Electronic Supplementary Information

Phosphine-catalyzed [4 + 3] Cycloaddition Reaction of Aromatic Azomethine Imines with Allenoates

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Contents

General Information:

All reactions were performed under a Nitrogen atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Dichloromethane employed in the reactions was freshly distilled from CaH_2. Organic solutions were concentrated under reduced pressure using a rotary evaporator or oil pump. Reactions were monitored through thin-layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching under UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, $CDCl_2$ or DMSO-d_6 using a Bruker 300 M spectrometer, as indicated. Chemical shifts (δ, ppm) are relative to tetramethylsilane (TMS) with the resonance of the non-deuterated solvent or TMS as the internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s =singlet; d = doublet; t = triplet; q = quartet; p = pentet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. Data were analyzed using instrument-supplied software. X-ray crystallographic data were collected using a Bruker SMART CCD-based diffractometer equipped with a low-temperature apparatus operated at 100 K.

Preparation of C, N-Cyclic Aromatic Azomethine Imines: N-acetyliminoisoquinolinium betaine **1**,[1] N-acetyliminoquinolinium betaine **2**,[1] N-acetyliminophenanthridinium betaine **3**[2] were prepared by the reported procedure.

General Procedure for Phosphine-Catalyzed [4 + 3] Annulation Reactions

An oven-dried 15 mL of Schlenk tube was charged with azomethine imine (0.125 mmol), 3 mL or 5 mL of CH_2Cl_2 and the allenoate (0.15 mmol) at room temperature, then catalyst (0.025 mmol) was added to the above solution. The reaction mixture was stirred at room temperature for 48 h, and then was concentrated. The residue was purified by flash column (ethyl acetate/ petroleum ether) to afford the corresponding product.

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[1] (a) C. Legault and A. B. Charette, *J. Org. Chem.,* 2003, **68**, 7119; (b) M. Alvarez and J. A. Joule, *Sci. Synth.,* 2005, **15**, 661; (c) J. J. Mousseau, J. A. Bull, C. L. Ladd, A. Fortier, D. Sustac Roman and A. B. Charette, *J. Org. Chem.,* 2011, **76**, 8243; (d) P. N. Anderson and J. T. Sharp, *J. Chem. Soc., Perkin Trans. 1,* 1980, 1331.

[2] (a) B. Agai, K. Lempert and J. Hegedus-Vajda, *Acta Chim. Acad. Sci. Hung.,* 1976, **91**, 91; (b) B. Agai and K. Lempert, *Tetrahedron,* 1972, **28**, 2069; (c) Y. Tamura, H. Ishibashi, N. Tsujimoto and M. Ikeda, *Chem. Pharm. Bull.,* 1971, **19**, 1285; (d) Y. Tamura, Y. Miki and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1,* 1976, 1702.

General procedure for the hydrolysis of 8a

To the product **8a** (0.15 mmol, 65 mg) in 1 mL of THF was added 4 mL of 20% NaOH solution and 2 mL of ethanol, the solution was stirred at 40 °C for about 6 h. The mixture was then neutralized with 1 M hydrochloric acid, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (5 mL), and the organic layers were combined, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column (ethyl acetate/ methanol) to afford the corresponding product **13**.

Characterization Data for all Products

Compounds **5a** + **6a**

88%yield, pale-yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 2H), 7.34 – 7.22 (m, 1H), 7.19 – 6.91 (m, 7H), 6.83 (dd, *J* =1.6, 7.2 Hz, 1H), 5.33 (d, *J* = 7.7 Hz, 1H), 5.01 (d, *J* = 7.6 Hz, 1H), 4.84 (dd, *J* = 2.3, 9.4 Hz, 1H), 4.17 – 4.00 (m, 2H), 3.39 – 3.25 (m, 1H), 2.58 – 2.37 (m, 1H), 2.14 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.63, 174.56, 148.8, 141.0, 136.0, 134.1, 131.9, 130.6, 130.0, 129.7, 129.6, 129.1, 128.5, 128.0, 126.2, 124.4, 122.8, 122.5, 122.2, 121.4, 121.0, 120.9, 119.2, 112.5, 74.2, 23.2, 22.0; IR (film) ν_{max} 2920, 2850, 1691, 1632, 1529, 1495, 1454, 1373, 1290, 1235, 1210, 1133, 1079, 1029, 770, 744, 703, 575 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{25}N_2O_3^+$ $[M + H]^+$ 389.1860, found 389.1862.

Compounds **5b** + **6b**

80% yield, pale-yellow solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.41 (dd, *J* = 4.4, 7.6 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.05 (m, 4H), 6.99 – 6.92 (m, 2H), 6.83 – 6.77 (m, 1H), 5.12 (d, *J* = 7.6 Hz, 1H), 5.00 – 4.93 (m, 1H), 4.90 (d, *J* = 7.6 Hz, 1H), 4.13 – 3.91 (m, 2H), 3.32 – 3.20 (m, 1H), 2.58 – 2.43 (m, 1H), 2.29 (s, 3H), 2.07 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.4, 165.6, 142.5, 136.9, 134.5, 134.2, 134.0, 131.6, 130.8, 129.9, 128.4, 128.4, 127.6, 125.9, 125.6, 125.5, 123.2, 97.2, 61.6, 60.8, 55.4, 34.1, 20.7, 19.2, 14.0; IR (film) ν_{max} 2920, 2850, 1691, 1632, 1529, 1495, 1454, 1373, 1235, 1210, 1136, 770, 744, 703, 575 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_3^+$ $[M + H]^+$ 403.2016, found 403.2012.

Compounds **5c** + **6c**

70% yield, pale-yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.50 – 7.41 (m, 1H), 7.21 – 7.05 (m, 7H), 7.03 – 6.96 (m, 1H), 6.89 – 6.82 (m, 1H), 5.17 (dd, *J* = 1.2, 7.6 Hz, 1H), 5.00 (d, *J* = 7.6 Hz, 1H), 4.80 (d, *J* = 9.9 Hz, 1H), 4.17 – 4.07 (m, 2H), 3.41 – 3.27 (m, 1H), 2.41 – 2.26 (m, 4H), 2.10 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 172.8, 166.1, 141.7, 138.5, 137.4, 134.0, 133.8, 131.4, 130.1, 129.4, 128.9, 128.5, 127.9, 125.6, 125.5, 125.5, 123.6, 97.6, 62.7, 61.2, 58.0, 35.7, 21.3, 20.9, 13.9; IR (film) ν_{max} 2920, 1731, 1529, 1389, 1290, 1267, 1232, 1129, 1032, 744, 703, 576 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_3^+$ $[M + H]^+$ 403.2016, found 403.2020.

Compounds **5d** + **6d**

85% yield, pale-yellow solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.47 – 7.36 (m, 1H), 7.22 – 7.02 (m, 8H), 6.87 – 6.79 (m, 1H), 5.18 (dd, *J* = 1.1, 7.6 Hz, 1H), 4.97 (d, *J* = 7.7 Hz, 2H), 4.13 – 3.97 (m, 2H), 3.24 – 3.10 (m, 1H), 2.42 – 2.30 (m, 1H), 2.29 (s, 3H), 2.01 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.3, 165.7, 143.1, 137.5, 134.3, 134.2, 132.8, 131.0, 130.4, 129.5, 128.3, 127.7, 125.9, 125.4, 123.2, 97.0, 61.5, 61.0, 56.9, 35.7, 20.8, 20.7, 14.1; IR (film) ν_{max} 2920, 1691, 1632, 1529, 1495, 1373, 1290, 1235, 1210, 1133, 1079, 1029, 770, 744, 703, 578 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_3^+$ $[M + H]^+$ 403.2016, found 403.2019.

Compounds **5e** + **6e**

90% yield, pale-yellow solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.49 – 7.29 (m, 2H), 7.29 – 6.95 (m, 7H), 6.81 (dd, *J* = 1.6,7.0 Hz, 1H), 5.29 (d, *J* = 7.7 Hz, 1H), 5.03 – 4.88 (m, 2H), 4.18 – 3.87 (m, 2H), 3.30 – 3.16 (m, 1H), 2.61 – 2.37 (m, 1H), 2.04 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.8, 165.4, 143.8, 134.0, 132.4, 131.4, 130.7 (d, *J* = 8.4 Hz), 130.03, 129.97, 127.7, 125.7, 124.4 (d, *J* = 3.5 Hz), 123.9, 123.7, 123.3, 115.7 (d, *J* = 21.3 Hz), 97.8, 61.6, 60.9, 51.8 (d, *J* = 3.1 Hz), 34.2, 20.6, 14.0; IR (film) ν_{max} 3445, 1707, 1680, 1624, 1488, 1457, 1372, 1294, 1240, 1095, 1057, 1036, 897, 838, 762, 636, 582, 529 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}FN_2O_3^+$ $[M + H]^+$ 407.1765, found 407.1760.

Compounds **5f** + **6f**

87% yield, pale-yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.35 (dd, *J* = 3.5, 8.3 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 3H), 7.10 – 6.82 (m, 5H), 6.78 (d, *J* = 7.0 Hz, 1H), 5.09 (d, *J* = 7.6 Hz, 1H), 4.95 (d, *J* = 7.6 Hz, 1H), 4.74 (d, *J* = 10.0 Hz, 1H), 4.06 – 3.83 (m, 2H), 3.30 – 3.14 (m, 1H), 2.35 – 2.23 (m, 1H), 1.99 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 173.5, 166.8, 142.6, 134.7, 134.6, 134.5, 132.2, 131.3, 131.2, 130.9, 128.7, 126.5, 126.3, 124.4, 116.5, 116.2, 98.8, 63.5, 62.1, 58.2, 36.4, 21.5, 14.7; IR (film) ν_{max} 3446, 1709 ,1674, 1621, 1507 ,1391, 1372, 1295, 1238, 1159, 1056, 835, 763, 741, 609, 579, 523 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}FN_2O_3^+$ $[M + H]^+$ 407.1765, found 407.1763.

Compounds **5g** + **6g**

78% yield, pale-yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.55 – 7.45 (m, 1H), 7.39 – 7.25 (m, 3H), 7.21 – 6.98 (m, 5H), 6.93 – 6.86 (m, 1H), 5.29 – 5.18 (m, 1H), 5.09 (t, *J* = 6.8 Hz, 1H), 4.87 (d, *J* = 9.9 Hz, 1H), 4.21 – 4.07 (m, 2H), 3.42 – 3.25 (m, 1H), 2.50 – 2.34 (m, 1H), 2.12 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 172.7, 165.9, 141.8, 133.8, 130.5, 130.4, 130.1, 127.9, 125.6, 125.4, 123.6, 115.6, 115.3, 97.9, 62.6, 61.2, 57.3, 35.5, 20.7, 13.8; IR (film) ν_{max} 3451, 1643, 1489, 1296, 1239, 1090, 1056, 1016, 799, 764 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}ClN_2O_3^+$ $[M + H]^+$ 423.1470, found 423.1467.

Compounds **5h** + **6h**

89% yield, pale-yellow solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.47 – 7.31 (m, 4H), 7.27 – 7.18 (m, 2H), 7.17 – 7.01 (m, 4H), 6.90 – 6.76 (m, 1H), 5.26 – 5.19 (m, 1H), 5.07 – 4.93 (m, 2H), 4.14 – 3.95 (m, 2H), 3.26 – 3.08 (m, 1H), 2.46 – 2.33 (m, 1H), 2.02 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.5, 165.6, 143.6, 136.4, 134.2, 132.9, 132.2, 131.0, 130.3, 128.9, 127.7, 125.8, 125.6, 123.3, 97.5, 61.5, 61.0, 56.8, 35.3, 20.7, 14.1; IR (film) ν_{max}3444, 1643, 1489, 1371, 1296, 1239, 1090, 1056, 1016, 799, 764 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}ClN_2O_3^+$ [M + H]$^+$ 423.1470, found 423.1473.

Compounds **5i** + **6i**

83% yield, pale-yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58 – 7.45 (m, 3H), 7.33 – 7.09 (m, 5H), 7.06 – 6.86 (m, 2H), 5.25 (dd, *J* = 1.2, 7.6 Hz, 1H), 5.10 (d, *J* = 7.6 Hz, 1H), 4.87 (d, *J* = 9.8 Hz, 1H), 4.20 – 4.06 (m, 2H), 3.42 – 3.27 (m, 1H), 2.49 – 2.36 (m, 1H), 2.12 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 172.8, 165.8, 142.3, 140.3, 133.7, 133.0, 131.6, 131.3, 130.3, 130.0, 127.9, 127.3, 125.7, 125.4, 123.7, 122.6, 98.1, 62.6, 61.3, 57.6, 35.4, 20.7, 13.8; IR (film) ν_{max} 3439, 1529, 1475, 1370, 1293, 1239, 1057 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}BrN_2O_3^+$ [M + H]$^+$ 467.0965, found 467.0968.

Compounds **5j** + **6j**

90% yield, pale-yellow solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.60 – 7.37 (m, 3H), 7.21 – 6.97 (m, 6H), 6.92 – 6.74 (m, 1H), 5.32 – 5.20 (m, 1H), 5.08 – 4.91 (m, 2H), 4.15 – 3.91 (m, 2H), 3.23 – 3.07 (m, 1H), 2.49 – 2.31 (m, 1H), 2.03 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.5, 165.6, 143.7, 136.9, 134.2, 132.2, 131.8, 131.0, 130.6, 130.3, 127.7, 125.8, 125.6, 123.3, 121.5, 97.5, 61.5, 61.0, 56.8, 35.3, 20.7, 14.1; IR (film) ν_{max} 3437, 1640, 1529, 1474, 1370, 1293, 1239, 1057 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}BrN_2O_3^+$ [M + H]$^+$ 467.0965, found 467.0970.

Compounds **5k** + **6k**

69% yield, pale-yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.86 – 7.51 (m, 4H), 7.49 – 7.28 (m, 5H), 7.08 – 6.82 (m, 3H), 6.73 – 6.64 (m, 1H), 5.05 (d, *J* = 8.2 Hz, 1H), 4.76 (d, *J* = 7.7 Hz, 2H), 4.08 – 3.88 (m, 2H), 3.43 – 3.18 (m, 1H), 2.39 – 2.21 (m, 1H), 2.01 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 173.7, 166.9, 143.1, 135.7, 134.7, 134.5, 134.1, 134.0, 132.2, 131.0, 129.5, 129.0, 128.7, 128.4, 128.2, 127.6, 127.2, 127.2, 127.1, 126.4, 126.4, 124.4, 98.5, 63.5, 62.1, 58.8, 36.5, 21.6, 14.7; IR (film) ν_{max} 3436, 1637, 1294, 1238, 526 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_3^+$ [M + H]$^+$ 439.2016, found 439.2019.

Compounds **5l** + **6l**

81% yield, pale-yellow solid; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.21 – 6.99 (m, 4H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.46 (dd, *J* = 1.1, 7.6 Hz, 1H), 5.92 (q, *J* = 7.1 Hz, 1H), 5.31 (d, *J* = 7.6 Hz, 1H), 4.87 (d, *J* = 9.9 Hz, 1H), 4.27 – 4.02 (m, 2H), 3.27 – 3.09 (m, 1H), 2.28 – 2.09 (m, 1H), 1.99 (s, 3H), 1.31 (d, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 172.2, 166.2, 141.4, 137.1, 136.2, 131.5, 130.9, 128.0, 126.5, 125.7, 123.4, 97.0, 61.8, 61.1, 50.5, 35.4, 21.2, 17.8, 14.5; IR (film) ν_{max} 2255, 2128, 1666, 1526, 1373, 1243, 1027, 825, 764, 629 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{22}N_2O_3Na^+$ $[M + Na]^+$ 349.1523, found 349.1523.

Compounds **5m** + **6m**

78% yield, pale-yellow solid; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.19 – 6.99 (m, 4H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.35 (dd, *J* = 1.0, 7.6 Hz, 1H), 5.75 (dd, *J* = 5.9, 8.7 Hz, 1H), 5.31 (d, *J* = 7.6 Hz, 1H), 4.88 (d, *J* = 10.2 Hz, 1H), 4.24 – 4.04 (m, 2H), 3.24 – 3.04 (m, 1H), 2.24 – 2.08 (m, 1H), 2.02 (s, 3H), 1.83 – 1.52 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, DMSO) δ 173.0, 166.5, 141.7, 136.3, 135.6, 131.4, 131.0, 128.1, 126.5, 125.8, 123.4, 97.1, 62.2, 61.1, 56.3, 35.7, 24.4, 21.3, 14.5, 11.6; IR (film) ν_{max} 2255, 2128, 1662, 1239, 1051, 1026, 1006, 825, 764, 629 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{24}N_2O_3Na^+$ $[M + Na]^+$ 363.1679, found 363.1676.

Compounds **5n** + **6n**

79% yield, pale-yellow solid; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.30 – 7.02 (m, 6H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.28 (dd, *J* = 1.0, 7.7 Hz, 1H), 5.36 (d, *J* = 7.7 Hz, 1H), 4.97 (d, *J* = 8.7 Hz, 1H), 4.21 – 4.05 (m, 4H), 3.14 – 3.00 (m, 1H), 2.37 – 2.22 (m, 1H), 2.08 (s, 3H), 1.25 – 1.12 (m, 6H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 172.5, 168.0, 165.6, 143.7, 133.6, 130.9, 130.5, 130.3, 127.8, 125.9, 125.8, 123.4, 98.8, 61.9, 61.7, 61.1, 57.1, 34.9, 20.4, 14.1, 13.9; IR (film) ν_{max} 2980, 1740, 1698, 1634, 1530, 1484, 1464, 1369, 1325, 1272, 1231, 1210, 1169, 1135, 1083, 779, 751 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{24}N_2O_5NaS^+$ $[M + Na]^+$ 407.1577, found 407.1575.

Compounds **7a**

89% yield, white solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.31 – 6.61 (m, 11H), 6.50 (d, *J* = 9.6 Hz, 50/100×1H), 6.45 – 6.30 (m, 50/100×2H), 6.24 (d, *J* = 1.5 Hz, 50/100×1H), 5.52 (dd, *J* = 3.6, 9.9 Hz, 50/100×1H), 5.45 (d, *J* = 8.0 Hz, 50/100×1H), 5.06 (d, *J* = 9.4 Hz, 50/100×1H), 4.69 – 4.50 (m, 50/100×1H), 4.08 – 3.84 (m, 50/100×2H+50/100×2H), 2.94 – 2.76 (m, 50/100×1H), 2.71 – 2.53 (m, 50/100×1H), 1.89 (s, 50/100×3H), 1.66 (s, 50/100×3H), 1.15 (t, *J* = 7.1 Hz, 50/100×3H), 1.00 (t, *J* = 7.1 Hz, 50/100×3H); ^{13}C NMR (75 MHz, CD_2Cl2) δ 174.3, 173.1, 166.9, 166.6, 149.9, 143.2, 142.2, 139.5, 138.8, 136.2, 135.6, 135.1, 131.0, 130.7, 130.2, 130.0, 129.3, 129.1, 129.0, 128.9, 128.8, 128.2, 127.7, 126.9, 126.6, 125.8, 124.6, 123.8, 123.5, 120.6, 119.2, 113.7, 111.7, 97.1, 65.2, 63.1, 61.8, 61.0, 60.1, 37.1, 22.0, 20.7, 14.9, 14.5; IR (film) ν_{max} 1691, 1535, 1483, 1369, 1295, 1245, 1226, 1078, 751 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}N_2O_3NaS^+$ $[M + Na]^+$ 411.1679, found 411.1682.

Compounds **7n**

77% yield, white solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.41 – 6.81 (m, 5H), 6.69 – 6.51 (m, 2H), 6.40 (s, 60/100×1H), 6.30 – 6.25 (m, 60/100×1H), 5.46 (dd, *J* = 3.3, 9.9 Hz, 60/100×1H), 5.03 (d, *J* = 9.4 Hz, 40/100×1H), 4.69 – 4.61 (m, 60/100×1H), 4.16 – 4.00 (m, 60/100×4H), 3.89 – 3.64 (m, 40/100×4H), 2.88 – 2.74 (m, 60/100×1H), 2.53 – 2.41 (m, 60/100×1H), 2.00 (s, 60/100×3H), 1.66 (s, 40/100×3H), 1.24 – 1.13 (m, 60/100×3H+40/100×3H), 1.01 (t, *J* = 7.2 Hz, 60/100×3H), 0.88 (t, *J* = 7.1 Hz, 40/100×3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 174.8, 173.2, 168.5, 167.1, 166.4, 148.6, 142.8, 142.0, 135.8, 132.7, 131.1, 130.4, 129.9, 128.6, 128.3, 126.9, 126.8, 125.2, 124.4, 124.0, 121.4, 120.2, 114.3, 111.5, 96.8, 63.4, 62.4, 62.3, 62.0, 61.2, 59.2, 35.3, 21.7, 20.2, 15.0, 14.7, 14.3, 14.2; IR (film) ν_{max} 3453 ,1639, 1245, 1226, 750, 488 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{24}N_2O_5NaS^+$ $[M + Na]^+$ 407.1577, found 407.1578.

Compound **8a**

57% yield; yellow solid; m.p. 200 – 202 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.53 (m, 2H), 7.43 – 7.10 (m, 5H), 7.05 – 6.79 (m, 5H), 6.78 – 6.53 (m, 2H), 5.91 (d, *J* = 8.0 Hz, 1H), 5.01 (t, *J* = 4.5 Hz, 1H), 4.06 – 3.79 (m, 2H), 3.34 – 3.14 (m, 1H), 3.02 – 2.77 (m, 1H), 2.09 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 165.8, 141.4, 137.6, 137.5, 134.3, 132.7, 131.2, 128. 8, 128.3, 128.0, 127.9, 127.6, 127.6, 124.3, 123.0, 122.8, 120.2, 119.1, 112.8, 63.1, 60.7, 60.3, 29.8, 21.5, 13.7; IR (film) ν_{max} 3437, 1639, 1241, 735, 700, 511 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_3^+$ $[M + H]^+$ 439.2016, found 439.2021.

Compound **9a**

29% yield; yellow solid; m.p. 182 – 184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.66 (m, 2H), 7.43 – 7.09 (m, 10H), 7.02 (dd, *J* = 1.2, 7.5 Hz, 1H), 6.93 – 6.84 (m, 1H), 6.57 (dd, *J* = 1.0, 8.2 Hz, 1H), 5.16 (dd, *J* = 5.4, 8.6 Hz, 1H), 4.33 – 3.96 (m, 2H), 2.88 – 2.63 (m, 1H), 2.41 – 2.16 (m, 1H), 2.14 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 165.9, 144.3, 143.6, 139.4, 136.8, 132.6, 129.7, 129.2, 128.3, 128.1, 127.6, 127.0, 126.1, 125.4, 123.7, 122.9, 120.6, 120.1, 111.9, 61.3, 60.1, 57.0, 35.8, 21.7, 14.2; IR (film) ν_{max} 3449, 1688.,1639, 1442, 1368, 1325, 1233, 754, 701 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_3^+$ [M + H]$^+$ 439.2016, found 439.2018.

Compound **8e**

76%yield, yellow solid; m.p. 181 – 183 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.20 (m, 7H), 6.95 – 6.20 (m, 7H), 5.00 (t, *J* = 4.1 Hz, 1H), 4.07 – 3.78 (m, 2H), 3.35 – 3.13 (m, 1H), 3.04 – 2.90 (m, 1H), 2.19 (s, 3H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 165.4 (d, J = 1.8 Hz), 160.0 (d, J = 247.0 Hz), 144.3, 142.1 (d, J = 1.5 Hz), 136.5, 132.0 (d, J = 1.3 Hz), 129.9, 129.2, 128.9 (d, J = 8.5 Hz), 128.2, 128.0 (d, J = 4.1 Hz), 127.8, 126.0, 125.9, 125.7, 123.6, 123.5, 123.4, 122.8, 120.2, 120.2, 116.3 (d, J = 22.1 Hz), 111.7, 61.2, 60.8 (d, J = 2.1 Hz), 55.5, 35.9, 29.7, 21.7, 14.1；IR (film) ν_{max} 3436, 1644, 1489, 1443, 1384, 1243, 1094, 750 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FN_2O_3^+$ [M + H]$^+$ 457.1922, found 457.1920.

Compound **9e**

15%yield,yellow solid; m.p. 198 – 201 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.76 – 7.66 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.35 – 6.92 (m, 8H), 6.91 – 6.78 (m, 2H), 6.53 (d, *J* = 8.2 Hz, 1H), 5.34 (dd, *J* =4.6, 9.0 Hz, 1H), 4.13 – 4.01 (m, 3H), 2.91 – 2.77 (m, 1H), 2.30 – 2.16 (m, 1H), 2.04 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); 13C NMR (75 MHz, $CDCl_3$) δ 173.7, 165.38 (d, *J* = 1.8 Hz), 144.3, 142.1, 136.5, 132.1, 129.9, 129.2, 128.89 (d, *J* = 8.5 Hz), 128.2, 127.95 (d, *J* = 4.1 Hz), 127.8, 125.7, 123.6, 123.44 (d, *J* = 3.3 Hz), 122.8, 120.24, 120.19, 116.27 (d, *J* = 22.1 Hz), 111.7, 61.2, 60.78 (d, *J* = 2.1 Hz), 55.5, 35.9, 21.70, 14.1; IR (film) ν_{max} 3437, 2059, 1638, 1486, 1441, 1375, 1260, 1017 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FN_2O_3^+$ [M + H]$^+$ 457.1922, found 457.1927.

Compound **8h**

71% yield; yellow solid; m.p. 145 – 147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.54 (m, 2H), 7.47 – 7.21 (m, 4H), 7.10 (s, 1H), 6.95 – 6.62 (m, 6H), 5.96 (dd, *J* = 1.3, 8.2 Hz, 1H), 5.02 (t, *J* = 4.5 Hz, 1H), 4.07 – 3.83 (m, 2H), 3.33 – 3.18 (m, 1H), 2.99 – 2.84 (m, 1H), 2.11 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 165.2, 141.0, 137.6, 135.8, 133.6, 133.2, 132.3, 131.0, 129.8, 128.2, 127.8, 127.7, 127.5, 123.9, 122.8, 122.8, 120.3, 119.3, 112.5, 62.6, 60.6, 59.5, 28.6, 21.2, 13.4; IR (film) ν_{max} 3448, 1638, 1489, 1442, 1241, 1015 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClN_2O_3^+$ [M + H]$^+$ 473.1626, found 473.1623.

Compound **9h**

26% yield; yellow solid; m.p. 151 – 153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 2H), 7.39 – 6.99 (m, 11H), 6.95 – 6.83 (m, 1H), 6.53 (dd, *J* = 1.0, 8.2 Hz, 1H), 5.12 (dd, *J* =5.4, 8.5 Hz, 1H), 4.25 – 4.05 (m, 2H), 2.85 – 2.65 (m, 1H), 2.43 – 2.20 (m, 1H), 2.12 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 165.4, 143.8, 143.2, 137.8, 136.3, 132.6, 132.0, 129.5, 128.9, 128.2, 127.9, 127.4, 127.3, 125.2, 123.5, 122.6, 120.4, 120.0, 111.4, 61.1, 60.0, 56.6, 35.5, 29.3, 21.4, 13.8; IR (film) ν_{max} 3448, 1639, 1489, 1441, 1373, 1260, 1093, 1014, 801, 753 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClN_2O_3^+$ [M + H]$^+$ 473.1626, found 473.1627.

Compound **8k**

61%yield, yellow solid; m.p.151 – 153 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.55 – 7.42 (m, 2H), 7.37 – 7.02 (m, 13H), 6.48 – 6.28 (m, 2H), 5.92 (dd, *J* = 1.1, 8.1 Hz, 1H), 4.95 (t, *J* = 4.5 Hz, 1H), 3.95 – 3.74 (m, 2H), 3.32 – 3.16 (m, 1H), 2.95 – 2.81 (m, 1H), 2.03 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 175.6, 166.5, 142.4, 138.6, 135.6, 135.2, 133.8, 133.6, 133.6, 132.3, 128.9, 128.8, 128.7, 128.6, 128.3, 128.2, 127.9, 126.5, 126.3, 125.2, 124.1, 123.5, 121.6, 119.8, 113.9, 63.7, 61.6, 61.4, 29.5, 22.2, 14.4; IR (film) ν_{max} 3448, 1644, 1537, 1442, 1367, 1237, 750, 479 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{29}N_2O_3^+$ [M + H]$^+$ 489.2172, found 489.2169.

Compound **9k**

19%yield; yellow solid; m.p. 251 – 253 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.87 – 7.63 (m, 6H), 7.47 – 7.34 (m, 3H), 7.31 – 7.21 (m, 1H), 7.19 – 7.03 (m, 4H), 6.93 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.87 – 6.77 (m, 1H), 6.49 (dd, *J* = 0.9, 8.2 Hz, 1H), 5.17 (dd, *J* = 5.2, 8.8 Hz, 1H), 4.19 – 4.03 (m, 2H), 2.77 – 2.62 (m, 1H), 2.24 – 2.10 (m, 1H), 2.06 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 174.2, 166.9, 145.5, 144.7, 138.0, 137.8, 134.0, 133.49, 133.47, 130.7, 130.1, 129.0, 128.96, 128.89, 128.6, 128.4, 127.1, 126.8, 126.5, 125.5, 125.3, 124.7, 123.7, 121.7, 121.0, 112.8, 62.3, 61.2, 58.0, 36.7, 22.4, 14.9; IR (film) ν_{max} 3437, 1635, 1238, 753, 728, 477 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{29}N_2O_3^+$ $[M + H]^+$ 489.2172, found 489.2174.

Compounds **8l** + **9l**

81% yield; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.39 – 7.17 (m, 3H), 7.16 – 7.06 (m, 2H), 6.94 – 6.80 (m, 2H), 6.17 (q, *J* = 7.1 Hz, 1H), 4.96 – 4.88 (m, 1H), 4.29 – 4.10 (m, 1H), 3.23 – 3.10 (m, 1H), 2.67 – 2.55 (m, 1H), 2.07 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 166.0, 142.3, 138.3, 137.8, 132.8, 130.2, 129.2, 128.1, 127.8, 125.4, 123.3, 122.6, 119.3, 119.2, 112.6, 63.1, 61.0, 52.2, 33.9, 21.3, 17.1, 14.2; IR (film) ν_{max} 2926, 1706, 1538, 1487, 1442, 1371, 1302, 1275, 1260, 1240, 1084, 1052, 751 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}N_2O_3Na^+$ $[M + Na]^+$ 399.1679, found 399.1682.

Compound **8m**

71%yield; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.68 (m, 2H), 7.36 – 7.07 (m, 5H), 6.93 – 6.81 (m, 2H), 6.02 (t, *J* = 7.3 Hz, 1H), 4.91 (dd, *J* = 2.5, 8.1 Hz, 1H), 4.31 – 4.12 (m, 2H), 3.26 – 3.10 (m, 1H), 2.62 – 2.48 (m, 1H), 2.07 (s, 3H), 1.67 (t, *J* = 7.4 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 166.3, 142.2, 138.6, 137.5, 132.8, 130.0, 129.0, 128.0, 127.7, 125.6, 123.2, 122.4, 119.2, 118.9, 112.5, 63.1, 60.9, 57.5, 34.5, 23.6, 21.3, 14.1; IR (film) ν_{max} 3064, 2977, 2937, 2905, 2878, 1681, 1603, 1567, 1537, 1488, 1443, 1372, 1240, 1186, 1159, 1130, 1094. 1049, 946, 903, 863, 753, 702, 617, 581 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}N_2O_3Na^+$ $[M + Na]^+$ 413.1836, found 413.1834.

Compound **9m**

23%yield; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.69 (m, 2H), 7.41 – 7.33 (m, 1H), 7.31 – 7.26 (m, 1H), 7.20 – 7.09 (m, 2H), 7.00 (dd, *J* = 7.9, 3.2 Hz, 1H), 6.93 – 6.85 (m, 1H), 6.55 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.78 (dd, *J* = 10.8, 3.8 Hz, 1H), 4.99 (t, *J* = 7.9 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.00 – 2.86 (m, 1H), 2.57 – 2.42 (m, 1H), 2.37 – 2.25 (m, 1H), 1.92 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H)；^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 166.7, 143.2, 142.7, 137.4, 130.8, 129.7, 129.4, 128.0, 127.4, 124.8, 123.6, 123.4, 121.1, 120.0, 112.6, 61.1, 59.8, 56.2, 36.0, 29.0, 21.8, 14.2, 10.7; IR (film) ν_{max} 2966, 2931, 1707, 1668, 1602, 1485, 1456, 1442, 1376, 1302, 1275, 1261, 1237, 1097, 1072, 1046, 800, 752, 730 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}N_2O_3Na^+$ $[M + Na]^+$ 413.1836, found 413.1832.

Compound **8n**

49%yield; yellow solid; m.p.169 – 171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.62 (m, 2H), 7.37 – 7.22 (m, 3H), 7.23 – 7.13 (m, 2H), 6.94 – 6.76 (m, 2H), 6.60 (s, 1H), 5.02 (dd, *J* = 4.1, 5.6 Hz, 1H), 4.37 – 4.03 (m, 2H), 3.91 – 3.57 (m, 2H), 3.39 – 3.15 (m, 1H), 2.80 – 2.61 (m, 1H), 2.16 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174. 6, 167.5, 165.47, 141.1, 140.3, 133.0, 131.2, 130.5, 129.1, 128.1, 127.8, 124.7, 123.5, 122.9, 120.6, 120.1, 112.3, 63.1, 61.4, 61.1, 58.7, 30.8, 21.1, 14.0, 13.4; IR (film) ν_{max} 2982, 1743, 1677, 1486, 1443, 1392, 1325, 1285, 1197, 1051, 1025 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_5^+$ $[M + H]^+$ 435.1914, found 435.1918.

Compound **9n**

40%yield; yellow solid; m.p.165 – 167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.60 (m, 2H), 7.42 – 7.25 (m, 2H), 7.21 – 7.05 (m, 3H), 6.98 – 6.82 (m, 1H), 6.59 (dd, *J* = 1.0, 8.1 Hz, 1H), 6.39 (s, 1H), 5.56 (t, *J* = 7.5 Hz, 1H), 4.39 – 4.11 (m, 4H), 3.06 – 2.91 (m, 1H), 2.53 – 2.37 (m, 1H)., 2.02 (s, 3H), 1.31-1.23 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 169.7, 165.2, 145.1, 143.2, 137.2, 129.6, 129.3, 128.0, 127.6, 125.4, 125.2, 123.6, 123.2, 121.0, 120.2, 112.0, 61.8, 61.5, 58.5, 57.8, 35.7, 20.8, 14.2, 14.0; IR (film) ν_{max} 3548, 2980, 1743, 1713, 1680, 1603, 1486, 1443, 1382, 1325, 1285, 1231, 1197, 1051, 1025, 757 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_5^+$ $[M + H]^+$ 435.1914, found 435.1915.

Compound **10**

49% yield; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 1H), 7.55 (d, *J* = 9.8 Hz, 1H), 7.45 – 7.30 (m, 2H), 7.25 – 7.22 (m, 5H), 7.21 – 7.10 (m, 2H), 6.01 (d, *J* = 7.5 Hz, 1H), 5.91 (d, *J* = 9.8 Hz, 1H), 5.80 (d, *J* = 7.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.90 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 166.0, 148.4, 136.1, 135.2, 134.6, 131.6, 130.1, 129.4, 128.4, 128.1, 128.0, 127.7, 126.5, 124.1, 123.4, 106.5, 91.5, 64.0, 60.2, 19.7, 14.2; IR (film) ν_{max} 2920, 2850, 1691, 1632, 1529, 1495, 1454, 1373, 1290, 1235, 1210, 1133, 1079, 1029, 770, 744, 703, 575 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}N_2NaO_3^+$ $[M + Na]^+$ 409.1523, found 409.1526.

Compound **11**

52% yield; yellow solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.05 – 7.96 (m, 1H), 7.49 – 7.25 (m, 4H), 7.24 – 7.12 (m, 2H), 7.13 – 7.02 (m, 2H), 6.90 (s, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 6.13 – 6.02 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.74 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 171.0, 165.1, 148.0, 134.5, 133.8, 131.4, 131.0, 130.5, 130.4, 129.7, 127.14, 127.08, 125.8, 122.9, 122.8, 114.7, 114.4, 106.1, 90.4, 62.6, 59.5, 18.8, 13.4; IR (film) ν_{max} 2961, 2927,1755, 1690, 1603, 1528, 1509, 1374, 1328, 1277, 1261, 1234, 1210, 1158, 1133, 1096, 1078, 1016, 799, 747 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}FN_2NaO_3^+$ $[M + Na]^+$ 427.1428, found 427.1427.

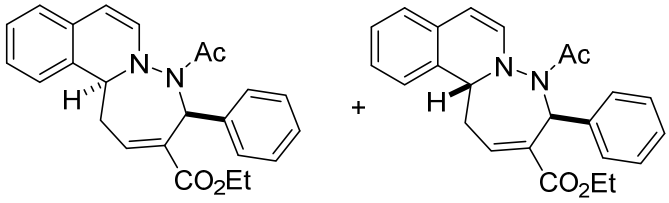
Compound **12**

46% yield; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 3H), 7.24 (s, 1H), 7.14 – 6.99 (m, 5H), 6.91 – 6.76 (m, 3H), 6.55 (d, *J* = 9.5 Hz, 1H), 5.13 (d, *J* = 9.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.78 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 165.9, 148.8, 141.3, 135.2, 134.3, 130.0, 129.8, 129.3, 128.2, 128.1, 127.3, 125.7, 125.3, 122.9, 122.4, 112.7, 96.4, 64.4, 60.2, 20.1, 14.2; IR (film) ν_{max} 2962, 2924, 2851, 1691, 1625, 1594, 1535, 1483, 1454, 1409, 1369, 1342, 1294, 1246, 1226, 1194, 1144, 1079, 801, 751 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}N_2NaO_3^+$ $[M + Na]^+$ 409.1523, found 409.1519.

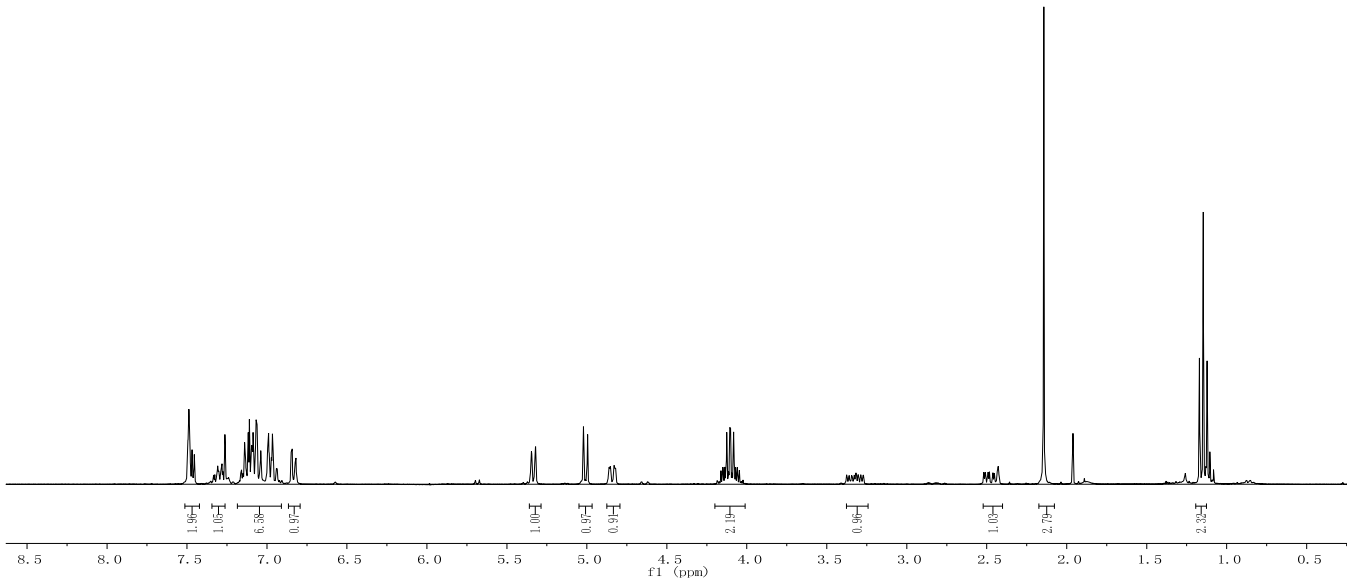
Compound **13**

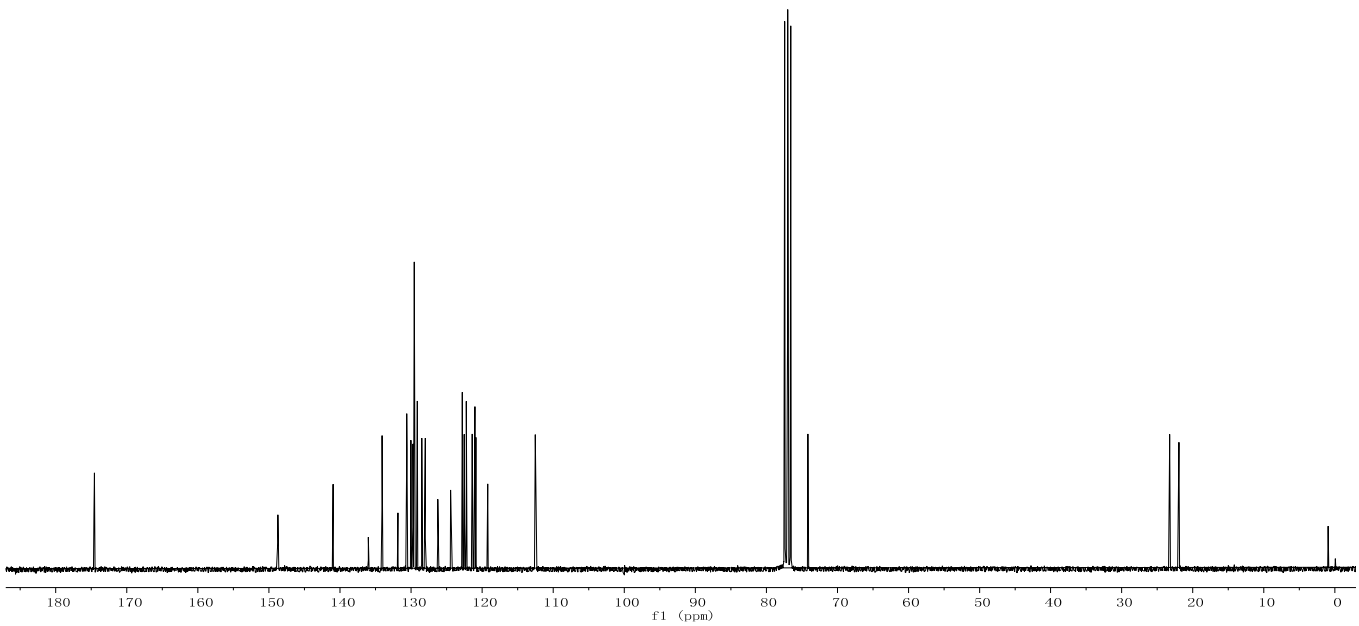
91% yield; yellow solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.45 (s, 1H), 7.77 – 7.59 (m, 2H), 7.48 – 7.23 (m, 4H), 7.01 – 6.83 (m, 5H), 6.73 – 6.50 (m, 2H), 5.88 (dd, *J* = 1.1, 8.1 Hz, 1H), 5.05 (t, *J* = 4.6 Hz, 1H), 3.63 – 3.10 (m, 2H), 2.90 – 2.69 (m, 1H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.3, 167.3, 141.8, 138.7, 137.8, 134.1, 133.4, 131.0, 128.9, 128.4, 128.1, 128.1, 127.9, 127.8, 125.2, 123.3, 123.1, 120.3, 119.1, 112.7, 62.7, 59.9, 29.5, 21.4; IR (film) ν_{max} 2254, 2127, 1659, 1027, 825, 763, 629 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{22}N_2O_3Na^+$ $[M + Na]^+$ 433.1523, found 433.1524.

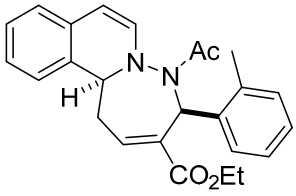
^{1}H and ^{13}C NMR Spectra of the Cycloadducts



5a **6a**

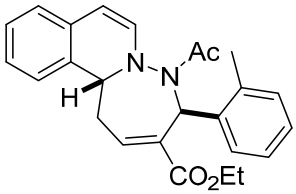




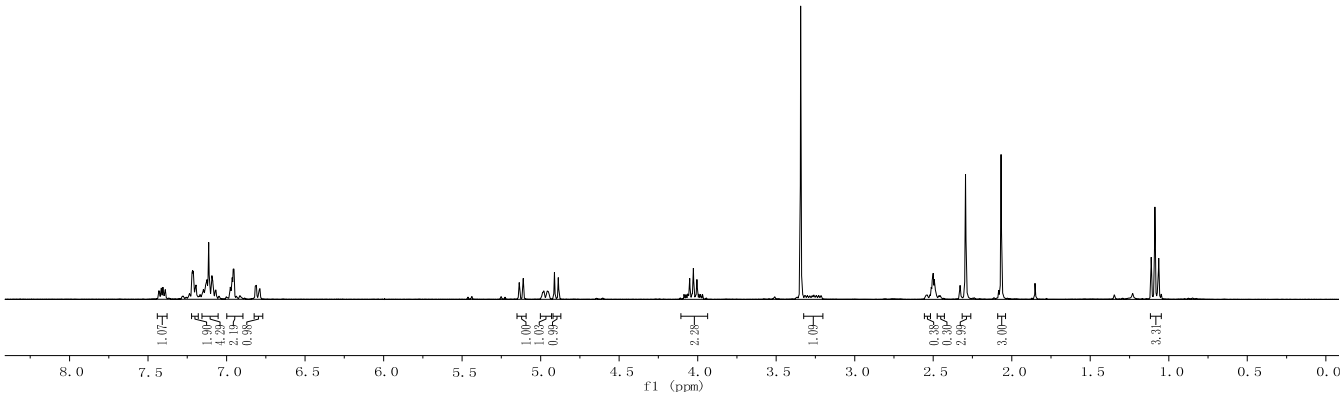

N
N
Ac
H
CO2Et

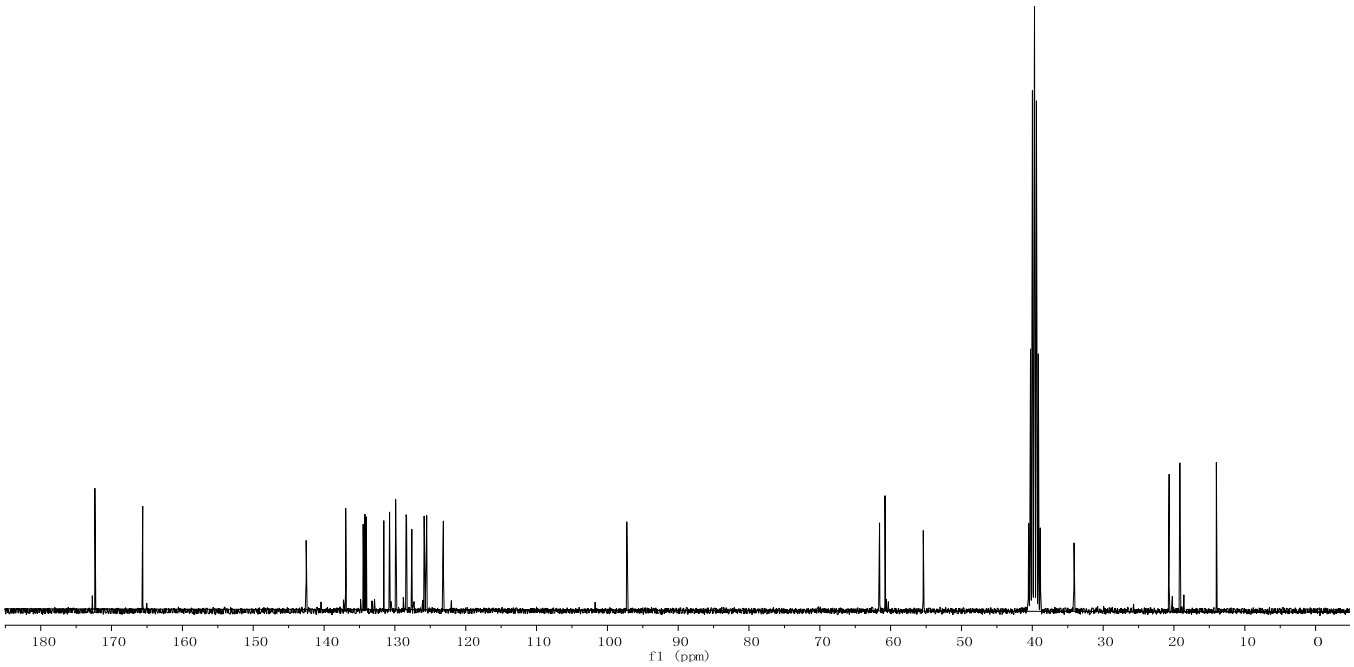
5b

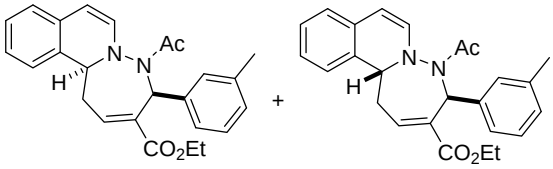
+


N
N
Ac
H
CO2Et

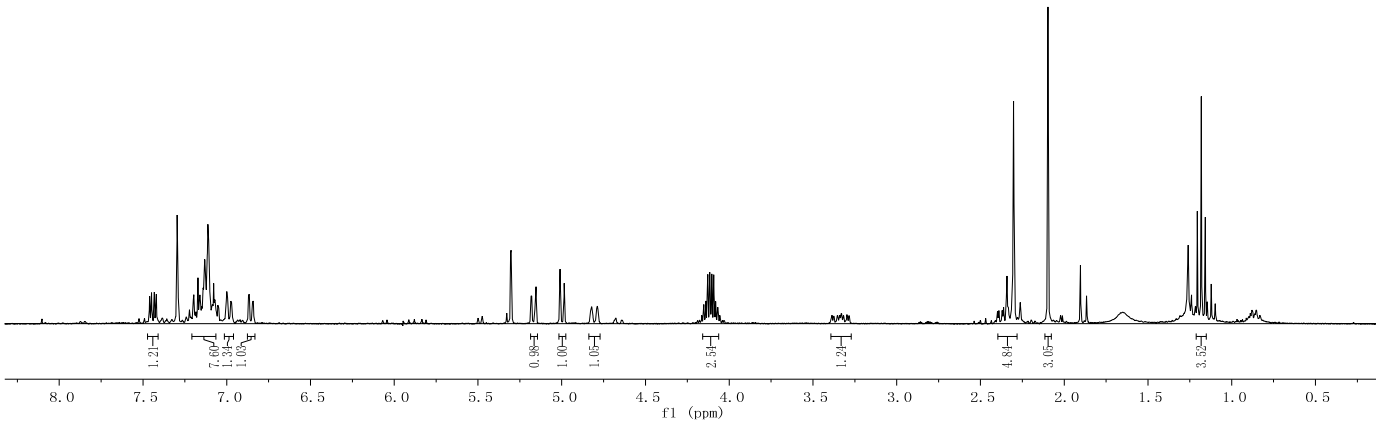
6b


1.07
1.90
4.29
2.11
0.98
1.00
1.05
0.95
2.28
1.09
0.38
0.30
2.99
3.00
3.31
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

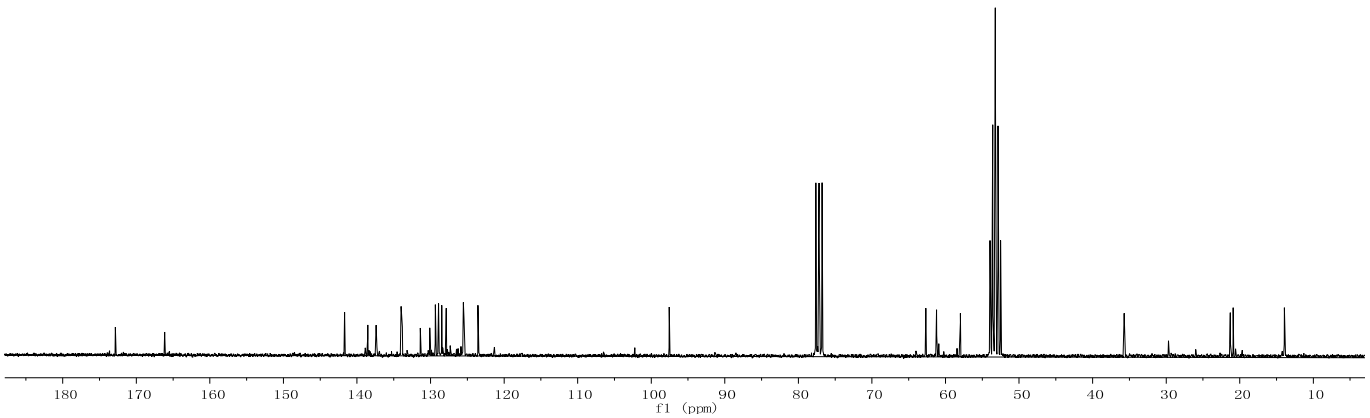

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

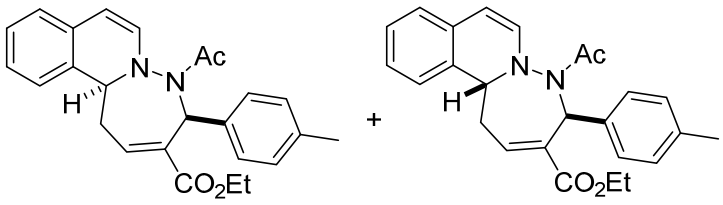

Ac
N
N
H
CO2Et
+
Ac
N
N
H
CO2Et

5c **6c**

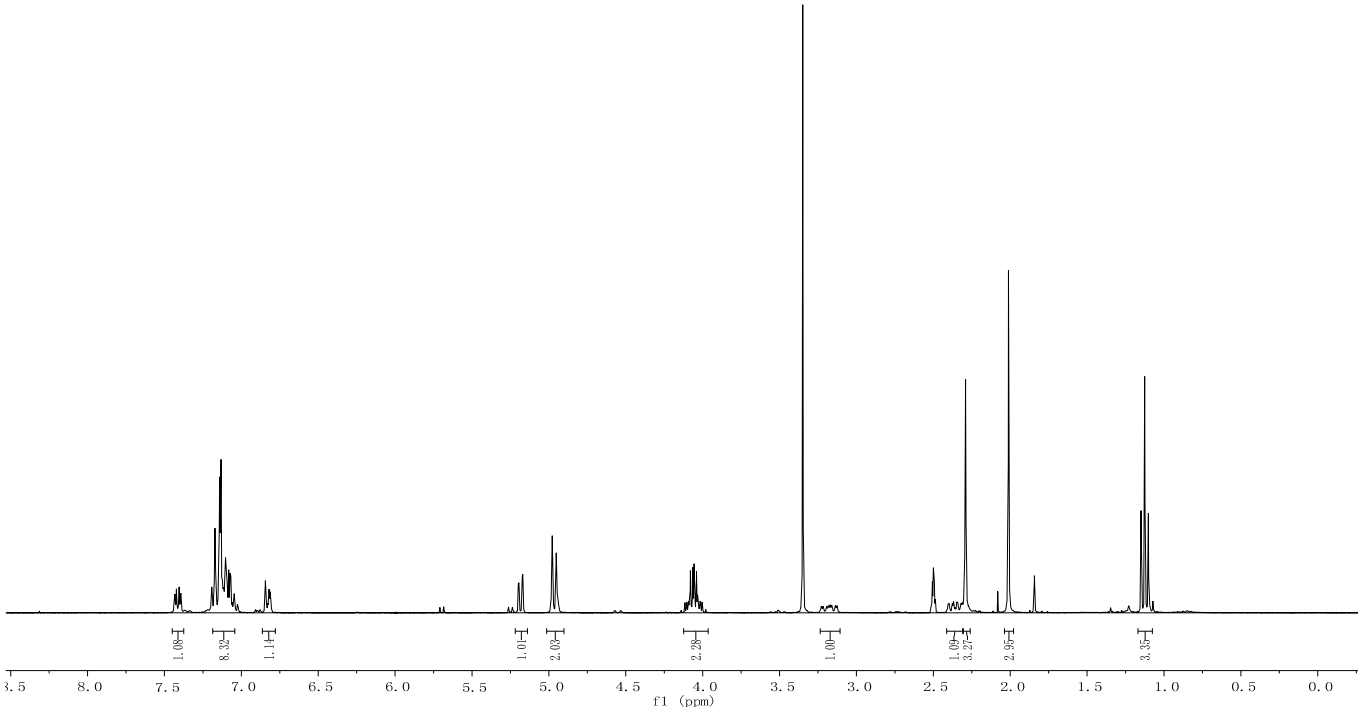

1.21
7.60
1.34
1.05
0.98
1.00
1.06
2.54
1.24
4.84
3.05
3.52
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

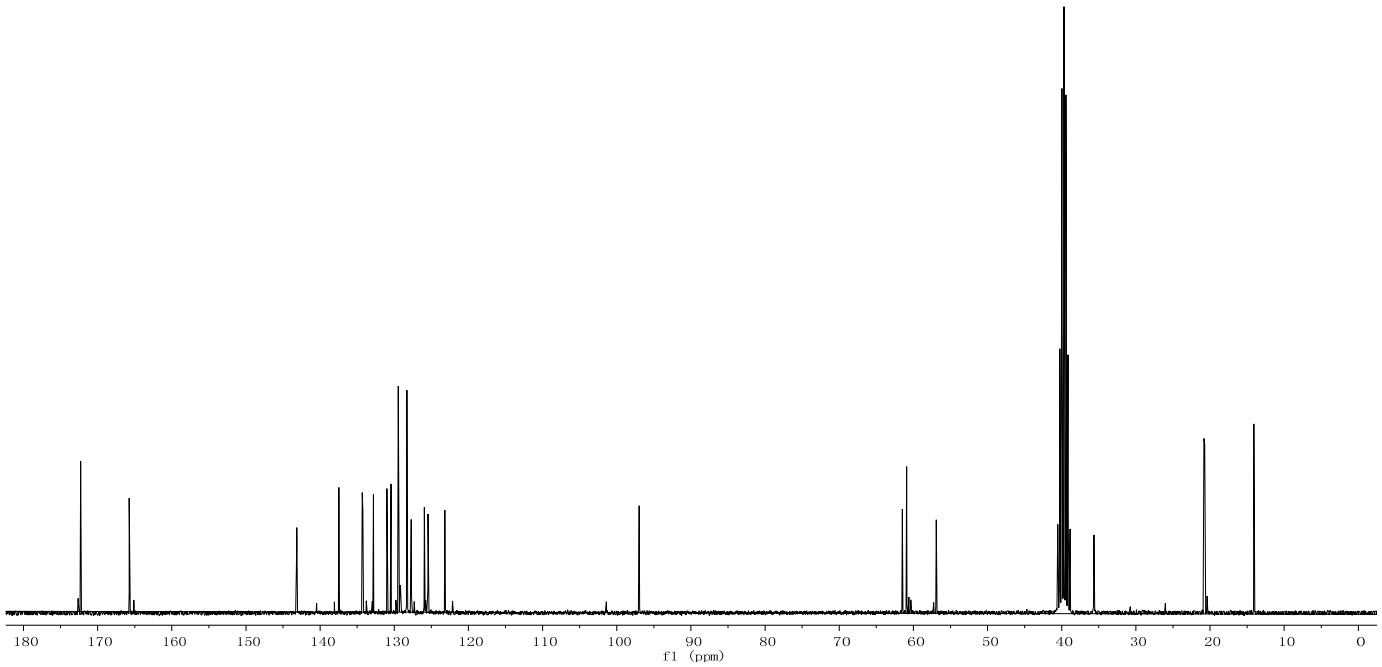

172.84
166.13
141.68
138.54
137.40
134.01
133.82
131.99
130.11
129.35
128.92
128.47
127.87
125.59
125.53
125.46
123.55
97.56
62.68
61.21
57.97
35.71
21.28
20.69
13.93

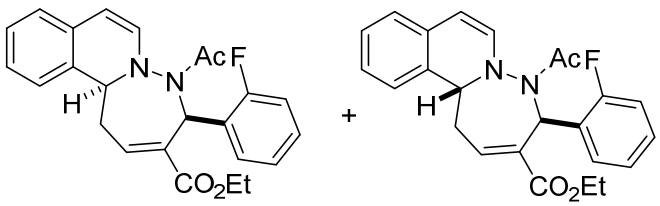

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ac
N
N
H
CO2Et
+
Ac
N
N
H
CO2Et

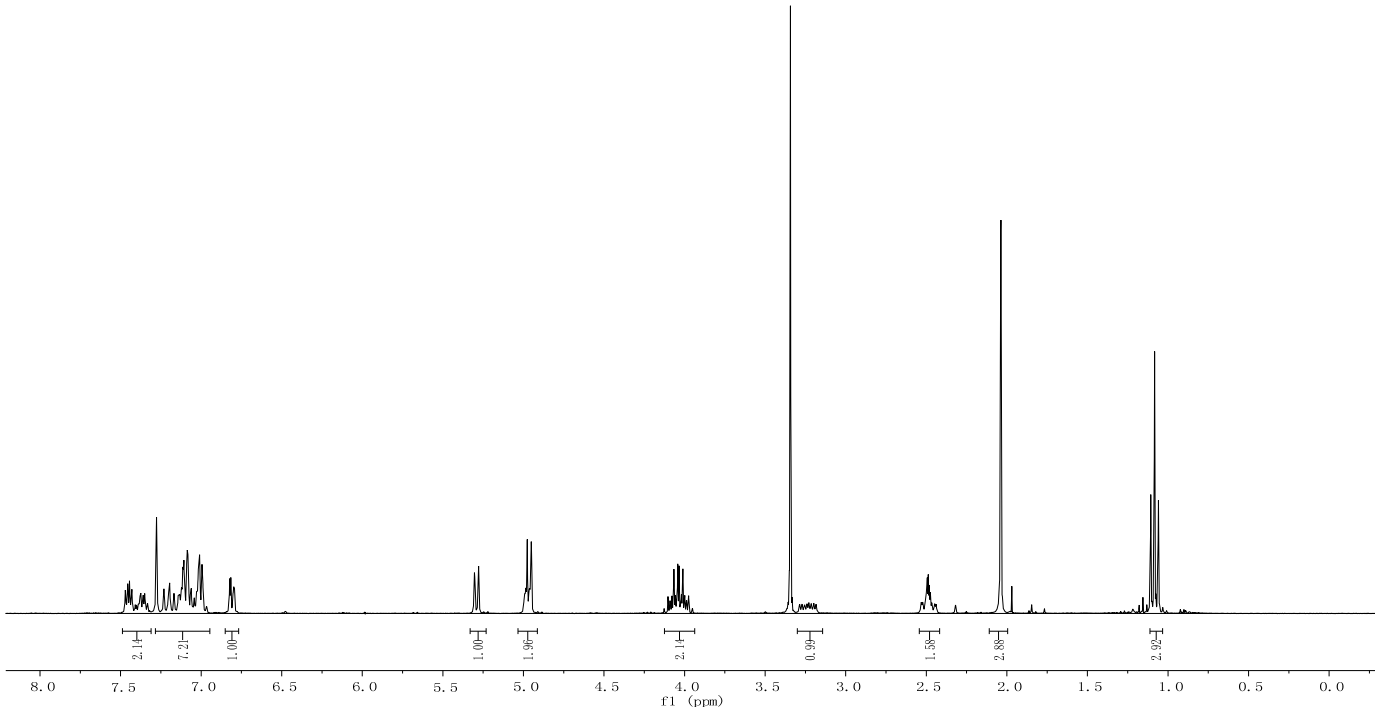
5d **6d**

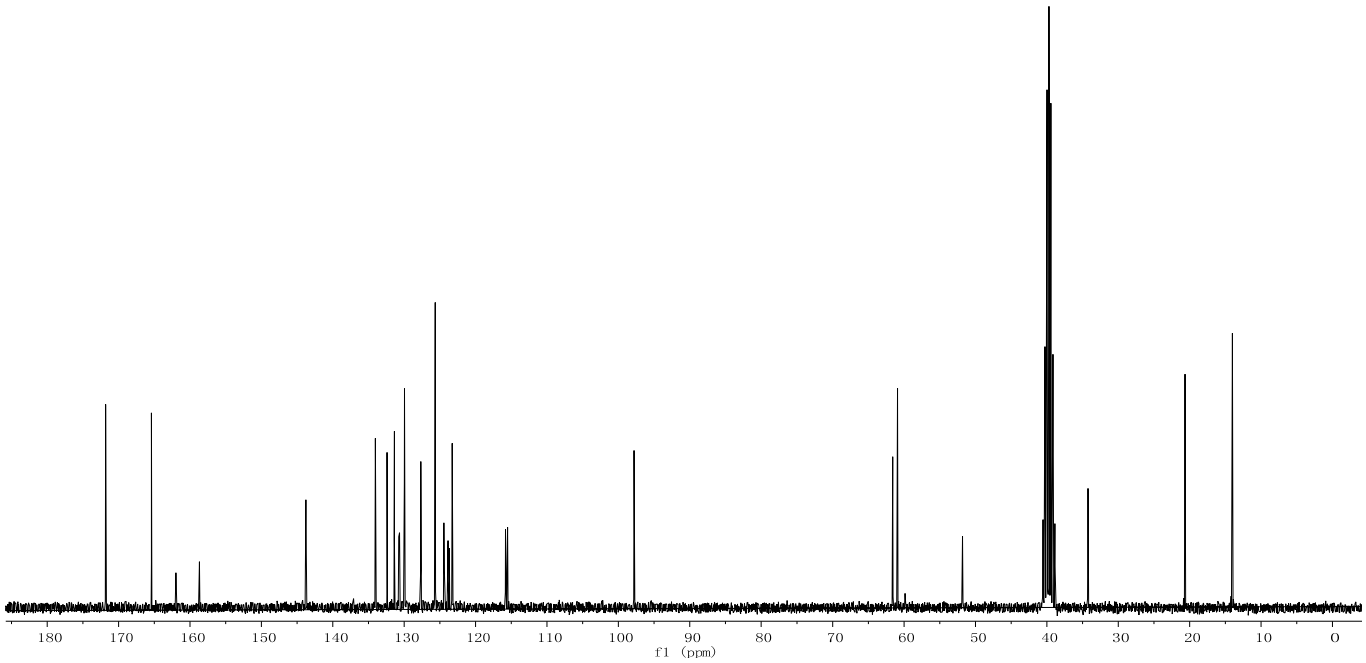

1.08
8.32
1.11
1.01
2.03
2.28
1.00
1.09
3.27
2.95
3.35
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

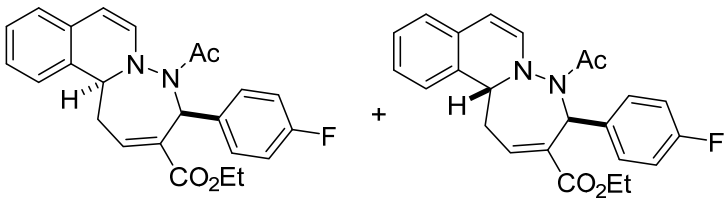

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
N
Ac
F
H
CO2Et
+
N
N
Ac
F
H
CO2Et

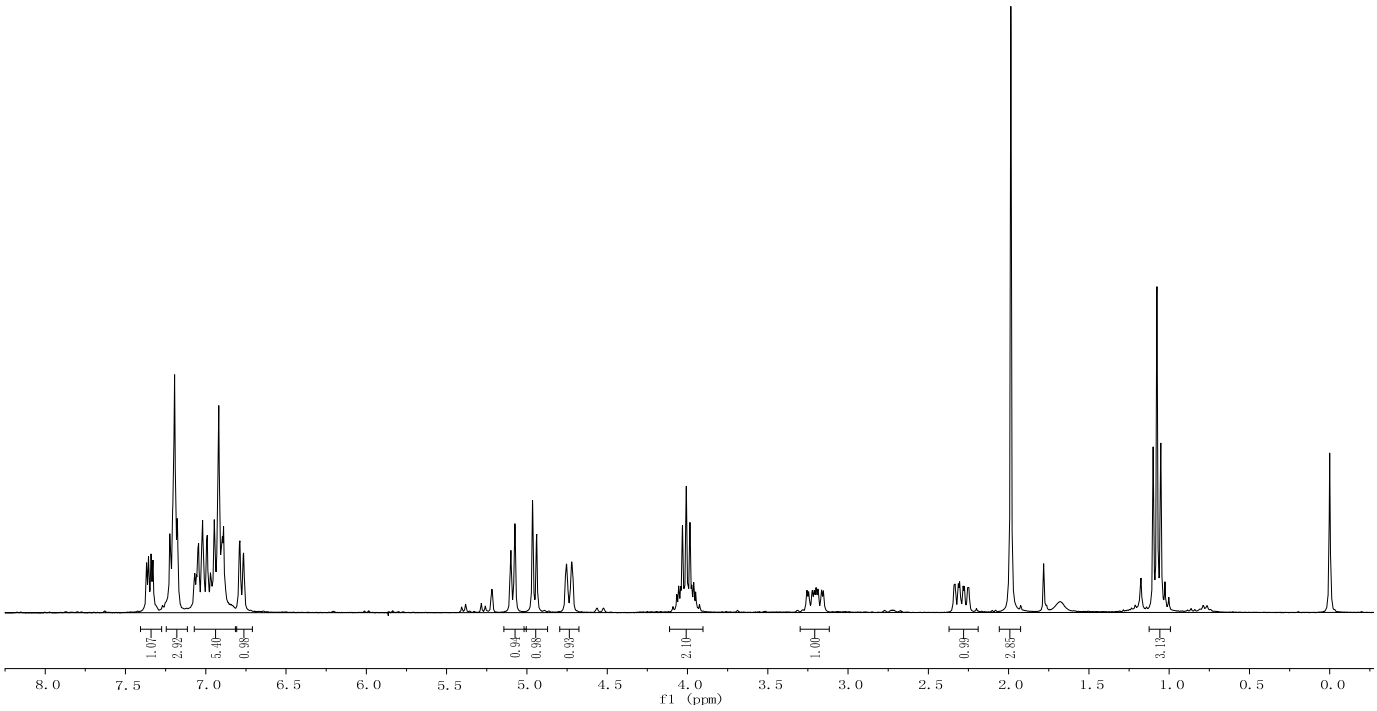
5e **6e**

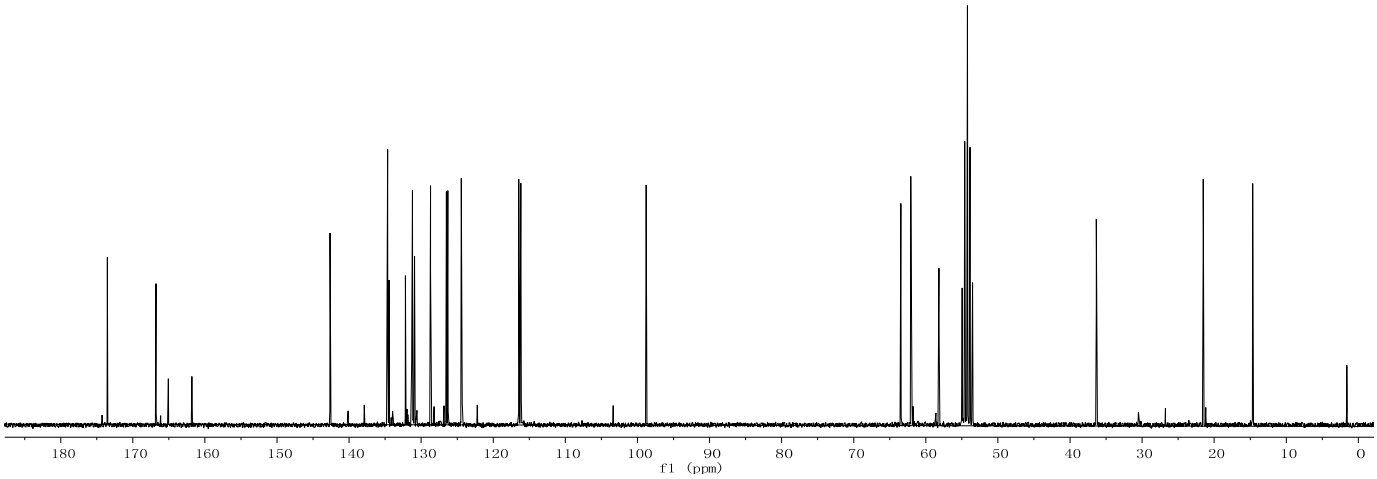

2.14
7.21
1.00
1.00
1.96
2.14
0.99
1.58
2.88
2.92
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

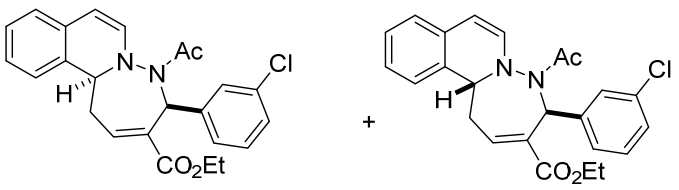

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
F
CO2Et
+
Ac
N
N
H
F
CO2Et

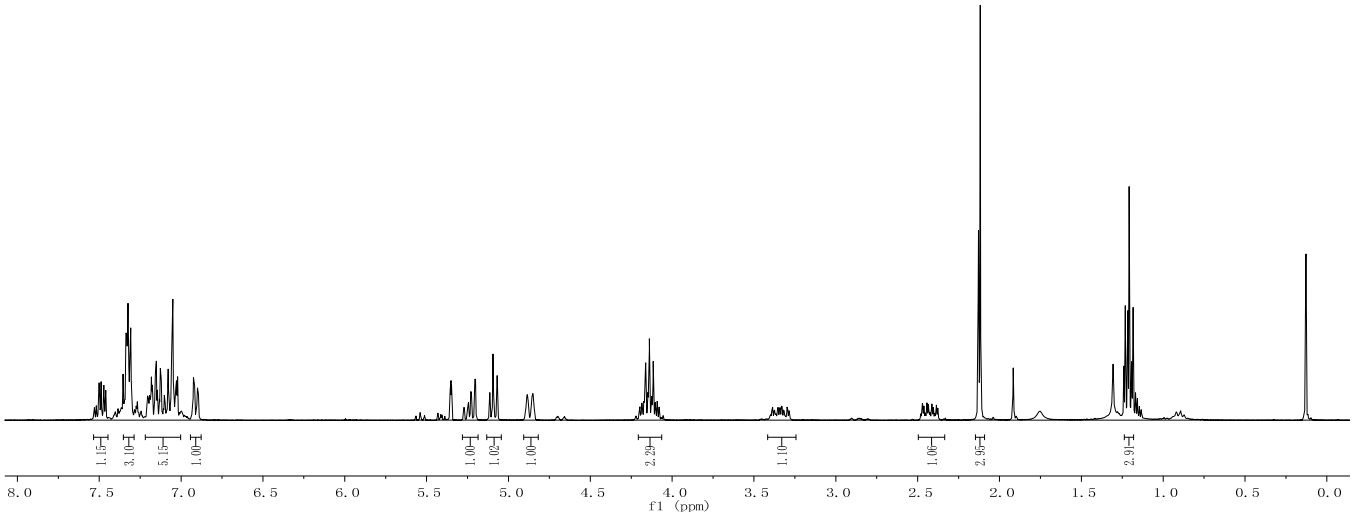
5f **6f**

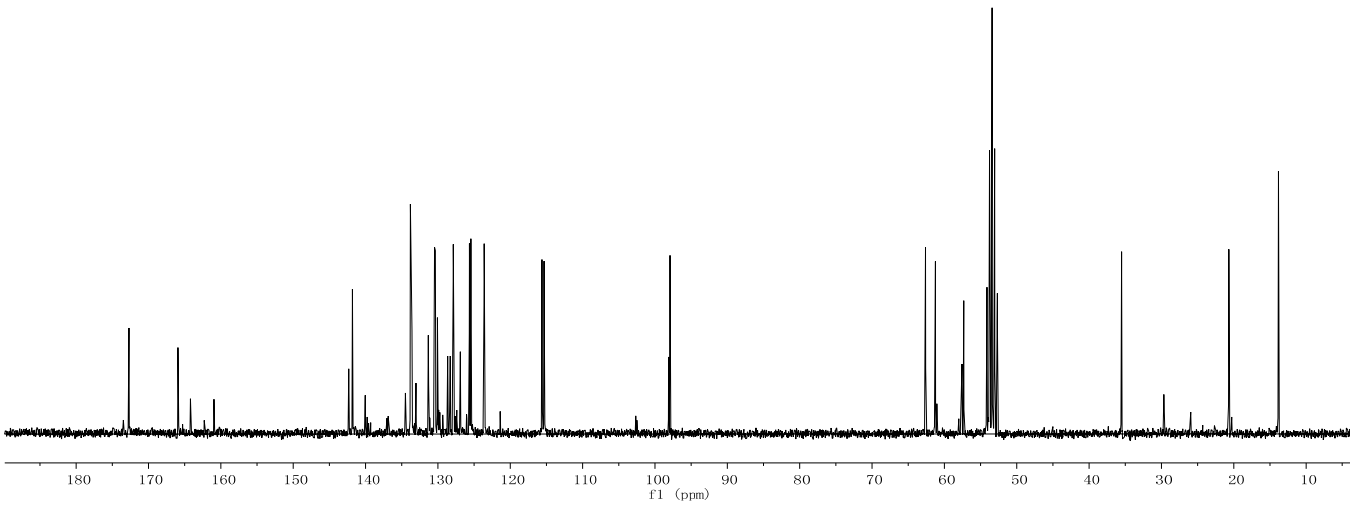

1.07
2.92
5.40
0.98
0.94
0.98
0.93
2.10
1.00
0.99
2.85
3.13
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

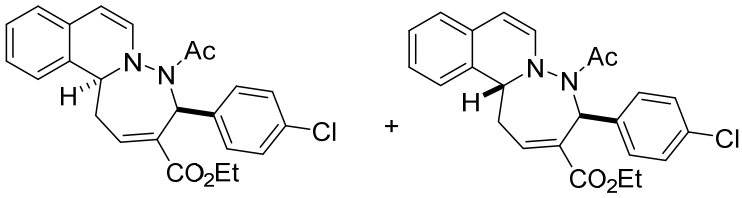

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
N
Ac
Cl
H
CO2Et
+
N
N
Ac
Cl
H
CO2Et

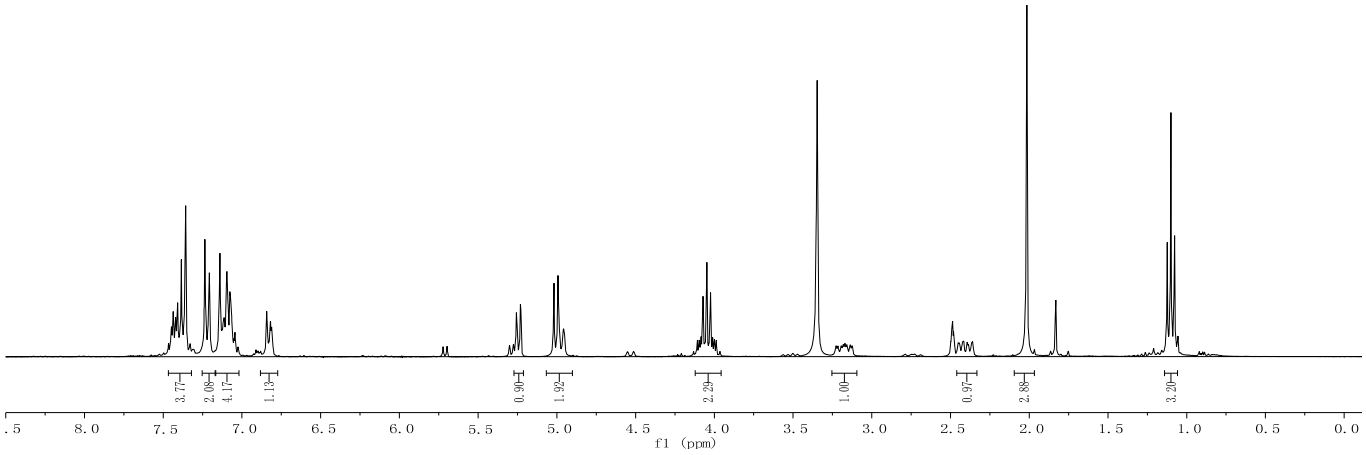
5g **6g**

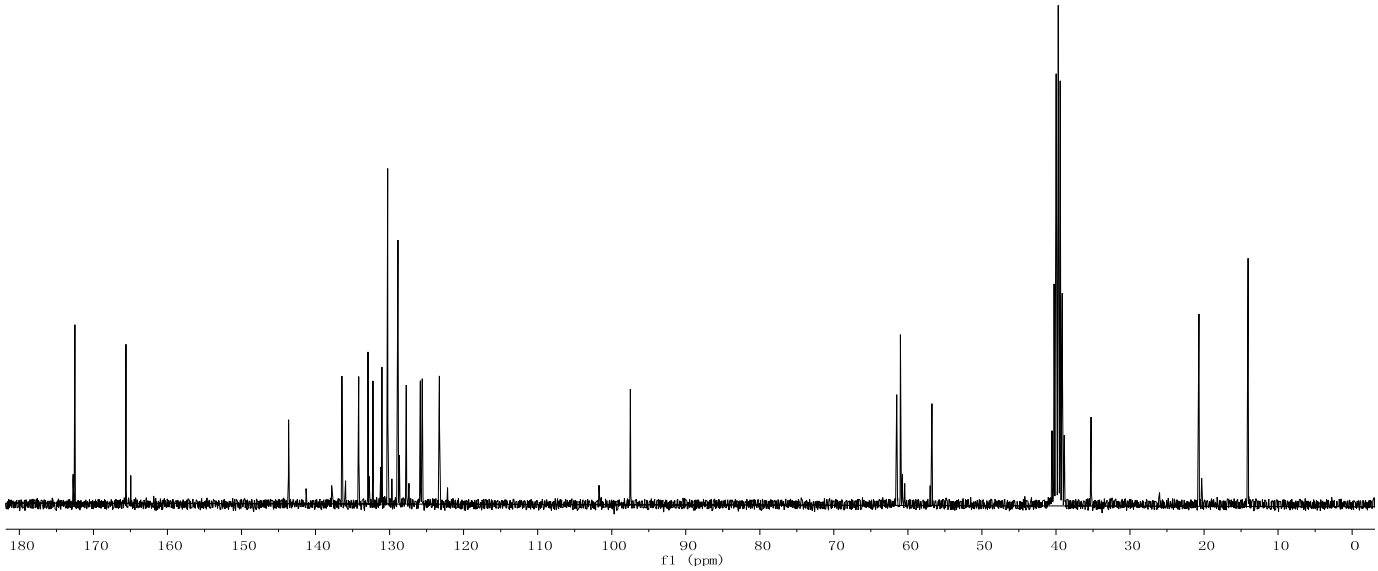

1.15
3.10
5.15
1.00
1.00
1.02
1.00
2.29
1.10
1.06
2.95
2.91
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

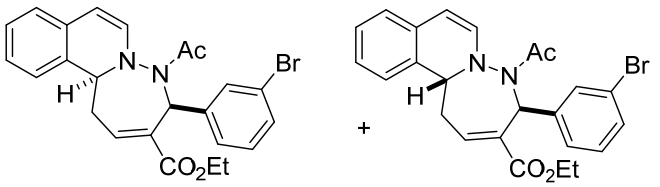

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ac
N
N
H
Cl
CO2Et
+
Ac
N
N
H
Cl
CO2Et

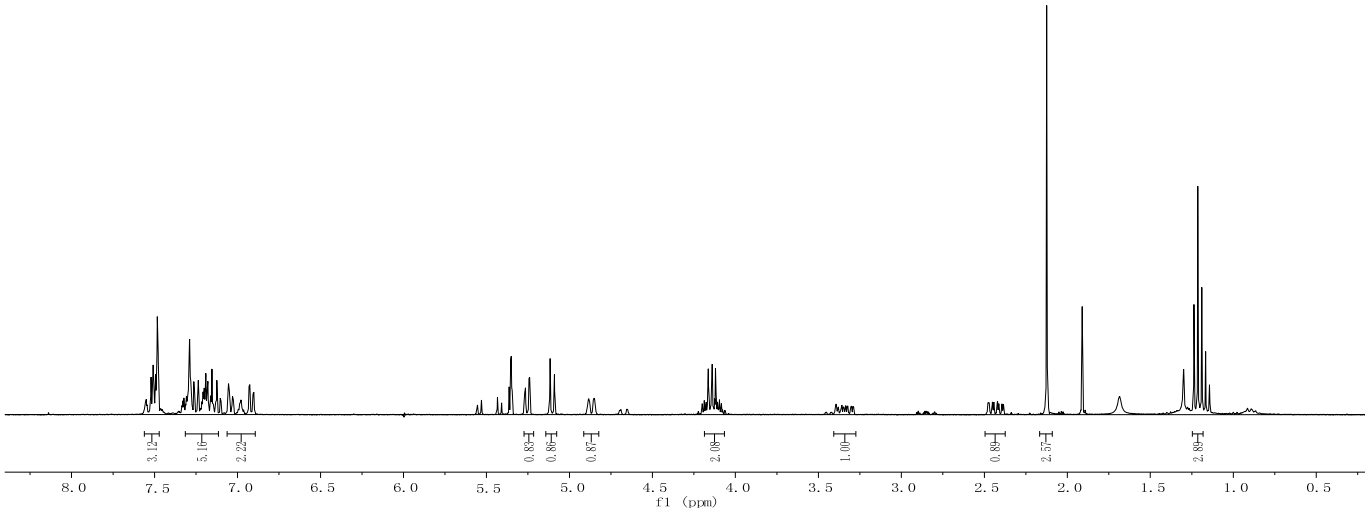
5h **6h**

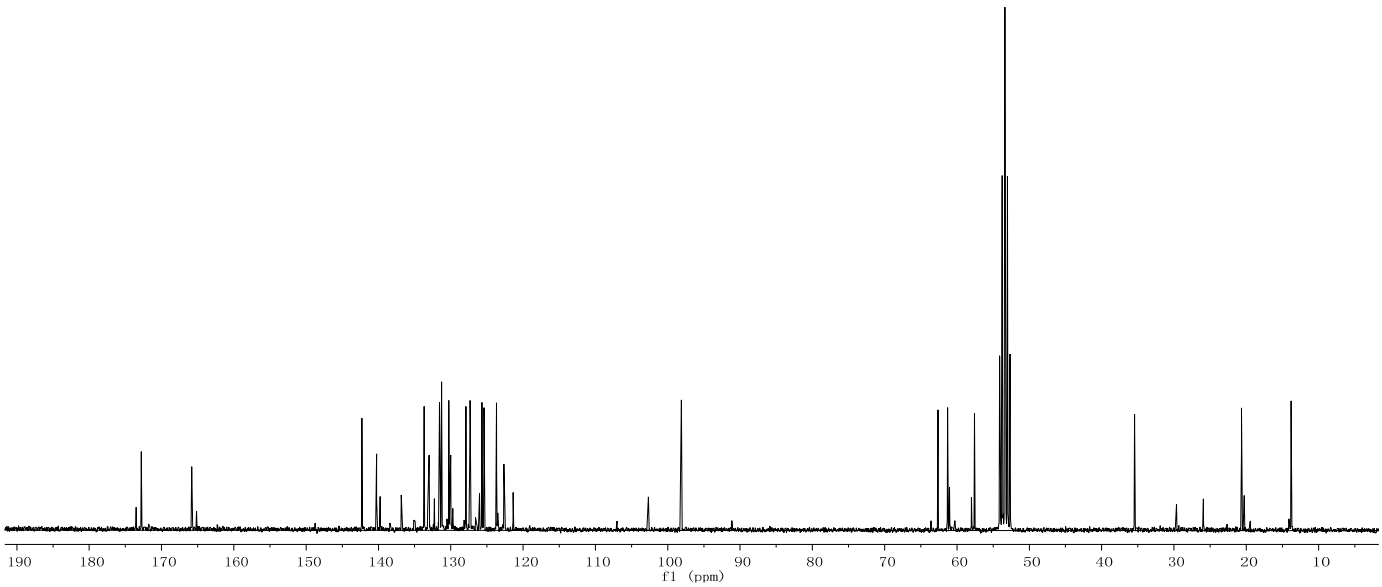

3.77
2.08
4.17
1.13
0.90
1.92
2.29
1.00
0.97
2.88
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

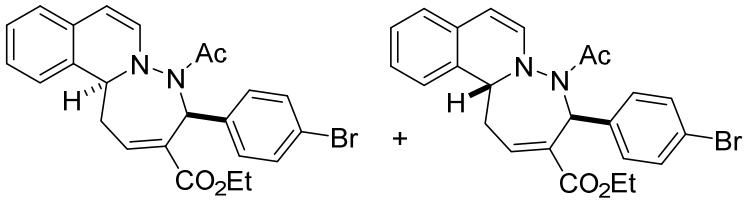

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ac
N
N
H
Br
CO2Et
+
Ac
N
N
H
Br
CO2Et

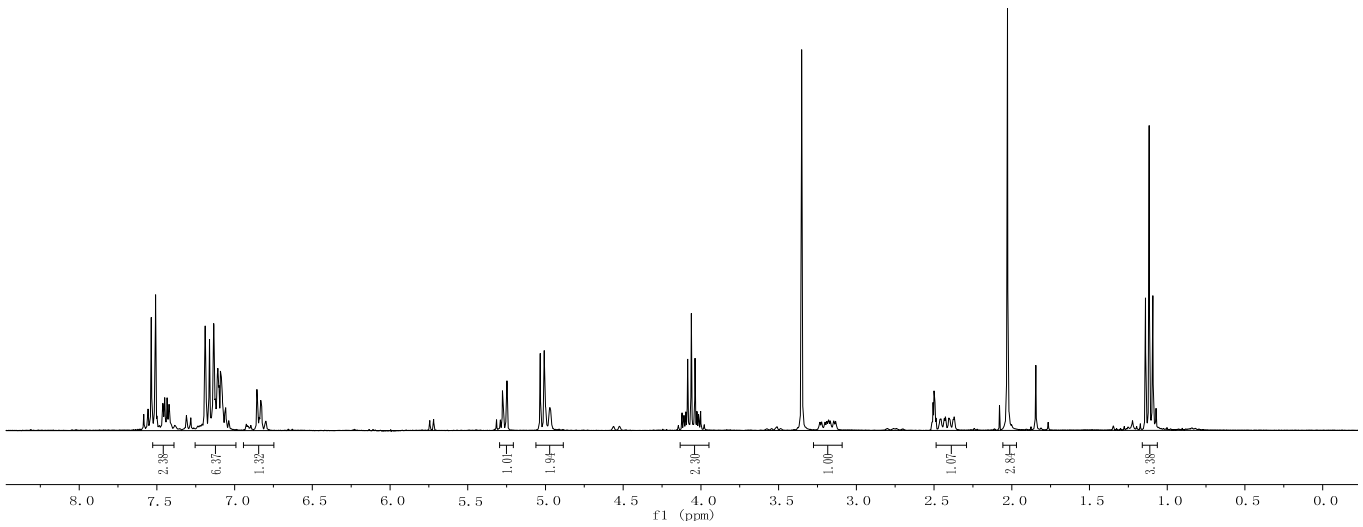
5i **6i**

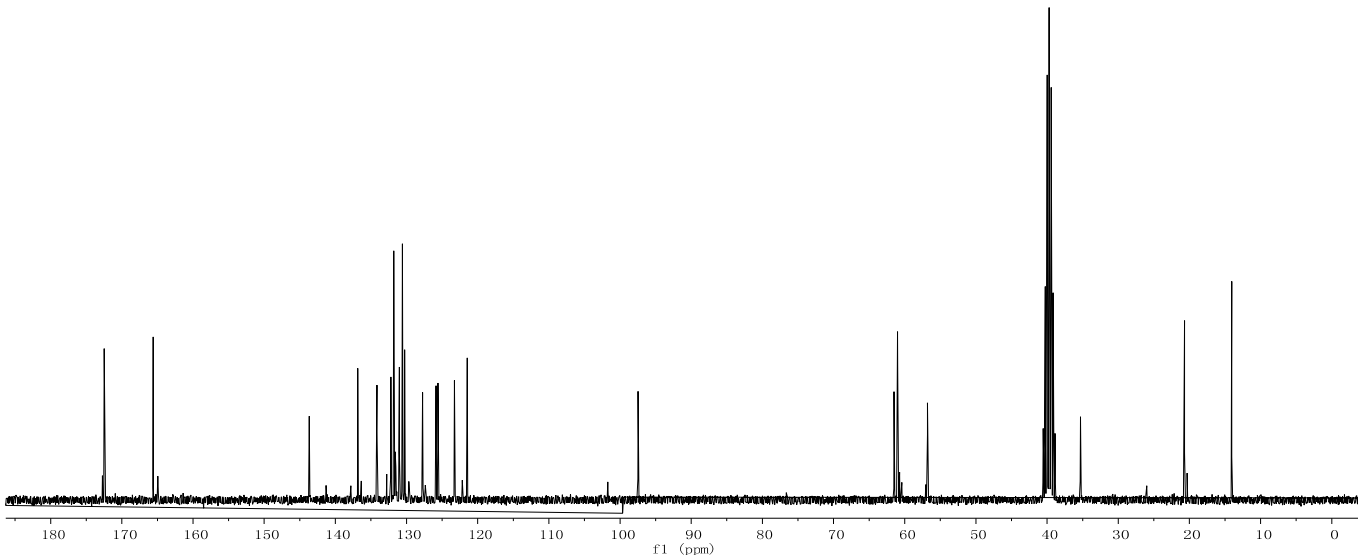

3.12
5.16
2.23
0.83
0.86
0.87
2.08
1.00
0.89
2.57
2.89
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

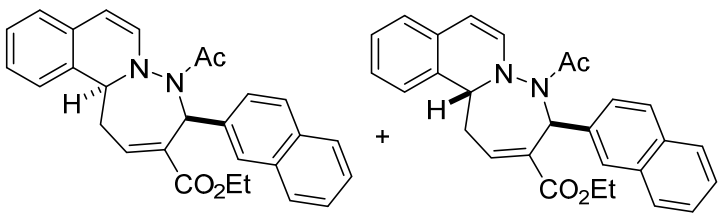

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ac
N
N
H
Br
CO2Et
+
Ac
N
N
H
Br
CO2Et

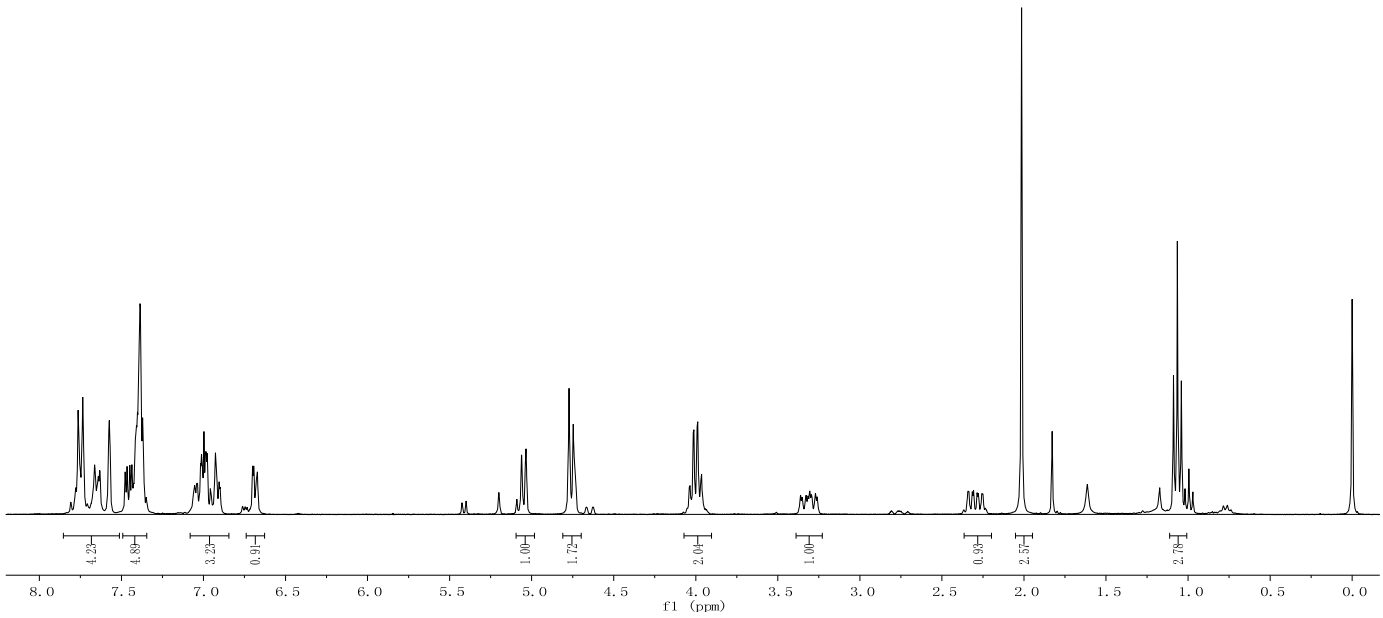
5j **6j**

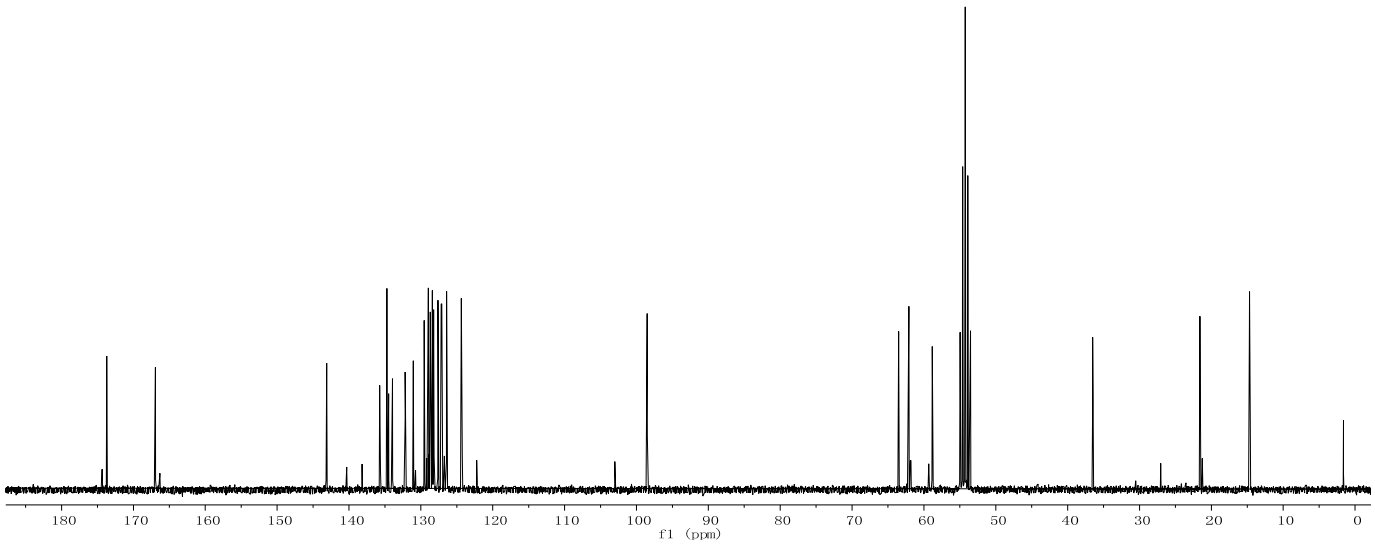

2.38
6.37
1.32
1.01
1.91
2.30
1.00
1.07
2.81
3.38
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

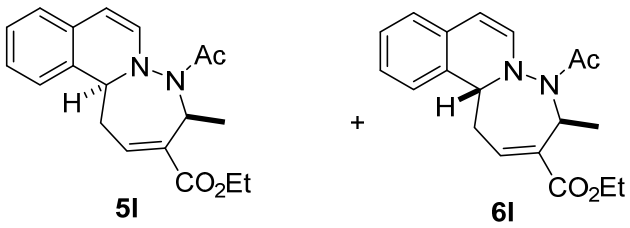

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
CO2Et
+
Ac
N
N
H
CO2Et

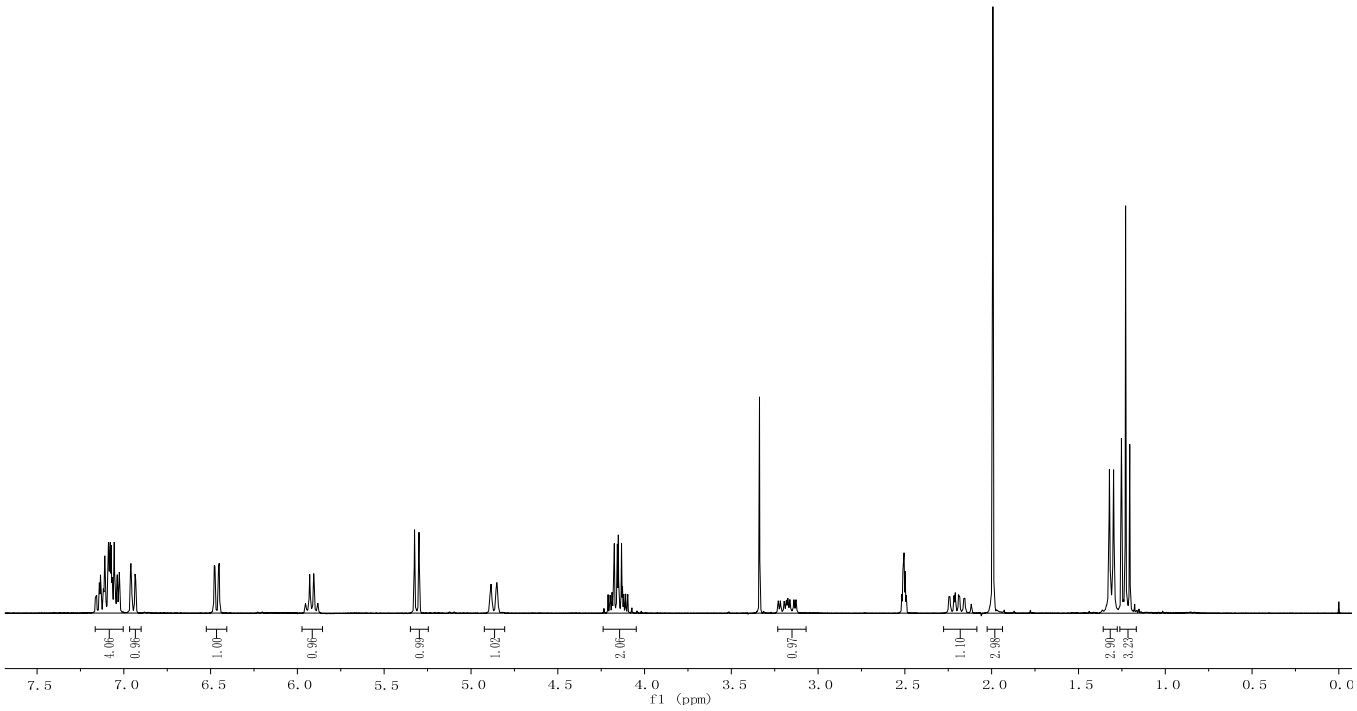
5k **6k**

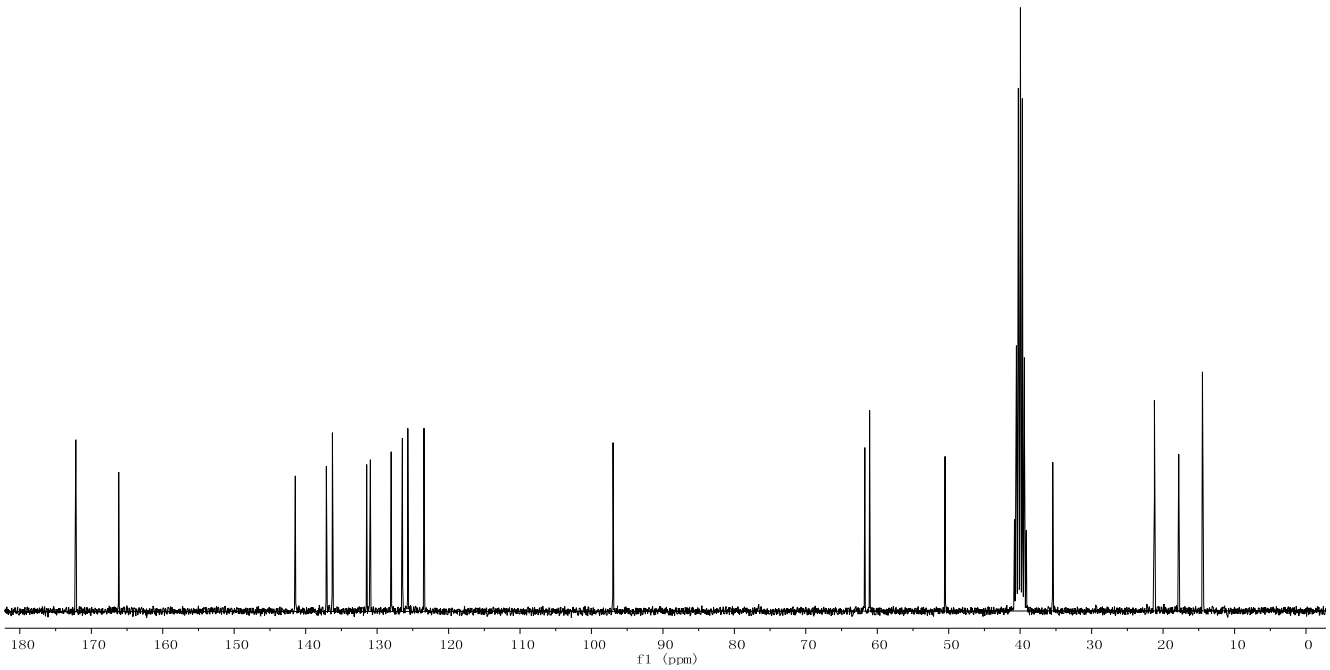

4.23
4.89
3.29
0.91
1.00
1.72
2.04
1.00
0.93
2.57
2.78
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

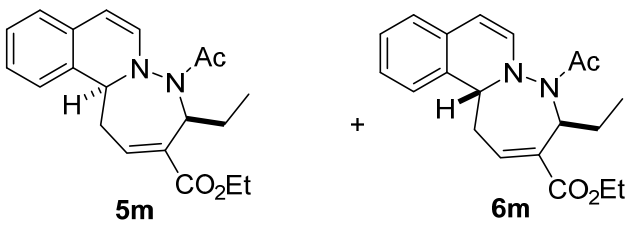

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

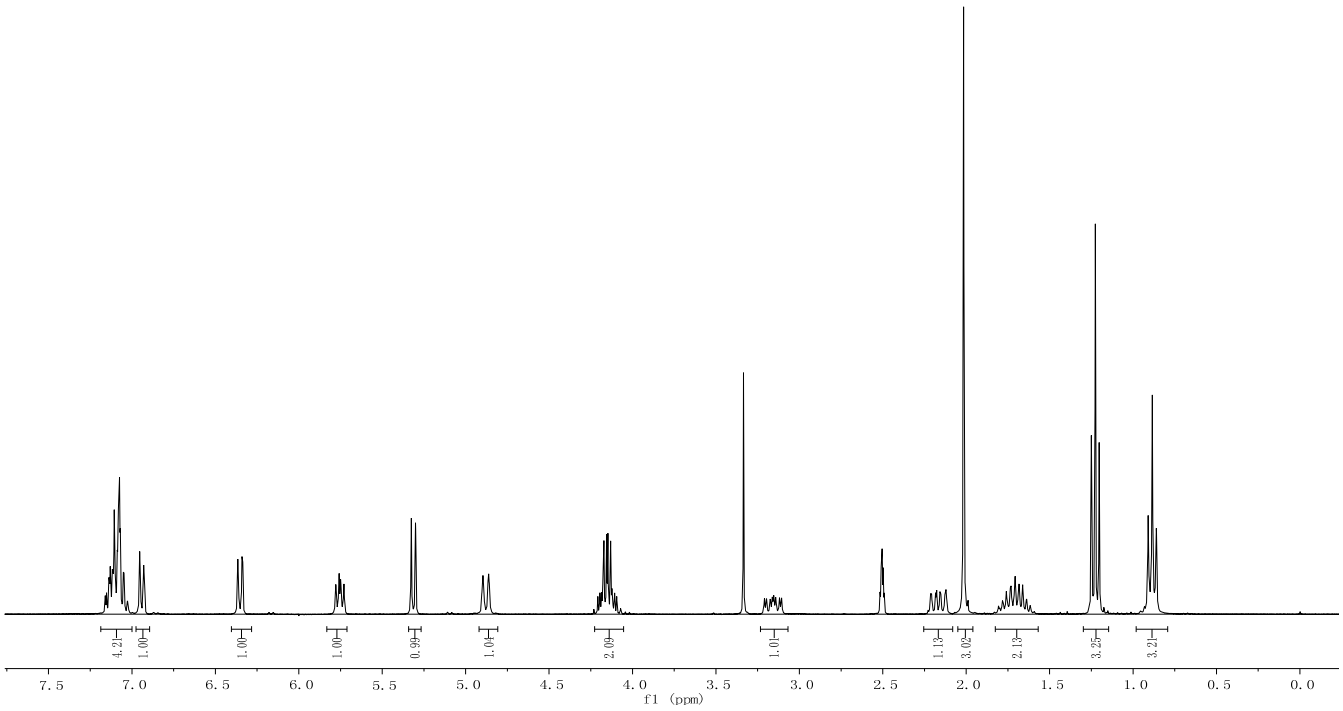

Ac
N
N
H
CO2Et
+
Ac
N
N
H
CO2Et

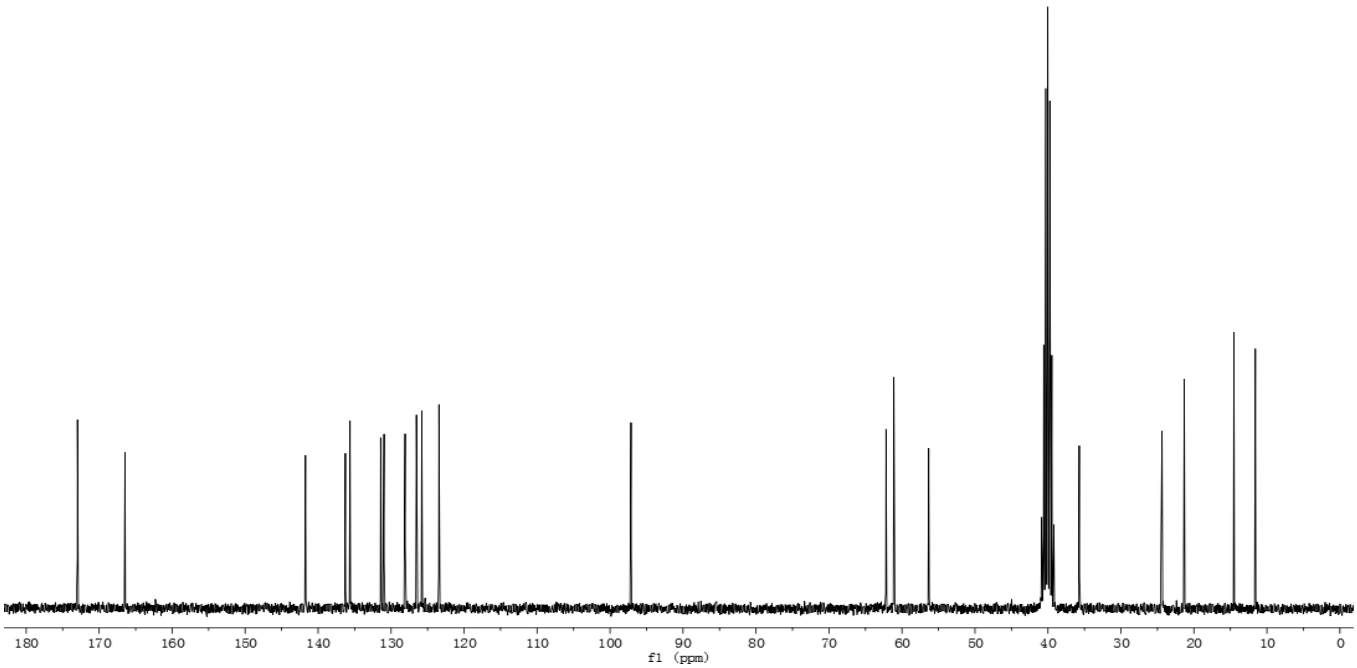
5l **6l**

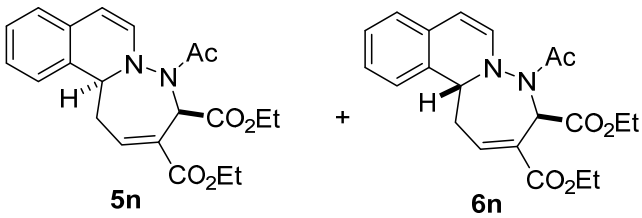

4.06
0.96
1.00
0.96
0.99
1.02
2.06
0.97
1.10
2.98
2.90
3.23
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

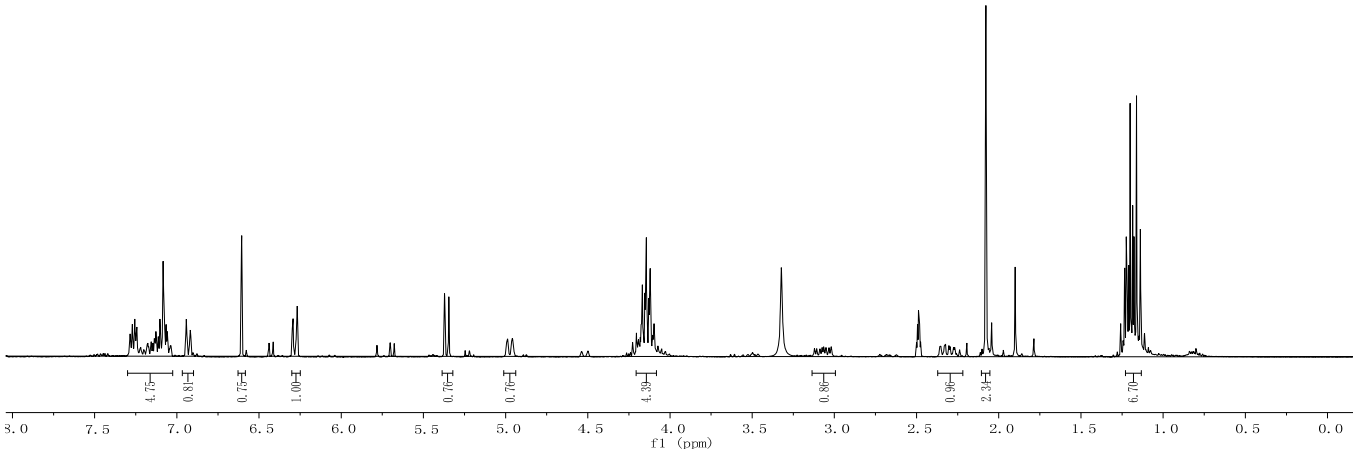

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

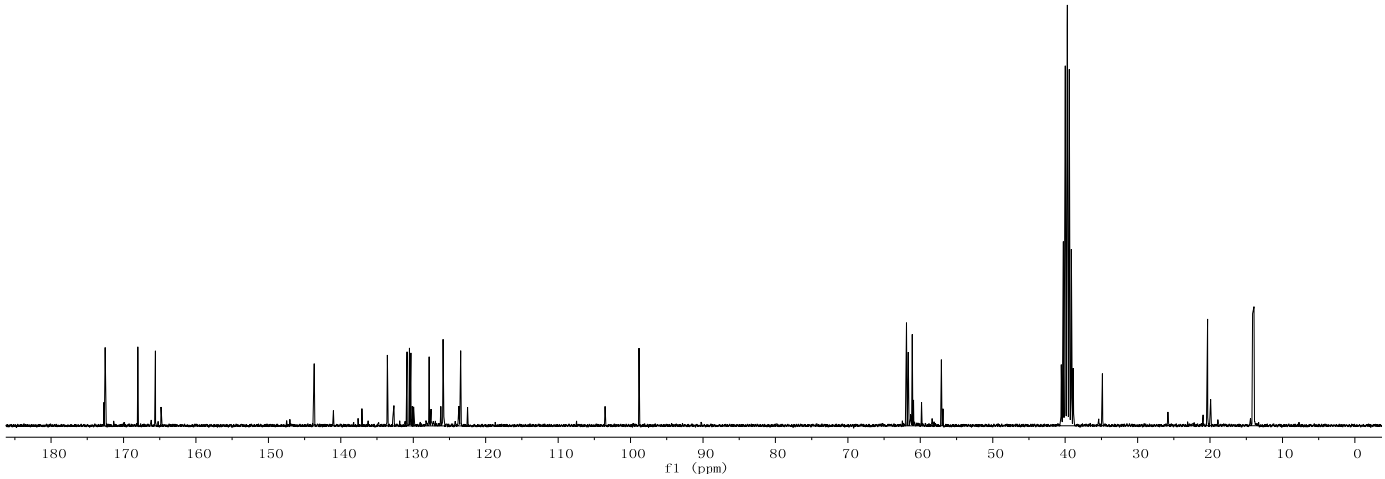

Ac
N
N
H
CO2Et
5m
+
Ac
N
N
H
CO2Et
6m

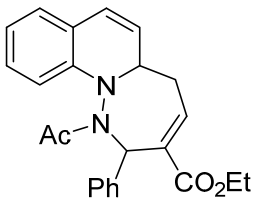

4.21
1.00
1.00
1.00
1.00
0.99
1.01
2.09
1.01
1.13
3.02
2.13
3.25
3.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

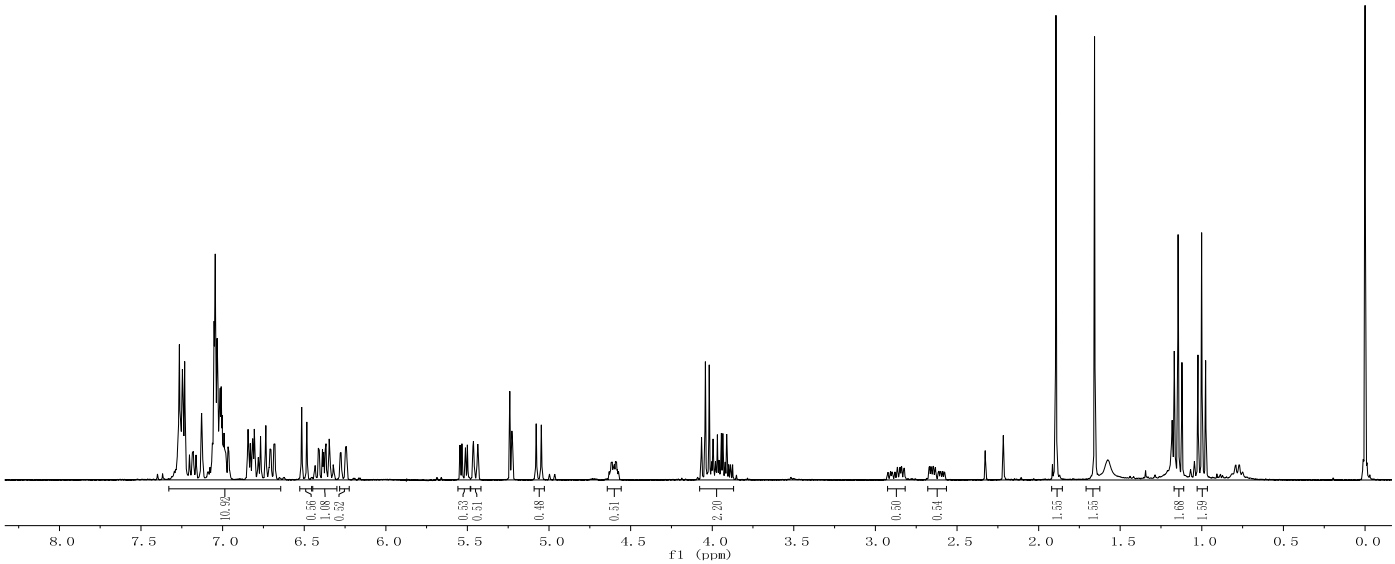

Ac
N
N
H
CO2Et
CO2Et
5n
+
Ac
N
N
H
CO2Et
CO2Et
6n

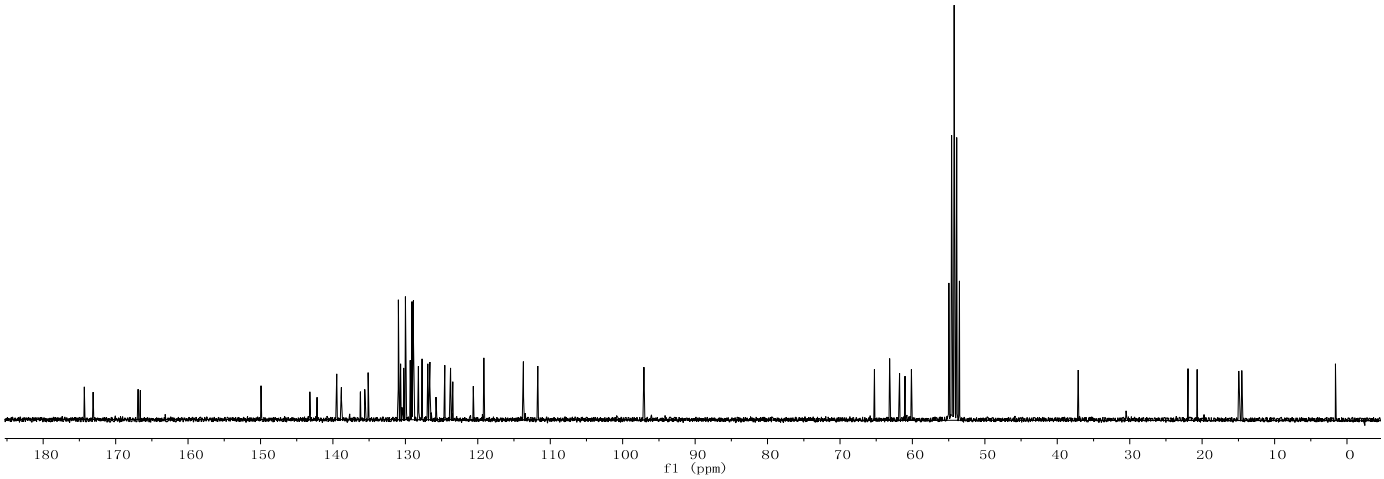

4.75
0.81
0.76
1.00
0.70
0.70
4.39
0.88
0.96
2.34
6.70
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

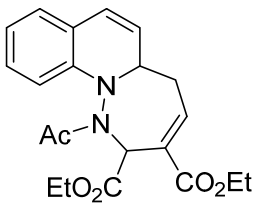

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
N
Ac
Ph
CO2Et

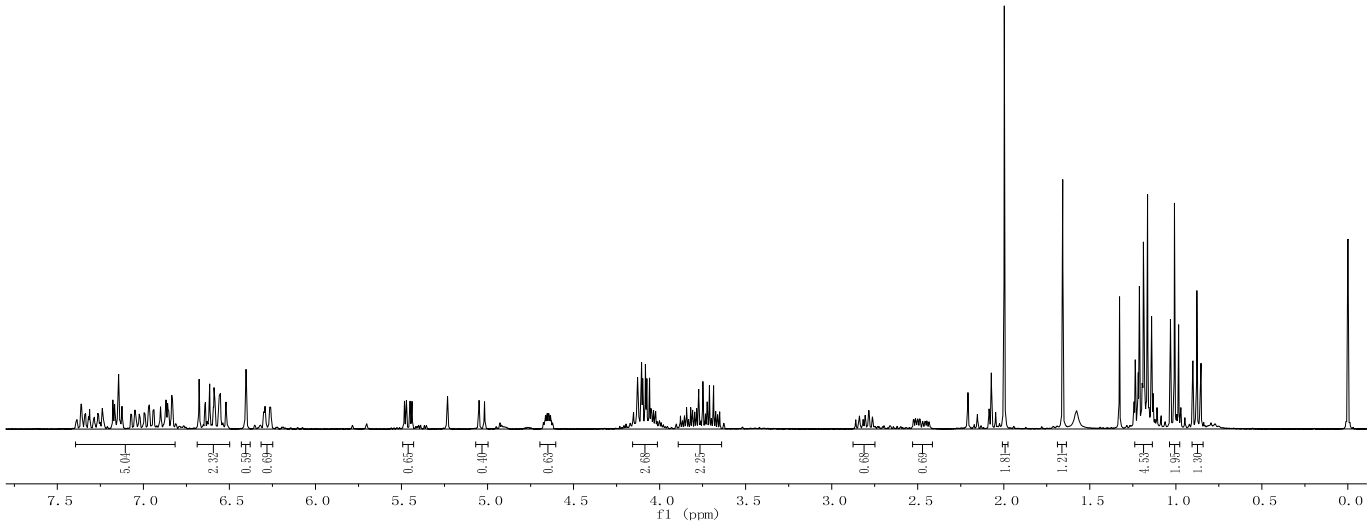
7a

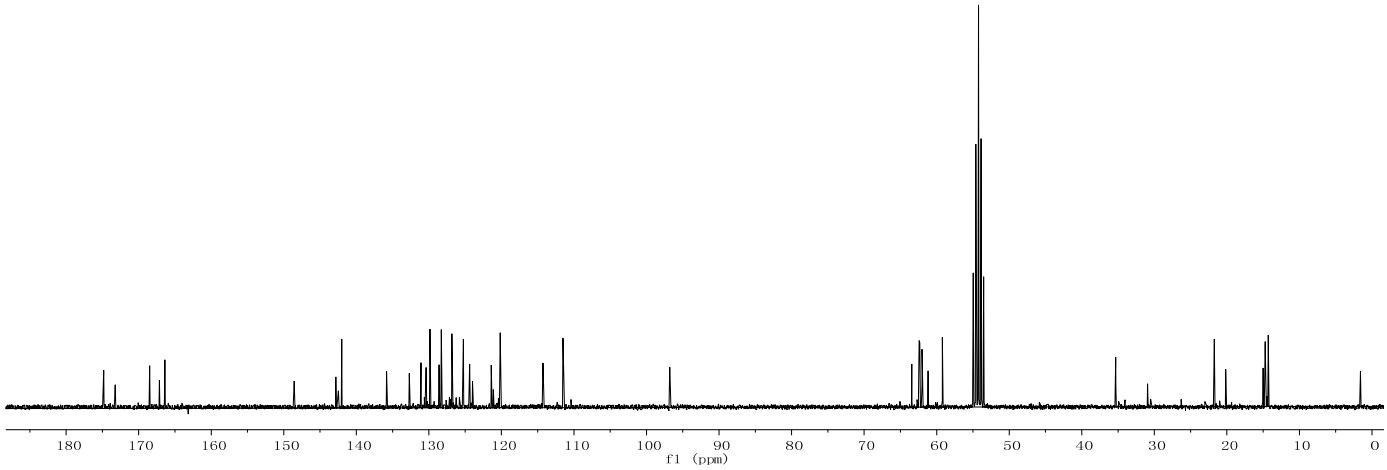

10.92
0.56
1.08
0.52
0.53
0.51
0.48
0.51
2.20
0.50
0.54
1.55
1.55
1.68
1.59
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

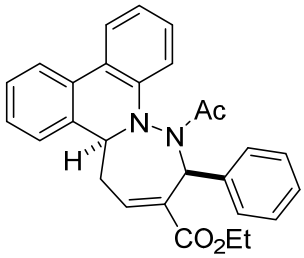

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
N
Ac
EtO2C
CO2Et

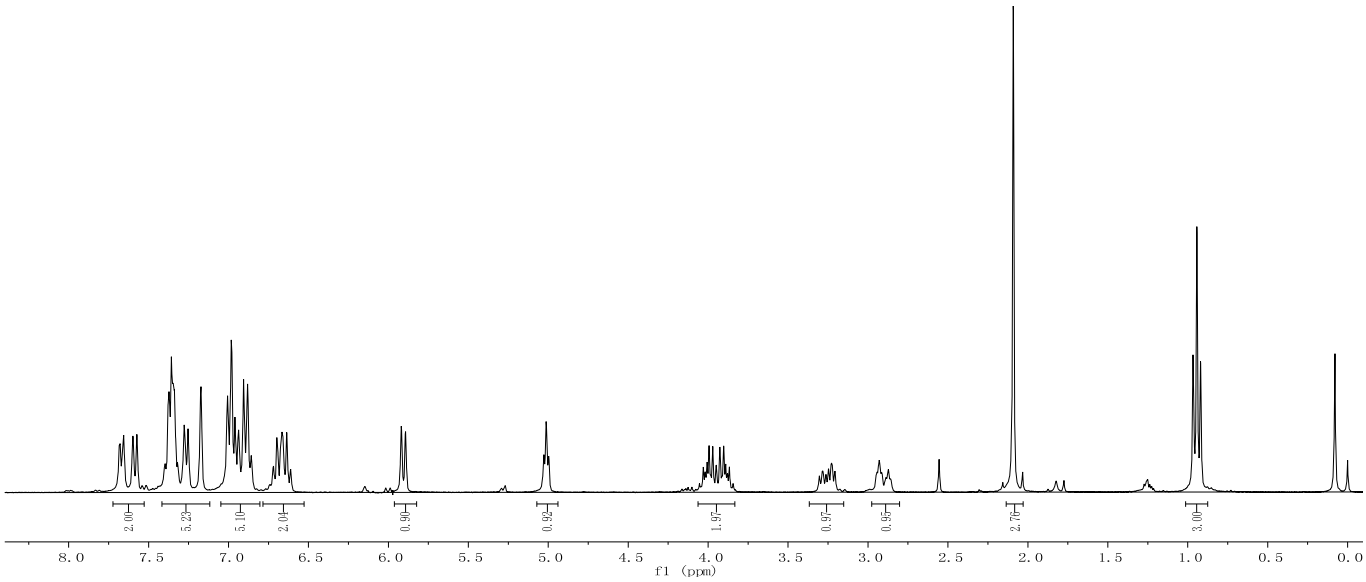
7n

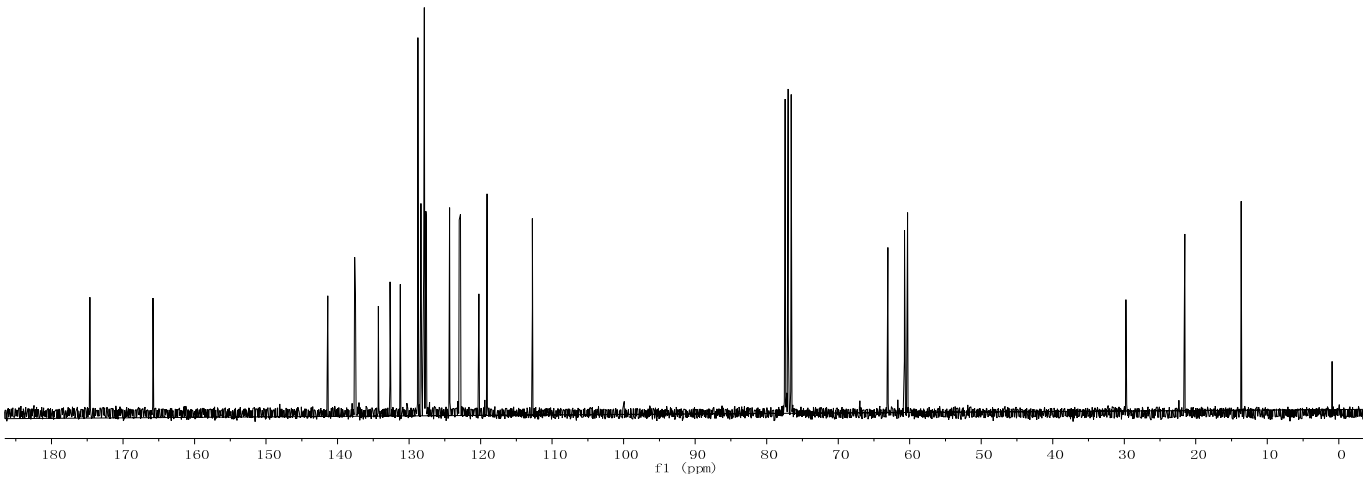

5.04
2.32
0.59
0.69
0.65
0.40
0.63
2.68
2.25
0.68
0.69
1.81
1.27
4.53
1.95
1.30
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

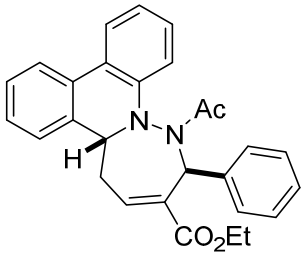

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ac
N
N
H
CO2Et

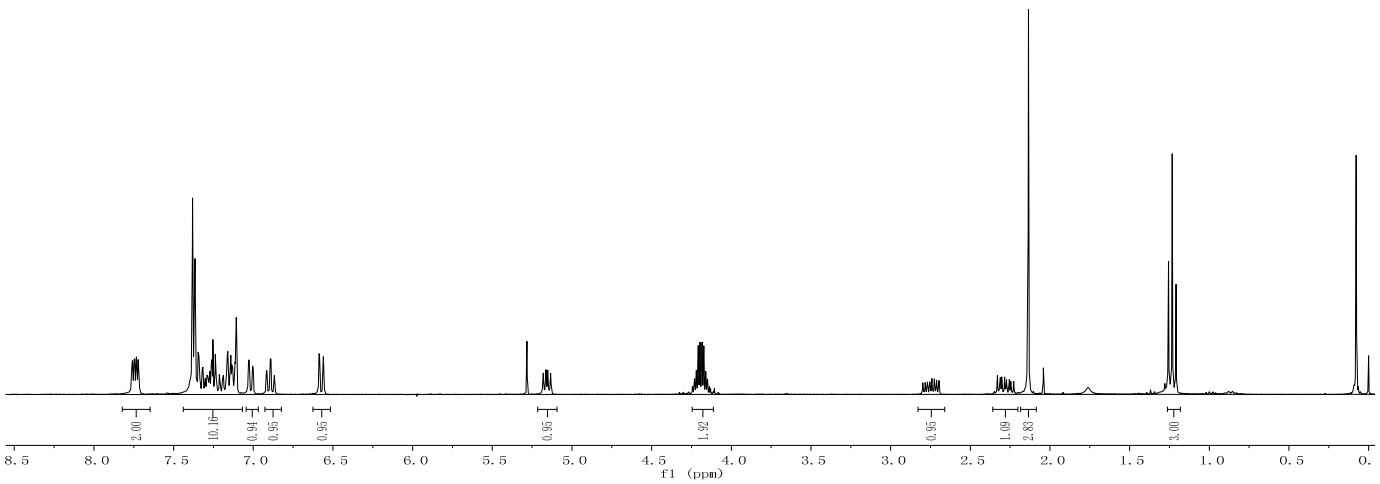
8a

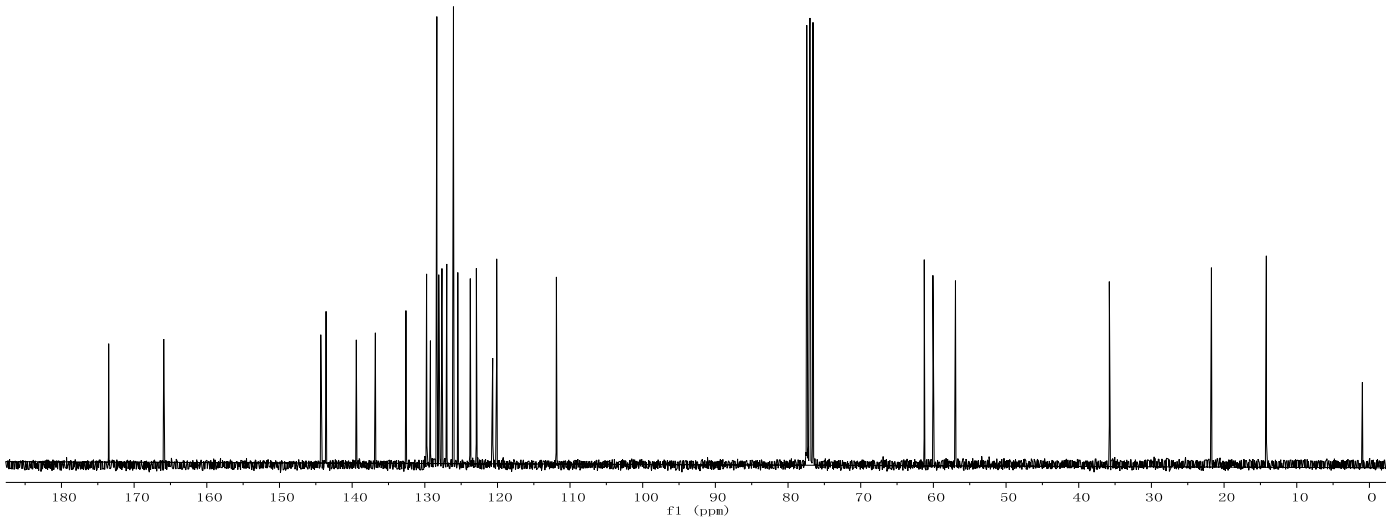

2.00
5.23
5.10
2.04
0.90
0.92
1.97
0.97
0.95
2.76
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

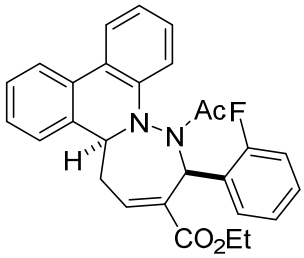

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
CO2Et

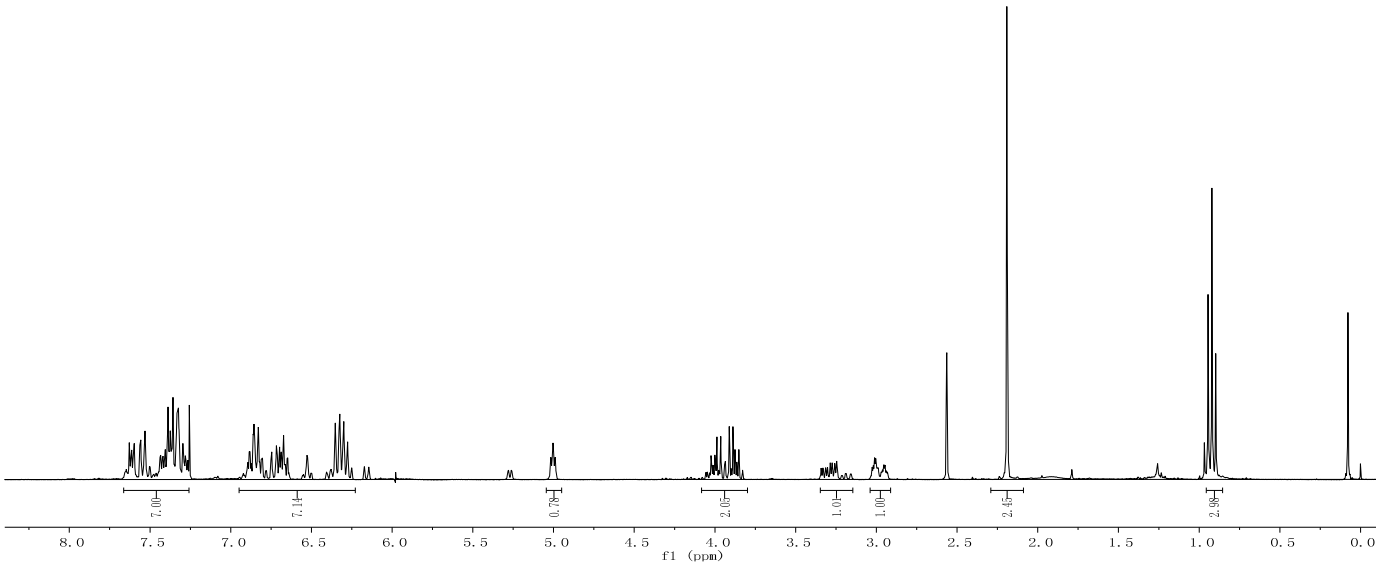
9a

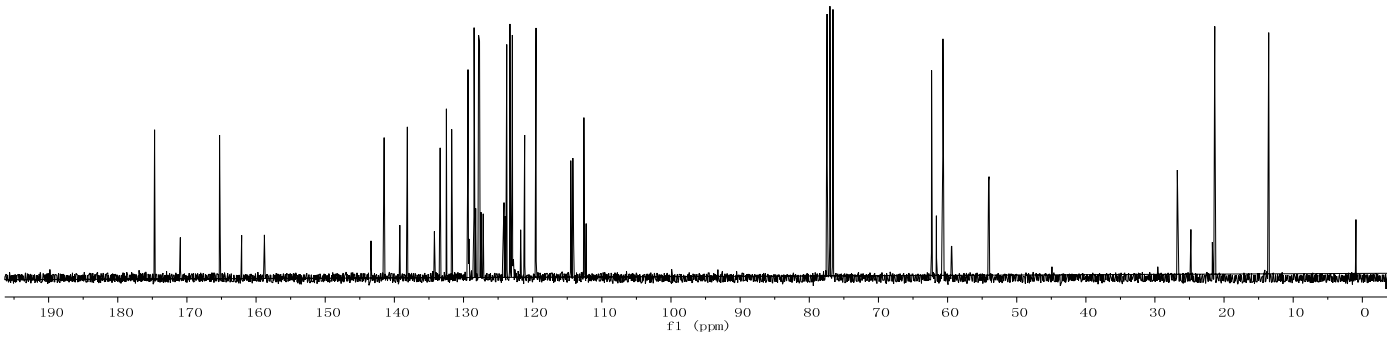

2.00
10.16
0.94
0.95
0.95
0.95
1.92
0.95
1.09
2.83
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

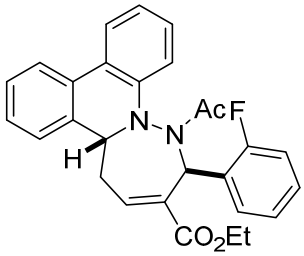

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
N
Ac
F
H
CO2Et

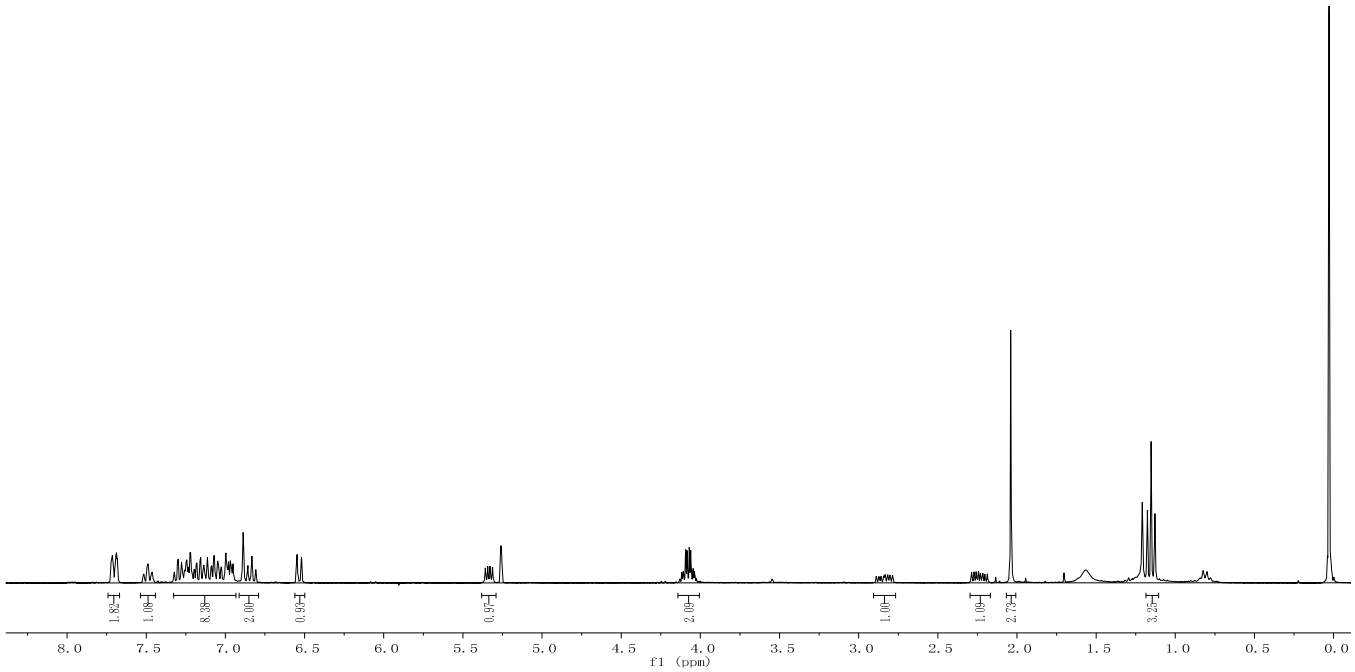
8e

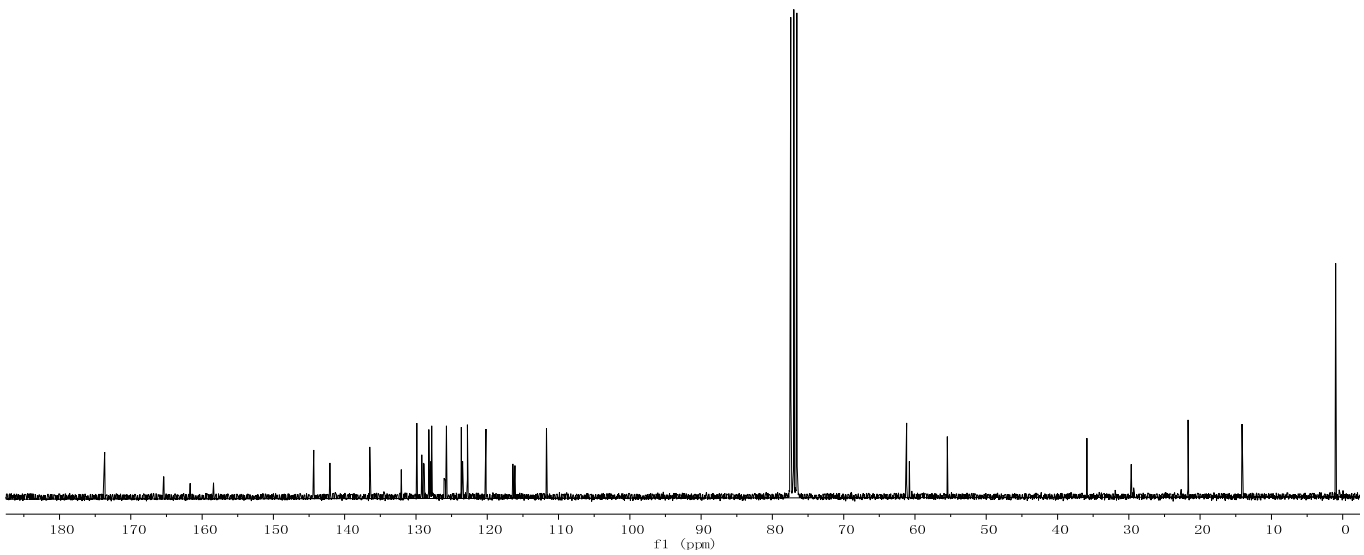

7.00
7.14
0.98
2.07
1.01
1.00
2.45
2.89
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

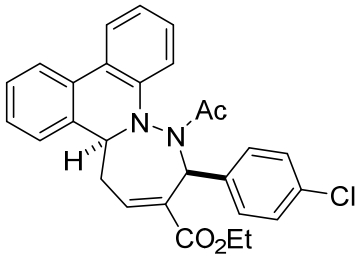

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
N
Ac
F
H
CO2Et

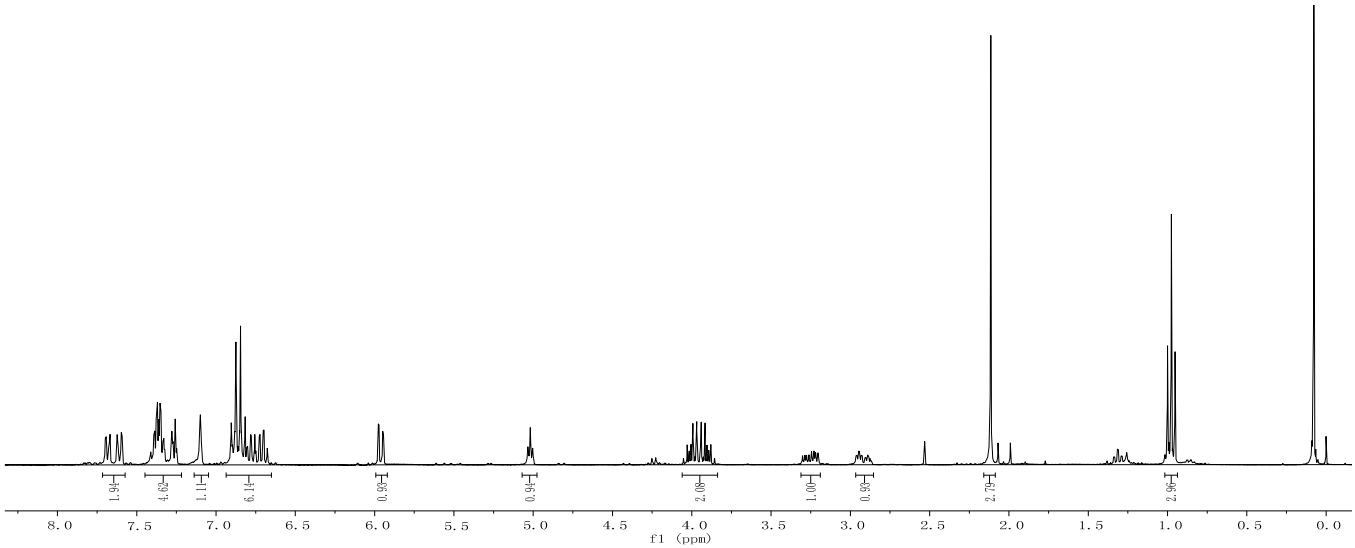
9e

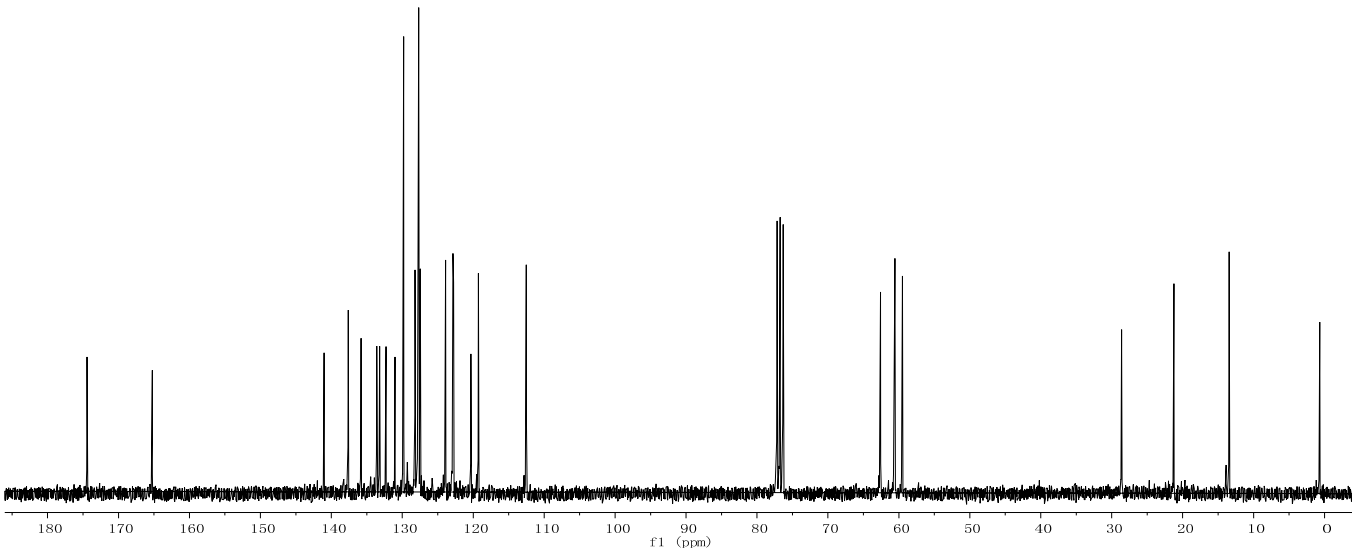

1.82
1.08
8.38
2.00
0.99
0.97
2.09
1.00
1.09
2.79
3.25
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

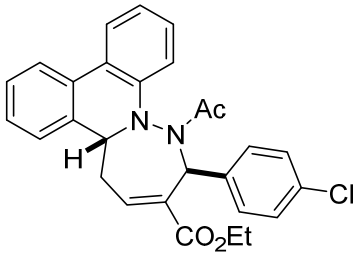

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
Cl
CO2Et

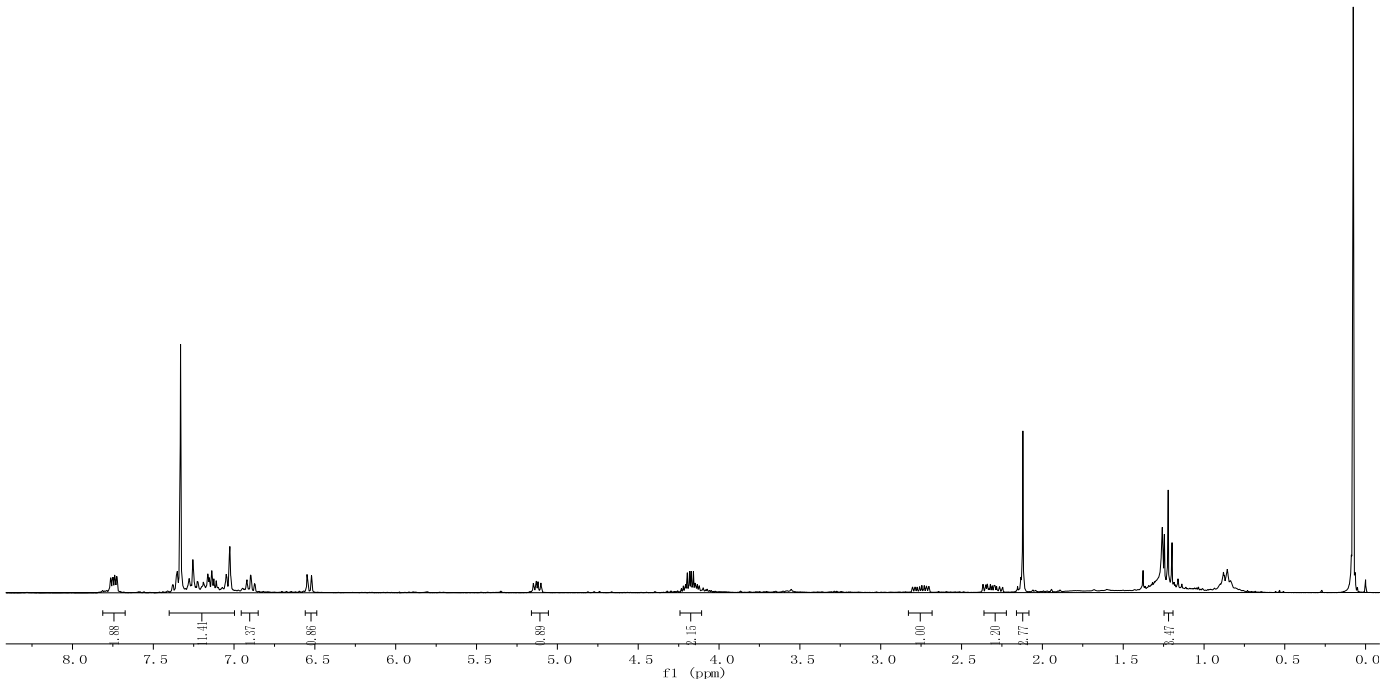
8h

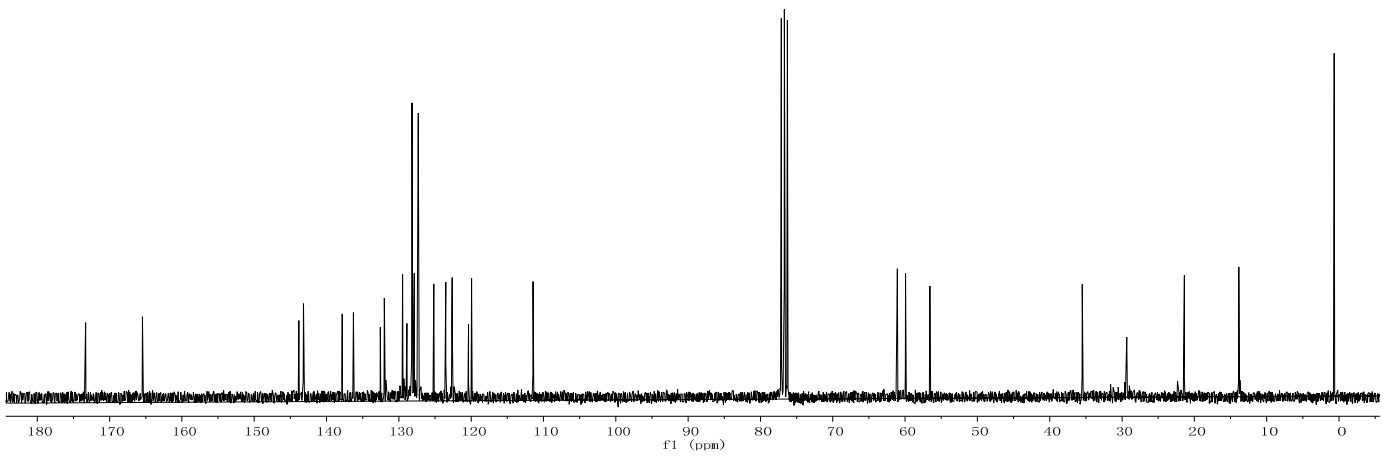

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

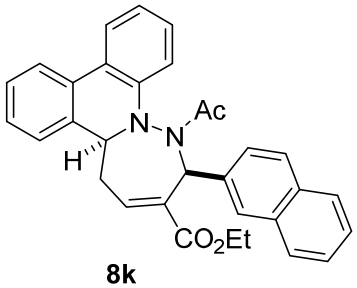

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ac
N
N
H
Cl
CO2Et

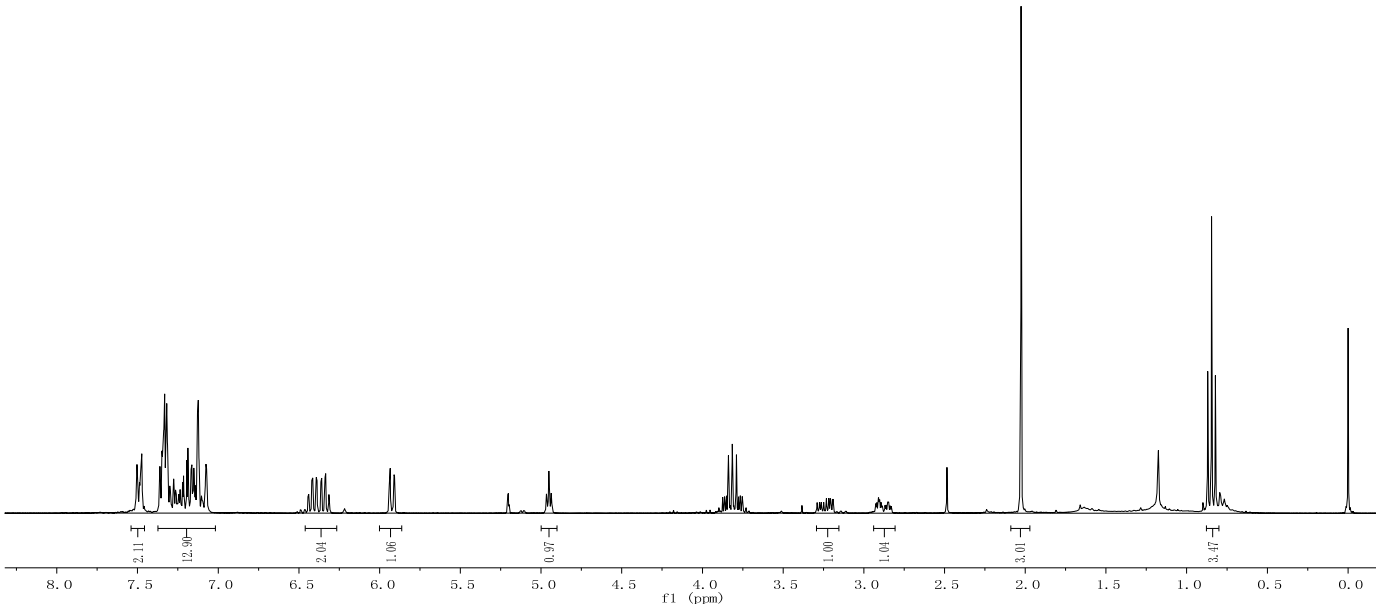
9h

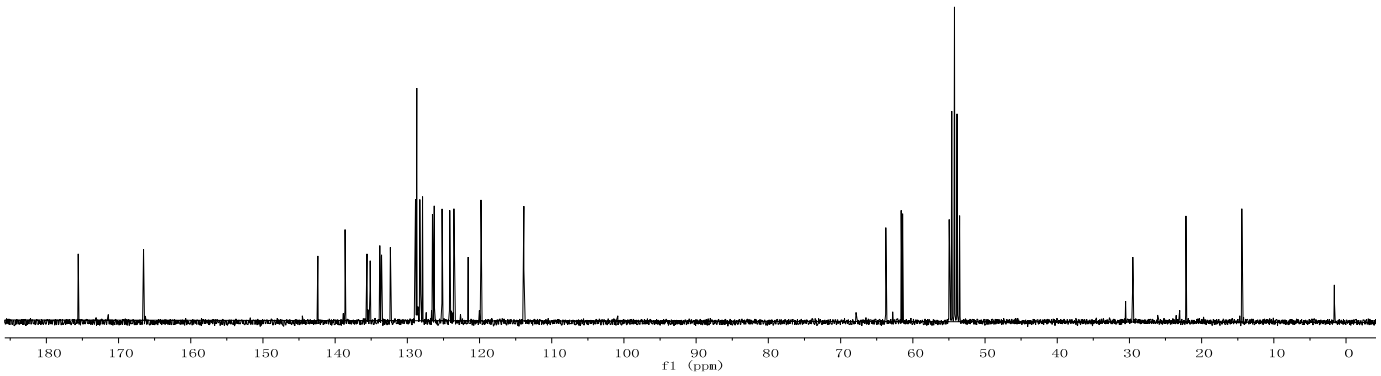

1.88
1.41
1.37
0.86
0.89
2.15
4.00
1.20
2.77
3.47
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

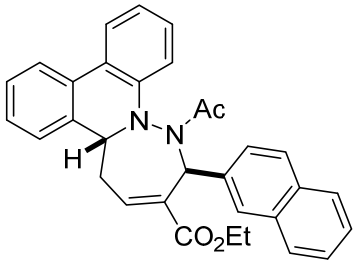

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
CO2Et

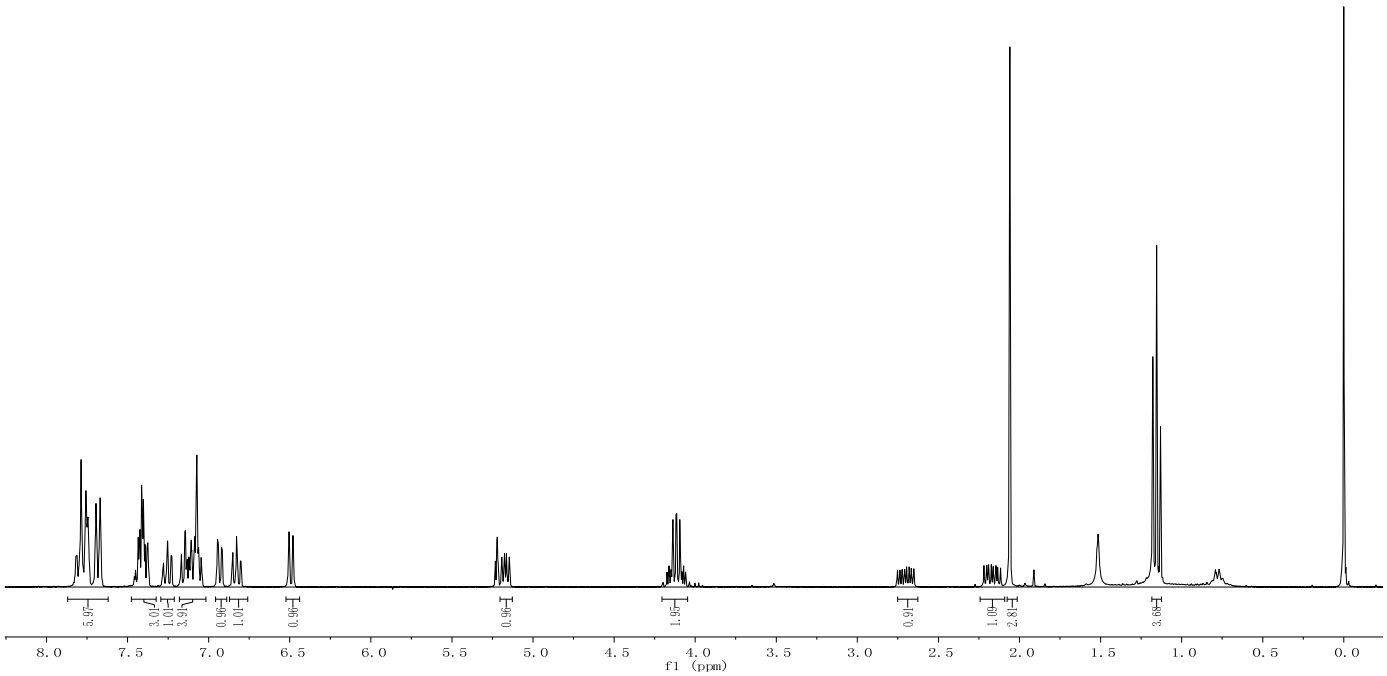
8k

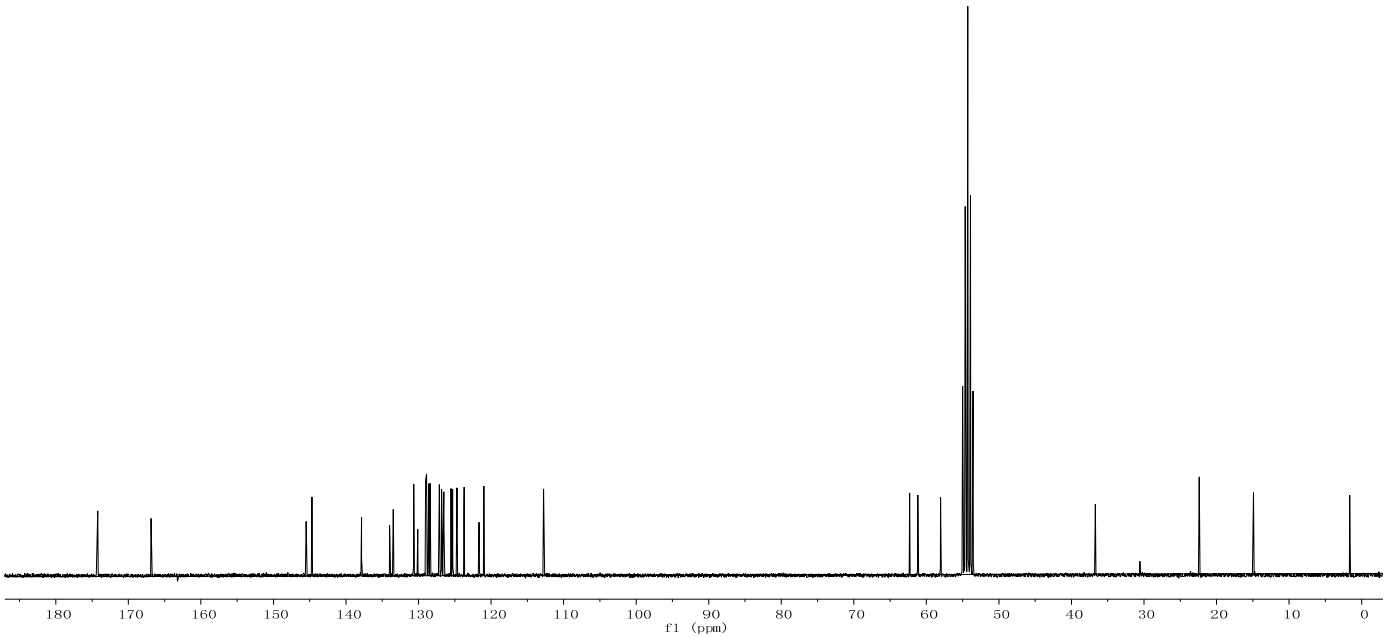

2.11
12.90
2.04
1.06
0.97
1.00
1.04
3.01
3.47
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

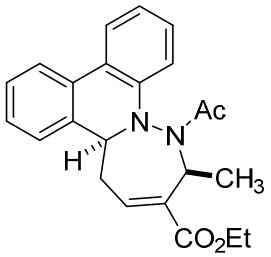

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
CO2Et

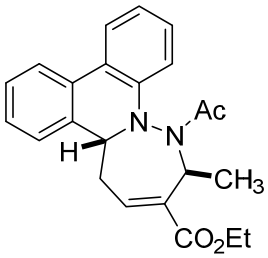
9k


5.97
3.01
1.01
3.94
0.96
1.01
0.96
0.96
1.95
0.91
1.09
2.81
3.68
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

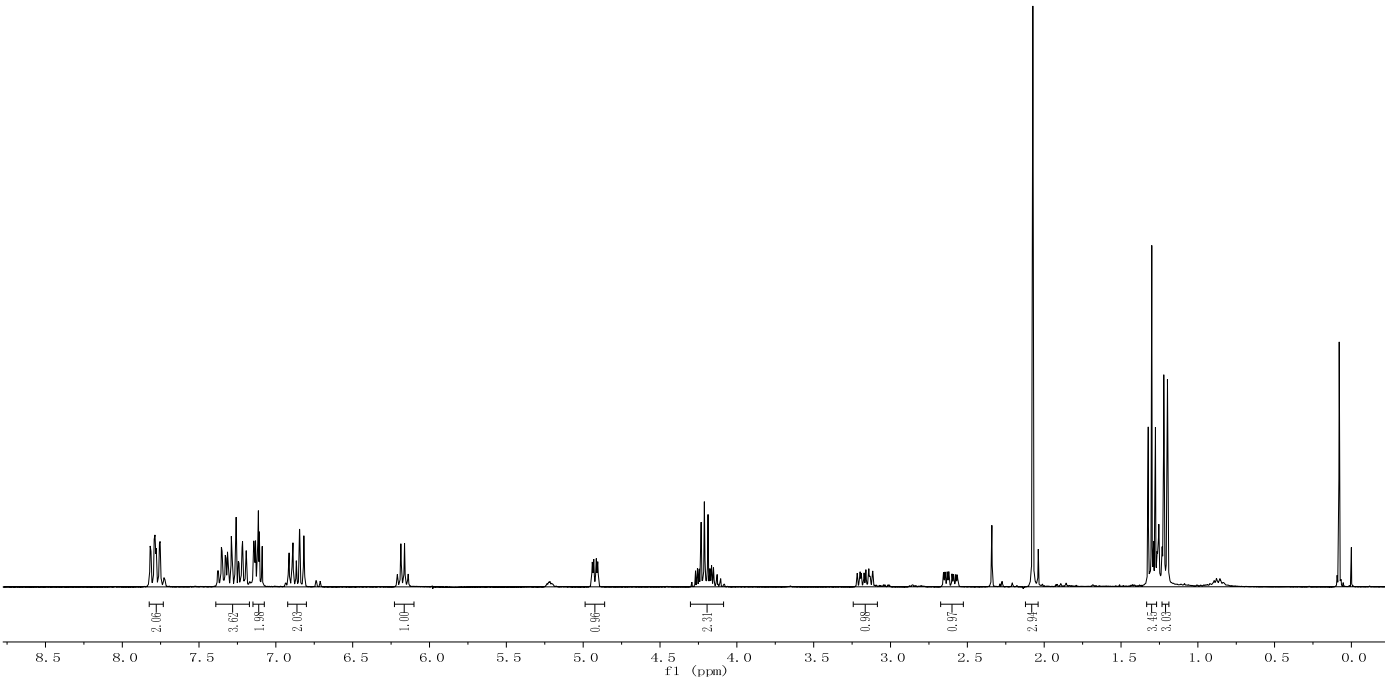

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

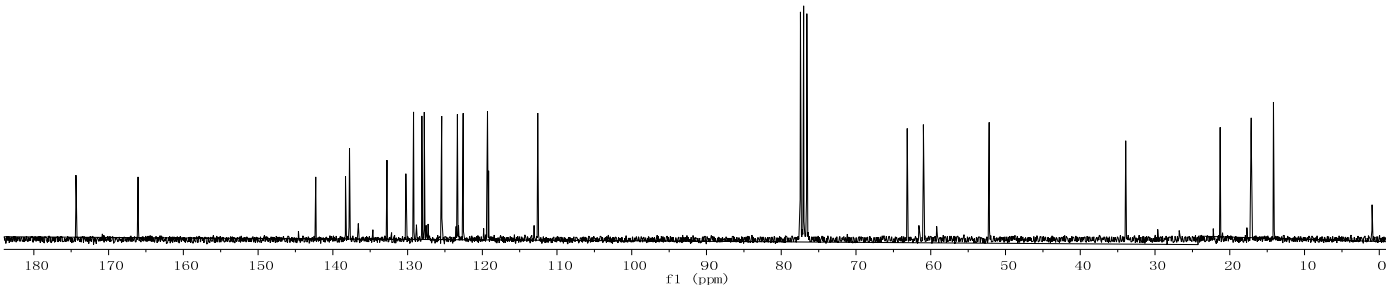

Ac
N
N
H
CH3
CO2Et

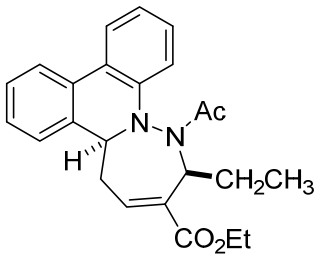
8l


Ac
N
N
H
CH3
CO2Et

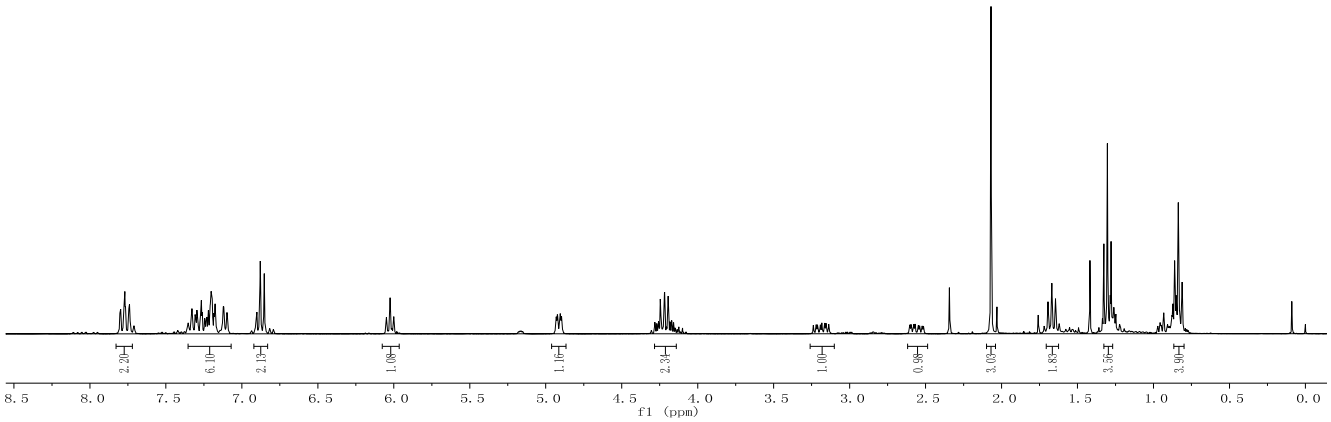
9l

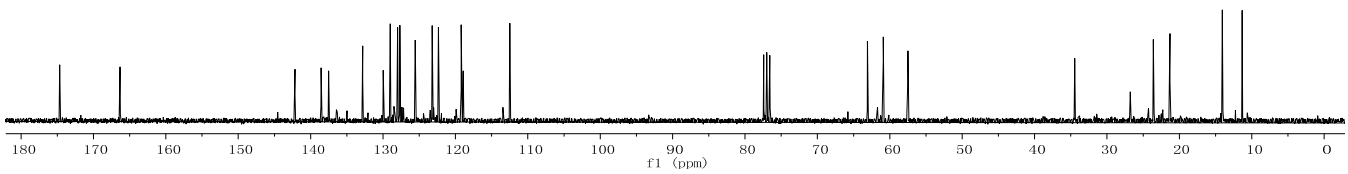

2.06
3.62
1.98
2.03
1.00
0.96
2.31
0.98
0.97
2.94
3.45
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

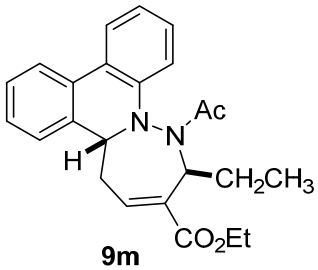

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
CH2CH3
CO2Et

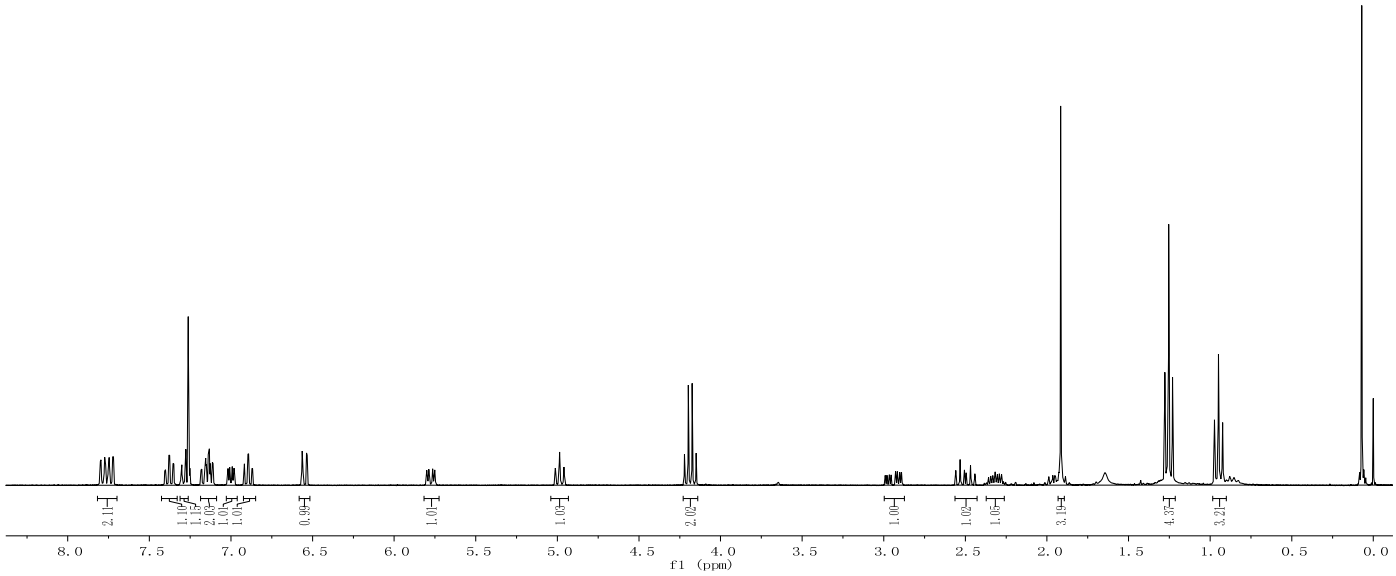
8m

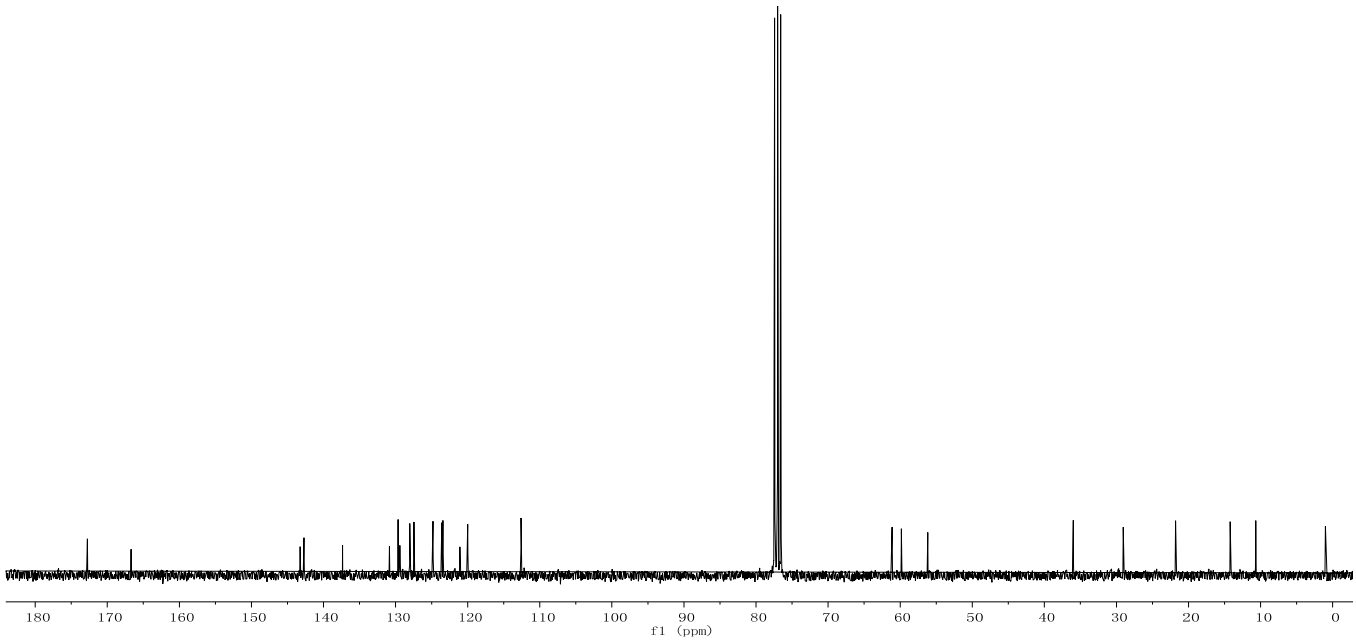

2.20
6.10
2.13
1.08
1.10
2.34
1.00
0.98
3.03
1.88
3.56
3.90
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

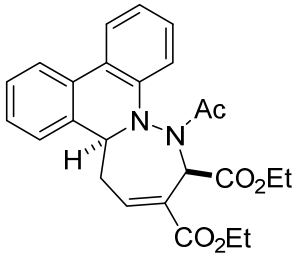

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



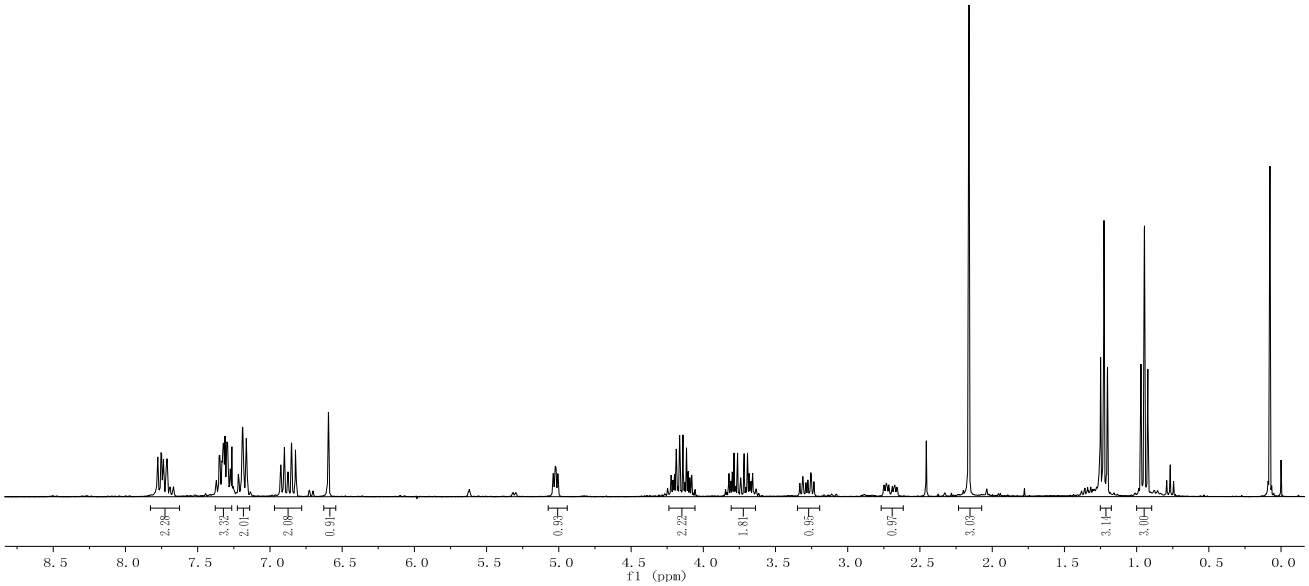
9m

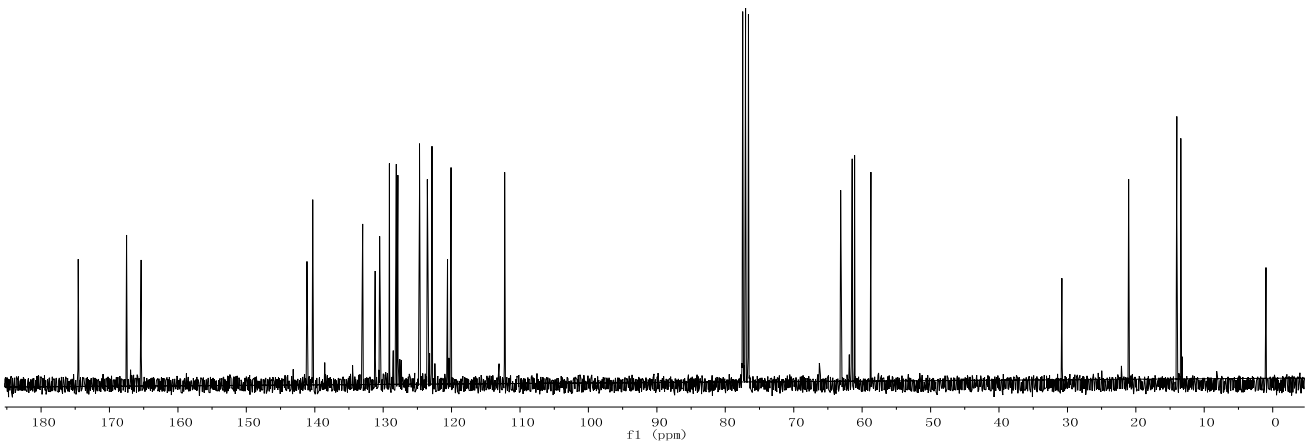


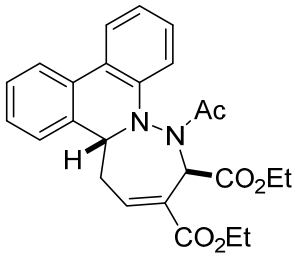



Ac
N
N
H
CO2Et
CO2Et

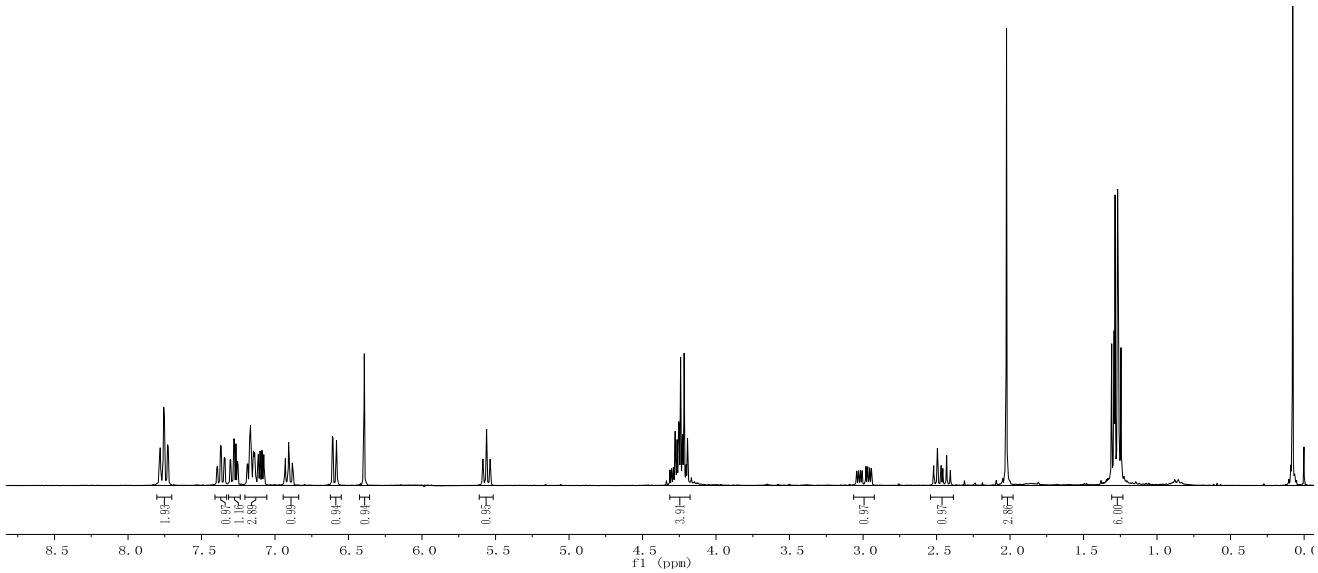
8n

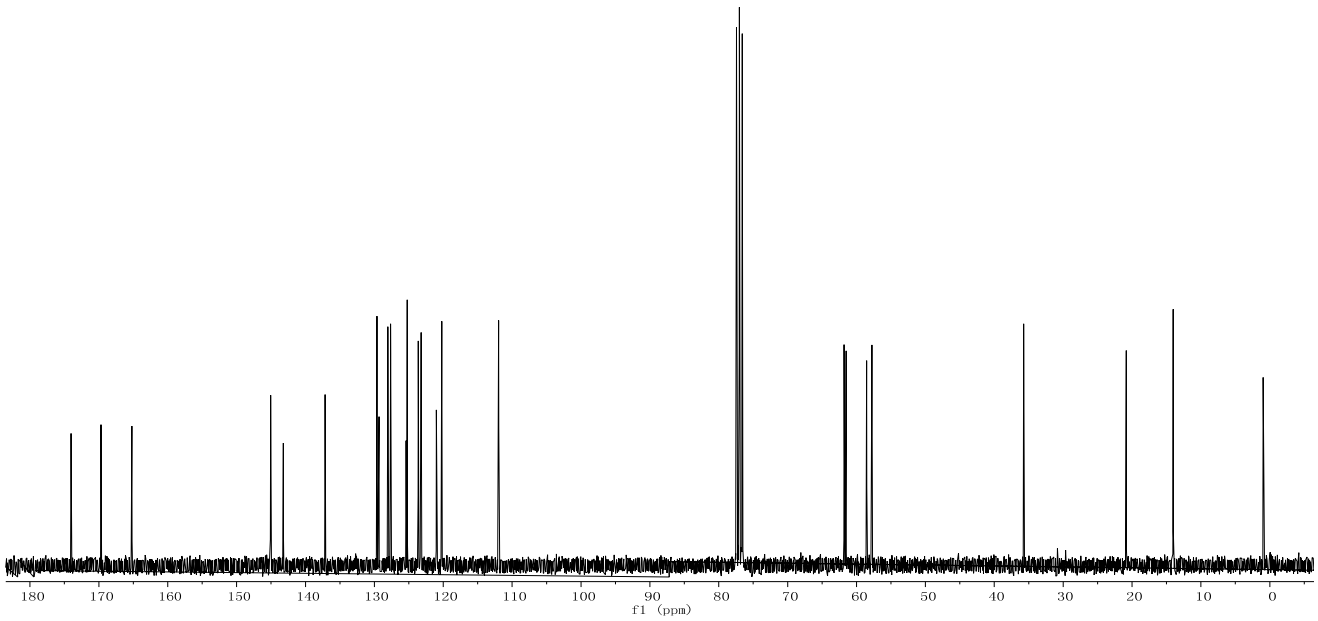

2.26
3.32
2.01
2.08
0.91
0.99
2.22
1.81
0.96
0.97
3.03
3.14
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

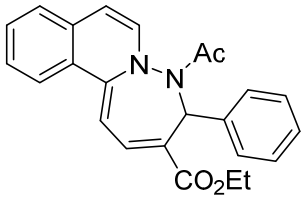

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
CO2Et
CO2Et

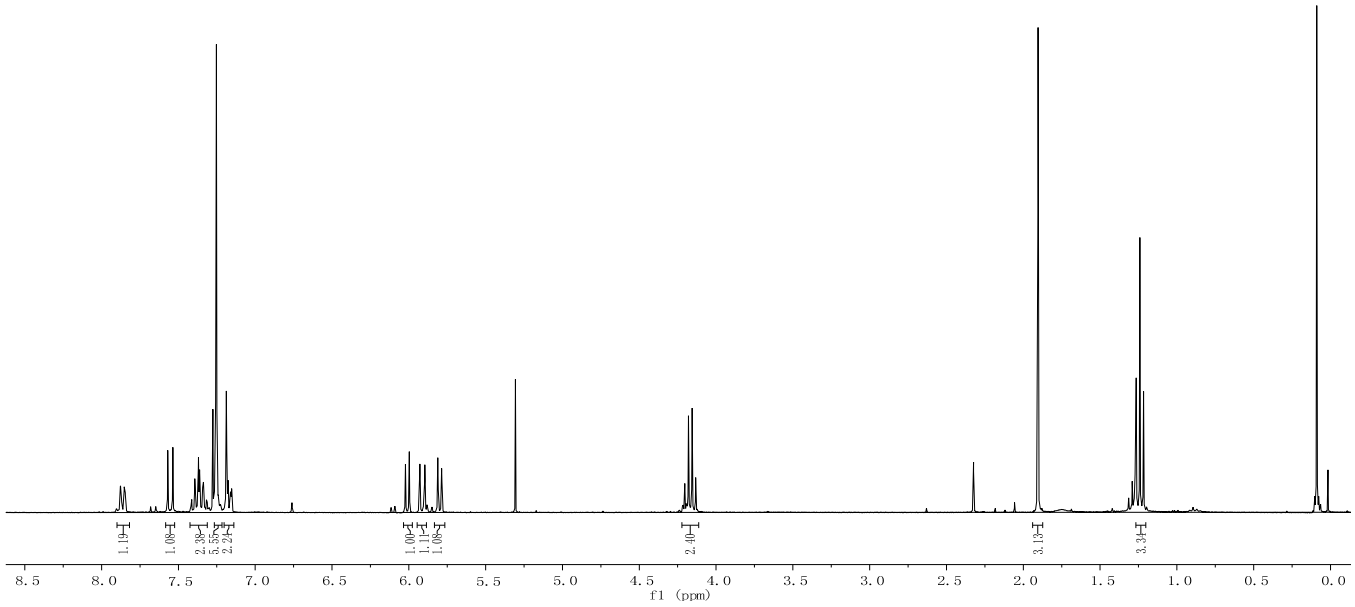
9n

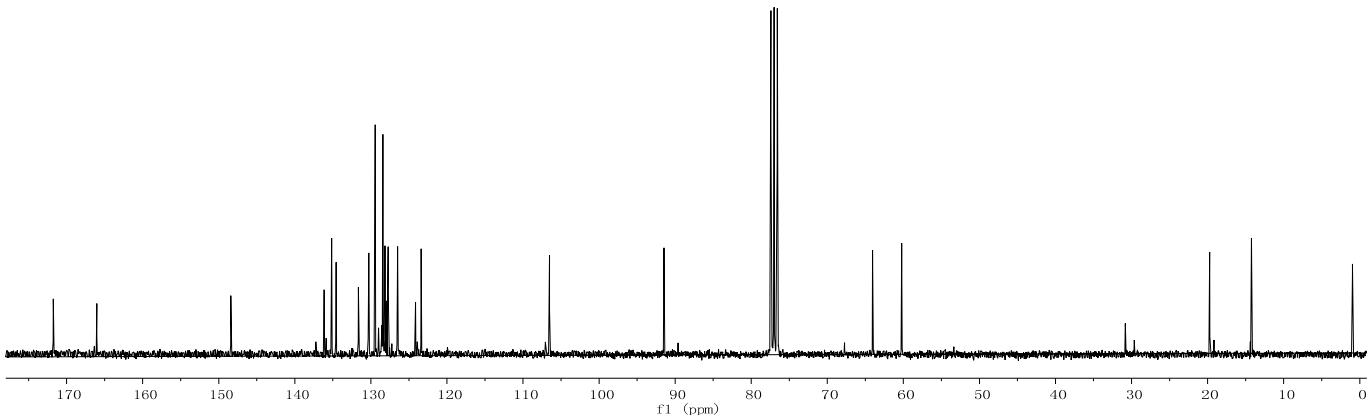

1.95
0.97
1.10
2.85
0.99
0.94
0.94
0.95
3.91
0.97
0.97
2.80
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

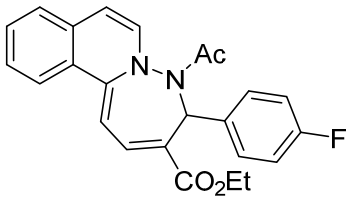

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ac
N
N
CO2Et

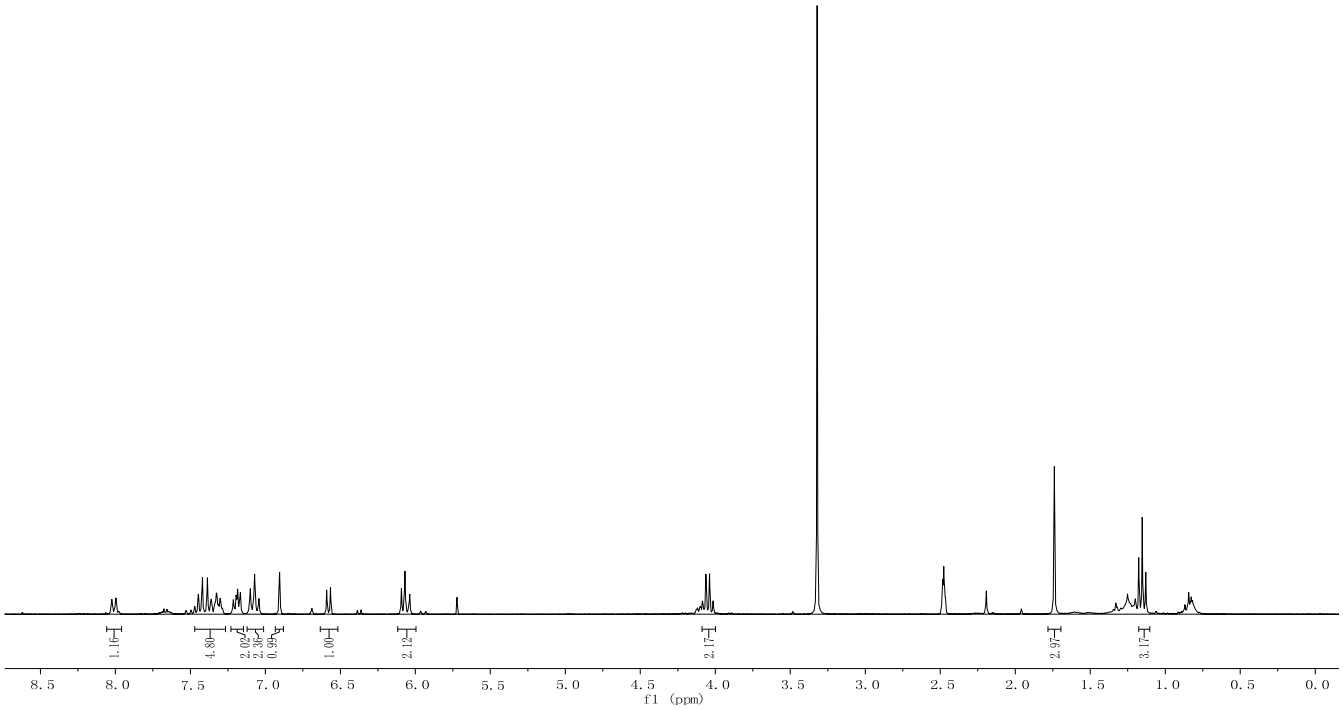
10

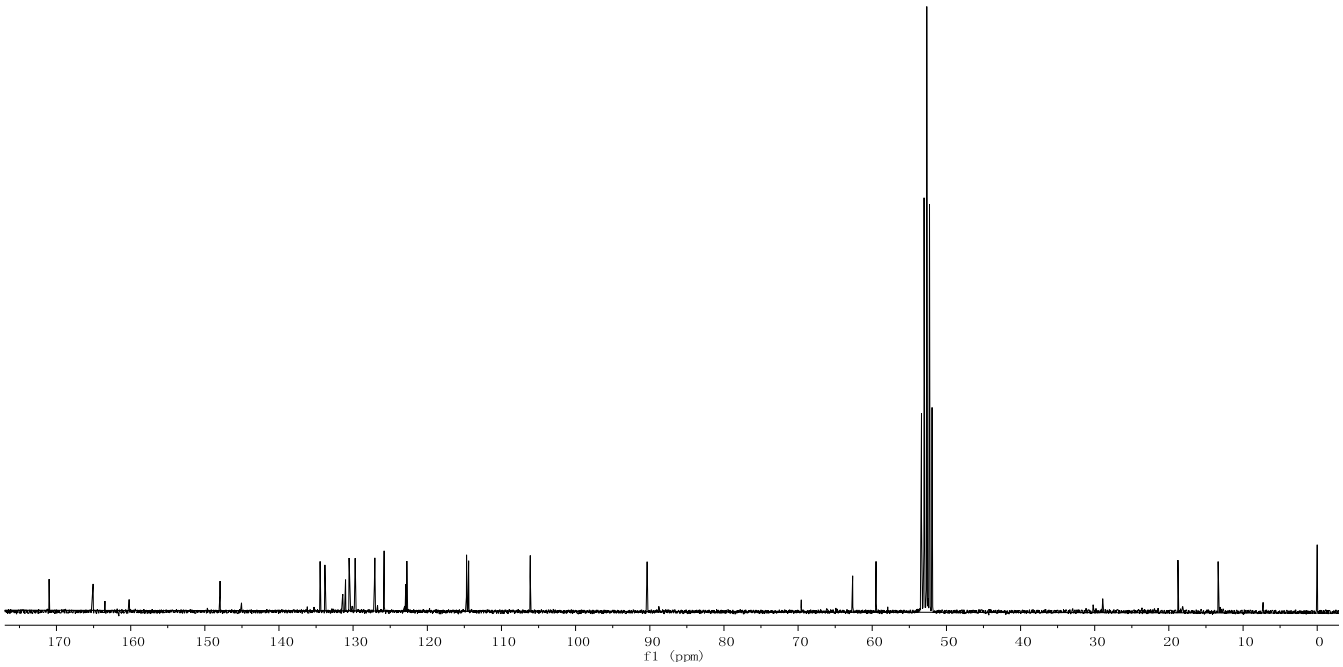

1.19
1.08
2.38
5.55
2.24
1.00
1.11
1.08
2.40
3.13
3.34
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

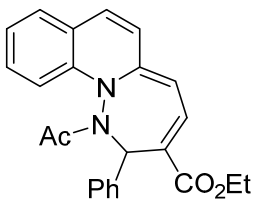

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
F
CO2Et

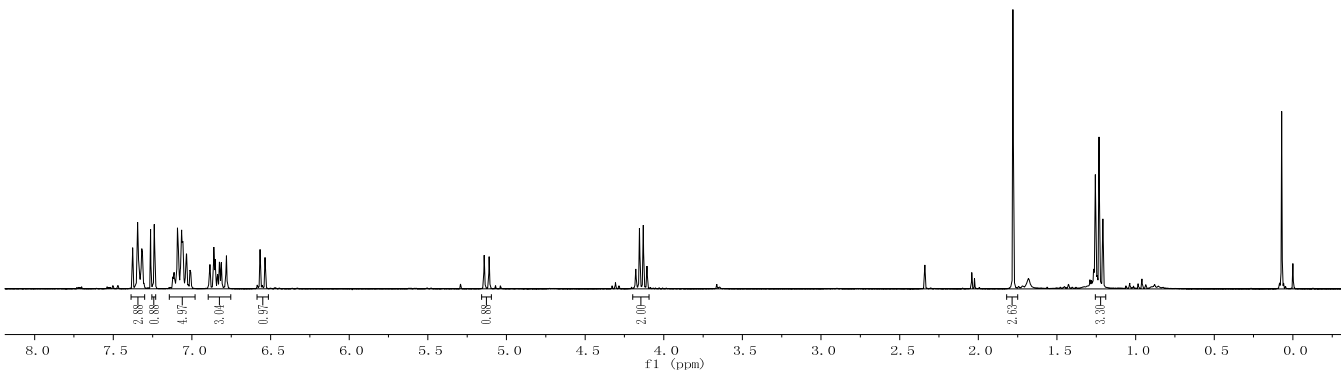
11


1.10
4.80
2.09
2.36
0.95
1.00
2.12
2.17
2.97
3.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
N
Ac
Ph
CO2Et

12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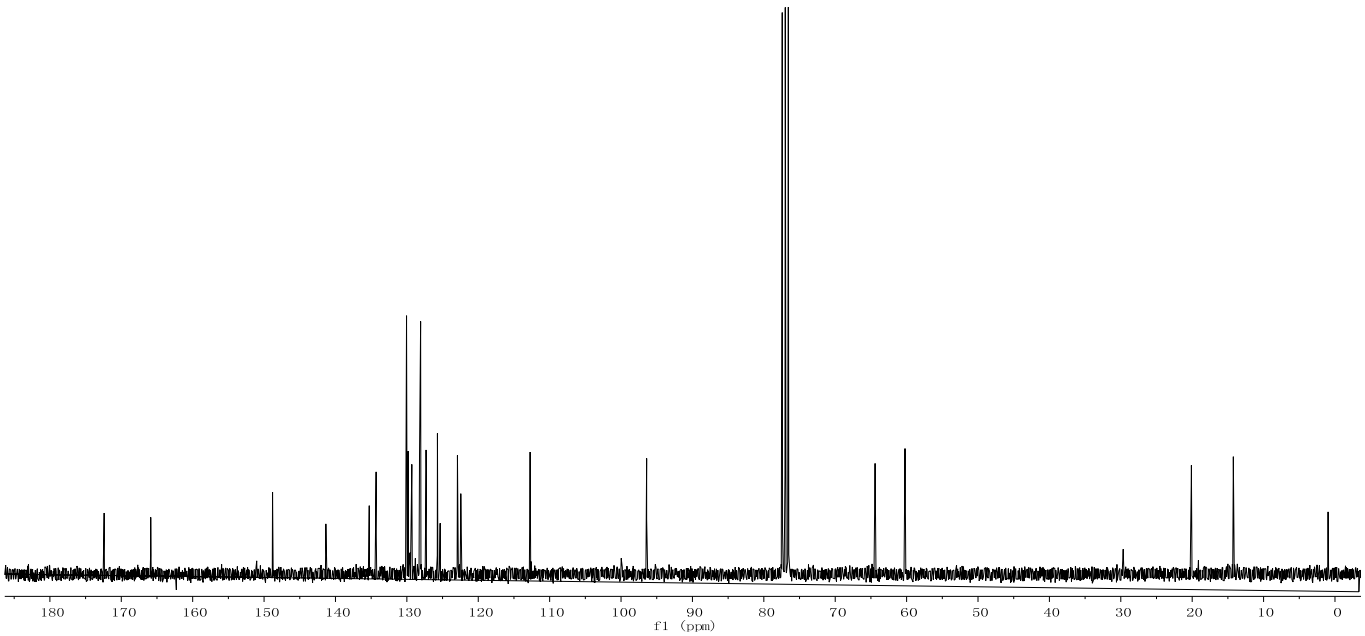
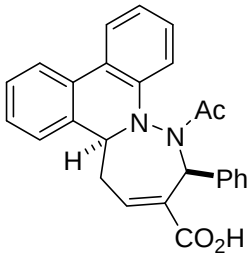
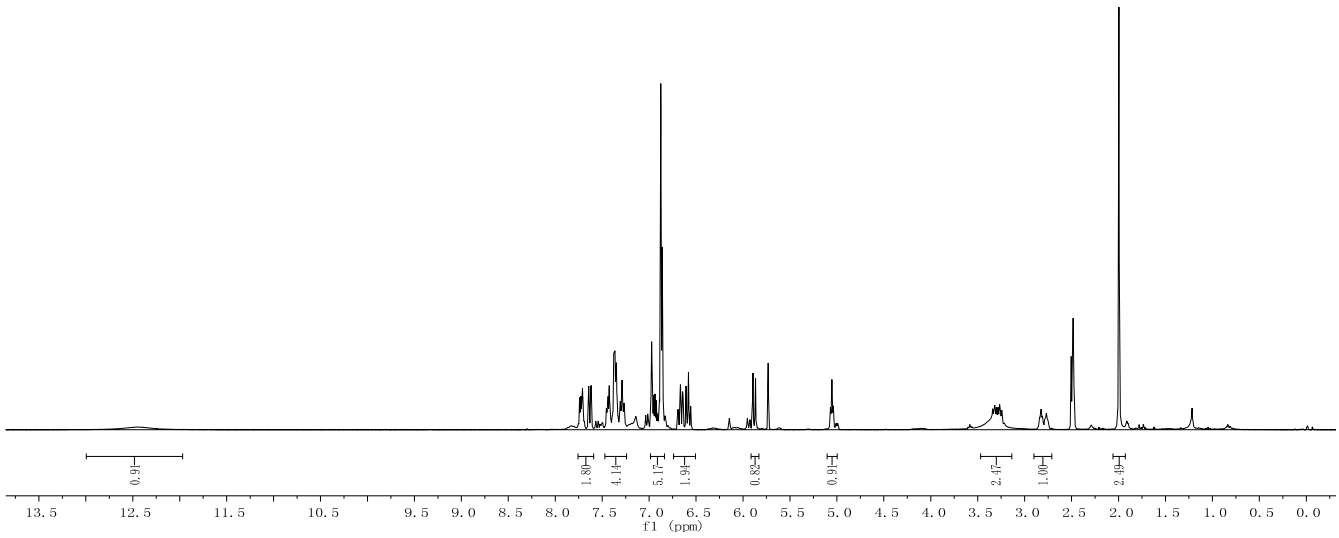
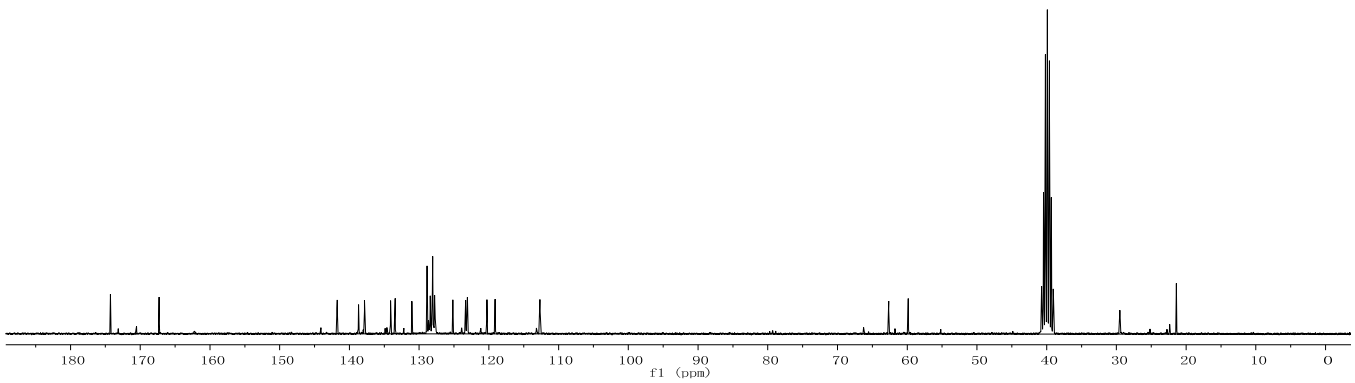
4.97
3.04
0.97
0.88
2.00
2.63
3.30
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
N
N
H
Ph
CO2H

13

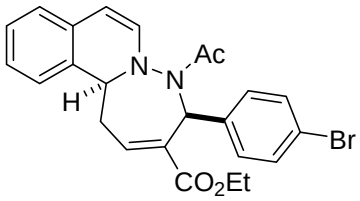

0.91
1.80
4.14
5.17
1.94
0.82
0.91
2.47
1.00
2.39
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

X-ray structure of **5j**, **8a**, **9a**, **11** and **13**:

Crystallographic data for **5j**, **8a**, **9a**, **11**, and **13** have been deposited with the Cambridge Crystallographic Data Centre as supplementary numbers CCDC 1049475–1049479. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

X-ray structure of **5j**



5j

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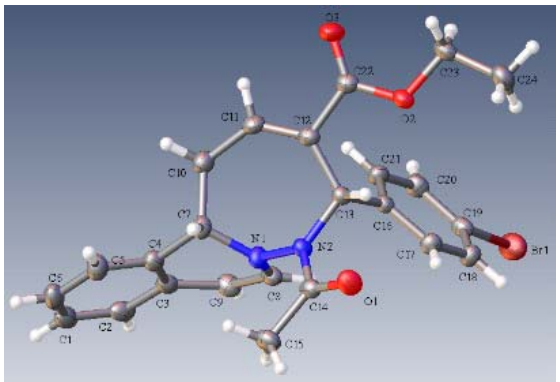
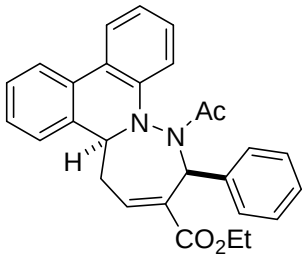


Table 1. Crystal data and structure refinement for **5j**.

Identification code	**5j**	
Empirical formula	$C_{24}H_{23}BrN_2O_3$	
Formula weight	466.09	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.3145(19) Å	α= 103.68(3)°.
	b = 9.4037(19) Å	β= 92.51(3)°.
	c = 12.365(3) Å	γ = 95.23(3)°.
Volume	1045.6(4) $Å^3$	
Z	2	
Density (calculated)	1.484 Mg/m^3	
Absorption coefficient	1.995 mm^{-1}	
F(000)	480	
Crystal size	0.39 x 0.25 x 0.09 mm^3	
Theta range for data collection	1.699 to 27.483°.	
Index ranges	-12<=h<=12, -12<=k<=12, -15<=l<=16	
Reflections collected	13133	
Independent reflections	4757 [R(int) = 0.0325]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6897	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4757 / 0 / 273	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0779	
R indices (all data)	R1 = 0.0424, wR2 = 0.0802	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.346 and -0.432 e.$Å^{-3}$	

X-ray structure of the product **8a**



8a

≡

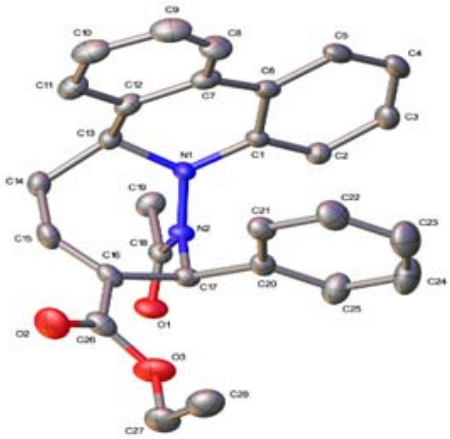


Table 3. Crystal data and structure refinement for **8a**.

Identification code	**8a**
Empirical formula	$C_{28}H_{26}N_2O_3$
Formula weight	438.51
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 (1)/n
Unit cell dimensions	a = 9.4797(19) Å alpha = 90 deg.
	b = 27.330(6) Å beta = 117.10(3) deg.
	c = 9.775(2) Å gamma = 90 deg.
Volume	2254.6(8) $Å^3$
Z, Calculated density	4, 1.292 Mg/m^3
Absorption coefficient	0.084 mm^{-1}
F (000)	928
Crystal size	0.29 x 0.28 x 0.25 mm
Theta range for data collection	2.46 to 27.48 deg.
Limiting indices	-12<=h<=12, -34<=k<=35, -12<=l<=12
Reflections collected / unique	15051 / 5138 [R (int) = 0.0401]
Completeness to theta = 27.48	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6199
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5138 / 568 / 357
Goodness-of-fit on F^2	1.135
Final R indices [I>2sigma (I)]	R1 = 0.0823, wR2 = 0.2255
R indices (all data)	R1 = 0.0938, wR2 = 0.2419
Largest diff. peak and hole	0.693 and -0.334 e. $Å^{-3}$

X-ray structure of the product **9a**

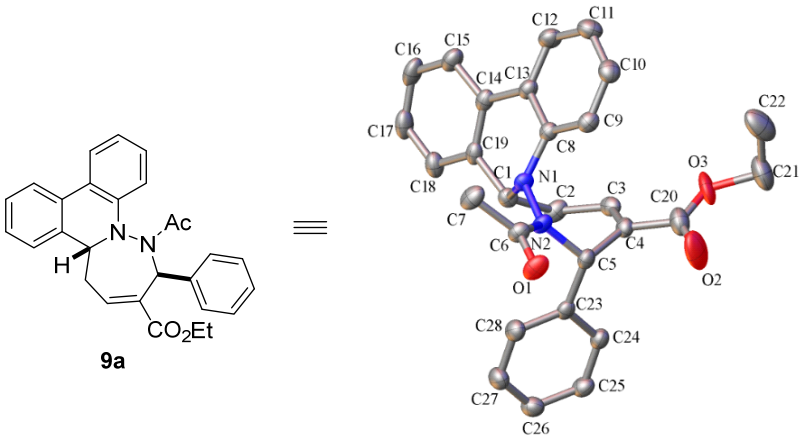
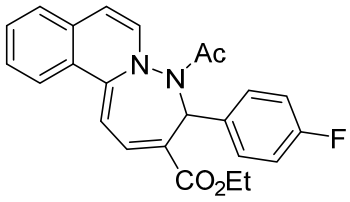


Table 2. Crystal data and structure refinement for **9a**.

Identification code	**9a**	
Empirical formula	$C_{28}H_{26}N_2O_3$	
Formula weight	438.51	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 8.5503(19) Å	α= 90°.
	b = 17.424(4) Å	β= 97.211(3)°.
	c = 15.187(3) Å	γ = 90°.
Volume	2244.6(9) $Å^3$	
Z	4	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	928	
Crystal size	0.51 x 0.28 x 0.25 mm^3	
Theta range for data collection	1.787 to 27.484°.	
Index ranges	-11<=h<=11, -22<=k<=22, -19<=l<=18	
Reflections collected	14344	
Independent reflections	5103 [R(int) = 0.0310]	
Completeness to theta = 26.000°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8314	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5103 / 116 / 338	
Goodness-of-fit on F^2	1.196	
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1260	
R indices (all data)	R1 = 0.0661, wR2 = 0.1298	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.228 and -0.185 e.$Å^{-3}$	

X-ray structure of the product **11**



11

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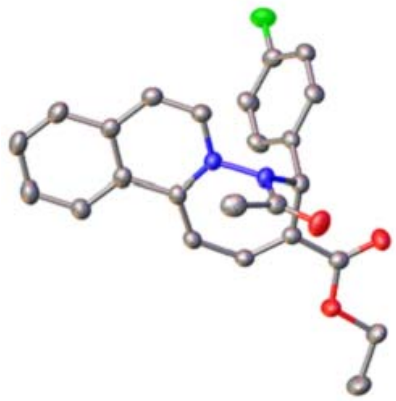
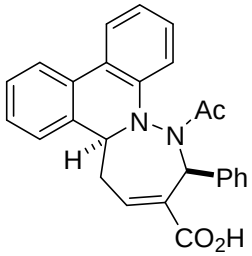


Table 4. Crystal data and structure refinement for **11**.

Identification code	**11**
Empirical formula	$C_{24}H_{21}FN_2O_3$
Formula weight	404.43
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.5283(17) Å alpha = 112.58(3) deg.
	b = 11.326(2) Å beta = 97.17(3) deg.
	c = 11.349(2) Å gamma = 97.42(3) deg.
Volume	985.3(3) $Å^3$
Absorption coefficient	0.097 mm^{-1}
F (000)	424
Crystal size	0.37 x 0.32 x 0.20 mm
Theta range for data collection	2.84 to 27.48 deg.
Limiting indices	-10<=h<=11, -14<=k<=14, -14<=l<=14
Reflections collected / unique	8769 / 4483 [R (int) = 0.0402]
Completeness to theta = 27.48	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.56725
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4483 / 0 / 273
Goodness-of-fit on F^2	1.121
Final R indices [I>2sigma (I)]	R1 = 0.0596, wR2 = 0.1294
R indices (all data)	R1 = 0.0689, wR2 = 0.1349
Largest diff. peak and hole	0.235 and -0.229 e. $Å^{-3}$

X-ray structure of the product **13**



13

≡

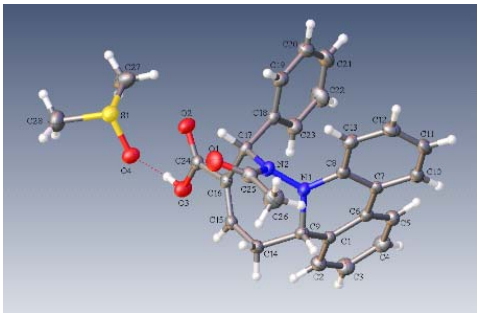


Table 5. Crystal data and structure refinement for **13**.

Identification code	**13**	
Empirical formula	$C_{26}H_{22}N_2O_3$	
Formula weight	410.16	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4629(19) Å	a= 97.33(3)°.
	b = 10.003(2) Å	b= 104.20(3)°.
	c = 14.426(3) Å	g = 110.31(3)°.
Volume	1207.1(5) $Å^3$	
Z	2	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	0.172 mm^{-1}	
F(000)	516	
Crystal size	0.42 x 0.31 x 0.04 mm^3	
Theta range for data collection	1.498 to 27.504°.	
Index ranges	-11<=h<=12, -12<=k<=12, -18<=l<=18	
Reflections collected	15687	
Independent reflections	5523 [R(int) = 0.0326]	
Completeness to theta = 26.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8984	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5523 / 0 / 320	
Goodness-of-fit on F^2	1.151	
Final R indices [I>2sigma(I)]	R1 = 0.0553, wR2 = 0.1086	
R indices (all data)	R1 = 0.0661, wR2 = 0.1145	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.258 and -0.289 e.$Å^{-3}$	