculated for $\text{C}_{18}\text{H}_{22}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 277.1563; found: 277.1564.



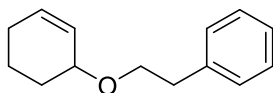
1-Methyl-4-(1-phenethoxyethyl)benzene (3ea): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.10 (m, 9H), 4.37 (q, $J = 6.5$ Hz, 1H), 3.57 – 3.42 (m, 2H), 2.95 – 2.79 (m, $J = 7.1$ Hz, 2H), 2.33 (s, 3H), 1.41 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.97, 139.15, 137.08, 129.18, 129.06, 128.35, 126.21, 126.20, 78.03, 69.62, 36.68, 24.29, 21.25. HRMS (ESI+) calculated for $\text{C}_{17}\text{H}_{20}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 263.1406; found: 263.1399.



2-methyl-5-(1-phenethoxyethyl)thiophene (3fa): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 2H), 7.19 (dt, $J = 5.9, 1.5$ Hz, 3H), 6.68 (d, $J = 3.4$ Hz, 1H), 6.56 (dq, $J = 3.5, 1.2$ Hz, 1H), 4.58 (q, $J = 6.4$ Hz, 1H), 3.61 (ddd, $J = 9.4, 8.4, 6.4$ Hz, 1H), 3.52 (ddd, $J = 9.3, 8.4, 6.4$ Hz, 1H), 2.94 – 2.80 (m, 2H), 2.45 (s, 3H), 1.51 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.36, 139.34, 139.09, 129.09, 128.40, 126.25, 124.46, 124.39, 73.79, 69.43, 36.58, 24.11, 15.59. HRMS (ESI+) calculated for $\text{C}_{15}\text{H}_{18}\text{NaOS}^+$ ($\text{M}+\text{Na}$) $^+$: 269.0971; found: 269.0974.

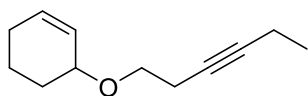


2-(1-Phenethoxypropyl)thiophene (3ga): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, DMSO-*d*₆) δ 7.46 (dd, $J = 4.9, 1.4$ Hz, 1H), 7.28 – 7.22 (m, 2H), 7.22 – 7.12 (m, 3H), 7.05 – 6.92 (m, 2H), 4.47 (t, $J = 6.7$ Hz, 1H), 3.55 – 3.42 (m, 2H), 2.78 (hept, $J = 6.9$ Hz, 2H), 1.78 (dq, $J = 14.4, 7.2$ Hz, 1H), 1.69 – 1.57 (m, 1H), 0.79 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO-*d*₆) δ 146.22, 138.96, 128.80, 128.16, 126.47, 126.02, 125.45, 125.24, 78.12, 68.88, 35.63, 30.86, 10.06. HRMS (ESI+) calculated for $\text{C}_{15}\text{H}_{18}\text{NaOS}^+$ ($\text{M}+\text{Na}$) $^+$: 269.0971; found: 269.0974.

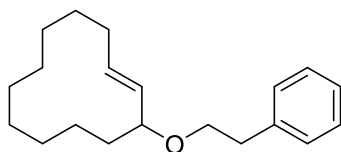


2-(Cyclohex-2-en-1-yloxy)ethylbenzene (3ha): The synthesis procedure is the same as for **3a**. ^1H

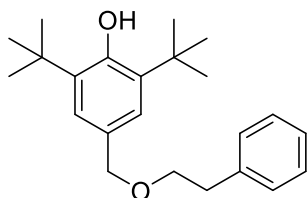
NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.16 (m, 5H), 5.94 – 5.69 (m, 2H), 3.84 (dq, $J = 4.7, 1.6$ Hz, 1H), 3.75 – 3.61 (m, 2H), 2.89 (t, $J = 7.5$ Hz, 2H), 2.08 – 1.88 (m, 2H), 1.84 – 1.61 (m, 3H), 1.56 – 1.47 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.13, 130.89, 129.00, 128.35, 127.87, 126.18, 73.04, 69.40, 36.94, 28.37, 25.30, 19.30. HRMS (ESI+) calculated for $\text{C}_{14}\text{H}_{18}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 225.1250; found: 225.1251.



3-(Hex-3-yn-1-yloxy)cyclohex-1-ene (3ia): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 5.90 – 5.61 (m, 2H), 3.89 (dp, $J = 6.2, 2.4, 1.9$ Hz, 1H), 3.64 – 3.51 (m, 2H), 2.42 (tt, $J = 7.4, 2.4$ Hz, 2H), 2.15 (qt, $J = 7.5, 2.4$ Hz, 2H), 2.09 – 1.89 (m, 2H), 1.84 – 1.66 (m, 3H), 1.55 (dddd, $J = 11.4, 4.6, 3.8, 2.0$ Hz, 1H), 1.11 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.06, 127.81, 82.81, 76.17, 73.06, 67.08, 28.34, 25.30, 20.71, 19.29, 14.32, 12.53. HRMS (ESI+) calculated for $\text{C}_{12}\text{H}_{18}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 201.1250; found: 201.1246.

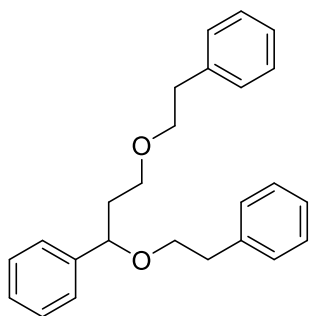


(E)-3-Phenethoxycyclododec-1-ene (3ja): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.02 (m, 5H), 5.55 (ddd, $J = 15.0, 10.1, 4.6$ Hz, 1H), 5.26 (dd, $J = 15.4, 8.6$ Hz, 1H), 3.78 – 3.53 (m, 2H), 3.45 (td, $J = 8.9, 6.7$ Hz, 1H), 2.98 – 2.69 (m, 2H), 2.29 – 2.13 (m, 1H), 2.00 (dtd, $J = 13.7, 10.2, 3.4$ Hz, 1H), 1.79 (tt, $J = 9.4, 4.2$ Hz, 1H), 1.57 – 1.09 (m, 15H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.30, 134.65, 131.98, 129.08, 128.38, 126.19, 81.97, 69.14, 36.69, 33.10, 31.82, 26.10, 25.68, 25.14, 25.11, 24.55, 22.63. HRMS (ESI+) calculated for $\text{C}_{20}\text{H}_{30}\text{NaO}^+$ ($\text{M}+\text{Na}$) $^+$: 309.2189; found: 309.2191.



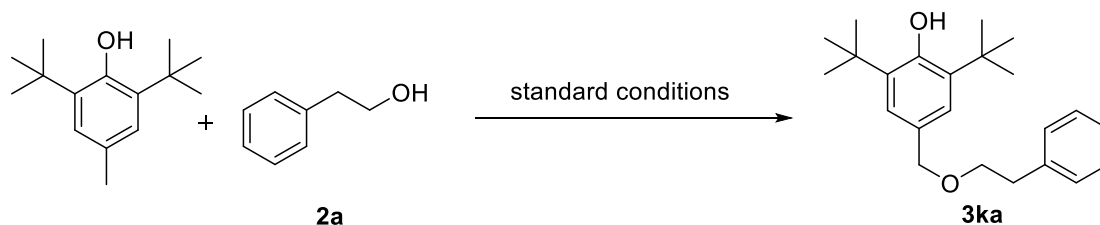
2,6-Di-tert-butyl-4-(phenethoxymethyl)phenol (3ka): The synthesis procedure is the same as for **3a**. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.19 (m, 5H), 7.12 (s, 2H), 5.18 (s, 1H), 4.42 (s, 2H), 3.71 (t, $J = 7.2$ Hz, 2H), 2.94 (t, $J = 7.2$ Hz, 2H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.52, 139.22, 135.83, 129.07, 128.91, 128.43, 126.25, 125.10, 73.77, 71.32, 36.49, 34.39,

30.37. HRMS (ESI+) calculated for $C_{23}H_{32}NaO_2^+$ ($M+Na$) $^+$: 363.2295; found: 363.2287.

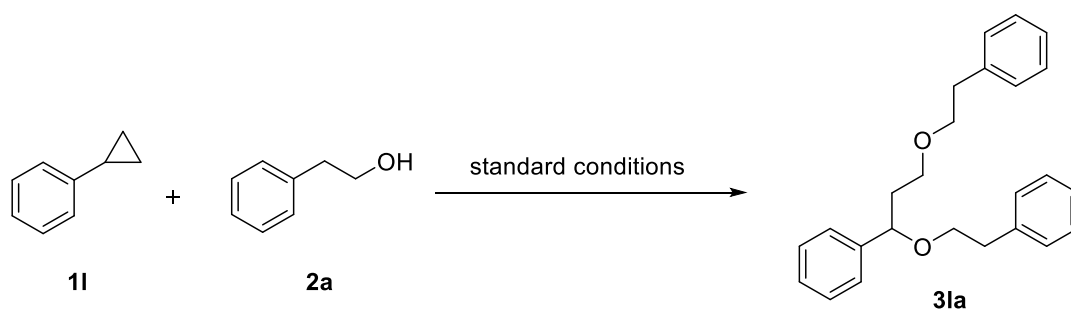


(((1-Phenylpropane-1,3-diyl)bis(oxy))bis(ethane-2,1-diyl)dibenzene (3a): The synthesis procedure is the same as for **3a**. 1H NMR (400 MHz, Chloroform-*d*) δ 7.23 (dddd, $J = 23.4, 21.1, 10.3, 4.7$ Hz, 15H), 4.34 (dd, $J = 8.3, 5.4$ Hz, 1H), 3.62 – 3.45 (m, 4H), 3.42 – 3.28 (m, 2H), 2.84 (dt, $J = 16.7, 7.0$ Hz, 4H), 2.03 (ddt, $J = 11.6, 8.7, 5.7$ Hz, 1H), 1.82 (ddd, $J = 13.6, 7.6, 5.5$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.58, 139.34, 139.24, 129.09, 129.05, 128.42, 128.40, 128.30, 127.48, 126.67, 126.26, 126.16, 79.00, 71.86, 69.73, 67.23, 38.49, 36.51, 36.48. HRMS (ESI+) calculated for $C_{25}H_{28}NaO_2^+$ ($M+Na$) $^+$: 383.1982; found: 383.1981.

3) Control experiments



Typical procedure for radical trapping experiments: A mixture of phenethyl alcohol (**2a**, 3 equiv.), BHT (0.5 mmol), CS_2CO_3 (2 equiv.), tBu_4NClO_4 (0.5 equiv.), DCE/ Et_2O (6 mL/ 0.5 mL), in an undivided cell with carbon rod electrode anode, nickel cathode, constant current = 10 mA, r.t., 3.5 h. Then, the system was concentrated under reduced pressure. The resulting crude product was separated on a silica gel column with hexane and ethyl acetate as eluent to afford the desired product.



Typical procedure for radical trapping experiments: A mixture of phenethyl alcohol (**2a**, 3 equiv.), cyclopropylbenzene (0.5 mmol), Cs_2CO_3 (2 equiv.), ${}^n\text{Bu}_4\text{NClO}_4$ (0.5 equiv.), DCE/ Et_2O (6 mL/ 0.5 mL), in an undivided cell with carbon electrode anode, nickel cathode, constant current = 10 mA, r.t., 3.5 h. Then, the system was concentrated under reduced pressure. The resulting crude product was separated on a silica gel column with hexane and ethyl acetate as eluent to afford the desired product.

3) EPR experiments

EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.4158 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3359.8 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^5 ; microwave power: 19.05 mW.

3.1 1a under the standard conditions: A mixture of indan (**1a**, 0.5 mmol), Cs_2CO_3 (2 equiv.), ${}^n\text{Bu}_4\text{NClO}_4$ (0.5 equiv.) in degassed dry CH_3CN (6 mL) was in an undivided cell with carbon electrode anode, nickel cathode, constant current = 10 mA, r.t., stirred under an argon atmosphere for 30 min. Afterwards, DMPO (40 μL) was added to the system to stir under electrolysis for 1 min. Finally, 20 μL of the mixture was quickly taken out into a small tube and analyzed by EPR.

3.2 2a under the standard conditions: A mixture of phenethyl alcohol (**1a**, 0.5 mmol), Cs_2CO_3 (2 equiv.), ${}^n\text{Bu}_4\text{NClO}_4$ (0.5 equiv.) in degassed dry CH_3CN (6 mL) was in an undivided cell with carbon electrode anode, nickel cathode, constant current = 10 mA, r.t., stirred under an argon atmosphere for 30 min. Afterwards, DMPO (40 μL) was added to the system to stir under electrolysis for 1 min. Finally, 20 μL of the mixture was quickly taken out into a small tube and

analyzed by EPR.

4) Cyclic voltammograms

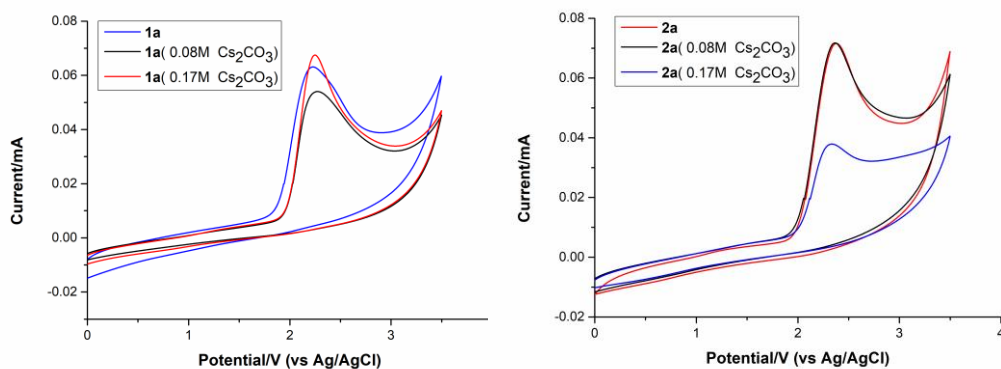
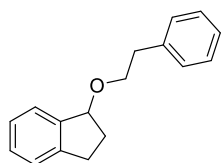
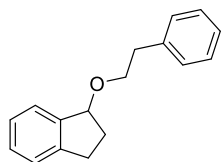
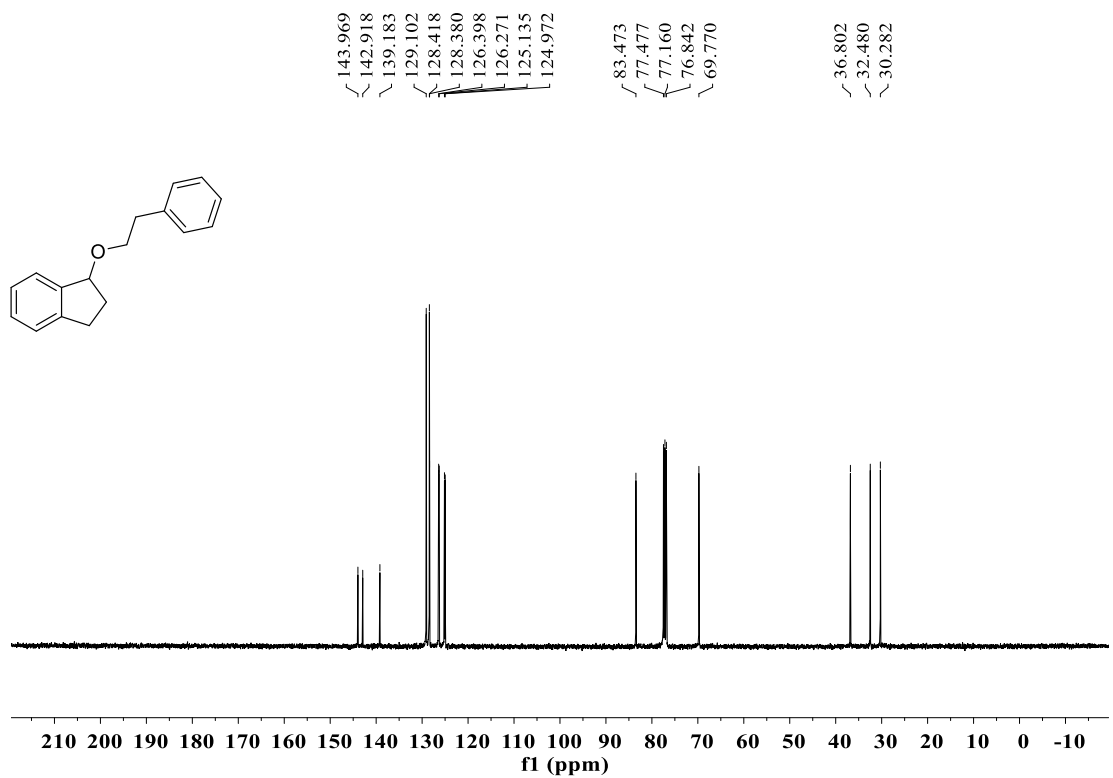
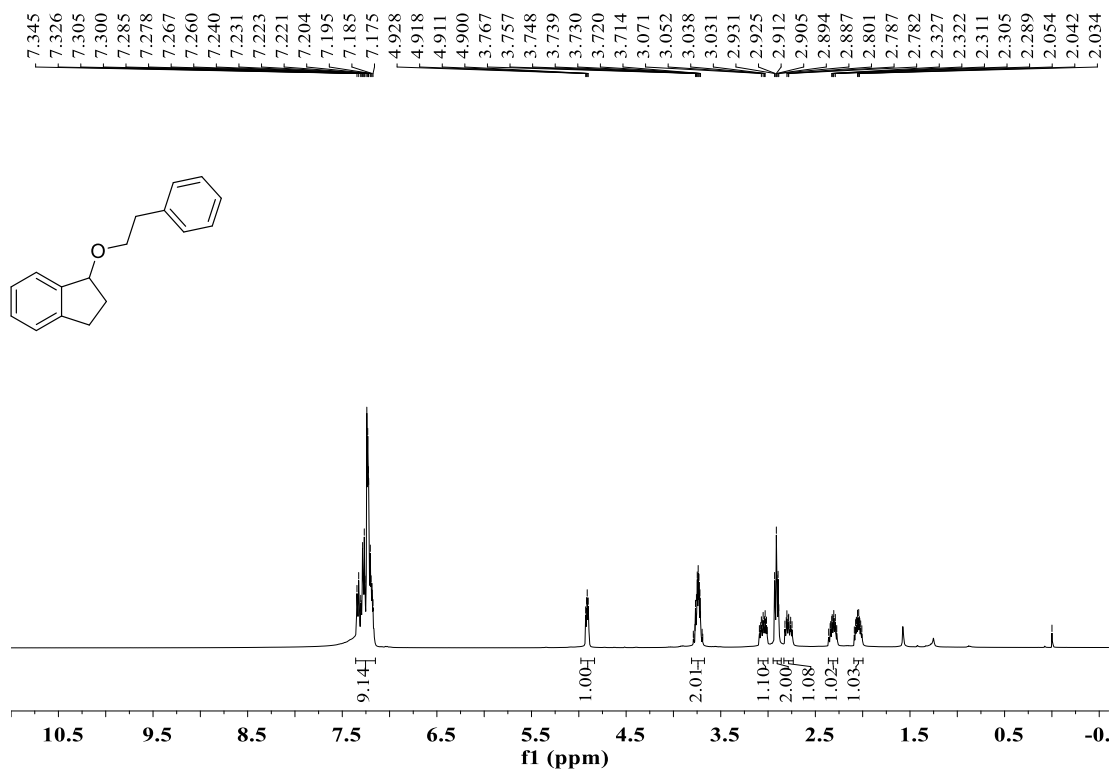
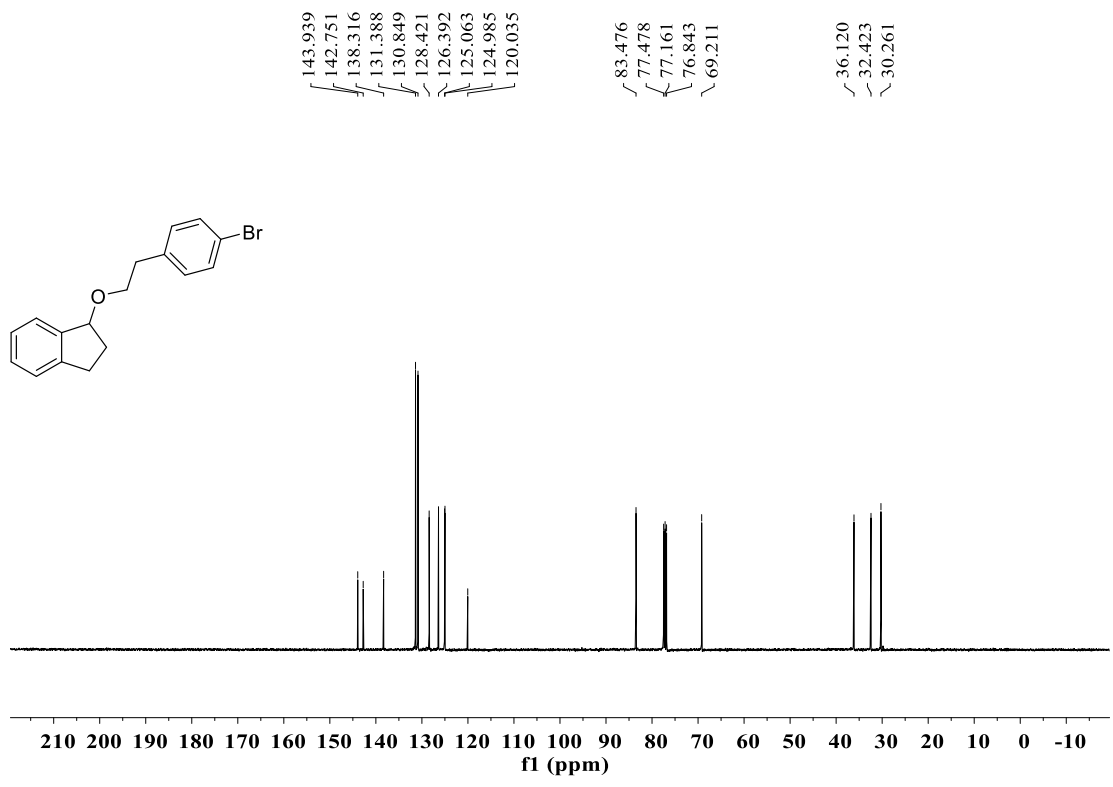
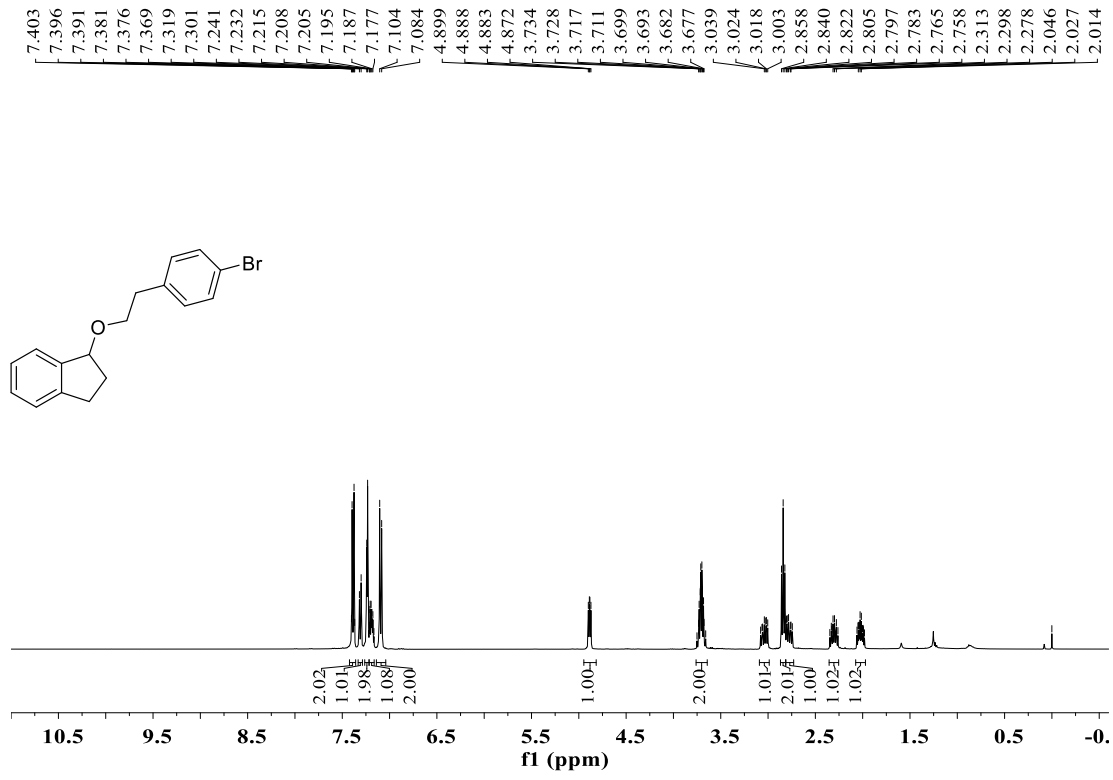
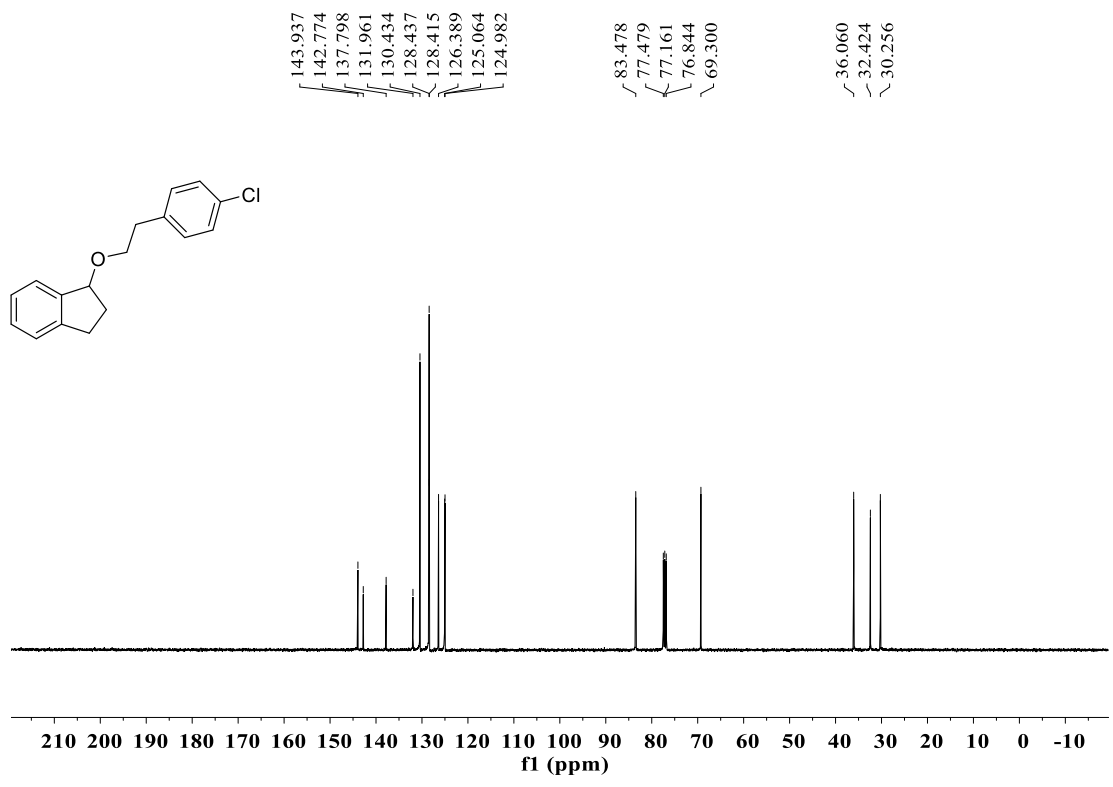
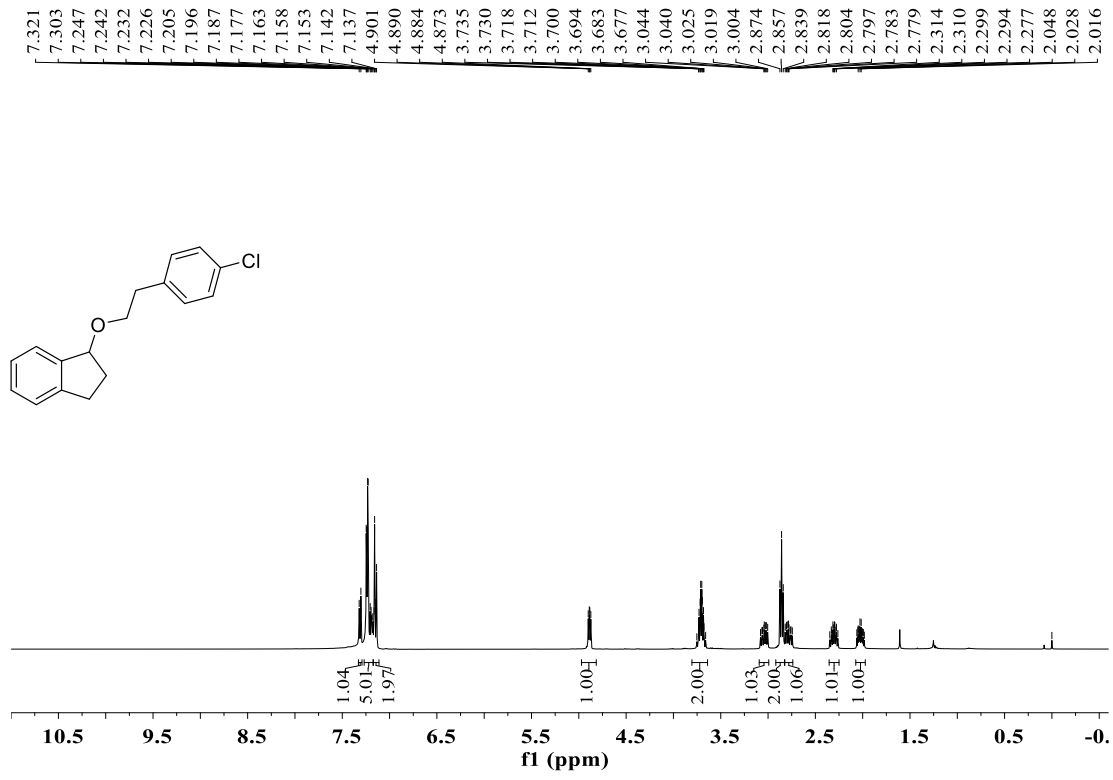


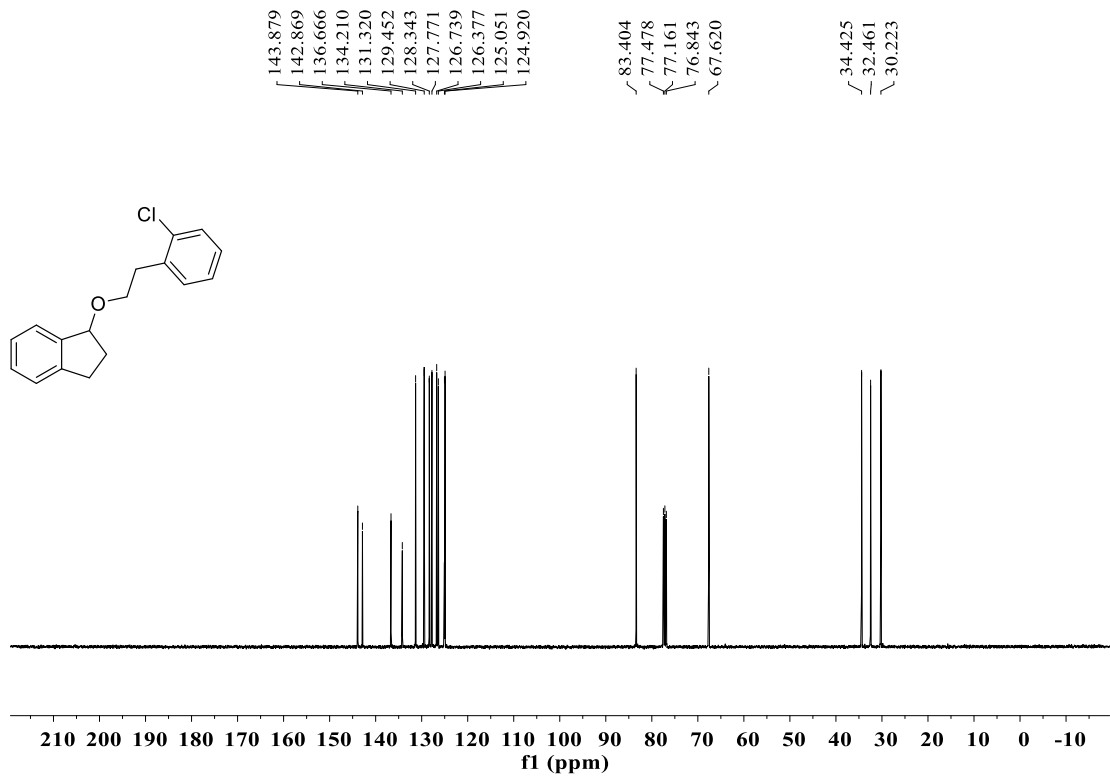
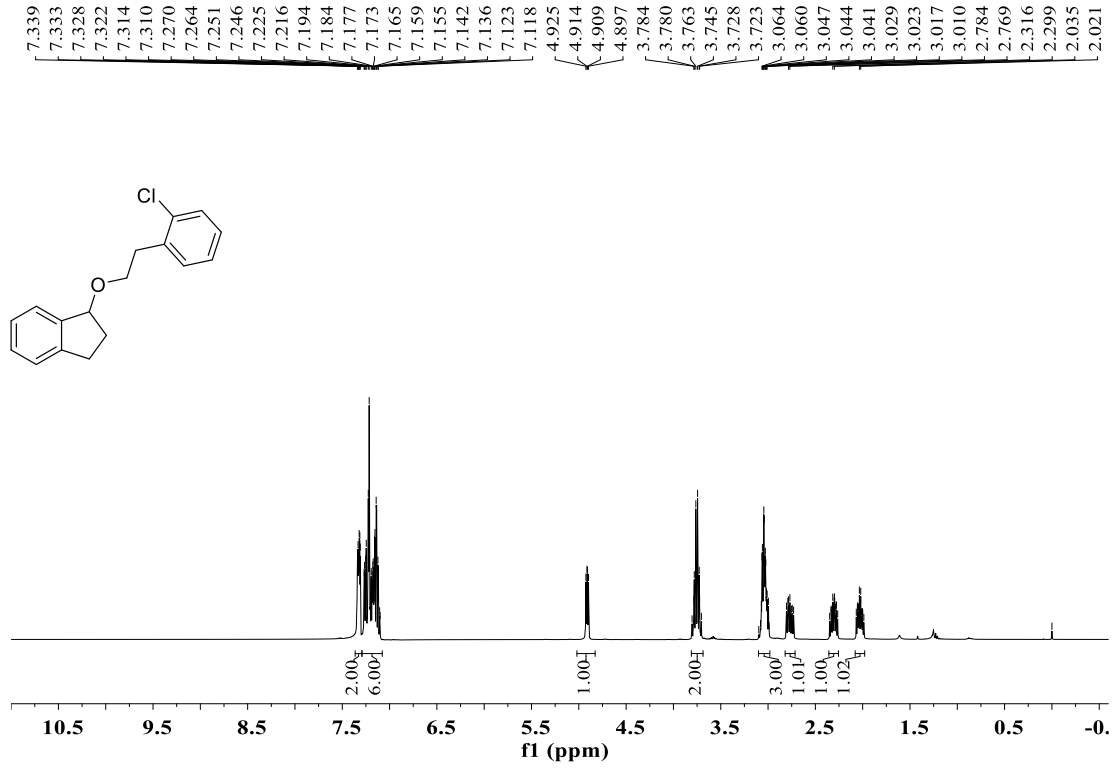
Figure S2. Cyclic voltammograms. Cyclic voltammetry of either 0.01 M **1a** or 0.01 M **2a** in 0.24 M ⁿBu₄NClO₄ in DCE (1,2-dichloroethane), with or without Cs₂CO₃ (0.08 M and 0.17 M, respectively), using glass carbon working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrode at 50 mV/s scan rate. An oxidation peak of **1a** in DCE was observed at 2.22 V (vs Ag|AgCl). An oxidation peak of **2a** in DCE was observed at 2.38 V (vs Ag|AgCl).

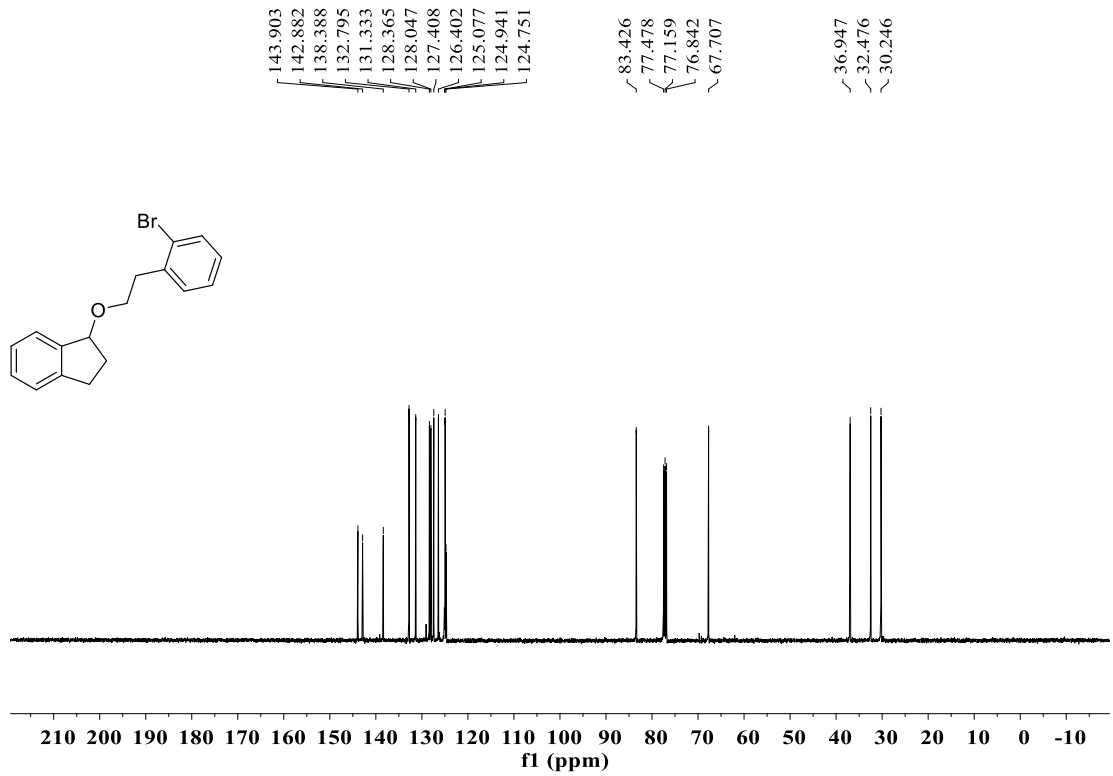
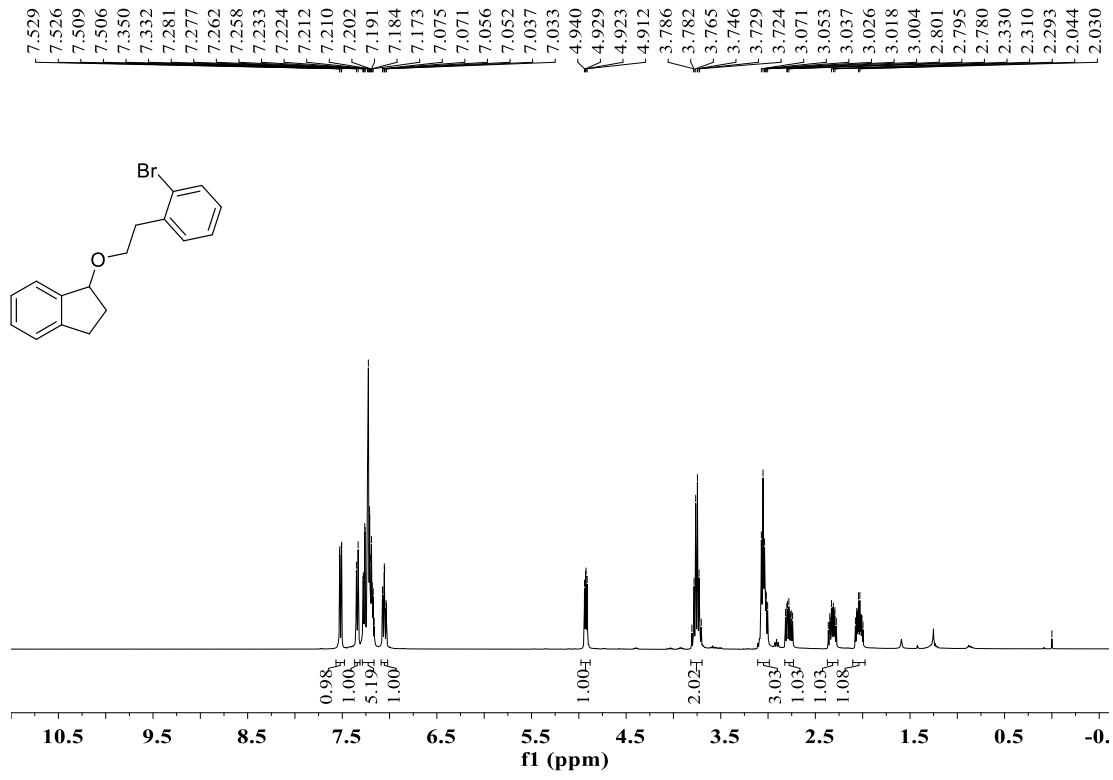
NMR Spectra of Products

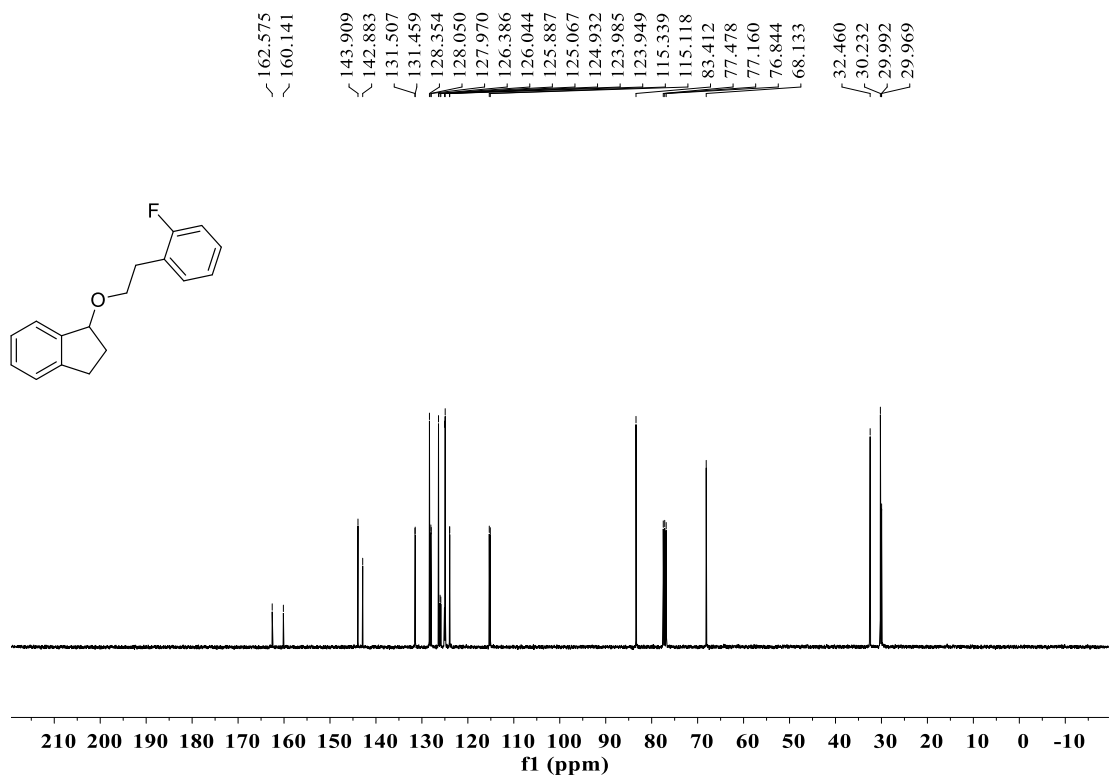
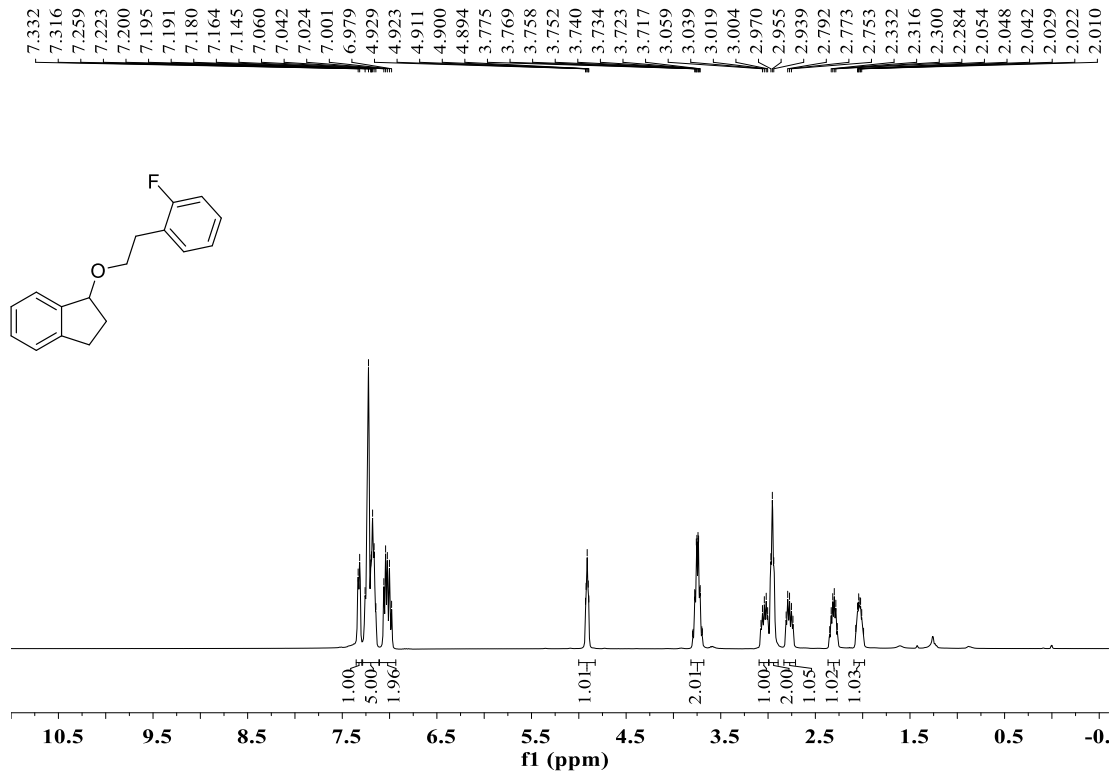


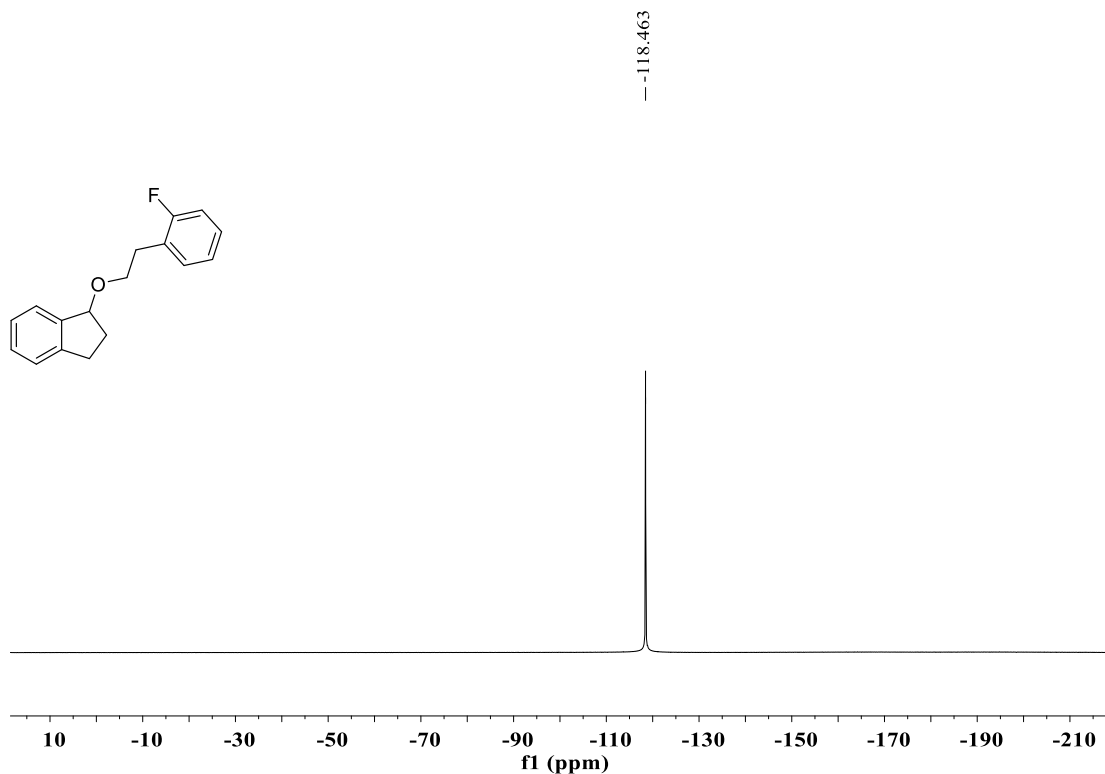
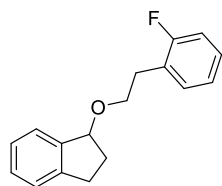




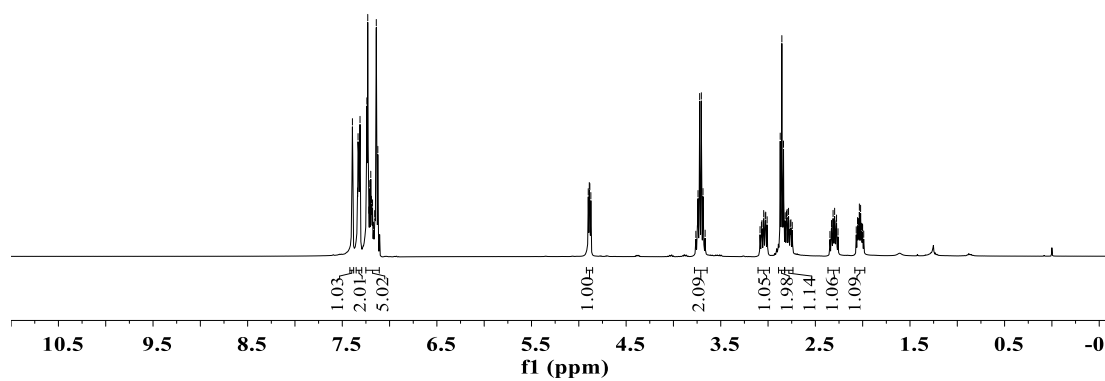
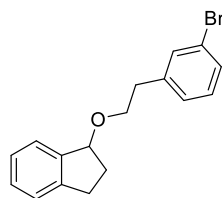








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