Supplementary Information

Direct C-H magnesiation of thiophenes with a Mg−Mg-bonded compound

Li Yang, Zhen-zhou Sun, Lin Wang, Jianqi Geng, Biao Wu, Xiao-Juan Yang*

Key Laboratory of Medical Molecule Science and Pharmaceutics Engineering, Ministry of Industry and Information Technology, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China.

**E-mail: yangxj@bit.edu.cn*

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S1. Experimental details

S1.1 General considerations

All reactions and manipulations of air- and moisture-sensitive compounds were carried out under argon or nitrogen with standard Schlenk or dry box techniques. The solvents (*n*-hexane, THF, toluene) were dried using appropriate methods and were distilled under argon prior to use. Tetrahydrofuran-d_8 was dried over Na/K alloy. The α-diimine ligand L was prepared according to literature procedures.[1] Compound **1** used in this work was *in-situ* generated by the reaction of α-diimine ligand L, $MgCl_2$, and K metal.[2] Potassium metal, anhydrous magnesium chloride ($MgCl_2$), thiophene, 2-methylthiophene, 2-ethylthiophene, 3-methylthiophene, 2-methoxythiophene, 2,3-dimethylthiophene, 3,4-ethylenedioxythiophene, thianaphthene, 2,2'-bithiophene, thieno[3,2-b]thiophene were commercially available. NMR spectra were acquired on a Bruker Advance 500 MHz or a 700 MHz spectrometer. Elemental analyses were performed with a Euro Vector EA3000 instrument.

S1.2 Synthesis

[K(thf)LMg(C_4H_3S)(thf)]$_\infty$ (2). Thiophene (2.0 equiv, 160 uL, 2 mmol) was added to a solution of *in situ* prepared compound **1** (1.0 mmol) in toluene (30 mL). After stirring for 2 days at room temperature, the reaction mixture was filtered. The resulted solution was concentrated to about 5 mL under reduced pressure, and a few drops of *n*-hexane were added. Orange-red crystals of **2** (yield: 0.876 g, 63%) suitable for X-ray diffraction were obtained in several days at room temperature. ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.06 (br, 12H, (CH_3)$_2$CH-), 1.18 (br, 12H, (CH_3)$_2$CH-), 1.58 (s, 6H, CH_3C-), 1.77 (thf), 2.30 (toluene), 3.62 (thf), 4.05 (br, 4H, C*H*(CH_3)$_2$), 6.44−6.45 (m, 2H, *p*-C_6H_3), 6.78 (br, 4H, *m*-C_6H_3), 6.96−6.98 (t, 1H, thienyl), 6.99−7.00 (d, 1H, thienyl), 7.03−7.20 (toluene), 7.33 (d, 1H, thienyl). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 17.1 (NCCH_3), 24.3 (CH(CH_3)$_2$), 25.6 (CH(CH_3)$_2$), 25.8 *C*H(CH_3)$_2$), 26.2 (thf), 26.9 (*C*H(CH_3)$_2$), 68.0 (thf), 116.0 (NC=*C*N), 120.5 (thienyl), 122.3 (Ar-*C*), 125.5 (toluene), 127.4 (thienyl), 128.2 (Ar-*C*), 128.7, 129.5 (toluene), 135.5 (thienyl), 143.9 (Ar-*C*), 154.5 (Ar-*C*), 163.4 (Mg-*C* of thienyl). Elemental analysis calcd. for $C_{40}H_{59}KMgN_2O_2S$ (695.36): C, 69.09; H, 8.55; N, 4.03. Found: C, 68.83; H, 8.56; N, 4.01%.

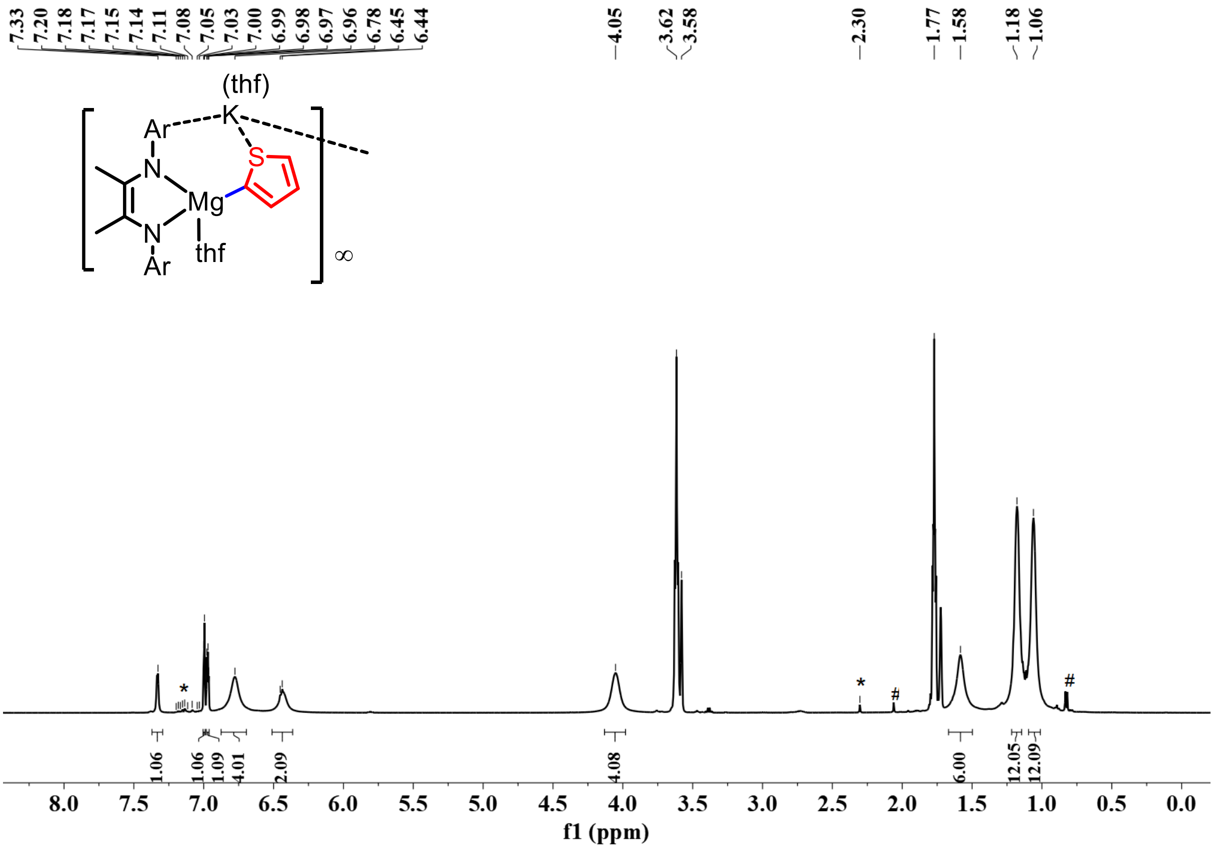


Fig. S1. ^{1}H NMR spectrum of **2** (THF-d_8, 500 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

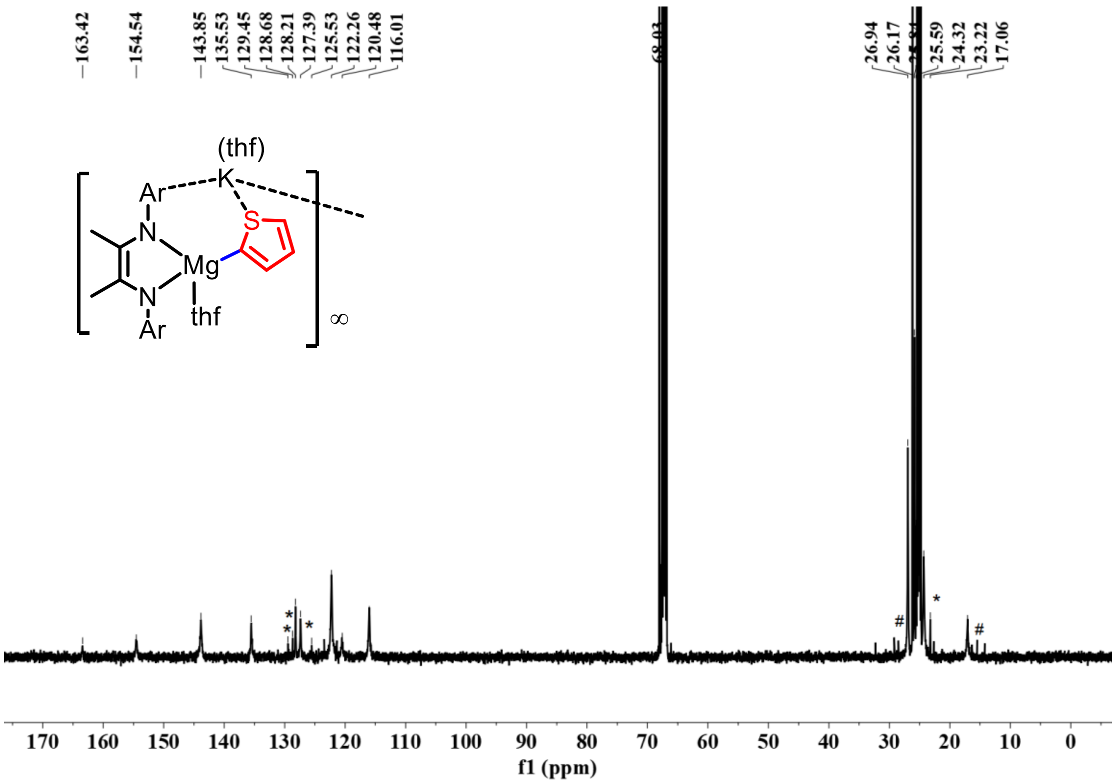


Fig. S2. ^{13}C NMR spectrum of **2** (THF-d_8, 126 MHz, 298 K, signals marked with * are from solvent toluene).

[K(thf)LMg(2-Me-C_4H_2S)(thf)]$_\infty$ (3). Complex **3** was synthesized by similar procedures as employed for **2**, from 2-methylthiophene (193 uL, 2 mmol) and **1** (1 mmol). Recrystallization from THF/toluene/*n*-hexane afforded orange-red crystals of complex **3** (yield: 0.922 g, 65%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.07 (d, 12H, (CH_3)$_2$CH-), 1.18 (d, 12H, (CH_3)$_2$CH-), 1.58 (s, 6H, NCCH$_3$), 1.77 (thf), 2.34 (s, 3H, C(CH_3) of 2-methylthienyl), 3.62 (thf), 4.04 (m, 4H, C*H*(CH$_3$)$_3$), 6.44 (t, 2H, Ar-*H*), 6.60 (s, 1H, C*H* of 2-methylthienyl), 6.74 (d, 1H, C*H* of 2-methylthienyl), 6.79 (d, 4H, Ar-*H*), 6.93−7.10 (toluene). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 14.7 (*C*H$_3$ of 2- methylthienyl), 17.0 (NC*C*H$_3$), 24.3 (CH(*C*H$_3$)$_2$), 25.9 *C*H(CH$_3$)$_2$), 26.2 (thf), 26.9 (*C*H(CH$_3$)$_2$), 68.0 (thf), 116.0 (N*C*=CN), 120.5 (2-methylthienyl), 122.3 (Ar-*C*), 127.0 (2-methylthienyl), 136.0 (2-methylthienyl), 142.4, 143.8 (Ar-*C*), 154.5 (Ar-*C*), 162.9 (Mg-*C* of 2-methylthienyl). Elemental analysis calcd. for $C_{41}H_{61}KMgN_2O_2S$ (709.38): C, 69.42; H, 8.67; N, 3.95. Found: C, 69.28; H, 8.63; N, 3.92%.

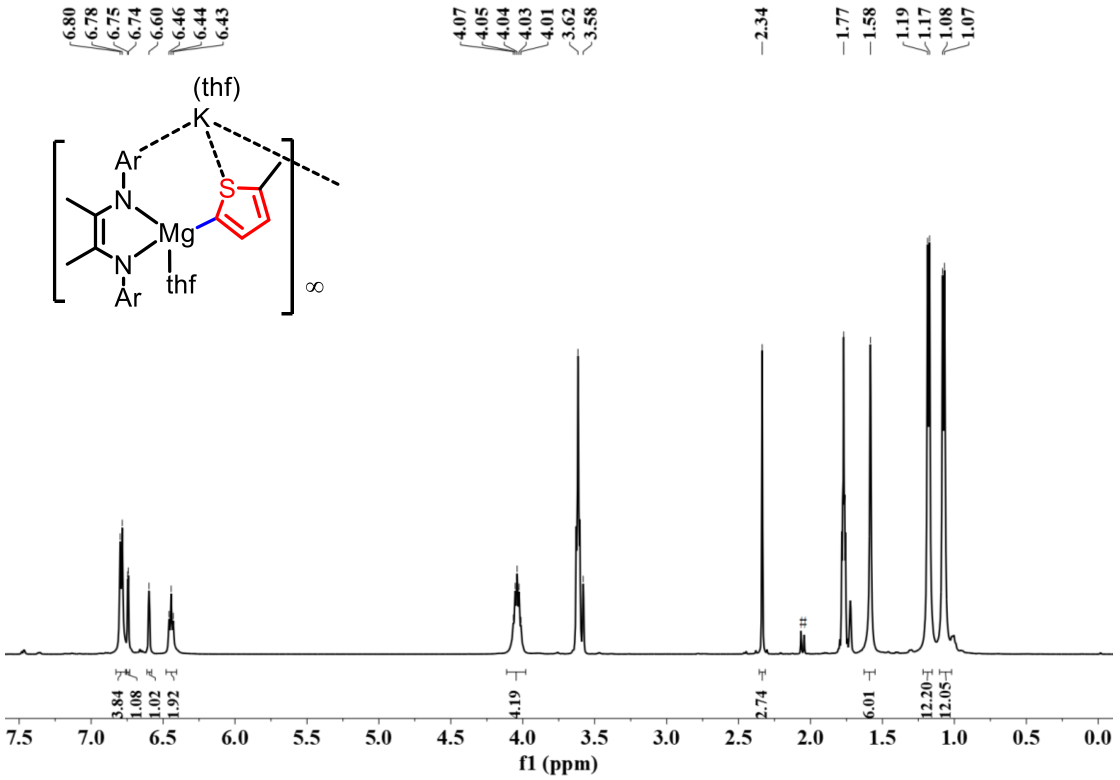


Fig. S3. ^{1}H NMR spectrum of **3** (THF-d_8, 500 MHz, 298 K, signals marked with # are due to unidentified impurities).

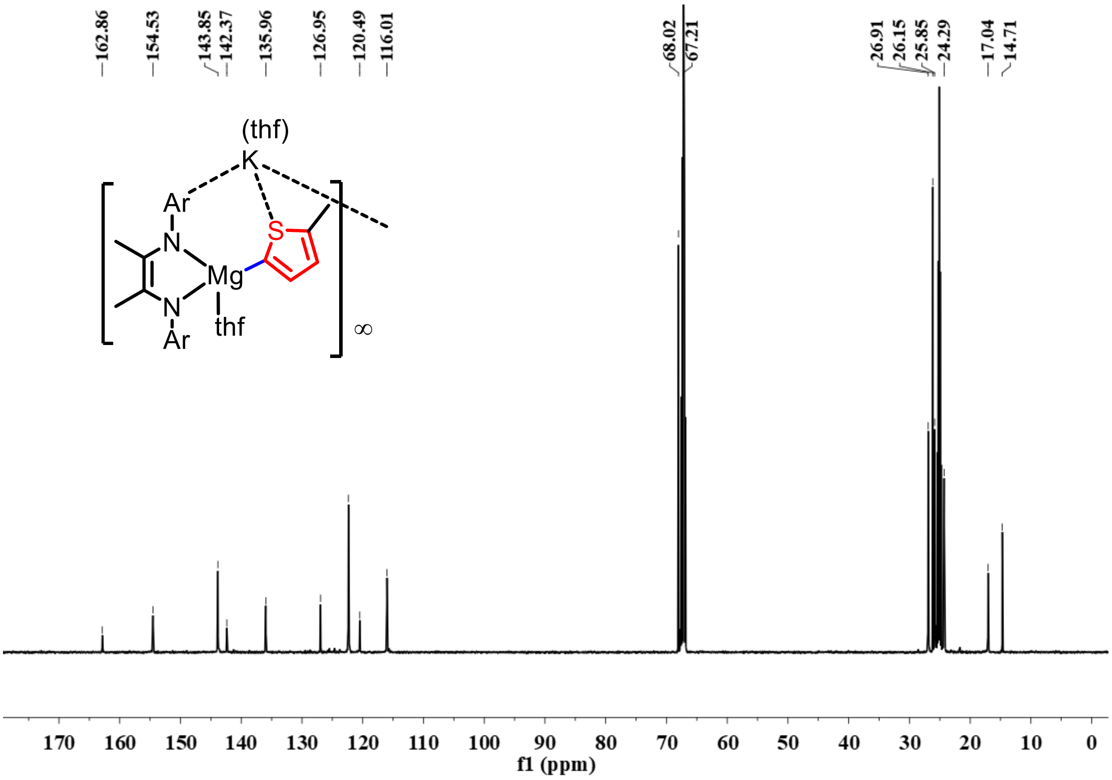


Fig. S4. ^{13}C NMR spectrum of **3** (THF-d_8, 126 MHz, 298 K).

$[\{LMg(thf)(2\text{-}Et\text{-}C_4H_2S)K\}_2]_\infty$ (4). Complex **4** was synthesized by similar procedures as employed for **2**, from 2-ethylthiophene (227 uL, 2 mmol) and **1** (1 mmol) in toluene. Orange crystals of **4** were obtained from a mixed solvent of toluene and *n*-hexane. Crystal yield: 0.865 g (62%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.07 (d, 12H, $(CH_3)_2CH$-), 1.13−1.16 (t, 3H, CH_3CH_2- of 2-ethylthiophene), 1.17 (d,12H, $(CH_3)_2CH$-), 1.58 (s, 6H, CH_3C-), 1.77 (thf), 2.30 (toluene), 2.69−2.73 (m, 2H, CH_3CH_2- of 2-ethylthienyl), 3.62 (thf), 4.01−4.07 (m, 4H, $CH(CH_3)_2$), 6.43−6.46 (t, 2H, *p*-C_6H_3), 6.65 (t, 1H, 2-ethylthienyl), 6.78−6.88 (t, 4H, *m*-C_6H_3), 6.78−6.88 (t, 1H, 2-ethylthienyl), 7.09−7.20 (toluene). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 16.6 (CH_3CH_2- of 2-ethylthienyl), 17.1 ($NCCH_3$), 21.3 (toluene), 23.6 (CH_3CH_2- of 2-ethylthienyl), 24.3 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 26.2 (thf), 26.9 ($CH(CH_3)_2$), 68.0 (thf), 116.1 (NC=CN), 120.5 (2-ethylthienyl), 122.4, 124.9 (Ar-*C*), 125.8, 128.7, 129.5 (toluene), 135.9 (2-ethylthienyl), 143.8, 150.6 (Ar-*C*), 154.6 (Ar-*C*), 161.9 (Mg-*C* of 2-ethylthienyl). Elemental analysis calcd. for $C_{83}H_{118}K_2Mg_2N_4O_2S_2$ (1394.75): C, 71.47; H, 8.53; N, 4.02. Found: C, 71.25; H, 8.65; N, 3.98%.

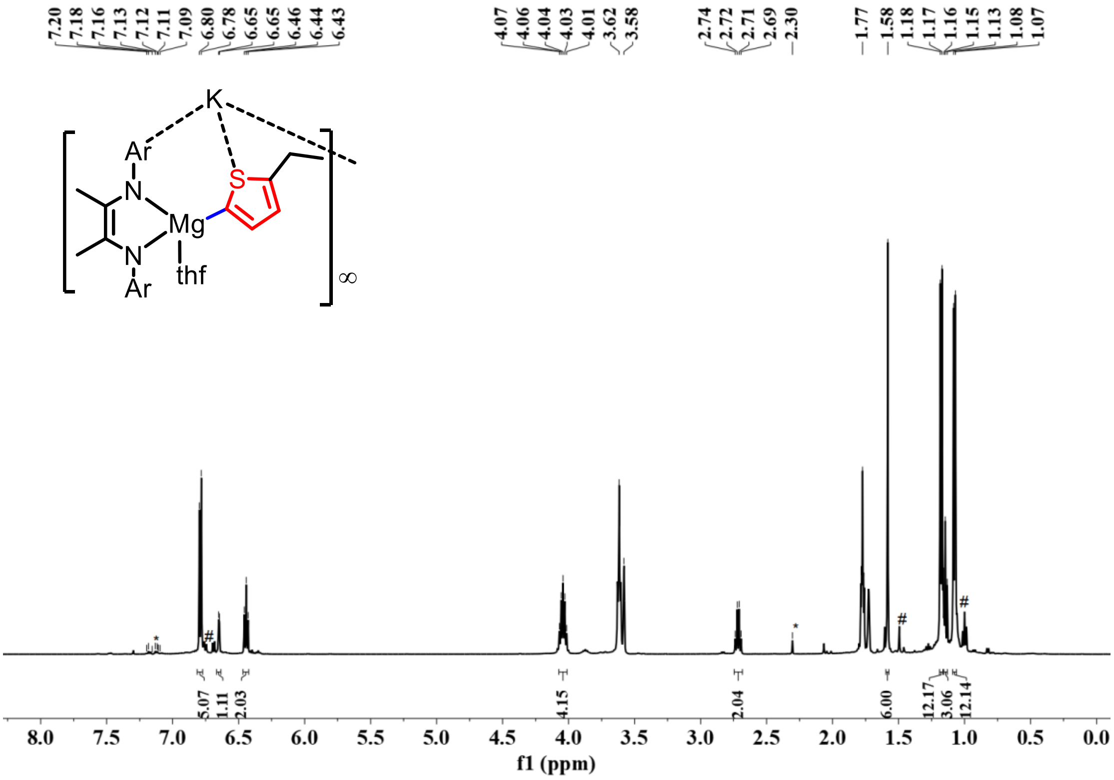


Fig. S5. ^{1}H NMR spectrum of **4** (THF-d_8, 500 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

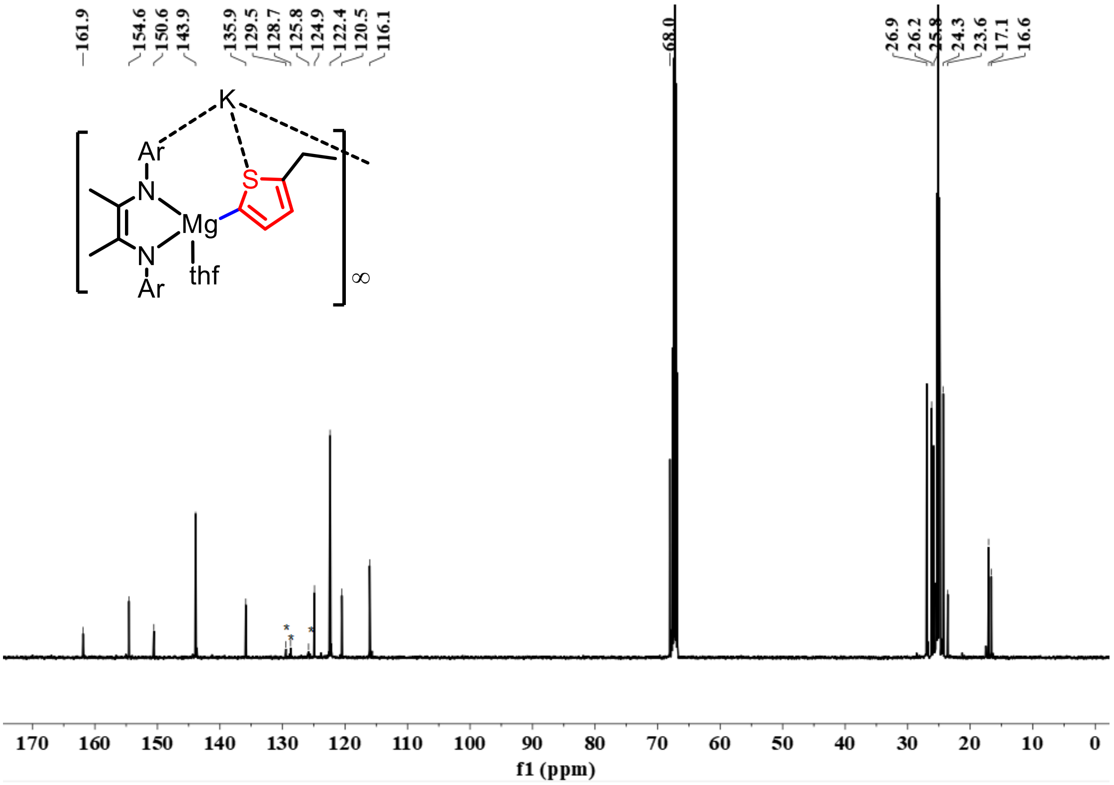


Fig. S6. ^{13}C NMR spectrum of **4** (THF-d_8, 126 MHz, 298 K, signals marked with * are from solvent toluene).

[K(thf)LMg(2-MeO-C_4H_2S)(thf)]$_\infty$ (5). Complex **5** was synthesized by similar procedures as employed for **2**, from 2-methoxythiophene (2.0 equiv, 206 uL, 2 mmol) and **1** (1 mmol), as orange crystals (yield: 0.986 g, 68%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.07 (d, 12H, $(CH_3)_2CH$-), 1.13−1.16 (t, 3H, CH_3O- of 2-methoxythienyl), 1.18 (d, 12H, $(CH_3)_2CH$-), 1.57 (s, 6H, CH_3C-), 1.77 (thf), 3.62 (thf), 3.63 (-OCH_3), 4.00−4.05 (m, 4H, $CH(CH_3)_2$), 6.06−6.07 (d, 1H, 2-methoxythienyl), 6.43−6.46 (2H, p-C_6H_3), 6.50−6.51 (d, 1H, 2-methoxythienyl), 6.78−6.80 (d, 4H, m-C_6H_3). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 17.0 (NCCH_3), 24.3 (CH(CH_3)$_2$), 25.9 (CH(CH_3)$_2$), 26.2 (thf), 26.9 (CH(CH_3)$_2$), 60.0 (-OCH_3), 68.0 (thf), 105.9 (2-methoxythienyl), 116.0 (NC=CN), 120.5 (2-methoxythienyl), 122.3, 124.9 (Ar-C), 133.1 (2-methoxythienyl), 143.8, 149.0 (Ar-C), 154.5 (Ar-C), 171.9 (Mg-C of 2-methoxythienyl). Elemental analysis calcd. for $C_{41}H_{61}KMgN_2O_3S$ (725.38): C, 67.89; H, 8.48; N, 3.86. Found: C, 67.85; H, 8.45; N, 3.79%.

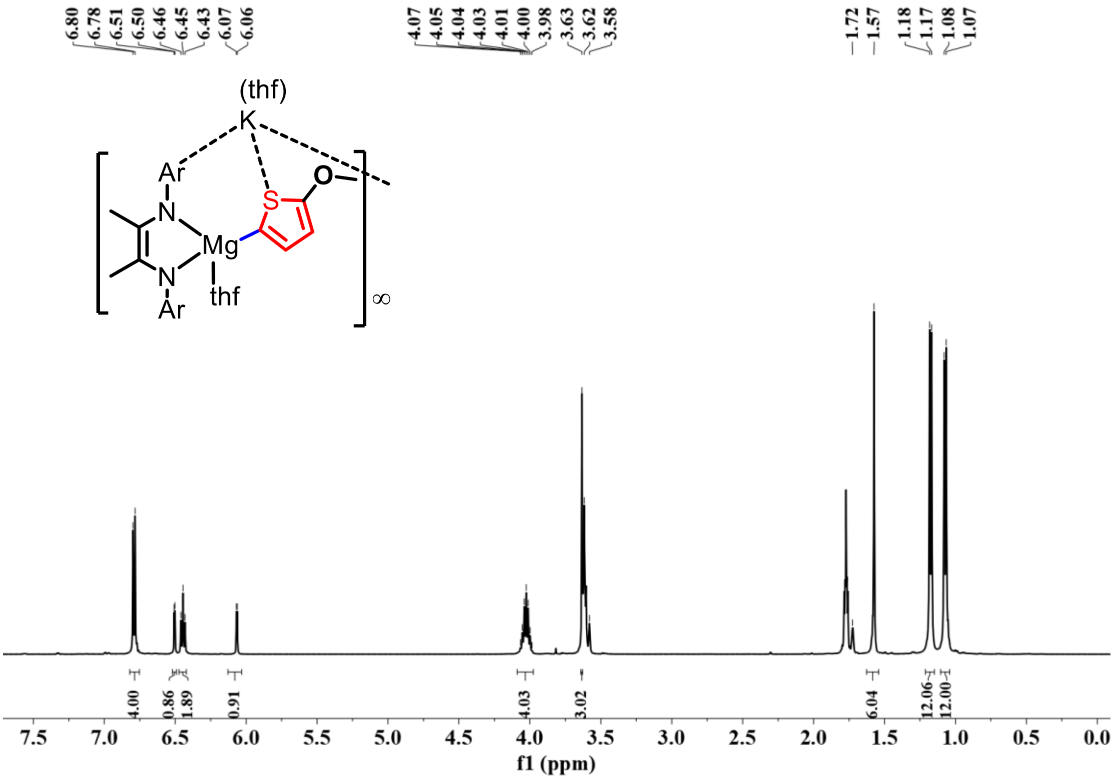


Fig. S7. ^{1}H NMR spectrum of **5** (THF-d_8, 500 MHz, 298 K).

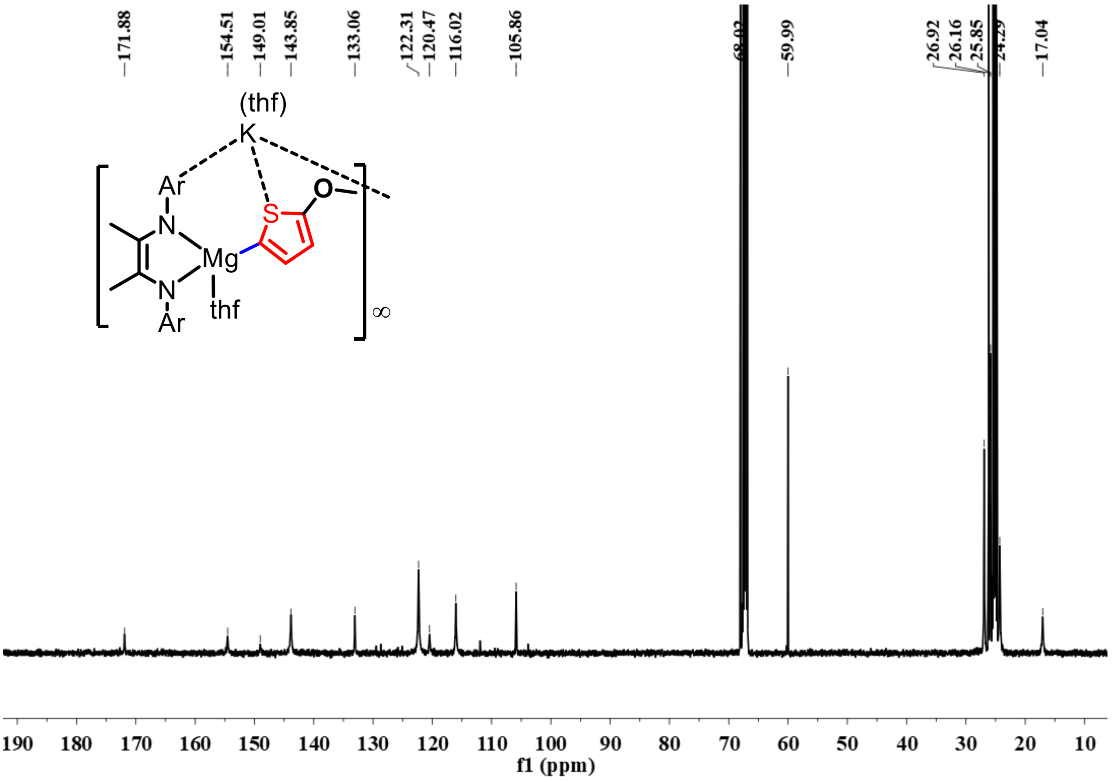


Fig. S8. ^{13}C NMR spectrum of **5** (THF-d_8, 126 MHz, 298 K).

[K(thf)LMg(3-Me-C_4H_2S)(thf)]$_\infty$ (6). Complex **6** was synthesized by similar procedures as employed for **2**, from 3-methylthiophene (193 uL, 2 mmol) and **1** (1 mmol). Orange crystals of **6** were obtained from toluene/*n*-hexane. Crystal yield: 0.894 g (63%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.09 (d, 12H, $(CH_3)_2CH$-), 1.19 (d,12H, $(CH_3)_2CH$-), 1.59 (s, 6H, CH_3C-), 1.76 (thf), 2.76 (s, 3H, CH_3- of 3-methylthienyl), 2.30 (toluene), 3.61 (thf), 4.05 (br, 4H, $CH(CH_3)_2$), 6.46 (br, 2H, *p*-C_6H_3), 6.61−6.69 (t, 1H, 3-methylthienyl), 6.74−6.81 (m, 4H, *m*-C_6H_3), 6.86 (s, 1H, 3-methylthienyl), 6.97−7.21 (toluene). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 14.6 (CH_3 of 3-methylthienyl), 17.0 (NCCH_3), 21.6, 23.2, 24.3 (CH(CH_3)$_2$), 25.8 (CH(CH_3)$_2$), 26.1 (thf), 26.9 (CH(CH_3)$_2$), 68.0 (thf), 116.0 (NC=CN), 120.4 (3-methylthienyl), 122.3, 123.8, 124.6 (Ar-*C*), 125.5, 128.6, 129.5, 138.1 (toluene), 139.0, 143.8 (3-methylthienyl), 144.8, 149.0 (Ar-*C*), 154.6 (Ar-*C*), 164.7 (Mg-*C* of 3-methylthienyl). Elemental analysis calcd. for $C_{41}H_{61}KMgN_2O_2S$ (709.38): C, 69.42; H, 8.67; N, 3.95. Found: C, 69.13; H, 8.71; N, 3.93%.

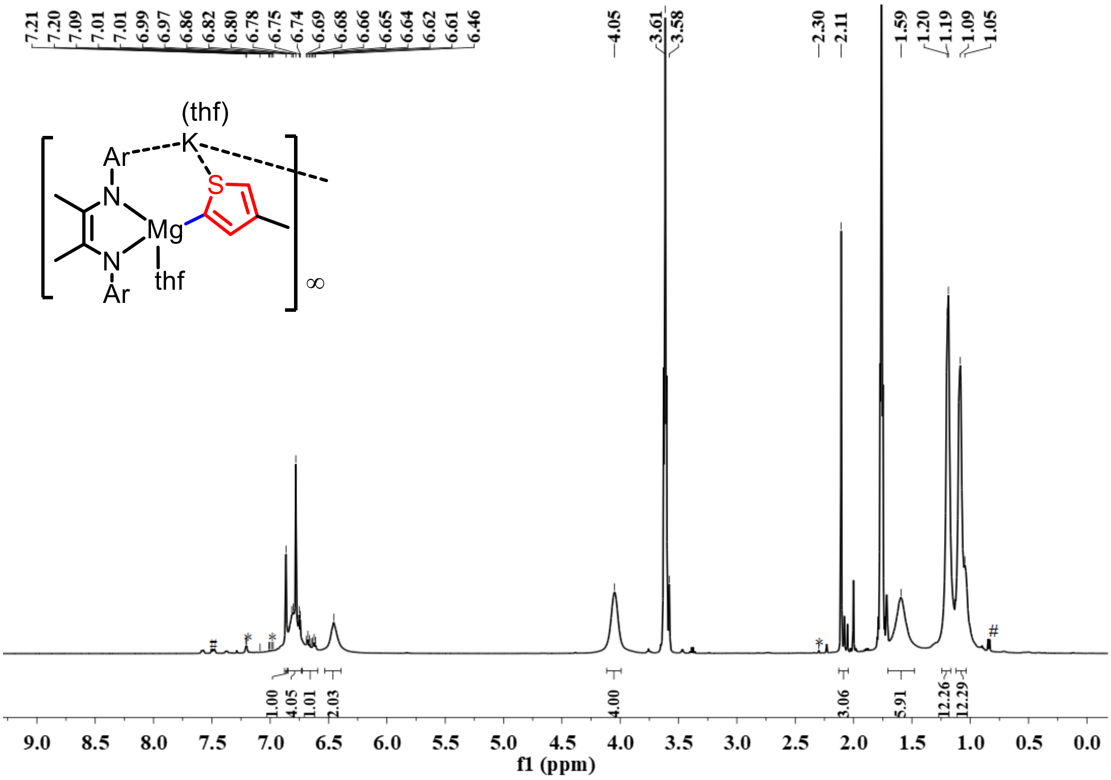


Fig. S9. ^{1}H NMR spectrum of **6** (THF-d_8, 500 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

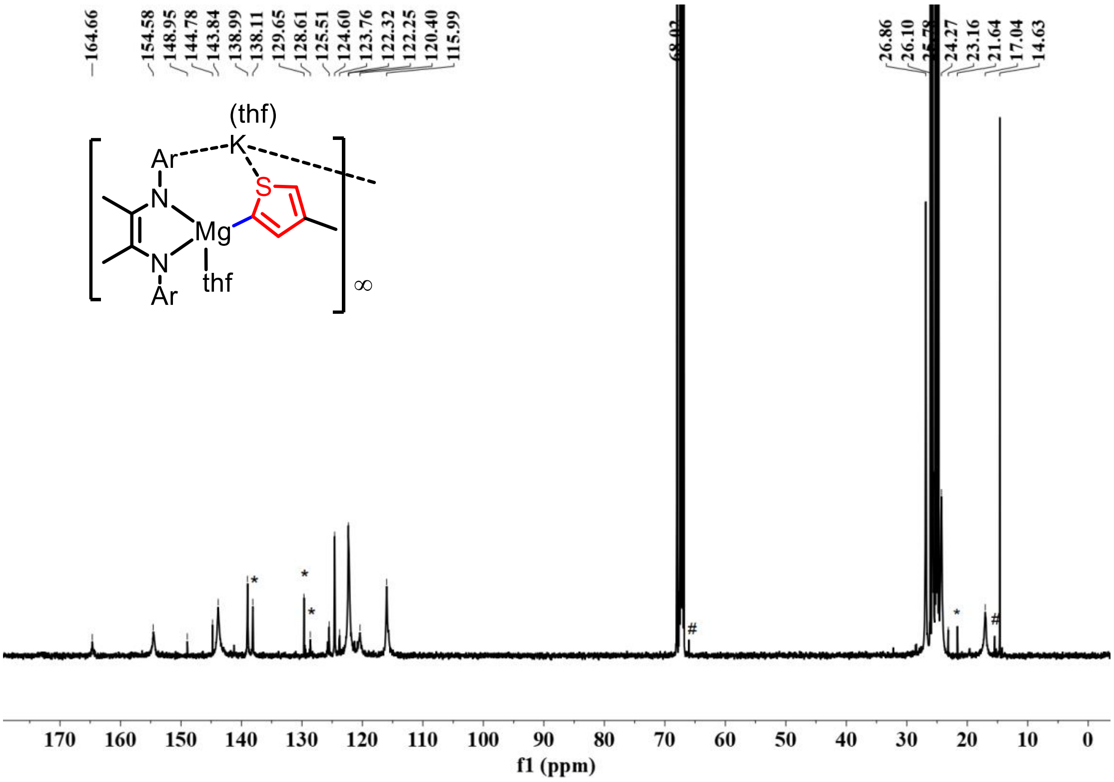


Fig. S10. ^{13}C NMR spectrum of **6** (THF-d_8, 126 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

[K(thf)LMg(2,3-Me$_2$-C$_4$HS)(thf)]$_\infty$ (7). Complex **7** was synthesized by similar procedures as employed for **2**, from 2,3-dimethylthiophene (224 uL, 2 mmol) and **1** (1 mmol), as orange crystals obtained from THF/toluene/*n*-hexane. Crystal yield: 0.868 g (60%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.08 (d, 12H, (C*H*$_3$)$_2$CH-), 1.19 (d, 12H, (C*H*$_3$)$_2$CH-), 1.59 (s, 6H, C*H*$_3$C-), 1.77 (thf), 1.94 (s, 3H, C*H*$_3$- of 2,3-dimethylthienyl), 2.17 (s, 3H, C*H*$_3$- of 2,3-dimethylthienyl), 2.30 (toluene), 3.62 (thf), 4.01−4.07 (m, 4H, C*H*(CH$_3$)$_2$), 6.44−6.47 (t, 2H, *p*-C$_6$H$_3$), 6.65 (s, 1H, 2,3-dimethylthienyl), 6.80−6.81 (d, 4H, *m*-C$_6$H$_3$), 7.06−7.19 (toluene). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 13.0 (*C*H$_3$- of 2,3-dimethylthienyl), 13.3 (C*H*$_3$- of 2,3-dimethylthienyl), 17.0 (NC*C*H$_3$), 21.3 (toluene), 24.3 (CH(*C*H$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 26.1 (thf), 26.9 (*C*H(CH$_3$)$_2$), 68.0 (thf), 116.0 (NC=*C*N), 120.5 (2,3-dimethylthienyl), 122.4 (Ar-*C*), 125.8, 128.7, 129.4 (toluene), 135.6 (2,3-dimethylthienyl), 138.2 (toluene), 139.9 (2,3-dimethylthienyl), 143.9, 150.6 (Ar-*C*), 154.5 (Ar-*C*), 159.0 (Mg-*C* of 2,3-dimethylthienyl). Elemental analysis calcd. for $C_{42}H_{63}KMgN_2O_2S$ (723.41): C, 69.73; H, 8.78; N, 3.87. Found: C, 69.72; H, 8.76; N, 3.85%.

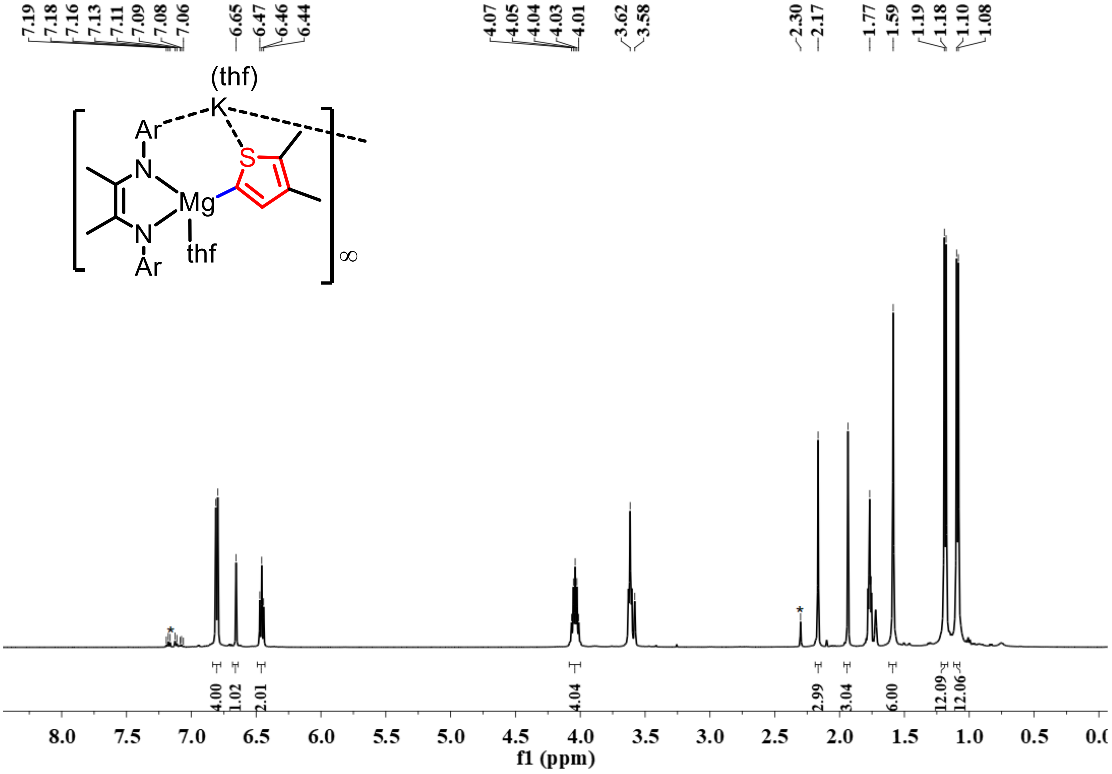


Fig. S11. ^{1}H NMR spectrum of **7** (THF-d_8, 500 MHz, 298 K, signals marked with * are from toluene).

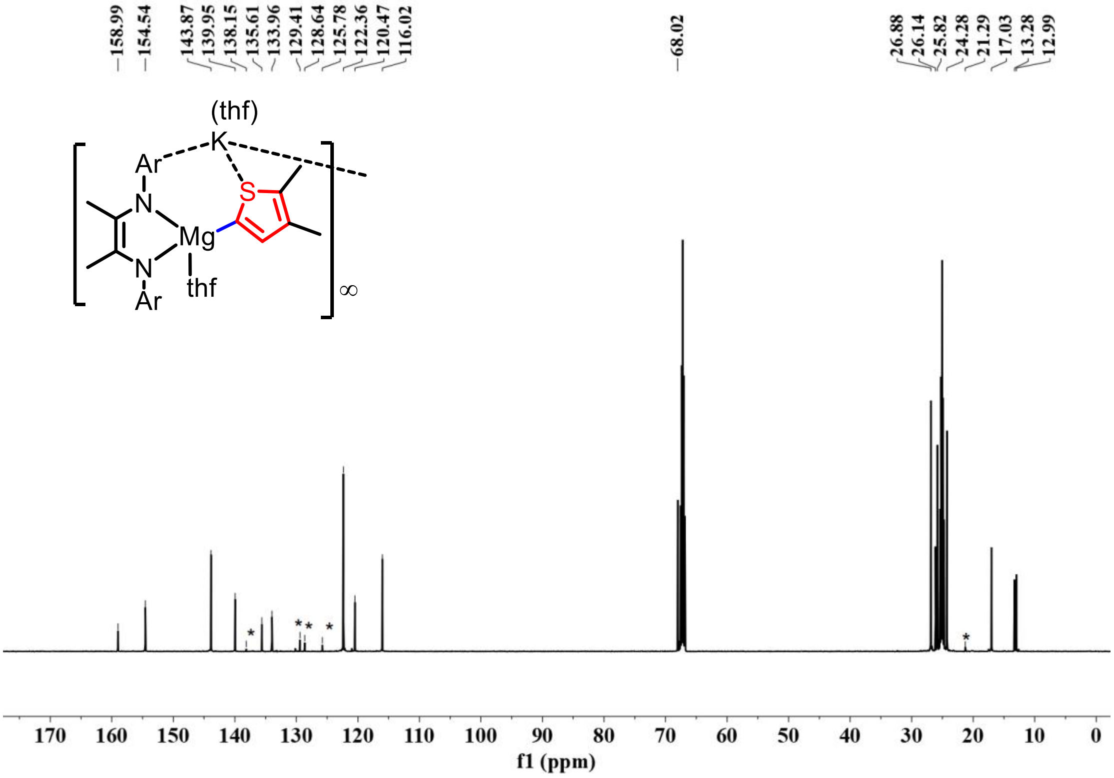


Fig. S12. ^{13}C NMR spectrum of **7** (THF-d_8, 126 MHz, 298 K, signals marked with * are from toluene).

[K(thf)LMg($C_2H_4O_2$-C_4HS)(thf)]$_{\infty}$ (8). Complex **8** was synthesized by similar procedures as employed for **2**, from 3,4-ethylenedioxythiophene (214 uL, 2 mmol) and **1** (1 mmol). Orange crystals were obtained from THF/toluene/*n*-hexane. Crystal yield: 1.205 g (80%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.02 (d, 12H, (CH_3)$_2$CH-), 1.18 (d, 12H, (CH_3)$_2$CH-), 1.58 (s, 6H, CH_3C-), 1.77 (thf), 2.30 (toluene), 3.62 (thf), 3.91−3.94 (CH_2O- of 3,4-ethylenedioxythienyl), 3.99 (br, 4H, CH(CH$_3$)$_2$), 6.22 (s, 1H, 3,4-ethylenedioxythienyl), 6.48 (s, 2H, *p*-C_6H_3), 6.81 (s, 4H, *m*-C_6H_3); 7.03−7.19 (toluene). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 16.9 (NCCH$_3$), 24.2, 24.4 (CH(CH$_3$)$_2$), 25.5 (CH(CH$_3$)$_2$), 26.2 (thf), 27.0 (CH(CH$_3$)$_2$), 65.2 ((OCH$_2$)$_2$ of 3,4-ethylenedioxythienyl), 68.0 (thf), 99.6 (3,4-ethylenedioxythienyl), 104.5 (3,4-ethylenedioxythienyl), 116.6 (NC=CN), 120.4, 121.3, 122.4 (Ar-C), 125.8, 128.7, 129.4 (toluene), 131.1, 134.3, 135.3 (Ar-C), 142.8 (3,4-ethylenedioxythienyl), 143.7, 147.1, 153.7 (Ar-C), 155.7 (Ar-C), 159.5 (Mg-C of 3,4-ethylenedioxythienyl). Elemental analysis calcd. for $C_{42}H_{61}KMgN_2O_4S$ (753.39): C, 66.96; H, 8.16; N, 3.72. Found: C, 67.19; H, 8.15; N, 3.70%.

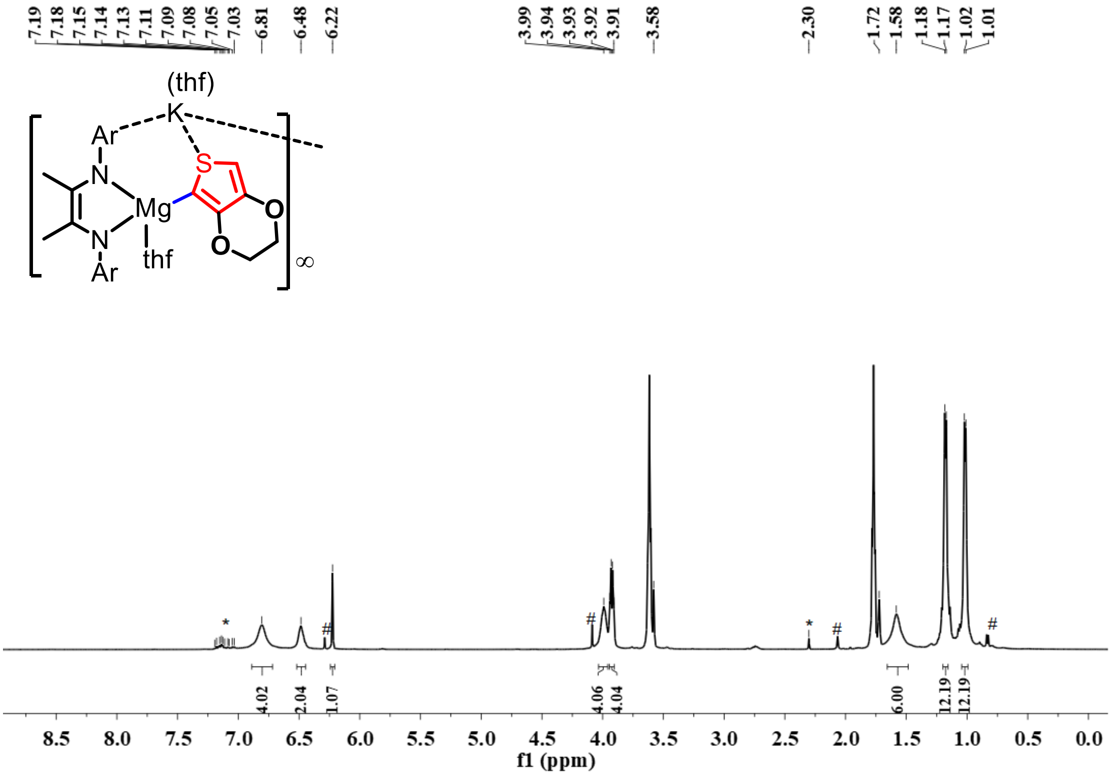


Fig. S13. ^{1}H NMR spectrum of **8** (THF-d_8, 500 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

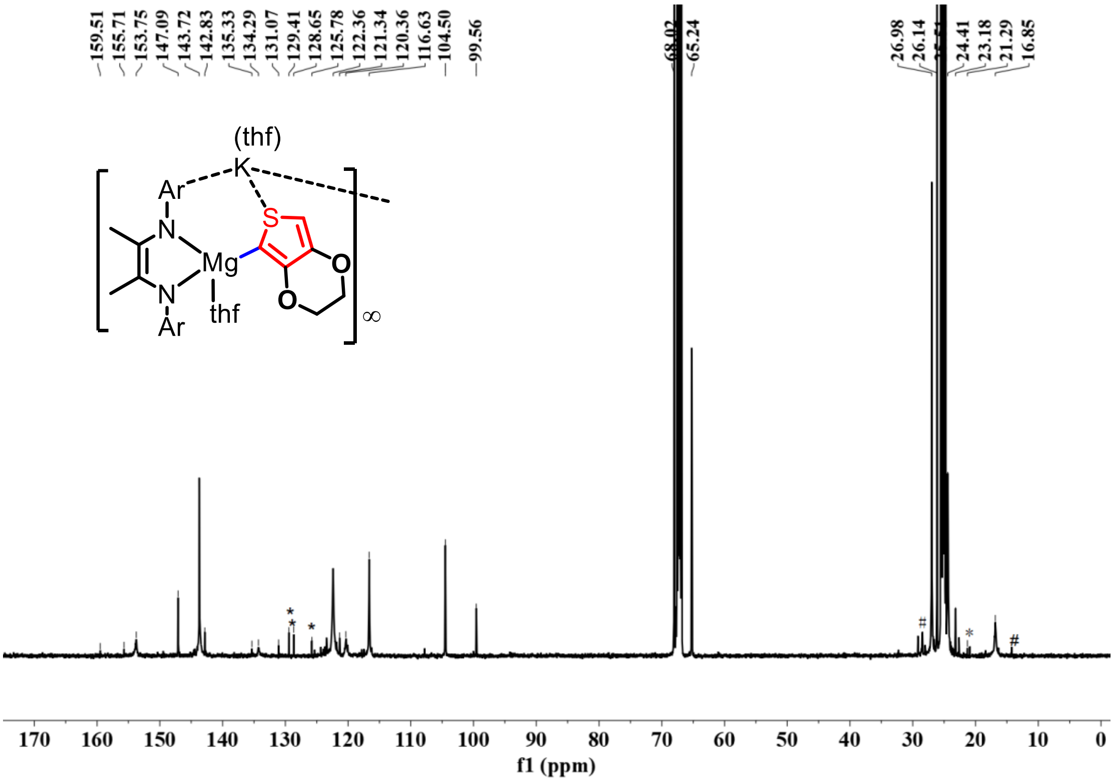


Fig. S14. ^{13}C NMR spectrum of **8** (THF-d_8, 126 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

[K(thf)LMg(C_4H_4-C_4HS)(thf)]$_\infty$ (9). Complex **9** was synthesized by similar procedures as employed for **2**, from thianaphthene (268.4 mg, 2 mmol) and **1** (1 mmol), as orange-red crystals (0.821 g, 61%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.06 (br, 12H, $(CH_3)_2CH$-), 1.20 (d, 12H, $(CH_3)_2CH$-), 1.59 (s, 6H, CH_3C-), 1.77 (thf), 2.30 (toluene), 3.63 (thf), 4.09 (br, 4H, $CH(CH_3)_2$), 6.44 (br, 2H, *p*-C_6H_3), 6.78–6.84 (d, 4H, *m*-C_6H_3), 6.92–6.95 (t, 1H, thianaphthene-5-yl), 7.07–7.10 (toluene), 7.12–7.14 (m, 3H, thianaphthene-5-yl), 7.16–7.20 (toluene), 7.44–7.46 (d, 1H, thianaphthene-5-yl). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 17.1, 20.9 ($NCCH_3$), 21.3 (toluene), 24.4 ($CH(CH_3)_2$), 26.0 ($CH(CH_3)_2$), 26.2 (thf), 27.0 ($CH(CH_3)_2$), 68.0 (thf), 116.1 (NC=*C*N), 120.0 (thianaphthene-5-yl), 121.3, 121.8, 122.0 (Ar-*C*), 122.9 (thianaphthene-5-yl), 124.1 (Ar-*C*), 124.6, 124.7 (thianaphthene-5-yl), 125.8 (toluene), 126.9 (Ar-*C*), 128.7, 129.5 (toluene), 134.8 (Ar-*C*), 138.2 (toluene), 140.6 ,143.8 (thianaphthene-5-yl), 144.2, 147.0, 154.5 (Ar-*C*), 159.6 (Mg-*C* of thianaphthene-5-yl). Elemental analysis calcd. for $C_{40}H_{53}KMgN_2OS$ (673.31): C, 71.35; H, 7.93; N, 4.16. Found: C, 71.14; H, 7.95; N, 4.12%.

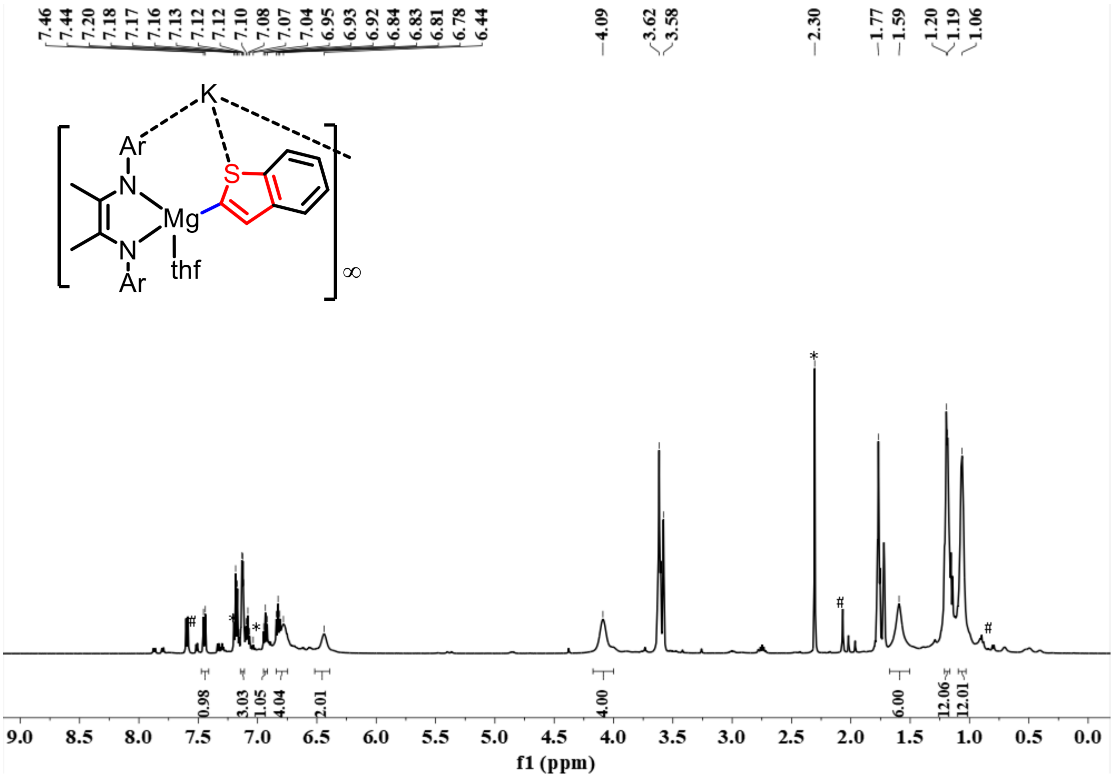


Fig. S15. ^{1}H NMR spectrum of **9** (THF-d_8, 500 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

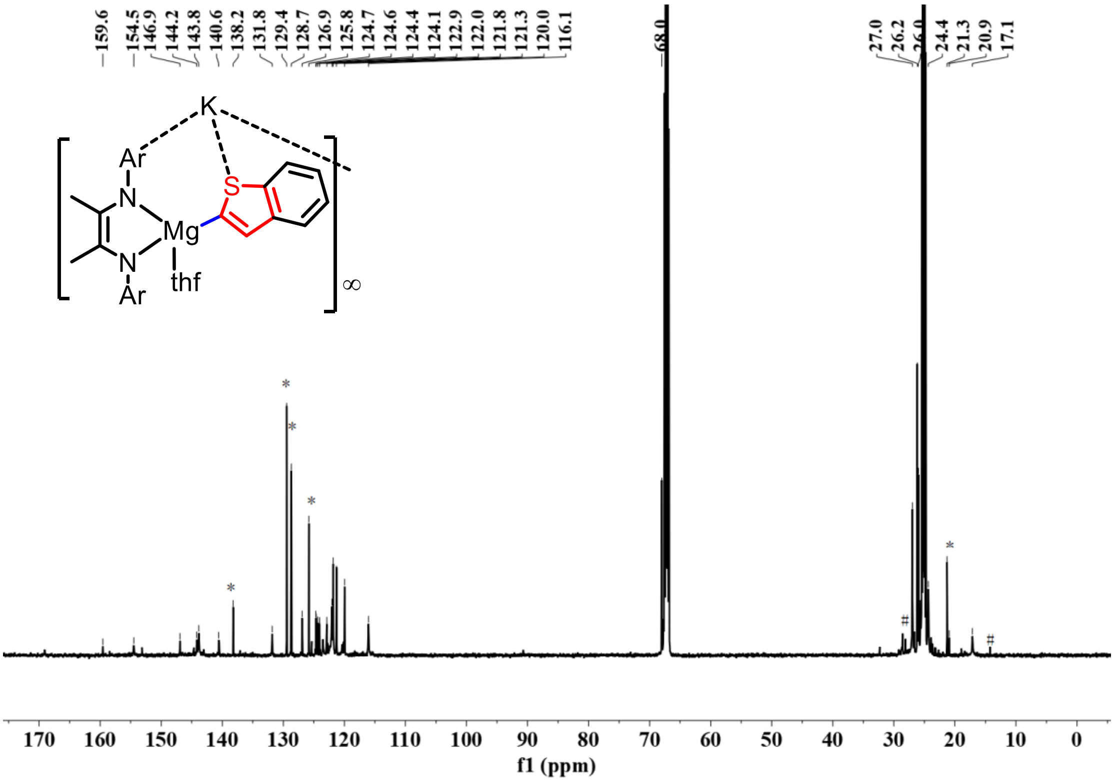


Fig. S16. ^{13}C NMR spectrum of **9** (THF-d_8, 126 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

$[\mathrm{K(thf)_2LMg(C_4H_2S)_2(thf)}]_2$ (10). Complex **10** was synthesized by similar procedures as employed for **2**, from 2,2'-bithiophene (166.2 mg, 1 mmol) and **1** (1 mmol), as orange-red crystals (1.073 g, 70%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.06 (d, 24H, $(\mathrm{C}H_3)_2\mathrm{CH}$-), 1.17 (d, 24H, $(\mathrm{C}H_3)\mathrm{CH_2}$-), 1.56 (s, 12H, $\mathrm{C}H_3\mathrm{C}$-), 1.77 (thf), 3.62 (thf), 4.01−4.03 (m, 8H, $\mathrm{C}H(\mathrm{CH_3})_2$), 6.40−6.43 (t, 4H, *p*-$\mathrm{C_6H_3}$), 6.74−6.76 (t, 8H, *m*-$\mathrm{C_6H_3}$), 6.74−6.76 (t, 2H, 2,2'-bithiophene-5,5'-diyl), 6.84−6.85 (d, 2H, 2,2'-bithiophene-5,5'-diyl). ^{13}C NMR (126 MHz, THF-d_8, 298 K): 17.1 ($\mathrm{NC}C\mathrm{H_3}$), 24.3 ($\mathrm{CH}(C\mathrm{H_3})_2$), 26.0 ($\mathrm{CH}(C\mathrm{H_3})_2$), 26.2 (thf), 26.9 ($C\mathrm{H(CH_3)_2}$), 68.0 (thf), 116.0 ($\mathrm{N}C\mathrm{{=}CN}$), 120.4 (2,2'-bithiophene-5,5'-diyl), 122.2, 123.3 (Ar-*C*), 136.4, 143.3 (2,2'-bithiophene-5,5'-diyl), 143.9, 154.6 (Ar-*C*), 162.7 (Mg-*C* of 2,2'-bithiophene-5,5'-diyl). Elemental analysis calcd. for $\mathrm{C_{88}H_{132}K_2Mg_2N_4O_6S_2}$ (1532.91): C, 68.95; H, 8.68; N, 3.65. Found: C, 68.70, H, 8.72; N, 3.63%.

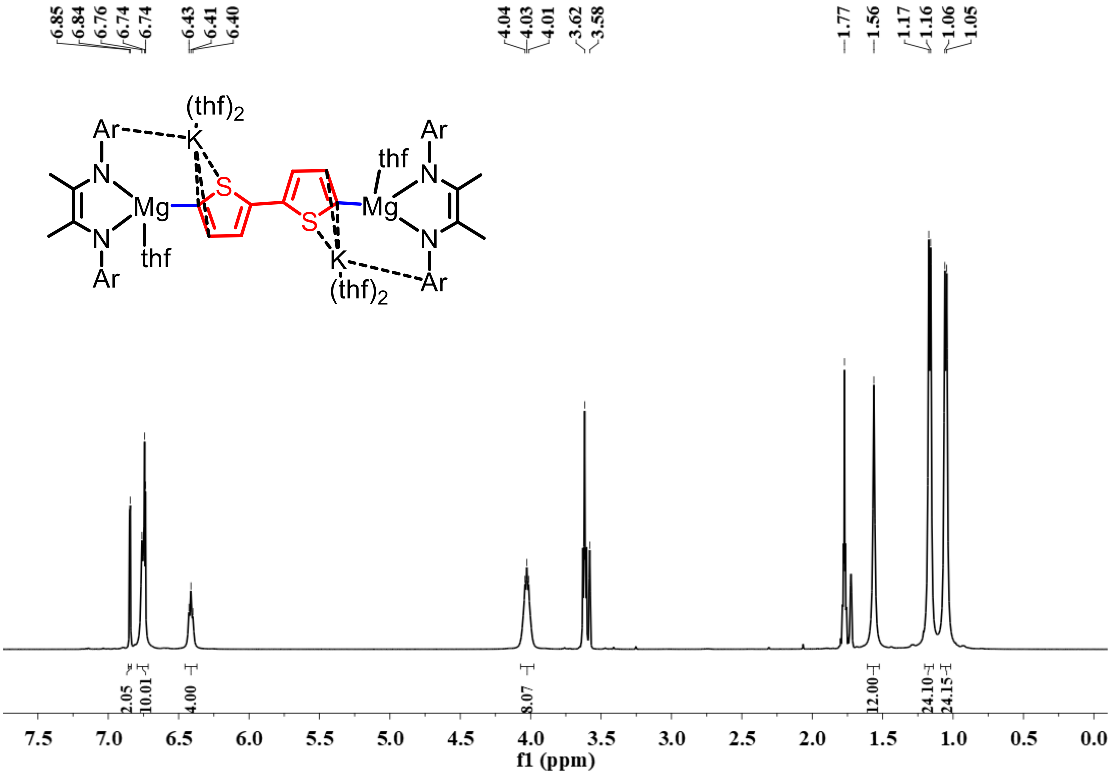


Fig. S17. ^{1}H NMR spectrum of **10** (THF-d_8, 500 MHz, 298 K).

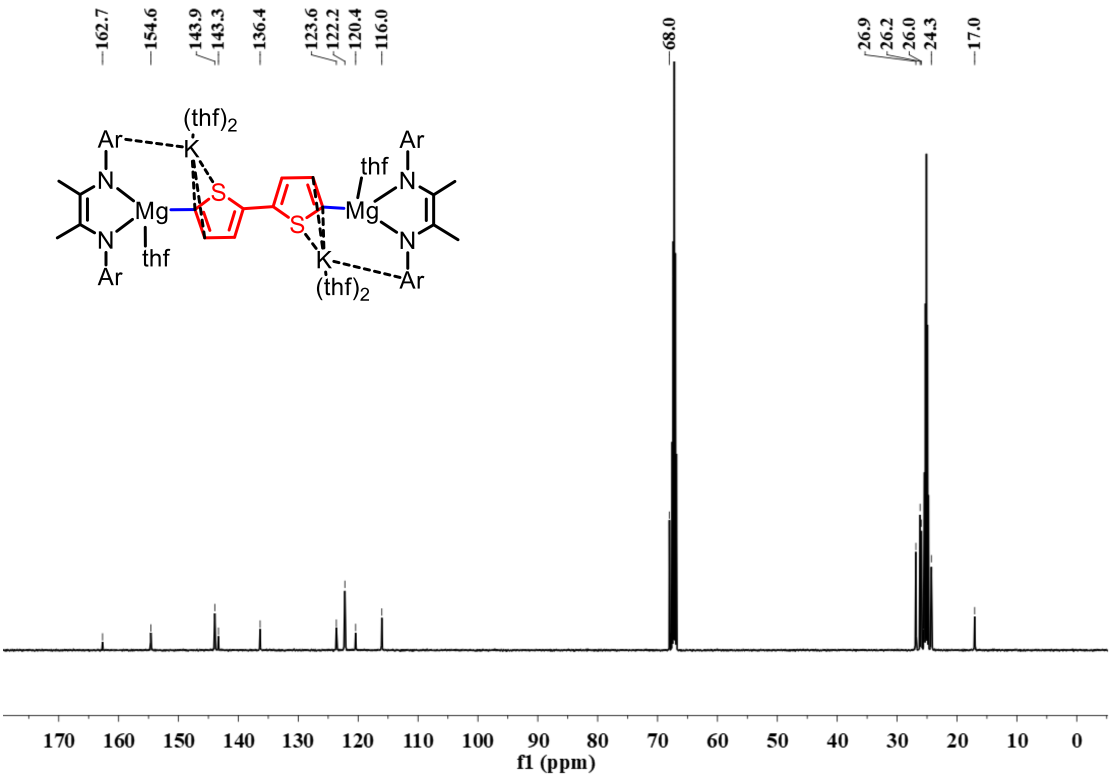


Fig. S18. ^{13}C NMR spectrum of **10** (THF-d_8, 126 MHz, 298 K).

[{K(thf)$_2$}$_2$LMg(C$_3$H$_2$S)$_2$MgL] (11). Complex **11** was synthesized by similar procedures as employed for **2**, from thieno[3,2-b]thiophene (140.2 mg, 1 mmol) and **1** (1 mmol), as orange crystals (0.814 g, 54%). ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ/ppm 1.03 (br, 24H, (CH_3)$_2$CH-), 1.15 (br, 24H, (CH_3)CH$_2$-), 1.55 (s, 12H, CH_3C-),1.77 (thf), 2.31 (toluene), 3.62 (thf), 4.00 (br, 8H, CH(CH$_3$)$_2$), 6.40 (br, 4H, *p*-C$_6$H$_3$),6.74 (br, 8H, *m*-C$_6$H$_3$), 6.79 (s, 2H, thieno[3,2-b]thiophene-5,5'-diyl), 7.03−7.15 (toluene). ^{13}C NMR (176 MHz, THF-d_8, 298 K): 17.0 (NCCH$_3$), 24.3 (CH(CH$_3$)$_2$), 26.0 (CH(CH$_3$)$_2$), 21.3 (toluene), 26.2 (thf), 26.9 (CH(CH$_3$)$_2$), 68.0 (thf), 116.0, 118.9 (NC=CN), 120.6 (thieno[3,2-b]thiophene-5,5'-diyl), 122.4, 122.9 (Ar-C), 125.6, 128.7, 129.5 (toluene), 137.1 (thieno[3,2-b]thiophene-5,5'-diyl), 143.9, 151.4, 154.6 (Ar-C), 167.2 (Mg-C of thieno[3,2-b]thiophene-5,5'-diyl). Elemental analysis calcd. for $C_{86}H_{130}K_2Mg_2N_4O_6S_2$ (1506.87): C, 68.55; H, 8.70; N, 3.72. Found: C, 68.65; H, 8.64; N, 3.74%.

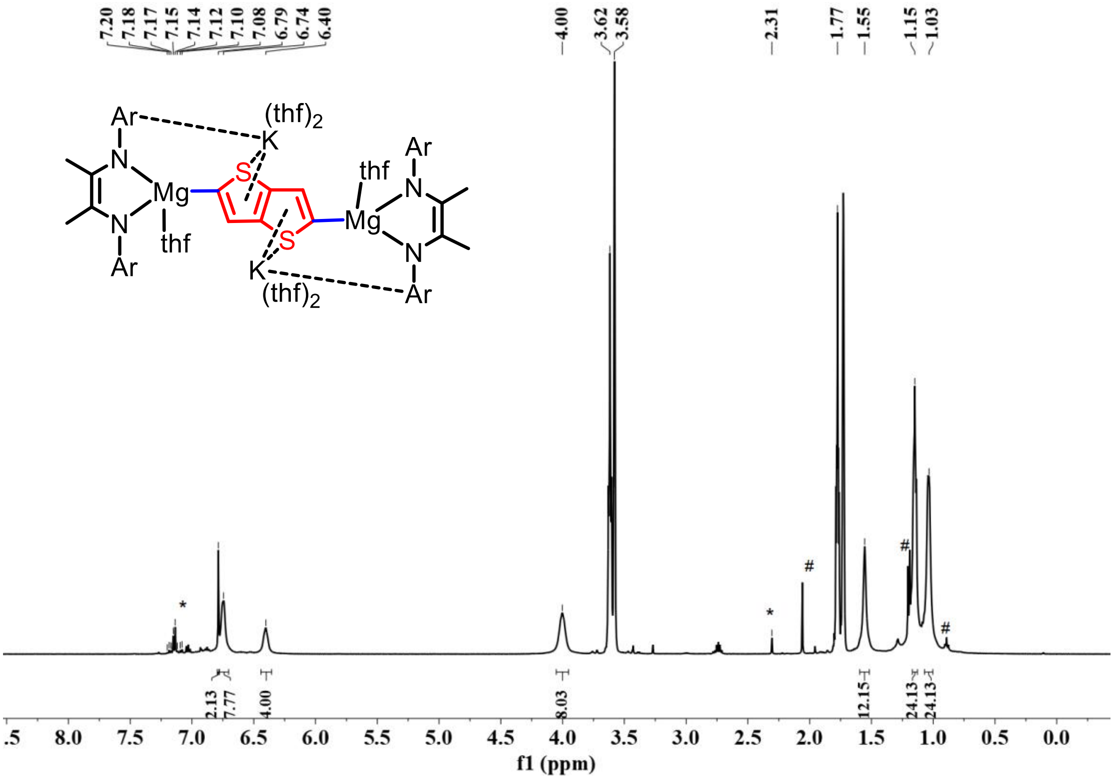


Fig. S19. ^{1}H NMR spectrum of **11** (THF-d_8, 500 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).

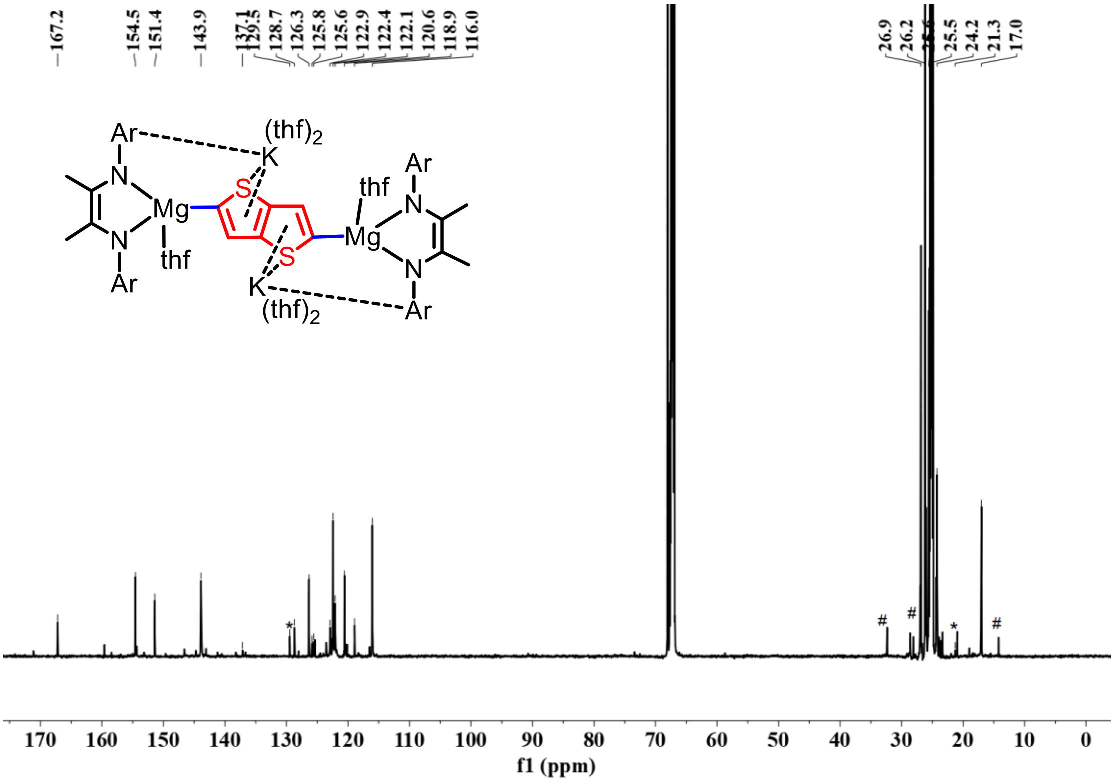
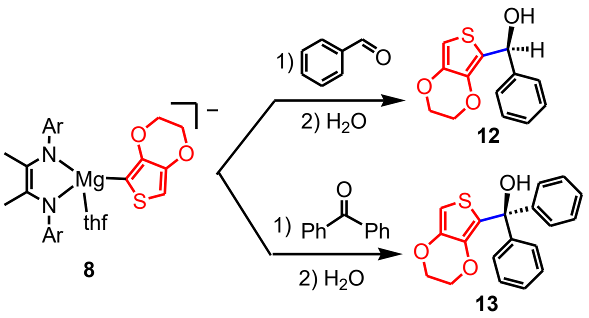


Fig. S20. ^{13}C NMR spectrum of **11** (THF-d_8, 176 MHz, 298 K, signals marked with * are from toluene and those with # are due to unidentified impurities).



$C_{13}H_{12}O_3S$ (12). At room temperature, a solution of benzaldehyde (2 mmol) in THF was added slowly to a solution of *in situ* generated complex **8** (2 mmol) in THF (20 mL). The mixture was stirred for 2 hours and quenched with water. The mixture was extracted with EtOAc and the combined organic phases were dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by column chromatography on silica gel to afford the colorless oily alcohol **12** (0.358 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ/ppm 2.53 (s, 1H, -OH), 4.18-4.20 (q, 2H, -CH_2O-), 4.13-4.24 (q, 2H,-CH_2O-), 6.10 (s, 1H, -HOC*H*-), 6.26 (s, 1H, -C_4*H*S-), 7.28-7.31 (t, 1H, *p*-C_6H_5), 7.35-7.38 (t, 2H, *m*-C_6H_5), 7.46-7.48 (d, 2H, *o*-C_6H_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 64.8 (-$C$$H_2$O-), 64.9 (-$C$$H_2$O-), 69.2 (-HO*C*H-), 98.7, 120.7 (C_4HS-*C*), 126.4, 128.0, 128.6 (C_6H_5-*C*), 138.5, 141.6 (C_4HS-*C*), 142.5 (C_6H_5-*C*).

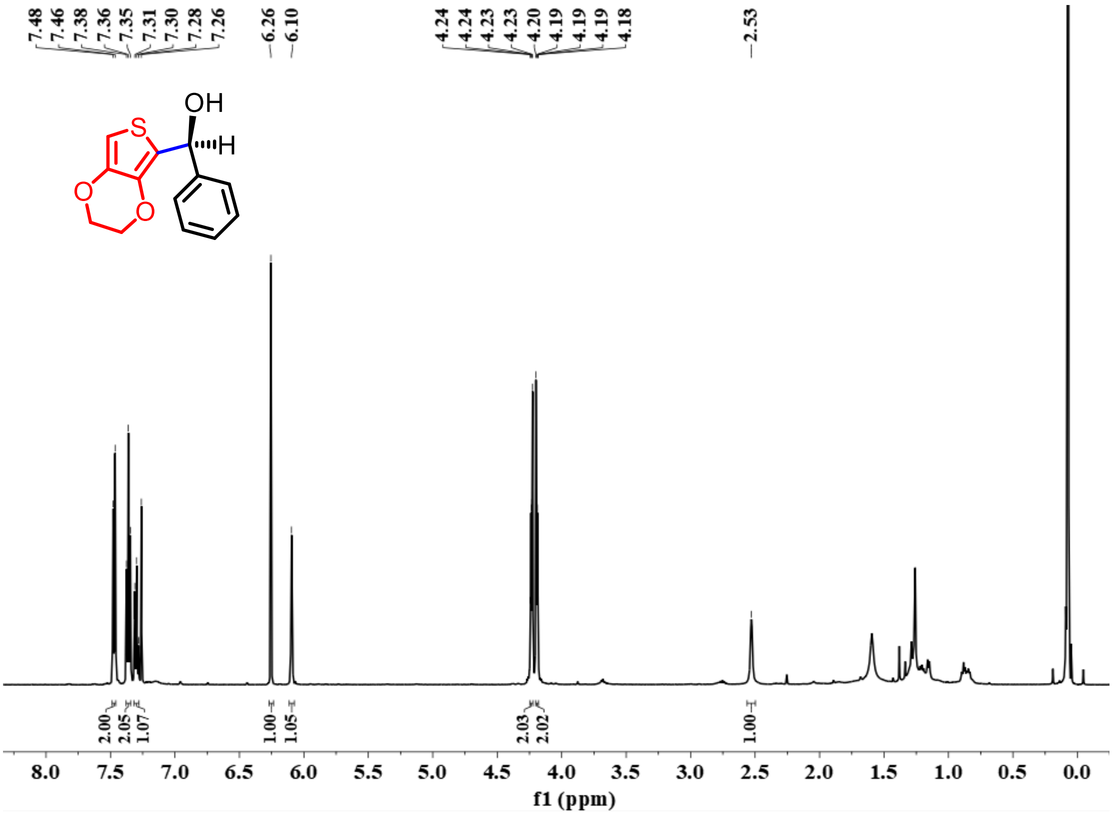


Fig. S21. ^{1}H NMR spectrum of **12** ($CDCl_3$, 298 K).

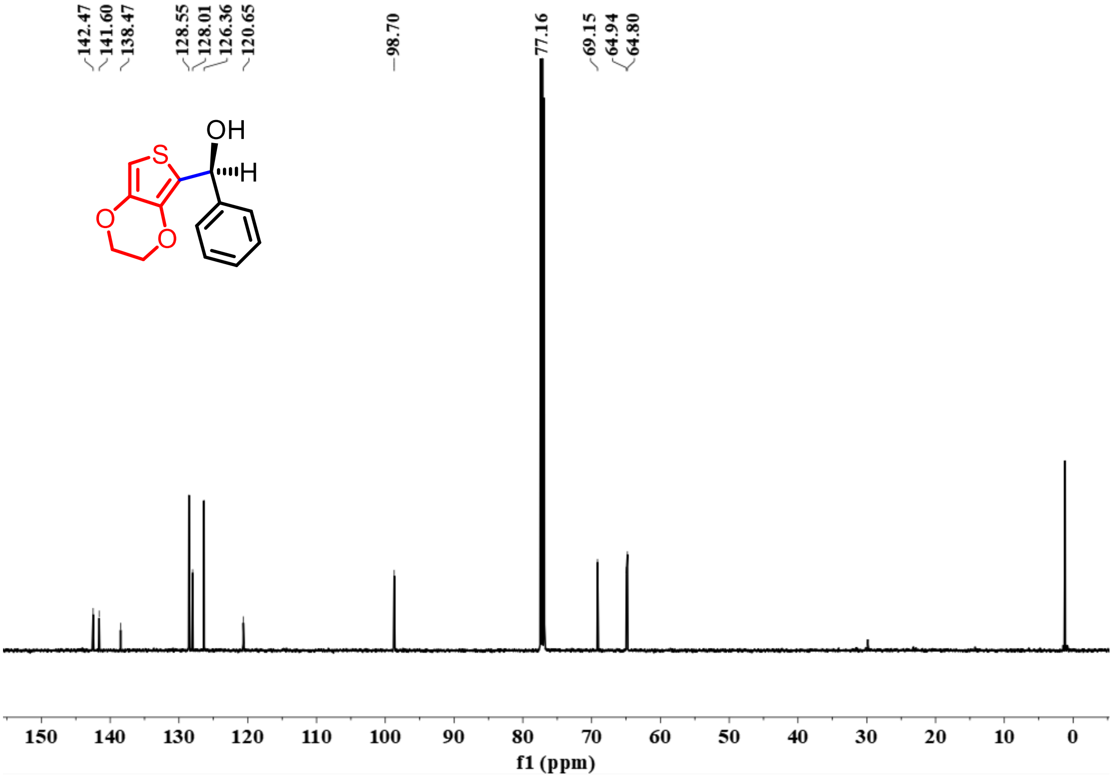


Fig. S22. ^{13}C NMR spectrum of **12** ($CDCl_3$, 298 K).

$C_{19}H_{16}O_3S$ (13). At room temperature, a solution of benzophenone (2 mmol) in THF was added slowly to a solution of *in situ* generated **8** (2 mmol) in THF (20 mL). The mixture was stirred at for 2 hours and quenched with water. The mixture was extracted with EtOAc and the combined organic phases were dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by column chromatography on silica gel to afford the colorless oily alcohol **13** (0.467 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ/ppm 4.05 (s, 1H, -OH), 4.14-4.16 (m, 2H, -$C\mathit{H}_2O$-), 4.18-4.19 (m, 2H,-$C\mathit{H}_2O$-), 6.25 (s, 1H, -$C_4\mathit{H}S$-), 7.29-7.30 (m, 3H, C_6H_5-*H*), 7.32-7.33 (m, 3H, C_6H_5-*H*), 7.34-7.36 (m, 4H, o-C_6H_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): 64.6 (-$\mathit{C}H_2O$-), 64.9 (-$\mathit{C}H_2O$-), 79.4 (-HO*C*-), 98.6, 124.0 (C_4HS-*C*), 127.5, 127.8, 128.0 (C_6H_5-*C*), 138.2, 141.9 (C_4HS-*C*), 145.9 (C_6H_5-*C*). HRMS (ESI): *m*/*z* calcd for $[C_{19}H_{16}O_3SNa]^+$: 347.0712, found: 347.0662.

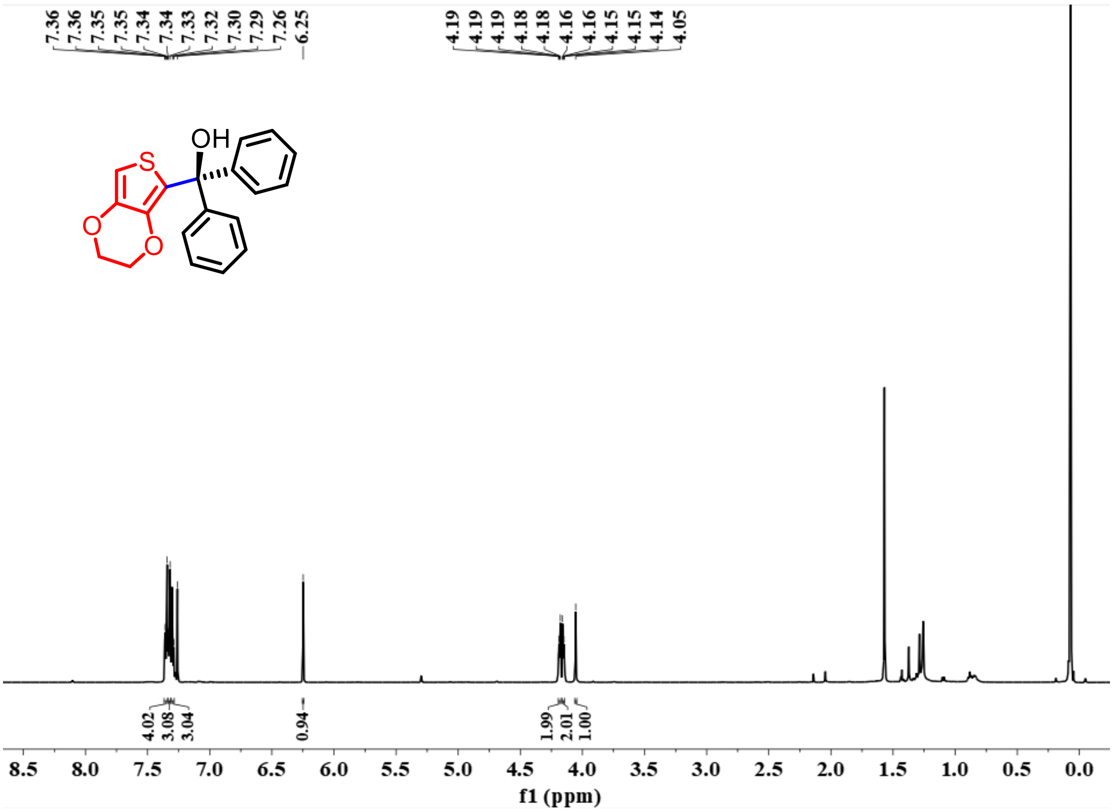


Fig. S23. ^{1}H NMR spectrum of **13** ($CDCl_3$, 298 K).

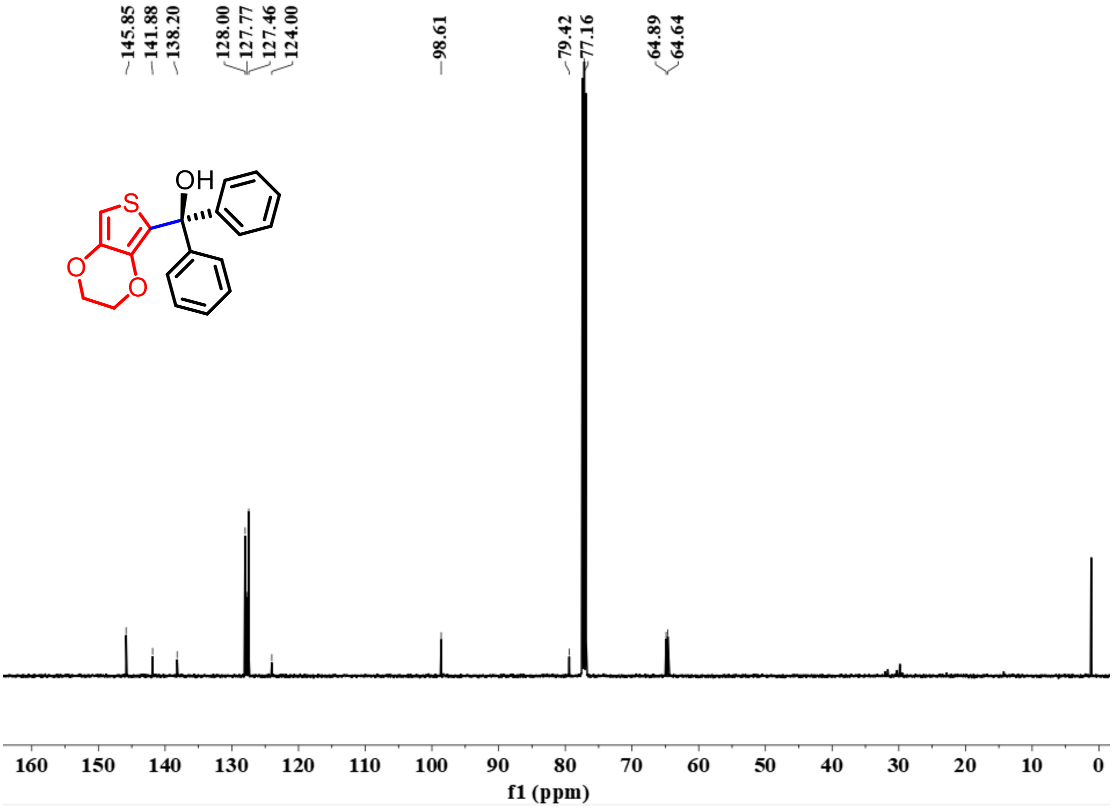


Fig. S24. ^{13}C NMR spectrum of **13** ($CDCl_3$, 298 K).

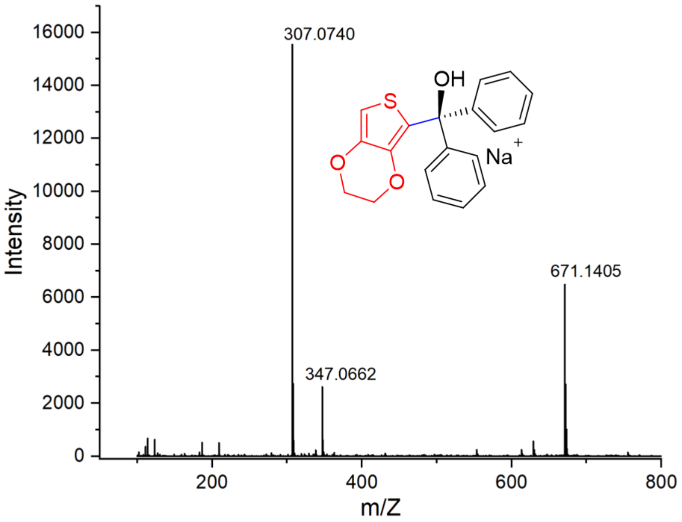


Fig. S25. HR ESI-MS spectrum of the alcohol product **13**.

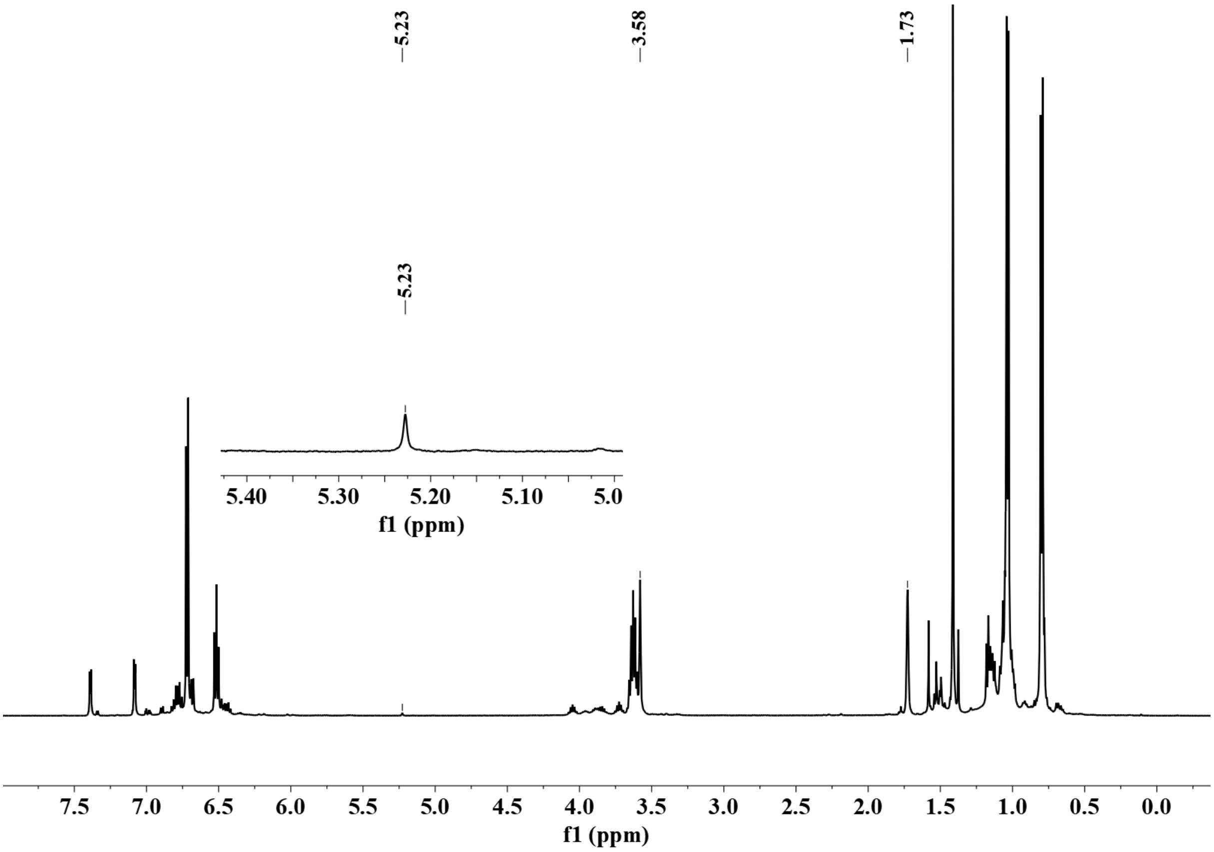


Fig. S26. ^{1}H NMR monitoring of the reaction of **1** with thiophene (THF-d_8, 298 K), indicating the formation of H_2 (at 5.23 ppm).

S2. X-ray Crystallographic Analysis

Diffraction data for compounds **2−4** and **6−11** were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). For complex **5**, data were collected with an XtaLAB Synergy R, DW system, HyPix diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data.[3] The structures were solved and refined to convergence on F^2 for all independent reflections by the full-matrix least squares method using the SHELXL−2014 programs[4] and OLEX$_2$ 1.2.[5]

In compound **3**, the *i*Pr group of the ligand L, the 2-Me-$C_4H_2S^-$ fragment, and THF molecules were disordered into two positions. Moreover, SIMU and ISOR instructions of some atoms, SADI instructions of some distances were used. In **4**, some atoms in 2-Et-$C_4H_2S^-$ fragment and THF molecules were disordered into two positions. SIMU, ISOR, RIGU and DELU instructions of some atoms, and DFIX and DANG instructions of some distances were also used. In **6**, one THF solvent molecule was disordered into two positions. RIGU instructions of some atoms and SADI instructions of some distances were used. In **7**, one THF solvent molecule was disordered into two positions. RIGU and ISOR instructions for some atoms and SADI instructions for some distances were used. In **8**, one S atom was disordered into two positions. SADI instructions of some distances were used. In **9**, some atoms in the C_4H_4-C_4HS^- fragment was disordered into two positions. Moreover, SIMU and ISOR instructions for some atoms, and DFIX and SADI instructions for some distances were used. In **10**, two THF solvent molecules were disordered into two positions. RIGU instructions of some atoms and SADI instructions of some distances were used. In **11**, some atoms in $(C_3H_2S)_2^{2-}$ fragment and the THF molecule were disordered into two positions. ISOR, RIGU and DELU instructions of some atoms, and SADI instructions of some distances were used.

Crystallographic data and refinement details for compounds **2–11** are given in Tables S1 and S2. CCDC Number(s) 2523301 (for **2**), 2523300 (for **3**), 2523302 (for **4**), 2523305 (for **5**), 2523306 (for **6**), 2523308 (for **7**), 2523309 (for **8**), 2523307 (for **9**), 2523304 (for **10**), 2523303 (for **11**).

Table S1. Crystallographic data and refinement details for compounds **2–6**.

Compound	**2**	**3**	**4.toluene**	**5**	**6**
formula	$C_{40}H_{59}KMgN_2O_2S$	$C_{41}H_{61}KMg N_2O_2S$	$C_{83}H_{118}K_2Mg_2 N_4O_2S_2$	$C_{41}H_{61}KMg N_2O_3S$	$C_{41}H_{61}KMg N_2O_2S$
M_r [g mol^{-1}]	695.36	709.38	1394.75	725.38	709.38
crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
space group	*Pbca*	*C*2/*c*	*P*-1	*C*2/*C*	*Pbca*
a [Å]	15.971(4)	17.84(4)	14.3040(8)	17.3049(4)	15.9820(19)
b [Å]	22.010(5)	13.453(14)	14.3229(8)	13.2052(3)	21.314(2)
c [Å]	22.603(5)	36.71(4)	20.2313(11)	36.1133(9)	23.857(3)
α[°]	90	90	91.745(2)	90	90
β [°]	90	101.14(5)	92.462(2)	95.887(2)	90
γ[°]	90	90	90.652(2)	90	90
V [Å^3]	7945(3)	8645(23)	4138.8(4)	8208.9(3)	8126.8(16)
Z	8	8	2	8	8
ρ_{calc}, [g cm^{-3}]	1.163	1.090	1.119	1.174	1.160
μ [mm^{-1}]	0.236	0.218	0.225	0.233	0.232
F(000)	3008	3072	1508	3136	3072
$\theta_{min}/\theta_{max}$ [°]	2.394 / 24.836	2.262 / 25.212	2.216 / 25.415	2.058 / 30.891	2.335 / 25.270
index ranges	$-18 \leq h \leq 18$, $-25 \leq k \leq 25$, $-26 \leq l \leq 26$	$-18 \leq h \leq 21$, $-13 \leq k \leq 16$, $-43 \leq l \leq 43$	$-17 \leq h \leq 17$, $-17 \leq k \leq 16$, $-24 \leq l \leq 24$	$-21 \leq h \leq 24$, $-18 \leq k \leq 18$, $-50 \leq l \leq 52$	$-19 \leq h \leq 19$, $-25 \leq k \leq 25$, $-28 \leq l \leq 28$
reflections collected	38738	30279	43390	55837	63089
independent reflections	6784	7735	15231	10910	7174
R_{int}	0.1694	0.0592	0.0570	0.0508	0.1010
data/restraints/ parameters	6784 / 0 / 434	7735 / 220 / 634	15231 / 298 / 981	10910/ 0 / 453	7274 / 74 / 481
GOF on F^2	1.023	1.014	1.035	1.020	1.029
final *R* indices [I>2σ (I)]	0.0942 / 0.2287	0.0505 / 0.1173	0.0821 / 0.2274	0.0485 / 0.1222	0.0744 / 0.1787
R indices (all data)	0.1796 / 0.2797	0.1080/ 0.1430	0.1337 / 0.2674	0.0643/ 0.1299	0.1276/ 0.2096
largest diff. peak/hole [e Å^{-3}]	0.546 / -0.524	0.289 / -0.262	0.890/ -1.118	0.440 / -0.419	0.782 / -0.506

Table S2. Crystallographic data and refinement details for compounds **7**−**11**.

Compound	**7**	**8**	**9**	**10**	**11**
formula	$C_{42}H_{63}KMgN_2O_2S$	$C_{42}H_{61}KMgN_2O_4S$	$C_{40}H_{53}KMgN_2OS$	$C_{88}H_{132}K_2Mg_2N_4O_6S_2$	$C_{86}H_{130}K_2Mg_2N_4O_6S_2$
M_r [g mol^{-1}]	723.41	753.39	673.31	1532.91	1506.87
crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
space group	*Pbca*	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	16.0887(19)	16.1294(14)	38.2556(19)	18.0904(10)	17.214(2)
b [Å]	21.608(3)	21.3984(18)	10.5263(6)	13.4627(8)	19.393(2)
c [Å]	23.849(3)	23.591(2)	19.3654(11)	20.4918(12)	27.132(3)
α [°]	90	90	90	90	90
β [°]	90	90	93.559(2)	113.102(2)	107.346(3)
γ [°]	90	90	90	90	90
V [Å^3]	8291.0(18)	8142.4(12)	7783.2(7)	4590.5(5)	8645.4(17)
Z	8	8	8	2	4
ρ_{calc}, [g cm^{-3}]	1.159	1.229	1.149	1.109	1.158
μ [mm^{-1}]	0.229	0.239	0.238	0.212	0.224
F(000)	3136	3248	2896	1660	3264
$\theta_{min}/\theta_{max}$ [°]	2.126 / 25.391	2.442/ 25.026	2.251/25.436	2.448/ 25.445	2.243/25.121
index ranges	$-19 \leq h \leq 19$, $-24 \leq k \leq 26$, $-28 \leq l \leq 28$	$-19 \leq h \leq 18$, $-24 \leq k \leq 25$, $-28 \leq l \leq 28$	$-46 \leq h \leq 42$, $-12 \leq k \leq 12$, $-23 \leq l \leq 23$	$-21 \leq h \leq 21$, $-16 \leq k \leq 16$, $-24 \leq l \leq 24$	$-19 \leq h \leq 20$, $-23 \leq k \leq 23$, $-32 \leq l \leq 32$
reflections collected	65236	74422	65196	56228	48970
independent reflections	7616	7175	7162	8456	15196
R_{int}	0.1669	0.1128	0.0633	0.0799	0.1145
data/restraints/ parameters	7616 / 58 / 491	7175 / 5 / 480	7162 / 190 / 465	8456 / 84 / 544	15196 / 174 / 1022
GOF on F^2	1.022	1.037	1.112	1.016	1.021
final R indices [I>2σ (I)]	0.0849 / 0.2257	0.0967 / 0.2444	0.0897/ 0.2285	0.0547/ 0.1316	0.0816/ 0.1961
R indices (all data)	0.1759 / 0.2818	0.1639 / 0.2875	0.1318 /0.2519	0.0926 / 0.1543	0.2013 / 0.2563
largest diff. peak/hole [e Å^{-3}]	0.612 / -0.698	0.851 / -0.461	0.660 / -0.473	0.812 / -0.466	0.664 / -0.579

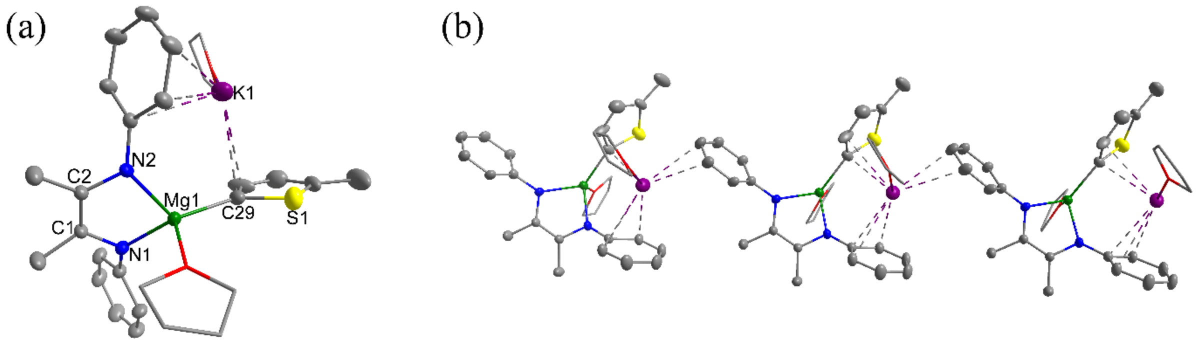


Fig. S27. Crystal structure of complex **3**: (a) the repeating unit [K(thf)LMg(thf)(2-Me-C_4H_2S)] with 30% probability thermal ellipsoids; (b) part of the infinite 1D chain connected by K^+ ions. Hydrogen atoms and isopropyl groups have been omitted for clarity. C1−C2 1.369(3), N1−C1 1.440(3), N2−C2 1.448(4), Mg1−N1 2.041(5), Mg1−N2 2.033(3), Mg1−C29 2.172(4); N1−Mg1−N2 87.23(11), N1−Mg1−C29 127.70(18), N2−Mg1−C29 121.40(18), Mg1−C29−S1 129.5(3), Mg1−C29−C30 122.6(3).

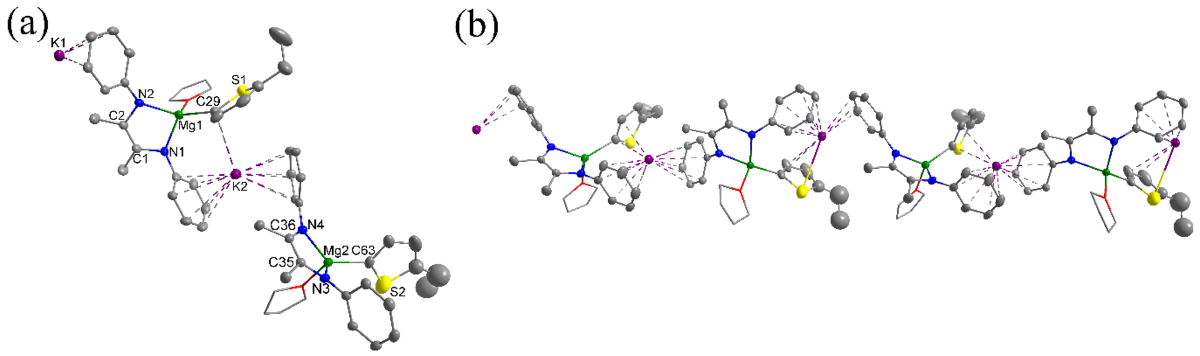


Fig. S28. Crystal structure of complex **4**: (a) the repeating unit [KLMg(thf)(2-Et-C_4H_2S)]$_2$ with 30% probability thermal ellipsoids; (b) part of the infinite 1D chain connected by K^+ ions. Hydrogen atoms and isopropyl groups have been omitted for clarity. C1−C2 1.363(6), N1−C1 1.402(5), N2−C2 1.432(5), Mg1−N1 1.995(3), Mg1−N2 2.031(4), Mg1−C29 2.152(5), C35−C36 1.375(5), N3−C35 1.414(5), N4−C36 1.433(5), Mg2−N3 1.998(3), Mg2−N4 2.028(3), Mg2−C63 2.134(6); N1−Mg1−N2 86.79(13), N1−Mg1−C29 118.44(16), N2−Mg1−C29 129.69(16), Mg1−C29−S1 122.1(3), Mg1−C29−C30 126.0(4), N3−Mg2−N4 85.91(13), N3−Mg2−C63 114.3(3), N4−Mg2−C63 131.0(3), Mg2−C63−S2 118.7(13), Mg2−C63−C64 128.9(14).

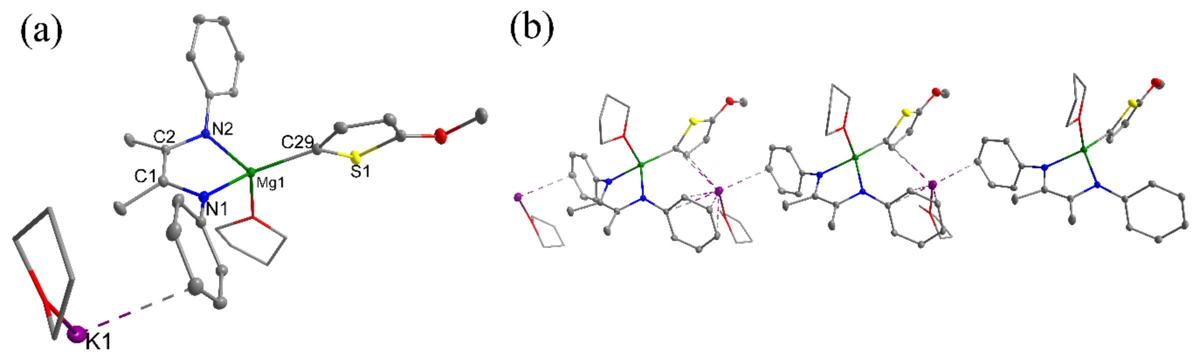


Fig. S29. Crystal structure of complex **5**: (a) the repeating unit [K(thf)LMg(thf)(2-MeO-C_4H_2S)] with 30% probability thermal ellipsoids; (b) part of the infinite 1D chain connected by K^+ ions. Hydrogen atoms and isopropyl groups have been omitted for clarity. C1−C2 1.361(2) , N1−C1 1.4214(19), N2−C2 1.4218(19), Mg1−N1 2.0078(14), Mg1−N2 2.0209(13), Mg1−C29 2.1520(16); N1−Mg1−N2 87.17(5), N1−Mg1−C29 131.08(6), N2−Mg1−C29 121.02(6), Mg1−C29−S1 125.13(9), Mg1−C29−C30 128.61(12).

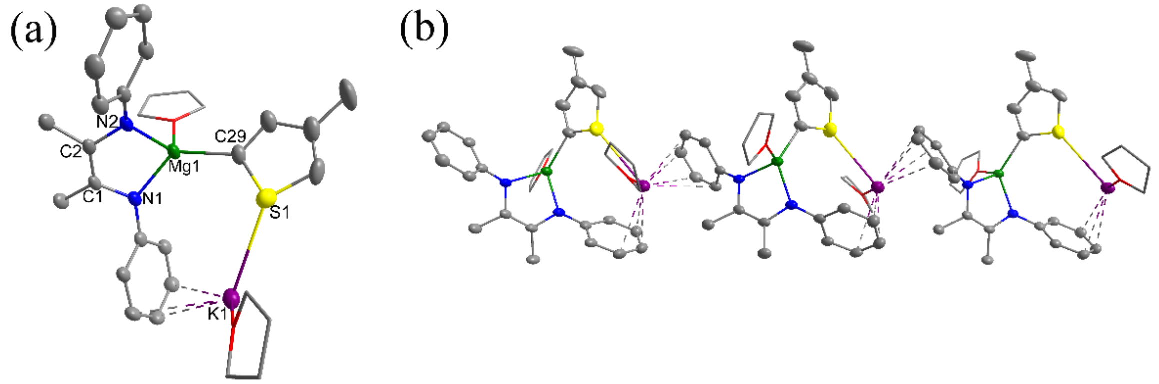


Fig. S30. Crystal structure of complex **6**: (a) the repeating unit [K(thf)LMg(thf)(3-Me-C_4H_2S)] with 30% probability thermal ellipsoids; (b) part of the infinite 1D chain connected by K^+ ions. Hydrogen atoms and isopropyl groups have been omitted for clarity. C1−C2 1.346(5), N1−C1 1.430(5), N2−C2 1.416(5), Mg1−N1 2.011(3), Mg1−N2 2.017(3), Mg1−C29 2.122(4), K1−S1 3.4107(18); N1−Mg1−N2 86.61(13), N1−Mg1−C29 124.98(16), N2−Mg1−C29 127.77(17), Mg1−C29−S1 126.3(2), Mg1−C29−C30 128.3(4).

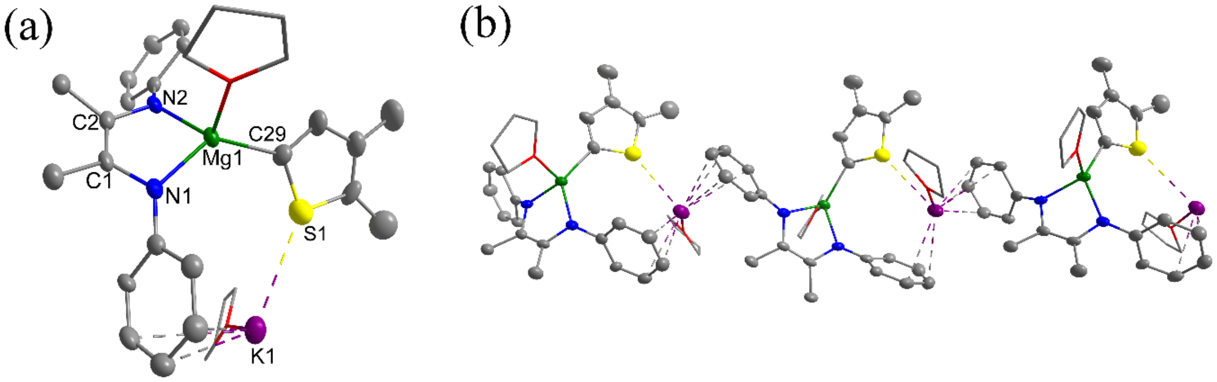


Fig. S31. Crystal structure of complex **7**: (a) the repeating unit [K(thf)LMg(thf)(2,3-Me_2C_4HS)] with 30% probability thermal ellipsoids; (b) part of the infinite 1D chain connected by K^+ ions. Hydrogen atoms and isopropyl groups have been omitted for clarity. C1−C2 1.342(7), N1−C1 1.416(6), N2−C2 1.444(6), Mg1−N1 2.029(4), Mg1−N2 2.012(4), Mg1−C29 2.131(5), K1−S1 3.448(2); N1−Mg1−N2 86.51(16), N1−Mg1−C29 128.3(2), N2−Mg1−C29 125.8(2), Mg1−C29−S1 125.3(3), Mg1−C29−C30 128.1(5).

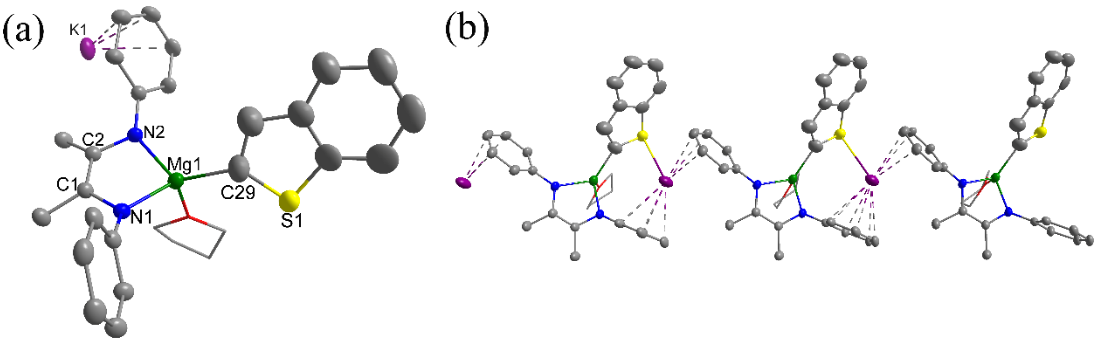


Fig. S32. Crystal structure of complex **9**: (a) the repeating unit [K(thf)LMg(thf)(C_4H_4-C_4HS)] with 30% probability thermal ellipsoids; (b) part of the infinite 1D chain connected by K^+ ions. Hydrogen atoms and isopropyl groups have been omitted for clarity. C1−C2 1.358(6), N1−C1 1.413(5), N2−C2 1.427(5), Mg1−N1 1.984(3), Mg1−N2 2.011(4), Mg1−C29 2.122(8), K1−S1 3.501(2); N1−Mg1−C29 120.9(3), N1−Mg1−N2 87.24(14), N2−Mg1−C29 125.2(3), Mg1−C29−S1 132.3(5), Mg1−C29−C30 120.6(6).

S3. References

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