

Supporting Information

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Regioselective pyrrole C–benzylation using hexaethylene glycolic ionic liquids as a recyclable catalyst

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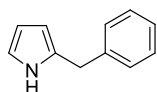
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General:

The ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at room temperature, and the chemical shifts are reported in δ units (ppm) relative to tetramethylsilane (TMS). TLC analysis was performed on 0.25 mm silica gel 60 aluminium sheets containing F254. Flash chromatography was performed using 230–400 mesh silica gel. All other known compounds including the ionic liquid, [bmim][BF₄] were commercially available. Tailor-made ionic liquid [hexaEGmim][OMs] and [dihexaEGim][OMs] were synthesized according to the reported procedure and was duly characterized before use.¹⁻²

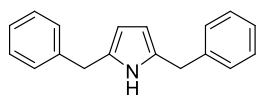
Typical Procedure for Pyrrole C-Benzylation in IL (Table 2). In a pre-dried pressure vial benzyl halides/ mesylate/ tosylate (**2**) (1.0 mmol), pyrrole (**1**, 0.14 mL, 2.0 mmol), NaHCO₃ (84 mg, 1.0 mmol) and [hexaEGmim][OMs] (45 mg, 0.1 mmol) or [dihexaEGim][OMs] (70 mg, 0.1 mmol) in 3.0 mL of anhydrous acetonitrile was heated at 80 °C in oil bath. Reaction was monitored using TLC, after completion the reaction mixture was extracted from IL phase with ethyl ether (10 mL x 3). The organic layer was dried over anhydrous sodium sulfate, evaporated under reduced pressure and was purified by short flash column chromatography (silica gel) (5% EtOAc/hexanes) to obtain of 2-benzyl-*1H*-pyrrole (**3**) as colorless oil.



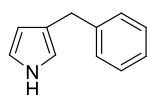
2-Benzyl-1H-pyrrole (3). colorless oil; ^1H NMR (400 MHz, CDCl₃) δ 3.97 (s, 2H), 5.98-6.00 (m, 1H), 6.13-6.15 (m, 1H), 6.65-6.66 (m, 1H), 7.18-7.31 (m, 5H), 7.80 (bs, NH); ^{13}C NMR (100 MHz, CDCl₃) δ 34.0, 106.4, 108.3, 116.9, 126.4, 128.6, 128.7, 130.6, 139.5; MS (EI) 157 (M^+), 80 (100). HR MS (EI) Calcd for C₁₁H₁₁N (M^+) 157.0891, found 157.0891; CAS Registry No. 33234-48-9.

¹ Jadhav, V. H.; Jeong, H.-J.; Lim, S. T.; Sohn, M. H.; Kim, D. W. *Org. Lett.*, **2011**, *13*, 2502–2505.

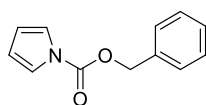
² Jadhav, V. H.; Kim, J. G.; Park, S. H.; Kim, D. W. *Chem. Eng. J.* **2017**, *308*, 664–668.



2,5-Dibenzyl-1H-pyrrole (4). light brown solid; m.p. 74-76 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.89 (s, 4H), 5.85 (d, J = 2.4 Hz, 2H), 7.16-7.21 (m, 6H), 7.24-7.29 (m, 4H), 7.45 (bs, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 34.1, 106.6, 126.3, 128.5, 128.6, 130.0, 139.7; MS (EI) 247 (M^+), 156 (100). HR MS (EI) Calcd for $\text{C}_{18}\text{H}_{17}\text{N}$ (M^+) 247.1361, found 247.1362; CAS Registry No. 850662-64-5.



3-Benzyl-1H-pyrrole (5). colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 3.89 (s, 2H), 6.10-6.12 (m, 1H), 6.54-6.56 (m, 1H), 6.73-6.25 (m, 1H), 7.19-7.35 (m, 5H), 8.02 (s, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 33.3, 108.9, 115.3, 117.9, 123.1, 125.6, 128.2, 128.6, 142.2; MS (EI) 157 (M^+ , 100), 156 (83). HR MS (EI) Calcd for $\text{C}_{11}\text{H}_{11}\text{N}$ (M^+ , 100), found 157.0888 (M^+ , 100); CAS Registry No. 33234-57-0.



1-Benzyloxycarbonylpyrrole (6). colorless liquid; ^1H NMR (200 MHz, CDCl_3) δ 5.25 (s, 2H), 6.12 (t, J = 2.6 Hz, 2H), 7.18 (t, J = 2.6 Hz, 2H), 7.25-7.32 (m, 5H); MS (EI) 201 (M^+), 91 (100). HR MS (EI) Calcd for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}$ (M^+ , 100), found 201.0791 (M^+); CAS Registry No. 56857-08-0.

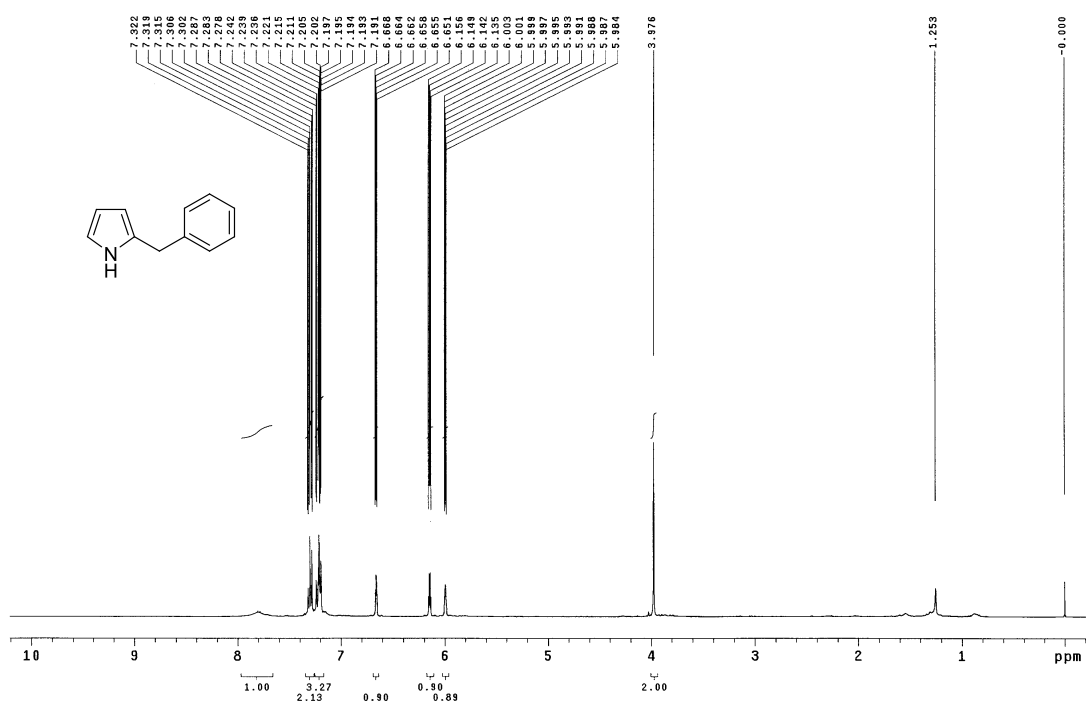


Figure S1: 2-Benzyl-1*H*-pyrrole (3) ¹H NMR (400 MHz, CDCl₃)

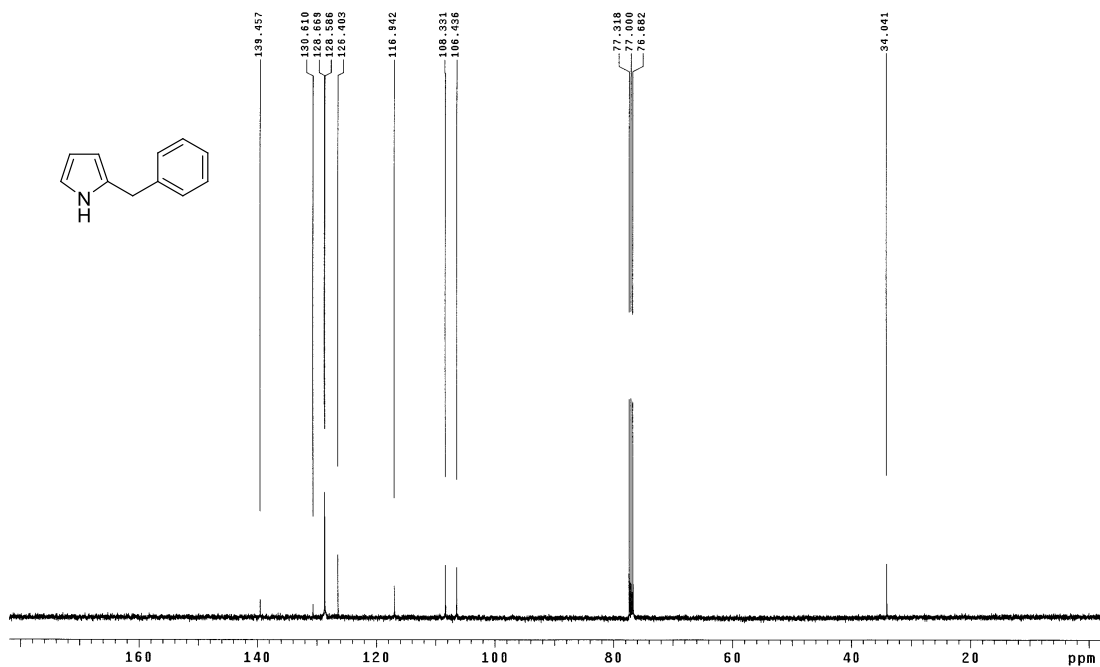


Figure S2: 2-Benzyl-1*H*-pyrrole (3) ¹³C NMR (100 MHz, CDCl₃)

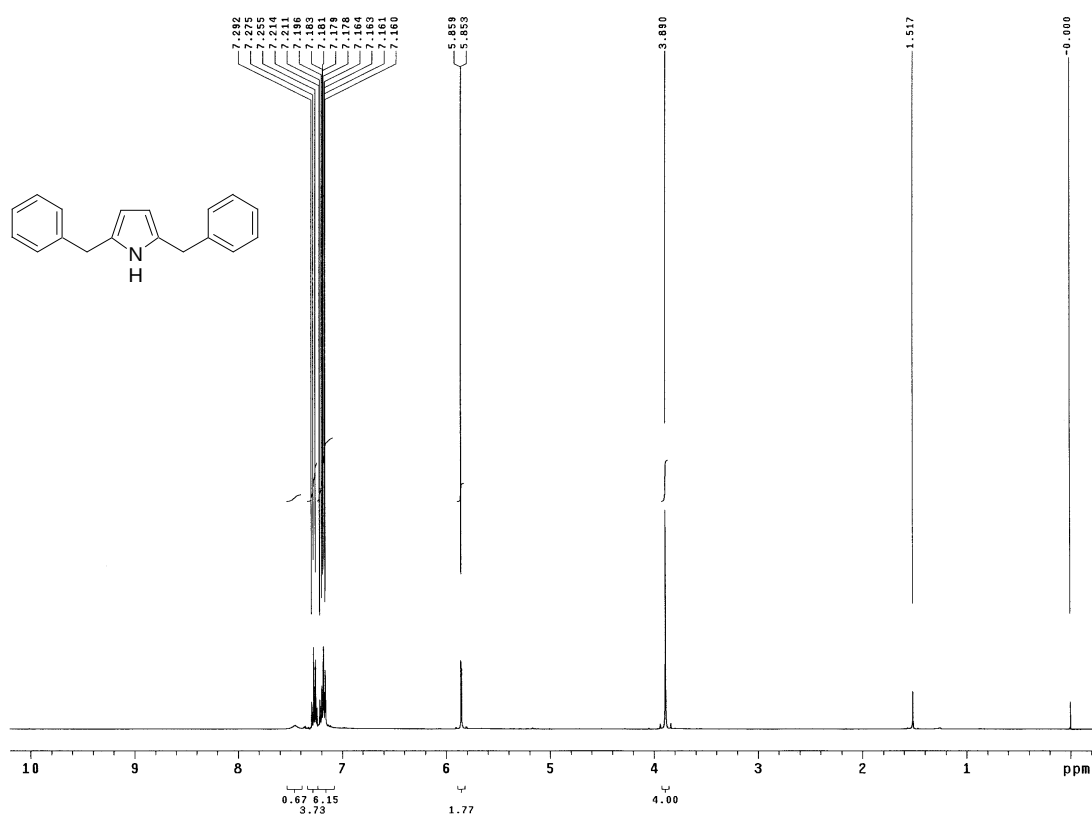


Figure S3: 2,5-Dibenzyl-1*H*-pyrrole (**4**) ¹H NMR (400 MHz, CDCl₃)

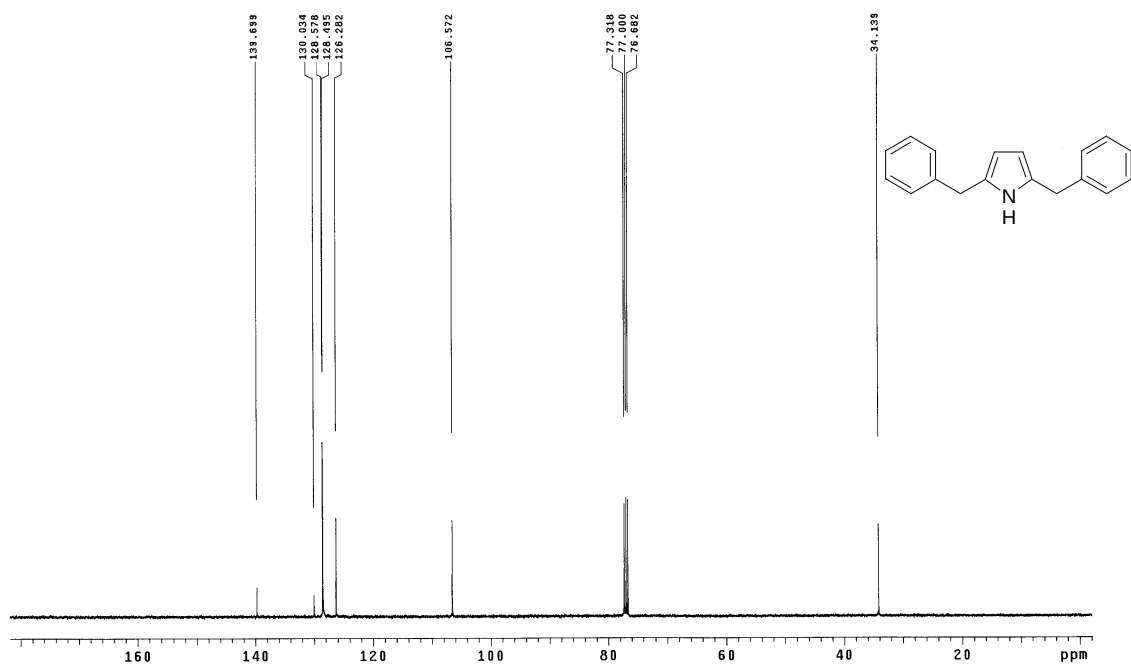
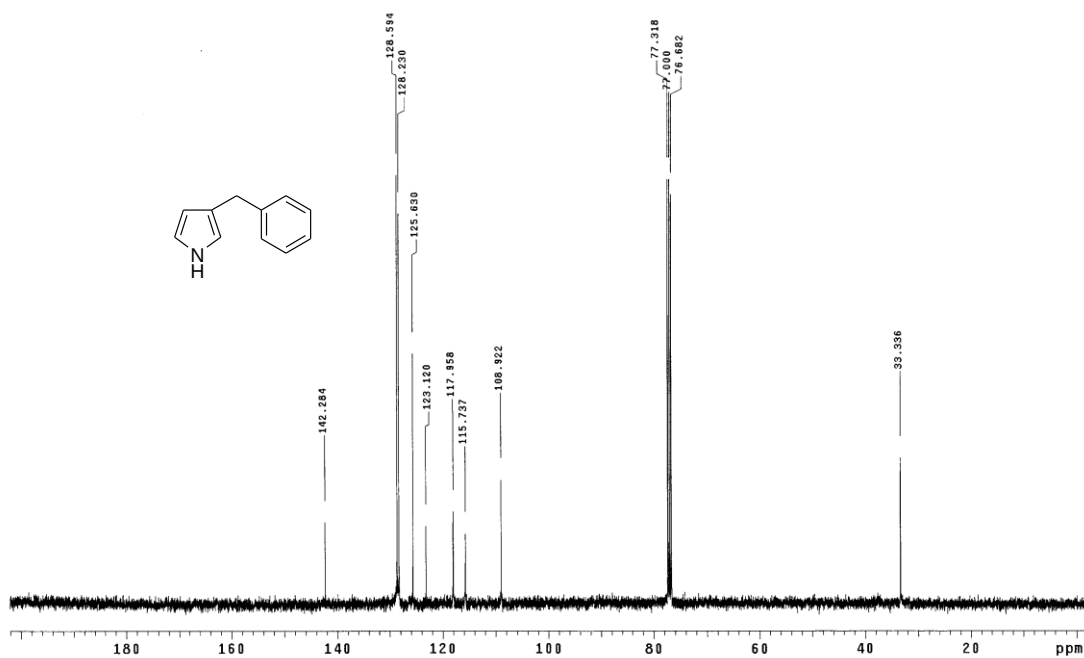
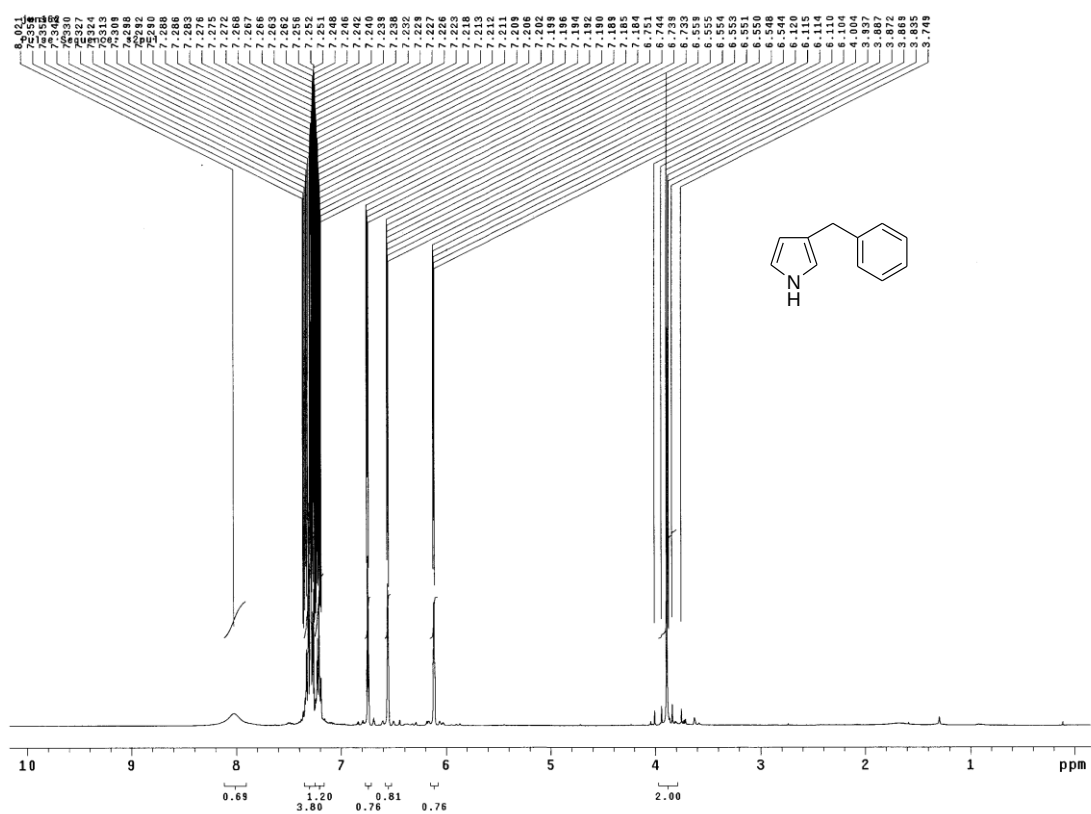


Figure S4: 2,5-Dibenzyl-1*H*-pyrrole (**4**) ¹³C NMR (100 MHz, CDCl₃)



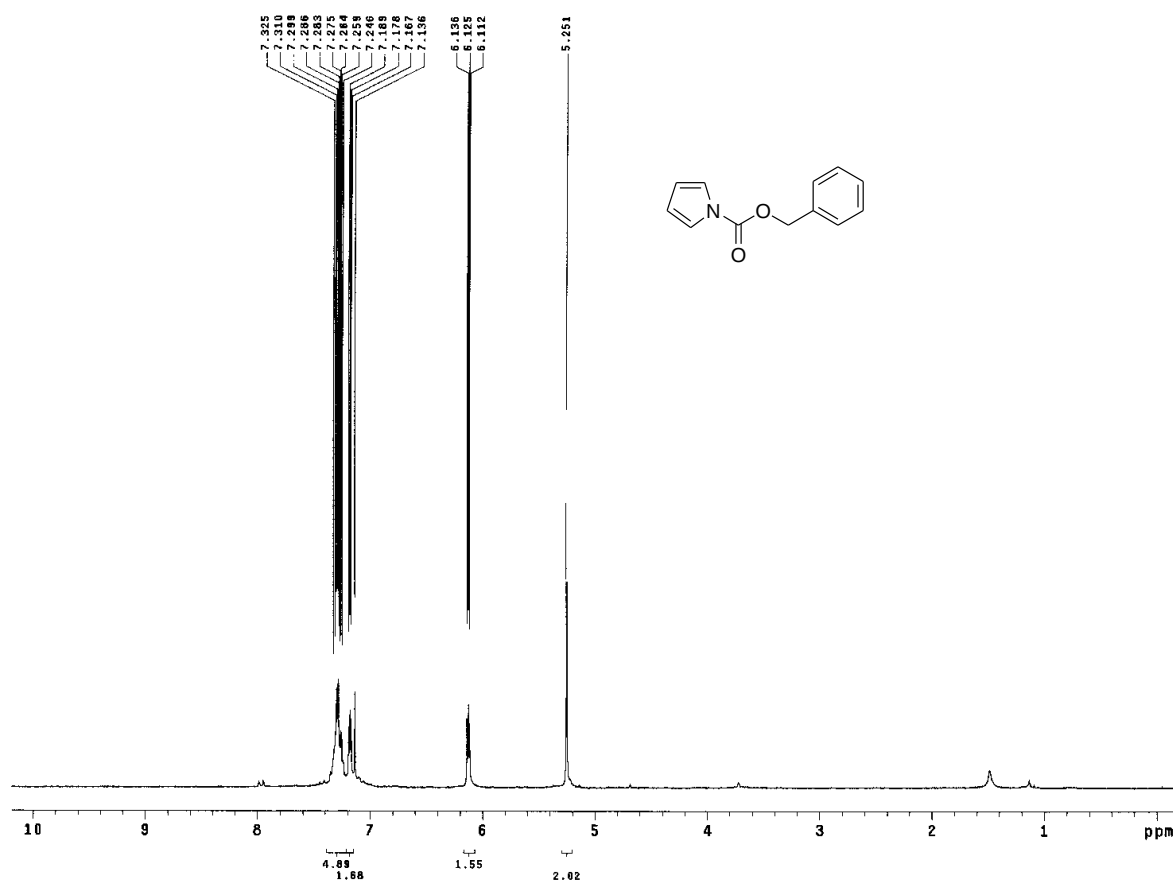


Figure S7: 1-Benzyloxycarbonylpyrrole (**6**) ^1H NMR (400 MHz, CDCl_3)