Supporting Information

Direct Hydroacylation of Arylacrylonitriles toward β-Ketonitriles Assisted by EDA Complex

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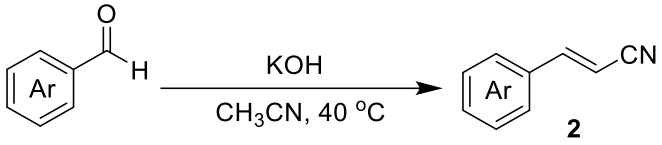
Contents

1. General considerations

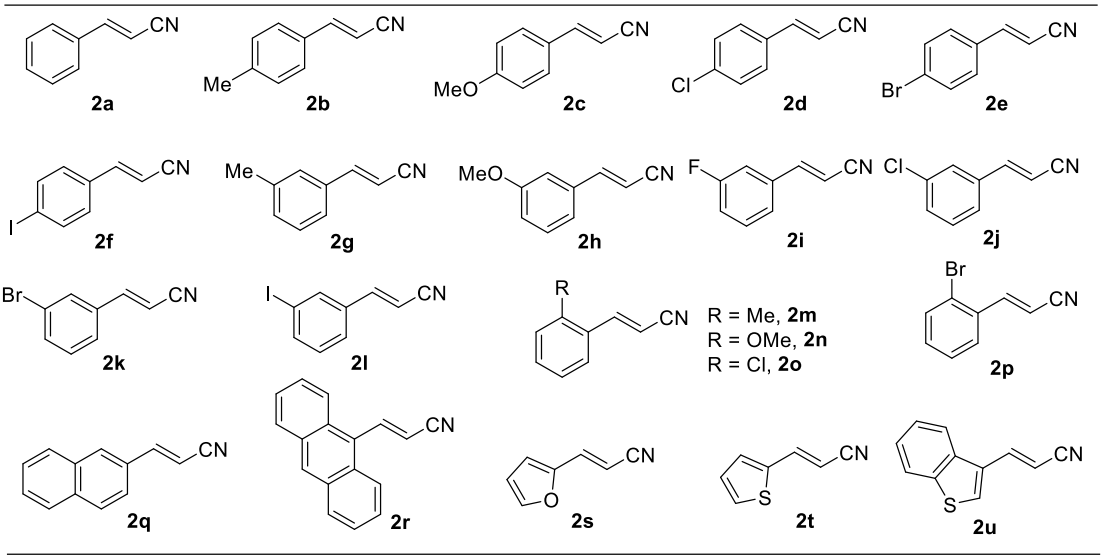
All manipulations were conducted in sealed tubes under nitrogen atmosphere. Reactions that require heating were carried out in the oil bath. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 or 500 MHz spectrometer, and the chemical shifts were reported in parts per million (δ) relative to the internal standard TMS (0 ppm) for ^{1}H, and referenced to the internal solvent signals for ^{13}C (77.16 ppm for $CDCl_3$). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). An APEX II (Bruker Inc.) spectrometer was used for ESI-MS and EI-MS. Flash column chromatography was performed over silica gel 200-300 mesh. All chemical reagents and deuterated solvents were purchased from Alfa, Acros, Aldrich, or J&K and used without further purification, unless otherwise stated.

2. Experiment procedures for hydroacylation of arylacrylonitriles

2.1. Preparation of arylacrylonitriles[1]

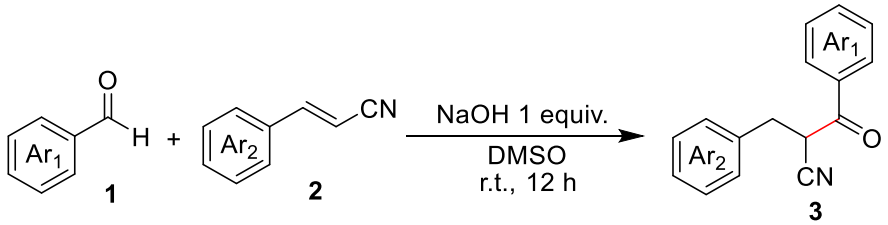


A 50 mL round-bottom flask was charged with aryl aldehyde (10 mmol), KOH (0.80 g, 20 mmol) and anhydrous CH_3CN (25 mL) under nitrogen atmosphere. Then, the reaction mixture was stirred at 40 °C and the reaction was monitored by TLC. After the reaction was completed, the mixture was filtered and washed by AcOEt. The combined organic volatiles were removed in vacuo and the crude product was purified by silica gel chromatography to give arylacrylonitriles **2**.



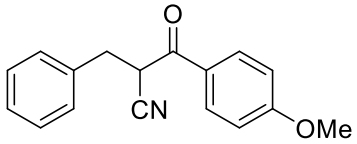
Scheme S1. The molecular structure of arylacrylonitriles

2.2. General procedure for hydroacylation of arylacrylonitriles

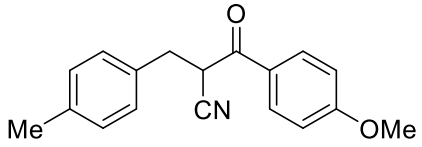


To an oven-dried glass tube equipped with a stir bar was added aryl aldehyde **1** (1.0 mmol), arylacrylonitrile **2** (0.5 mmol) and NaOH (20.0 mg, 0.5 mmol). The tube was sealed with a septum, evacuated and refilled with argon three times. Then, anhydrous DMSO (2 mL) was added to the reaction system and the mixture was stirred at room temperature for 12 h. The mixture was added H_2O (10 mL) and extracted with ethyl

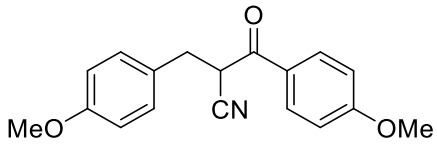
acetate (3 x 15 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel chromatography: PE/AcOEt → 6/1 – 20/1 to give the product **3**.



2-Benzyl-3-(4-methoxyphenyl)-3-oxopropanenitrile[2] (**3a**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 12:1) as yellow liquid (108.8 mg, 82% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 8.9 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 6.99 (d, J = 8.9 Hz, 2H), 4.52 (dd, J = 8.9, 5.8 Hz, 1H), 3.90 (s, 3H), 3.36 (dd, J = 14.0, 5.8 Hz, 1H), 3.25 (dd, J = 14.0, 9.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.4, 164.7, 136.2, 131.3, 129.1, 128.9, 127.6, 127.0, 117.4, 114.4, 55.7, 41.5, 35.7. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{15}NO_2Na$ 288.0995; found 288.1004.

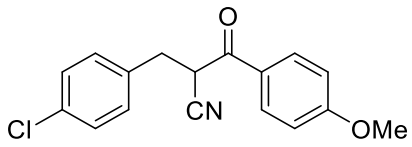


3-(4-Methoxyphenyl)-2-(4-methylbenzyl)-3-oxopropanenitrile (**3b**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2b** (71.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 12:1) as yellow liquid (68.4 mg, 49% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.9 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 4.45 (dd, J = 8.9, 5.8 Hz, 1H), 3.87 (s, 3H), 3.29 (dd, J = 14.0, 5.7 Hz, 1H), 3.18 (dd, J = 14.0, 8.9 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.5, 164.6, 137.3, 133.1, 131.3, 129.6, 128.9, 127.0, 117.4, 114.4, 55.7, 41.7, 35.3, 21.1. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{17}NO_2Na$ 302.1151; found 302.1162.

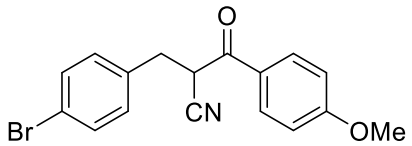


2-(4-Methoxybenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3c**). The

compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2c** (79.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as yellow solid (32.5 mg, 22% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 4.44 (dd, J = 8.7, 5.9 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.28 (dd, J = 14.0, 5.8 Hz, 1H), 3.18 (dd, J = 14.0, 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 164.6, 159.0, 131.3, 130.2, 128.1, 127.1, 117.4, 114.4, 114.3, 55.7, 55.3, 41.8, 35.0. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{17}NO_3Na$ 318.1101; found 318.1105.

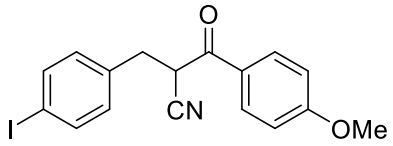


2-(4-Chlorobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3d**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2c** (81.8 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as yellow liquid (85.4 mg, 57% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 8.8 Hz, 2H), 7.27 (t, J = 7.9 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 4.46 (dd, J = 8.6, 6.0 Hz, 1H), 3.87 (s, 3H), 3.30 (dd, J = 14.1, 5.9 Hz, 1H), 3.19 (dd, J = 14.0, 8.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.0, 164.8, 134.6, 133.5, 131.3, 130.5, 129.0, 126.8, 117.2, 114.4, 55.7, 41.1, 34.8. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}ClNO_2Na$ 322.0605; found 322.0618.

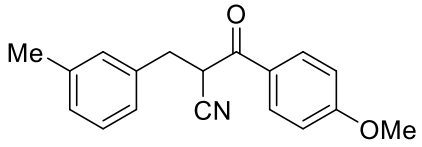


2-(4-Bromobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3e**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2e** (104.0 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 6:1) as yellow solid (117.0 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 4.45 (dd, J = 8.5, 6.0 Hz, 1H), 3.88 (s, 3H), 3.29 (dd, J = 14.0, 5.9 Hz, 1H), 3.18 (dd, J = 14.0, 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 164.8, 135.2,

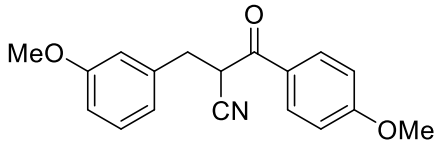
132.0, 131.3, 130.9, 126.8, 121.6, 117.2, 114.4, 55.7, 41.0, 34.8. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}BrNO_2Na$ 366.0100; found 366.0093.



2-(4-Iodobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3f**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2f** (127.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as yellow solid (95.8 mg, 49% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 4.43 (dd, J = 8.6, 6.0 Hz, 1H), 3.89 (s, 3H), 3.28 (dd, J = 14.1, 5.9 Hz, 1H), 3.17 (dd, J = 14.0, 8.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 164.8, 138.0, 135.8, 131.4, 131.1, 126.8, 117.1, 114.5, 93.2, 55.8, 41.0, 34.9. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}INO_2Na$ 413.9961; found 413.9968.

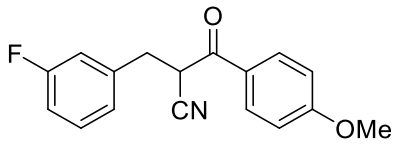


3-(4-Methoxyphenyl)-2-(3-methylbenzyl)-3-oxopropanenitrile (**3g**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2g** (71.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 10:1) as yellow liquid (78.2 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 8.1 Hz, 3H), 6.96 (d, J = 8.8 Hz, 2H), 4.50 (dd, J = 9.0, 5.7 Hz, 1H), 3.86 (s, 3H), 3.28 (dd, J = 13.9, 5.6 Hz, 1H), 3.17 (dd, J = 13.9, 9.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 164.7, 138.6, 136.1, 131.3, 129.8, 128.8, 128.4, 127.0, 126.1, 117.5, 114.4, 55.7, 41.5, 35.6, 21.4. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{17}NO_2Na$ 302.1151; found 302.1155.

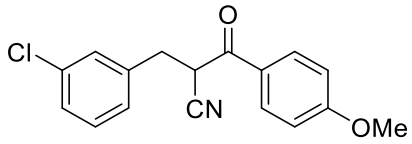


2-(3-Methoxybenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3h**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b**

(121.5 μL, 1.0 mmol), **2h** (79.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as yellow liquid (112.2 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.9 Hz, 2H), 7.24 (t, J = 7.8 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 7.5 Hz, 1H), 6.85 – 6.79 (m, 2H), 4.52 (dd, J = 8.9, 5.8 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.31 (dd, J = 14.0, 5.8 Hz, 1H), 3.20 (dd, J = 14.0, 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 164.7, 159.9, 137.7, 131.3, 129.9, 127.0, 121.3, 117.5, 114.8, 114.4, 113.0, 55.7, 55.2, 41.3, 35.7. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{17}NO_3Na$ 318.1101; found 318.1105.

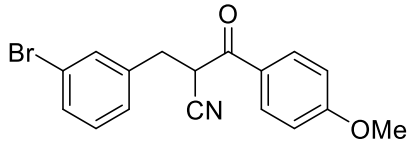


2-(3-Fluorobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3i**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2i** (73.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as yellow liquid (83.6 mg, 59% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.98 (t, J = 11.7 Hz, 4H), 4.48 (dd, J = 8.5, 6.1 Hz, 1H), 3.88 (s, 3H), 3.33 (dd, J = 14.0, 5.8 Hz, 1H), 3.22 (dd, J = 14.0, 8.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 164.8, 162.9 (d, J = 246.8 Hz), 138.6 (d, J = 7.4 Hz), 131.3, 130.5 (d, J = 8.3 Hz), 126.8, 124.8 (d, J = 2.8 Hz), 117.1, 116.1 (d, J = 21.5 Hz), 114.6 (d, J = 20.9 Hz), 114.4, 55.7, 40.9, 35.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.34 (s) ppm. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}FNO_2Na$ 306.0901; found 306.0901.

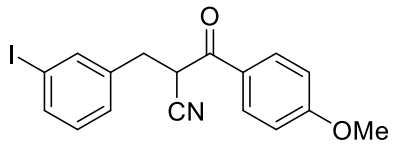


2-(3-Chlorobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3j**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2j** (81.8 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as yellow liquid (136.4 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 8.9 Hz, 2H), 7.21 – 7.10 (m, 3H), 7.10 – 7.04 (m, 1H), 6.86 (d, J = 8.9 Hz, 2H), 4.40 (dd, J = 8.8, 5.9 Hz, 1H), 3.77 (s, 3H), 3.20 (dd, J = 14.1, 5.8 Hz, 1H),

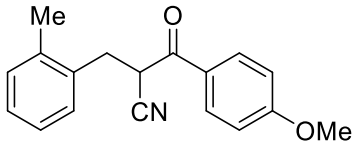
3.08 (dd, J = 14.0, 8.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 164.8, 138.2, 134.6, 131.4, 130.2, 129.2, 127.8, 127.4, 126.8, 117.2, 114.4, 55.7, 40.9, 34.9. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}ClNO_2Na$ 322.0605; found 322.0605.



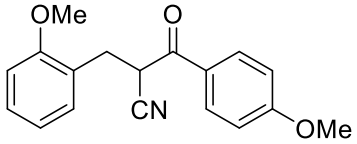
2-(3-Bromobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile[3] (**3k**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2k** (104.0 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 10:1) as yellow liquid (111.9 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.9 Hz, 2H), 7.41 (s, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 8.9 Hz, 2H), 4.47 (dd, J = 8.9, 5.9 Hz, 1H), 3.86 (s, 3H), 3.28 (dd, J = 14.1, 5.9 Hz, 1H), 3.16 (dd, J = 14.1, 8.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.9, 164.8, 138.5, 132.1, 131.4, 130.8, 130.5, 127.9, 126.8, 122.8 117.1, 114.4, 55.7, 41.0, 34.9. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+ Na]^+$ Calcd. for $C_{17}H_{14}BrNO_2Na$ 366.0100; found 366.0100.



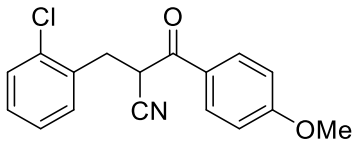
2-(3-Iodobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3l**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2l** (127.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as yellow liquid (80.2 mg, 41% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.9 Hz, 2H), 7.62 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 7.7 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 4.45 (dd, J = 8.9, 5.9 Hz, 1H), 3.88 (s, 3H), 3.27 (dd, J = 14.0, 5.9 Hz, 1H), 3.15 (dd, J = 14.0, 8.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 164.8, 138.6, 137.9, 136.7, 131.4, 130.6, 128.5, 126.8, 117.1, 114.4, 94.7, 55.7, 40.9, 34.8. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}INO_2Na$ 413.9961; found 413.9974.



3-(4-Methoxyphenyl)-2-(2-methylbenzyl)-3-oxopropanenitrile (**3m**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2m** (71.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as yellow liquid (72.6 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.24 (dd, J = 9.0, 4.3 Hz, 1H), 7.20 – 7.12 (m, 3H), 6.95 (d, J = 8.8 Hz, 2H), 4.46 (dd, J = 9.2, 6.0 Hz, 1H), 3.87 (s, 3H), 3.34 (dd, J = 14.3, 6.0 Hz, 1H), 3.25 (dd, J = 14.3, 9.2 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 164.7, 136.2, 134.4, 131.3, 130.8, 129.7, 127.7, 127.0, 126.5, 117.4, 114.4, 55.7, 40.0, 32.8, 19.5. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{17}NO_2Na$ 302.1151; found 302.1161.

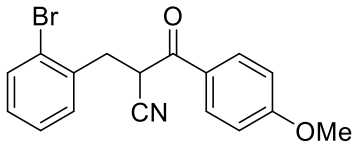


2-(2-Methoxybenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3n**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2n** (79.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as white solid (38.4 mg, 26% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 7.4 Hz, 2H), 6.96 – 6.81 (m, 4H), 4.72 (dd, J = 9.7, 5.4 Hz, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.40 (dd, J = 13.4, 5.3 Hz, 1H), 3.04 (dd, J = 13.4, 9.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 164.5, 157.3, 131.5, 131.3, 129.2, 127.1, 124.2, 121.0, 117.6, 114.2, 110.4, 55.7, 55.3, 39.9, 32.2. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{17}NO_3Na$ 318.1101; found 318.1107.

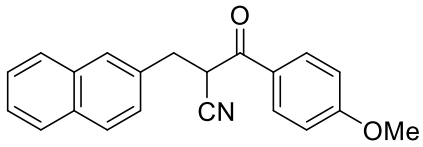


2-(2-Chlorobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3o**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2o** (81.8 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous

DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as yellow liquid (54.0 mg, 36% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.19 – 7.12 (m, 2H), 6.88 (d, J = 8.2 Hz, 2H), 4.64 (dd, J = 9.5, 6.0 Hz, 1H), 3.80 (s, 3H), 3.44 (dd, J = 13.8, 5.7 Hz, 1H), 3.15 (dd, J = 13.5, 10.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.3, 164.8, 133.8, 133.7, 132.2, 131.4, 129.8, 129.3, 127.4, 126.9, 117.0, 114.4, 55.7, 38.9, 33.9. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}ClNO_2Na$ 322.0605; found 322.0612.

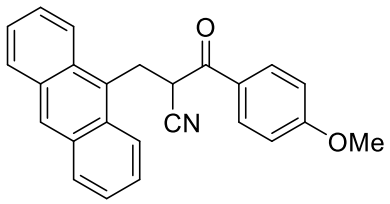


2-(2-Bromobenzyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3p**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2p** (104.0 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as yellow solid (108.4 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.9 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 7.1 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.9 Hz, 2H), 4.75 (dd, J = 9.7, 5.9 Hz, 1H), 3.85 (s, 3H), 3.49 (dd, J = 13.8, 5.9 Hz, 1H), 3.23 (dd, J = 13.8, 9.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.3, 164.8, 135.4, 133.1, 132.3, 131.4, 129.6, 128.1, 127.0, 124.3, 117.0, 114.4, 55.7, 39.0, 36.2. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}BrNO_2Na$ 366.0100; found 366.0101.

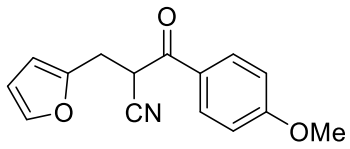


3-(4-Methoxyphenyl)-2-(naphthalen-2-ylmethyl)-3-oxopropanenitrile (**3q**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2q** (139.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 12:1) as yellow solid (113.5 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.9 Hz, 2H), 7.78 (dd, J = 8.5, 4.8 Hz, 3H), 7.71 (s, 1H), 7.51 – 7.41 (m, 2H), 7.37 (dd, J = 8.4, 1.6 Hz, 1H), 6.91 (d, J = 8.9 Hz, 2H), 4.57 (dd, J = 7.9, 4.8 Hz, 1H), 3.81 (s, 3H), 3.46 (dd, J = 14.0, 5.8 Hz, 1H), 3.35 (dd, J = 14.0, 8.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 164.7, 133.7, 133.5, 132.7, 131.4, 128.7, 128.0, 127.8, 127.7, 126.9, 126.4, 126.1, 117.5, 114.4, 114.0, 55.7, 41.4, 35.8. HRMS

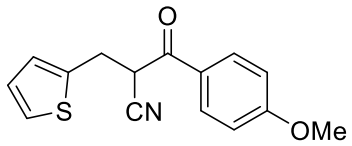
(ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{17}NO_2Na$ 338.1151; found 338.1151.



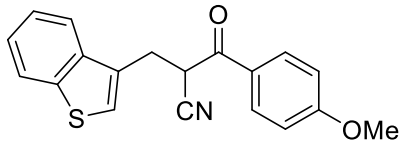
2-(Anthracen-9-ylmethyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3r**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2r** (114.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 7:1) as yellow liquid (84.0 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.22 (d, J = 8.7 Hz, 2H), 7.99 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.50 – 7.42 (m, 2H), 6.76 (d, J = 8.7 Hz, 2H), 4.76 (dd, J = 8.3, 6.5 Hz, 1H), 4.40 (dd, J = 14.8, 8.8 Hz, 1H), 4.28 (dd, J = 14.9, 6.2 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 164.6, 131.5, 131.2, 130.1, 129.5, 127.9, 127.8, 127.1, 126.7, 126.6, 125.2, 123.6, 114.1, 55.6, 39.7, 27.2. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{19}NO_2Na$ 388.1308; found 388.1321.



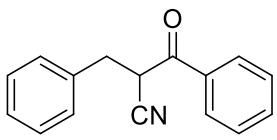
2-(Furan-2-ylmethyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3s**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2s** (59.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as brown liquid (66.4 mg, 52% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 9.0 Hz, 2H), 7.36 (dd, J = 1.8, 0.7 Hz, 1H), 6.99 (d, J = 9.0 Hz, 2H), 6.31 (dd, J = 3.1, 1.9 Hz, 1H), 6.25 (d, J = 3.2 Hz, 1H), 4.66 (dd, J = 8.6, 6.1 Hz, 1H), 3.90 (s, 3H), 3.39 (dd, J = 15.3, 6.1 Hz, 1H), 3.32 (dd, J = 15.2, 8.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.8, 164.8, 149.6, 142.4, 131.4, 126.8, 117.1, 114.4, 110.7, 108.4, 55.7, 38.4, 28.3. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{13}NO_3Na$ 278.0788; found 278.0796.



3-(4-Methoxyphenyl)-3-oxo-2-(thiophen-2-ylmethyl)propanenitrile (**3t**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2t** (67.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 7:1) as yellow liquid (109.9 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 8.9 Hz, 2H), 7.18 (dd, J = 5.1, 0.8 Hz, 1H), 6.99 – 6.94 (m, 3H), 6.93 (dd, J = 5.0, 3.5 Hz, 1H), 4.53 (dd, J = 8.1, 6.2 Hz, 1H), 3.86 (s, 3H), 3.55 (dd, J = 15.1, 6.1 Hz, 1H), 3.46 (dd, J = 15.0, 8.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 164.8, 137.9, 131.4, 127.4, 127.2, 126.9, 125.2, 117.2, 114.4, 55.8, 41.4, 29.7. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{13}NO_2SNa$ 294.0559; found 294.0572.

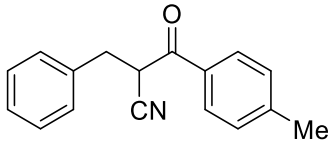


2-(Benzo[*b*]thiophen-3-ylmethyl)-3-(4-methoxyphenyl)-3-oxopropanenitrile (**3u**). The compound was prepared according to the general procedure using *p*-anisaldehyde **1b** (121.5 μL, 1.0 mmol), **2u** (92.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as red solid (65.9 mg, 41% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.44 – 7.34 (m, 3H), 6.93 (d, J = 8.7 Hz, 2H), 4.60 (dd, J = 8.3, 6.2 Hz, 1H), 3.86 (s, 3H), 3.62 (dd, J = 14.8, 6.1 Hz, 1H), 3.49 (dd, J = 14.8, 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.1, 164.8, 140.5, 137.9, 131.3, 130.4, 127.0, 125.1, 124.7, 124.4, 123.2, 121.0, 117.4, 114.4, 55.7, 39.1, 28.3. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{15}NO_2SNa$ 344.0716, found 344.0718.

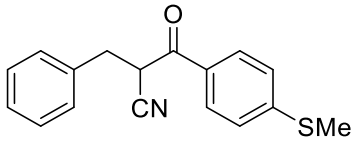


2-Benzyl-3-oxo-3-phenylpropanenitrile[4] (**3v**). The compound was prepared according to the general procedure using benzaldehyde **1a** (101.6 μL, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 15:1)

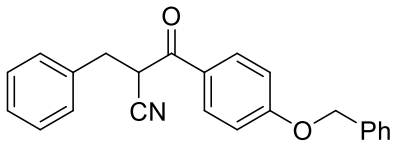
as faint yellow liquid (91.8 mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 3H), 4.55 (dd, J = 8.9, 5.8 Hz, 1H), 3.36 (dd, J = 14.0, 5.7 Hz, 1H), 3.25 (dd, J = 14.0, 8.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.1, 135.9, 134.6, 134.1, 129.2, 129.1, 129.0, 128.9, 127.7, 117.1, 41.9, 35.5. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{14}NO$ 236.1070; found 236.1079.



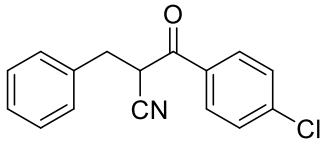
2-Benzyl-3-oxo-3-(*p*-tolyl)propanenitrile[2] (**3w**). The compound was prepared according to the general procedure using *p*-tolualdehyde **1c** (118.0 μL, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 20:1) as yellow liquid (51.1 mg, 41% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.41 – 7.27 (m, 7H), 4.54 (dd, J = 8.9, 5.7 Hz, 1H), 3.37 (dd, J = 14.0, 5.5 Hz, 1H), 3.26 (dd, J = 13.8, 9.1 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.6, 145.9, 136.1, 131.6, 129.9, 129.1, 129.0, 128.9, 127.7, 117.2, 41.7, 35.6, 21.8. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{15}NONa$ 272.1046; found 272.1057.



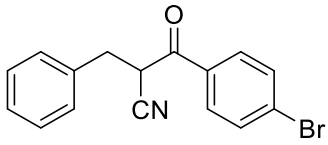
2-Benzyl-3-(4-(methylthio)phenyl)-3-oxopropanenitrile (**3x**). The compound was prepared according to the general procedure using 4-(methylthio)benzaldehyde **1d** (133.0 μL, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as yellow liquid (102.7 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 2H), 7.44 – 7.31 (m, 7H), 4.55 (dd, J = 8.8, 5.8 Hz, 1H), 3.39 (dd, J = 14.0, 5.8 Hz, 1H), 3.28 (dd, J = 13.9, 8.9 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 148.5, 136.1, 130.1, 129.2, 129.1, 128.9, 127.7, 125.1, 117.2, 41.6, 35.6, 14.6. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{15}NOSNa$ 304.0767; found 304.0774.



2-Benzyl-3-oxo-3-(4-phenoxyphenyl)propanenitrile (**3y**). The compound was prepared according to the general procedure using 4-(benzyloxy)benzaldehyde **1e** (106.1 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as yellow liquid (157.0 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 9.0 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.44 – 7.29 (m, 6H), 7.07 (d, J = 9.0 Hz, 2H), 5.18 (s, 2H), 4.52 (dd, J = 8.9, 5.8 Hz, 1H), 3.37 (dd, J = 14.0, 5.8 Hz, 1H), 3.26 (dd, J = 14.0, 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 163.8, 136.2, 135.8, 131.4, 129.1, 128.9, 128.8, 128.5, 127.6, 127.6, 127.2, 117.4, 115.2, 70.4, 41.5, 35.7. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{19}NO_2Na$ 364.1308; found 364.1322.

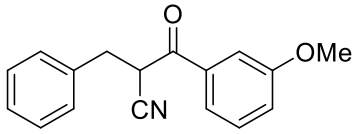


2-Benzyl-3-(4-chlorophenyl)-3-oxopropanenitrile (**3z**). The compound was prepared according to the general procedure using 4-chlorobenzaldehyde **1f** (140.6 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as faint yellow solid (48.6 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.37 – 7.24 (m, 5H), 4.46 (dd, J = 8.7, 6.0 Hz, 1H), 3.35 (dd, J = 14.0, 5.9 Hz, 1H), 3.24 (dd, J = 14.0, 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 141.3, 135.8, 132.4, 130.2, 129.5, 129.1, 129.0, 127.8, 116.8, 41.8, 35.4. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{13}ClNO$ 270.0680; found 270.0682.

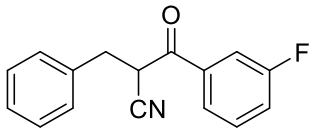


2-Benzyl-3-(4-bromophenyl)-3-oxopropanenitrile (**3aa**). The compound was prepared according to the general procedure using 4-bromobenzaldehyde **1g** (185.0 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel

(PE/AcOEt 8:1) as faint yellow solid (62.8 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.41 – 7.19 (m, 5H), 4.45 (dd, J = 8.6, 6.0 Hz, 1H), 3.35 (dd, J = 14.0, 5.9 Hz, 1H), 3.24 (dd, J = 14.0, 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 135.7, 132.8, 132.5, 130.2, 130.1, 129.1, 129.0, 127.8, 116.7, 41.8, 35.4. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{13}BrNO$ 314.0175; found 314.0179.

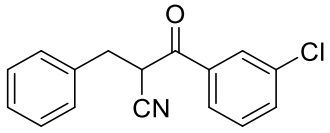


2-Benzyl-3-(3-methoxyphenyl)-3-oxopropanenitrile (**3ab**). The compound was prepared according to the general procedure using 3-methoxybenzaldehyde **1h** (136.2 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as yellow liquid (67.7 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 3H), 7.21 (dd, J = 8.0, 2.3 Hz, 1H), 4.56 (dd, J = 8.9, 5.8 Hz, 1H), 3.87 (s, 3H), 3.37 (dd, J = 14.0, 5.7 Hz, 1H), 3.25 (dd, J = 14.0, 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 160.2, 136.0, 135.4, 130.1, 129.1, 129.0, 127.70, 121.3, 121.2, 117.1, 113.1, 55.6, 42.0, 35.7. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{15}NO_2Na$ 288.0995; found 288.1007.

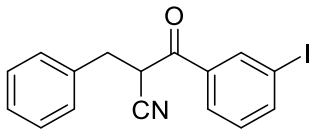


2-Benzyl-3-(3-fluorophenyl)-3-oxopropanenitrile (**3ac**). The compound was prepared according to the general procedure using 3-fluorobenzaldehyde **1i** (124.1 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as white solid (49.4 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 9.3 Hz, 1H), 7.42 – 7.24 (m, 6H), 7.20 (t, J = 8.0 Hz, 1H), 4.80 (t, J = 7.2 Hz, 1H), 3.08 (dd, J = 16.8, 6.7 Hz, 1H), 2.87 (dd, J = 16.8, 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 162.8 (d, J = 248.7 Hz), 137.1 (d, J = 6.4 Hz), 136.0, 130.4 (d, J = 7.6 Hz), 129.8, 128.7, 127.9, 124.8 (d, J = 2.9 Hz), 120.7 (d, J = 21.3 Hz), 118.1, 115.7 (d, J = 22.6 Hz), 50.7, 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.15 (s) ppm. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{13}FNO$

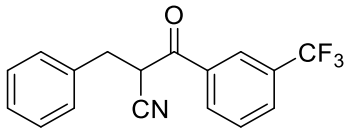
254.0976; found 254.0975.



2-Benzyl-3-(3-chlorophenyl)-3-oxopropanenitrile (**3ad**). The compound was prepared according to the general procedure using 3-chlorobenzaldehyde **1j** (140.6 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as white solid (56.6 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.39 – 7.24 (m, 5H), 4.47 (dd, J = 8.5, 6.1 Hz, 1H), 3.35 (dd, J = 14.0, 5.9 Hz, 1H), 3.25 (dd, J = 13.9, 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 135.6, 135.6, 135.6, 134.5, 130.4, 129.0, 129.0, 128.9, 127.8, 126.8, 116.6, 41.9, 35.4. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{13}ClNO$ 270.0680; found 270.0683.

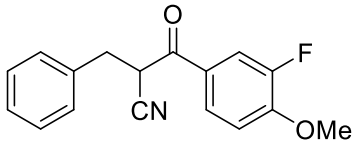


2-Benzyl-3-(3-iodophenyl)-3-oxopropanenitrile (**3ae**). The compound was prepared according to the general procedure using 3-iodobenzaldehyde **1k** (232.0 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as yellow solid (54.2 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.41 – 7.27 (m, 6H), 4.48 (dd, J = 8.5, 6.0 Hz, 1H), 3.38 (dd, J = 14.0, 6.0 Hz, 1H), 3.28 (dd, J = 14.0, 8.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 143.3, 137.7, 135.8, 135.7, 130.7, 129.1, 129.0, 127.8, 127.8, 116.6, 94.8, 41.8, 35.5. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{13}INO$ 362.0036; found 362.0037.

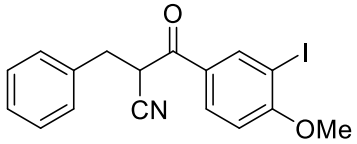


2-Benzyl-3-oxo-3-(3-(trifluoromethyl)phenyl)propanenitrile (**3af**). The compound was prepared according to the general procedure using 3-(trifluoromethyl)benzalde-hyde **1l** (174.1 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on

silica gel (PE/AcOEt 8:1) as white solid (81.9 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.43 – 7.24 (m, 5H), 4.86 (t, J = 7.1 Hz, 1H), 3.11 (dd, J = 16.8, 6.7 Hz, 1H), 2.90 (dd, J = 16.8, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 135.7, 135.5, 132.1, 131.4 (q, J = 32.9 Hz), 130.0 (q, J = 3.6 Hz), 129.9, 129.4, 128.8, 127.9, 125.9 (q, J = 3.8 Hz), 123.5 (q, J = 273.0 Hz), 118.0, 50.7, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.01 (s) ppm. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{13}F_3NO$ 304.0944; found 304.0946.

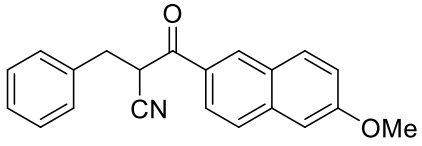


2-Benzyl-3-(3-fluoro-4-methoxyphenyl)-3-oxopropanenitrile (**3ag**). The compound was prepared according to the general procedure using 3-fluoro-4-methoxybenzaldehyde **1m** (154.1 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 7:1) as white solid (79.3 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.6 Hz, 1H), 7.68 (dd, J = 11.6, 2.1 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.30 – 7.22 (m, 3H), 7.01 (t, J = 8.3 Hz, 1H), 4.44 (dd, J = 8.7, 6.0 Hz, 1H), 3.96 (s, 3H), 3.33 (dd, J = 14.0, 5.9 Hz, 1H), 3.23 (dd, J = 14.0, 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 153.3 (d, J = 16.3 Hz), 152.0 (d, J = 222.8 Hz), 135.9, 129.1, 129.0, 127.7, 127.1 (d, J = 5.4 Hz), 126.5 (d, J = 3.3 Hz), 117.1, 116.4 (d, J = 19.3 Hz), 112.7, 56.5, 41.4, 35.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.61 (s) ppm. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{15}FNO_2$ 284.1081; found 284.1082.

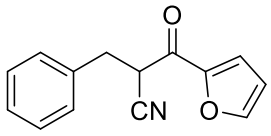


2-Benzyl-3-(3-iodo-4-methoxyphenyl)-3-oxopropanenitrile (**3ah**). The compound was prepared according to the general procedure using 3-iodo-4-methoxybenzaldehyde **1n** (262.0 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 7:1) as white solid (90.0 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 2.2 Hz, 1H), 7.92 (dd, J = 8.7, 2.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.30 – 7.23 (m, 3H), 6.85 (d, J = 8.7 Hz, 1H), 4.44 (dd, J = 8.6, 6.0 Hz, 1H), 3.95 (s,

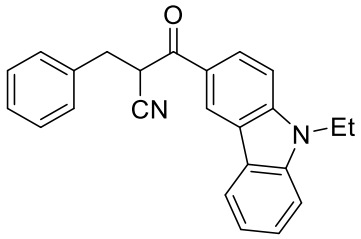
3H), 3.32 (dd, J = 14.0, 6.0 Hz, 1H), 3.22 (dd, J = 14.0, 8.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 162.9, 140.6, 135.9, 131.2, 129.1, 129.0, 128.6, 127.7, 117.1, 110.4, 86.6, 56.9, 41.4, 35.6. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{15}INO_2$ 392.0142; found 392.0142.



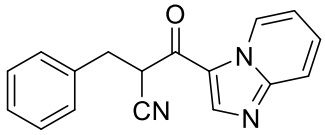
2-Benzyl-3-(6-methoxynaphthalen-2-yl)-3-oxopropanenitrile (**3ai**). The compound was prepared according to the general procedure using 6-methoxynaphthalene-2-carbaldehyde **1o** (186.2 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 9:1) as white solid (140.4 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.95 (dd, J = 8.7, 1.6 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.32 – 7.25 (m, 1H), 7.22 (dd, J = 9.0, 2.4 Hz, 1H), 7.14 (d, J = 2.2 Hz, 1H), 4.73 (dd, J = 8.8, 5.8 Hz, 1H), 3.94 (s, 3H), 3.41 (dd, J = 14.0, 5.8 Hz, 1H), 3.30 (dd, J = 14.0, 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 160.5, 138.0, 136.2, 131.5, 131.0, 129.3, 129.2, 128.9, 127.8, 127.7, 127.6, 124.6, 120.3, 117.6, 105.9, 55.6, 41.7, 35.8. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{17}NO_2Na$ 338.1151; found 338.1164.



2-Benzyl-3-(furan-2-yl)-3-oxopropanenitrile[5] (**3aj**). The compound was prepared according to the general procedure using furfural **1p** (82.8 μL, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 8:1) as red solid (65.3 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 1.0 Hz, 1H), 7.40 (d, J = 3.7 Hz, 1H), 7.38 – 7.25 (m, 5H), 6.63 (dd, J = 3.7, 1.6 Hz, 1H), 4.44 (dd, J = 8.8, 6.0 Hz, 1H), 3.36 (dd, J = 13.8, 6.0 Hz, 1H), 3.25 (dd, J = 13.8, 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 150.3, 148.0, 135.7, 129.1, 128.9, 127.7, 120.1, 116.6, 113.4, 42.1, 35.5. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{11}NO_2Na$ 248.0682; found 248.0693.

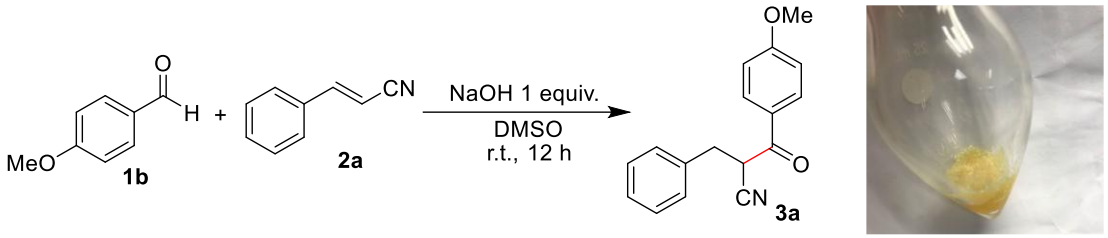


2-Benzyl-3-(9-ethyl-*9H*-carbazol-3-yl)-3-oxopropanenitrile (**3ak**). The compound was prepared according to the general procedure using 9-ethyl-*9H*-carbazole-3-carbaldehyde **1q** (223.3 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 7:1) as yellow liquid (125.1 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.10 (dd, J = 16.4, 8.2 Hz, 2H), 7.67 – 7.47 (m, 1H), 7.47 – 7.23 (m, 8H), 4.78 (dd, J = 8.6, 5.7 Hz, 1H), 4.29 (q, J = 8.6 Hz, 2H), 3.47 (dd, J = 13.9, 5.5 Hz, 1H), 3.36 (dd, J = 12.9, 9.8 Hz, 1H), 1.43 (t, J = 8.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 143.3, 140.7, 136.5, 129.2, 128.9, 127.6, 127.0, 126.8, 125.2, 123.1, 122.9, 122.5, 120.8, 120.5, 118.0, 109.3, 108.6, 41.7, 37.9, 35.9, 13.8. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{20}N_2ONa$ 375.1468; found 375.1476.



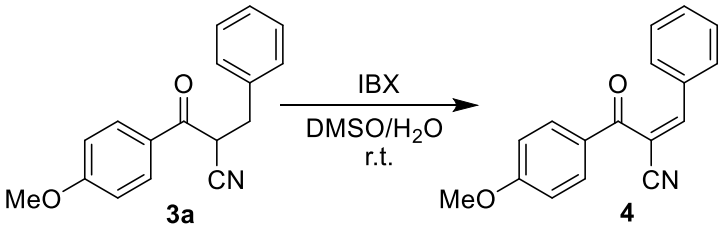
2-Benzyl-3-(imidazo[1,2-a]pyridin-3-yl)-3-oxopropanenitrile (**3al**). The compound was prepared according to the general procedure using imidazo[1,2-*a*]pyridine-3-carbaldehyde **1r** (146.1 mg, 1.0 mmol), **2a** (64.6 mg, 0.5 mmol) and NaOH (20.0 mg, 0.5 mmol) in 2 mL anhydrous DMSO. The crude product was purified by column chromatography on silica gel (PE/AcOEt 10:1) as faint yellow solid (110.1 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, J = 6.9 Hz, 1H), 8.39 (s, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.35 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 7.17 (t, J = 6.9 Hz, 1H), 4.43 (dd, J = 8.3, 6.7 Hz, 1H), 3.41 (dd, J = 13.8, 6.7 Hz, 1H), 3.34 (dd, J = 13.8, 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 149.7, 144.4, 135.8, 130.6, 129.0, 128.9, 128.9, 127.7, 121.9, 118.0, 117.4, 116.1, 42.7, 36.5. HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{13}N_3ONa$ 298.0951; found 298.0958.

3. Gram-scale synthesis

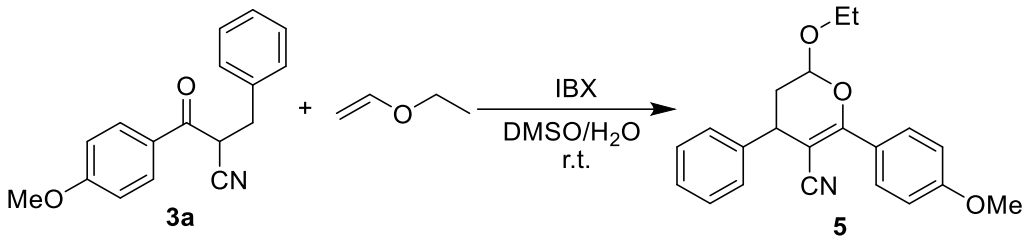


To an oven-dried 50 mL round-bottom flask equipped with a stir bar was added *p*-anisaldehyde **1b** (0.60 mL, 10 mmol), cinnamonitrile **2a** (0.65 g, 5 mmol), NaOH (200.0 mg, 5 mmol) and 10 mL anhydrous DMSO. The round-bottom flask was sealed with a septum, evacuated and refilled with argon three times. Then the mixture was stirred at room temperature for 12 h. The mixture was added 50 mL H_2O and extracted with ethyl acetate (3 x 60 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel chromatography (PE/AcOEt 12:1) as yellow solid **3a** (1.06 g, 80%).

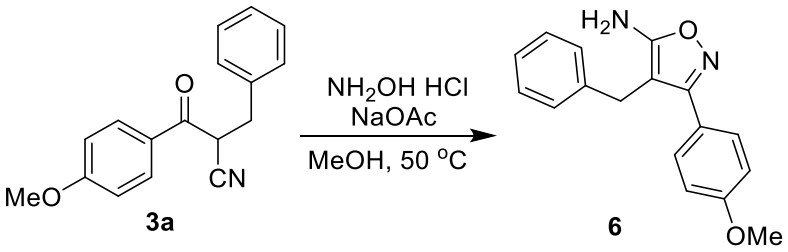
4. Synthetic applications



Water (0.4 mL) was added dropwise into the mixture of IBX (80.3 mg, 0.8 mmol) and DMSO (1.6 mL). Then, the resulting solution was added to 2-benzyl-3-(4-methoxyphenyl)-3-oxopropanenitrile **3a** (132.7 mg, 0.5 mmol) and the mixture was stirred at room temperature for 12 h. Then, the mixture was added water (4 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel column chromatography (PE/AcOEt 12:1) to afford the desired product **4**[6] (114.5 mg, 87%) as a brown oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 3H), 7.98 (d, J = 8.9 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.03 (d, J = 8.9 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.2, 164.1, 154.9, 133.2, 132.1, 132.0, 130.9, 129.3, 128.3, 117.3, 114.0, 110.2, 55.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{13}NO_2Na$ 286.0838; found 286.0851.

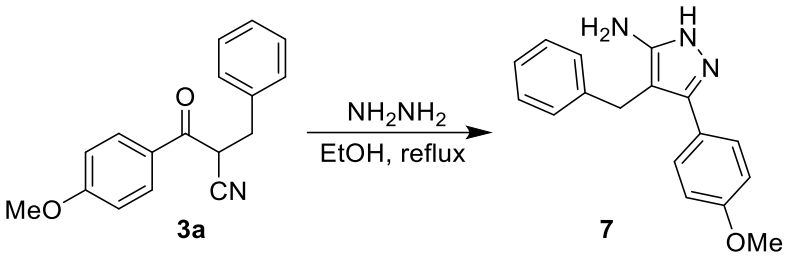


Water (0.4 mL) was added dropwise into the mixture of IBX (80.3 mg, 0.8 mmol) and DMSO (1.6 mL). Then, the resulting solution was added to a solution of 2-benzyl-3-(4-methoxyphenyl)-3-oxopropanenitrile **3a** (132.7 mg, 0.5 mmol) in ethyl vinyl ether (239.4 μL, 2.5 mmol), and the mixture was stirred at room temperature for 12 h. Following, the mixture was added water (4 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel gel column chromatography (PE/AcOEt 10:1) to afford the desired product **5** (87.2 mg, 52%) as a faint yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.9 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.34 – 7.27 (m, 3H), 6.94 (d, J = 8.9 Hz, 2H), 5.29 (dd, J = 8.7, 1.8 Hz, 1H), 4.16 – 4.04 (m, 1H), 3.90 – 3.85 (m, 1H), 3.84 (s, 3H), 3.79 – 3.63 (m, 1H), 2.48 – 2.35 (m, 1H), 2.12 – 2.05 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 161.7, 141.2, 129.9, 128.9, 127.8, 127.6, 125.3, 119.9, 113.8, 101.3, 86.6, 65.3, 55.5, 40.7, 36.7, 15.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{21}NO_3Na$ 358.1414; found 358.1426.



A 25 mL sealed tube was charged with $NH_2OH{\cdot}HCl$ (104.3 mg, 1.5 mmol), NaOAc (123.0 mg, 1.5 mmol), 2-benzyl-3-(4-methoxyphenyl)-3-oxopropanenitrile **3a** (132.7 mg, 0.5 mmol) and MeOH (2 mL) at 50 °C for 12 h. Then the mixture was quenched with water and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel column chromatography (PE/AcOEt 1:1) to afford the desired product **6** (116.3 mg, 83%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H),

7.18 (d, J = 7.3 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.34 (s, 2H), 3.79 (s, 3H), 3.71 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 163.6, 160.5, 138.9, 129.4, 128.8, 128.1, 126.6, 122.3, 114.2, 89.0, 55.3, 27.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}N_2O_2$ 281.1285; found 281.1294.



A 25 mL sealed tube was charged with $NH_2NH_2 \cdot H_2O$ (55.1 mg, 1.1 mmol), AcOH (114.5 μL, 2.0 mmol), 2-benzyl-3-(4-methoxyphenyl)-3-oxopropanenitrile **3a** (132.7 mg, 0.5 mmol) and EtOH (1.5 mL) and the mixture was heated to reflux overnight. The mixture was evaporated to move violate and adjusted to Ph 8 with a saturated $NaHCO_3$ solution. Then, the mixture was extracted with ethyl acetate (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel column chromatography (PE/AcOEt 9:1) to afford the desired product **7** (90.8 mg, 65%) as a faint yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 8.8 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 6.88 (d, J = 8.8 Hz, 2H), 3.84 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 153.8, 142.6, 140.2, 128.8, 128.7, 128.1, 126.3, 123.3, 114.4, 101.5, 55.3, 28.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{18}N_3O$ 280.1444; found 280.1454.

5. Mechanism studies

5.1 NMR titration experiments

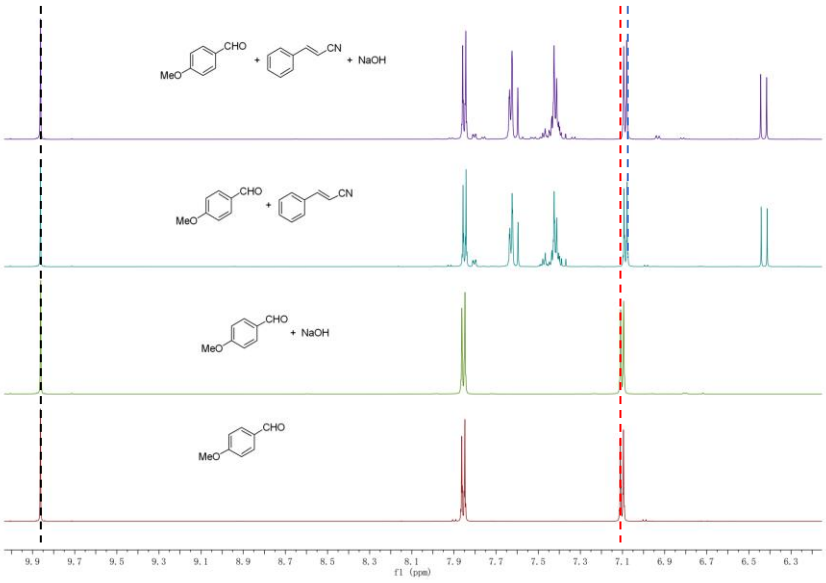


Figure S1. ^{1}H NMR Spectroscopy Experiments of *p*-Anisaldehydes **1b**

^{1}H NMR spectra experiments were conducted on a Bruker 500 MHz spectrometer in DMSO-d_6 (0.1 M) at room temperature. DMSO-d_6 (δ = 2.500 ppm) was used as internal standard. The total volume of the mixture was 1 mL. ^{1}H NMR spectra experiments were conducted on a Bruker 500 MHz spectrometer (Figure S1). The aryl C-H signal in the ^{1}H NMR spectrum of **1b**, when present in the mixture containing both benzaldehyde **1b** and cinnamonitriles **2a**, exhibited a migration phenomenon compared to the individual. The result indicated that there has an interaction force between **1b** and **2a** speculated to be π--π interaction. It was noteworthy that when NaOH was necessary, the substrates (**1b** and/or **2a**), NaOH, and DMSO-d_6 were added into the reaction bottle and stirred at 20 ºC for 15 minutes under N_2 atmosphere, preceding the execution of nuclear magnetic titration experiments.

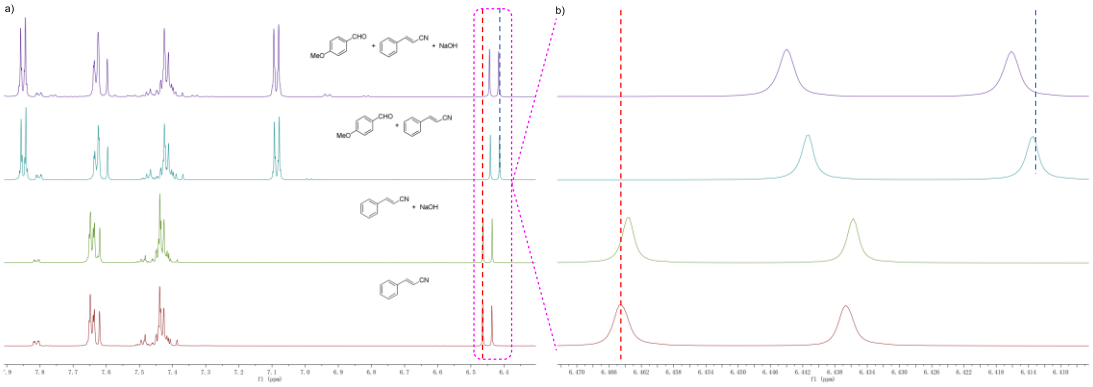
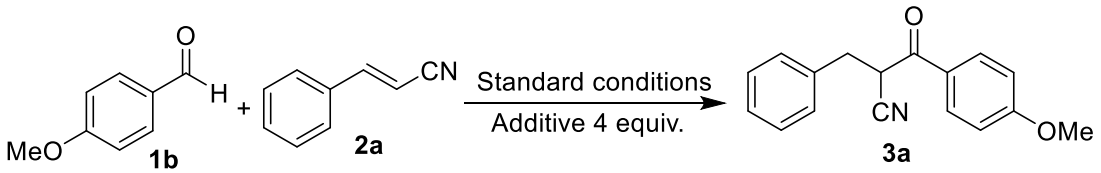


Figure S2. ^{1}H NMR Spectroscopy Experiments of Cinnamonitriles **2a**

^{1}H NMR spectra experiments were conducted on a Bruker 500 MHz spectrometer in DMSO-d_6 (0.1 M) at room temperature. DMSO-d_6 (δ = 2.500 ppm) was used as internal standard. The total volume of the mixture was 1 mL. ^{1}H NMR spectra experiments were conducted on a Bruker 500 MHz spectrometer. The ^{1}H NMR signal of cinnamonitriles **2a** on α C-H of cyanogroup (CH-CN) was exhibited distinctly migration compared with the mixture of benzaldehyde **1b** and cinnamonitriles **2a** (Figure S2a). Furthermore, when NaOH was added to the mixture (**1b** and **2a**), the α C-H signal of CH-CN was slightly shift to downfield (Figure S2b). We speculate that sodium ion may act as a chelating bridge with CN group. It was noteworthy that when NaOH was necessary, the substrates (**1b** and/or **2a**), NaOH, and DMSO-d_6 were added into the reaction bottle and stirred at 20 °C for 15 minutes under N_2 atmosphere, preceding the execution of nuclear magnetic titration experiments.

In a word, the NMR titration experiments have showed that there have π--π interaction between **1b** and **2a** and a coordination bond forces of sodium cation with CN of **2a** under the standard reaction conditions in the mixture (**1b**, **2a**, and NaOH).

5.2 Sodium ion capture experiments



w/o	82%
15-crown-5	31%
18-crown-6	47%

Under standard reaction conditions, different kinds of cation trapping agents, 15-crown-5 and 18-crown-6, were added to the reaction system and the yield of **3a** was decreased significantly compared to without trapping agents. When sodium ions trapping reagents (15-Crow-5) were added to the reaction, the yield of **3a** was distinctly decrease to 31%. The reaction in the presence of 18-crown-6, potassium ions trapping agents, resulted **3a** in 47% yields. The result indicated the contribution of sodium ions in reaction system. We speculated that sodium ions may play an indispensable bridging role in the formation of activated intermediate.

5.3 UV/vis studies

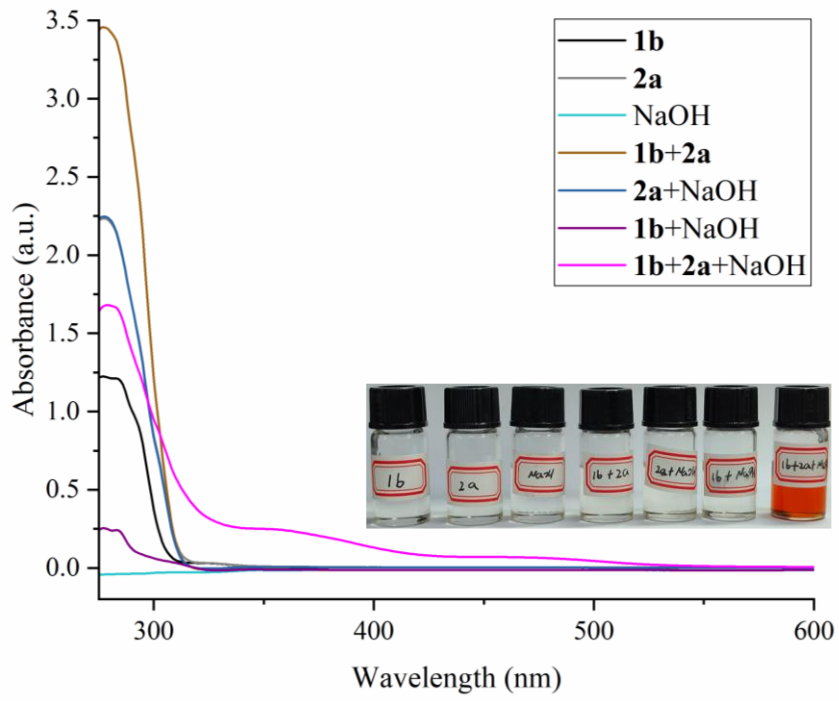
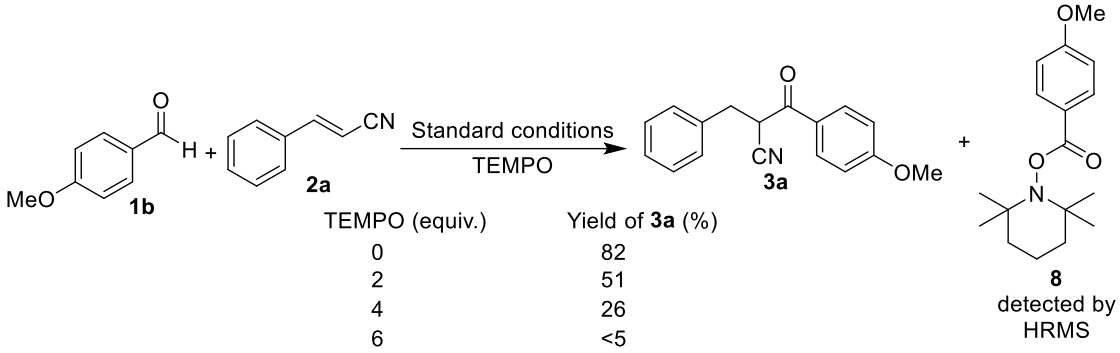


Figure S3. UV/vis Absorption Spectra of Individual Reaction Components and The Mixture. All spectra experiments were measured in DMSO and with a concentration of 10^{-3} M. The visual appearance of substrates and mixtures was placed in the picture (10^{-2} M in DMSO)

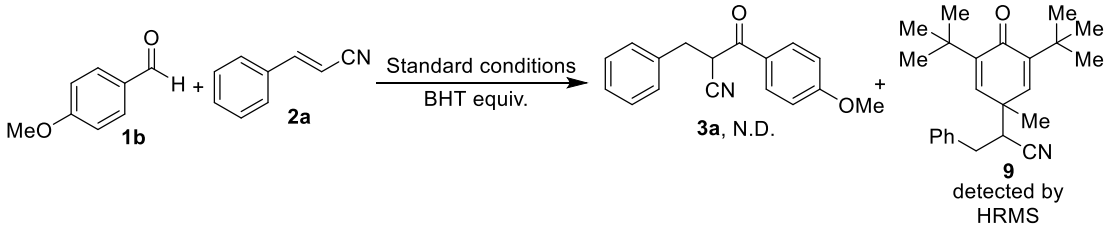
UV-vis absorption spectra were measured in a 1 cm quartz cuvette using a cary series UV-Vis-NIR spectrophotometer from Agilent Technologies. As shown in Figure S3, the mixture of **1b**, **2a** and NaOH in DMSO (10^{-3} M) exhibits a bathochromic shift compared to the individual reaction components (purple band). The mixture solution visual appearance was changed to distinct brown. These phenomena have indicated the formation of a mutual interacted electron donor-acceptor (EDA) complex between **1b**, **2a** and NaOH. (Tip: when NaOH was used, the mixture should be stirred at 20 °C for 15 minutes under N_2 atmosphere prior to conducting spectra experiments.)

5.4 Radical trapping experiments



TEMPO (equiv.)	Yield of **3a** (%)
0	82
2	51
4	26
6	<5

The reaction was conducted under standard reaction conditions and a series of different molar quantities of TEMPO were added to the reaction system. Significantly, as the amount of TEMPO was increase, the yield of **3a** was decrease rapidly. Furthermore, The TEMPO-aldehyde and -OH adducted products were detected by HRMS, TEMPO-aldehyde: HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{26}NO_3$ 292.1907; found 292.1906, TEMPO-OH: HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calcd. for $C_9H_{20}NO_2$ 174.1489; found 174.1488. In conclusion, these phenomena indicated that the reaction was conducted in a free radical mechanism model under standard reaction conditions. The yield was determined by ^{1}H NMR using mesitylene as an internal standard.

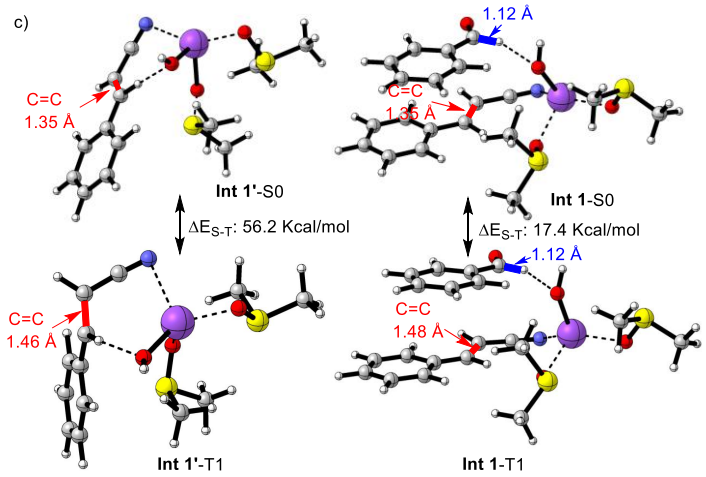


The reaction was conducted under standard reaction conditions and BHT (220.4 mg, 1.0 mmol) was added to the reaction system. The yield was determined by ^{1}H NMR using mesitylene as an internal standard. BHT capture products **9** was detected by HRMS, HRMS (ESI, Xevo G2-XS Tof) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{31}NONa$ 372.2298; found 372.2296.

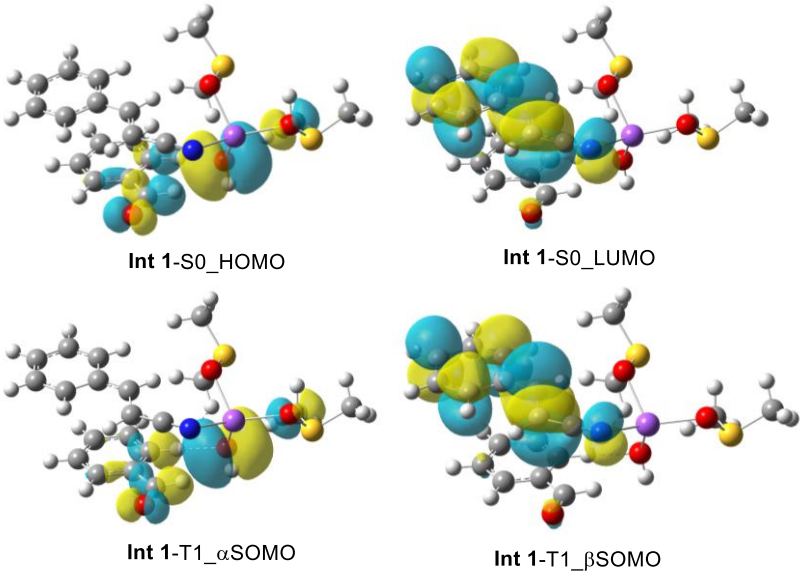
6. Computational details

All the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were done with GAUSSIAN 16[7]. Geometry optimization was performed using density functional of M06-2X[8] in combination with basis set of def2-SVP.[9] Frequency analysis was performed at the same level to confirm that we have obtained stable structures in the potential energy surfaces. All vibrational modes are

positive. When the solvent effect (in dimethyl sulfoxide) was applicable, it was accounted for using the solvation model based in the density (SMD) model.[10]



Scheme S2. The optimized geometry of the ground state (S0) and the triplet state (T1) of **Int 1'** and **Int 1**.



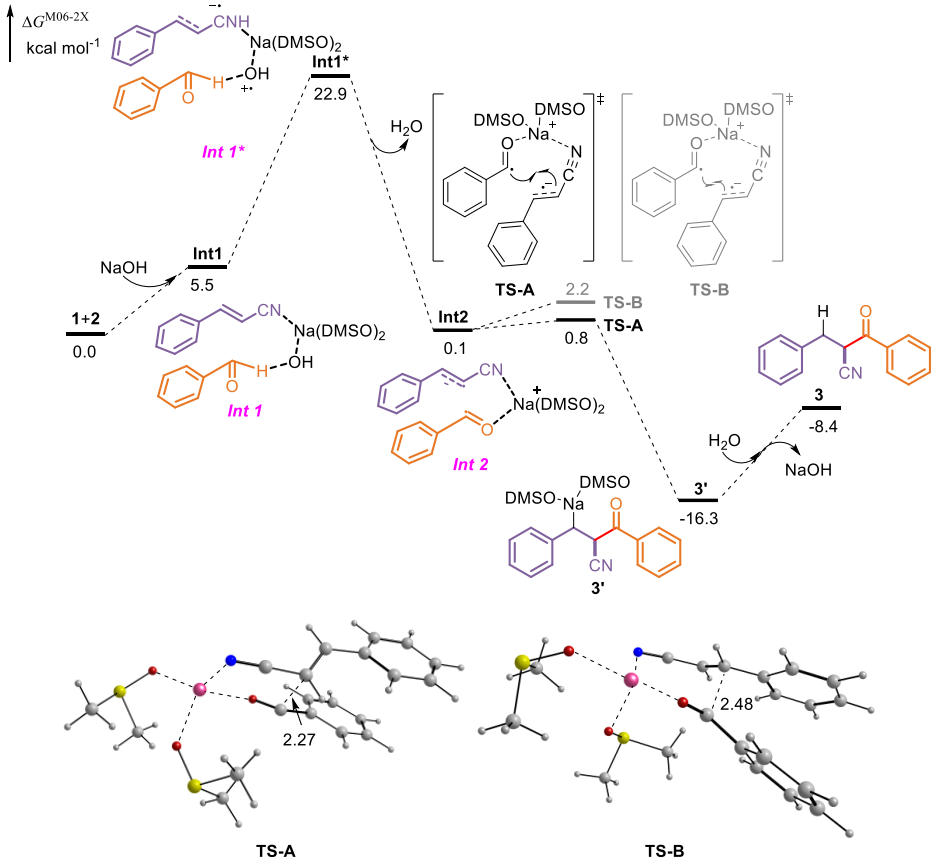
Scheme S3. The frontier molecular orbitals of S0 and T1 of **Int 1**

To better understand the reaction mechanism, DFT calculations at the SMD^{DMSO}-M06-2X/def2-SVP level were performed (Scheme S4). The process initiates with the formation of the EDA complex **Int 1** at 5.5 kcal mol^{-1} relative to the reactants. Upon thermal excitation at room temperature, as consistent with experimental conditions, a single electron transfer (SET) generates the high-energy radical anionic species **Int 1*** at 22.9 kcal mol^{-1}. The subsequent elimination of water furnishes the key radical intermediate **Int 2**, which is nearly thermoneutral (0.1 kcal mol^{-1}).

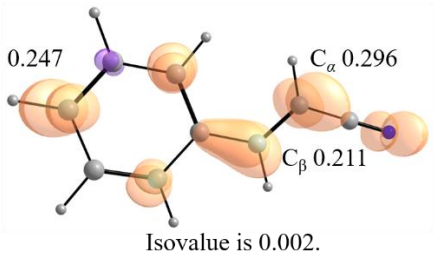
The radical **Int 2** then undergoes radical cross-coupling via two potential transition states. Among then, **TS-A**, which involves the coupling site at the αC, is identified as

the productive pathway with a barrier of only 0.8 kcal mol^{-1}. In contrast, **TS-B**, where the coupling site the βC, exhibits a slightly higher barrier (2.2 kcal mol^{-1}) and is thus disfavored. This computational observation aligns well with the experimental results, where the cross-coupling is selectively achieved via the lower-energy **TS-A** pathway.

Finally, the system proceeds to sodium salt intermediate **3'** (−16.3 kcal mol^{-1}) and subsequent protonation leads to the target product **3** (−8.4 kcal mol^{-1}), completing the reaction. Overall, the computational data support a thermally induced radical generation step and a regioselective cross-coupling via **TS-A**.

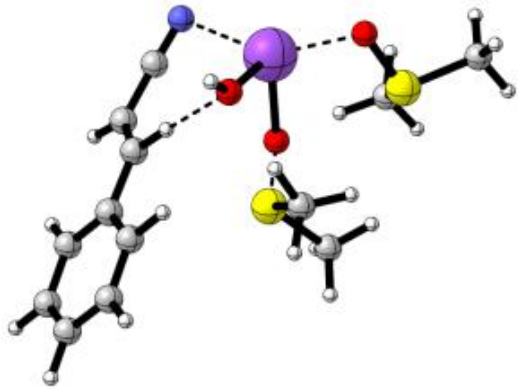


Scheme S4. The potential energy surface of the proposed mechanism



Scheme S5. Spin density plot of single-electron reductive **2a**

Cartesian Coordinates



Int 1'-S0

Zero-point correction= 0.309090 (Hartree/Particle)

Thermal correction to Energy= 0.335800

Thermal correction to Enthalpy= 0.336745

Thermal correction to Gibbs Free Energy= 0.249575

Sum of electronic and zero-point Energies= -1744.890174

Sum of electronic and thermal Energies= -1744.863463

Sum of electronic and thermal Enthalpies= -1744.862519

Sum of electronic and thermal Free Energies= -1744.949688

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6	-3.424805000	-0.394226000	1.112637000
6	-3.249630000	0.442899000	-0.001746000
6	-4.189666000	0.396497000	-1.044545000
6	-2.064698000	1.305238000	-0.004560000
6	-1.671107000	2.115189000	-1.008456000
11	1.442559000	1.488144000	0.879541000
8	0.939433000	-0.030745000	-0.676923000
8	-0.130229000	1.101748000	2.232846000
6	5.543222000	-0.836295000	0.437046000
16	3.792352000	-0.549239000	0.135991000
6	3.873915000	-0.347138000	-1.648637000
8	3.544294000	0.851771000	0.704352000
6	-0.440386000	2.824496000	-0.837748000

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1	-4.072235000	1.041282000	-1.917905000
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1	-2.198639000	2.251071000	-1.955400000
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1	5.841770000	-1.783555000	-0.031779000
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1	2.852906000	-0.105038000	-1.967168000
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1	0.214169000	-3.510001000	-1.073101000
1	0.822618000	-2.391922000	-2.345422000
1	1.805563000	-2.672282000	-0.854316000
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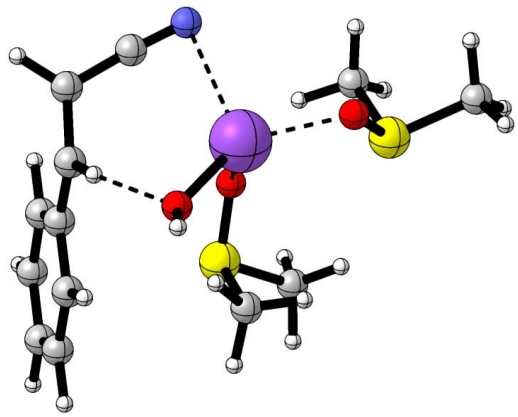
1	-0.555050000	1.396293000	3.044452000



Int 1'-T1

Zero-point correction=	0.304556 (Hartree/Particle)	
Thermal correction to Energy=	0.331758	
Thermal correction to Enthalpy=	0.332702	
Thermal correction to Gibbs Free Energy=	0.244477	
Sum of electronic and zero-point Energies=	-1744.805094	
Sum of electronic and thermal Energies=	-1744.777892	
Sum of electronic and thermal Enthalpies=	-1744.776948	
Sum of electronic and thermal Free Energies=	-1744.865173	
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6	-4.320326000	-1.619325000	-0.391330000
6	-3.905072000	-1.290218000	0.905658000
6	-3.168251000	-0.137560000	1.132705000
6	-2.834544000	0.734203000	0.061409000
6	-3.266964000	0.387899000	-1.244280000
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1	5.573224000	-1.543195000	-0.850461000

1	5.607276000	0.233923000	-0.485723000
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1	3.567400000	-0.950705000	-2.503342000
1	3.666727000	0.782200000	-1.977085000
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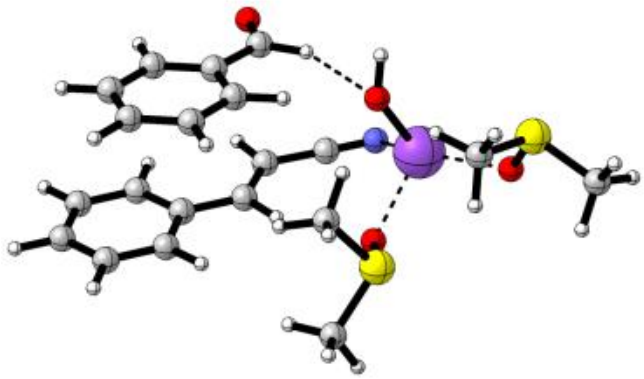


Int 1-S0

Zero-point correction= 0.421861 (Hartree/Particle)

Thermal correction to Energy= 0.456529

Thermal correction to Enthalpy= 0.457473

Thermal correction to Gibbs Free Energy= 0.352059

Sum of electronic and zero-point Energies= -2089.969413

Sum of electronic and thermal Energies= -2089.934745

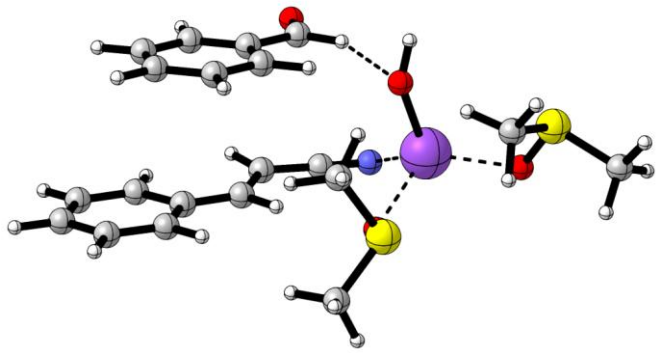
Sum of electronic and thermal Enthalpies= -2089.933801

Sum of electronic and thermal Free Energies= -2090.039216

6	5.391329000	0.667378000	-1.028330000
6	5.410697000	1.748482000	-0.140545000
6	4.213805000	2.338071000	0.263273000

6	3.000389000	1.845659000	-0.216374000
6	2.967804000	0.755895000	-1.099692000
6	4.182335000	0.172525000	-1.503609000
6	1.661337000	0.260693000	-1.544338000
6	1.462674000	-0.815456000	-2.331249000
11	-2.386503000	-0.776520000	-1.100284000
8	-4.544223000	-0.374059000	-0.887184000
6	4.037979000	-1.088398000	1.965411000
6	3.306922000	-0.192167000	2.754605000
6	1.912051000	-0.166645000	2.691244000
6	1.237606000	-1.040610000	1.836525000
6	1.972587000	-1.937995000	1.052718000
6	3.371413000	-1.963755000	1.112779000
6	1.224790000	-2.835328000	0.136823000
8	1.742994000	-3.664985000	-0.575576000
6	-0.965178000	3.712511000	-0.420285000
16	-1.882519000	2.194916000	-0.127182000
6	-0.980657000	1.587777000	1.302584000
8	-1.480008000	1.265791000	-1.282646000
8	-1.761642000	-1.393552000	0.854647000
6	0.133722000	-1.236127000	-2.646108000
7	-0.943959000	-1.589098000	-2.877808000
1	6.327689000	0.207327000	-1.348385000
1	6.362617000	2.130990000	0.232094000
1	4.222921000	3.183632000	0.953013000
1	2.059914000	2.307059000	0.094442000
1	4.184747000	-0.674356000	-2.192254000
1	0.777760000	0.811406000	-1.197561000
1	2.267687000	-1.438967000	-2.725743000
1	0.120670000	-2.671811000	0.155842000
1	5.128556000	-1.095733000	2.017704000
1	3.833852000	0.495194000	3.419927000
1	1.350741000	0.539313000	3.307546000
1	0.141943000	-1.053694000	1.735752000

1	3.918666000	-2.668102000	0.482326000
1	-1.374290000	4.168523000	-1.330597000
1	-1.106874000	4.385817000	0.436111000
1	0.095586000	3.459861000	-0.555487000
1	-1.268026000	0.522314000	1.387672000
1	-1.279879000	2.167393000	2.187616000
1	0.097011000	1.689095000	1.111582000
16	-5.244716000	-0.734370000	0.428301000
6	-6.739176000	0.266449000	0.426106000
1	-7.257278000	0.145108000	1.386957000
1	-6.454948000	1.313564000	0.255592000
1	-7.372041000	-0.099535000	-0.392377000
6	-4.335968000	0.125825000	1.718631000
1	-3.336371000	-0.349571000	1.698462000
1	-4.292117000	1.193490000	1.460081000
1	-4.845522000	-0.032033000	2.679684000
1	-1.863736000	-2.233907000	1.314933000



Int 1-T1

Zero-point correction= 0.415232 (Hartree/Particle)

Thermal correction to Energy= 0.448407

Thermal correction to Enthalpy= 0.449351

Thermal correction to Gibbs Free Energy= 0.348167

Sum of electronic and zero-point Energies= -2089.890041

Sum of electronic and thermal Energies= -2089.856866

Sum of electronic and thermal Enthalpies= -2089.855922

Sum of electronic and thermal Free Energies= -2089.957107

6	-5.532226000	-0.773381000	-0.983313000
6	-5.618173000	-1.907737000	-0.159145000
6	-4.437417000	-2.540386000	0.284571000
6	-3.204263000	-2.051108000	-0.078405000
6	-3.081344000	-0.878384000	-0.912531000
6	-4.306259000	-0.259608000	-1.358127000
6	-1.822018000	-0.393218000	-1.217504000
6	-1.593175000	0.843588000	-2.000147000
11	2.337050000	0.660786000	-0.954374000
8	4.522972000	0.365810000	-1.026125000
6	-3.944352000	1.635443000	1.482535000
6	-3.434418000	0.594647000	2.269796000
6	-2.056643000	0.389564000	2.366598000
6	-1.177242000	1.220458000	1.669260000
6	-1.692185000	2.263770000	0.889016000
6	-3.074394000	2.473450000	0.792727000
6	-0.731994000	3.135780000	0.165466000
8	-1.054456000	4.078585000	-0.520224000
6	0.795885000	-3.797792000	-0.290310000
16	1.737716000	-2.304606000	0.049123000
6	0.833763000	-1.715010000	1.484208000
8	1.366761000	-1.346192000	-1.092642000
8	1.914952000	1.152068000	1.083424000
6	-0.301635000	1.223440000	-2.358716000
7	0.793385000	1.538502000	-2.616275000
1	-6.446492000	-0.288306000	-1.330340000
1	-6.592758000	-2.300012000	0.133704000
1	-4.504135000	-3.423755000	0.922225000
1	-2.287840000	-2.534993000	0.267899000
1	-4.267704000	0.624706000	-1.994708000
1	-0.926755000	-0.922204000	-0.880149000
1	-2.406536000	1.504163000	-2.303554000
1	0.334922000	2.841919000	0.309644000
1	-5.023402000	1.785096000	1.411599000

1	-4.121864000	-0.060374000	2.809655000
1	-1.669101000	-0.425038000	2.982794000
1	-0.083902000	1.088982000	1.688509000
1	-3.447177000	3.292681000	0.173939000
1	1.203825000	-4.236282000	-1.209729000
1	0.918102000	-4.497041000	0.547984000
1	-0.259181000	-3.523300000	-0.427388000
1	1.186486000	-0.673397000	1.621378000
1	1.083736000	-2.350866000	2.345549000
1	-0.243184000	-1.754901000	1.265172000
16	5.328379000	0.609263000	0.255361000
6	6.856037000	-0.305970000	0.001704000
1	7.459938000	-0.265188000	0.918282000
1	6.600975000	-1.341130000	-0.262248000
1	7.389740000	0.182308000	-0.823492000
6	4.583248000	-0.438905000	1.511331000
1	3.570628000	-0.013595000	1.644786000
1	4.551566000	-1.470185000	1.132719000
1	5.179120000	-0.368770000	2.432336000
1	2.113220000	1.902784000	1.654173000

1

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.111049

Thermal correction to Energy: 0.117325

Thermal correction to Enthalpy: 0.118269

Thermal correction to Gibbs Free Energy: 0.080502

Sum of electronic and zero-point Energies: -345.066146

Sum of electronic and thermal Energies: -345.059870

Sum of electronic and thermal Enthalpies: -345.058926

Sum of electronic and thermal Free Energies: -345.096693

Optimized Coordinates:

C	-1.326737	-1.329527	0.000122
C	-2.212844	-0.246904	-0.000222
C	-1.730015	1.062675	-0.000307

C	-0.354882	1.292180	0.000052
C	0.532262	0.211329	0.000322
C	0.045476	-1.102294	0.000355
C	1.993737	0.467776	0.000443
O	2.834111	-0.397819	-0.000792
H	2.278413	1.545802	0.001759
H	-1.713274	-2.350040	0.000250
H	-3.289349	-0.428233	-0.000400
H	-2.426304	1.902721	-0.000470
H	0.039160	2.311682	0.000032
H	0.756482	-1.930794	0.000573

2

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.134038

Thermal correction to Energy: 0.142333

Thermal correction to Enthalpy: 0.143277

Thermal correction to Gibbs Free Energy: 0.100202

Sum of electronic and zero-point Energies: -401.300282

Sum of electronic and thermal Energies: -401.291987

Sum of electronic and thermal Enthalpies: -401.291042

Sum of electronic and thermal Free Energies: -401.334118

Optimized Coordinates:

C	-2.278071	1.295712	0.000005
C	-3.140649	0.195032	0.000017
C	-2.617900	-1.097660	-0.000001
C	-1.237481	-1.289038	-0.000010
C	-0.362389	-0.191743	-0.000012
C	-0.900500	1.107038	-0.000008
C	1.080860	-0.453670	0.000006
C	2.051726	0.478810	-0.000006
C	3.432764	0.103169	0.000027
N	4.552573	-0.186144	-0.000004
H	-2.685092	2.308202	-0.000007
H	-4.221157	0.348987	0.000043

H	-3.286346	-1.960159	-0.000006
H	-0.824014	-2.299989	-0.000043
H	-0.240874	1.976589	-0.000030
H	1.370350	-1.508739	0.000025
H	1.848966	1.552212	-0.000064

3

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.249320

Thermal correction to Energy: 0.264380

Thermal correction to Enthalpy: 0.265325

Thermal correction to Gibbs Free Energy: 0.204565

Sum of electronic and zero-point Energies: -746.399470

Sum of electronic and thermal Energies: -746.384409

Sum of electronic and thermal Enthalpies: -746.383465

Sum of electronic and thermal Free Energies: -746.444224

Optimized Coordinates:

C	3.899984	0.332588	0.301232
C	3.617630	1.664627	-0.009461
C	2.429067	1.984852	-0.664895
C	1.524836	0.977390	-1.006130
C	1.800014	-0.360203	-0.699491
C	2.995842	-0.671824	-0.040205
C	0.800202	-1.443225	-1.022639
C	0.059471	-1.914743	0.256311
C	-0.471685	-0.731311	1.092659
C	-1.472217	0.213543	0.505802
O	-0.000366	-0.547498	2.187919
C	-2.221000	-0.068292	-0.644690
C	-3.118904	0.876292	-1.140744
C	-3.266923	2.106578	-0.500618
C	-2.523023	2.392905	0.646920
C	-1.634532	1.449073	1.149939
C	-0.976896	-2.902173	-0.053871
N	-1.786078	-3.683896	-0.309269

H	4.830512	0.075355	0.810708
H	4.325588	2.451319	0.257407
H	2.203070	3.023303	-0.913993
H	0.593212	1.229403	-1.519847
H	3.220021	-1.713851	0.202799
H	1.304799	-2.321008	-1.450492
H	0.779531	-2.418486	0.917424
H	-2.128590	-1.023830	-1.161585
H	-3.703859	0.648050	-2.032817
H	-3.965293	2.845904	-0.896877
H	-2.637360	3.355452	1.147866
H	-1.044206	1.657210	2.043331
H	0.076855	-1.078008	-1.763098

3’

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.397489

Thermal correction to Energy: 0.428797

Thermal correction to Enthalpy: 0.429741

Thermal correction to Gibbs Free Energy: 0.331932

Sum of electronic and zero-point Energies: -2013.639927

Sum of electronic and thermal Energies: -2013.608619

Sum of electronic and thermal Enthalpies: -2013.607675

Sum of electronic and thermal Free Energies: -2013.705484

Optimized Coordinates:

C	-5.262404	0.204319	-0.532978
C	-5.422064	0.954540	-1.698429
C	-4.337306	1.740729	-2.125359
C	-3.144361	1.763779	-1.423476
C	-2.942531	0.992887	-0.232490
C	-4.068077	0.220198	0.188465
C	-1.690427	0.992226	0.437485
C	-1.577178	0.375143	1.812634
C	-1.733131	-1.171690	1.906516
C	-1.001464	-2.029501	0.910236

O	-2.377601	-1.662639	2.797827
C	-1.445192	-2.154393	-0.414817
C	-0.777750	-3.012292	-1.289558
C	0.333349	-3.736864	-0.853356
C	0.775574	-3.610275	0.461712
C	0.107470	-2.761829	1.346928
Na	0.253965	0.024986	-0.910383
C	-0.229116	0.637485	2.332240
N	0.854678	0.809549	2.692739
H	-6.090560	-0.407652	-0.164632
H	-6.358621	0.937312	-2.257249
H	-4.432204	2.348663	-3.029386
H	-2.318054	2.383387	-1.785854
H	-4.010040	-0.370789	1.105624
H	-1.038445	1.853722	0.263784
H	-2.296213	0.748753	2.572184
H	-2.325472	-1.599354	-0.747529
H	-1.129061	-3.113504	-2.317907
H	0.857449	-4.398743	-1.544843
H	1.643882	-4.175474	0.805740
H	0.448594	-2.663918	2.380357
S	1.700432	2.932928	0.429147
C	3.232410	2.779430	1.357953
H	4.025010	2.473486	0.661315
H	3.463275	3.746681	1.824815
H	3.064100	2.019756	2.130882
C	2.233179	4.202266	-0.727614
H	2.411321	5.138026	-0.180957
H	3.142778	3.854583	-1.235324
H	1.416328	4.337663	-1.447979
O	1.625668	1.657055	-0.418966
S	3.406148	-0.606956	-1.195631
C	3.372121	-0.789932	0.595579
H	3.088481	-1.822202	0.841874

H	4.366235	-0.547545	0.997274
H	2.627226	-0.074468	0.965583
C	4.420731	-2.048044	-1.562125
H	5.423488	-1.903318	-1.137508
H	3.931971	-2.936305	-1.139293
H	4.483151	-2.126707	-2.654943
O	2.009527	-1.012962	-1.680677

H_2O

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.021310

Thermal correction to Energy: 0.024146

Thermal correction to Enthalpy: 0.025090

Thermal correction to Gibbs Free Energy: 0.003649

Sum of electronic and zero-point Energies: -76.309185

Sum of electronic and thermal Energies: -76.306350

Sum of electronic and thermal Enthalpies: -76.305406

Sum of electronic and thermal Free Energies: -76.326846

Optimized Coordinates:

O	0.000000	0.000000	0.120541
H	0.000000	0.754342	-0.482165
H	0.000000	-0.754342	-0.482165

NaOH_2DMSO

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.174619

Thermal correction to Energy: 0.191141

Thermal correction to Enthalpy: 0.192085

Thermal correction to Gibbs Free Energy: 0.129007

Sum of electronic and zero-point Energies: -1343.572081

Sum of electronic and thermal Energies: -1343.555559

Sum of electronic and thermal Enthalpies: -1343.554615

Sum of electronic and thermal Free Energies: -1343.617693

Optimized Coordinates:

Na	0.085466	1.469642	0.000955
S	-2.982289	0.103450	-0.001711

C	-2.390650	-0.932409	-1.351324
H	-1.318032	-1.119921	-1.195096
H	-2.970389	-1.865773	-1.357772
H	-2.571785	-0.374612	-2.279178
C	-2.391784	-0.916032	1.360834
H	-2.971823	-1.849055	1.378347
H	-1.319163	-1.106104	1.207721
H	-2.573386	-0.346801	2.281644
O	-2.087249	1.346506	-0.008770
S	1.981720	-1.247320	0.000546
C	2.790843	-0.375479	-1.351946
H	2.673165	0.705459	-1.121282
H	3.843044	-0.692071	-1.388547
H	2.278395	-0.678570	-2.274590
C	2.800239	-0.375165	1.347108
H	3.852947	-0.690843	1.375803
H	2.679887	0.705649	1.117179
H	2.294852	-0.678764	2.273474
O	0.532640	-0.718545	0.005608
O	2.014920	2.218365	-0.001612
H	2.636886	2.951158	0.000599

Int1

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.421861

Thermal correction to Energy: 0.456529

Thermal correction to Enthalpy: 0.457473

Thermal correction to Gibbs Free Energy: 0.352059

Sum of electronic and zero-point Energies: -2089.969413

Sum of electronic and thermal Energies: -2089.934745

Sum of electronic and thermal Enthalpies: -2089.933801

Sum of electronic and thermal Free Energies: -2090.039216

Optimized Coordinates:

C	5.391329	0.667378	-1.028330
C	5.410697	1.748482	-0.140545

C	4.213805	2.338071	0.263273
C	3.000389	1.845659	-0.216374
C	2.967804	0.755895	-1.099692
C	4.182335	0.172525	-1.503609
C	1.661337	0.260693	-1.544338
C	1.462674	-0.815456	-2.331249
Na	-2.386503	-0.776520	-1.100284
O	-4.544223	-0.374059	-0.887184
C	4.037979	-1.088398	1.965411
C	3.306922	-0.192167	2.754605
C	1.912051	-0.166645	2.691244
C	1.237606	-1.040610	1.836525
C	1.972587	-1.937995	1.052718
C	3.371413	-1.963755	1.112779
C	1.224790	-2.835328	0.136823
O	1.742994	-3.664985	-0.575576
C	-0.965178	3.712511	-0.420285
S	-1.882519	2.194916	-0.127182
C	-0.980657	1.587777	1.302584
O	-1.480008	1.265791	-1.282646
O	-1.761642	-1.393552	0.854647
C	0.133722	-1.236127	-2.646108
N	-0.943959	-1.589098	-2.877808
H	6.327689	0.207327	-1.348385
H	6.362617	2.130990	0.232094
H	4.222921	3.183632	0.953013
H	2.059914	2.307059	0.094442
H	4.184747	-0.674356	-2.192254
H	0.777760	0.811406	-1.197561
H	2.267687	-1.438967	-2.725743
H	0.120670	-2.671811	0.155842
H	5.128556	-1.095733	2.017704
H	3.833852	0.495194	3.419927
H	1.350741	0.539313	3.307546

H	0.141943	-1.053694	1.735752
H	3.918666	-2.668102	0.482326
H	-1.374290	4.168523	-1.330597
H	-1.106874	4.385817	0.436111
H	0.095586	3.459861	-0.555487
H	-1.268026	0.522314	1.387672
H	-1.279879	2.167393	2.187616
H	0.097011	1.689095	1.111582
S	-5.244716	-0.734370	0.428301
C	-6.739176	0.266449	0.426106
H	-7.257278	0.145108	1.386957
H	-6.454948	1.313564	0.255592
H	-7.372041	-0.099535	-0.392377
C	-4.335968	0.125825	1.718631
H	-3.336371	-0.349571	1.698462
H	-4.292117	1.193490	1.460081
H	-4.845522	-0.032033	2.679684
H	-1.863736	-2.233907	1.314933

Int1*

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.417135

Thermal correction to Energy: 0.452495

Thermal correction to Enthalpy: 0.453439

Thermal correction to Gibbs Free Energy: 0.344162

Sum of electronic and zero-point Energies: -2089.878535

Sum of electronic and thermal Energies: -2089.843175

Sum of electronic and thermal Enthalpies: -2089.842231

Sum of electronic and thermal Free Energies: -2089.951508

Optimized Coordinates:

C	-5.532226	-0.773381	-0.983313
C	-5.618173	-1.907737	-0.159145
C	-4.437417	-2.540386	0.284571
C	-3.204263	-2.051108	-0.078405
C	-3.081344	-0.878384	-0.912531

C	-4.306259	-0.259608	-1.358127
C	-1.822018	-0.393218	-1.217504
C	-1.593175	0.843588	-2.000147
Na	2.337050	0.660786	-0.954374
O	4.522972	0.365810	-1.026125
C	-3.944352	1.635443	1.482535
C	-3.434418	0.594647	2.269796
C	-2.056643	0.389564	2.366598
C	-1.177242	1.220458	1.669260
C	-1.692185	2.263770	0.889016
C	-3.074394	2.473450	0.792727
C	-0.731994	3.135780	0.165466
O	-1.054456	4.078585	-0.520224
C	0.795885	-3.797792	-0.290310
S	1.737716	-2.304606	0.049123
C	0.833763	-1.715010	1.484208
O	1.366761	-1.346192	-1.092642
O	1.914952	1.152068	1.083424
C	-0.301635	1.223440	-2.358716
N	0.793385	1.538502	-2.616275
H	-6.446492	-0.288306	-1.330340
H	-6.592758	-2.300012	0.133704
H	-4.504135	-3.423755	0.922225
H	-2.287840	-2.534993	0.267899
H	-4.267704	0.624706	-1.994708
H	-0.926755	-0.922204	-0.880149
H	-2.406536	1.504163	-2.303554
H	0.334922	2.841919	0.309644
H	-5.023402	1.785096	1.411599
H	-4.121864	-0.060374	2.809655
H	-1.669101	-0.425038	2.982794
H	-0.083902	1.088982	1.688509
H	-3.447177	3.292681	0.173939
H	1.203825	-4.236282	-1.209729

H	0.918102	-4.497041	0.547984
H	-0.259181	-3.523300	-0.427388
H	1.186486	-0.673397	1.621378
H	1.083736	-2.350866	2.345549
H	-0.243184	-1.754901	1.265172
S	5.328379	0.609263	0.255361
C	6.856037	-0.305970	0.001704
H	7.459938	-0.265188	0.918282
H	6.600975	-1.341130	-0.262248
H	7.389740	0.182308	-0.823492
C	4.583248	-0.438905	1.511331
H	3.570628	-0.013595	1.644786
H	4.551566	-1.470185	1.132719
H	5.179120	-0.368770	2.432336
H	2.113220	1.902784	1.654173

Int2

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.396137

Thermal correction to Energy: 0.428366

Thermal correction to Enthalpy: 0.429310

Thermal correction to Gibbs Free Energy: 0.329609

Sum of electronic and zero-point Energies: -2013.612837

Sum of electronic and thermal Energies: -2013.580607

Sum of electronic and thermal Enthalpies: -2013.579663

Sum of electronic and thermal Free Energies: -2013.679364

Optimized Coordinates:

C	-5.066060	-0.426391	0.198996
C	-5.346511	0.460068	-0.845144
C	-4.480824	1.522638	-1.107082
C	-3.336013	1.693474	-0.331249
C	-3.045439	0.809269	0.720051
C	-3.925670	-0.255270	0.977876
C	-1.798934	0.997627	1.466486
C	-1.452566	0.340627	2.591278

Na	2.249719	0.190097	1.625414
O	4.187793	-0.229168	0.725015
C	-2.670069	-3.105013	-1.105789
C	-2.593128	-2.056597	-2.027192
C	-1.630497	-1.055079	-1.864088
C	-0.737720	-1.116128	-0.793568
C	-0.806021	-2.161876	0.138499
C	-1.794816	-3.139814	-0.018287
C	0.106655	-2.186622	1.370733
O	1.217907	-1.662493	1.146894
C	0.941058	4.086370	-0.644020
S	1.599736	2.432581	-0.887867
C	0.447815	1.886760	-2.157934
O	1.206139	1.671782	0.385807
C	-0.158782	0.552089	3.158769
N	0.903647	0.722129	3.587314
H	-5.737500	-1.263159	0.399664
H	-6.239578	0.318242	-1.456349
H	-4.695123	2.216798	-1.921375
H	-2.649966	2.518858	-0.537162
H	-3.707190	-0.968689	1.775012
H	-1.073833	1.696933	1.035694
H	-2.089119	-0.390939	3.093178
H	-3.423749	-3.885716	-1.230951
H	-3.291659	-2.012684	-2.865659
H	-1.588336	-0.222600	-2.572168
H	0.010237	-0.333935	-0.626872
H	-1.867853	-3.936442	0.729246
H	1.476675	4.515572	0.212092
H	1.129472	4.684958	-1.545200
H	-0.134288	4.011485	-0.431817
H	0.736948	0.870611	-2.456450
H	0.530496	2.565618	-3.017880
H	-0.566602	1.901702	-1.733924

S	4.286739	-1.339146	-0.327907
C	5.742659	-0.913524	-1.292720
H	5.828942	-1.607543	-2.139729
H	5.644102	0.125544	-1.634385
H	6.608483	-1.021244	-0.627282
C	3.033112	-0.940578	-1.555808
H	2.069391	-1.080782	-1.045105
H	3.188358	0.098545	-1.878870
H	3.121439	-1.635194	-2.402658

TS-A

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.395645

Thermal correction to Energy: 0.426850

Thermal correction to Enthalpy: 0.427794

Thermal correction to Gibbs Free Energy: 0.329162

Sum of electronic and zero-point Energies: -2013.611617

Sum of electronic and thermal Energies: -2013.580412

Sum of electronic and thermal Enthalpies: -2013.579468

Sum of electronic and thermal Free Energies: -2013.678100

Optimized Coordinates:

C	5.199467	1.653230	-0.941569
C	6.139323	0.622435	-0.848289
C	5.739571	-0.689099	-1.118714
C	4.420181	-0.966787	-1.465923
C	3.452862	0.057853	-1.541280
C	3.878120	1.378832	-1.281413
C	2.069039	-0.282090	-1.824170
C	1.001361	0.486486	-1.417148
C	0.507507	-0.592519	0.530811
C	1.866642	-0.810712	1.194903
O	-0.227757	-1.574907	0.445947
C	2.343528	-2.099639	1.465762
C	3.588686	-2.281780	2.064346
C	4.362307	-1.170548	2.415806

C	3.885476	0.118117	2.167852
C	2.642975	0.292903	1.556273
C	-0.329717	0.211289	-1.863111
N	-1.419469	-0.032643	-2.175078
H	5.501336	2.684733	-0.747436
H	7.173572	0.840516	-0.576831
H	6.463233	-1.504620	-1.054326
H	4.115026	-1.997348	-1.664876
H	3.162947	2.201252	-1.354933
H	1.872092	-1.276153	-2.234495
H	1.137668	1.500068	-1.033349
H	1.718878	-2.952524	1.188148
H	3.963516	-3.289337	2.257878
H	5.338237	-1.311081	2.885027
H	4.487768	0.986342	2.443744
H	2.268700	1.298193	1.339715
Na	-2.325124	-1.059581	-0.139163
S	-5.552539	-1.401199	-0.873356
C	-6.064475	-0.896509	0.777030
H	-5.264449	-0.274361	1.203880
H	-7.013821	-0.348794	0.701733
H	-6.208187	-1.816714	1.357629
C	-5.228132	0.242319	-1.537882
H	-6.181935	0.781548	-1.620988
H	-4.533582	0.756106	-0.857811
H	-4.789060	0.104746	-2.534523
O	-4.181493	-2.058992	-0.689833
S	-2.717462	1.968007	1.577042
C	-1.617929	1.568525	2.942240
H	-0.815850	0.915899	2.567275
H	-1.211401	2.502064	3.354587
H	-2.222327	1.053192	3.699322
C	-1.473383	2.578247	0.431528
H	-1.067606	3.521866	0.821827

H	-0.692185	1.806454	0.349784
H	-1.975103	2.752243	-0.529347
O	-3.160799	0.610484	1.010182

TS-B

Thermodynamic Data (given by Hartree):

Zero-point correction: 0.395597

Thermal correction to Energy: 0.426940

Thermal correction to Enthalpy: 0.427884

Thermal correction to Gibbs Free Energy: 0.330076

Sum of electronic and zero-point Energies: -2013.610422

Sum of electronic and thermal Energies: -2013.579079

Sum of electronic and thermal Enthalpies: -2013.578135

Sum of electronic and thermal Free Energies: -2013.675943

Optimized Coordinates:

C	4.128806	-2.349407	0.028821
C	5.109953	-1.472330	-0.439757
C	4.757137	-0.449026	-1.322290
C	3.430632	-0.298380	-1.718015
C	2.432947	-1.165571	-1.243118
C	2.802312	-2.203185	-0.372653
C	1.039978	-0.937875	-1.657334
C	0.041556	-1.883505	-1.583178
C	0.880809	1.134788	-0.211417
O	0.186995	2.007312	-0.742803
C	2.158685	1.608060	0.460383
C	2.739700	0.829923	1.468501
C	3.967878	1.190656	2.022136
C	4.637812	2.323096	1.551215
C	4.065545	3.106086	0.544555
C	2.826478	2.754541	0.010621
C	-1.228279	-1.556691	-2.109550
N	-2.257634	-1.194588	-2.516005
H	4.399497	-3.154407	0.714592
H	6.146980	-1.588520	-0.119629

H	5.517599	0.238525	-1.697601
H	3.150539	0.514223	-2.393154
H	2.047603	-2.892418	0.011341
H	0.886974	-0.092697	-2.331010
H	0.144082	-2.832397	-1.054701
H	2.224284	-0.073208	1.807231
H	4.413762	0.581870	2.811503
H	5.609463	2.595367	1.968250
H	4.591222	3.990820	0.178445
H	2.361396	3.353500	-0.776698
Na	-1.720209	0.802296	-0.789439
S	-1.832157	-1.968703	1.171916
C	-0.176071	-1.779534	1.840317
H	-0.223301	-1.122099	2.719258
H	0.220861	-2.770087	2.102512
H	0.418010	-1.310881	1.042128
C	-2.694724	-2.384217	2.692213
H	-2.316069	-3.345076	3.066425
H	-2.526488	-1.578223	3.418851
H	-3.760782	-2.470781	2.445674
O	-2.295678	-0.537808	0.853111
S	-4.969610	1.597284	-0.407321
C	-5.211700	-0.169885	-0.660063
H	-4.349224	-0.693528	-0.224283
H	-6.154554	-0.466155	-0.179822
H	-5.274769	-0.335347	-1.743187
C	-4.754591	1.556242	1.380377
H	-5.708280	1.272112	1.846109
H	-3.955844	0.837332	1.613574
H	-4.477383	2.573162	1.686738
O	-3.586408	1.921216	-0.977908

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8. Copies of ^{1}H and ^{13}C NMR spectra

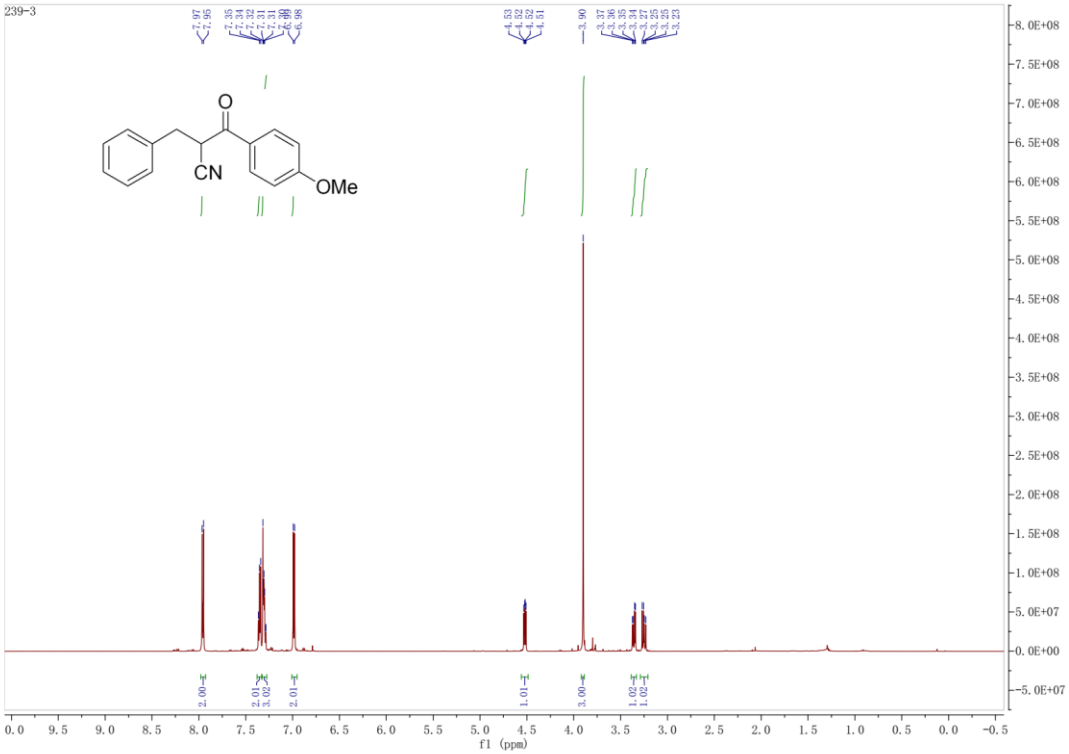

Figure S4. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3a**

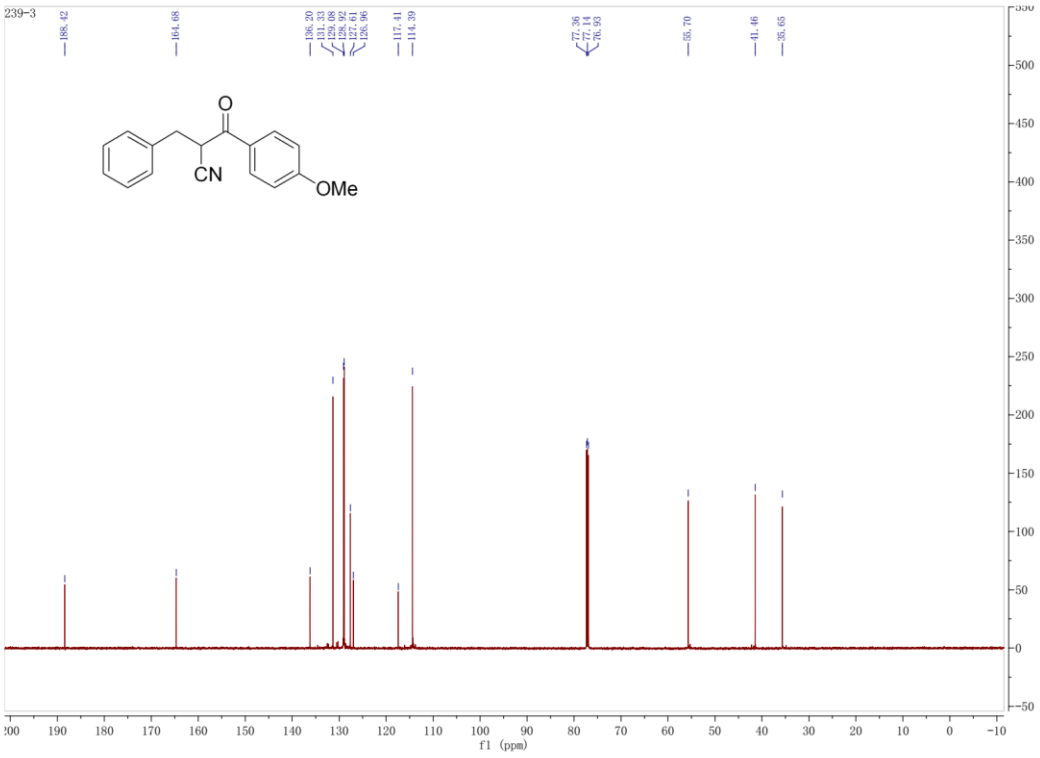

Figure S5. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3a**

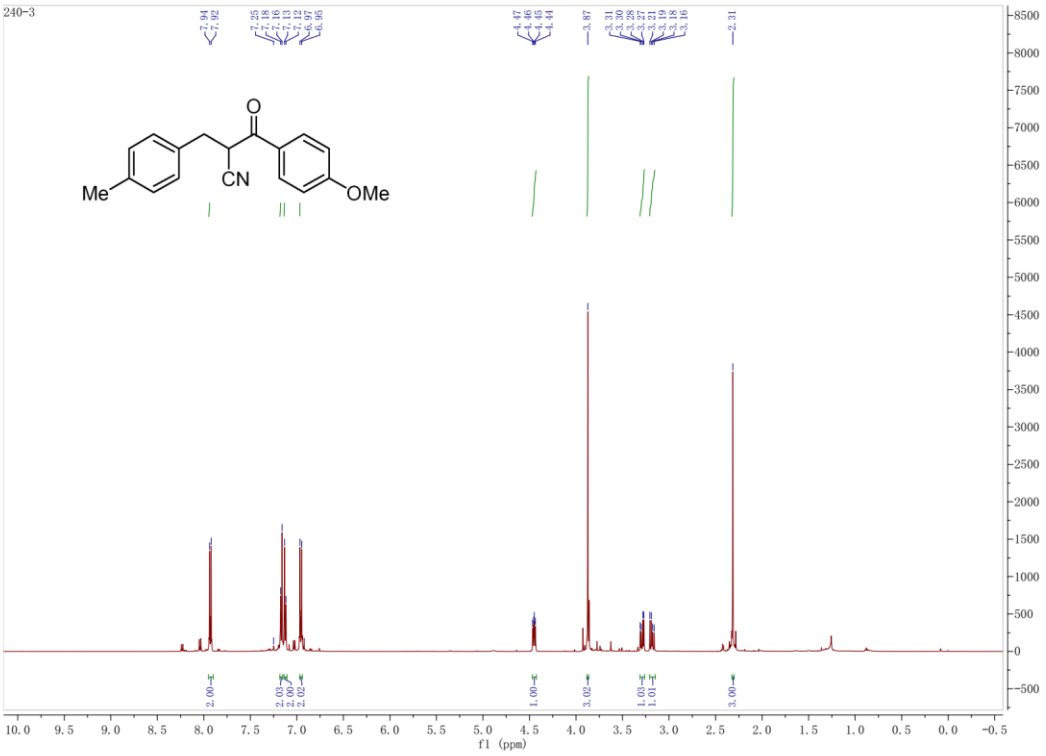

Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3b**

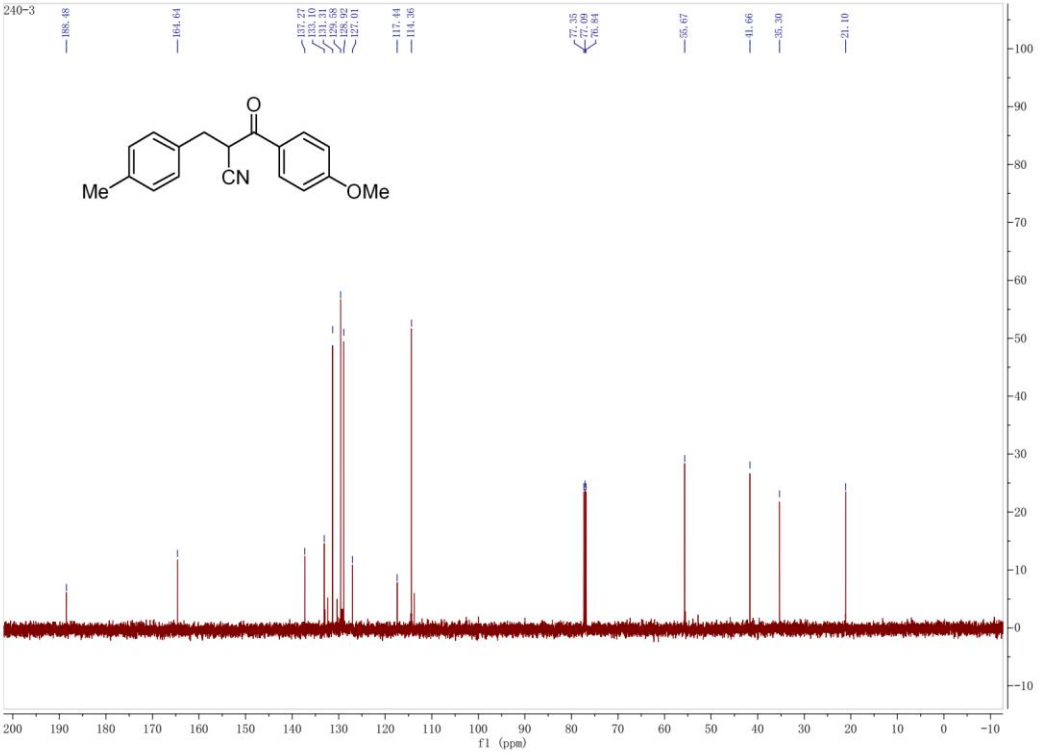

Figure S7. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3b**

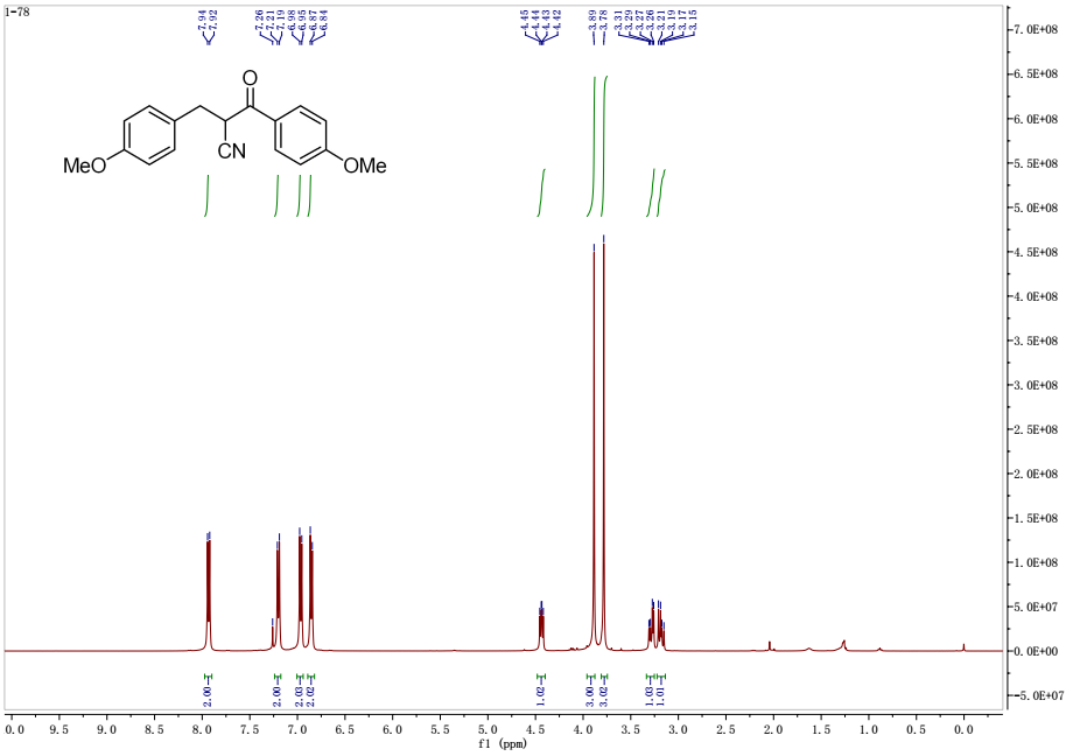

Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3c**

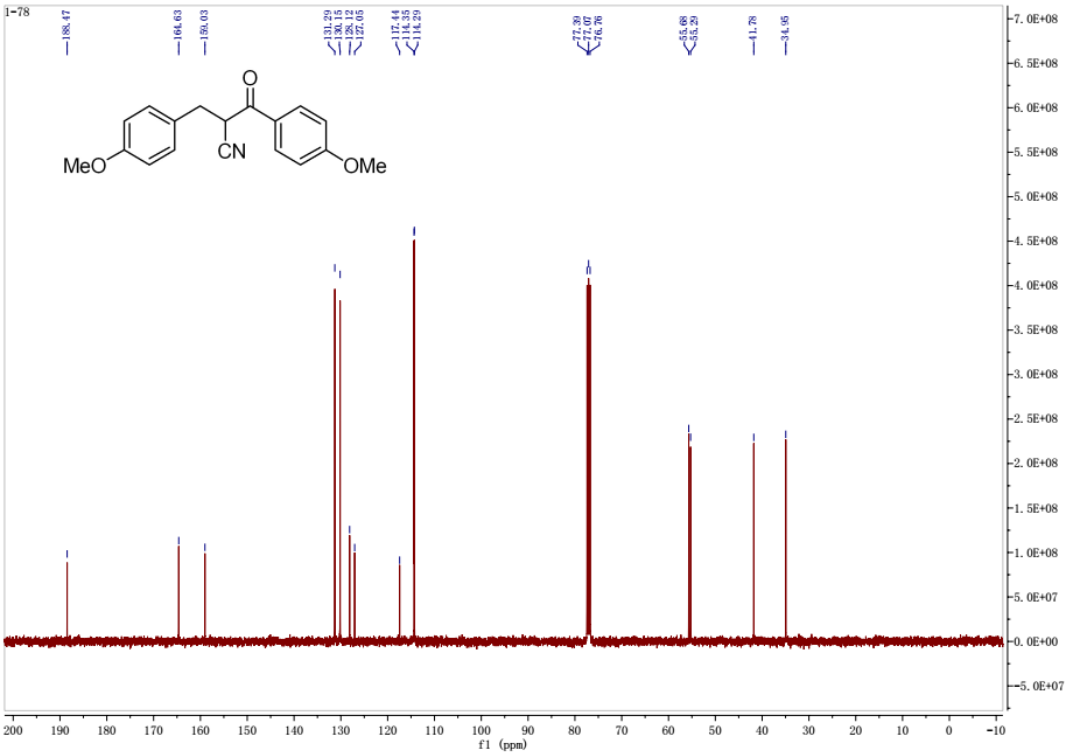

Figure S9. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3c**

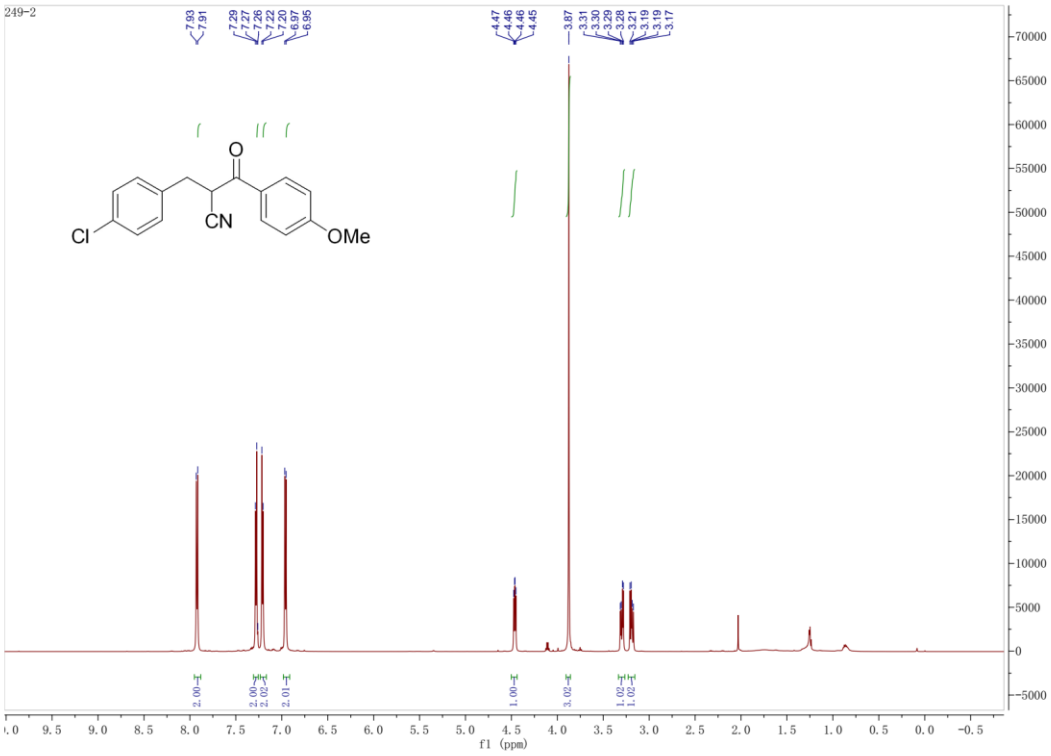

Figure S10. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3d**

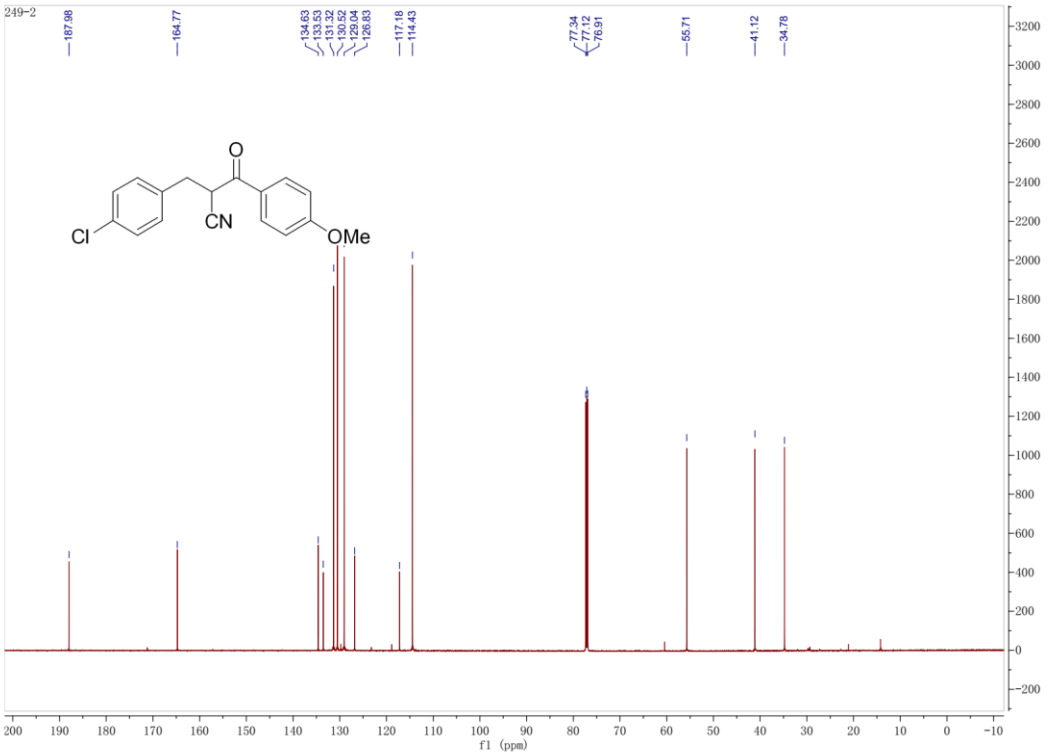

Figure S11. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3d**

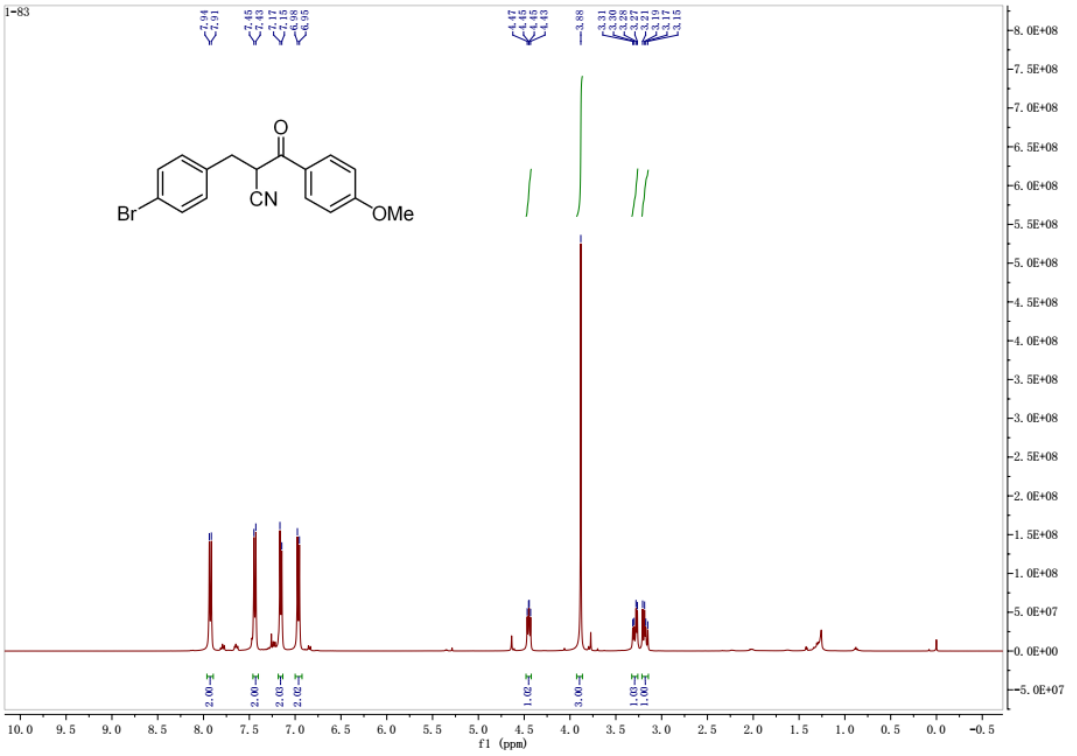

Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3e**

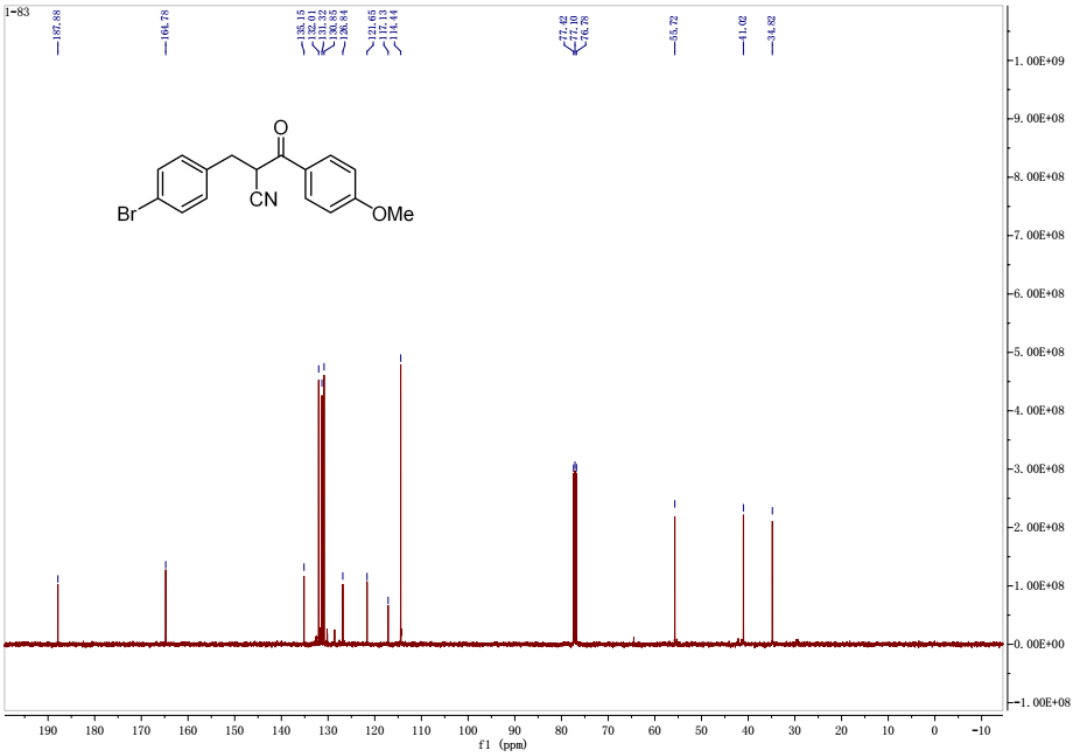

Figure S13. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3e**

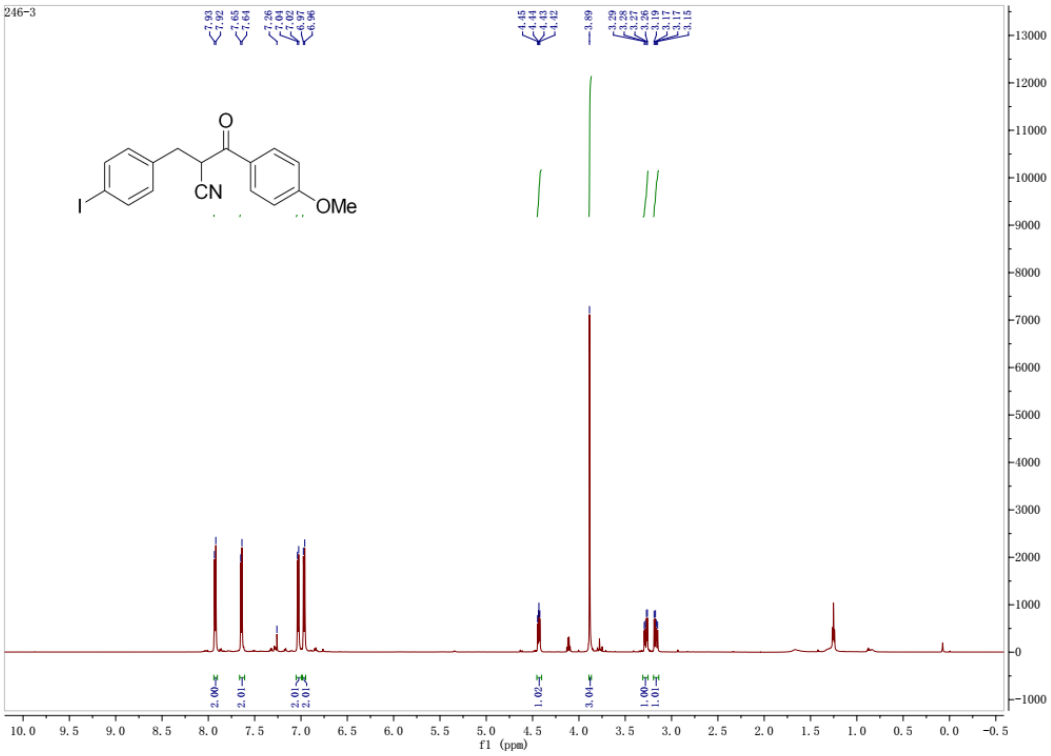

Figure S14. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3f**

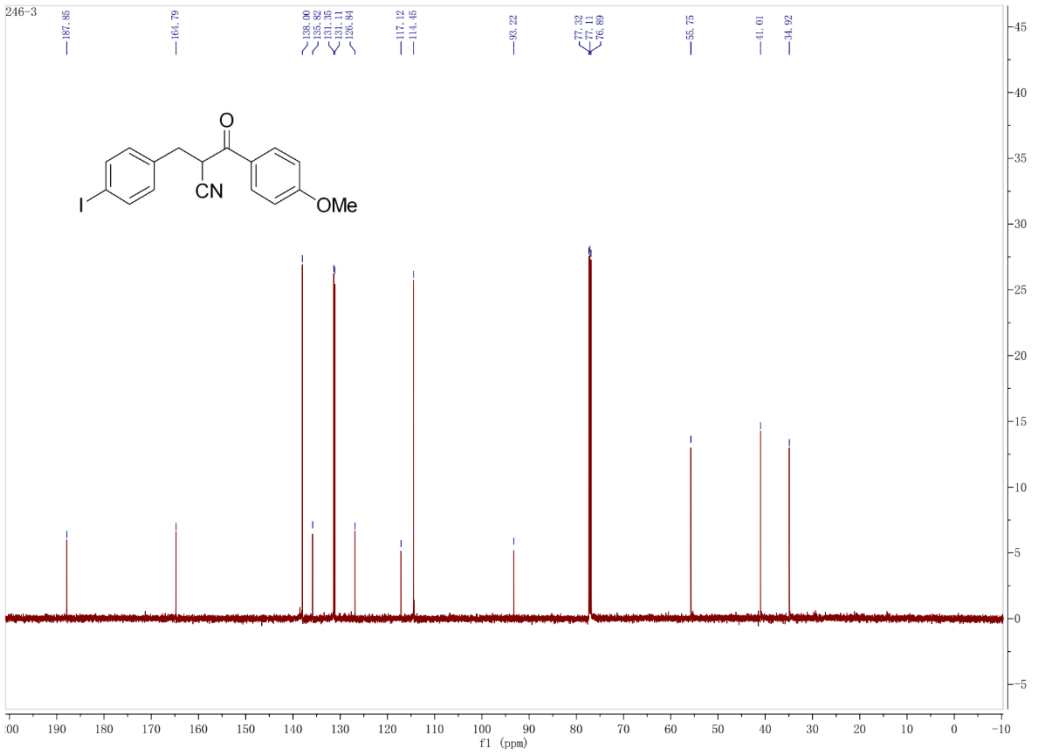

Figure S15. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3f**

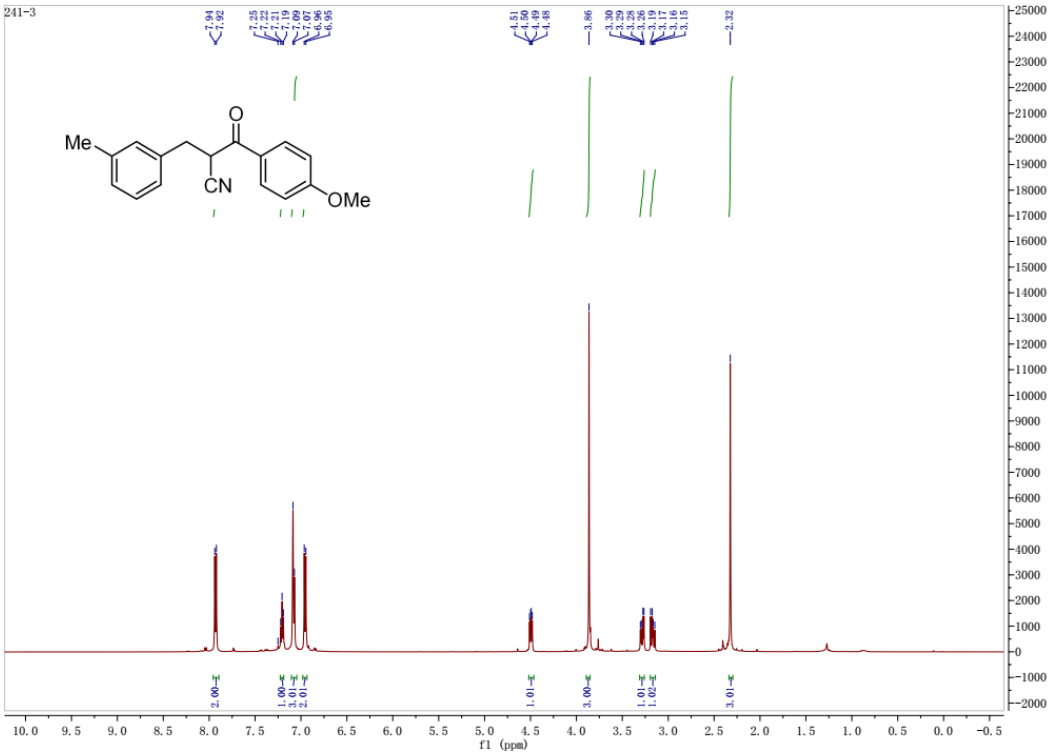

Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3g**

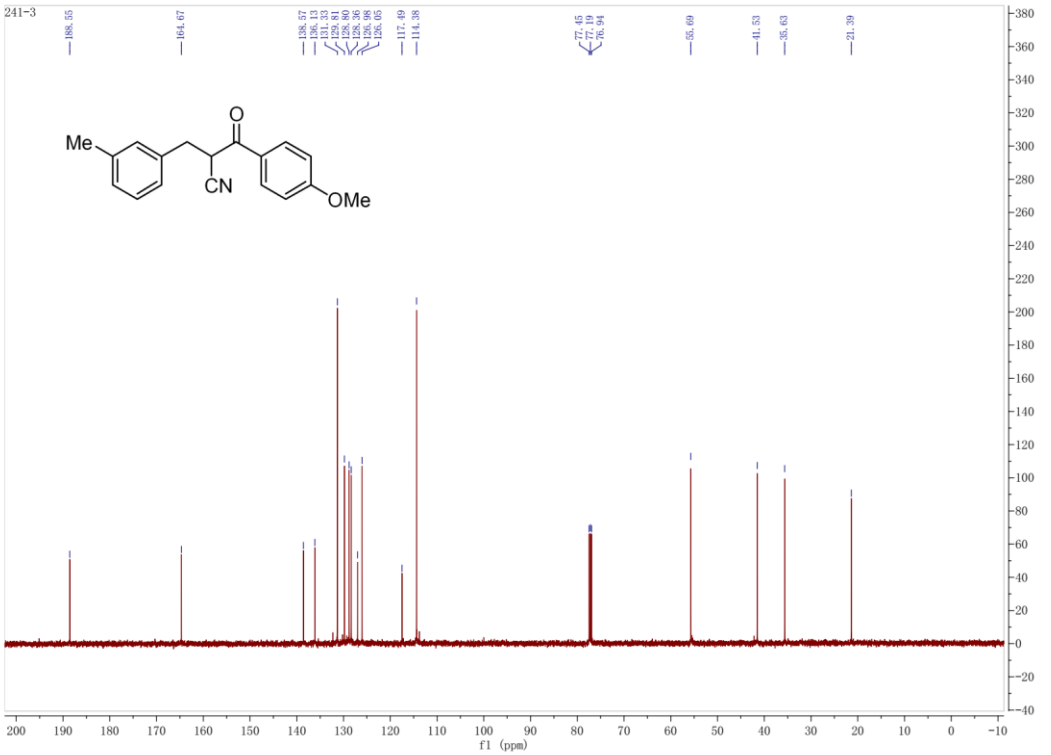

Figure S17. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3g**

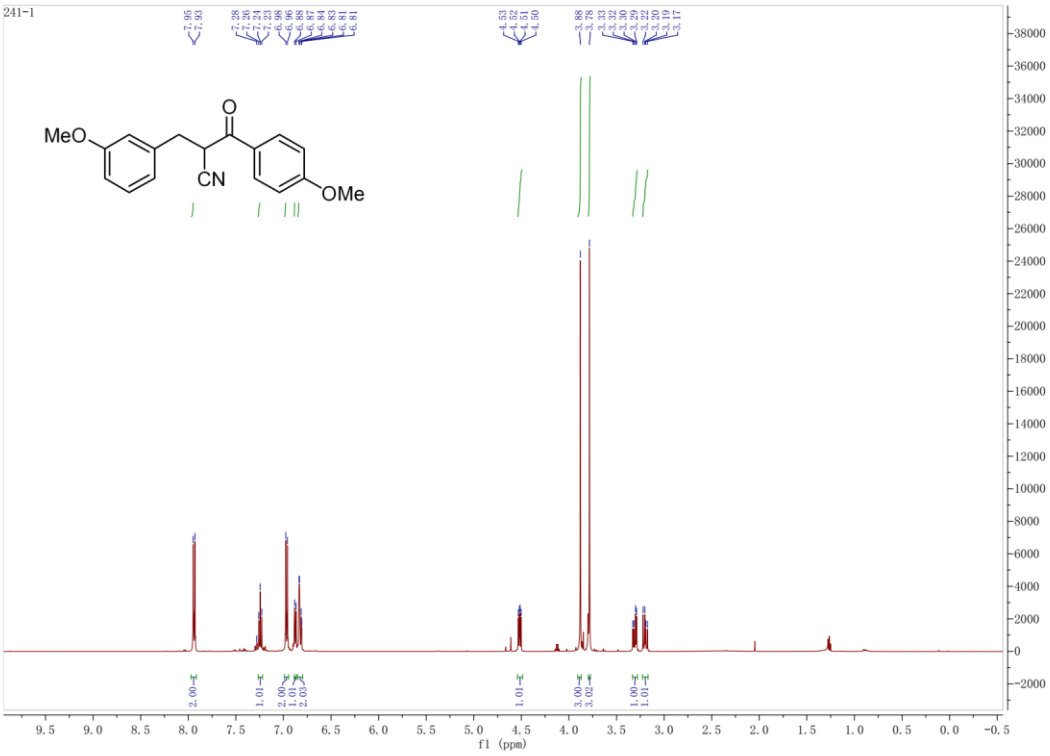

Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3h**

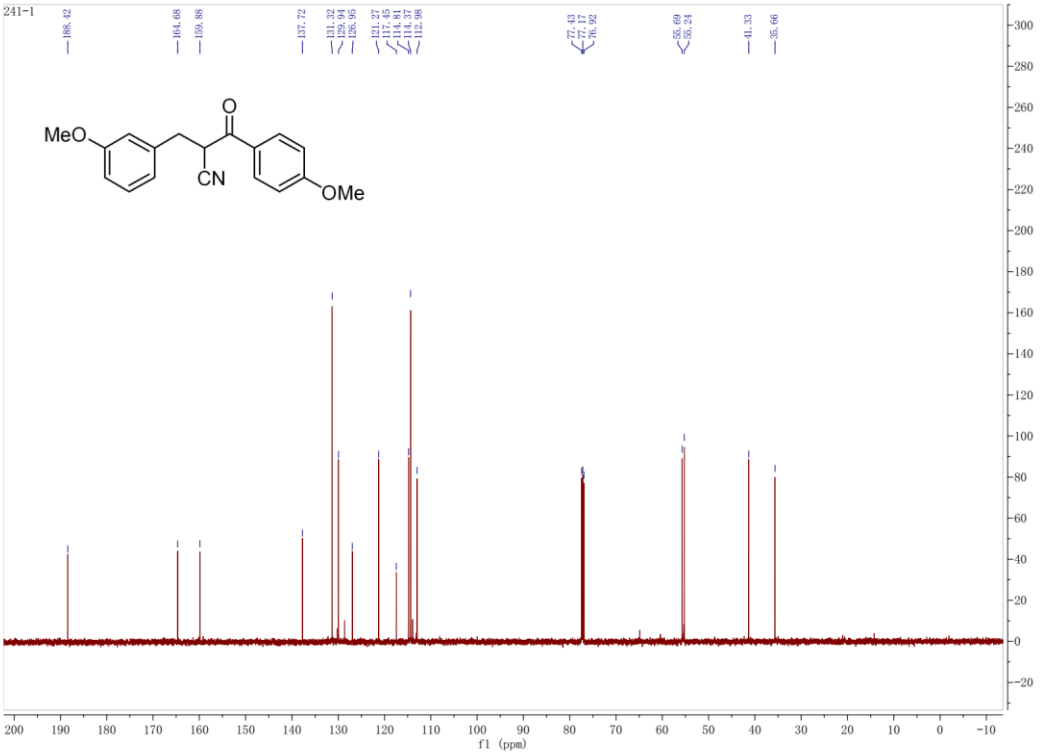

Figure S19. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3h**

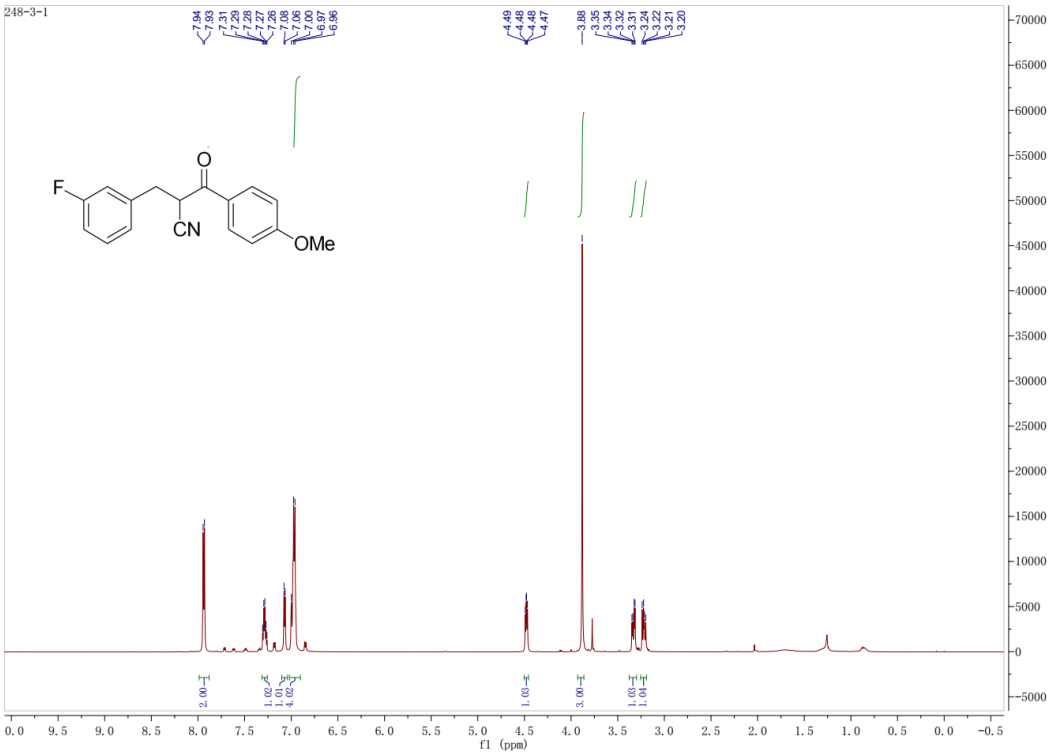

Figure S20. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3i**

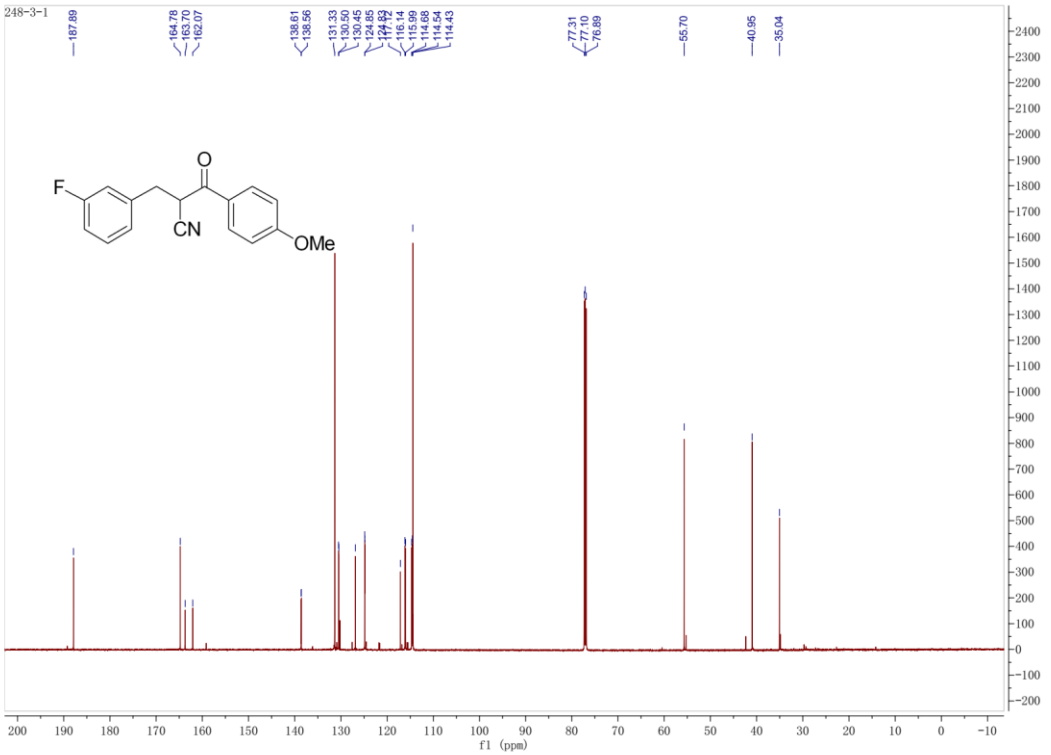

Figure S21. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3i**

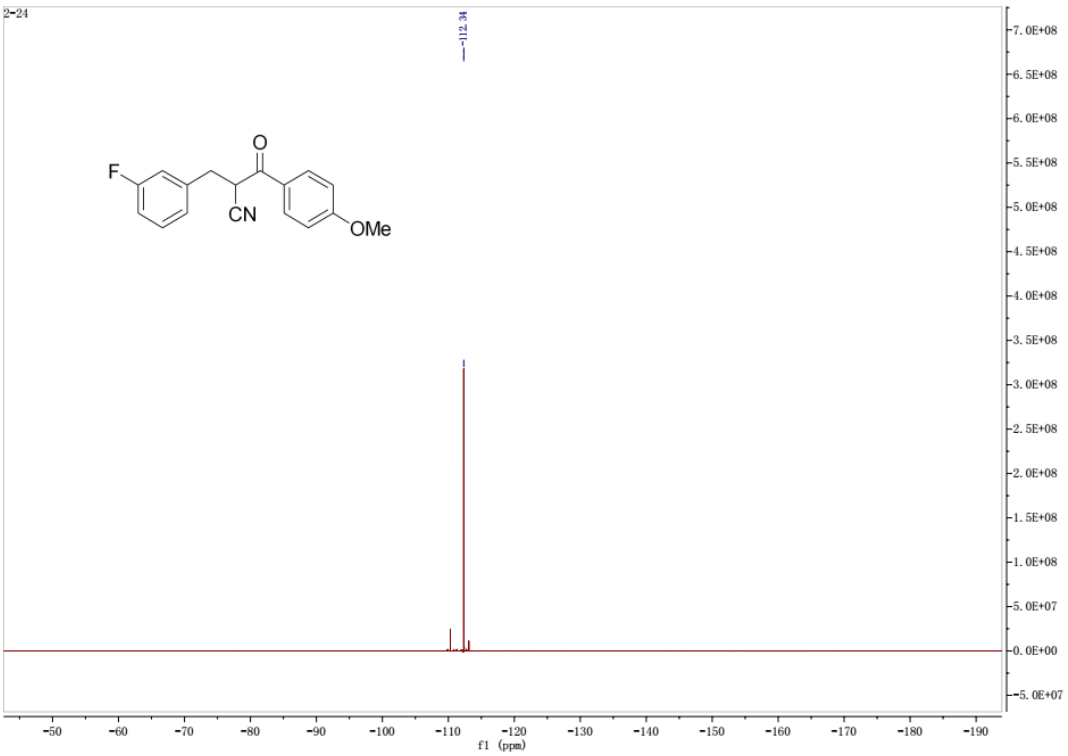

Figure S22. ^{19}F NMR (376 MHz, $CDCl_3$) of Compound **3i**

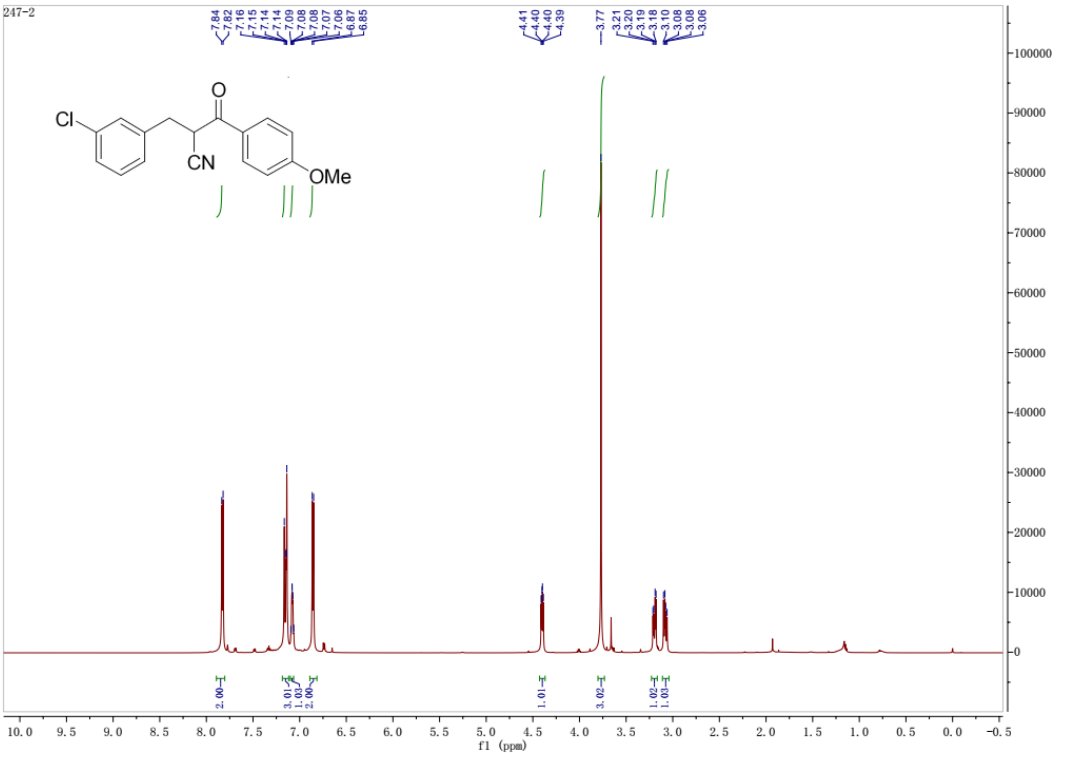

Figure S23. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3j**

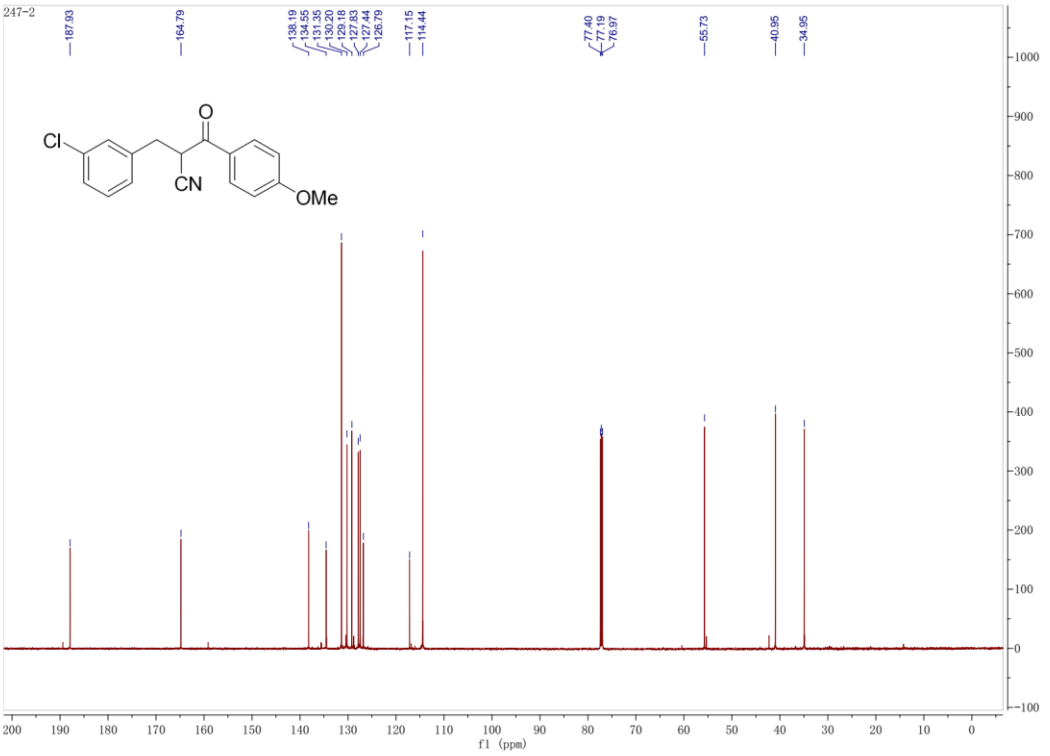

Figure S24. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3j**

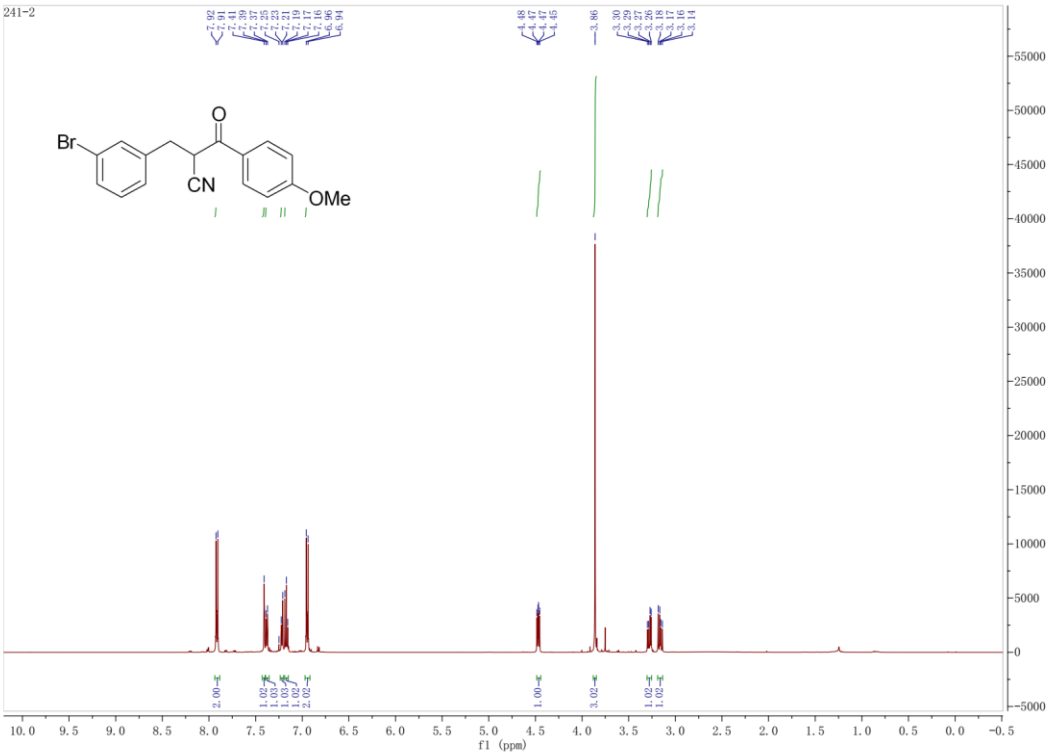

Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3k**

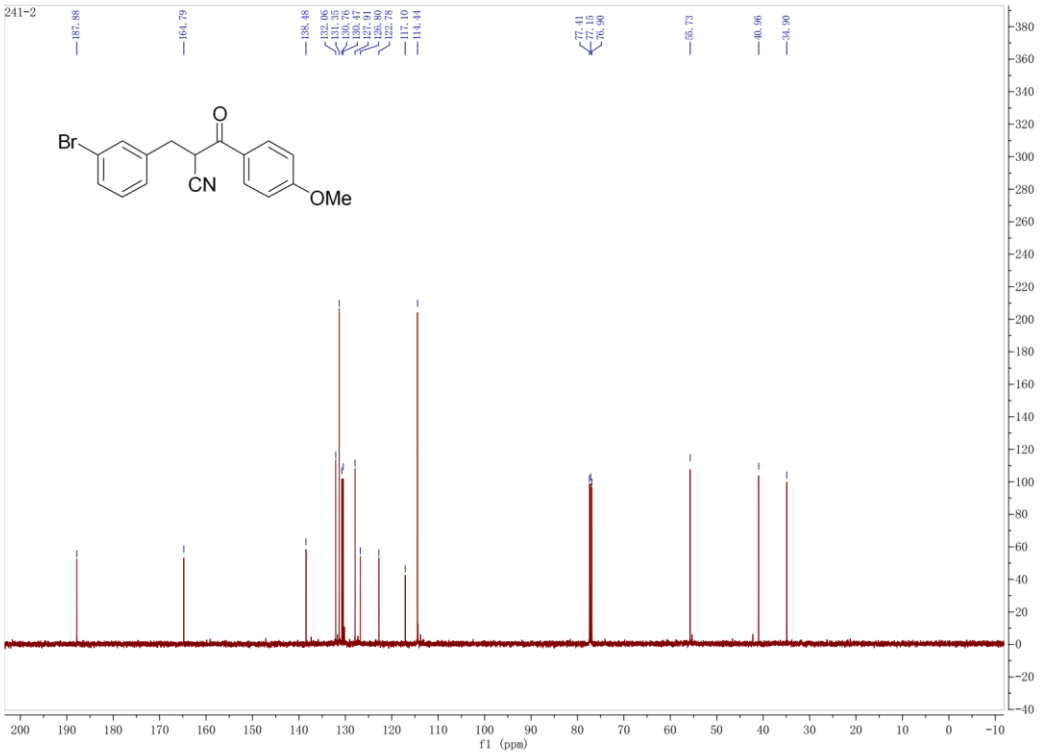

Figure S26. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3k**

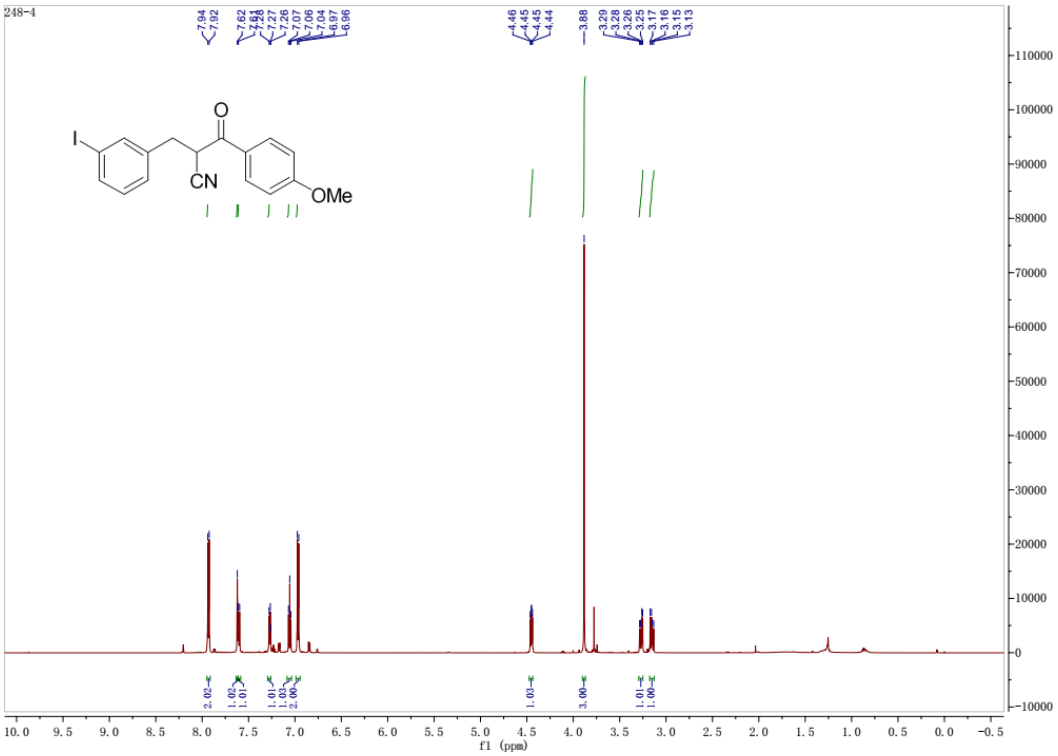

Figure S27. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3l**

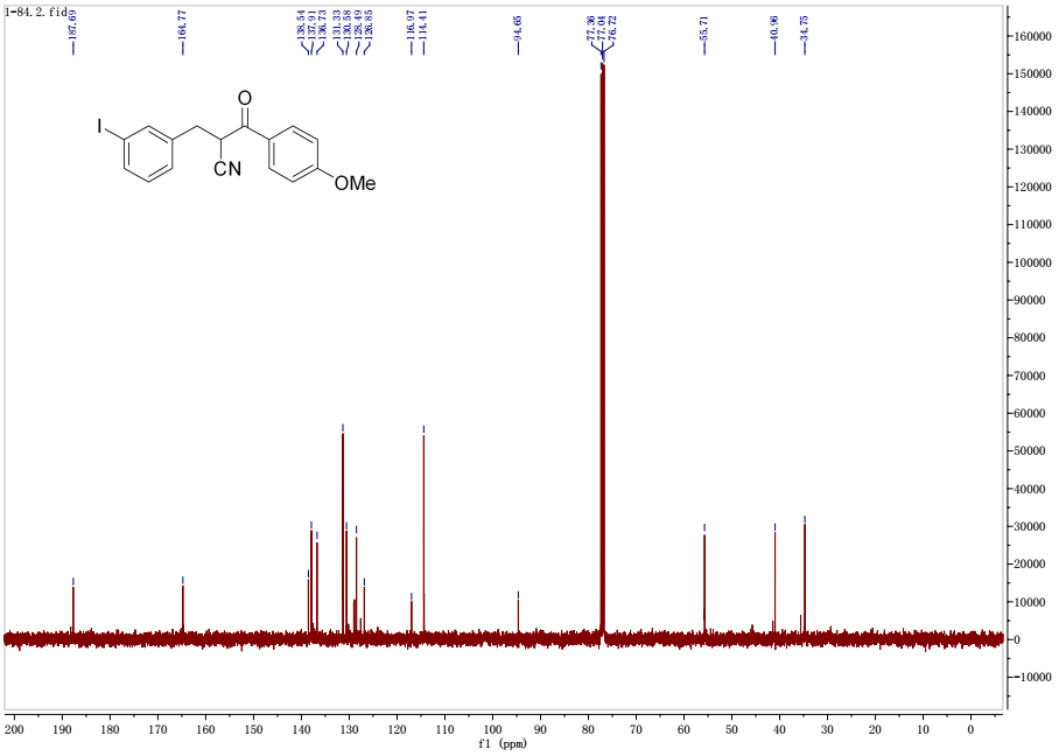

Figure S28. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3l**

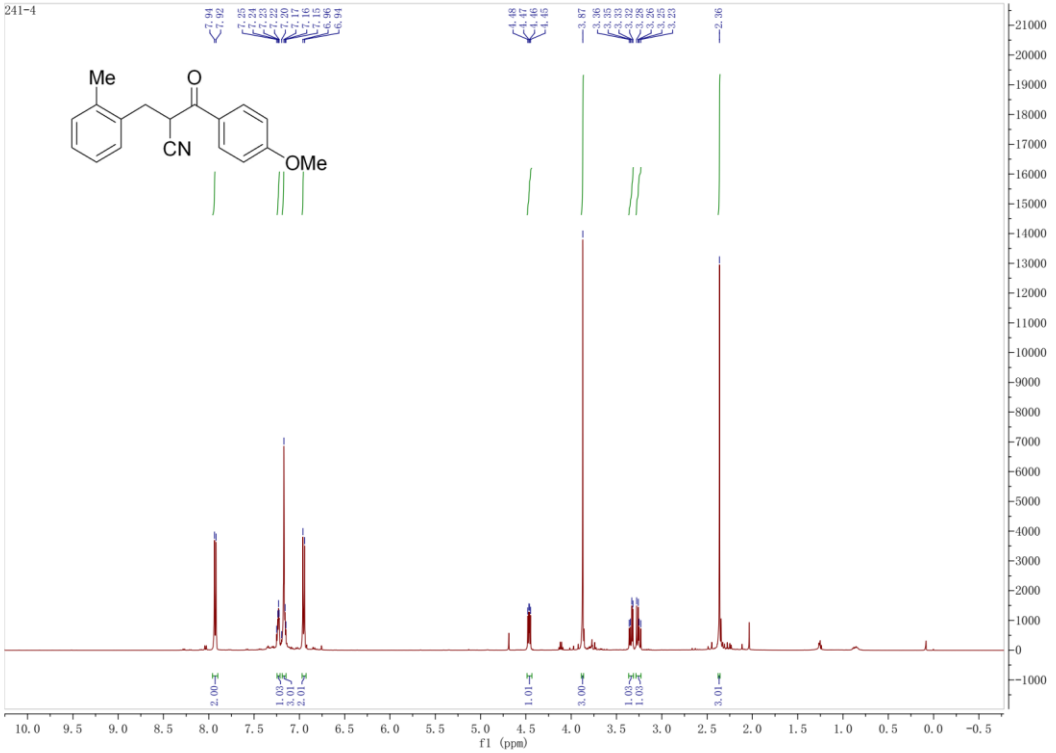

Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3m**

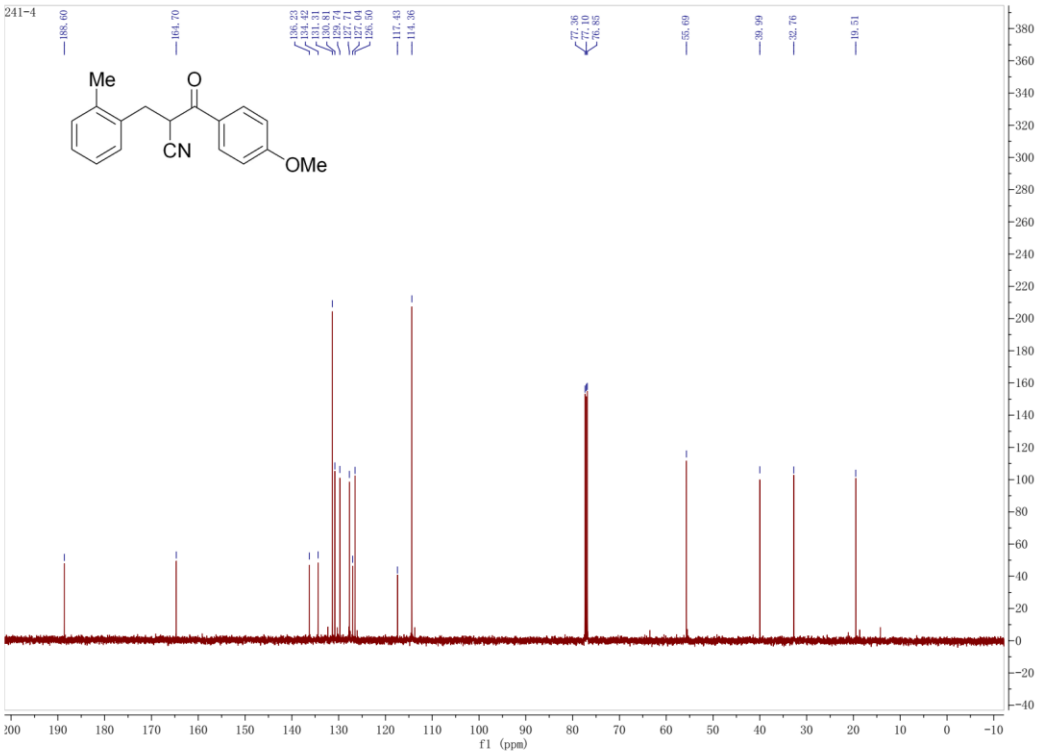

Figure S30. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3m**

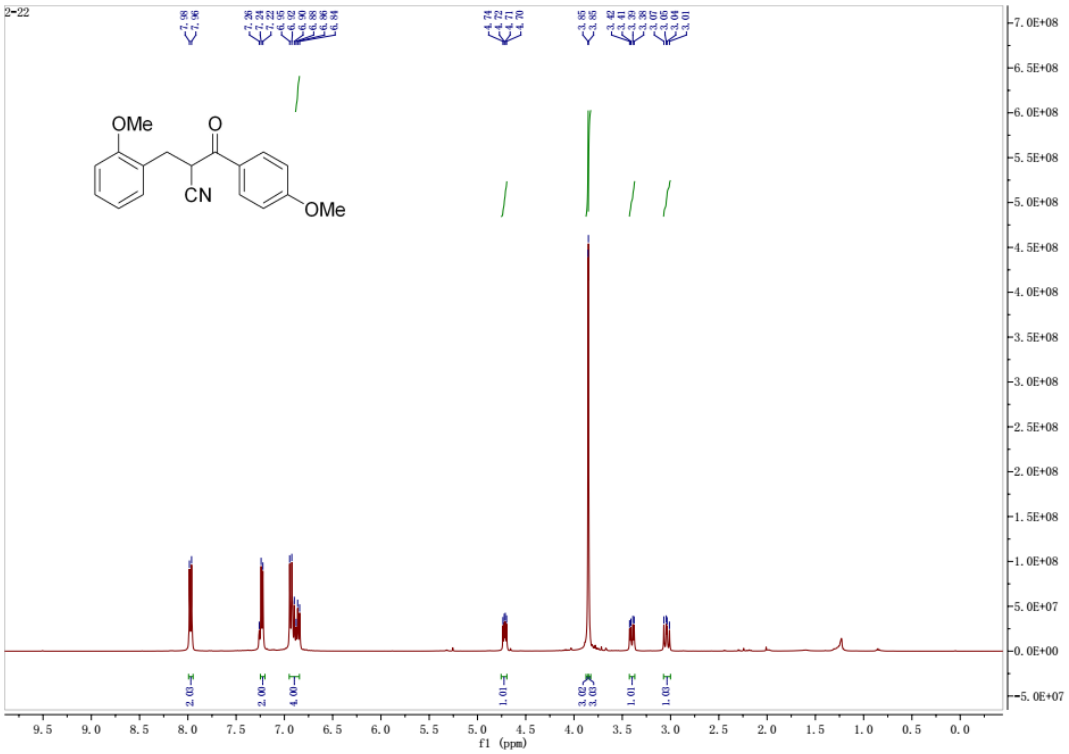

Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3n**

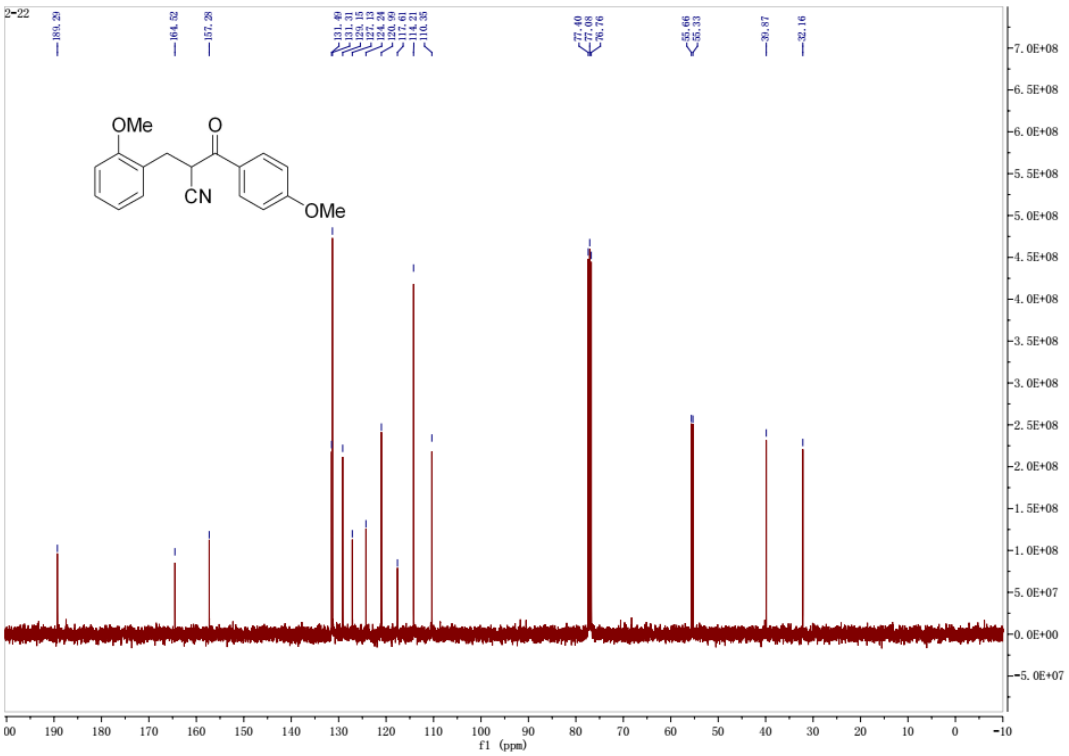

Figure S32. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3n**

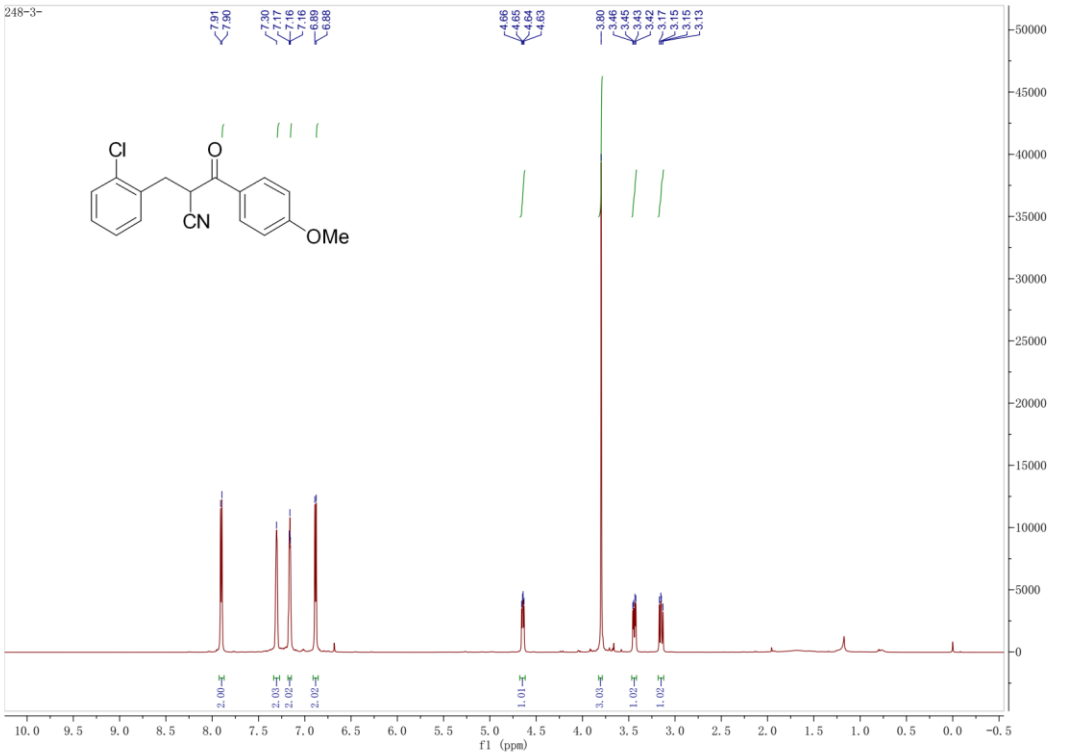

Figure S33. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3o**

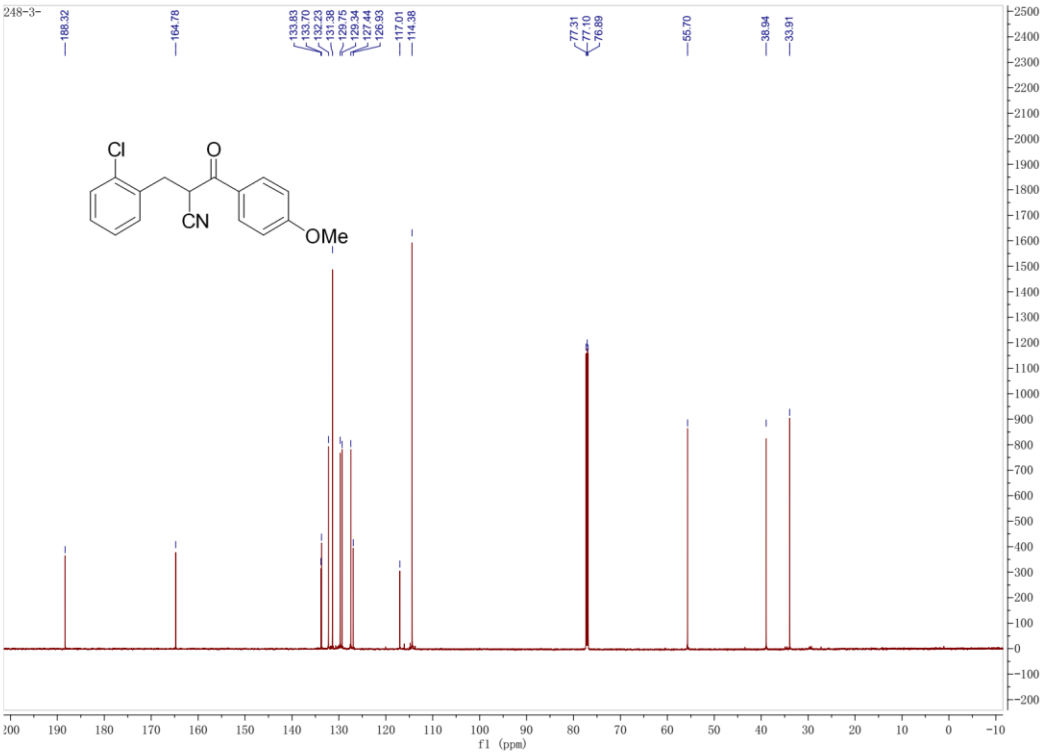

Figure S34. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3o**

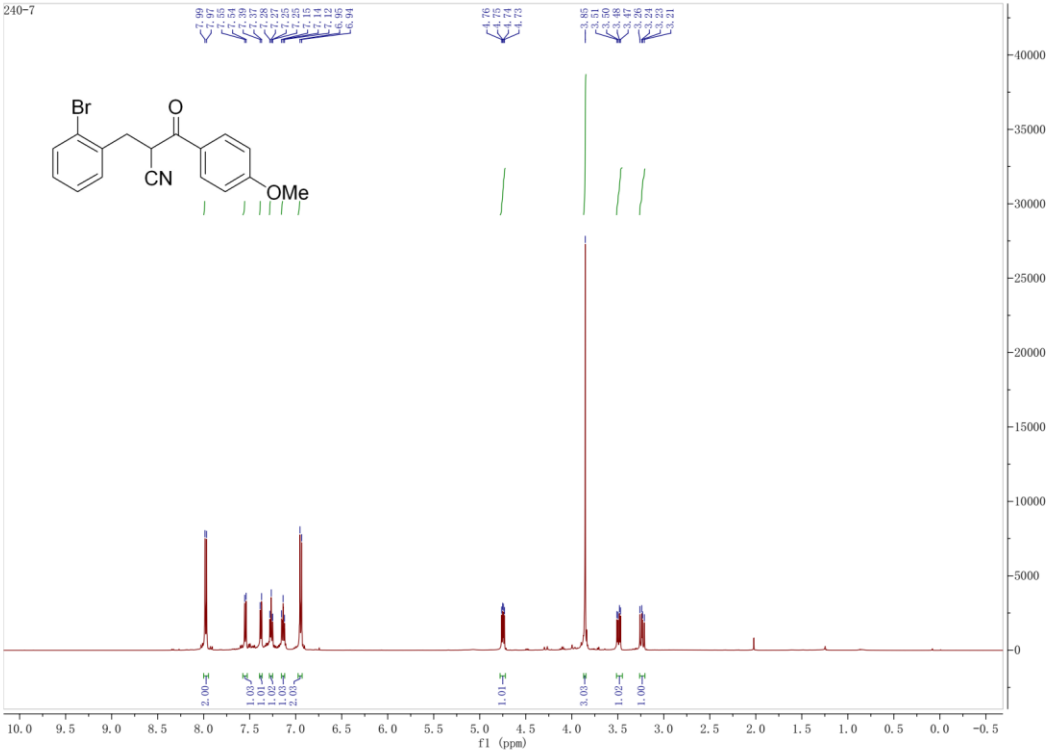

Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3p**

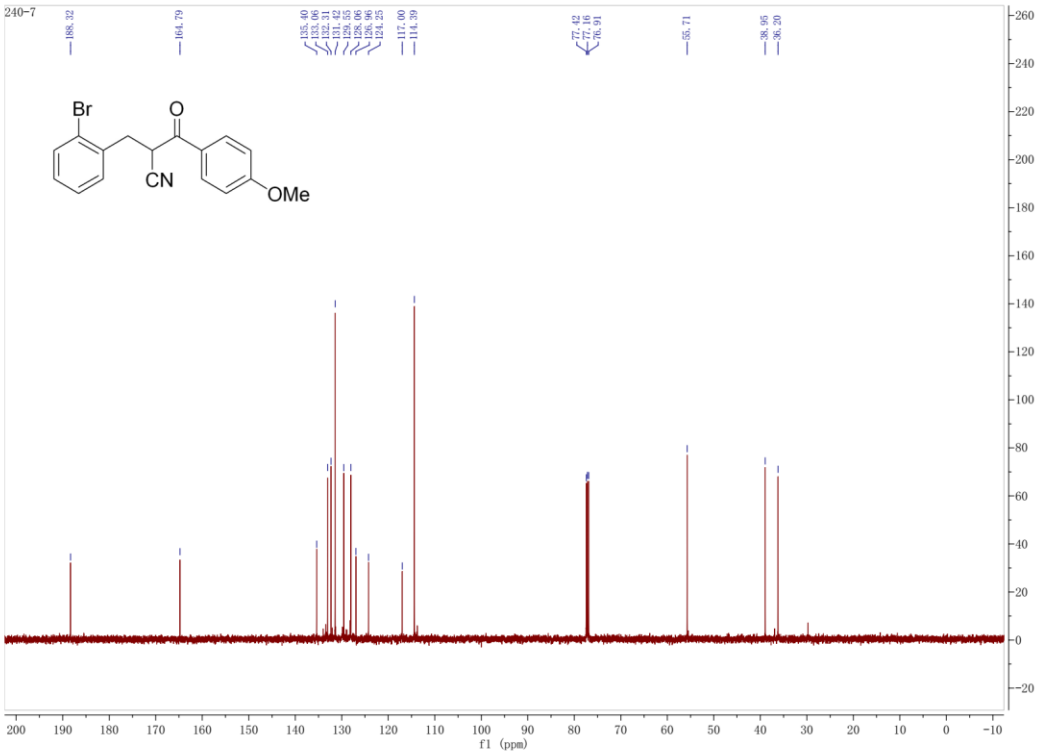

Figure S36. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3p**

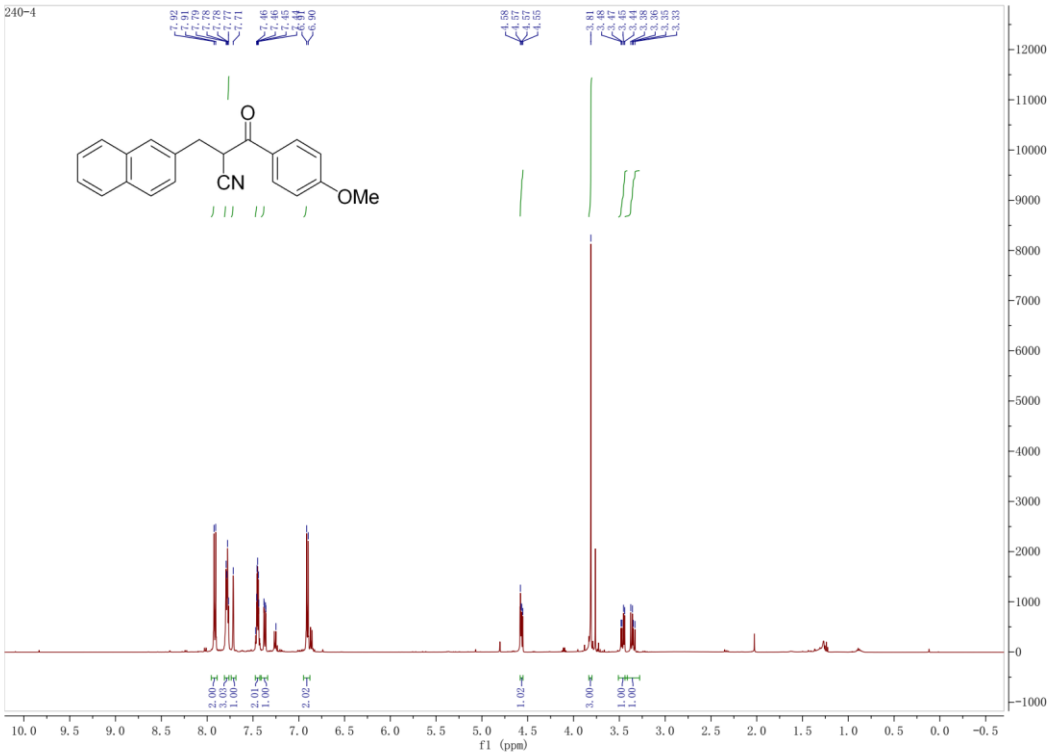

Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3q**

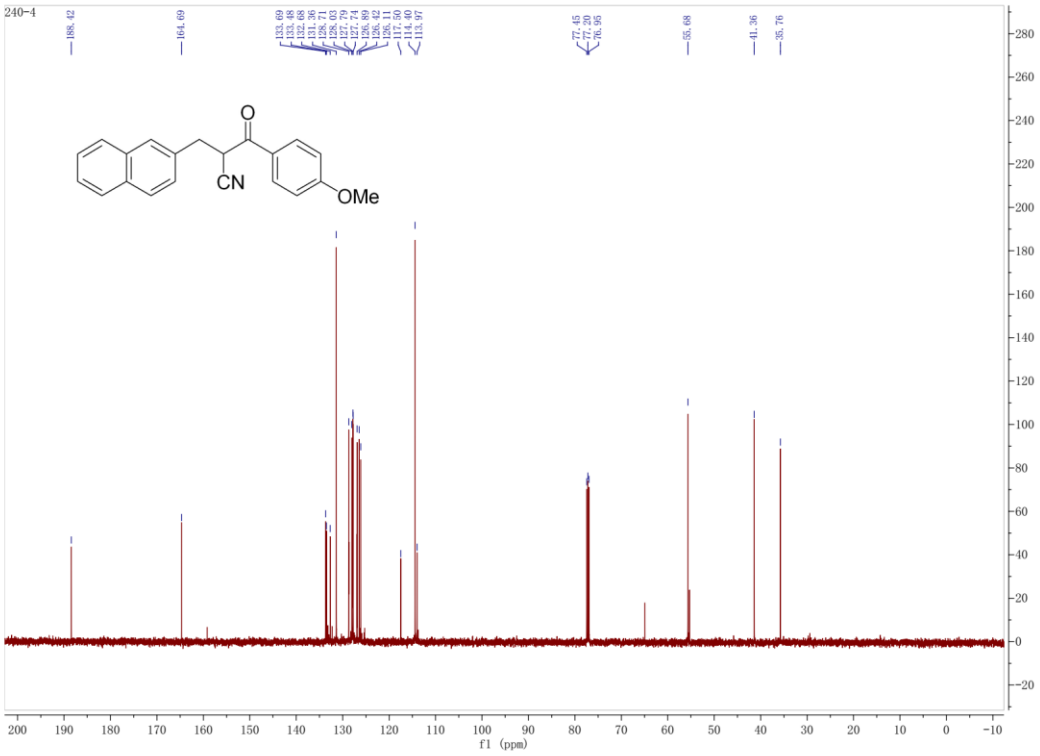

Figure S38. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3q**

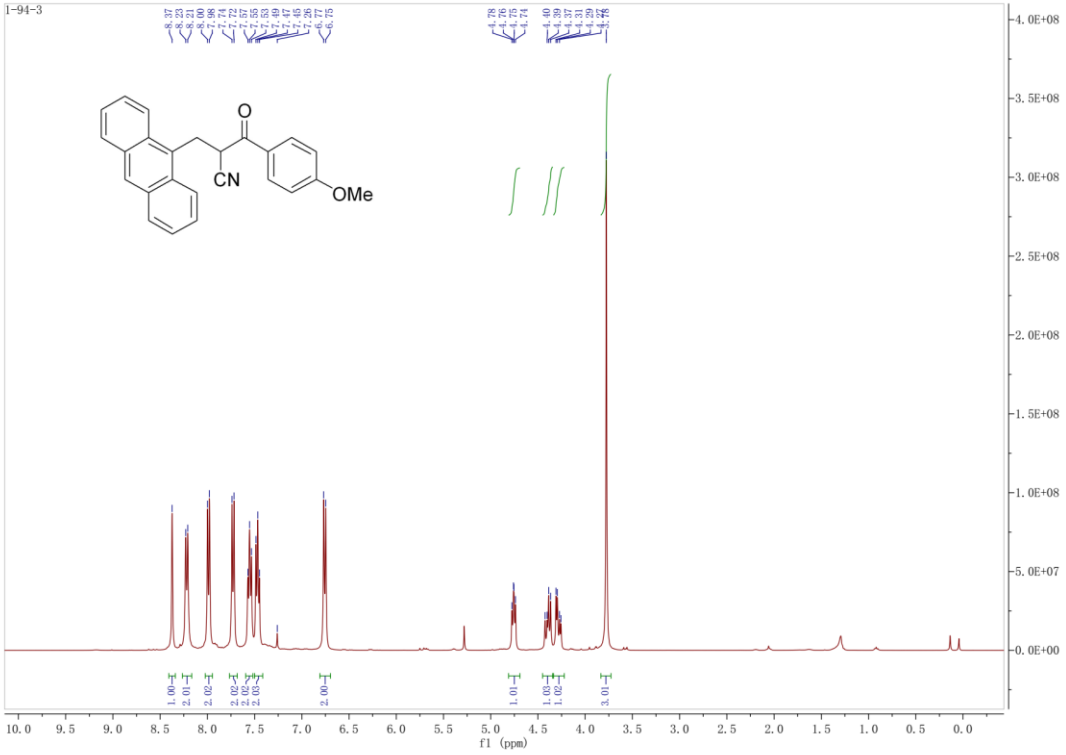

Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3r**

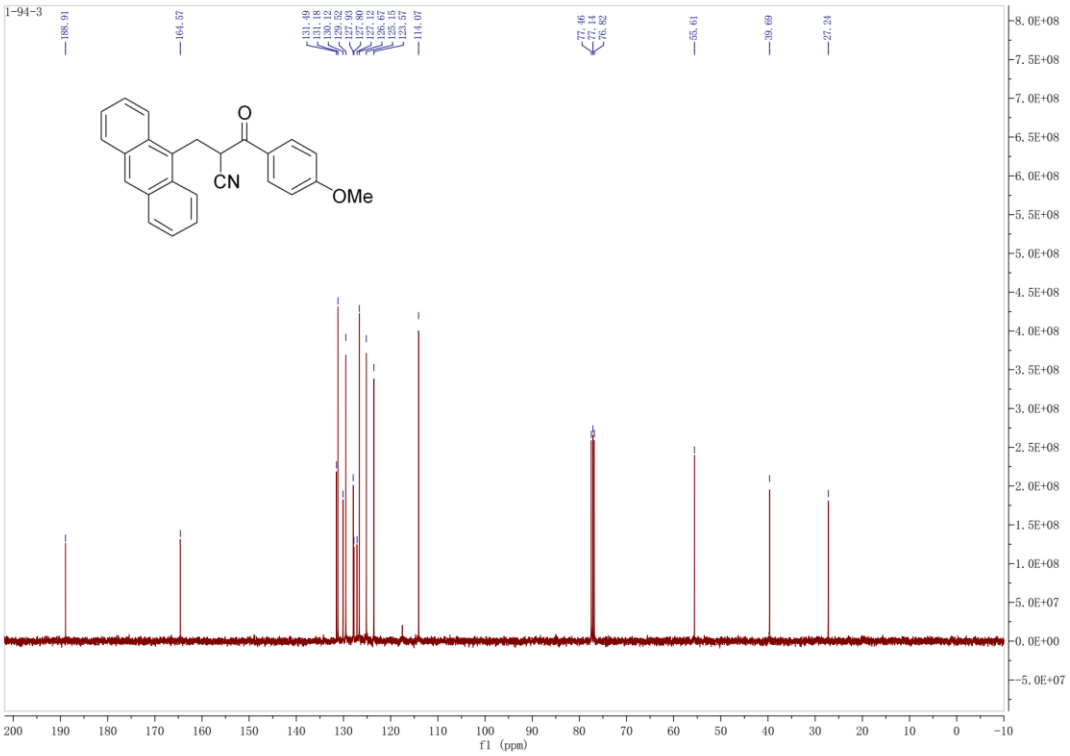

Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3r**

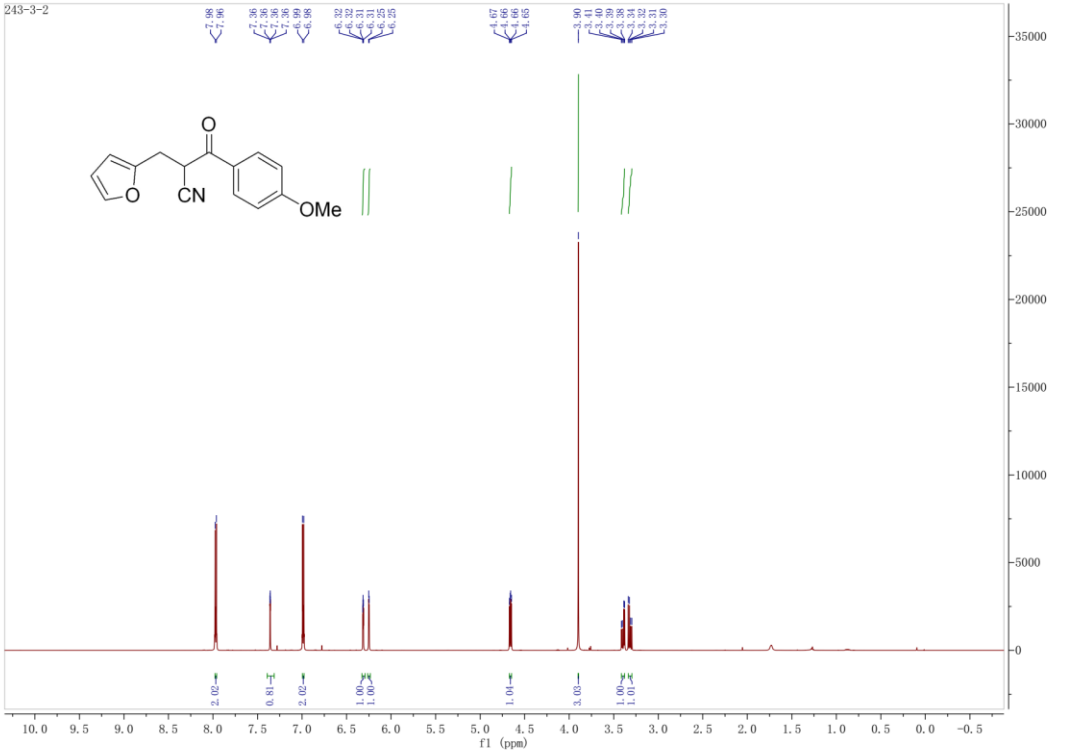

Figure S41. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3s**

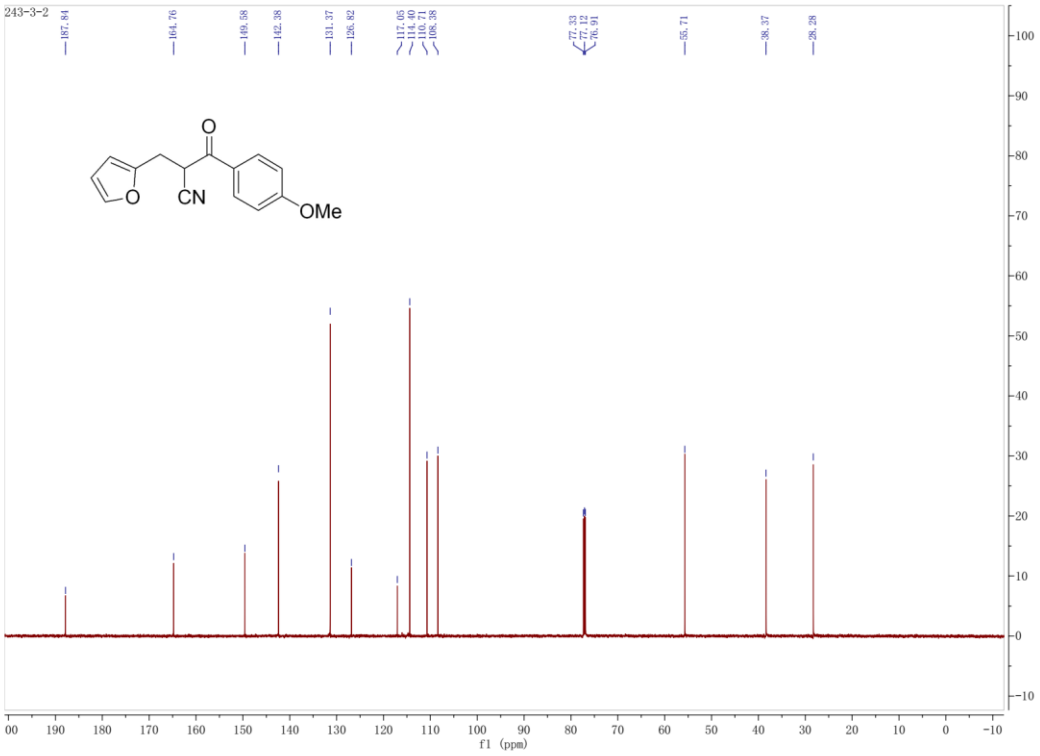

Figure S42. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3s**

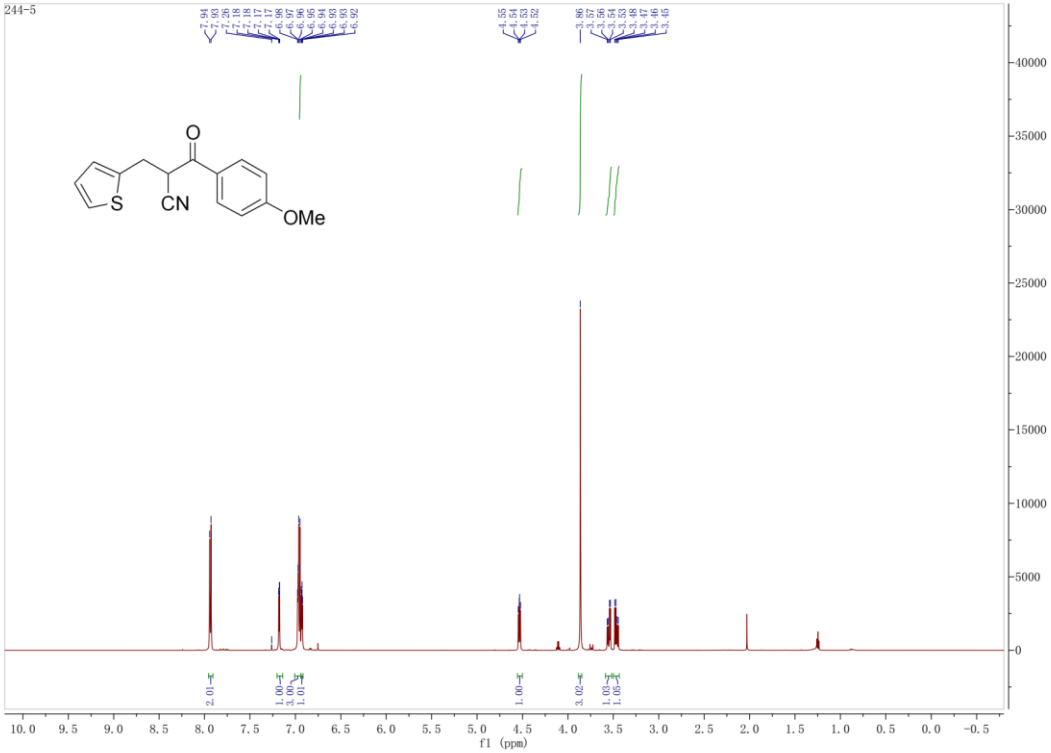

Figure S43. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3t**

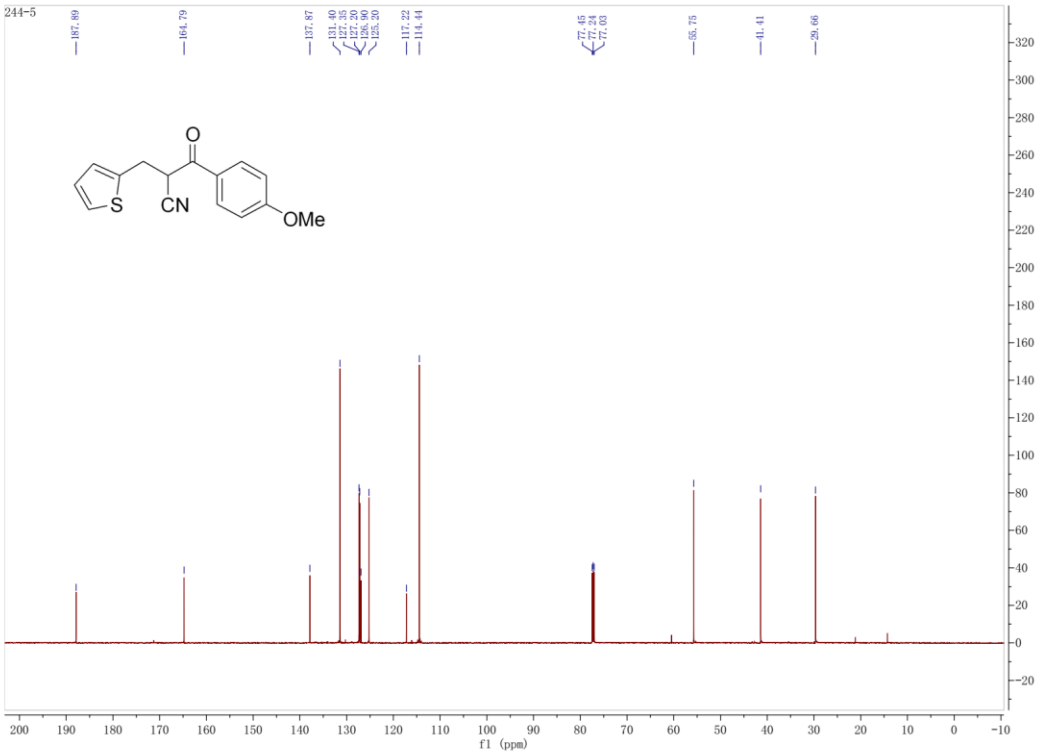

Figure S44. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3t**

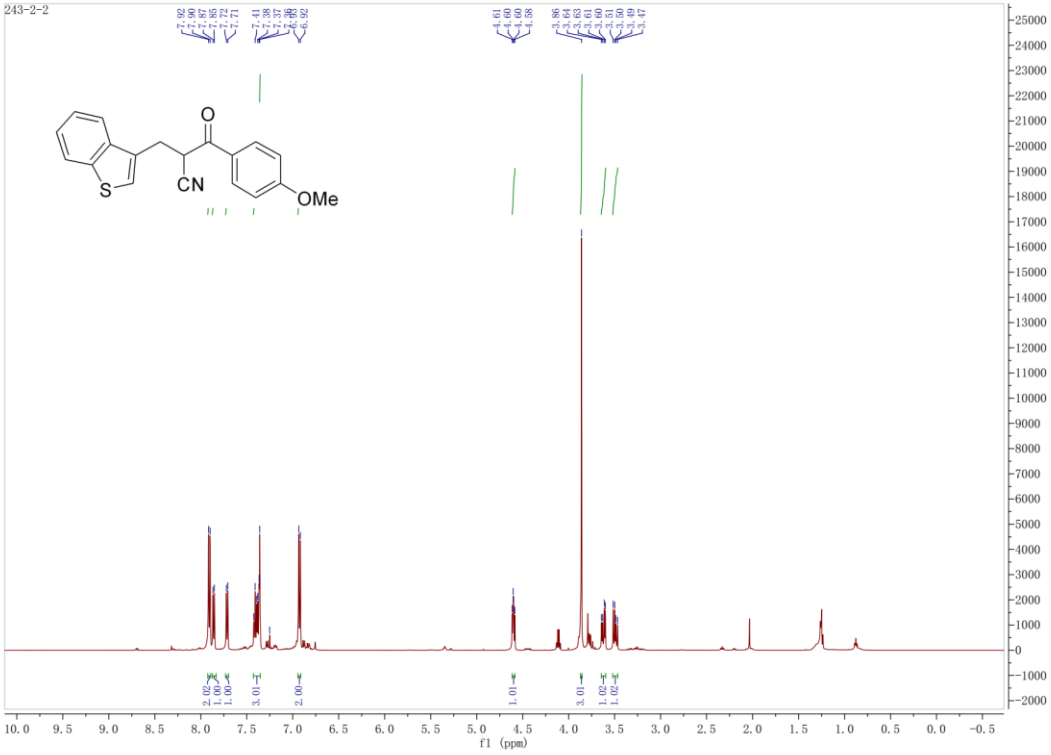

Figure S45. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **3u**

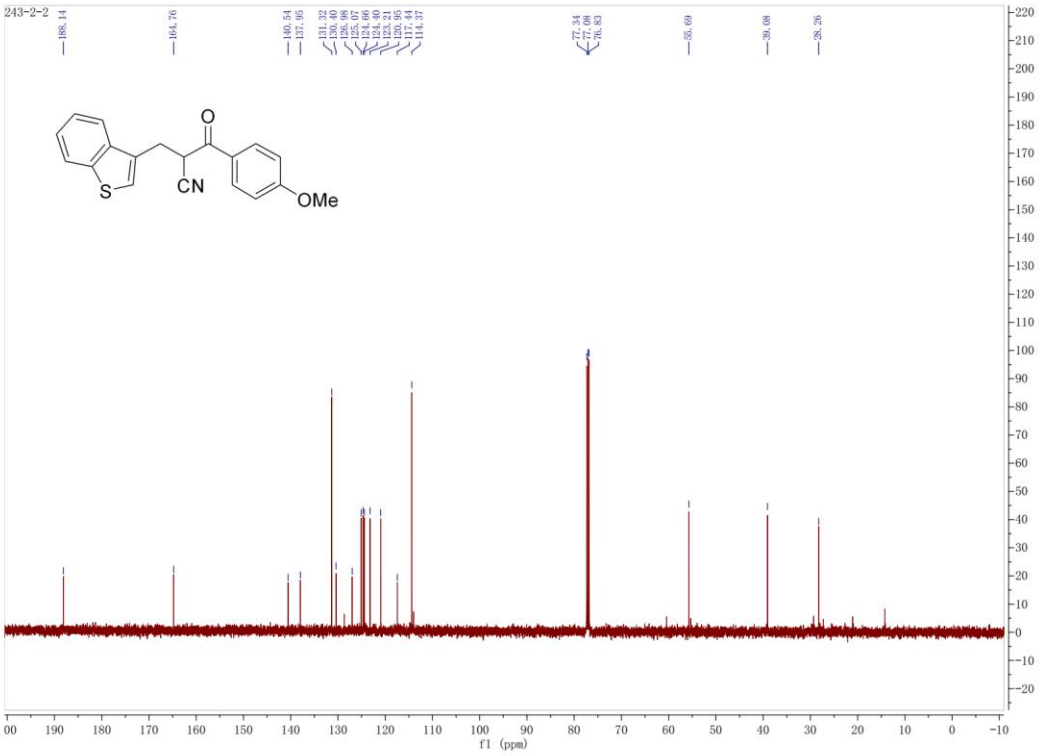

Figure S46. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **3u**

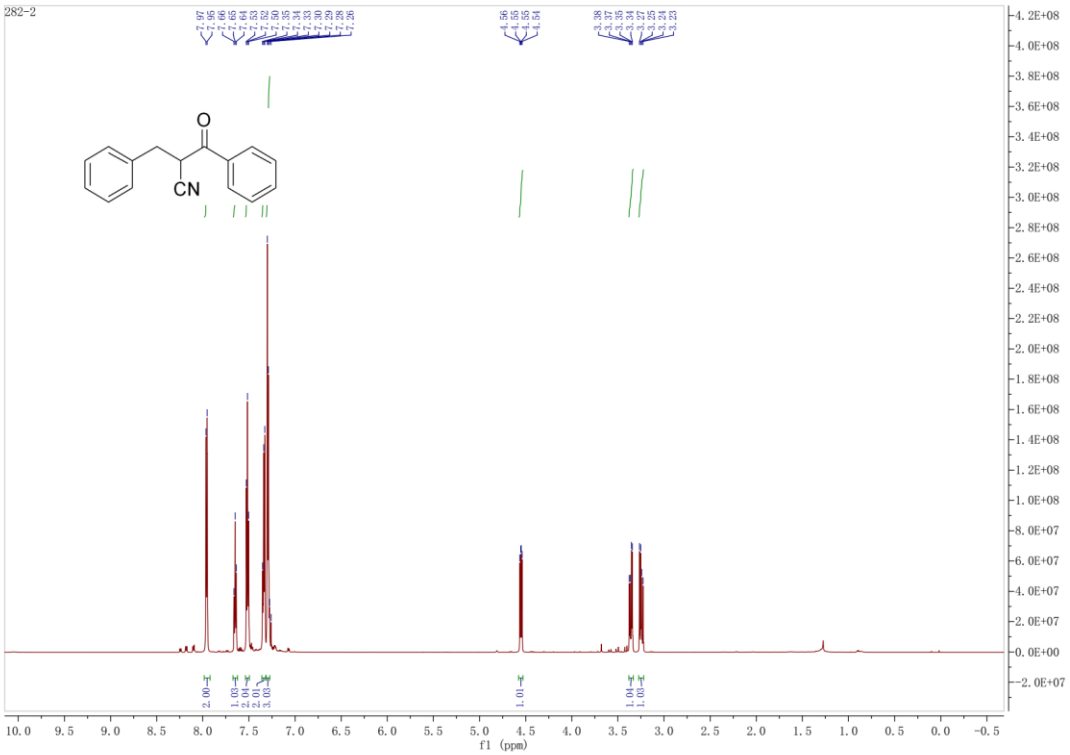

Figure S47. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3v**

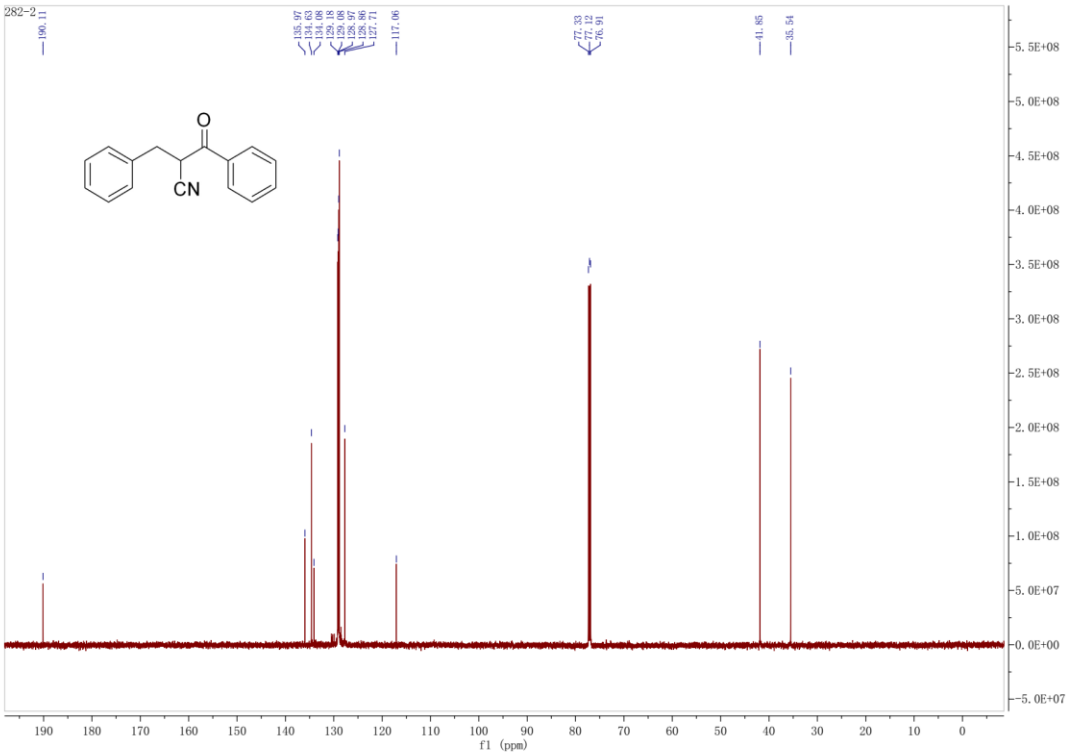

Figure S48. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3v**

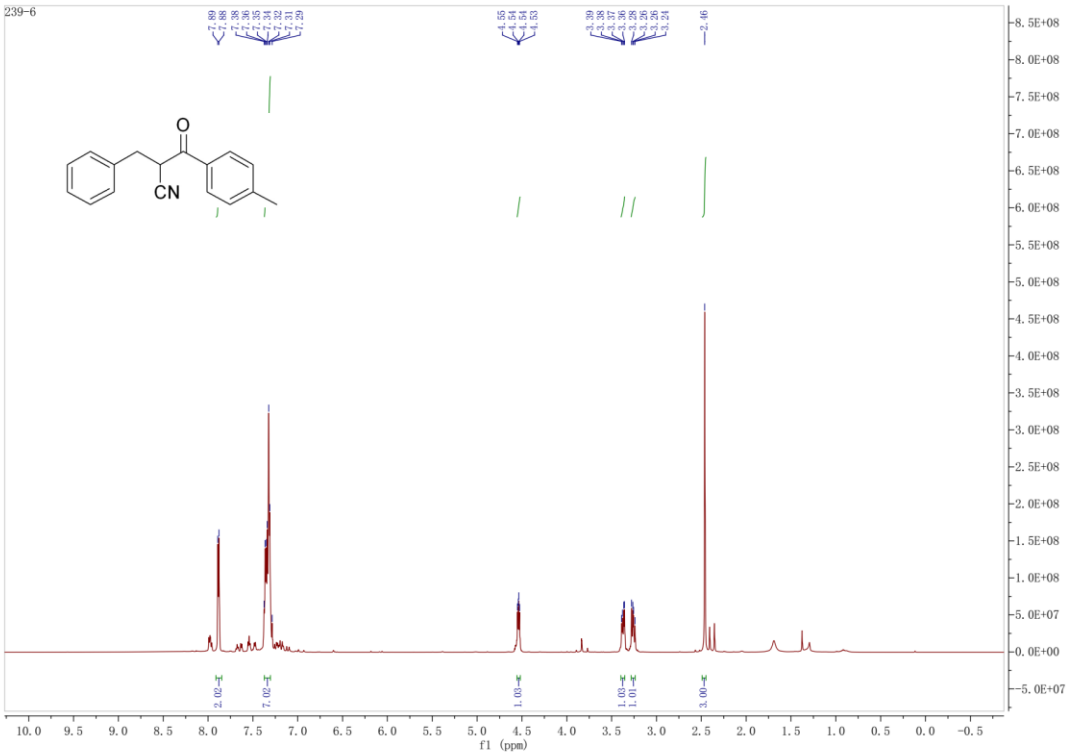

Figure S49. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **3w**

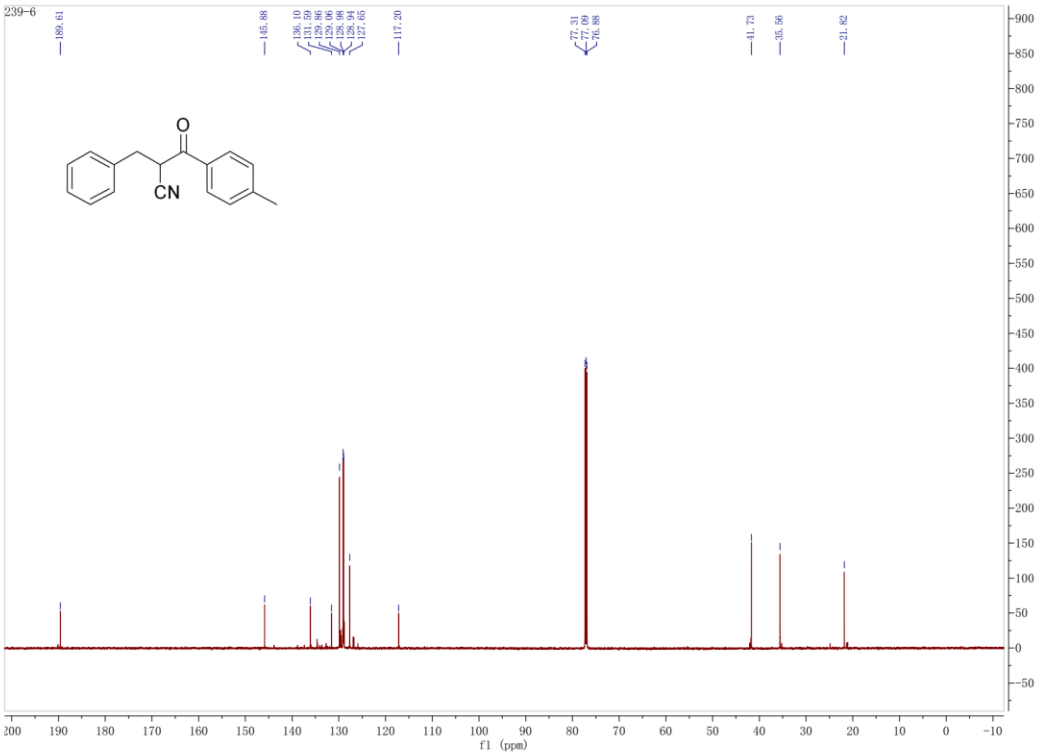

Figure S50. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **3w**

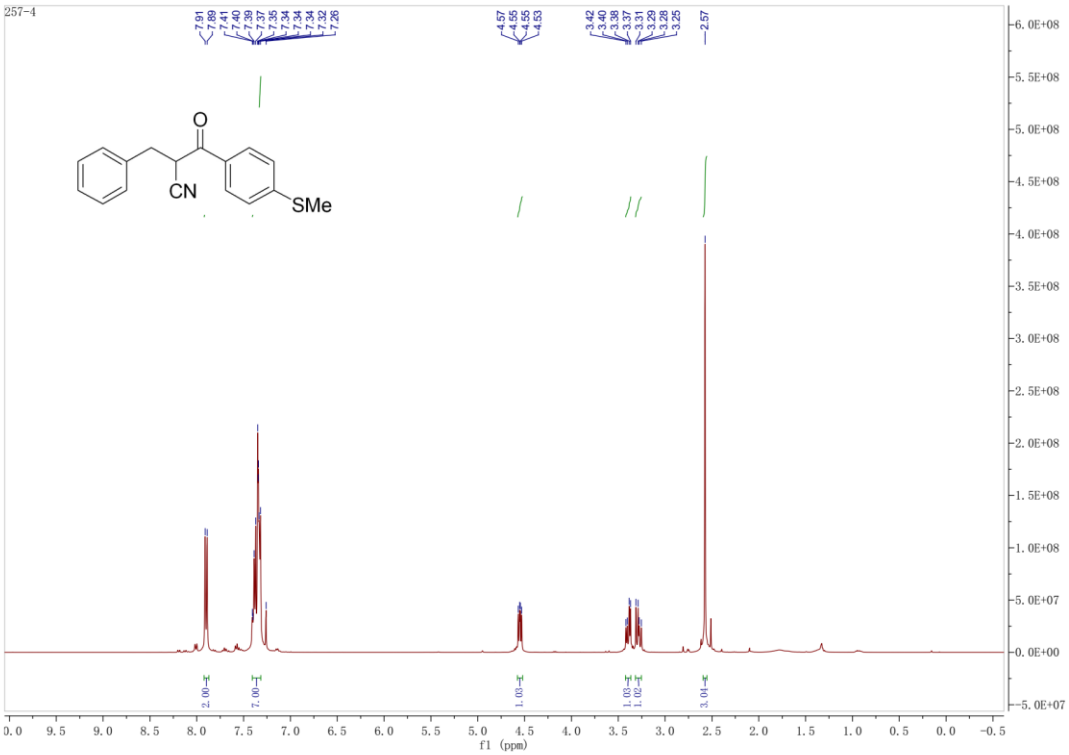

Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3x**

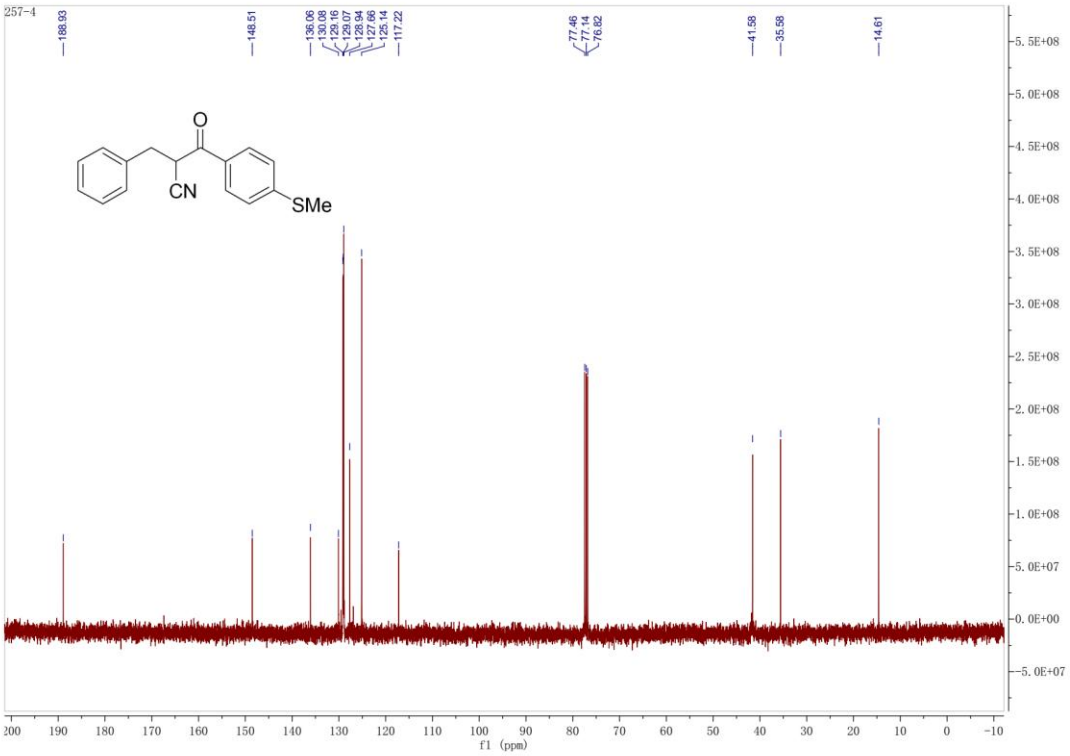

Figure S52. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3x**

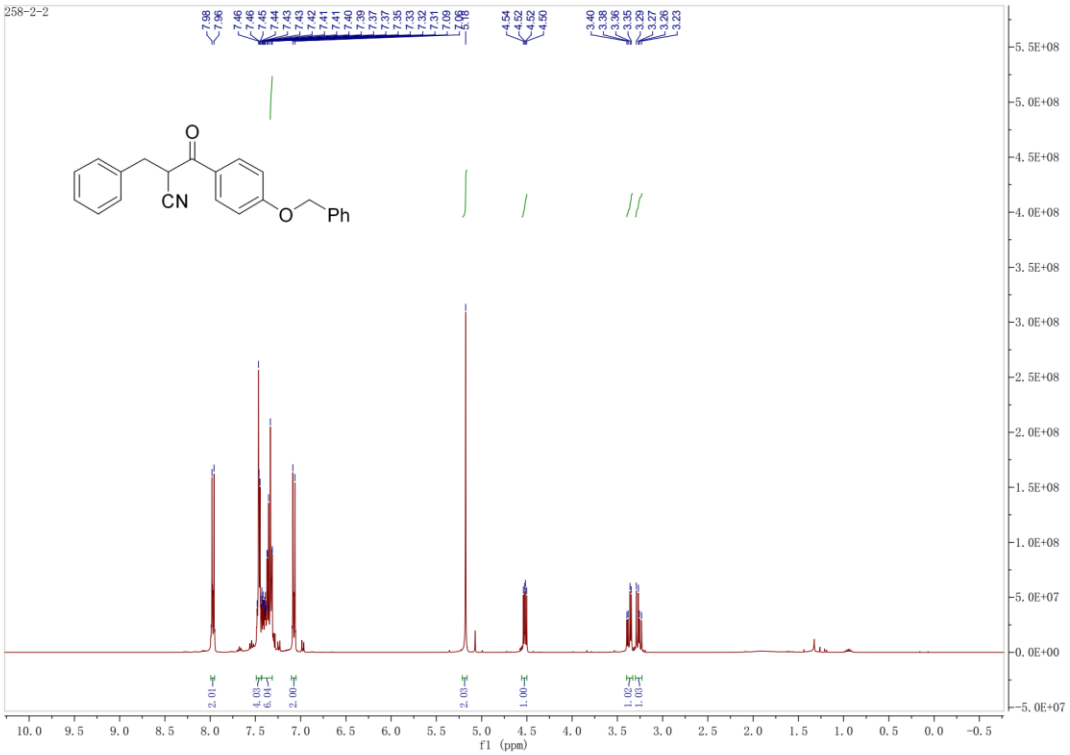

Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3y**

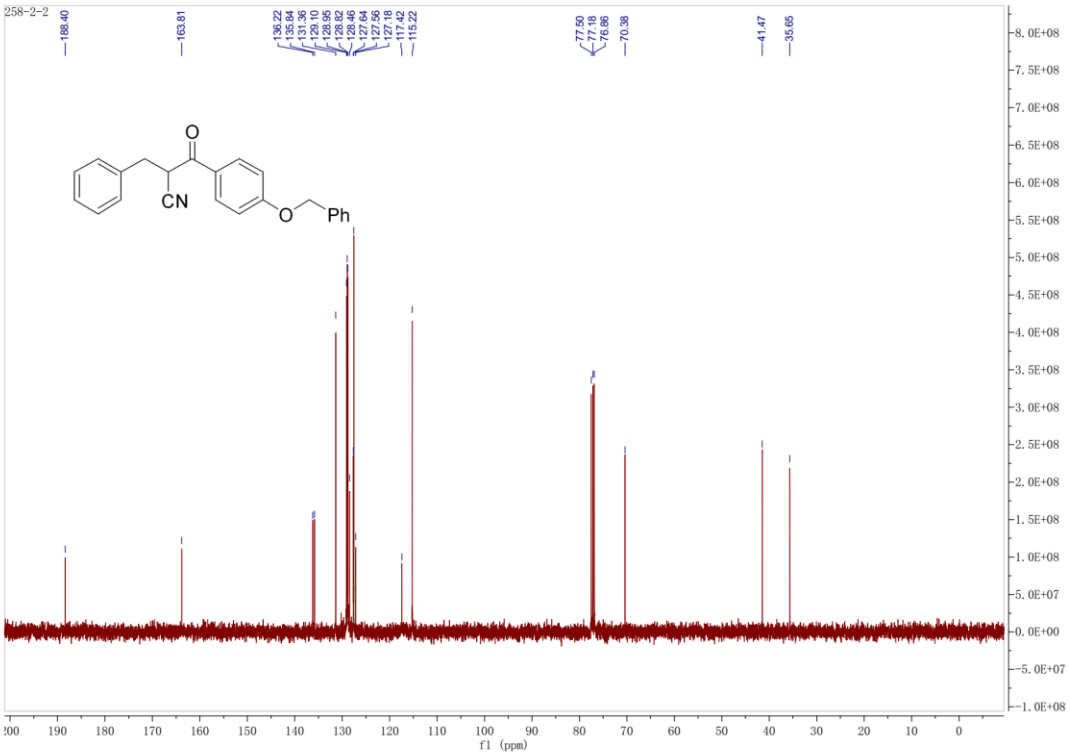

Figure S54. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3y**

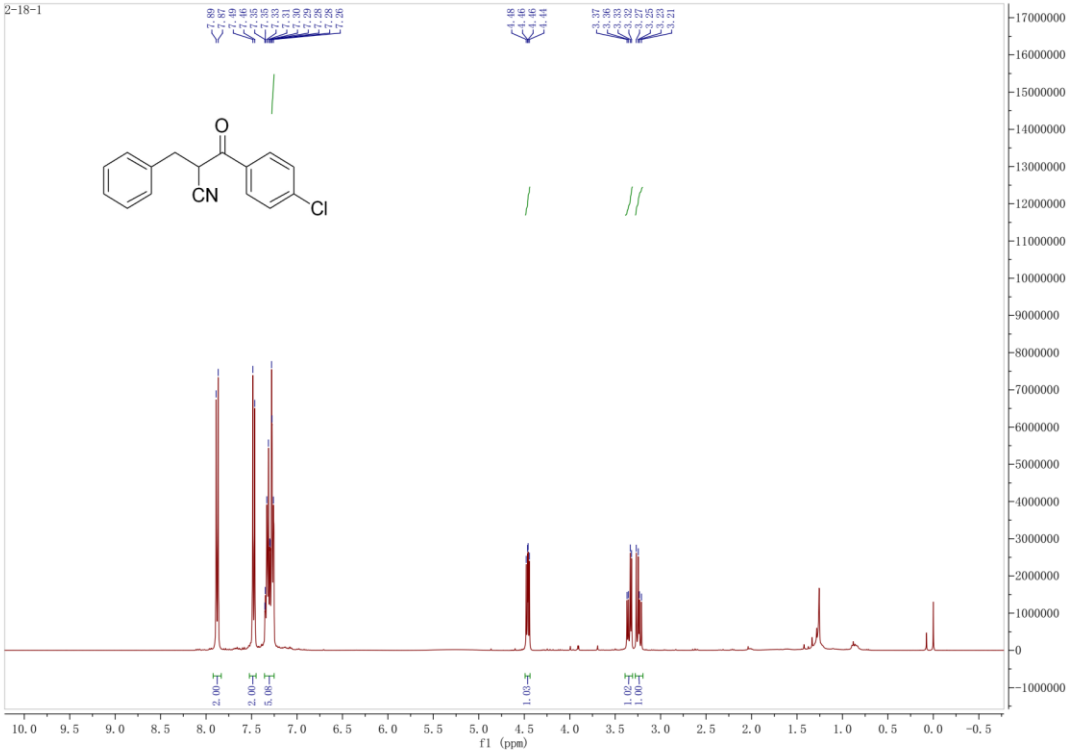

Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3z**

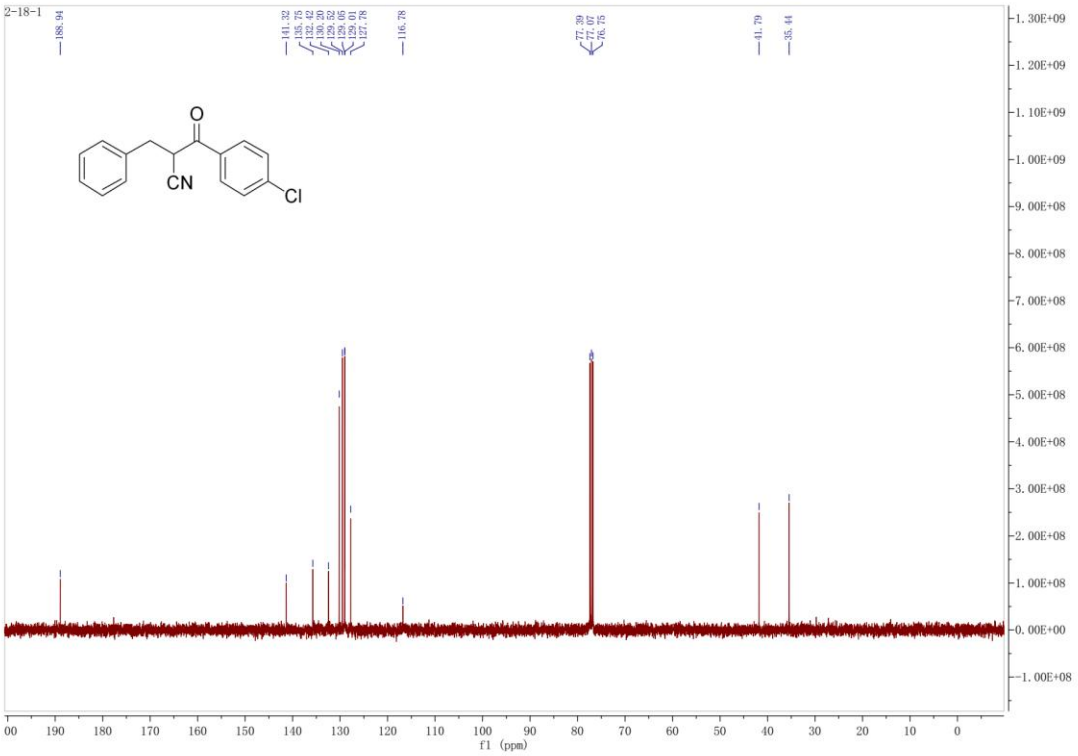

Figure S56. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3z**

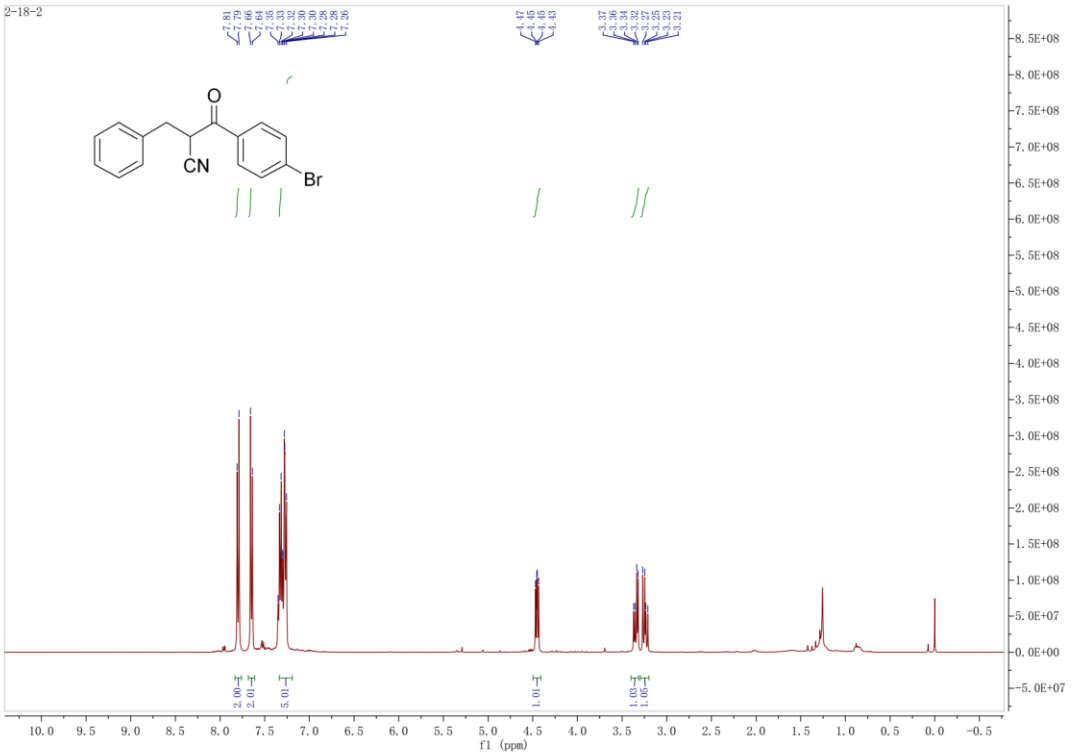

Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3aa**

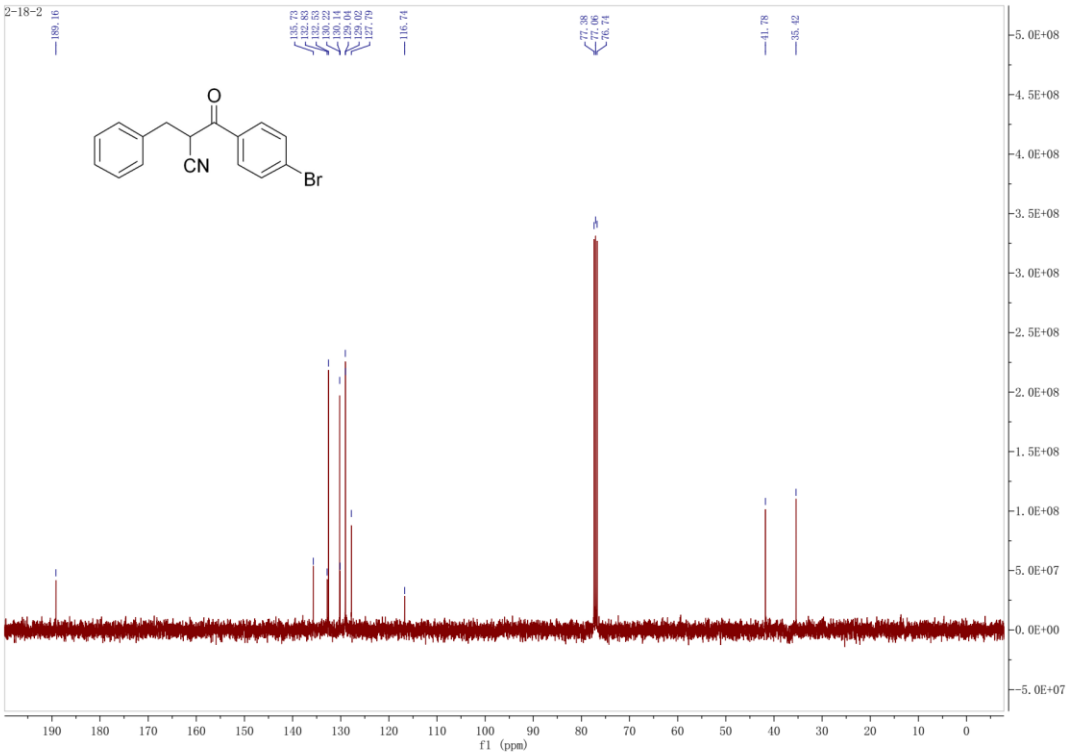

Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3aa**

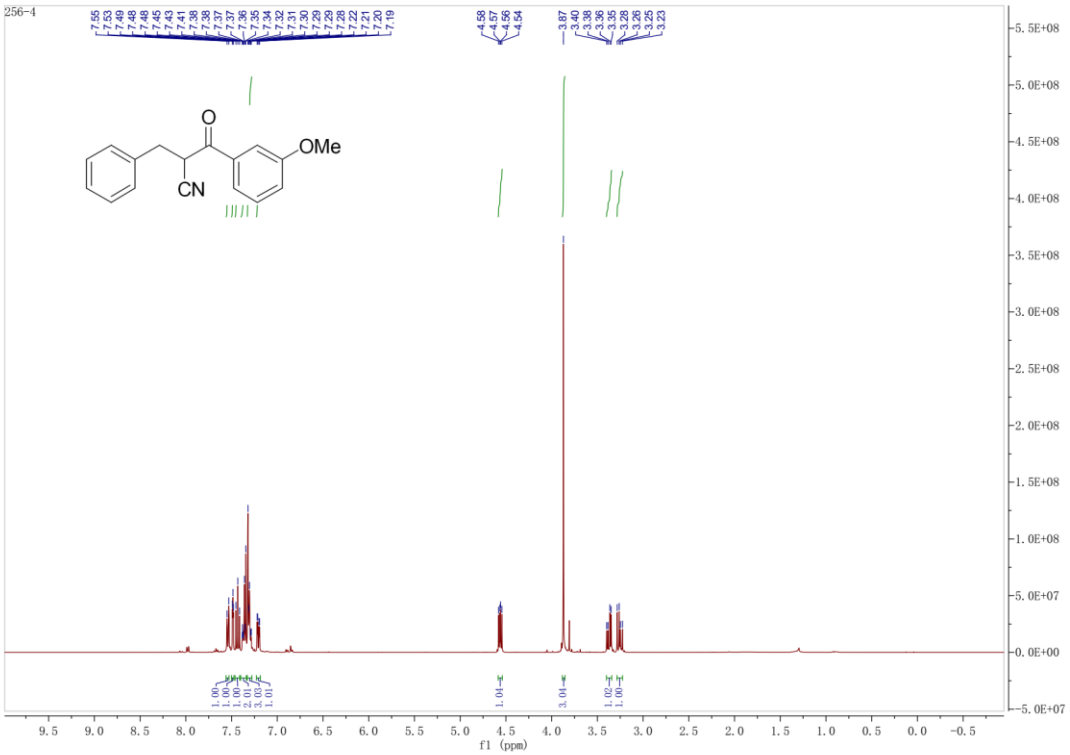

Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3ab**

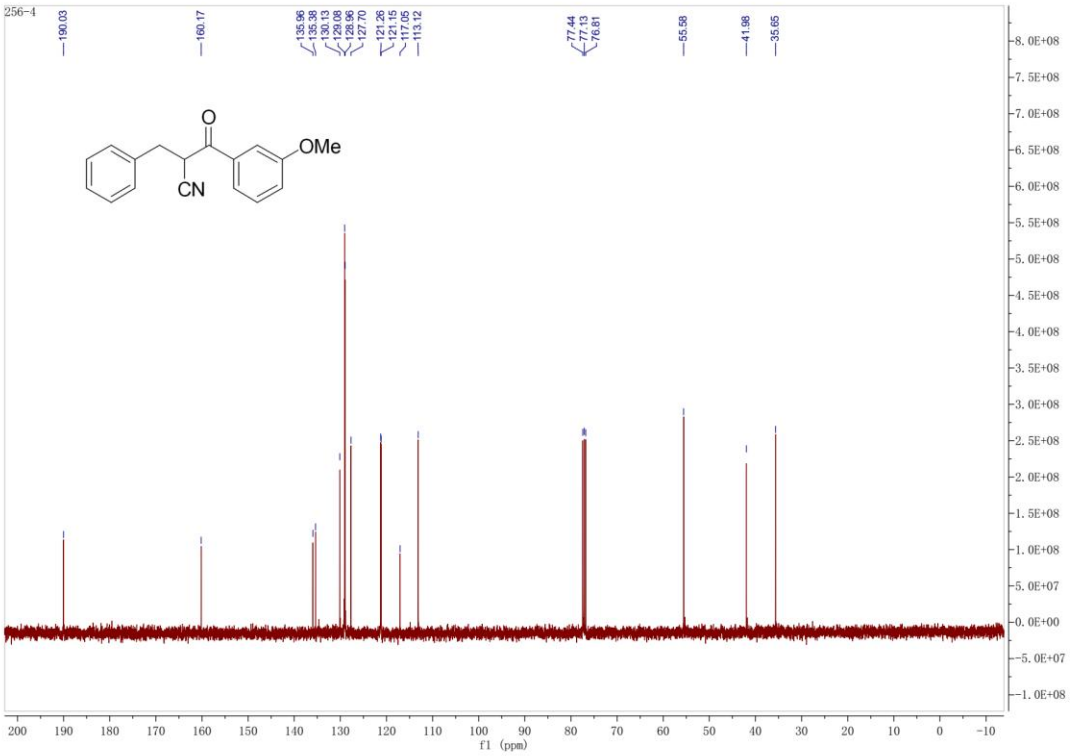

Figure S60. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3ab**

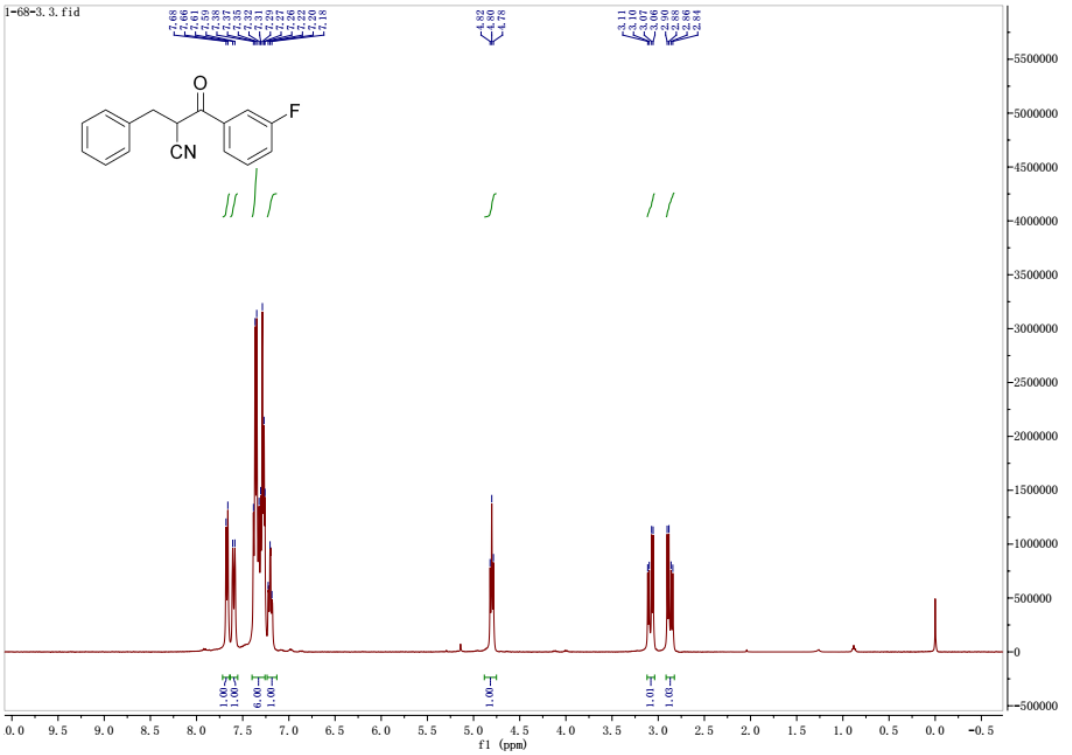

Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3ac**

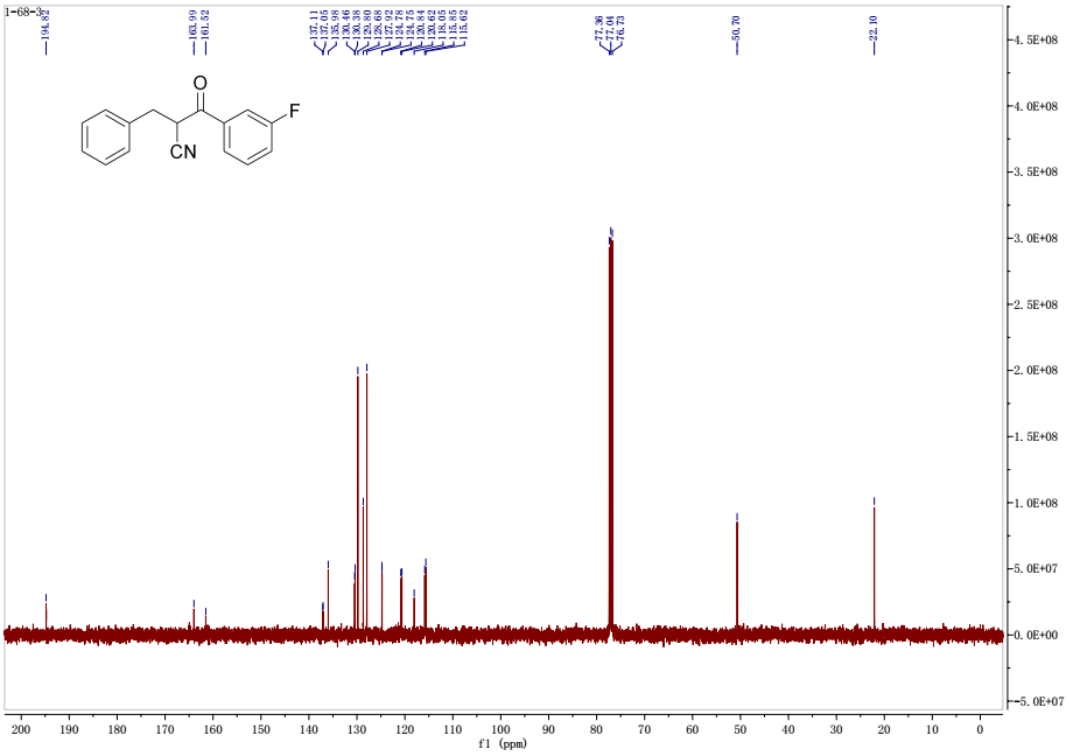

Figure S62. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3ac**

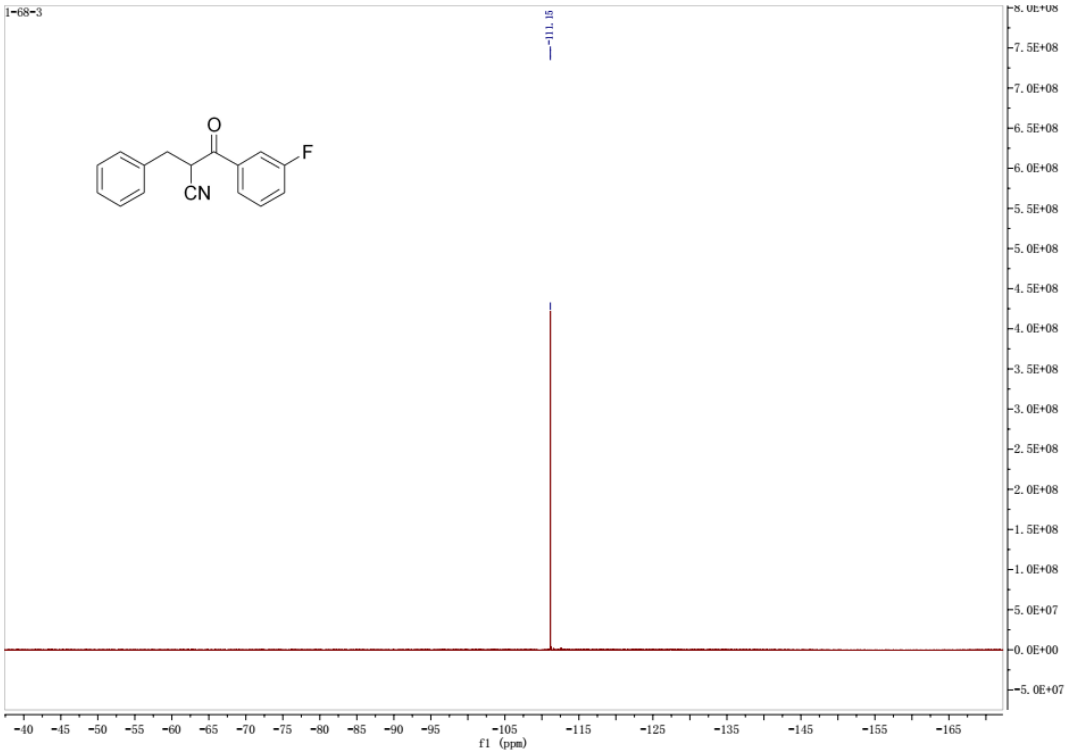

Figure S63. ^{19}F NMR (376 MHz, $CDCl_3$) of Compound **3ac**

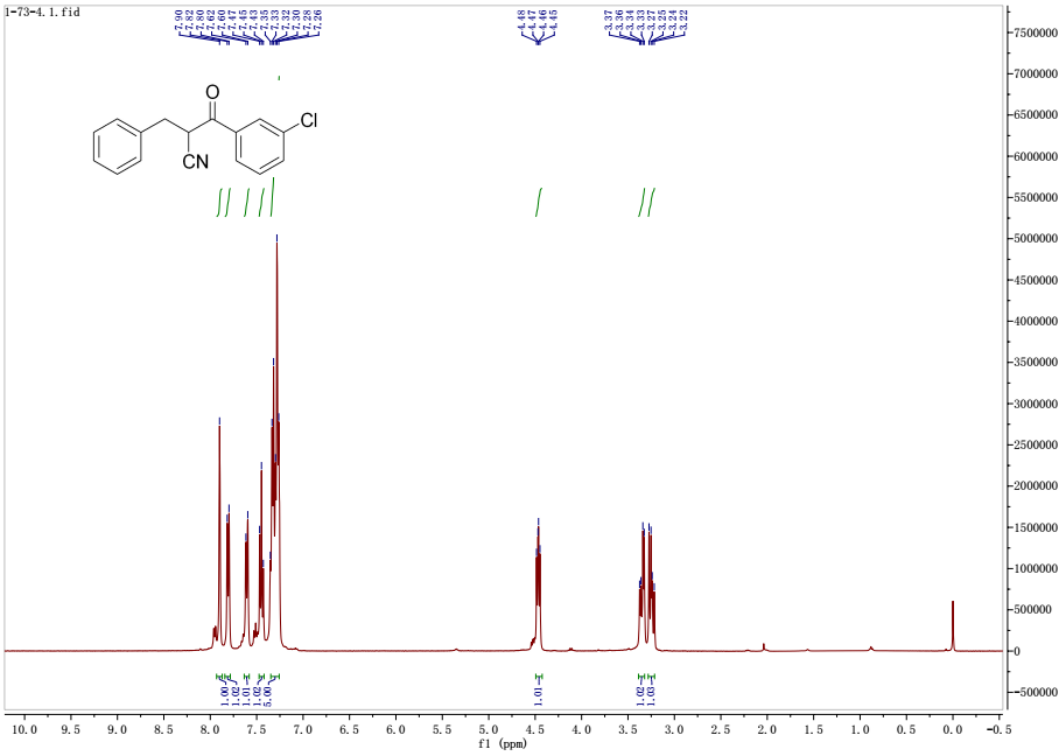

Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3ad**

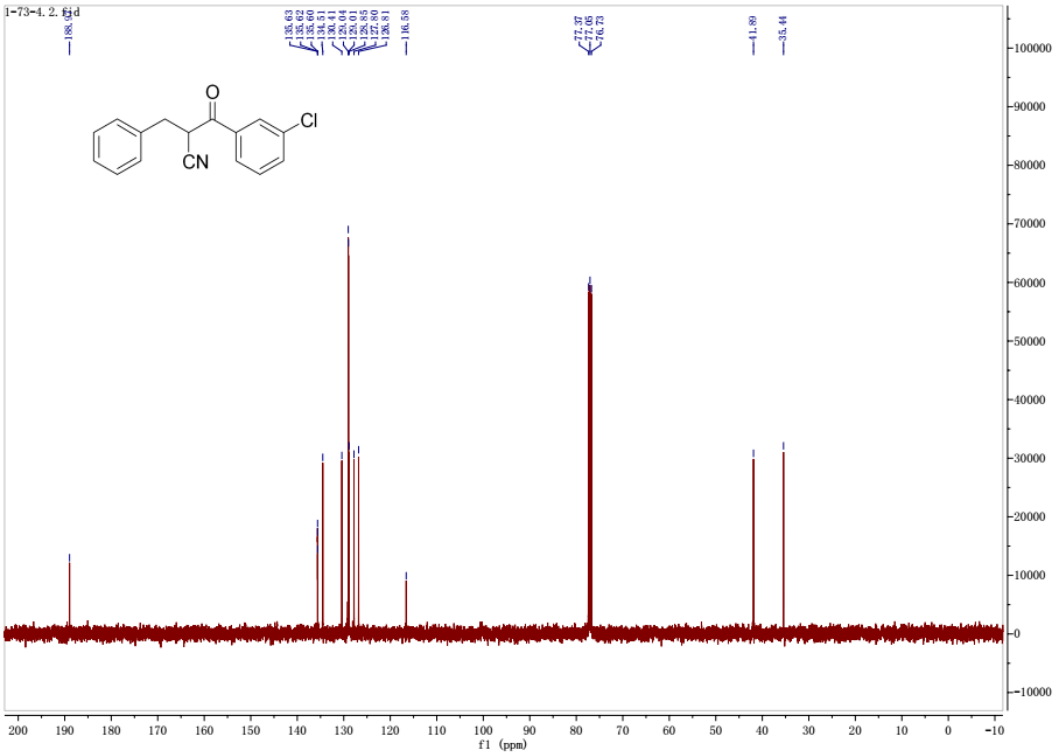

Figure S65. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3ad**

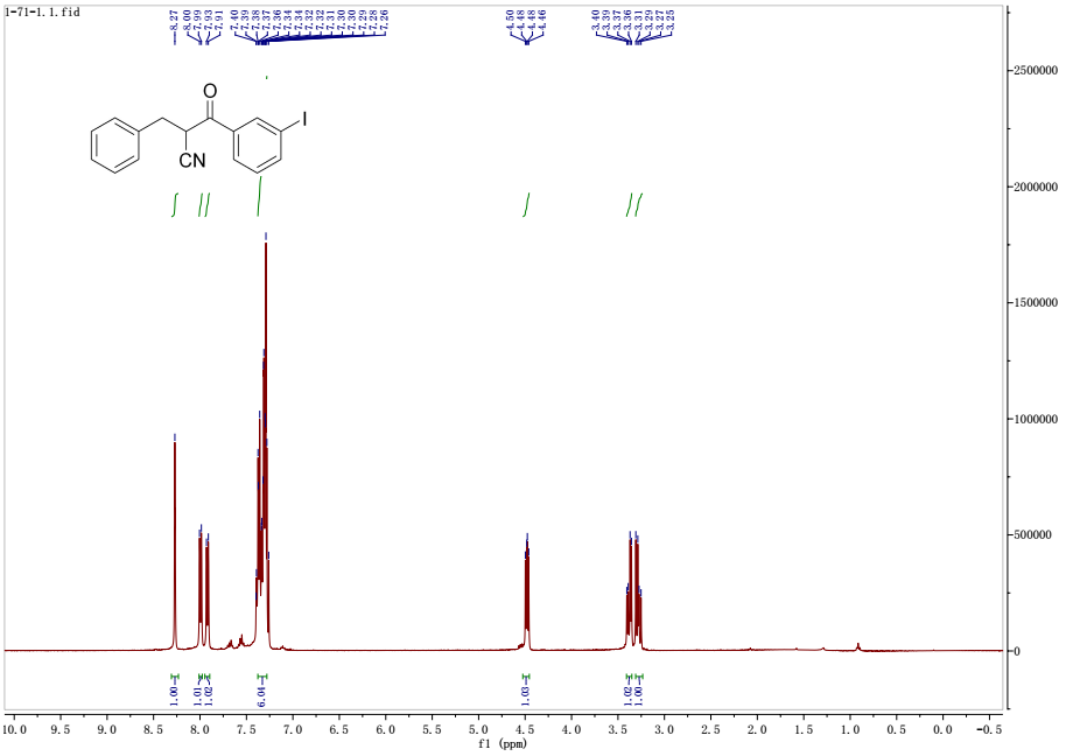

Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3ae**

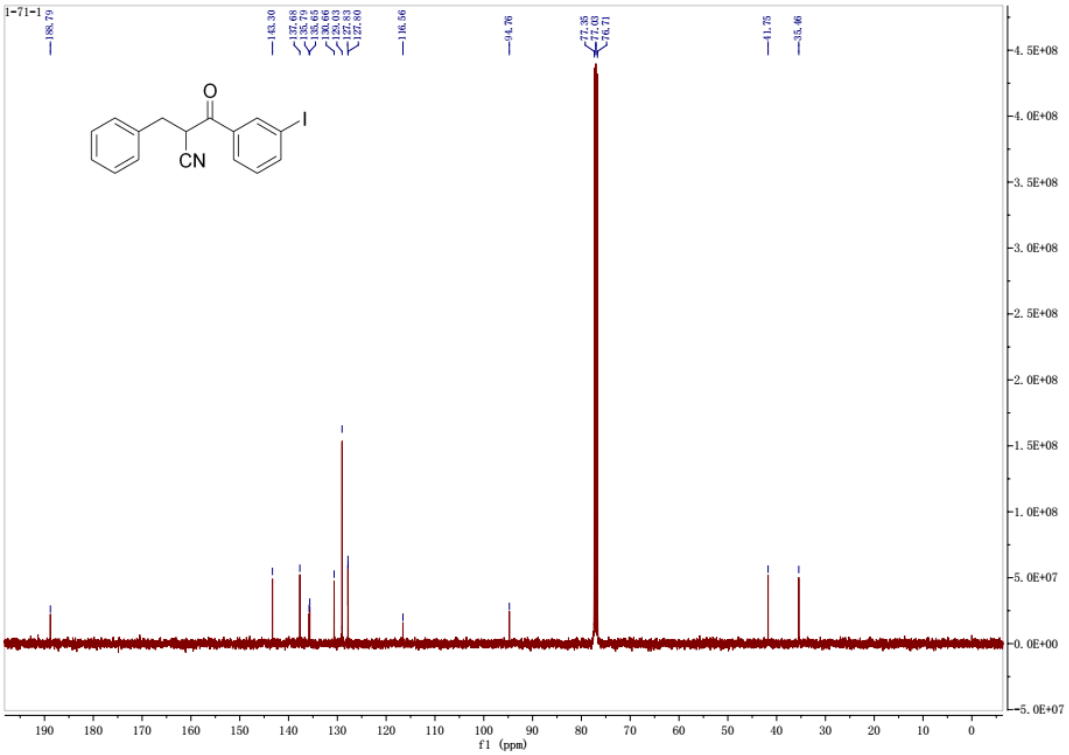

Figure S67. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3ae**

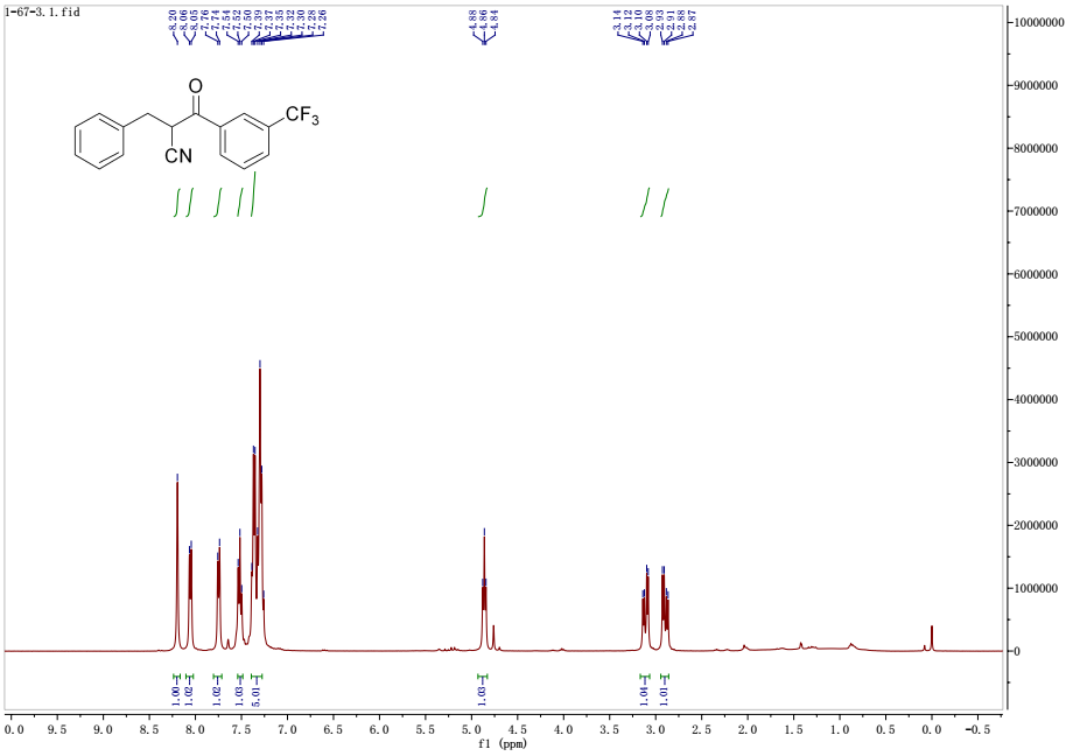

Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3af**

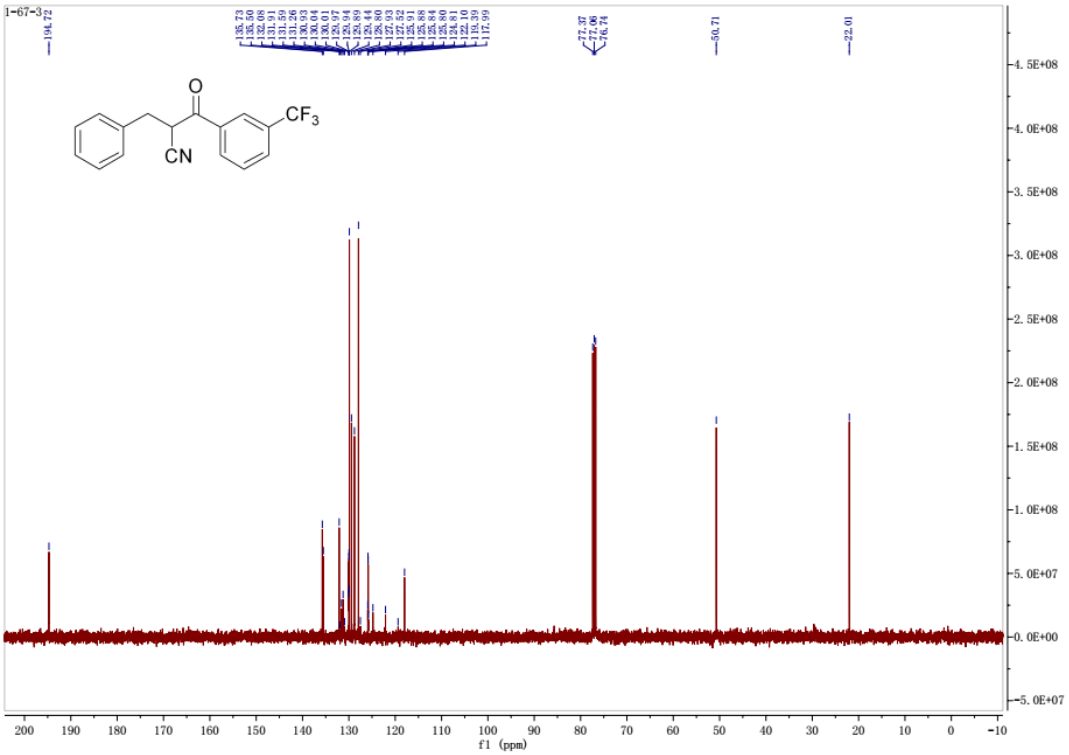

Figure S69. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3af**

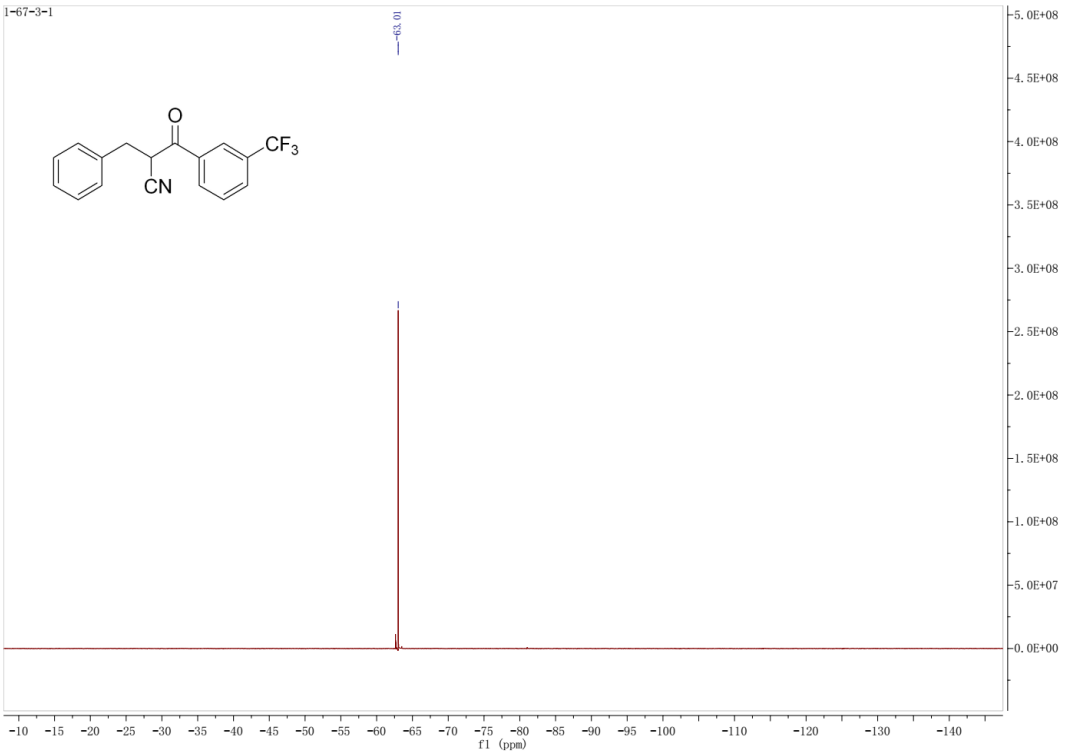

Figure S70. ^{19}F NMR (376 MHz, $CDCl_3$) of Compound **3af**

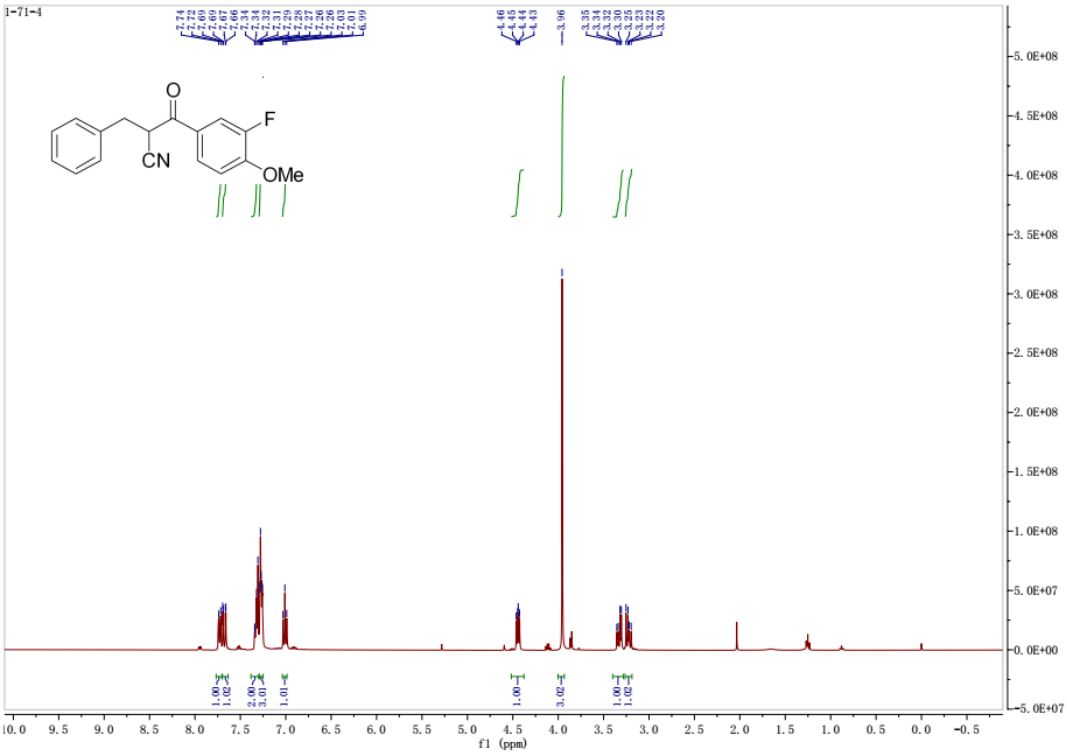

Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3ag**

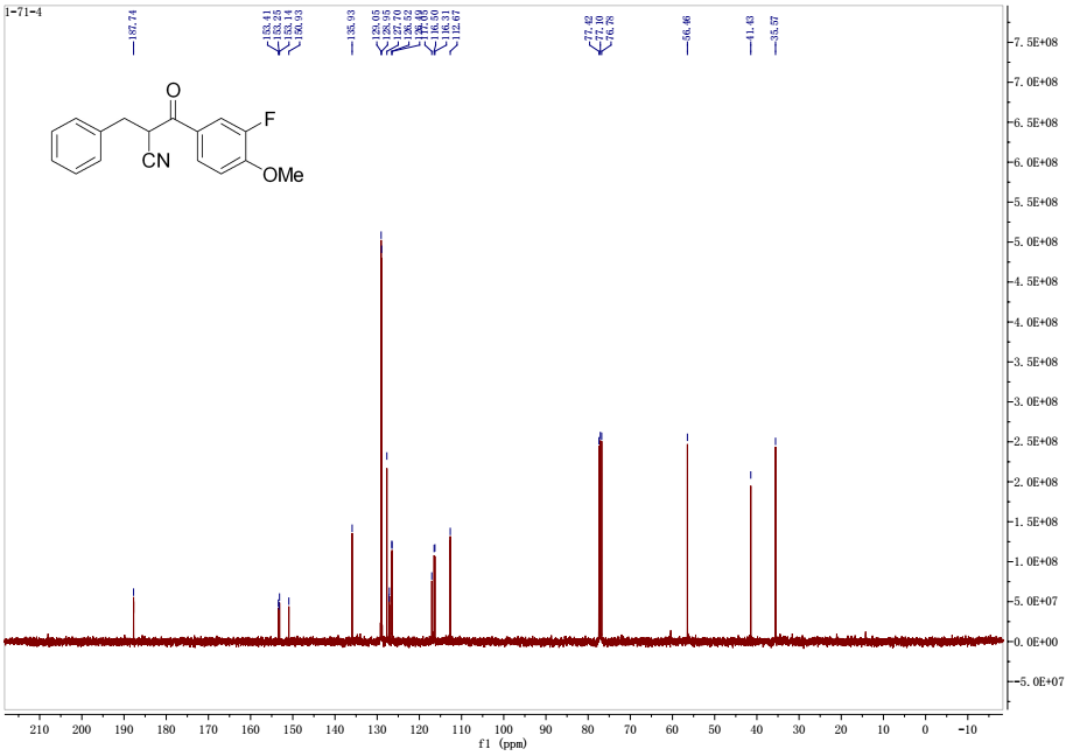

Figure S72. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3ag**

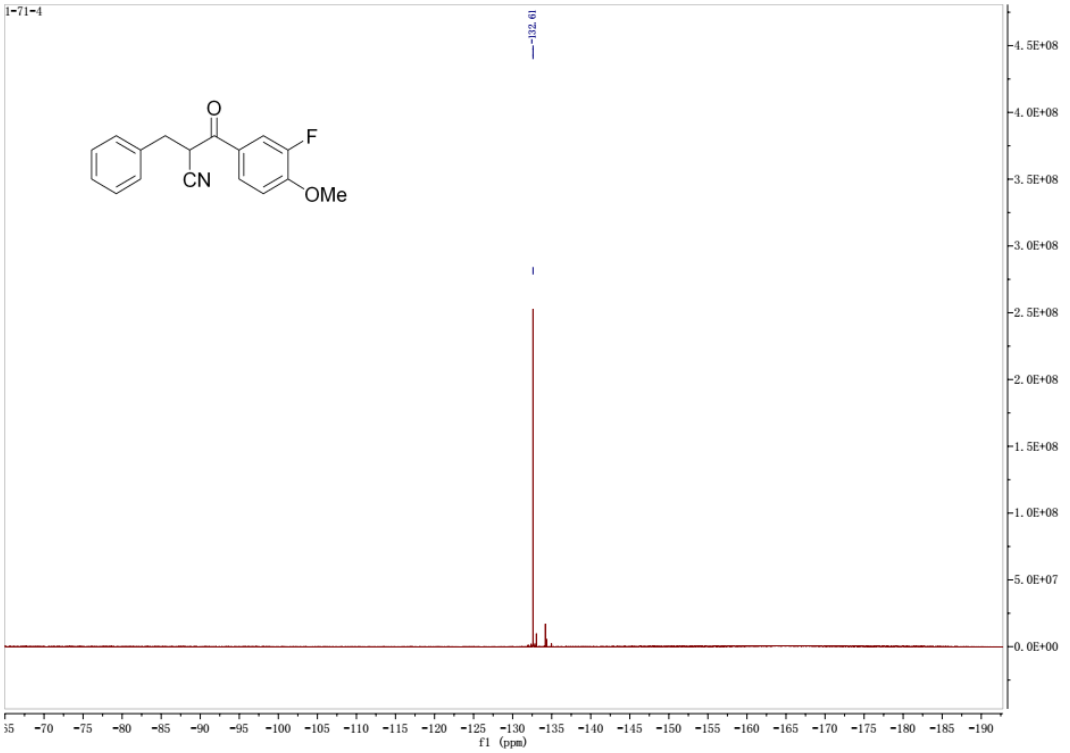

Figure S73. ^{19}F NMR (376 MHz, $CDCl_3$) of Compound **3ag**

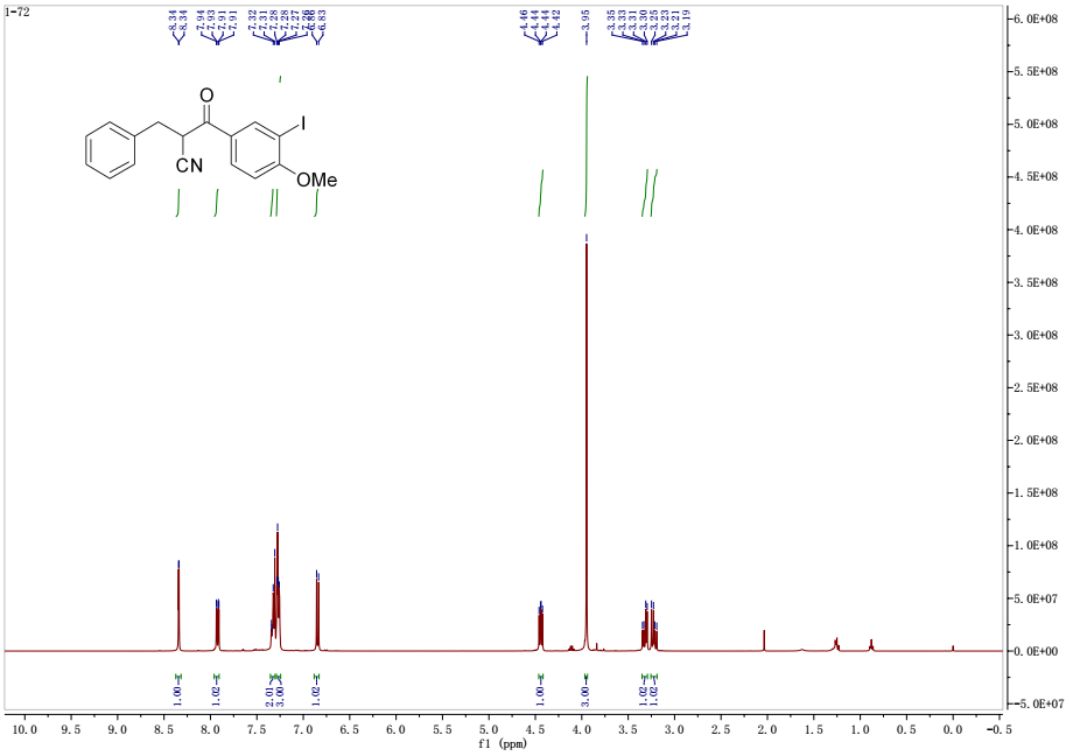

Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3ah**

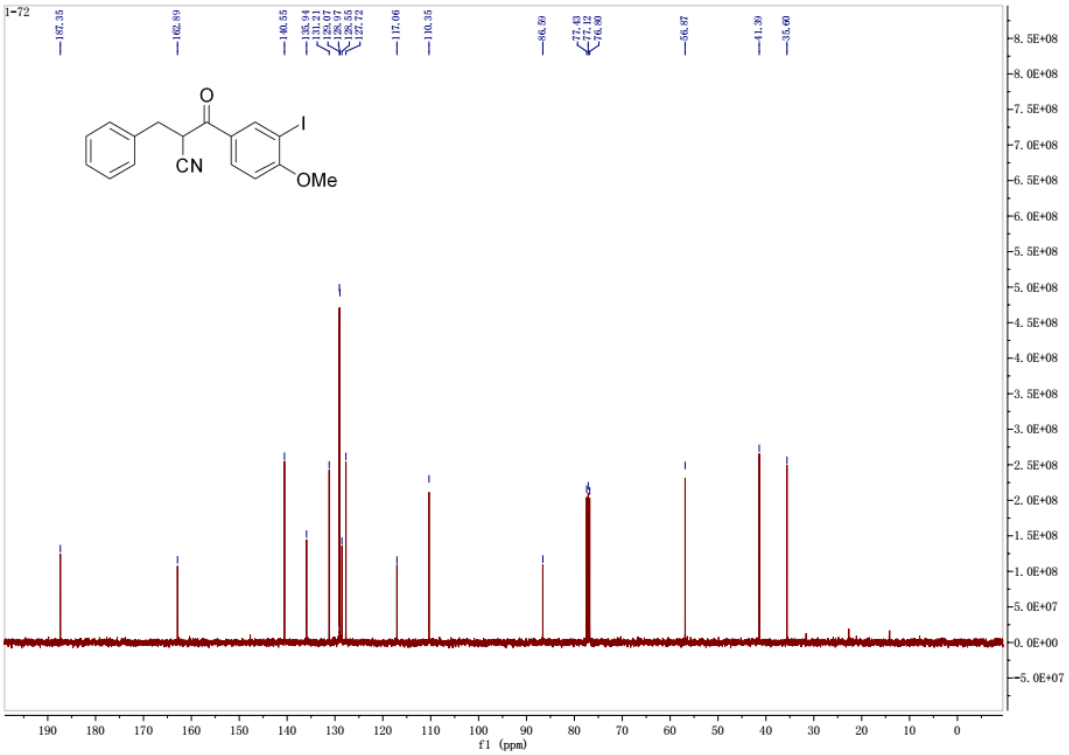

Figure S75. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3ah**

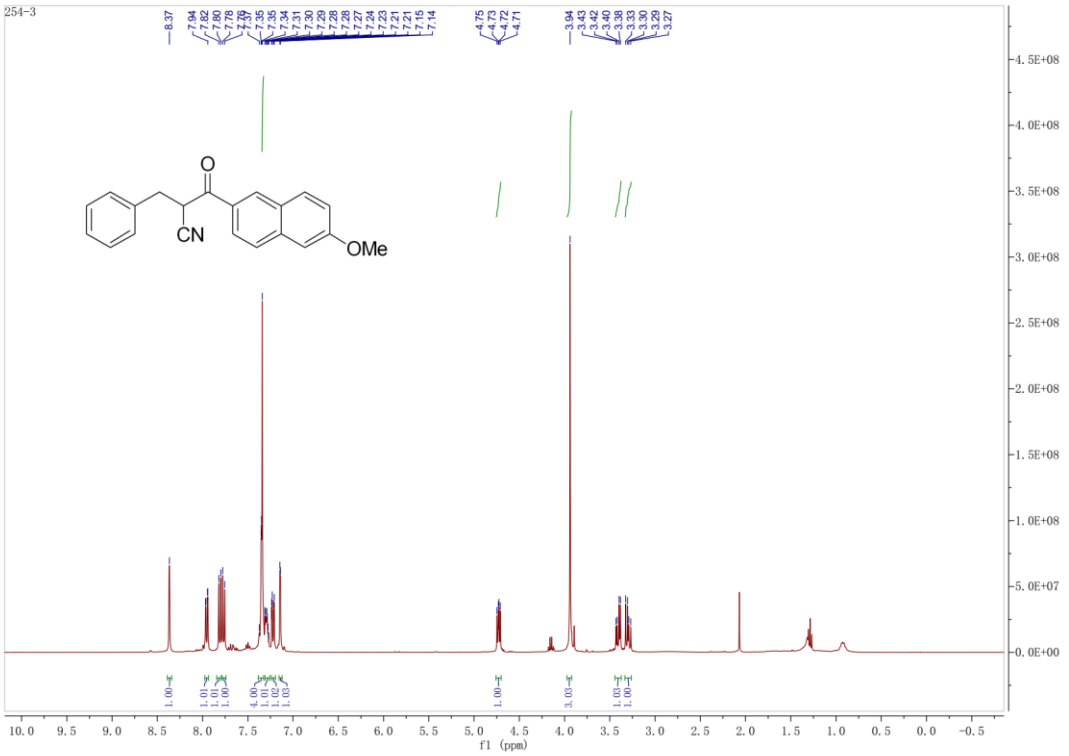

Figure S76. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3ai**

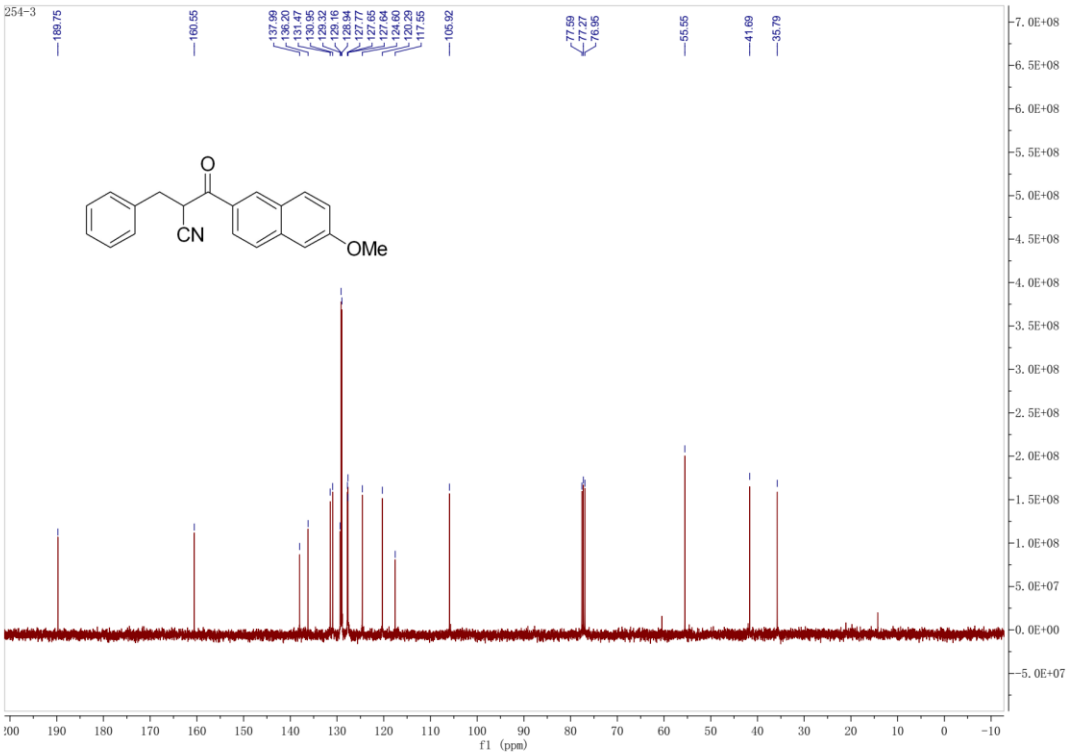

Figure S77. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3ai**

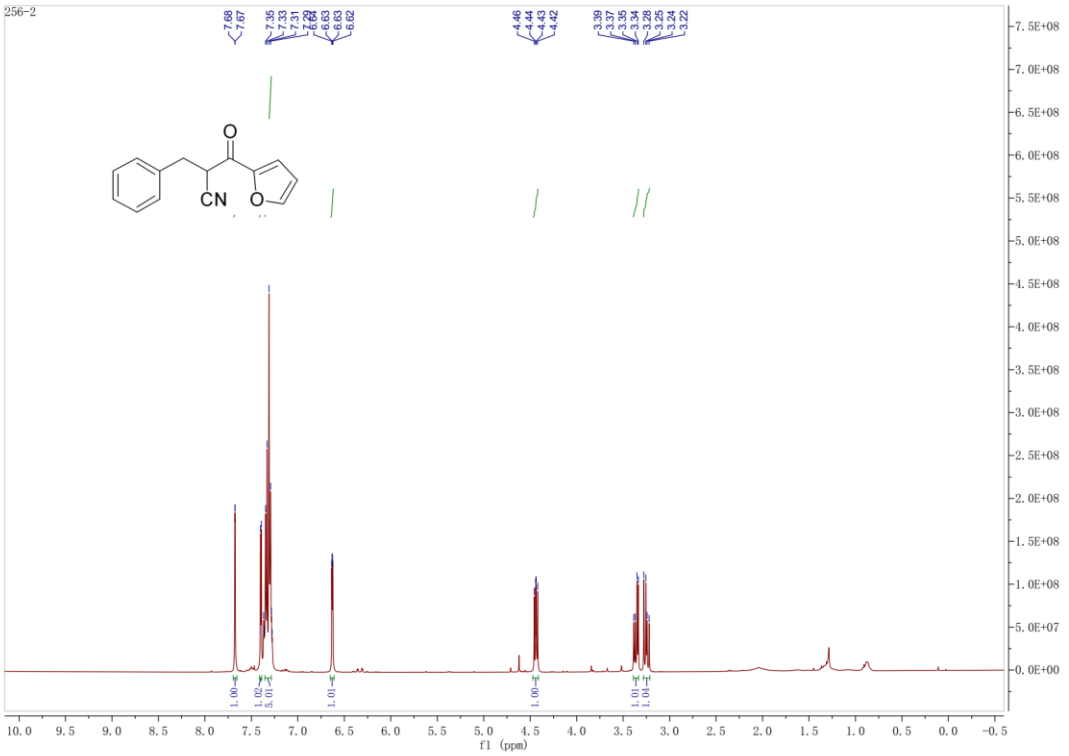

Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3aj**

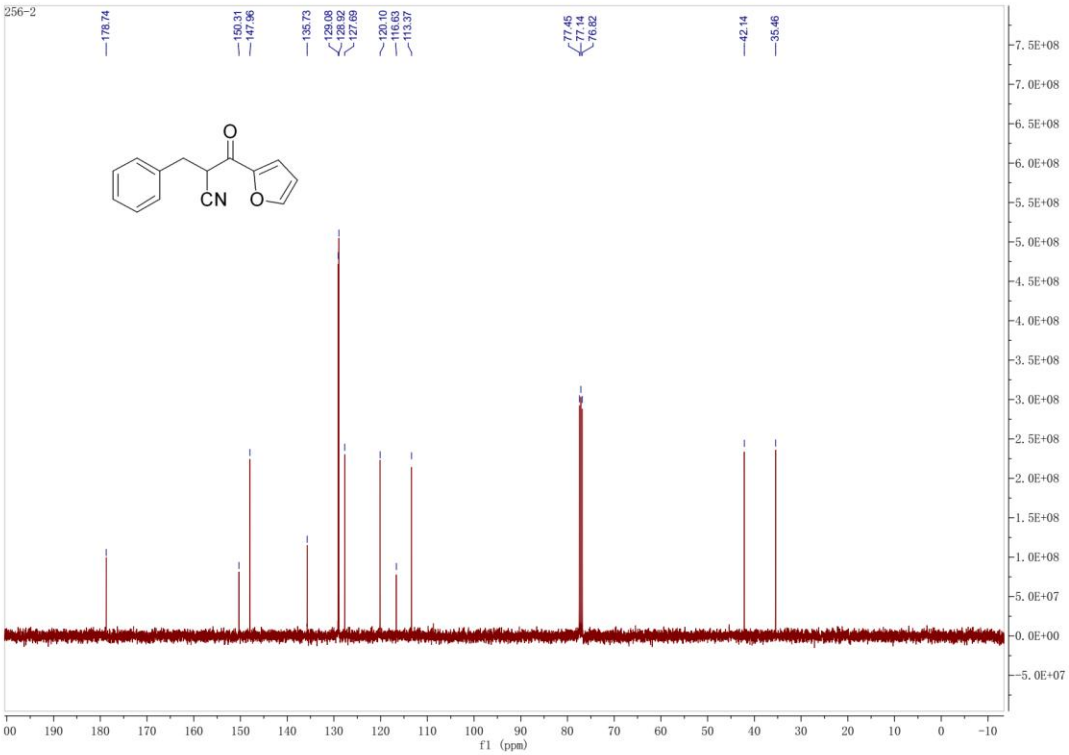

Figure S79. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3aj**

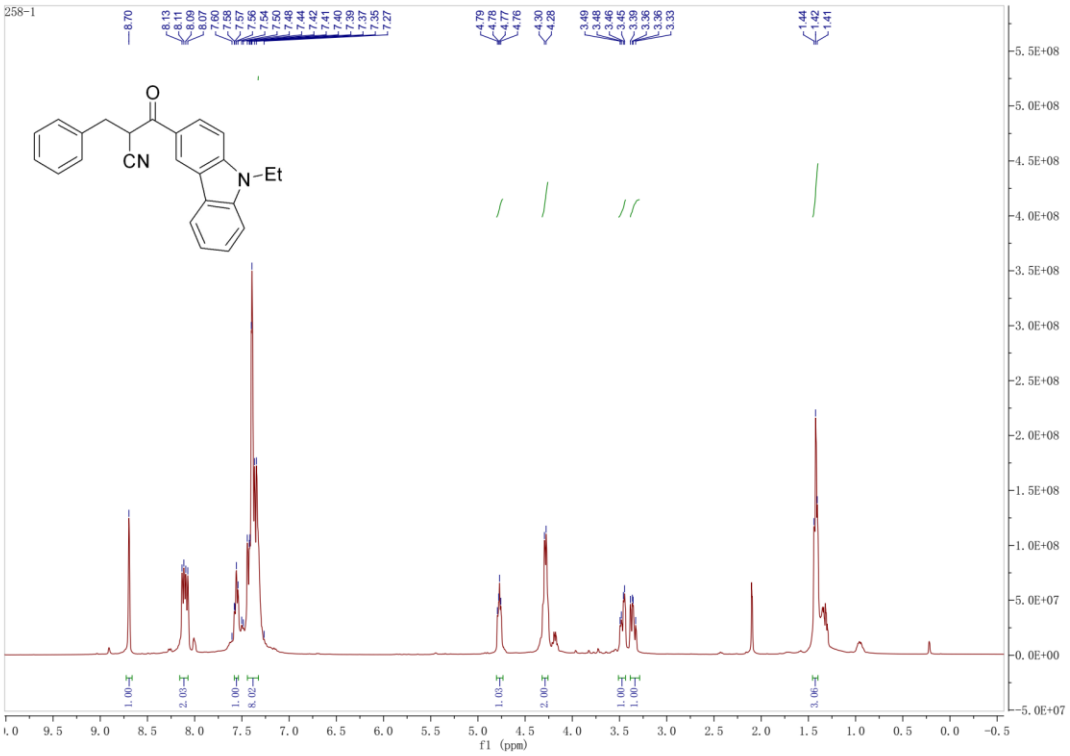

Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3ak**

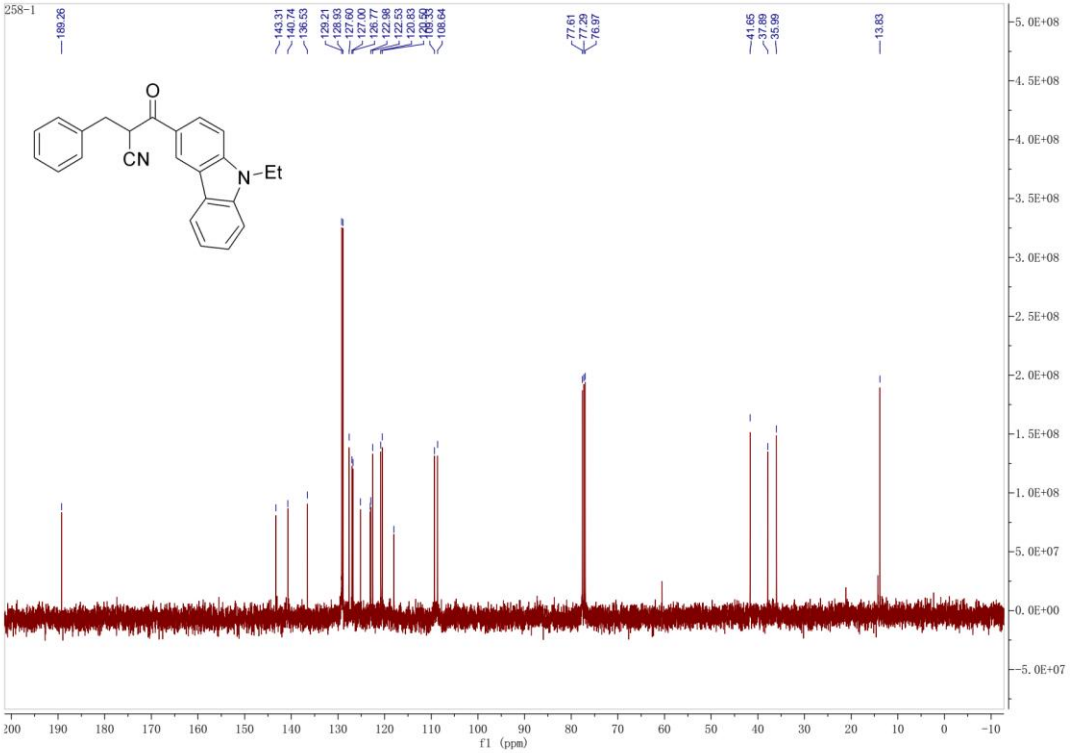

Figure S81. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3ak**

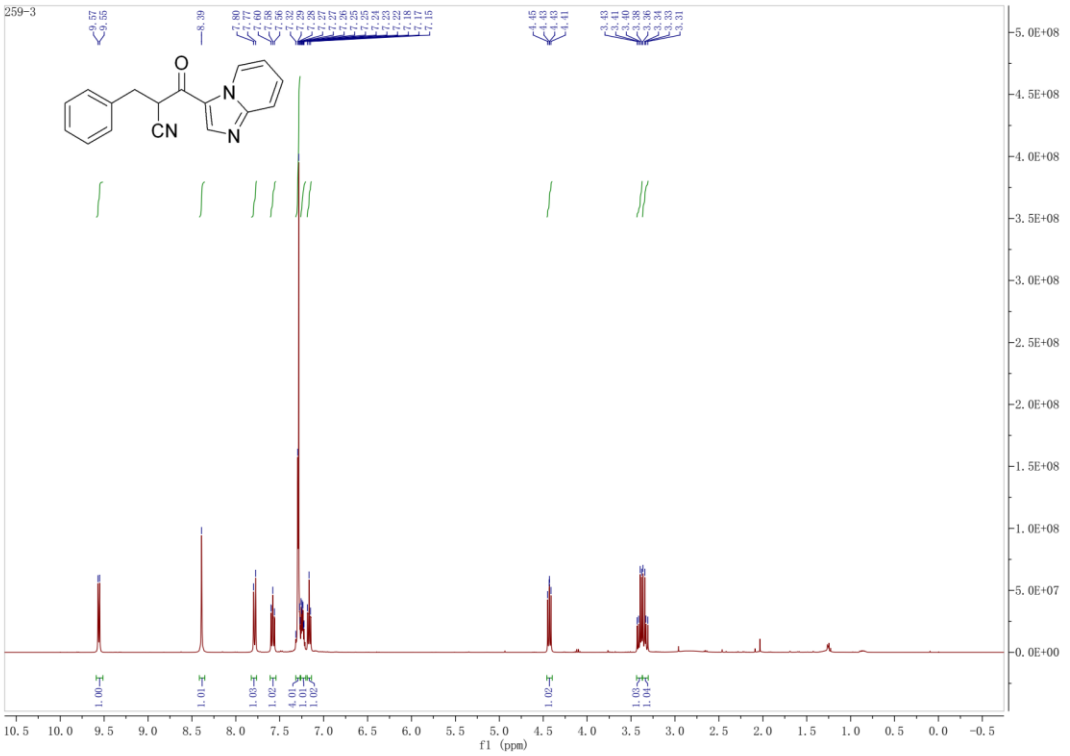

Figure S82. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3al**

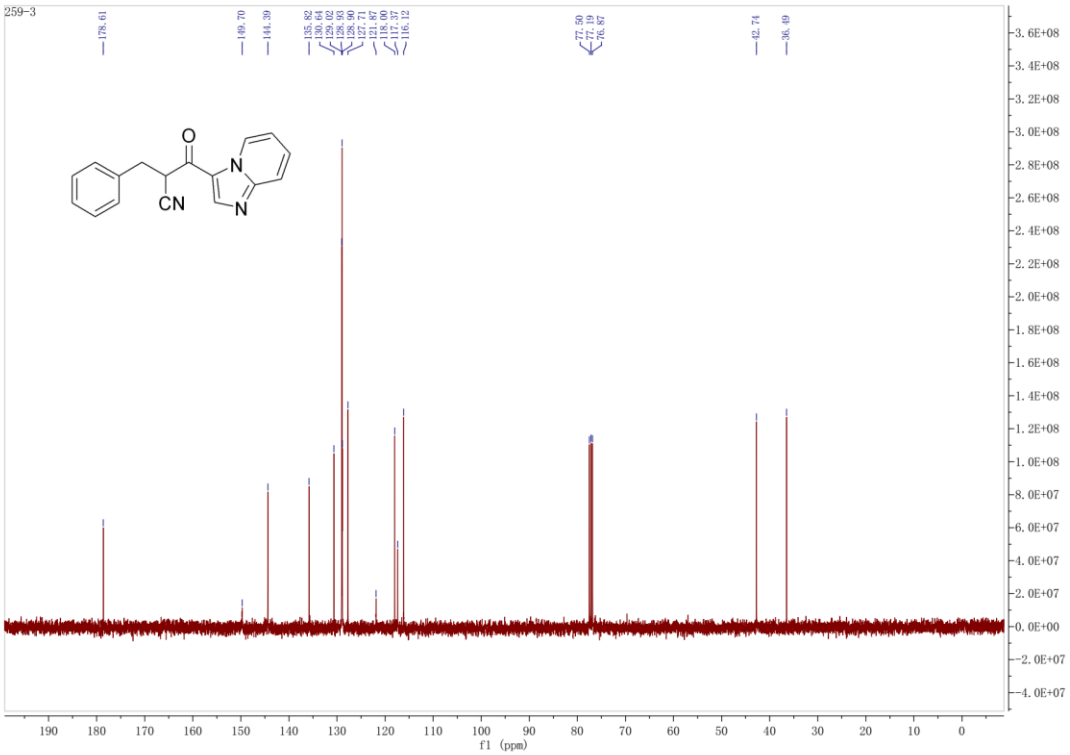

Figure S83. ^{13}C NMR (400 MHz, $CDCl_3$) of Compound **3al**

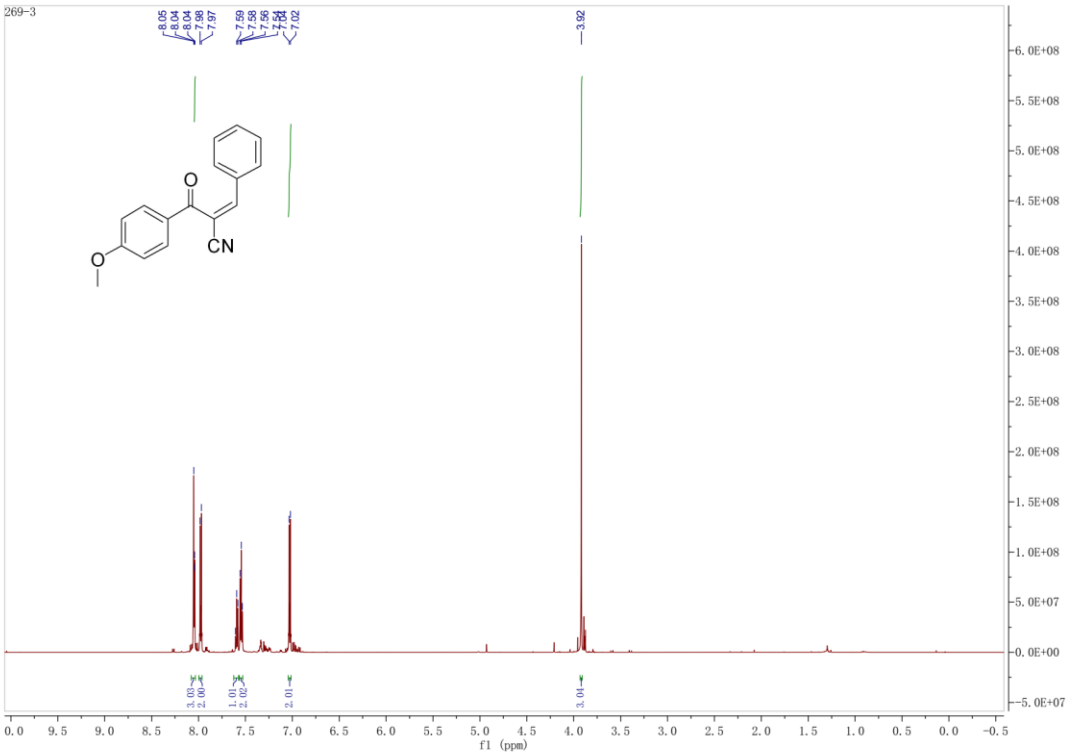

Figure S84. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **4**

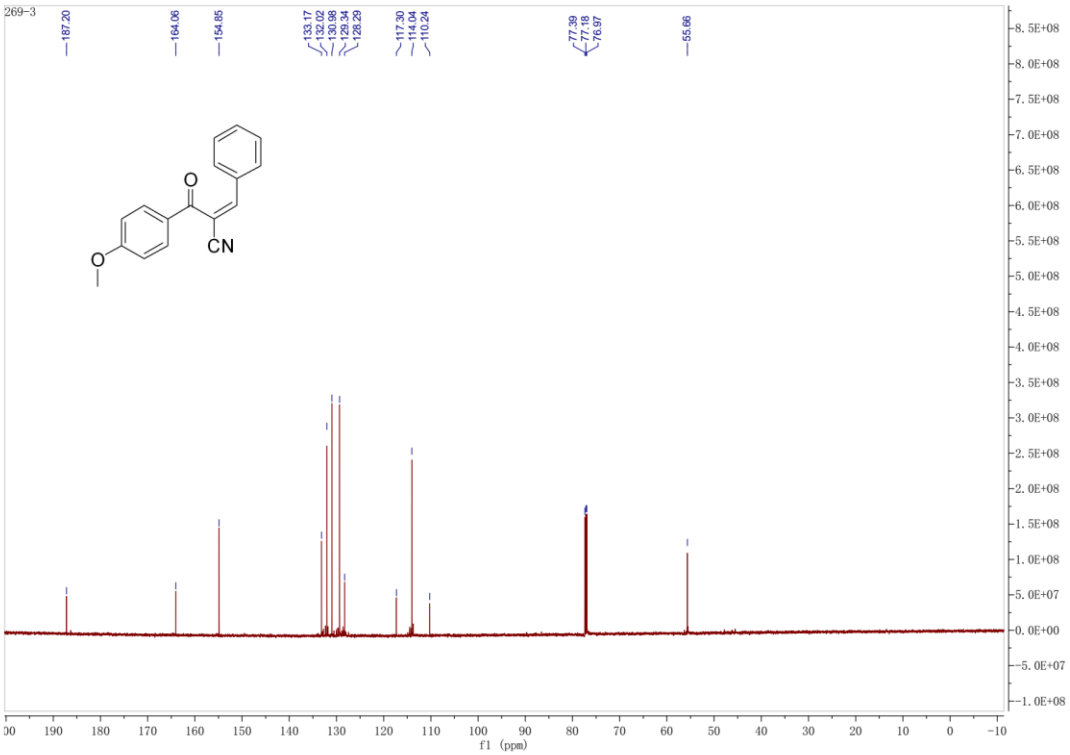

Figure S85. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **4**

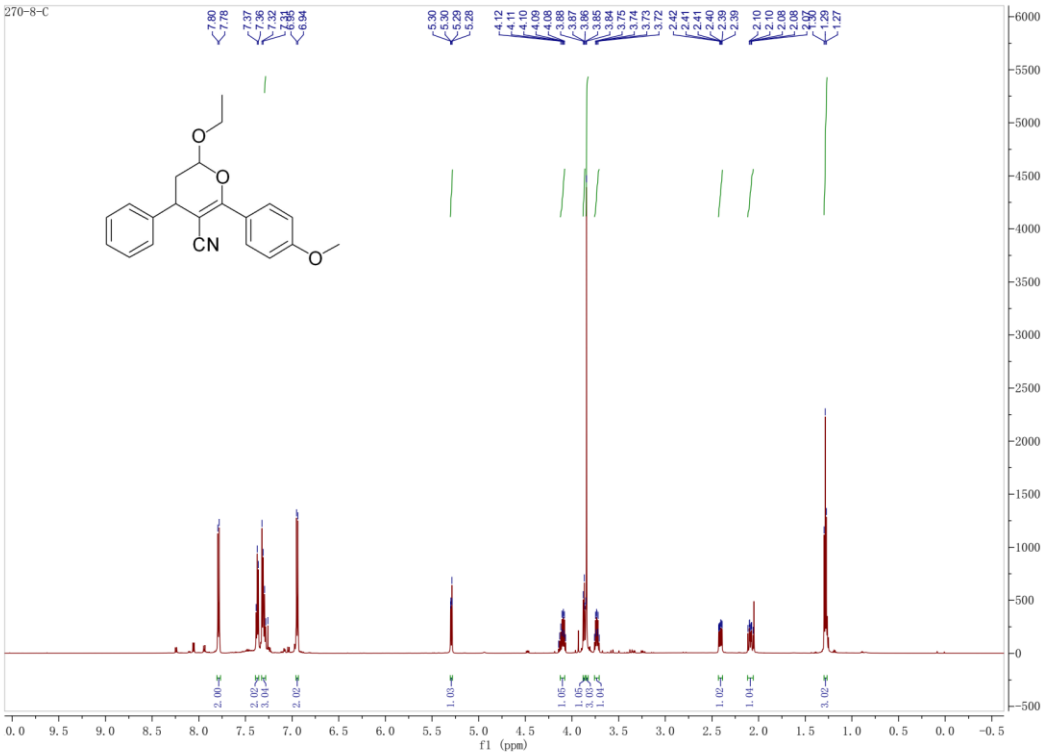

Figure S86. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **5**

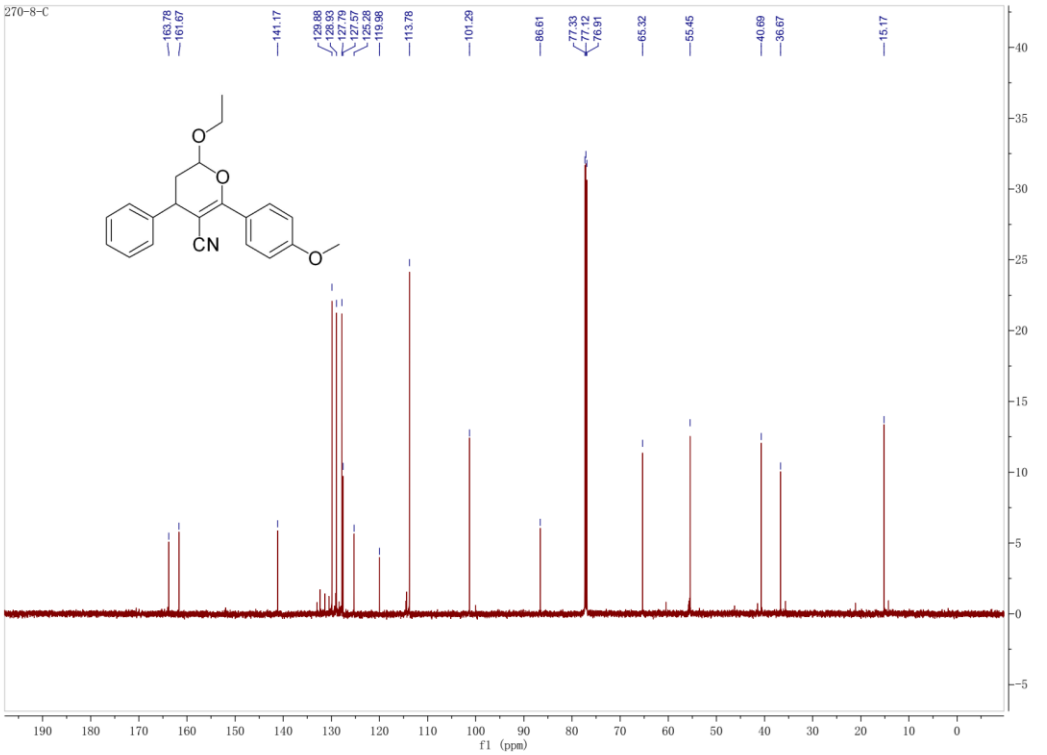

Figure S87. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **5**

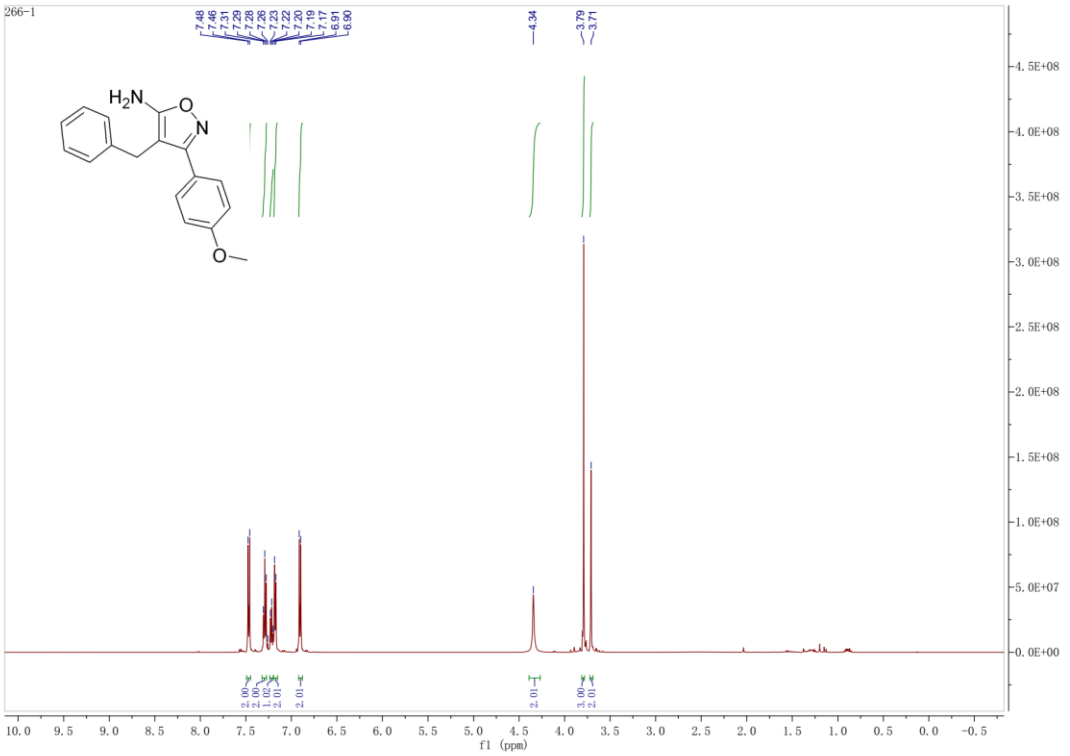

Figure S88. ^{1}H NMR (500 MHz, $CDCl_3$) of Compound **6**

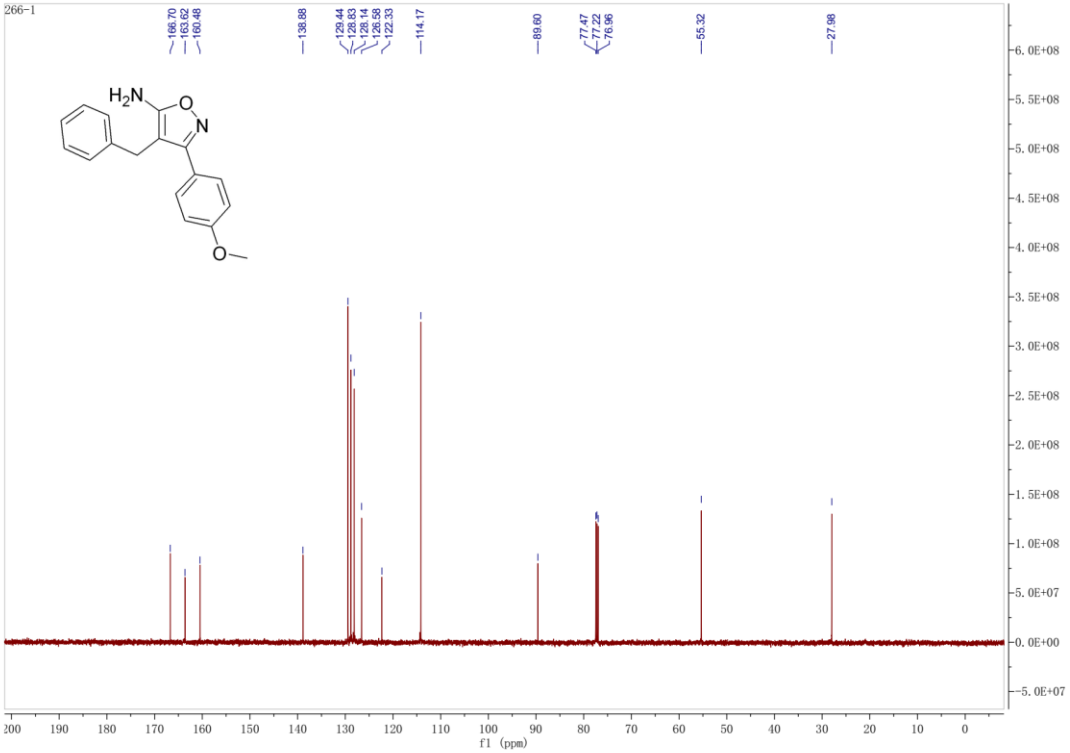

Figure S89. ^{13}C NMR (125 MHz, $CDCl_3$) of Compound **6**

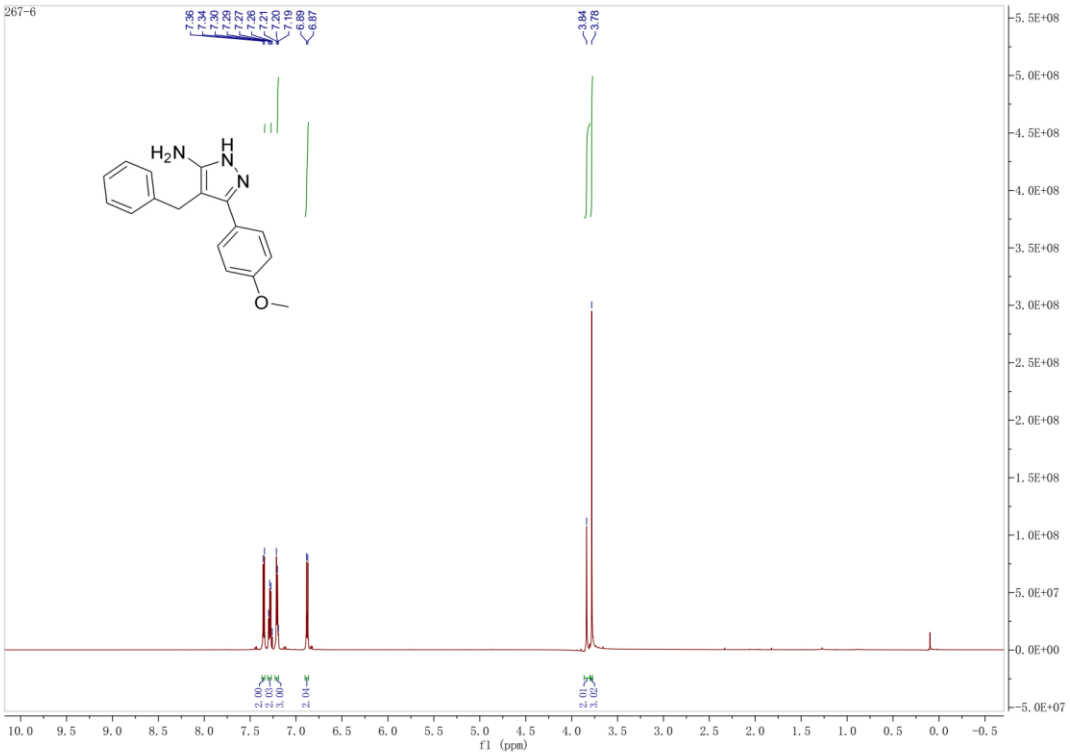

Figure S90. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound **7**

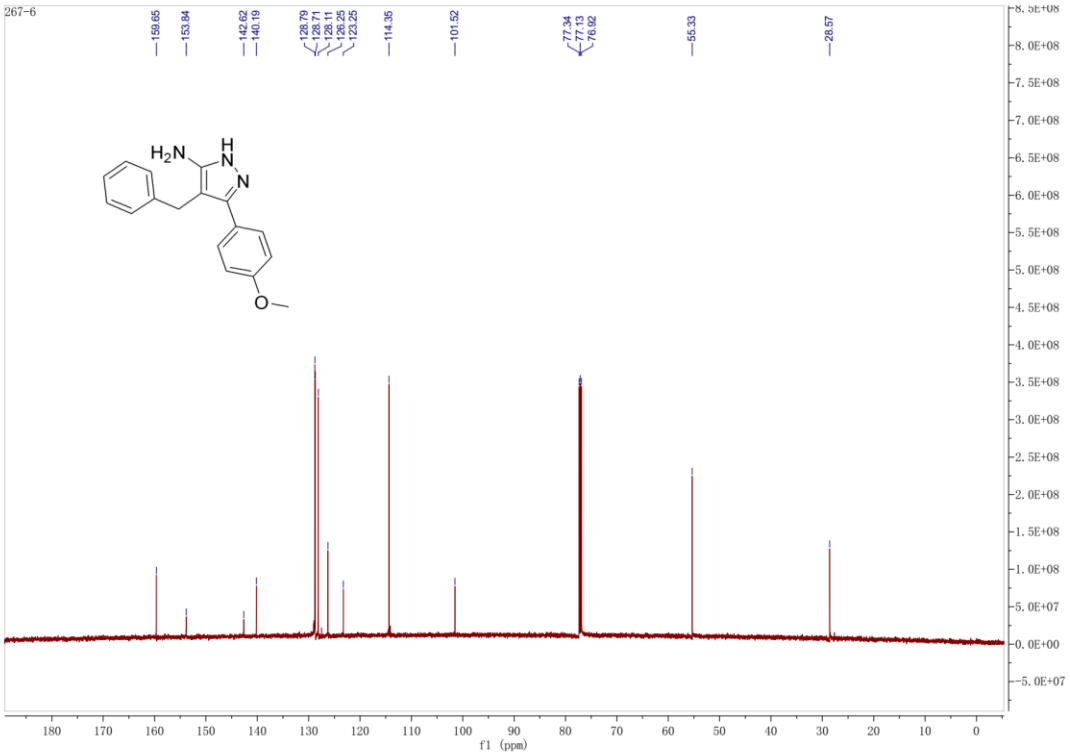

Figure S91. ^{13}C NMR (150 MHz, $CDCl_3$) of Compound **7**