

Supporting Information

An efficient combination of Zr-MOF and microwave irradiation in catalytic Lewis acid Friedel-Crafts benzoylation

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Section S1: Materials

Methyl 4-iodobenzoate (purity > 97%), 1,4-diethynylbenzene (purity > 96%), bis(triphenylphosphine)palladium dichloride (purity \geq 99%), copper(I) iodide (purity \geq 99.5%), potassium hydroxide (purity > 90%), ammonium chloride (NH₄Cl, purity > 99.5%), sodium chloride (NaCl, purity > 99%), triethylamine (TEA, purity > 99.5%), toluene (purity > 99.8%), methanol (MeOH, purity > 99.8%), acetic acid (purity \geq 99.7%), chloroform (purity > 99.5%), 1,4-benzenedicarboxylic acid (H₂BDC, purity > 98%), mesitylene (purity \geq 99%), naphthalene (purity > 99%), anisole (purity > 99%), 1,2-dimethoxybenzene (purity > 99%), 1,3-dimethoxybenzene (purity \geq 98%), 1,4-dimethoxybenzene (purity > 99%), 1,2,4-trimethoxybenzene (purity > 97%), ethoxybenzene (purity > 99%), 4-fluoroanisole (purity > 99%), thioanisole (purity > 99%), ethylbenzene (purity > 99.8%), *m*-xylene (purity \geq 99%), anthracene (purity > 97%), fluorene (purity > 98%) and *N,N*-dimethylformamide (DMF, purity \geq 99.5%) were obtained from the Sigma-Aldrich Chemical Company. Zirconyl chloride octahydrate (ZrOCl₂·8H₂O, purity \geq 98%), 1,4-biphenyldicarboxylic acid (H₂BPDC, purity > 98%), tetrahydrofuran (THF, purity > 99.5%) were obtained from Acros Organics. Benzoyl chloride (purity > 98%) was obtained from Merck. All chemicals were used without further purification.

Section S2: UiO-66, and UiO-67

Synthesis of Zr-MOFs was modified from reported literature.² An equimolar solution (8.5 mM) of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and the dicarboxylic acid (H_2BDC or H_2BPDC) in 40 mL solvent mixture of DMF and acetic acid (v/v = 39:1) in 100-mL capped bottle was heated in an oven at 120 °C for 24 h under static conditions. After cooling the bottle to room temperature, the precipitates were collected by centrifugation. The products were washed with DMF for 3 days and dispersed in a large amount of chloroform for 3 days. Finally, the materials were dried under reduced pressure at 120 °C for 24 h.

Section 3: Characterization of UiO-66, UiO-67, and VNU-1

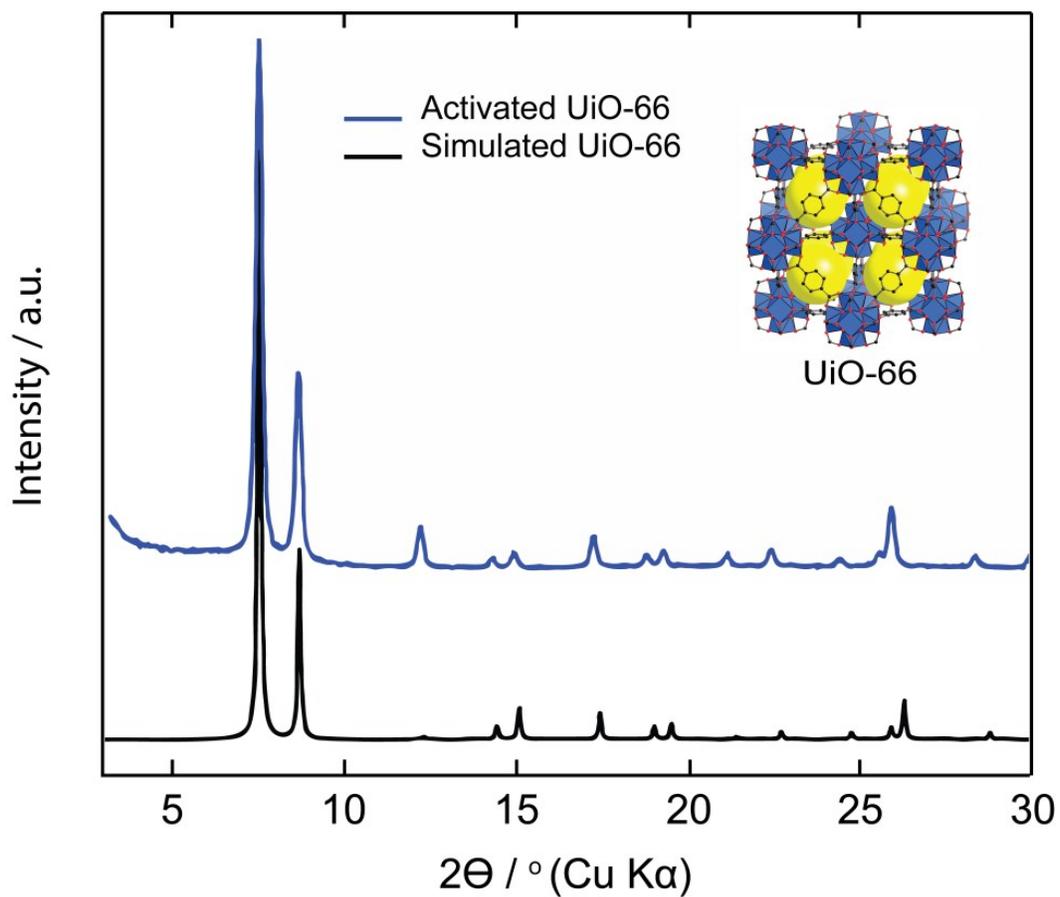


Figure S1. PXRD patterns of UiO-66: simulated (black) and experimental (blue). Inset: structure of UiO-66 (Zr, blue polyhedra; O, red; C, black; H atoms are omitted for clarity. The yellow colored balls represent the free pore).

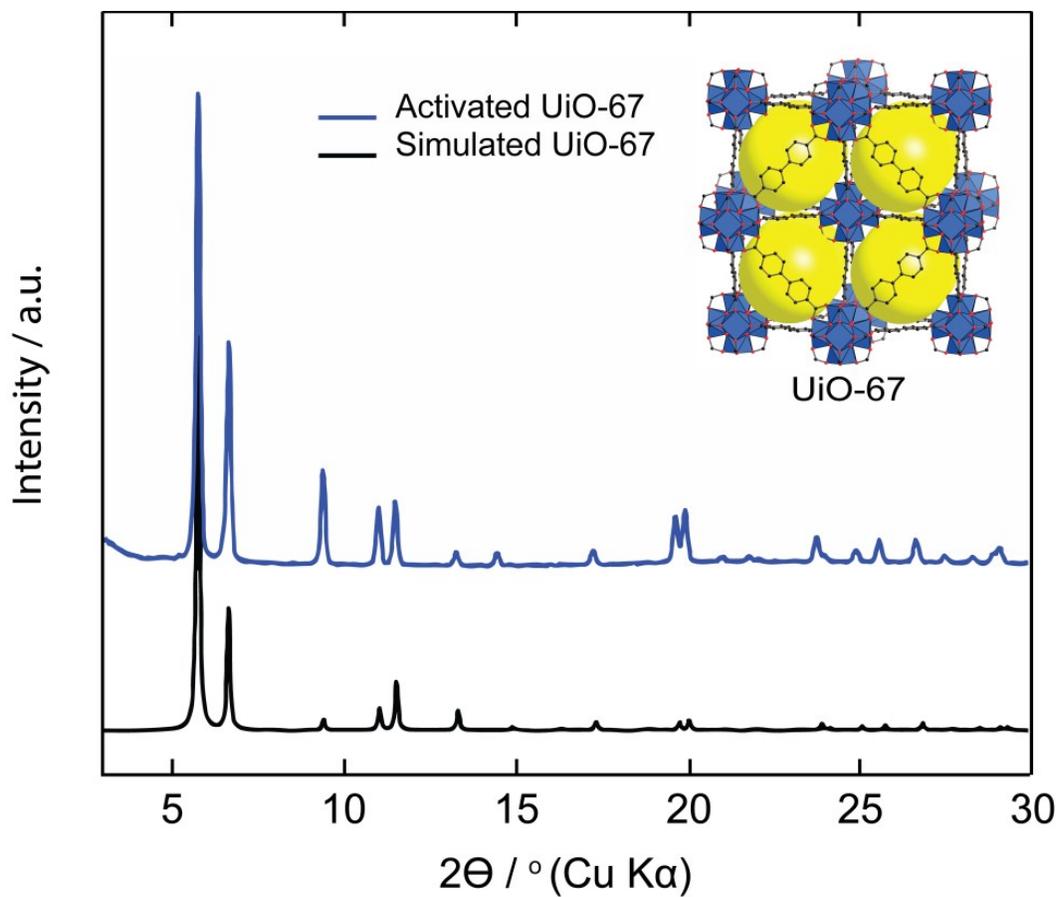


Figure S2. PXRD patterns of UiO-67: simulated (black) and experimental (blue). Inset: structure of UiO-67 (Zr, blue polyhedra; O, red; C, black; H atoms are omitted for clarity. The yellow colored balls represent the free pore).

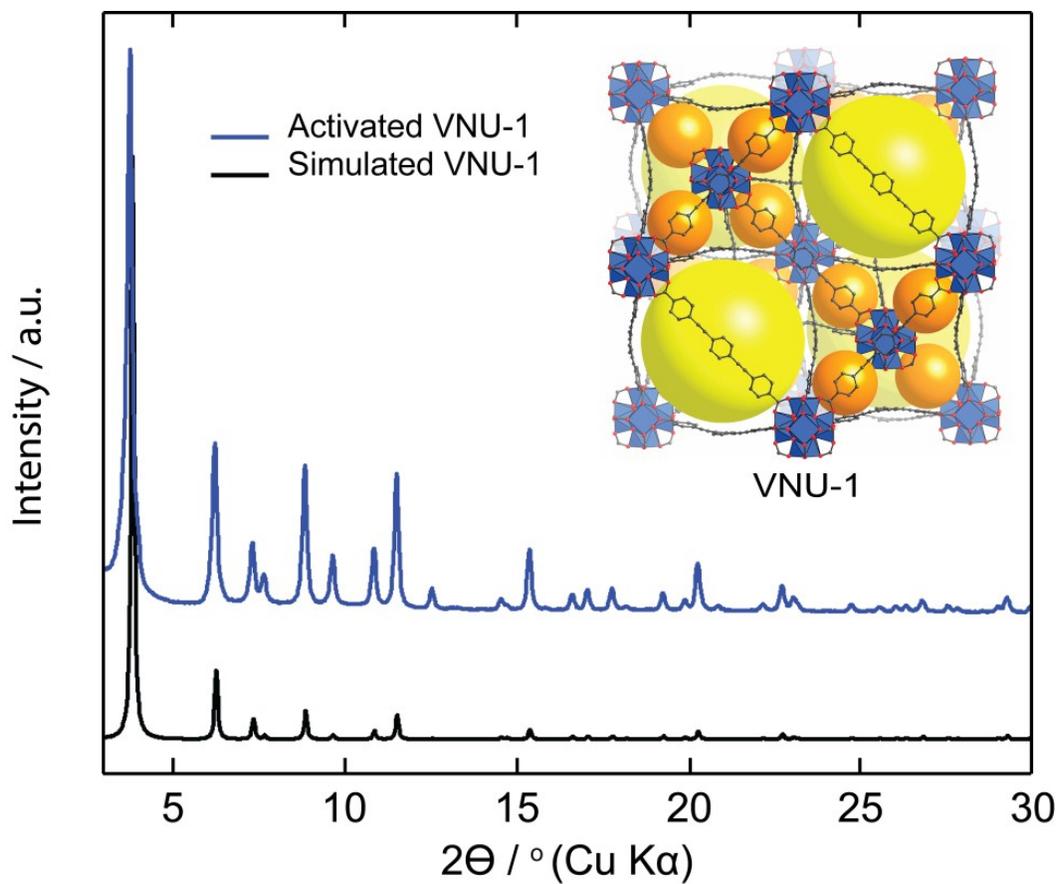


Figure S3. PXRD patterns of VNU-1: simulated (black) and experimental (blue). Inset: structure of VNU-1 (Zr, blue polyhedra; O, red; C, black; H atoms are omitted for clarity. The yellow and orange colored balls represent the free pore).

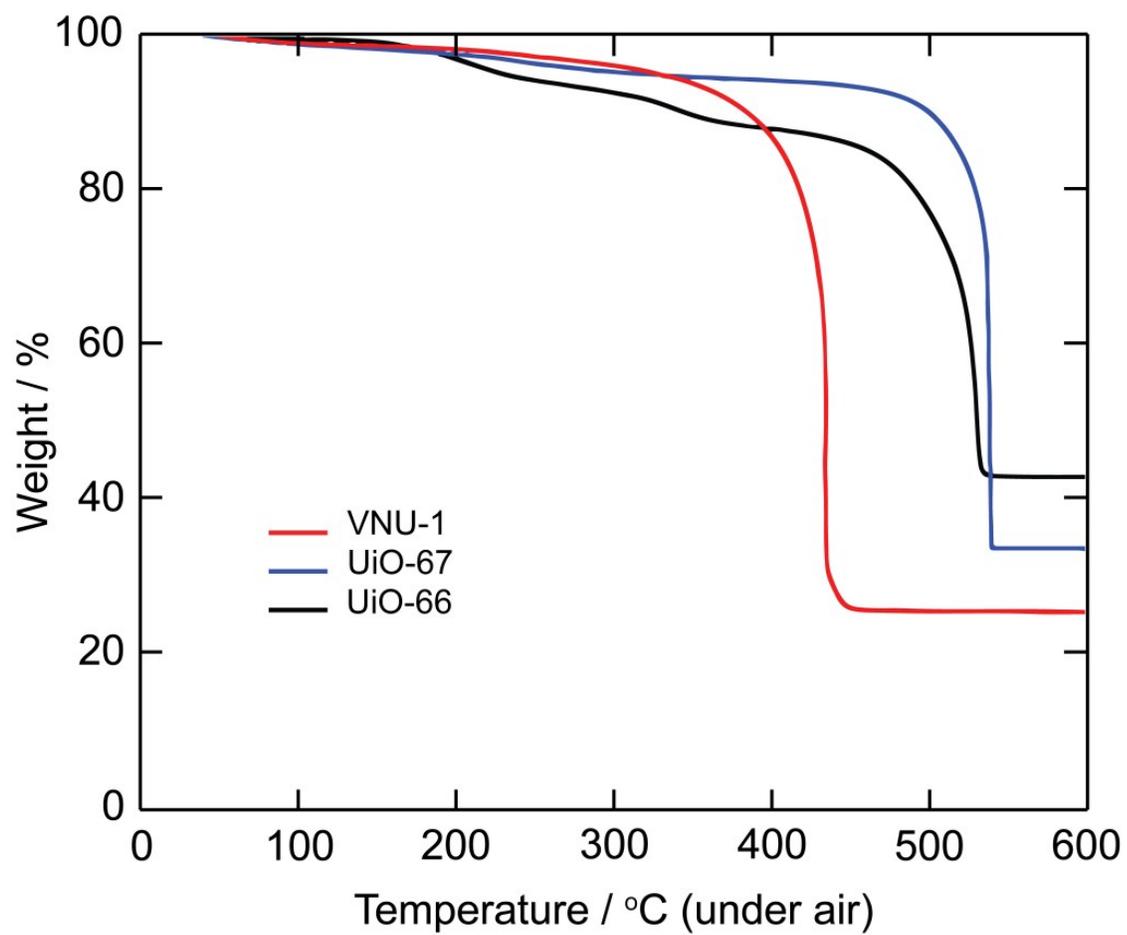


Figure S4. TGA curves of UiO-66 (black), UiO-67 (blue), and VNU-1 (red).

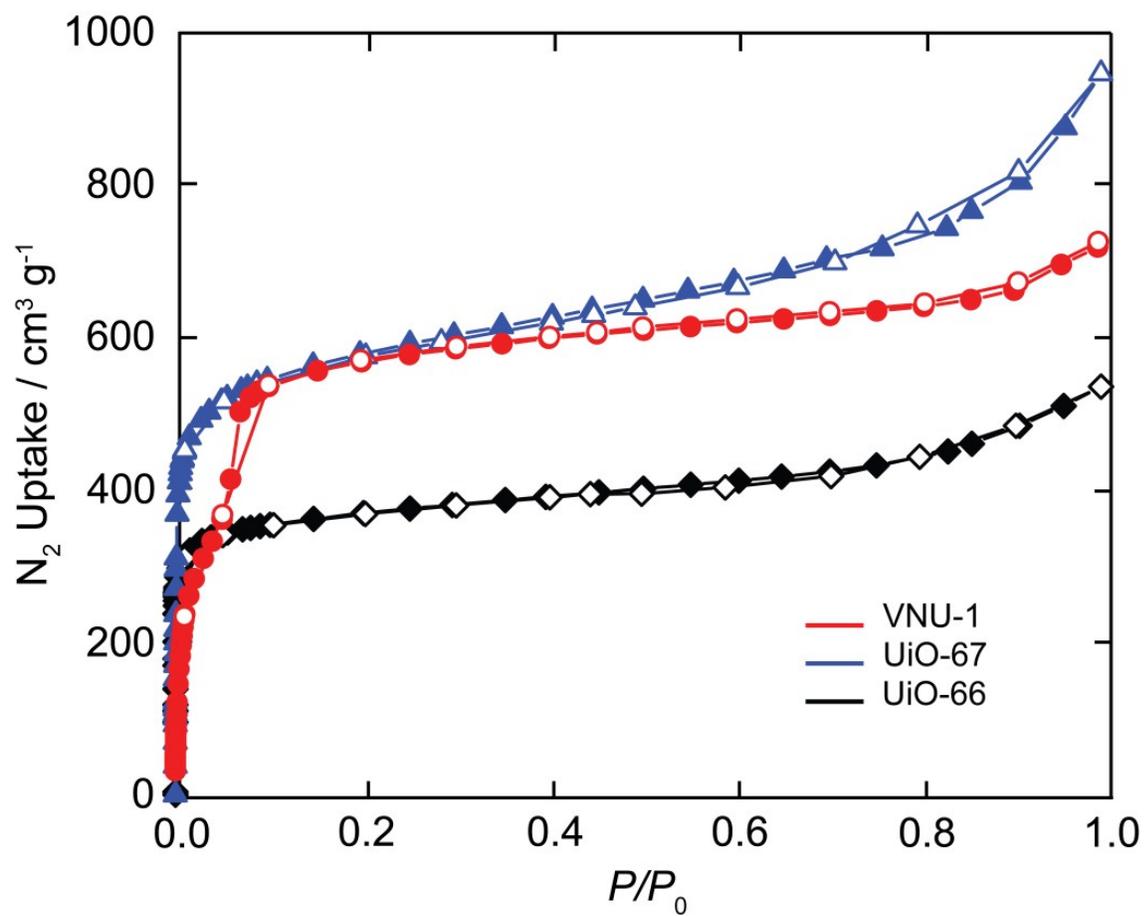


Figure S5. Nitrogen isotherms at 77 K of UiO-66 (black), UiO-67 (blue), and VNU-1 (red) (Closed circles, adsorption; opened circles, desorption).

Digested ¹H-NMR spectrum of VNU-1

An activated sample of VNU-1 (5 mg) was digested by 20 μL of HF (48%) and 580 μL of DMSO-*d*₆. The sample was then sonicated to completely dissolve VNU-1. The signals of CPEB linker were identified in the spectrum. In addition, no signal of acetic acid as modulator was presented.

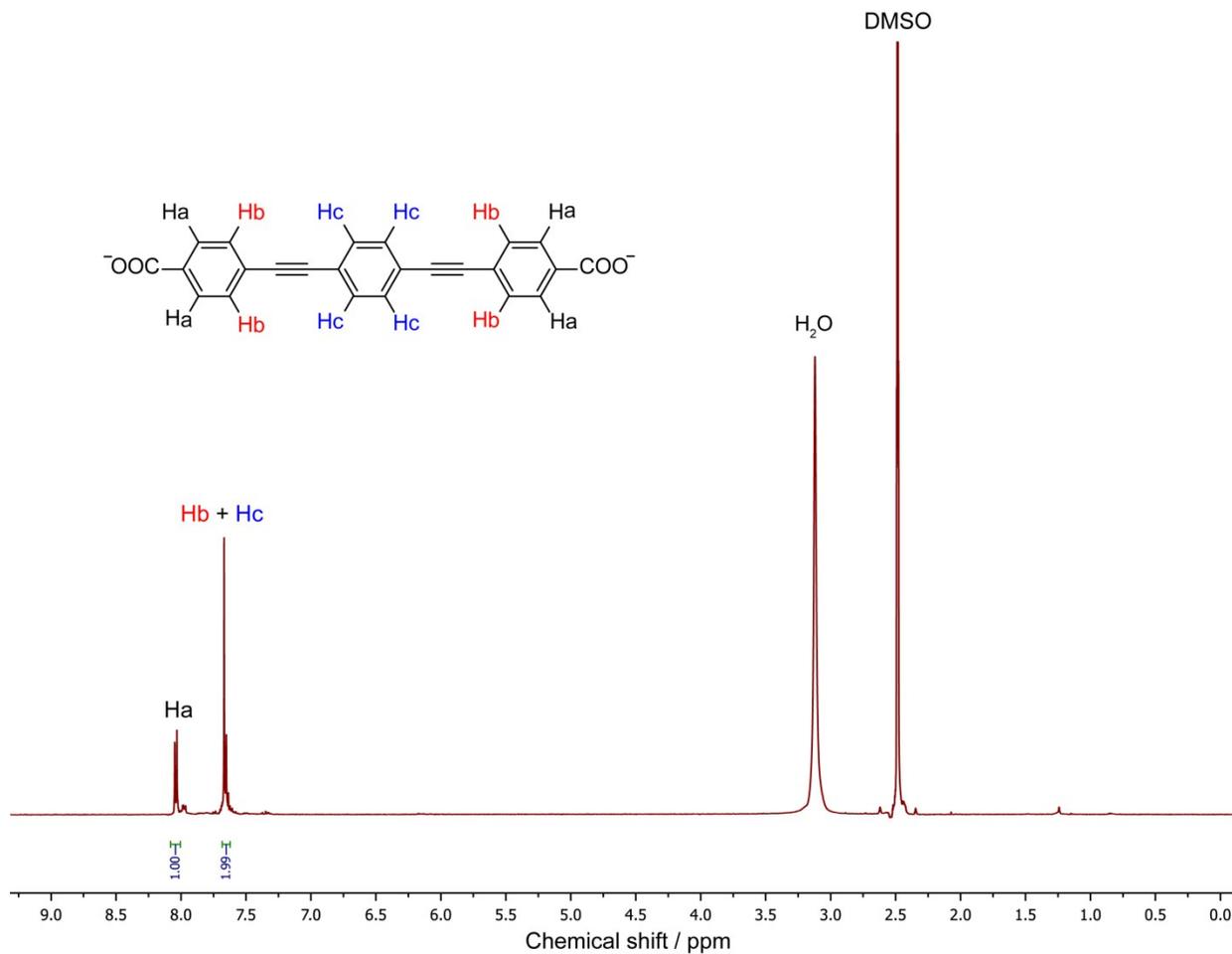


Figure S6. Post-digestion ¹H NMR spectrum of VNU-1 displaying the presence of CPEB.

Section 4: Procedure of benzoylation reaction

Procedure for Zr-MOFs catalyzed Friedel-Crafts acylation of aromatic compounds. A mixture of Zr-MOF (7.50 μmol), arene (1.00 mmol), nitrobenzene (1 mL) and benzoyl chloride (140 mg, 1.00 mmol) was heated under microwave irradiation at 120 $^{\circ}\text{C}$ for 5 min in a CEM Discover apparatus. After being cooled, the catalyst was filtered from the reaction mixture. The filtrate was diluted with ethyl acetate (50 mL), washed with H_2O (3 x 20 mL), aqueous NaHCO_3 (2 x 20 mL), and brine (20 mL), and dried over Na_2SO_4 . The solvent was removed on a rotary evaporator. The crude product was purified by flash chromatography (*n*-hexane, then 10% ethyl acetate in *n*-hexane) to give corresponding product. The purity and identity of the products were confirmed by GC-MS spectra, which were compared with the spectra in the NIST library, and by ^1H and ^{13}C NMR spectroscopy.

Table S1. Optimized condition of reaction between mesitylene and benzoyl chloride catalyzed by VNU-1 under microwave irradiation.

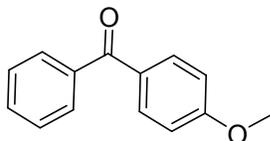
| Entry | Temperature ($^{\circ}\text{C}$) | Time (min) | Yield (%) |
|-------|------------------------------------|------------|-----------|
| 1 | 120 | 1 | 40 |
| 2 | 120 | 3 | 72 |
| 3 | 120 | 5 | 94 |
| 4 | 120 | 10 | 94 |
| 5 | 100 | 5 | 67 |
| 7 | 140 | 5 | 93 |
| 8 | 160 | 5 | 90 |

Procedure for metal halide catalyzed Friedel-Crafts acylation of aromatic compounds.

A mixture of ZrCl_4 or $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (7.50 μmol), arene (1.00 mmol), nitrobenzene (1 mL) and benzoyl chloride (140 mg, 1.00 mmol) was heated under microwave irradiation at 120 °C for 5 min in a CEM Discover apparatus. After being cooled, the reaction mixture was diluted with HCl 10% (10 mL). The mixture was then extracted with ethyl acetate (3 x 15 mL), washed with, aqueous NaHCO_3 (3 x 20 mL), and brine (10 mL), and dried over Na_2SO_4 . The solvent was removed on a rotary evaporator. The crude product was purified by flash chromatography (*n*-hexane, then 10% ethyl acetate in *n*-hexane) to give corresponding product. The purity and identity of the products were confirmed by GC-MS spectra which were compared with the spectra in the NIST library, and by ^1H and ^{13}C NMR spectroscopy.

Section 5: NMR data and spectra

4-Methoxybenzophenone

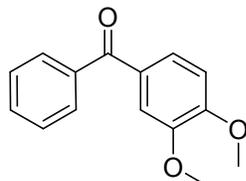


¹H NMR (300 MHz, CDCl₃) δ = 7.86 – 7.81 (m, 2H), 7.75 (dd, J = 8.3, 1.4 Hz, 2H), 7.55 (d, J = 7.5 Hz, 1H), 7.50-7.44 (m, 2H), 6.96 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ = 195.6, 163.2, 138.3, 132.6, 131.9, 130.2, 129.8, 128.2, 113.6, 55.5.

GC-MS (EI, 70 eV) m/z : 212 ([M]⁺)

3,4-Dimethoxybenzophenone

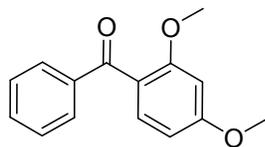


¹H NMR (300 MHz, CDCl₃) δ = 7.77 (dd, J = 8.4, 1.4 Hz, 2H), 7.49 (s, 1H), 7.46 – 7.36 (m, 3H), 6.90 (m, 2H), 3.96 (s, 3H), 3.95 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 195.6, 153.0, 149.0, 138.3, 131.9, 130.2, 129.7, 128.2, 125.5, 112.1, 109.7, 56.1, 56.1.

GC-MS (EI, 70 eV) m/z : 242 ([M]⁺)

2,4-Dimethoxybenzophenone

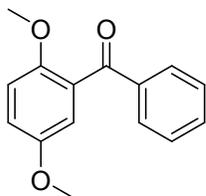


¹H NMR (300 MHz, CDCl₃) δ = 7.77 (dd, J = 8.4, 1.4 Hz, 2H), 7.49 (s, 1H), 7.42 (m, 1H), 7.39 (s, 2H), 6.53 (dd, J = 9.6, 5.3 Hz, 2H), 3.86 (s, 3H), 3.69 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ = 195.6, 163.4, 159.6, 138.8, 132.3, 132.2, 129.7, 128.0, 121.5, 104.6, 98.8, 55.6, 55.5.

GC-MS (EI, 70 eV) m/z : 242 ($[M]^+$).

2,5-Dimethoxybenzophenone

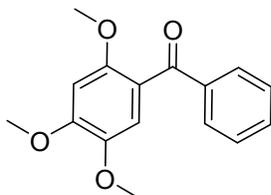


$^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 7.84 – 7.80 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.38 (m, 2H), 7.01 (dd, J = 9.0, 3.0 Hz, 1H), 6.92 (dd, J = 6.0, 3.0 Hz, 2H), 3.78 (s, 3H), 3.66 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ = 196.2, 153.5, 151.5, 137.6, 133.0, 129.8, 128.2, 117.3, 114.4, 113.1, 56.3, 55.8.

GC-MS (EI, 70 eV) m/z : 242 ($[M]^+$)

2,4,5-Trimethoxybenzophenone

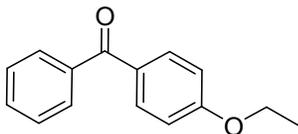


$^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 7.76 (d, J = 8.2 Hz, 2H), 7.51 (t, J = 6.8 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.02 (s, 1H), 6.55 (s, 1H), 3.94 (s, 3H), 3.83 (s, 3H), 3.64 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ = 195.5, 153.4, 152.7, 143.3, 139.0, 132.3, 129.5, 128.0, 120.1, 113.6, 97.7, 56.7, 56.5, 56.2.

GC-MS (EI, 70 eV) m/z : 272 ($[M]^+$).

4-Ethoxybenzophenone

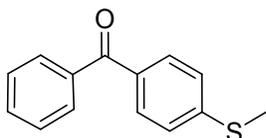


$^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 7.81 (d, J = 8.9 Hz, 2H), 7.75 (dd, J = 8.3, 1.3 Hz, 2H), 7.55 (t, J = 6.8 Hz, 1H), 7.47 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.12 (q, J = 7.0 Hz, 2H), 1.45 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 195.6, 162.7, 138.4, 132.6, 131.8, 130.0, 129.7, 128.2, 114.0, 63.8, 14.7.

GC-MS (EI, 70 eV) m/z : 226 ($[\text{M}]^+$).

4-Methylthiobenzophenone

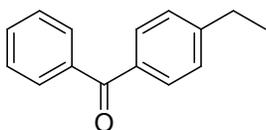


^1H NMR (500 MHz, CDCl_3) δ = 7.75 (m, 4H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.31 – 7.27 (m, 2H), 2.53 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 195.8, 145.3, 137.9, 133.7, 132.2, 130.6, 129.8, 128.3, 124.9, 14.9.

GC-MS (EI, 70 eV) m/z : 228 ($[\text{M}]^+$).

4-Ethylbenzophenone

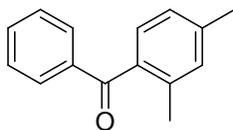


^1H NMR (500 MHz, CDCl_3) δ = 7.78 (dd, J = 8.3, 1.3 Hz, 2H), 7.76 – 7.72 (m, 2H), 7.56 (s, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 2.73 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 196.5, 149.4, 138.0, 135.2, 132.1, 130.3, 130.1, 130.0, 129.9, 128.4, 128.2, 127.8, 28.9, 15.2.

GC-MS (EI, 70 eV) m/z : 210 ($[\text{M}]^+$).

2,4-Dimethylbenzophenone

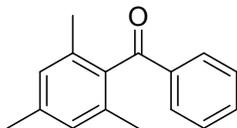


^1H NMR (500 MHz, CDCl_3) δ = 7.77 (dd, J = 8.3, 1.2 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (m, 2H), 7.21 (d, J = 7.7 Hz, 1H), 7.09 (s, 1H), 7.02 (d, J = 7.7 Hz, 1H), 2.36 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 198.5, 140.6, 138.3, 137.3, 135.7, 132.8, 131.9, 130.1, 129.2, 128.4, 127.5, 125.8, 21.4, 20.1.

GC-MS (EI, 70 eV) m/z : 209 ($[M - H]^+$).

2,4,6-Trimethylbenzophenone

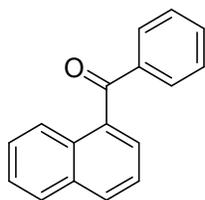


$^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 7.80 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 6.90 (s, 2H), 2.33 (s, 3H), 2.08 (s, 6H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ = 200.8, 138.5, 137.4, 136.9, 134.2, 133.5, 129.4, 128.8, 128.4, 21.2, 19.4.

GC-MS (EI, 70 eV) m/z : 223 (100 $[M+H]^+$).

1-Benzoylnaphthalene

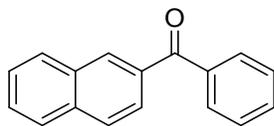


$^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 8.09 (d, J = 9.1 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 7.3 Hz, 1H), 7.87 (dd, J = 8.4, 1.3 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.57 – 7.49 (m, 3H), 7.46 (dd, J = 8.0, 7.5 Hz, 2H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ = 196.9, 138.1, 135.4, 135.0, 132.5, 132.4, 132.0, 130.3, 129.6, 128.5, 128.5, 128.5, 128.0, 127.0, 125.9.

GC-MS (EI, 70 eV) m/z : 232 ($[M]^+$)

2-Benzoylnaphthalene

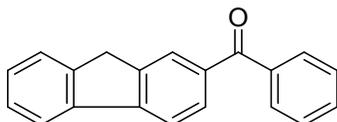


$^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 8.27 (s, 1H), 7.95 (d, J = 1.1 Hz, 2H), 7.94 – 7.89 (m, 2H), 7.89 – 7.83 (m, 2H), 7.62 (d, J = 3.8 Hz, 2H), 7.53 (dd, J = 17.0, 9.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ = 198.2, 138.5, 136.5, 133.9, 133.4, 131.4, 131.1, 130.6, 128.6, 128.5, 127.9, 127.4, 126.6, 125.8, 124.5.

GC-MS (EI, 70 eV) m/z : 232 ($[\text{M}]^+$).

2-Benzoylfluorene

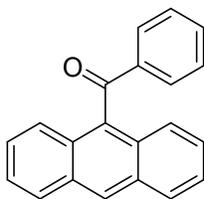


^1H NMR (500 MHz, CDCl_3) δ = 8.03 (s, 1H), 7.89 – 7.82 (m, 5H), 7.59 (dd, J = 6.8, 5.2 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.45 – 7.36 (m, 2H), 3.95 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ = 196.7, 146.0, 144.5, 143.1, 140.6, 138.3, 135.9, 132.2, 130.0, 129.7, 128.3, 128.0, 127.1, 126.8, 125.3, 120.9, 119.4, 36.9.

GC-MS (EI, 70 eV) m/z : 270 ($[\text{M}]^+$).

9-Benzoylanthracene



^1H NMR (500 MHz, CDCl_3) δ = 8.57 (s, 1H), 8.07 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 7.4 Hz, 2H), 7.73 (dd, J = 8.7, 0.5 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.40 (td, J = 8.1, 4.3 Hz, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ = 200.2, 138.2, 134.0, 131.1, 130.1, 128.9, 128.7, 128.4, 126.6, 125.5, 125.3.

GC-MS (EI, 70 eV) m/z : 282 ($[\text{M}]^+$).

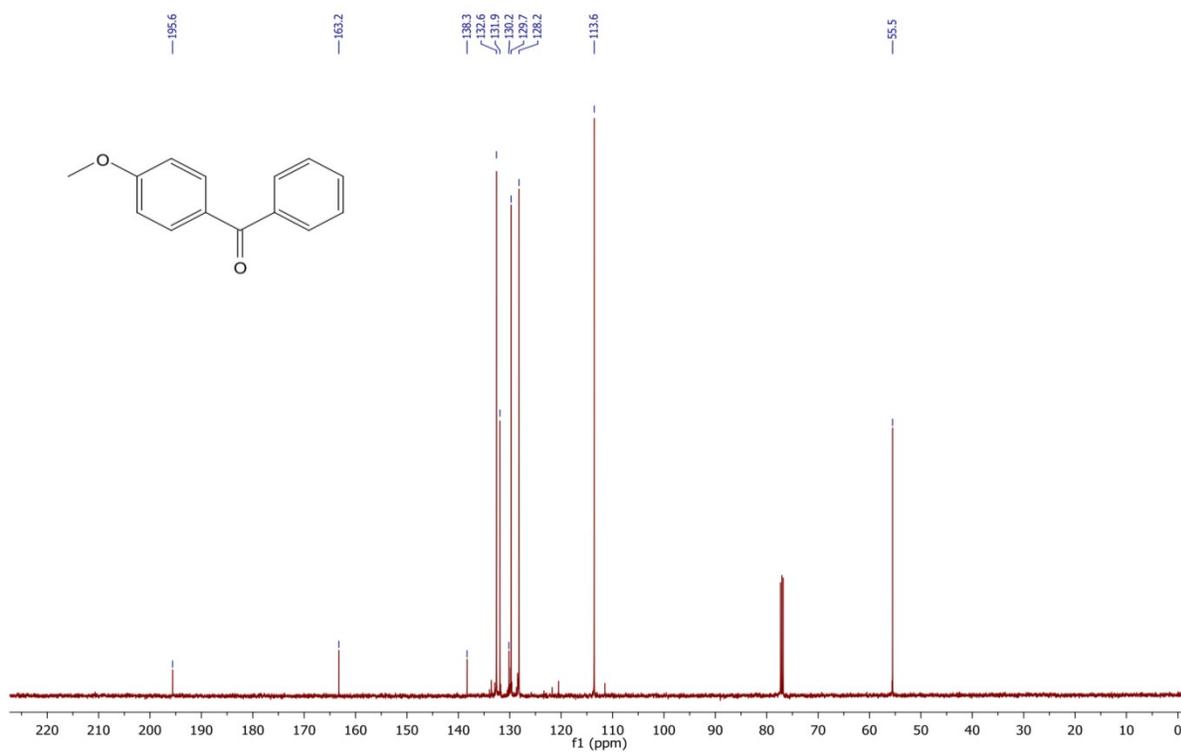
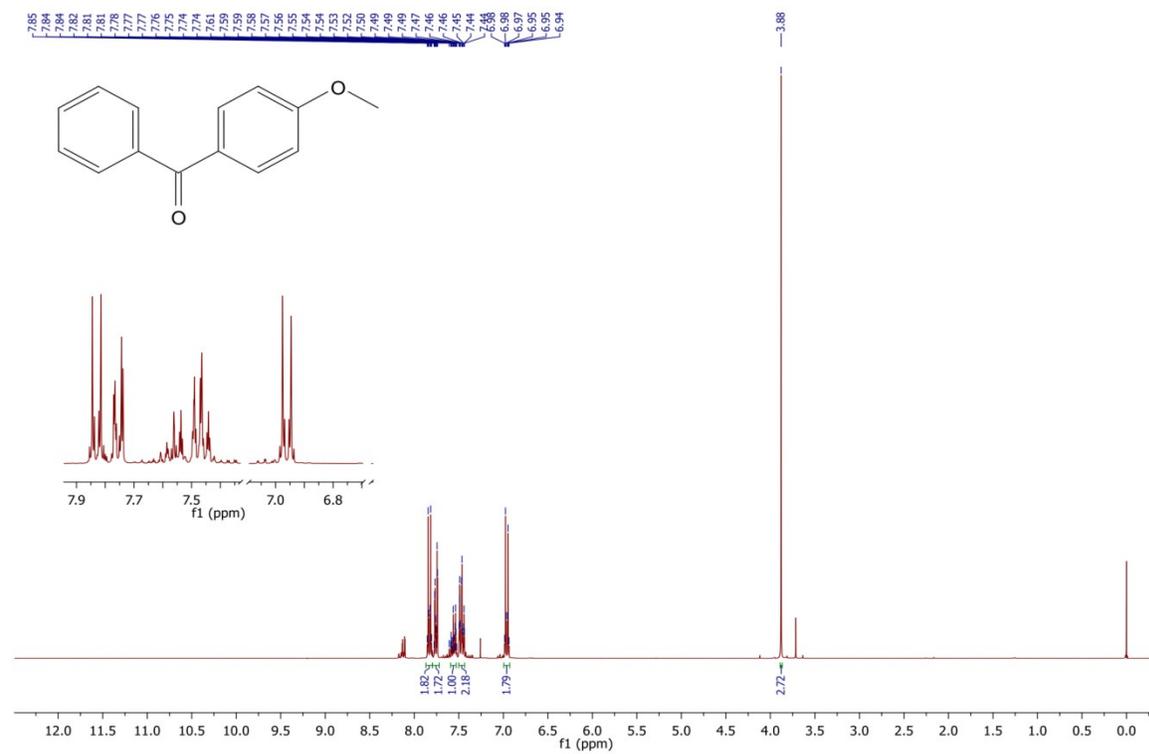


Figure S7. ¹H and ¹³C NMR of 4-methoxyacetophenone.

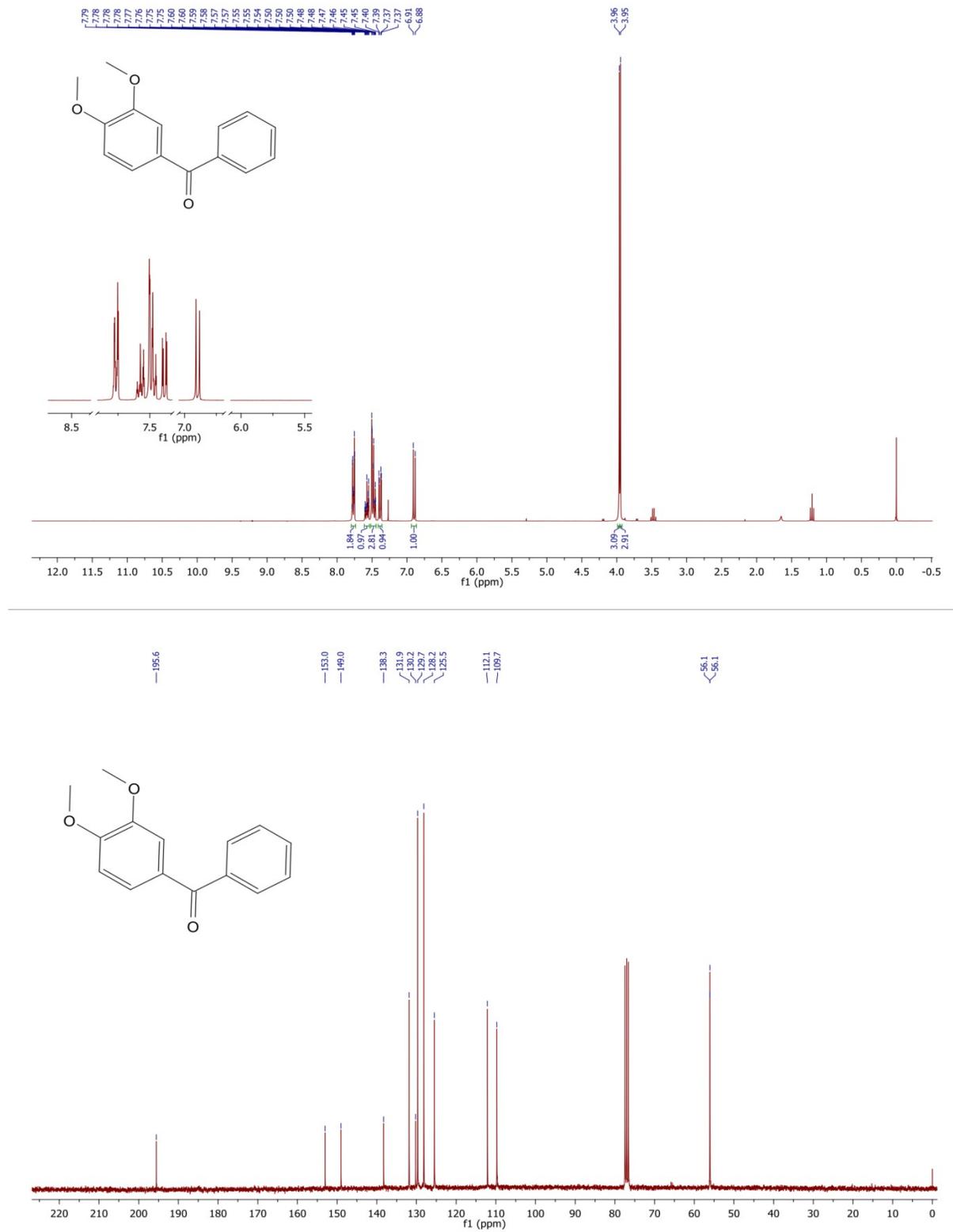


Figure S8. ^1H and ^{13}C NMR of 3,4-dimethoxybenzophenone.

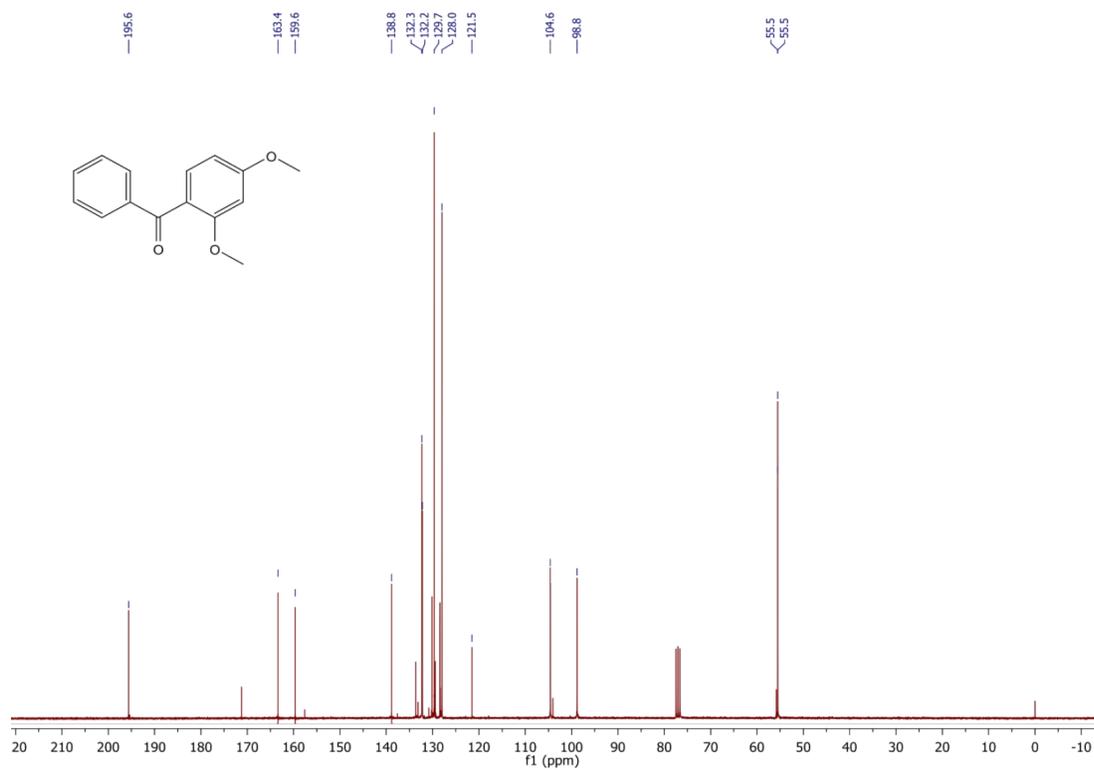
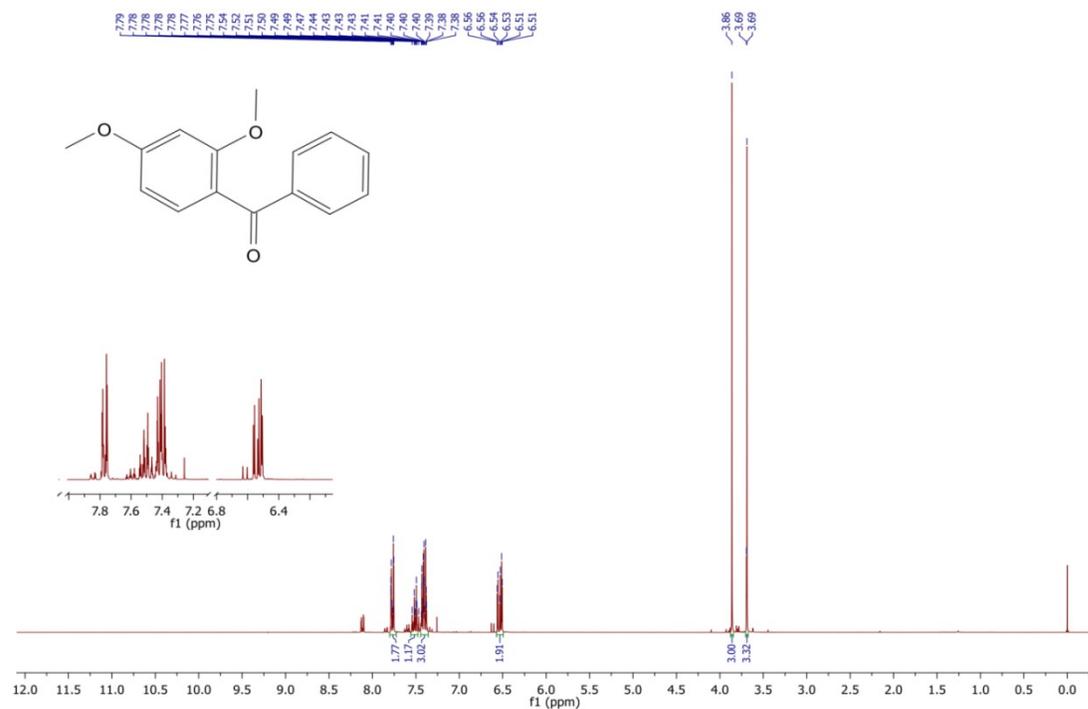


Figure S9. ¹H and ¹³C NMR of 2,4-dimethoxyacetophenone.

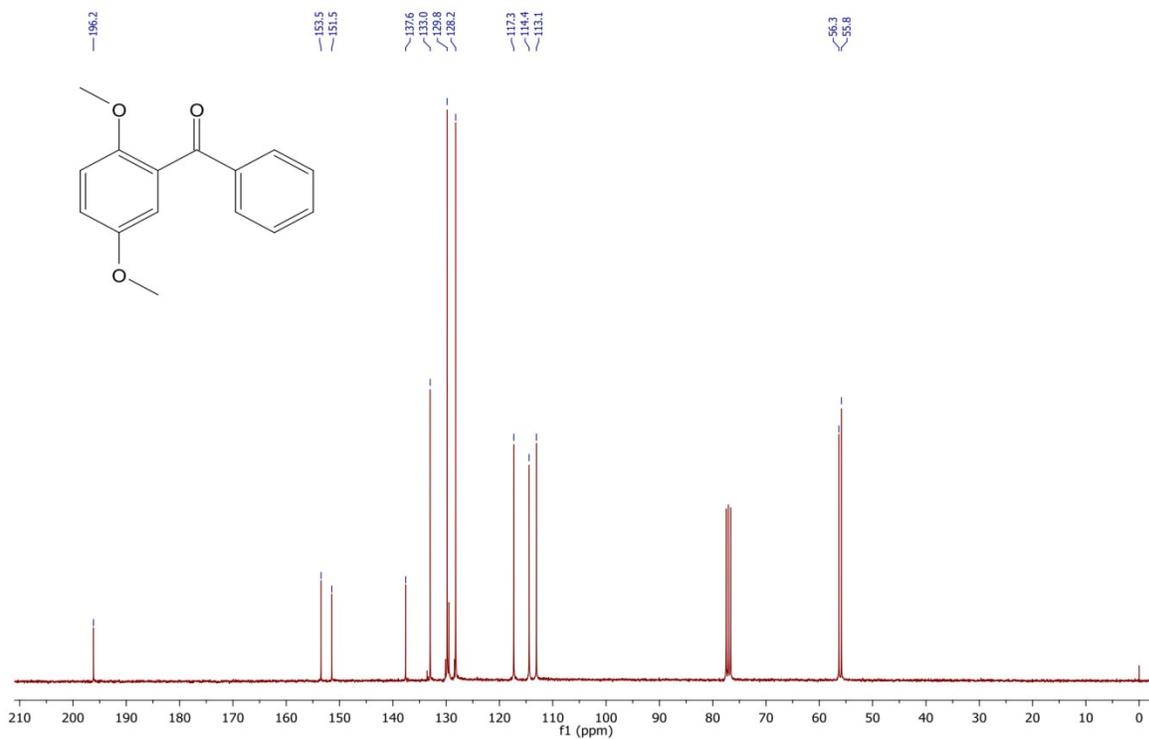
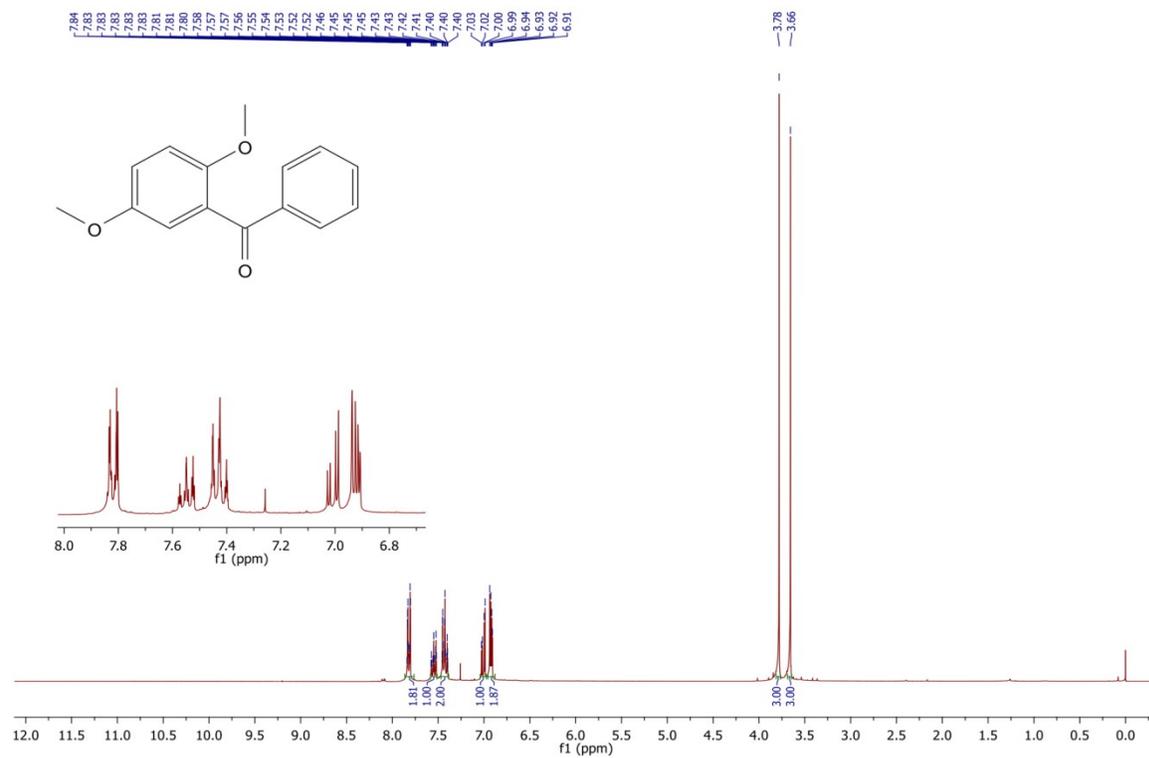


Figure S10. ¹H and ¹³C NMR of 2,5-dimethoxyacetophenone.

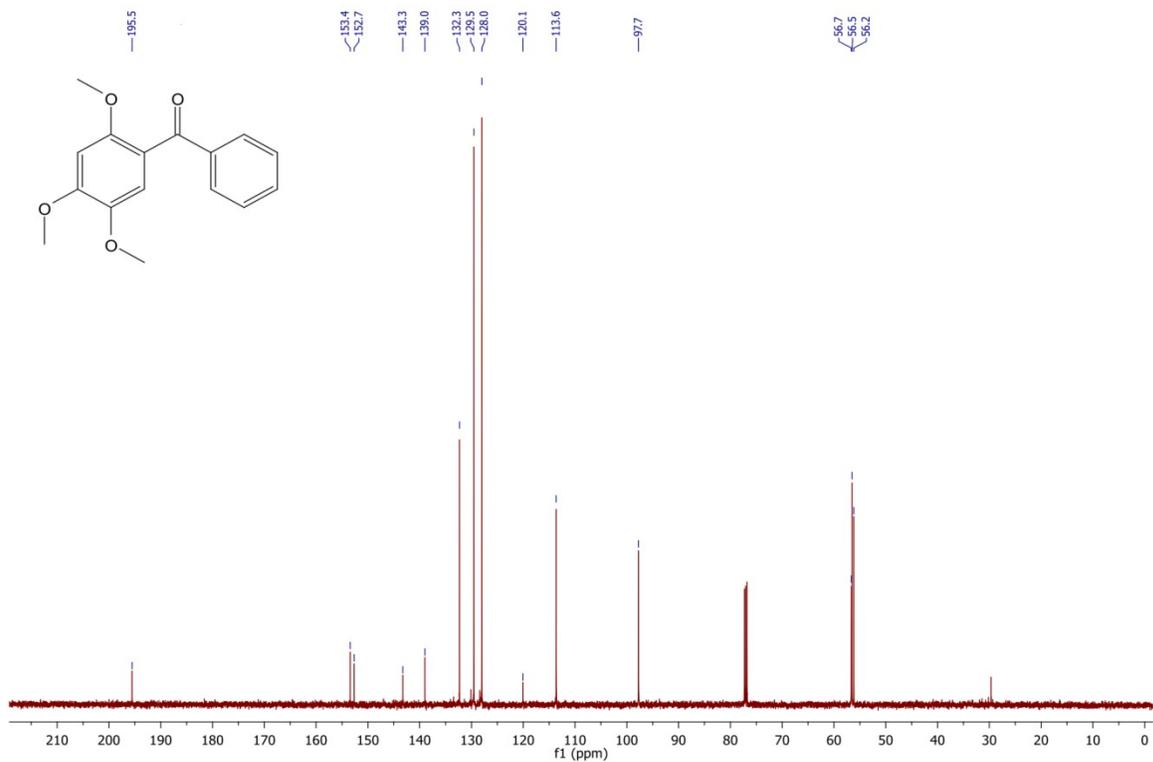
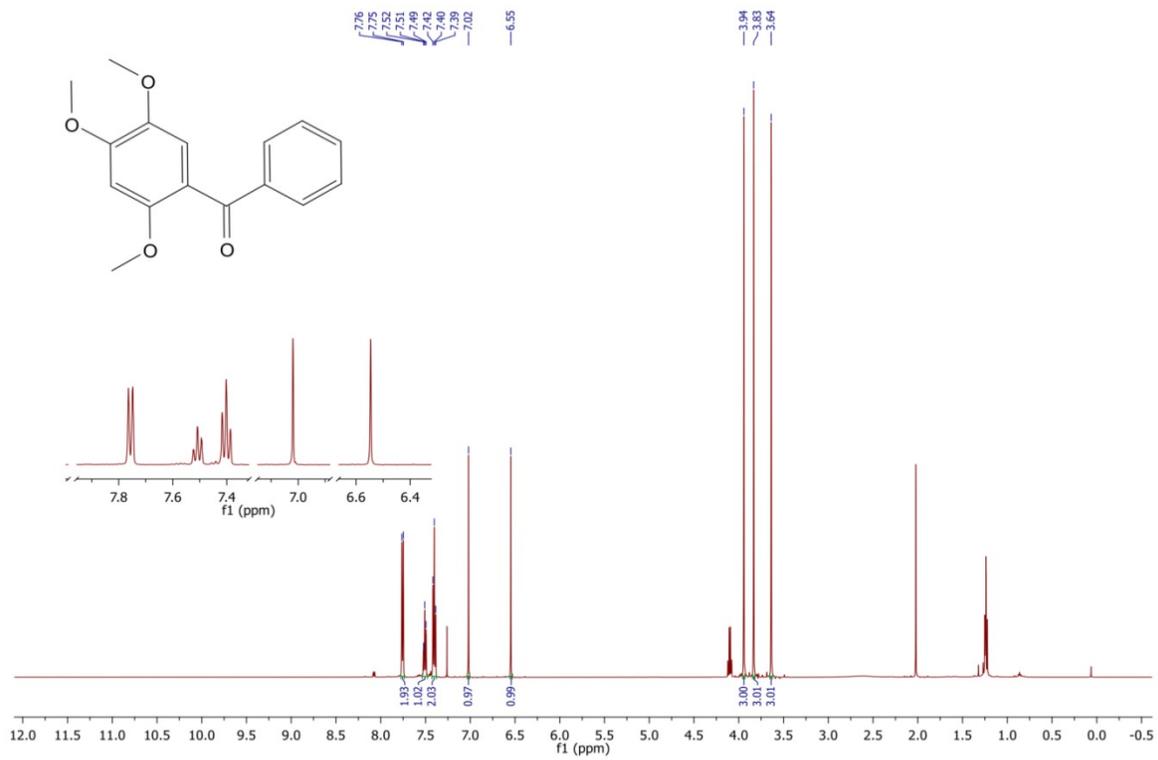


Figure S11. ¹H and ¹³C NMR of 2,4,5-trimethoxybenzophenone.

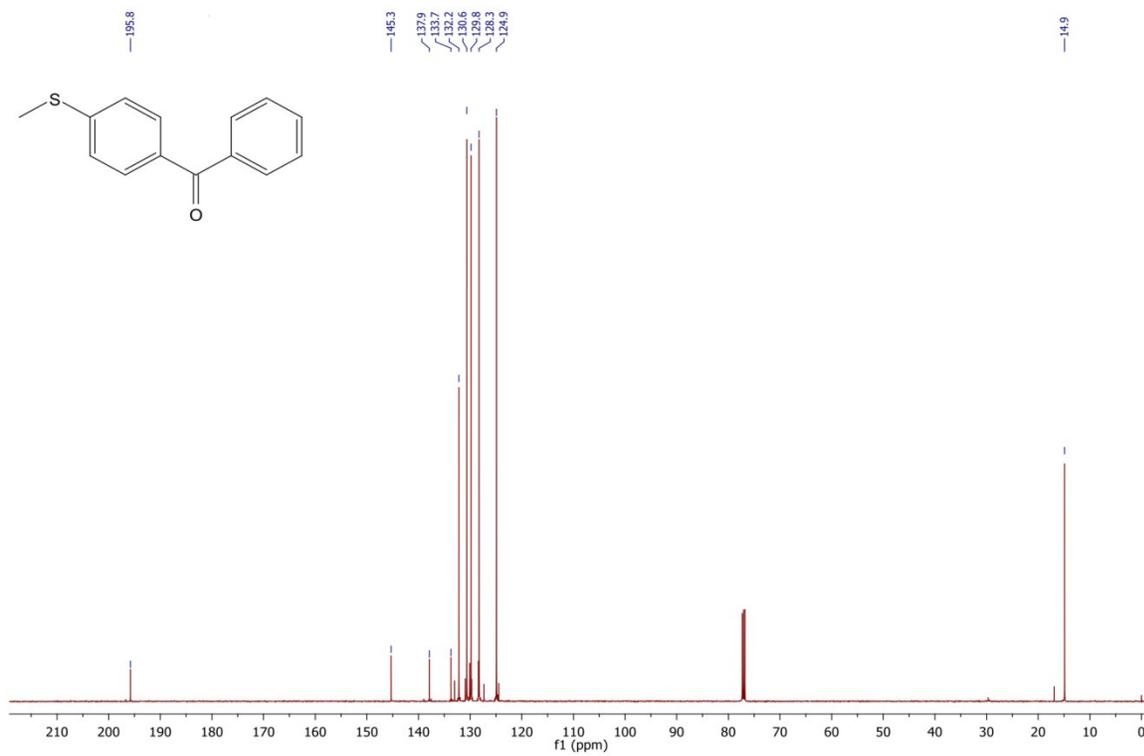
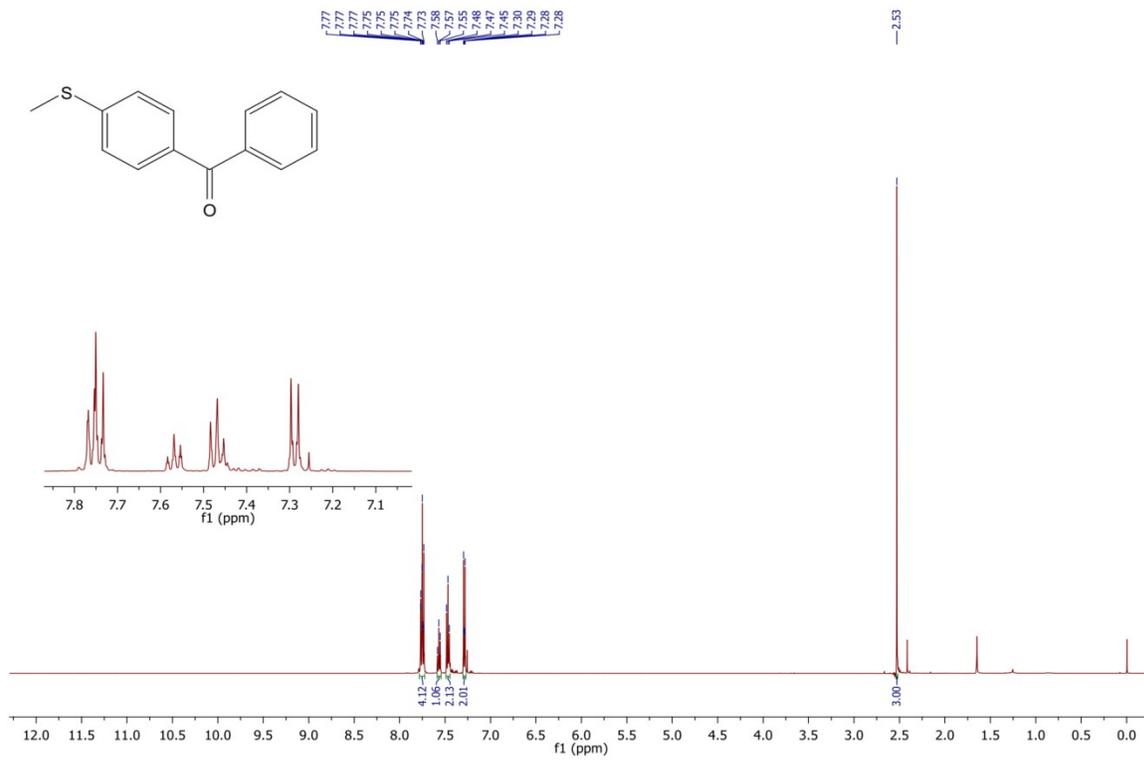


Figure S12. ¹H and ¹³C NMR of 4-methylthiobenzophenone.

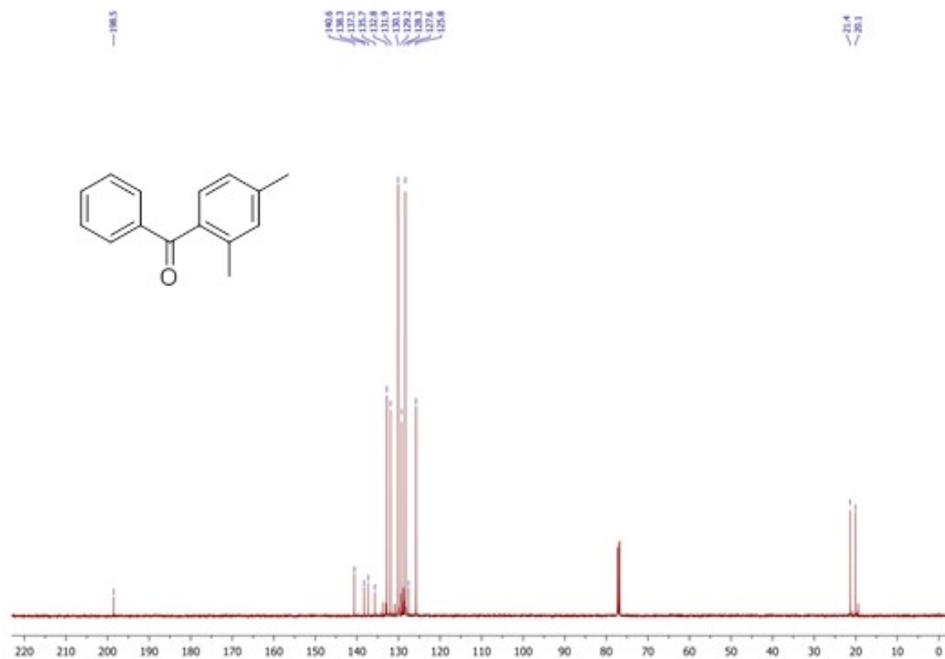
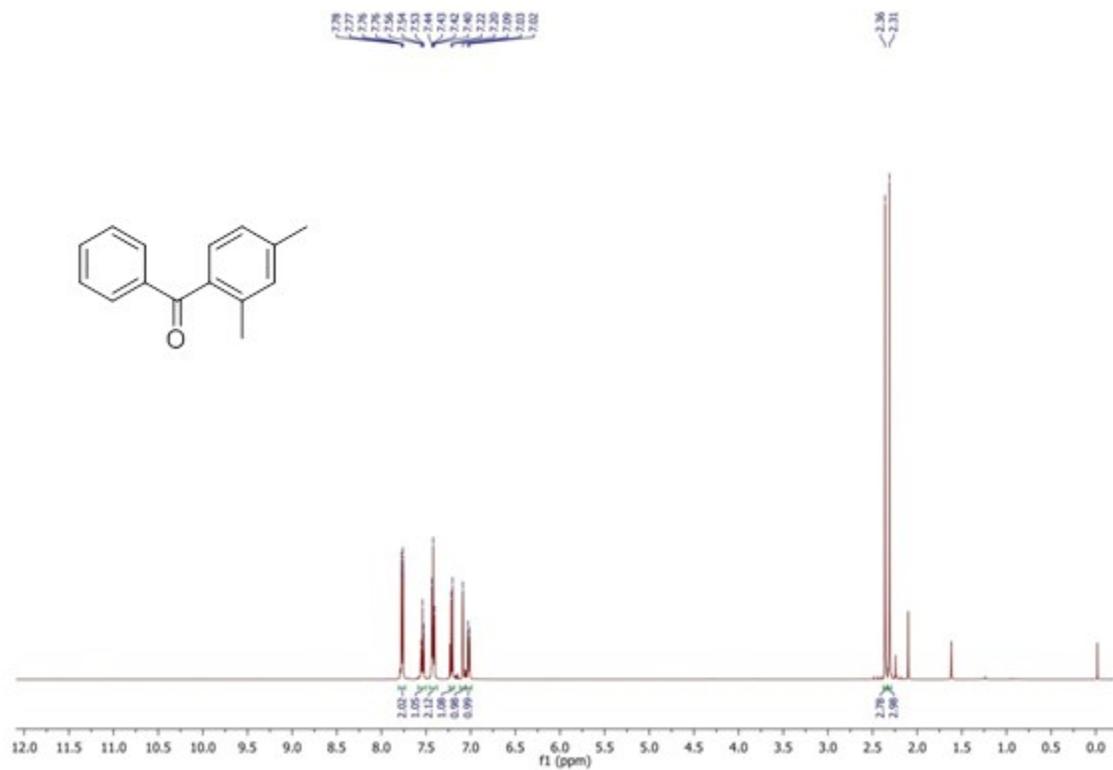


Figure S14. ¹H and ¹³C NMR of 2,4-dimethylbenzophenone.

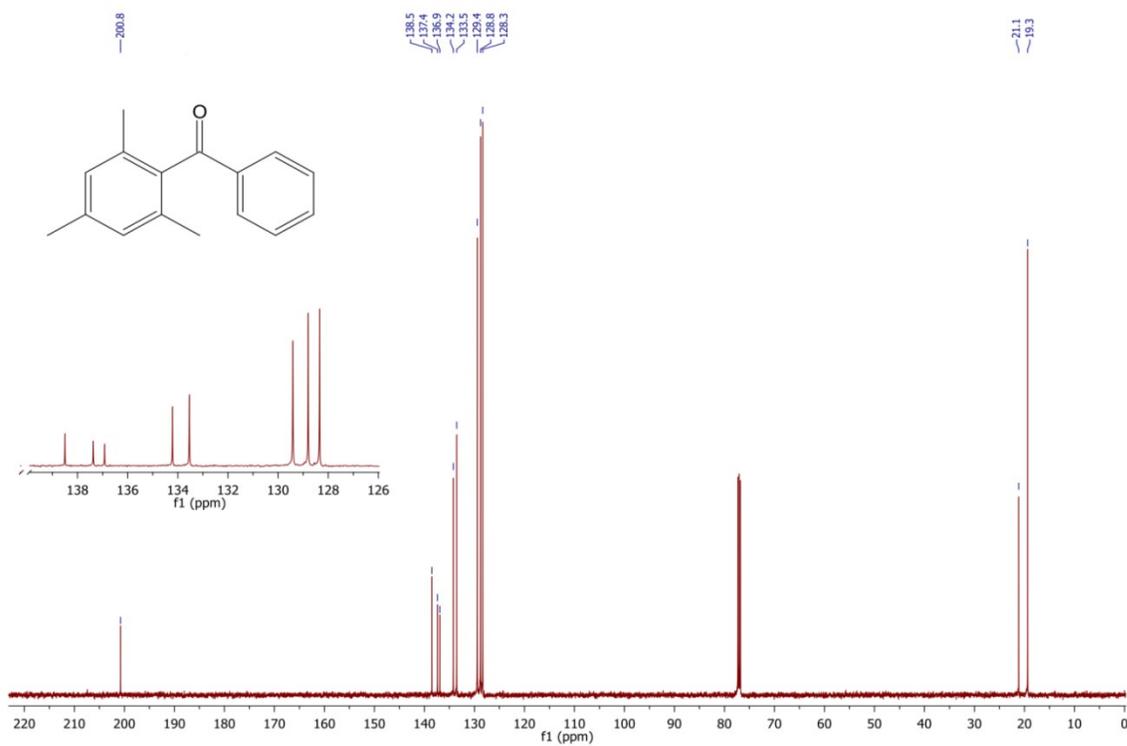
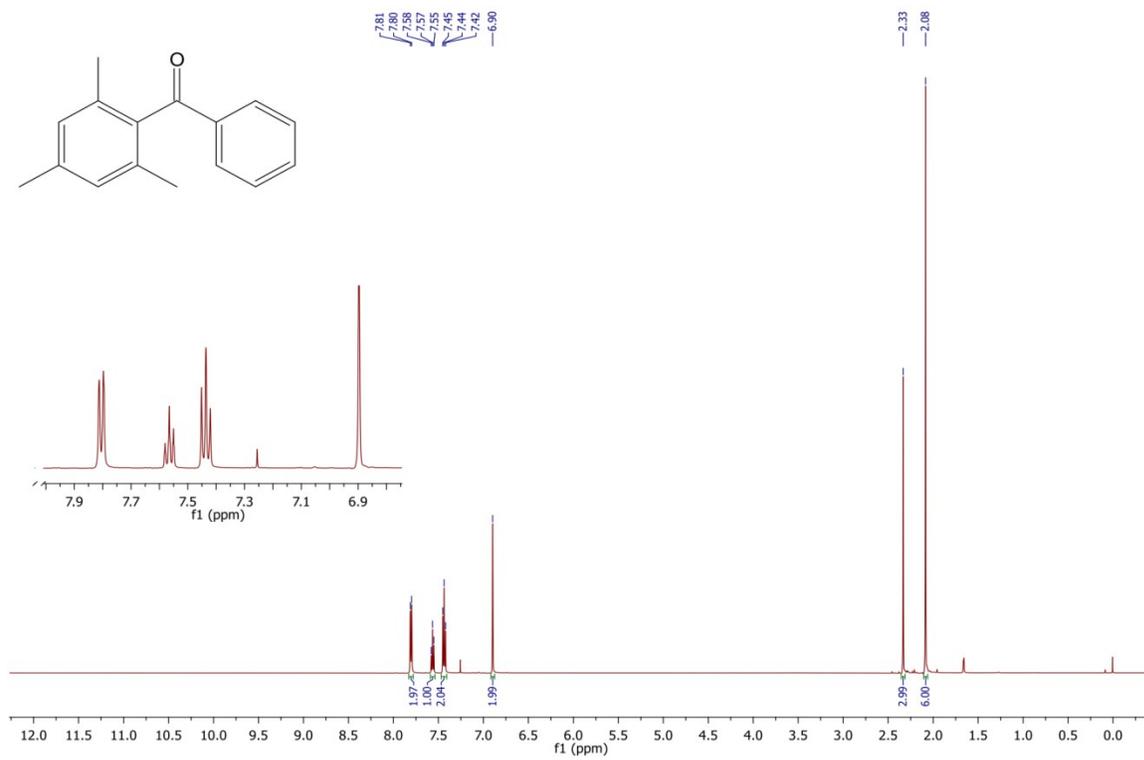


Figure S15. ^1H and ^{13}C NMR of 2,4,6-trimethylbenzophenone.

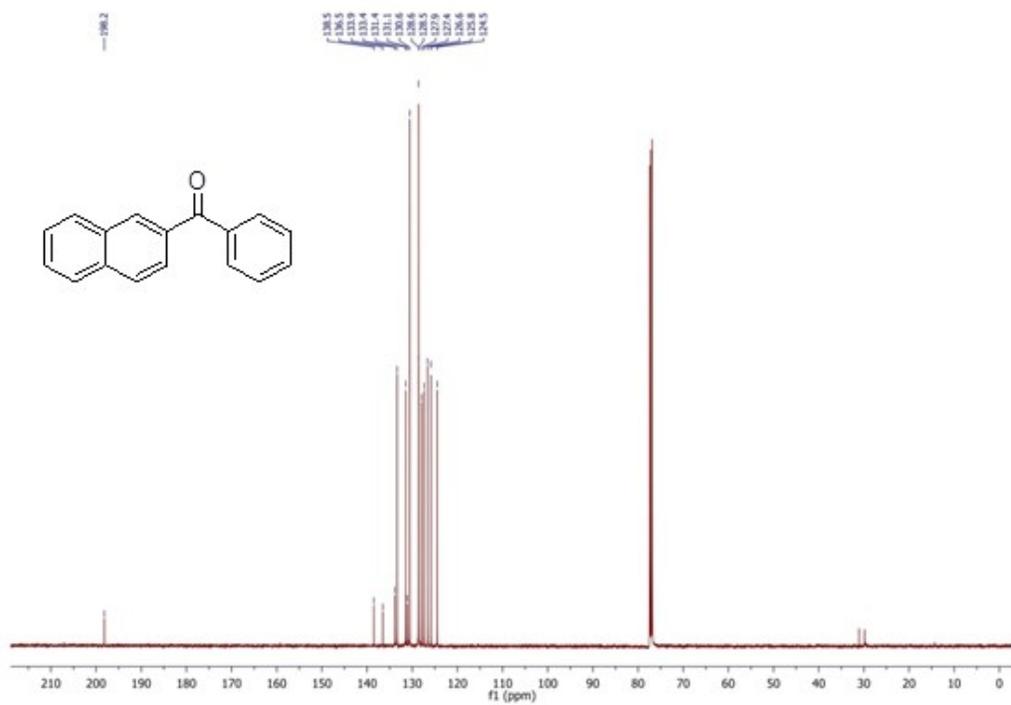
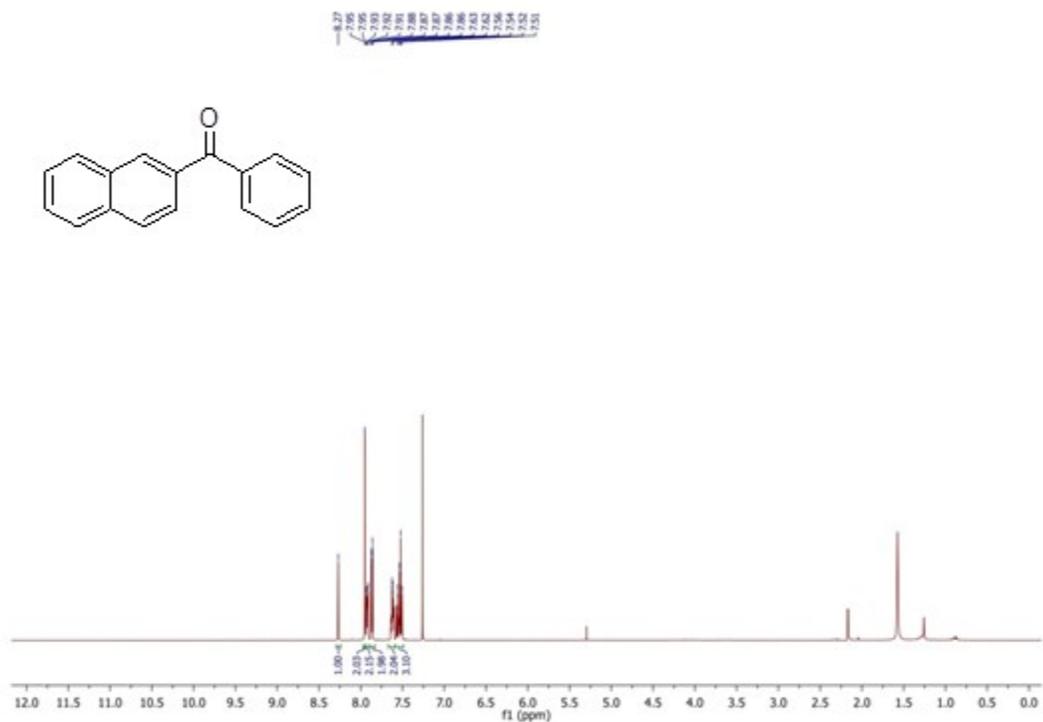


Figure S17. ^1H and ^{13}C NMR of 2-benzoylnaphthalene.

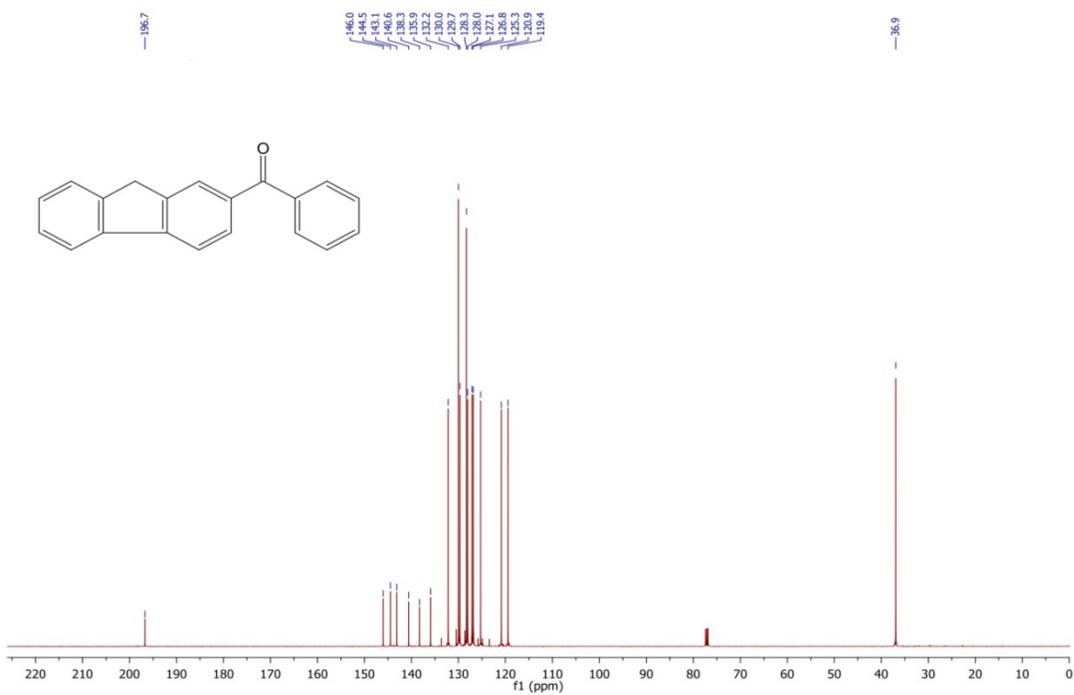
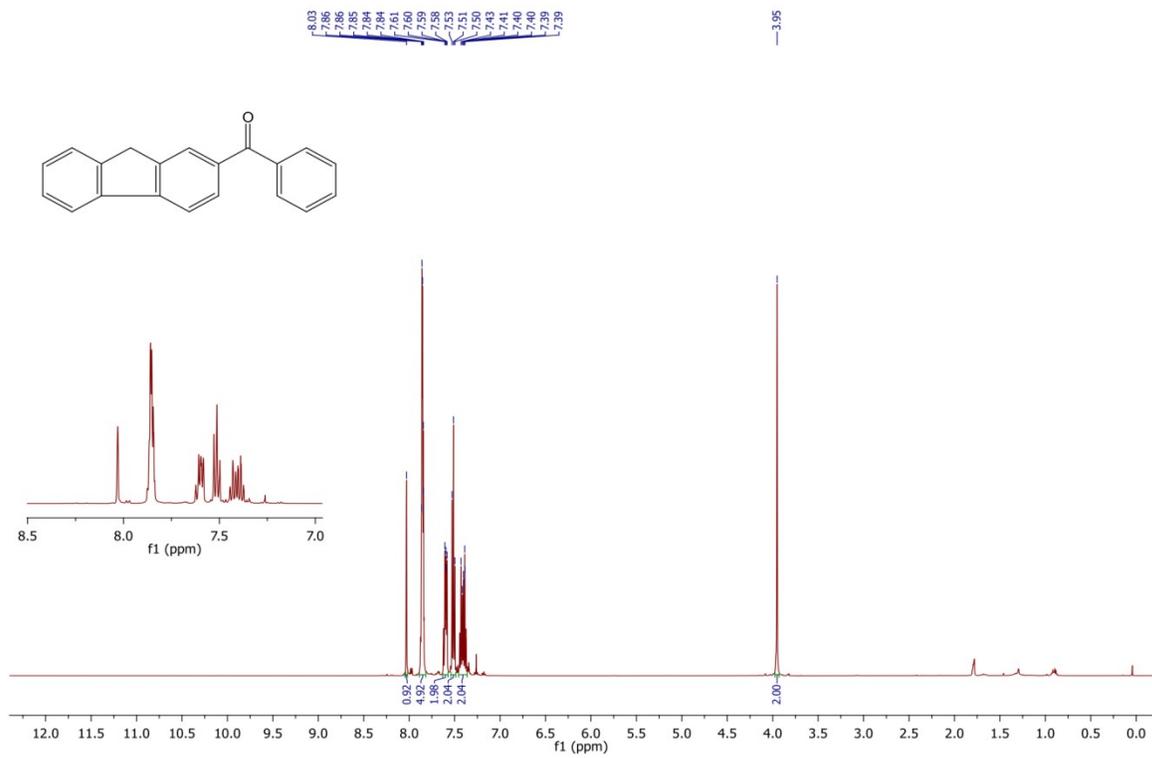


Figure S18. ^1H and ^{13}C NMR of 2-benzoylfluorene.

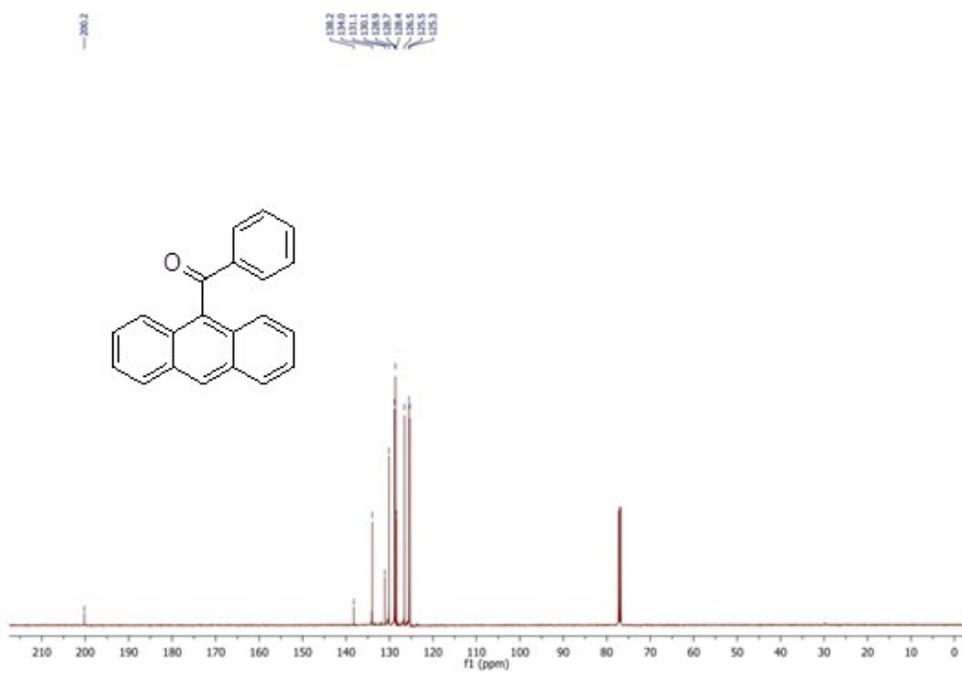
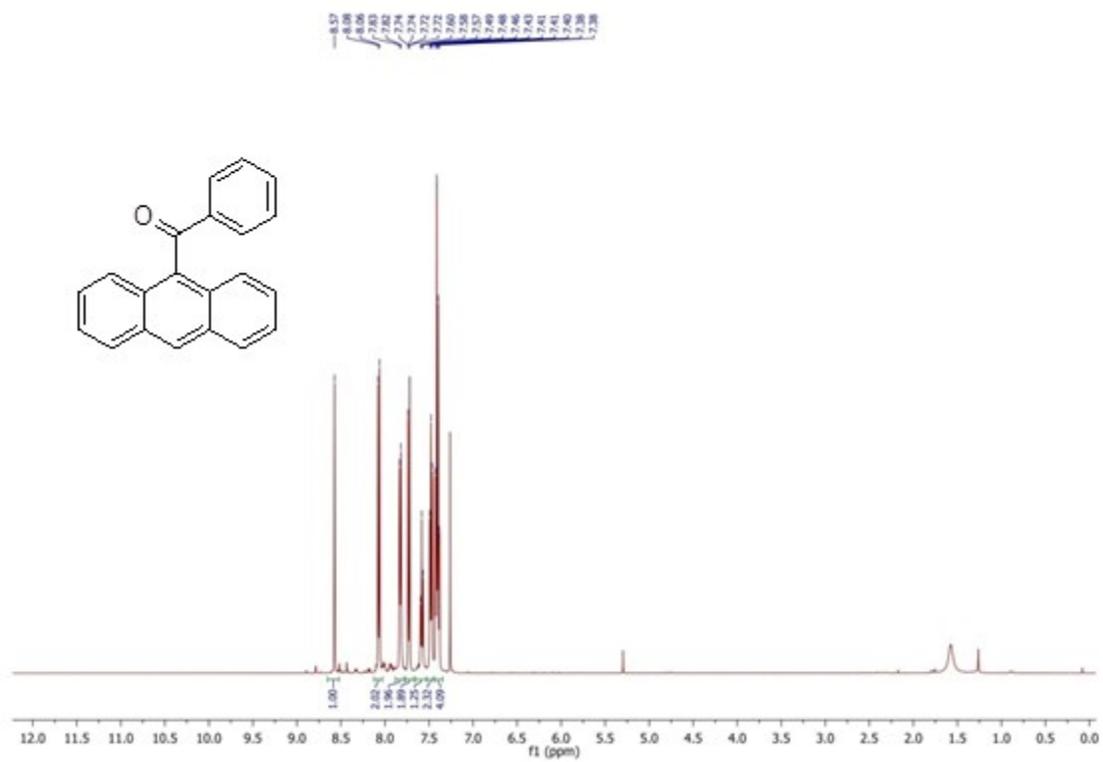


Figure S19. ¹H and ¹³C NMR of 9-benzoylanthracene.

Reference

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