

Electronic Supplementary Information

for

**Three-component reaction for the synthesis of imides enabled by
electrochemical C(sp³)-H functionalization**

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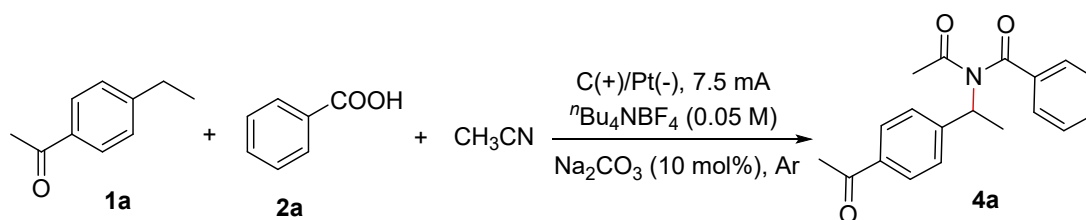
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1 General information

All reagents were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography. Column chromatography was performed using silica gel (300–400 mesh). The anodic electrode, graphite felt (10 mm×10 mm), was purchased from Tianjin Carbon Factory; cathodic electrode, platinum sheet (10 mm×10 mm×0.2 mm), was purchased from Chengxin Technology Co., LTD. The instrument for electrochemical reaction is Adjustable DC power supply (UTP1303). The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^1H), 100 MHz (^{13}C) and 376 MHz (^{19}F) in CDCl_3 using tetramethylsilane as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer. Melting points are uncorrected.

2 Experimental procedures

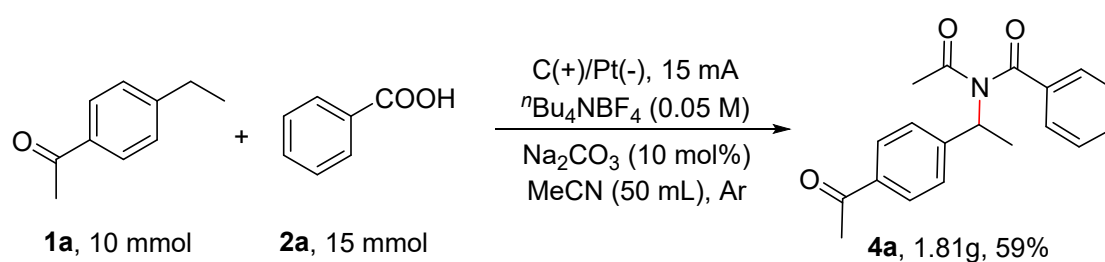
2.1 General procedure for the electrochemical reactions



An undivided four-necked flask (25 mL) was charged with benzoic acid (**2a**, 91.6 mg, 0.75 mmol), $n\text{Bu}_4\text{NBF}_4$ (164.6 mg, 0.5 mmol), Na_2CO_3 (5.2 mg, 0.05 mmol, 10 mol%). The flask equipped with a graphite felt electrode as the anode and a platinum plate electrode (10 mm × 10 mm) as the cathode was evacuated and backfilled with Ar for 3 times, then CH_3CN (10 mL) and 1-(4-ethylphenyl)ethan-1-one (**1a**, 74.1 mg, 0.5 mmol) were added in sequence. The reaction was equipped with platinum plate electrode (10 mm × 10 mm) as the cathode and graphite felt electrode as the anode, and was electrolyzed at room temperature under air atmosphere and constant current (7.5 mA) for 12 h. After the reaction was completed, the mixture was diluted with saturated NaHCO_3 (20 mL) and then extracted with CH_2Cl_2 (30 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated in *vacuo*. Subsequently, the crude residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (8:1, v/v) as eluent to afford the desired product **4a**.

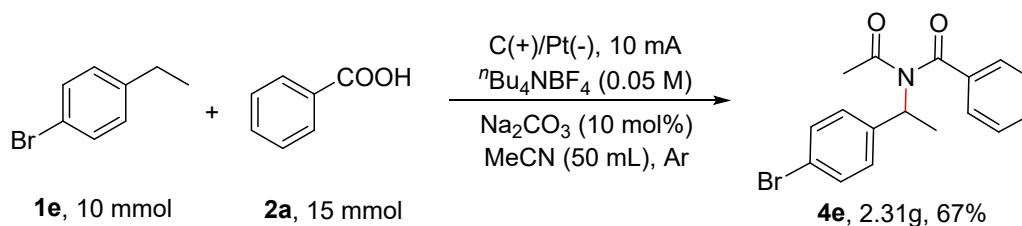


2.2 10 mmol-scale synthesis of 4a



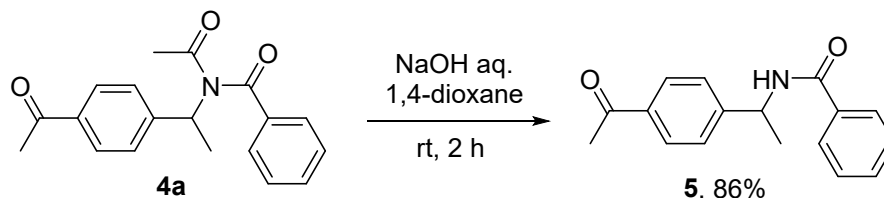
An undivided three-necked flask (100 mL) was charged with benzoic acid (**2a**, 1.83 g, 15 mmol), $^t\text{Bu}_4\text{NBF}_4$ (0.82 g, 2.5 mmol), Na_2CO_3 (106.00 mg, 1 mmol, 10 mol%). The flask equipped with a graphite felt electrode as the anode and a platinum plate electrode (10 mm \times 10 mm) as the cathode was evacuated and backfilled with Ar for 3 times, then CH_3CN (50 mL) and 1-(4-ethylphenyl)ethan-1-one (**1a**, 1.48 g, 10 mmol) were added in sequence. The reaction was equipped with platinum plate electrode (10 mm \times 10 mm) as the cathode and graphite felt electrode as the anode, and was electrolyzed at room temperature under air atmosphere and constant current (15 mA) for 96 h. After the reaction was completed, the mixture was diluted with saturated NaHCO_3 (50 mL) and then extracted with CH_2Cl_2 (80 mL \times 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated in *vacuo*. Subsequently, the crude residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (8:1, v/v) as eluent to afford the desired product **4a**.

2.3 10 mmol-scale synthesis of 4e



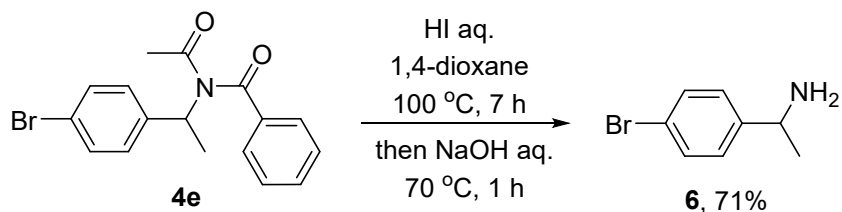
An undivided three-necked flask (100 mL) was charged with benzoic acid (**2a**, 1.83 g, 15 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (0.82 g, 2.5 mmol) and Na_2CO_3 (106.0 mg, 1 mmol, 10 mol%). The flask equipped with a graphite felt electrode as the anode and a platinum plate electrode (10 mm \times 10 mm) as the cathode was evacuated and backfilled with Ar for 3 times, then CH_3CN (50 mL) and 1-bromo-4-ethylbenzene (**1e**, 1.85 g, 10 mmol) was added in sequence. The reaction mixture was stirred and electrolyzed at a constant current (15 mA) at room temperature for 24 h. After the reaction was completed, the mixture was diluted with saturated NaHCO_3 (50 mL) and then extracted with CH_2Cl_2 (80 mL \times 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated in *vacuo*. Subsequently, the crude residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1, v/v) as eluent to afford the desired product **4e**.

2.4 The transformation of 4a to 5



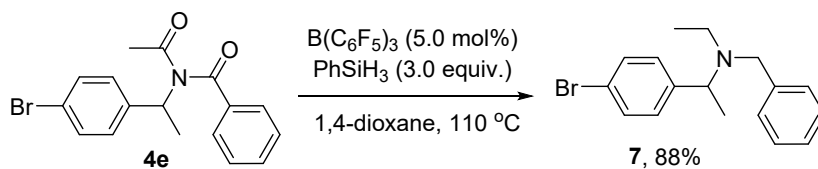
In a Schlenk flask (25 mL), **4a** (0.2 mmol, 61.8 mg), 1,4-dioxane (5 mL) and NaOH solution (4.0 mol/L, 5 mL) were added in sequence. The reaction mixture was stirred at room temperature for 2 h. After the reaction was completed, the mixture was diluted with water (20 mL) and then extracted with CH_2Cl_2 (30 mL \times 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated in *vacuo*. Subsequently, the crude residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (2:1, v/v) as eluent to afford the desired product **5**.

2.5 The transformation of 4e to 6



In a Schlenk flask (25 mL), **4e** (69.0 mg 0.2 mmol), 1,4-dioxane (5 mL) and HI solution (20%, 3 mL) were added in sequence. The reaction mixture was stirred at 100 °C for 7h. Next, NaOH solution (4 mol/L, 15 mL) was added and the mixture was heated at 70 °C for 1h. After the reaction was completed, the mixture was diluted with water (20 mL) and then extracted with CH₂Cl₂ (30 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered, concentrated in *vacuo*. Subsequently, the crude residue was purified by silica gel chromatography using ether/ethyl acetate (1:1, v/v) as eluent to afford the desired product **6**.

2.6 The transformation of 4e to 7

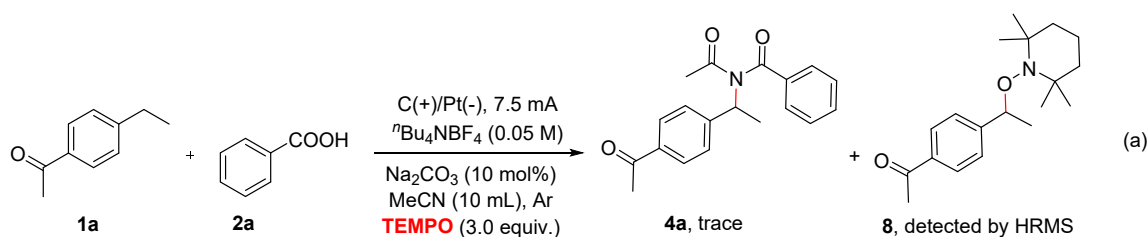


A Schlenk flask (25 mL) was charged with B(C₆F₅)₃ (12.8 mg, 0.025 mol, 5.0 mol%), **4e** (172.5 mg, 0.5 mmol), 1,4-dioxane (2 mL) and PhSiH₃ (162.3 mg, 1.5 mmol, 3.0 equiv) under Ar atmosphere. The reaction mixture was stirred and refluxed at 110 °C for 16 h. After the imide **4e** was consumed completely, the mixture was diluted with water (20 mL) and then extracted with CH₂Cl₂ (30 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered, concentrated in *vacuo*. Subsequently, the crude residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (2:1, v/v) as eluent to afford the desired product **7**.

3. Mechanistic studies

3.1 Control experiments

3.1.1 Reaction with TEMPO



An undivided four-necked flask (25 mL) was charged with benzoic acid (**2a**, 91.6 mg, 0.75 mmol), TEMPO (234.4 mg, 1.5 mmol, 3 equiv.), $n\text{Bu}_4\text{NBF}_4$ (164.6 mg, 0.5 mmol), Na_2CO_3 (5.2 mg, 0.05 mmol, 10 mol%). The flask equipped with a graphite felt electrode as the anode and a platinum plate electrode (10 mm \times 10 mm) as the cathode was evacuated and backfilled with Ar for 3 times, then CH_3CN (10 mL) and 1-(4-ethylphenyl)ethan-1-one (**1a**, 74.1 mg, 0.5 mmol) were added in sequence. The reaction was equipped with platinum plate electrode (10 mm \times 10 mm) as the cathode and graphite felt electrode as the anode, and was electrolyzed at room temperature under air atmosphere and constant current (7.5 mA) for 12 h. The reaction was obviously suppressed by the addition of TEMPO, and a trapping product **8** was observed through the HRMS analysis from the reaction solution (Figure S1).

8, HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{30}\text{NO}_2^+$, 304.2271; found 304.2276.

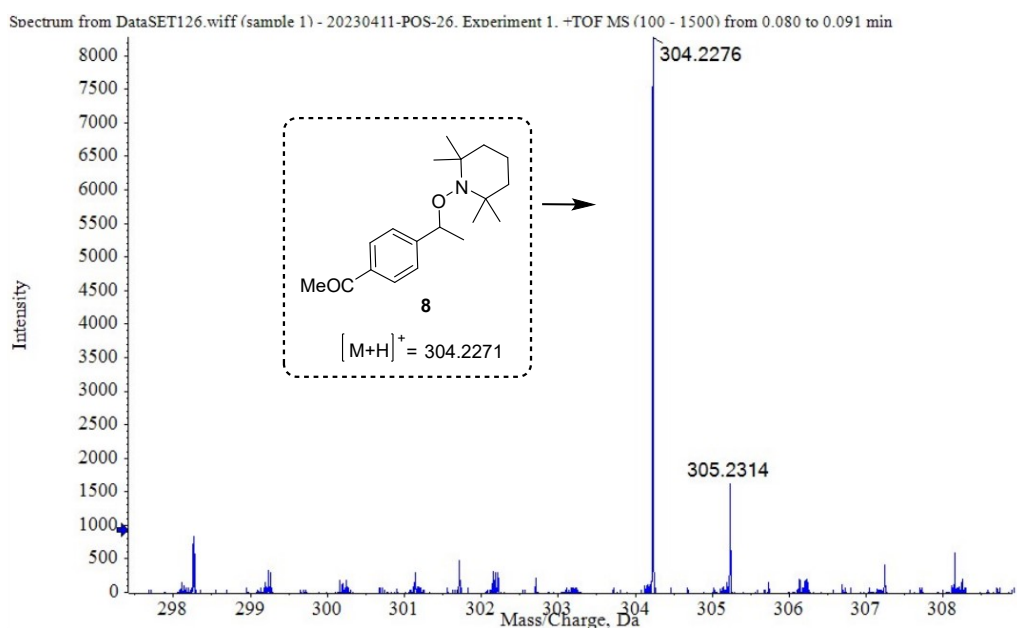
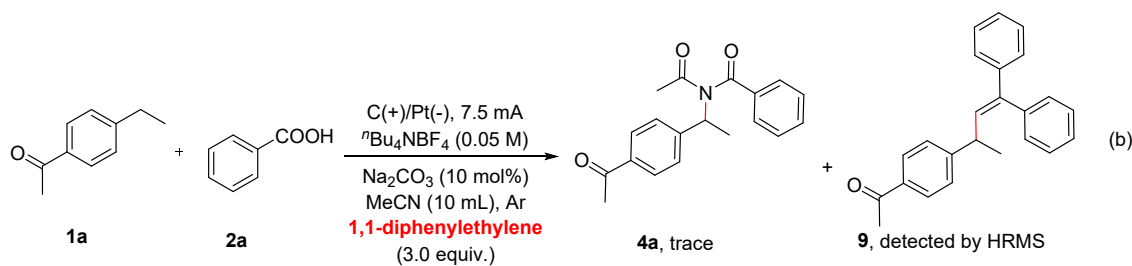


Figure S1. HRMS analysis of the radical-trapping product **8**.

3.1.2 Reaction with 1,1-diphenylethylene



An undivided four-necked flask (25 mL) was charged with benzoic acid (**2a**, 91.6 mg, 0.75 mmol), $n\text{Bu}_4\text{NBF}_4$ (164.6 mg, 0.5 mmol), Na_2CO_3 (5.2 mg, 0.05 mmol, 10 mol%). The flask equipped with a graphite felt electrode as the anode and a platinum plate electrode (10 mm \times 10 mm) as the cathode was evacuated and backfilled with Ar for 3 times, then CH_3CN (10 mL), 1-(4-ethylphenyl)ethan-1-one (**1a**, 74.1 mg, 0.5 mmol) and 1,1-diphenylethylene (270.4 mg, 264.8 μL , 1.5 mmol, 3 equiv.) were added in sequence. The reaction was equipped with platinum plate electrode (10 mm \times 10 mm) as the cathode and graphite felt electrode as the anode, and was electrolyzed at room temperature under air atmosphere and constant current (7.5 mA) for 12 h. The reaction was obviously suppressed by the addition of 1,1-diphenylethylene, and a trapping product **9** was observed through the HRMS analysis from the reaction solution (Figure S2).

9, HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{O}^+$, 327.1743; found 327.1744.

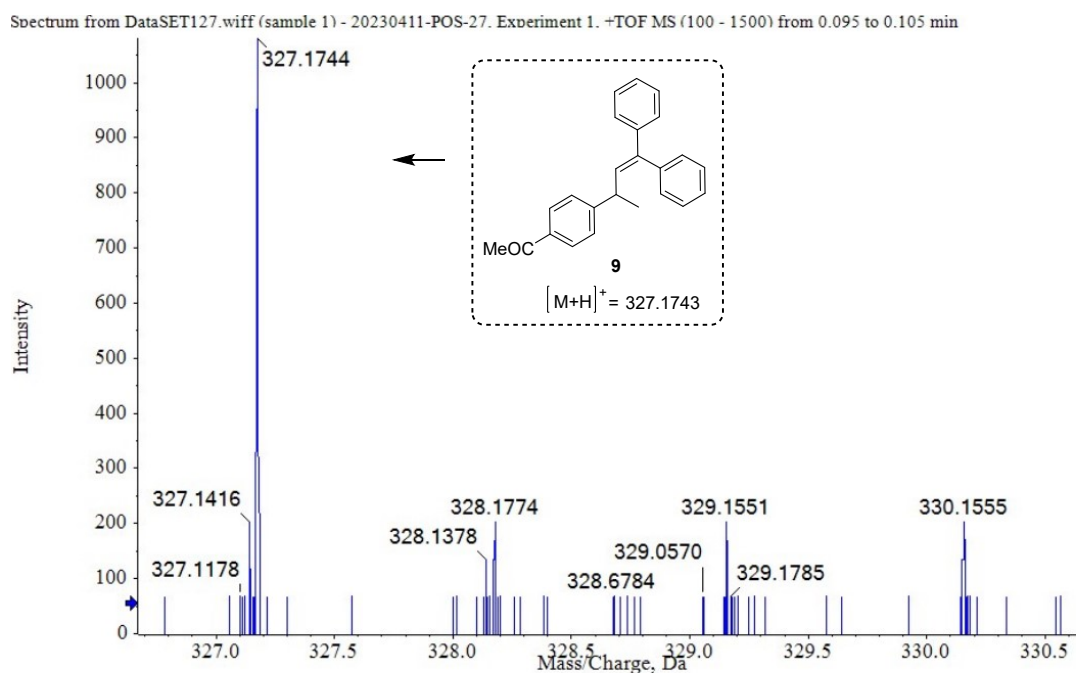
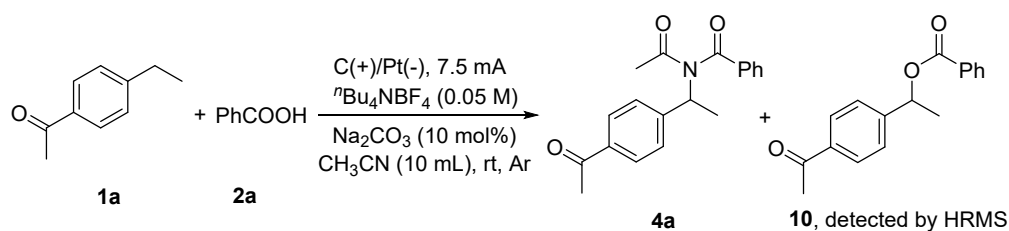


Figure S2. HRMS analysis of the radical-trapping product **9**.

3.1.3 Detection of carbocation



Reaction was performed under standard conditions for 12 h, **10** was found by HRMS analysis (Figure S3).

10 HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{17}H_{17}O_3^+$, 269.1172; found 269.1173.

Spectrum from 20230717-POS-C2.wiff (sample 1) - 20230717-POS-C2. Experiment 1. -TOF MS (50 - 1500) from 0.231 to 0.262 min

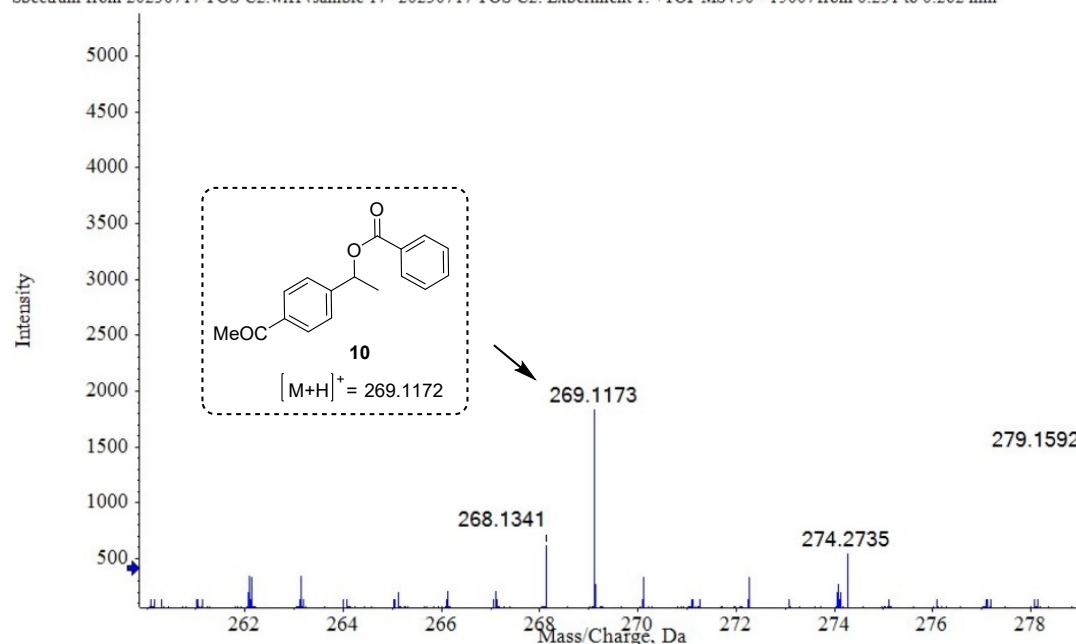
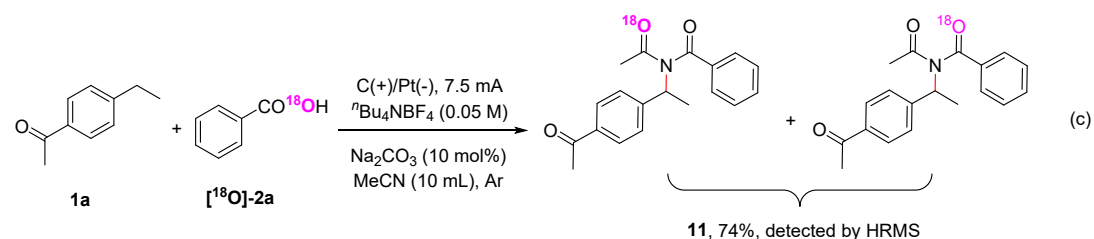


Figure S3. HRMS analysis of the product **10**.

3.1.4 Reaction with $PhCO^{18}OH$



An undivided four-necked flask (25 mL) was charged with ^{18}O -labeled benzoic acid ($[^{18}O]$ -**2a**, 93.0 mg, 0.75 mmol), nBu_4NBF_4 (164.6 mg, 0.5 mmol), Na_2CO_3 (5.2 mg, 0.05 mmol, 10 mol%). The flask equipped with a graphite felt electrode as the anode and a platinum plate electrode (10 mm \times 10 mm) as the cathode was evacuated and backfilled with Ar for 3 times, then CH_3CN (10 mL) and 1-(4-ethylphenyl)ethan-1-one (**1a**, 74.1 mg, 0.5 mmol) were added in sequence. The reaction was equipped with platinum plate electrode (10 mm \times 10 mm) as the cathode and graphite felt electrode as the anode, and was electrolyzed at room temperature under air atmosphere and constant current (7.5 mA) for 12 h. After the reaction was stopped, the ^{18}O -labelled product **11** was found by HRMS analysis (Figure S4).

11, HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{19}H_{20}NO_2^{18}O^+$, 312.1480; found 312.1481.

Spectrum from DataSET128.wiff (sample 1) - 20230411-POS-28. Experiment 1. +TOF MS (100 - 1500) from 0.166 min

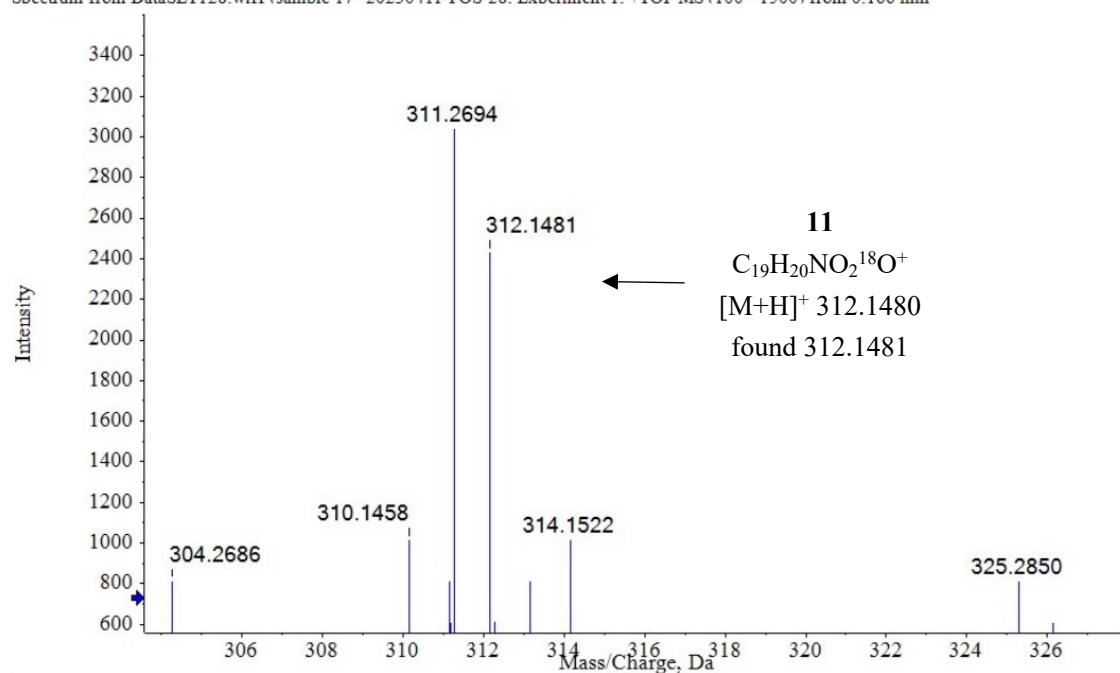


Figure S4. HRMS analysis of the product **11**.

3.2 Cyclic voltammetry analysis

Cyclic voltammetry was performed in a three electrodes cell in a three-necked flask at room temperature. The working electrode was a 3 mm diameter glassy carbon disc electrode, and the counter electrode was a Pt wire. The reference was saturated calomel electrode (SCE) submerged in saturated aqueous KCl solution. As shown in the Figure S5, 1-(4-ethylphenyl)ethan-1-one (**1a**) gave an oxidation peak at 1.93 V vs SCE in the range of 0–4.0 V, which indicated that **1a** could be oxidized under the electrochemical conditions (Figure S5).

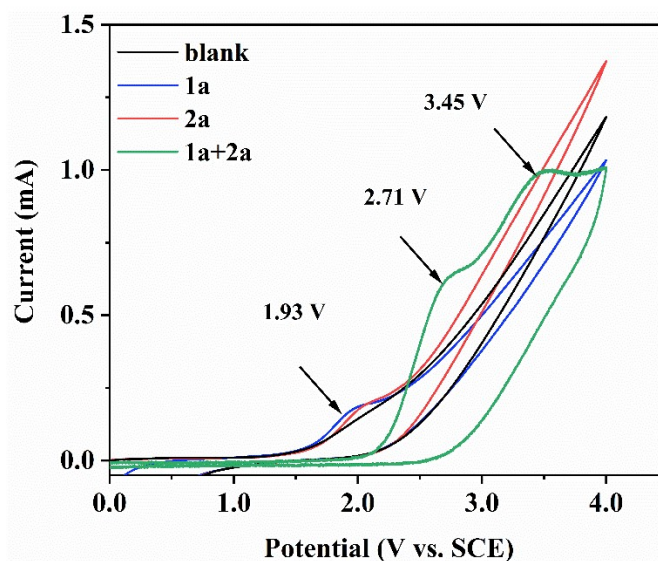
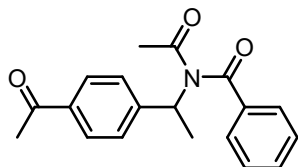


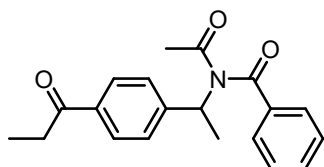
Figure S5 CV scans (scan rate 100 $\text{mv}\cdot\text{s}^{-1}$) of substrates: Blank ($n\text{-Bu}_4\text{NBF}_4$ (0.02 M) and Na_2CO_3

(10 mol %) in CH₃CN (10 mL), black curve); 1-(4-Ethylphenyl)ethan-1-one (**1a**, 0.01 M, blue curve). benzoic acid (**2a**, 0.01 M, red curve); **1a** and **2a** (0.01 M, green curve).

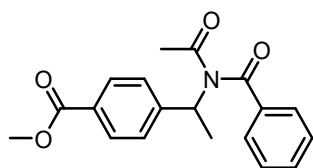
4 Experimental data for the products 4, 5, 6 and 7



N-Acetyl-N-(1-(4-acetylphenyl)ethyl)benzamide (4a). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Colorless oil (123.7 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.92 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.60–7.53 (m, 3H), 7.46 (t, J = 7.6 Hz, 2H), 5.89–5.84 (m, 1H), 2.57 (s, 3H), 1.90 (s, 3H), 1.83 (d, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 197.7, 174.3, 172.5, 146.4, 136.5, 136.0, 133.2, 129.1, 128.8, 128.4, 127.4, 55.1, 27.5, 26.6, 17.6. HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₉H₂₀NO₃⁺ 310.1438; Found 310.1443.

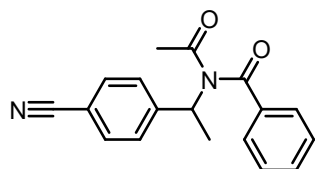


N-Acetyl-N-(1-(4-propionylphenyl)ethyl)benzamide (4b). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (6:1, v/v). Colorless oil (126.0 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.93 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 5.89–5.84 (m, 1H), 3.01–2.95 (m, 2H), 1.90 (s, 3H), 1.83 (d, J = 7.1 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 200.4, 174.4, 172.5, 146.1, 136.5, 135.8, 133.2, 129.1, 128.8, 128.1, 127.4, 55.1, 31.8, 27.5, 17.7, 8.2. HRMS (ESI) m/z : [M + H]⁺ Calcd for C₂₀H₂₂NO₃⁺ 324.1594; Found 324.1605.

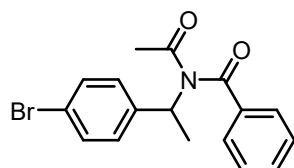


Methyl 4-(1-(N-acetylbenzamido)ethyl)benzoate (4c). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Colorless oil (108.9 mg,

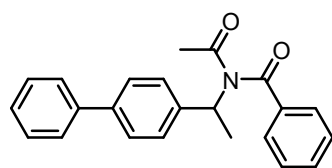
67%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.00 (d, $J = 8.4$ Hz, 2H), 7.68–7.66 (m, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.47 (t, $J = 7.7$ Hz, 2H), 5.91–5.86 (m, 1H), 3.91 (s, 3H), 1.90 (s, 3H), 1.83 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.3, 172.5, 166.9, 146.1, 136.5, 133.2, 129.6, 129.1, 129.0, 128.8, 127.2, 55.1, 52.1, 27.5, 17.7. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_4^+$ 326.1387; Found 326.1395.



***N*-Acetyl-*N*-(1-(4-cyanophenyl)ethyl)benzamide (4d)**. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Colorless oil (113.9 mg, 78%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.68 (d, $J = 6.9$ Hz, 2H), 7.63–7.56 (m, 5H), 7.49 (t, $J = 7.6$ Hz, 2H), 5.88–5.82 (m, 1H), 1.88 (s, 3H), 1.80 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.2, 172.4, 146.5, 136.3, 133.4, 132.2, 129.2, 128.9, 128.0, 118.8, 111.0, 54.9, 27.5, 17.5. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_2^+$ 293.1285; Found 293.1292.

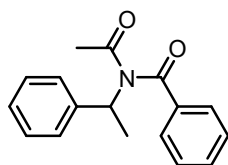


***N*-Acetyl-*N*-(1-(4-bromophenyl)ethyl)benzamide (4e)**. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Colorless oil (132.8 mg, 77%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.66 (d, $J = 7.1$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.48–7.44 (m, 4H), 7.35 (d, $J = 8.2$ Hz, 2H), 5.83–5.78 (m, 1H), 1.89 (s, 3H), 1.79 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.4, 172.5, 139.9, 136.6, 133.2, 131.4, 129.2, 129.1, 128.9, 121.3, 54.8, 27.5, 17.8. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{17}\text{BrNO}_2^+$ 346.0437; Found 346.0430.

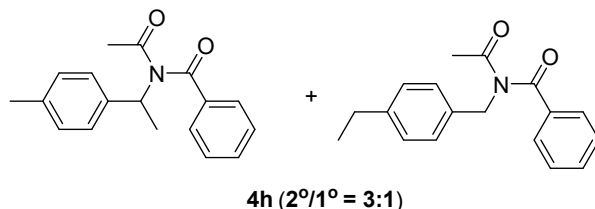


***N*-(1-([1,1'-Biphenyl]-4-yl)ethyl)-*N*-acetylbenzamide (4f)**. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (104.7 mg,

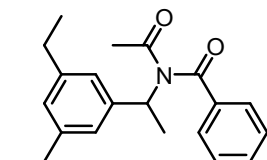
61%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.71–7.69 (m, 2H), 7.61–7.52 (m, 7H), 7.49–7.43 (m, 4H), 7.35 (t, $J = 7.3$ Hz, 1H), 5.94–5.89 (m, 1H), 1.95 (s, 3H), 1.87 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.6, 172.6, 140.8, 140.1, 139.9, 136.8, 133.0, 129.0, 128.9, 128.8, 127.8, 127.3, 127.1, 127.0, 55.2, 27.4, 17.9. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2^+$ 344.1645; Found 344.1654.



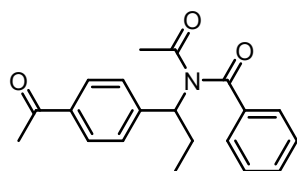
***N*-Acetyl-*N*-(1-phenylethyl)benzamide (4g).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Colorless oil (88.2 mg, 66%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.67 (d, $J = 7.4$ Hz, 2H), 7.59–7.55 (m, 1H), 7.46 (d, $J = 7.9$ Hz, 4H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.29–7.23 (m, 1H), 5.90–5.84 (m, 1H), 1.92 (s, 3H), 1.83 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.6, 172.6, 140.8, 136.8, 132.9, 129.0, 128.8, 128.3, 127.3, 127.3, 55.4, 27.4, 17.9. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2^+$ 268.1332; Found 268.1329.



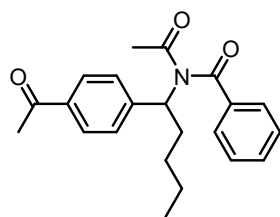
***N*-Acetyl-*N*-(1-(*p*-tolyl)ethyl)benzamide and *N*-acetyl-*N*-(4-ethylbenzyl)benzamide (4h).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Colorless oil (73.1 mg, 52%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.68–7.66 (m, 2H), 7.61–7.54 (m, 2H), 7.45 (t, $J = 7.6$ Hz, 3H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.15 (t, $J = 8.8$ Hz, 4H), 5.87–5.81 (m, 1H), 5.01 (s, 1H), 2.66–2.60 (m, 1H), 2.33 (s, 3H), 2.18 (s, 1H), 1.91 (s, 3H), 1.82 (d, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.6, 174.4, 173.3, 172.6, 143.5, 137.8, 136.9, 136.9, 135.9, 134.6, 132.9, 132.4, 129.0, 128.9, 128.8, 128.8, 128.4, 128.1, 127.9, 127.3, 55.2, 49.1, 28.5, 27.4, 26.4, 21.1, 18.0, 15.5. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_2^+$ 282.1489; Found 282.1481.



***N*-Acetyl-*N*-(1-(3,5-diethylphenyl)ethyl)benzamide (4i).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Colorless oil (75.9 mg, 47%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.67–7.64 (m, 2H), 7.58–7.53 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.08 (s, 2H), 6.92 (s, 1H), 5.87–5.82 (m, 1H), 2.65–2.59 (m, 4H), 1.94 (s, 3H), 1.82 (d, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 174.7, 172.5, 144.1, 140.6, 136.9, 132.8, 128.9, 128.8, 126.5, 124.3, 55.4, 28.9, 27.2, 18.0, 15.6. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₆NO₂⁺ 324.1958; Found 324.1953.

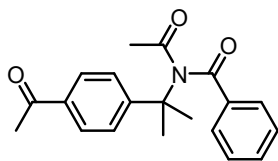


***N*-Acetyl-*N*-(1-(4-acetylphenyl)propyl)benzamide (4j).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (130.9 mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.89 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.58–7.51 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 5.68–5.64 (m, 1H), 2.55 (s, 3H), 2.44–2.33 (m, 1H), 2.30–2.20 (m, 1H), 1.82 (s, 3H), 0.99 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 197.7, 174.1, 173.2, 145.4, 136.5, 136.1, 133.1, 129.1, 128.9, 128.4, 61.6, 27.7, 26.7, 24.8, 11.7. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂NO₃⁺ 324.1594; Found 324.1602.

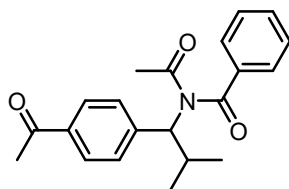


***N*-Acetyl-*N*-(1-(4-acetylphenyl)pentyl)benzamide (4k).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (131.7 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.92 (d, *J* = 8.0 Hz, 2H), 7.64–7.55 (m, 5H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.75 (t, *J* = 7.8 Hz, 1H), 2.58 (s, 3H), 2.42–2.32 (m, 1H), 2.29–2.20 (m, 1H), 1.84 (s, 3H), 1.39–1.35 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 197.8, 174.1, 173.2, 145.5, 136.6, 136.2, 133.1, 129.1, 128.9, 128.5, 128.4, 60.1, 31.5, 29.2, 27.8, 26.6,

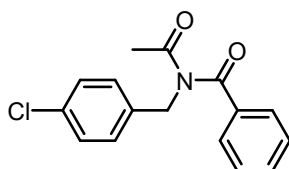
22.5, 14.0. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{22}H_{26}NO_3^+$ 352.1907; Found 352.1909.



***N*-Acetyl-*N*-(2-(4-acetylphenyl)propan-2-yl)benzamide (4l)**. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Colorless oil (134.1 mg, 83%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (d, $J = 7.2$ Hz, 2H), 7.98 (d, $J = 8.5$ Hz, 2H), 7.75–7.71 (m, 3H), 7.61 (t, $J = 7.7$ Hz, 2H), 2.61 (s, 3H), 1.86 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 175.6, 168.4, 152.9, 135.6, 135.3, 134.8, 130.6, 129.5, 128.6, 125.3, 62.4, 28.6, 26.7, 25.8. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{20}H_{22}NO_3^+$ 324.1594; Found 324.1597.

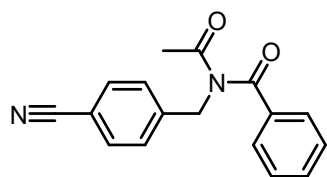


***N*-Acetyl-*N*-(1-(4-acetylphenyl)-2-methylpropyl)benzamide (4m)**. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Colorless oil (99.5 mg, 59%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.54–7.49 (m, 3H), 7.39 (t, $J = 7.6$ Hz, 2H), 5.37 (d, $J = 11.2$ Hz, 1H), 3.18–3.09 (m, 1H), 2.57 (s, 3H), 1.76 (s, 3H), 1.10 (d, $J = 6.5$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.9, 174.1, 173.6, 144.3, 136.8, 136.3, 133.1, 129.7, 129.0, 128.8, 128.4, 67.2, 29.0, 27.9, 26.7, 21.0, 20.1. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{21}H_{24}NO_3^+$ 338.1751; Found 338.1756.

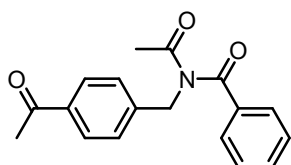


***N*-Acetyl-*N*-(4-chlorobenzyl)benzamide (4n)**. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Colorless oil (83.3 mg, 58%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 (d, $J = 7.4$ Hz, 3H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.27 (d, $J = 8.3$ Hz, 2H), 7.21 (d, $J = 8.2$ Hz, 2H), 4.99 (s, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

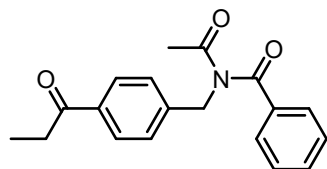
(ppm) 174.2, 173.2, 135.8, 135.7, 133.4, 132.7, 129.5, 128.9, 128.7, 128.4, 48.6, 26.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}ClNO_2^+$ 288.0786; Found 288.0780.



***N*-Acetyl-*N*-(4-cyanobenzyl)benzamide (4o).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (111.2 mg, 80%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62–7.57 (m, 5H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.40 (d, $J = 7.9$ Hz, 2H), 5.06 (s, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.0, 173.2, 142.7, 135.3, 133.0, 132.4, 129.1, 128.7, 128.4, 118.7, 111.5, 49.0, 26.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O_2^+$ 279.1128; Found 279.1134.

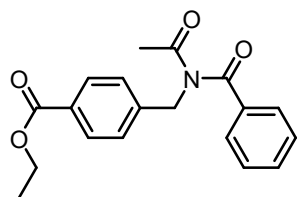


***N*-Acetyl-*N*-(4-acetylbenzyl)benzamide (4p).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (106.2 mg, 72%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, $J = 8.0$ Hz, 2H), 7.59–7.55 (m, 3H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 5.06 (s, 2H), 2.59 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.7, 174.1, 173.3, 142.7, 136.3, 135.5, 132.8, 129.0, 128.7, 128.4, 127.9, 49.1, 26.7, 26.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_3^+$ 296.1281; Found 296.1280.



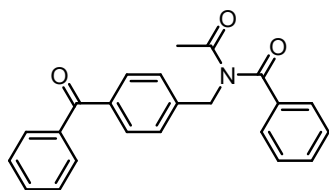
***N*-Acetyl-*N*-(4-propionylbenzyl)benzamide (4q).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (109.7 mg, 71%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (d, $J = 8.3$ Hz, 2H), 7.59–7.57 (m, 3H), 7.48–7.44 (m, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 5.07 (s, 2H), 3.02–2.96 (m, 2H), 2.17 (s, 3H), 1.22 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.4, 174.2, 173.3, 142.4, 136.1, 135.5, 132.8, 129.0, 128.4, 128.4, 127.9, 49.1, 31.8, 26.5, 8.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}NO_3^+$

310.1438; Found 310.1441.

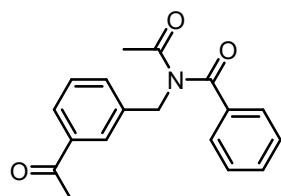


Ethyl 4-((*N*-acetylbenzamido)methyl)benzoate (4r). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (100.8 mg, 62%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.99 (d, $J = 7.9$ Hz, 2H), 7.57 (d, $J = 6.3$ Hz, 3H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 5.07 (s, 2H), 4.40–4.35 (m, 2H), 2.17 (s, 3H), 1.40 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.2, 173.2, 166.3, 142.3, 135.5, 132.7, 129.9, 129.7, 128.9, 128.4, 127.7, 61.0, 49.1, 26.5, 14.3. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_4^+$ 326.1387; Found 326.1391.

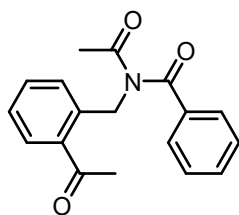


***N*-Acetyl-*N*-(4-benzoylbenzyl)benzamide (4s).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). White solid (101.8 mg, 57%). mp 87–89 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.81–7.76 (m, 4H), 7.62–7.57 (m, 4H), 7.51–7.46 (m, 4H), 7.39 (d, $J = 7.9$ Hz, 2H), 5.10 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 196.3, 174.2, 173.3, 142.0, 137.5, 136.7, 135.5, 132.8, 132.5, 130.5, 130.0, 129.0, 128.4, 128.3, 127.7, 49.1, 26.6. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_3^+$ 358.1438; Found 358.1436.

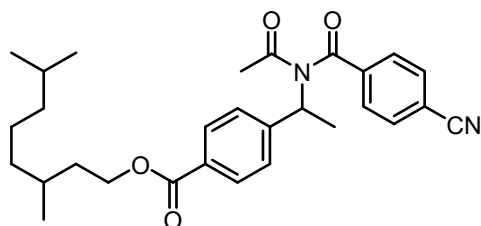


***N*-Acetyl-*N*-(3-acetylbenzyl)benzamide (4t).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (101.8 mg, 69%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.85–7.82 (m, 2H), 7.58 (d, $J = 7.7$ Hz, 3H), 7.50–7.39 (m, 4H), 5.07 (s, 2H), 2.57 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.9, 174.2, 173.3, 137.9, 137.3, 135.6, 132.7, 132.6, 129.0, 128.4, 127.8, 127.5, 49.0, 26.7, 26.6. HRMS (ESI) m/z :

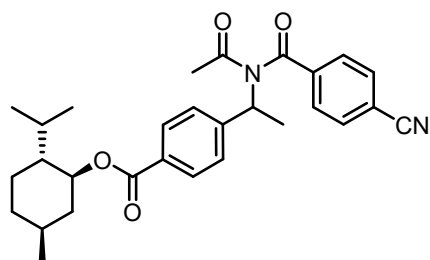
$[M + H]^+$ Calcd for $C_{18}H_{18}NO_3^+$ 296.1281; Found 296.1288.



***N*-Acetyl-*N*-(2-acetylbenzyl)benzamide (4u).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (95.9 mg, 65%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, $J = 7.8$ Hz, 1H), 7.59 (d, $J = 7.9$ Hz, 2H), 7.53–7.48 (m, 2H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.40–7.34 (m, 2H), 5.30 (s, 2H), 2.55 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 201.4, 174.6, 173.5, 138.1, 136.5, 135.2, 132.4, 132.3, 129.8, 128.8, 128.3, 127.4, 126.9, 48.4, 29.1, 26.1. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{18}H_{18}NO_3^+$ 296.1281; Found 296.1289.

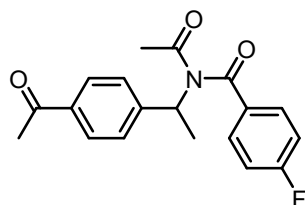


3,7-Dimethyloctyl 4-(1-(*N*-acetyl-4-cyanobenzamido)ethyl)benzoate (4v). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (95.3 mg, 40%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, $J = 8.0$ Hz, 2H), 7.77–7.70 (m, 4H), 7.48 (d, $J = 8.0$ Hz, 2H), 5.84–5.78 (m, 1H), 4.39–4.33 (m, 2H), 2.00 (s, 3H), 1.85 (d, $J = 7.1$ Hz, 3H), 1.82–1.77 (m, 1H), 1.65 (s, 2H), 1.61–1.51 (m, 2H), 1.35 (d, $J = 5.5$ Hz, 2H), 1.17 (t, $J = 7.1$ Hz, 3H), 0.97 (d, $J = 6.4$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.6, 172.6, 166.3, 145.2, 140.3, 132.8, 129.8, 129.8, 128.8, 127.0, 117.6, 116.1, 63.7, 55.4, 39.2, 37.2, 35.6, 30.0, 28.0, 27.2, 24.7, 22.7, 22.6, 19.6, 17.8. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{29}H_{37}N_2O_4^+$ 477.2748; Found 477.2755.



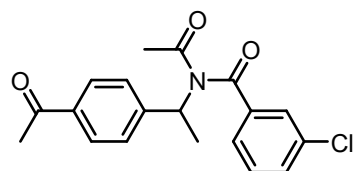
(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl-4-(1-(*N*-acetyl-4-cyanobenzamido)ethyl)benzoate

(**4w**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (85.4 mg, 36%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.03 (d, *J* = 8.0 Hz, 2H), 7.78–7.71 (m, 4H), 7.48 (d, *J* = 8.0 Hz, 2H), 5.83–5.78 (m, 1H), 4.96–4.90 (m, 1H), 2.12 (d, *J* = 13.7 Hz, 1H), 2.01 (s, 4H), 1.85 (d, *J* = 6.2 Hz, 3H), 1.74 (d, *J* = 11.6 Hz, 2H), 1.61–1.52 (m, 2H), 1.20–1.04 (m, 2H), 0.93 (t, *J* = 6.0 Hz, 7H), 0.80 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.6, 165.7, 145.1, 140.3, 132.8, 130.1, 130.1, 129.8, 128.8, 126.9, 117.6, 116.1, 55.4, 47.3, 40.9, 34.3, 31.4, 27.2, 26.5, 23.6, 22.1, 20.8, 17.8, 16.5. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₉H₃₅N₂O₄⁺ 475.2591; Found 475.2594.



***N*-Acetyl-*N*-(1-(4-acetylphenyl)ethyl)-4-fluorobenzamide (4x)**

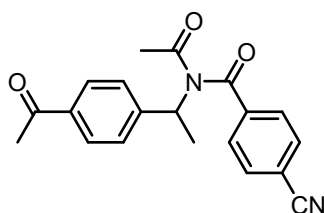
The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Colorless oil (101.4 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.91 (d, *J* = 8.0 Hz, 2H), 7.72–7.68 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.4 Hz, 2H), 5.87–5.81 (m, 1H), 2.57 (s, 3H), 1.92 (s, 3H), 1.81 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 197.7, 173.1, 172.2, 165.7 (d, *J* = 256.1 Hz), 146.1, 136.1, 132.7 (d, *J* = 3.2 Hz), 131.5 (d, *J* = 9.3 Hz), 128.5, 127.4, 116.4 (d, *J* = 22.2 Hz), 55.2, 27.3, 26.6, 17.7. ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -104.0. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₉H₁₉FNO₃⁺ 328.1343; Found 328.1346.



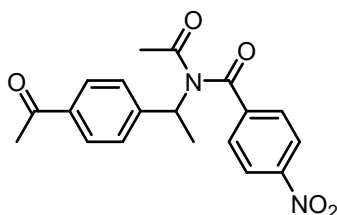
***N*-Acetyl-*N*-(1-(4-acetylphenyl)ethyl)-3-chlorobenzamide (4y)**

The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (7:1, v/v). Colorless oil (94.4 mg, 55%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.91 (d, *J* = 8.1 Hz, 2H), 7.62 (s, 1H), 7.51 (t, *J* = 10.2 Hz, 4H), 7.39 (t, *J* = 7.8 Hz, 1H), 5.85–5.80 (m, 1H), 2.57 (s, 3H), 1.95 (s, 3H), 1.81 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 197.6, 172.9, 172.4, 146.0, 138.1, 136.1, 135.3,

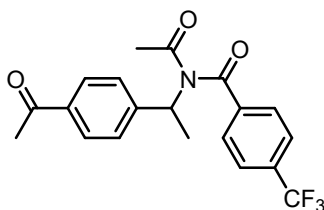
133.1, 130.3, 128.7, 128.5, 127.3, 126.7, 55.2, 27.4, 26.6, 17.7. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{19}H_{19}ClNO_3^+$ 344.1048; Found 344.1046.



***N*-Acetyl-*N*-(1-(4-acetylphenyl)ethyl)-4-cyanobenzamide (4z).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). Colorless oil (137.0 mg, 82%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, $J = 8.5$ Hz, 2H), 7.77–7.70 (m, 4H), 7.49 (d, $J = 8.0$ Hz, 2H), 5.81–5.76 (m, 1H), 2.58 (s, 3H), 1.99 (s, 3H), 1.84 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.6, 172.6, 172.5, 145.6, 140.2, 136.2, 132.8, 128.8, 128.6, 127.2, 117.6, 116.1, 55.4, 27.2, 26.7, 17.8. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_3^+$ 335.1390; Found 335.1391.

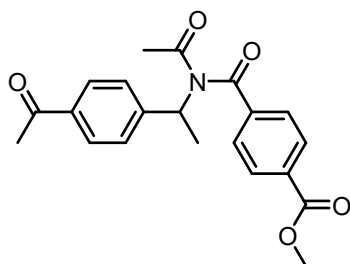


***N*-Acetyl-*N*-(1-(4-acetylphenyl)ethyl)-4-nitrobenzamide (4aa).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Colorless oil (125.7 mg, 71%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30 (d, $J = 8.4$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.78 (d, $J = 8.3$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 5.82–5.76 (m, 1H), 2.59 (s, 3H), 2.03 (s, 3H), 1.87 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.6, 172.6, 172.3, 149.9, 145.5, 141.9, 136.3, 129.2, 128.6, 127.1, 124.2, 55.4, 27.1, 26.7, 17.8. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O_5^+$ 355.1288; Found 355.1291.

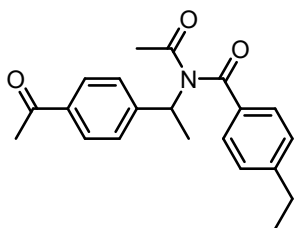


***N*-Acetyl-*N*-(1-(4-acetylphenyl)ethyl)-4-(trifluoromethyl)benzamide (4ab).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (6:1, v/v).

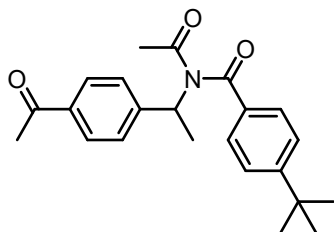
Colorless oil (99.9 mg, 53%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.94 (d, $J = 8.0$ Hz, 2H), 7.76 (t, $J = 6.9$ Hz, 4H), 7.52 (d, $J = 8.0$ Hz, 2H), 5.86–5.81 (m, 1H), 2.59 (s, 3H), 1.98 (s, 3H), 1.85 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.6, 173.0, 172.5, 145.8, 139.7, 136.2, 134.3 (q, $J = 32.9$ Hz), 128.8, 128.5, 127.3, 126.1 (q, $J = 3.7$ Hz), 123.3 (q, $J = 272.9$ Hz), 55.3, 27.4, 26.6, 17.7. ^{19}F NMR (376 MHz, CDCl_3) δ (ppm) -63.2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NO}_3^+$ 378.1312; Found 378.1319.



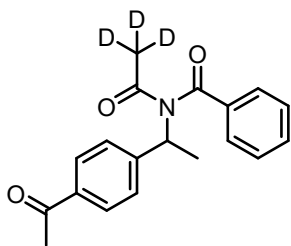
Methyl 4-(acetyl(1-(4-acetylphenyl)ethyl)carbamoyl)benzoate (4ac). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (101.0 mg, 55%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.12 (d, $J = 8.4$ Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 5.87–5.82 (m, 1H), 3.96 (s, 3H), 2.58 (s, 3H), 1.93 (s, 3H), 1.84 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.7, 173.4, 172.5, 165.8, 145.9, 140.2, 136.1, 133.9, 130.2, 128.5, 128.5, 127.3, 55.2, 52.6, 27.5, 26.6, 17.7. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_5^+$ 368.1492; Found 368.1487.



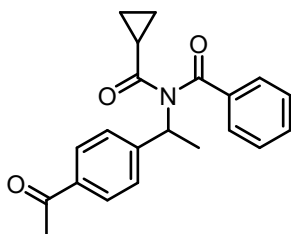
***N*-Acetyl-*N*-(1-(4-acetylphenyl)ethyl)-4-ethylbenzamide (4ad).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Colorless oil (74.2 mg, 44%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.92 (d, $J = 8.5$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.55 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 5.89–5.84 (m, 1H), 2.75–2.69 (m, 2H), 2.59 (s, 3H), 1.90 (s, 3H), 1.82 (d, $J = 7.1$ Hz, 3H), 1.27 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.8, 174.3, 172.4, 150.6, 146.5, 135.9, 133.9, 129.2, 128.6, 128.4, 127.4, 55.0, 28.9, 27.4, 26.7, 17.7, 15.1. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_3^+$ 338.1751; Found 338.1750.



***N*-Acetyl-*N*-(1-(4-acetylphenyl)ethyl)-4-(*tert*-butyl)benzamide (4ae).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (131.5 mg, 72%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.91 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 7.9$ Hz, 2H), 7.54 (d, $J = 7.9$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 5.88–5.82 (m, 1H), 2.57 (s, 3H), 1.91 (s, 3H), 1.81 (d, $J = 7.2$ Hz, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.8, 174.3, 172.4, 157.3, 146.5, 135.9, 133.5, 129.0, 128.4, 127.4, 126.1, 55.0, 35.2, 31.1, 27.4, 26.7, 17.7. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_3^+$ 366.2064; Found 366.2067.

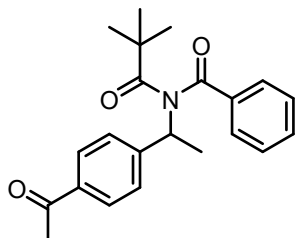


***N*-(Acetyl- d_3)-*N*-(1-(4-acetylphenyl)ethyl)benzamide (4ag).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (104.6 mg, 67%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.93 (d, $J = 8.1$ Hz, 2H), 7.68 (d, $J = 7.5$ Hz, 2H), 7.62–7.54 (m, 3H), 7.48 (t, $J = 7.6$ Hz, 2H), 5.91–5.86 (m, 1H), 2.59 (s, 3H), 1.84 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.7, 174.3, 172.5, 146.3, 136.5, 136.0, 133.2, 129.1, 128.8, 128.4, 127.4, 55.1, 26.6, 17.6. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{D}_3\text{NO}_3^+$ 313.1626; Found 313.1621.

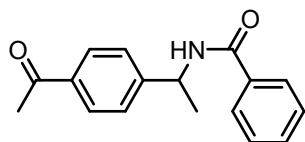


***N*-(1-(4-Acetylphenyl)ethyl)-*N*-(cyclopropanecarbonyl)benzamide (4ah).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Colorless oil (95.5 mg, 57%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.94 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 7.3$ Hz, 2H), 7.57 (d, $J = 7.9$ Hz, 3H), 7.46 (t, $J = 7.6$ Hz, 2H), 6.04–5.99 (m, 1H), 2.59 (s,

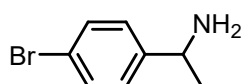
3H), 1.85 (d, $J = 7.1$ Hz, 3H), 1.23–1.17 (m, 1H), 1.02–0.90 (m, 2H), 0.54–0.52 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.8, 177.7, 173.6, 146.7, 136.9, 135.9, 132.8, 129.1, 128.8, 128.4, 127.3, 54.8, 26.7, 20.3, 17.5, 12.1, 12.1. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_3^+$ 336.1594; Found 336.1587.



***N*-(1-(4-Acetylphenyl)ethyl)-*N*-pivaloylbenzamide (4ai).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Colorless oil (84.3 mg, 48%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.92 (d, $J = 8.5$ Hz, 2H), 7.70–7.68 (m, 2H), 7.58–7.54 (m, 1H), 7.52–7.45 (m, 4H), 5.49–5.44 (m, 1H), 2.60 (s, 3H), 1.78 (d, $J = 7.1$ Hz, 3H), 1.06 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.8, 188.1, 174.1, 146.3, 136.0, 135.9, 132.6, 129.0, 129.0, 128.4, 127.5, 57.5, 44.2, 28.5, 26.7, 18.4. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_3^+$ 352.1907; Found 352.1903.

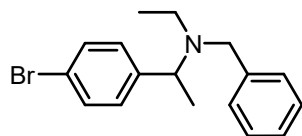


***N*-(1-(4-Acetylphenyl)ethyl)benzamide (5).** The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2:1, v/v). White solid (45.9 mg, 86%). mp 141–143 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.96 (d, $J = 8.3$ Hz, 2H), 7.82–7.79 (m, 2H), 7.55–7.44 (m, 5H), 6.47 (d, $J = 7.6$ Hz, 1H), 5.42–5.35 (m, 1H), 2.61 (s, 3H), 1.63 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.7, 166.7, 148.7, 136.3, 134.2, 131.7, 128.9, 128.7, 127.0, 126.4, 49.2, 26.7, 21.9. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2^+$ 268.1312; Found 268.1314.



1-(4-Bromophenyl)ethan-1-amine (6).¹ The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1:1, v/v). Colorless oil (28.3 mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.45 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 4.13–4.08 (m,

1H), 1.87 (s, 2H), 1.37 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 146.4, 131.5, 127.6, 120.5, 50.8, 25.6.

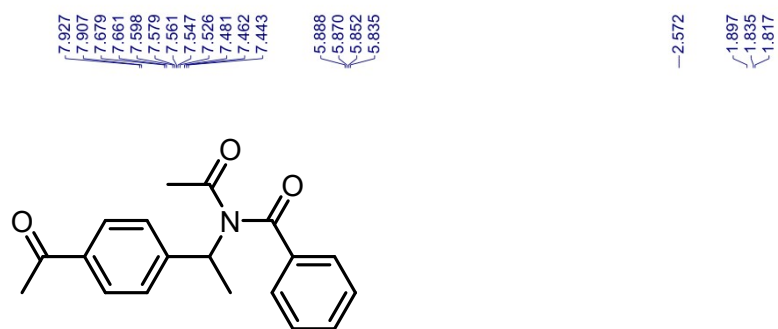


***N*-Benzyl-1-(4-bromophenyl)-*N*-ethylethan-1-amine (7)**. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2:1, v/v). Colorless oil (139.5 mg, 88%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.49 (d, $J = 8.1$ Hz, 2H), 7.41–7.33 (m, 6H), 7.27 (t, $J = 7.2$ Hz, 1H), 3.94–3.89 (m, 1H), 3.58 (s, 2H), 2.68–2.59 (m, 1H), 2.52–2.44 (m, 1H), 1.40 (d, $J = 6.8$ Hz, 3H), 1.06 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 143.8, 140.8, 131.2, 129.5, 128.5, 128.2, 126.7, 120.3, 57.4, 53.8, 42.9, 15.7, 12.2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{21}\text{BrN}^+$ 318.0852; Found 318.0847.

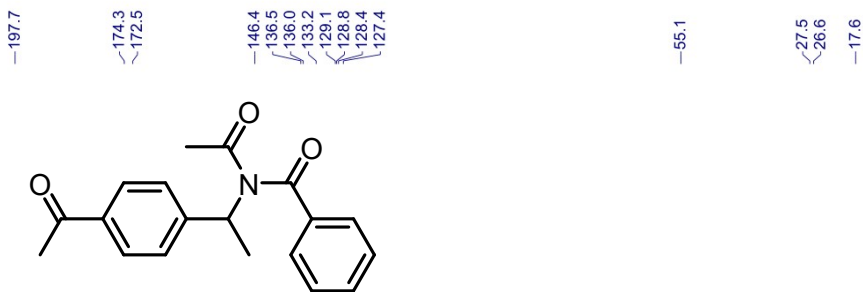
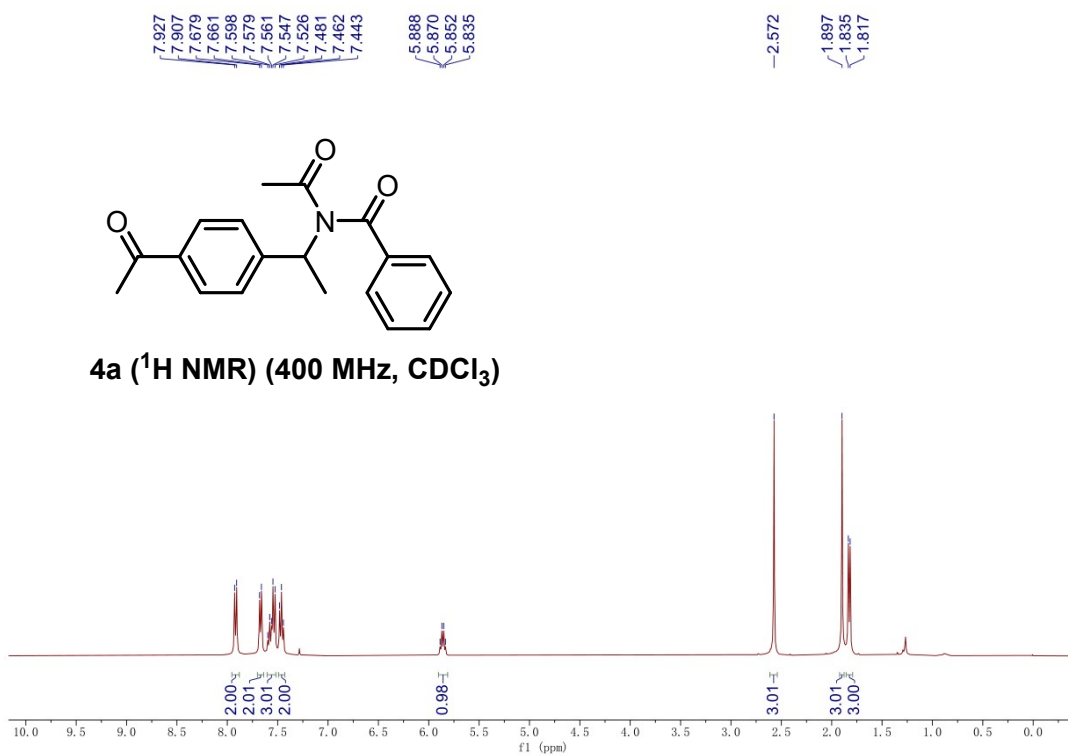
5 References

(1) D. Talwar, N.- P. Salguero, C. M. Robertson and J. Xiao, *Chem. Eur. J.*, 2014, **20**, 245–252.

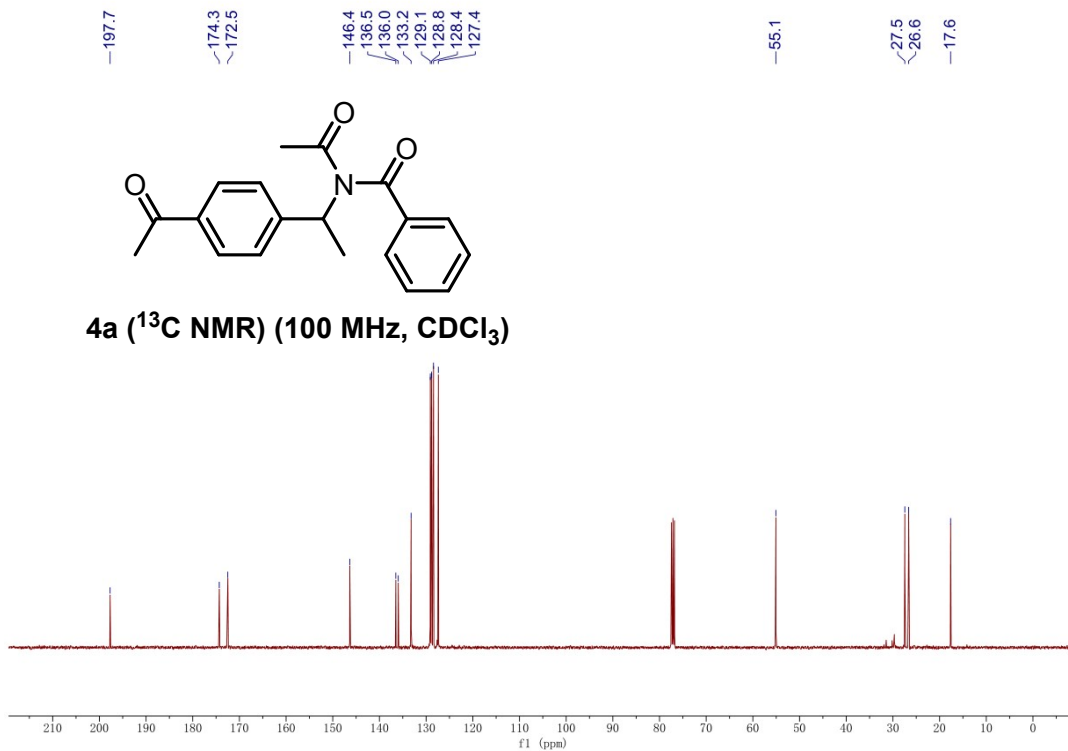
6 ^1H and ^{13}C NMR spectra of the products 4, 5, 6 and 7

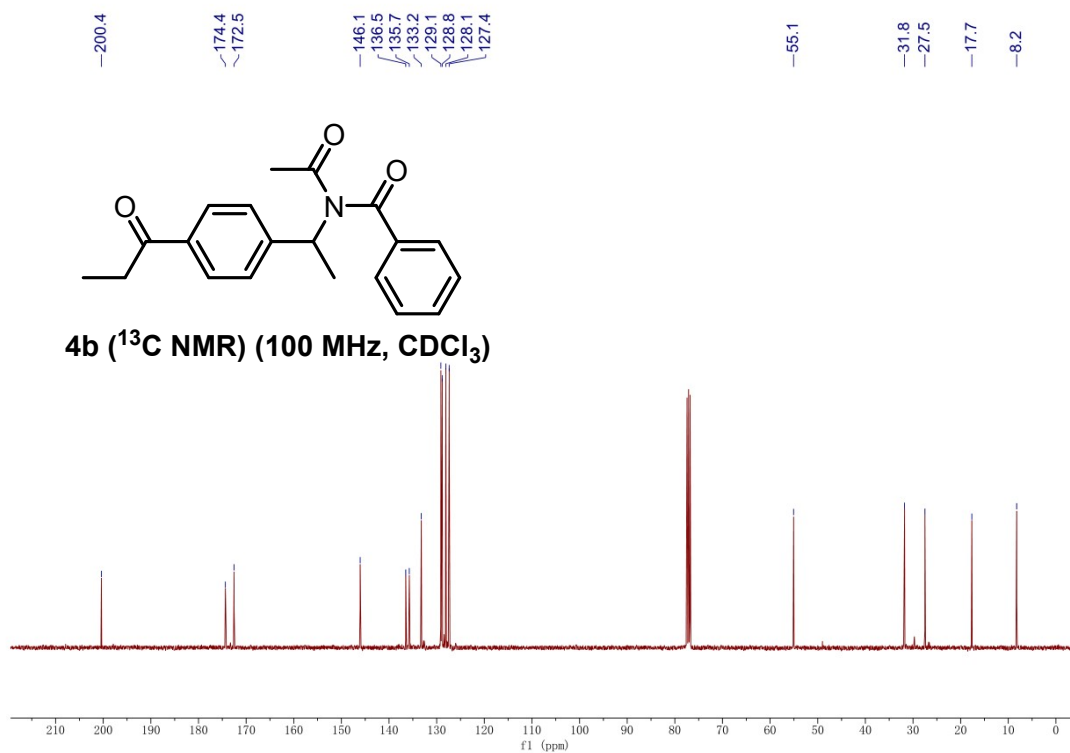
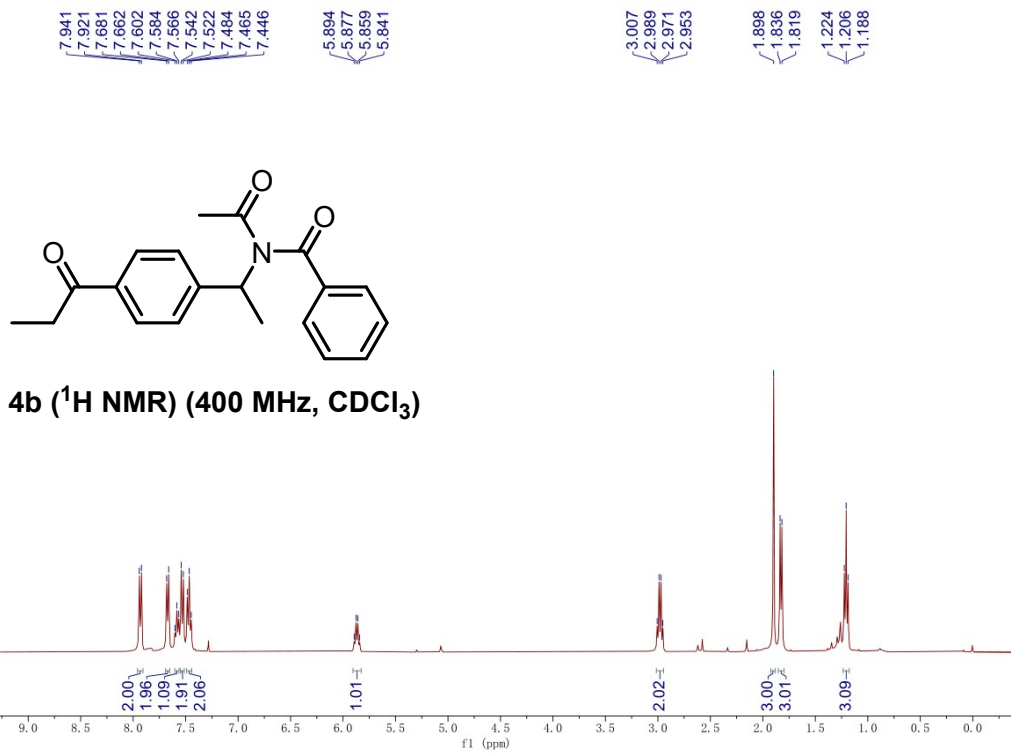


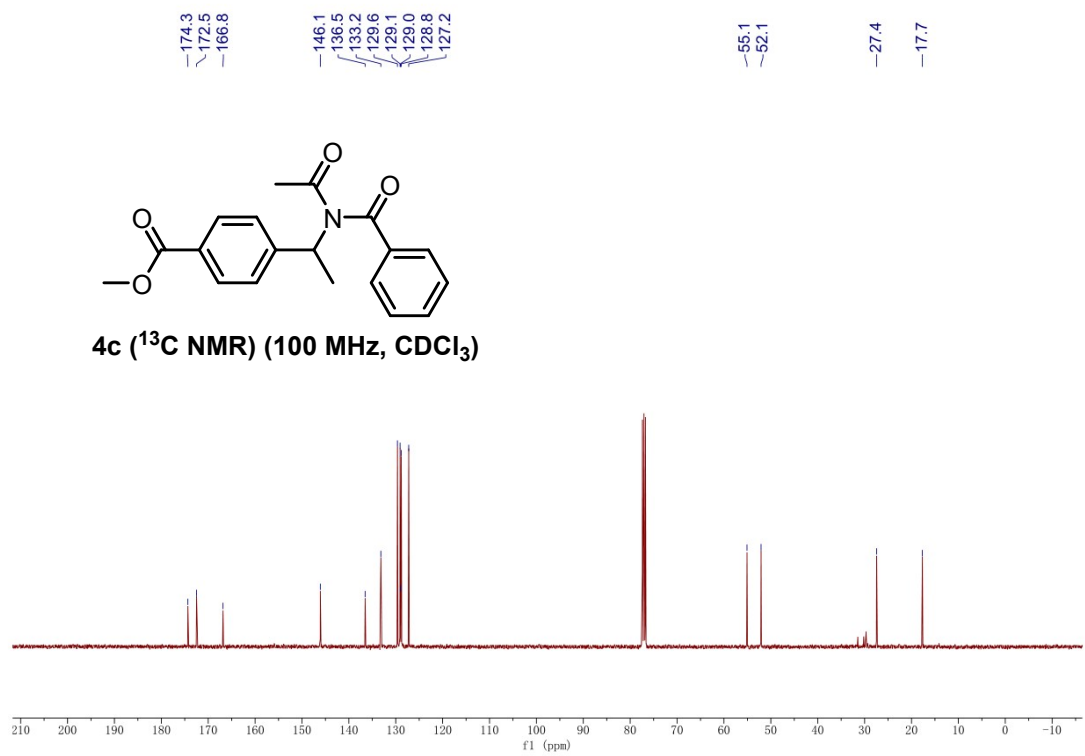
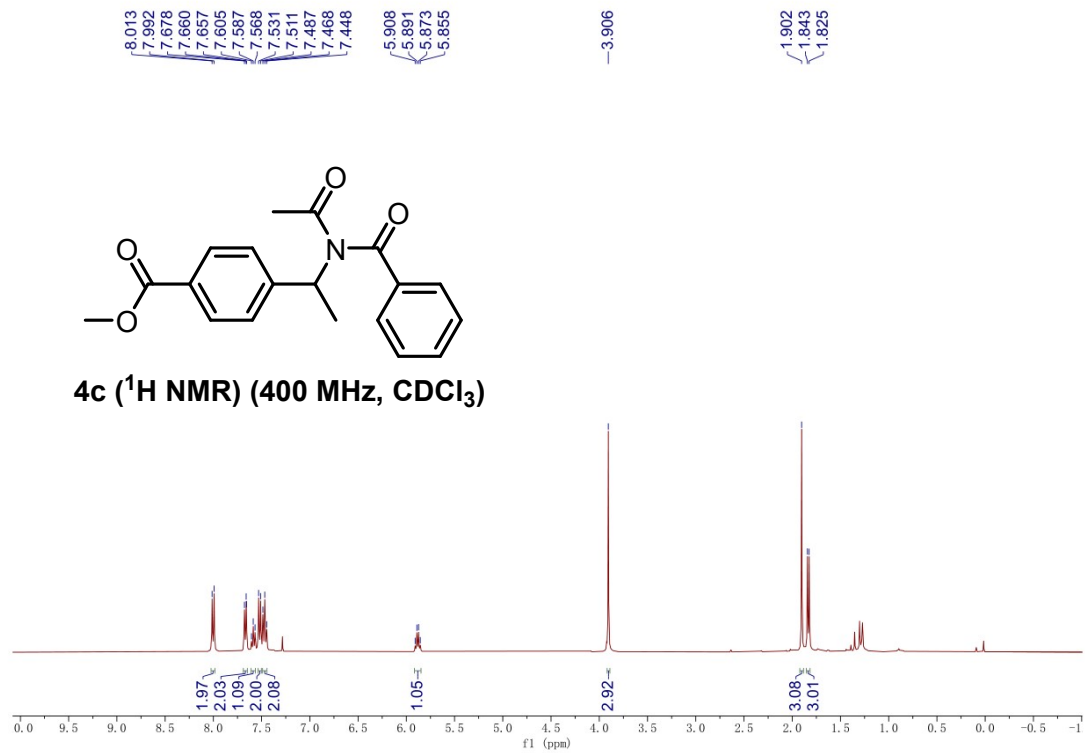
4a (^1H NMR) (400 MHz, CDCl_3)

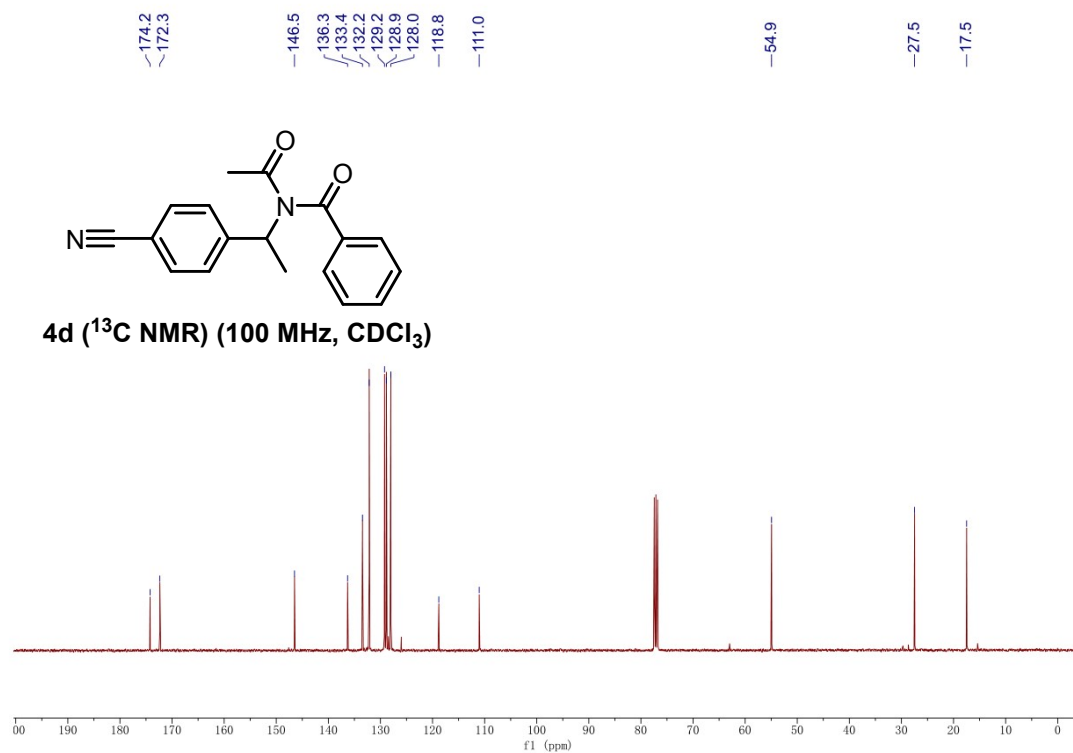
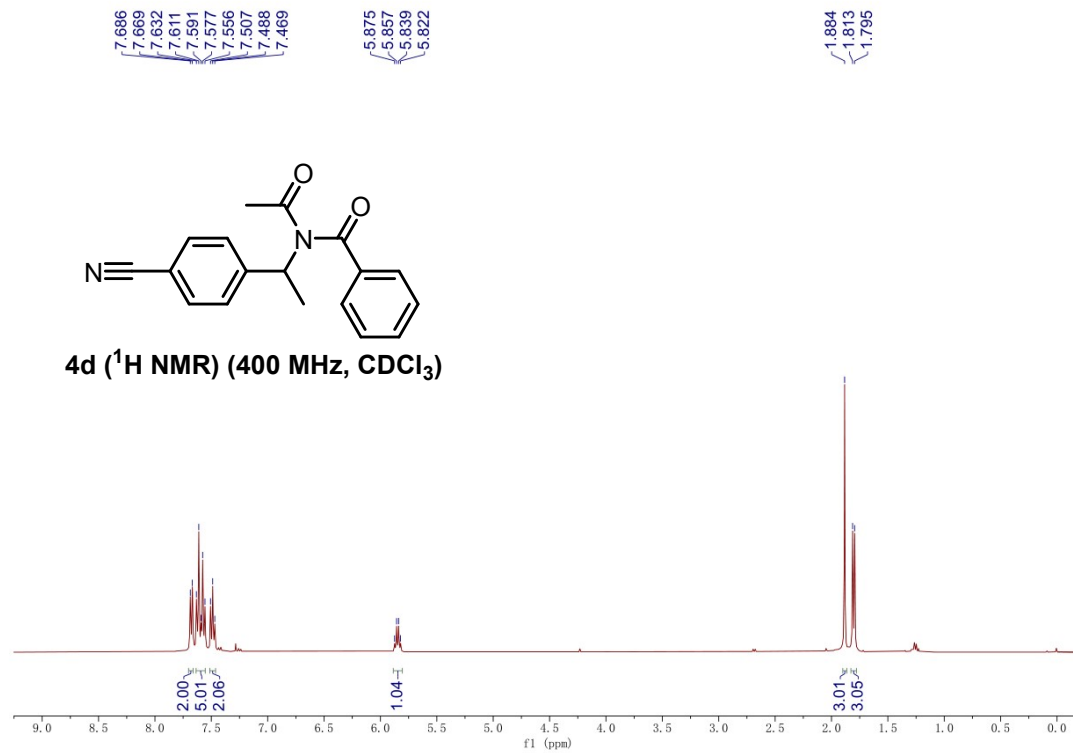


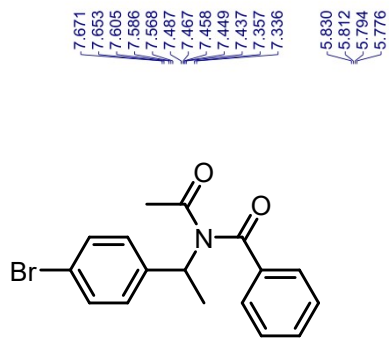
4a (^{13}C NMR) (100 MHz, CDCl_3)



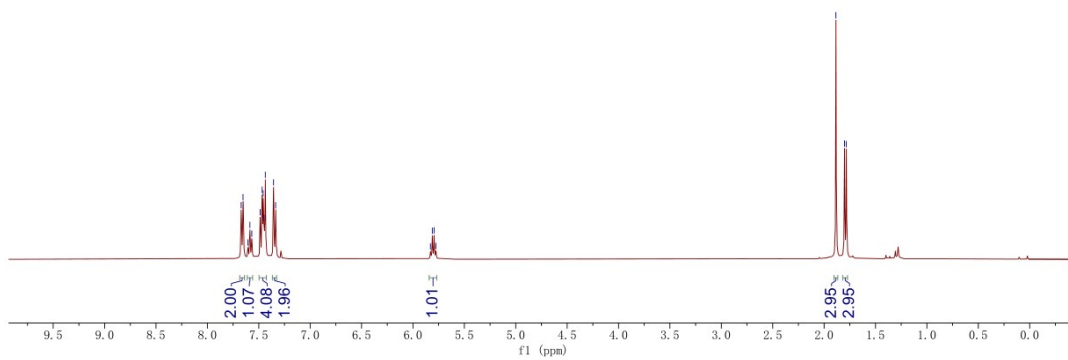




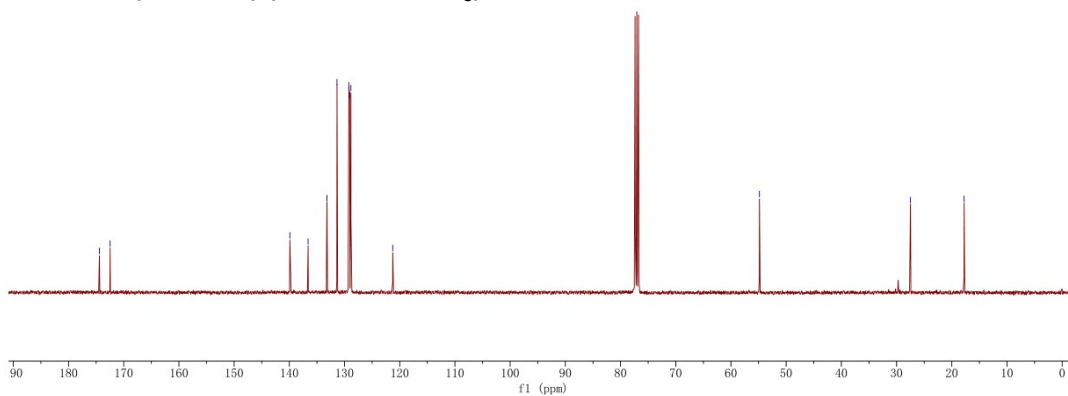


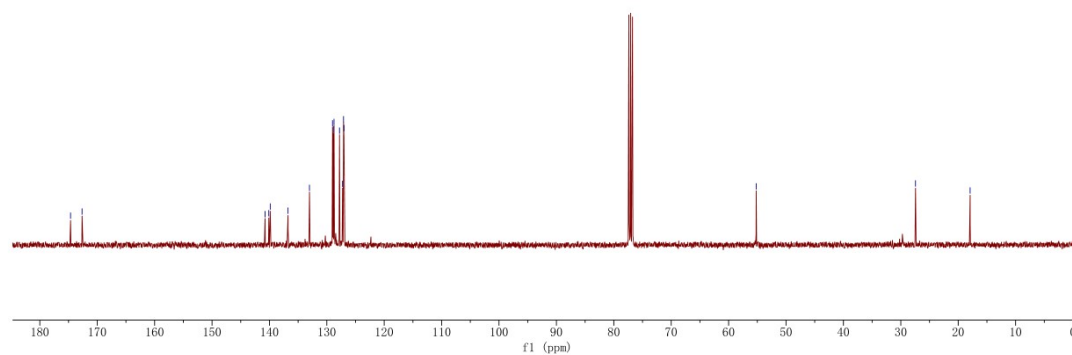
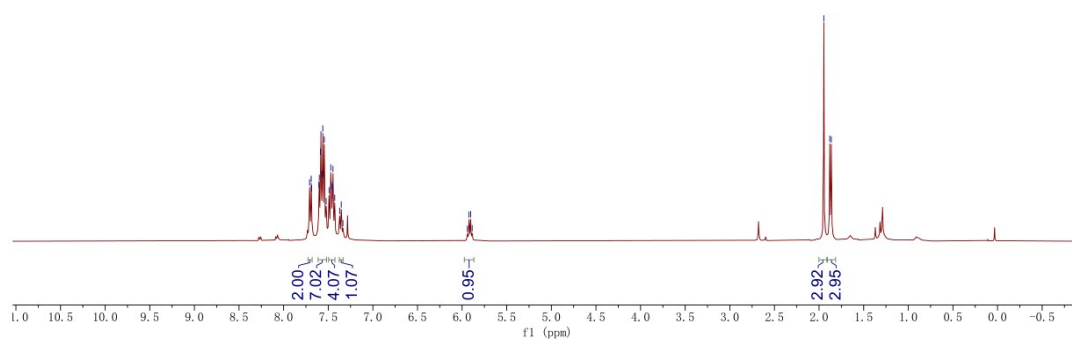
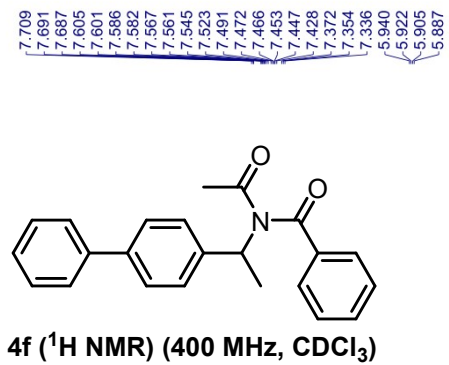


4e (¹H NMR) (400 MHz, CDCl₃)



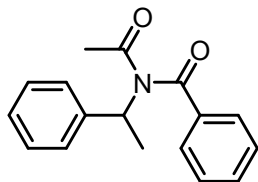
4e (¹³C NMR) (100 MHz, CDCl₃)



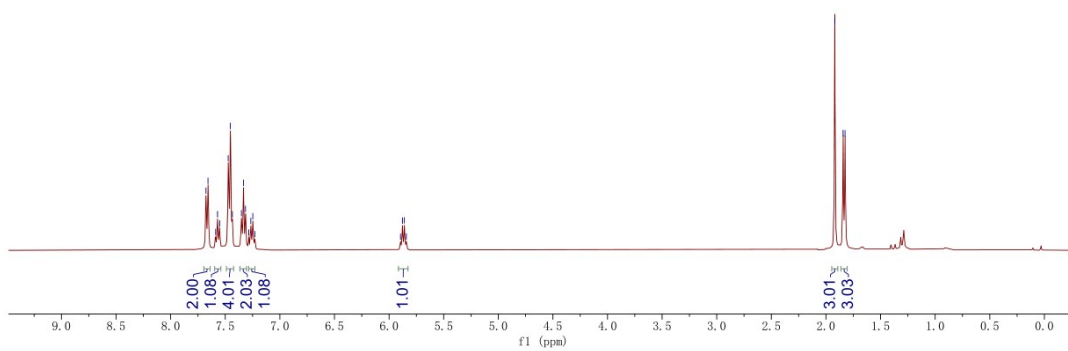


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7.453
7.435
7.352
7.333
7.315
7.285
7.266
7.248
7.229
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5.878
5.860
5.842

1.920
1.843
1.825



4g (^1H NMR) (400 MHz, CDCl_3)



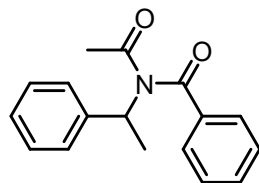
174.6
172.6

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128.3
127.3

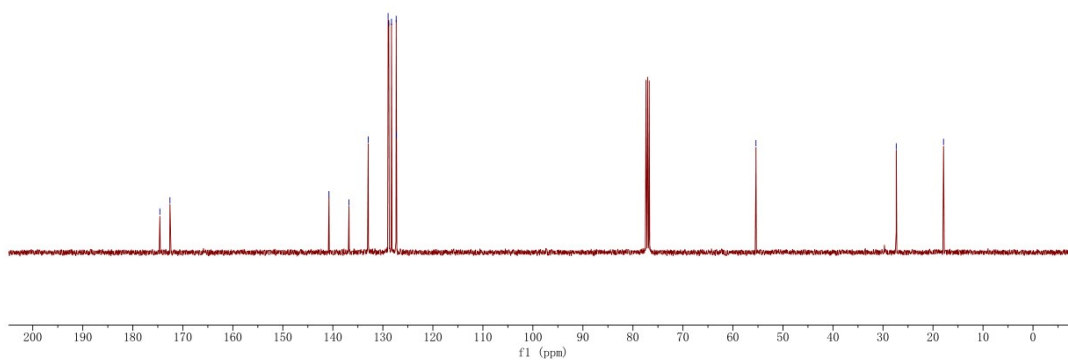
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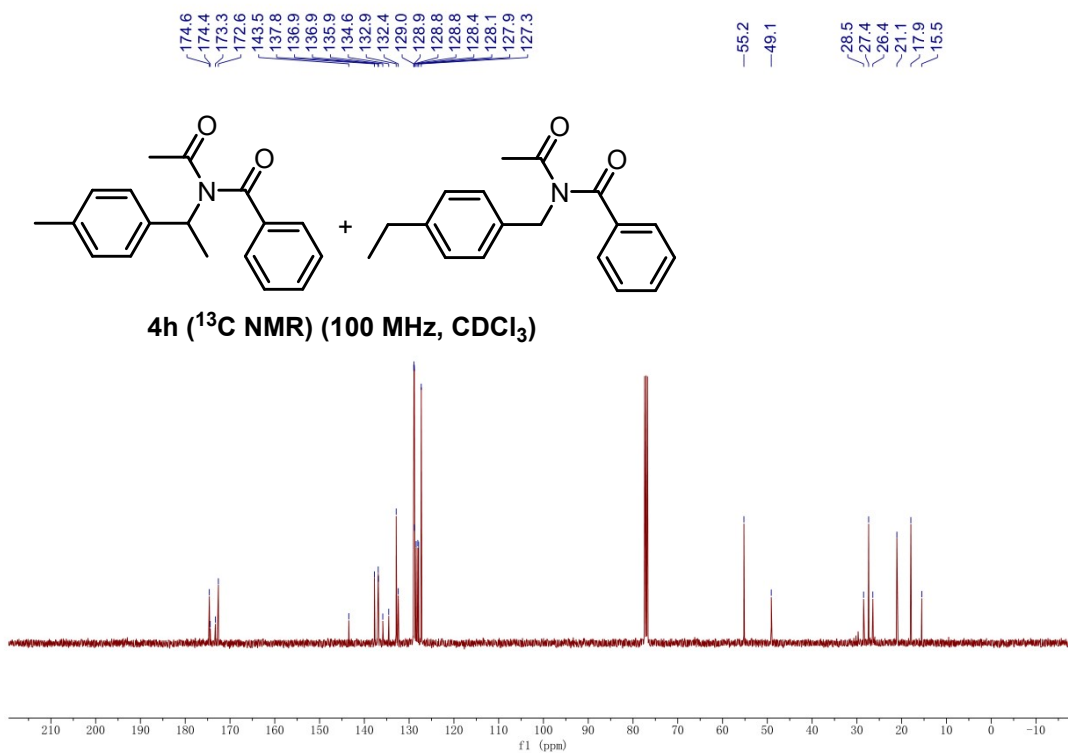
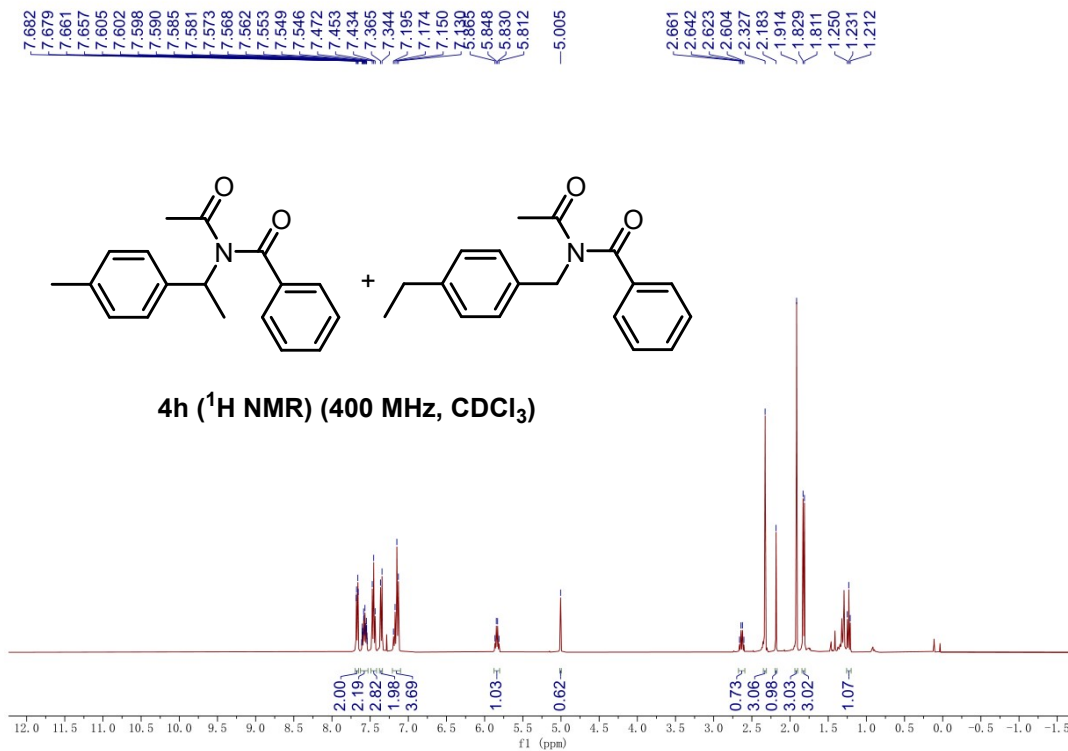
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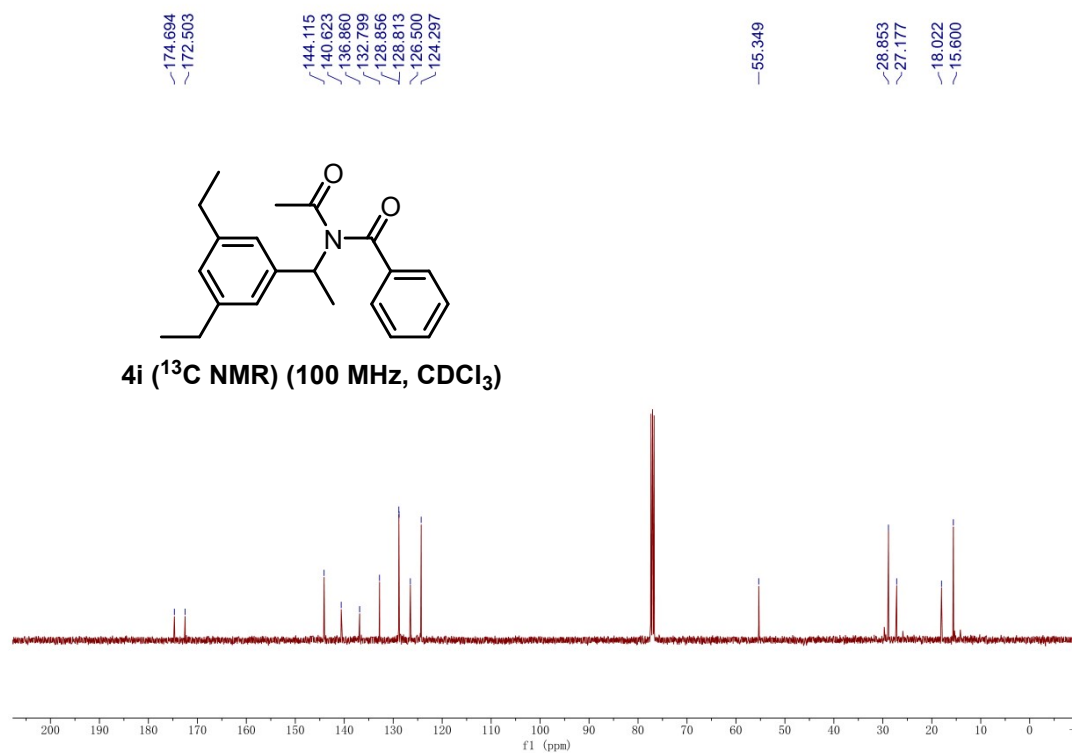
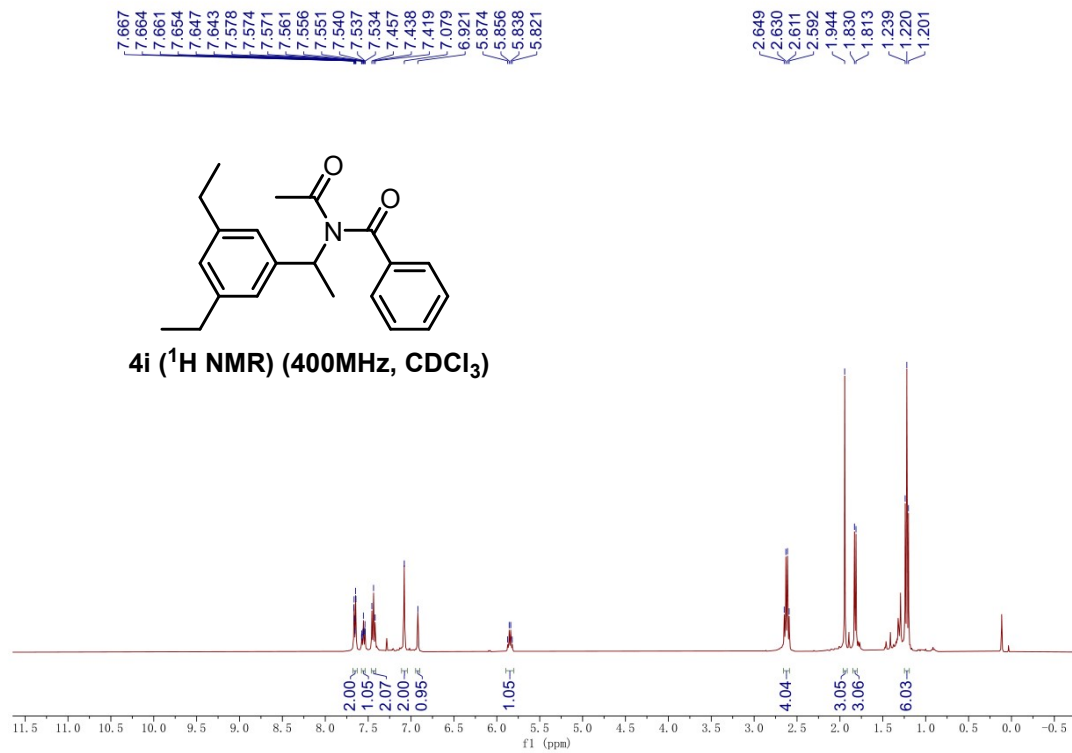
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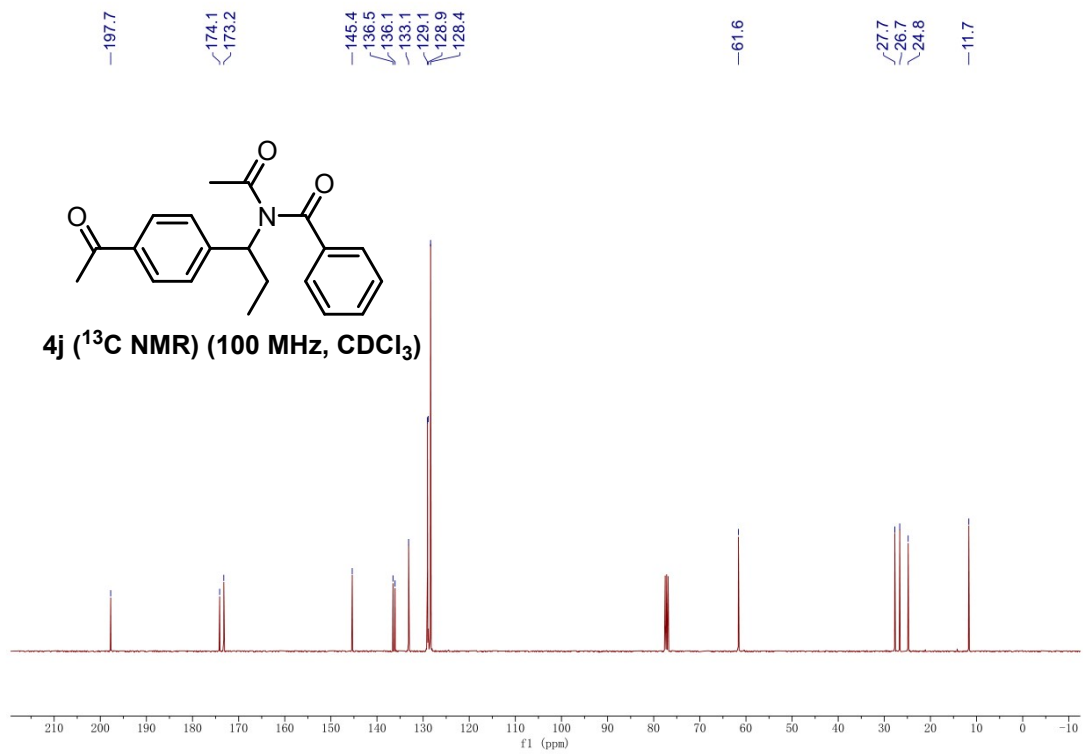
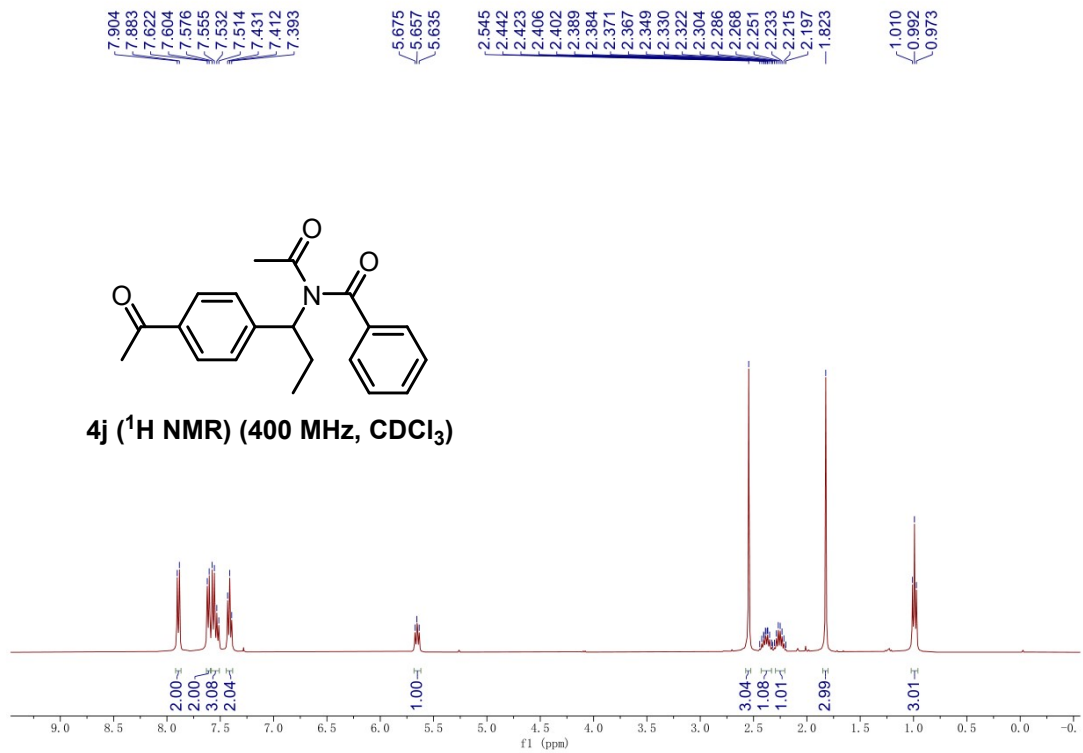


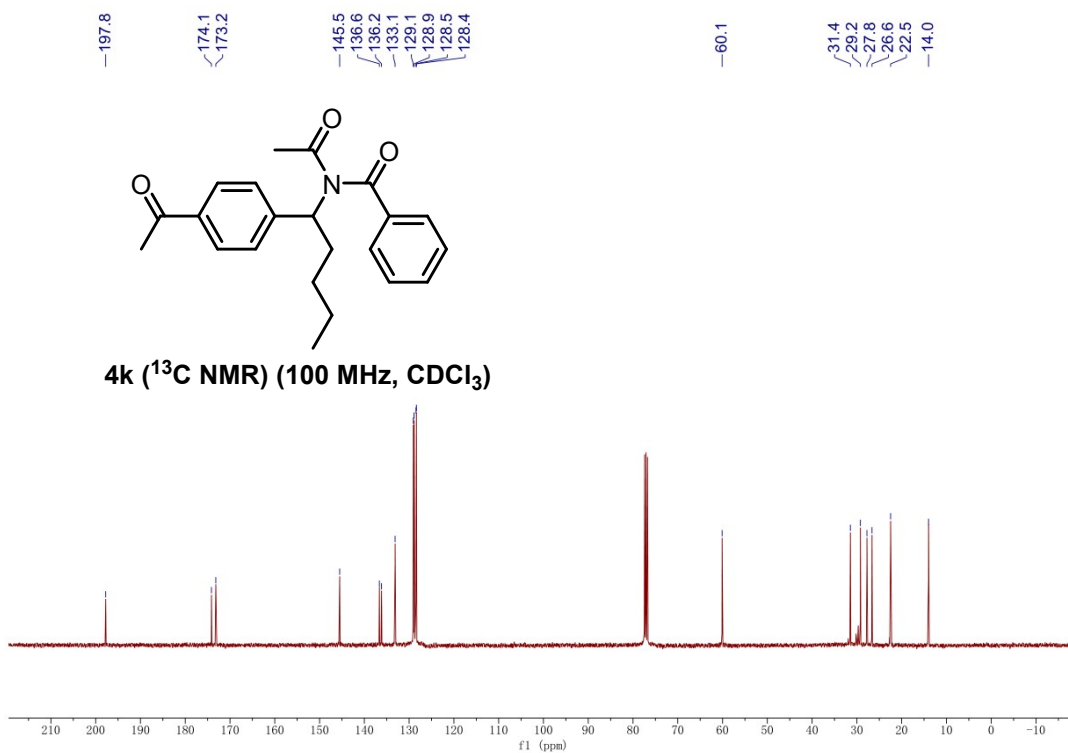
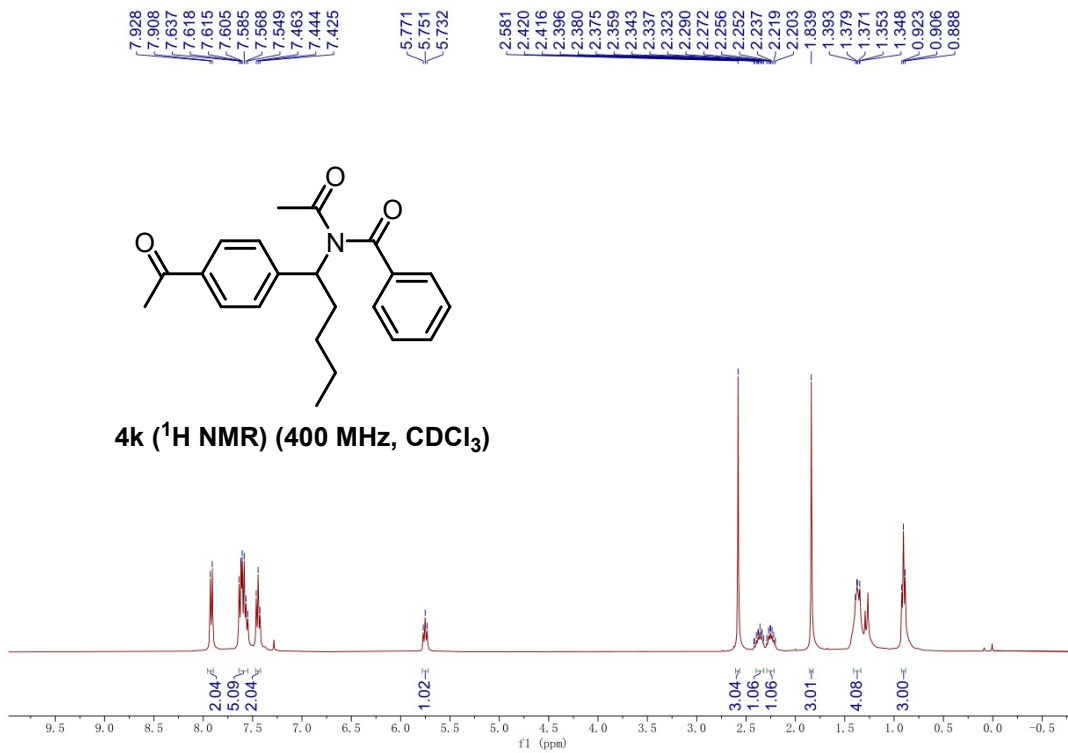
4g (^{13}C NMR) (100 MHz, CDCl_3)

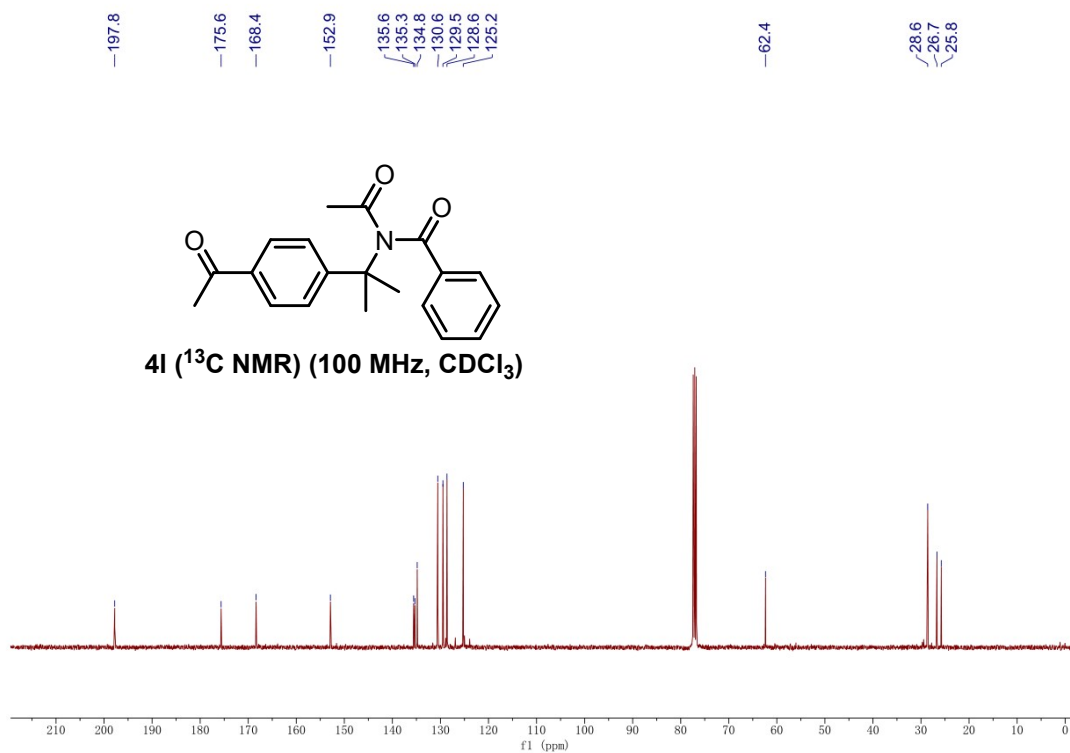
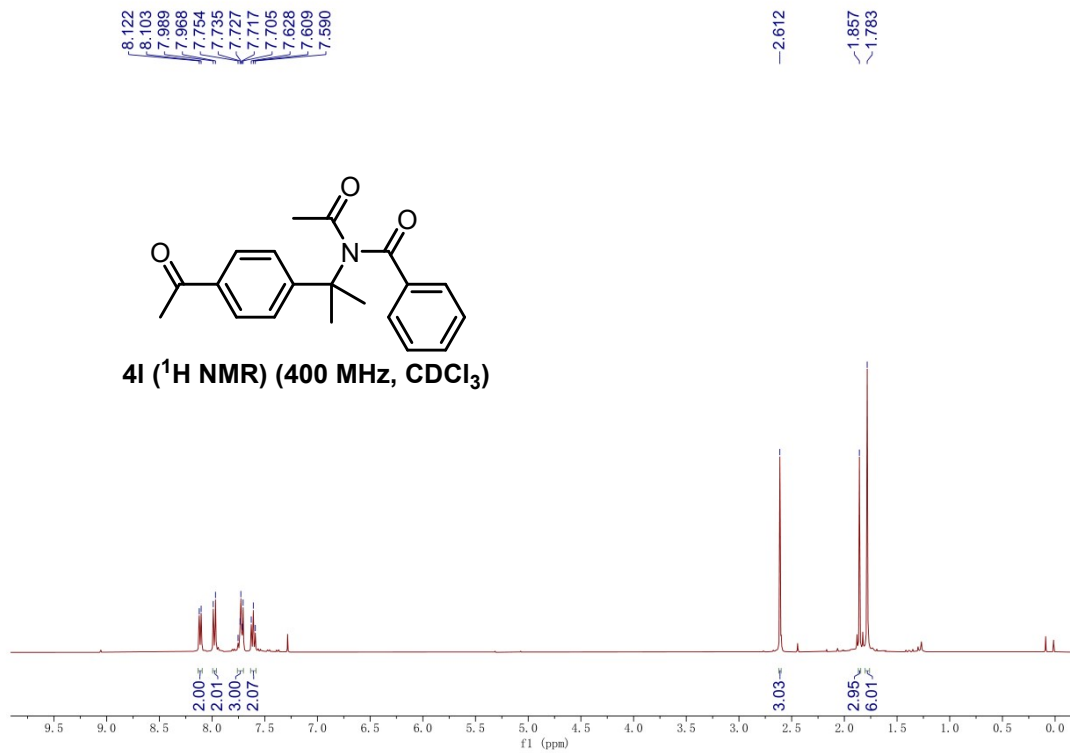


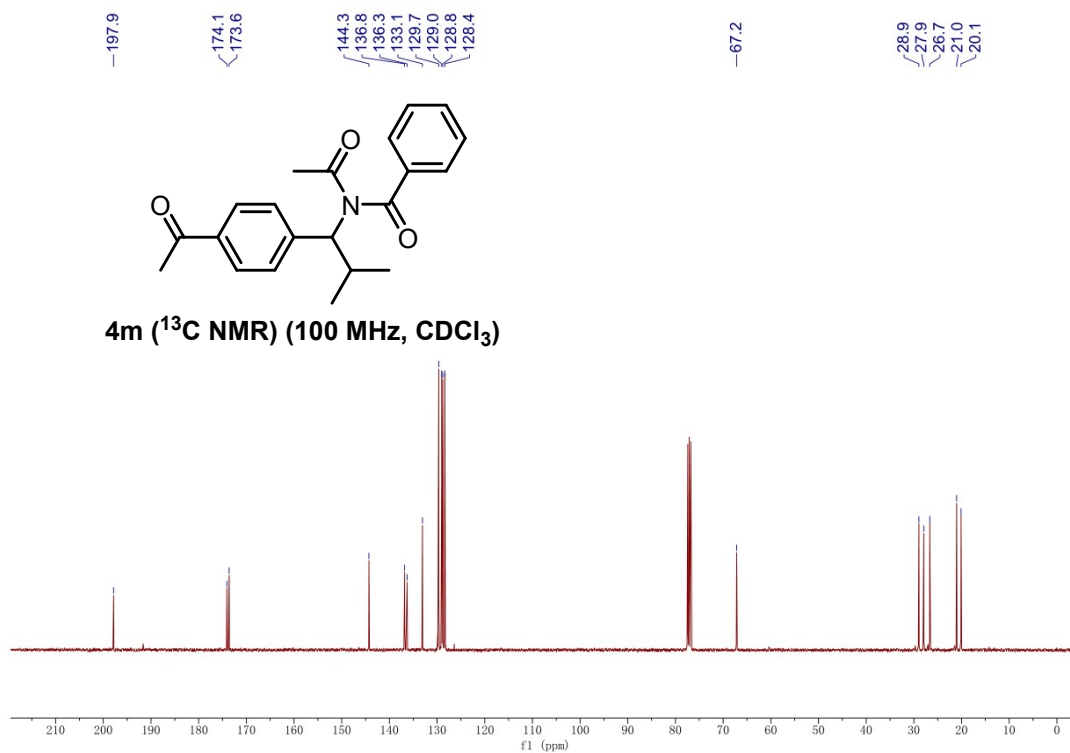
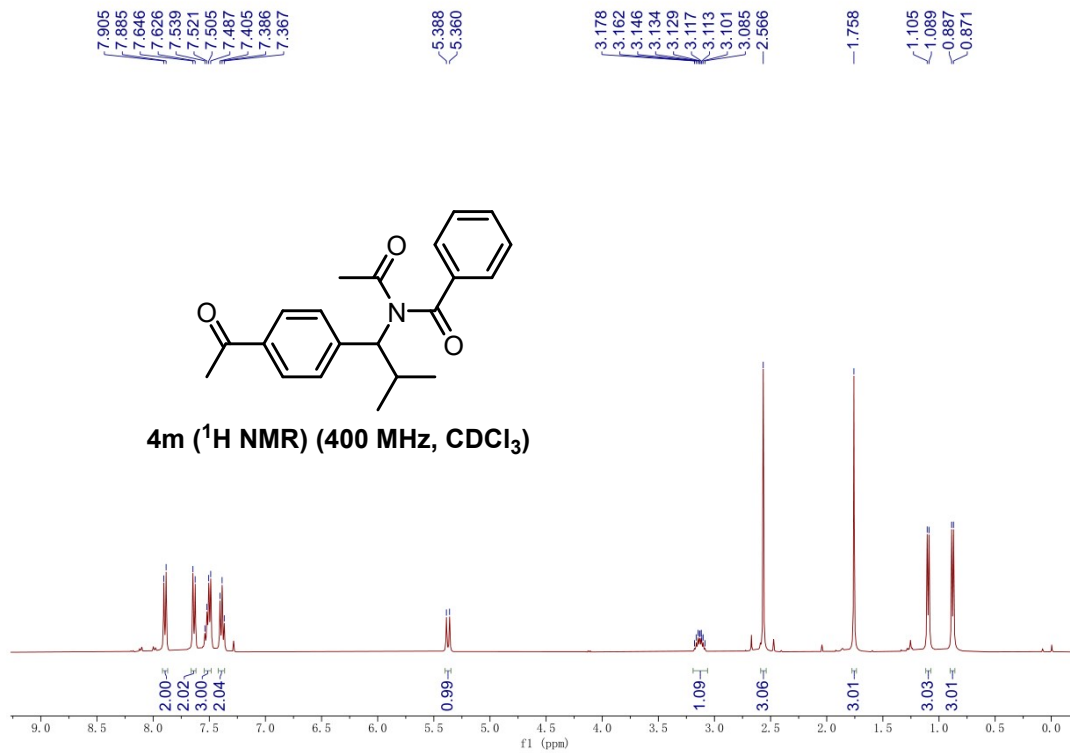








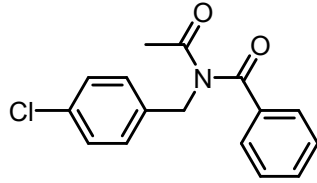




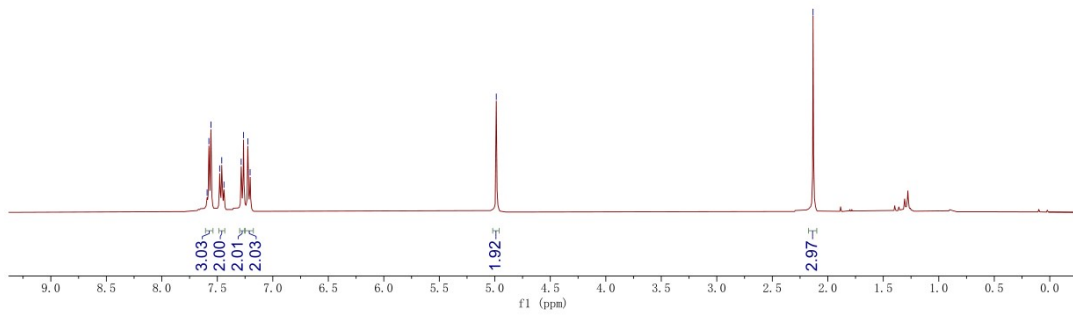
7.592
7.576
7.557
7.479
7.460
7.440
7.285
7.264
7.225
7.205

-4.987

-2.133



4n (¹H NMR) (400 MHz, CDCl₃)

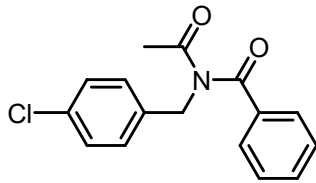


174.2
173.2

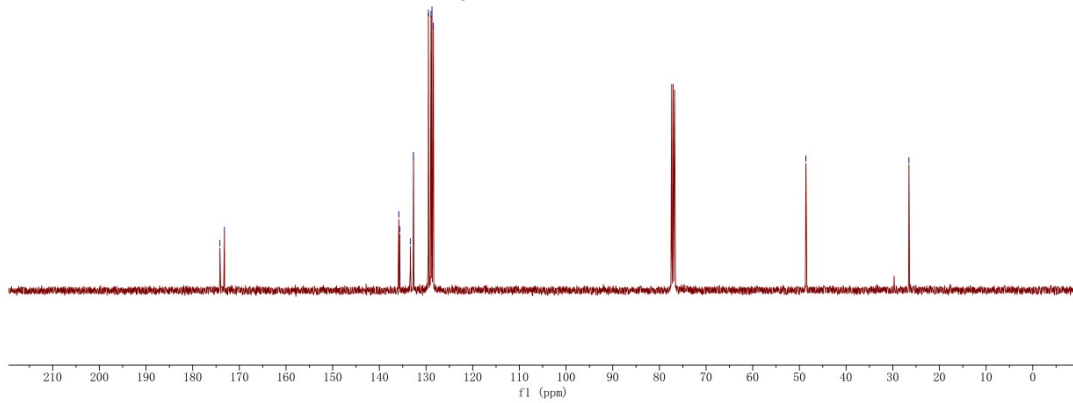
135.8
135.7
133.4
132.7
129.5
128.9
128.7
128.4

-48.6

-26.5



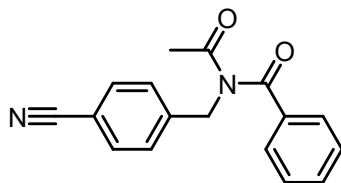
4n (¹³C NMR) (100 MHz, CDCl₃)



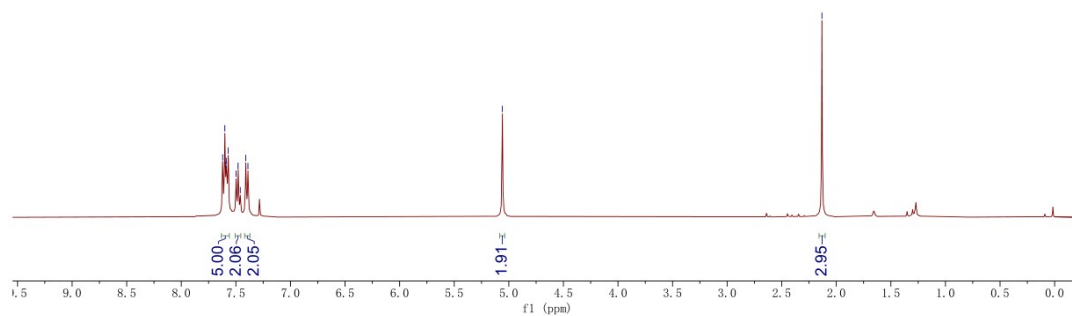
7.621
7.601
7.591
7.588
7.571
7.498
7.480
7.460
7.409
7.390

-5.059

-2.132



4o (¹H NMR) (400 MHz, CDCl₃)

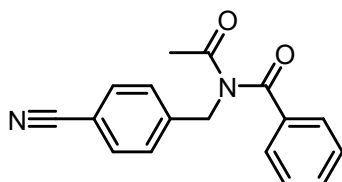


174.0
173.2

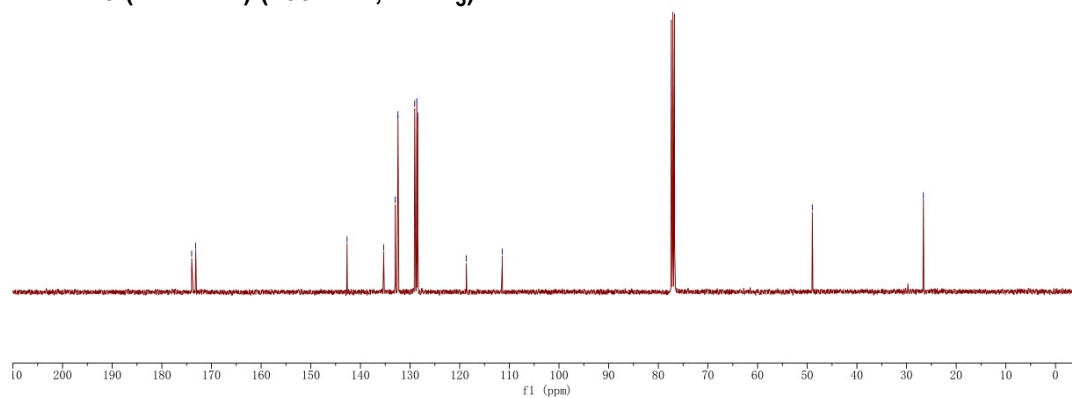
142.7
135.3
133.0
132.4
129.1
128.6
128.4
118.7
111.4

-49.0

-26.6



4o (¹³C NMR) (100 MHz, CDCl₃)

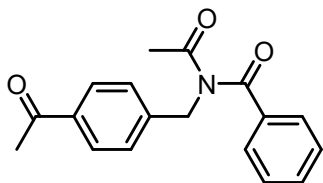


7.910
7.890
7.585
7.572
7.566
7.563
7.554
7.472
7.453
7.433
7.363
7.343

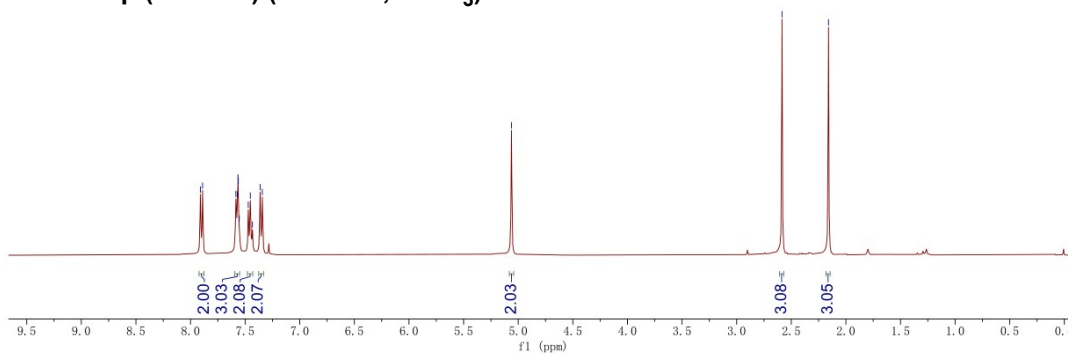
-5.062

-2.585

-2.160



4p (¹H NMR) (400 MHz, CDCl₃)



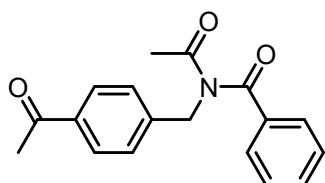
-197.7

174.1
173.3

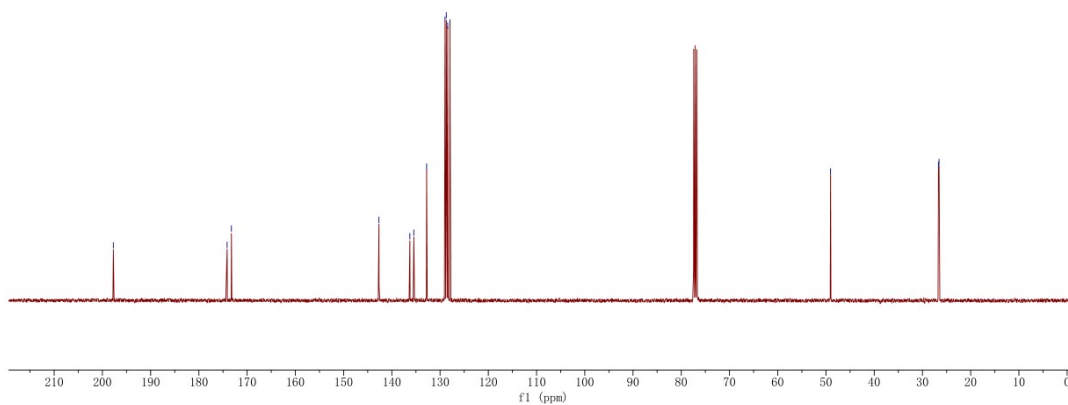
142.7
136.3
135.4
132.8
129.0
128.7
128.4
127.9

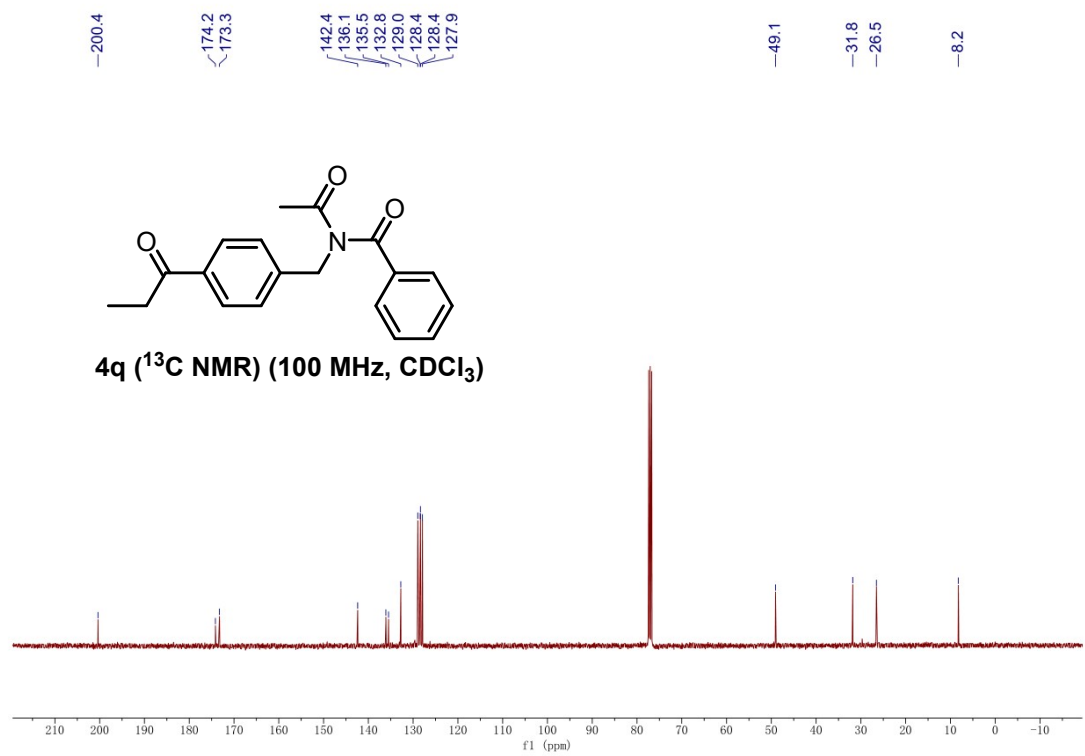
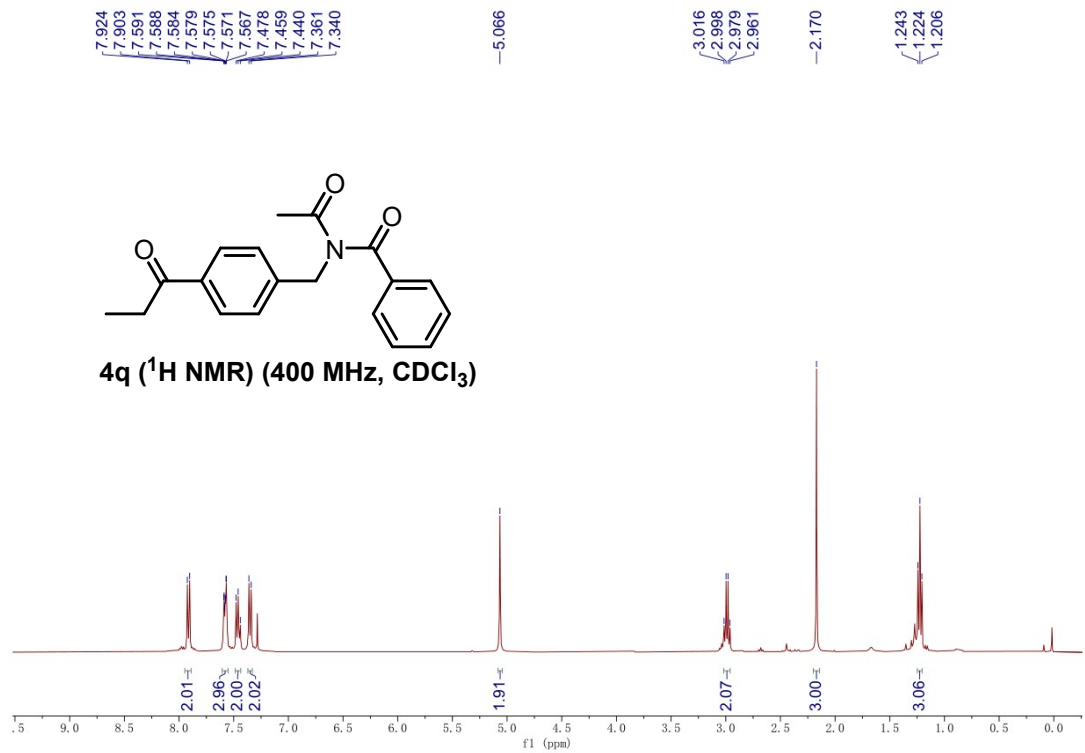
-49.1

26.7
26.6



4p (¹³C NMR) (100 MHz, CDCl₃)

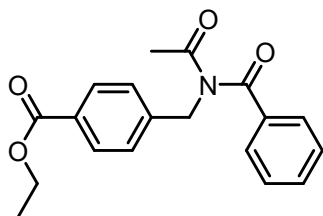




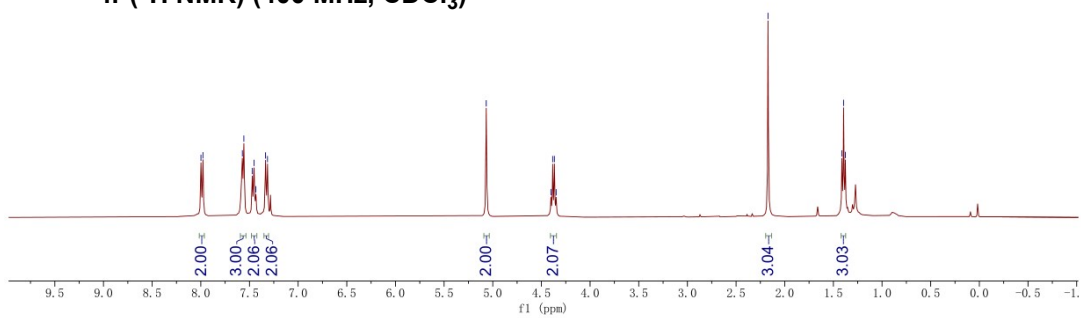
7.998
7.978
7.573
7.558
7.472
7.453
7.434
7.335
7.315

5.067
4.402
4.385
4.367
4.349

2.172
1.413
1.395
1.377

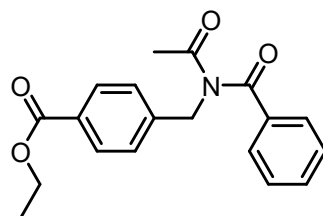


4r (¹H NMR) (400 MHz, CDCl₃)

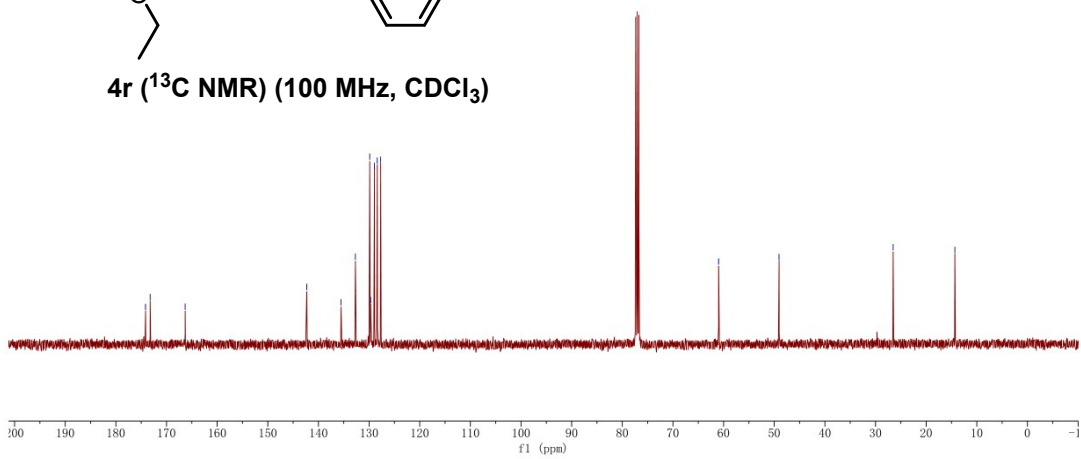


174.1
173.2
166.3
142.3
135.5
132.7
129.9
129.7
128.9
128.4
127.7

61.0
49.1
26.5
14.3



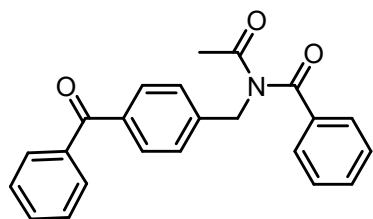
4r (¹³C NMR) (100 MHz, CDCl₃)



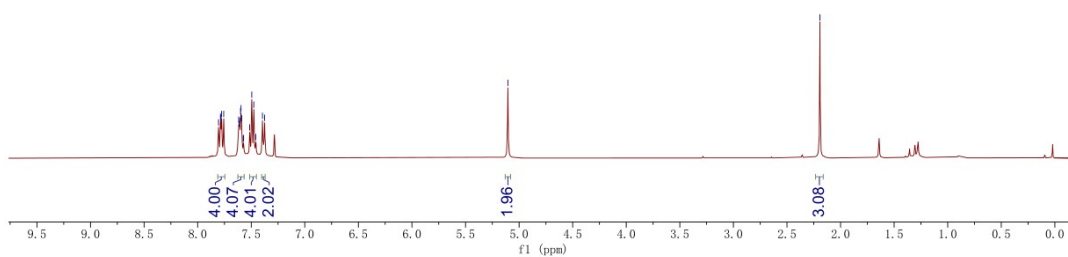
7.805
7.787
7.783
7.777
7.757
7.617
7.612
7.607
7.600
7.595
7.590
7.575
7.572
7.514
7.495
7.476
7.457
7.395
7.375

—5.105

—2.193



4s (¹H NMR) (400 MHz, CDCl₃)



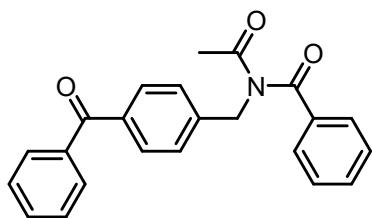
—196.3

174.2
173.3

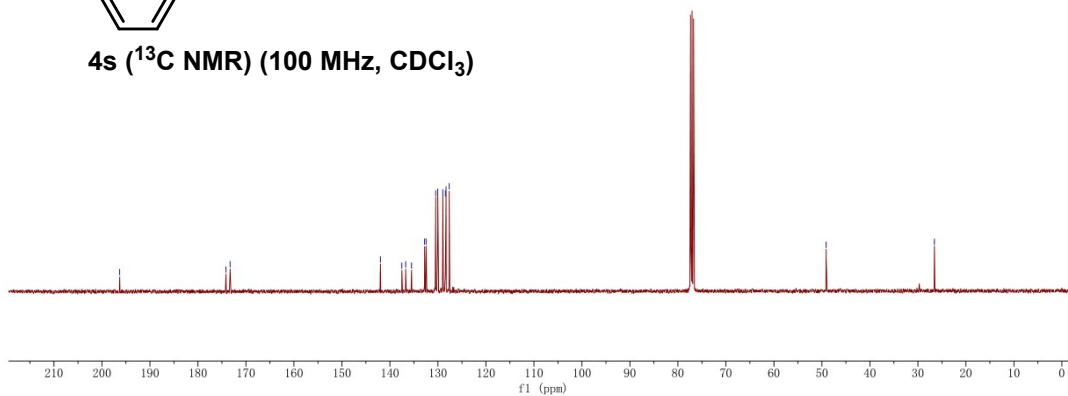
142.0
137.5
136.7
135.5
132.8
132.5
130.5
130.0
129.0
128.4
128.3
127.7

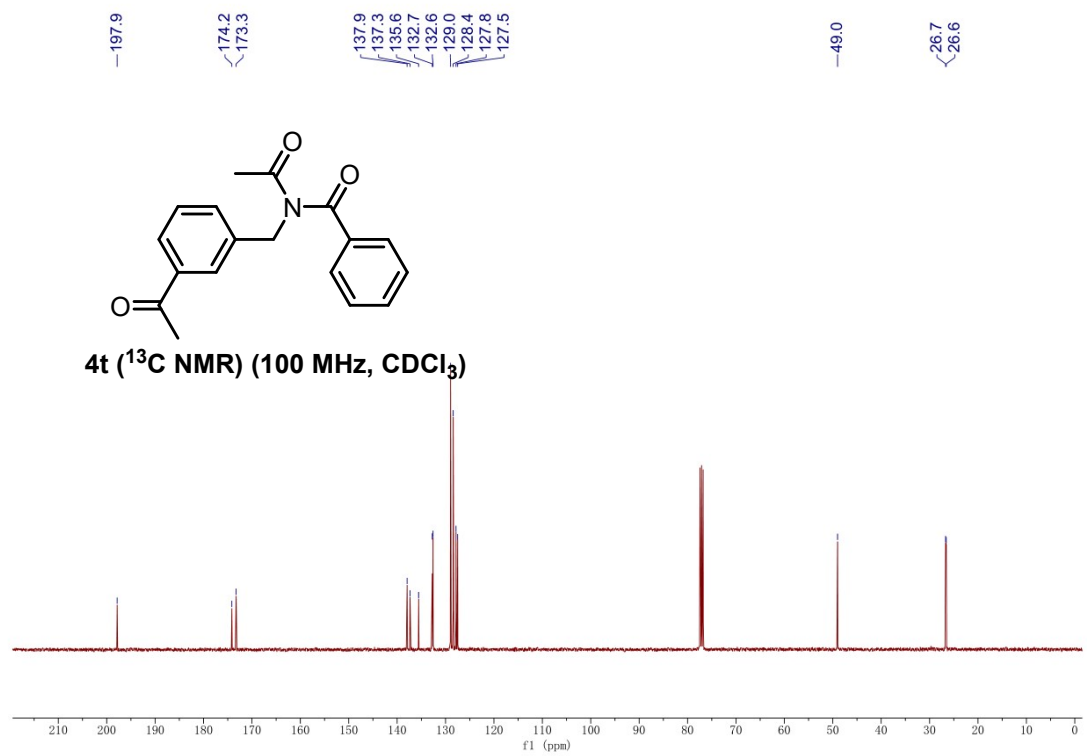
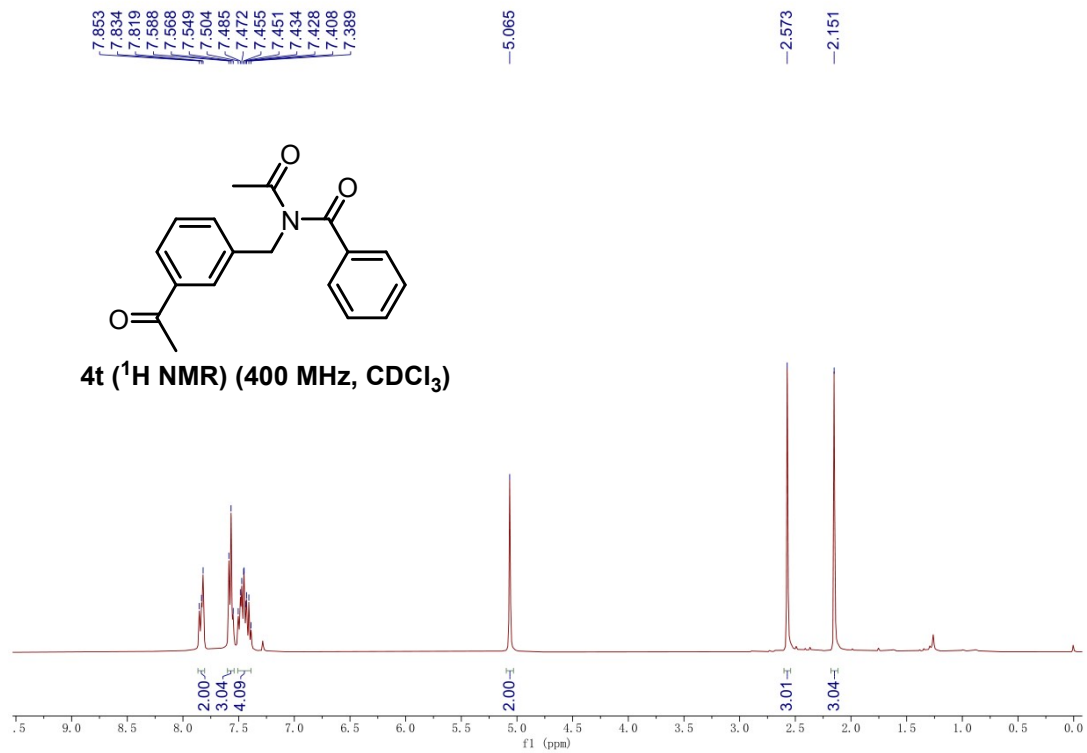
—49.1

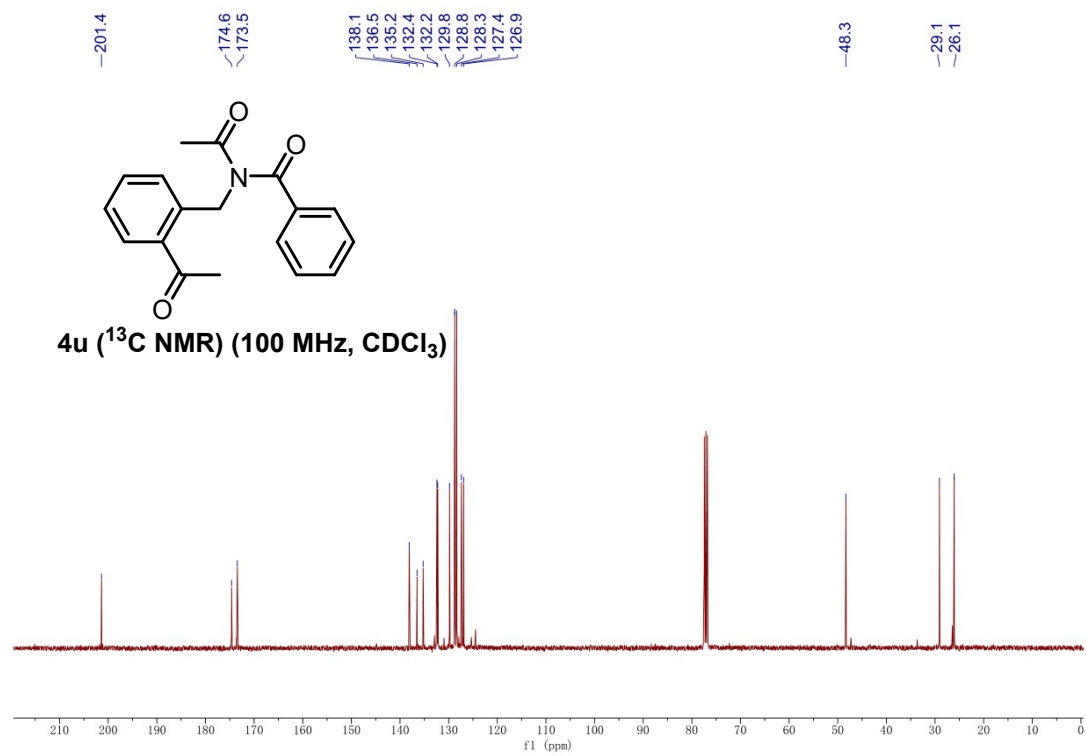
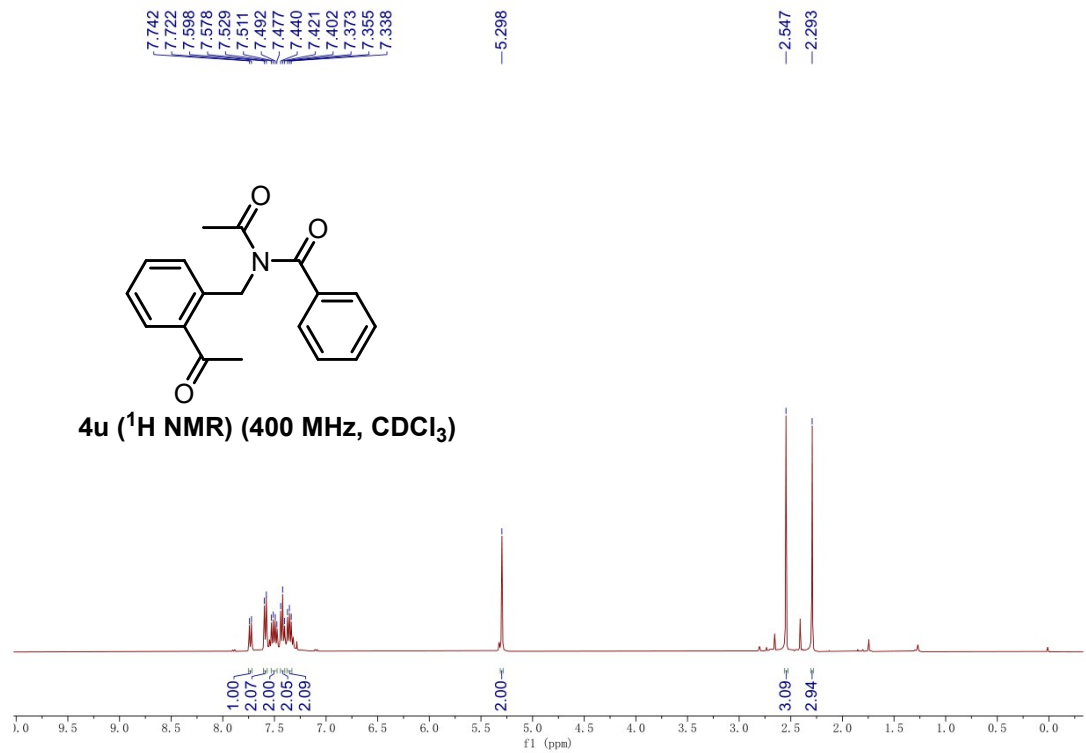
—26.6

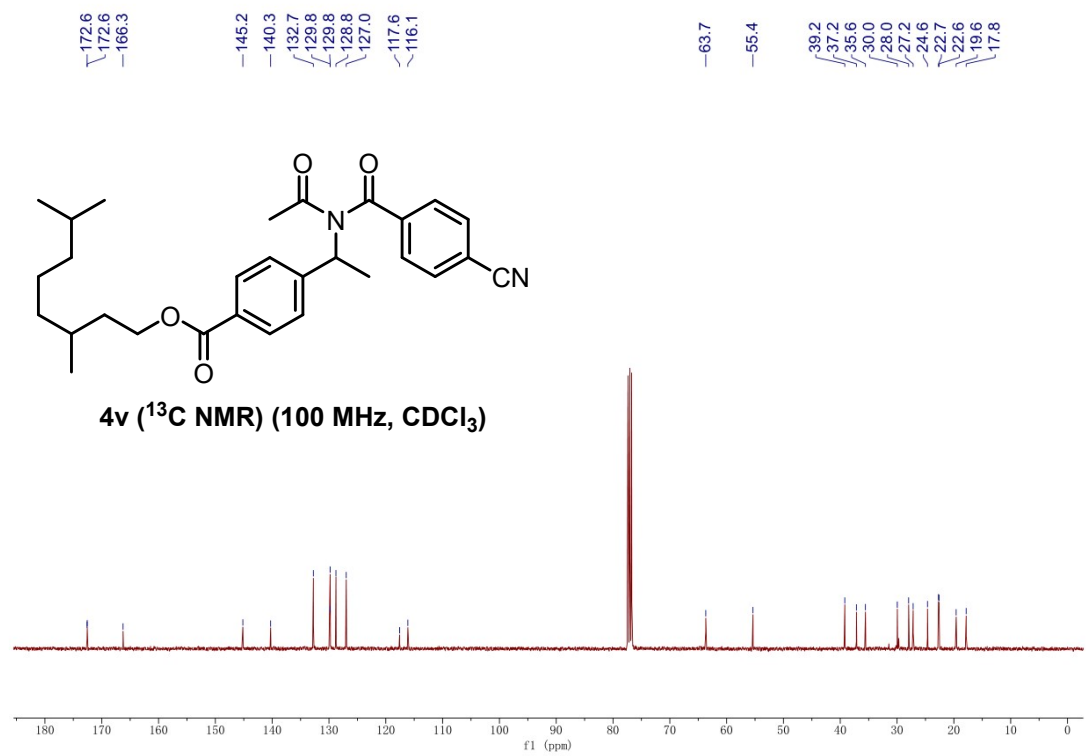
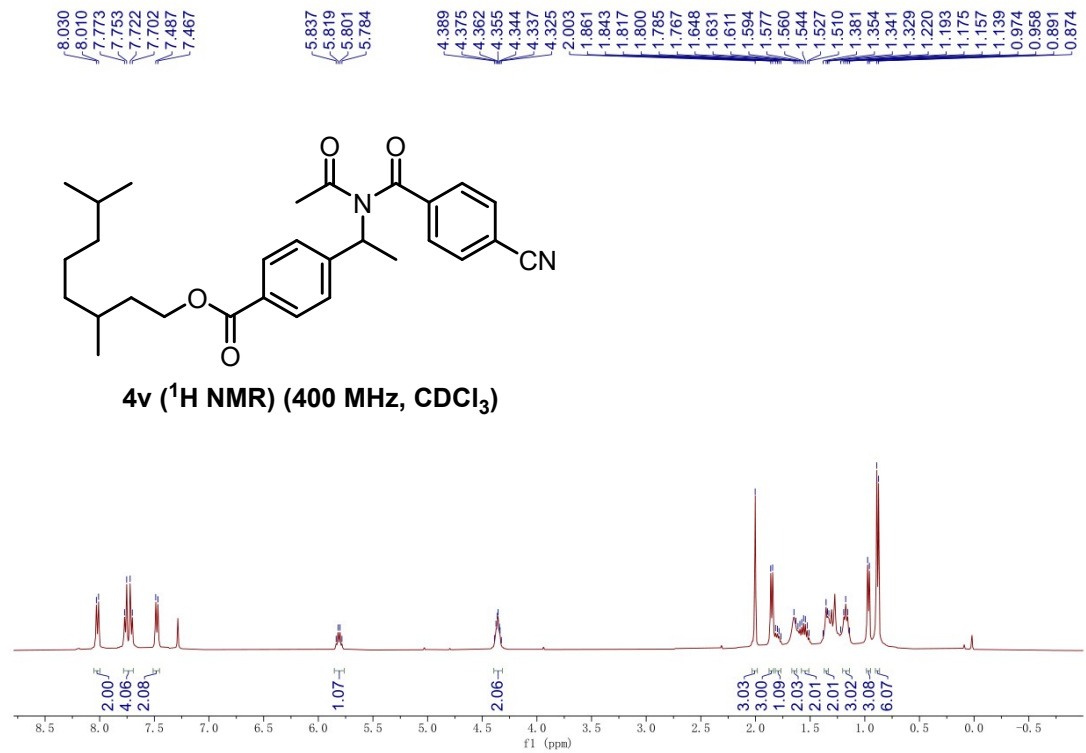


4s (¹³C NMR) (100 MHz, CDCl₃)

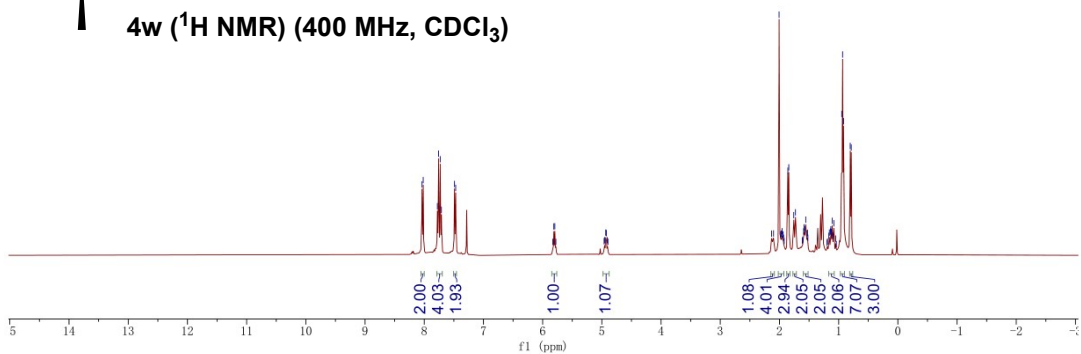
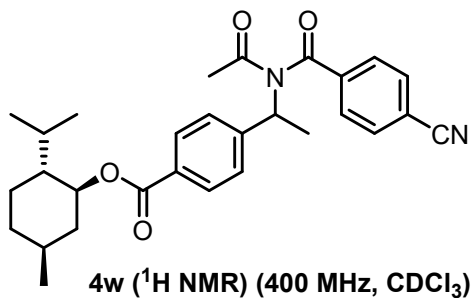




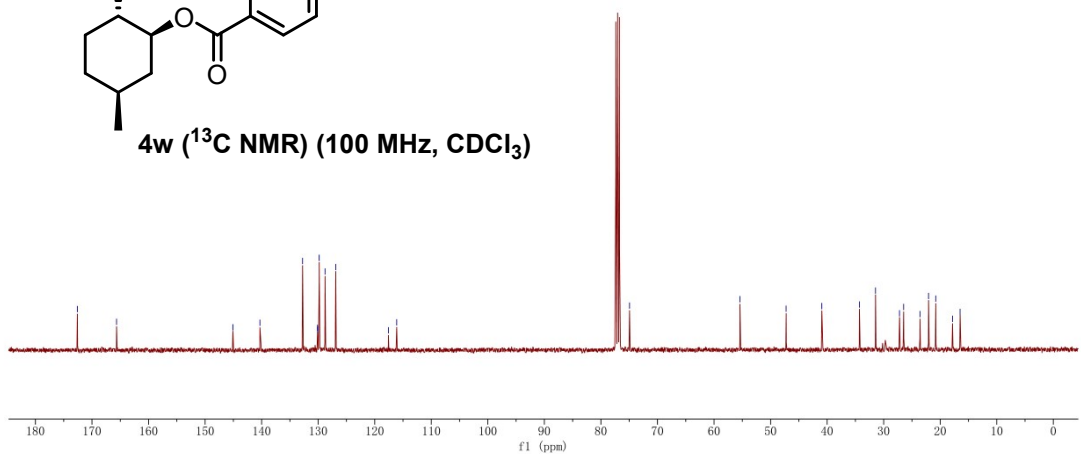
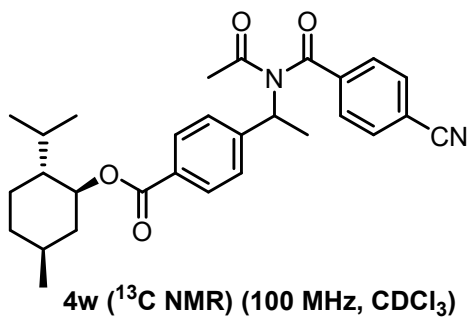


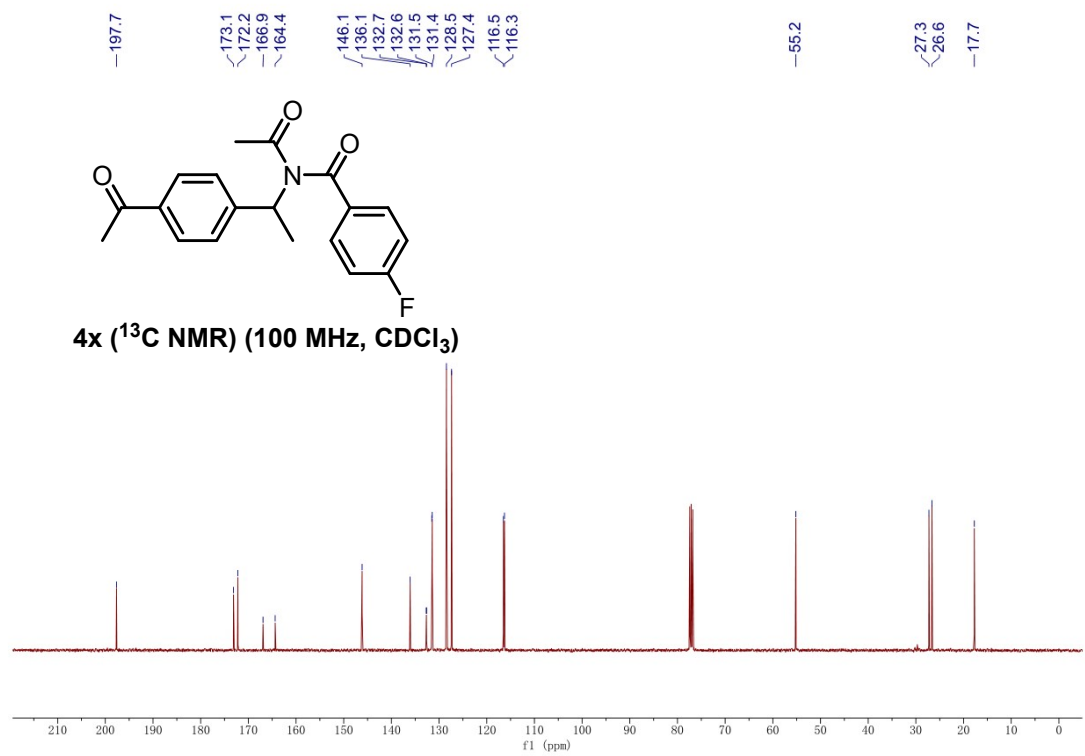
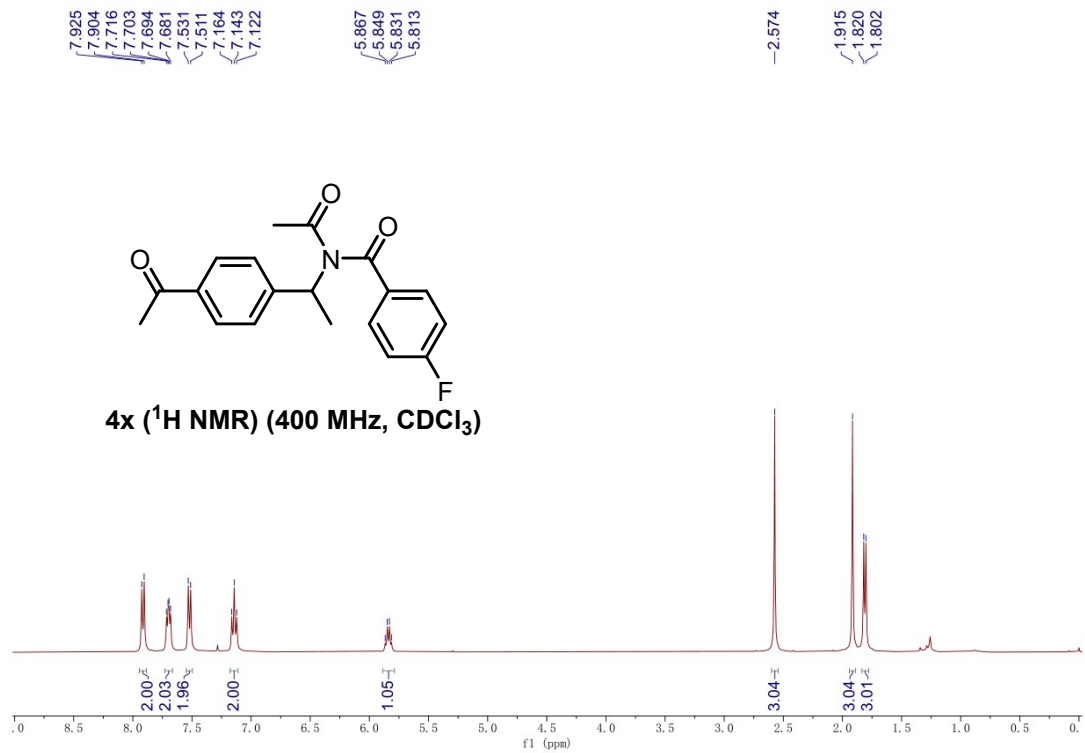


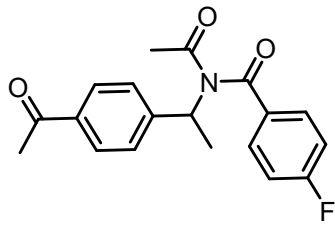
8.038
8.018
7.778
7.758
7.730
7.710
7.489
7.469
5.829
5.811
5.794
5.776
4.962
4.951
4.935
4.924
4.908
4.897
2.134
2.100
2.007
1.980
1.973
1.963
1.955
1.947
1.938
1.931
1.920
1.858
1.843
1.759
1.730
1.613
1.607
1.592
1.585
1.576
1.556
1.535
1.527
1.520
1.186
1.189
1.166
1.157
1.139
1.132
1.124
1.110
1.099
1.081
1.052
1.039
0.949
0.934
0.918
0.805
0.788



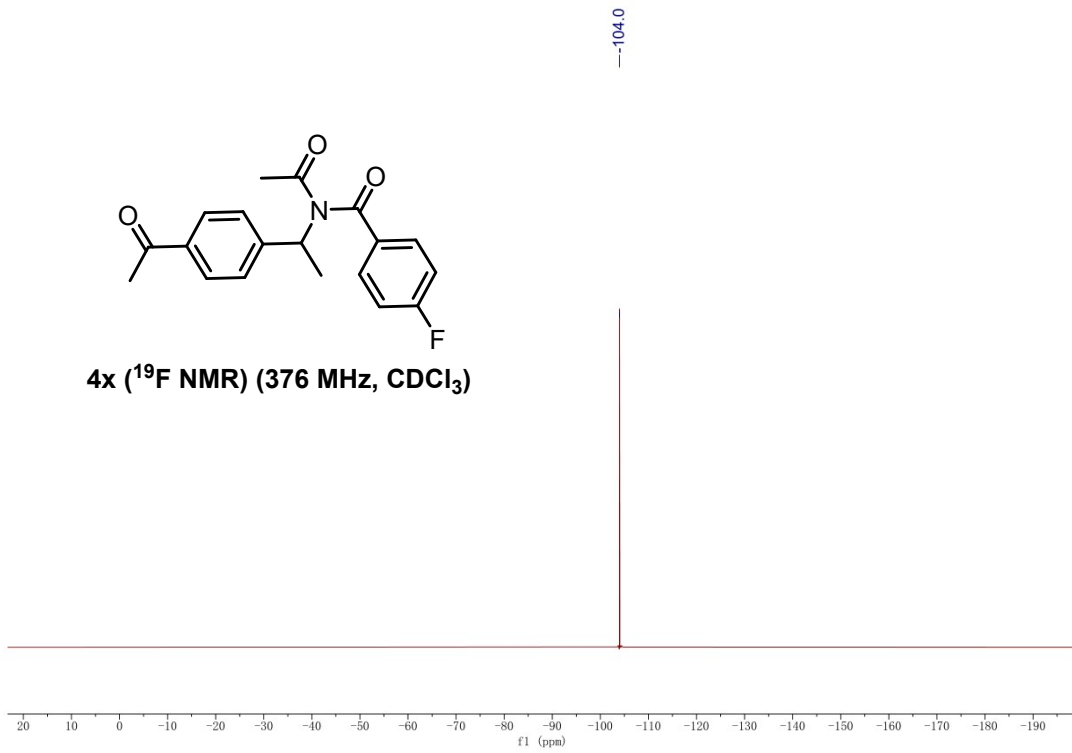
172.6
165.7
145.1
140.3
132.8
130.1
129.8
128.8
126.9
117.6
116.1
74.9
55.4
47.3
40.9
34.3
31.4
27.2
26.5
23.6
22.1
20.8
17.8
16.5







4x (¹⁹F NMR) (376 MHz, CDCl₃)

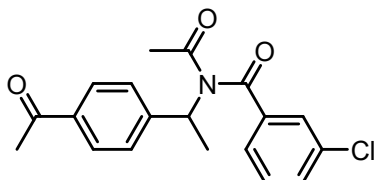


7.925
7.905
7.625
7.542
7.512
7.491
7.413
7.394
7.374

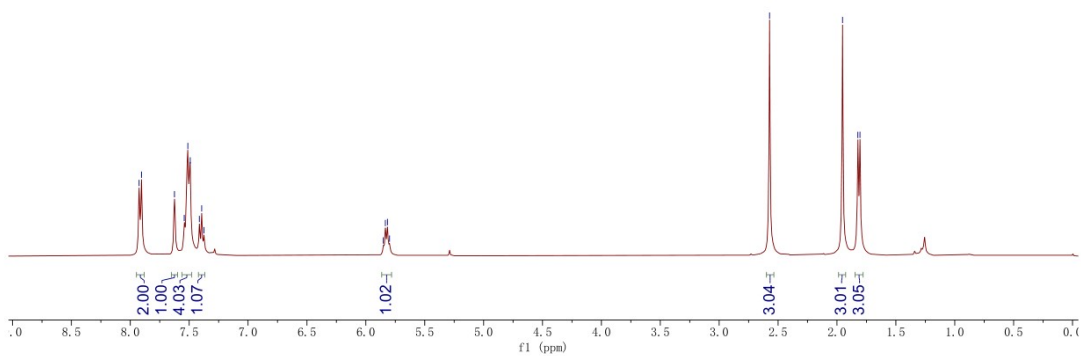
5.852
5.834
5.816
5.799

-2.572

1.952
1.823
1.805



4y (¹H NMR) (400 MHz, CDCl₃)



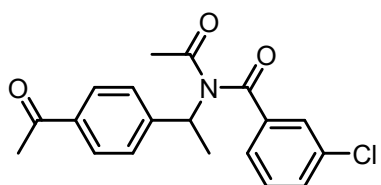
-197.6

172.9
172.4

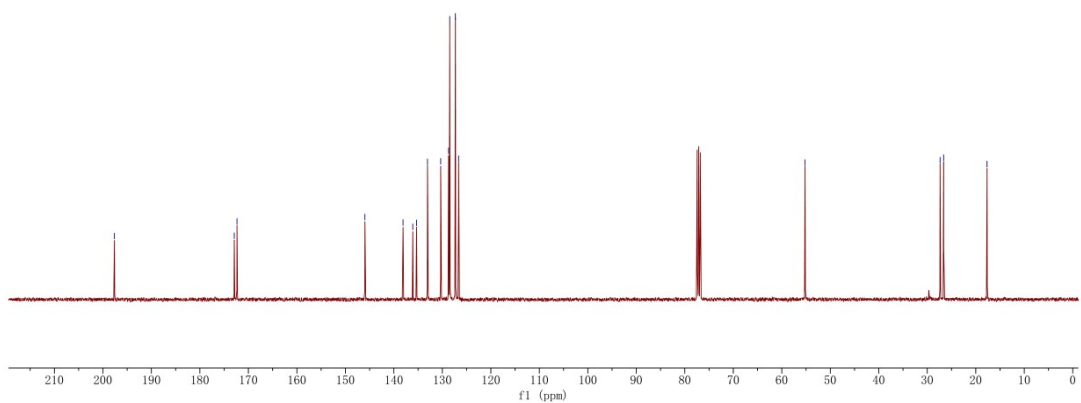
146.0
138.1
136.1
135.3
133.1
130.3
128.7
128.5
127.3
126.6

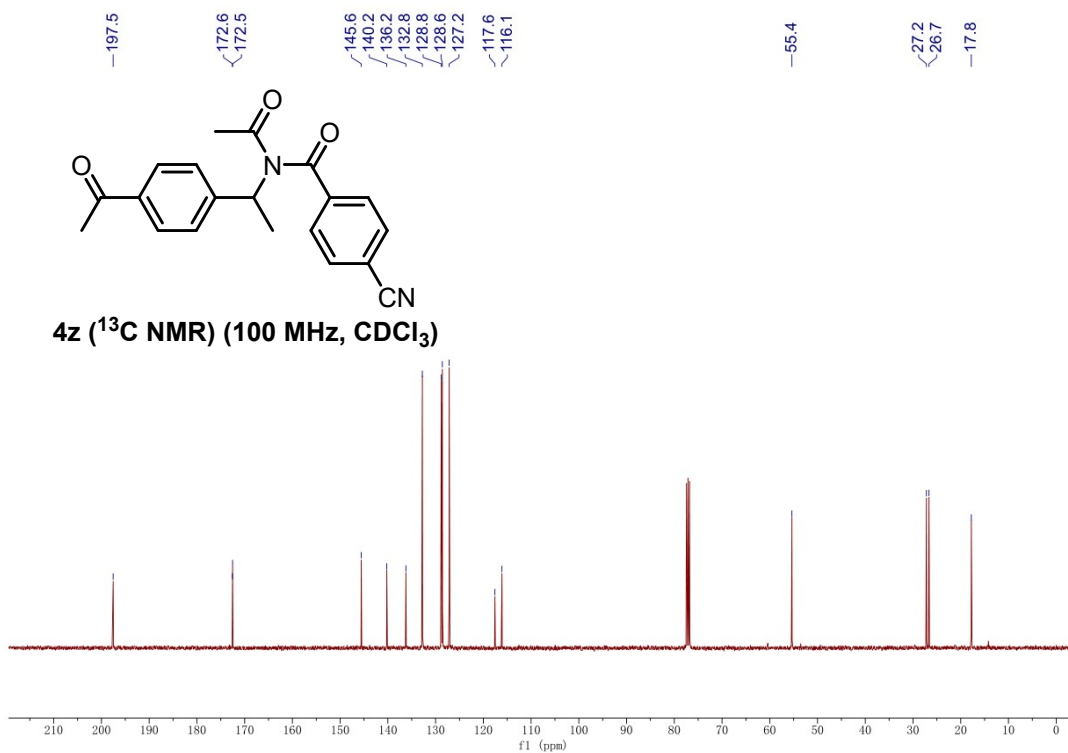
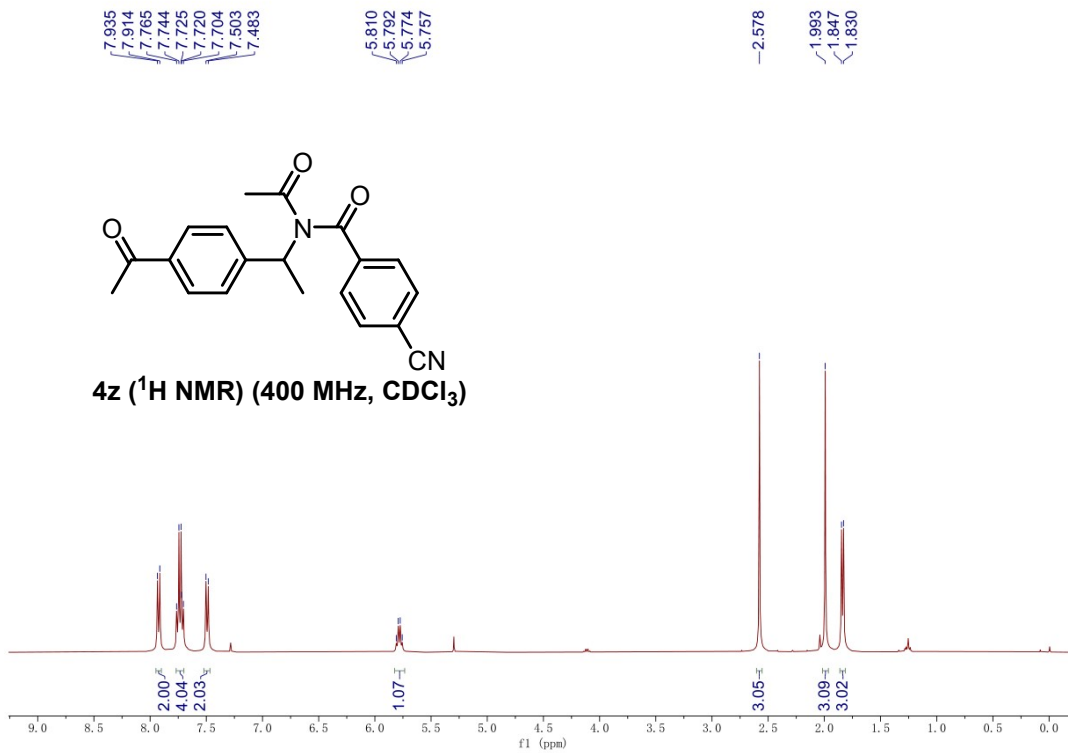
-55.2

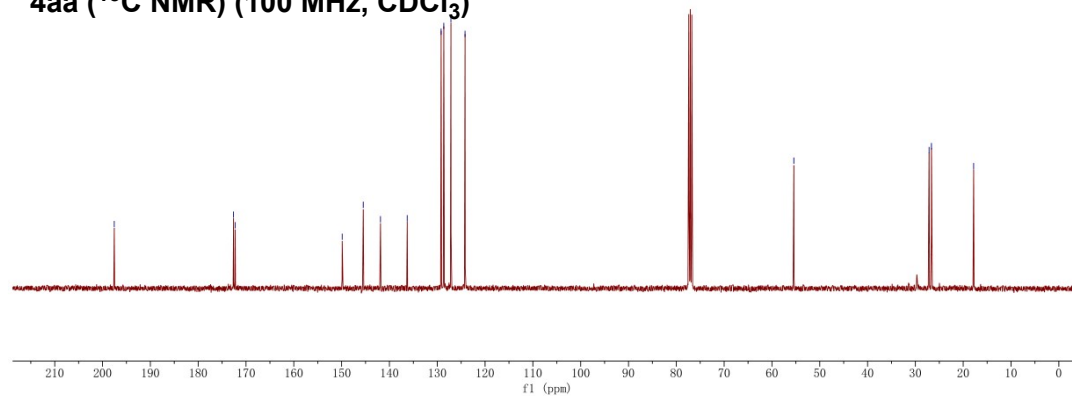
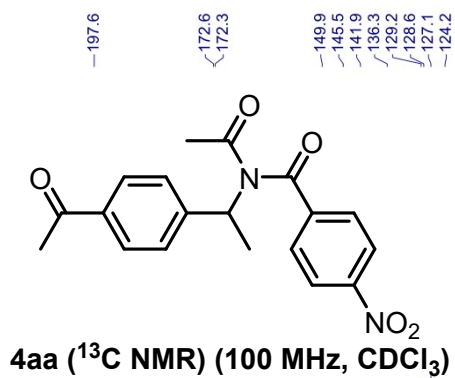
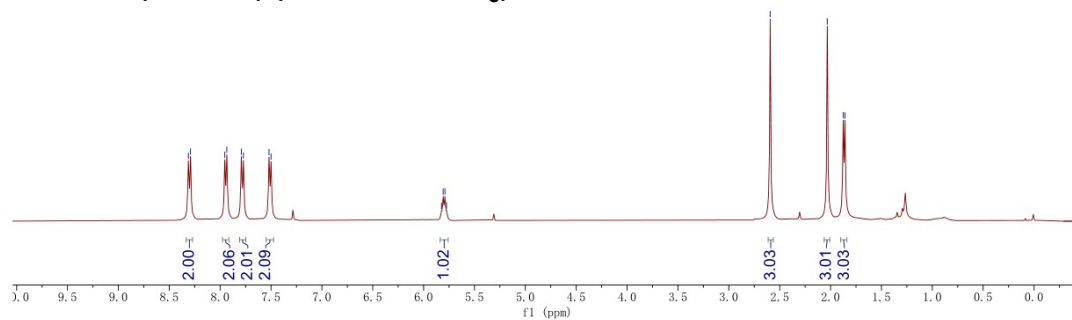
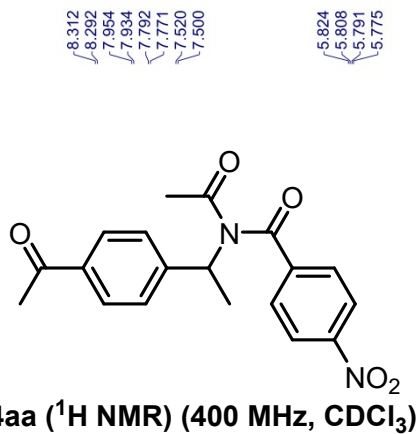
27.4
26.6
17.7

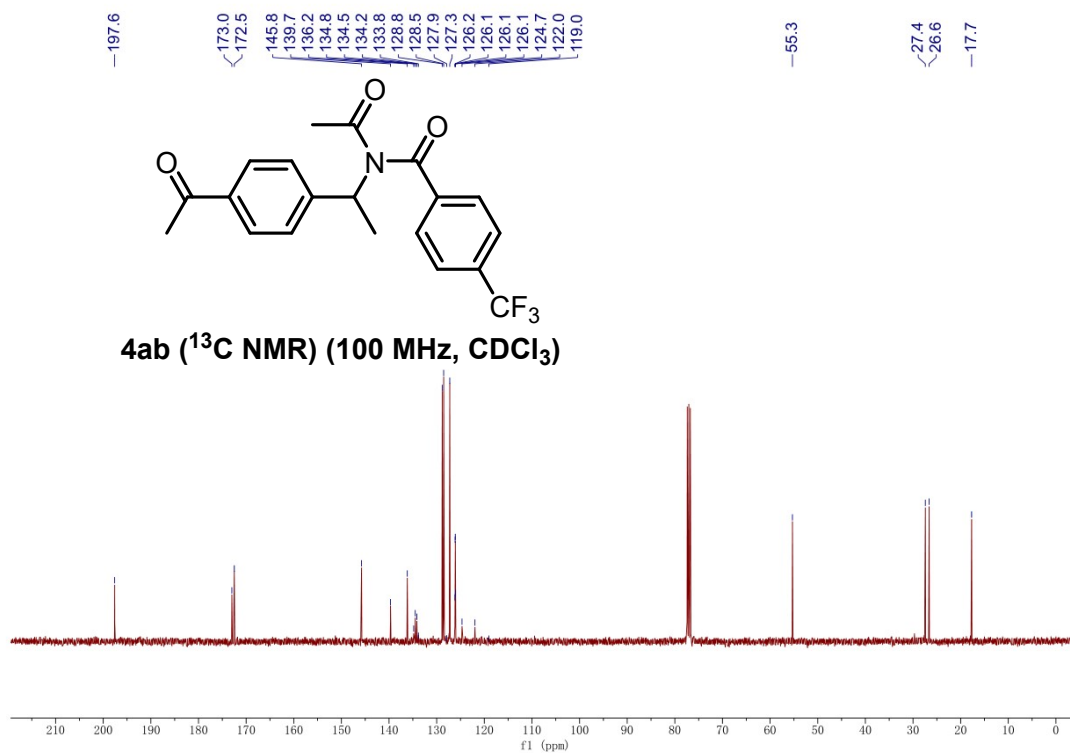
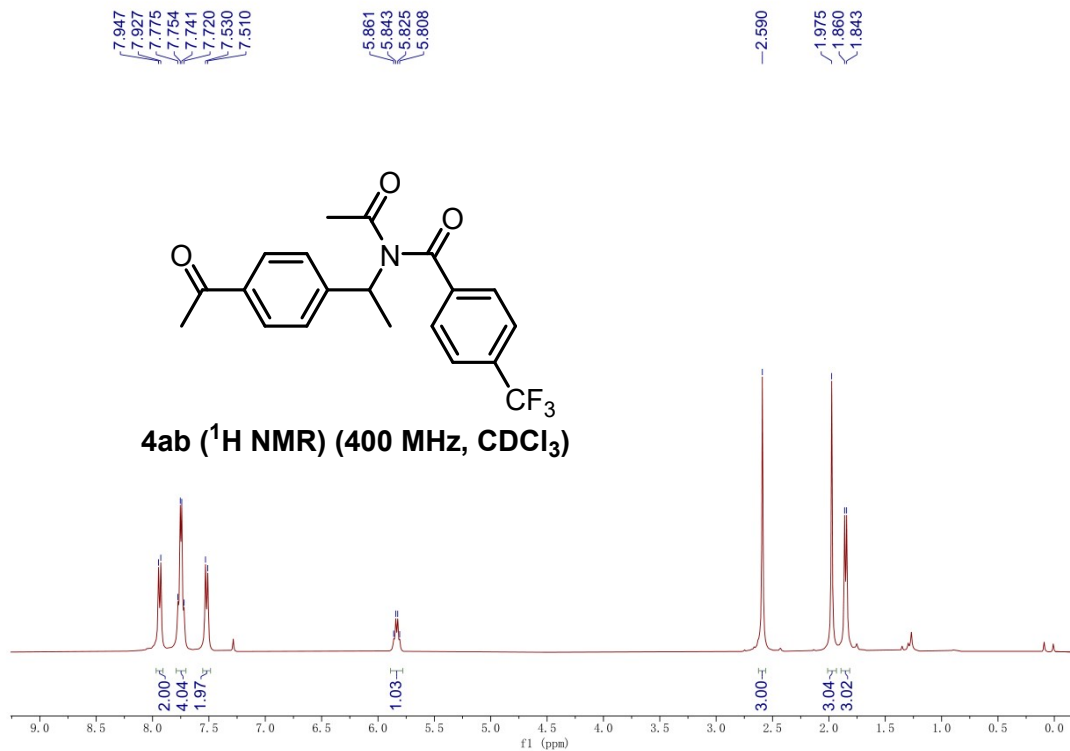


4y (¹³C NMR) (100 MHz, CDCl₃)

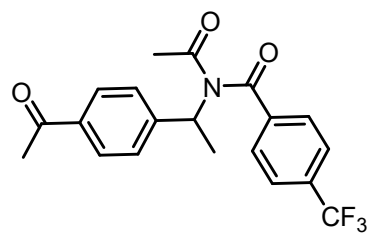




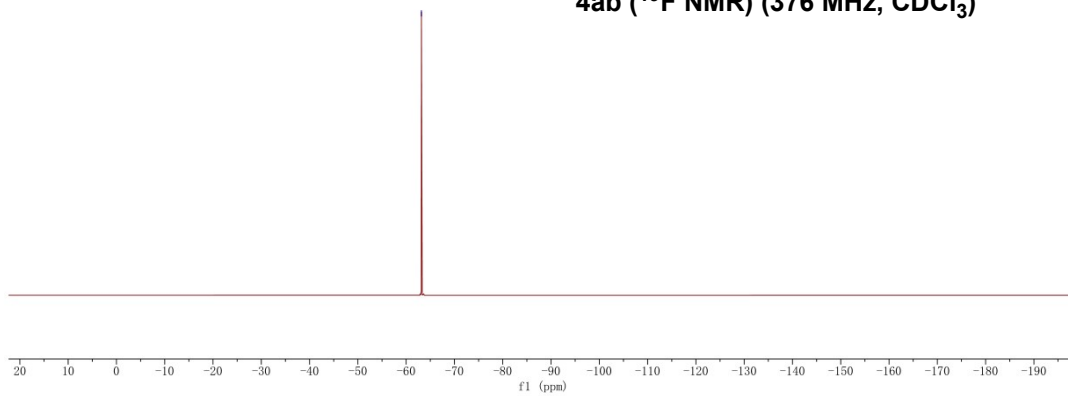


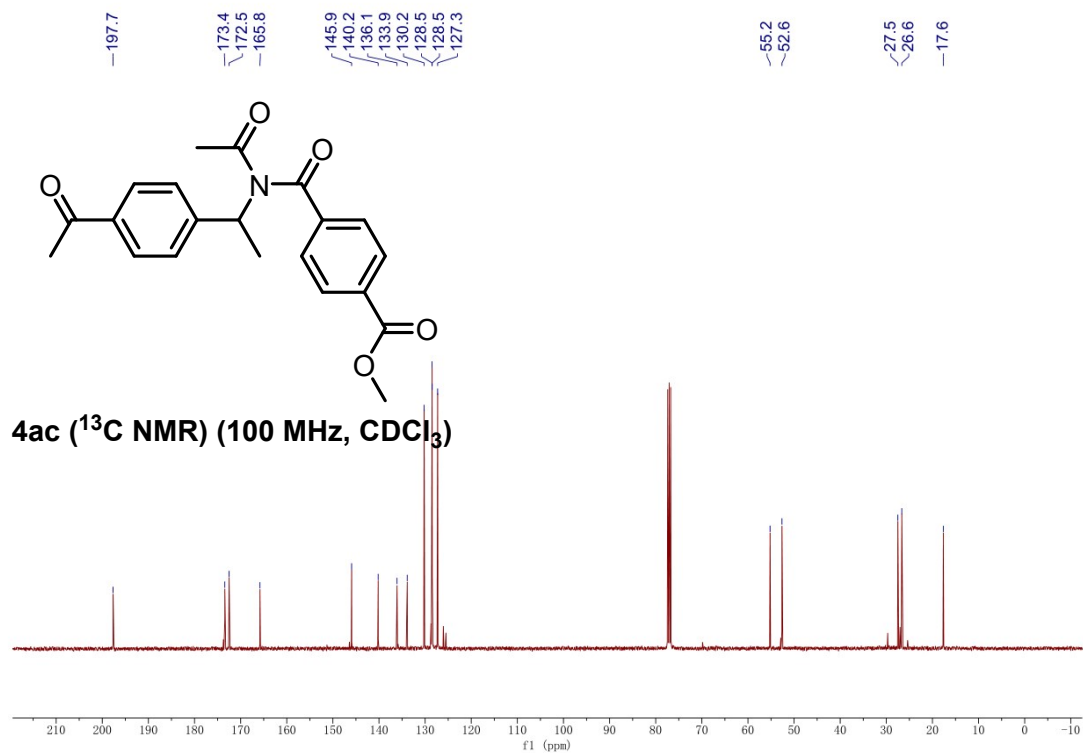
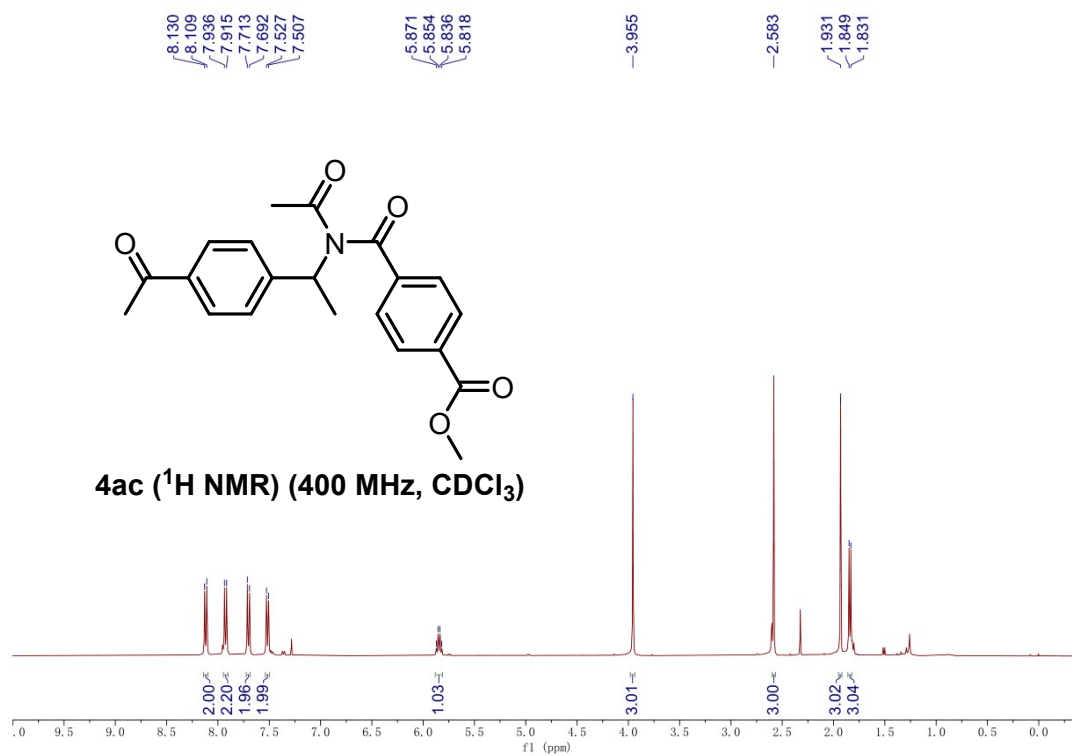


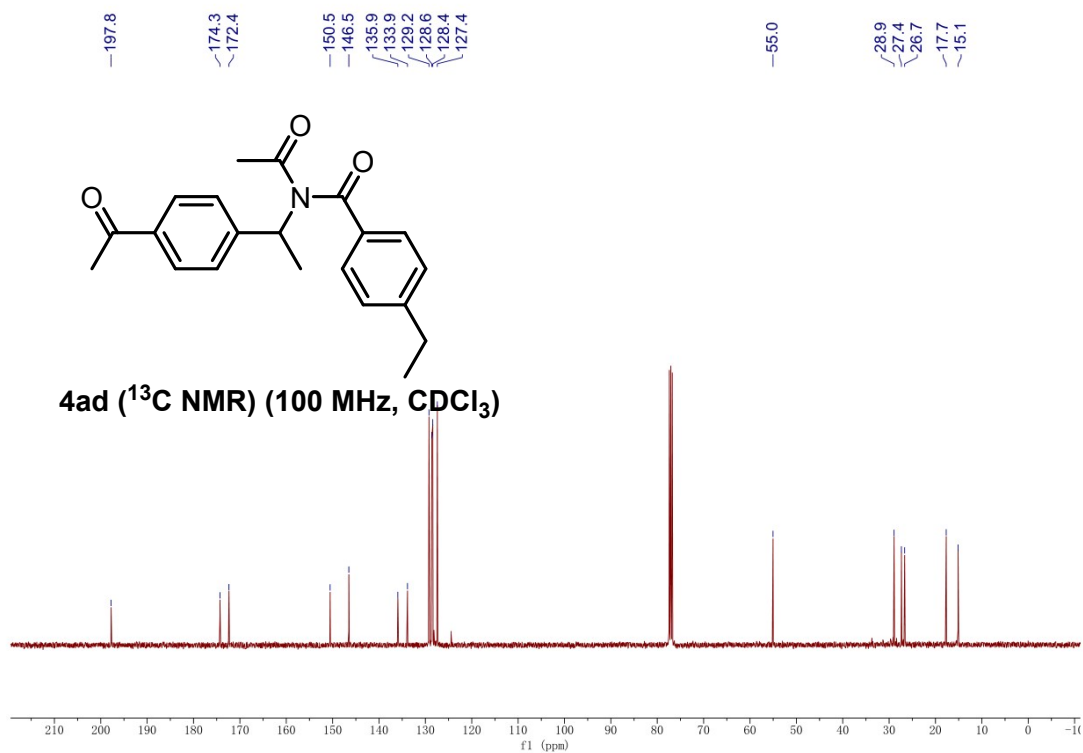
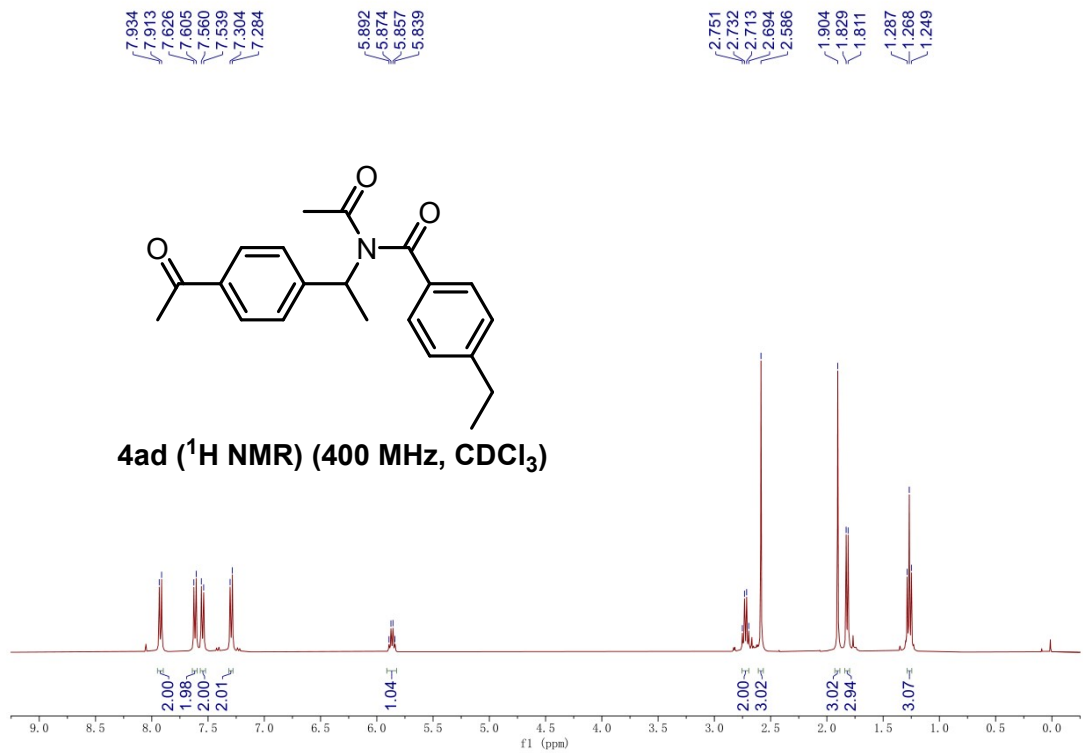
-63.2

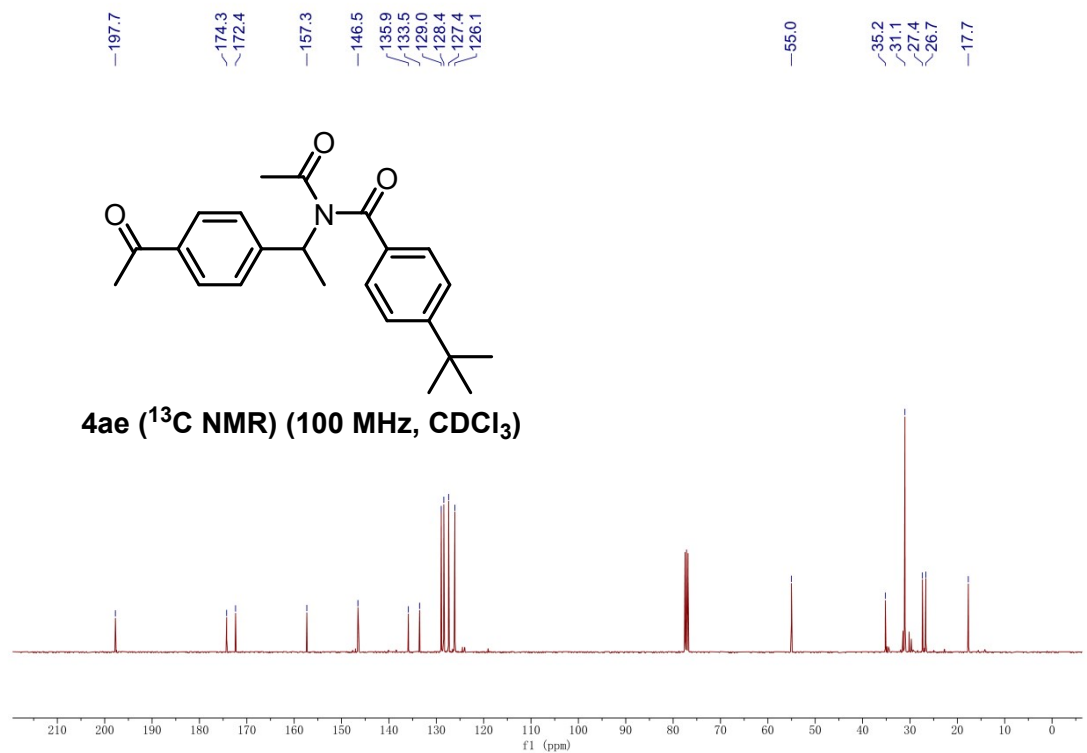
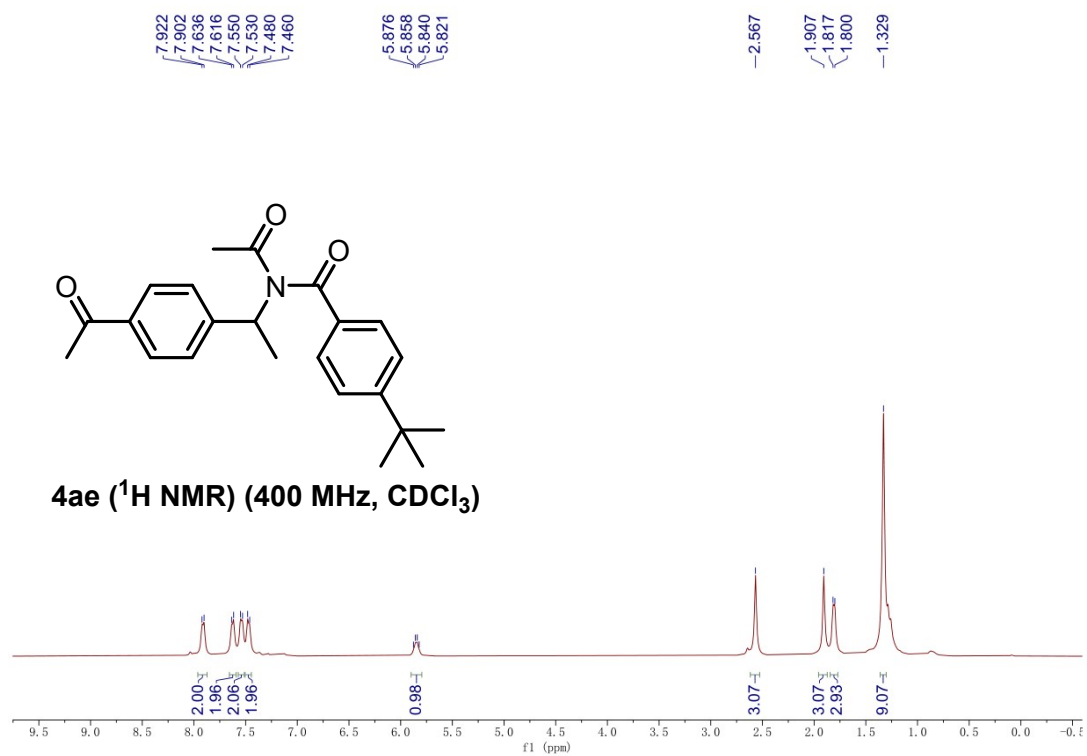


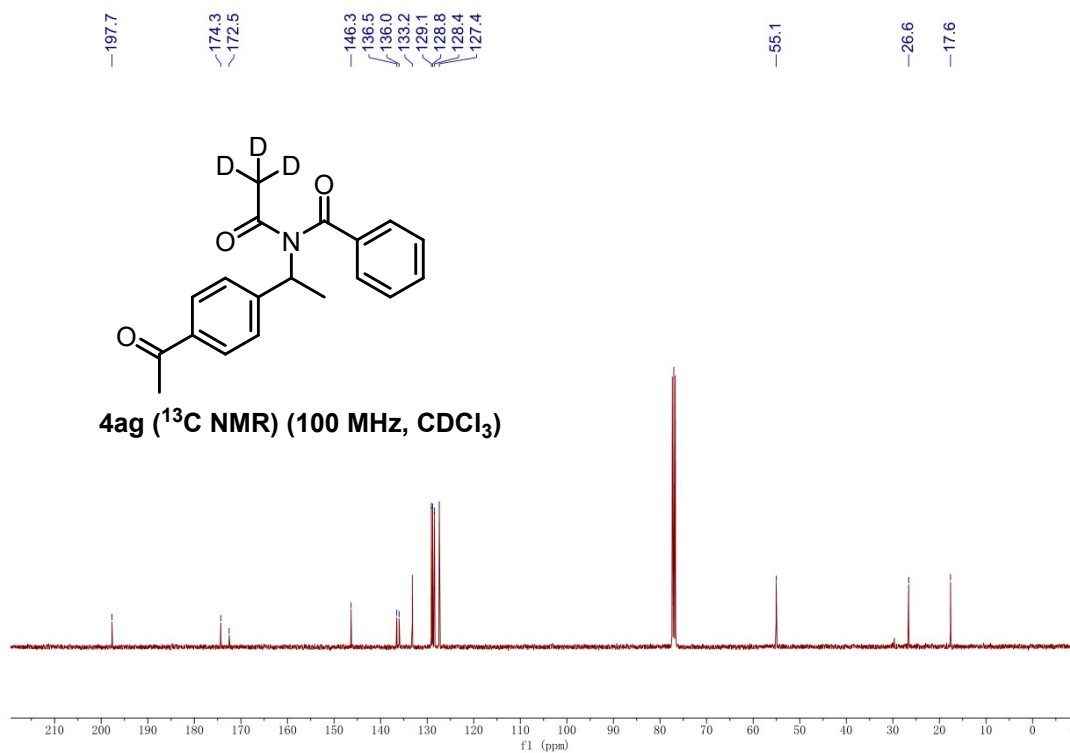
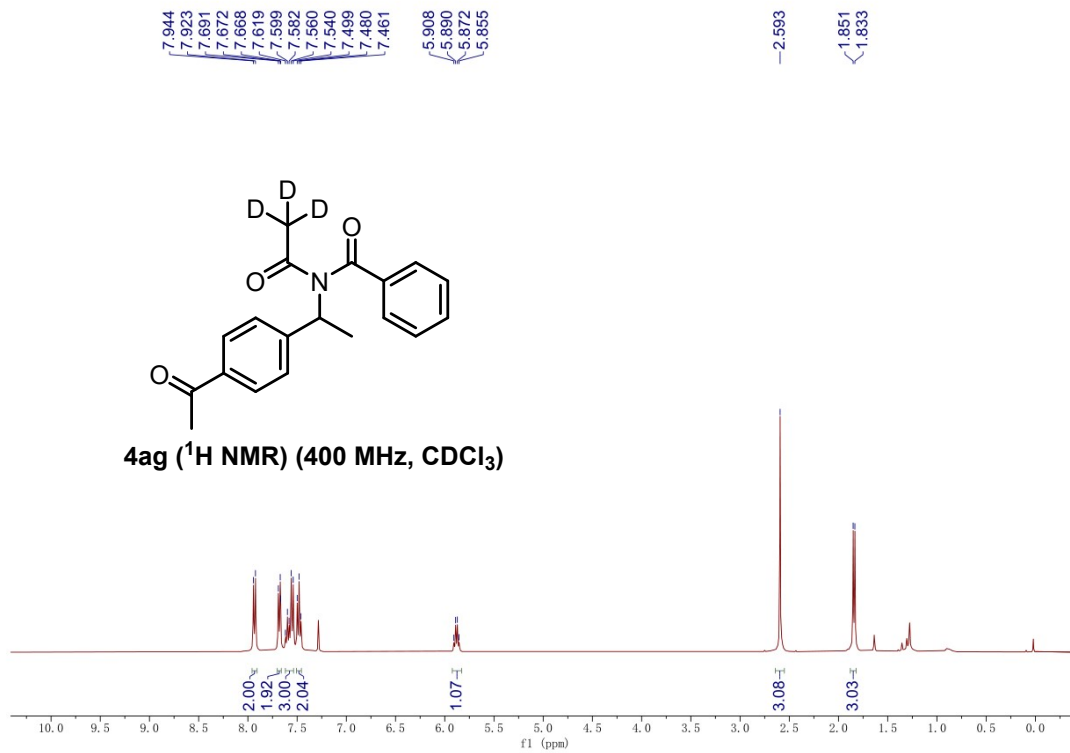
4ab (^{19}F NMR) (376 MHz, CDCl_3)

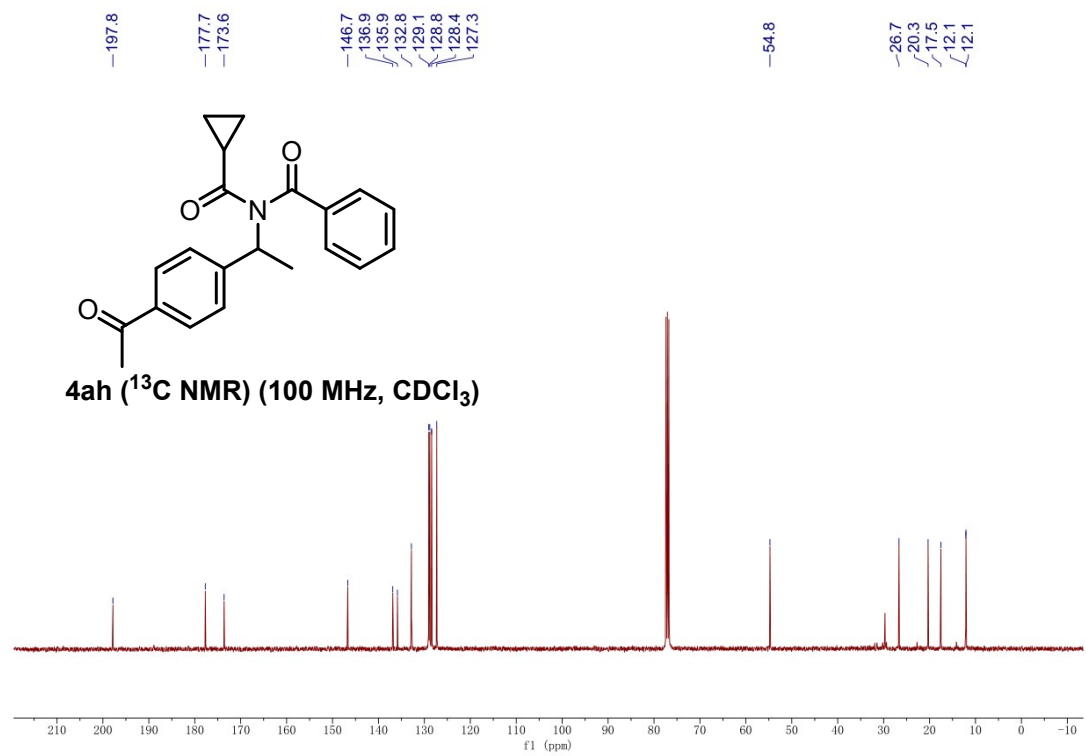
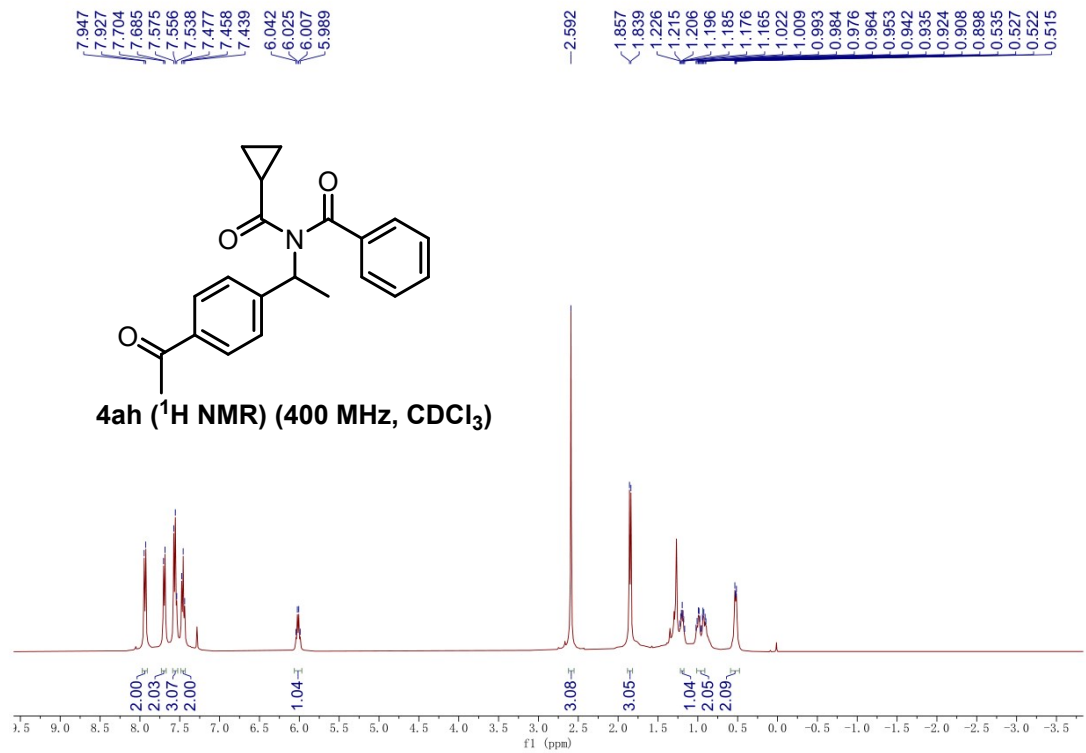


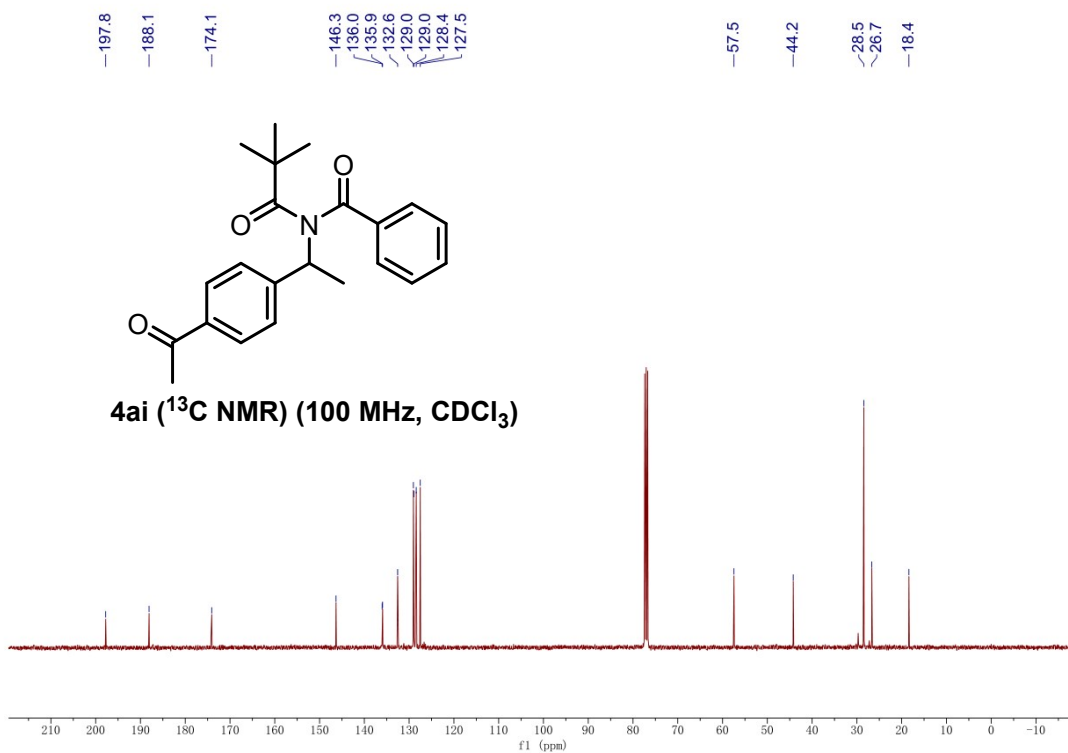
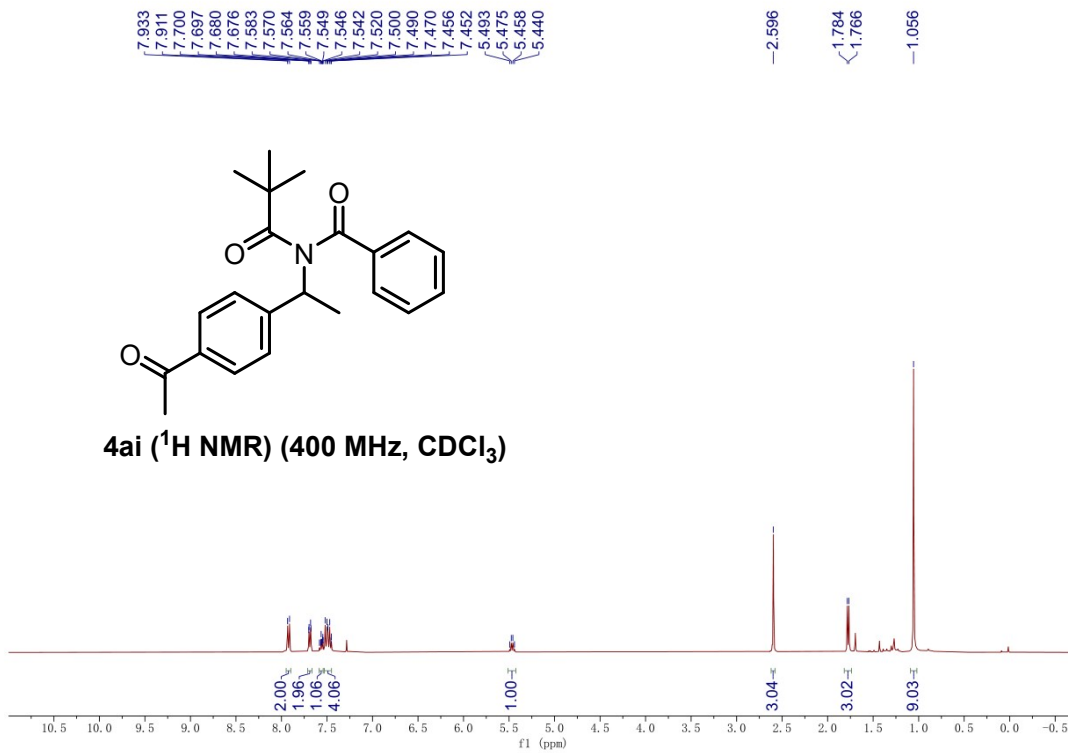


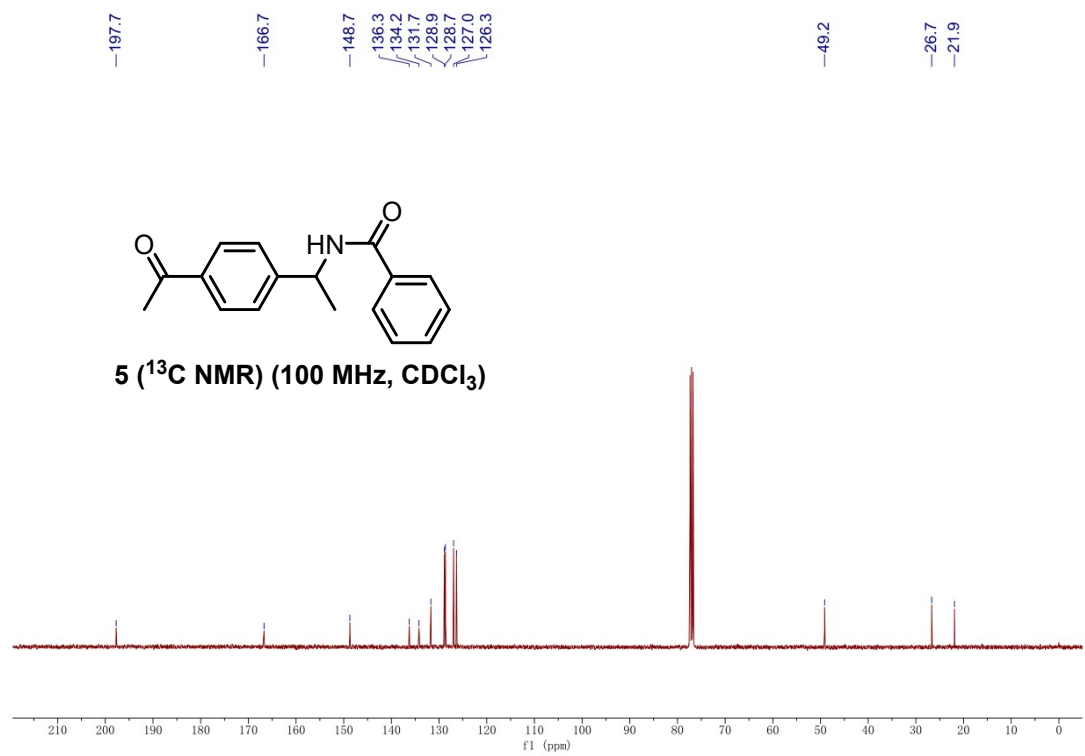
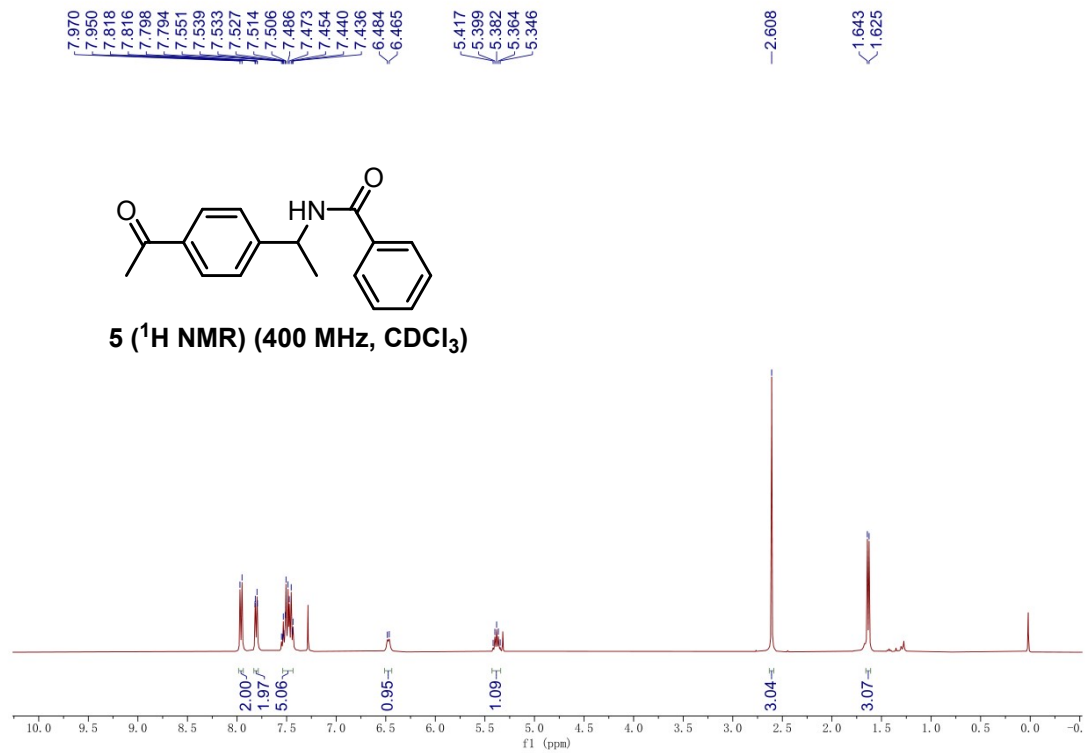








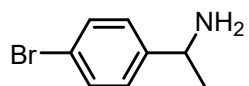




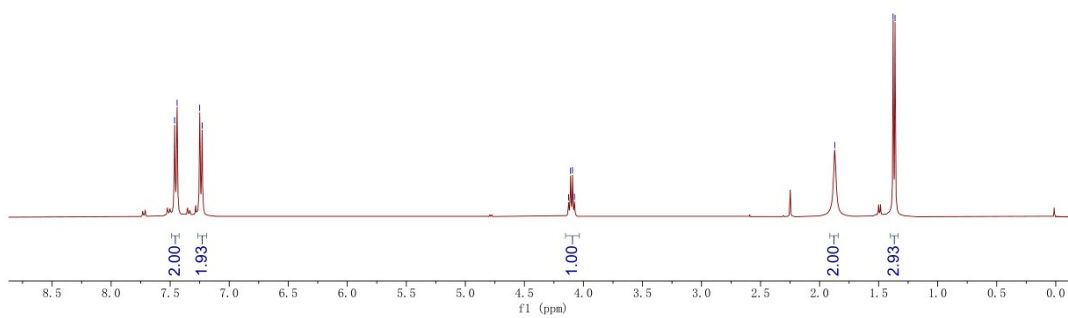
7.463
7.441
7.250
7.229

4.125
4.109
4.092
4.076

-1.872
-1.377
-1.361



6 (^1H NMR) (400 MHz, CDCl_3)



-146.4

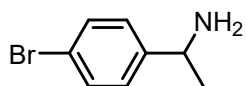
-131.5

-127.6

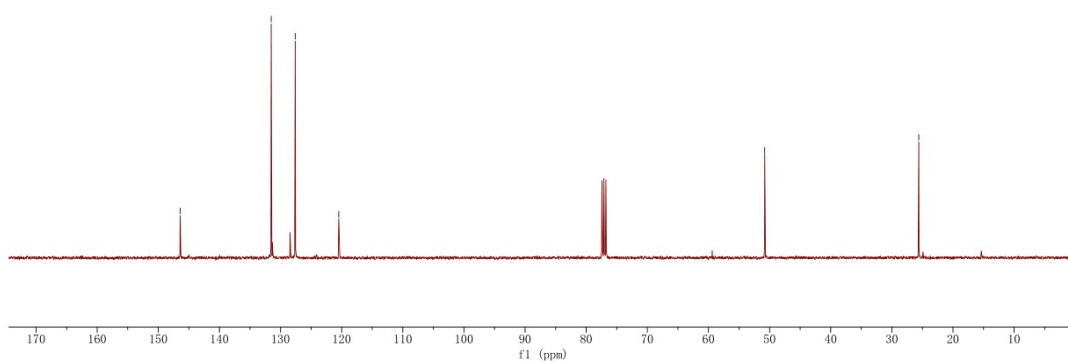
-120.5

-50.8

-25.6

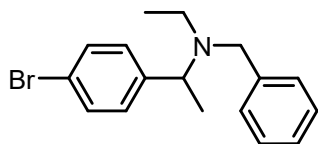


6 (^{13}C NMR) (100 MHz, CDCl_3)

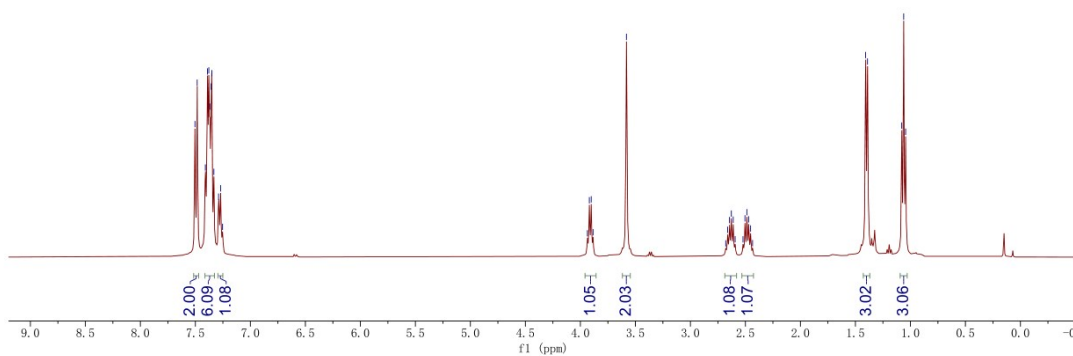


7.504
7.484
7.409
7.390
7.378
7.369
7.357
7.350
7.332
7.289
7.271
7.253

3.936
3.919
3.902
3.885
3.582
2.679
2.661
2.644
2.628
2.611
2.593
2.522
2.504
2.487
2.470
2.453
2.435
1.407
1.390
1.079
1.061
1.044

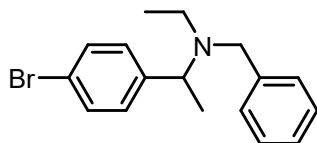


7 ($^1\text{H NMR}$) (400 MHz, CDCl_3)



143.8
140.8
131.1
129.5
128.5
128.2
126.7
120.3

57.4
53.8
42.9
15.6
12.2



7 ($^{13}\text{C NMR}$) (100 MHz, CDCl_3)

