

Electronic Supplementary Information

Iron-Catalyzed Aerobic Oxidative Cleavage of C–C σ -Bond Using Air as Oxidant: Chemoselectively to Carbon Chain-Shortened Aldehydes, Ketones and 1,2-Dicarbonyl Compounds

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1) General Information

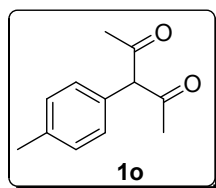
Reagents including 2-iodoaniline and its derivatives, 1,3-diones, α -aryl ketones, benzenacetaldehyde and 3-phenylpropanal were purchased and used as received without further purification. FeCl_3 (99.99%) was purchased from Sigma-Aldrich. NMR spectra of the products were recorded using a Bruker Advance TM spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C in CDCl_3 unless otherwise noted. High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. Isolated yield was obtained by column chromatography (300-400 mesh), and ethyl acetate/petroleum ether (boiling range: 30-60 $^\circ\text{C}$) was used as the eluent.

2) General Procedures for Preparation of Substrates (1o to 1r, 1u to 1x) and Spectra Analytical Data

1,3-Dicarbonyl compounds **1o**¹, **1p**¹, **1q**¹, **1r**², and substituted *N*-(2-(2-oxopropyl)phenyl)acetamides including **1u**³, **1v**³, **1w**³, **1x**³ were prepared through previously reported methods.

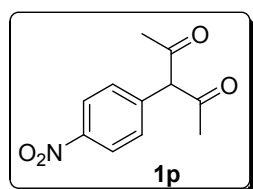
General procedure for the preparation of 1o to 1q: In the glove box, a mixture of iodobenzene (1.0 mmol), 1,3-dione (3.0 mmol), K₂CO₃ (4 mmol), CuI (0.1 mmol), L-proline (0.2 mmol) in 2 mL of DMSO was added into a 50 mL Schlenk tube with a magnetic bar. Then the tube was tightly screw-capped and stirred at 90 °C for 9-12 h. After cooling to room temperature, the mixture was purified by flash column chromatography using petroleum ether/ethyl acetate (10:1) as the eluent to afford the corresponding product.

3-*p*-tolylpentane-2,4-dione (**1o**)



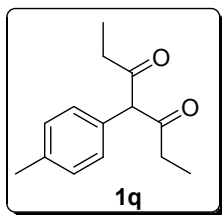
White solid; 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 16.68 (s, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.08–7.02 (m, 2H), 2.37 (s, 3H), 1.88 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 190.9, 137.1, 133.9, 130.9, 129.5, 115.0, 24.1, 21.2. HRMS (ESI) Calcd for C₁₂H₁₄NaO₂: [M+Na]⁺, 213.0886; Found: 213.0882.

3-(4-nitrophenyl)pentane-2,4-dione (**1p**)



Yellow solid; 66% yield. ¹H NMR (400 MHz, CDCl₃) δ 16.71 (s, 1H), 8.24–8.15 (m, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 1.84 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 190.5, 147.4, 144.1, 132.2, 124.1, 113.7, 24.2. HRMS (ESI) Calcd for C₁₁H₁₁NNaO₄: [M+Na]⁺, 244.0580; Found: 244.0582.

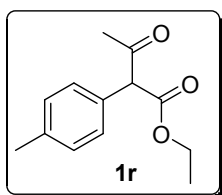
4-*p*-tolylheptane-3,5-dione (**1q**)



Colorless oil; 64% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 16.62 (s, 1H), 7.10 (d, $J = 7.8$ Hz, 2H), 6.96 (d, $J = 7.9$ Hz, 2H), 2.29 (s, 3H), 2.03 (q, $J = 7.5$ Hz, 4H), 0.93 (t, $J = 7.5$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 194.2, 137.1, 133.4, 131.1, 129.5, 113.7, 29.9, 21.2, 9.6. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_2$: $[\text{M}+\text{Na}]^+$, 241.1199; Found: 241.1196.

Preparation of 1r: In the glove box, a mixture of 1-iodo-4-methylbenzene (0.5 mmol), ethyl acetoacetate (0.6 mmol), CuI (0.1 mmol), L-proline (0.2 mmol), Cs_2CO_3 (2 mmol) in DMSO (2 mL) was added into a 50 mL Schlenk tube with a magnetic bar. Then the tube was tightly screw-capped and stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was purified by flash column chromatography using petroleum ether/ethyl acetate (10:1) as the eluent to afford **1r** in 62% yield.

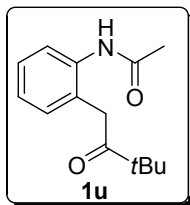
ethyl 3-oxo-2-p-tolylbutanoate (1r)



Colorless oil; 62% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.13 (d, $J = 0.6$ Hz, 0.3 H), 7.27–7.00 (m, 4H), 4.65 (s, 0.7H), 4.25–4.12 (m, 2H), 2.36–2.35 (s, 3H), 2.17 (s, 2H), 1.85 (s, 1H), 1.18–1.25 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 201.8, 173.8, 172.8, 168.7, 138.1, 136.5, 132.2, 131.1, 129.8, 129.6, 129.2 (two peaks overlap), 129.1, 128.8, 126.2, 104.1, 65.4, 61.5, 60.6, 41.0, 28.7, 21.2, 21.1, 19.9, 14.2, 14.1. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{16}\text{NaO}_3$: $[\text{M}+\text{Na}]^+$, 243.0992; Found: 243.0995.

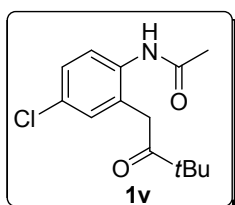
General procedure for the preparation of 1u to 1x: A mixture of 2-iodoaniline derivatives (0.5 mmol), 1,3-dione (2.5 mmol), Cs_2CO_3 (1.5 mmol) and CuI (0.05 mmol) in 2 mL CH_3CN was added to a 50 mL Schlenk tube with a magnetic bar. Then the tube was tightly screw-capped and stirred at 90 °C for 12 h. After cooling to room temperature, the mixture was purified by flash column chromatography using petroleum ether/ethyl acetate (5:1 then 2:1) as the eluent to afford the corresponding *N*-(2-(2-oxopropyl)phenyl)acetamide.

N-(2-(3,3-dimethyl-2-oxobutyl)phenyl)acetamide (1u)



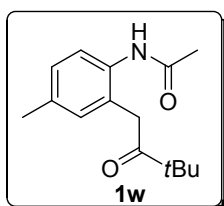
Pale yellow solid; 82% yield; $R_f = 0.62$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.08 (s, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.28–7.24 (m, 1H), 7.17–7.03 (m, 2H), 3.79 (s, 2H), 2.19 (s, 3H), 1.23 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.5 (C=O), 168.8 (C=O), 137.2, 130.6, 127.9, 127.4, 125.1, 45.3 (C), 40.7 (CH_2), 26.1 (CH_3), 24.4 (CH_3). HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$, 256.1308; Found: 256.1311.

N-(4-chloro-2-(3,3-dimethyl-2-oxobutyl)phenyl)acetamide (1v)



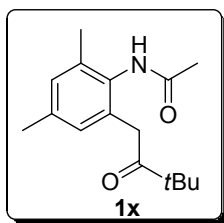
Pale yellow solid; 73% yield; $R_f = 0.63$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.94 (s, 1H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.20 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.10 (d, $J = 2.3$ Hz, 1H), 3.73 (s, 2H), 2.16 (s, 3H), 1.22 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 215.6 (C=O), 168.9 (C=O), 135.7, 130.3, 130.1, 129.6, 127.8, 126.5, 45.3 (C), 40.3 (CH_2), 26.0 (CH_3), 24.2 (CH_3). HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{18}\text{ClNNaO}_2$: $[\text{M}+\text{Na}]^+$, 290.0918; Found: 290.0925.

N-(2-(3,3-dimethyl-2-oxobutyl)-4-methylphenyl)acetamide (1w)



Pale yellow solid; 84% yield; $R_f = 0.65$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.80 (s, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.04 (d, $J = 7.4$ Hz, 1H), 6.92 (s, 1H), 3.73 (s, 2H), 2.27 (s, 3H), 2.13 (s, 3H), 1.21 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.0 (C=O), 168.9 (C=O), 134.9, 134.4, 131.2, 128.4, 128.1, 125.4, 45.1 (C), 40.6 (CH_2), 26.1 (CH_3), 24.1 (CH_3), 20.8 (CH_3). HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{21}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$, 270.1465; Found: 270.1472.

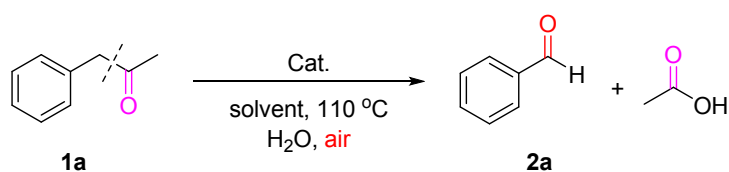
N-(2-(3,3-dimethyl-2-oxobutyl)-4,6-dimethylphenyl)acetamide (1x)



Pale yellow solid; 86% yield; $R_f = 0.66$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (s, 1H), 6.95 (s, 1H), 6.75 (s, 1H), 3.76 (s, 2H), 2.26 (s, 3H), 2.12 2.11 (s, 6H), 1.22 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 215.1 (C=O), 168.8 (C=O), 136.8, 136.3, 132.5, 132.2, 130.6, 128.8, 44.8 (C), 41.0 (CH_2), 26.4 (CH_3), 23.2 (CH_3), 20.9 (CH_3), 18.4 (CH_3). HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{23}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$, 284.1621; Found: 284.1623.

3) Experimental Procedure for C–C Cleavage and Spectra Analytical Data

Table S1. Optimization of the C–C cleavage of 1-phenylpropan-2-one



Entry	Solvent	Catalyst	Temperature ($^\circ\text{C}$)	Yield (%) ^a
1	DMSO	FeCl_3	90	77
2	DMSO	---	90	n.r.
3 ^b	DMSO	FeCl_3	90	64
4	1,4-dioxane	FeCl_3	90	44
5	CH_3CN	FeCl_3	90	29
6	DMF	FeCl_3	90	54
7	DMSO	FeCl_3	110	83
8	DMSO	FeCl_2	110	47
9	DMSO	$\text{Fe}(\text{OTf})_3$	110	49
10	DMSO	CuI	110	78

11 ^c	DMSO	HCl	110	trace
12 ^d	DMSO	FeCl ₃	110	90
13 ^e	DMSO	FeCl ₃	110	Trace

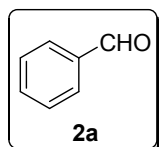
^aReaction conditions: **1a** (0.5 mmol), H₂O (0.5 mmol), 10.0 mol % of metal catalyst, air (1 atm), solvent (2 mL), 110 °C. 12 h. Isolated yield. ^bO₂ (1 atm) was inflated instead of air. ^cHCl (30 mol %). ^d20 h. ^eThe reaction was conducted in the glove box and no air was inflated.

Experimental procedure of Table S1, entry 12: A 50 mL Schlenk tube with a magnetic bar was charged with 1-phenylpropan-2-one (0.5 mmol), H₂O (0.5 mmol), FeCl₃ (0.05 mmol), and DMSO (2 mL). Then the tube was sealed and pressurized with 1.0 atm air after it was vacuumed and flushed with air three times. After that, it was stirred at 110 °C for 20 h. After cooling to room temperature, the reaction mixture was purified by column chromatography (300-400 mesh), and petroleum ether (boiling range: 30-60 °C) was used as the eluent and finally concentrated at 10 °C.

C-C bond cleavage of different β-carbonyl compounds (**1a** to **1n**) (Scheme 2)

A mixture of β-carbonyl compounds **1** (0.5 mmol), FeCl₃ (0.05 mmol), H₂O (0.5 mmol), and DMSO (2 mL) was added into a 50 mL Schlenk tube with a magnetic bar. Then the tube was sealed and pressurized with 1.0 atm air after it was vacuumed and flushed with air three times. After that, it was stirred at 110 °C for 20 h. After cooling to room temperature, the reaction mixture was purified by column chromatography on silica gel to give product **2**. Considering the volatility of the product, petroleum ether (boiling range: 30-60 °C) was used as the eluent and finally concentrated at 10 °C. The spectroscopic data of all the products are presented below. All the known compounds gave satisfactory spectroscopic values and are analogue to spectroscopic data reported in the literature.

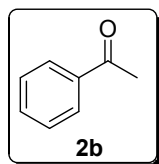
Benzaldehyde (**2a**)⁴



Purified by column chromatography (PE with boiling range: 30-60 °C) and finally concentrated at 10 °C; pale yellow liquid; 90% yield; *R*_f = 0.50 (10:1 PE/EA). ¹H NMR (400 MHz,

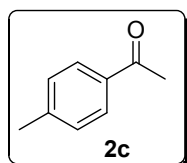
CDCl₃) δ 10.02 (s, 1H), 7.88 (dd, $J = 7.9, 0.9$ Hz, 2H), 7.67–7.59 (m, 1H), 7.53 (t, $J = 7.6$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 192.4 (C=O), 136.4, 134.5, 130.2, 129.8, 129.0, 128.5. ¹H NMR and ¹³C NMR data are consistent with the literature (4) and match a commercial sample.

Acetophenone (2b)⁴



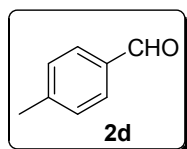
Purified by column chromatography (PE with boiling range: 30-60 °C) and finally concentrated at 10 °C; pale yellow liquid; 72% yield; $R_f = 0.44$ (10:1 PE/EA). ¹H NMR (400 MHz, CDCl₃) δ 8.00–7.92 (m, 2H), 7.59–7.53 (m, 1H), 7.49–7.41 (m, 2H), 2.60 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 198.2 (C=O), 137.1, 133.1, 128.6, 128.3, 26.6 (CH₃). ¹H NMR and ¹³C NMR data are consistent with the literature (4) and match a commercial sample.

1-p-tolyethanone (2c)⁴



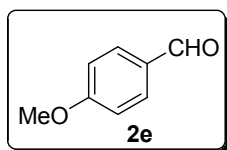
Purified by column chromatography (PE with boiling range: 30-60 °C) and finally concentrated at 10 °C; pale yellow liquid; 75% yield. $R_f = 0.38$ (10:1 PE/EA). ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 2.56 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.8 (C=O), 143.9, 134.7, 129.2, 128.4, 26.5 (CH₃), 21.6 (CH₃). ¹H NMR and ¹³C NMR data are consistent with the literature (4) and match a commercial sample.

4-methylbenzaldehyde (2d)⁴



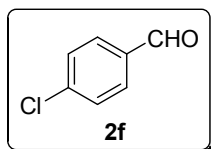
Purified by column chromatography (PE with boiling range: 30-60 °C) and finally concentrated at 10 °C; colorless liquid; 86% yield; $R_f = 0.47$ (10:1 PE/EA). ¹H NMR (400 MHz, CDCl₃) δ 9.88 (s, 1H), 7.70 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.0 (C=O), 145.6, 134.2, 129.9, 129.7, 21.9 (CH₃). ¹H NMR and ¹³C NMR data are consistent with the literature (4) and match a commercial sample.

4-methoxybenzaldehyde (2e)⁴



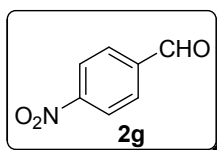
Purified by column chromatography (PE with boiling range: 30-60 °C) and finally concentrated at 10 °C; colorless liquid; 75% yield; $R_f = 0.23$ (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.87 (s, 1H), 7.83 (d, $J = 8.6$ Hz, 2H), 7.00 (d, $J = 8.5$ Hz, 2H), 3.88 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 190.9 (C=O), 164.6, 132.0, 129.9, 114.3, 55.6 (CH_3). $^1\text{H NMR}$ and $^{13}\text{C NMR}$ data are consistent with the literature (4) and match a commercial sample.

4-chlorobenzaldehyde (2f)⁴



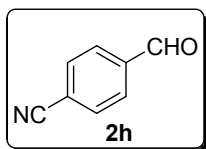
Purified by column chromatography (PE with boiling range: 30-60 °C) and finally concentrated at 10 °C; white solid; 91% yield; $R_f = 0.38$ (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.99 (s, 1H), 7.85–7.81 (m, 2H), 7.55–7.48 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 190.9 (C=O), 140.9, 134.7, 130.9, 129.5. $^1\text{H NMR}$ and $^{13}\text{C NMR}$ data are consistent with the literature (4) and match a commercial sample.

4-nitrobenzaldehyde (2g)⁴



Purified by column chromatography (20:1 PE/EA); yellow solid; 84% yield; $R_f = 0.18$ (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.17 (s, 1H), 8.41 (d, $J = 8.7$ Hz, 2H), 8.09 (d, $J = 8.7$ Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 190.3 (C=O), 151.1, 140.1, 130.8, 130.5, 124.3, 123.9. $^1\text{H NMR}$ and $^{13}\text{C NMR}$ data are consistent with the literature (4) and match a commercial sample.

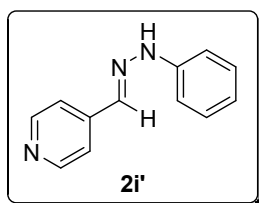
4-formylbenzonitrile (2h)⁵



Purified by column chromatography (20:1 PE/EA); white solid; 82% yield; R_f = 0.13 (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.11 (s, 1H), 8.10–7.97 (m, 2H), 7.86 (d, J = 8.3 Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 190.6 (C=O), 138.7, 132.9, 129.9, 117.7, 117.6. $^1\text{H NMR}$ and $^{13}\text{C NMR}$ data are consistent with the literature (5) and match a commercial sample.

In order to isolate **2i** successfully, this aldehyde product was transformed into corresponding hydrazone **2i'**. The general operation is as follow: when the degradation reaction was complete, the reaction mixture was cooled to room temperature, and then phenylhydrazine (1.0 mmol) was added directly into the reaction system and continued to stir for 6 h. The final reaction mixture was partitioned between ethyl acetate and water. The organic layer was washed with 6 \times 50 mL water and dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with PE/EA = 2:1) to provide **2i'** in 79% yield.

(E)-4-((2-phenylhydrazono)methyl)pyridine (**2i'**)



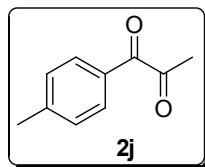
Purified by column chromatography (2:1 PE/EA); yellow liquid; 79% yield; R_f = 0.51 (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (d, J = 3.3 Hz, 2H), 8.33 (s, 1H), 7.58 (s, 1H), 7.50 (d, J = 4.7 Hz, 2H), 7.30 (t, J = 7.9 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 6.93 (t, J = 7.3 Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.9, 143.8, 143.0, 133.5, 129.4, 121.1, 120.2, 113.1. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{Na}$: $[\text{M}+\text{Na}]^+$, 220.0845; Found: 220.0849.

Carbon-carbon bond cleavage of 1,3-dicarbonyl compounds **1o** to **1r** (Scheme 2)

A mixture of 1,3-dicarbonyl compounds **1** (0.5 mmol), FeCl_3 (0.05 mmol), H_2O (0.5 mmol), and CH_3CN (2 mL) was added into a 50 mL Schlenk tube with a magnetic bar. Then the tube was sealed and pressurized with 1.0 atm air after it was vacuumed and flushed with air three times. After that, it was stirred at 90 $^\circ\text{C}$ for 20 h. After cooling to room temperature, the reaction mixture

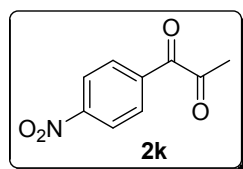
was purified by column chromatography on silica gel to give products (**2j** to **2m**).

1-p-tolylpropane-1,2-dione (**2j**)



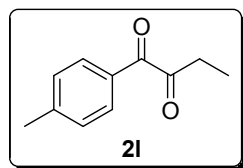
Purified by column chromatography (20:1 PE/EA); yellow oil; 91% yield; $R_f = 0.60$ (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 2.34 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 200.9 (C=O), 191.2 (C=O), 145.8, 130.4, 129.6, 129.2, 26.4 (CH_3), 21.9 (CH_3). HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{10}\text{NaO}_2$: $[\text{M}+\text{Na}]^+$, 185.0573; Found: 185.0566.

1-(4-nitrophenyl)propane-1,2-dione (**2k**)



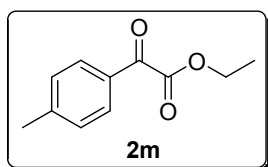
Purified by column chromatography (10:1 PE/EA); yellow solid; 66% yield; $R_f = 0.19$ (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (d, $J = 8.9$ Hz, 2H), 8.22 (d, $J = 8.9$ Hz, 2H), 2.57 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 198.6 (C=O), 188.3 (C=O), 150.9, 136.6, 131.6, 123.8, 26.0 (CH_3). HRMS (ESI) Calcd for $\text{C}_9\text{H}_7\text{NNaO}_4$: $[\text{M}+\text{Na}]^+$, 216.0267; Found: 216.0262.

1-p-tolylbutane-1,2-dione (**2l**)



Purified by column chromatography (20:1 PE/EA); yellow oil; 81% yield; $R_f = 0.56$ (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (d, $J = 3.9$ Hz, 2H), 7.31 (d, $J = 4.6$ Hz, 2H), 2.92 (d, $J = 4.6$ Hz, 2H), 2.45 (s, 3H), 1.21 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 204.1 (C=O), 192.4 (C=O), 145.9, 130.3, 129.6, 127.5, 32.2 (CH_2), 21.9 (CH_3), 6.8 (CH_3). HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{12}\text{NaO}_2$: $[\text{M}+\text{Na}]^+$, 199.0730; Found: 199.0726.

ethyl 2-oxo-2-p-tolylacetate (**2m**)

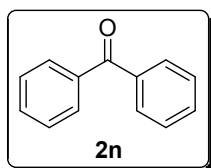


Purified by column chromatography (20:1 PE/EA); pale yellow oil; 73% yield; $R_f = 0.48$ (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 4.44 (q, $J = 7.1$ Hz, 2H), 2.44 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 186.1 (C=O), 164.1 (C=O), 146.2, 130.2, 130.1, 129.6, 62.2 (CH_2), 21.9 (CH_3), 14.1 (CH_3). HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{12}\text{NaO}_3$: $[\text{M}+\text{Na}]^+$, 215.0679; Found: 215.0675.

Carbon-carbon bond cleavage of **1s** and **1t** (Scheme 2)

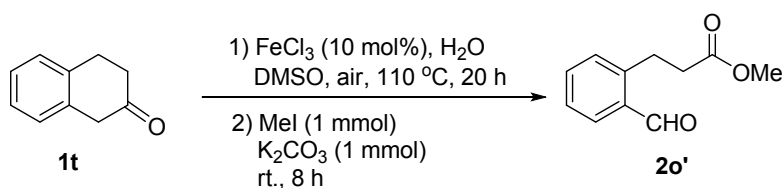
A mixture of **1s** (0.5 mmol), FeCl_3 (0.05 mmol), H_2O (0.5 mmol), and DMSO (2 mL) was added into a 50 mL Schlenk tube with a magnetic bar. Then the tube was sealed and pressurized with 1.0 atm air after it was vacuumed and flushed with air three times. After that, it was stirred at 110 °C for 20 h. After cooling to room temperature, the reaction mixture was purified by column chromatography on silica gel to give products **2n** in 64% yield.

benzophenone (**2n**)

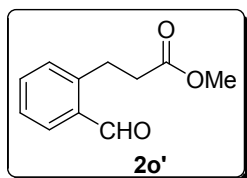


Purified by column chromatography (20:1 PE/EA); white solid; 64% yield; $R_f = 0.51$ (10:1 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77–7.67 (m, 4H), 7.50 (t, $J = 7.4$ Hz, 2H), 7.39 (t, $J = 7.6$ Hz, 4H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 196.8 (C=O), 137.6, 132.4, 130.1, 128.3. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{10}\text{NaO}$: $[\text{M}+\text{Na}]^+$, 205.0624; Found: 205.0622.

A mixture of **1t** (0.5 mmol), FeCl_3 (0.05 mmol), H_2O (0.5 mmol), and DMSO (2 mL) was added into a 50 mL Schlenk tube with a magnetic bar. Then the tube was sealed and pressurized with 1.0 atm air after it was vacuumed and flushed with air three times. After that, it was stirred at 110 °C for 20 h. In order to isolate the acid **2o** successfully, this product was converted into corresponding methyl ester **2o'**. The general operation is as follow: After the C–C cleavage is complete, the mixture was cooled to room temperature, and then K_2CO_3 (1 mmol) and MeI (1 mmol) were directly added. Then the mixture continued to stir at room temperature for 8 h. Finally, the reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate (10:1) as the eluent to afford **2o'** in 85% yield.



methyl 3-(2-formylphenyl)propanoate (**2o'**)

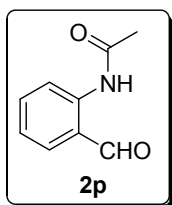


Purified by column chromatography (10:1 PE/EA); light red oil; 85% yield; R_f = 0.19 (10:1 PE/EA). ^1H NMR (400 MHz, CDCl_3) δ 10.21 (s, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 3.66 (s, 3H), 3.36 (t, J = 7.6 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.7 (C=O), 173.1 (C=O), 142.8, 133.8, 133.6, 131.2, 127.1, 51.6 (CH_3), 35.3 (CH_2), 28.1 (CH_2).

C–C bond cleavage of *o*-(*N*-acylamino)aryl ketones (**1u** to **1x**) (Scheme 3)

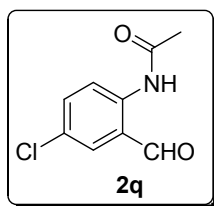
A mixture of *o*-(*N*-acylamino)aryl ketones **1** (0.25 mmol), FeCl_3 (0.025 mmol), H_2O (0.25 mmol), and CH_3CN (1 mL) was added into a 50 mL Schlenk tube with a magnetic bar. Then the tube was sealed and pressurized with 1.0 atm air after it was vacuumed and flushed with air three times. After that, it was stirred at $90\text{ }^\circ\text{C}$ ($110\text{ }^\circ\text{C}$ for **1v**) for 20 h. After cooling to room temperature, the reaction mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5:1 then 2:1) as the eluent to give product **2**.

N-(2-formylphenyl)acetamide (**2p**)



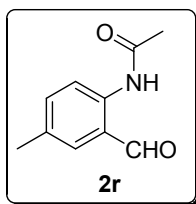
Purified by column chromatography (5:1 then 2:1 PE/EA); white solid; 82% yield; R_f = 0.38 (1:2 PE/EA). ^1H NMR (400 MHz, CDCl_3) δ 11.13 (s, 1H), 9.93 (d, J = 0.4 Hz, 1H), 8.74 (d, J = 8.5 Hz, 1H), 7.75–7.45 (m, 2H), 7.27–7.18 (m, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.6 (C=O), 169.6 (C=O), 141.0, 136.2, 136.0, 122.8, 121.5, 119.8, 25.4 (CH_3). HRMS (ESI) Calcd for $\text{C}_9\text{H}_9\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$, 186.0525; Found: 186.0521.

N-(4-chloro-2-formylphenyl)acetamide (2q)



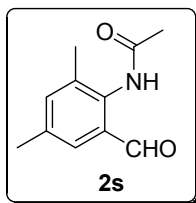
Purified by column chromatography (5:1 then 2:1 PE/EA); pale yellow solid; 65% yield; $R_f = 0.35$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.95 (s, 1H), 9.79 (d, $J = 0.4$ Hz, 1H), 8.66 (d, $J = 9.0$ Hz, 1H), 7.56 (d, $J = 2.5$ Hz, 1H), 7.48 (dd, $J = 9.0, 2.5$ Hz, 1H), 2.18 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 194.3 (C=O), 169.6 (C=O), 139.4, 136.0, 135.0, 127.9, 122.4, 121.5, 25.4 (CH_3). HRMS (ESI) Calcd for $\text{C}_9\text{H}_8\text{ClNNaO}_2$: $[\text{M}+\text{Na}]^+$, 220.0136; Found: 220.0138.

N-(2-formyl-4-methylphenyl)acetamide (2r)



Purified by column chromatography (5:1 then 2:1 PE/EA); white solid; 84% yield; $R_f = 0.34$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 11.02 (s, 1H), 9.86 (s, 1H), 8.61 (d, $J = 8.5$ Hz, 1H), 7.43 (s, 1H), 7.43–7.34 (m, 1H), 2.38 (s, 3H), 2.24 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.6 (C=O), 169.4 (C=O), 138.6, 136.9, 136.1, 132.5, 121.4, 119.8, 25.3 (CH_3), 20.4 (CH_3). HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{11}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$, 200.0682; Found: 200.0685.

N-(2-formyl-4,6-dimethylphenyl)acetamide (2s)

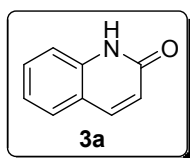


Purified by column chromatography (5:1 then 2:1 PE/EA); pale yellow solid; 87% yield; $R_f = 0.35$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.92 (s, 1H), 8.89 (s, 1H), 7.37 (s, 1H), 7.31 (s, 1H), 2.38 (s, 3H), 2.24 2.23 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 193.8 (C=O), 169.1 (C=O), 137.9, 135.6, 134.3, 132.5, 128.5, 23.9 (CH_3), 20.6 (CH_3), 18.8 (CH_3). HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{13}\text{NNaO}_2$: $[\text{M}+\text{Na}]^+$, 214.0839; Found: 214.0831.

4) Transformation of 2-acetylamino-benzaldehydes (2p to 2s) to quinolin-2(1 H)-ones (Scheme 3)⁶

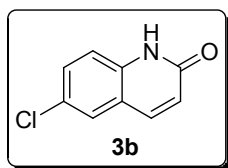
A 50 mL Schlenk tube with a magnetic bar was charged with **2** (0.125 mmol), Cs₂CO₃ (0.625 mmol), DMF (1 mL). Then the tube was tightly screw-capped and stirred at 60 °C for 12 h. After cooling to room temperature, the mixture was purified by flash column chromatography using petroleum ether/ethyl acetate (2:1) as the eluent to afford the corresponding products **3**.

quinolin-2(1 H)-one (**3a**)⁷



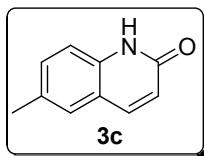
Purified by column chromatography (2:1 PE/EA); white solid; 79% yield; *R_f* = 0.33 (1:2 PE/EA). ¹H NMR (400 MHz, CDCl₃) δ 12.30 (s, 1H), 7.82 (d, *J* = 9.5 Hz, 1H), 7.61–7.49 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 9.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 164.5 (C=O), 141.0, 138.5, 130.7, 127.8, 122.7, 121.4, 119.9, 116.1.

6-chloroquinolin-2(1 H)-one (**3b**)⁷



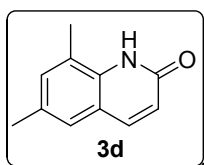
Purified by column chromatography (2:1 PE/EA); white solid; 84% yield; *R_f* = 0.34 (1:2 PE/EA). ¹H NMR (400 MHz, DMSO) δ 11.88 (s, 1H), 7.88 (d, *J* = 9.6 Hz, 1H), 7.80 (d, *J* = 2.2 Hz, 1H), 7.54 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 6.56 (d, *J* = 9.6 Hz, 1H). ¹³C NMR (100 MHz, DMSO) δ 161.6 (C=O), 139.2, 137.6, 130.2, 126.9, 125.5, 123.2, 120.2, 117.0.

6-methylquinolin-2(1 H)-one (**3c**)⁷



Purified by column chromatography (2:1 PE/EA); white solid; 70% yield; $R_f = 0.36$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.33 (s, 1H), 7.75 (d, $J = 9.5$ Hz, 1H), 7.34 (d, $J = 4.1$ Hz, 3H), 6.69 (d, $J = 9.4$ Hz, 1H), 2.41 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.4 (C=O), 140.8, 136.5, 132.2, 132.1, 127.3, 121.3, 119.9, 116.0, 20.9 (CH_3).

6,8-dimethylquinolin-2(1 H)-one (3d)

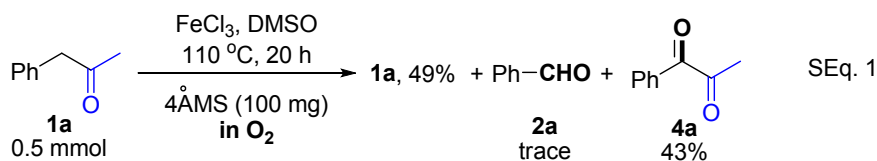


Purified by column chromatography (2:1 PE/EA); pale yellow solid; 64% yield; $R_f = 0.35$ (1:2 PE/EA). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.87 (s, 1H), 7.69 (d, $J = 9.5$ Hz, 1H), 7.18 (d, $J = 6.1$ Hz, 2H), 6.63 (d, $J = 9.5$ Hz, 1H), 2.47 (s, 3H), 2.37 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.3 (C=O), 141.0, 134.9, 133.3, 131.7, 125.7, 123.0, 121.3, 119.8, 20.7 (CH_3), 16.6 (CH_3). HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{11}\text{NNaO}$: $[\text{M}+\text{Na}]^+$, 196.0738; Found: 196.0731.

5) Mechanistic Study on the C–C Bond Cleavage

5.1 Control C–C bond cleavage reactions of 1a to investigate the role of H_2O .

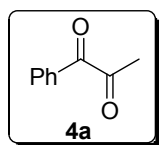
C–C bond cleavage reaction of 1a in the absence of H_2O



In the glove-box, a mixture of **1a** (0.5 mmol), FeCl_3 (0.05 mmol) and molecular sieve (100 mg)

in 2mL anhydrous DMSO loaded in a Schlenk tube was stirred in 1 atm O₂ at 110 °C for 20 h. After cooling to room temperature, the mixture was purified by column chromatography using petroleum ether (boiling range: 30-60 °C) as the eluent and **4a** was obtained in 43% yield while only trace of benzaldehyde was obtained. 49% yield of **1a** was recovered. **This control experiment suggested that the presence of H₂O is essential for this C–C bond cleavage.**

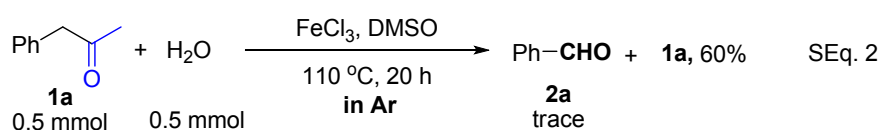
1-phenylpropane-1,2-dione (**4a**)



Purified by column chromatography (PE with boiling range: 30-60 °C); yellow oil, 43% yield; *R_f* = 0.58 (10:1 PE/EA). ¹H NMR (400 MHz, CDCl₃) δ 7.98–7.87 (m, 2H), 7.58–7.52 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 200.6 (C=O), 191.4 (C=O), 134.6, 131.8, 130.3, 128.8, 26.4 (CH₃). HRMS (ESI) Calcd for C₉H₈NaO₂: [M+Na]⁺, 171.0417; Found: 171.0415.

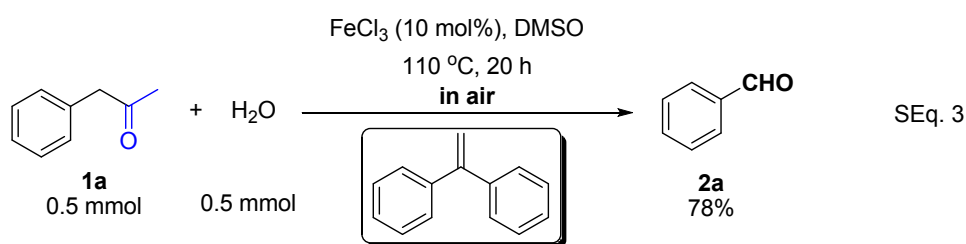
5.2 Control C–C bond cleavage reactions of **1a** to investigate the role of air.

C–C bond cleavage reaction of **1a** in the absence of air

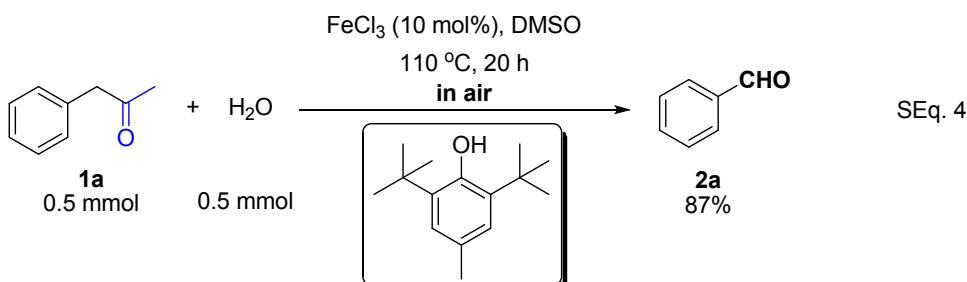


In the glove box, a mixture of **1a** (0.5 mmol), FeCl₃ (0.05 mmol) and H₂O (0.5 mmol) in 2mL degassed DMSO loaded in a Schlenk tube was stirred at 110 °C for 20 h. After cooling to room temperature, the mixture was purified by column chromatography using petroleum ether (boiling range: 30-60 °C) as the eluent. Only trace of benzaldehyde was obtained and 60% of **1a** was recovered. **This control experiment suggested that the presence of O₂ (or air) is essential for this C–C bond cleavage.**

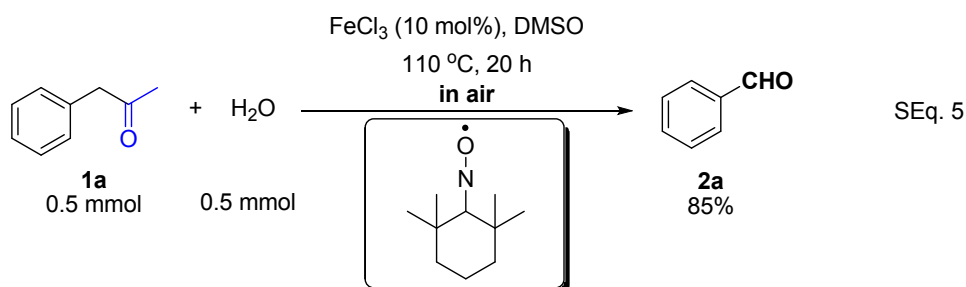
5.3 Control C–C bond cleavage reactions of **1a** in the presence of radical scavengers.



A mixture of **1a** (0.5 mmol), FeCl_3 (0.05 mmol), ethene-1,1-diylidibenzene (1 mmol) and H_2O (0.5 mmol) in 2mL DMSO loaded in a Schlenk tube was stirred in 1 atm air at 110°C for 20 h. After cooling to room temperature, the mixture was purified by column chromatography using petroleum ether (boiling range: $30\text{--}60^\circ\text{C}$) as the eluent and 78% of benzaldehyde was obtained.

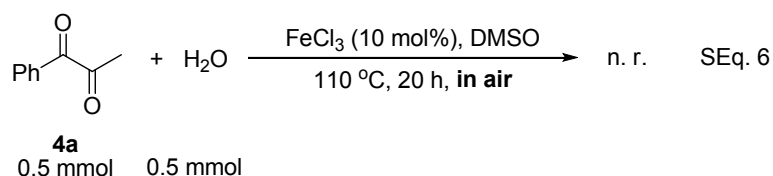


A mixture of **1a** (0.5 mmol), FeCl_3 (0.05 mmol), 2,6-di-tert-butyl-4-methylphenol (1 mmol) and H_2O (0.5 mmol) in 2mL DMSO loaded in a Schlenk tube was stirred in 1 atm air at 110°C for 20 h. After cooling to room temperature, the mixture was purified by column chromatography using petroleum ether (boiling range: $30\text{--}60^\circ\text{C}$) as the eluent and 87% of benzaldehyde was obtained.



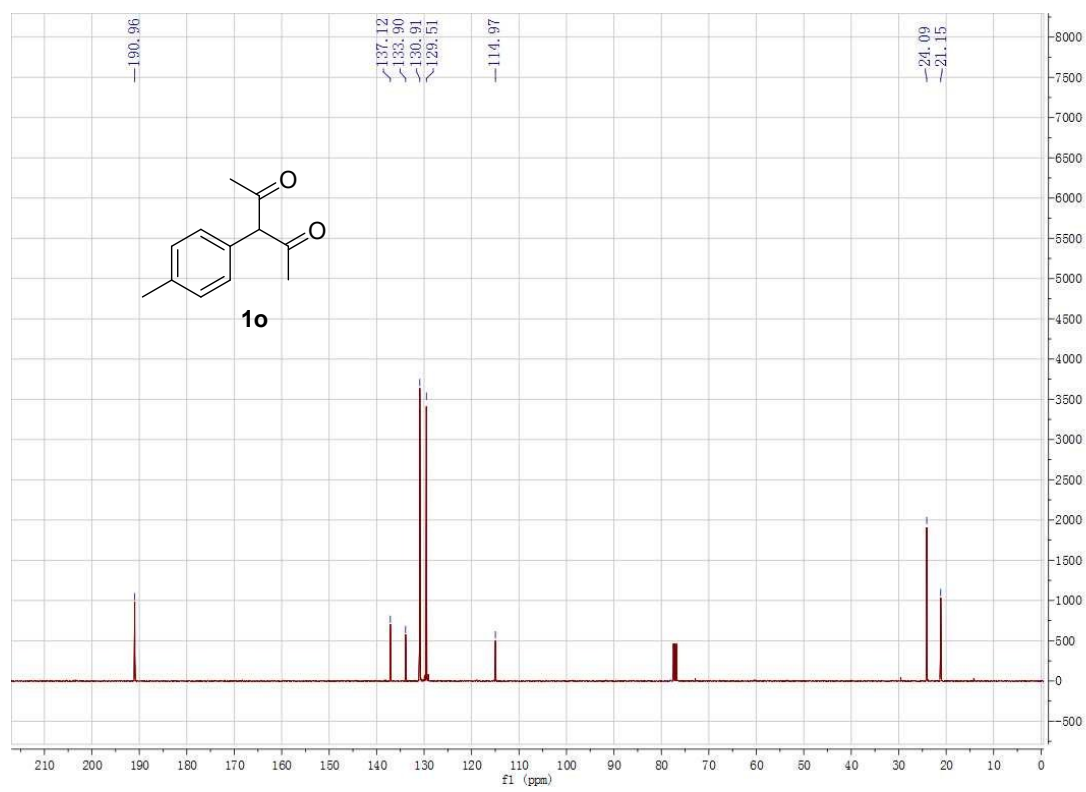
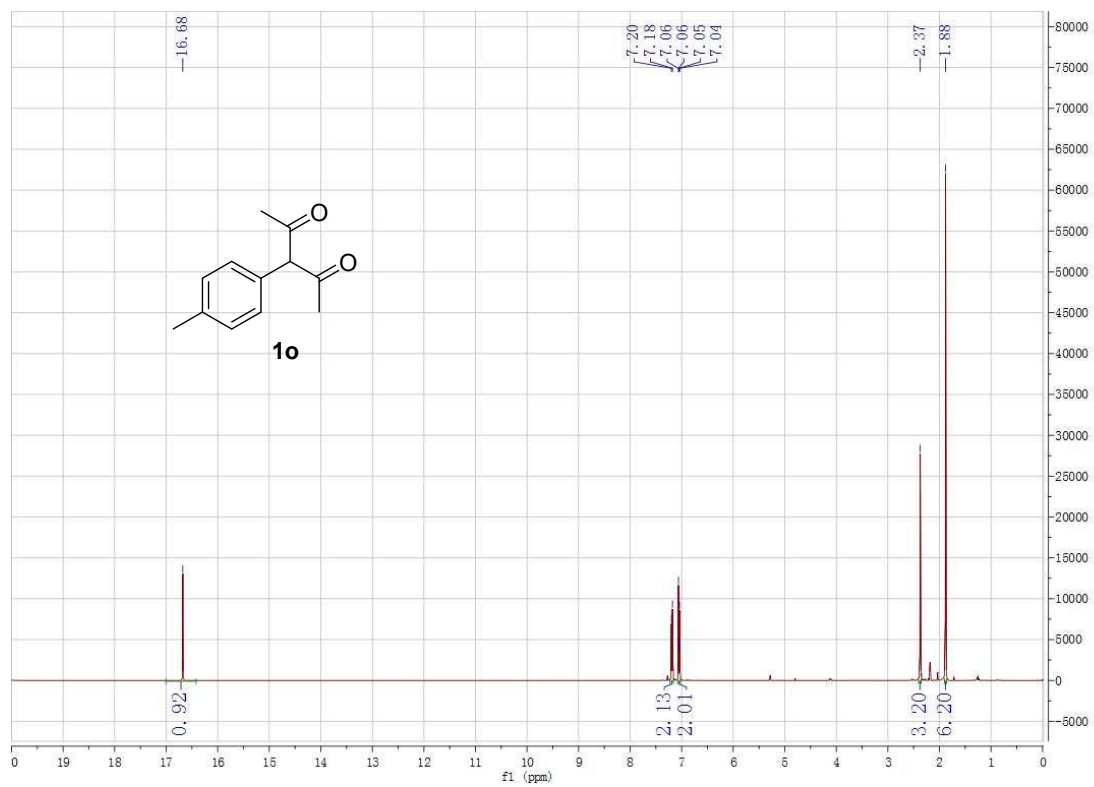
A mixture of **1a** (0.5 mmol), FeCl₃ (0.05 mmol), 1,1,5,5-Tetramethylpentamethylene nitroxide (1 mmol) and H₂O (0.5 mmol) in 2mL DMSO loaded in a Schlenk tube was stirred in 1 atm air at 110 °C for 20 h. After cooling to room temperature, the mixture was purified by column chromatography using petroleum ether (boiling range: 30-60 °C) as the eluent and 85% of benzaldehyde was obtained. **The results of SEq. 3, SEq. 4 and SEq. 5 suggested that a radical process might not be involved in the present transformation.**

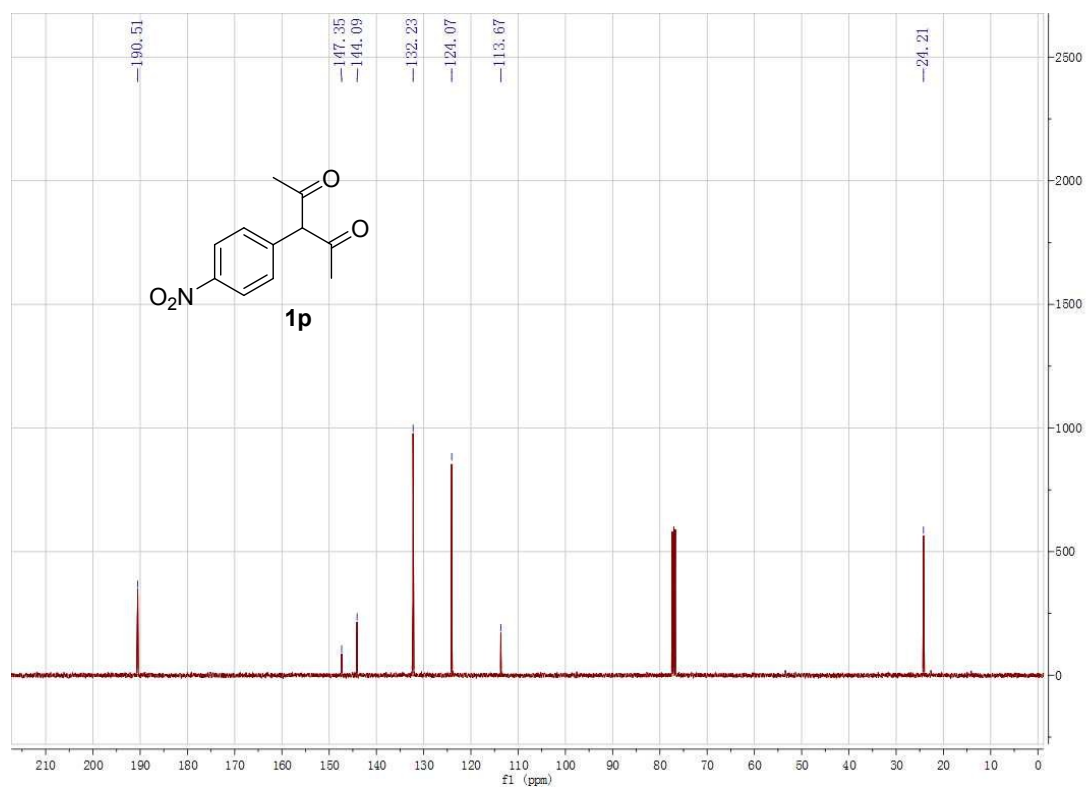
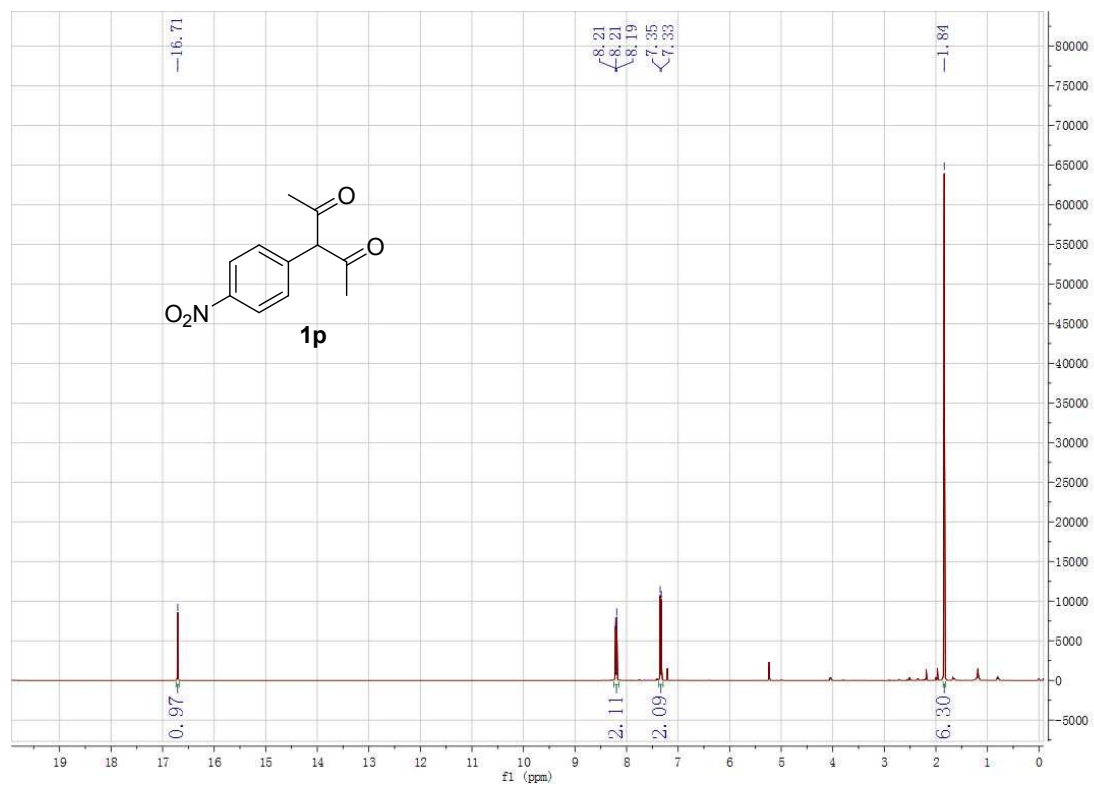
5.4 Reactions of **4a** under standard conditions for C–C bond cleavage.

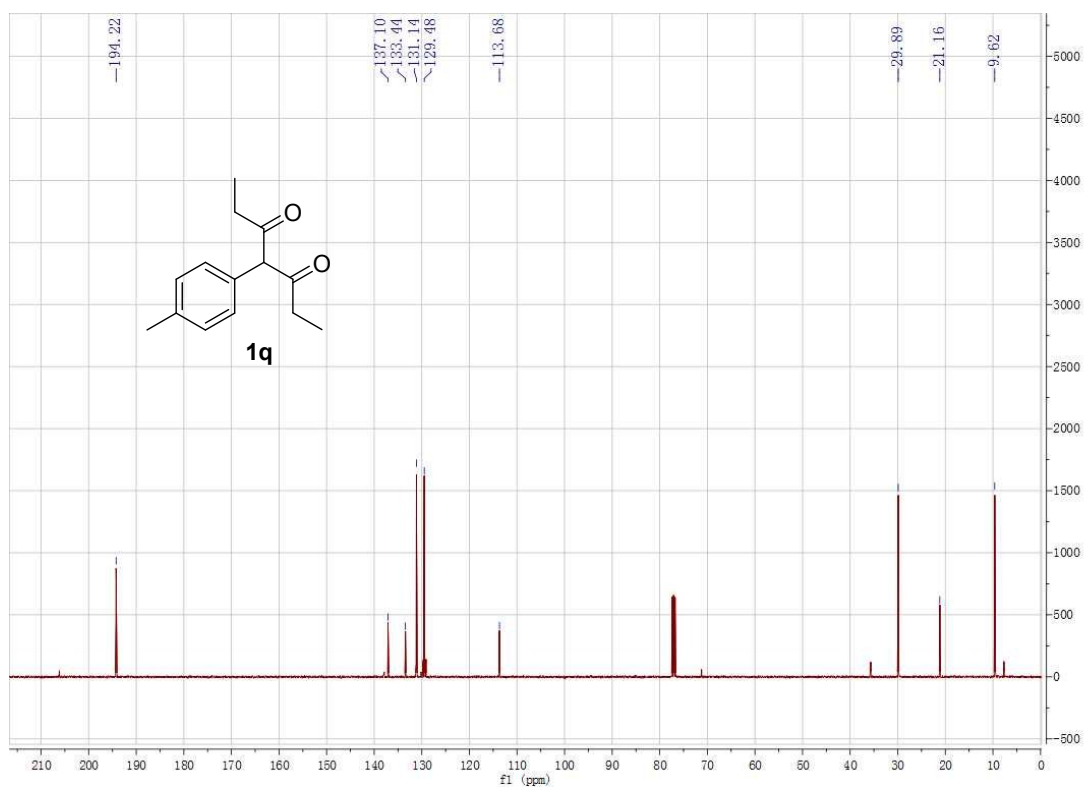
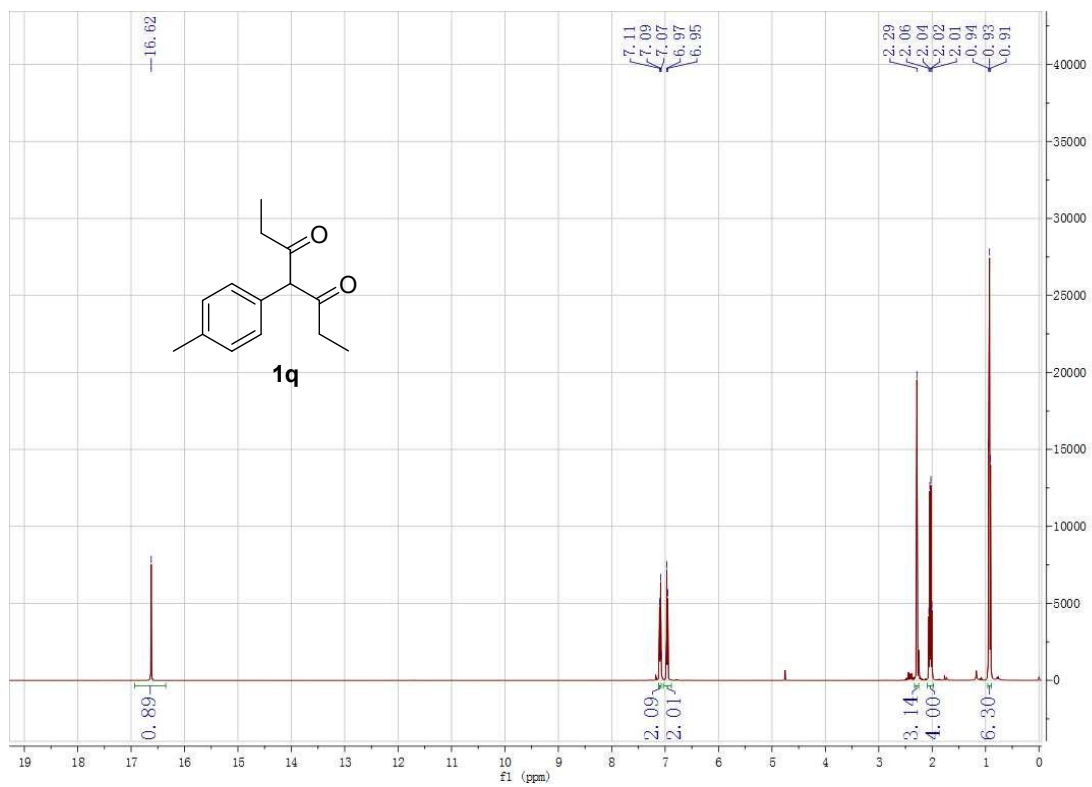


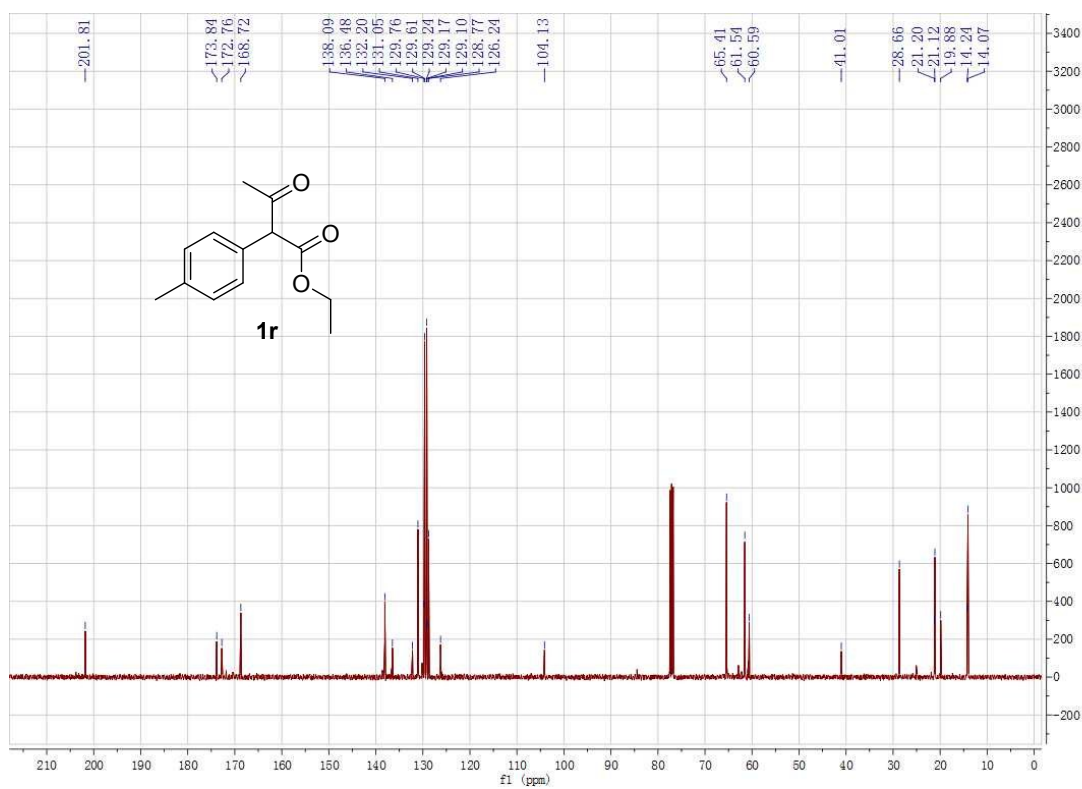
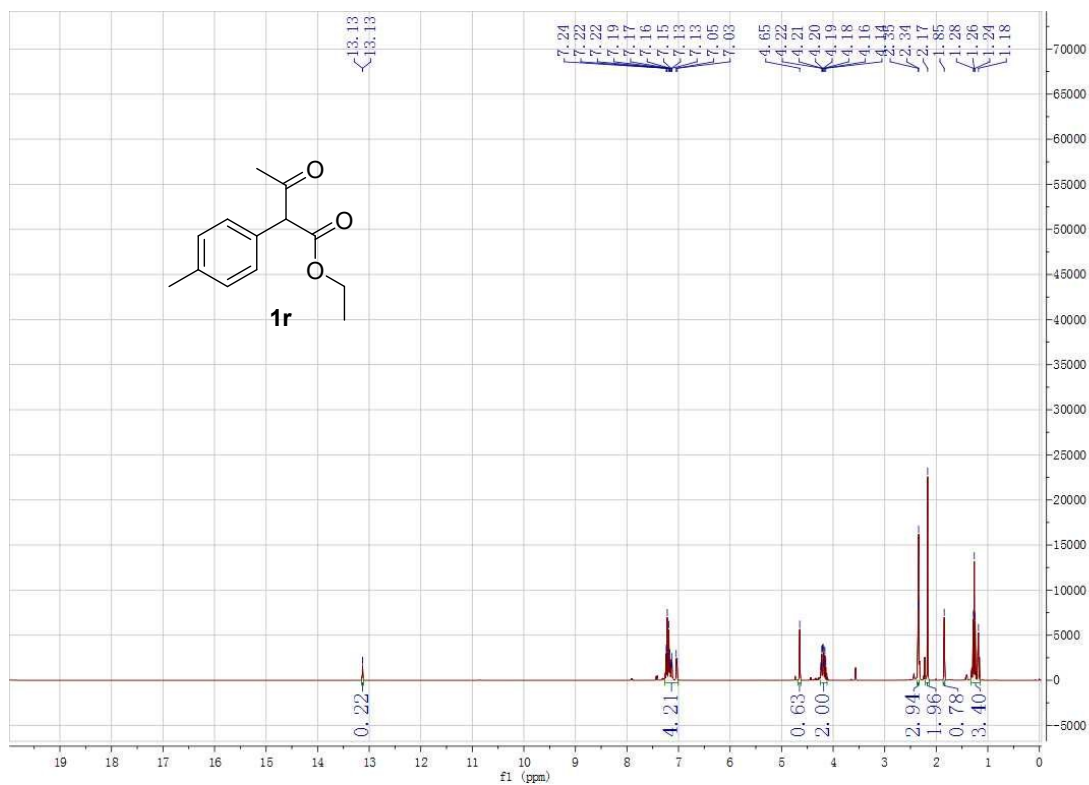
A mixture of **4a** (0.5 mmol), FeCl₃ (0.05 mmol), and H₂O (0.5 mmol) in 2 mL DMSO loaded in a schlenk tube was stirred in 1 atm air at 110 °C for 20 h. After cooling to room temperature, the mixture was detected by GC-MS and **4a** was totally intact. **This control experiment suggested that 4a was not the intermediate for this oxidative C–C bond cleavage.**

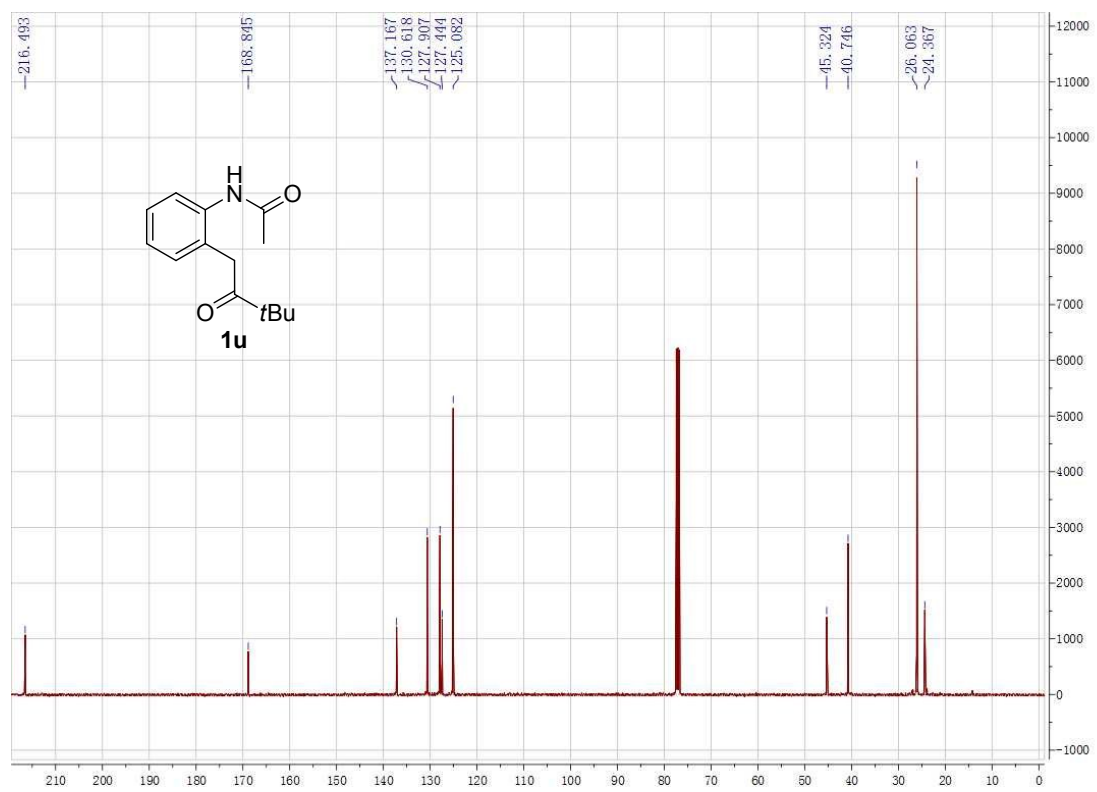
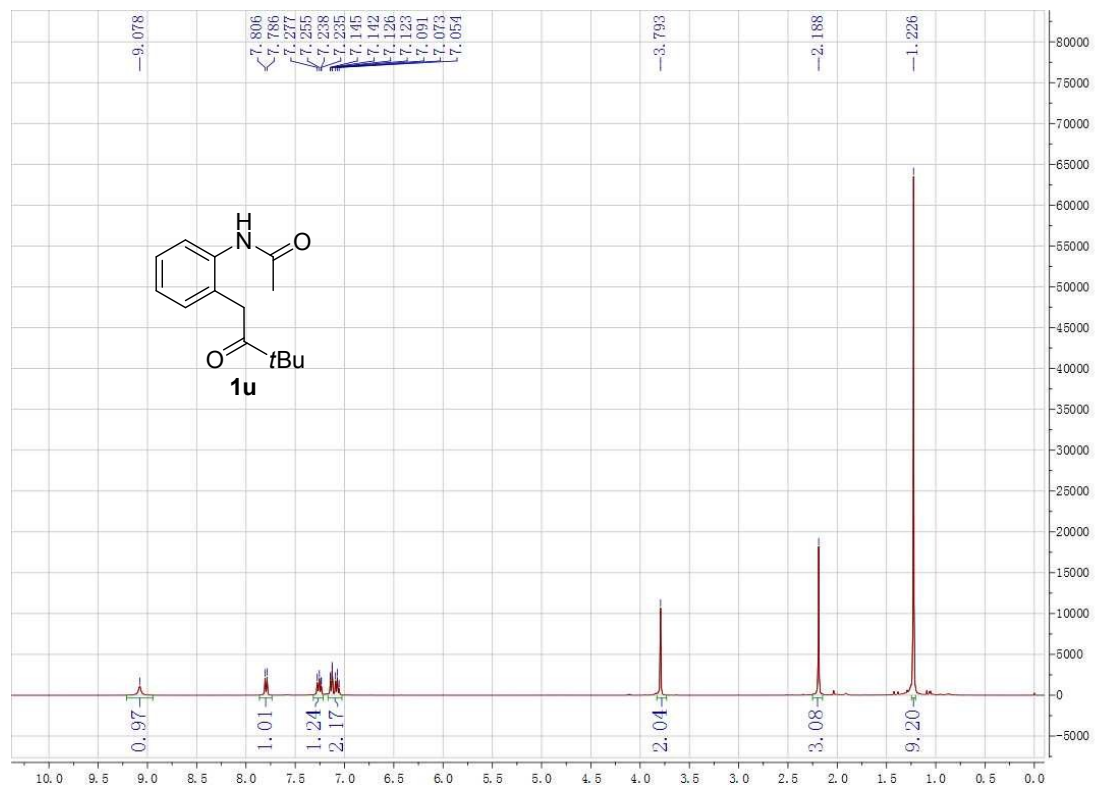
6) ¹H NMR and ¹³C NMR Copies of Products

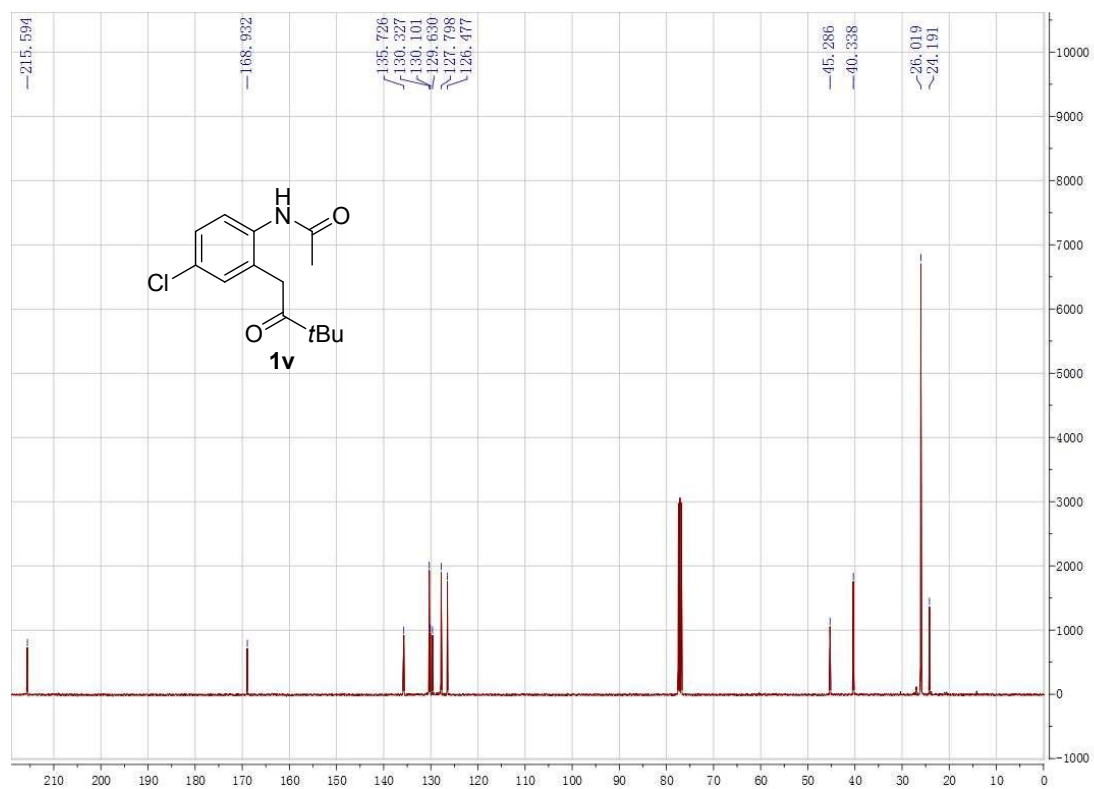
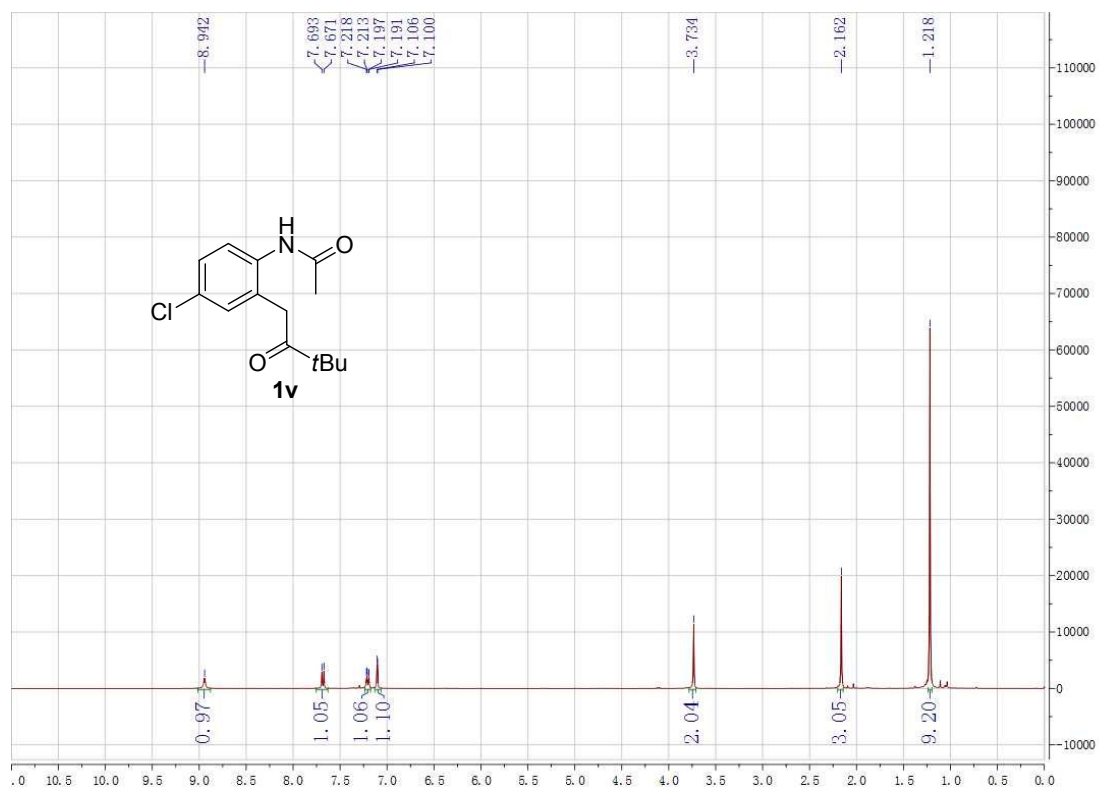


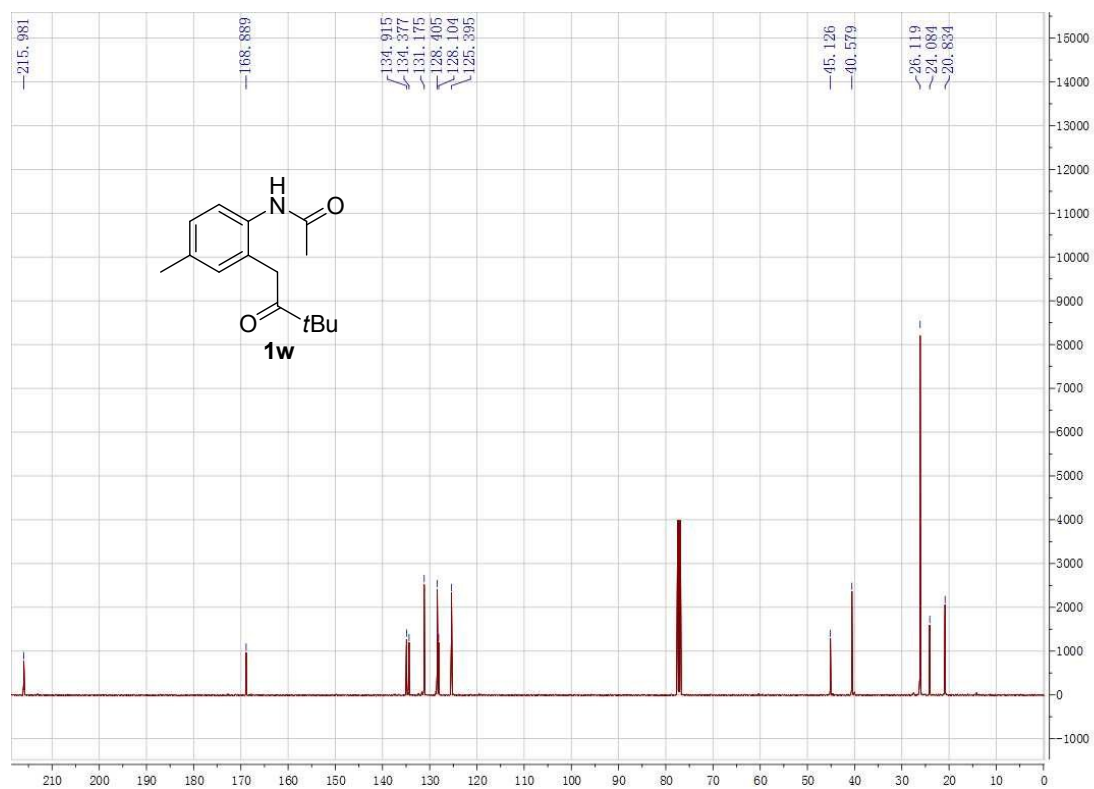
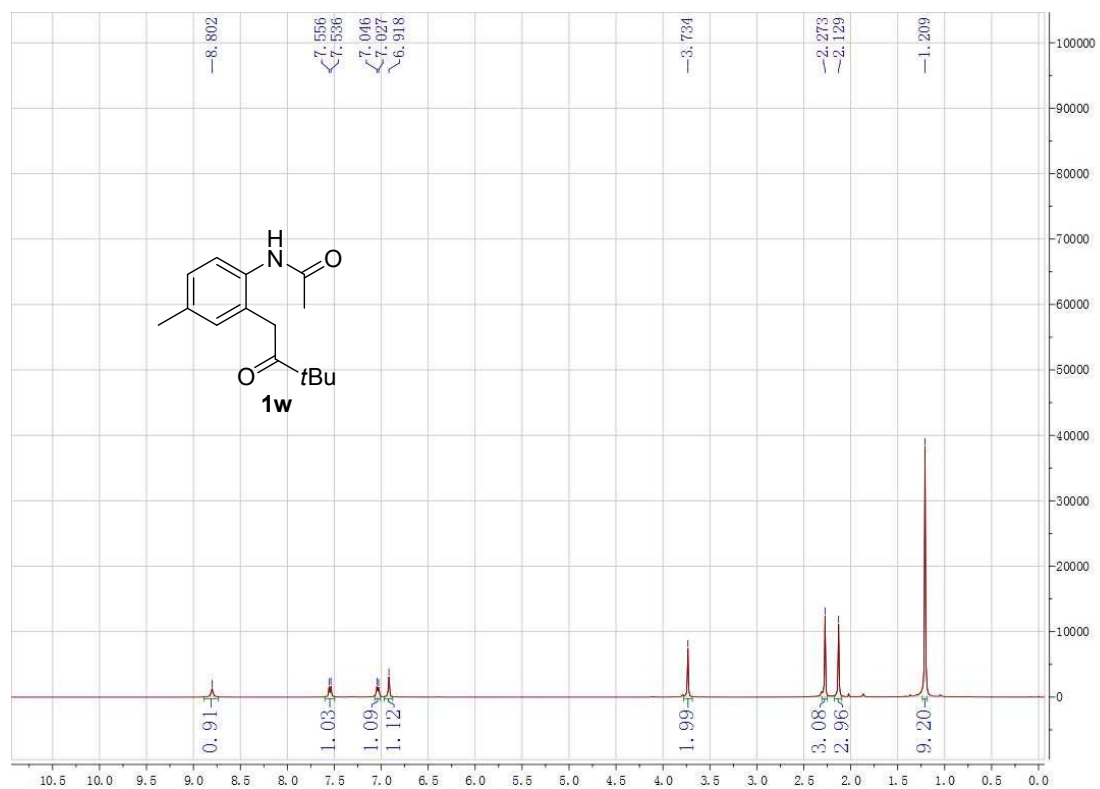


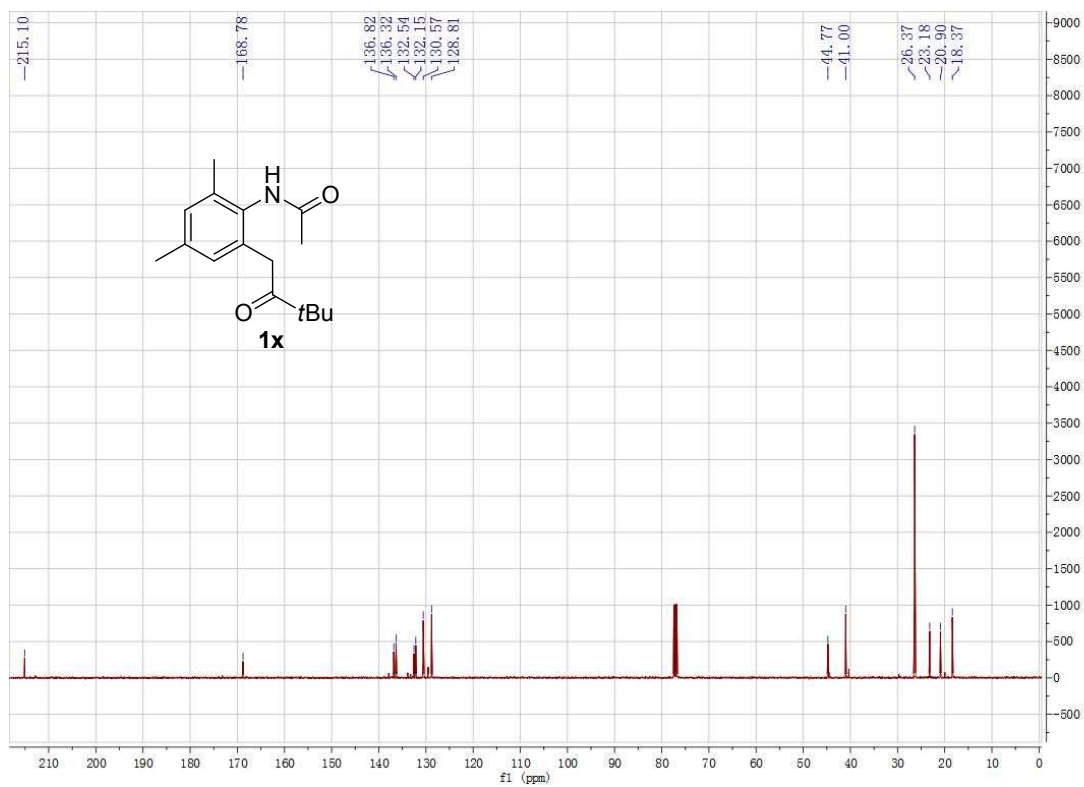
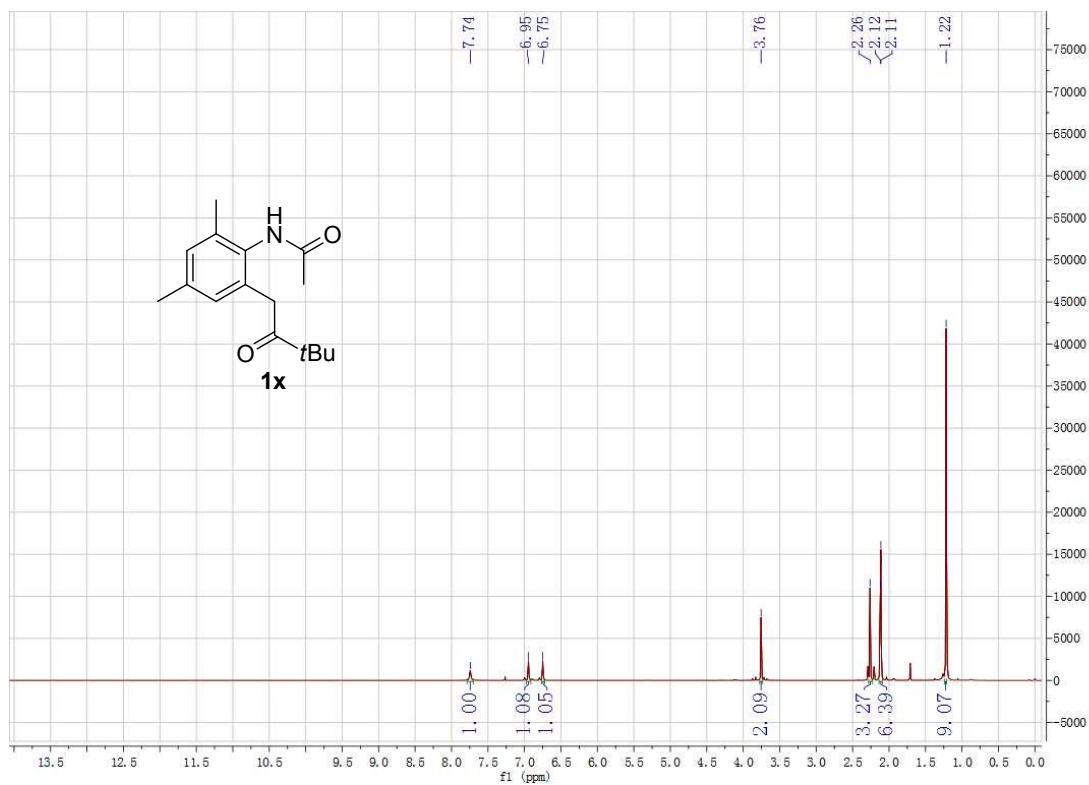


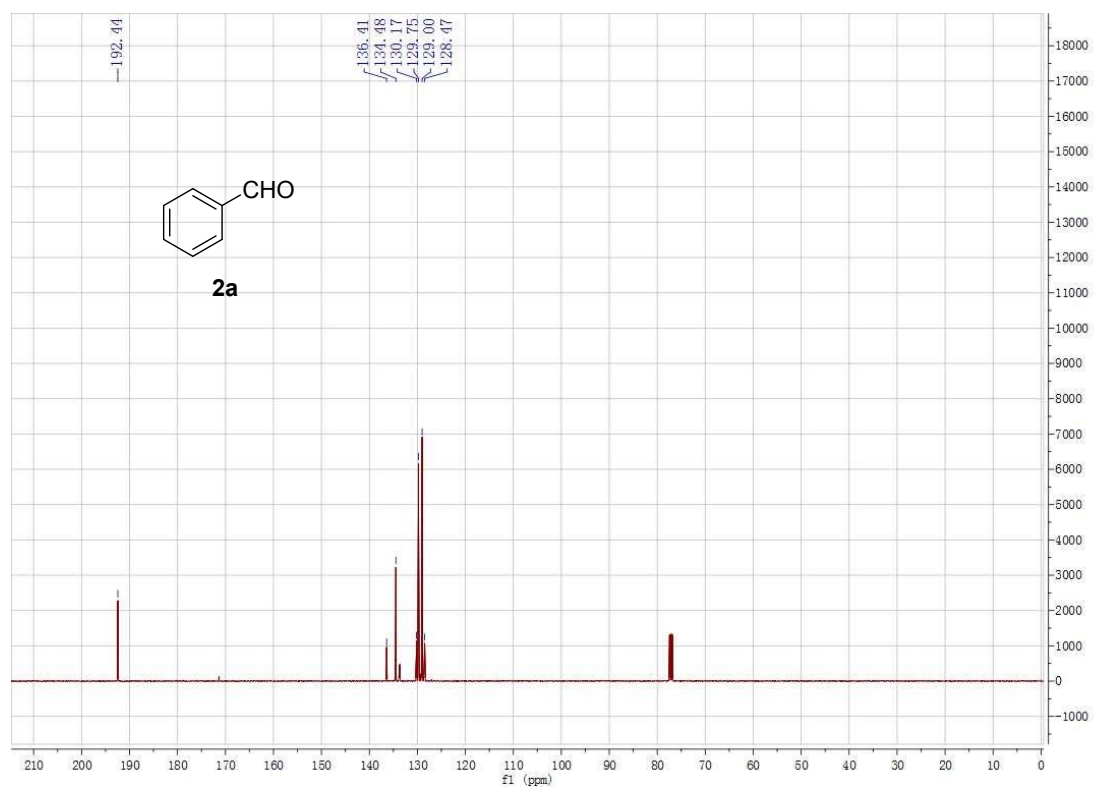
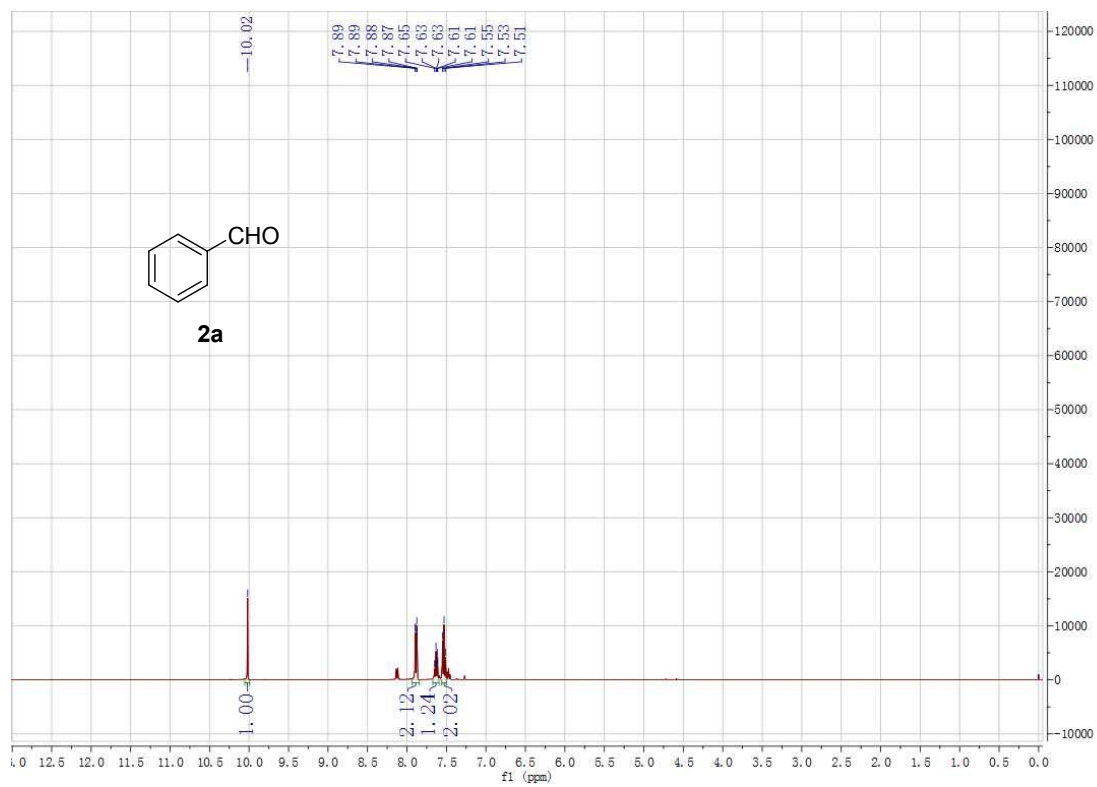


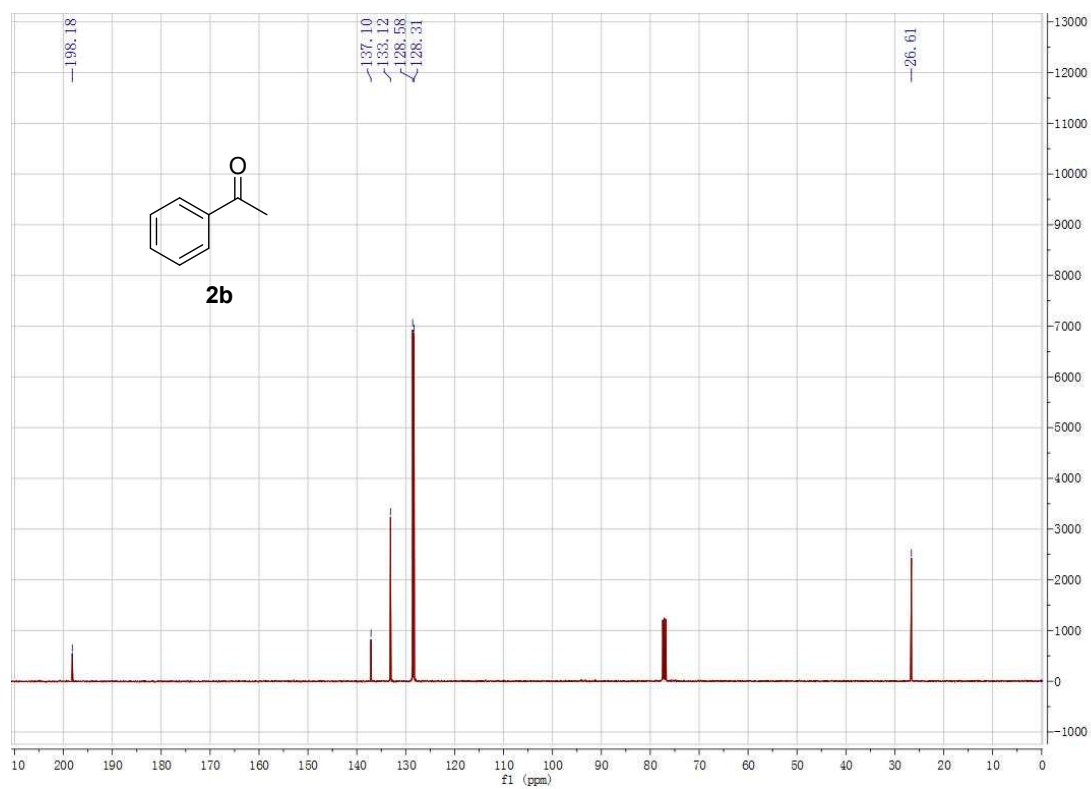
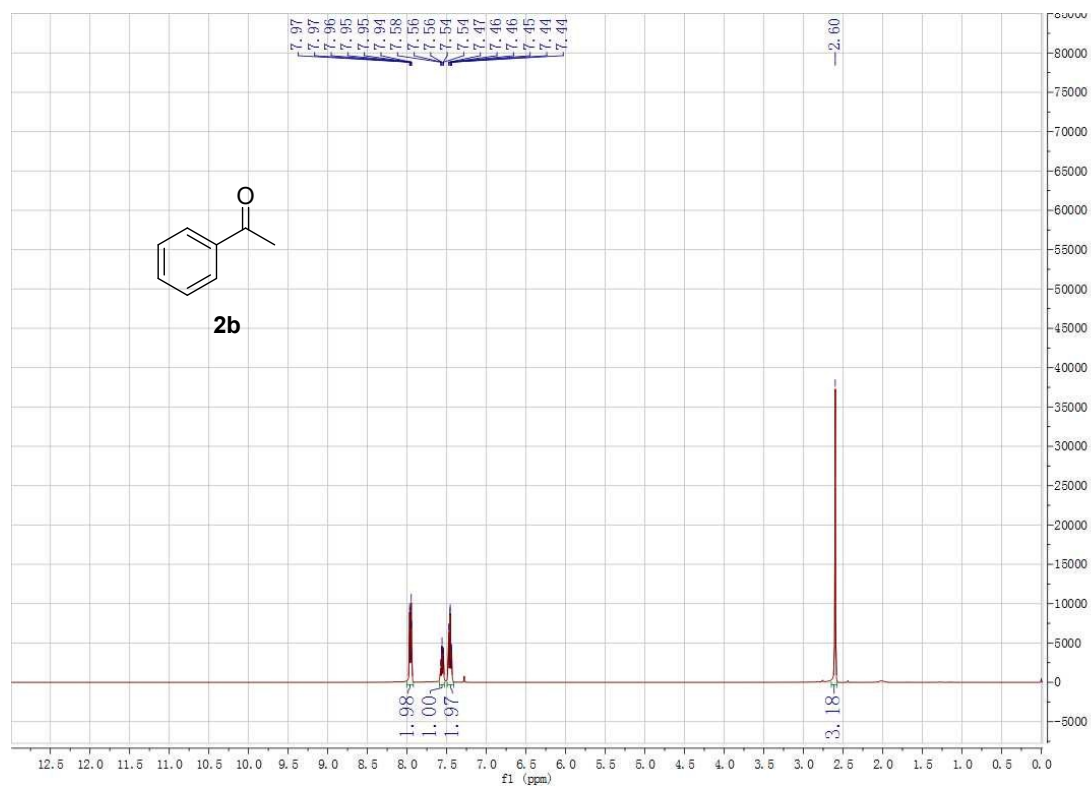


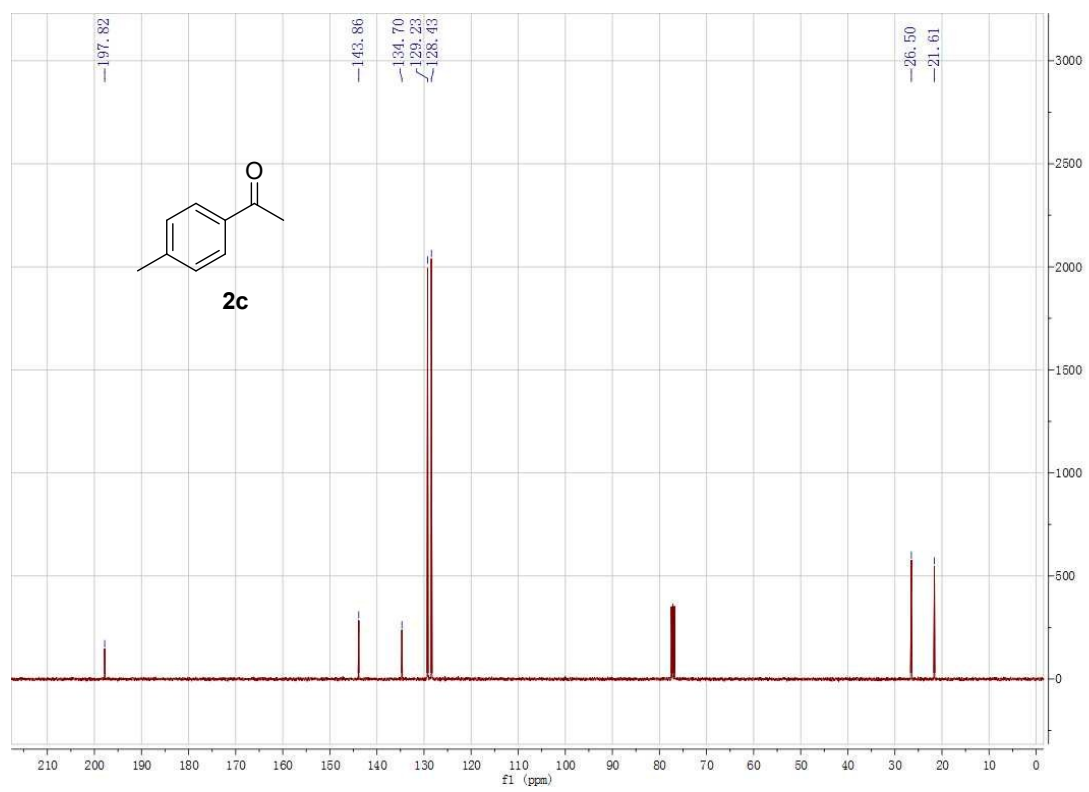
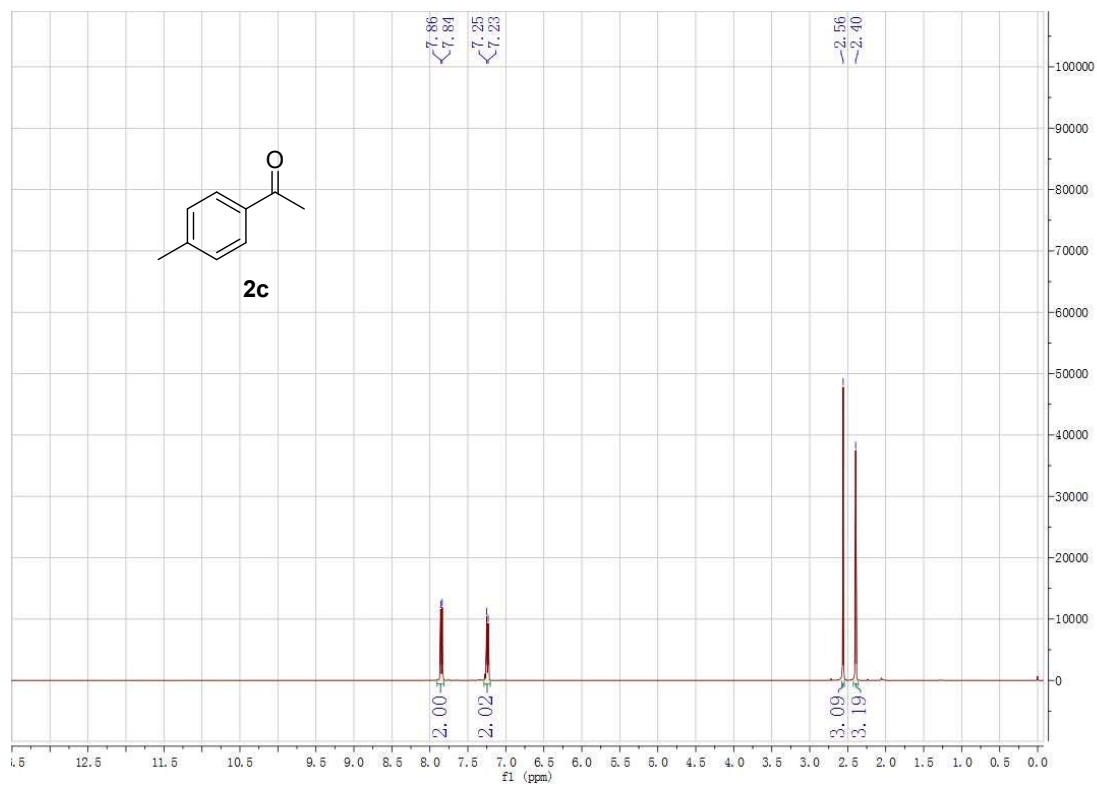


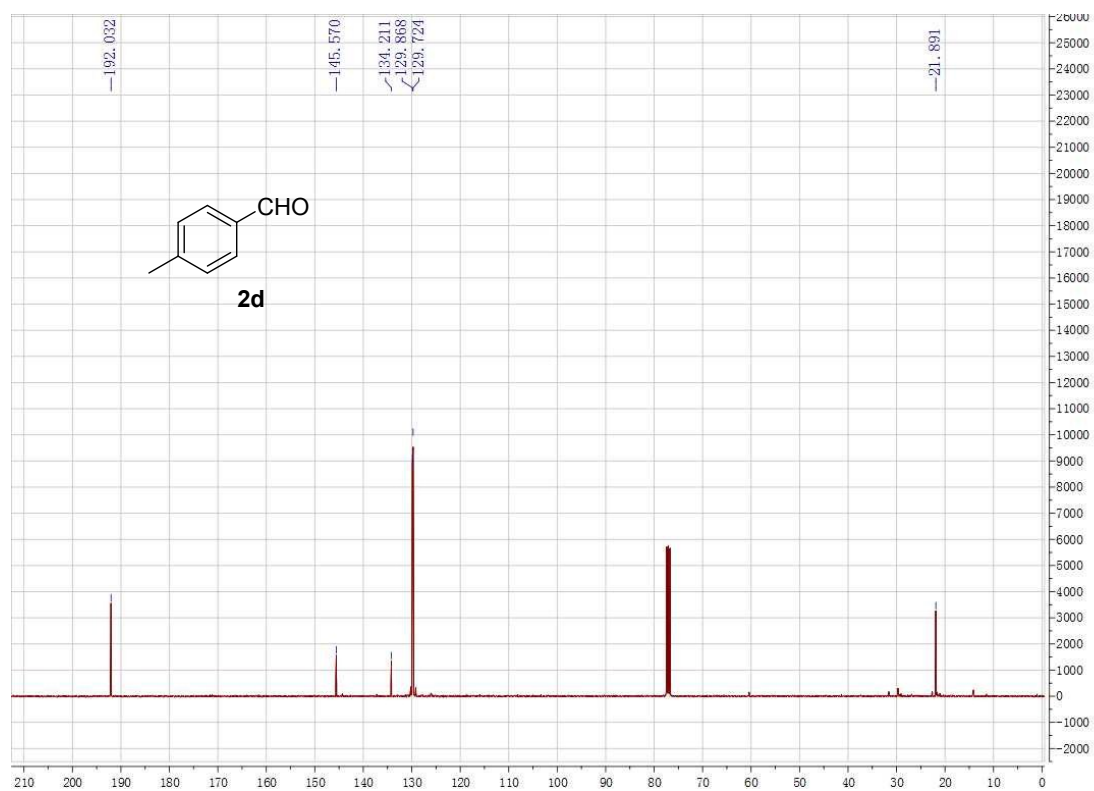
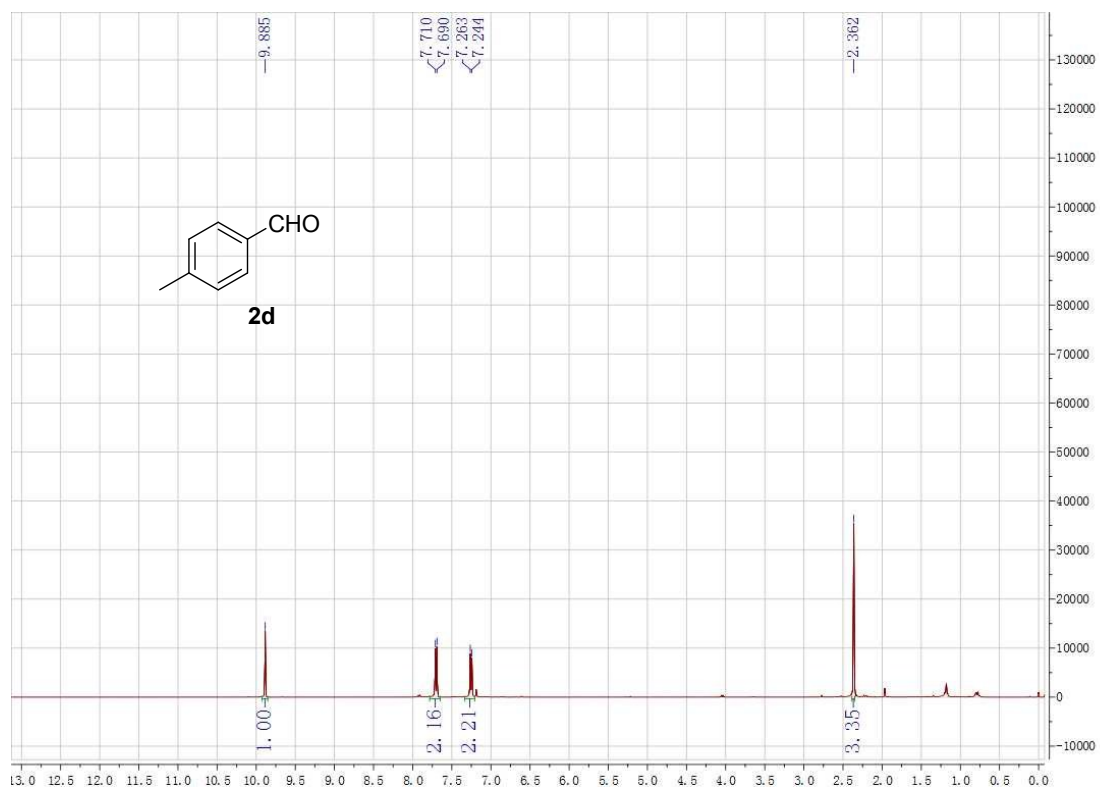


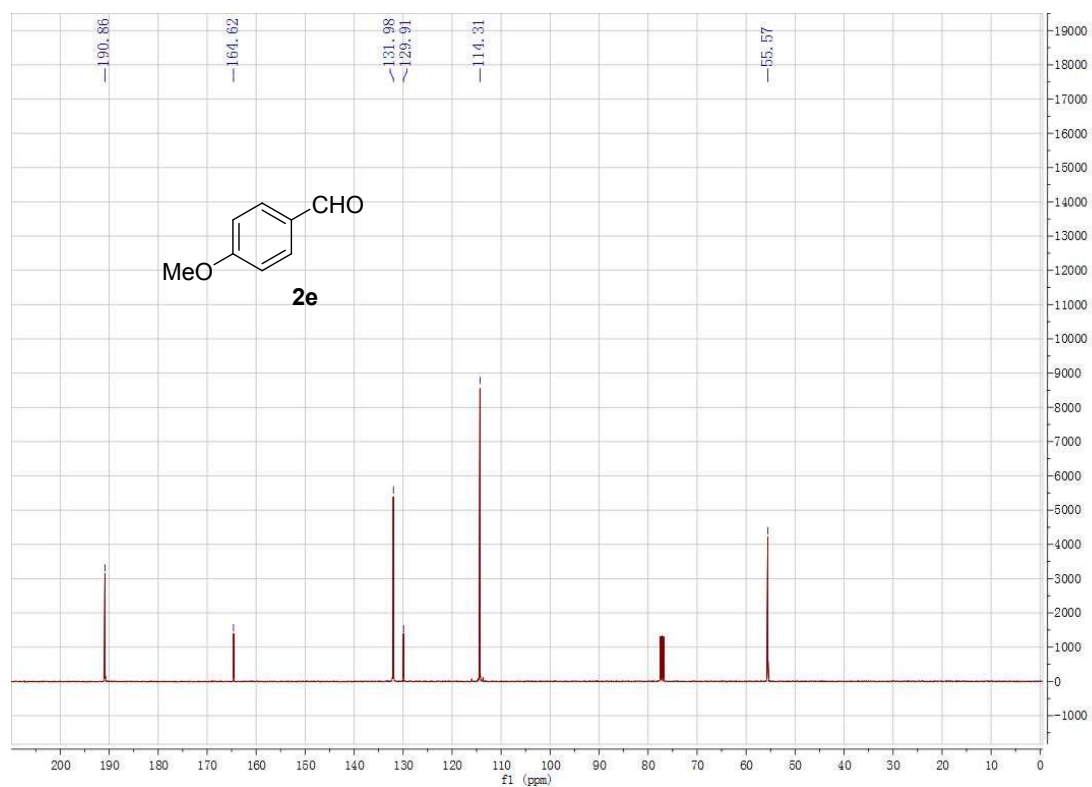
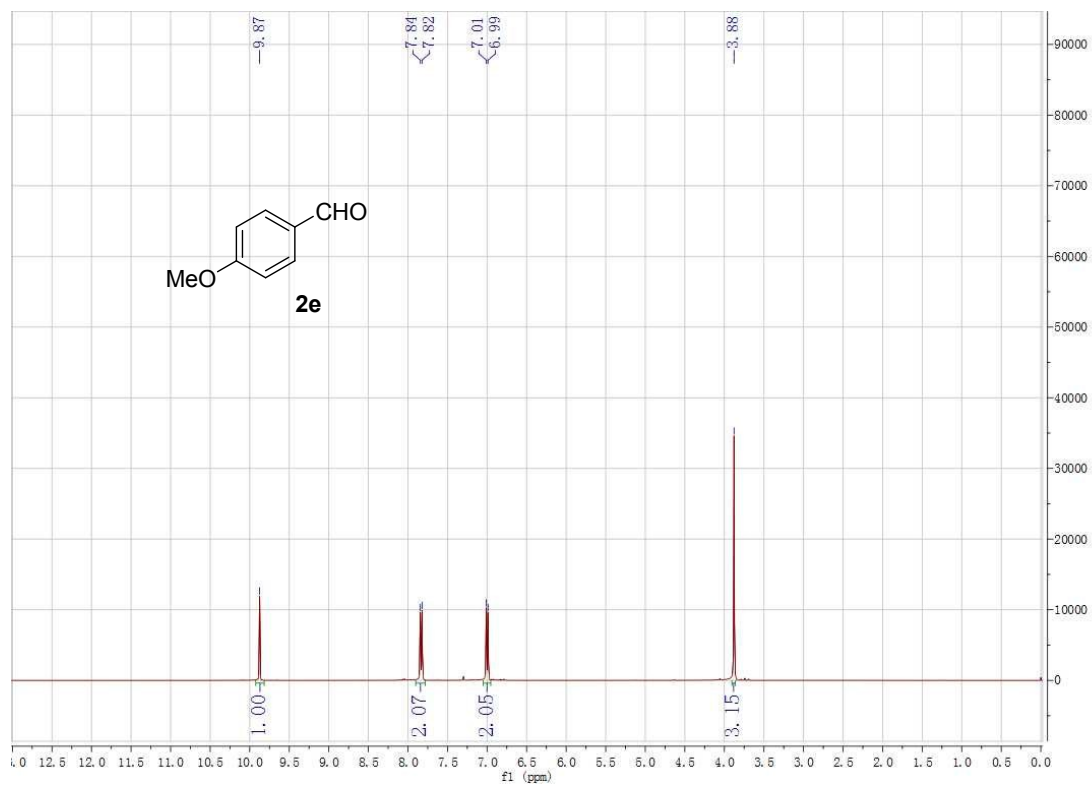


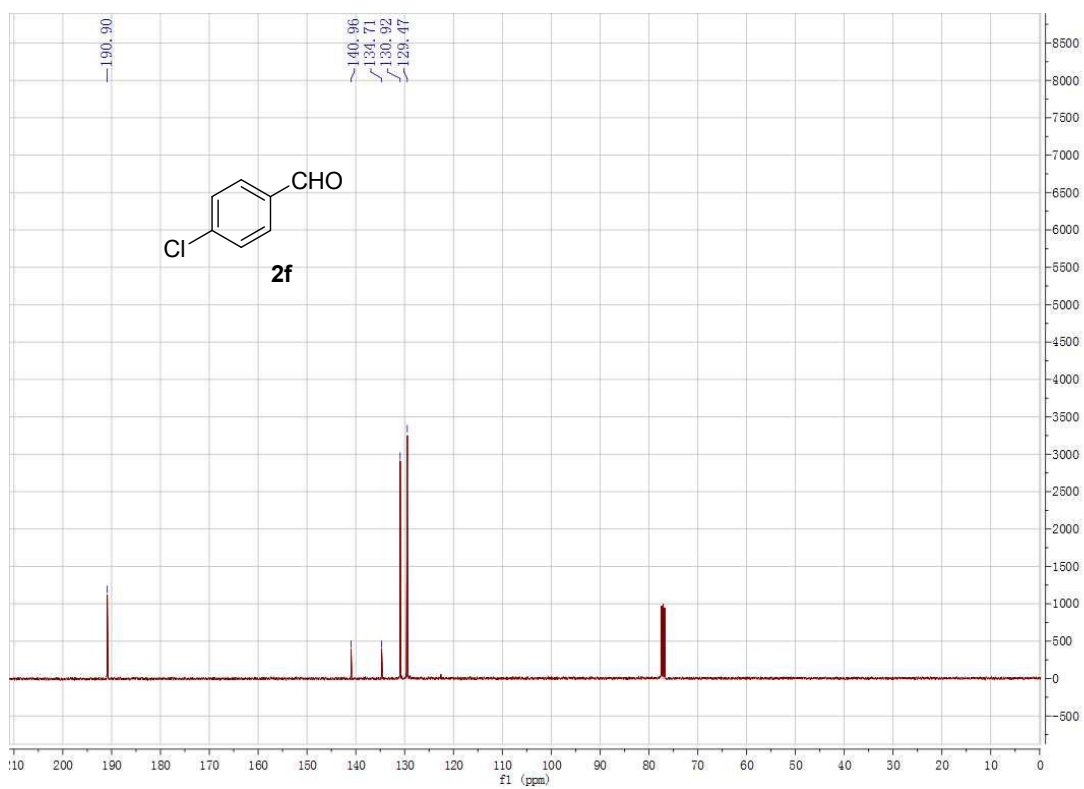
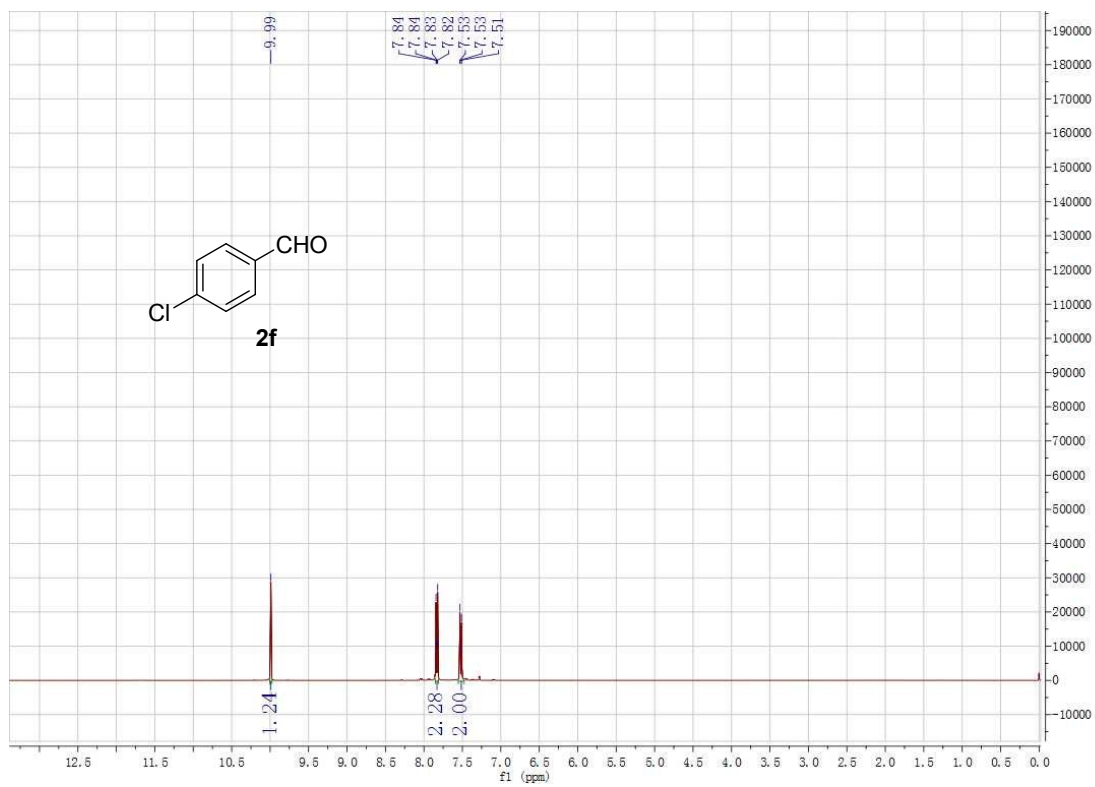


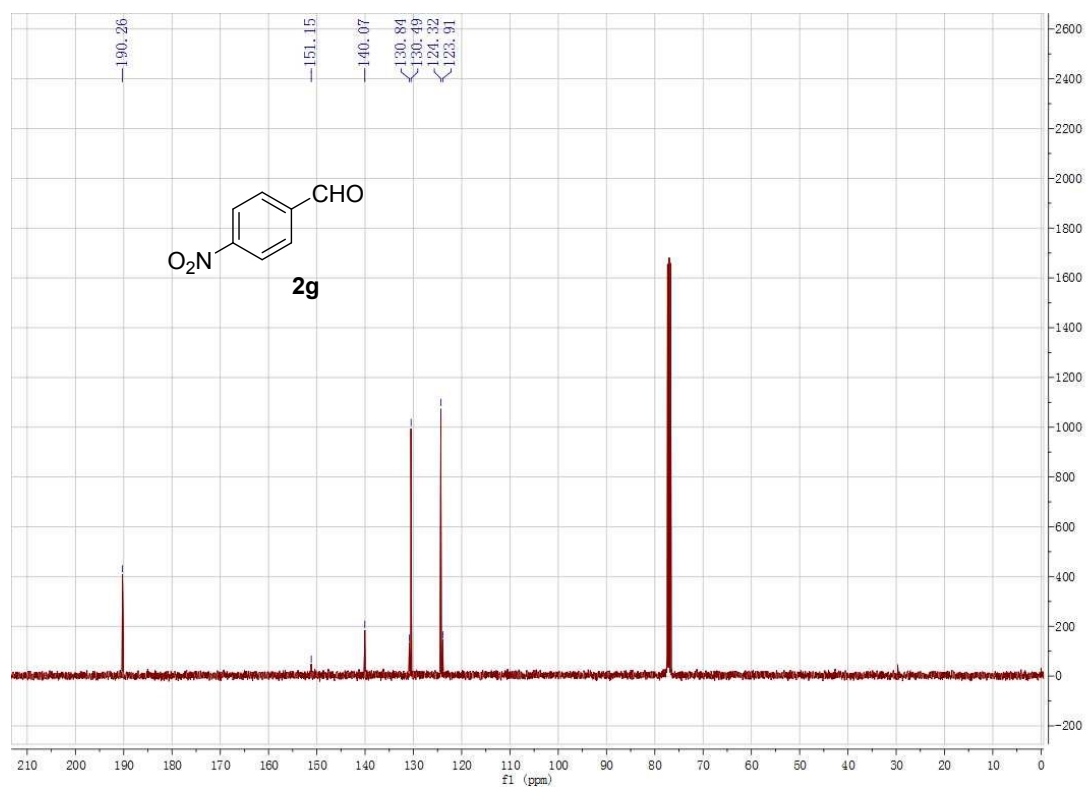
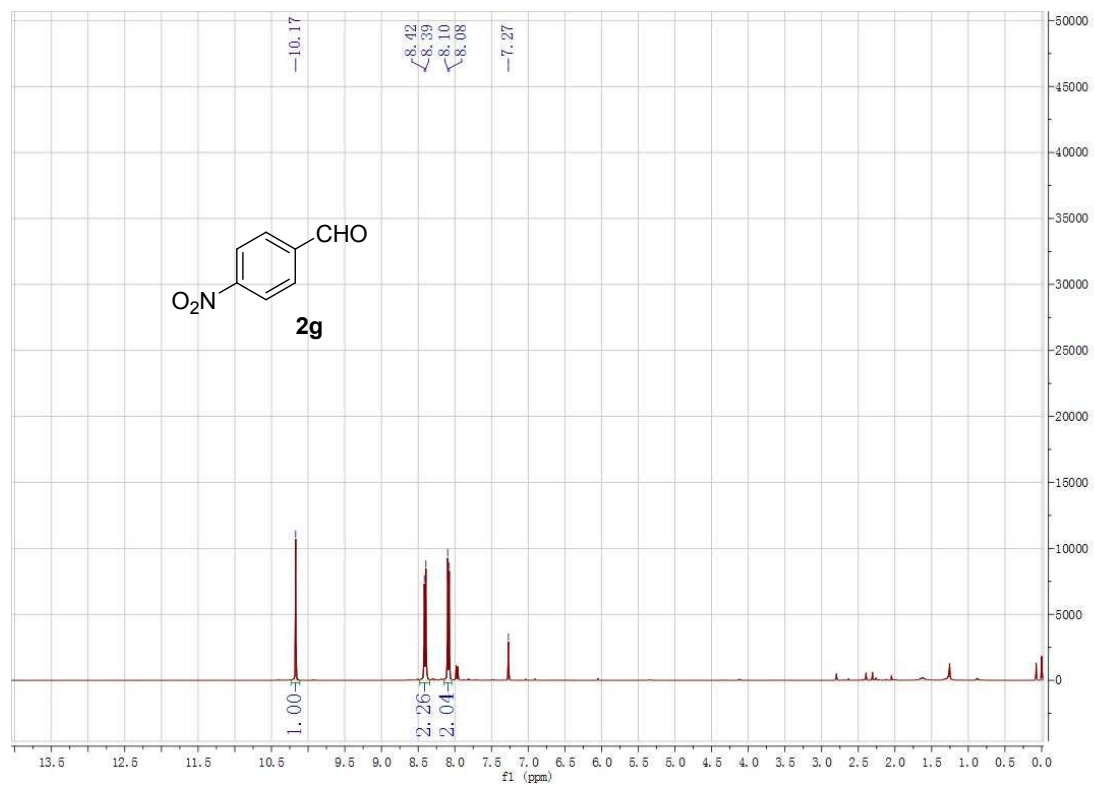


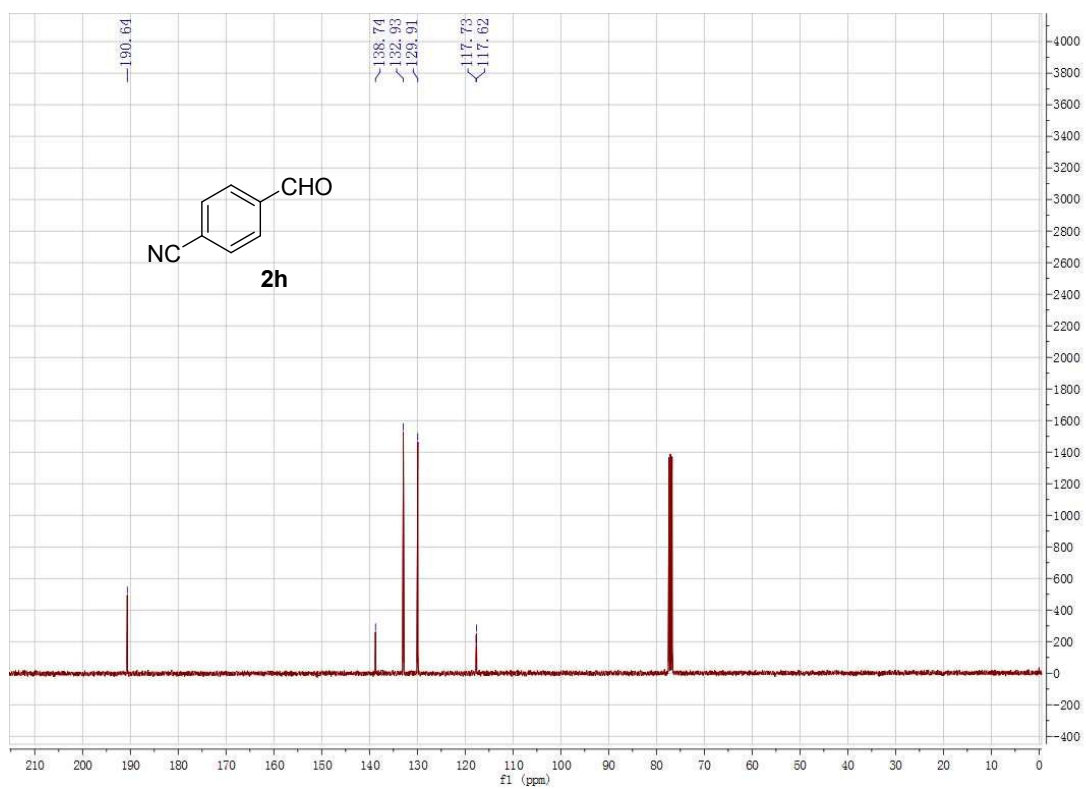
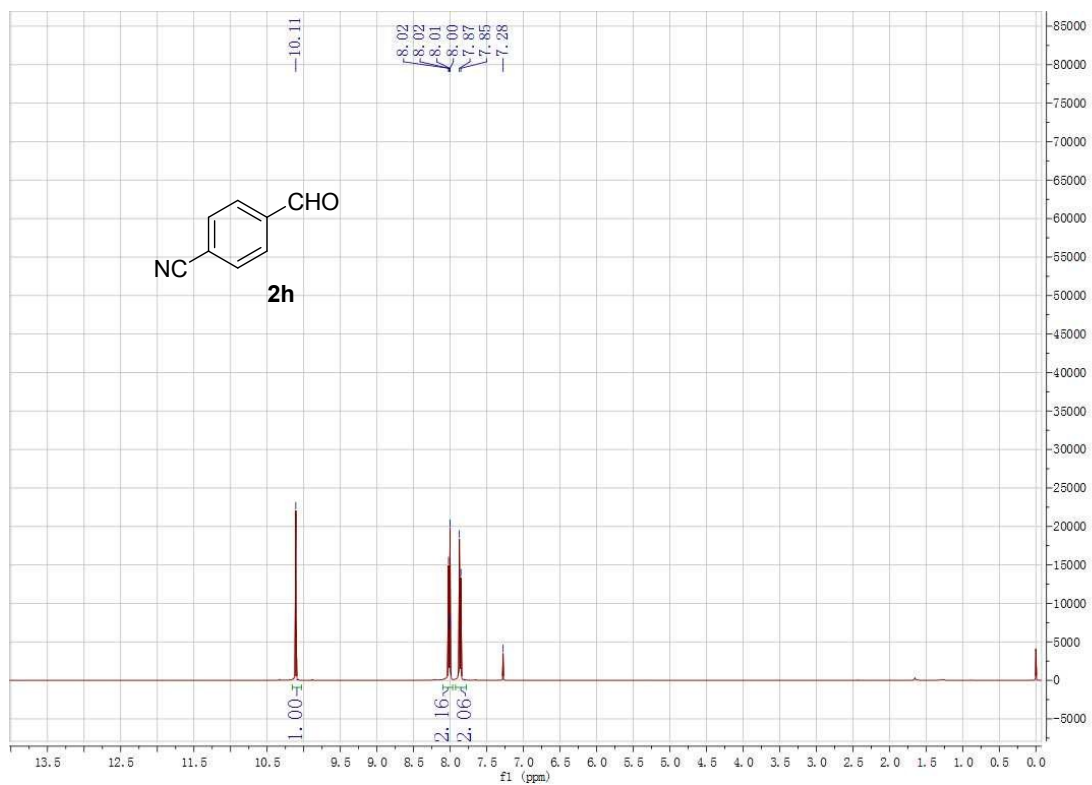


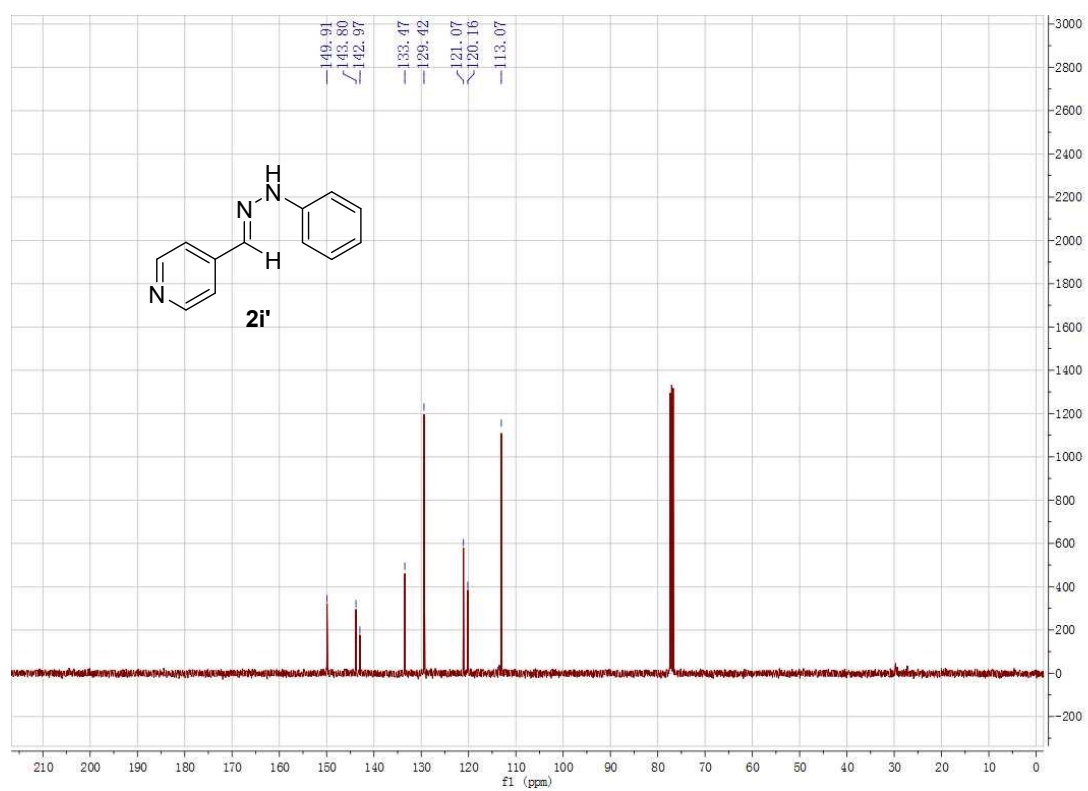
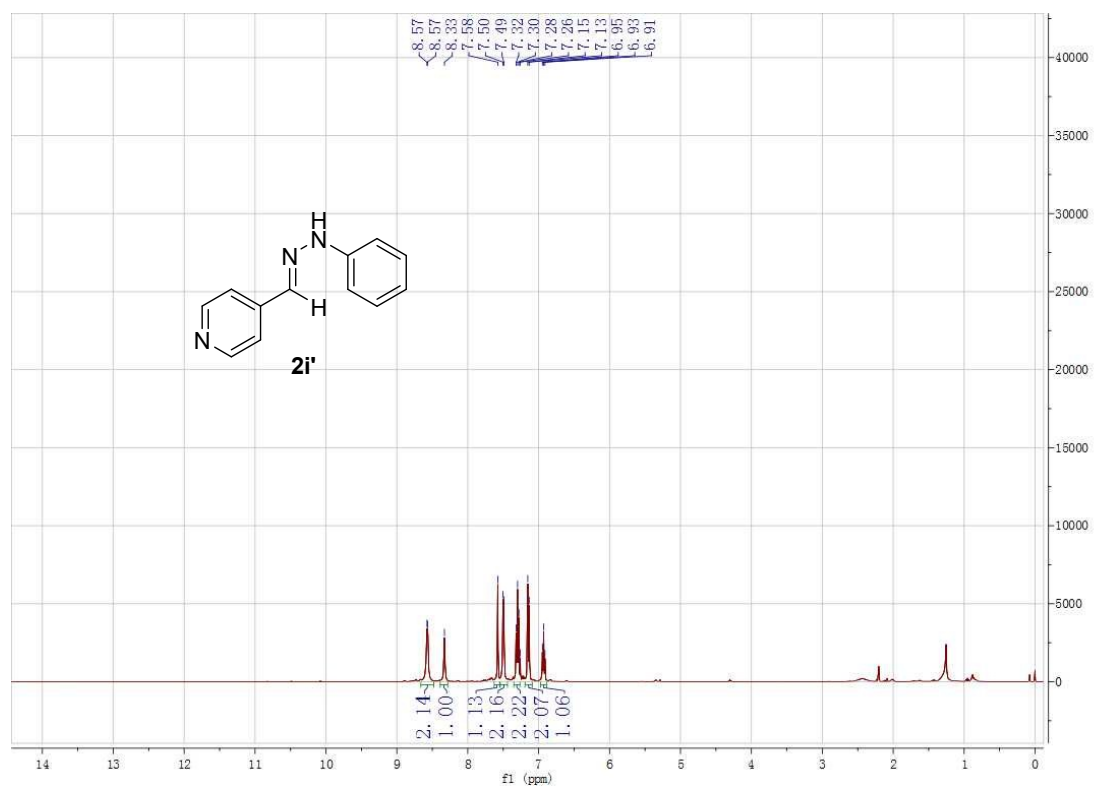


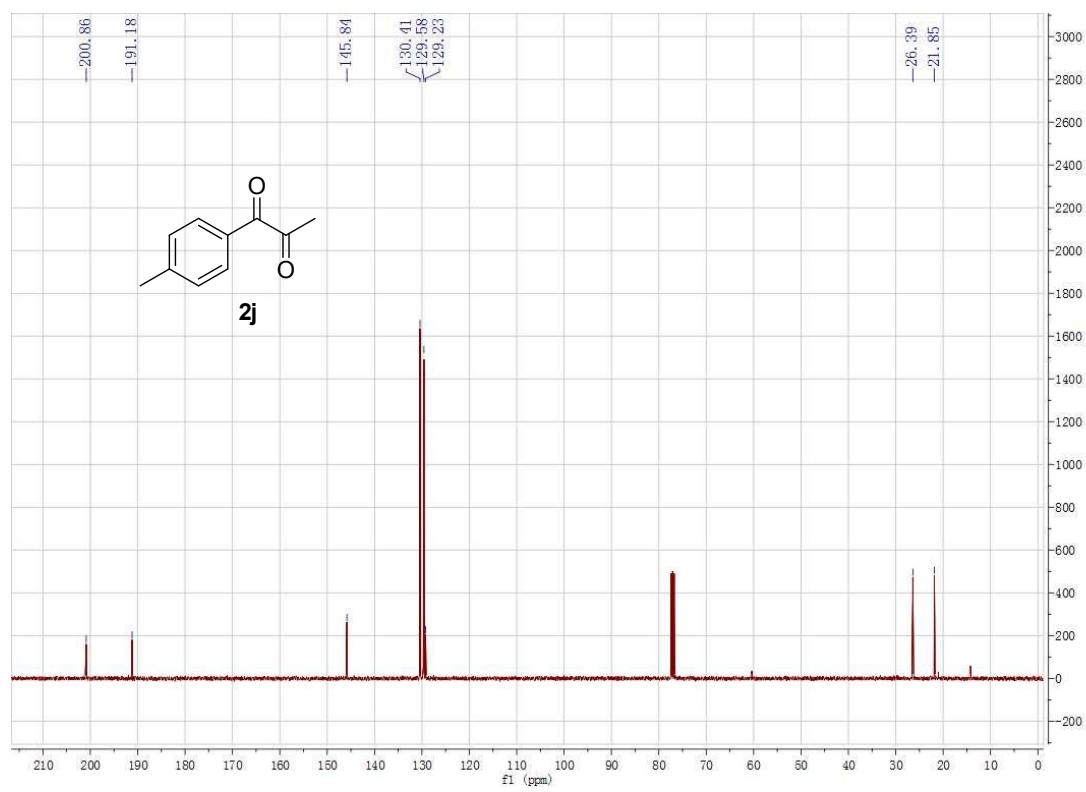
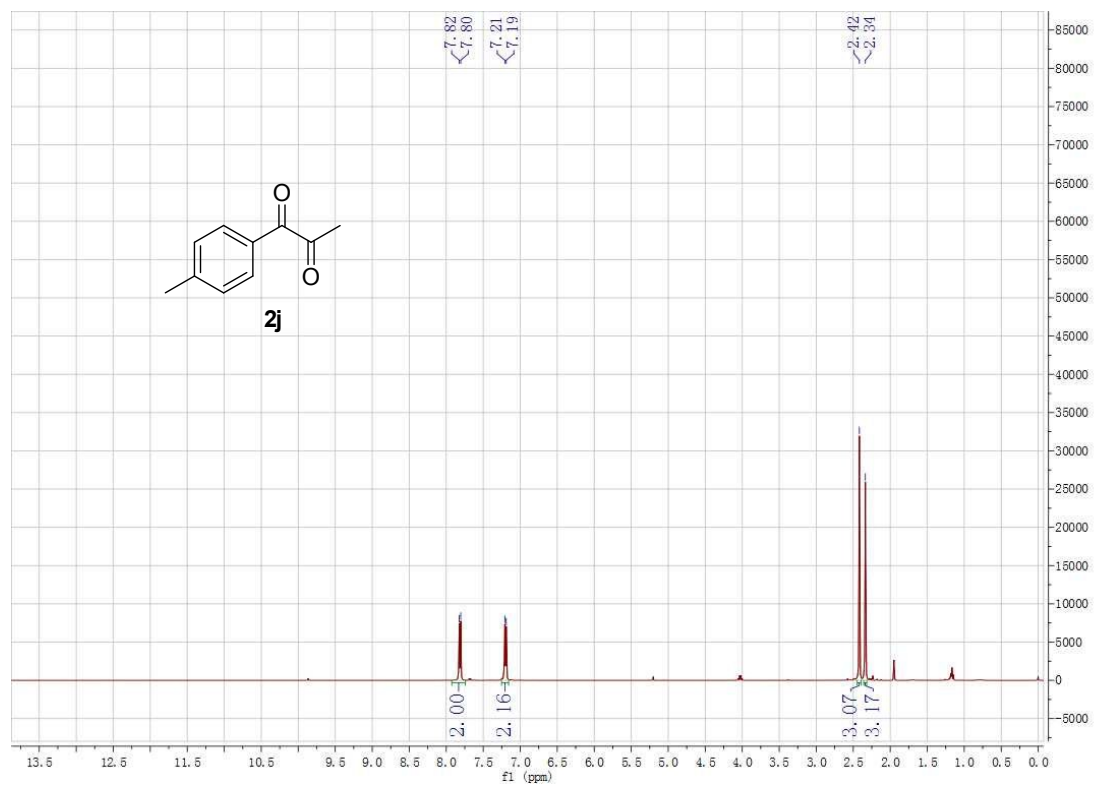


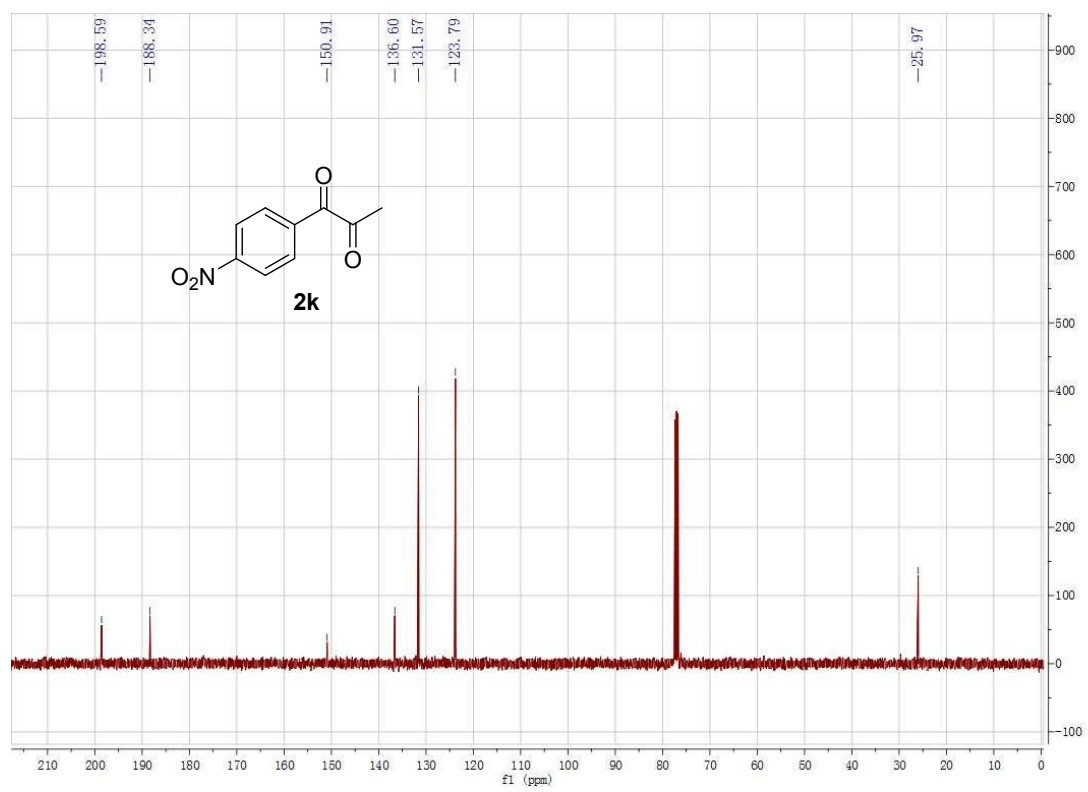
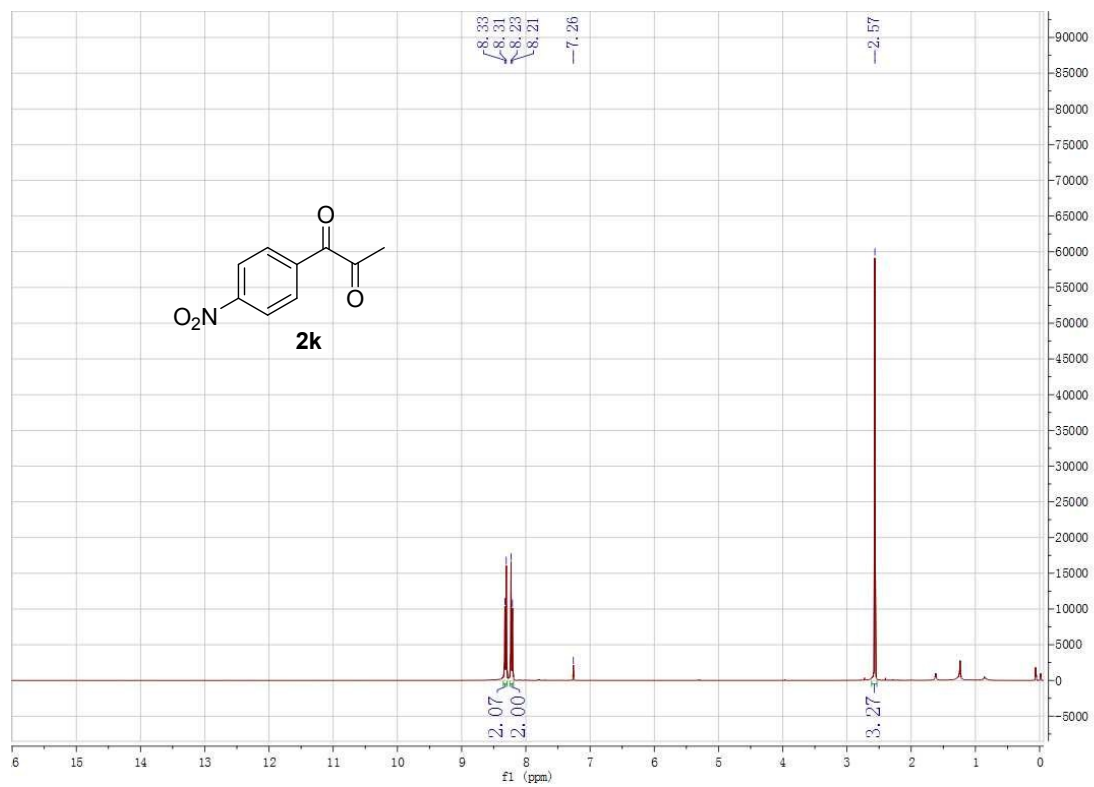


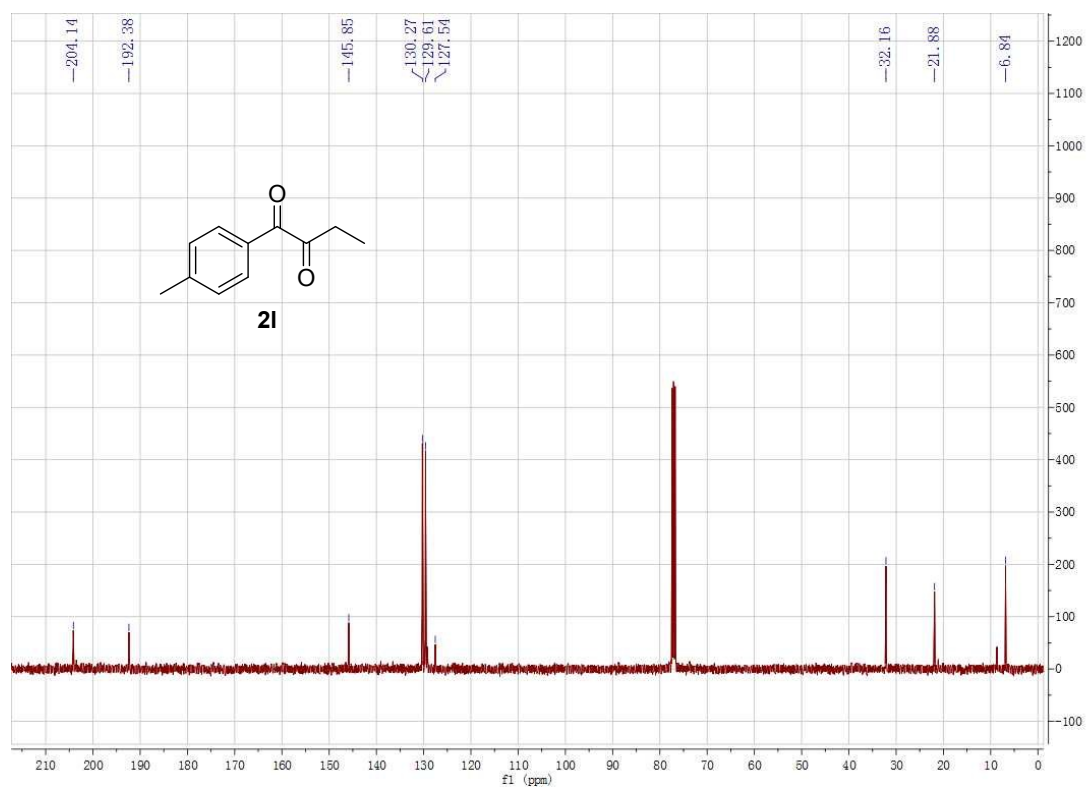
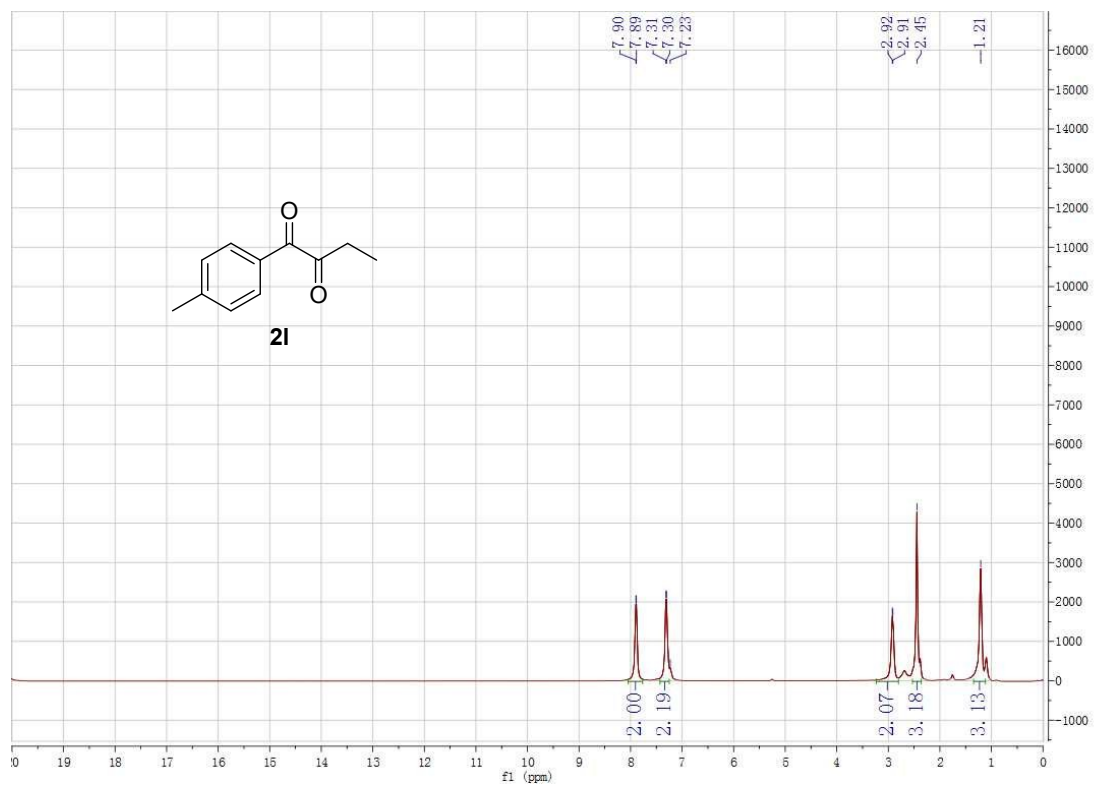


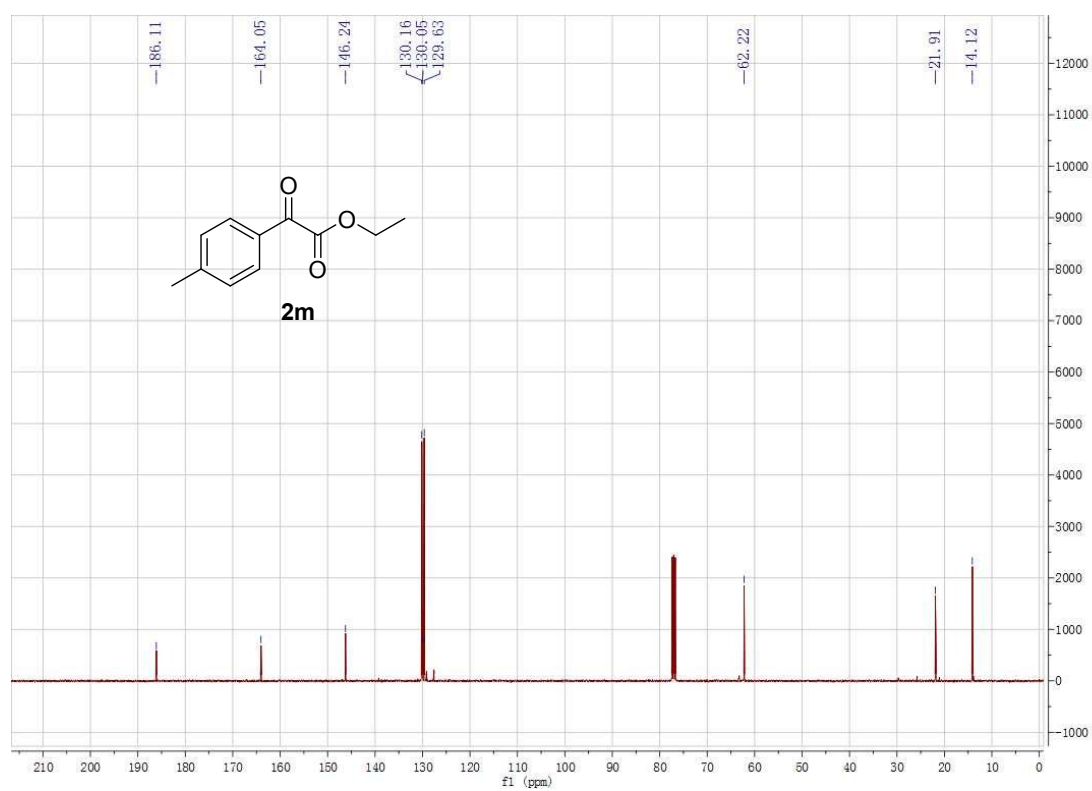
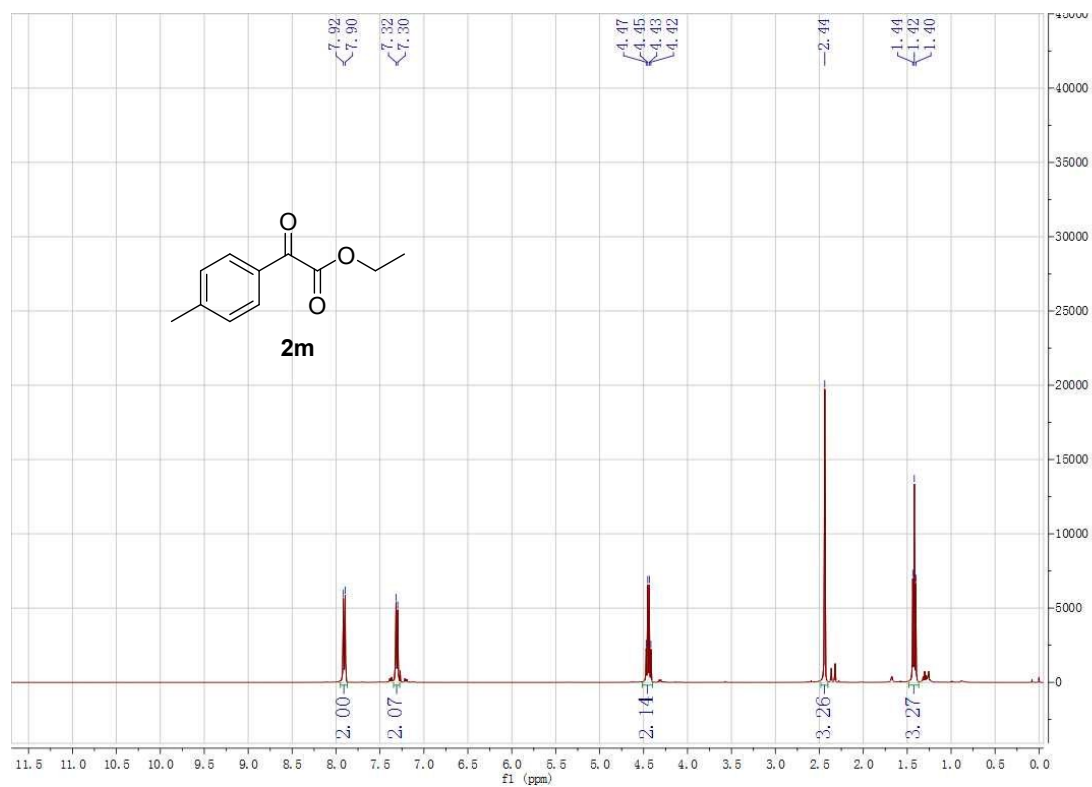


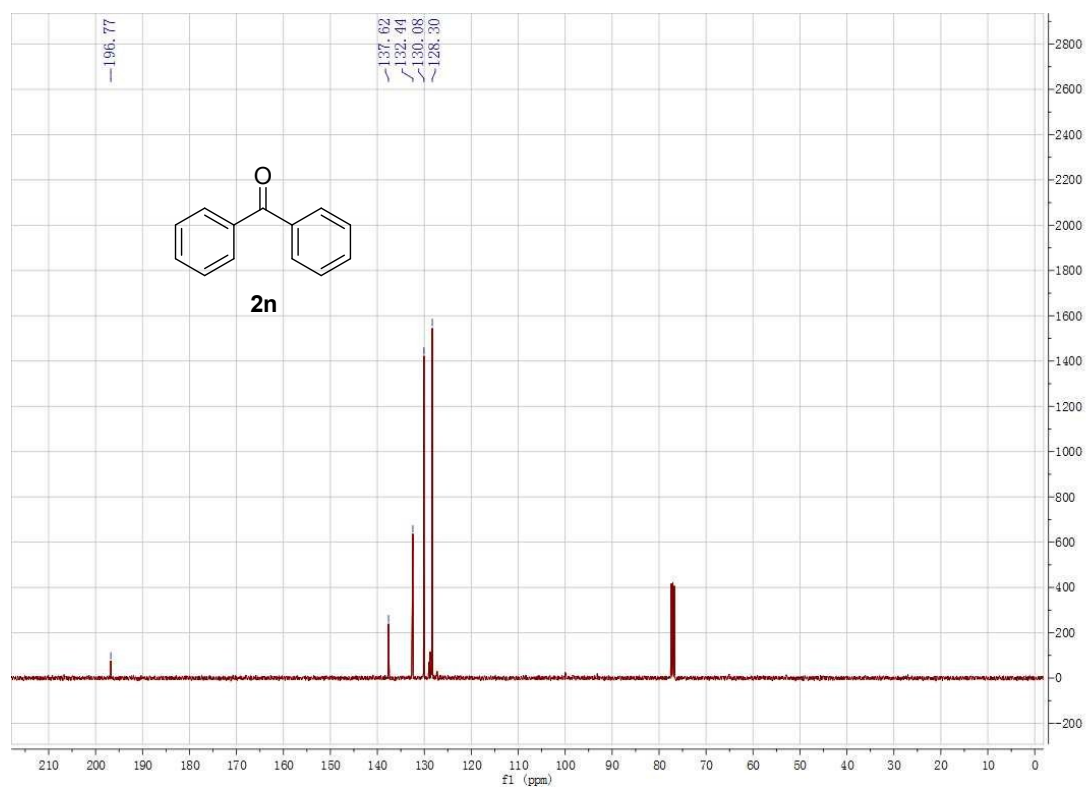
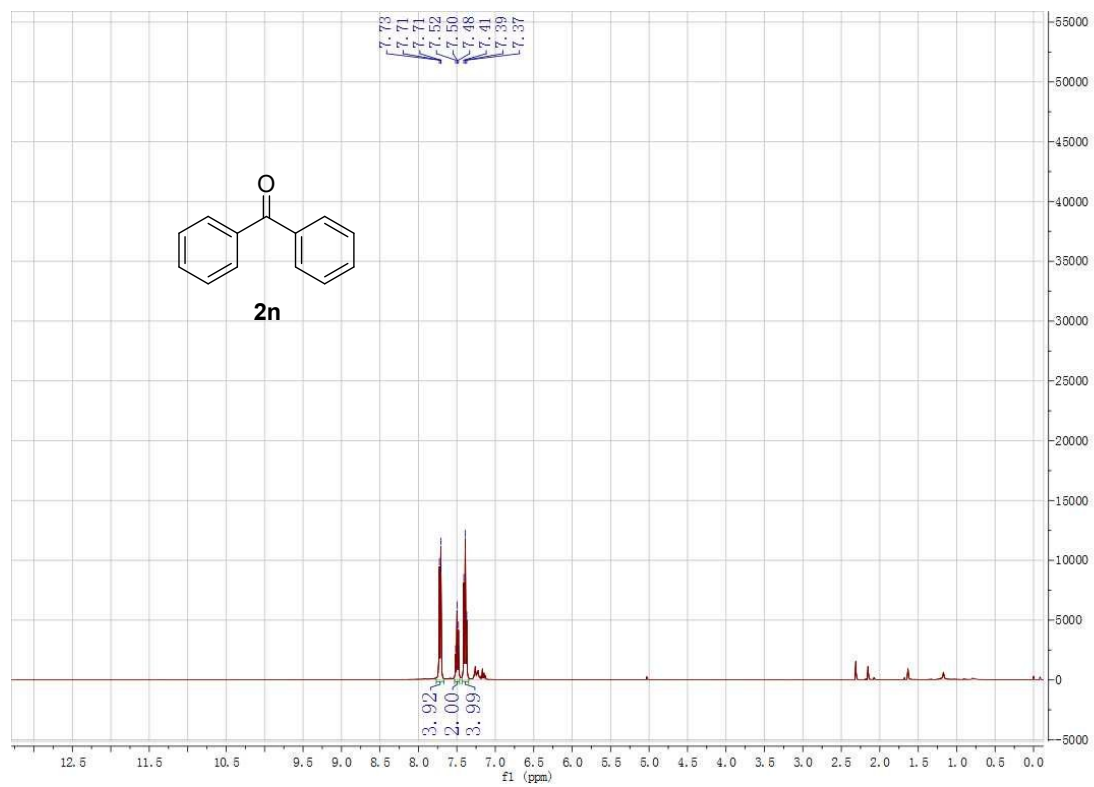


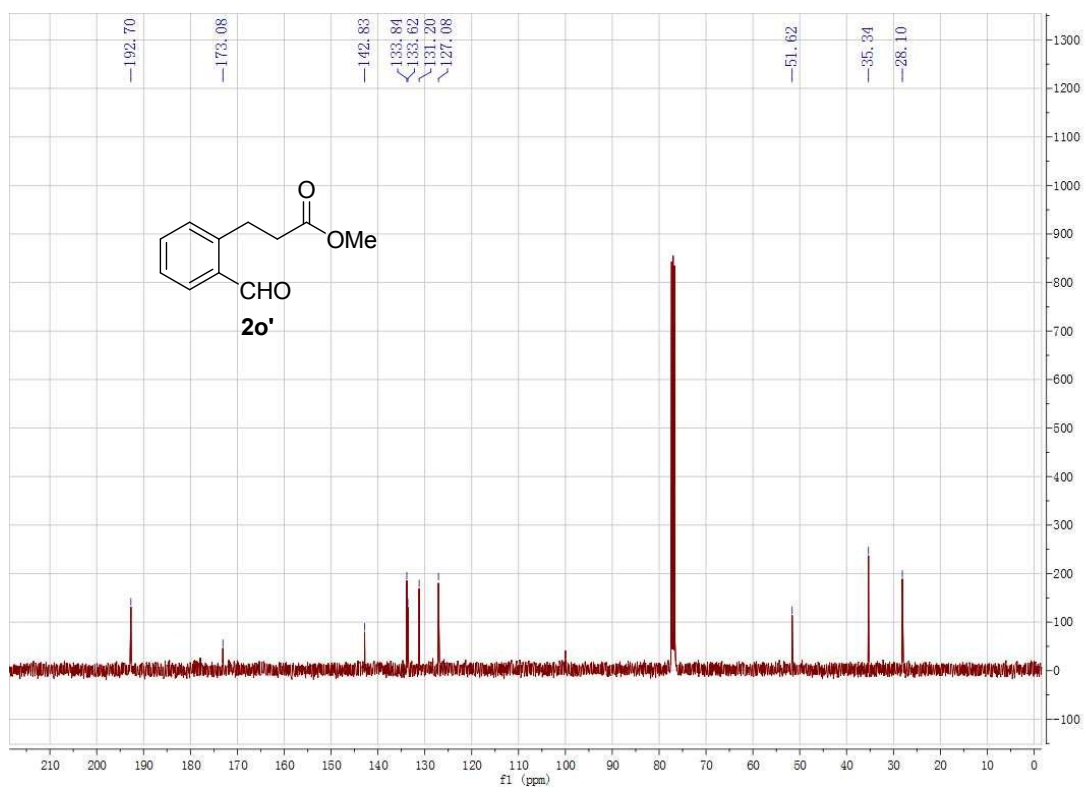
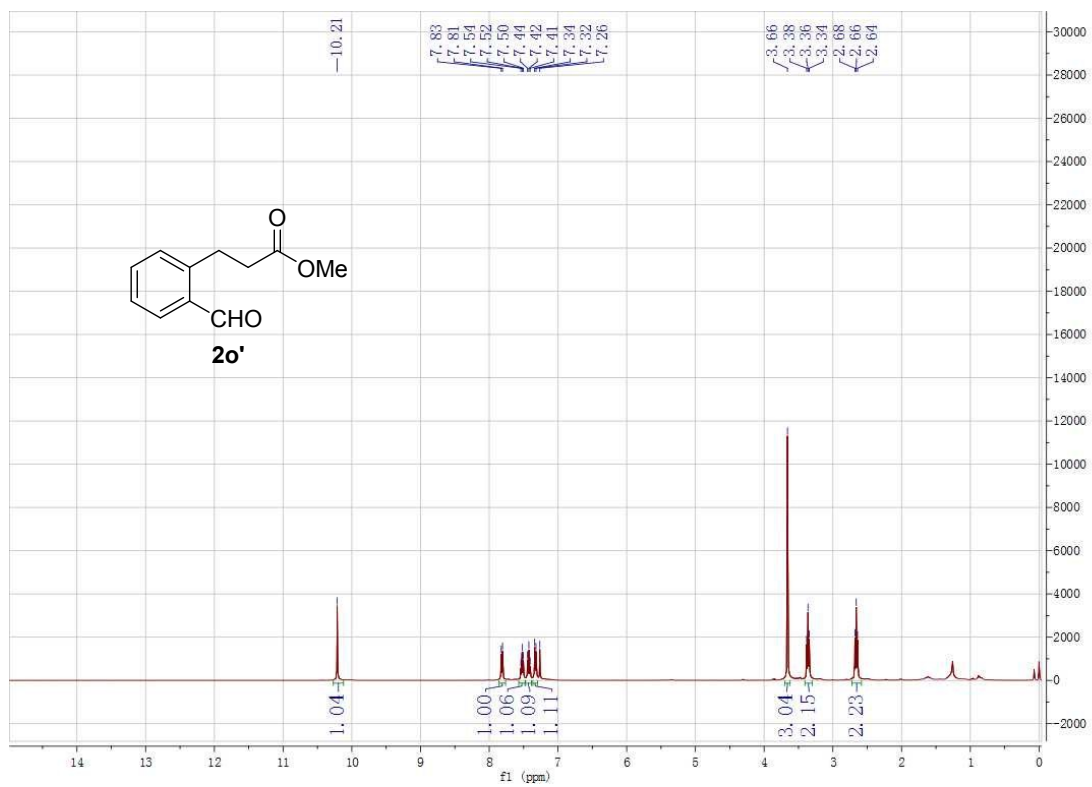


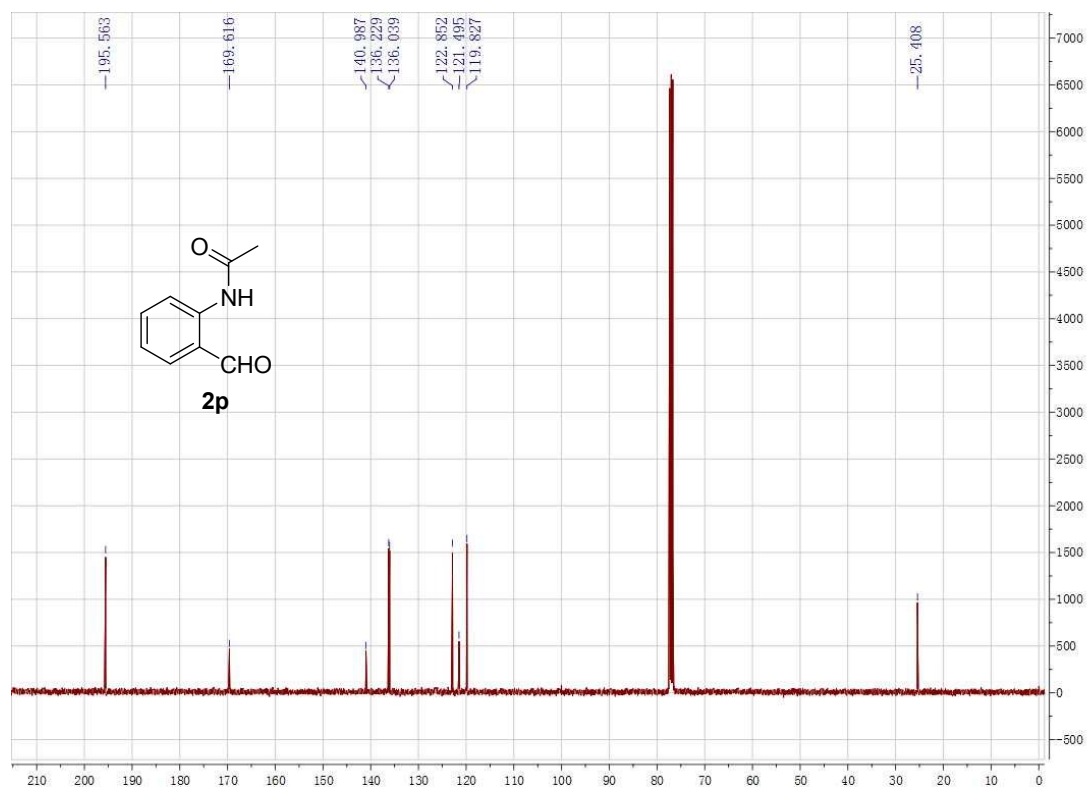
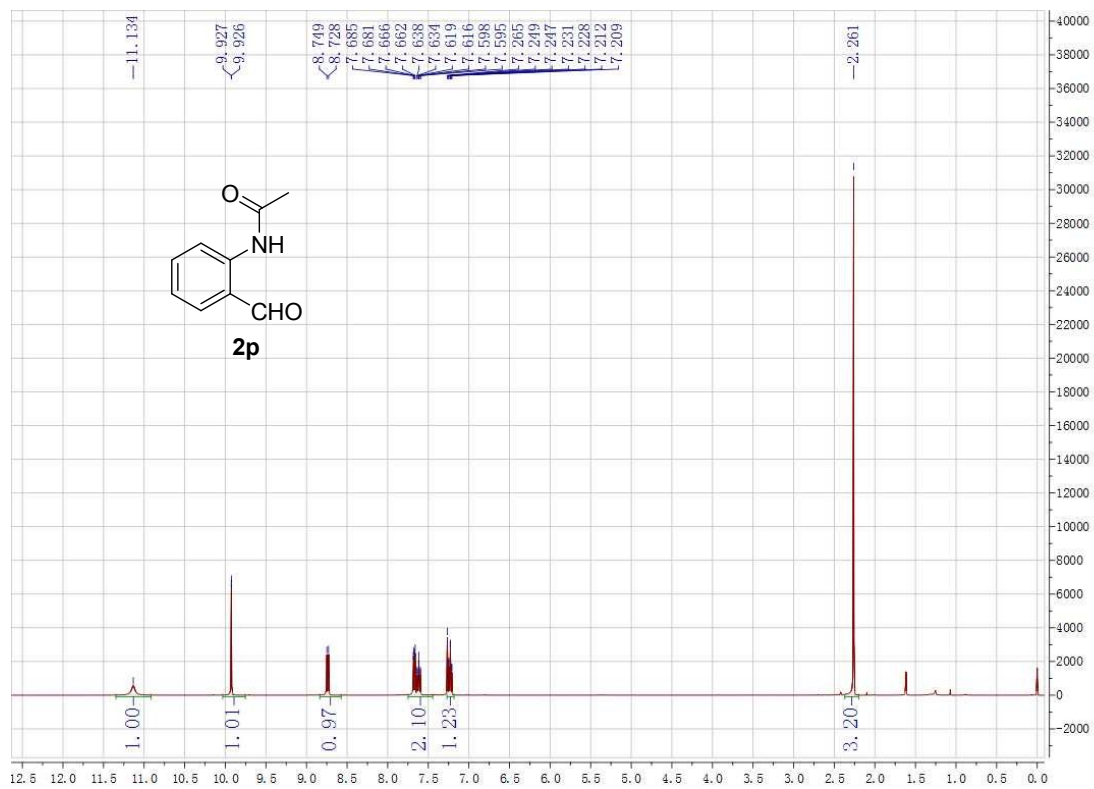


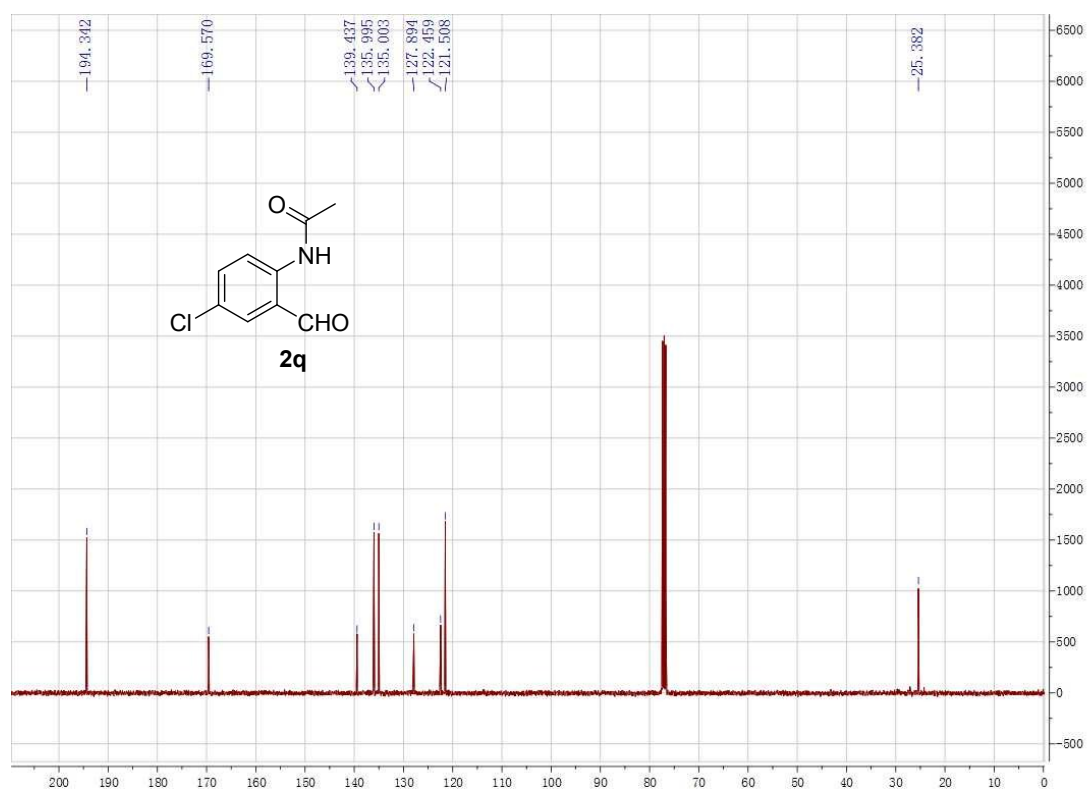
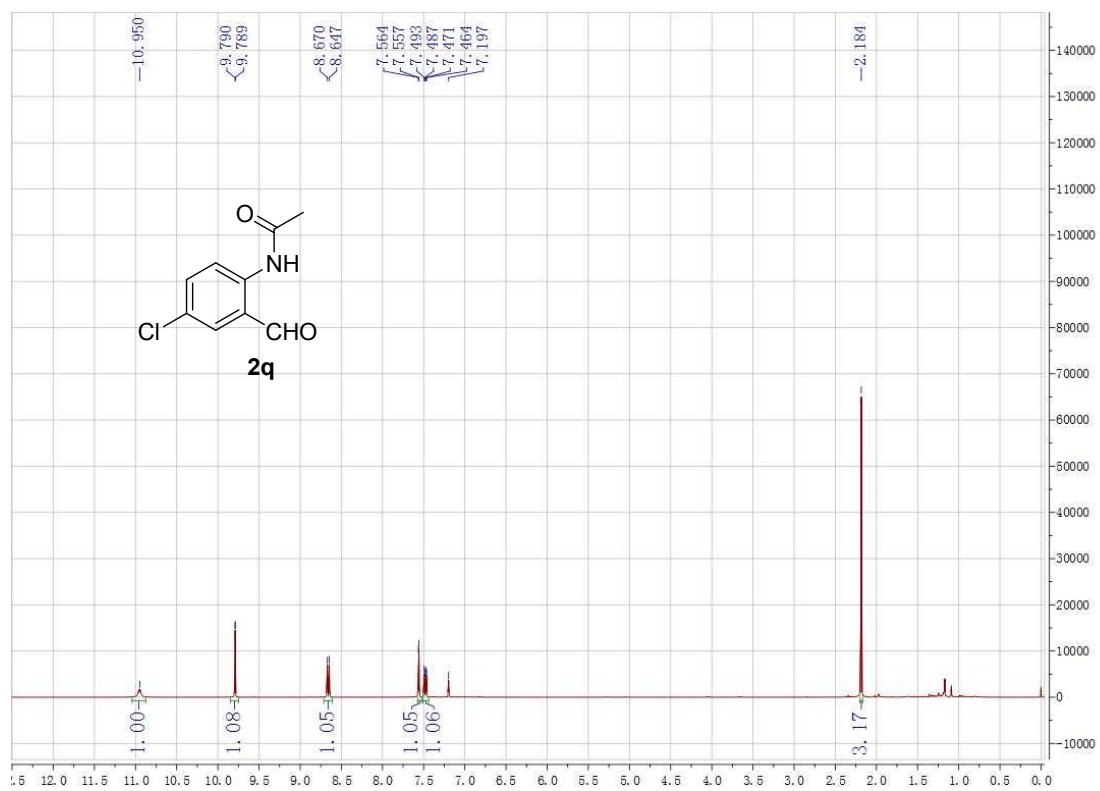


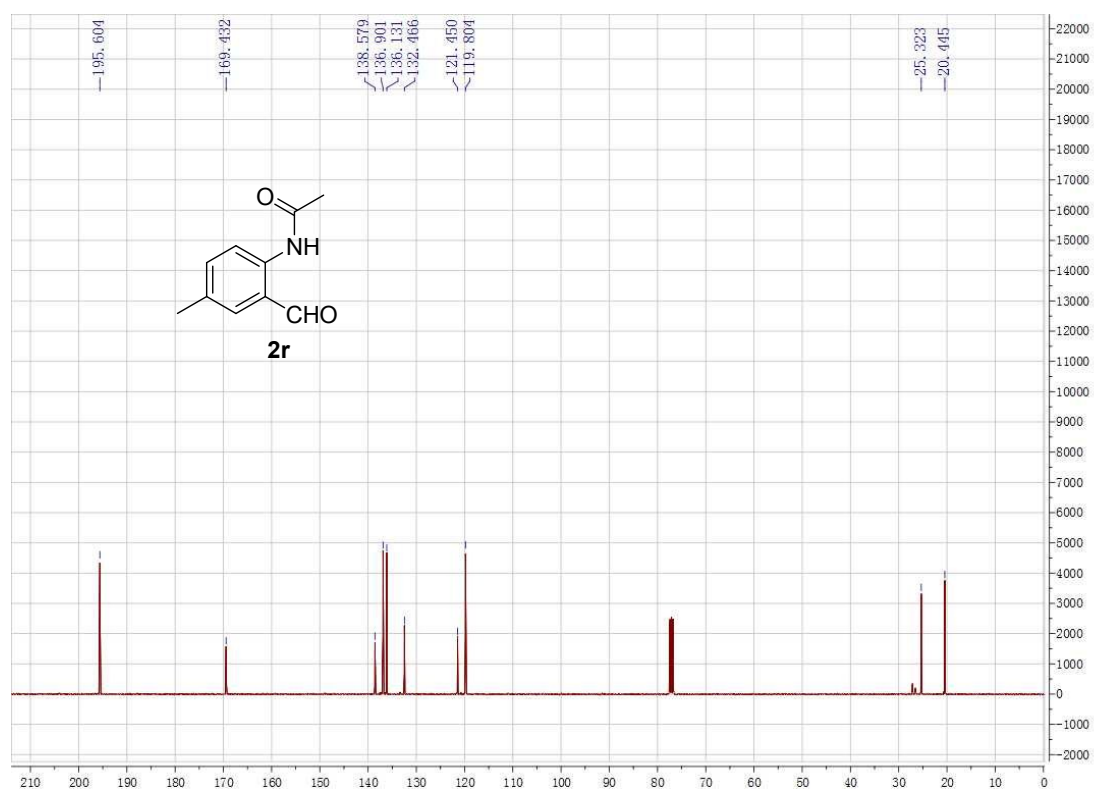
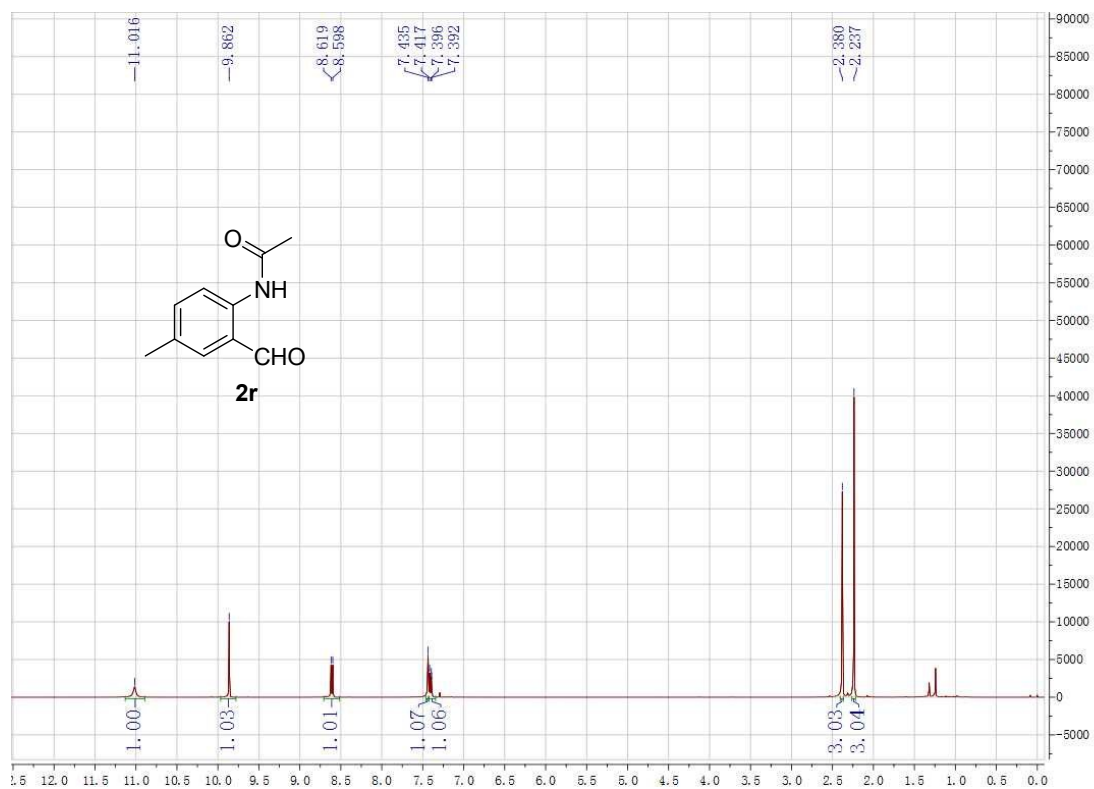


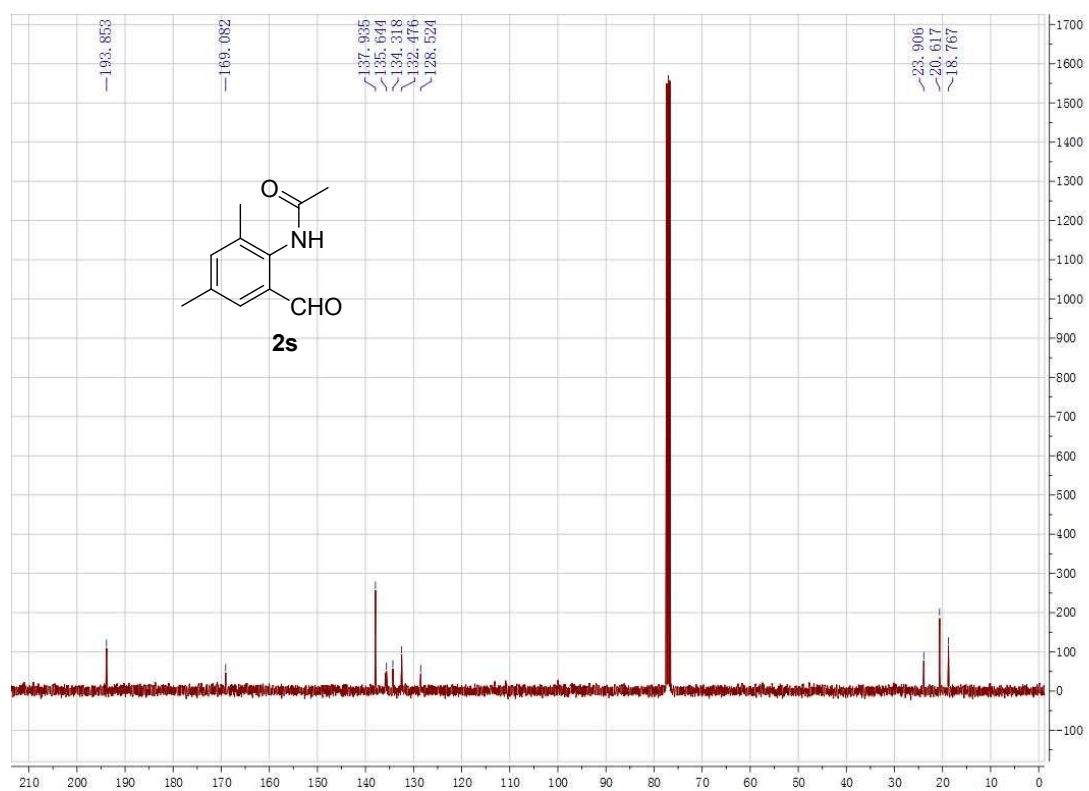
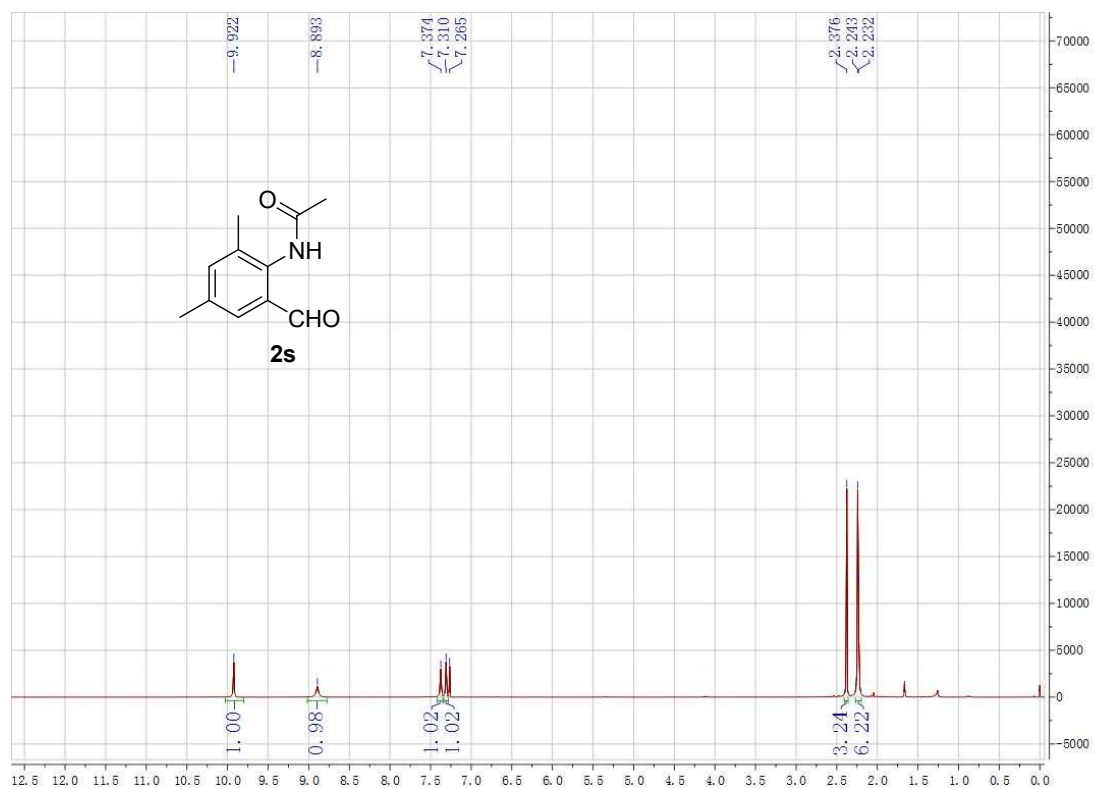


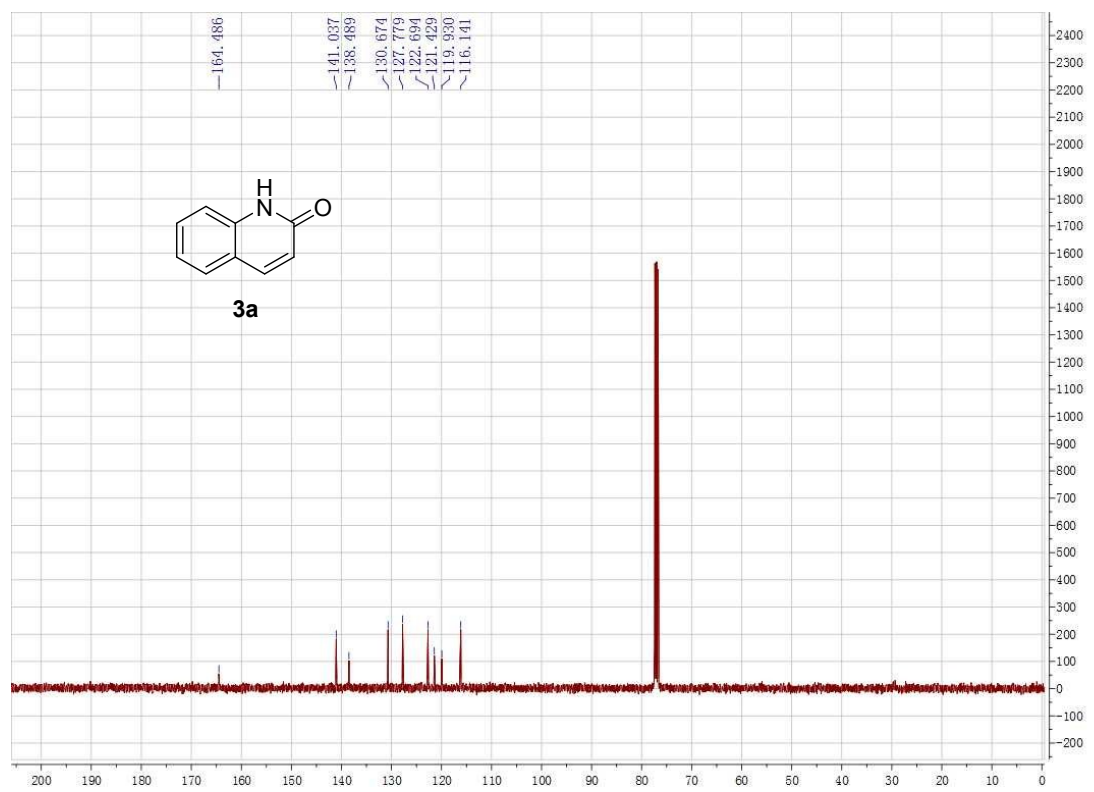
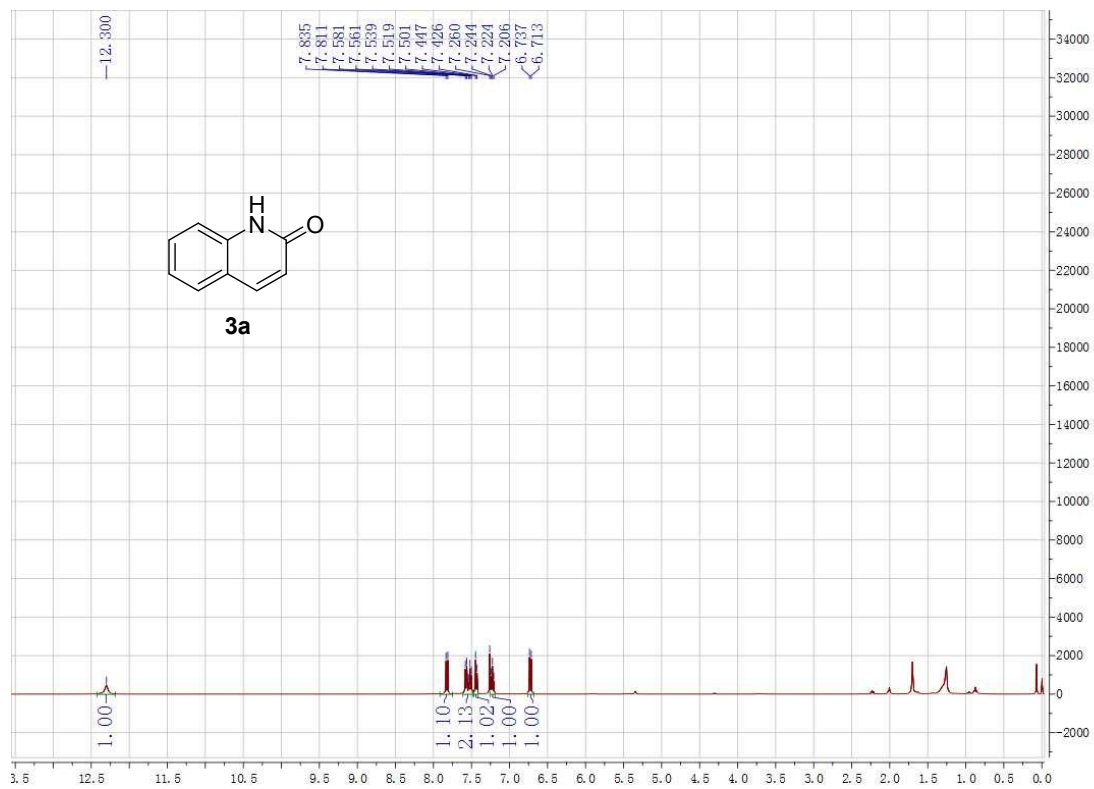


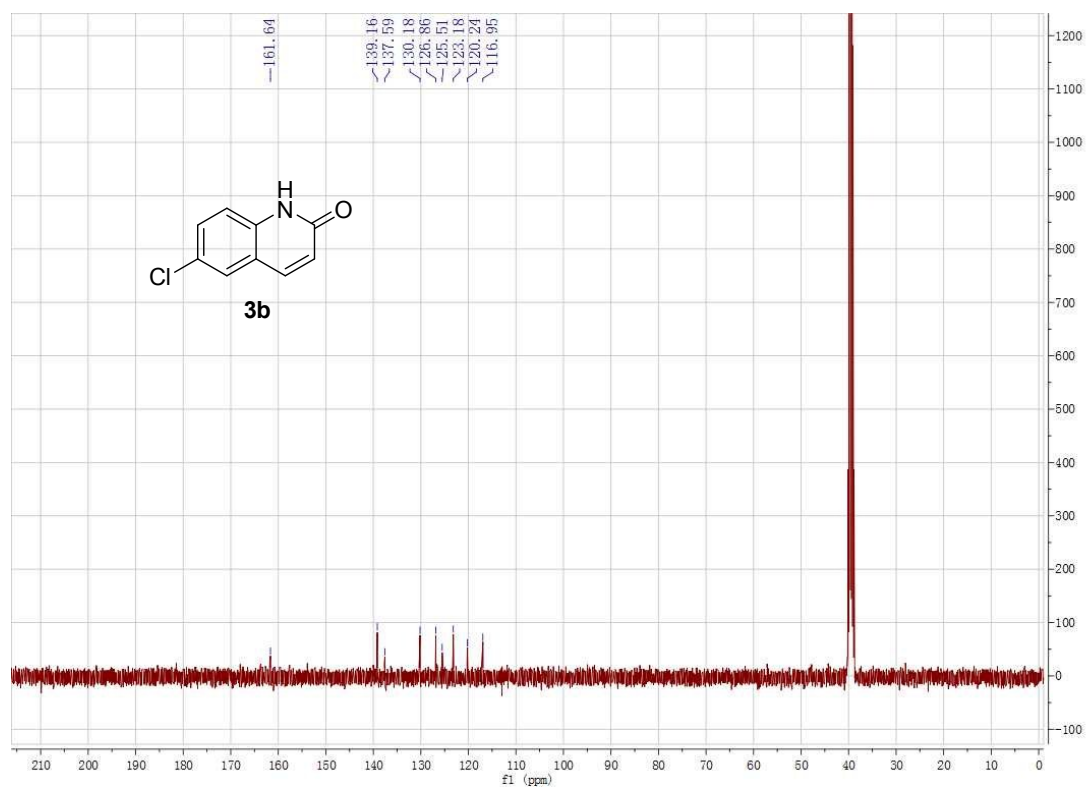
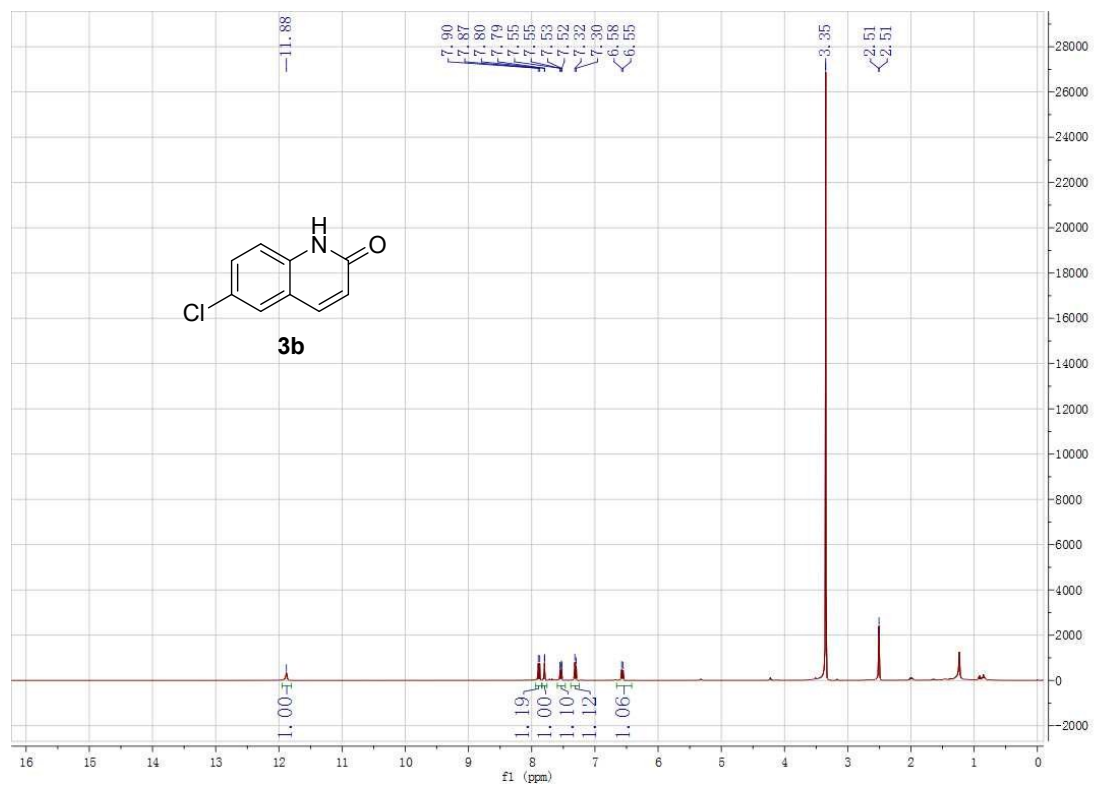


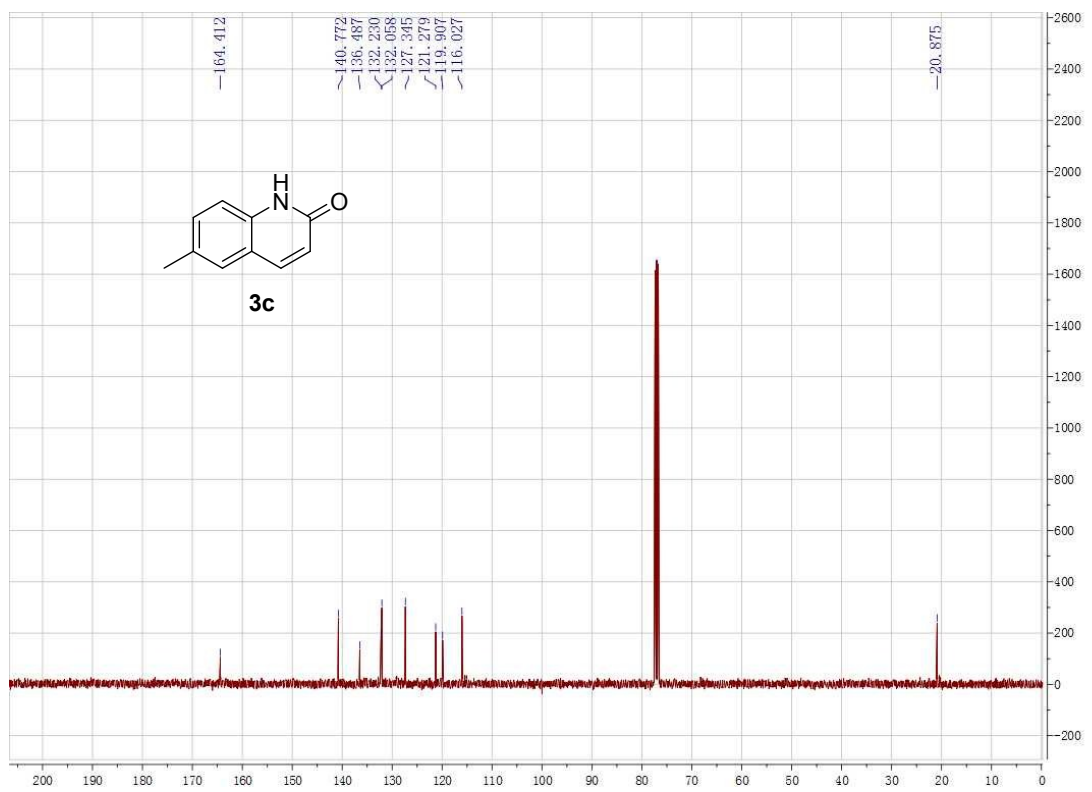
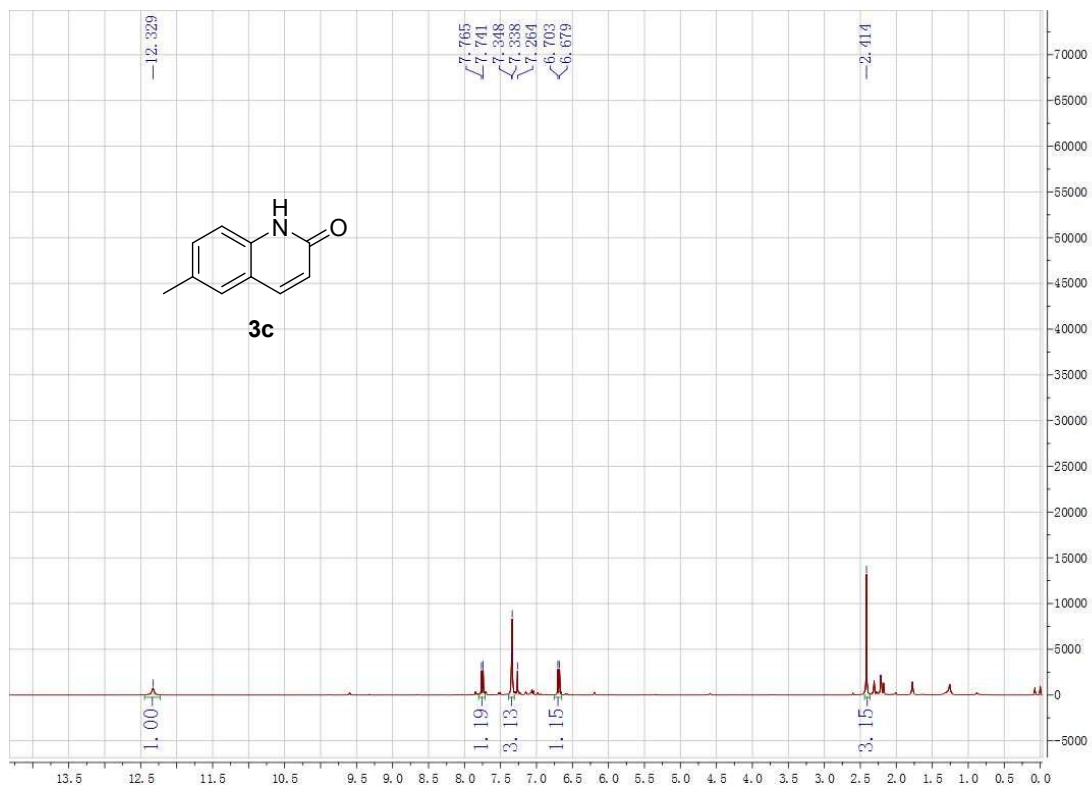


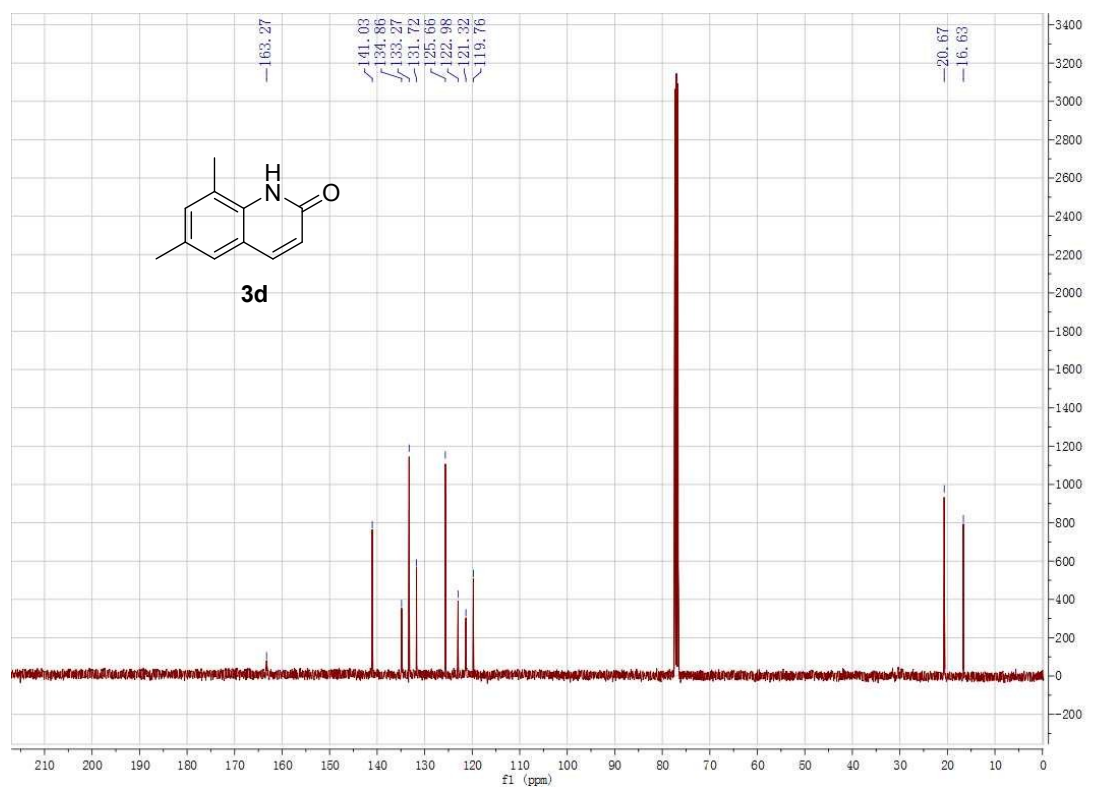
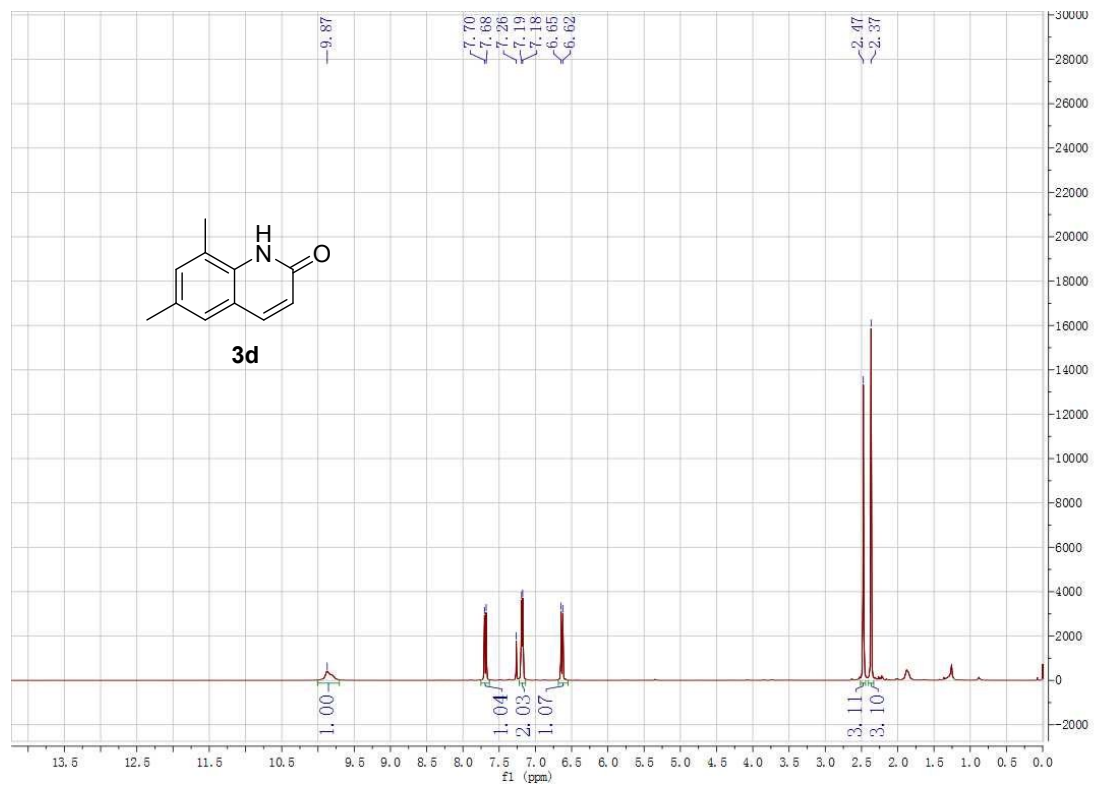


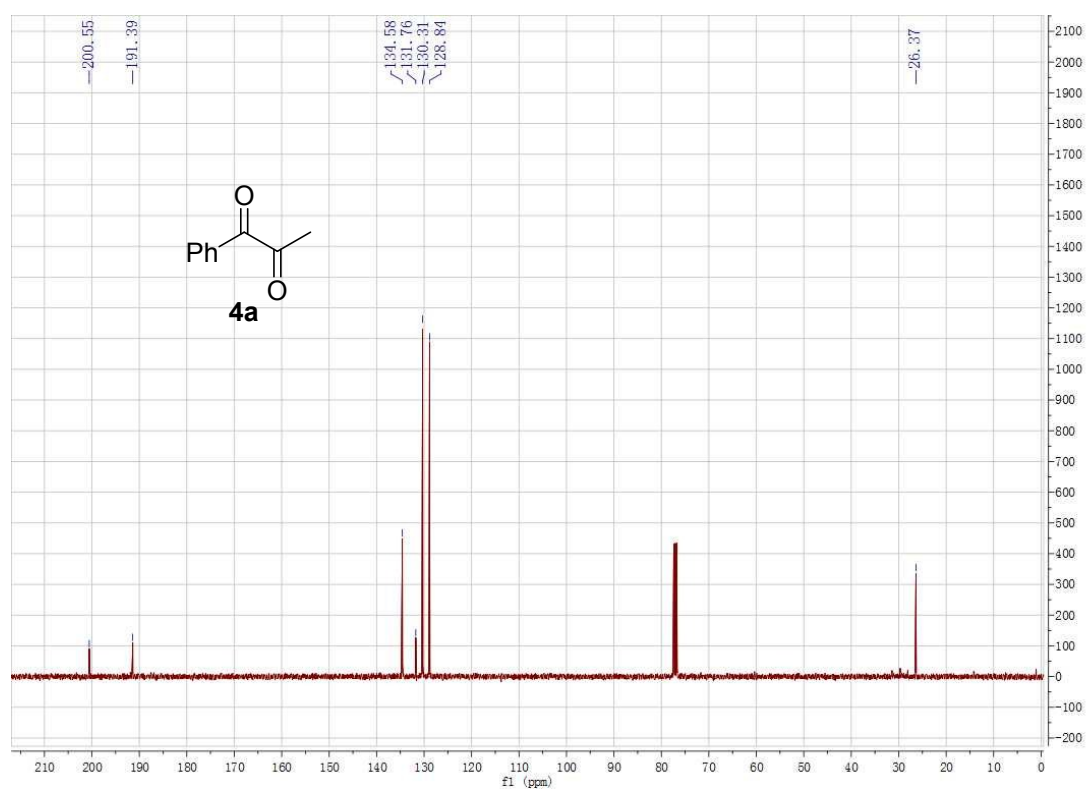
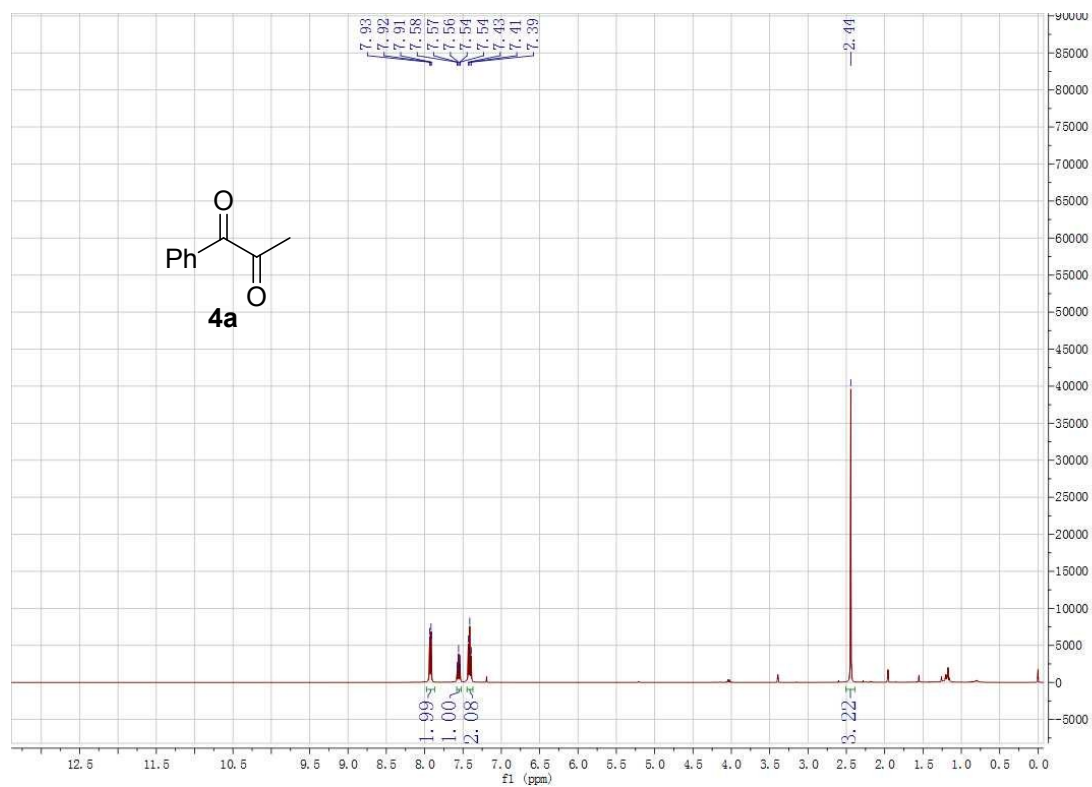












7) References

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