Supporting Information for

Phosphine-Catalyzed Annulations of Azomethine Imines: Allene-Dependent [3 + 2], [3 + 3], [4 + 3], and [3 + 2 + 3] Pathways

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General Information

All reactions were performed under an Ar 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 (SiliCycle silica gel; thickness: 0.25 mm). Chromatograms were visualized by fluorescence quenching under UV light at 254 nm. Flash column chromatography was performed using SiliCycle Silica-P Flash silica gel (60 Å pore size, 40–63 μm) or 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 $CDCl_3$ using a Bruker Avance 500, ARX-500, ARX-400, or AV-300 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 and samples dissolved in $CHCl_3$. 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 Allenoates

Ethyl 2,3-butadienoate (**2o**), α-alkylallenoates (**2a**–**2n**), and γ-substituted allenoates (**2p**–**2r**) were prepared using either a literature method[1] or a one-pot procedure developed in this laboratory from commercially available (carbethoxymethylene)triphenylphosphorane,[2] except for **2d** and **2e**.

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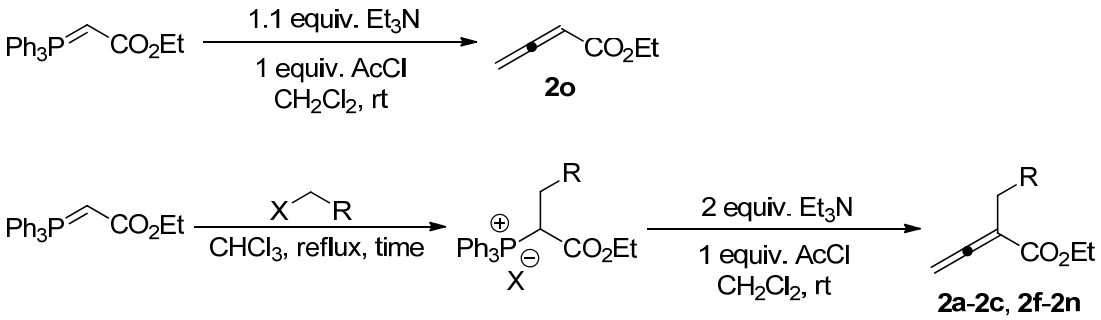
[1] (a) Lang, R. W.; Hansen, H.-J. *Org. Synth.* **1984**, *62*, 202. (b) Lu, K.; Kwon, O. *Org. Synth*. **2009**, *86*, 212.

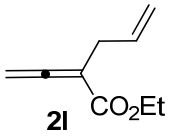
[2] (a) Buono, G. *Tetrahedron Lett.* **1972**, *13*, 3257. (b) Zhu, X.-F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716.



Ethyl 2,3-Butadienoate (2o). Triethylamine (14.8 mL, 0.105 mol) was added slowly to a stirred solution of (carbethoxymethylene)triphenylphosphorane (34.8 g, 0.1 mol)[1a] in DCM (300 mL)/pentane (100 mL) at 0 °C under Ar. AcCl (6.9 mL, 0.1 mol) was then added dropwise over 1 h using a syringe pump. The resulting orange/yellow suspension was stirred at 0 °C for 1 h and then overnight at room temperature. The suspension was filtered through silica gel in a Buchner funnel and concentrated (rotary evaporator) at 0 °C. Pentane (300 mL) was added to the residue and the mixture stirred for 30 min. The triphenylphosphine oxide was filtered off and the solution concentrated (rotary evaporator) at 0 °C. The residue was distilled under reduced pressure to give the product as a colorless liquid (46%).

General Procedure for the Synthesis of the Alleneoates 2a–2c and **2f–2n**. The pertinent alkyl halide (1.0 – 1.2 equiv) was added to a stirred solution of (carbethoxymethylene)triphenylphosphorane[1a] in $CHCl_3$ (80 mL) at room temperature. The mixture was heated under reflux until all of the (carbethoxymethylene)triphenylphosphorane had disappeared (monitored using TLC or ^{1}H NMR). The solvent was evaporated under reduced pressure. DCM (100 mL) and triethylamine (8.4 mL, 2.2 equiv) were added to the resulting phosphonium salt. After stirring for 1 h, AcCl (1.96 mL, 1.0 equiv) was added dropwise over 30 min using a syringe pump. The mixture was stirred overnight and then passed through a Buchner funnel packed with silica gel and washed several times with DCM. The combined filtrates were carefully concentrated and the residue subjected to a flash column chromatography (eluent: 10–15% EtOAc in hexanes) to afford the corresponding allenoates **2a**–**2c** and **2f**–**2n** in 50–85% yield. Spectroscopic data of previously unknown allenoates are provided.

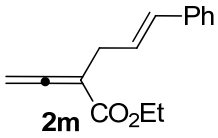
Ethyl 2-Allyl-2,3-butadienoate (2l)



2l

The general procedure outlined above was followed (27.3 mmol scale, using 1.2 equiv of allyl bromide). Formation of the phosphonium salt took ca. 24 h. The allenoate **2l** (2.95 g, 19.16 mmol, 70%) was formed as a colorless oil. IR (neat) ν_{max} 3080, 2983, 1967, 1941, 1718, 1641, 1255, 1127, 1071 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.85–5.73 (m, 1H), 5.12–5.00 (m, 4H), 4.18 (q, *J* = 7.20 Hz, 2H), 2.98–2.95 (m, 2H), 1.25 (t, *J* = 7.20 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.9, 167.7, 134.8, 116.3, 98.9, 79.1, 77.1, 61.0, 32.7, 14.2; HRMS (EI) calcd for $C_9H_{11}O_2$ [$(M - H)^+$] 151.0759, found 151.0763.

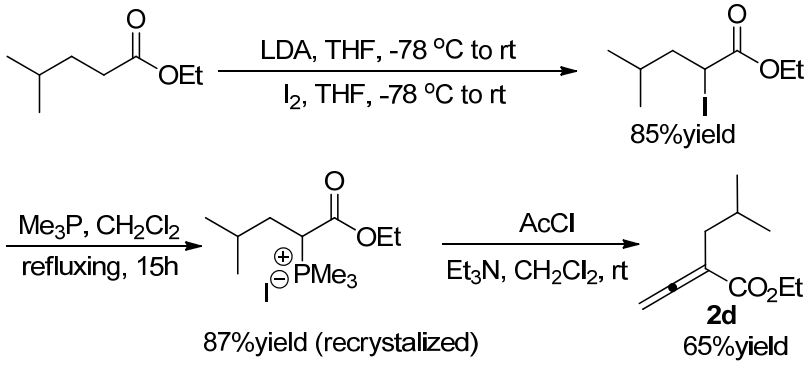
Ethyl 5-Phenyl-2-vinylidenepent-4-enoate (2m)



2m

The general procedure outlined above was followed (27.3 mmol scale, using 1.2 equiv of cinnamyl bromide). Formation of the phosphonium salt took ca. 12 h. The allenoate **2m** (4.70 g, 20.45 mmol, 75%) was formed as a yellow oil. IR (neat) ν_{max} 3060, 3027, 2982, 1966, 1941, 1709, 1255, 1099, 965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51–7.32 (m, 5H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.43–6.33 (m, 1H), 5.31 (t, *J* = 2.9 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.33–3.28 (m, 2H), 1.44 (t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.1, 166.9, 137.4, 131.7, 128.5, 128.4, 127.2, 126.7, 126.2, 99.2, 79.5, 77.1, 61.2, 32.1, 14.3; HRMS (EI) calcd for $C_{15}H_{16}O_2$ [M^+] 228.1150, found 228.1153.

Preparation of Allenoate 2d

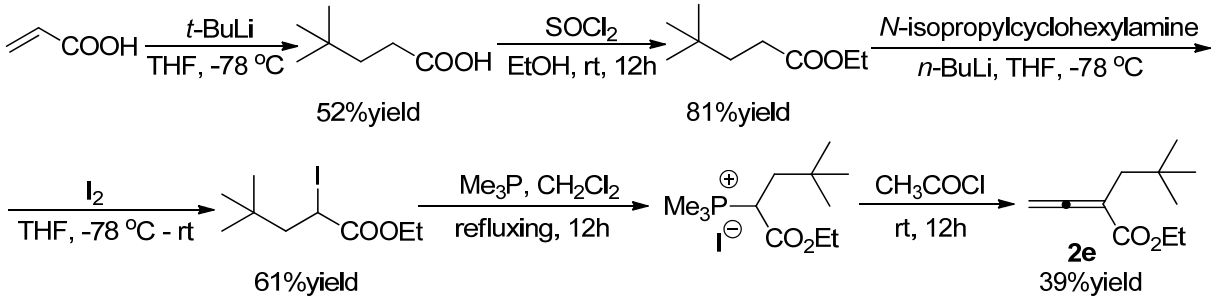


Ethyl 2-Iodo-4-methylpentanoate. *n*-BuLi (2 M in pentane, 25 mL, 50 mmol) was added dropwise to a stirred solution of diisopropylamine (6.95 mL, 50 mmol) in dry THF (25 mL) at –20 °C; the mixture was then stirred for 0.5 h at –78 °C. Ethyl isocaprate (8.29 mL, 50 mmol) was added dropwise over a period of 5 min to the resulting solution; the mixture was warmed to room temperature and the solution of the ester enolate was withdrawn and added dropwise, via syringe, to a solution of I_2 (15.2 g, 60 mmol, 20% excess) in THF (50 mL) maintained at dry ice–acetone temperatures. Conc. HCl (10 mL) was injected and the solution warmed to room temperature before being extracted with water (2 × 30 mL) containing sufficient sodium thiosulfate to remove the I_2 color, dried ($MgSO_4$), and concentrated to give the crude product, which was purified through flash column chromatography (hexane/EtOAc), giving the product as a yellow oil (11.5 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (d, *J* = 5.6 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.62–1.68 (m, 2H), 4.16–4.22 (m, 2H), 4.34 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 20.2, 21.6, 22.1, 28.3, 44.6, 61.7, 171.6.

Ethyl 2-Isobutyl-2,3-butadienoate (2d). Me_3P (3.1 mL, 30.2 mmol) was added dropwise over 5 min to a stirred solution of ethyl 2-iodo-4-methylpentanoate (6.81 g, 25.2 mmol) in DCM (50 mL). The mixture was stirred for 12 h under reflux, cooled to room temperature, and then concentrated to give the phosphonium iodide as a white solid. This solid was kept under high vacuum for 2 h and then recrystallized (hexanes and a minimal amount of DCM) to afford (1-ethoxy-4-methyl-1-oxopentan-2-yl)trimethylphosphonium iodide as a white solid (7.6 g, 87%). IR (film) ν_{max} 3423, 2955, 2271, 2073, 1730, 1638, 1320, 1252, 1160, 968 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (qd, *J* = 7.2, 1.8 Hz, 2H), 3.89 (td, *J* = 11.7, 2.6 Hz, 1H), 2.32 (d, *J* = 11.7 Hz, 9H), 1.98–1.86 (m, 1H), 1.80–1.51 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 77.1, 63.2, 40.6, 39.9, 34.4, 27.3, 23.0, 21.3, 14.2, 8.7, 7.9.

Et_3N (6.71 mL, 48.2 mmol) was added dropwise over 5 min to a solution of (1-ethoxy-4-methyl-1-oxopentan-2-yl)trimethylphosphonium iodide (7.6 g, 21.9 mmol) in DCM (50 mL) and then the mixture was stirred for 1 h. AcCl (1.71 mL, 24.1 mmol) was added dropwise (syringe pump) over 30 min. The resulting mixture was stirred overnight at room temperature and then concentrated. The residue was diluted with Et_2O (50 mL) and passed through a pad of celite under reduced pressure. The filtrate was concentrated and the residue purified through flash column chromatography (hexane/EtOAc, 50:1) to afford **2d** as a colorless oil (2.39 g, 65%). IR (neat) ν_{max} 2958, 2871, 1967, 1941, 1715, 1466, 1368, 1254, 1135, 1061 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.6 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.71–1.79 (m, 1H), 2.06–2.09 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 5.06–5.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.2, 27.3, 37.4, 60.9, 78.1, 99.1, 167.4, 214.4.

Preparation of the Allenoate 2e



4,4-Dimethylpentanoic Acid.[3] A solution of *t*-BuLi (1.7 M in pentane, 84 mL, 135–150 mmol) was added slowly, via syringe, to a stirred solution of acrylic acid (67.5 mmol) in THF (600 mL) at –78 °C and then the solution was stirred for 2 h at the same temperature. Water (200 mL) was added and them most of the solvent was evaporated under reduced pressure. The mixture was acidified through the slow addition of conc. HCl under stirring and ice water cooling. The aqueous phase was saturated with NaCl and extracted with EtOAc. The combined organic layers were dried (Na_2SO_4). The crude acid obtained after evaporation of the solvent was purified through distillation under reduced pressure to give a colorless oil (4.6 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9H), 1.54–1.58 (m, 2H), 2.30–2.34 (m, 2H), 11.4 (broad s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.0, 29.95, 30.04, 38.3, 181.3.

Ethyl 4,4-Dimethylpentanoate. $SOCl_2$ (0.048 mol) was added dropwise to a stirred solution of 4,4-dimethylpentanoic acid (0.04 mol) in dry EtOH (100 mL) at 0 °C. After stirring at room temperature for 12 h, the mixture was concentrated and purified through flash chromatography (SiO_2; EtOAc/hexane) to afford the ester as a colorless oil (5.1 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 9H), 1.25 (t, J = 7.2 Hz, 3H), 1.52–1.56 (m, 3H), 2.23–2.28 (m, 2H), 4.11 (q, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 29.0, 30.2, 32.1, 38.6, 60.2, 174.5.

Ethyl 2-Iodo-4,4-dimethylpentanoate.[4] *n*-BuLi (2.56 M in hexane, 9.88 mL, 25.28 mmol) was added dropwise to a stirred solution of *N*-isopropylcyclohexylamine (4.2 mL, 25.28 mmol) in dry THF (60 mL) at –20 °C and then the mixture was stirred for 0.5 h at –78 °C. Ethyl 4,4-dimethylpentanoate (4.0 g, 25.28 mmol) was added dropwise over a period of 5 min to the resulting solution. The mixture was then warmed to room temperature and the solution of the ester enolate was withdrawn and added dropwise, via syringe, to a solution of I_2 (7.72 g, 30.32 mmol, 20% excess) in THF (60 mL) maintained at dry ice–acetone temperatures. Conc. HCl (5.6

[3] Aurell, M. J.; Domingo, L. R.; Mestres, R.; Muñoz, E.; Zaragozá, R. J. *Tetrahedron* **1999**, *55*, 815.
[4] Rathke, M. W.; Lindert, A. *Tetrahedron Lett.* **1971**, *43*, 3995.

mL) was injected and the solution warmed to room temperature; it was then extracted with water (2 × 30 mL) containing sufficient sodium thiosulfate to remove the I_2 color, dried ($MgSO_4$), and concentrated to give the crude product, which was purified through flash column chromatography (hexane/EtOAc) to give the product as a yellow oil (4.4 g, 61%). IR (neat) ν_{max} 2957, 2908, 2870, 1733, 1476, 1447, 1396, 1368, 1352, 1326, 1280, 1245, 1214, 1195, 1154, 1114, 1097, 1063, 1047, 1028, 1011, 853, 793, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.94 (dd, *J* = 2.8, 14.4 Hz, 1H), 2.46 (dd, *J* = 2.8, 14.4 Hz, 1H), 4.14–4.20 (m, 2H), 4.40 (dd, *J* = 2.8, 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 16.7, 28.9, 33.4, 50.4, 61.7, 172.5; MS (EI): 57.2, 73.1, 83.2, 101.1 (100), 142.2, 157.2, 239.1, 284.1 [M].

Ethyl 4,4-Dimethyl-2-vinylidenepentanoate (2e). Me_3P (2.24 mL, 25.3 mmol) was added dropwise over 5 min to a stirred solution of ethyl 2-iodo-4,4-dimethylpentanoate (6.0 g, 21.1 mmol) in DCM (50 mL) and then the mixture was stirred for 12 h under reflux. After cooling, the mixture was concentrated to give the phosphonium iodide as a white solid, which was kept under high vacuum for 2 h and then dissolved in DCM (50 mL). Et_3N (6.5 mL, 46.41 mmol) was added dropwise over 5 min and then the mixture was stirred for an additional 1 h. AcCl (1.66 mL, 23.20 mmol) was added dropwise (syringe pump) over 1 h. The resulting mixture was stirred overnight at room temperature and then concentrated. The residue was diluted with Et_2O (50 mL) and passed through a pad of celite under reduced pressure. The filtrate was concentrated and the residue purified through gravity column chromatography (pentane/ether, 100:1) to afford the product as a colorless oil (1.5 g, 39%). IR (neat) ν_{max} 2958, 2869, 1965, 1941, 1715, 1476, 1466, 1446, 1393, 1366, 1312, 1260, 1214, 1161, 1091, 1033, 909, 842, 792, 674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.17 (t, *J* = 2.0 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 5.05 (t, *J* = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 29.1, 32.5, 41.3, 61.0, 77.5, 97.7, 167.7, 215.6; MS (EI): 41.2, 57.2, 98.1 (100), 99.1, 126.2, 135.2, 137.2, 139.2, 141.2, 153.2, 154.2, 167.2, 168.2, 182.2 [M], 183.2 $[M + H]^+$.

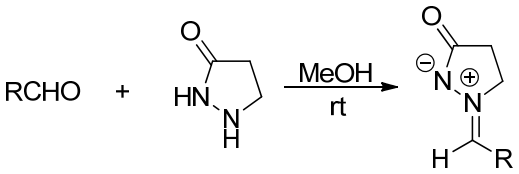
Preparation of *N, N′*-Cyclic Azomethine Imines 1

All *N*,*N′*-cyclic azomethine imines were prepared using the reported procedure (Method A) or a modified procedure (Method B) from the corresponding aldehydes.[5] Aromatic imines are tolerant

[5] (a) Shintani, R.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 10778. (b) Suárez, A.; Downey, C. W.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 11244. (c) Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 6330.

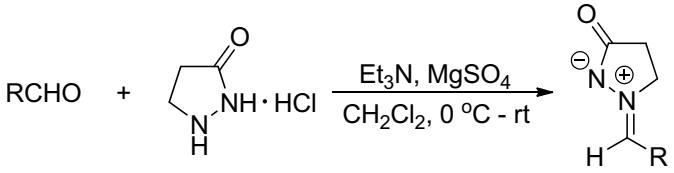
to water and flash column chromatography, but aliphatic imines are sensitive to moisture and decompose on silica gel. Therefore, whereas the aromatic *N*,*N*′-cyclic azomethine imines could be prepared using either Method A or B, the aliphatic imines could be prepared only using Method A.

Method A (reported procedure)[5]



The aldehyde (5 mmol) was added to a solution of pyrazolidin-3-one (5 mmol) in MeOH (1 mL). The resulting mixture was stirred for 1–24 h (depending on TLC monitor) at room temperature and then diluted with Et_2O (20 mL). The precipitate was filtered off, washed with Et_2O, and dried under vacuum to afford the corresponding azomethine imine as a solid (40–90%).

Method B (modified procedure)

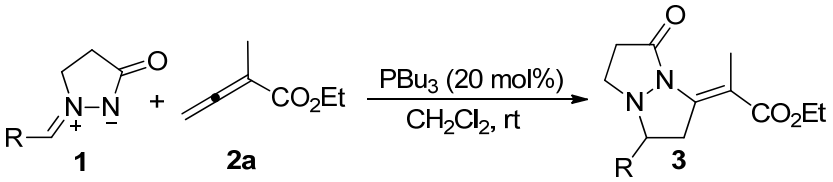


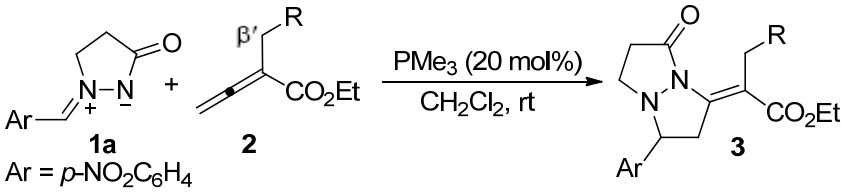
Et_3N (5 mmol) was added dropwise to a stirred mixture of pyrazolidin-3-one hydrochloride (2.5 mmol), $MgSO_4$ (1.5 g), and DCM (15 mL) at 0 °C. The resulting mixture was stirred for 10 min and then the aldehyde (3.75 mmol) was added at 0 °C. The mixture was stirred at room temperature for 48 h and then the $MgSO_4$ was filtered off. The filtrate was washed successively with water (2 × 5 mL) and sat. NaCl (5 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was purified through flash column chromatography (MeOH/EtOAc) to give the corresponding imine as a solid (30–80%).

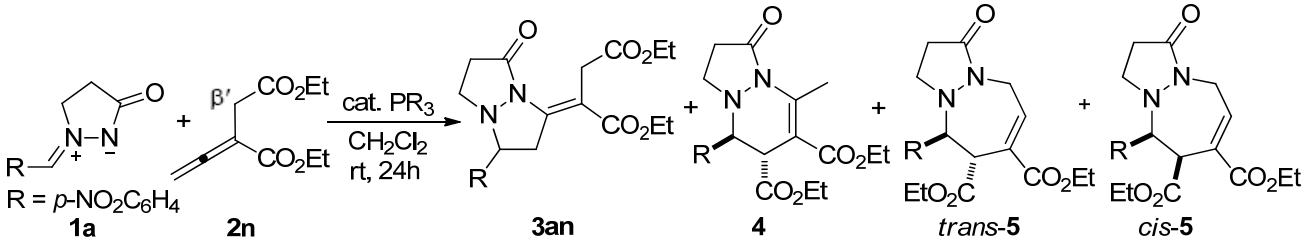
General Procedure for the [3 + 2], [3 + 3], and [4 + 3] Annulations of Azomethine Imines 1 and Allenoates 2

The phosphine (0.025 mmol) was added to a solution of the azomethine imine (0.125 mmol), the allenoate (0.15 mmol), and DCM (5–8 mL) at room temperature in an oven-dried 15-mL Schlenk tube. The mixture was stirred at room temperature (or the given temperature) for the given time

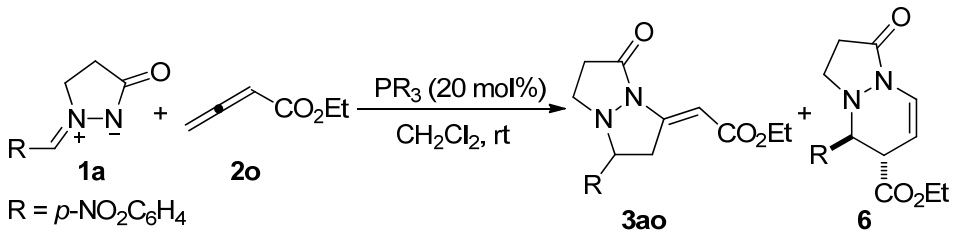
and then concentrated. The residue was purified through flash column chromatography (EtOAc/hexane) to afford the corresponding cycloaddition product.

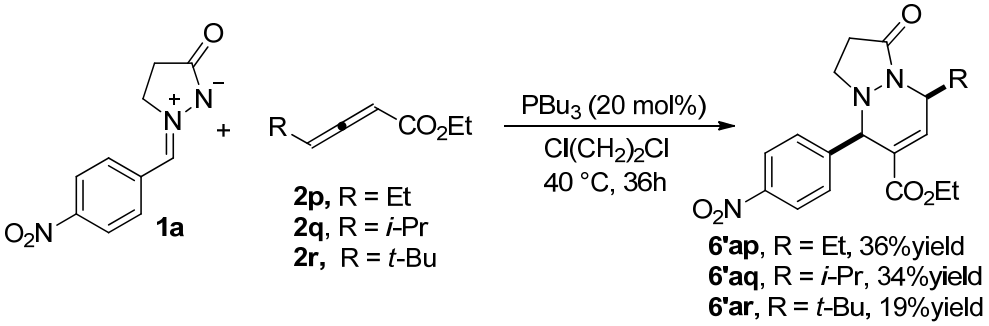






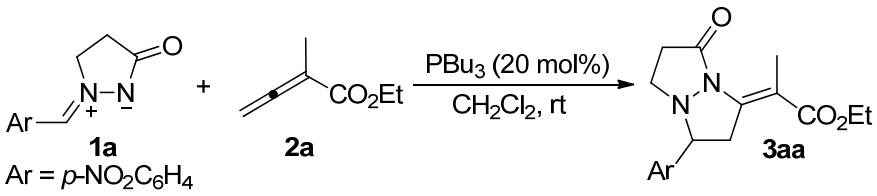
	3an	4	*trans*-**5**	*cis*-**5**
PBu_3 (20 mol%)	6%	23%	48%	15%
PMe_3 (20 mol%)	40%	42%	7%	5%





Screening of Reaction Solvents

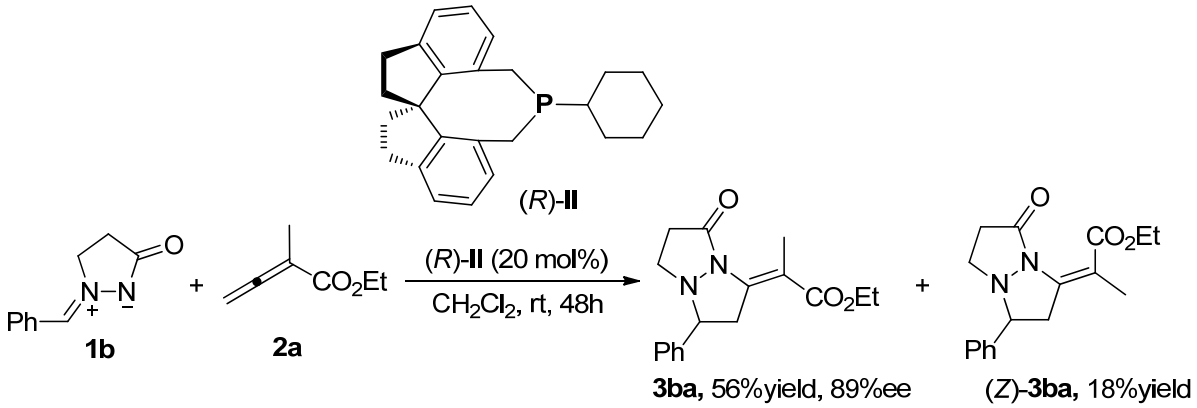
Table S1. Phosphine-Catalyzed [3 + 2] Cycloadditions of the Azomethine Imine **1a** and the Allenoate **2a**: Screening Solvents[a]



entry	solvent	time (h)	yield (%)[b]
1	DCM	14	88
2	$CHCl_3$	24	71
3	$Cl(CH_2)_2Cl$	24	59
4	Et_2O	24	3
5	THF	24	4
6	toluene	24	12
7	benzene	24	10
8	MeCN	24	4
9	EtOAc	24	6
10	acetone	24	5
11	DMF	24	trace
12	MeOH	24	0

[a] 1.2 equiv. of the allenoate was used. [b] Isolated yields.

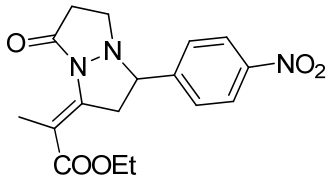
General Procedure for Asymmetric [3 + 2] Annulation of Azomethine Imine 1b and Allenoates 2a



The phosphine (*R*)-**II** (0.020 mmol) was added to a solution of the azomethine imine (0.10 mmol), the allenoate (0.15 mmol), and DCM (1 mL) at room temperature in an oven-dried 5 mL Schlenk tube. The mixture was stirred at room temperature for 48h and then concentrated. The residue was purified through flash column chromatography (EtOAc/hexane = 1 : 2) to afford the corresponding cycloaddition product **3ba** in 56%yield and 89%ee, and (*Z*)-**3ba** in 18%yield. The enantiomer excess was determined by HPLC analysis on a chiral stationary phase (chiral column: (*R*, *R*)-DACH DNB 5/100; eluent: DCM 40%, hexane 60%; flow rate: 1.0 mL/min).

Characterization Data for the [3 + 2], [3 + 3] and [4 + 3] Annulation Products 3–6, and 6′

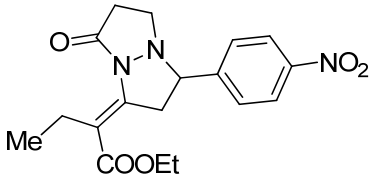
(*E*)-Ethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3aa)



3aa

92% yield; pale-yellow solid. IR (film) ν_{max} 3078, 2981, 2930, 1729, 1649, 1604, 1522, 1493, 1445, 1420, 1348, 1096, 1059, 1016, 980, 767, 736, 700, 669, 577 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.07–2.08 (m, 3H), 2.74–2.90 (m, 2H), 2.94–3.05 (m, 2H), 3.60–3.68 (m, 1H), 3.78–3.91 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 8.23 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.0, 31.4, 43.9, 45.6, 60.5, 68.4, 114.1, 124.1, 128.4, 142.5, 145.6, 147.9, 167.6, 171.8; HRMS (ESI) calcd for $C_{17}H_{20}N_3O_5^+$ $[M + H]^+$ 346.1397, found 346.1396.

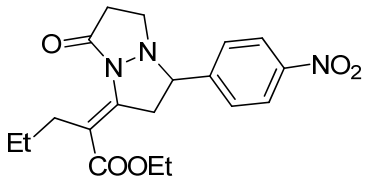
(*E*)-Ethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)butanoate (3ab)



3ab

96% yield; pale-yellow solid. IR (film) ν_{max} 3078, 2891, 2931, 1729, 1649, 1604, 1522, 1445, 1420, 1348, 1096, 1059, 1016, 980, 767, 736, 700, 669, 577 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.3 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 2.47–2.68 (m, 2H), 2.73–3.04 (m, 4H), 3.59–3.66 (m, 1H), 3.75–3.88 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 8.24 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6, 14.1, 24.2, 31.2, 43.8, 45.2, 60.3, 67.9, 120.5, 124.0, 128.2, 141.3, 145.5, 147.8, 167.4, 171.6; HRMS (ESI) calcd for $C_{18}H_{22}N_3O_5^+$ $[M + H]^+$ 360.1554, found 360.1549.

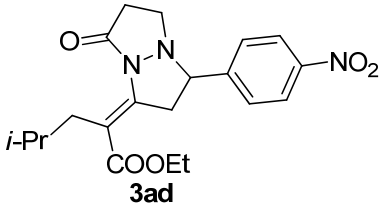
(*E*)-Ethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)pentanoate (3ac)



3ac

92% yield; pale-yellow solid. IR (film) ν_{max} 2960, 2871, 1730, 1644, 1606, 1522, 1493, 1463, 1420, 1347,1286, 1223, 1156, 1109, 1072, 1036, 866, 786, 750, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.39–1.66 (m, 2H), 2.44–2.60 (m, 2H), 2.72–2.90 (m, 2H), 2.94–3.03 (m, 2H), 3.57–3.65 (m, 1H), 3.75 (dd, *J* = 18.1, 7.7 Hz, 1H), 3.86 (dd, *J* = 10.0, 7.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.3, 22.4, 31.4, 32.8, 44.0, 45.4, 60.4, 68.0, 119.2, 124.0, 128.4, 141.6, 145.7, 147.9, 167.6, 171.6; HRMS (ESI) calcd for $C_{19}H_{24}N_3O_5^+$ $[M + H]^+$ 374.1710, found 374.1716.

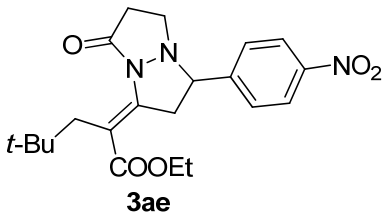
(*E*)-Ethyl 4-Methyl-2-(3-(4-nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)pentanoate (3ad)



3ad

95% yield; pale-yellow solid. IR (film) ν_{max} 2956, 2920, 2849, 1714, 1646, 1605, 1522, 1464, 1347, 1298, 1222, 1132, 1027, 856, 737, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 1.26 (t, *J* = 6.9 Hz, 3H), 1.75–1.82 (m, 1H), 2.48–2.57 (m, 2H), 2.72–2.90 (m, 2H), 2.96–3.09 (m, 2H), 3.57–3.72 (m, 2H), 3.82–3.86 (m, 1H), 4.11–4.20 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 8.23 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.7, 23.2, 28.1, 31.4, 39.0, 44.0, 45.4, 60.4, 67.9, 118.3, 124.0, 128.4, 142.0, 145.6, 147.9, 167.8, 171.4; HRMS (ESI) calcd for $C_{20}H_{26}N_3O_5^+$ $[M + H]^+$ 388.1867, found 388.1874.

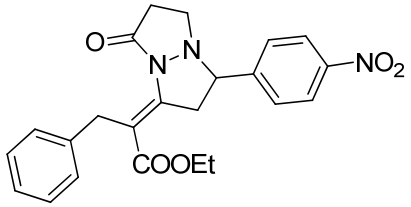
(*E*)-Ethyl 4,4-Dimethyl-2-(3-(4-nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)pentanoate (3ae)



3ae

98% yield; pale-yellow solid. IR (film) ν_{max} 3058, 2958, 1714, 1465, 1605, 1520, 1493, 1475, 1421, 1346, 1178, 1081, 1052, 1030, 978, 908, 856, 828, 788, 737, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H), 2.58 (d, *J* = 14.0 Hz, 1H), 2.71–2.90 (m 3H), 2.94–3.01 (m, 1H), 3.17 (dd, *J* = 18.3, 10.5 Hz, 1H), 3.55–3.62 (m, 2H), 3.80 (dd, *J* = 10.3, 7.6 Hz, 1H), 4.14 (qd, *J* = 7.1, 1.8 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 29.3, 31.7, 33.4, 41.4, 44.3, 45.5, 60.4, 67.7, 117.0, 123.9, 128.3, 141.8, 145.5, 147.8, 168.4, 170.2; HRMS (ESI) calcd for $C_{21}H_{28}N_3O_5^+$ $[M + H]^+$ 402.2023, found 402.2004.

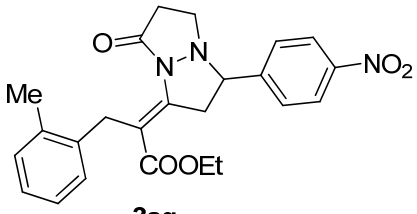
(*E*)-Ethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)-3-phenylpropanoate (3af)



3af

87% yield; pale-yellow solid. IR (film) ν_{max} 3050, 3028, 2982, 2862, 1714, 1650, 1605, 1494, 1453, 1420, 1274, 1197, 1084, 1029, 978, 856, 833, 742, 670, 557 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (t, *J* = 7.1 Hz, 3H), 2.74–2.93 (m, 2H), 3.00–3.16 (m, 2H), 3.60–3.68 (m, 1H), 3.78–3.94 (m, 3H), 3.99–4.13 (m, 3H), 7.15–7.27 (m, 5H), 7.61 (d, *J* = 8.7 Hz, 2H), 8.25 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 31.3, 36.1, 43.9, 45.4, 60.3, 68.0, 117.2, 124.0, 125.7, 127.9, 128.28, 128.33, 140.2, 142.7, 145.3, 147.9, 167.0, 171.8; HRMS (ESI) calcd for $C_{23}H_{24}N_3O_5^+$ $[M + H]^+$ 422.1710, found 422.1708.

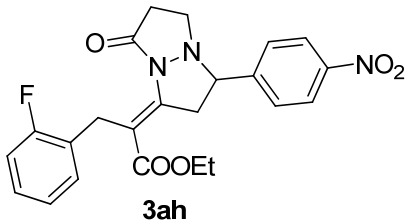
(*E*)-Ethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)-3-(*o*-tolyl)propanoate (3ag)



3ag

95% yield; pale-yellow solid. IR (film) ν_{max} 2979, 1745, 1647, 1603, 1522, 1491, 1461, 1346, 1299, 1195, 1089, 1028, 855, 787, 739, 699, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.1 Hz, 3H), 2.34 (s, 3H), 2.71–2.80 (m, 1H), 2.83–2.92 (m, 1H), 3.03 (ddd, *J* = 11.9, 9.5, 5.7 Hz, 1H), 3.17 (dd, *J* = 18.2, 10.3 Hz, 1H), 3.59–3.66 (m, 1H), 3.76–4.03 (m, 6H), 7.04–7.12 (m, 4H), 7.60–7.64 (m, 2H), 8.23–8.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 19.7, 31.3, 33.7, 44.0, 45.4, 60.4, 68.0, 116.8, 124.1, 125.6, 125.9, 128.2, 128.4, 129.9, 136.2, 138.3, 142.9, 145.5, 148.0, 167.2, 172.2; HRMS (ESI) calcd for $C_{24}H_{26}N_3O_5^+$ $[M + H]^+$ 436.1867, found 436.1852.

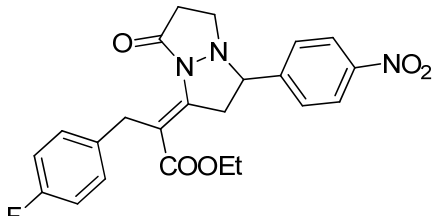
(*E*)-Ethyl 3-(2-Fluorophenyl)-2-(3-(4-nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ah)



3ah

91% yield; pale-yellow solid. IR (film) ν_{max} 2918, 2849, 1715, 1647, 1603, 1522, 1489, 1456, 1419, 1347, 1298, 1196, 1097, 1030, 856, 757, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (td, *J* = 7.1, 2.0 Hz, 3H), 2.74–2.93 (m, 2H), 2.99–3.15 (m, 2H), 3.60–3.68 (m, 1H), 3.81–4.10 (m, 6H), 6.83–7.23 (m, 4H), 7.59–7.63 (m, 2H), 8.22–8.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.88, 13.96, 29.39, 29.42, 31.50, 31.64, 36.05, 36.07, 44.12, 44.19, 45.58, 45.80, 60.50, 60.57, 68.07, 68.17, 115.46, 115.47, 116.50, 123.56, 123.59, 124.09, 124.12, 127.16, 127.31, 128.42, 142.96, 143.04, 143.46, 143.52, 145.31, 145.43, 147.96, 147.99, 159.78, 161.57, 162.22, 163.99, 166.92, 166.97, 171.58, 171.91; HRMS (ESI) calcd for $C_{23}H_{23}FN_3O_5^+$ $[M + H]^+$ 440.1616, found 440.1596.

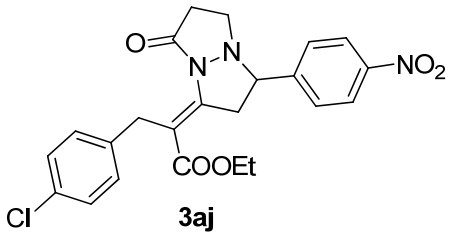
(*E*)-Ethyl 3-(4-Fluorophenyl)-2-(3-(4-nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ai)



3ai

99% yield; pale-yellow solid. IR (film) ν_{max} 2691, 1707, 1647, 1603, 1522, 1506, 1419, 1347, 1273, 1189, 1156, 1095, 1016, 856, 747, 699, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (t, *J* = 7.1 Hz, 3H), 2.73–2.93 (m, 2H), 3.00–3.13 (m, 2H), 3.60–3.67 (m, 1H), 3.79–3.85 (m, 2H), 3.90–3.94 (m, 1H), 3.98–4.05 (m, 3H), 6.92 (app. t, *J* = 8.7 Hz, 2H), 7.14–7.18 (m, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 8.23 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 31.4, 35.5, 44.1, 45.5, 60.5, 68.0, 114.7, 114.9, 117.2, 124.1, 128.4, 129.8, 129.9, 135.92, 135.95, 143.0, 145.4, 148.0, 160.1, 162.5, 167.0, 172.0; HRMS (ESI) calcd for $C_{23}H_{23}FN_3O_5^+$ $[M + H]^+$ 440.1616, found 440.1595.

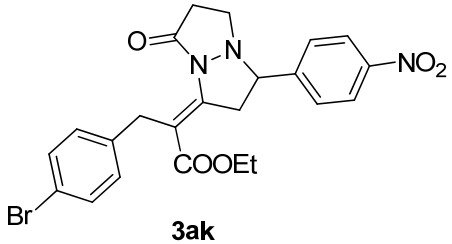
(*E*)-Ethyl 3-(4-Chlorophenyl)-2-(3-(4-nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3aj)



3aj

88% yield; pale-yellow solid. IR (film) ν_{max} 2925, 2850, 1708, 1647, 1606, 1522, 1490, 1419, 1347, 1284, 1191, 1091, 1015, 866, 804, 736, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, *J* = 7.1 Hz, 3H), 2.73–2.92 (m, 2H), 3.00–3.13 (m, 2H), 3.59–3.67 (m, 1H), 3.80–3.94 (m, 3H), 4.00–4.05 (m, 3H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 8.23 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 31.5, 35.7, 44.1, 45.6, 60.6, 68.1, 116.7, 124.1, 128.1, 128.4, 129.9, 131.5, 138.9, 143.3, 145.3, 148.0, 166.9, 171.9; HRMS (ESI) calcd for $C_{23}H_{23}ClN_3O_5^+$ $[M + H]^+$ 456.1321, found 456.1304.

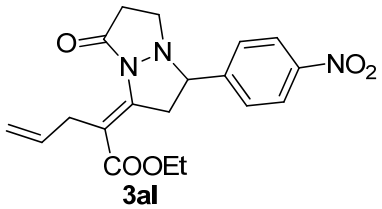
(*E*)-Ethyl 3-(4-Bromophenyl)-2-(3-(4-nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ak)



3ak

81% yield; pale-yellow solid. IR (film) ν_{max} 2918, 2849, 1715, 1647, 1606, 1522, 1487, 1419, 1347, 1284, 1192, 1091, 1012, 856, 800, 736, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, *J* = 7.1 Hz, 3H), 2.73–2.93 (m, 2H), 3.00–3.12 (m, 2H), 3.59–3.67 (m, 1H), 3.80–3.94 (m, 3H), 4.00–4.05 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 8.24 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 31.5, 35.8, 44.1, 45.6, 60.6, 68.1, 116.6, 119.6, 124.1, 128.4, 130.3, 131.1, 139.4, 143.3, 145.3, 148.0, 166.9, 171.89; HRMS (ESI) calcd for $C_{23}H_{23}BrN_3O_5^+$ $[M + H]^+$ 500.0816, found 500.0796.

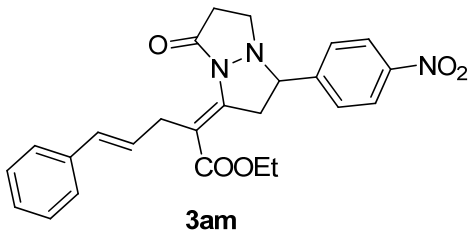
(*E*)-Ethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)pent-4-enoate (3al)



3al

45% yield; pale-yellow solid. IR (film) ν_{max} 2917, 2849, 1704, 1646, 1605, 1522, 1457, 1419, 1347, 1286, 1212, 1156, 1109, 1028, 856, 749, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.1 Hz, 3H), 2.75–2.91 (m, 2H), 2.97–3.05 (m, 2H), 3.36 (ddd, *J* = 21.0, 15.3, 6.2 Hz, 2H), 3.59–3.66 (m, 1H), 3.79–3.90 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 5.04 (ddd, *J* = 13.6, 11.5, 1.5 Hz, 2H), 5.90 (ddt, *J* = 16.8, 10.1, 6.3 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 8.23 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 31.6, 34.7, 44.1, 45.6, 60.6, 68.1, 115.6, 116.4, 124.1, 128.4, 142.4, 145.5, 148.0, 167.2, 171.4; HRMS (ESI) calcd for $C_{19}H_{22}N_3O_5^+$ $[M + H]^+$ 372.1554, found 372.1538.

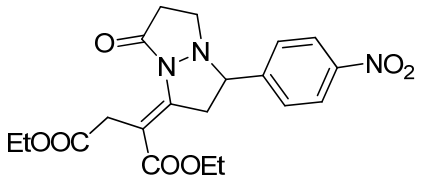
(2*E*,4*E*)-Ethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)-5-phenylpent-4-enoate (3am)



3am

30% yield; pale-yellow solid. IR (film) ν_{max} 2918, 2849, 1704, 1637, 1601, 1522, 1491, 1457, 1419, 1347, 1282, 1094, 968, 856, 744, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.77–2.93 (m, 2H), 2.99–3.09 (m, 2H), 3.45 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.54–3.68 (m, 2H), 3.82–3.91 (m, 2H), 4.17 (q, *J* = 7.0 Hz, 2H), 6.30 (dt, *J* = 15.8, 6.6 Hz, 1H), 6.45 (app. d, *J* = 15.9 Hz, 1H), 7.19 (app. t, *J* = 7.2 Hz, 1H), 7.26–7.36 (m, 4H), 7.60 (d, *J* = 8.7 Hz, 2H), 8.24 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 31.5, 34.0, 44.0, 45.5, 60.5, 68.0, 116.3, 124.0, 126.0, 126.8, 127.9, 128.27, 128.33, 131.1, 137.7, 142.4, 145.3, 147.8, 167.1, 171.4; HRMS (ESI) calcd for $C_{25}H_{26}N_3O_5^+$ $[M + H]^+$ 448.1867, found 448.1880.

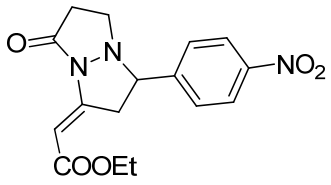
(*E*)-Diethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)succinate (3an)



3an

Pale-yellow solid. IR (film) ν_{max} 2925, 2851, 1732, 1652, 1558, 1541, 1521, 1457, 1346, 1287, 1178, 855, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (dt, *J* = 15.4, 7.1 Hz, 6H), 2.84 (td, *J* = 8.0, 2.0 Hz, 2H), 2.95–3.11 (m, 2H), 3.62 (ddd, *J* = 15.8, 12.6, 11.5 Hz, 3H), 3.95 (ddd, *J* = 17.9, 14.1, 7.7 Hz, 2H), 4.14–4.22 (m, 4H), 7.58–7.61 (m, 2H), 8.22–8.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.1, 32.1, 36.6, 44.1, 46.4, 60.5, 60.6, 68.3, 110.2, 124.0, 128.2, 144.2, 145.0, 147.9, 166.5, 170.6, 171.3; HRMS (ESI) calcd for $C_{20}H_{24}N_3O_7^+$ $[M + H]^+$ 418.1609, found 418.1611.

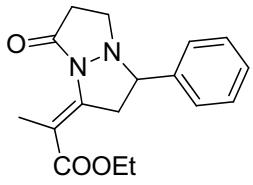
(*E*)-Ethyl 2-(3-(4-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)acetate (3ao)



3ao

Pale-yellow solid. IR (film) ν_{max} 2988, 2356, 2345, 1721, 1626, 1601, 1520, 1386, 1346, 1267, 1229, 1149, 1127, 1038, 860, 854, 839, 726, 680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.77–2.86 (m, 2H), 3.04–3.19 (m, 2H), 3.51 (t, *J* = 8.1 Hz, 1H), 3.88 (dd, *J* = 11.7, 6.7 Hz, 1H), 4.11–4.20 (m, 3H); 6.46 (s, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 8.25 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 37.1, 44.4, 51.8, 60.0, 69.5, 96.6, 96.7, 124.2, 128.0, 144.1, 144.2, 148.1, 164.6, 167.6; HRMS (ESI) calcd for $C_{16}H_{18}N_3O_5^+$ $[M + H]^+$ 332.1241, found 332.1225.

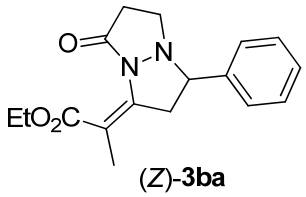
(*E*)-Ethyl 2-(7-Oxo-3-phenyltetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ba)



3ba

97% yield; pale-yellow solid. IR (film) ν_{max} 2979, 2930, 1729, 1648, 1603, 1541, 1496, 1456, 1366, 1279, 1247, 1156, 1098, 1029, 978, 766, 701, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.08 (s, 3H), 2.70–2.88 (m, 2H), 3.00–3.10 (m, 2H), 3.53–3.61 (m, 1H), 3.71–3.78 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 7.31–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.1, 31.5, 43.8, 45.1, 60.4, 69.4, 113.7, 127.6, 128.4, 128.8, 137.7, 143.6, 167.7, 172.2; HRMS (ESI) calcd for $C_{17}H_{21}N_2O_3^+$ $[M + H]^+$ 301.1547, found 301.1545.

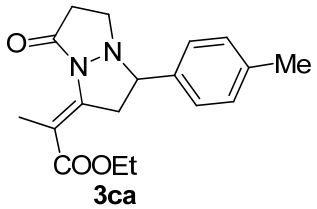
(*Z*)-Ethyl 2-(7-oxo-3-phenyltetrahydropyrazolo[1,2-a]pyrazol-1(5H)-ylidene)propanoate ((*Z*)-3ba)



(*Z*)-**3ba**

18% yield; pale-yellow solid. IR (film) ν_{max} 2970, 2932, 1730, 1641, 1600, 1545, 1501, 1460, 1365, 1280, 1246, 1155, 1100, 1025, 980, 765, 703, 675 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.84 (s, 3H), 2.70 (t, *J* = 8.4 Hz, 2H), 2.78 (ddd, *J* = 1.2, 10.8, 16.8 Hz, 1H), 2.91 (dt, *J* = 8.4 , 11.6 Hz, 1H), 3.19 (ddd, *J* = 1.2, 7.2, 16.8 Hz, 1H), 3.50 (dt, *J* = 8.4 , 11.6 Hz, 1H), 3.65(dd, *J* = 7.2, 10.8Hz, 1H), 4.11–4.24 (m, 2H), 7.25–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.28, 15.94, 32.31, 42.43, 46.58, 60.68, 69.66, 111.13, 127.57, 128.55, 128.91, 134.74, 137.42, 168.42, 169.00; HRMS (ESI) calcd for $C_{17}H_{21}N_2O_3^+$ $[M + H]^+$ 301.1552, found 301.1557.

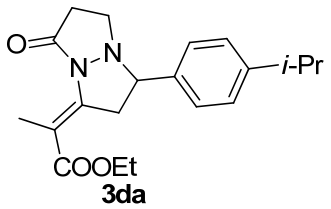
(*E*)-Ethyl 2-(7-Oxo-3-(*p*-tolyl)tetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ca)



3ca

85% yield; pale-yellow solid. IR (film) ν_{max} 2926, 1729, 1649, 1605, 1541, 1516, 1445, 1366, 1279, 1247, 1174, 1096, 1022, 820, 766, 736, 669, 562 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.08 (s, 3H), 2.35 (s, 3H), 2.67–2.87 (m, 2H), 2.99–3.09 (m, 2H), 3.51–3.58 (m, 1H), 3.68–3.74 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.25–7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.1, 21.2, 31.5, 43.7, 45.0, 60.4, 69.2, 113.7, 127.6, 129.5, 134.6, 138.2, 143.7, 167.8, 172.2; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_3^+$ $[M + H]^+$ 315.1703, found 315.1691.

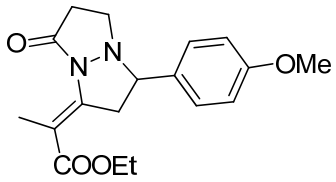
(*E*)-Ethyl 2-(3-(4-Isopropylphenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3da)



3da

89% yield; pale-yellow solid. IR (film) ν_{max} 2996, 1714, 1650, 1614, 1513, 1462, 1278, 1096, 1057, 1020, 978, 919, 836, 789, 767, 736, 702, 670, 574 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24–1.26 (m, 9H), 2.08 (app. t, 3H), 2.67–2.94 (m, 3H), 3.00–3.11 (m, 2H), 3.52–3.60 (m, 1H), 3.68–3.75 (m, 2H), 4.13–4.20 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.1, 24.0, 31.5, 33.8, 43.7, 45.1, 60.4, 69.2, 113.7, 126.9, 127.6, 134.9, 143.7, 149.2, 167.8, 172.2; HRMS (ESI) calcd for $C_{20}H_{27}N_2O_3^+$ $[M + H]^+$ 343.2016, found 343.2008.

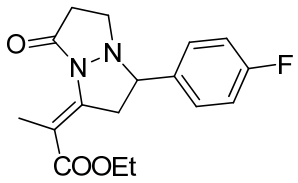
(*E*)-Ethyl 2-(3-(4-Methoxyphenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ea)



3ea

77% yield; pale-yellow solid. IR (film) ν_{max} 3054, 2986, 2931, 2849, 1722, 1650, 1614, 1514, 1444, 1421, 1367, 1265, 1198, 1176, 1097, 1034, 896, 836 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.07 (s, 3H), 2.70–2.87 (m, 2H), 2.98–3.09 (m, 2H), 3.49–3.57 (m, 1H), 3.66–3.73 (m, 2H), 3.81 (s, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 6.88–6.91 (m, 2H), 7.27–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.1, 31.5, 43.7, 44.8, 55.3, 60.4, 68.9, 113.7, 114.2, 128.8, 129.5, 143.7, 159.7, 167.8, 172.3; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_4^+$ $[M + H]^+$ 331.1652, found 331.1645.

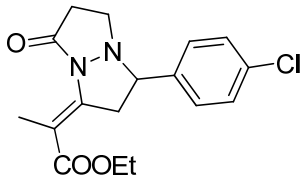
(*E*)-Ethyl 2-(3-(4-Fluorophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3fa)



3fa

91% yield; pale-yellow solid. IR (film) ν_{max} 2927, 1725, 1647, 1607, 1510, 1445, 1365, 1278, 1246, 1224, 1196, 1174, 1128, 1093, 1059, 1025, 979, 837, 809, 767, 701, 690, 683, 676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.1 Hz, 3H), 2.06 (s, 3H), 2.71–2.86 (m, 2H), 2.94–3.09 (m, 3H), 3.52–3.58 (m, 1H), 3.69–3.75 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.03–7.10 (m, 2H), 7.33–7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.0, 31.5, 43.9, 45.1, 60.4, 68.6, 113.8, 115.6, 115.9, 129.1, 129.2, 133.51, 133.55, 143.3, 161.0, 164.3, 167.7, 172.0; HRMS (ESI) calcd for $C_{17}H_{20}FN_2O_3^+$ $[M + H]^+$ 319.1452, found 319.1448.

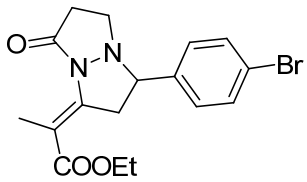
(*E*)-Ethyl 2-(3-(4-Chlorophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ga)



3ga

93% yield; pale-yellow solid. IR (film) ν_{max} 2979, 2930, 1731, 1648, 1605, 1567, 1541, 1491, 1457, 1418, 1280, 1175, 1094, 1015, 832, 767, 737, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.07 (app. t, 3H), 2.70–2.88 (m, 2H), 2.93–3.06 (m, 2H), 3.53–3.61 (m, 1H), 3.70–3.77 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 7.30–7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.0, 31.4, 43.8, 45.2, 60.4, 68.6, 113.8, 128.91, 129.04, 134.2, 136.4, 143.2, 167.7, 172.0; HRMS (ESI) calcd for $C_{17}H_{20}ClN_2O_3^+$ $[M + H]^+$ 335.1157, found 335.1153.

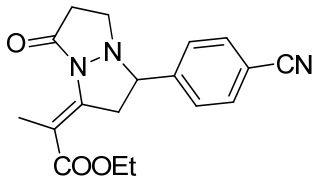
(*E*)-Ethyl 2-(3-(4-Bromophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ha)



3ha

97% yield; pale-yellow solid. IR (film) ν_{max} 2979, 2929, 1728, 1649, 1605, 1541, 1507, 1488, 1364, 1280, 1247, 1174, 1156, 1096, 1010, 828, 767, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.07 (app. d, 3H), 2.69–2.88 (m, 2H), 2.93–3.05 (m, 2H), 3.53–3.61 (m, 1H), 3.69–3.77 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.24–7.28 (m, 2H), 7.48–7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.0, 31.4, 43.8, 45.2, 60.5, 68.7, 113.9, 122.3, 129.2, 132.0, 136.9, 143.2, 167.7, 172.0; HRMS (ESI) calcd for $C_{17}H_{20}BrN_2O_3^+$ $[M + H]^+$ 379.0652, found 379.0668.

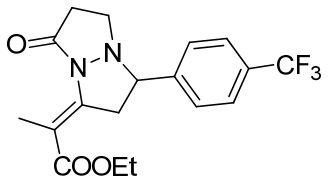
(*E*)-Ethyl 2-(3-(4-Cyanophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ia)



3ia

87% yield; pale-yellow solid. IR (film) ν_{max} 2929, 1729, 1650, 1610, 1506, 1445, 1417, 1366, 1280, 1249, 1175, 1097, 1022, 842, 767, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.07 (s, 3H), 2.73–3.04 (m, 4H), 3.58–3.66 (m, 1H), 3.75–3.85 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.0, 31.4, 43.9, 45.6, 60.5, 68.7, 112.3, 114.1, 118.5, 128.2, 132.7, 142.6, 143.6, 167.6, 171.8; HRMS (ESI) calcd for $C_{18}H_{20}N_3O_3^+$ $[M + H]^+$ 326.1499, found 326.1491.

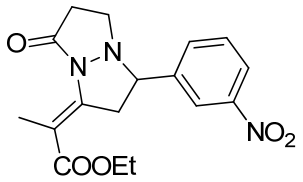
(*E*)-Ethyl 2-(7-Oxo-3-(4-(trifluoromethyl)phenyl)tetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ja)



3ja

98% yield; pale-yellow solid. IR (film) ν_{max} 2931, 1730, 1650, 1621, 1541, 1419, 1326, 1280, 1249, 1164, 1126, 1068, 1019, 979, 844, 767, 738, 669, 605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.08 (app. d, 3H), 2.72–2.89 (m, 2H), 2.96–3.06 (m, 2H), 3.57–3.65 (m, 1H), 3.75–3.85 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.0, 31.4, 43.9, 45.4, 60.5, 68.8, 114.0, 116.7, 116.9, 117.9, 125.3, 125.8, 127.9, 130.5, 130.8, 142.12, 142.14, 142.9, 167.6, 172.0; HRMS (ESI) calcd for $C_{18}H_{20}F_3N_2O_3^+$ $[M + H]^+$ 369.1421, found 369.1430.

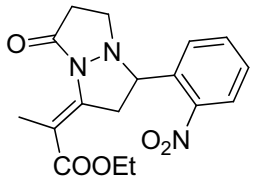
(*E*)-Ethyl 2-(3-(3-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ka)



3ka

97% yield; pale-yellow solid. IR (film) ν_{max} 2980, 2930, 2849, 1730, 1649, 1605, 1531, 1445, 1349, 1531, 1445, 1349, 1280, 1156, 1098, 1059, 1025, 811, 767, 736, 690, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.07 (t, *J* = 1.7 Hz, 3H), 2.74–2.91 (m, 2H), 2.96–3.06 (m, 2H), 3.60–3.67 (m, 1H), 3.78–3.91 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 8.18 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 8.28 (t, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.00, 17.01, 31.4, 44.0, 45.6, 60.5, 68.3, 114.1, 122.6, 123.4, 129.9, 133.6, 140.5, 142.6, 148.6, 167.6, 171.8; HRMS (ESI) calcd for $C_{17}H_{20}N_3O_5^+$ $[M + H]^+$ 346.1397, found 346.1384.

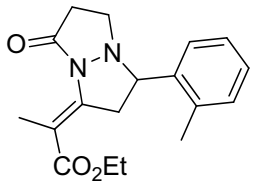
(*E*)-Ethyl 2-(3-(2-Nitrophenyl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3la)



3la

94% yield; pale-yellow solid. IR (film) ν_{max} 2981, 2930, 1714, 1650, 1605, 1577, 1530, 1446, 1349, 1284, 1099, 1060, 1026, 981, 854, 789, 767, 738, 703, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.07 (t, *J* = 1.7 Hz, 3H), 2.71–3.04 (m, 4H), 3.59–3.66 (m, 1H), 4.00 (ddd, *J* = 18.4, 7.8, 1.6 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 6H), 4.33 (dd, *J* = 9.8, 7.9 Hz, 3H), 7.45–7.49 (m, 1H), 7.64–7.68 (m, 1H), 7.94–7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.0, 31.4, 43.5, 45.8, 60.5, 63.8, 114.0, 124.7, 128.8, 133.87, 133.9, 142.8, 149.5, 167.6, 172.0; HRMS (ESI) calcd for $C_{17}H_{20}N_3O_5^+$ $[M + H]^+$ 346.1397, found 346.1408.

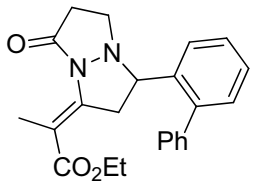
(*E*)-Ethyl 2-(7-oxo-3-(o-tolyl)tetrahydropyrazolo[1,2-a]pyrazol-1(5H)-ylidene)propanoate (3ma)



3ma

70%yield; white solid. IR (film) ν_{max} 2980, 2929, 2851, 1708, 1648, 1491, 1460, 1444, 1365, 1302, 1279, 1249, 1200, 1174, 1157, 1112, 1095, 1057, 1112, 1095, 1057, 1026, 798, 761, 726; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 1H), 7.25 – 7.14 (m, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.99 (dd, *J* = 10.4, 7.5 Hz, 1H), 3.81 (ddd, *J* = 18.3, 7.5, 1.6 Hz, 1H), 3.66 (ddd, *J* = 11.7, 9.6, 8.2 Hz, 1H), 3.02 (ddd, *J* = 11.7, 8.9, 6.7 Hz, 1H), 2.94 – 2.77 (m, 3H), 2.33 (s, 3H), 2.09 (t, *J* = 1.8 Hz, 3H), 1.26 (dd, *J* = 9.2, 5.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 167.7, 143.5, 136.1, 135.9, 130.6, 127.6, 126.6, 126.1, 113.7, 65.7, 60.4, 45.6, 42.3, 31.6, 19.3, 17.0, 14.3; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_3^+$ $[M + H]^+$ 315.1703, found 315.1695.

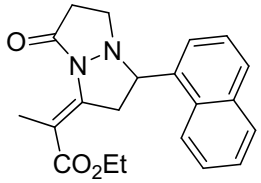
(*E*)-Ethyl 2-(3-([1,1'-biphenyl]-2-yl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5H)-ylidene)propanoate (3na)



3na

50% yield; white solid. IR (film) ν_{max} 3059, 3025, 2978, 2929, 2854, 1728, 1651, 1479, 1441, 1420, 1366, 1281, 1242, 1195, 1175, 1155, 1095, 1053, 1026, 862, 800, 759, 738, 705; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.54 – 7.27 (m, 5H), 7.28 – 7.14 (m, 3H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.79 (dd, *J* = 10.5, 7.5 Hz, 1H), 3.65 – 3.40 (m, 2H), 3.03 (ddd, *J* = 18.3, 10.5, 2.1 Hz, 1H), 2.85 (ddd, *J* = 12.0, 9.8, 5.5 Hz, 1H), 2.68 – 2.41 (m, 2H), 2.03 (t, *J* = 1.8 Hz, 3H), 1.27 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.42, 167.69, 143.86, 142.86, 140.53, 135.35, 129.81, 128.95, 128.40, 128.11, 127.49, 127.07, 113.62, 65.05, 60.33, 44.91, 44.08, 31.21, 16.92, 14.29; HRMS (ESI) calcd for $C_{23}H_{25}N_2O_3^+$ $[M + H]^+$ 377.1860, found 377.1855.

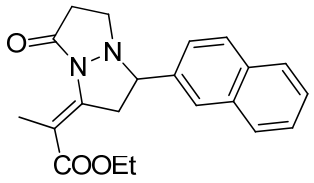
(*E*)-Ethyl 2-(3-(naphthalen-1-yl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5H)-ylidene)propanoate (3oa)



3oa

57% yield; white solid. IR (film) ν_{max} 3052, 2980, 2930, 1709, 1650, 1597, 1512, 1444, 1421, 1388, 1281, 1201, 1172, 1100, 1060, 1022, 978, 863, 803, 781, 737; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 1H), 7.92 – 7.72 (m, 3H), 7.52 (tdd, *J* = 14.1, 9.6, 4.8 Hz, 3H), 4.51 (dd, *J* = 10.3, 7.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.09 – 3.97 (m, 1H), 3.72 (m, *J* = 11.7, 9.7, 8.2 Hz, 1H), 3.15 – 2.98 (m, 2H), 2.96 – 2.72 (m, 2H), 2.13 (t, *J* = 1.8 Hz, 3H), 1.24 (m, *J* = 9.9, 4.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.00, 167.64, 143.41, 133.83, 133.72, 131.25, 128.98, 128.39, 126.37, 125.80, 125.62, 123.86, 122.82, 113.86, 60.33, 45.83, 43.00, 31.61, 17.02, 14.23; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3^+$ $[M + H]^+$ 351.1703, found 351.1697.

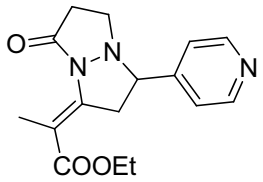
(*E*)-Ethyl 2-(3-(Naphthalen-2-yl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3pa)



3pa

96% yield; pale-yellow solid. IR (film) ν_{max} 3055, 2980, 2930, 2849, 1726, 1649, 1605, 1508, 1445, 1280, 1198, 1174, 1097, 1058, 1020, 860, 822, 736, 702, 479 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.1 Hz, 3H), 2.12 (app. t, 3H), 2.72–2.93 (m, 2H), 3.07–3.19 (m, 2H), 3.56–3.64 (m, 1H), 3.82 (ddd, *J* = 18.3, 7.5, 1.4 Hz, 1H), 3.92 (dd, *J* = 10.0, 7.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 7.48–7.53 (m, 3H), 7.83–7.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.1, 31.5, 43.8, 45.2, 60.4, 69.6, 113.8, 125.0, 126.3, 126.5, 127.0, 127.80, 127.83, 128.8, 133.3, 133.4, 135.2, 143.5, 167.8, 172.2; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3^+$ $[M + H]^+$ 351.1703, found 351.1713.

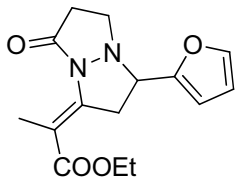
(*E*)-Ethyl 2-(7-Oxo-3-(pyridin-4-yl)tetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3qa)



3qa

86% yield; pale-yellow solid. IR (film) ν_{max} 2980, 2931, 1730, 1650, 1601, 1560, 1445, 1415, 1281, 1101, 1051, 1025, 992, 828, 767, 734, 670, 578 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.07 (app. d, 3H), 2.73–3.05 (m, 4H), 3.61–3.68 (m, 1H), 3.73–3.82 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.31 (d, *J* = 4.0 Hz, 2H), 8.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.0, 31.4, 43.5, 45.7, 60.5, 68.0, 114.1, 129.1, 142.6, 147.2, 150.4, 167.6, 171.8; HRMS (ESI) calcd for $C_{16}H_{20}N_3O_3^+$ $[M + H]^+$ 302.1499, found 302.1497.

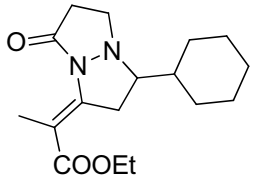
(*E*)-Ethyl 2-(3-(Furan-2-yl)-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ra)



3ra

99% yield; pale-yellow solid. IR (film) ν_{max} 2976, 2928, 2867, 1714, 1628, 1601, 1520, 1464, 1394, 1350, 1285, 1232, 1151, 1038, 996, 949, 857, 738, 697, 650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.1 Hz, 3H), 2.06 (s, 3H), 2.70 (s, br, 2H), 3.47 (app. d, br, 4H), 3.95 (s, br, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 6.31 (s, 1H), 6.36 (dd, *J* = 3.2, 1.9 Hz, 1H), 7.42 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 17.0, 31.2, 39.2, 45.0, 60.4, 60.9, 77.2, 109.0, 110.6, 114.1, 143.1, 150.6, 167.7, 172.4; HRMS (ESI) calcd for $C_{15}H_{19}N_2O_4^+$ $[M + H]^+$ 291.1339, found 291.1334.

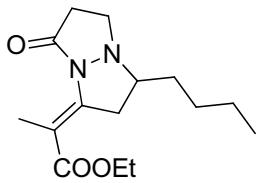
(*E*)-Ethyl 2-(3-Cyclohexyl-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3sa)



3sa

55% yield; white solid. IR (film) ν_{max} 3055, 2925, 2852, 1715, 1634, 1601, 1541, 1521, 1507, 1448, 1338, 1278, 1112, 801, 767, 736, 702, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97–1.30 (m, 8H), 1.44–1.52 (m, 1H), 1.63–1.78 (m, 5H), 1.99 (t, *J* = 1.7 Hz, 3H), 2.56 (td, *J* = 9.0, 6.2 Hz, 1H), 2.73 (ddd, *J* = 16.7, 9.2, 5.1 Hz, 1H), 2.85–2.94 (m, 2H), 3.03 (dd, *J* = 19.8, 9.4 Hz, 1H), 3.42 (ddd, *J* = 18.5, 8.5, 1.7 Hz, 1H), 3.68–3.74 (m, 1H), 4.14–4.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 16.9, 25.8, 26.1, 26.3, 28.1, 30.3, 33.4, 37.7, 40.6, 50.1, 60.2, 70.7, 111.9, 142.5, 168.0, 168.2; HRMS (ESI) calcd for $C_{17}H_{27}N_2O_3^+$ $[M + H]^+$ 307.2016, found 307.2010.

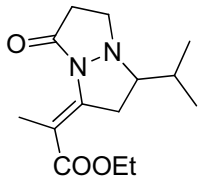
(*E*)-Ethyl 2-(3-Butyl-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ta)



3ta

41% yield; white solid. IR (film) ν_{max} 2930, 1716, 1647, 1557, 1541, 1522, 1508, 1457, 1339, 1279, 1121 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 6.7 Hz, 3 H), 1.26–1.46 (m, 9H), 2.02 (d, *J* = 1.9 Hz, 3H), 2.63–2.86 (m, 4H), 3.06–3.15 (m, 1H), 3.47–3.58 (m, 1H), 3.65–3.74 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.3, 16.9, 22.8, 28.1, 32.0, 32.4, 40.5, 47.0, 60.3, 65.8, 112.9, 143.4, 168.0, 170.2; HRMS (ESI) calcd for $C_{15}H_{25}N_2O_3^+$ $[M + H]^+$ 281.1860, found 281.1865.

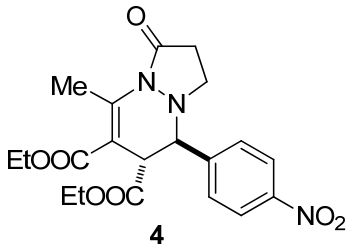
(*E*)-Ethyl 2-(3-Isopropyl-7-oxotetrahydropyrazolo[1,2-a]pyrazol-1(5*H*)-ylidene)propanoate (3ua)



3ua

48% yield; yellow solid. IR (film) ν_{max} 2961, 1710, 1636, 1557, 1541, 1522, 1508, 1457, 1388, 1349, 1280, 1198, 1125, 767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (dd, *J* = 11.9, 6.8 Hz, 6H), 1.30 (t, *J* = 7.1 Hz, 3 H), 1.77–1.88 (m, 1H), 2.00 (d, *J* = 1.9 Hz, 3H), 2.55–2.63 (m, 1H), 2.72–3.09 (m, 4H), 3.34–3.45 (m, 1H), 3.67–3.76 (m, 1H), 4.14–4.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 17.0, 17.2, 19.7, 29.9, 33.3, 36.8, 49.5, 60.2, 71.2, 112.2, 142.7, 168.0, 168.5; HRMS (ESI) calcd for $C_{14}H_{23}N_2O_3^+$ $[M + H]^+$ 267.1703, found 267.1706.

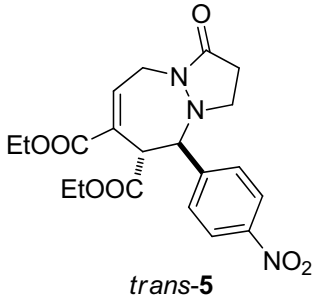
Diethyl 8-Methyl-5-(4-nitrophenyl)-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a]pyridazine-6,7-dicarboxylate (4)



4

Pale-yellow solid. IR (film) ν_{max} 2918, 1710, 1647, 1607, 1558, 1523, 1457, 1348, 1211, 1176, 1127, 1092, 1025, 896, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 311H), 2.50–2.75 (m, 3H), 2.86 (d, *J* = 1.7 Hz, 3H), 3.09 (ddd, *J* = 9.5, 8.3, 4.0 Hz, 1H), 3.77–3.80 (m, 1H), 3.90–4.02 (m, 3H), 4.11–4.19 (m, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 8.26 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1, 16.0, 31.8, 48.4, 51.3, 60.6, 61.1, 68.3, 106.8, 124.2, 129.4, 144.0, 145.4, 148.3, 166.3, 169.2, 171.1; HRMS (ESI) calcd for $C_{20}H_{24}N_3O_7^+$ $[M + H]^+$ 418.1609, found 418.1592.

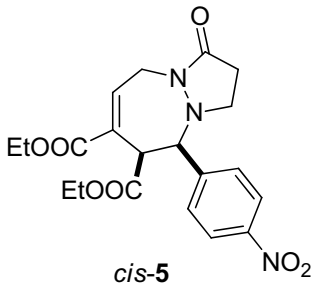
***trans*-Diethyl 5-(4-Nitrophenyl)-1-oxo-1,2,3,5,6,9-hexahydropyrazolo[1,2-a][1,2]diazepine-6,7-dicarboxylate (*trans*-5)**



trans-**5**

Pale-yellow solid. IR (film) ν_{max} 2917, 1714, 1653, 1606, 1521, 1457, 1347, 1231, 1107, 1034, 856, 777, 748, 708, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 2.23 (dd, *J* = 16.2, 7.1 Hz, 1H), 2.94 (dd, *J* = 11.9, 8.0 Hz, 1H), 3.11–3.18 (m, 1H), 3.55 (td, *J* = 12.7, 7.3 Hz, 1H), 3.95–4.07 (m, 4H), 4.09–4.16 (m, 1H), 4.26 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.78 (dd, *J* = 19.6, 2.0 Hz, 1H), 5.32 (s, 1H), 7.13 (dd, *J* = 4.2, 2.3 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 14.3, 29.2, 46.8, 47.6, 51.3, 61.3, 62.2, 69.8, 123.6, 125.8, 128.3, 138.9, 147.2, 147.6, 165.5, 170.5, 174.5; HRMS (ESI) calcd for $C_{20}H_{24}N_3O_7^+$ $[M + H]^+$ 418.1609, found 418.1593.

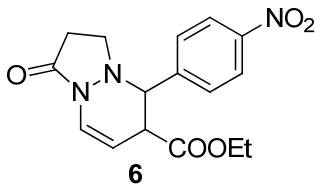
***cis*-Diethyl 5-(4-Nitrophenyl)-1-oxo-1,2,3,5,6,9-hexahydropyrazolo[1,2-a][1,2]diazepine-6,7-dicarboxylate (*cis*-5)**



cis-**5**

Pale-yellow solid. IR (film) ν_{max} 2980, 2919, 2850, 1710, 1655, 1605, 1522, 1457, 1347, 1231, 1034, 854, 649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (dt, *J* = 12.2, 7.1 Hz, 6H), 2.26 (ddd, *J* = 16.2, 8.1, 2.0 Hz, 1H), 2.73–2.82 (m, 1H), 2.97 (t, *J* = 9.2 Hz, 1H), 3.47 (td, *J* = 11.6, 8.4 Hz, 1H), 3.95–4.07 (m, 4H), 4.33–4.43 (m, 3H), 4.81 (dd, *J* = 17.6, 3.9 Hz, 1H), 7.20 (t, *J* = 4.9 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 2H), 8.17 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 14.4, 29.3, 47.0, 47.8, 51.4, 61.4, 62.3, 70.0, 123.7, 126.0, 128.4, 139.0, 147.3, 147.8, 165.6, 170.6, 174.6; HRMS (ESI) calcd for $C_{20}H_{24}N_3O_7^+$ $[M + H]^+$ 418.1609, found 418.1610.

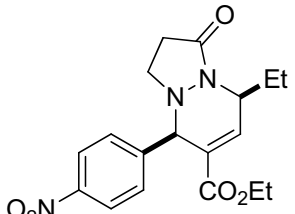
Ethyl 5-(4-Nitrophenyl)-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a]pyridazine-6-carboxylate (6)



6

Pale-yellow solid. IR (film) ν_{max} 2985, 2950, 2905, 1701, 1647, 1601, 1567, 1541, 1523, 1473, 1457, 1410, 1348, 1280, 1178, 1119, 852 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (t, *J* = 7.1 Hz, 3H), 2.52–2.65 (m, 3H), 3.10 (dd, *J* = 8.1, 4.6 Hz, 1H), 3.59 (dt, *J* = 8.8, 2.4 Hz, 1H), 3.98–4.09 (m, 3H), 5.24 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.09 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 8.25 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 30.8, 49.2, 50.2, 61.4, 67.6, 104.3, 120.7, 124.0, 144.7, 147.8, 148.2, 165.1, 170.0; HRMS (ESI) calcd for $C_{16}H_{18}N_3O_5^+$ [M + H]$^+$ 332.1241, found 332.1229.

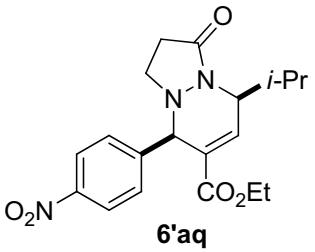
Ethyl 8-Ethyl-5-(4-nitrophenyl)-1-oxo-2,3,5,8-tetrahydro-1*H*-pyrazolo[1,2-a]pyridazine-6-carboxylate (6'ap)



6'ap

Yellow semi-solid. IR (neat) ν_{max} 2973, 1712, 1685, 1650, 1605, 1521, 1490, 1460 1411, 1373, 1347, 1263, 1249, 1204, 1180, 1099, 1033, 917, 857, 839, 812, 749, 732, 711, 697, 694, 683, 676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.30 (s, 1H), 4.87 (s, 1H), 4.78 (tt, *J* = 10.7, 5.3 Hz, 1H), 4.25–3.93 (m, 2H), 3.57 (td, *J* = 12.2, 9.5 Hz, 1H), 3.34–3.14 (m, 1H), 2.09–1.73 (m, 3H), 1.19 (t, *J* = 7.1 Hz, 4H), 1.08 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 170.0, 163.7, 148.0, 143.3, 137.6, 130.2, 130.0, 123.7, 63.1, 61.1, 52.1, 45.6, 30.0, 26.7, 13.9, 10.5; HRMS (EI) calcd for $C_{18}H_{21}N_3O_5^+$ [M^+] 359.1481, found 359.1473.

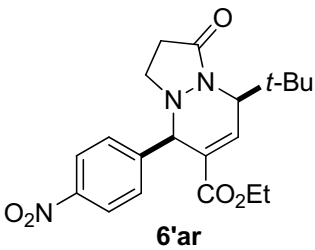
Ethyl 8-Isopropyl-5-(4-nitrophenyl)-1-oxo-2,3,5,8-tetrahydro-1*H*-pyrazolo[1,2-a]pyridazine-6-carboxylate (6′aq)



6'aq

Yellow semi-solid. IR (neat) ν_{max} 2959, 2925, 1713, 1689, 1521, 1462, 1408, 1374, 1348, 1283, 1263, 1249, 1100, 1076, 837, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.28 (dd, *J* = 2.8, 2.1 Hz, 1H), 4.87 (s, 1H), 4.65 (dd, *J* = 6.1, 3.6 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.59 (td, *J* = 12.3, 9.4 Hz, 1H), 3.26 (t, *J* = 10.6 Hz, 1H), 2.19 (dq, *J* = 13.3, 6.7 Hz, 1H), 1.96 (ddd, *J* = 16.9, 9.3, 1.6 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.12–1.03 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 163.8, 148.1, 143.4, 136.7, 130.8, 130.0, 123.8, 63.1, 61.2, 56.2, 45.5, 33.3, 30.0, 19.3, 14.0; HRMS (ESI) calcd for $C_{19}H_{24}N_3O_5^+$ $[M + H]^+$ 374.1710, found 374.1694.

Ethyl 8-(*tert*-Butyl)-5-(4-nitrophenyl)-1-oxo-2,3,5,8-tetrahydro-1*H*-pyrazolo[1,2-a]pyridazine-6-carboxylate (6′ar)

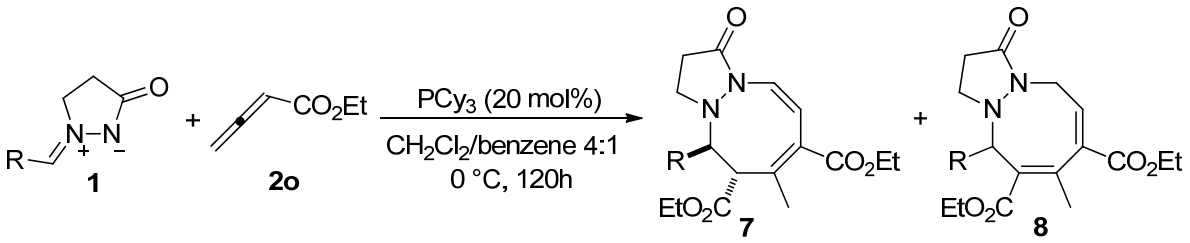


6'ar

Yellow semi-solid. IR (neat) ν_{max} 2959, 2924, 1691, 1522, 1401, 1393, 1374, 1347, 1283, 1262, 1230, 1097, 1077, 1057, 858, 840, 812, 750, 738, 676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.65–7.27 (m, 3H), 4.87 (s, 1H), 4.59 (d, *J* = 3.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.60 (td, *J* = 12.5, 9.3 Hz, 1H), 3.35–3.21 (m, 1H), 1.98–1.85 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.11 (s, 9H), 1.05–0.98 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 163.8, 148.2, 143.5, 136.0, 131.3, 123.8, 63.0, 61.2, 59.3, 45.5, 37.9, 29.9, 27.4, 14.0; HRMS (ESI) calcd for $C_{20}H_{25}N_3NaO_5$ [M + Na] 410.1686, found 410.1681.

General Procedure for the [3 + 2 + 3] Cycloadditions of Azomethine Imines and Allenoates

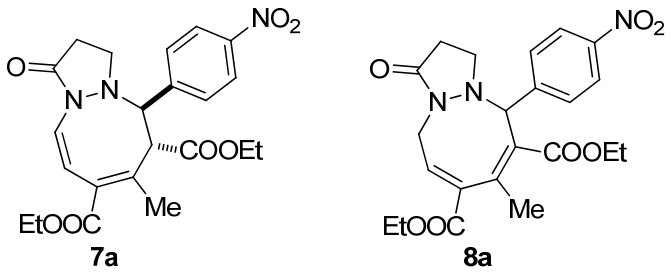
Tricyclohexylphosphine (7.01 mg, 0.025 mmol) was added to a solution of the azomethine imine **1** (0.125 mmol) and ethyl 2,3-butadienoate (**2o**, 28 mg, 0.25 mmol) in DCM (4 mL) and benzene (1 mL) in an oven-dried 15 mL Schlenk tube at 0 °C. The mixture was stirred at 0 °C for 120 h and then concentrated. The residue was purified through flash column chromatography (EtOAc/hexane) to afford the corresponding cycloaddition products **7**/**8**.



Notes:

1. The NMR spectroscopic data were read using the following principles: (a) If the peaks of two isomers did not overlap, the peaks of each isomer were read and are reported separately. (b) If the peaks of the two isomers overlap, the peaks of each isomer were not read and are not described.
2. The IR data were recorded using the thin film method. The samples were dissolved in DCM; the solution was placed on the salt plate; DCM was evaporated; the data were collected. In principle, the data collected were those of the mixture.
3. HRMS data were recorded from a solution of the mixture of the two isomers in $CHCl_3$.

(7*E*,9*Z*)-Diethyl 7-Methyl-5-(4-nitrophenyl)-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7a**); **(6*E*,8*E*)-Diethyl 7-Methyl-5-(4-nitrophenyl)-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8a**)

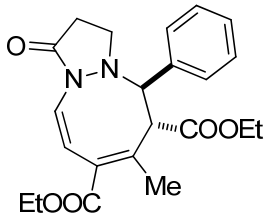


7a + **8a**: 65% yield; yellow solid. IR (film) ν_{max} 2918, 1715, 1698, 1652, 1541, 1521, 1473, 1456, 1418, 1396, 1347, 1243 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}N_3O_7^+$ $[M + H]^+$ 444.1765, found 444.1744.

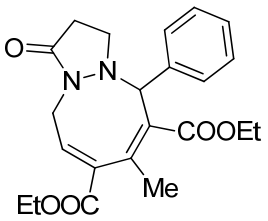
8a (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 8.10–7.98 (m, 2H), 7.62 (dd, *J* = 9.0, 1.1 Hz, 2H), 6.05 (dd, *J* = 4.7, 2.8 Hz, 1H), 5.64 (s, 1H), 4.87 (dd, *J* = 19.2, 2.8 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.05–3.87 (m, 3H), 3.66 (dd, *J* = 19.2, 4.7 Hz, 1H), 3.57–3.45 (m, 1H), 2.71 (ddd, *J* = 16.7, 12.7, 9.0 Hz, 1H), 2.30 (dd, *J* = 15.1, 7.5 Hz, 1H), 2.22 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.14 (dd, *J* = 10.0, 4.3 Hz, 3H).

7a (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.9 Hz, 2H), 7.52–7.19 (m, 2H), 6.78 (t, *J* = 3.5 Hz, 1H), 5.43 (s, 1H), 4.30–4.20 (m, 2H), 4.12 (m, 3H), 2.61–2.38 (m, 1H), 2.18 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

(7*E*,9*Z*)-Diethyl 7-Methyl-1-oxo-5-phenyl-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7b**); **(6*E*,8*E*)-Diethyl 7-Methyl-1-oxo-5-phenyl-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8b**)



7b



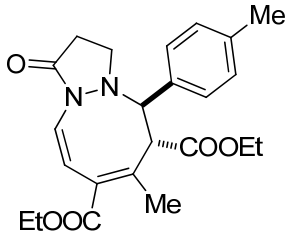
8b

7b + **8b**: 81% yield; yellow solid. IR (film) ν_{max} 2980, 1716, 1699, 1662, 1567, 1541, 1491, 1417, 1396, 1366, 1241, 1201, 1098, 1039, 760, 736, 705, 668 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_5^+$ $[M + H]^+$ 399.1914, found 399.1918.

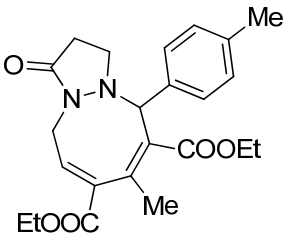
8b (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.43–7.07 (m, 4H), 6.13 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.48 (s, 1H), 4.68 (dd, *J* = 18.3, 3.6 Hz, 1H), 4.34–4.26 (m, 2H), 4.10–3.95 (m, 2H), 3.85–3.71 (m, 1H), 3.39 (ddd, *J* = 37.9, 20.0, 15.5 Hz, 1H), 2.74 (ddd, *J* = 16.8, 12.2, 9.0 Hz, 1H), 2.35–2.17 (m, 1H), 2.15 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 168.8, 164.4, 146.4, 141.0, 135.0, 133.7, 128.3, 127.9, 126.7, 125.8, 71.5, 61.2, 60.8, 53.2, 43.6, 30.5, 22.7, 14.2, 14.0.

7b (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81 (s, 1H), 5.14 (s, 1H), 2.65–2.45 (m, 1H), 2.07 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 165.5, 137.2, 136.1, 127.4, 127.3, 61.3, 60.6, 30.7, 14.1, 13.8.

(7*E*,9*Z*)-Diethyl 7-Methyl-1-oxo-5-(*p*-tolyl)-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7c**); **(6*E*,8*E*)-Diethyl 7-Methyl-1-oxo-5-(*p*-tolyl)-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8c**)



7c



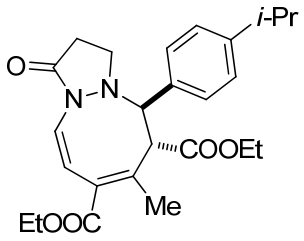
8c

7c + **8c**: 64% yield; yellow solid. IR (film) ν_{max} 2980, 1716, 1699, 1652, 1557, 1541, 1508, 1417, 1395, 1366, 1240, 1200, 1097, 1040, 762, 668 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{29}N_2O_5^+$ $[M + H]^+$ 413.2071, found 413.2081.

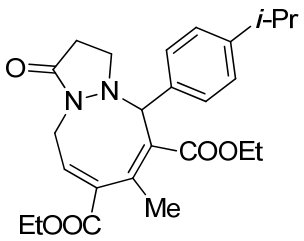
8c (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–6.94 (m, 1H), 6.18 (dd, *J* = 5.1, 4.0 Hz, 2H), 5.40 (s, 1H), 4.63 (dd, *J* = 17.9, 3.9 Hz, 1H), 4.35–4.18 (m, 2H), 4.17–3.95 (m, 2H), 3.91–3.64 (m, 2H), 3.37 (ddd, *J* = 11.6, 8.9, 2.3 Hz, 1H), 2.88–2.64 (m, 1H), 2.27 (s, 3H), 2.26–2.19 (m, 1H), 2.13 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 168.9, 164.5, 145.4, 137.9, 136.3, 135.4, 133.6, 129.0, 128.7, 125.9, 71.4, 61.2, 60.8, 52.9, 43.6, 30.5, 22.7, 21.0, 14.1, 13.8.

7c (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 1H), 5.05 (s, 1H), 2.65–2.45 (m, 1H), 2.32 (s, 3H), 2.06 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 168.9, 164.5, 137.0, 136.1, 134.1, 127.1, 61.3, 60.7, 30.8, 21.0, 14.1, 13.8.

(7*E*,9*Z*)-Diethyl 5-(4-Isopropylphenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7d**); **(6*E*,8*E*)-Diethyl 5-(4-Isopropylphenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8d**)



7d



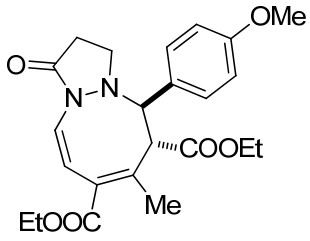
8d

7d + **8d**: 67% yield; yellow solid. IR (film) ν_{max} 2960, 1716, 1698, 1652, 1567, 1541, 1508, 1457, 1417, 1396, 1365, 1240, 1198, 1097, 1040, 755 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{33}N_2O_5^+$ $[M + H]^+$ 441.2384, found 441.2385.

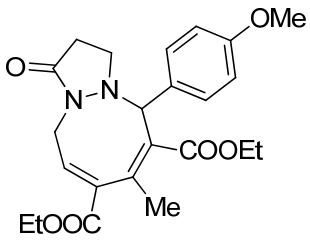
8d (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.7 Hz, 1H), 7.22–7.13 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.19 (dd, *J* = 5.1, 3.9 Hz, 1H), 5.43 (s, 1H), 4.65 (dd, *J* = 18.0, 3.8 Hz, 1H), 4.37–3.95 (m, 4H), 3.90–3.66 (m, 2H), 2.80–2.90 (m, 2H), 2.36–2.17 (m, 1H), 2.14 (s, 3H), 1.37–1.28 (m, 3H), 1.27–1.16 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 168.8, 164.4, 147.4, 145.6, 138.3, 135.3, 133.6, 126.4, 126.0, 125.9, 71.4, 61.1, 60.8, 53.0, 43.6, 33.6, 30.5, 24.0, 23.9, 22.7, 14.2, 14.0.

7d (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 6.83 (s, 1H), 5.02 (s, 1H), 2.67–2.47 (m, 1H), 2.05 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 165.5, 148.1, 145.6, 136.1, 134.5, 127.2, 61.3, 60.6, 33.7, 30.8, 29.6, 23.9, 23.9, 14.1, 13.8.

(7*E*,9*Z*)-Diethyl 5-(4-Methoxyphenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7e**); **(6*E*,8*E*)-Diethyl 5-(4-Methoxyphenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8e**)



7e



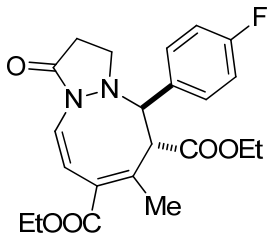
8e

7e + **8e**: 76% yield; yellow solid. IR (film) ν_{max} 2930, 1719, 1699, 1608, 1541, 1506, 1457, 1366, 1338, 1277, 1251, 1201, 1143, 1110, 1074, 1046, 931, 772, 742 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{29}N_2O_6^+$ $[M + H]^+$ 429.2020, found 429.2022.

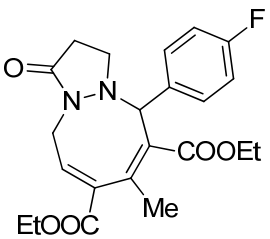
8e (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 3.0, 1.5 Hz, 2H), 6.77–6.70 (m, 2H), 6.22 (dd, *J* = 5.2, 4.2 Hz, 1H), 5.34 (s, 1H), 4.60 (dd, *J* = 17.7, 4.2 Hz, 1H), 4.34–4.20 (m, 2H), 4.07 (ttd, *J* = 14.2, 7.1, 3.5 Hz, 2H), 3.85 (dd, *J* = 17.7, 5.3 Hz, 1H), 3.76 (s, 3H), 3.72–3.61 (m, 1H), 3.35 (ddd, *J* = 11.6, 8.8, 2.5 Hz, 1H), 2.76 (ddd, *J* = 16.8, 11.9, 8.9 Hz, 1H), 2.37–2.15 (m, 1H), 2.12 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 168.9, 164.6, 158.6, 144.6, 135.7, 133.4, 132.9, 127.3, 113.8, 113.4, 71.2, 61.2, 60.9, 55.2, 52.7, 43.6, 30.5, 22.7, 14.2, 14.1.

7e (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.01 (s, 1H), 3.79 (s, 3H), 2.66–2.37 (m, 1H), 2.04 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 165.5, 162.3, 158.8, 136.0, 129.1, 128.52, 128.46, 100.0, 61.3, 60.7, 55.2, 30.8, 14.1, 13.9.

(7*E*,9*Z*)-Diethyl 5-(4-Fluorophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (7f); (6*E*,8*E*)-Diethyl 5-(4-Fluorophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (8f)



7f



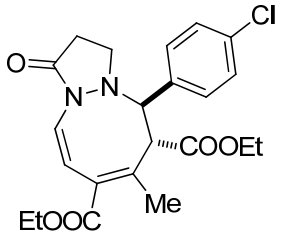
8f

7f + **8f**: 68% yield; yellow solid. IR (film) ν_{max} 2931, 1715, 1699, 1614,1567, 1541, 1417, 1396, 1367, 1242, 1096, 1039, 862, 758 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}FN_2O_5^+$ $[M + H]^+$ 417.1820, found 417.1812.

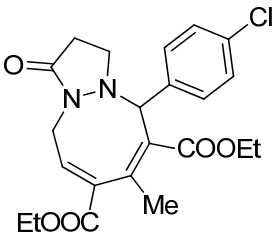
8f (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.9, 5.5 Hz, 1H), 6.87 (dd, *J* = 17.7, 9.0 Hz, 1H), 6.15 (dd, *J* = 4.9, 3.6 Hz, 1H), 5.39 (d, *J* = 26.0 Hz, 1H), 4.71 (dd, *J* = 18.4, 3.5 Hz, 1H), 4.38–4.27 (m, 1H), 4.14–3.99 (m, 2H), 3.87–3.68 (m, 1H), 3.48–3.36 (m, 1H), 2.75 (ddd, *J* = 16.8, 12.2, 9.0 Hz, 1H), 2.39–2.17 (m, 1H), 2.15 (s, 1H), 1.36 (t, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 168.8, 164.4, 161.7, 146.7, 136.8, 135.1, 133.8, 127.4, 115.3, 114.7, 71.0, 61.4, 61.0, 53.3, 43.8, 30.4, 22.8, 14.2, 14.0.

7f (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.20 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.81 (s, 1H), 5.12 (s, 1H), 4.28–4.16 (m, 1H), 2.66–2.46 (m, 1H), 2.08 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 165.5, 136.2, 133.0, 61.4, 60.8, 30.6, 14.1, 13.9.

(7*E*,9*Z*)-Diethyl 5-(4-Chlorophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (7g); (6*E*,8*E*)-Diethyl 5-(4-Chlorophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (8g)



7g



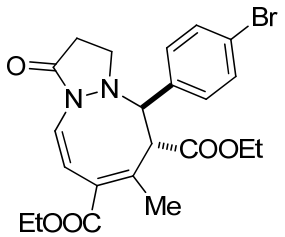
8g

7g + **8g**: 63% yield; yellow solid. IR (film) ν_{max} 2980, 1715, 1698, 1647, 1636, 1557, 1541, 1521, 1508, 1489, 1473, 1456, 1418, 1396, 1241 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}ClN_2O_5^+$ $[M + H]^+$ 433.1525, found 433.1527.

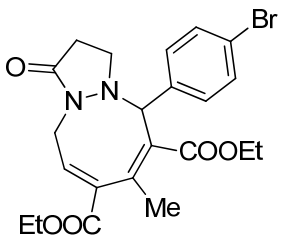
8g (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.11 (m, 1H), 6.14 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.49 (s, 1H), 4.70 (dd, *J* = 18.3, 3.6 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.13–3.94 (m, 2H), 3.88–3.68 (m, 1H), 3.50–3.35 (m, 1H), 2.75 (ddd, *J* = 16.7, 12.2, 9.0 Hz, 1H), 2.37–2.18 (m, 1H), 2.16 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 168.8, 164.4, 146.4, 141.0, 135.1, 133.8, 128.4, 128.0, 126.7, 125.8, 71.5, 61.2, 60.8, 53.2, 43.7, 30.5, 22.8, 14.2, 14.0.

7g (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 1H), 5.14 (s, 1H), 4.27–4.16 (m, 2H), 2.67–2.47 (m, 1H), 2.08 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 165.5, 137.3, 136.2, 127.5, 127.3, 61.3, 60.7, 30.7, 14.1, 13.8.

(7*E*,9*Z*)-Diethyl 5-(4-Bromophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (7h); (6*E*,8*E*)-Diethyl 5-(4-Bromophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (8h)



7h



8h

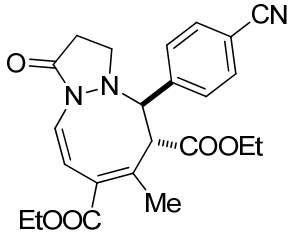
7h + **8h**: 77% yield; yellow solid. IR (film) ν_{max} 2924, 2853, 1715, 1699, 1652, 1557, 1541, 1522, 1508, 1488, 1456, 1396, 1243, 1097, 1038, 1010, 822 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}BrN_2O_5^+$ $[M + H]^+$ 477.1020, found 477.1013.

8h (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.26 (m, 4H), 6.13 (dd, *J* = 4.9, 3.3 Hz, 1H), 5.45 (s, 1H), 4.75 (dd, *J* = 18.6, 3.3 Hz, 1H), 4.37–4.28 (m, 2H), 4.15–3.95 (m, 2H), 3.83 (td, *J* = 12.1, 8.6 Hz, 1H), 3.71 (dd, *J* = 18.6, 4.9 Hz, 1H), 3.51–3.38 (m, 1H), 2.73 (ddd, *J* = 16.8, 12.4, 8.9 Hz, 1H), 2.34–2.19 (m, 1H), 2.17 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 168.7, 164.2, 147.6, 140.4, 134.9, 133.9, 131.5, 131.0, 127.6, 126.7, 120.4, 70.9, 61.4, 61.0, 53.6, 43.7, 30.4, 22.8, 14.2, 14.0.

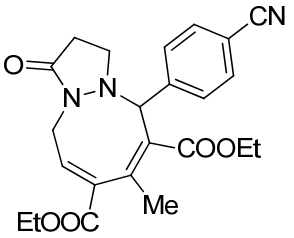
7h (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.80 (s, 1H), 5.15 (s, 1H), 4.27–4.18 (m, 2H), 2.64–2.46 (m, 1H), 2.10 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 165.4, 136.4, 136.2, 128.6, 121.1, 70.9, 60.8, 30.6, 14.1, 13.9.

At –10 °C, only the isomer **7h** exists in CD_2Cl_2 solution: ^1H NMR (300 MHz, CD_2Cl_2) δ 7.60–7.49 (m, 2H), 7.39 (d, *J* = 6.8 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 10.4 Hz, 1H), 5.37 (s, 1H), 4.38–4.16 (m, 3H), 4.03–3.85 (m, 3H), 3.62–3.43 (m, 1H), 3.31–3.16 (m, 1H), 2.04 (s, 3H), 1.82–1.74 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), 1.03–0.93 (m, 1H).

(7*E*,9*Z*)-Diethyl 5-(4-Cyanophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (7i); (6*E*,8*E*)-Diethyl 5-(4-Cyanophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (8i)



7i



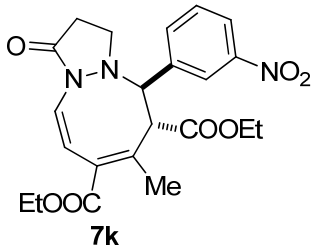
8i

7i + **8i**: 51% yield; yellow solid. IR (film) ν_{max} 2923, 1715, 1697, 1652, 1636, 1557, 1541, 1521, 1507, 1489, 1473, 1456, 1418, 1396, 1242, 1039, 855, 737 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{26}N_3O_5^+$ $[M + H]^+$ 424.1867, found 424.1857.

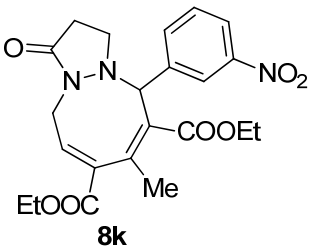
8i (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 6.04 (dt, *J* = 18.1, 9.1 Hz, 1H), 5.59 (s, 1H), 4.84 (dd, *J* = 19.1, 2.8 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.16–3.82 (m, 2H), 3.64 (dd, *J* = 19.1, 4.8 Hz, 1H), 3.53–3.44 (m, 1H), 2.70 (ddd, *J* = 16.8, 12.7, 9.0 Hz, 1H), 2.31–2.22 (m, 1H), 2.19 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 168.5, 163.9, 149.2, 147.1, 134.6, 134.2, 132.1, 131.8, 126.4, 125.7, 118.7, 110.4, 71.2, 61.6, 61.1, 54.0, 43.8, 30.3, 22.8, 14.2, 14.0.

7i (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 6.77 (t, *J* = 3.6 Hz, 1H), 5.37 (s, 1H), 4.30–4.16 (m, 2H), 2.61–2.38 (m, 1H), 2.16 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 165.3, 143.2, 136.4, 127.4, 118.5, 111.0, 61.5, 61.0, 43.1, 30.4, 22.1, 14.1, 13.9.

(7*E*,9*Z*)-Diethyl 7-Methyl-5-(3-nitrophenyl)-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (7k); (6*E*,8*E*)-Diethyl 7-Methyl-5-(3-nitrophenyl)-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (8k)



7k



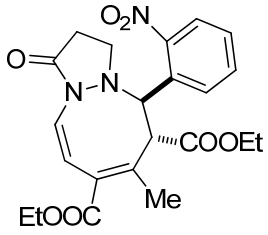
8k

7k + **8k**: 77% yield; yellow solid. IR (film) ν_{max} 2918, 1716, 1698, 1683, 1647, 1557, 1541, 1522, 1508, 1457, 669 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}N_3O_7^+$ $[M + H]^+$ 444.1765, found 444.1762.

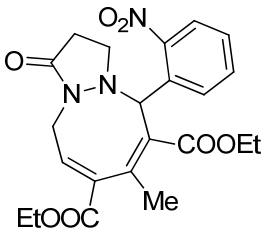
8k (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (t, *J* = 2.5 Hz, 1H), 8.06–7.97 (m, 1H), 7.73 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 6.05 (dt, *J* = 23.7, 11.8 Hz, 1H), 5.64 (s, 1H), 4.86 (dd, *J* = 19.2, 2.8 Hz, 1H), 4.36 (p, *J* = 7.2 Hz, 2H), 4.08–3.81 (m, 3H), 3.67 (dd, *J* = 19.2, 4.7 Hz, 1H), 3.58–3.41 (m, 1H), 2.72 (ddd, *J* = 16.8, 12.6, 8.9 Hz, 1H), 2.30 (dd, *J* = 15.1, 7.6 Hz, 1H), 2.21 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 168.5, 164.0, 149.4, 148.2, 144.0, 134.6, 134.4, 131.8, 128.9, 125.6, 121.8, 120.7, 70.8, 61.7, 61.2, 54.1, 44.0, 30.4, 23.0, 14.2, 13.9.

7k (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.17–8.09 (m, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 3.6 Hz, 1H), 5.41 (s, 1H), 4.31–4.18 (m, 2H), 4.18–4.08 (m, 2H), 2.62–2.48 (m, 1H), 2.17 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 165.4, 148.4, 139.8, 136.5, 132.9, 129.3, 122.2, 61.5, 61.1, 22.1, 14.1.

(7*E*,9*Z*)-Diethyl 7-Methyl-5-(2-nitrophenyl)-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (7l); (6*E*,8*E*)-Diethyl 7-Methyl-5-(2-nitrophenyl)-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (8l)



7l



8l

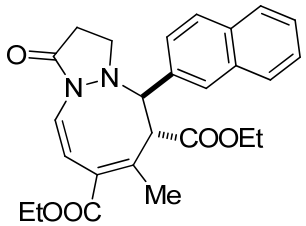
7l + **8l**: 73% yield; yellow solid. IR (film) ν_{max} 2918, 2860, 1716, 1697, 1652, 1567, 1526, 1508, 1457, 1418, 1396, 1362, 1265, 1040, 739, 704 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}N_3O_7$ $[M + H]^+$ 444.1765, found 444.1757.

8l (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.46 (td, *J* = 7.8, 1.3 Hz, 1H), 7.31 (m, 1H), 6.26 (dd, *J* = 5.3, 3.0 Hz, 1H), 4.78 (dd, *J* = 18.6, 3.0 Hz, 1H), 4.41–4.27 (m, 2H), 4.09 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.97–3.73 (m, 3H), 3.71–3.58 (m, 1H), 3.02 (ddd, *J* = 16.6, 12.8, 8.8 Hz, 1H), 2.22 (dt, *J* = 14.9, 7.5 Hz, 1H), 2.10 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 168.3,

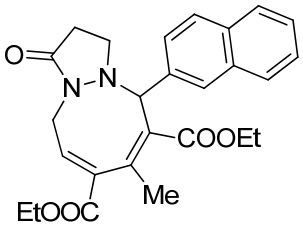
164.0, 148.2, 147.0, 136.2, 135.0, 134.3, 131.6, 129.5, 127.6, 127.1, 124.5, 69.0, 61.4, 61.0, 54.7, 43.8, 30.3, 22.6, 14.1, 13.8.

7l (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (s, 1H), 4.27–4.17 (m, 2H), 2.71–2.55 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 2H).

(7*E*,9*Z*)-Diethyl 7-Methyl-5-(naphthalen-2-yl)-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7p**); **(6*E*,8*E*)-Diethyl 7-Methyl-5-(naphthalen-2-yl)-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8p**)



7p



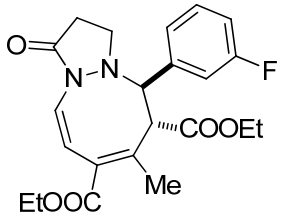
8p

7p + **8p**: 76% yield; yellow solid. IR (film) ν_{max} 2940, 1715, 1697, 1662, 1557, 1541, 1521, 1508, 1473, 1456, 1417, 1396, 1363, 1231, 1198, 1039 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{29}N_2O_5$ $[M + H]^+$ 449.2098, found 449.2085.

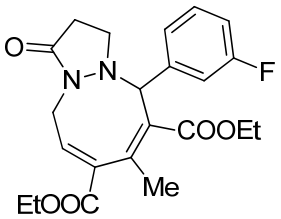
8p (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.63 (m, 4H), 7.60–7.34 (m, 3H), 6.14–6.00 (m, 1H), 5.67 (s, 1H), 4.71 (dd, *J* = 18.2, 3.6 Hz, 1H), 4.42–4.21 (m, 2H), 4.06 (dt, *J* = 14.0, 5.3 Hz, 1H), 3.95–3.73 (m, 2H), 3.55–3.42 (m, 1H), 2.81 (ddd, *J* = 16.8, 12.3, 9.0 Hz, 1H), 2.30 (ddd, *J* = 11.9, 10.3, 5.1 Hz, 1H), 2.20 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 168.8, 164.2, 138.5, 135.2, 133.6, 133.0, 132.5, 127.8, 127.7, 127.43, 125.9, 125.5, 124.4, 124.4, 71.6, 61.3, 60.7, 53.2, 43.7, 30.5, 30.5, 22.8, 14.2, 13.7.

7p (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (s, 1H), 5.31 (s, 1H), 2.71–2.52 (m, 1H), 2.12 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 167.6, 165.5, 146.9, 136.3, 134.7, 133.1, 132.3, 130.8, 128.8, 128.0, 127.8, 127.5, 127.4, 126.2, 126.0, 125.1, 70.9, 65.6, 61.3, 30.7, 30.5, 19.0, 14.1, 13.8, 13.6.

(7*E*,9*Z*)-Diethyl 5-(3-Fluorophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7v**); **(6*E*,8*E*)-Diethyl 5-(3-Fluorophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8v**)



7v



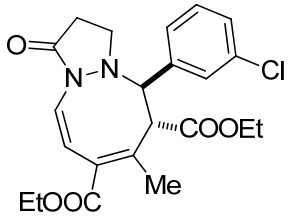
8v

7v + **8v**: 79% yield; yellow solid. IR (film) ν_{max} 2982, 2934, 1718, 1698, 1615, 1588, 1541, 1508, 1486, 1438, 1416, 1395, 1367, 1243, 1198, 1065, 1040, 870, 757, 686 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}FN_2O_5^+$ $[M + H]^+$ 417.1820, found 417.1831.

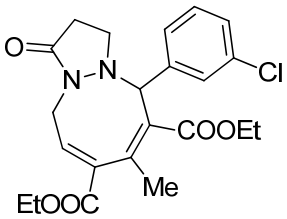
8v (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–6.75 (m, 4H), 6.12 (dd, *J* = 4.8, 3.1 Hz, 1H), 5.53 (s, 1H), 4.79 (dd, *J* = 18.8, 3.1 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.17–3.95 (m, 2H), 3.87 (td, *J* = 12.2, 8.6 Hz, 1H), 3.72 (dd, *J* = 18.8, 4.8 Hz, 1H), 3.53–3.39 (m, 1H), 2.72 (ddd, *J* = 16.9, 12.5, 9.0 Hz, 1H), 2.34–2.20 (m, 1H), 2.19 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 168.6, 164.2, 162.8, 148.1, 144.2, 136.3, 134.6, 134.0, 129.4, 126.2, 121.2, 113.4, 112.7, 71.02, 71.00, 61.4, 61.0, 53.6, 43.8, 30.6, 30.4, 22.9, 14.2, 13.9.

7v (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (s, 1H), 4.28–4.21 (m, 2H), 2.63–2.37 (m, 1H), 2.12 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 165.4, 140.0, 136.3, 129.8, 122.5, 114.2, 113.9, 60.8, 53.6, 43.8, 30.6, 14.1, 13.8.

(7*E*,9*Z*)-Diethyl 5-(3-Chlorophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7w**); **(6*E*,8*E*)-Diethyl 5-(3-Chlorophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8w**)



7w



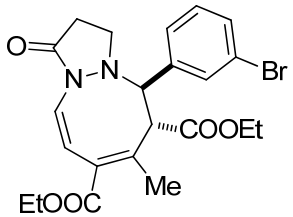
8w

7w + **8w**: 82% yield; yellow solid. IR (film) ν_{max} 2981, 1715, 1698, 1652, 1594, 1570, 1541, 1508, 1473, 1416, 1395, 1366, 1242, 1200, 1039, 792, 749, 686 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}ClN_2O_5^+$ $[M + H]^+$ 433.1525, found 433.1522.

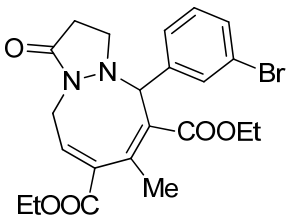
8w (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.46–7.08 (m, 4H), 6.13 (dd, *J* = 4.8, 3.1 Hz, 1H), 5.52 (s, 1H), 4.79 (dd, *J* = 18.8, 3.1 Hz, 1H), 4.40–4.29 (m, 2H), 4.17–3.97 (m, 2H), 3.87 (td, *J* = 12.2, 8.6 Hz, 1H), 3.71 (dd, *J* = 18.9, 4.8 Hz, 1H), 3.53–3.41 (m, 1H), 2.35–2.22 (m, 1H), 2.20 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 168.6, 164.2, 148.3, 143.5, 134.6, 134.2, 134.0, 129.2, 126.8, 126.1, 125.8, 123.8, 70.9, 61.4, 61.1, 53.6, 43.8, 30.4, 22.9, 14.2, 14.0.

7w (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 6.80 (s, 1H), 5.23 (s, 1H), 4.23 (ddd, *J* = 11.2, 9.2, 3.8 Hz, 2H), 3.40–3.27 (m, 1H), 2.64–2.51 (m, 1H), 2.12 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 165.4, 139.4, 136.3, 134.4, 129.6, 127.4, 60.9, 30.5, 14.1, 13.8.

(7*E*,9*Z*)-Diethyl 5-(3-Bromophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (7x); (6*E*,8*E*)-Diethyl 5-(3-Bromophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (8x)



7x



8x

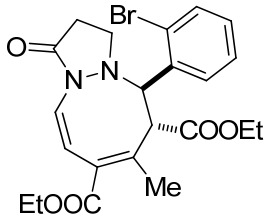
7x + **8x**: 75% yield; yellow solid. IR (film) ν_{max} 3058, 1715, 1698, 1652, 1558, 1541, 1522, 1508, 1489, 1473, 1357, 1417, 1396, 1364, 1241, 1200, 1039, 747 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}BrN_2O_5^+$ $[M + H]^+$ 477.1020, found 477.0997.

8x (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.60–6.97 (m, 4H), 6.12 (dd, *J* = 4.8, 3.1 Hz, 1H), 5.52 (s, 1H), 4.78 (dd, *J* = 18.9, 3.1 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.18–3.97 (m, 2H),

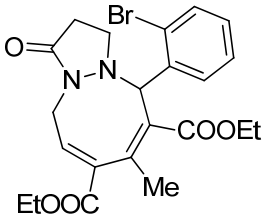
3.86 (td, *J* = 12.3, 8.6 Hz, 1H), 3.69 (dd, *J* = 18.9, 4.8 Hz, 1H), 3.54–3.39 (m, 1H), 2.79–2.63 (m, 1H), 2.35–2.22 (m, 1H), 2.19 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 168.6, 164.2, 148.3, 143.8, 134.6, 134.0, 129.7, 129.5, 128.7, 126.0, 124.3, 122.4, 70.8, 61.4, 61.2, 53.6, 43.8, 30.4, 22.9, 14.2, 14.0.

7x (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (s, 1H), 5.21 (s, 1H), 4.23 (ddt, *J* = 10.4, 6.7, 3.5 Hz, 2H), 3.39–3.27 (m, 1H), 2.62–2.52 (m, 1H), 2.11 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 165.4, 164.3, 164.2, 139.7, 136.3, 130.3, 129.9, 129.8, 125.5, 122.6, 60.9, 53.6, 42.9, 30.5, 21.7, 14.1, 13.9.

(7*E*,9*Z*)-Diethyl 5-(2-Bromophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7y**); **(6*E*,8*E*)-Diethyl 5-(2-Bromophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8y**)



7y



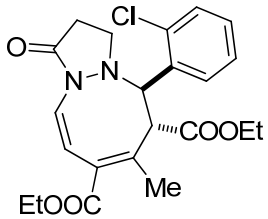
8y

7y + **8y**: 92% yield; yellow solid. IR (film) ν_{max} 3058, 2981, 1715, 1693, 1652, 1566, 1541, 1366, 1252, 1097, 1043, 972, 920, 864, 743, 701, 660, 603 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}BrN_2O_5^+$ $[M + H]^+$ 477.1020, found 477.0998.

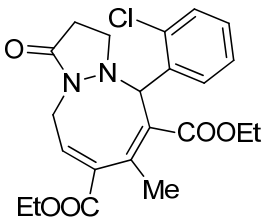
8y (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (ddd, *J* = 9.3, 7.9, 1.5 Hz, 1H), 7.43 (td, *J* = 8.3, 1.4 Hz, 1H), 7.24 (td, *J* = 7.8, 1.2 Hz, 1H), 7.06 (td, *J* = 7.6, 1.6 Hz, 1H), 6.62 (dd, *J* = 6.7, 5.2 Hz, 1H), 5.51 (s, 1H), 4.43 (dd, *J* = 15.8, 5.1 Hz, 1H), 4.36–3.83 (m, 5H), 3.58 (td, *J* = 11.7, 8.0 Hz, 1H), 3.29–3.01 (m, 2H), 2.26 (ddd, *J* = 16.3, 8.0, 1.7 Hz, 1H), 2.04 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 168.6, 164.2, 148.3, 143.8, 134.6, 134.0, 129.7, 129.5, 128.7, 126.0, 124.3, 122.4, 70.8, 61.4, 61.2, 53.6, 43.8, 30.4, 22.9, 14.2, 14.0.

7y (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37–7.29 (m, 1H), 7.15 (ddd, *J* = 9.1, 6.6, 2.7 Hz, 1H), 4.98 (s, 1H), 3.00–2.56 (m, 1H), 2.01 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 6H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 165.4, 139.7, 136.3, 130.3, 129.8, 125.5, 122.6, 60.9, 42.9, 30.5, 29.6, 22.9, 14.1, 13.9.

(7*E*,9*Z*)-Diethyl 5-(2-Chlorophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7z**); **(6*E*,8*E*)-Diethyl 5-(2-Chlorophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8z**)



7z



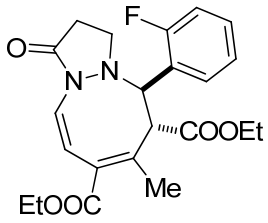
8z

7z + **8z**: 90% yield; yellow solid. IR (film) ν_{max} 2932, 1715, 1541, 1508, 1458, 1396, 1366, 1252, 1199, 1097, 1042, 864, 748, 668 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}ClN_2O_5^+$ $[M + H]^+$ 433.1525, found 433.1534.

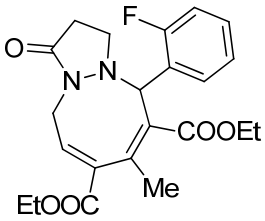
8z (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.47–7.31 (m, 1H), 7.27–7.09 (m, 2H), 6.61 (dd, *J* = 6.7, 4.9 Hz, 1H), 5.57 (s, 1H), 4.46 (dd, *J* = 16.0, 4.9 Hz, 1H), 4.28 (qd, *J* = 7.1, 4.9 Hz, 2H), 4.16 (dd, *J* = 16.1, 6.6 Hz, 1H), 4.07–3.81 (m, 2H), 3.63 (td, *J* = 11.9, 8.0 Hz, 1H), 3.30–3.18 (m, 1H), 3.09 (ddd, *J* = 16.3, 12.1, 8.4 Hz, 1H), 2.25 (ddd, *J* = 16.3, 7.9, 1.6 Hz, 1H), 2.04 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.19–1.09 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 168.1, 164.2, 142.8, 138.6, 138.1, 133.2, 132.9, 130.5, 130.2, 129.4, 128.2, 126.1, 69.1, 61.1, 60.9, 53.4, 43.2, 30.6, 22.0, 14.2, 13.9.

7z (minor isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 1H), 5.01 (s, 1H), 2.02 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 165.1, 129.8, 128.8, 126.4, 61.2, 60.6, 30.9, 14.1, 13.7.

(7*E*,9*Z*)-Diethyl 5-(2-Fluorophenyl)-7-methyl-1-oxo-2,3,5,6-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate (**7zz**); **(*6E*,*8E*)-Diethyl 5-(2-Fluorophenyl)-7-methyl-1-oxo-2,3,5,10-tetrahydro-1*H*-pyrazolo[1,2-a][1,2]diazocine-6,8-dicarboxylate** (**8zz**)



7zz



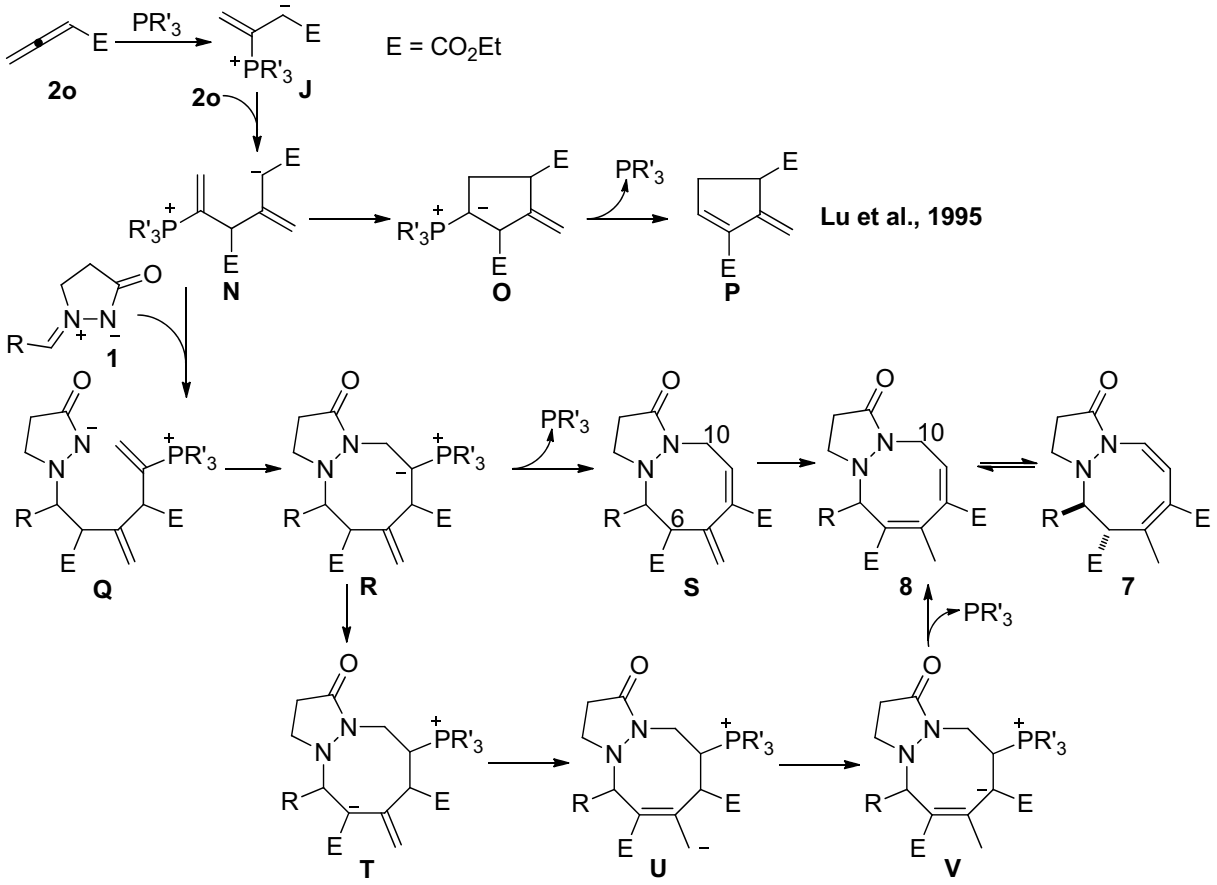
8zz

7zz + **8zz**: 88% yield; yellow solid. IR (film) ν_{max} 2932, 1715, 1699, 1652, 1541, 1484, 1455, 1366, 1241, 1198, 1097, 1041, 864, 812, 761, 650 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{26}FN_2O_5^+$ $[M + H]^+$ 417.1820, found 417.1817.

8zz (major isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (td, *J* = 7.7, 0.9 Hz, 1H), 7.21–7.09 (m, 1H), 7.04 (tt, *J* = 7.9, 4.0 Hz, 1H), 6.91 (ddd, *J* = 10.5, 8.1, 1.2 Hz, 1H), 6.58 (dd, *J* = 6.5, 5.0 Hz, 1H), 5.56 (s, 1H), 4.45 (dd, *J* = 16.1, 4.9 Hz, 1H), 4.29 (dd, *J* = 14.1, 7.1 Hz, 2H), 4.18–3.83 (m, 3H), 3.64 (td, *J* = 11.9, 8.0 Hz, 1H), 3.31–3.18 (m, 1H), 2.99 (ddd, *J* = 16.4, 12.1, 8.4 Hz, 1H), 2.26 (ddd, *J* = 16.4, 8.0, 2.0 Hz, 1H), 2.07 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 167.9, 164.2, 159.7, 143.6, 138.1, 133.2, 130.2, 129.0, 128.5, 127.8, 123.4, 115.1, 65.5, 61.2, 60.8, 53.5, 43.1, 30.5, 22.1, 14.1, 13.9.

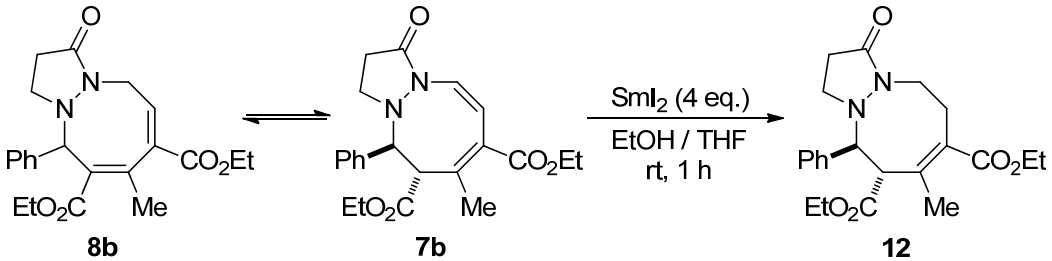
7zz (minor isomer): ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.4 Hz, 1H), 7.33–7.22 (m, 1H), 5.24–4.97 (s, 1H), 2.04 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 165.2, 160.3, 123.8, 115.5, 61.3, 60.6, 30.9, 14.1, 13.7.

Mechanism of the [3 + 2 + 3] Annulation: An Alternative Route toward the Tetrahydrodiazocine 8



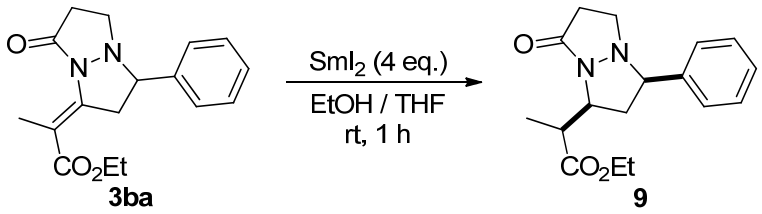
Transformations of the Fused Pyrazolidinone Heterocycles from Phosphine-catalyzed Annulations of Azomethine Imines with Allenoates

1. Samarium Iodide-Mediated Reduction of the C=C Bond of the Cycloadduct 7b and 3ba



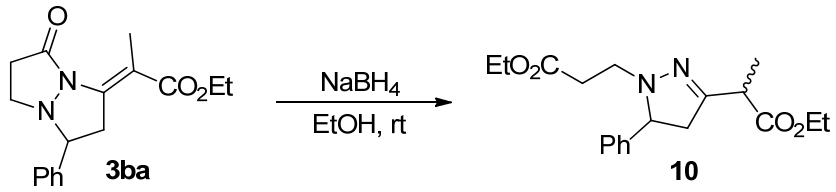
To a stirred solution of the mixture of **8b** and **7b** (79.6 mg, 0.20 mmol) in EtOH (1 mL) was added THF solution of SmI_2 (0.1M, 8.0 mL, 0.80 mmol) at room temperature. After stirring for 1

hour at room temperature, the reaction solution was poured into saturated aq. $NaHCO_3$ and extracted with ethyl acetate. The organic extracts were combined and washed with brine, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography (eluting with EtOAc/Hexane = 1 : 1) to give **12** as a colorless semi-solid, 58.8 mg, 73% yield. IR (neat) ν_{max} 2892, 2359, 1735, 1701, 1635, 1494, 1454, 1367, 1327, 1281, 1251, 1233, 1217, 1196, 1177, 1111, 1074, 1043, 1032, 914, 857, 833, 782, 758, 754, 735, 718, 703, 680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 5H), 4.45 – 4.11 (m, 5H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.53 – 3.40 (m, 1H), 3.20 (dd, *J* = 11.9, 8.3 Hz, 1H), 3.05 (s, 1H), 2.90 – 2.68 (m, 2H), 2.06 (s, 3H), 1.54 (s, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H), 0.92 – 0.81 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.03, 170.13, 168.51, 143.07, 137.25, 130.24, 129.28, 128.76, 128.62, 70.76, 60.89, 60.59, 53.55, 51.20, 48.75, 30.66, 29.98, 16.63, 14.25, 13.82; HRMS (ESI) calcd for $C_{22}H_{29}N_2O_5^+$ $[M + H]^+$ 401.2071, found 401.2071.



A colorless semi-solid, 68%yield. IR (film) ν_{max} 3062, 3032, 2981, 2943, 2903, 2843, 1732, 1604, 1496, 1455, 1421, 1370, 1341, 1272, 1201, 1095, 1068, 1029, 974, 911, 860, 830, 757, 702cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 5H), 4.36 – 4.27 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.47 – 3.29 (m, 2H), 2.98 – 2.76 (m, 2H), 2.65 – 2.52 (m, 3H), 2.01 (m, *J* = 12.7, 10.8, 7.5 Hz, 1H), 1.16 (m, *J* = 10.1, 4.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.13, 172.76, 137.70, 128.46, 127.92, 127.11, 69.72, 60.36, 54.87, 46.11, 42.76, 40.56, 31.65, 13.90, 11.65; HRMS (ESI) calcd for $C_{17}H_{23}N_2O_3^+$ $[M + H]^+$ 303.1703, found 303.1696.

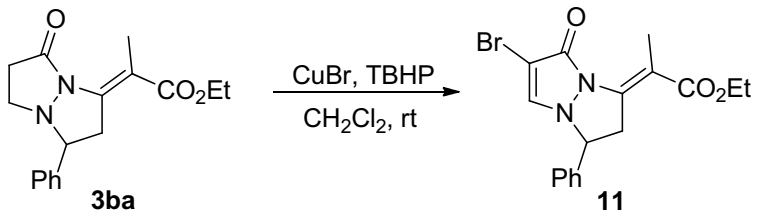
2. Reduction of the Cycloadduct by Sodium Borohydride



To a stirred solution of **3ba** (30.0 mg, 0.10 mmol) in EtOH (2 mL) was added $NaBH_4$ (7.6 mg, 0.2 mmol) at room temperature. After stirring at room temperature overnight, the reaction

solution was concentrated under vacuum and the residue was purified by flash column (eluting with EtOAc/Hexane = 1 : 3) to give **10** as a colorless semi-solid, 20.9 mg, 63% yield. The product is the mixture of diastereomers, which couldn't be separated by flash column chromatography. The spectra were recorded by using this mixture. IR (neat) ν_{max} 2984, 1731, 1495, 1456, 1369, 1323, 1250, 1184, 1096, 1029, 943, 861, 758, 732, 720, 714, 701, 683 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 10H), 4.25 – 4.02 (m, 10H), 3.51 (dq, *J* = 14.4, 7.2 Hz, 2H), 3.20 – 2.92 (m, 6H), 2.80 – 2.55 (m, 6H), 1.40 (dd, *J* = 16.8, 7.2 Hz, 6H), 1.27 (td, *J* = 7.1, 2.8 Hz, 6H), 1.20 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.64, 172.61, 172.34, 151.92, 140.40, 128.54, 127.72, 127.47, 127.45, 71.81, 71.69, 60.94, 60.23, 49.67, 49.64, 43.54, 43.49, 41.63, 41.53, 33.18, 15.07, 14.68, 14.13; HRMS (ESI) calcd for $C_{19}H_{26}N_2O_4^+$ $[M]^+$ 346.1893, found 346.1897.

3. Cuprous Bromide-Mediated Oxidation/Bromination of the Cycloadduct



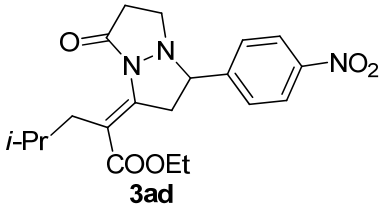
3ba **11**

To a mixture of CuBr (14.0 mg, 0.1 mmol) and **3ba** (30.0 mg, 0.1 mmol) in 2 mL of CH_2Cl_2 was added tert-butyl hydroperoxide (0.1 mL, 5 – 6 M in decane) under nitrogen over 30 seconds at 0 °C. The reaction temperature was allowed to warm to room temperature. The reaction mixture was stirred for 4 hours, and then diluted with EtOAc and filtered through a short celite column eluting with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography (eluting with hexane/EtOAc = 2 : 1) to give 11 as a pale yellow semi-solid, 21.4 mg, 57% yield. IR (neat) ν_{max} 2981, 1701, 1633, 1539, 1457, 1366, 1274, 1137, 1030, 946, 912, 838, 767, 731, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 3H), 7.35 – 7.27 (m, 3H), 4.79 (t, *J* = 8.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.14 – 4.06 (m, 1H), 3.52 (ddd, *J* = 17.6, 7.6, 1.9 Hz, 1H), 2.35 (t, *J* = 1.8 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.80, 157.76, 139.42, 138.60, 136.41, 129.33, 126.74, 111.91, 90.66, 62.07, 60.71, 44.49, 17.11, 14.18; HRMS (EI) calcd for $C_{17}H_{17}BrN_2O_3^+$ $[M]^+$ 376.0423, found 376.0427.

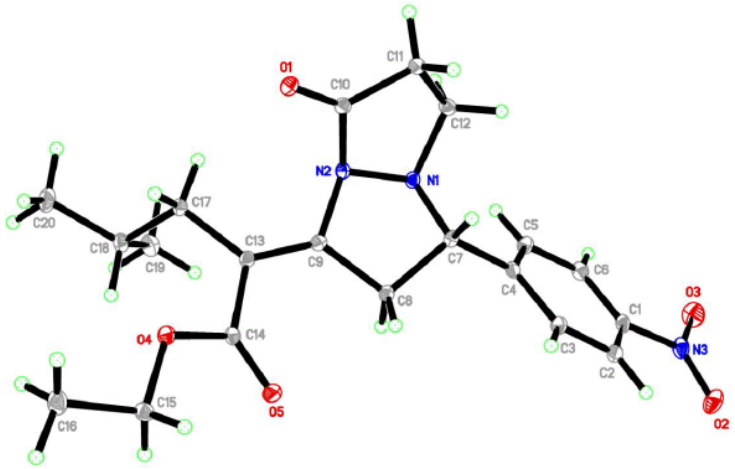
Crystallographic Data for 3ad, 3ao, 3an, 4, *trans*-5, 6, 7h, 7i, and 8a

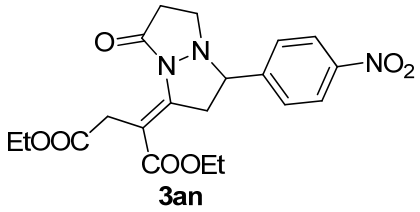
Crystallographic data for **3ad**, **3ao**, **3an**, **4**, ***trans*-5**, **6**, **7h**, **7i**, and **8a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary numbers CCDC 804940–804949. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, 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.

ORTEP Representations of 3ad, 3an, 3ao, 4, *trans*-5, 6, 7h, 7i, and 8a



3ad





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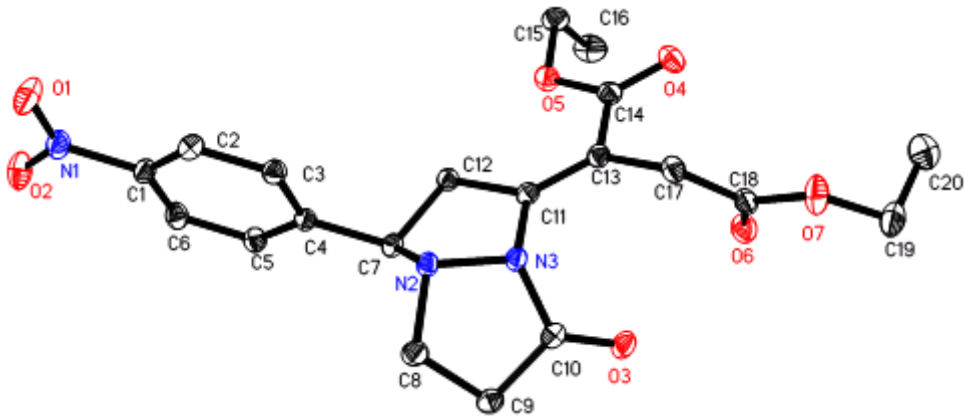

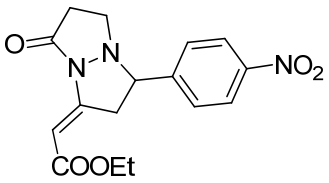
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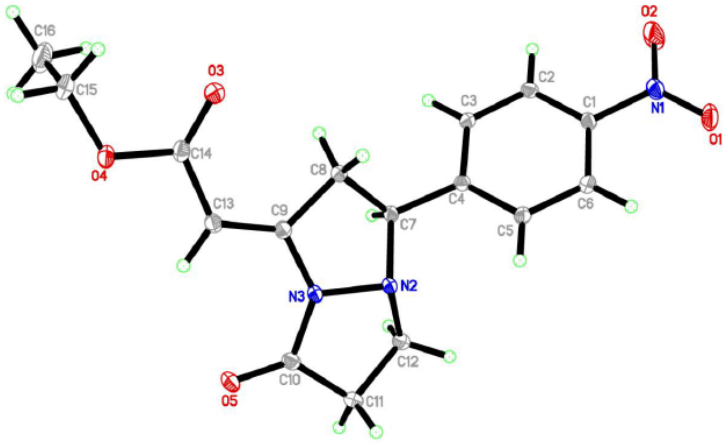
3ao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C3
C2
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O1
C5
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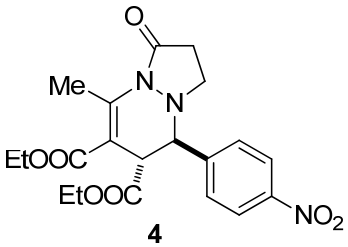
N3
N2
C12
C10
O5
C11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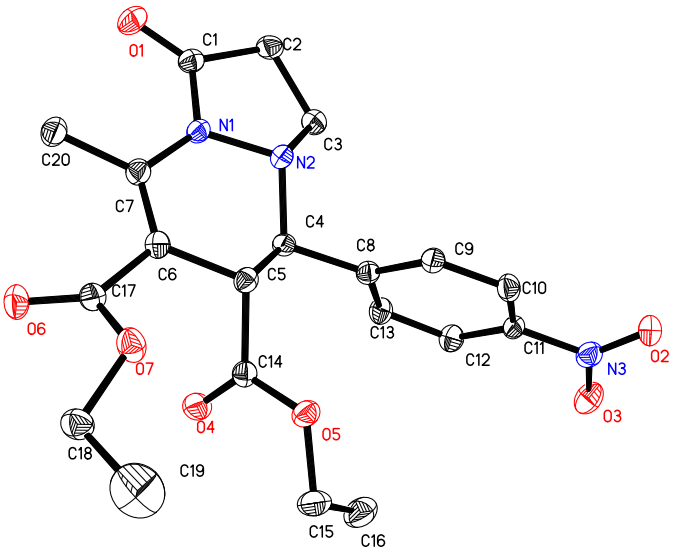
EtOOC
NO2

4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O4
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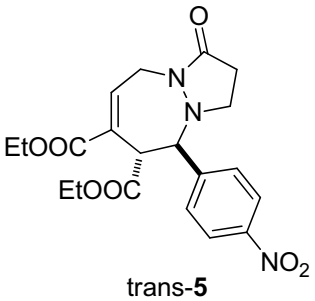
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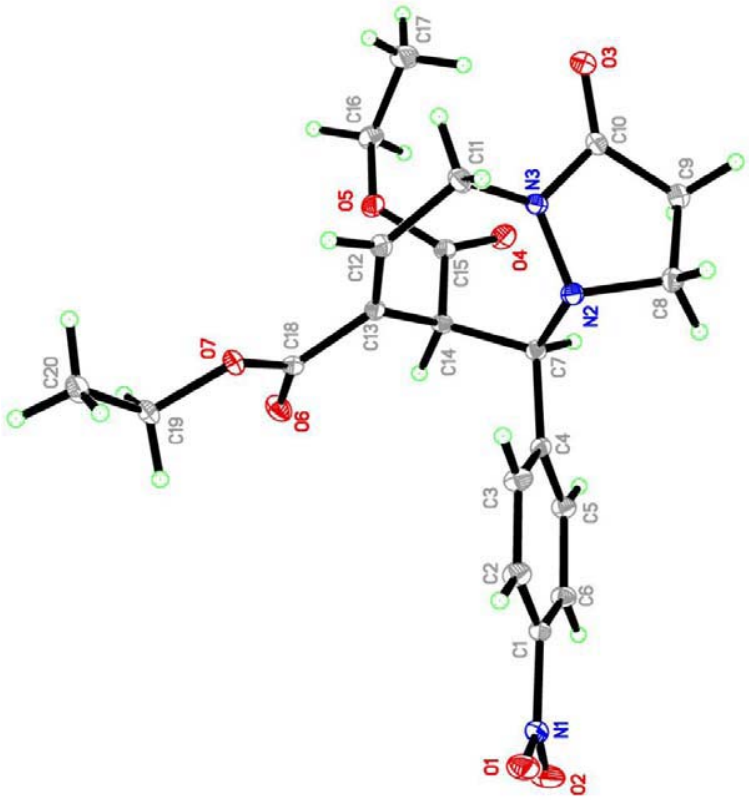
EtOOC
NO2

trans-**5**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C11
C10
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O5
N3
C12
C15
O4
N2
C8
C13
C14
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C2
C6
C1
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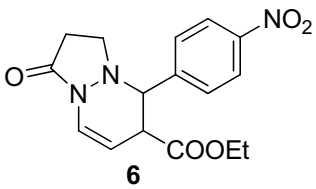
O1
O2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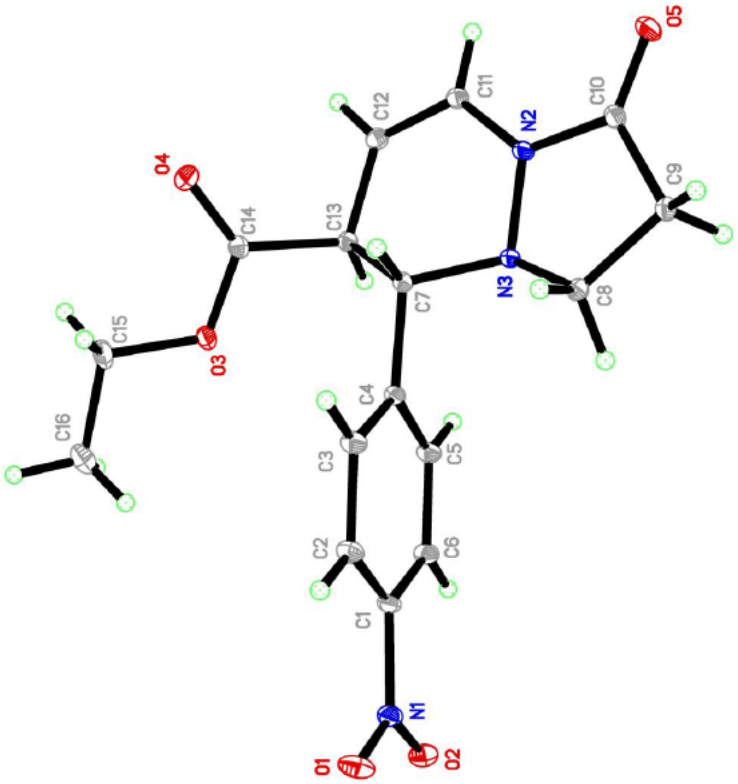
6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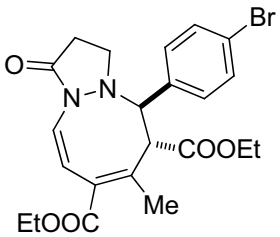
O2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Me
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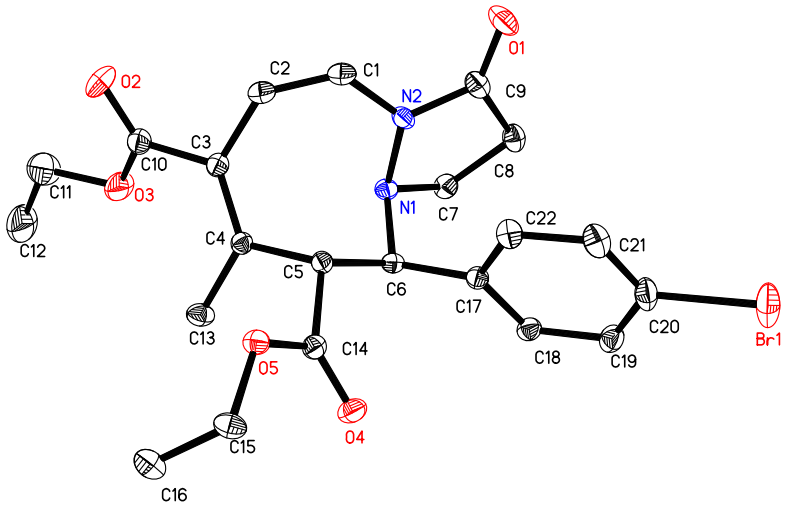
7h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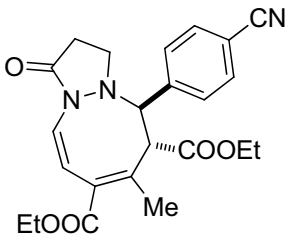
C16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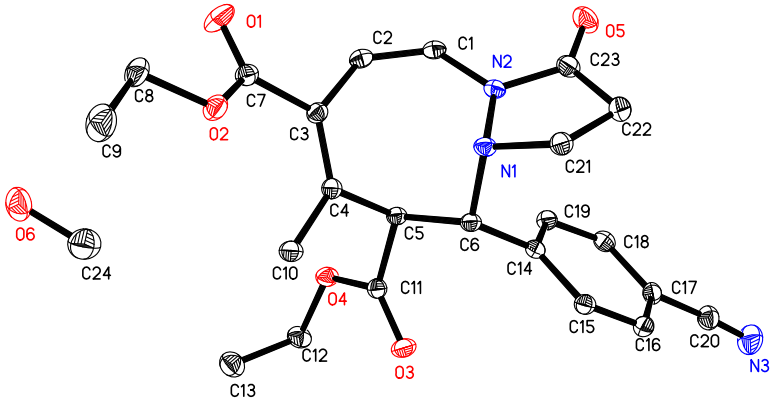
7i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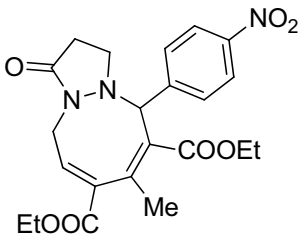
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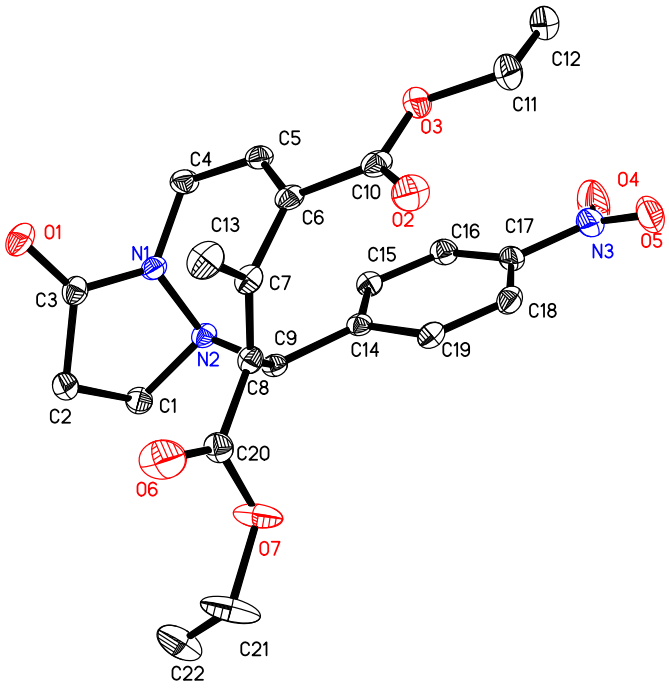
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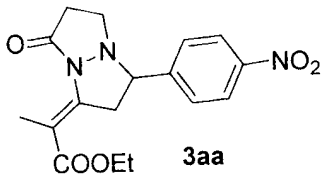
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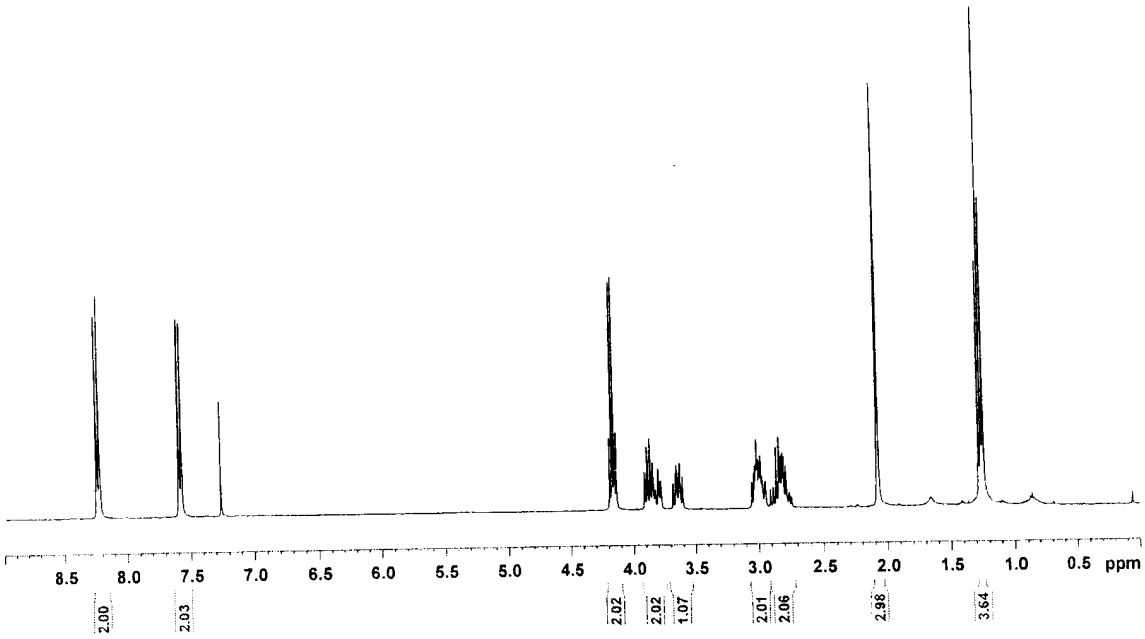
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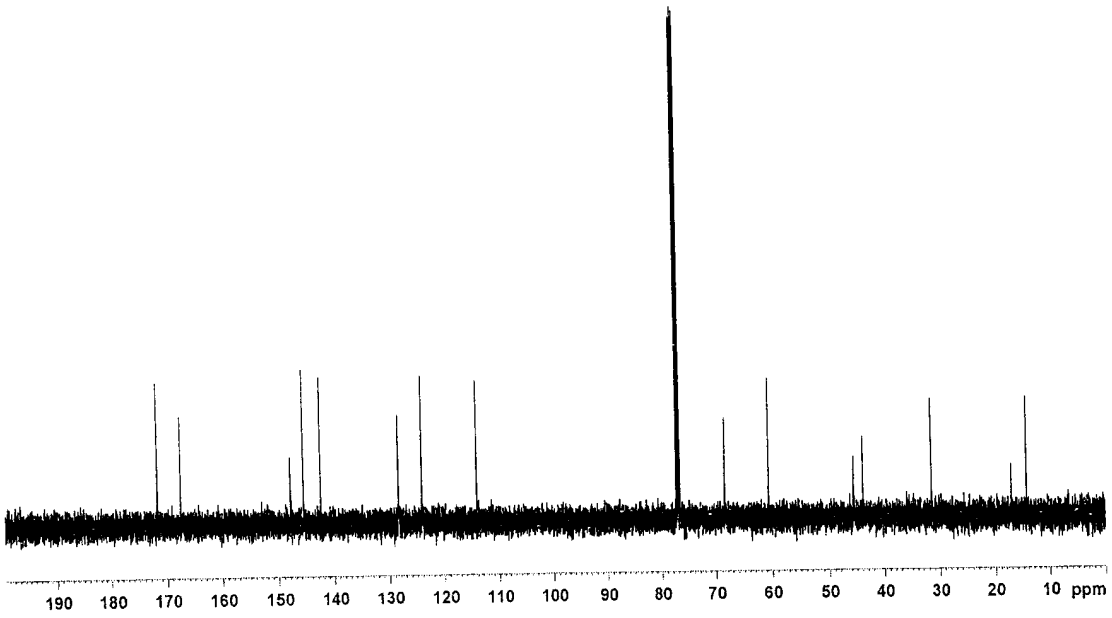
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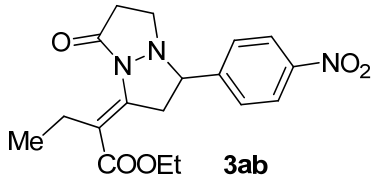
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Me
COOEt

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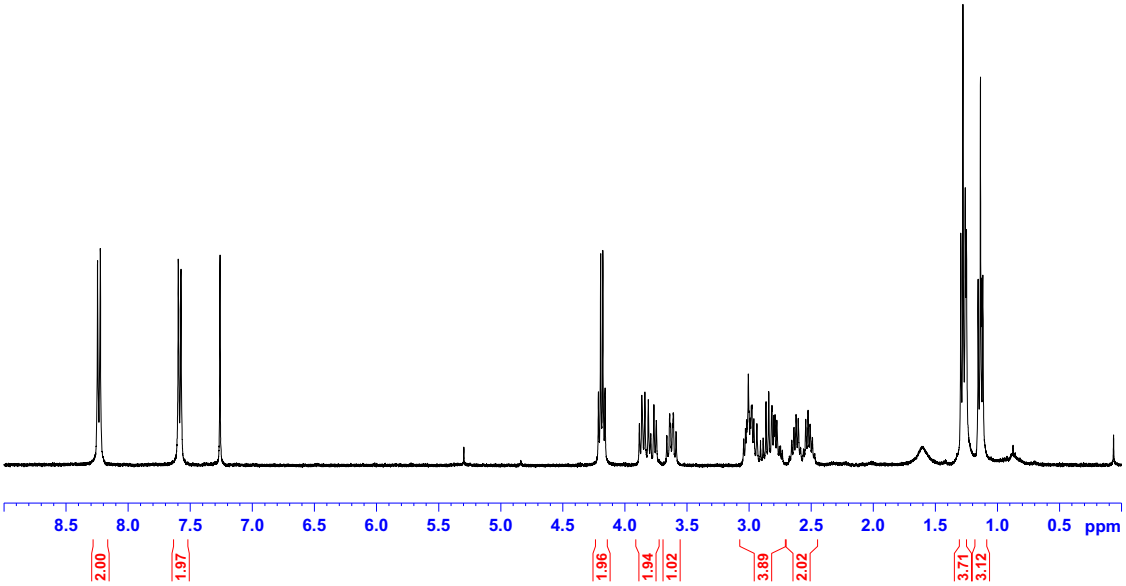
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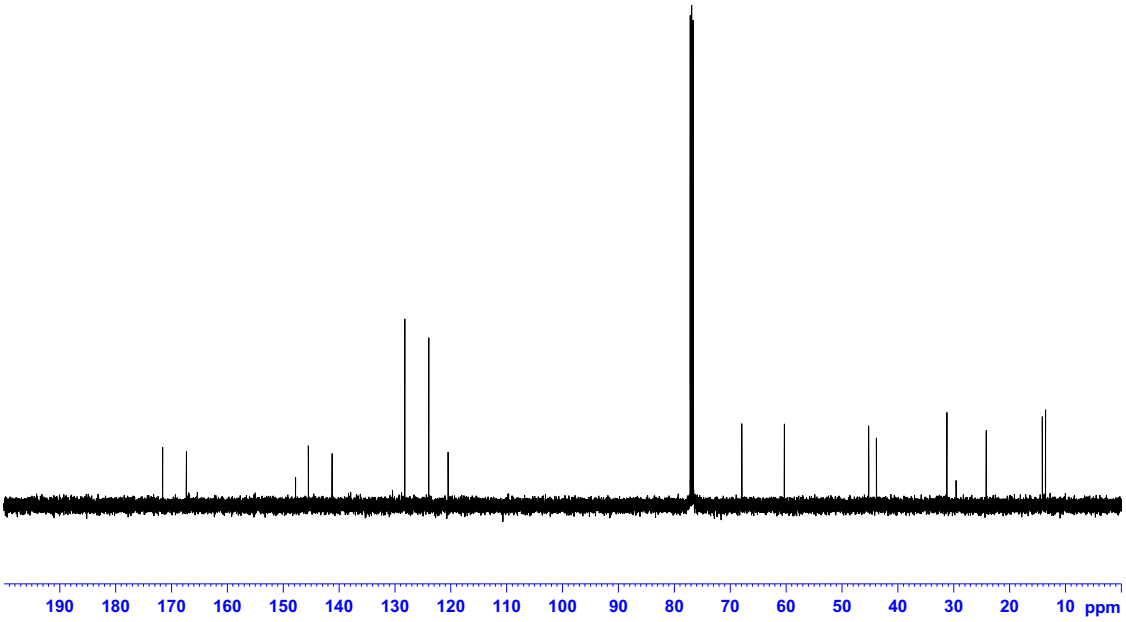
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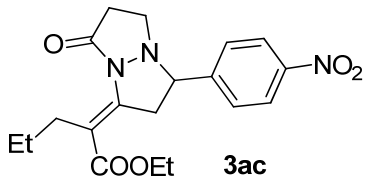
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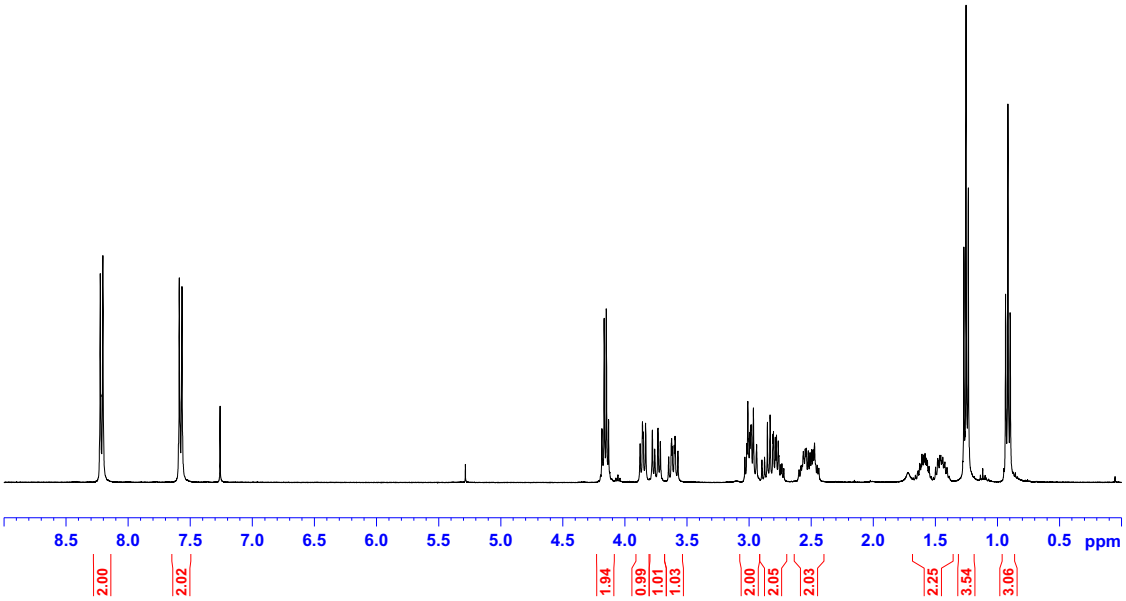
Et
COOEt

3ac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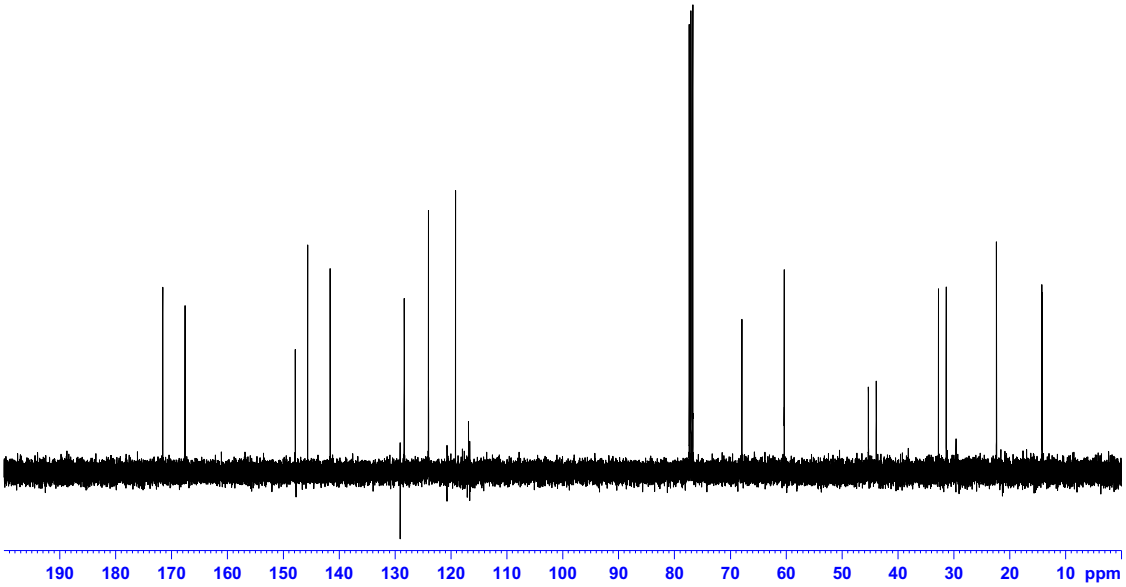
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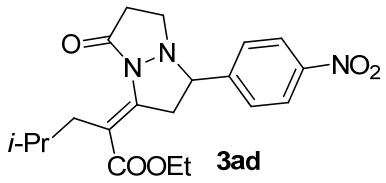
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N
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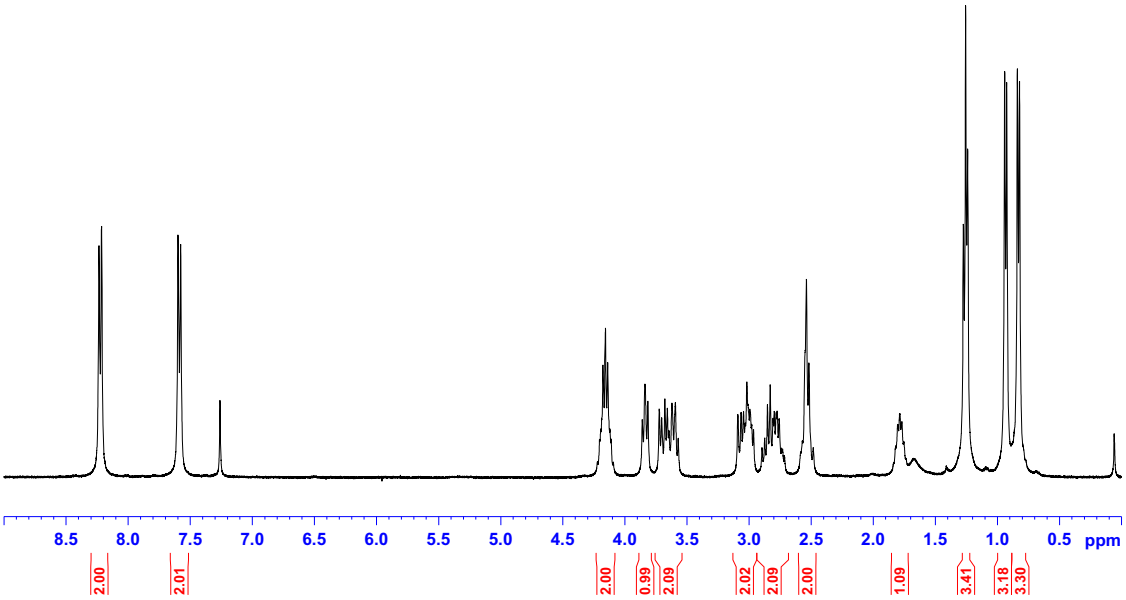
i-Pr
COOEt

3ad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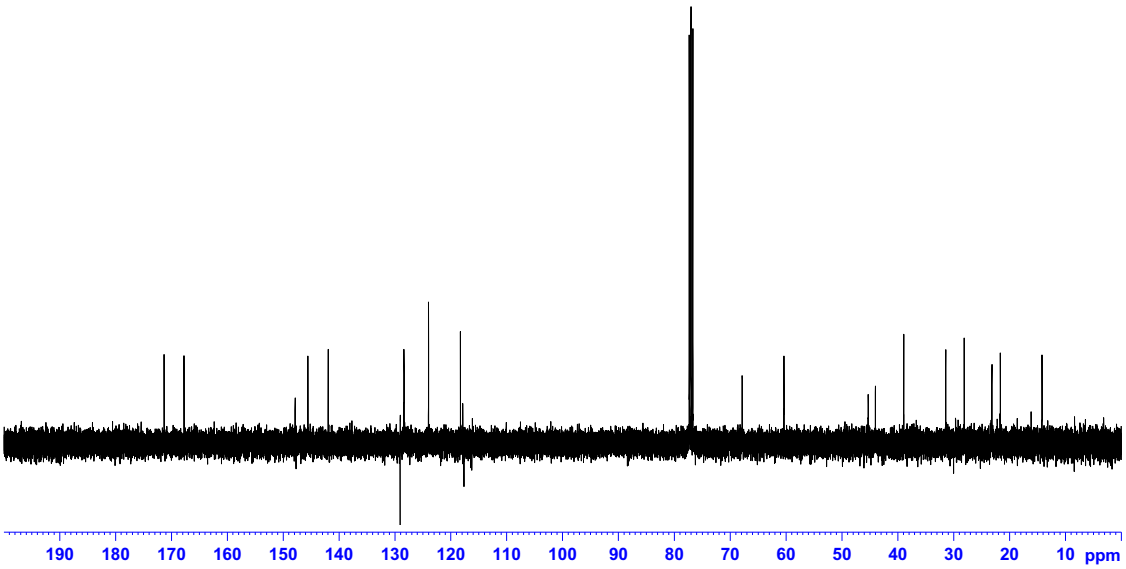
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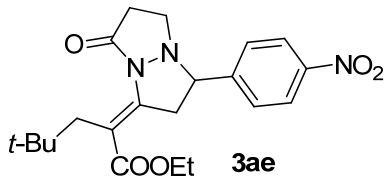
O
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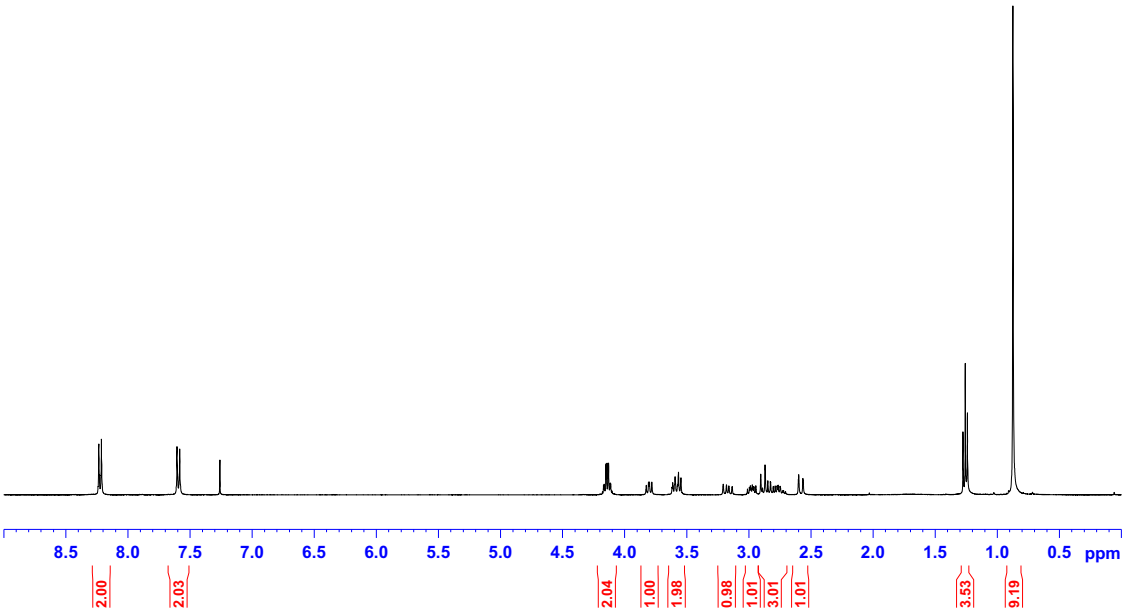
N
NO2
t-Bu
COOEt

3ae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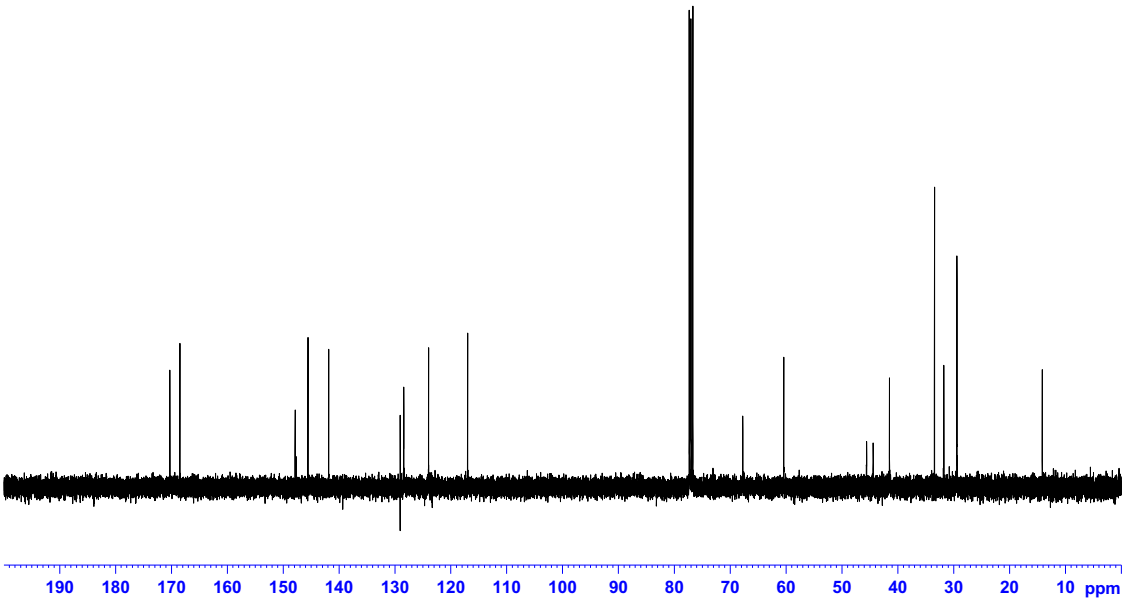
2.00 2.03 2.04 1.00 1.98 0.98 1.01 3.01 1.01 3.53 9.19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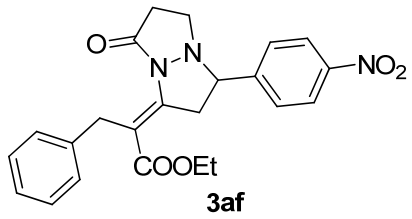
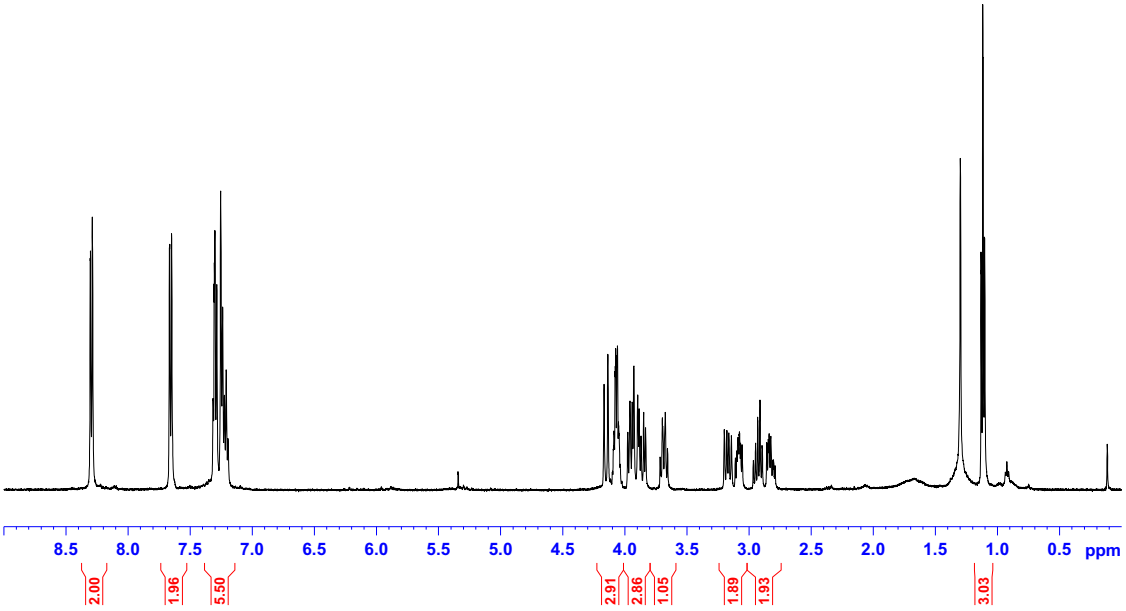

O
N
N
NO2
COOEt

3af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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
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ppm
2.00
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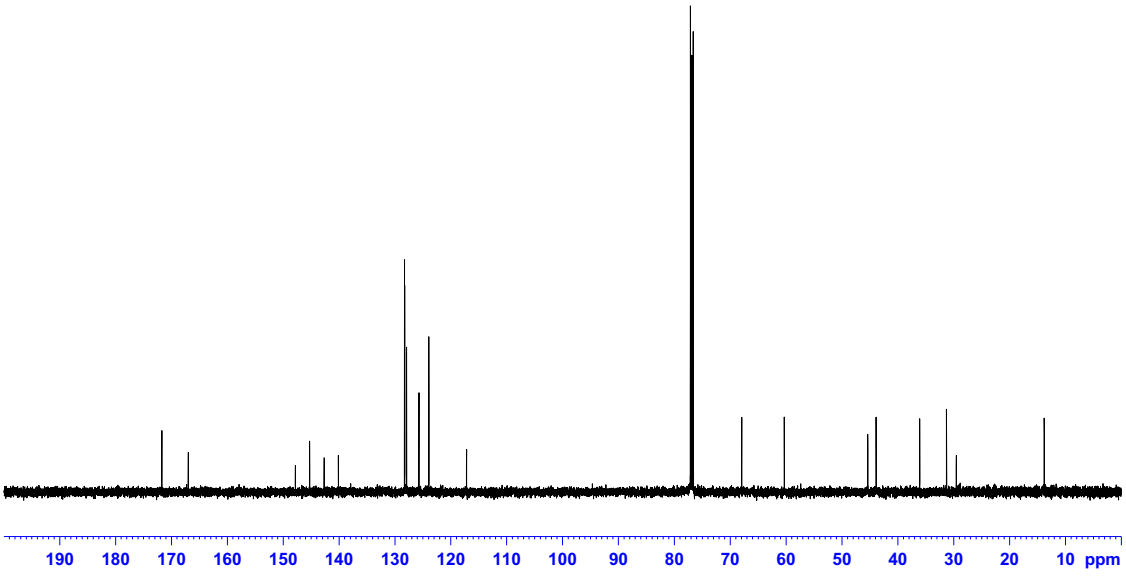
5.50
2.91
2.86
1.05
1.89
1.93
3.03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70
60
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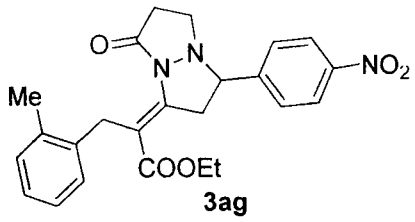
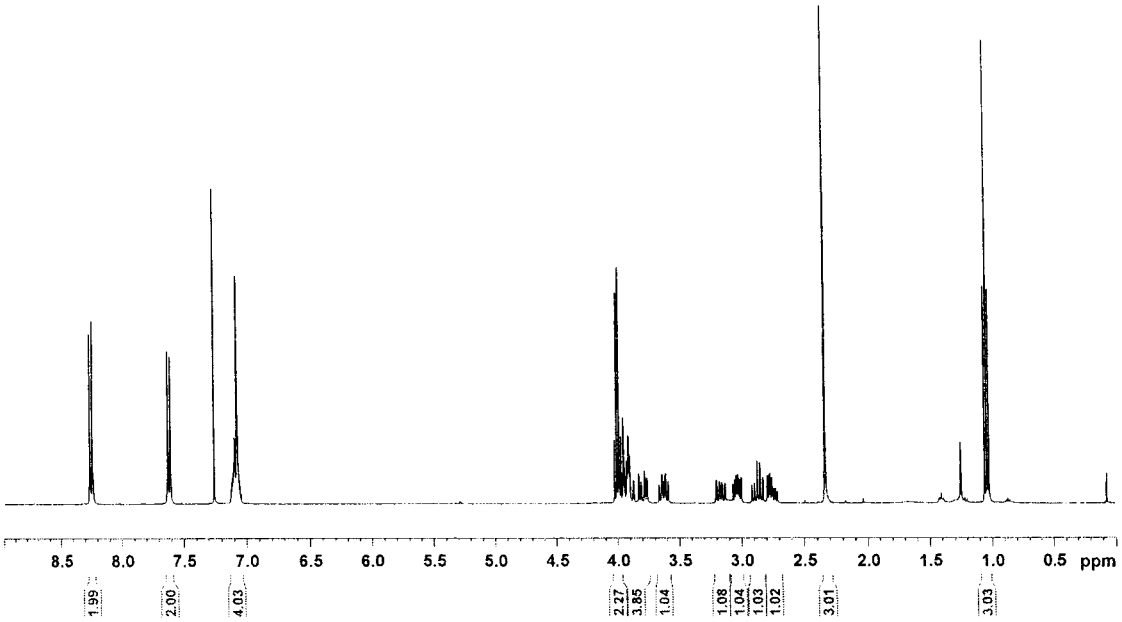
40
30
20
10
ppm


O
N
N
NO2
Me
COOEt

3ag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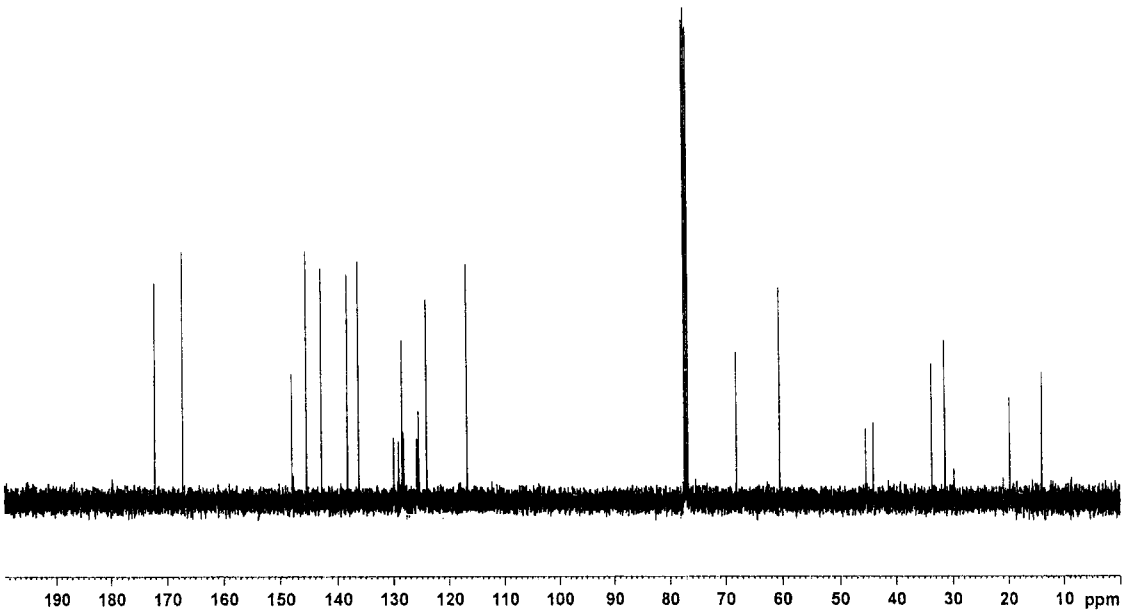
1.04
1.08
1.04
1.03
1.02
3.01
3.03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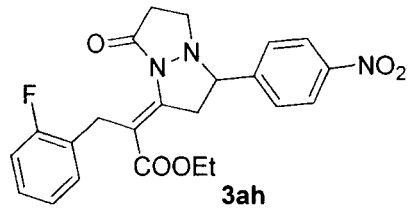
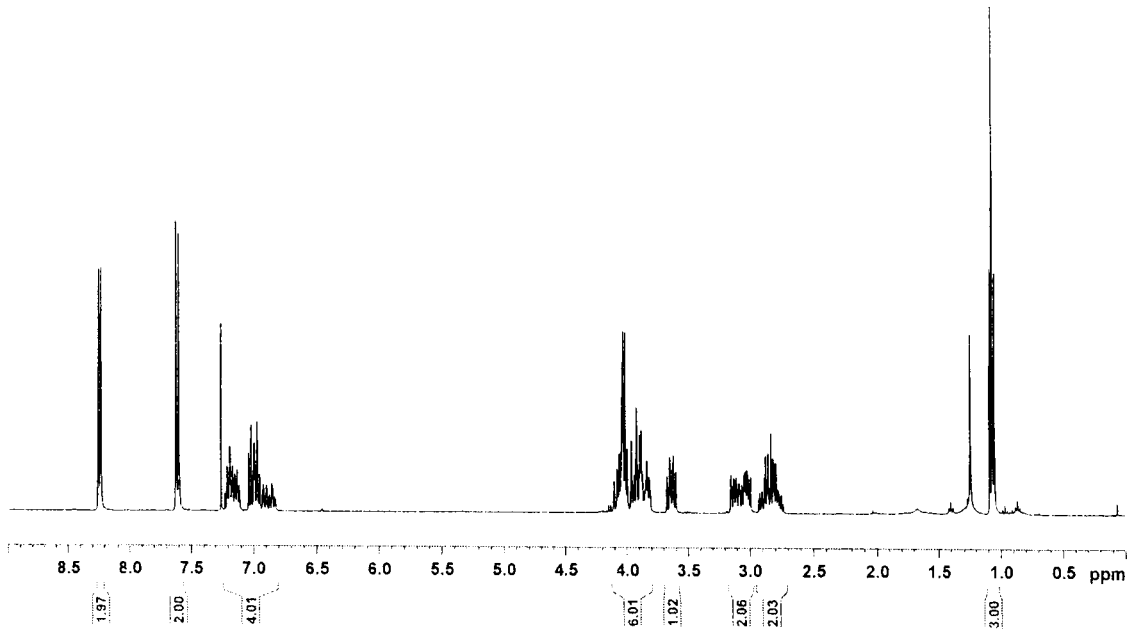

O
N
N
NO2
F
COOEt

3ah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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
ppm
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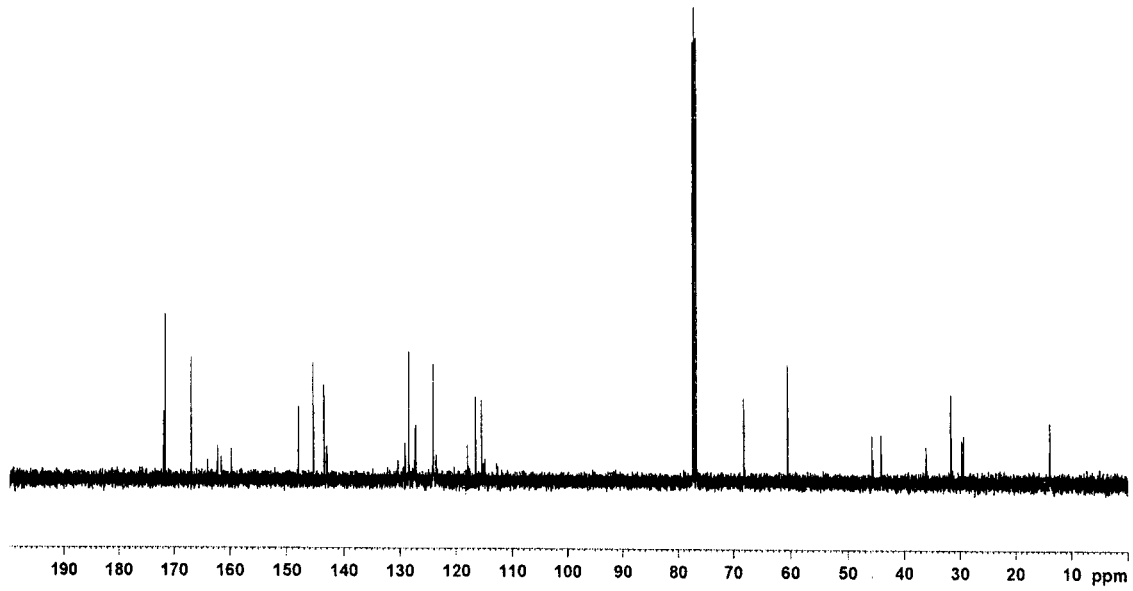
2.00
4.01
6.01
1.02
2.06
2.03
3.00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180
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90
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70
60
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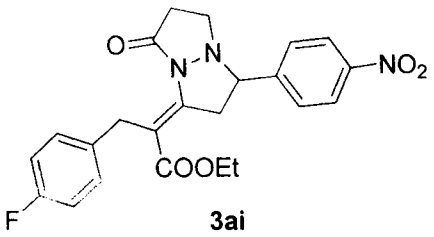
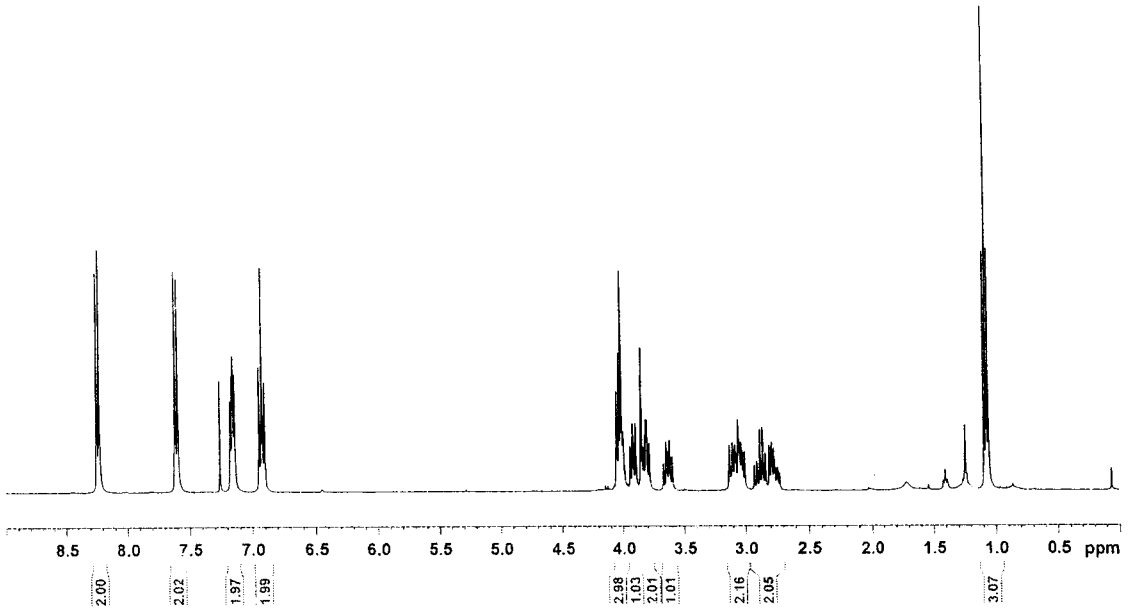
40
30
20
10
ppm


O
N
N
NO2
COOEt
F

3ai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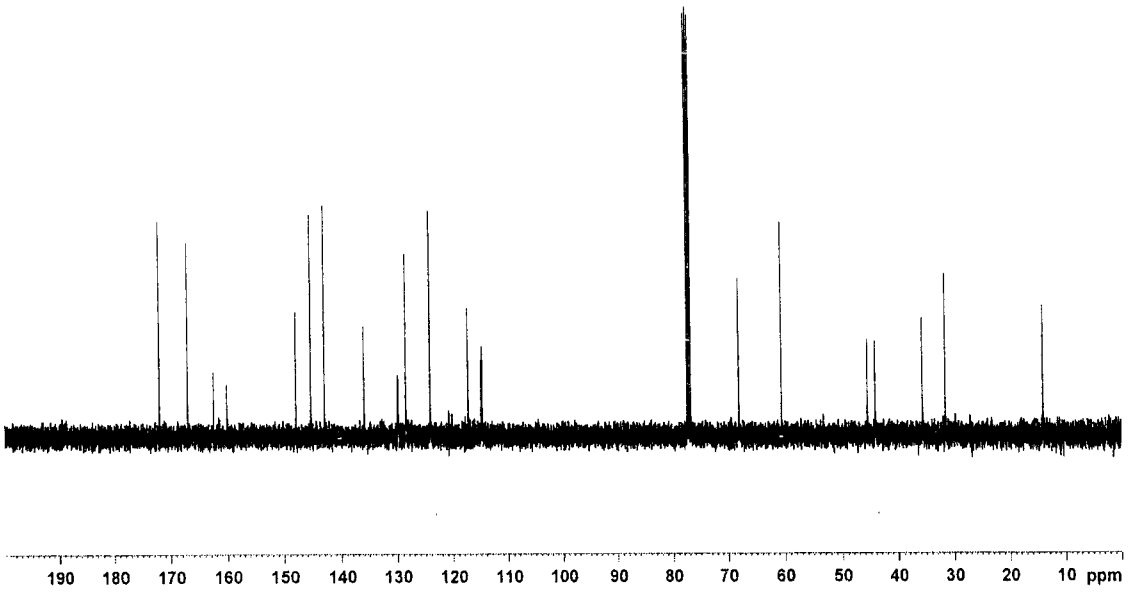
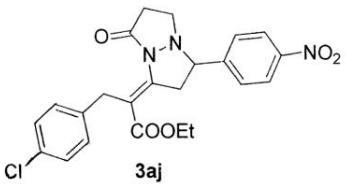
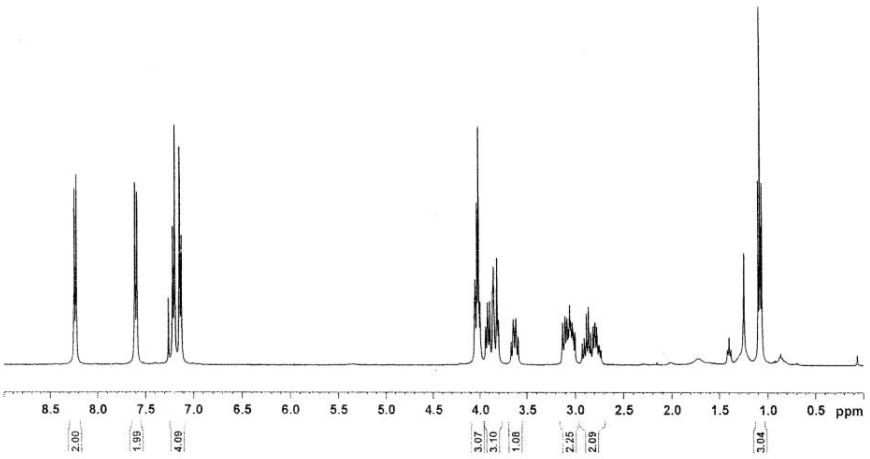
2.02
1.97
1.99
2.98
1.03
2.01
1.01
2.16
2.05
3.07


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


O
N
N
NO2
COOEt
Cl

3aj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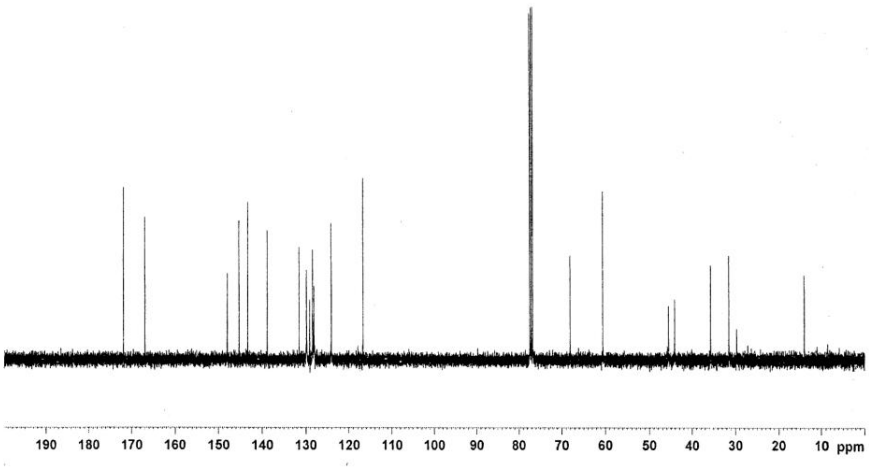
2.00
1.99
4.09
3.07
3.10
1.08
2.25
2.09
3.04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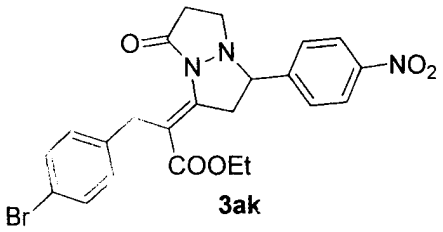
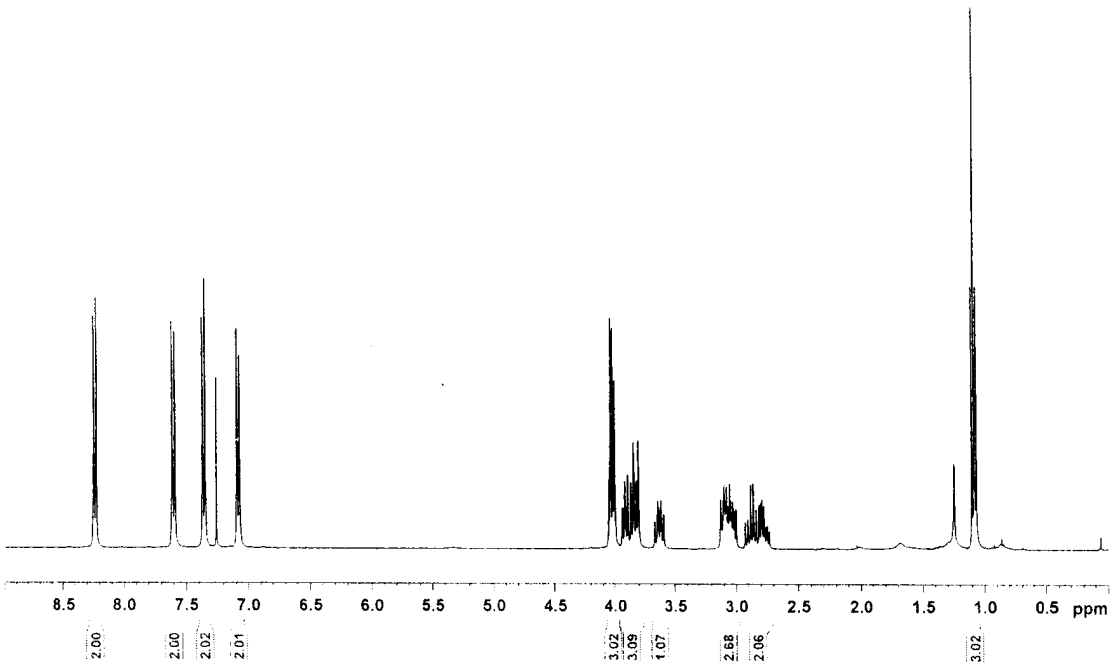

O
N
N
NO2
COOEt
Br

3ak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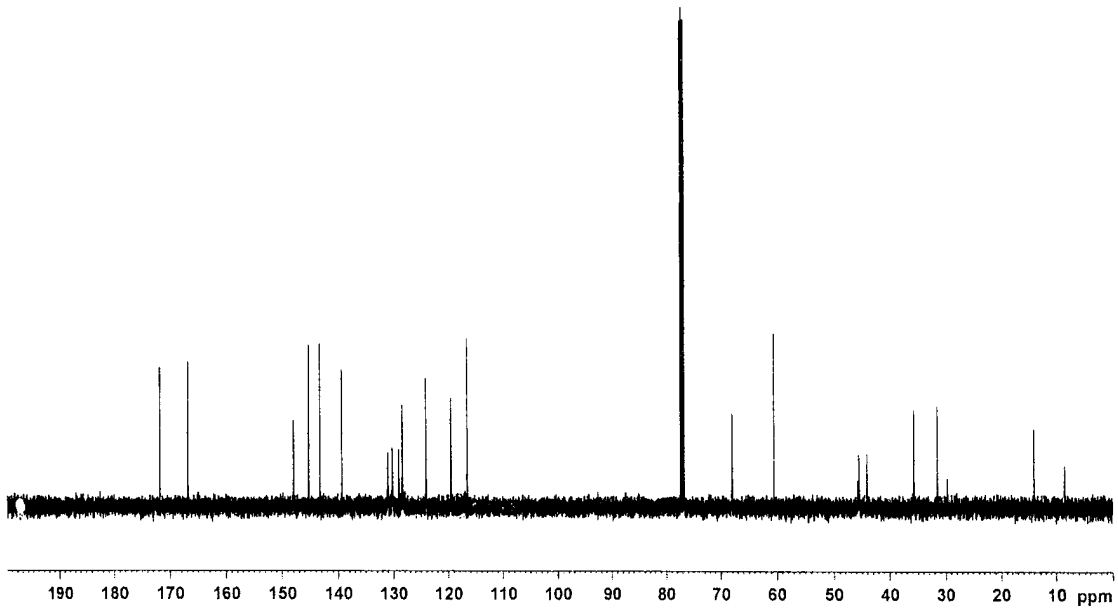
2.00 2.00 2.02 2.01 3.02 3.09 1.07 2.68 2.06 3.02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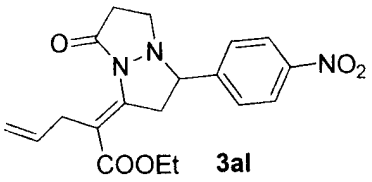
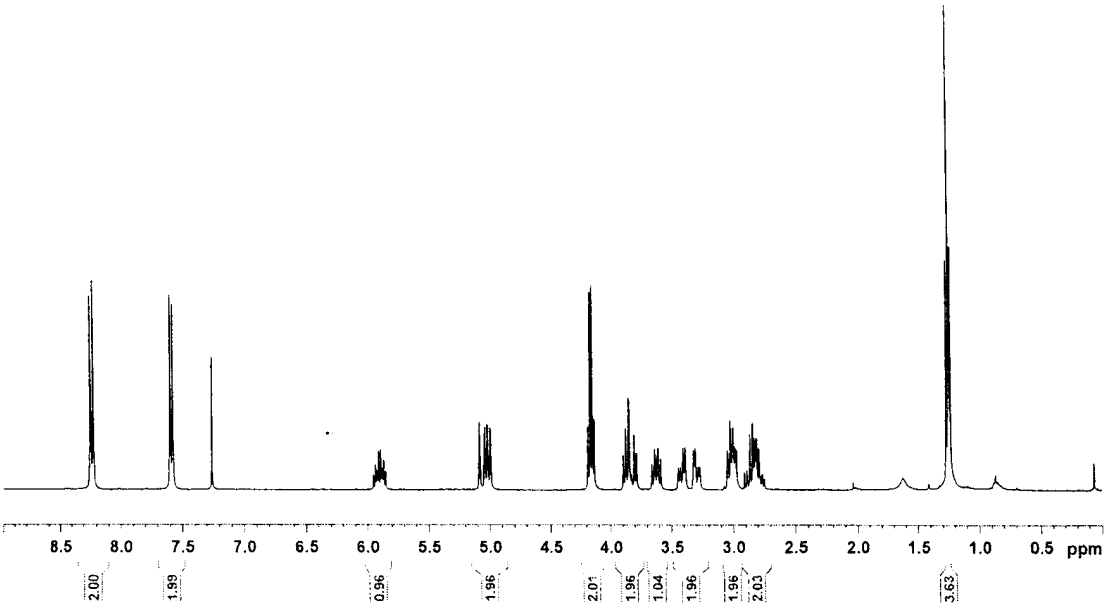

O
N
N
NO2
COOEt

3al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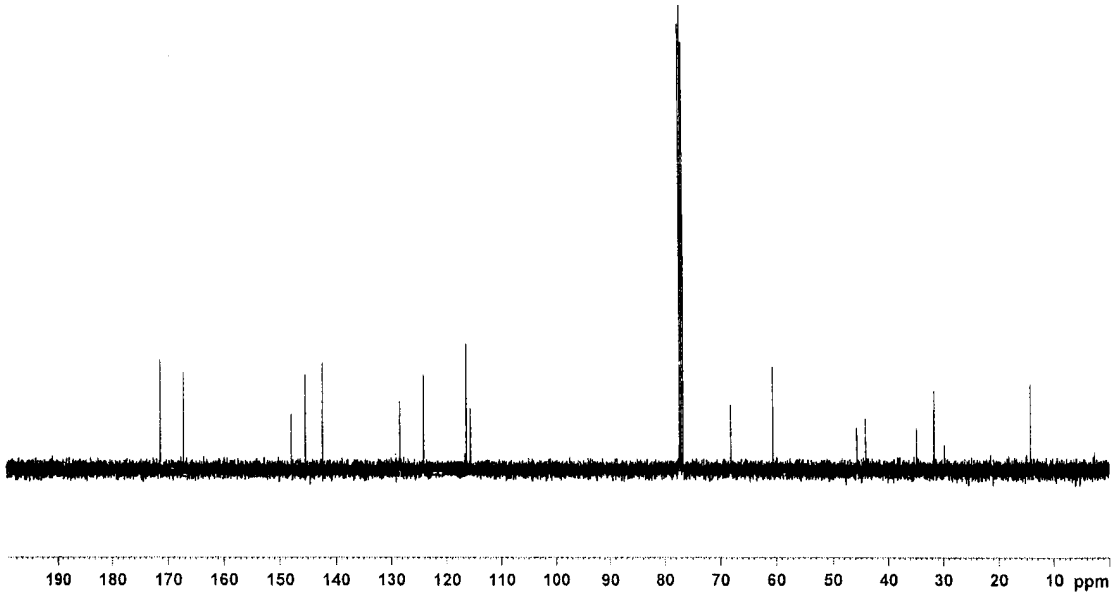
2.00
1.99
0.96
1.96
2.01
1.96
1.04
1.96
1.96
2.03
3.63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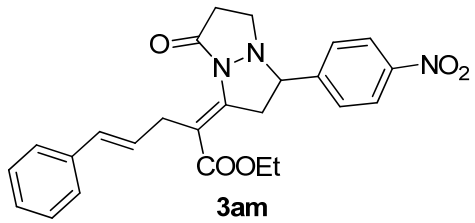
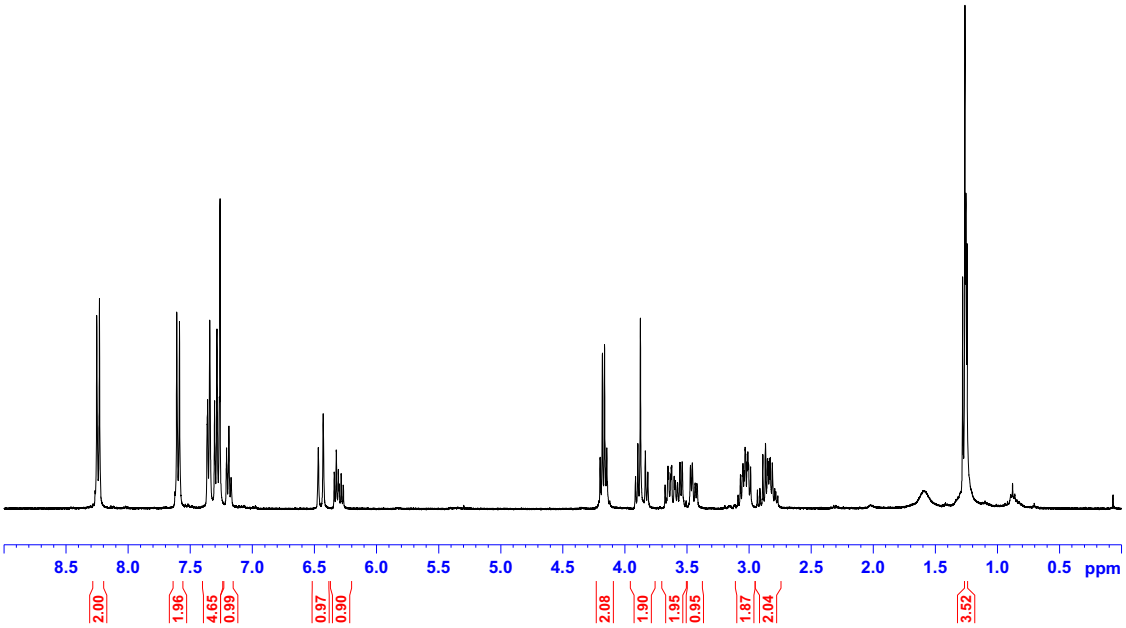

O
N
N
NO2
COOEt

3am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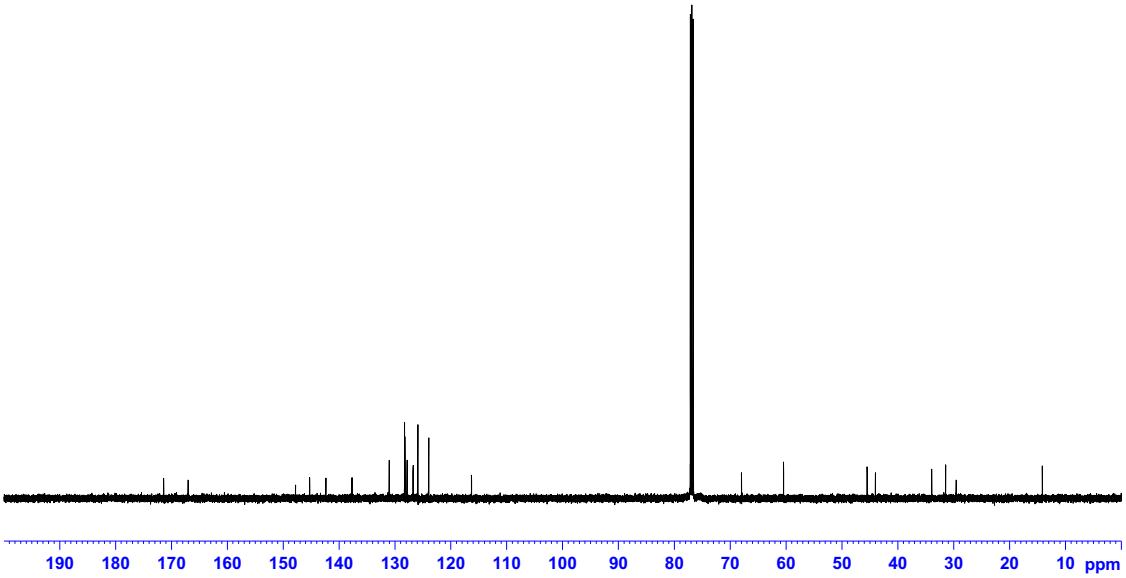
2.00 1.96 4.65 0.99 0.97 0.90 2.08 1.90 1.95 0.95 1.87 2.04 3.52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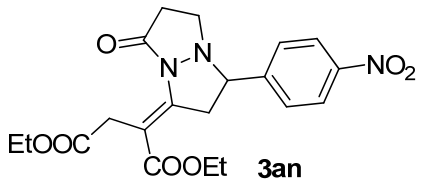
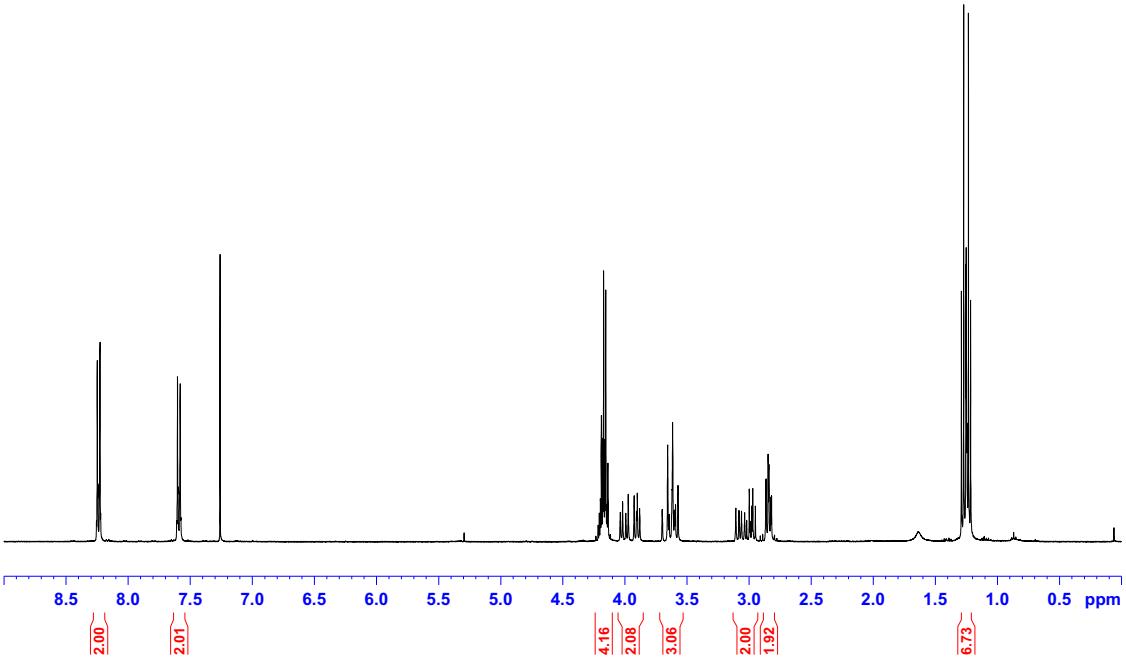

O
N
N
NO2
EtOOC
COOEt

3an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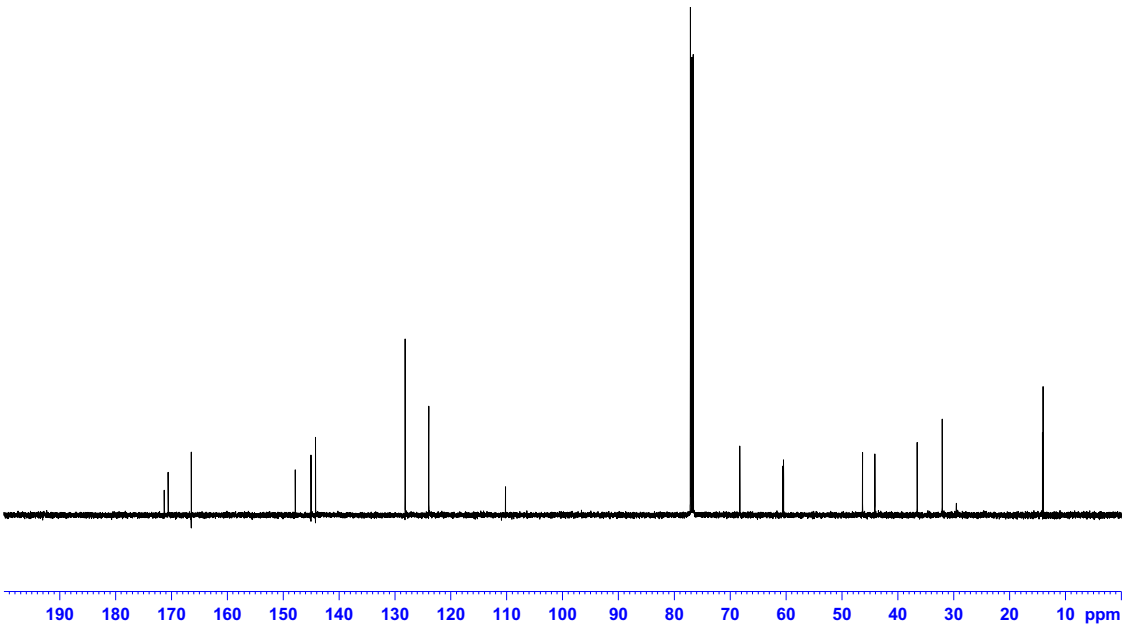
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.01
4.16
2.08
3.06
2.00
1.92
6.73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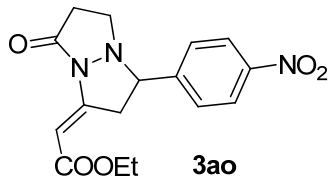
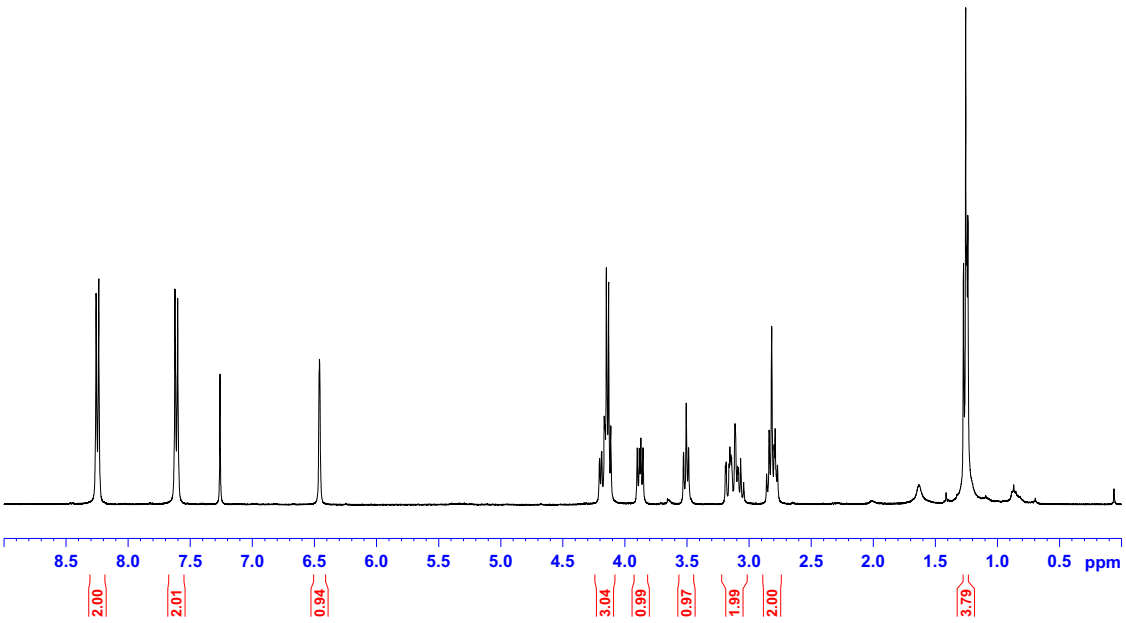
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
N
N
NO2
COOEt

3ao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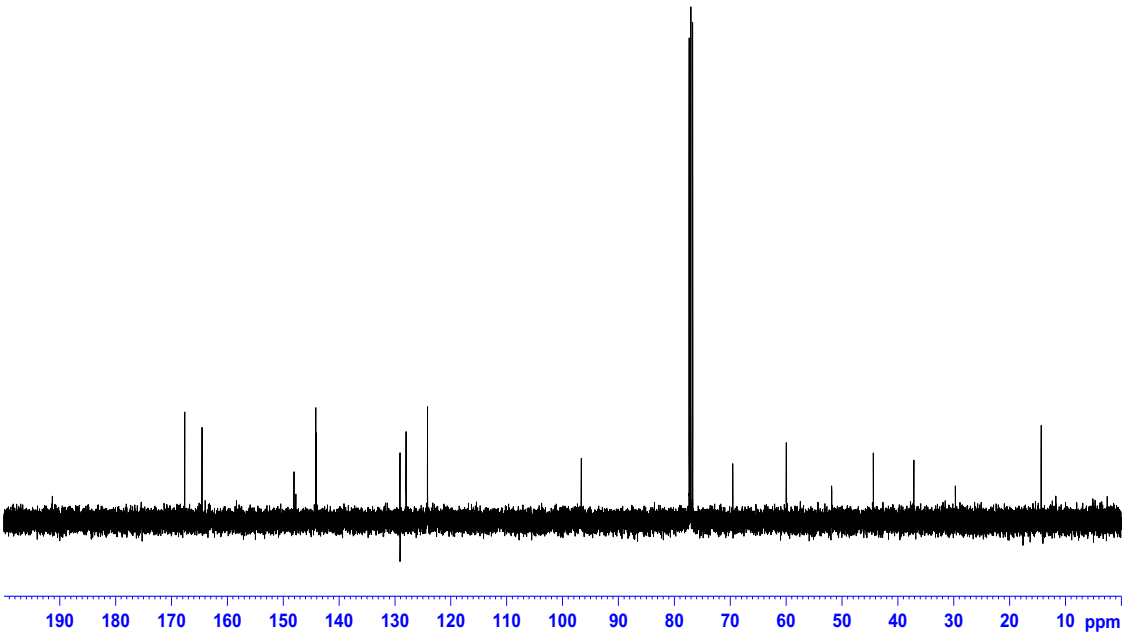
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.01
0.94
3.04
0.99
0.97
1.99
2.00
3.79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150
140
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120
110
100
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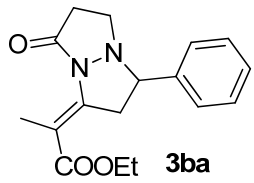
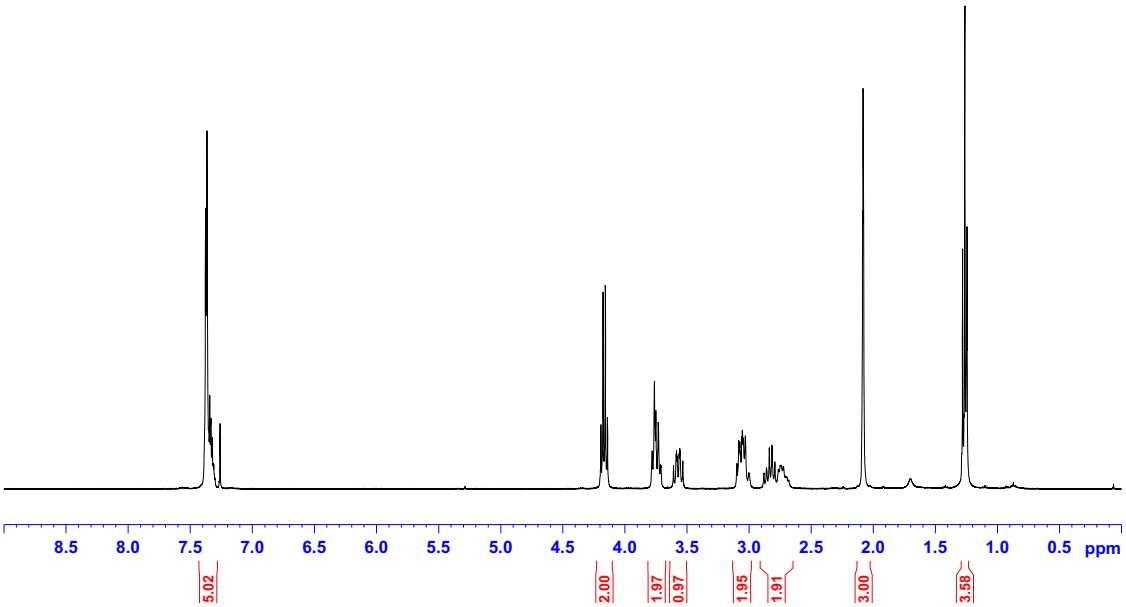
80
70
60
50
40
30
20
10
ppm


O
N
N
COOEt

3ba


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
ppm
5.02
2.00
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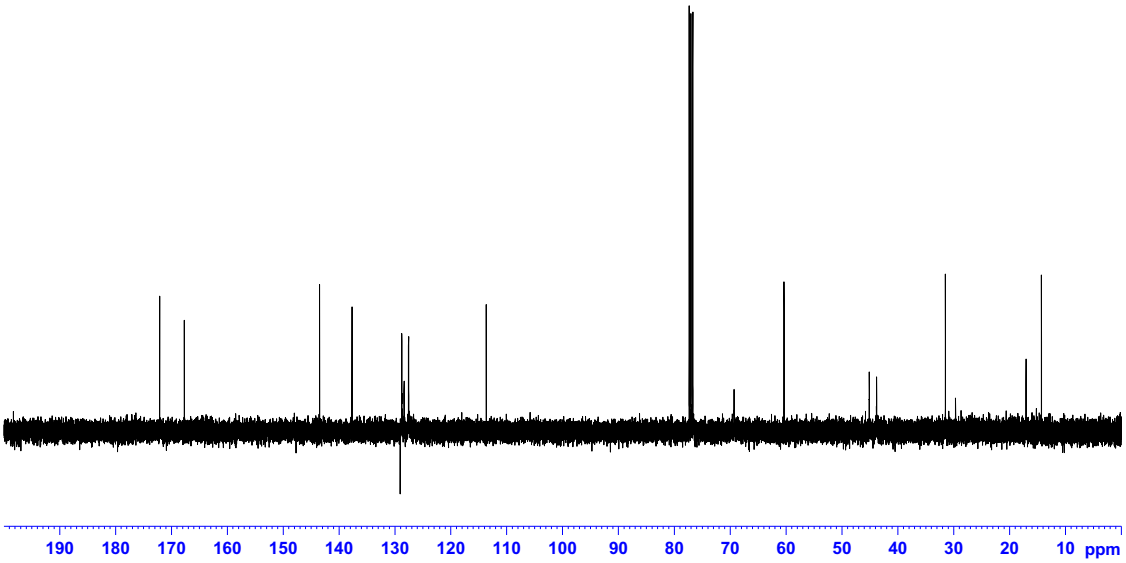
0.97
1.95
1.91
3.00
3.58


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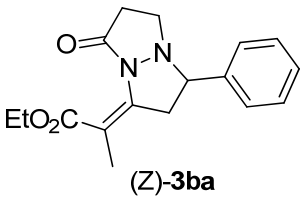
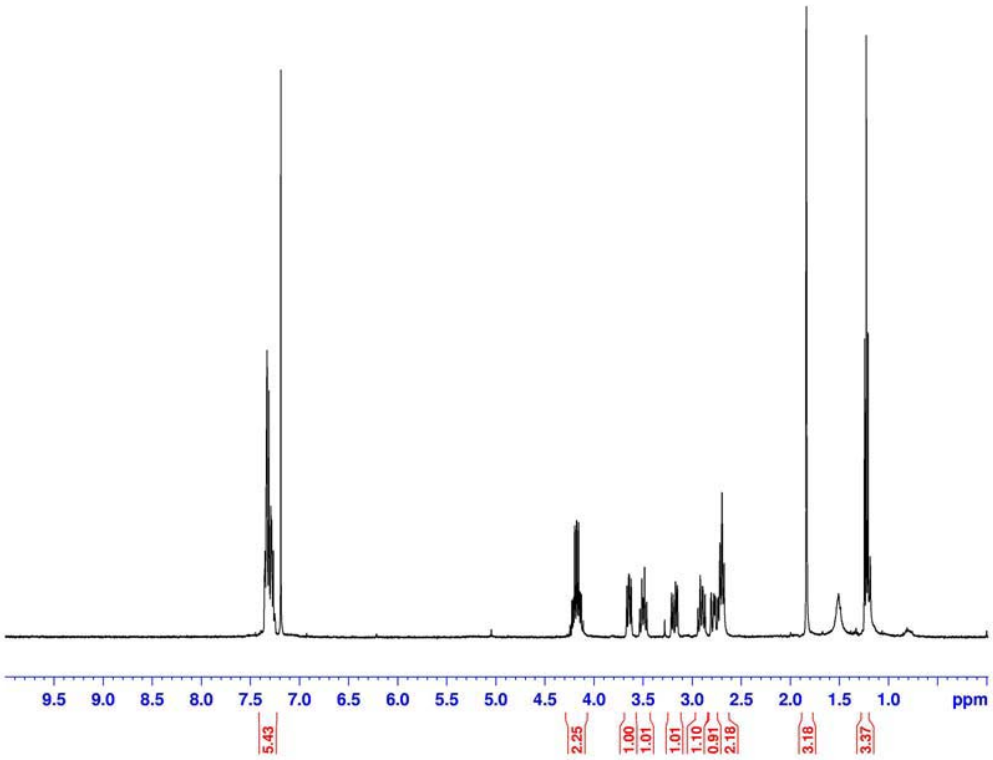
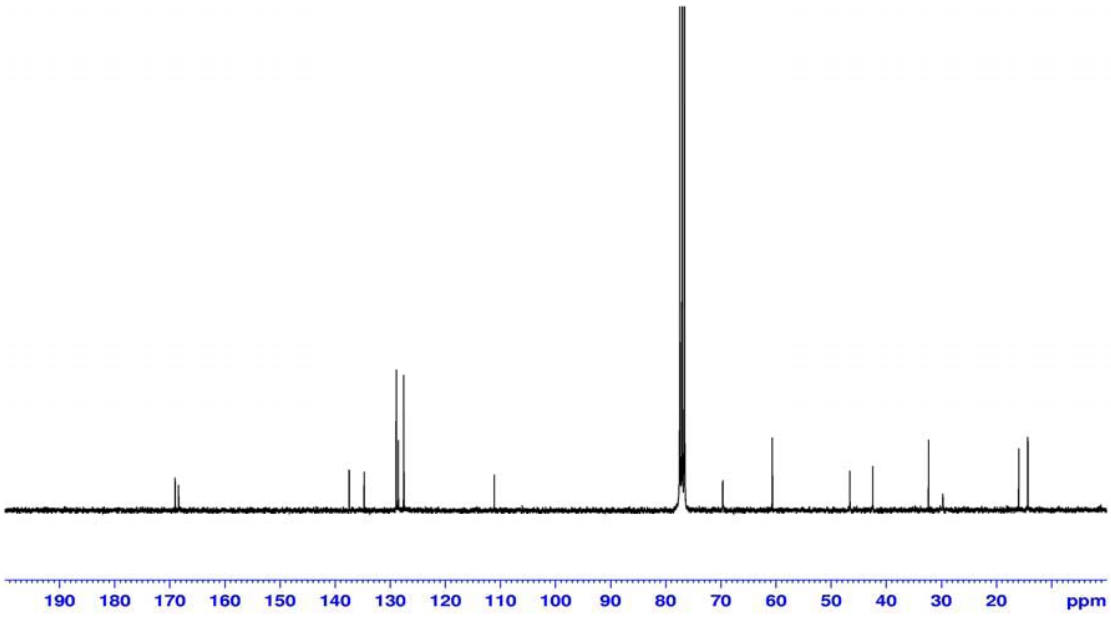
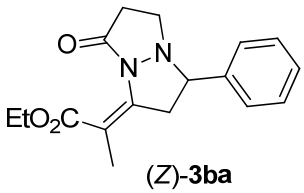
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
N
N
EtO2C

(Z)-**3ba**

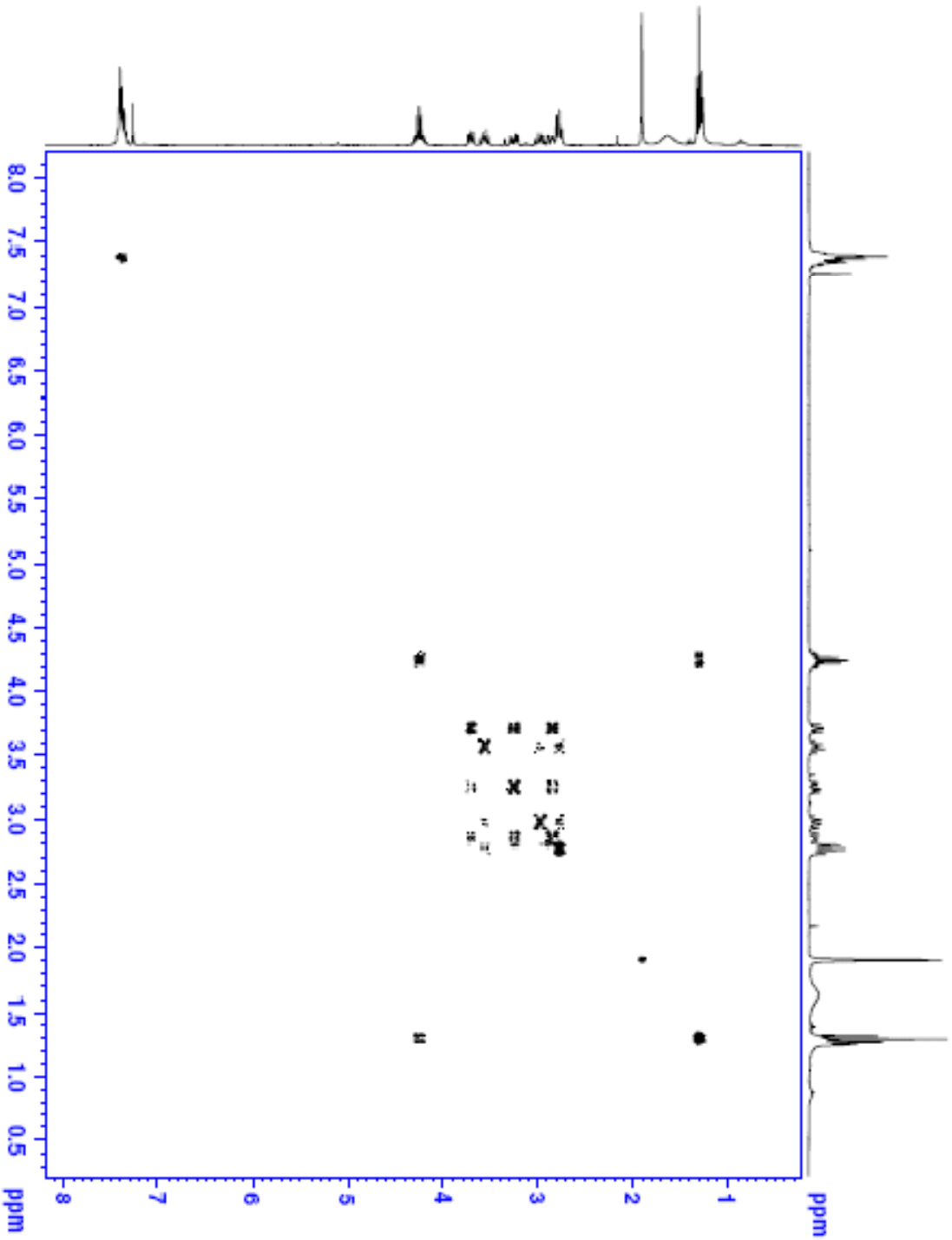

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
5.43
2.25
1.00
1.01
1.01
1.10
0.91
2.18
3.18
3.37

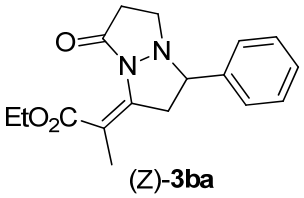

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



(*Z*)-**3ba**

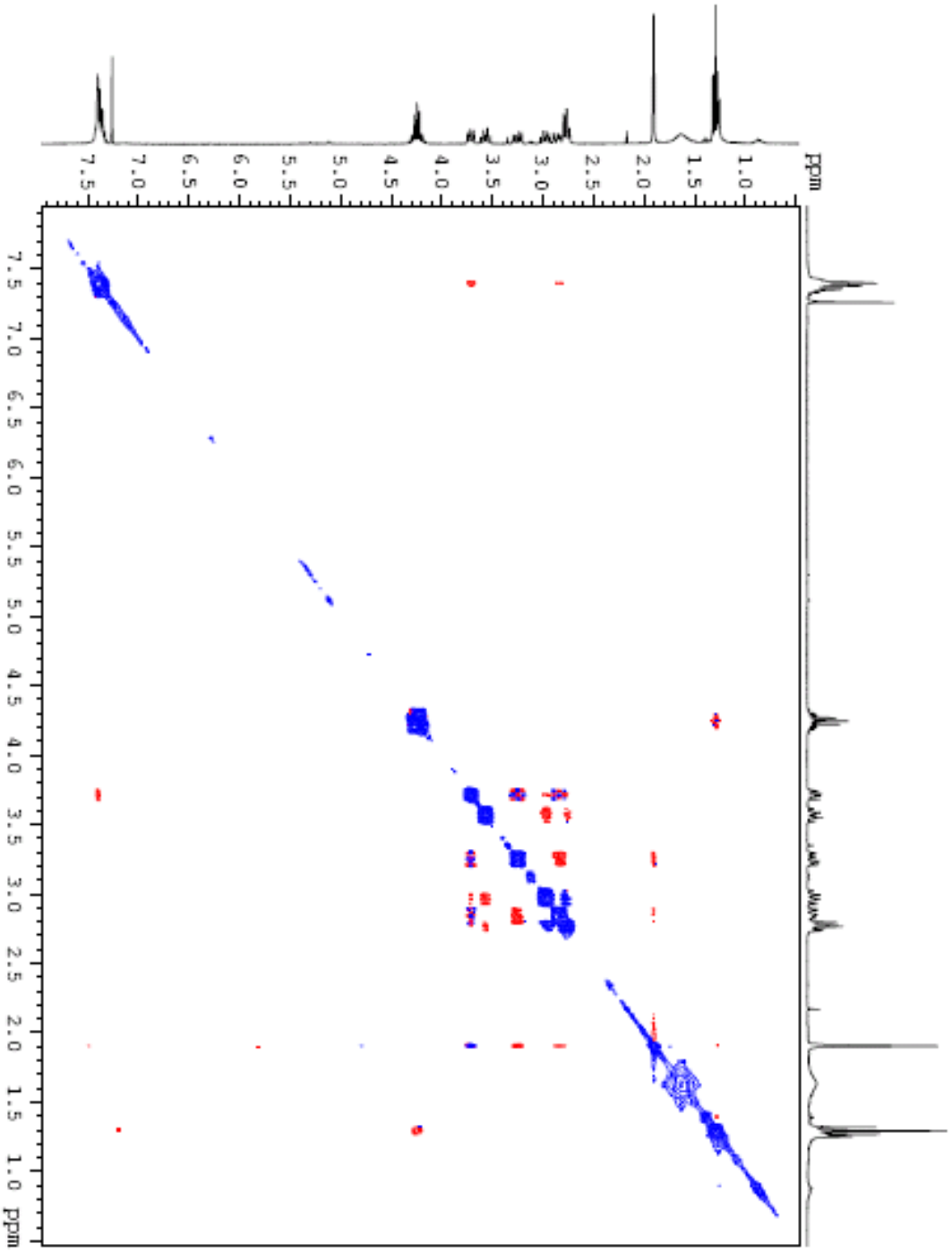
2D NMR COSY

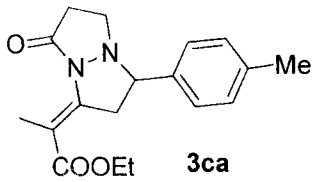




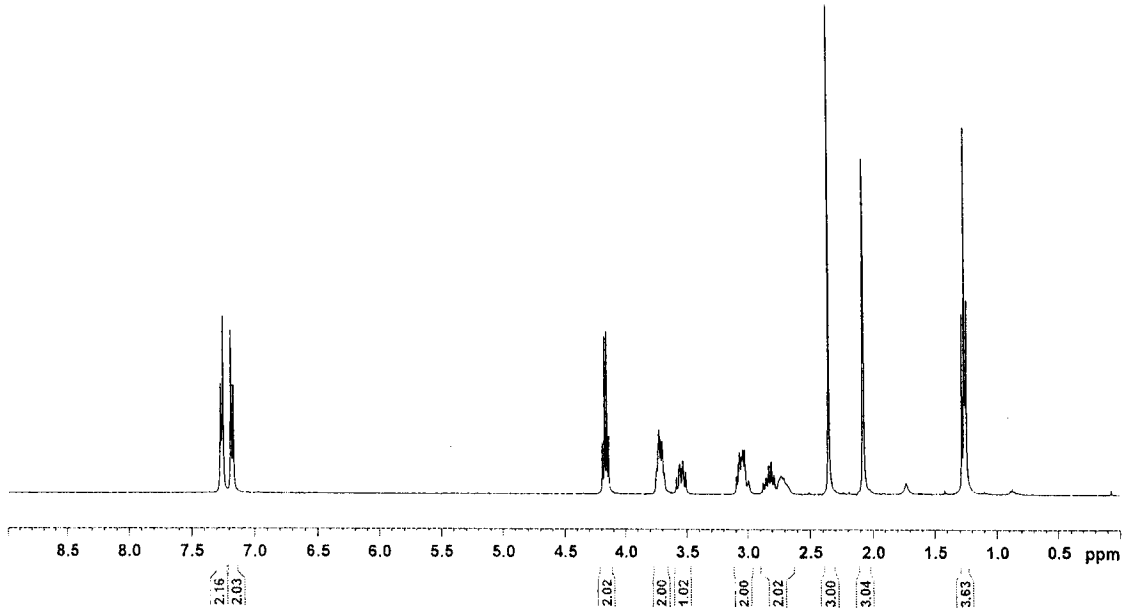
(Z)-**3ba**

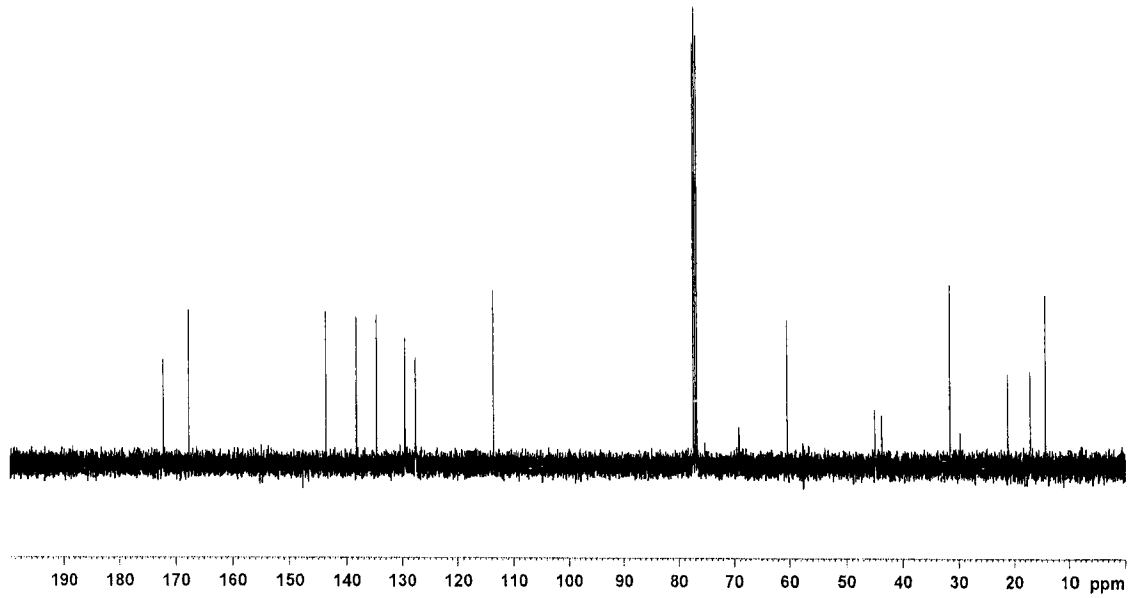
2D NMR NOESY

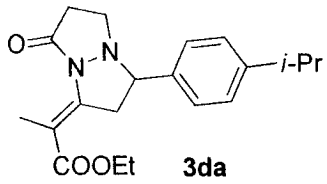



O
N
N
Me
COOEt

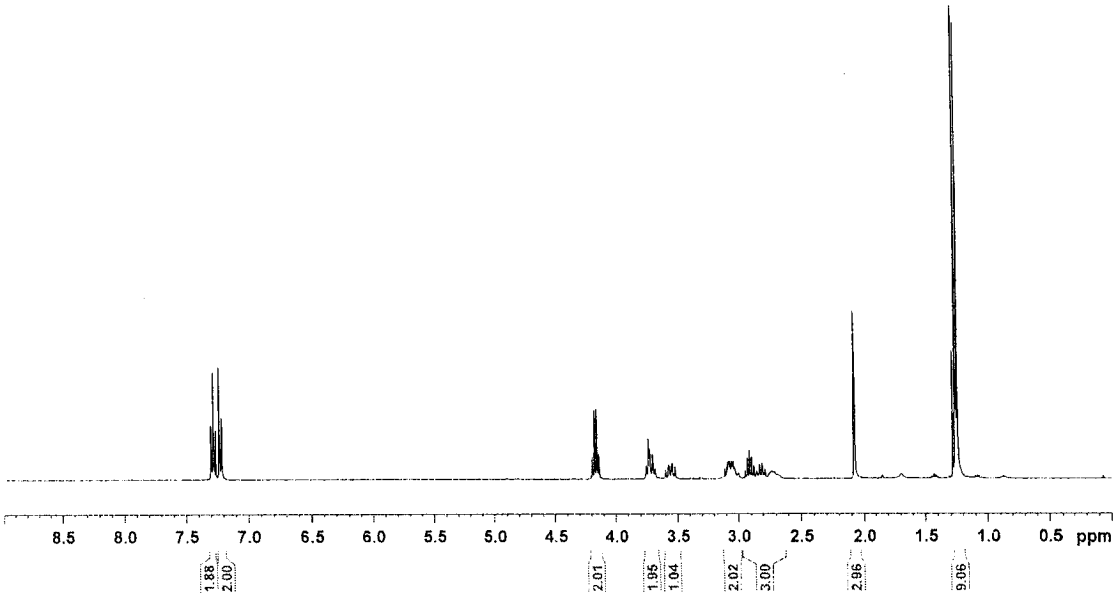
3ca

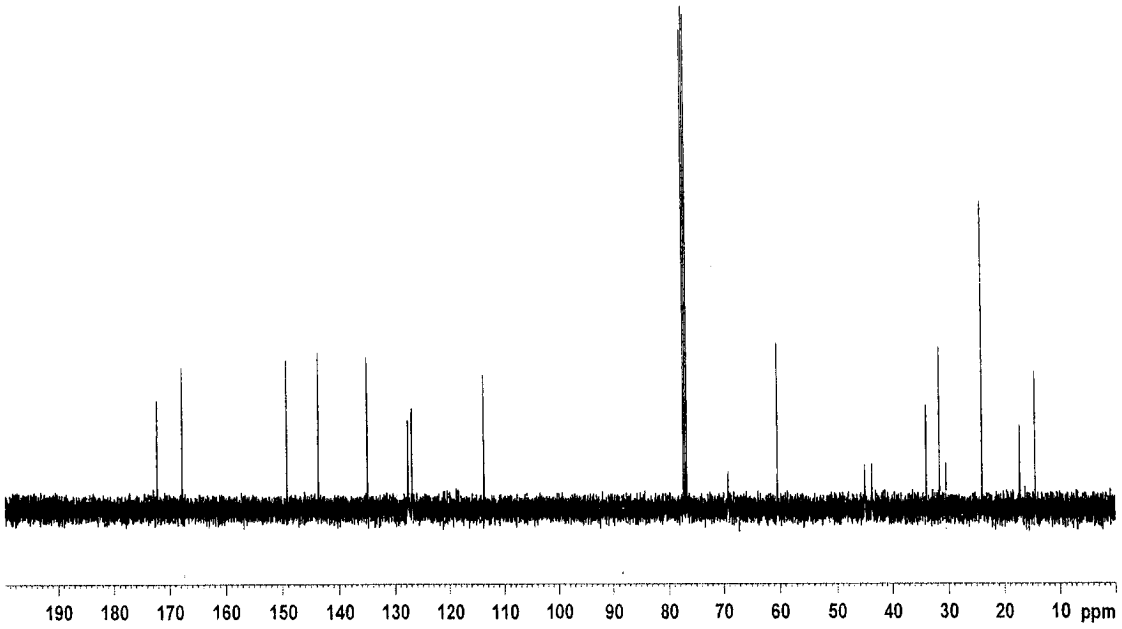

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.16
2.03
2.02
2.00
1.02
2.00
2.02
3.00
3.04
3.63

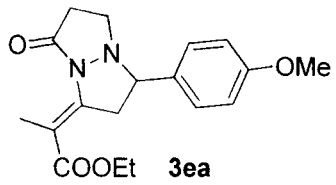

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
i-Pr
COOEt

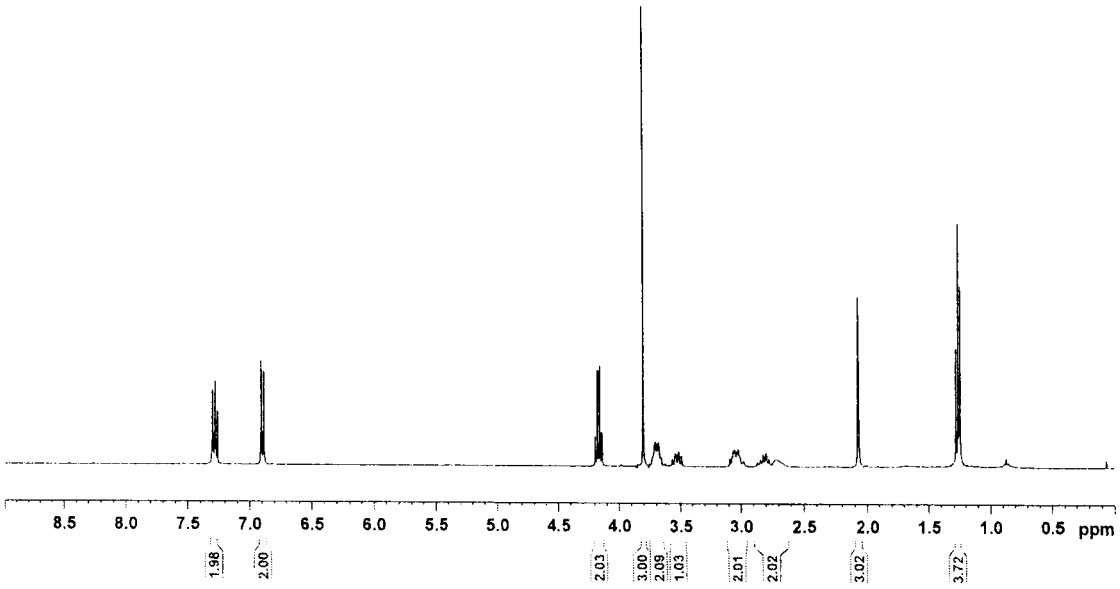
3da

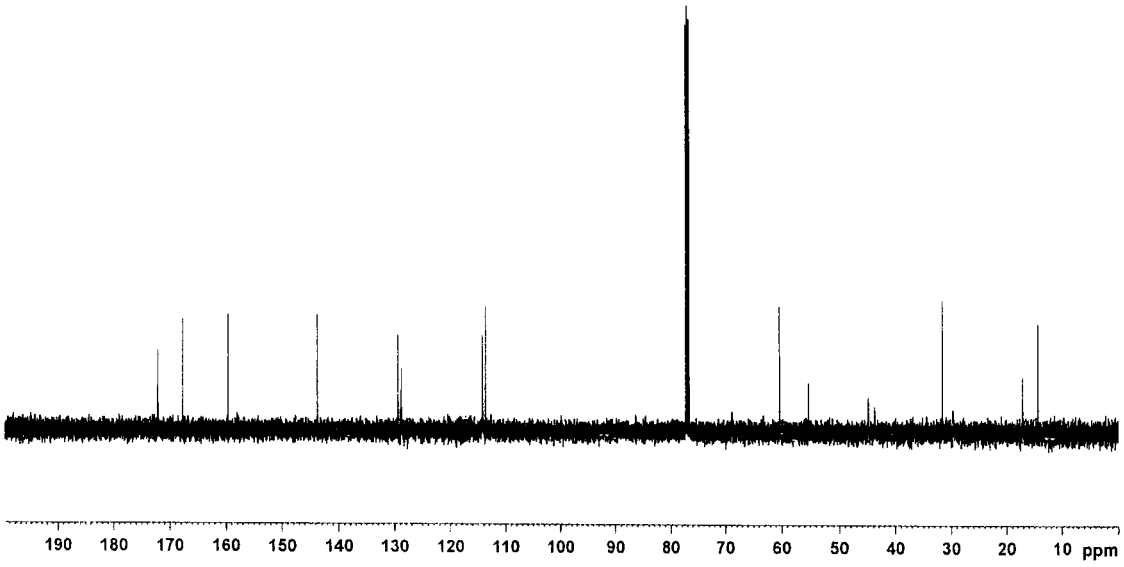

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.88
2.00
2.01
1.95
1.04
2.02
3.00
2.96
9.06

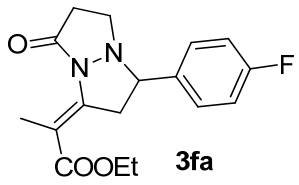

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
OMe
COOEt

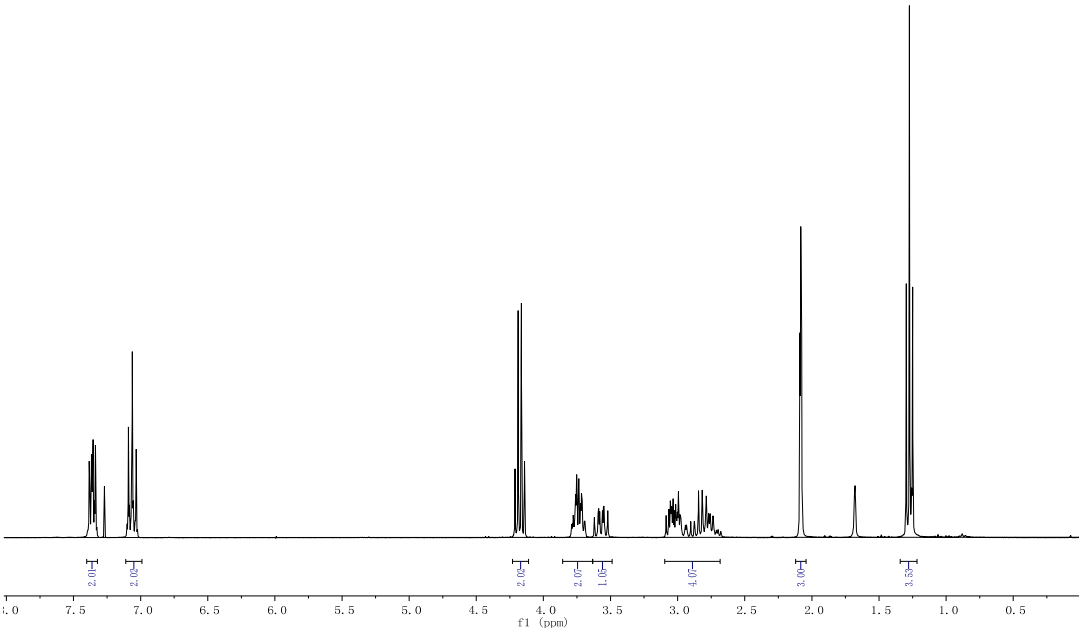
3ea

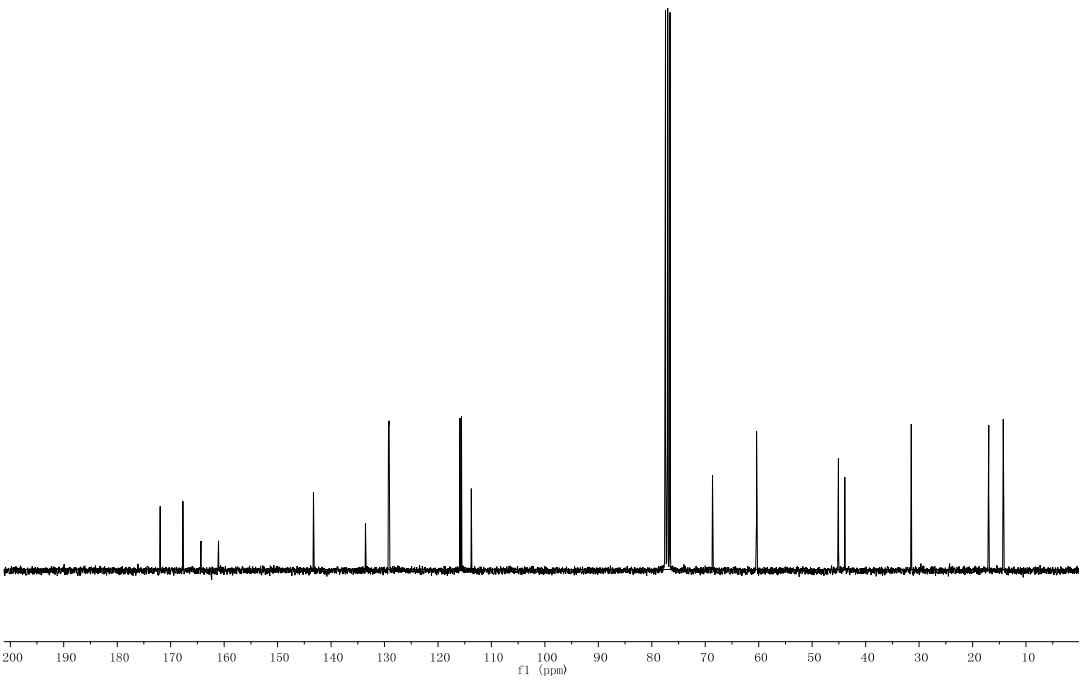

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98
2.00
2.03
3.00
2.09
1.03
2.01
2.02
3.02
3.72

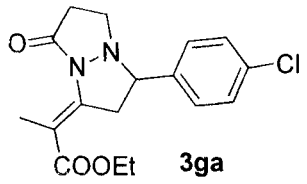

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
F
COOEt

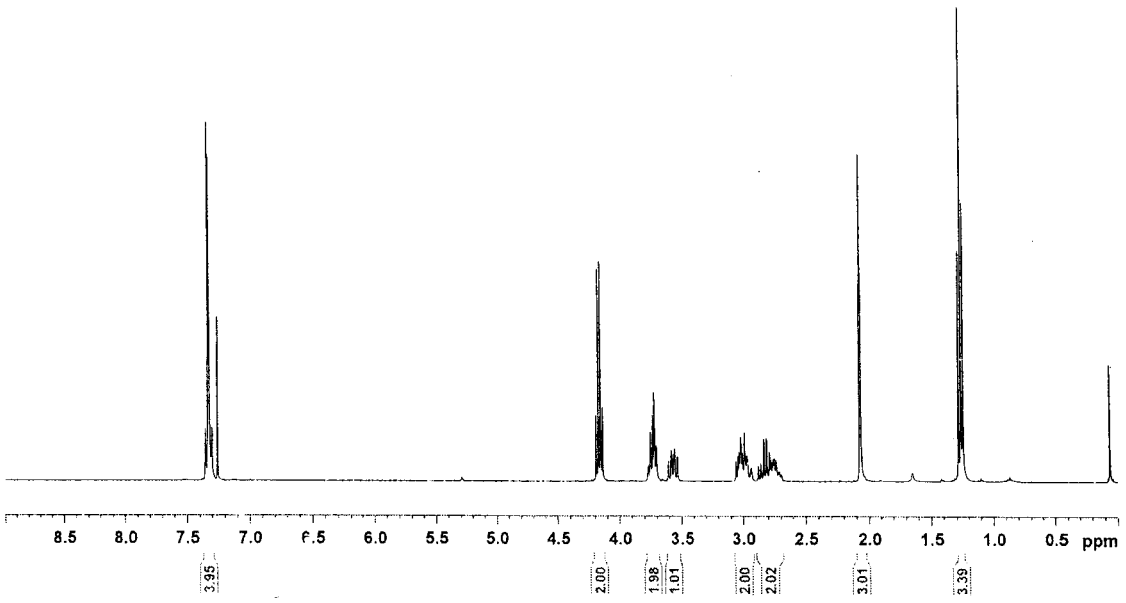
3fa

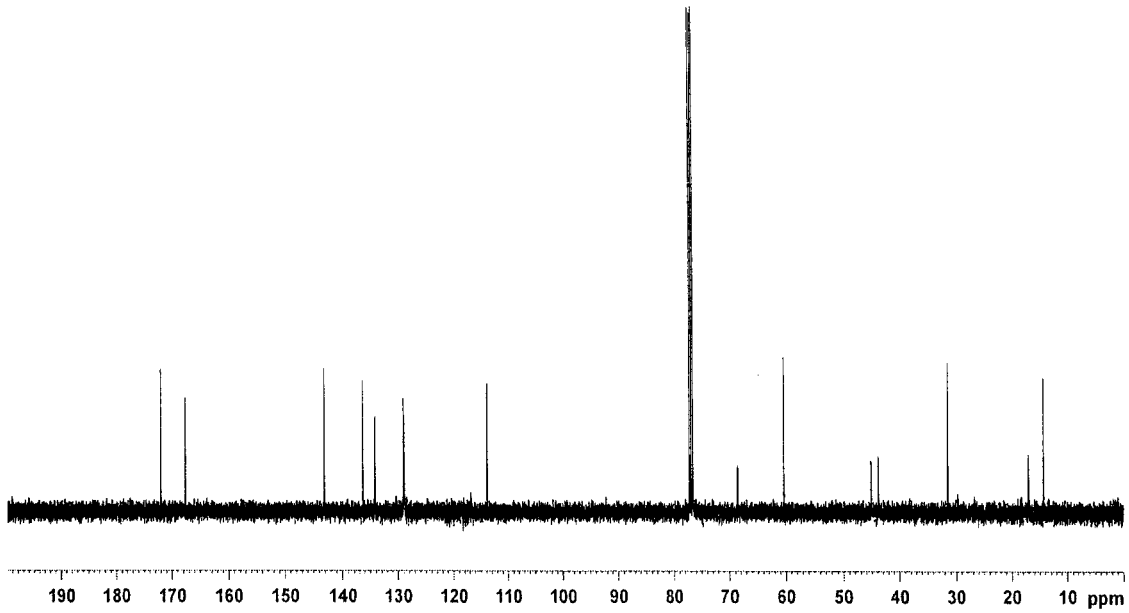

2.01
2.02
2.02
2.07
1.05
4.07
3.00
3.53
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

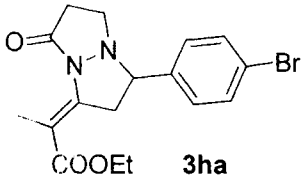

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
N
N
Cl
COOEt

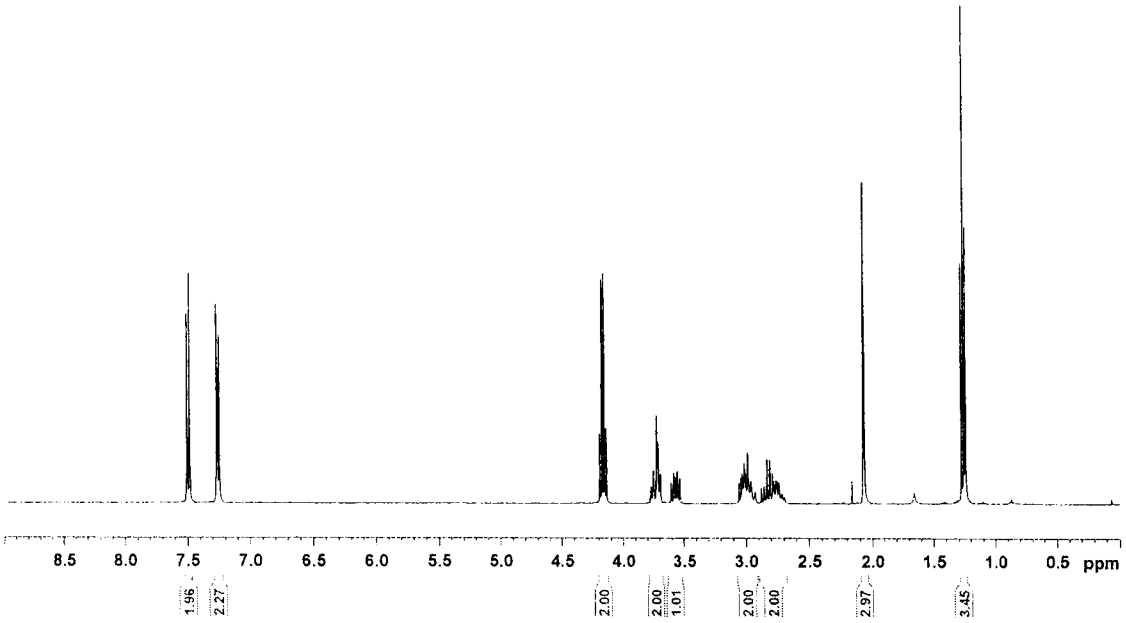
3ga

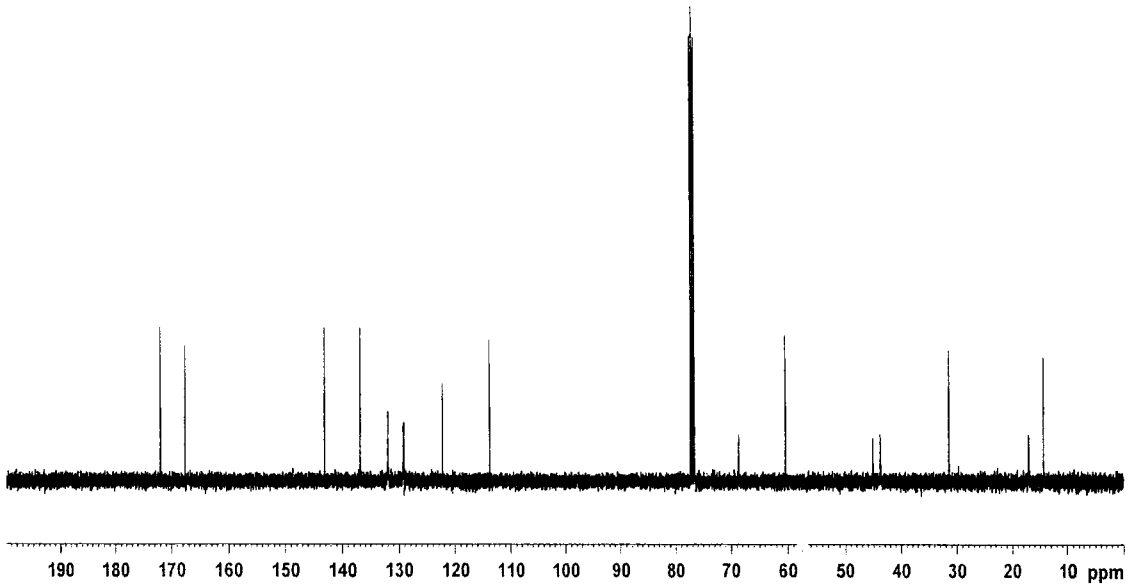

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.95
2.00
1.98
1.01
2.00
2.02
3.01
3.39

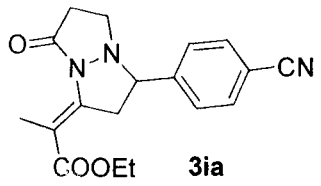

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
N
N
Br
COOEt

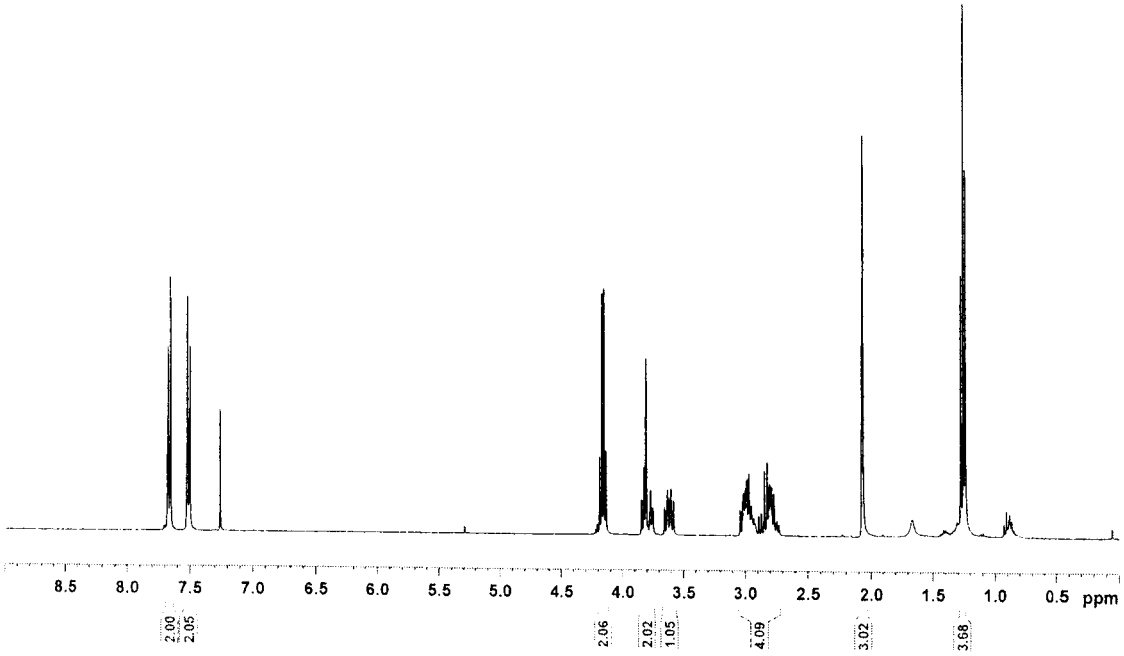
3ha

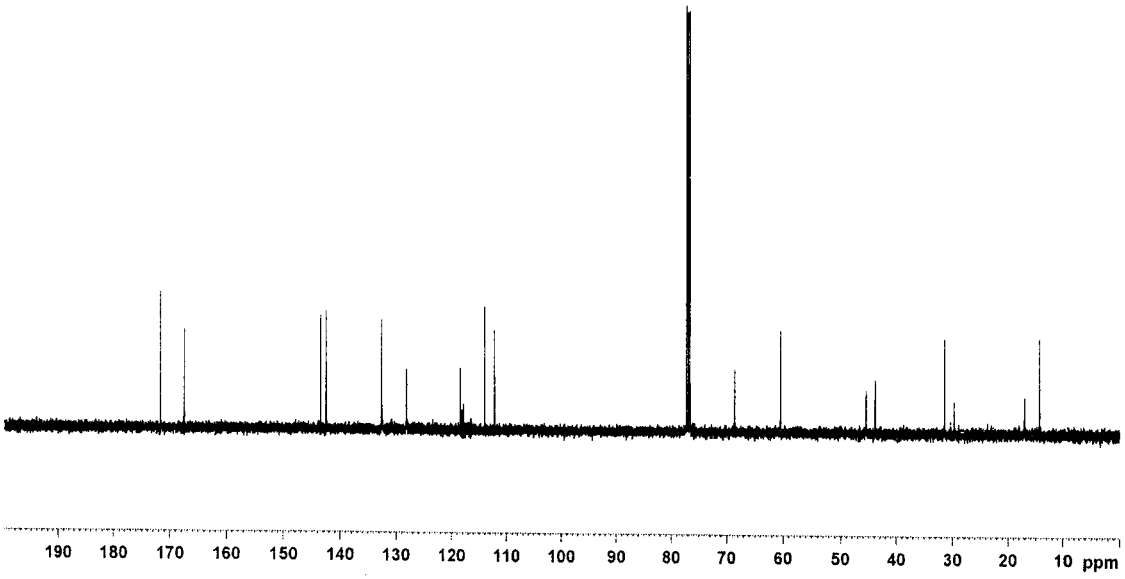

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.96
2.27
2.00
2.00
1.01
2.00
2.00
2.97
3.45

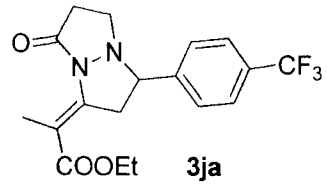

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
CN
COOEt

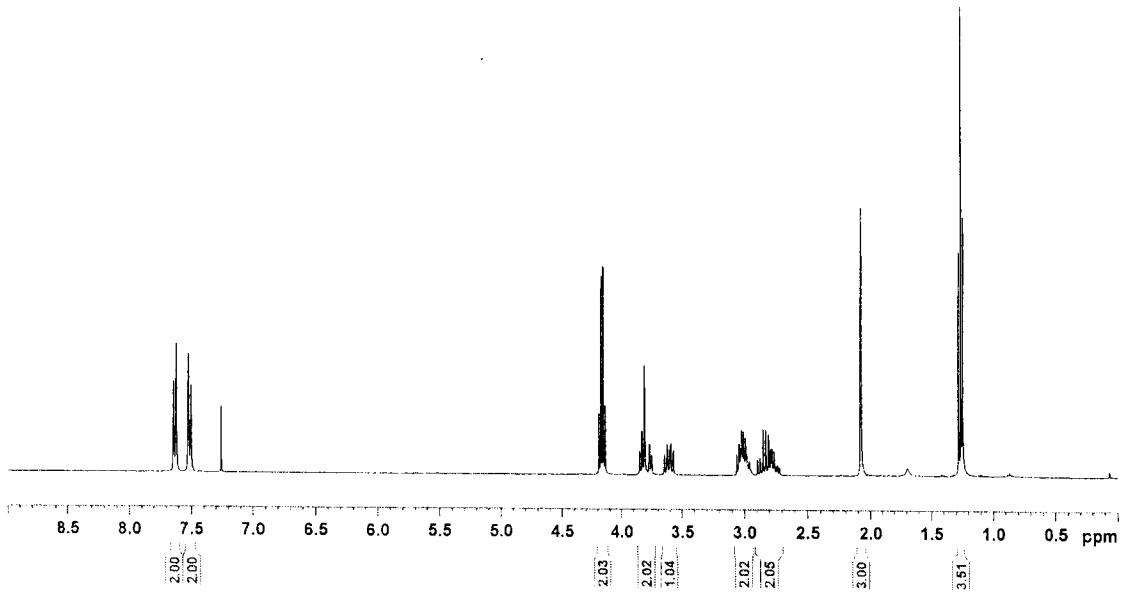
3ia

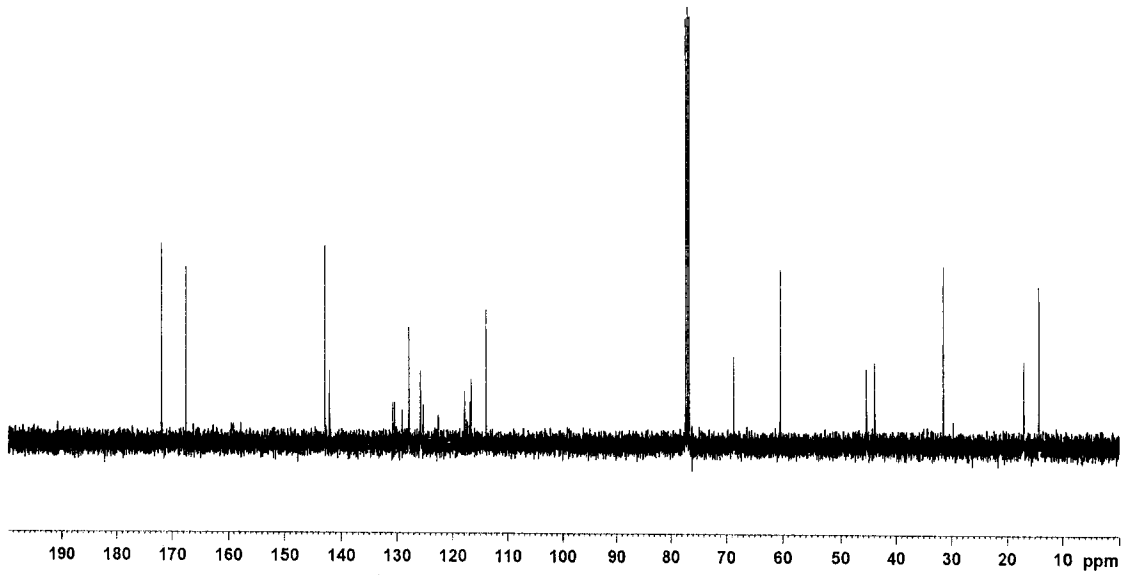

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.05
2.06
2.02
1.05
4.09
3.02
3.68

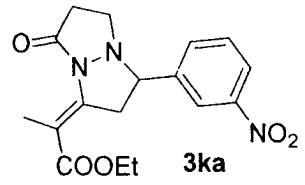

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
CF3
COOEt

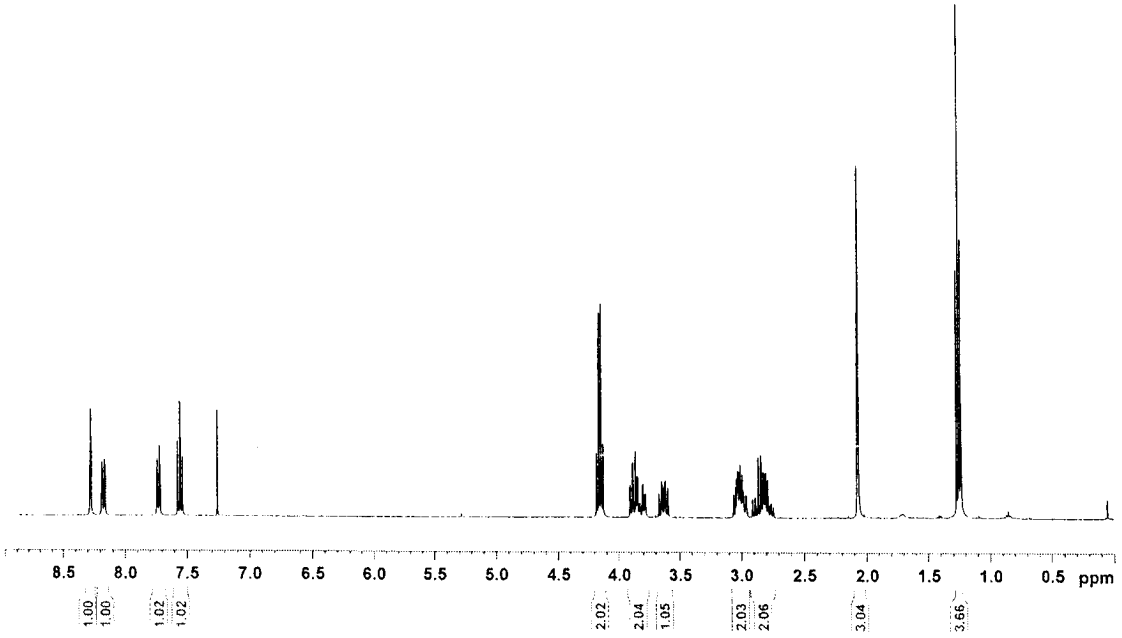
3ja

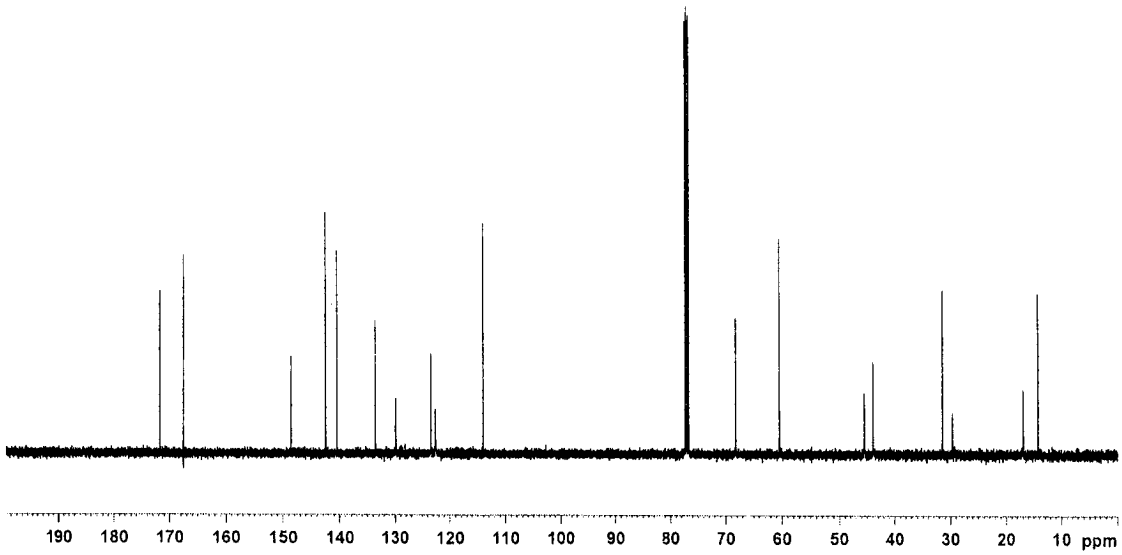

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.00
2.03
2.02
1.04
2.02
2.05
3.00
3.51

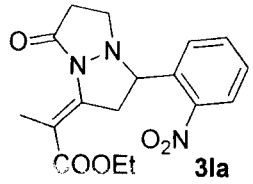

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
NO2
COOEt

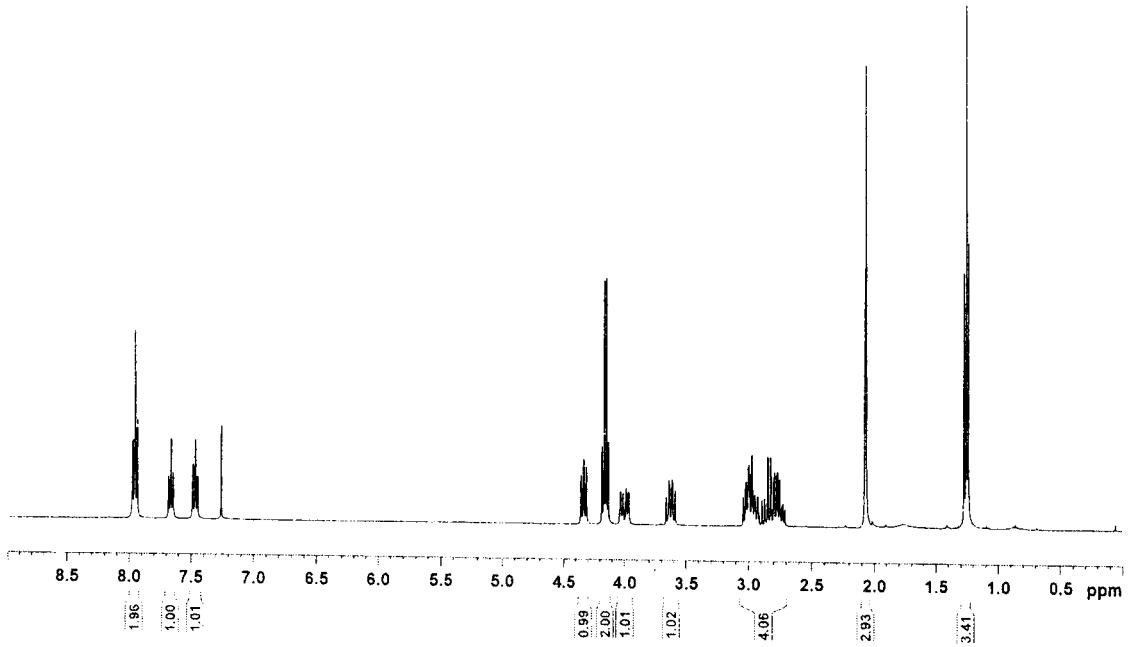
3ka

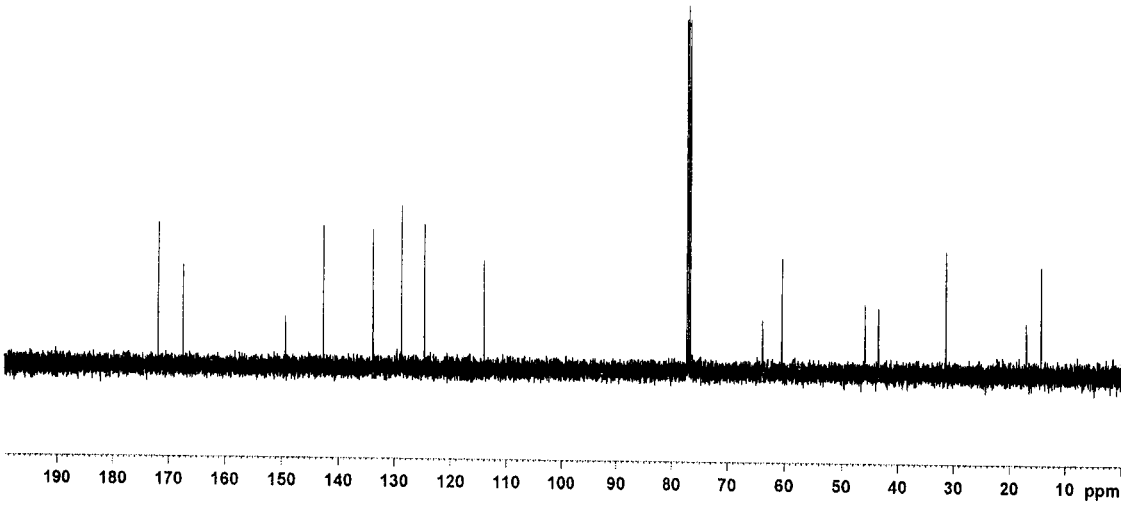

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.00
1.02
1.02
2.02
2.04
1.05
2.03
2.06
3.04
3.66

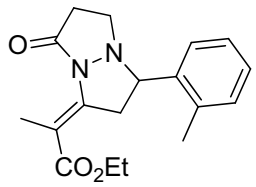

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
O_2N
COOEt

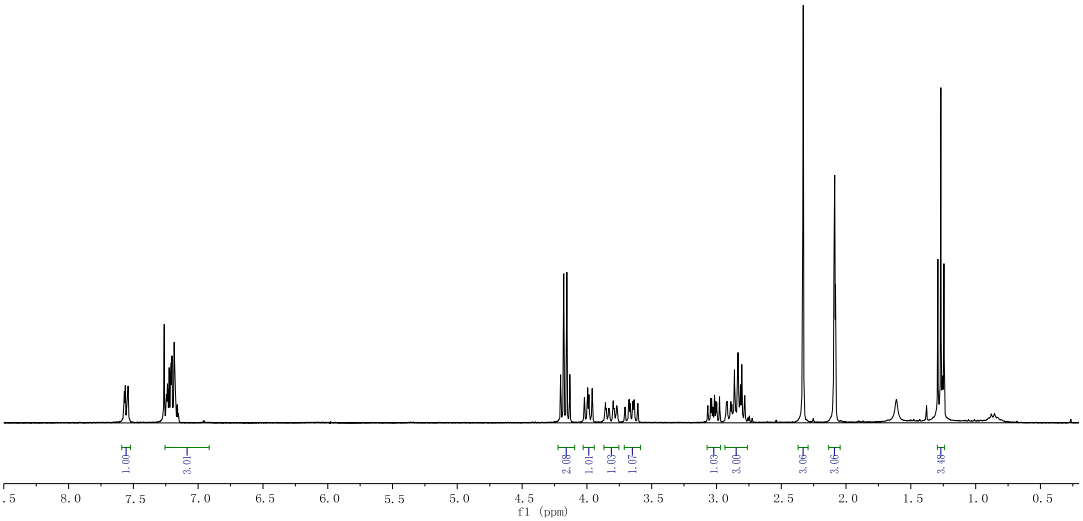
3la

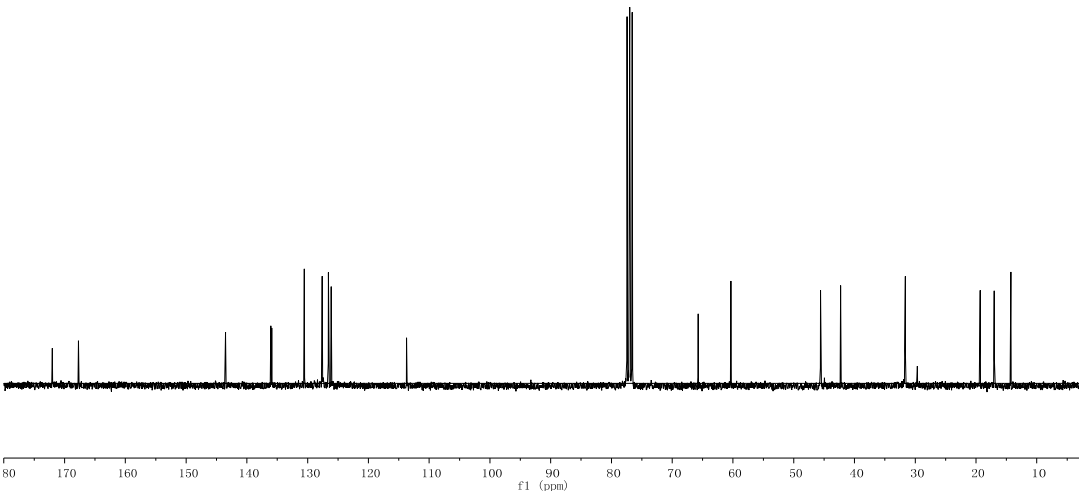

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.96
1.00
1.01
0.99
2.00
1.01
1.02
4.06
2.93
3.41

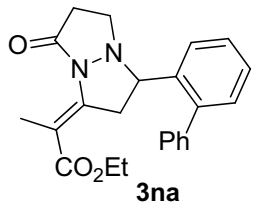

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
CO2Et

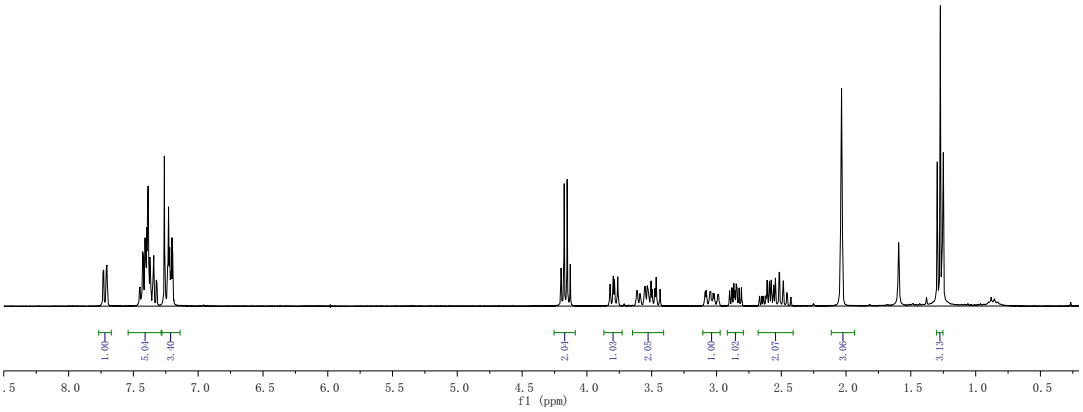
3ma

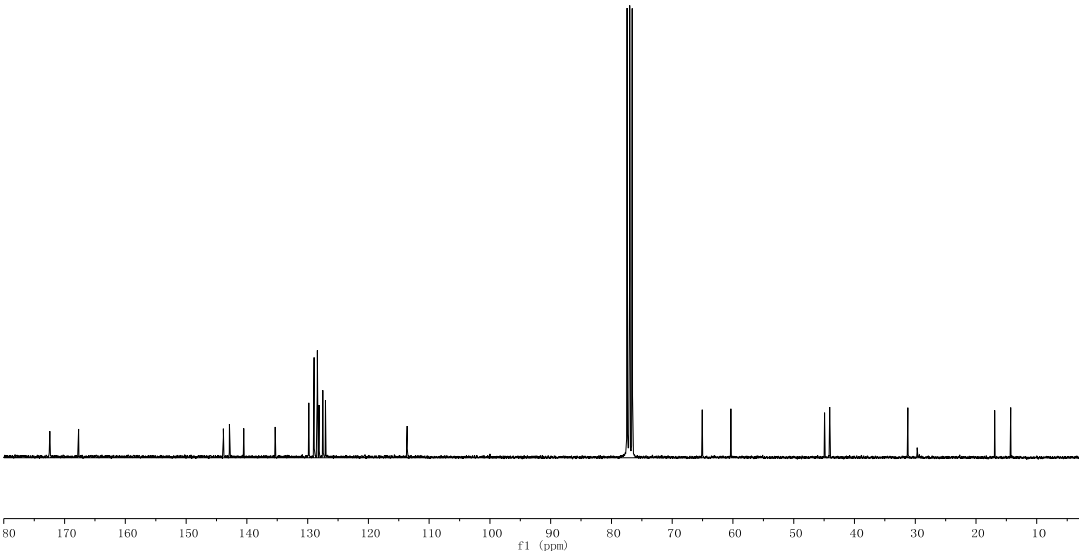

1.00
3.01
2.08
1.01
1.02
1.07
1.03
3.00
3.06
3.06
3.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

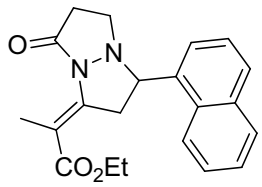

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
N
N
Ph
CO2Et

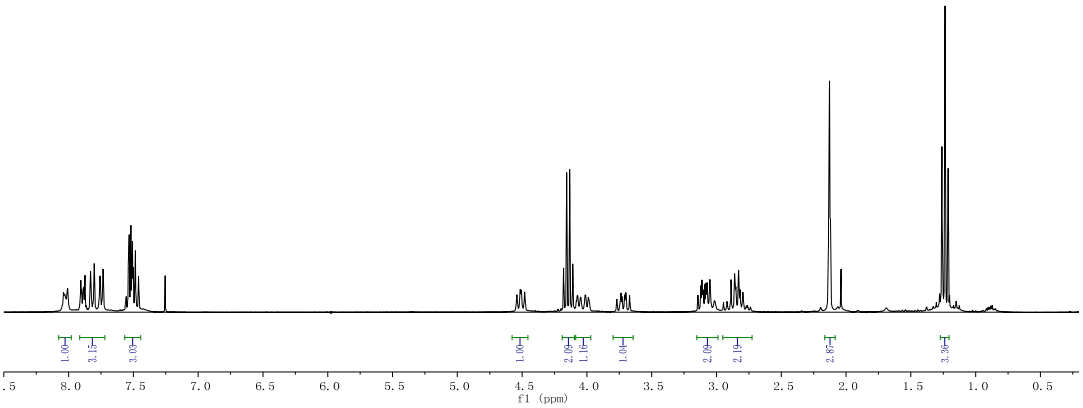
3na

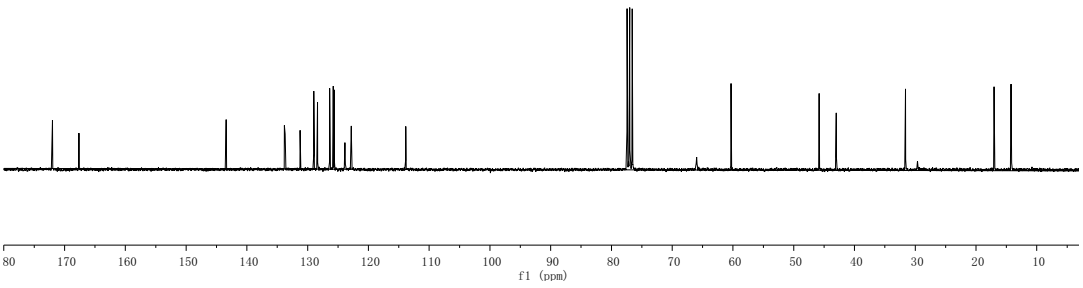

1.00
5.04
3.40
2.04
1.03
2.05
1.00
1.02
2.07
3.06
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

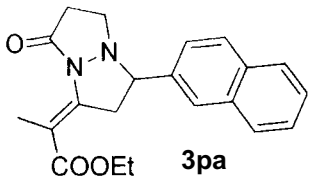

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
N
N
CO2Et

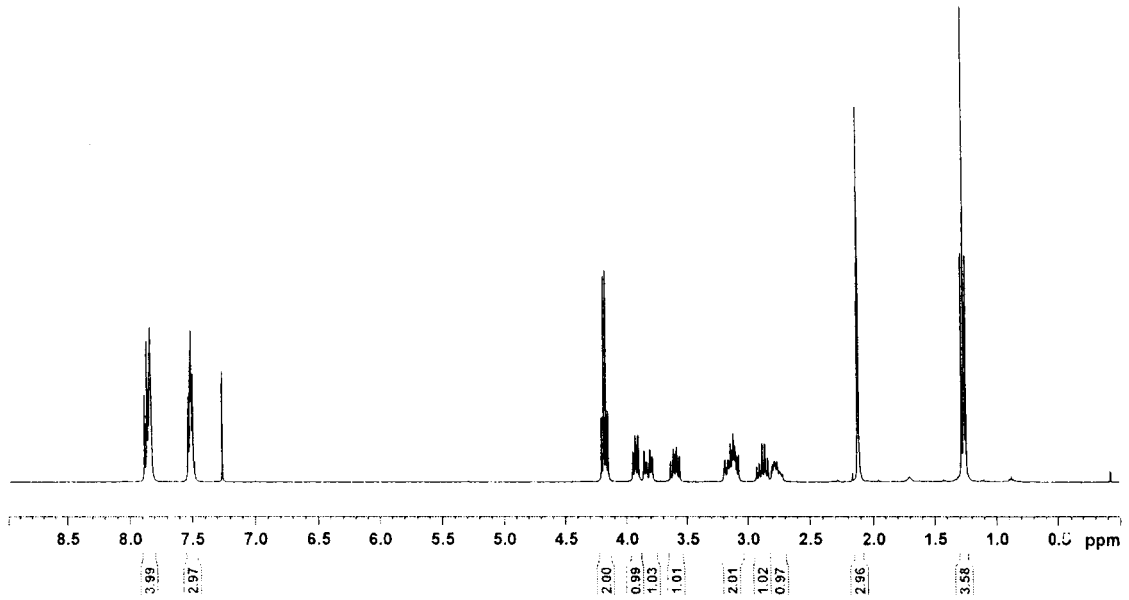
3oa

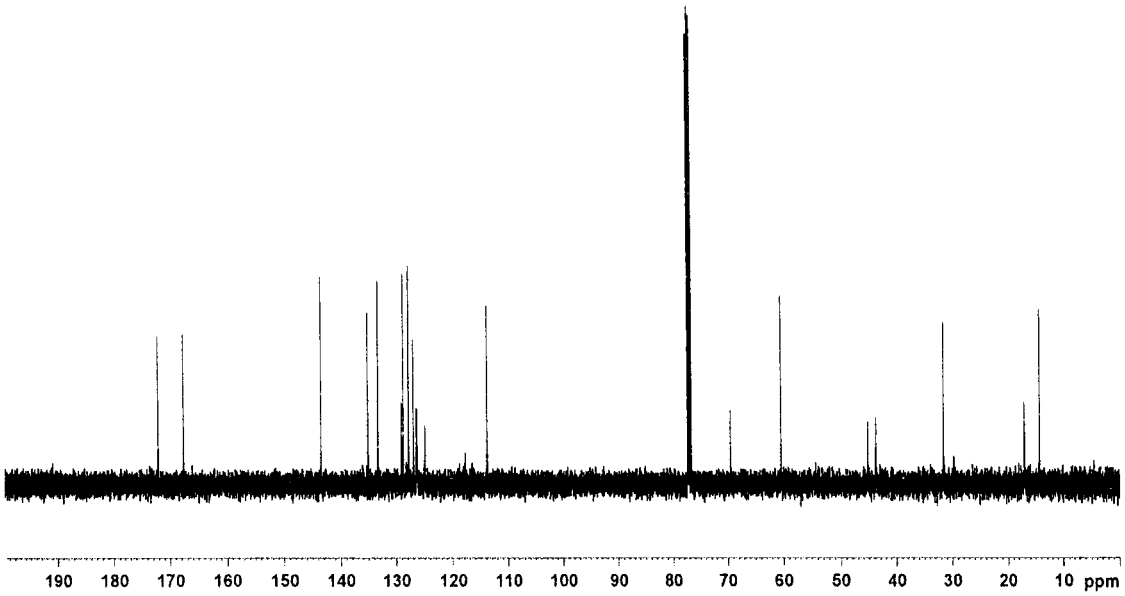

1.00
3.15
3.05
1.00
2.02
1.11
1.04
2.09
2.10
2.85
3.36
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

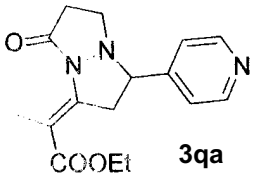

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
N
N
COOEt

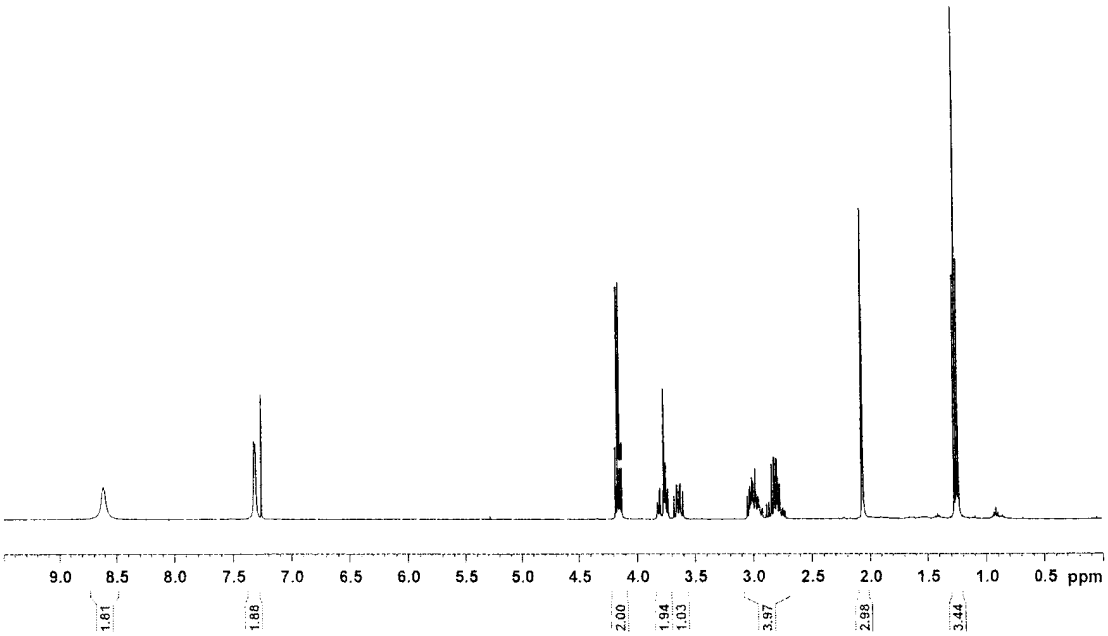
3pa

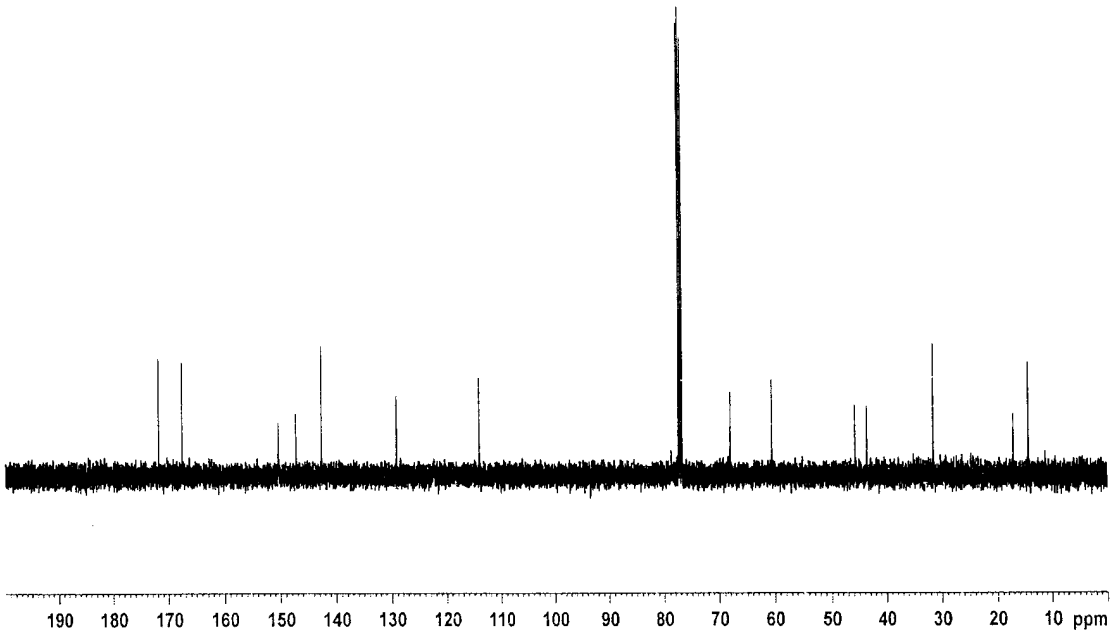

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.99
2.97
2.00
0.99
1.03
1.01
2.01
1.02
0.97
2.96
3.58

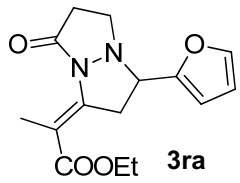

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
N
COOEt

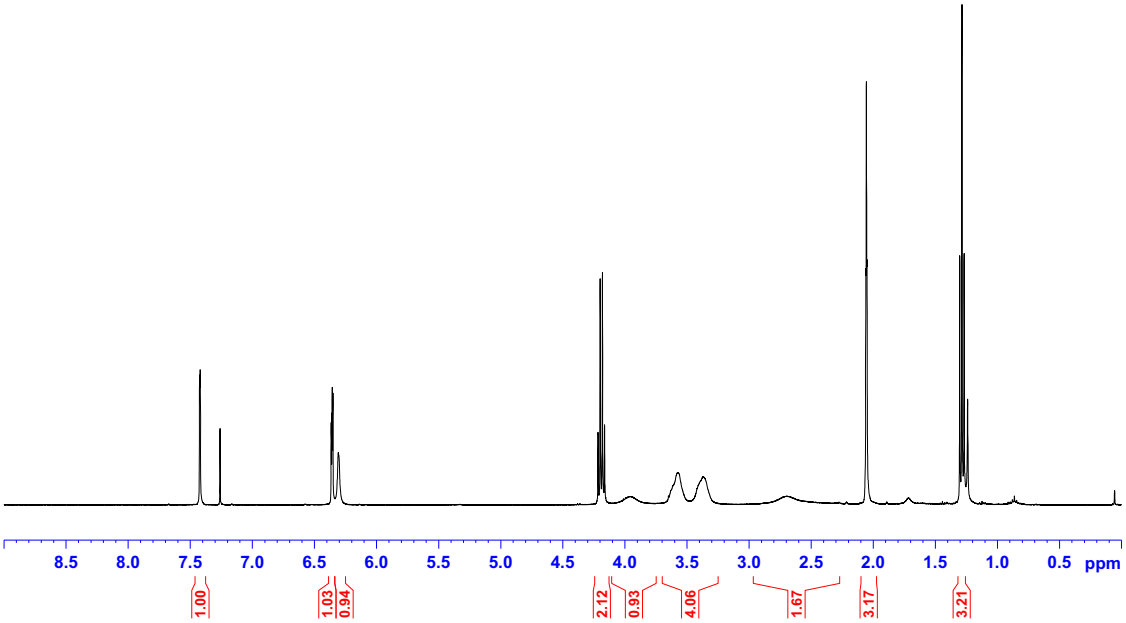
3qa

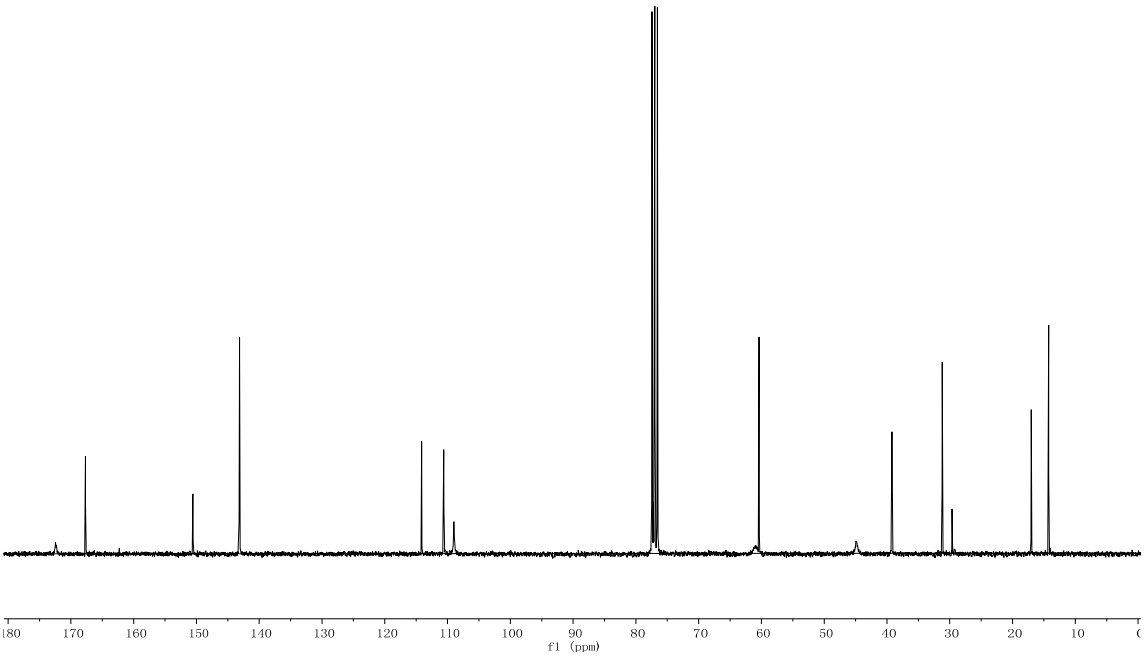

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.61
1.88
2.00
1.94
1.03
3.97
2.98
3.44

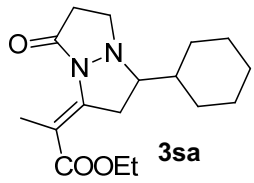

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
N
N
O
COOEt

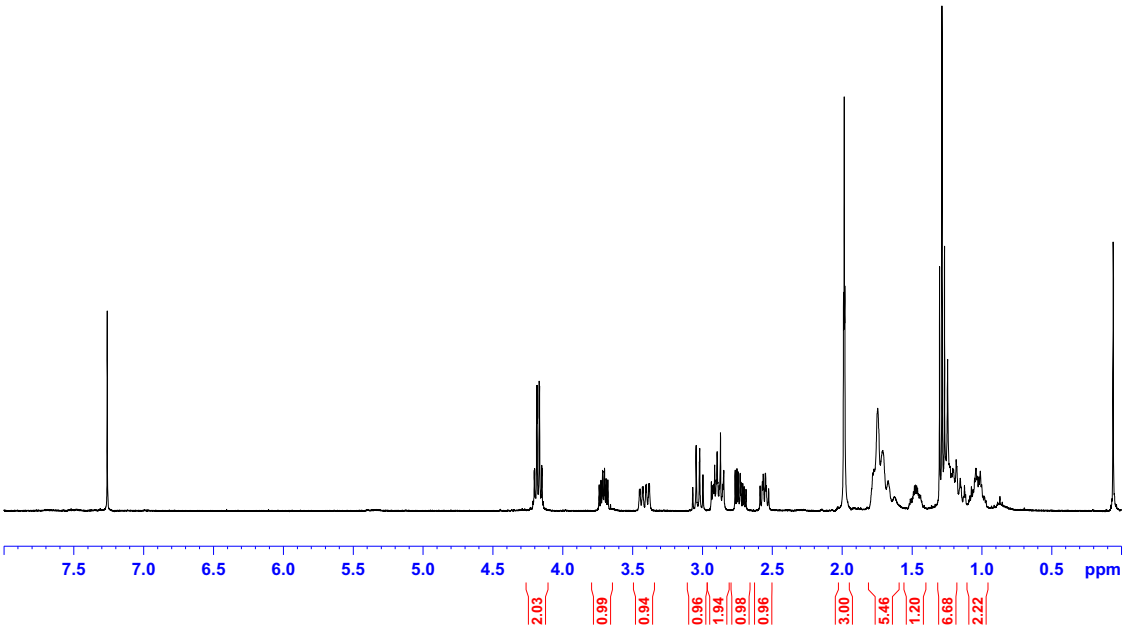
3ra

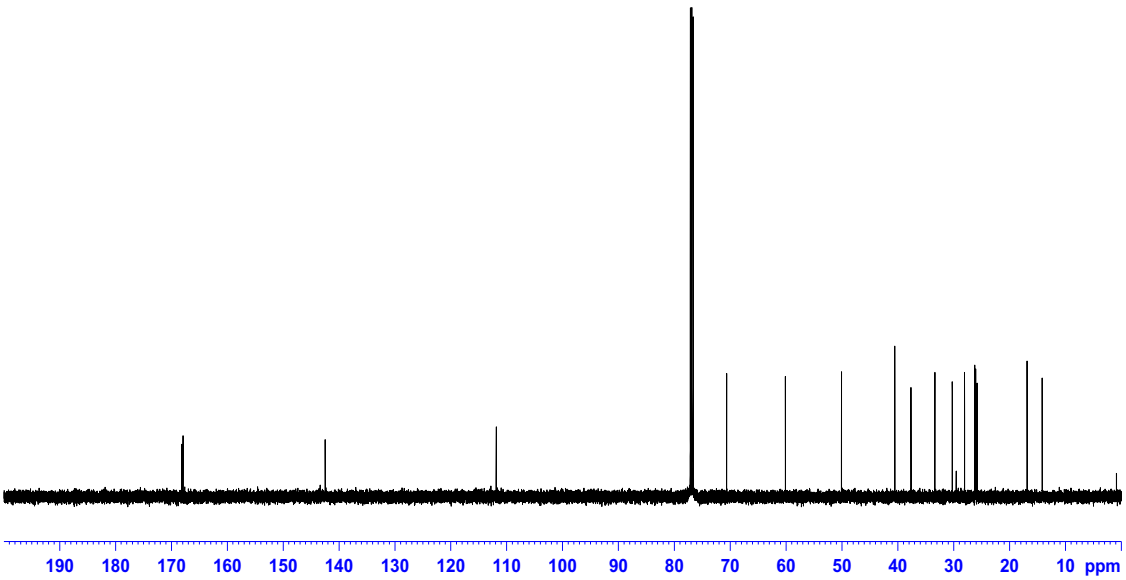

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
0.94
2.12
0.93
4.06
1.67
3.17
3.21

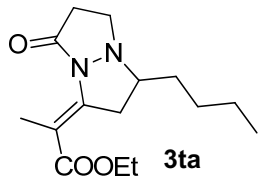

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
N
N
COOEt

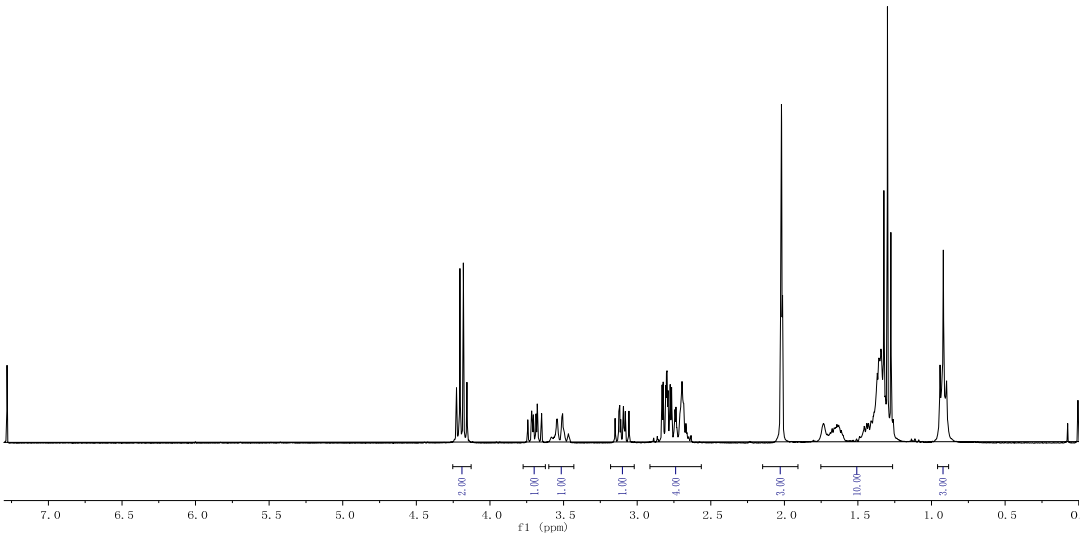
3sa

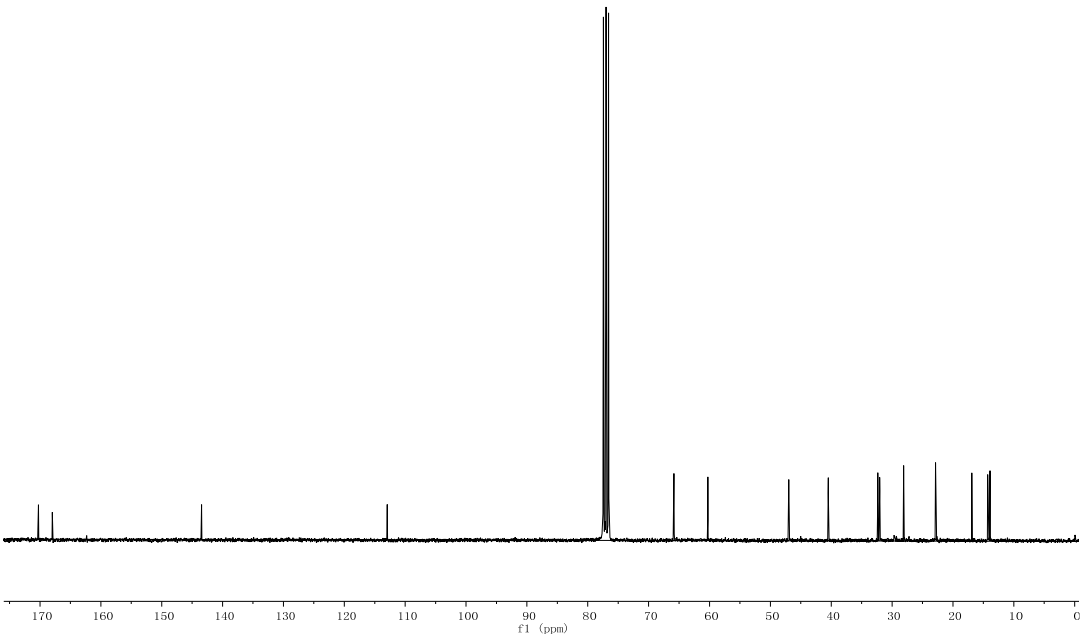

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
0.99
0.94
0.96
1.94
0.98
0.96
3.00
5.46
1.20
6.68
2.22

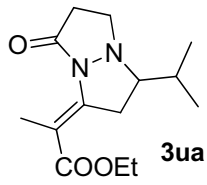

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
N
N
COOEt

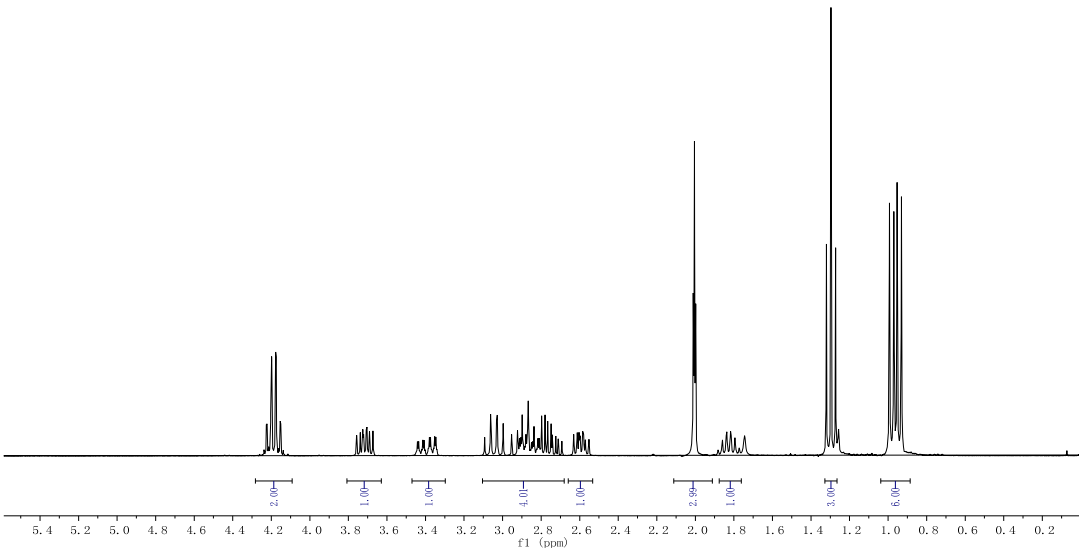
3ta

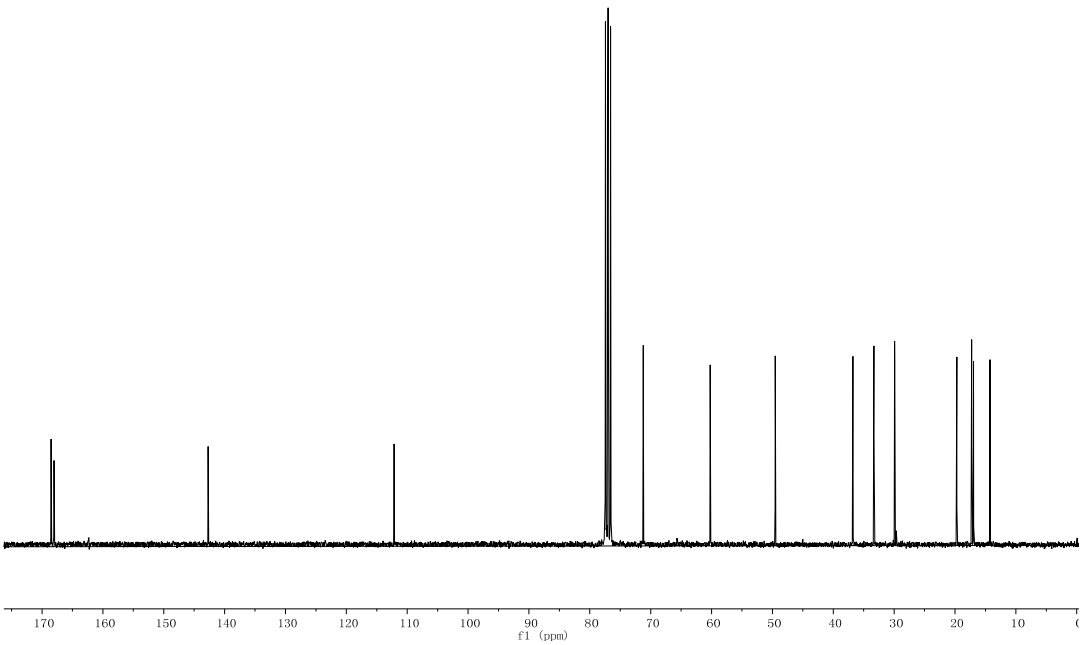

2.00
1.00
1.00
1.00
4.00
3.00
10.00
3.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

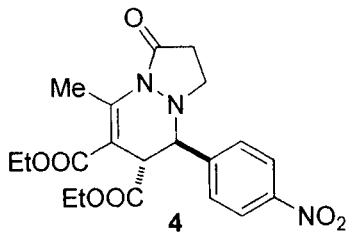

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
N
COOEt

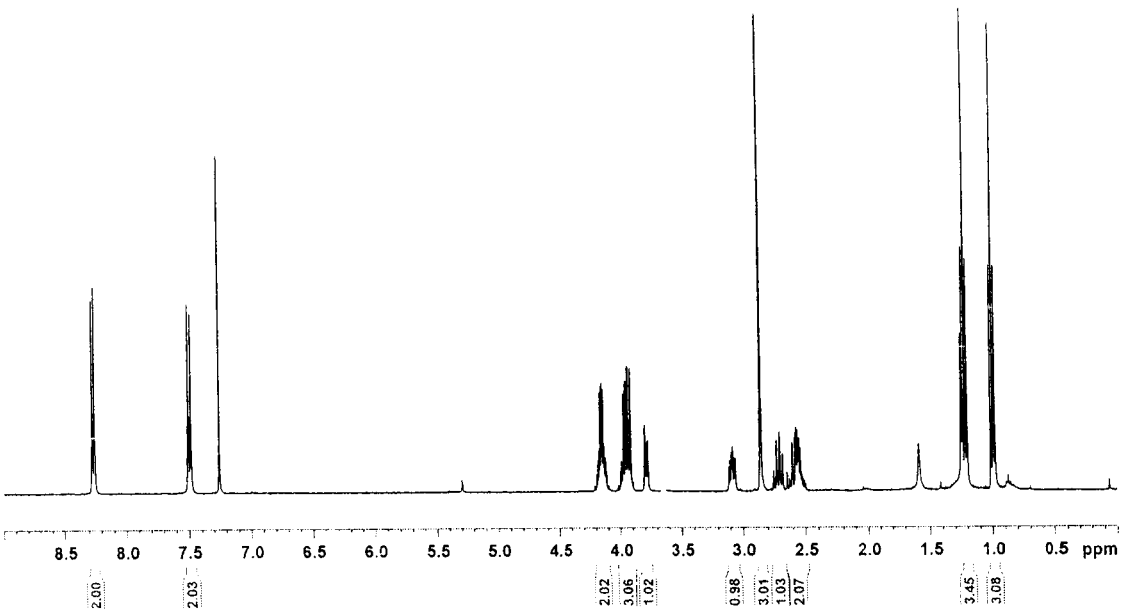
3ua

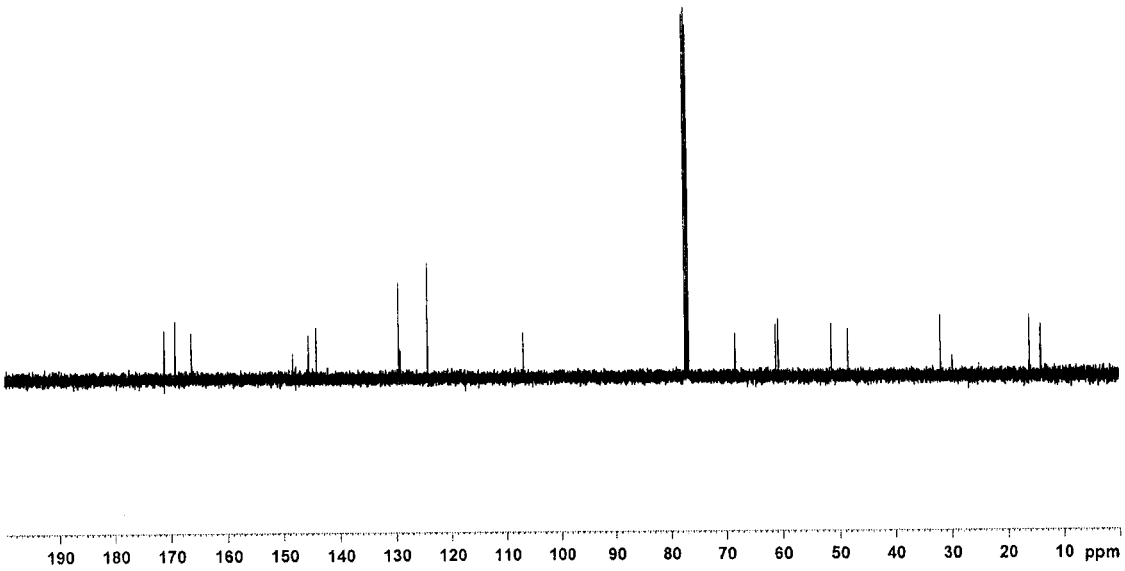

2.00
1.01
1.00
4.01
1.00
2.98
1.01
3.03
6.00
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2
f1 (ppm)

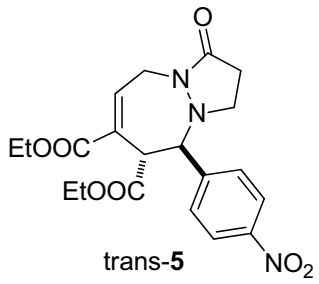

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
Me
N
N
EtOOC
EtOOC
NO2

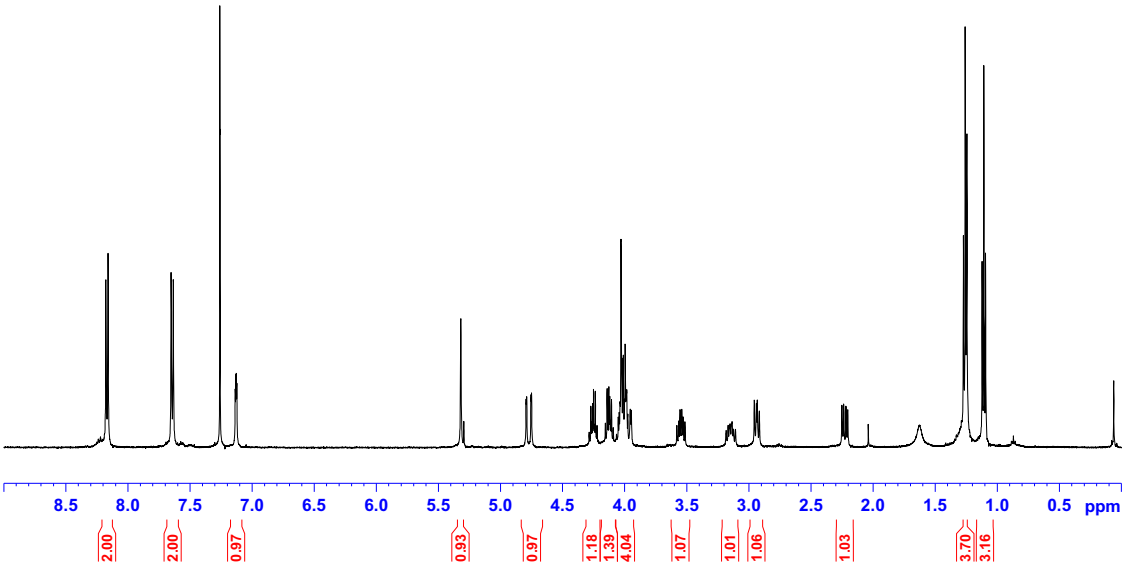
4

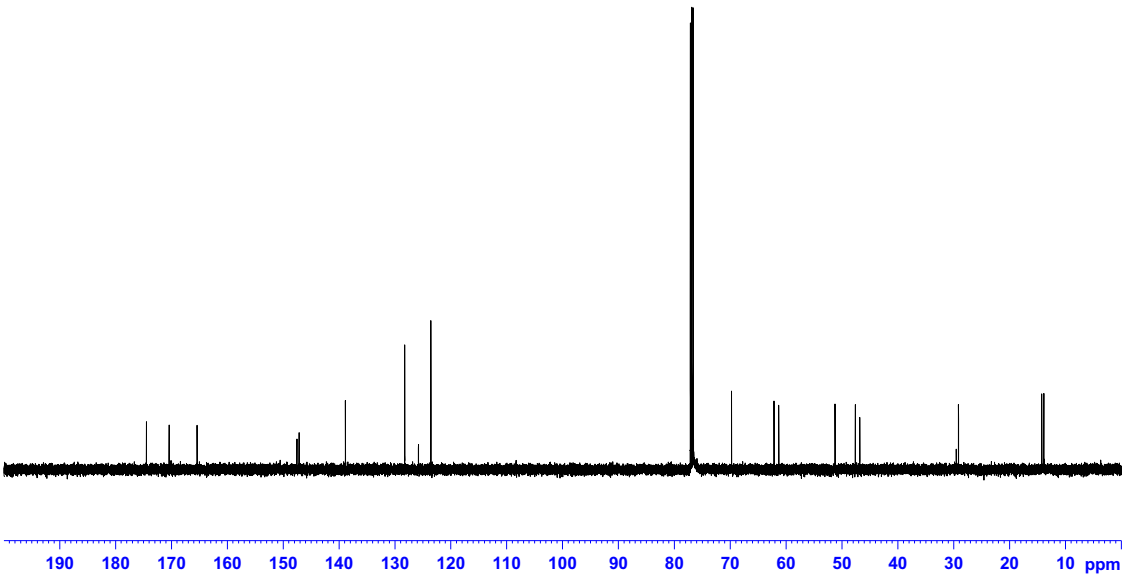

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.03
2.02
3.06
1.02
0.98
3.01
1.03
2.07
3.45
3.08

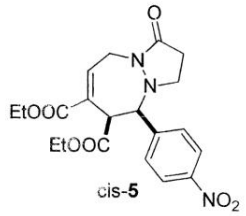

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

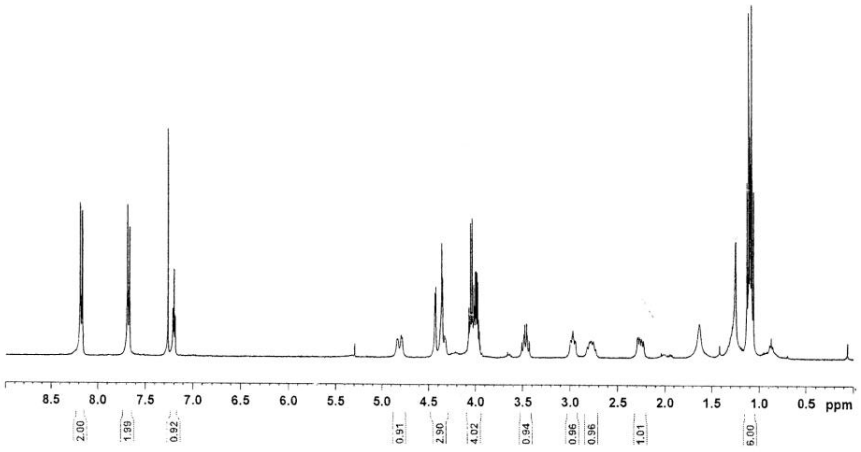

O
N
N
EtOOC
EtOOC
NO2

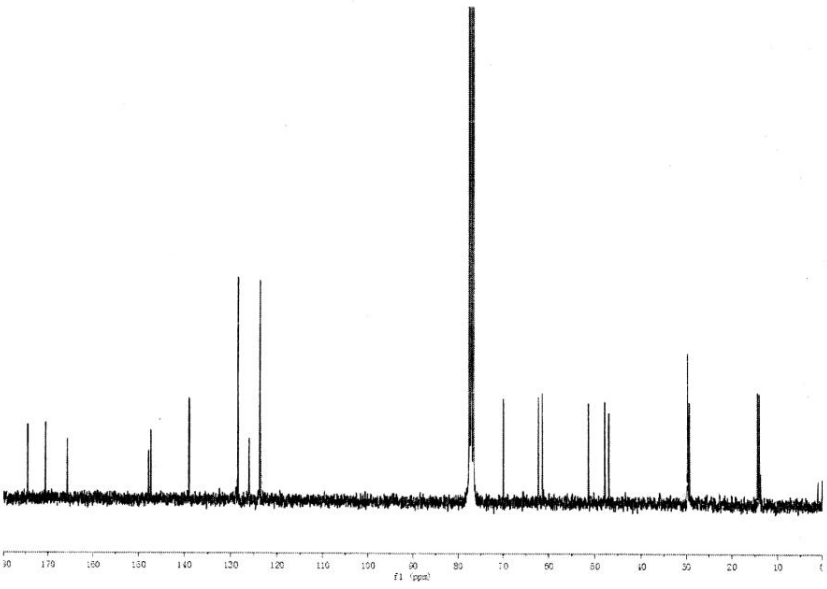
trans-**5**

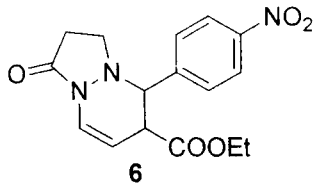

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 2.00 0.97 0.93 0.97 1.18 1.39 4.04 1.07 1.01 1.06 1.03 3.70 3.16


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

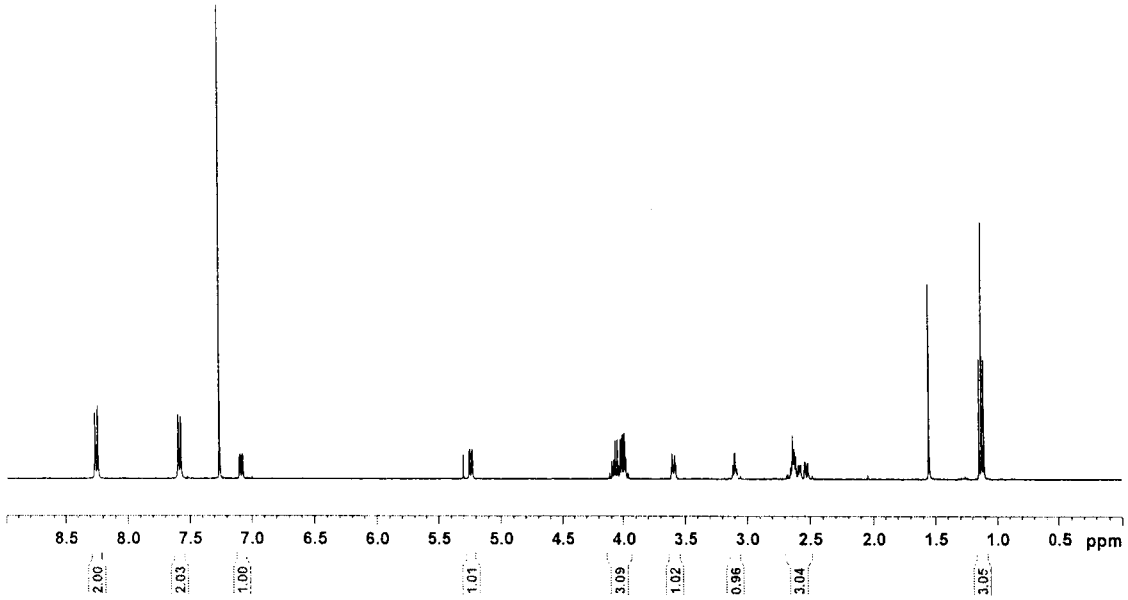

O
N
N
EtOOC
EtOOC
cis-5
NO2

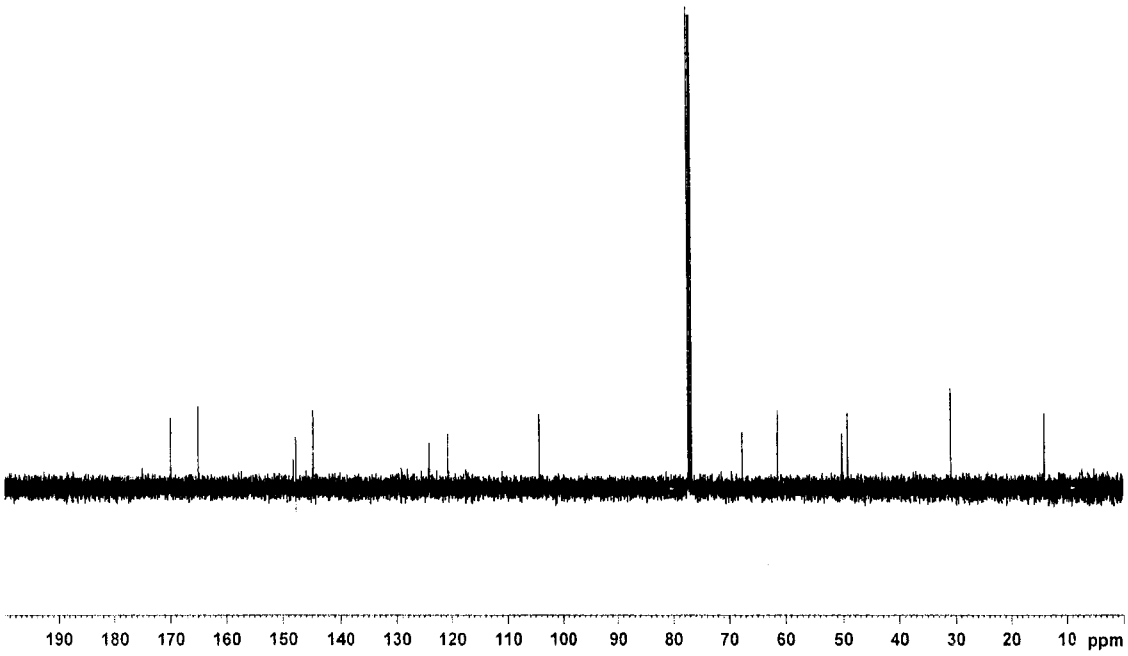

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.99
0.92
0.91
2.90
4.02
0.94
0.96
0.96
1.01
6.00

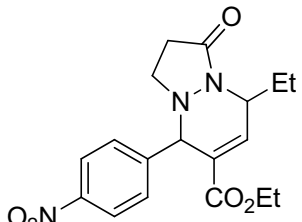



NO2
O
N
N
COOEt

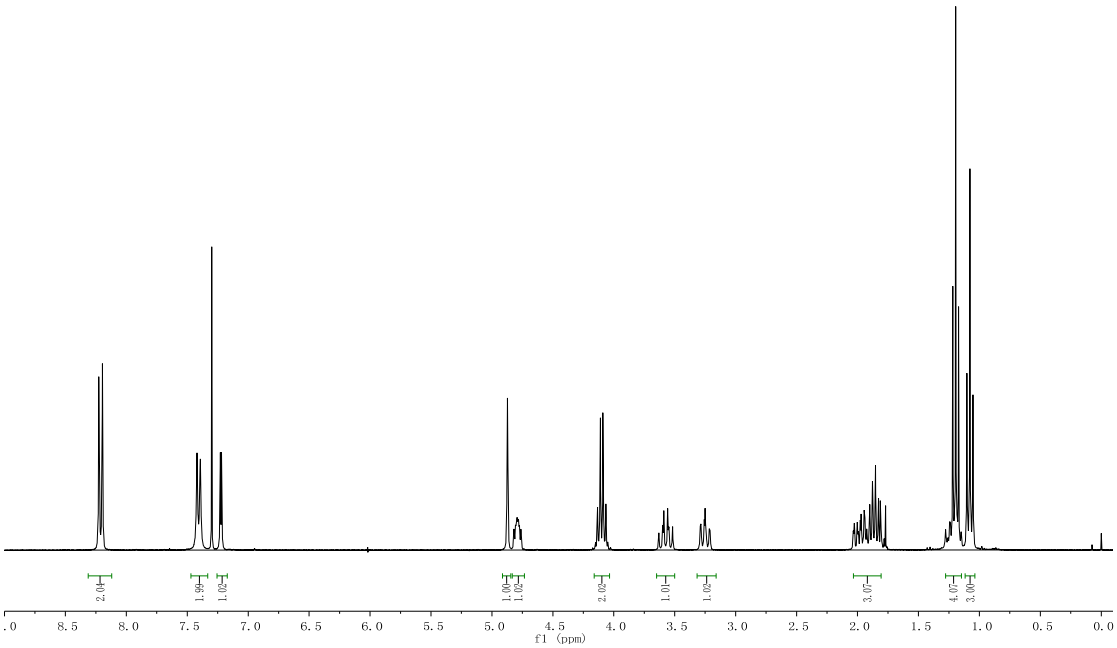
6

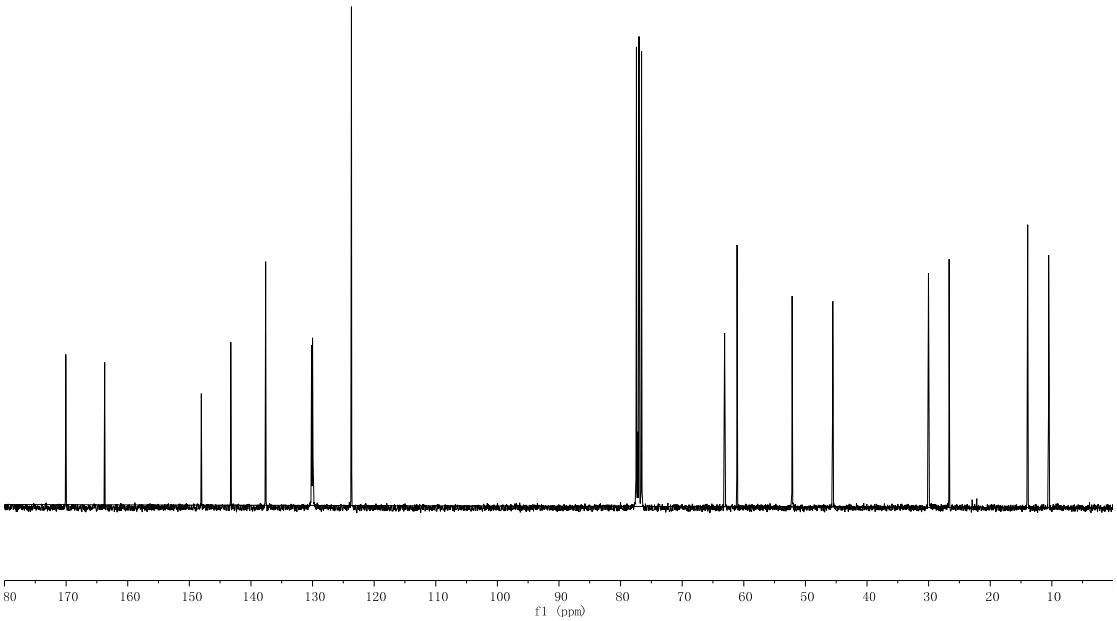

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.03
1.00
1.01
3.09
1.02
0.96
3.04
3.05

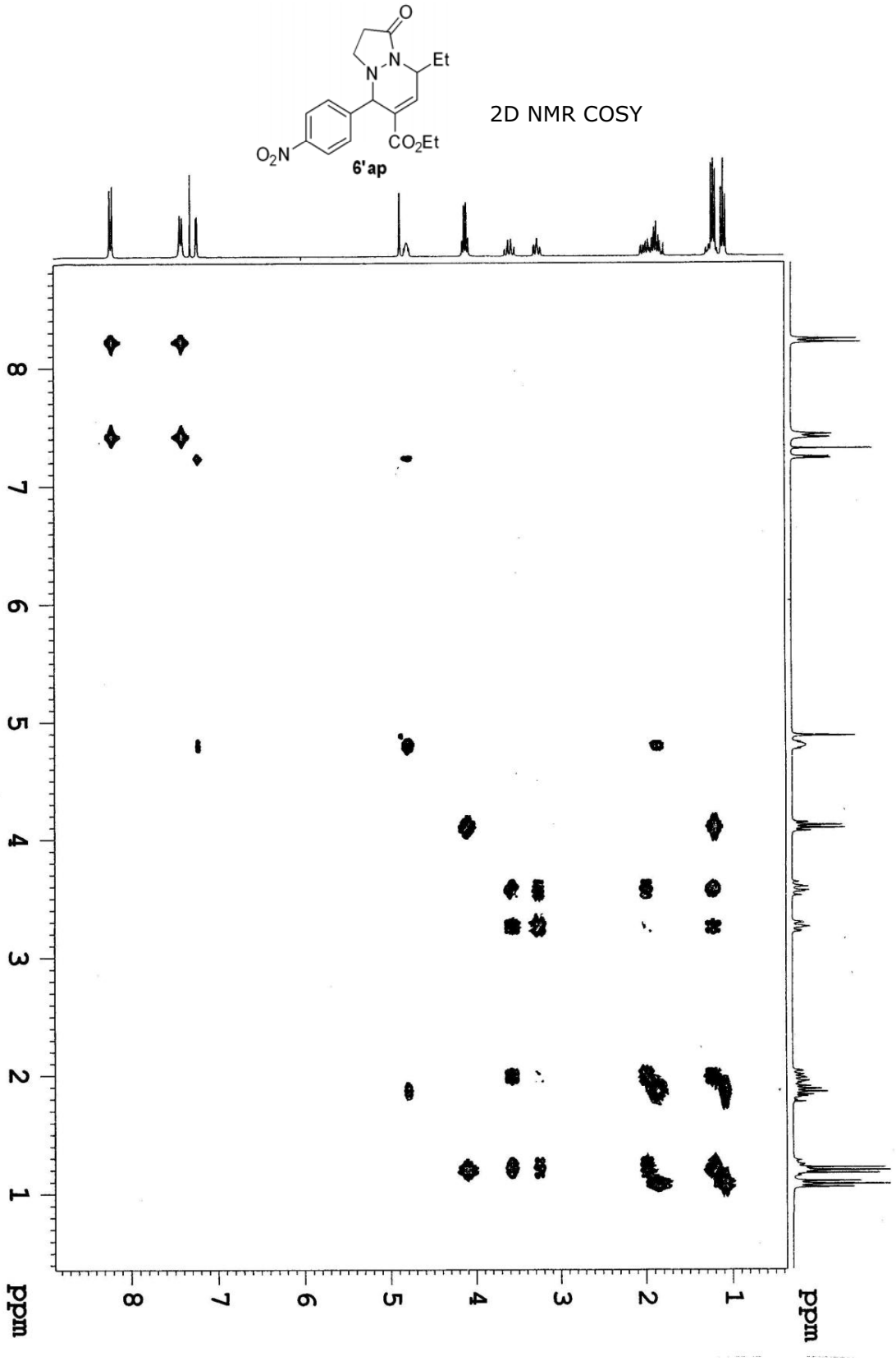

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

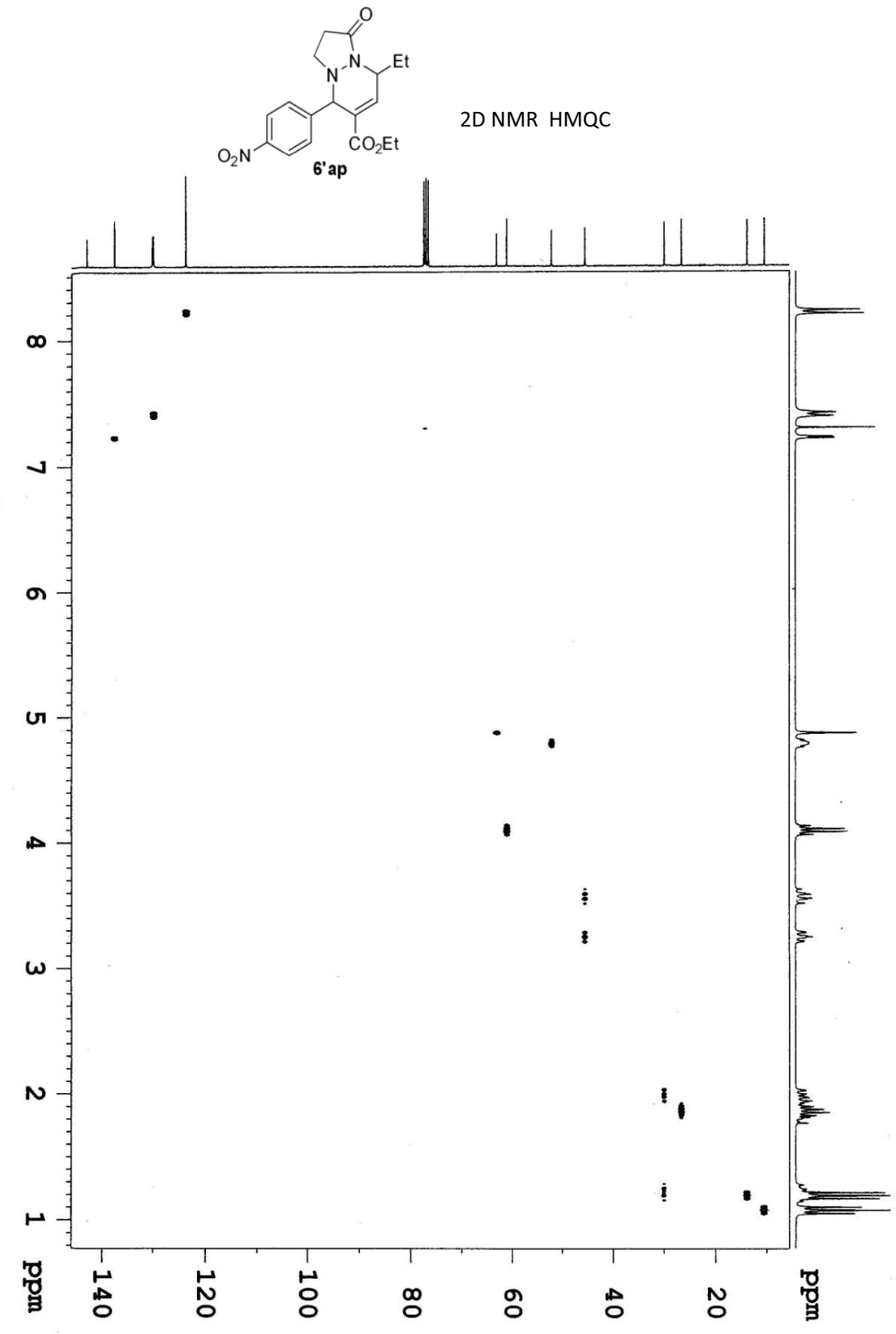

O
N
N
Et
O_2N
CO_2Et

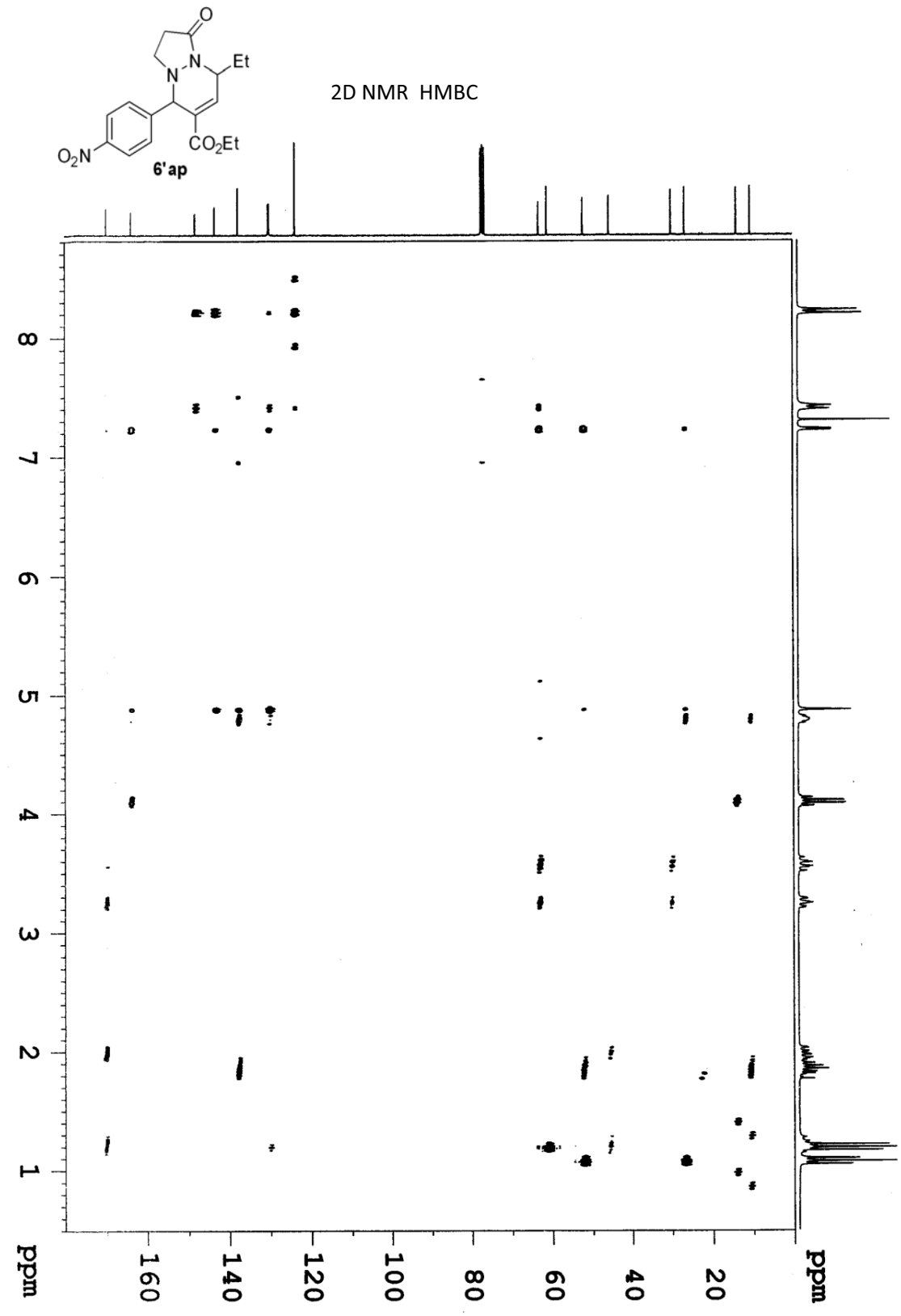
6'ap

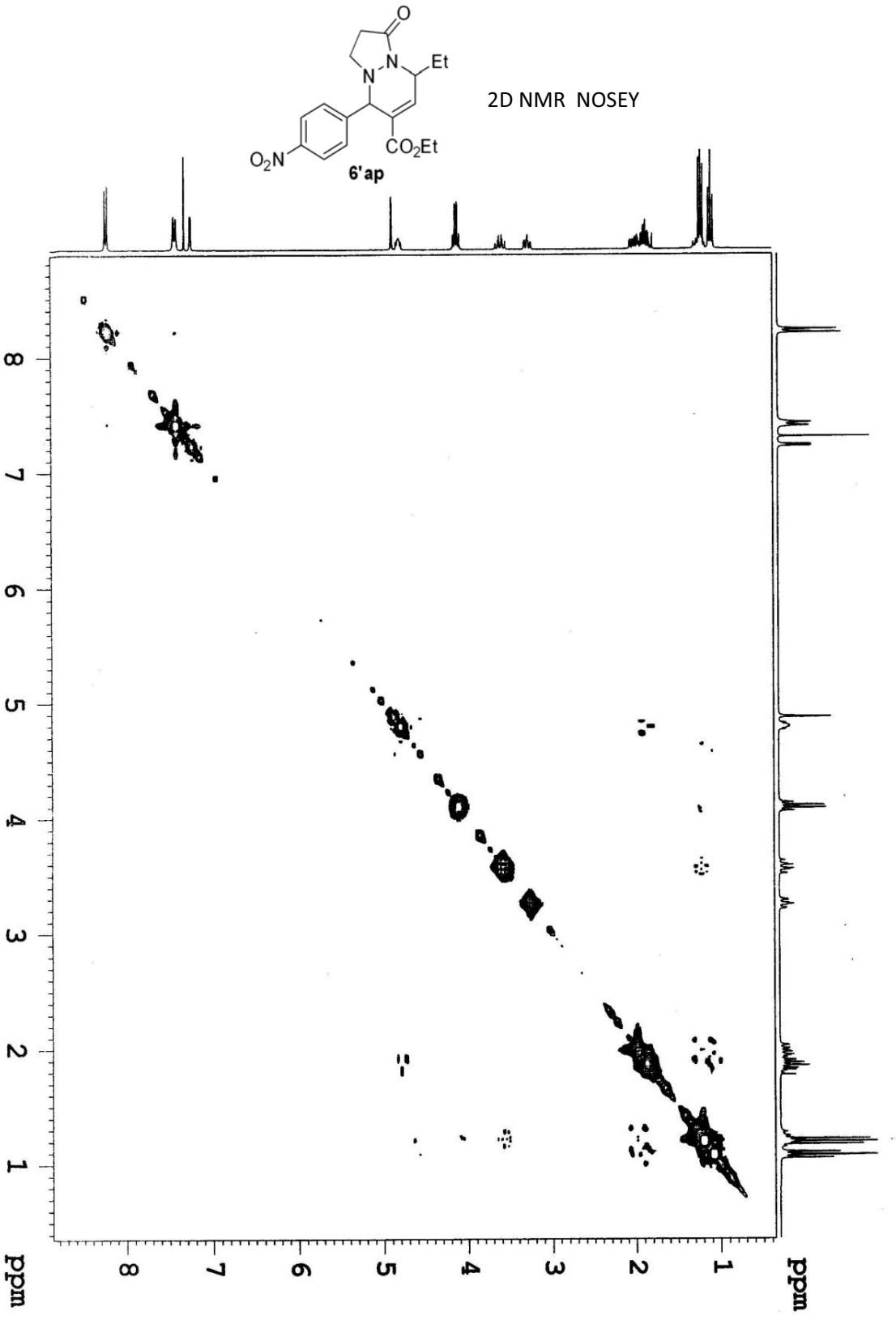

2.04
1.99
1.02
1.00
1.02
2.02
1.01
1.02
3.07
4.07
3.00
f1 (ppm)

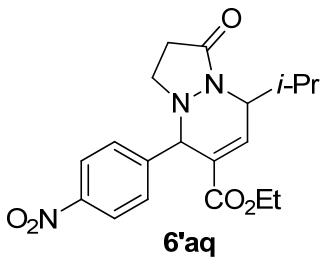

f1 (ppm)


O
N
N
Et
O_2N
CO_2Et
6'ap
2D NMR COSY
ppm
ppm

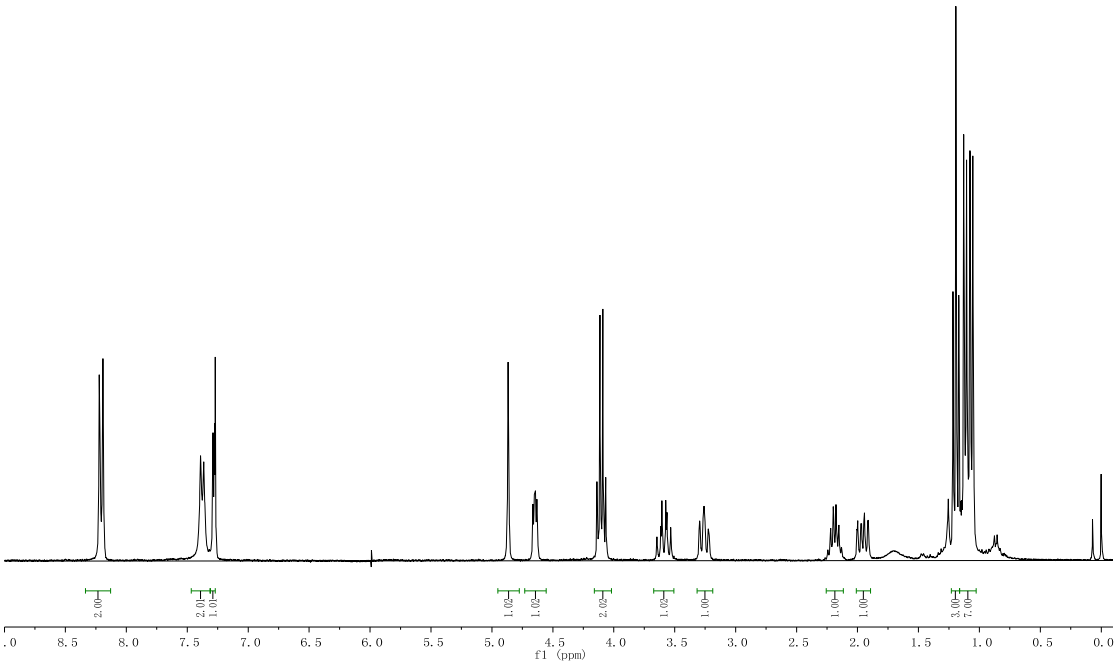

O
N
N
Et
O_2N
CO_2Et
6'ap
2D NMR HMQC
ppm
140
120
100
80
60
40
20
ppm
1
2
3
4
5
6
7
8
ppm

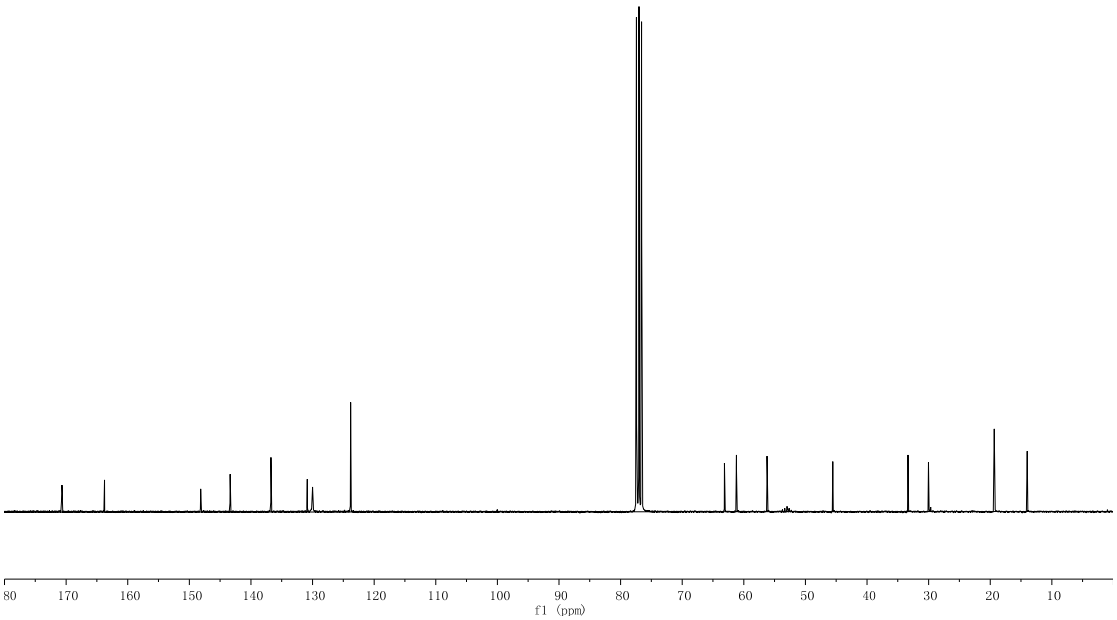

2D NMR HMBC
6'ap
ppm
ppm

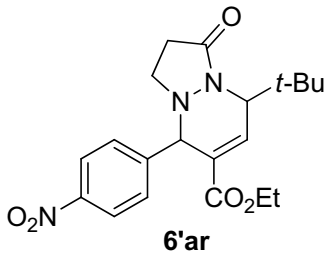

O
N
N
Et
O_2N
CO_2Et
6'ap
2D NMR NOSEY
8
7
6
5
4
3
2
1
ppm
ppm


O
N
N
i-Pr
O2N
CO2Et

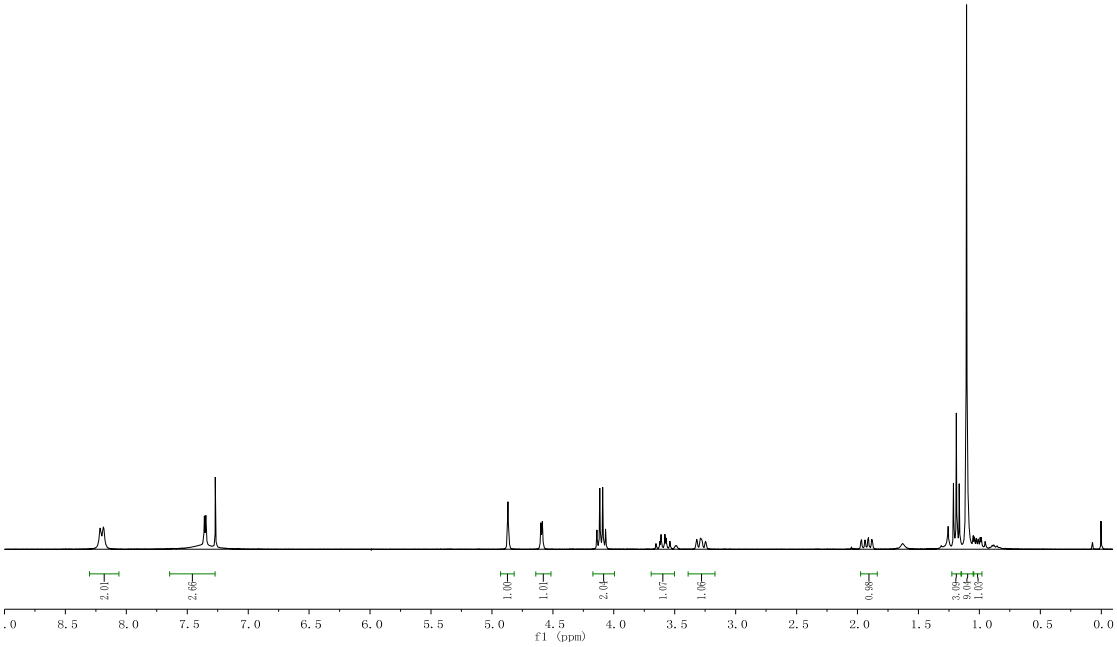
6'aq

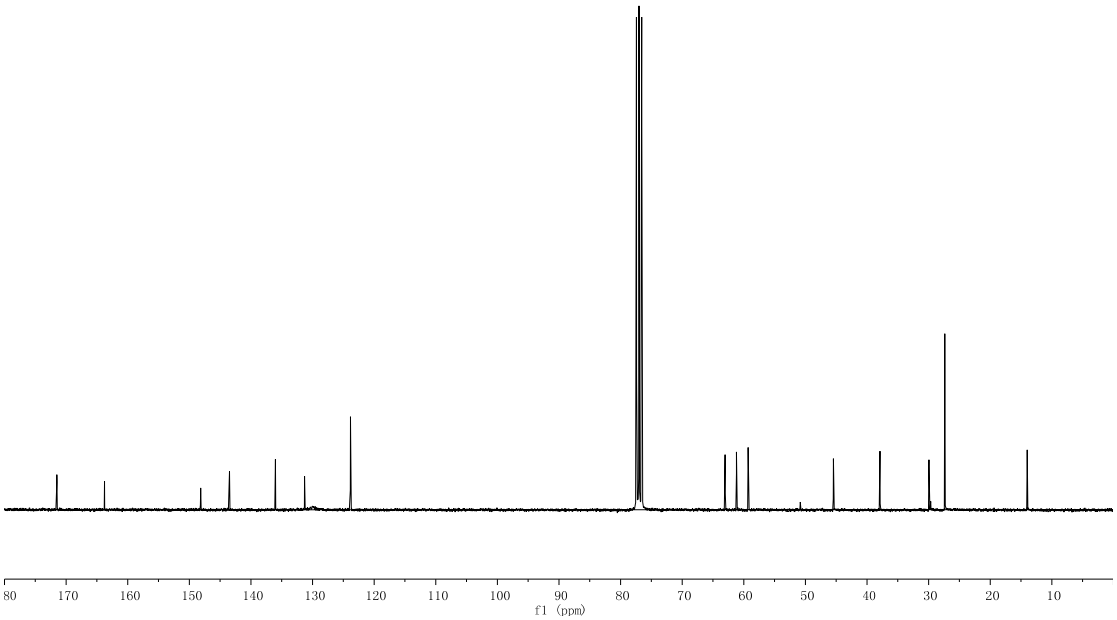

2.00
2.01
1.00
1.02
1.02
2.02
1.02
1.00
1.00
1.00
3.00
7.06
f1 (ppm)

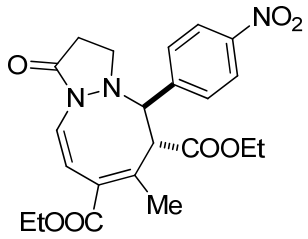

f1 (ppm)


O
N
N
t-Bu
O2N
CO2Et

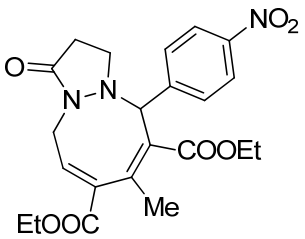
6'ar


2.01
2.86
1.00
1.01
2.04
1.07
1.06
0.88
3.08
3.04
1.00
f1 (ppm)

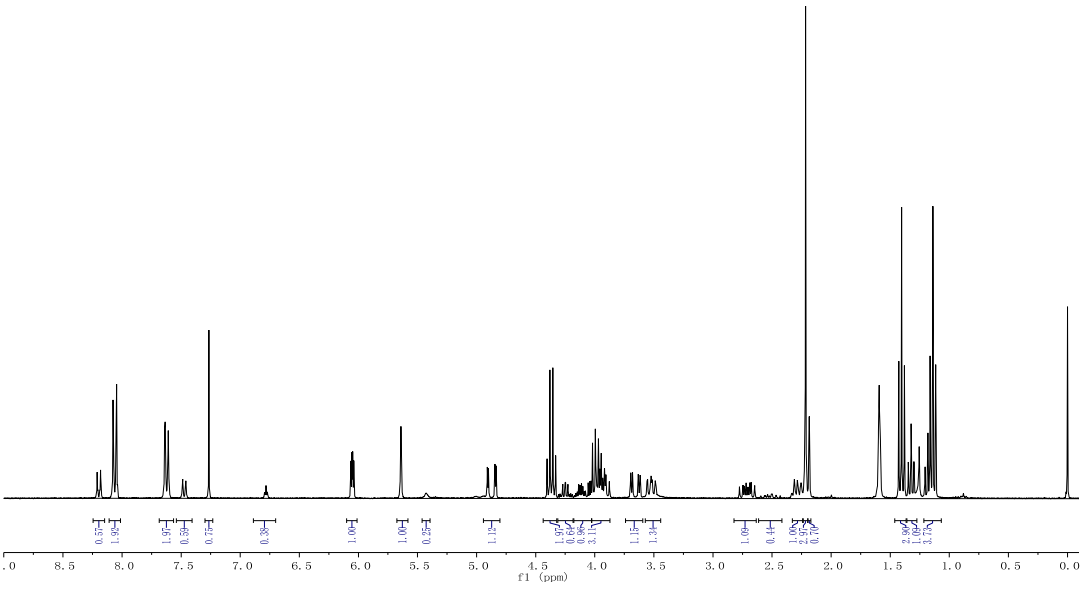

f1 (ppm)

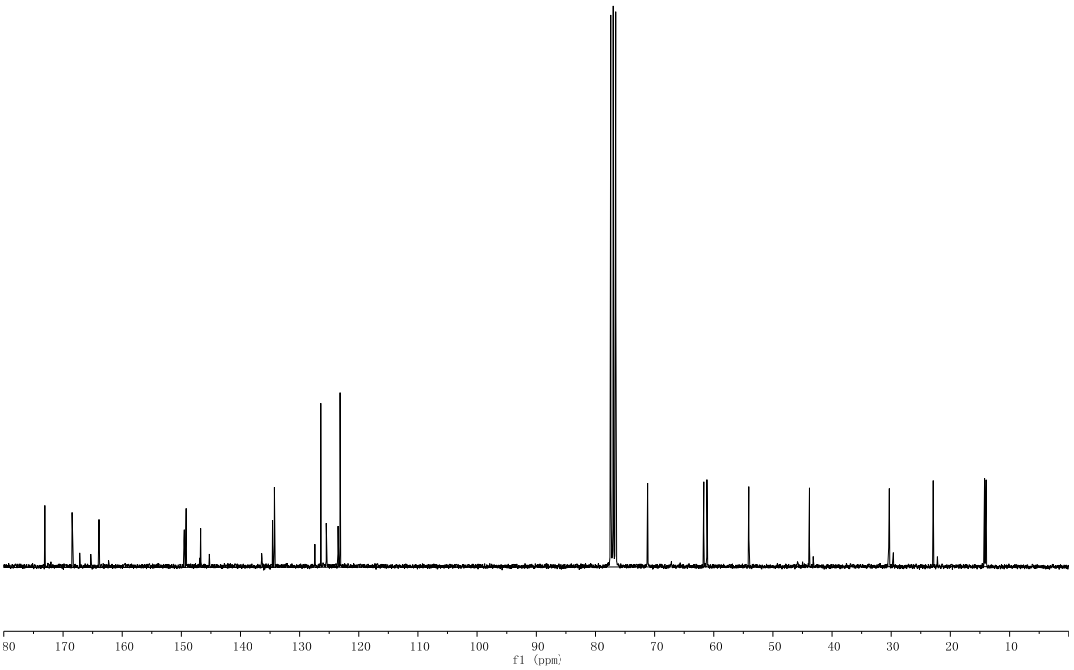


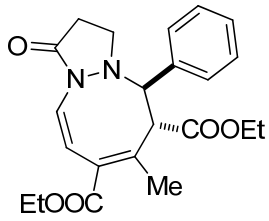
7a



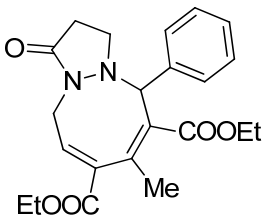
8a



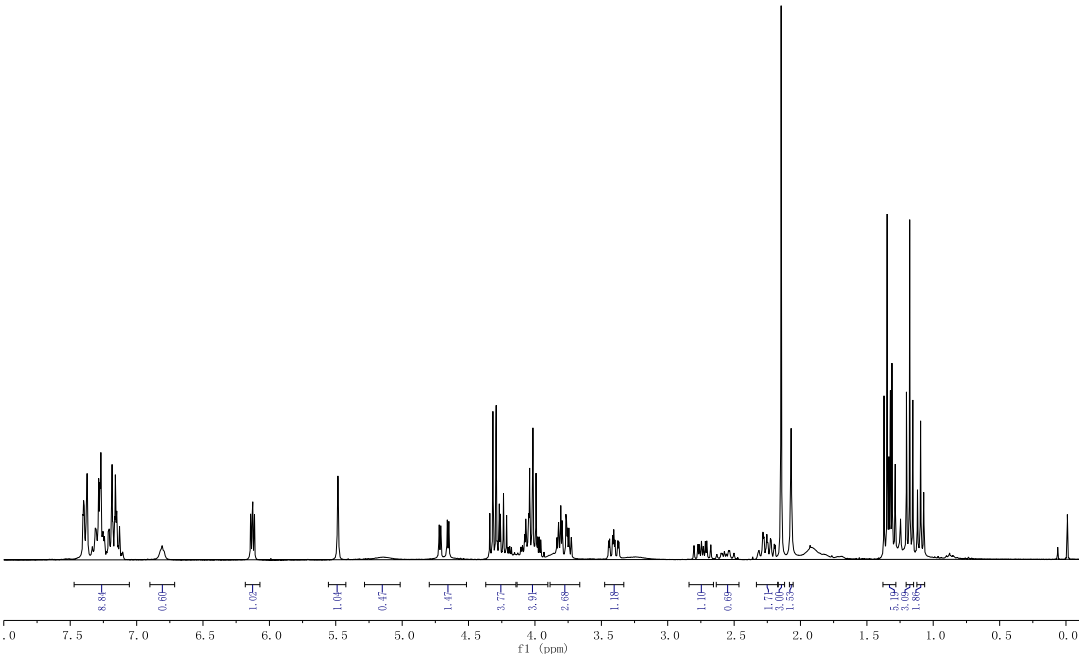


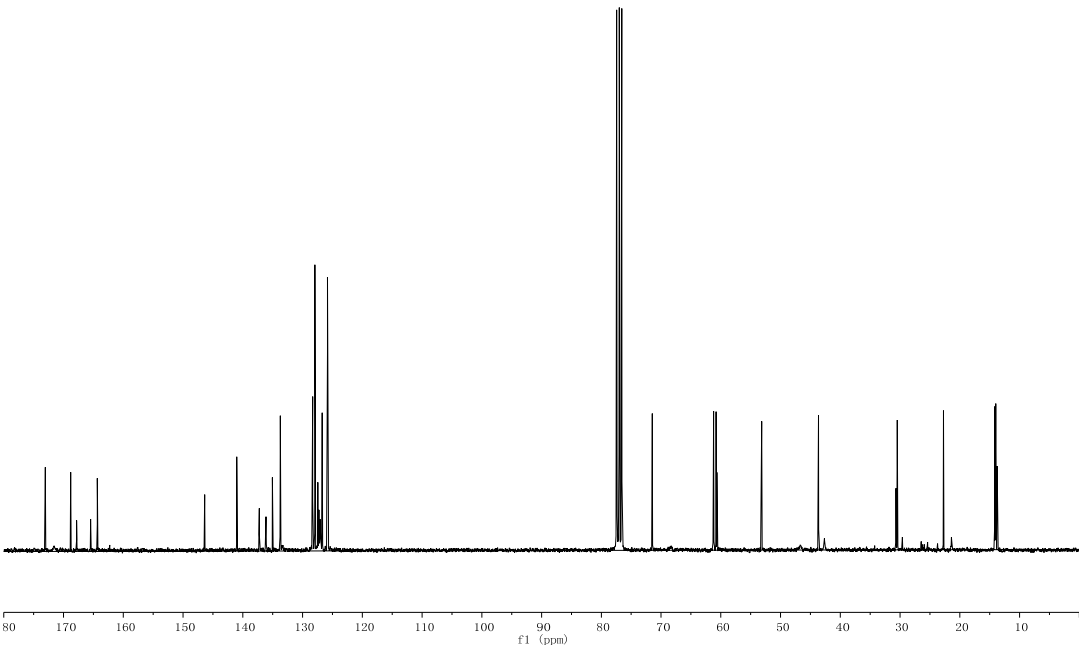

O
N
N
COOEt
Me
EtOOC

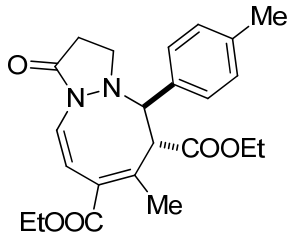
7b


O
N
N
COOEt
Me
EtOOC

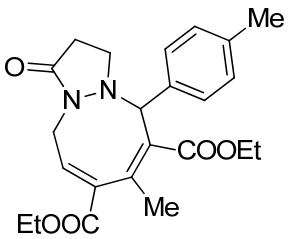
8b


8.84
0.60
1.00
1.01
0.45
1.46
3.77
3.89
2.68
1.18
1.10
0.89
1.77
15.00
1.98
f1 (ppm)

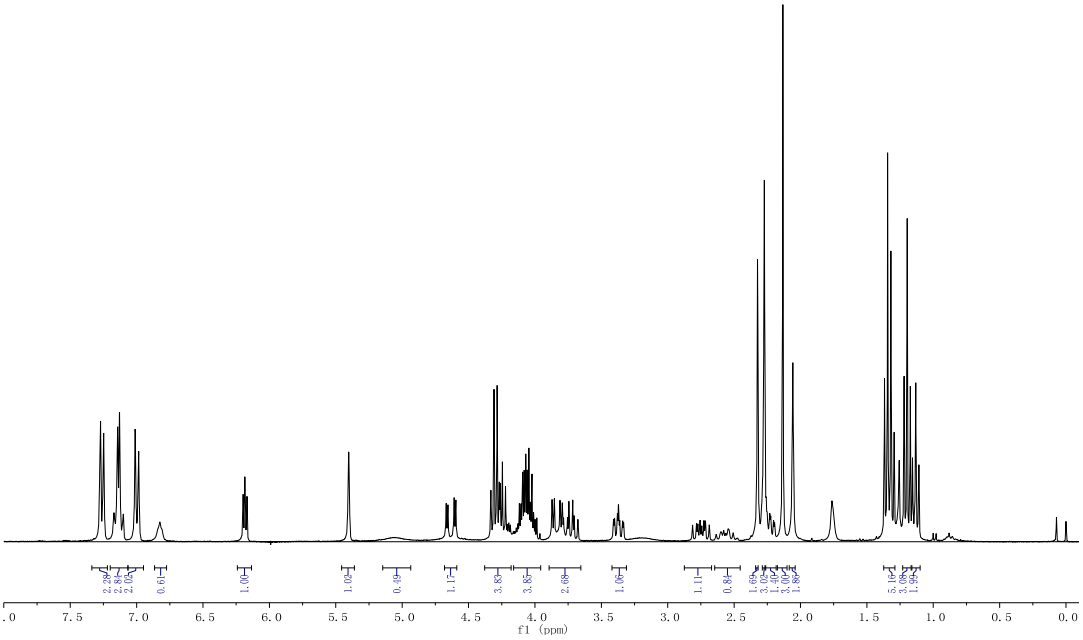

f1 (ppm)

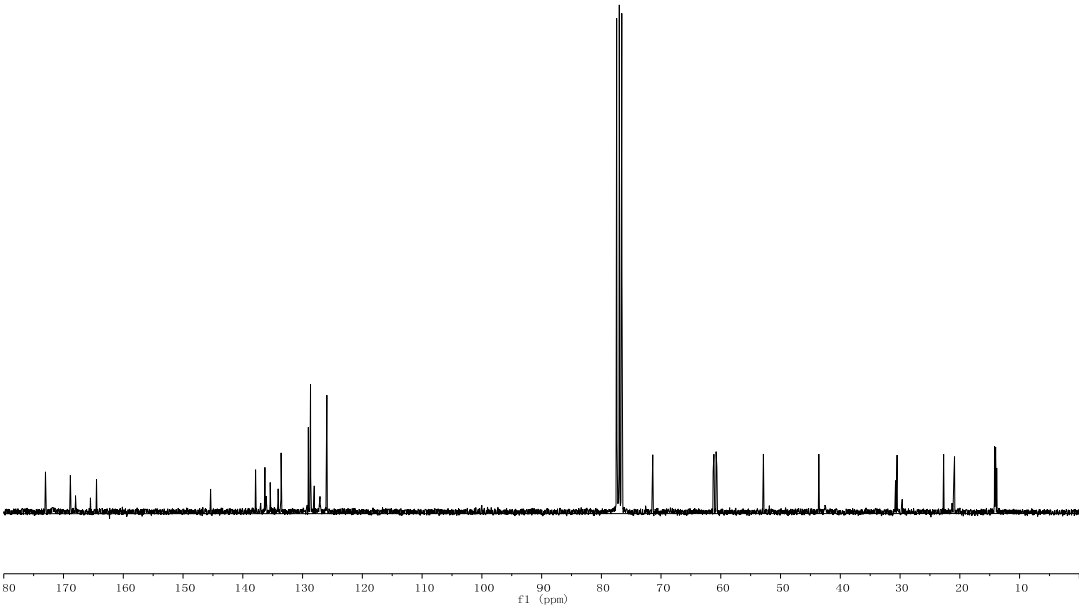


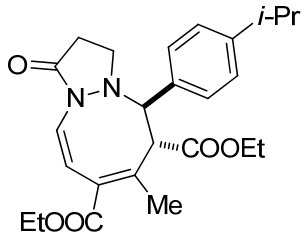
7c



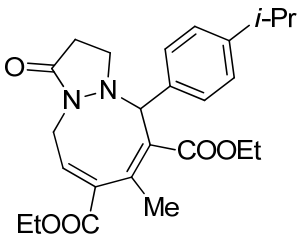
8c



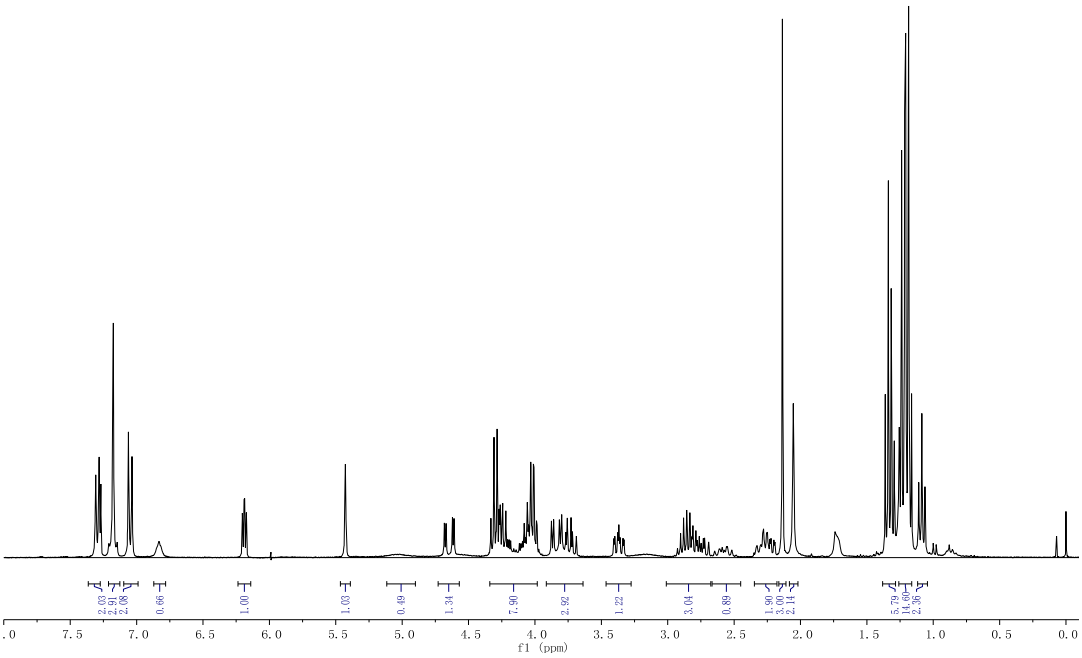


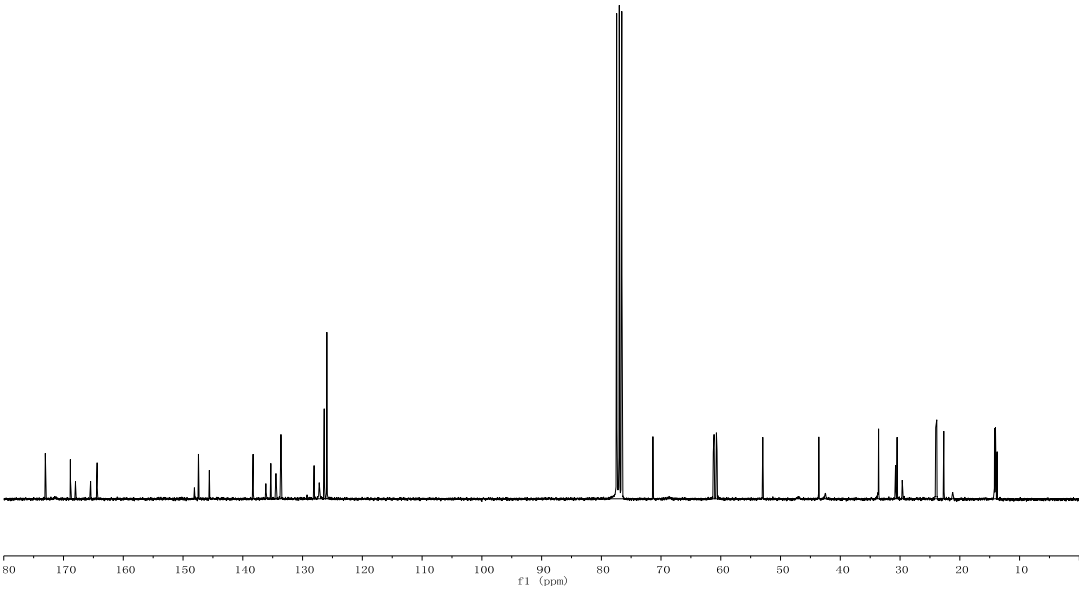

i-Pr
O
N
N
COOEt
Me
EtOOC

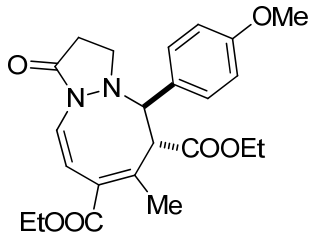
7d


i-Pr
O
N
N
COOEt
Me
EtOOC

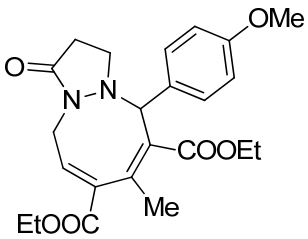
8d


2.03
2.91
2.08
0.66
1.00
1.03
0.49
1.34
7.90
2.92
1.22
3.04
0.89
1.90
3.00
2.14
5.79
14.68
2.36
f1 (ppm)

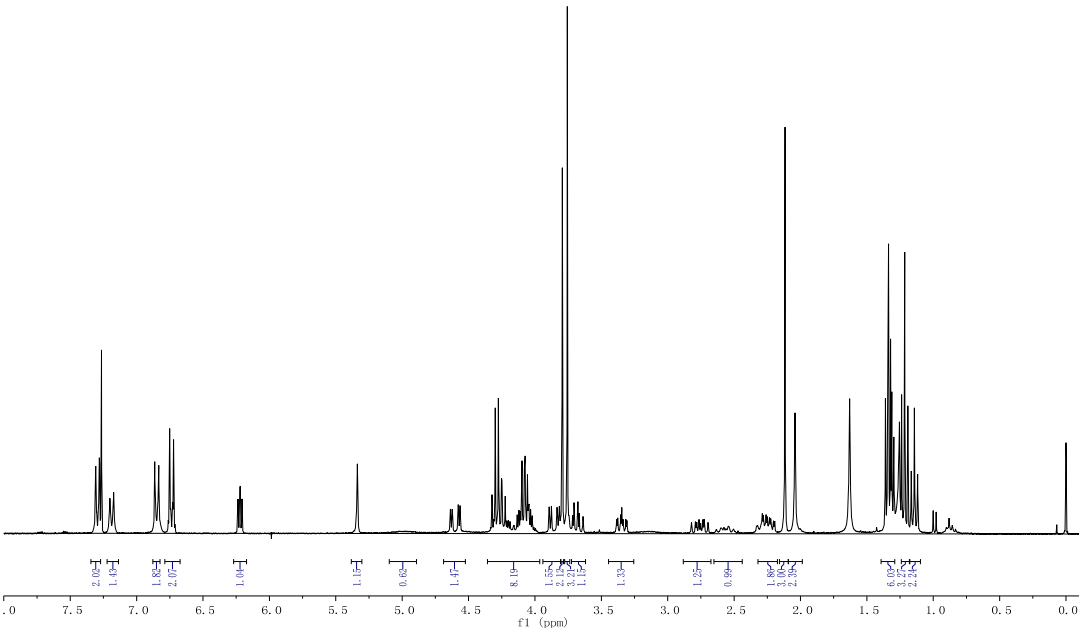

f1 (ppm)

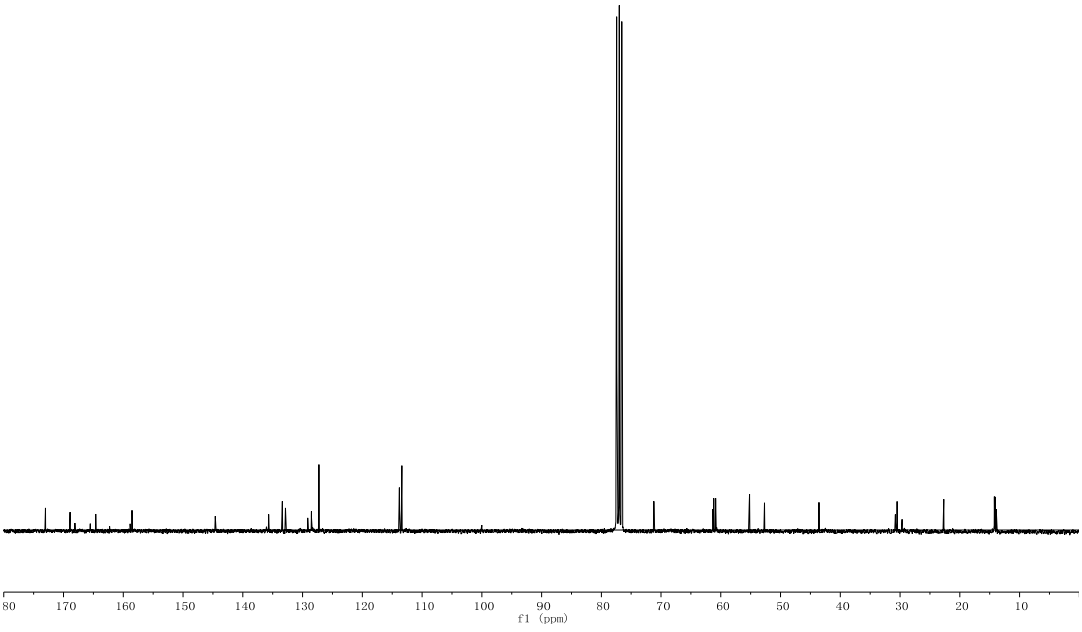

OMe
O
N
N
COOEt
Me
EtOOC

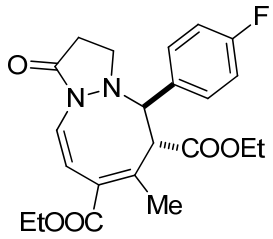
7e


OMe
O
N
N
COOEt
Me
EtOOC

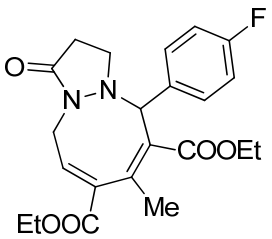
8e


2.02
1.43
1.82
2.07
1.04
1.15
0.62
1.47
8.19
1.55
2.12
3.22
1.14
1.39
1.25
0.99
1.86
3.00
2.38
6.02
2.27
2.24
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)

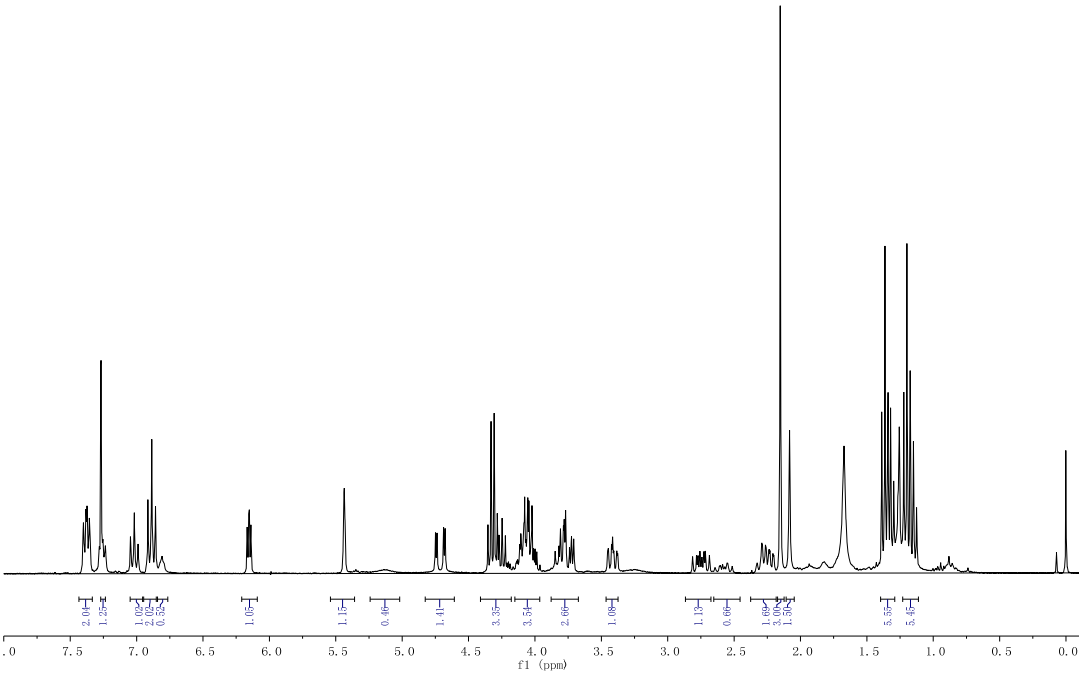

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

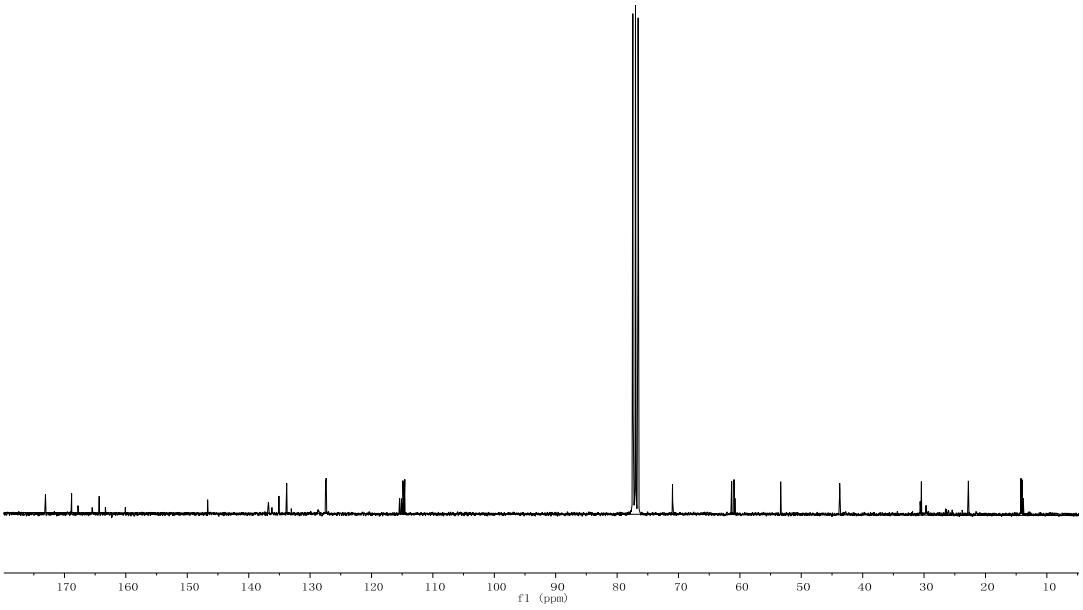

O
N
N
F
COOEt
Me
EtOOC

7f


O
N
N
F
COOEt
Me
EtOOC

8f


2.04
1.25
1.02
2.92
0.52
1.05
1.15
0.46
1.41
3.35
3.54
2.66
1.08
1.13
0.66
1.69
3.00
1.50
5.55
5.45
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
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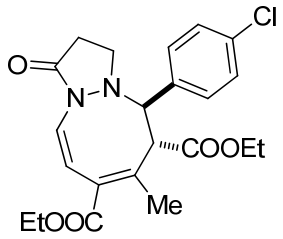
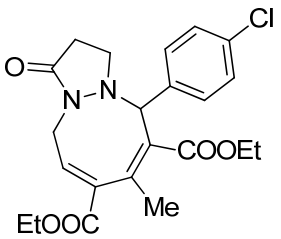
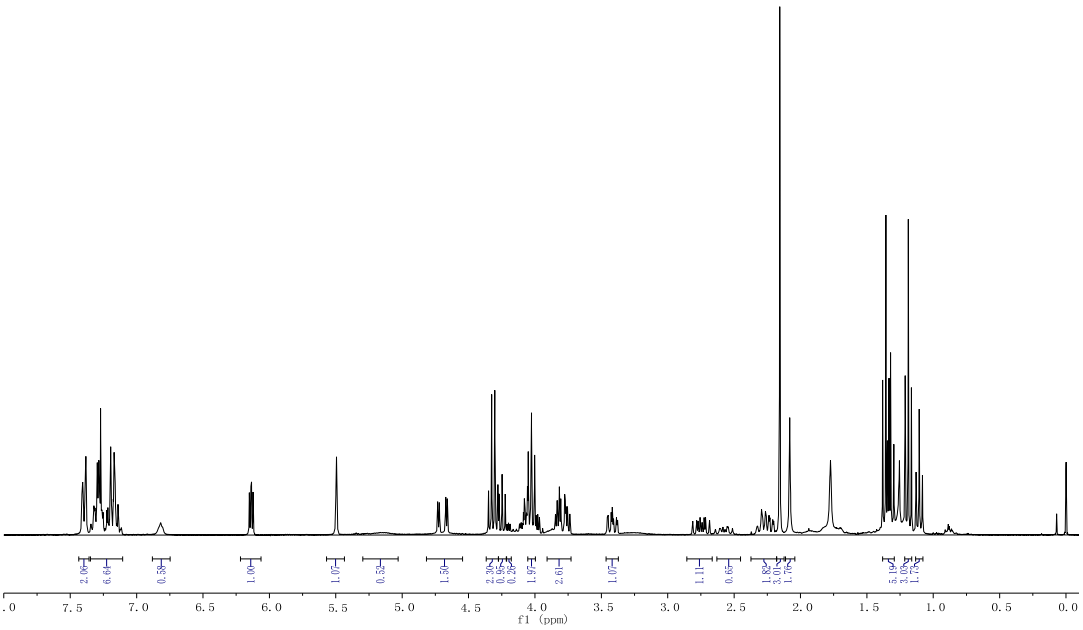
60
50
40
30
20
10
f1 (ppm)

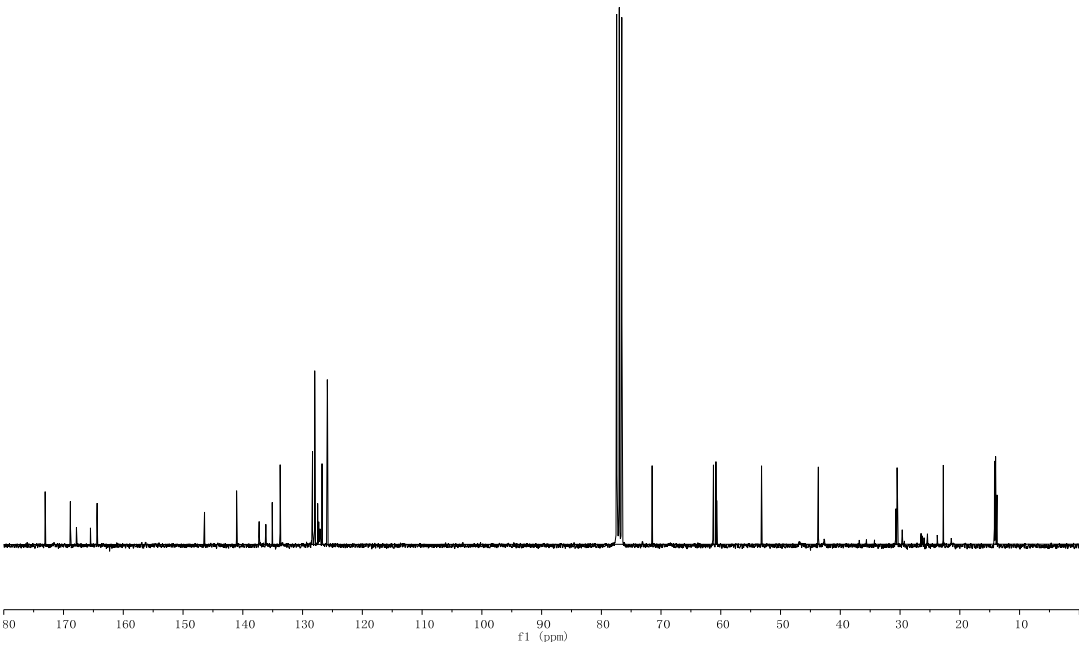


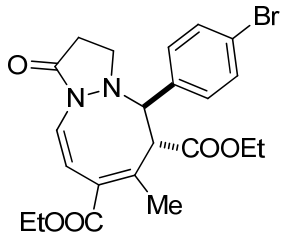
7g



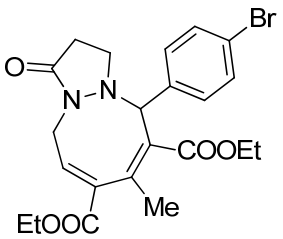
8g



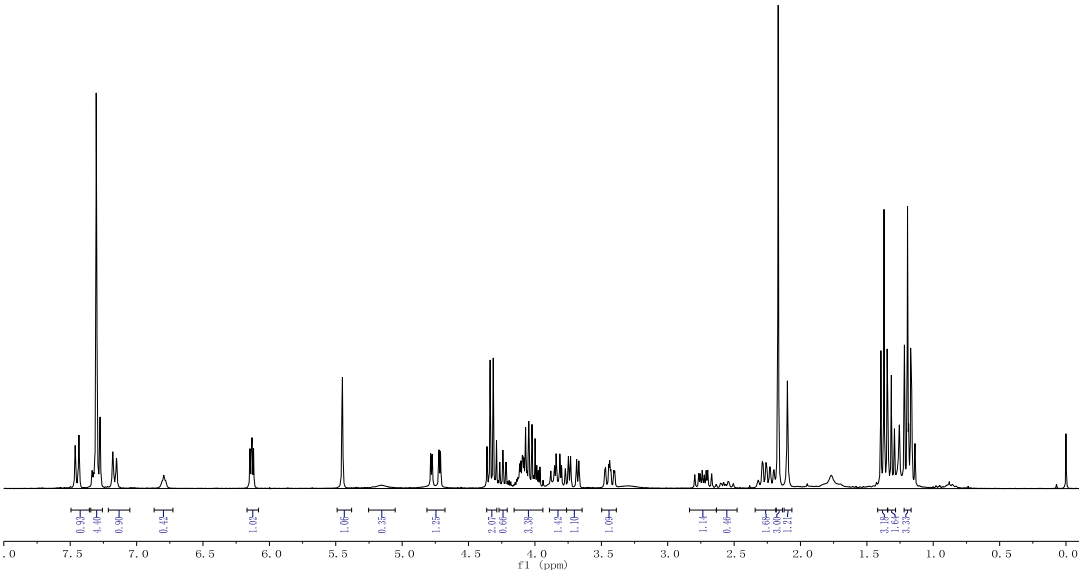


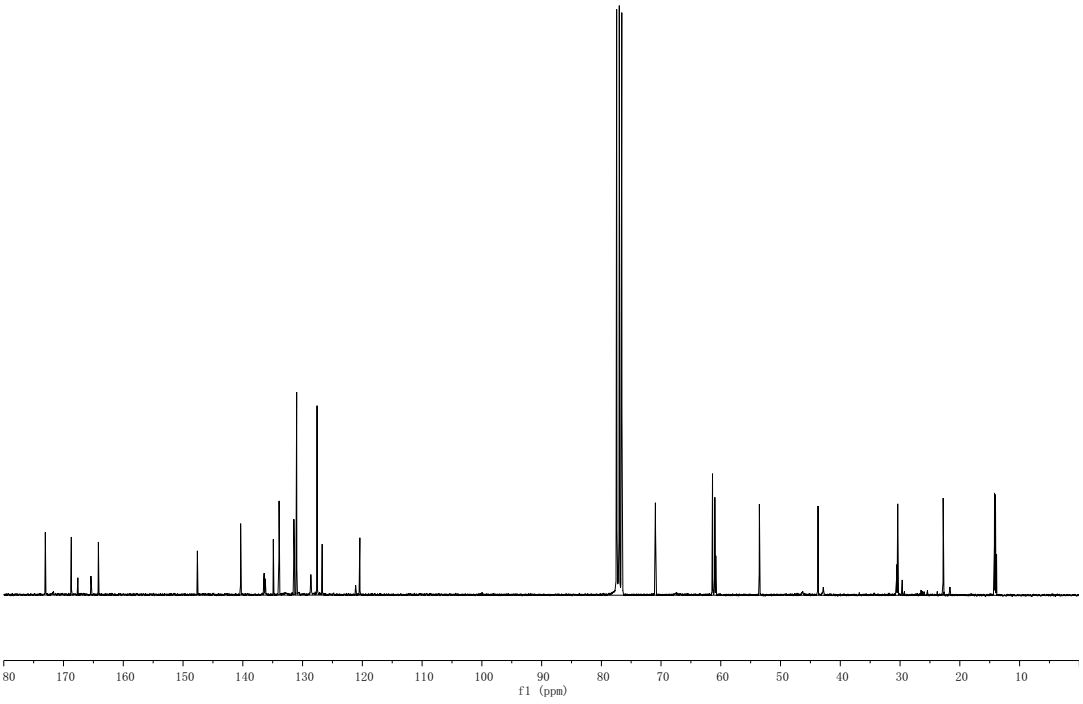


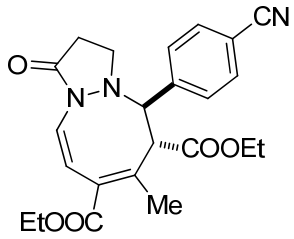
7h



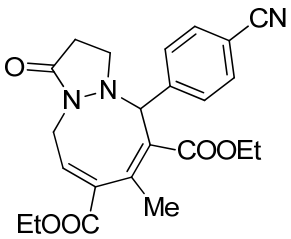
8h



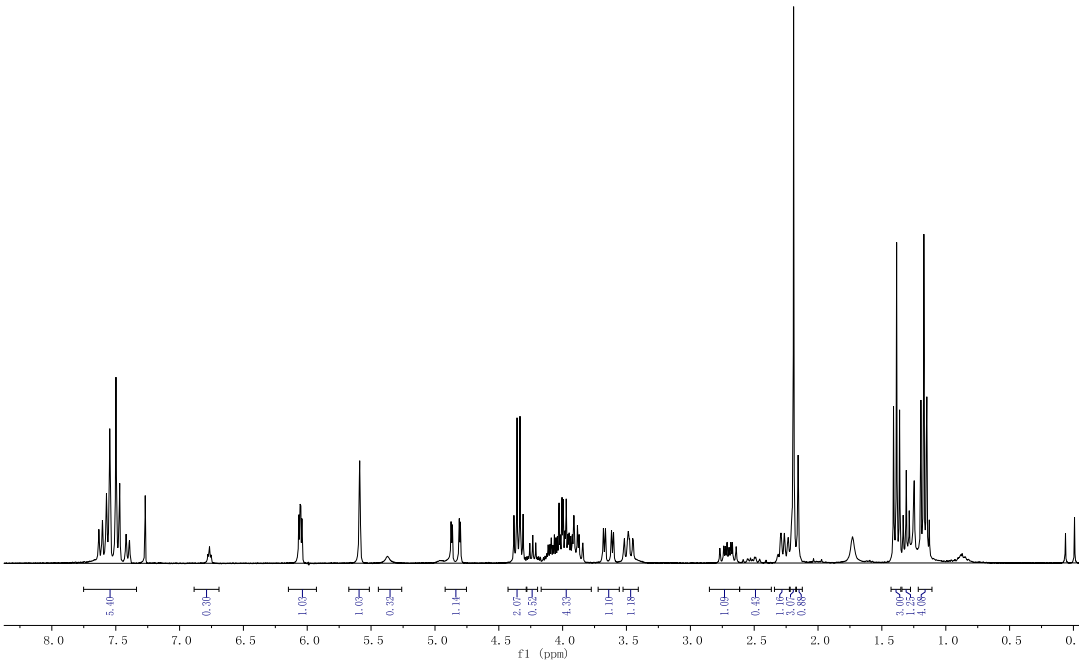


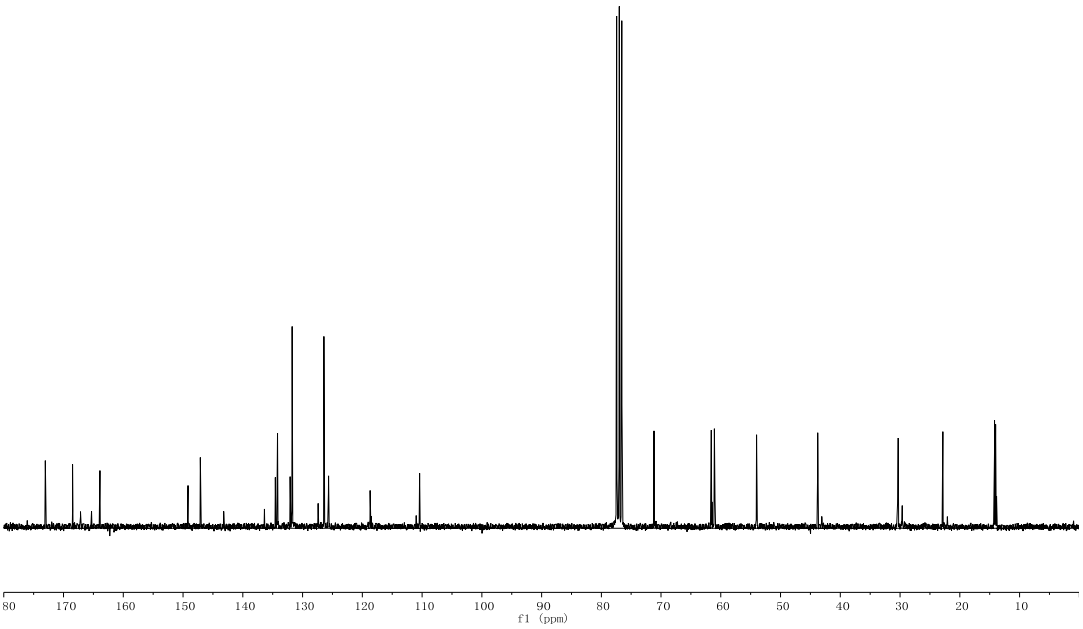

CN
O
N
N
COOEt
Me
EtOOC

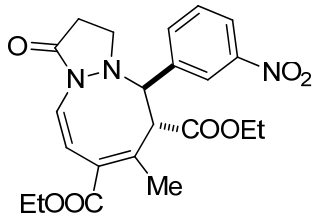
7i


CN
O
N
N
COOEt
Me
EtOOC

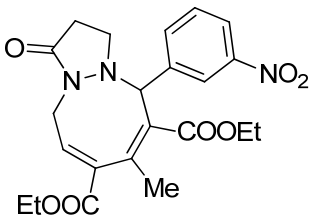
8i


3.40
0.30
1.03
1.03
0.32
1.14
2.07
0.52
4.33
1.10
1.18
1.09
0.43
1.16
0.88
3.00
1.25
4.08
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)

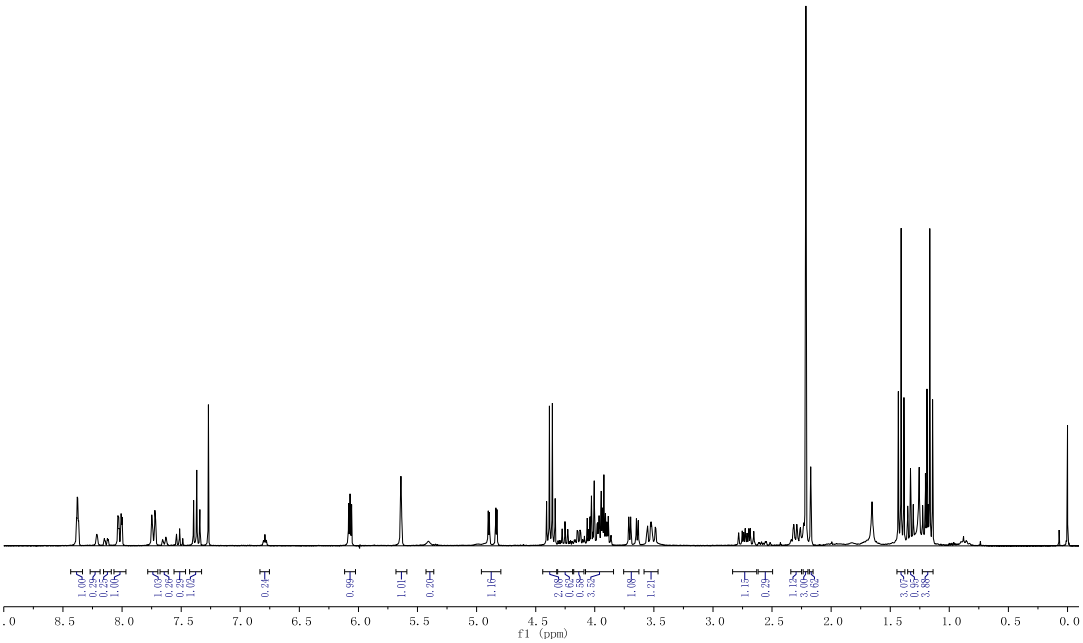

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

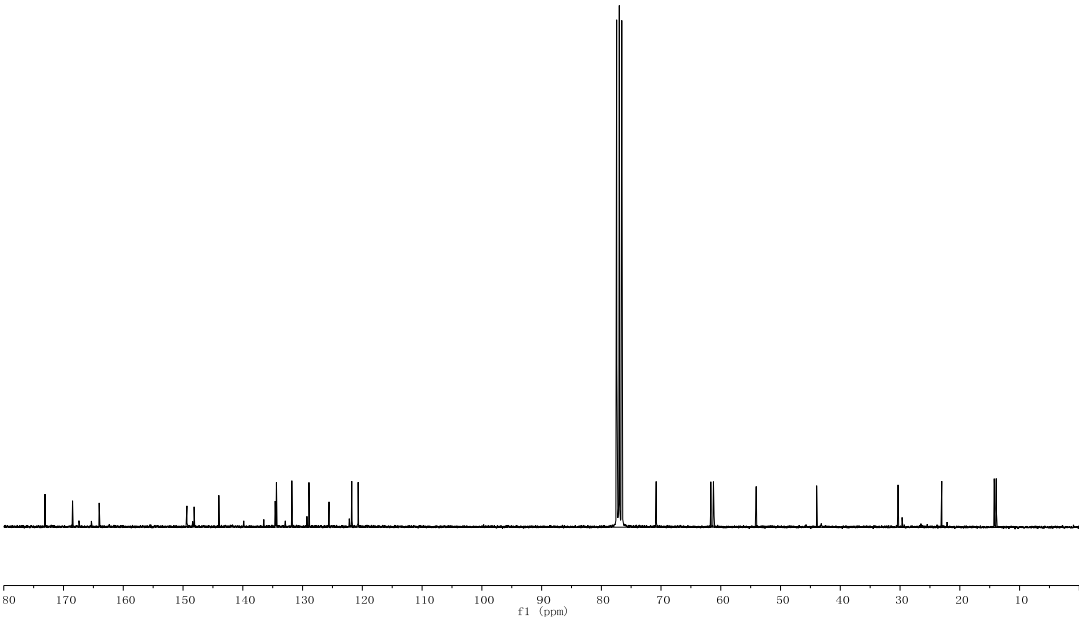


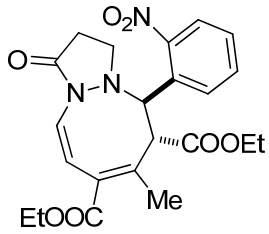
7k



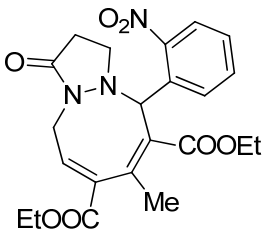
8k



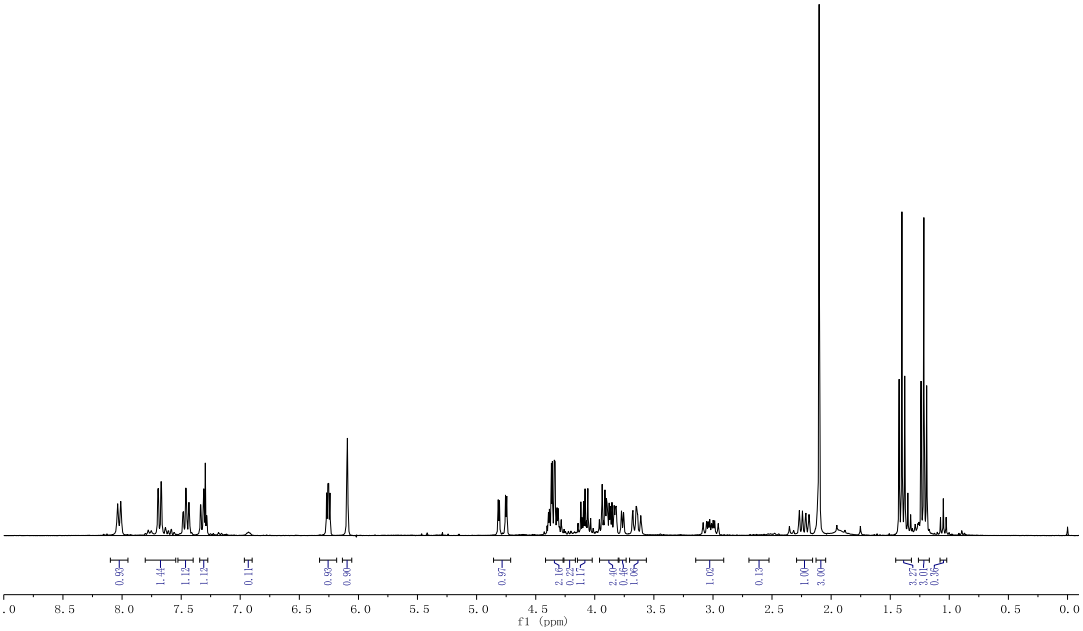


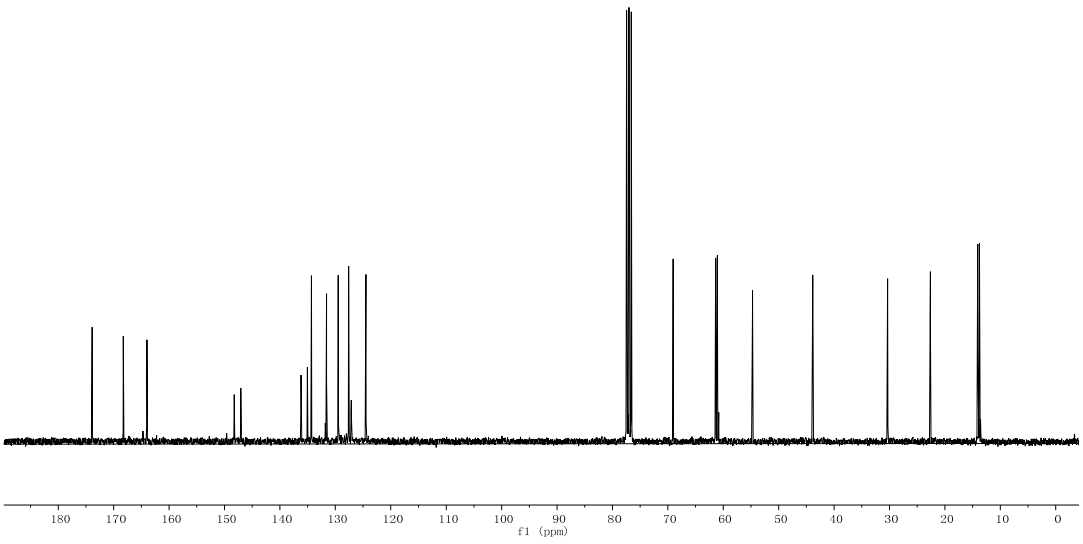


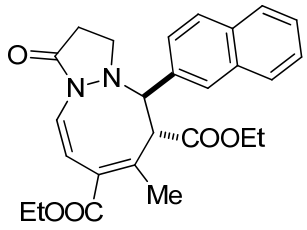
7l



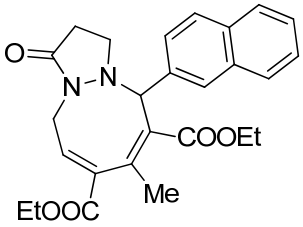
8l



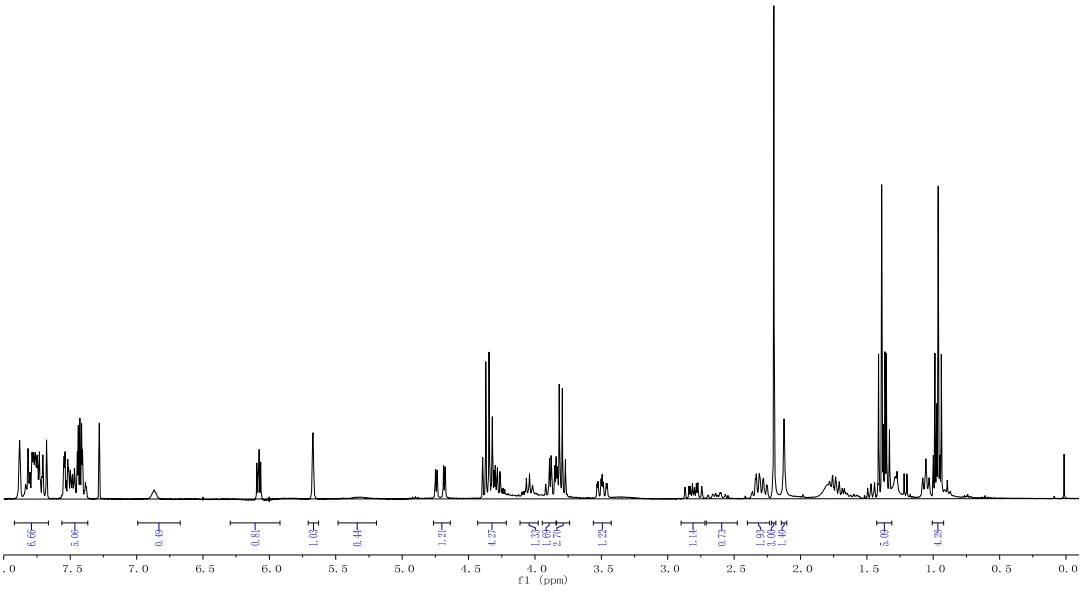


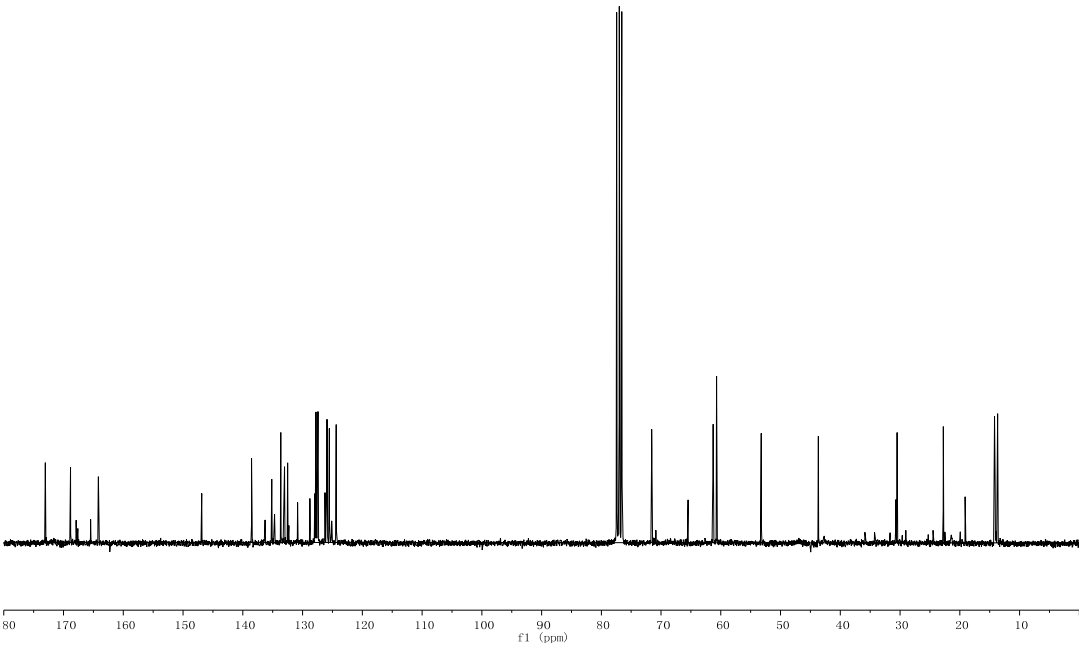

O
N
N
COOEt
Me
EtOOC

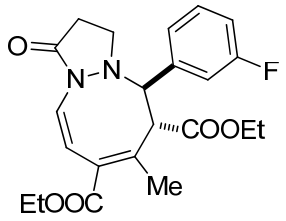
7p


O
N
N
COOEt
Me
EtOOC

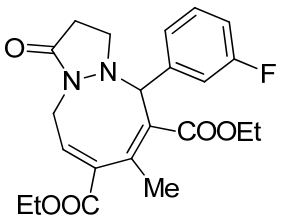
8p


6.68
5.06
0.89
0.81
1.03
0.44
1.21
4.27
1.39
1.68
2.70
1.24
1.14
0.77
1.91
3.06
1.40
5.09
4.28
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)

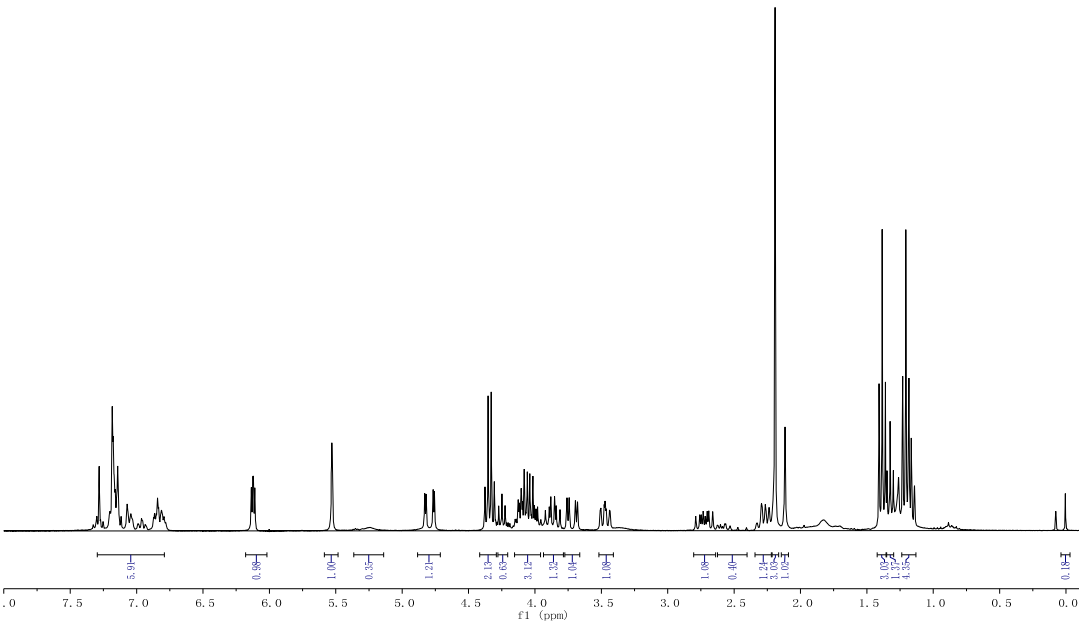

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

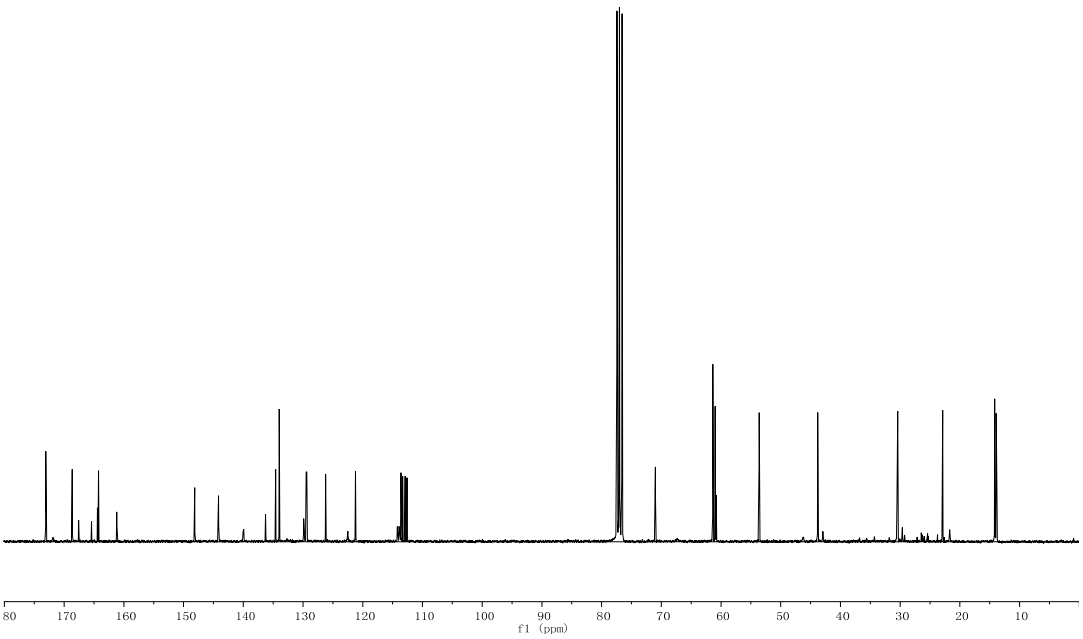

O
N
N
F
COOEt
Me
EtOOC

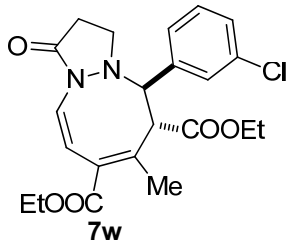
7v


O
N
N
F
COOEt
Me
EtOOC

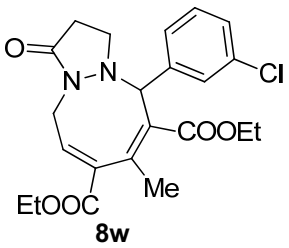
8v


5.91
0.98
1.00
0.35
1.21
2.13
0.65
3.12
1.32
1.04
1.08
1.08
0.40
1.24
3.03
1.02
3.03
1.37
4.55
0.18
f1 (ppm)

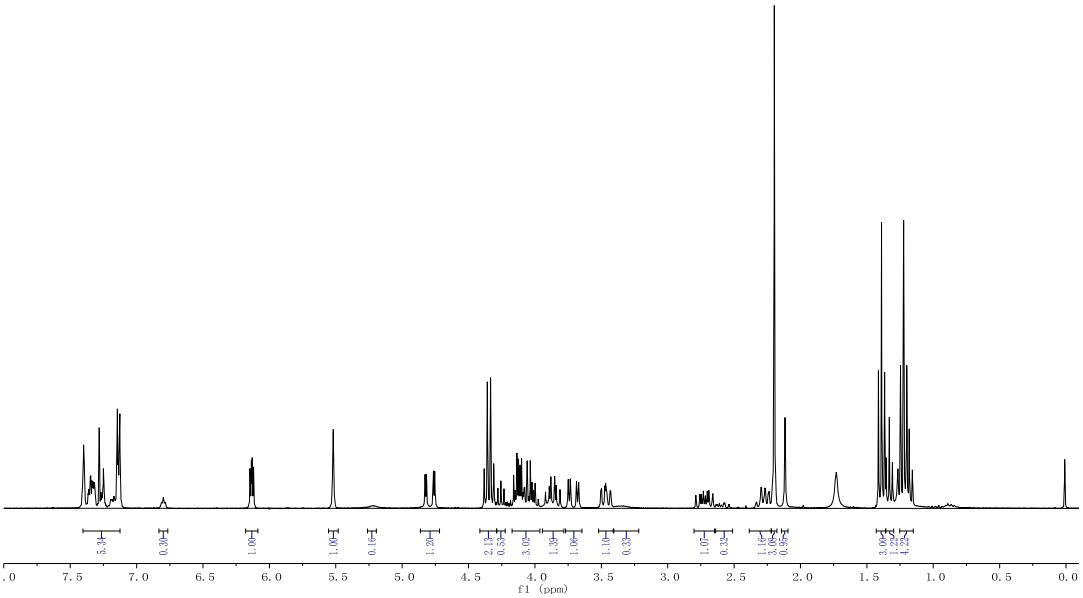

f1 (ppm)

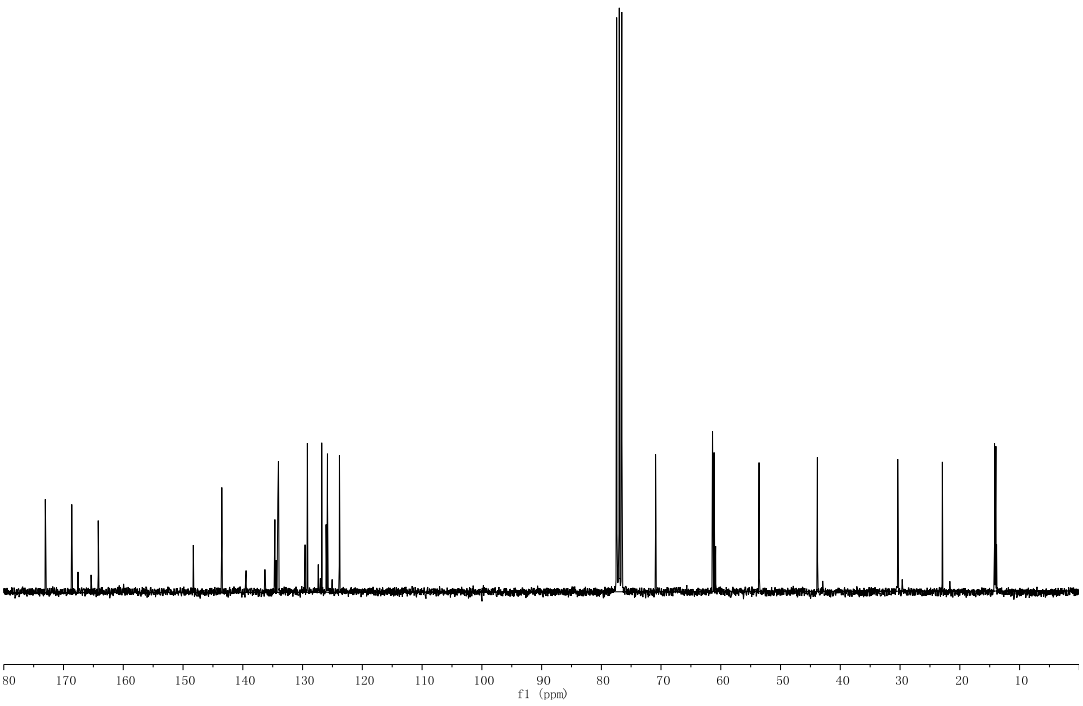

O
N
N
Cl
COOEt
Me
EtOOC

7w


O
N
N
Cl
COOEt
Me
EtOOC

8w


5.34
0.30
1.00
1.00
0.16
1.20
2.13
0.58
3.02
1.39
1.06
1.10
0.33
1.07
0.32
1.16
3.08
0.95
3.00
1.23
4.22
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
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140
130
120
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100
90
80
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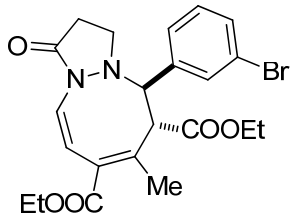
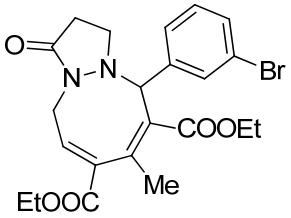
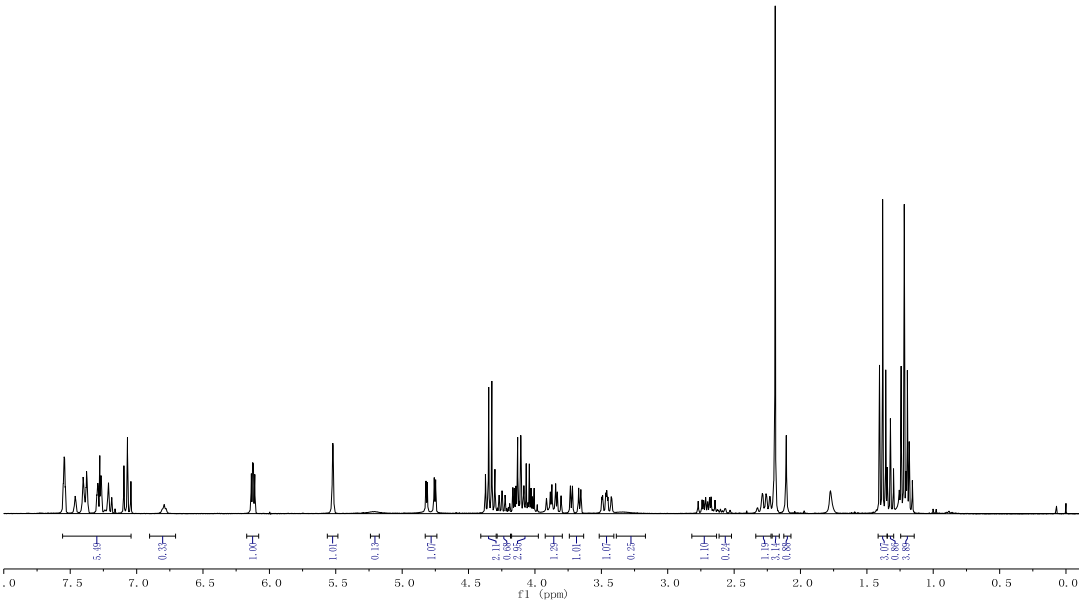
60
50
40
30
20
10
f1 (ppm)

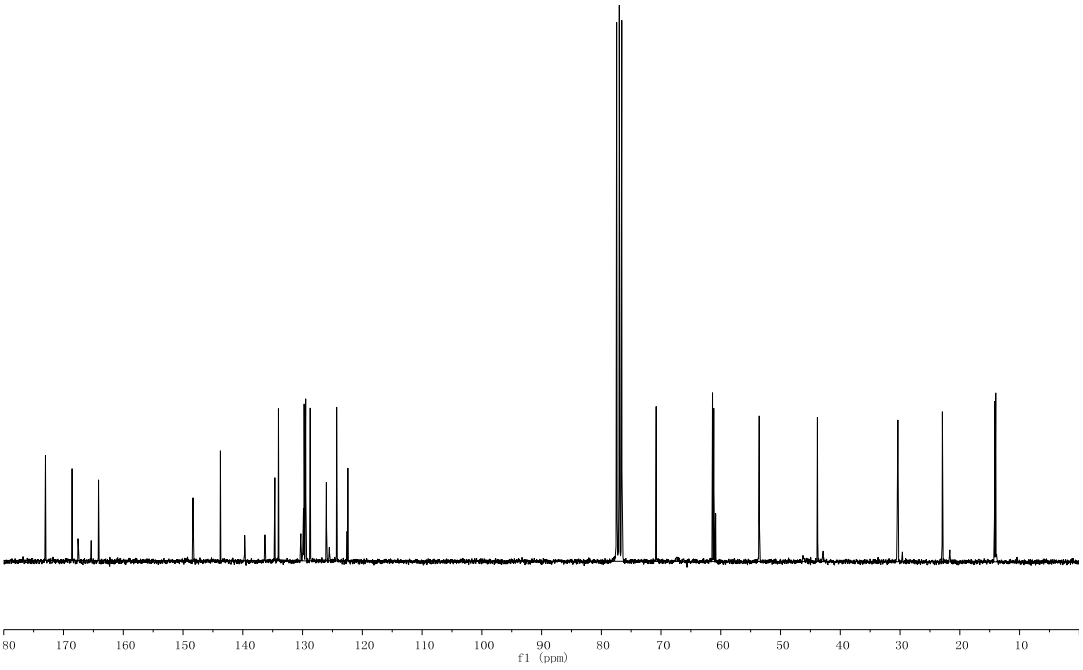


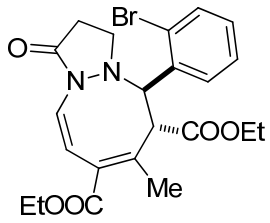
7x



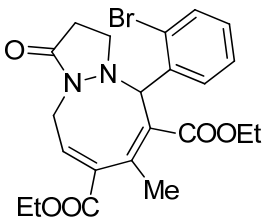
8x






Br
O
N
N
COOEt
Me
EtOOC

7y


Br
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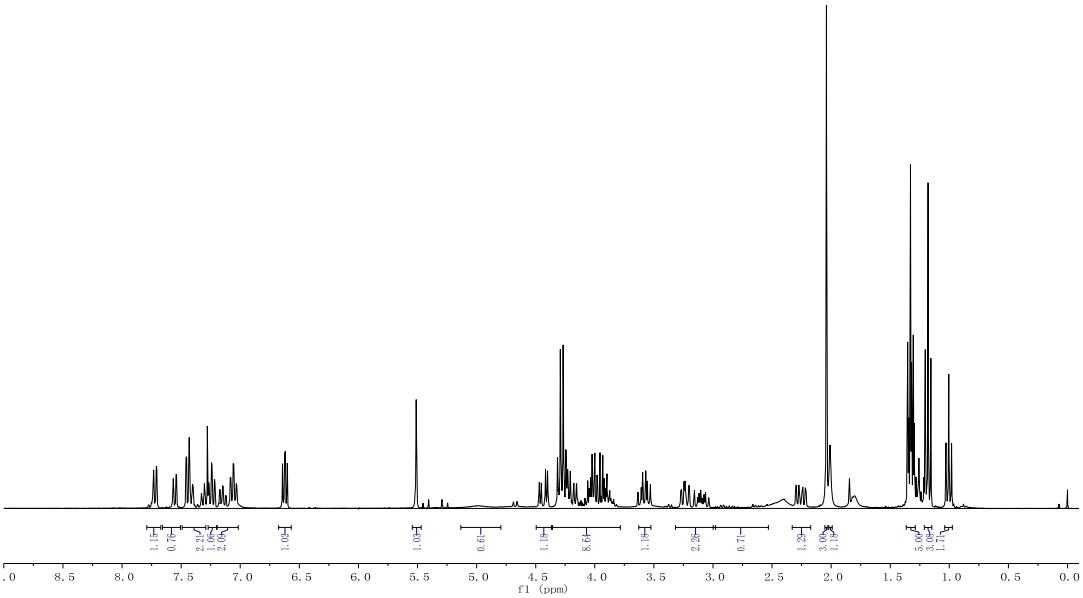
N
N
COOEt
Me
EtOOC

8y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1.29
3.00
1.18
5.00
3.08
1.71
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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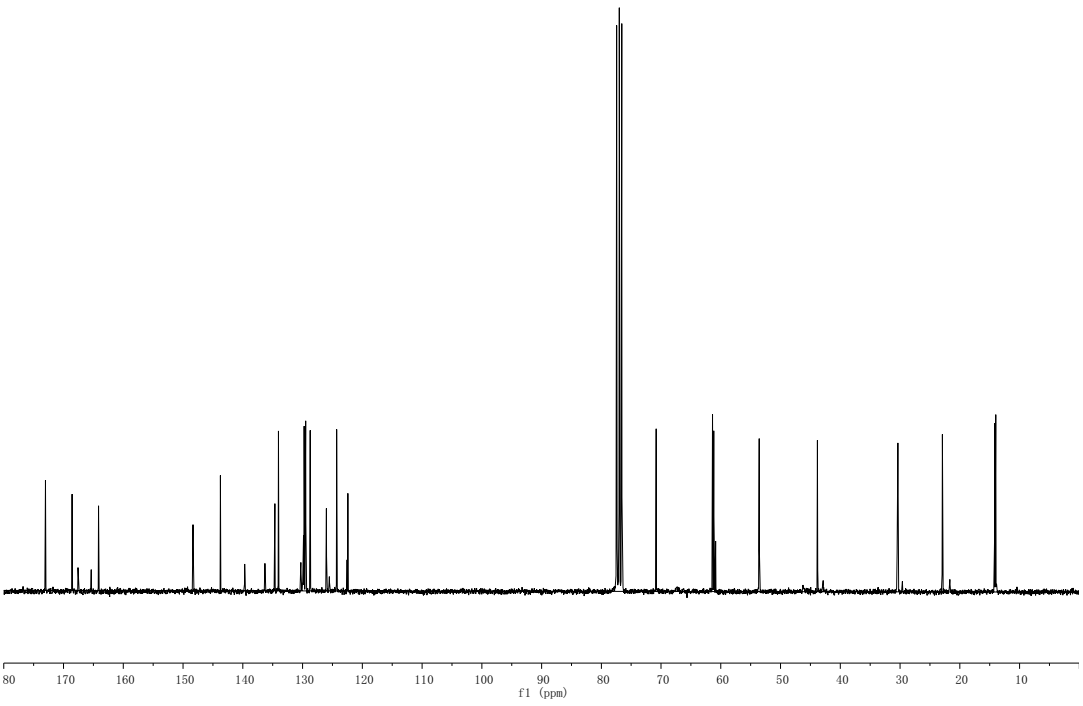
0.0
f1 (ppm)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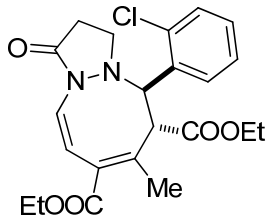
10
f1 (ppm)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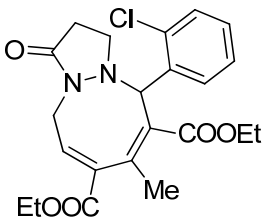
N
N
COOEt
Me
EtOOC

7z


Cl
O
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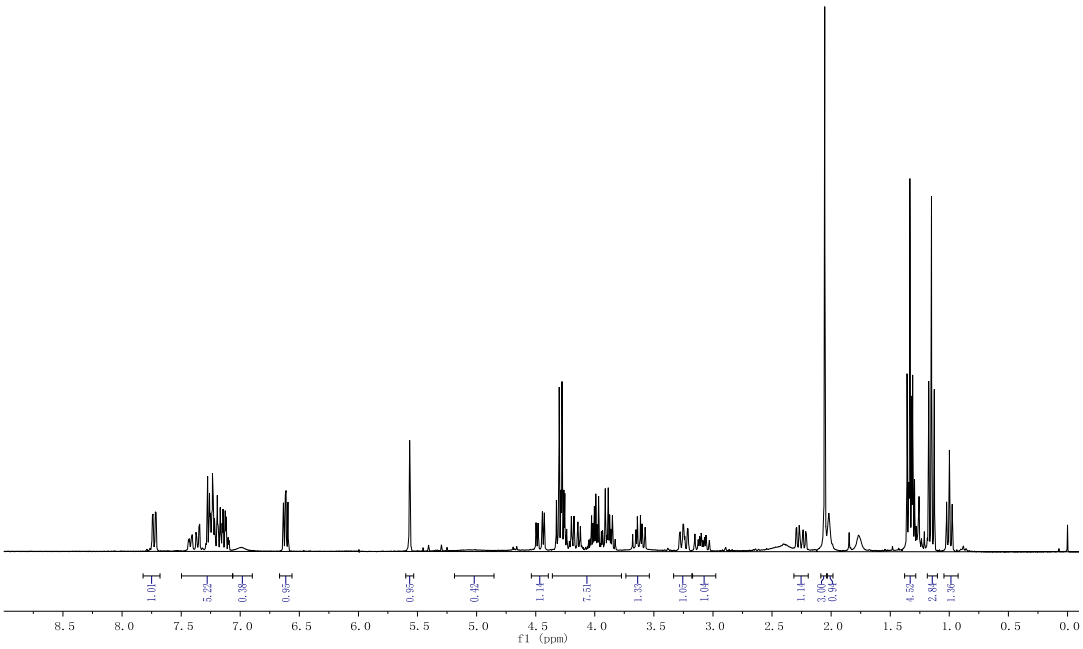
N
COOEt
Me
EtOOC

8z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3.00
0.94
4.58
2.84
1.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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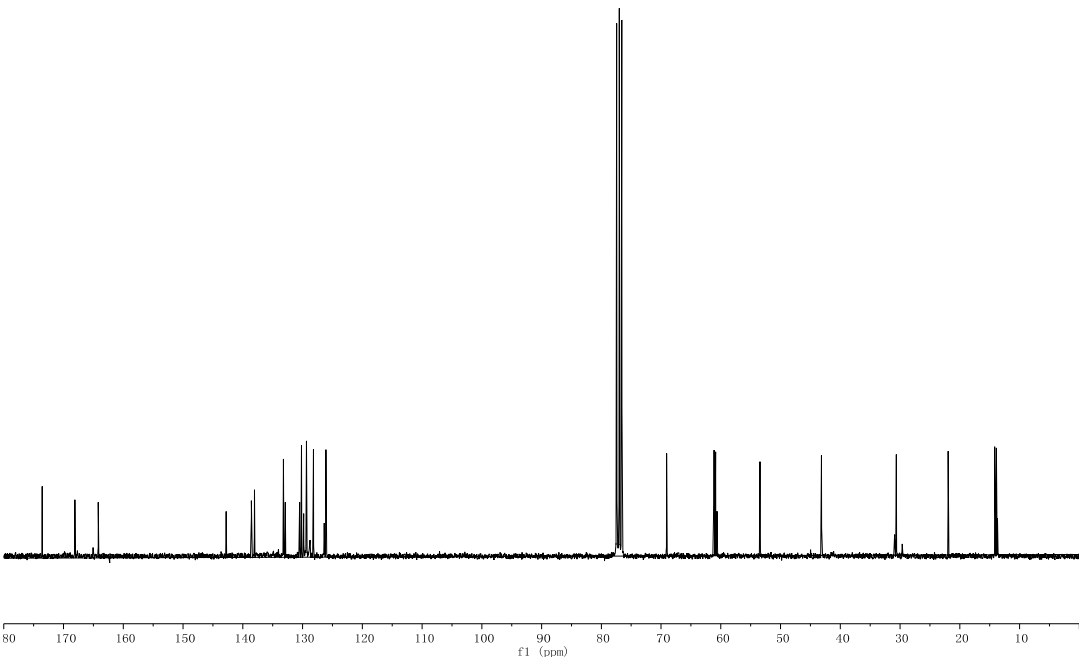
f1 (ppm)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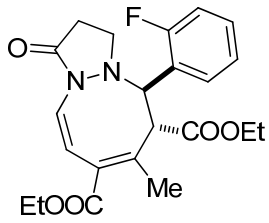
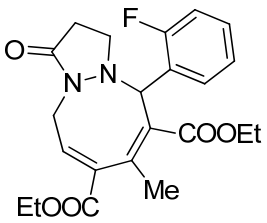
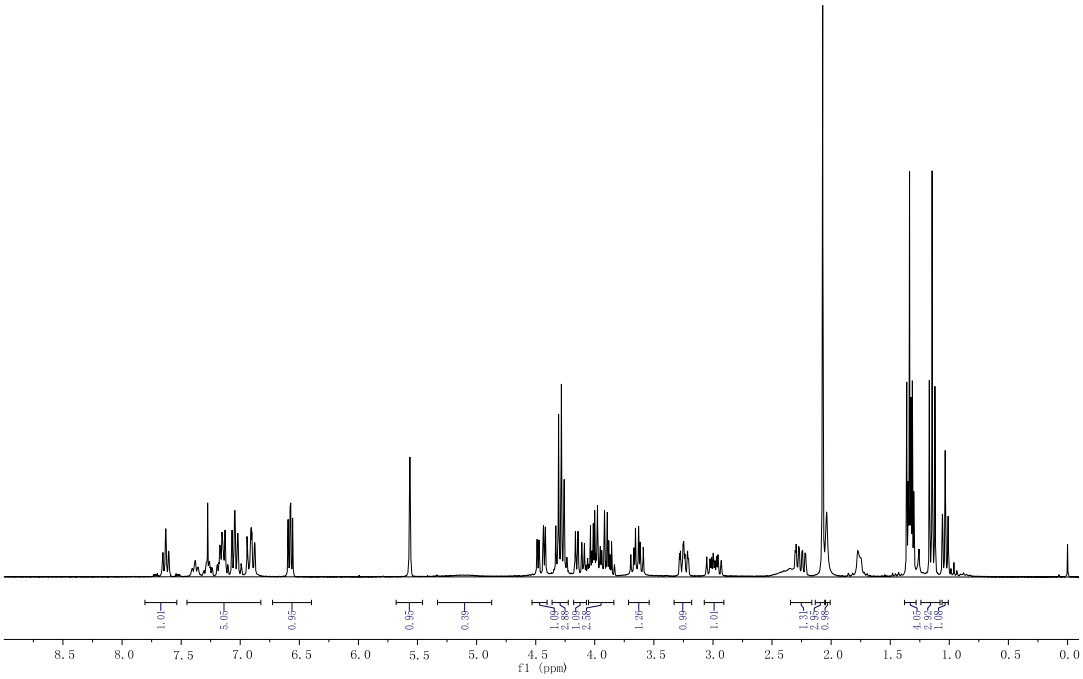
f1 (ppm)


F
O
N
N
COOEt
Me
EtOOC

7zz


F
O
N
N
COOEt
Me
EtOOC

8zz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1.09
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0.99
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1.31
2.95
0.98
4.05
2.92
1.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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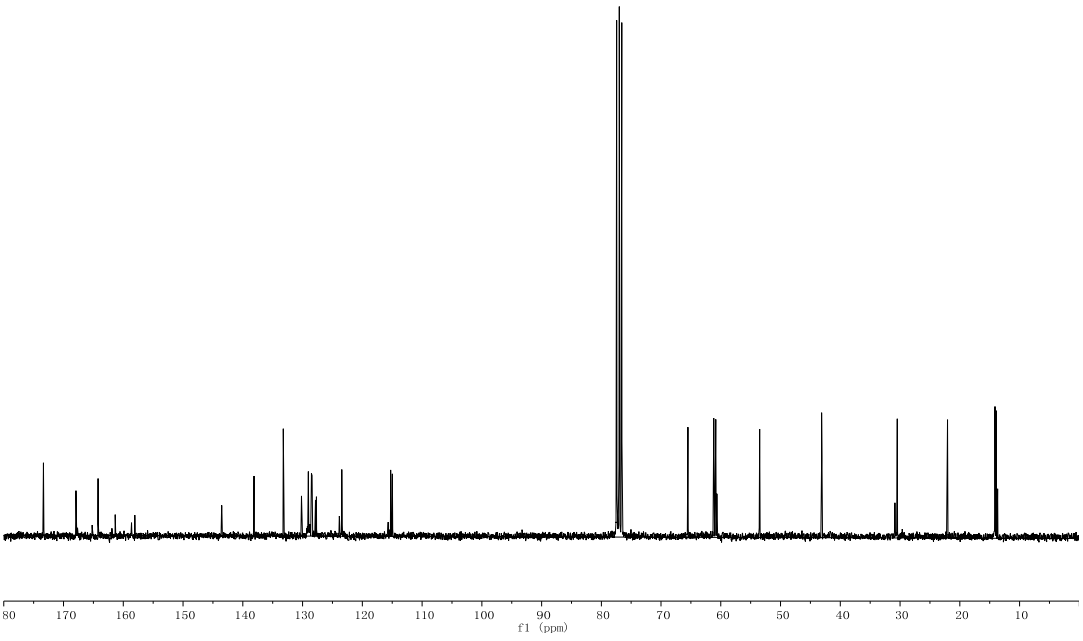
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


80
170
160
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140
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100
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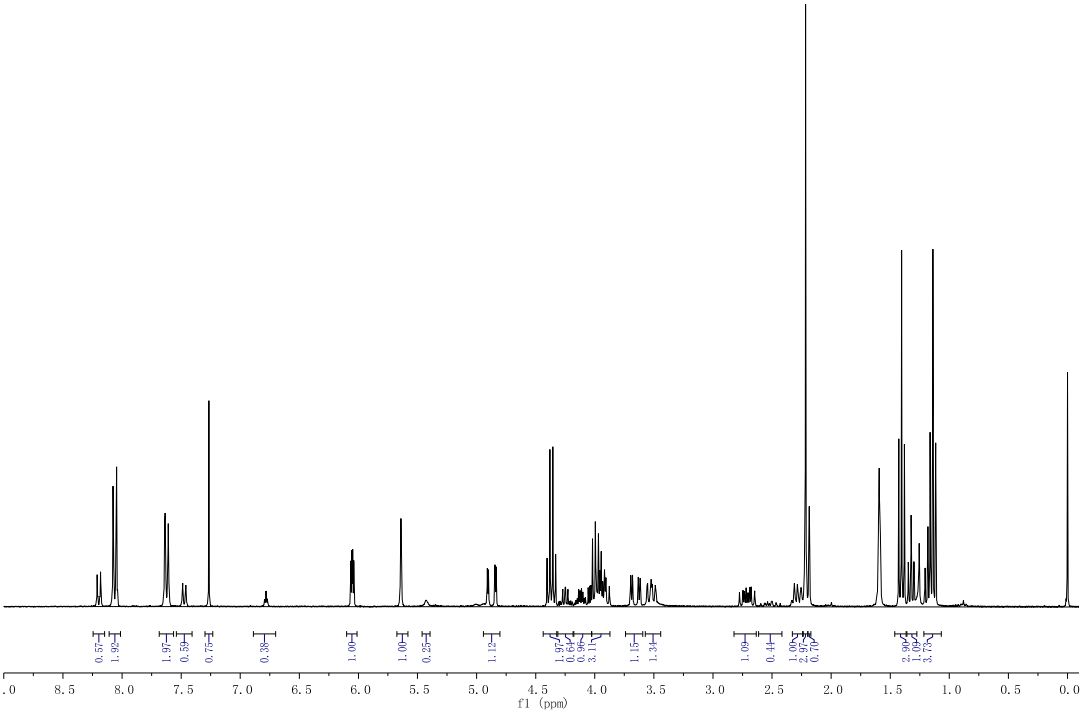
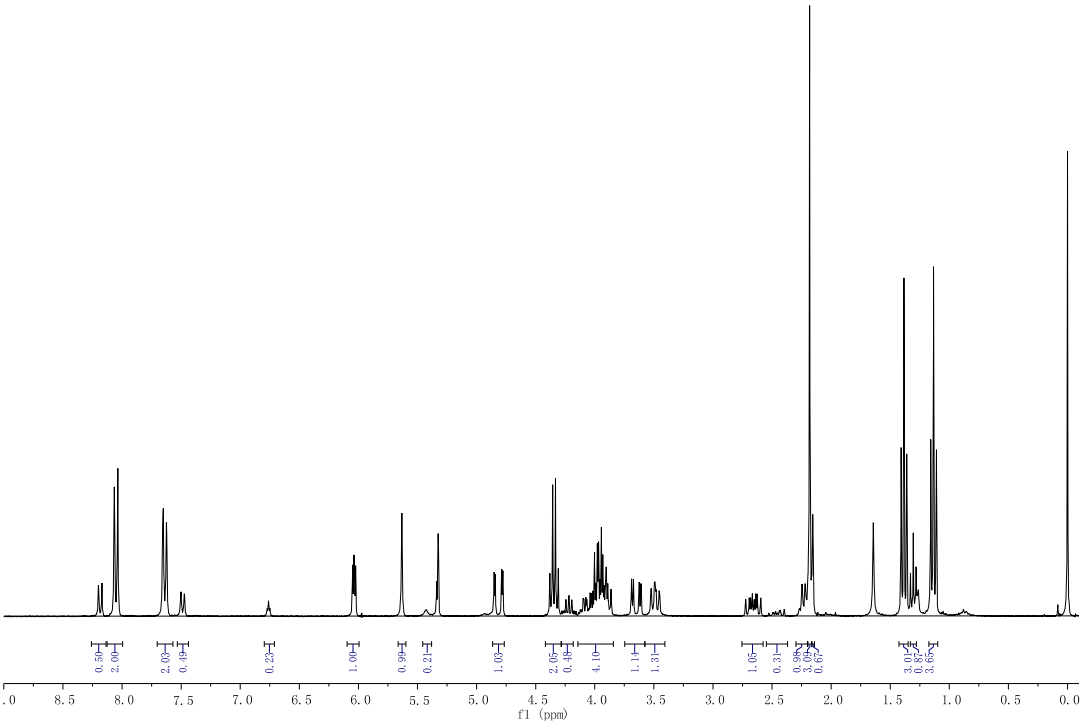
50
40
30
20
10
f1 (ppm)

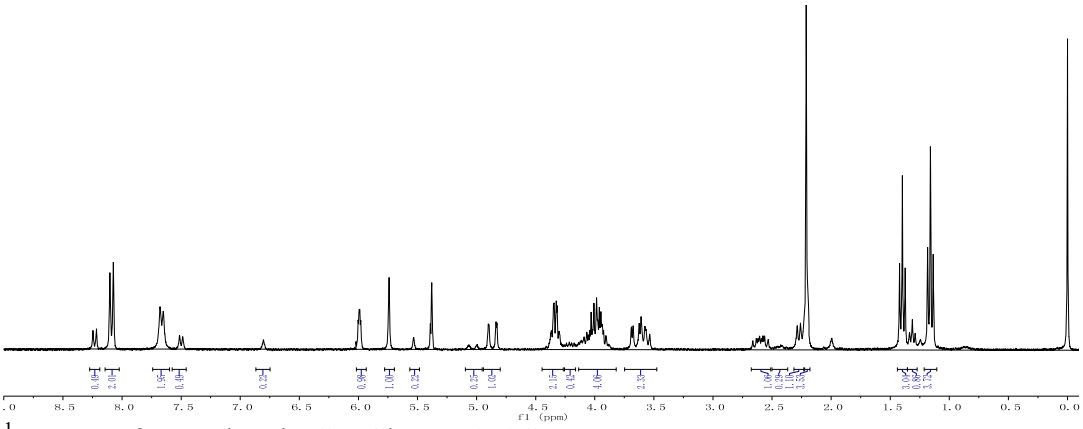
^{1}HNMR of **7a** and **8a** in $CDCl_3$ at room temperature



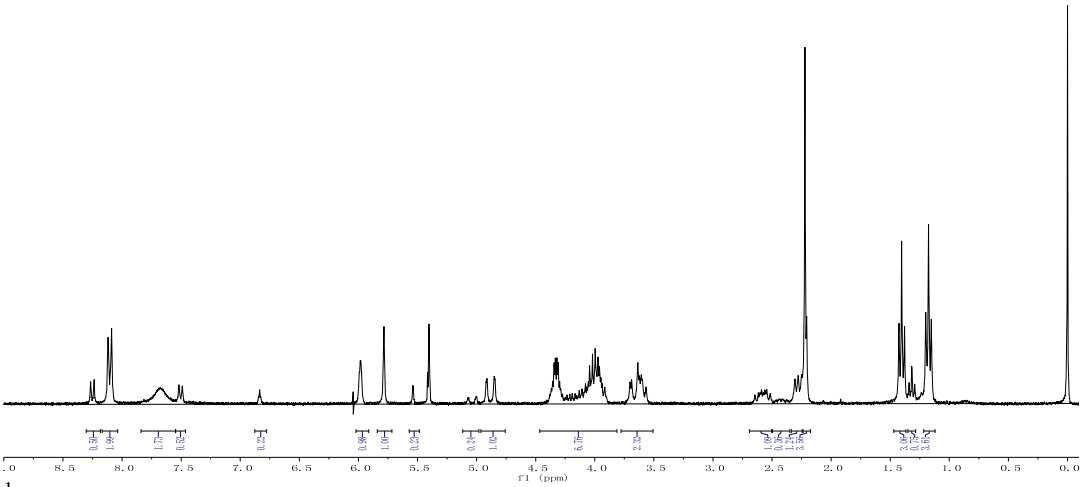
^{1}HNMR of **7a** and **8a** in CD_2Cl_2 at room temperature



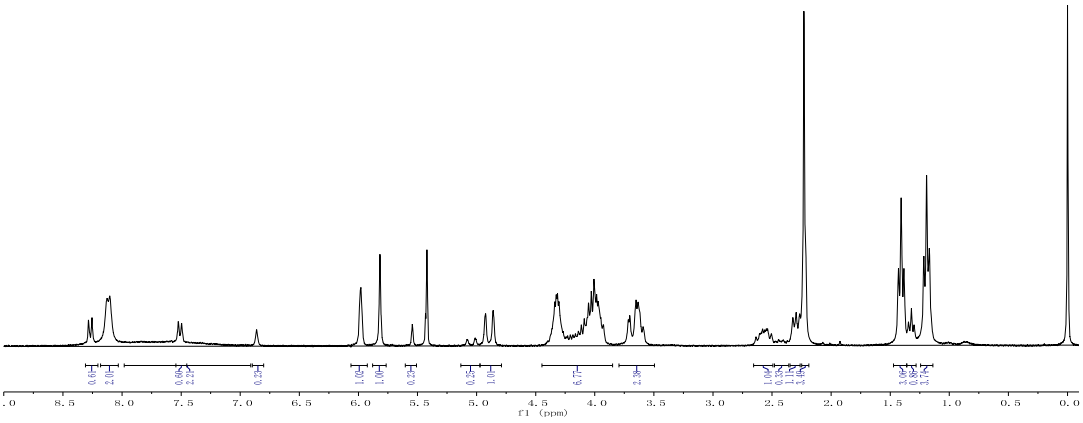
1HNMR of **7a** and **8a** in CD_2Cl_2 at – 40 °C



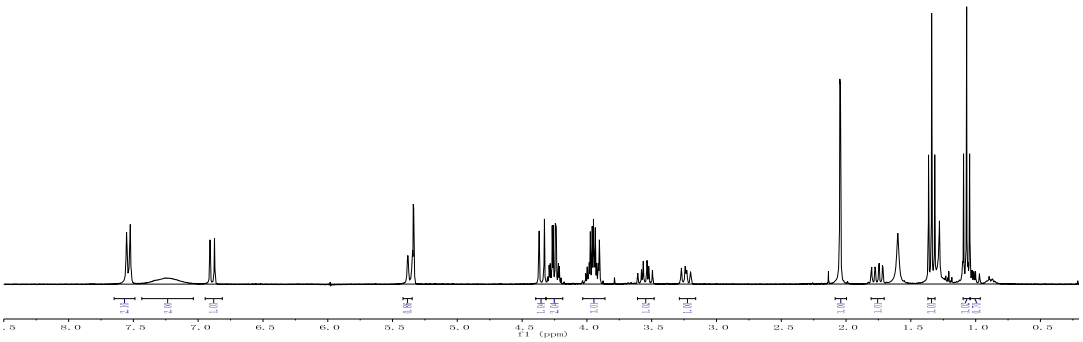
^{1}HNMR of **7a** and **8a** in CD_2Cl_2 at – 60 °C



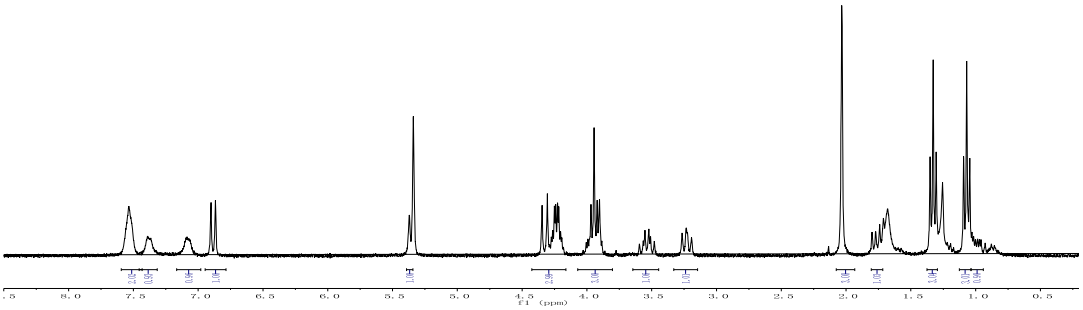
^{1}HNMR of **7a** and **8a** in CD_2Cl_2 at – 80 °C



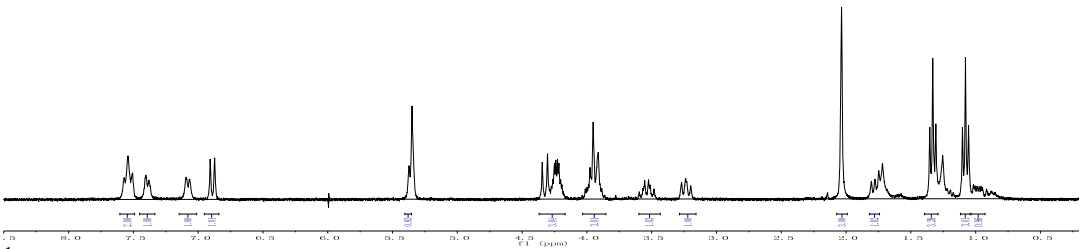
^{1}HNMR of **7h** and **8h** in CD_2Cl_2 at room temperature



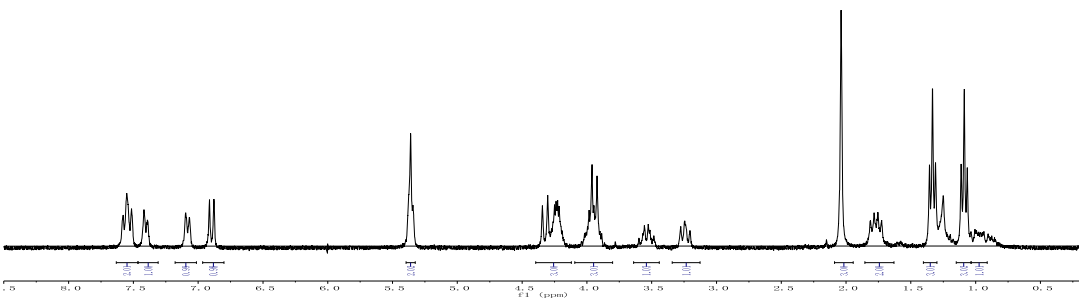
^{1}H NMR of **7h** and **8h** in CD_2Cl_2 at 0 °C



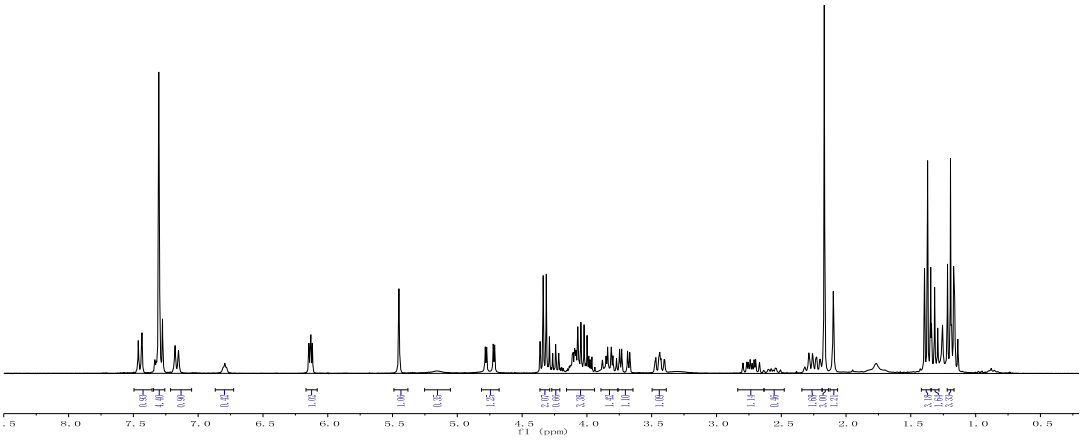
^{1}HNMR of **7h** and **8h** in CD_2Cl_2 at – 10 °C



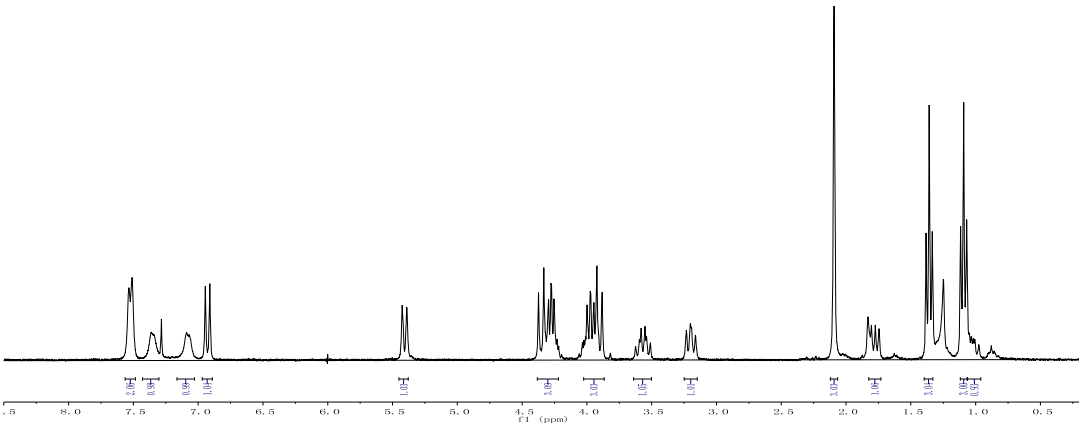
^{1}HNMR of **7h** and **8h** in CD_2Cl_2 at – 20 °C



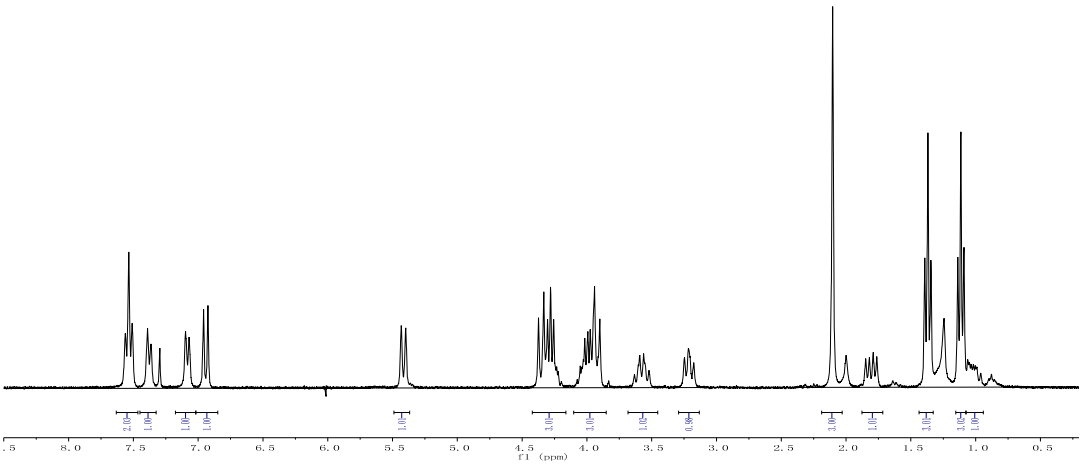
^{1}HNMR of **7h** and **8h** in $CDCl_3$ at room temperature

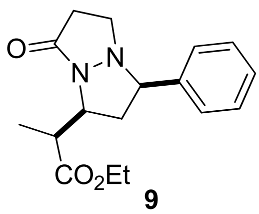


^{1}HNMR of **7h** and **8h** in $CDCl_3$ at 0 °C



^{1}HNMR of **7h** and **8h** in $CDCl_3$ at –20 °C





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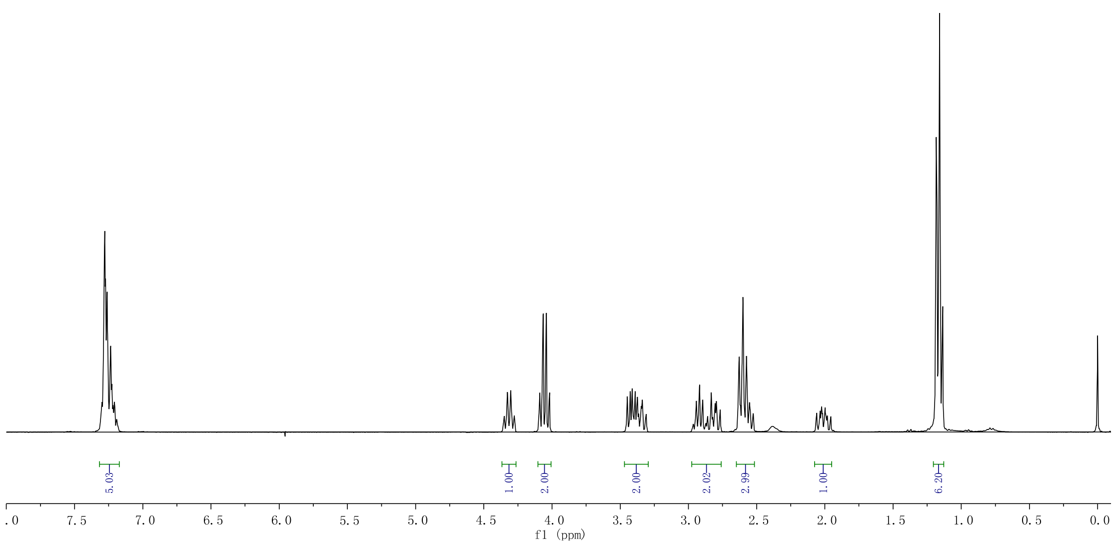
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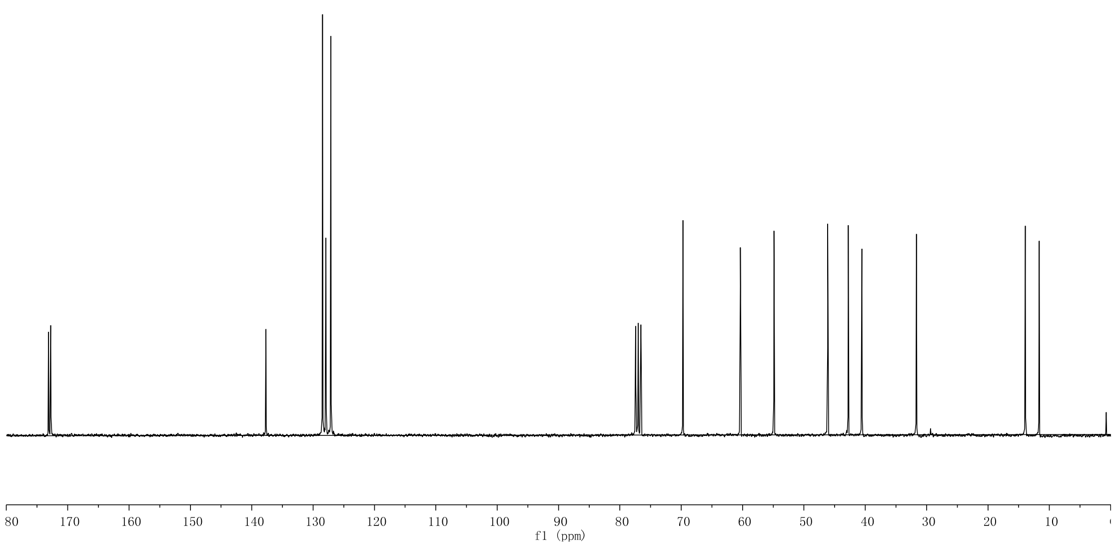
2.00
2.00
2.02
2.99
1.00
6.20
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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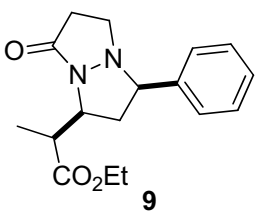
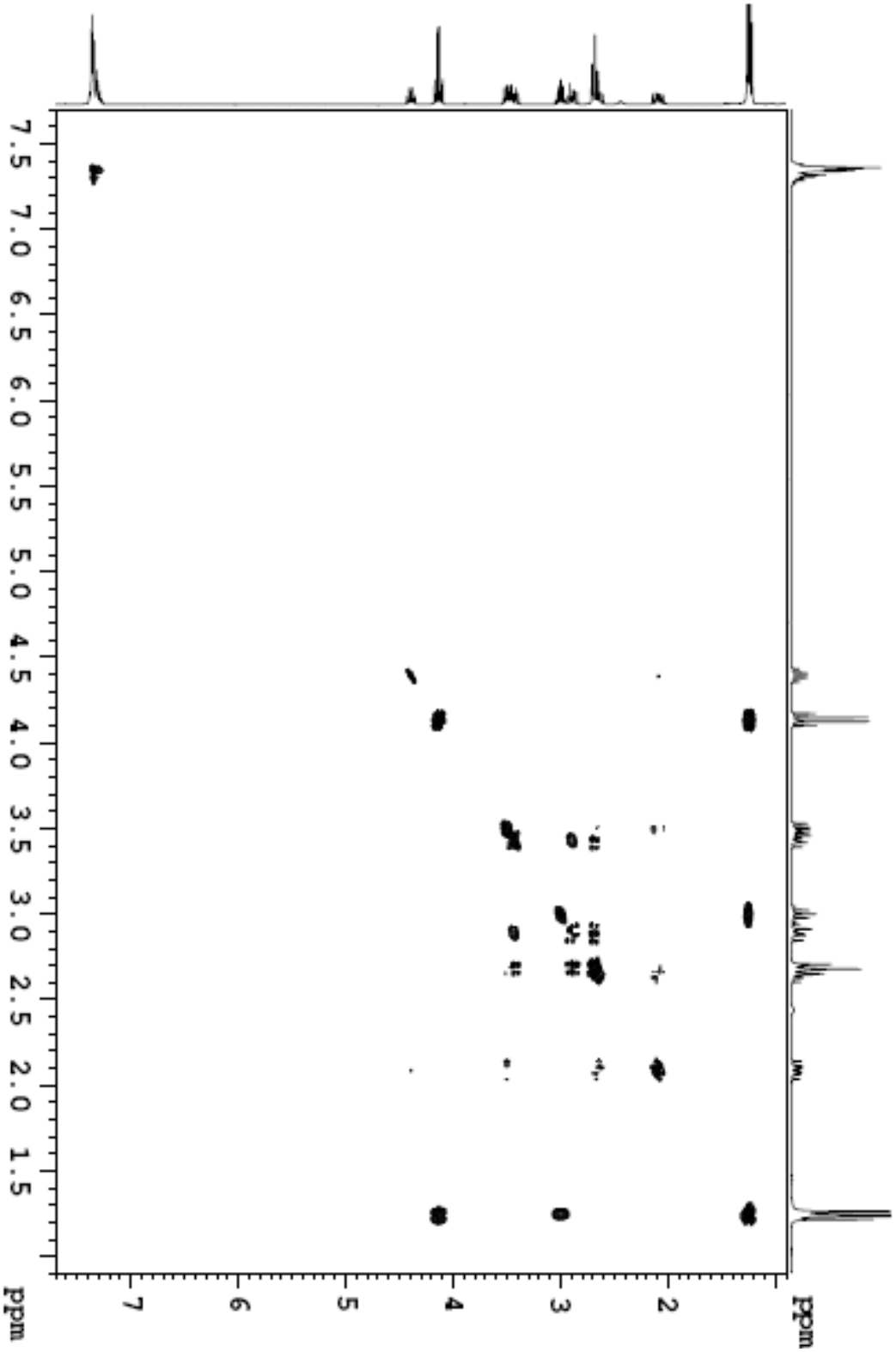
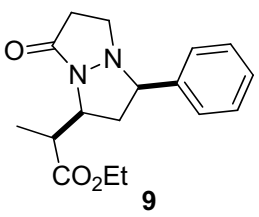
f1 (ppm)



9

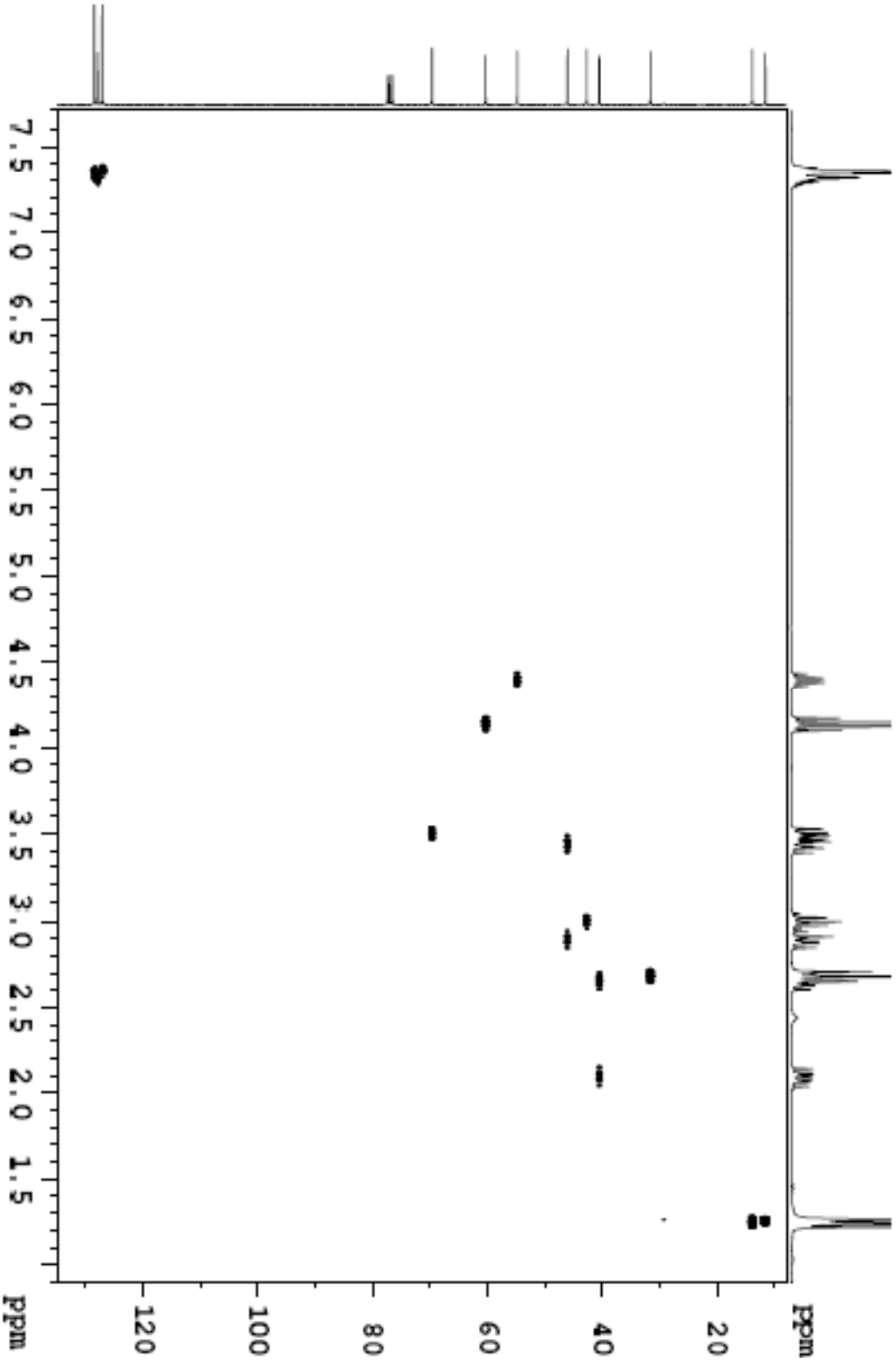
2D NMR COSY




O
N
N
CO2Et

9

2D NMR HMQC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ppm
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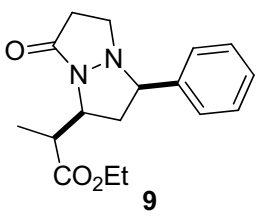
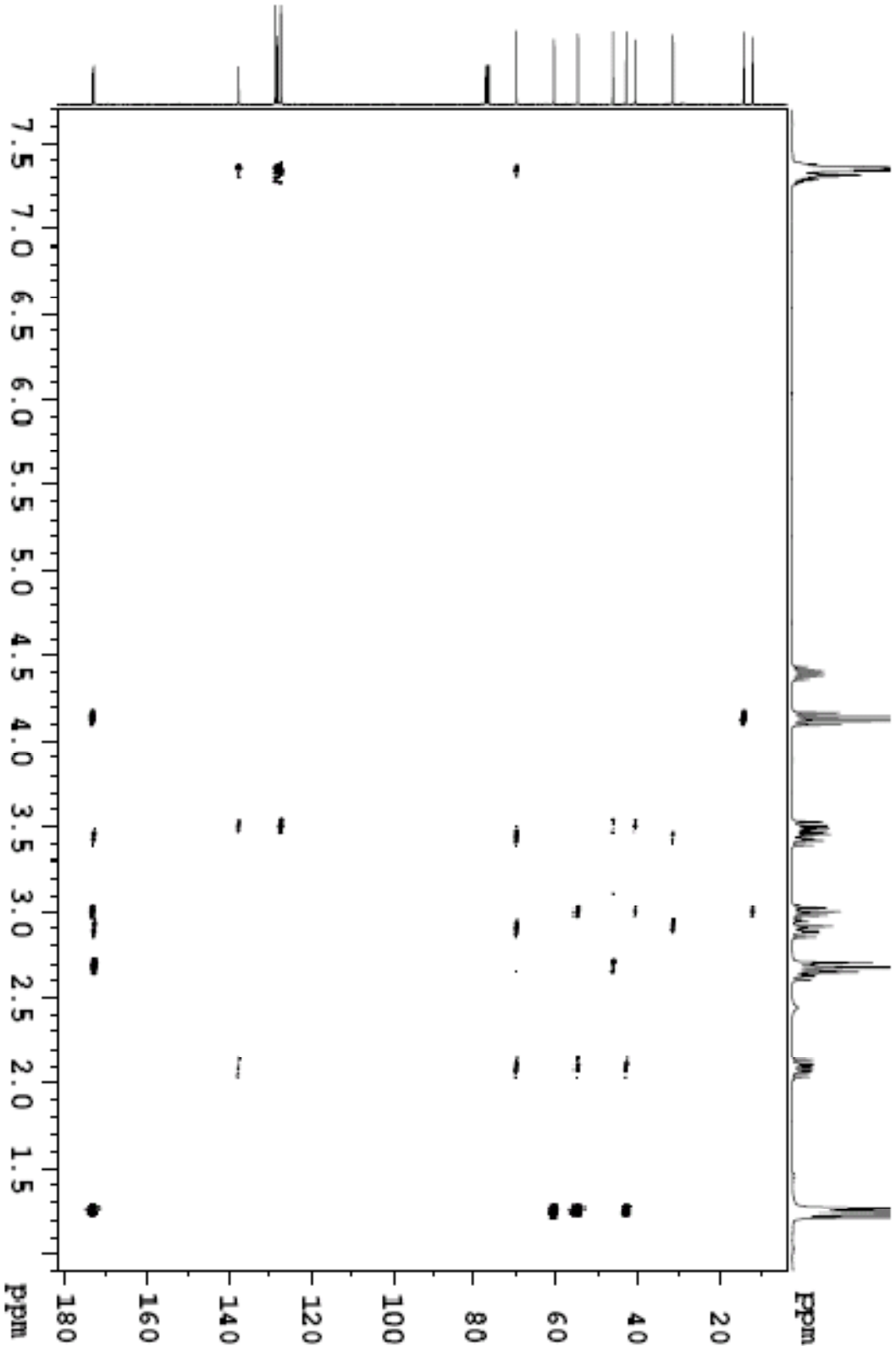
ppm


O
N
N
CO2Et

9

2D NMR HMBC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2.0
1.5
ppm
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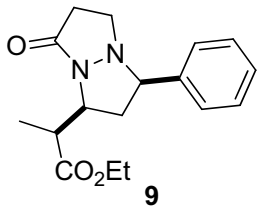
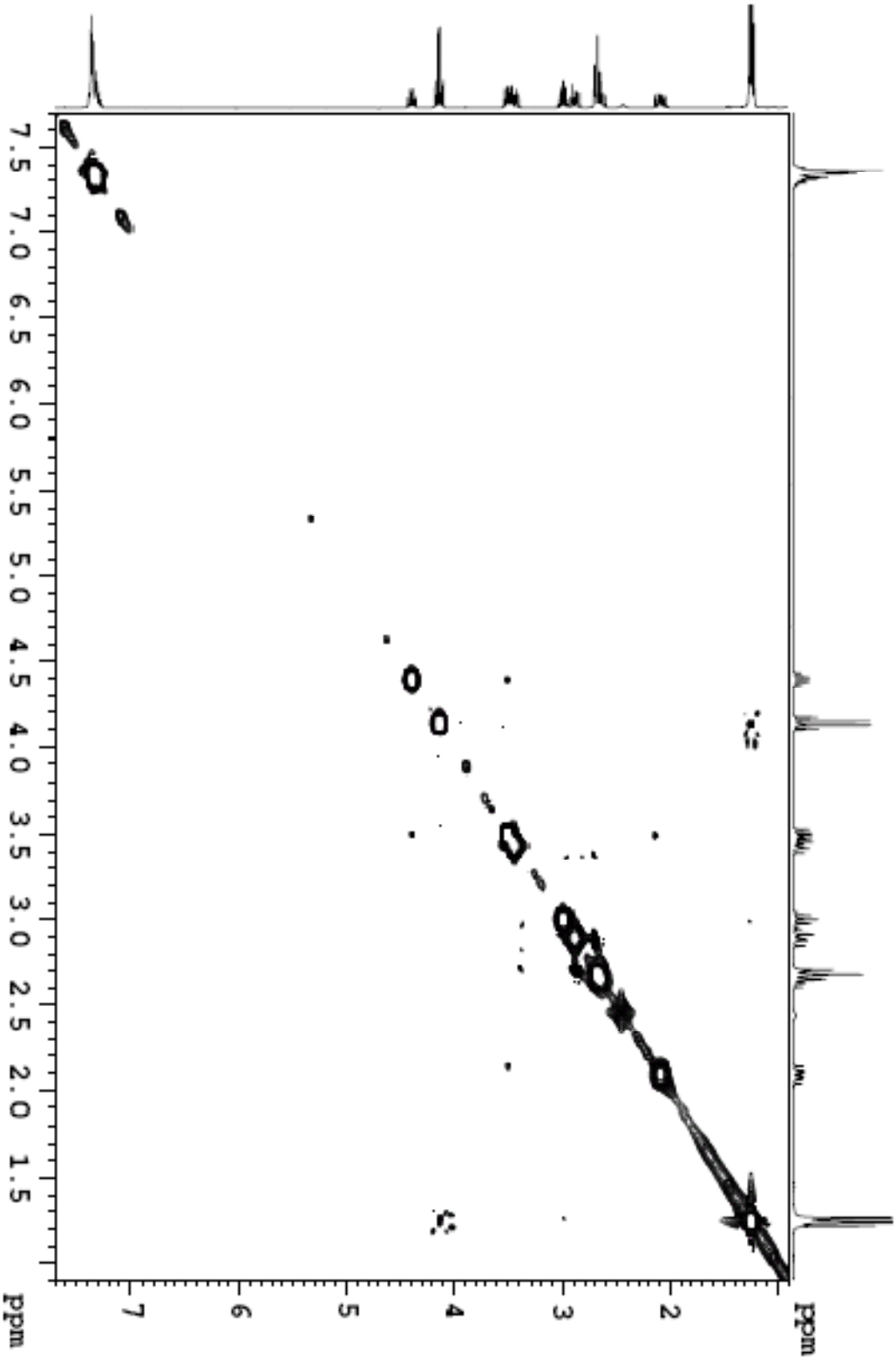
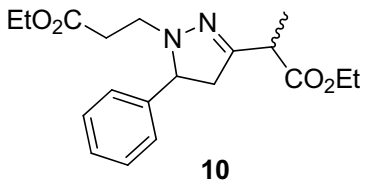
ppm



9

2D NMR NOESY





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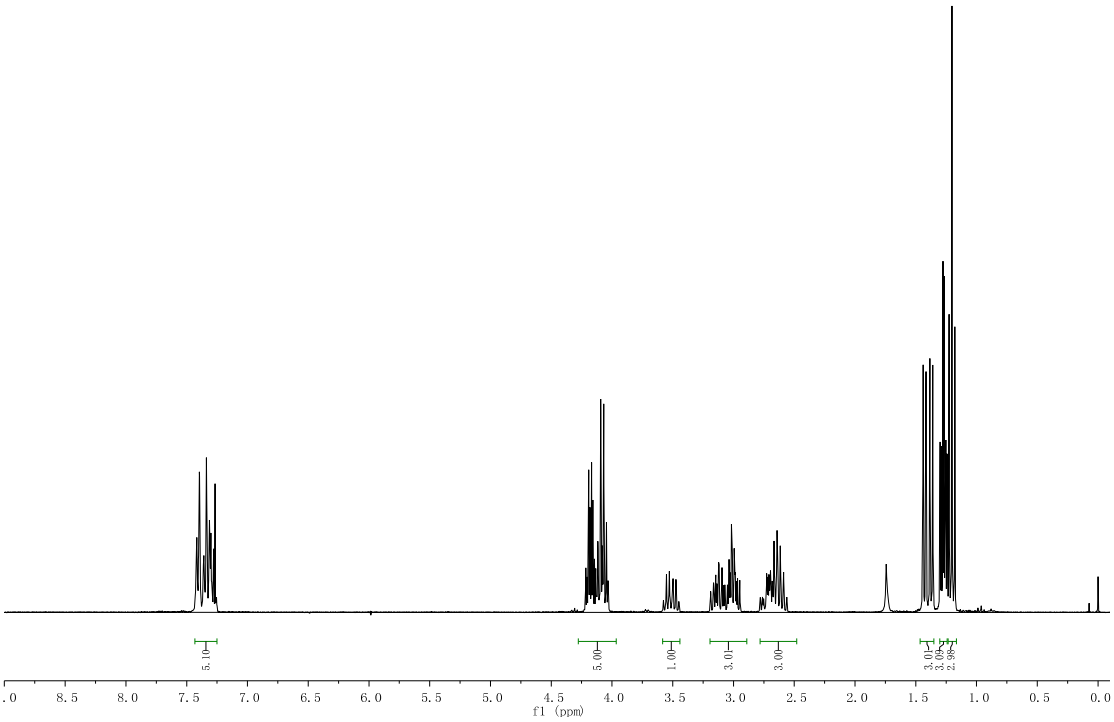

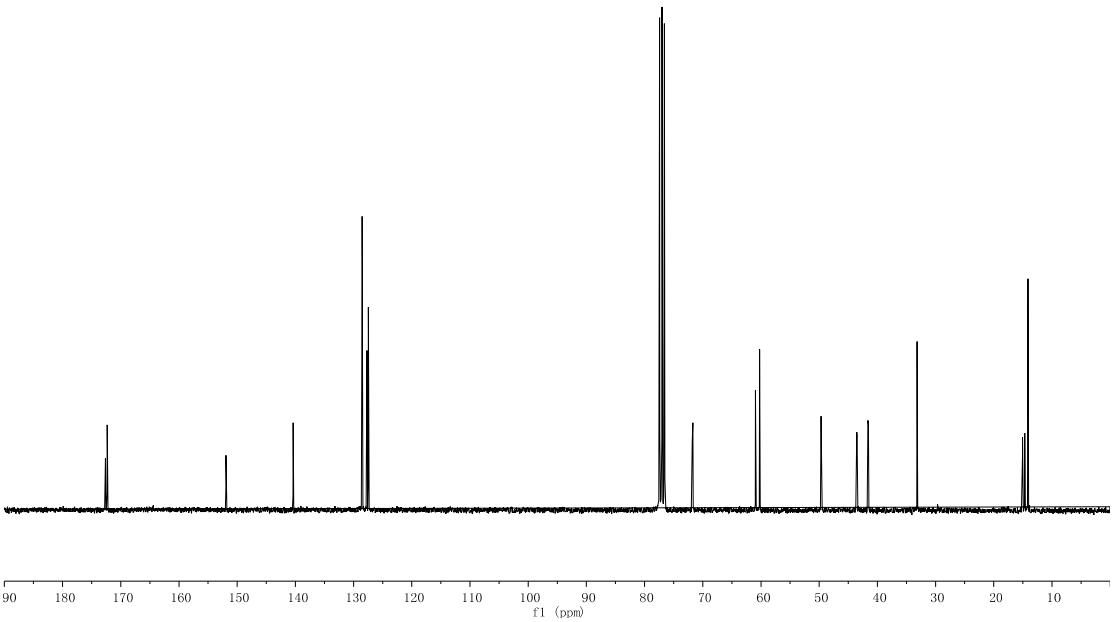

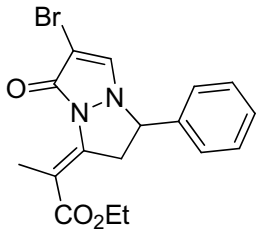

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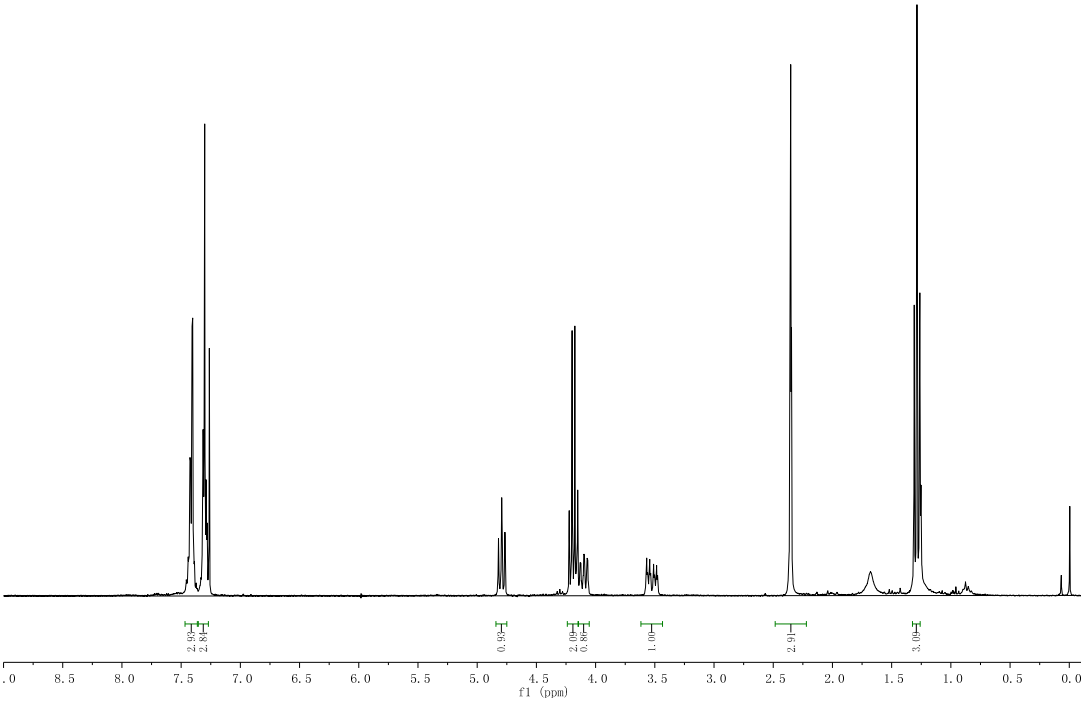
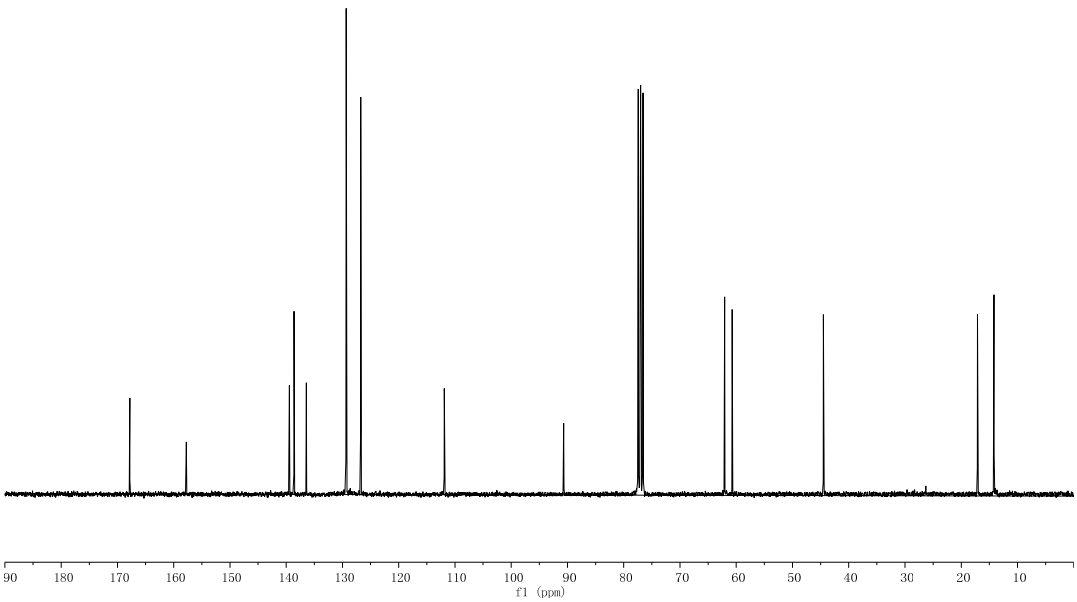
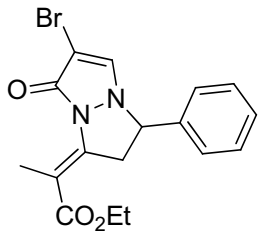
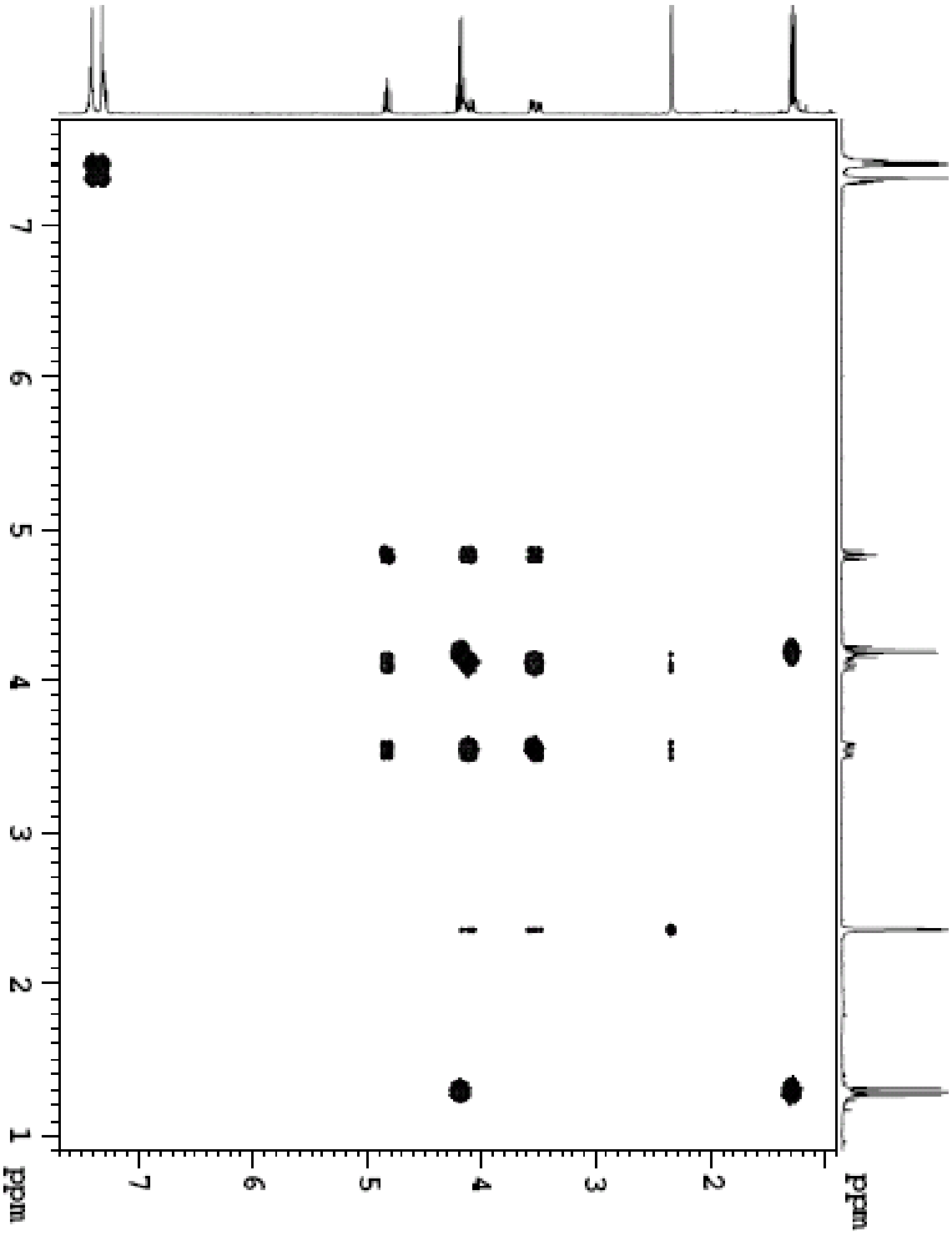


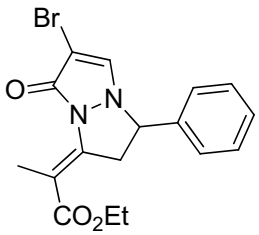




11

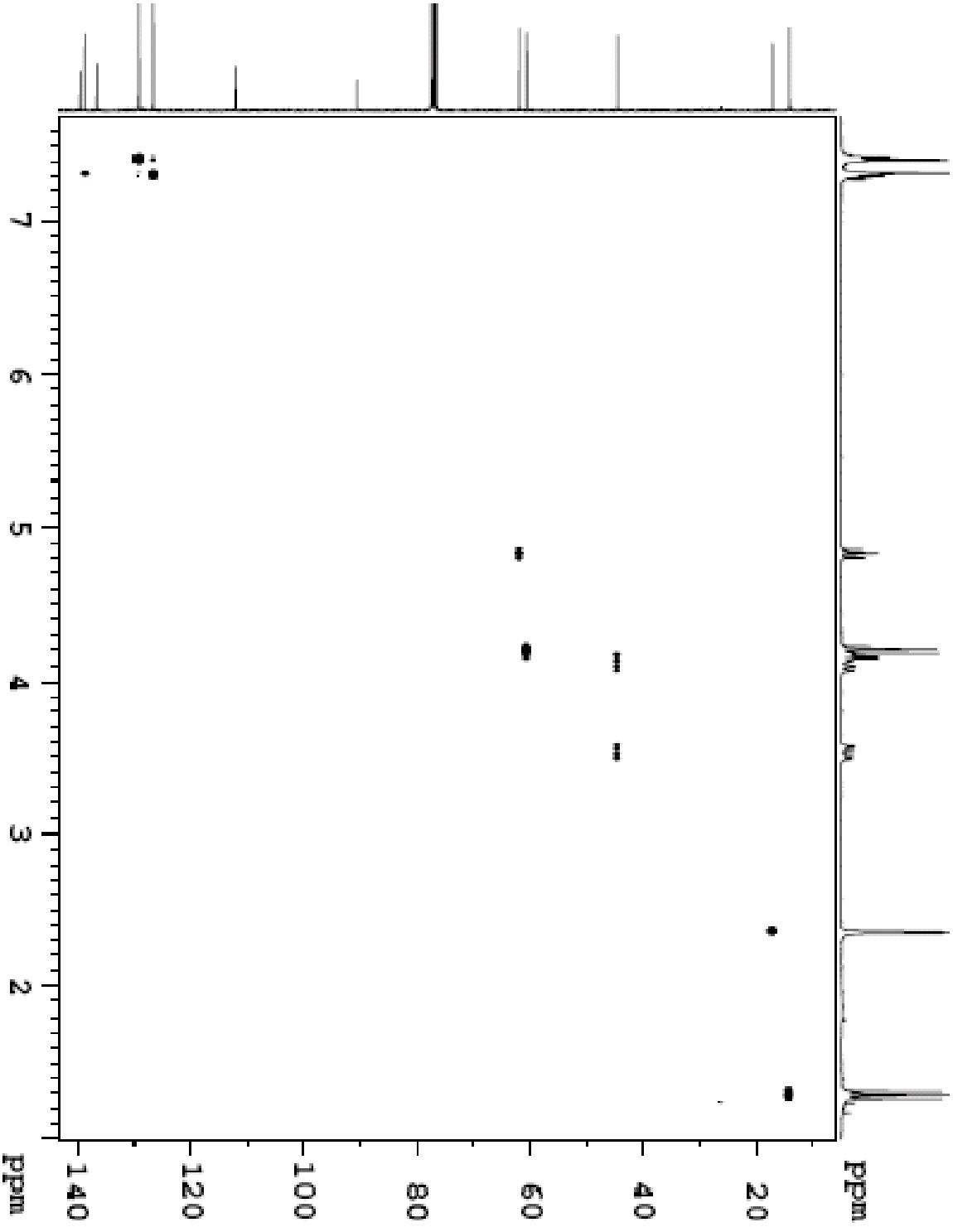
2D NMR COSY

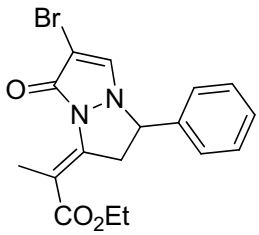




11

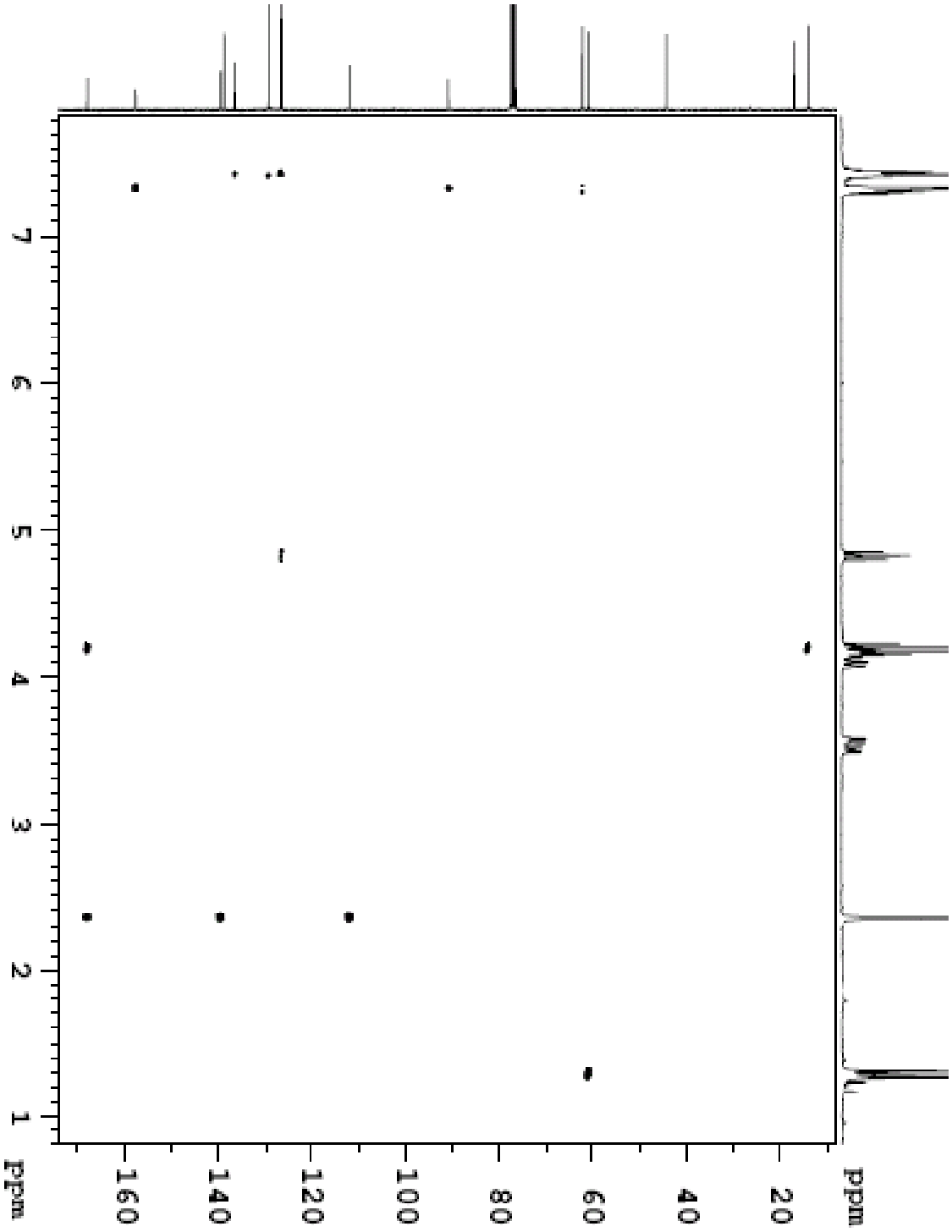
2D NMR HMQC

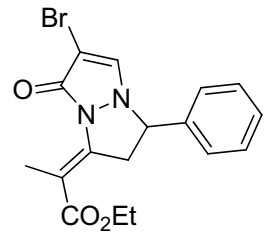




11

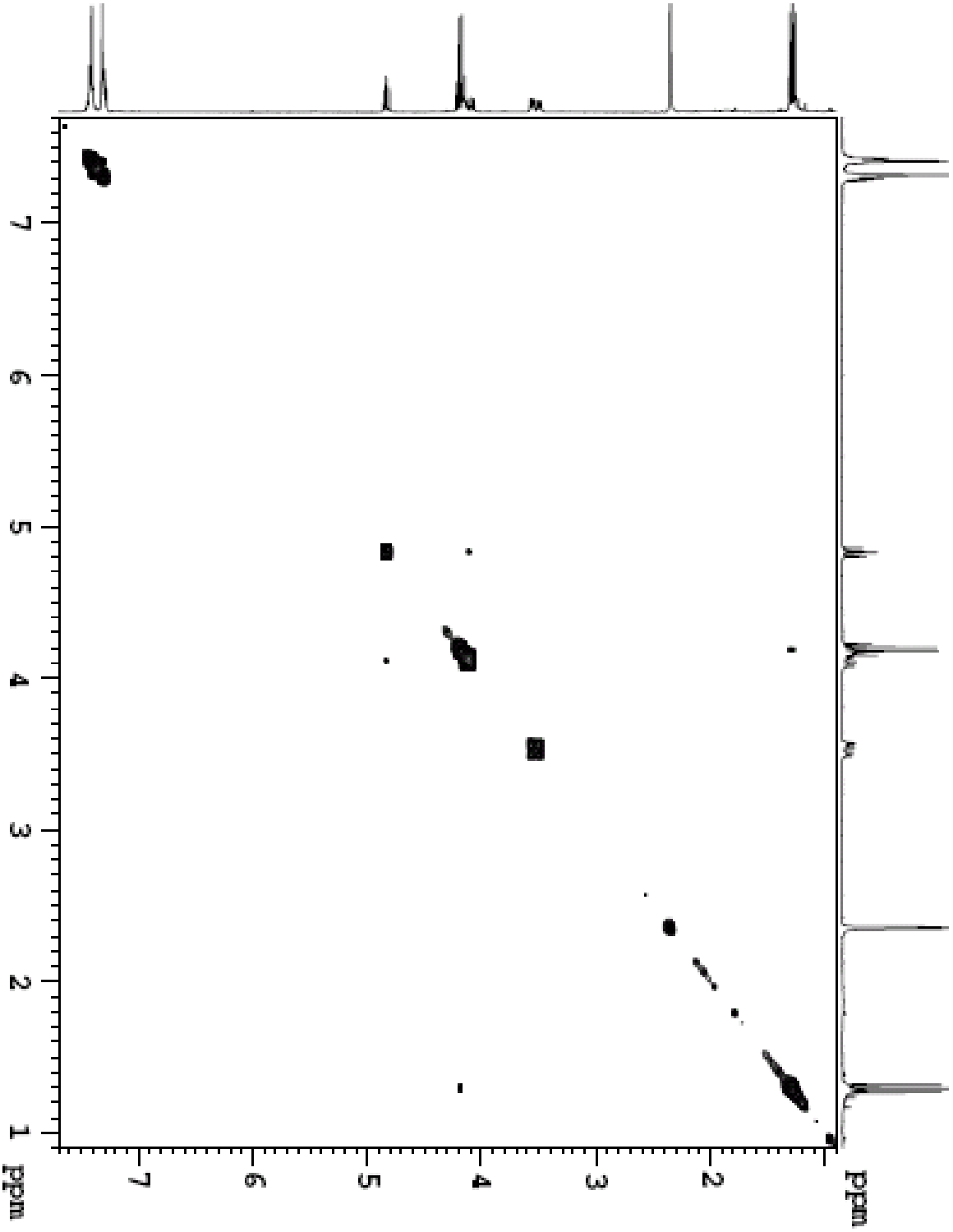
2D NMR HMBC

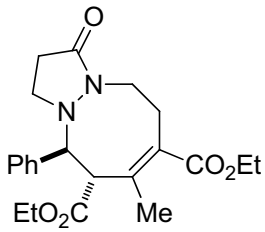




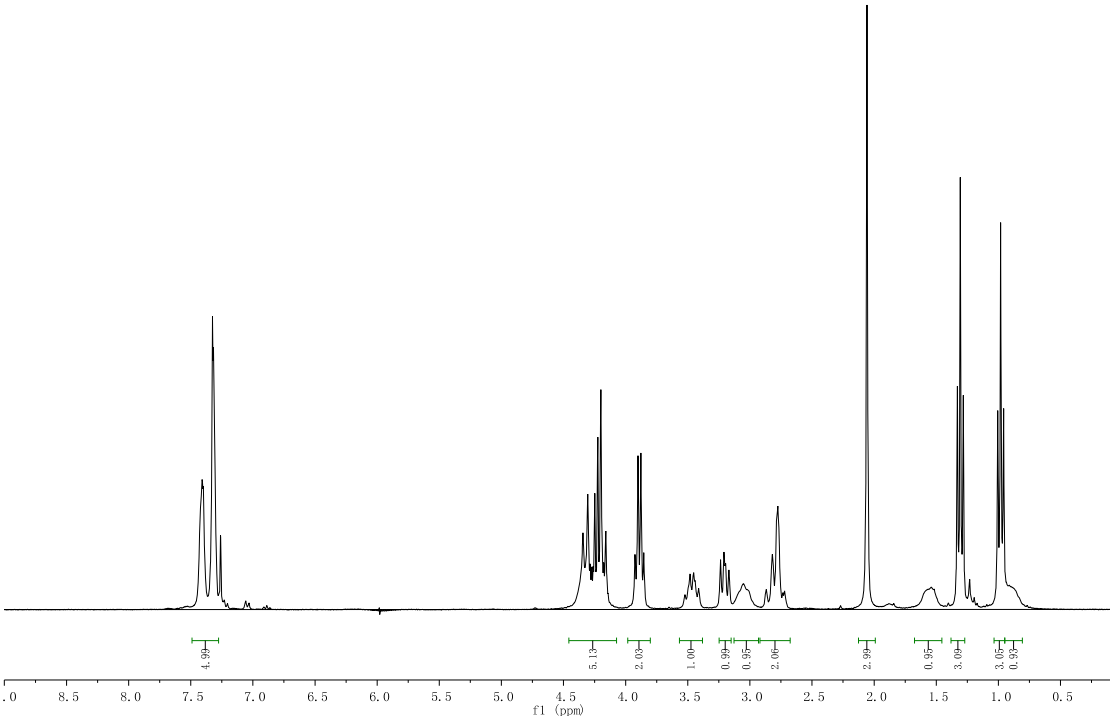
11

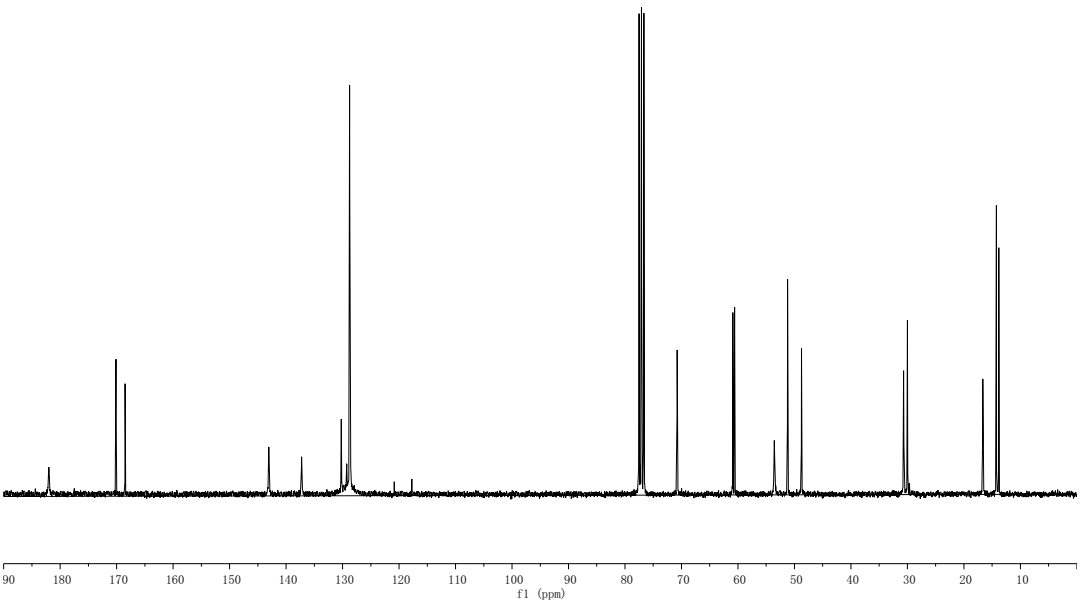
2D NMR NOESY

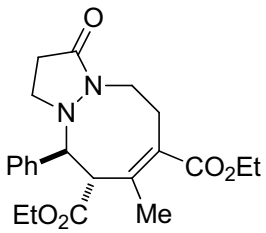



O
N
N
Ph
CO2Et
EtO2C
Me

12

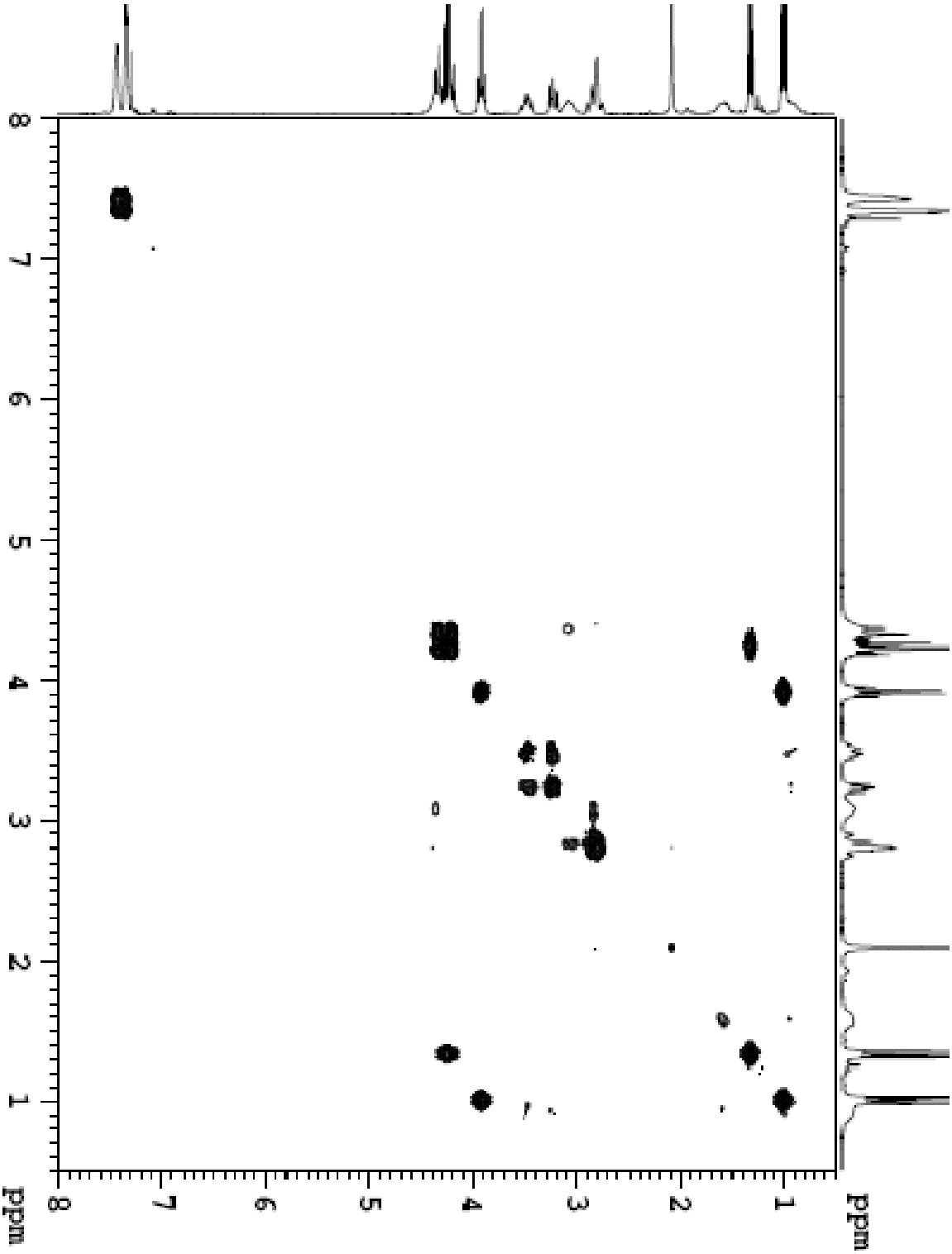

4.99
5.13
2.03
1.00
0.69
0.95
2.00
2.99
0.95
3.09
3.05
0.83
f1 (ppm)

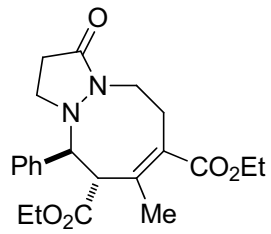

f1 (ppm)



12

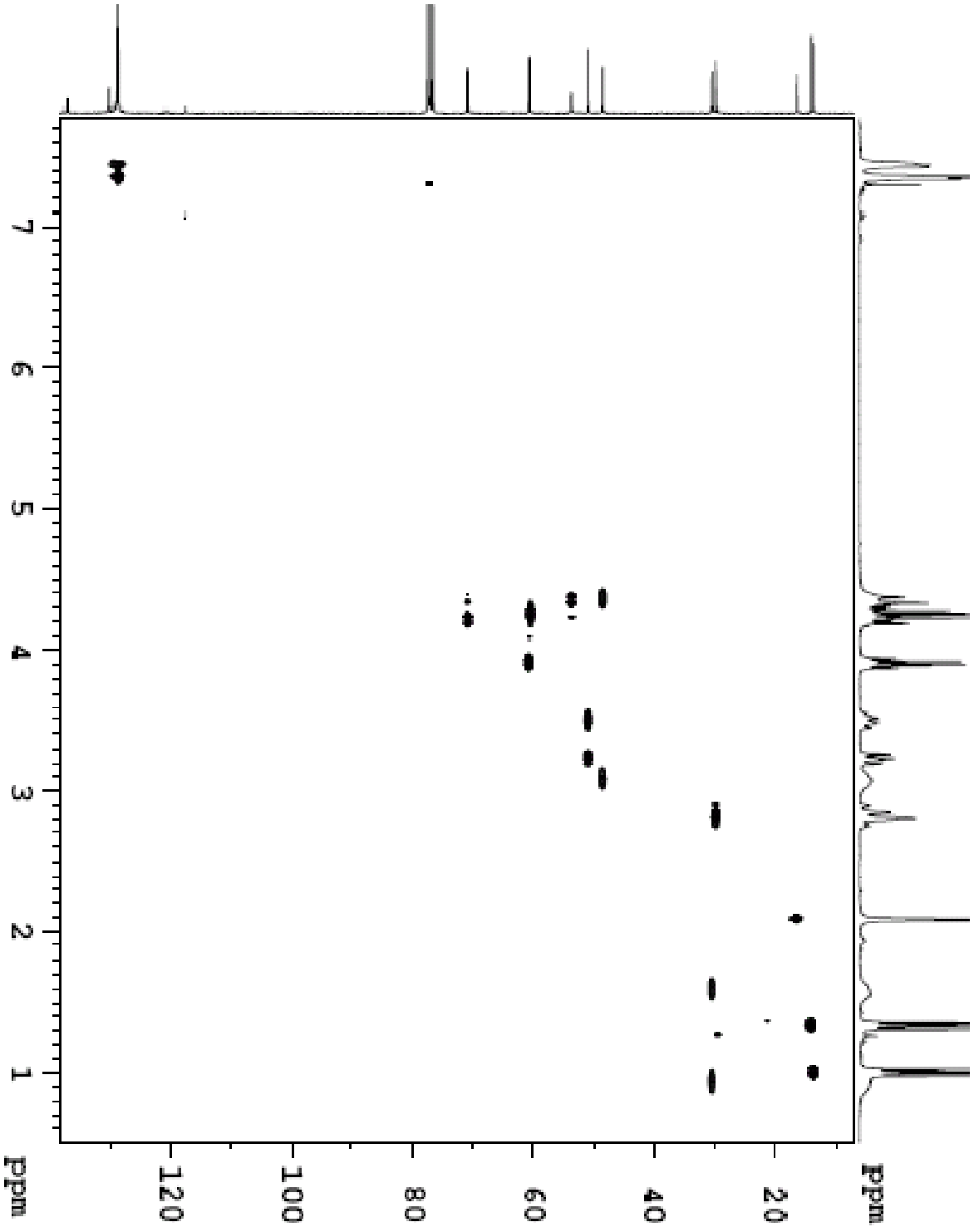
2D NMR COSY

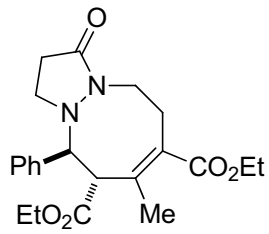




12

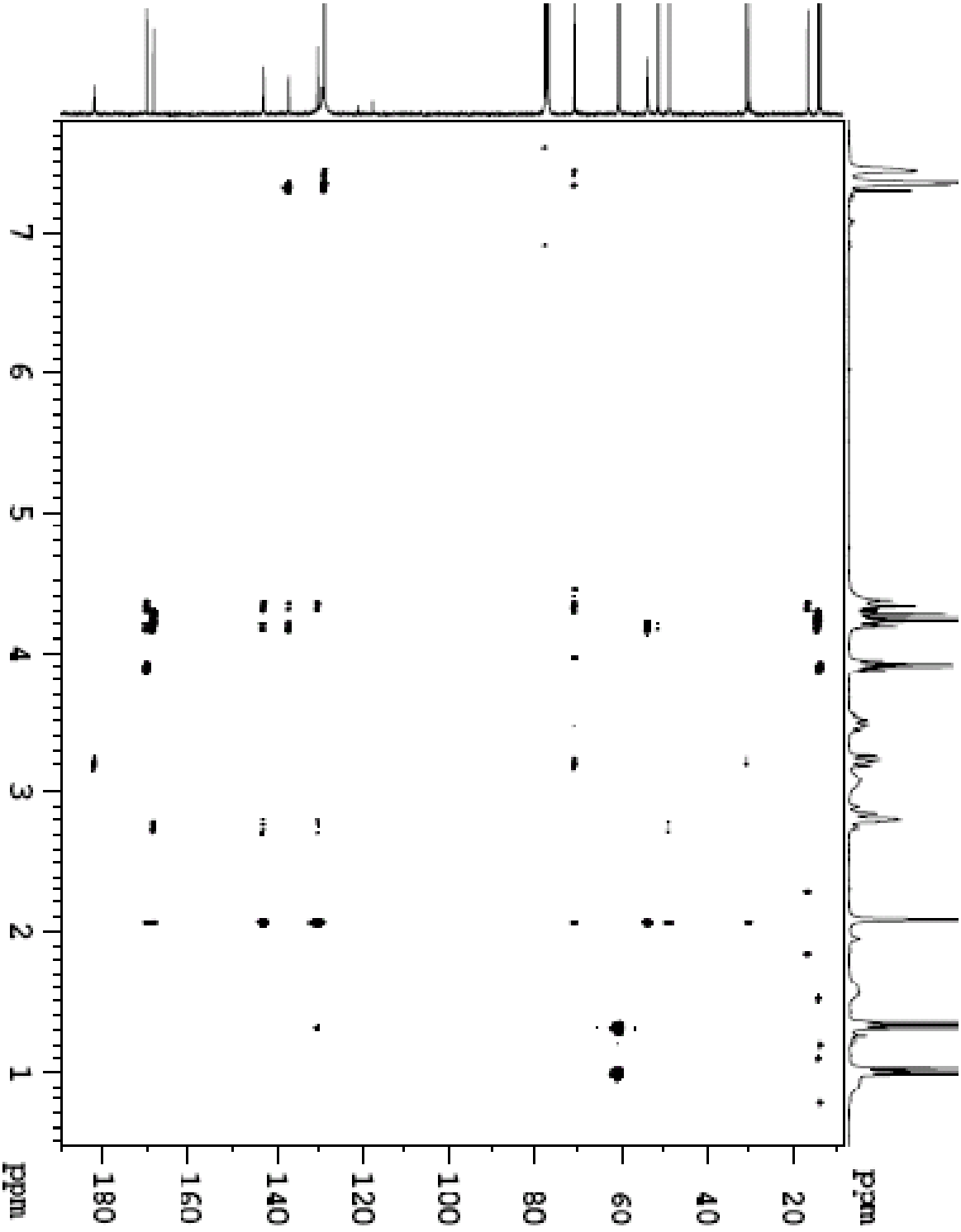
2D NMR HMQC

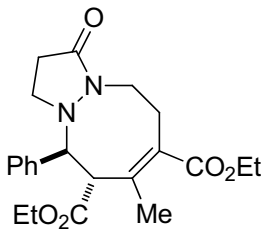




12

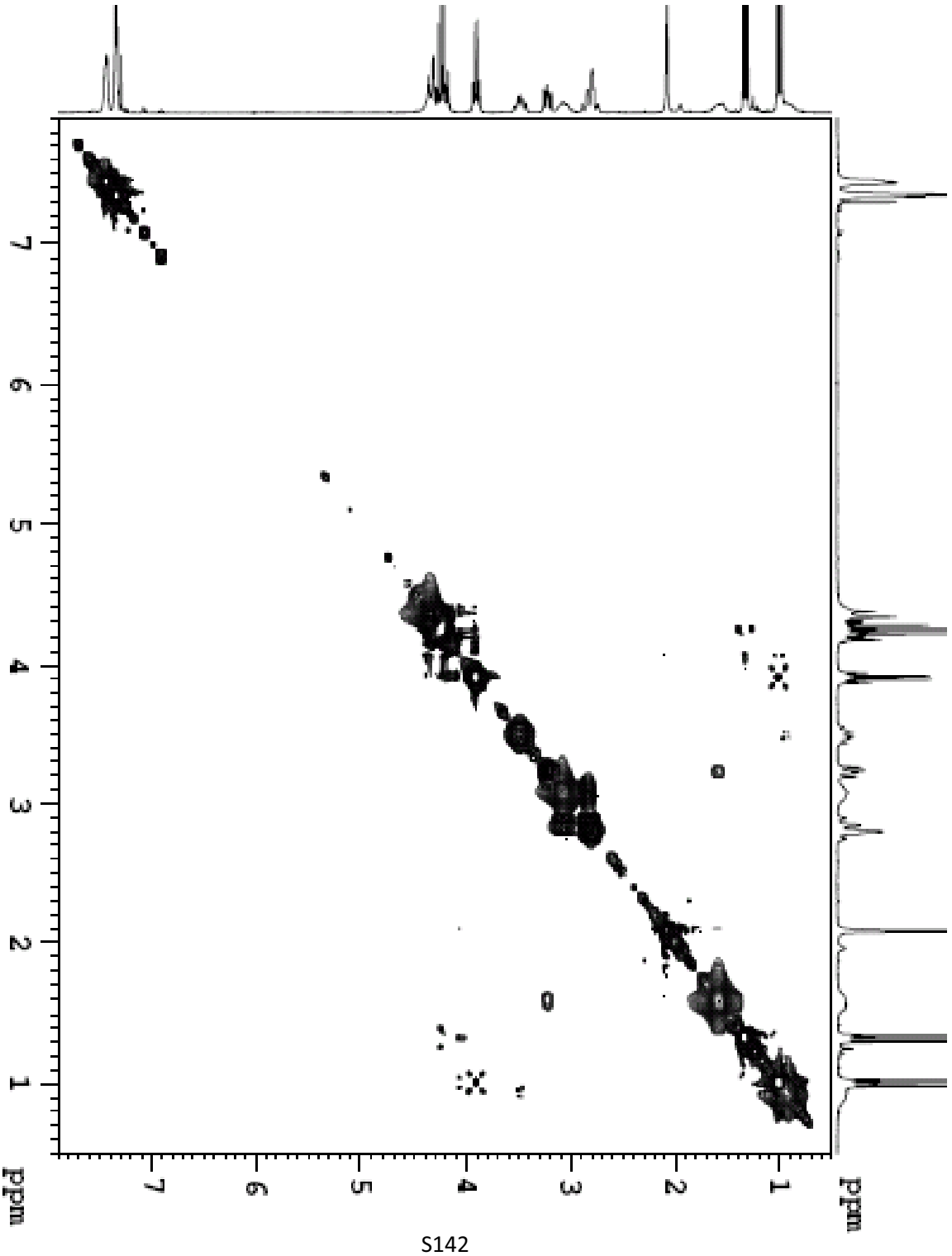
2D NMR HMBC



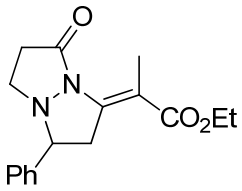


12

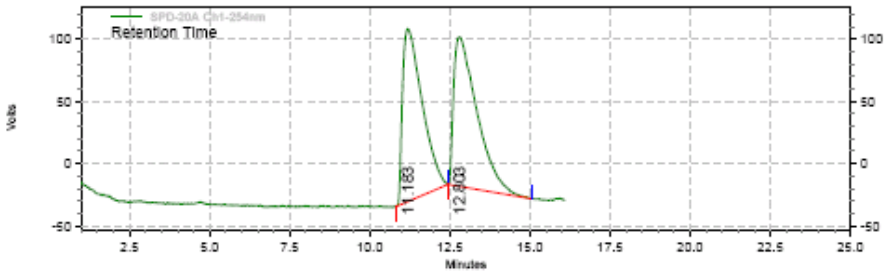
2D NMR NOESY



HPLC chromatogram of racemic 3ba



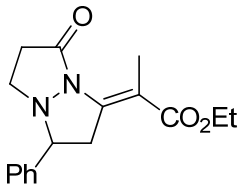
rac-**3ba**



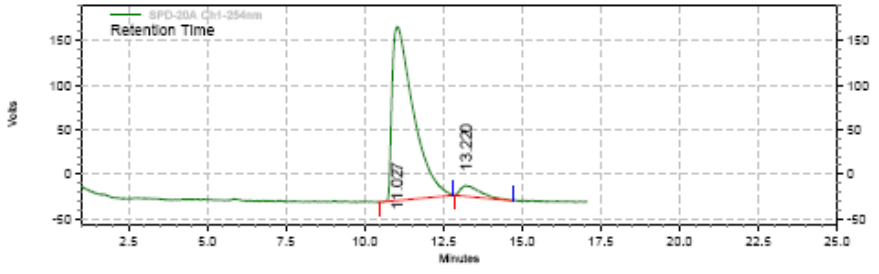
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.183	5897071	49.17	138860	53.65
12.803	6095423	50.83	119953	46.35
Totals	11992494	100.00	258813	100.00

HPLC chromatogram of chiral 3ba



chiral **3ba**



SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
11.027	9174997	94.51	194979	94.20
13.220	532587	5.49	12015	5.80
Totals	9707584	100.00	206994	100.00

Computational Methods

Calculations were performed using density functional theory (DFT) with the M06 functional,[6] as implemented in Jaguar 7.6.110.[7] Geometry optimizations were performed using the 6-31G** basis set,[8, 9] while energies were computed using the correlation-consistent polarized triple-ζ basis set cc-pVTZ++ basis set for all atoms. For each optimized structure, the M06 analytic Hessian was calculated to obtain the vibrational frequencies, which in turn were used to obtain the zero point energies and free energy corrections (without translational or rotational components). Solvent corrections were based on single point self-consistent Poisson-Boltzmann continuum solvation calculations (using the 6-31G** basis set) for CH_2Cl_2 ($\varepsilon = 8.93$ and $R_0 = 2.33$ Å using the PBF[10] module in Jaguar.

XYZ Coordinates

7b

N1	0.3834869123	-0.0155129298	0.8850189423
N2	0.1402691904	-0.2728011462	-0.4981513086
C3	-1.2030566760	-0.4578810475	-0.7882957908
C4	-1.9762882821	-0.1291077792	0.4740236501
H5	-2.8308074044	-0.8034013341	0.5669501175
H6	-2.3540883834	0.9003145998	0.4174480503

[6] Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.
[7] Jaguar 7.6, Schrodinger, LLC, New York, NY (2006).
[8] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.
[9] Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
[10] Tannor, D. J. *et al. J. Am. Chem. Soc.* **1994**, *116*, 11875–11882.

C7	-0.9101291131	-0.3141719060	1.5431631388
H8	-0.8846836959	-1.3571032635	1.8858461081
H9	-1.0378799858	0.3266025933	2.4205641683
O10	-1.6216317749	-0.8573177773	-1.8508472589
C11	1.1276776935	-0.9879096489	-1.2199633151
H12	0.9323228314	-2.0514103371	-1.3565655316
C13	0.8690796013	1.3507877266	1.1437732540
H14	0.9263144317	1.3771280074	2.2397164443
C15	2.3430695852	1.5253015423	0.6993170597
C16	2.6215569430	1.8710876864	-0.7484982112
C17	2.5739524168	0.9909642441	-1.7680643115
C18	2.2277275314	-0.4325971828	-1.7237735580
H19	2.9116435086	-1.0814038837	-2.2686316108
C20	2.9501435522	1.3660067272	-3.1687516991
O21	3.7294870534	0.7445928438	-3.8508395658
O22	2.2592067520	2.4281892294	-3.6236345489
C23	3.2007938195	0.3883373481	1.2407654012
O24	3.9672842099	-0.2992631190	0.6190012646
O25	3.0396421853	0.2961539362	2.5743356522
C26	2.5275667791	2.7739395837	-4.9815547411
H27	1.8913714033	3.6307799163	-5.2058318357
H28	2.2905063328	1.9367290141	-5.6443874650
H29	3.5818617197	3.0333727351	-5.1164636446

C30	3.7989547160	-0.7350564948	3.1973333267
H31	4.8698820304	-0.5787098271	3.0370167051
H32	3.5264367917	-1.7128589244	2.7896011572
H33	3.5621846538	-0.6860534513	4.2609810648
C34	-0.0566968682	2.4716515807	0.7228785008
C35	-1.9395778385	4.4555885860	0.0907514891
C36	-0.7156794239	3.1876889779	1.7259043365
C37	-0.3461036840	2.7815588957	-0.6125780267
C38	-1.2812567431	3.7626711262	-0.9195784035
C39	-1.6488999452	4.1705388986	1.4189069379
H40	-0.4938019799	2.9647679446	2.7702216173
H41	0.1551969003	2.2537055907	-1.4193570268
H42	-1.4986816020	3.9836742806	-1.9618213351
H43	-2.1497483766	4.7113247464	2.2184837138
H44	-2.6734675789	5.2185539788	-0.1577661394
C45	3.0523346821	3.2994988505	-0.9118402040
H46	3.9314641106	3.4910486308	-0.2809901290
H47	2.2604974920	3.9759483826	-0.5607997775
H48	3.2955562502	3.5752156205	-1.9371641415
H49	2.6702796530	2.4004786688	1.2835396399

8b

N1	0.2662000880	-0.0069175458	-0.7875658401

N2	-0.6394329637	0.8296189140	-1.4791152457
C3	-1.9673030257	0.5575604397	-1.2651504264
C4	-2.0101589363	-0.6036891685	-0.2903319251
H5	-2.7707917152	-1.3237726696	-0.6019053740
H6	-2.2870522873	-0.2231928738	0.7016199258
C7	-0.5836639122	-1.1388459623	-0.3580874115
H8	-0.5047539519	-1.9271068705	-1.1180591048
H9	-0.2108846531	-1.5411011561	0.5879991806
O10	-2.8890132328	1.1406744178	-1.7984975334
C11	-0.1680932341	1.7758823186	-2.4772739882
H12	-1.0204300818	1.9605884993	-3.1392090188
H13	0.1031219503	2.7329564961	-2.0022950461
C14	0.9623773923	0.6872326794	0.3120254426
H15	1.5379378020	-0.1035526131	0.8198731315
C16	1.9987986723	1.6936684593	-0.1658613524
C17	2.5866008916	1.8502018930	-1.3666125386
C18	2.2189138616	1.1321106534	-2.6128717432
C19	1.0056693987	1.1864312784	-3.1773536738
H20	0.8607825148	0.6698003671	-4.1241823527
C21	3.2474020609	0.3382691858	-3.3460426093
O22	3.1241982318	-0.0938052396	-4.4690368607
O23	4.3335374499	0.1083630610	-2.5855748935
C24	2.4867192220	2.4767964547	1.0125155563

O25	2.9631010037	1.9734110303	2.0027016800
O26	2.2682653069	3.7951192797	0.8796636537
C27	5.3341650816	-0.6979178596	-3.1991658746
H28	6.1356399033	-0.7952553297	-2.4661271331
H29	5.7060279017	-0.2266857219	-4.1139583775
H30	4.9309345042	-1.6813740119	-3.4582482734
C31	2.5621070346	4.5647228905	2.0438948204
H32	3.6102276291	4.4515589847	2.3356565468
H33	1.9297729273	4.2391521875	2.8768441934
H34	2.3466305646	5.6016759371	1.7841208257
C35	0.0188325886	1.2830331817	1.3389002930
C36	-1.8708802543	2.2272089370	3.1737263056
C37	-0.1769614169	0.6329159662	2.5576834692
C38	-0.7183479088	2.4382975093	1.0675451350
C39	-1.6638053997	2.9010377002	1.9752262810
C40	-1.1159183479	1.0972132194	3.4699201045
H41	0.4256539770	-0.2439842131	2.7952903973
H42	-0.5533856816	2.9833635970	0.1395877317
H43	-2.2423792524	3.7917719839	1.7429620635
H44	-1.2565159080	0.5783028461	4.4151423710
H45	-2.6127806724	2.5891768239	3.8815101262
C46	3.6616828256	2.8857091422	-1.5865998087
H47	4.1766355302	3.1742042884	-0.6681035864

H48	3.2197433392	3.7914685669	-2.0211522025
H49	4.4142779093	2.5199423295	-2.2902814678

S

N1	-0.2175335147	-0.3500545364	-0.2284600502
N2	-0.7462566069	0.2571943091	-1.4009786481
C3	-2.1370850888	0.3942976746	-1.3360599596
C4	-2.5839050336	-0.1088020834	0.0220278215
H5	-3.5202705984	-0.6598886395	-0.0969890741
H6	-2.7672470768	0.7345528585	0.6989508593
C7	-1.3936908878	-0.9630647130	0.4324738512
H8	-1.5041587948	-1.9878426675	0.0525958743
H9	-1.2271804652	-1.0202812802	1.5119582333
O10	-2.8283680370	0.7780614587	-2.2516658684
C11	-0.1968514395	-0.1903480167	-2.6682797940
H12	-0.1830704649	-1.2953726526	-2.6805770623
H13	-0.9285133207	0.1167112591	-3.4294773099
C14	0.4767346804	0.6173604669	0.6488102475
H15	0.7022813755	0.0206206487	1.5407085683
C16	1.8683834573	0.9914382695	0.0955373885
H17	2.2947863560	1.6364901879	0.8814213528
C18	1.9289303526	1.7851559499	-1.1943897732
C19	1.9637130835	3.1182331783	-1.1423324513

H20	2.0225828032	3.7183535625	-2.0468778348
H21	1.9383066798	3.6549686562	-0.1960277917
C22	2.0412601494	1.0903872417	-2.5042019195
C23	1.1459506543	0.2787447012	-3.0796528354
H24	1.4599097795	-0.1337999672	-4.0399677902
C25	3.3047485869	1.2501206643	-3.2971743721
O26	3.5125157045	0.7318132374	-4.3723245840
O27	4.2024306085	2.0431394283	-2.6938814362
C28	2.7972829091	-0.2124891692	0.0613063019
O29	3.5993578400	-0.4599899304	-0.8044123733
O30	2.6847287942	-0.9510189820	1.1806601466
C31	5.4291946104	2.1857461222	-3.3969539618
H32	6.0462305373	2.8555117290	-2.7961102595
H33	5.2624231524	2.6090402159	-4.3924563161
H34	5.9214343632	1.2155438591	-3.5142676980
C35	3.5726609099	-2.0624286603	1.2557285018
H36	4.6139365608	-1.7291445604	1.2149311587
H37	3.3978822486	-2.7526834148	0.4254132001
H38	3.3659848570	-2.5514748259	2.2084896496
C39	-0.3382819064	1.8000049851	1.1313833645
C40	-1.9446683704	3.8586418296	2.1664857147
C41	-0.6301579635	1.8726841321	2.4960647268
C42	-0.8563985734	2.7937954008	0.2916398916

C43	-1.6555070088	3.8072814572	0.8071381198
C44	-1.4234738583	2.8892265890	3.0143052469
H45	-0.2317041441	1.1090899588	3.1649390510
H46	-0.6499083483	2.7658329313	-0.7728103238
H47	-2.0596076752	4.5615358563	0.1359237128
H48	-1.6384592225	2.9196673051	4.0799358865
H49	-2.5736430245	4.6525111765	2.5625361438