Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Polyenolate-mediated reaction cascade initiated by the higher-order-cycloaddition for the construction of polycarbocyclic scaffold

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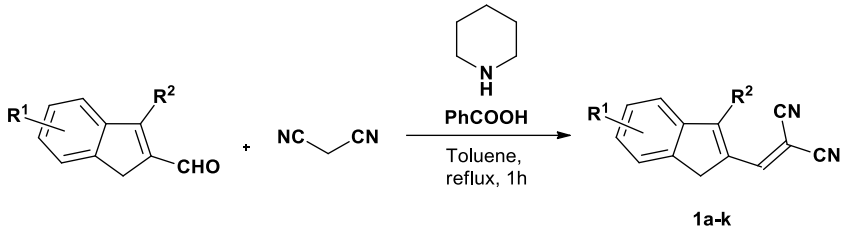
Contents

1. General methods

NMR spectra were acquired on a Bruker Ultra Shield 700 instrument, running at 700 MHz for ^{1}H and 176 MHz for ^{13}C, respectively or on a Jeol 400YH instrument, running at 376 MHz for ^{19}F. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). Chemical shifts (δ) for ^{19}F NMR are reported in ppm relative to $C_6H_5CF_3$ (trifluorotoluene) as external reference. High-resolution mass spectra (HRMS) were obtained on Bruker ESI-Q-TOF Impact II spectrometer using electrospray (ESI+) ionization. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or Hanessian's stain. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Fluka). The enantiomeric ratio (er) of the products were determined by Ultra Performance Convergence Chromatography (UPC[2]) using Daicel Chiralpak IA,IB,IC,IG columns as chiral stationary phases. Indene-2-carbaldehydes used for the synthesis of the corresponding malononitriles **1** were synthesized according to the literature procedure[1]. Aldehydes **2** were prepared from the corresponding starting materials following the literature procedure.[2]

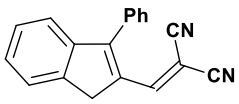
[1] B. S. Donslund, N. I. Jessen, G. Bertuzzi, M. Giardinetti, T. A. Palazzo, M. Louise Christensen, K. A. Jørgensen, *Angew. Chem., Int. Ed*. 2018, **57**, 13182–13186.
[2] N. Daubresse, C. Francesch, C. Rolando, *Tetrahedron* 1998, **54**, 10761-10770.

2. Synthesis of 2-((1*H*-inden-2-yl)methylene)malononitriles 1 - general procedure



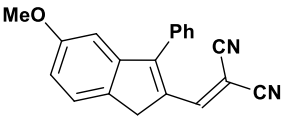
In a flame-dried round-bottom flask equipped with a magnetic stirring bar the corresponding indene-2-carbaldehyde (3 mmol, 1.0 equiv.), malononitrile (3.6 mmol, 1.2 equiv.) and benzoic acid (0.6 mmol, 0.2 equiv.) were dissolved in toluene (18 ml, 0.16 M) and piperidine (0.6 mmol. 0.2 equiv.) was added. The reaction mixture was refluxed for 1 hour. After full conversion of the starting indene-2-carbaldehyde (as confirmed by TLC analysis), mixture was cooled to rt and diluted with Et_2O (20 mL) and washed with water (2×15 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting solid was subjected to column chromatography on silica gel (eluent: petroleum ether: dichloromethane 40:60) to afford pure product **1**.

2-((3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1a



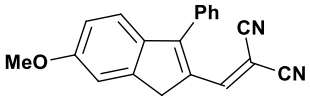
Following the general procedure product **1a** was isolated in 82% yield (660.2 mg) as light-orange solid; mp = 180 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.53 – 7.48 (m, 2H), 7.43 – 7.39 (m, 3H), 4.19 (s, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.6, 153.0, 145.1, 142.6, 135.6, 132.1, 130.5, 130.2, 129.6 (2C), 129.3 (2C), 127.8, 124.9, 124.1, 115.1, 114.1, 78.8, 38.0. HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{19}H_{13}N_2^+$: 269.1073; found: 269.1070.

2-((5-methoxy-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1b



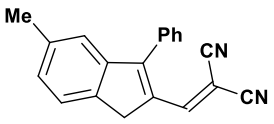
Following the general procedure product **1b** was isolated in 80% yield (715.0 mg) as brown solid; mp = 188 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.61 – 7.56 (m, 3H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.08 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 4.11 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.4, 159.8, 152.9, 143.9, 137.5, 136.8, 132.1, 130.1, 129.6 (2C), 129.4 (2C), 125.5, 117.8, 115.1, 114.1, 108.1, 78.7, 55.8, 37.3. HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{20}H_{15}N_2O^+$: 299.1179; found: 299.1172.

2-((6-methoxy-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1c



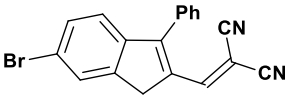
Following the general procedure product **1c** was isolated in 88% yield (786.7 mg) as brown solid; mp = 192 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.41 – 7.36 (m, 3H), 7.18 (d, *J* = 2.0 Hz, 1H), 6.95 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.14 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.7, 161.9, 152.6, 148.1, 135.9, 133.8, 132.3, 130.1, 129.6 (2C), 129.3 (2C), 125.4, 115.6, 115.0, 114.7, 109.9, 76.3, 55.9, 37.9. HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{20}H_{15}N_2O^+$: 299.1179; found: 299.1169.

2-((5-methyl-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1d



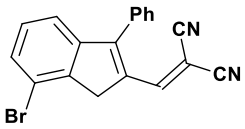
Following the general procedure product **1d** was isolated in 97% yield (820.1 mg) as light-yellow solid; mp = 196 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.63 – 7.56 (m, 3H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.40 (dt, *J* = 4.2, 2.3 Hz, 2H), 7.33 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.28 (d, *J* = 0.6 Hz, 1H), 4.13 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.7, 153.0, 142.9, 142.4, 137.7, 135.9, 132.2, 131.7, 1301, 129.6 (2C), 129.3 (2C), 124.6, 124.4, 115.2, 114.2, 78.4, 37.6, 21.5. HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{20}H_{15}N_2^+$: 283.1230; found: 283.1224.

2-((6-bromo-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1e



Following the general procedure product **1e** was isolated in 78% yield (812.0 mg) as dark yellow solid; mp = 198 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.0 Hz, 1H), 7.64 (s, 1H), 7.62 – 7.56 (m, 3H), 7.54 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 4.15 (s, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.5, 152.7, 146.5, 141.6, 135.5, 131.6, 131.2, 130.4, 129.6 (2C), 129.5 (2C), 128.2, 125.3, 125.0, 114.9, 114.0, 79.6, 37.8. HRMS (ESI) m/z $[M-H]^-$ Calcd. for $C_{19}H_{10}BrN_2^-$: 345.0033; found: 345.0036.

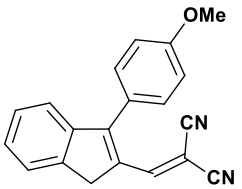
2-((7-bromo-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1f



Following the general procedure product **1f** was isolated in 64 % yield (666.2 mg) as dark yellow solid; mp = 204 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.63 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.44 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 4.14 (s, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.7, 152.6, 144.9, 144.0, 135.6, 133.2, 131.8, 130.4, 129.6 (2C), 129.5, 129.4 (2C),

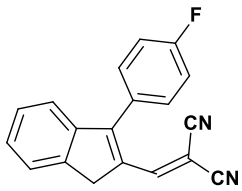
123.0, 119.8, 114.8, 113.6, 80.3, 39.5. HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{19}H_{12}BrN_2^+$: 347.0179; found: 347.0176.

2-((3-(4-methoxyphenyl)-1*H*-inden-2-yl)methylene)malononitrile 1g



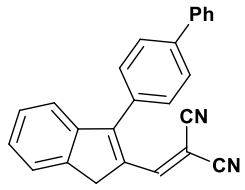
Following the general procedure product **1g** was isolated in 80% yield (715.2 mg) as red solid; mp = 158 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.14 – 7.09 (m, 2H), 4.16 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.5, 161.3, 153.2, 145.2, 142.7, 135.0, 131.3 (2C), 130.4, 127.7, 124.9, 124.4, 124.1, 115.3, 114.9 (2C), 114.3, 78.1, 55.6, 37.9. HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{20}H_{15}N_2O^+$: 299.1179; found: 299.1170.

2-((3-(4-fluorophenyl)-1*H*-inden-2-yl)methylene)malononitrile 1h



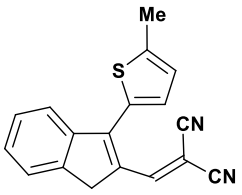
Following the general procedure product **1h** was isolated in 81% yield (696 mg) as light-yellow solid; mp = 184°C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.62 (s, 1H), 7.52 (td, *J* = 7.4, 1.2 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.39 (m, 2H), 7.32 – 7.28 (m, 2H), 4.18 (s, *J* = 46.5 Hz, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 163.8 (d, *J* = 251.5 Hz), 160.3, 152.6, 145.0, 142.5, 135.8, 131.6 (d, *J* = 8.5 Hz) (2C), 130.7, 128.1 (d, *J* = 3.5 Hz), 127.9, 125.0, 123.8, 116.67 (d, *J* = 21.8 Hz) (2C), 115.0, 114.0, 79.2, 38.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ - 109.6. HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{19}H_{12}FN_2^+$: 287.0979; found: 287.0974.

2-((3-([1,1'-biphenyl]-4-yl)-1*H*-inden-2-yl)methylene)malononitrile 1i



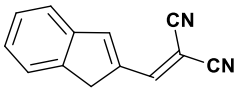
Following the general procedure product **1i** was isolated in 78% yield (804.9 mg) as light-yellow solid; mp = 240 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.74 (s, 1H), 7.71 – 7.66 (m, 3H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.51 (m, 3H), 7.50 – 7.48 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 4.21 (s, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.1, 152.9, 145.1, 143.1, 142.5, 139.9, 135.5, 130.8, 130.5, 130.1 (2C), 129.1 (2C), 128.1, 127.9 (2C), 127.7, 127.2 (2C), 124.9, 124.0, 115.0, 114.1, 78.7, 38.0. HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{25}H_{16}N_2Na^+$: 367.1206; found: 367.1199.

2-((3-(5-methylthiophen-2-yl)-1*H*-inden-2-yl)methylene)malononitrile 1j



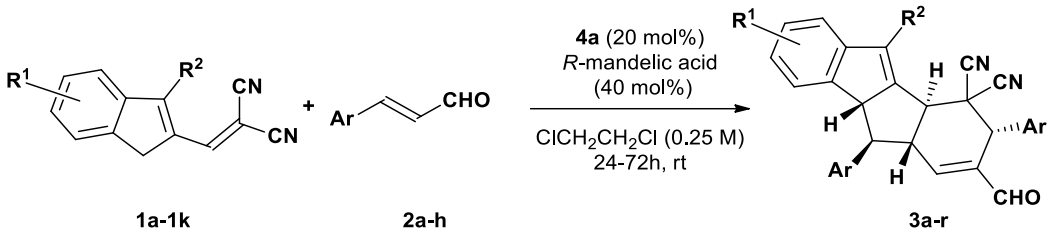
Following the general procedure product **1j** was isolated in 87% yield (751.7 mg) as orange solid; mp = 191 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.50 (td, *J* = 7.4, 1.1 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.00 – 6.95 (m, 1H), 4.14 (s, 2H), 2.64 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 153.2, 152.8, 145.8, 145.0, 141.8, 135.2, 131.4, 130.5, 130.5, 127.8, 127.1, 124.9, 124.2, 115.4, 114.3, 78.4, 38.0, 15.7. HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{18}H_{12}N_2Na^+$: 311.0614; found: 311.0619.

2-((1*H*-inden-2-yl)methylene)malononitrile 1k



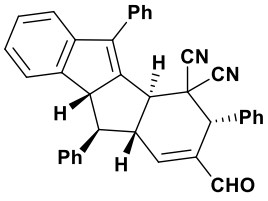
Following the general procedure product **1k** was isolated in 46% yield (265.0 mg) as orange solid; mp = 175 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.65 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.46 (td, *J* = 7.5, 1.1 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 4.00 (s, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 153.9, 150.0, 145.9, 141.7, 140.7, 130.2, 127.9, 124.8, 124.5, 114.5, 113.6, 79.7, 37.9. HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{13}H_9N_2^+$: 193.0760; found: 193.0762.

3. Polyenolate-mediated reaction cascade initiated by the higher-order-cycloaddition - general procedure



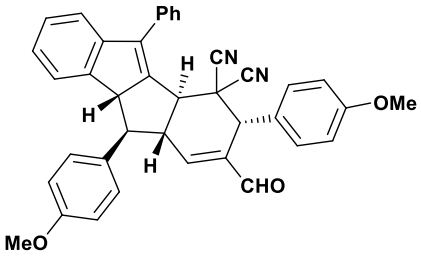
In an ordinary 4 mL glass vial equipped with a magnetic stirring, corresponding malononitrile **1** (0.2 mmol), α,β-unsaturated aldehyde **2** (0.2 mmol) and *R*-mandelic acid (0.04 mmol) were dissolved in DCE (0.4 mL) and catalyst **4a** (6.6 mg, 0.02 mmol) was added. The reaction mixture was stirred in room temperature for the indicated time. The progress of the reaction was controlled by ^{1}H NMR spectroscopy. After full conversion of the starting material **1**, the reaction mixture was directly subjected to column chromatography on silica gel (hexanes: ethyl acetate 80:20) to afford pure product **3**.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3a



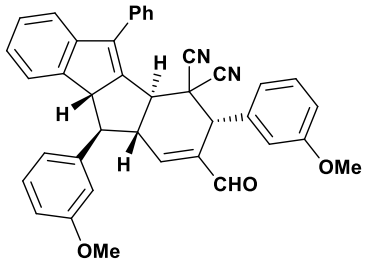
Following the general procedure product **3a** (>20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 65% yield (33.4 mg) as yellow solid; mp = 226 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.57 (d, *J* = 4.8 Hz, 4H), 7.51 – 7.46 (m, 2H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 0.9 Hz, 1H), 7.13 – 7.07 (m, 3H), 7.03 – 7.00 (m, 3H), 4.62 (s, 1H), 4.35 (dd, *J* = 10.6, 1.9 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.88 (dd, *J* = 11.9, 2.1 Hz, 1H), 2.81 (t, *J* = 11.1 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 148.2, 148.2, 143.5, 142.8, 141.4, 138.9, 137.7, 134.9, 133.9, 130.0 (2C), 129.7 (2C), 129.5, 129.0 (2C), 128.6 (2C), 128.4, 128.2, 127.9 (2C), 127.8 (2C), 127.7, 125.6, 123.7, 121.5, 114.9, 112.0, 64.7, 53.8, 49.8, 49.7, 41.1, 39.8. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 5.33 min, τ_{minor} = 6.88 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 81.3 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{37}H_{27}N_2O^+$: 515.2118; found: 515.2116.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-bis(4-methoxyphenyl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3b



Following the general procedure product **3b** (17:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 60% yield (34.3 mg) as yellow solid; mp = 194 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.50 – 7.45 (m, 2H), 7.26 – 7.23 (m, 2H), 7.22 – 7.16 (m, 4H), 7.15 – 7.08 (m, 6H), 7.07 – 7.02 (m, 3H), 6.98 – 6.93 (m, 2H), 4.58 (s, 1H), 4.29 (dd, *J* = 10.6, 2.1 Hz, 1H), 3.97 – 3.92 (m, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 3.83 (dd, *J* = 11.9, 2.2 Hz, 1H), 2.75 (t, *J* = 11.0 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.6, 160.6, 159.7, 148.2, 148.1, 143.7, 142.7, 141.6, 139.1, 134.1, 131.2 (2C), 129.4, 128.9 (2C), 128.6 (2C), 128.2, 128.0 (2C), 127.7, 126.9, 125.5, 123.7, 121.5, 115.0 (2C), 114.9, 114.3 (2C), 112.2, 65.0, 55.6, 55.5, 53.9, 49.2, 49.0, 41.3, 39.8. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 7.10 min, τ_{minor} = 4.94 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 45.2 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{39}H_{31}N_2O_3^+$: 575.2329; found: 575.2313.

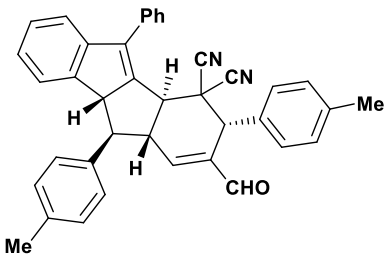
3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-bis(3-methoxyphenyl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3c



Following the general procedure product **3c** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 44% yield (25.2 mg) as yellow solid; mp = 170 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.49 (dd, *J* = 8.3, 7.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.17 – 7.15 (m, 2H), 7.14 – 7.10 (m, 3H), 7.09 – 7.04 (m, 4H), 7.01 (dddd, *J* = 9.5, 8.4, 2.5, 0.9 Hz, 2H), 6.85 – 6.81 (m, 2H), 4.59 – 4.56 (m, 1H), 4.34 (dd, *J* = 10.6, 2.4 Hz, 1H), 3.97 (tt, *J* = 11.7, 2.0 Hz, 1H), 3.92 (s, 3H), 3.90 (dd, *J* = 11.9, 2.4 Hz, 1H), 3.84 (s, 3H), 2.76 (t, *J* = 11.1 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 160.6, 160.0, 148.3, 148.2, 143.6, 142.9, 141.4, 139.4, 138.9, 136.4, 134.0, 130.7, 130.0, 128.6 (2C), 128.2, 127.9 (2C) , 127.7, 125.6, 123.8, 122.2, 121.5, 120.0, 116.3, 114.9, 114.6, 114.2, 113.1, 112.0, 64.6, 55.6, 55.5, 53.8, 49.8, 49.7, 41.1, 39.9. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow

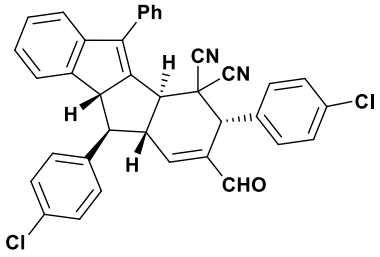
rate = 2.2 mL/min τ_{major} = 6.21 min, τ_{minor} = 5.51 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 167.1 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{39}H_{30}N_2O_3^+$: 575.2329; found: 575.2334.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-phenyl-3,10-di-*p*-tolyl-4a,9b,10,10a-tetrahydroindeno [2,1-a]indene-4,4(3*H*)-dicarbonitrile 3d



Following the general procedure product **3d** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 59% yield (31.8 mg) as yellow solid; mp = 217 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.25 – 7.19 (m, 4H), 7.18 – 7.12 (m, 4H), 7.12 – 7.06 (m, 3H), 7.06 – 7.01 (m, 3H), 4.59 (s, 1H), 4.33 (dd, *J* = 10.6, 2.1 Hz, 1H), 3.97 (tt, *J* = 11.6, 1.9 Hz, 1H), 3.87 (dd, *J* = 12.0, 2.2 Hz, 1H), 2.77 (t, *J* = 11.0 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.6, 148.2, 148.2, 143.7, 142.6, 141.7, 139.6, 139.0, 138.2, 134.6, 134.1, 132.0, 130.3 (2C), 129.9 (2C), 129.7 (2C), 128.5 (2C), 128.1, 128.0 (2C), 127.7 (2C), 127.7, 125.5, 123.7, 121.4, 115.0, 112.1, 64.8, 53.9, 49.5, 49.4, 41.2, 39.8, 21.4, 21.3. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 4.79 min, τ_{minor} = 4.17 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 100.1 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{39}H_{31}N_2O^+$: 543.2431; found: 543.2445.

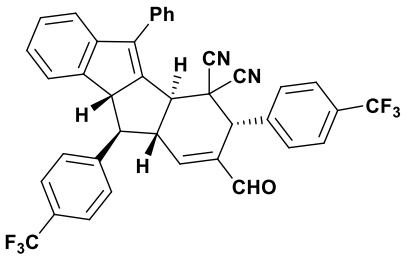
(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-3,10-bis(4-chlorophenyl)-2-formyl-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3e



Following the general procedure product **3e** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 55% yield (32.1 mg) as brown solid; mp = 188 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.30-7.26 (m, 1H), 7.26-7.10 (m, 8H), 7.04-7.00 (m, 3H), 4.58 (s, 1H), 4.29 (dd, *J* = 10.6, 1.9 Hz, 1H), 4.02 – 3.91 (m, 1H), 3.76 (dd, *J* = 11.9, 2.2 Hz, 1H), 2.78 (t, *J* = 11.1 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.1, 149.0, 148.0, 143.4, 143.1, 140.5, 138.7, 136.0, 135.8, 134.3, 133.7, 133.3, 131.1 (2C), 129.8 (2C), 129.1 (2C), 129.0 (2C), 128.6 (2C), 128.3, 127.8, 127.7 (2C), 125.7, 123.5, 121.6, 114.5, 111.7, 64.61, 53.6, 49.0, 49.0, 40.9, 39.7. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major}

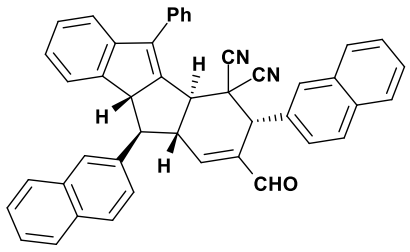
= 5.54 min, τ_{minor} = 4.89 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 85.0 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{37}H_{25}Cl_2N_2O^+$: 583.1338; found: 583.1343.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-phenyl-3,10-bis(4-(trifluoromethyl)phenyl)-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3f



Following the general procedure product **3f** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 36% yield (23.1 mg) as yellow solid; mp = 200 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.71 (dd, *J* = 8.0, 3.1 Hz, 4H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 1.0 Hz, 1H), 7.14 (td, *J* = 7.5, 0.9 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.99 (dd, *J* = 14.9, 7.2 Hz, 3H), 4.66 (s, 1H), 4.35 (dd, *J* = 10.6, 2.1 Hz, 1H), 4.06 (tt, *J* = 11.8, 2.0 Hz, 1H), 3.78 (dd, *J* = 11.9, 2.2 Hz, 1H), 2.88 (t, *J* = 11.2 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.1, 148.2, 148.1, 144.0, 143.0, 141.8, 140.1, 138.8, 138.7, 133.6, 131.9 (q, *J* = 32.7 Hz), 131.0 (q, *J* = 32.9 Hz), 130.4 (2C), 128.7 (2C), 128.6, 128.3 (2C), 128.1, 127.7 (2C), 126.8 (q, *J* = 3.5 Hz, 2C), 126.0, 126.0 (q, *J* = 3.7 Hz, 2C), 124.1 (q, *J* = 272.1 Hz), 123.9 (q, *J* = 272.2 Hz), 123.6, 121.9, 114.4, 111.6, 64.6, 53.7, 49.5, 49.3, 41.0, 39.9. ^{19}F NMR (376 MHz $CDCl_3$) δ -62.44, -62.64. The er was determined by UPC^2 using a chiral Chiralpack IA column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.08 min, τ_{minor} = 2.89 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 78.6 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{39}H_{25}F_6N_2O^+$: 651.1865; found: 651.1859.

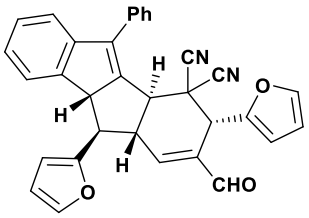
(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-di(naphthalen-2-yl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3g



Following the general procedure product **3g** (>20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 50% yield (30.7 mg) as yellow solid; mp = 190 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.06 – 8.04 (m, 1H), 8.01 – 7.96 (m, 2H), 7.95 – 7.92 (m, 2H), 7.90 – 7.85 (m, 1H), 7.75 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.68 – 7.66 (m, 1H), 7.65 – 7.56 (m, 4H), 7.47 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.18 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.07 (td, *J* = 7.4, 1.2 Hz, 1H), 6.98 (ddt, *J* = 16.4, 7.6, 1.0 Hz, 2H), 6.92 (dt, *J* = 6.7, 1.3 Hz, 2H), 6.66 – 6.62 (m, 2H), 4.83 – 4.79 (m, 1H), 4.50 (dd, *J* = 10.6, 2.4 Hz, 1H), 4.19 (tt, *J* = 11.7, 2.1 Hz, 1H), 4.11 (dd,

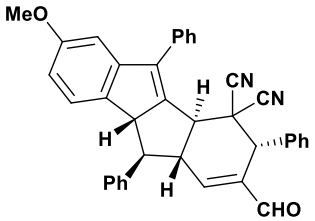
J = 11.9, 2.3 Hz, 1H), 3.04 (t, *J* = 11.0 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 148.4, 148.1, 143.6, 143.1, 141.4, 139.1, 135.2, 133.9, 133.8, 133.7, 133.4, 133.0, 132.7, 129.6, 129.0, 128.8, 128.3 (2C), 128.2, 128.1, 128.1, 128.0, 127.9 (2C), 127.8, 127.7 (2C), 127.3, 127.2, 127.0 (2C), 126.6, 125.7, 125.3, 123.8, 121.5, 115.0, 112.0, 64.8, 53.9, 50.1, 50.0, 41.1, 40.0.The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; ACN flow rate = 2.2 mL/min τ_{major} = 5.91 min, τ_{minor} = 5.40 min, (> 99:1 er). $[\alpha]_D^{21}$ = - 16.7 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{45}H_{30}N_2O_6^+$: 615.2431; found: 615.2440.

(3*S*,4a*S*,9b*R*,10*R*,10a*S*)-2-formyl-3,10-di(furan-2-yl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3h



Following the general procedure product **3h** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 52% yield (25.6 mg) as yellow solid; mp = 174 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.61 (dt, *J* = 1.9, 1.0 Hz, 1H), 7.46 (dd, *J* = 1.9, 1.0 Hz, 1H), 7.34 – 7.27 (m, 5H), 7.28 – 7.17 (m, 5H), 6.55 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.51 (d, *J* = 3.2 Hz, 1H), 6.46 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.43 (dd, *J* = 3.4, 1.0 Hz, 1H), 4.72 (d, *J* = 1.6 Hz, 1H), 4.42 (dd, *J* = 10.7, 2.3 Hz, 1H), 4.05 (dd, *J* = 11.9, 2.3 Hz, 1H), 3.97 (tt, *J* = 12.1, 2.1 Hz, 1H), 2.95 (t, *J* = 10.9 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.2, 152.0, 148.6, 148.3, 148.1, 143.7, 143.4, 143.3, 143.1, 141.0, 136.8, 134.1, 128.8 (2C), 128.4, 128.0 (2C), 127.9, 125.8, 123.9, 121.6, 114.1, 112.4, 111.7, 111.4, 111.0, 108.0, 62.4, 52.2, 43.8, 42.8, 41.3, 40.5. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 4.03 min, τ_{minor} = 4.25 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 58.2 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{33}H_{23}N_2O_3^+$: 495.1703; found: 495.1716.

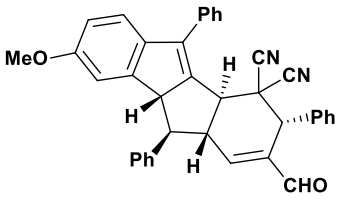
(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-7-methoxy-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3i



Following the general procedure product **3i** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 53% yield (28.8 mg) as yellow solid; mp = 170 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.58 – 7.54 (m, 4H), 7.50 – 7.46 (m, 2H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.15 (d, *J* = 1.1 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 2H), 7.00 (d, *J* = 7.0 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.72 (t, *J* = 2.9 Hz, 1H), 6.66 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.61 (s, 1H), 4.29 (dd, *J* = 10.6, 1.9 Hz, 1H), 3.99 (tt, *J* = 11.8, 2.0 Hz, 1H), 3.86 (dd,

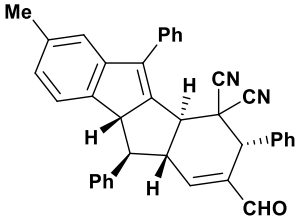
J = 11.9, 2.1 Hz, 1H), 3.71 (s, 3H), 2.76 (t, *J* = 11.2 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 160.0, 149.7, 148.3, 142.8, 142.7, 138.9, 137.8, 135.8, 134.9, 133.9, 130.0 (2C), 129.7 (2C), 129.5, 129.0 (2C), 128.7 (2C), 128.4, 128.2, 127.8 (2C), 127.8 (2C), 124.3, 114.9, 112.0, 111.7, 107.0, 64.2, 55.6, 53.6, 50.0, 49.8, 41.1, 39.8. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 5.39. min, τ_{minor} = 6.61 min, (>99:1 er). $[\alpha]_D^{21}$ = + 124.6 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{38}H_{29}N_2O_2^+$: 545.2223; found: 545.2211.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-8-methoxy-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3j



Following the general procedure product **3j** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 47% yield (25.6 mg) as yellow solid; mp = 162 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.59 – 7.54 (m, 4H), 7.53 – 7.38 (m, 4H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.15 (d, *J* = 1.1 Hz, 1H), 7.09 (dd, *J* = 12.1, 5.0 Hz, 3H), 7.01 (dd, *J* = 7.9, 1.0 Hz, 2H), 6.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.58 (d, *J* = 2.3 Hz, 1H), 4.61 (s, 1H), 4.29 (dd, *J* = 10.6, 2.0 Hz, 1H), 3.99 (tt, *J* = 11.7, 2.0 Hz, 1H), 3.86 (dd, *J* = 11.9, 2.4 Hz, 1H), 3.70 (s, 3H), 2.80 (t, *J* = 11.3 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 158.4, 148.3, 145.4, 142.7, 141.3, 139.0, 138.8, 137.6, 134.9, 134.2, 130.0 (2C), 129.7 (2C), 129.5, 129.0 (2C), 128.6 (2C), 128.4, 128.1, 127.9 (2C), 127.8 (2C), 122.0, 115.0, 112.6, 112.1, 110.8, 64.5, 55.6, 53.8, 49.8 (2C), 41.3, 39.8. The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; ACN, flow rate = 2.2 mL/min τ_{major} = 4.91 min, τ_{minor} = 4.59 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 49.5 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{38}H_{29}N_2O_2^+$: 545.2223; found: 545.2206.

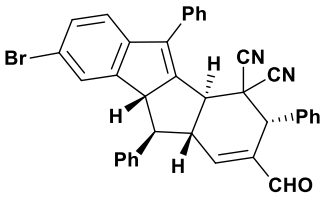
(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-7-methyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3k



Following the general procedure product **3k** (>20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 54% yield (28.5 mg) as yellow solid; mp = 175 °C. NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), δ 7.61 – 7.54 (m, 4H), 7.52 – 7.40 (m, 4H), 7.30 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 7.16 – 7.14 (m, 1H), 7.10 (t, *J* = 7.7 Hz, 2H), 7.04 – 6.98 (m, 3H), 6.95 – 6.87 (m, 2H), 4.61 (s, 1H), 4.31 (dd, *J* = 10.6, 1.9 Hz, 1H), 4.00 (tt, *J* = 11.7, 1.9 Hz, 1H),

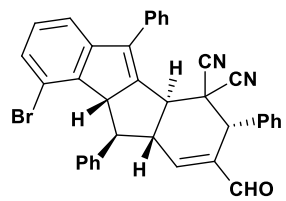
3.86 (dd, *J* = 12.0, 2.2 Hz, 1H), 2.77 (t, *J* = 11.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 148.4, 148.3, 142.9, 141.6, 140.7, 138.9, 137.8, 137.7, 134.9, 134.1, 130.0 (2C), 129.6 (2C), 129.5, 129.0 (2C), 128.6 (2C), 128.4, 128.1, 127.9 (4C), 126.4, 123.4, 122.1, 114.9, 112.0, 64.5, 53.7, 49.9, 49.8, 41.2, 39.8, 21.6. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 5.23. min, τ_{minor} = 6.72 min, (> 99:1 er). $[\alpha]_D^{21}$ = - 46.5 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{38}H_{29}N_2O^+$: 529.2274; found: 529.2265.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-8-bromo-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3l



Following the general procedure product **3l** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 40% yield (23.7 mg) as yellow solid; mp = 169 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.61 – 7.58 (m, 2H), 7.56 – 7.54 (m, 2H), 7.53 – 7.50 (m, 1H), 7.50 – 7.46 (m, 1H), 7.46 – 7.43 (m, 2H), 7.38 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.21 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.14 – 7.11 (m, 2H), 7.11 – 7.07 (m, 2H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.99 – 6.97 (m, 2H), 4.61 (s, 1H), 4.33 (dd, *J* = 10.7, 2.4 Hz, 1H), 3.97 (tt, *J* = 11.8, 2.1 Hz, 1H), 3.85 (dd, *J* = 12.0, 2.4 Hz, 1H), 2.82 (t, *J* = 11.2 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.4, 147.8, 147.1, 145.4, 142.2, 141.9, 139.0, 137.1, 134.8, 133.4, 130.9, 130.0 (2C), 129.9 (2C), 129.6, 129.1 (2C), 128.7 (2C), 128.7, 128.4, 127.8 (4C), 126.9, 122.8, 120.1, 114.8, 111.9, 64.3, 53.9, 49.8, 49.5, 41.0, 39.8. The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 5.70 min, τ_{minor} = 5.34 min, (99:1 er). $[\alpha]_D^{21}$ = + 30.9 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{37}H_{26}BrN_2O^+$: 593.1223; found: 593.1204.

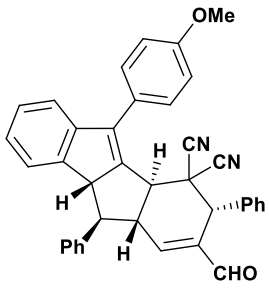
(3*S*,4a*S*,9b*S*,10*R*,10a*R*)-9-bromo-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3m



Following the general procedure product **3m** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 30% yield (17.8 mg) as yellow solid; mp = 210 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.79 (s, 1H), 7.60 – 7.55 (m, 1H), 7.49 – 7.41 (m, 5H), 7.35 – 7.30 (m, 1H), 7.28 (dd, *J* = 5.2, 3.6 Hz, 2H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.21 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.12 – 7.07 (m, 4H), 7.01 – 6.98 (m, 3H), 4.59 (s, 1H), 4.49 (dd, *J* = 10.0, 2.3 Hz, 1H),

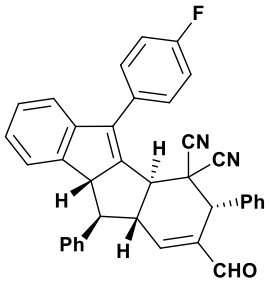
4.06 (tt, *J* = 11.9, 2.1 Hz, 1H), 3.83 (dd, *J* = 12.3, 2.3 Hz, 1H), 2.84 (dd, *J* = 11.8, 10.1 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.40, 149.93, 148.11, 143.42, 143.06, 142.34, 138.96, 138.68, 134.88, 133.38, 130.21, 130.01 (2C), 129.52, 129.37 (4C), 129.01 (2C), 128.73 (2C), 128.44, 128.41, 127.87 (2C), 126.30, 120.33, 119.29, 114.79, 111.83, 66.43, 54.66, 50.56, 49.77, 41.17, 39.00. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 4.43. min, τ_{minor} = 6.50 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 99.5 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{37}H_{26}BrN_2O^+$: 593.1223; found: 593.1217.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-(4-methoxyphenyl)-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3n



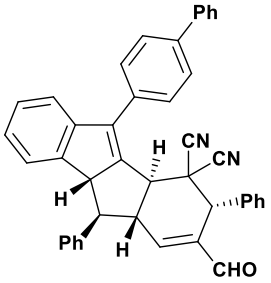
Following the general procedure product **3n** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 46% yield (25.1 mg) as yellow solid; mp = 173 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.59 – 7.54 (m, 4H), 7.47 – 7.44 (m, 2H), 7.45 (dd, *J* = 11.4, 4.5 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.25 – 7.24 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 1.2 Hz, 1H), 7.10 (td, *J* = 7.4, 1.1 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.94 – 6.91 (m, 2H), 6.60 (t, *J* = 5.7 Hz, 2H), 4.63 (s, 1H), 4.33 (dd, *J* = 10.6, 2.2 Hz, 1H), 4.01 (tt, *J* = 11.8, 2.0 Hz, 1H), 3.85 (dd, *J* = 11.9, 2.3 Hz, 1H), 3.73 (s, 3H), 2.78 (t, *J* = 11.1 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 159.4, 148.4 (2C), 143.6, 142.6, 141.1, 139.0, 137.8, 134.9, 130.1 (2C), 129.7 (2C), 129.5, 129.0 (2C), 129.0 (2C), 128.4, 127.9 (2C), 127.7, 126.2, 125.5, 123.7, 121.5, 115.0, 114.1 (2C), 112.1, 64.7, 55.3, 53.9, 49.8, 49.8, 41.2, 39.8. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 5.38. min, τ_{minor} = 6.61 min, (> 99:1 er). $[\alpha]_D^{21}$ = -39.6 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{38}H_{29}N_2O_2^+$: 545.2223; found: 545.2211.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-5-(4-fluorophenyl)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3o



Following the general procedure product **3o** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 56% yield (29.8 mg) as yellow solid; mp = 176 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.60 – 7.55 (m, 4H), 7.52 – 7.48 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.1 Hz, 3H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.12 (td, *J* = 7.5, 0.9 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 5.3 Hz, 2H), 6.78 (t, *J* = 8.7 Hz, 2H), 4.63 (s, 1H), 4.34 (dd, *J* = 10.6, 2.1 Hz, 1H), 4.01 (tt, *J* = 11.7, 2.0 Hz, 1H), 3.81 (dd, *J* = 11.9, 2.3 Hz, 1H), 2.82 – 2.78 (m, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.4, 162.6 (d, *J* = 247.4 Hz), 148.1, 148.1, 143.5, 141.9, 141.9, 138.9, 137.6, 134.8, 130.0 (2C), 129.9 (d, *J* = 3.4 Hz), 129.7 (2C), 129.6 (d, *J* = 8.2 Hz, 2C), 129.6, 129.0 (2C), 128.5, 127.9 (2C), 127.8, 125.8, 123.8, 121.3, 115.7 (d, *J* = 21.6 Hz, 2C), 114.8, 112.2, 64.8, 53.8, 49.7, 49.7, 41.1, 39.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.0. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 5.13. min, τ_{minor} = 6.12 min, (> 99:1 er). $[\alpha]_D^{21}$ = -19.5 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{37}H_{26}FN_2O^+$: 533.2024; found: 533.2017.

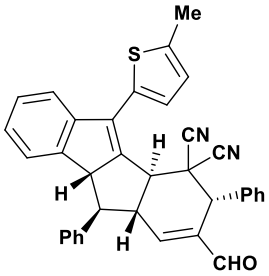
(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-5-([1,1'-biphenyl]-4-yl)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3p



Following the general procedure product **3p** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 49% yield (28.9 mg) as yellow solid; mp = 226 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.58 (d, *J* = 4.5 Hz, 4H), 7.52 – 7.49 (m, 4H), 7.48 – 7.45 (m, 2H), 7.45 – 7.41 (m, 2H), 7.34 (ddt, *J* = 7.8, 6.9, 1.3 Hz, 1H), 7.32 – 7.29 (m, 4H), 7.28 – 7.26 (m, 2H), 7.17 (dd, *J* = 2.3, 1.1 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.09 – 7.07 (m, 2H), 7.05 – 7.01 (m, 1H), 4.64 (s, 1H), 4.37 (dd, *J* = 10.7, 2.9 Hz, 1H), 4.04 (tt, *J* = 11.8, 2.1 Hz, 1H), 3.90 (dd, *J* = 11.9, 2.4 Hz, 1H), 2.82 (dd, *J* = 11.7, 10.6 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.49, 148.33, 148.12, 143.62, 142.64, 141.65, 140.99, 140.94, 138.98, 137.70, 134.91, 132.83, 130.13 (2C), 129.68 (2C), 129.52, 129.02 (2C), 128.81 (2C), 128.45, 128.25 (2C), 127.89 (2C), 127.78, 127.42, 127.34 (2C), 127.23 (2C), 125.66, 123.76, 121.55, 114.98, 112.07, 64.81, 53.92, 49.83, 49.80, 41.23, 39.86. The er was determined by UPC^2 using a chiral Chiralpack IA

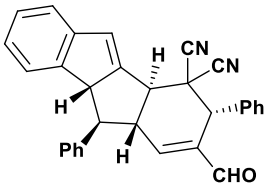
column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 4.50. min, τ_{minor} = 4.28 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 96.2 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{43}H_{31}N_2O^+$: 591.2431; found: 591.2429.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-(5-methylthiophen-2-yl)-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3q



Following the general procedure product **3q** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 47% yield (25.1 mg) as orange solid; mp = 148 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.57 – 7.53 (m, 4H), 7.50 – 7.44 (m, 4H), 7.43 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.29 (td, *J* = 7.6, 1.4 Hz, 1H), 7.16 (dd, *J* = 2.3, 1.1 Hz, 1H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 6.98 (dq, *J* = 7.6, 1.0 Hz, 1H), 6.66 (d, *J* = 3.4 Hz, 1H), 6.54 (dq, *J* = 3.3, 1.1 Hz, 1H), 4.67 (s, 1H), 4.32 (dd, *J* = 10.6, 2.4 Hz, 1H), 4.04 (tt, *J* = 11.8, 2.1 Hz, 1H), 3.85 (dd, *J* = 11.9, 2.4 Hz, 1H), 2.77 (dd, *J* = 11.7, 10.5 Hz, 1H), 2.28 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 148.4, 147.6, 143.5, 143.3, 140.4, 139.0, 137.6, 137.1, 134.8, 131.5, 130.3 (2C), 129.7 (2C), 129.4, 129.1 (2C), 128.4, 127.9 (2C), 127.8, 127.2, 125.8, 125.5, 123.8, 121.6, 115.1, 112.0, 64.6, 54.0, 49.9, 49.8, 41.5, 40.0, 15.0. The er was determined by UPC^2 using a chiral Chiralpack IB column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 5.35. min, τ_{minor} = 6.85 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 125.0 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{27}N_2O^+$: 535.1839; found: 535.1836.

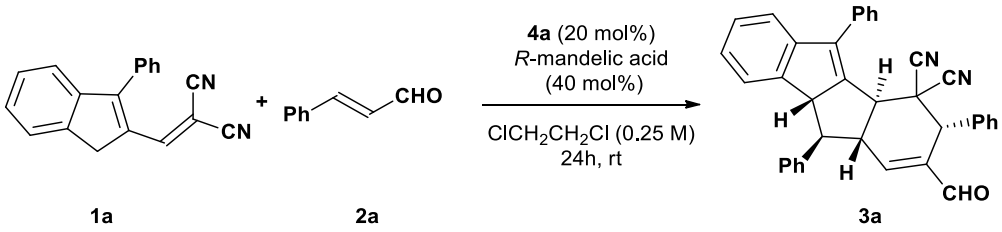
(3S,4aS,9bS,10R,10aR)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3r



Following the general procedure product **3r** (20:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 56% yield (24.6 mg) as yellow solid; mp = 158 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.59 – 7.52 (m, 4H), 7.50 – 7.46 (m, 1H), 7.45 – 7.39 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.12 (dd, *J* = 2.3, 1.3 Hz, 1H), 7.07 (td, *J* = 7.4, 1.2 Hz, 1H), 7.00 (dt, *J* = 7.6, 1.0 Hz, 1H), 6.93 (t, *J* = 2.4 Hz, 1H), 4.70 (s, 1H), 4.24 (dt, *J* = 10.9, 2.6 Hz, 1H), 3.77 (tt, *J* = 11.8, 2.1 Hz, 1H), 3.32 (dt, *J* = 12.2, 2.4 Hz, 1H), 2.78 (t, *J* = 11.1 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.5, 147.7, 147.6, 146.8, 143.8, 139.1, 137.6, 135.2, 129.9, 129.8 (2C), 129.7, 129.7 (2C), 129.3 (2C), 128.4, 127.8, 127.8 (2C), 125.3, 123.7, 122.4, 114.4, 113.2, 65.6, 52.4, 49.4, 48.9, 41.3, 40.9. The er was determined by UPC^2 using a chiral Chiralpack IB column

gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 4.82 min, τ_{minor} = 5.41 min, (> 99:1 er). $[\alpha]_D^{21}$ = + 83.3 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{31}H_{22}N_2ONa^+$: 461.1625; found: 461.1618.

4. Enantioselective synthesis of (3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3a on a 1 mmol scale

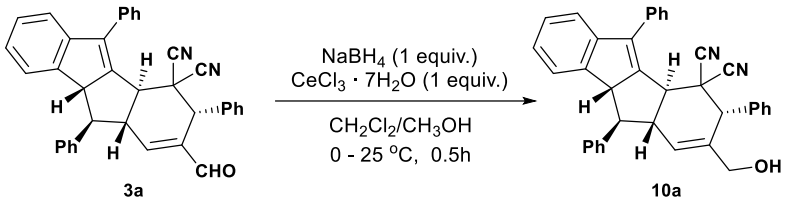


1a 2a 3a

In an ordinary 8 mL glass vial equipped with a magnetic stirring, malononitrile **1a** (1 mmol), α,β-unsaturated aldehyde **2a** (1 mmol) and *R*-mandelic acid (0.4 mmol) were dissolved in DCE (4 mL) and catalyst **4a** (66 mg, 0.2 mmol) was added. The reaction mixture was stirred in room temperature for 24h. After this time, the reaction mixture was directly subjected to column chromatography on silica gel (hexanes: ethyl acetate 80:20) to afford pure product **3a**.

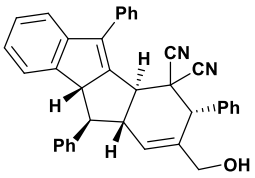
5. Selective transformations of products 3

5.1. Selective reduction of aldehyde 3a



In an ordinary 4 mL glass vial equipped with a magnetic stirring bar, the aldehyde **3a** (0.1 mmol, 1.0 equiv.) and $CeCl_3 \cdot 7H_2O$ (0.1 mmol, 1.0 equiv.) were dissolved in the mixture of CH_2Cl_2 (0.2 mL) and MeOH (0.2 mL). Then $NaBH_4$ (0,1 mmol, 1.0 equiv.) was added to the cold reaction mixture and was stirred at room temperature for 30 minutes. After full conversion of the starting material **3a** (as confirmed by TLC analysis), the reaction mixture was directly subjected to column chromatography on silica gel (eluent: hexanes/ethyl acetate 80:20) to afford pure product **10a** in 94 % yield (48.5 mg) as light-yellow solid; mp = 152°C.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-(Hydroxymethyl)-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno [2,1-a]indene-4,4(3*H*)-dicarbonitrile 10a



^{1}H NMR (700 MHz, CDCl3) δ 7.55 – 7.51 (m, 4H), 7.51 – 7.46 (m, 3H), 7.44 (ddd, *J* = 8.5, 6.3, 2.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.12 – 7.07 (m, 3H), 7.05 (d, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.19 (s, 1H), 4.31 (dd, *J* = 10.6, 1.9 Hz, 1H), 4.27 (s, 1H), 3.87 (dd, *J* = 12.9, 3.7 Hz, 1H), 3.82 (dt, *J* = 11.8, 7.6 Hz, 2H), 3.73 (dd, *J* = 11.8, 2.0 Hz, 1H), 2.66 (t, *J* = 11.1 Hz, 1H), 1.37 (dd, *J* = 6.8, 5.1 Hz, 1H). ^{13}C NMR (176 MHz, CDCl3) δ 148.4, 143.8, 143.2, 141.9, 138.6, 135.9, 135.1, 134.3, 130.6 (2C), 129.5, 129.4 (2C), 129.1 (2C), 128.5 (2C), 128.0 (2C), 128.0, 127.9 (3C), 127.5, 125.9, 125.3, 123.7, 121.3, 115.5, 112.6, 64.8, 64.7, 52.6 (2C), 50.2, 41.6, 40.1. $[\alpha]_D^{21}$ = + 115.0 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{37}H_{29}N_2O^+$: 517.2274; found: 517.2268.

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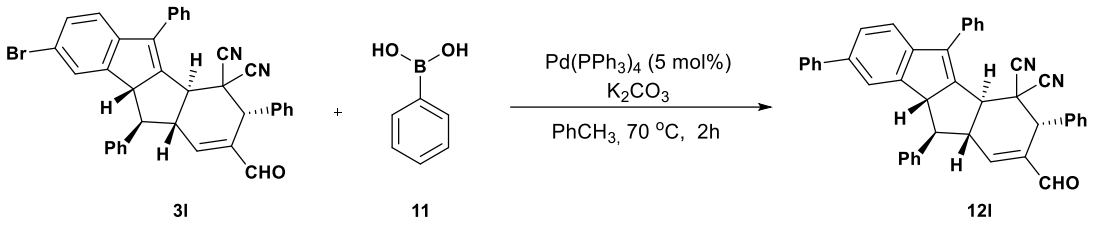
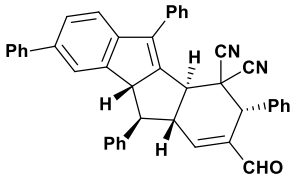
5.2. Selective Suzuki coupling of aldehyde 3l



In an ordinary 4 mL glass vial equipped with a magnetic stirring bar and a screw septum cap, the $Pd(PPh_3)_4$ (0.005mmol, 0.05 equiv.) was placed. The vial was evacuated and filled with argon. Phenylboronic acid **11** (0.11 mmol, 1.1 equiv.) was dissolved in the mixture of $PhCH_3$ (0.4 mL) and EtOH (0.1 mL), the solution was degassed and then was added *via* syringe to the reaction vial. Aldehyde **3l** (0.1 mmol, 1.0 equiv.) was dissolved in the $PhCH_3$ (0.5 mL), the solution was degassed and then was added *via* syringe to the reaction vial. Then, degassed, aqueous solution of K_2CO_3 (2M, 50µL) was added and the reaction mixture was stirred at 70 ^oC for 2h. After full conversion of the starting material **3l** (as confirmed by TLC analysis), the mixture was cooled to rt, quenched with brine (5 mL), extracted with $CHCl_3$ (3×5 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting solid was subjected to column chromatography on silica gel (eluent: hexanes/ethyl acetate 80:20) to afford pure product **12l** in 62 % yield (36.6 mg) as brown solid; mp = 160 °C.

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,5,8,10-tetraphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 12l



^1H NMR (700 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.61 – 7.57 (m, 4H), 7.53 – 7.47 (m, 3H), 7.48 – 7.44 (m, 4H), 7.41 – 7.38 (m, 2H), 7.33 – 7.29 (m, 3H), 7.27 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.17 (dd, *J* = 2.2, 1.1 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 2H), 7.06 – 7.04 (m, 2H), 4.64 (s, 1H), 4.42 (dd, *J* = 10.6, 2.5 Hz, 1H), 4.04 (tt, *J* = 11.8, 2.0 Hz, 1H), 3.91 (dd, *J* = 12.0, 2.4 Hz, 1H), 2.88 (dd, *J* = 11.6, 10.6 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 190.4, 148.2, 147.4, 144.3, 142.7, 141.7, 141.2, 139.0, 138.9, 137.6, 134.9, 133.9, 130.0 (2C), 129.7 (2C), 129.5, 129.0 (2C), 128.9 (2C), 128.7 (2C), 128.5, 128.2, 127.8 (2C), 127.8 (2C), 127.3 , 127.3 (2C), 127.0, 122.5, 121.7, 114.9, 112.0, 64.8, 53.8, 49.8, 49.7, 41.2, 39.9. $[\alpha]_D^{21}$ = + 224.7 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{46}H_{31}N_2O^+$: 591.2431; found: 591.2430.

6. Crystal and X-ray data for (3*S*,4a*S*,9b*S*,10*R*,10a*R*)-9-bromo-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3*H*)-dicarbonitrile 3m

The crystal structure of the compound **3m**, $C_{37}H_{25}BrN_2O \cdot CHCl_3$, was established by single-crystal X-ray diffraction at 100 K. The compound crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ (Z = 4), with one crystallographically independent formula unit per unit cell (Figure 1).

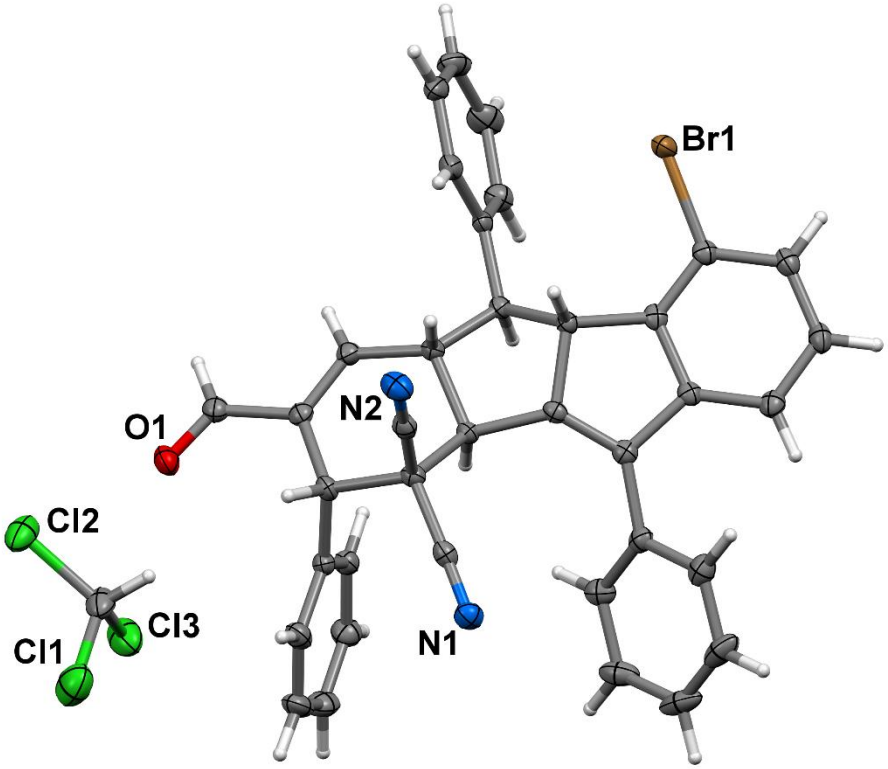


Figure 1. The molecular structure of the compound **3m** at 100 K, showing 50% probability displacement ellipsoids. Hydrogen atoms are drawn with an arbitrary radius.

Single crystal X-ray diffraction data were collected at 100 K by the ω-scan technique using a RIGAKU XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer[3] with PhotonJet micro-focus X-ray Source Cu-Kα (λ = 1.54184 Å). Data collection, cell refinement, data reduction and absorption correction were performed using CrysAlis PRO software.[3] The crystal structure was

[3] Rigaku OD. CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England, 2019.

solved using direct methods and the SHELXT 2018/2 program,[4] with atomic scattering factors taken from the International Tables for X-ray Crystallography. Positional parameters of non-H-atoms were refined by a full-matrix least-squares method on F^2 with anisotropic thermal parameters by using the SHELXL 2019/3 program.[5] All hydrogen atoms were found from the difference Fourier maps and for further calculations they were positioned geometrically in calculated positions (C–H = 0.95–1.00 Å) and constrained to ride on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the parent atom.

3m: Formula $C_{38}H_{26}Cl_3BrN_2O$, orthorhombic, space group $P2_12_12_1$, $Z = 4$, unit cell constants a = 10.9432(1), b = 15.0034(1), c = 19.5901(1) Å, V = 3216.41(4) Å^3. The integration of the data yielded a total of 117789 reflections with θ angles in the range of 3.71 to 67.73°, of which 5828 were unique (R_{int} = 2.54%). The final anisotropic full-matrix least-squares refinement on F^2 with 406 parameters. The final R_1 was 0.0181 (for $I > 2\sigma(I)$) and wR_2 was 0.0467 (all data). The largest peak in the final difference electron density synthesis was 0.279 eÅ^{-3} and the largest hole was -0.281 eÅ^{-3}. The goodness-of-fit was 1.084. The absolute configuration was unambiguously established from anomalous scattering, by calculating the x Flack parameter[6] of -0.0070(18) using 2538 quotients.

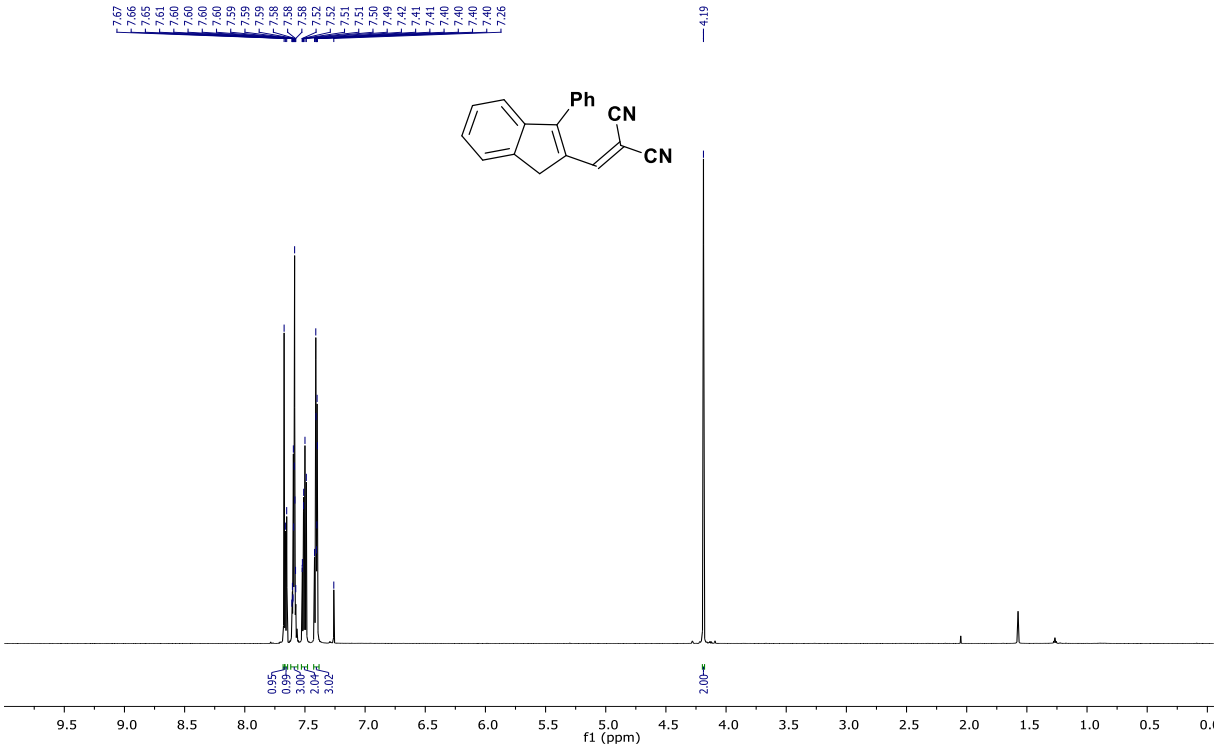
CCDC 2279932 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

[4] Sheldrick, G.M. "SHELXT - integrated space-group and crystal-structure determination", *Acta Cryst.* 2015, A**71**, 3-8.
[5] Sheldrick, G.M. "Crystal structure refinement with SHELXL", *Acta Cryst.* 2015, C**71**, 3-8.
[6] Parsons, S.; Flack, H.D.; Wagner, T. "Use of intensity quotients and differences in absolute structure refinement" *Acta Cryst.* 2013, B**69**, 249-259.

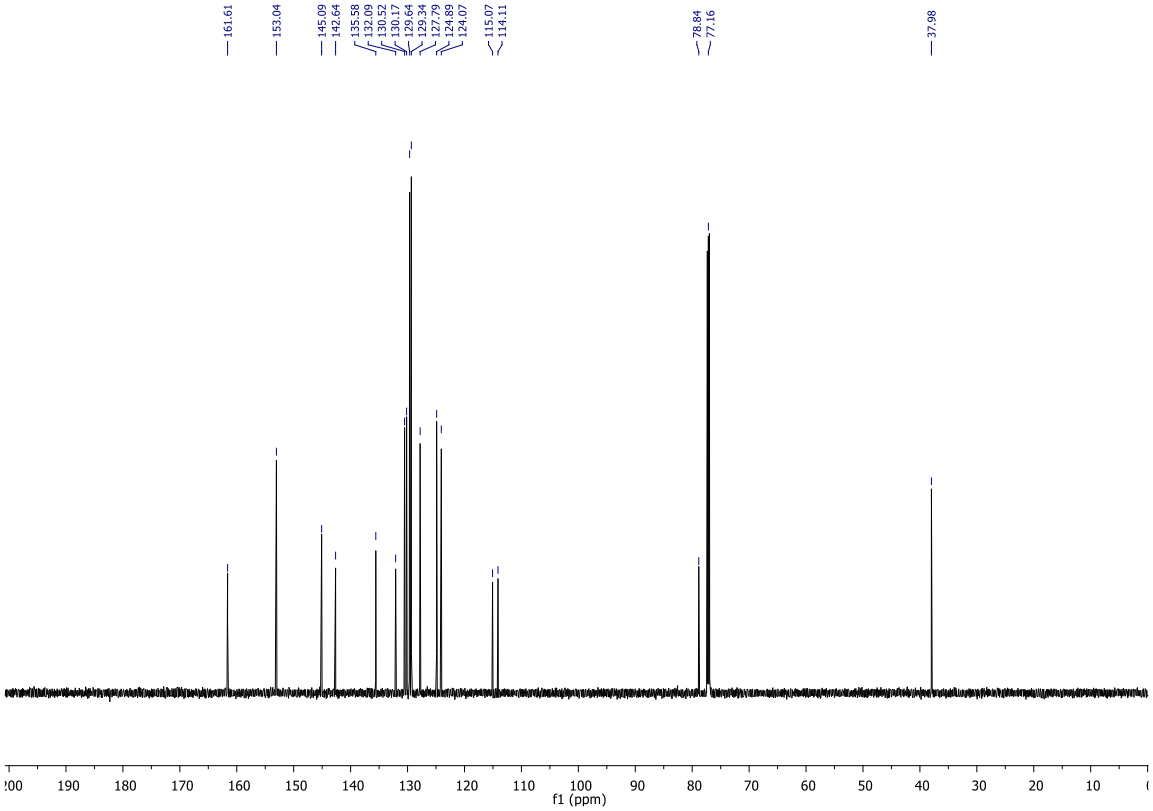
7. NMR spectra

2-((3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1a

^{1}H NMR (700 MHz, $CDCl_3$)

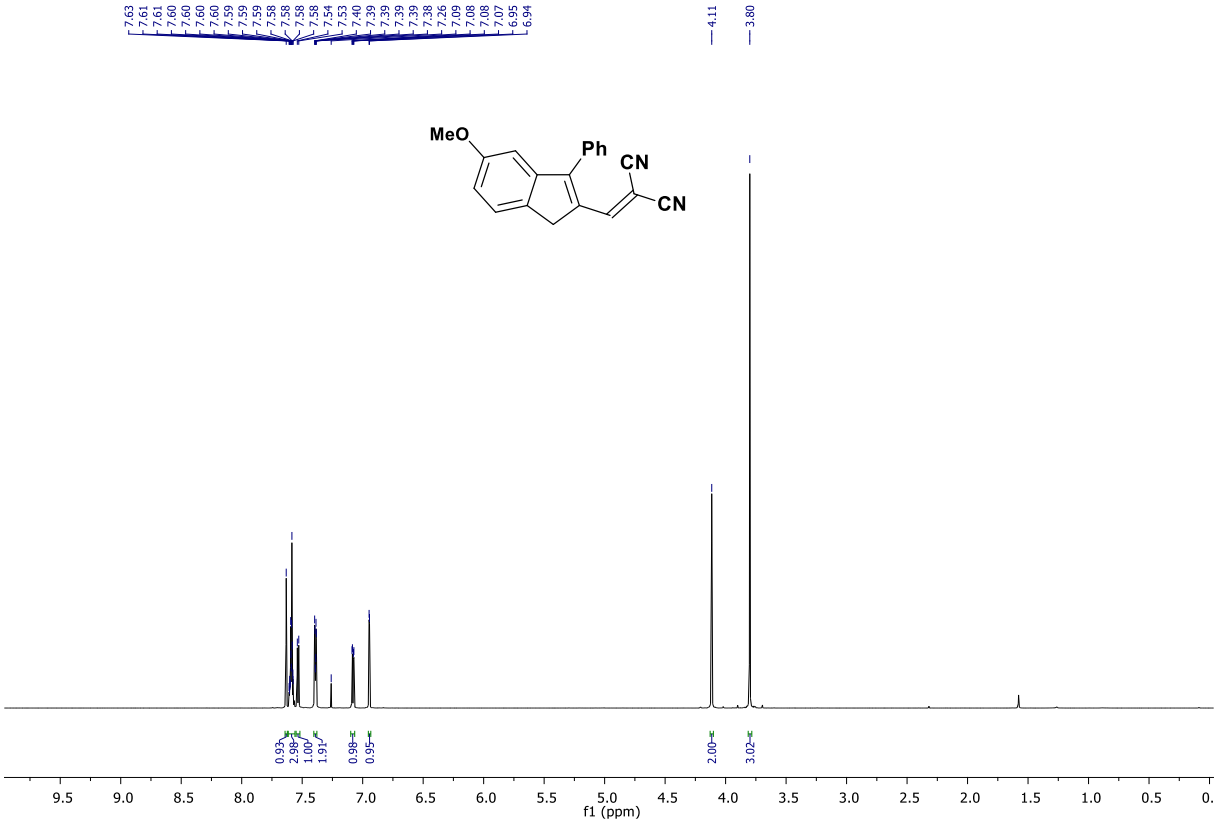


^{13}C NMR (176 MHz, $CDCl_3$)

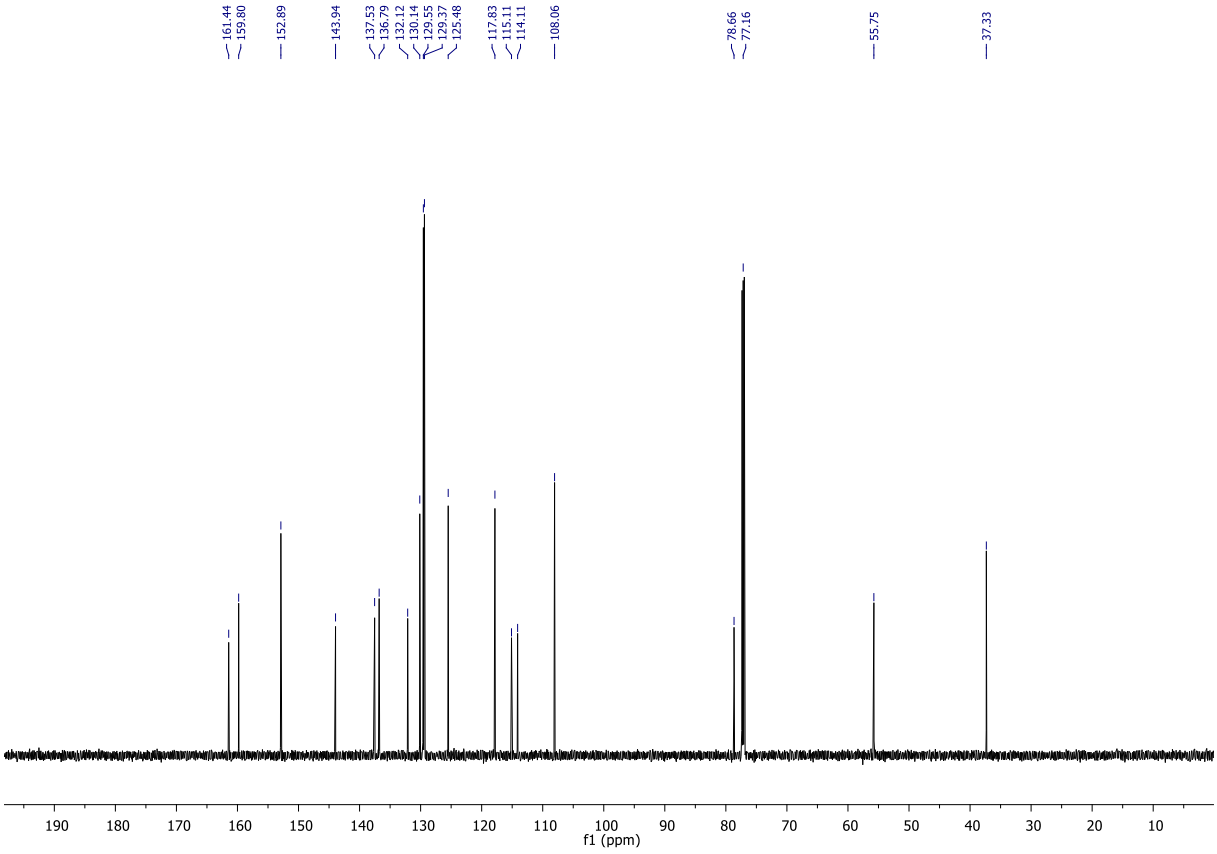


2-((5-methoxy-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1b

^{1}H NMR (700 MHz, $CDCl_3$)

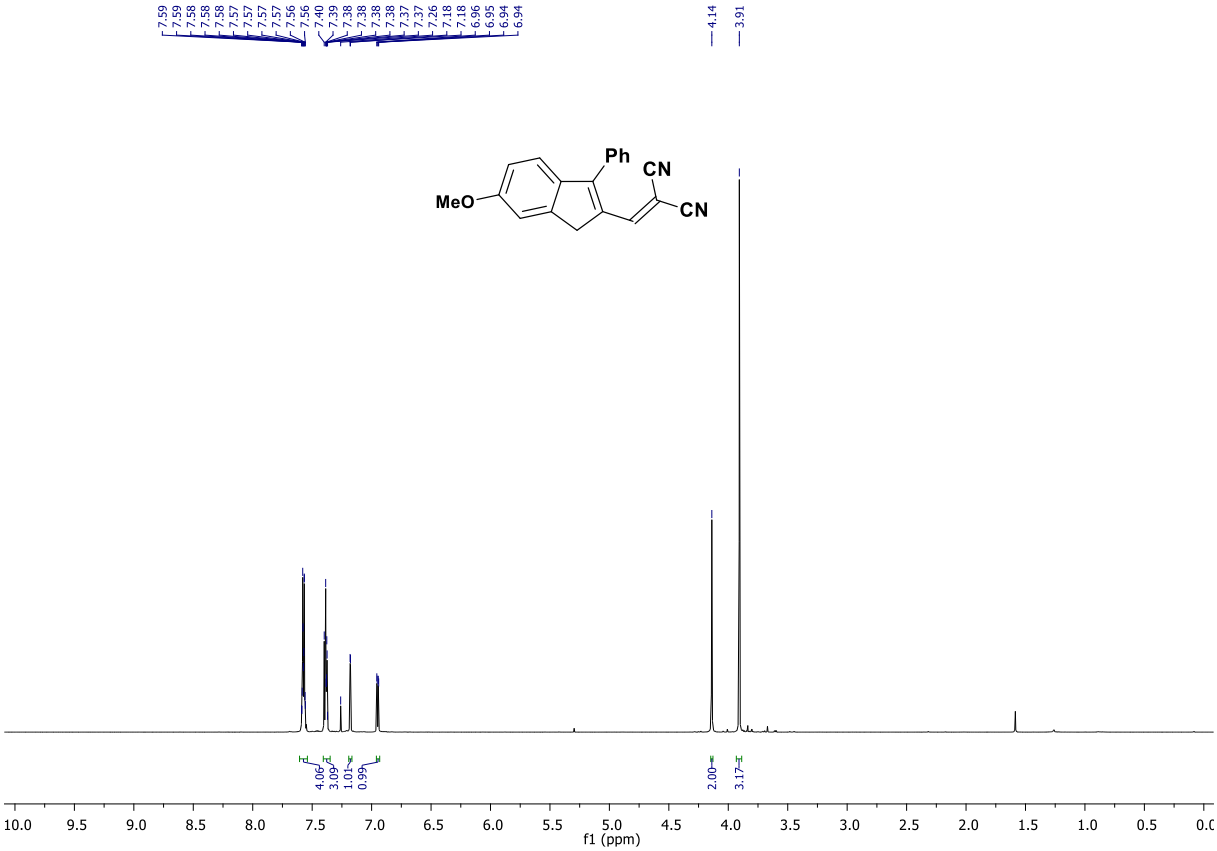


^{13}C NMR (176 MHz, $CDCl_3$)

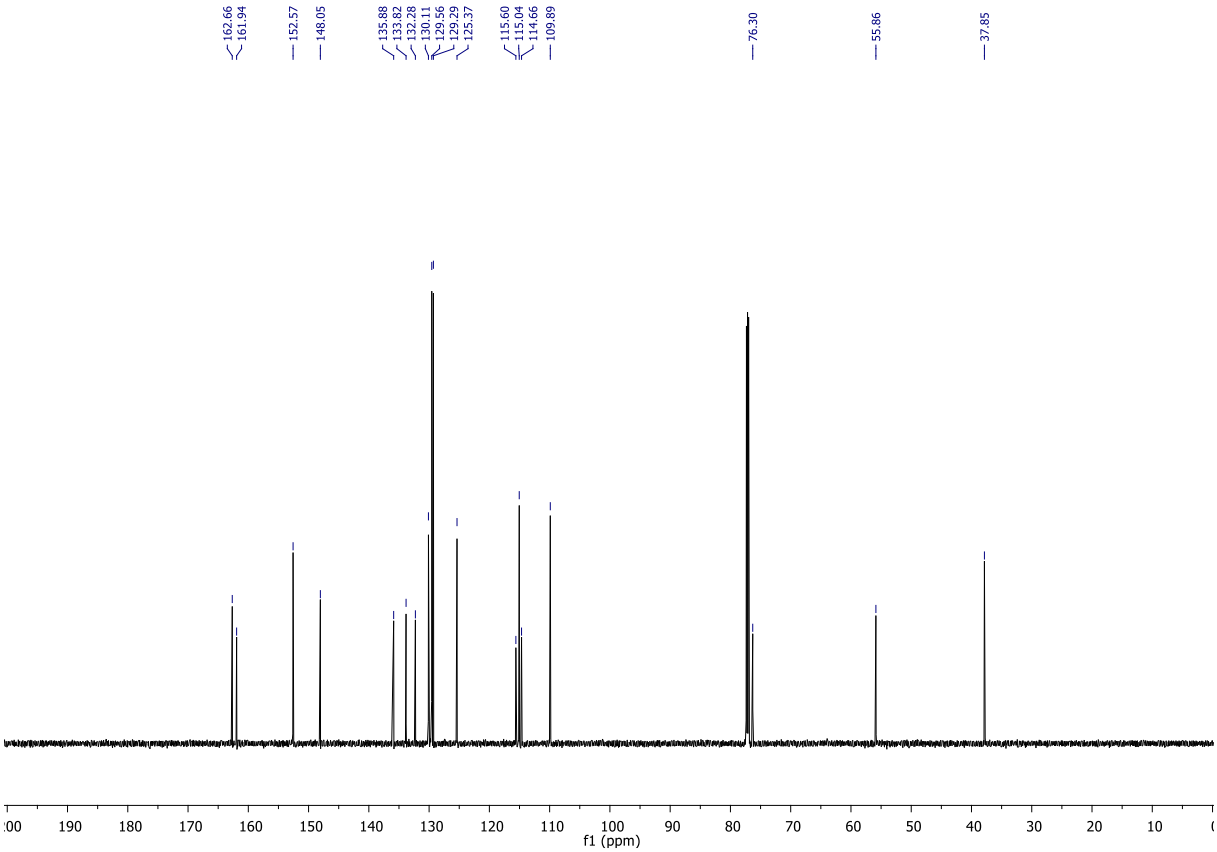


2-((6-methoxy-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1c

^{1}H NMR (700 MHz, $CDCl_3$)

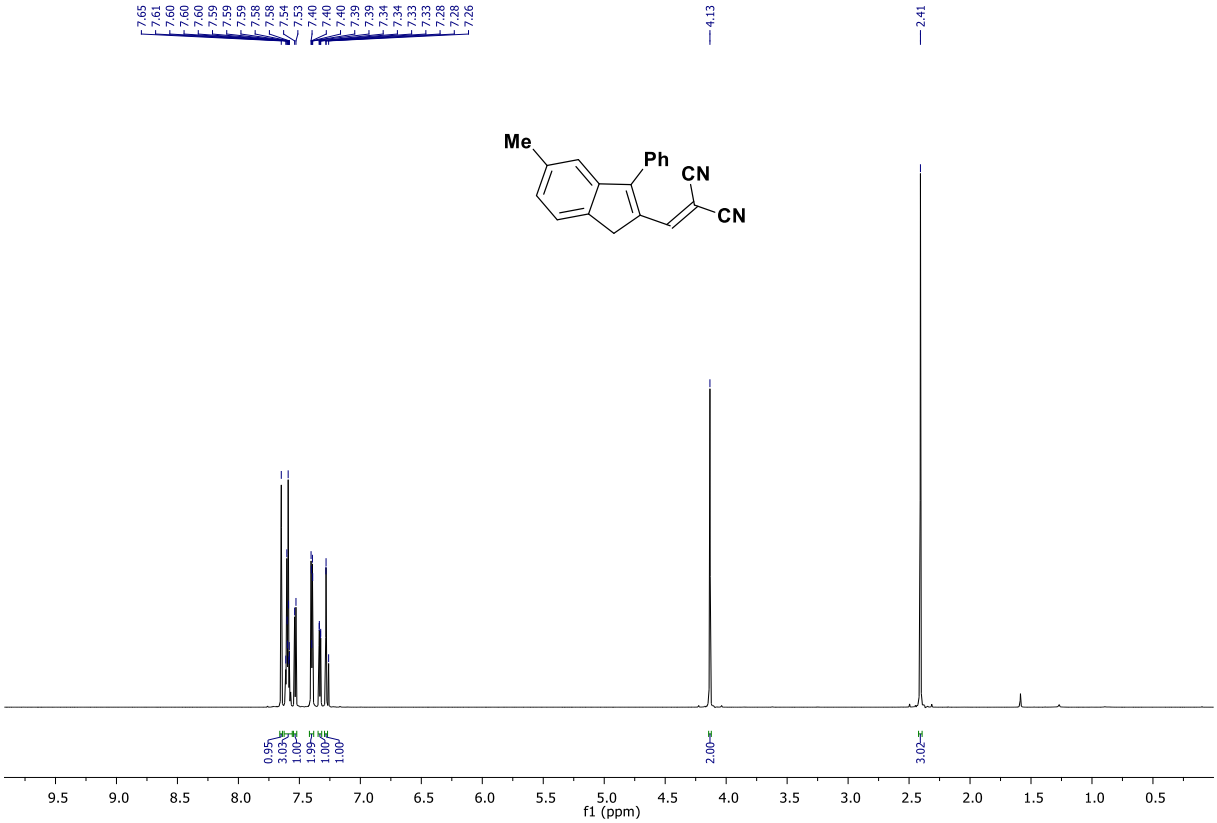


^{13}C NMR (176 MHz, $CDCl_3$)

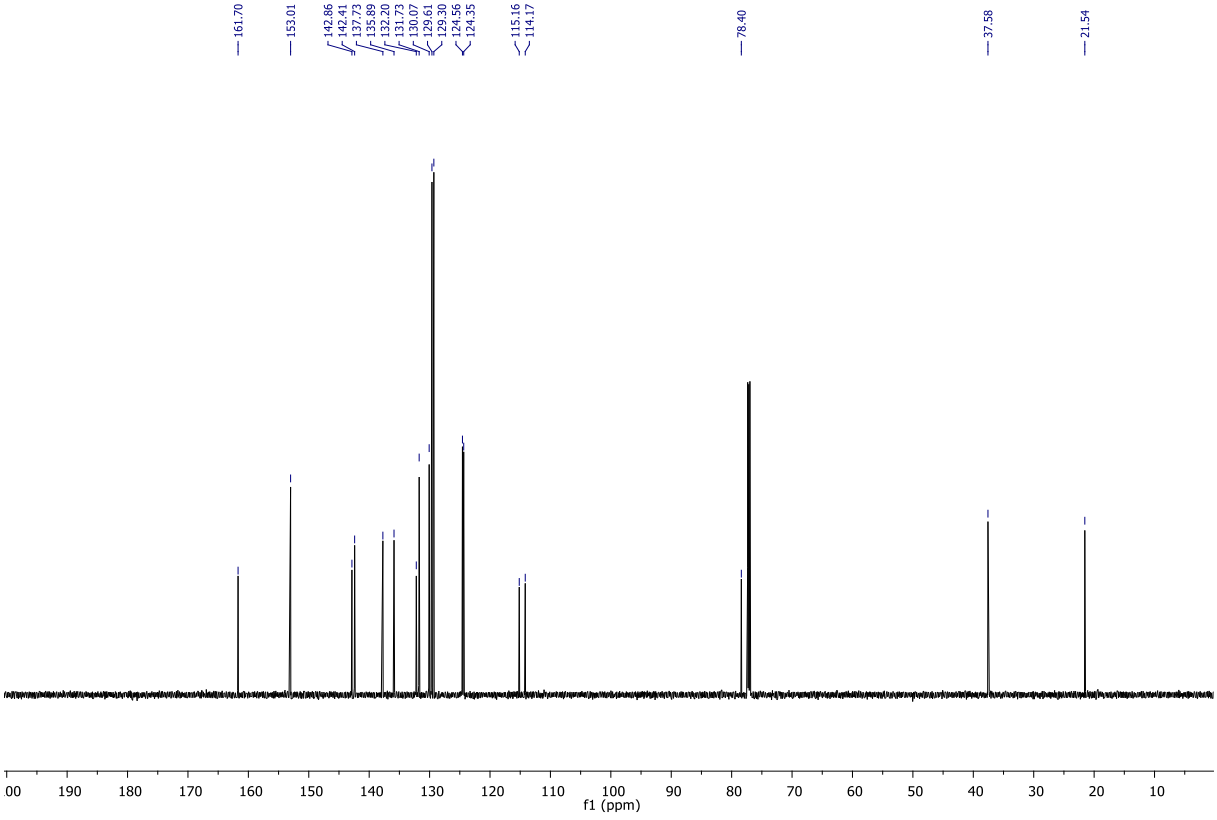


2-((5-methyl-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1d

^{1}H NMR (700 MHz, $CDCl_3$)

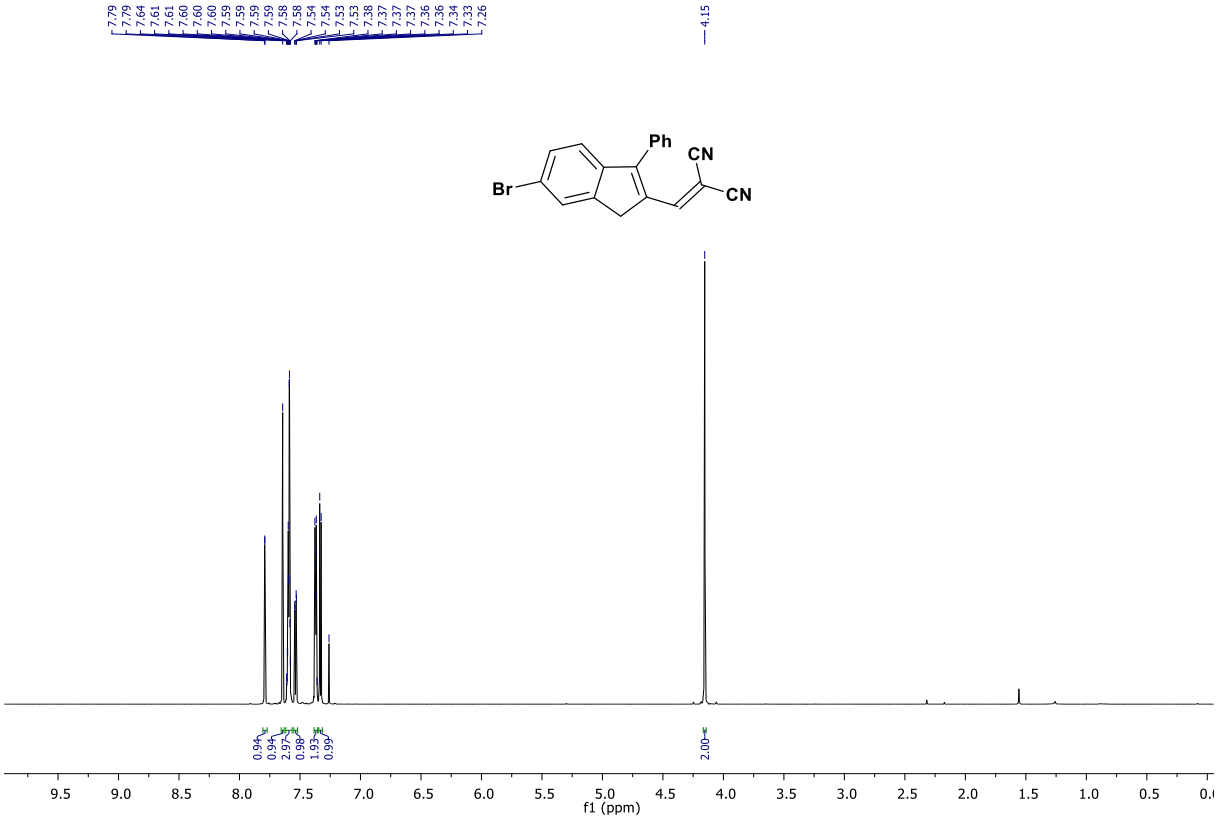


^{13}C NMR (176 MHz, $CDCl_3$)

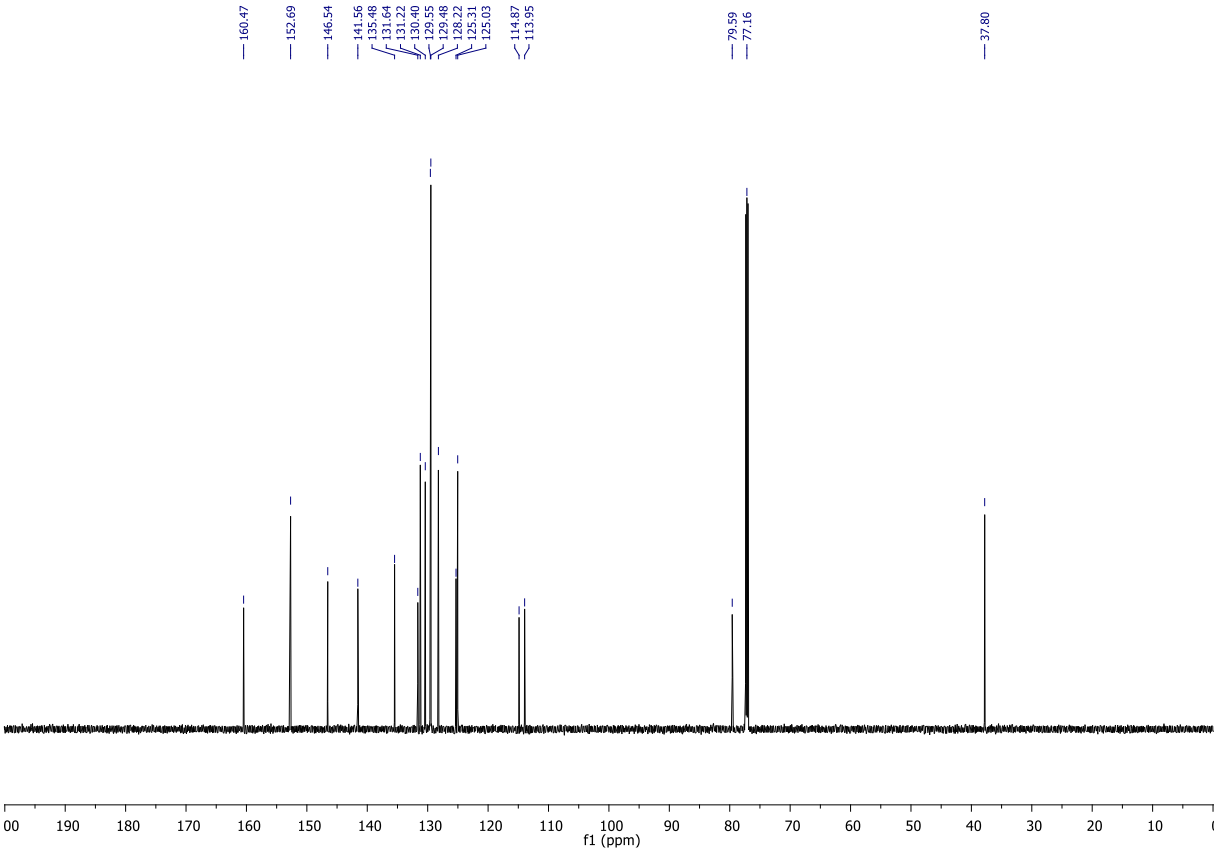


2-((6-bromo-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1e

^{1}H NMR (700 MHz, $CDCl_3$)

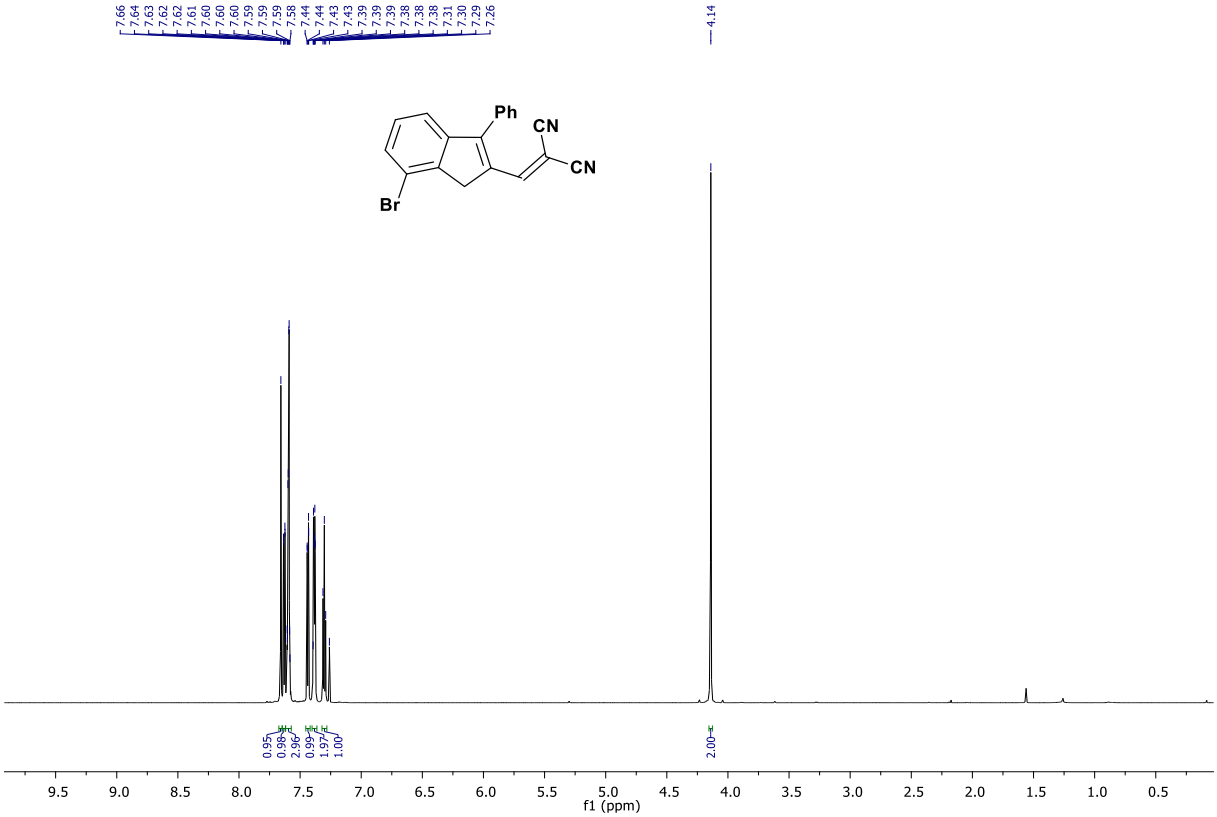


^{13}C NMR (176 MHz, $CDCl_3$)

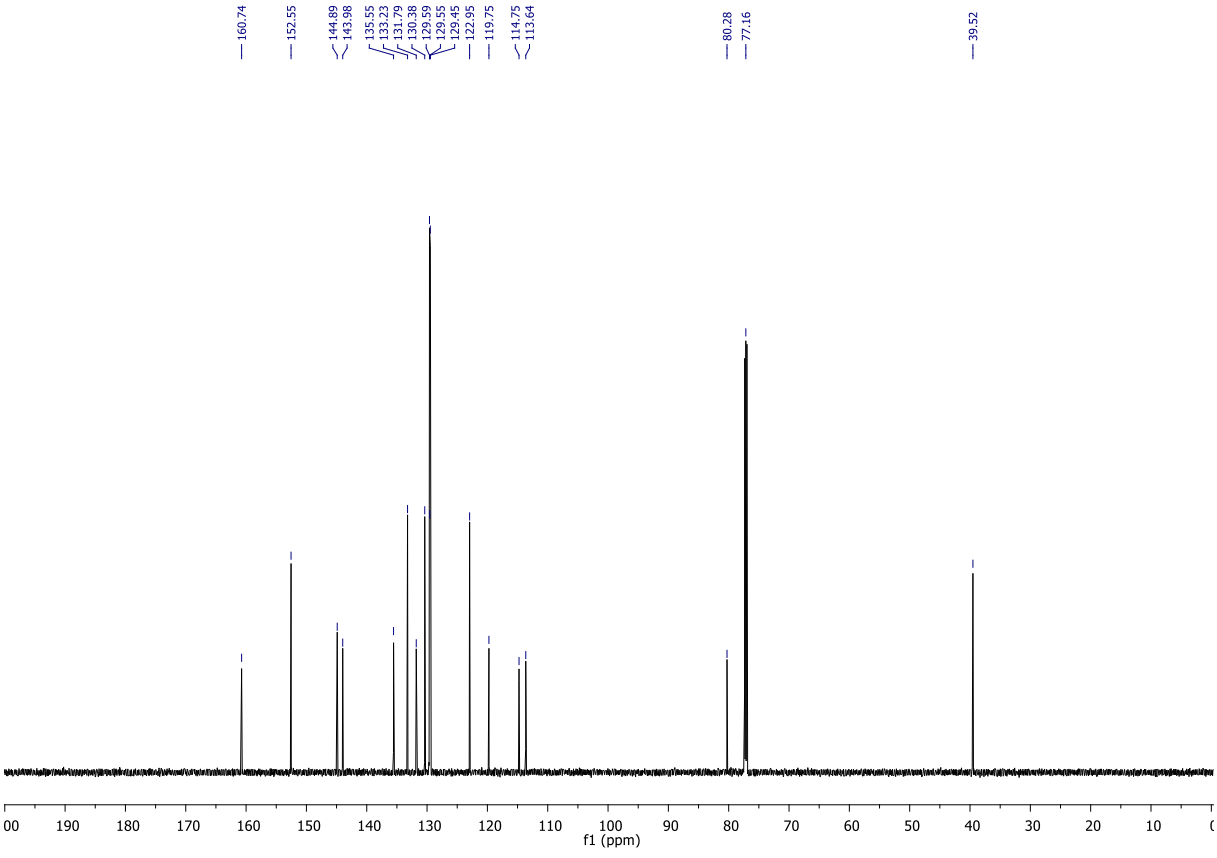


2-((7-bromo-3-phenyl-1*H*-inden-2-yl)methylene)malononitrile 1f

^{1}H NMR (700 MHz, $CDCl_3$)

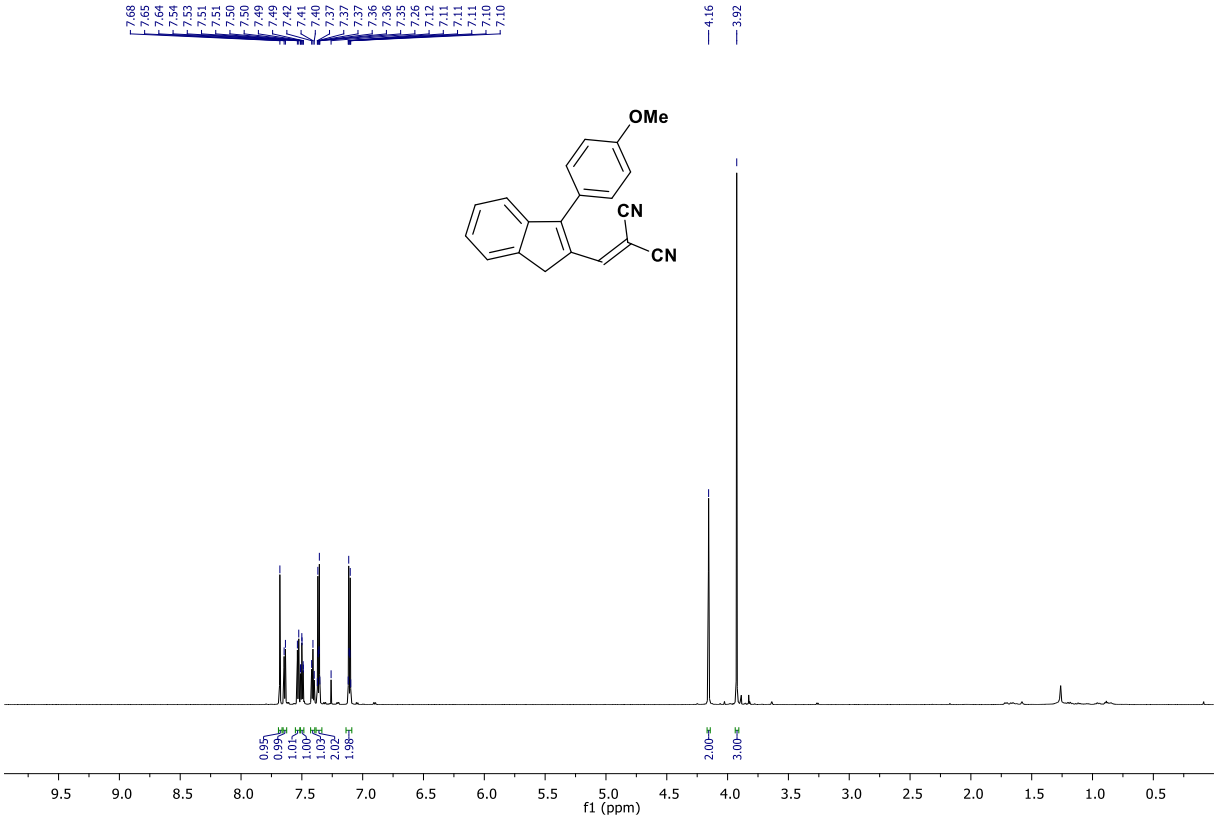


^{13}C NMR (176 MHz, $CDCl_3$)

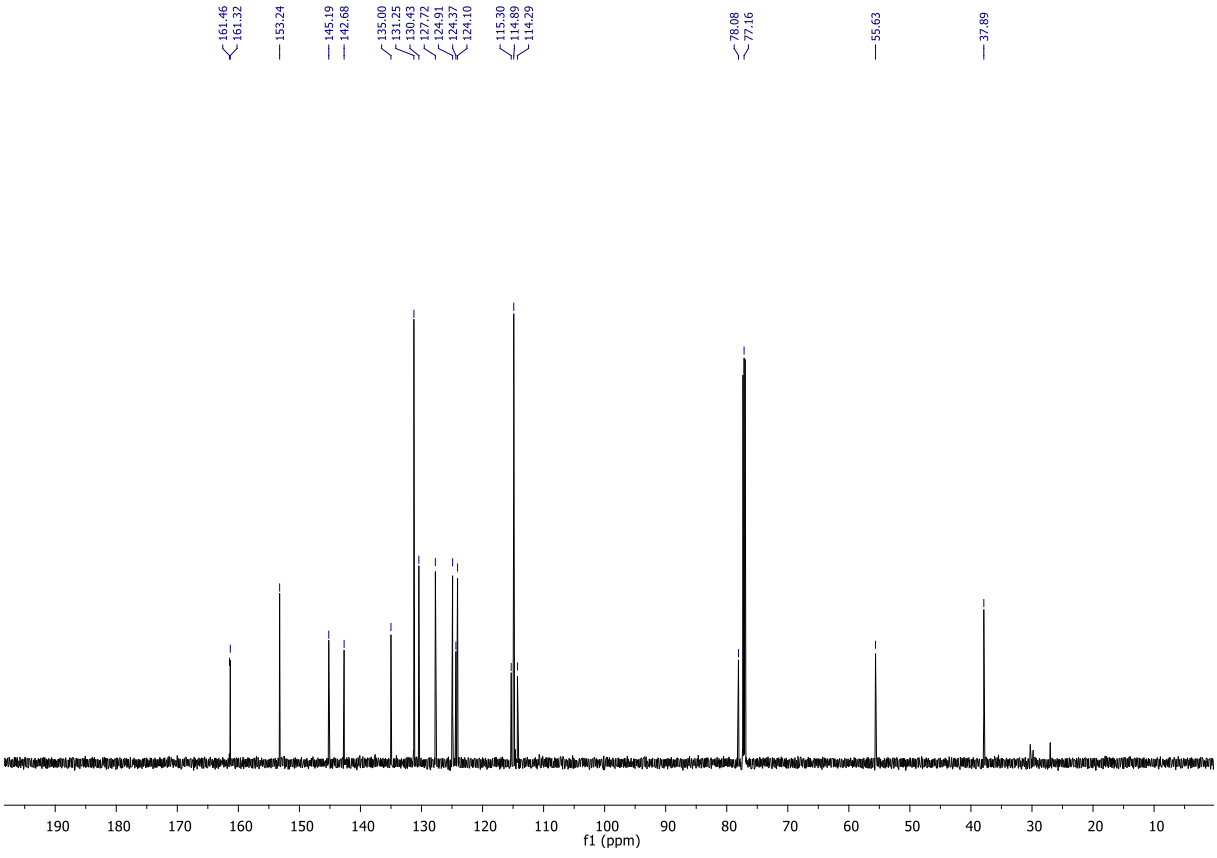


2-((3-(4-methoxyphenyl)-1*H*-inden-2-yl)methylene)malononitrile 1g

^{1}H NMR (700 MHz, $CDCl_3$)

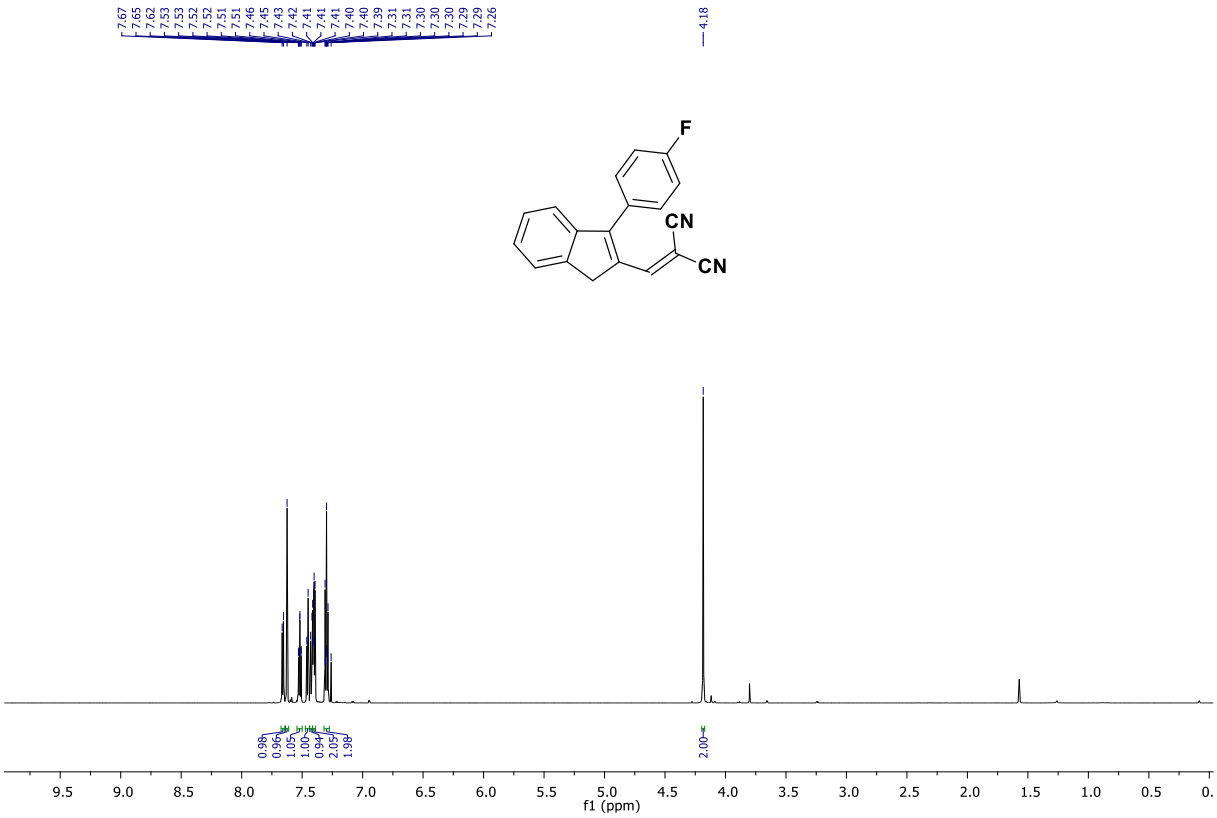


^{13}C NMR (176 MHz, $CDCl_3$)

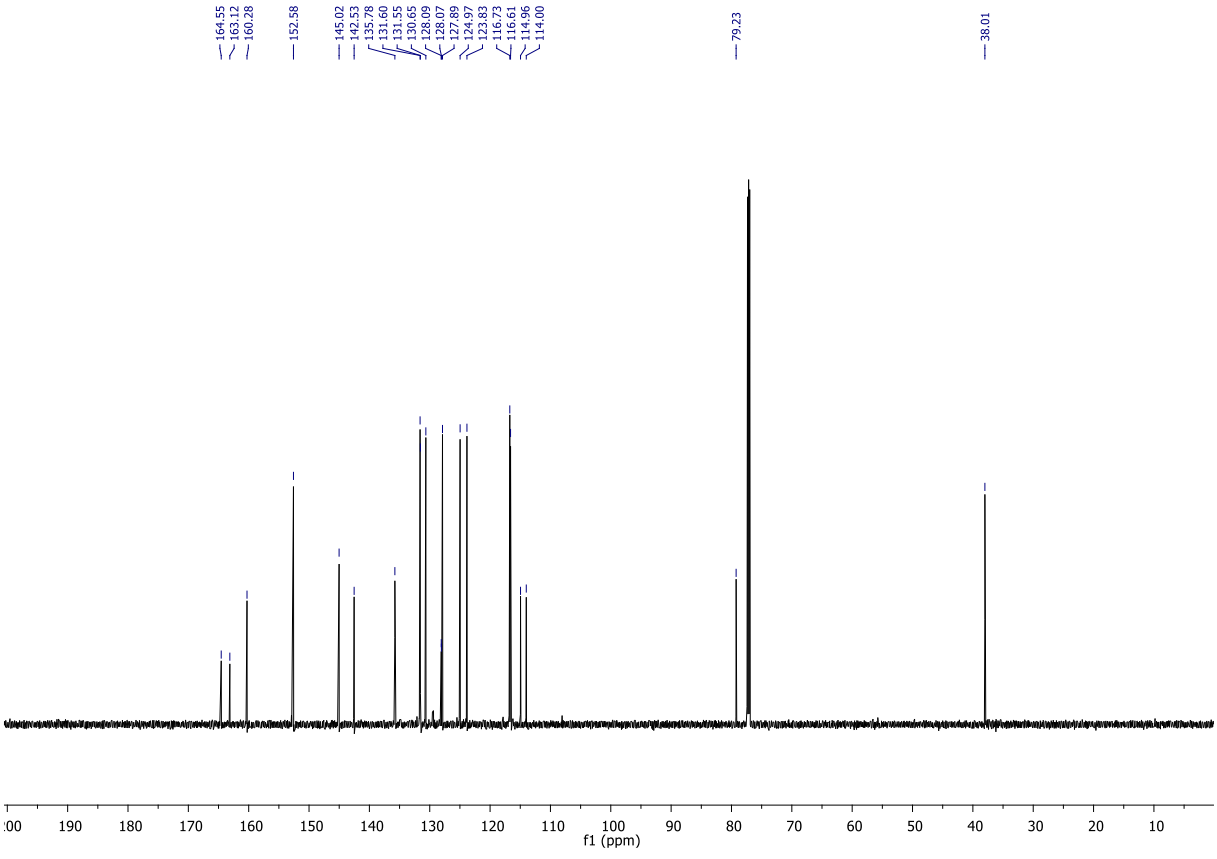


2-((3-(4-fluorophenyl)-1*H*-inden-2-yl)methylene)malononitrile 1h

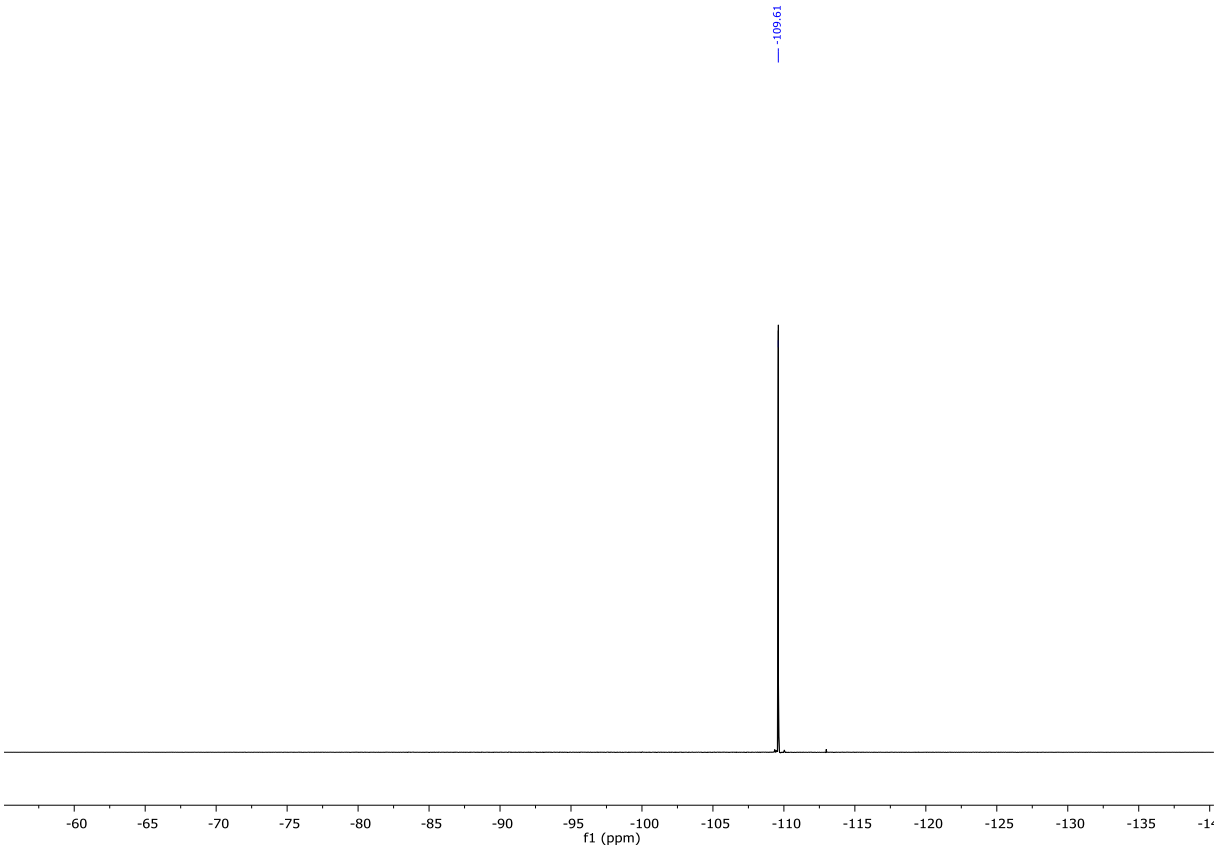
^{1}H NMR (700 MHz, $CDCl_3$)



^{13}C NMR (176 MHz, $CDCl_3$)

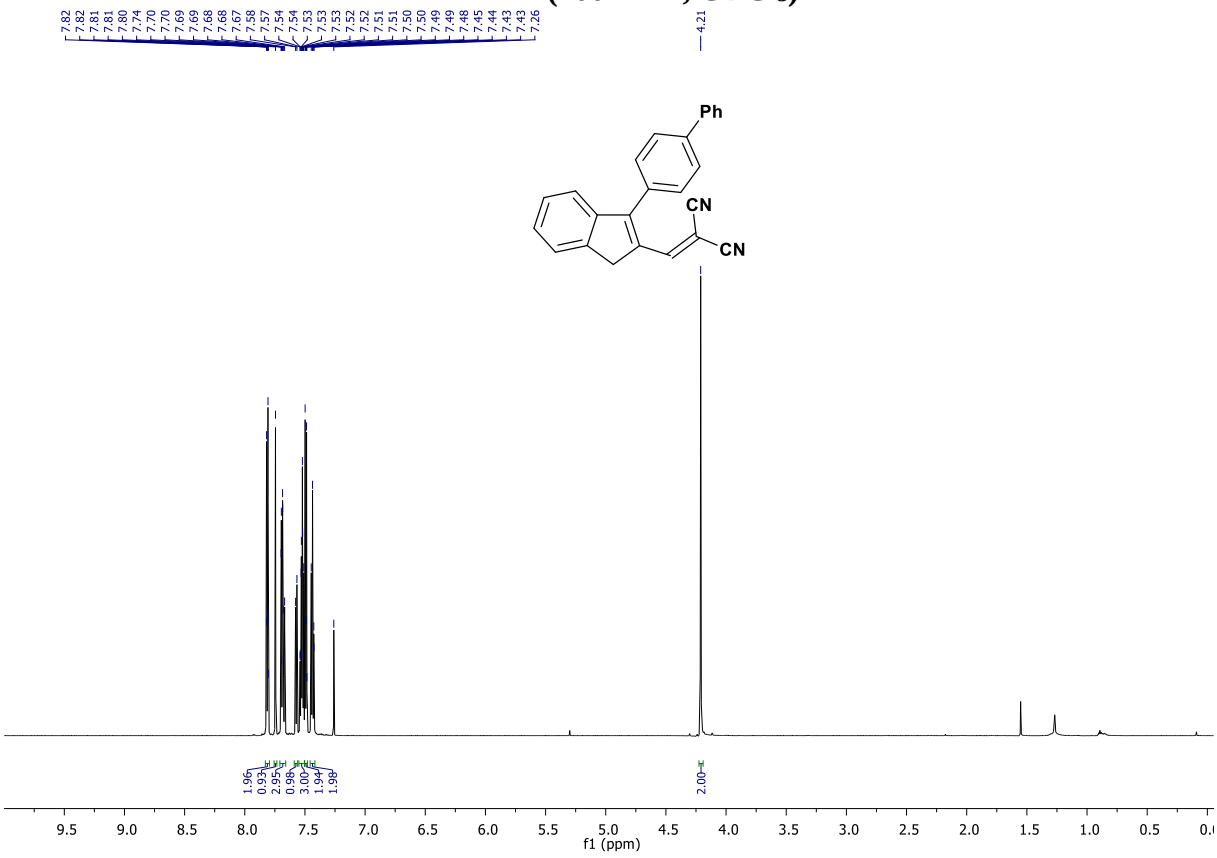


^{19}F NMR (376 MHz, $CDCl_3$)

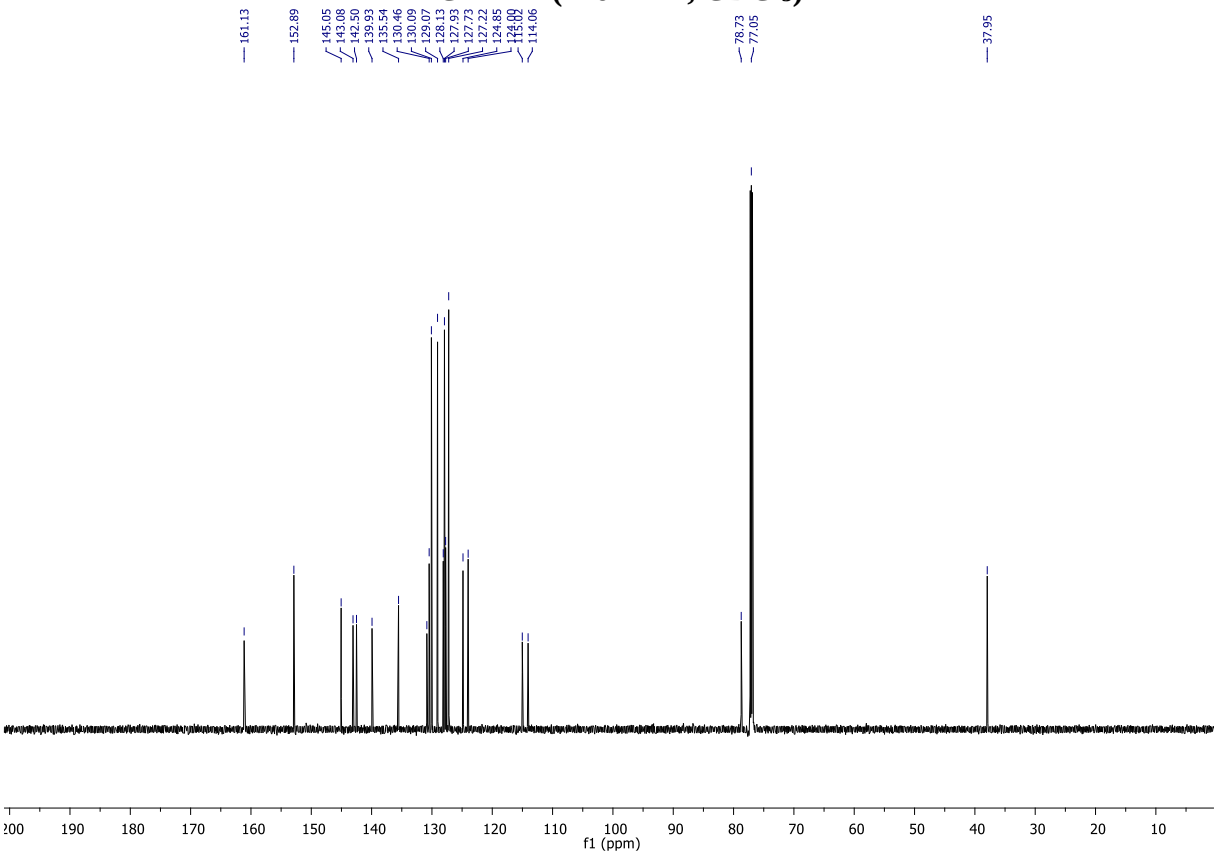


2-((3-([1,1'-biphenyl]-4-yl)-1*H*-inden-2-yl)methylene)malononitrile 1i

^{1}H NMR (700 MHz, $CDCl_3$)

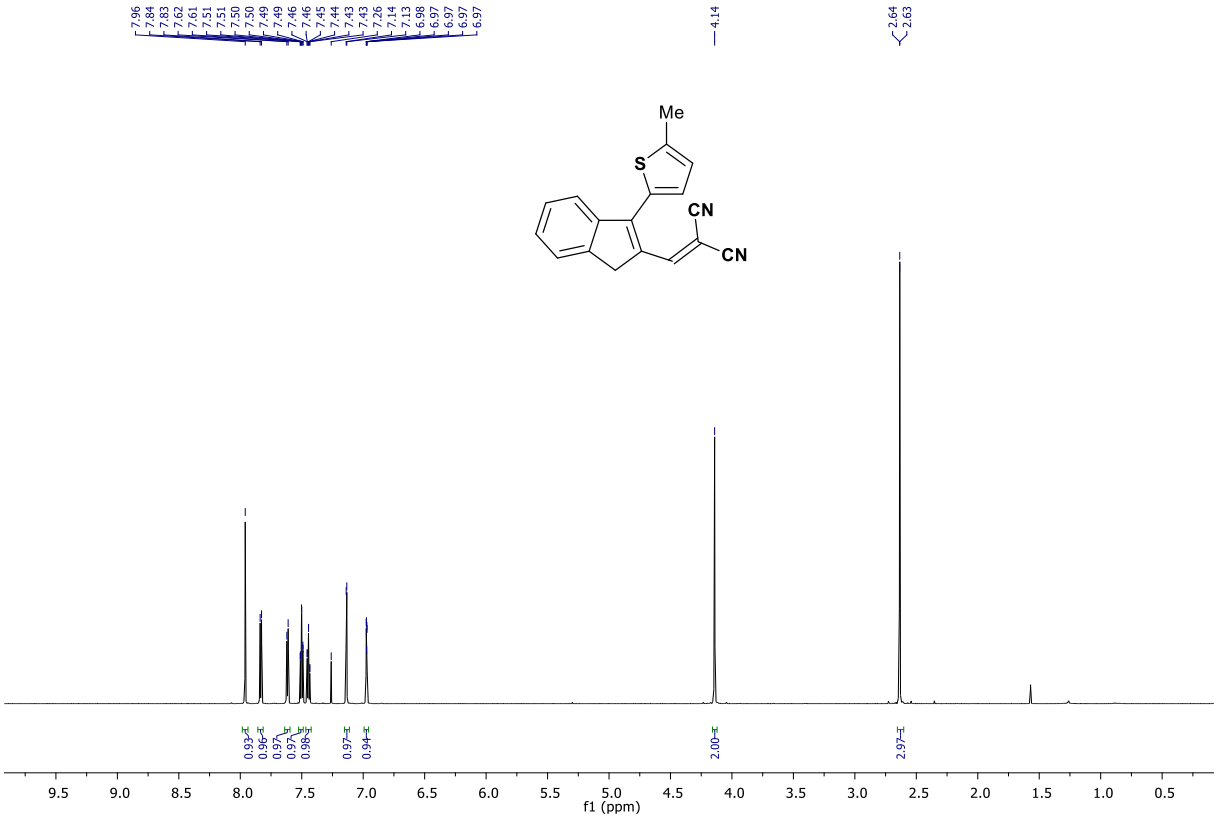


^{13}C NMR (176 MHz, $CDCl_3$)

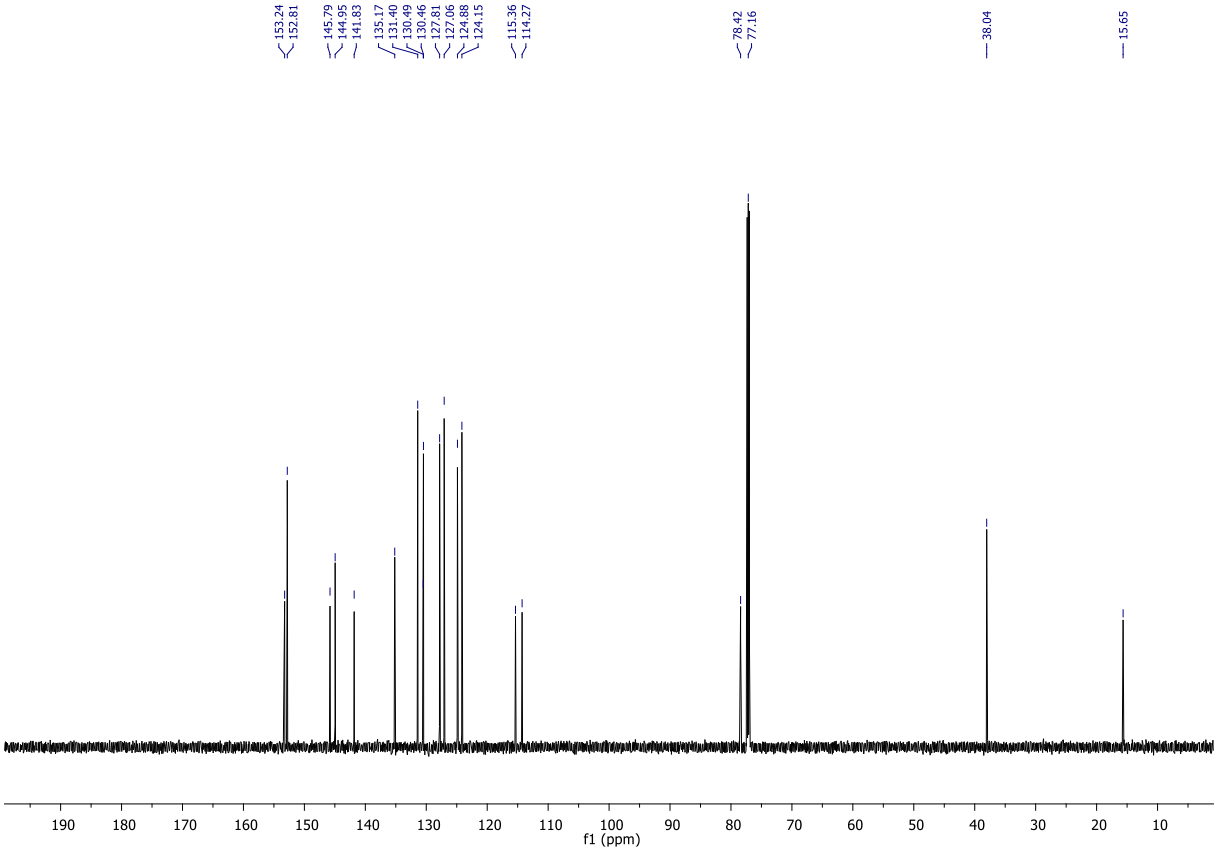


2-((3-(5-methylthiophen-2-yl)-1*H*-inden-2-yl)methylene)malononitrile 1j

^{1}H NMR (700 MHz, $CDCl_3$)

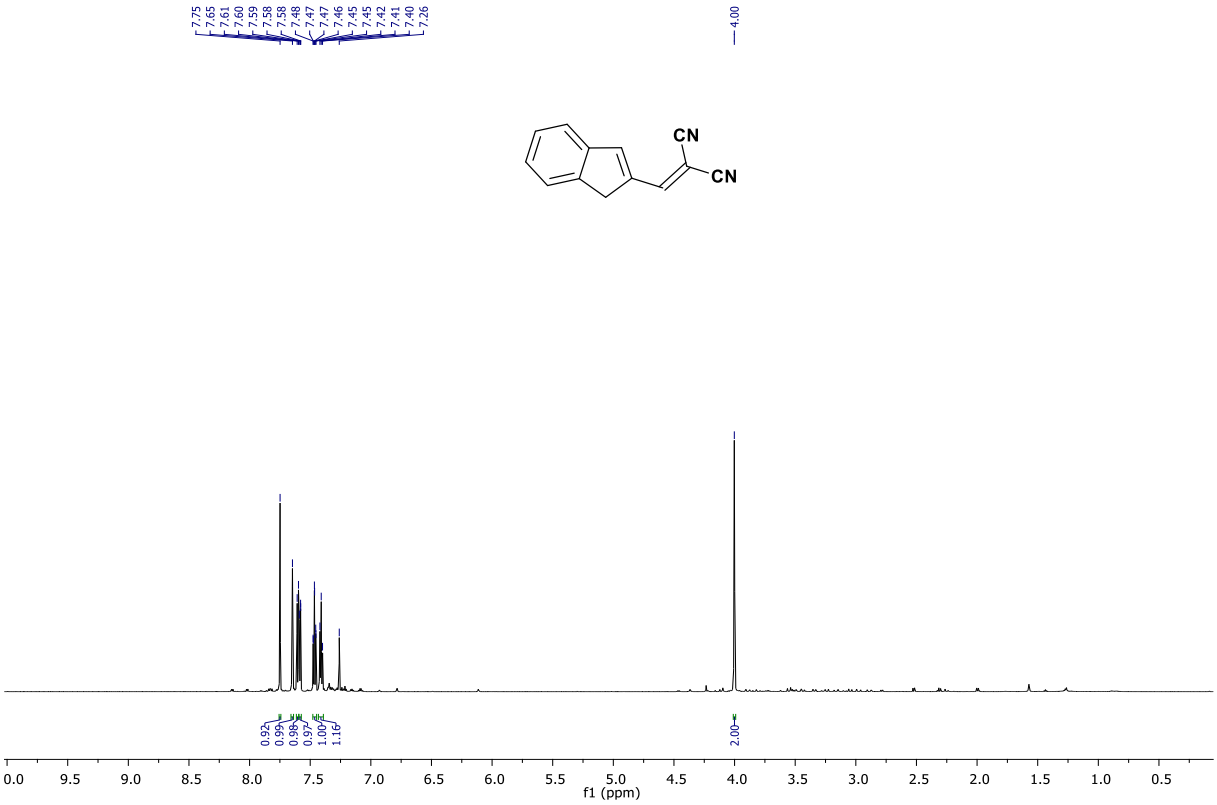


^{13}C NMR (176 MHz, $CDCl_3$)

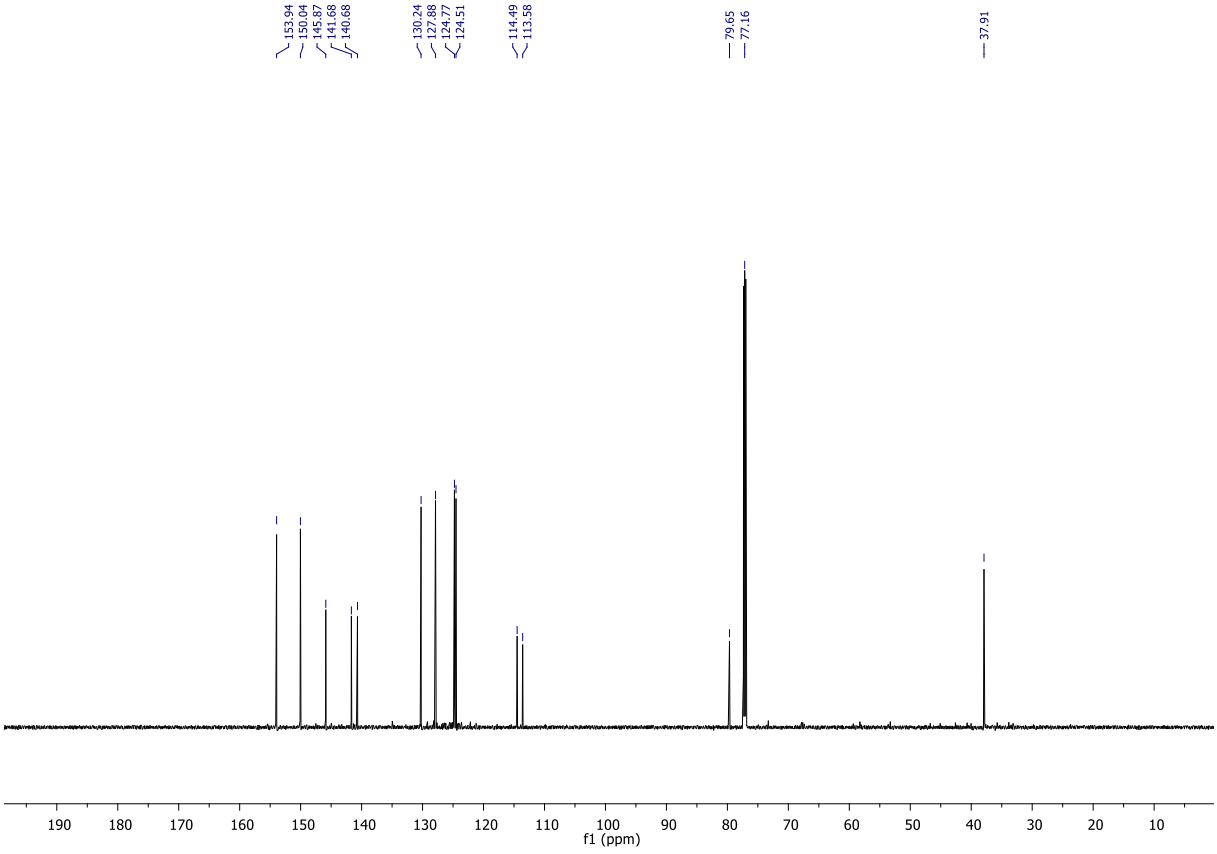


2-((1*H*-inden-2-yl)methylene)malononitrile 1k

^{1}H NMR (700 MHz, $CDCl_3$)

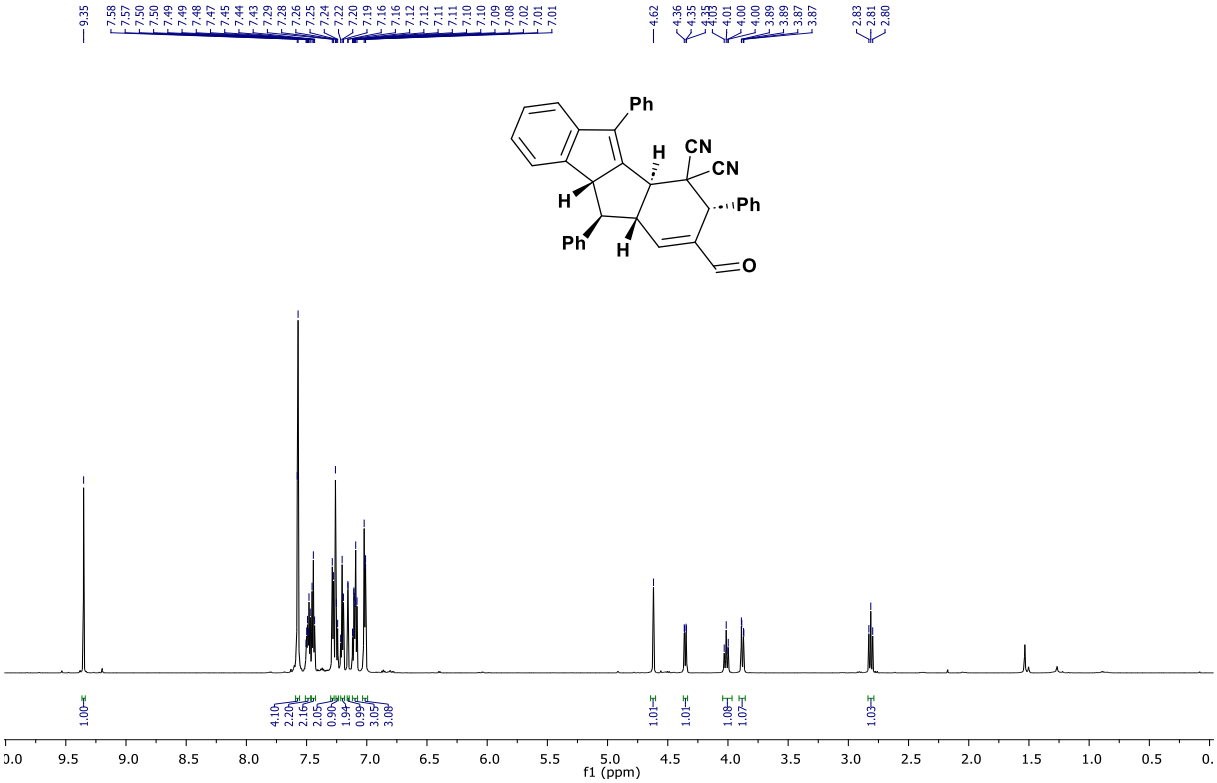


^{13}C NMR (176 MHz, $CDCl_3$)

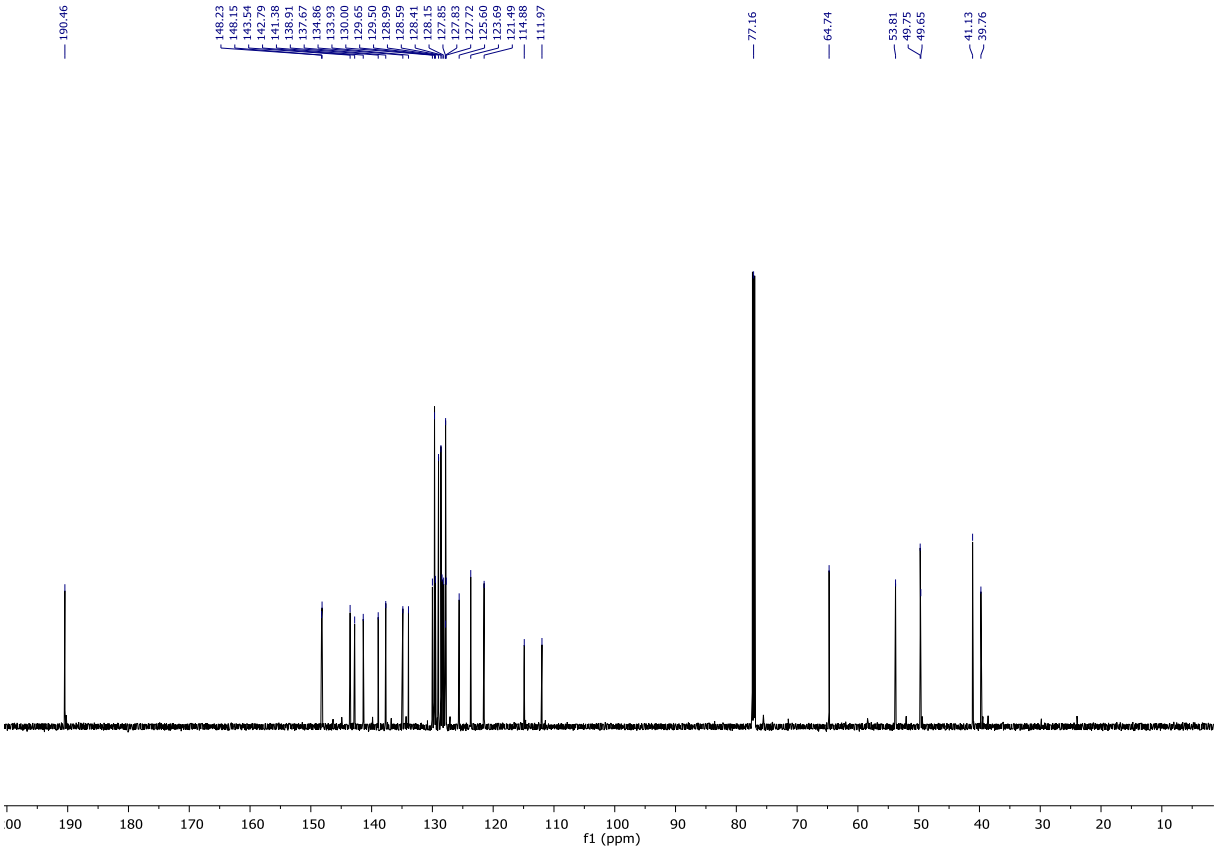


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3a

^{1}H NMR (700 MHz, $CDCl_3$)

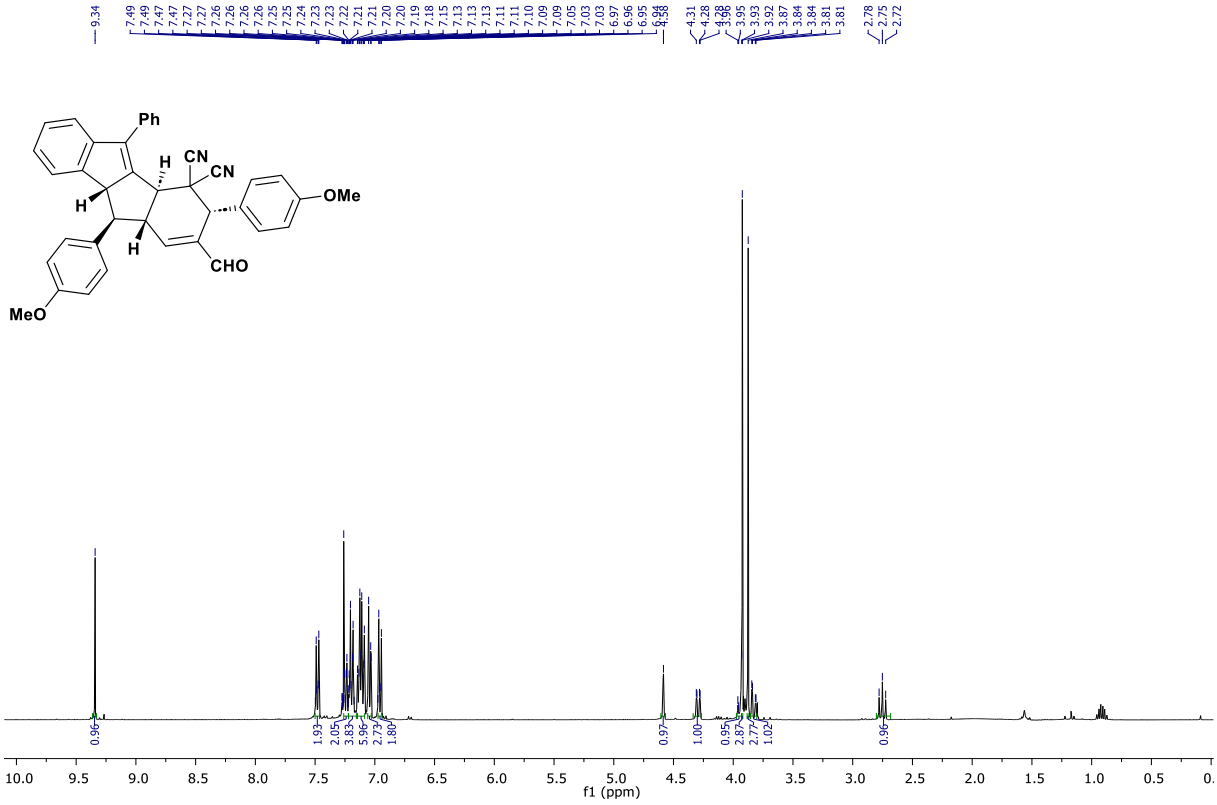


^{13}C NMR (176 MHz, $CDCl_3$)

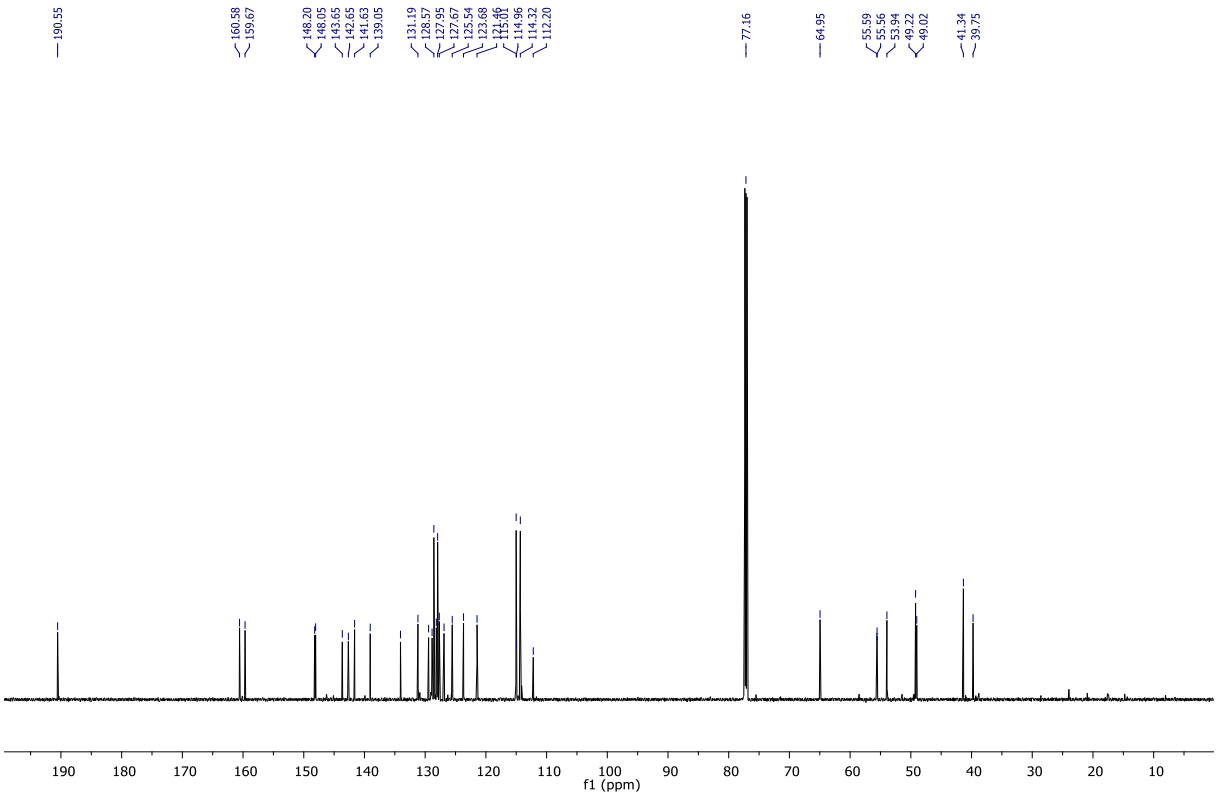


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-bis(4-methoxyphenyl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3b

^{1}H NMR (700 MHz, CDCl$_3$)

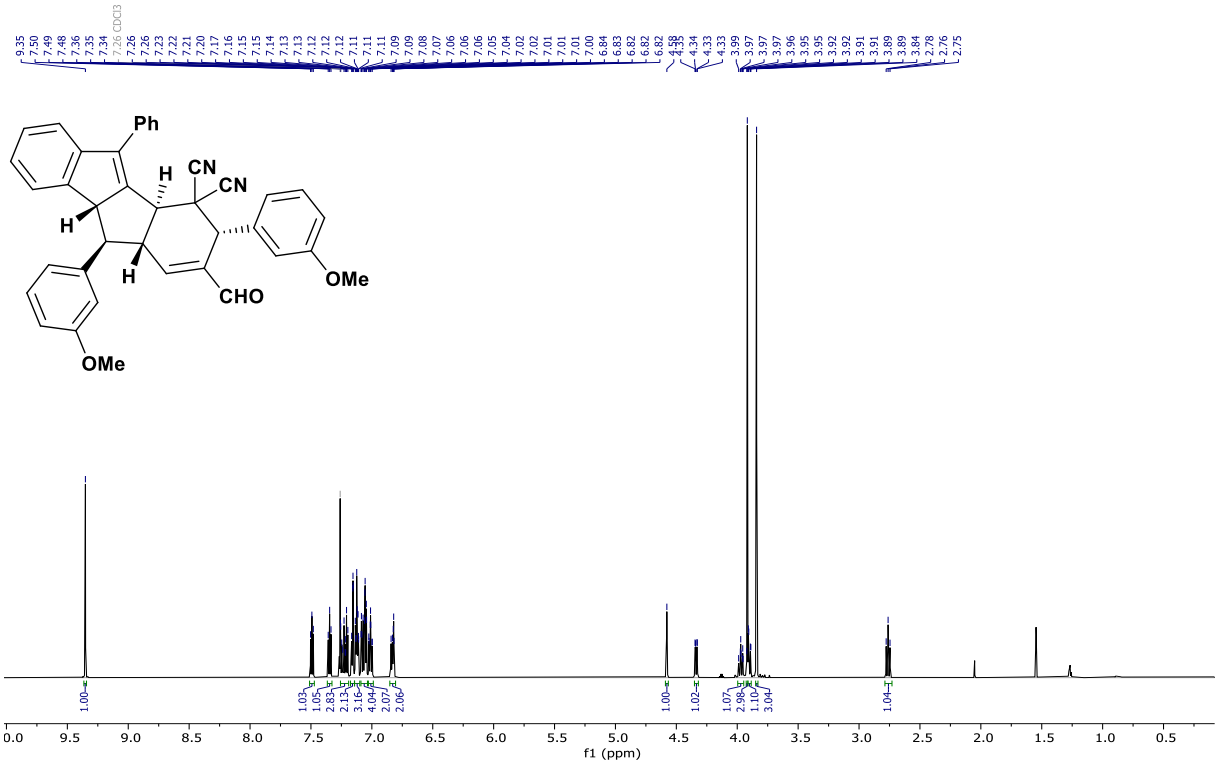


^{13}C NMR (176 MHz, CDCl$_3$)

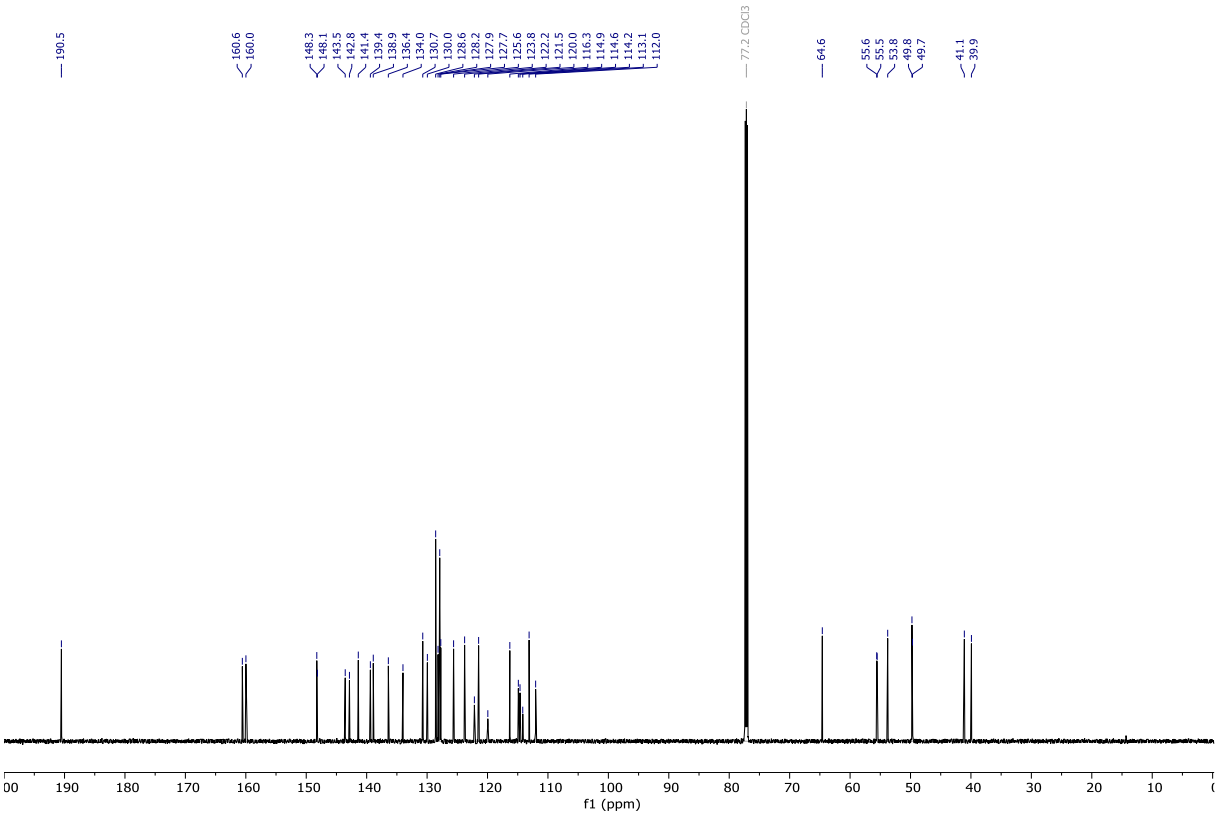


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-bis(3-methoxyphenyl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3c

^{1}H NMR (700 MHz, $CDCl_3$)

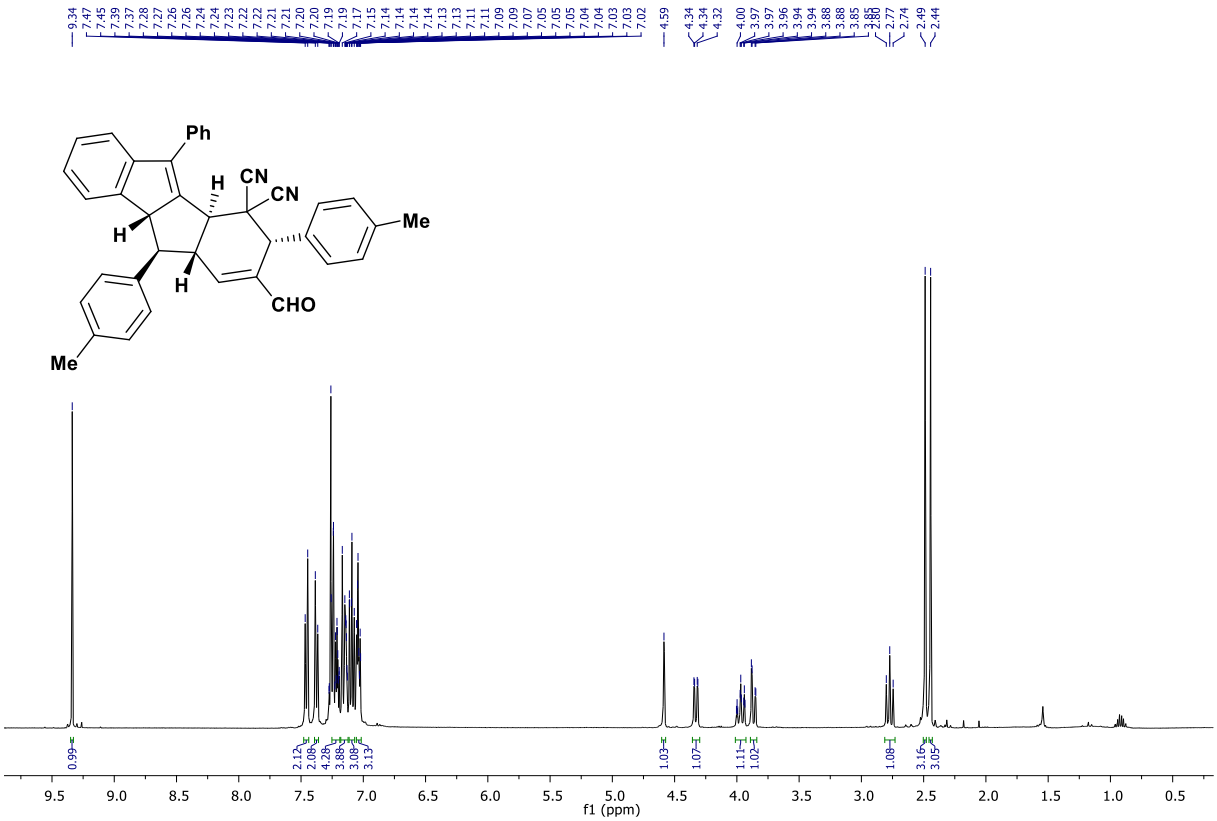


^{13}C NMR (176 MHz, $CDCl_3$)

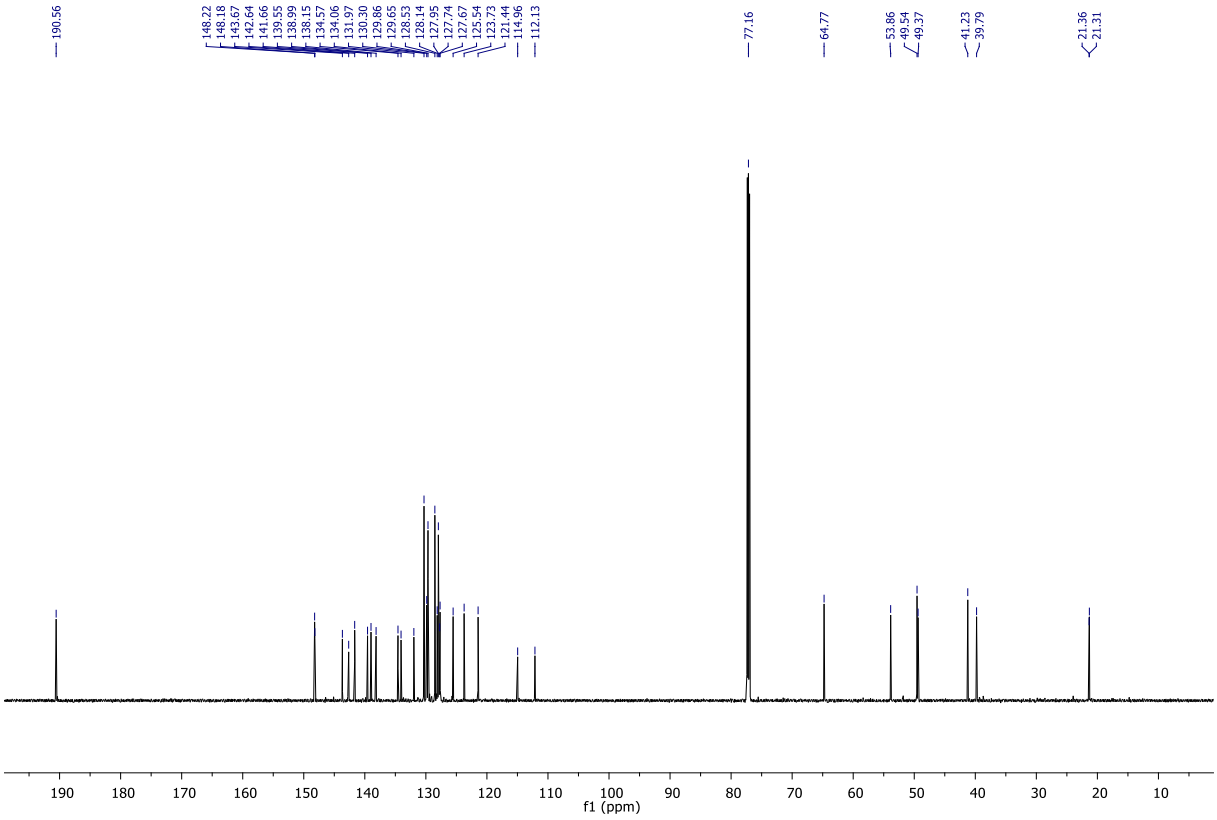


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-phenyl-3,10-di-p-tolyl-4a,9b,10,10a-tetrahydroindeno [2,1-a]indene-4,4(3H)-dicarbonitrile 3d

^{1}H NMR (700 MHz, $CDCl_3$)

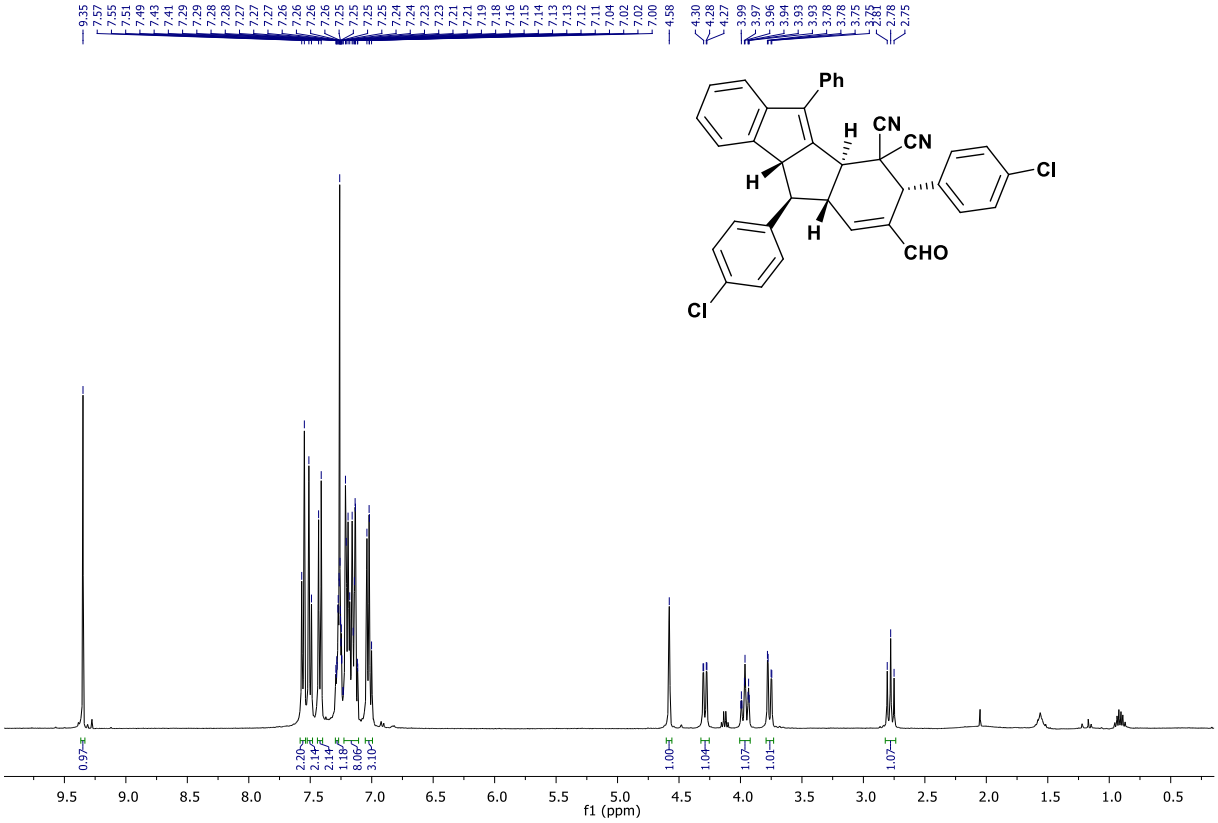


^{13}C NMR (176 MHz, $CDCl_3$)

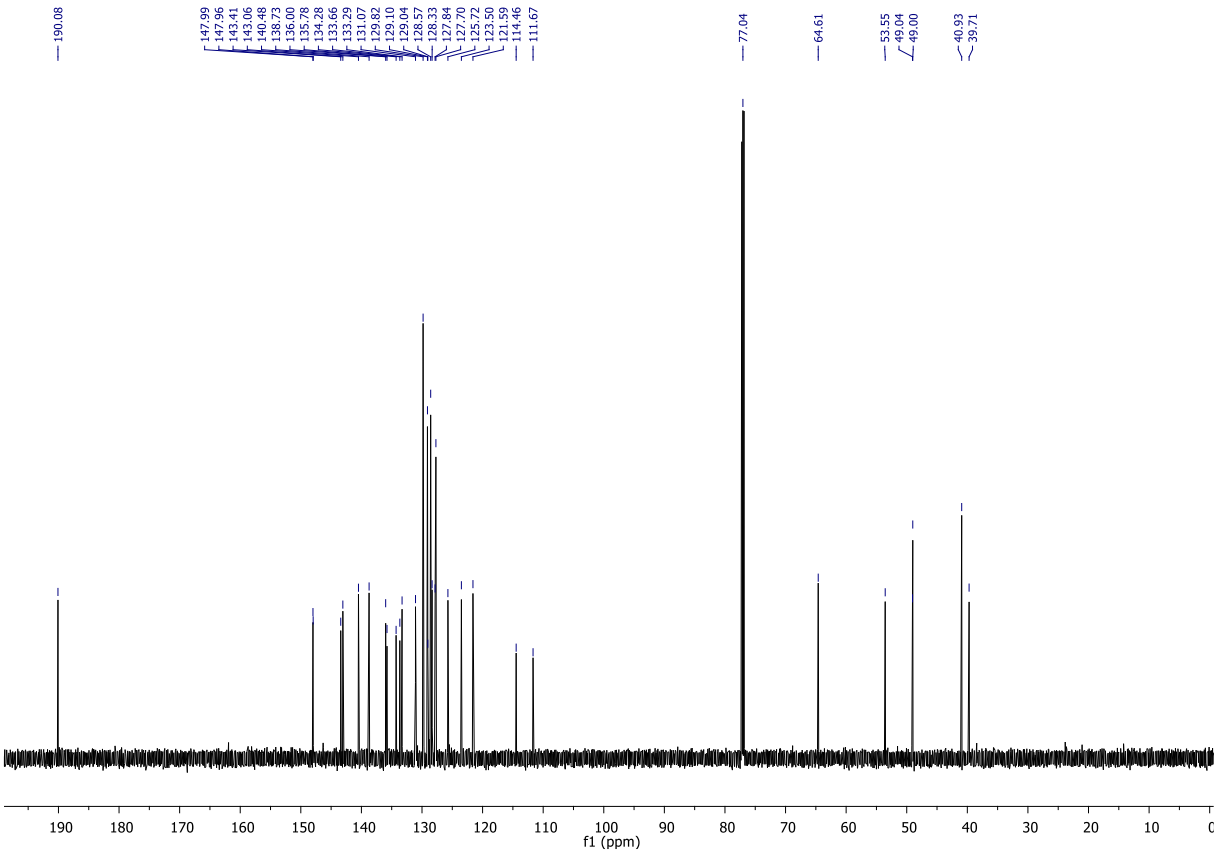


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-3,10-bis(4-chlorophenyl)-2-formyl-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3e

^{1}H NMR (700 MHz, $CDCl_3$)

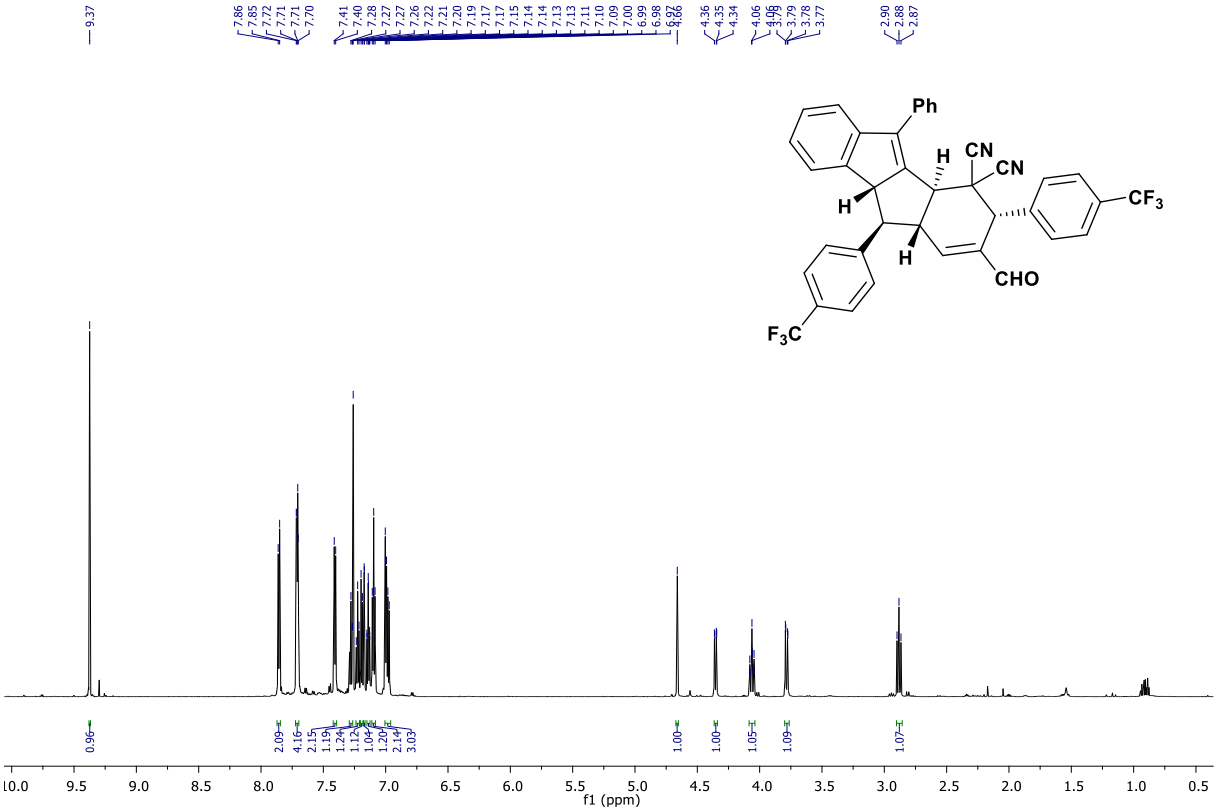


^{13}C NMR (176 MHz, $CDCl_3$)

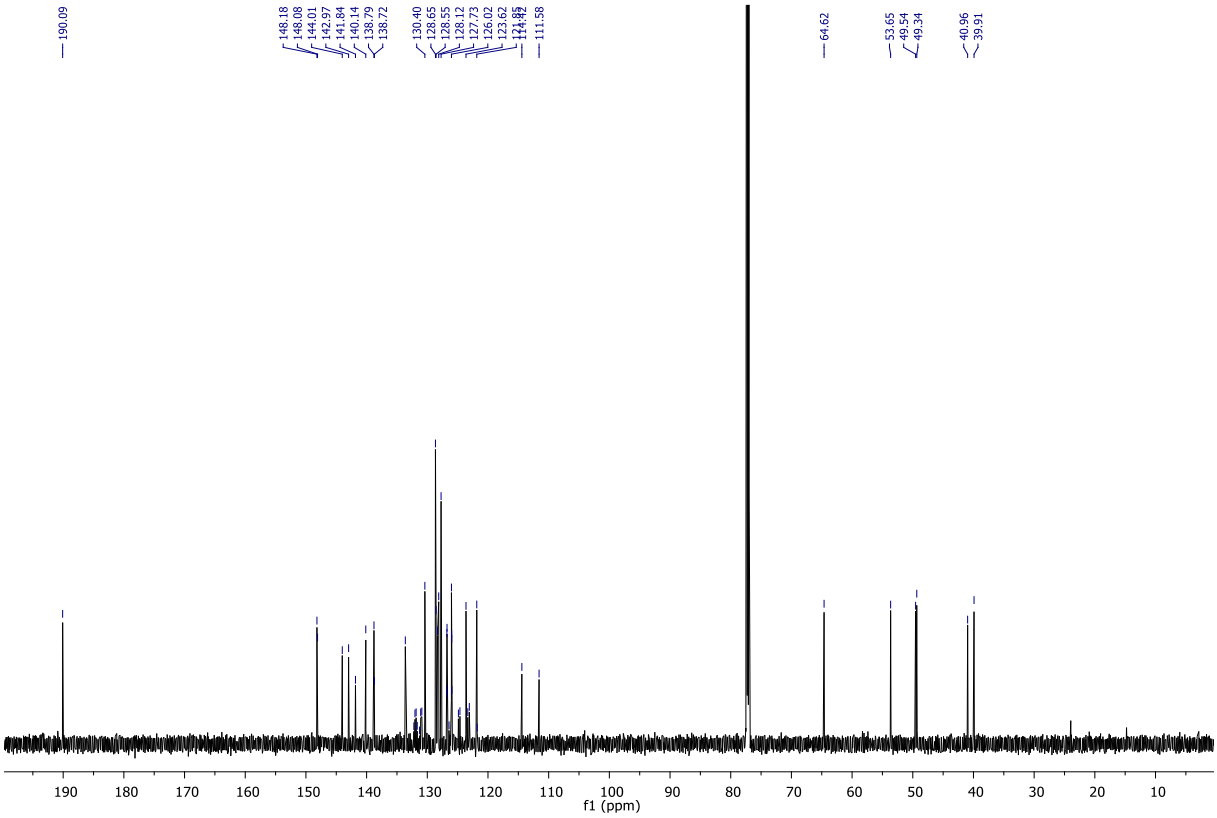


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-phenyl-3,10-bis(4-(trifluoromethyl)phenyl)-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3f

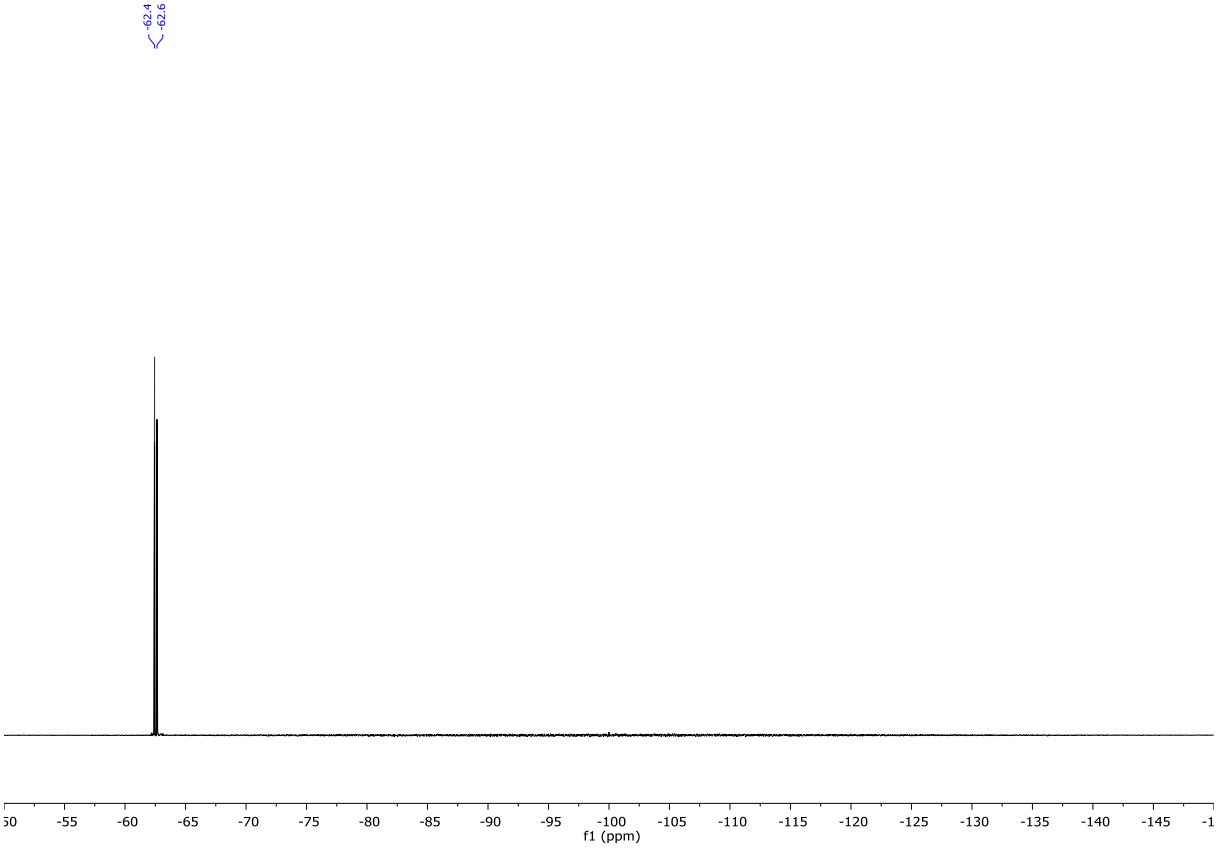
^{1}H NMR (700 MHz, CDCl$_3$)



^{13}C NMR (176 MHz, CDCl$_3$)

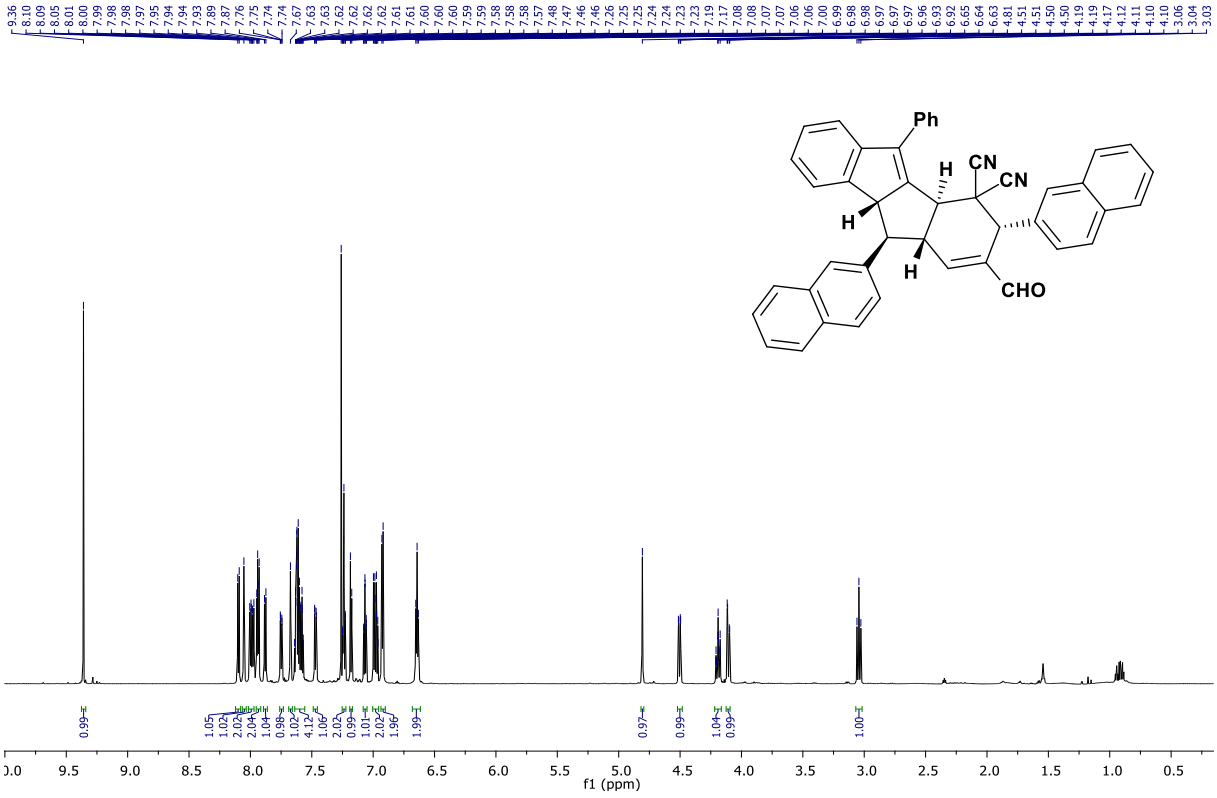


^{19}F NMR (376 MHz, $CDCl_3$)

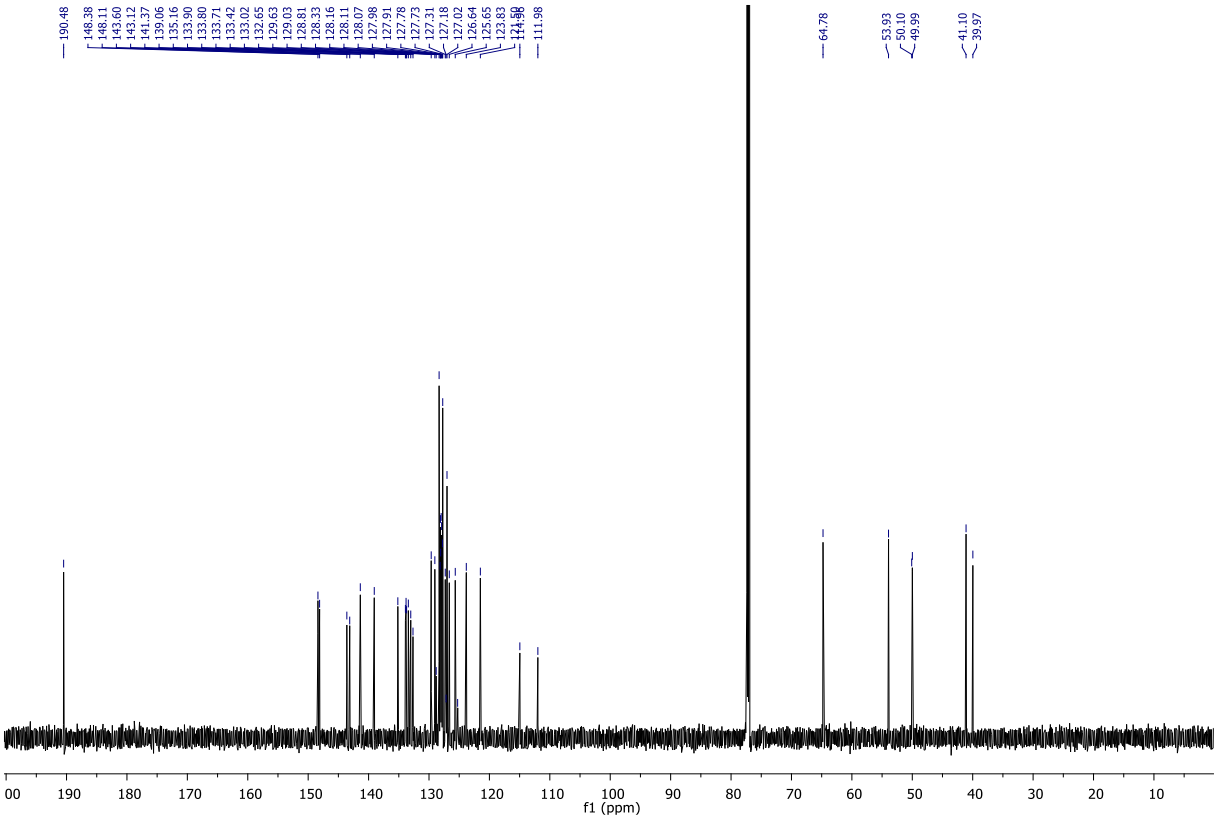


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-di(naphthalen-2-yl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3g

^{1}H NMR (700 MHz, $CDCl_3$)

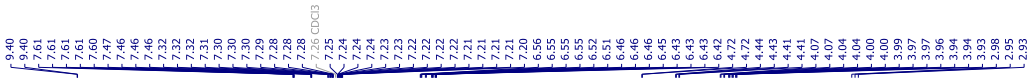


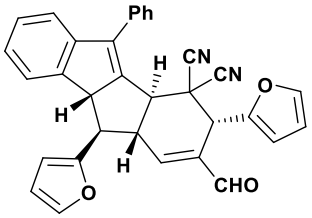
^{13}C NMR (176 MHz, $CDCl_3$)

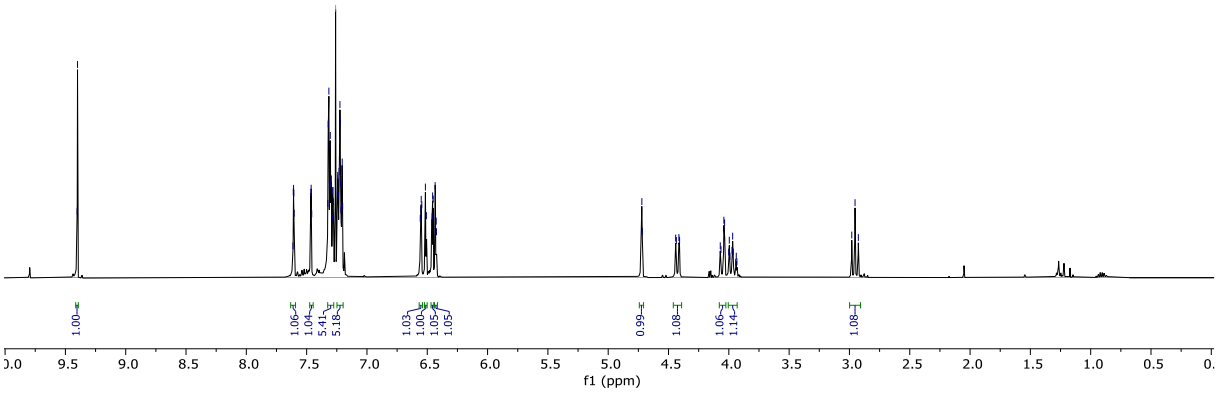


(3S,4aS,9bR,10R,10aS)-2-formyl-3,10-di(furan-2-yl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3h

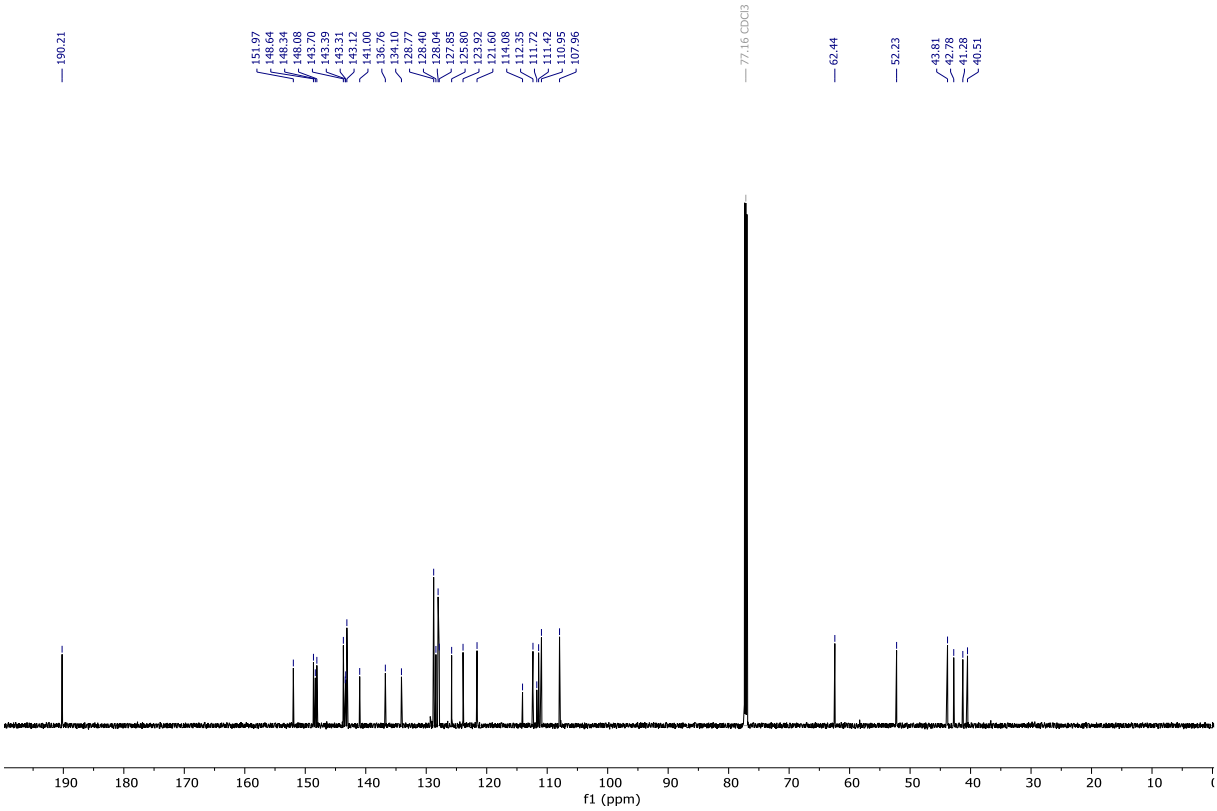
^{1}H NMR (700 MHz, $CDCl_3$)





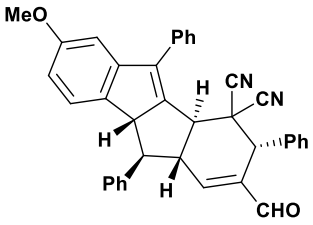


^{13}C NMR (176 MHz, $CDCl_3$)

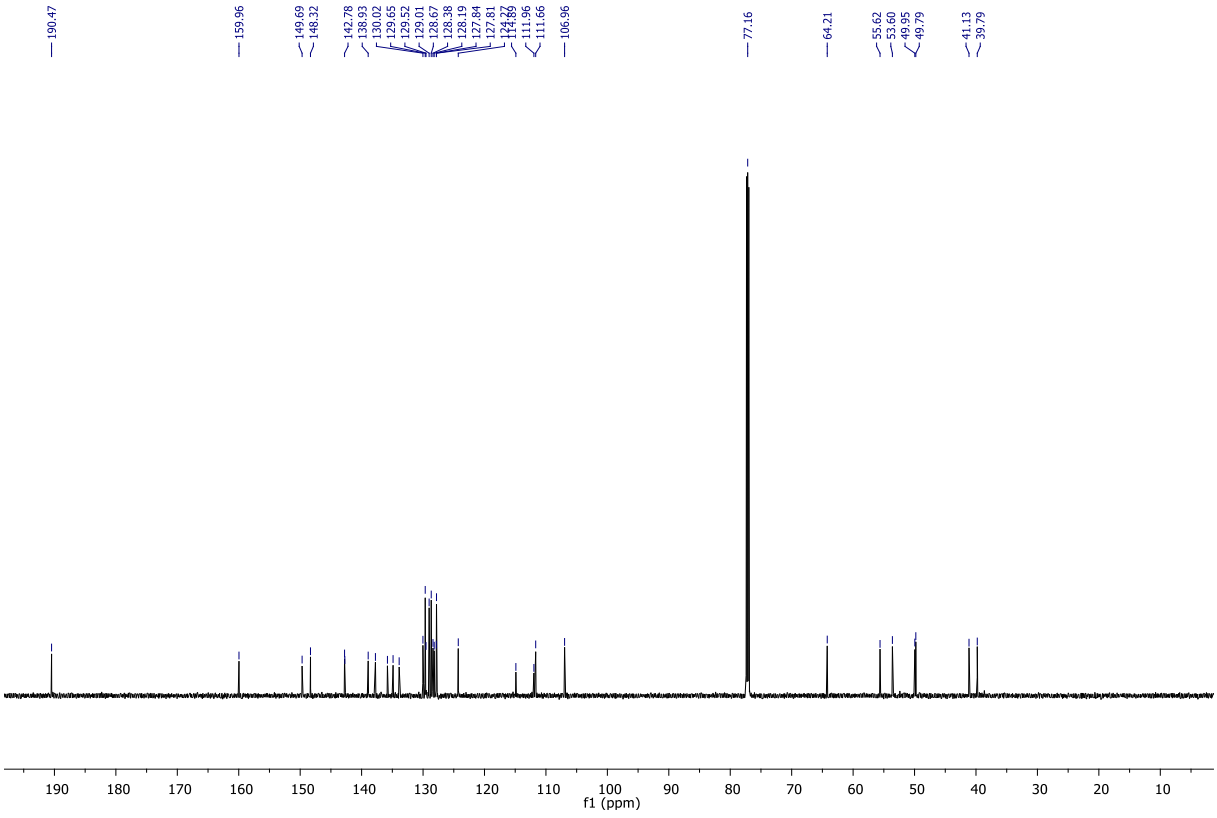


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-7-methoxy-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3i

^{1}H NMR (700 MHz, $CDCl_3$)

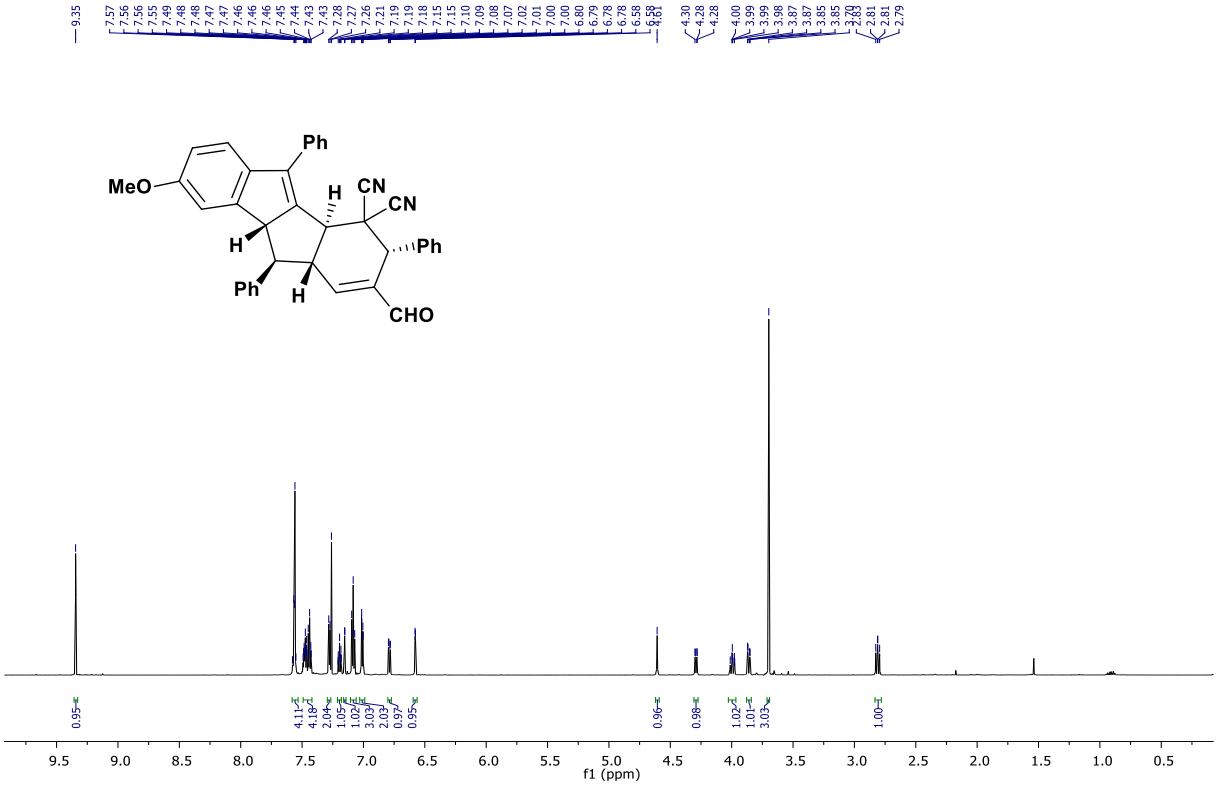


^{13}C NMR (176 MHz, $CDCl_3$)

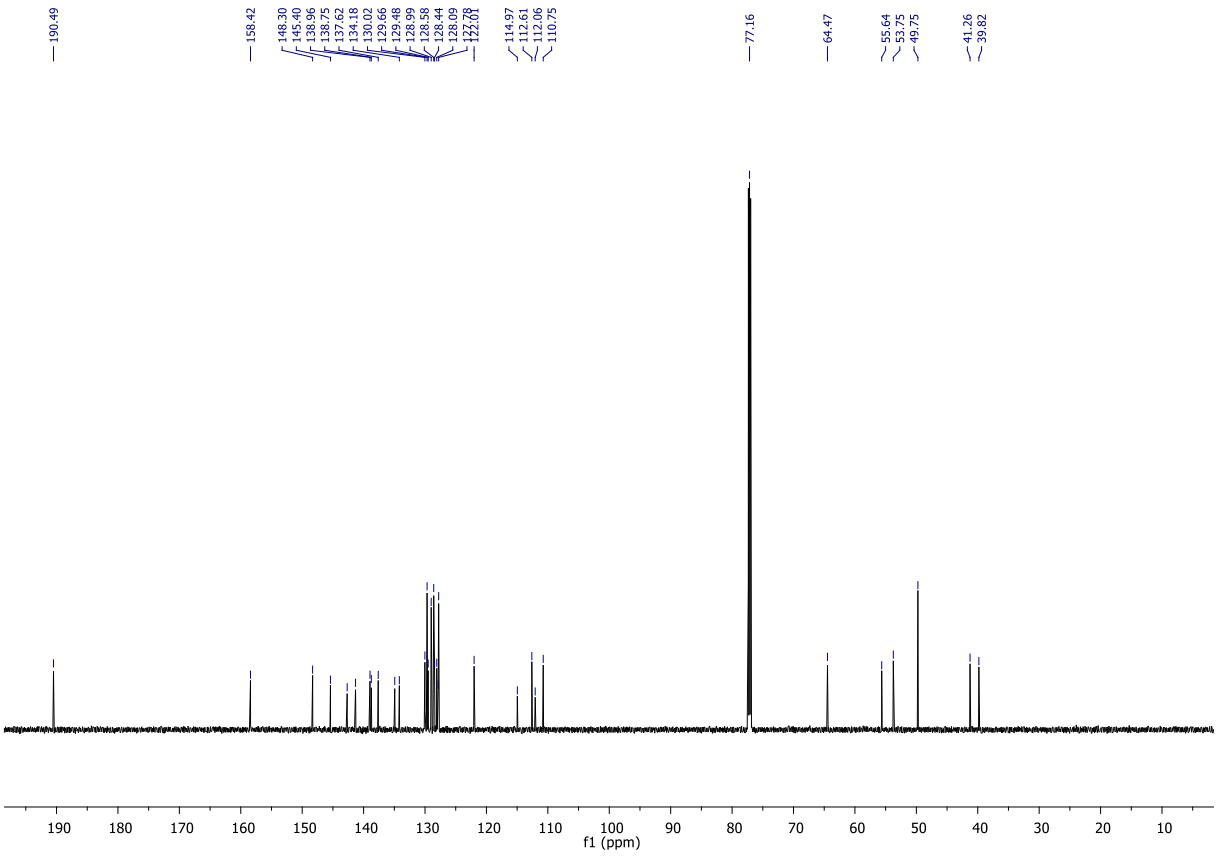


(3S,4aS,9bR,10R,10aR)-2-formyl-8-methoxy-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3j

^{1}H NMR (700 MHz, $CDCl_3$)

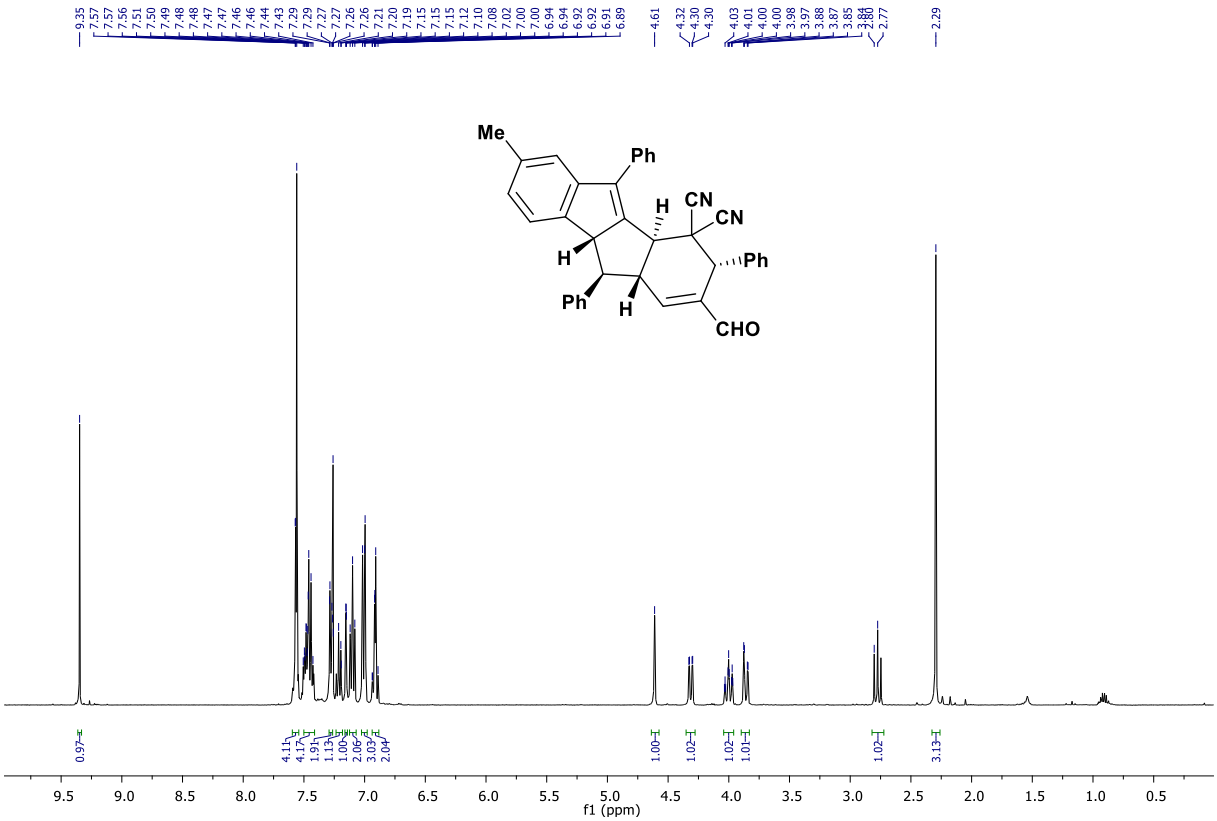


^{13}C NMR (176 MHz, $CDCl_3$)

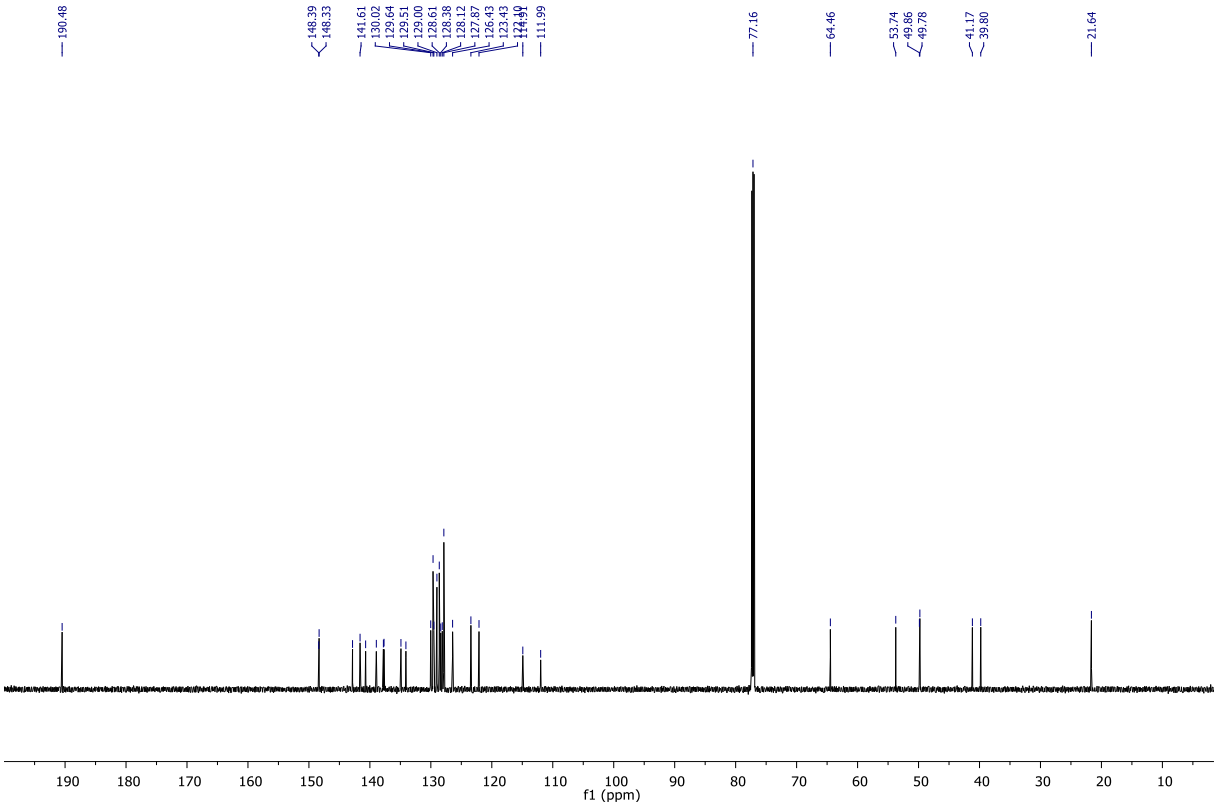


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-7-methyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3k

^{1}H NMR (700 MHz, $CDCl_3$)

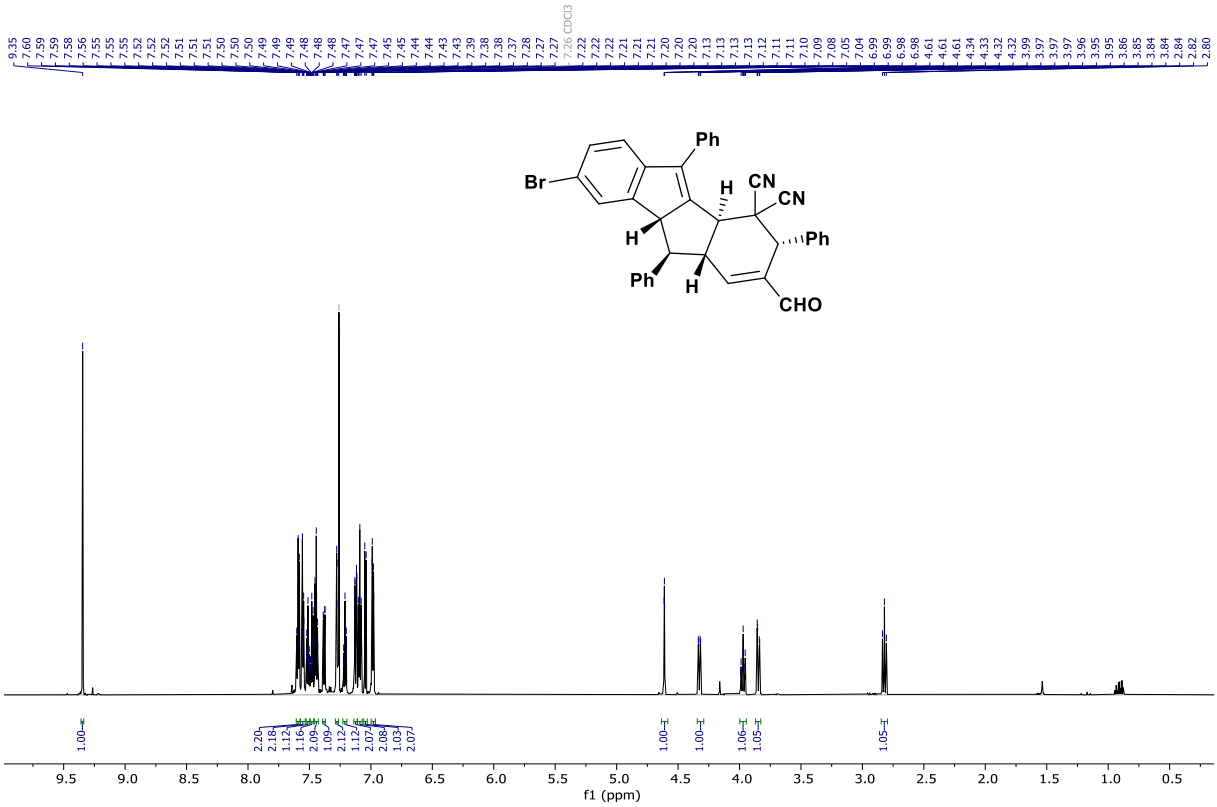


^{13}C NMR (176 MHz, $CDCl_3$)

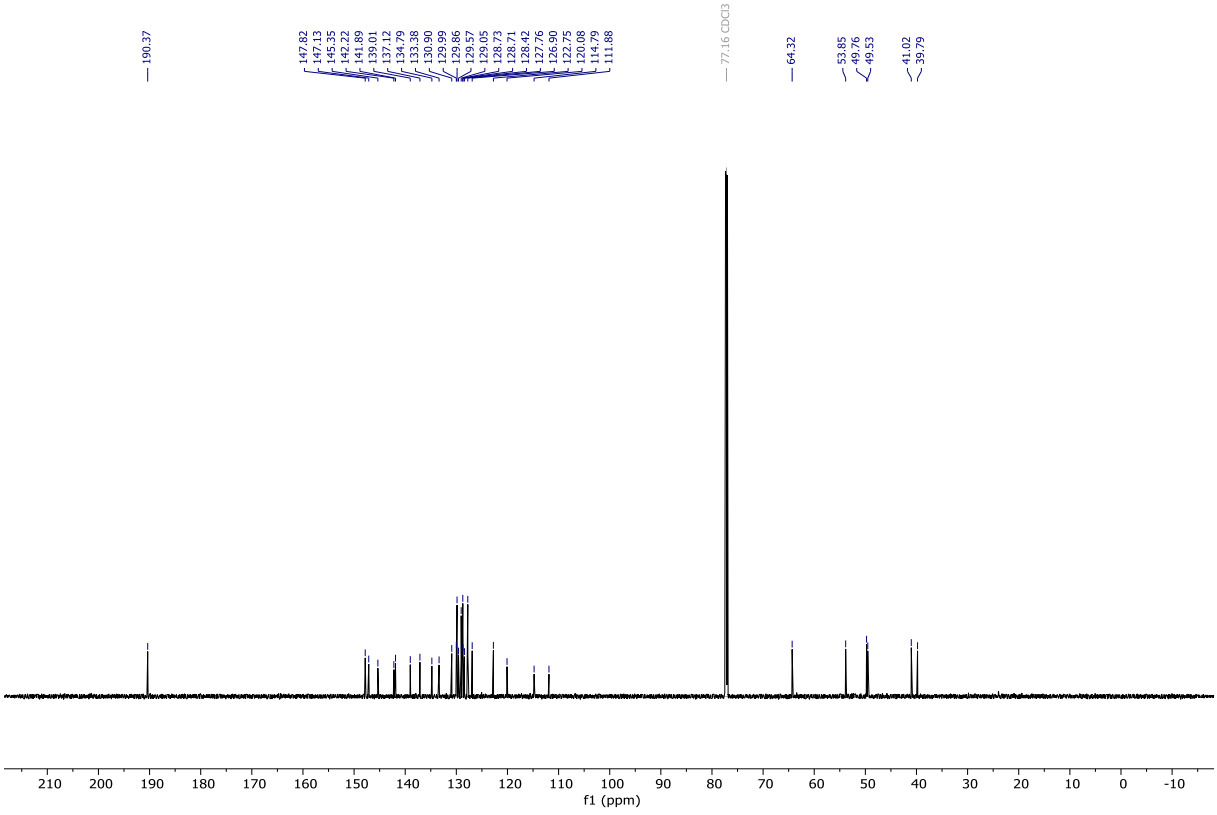


(3S,4aS,9bR,10R,10aR)-8-bromo-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3l

^{1}H NMR (700 MHz, $CDCl_3$)

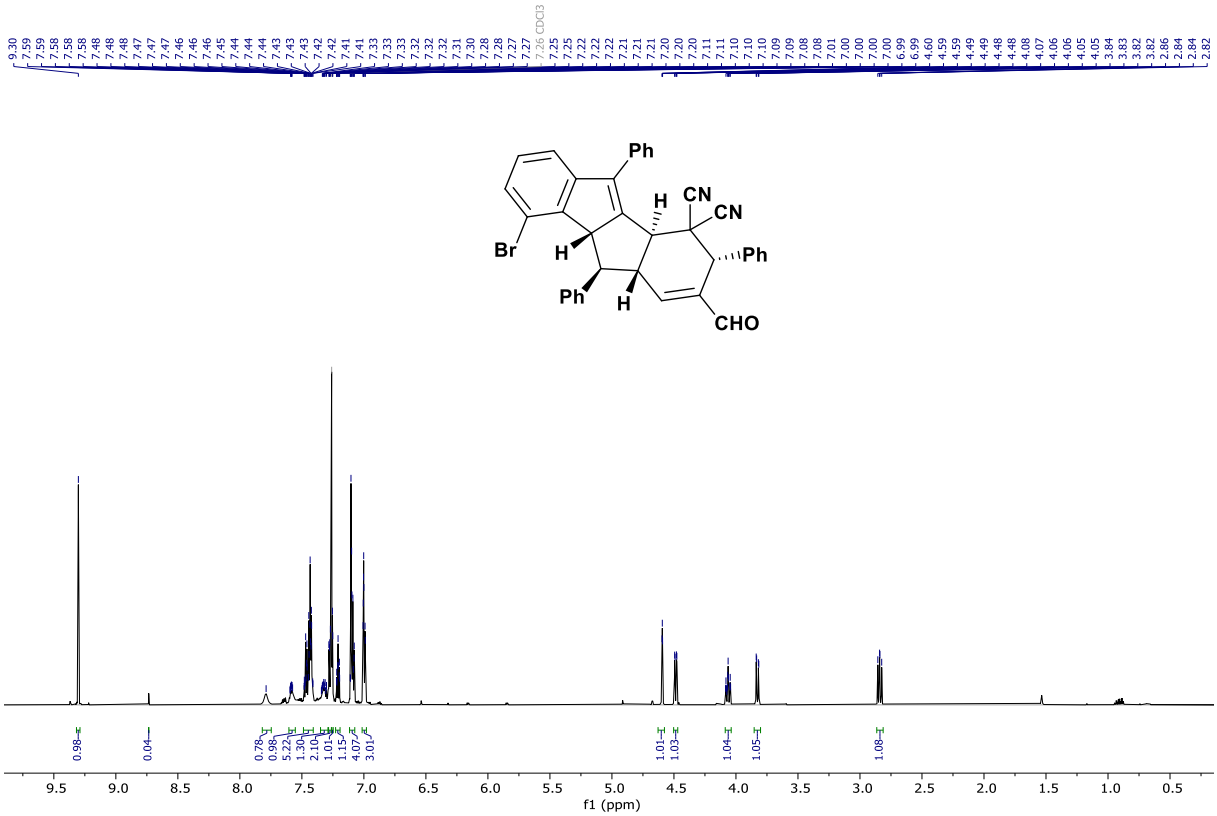


^{13}C NMR (176 MHz, $CDCl_3$)

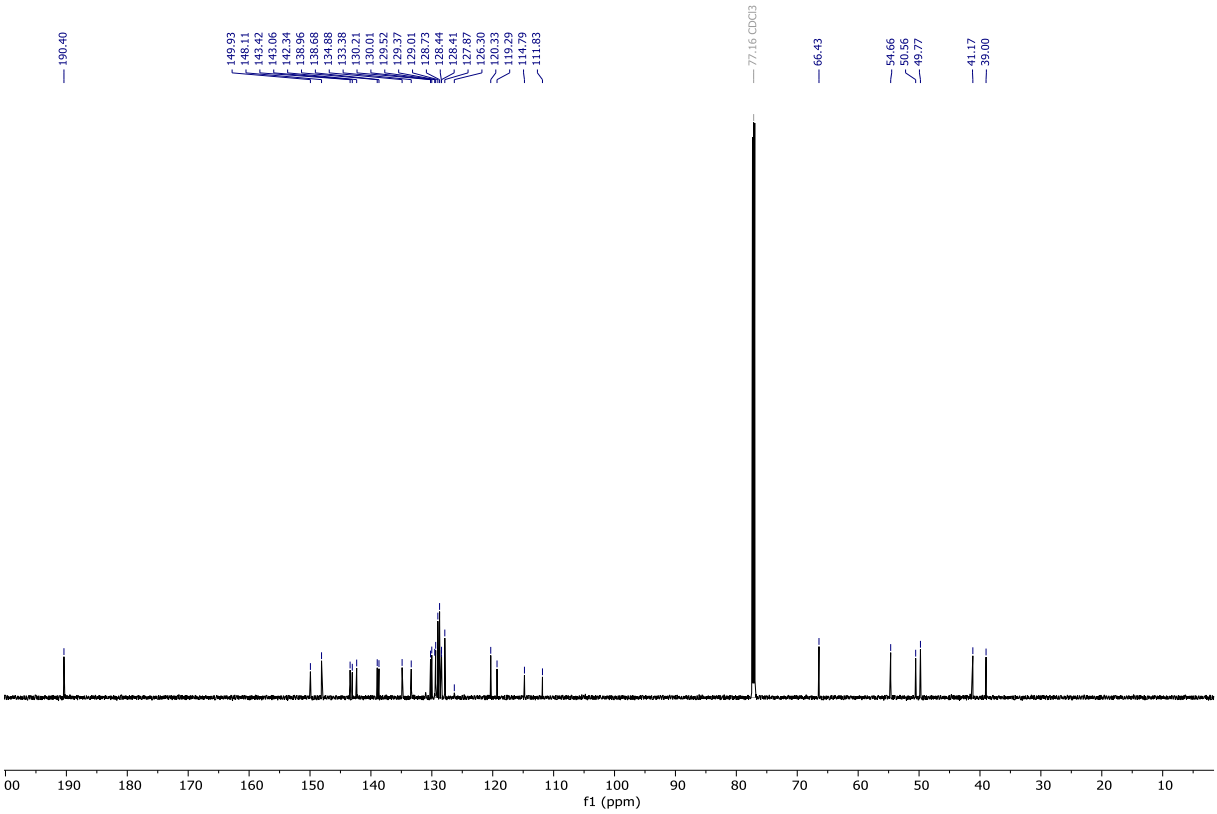


(3S,4aS,9bS,10R,10aR)-9-bromo-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3m

^{1}H NMR (700 MHz, $CDCl_3$)

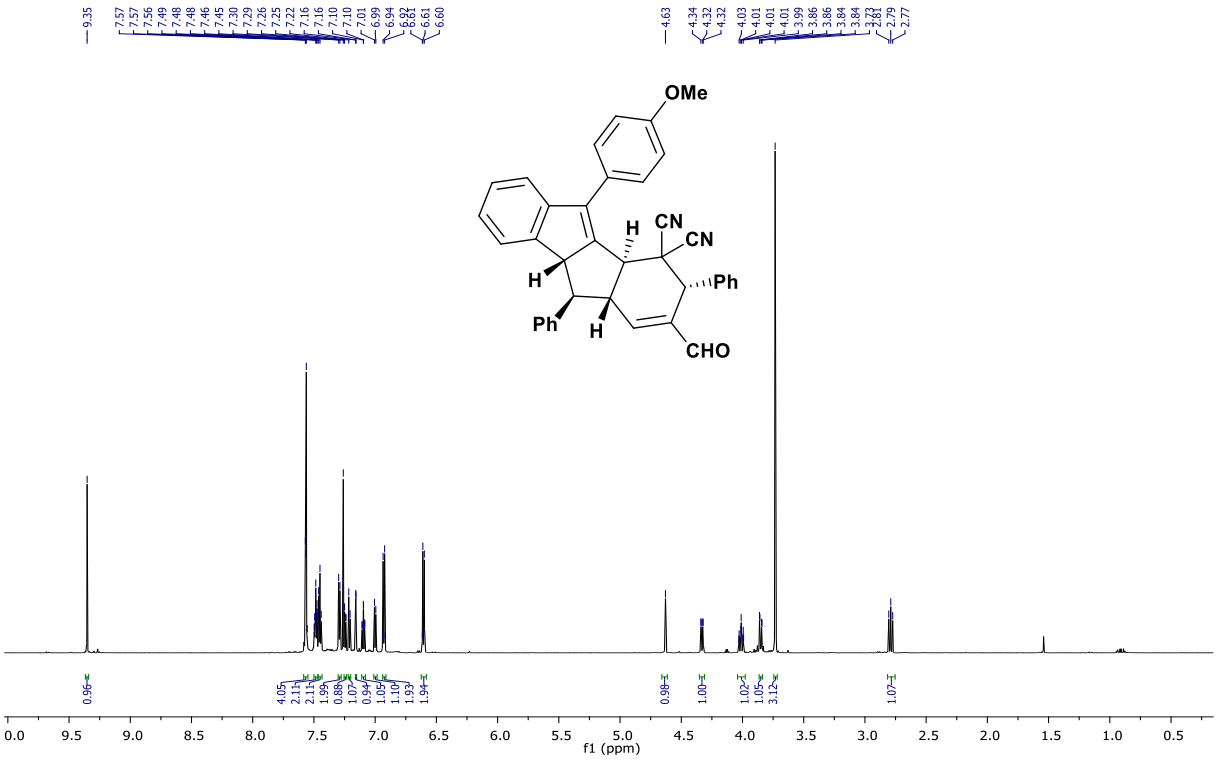


^{13}C NMR (176 MHz, $CDCl_3$)

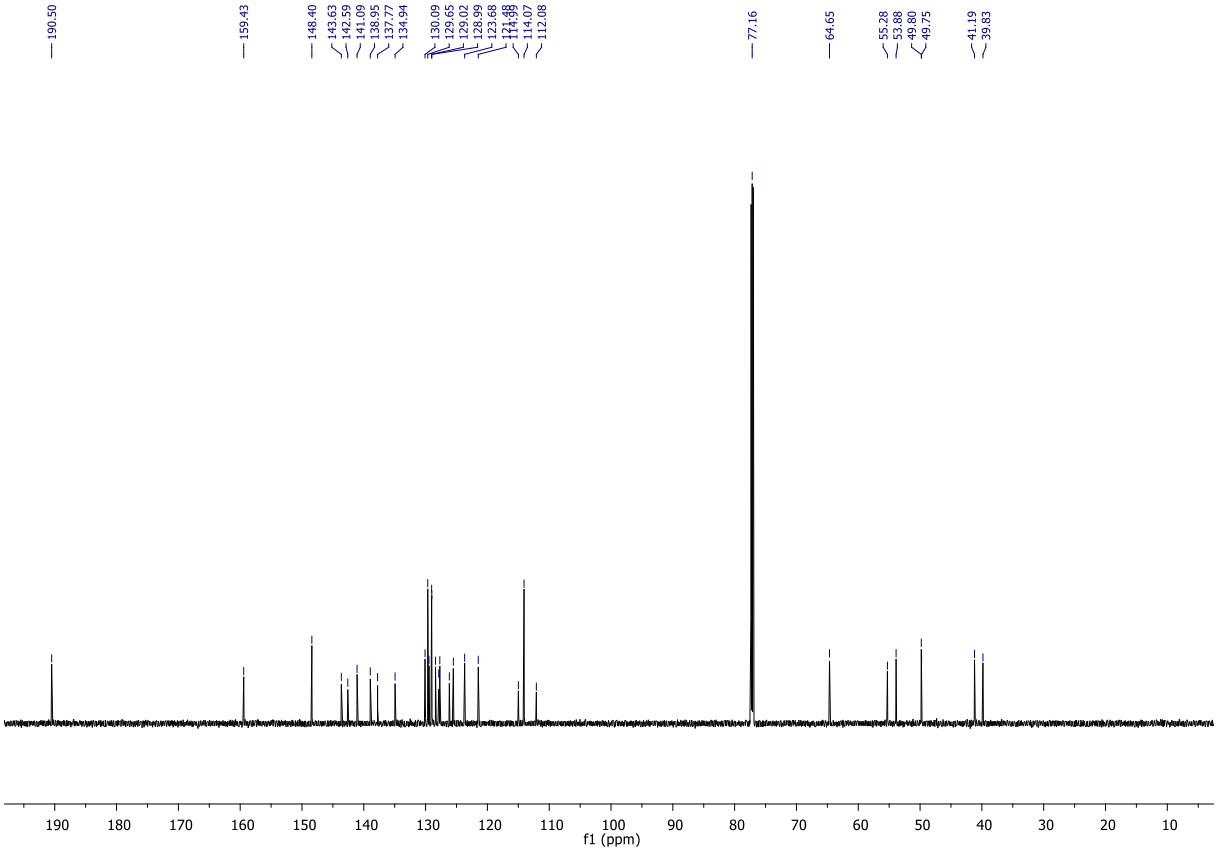


(3S,4aS,9bR,10R,10aR)-2-formyl-5-(4-methoxyphenyl)-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3n

^{1}H NMR (700 MHz, $CDCl_3$)

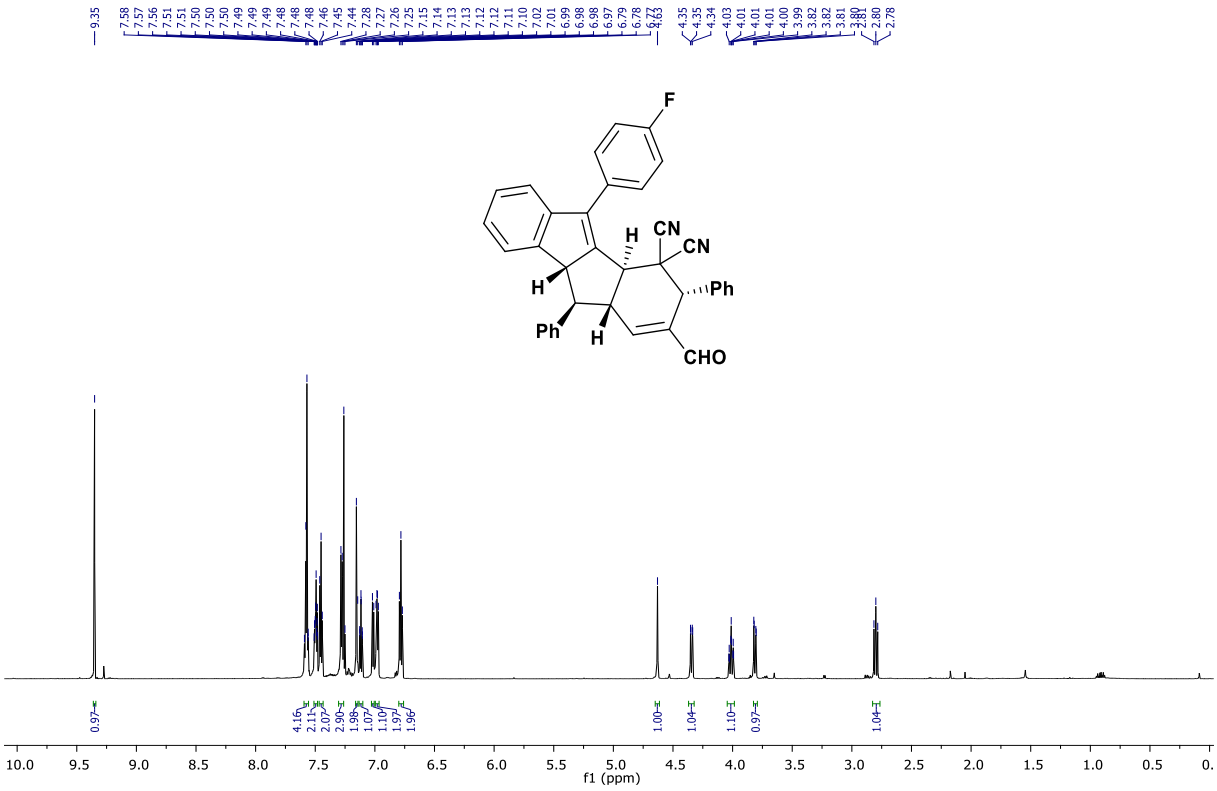


^{13}C NMR (176 MHz, $CDCl_3$)

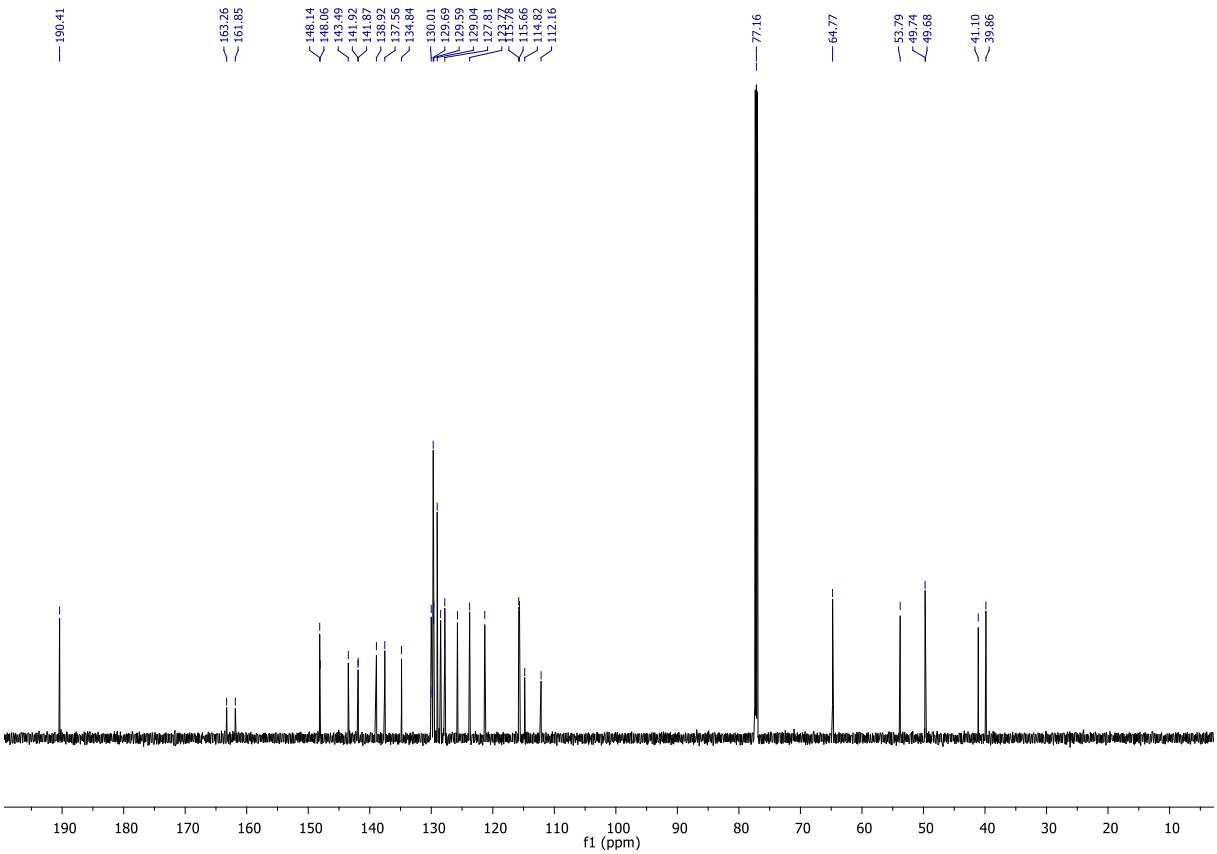


(3S,4aS,9bR,10R,10aR)-5-(4-fluorophenyl)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3o

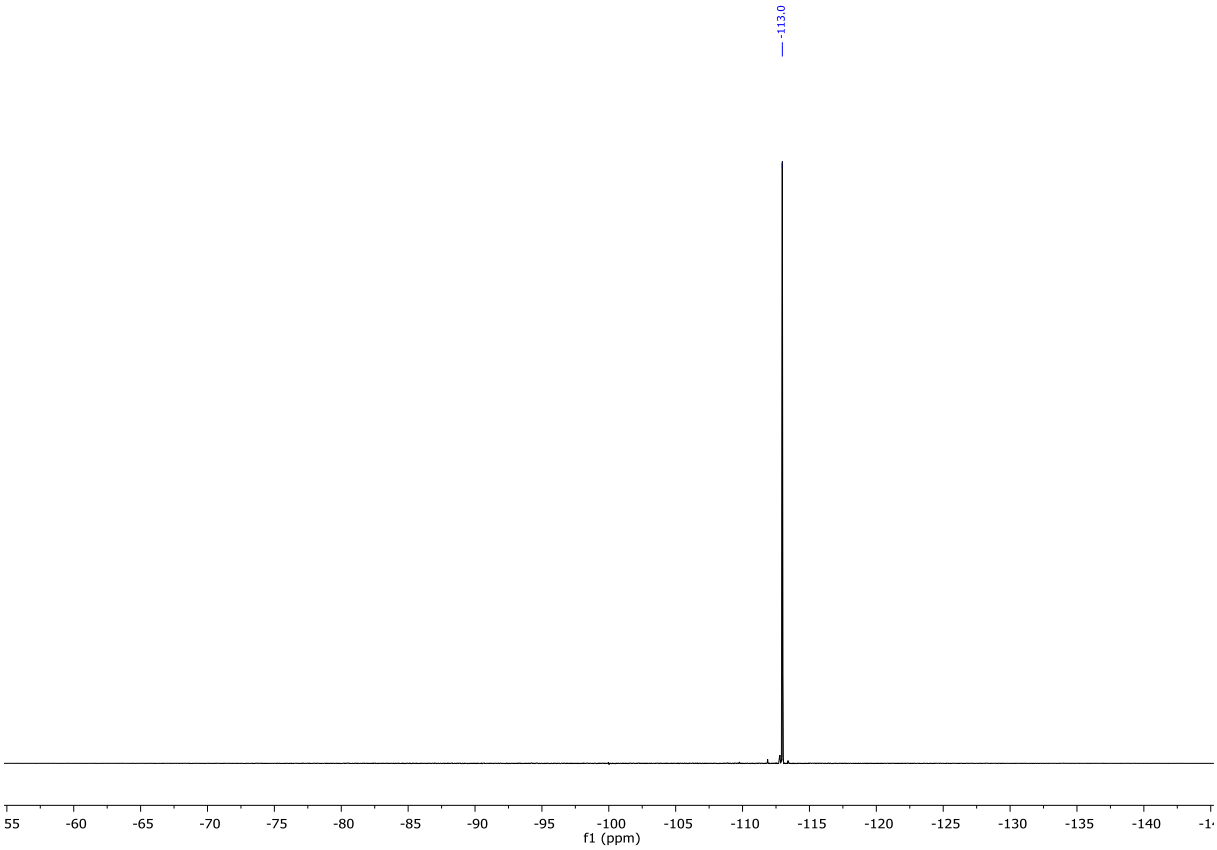
^{1}H NMR (700 MHz, $CDCl_3$)



^{13}C NMR (176 MHz, $CDCl_3$)

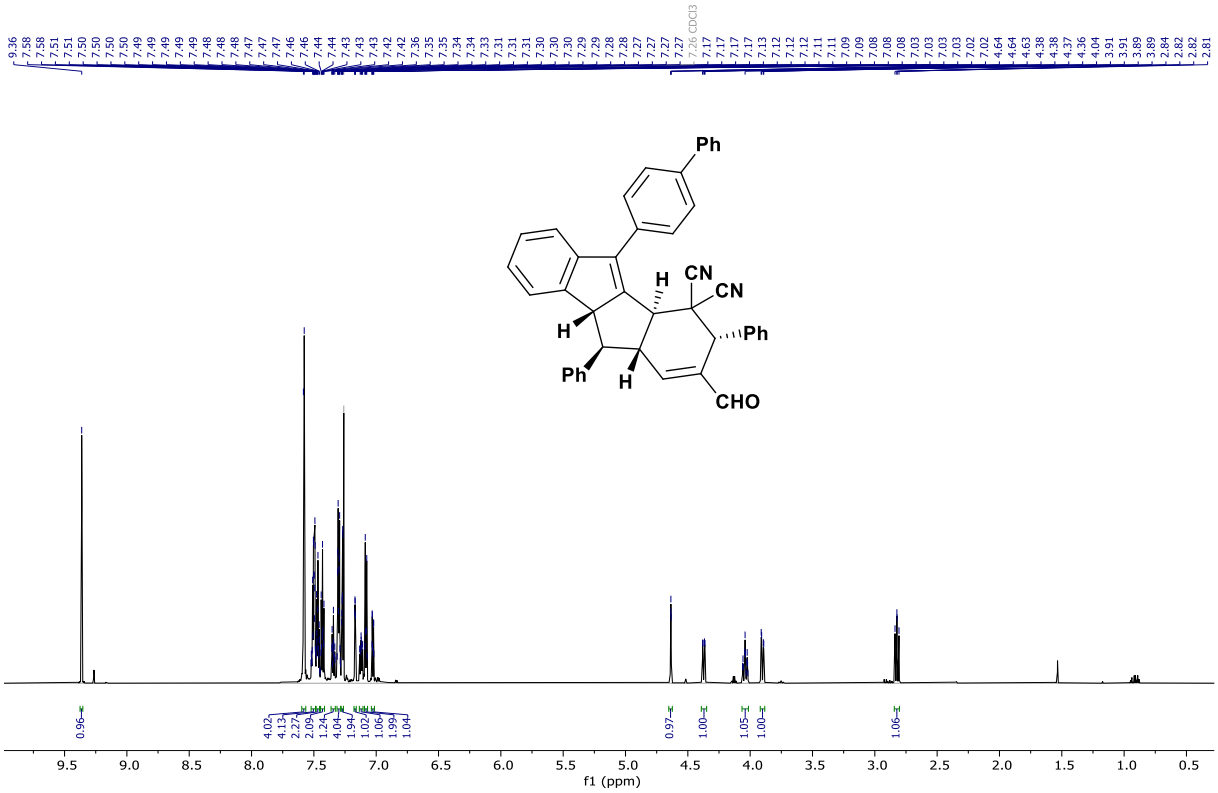


^{19}F NMR (376 MHz, $CDCl_3$)

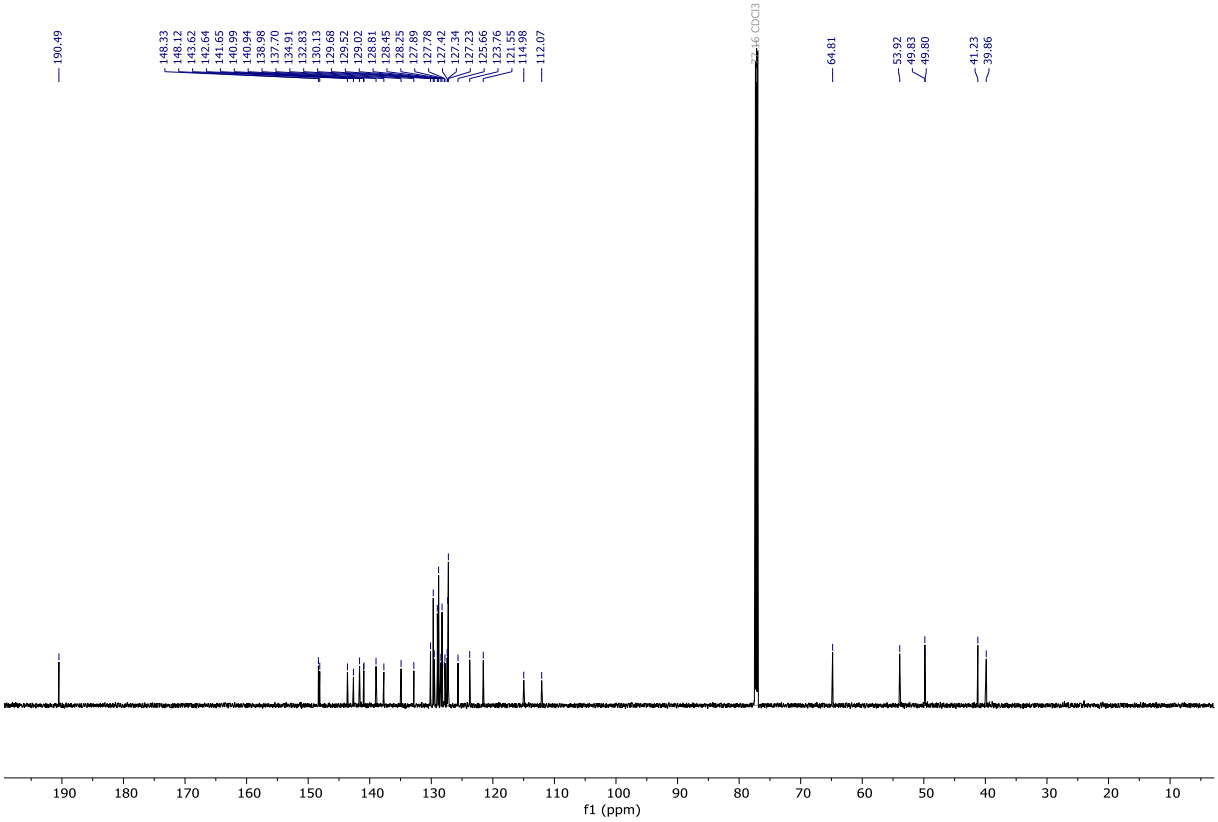


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-5-([1,1'-biphenyl]-4-yl)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3p

^{1}H NMR (700 MHz, $CDCl_3$)

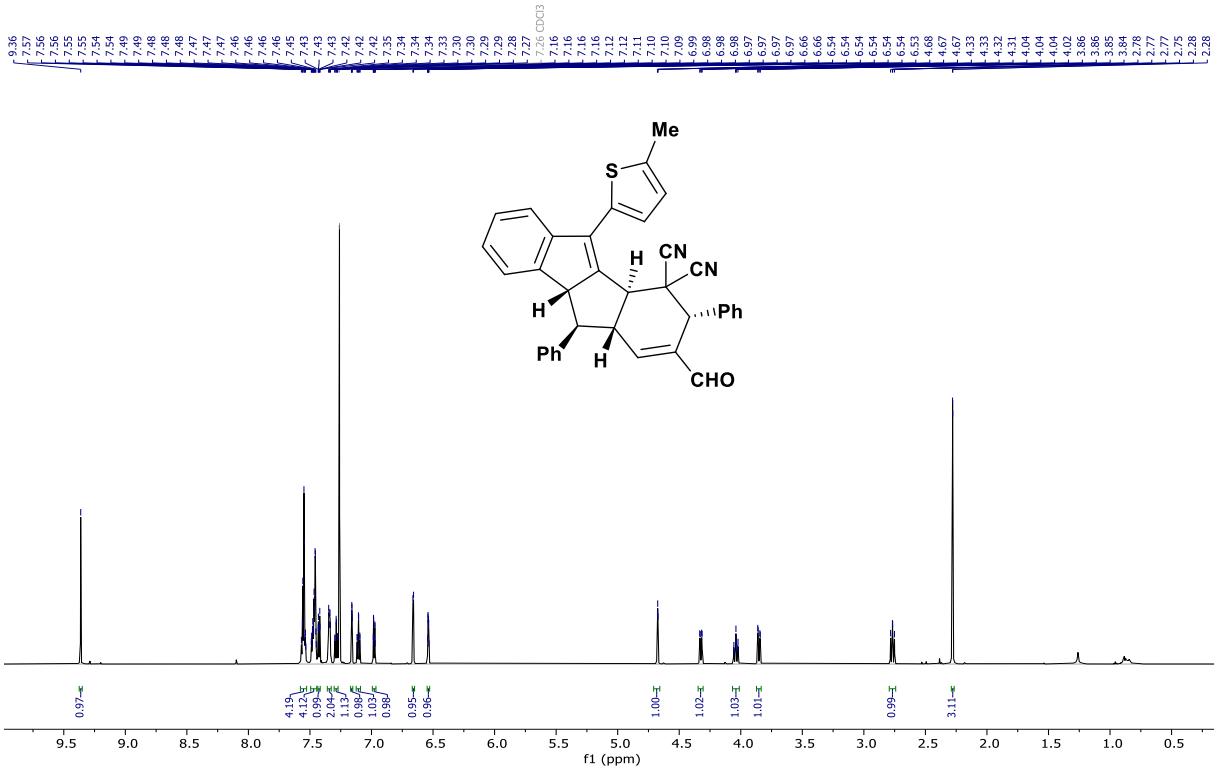


^{13}C NMR (176 MHz, $CDCl_3$)

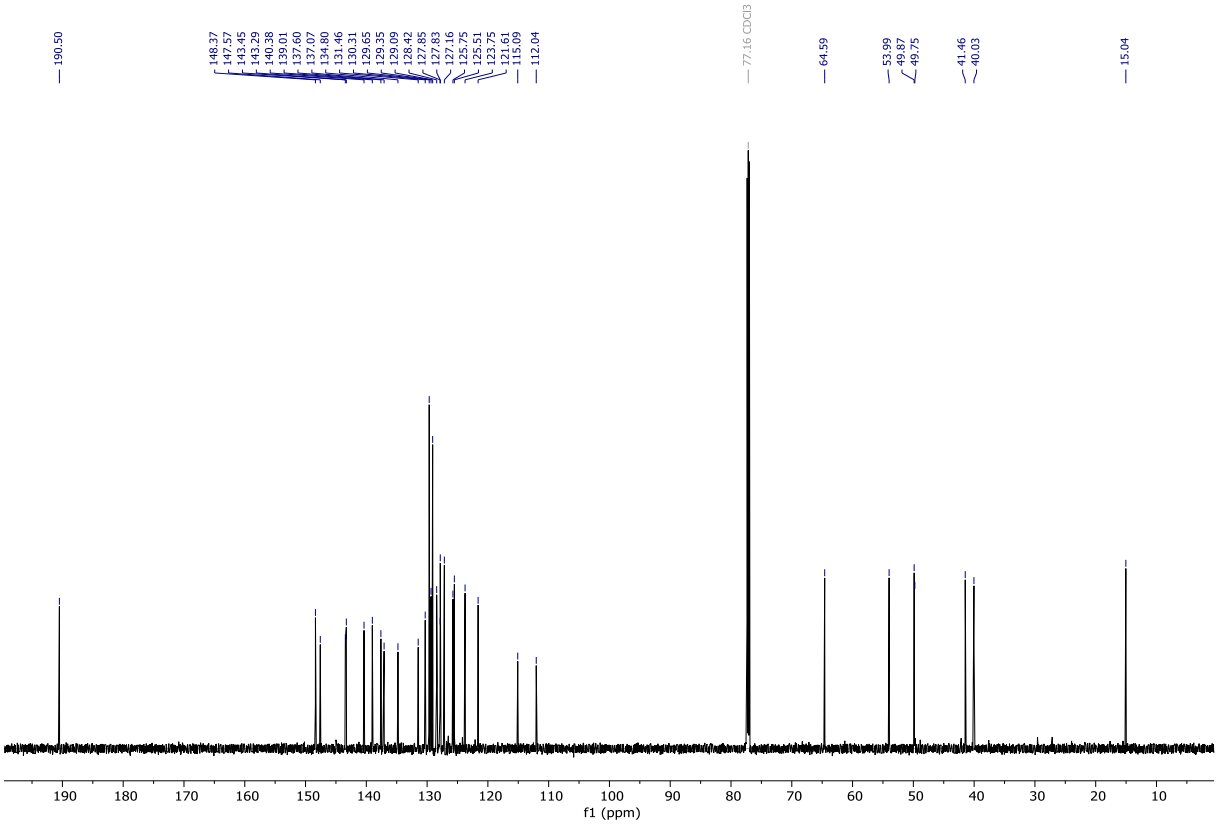


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-(5-methylthiophen-2-yl)-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3q

^{1}H NMR (700 MHz, $CDCl_3$)

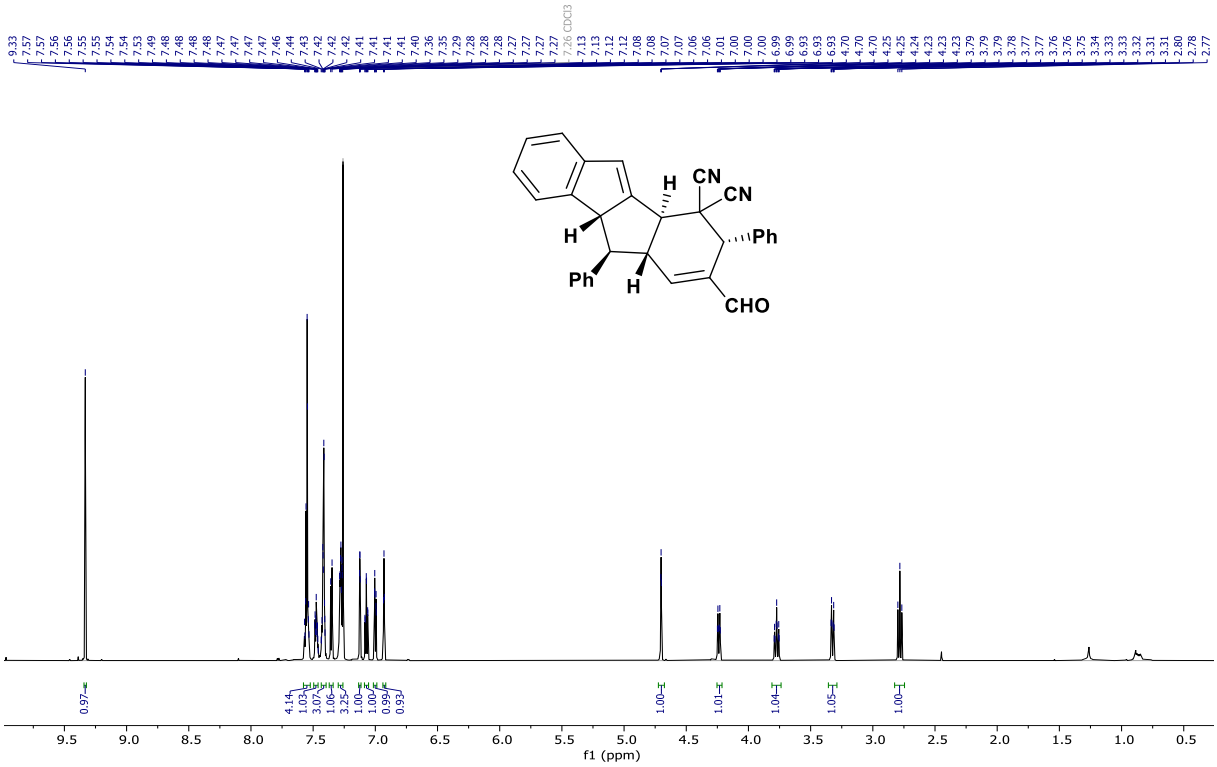


^{13}C NMR (176 MHz, $CDCl_3$)

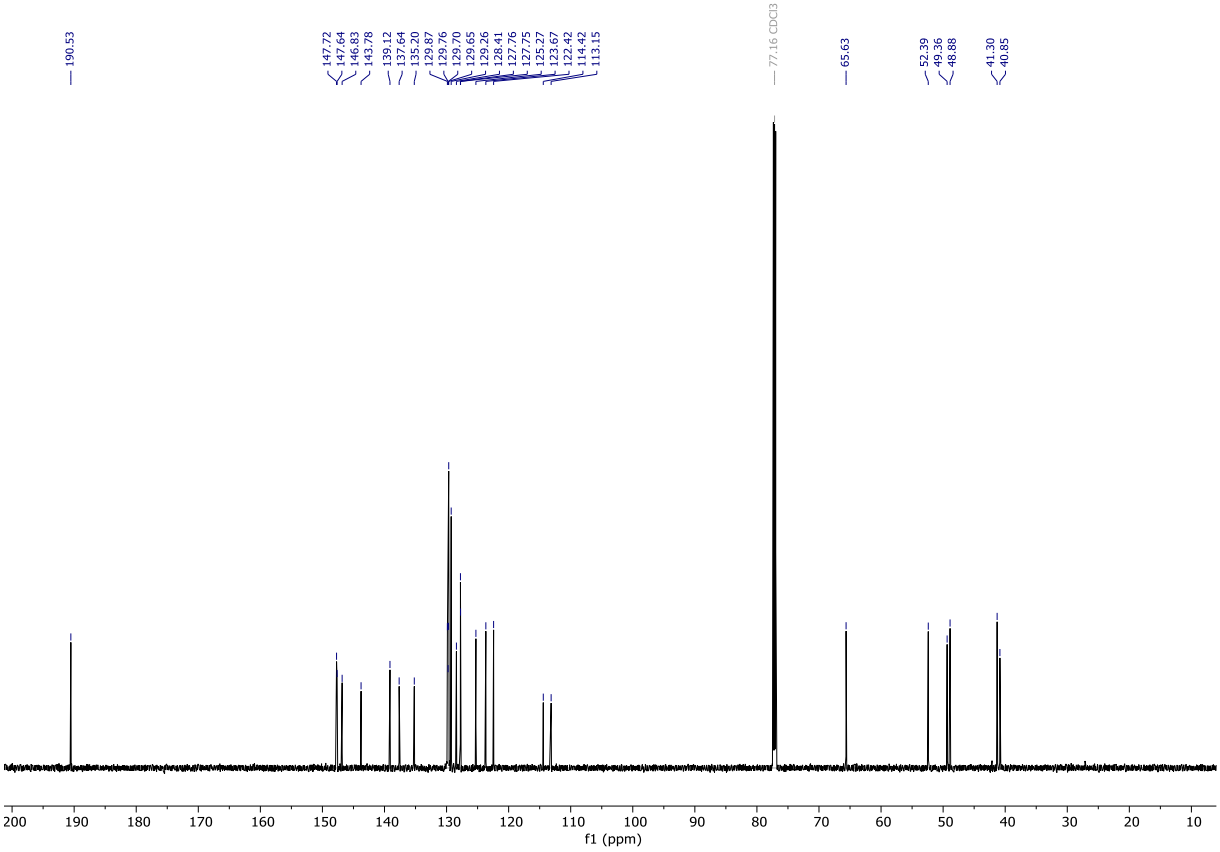


(3S,4aS,9bS,10R,10aR)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3r

^{1}H NMR (700 MHz, $CDCl_3$)

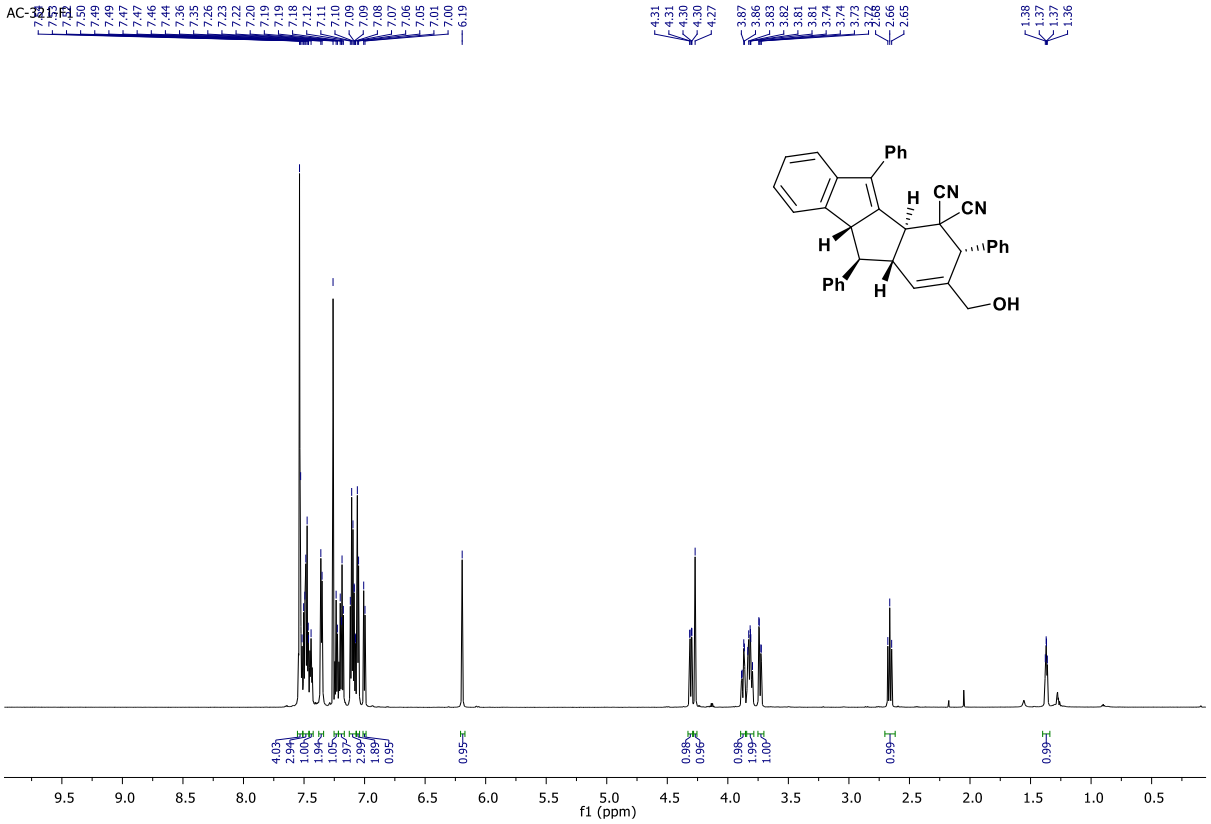


^{13}C NMR (176 MHz, $CDCl_3$)

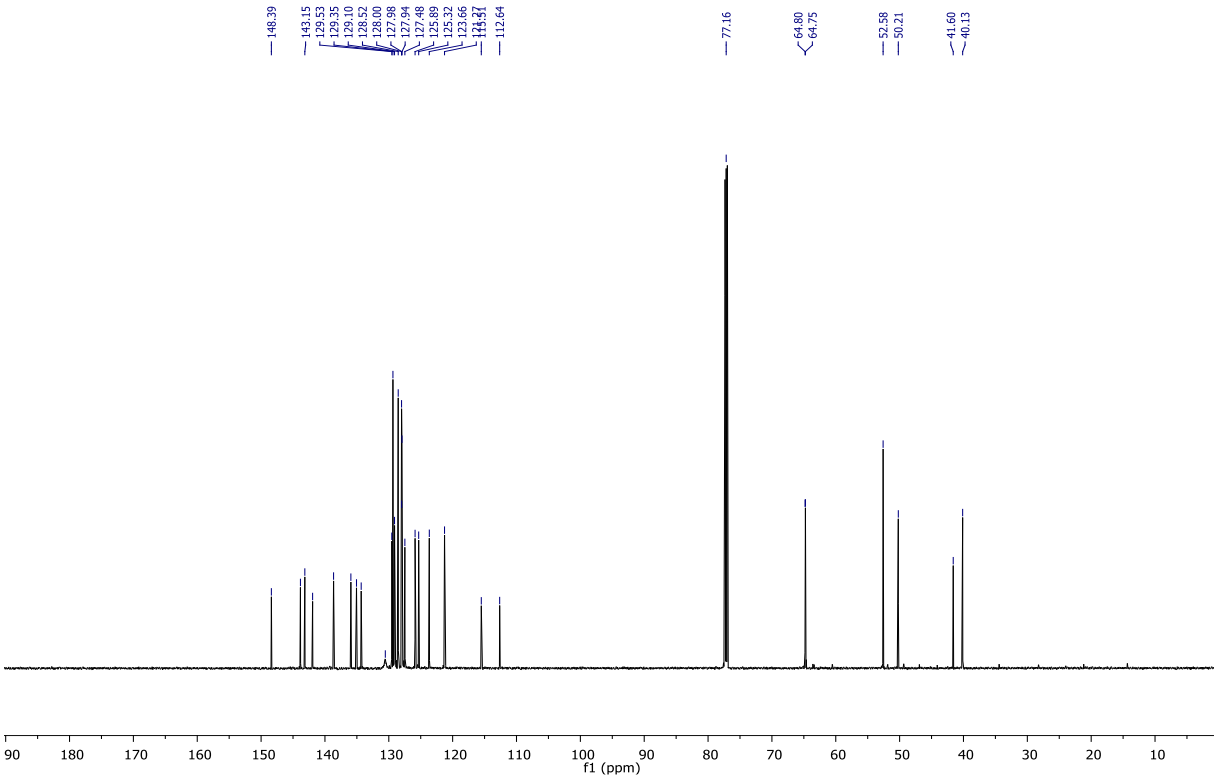


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-(hydroxymethyl)-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno [2,1-a]indene-4,4(3*H*)-dicarbonitrile 10a

^{1}H NMR (700 MHz, $CDCl_3$)

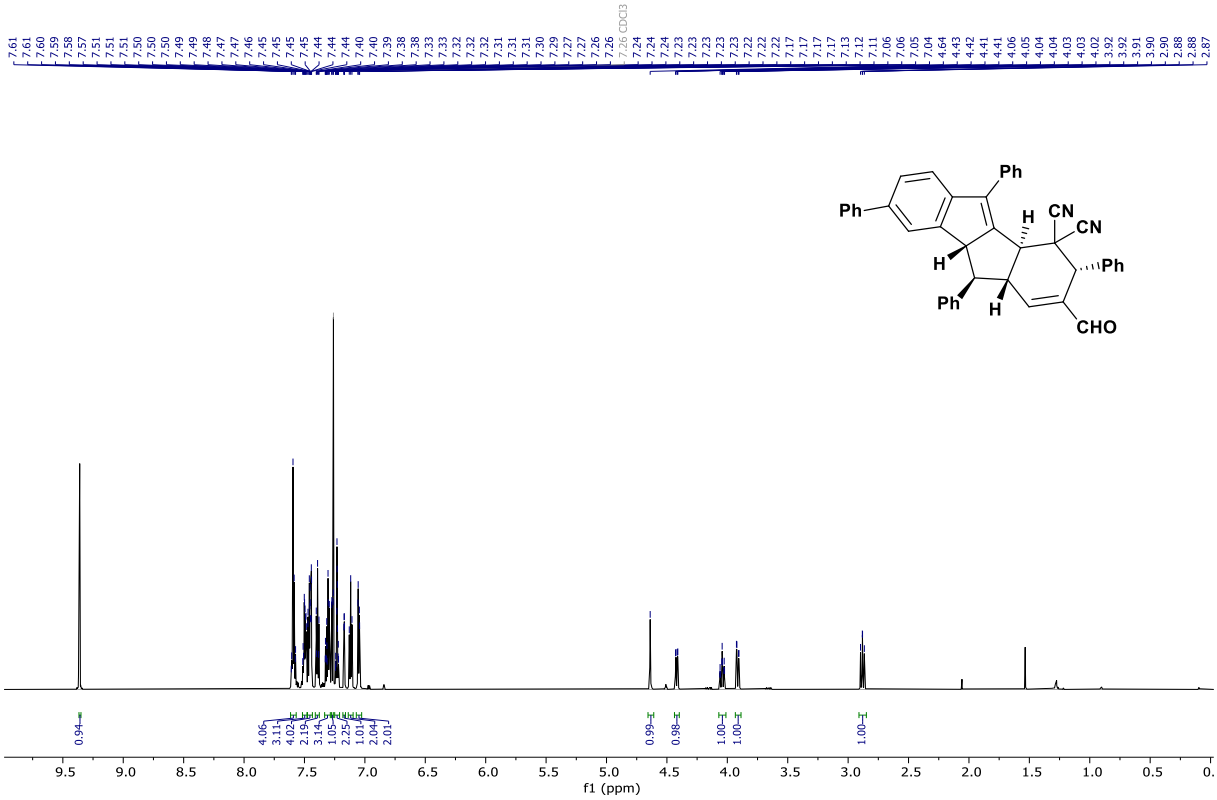


^{13}C NMR (176 MHz, $CDCl_3$)

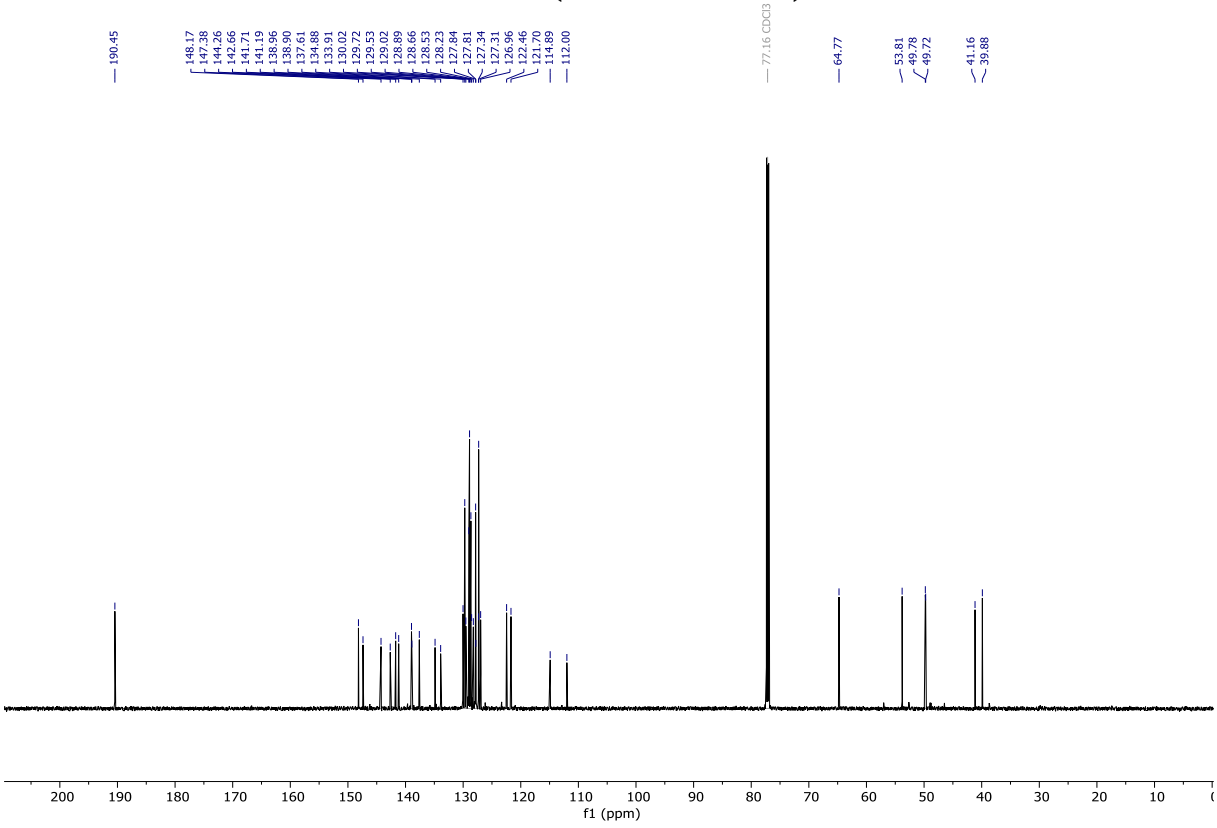


(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,5,8,10-tetraphenyl-4a,9b,10,10a-tetrahydroindeno [2,1-a]indene-4,4(3*H*)-dicarbonitrile 12l

^{1}H NMR (700 MHz, $CDCl_3$)



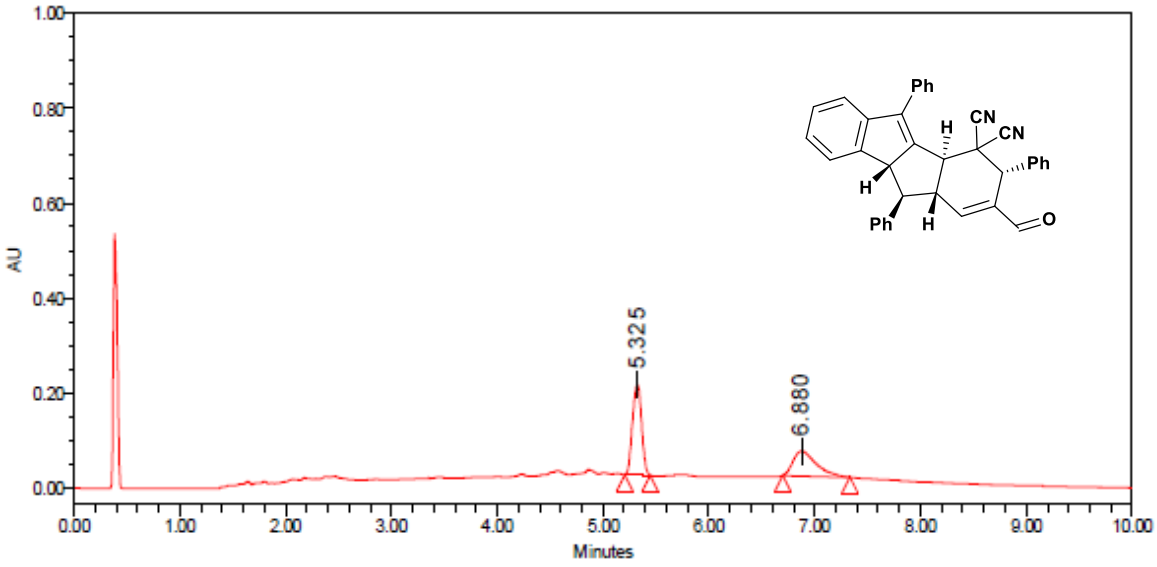
^{13}C NMR (176 MHz, $CDCl_3$)



8. UPC^2 data

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3a

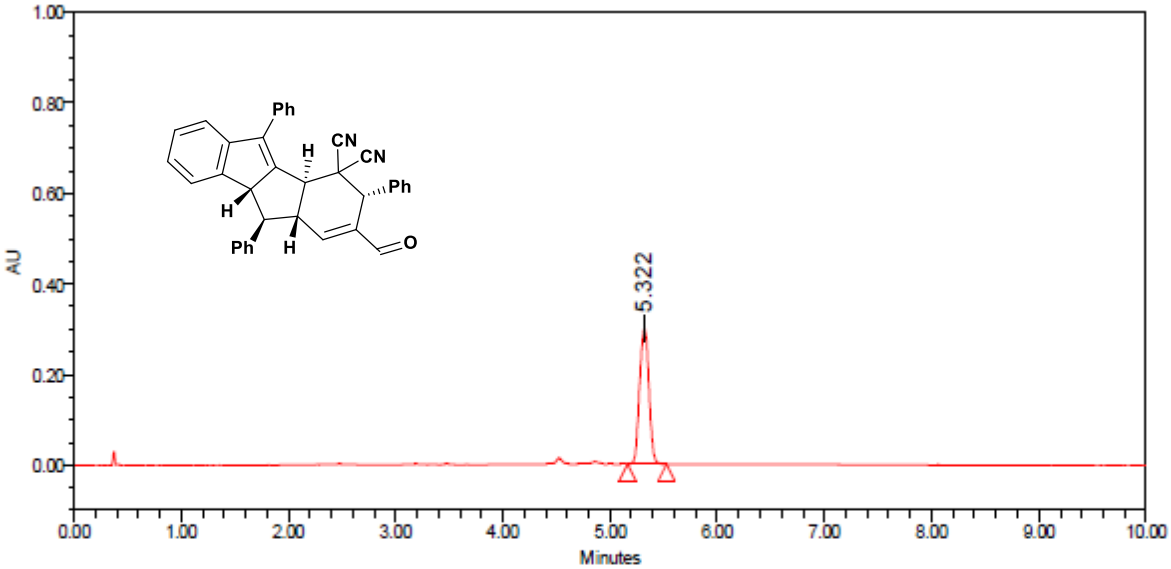
Racemic sample



Peak Results

	RT	% Area
1	5.325	58.91
2	6.880	41.09

Enantiomerically enriched sample

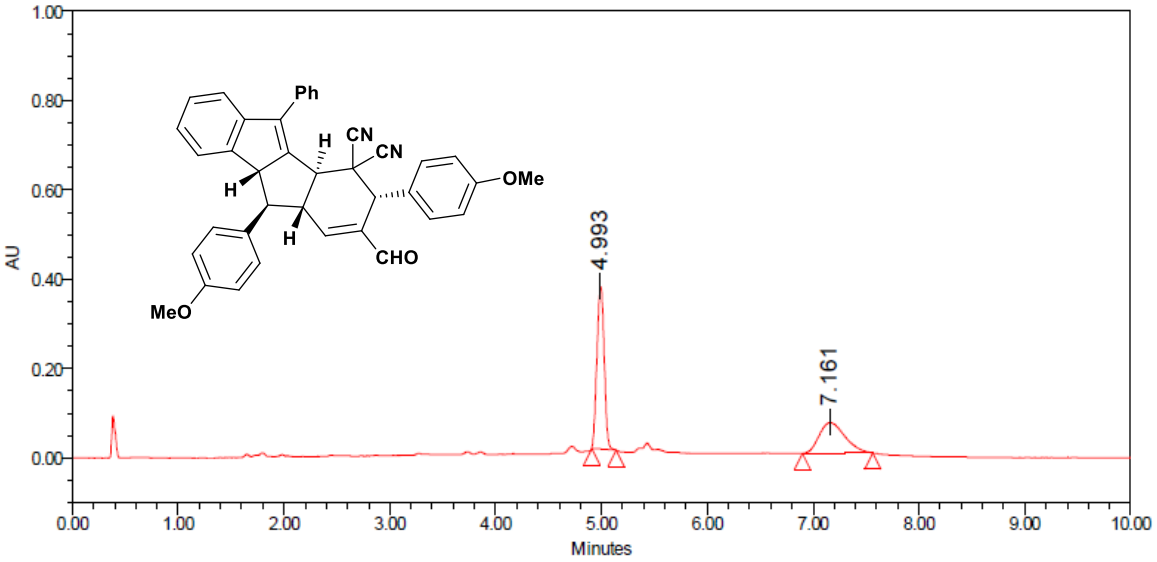


Peak Results

	RT	% Area
1	5.322	100.00

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-bis(4-methoxyphenyl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3b

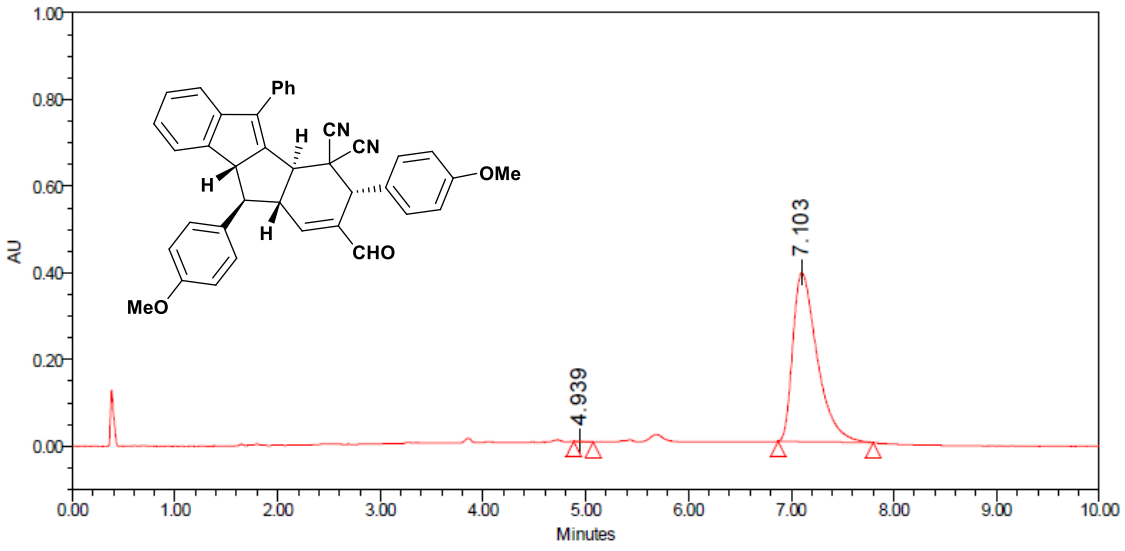
Racemic sample



Peak Results

	RT	% Area
1	4.993	59.86
2	7.161	40.14

Enantiomerically enriched sample

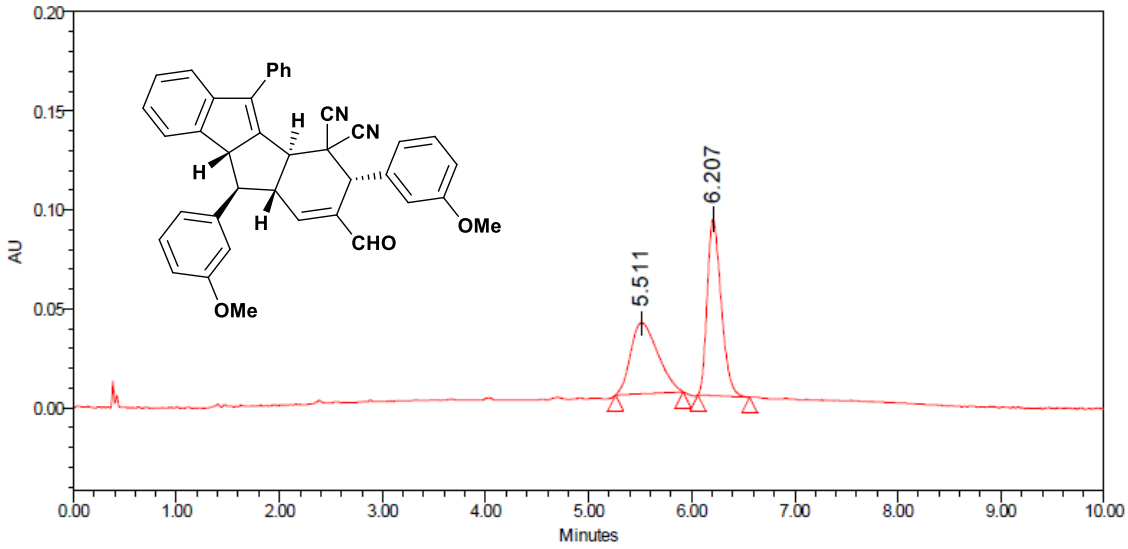


Peak Results

	RT	% Area
1	4.939	0.06
2	7.103	99.94

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-bis(3-methoxyphenyl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3c

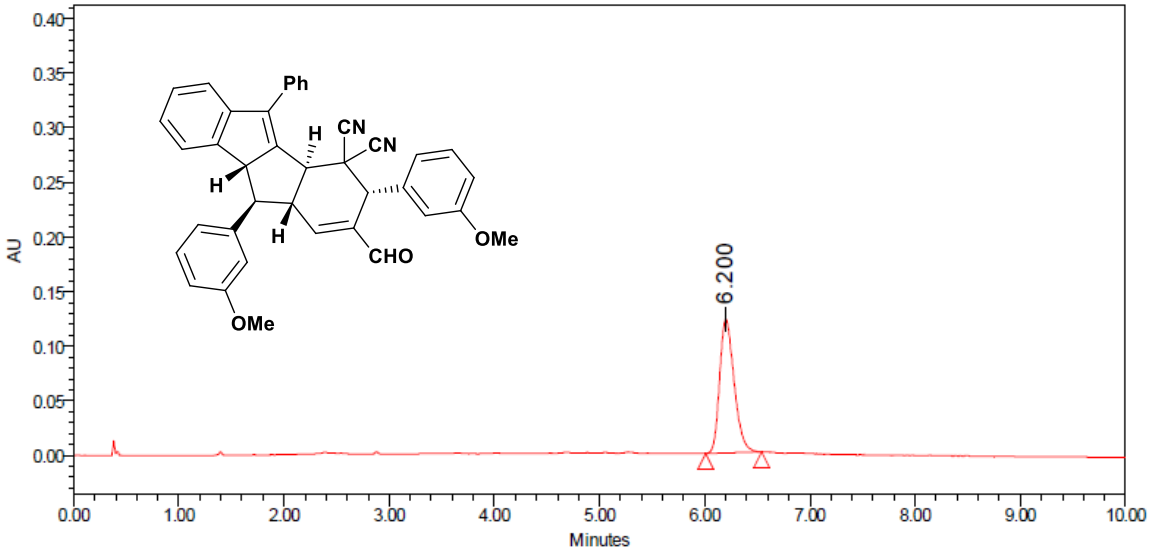
Racemic sample



Peak Results

	RT	% Area
1	5.511	43.94
2	6.207	56.06

Enantiomerically enriched sample

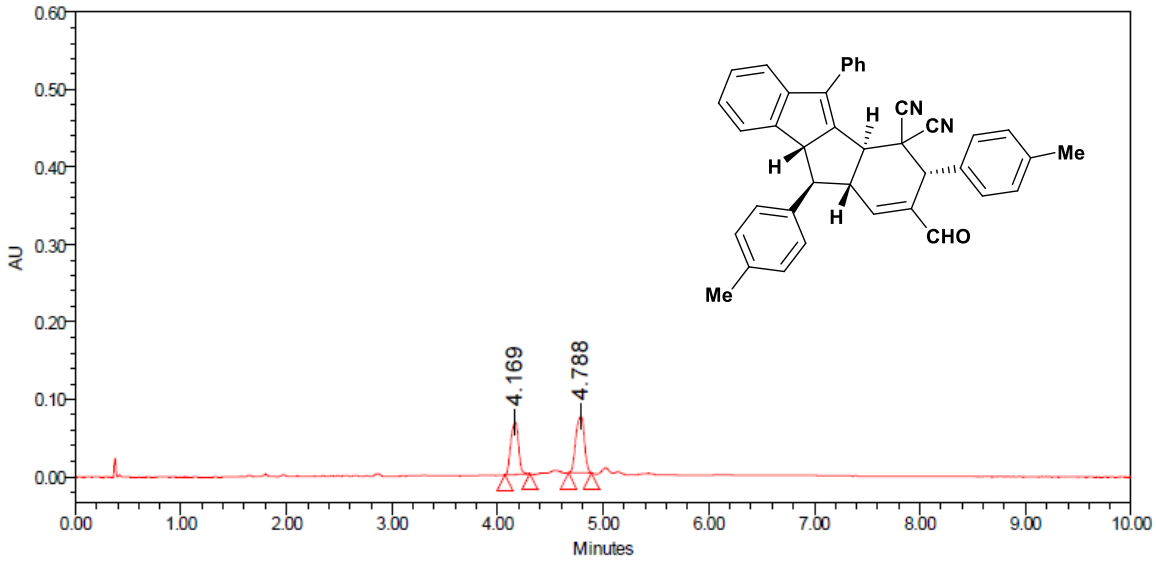


Peak Results

	RT	% Area
1	6.200	100.00

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-phenyl-3,10-di-p-tolyl-4a,9b,10,10a-tetrahydroindeno [2,1-a]indene-4,4(3H)-dicarbonitrile 3d

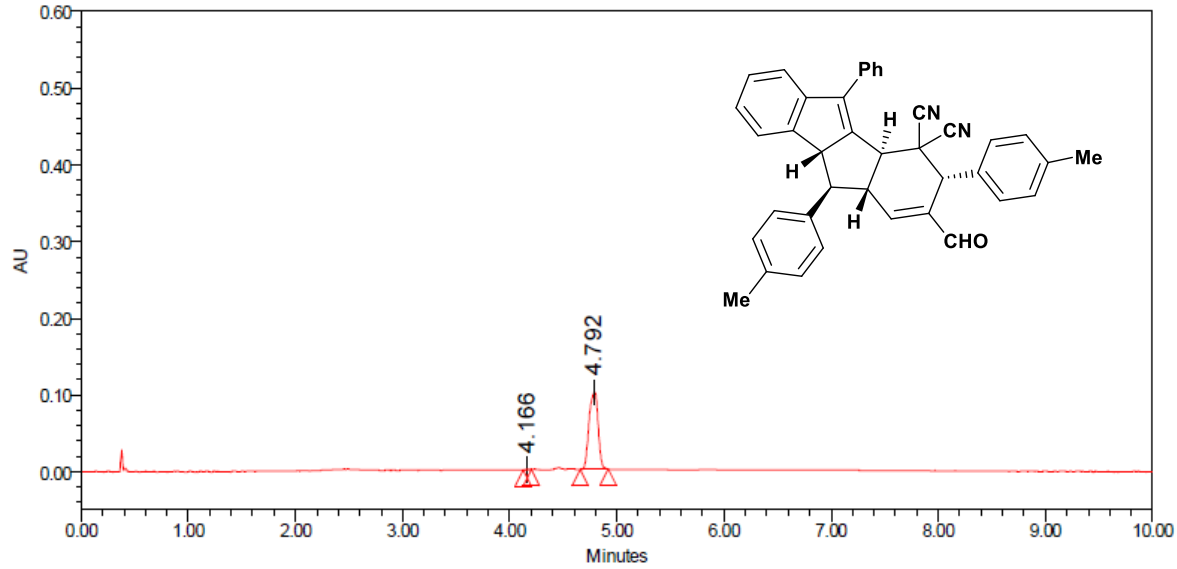
Racemic sample



Peak Results

	RT	% Area
1	4.169	45.44
2	4.788	54.56

Enantiomerically enriched sample

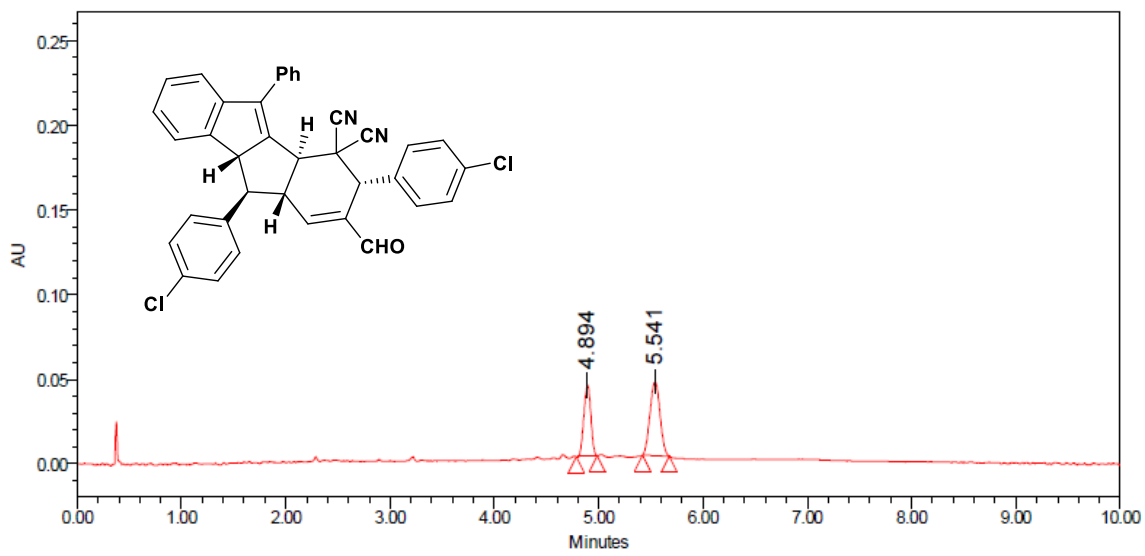


Peak Results

	RT	% Area
1	4.166	0.04
2	4.792	99.96

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-3,10-bis(4-chlorophenyl)-2-formyl-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3e

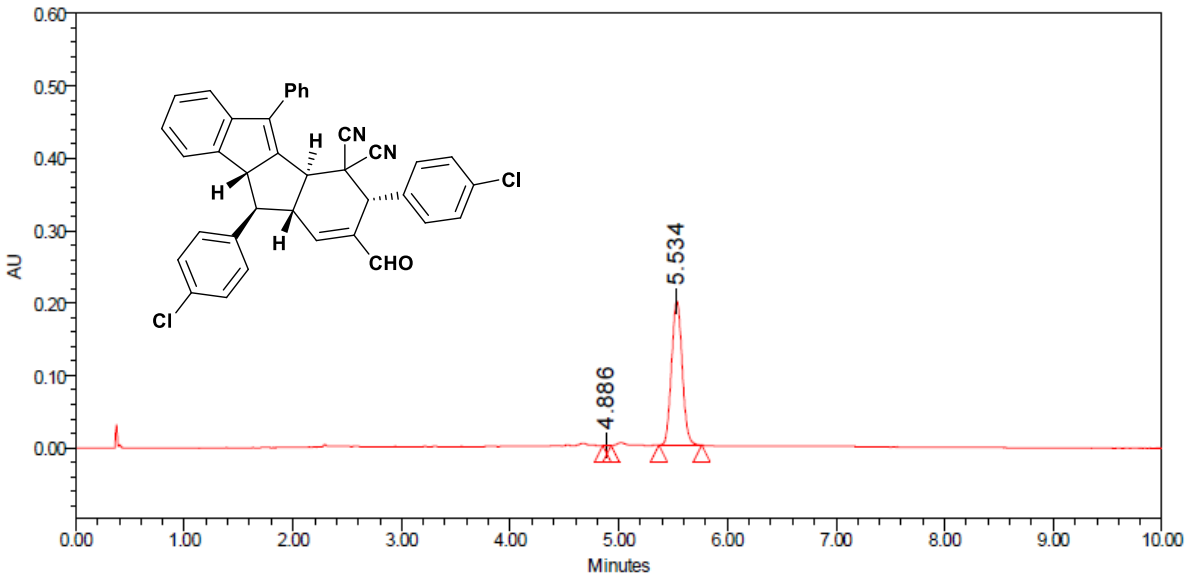
Racemic sample



Peak Results

	RT	% Area
1	4.894	39.97
2	5.541	60.03

Enantiomerically enriched sample

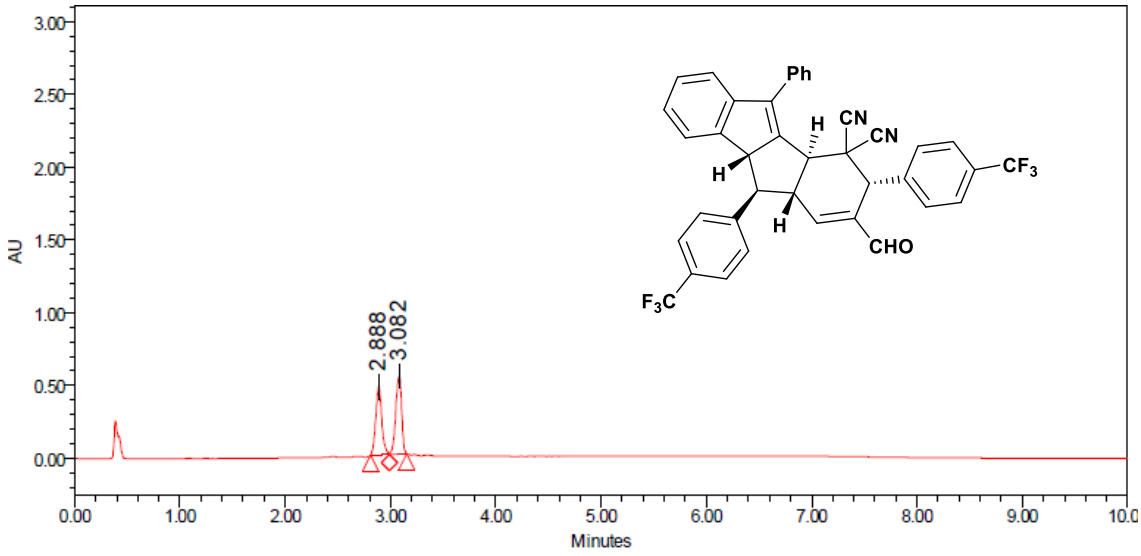


Peak Results

	RT	% Area
1	4.886	0.06
2	5.534	99.94

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-phenyl-3,10-bis(4-(trifluoromethyl)phenyl)-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3f

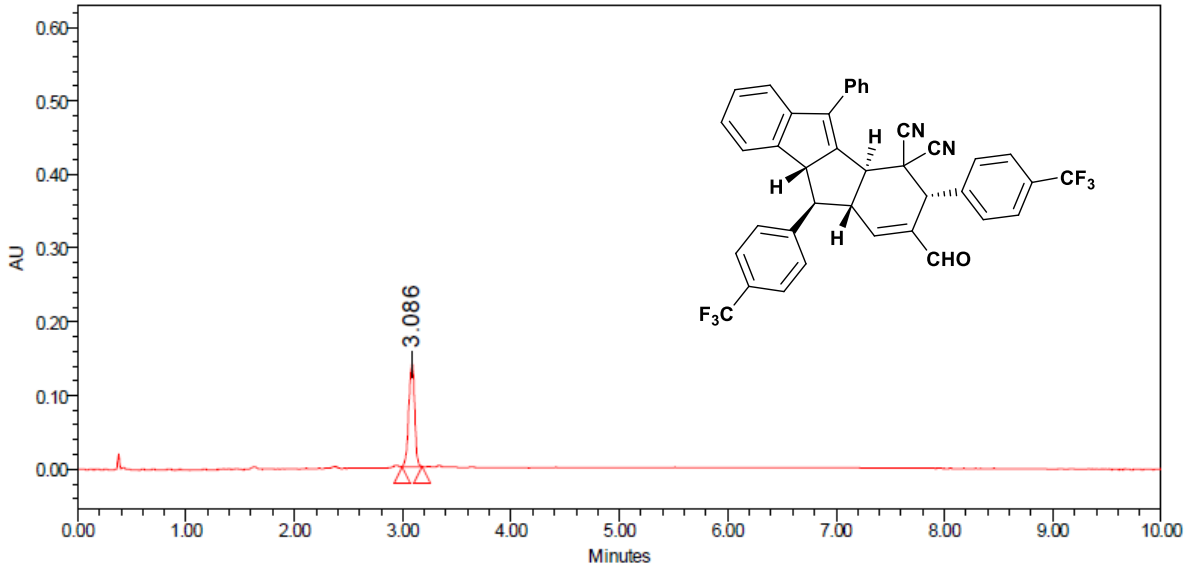
Racemic sample



Peak Results

	RT	% Area
1	2.888	47.44
2	3.082	52.56

Enantiomerically enriched sample

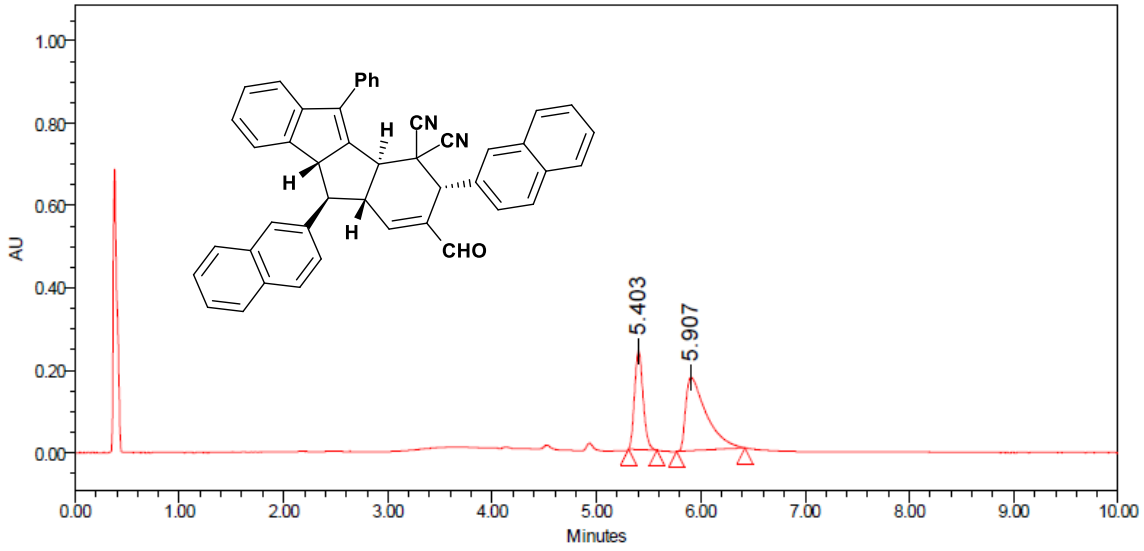


Peak Results

	RT	% Area
1	3.086	100.00

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-3,10-di(naphthalen-2-yl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3g

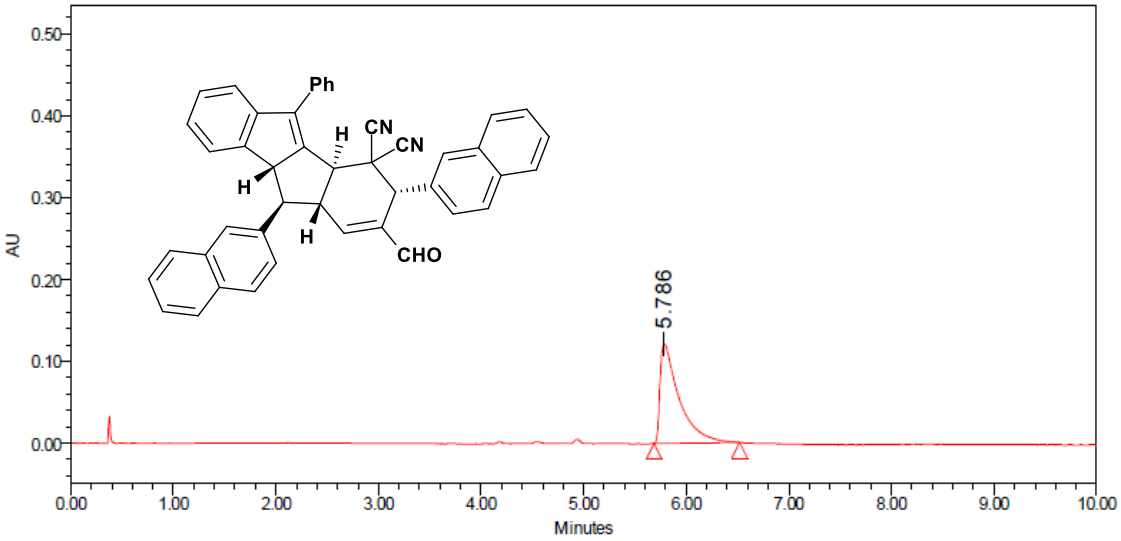
Racemic sample



Peak Results

	RT	% Area
1	5.403	35.83
2	5.907	64.17

Enantiomerically enriched sample

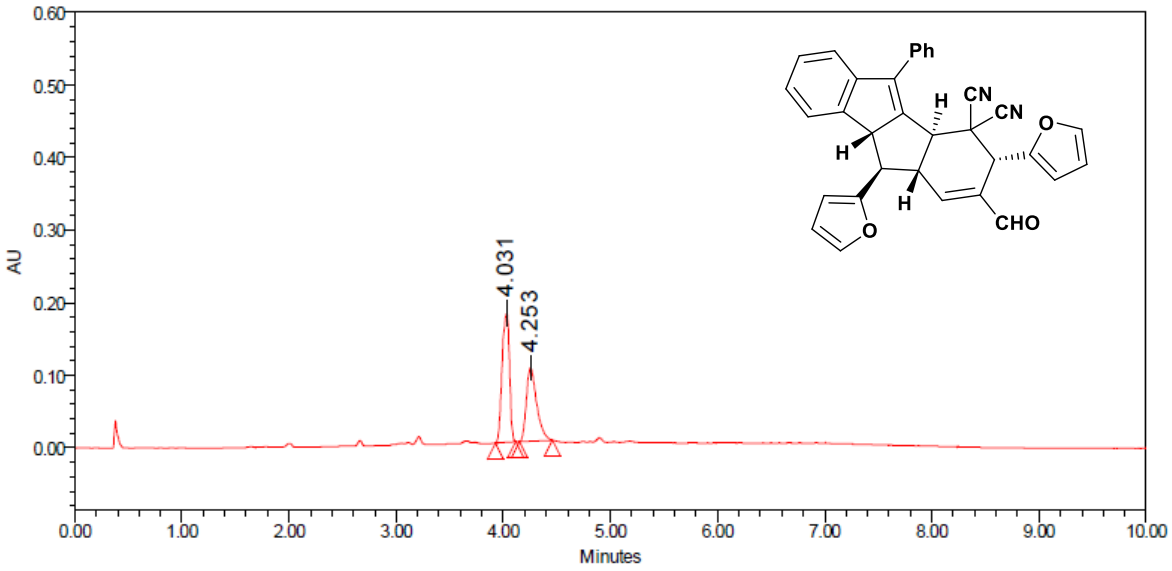


Peak Results

	RT	% Area
1	5.786	100.00

(3S,4aS,9bR,10R,10aS)-2-formyl-3,10-di(furan-2-yl)-5-phenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3h

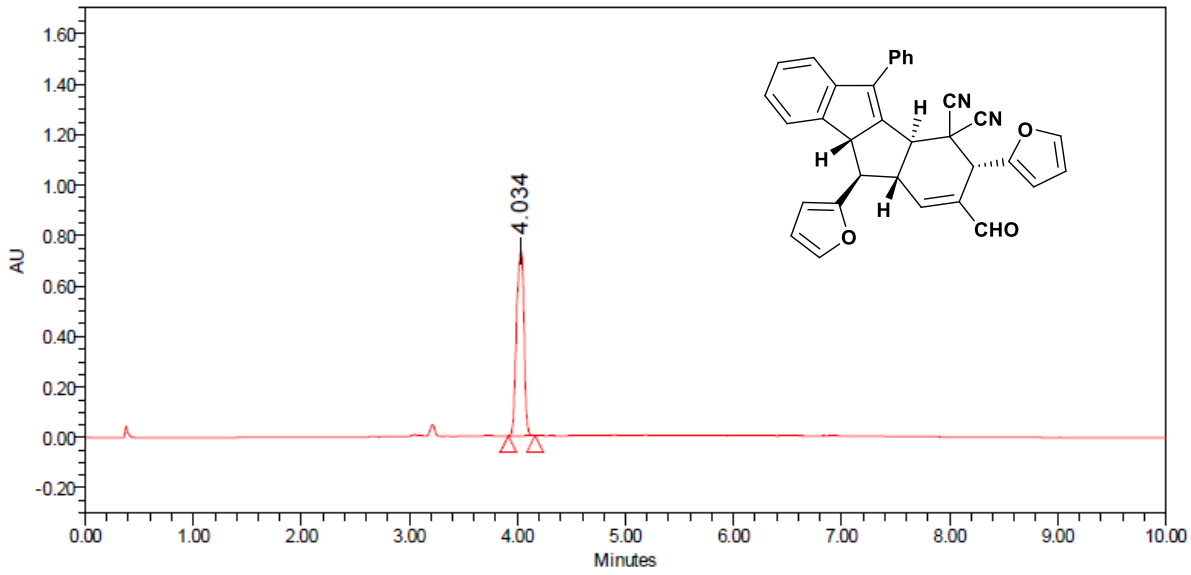
Racemic sample



Peak Results

	RT	% Area
1	4.031	55.59
2	4.253	44.41

Enantiomerically enriched sample

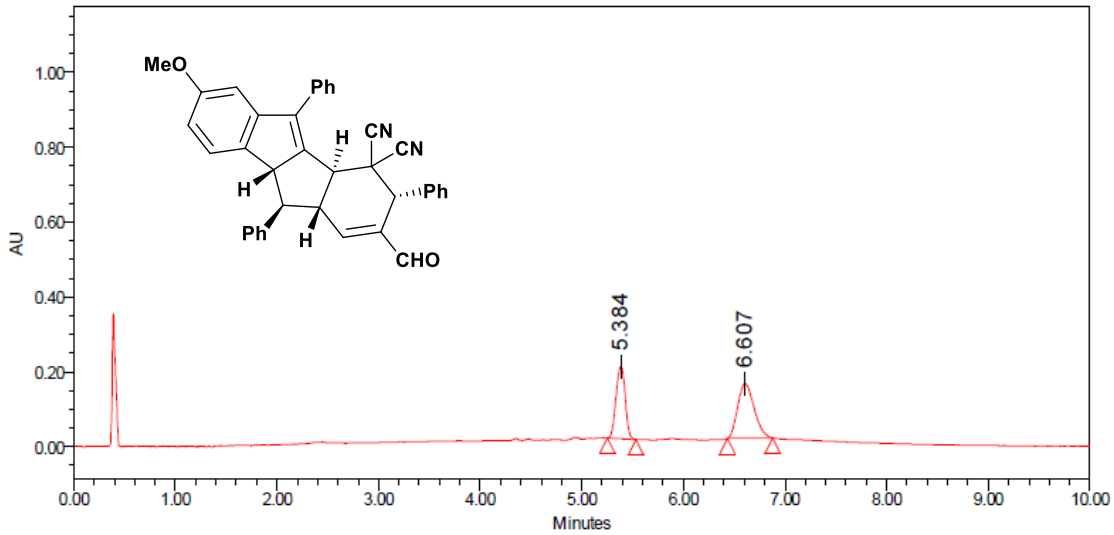


Peak Results

	RT	% Area
1	4.034	100.00

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-7-methoxy-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3i

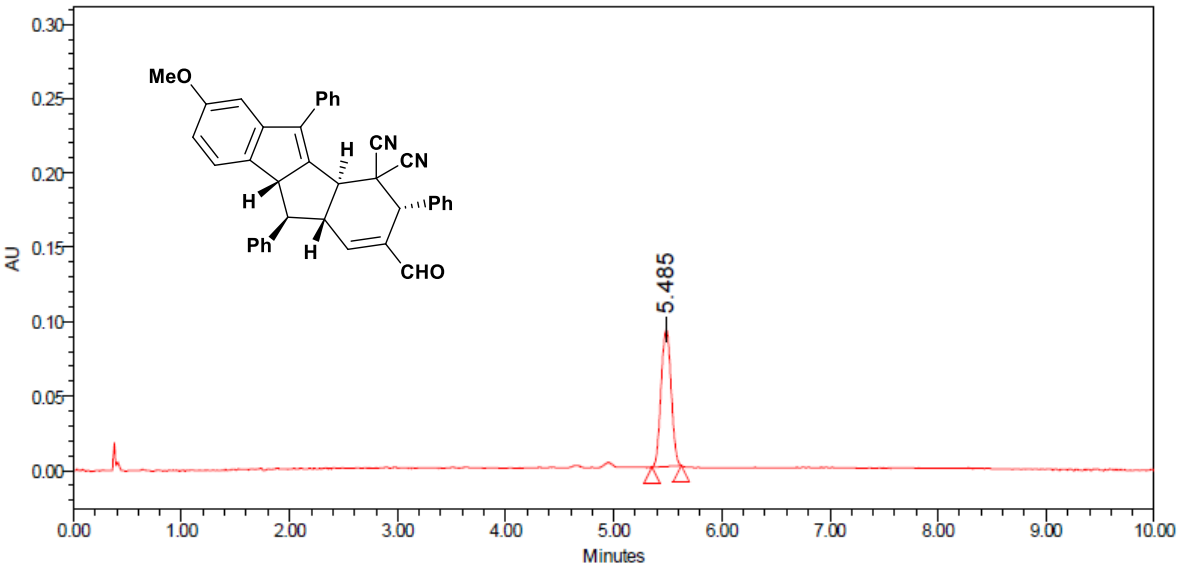
Racemic sample



Peak Results

	RT	% Area
1	5.384	42.53
2	6.607	57.47

Enantiomerically enriched sample

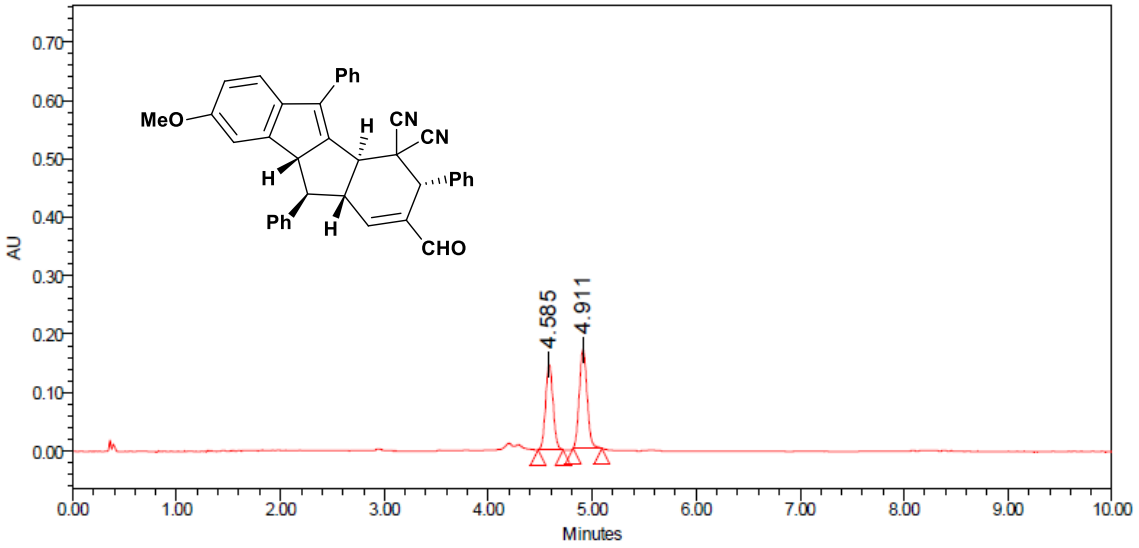


Peak Results

	RT	% Area
1	5.485	100.00

(3S,4aS,9bR,10R,10aR)-2-formyl-8-methoxy-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3j

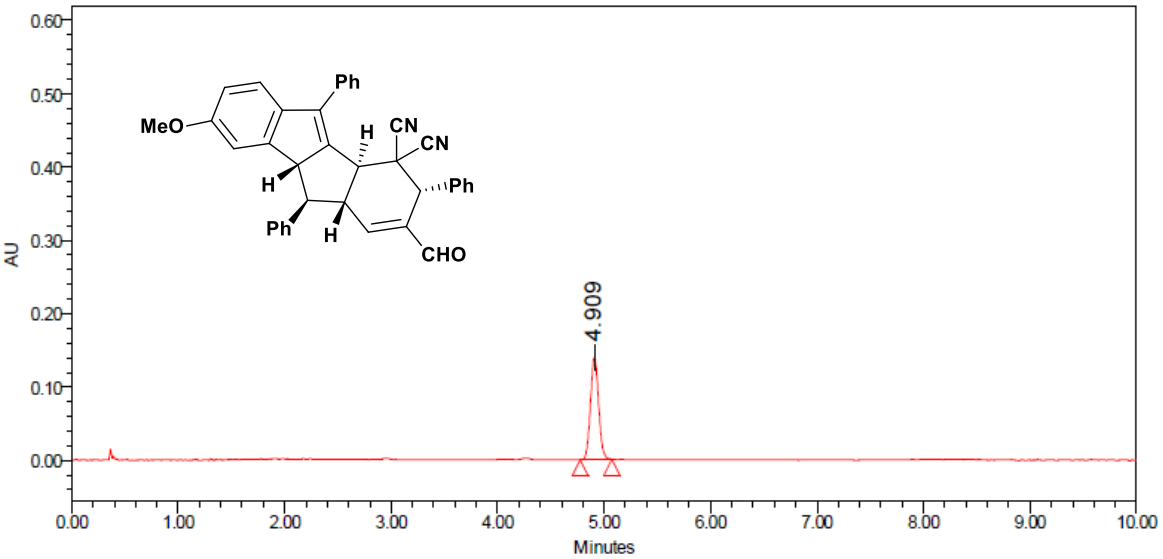
Racemic sample



Peak Results

	RT	% Area
1	4.585	45.08
2	4.911	54.92

Enantiomerically enriched sample

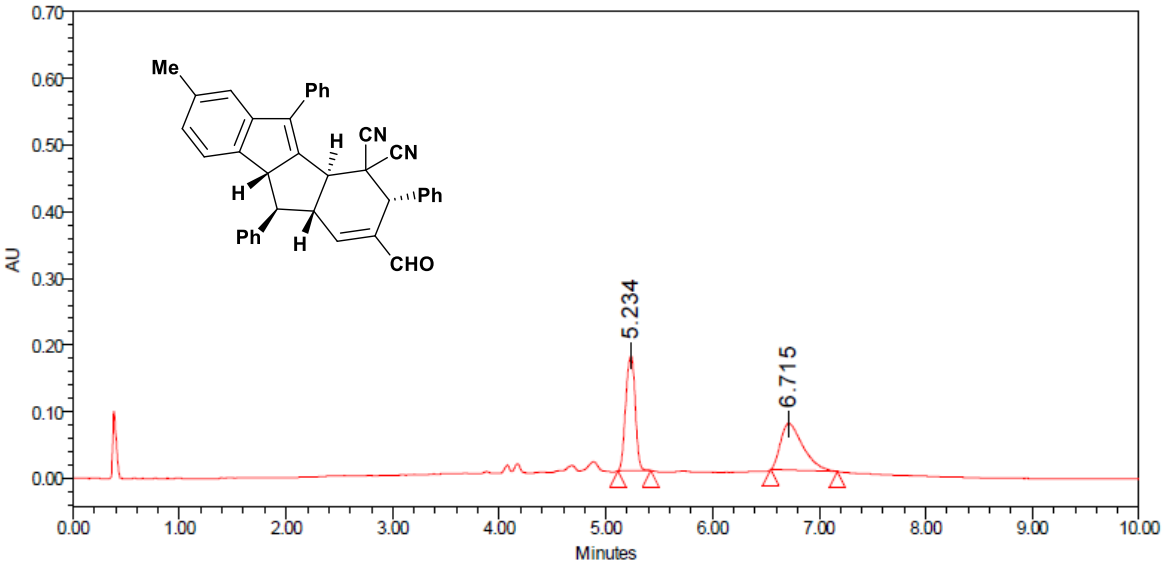


Peak Results

	RT	% Area
1	4.909	100.00

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-7-methyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3k

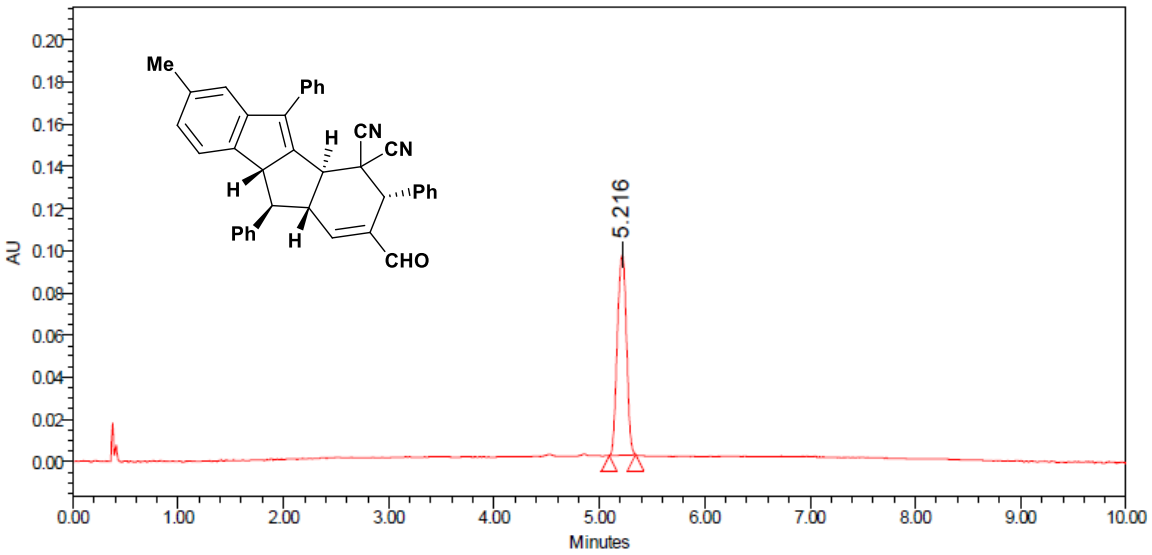
Racemic sample



Peak Results

	RT	% Area
1	5.234	51.16
2	6.715	48.84

Enantiomerically enriched sample

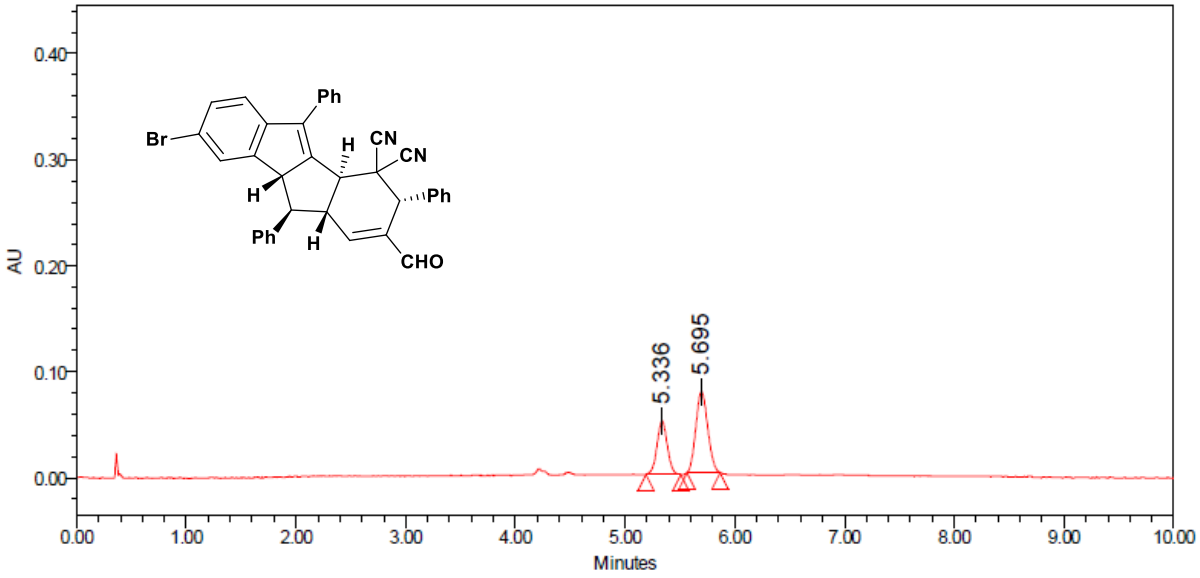


Peak Results

	RT	% Area
1	5.216	100.00

(3S,4aS,9bR,10R,10aR)-8-bromo-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3l

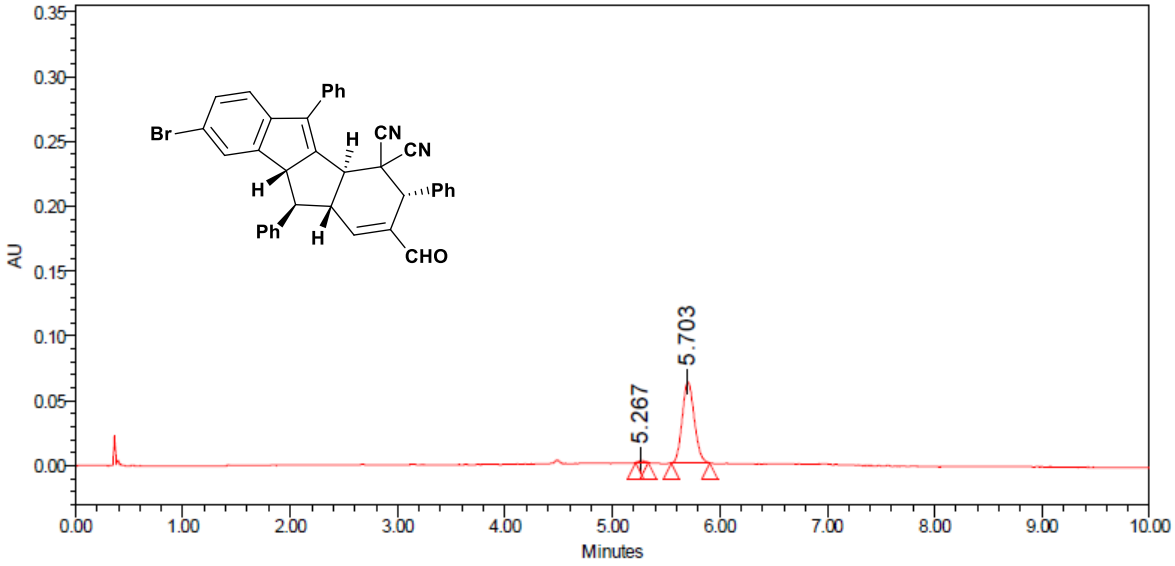
Racemic sample



Peak Results

	RT	% Area
1	5.336	36.06
2	5.695	63.94

Enantiomerically enriched sample

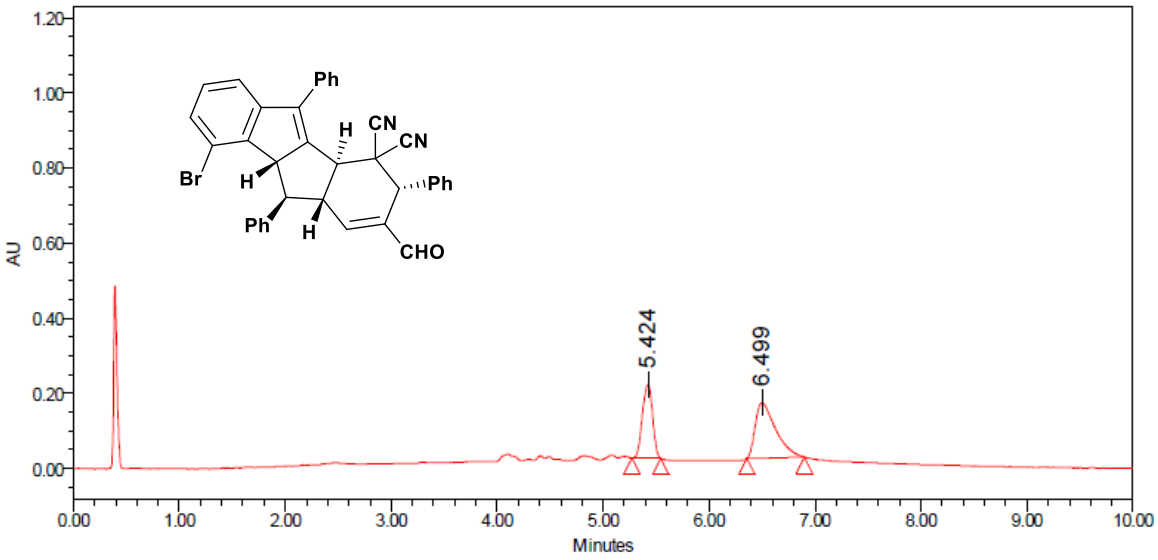


Peak Results

	RT	% Area
1	5.267	1.17
2	5.703	98.83

(3S,4aS,9bS,10R,10aR)-9-bromo-2-formyl-3,5,10-triphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3m

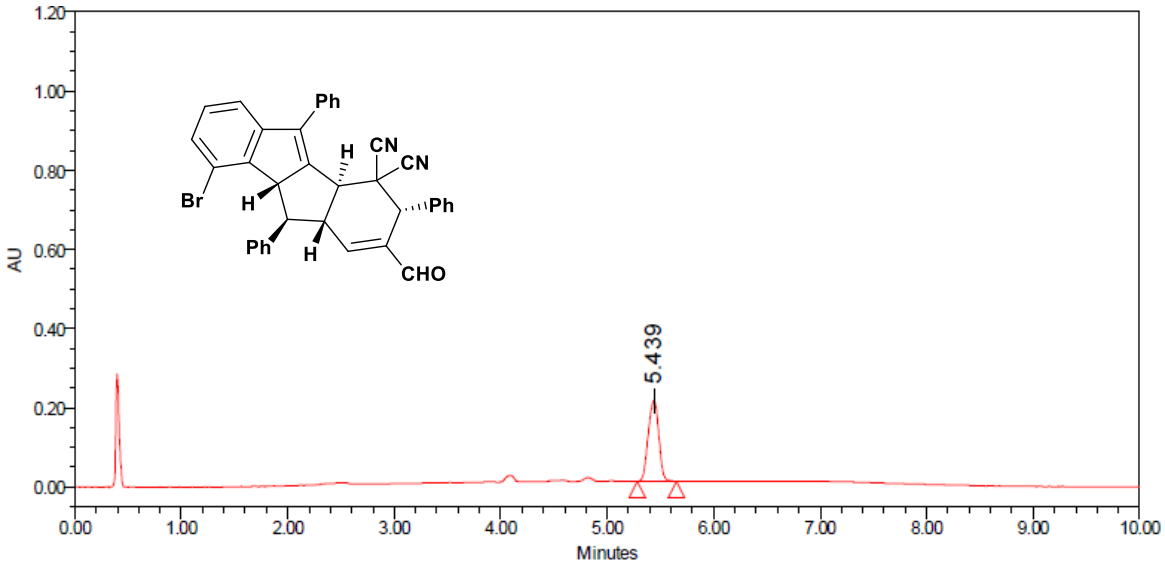
Racemic sample



Peak Results

	RT	% Area
1	5.424	39.82
2	6.499	60.18

Enantiomerically enriched sample

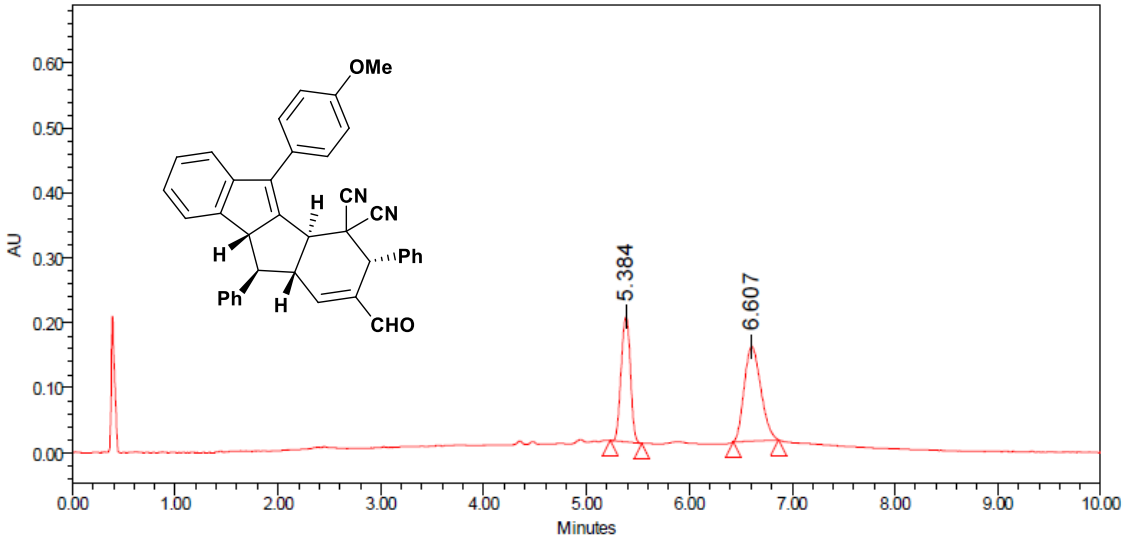


Peak Results

	RT	% Area
1	5.439	100.00

(3S,4aS,9bR,10R,10aR)-2-formyl-5-(4-methoxyphenyl)-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3n

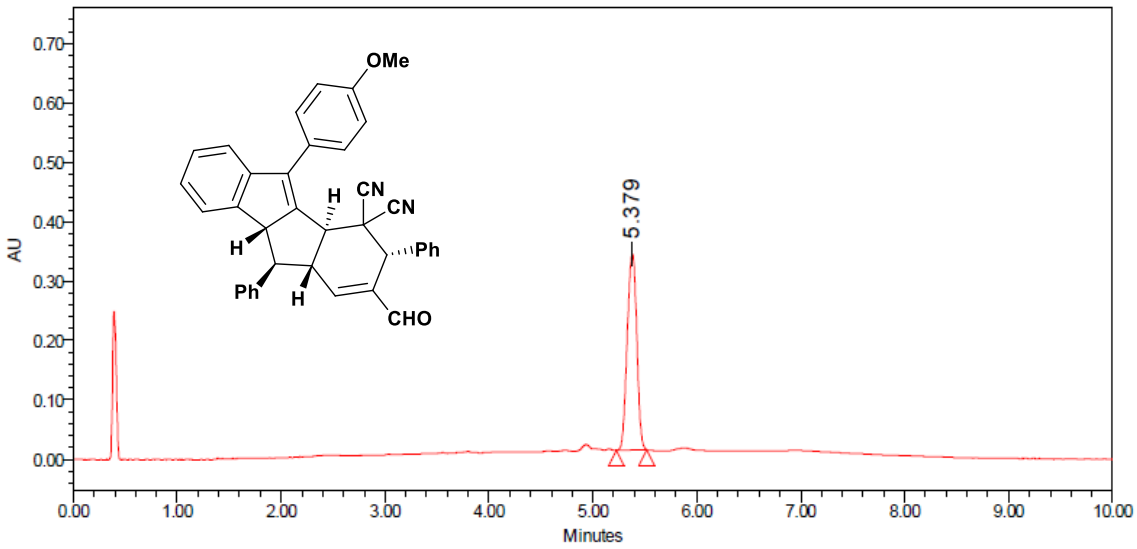
Racemic sample



Peak Results

	RT	% Area
1	5.384	42.42
2	6.607	57.58

Enantiomerically enriched sample

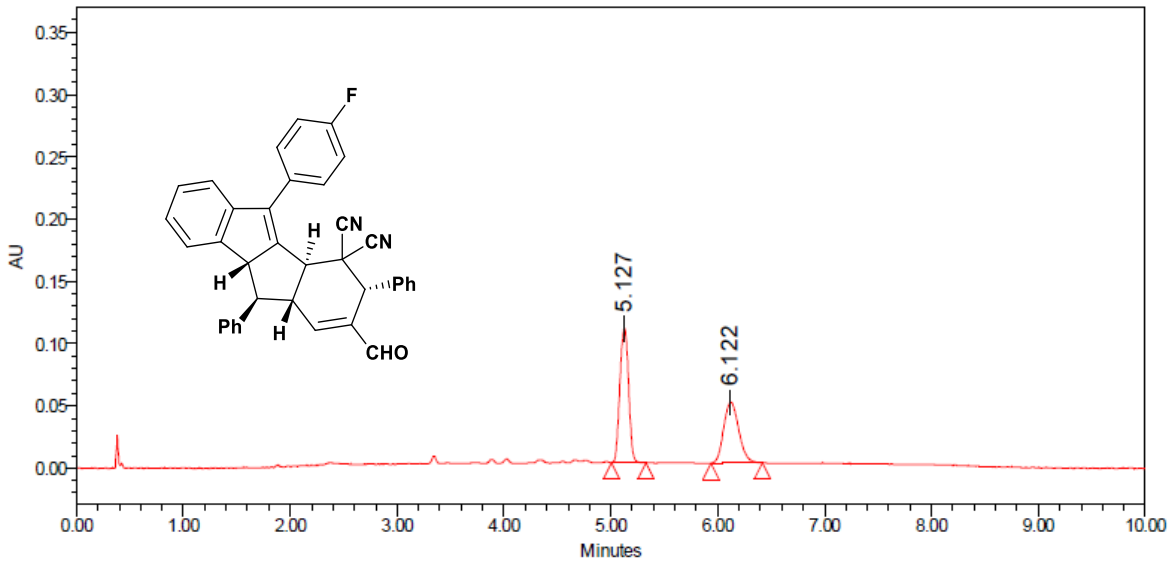


Peak Results

	RT	% Area
1	5.379	100.00

(3S,4aS,9bR,10R,10aR)-5-(4-fluorophenyl)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3o

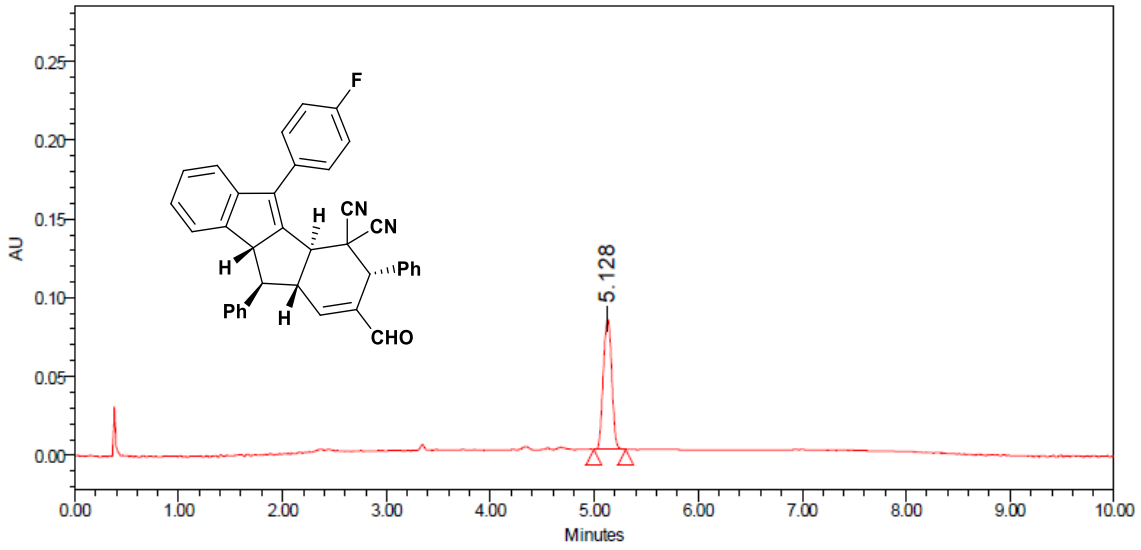
Racemic sample



Peak Results

	RT	% Area
1	5.127	55.99
2	6.122	44.01

Enantiomerically enriched sample

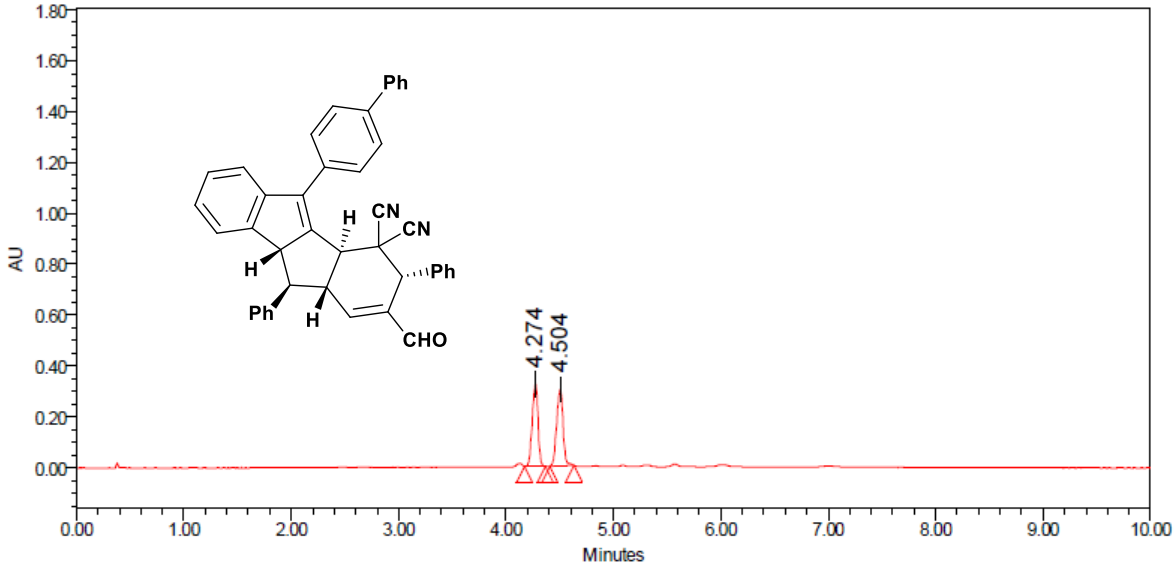


Peak Results

	RT	% Area
1	5.128	100.00

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-5-([1,1'-biphenyl]-4-yl)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3p

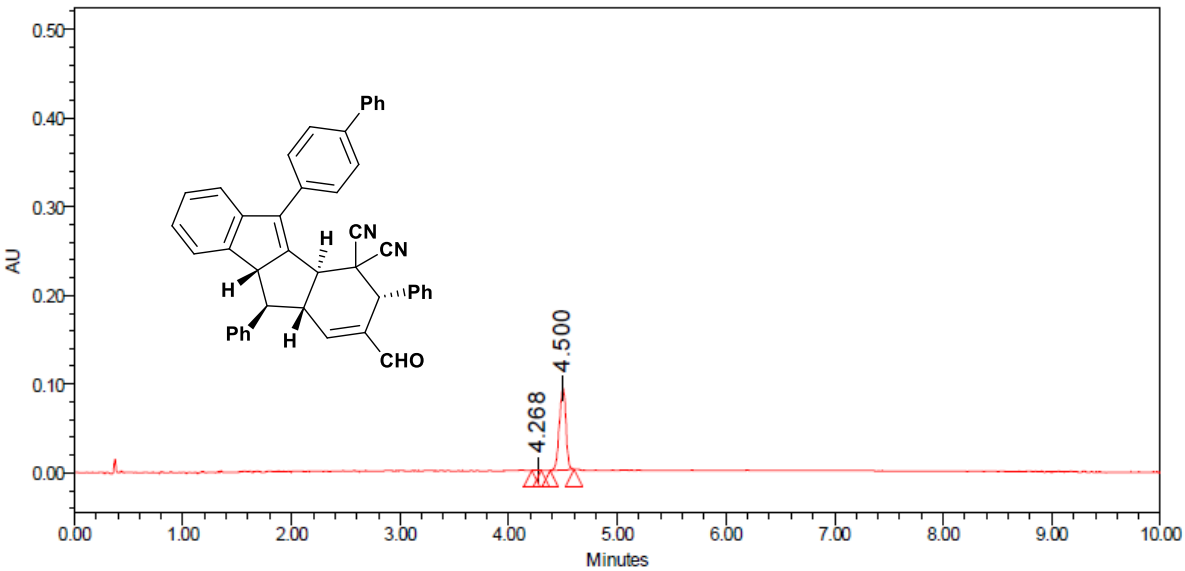
Racemic sample



Peak Results

	RT	% Area
1	4.274	49.36
2	4.504	50.64

Enantiomerically enriched sample

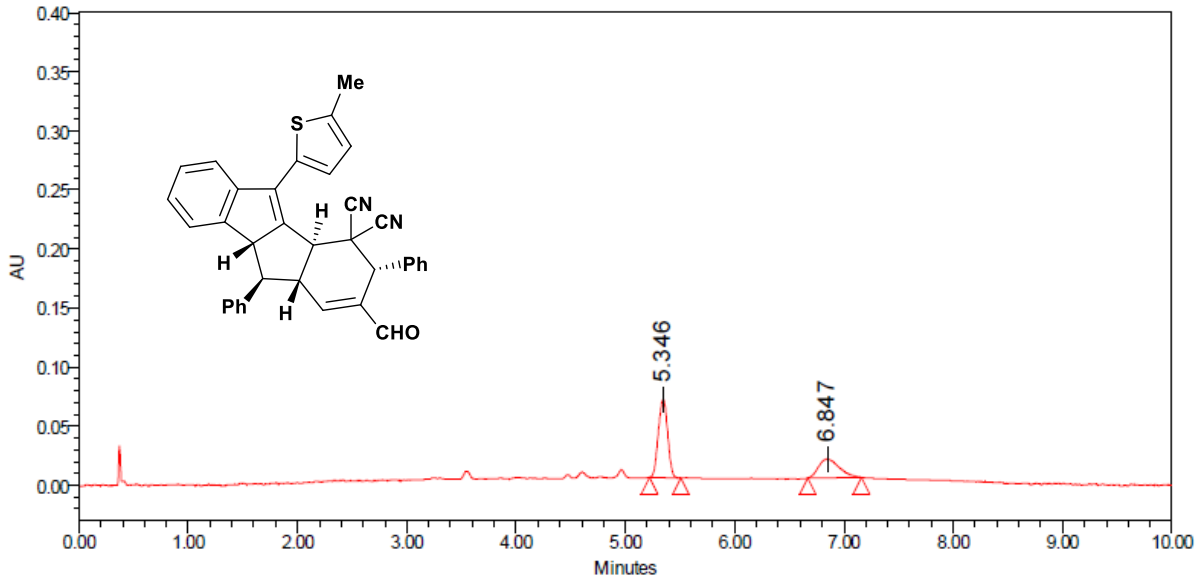


Peak Results

	RT	% Area
1	4.268	0.36
2	4.500	99.64

(3*S*,4a*S*,9b*R*,10*R*,10a*R*)-2-formyl-5-(5-methylthiophen-2-yl)-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3q

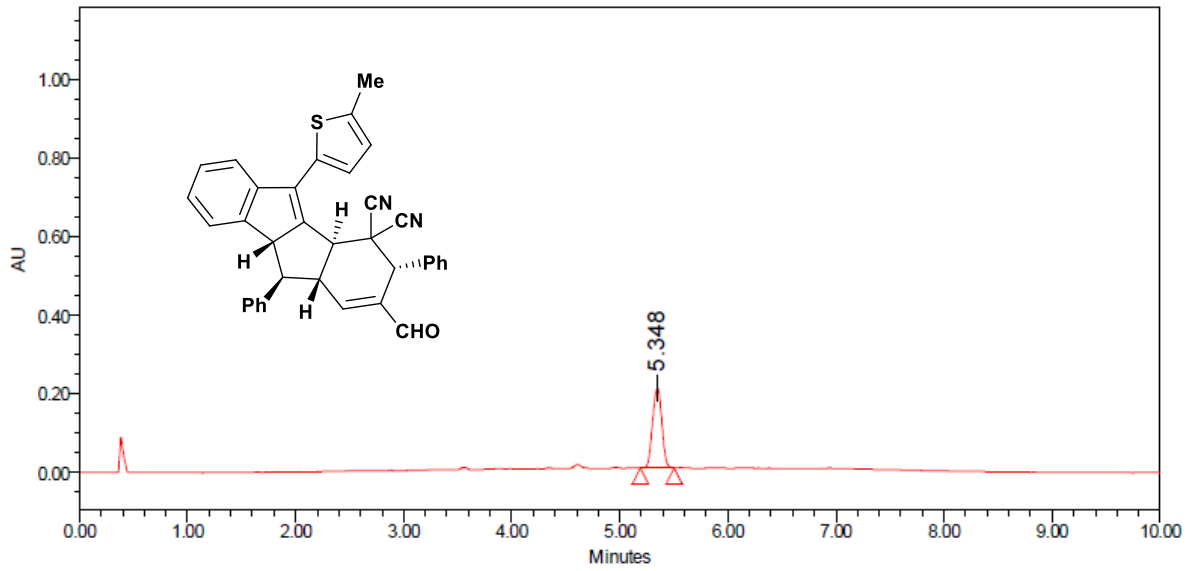
Racemic sample



Peak Results

	RT	% Area
1	5.346	65.32
2	6.847	34.68

Enantiomerically enriched sample

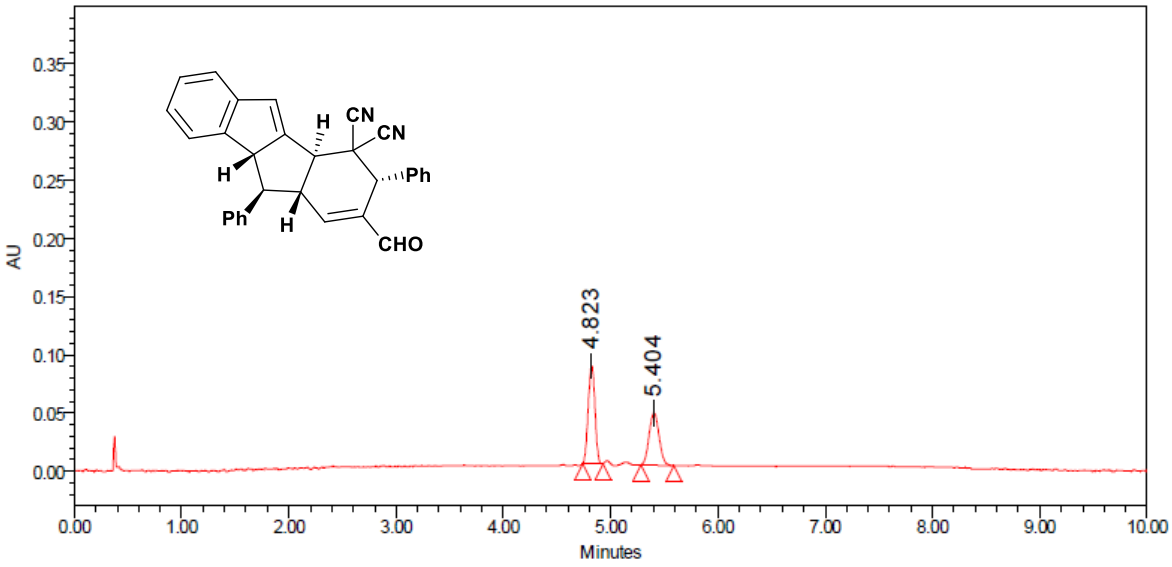


Peak Results

	RT	% Area
1	5.348	100.00

(3S,4aS,9bS,10R,10aR)-2-formyl-3,10-diphenyl-4a,9b,10,10a-tetrahydroindeno[2,1-a]indene-4,4(3H)-dicarbonitrile 3r

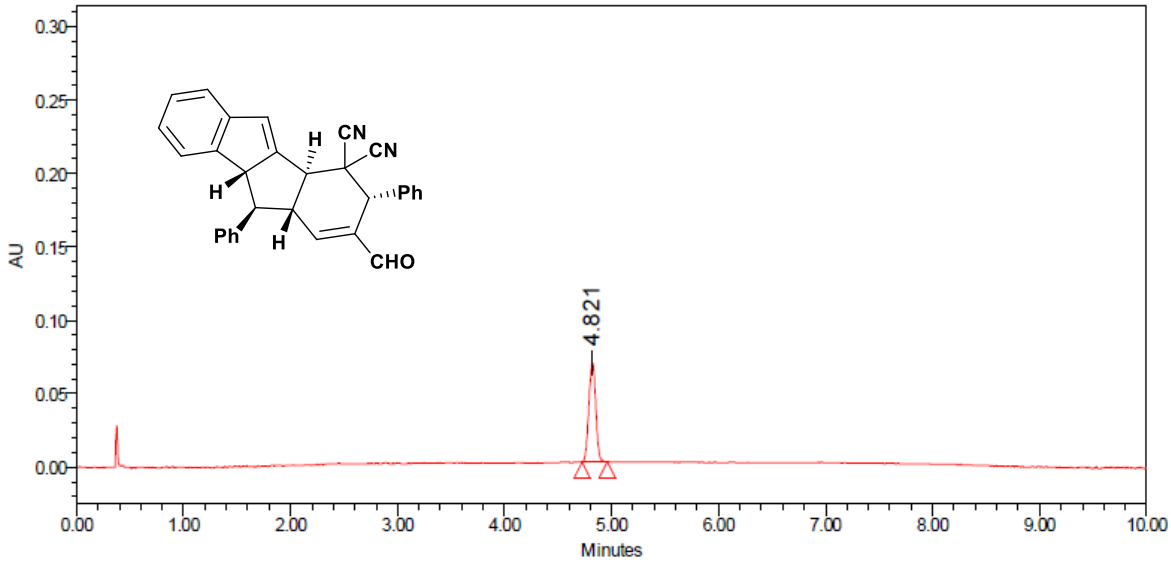
Racemic sample



Peak Results

	RT	% Area
1	4.823	55.88
2	5.404	44.12

Enantiomerically enriched sample



Peak Results

	RT	% Area
1	4.821	100.00