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## Electronic Supplementary Information (ESI)

# Water opens the door to organolithium and Grignard reagents: exploring and comparing the reactivity of highly polar organometallic compounds in unconventional reaction media towards the synthesis of tetrahydrofurans

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# 1. General Methods

Tetrahydrofuran (THF), was freshly distilled, under a nitrogen atmosphere, over sodium/benzophenone ketyl. Eutectic mixtures of solvents [choline chloride (ChCl)−glycerol (Gly) (1:2 mol/mol); D-fructose−ChCl (2:1 mol/mol); L-tartaric acid−ChCl (1:2 mol/mol); L-lactic acid−L-alanine (9:1 mol/mol)] and the low melting mixture of D-fructose−urea (3:2 weight/weight) were prepared by heating under stirring up to 90 °C for 10–30 min the corresponding individual components until a clear solution was obtained. For $^1$H and $^{13}$C NMR spectra ($^1$H NMR 400, 500 or 600 MHz; $^{13}$C NMR 100, 125 or 150 MHz), $CDCl_3$ was used as the solvent. GC-MS spectrometry analyses were performed on a gas chromatograph (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass selective detector operating at 70 eV (EI). Elemental analyses were performed by using a Carlo Erba CHNS-O EA1108-Elemental Analyzer. Analytical thin layer chromatography (TLC) was carried out on precoated 0.25 mm thick plates of Kieselgel 60 F254; visualization was accomplished by UV light (254 nm) or by spraying with a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 ml 17.6 % (w/v) aq. sulfuric acid and heating to 473 K for some time until blue spots appear. Some reactions involving air-sensitive reagents were performed under argon in oven-dried glassware using syringe-septum cap technique. The following solutions of Grignard reagents and organolithium reagents were commercially available and were used with the following concentration: MeMgCl 3.0 M in THF, EtMgCl 2.0 M in THF, *i*-PrMgCl 2.0 M in THF, allylMgCl 2.0 M in THF, 4-$MeOC_6H_4MgBr$ 0.5 M in THF, 4-$ClC_6H_4MgBr$ 1.0 M in 2-MeTHF, 4-$FC_6H_4MgBr$ 2.0 M in $Et_2O$, MeLi 1.6 M in $Et_2O$, EtLi 0.5 M in benzene/cyclohexane, *i*-PrLi 0.7 M in pentane, *n*-BuLi 2.5 M in hexanes, PhLi 1.8 M in dibutyl ether. Spectroscopic data of compounds **3a**,[1] **3b**,[2] **3c**,[3] **3d,e**,[4] **3f**,[5] **3g**,[3] **3j**,[6] **3k**,[7] **3l**,[4] **3n**[8] and **4a**[9] are in agreement with the literature. γ−Chloroketones **1a**–**d** and cyclopropyl phenyl ketone **4a** are commercially available. Fully characterization data, including elemental analysis and copies of $^1$H and $^{13}$C NMR spectra, have been reported for the new compounds **2a**, **3h**, **3i** and **3m**.

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[1] E. D. Butova, A. V. Barabash, A. A. Petrova, C. M. Kleiner, P. R. Schreiner and A. A. Fokin, *J. Org. Chem.* 2010, **75**, 6229.

[2] G. A. Moniz and J. L. Wood, *J. Am. Chem. Soc.*, 2001, **123**, 5095.

[3] R. Mansueto, V. Mallardo, F. M. Perna, A. Salomone and V. Capriati, *Chem. Commun.* 2013, **49**, 10160.

[4] V. Mallardo, R. Rizzi, F. C. Sassone, R. Mansueto, F. M. Perna, A. Salomone and V. Capriati, *Chem. Commun.* 2014, **50**, 8655.

[5] Y. Maeda, T. Nishimura and S. Uemura, *Chem. Lett.* 2005**, 34**, 790.

[6] C. Zhu and J. R. Falck, *Angew. Chem. Int. Ed.* 2011**, 50***,* 6626.

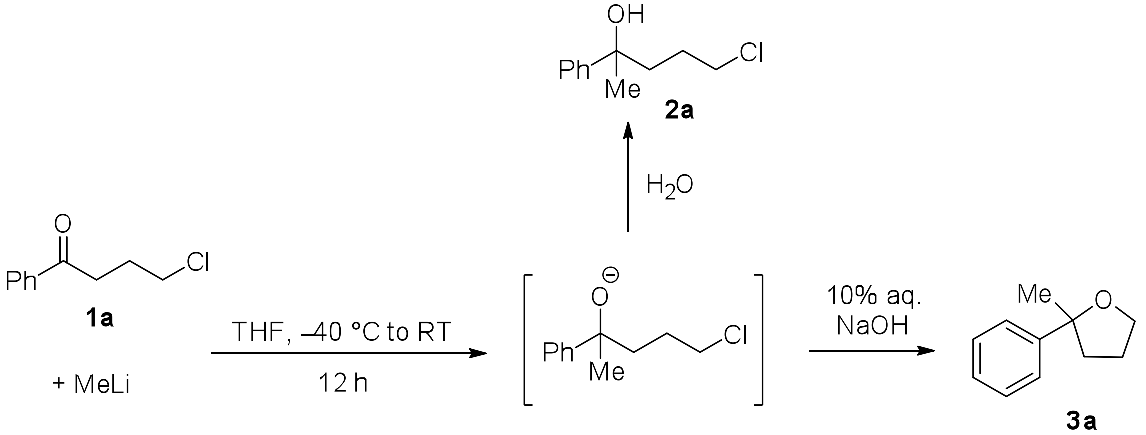
[7] P. P. Singh, S. Gudup, H. Aruri, U. Singh, S. Ambala, M. Yadav, S. D. Sawant and R. A. Vishwakarma, *Org. Biomol. Chem.,* 2012*,* **10**, 1587.

[8] A. K. Diba, J. Begouin and M. Niggemann, *Tetrahedron Lett.,* 2012*,* **53,** 6629.

[9] C. Clarke, S. Foussat, D. J. Fox, D. S. Pedersen and S. Warren, *Org. Biomol. Chem.,* 2009*,* **7**, 1323.

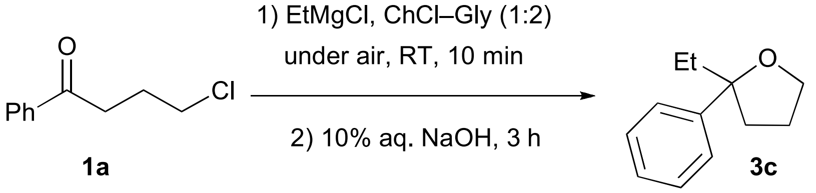
# 2. Experimental Procedures

## 2.1 Preparation of 5-chloro-2-phenylpentan-2-ol (2a) and 2-methyl-2-phenyltetrahydrofuran (3a) in THF. Typical Procedure.



To an anhydrous THF solution (1 mL) of the ketone **1a** (0.5 mmol), 0.94 mL of the commercially available MeLi (1.5 mmol in 1.6 M $Et_2O$ solution) were added dropwise, under argon, at –40 °C. After 12 h stirring at RT, the reaction mixture was treated with 10% aq. NaOH for 3 h (or quenched with $H_2O$ to isolate chlorohydrin **2a**), and then extracted with $Et_2O$ (3 × 20 mL). The combined organic phases were dried over $Na_2SO_4$ and the solvent was concentrated *in vacuo*. The crude product was purified by flash-chromatography (silica gel, hexane/$Et_2O$ 80:20, $Et_3N$ 2%), to give **3a** in 70% yield. Spectroscopic data are in accord with the literature.[1] The chlorohydrin **2a** could be purified by flash-chromatography on silica gel with hexane/AcOEt 80:20 as the eluent in 38% yield (see Table 1 of the main text).

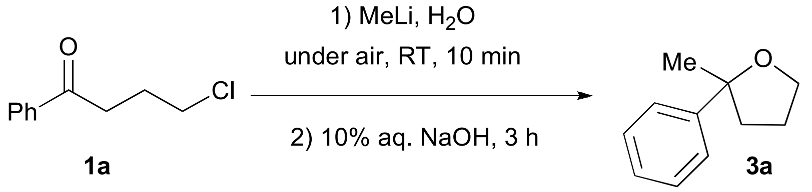
## 2.2 Preparation of 2-ethyl-2-phenyltetrahydrofuran (3c) in deep eutectic solvents. Typical procedure.



**1a** **3c**

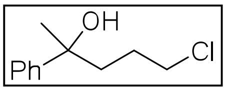
To a mixture of the ketone **1a** (0.5 mmol) in 1 g of ChCl−Gly (1:2), 0.75 mL of the commercially available EtMgCl (1.5 mmol in 2.0 M THF solution), handled under argon using conventional Schlenk techniques, were quickly spread out at RT, under air, and vigorous stirring. After 10 min, 10 mL of 10% aq. NaOH were added and the mixture was stirred for additional 3 h, and then extracted with $Et_2O$ (3 × 10 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$ and the solvent was concentrated *in vacuo*. The crude product was purified by flash-chromatography to give **3c** in 75% yield.

### 2.3 Preparation of 2-methyl-2-phenyltetrahydrofuran (3a) in water. Typical procedure.

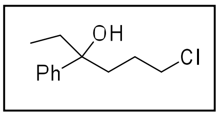


To a suspension of the ketone **1a** (0.5 mmol) in 1 mL of water, 0.94 mL of the commercially available MeLi (1.5 mmol in 1.6 M $Et_2O$ solution), handled under argon using conventional Schlenk techniques, were quickly spread out at RT, under air, and vigorous stirring. After 10 min, 10 mL of 10% aq. NaOH were added and the mixture was stirred for additional 3 h, and then extracted with $Et_2O$ (3 × 10 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$ and the solvent was concentrated *in vacuo*. The crude product was purified by flash-chromatography to give **3a** in 75% yield.

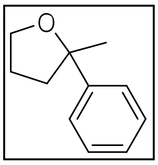
## 3. Characterization Data



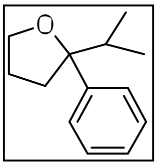
**5-Chloro-2-phenylpentan-2-ol (2a)**: colourless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 1.51 (s, 3 H); 1.54−1.61 (m, 1 H), 1.65−1.77 (m, 1 H), 1.81−1.92 (m, 2 H), 3.36−3.44 (m, 2 H); 7.15−7.19 (m, 1 H), 7.25−7.29 (m, 2 H), 7.34−7.36 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 27.4, 30.6, 41.4, 45.5, 74.4, 124.7, 126.8, 128.3, 147.3; FT-IR (film, cm$^{-1}$): 3436, 3058, 2956, 2925, 1601, 1445, 1028, 760, 700; GC-MS (70 eV) *m/z* (%): 198 (M$^+$, 5), 183 (9), 147 (11), 121 (100), 105 (19), 77 (10), 43 (15). Anal. Calcd. for $C_{11}H_{15}ClO$: C, 66.49; H, 7.61; Found: C, 66.84; H, 7.69.



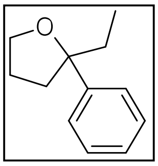
**6-Chloro-3-phenylhexan-3-ol (2c)**: colourless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 0.76 (t, $J$ = 7.4 Hz, 3 H); 1.49−1.59 (m, 1 H), 1.77−2.01 (m, 5 H), 3.46−3.50 (m, 2 H); 7.23−7.26 (m, 1 H), 7.33−7.40 (m, 4 H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 7.6, 27.0, 35.7, 39.9, 45.7, 76.9, 125.3, 126.5, 128.2, 145.2; FT-IR (film, cm$^{-1}$): 3467, 3027, 2963, 2929, 1602, 1446, 1310, 760, 701; GC-MS (70 eV) *m/z* (%): 212 (M$^+$, 2), 194 (6) 183 (75), 147 (61), 135 (55), 105 (100), 77 (10). HRMS calcd. for $C_{12}H_{17}ClO$ (M + Na)$^+$: 235.0866. Found: 235.0860.



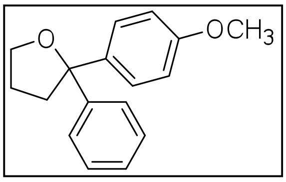
**2-Methyl-2-phenyltetrahydrofuran (3a)**:[1] colourless oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 1.47−1.53 (m, 2 H), 1.57 (s, 3 H), 1.80−2.05 (m, 2 H), 3.55−3.65 (m, 2 H), 7.21−7.44 (m, 5 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 26.9, 30.2, 40.9, 62.5, 74.2, 124.9, 125.8, 125.9, 126.3, 127.2, 127.2, 128.0, 128.2, 128.2, 144.7, 144.8, 148.0; FT-IR (film, cm$^{-1}$): 3016, 2972, 2927, 2869, 1492, 1445, 1098, 1068, 1037, 763, 701; ESI-MS: 163.2 (M$^+$ + 1).



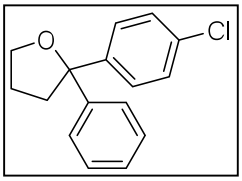
**2-Isopropyl-2-phenyltetrahydrofuran (3b)**:[2] colourless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 0.82 (d, $J$=6.5 Hz, 3 H), 0.87 (d, $J$=6.5 Hz, 3 H), 1.70−1.73 (m, 1 H), 1.90−1.93 (m, 1 H), 2.00−2.04 (m, 1 H), 2.06−2.10 (m, 1 H), 2.22−2.26 (m, 1 H), 3.76−3.82 (m, 1 H), 3.93−3.97 (m, 1 H), 7.21−7.38 (m, 5 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 17.5, 18.5, 25.7, 35.5, 37.9, 67.1, 89.5, 126.2, 126.3, 127.5, 145.0; FT-IR (film, $cm^{-1}$): 2965, 2873, 1489, 1469, 1445, 1382, 1364, 1055, 760, 703; ESI-MS: 189.1 ($M^{-}$ − 1).



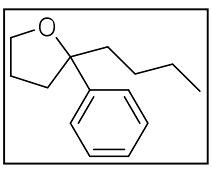
**2-Ethyl-2-phenyltetrahydrofuran (3c)**:[3] colourless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 0.76 (t, $J$ = 7.4 Hz, 3 H), 1.86−1.74 (m, 3 H), 1.98−1.90 (m, 1 H), 2.07−2.00 (m, 1 H), 3.86−3.90 (m, 1 H), 3.94−4.00 (m, 1 H), 7.19−7.23 (m, 1 H), 7.37−7.29 (m, 4 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 8.7, 25.6, 35.0, 37.7, 67.4, 77.4, 87.1, 125.3, 127.8, 146.5; FT-IR (film, $cm^{-1}$): 3024, 2967, 2929, 1492, 1446, 1057, 758, 701; GC-MS (70 eV) *m/z* (%): 176 ($M^{+}$, 3), 147 (100), 105 (55), 77 (16).



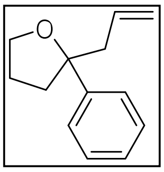
**2-(4-Methoxyphenyl)-2-phenyltetrahydrofuran (3d)**:[4] colourless oil: $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.91−1.98 (m, 2 H), 2.50−2.57 (m, 2 H), 3.76 (s, 3 H), 4.02−4.06 (m, 2 H), 6.81−6.84 (m, 2 H), 7.16−7.20 (m, 1 H), 7.27−7.36 (m, 4 H), 7.41−7.42 (m, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ: 25.5, 38.7, 55.5, 67.3, 87.8, 113.5, 125.8, 126.6, 127.1, 128.1, 138.5, 146.7, 158.4; FT-IR (film, $cm^{-1}$): 3059, 2953, 2876, 1610, 1509, 1250, 1055, 829; GC-MS (70eV), *m/z* (%): 254 ($M^{+}$, 25), 223 (10), 177 (100), 135 (50).



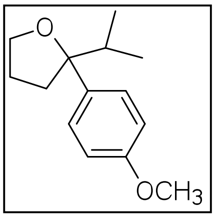
**2-(4-Chlorophenyl)-2-phenyltetrahydrofuran (3e)**:[4] colourless oil. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 1.95−2.03 (m, 1 H), 2.07−2.14 (m, 1 H), 2.55−2.60 (m, 1 H), 3.03−3.07 (m, 1 H), 3.96−4.05 (m, 2 H), 7.20−7.23 (m, 2 H), 7.27−7.33 (m, 6 H), 7.92−7.93 (m, 1 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 26.6, 36.3, 67.6, 87.6, 126.5, 126.8, 127.1, 127.6, 127.9, 128.4, 131.0, 132.0, 143.6, 143.8; FT-IR (film, $cm^{-1}$): 2918, 1492, 1459, 758, 697; GC-MS (70 eV) *m/z* (%): 258 ($M^{+}$, 22), 223 (28), 181 (80), 147 (100), 105 (57).



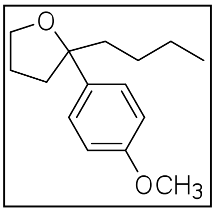
**2-Butyl-2-phenyltetrahydrofuran (3f)**:[5] colourless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, $J$ = 7.2 Hz, 3 H), 0.92–1.08 (m, 1 H), 1.18–1.29 (m, 3 H), 1.73–2.18 (m, 6 H), 3.85–3.97 (m, 2 H), 7.20–7.37 (m, 5 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.0, 23.1, 25.5, 26.6, 30.3, 67.4, 86.8, 125.2, 126.1, 127.9, 146.9; FT-IR (film, cm$^{-1}$): 2957, 2933, 2871, 1458, 1446, 1118, 1048, 763, 702; ESI-MS: 205 (M$^+$ + 1).



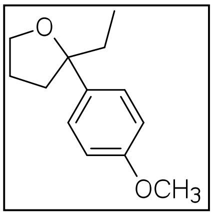
**2-Allyl-2-phenyltetrahydrofuran (3g)**:[3] colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.66–1.77 (m, 1 H), 1.85–1.92 (m, 1 H), 2.04–2.10 (m, 2 H), 2.43–2.48 (m, 1 H), 2.52–2.56 (m, 1 H), 3.81–3.85 (m, 1 H), 3.90–3.95 (m, 1 H), 4.91–4.96 (m, 2 H), 5.58–5.67 (m, 1 H), 7.12–7.17 (m, 1 H), 7.23–7.34 (m, 4 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 25.5, 37.2, 46.9, 67.7, 86.2, 117.4, 125.2, 126.3, 127.9, 134.3, 146.6; FT-IR (film, cm$^{-1}$): 2976, 2872, 1446, 1055, 914, 762, 703; GC-MS (70 eV) *m/z* (%): 188 (M+, 2), 147 (100), 105 (70), 77 (21).



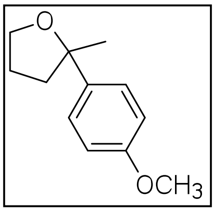
**2-Isopropyl-2-(4-methoxyphenyl)tetrahydrofuran (3h)**: colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 0.81 (d, *J* = 6.5 Hz, 3 H), 0.82 (d, *J* = 6.5 Hz, 3 H), 1.66–1.72 (m, 1 H), 1.85–1.91 (m, 1 H), 1.93–2.05 (m, 2 H), 2.19–2.24 (m, 1 H), 3.72–3.77 (m, 1 H), 3.80 (s, 3 H), 3.89–3.94 (m, 1 H), 6.83–6.86 (m, 2 H), 7.25–7.28 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 17.6, 18.5, 25.6, 35.3, 38.1, 55.2, 67.0, 89.3, 112.9, 127.5, 136.7, 158.1; FT-IR (film, cm$^{-1}$): 2962, 2874, 1610, 1508, 1464, 1294, 1246, 1176, 1058, 1039, 826, 799; GC-MS (70 eV) *m/z* (%): 220 (M$^+$, 13), 177 (100), 135 (30), 92 (23), 77 (14). Anal.Calcd. for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15; Found: C, 76.40; H, 9.28.



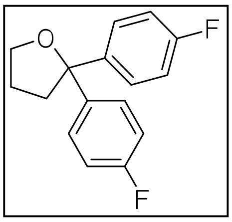
**2-Butyl-2-(4-methoxyphenyl)tetrahydrofuran (3i)**: colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 0.79 (t, *J* = 6.9 Hz, 3 H), 1.14–1.30 (m, 4 H), 1.67–1.79 (m, 3 H), 1.84–1.99 (m, 2 H), 2.10–2.16 (m, 1 H), 3.77 (s, 3 H), 3.80–3.85 (m, 1 H), 3.89–3.95 (m, 1 H), 6.81–6.84 (m, 2 H), 7.22–7.25 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.0, 23.1, 25.5, 26.7, 38.1, 42.4, 55.2, 67.2, 86.5, 113.2, 126.3, 138.8, 157.9; FT-IR (film, cm$^{-1}$): 2932, 1611, 1509, 1463, 1298, 1246, 1175, 1039, 830; GC-MS (70 eV) *m/z* (%): 234 (M$^+$, 15), 177 (100), 135 (43), 128 (12), 92 (14), 77 (5). Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46; Found: C, 77.11; H, 9.69.



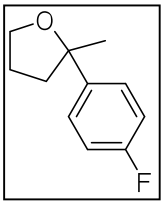
**2-Ethyl-2-(4-methoxyphenyl)tetrahydrofuran (3j)**:[6] colourless oil. $^1$H NMR (500 MHz, $CDCl_3$): δ 0.77 (t, $J$ = 7.5 Hz, 3 H), 1.76–1.84 (m, 3 H), 1.92–2.05 (m, 2 H), 2.13–2.18 (m, 1 H), 3.81 (s, 3 H), 3.86–3.90 (m, 1 H), 3.94–3.98 (m, 1 H), 6.87 (d, $J$ = 8.5 Hz, 2 H), 7.28 (d, $J$ = 8.5 Hz, 2 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 9.1, 25.8, 35.4, 37.9, 55.5, 67.6, 87.2, 113.5, 126.7, 138.8, 158.2; FT-IR (film, cm$^{-1}$): 2966, 2934, 2875, 1610, 1582, 1510, 1442, 1299, 1176, 1037, 911, 830; ESI-MS: 207 ($M^+$ + 1).



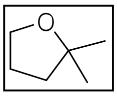
**2-(4-Methoxyphenyl)-2-methyltetrahydrofuran (3k)**:[7] colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 3 H), 1.87–1.93 (m, 1 H), 2.05–2.12 (m, 1 H), 3.80 (s, 3 H), 3.81–3.84 (m, 1 H) 3.89–3.94 (m, 1 H), 6.77–6.80 (m, 2H), 7.22–7.25 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 27.2, 30.4, 41.1, 55.3, 67.1, 87.1, 113.3, 126.8, 140.3, 158.8; FT-IR (film, cm$^{-1}$): 2969, 2877, 1609, 1512, 1444, 1297, 1176, 1036, 910, 830; GC-MS (70 eV) *m/z* (%): 193 ($M^+$ + 1, 13), 177 (100), 175 (13), 151 (32), 135 (84) 77 (20).



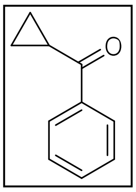
**2,2-Bis(4-fluorophenyl)tetrahydrofuran (3l)**:[4] colourless oil. $^1$H NMR (600 MHz; $CDCl_3$): δ 1.93−2.00 (m, 2 H), 2.50−2.54 (m, 2 H), 4.03−4.06 (m, 2 H), 6.96−7.01 (m, 4 H), 7.36−7.40 (m, 4 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 25.4, 38.8, 67.4, 87.2, 114.9 (d, $^2J_{\text{C-F}}$ = 21.2 Hz), 127.4 (d, $^3J_{\text{C-F}}$ = 8.0 Hz), 141.9 (d, $^4J_{\text{C-F}}$ = 3.3 Hz), 161.6 (d, $^1J_{\text{C-F}}$ = 240 Hz); FT-IR (film, cm$^{-1}$): 3055, 2959, 1598, 1506, 1266, 743; GC-MS (70eV), m/z (%): 260 (3), 219 (100), 123 (60). Anal. Calcd. for $C_{16}H_{14}F_2O$: C, 73.83; H, 5.42. Found: C, 74.02; H, 5.55.



**2-(4-Fluorophenyl)-2-methyltetrahydrofuran (3m)**: colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.47 (s, 3 H), 1.72−1.80 (m, 1 H), 1.91−2.01 (m, 2 H), 2.08−2.15 (m, 1 H), 3.83−3.89 (m, 1 H), 3.94−3.99 (m, 1 H), 6.93−6.98 (m, 2 H), 7.08−7.13 (m, 1 H), 7.30−7.33 (m, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 17.0, 25.7, 39.5, 67.5, 83.9, 115.5 (d, $^2J_{\text{C-F}}$ = 21.4 Hz), 126.2 (d, $^3J_{\text{C-F}}$ = 7.5 Hz), 141.8, 161.3 (d, $^1J_{\text{C-F}}$ = 243.0 Hz); FT-IR (film, cm$^{-1}$): 3055, 2959, 1600, 1590, 1266, 1176, 912, 831; GC-MS (70 eV) *m/z* (%): 180 ($M^+$,6), 165 (100), 135 (7), 123 (77). Anal. Calcd. for $C_{11}H_{13}FO$: C, 73.31; H, 7.27. Found: C, 73.58; H, 7.51.



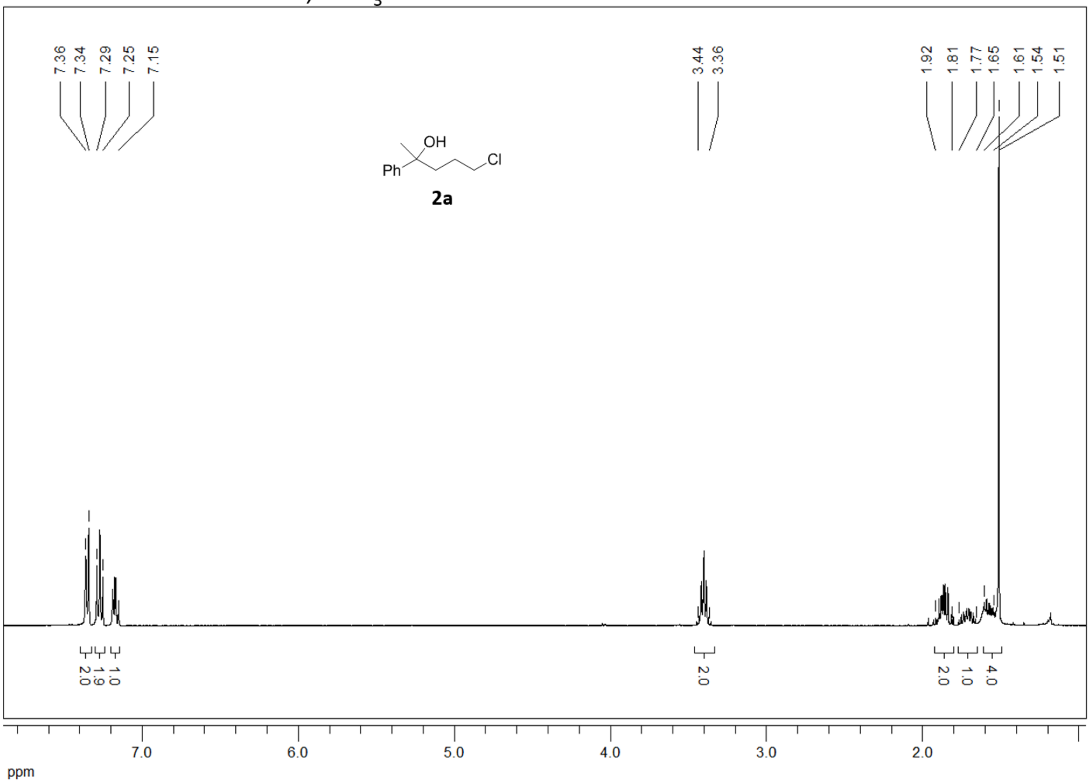
**2,2-Dimethyltetrahydrofuran (3n)**:[8] colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.24 (s, 6 H), 1.71 (t, *J* = 7.7 Hz, 2 H), 1.91−2.00 (m, 2 H), 3.84 (t, *J* = 6.9 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 25.9, 27.7, 38.1, 67.1, 81.4; FT-IR (film, cm$^{-1}$): 2962, 1467, 1140, 609; ESI-MS: 100 (M$^+$).



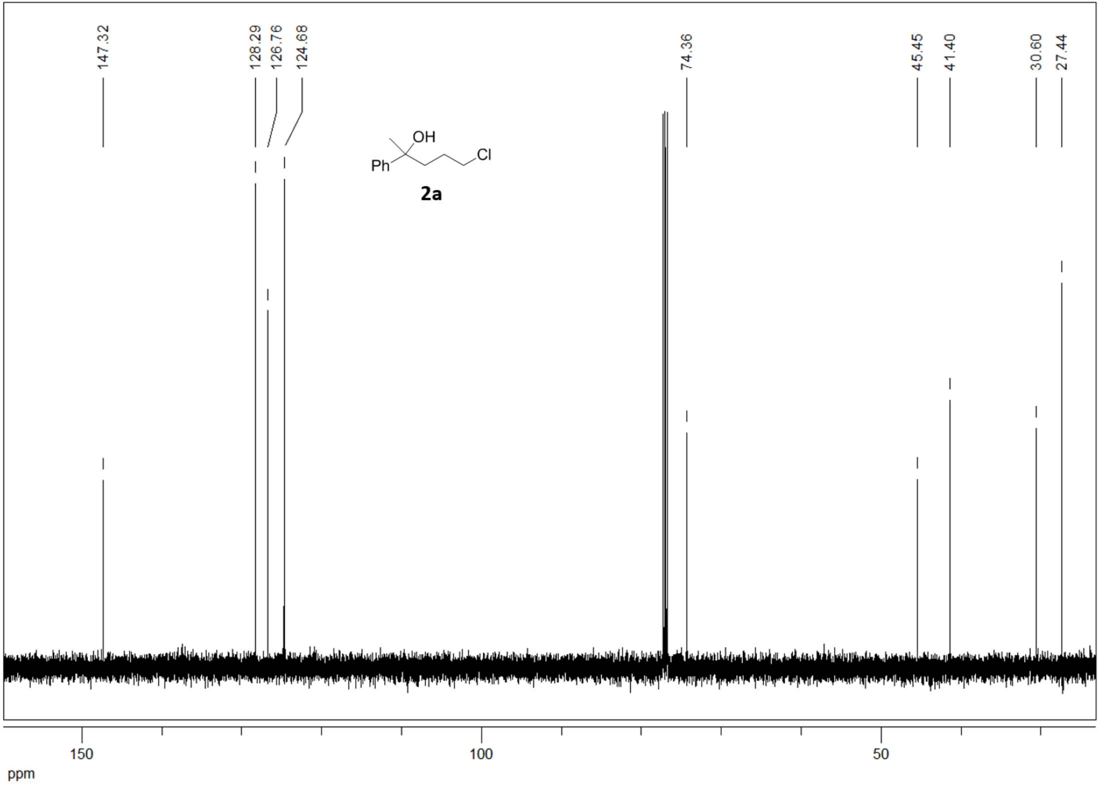
**Cyclopropyl(phenyl)methanone (4a)**:[9] colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.02 (ddd, *J* = 8.0, 7.0, 3.5 Hz, 2 H), 1.22 (ddd, *J* = 7.0, 4.5, 3.5 Hz, 2 H), 2.60−2.70 (m, 1 H), 7.43−7.47 (m, 2 H), 7.49−7.55 (m, 1 H), 7.96−8.02 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 11.6, 17.1, 127.9, 128.3, 132.7, 138.0, 200.5; FT-IR (film, cm$^{-1}$): 3031, 2960, 1668, 1597, 1579, 752, 700; ESI-MS: 146 (M$^+$).

## $^1$H and $^{13}$C NMR spectra of 2a

$^1$H NMR 400 MHz , CDCl$_3$

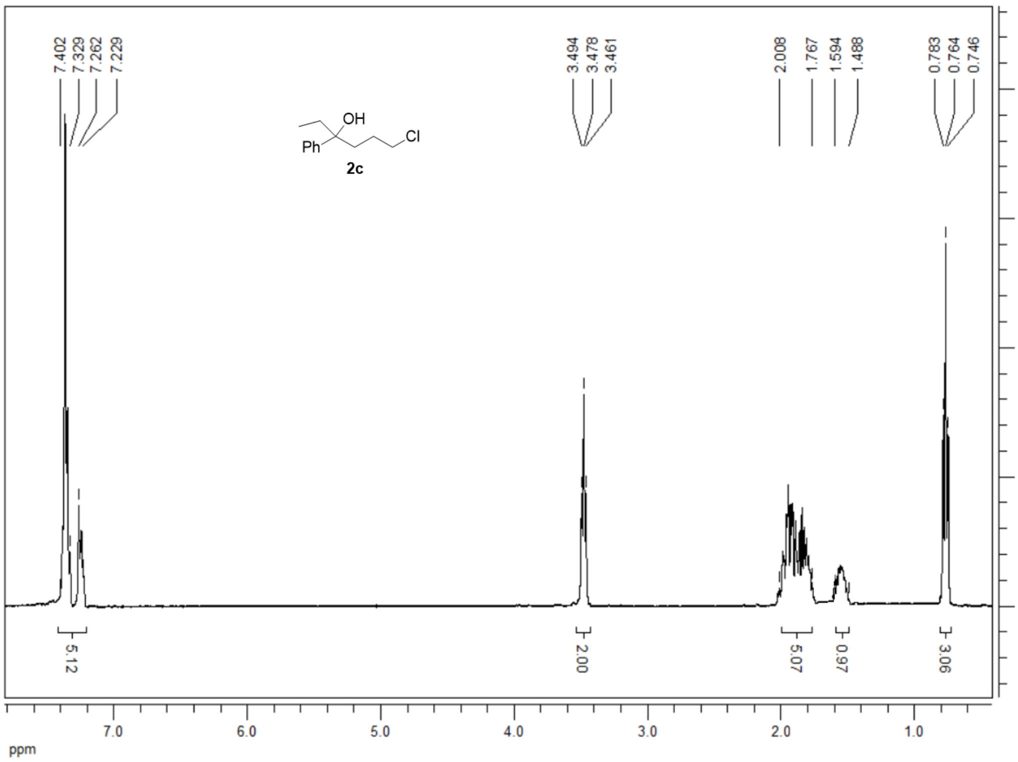


$^{13}$C NMR 100 MHz, CDCl$_3$

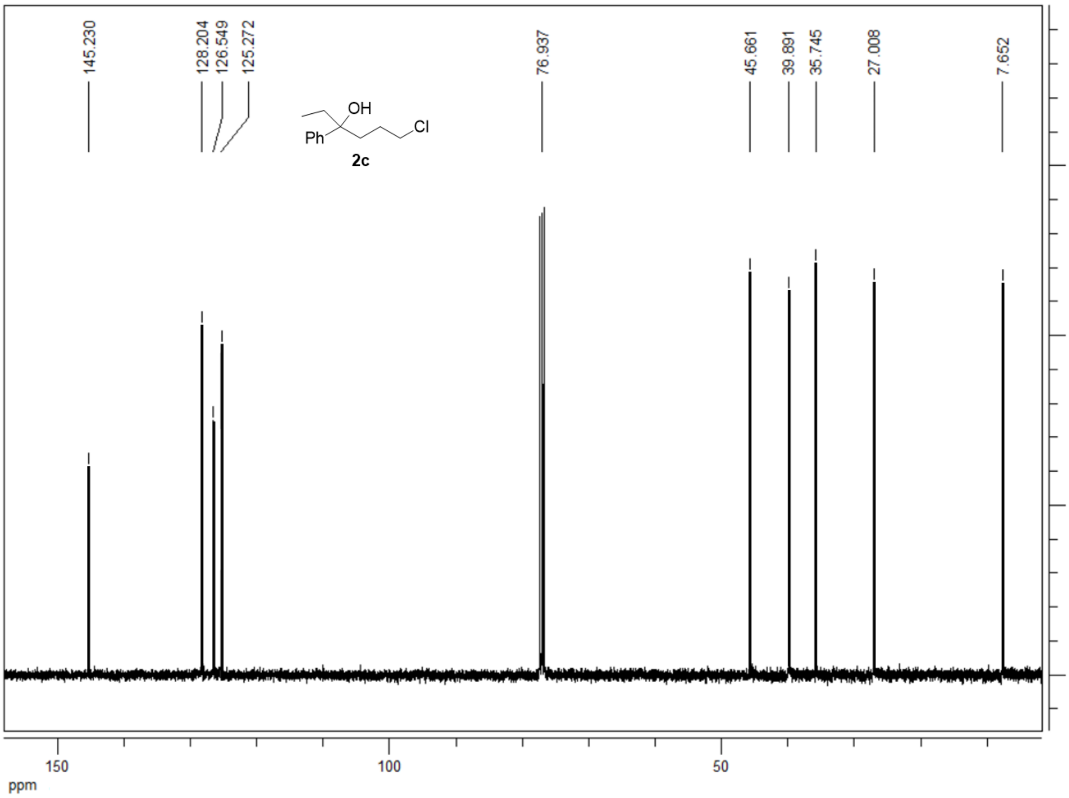


## $^{1}$H and $^{13}$C NMR spectra of 2c

$^{1}$H NMR 400 MHz , $CDCl_3$

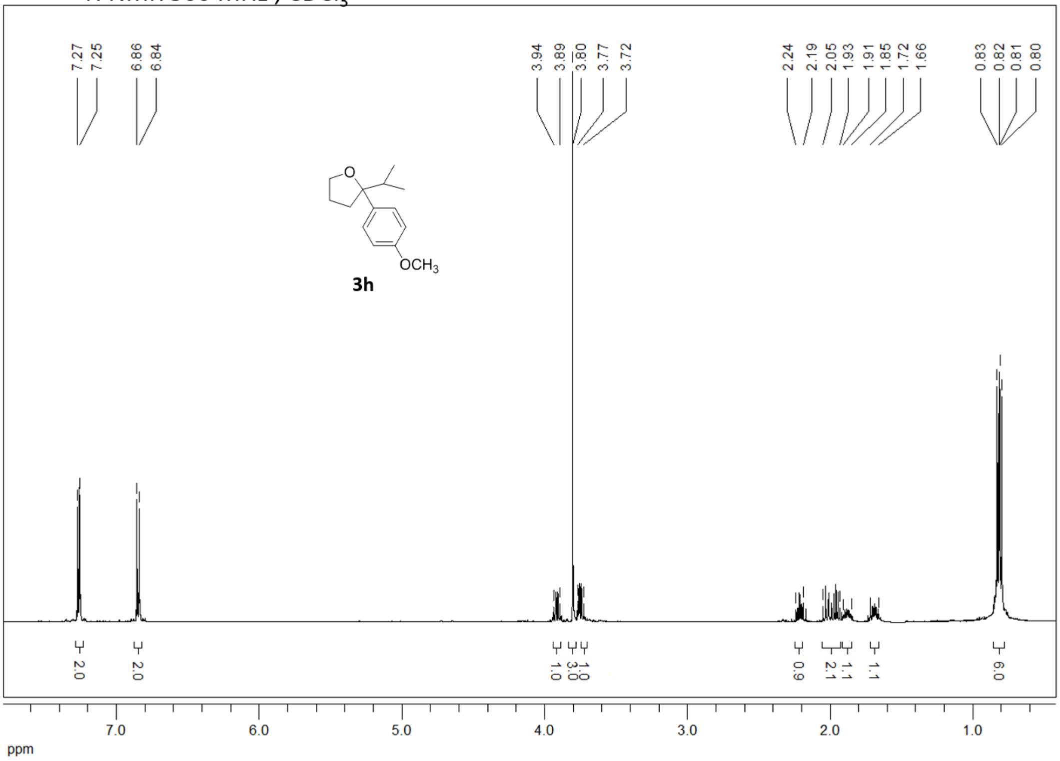


$^{13}$C NMR 125 MHz, $CDCl_3$

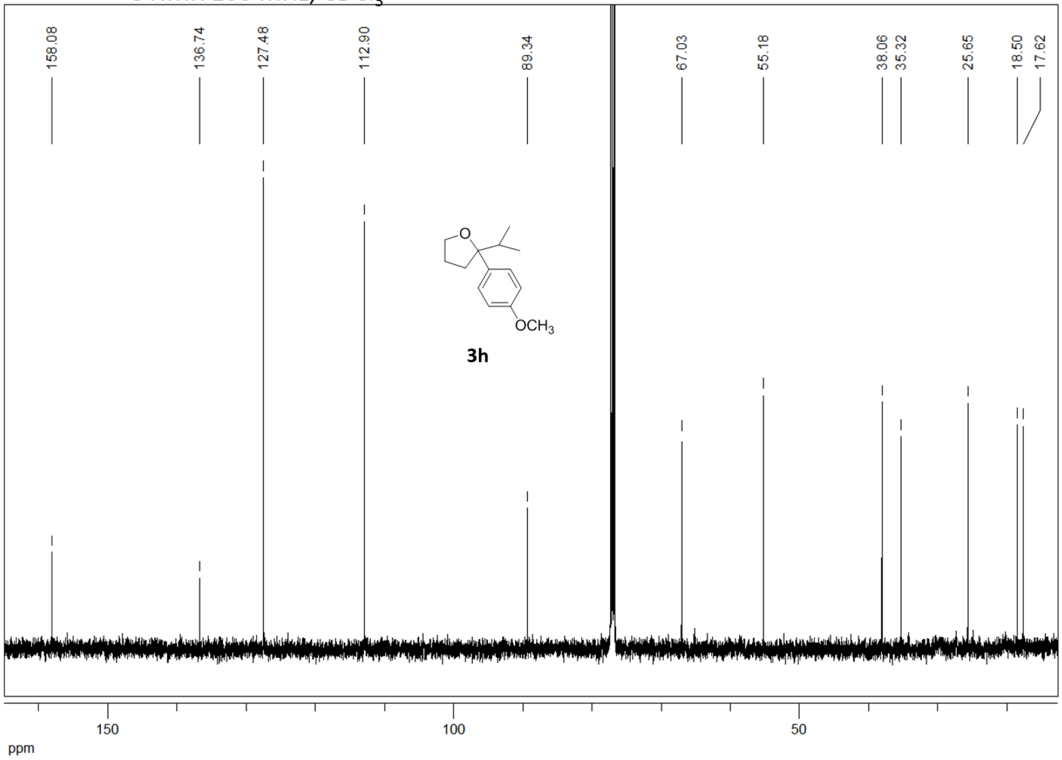


## $^1$H and $^{13}$C NMR spectra of 3h

$^1$H NMR 500 MHz , $CDCl_3$

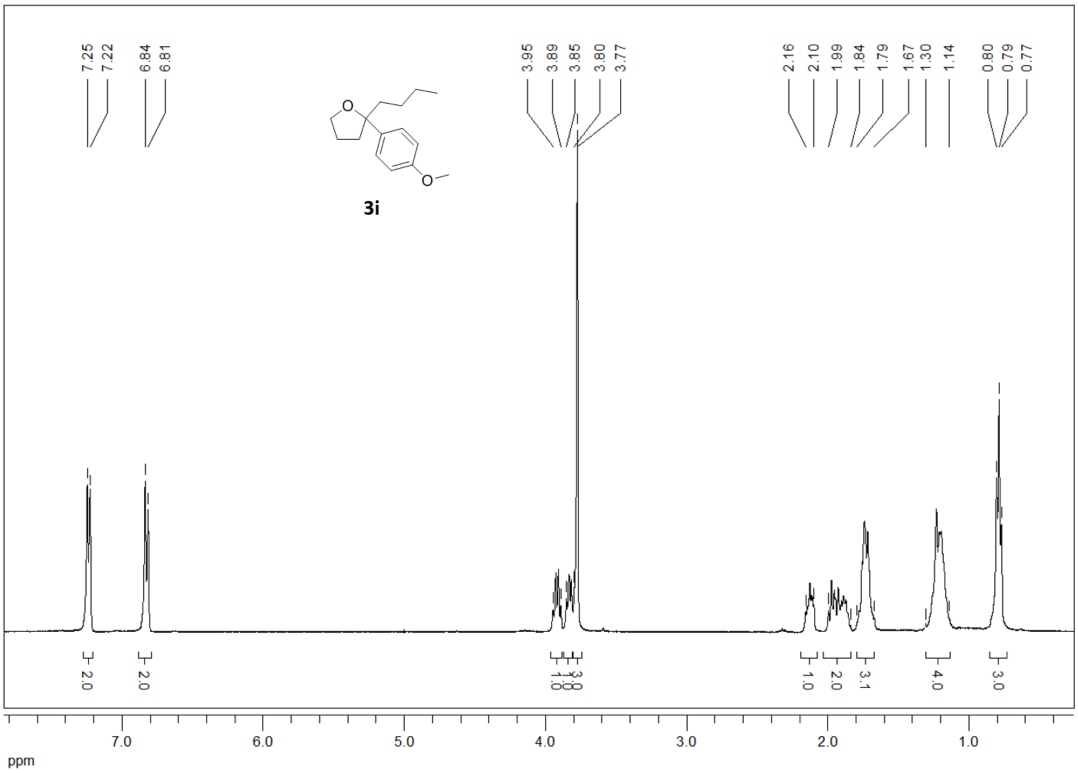


$^{13}$C NMR 100 MHz, $CDCl_3$

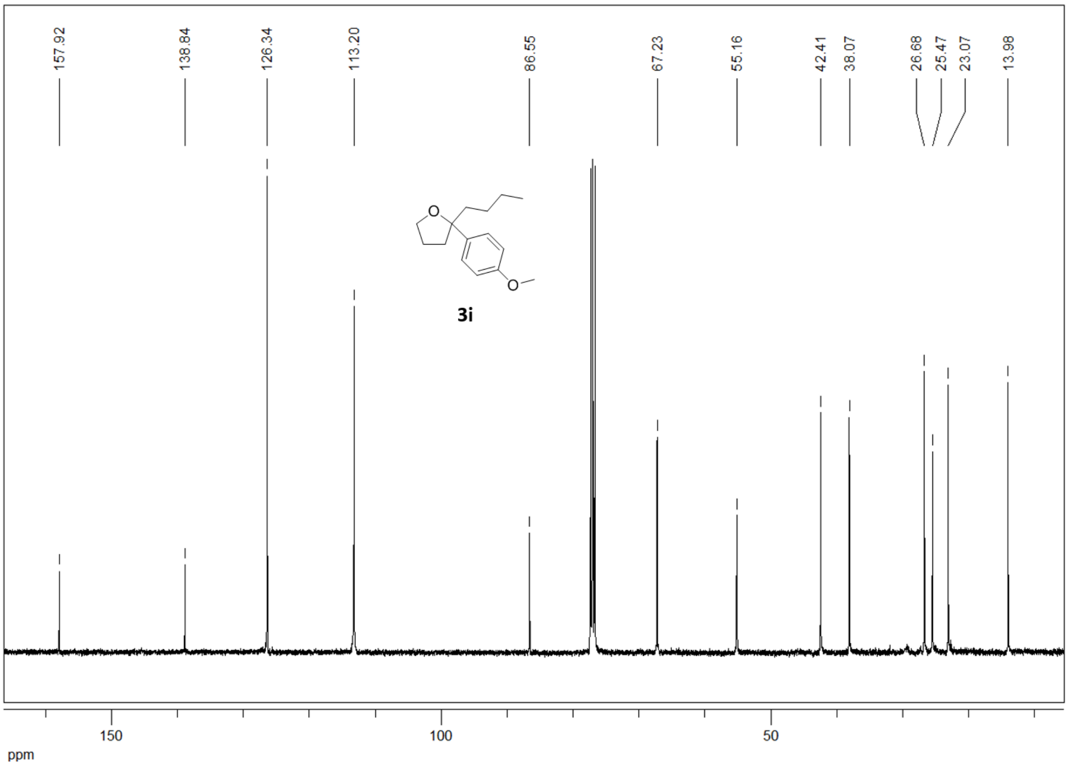


## $^{1}$H and $^{13}$C NMR spectra of 3i

$^{1}$H NMR 400 MHz , $CDCl_3$

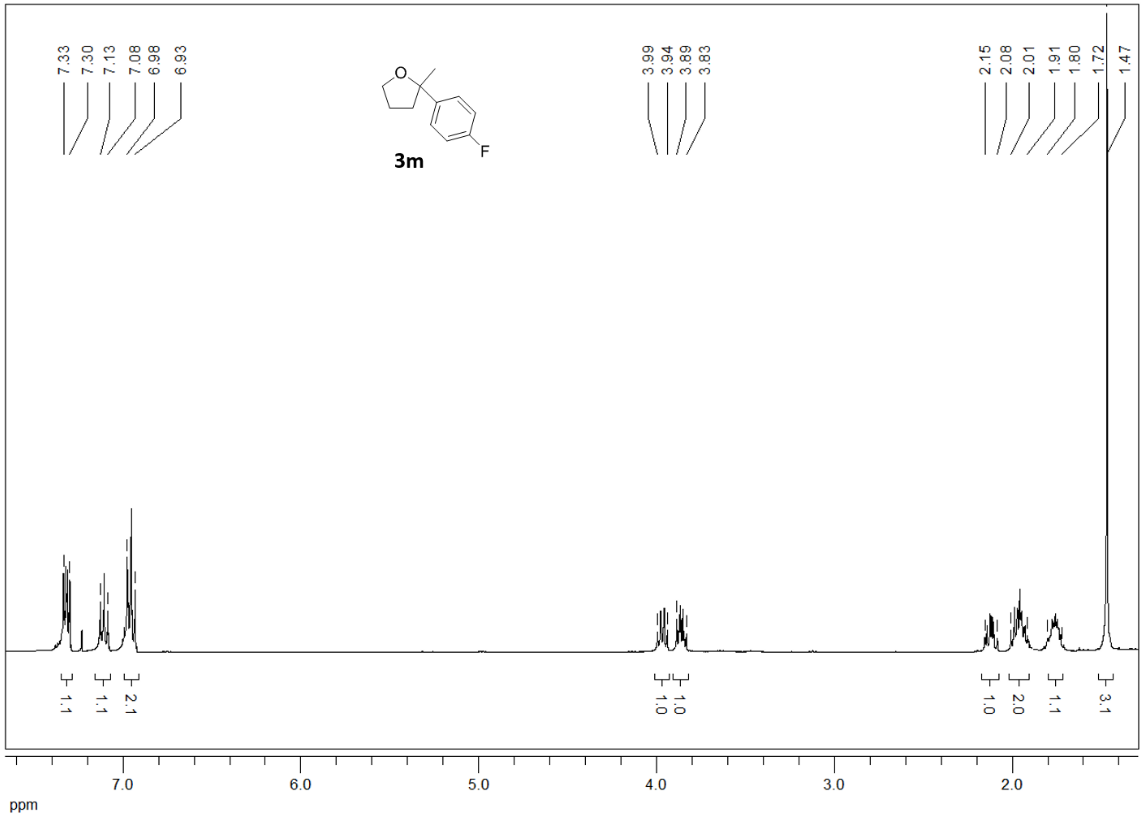


$^{13}$C NMR 100 MHz, $CDCl_3$



## $^1$H and $^{13}$C NMR spectra of 3m

$^1$H NMR 400 MHz , $CDCl_3$



$^{13}$C NMR 100 MHz, $CDCl_3$