Electronic Supplementary Material (ESI) for ChemComm.

Ir-Photoredox-Catalyzed Decarboxylative Michael Addition of Glyoxylic Acid Acetal as Formyl Equivalent

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1. General Information

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity≥99.999%) unless otherwise mentioned. Commercial reagents were purchased from Energy Chemical and TCI. Glyoxylic acid acetals were prepared by the hydrolysis of ethyl diethoxyacetate according to the previous report (*Eur. J. Med. Chem.*, 2011, **46**, 787−793). $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**Ir-cat.**) was prepared according to the previous report (*Chem. Mater.*, 2005, **17**, 5712−5719). ^1H NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^1H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS was recorded on a Waters™ Q-TOF Premier and a Thermo Scientific™ LTQ Orbitrap XL™ Hybrid Ion Trap Orbitrap Mass Spectrometer.

2. Experimental Procedures and Spectral Data

2.1 Experimental Procedures

General Procedure for the Decarboxylative Michael Addition Reaction:

Glyoxylic acid acetals (1.5 equiv., 0.3 mmol), Michael acceptor (1.0 equiv., 0.2 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.0 mol %, 4.5 mg) and K_2HPO_4 (1.2 equiv., 55 mg) were placed in a Schlenk tube (10 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Then, anhydrous *N*,*N*-dimethyl acetamide (DMF, 2.0 mL) was added via a syringe under argon atmosphere. The resulting reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 12 h. After the reaction was completed, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether:

ethyl acetate 2:1-10:1).

General Procedure for the Gram-scale Synthesis:

Diethoxyacetic acid (1.5 equiv., 9 mmol, 1.34g), *N*-methyl-*N*-phenylacrylamide (1.0 equiv., 6 mmol, 968 mg), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.0 mol %, 135 mg) and K_2HPO_4 (1.2 equiv., 7.2 mmol, 1.65g) were placed in a Schlenk tube (100 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Then, anhydrous *N*, *N*-dimethylacetamide (DMF, 40 mL) was added via a syringe under argon atmosphere. The resulting reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 16 h. After the reaction was completed, the mixture was quenched with water and extracted with ethyl acetate (3 x 30 mL). The organic layers were combined and concentrated under vacuo. The crude was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate 2:1) to give product **1** as a colorless oil (1.29g, 81% yield).

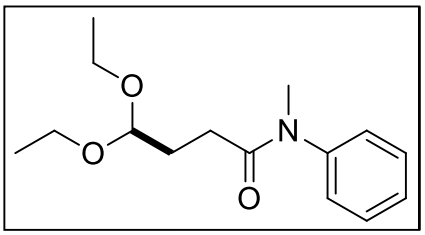
General Procedure for the Preparation of Aldehyde from Product 1:

Product **1** (4.86 mmol, 1.29g) and EtOAc (15 mL) were placed in a round-bottom flask (50 mL) equipped with a stirring bar. The mixture was cooled to 0 ^oC in an ice bath. Then, 1M HCl in EtOAc (8 mL) was added slowly. After the addition, the mixture was stirred at room temperature for 1 h. After the reaction was completed, the mixture was quenched with $NaHCO_3$ and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The crude was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate 1:1) to give the corresponding aldehyde as a colorless oil (882 mg, 95% yield). Note, the aldehyde was not stable at room temperature. However, the aldehyde could be stored at -20 ^oC for three days without detectable decomposition.

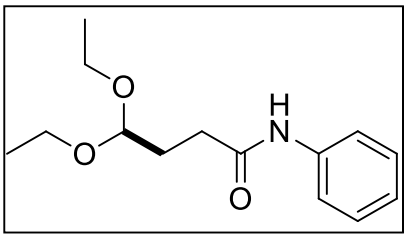
General Procedure for One-pot Synthesis of Aldehyde from *N*-methyl-*N*-phenylacrylamide:

Diethoxyacetic acid (1.5 equiv., 9 mmol, 1.34g), *N*-methyl-*N*-phenylacrylamide (1.0 equiv., 6 mmol, 968 mg), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.0 mol %, 135 mg) and K_2HPO_4 (1.2 equiv., 7.2 mmol, 1.65g) were placed in a Schlenk tube (100 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Then, anhydrous *N*,*N*-dimethylacetamide (DMF, 40 mL) was added via a syringe under argon atmosphere. The resulting reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 16 h. After the reaction was completed, the mixture was cooled to 0 ^oC in an ice bath. Then, 1M HCl in EtOAc (20 mL) was added slowly. After the addition, the mixture was stirred at room temperature for 1 h. After the reaction was completed, the mixture was quenched with $NaHCO_3$ and extracted with ethyl acetate (3 x 30 mL). The organic layers were combined and concentrated under vacuo. The crude was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate 3:1-1:1) to give the corresponding aldehyde as a colorless oil (808 mg, 71% overall yield).

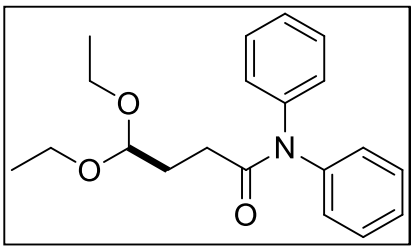
2.3 Spectral Data



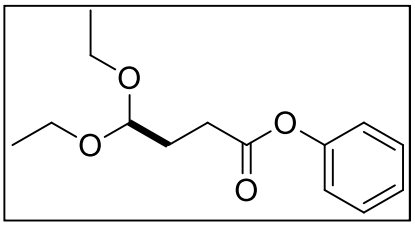
4,4-Diethoxy-N-methyl-N-phenylbutanamide 1: Colorless oil in 92% yield, 49 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.49-7.45 (t, *J* = 7.3 Hz, 2H), 7.38-7.35 (t, *J* = 6.6 Hz, 1H), 7.33-7.31 (d, *J* = 7.5 Hz, 2H), 4.42 (m, 1H), 3.52-3.47 (m, 2H), 3.41-3.33 (m, 2H), 3.20 (s, 3H), 2.10 (m, 2H), 1.81-1.76 (m, 2H), 1.07-1.04 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone) δ 171.3, 144.6, 129.6, 127.5, 101.8, 60.6, 36.3, 29.2, 14.8; HRMS (ESI) m/z calcd for $C_{15}H_{24}NO_3^+$ $[M+H]^+$: 266.1751, found 266.1763.



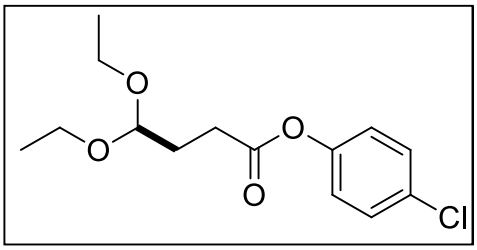
4,4-Diethoxy-N-phenylbutanamide 2: Colorless oil in 58 % yield, 29 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 9.16 (s, 1H), 7.68-7.66 (d, *J* = 7.9 Hz, 2H), 7.30-7.26 (t, *J* = 7.9 Hz, 2H), 7.04-7.01 (t, *J* = 7.4 Hz, 1H), 4.57-4.54 (t, *J* = 5.5 Hz, 1H), 3.64-3.59 (m, 2H), 3.51-3.44 (m, 2H), 2.45-2.41 (t, *J* = 7.5 Hz, 2H), 1.96-1.91 (dd, *J* = 7.5 Hz, 5.9 Hz, 2H), 1.15-1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 170.8, 139.7, 128.6, 123.0, 119.1, 102.0, 60.9, 31.8, 14.8; HRMS (ESI) m/z calcd for $C_{14}H_{22}NO_3^+$ $[M+H]^+$: 252.1594, found 252.1599.



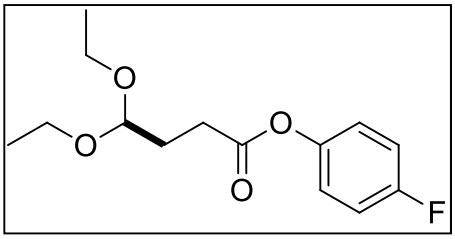
4,4-Diethoxy-*N,N*-diphenylbutanamide 3: Colorless oil in 78% yield, 51 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.37-7.28 (m, 10H), 4.50-4.47 (t, *J* = 5.5 Hz, 1H), 3.58-3.50 (m, 2H), 3.44-3.37 (m, 2H), 2.31-2.27 (t, *J* = 7.3 Hz, 2H), 1.89-1.84 (q, *J* = 6.7 Hz, 2H), 1.10-1.06 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 171.6, 143.5, 129.1, 127.4, 101.8, 60.7, 30.0, 29.2, 14.8; HRMS (ESI) m/z calcd for $C_{20}H_{26}NO_3^+$ $[M+H]^+$: 328.1907, found 328.1919.



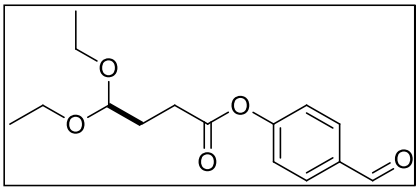
Phenyl 4,4-diethoxybutanoate 4: Colorless oil in 75% yield, 38 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.42-7.38 (t, *J* = 7.8 Hz, 2H), 7.25-7.22 (t, *J* = 7.4 Hz, 1H), 7.14-7.12 (d, *J* = 7.7 Hz, 2H), 4.62-4.60 (t, *J* = 5.5 Hz, 1H), 3.68-3.62 (m, 2H), 3.55-3.49 (m, 2H), 2.65-2.62 (t, *J* = 7.4 Hz, 2H), 2.01-1.95 (m, 2H), 1.18-1.14 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 171.4, 144.6, 129.6, 127.5, 101.8, 60.6, 36.4, 28.9, 14.80; HRMS (ESI) m/z calcd for $C_{14}H_{21}O_4^+$ $[M+H]^+$: 253.1434, found 253.1447.



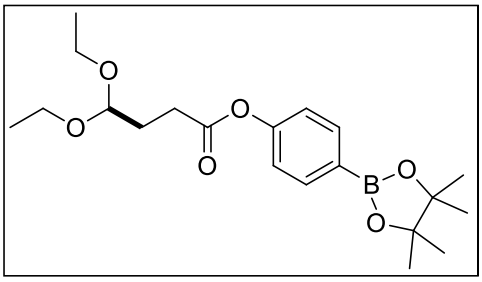
4-Chlorophenyl 4,4-diethoxybutanoate 5: white foam in 65% yield, 37 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.44-7.42 (d, *J* = 8.3 Hz, 2H), 7.18-7.16 (d, *J* = 8.4 Hz, 2H), 4.62-4.59 (t, *J* = 5.4 Hz, 1H), 3.69-3.62 (m, 2H), 3.55-3.47 (m, 2H), 2.66-2.62 (t, *J* = 7.4 Hz, 2H), 2.00-1.95 (q, *J* = 6.7 Hz, 2H), 1.17-1.14 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 171.2, 149.8, 130.3, 129.2, 123.5, 101.7, 61.2, 29.1, 28.8, 14.8; HRMS (ESI) m/z calcd for $C_{14}H_{20}ClO_4^+$ $[M+H]^+$: 287.1045, found 287.1053.



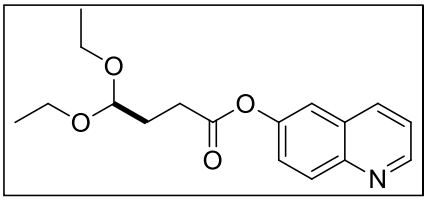
4-Fluorophenyl 4,4-diethoxybutanoate 6: Colorless oil in 72% yield, 39 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.06 (s, 2H), 7.04 (s, 2H), 4.61-4.58 (t, *J* = 5.5 Hz, 1H), 3.73-3.65 (m, 2H), 3.57-3.49 (m, 2H), 2.67-2.63 (t, *J* = 7.4 Hz, 2H), 2.08-2.03 (m, 2H), 1.24-1.20 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 171.4, 161.2-158.8 (d, *J* = 240.3 Hz), 147.1, 123.5-123.4 (d, *J* = 8.6 Hz), 115.8-115.6 (d, *J* = 23.5 Hz), 101.7, 61.2, 29.0, 28.8, 14.8; HRMS (ESI) m/z calcd for $C_{14}H_{20}FO_4^+$ $[M+H]^+$: 271.1340, found 271.1352.



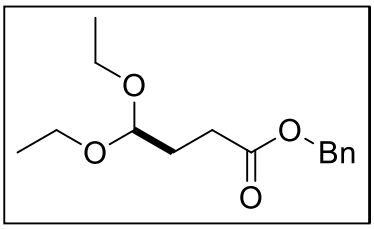
4-Formylphenyl 4,4-diethoxybutanoate 7: Colorless oil in 40% yield, 23 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 10.04 (s, 1H), 8.00-7.98 (d, *J* = 8.2 Hz, 2H), 7.40-7.38 (d, *J* = 8.1 Hz, 2H), 4.64-4.61 (t, *J* = 5.3 Hz, 1H), 3.69-3.63 (m, 2H), 3.56-3.48 (m, 2H), 2.71-2.68 (t, *J* = 7.3 Hz, 2H), 2.03-1.98 (q, *J* = 6.7 Hz, 2H), 1.18-1.15 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 190.9, 171.0, 155.7, 130.8, 122.6, 101.7, 61.3, 14.8; HRMS (ESI) m/z calcd for $C_{15}H_{21}O_5^+$ $[M+H]^+$: 281.1384, found 281.1395.



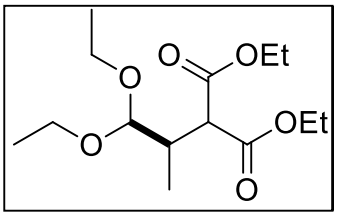
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl 4,4-diethoxybutanoate 8: white foam in 57% yield, 43 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.79-7.77 (d, *J* = 7.6 Hz, 2H), 7.16-7.14 (d, *J* = 7.6 Hz, 2H), 4.62-4.60 (t, *J* = 5.2 Hz, 1H), 3.70-3.62 (m, 2H), 3.55-3.49 (m, 2H), 2.67-2.63 (t, *J* = 7.3 Hz, 2H), 2.01-1.96 (q, *J* = 6.5 Hz, 2H), 1.33 (s, 12H), 1.18-1.15 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 176.4, 158.9, 141.05-141.00 (d, *J* = 6.0 Hz), 126.43, 126.40-126.38 (d, *J* = 2.1 Hz), 106.9, 88.9, 66.4, 34.1, 29.5, 20.0; HRMS (ESI) m/z calcd for $C_{20}H_{32}BO_6^+$ $[M+H]^+$: 379.2286, found 379.2299.



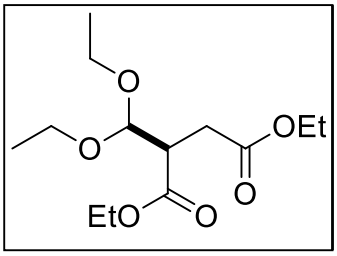
Quinolin-6-yl 4,4-diethoxybutanoate 9: pale yellow foam in 35 % yield, 22 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 8.90 (s, 1H), 8.33-8.31 (d, *J* = 8.1 Hz, 1H), 8.09-8.07 (d, *J* = 9.0 Hz, 1H), 7.70 (s, 1H), 7.58-7.51 (m, 2H), 4.66-4.64 (t, *J* = 5.3 Hz, 1H), 3.72-3.65 (m, 2H), 3.58-3.50 (m, 2H), 2.74-2.71 (t, *J* = 7.2 Hz, 2H), 2.06-2.01 (m, 2H), 1.20-1.16 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 172.4, 151.1, 149.8, 147.3, 136.4, 131.6, 129.5, 125.9, 122.6, 119.5, 102.6, 62.2, 30.1, 15.7; HRMS (ESI) m/z calcd for $C_{17}H_{22}NO_4^+$ $[M+H]^+$: 304.1543, found 304.1560.



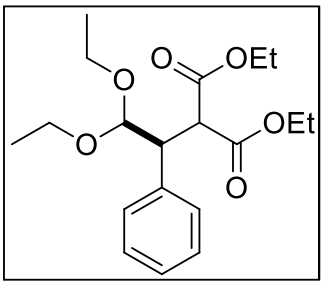
Benzyl 4,4-diethoxybutanoate 10: Colorless oil in 75% yield, 40 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.38-7.30 (m, 5H), 5.11 (s, 2H), 4.53-4.50 (t, *J* = 5.6 Hz, 1H), 3.66-3.60 (m, 2H), 3.51-3.43 (m, 2H), 2.47-2.43 (t, *J* = 7.5 Hz, 2H), 1.98-1.93 (q, *J* = 6.9 Hz, 2H), 1.17-1.14 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 172.5, 136.7, 128.4, 128.0, 127.9, 101.7, 65.5, 61.0, 29.0, 28.9, 14.8; HRMS (ESI) m/z calcd for $C_{15}H_{23}O_4^+$ $[M+H]^+$: 267.1591, found 267.1602.



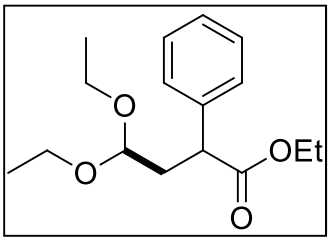
Diethyl 2-(1,1-diethoxypropan-2-yl)malonate 11: Colorless oil in 95% yield, 55 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 4.44-4.43 (d, *J* = 5.8 Hz, 1H), 4.18-4.12 (q, *J* = 7.1 Hz, 4H), 3.68-3.60 (m, 2H), 3.52-3.45 (m, 3H), 2.49-2.44 (m, 1H), 1.25-1.22 (t, *J* = 7.1 Hz, 6H), 1.16-1.12 (m, 6H), 0.99-0.98 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 168.4, 168.2, 104.1, 63.0, 61.9, 60.7, 60.6, 53.2, 36.9, 14.74, 14.67, 13.53, 13.49, 11.4; HRMS (ESI) m/z calcd for $C_{14}H_{27}O_6^+$ $[M+H]^+$: 291.1802, found 291.1809.



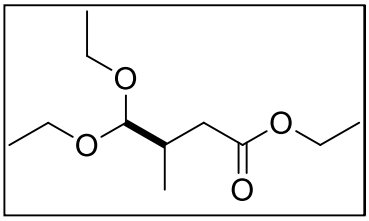
Diethyl 2-(diethoxymethyl)succinate 12: Colorless oil in 94% yield, 52 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 4.72-4.71 (d, *J* = 5.6 Hz, 1H), 4.17-4.05 (m, 4H), 3.71-3.64 (m, 2H), 3.55-3.48 (m, 2H), 3.13-3.08 (m, 1H), 2.70-2.55 (m, 2H), 1.24-1.19 (q, *J* = 6.8 Hz, 6H), 1.16-1.11 (q, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 171.5, 171.0, 102.3, 63.0, 62.5, 60.1, 60.0, 46.0, 30.9, 14.6, 14.5, 13.6; HRMS (ESI) m/z calcd for $C_{13}H_{25}O_6^+$ $[M+H]^+$: 277.1646, found 277.1655.



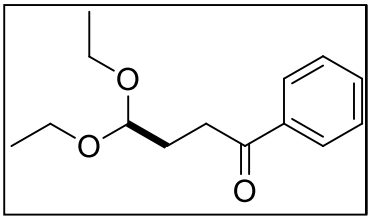
Diethyl 2-(2,2-diethoxy-1-phenylethyl)malonate 13: Colorless oil in 88% yield, 62 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.33-7.31 (d, *J* = 7.5 Hz, 2H), 7.27-7.24, (t, *J* = 7.3 Hz, 2H), 7.22-7.18 (t, *J* = 7.1 Hz, 1H), 4.74-4.72 (d, *J* = 5.7 Hz, 1H), 4.18-4.13 (q, *J* = 7.0 Hz, 2H), 3.95-3.92 (d, *J* = 10.4 Hz, 1H), 3.84-3.79 (m, 2H), 3.74-3.62 (m, 2H), 3.59-3.52 (m, 1H), 3.48-3.31 (m, 2H), 1.26-1.22 (t, *J* = 7.1 Hz, 3H), 1.12-1.09 (t, *J* = 7.0 Hz, 3H), 1.01-0.98 (t, *J* = 7.0 Hz, 3H), 0.92-0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 167.7, 167.3, 138.1, 129.7, 127.7, 126.8, 104.4, 63.5, 62.3, 60.8, 60.5, 54.2, 49.1, 14.6, 14.5, 13.5, 13.1; HRMS (ESI) m/z calcd for $C_{19}H_{29}O_6^+$ $[M+H]^+$: 353.1959, found 353.1966.



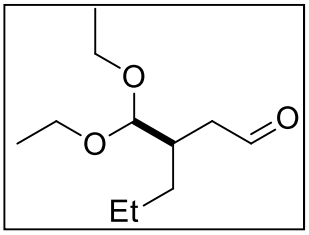
Ethyl 4,4-diethoxy-2-phenylbutanoate 14: Colorless oil in 81% yield, 45 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.33 (m, 4H), 7.27-7.25 (m, 1H), 4.39-4.36 (t, *J* = 5.4 Hz, 1H), 4.13-4.02 (m, 2H), 3.74-3.70 (m, 1H), 3.65-3.55 (m, 2H), 3.46-3.40 (m, 2H), 2.41-2.38 (m, 1H), 1.96-1.92 (m, 1H), 1.18-1.14 (t, *J* = 6.7 Hz, 6H), 1.30-1.10 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 173.0, 139.4, 128.6, 127.8, 127.1, 100.8, 61.2, 60.9, 60.2, 47.3, 37.5, 14.8, 13.5; HRMS (ESI) m/z calcd for $C_{16}H_{25}O_4^+$ $[M+H]^+$: 281.1747, found 281.1759.



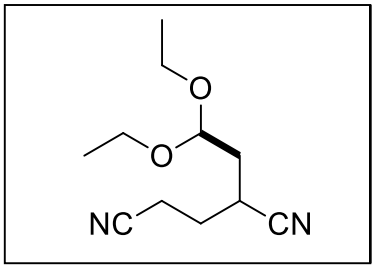
Ethyl 4,4-diethoxy-3-methylbutanoate 15: Colorless oil in 47% yield, 21 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 4.28-4.27 (d, *J* = 5.7 Hz, 1H), 4.11-4.06 (q, *J* = 7.1 Hz, 2H), 3.68-3.60 (m, 2H), 3.51-3.45 (m, 2H), 2.50-2.45 (dd, *J* = 4.9 Hz, 15.2 Hz, 1H), 2.22-2.17 (m, 1H), 2.10-2.04 (m, 1H), 1.23-1.20 (t, *J* = 7.2 Hz, 3H), 1.16-1.13 (t, *J* = 7.0 Hz, 6H), 0.94-0.92 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 172.3, 105.6, 62.5, 61.8, 59.5, 36.4, 34.0, 14.8, 14.7, 14.4, 13.7; HRMS (ESI) m/z calcd for $C_{11}H_{23}O_4^+$ $[M+H]^+$: 219.1591, found 219.1602.



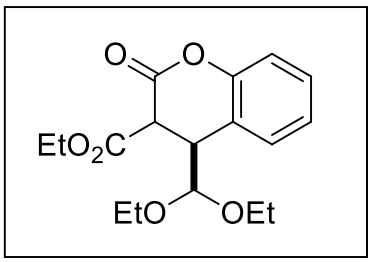
4,4-Diethoxy-1-phenylbutan-1-one 16: Colorless oil in 48% yield, 23 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 8.02-8.00 (d, *J* = 7.1 Hz, 2H), 7.64-7.60 (t, *J* = 7.3 Hz, 1H), 7.54-7.50 (t, *J* = 7.6 Hz, 2H), 4.62-4.59 (t, *J* = 5.6 Hz, 1H), 3.68-3.60 (m, 2H), 3.52-3.44 (m, 2H), 3.12-3.10 (t, *J* = 7.2 Hz, 2H), 2.00-1.95 (m, 2H), 1.15-1.12 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 199.0, 137.3, 132.8, 128.5, 127.8, 101.9, 60.9, 33.2, 28.1, 14.8; HRMS (ESI) m/z calcd for $C_{14}H_{21}O_3^+$ $[M+H]^+$: 237.1485, found 237.1497.



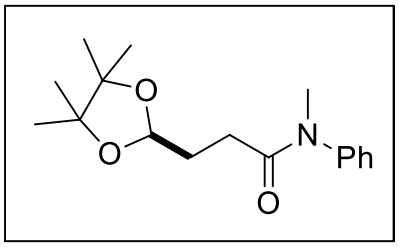
3-(Diethoxymethyl)hexanal 17: Colorless oil in 60% yield, 24 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 4.41-4.40 (d, *J* = 4.3 Hz, 1H), 3.70-3.60 (m, 2H), 3.54-3.45 (m, 2H), 2.50-2.43 (m, 1H), 2.21-2.13 (m, 2H), 1.53-1.46 (m, 1H), 1.43-1.32 (m, 3H), 1.16-1.23 (t, *J* = 7.0 Hz, 6H), 0.91-0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 173.7, 104.7, 62.7, 62.2, 38.5, 33.7, 32.0, 19.8, 14.8, 14.7, 13.8; HRMS (ESI) m/z calcd for $C_{11}H_{23}O_3^+$ $[M+H]^+$: 203.1642, found 203.1655.



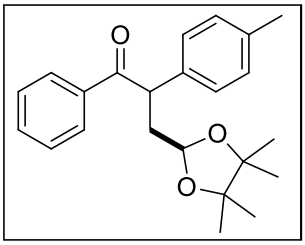
2-(2,2-Diethoxyethyl)pentanedinitrile 18: Colorless oil in 36% yield, 15 mg; ^{1}H NMR (400 MHz, d^{6}-acetone) δ 4.78-4.64 (m, 1H), 3.74-3.65 (m, 2H), 3.60-3.52 (m, 2H), 3.03-2.89 (m, 1H), 2.75-2.67 (m, 2H), 2.12-2.05 (m, 2H), 2.00-1.94 (m, 2H), 1.18 (td, *J* = 7.0, 1.2 Hz, 6H). ^{13}C NMR (100 MHz, d^{6}-acetone) δ 120.4, 118.6, 100.4, 61.60, 61.57, 35.4, 27.9, 26.6, 14.73, 14.69, 14.5; HRMS (ESI) m/z calcd for $C_{11}H_{19}N_2O_2^+$ $[M+H]^+$: 211.1441, found 211.1456.



Ethyl 4-(diethoxymethyl)-2-oxochroman-3-carboxylate 19: Colorless oil in 54% yield, 35 mg; ^{1}H NMR (400 MHz, d^{6}-acetone) δ 7.43 – 7.31 (m, 2H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.69 (d, *J* = 3.3 Hz, 1H), 4.12 – 4.02 (m, 3H), 3.79 – 3.52 (m, 4H), 3.34 (dq, *J* = 9.5, 7.0 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, d^{6}-acetone) δ 167.6, 163.0, 152.3, 129.9, 129.0, 124.0, 119. 8, 116.2, 104.40, 104.39, 64.8, 63.8, 61.7, 46.6, 44.9, 14.5, 14.4, 13.3; HRMS (ESI) m/z calcd for $C_{17}H_{23}O_6^+$ $[M+H]^+$: 323.1489, found 323.1495.

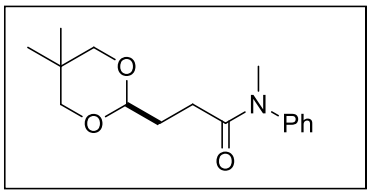


***N*-Methyl-*N*-phenyl-3-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)propanamide 20**: Colorless oil in 85% yield, 50 mg; ^{1}H NMR (400 MHz, d^{6}-acetone) δ 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.26 (m, 3H), 4.91 (m, 1H), 3.21 (s, 3H), 2.15 (m, 2H), 1.77 (dt, *J* = 12.6, 6.4 Hz, 2H), 1.11 (s, 6H), 1.08 (s, 6H). ^{13}C NMR (100 MHz, d^{6}-acetone) δ 171.1, 144.6, 129.6, 127.5, 99.7, 81.3, 36.3, 32.0, 28.9, 23.6, 21.5; HRMS (ESI) m/z calcd for $C_{17}H_{26}NO_3^+$ $[M+H]^+$: 292.1907, found 292.1916.

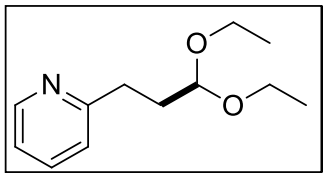


1-Phenyl-3-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-2-(p-tolyl)propan-1-one 21: Colorless oil in 71% yield, 50 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 8.03-8.01 (m, 2H), 7.55-7.51 (m, 1H), 7.46-7.42 (t, *J* = 5.3 Hz, 2H), 7.25-7.23 (d, *J* = 8.0 Hz, 2H), 7.12-7.10 (d, *J* = 8.0 Hz, 2H), 4.91-4.87 (m, 2H), 2.53-2.47 (m, 1H), 2.23 (s, 3H), 1.99-1.93 (m, 1H), 1.16 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 198.5, 136.8, 136.6, 136.5, 132.8, 129.5, 128.6, 128.5, 128.1, 98.6, 81.59, 81.57, 48.3, 40.6, 23.7, 21.6, 21.5, 20.1; HRMS (ESI) m/z calcd

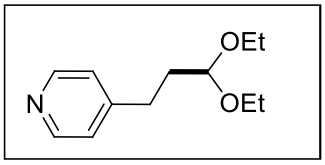
for $C_{23}H_{29}O_3^+$ [M+H]$^+$: 353.2111, found 353.2119.



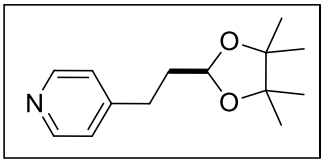
3-(5,5-Dimethyl-1,3-dioxan-2-yl)-*N*-methyl-*N*-phenylpropanamide 22: Colorless oil in 83% yield, 46 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.23 – 7.15 (m, 2H), 4.46 (t, *J* = 4.7 Hz, 1H), 3.54 (d, *J* = 10.9 Hz, 2H), 3.38 (d, *J* = 10.8 Hz, 2H), 3.28 (s, 3H), 2.22 (t, *J* = 7.1 Hz, 2H), 1.94 (dd, *J* = 12.3, 7.0 Hz, 2H), 1.11 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 144.2, 129.8, 127.8, 127.5, 101.1, 77.2, 37.5, 30.3, 28.6, 23.0, 22.0; HRMS (ESI) m/z calcd for $C_{16}H_{24}NO_3^+$ [M+H]$^+$: 278.1751, found 278.1760.



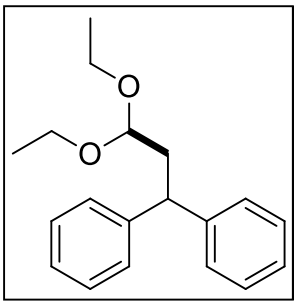
2-(3,3-Diethoxypropyl)pyridine 24: Colorless oil in 75% yield, 31 mg; ^{1}H NMR (400 MHz, d^6-acetone): δ 8.49-8.48 (d, *J* = 4.6 Hz, 1H), 7.68-7.64 (m, 1H), 7.24-7.22 (d, *J* = 7.8 Hz, 1H), 7.17-7.14 (m, 1H), 4.54-4.51 (t, *J* = 5.6 Hz, 1H), 3.67-3.59 (m, 2H), 3.51-3.44 (m, 2H), 2.83-2.79 (m, 2H), 2.03-1.97 (m, 2H), 1.16-1.13 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, d^6-acetone): δ 161.6, 149.1, 136.1, 122.7, 120.9, 102.1, 60.6, 33.3, 33.1, 14.9; HRMS (ESI) m/z calcd for $C_{12}H_{20}NO_2^+$ [M+H]$^+$: 210.1489, found 210.1496.



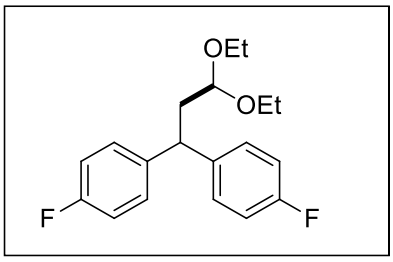
4-(3,3-Diethoxypropyl)pyridine 25: Colorless oil in 61% yield, 36 mg; ^{1}H NMR (400 MHz, d^6-acetone) δ 8.47 (d, *J* = 4.1 Hz, 2H), 7.24 (d, *J* = 5.8 Hz, 2H), 4.51 (t, *J* = 5.6 Hz, 1H), 3.65 (dq, *J* = 9.5, 7.1 Hz, 2H), 3.49 (dq, *J* = 9.4, 7.1 Hz, 2H), 2.70 (dd, *J* = 9.1, 6.9 Hz, 2H), 1.98 – 1.84 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, d^6-acetone) δ 149.6, 123.8, 101.8, 60.7, 34.1, 30.0, 14.8; HRMS (ESI) m/z calcd for $C_{12}H_{20}NO_2^+$ [M+H]$^+$: 210.1489, found 210.1496.



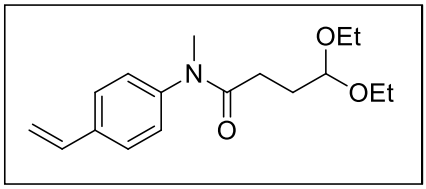
4-(2-(4,4,5,5-Tetramethyl-1,3-dioxolan-2-yl)ethyl)pyridine 26: Colorless oil in 63% yield, 30 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 8.46-8.44 (d, *J* = 1.6 Hz, 4.4 Hz, 2H), 7.23-7.22 (m, 2H), 5.04-5.02 (t, *J* = 5.2Hz, 1H), 2.73-2.69 (m, 2H), 1.89-1.83 (m, 2H), 1.19 (s, 6H), 1.17 (s, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 150.7, 149.7, 123.7, 99.6, 81.5, 36.8, 29.7, 23.7, 21.5; HRMS (ESI) m/z calcd for $C_{14}H_{22}NO_2^+$ $[M+H]^+$: 236.1645, found 236.1659.



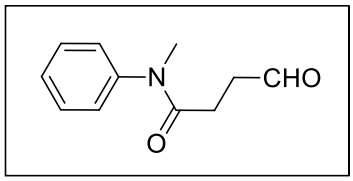
(3,3-Diethoxypropane-1,1-diyl)dibenzene 27: Colorless oil in 62% yield, 35 mg; ^{1}H NMR (400 MHz, d^{6}-acetone): δ 7.35-7.33 (d, *J* = 7.7 Hz, 4H), 7.30-7.26 (t, *J* = 7.5 Hz, 4H), 7.18-7.14 (t, *J* = 7.1 Hz, 2H), 4.26-4.23 (t, *J* = 5.8 Hz, 1H), 4.15-4.11 (t, *J* = 7.9 Hz, 1H), 3.59-3.54 (m, 2H), 3.40-3.36 (m, 2H), 2.36-2.33 (t, *J* = 6.9 Hz, 2H), 1.13-1.10 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, d^{6}-acetone): δ 144.96, 144.93, 128.45, 128.42, 127.79, 127.76, 126.15, 126.11, 101.03, 101.00, 60.7, 60.6, 47.1, 39.2, 14.90, 14.87; HRMS (ESI) m/z calcd for $C_{19}H_{25}O_2^+$ $[M+H]^+$: 285.1849, found 285.1856.



4,4'-(3,3-Diethoxypropane-1,1-diyl)bis(fluorobenzene) 28: Colorless oil in 53% yield, 34 mg; ^{1}H NMR (400 MHz, d^{6}-acetone) δ 7.52 – 7.26 (m, 4H), 7.24 – 6.92 (m, 4H), 4.25 (t, *J* = 5.9 Hz, 1H), 4.19 (t, *J* = 8.0 Hz, 1H), 3.59 (dq, *J* = 9.4, 7.0 Hz, 2H), 3.41 (dq, *J* = 9.4, 7.1 Hz, 2H), 2.33 (dd, *J* = 8.0, 5.9 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, d^{6}-acetone) δ 161.3 (d, *J* = 242.6 Hz), 140.8 (dd, *J* = 3.2, 0.9 Hz), 129.4 (d, *J* = 7.8 Hz), 115.0 (d, *J* = 21.2 Hz), 100.9, 60.7, 45.5, 39.4, 14.8; HRMS (ESI) m/z calcd for $C_{19}H_{23}F_2O_2^+$ $[M+H]^+$: 321.1661, found 321.1677.



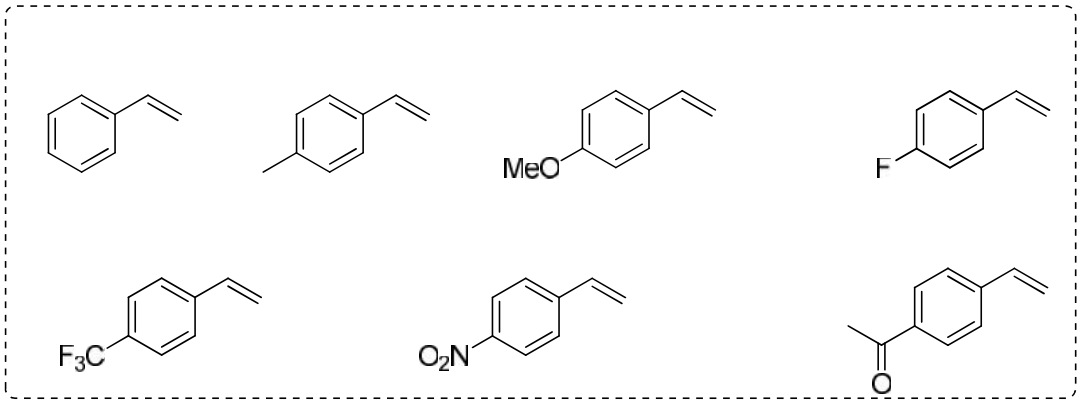
4,4-Diethoxy-*N*-methyl-*N*-(4-vinylphenyl)butanamide: Colorless oil in 77% yield, 45 mg; ^{1}H NMR (400 MHz, d^{6}-acetone) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.28 (m, 2H), 6.82 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.87 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.31 (dd, *J* = 11.0, 0.7 Hz, 1H), 4.44 (t, *J* = 5.5 Hz, 1H), 3.56 – 3.49 (m, 2H), 3.44 – 3.32 (m, 2H), 3.21 (s, 3H), 2.24 – 2.09 (m, 2H), 1.82 – 1.76 (m, 2H), 1.07 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, d^{6}-acetone) δ 171.6, 144.3, 136.4, 131.4, 129.0, 114.4, 101.9, 60.7, 36.6, 30.8, 29.1, 15.1. HRMS (ESI) m/z calcd for $C_{17}H_{26}NO_3^+$ $[M+H]^+$: 292.1907, found 292.1916.



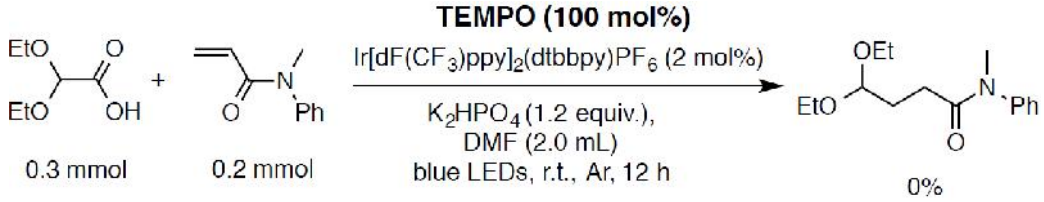
***N*-Methyl-4-oxo-*N*-phenylbutanamide**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.26 – 7.22 (m, 2H), 3.27 (s, 3H), 2.74 (t, *J* = 6.5 Hz, 2H), 2.37 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.19 (s), 171.33 (s), 143.82 (s), 130.00 (s), 128.11 (s), 127.45 (s), 77.48 (s), 77.16 (s), 76.84 (s), 39.11 (s), 37.53 (s), 27.14 (s); HRMS (EI) m/z calcd for $C_{11}H_{13}NO_2$ $[M]^+$ 191.0946, found 191.0951.

3. Failed Substrates and Mechanism Study

We have tried some styrene derivatives under the standard conditions, however, the reaction didn't occur and the starting materials were recovered. The failed substrates are shown as below:

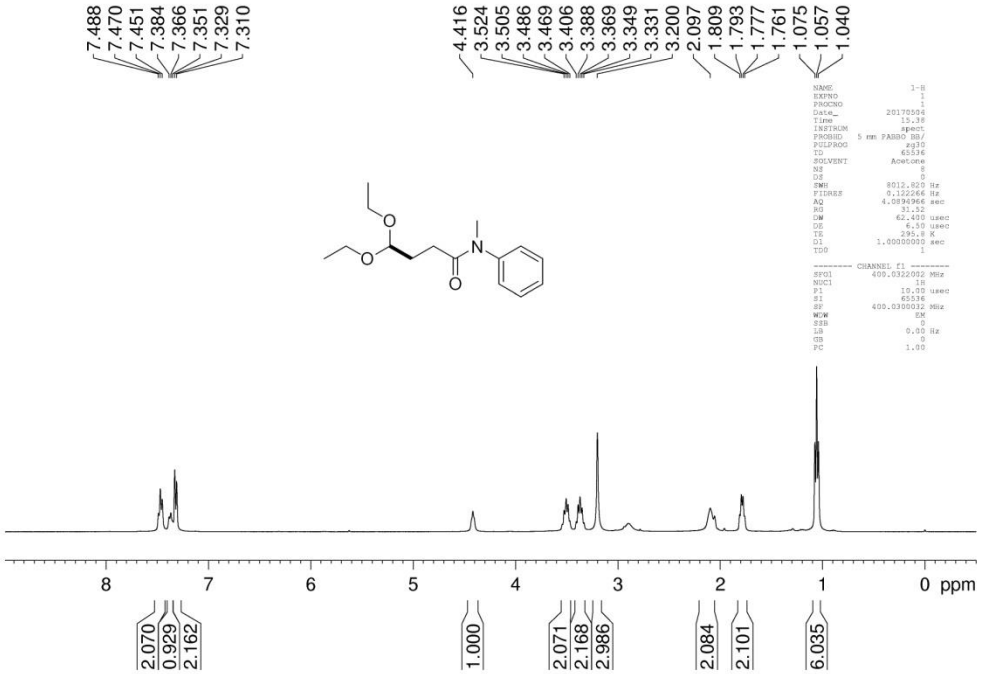


To gain insight into the mechanism, the radical trapping experiment was carried out using TEMPO as the radical trapping regents. When 1equiv of TEMPO was added to the standard reaction, the reaction was inhibited and no desired product was obtained. The results showed that a radical intermediate may be involved in this decarboxylative reaction.

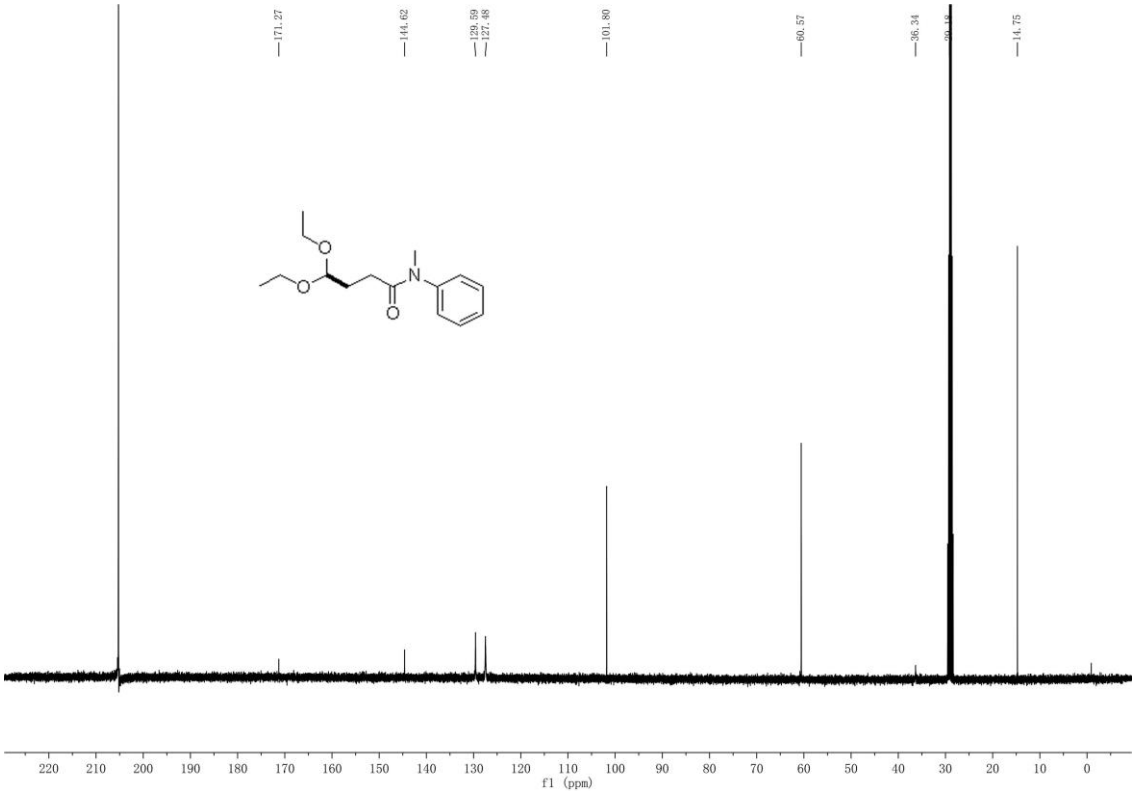


4. NMR Spectra

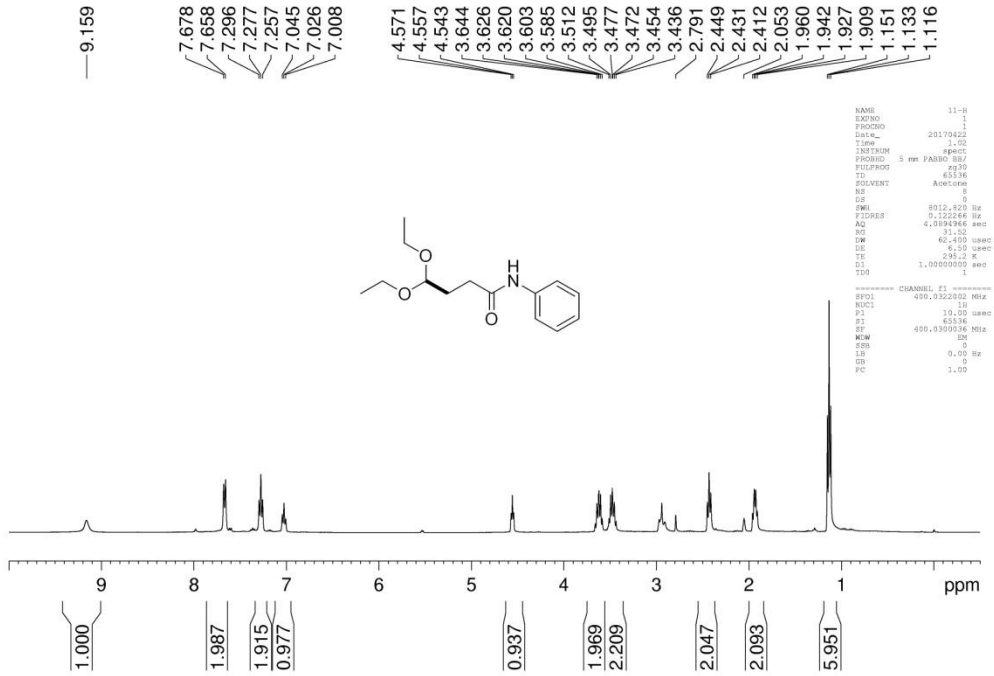
^{1}H NMR of **1**



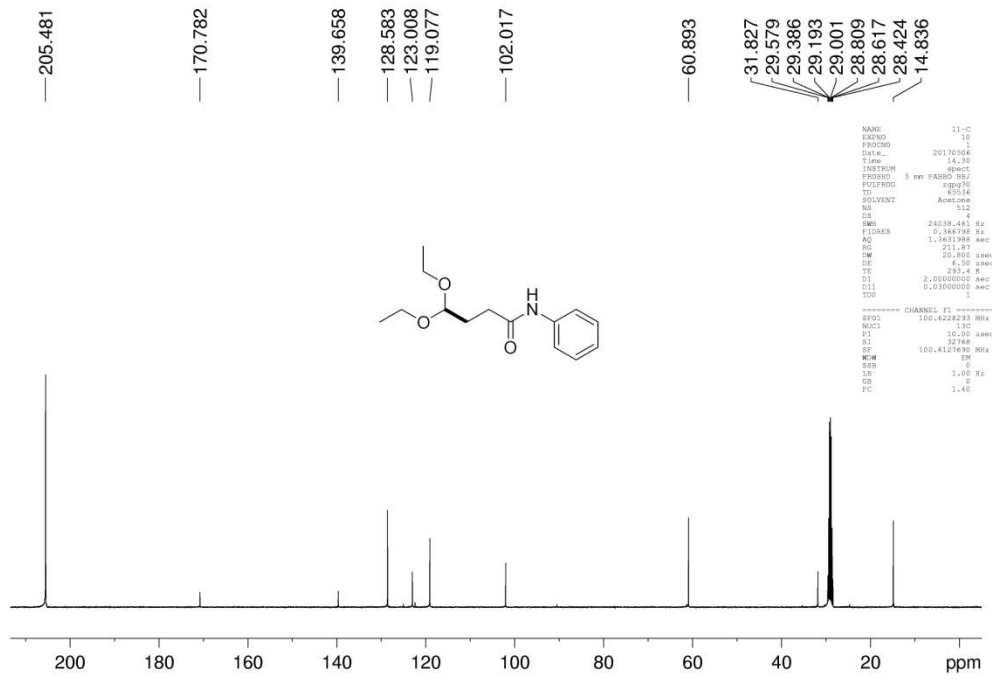
^{13}C NMR of **1**



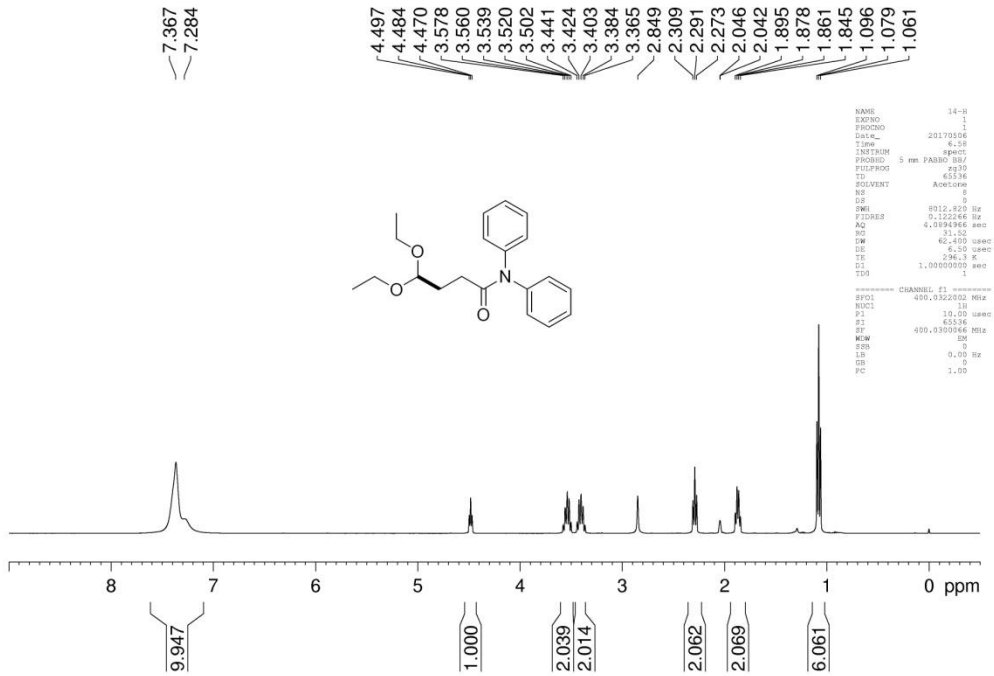
^{1}H NMR of **2**



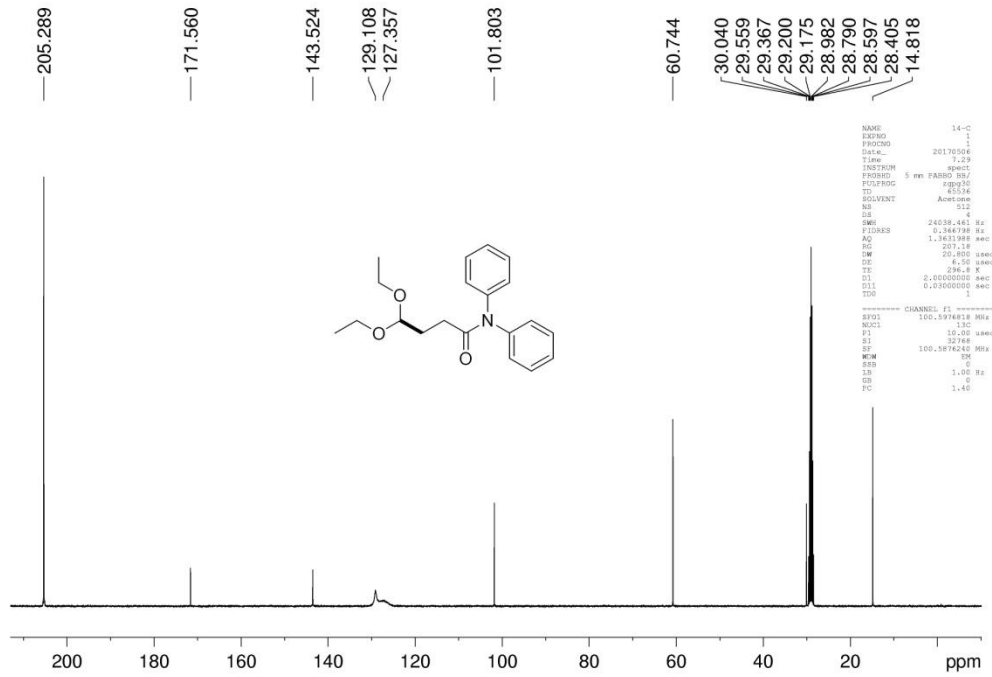
^{13}C NMR of **2**



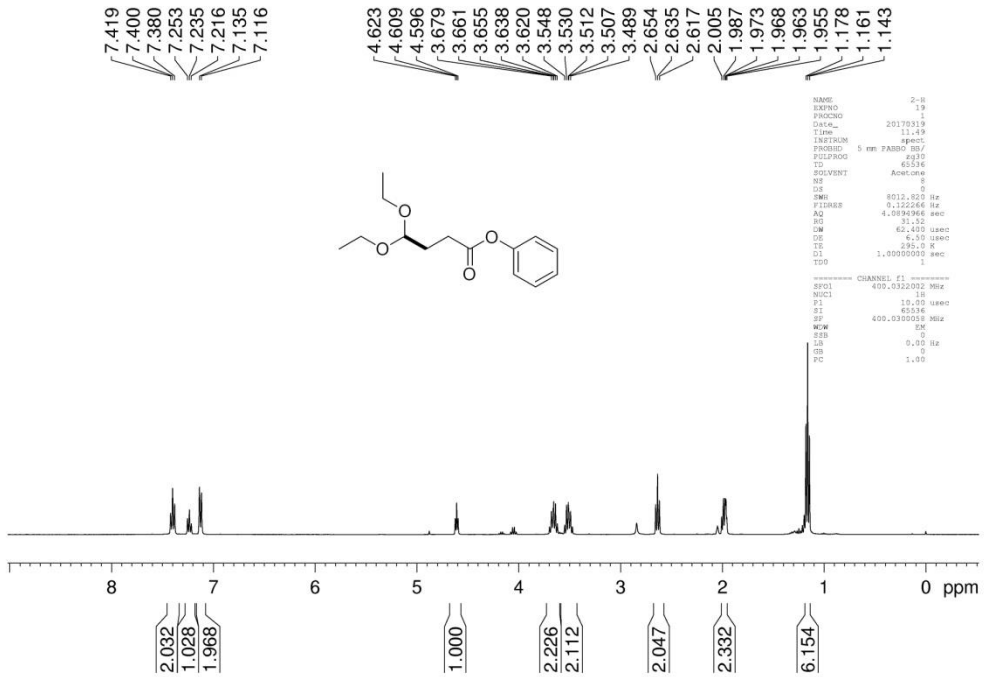
^{1}H NMR of **3**



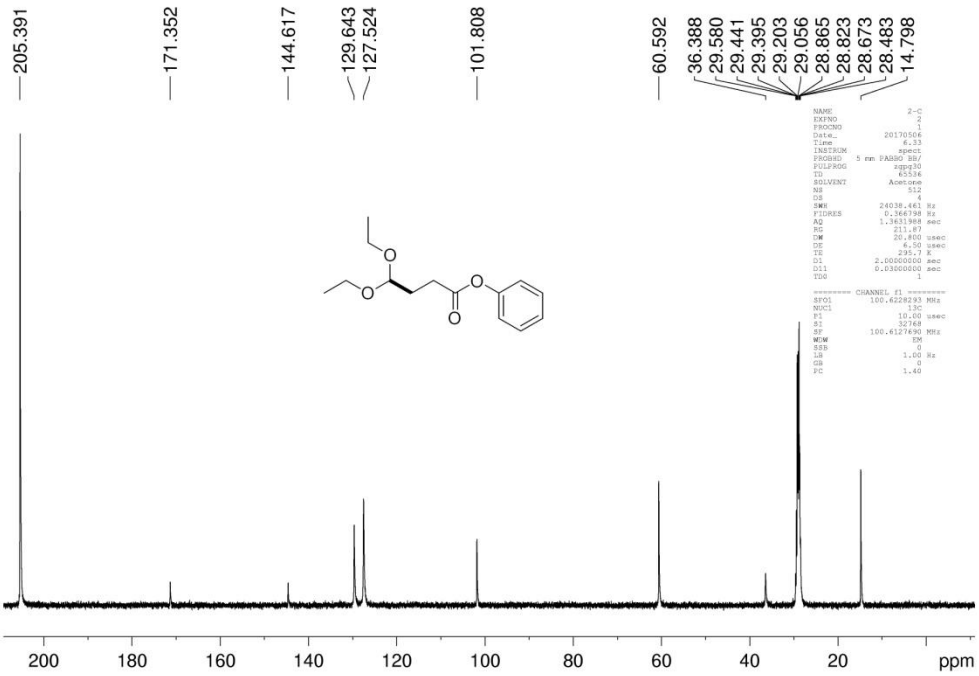
^{13}C NMR of **3**



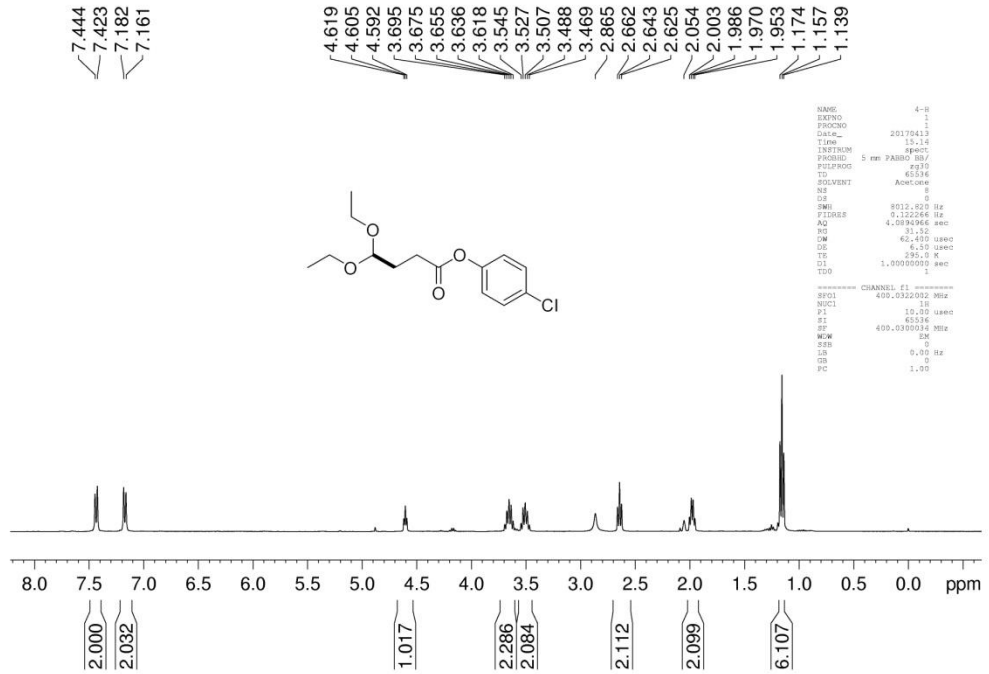
^{1}H NMR of **4**



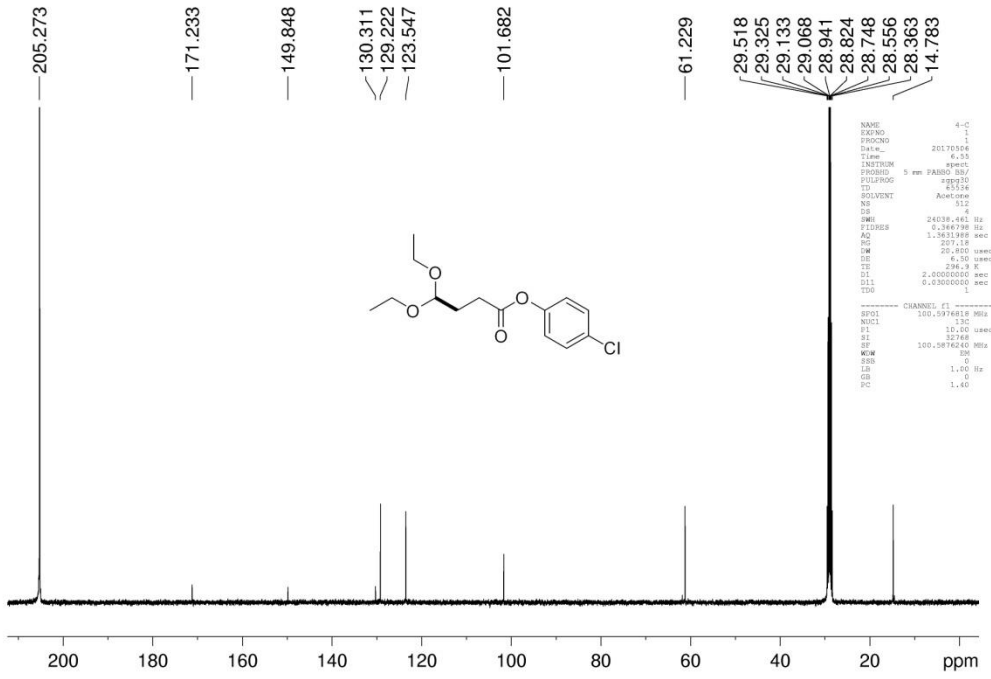
^{13}C NMR of **4**



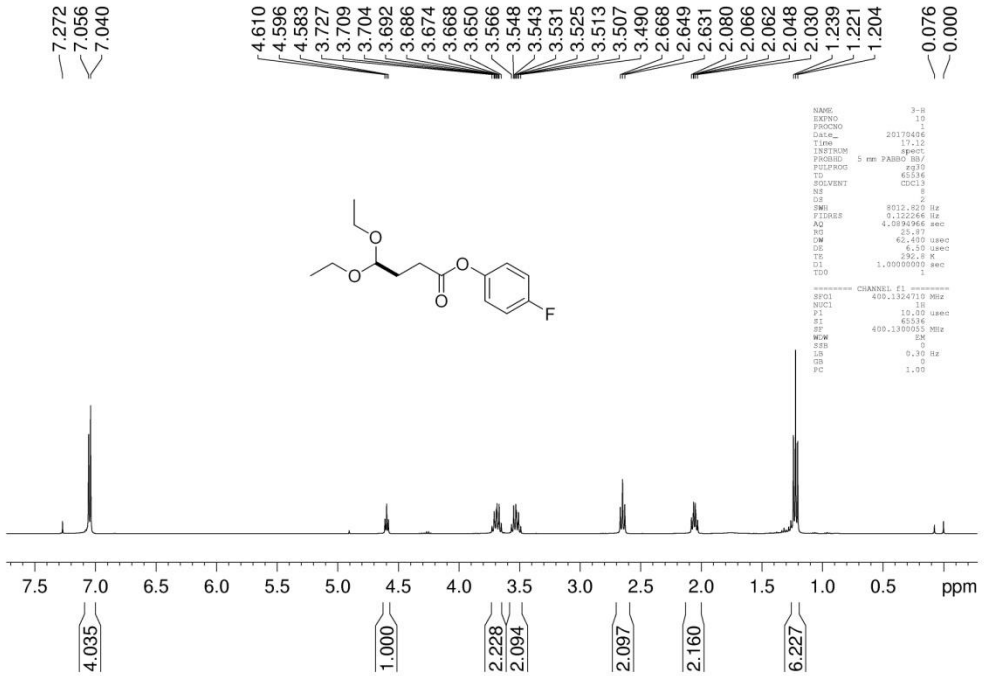
^{1}H NMR of **5**



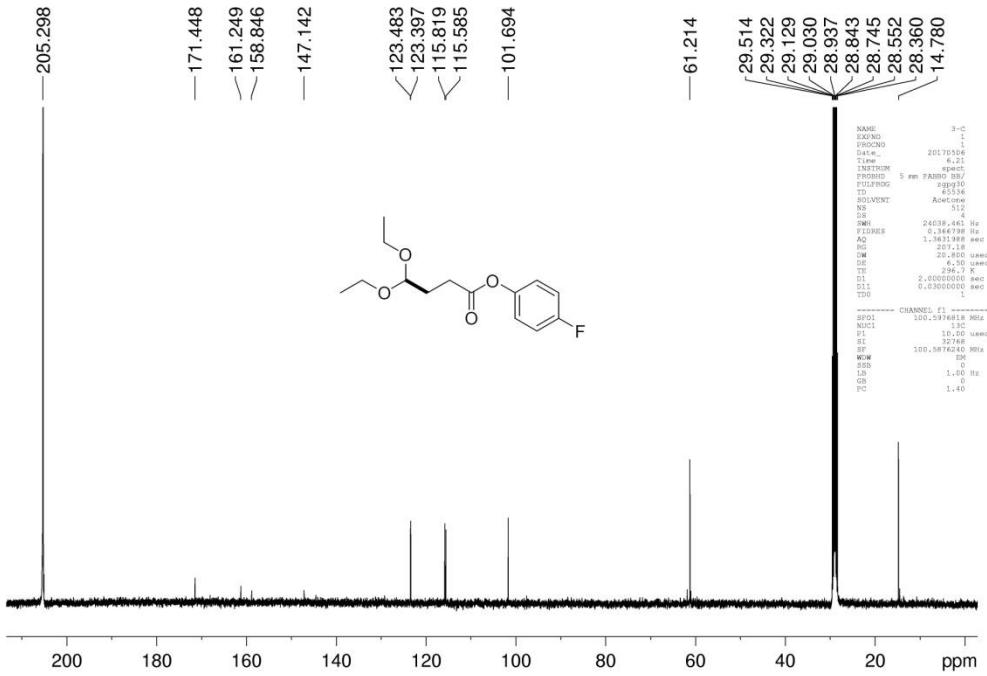
^{13}C NMR of **5**



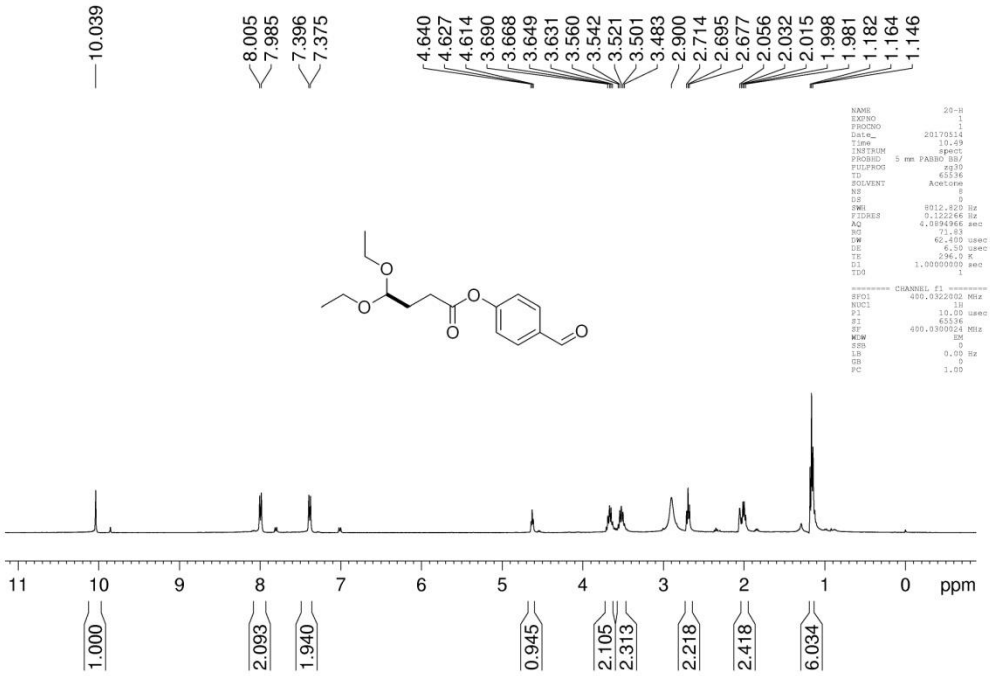
^{1}H NMR of **6**



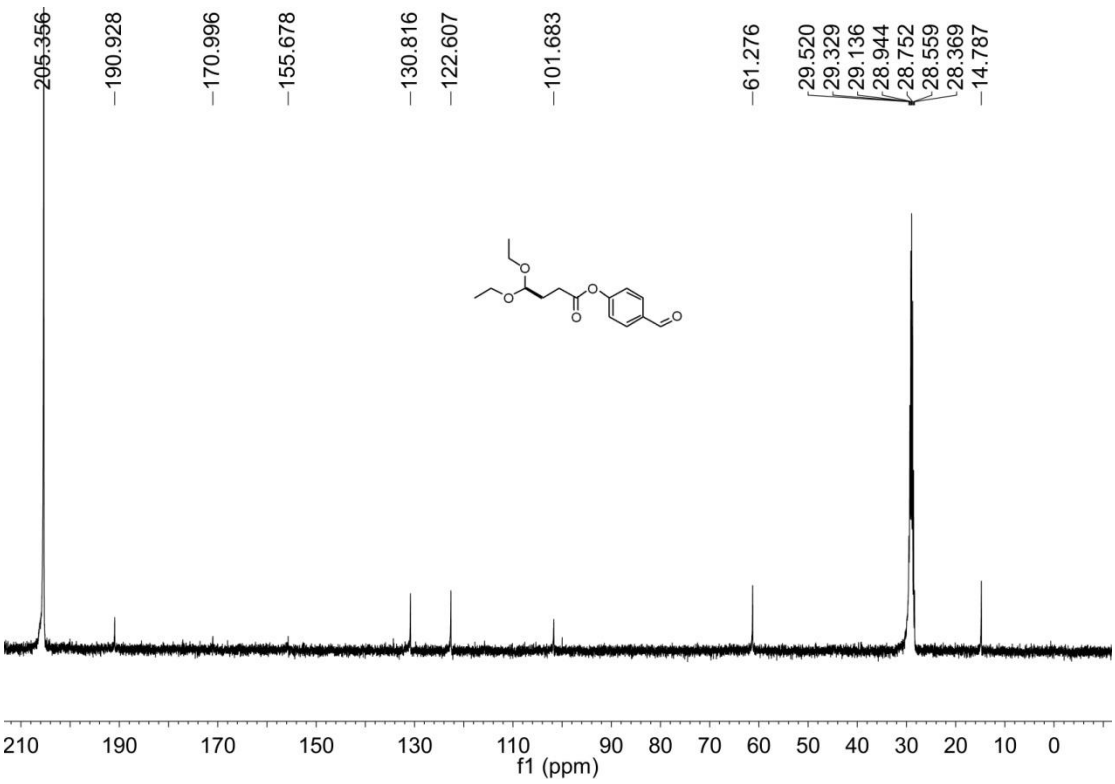
^{13}C NMR of **6**



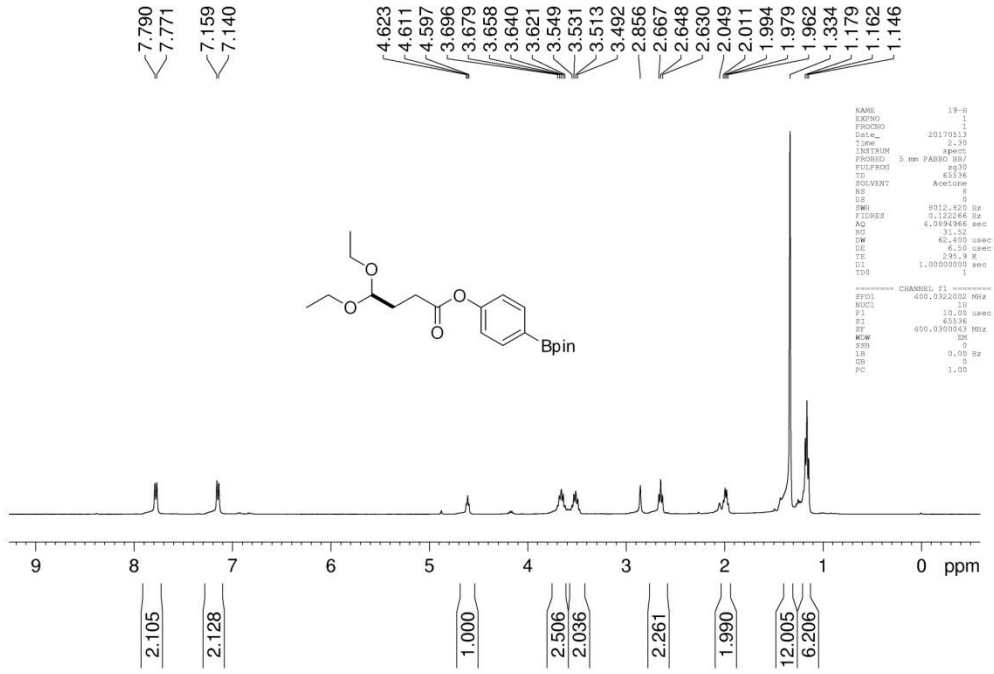
^{1}H NMR of **7**



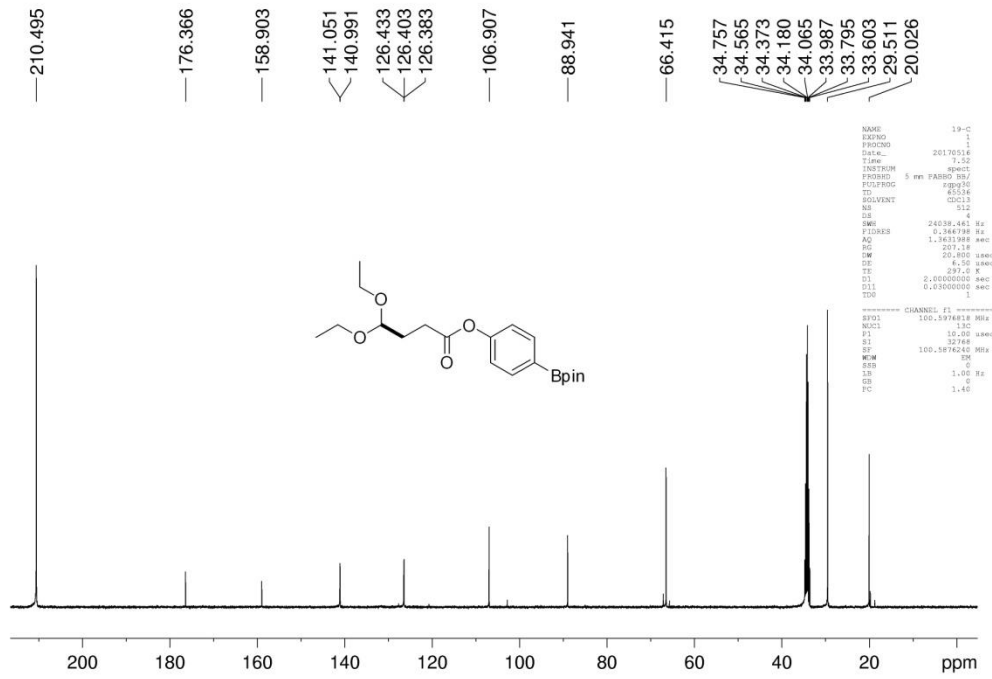
^{13}C NMR of **7**



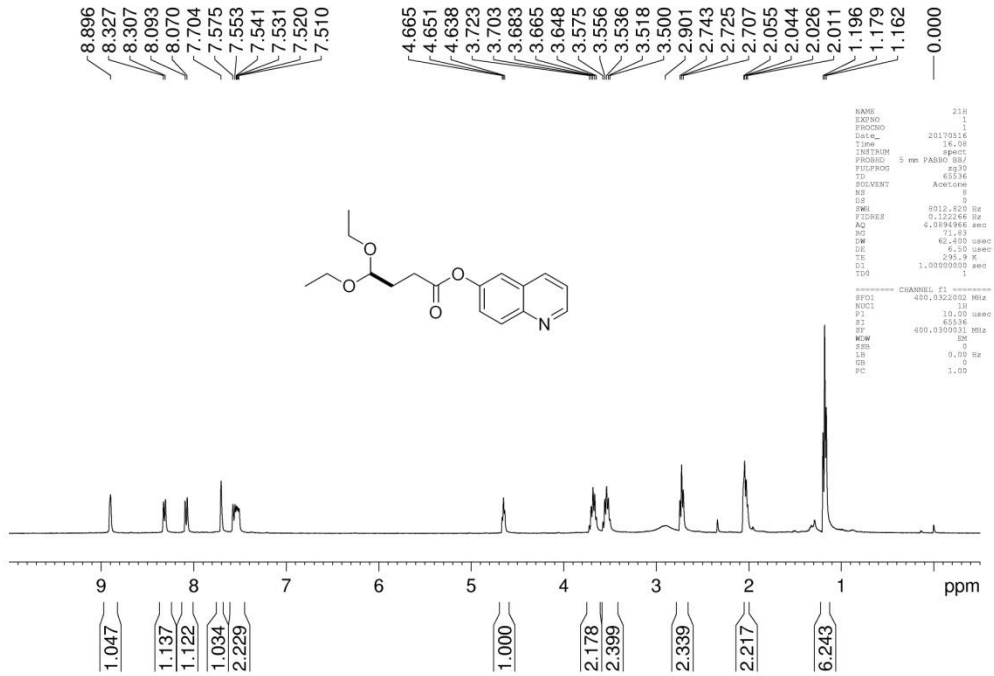
^{1}H NMR of **8**



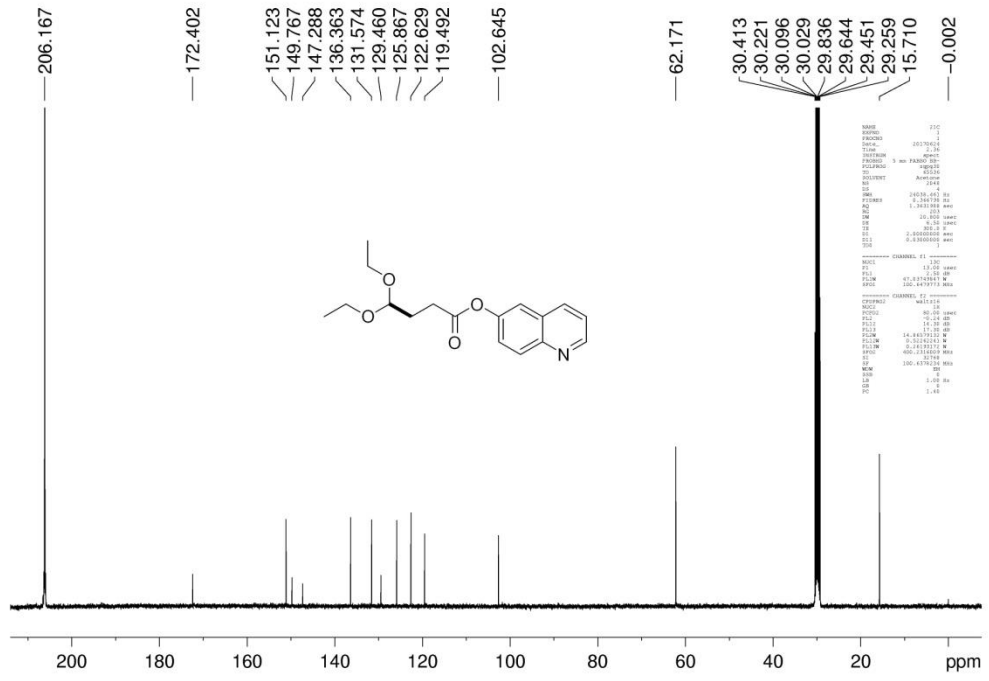
^{13}C NMR of **8**



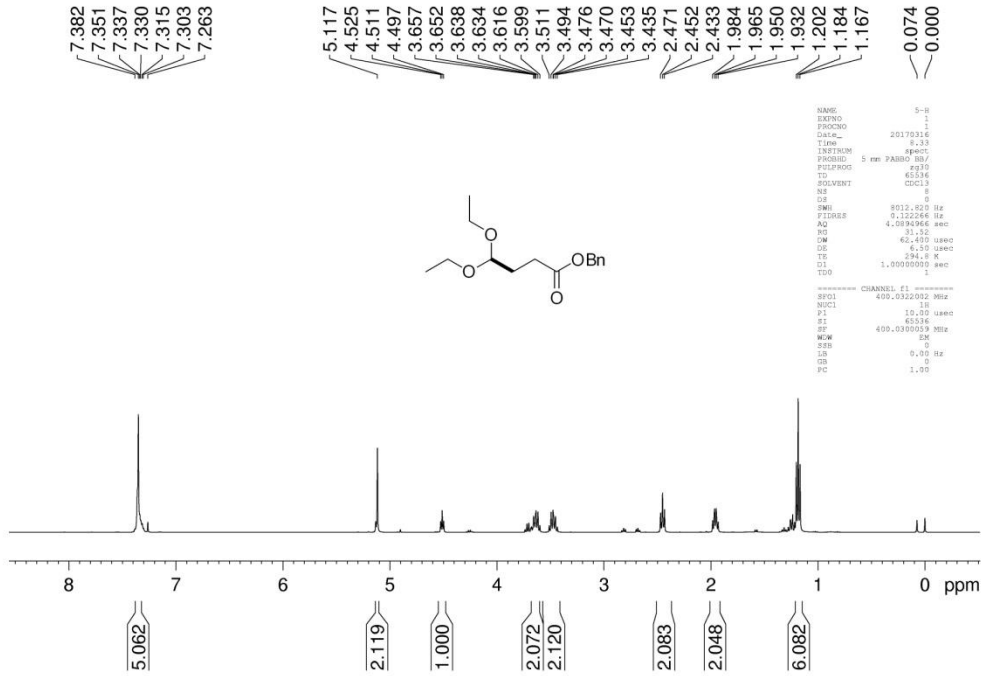
^{1}H NMR of **9**



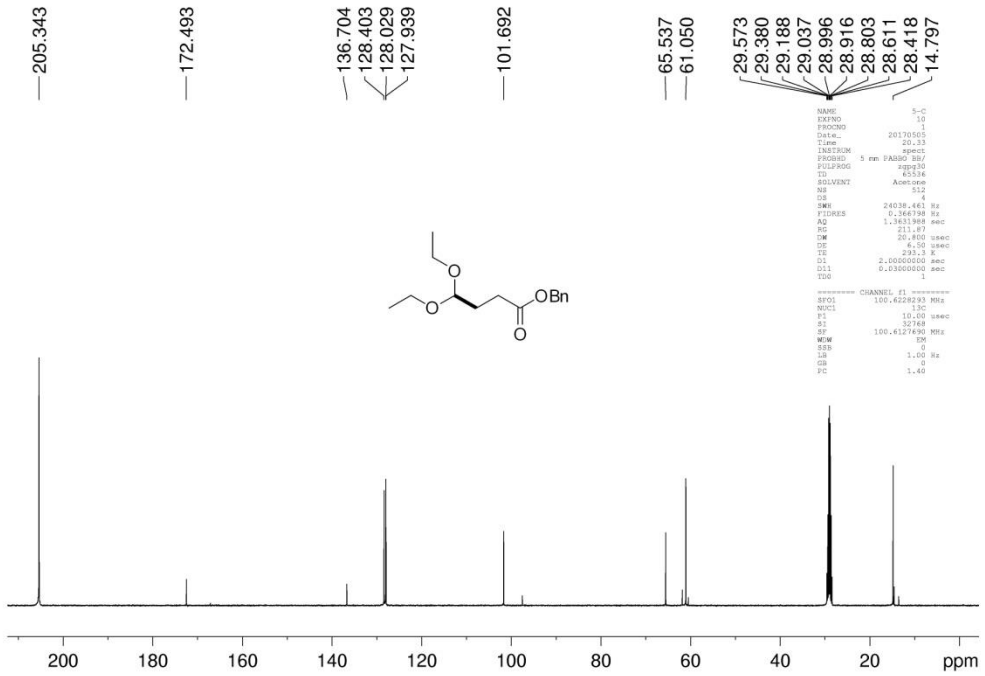
^{13}C NMR of **9**



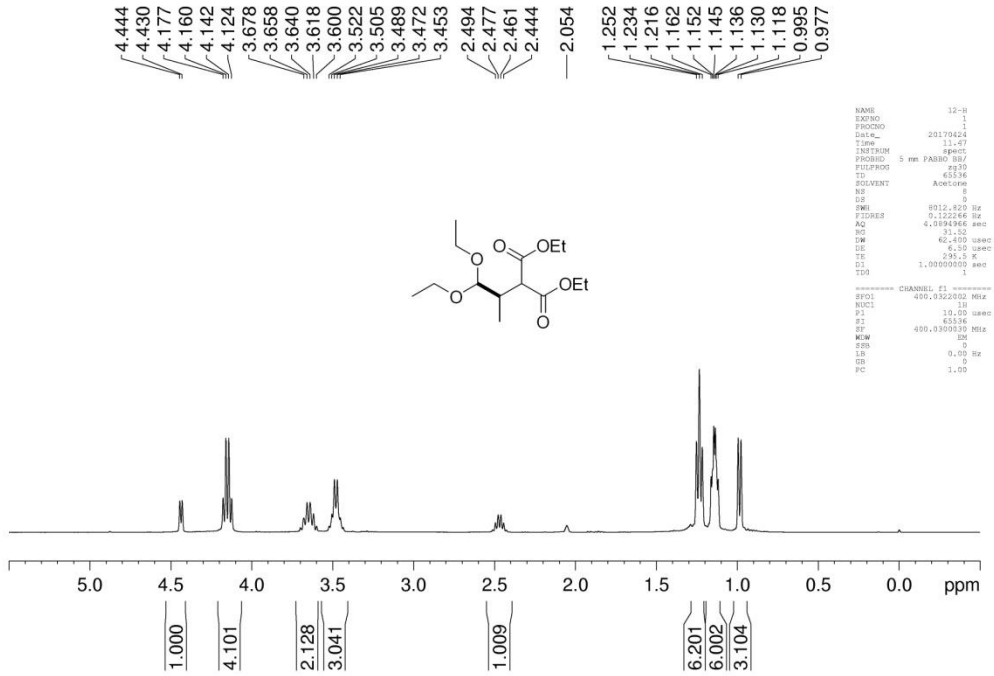
^{1}H NMR of **10**



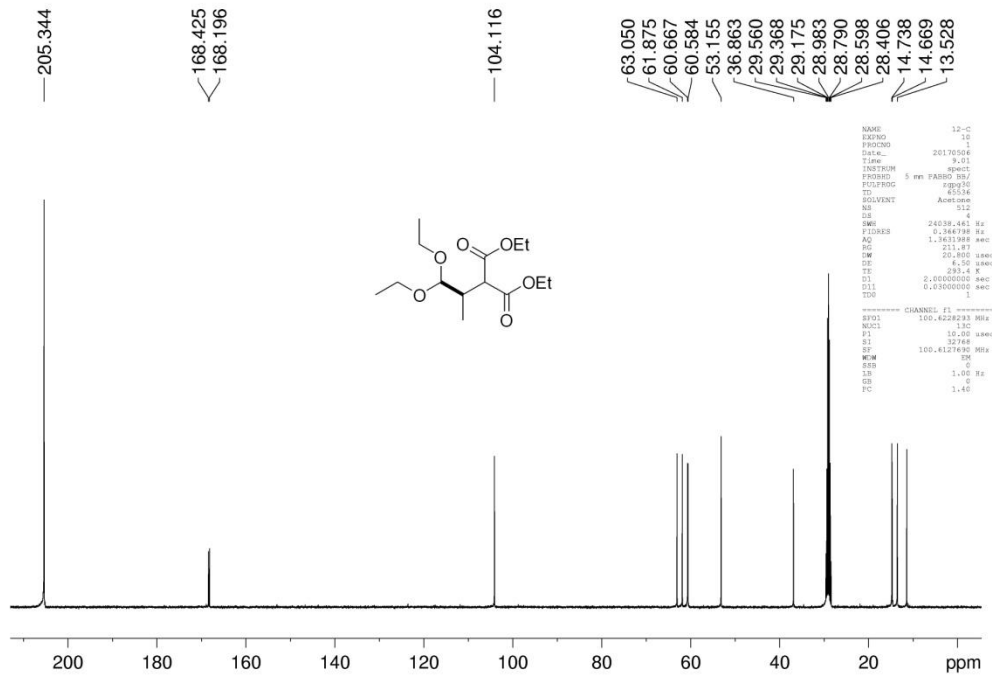
^{13}C NMR of **10**



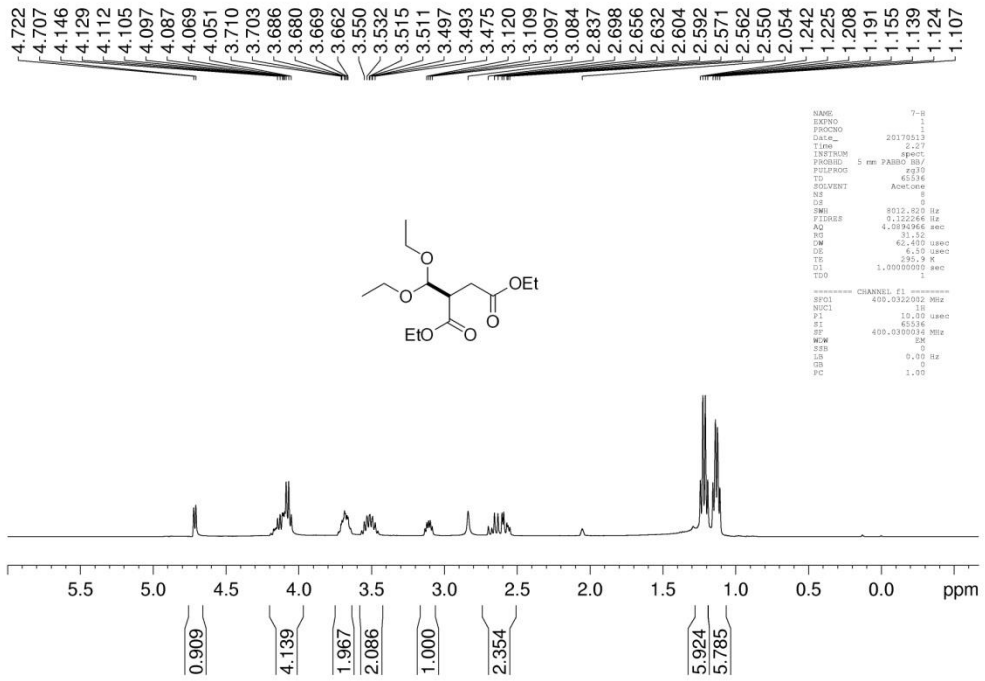
^{1}H NMR of **11**



^{13}C NMR of **11**



^{1}H NMR of **12**



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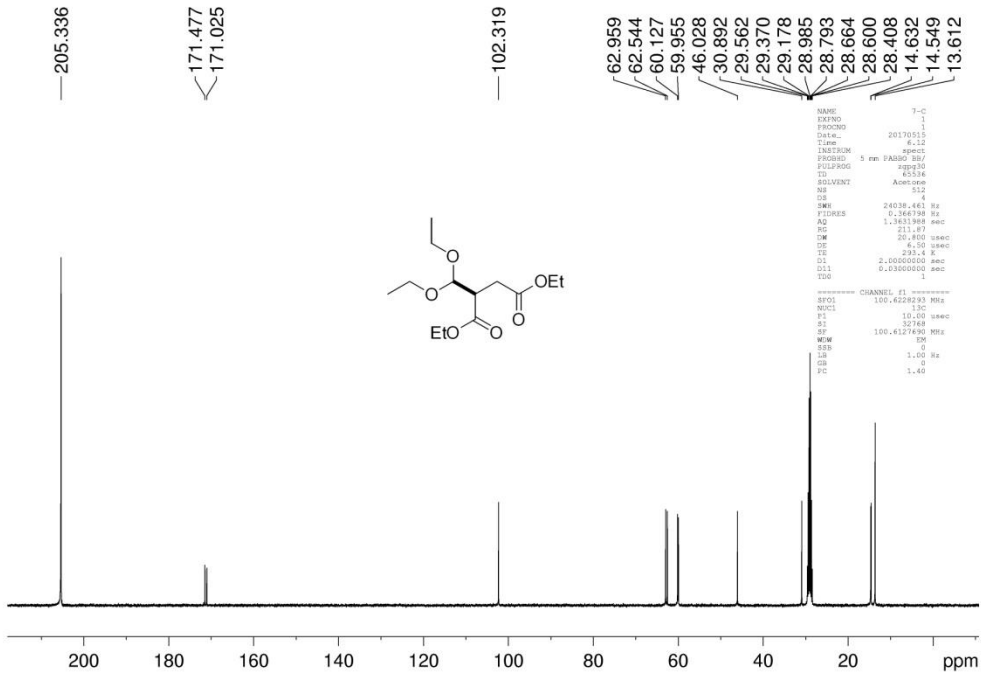
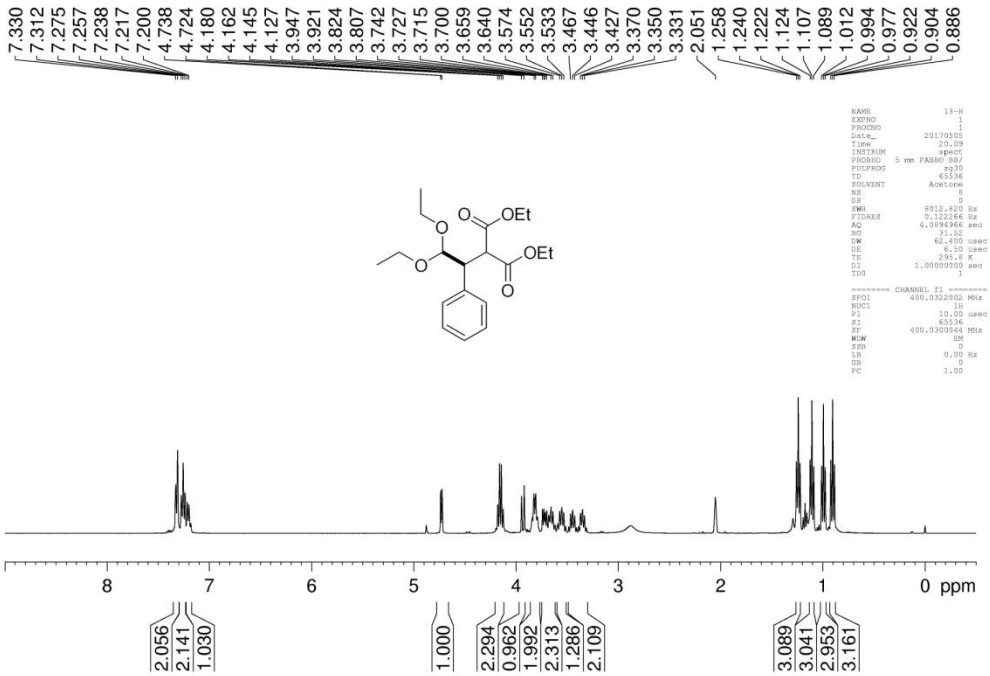
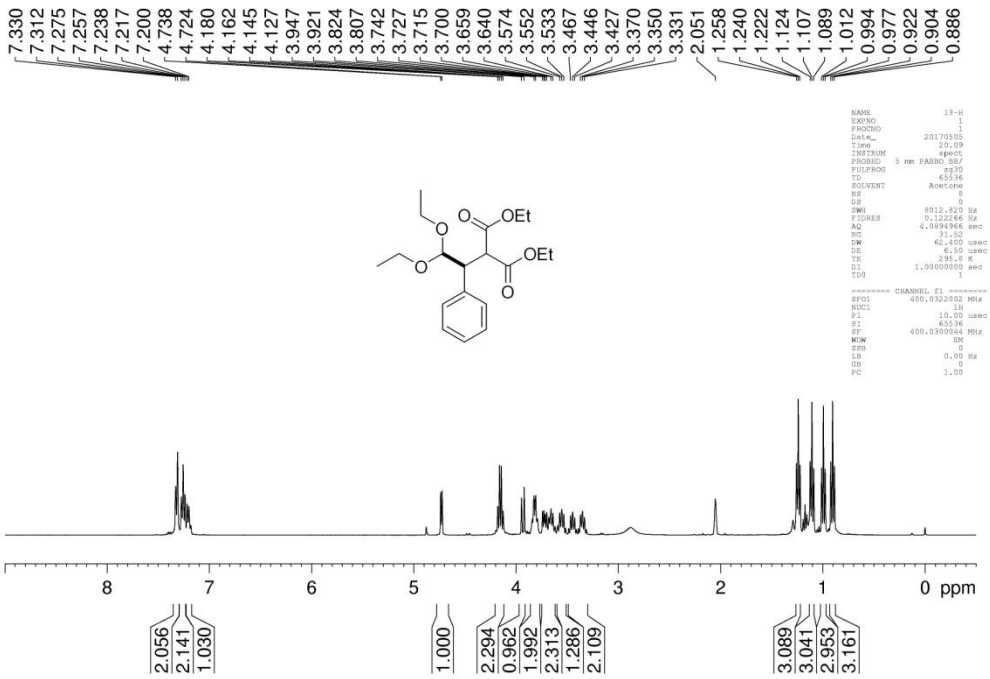


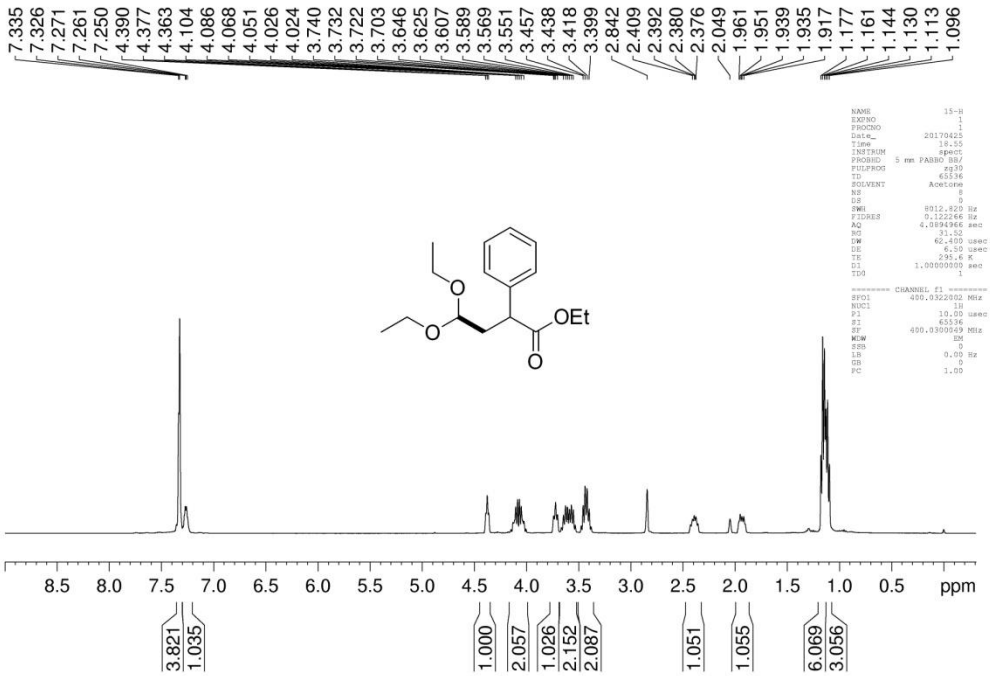
^{1}H NMR of **13**



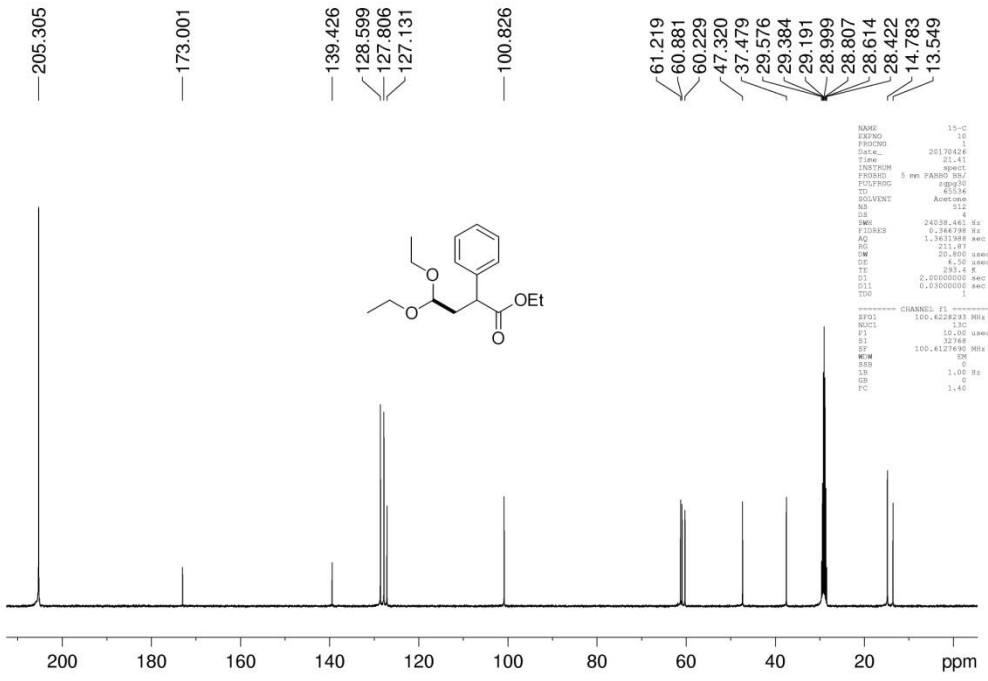
^{13}C NMR of **13**



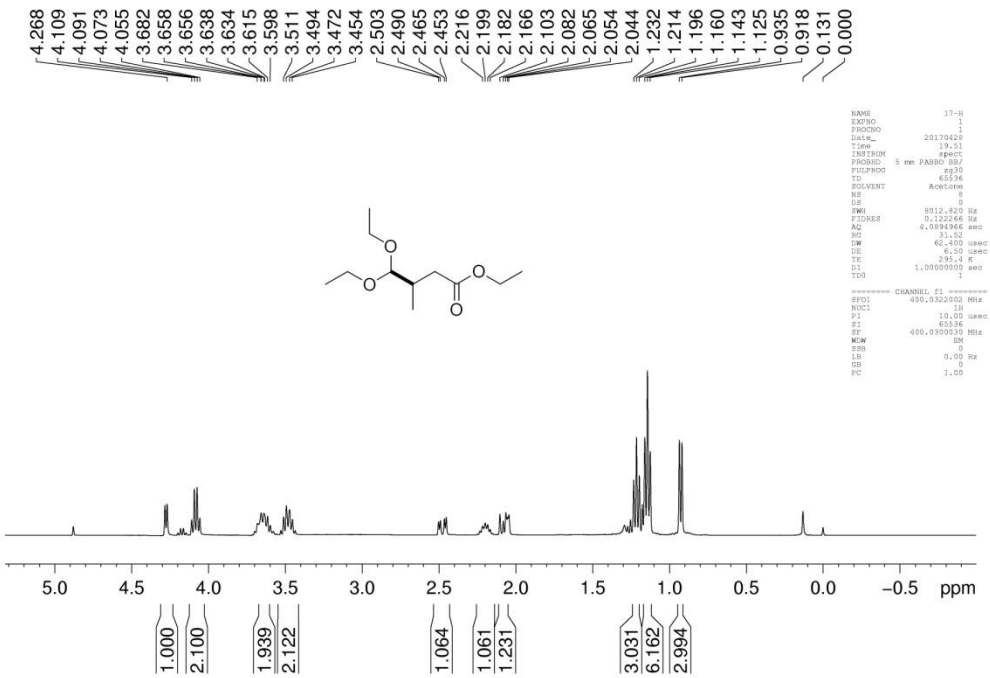
^{1}H NMR of **14**



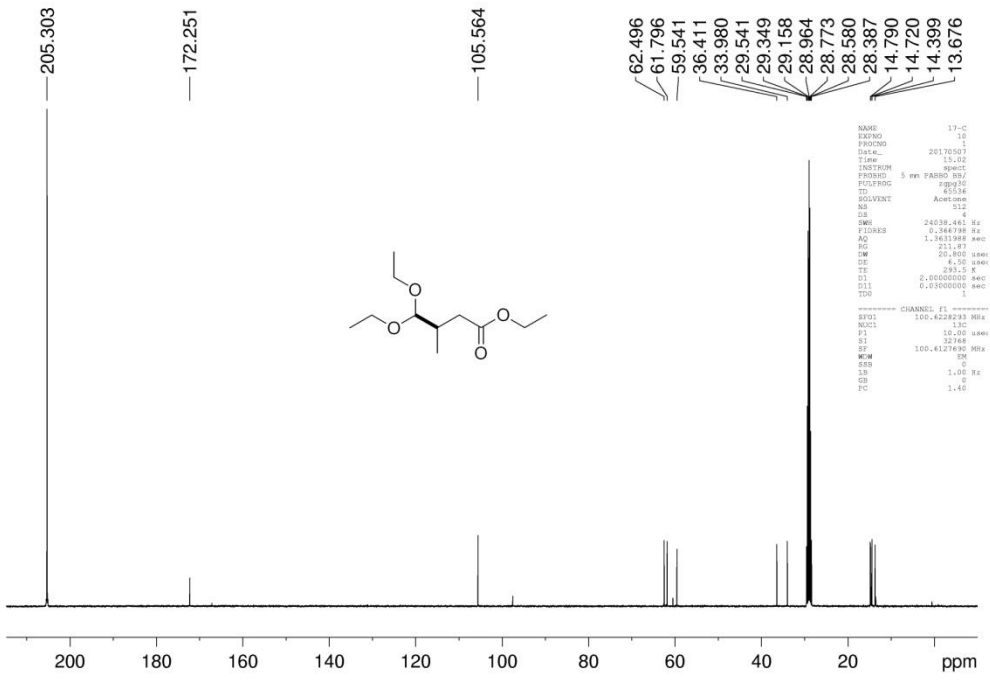
^{13}C NMR of **14**



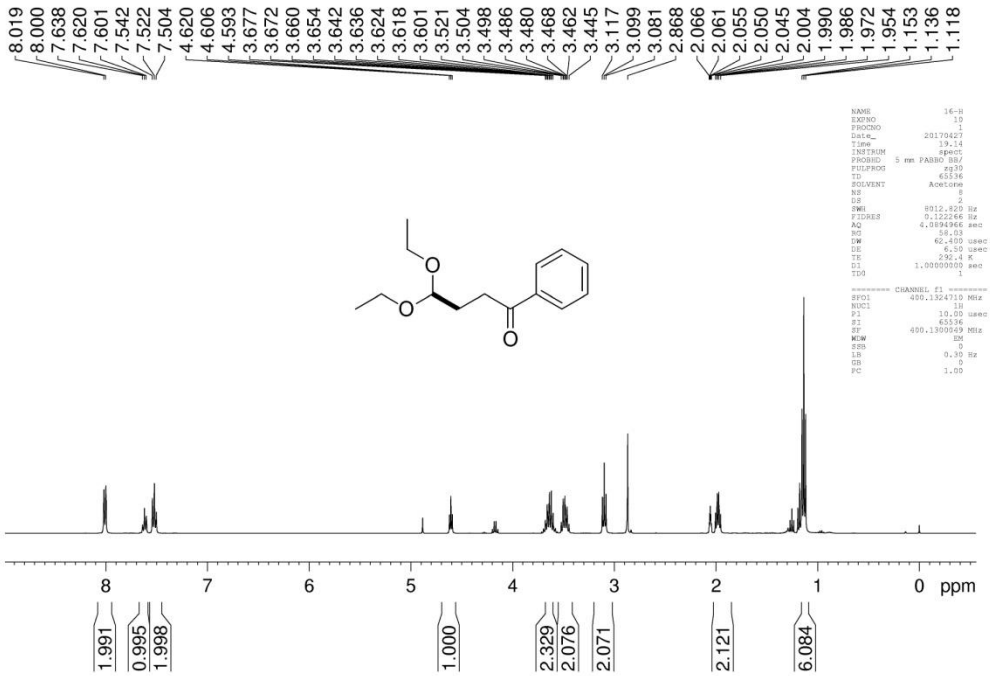
^{1}H NMR of **15**



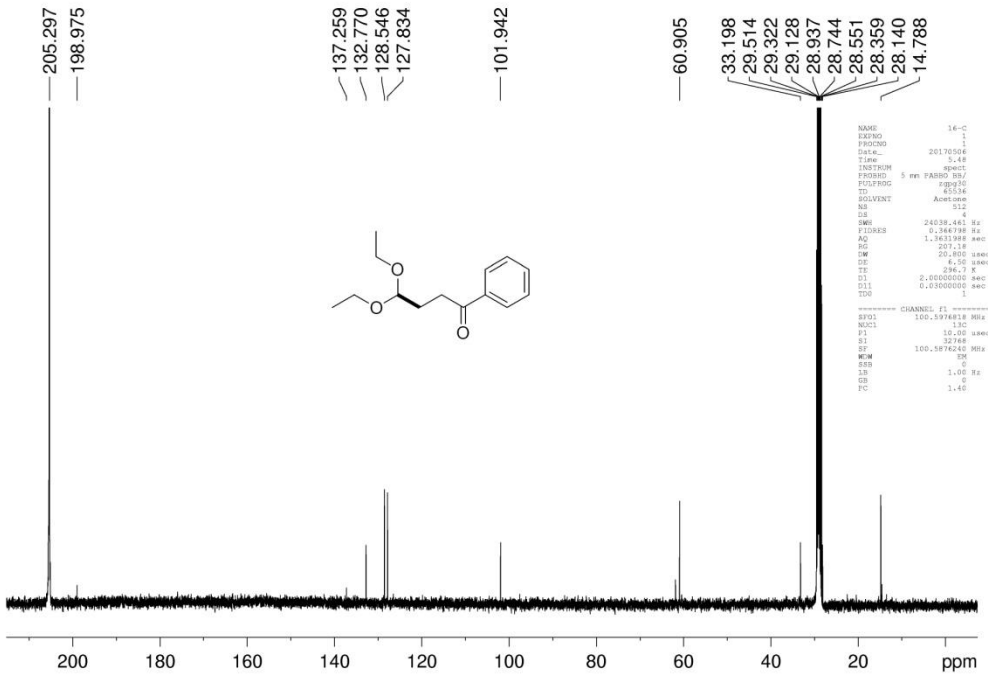
^{13}C NMR of **15**



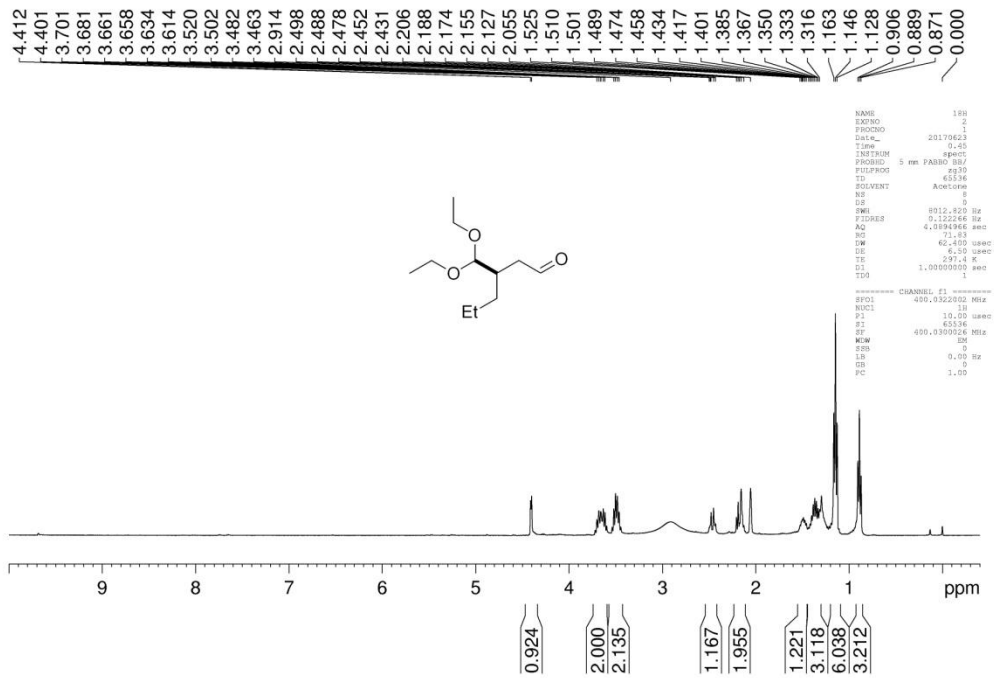
^{1}H NMR of **16**



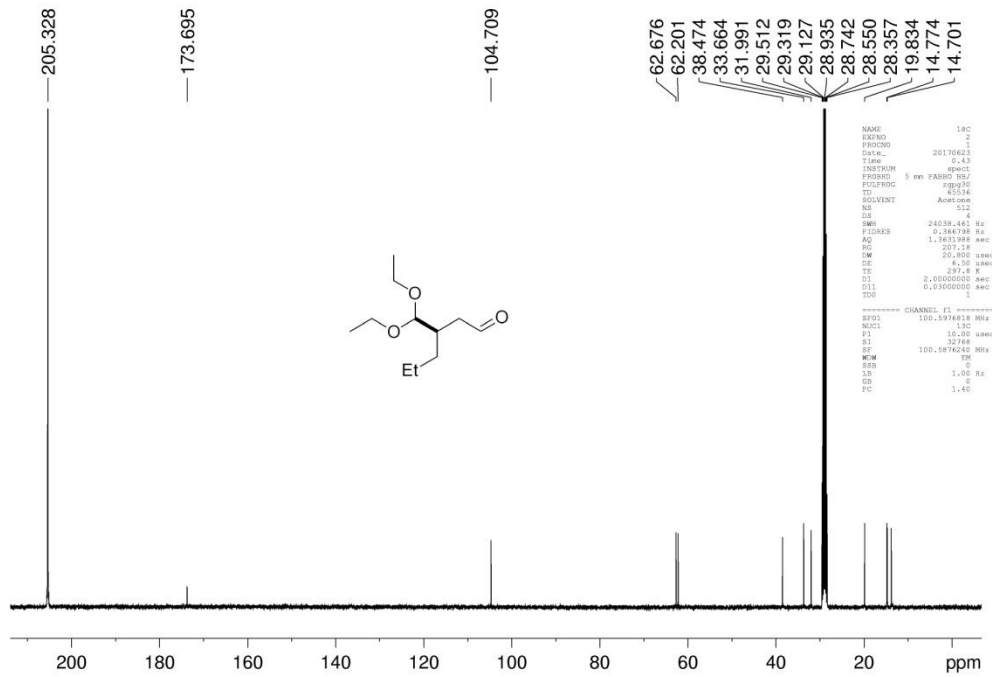
^{13}C NMR of **16**



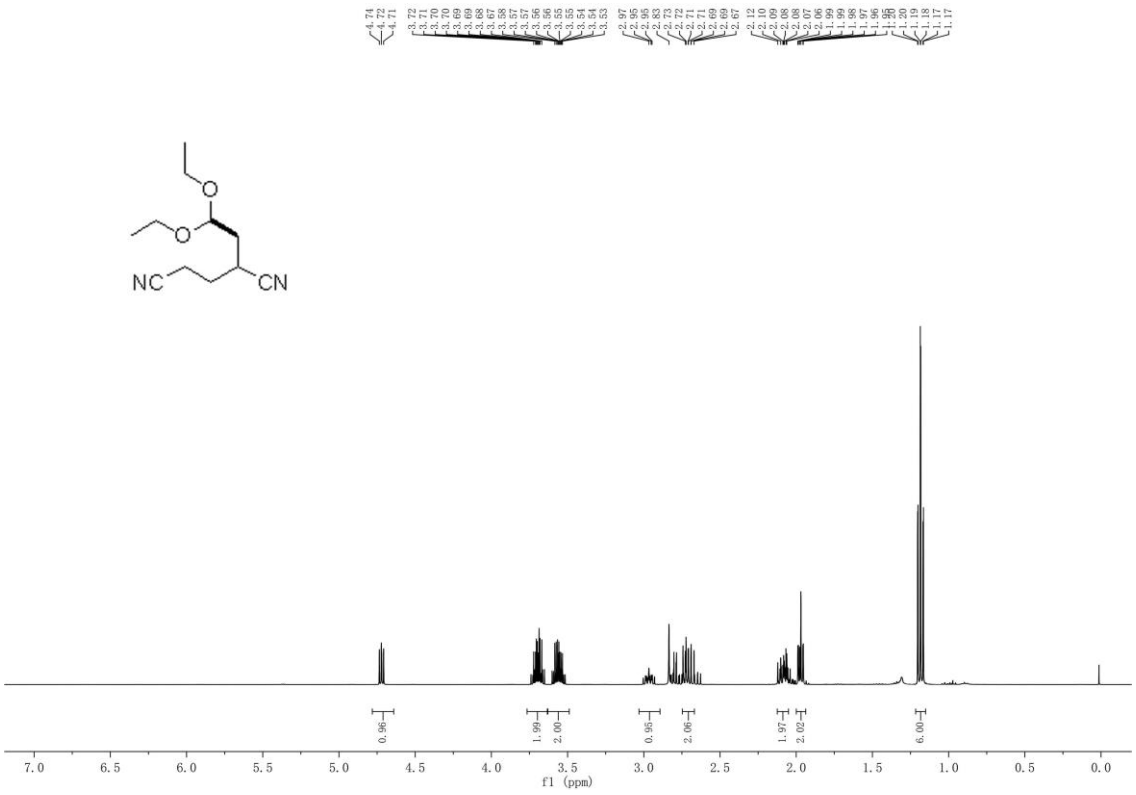
^{1}H NMR of **17**



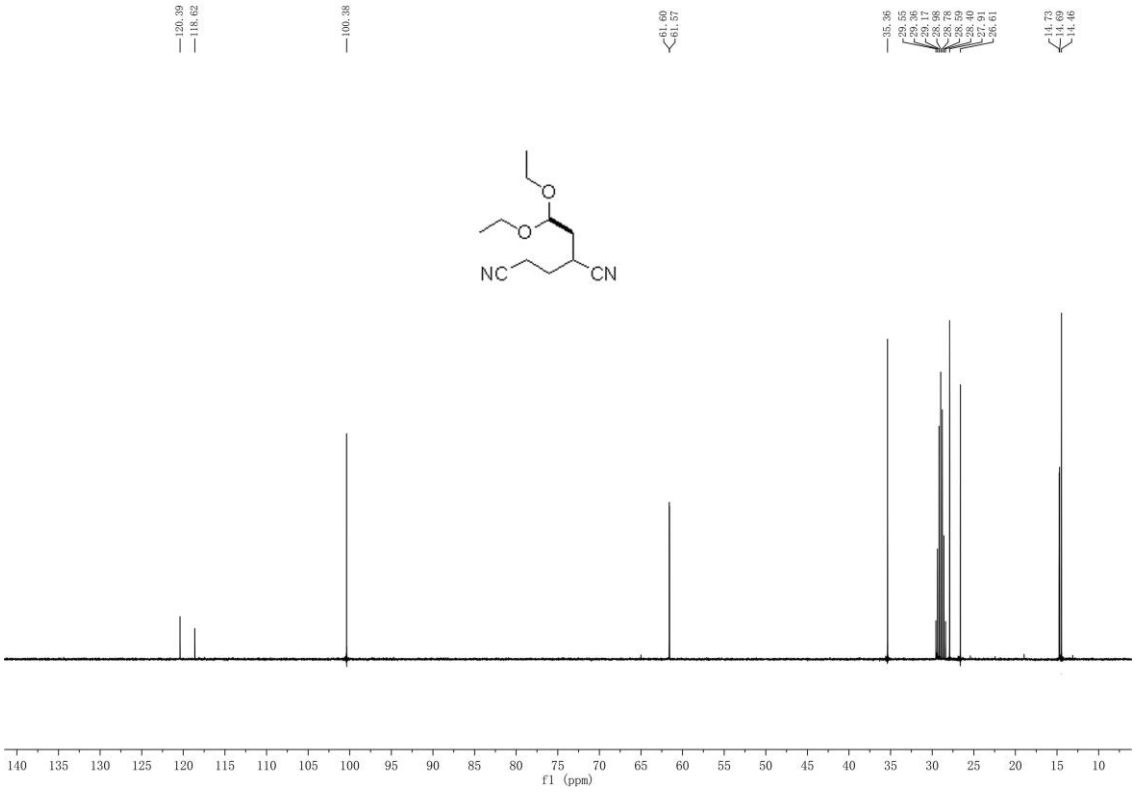
^{13}C NMR of **17**



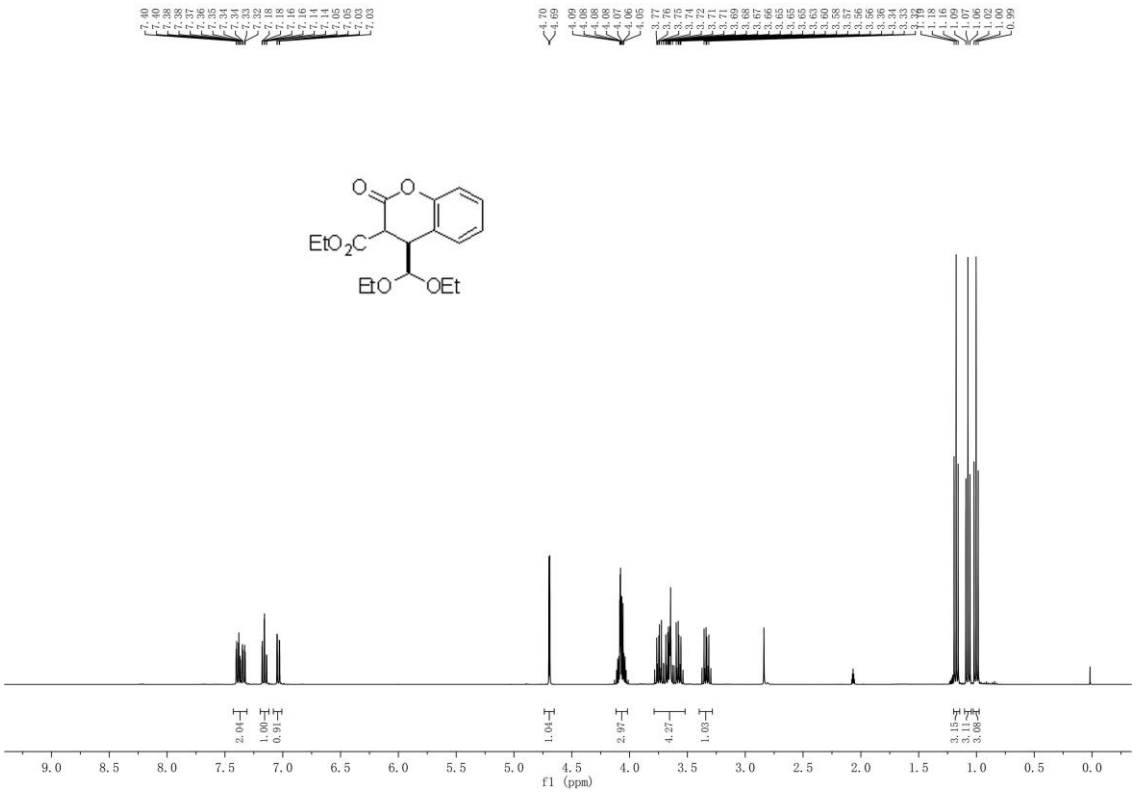
^{1}H NMR of **18**



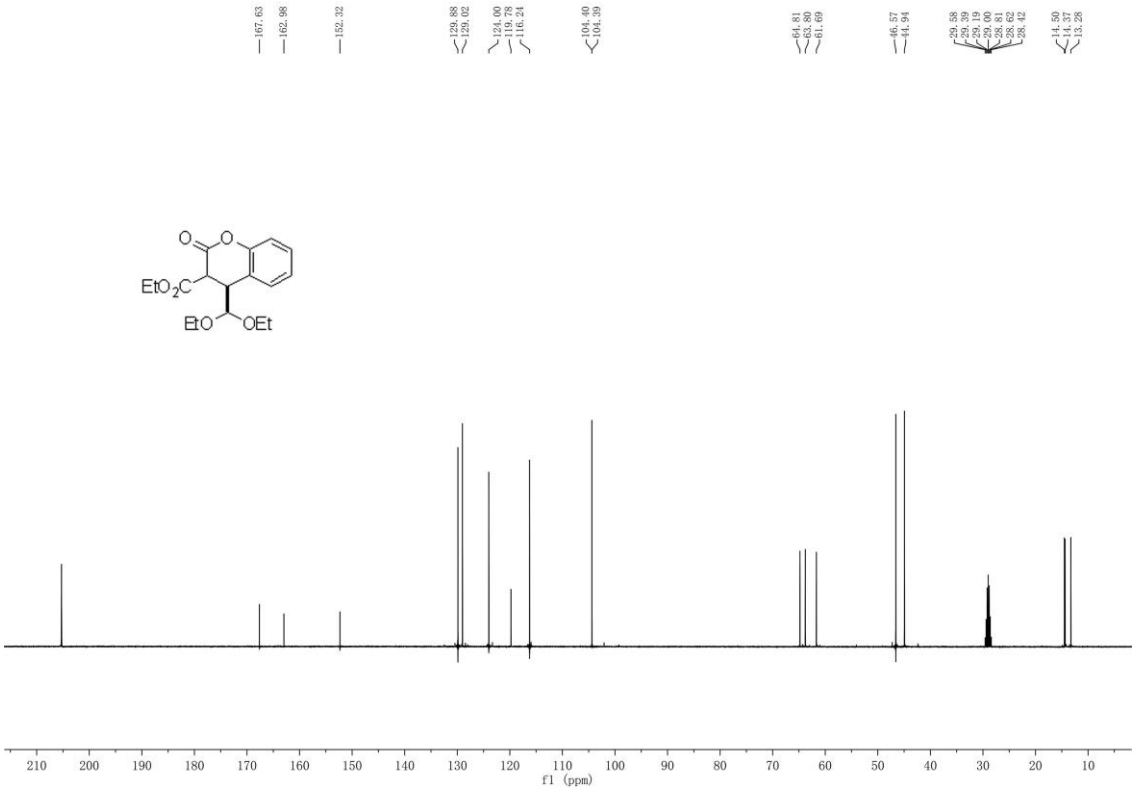
^{13}C NMR of **18**



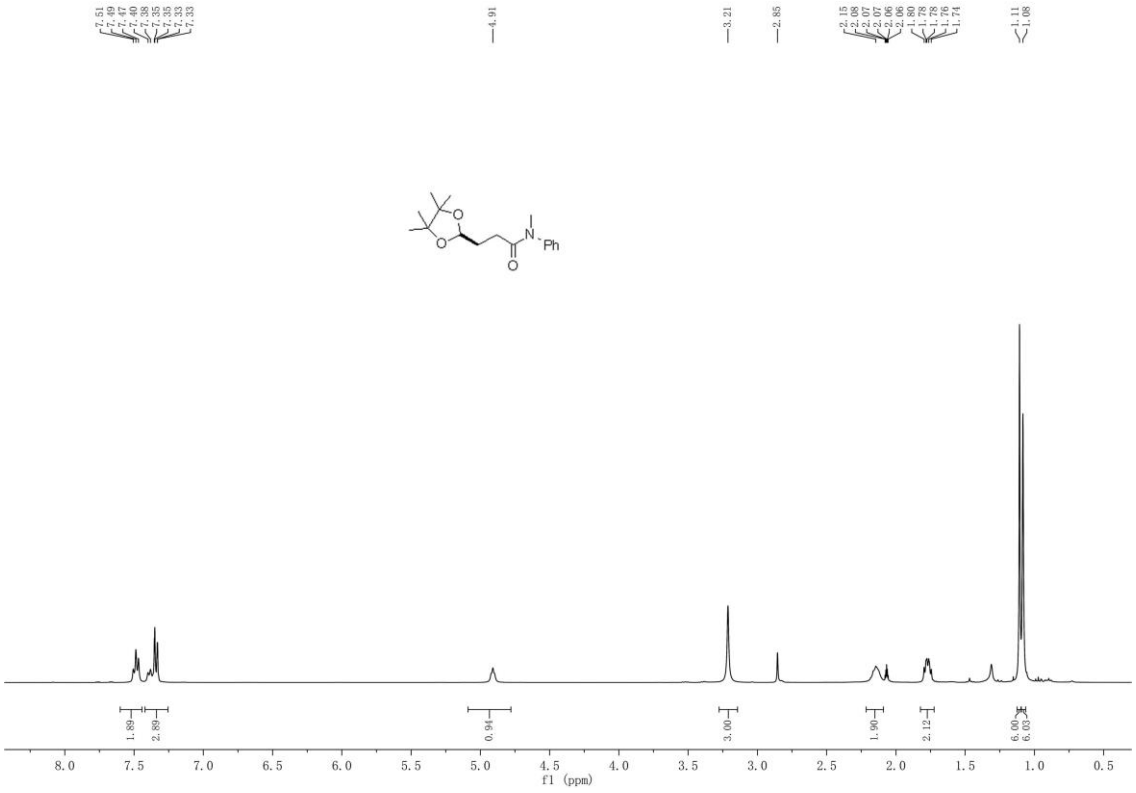
^{1}H NMR of **19**



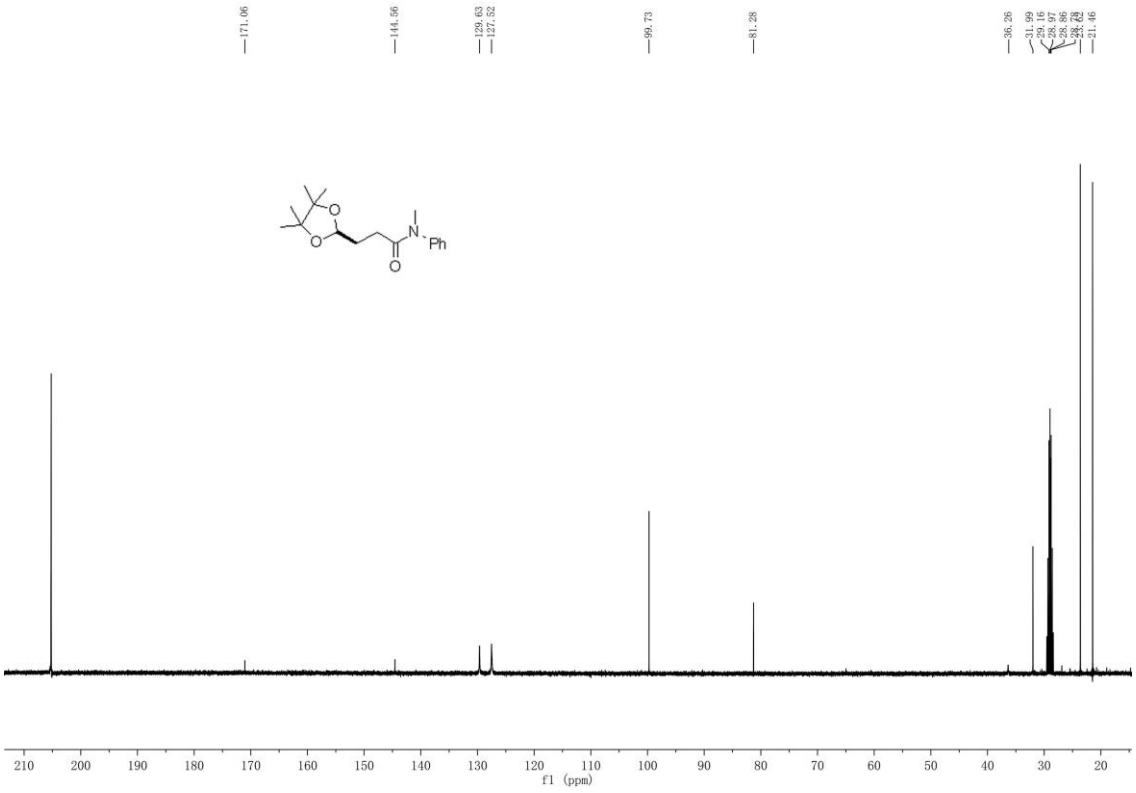
^{13}C NMR of **19**



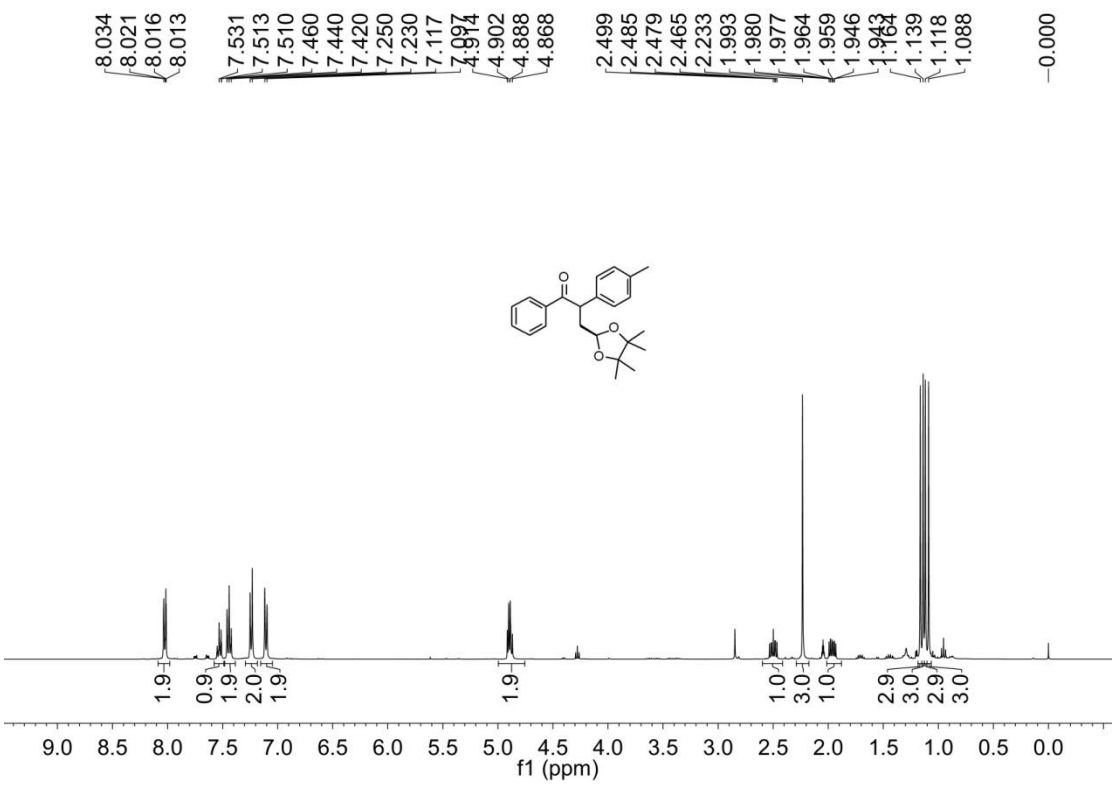
^{1}H NMR of **20**



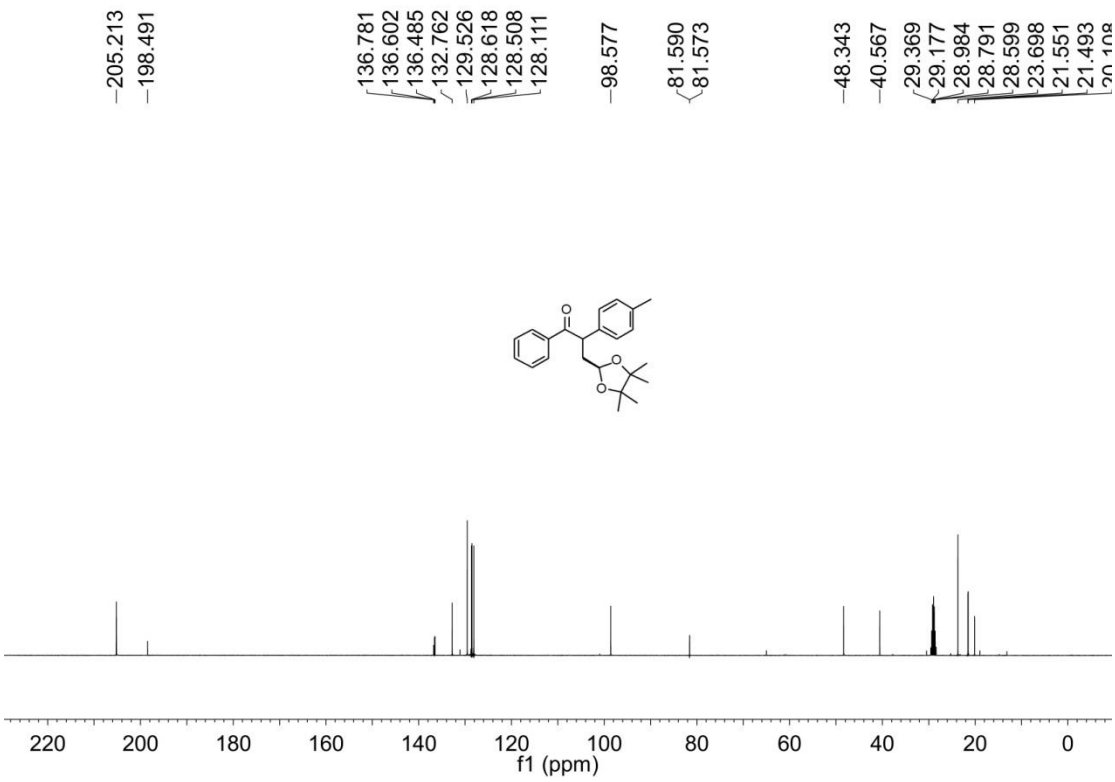
^{13}C NMR of **20**



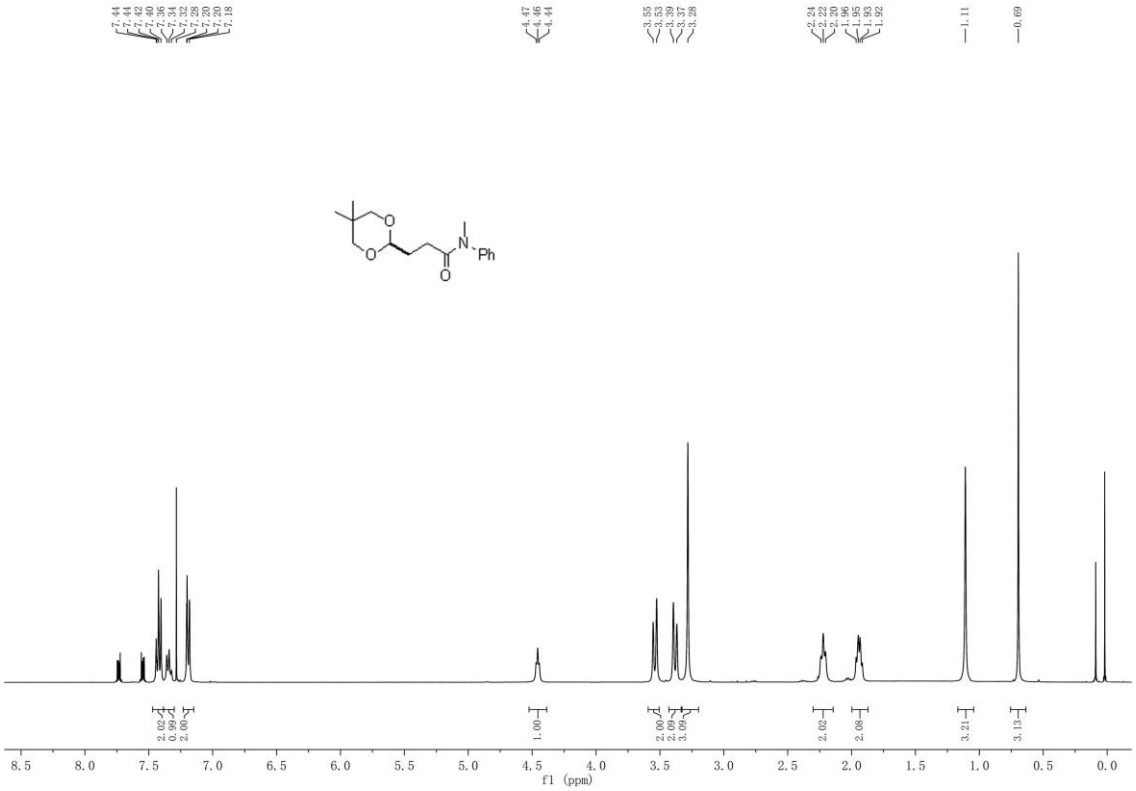
^{1}H NMR of **21**



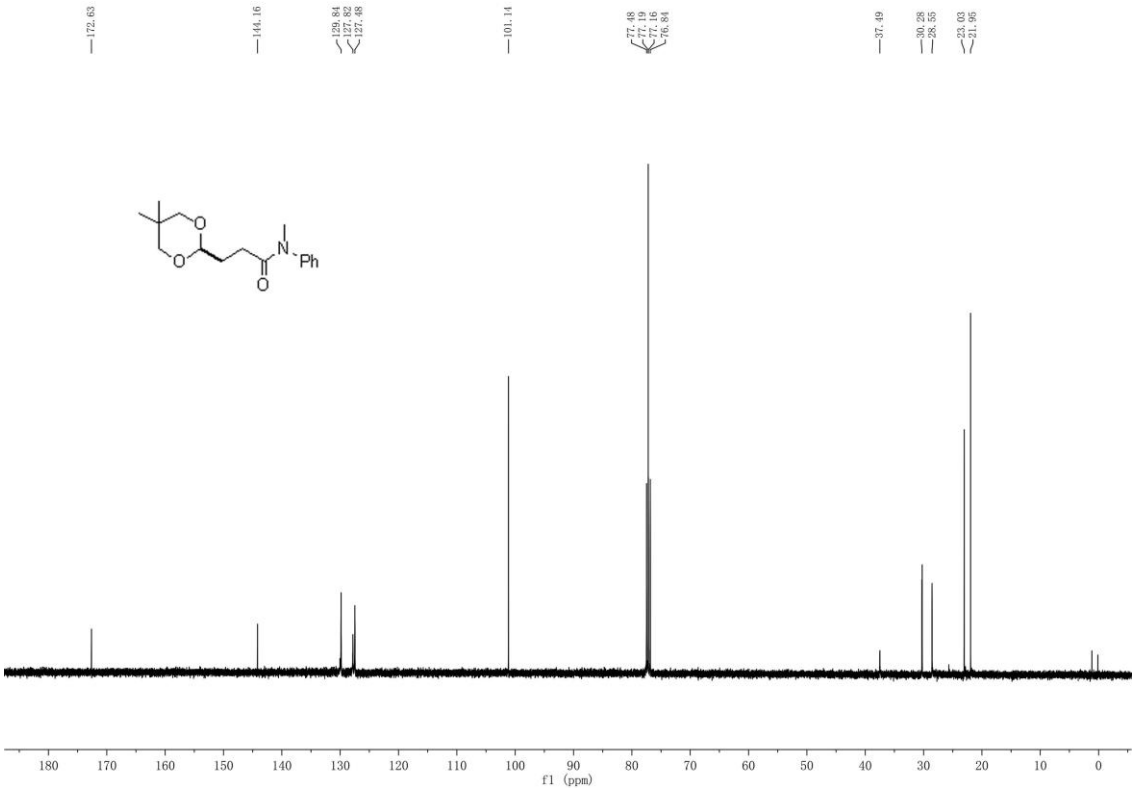
^{13}C NMR of **21**



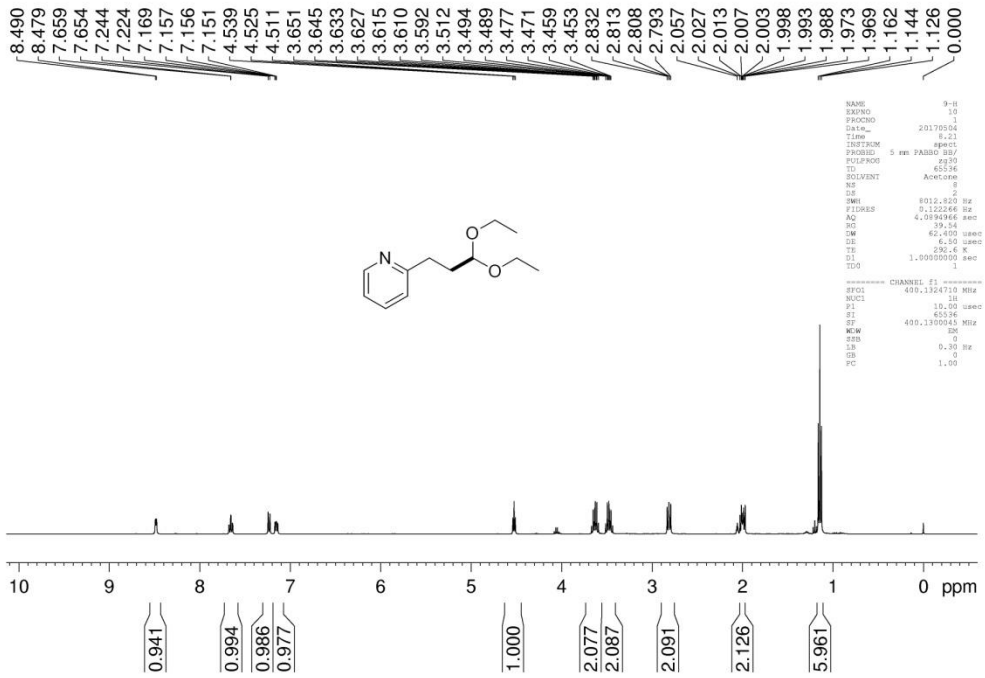
^{1}H NMR of **22**



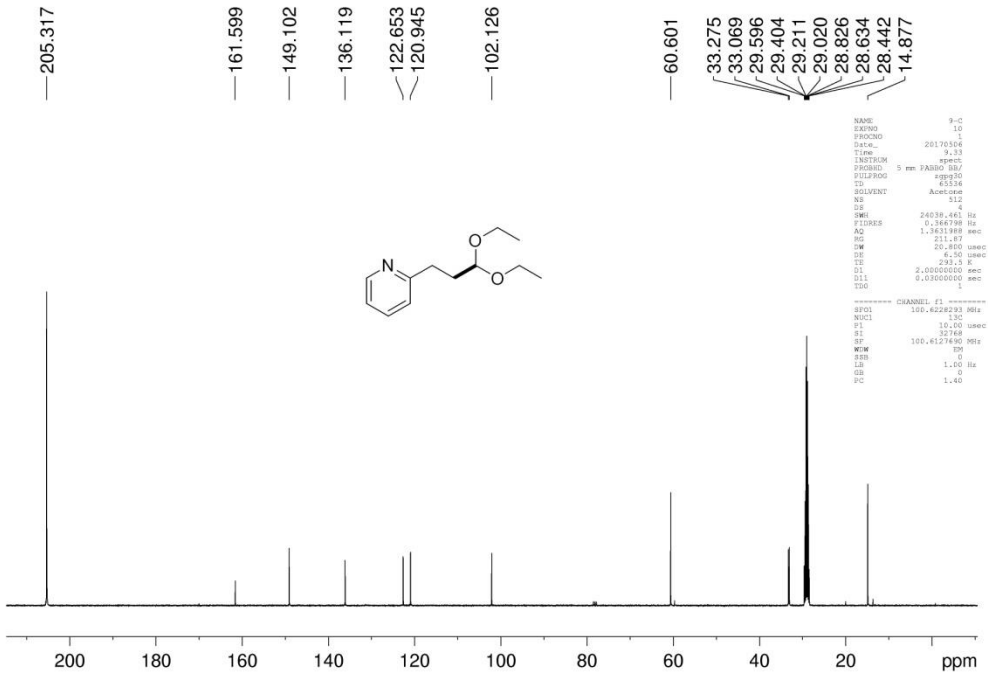
^{13}C NMR of **22**



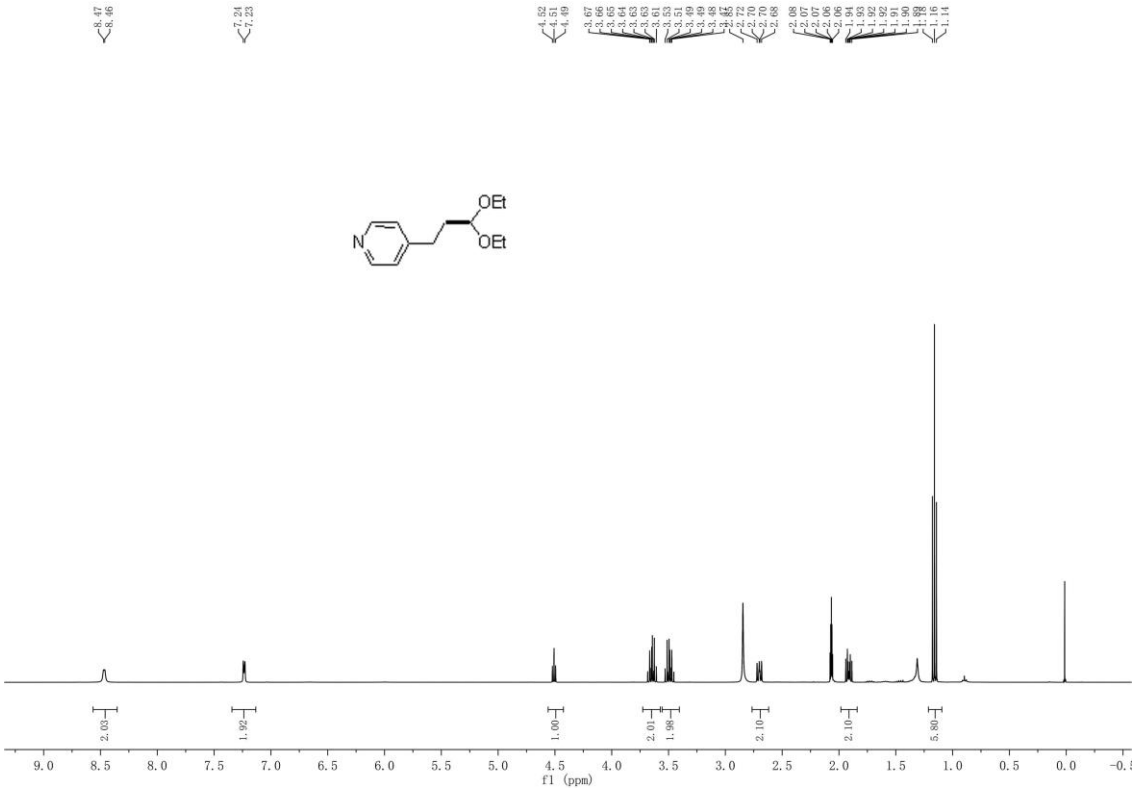
^{1}H NMR of **24**



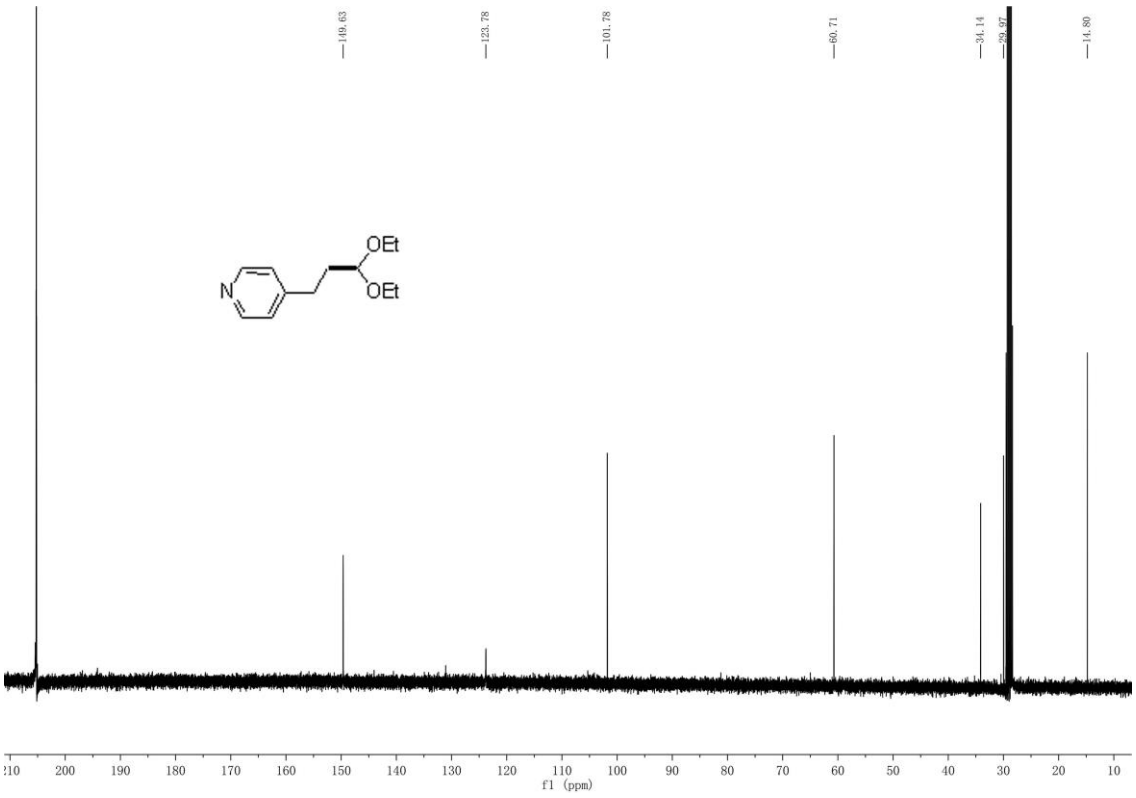
^{13}C NMR of **24**



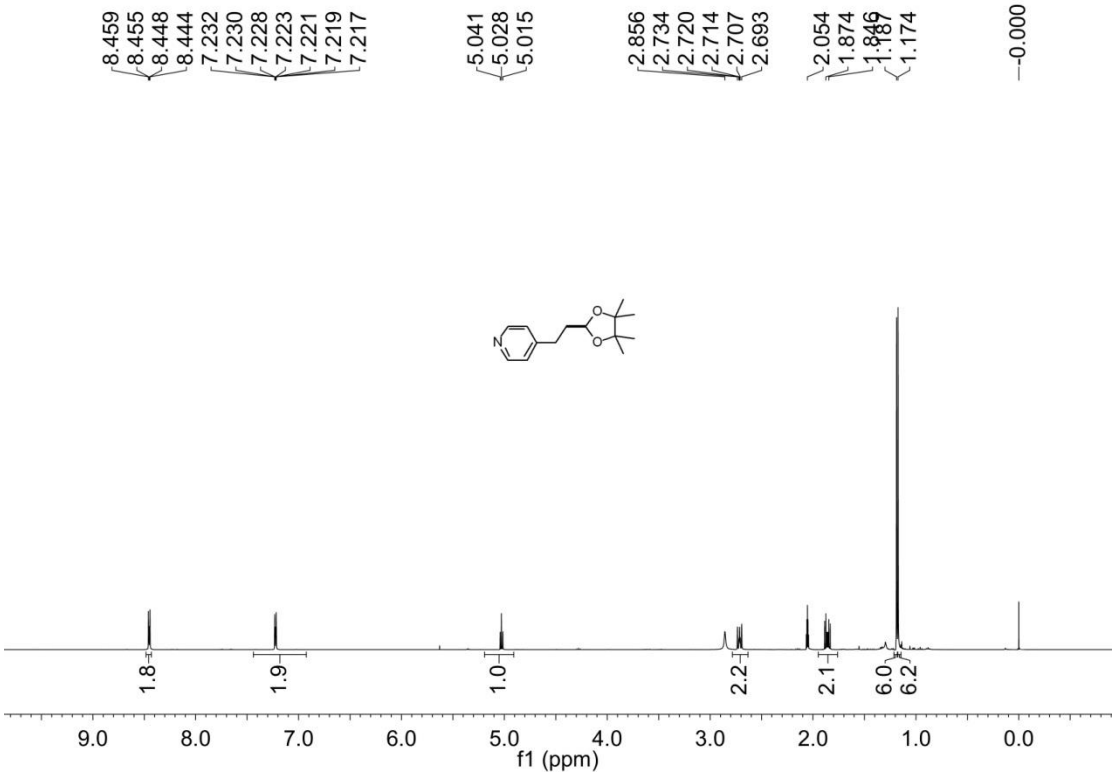
^{1}H NMR of **25**



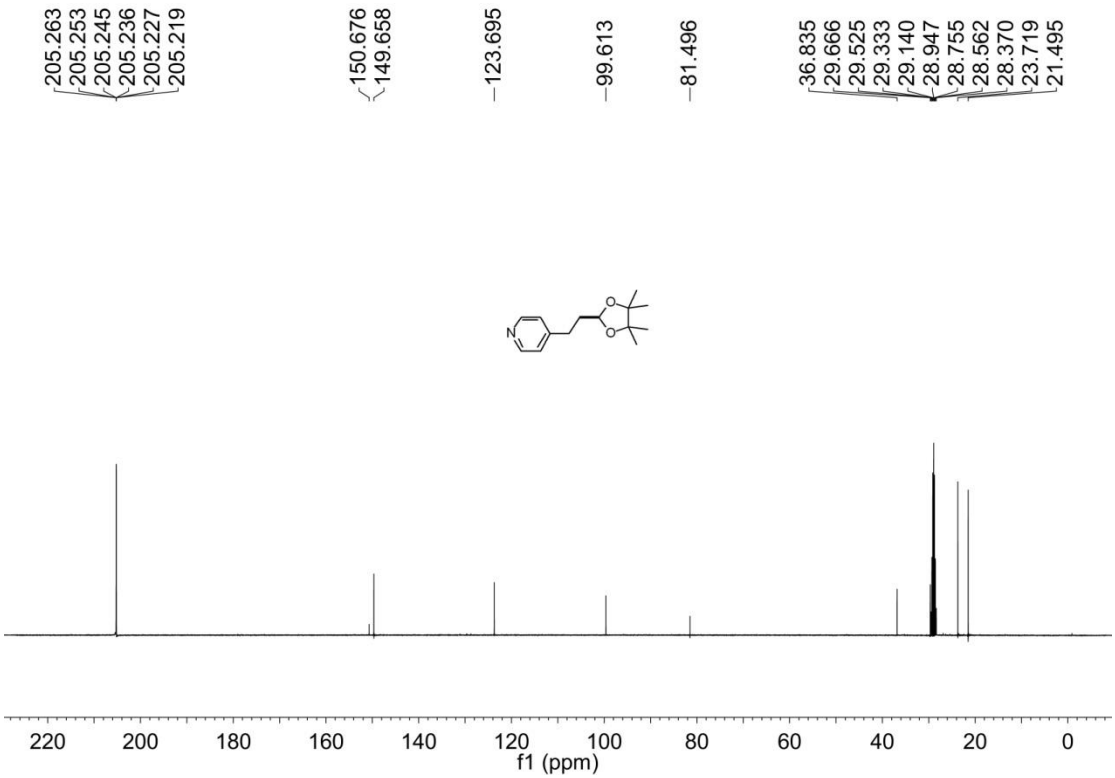
^{13}C NMR of **25**



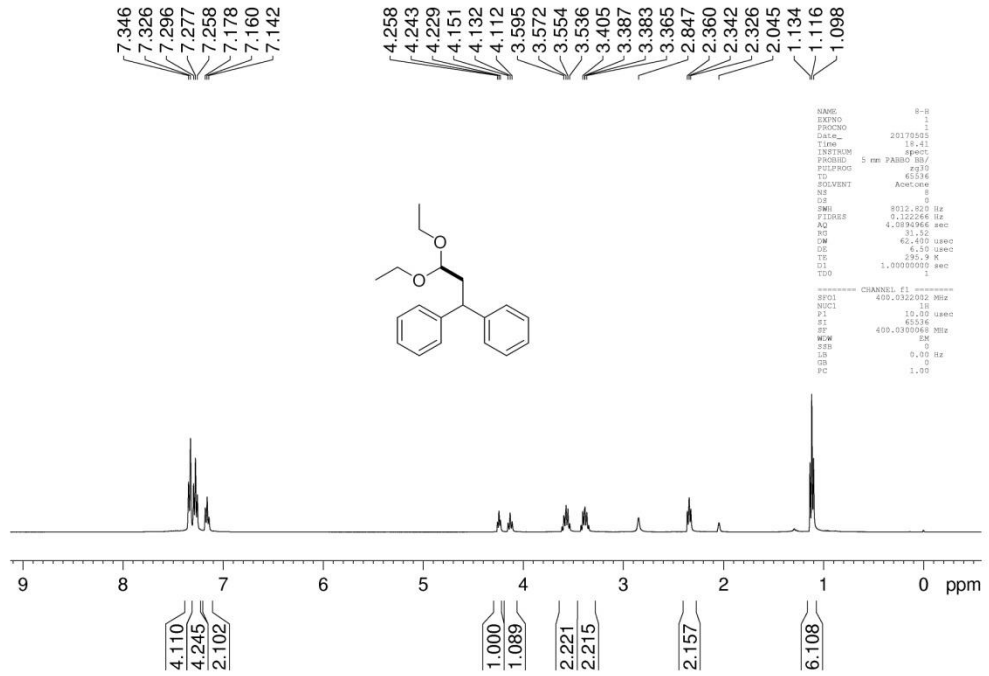
^{1}H NMR of **26**



^{13}C NMR of **26**



^{1}H NMR of **27**



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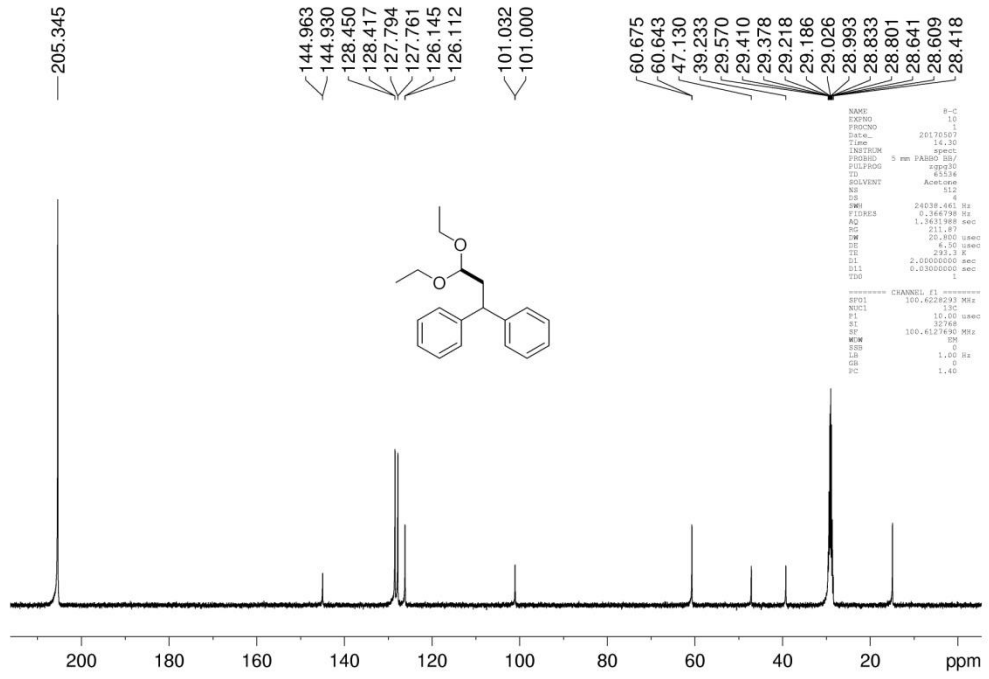
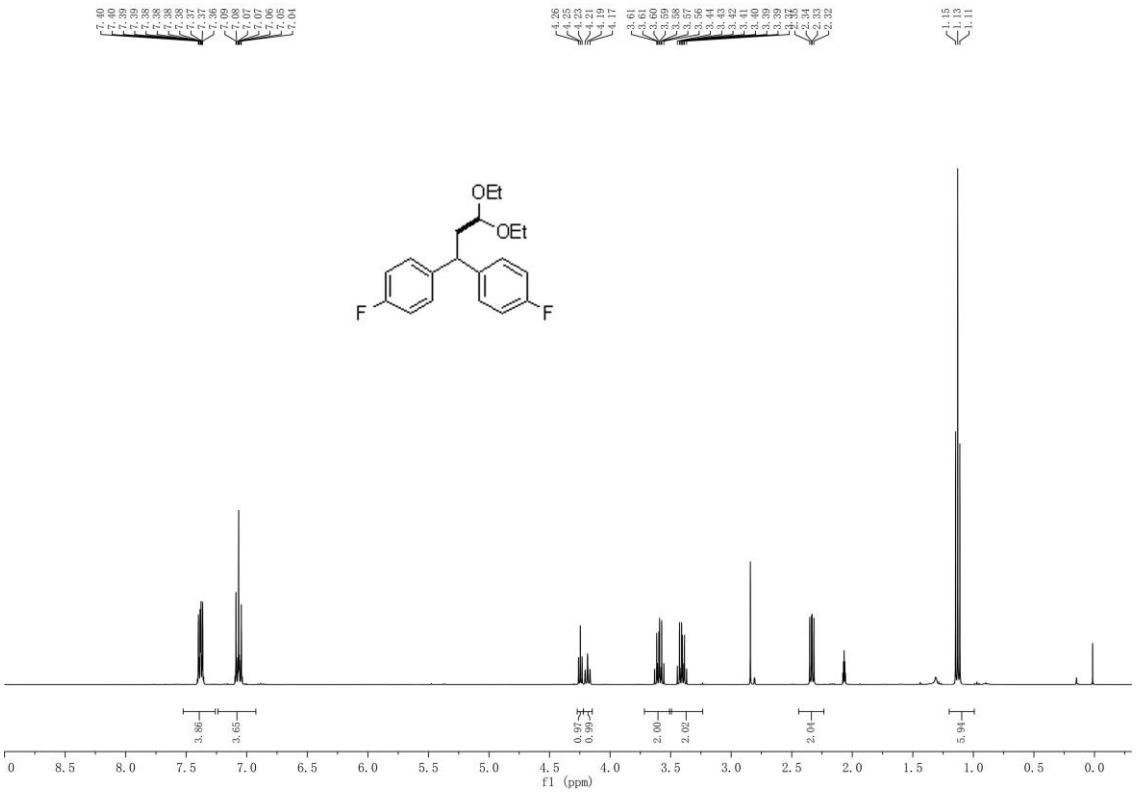
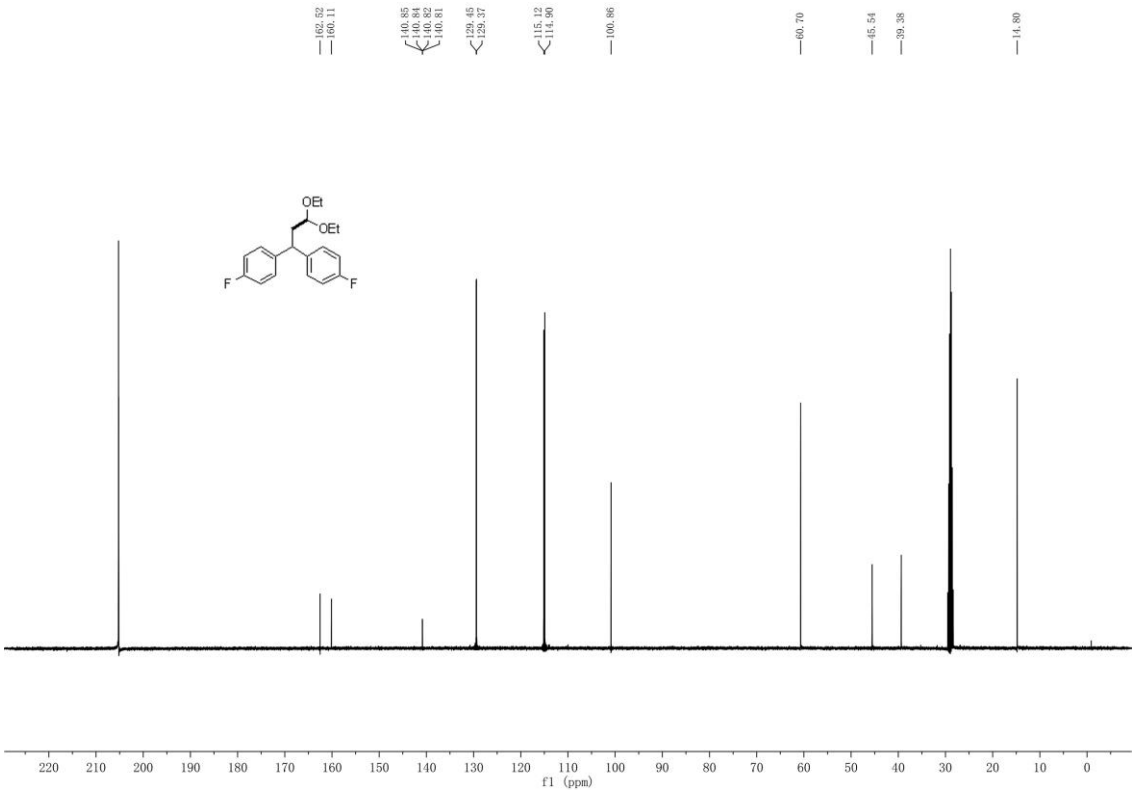


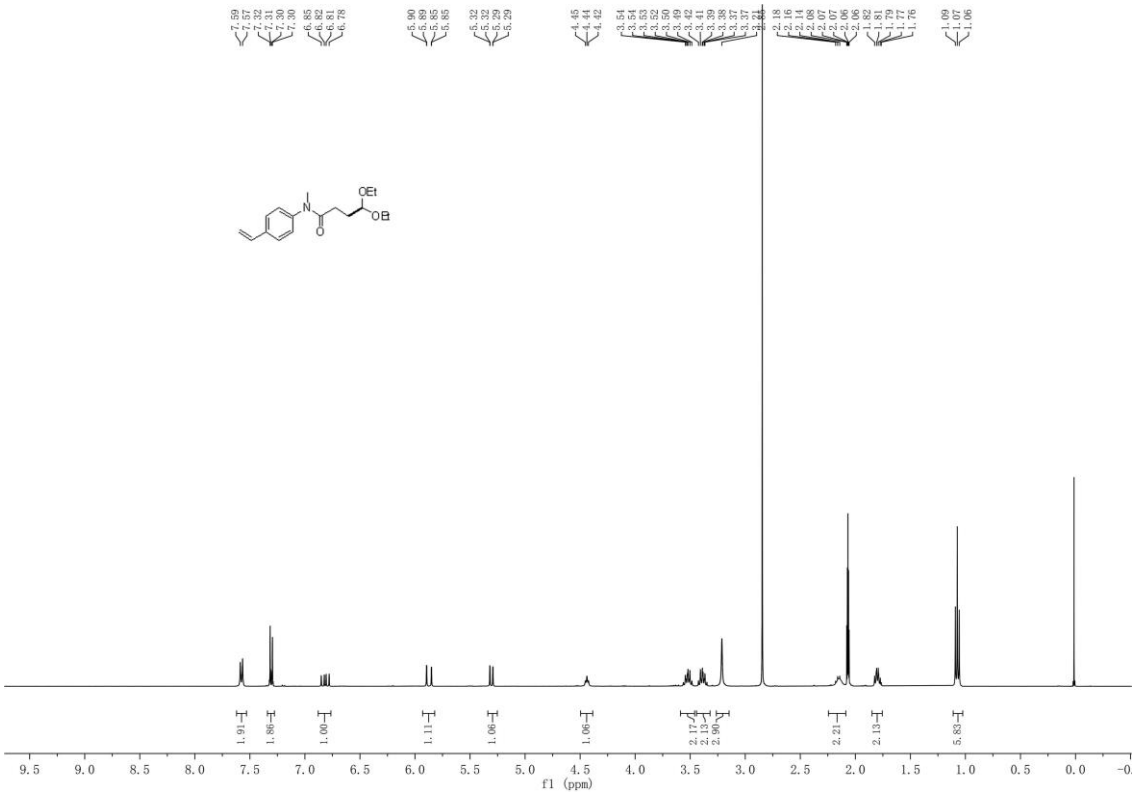
^{1}H NMR of **28**



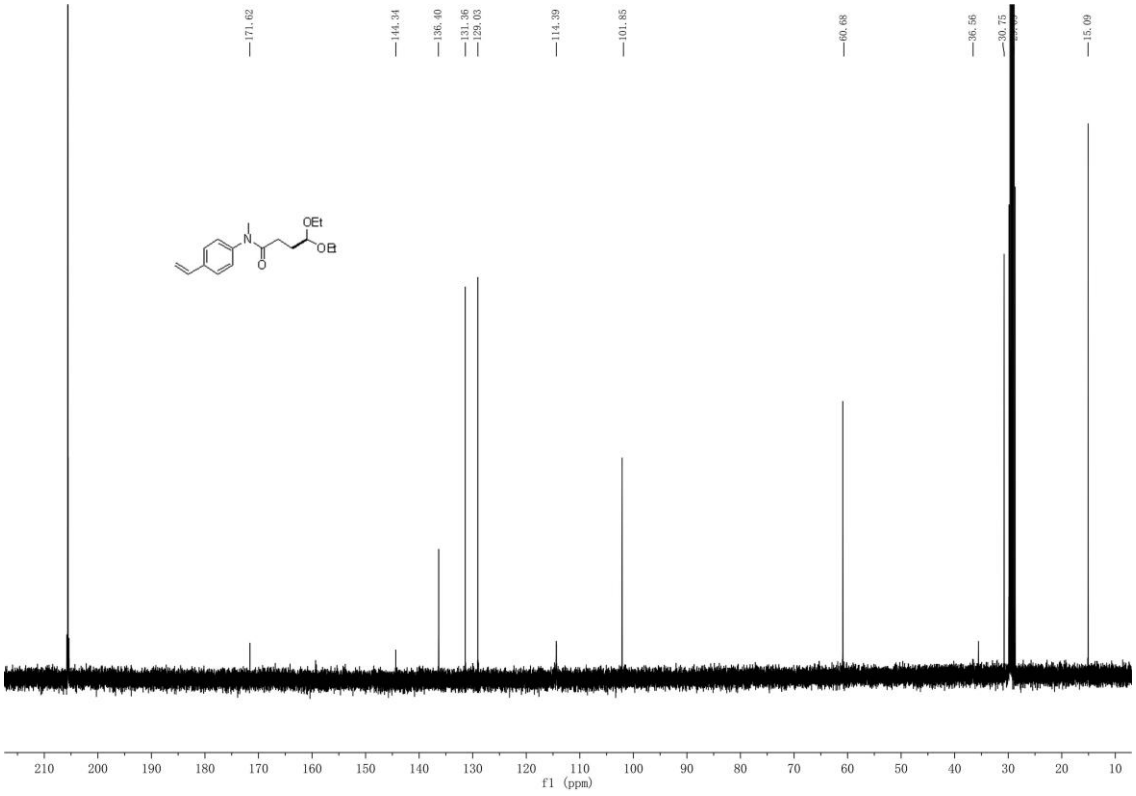
^{13}C NMR of **28**



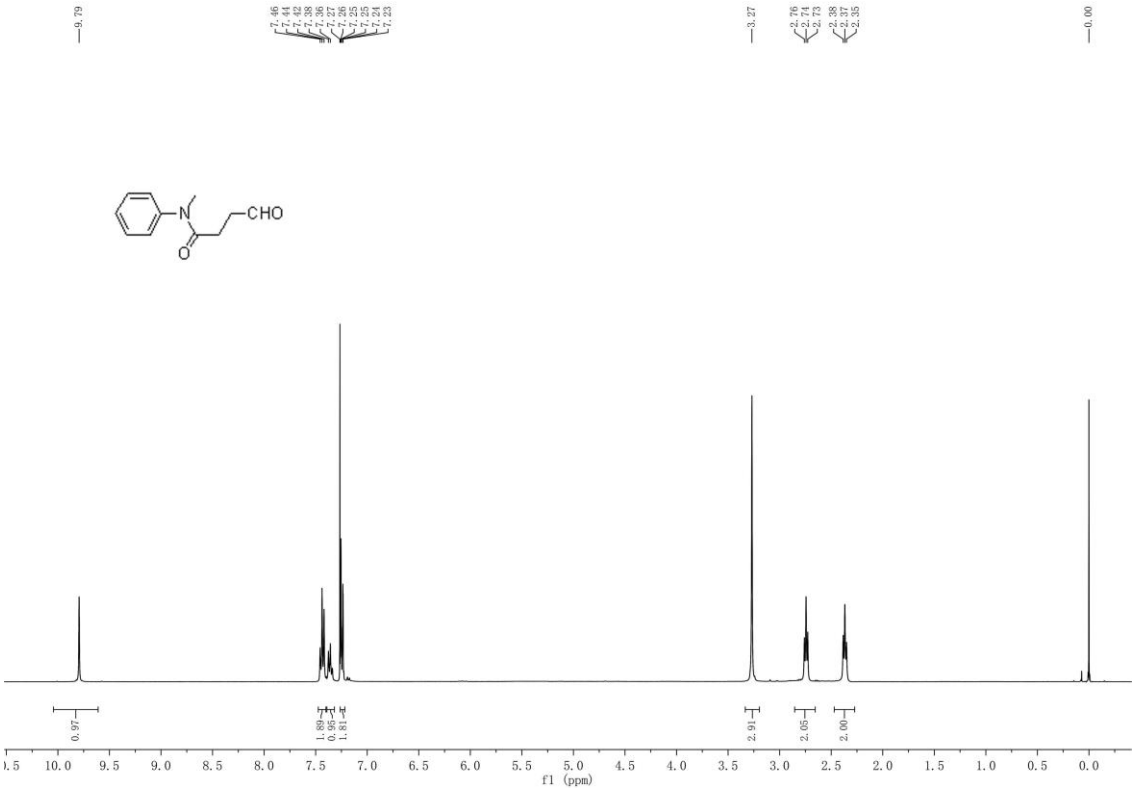
^{1}H NMR of **29**



^{13}C NMR of **29**



^{1}H NMR of **30**



^{13}C NMR of **30**