Electronic Supplementary Information for

A supramolecular naphthalenediimide radical anion through host-guest interactions for photooxidation of alkylarenes to carbonyls

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1. Experimental Section

1.1 Materials

Unless specifically mentioned, the chemicals used are commercially available.

1.2 Characterizations

^{1}H NMR and ^{13}C NMR were characterized on Bruker Avance 400 NMR instrument. UV-vis absorption spectra were characterized by a Shimadzu UV-2450 spectrophotometer. Fluorescence emission spectra were obtained by fluorescence spectrophotometer F-380A. DLS and Zeta potential tests were constructed on Malvern Zeta sizer Nano ZS90. The photocatalytic reaction was performed on WATTCAS Parallel Photocatalytic Reactor (WP-TEC-HSL) with 10W COB LED. Cyclic voltammetry (CV) was performed on CHI660C electrochemical workstation (Shanghai Chenhua, China). The fluorescence lifetime was measured by the FS-5 fluorescence spectrophotometer.

2. General procedure for photooxidation of alkylarenes to carbonyls

Alkylarenes derivatives (0.20 mmol) and TBACl (40 mM) was dissolved in the freshly prepared NDI-2CB[7] aqueous solution (1.0 mol%, 2.0 mL). The mixture was subsequently irradiated by UV light (365-367 nm) at room temperature for 24 h. After that, it was extracted with ethyl acetate, and the combined organic layer was dried with anhydrous Na_2SO_4. Then the organic solvent was concentrated in a vacuum. The crude product was separated by flash column chromatography with petroleum ether/ethyl acetate to obtain the product.

3. General procedure for Cyclic voltammetry in solution.

Cyclic voltammetry (CV) of NDI-2CB[7] was carried out on a CHI660C electrochemical workstation. The CV curves were performed using a typical three-electrode cell system with SCE as the reference electrode, glassy carbon (GC) as the working electrode, and Pt wire as the counter electrode. The NDI-2CB[7] aqueous solution with 0.5 M $KHCO_3$ as the electrolyte with a scan rate of 100 mV s^{-1}. Using the same three-electrode cell system, CV curves were obtained for substrates at a working concentration of 5 mM by the same method.

4. Transition state free energy calculation.

$\mathbf{E_{0\text{-}0}}$ = 1240/(The wavelength at the intersection of UV-vis absorption spectrum and fluorescence spectrum).

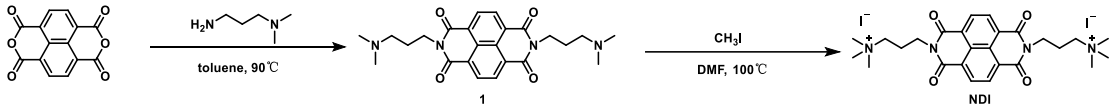
5. General procedure for fluorescence lifetime detection in solution.

The fluorescence lifetime was measured by the FS-5 fluorescence spectrophotometer. The light source was picosecond pulsed diode laser EPL-375, whose excitation wavelength was fixed at 375 nm and pulse width was 60.5 ps.

Fluorescence lifetime decay of NDI (1 mM) and NDI-2CB[7] (1 mM) (λ_{ex} =375 nm) at 418 nm were obtained by kinetic fitting to the single exponential decay model. Each sample was measured three times and its average value was taken as the fluorescence lifetime of the sample.

Fluorescence lifetime decay of NDI-2CB[7] (1 mM) (λ_{ex} = 375 nm) at 418 nm upon titration with different TBACl concentrations (0, 10, 30, 50, 70, 100 mM) in an air saturated aqueous solution were investigated. The fluorescence lifetimes of NDI-2CB[7] at corresponding concentrations of TBACl were obtained by kinetic fitting to the single exponential decay model. Each sample was measured three times and its average value was taken as the fluorescence lifetime of the sample.

6. Synthesis of NDI



Scheme S1. The synthetic route of the NDI target molecule.

Synthetic of compound 1: 1,4,5,8-naphthalenetetracarboxylic dianhydride (540 mg, 2 mmol) was dissolved in 100 mL toluene and heated to 90 °C, and N,N-dimethyl-1,3-propanediamine (1.5 mL, 12 mmol) was added dropwise over 10 min. The reaction mixture was heated at 120 °C for 24 h. The crude mixture was concentrated on a rotary evaporator, and the yellow crystalline Compound 1 was purified by recrystallizing from ethanol (510 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 4H), 4.31 – 4.23 (m, 4H), 2.44 (s, 4H), 2.24 (s, 12H), 1.95 – 1.89 (m, 4H).

Synthetic of NDI: Compound 1 (200 mg, 0.46 mmol) was first dissolved in 10 mL DMF and then methyl iodide (0.4 mL, 7.2 mmol) was added. The mixture was heated at 100 °C for 12 h. After precipitated in toluene, the orange product NDI was collected by filtration and dried under vacuum (330 mg, 83%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (s, 4H), 4.17 (t, J = 6.3 Hz, 4H), 3.50 - 3.44 (m, 4H), 3.04 (s, 18H), 2.17 (dd, J = 11.0, 6.4 Hz, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.41, 131.02, 126.84, 126.70, 63.66, 52.74, 52.70, 52.66, 37.85, 22.07.

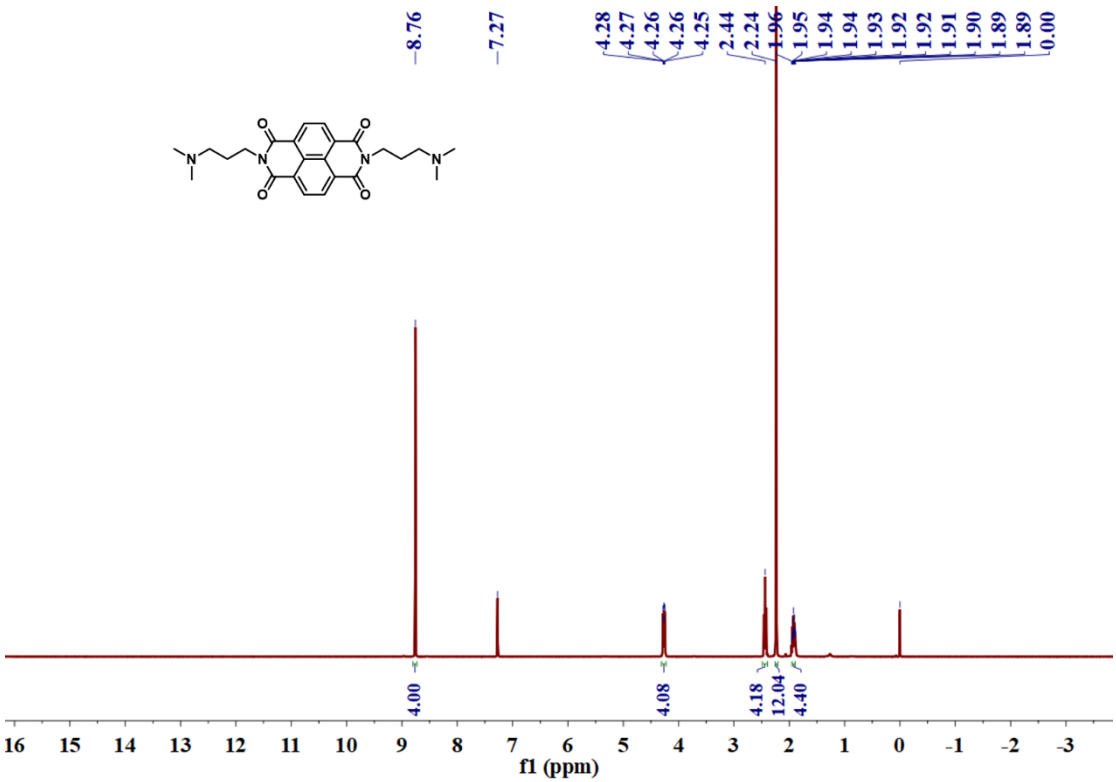


Fig. S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

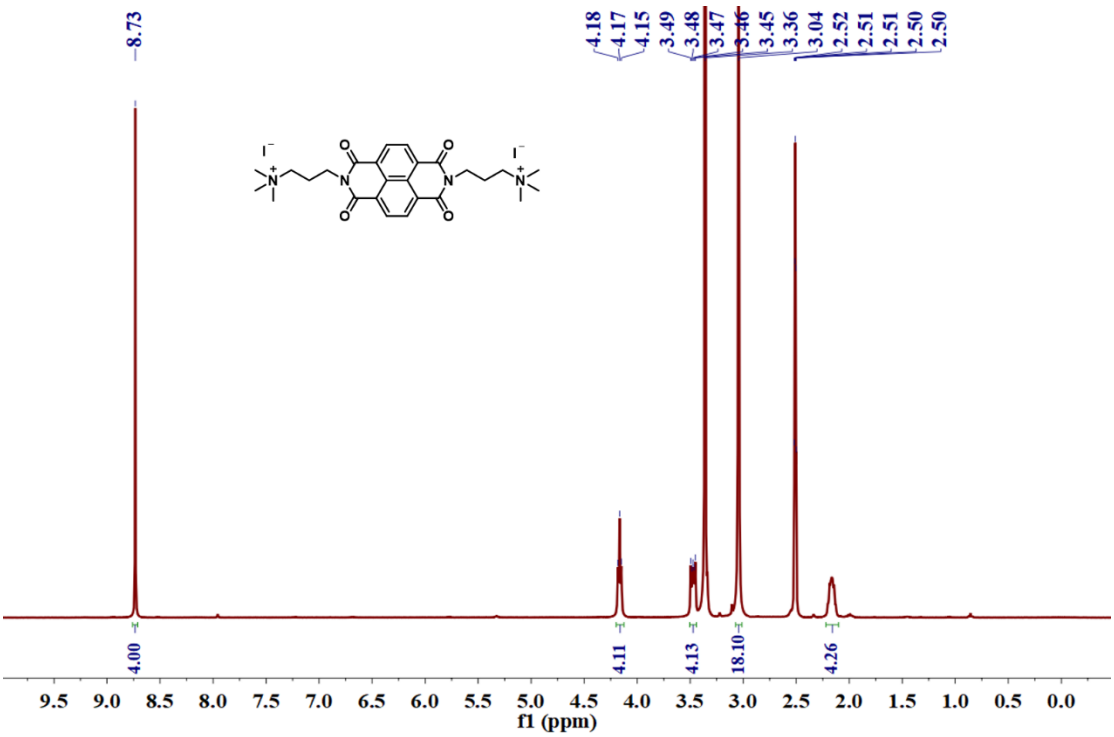


Fig. S2. ^{1}H NMR spectrum of **NDI** in DMSO-d_6.

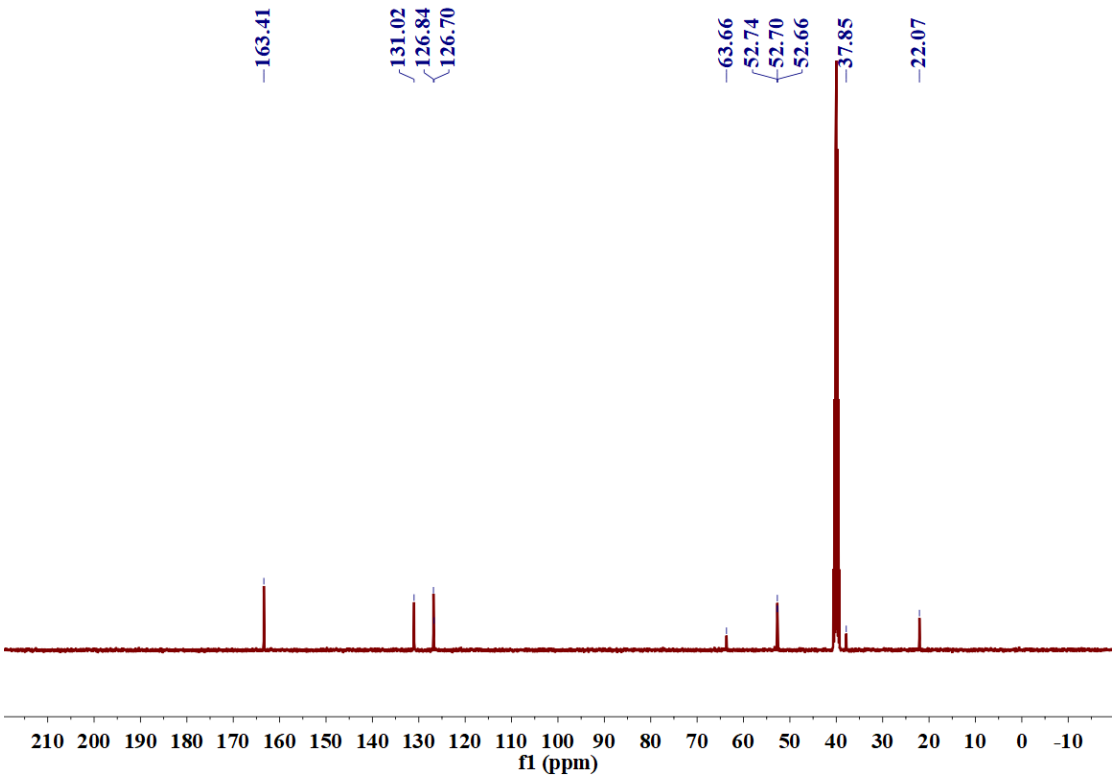


Fig. S3. ^{13}C NMR spectrum of **NDI** in DMSO-d_6.

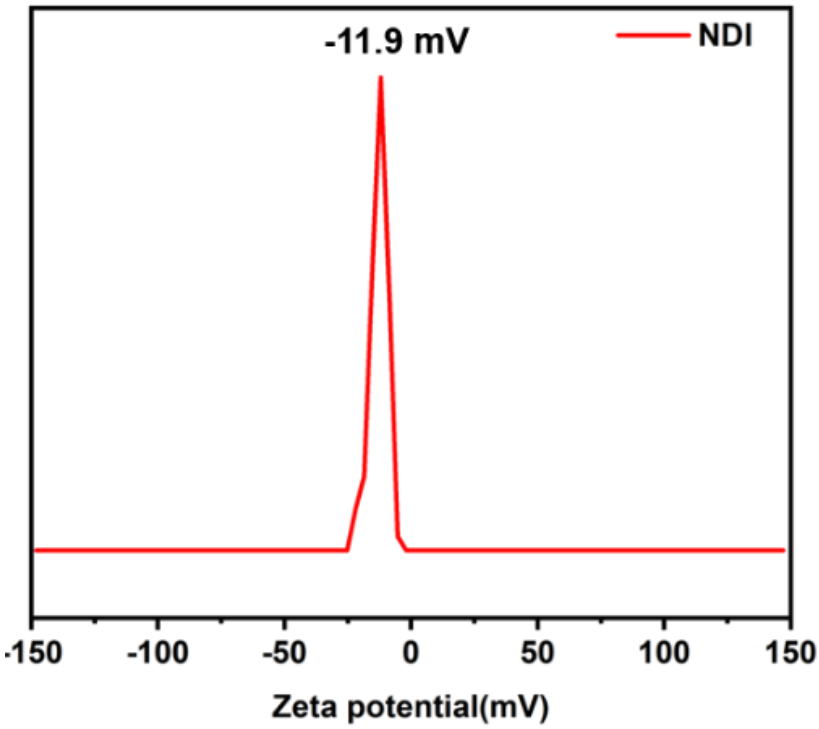


Fig. S4. Zeta potential of NDI.

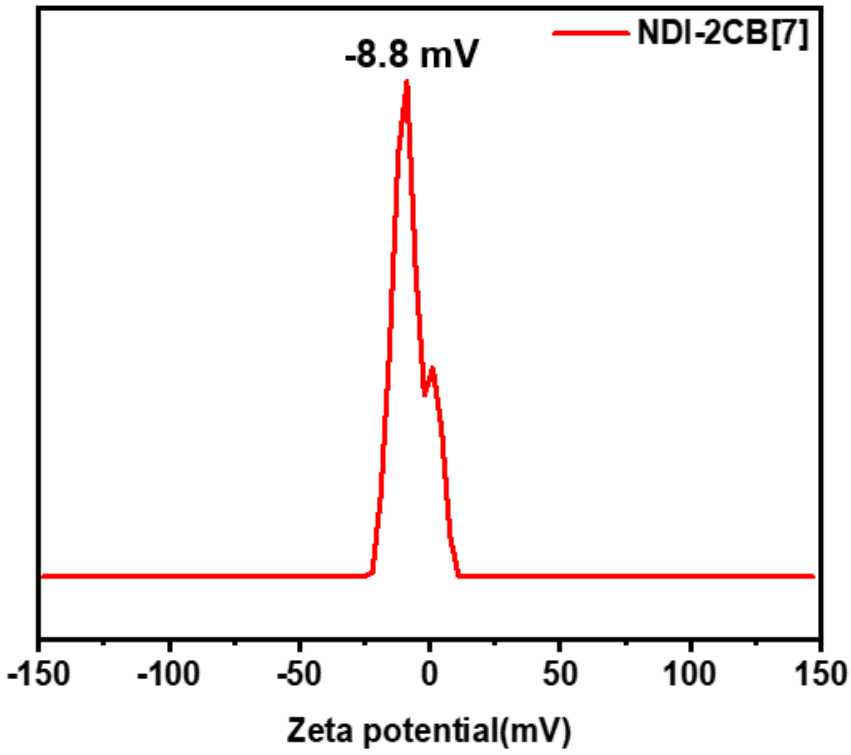


Fig. S5. Zeta potential of NDI-2CB[7].

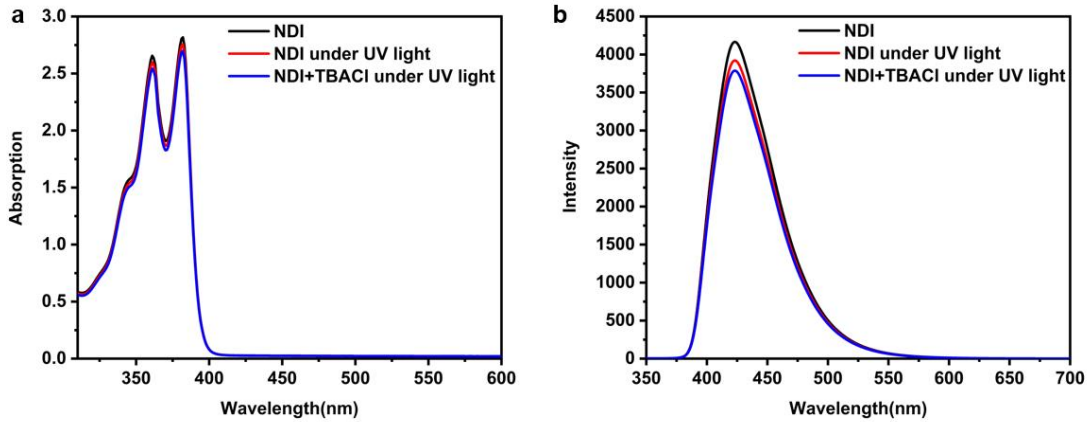


Fig. S6. (a) UV-vis absorption spectra and (b) fluorescence emission spectra of NDI and NDI+TBACl in aqueous solution after irradiated by UV light for 30 s.

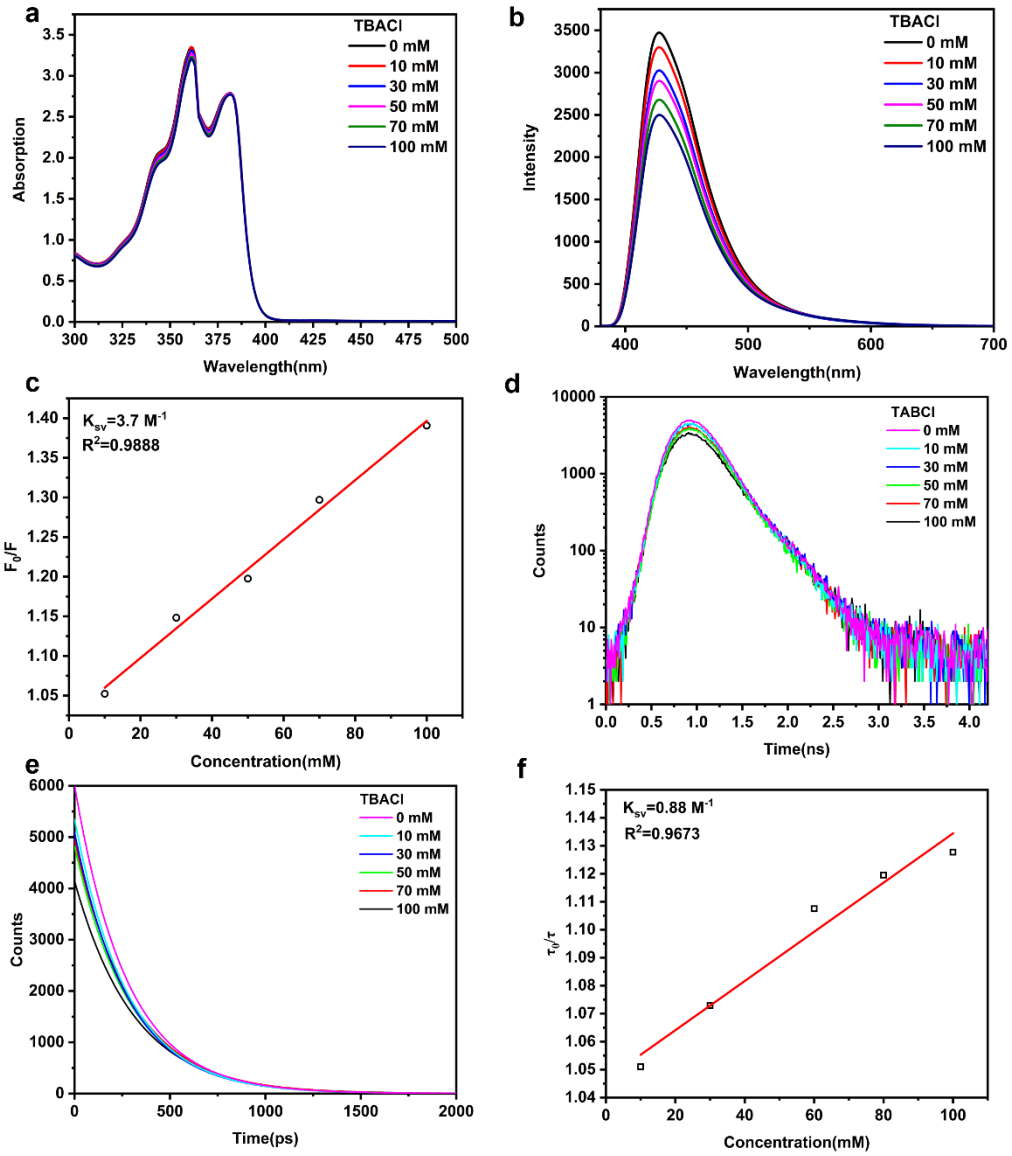
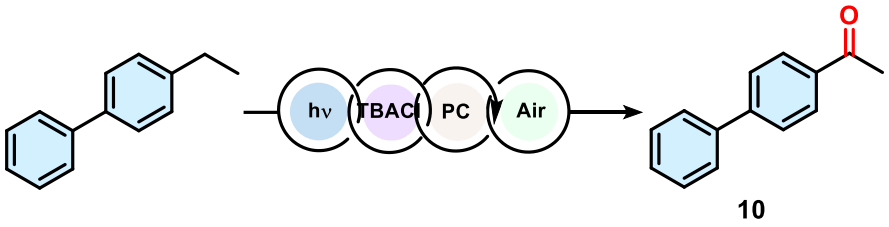


Fig. S7. (a) Ground state UV-vis absorption changes of NDI-2CB[7] after titration with different concentrations of TBACl; (b) Fluorescence spectra of NDI-2CB[7] (λ_{ex} = 381 nm) upon titration of TBACl at indicated concentrations; (c) The corresponding Stern−Volmer plots for fluorescence intensity quenching; (d) Time-resolved fluorescence measurements of NDI and NDI-2CB[7]; (e) Fitted fluorescence lifetime decay of NDI-2CB[7] (λ_{ex} = 375 nm) monitored at 418 nm upon titration of TBACl at indicated concentrations; (f) Stern-Volmer plot for fluorescence lifetime quenching of excited state NDI-2CB[7] with various concentrations of TBACl by monitoring the emission intensity at 418 nm (λ_{ex} =375 nm).

Table S1 Fluorescence lifetimes of NDI-2CB[7] at different TBACl concentrations.

TBACl concentrations (mM)	0	10	30	50	70	100
Fluorescence lifetime (ps)	309	294	288	279	276	274

Table S2 Control experiment under different conditions for photooxidation reaction of 4-ethylbiphenyl.[a,b]



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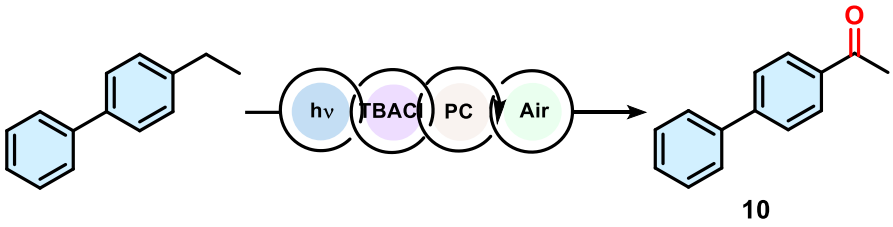
Entry	Deviation from standard conditions	Yield[b] (%)
1	standard conditions[a]	92
2	1.0 mol% NDI instead of 1.0 mol% NDI-2CB[7]	15
3	0.5 mol% NDI-2CB[7] instead of 1.0 mol% NDI-2CB[7]	43
4	1.5 mol% NDI-2CB[7] instead of 1.0 mol% NDI-2CB[7]	94
5	1.0 mol% CB[7] instead of 1.0 mol% NDI-2CB[7]	No reaction
6	TBACl (40 mM) instead of 1.0 mol% NDI-2CB[7]	No reaction
7	12 h instead of 24 h	33
8	48 h instead of 24 h	93
9	40 mM TBABr instead of 40 mM TBACl	No reaction
10	Without TBACl	No reaction
11	Without light	No reaction
12	Without PC	No reaction

[a]Reaction conditions: 4-ethylbiphenyl (0.2 mmol, 36.4 mg), NDI-2CB[7] as photocatalyst, TBACl (40 mM), UV light (365-367 nm), room temperature, air, 24 h; [b]Isolated yield.

Table S3 Control experiment under different chlorine source for photooxidation reaction of 4-ethylbiphenyl.[a,b]



Entry	Deviation from standard conditions	Yield[b] (%)
1	standard conditions[a]	92
2	NaCl instead of TBACl	82
3	KCl instead of TBACl	79
4	NH_4Cl instead of TBACl	77
5	$CaCl_2$ instead of TBACl	75
6	HCl instead of TBACl	91

[a]Reaction conditions: 4-ethylbiphenyl (0.2 mmol, 36.4 mg), NDI-2CB[7] as photocatalyst, TBACl (40 mM), UV light (365-367 nm), room temperature, air, 24 h; [b]Isolated yield.

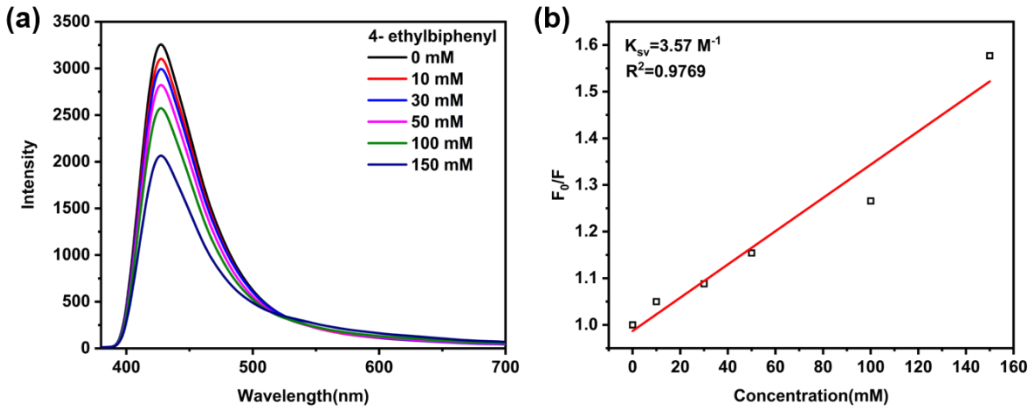


Fig. S8. (a) Fluorescence spectra of NDI-2CB[7] (λ_{ex} = 381 nm) upon titration of 4-ethylbiphenyl at indicated concentrations. (b) The corresponding Stern−Volmer plots for fluorescence intensity quenching with various concentrations of 4-ethylbiphenyl by monitoring the emission intensity at 418 nm (λ_{ex} =381 nm).

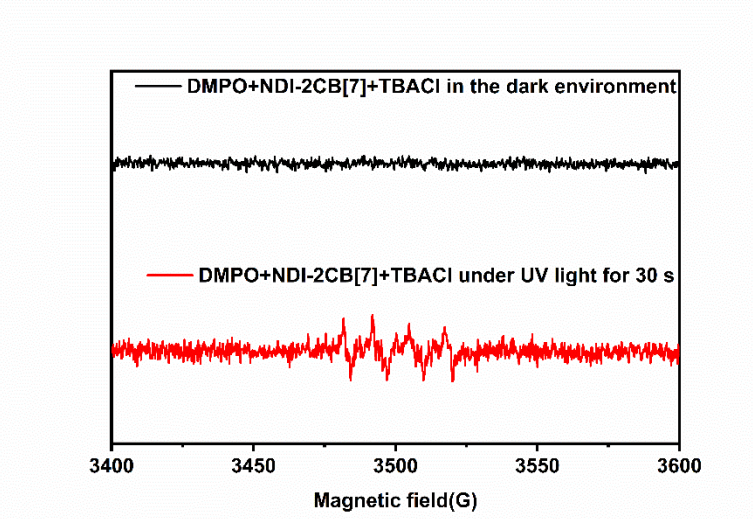
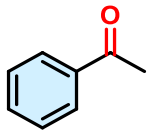


Fig. S9. EPR spectrum of NDI-2CB[7] and TBACl after addition of DMPO in the aqueous solution under dark and UV light irradiation for 30 s.

6. ^{1}H NMR spectra and data of 1-15

1.



Colorless oil (17.3 mg); 72% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.58 – 7.52 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.12, 137.11, 133.11, 128.57, 128.30, 26.60.

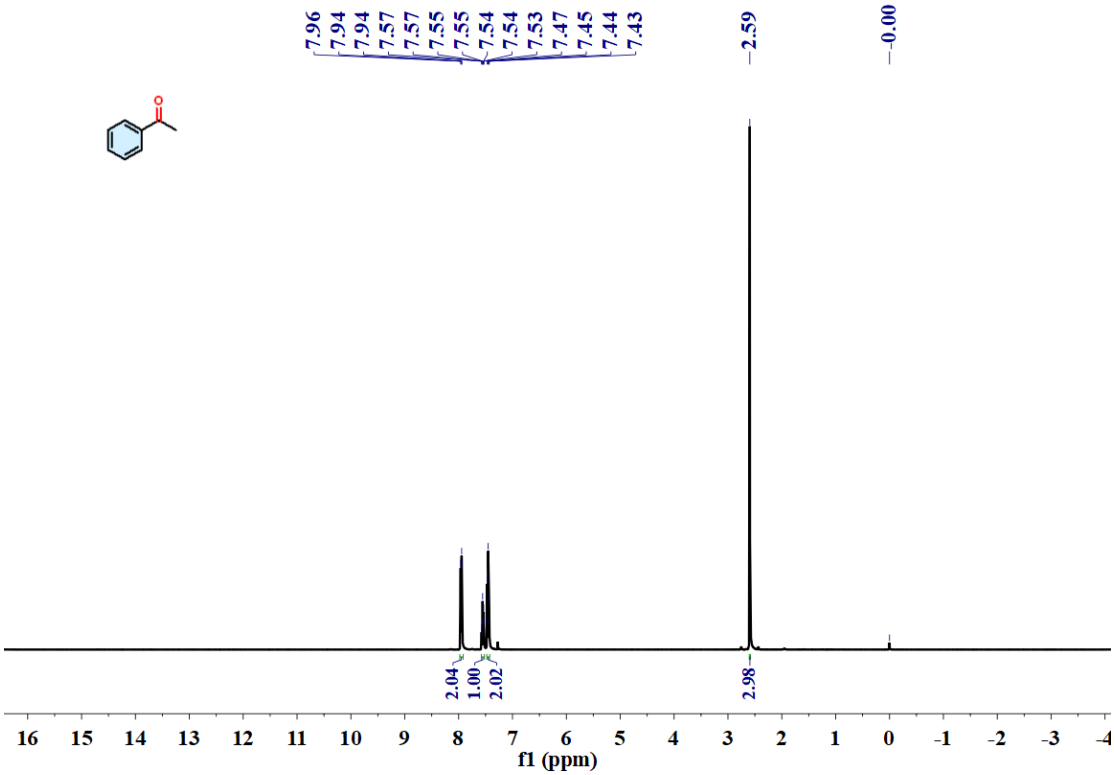


Fig. S10. ^{1}H NMR spectra of **1** in $CDCl_3$.

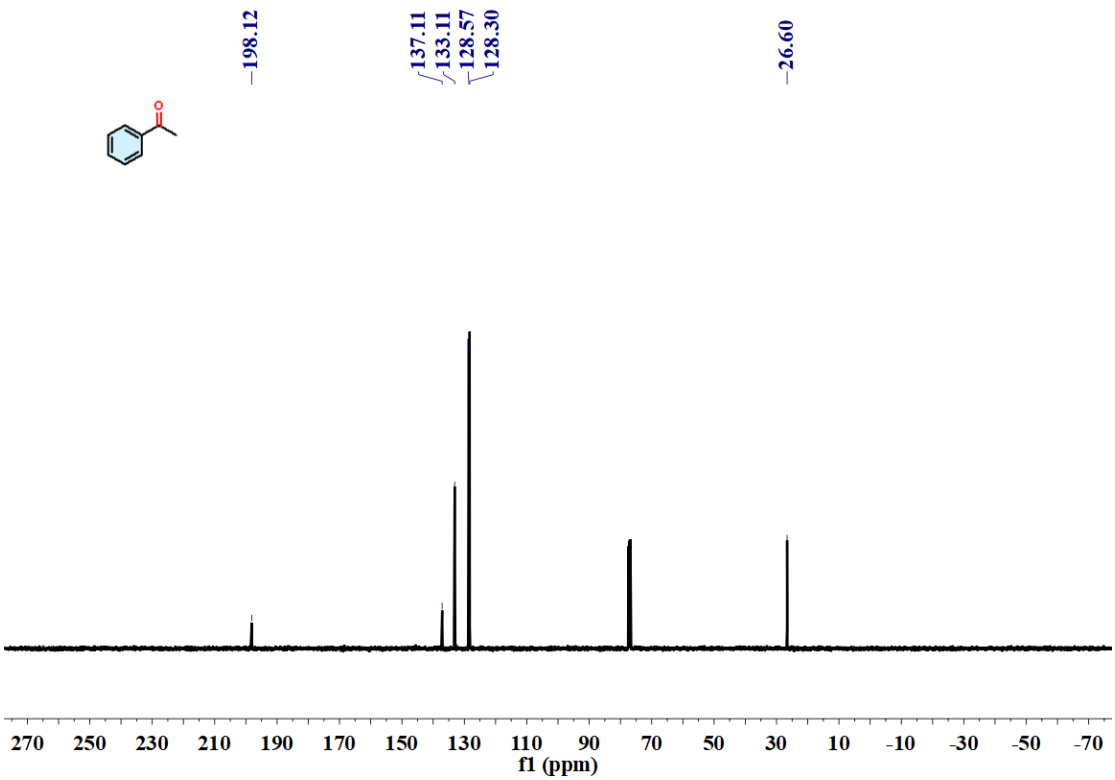
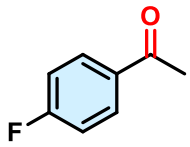


Fig. S11. ^{13}C NMR spectra of **1** in $CDCl_3$.

2.



Colorless oil (21.2 mg); 77% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.47 – 7.40 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.44, 166.98, 164.45, 133.57, 133.54, 130.96, 130.87, 115.71, 115.50, 26.49.

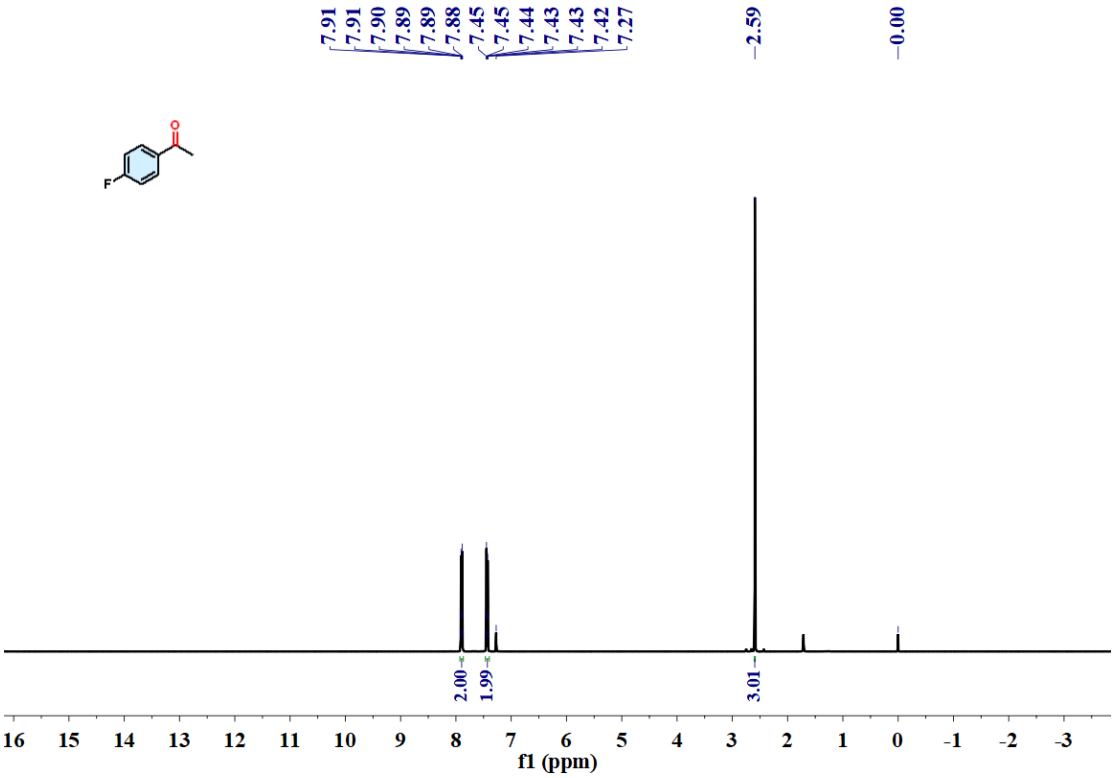


Fig. S12. ^{1}H NMR spectra of **2** in $CDCl_3$.

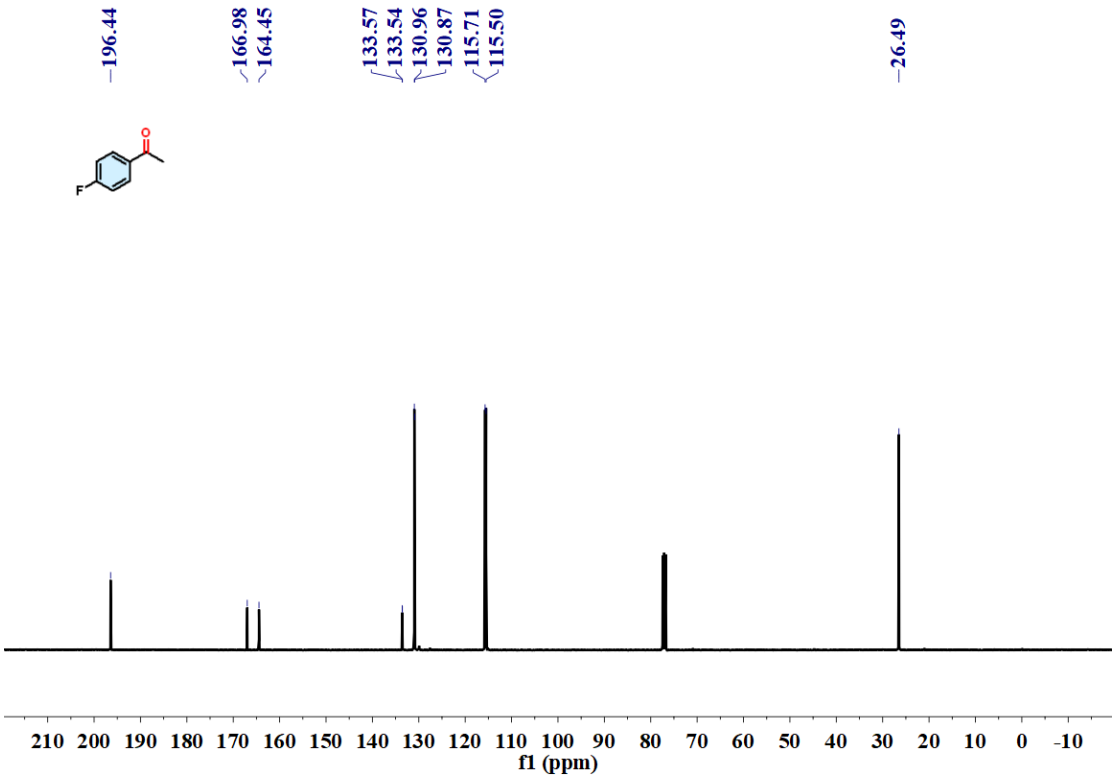
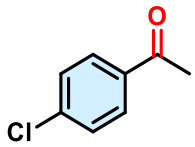


Fig. S13. ^{13}C NMR spectra of **2** in $CDCl_3$.

3.



Colorless oil (24.6 mg); 82% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.93, 139.59, 135.41, 129.75, 128.91, 26.62, 26.59.

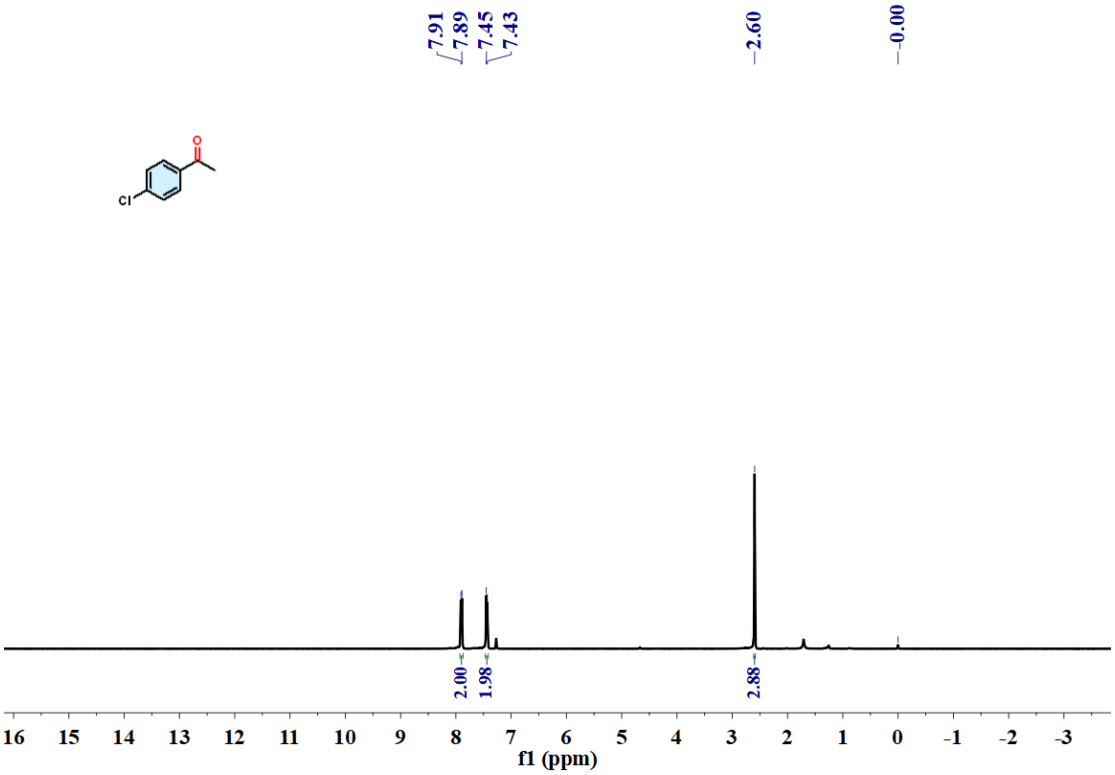


Fig. S14. ^{1}H NMR spectra of **3** in $CDCl_3$.

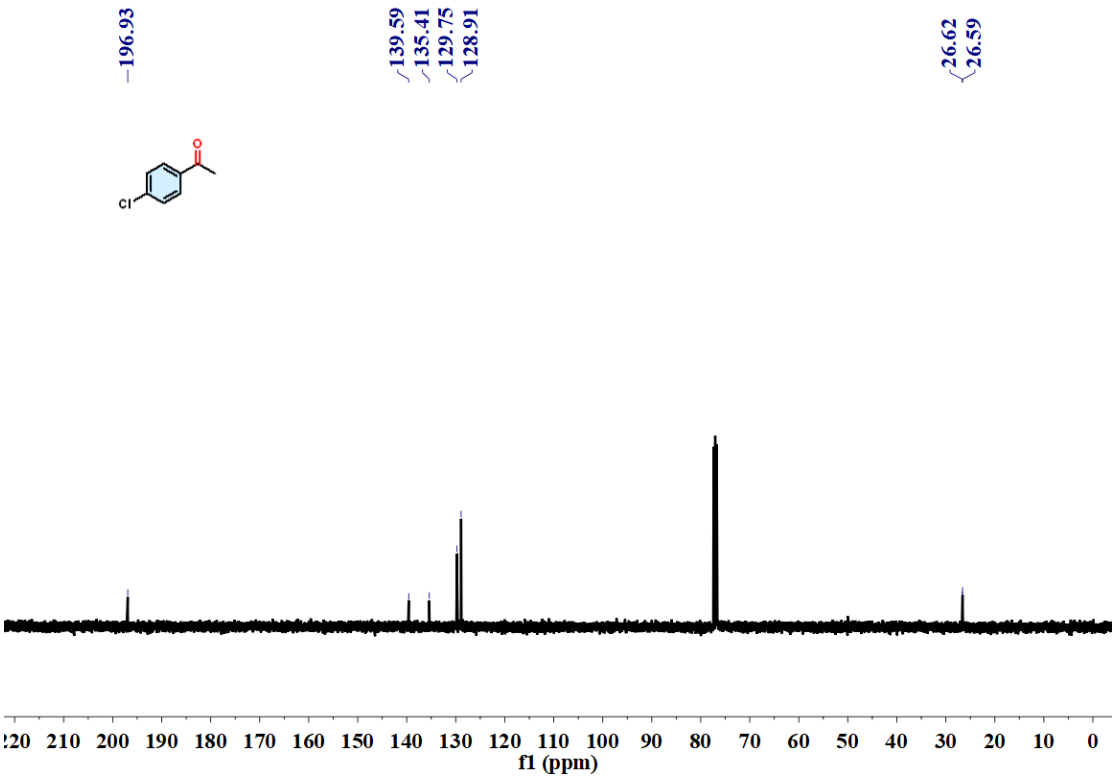
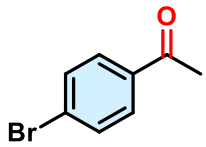


Fig. S15. ^{13}C NMR spectra of **3** in $CDCl_3$.

4.



Colorless oil (32.4 mg); 81% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.60 (dd, *J* = 8.5, 1.6 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.09, 135.79, 131.91, 129.86, 128.33, 26.60, 26.57.

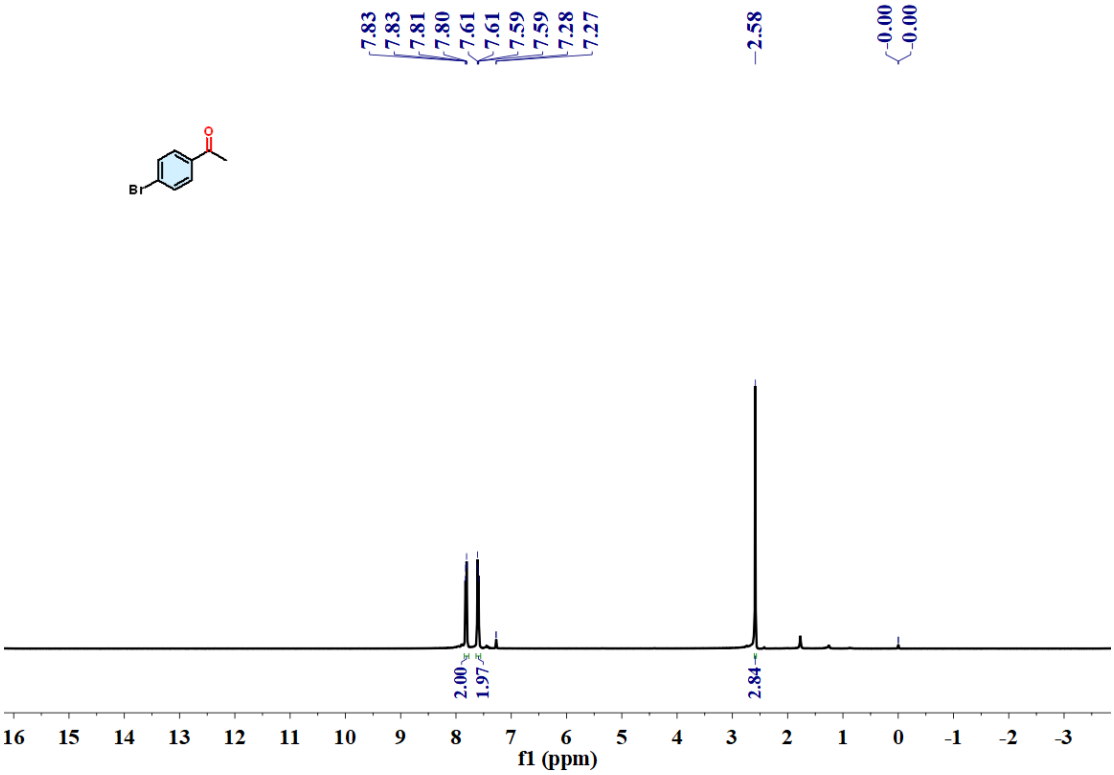


Fig. S16. ^{1}H NMR spectra of **4** in $CDCl_3$.

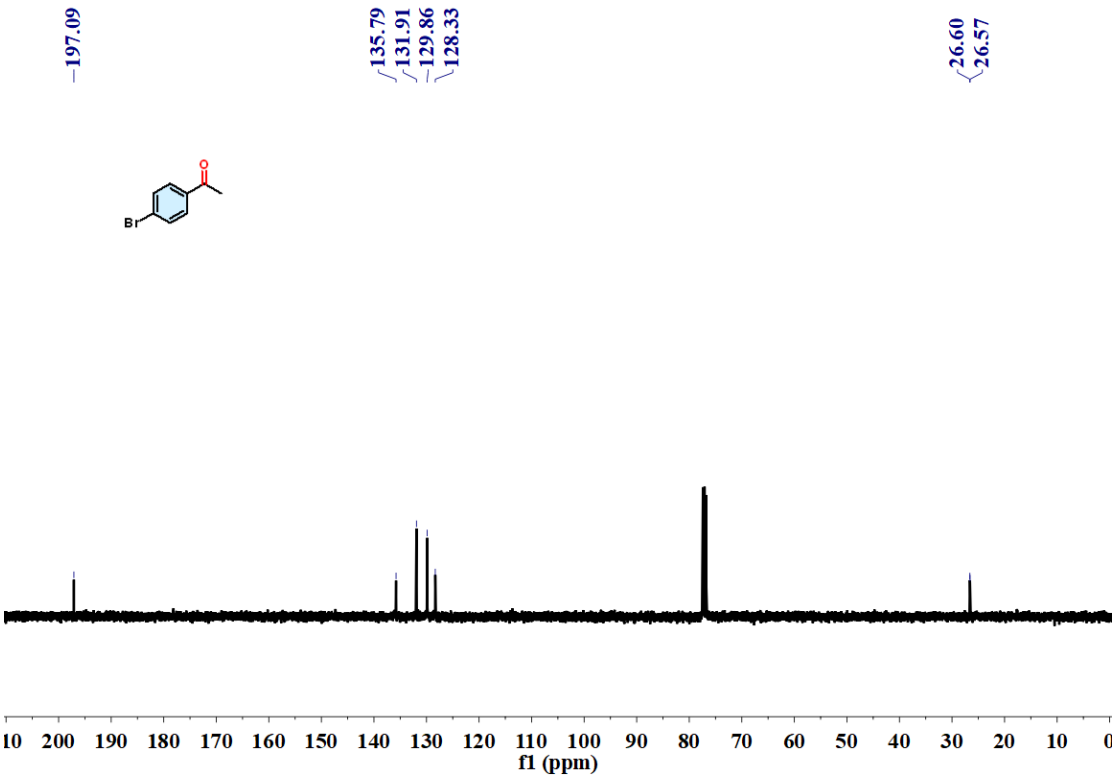
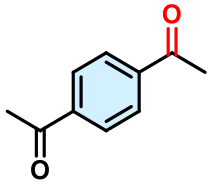


Fig. S17. ^{13}C NMR spectra of **4** in $CDCl_3$.

5.



White solid (23.9 mg); 74% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.4 Hz, 4H), 2.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.46, 140.05, 128.41, 26.84.

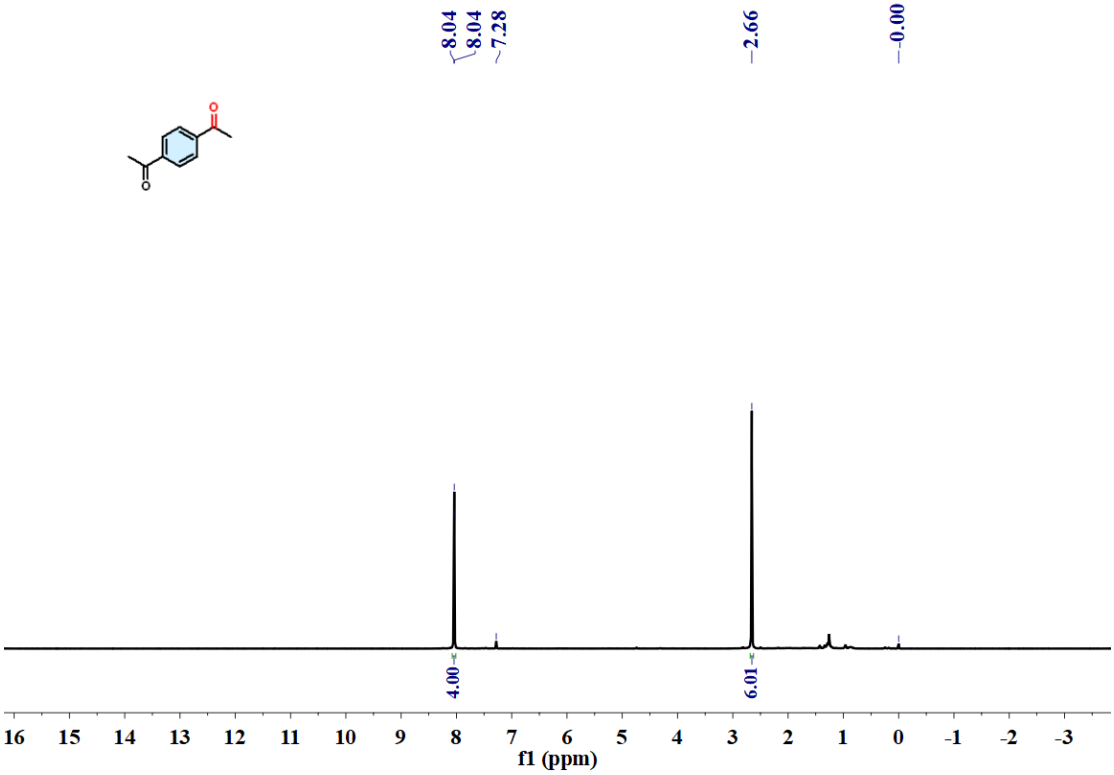


Fig. S18. ^{1}H NMR spectra of **5** in $CDCl_3$.

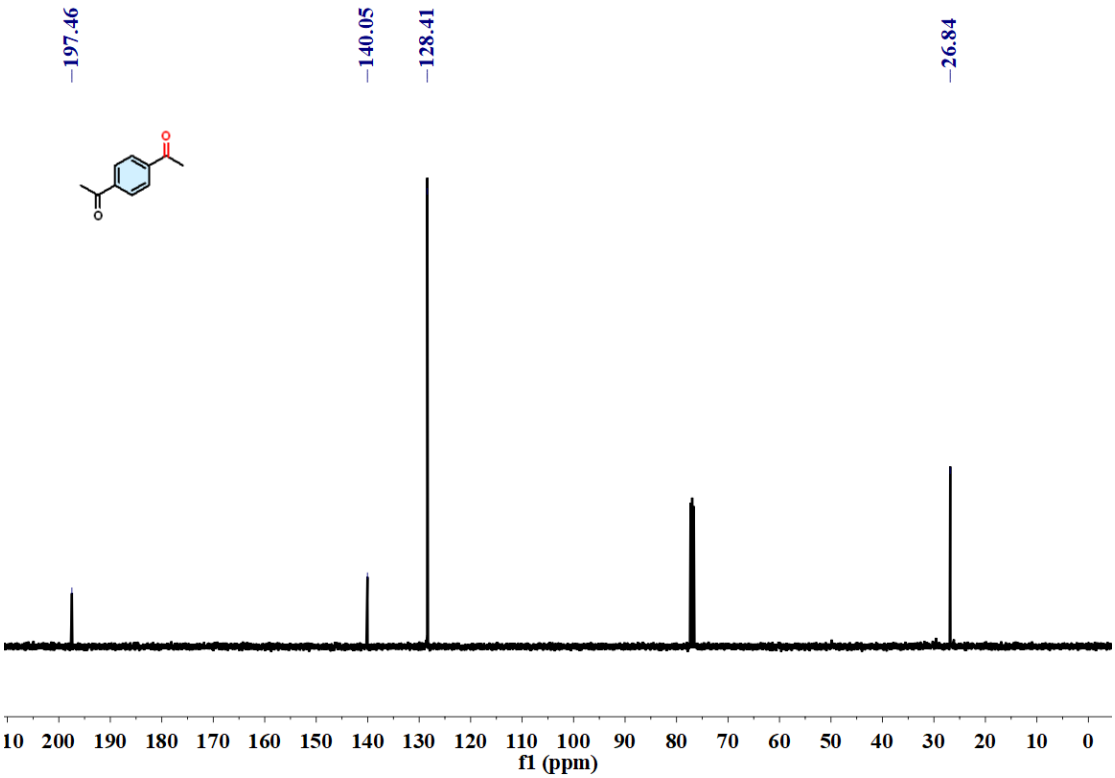
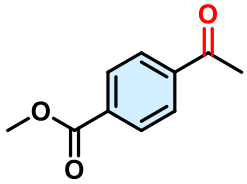


Fig. S19. ^{13}C NMR spectra of **5** in $CDCl_3$.

6



yellow oil (26.7 mg); 75% yield; eluent: PE/EA=10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 2.61 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.93, 168.90, 154.34, 134.69, 129.95, 121.78, 26.60, 21.14.

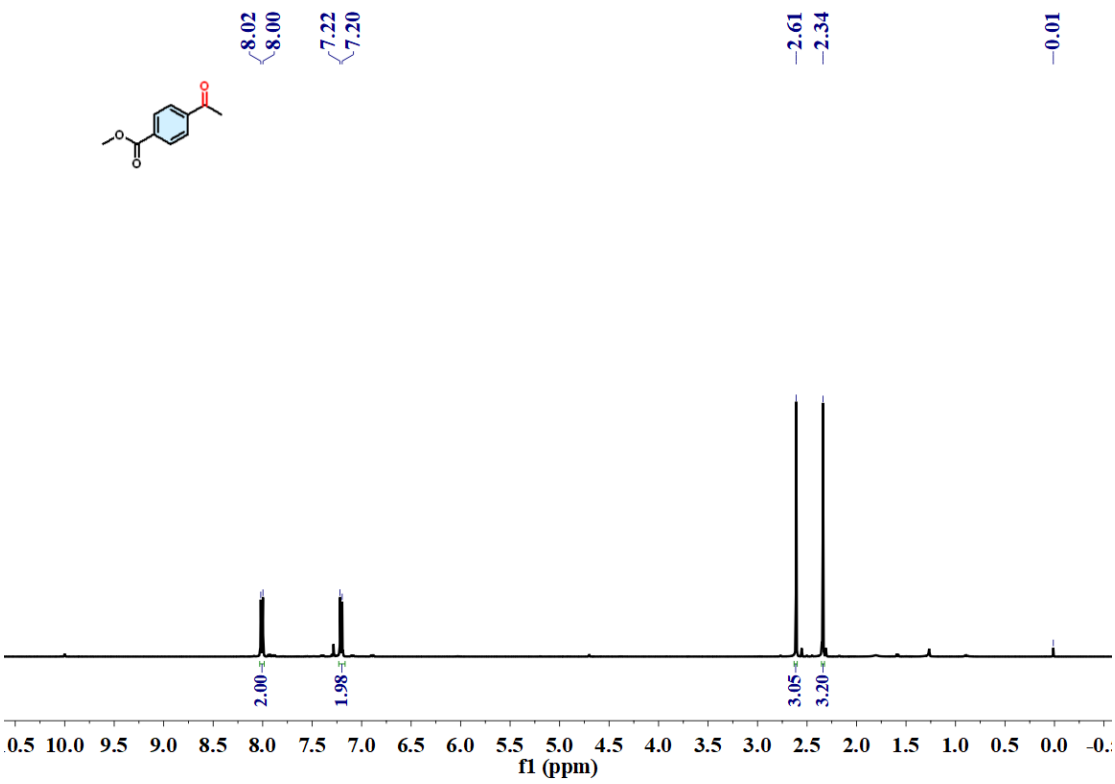


Fig. S20. ^{1}H NMR spectra of **6** in $CDCl_3$.

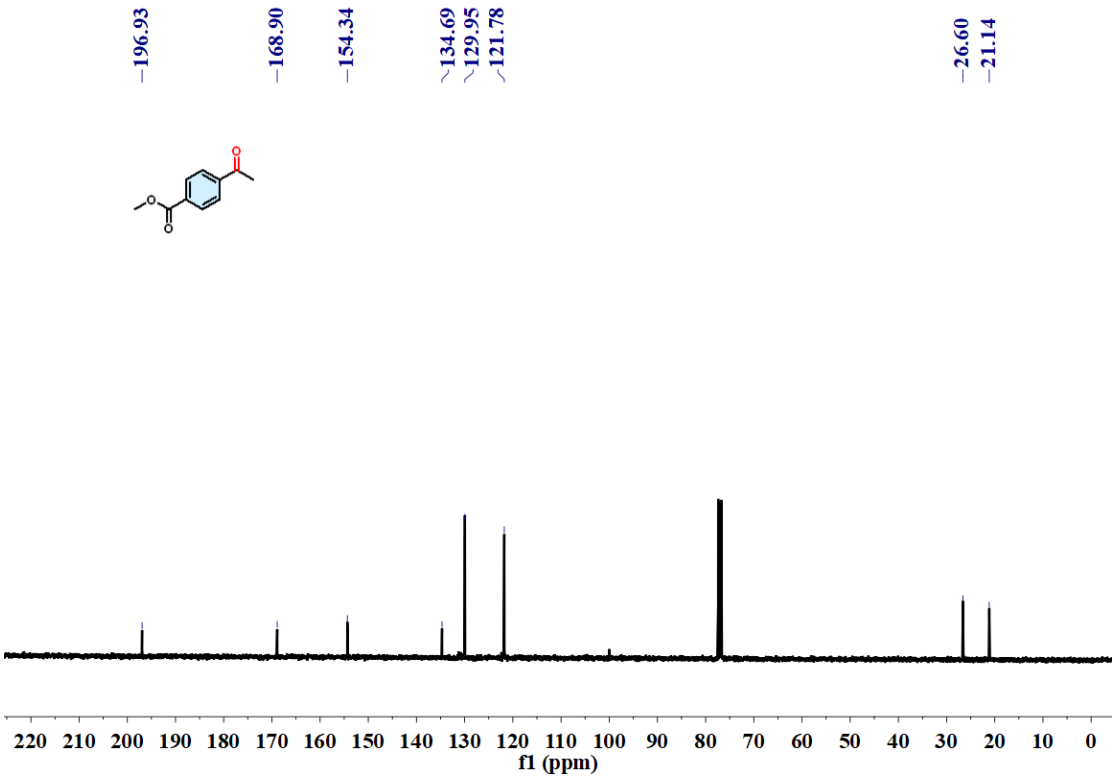
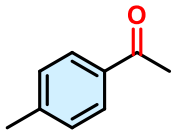


Fig. S21. ^{13}C NMR spectra of **6** in $CDCl_3$.

7.



Colorless oil (20.9 mg); 78% yield; eluent: PE/EA = 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 2.57 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.80, 143.85, 134.68, 129.23, 128.42, 26.51, 21.61.

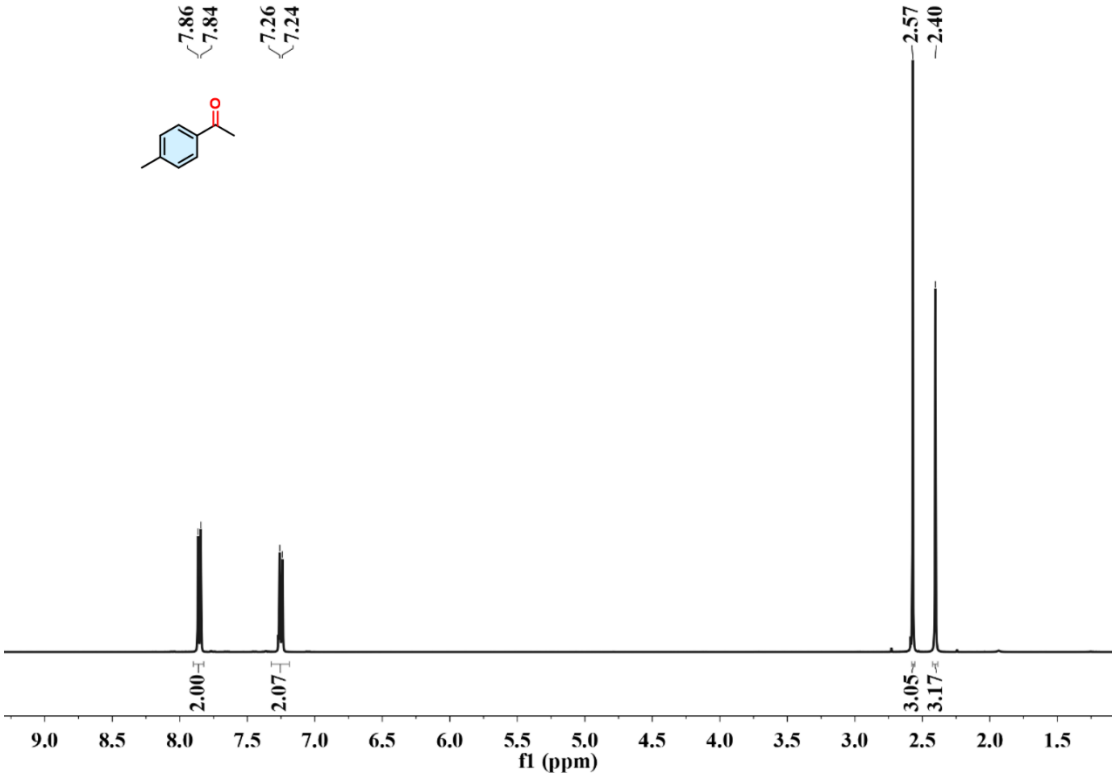


Fig. S22. ^{1}H NMR spectra of **7** in $CDCl_3$.

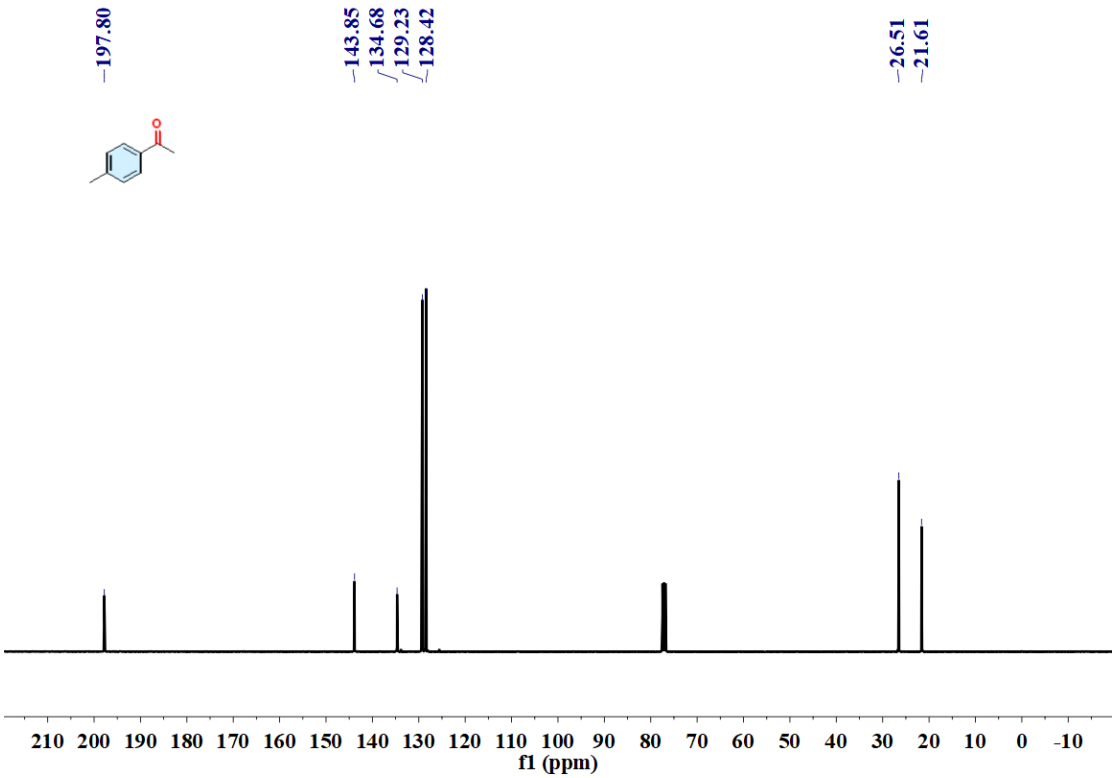
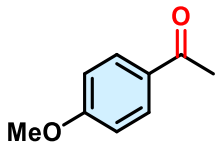


Fig. S23. ^{13}C NMR spectra of **7** in $CDCl_3$.

8



Yellow solid (23.7 mg); 79% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 6.95 – 6.88 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 163.31, 131.60, 122.60, 113.60, 55.43, 51.88.

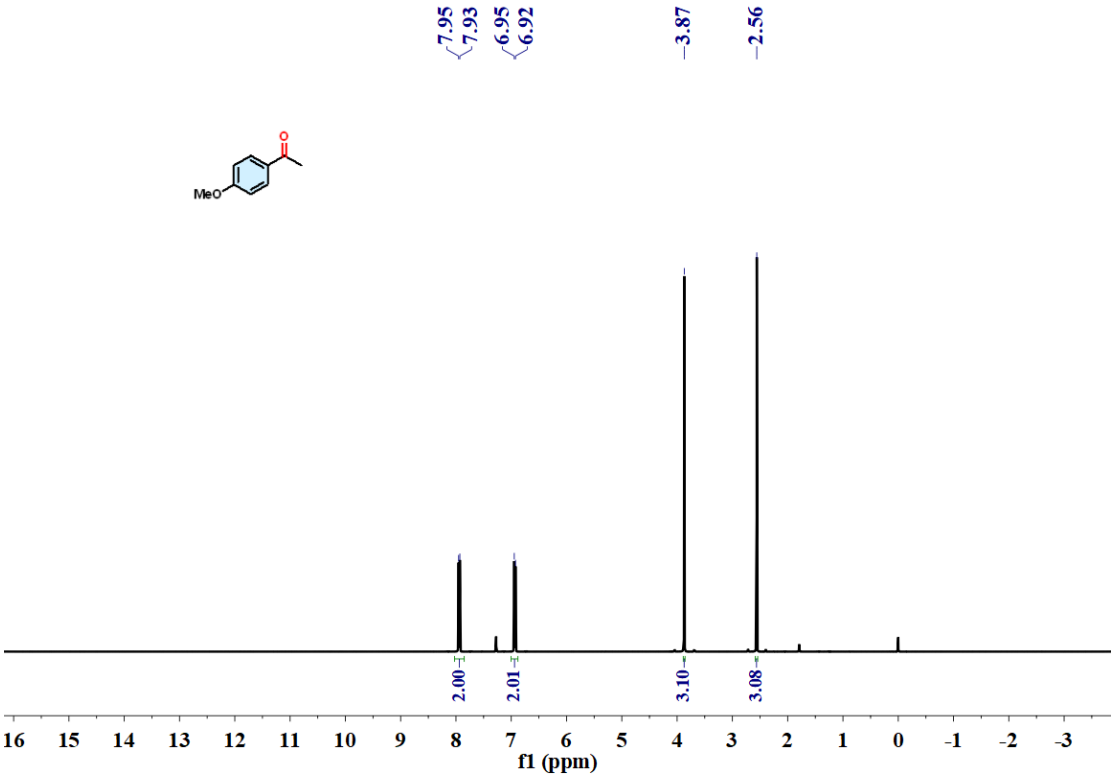


Fig. S24. ^{1}H NMR spectra of **8** in $CDCl_3$.

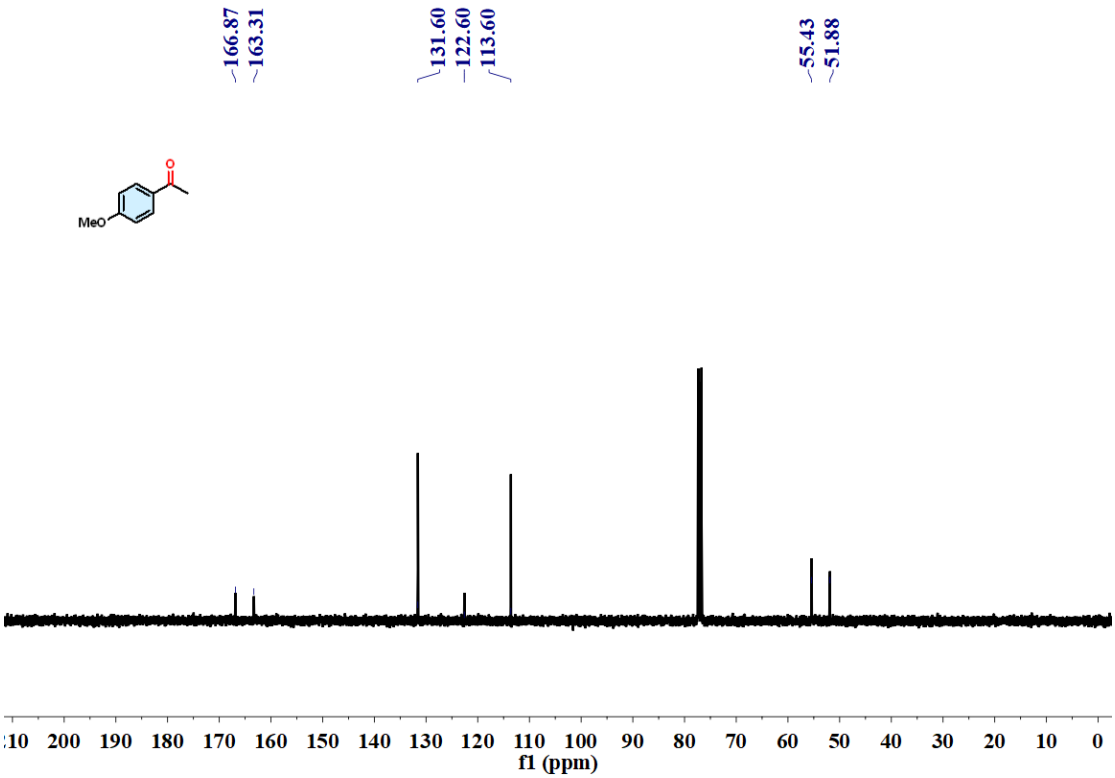
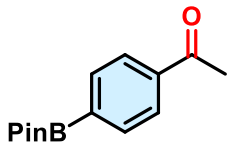


Fig. S25. ^{13}C NMR spectra of **8** in $CDCl_3$.

9



White solid (37.9 mg); 71% yield; eluent: PE/EA = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.84 (m, 4H), 2.64 – 2.58 (m, 3H), 1.38 – 1.34 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.56, 138.97, 134.94, 127.32, 84.24, 26.84, 24.88.

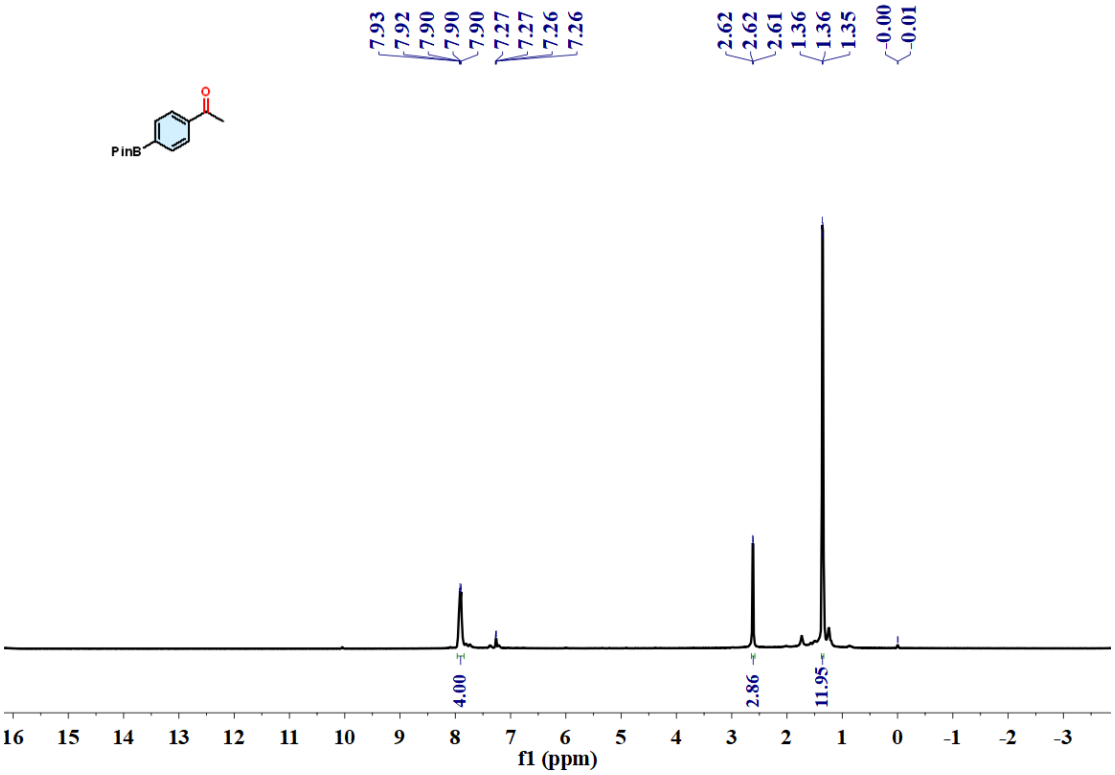


Fig. S26. ^{1}H NMR spectra of **9** in $CDCl_3$.

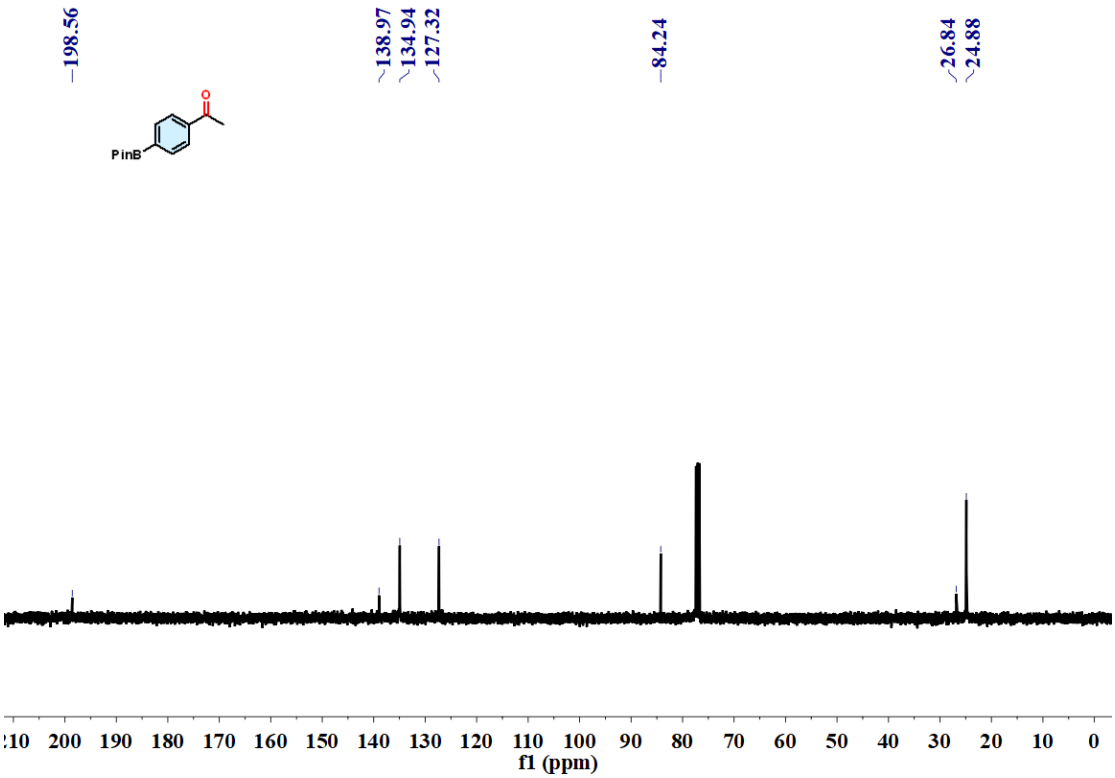
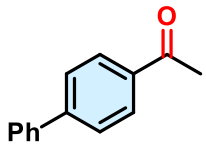


Fig. S27. ^{13}C NMR spectra of **9** in $CDCl_3$.

10



White solid (37.6 mg); 92% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.1 Hz, 2H), 7.43 – 7.36 (m, 1H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.78, 145.80, 139.89, 135.87, 128.99, 128.94, 128.26, 127.30, 127.25, 77.39, 77.07, 76.75, 26.70.

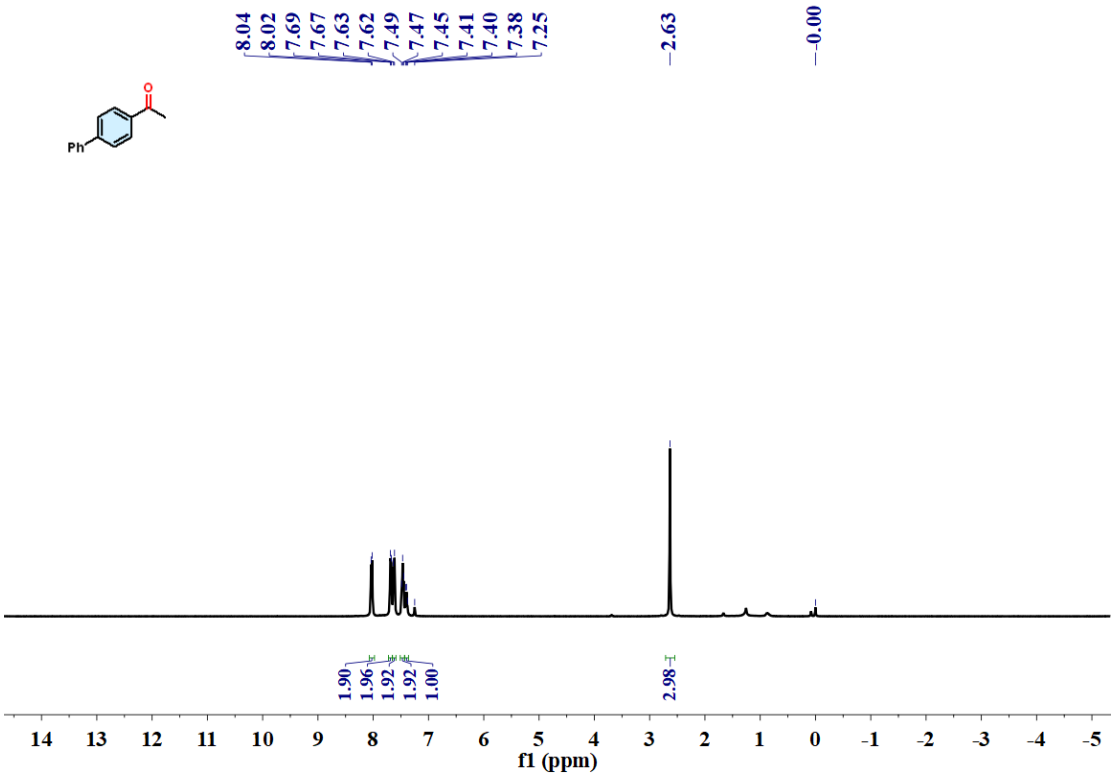


Fig. S28. ^{1}H NMR spectra of **10** in $CDCl_3$.

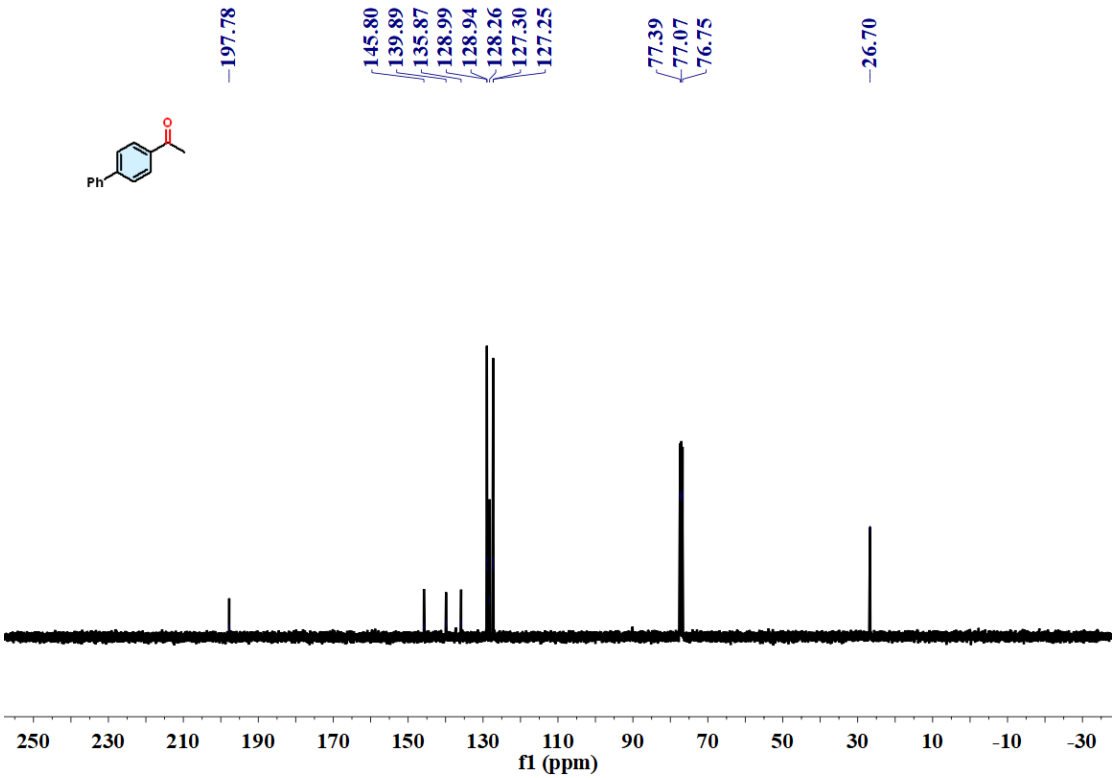
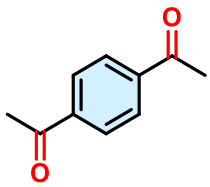


Fig. S29. ^{13}C NMR spectra of **10** in $CDCl_3$.

11



White solid (18.1 mg); 56% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.4 Hz, 4H), 2.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.56, 140.15, 128.51, 26.94.

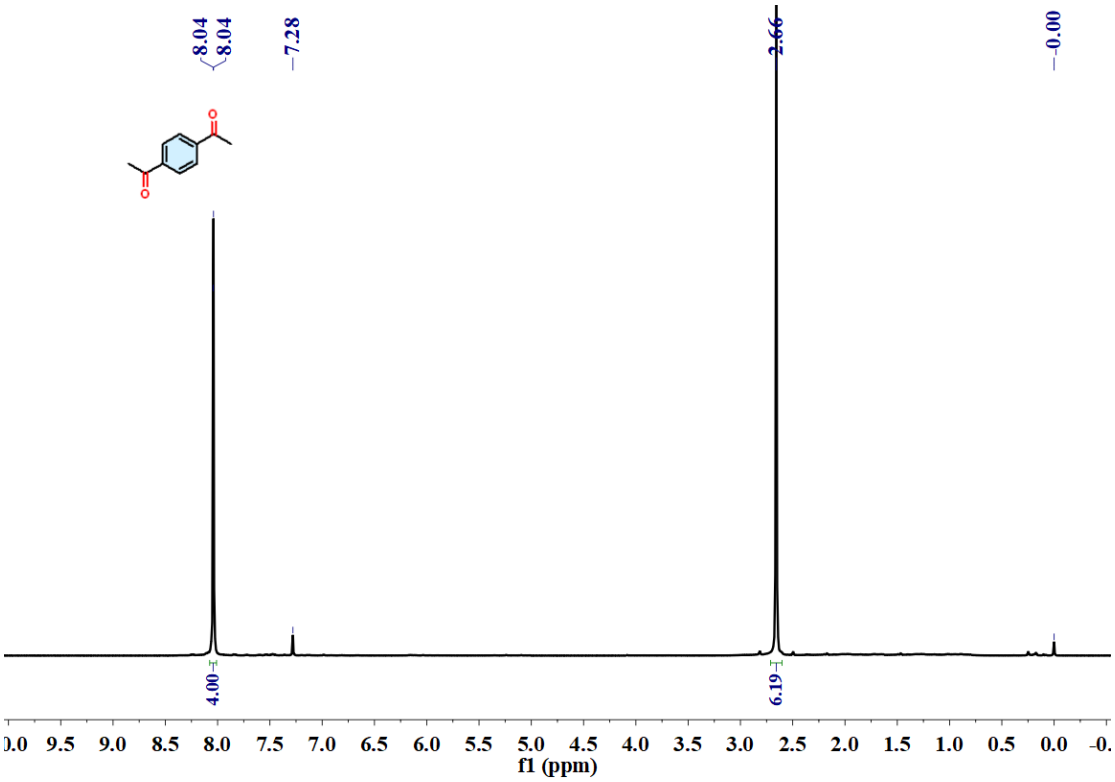


Fig. S30. ^{1}H NMR spectra of **11** in $CDCl_3$.

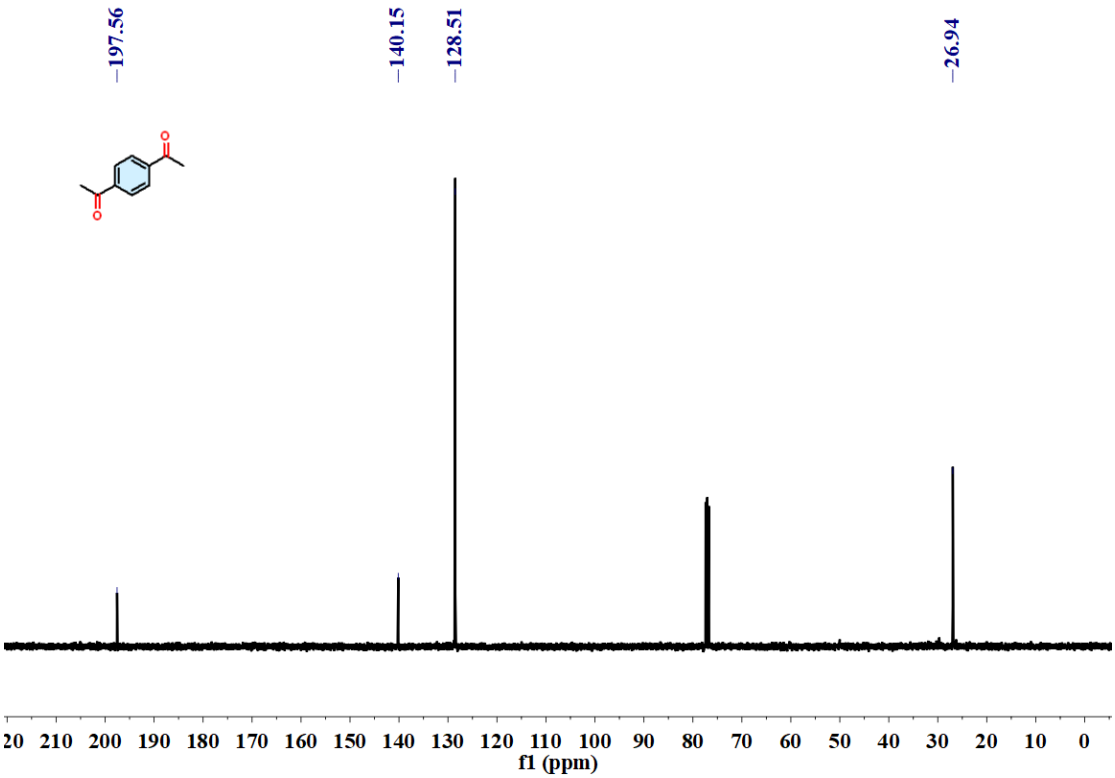
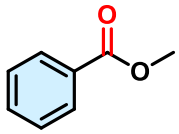


Fig. S31. ^{13}C NMR spectra of **11** in $CDCl_3$.

12



Colorless oil (18.7 mg); 69% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 132.95, 130.15, 129.60, 128.40, 52.15.

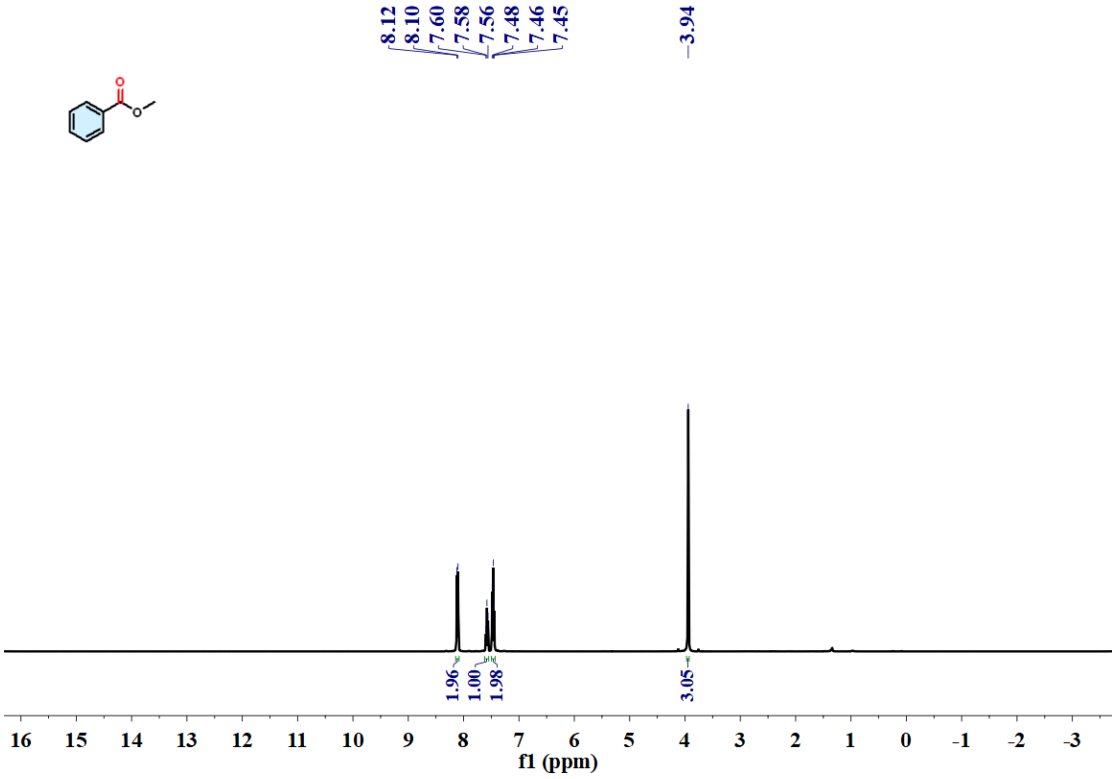


Fig. S32. ^{1}H NMR spectra of **12** in $CDCl_3$.

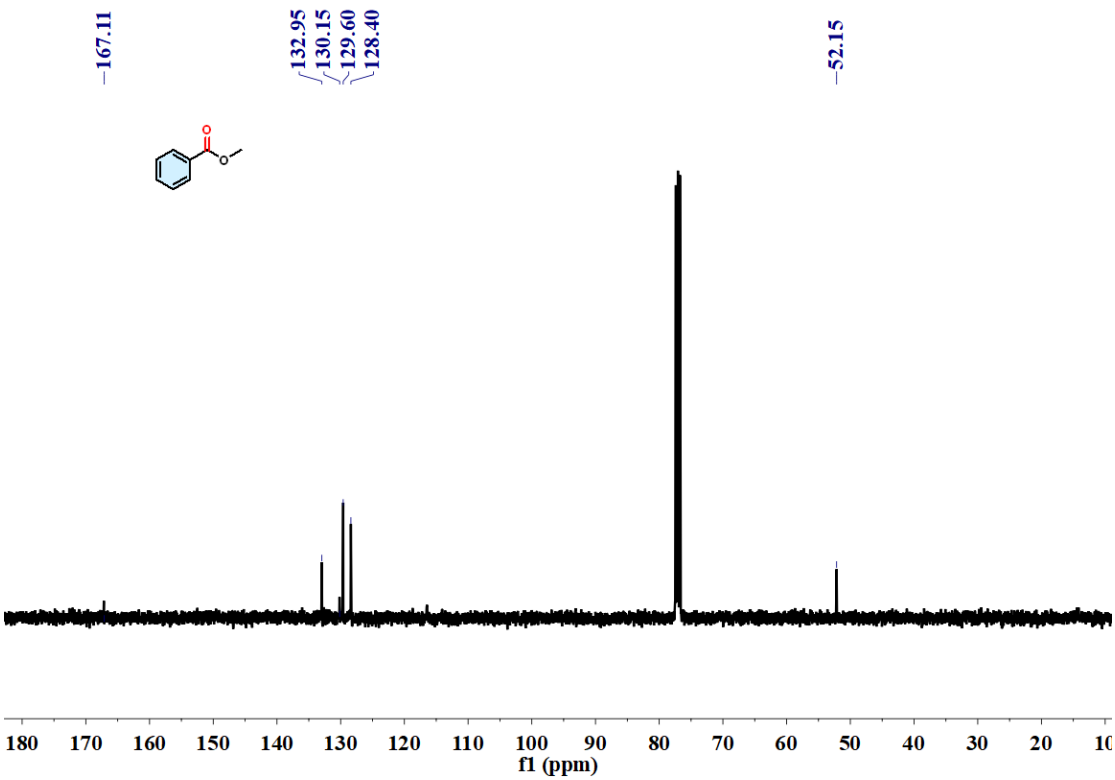
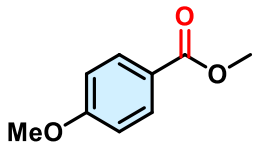


Fig. S33. ^{13}C NMR spectra of **12** in $CDCl_3$.

13



Yellow solid (20.5 mg); 62% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 6.95 – 6.88 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.89, 163.33, 131.60, 122.60, 113.60, 55.43, 51.88.

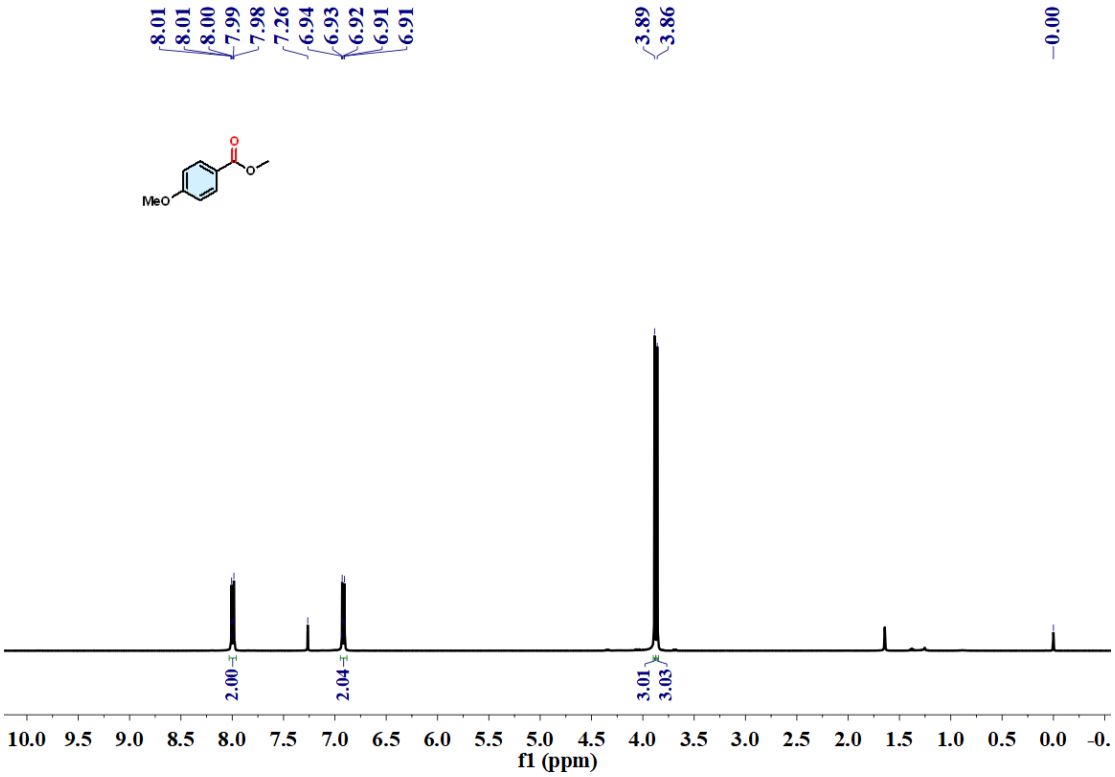


Fig. S34. ^{1}H NMR spectra of **13** in $CDCl_3$.

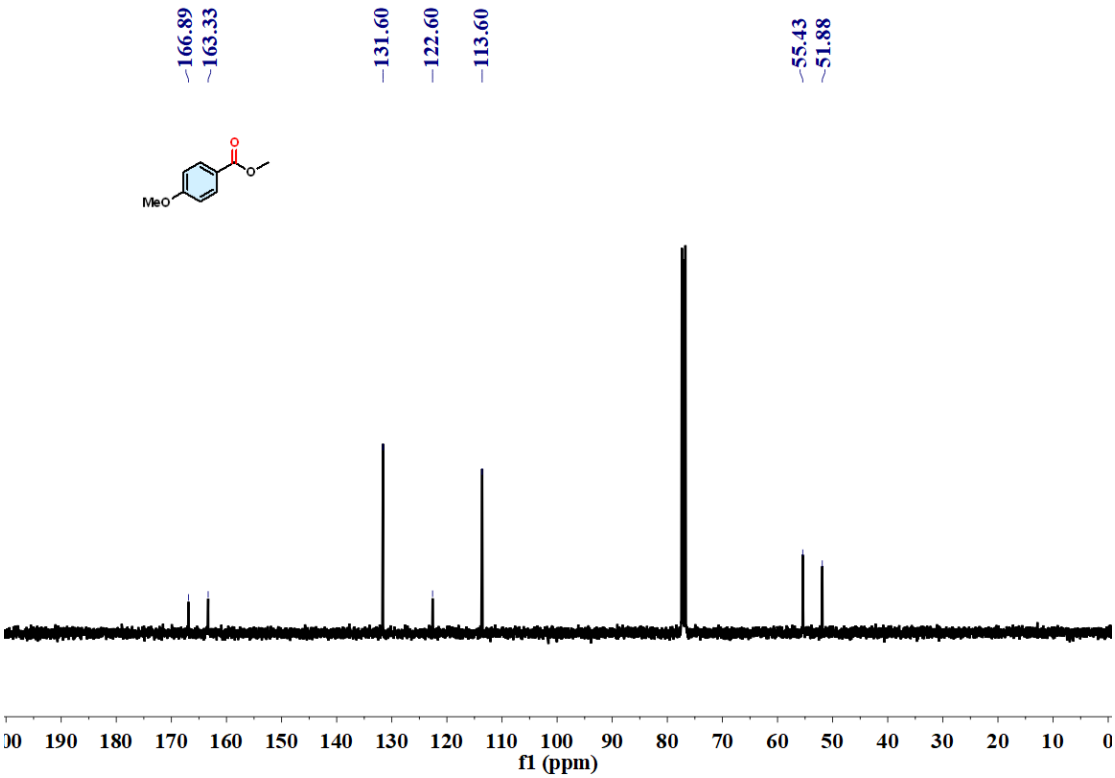
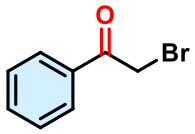


Fig. S35. ^{13}C NMR spectra of **13** in $CDCl_3$.

14.



Yellow solid (37.6 mg); 94% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.65 – 7.59 (m, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 4.47 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.33, 134.02, 128.98, 128.91, 128.56, 30.97.

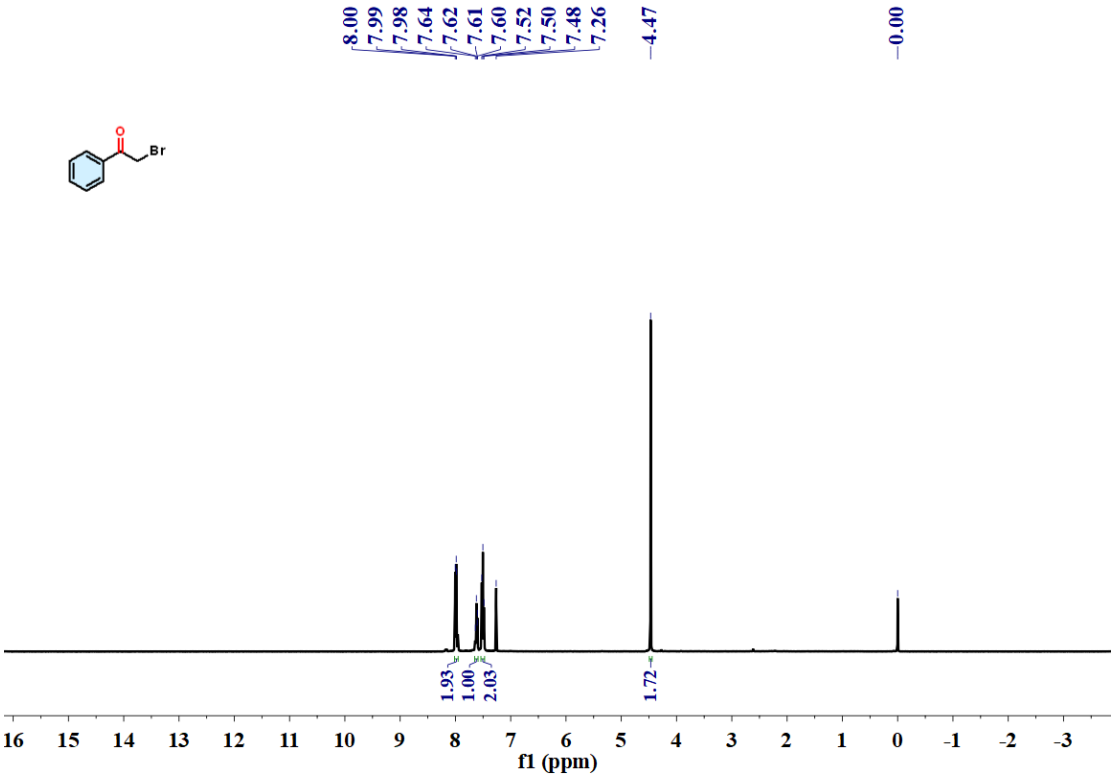


Fig. S36. ^{1}H NMR spectra of **14** in $CDCl_3$.

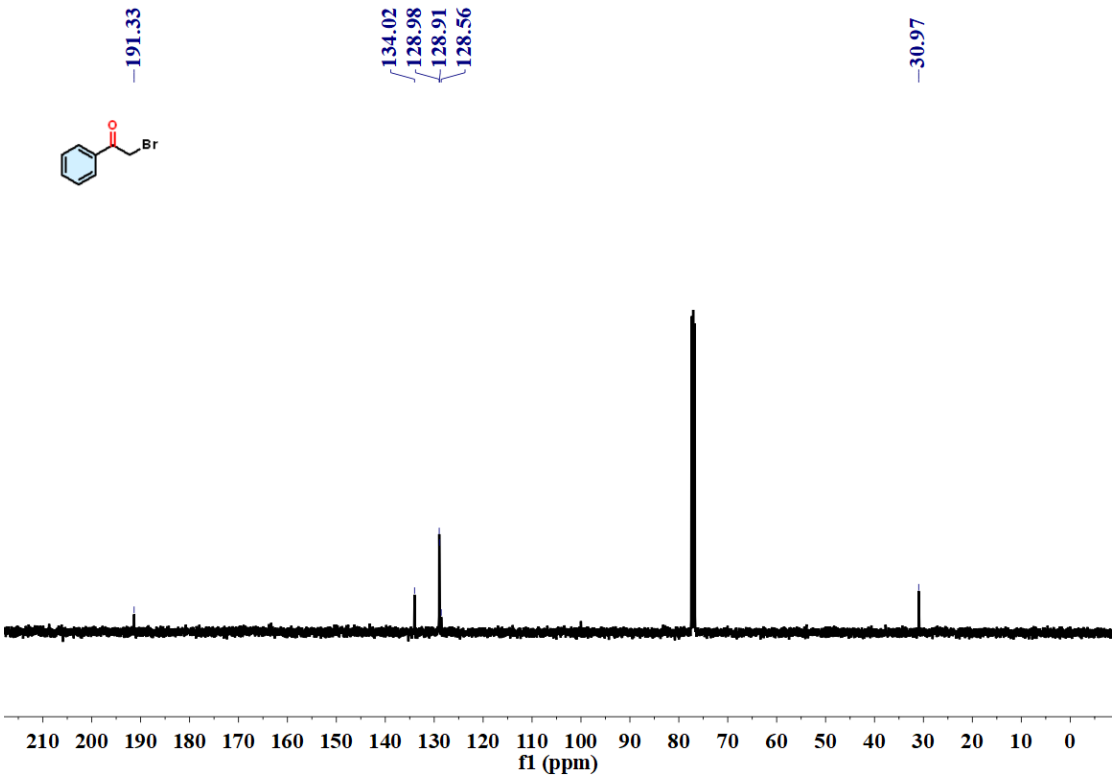
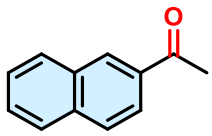


Fig. S37. ^{13}C NMR spectra of **14** in $CDCl_3$.

15.



Red solid (30.0 mg); 88% yield; eluent: PE/EA=20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.63 – 7.51 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.15, 135.59, 134.48, 132.51, 130.23, 129.57, 128.50, 128.44, 127.80, 126.80, 123.90, 77.39, 77.07, 76.75, 26.73.

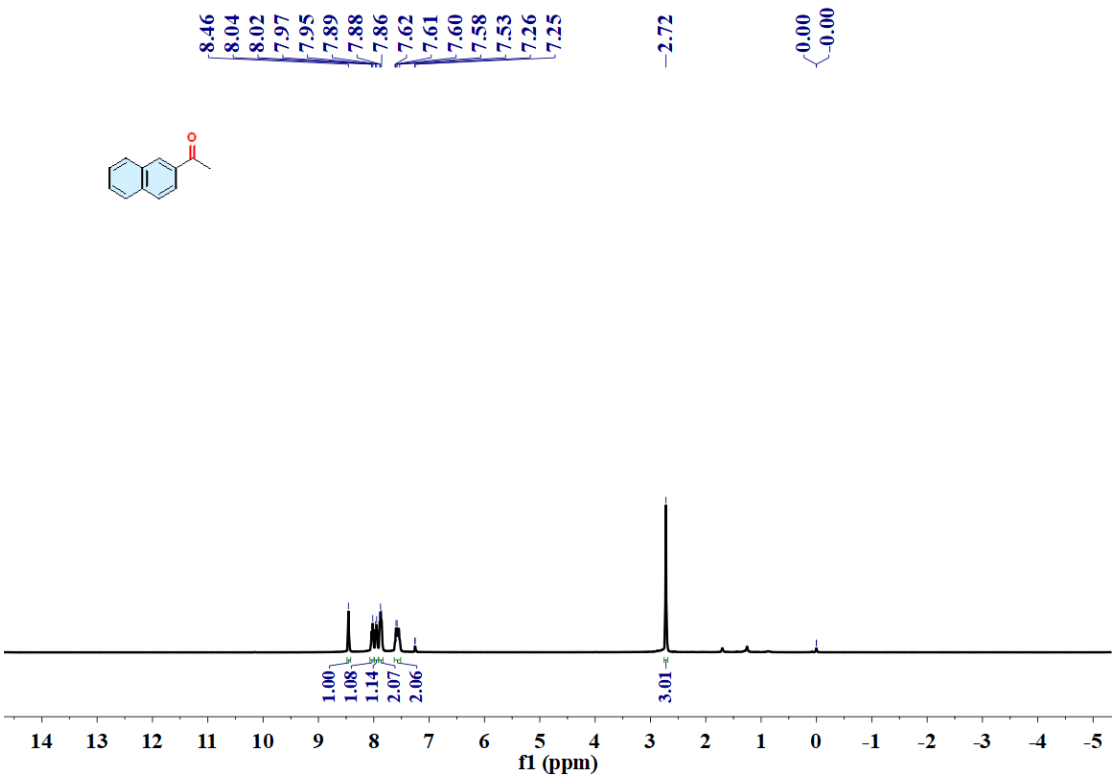


Fig. S38. ^{1}H NMR spectra of **15** in $CDCl_3$.

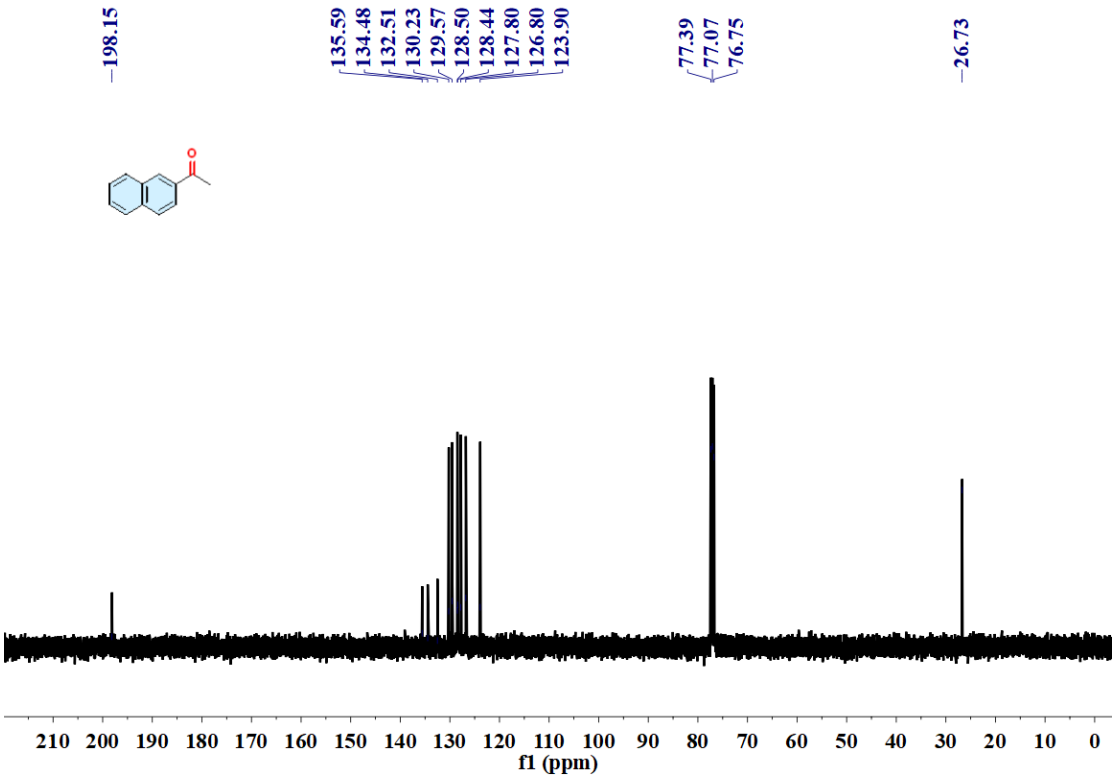


Fig. S39. ^{13}C NMR spectra of **15** in $CDCl_3$.