

Supplementary Information

Multicomponent Reactions in PEG-400: Ruthenium-Catalyzed Synthesis of Substituted Pyrroles

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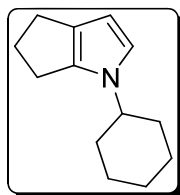
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Representative experimental procedure: To a stirred solution of ketone (1.0 mmol) in PEG-400 (4 mL) was added amine (1.5mmol) at 25 °C in a sealed tube. After 5 min, diol (2.2 mmol) was added followed by [Ru(*p*-cymene)Cl₂]₂ (0.01 mmol) and potassium tert.butoxide (0.2 mmol) were added successively. The sealed tube was tightly capped and heated to 130 °C. After completion of the reaction, it was cooled to room temperature. The solution was diluted with ether (10 mL), stirred for 10 min and was allowed to stand in ice-salt bath to solidify PEG-400. The ether layer was decanted, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography using 1-5 % ethyl acetate in petroleum ether as eluent to give pure products. The residual PEG-catalyst system was brought to room temperature and then utilized in next run by an addition of ketone, amine and ethyleneglycol along with base (KO^tBu) with further addition of Ru complex.

Spectral data for all compounds

All the substituted pyrroles have been prepared from the representative procedure.

1-Cyclohexyl-1,4,5,6-tetrahydrocyclopenta[*b*]pyrrole: (4a)



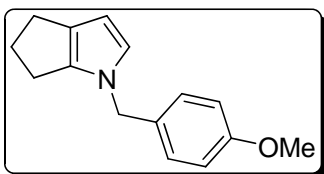
¹H NMR (300MHz, CDCl₃): δ 6.58 (d, *J* = 2.2 Hz, 1H), 5.9 (d, *J* = 3.0 Hz, 1H), 3.67 (tt, *J* = 12.0, 3.7 Hz, 1H), 2.69 (t, *J* = 6.7 Hz, 2H), 2.60 (t, *J* = 6.7 Hz, 2H), 2.39 (quin, *J* = 6.7 Hz, 2H), 2.03 (d, *J* = 12.8 Hz, 2H), 1.86 (d, *J* = 12.8 Hz, 2H), 1.78-1.51 (m, 2H), 1.46-1.11 (m, 4H);

^{13}C NMR (75 MHz, CDCl_3): δ 136.7, 125.8, 120.2, 102.2, 57.8, 34.0, 28.9, 25.7, 25.4, 25.3, 25.0;

IR (KBr): ν 2928, 2849, 1687, 1448, 1292, 698 cm^{-1} ;

EI-MS (m/z): 189 $[\text{M}^+]$;

1-(4-Methoxybenzyl)-1,4,5,6-tetrahydrocyclopenta[*b*]pyrrole: (4b)



^1H NMR (300MHz, CDCl_3): δ 7.06 (d, $J = 8.3\text{Hz}$, 2H), 6.84 (d, $J = 8.3\text{Hz}$, 2H), 6.55 (d, $J = 2.2\text{Hz}$, 1H), 5.92 (d, $J = 2.2\text{Hz}$, 1H), 4.87 (s, 2H), 3.79 (s, 3H), 2.61 (t, $J = 6.7\text{ Hz}$, 2H), 2.51 (t, $J = 7.5\text{ Hz}$, 2H), 2.42-2.30 (m, 2H);

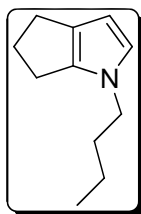
^{13}C NMR (75 MHz, CDCl_3): δ 158.9, 138.1, 130.2, 128.4, 126.4, 123.1, 113.9, 103.0, 55.2, 51.3, 29.2, 25.6, 24.5;

IR (KBr): ν 2998, 1050, 771, 697 cm^{-1} ;

ESI-MS (m/z): 227 $[\text{M}^+]$;

HRMS (ESI-MS): calcd for $\text{C}_{15}\text{H}_{18}\text{NO}$ $[\text{M} + \text{H}]^+ 228.1382$, found 228.1391;

1-Butyl-1,4,5,6-tetrahydrocyclopenta[*b*]pyrrole: (4c)



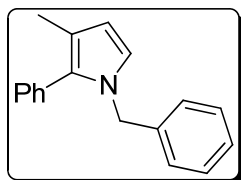
^1H NMR (300MHz, CDCl_3): δ 6.51 (d, $J = 2.2\text{ Hz}$, 1H), 5.89 (d, $J = 2.2\text{ Hz}$, 1H), 3.74 (t, $J = 7.5$, 6.7 Hz, 2H), 2.67-2.58 (m, 4H), 2.46-2.35 (m, 2H), 1.75-1.63 (m, 2H), 1.33 (sex, $J = 7.5\text{ Hz}$, 2H), 0.93 (t, $J = 7.5$, 6.7 Hz, 3H);

^{13}C NMR (75 MHz, CDCl_3): δ 137.7, 125.7, 122.7, 102.4, 47.8, 33.3, 29.1, 25.5, 24.5, 19.9, 13.6;

IR (KBr): ν 2990, 1200 cm^{-1} ;

EI-MS (m/z): 163 [M⁺];

1-Benzyl-3-methyl-2-phenyl-1H-pyrrole: (4d)



¹H NMR (300MHz, CDCl₃): δ 7.39-7.19 (m, 8H), 6.95 (d, J = 6.6 Hz, 2H), 6.66 (d, J = 2.6 Hz, 1H), 6.14 (d, J = 2.6 Hz, 1H), 4.98 (s, 2H), 2.08 (s, 3H);

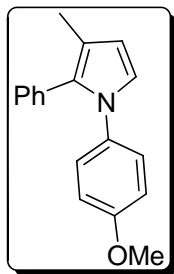
¹³CNMR (75 MHz, CDCl₃): δ 138.9, 132.6, 131.2, 130.3, 128.4, 128.1, 127.0, 126.9, 126.5, 120.8, 116.9, 109.7, 50.6, 11.9.;

IR (KBr): ν 2922, 2852, 771, 697 cm⁻¹;

ESI-MS (m/z): 247 [M⁺];

HRMS (ESI-MS): calcd. for C₁₈H₁₈N [M + H]⁺ 248.1433; found 248.1441;

1-(4-Methoxyphenyl)-3-methyl-2-phenyl-1H-pyrrole: (4e)



¹H NMR (300MHz, CDCl₃): δ 7.28-7.15 (m, 3H), 7.11-7.06 (m, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 2.8 Hz, 1H), 6.77 (d, J = 9.0 Hz, 2H), 6.22 (d, J = 2.6 Hz, 1H), 3.77 (s, 3H), 2.18 (s, 3H);

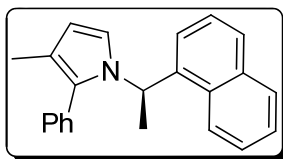
¹³CNMR (75 MHz, CDCl₃): δ 157.7, 133.9, 132.6, 130.2, 127.8, 126.6, 126.1, 122.3, 119.7, 118.4, 113.9, 110.6, 55.4, 12.2;

IR (KBr): ν 2927, 1514, 1248, 834, 768 cm⁻¹;

ESI-MS (m/z): 263 [M⁺];

HRMS (ESI-MS): calcd for C₁₈H₁₈NO [M + H]⁺264.1382, found264.1391;

(R)-3-Methyl-1-(1-(naphthalen-1-yl)ethyl)-2-phenyl-1H-pyrrole (4f)



¹H NMR (300MHz, CDCl₃): δ 7.8 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.3 Hz, 1H), 7.43-7.32 (m, 3H), 7.28-7.26 (m, 1H), 7.24-7.18 (m, 3H), 7.14-7.11 (m, 2H), 6.86 (d, J = 2.8 Hz, 1H), 6.14 (d, J = 2.8 Hz, 1H), 5.95 (q, J = 7.0 Hz, 1H), 2.04 (s, 3H), 1.85 (d, J = 7.0 Hz, 3H);

¹³CNMR (75 MHz, CDCl₃): δ 139.5, 133.6, 132.8, 130.9, 130.5, 130.0, 128.6, 128.0, 127.8, 126.9, 126.0, 125.4, 125.3, 122.9, 122.6, 117.8, 116.9, 109.1, 51.7, 23.3, 11.8;

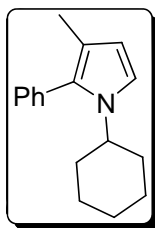
IR (KBr): ν 2933, 1377, 1218, 1077, 772 cm⁻¹;

ESI-MS (m/z): 311 [M⁺];

HRMS (ESI-MS): calcd.for C₂₃H₂₂N [M + H]⁺ 312.1746; found 312.1754;

$[\alpha]_D^{25}$: - 34.78 (c 1.935, CHCl₃);

1-Cyclohexyl-3-methyl-2-phenyl-1H-pyrrole: (4g)



¹H NMR (300MHz, CDCl₃): δ 7.44-7.23 (m, 5H), 6.76 (d, J = 3.0 Hz, 1H), 6.10 (d, J = 3.0 Hz, 1H), 3.79 (tt, J = 12.0, 3.7 Hz, 1H), 2.02 (s, 3H), 1.99-1.89 (m, 2H), 1.82-1.72 (m, 2H), 1.67-1.52 (m, 3H), 1.28-1.09 (m, 3H);

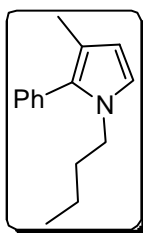
^{13}C NMR (75 MHz, CDCl_3): δ 133.0, 130.3, 130.0, 128.0, 126.6, 116.1, 115.7, 108.9, 54.9, 34.6, 25.6, 25.2, 11.5;

IR (KBr): ν 2931, 2856, 1318, 1213, 771 cm^{-1} ;

ESI-MS (m/z): 239 [M^+];

HRMS (ESI-MS): calcd. for $\text{C}_{17}\text{H}_{22}\text{N}$ [$\text{M} + \text{H}$] $^+$ 240.1746; found240.1755;

1-Butyl-3-methyl-2-phenyl-1H-pyrrole: (4h)



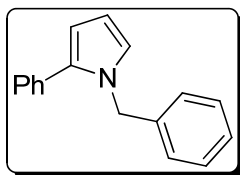
^1H NMR (300MHz, CDCl_3): δ 7.43-7.38 (m, 2H), 7.34-7.27 (m, 3H), 6.66 (d, $J = 2.7$ Hz, 1H), 6.07 (d, $J = 2.5$ Hz, 1H), 3.78 (t, $J = 7.3$ Hz, 2H), 2.04 (s, 3H), 1.58- 1.51 (m, 2H), 1.21-1.13 (m, 2H), 0.79 (t, $J = 7.3$ Hz, 3H);

^{13}C NMR (75 MHz, CDCl_3): δ 133.1, 130.8, 130.5, 128.2, 126.9, 120.1, 116.6, 109.0, 46.9, 33.6, 19.8, 11.9, 13.6;

IR (KBr): ν 1200, 772, 698 cm^{-1} ;

ESI-MS (m/z): 213 [M^+];

1-Benzyl-2-phenyl-1H-pyrrole: (4i)



^1H NMR (300MHz, CDCl_3): δ 7.37-7.20 (m, 10H), 7.01 (d, $J = 6.7$ Hz, 1H), 6.75 (t, $J = 2.2$ Hz, 1H), 6.28 (d, $J = 2.2$ Hz, 1H), 5.15 (s, 2H);

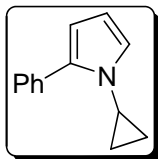
^{13}C NMR (75 MHz, CDCl_3): δ 138.7, 134.8, 133.1, 128.7, 128.5, 128.3, 127.2, 126.3, 122.8, 108.8, 108.4, 50.5;

IR (KBr): ν 1220, 772, 698 cm^{-1} ;

ESI-MS (m/z): 233 [M⁺];

HRMS (ESI-MS): calcd. for $\text{C}_{17}\text{H}_{16}\text{N}$ [M + H]⁺ 234.1277; found 234.1288.

1-Cyclopropyl-2-phenyl-1H-pyrrole: (4j)



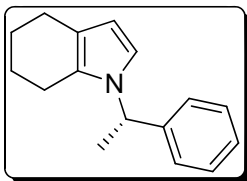
¹H NMR (300MHz, CDCl_3): δ 7.55 (d, $J = 7.1$ Hz, 2H), 7.37 (t, $J = 7.9$ Hz, 2H), 7.27 (t, $J = 7.5$ Hz, 1H), 6.79 (t, $J = 3.3, 1.8$ Hz, 1H), 6.22 (dd, $J = 3.3, 1.8$ Hz, 1H), 6.14 (t, $J = 3.3, 3.0$ Hz, 1H), 3.47-3.37 (m, 1H), 0.91-0.77 (m, 4H);

¹³CNMR (75 MHz, CDCl_3): δ 135.4, 133.7, 128.3, 128.1, 126.4, 122.6, 108.8, 107.5, 29.7, 8.3;

IR (KBr): ν 1219, 771 cm^{-1} ;

EI-MS (m/z): 183 [M⁺];

(S)-1-(1-Phenylethyl)-4,5,6,7-tetrahydro-1H-indole: (4k)



¹H NMR (300MHz, CDCl_3): δ 7.29 (t, $J = 7.6$ Hz, 2H), 7.22 (tt, $J = 7.3, 2.1$ Hz, 1H), 7.0 (d, $J = 7.3$ Hz, 2H), 6.73 (d, $J = 2.8$ Hz, 1H), 6.0 (d, $J = 2.8$ Hz, 1H), 5.2 (q, $J = 7.0$, 1H), 2.55-2.44 (m, 3H), 2.24-2.16 (m, 1H), 1.78 (d, $J = 7.0$ Hz, 3H), 1.75-1.59 (m, 4H);

¹³CNMR (75 MHz, CDCl_3): δ 143.8, 128.5, 128.0, 126.9, 125.6, 117.5, 115.7, 106.0, 54.4, 23.6, 23.2, 23.1, 22.1, 21.9;

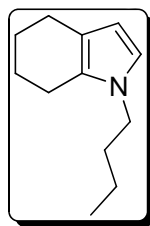
IR (KBr): ν 2928, 1292, 772, 698 cm^{-1} ;

ESI-MS (m/z): 225 [M⁺];

HRMS (ESI-MS): calcd for $\text{C}_{16}\text{H}_{20}\text{N}$ [M + H]⁺ 226.1590, found 226.1596;

$[\alpha]_D^{25}$: - 32.5 (c 0.96, CHCl₃);

1-Butyl-4,5,6,7-tetrahydro-1H-indole: (4l)



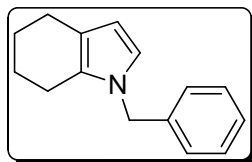
¹H NMR (300MHz, CDCl₃): δ 6.50 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 2.7 Hz, 1H), 3.71 (t, *J* = 7.3 Hz, 2H), 2.54-2.49 (m, 4H), 1.85-1.79 (m, 2H), 1.75-1.63 (m, 4H), 1.38-1.30 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H);

¹³CNMR (75 MHz, CDCl₃): δ 127.3, 118.4, 116.8, 116.8, 105.7, 45.7, 33.4, 23.5, 23.3, 23.1, 21.8, 19.9, 13.6;

IR (KBr): ν 2956, 2929, 1702, 1679 cm⁻¹.

EI-MS (*m/z*): 177 [M⁺];

1-Butyl-2-phenyl-4,5,6,7-tetrahydro-1H-indole: (4m)



¹H NMR (300MHz, CDCl₃): δ 7.33-7.28 (m, 2H), 7.25-7.22 (m, 1H), 7.04-7.01 (m, 2H), 6.56 (d, *J* = 2.7 Hz, 1H), 5.97 (d, *J* = 2.7 Hz, 1H), 4.95 (s, 2H), 2.53 (t, *J* = 6.1 Hz, 2H), 2.41 (t, *J* = 6.2 Hz, 2H), 1.80-1.68 (m, 4H);

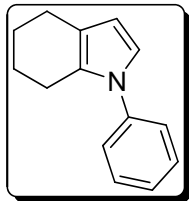
¹³CNMR (75 MHz, CDCl₃): δ 138.5, 128.5, 127.9, 127.1, 126.5, 119.3, 117.6, 106.4, 49.8, 23.5, 23.2 (2C), 21.7;

IR (KBr):ν 2998, 779, 698 cm⁻¹;

ESI-MS (*m/z*): 211 [M⁺];

HRMS (ESI-MS): calcd. for C₁₅H₁₈N [M + H]⁺ 212.1433; found 212.1436;

1-Phenyl-4,5,6,7-tetrahydro-1H-indole (4n):



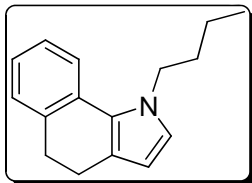
^1H NMR (300MHz, CDCl_3): δ 7.43-7.37 (m, 2H), 7.32-7.25 (m, 3H), 6.77 (d, $J = 2.8$ Hz, 1H), 6.10 (d, $J = 2.8$ Hz, 1H), 2.62-2.54 (m, 4H), 1.81-1.75 (m, 4H);

^{13}C NMR (75 MHz, CDCl_3): δ 140.2, 129.0, 128.1, 126.0, 124.5, 119.8, 118.9, 108.0, 23.6, 23.4, 23.2;

IR (KBr): ν 2932, 1500, 1475, 1384, 760, 704 cm^{-1} ;

EI-MS (m/z): 197 [M^+];

1-Butyl-4,5-dihydro-1H-benzo[g]indole: (4o)



^1H NMR (300MHz, CDCl_3): δ 7.35 (d, $J = 7.5$ Hz, 1H), 7.26-7.17 (m, 2H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.61 (d, $J = 2.2$ Hz, 1H), 6.02 (d, $J = 3.0$ Hz, 1H), 4.16 (t, $J = 7.5$ Hz, 2H), 2.85 (t, $J = 8.3$, 6.7 Hz, 2H), 2.65 (t, $J = 8.3$, 6.7 Hz, 2H), 1.82 (quin, $J = 7.5$ Hz, 2H), 1.39 (sex, $J = 7.5$ Hz, 2H), 0.95 (t, $J = 7.5$ Hz, 3H);

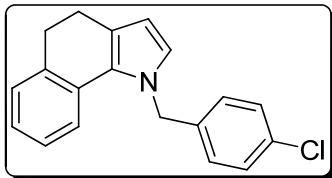
^{13}C NMR (75 MHz, CDCl_3): δ 136.4, 130.2, 128.4, 127.4, 126.4, 124.4, 123.3, 122.8, 120.1, 105.7, 48.7, 33.2, 31.3, 22.5, 19.9, 13.7;

IR (KBr): ν 2957, 2932, 1476, 758, 684 cm^{-1} ;

ESI-MS (m/z): 225 [M^+];

HRMS (ESI-MS): calcd. for $\text{C}_{16}\text{H}_{20}\text{N}$ [$\text{M} + \text{H}$] $^+$ 226.1590; found 226.1590;

1-(4-Chlorobenzyl)-4,5-dihydro-1H-benzo[g]indole: (4p)



^1H NMR (300MHz, CDCl_3): δ 7.3 (d, $J = 8.3$ Hz, 2H), 7.22 (d, $J = 5.3$ Hz, 1H), 7.07-6.99 (m, 5H), 6.61 (d, $J = 2.7$ Hz, 1H), 6.13 (d, $J = 2.5$ Hz, 1H), 5.37 (s, 2H), 2.87 (t, $J = 8.0, 6.7$ Hz, 2H), 2.70 (t, $J = 7.9, 6.8$ Hz, 2H);

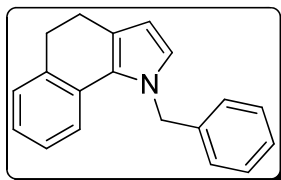
^{13}C NMR (75 MHz, CDCl_3): δ 136.9, 136.4, 133.0, 128.8, 128.4, 127.4, 126.4, 124.7, 123.7, 122.9, 120.0, 106.9, 51.7, 31.1, 22.4;

IR (KBr): ν 2931, 1492, 1477, 760 cm^{-1} ;

ESI-MS (m/z): 293 [M $^+$];

HRMS (ESI-MS): calcd. for $\text{C}_{19}\text{H}_{17}\text{ClN}$ [M + H] $^+$ 294.1044; found 294.1048;

1-Benzyl-4,5-dihydro-1H-benzo[g]indole: (4q)



^1H NMR (300MHz, CDCl_3): δ 7.37-6.94 (m, 9H), 6.62 (d, $J = 2.4$ Hz, 1H), 6.13 (d, $J = 2.0$ Hz, 1H), 5.4 (s, 2H), 2.88 (t, $J = 27.7, 6.7$ Hz, 2H), 2.71 (t, $J = 7.9, 6.6$ Hz, 2H);

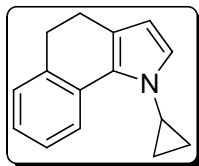
^{13}C NMR (75 MHz, CDCl_3): δ 138.4, 136.4, 129.7, 128.7, 128.3, 127.2, 126.4, 126.0, 124.6, 123.8, 122.6, 120.3, 106.6, 51.7, 31.2, 22.4;

IR (KBr): ν 2933, 1603, 1477, 1301, 760, 727, 689 cm^{-1} ;

ESI-MS (m/z): 259 [M $^+$];

HRMS (ESI-MS): calcd. for $\text{C}_{19}\text{H}_{18}\text{N}$ [M + H] $^+$ 260.1433; found 260.1441;

1-Cyclopropyl-4,5-dihydro-1H-benzo[g]indole: (4r)



^1H NMR (300MHz, CDCl_3): δ 7.90 (d, $J = 7.5$ Hz, 1H), 7.28-7.16 (m, 2H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.69 (d, $J = 2.4$ Hz, 1H), 5.97 (d, $J = 1.8$ Hz, 1H), 3.58-3.49 (m, 1H), 2.86 (t, $J = 6.7, 7.9$ Hz, 2H), 2.65 (t, $J = 8.1, 6.6$ Hz, 2H), 1.11-1.02 (m, 4H);

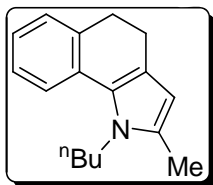
^{13}C NMR (75 MHz, CDCl_3): δ 135.9, 128.1, 127.7, 126.0, 124.5, 122.7, 122.2, 121.0, 120.0, 105.6, 30.9, 30.4, 22.3, 8.8;

IR (KBr): ν 2932, 1500, 1475, 1384, 760, 704 cm^{-1} ;

ESI-MS (m/z): 209 [M $^+$];

HRMS (ESI-MS): calcd. for $\text{C}_{15}\text{H}_{16}\text{N}$ [M + H] $^+$ 210.1277; found 210.1279;

1-Butyl-2-methyl-4,5-dihydro-1H-benzo[g]indole: (4s)

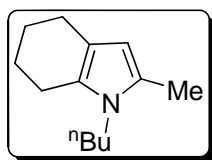


^1H NMR (300MHz, CDCl_3): 7.34-7.28 (m, 1H), 7.25-7.15 (m, 2H), 7.04-5.97 (m, 1H), 5.80 (s, 1H), 4.06 (t, $J = 8.1$ Hz, 2H), 2.82 (t, $J = 8.1$ Hz, 2H), 2.59 (t, $J = 7.9$ Hz, 2H), 2.29 (s, 3H), 1.86-1.74 (m, 2H), 1.49-1.35 (m, 2H), 0.98 (t, $J = 7.3$ Hz, 3H);

^{13}C NMR (75 MHz, CDCl_3): δ 136.1, 133.0, 130.5 (2C), 128.3, 126.4, 123.8, 121.8, 119.4, 105.5, 45.0, 33.0, 31.3, 22.3, 20.0, 13.7, 12.5;

ESI-MS (m/z): 301 [M $^+$];

1-Butyl-2-methyl-4,5,6,7-tetrahydro-1H-indole: (4t)



^1H NMR (300MHz, CDCl_3): δ 5.65 (s, 1H), 3.65 (t, $J = 7.7$ Hz, 2H), 2.51 (t, $J = 6.1$ Hz, 2H), 2.47 (t, $J = 6.1$ Hz, 2H), 2.20 (s, 3H), 1.84-1.78 (m, 2H), 1.74-1.67 (m, 2H), 1.62-1.55 (m, 2H), 1.39-1.31 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H);

^{13}C NMR (75 MHz, CDCl_3): δ 126.4 (2C), 115.7, 104.6, 42.9, 33.3, 23.8, 23.5, 22.9, 22.1, 20.1, 13.7, 11.9;

ESI-MS (m/z): 191 [M^+];