

## A highly stable metal-organic framework with cubane-like clusters for selective oxidation of aryl alkenes to aldehydes or ketones

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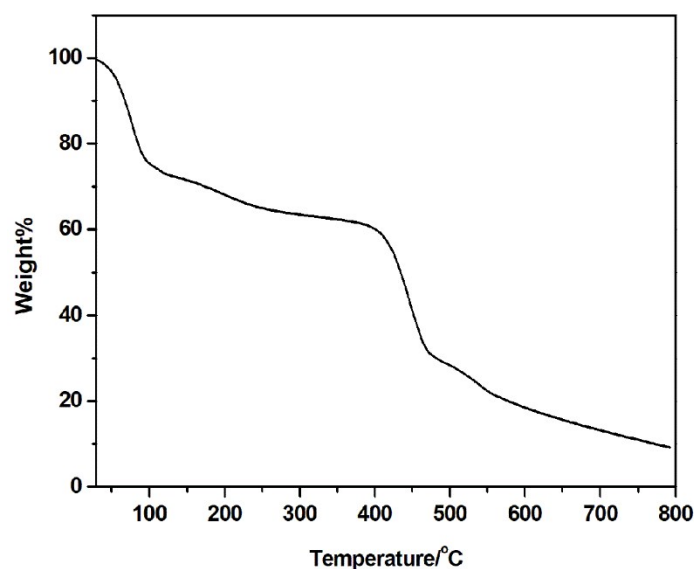


Figure S1. The TGA curve of compound 1.

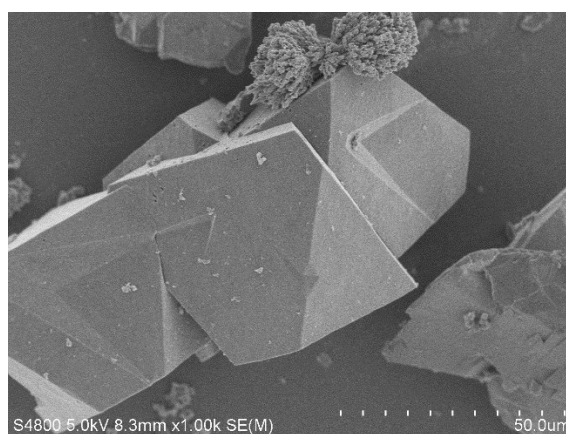


Figure S2. The SEM image of compound 1.

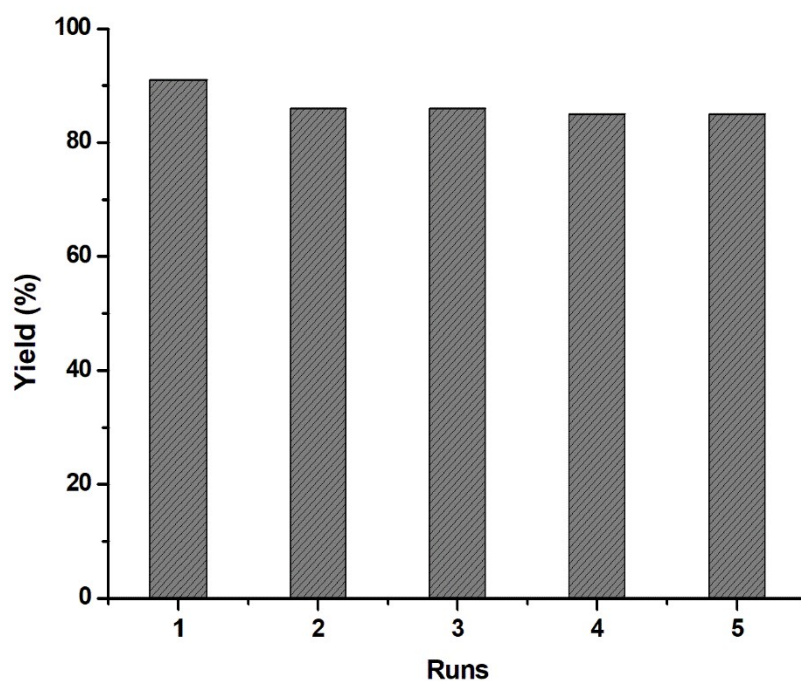


Figure S3. The recycle experiments for styrene oxidation to benzaldehyde by using compound 1 as catalyst.

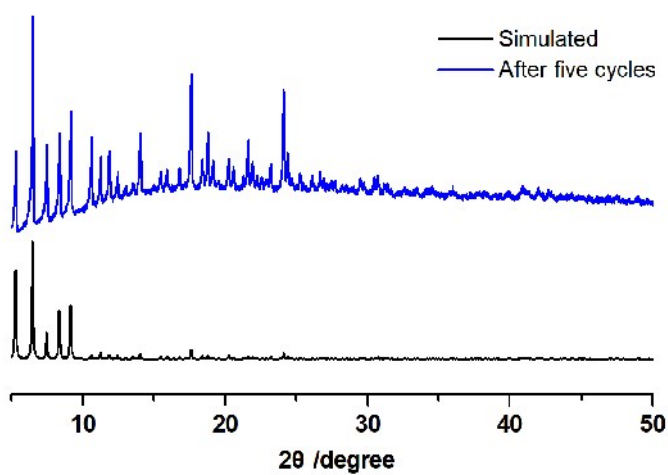


Figure S4. The PXRD patterns of compound 1 after seven cycles.

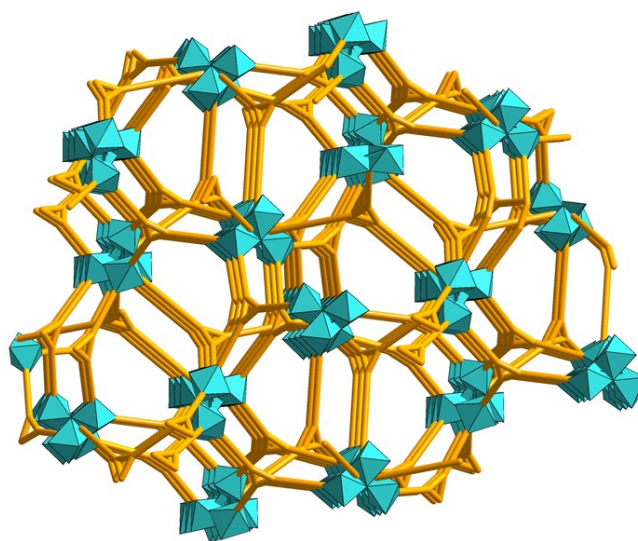
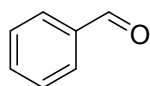
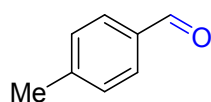


Figure S5. The 3D (3,9)-connected self-interpenetrating framework of compound 1;  $[\text{Co}_4(\text{SO}_4)(\text{F})_3]^{3+}$  cluster can be viewed as a 9-connecting node, while both tpt pairs and  $\text{tatb}^{3-}$  ligands can be viewed as 3-connecting triangles.



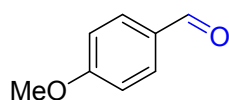
**3a**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.03 (s, 1H, ArCHO), 7.90 (d,  $J$  = 8.0 Hz, 2H, ArH) 7.63-7.67 (m, 1H, ArH), 7.53-7.57 (m, 2H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.5, 136.4, 134.5, 129.8, 129.0.



**3b**

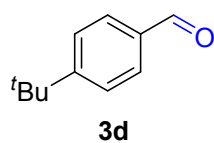
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.96 (s, 1H, ArCHO), 7.78 (d,  $J$  = 8.0 Hz, 2H, ArH) 7.33 (d,  $J$  = 7.6 Hz, 2H, ArH), 2.44 (s, 3H, ArCH<sub>3</sub>);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.1, 145.6, 134.2, 129.9, 129.7, 21.9.



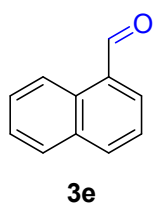
**3c**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.89 (s, 1H, ArCHO), 7.85 (d,  $J$  = 8.8 Hz, 2H, ArH) 7.00 (d,  $J$  = 8.8 Hz, 2H, ArH), 3.89 (s, 3H, ArOCH<sub>3</sub>);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$

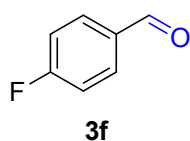
= 190.9, 164.6, 132.0, 129.9, 114.3, 55.6.



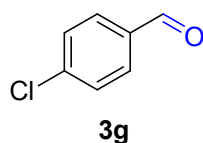
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.99 (s, 1H, ArCHO), 7.83 (d,  $J$  = 8.4 Hz, 2H, ArH) 7.56 (d,  $J$  = 8.4 Hz, 2H, ArH), 1.36 (s, 3H, Ar'tBu);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.2, 158.5, 134.0, 129.7, 126.0, 35.4, 31.1.



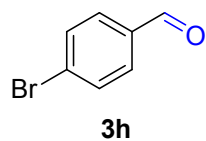
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.36 (s, 1H, ArCHO), 9.24-9.26 (m, 1H, ArH), 8.07 (d,  $J$  = 8.0 Hz, 1H, ArH), 7.96 (d,  $J$  = 7.2 Hz, 1H, ArH), 7.90 (d,  $J$  = 8.4 Hz, 1H, ArH), 7.65-7.70 (m, 1H, ArH), 7.55-7.62 (m, 2H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 193.7, 136.9, 135.4, 133.7, 131.4, 130.5, 129.1, 128.5, 127.0, 124.9.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.98 (s, 1H, ArCHO), 7.90-7.94 (m, 2H, ArH), 7.20-7.25 (m, 2H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 190.6, 167.8, 165.3, 132.9, 132.3, 116.5, 116.3.

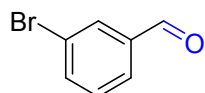


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.99 (s, 1H, ArCHO), 7.84 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.53 (d,  $J$  = 8.4 Hz, 2H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 191.0, 134.6, 130.9, 129.5.



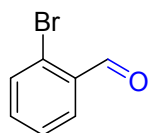
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.98 (s, 1H, ArCHO), 7.75-7.77 (m, 2H, ArH), 7.69-

7.71 (m, 2H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 191.2, 135.0, 132.5, 131.0, 129.8$ .



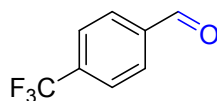
**3i**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.97$  (s, 1H, ArCHO), 8.02 (s, 1H, ArH), 7.82 (d,  $J = 7.6$  Hz, 1H, ArH), 7.75-7.77 (m, 1H, ArH), 7.41-7.45 (m, 1H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 190.9, 137.9, 137.4, 132.4, 130.7, 128.4, 123.4$ .



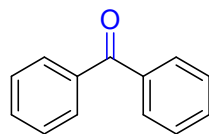
**3j**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 10.38$  (s, 1H, ArCHO), 7.92-7.94 (m, 1H, ArH), 7.65-7.68 (m, 1H, ArH), 7.44-7.47 (m, 2H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 192.0, 135.4, 133.9, 133.4, 129.9, 128.0, 127.2$ .



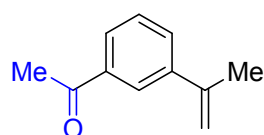
**3k**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 10.11$  (s, 1H, ArCHO), 8.02 (d,  $J = 8.0$  Hz, 2H, ArH), 7.82 (d,  $J = 8.0$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 191.2, 138.6, 136.1$  ( $J = 32.5$  Hz), 129.9, 126.1, 122.1 ( $J = 271.3$  Hz).



**3l**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.81$  (d,  $J = 7.6$  Hz, 4H, ArH), 7.58-7.61 (m, 2H, ArH), 7.47-7.50 (m, 4H, ArH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 196.9, 137.6, 132.5, 130.1, 128.3$ .



**3m**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.05 (s, 1H, ArH), 7.86 (d,  $J$  = 7.6 Hz, 1H, ArH), 7.67 (d,  $J$  = 7.6 Hz, 1H, ArH), 7.43 (t,  $J$  = 7.6 Hz, 1H, ArH), 5.44 (s, 1H,  $\text{CH}_2$ ), 5.17 (s, 1H,  $\text{CH}_2$ ), 2.63 (s, 3H,  $\text{CH}_3$ ), 2.19 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.4, 142.5, 141.7, 137.1, 130.2, 128.5, 127.4, 125.2, 113.7, 26.8, 21.8.

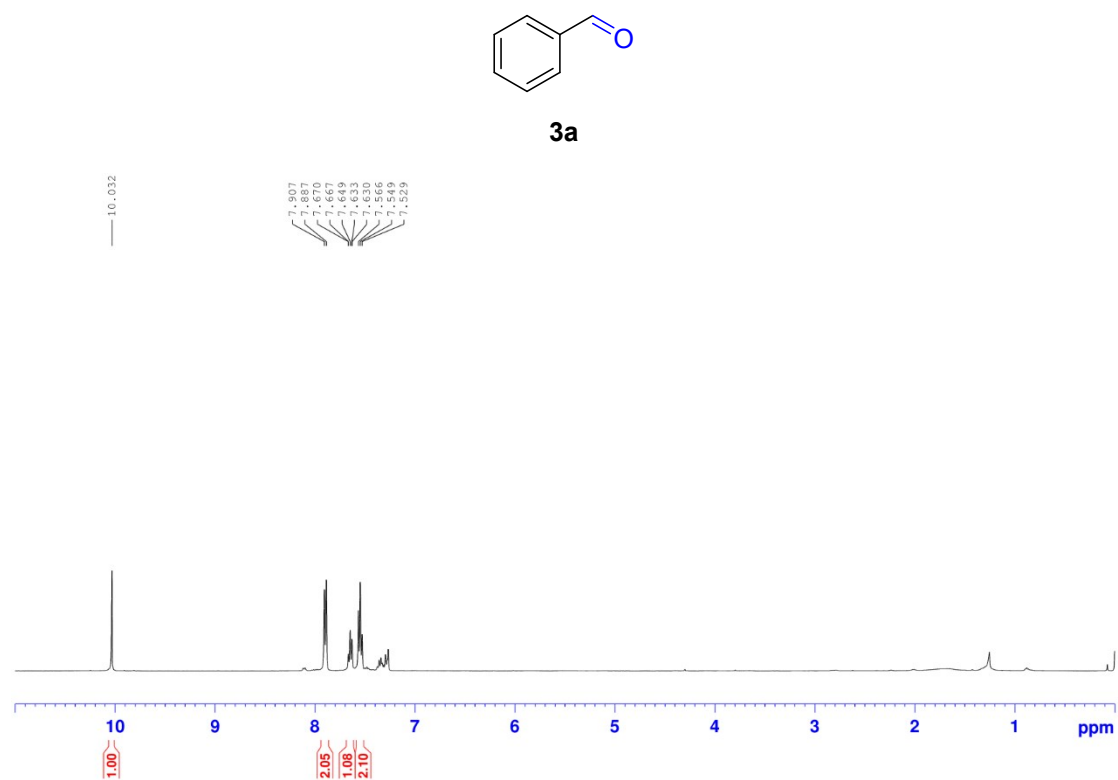


Figure S6.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3a**

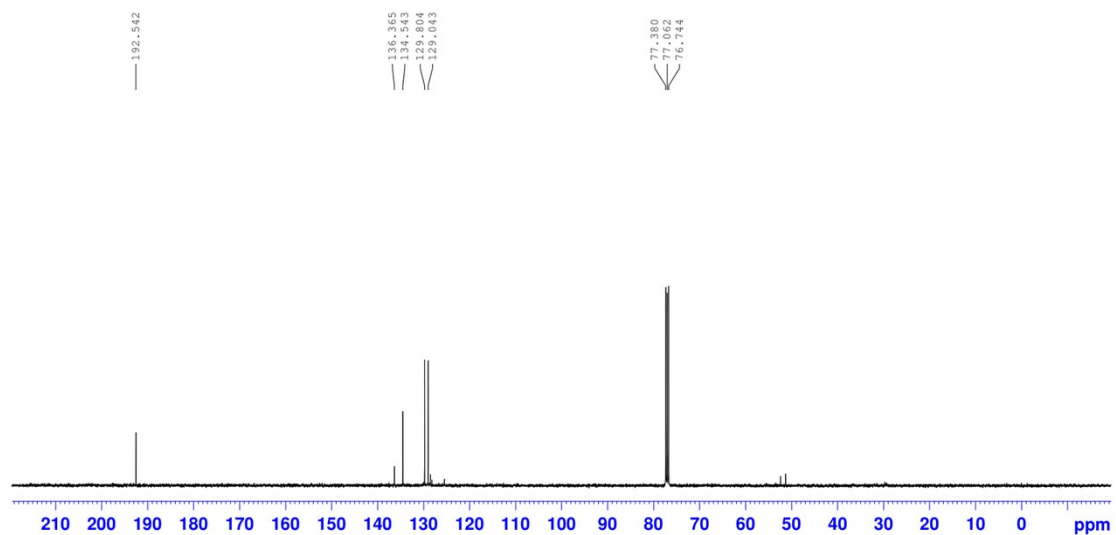


Figure S7. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of compound **3a**

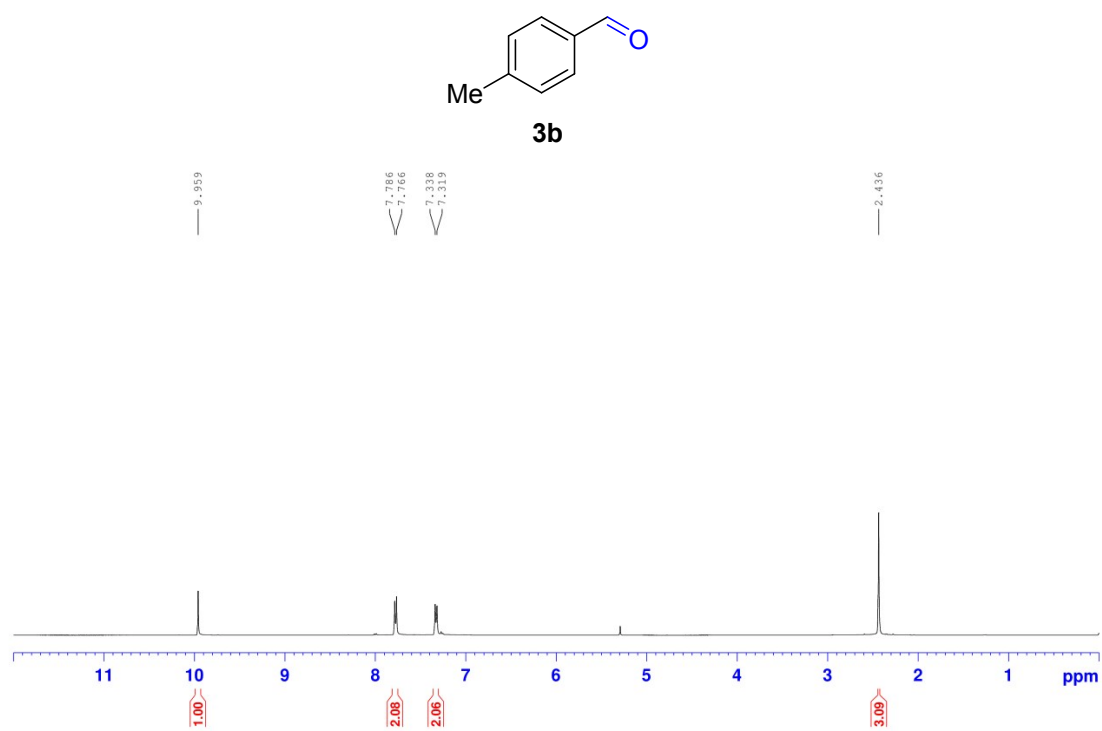


Figure S8. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3b**

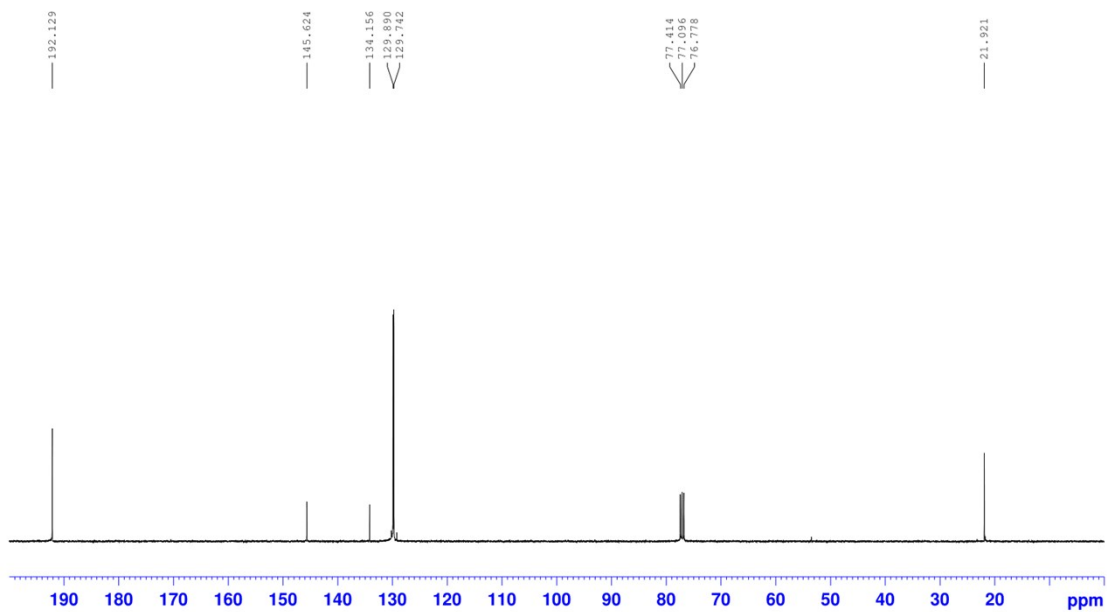


Figure S9.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3b**

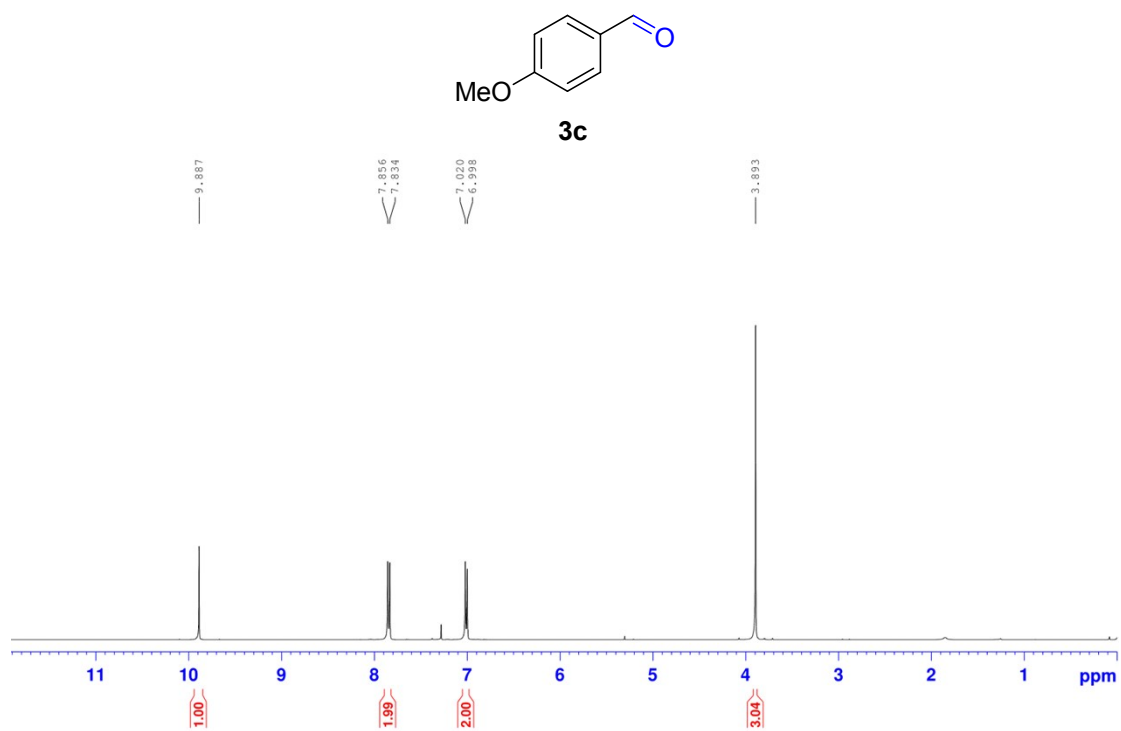




Figure S10.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3c**

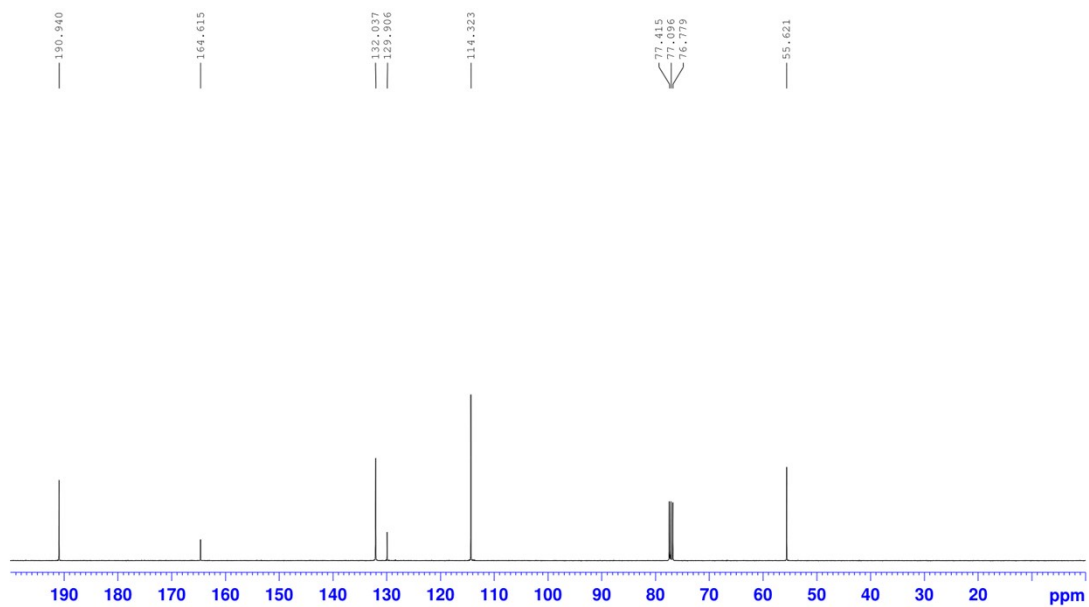


Figure S11.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3c**

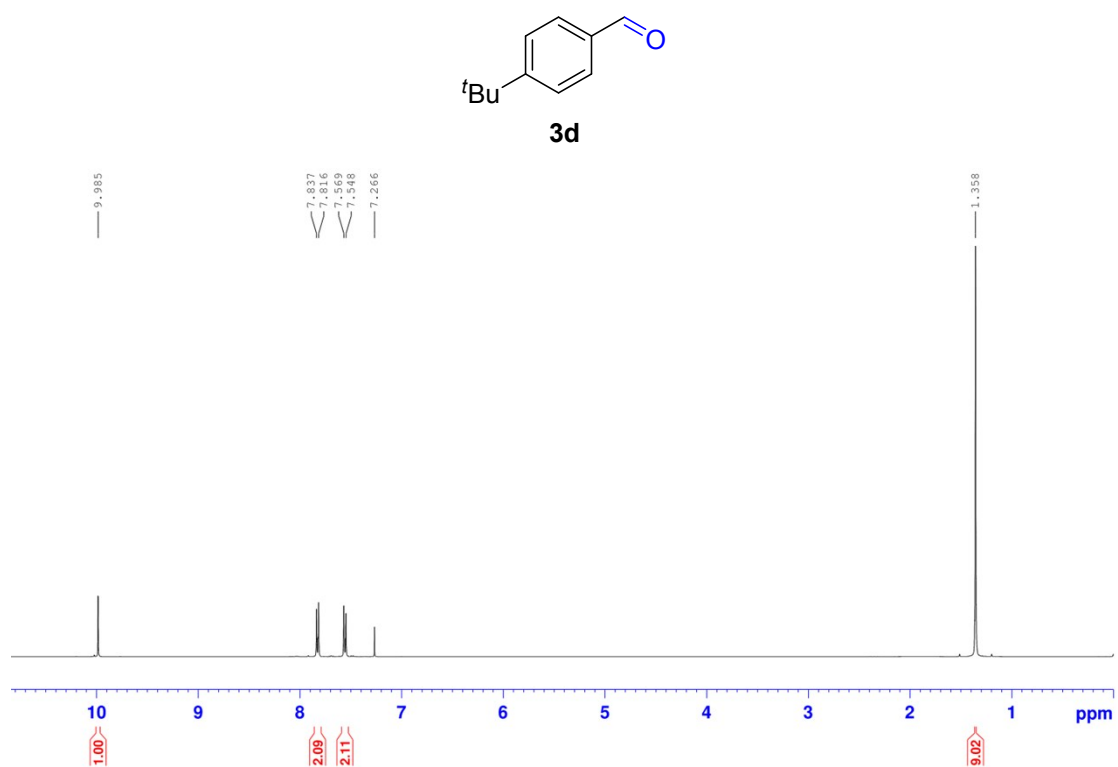


Figure S12.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3d**

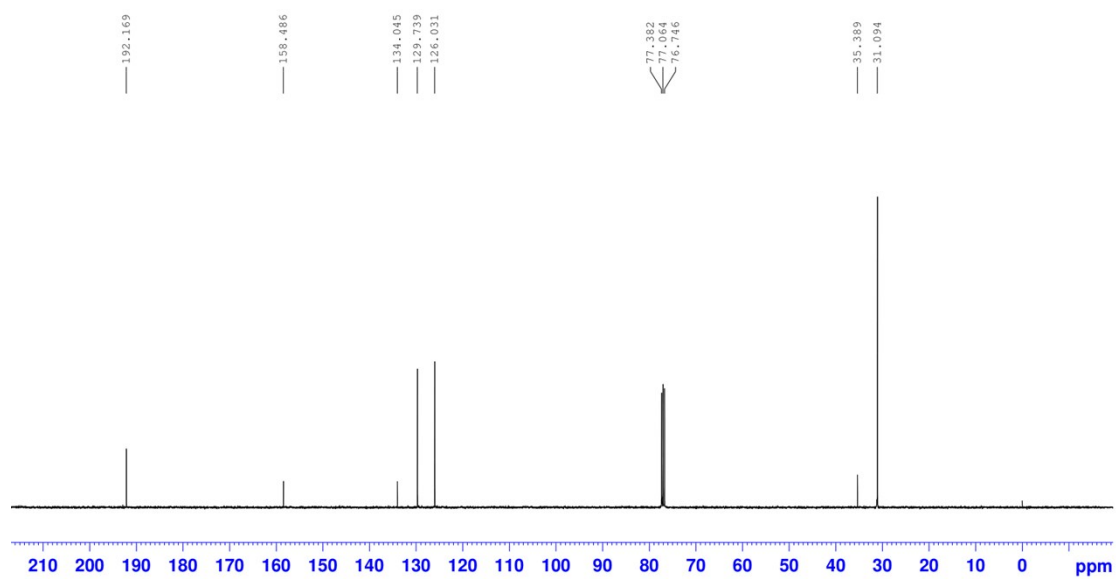


Figure S13.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3d**

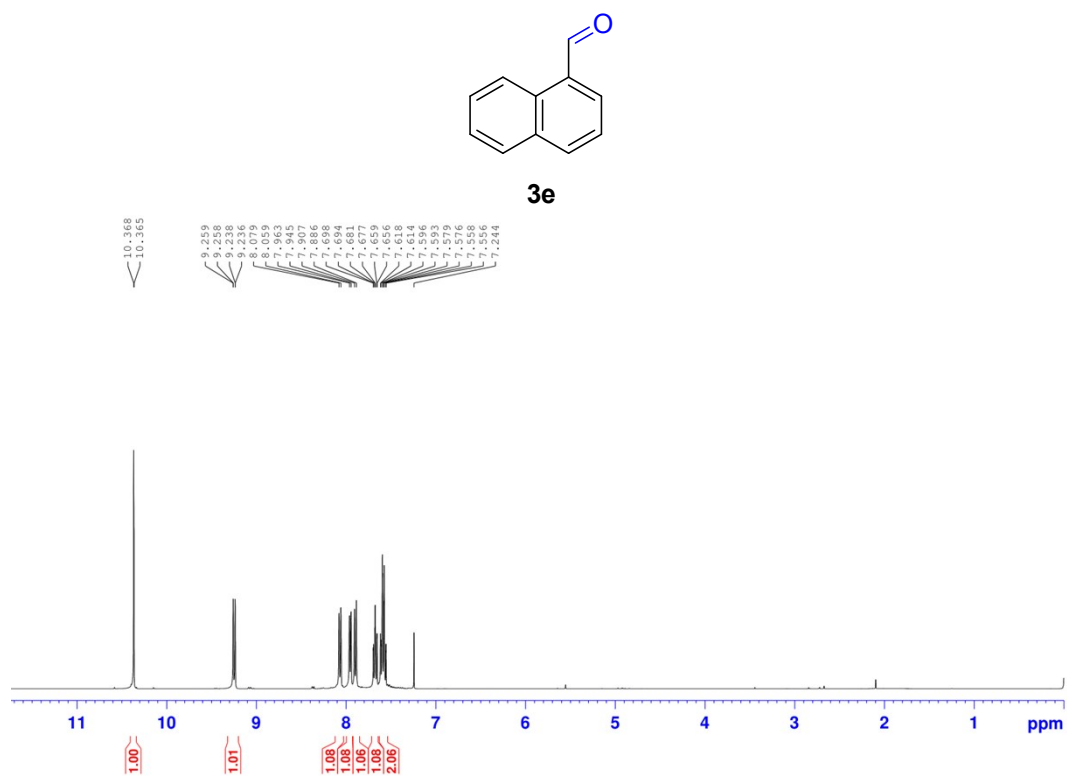


Figure S14.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3e**

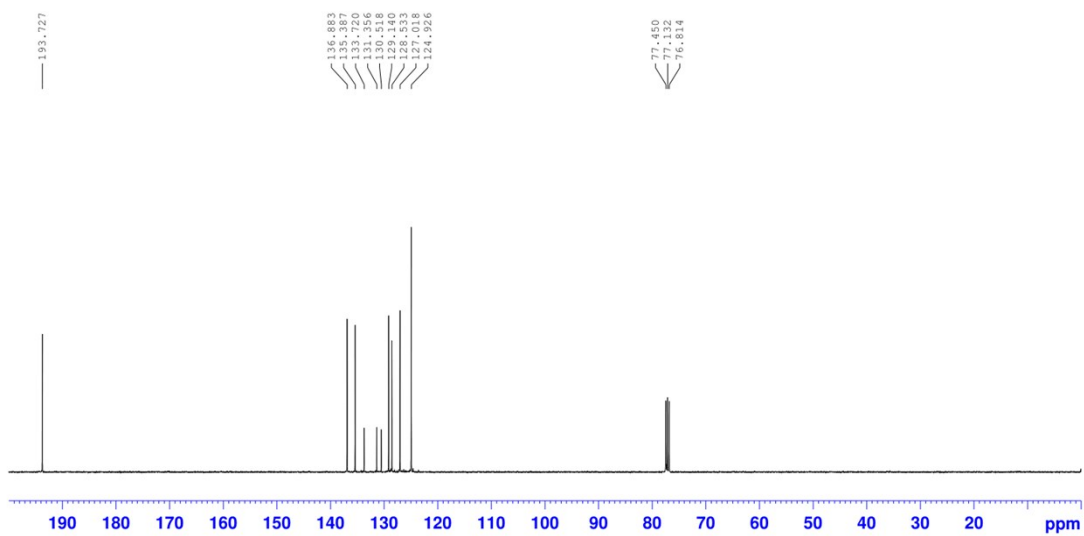


Figure S15. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of compound **3e**

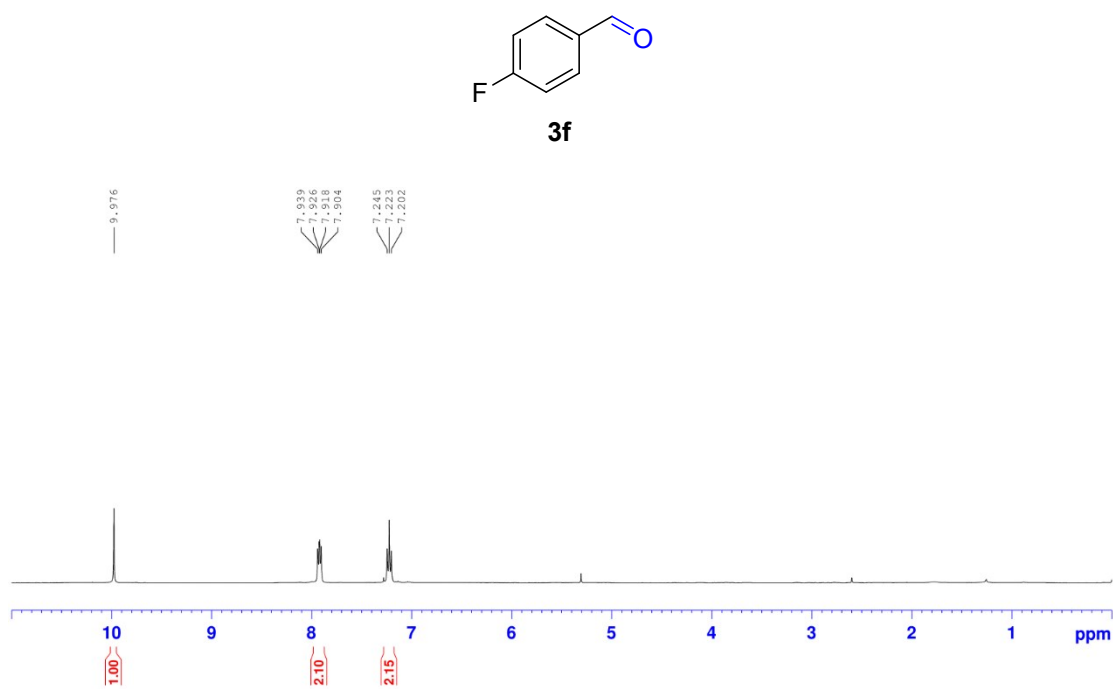


Figure S16. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of compound **3f**

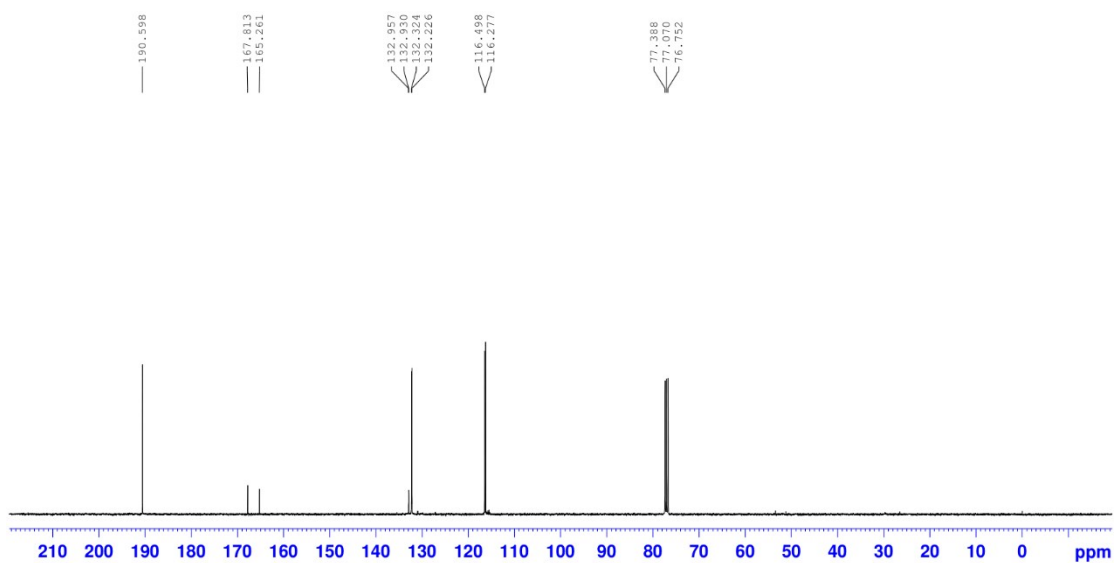


Figure S17.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3f**

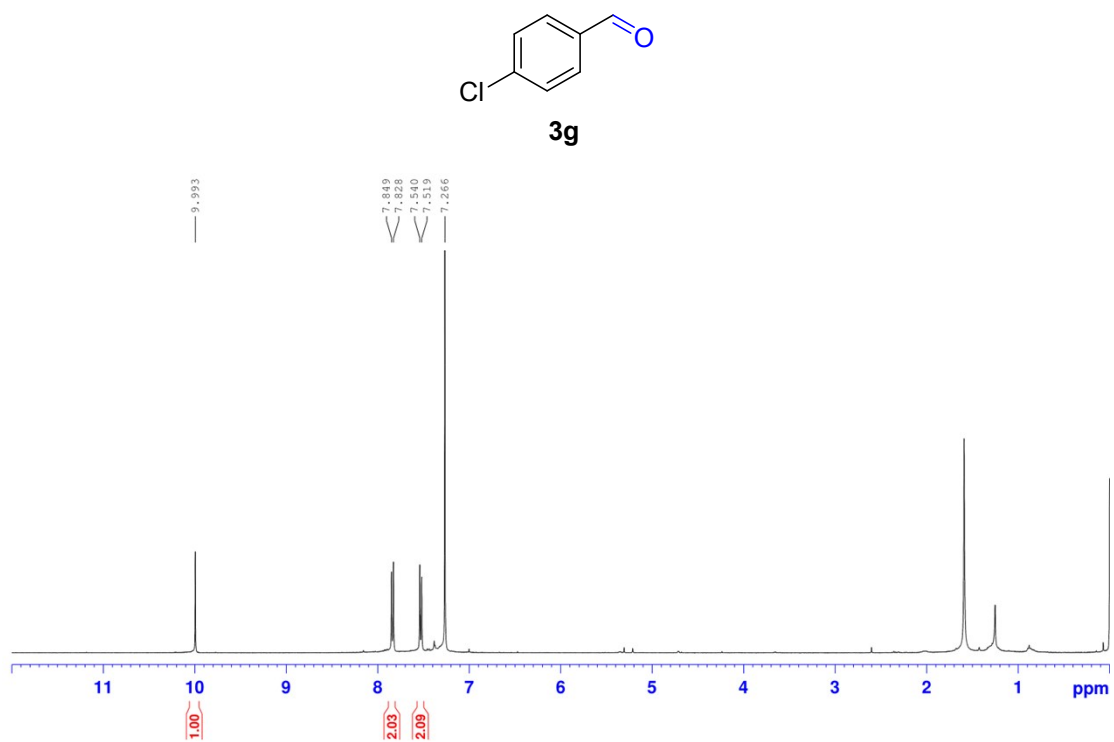


Figure S18.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3g**

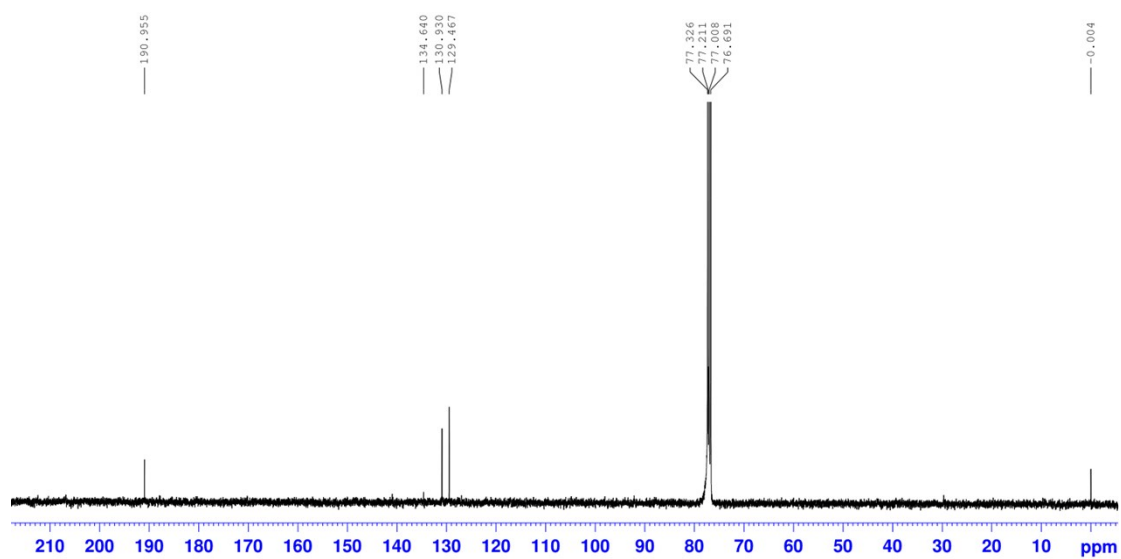


Figure S19.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3g**

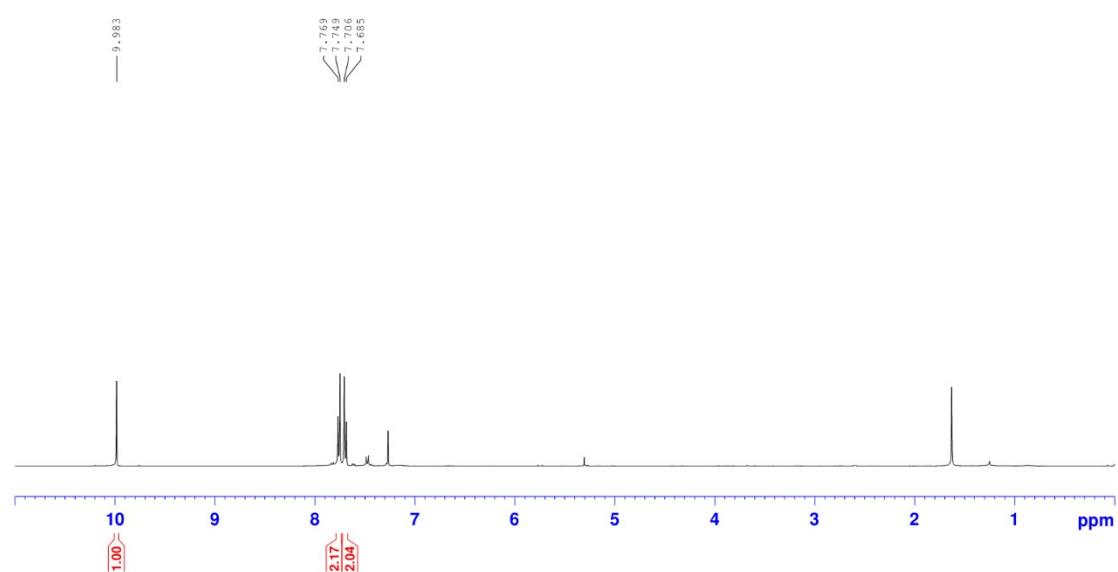
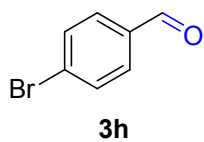


Figure S20.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3h**

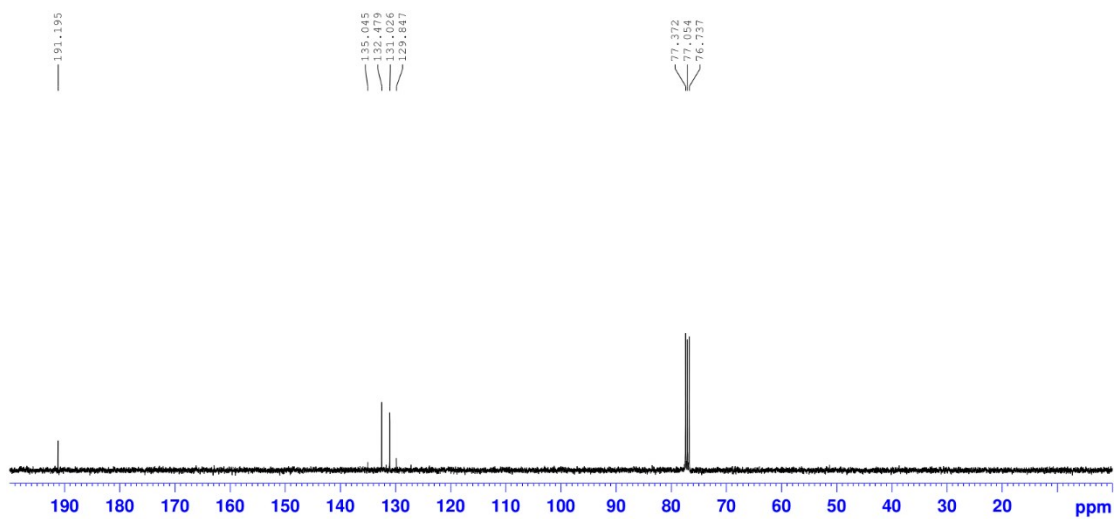


Figure S21.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3h**

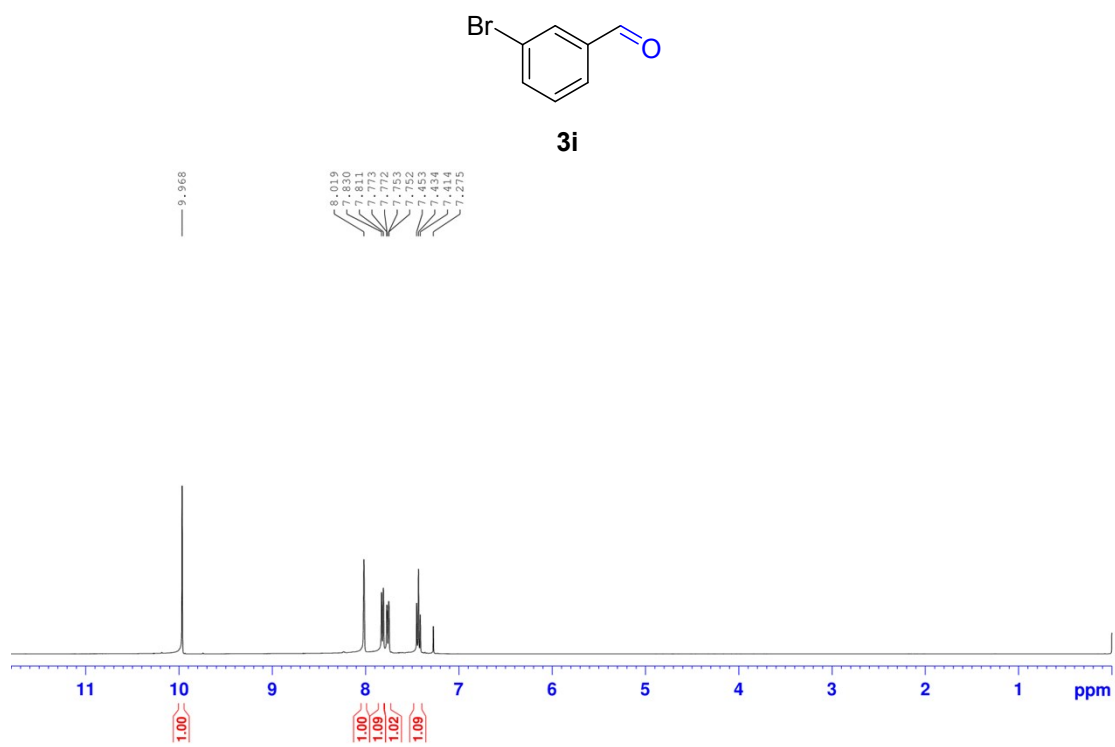


Figure S22.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3i**

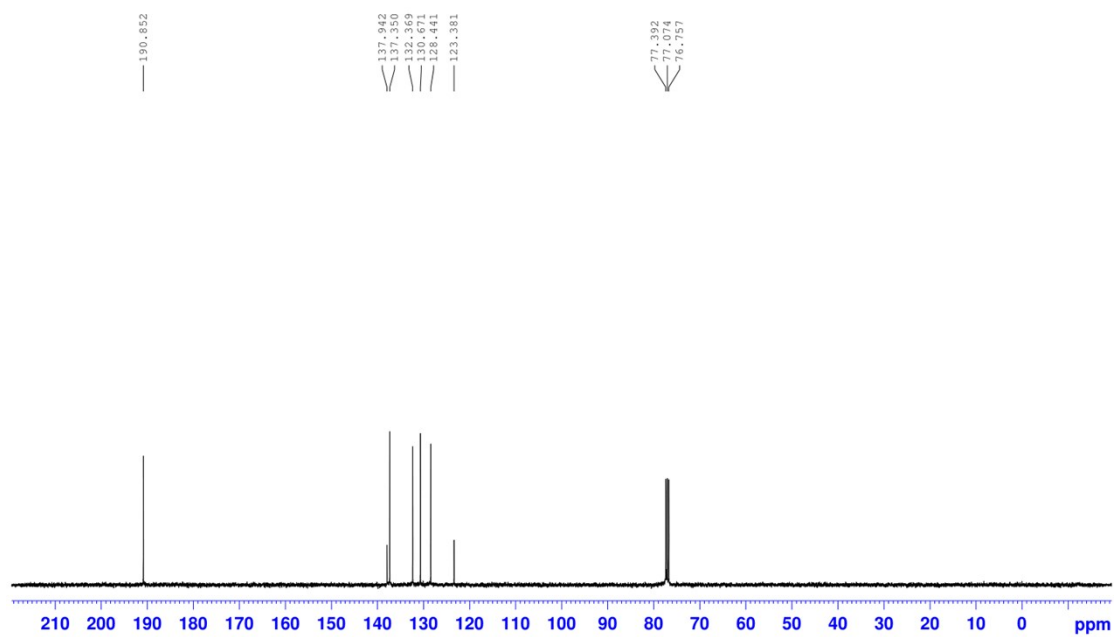


Figure 23.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3i**

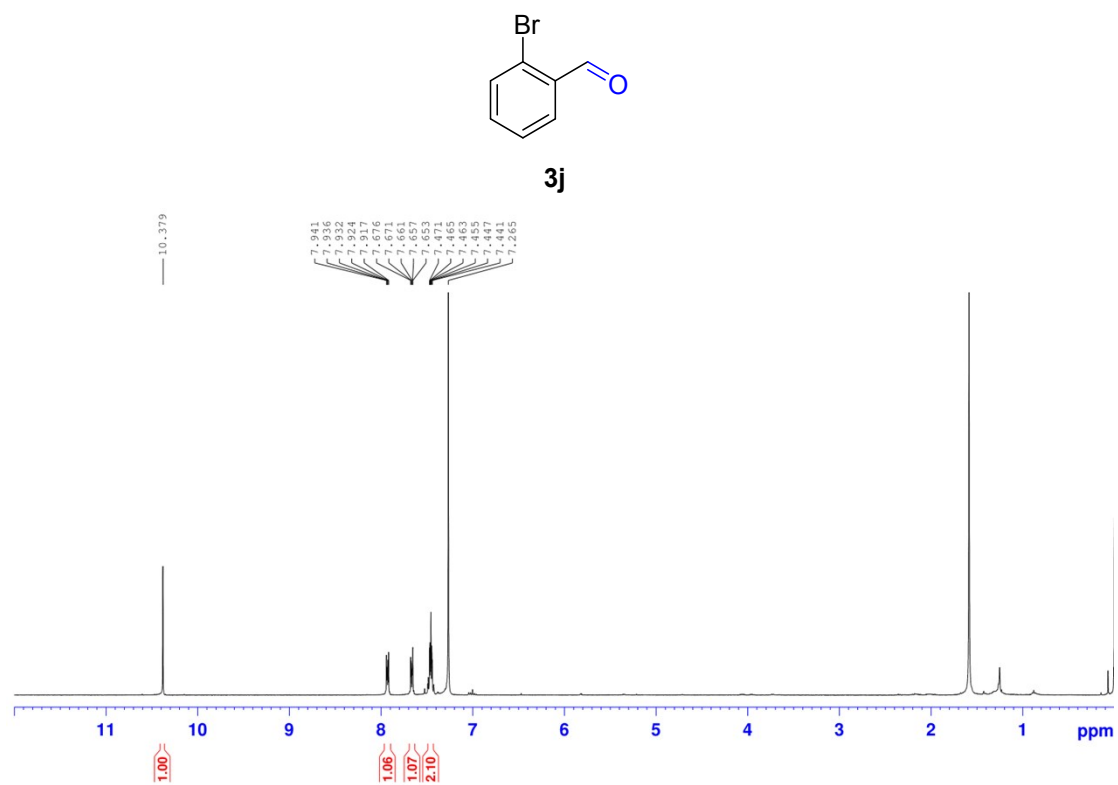


Figure S24.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3j**

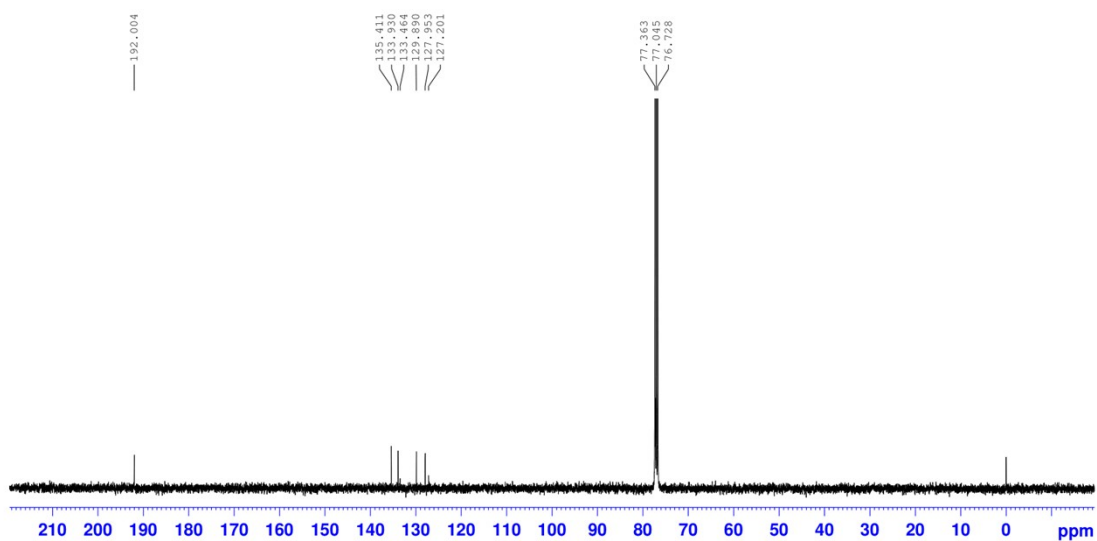


Figure 25.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3j**

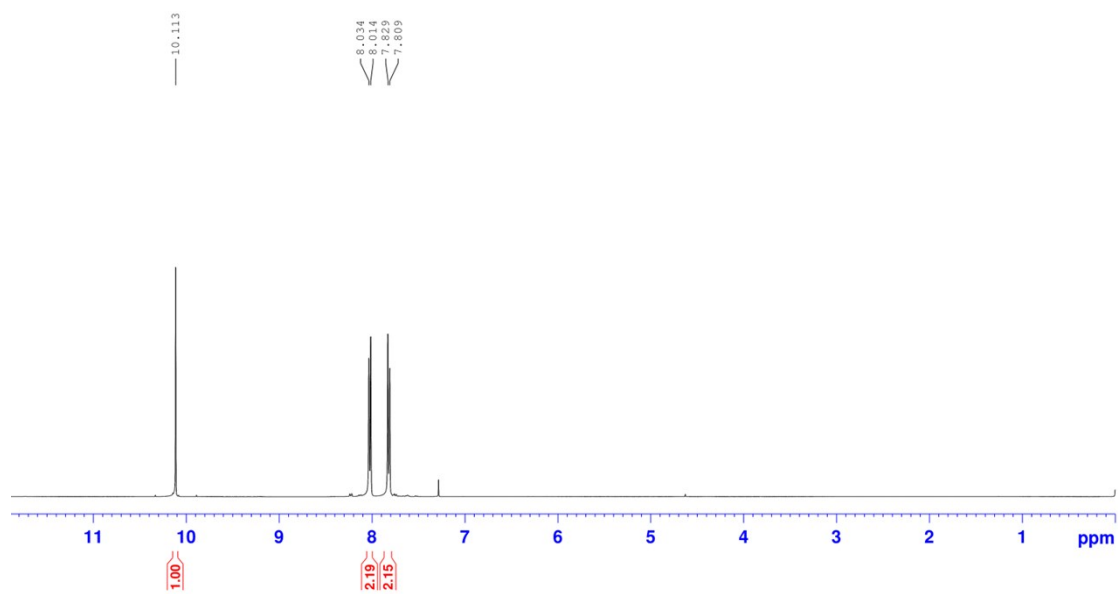
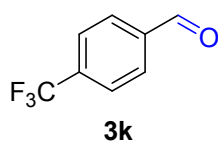


Figure S26.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3k**



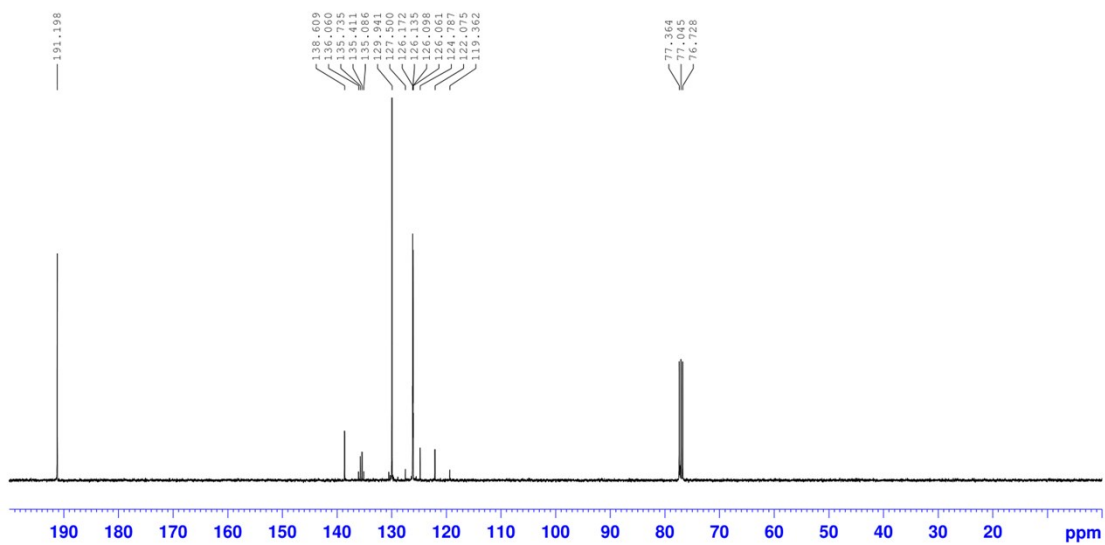


Figure S27.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **3k**

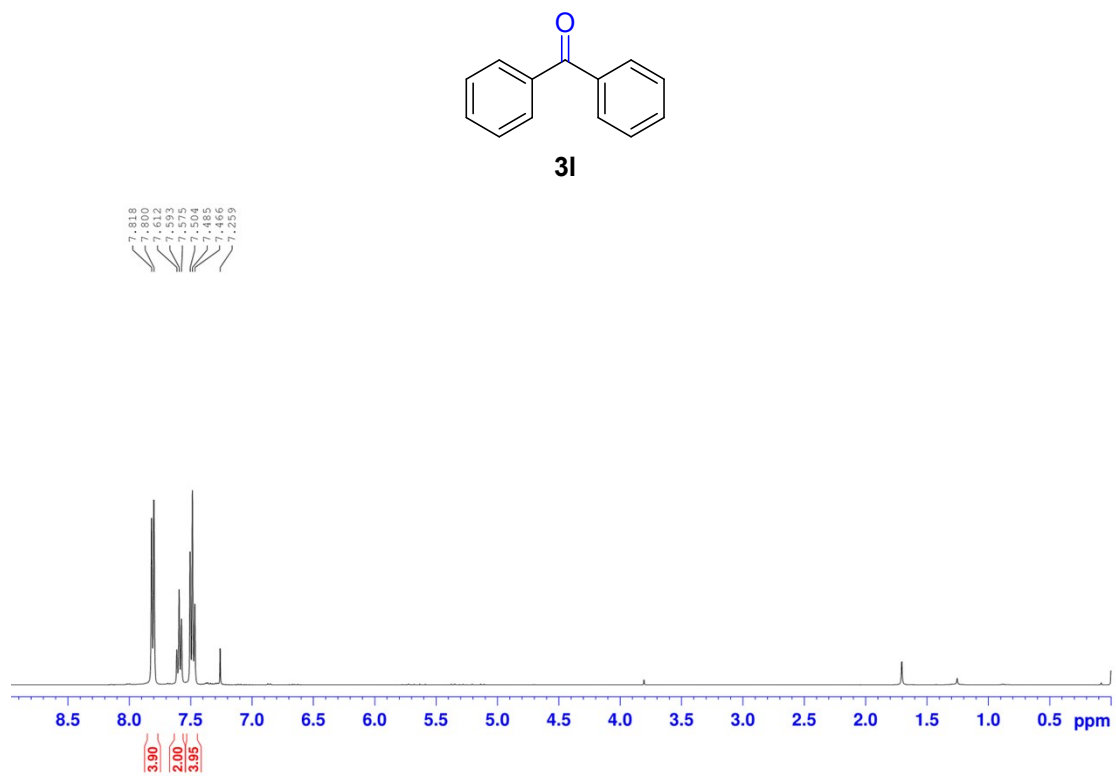


Figure S28.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3l**

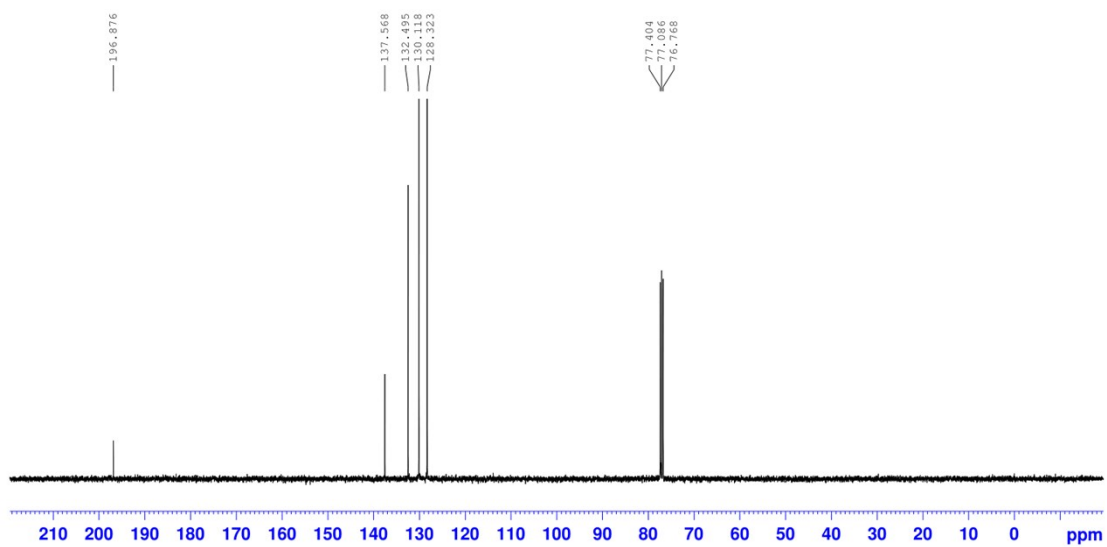


Figure S29.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of compound **31**

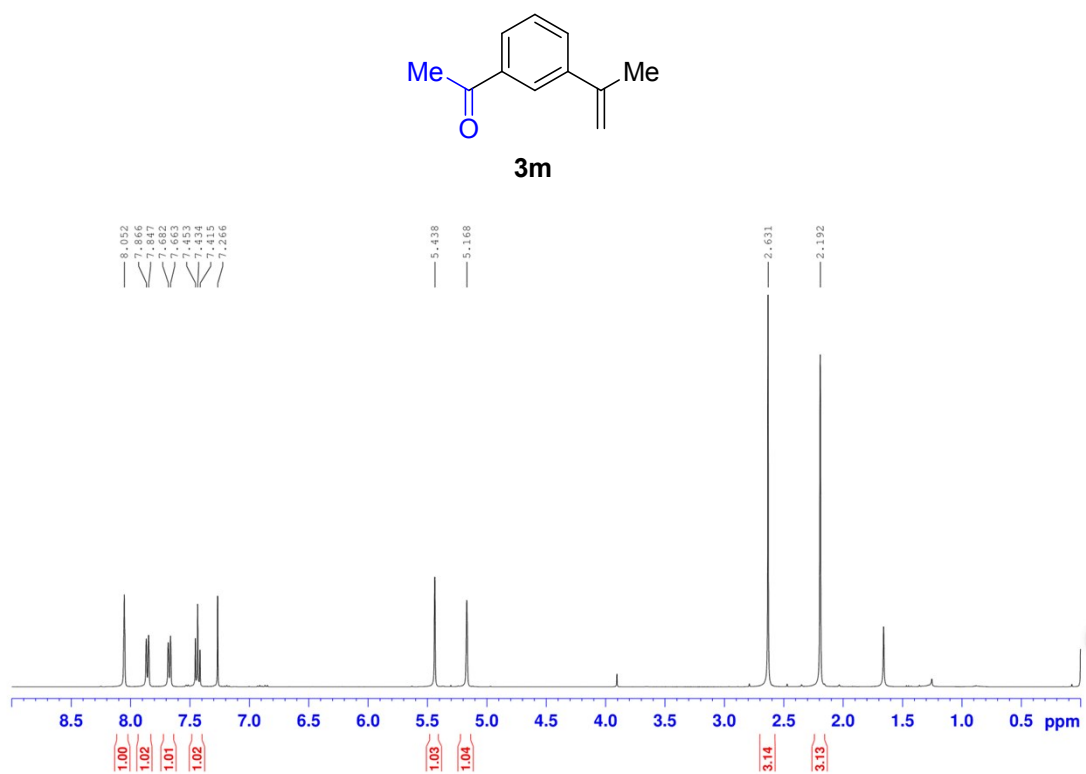


Figure S30.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3m**

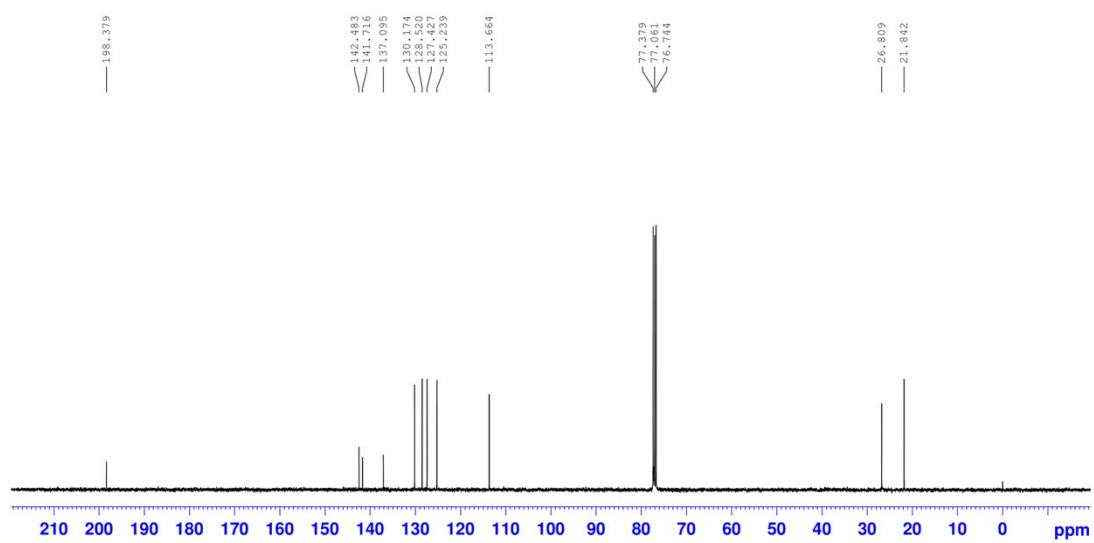


Figure S31.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of compound **3m**