Construction of All Carbon Quaternary Stereocenter by Organocatalytic Enantioselective α-Functionalization of α-Substituted β-Ketocarbonyls with Electron Deficient Vinylarenes

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Supporting Information

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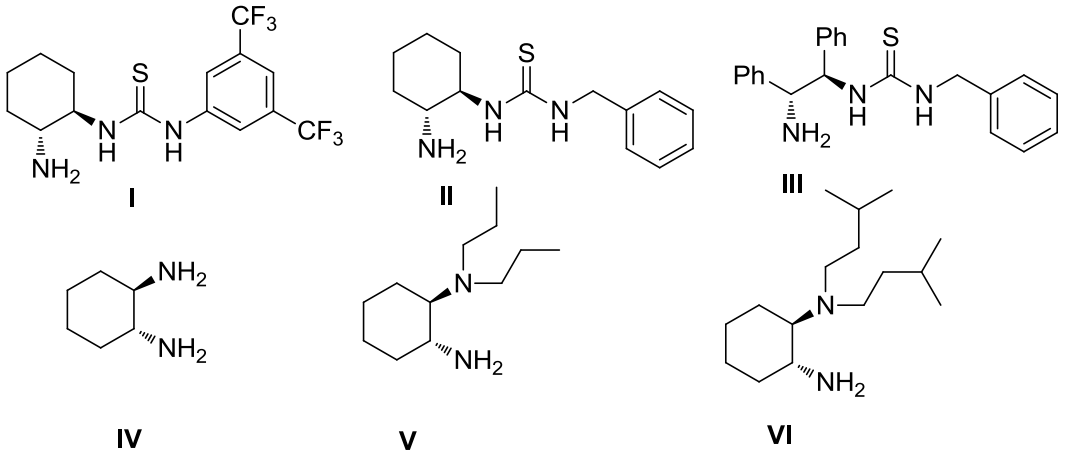
1. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification. Unless otherwise specified, all other reagents were purchased from Acros, Aldrich, Fisher, Adamas-beta Co. Ltd. or TCI and used without further purification. ^{1}H NMR spectra was recorded at 400 MHz, ^{13}C NMR spectra was recorded at 100 MHz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Chromatography was carried out with silica gel (200-300 mesh) using mixtures of petroleum ether (b.p. 60-80 ^{o}C) and ethyl acetate as eluents. The enantiomeric excess of products was detected on HPLC (Shimadzu LC-LabSolutions). Mass Spectra were obtained from East China University of Science and Technology mass spectral facility. Melting point (mp) was recorded on X4 microscopic instrument.

2. Procedure for the synthesis of catalysts

Optically pure amine **IV** is commercially available. Amines **I**[1], **II**[1], **III**[2], **V**[3] and **VI**[4] are known in the literature and were prepared according to the literature methods.

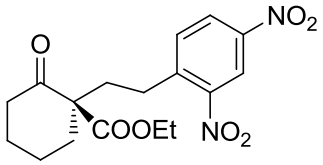


3. Procedure for the synthesis of compound 2

Compound **2** were prepared according to the literature methods.[5]

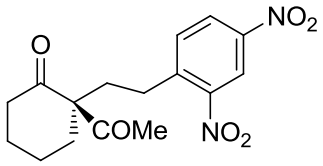
4. General procedure for the synthesis of compound 3

To a solution of vinylarenes (0.2 mmol) and ketones (1.5 mmol) in dioxane (600 μL) was added the catalyst (0.06 mmol) and benzoic acid (0.06 mmol). The resulting solution was stirred at 23 °C or 50 °C for a defined time (2-15 d). The crude reaction mixture was directly purified by column chromatography (petroleum ether/ethyl acetate 8/1 v/v) on silica gel to give the corresponding product.

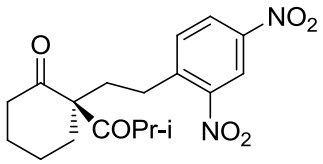


(*R*)-Ethyl 1-(2,4-dinitrophenethyl)-2-oxocyclohexanecarboxylate (3a): The title compound was prepared according to the general procedure, as described above in 80% yield as white solid; mp 60-62 °C. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.77 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.86-3.01 (m, 2H), 2.47-2.62 (m, 3H), 2.05-2.19 (m, 2H), 1.91-1.98 (m, 1H), 1.52-1.82 (m, 5H), 1.33 (t, *J* = 7.2 Hz, 2H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 207.9, 171.5, 148.9, 146.4, 144.2, 133.8, 127.2, 120.3, 61.77, 60.6, 41.1, 36.3, 35.5, 28.5, 27.6, 22.6, 14.2; 146.6, 144.2, 139.6, 137.8, 136.2, 131.5, 127.8, 126.0, 121.0, 114.4, 55.2, 33.4, 32.5; HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2O_7$ $(M+Na)^+$ 387.1168, found 387.1169; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 22.27 min, t_{major} =

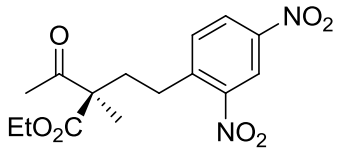
19.17 min, ee = 92%.



(*R*)-2-Acetyl-2-(2,4-dinitrophenethyl)cyclohexanone (3b): The title compound was prepared according to the general procedure, as described above in 70% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.78 (d, J = 2.0 Hz, 1H), 8.39 (dd, J_1 = 2.0Hz, J_2 = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 2.74-2.85 (m, 2H), 2.49-2.56 (m, 2H), 2.39-2.49 (m, 1H), 2.23 (s, 3H), 2.12-2.20 (m, 1H), 1.96-2.04 (m, 2H), 1.60-1.85 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 209.9, 207.1, 148.8, 146.5, 144.1, 134.0, 127.3, 120.4, 67.2, 41.4, 34.9, 34.7, 28.6, 27.1, 26.2, 22.2; HRMS (ESI) m/z calcd for $C_{16}H_{18}N_2O_6$ $(M+Na)^+$ 357.1063, found 357.1066; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 29.65 min, t_{major} = 27.26 min, ee = 80%.

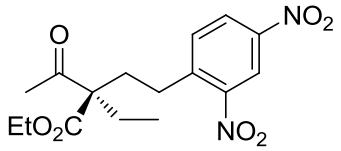


(*R*)-2-(2,4-dinitrophenethyl)-2-isobutyrylcyclohexanone (3c): The title compound was prepared according to the general procedure, as described above in 60% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.77 (d, J = 2.0 Hz, 1H), 8.39 (dd, J_1 = 3.0Hz, J_2 = 8.4 Hz, 1H), 7.75 (d, J = 8.4.Hz, 1H), 2.80-2.96 (m, 2H), 2.68-2.75 (m, 1H), 2.50-2.58 (m, 2H), 2.39-2.47 (m, 1H), 2.06-2.20 (m, 2H), 1.93-2.00 (m, 1H), 1.73-1.90 (m, 3H), 1.63-1.69 (m, 1H), 1.17 (s, 3H), 1.07 (s, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 213.7, 210.3, 148.9, 146.5, 144.2, 134.0, 127.3, 120.3, 67.8, 41.5, 36.8, 34.1, 33.5, 28.5, 26.7, 21.8, 20.9, 20.4; HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_6$ $(M+Na)^+$ 385.1376, found 385.1378; HPLC (Chiralpak OD-3, *i*-PrOH/hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 31.32 min, t_{major} = 36.39 min, ee = 91%.

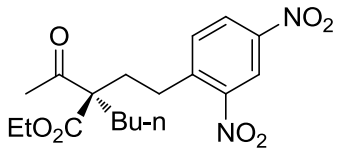


(*R*)-Ethyl 2-acetyl-4-(2,4-dinitrophenyl)-2-methylbutanoate (3d): The title compound was prepared according to the general procedure, as described above in 77% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.78 (s, 1H), 8.39 (d, J = 8 Hz, 1H), 7.65 (d, J = 8 Hz, 1H), 4.27 (q, J = 8 Hz, 2H), 2.84-2.98 (m, 2H), 2.06-2.22 (m, 5H), 1.49 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H);

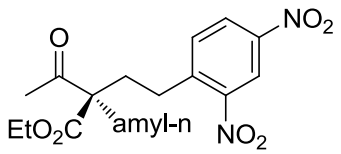
^{13}CNMR ($CDCl_3$, 100 MHz): δ 204.9, 172.2, 148.9, 146.5, 143.8, 133.7, 127.2, 120.4, 61.8, 59.3, 35.6, 28.5, 26.1, 19.0, 14.0; HRMS (ESI) m/z calcd for $C_{15}H_{18}N_2O_7$ $(M+Na)^+$ 361.1012, found 361.1008; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 26.33 min , t_{major} = 24.12 min, ee = 86%.



(*R*)-Ethyl 2-acetyl-4-(2,4-dinitrophenyl)-2-ethylbutanoate (3e): The title compound was prepared according to the general procedure, as described above in 65% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 2.4 Hz, 1H), 8.38 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 4.24-4.31 (m, 2H), 2.74-2.87 (m, 2H), 2.13-2.21 (m, 5H), 1.98-2.01 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.6 Hz, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 204.7, 171.8, 148.9, 146.5, 143.8, 133.6, 127.2, 120.4, 63.6, 61.7, 31.7, 28.3, 26.7, 24.7, 14.1, 8.2; HRMS (ESI) m/z calcd for $C_{16}H_{20}N_2O_7$ $(M+Na)^+$ 375.1168, found 375.1167; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 14.10 min, t_{major} = 13.11min, ee = 82%.

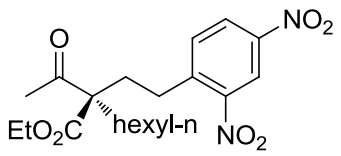


(*R*)-Ethyl 2-acetyl-2-(2,4-dinitrophenethyl)hexanoate (3f): The title compound was prepared according to the general procedure, as described above in 61% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 2.4 Hz, 1H), 8.38 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 4.23-4.31 (m, 2H), 2.75-2.88 (m, 2H), 2.11-2.23 (m, 5H), 1.90-2.04 (m, 2H), 1.28-1.40 (m, 5H), 1.16-1.22 (m, 1H), 1.08-1.12 (m, 1H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 204.8, 171.9, 48.9, 146.5, 143.8, 133.6, 127.2, 120.4, 63.2, 61.7, 32.2, 31.5, 28.4, 26.7, 25.9, 23.0, 14.1, 13.8; HRMS (ESI) m/z calcd for $C_{18}H_{24}N_2O_7$ $(M+Na)^+$ 403.1481, found 403.1473; HPLC (Chiralpak IC-3, *i*-PrOH/hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 123.64 min, t_{major} = 84.02 min, ee = 88%.

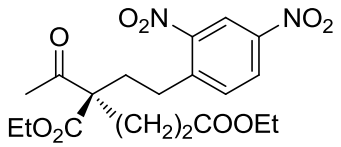


(*R*)-Ethyl 2-acetyl-2-(2,4-dinitrophenethyl)heptanoate (3g): The title compound was prepared according to the general procedure, as described above in 69% yield as yellow oil.. ^{1}HNMR

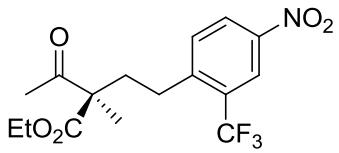
($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 2.4 Hz, 1H), 8.38 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 4.23-4.34 (m, 2H), 2.74-2.87 (m, 2H), 2.08-2.24 (m, 5H), 1.89-2.00 (m, 2H), 1.27-1.34 (m, 7H), 1.15-1.25 (m, 1H), 1.05-1.15 (m, 1H), 0.89 (t, *J* = 8.4 Hz, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 204.9, 171.9, 148.9, 146.5, 143.9, 33.6, 127.2, 120.4, 63.3, 61.7, 32.3, 32.0, 31.8, 28.4, 26.7, 23.4, 22.3, 14.1, 13.9; HRMS (ESI) m/z calcd for $C_{19}H_{26}N_2O_7$ $(M+Na)^+$ 417.1638, found 417.1642; HPLC (Chiralpak IC-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 81.27 min, t_{major} = 51.28 min, ee = 88%.



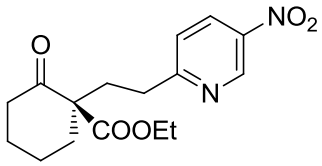
(*R*)-Ethyl 2-acetyl-2-(2,4-dinitrophenethyl)octanoate (3h): The title compound was prepared according to the general procedure, as described above in 67% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 2.4 Hz, 1H), 8.38 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 4.23-4.31 (m, 2H), 2.75-2.88 (m, 2H), 2.09-2.23 (m, 5H), 1.89-2.05 (m, 2H), 1.25-1.36 (m, 9H), 1.15-1.24 (m, 1H), 1.04-1.15 (m, 1H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 204.9, 171.9, 148.9, 146.5, 143.9, 133.6, 127.2, 120.4, 63.2, 61.7, 32.2, 31.8, 31.5, 29.6, 28.4, 26.7, 23.7, 22.5, 14.1, 14.0; HRMS (ESI) m/z calcd for $C_{20}H_{28}N_2O_7$ $(M+Na)^+$ 431.1794, found 431.1794; HPLC (Chiralpak IC-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 96.36 min, t_{major} = 48.75 min, ee = 89%.



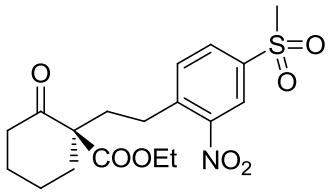
(*R*)-Diethyl 2-acetyl-2-(2,4-dinitrophenethyl)pentanedioate (3i): The title compound was prepared according to the general procedure, as described above in 83% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.80 (d, *J* = 2.4 Hz, 1H), 8.39 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.15 (*J* = 7.2 Hz, 2H), 2.78-2.91 (m, 1H), 2.14-2.40 (m, 9H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 204.2, 172.5, 171.3, 148.9, 146.6, 143.5, 133.8, 127.3, 120.5, 62.5, 62.0, 60.9, 32.4, 28.9, 28.3, 26.8, 26.5, 14.2, 14.1; HRMS (ESI) m/z calcd for $C_{19}H_{24}N_2O_9$ $(M+Na)^+$ 447.1380, found 447.1383; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 34.16 min, t_{major} = 44.72 min, ee = 81%.



(*R*)-Ethyl 2-acetyl-2-methyl-4-(4-nitro-2-(trifluoromethyl)phenyl)butanoate (3j): The title compound was prepared according to the general procedure, as described above in 83% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.50 (d, J = 2.4 Hz, 1H), 8.34 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.61 (d, J = 2.4 Hz, 1H), 4.22-4.29 (m, 2H), 2.74-2.86 (m, 2H), 2.13-2.20 (m, 3H), 1.97-2.04 (m, 1H), 1.47 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 204.9, 172.3, 148.2, 146.1, 132.9, 130.3, 129.9, 129.7, 129.3, 126.6, 124.6, 121.8, 121.8, 121.7, 121.7, 121.6, 61.7, 59.4, 36.7, 27.9, 26.1, 19.1, 14.1; HRMS (ESI) m/z calcd for $C_{16}H_{18}F_3NO_5$ $(M+Na)^+$ 384.1035, found 384.1033; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 7.37 min, t_{major} = 7.93 min, ee = 81%.



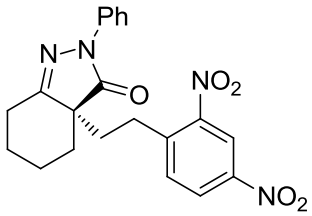
(*R*)-Ethyl 1-(2-(5-nitropyridin-2-yl)ethyl)-2-oxocyclohexanecarboxylate (3k): The title compound was prepared according to the general procedure, as described above in 63% yield as yellow oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 9.34 (s, 1H), 8.38 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 4.18-4.29 (m, 2H), 2.95-3.02 (m, 1H), 2.78-2.85 (m, 1H), 2.46-2.59 (m, 3H), 2.23-2.30 (m, 1H), 2.03-2.09 (m, 2H), 1.52-1.91 (m, 4H), 1.28-1.32 (m, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 207.8, 171.8, 168.4, 144.7, 142.7, 131.4, 123.1, 61.5, 60.5, 41.1, 36.5, 34.2, 33.5, 27.6, 22.6, 14.2; HRMS (ESI) m/z calcd for $C_{16}H_{20}N_2O_5$ $(M+Na)^+$ 342.1270, found 342.1265; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{minor} = 31.20 min, t_{major} = 21.87 min, ee = 95%.



(*R*)-Ethyl 1-(4-(methylsulfonyl)-2-nitrophenethyl)-2-oxocyclohexanecarboxylate (3l): The title compound was prepared according to the general procedure. The crude reaction mixture was directly purified by column chromatography (petroleum ether/ethyl acetate 2/1 v/v) on silica gel to give the corresponding product in 72% yield as white solid; mp59-60 °C. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.45 (d, J = 1.6 Hz, 1H), 8.08 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H),

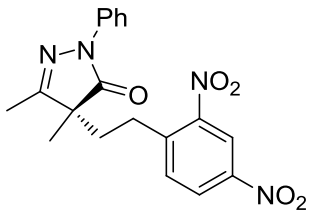
4.29 (q, *J* = 7.2 Hz, 2H), 3.11 (s, 3H), 2.84-3.00 (m, 2H), 2.46-2.62 (m, 3H), 2.11-2.19 (m, 1H), 2.03-2.11 (m, 1H), 1.90-1.98 (m, 1H), 1.77-1.87 (m, 1H), 1.63-1.76 (m, 2H), 1.50-1.58 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 207.8, 171.5, 149.2, 143.2, 140.1, 133.9, 131.2, 124.2, 61.7, 60.6, 44.4, 41.1, 36.3, 35.6, 28.4, 27.6, 22.5, 14.1; HRMS (ESI) m/z calcd for $C_{18}H_{23}NO_7S$ $(M+Na)^+$ 420.1093, found 420.1094; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 25/75, flow rate = 1.0 mL/min, λ= 254 nm): t_{minor} = 16.93 min, t_{major} = 14.39 min, ee = 93%.

5. The synthesis of compound 5



(*R*)-3a-(2,4-Dinitrophenethyl)-2-phenyl-4,5,6,7-tetrahydro-2H-indazol-3(3aH)-one (5a):

Phenylhydrazine (**4**, 88 mg, 0.82 mmol) and AcOH (59 mg, 0.98 mmol) were added to a solution of **3a** (300 mg, 0.82 mmol) in EtOH (2 mL) and the reaction mixture was stirred for 4 h at 23 ℃. The precipitated solid was filtered off and dried as a yellow solid (260.6 mg). TFA (98.2 mg, 0.86 mmol) was added to a solution of the yellow solid (260.6 mg) in CH_2Cl_2 (5 mL) and the solution was stirred overnight h at 23℃. After removal of all volatile materials in vacuo, the residue was purified by using chromatography (petroleum ether/ethyl acetate 4/1 v/v), to yield **5a** (166 mg, 0.41 mmol, 71 %) as a white solid; mp 127-128 ℃. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.79 (d, *J* = 2.0 Hz, 1H), 8.30 (dd, J_1 = 3.0 Hz, J_2 = 7.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 2.93-3.00 (m, 1H), 2.78-2.83 (m, 1H), 2.53-2.69 (m, 3H), 2.35-2.43 (m, 1H), 2.09-2.24 (m, 3H), 1.49-1.81 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 176.0, 166.5, 148.8, 146.7, 142.7, 138.0, 134.1, 128.9, 127.3, 125.2, 120.5, 118.6, 54.8, 35.4, 33.1, 28.8, 28.8, 27.2, 20.8; HRMS (ESI) m/z calcd for $C_{21}H_{20}N_4O_5$ $(M+Na)^+$ 431.1331, found 431.1323; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ= 254 nm): t_{minor} = 30.84 min, t_{major} = 45.10 , ee = 95%.



(*R*)-4-(2,4-Dinitrophenethyl)-3,4-dimethyl-1-phenyl-1H-pyrazol-5(4H)-one (5d):

Phenylhydrazine (**4**, 142 mg, 1.34 mmol) was added to a solution of **3d** (300 mg, 0.89 mmol) in

AcOH (2 mL) and the reaction mixture was refluxed for 1 h. After removal of AcOH in vacuo, the residue was purified by using chromatography (petroleum ether/ethyl acetate 4/1 v/v), to yield **5d** (305 mg, 0.80 mmol, 90 %) as a light yellow liquid. ^{1}HNMR ($CDCl_3$, 400 MHz): δ 8.78 (d, J = 2.4 Hz, 1H), 8.30 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 8.4 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 2.93-3.00 (m, 1H), 2.54-2.61 (m, 1H), 2.25 (s, 3H), 2.10-2.15 (m, 2H), 1.38 (s, 3H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 175.3, 163.4, 148.7, 146.6, 142.5, 137.8, 134.0, 128.9, 127.4, 125.2, 120.5, 118.6, 54.4, 35.9, 29.1, 20.73, 13.61; HRMS (ESI) m/z calcd for $C_{19}H_{18}N_4O_5$ $(M+Na)^+$ 405.1175, found 405.1181; HPLC (Chiralpak AD-3, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ= 254 nm): t_{minor} = 22.22 min, t_{major} = 25.96 , ee = 90%.

6. Determination of X-ray crystallographic structure

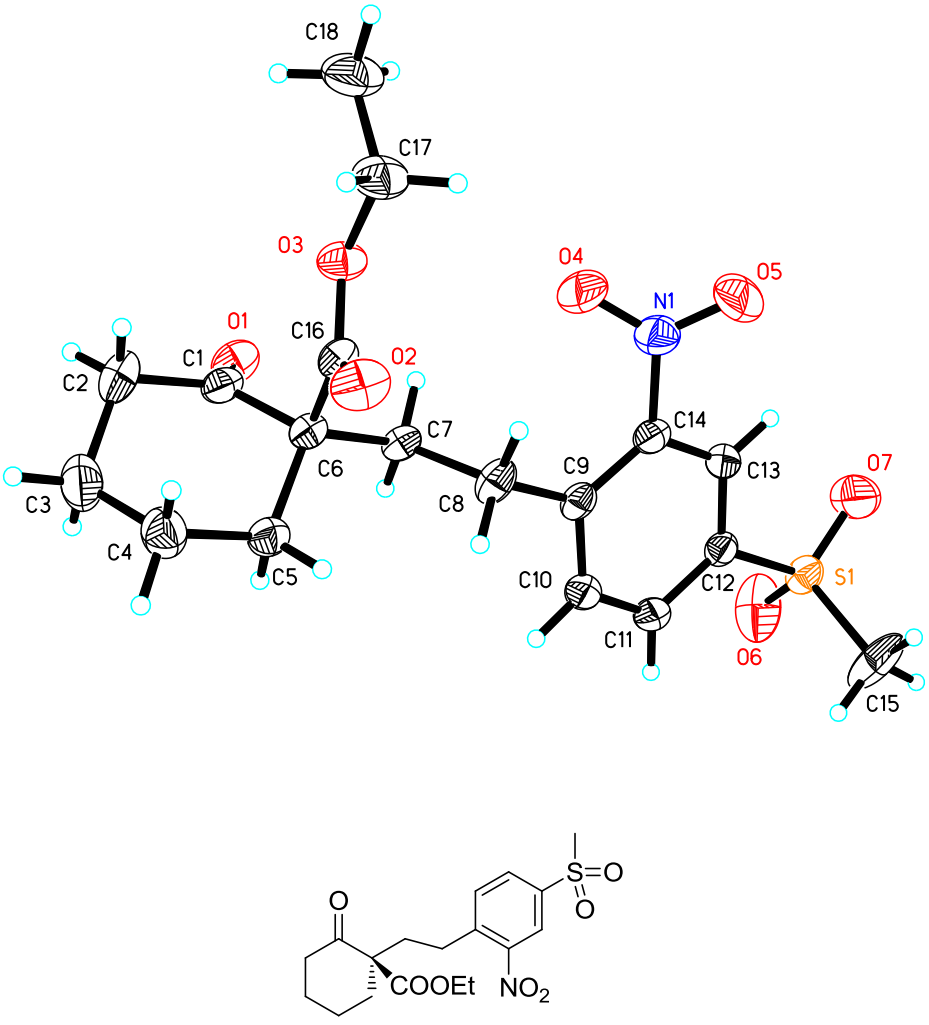


Fig S1. The X-ray crystallographic structure of compound **3l**.

Table 1. Crystal data and structure refinement for cd214673.

Identification code	cd214673	
Empirical formula	C18 H23 N O7 S	
Formula weight	397.43	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.5125(13) Å	α= 90°.
	b = 13.887(2) Å	β= 90.249(3)°.
	c = 14.680(2) Å	γ = 90°.
Volume	1939.2(5) $Å^3$	
Z	4	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	0.206 mm^{-1}	
F(000)	840	
Crystal size	0.211 x 0.176 x 0.145 mm^3	
Theta range for data collection	1.387 to 25.993°.	
Index ranges	-9<=h<=11, -17<=k<=17, -18<=l<=17	
Reflections collected	11823	
Independent reflections	7463 [R(int) = 0.0224]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6380	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7463 / 5 / 516	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1167	
R indices (all data)	R1 = 0.0523, wR2 = 0.1232	
Absolute structure parameter	-0.01(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.248 and -0.149 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for cd214673. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	3872(1)	1802(1)	4061(1)	53(1)
S(2)	3762(1)	6833(1)	950(1)	51(1)
N(1)	8371(4)	3235(3)	2737(3)	65(1)
N(2)	8315(4)	8269(3)	2200(3)	61(1)
O(1)	12278(3)	128(2)	1795(2)	65(1)
O(2)	10847(3)	2397(2)	-234(2)	68(1)
O(3)	12194(3)	2349(2)	1009(2)	54(1)
O(4)	9568(4)	3096(3)	2519(3)	92(1)
O(5)	7965(5)	3990(3)	3042(4)	106(1)
O(6)	3766(5)	876(3)	4447(3)	110(2)
O(7)	4148(4)	2553(4)	4669(3)	99(1)
O(9)	10857(4)	7341(3)	5245(2)	71(1)
O(10)	12141(3)	7346(2)	3980(2)	59(1)
O(11)	9514(3)	8132(3)	2440(3)	84(1)
O(12)	7934(4)	9007(3)	1841(4)	112(2)
O(13)	4161(4)	7451(3)	227(2)	87(1)
O(14)	3427(4)	5868(3)	735(3)	92(1)
O(8)	12176(6)	5179(5)	3115(4)	64(1)
O(8')	9031(8)	5221(8)	5119(7)	77(2)
C(1)	12142(4)	394(3)	1020(3)	49(1)
C(2)	13183(4)	164(4)	285(3)	70(1)
C(3)	12476(6)	-370(4)	-505(4)	81(1)
C(4)	11227(5)	208(4)	-863(3)	67(1)
C(5)	10199(4)	412(3)	-103(3)	52(1)
C(6)	10847(3)	969(3)	708(2)	42(1)
C(7)	9795(3)	1085(3)	1490(2)	42(1)
C(8)	8539(3)	1721(3)	1246(2)	53(1)
C(9)	7432(3)	1757(3)	1980(2)	42(1)
C(10)	6376(4)	1071(3)	1968(2)	49(1)
C(11)	5304(4)	1059(3)	2589(3)	49(1)
C(12)	5236(3)	1782(3)	3242(2)	43(1)
C(13)	6238(4)	2490(3)	3273(2)	45(1)

C(14)	7331(3)	2460(3)	2653(2)	44(1)
C(15)	2360(4)	2058(6)	3445(3)	102(2)
C(16)	11286(3)	1979(3)	416(2)	45(1)
C(17)	12614(5)	3345(3)	862(4)	68(1)
C(18)	13873(7)	3539(4)	1436(4)	88(2)
C(19)	10155(4)	5400(4)	5048(3)	54(1)
C(20)	11218(5)	5138(4)	5796(3)	79(1)
C(21)	12405(6)	4552(5)	5385(4)	89(2)
C(22)	13095(5)	5101(4)	4605(4)	77(1)
C(23)	12027(4)	5373(3)	3880(3)	53(1)
C(24)	10776(3)	5963(3)	4248(2)	43(1)
C(25)	9697(3)	6116(3)	3482(2)	42(1)
C(26)	8494(3)	6805(3)	3738(2)	51(1)
C(27)	7361(3)	6828(3)	3015(2)	42(1)
C(28)	6301(4)	6147(3)	3046(2)	49(1)
C(29)	5216(3)	6127(3)	2427(2)	49(1)
C(30)	5151(3)	6824(3)	1761(2)	44(1)
C(31)	6163(3)	7529(3)	1706(2)	44(1)
C(32)	7263(3)	7511(3)	2325(2)	43(1)
C(33)	2352(4)	7369(5)	1517(3)	74(1)
C(34)	11260(3)	6954(3)	4569(2)	47(1)
C(35)	12618(6)	8326(4)	4173(4)	80(2)
C(36)	13876(7)	8528(4)	3642(4)	88(2)

Table 3. Bond lengths [Å] and angles [°] for cd214673.

S(1)-O(7)	1.397(4)
S(1)-O(6)	1.409(4)
S(1)-C(15)	1.732(4)
S(1)-C(12)	1.773(3)
S(2)-O(14)	1.413(4)
S(2)-O(13)	1.418(4)
S(2)-C(33)	1.748(4)
S(2)-C(30)	1.775(3)
N(1)-O(4)	1.200(5)
N(1)-O(5)	1.204(5)
N(1)-C(14)	1.466(5)
N(2)-O(11)	1.207(4)
N(2)-O(12)	1.207(5)
N(2)-C(32)	1.465(5)
O(1)-C(1)	1.203(5)
O(2)-C(16)	1.191(4)
O(3)-C(16)	1.327(4)
O(3)-C(17)	1.456(5)
O(9)-C(34)	1.194(5)
O(10)-C(34)	1.324(5)
O(10)-C(35)	1.462(5)
O(8)-C(23)	1.164(7)
O(8')-C(19)	1.103(9)
C(1)-C(2)	1.503(6)
C(1)-C(6)	1.536(5)
C(2)-C(3)	1.529(7)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.525(7)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.513(6)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.546(5)
C(5)-H(5A)	0.9700

C(5)-H(5B)	0.9700
C(6)-C(16)	1.526(5)
C(6)-C(7)	1.535(5)
C(7)-C(8)	1.527(5)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.511(5)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.385(5)
C(9)-C(14)	1.392(5)
C(10)-C(11)	1.371(5)
C(10)-H(10)	0.9300
C(11)-C(12)	1.389(5)
C(11)-H(11)	0.9300
C(12)-C(13)	1.370(5)
C(13)-C(14)	1.386(5)
C(13)-H(13)	0.9300
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(17)-C(18)	1.485(7)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-C(24)	1.531(6)
C(19)-C(20)	1.534(6)
C(19)-H(19A)	0.96(3)
C(19)-H(19B)	0.94(3)
C(20)-C(21)	1.520(8)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(22)	1.526(8)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(23)	1.516(6)

C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-C(24)	1.544(5)
C(23)-H(23A)	0.95(3)
C(23)-H(23B)	0.97(3)
C(24)-C(34)	1.526(5)
C(24)-C(25)	1.535(5)
C(25)-C(26)	1.540(5)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-C(27)	1.509(4)
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
C(27)-C(28)	1.384(5)
C(27)-C(32)	1.390(5)
C(28)-C(29)	1.373(5)
C(28)-H(28)	0.9300
C(29)-C(30)	1.377(5)
C(29)-H(29)	0.9300
C(30)-C(31)	1.376(5)
C(31)-C(32)	1.382(5)
C(31)-H(31)	0.9300
C(33)-H(33A)	0.9600
C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600
C(35)-C(36)	1.458(8)
C(35)-H(35A)	0.9700
C(35)-H(35B)	0.9700
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600

O(7)-S(1)-O(6)	115.9(3)
O(7)-S(1)-C(15)	109.5(3)
O(6)-S(1)-C(15)	109.7(3)
O(7)-S(1)-C(12)	108.0(2)
O(6)-S(1)-C(12)	108.2(2)
C(15)-S(1)-C(12)	104.97(18)

O(14)-S(2)-O(13)	117.9(3)
O(14)-S(2)-C(33)	109.7(3)
O(13)-S(2)-C(33)	107.9(3)
O(14)-S(2)-C(30)	108.1(2)
O(13)-S(2)-C(30)	107.73(18)
C(33)-S(2)-C(30)	104.74(18)
O(4)-N(1)-O(5)	123.0(4)
O(4)-N(1)-C(14)	120.0(4)
O(5)-N(1)-C(14)	117.0(4)
O(11)-N(2)-O(12)	122.9(4)
O(11)-N(2)-C(32)	119.6(4)
O(12)-N(2)-C(32)	117.4(3)
C(16)-O(3)-C(17)	116.6(3)
C(34)-O(10)-C(35)	116.9(3)
O(1)-C(1)-C(2)	123.1(4)
O(1)-C(1)-C(6)	121.7(4)
C(2)-C(1)-C(6)	115.2(3)
C(1)-C(2)-C(3)	111.0(4)
C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2A)	109.4
C(1)-C(2)-H(2B)	109.4
C(3)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
C(4)-C(3)-C(2)	110.2(4)
C(4)-C(3)-H(3A)	109.6
C(2)-C(3)-H(3A)	109.6
C(4)-C(3)-H(3B)	109.6
C(2)-C(3)-H(3B)	109.6
H(3A)-C(3)-H(3B)	108.1
C(5)-C(4)-C(3)	110.4(4)
C(5)-C(4)-H(4A)	109.6
C(3)-C(4)-H(4A)	109.6
C(5)-C(4)-H(4B)	109.6
C(3)-C(4)-H(4B)	109.6
H(4A)-C(4)-H(4B)	108.1
C(4)-C(5)-C(6)	113.9(3)
C(4)-C(5)-H(5A)	108.8
C(6)-C(5)-H(5A)	108.8

C(4)-C(5)-H(5B)	108.8
C(6)-C(5)-H(5B)	108.8
H(5A)-C(5)-H(5B)	107.7
C(16)-C(6)-C(7)	107.1(3)
C(16)-C(6)-C(1)	110.0(3)
C(7)-C(6)-C(1)	110.9(3)
C(16)-C(6)-C(5)	110.7(3)
C(7)-C(6)-C(5)	111.7(3)
C(1)-C(6)-C(5)	106.6(3)
C(8)-C(7)-C(6)	113.4(3)
C(8)-C(7)-H(7A)	108.9
C(6)-C(7)-H(7A)	108.9
C(8)-C(7)-H(7B)	108.9
C(6)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.7
C(9)-C(8)-C(7)	113.5(3)
C(9)-C(8)-H(8A)	108.9
C(7)-C(8)-H(8A)	108.9
C(9)-C(8)-H(8B)	108.9
C(7)-C(8)-H(8B)	108.9
H(8A)-C(8)-H(8B)	107.7
C(10)-C(9)-C(14)	116.1(3)
C(10)-C(9)-C(8)	118.4(3)
C(14)-C(9)-C(8)	125.4(3)
C(11)-C(10)-C(9)	122.7(3)
C(11)-C(10)-H(10)	118.6
C(9)-C(10)-H(10)	118.6
C(10)-C(11)-C(12)	119.2(3)
C(10)-C(11)-H(11)	120.4
C(12)-C(11)-H(11)	120.4
C(13)-C(12)-C(11)	120.5(3)
C(13)-C(12)-S(1)	118.5(3)
C(11)-C(12)-S(1)	121.0(3)
C(12)-C(13)-C(14)	118.7(3)
C(12)-C(13)-H(13)	120.7
C(14)-C(13)-H(13)	120.7
C(13)-C(14)-C(9)	122.8(3)
C(13)-C(14)-N(1)	115.5(3)

C(9)-C(14)-N(1)	121.7(3)
S(1)-C(15)-H(15A)	109.5
S(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
S(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(2)-C(16)-O(3)	124.3(4)
O(2)-C(16)-C(6)	125.2(3)
O(3)-C(16)-C(6)	110.4(3)
O(3)-C(17)-C(18)	108.0(4)
O(3)-C(17)-H(17A)	110.1
C(18)-C(17)-H(17A)	110.1
O(3)-C(17)-H(17B)	110.1
C(18)-C(17)-H(17B)	110.1
H(17A)-C(17)-H(17B)	108.4
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(8')-C(19)-C(24)	124.4(6)
O(8')-C(19)-C(20)	121.1(6)
C(24)-C(19)-C(20)	114.5(4)
C(24)-C(19)-H(19A)	109(3)
C(20)-C(19)-H(19A)	108(3)
C(24)-C(19)-H(19B)	104(5)
C(20)-C(19)-H(19B)	110(4)
H(19A)-C(19)-H(19B)	111(6)
C(21)-C(20)-C(19)	109.4(4)
C(21)-C(20)-H(20A)	109.8
C(19)-C(20)-H(20A)	109.8
C(21)-C(20)-H(20B)	109.8
C(19)-C(20)-H(20B)	109.8
H(20A)-C(20)-H(20B)	108.2
C(20)-C(21)-C(22)	110.6(5)
C(20)-C(21)-H(21A)	109.5

C(22)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
C(22)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	108.1
C(23)-C(22)-C(21)	111.3(4)
C(23)-C(22)-H(22A)	109.4
C(21)-C(22)-H(22A)	109.4
C(23)-C(22)-H(22B)	109.4
C(21)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0
O(8)-C(23)-C(22)	122.4(4)
O(8)-C(23)-C(24)	123.9(4)
C(22)-C(23)-C(24)	113.7(4)
C(22)-C(23)-H(23A)	110(4)
C(24)-C(23)-H(23A)	106(4)
C(22)-C(23)-H(23B)	113(10)
C(24)-C(23)-H(23B)	114(10)
H(23A)-C(23)-H(23B)	99(10)
C(34)-C(24)-C(19)	109.9(3)
C(34)-C(24)-C(25)	107.5(3)
C(19)-C(24)-C(25)	111.9(3)
C(34)-C(24)-C(23)	110.7(3)
C(19)-C(24)-C(23)	107.4(3)
C(25)-C(24)-C(23)	109.3(3)
C(24)-C(25)-C(26)	113.8(3)
C(24)-C(25)-H(25A)	108.8
C(26)-C(25)-H(25A)	108.8
C(24)-C(25)-H(25B)	108.8
C(26)-C(25)-H(25B)	108.8
H(25A)-C(25)-H(25B)	107.7
C(27)-C(26)-C(25)	111.7(3)
C(27)-C(26)-H(26A)	109.3
C(25)-C(26)-H(26A)	109.3
C(27)-C(26)-H(26B)	109.3
C(25)-C(26)-H(26B)	109.3
H(26A)-C(26)-H(26B)	107.9
C(28)-C(27)-C(32)	116.3(3)
C(28)-C(27)-C(26)	118.7(3)

C(32)-C(27)-C(26)	124.9(3)
C(29)-C(28)-C(27)	122.5(3)
C(29)-C(28)-H(28)	118.7
C(27)-C(28)-H(28)	118.7
C(28)-C(29)-C(30)	119.2(3)
C(28)-C(29)-H(29)	120.4
C(30)-C(29)-H(29)	120.4
C(31)-C(30)-C(29)	120.8(3)
C(31)-C(30)-S(2)	118.4(3)
C(29)-C(30)-S(2)	120.8(3)
C(30)-C(31)-C(32)	118.5(3)
C(30)-C(31)-H(31)	120.8
C(32)-C(31)-H(31)	120.8
C(31)-C(32)-C(27)	122.6(3)
C(31)-C(32)-N(2)	114.9(3)
C(27)-C(32)-N(2)	122.5(3)
S(2)-C(33)-H(33A)	109.5
S(2)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
S(2)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
O(9)-C(34)-O(10)	124.4(4)
O(9)-C(34)-C(24)	124.4(4)
O(10)-C(34)-C(24)	111.2(3)
C(36)-C(35)-O(10)	109.2(4)
C(36)-C(35)-H(35A)	109.8
O(10)-C(35)-H(35A)	109.8
C(36)-C(35)-H(35B)	109.8
O(10)-C(35)-H(35B)	109.8
H(35A)-C(35)-H(35B)	108.3
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cd214673. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	44(1)	75(1)	41(1)	-3(1)	5(1)	2(1)
S(2)	39(1)	67(1)	47(1)	-3(1)	-10(1)	3(1)
N(1)	56(2)	52(2)	87(3)	3(2)	0(2)	-11(2)
N(2)	46(2)	49(2)	88(2)	-2(2)	-5(2)	-10(2)
O(1)	54(2)	71(2)	68(2)	18(2)	-14(1)	4(1)
O(2)	72(2)	70(2)	63(2)	25(2)	-14(1)	-5(2)
O(3)	56(2)	48(2)	58(2)	10(1)	-8(1)	-11(1)
O(4)	52(2)	75(2)	151(4)	-8(2)	12(2)	-20(2)
O(5)	90(3)	55(2)	173(4)	-26(3)	25(3)	-19(2)
O(6)	117(3)	105(3)	107(3)	40(3)	61(3)	23(2)
O(7)	74(2)	133(4)	91(3)	-53(3)	24(2)	-16(2)
O(9)	80(2)	74(2)	60(2)	-23(2)	6(2)	-6(2)
O(10)	57(2)	50(2)	71(2)	-15(1)	8(1)	-13(1)
O(11)	42(2)	78(2)	132(3)	4(2)	-12(2)	-15(2)
O(12)	78(2)	48(2)	209(5)	31(3)	-27(3)	-16(2)
O(13)	66(2)	138(3)	57(2)	27(2)	-12(1)	-6(2)
O(14)	80(2)	74(2)	120(3)	-19(2)	-52(2)	1(2)
O(8)	52(3)	78(4)	63(3)	-15(3)	17(2)	1(3)
O(8')	51(5)	86(7)	95(6)	25(5)	22(4)	2(5)
C(1)	38(2)	43(2)	66(2)	7(2)	-7(2)	-4(2)
C(2)	45(2)	81(3)	85(3)	6(3)	7(2)	16(2)
C(3)	76(3)	82(4)	84(3)	-15(3)	9(3)	20(3)
C(4)	70(3)	73(3)	58(2)	-7(2)	2(2)	8(2)
C(5)	44(2)	62(2)	51(2)	-5(2)	-7(2)	1(2)
C(6)	35(2)	45(2)	45(2)	4(2)	-2(1)	-1(1)
C(7)	35(2)	51(2)	40(2)	8(2)	-3(1)	-3(2)
C(8)	39(2)	74(3)	45(2)	13(2)	1(1)	8(2)
C(9)	35(2)	54(2)	39(2)	6(2)	-5(1)	6(2)
C(10)	44(2)	57(2)	46(2)	-11(2)	-2(1)	1(2)
C(11)	39(2)	51(2)	56(2)	-6(2)	1(2)	-7(2)
C(12)	34(2)	54(2)	41(2)	-4(2)	1(1)	4(2)
C(13)	43(2)	46(2)	47(2)	-6(2)	-3(1)	2(2)
C(14)	36(2)	45(2)	53(2)	5(2)	-4(1)	-2(2)

C(15)	37(2)	207(8)	62(3)	19(4)	5(2)	13(3)
C(16)	36(2)	52(2)	48(2)	5(2)	4(1)	-2(2)
C(17)	76(3)	46(2)	82(3)	13(2)	-9(2)	-15(2)
C(18)	93(4)	57(3)	113(4)	1(3)	-13(3)	-24(3)
C(19)	49(2)	60(3)	53(2)	4(2)	7(2)	7(2)
C(20)	76(3)	95(4)	65(3)	22(3)	-5(2)	10(3)
C(21)	74(3)	95(4)	96(4)	25(3)	-9(3)	27(3)
C(22)	43(2)	81(3)	108(4)	3(3)	0(2)	17(2)
C(23)	39(2)	46(2)	75(3)	-3(2)	10(2)	-1(2)
C(24)	32(2)	48(2)	49(2)	-2(2)	0(1)	-1(1)
C(25)	35(2)	50(2)	40(2)	-6(2)	1(1)	-5(2)
C(26)	40(2)	70(2)	43(2)	-9(2)	-5(1)	9(2)
C(27)	33(2)	55(2)	40(2)	-4(2)	2(1)	6(2)
C(28)	42(2)	60(2)	44(2)	11(2)	1(1)	-2(2)
C(29)	37(2)	54(2)	56(2)	6(2)	2(1)	-6(2)
C(30)	34(2)	55(2)	43(2)	-2(2)	-5(1)	3(2)
C(31)	40(2)	48(2)	44(2)	4(2)	2(1)	1(2)
C(32)	36(2)	46(2)	46(2)	-7(2)	2(1)	-3(2)
C(33)	44(2)	118(4)	59(2)	-12(3)	-8(2)	19(2)
C(34)	39(2)	51(2)	51(2)	-6(2)	-10(1)	2(2)
C(35)	84(4)	51(3)	104(4)	-21(3)	17(3)	-20(2)
C(36)	105(4)	62(3)	96(4)	0(3)	3(3)	-33(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cd214673.

	x	y	z	U(eq)
H(19A)	9750(60)	4810(30)	4820(30)	23(13)
H(19B)	9460(60)	5810(50)	5280(40)	50(20)
H(23A)	11630(60)	4810(30)	3610(40)	46(14)
H(23B)	12450(170)	5650(130)	3340(70)	110(70)
H(2A)	13931	-232	535	84
H(2B)	13598	756	61	84
H(3A)	13149	-468	-991	97
H(3B)	12158	-997	-299	97
H(4A)	11557	811	-1119	80
H(4B)	10759	-151	-1343	80
H(5A)	9827	-195	118	63
H(5B)	9419	781	-348	63
H(7A)	9454	454	1666	50
H(7B)	10278	1361	2011	50
H(8A)	8871	2370	1130	63
H(8B)	8113	1483	688	63
H(10)	6395	597	1520	59
H(11)	4631	574	2574	58
H(13)	6185	2982	3702	55
H(15A)	1557	2004	3835	153
H(15B)	2271	1611	2949	153
H(15C)	2415	2702	3209	153
H(17A)	11855	3776	1029	81
H(17B)	12834	3448	225	81
H(18A)	13620	3501	2067	132
H(18B)	14225	4171	1304	132
H(18C)	14586	3070	1307	132
H(20A)	11593	5721	6069	95
H(20B)	10757	4768	6269	95
H(21A)	12038	3945	5160	107
H(21B)	13102	4412	5851	107
H(22A)	13535	5679	4842	93

H(22B)	13822	4704	4336	93
H(25A)	9298	5497	3314	50
H(25B)	10177	6370	2952	50
H(26A)	8087	6602	4311	61
H(26B)	8869	7449	3820	61
H(28)	6325	5684	3504	59
H(29)	4533	5650	2458	59
H(31)	6109	8007	1264	53
H(33A)	1530	7347	1135	111
H(33B)	2578	8027	1653	111
H(33C)	2173	7027	2073	111
H(35A)	11884	8782	4016	95
H(35B)	12826	8392	4818	95
H(36A)	14563	8034	3751	132
H(36B)	14255	9141	3820	132
H(36C)	13638	8542	3006	132

Table 6. Torsion angles [°] for cd214673.

O(1)-C(1)-C(2)-C(3)	122.2(5)
C(6)-C(1)-C(2)-C(3)	-55.6(5)
C(1)-C(2)-C(3)-C(4)	54.9(6)
C(2)-C(3)-C(4)-C(5)	-56.4(6)
C(3)-C(4)-C(5)-C(6)	58.3(6)
O(1)-C(1)-C(6)-C(16)	115.2(4)
C(2)-C(1)-C(6)-C(16)	-66.9(4)
O(1)-C(1)-C(6)-C(7)	-3.0(5)
C(2)-C(1)-C(6)-C(7)	174.9(3)
O(1)-C(1)-C(6)-C(5)	-124.8(4)
C(2)-C(1)-C(6)-C(5)	53.1(4)
C(4)-C(5)-C(6)-C(16)	65.4(4)
C(4)-C(5)-C(6)-C(7)	-175.4(3)
C(4)-C(5)-C(6)-C(1)	-54.2(5)
C(16)-C(6)-C(7)-C(8)	55.3(4)
C(1)-C(6)-C(7)-C(8)	175.2(3)
C(5)-C(6)-C(7)-C(8)	-66.0(4)
C(6)-C(7)-C(8)-C(9)	174.3(3)
C(7)-C(8)-C(9)-C(10)	-88.6(4)
C(7)-C(8)-C(9)-C(14)	94.9(5)
C(14)-C(9)-C(10)-C(11)	-1.4(5)
C(8)-C(9)-C(10)-C(11)	-178.2(3)
C(9)-C(10)-C(11)-C(12)	2.2(6)
C(10)-C(11)-C(12)-C(13)	-0.8(5)
C(10)-C(11)-C(12)-S(1)	179.9(3)
O(7)-S(1)-C(12)-C(13)	-4.5(4)
O(6)-S(1)-C(12)-C(13)	-130.6(4)
C(15)-S(1)-C(12)-C(13)	112.3(4)
O(7)-S(1)-C(12)-C(11)	174.8(3)
O(6)-S(1)-C(12)-C(11)	48.6(4)
C(15)-S(1)-C(12)-C(11)	-68.5(4)
C(11)-C(12)-C(13)-C(14)	-1.2(5)
S(1)-C(12)-C(13)-C(14)	178.0(3)
C(12)-C(13)-C(14)-C(9)	2.1(5)
C(12)-C(13)-C(14)-N(1)	-179.1(3)
C(10)-C(9)-C(14)-C(13)	-0.8(5)

C(8)-C(9)-C(14)-C(13)	175.7(3)
C(10)-C(9)-C(14)-N(1)	-179.5(3)
C(8)-C(9)-C(14)-N(1)	-2.9(5)
O(4)-N(1)-C(14)-C(13)	150.6(4)
O(5)-N(1)-C(14)-C(13)	-28.4(6)
O(4)-N(1)-C(14)-C(9)	-30.7(6)
O(5)-N(1)-C(14)-C(9)	150.3(4)
C(17)-O(3)-C(16)-O(2)	2.9(6)
C(17)-O(3)-C(16)-C(6)	-174.8(3)
C(7)-C(6)-C(16)-O(2)	-101.2(4)
C(1)-C(6)-C(16)-O(2)	138.3(4)
C(5)-C(6)-C(16)-O(2)	20.8(5)
C(7)-C(6)-C(16)-O(3)	76.5(3)
C(1)-C(6)-C(16)-O(3)	-44.0(4)
C(5)-C(6)-C(16)-O(3)	-161.6(3)
C(16)-O(3)-C(17)-C(18)	-165.8(4)
O(8')-C(19)-C(20)-C(21)	125.4(9)
C(24)-C(19)-C(20)-C(21)	-57.7(6)
C(19)-C(20)-C(21)-C(22)	56.4(7)
C(20)-C(21)-C(22)-C(23)	-56.7(7)
C(21)-C(22)-C(23)-O(8)	-126.4(6)
C(21)-C(22)-C(23)-C(24)	56.0(6)
O(8')-C(19)-C(24)-C(34)	110.6(9)
C(20)-C(19)-C(24)-C(34)	-66.2(5)
O(8')-C(19)-C(24)-C(25)	-8.8(10)
C(20)-C(19)-C(24)-C(25)	174.4(4)
O(8')-C(19)-C(24)-C(23)	-128.8(9)
C(20)-C(19)-C(24)-C(23)	54.4(5)
O(8)-C(23)-C(24)-C(34)	-110.5(6)
C(22)-C(23)-C(24)-C(34)	67.1(4)
O(8)-C(23)-C(24)-C(19)	129.5(6)
C(22)-C(23)-C(24)-C(19)	-53.0(5)
O(8)-C(23)-C(24)-C(25)	7.8(7)
C(22)-C(23)-C(24)-C(25)	-174.6(4)
C(34)-C(24)-C(25)-C(26)	-52.3(4)
C(19)-C(24)-C(25)-C(26)	68.6(4)
C(23)-C(24)-C(25)-C(26)	-172.6(3)
C(24)-C(25)-C(26)-C(27)	-172.2(3)

C(25)-C(26)-C(27)-C(28)	86.3(4)
C(25)-C(26)-C(27)-C(32)	-96.2(4)
C(32)-C(27)-C(28)-C(29)	0.9(5)
C(26)-C(27)-C(28)-C(29)	178.7(3)
C(27)-C(28)-C(29)-C(30)	-1.7(6)
C(28)-C(29)-C(30)-C(31)	0.5(5)
C(28)-C(29)-C(30)-S(2)	-179.6(3)
O(14)-S(2)-C(30)-C(31)	143.4(3)
O(13)-S(2)-C(30)-C(31)	15.0(4)
C(33)-S(2)-C(30)-C(31)	-99.7(3)
O(14)-S(2)-C(30)-C(29)	-36.4(4)
O(13)-S(2)-C(30)-C(29)	-164.8(3)
C(33)-S(2)-C(30)-C(29)	80.5(4)
C(29)-C(30)-C(31)-C(32)	1.3(5)
S(2)-C(30)-C(31)-C(32)	-178.6(3)
C(30)-C(31)-C(32)-C(27)	-2.1(5)
C(30)-C(31)-C(32)-N(2)	178.2(3)
C(28)-C(27)-C(32)-C(31)	1.0(5)
C(26)-C(27)-C(32)-C(31)	-176.6(3)
C(28)-C(27)-C(32)-N(2)	-179.3(3)
C(26)-C(27)-C(32)-N(2)	3.1(5)
O(11)-N(2)-C(32)-C(31)	-152.2(4)
O(12)-N(2)-C(32)-C(31)	26.4(6)
O(11)-N(2)-C(32)-C(27)	28.1(6)
O(12)-N(2)-C(32)-C(27)	-153.3(5)
C(35)-O(10)-C(34)-O(9)	-1.3(6)
C(35)-O(10)-C(34)-C(24)	176.1(4)
C(19)-C(24)-C(34)-O(9)	-20.3(5)
C(25)-C(24)-C(34)-O(9)	101.8(4)
C(23)-C(24)-C(34)-O(9)	-138.8(4)
C(19)-C(24)-C(34)-O(10)	162.3(3)
C(25)-C(24)-C(34)-O(10)	-75.6(3)
C(23)-C(24)-C(34)-O(10)	43.8(4)
C(34)-O(10)-C(35)-C(36)	162.4(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd214673 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11)...O(1)#1	0.93	2.58	3.360(4)	141.2
C(18)-H(18B)...O(14)#2	0.96	2.61	3.420(7)	142.0
C(20)-H(20A)...O(9)	0.97	2.65	3.182(7)	115.1
C(29)-H(29)...O(8)#1	0.93	2.53	3.338(7)	145.4
C(33)-H(33A)...O(2)#3	0.96	2.62	3.572(5)	173.7
C(35)-H(35A)...O(8')#4	0.97	2.52	3.237(11)	130.3
C(36)-H(36B)...O(6)#5	0.96	2.62	3.471(8)	147.5
C(11)-H(11)...O(1)#1	0.93	2.58	3.360(4)	141.2
C(18)-H(18B)...O(14)#2	0.96	2.61	3.420(7)	142.0
C(20)-H(20A)...O(9)	0.97	2.65	3.182(7)	115.1
C(29)-H(29)...O(8)#1	0.93	2.53	3.338(7)	145.4
C(33)-H(33A)...O(2)#3	0.96	2.62	3.572(5)	173.7
C(35)-H(35A)...O(8')#4	0.97	2.52	3.237(11)	130.3
C(36)-H(36B)...O(6)#5	0.96	2.62	3.471(8)	147.5
C(11)-H(11)...O(1)#1	0.93	2.58	3.360(4)	141.2
C(18)-H(18B)...O(14)#2	0.96	2.61	3.420(7)	142.0
C(20)-H(20A)...O(9)	0.97	2.65	3.182(7)	115.1
C(29)-H(29)...O(8)#1	0.93	2.53	3.338(7)	145.4
C(33)-H(33A)...O(2)#3	0.96	2.62	3.572(5)	173.7
C(35)-H(35A)...O(8')#4	0.97	2.52	3.237(11)	130.3
C(36)-H(36B)...O(6)#5	0.96	2.62	3.471(8)	147.5
C(11)-H(11)...O(1)#1	0.93	2.58	3.360(4)	141.2
C(18)-H(18B)...O(14)#2	0.96	2.61	3.420(7)	142.0
C(20)-H(20A)...O(9)	0.97	2.65	3.182(7)	115.1
C(29)-H(29)...O(8)#1	0.93	2.53	3.338(7)	145.4
C(33)-H(33A)...O(2)#3	0.96	2.62	3.572(5)	173.7
C(35)-H(35A)...O(8')#4	0.97	2.52	3.237(11)	130.3
C(36)-H(36B)...O(6)#5	0.96	2.62	3.471(8)	147.5

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 x+1,y,z #3 -x+1,y+1/2,-z #4 -x+2,y+1/2,-z+1

#5 x+1,y+1,z

7. References

(1). X.-J. Zhang, S.-P. Liu, J.-H. Lao, G.-J. Du, M. Yan, A.S.C. Chan, *Tetrahedron: Asymmetry* 2009, **20**, 1451.

(2). T.-X. He, J.-Y. Qian, H.-L. Song, X.-Y. Wu, *Synlett.* 2009, **19**, 3195.

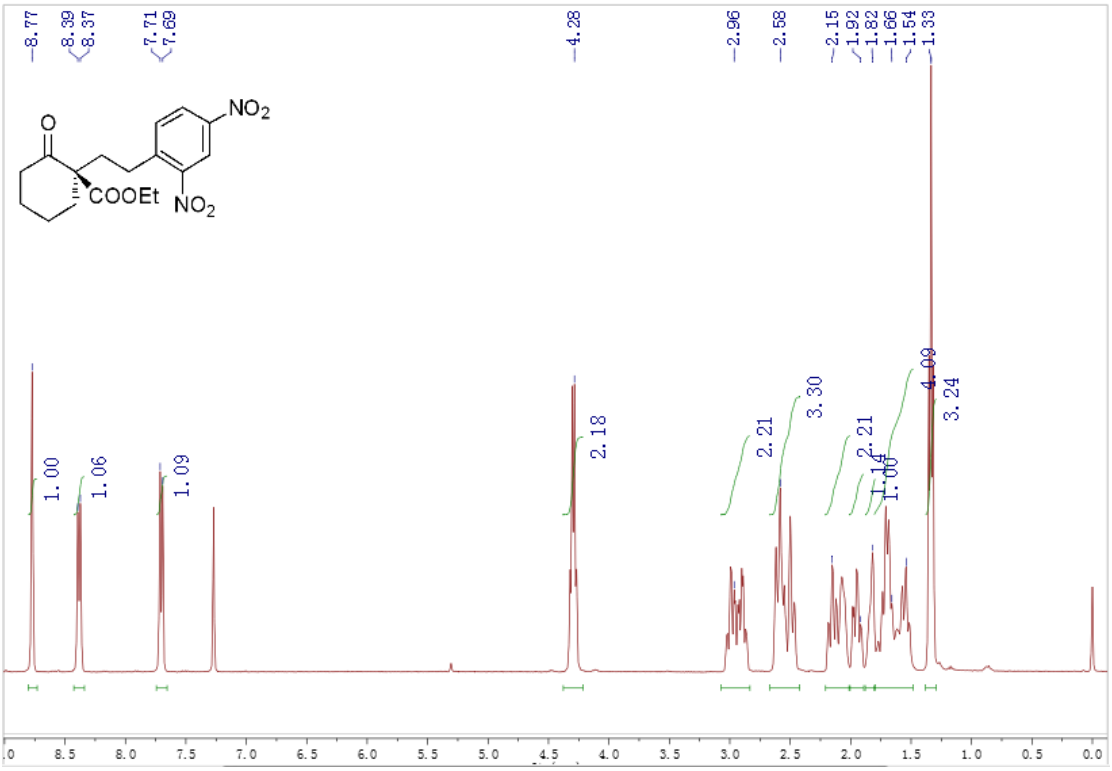
(3). S.-Z. Luo, H. Xu, J.-Y. Li, L. Zhang, J.-P. Cheng, *J. Am. Chem. Soc.* 2007, **129**, 3074.

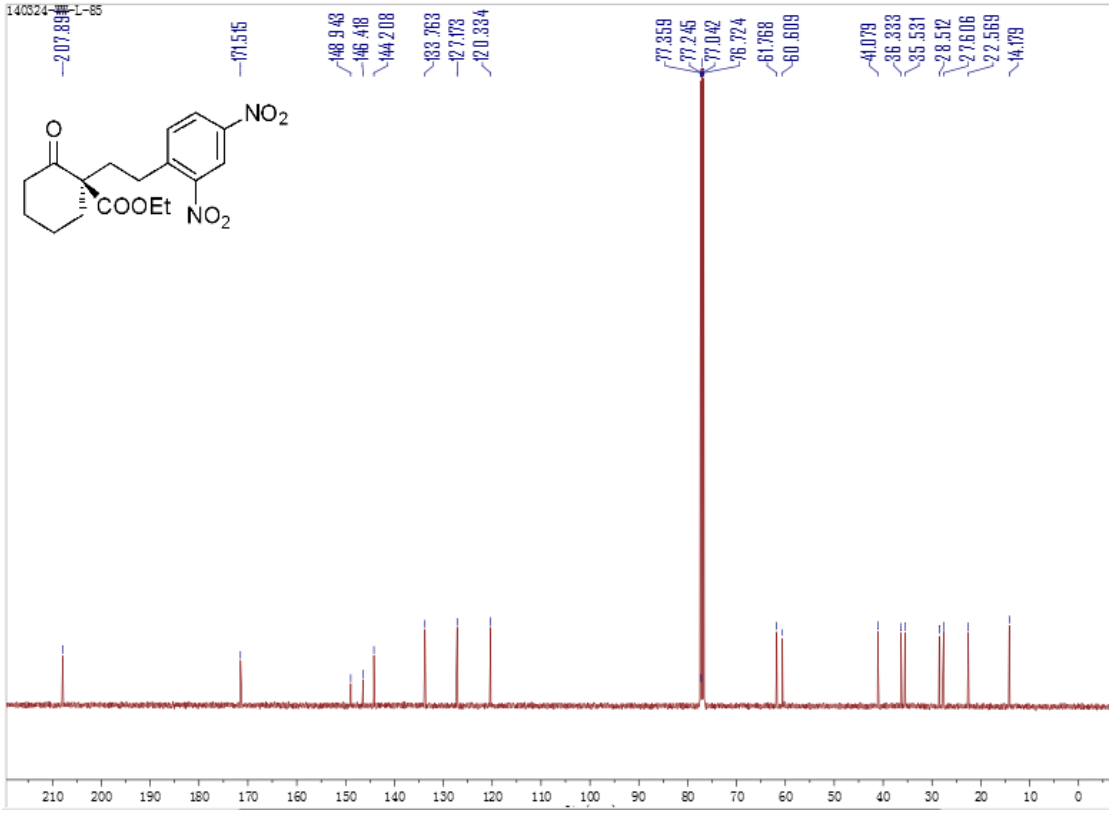
(4). S.-Z. Luo, Y.-P. Qiao, L. Zhang, J.-Y. Li, X. Li, J.-P. Cheng, *J. Org. Chem*. 2009, **74**, 9521.

(5). S.-N. Wang, X.-M. Li, H.-W. L. Liu, Xu, J.-C. Zhuang, J. Li, H. Li, W. Wang, *J. Am. Chem. Soc*. 2015, **137**, 2303.

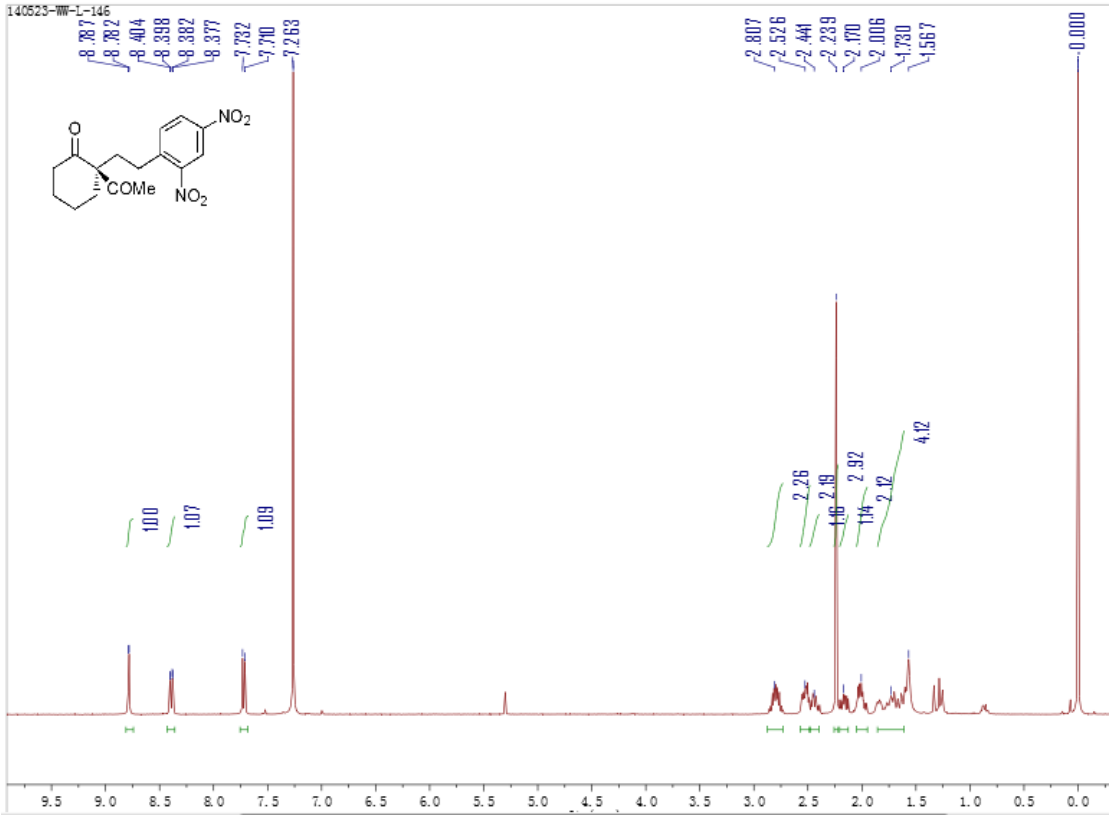
8. 1H and 13C-NMR spectra

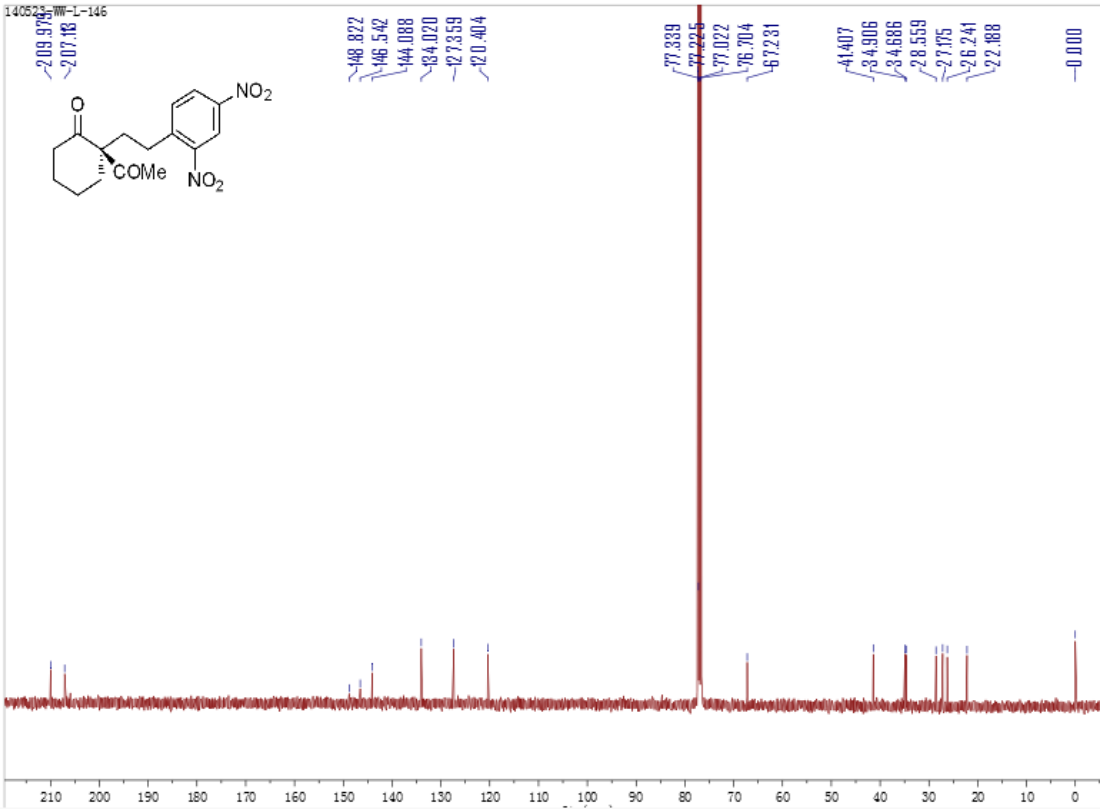
(*R*)-Ethyl 1-(2,4-dinitrophenethyl)-2-oxocyclohexanecarboxylate (3a)



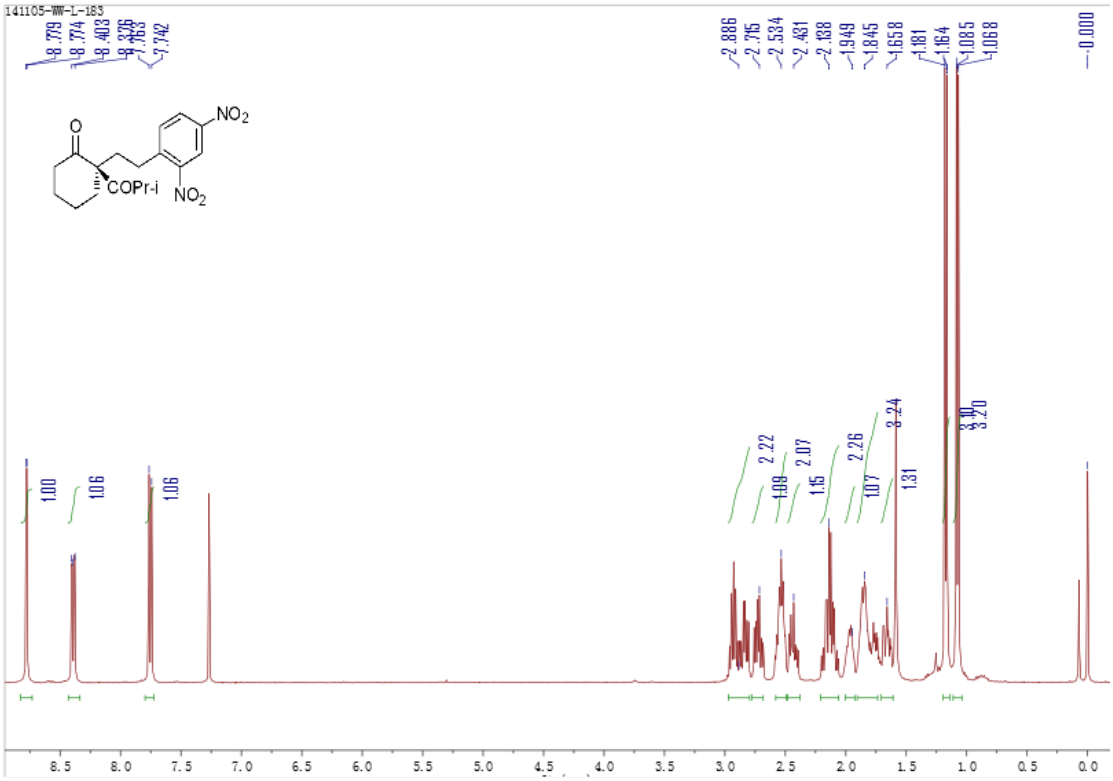


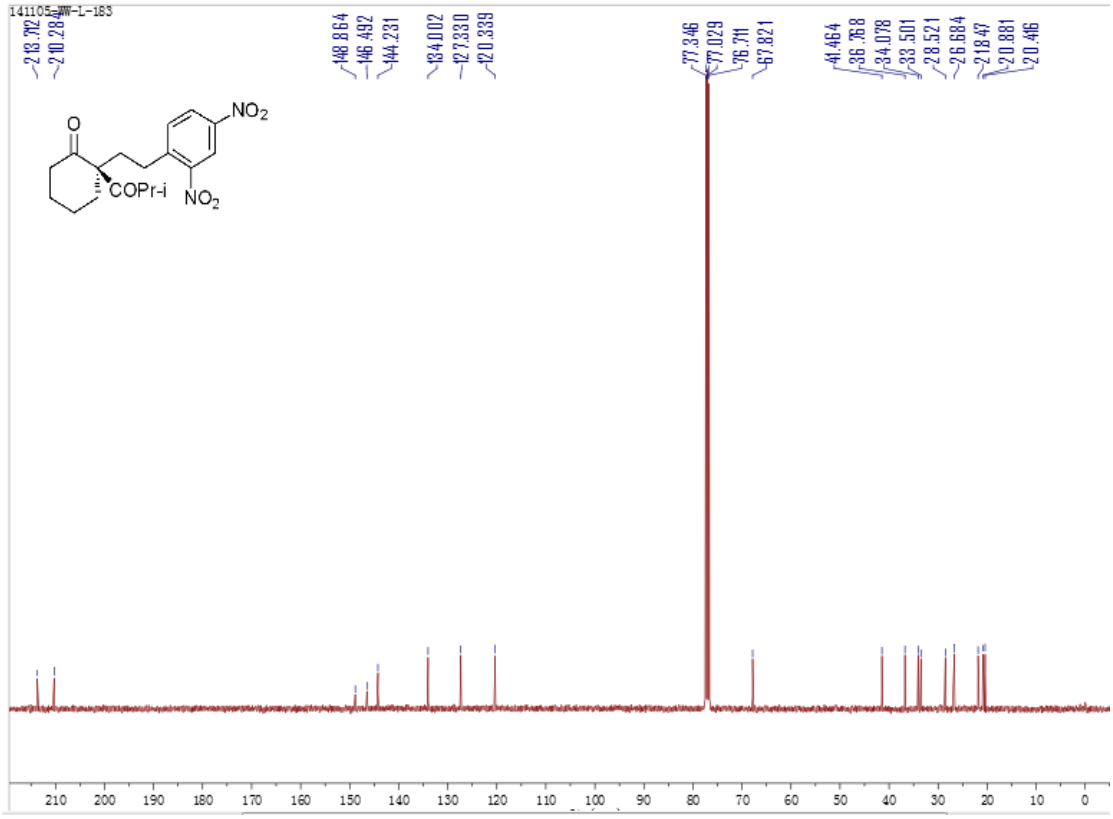
(*R*)-2-Acetyl-2-(2,4-dinitrophenethyl)cyclohexanone (3b)



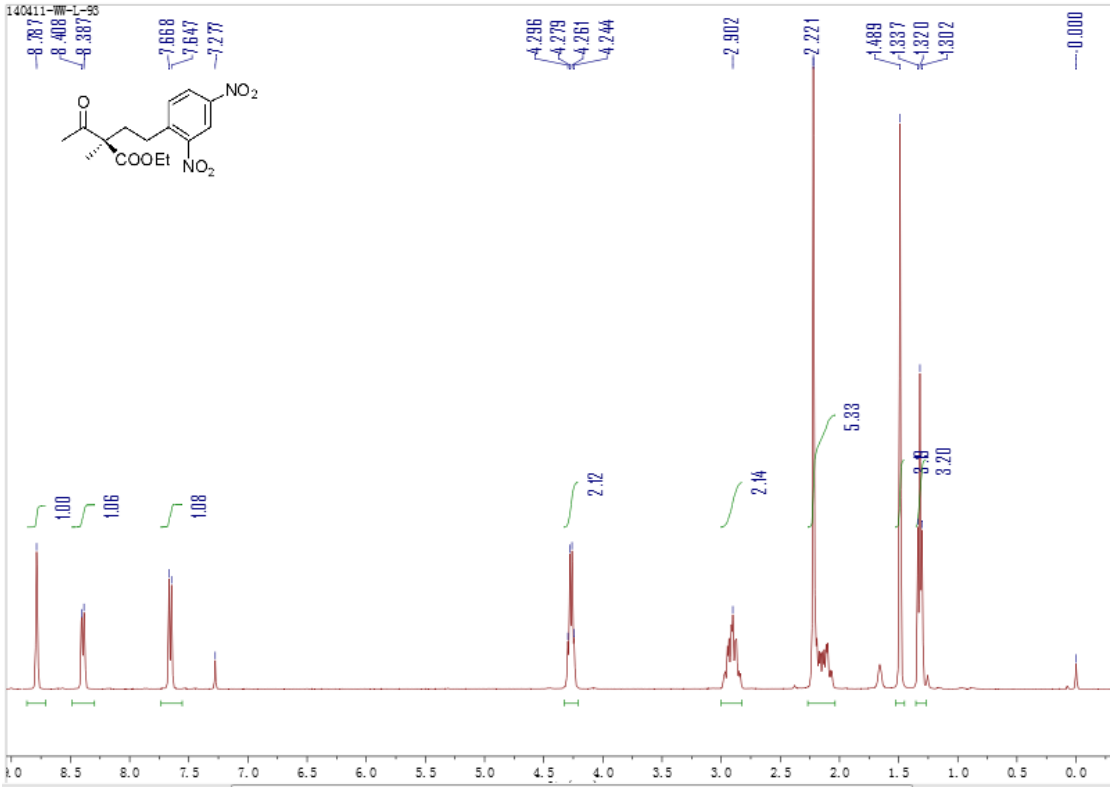


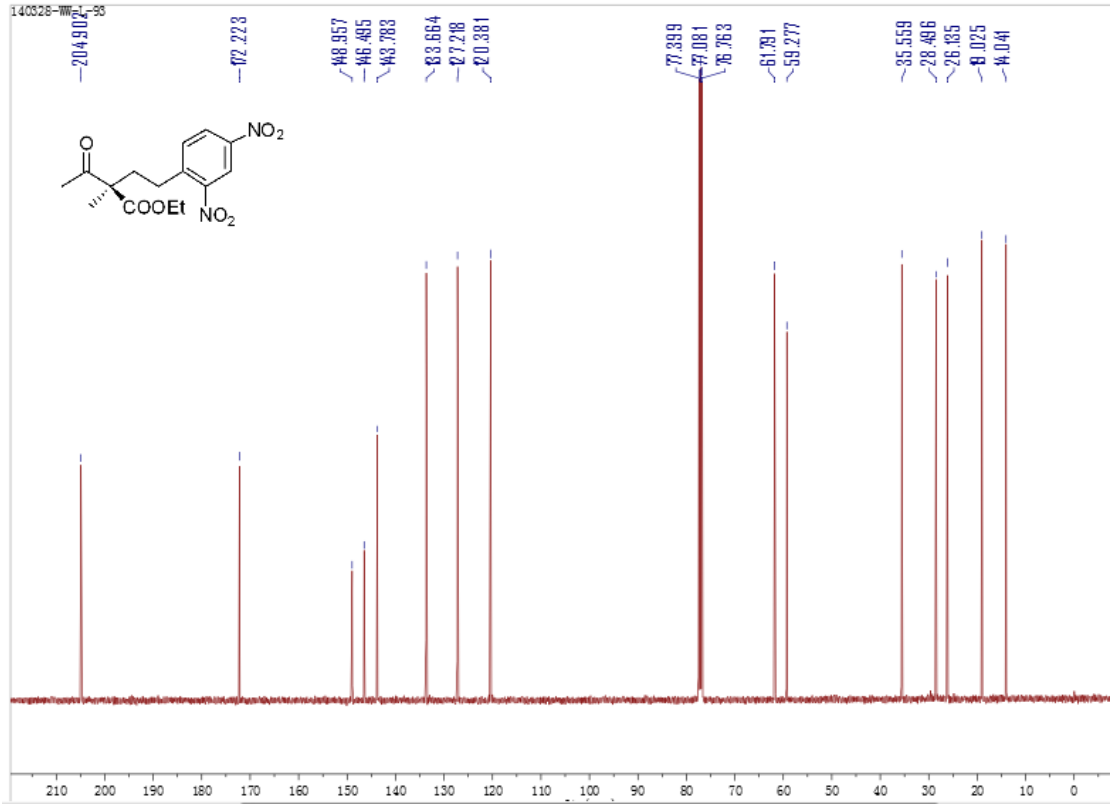
(*R*)-2-(2,4-Dinitrophenethyl)-2-isobutyrylcyclohexanone (3c)



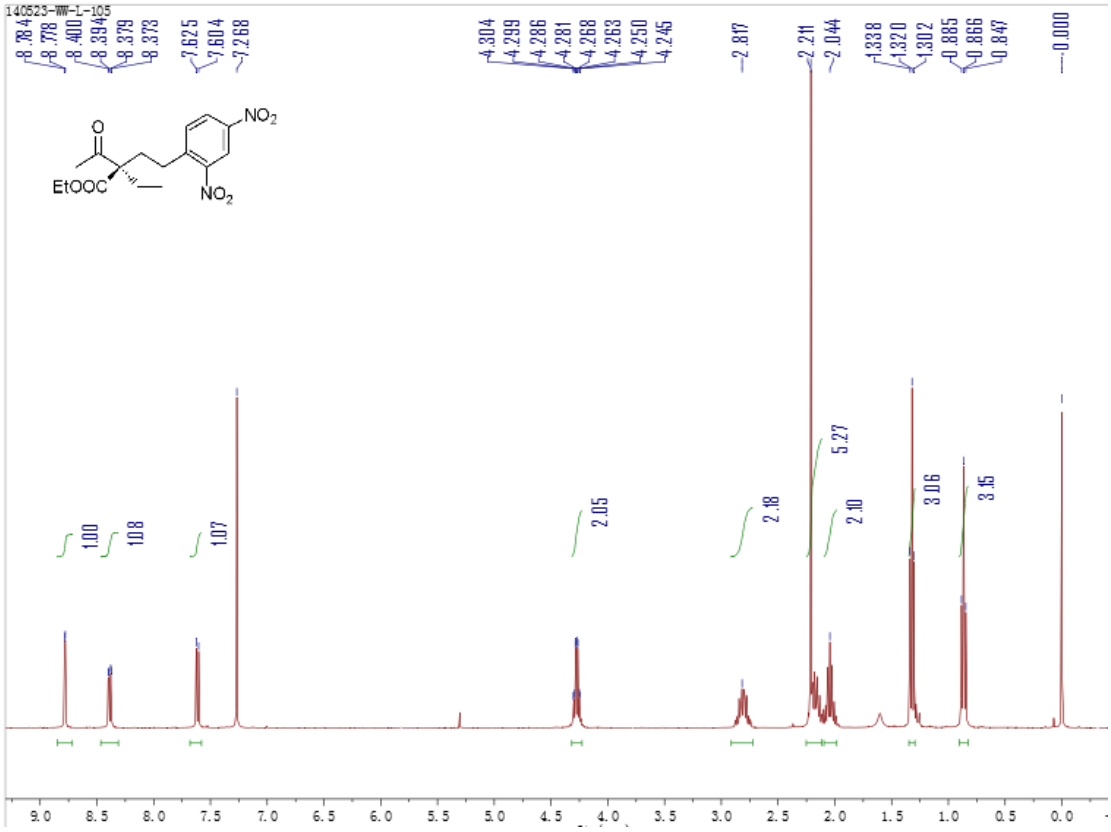


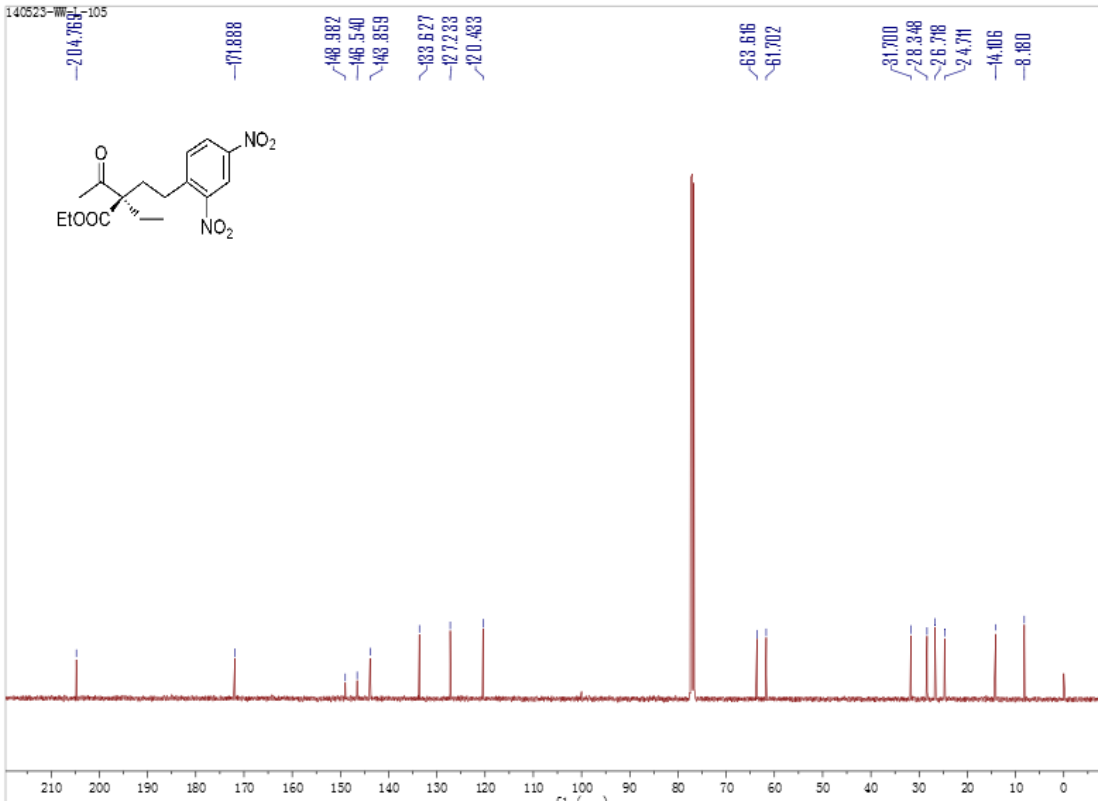
(*R*)-Ethyl 2-acetyl-4-(2,4-dinitrophenyl)-2-methylbutanoate (3d)



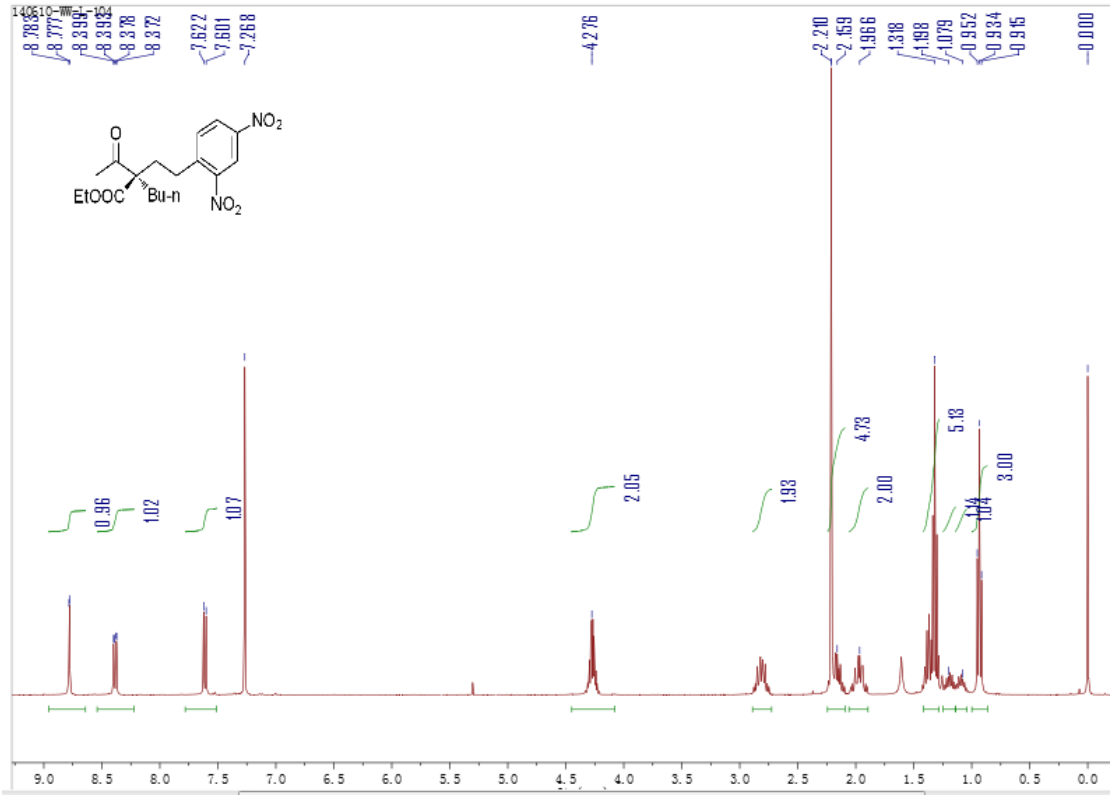


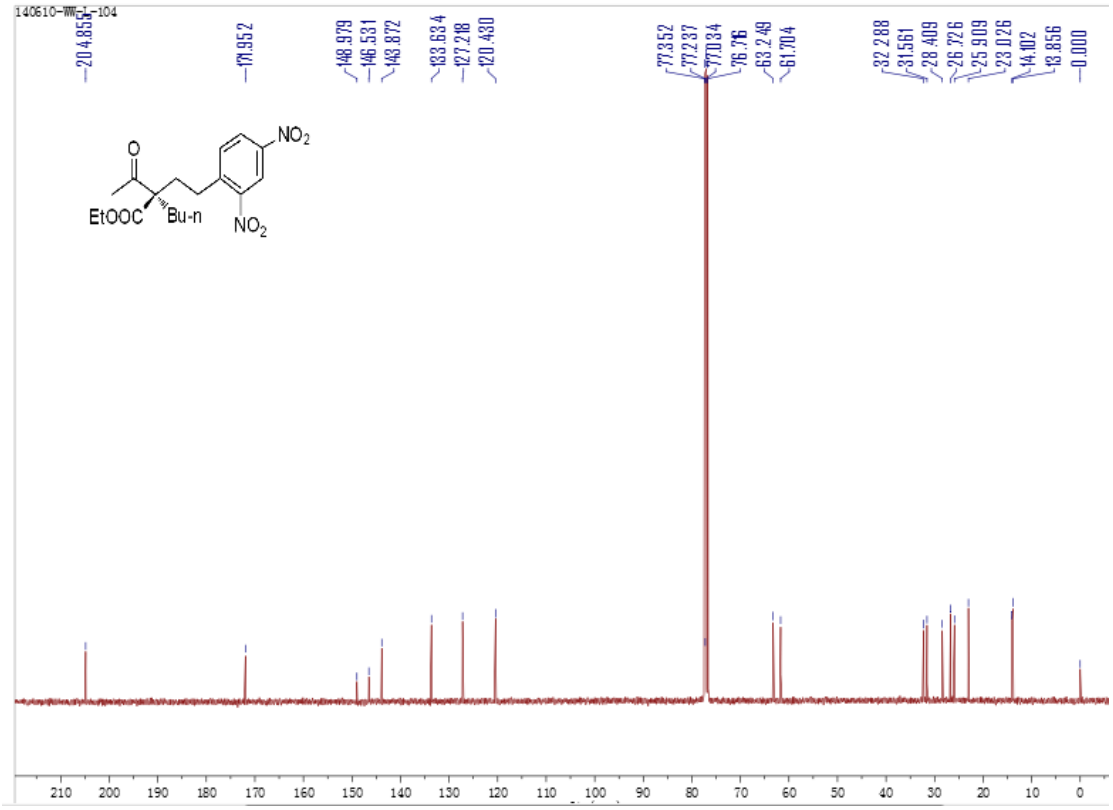
(*R*)-Ethyl 2-acetyl-4-(2,4-dinitrophenyl)-2-ethylbutanoate (3e)



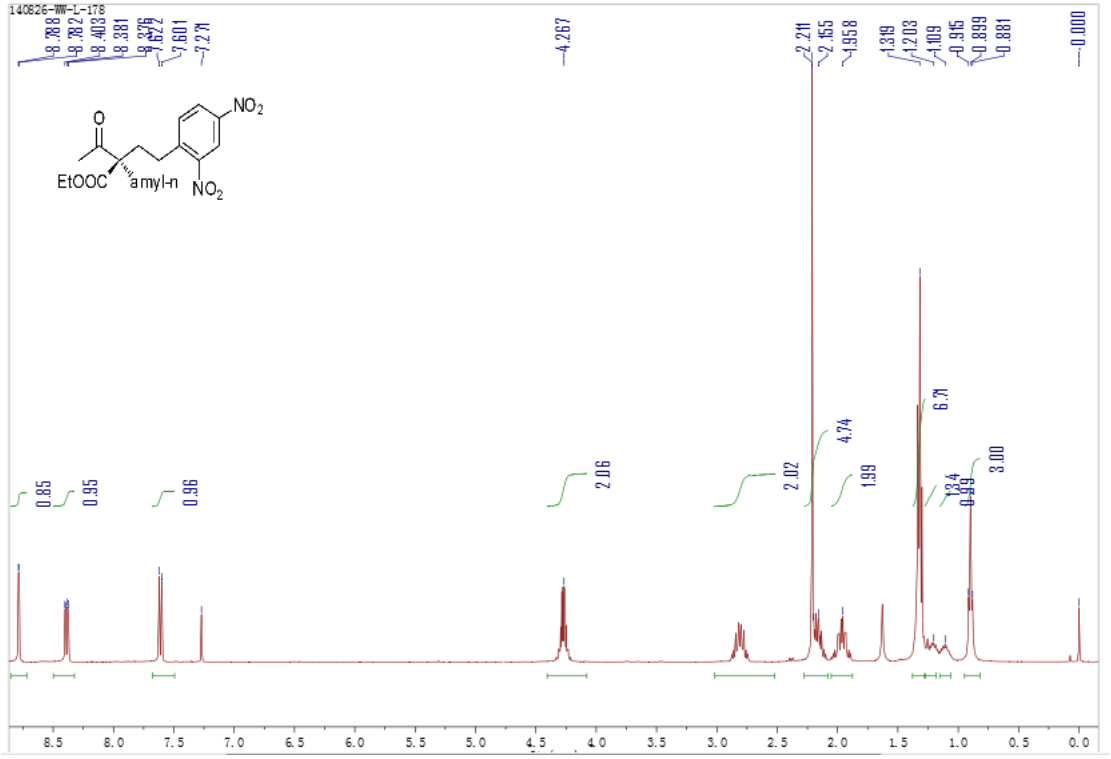


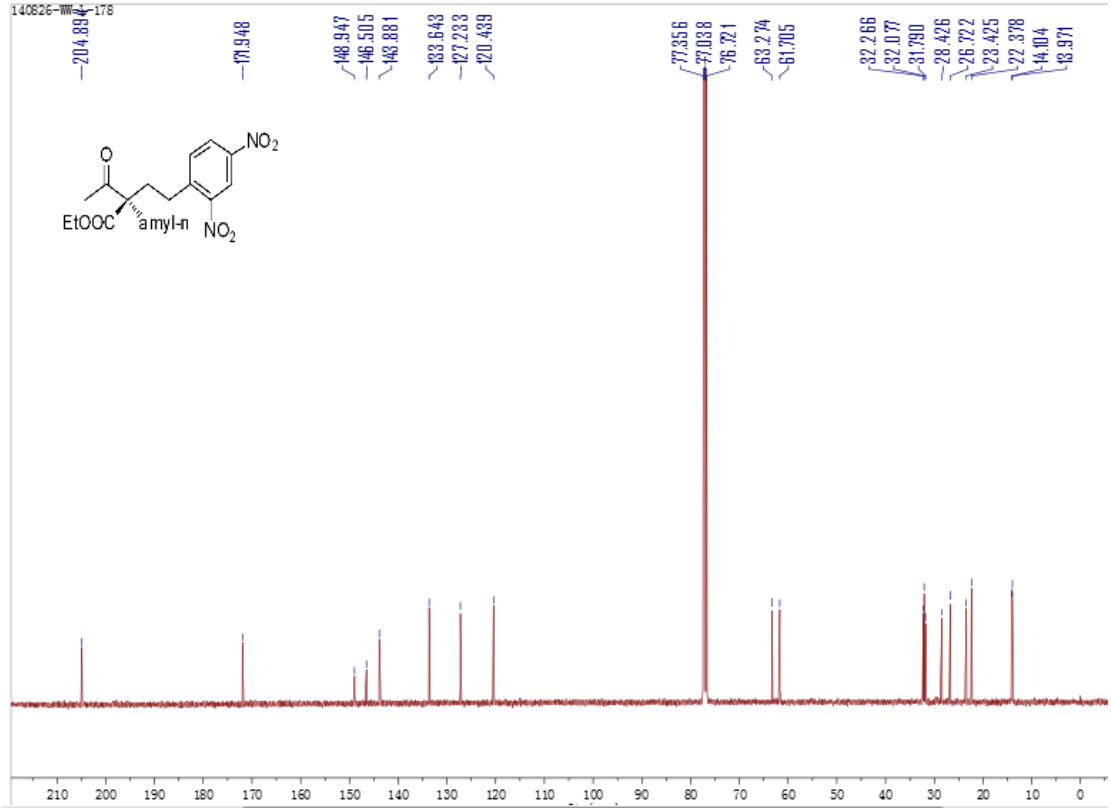
(*R*)-Ethyl 2-acetyl-2-(2,4-dinitrophenethyl)hexanoate (3f)



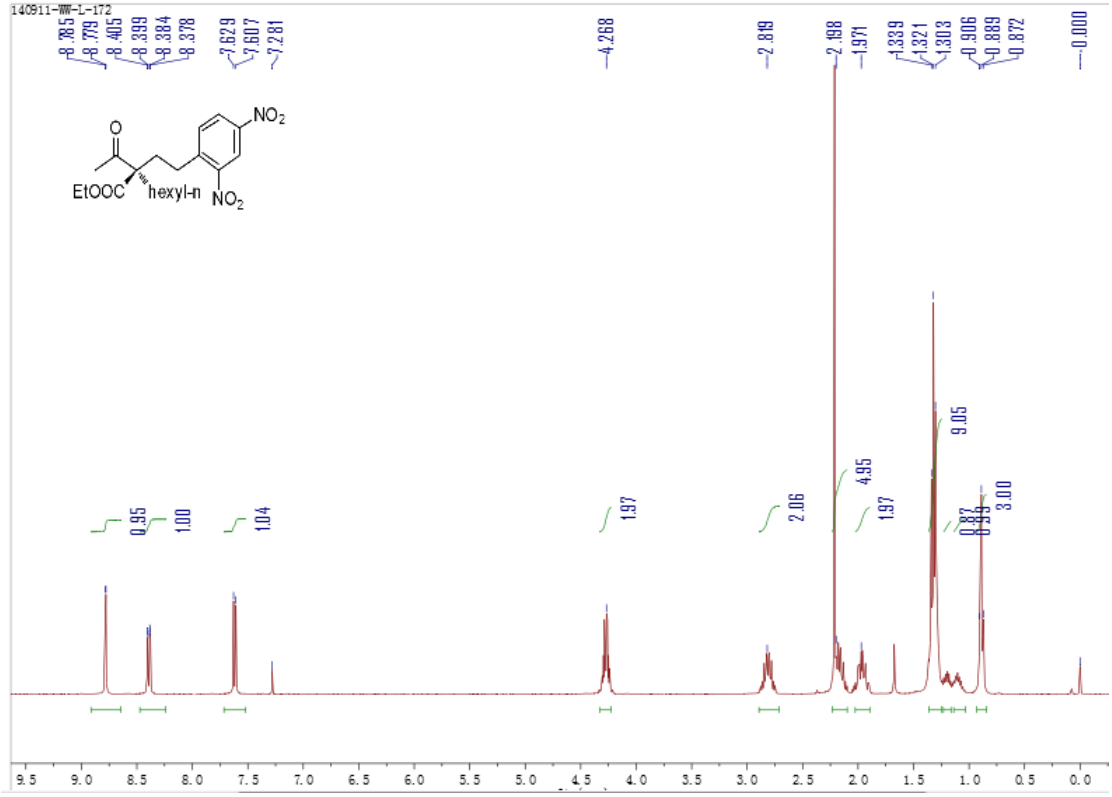


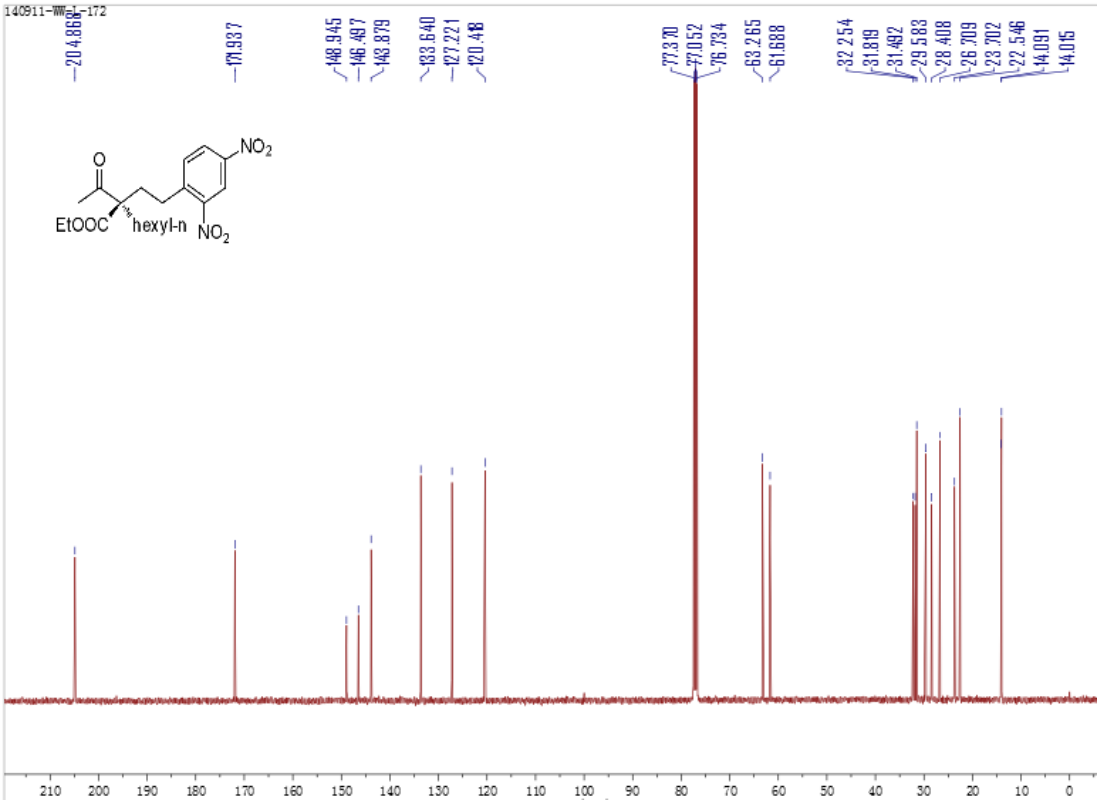
(*R*)-Ethyl 2-acetyl-2-(2,4-dinitrophenethyl)heptanoate (3g)



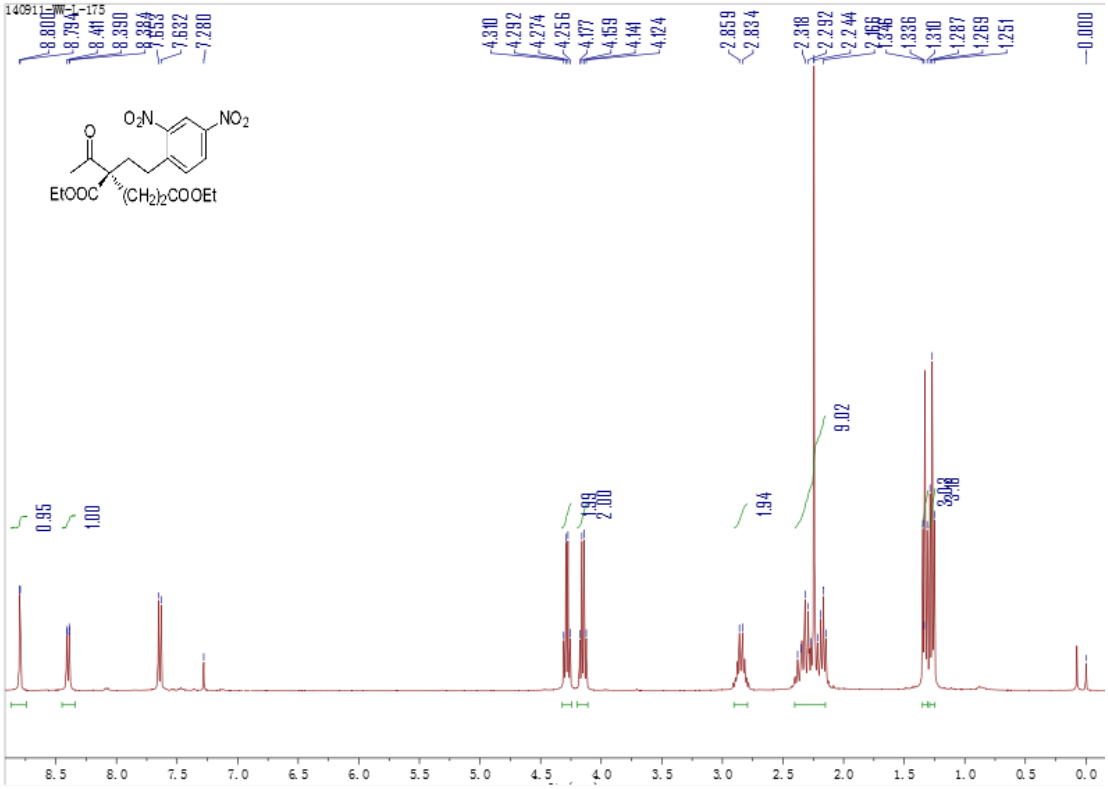


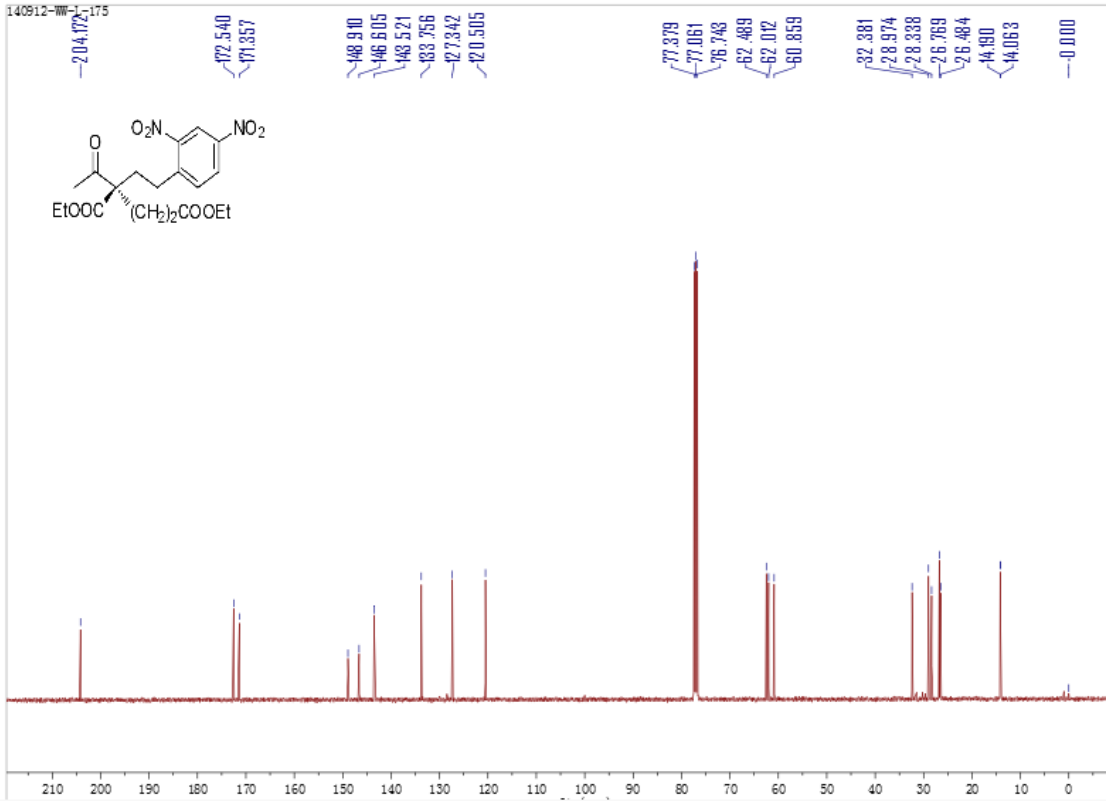
(*R*)-Ethyl 2-acetyl-2-(2,4-dinitrophenethyl)octanoate (3h)



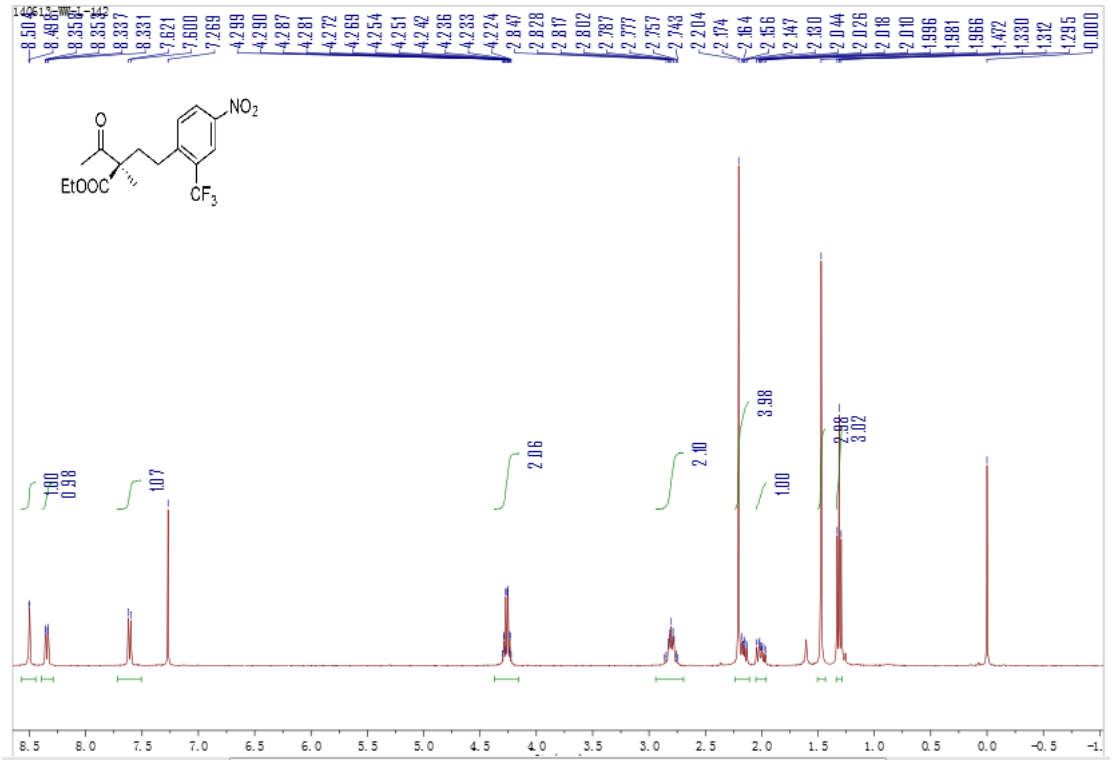


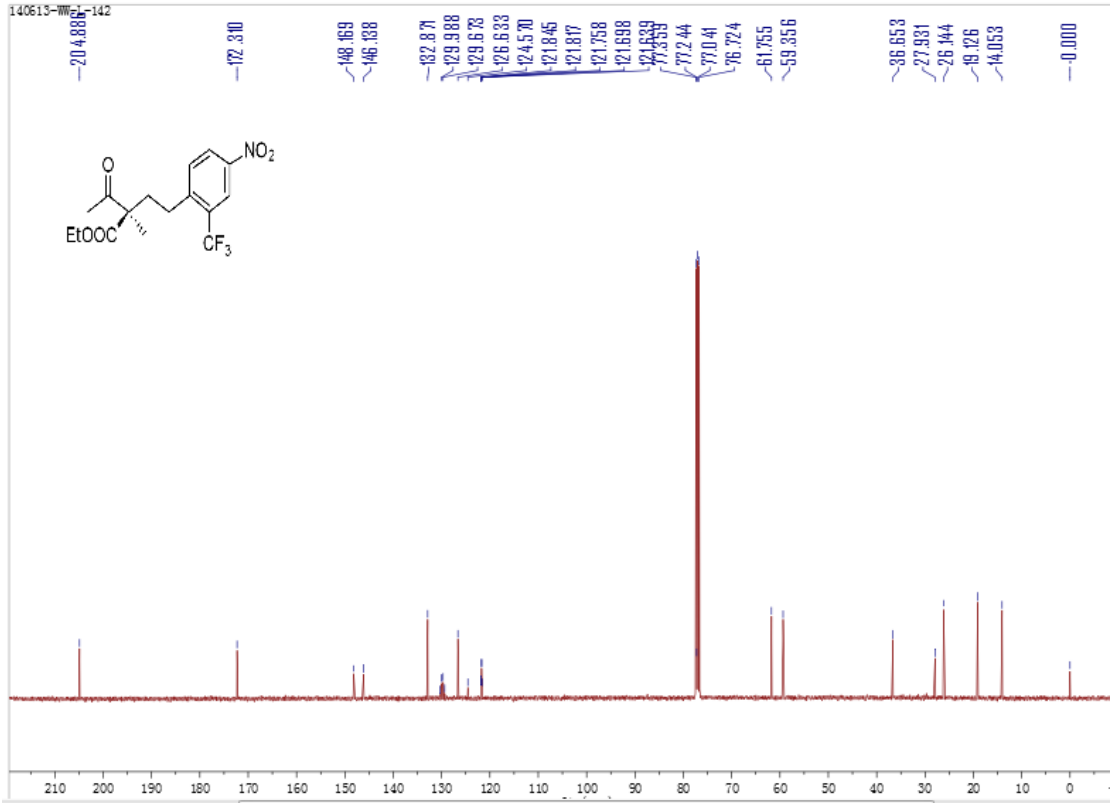
(*R*)-Diethyl 2-acetyl-2-(2,4-dinitrophenethyl)pentanedioate (3i)



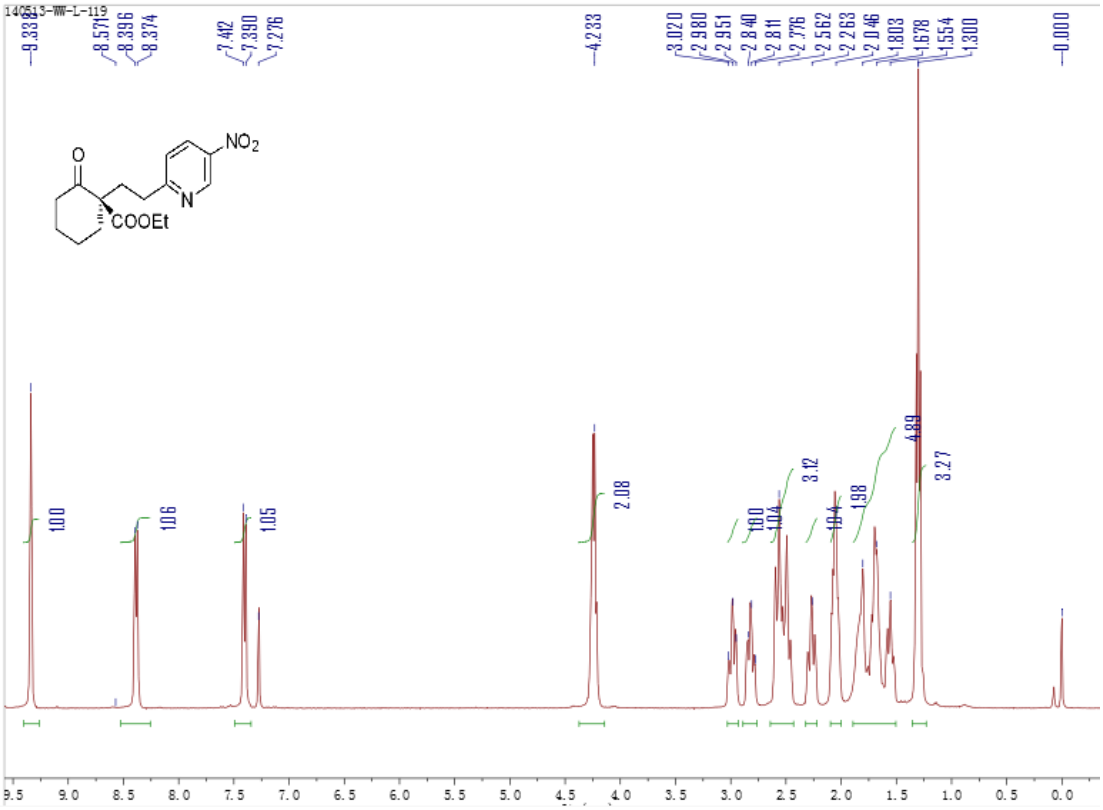


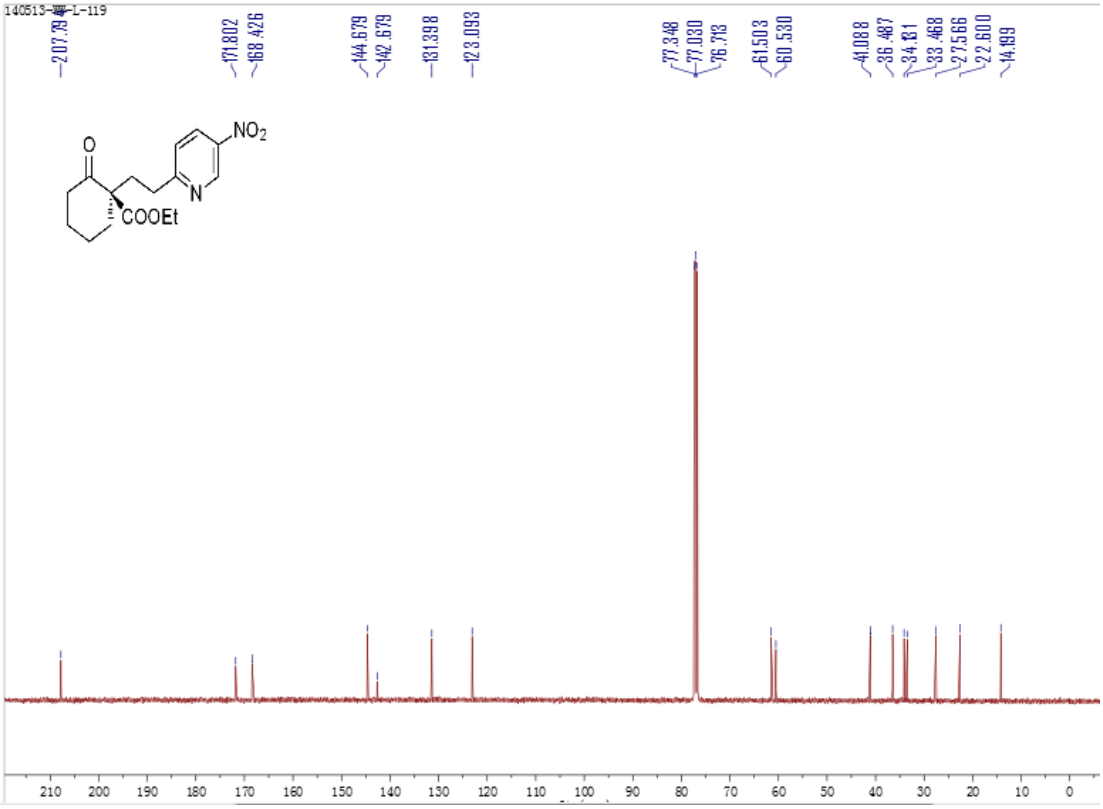
(*R*)-Ethyl 2-acetyl-2-methyl-4-(4-nitro-2-(trifluoromethyl)phenyl)butanoate (3j)



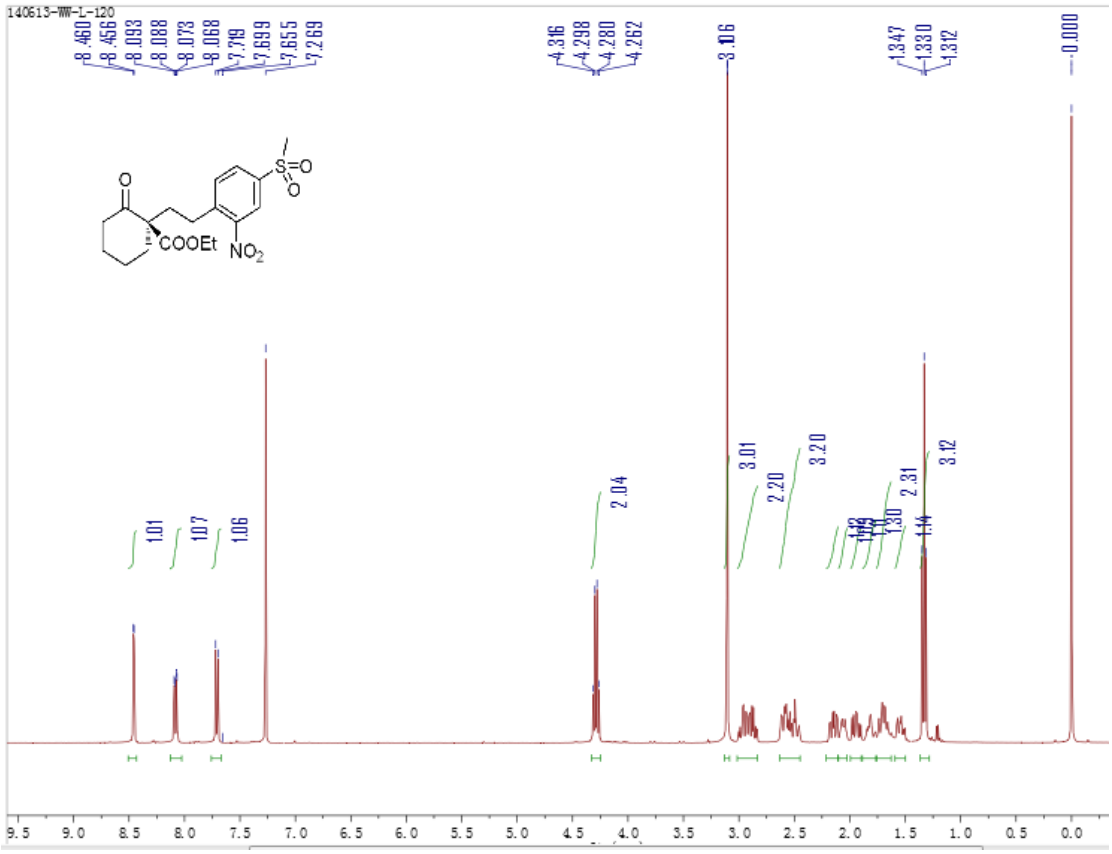


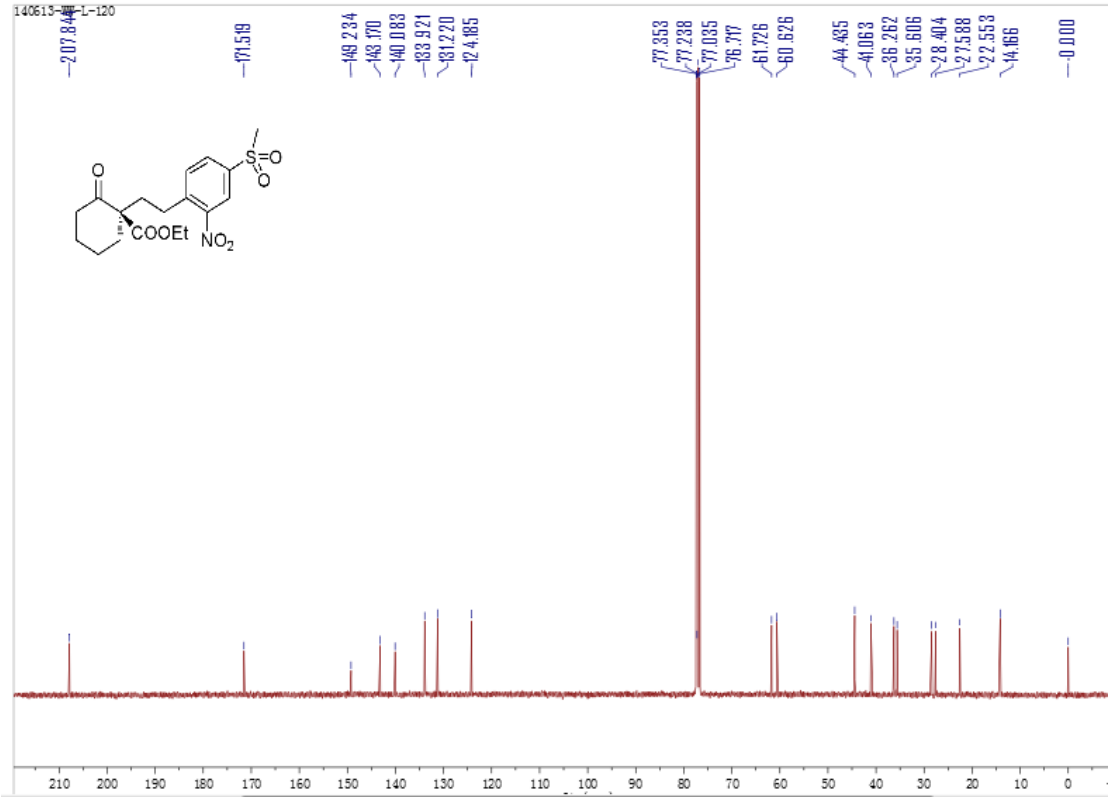
(*R*)-Ethyl 1-(2-(5-nitropyridin-2-yl)ethyl)-2-oxocyclohexanecarboxylate (3k)



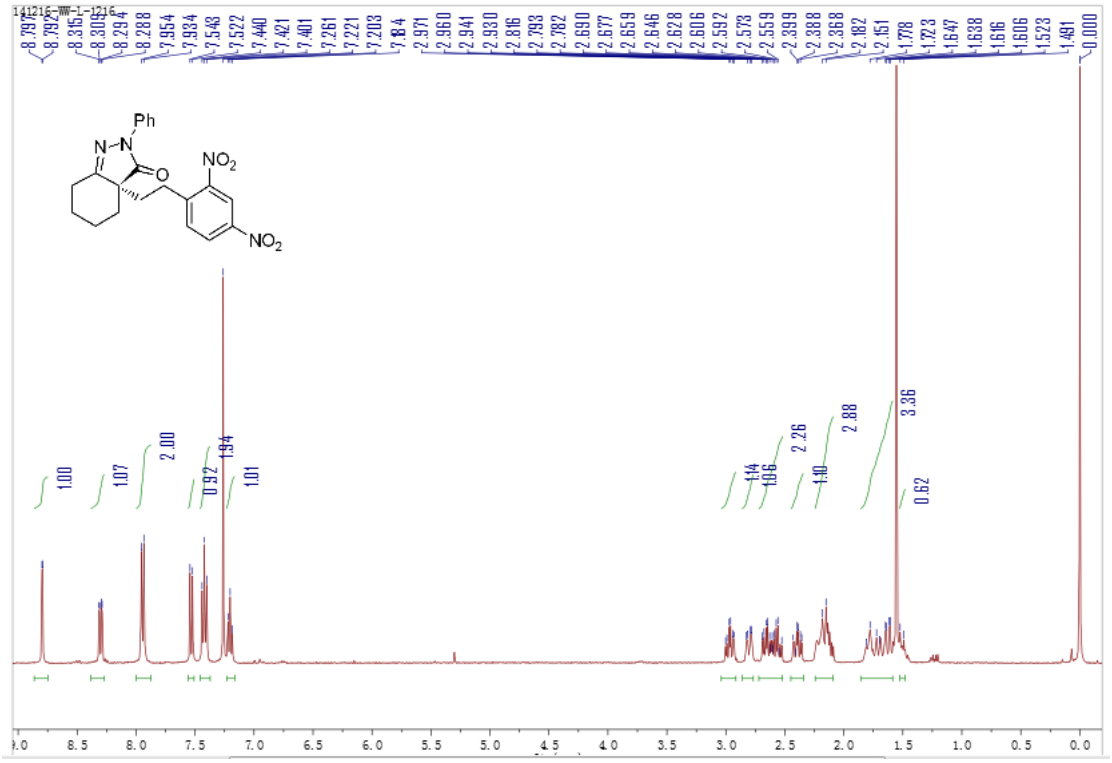


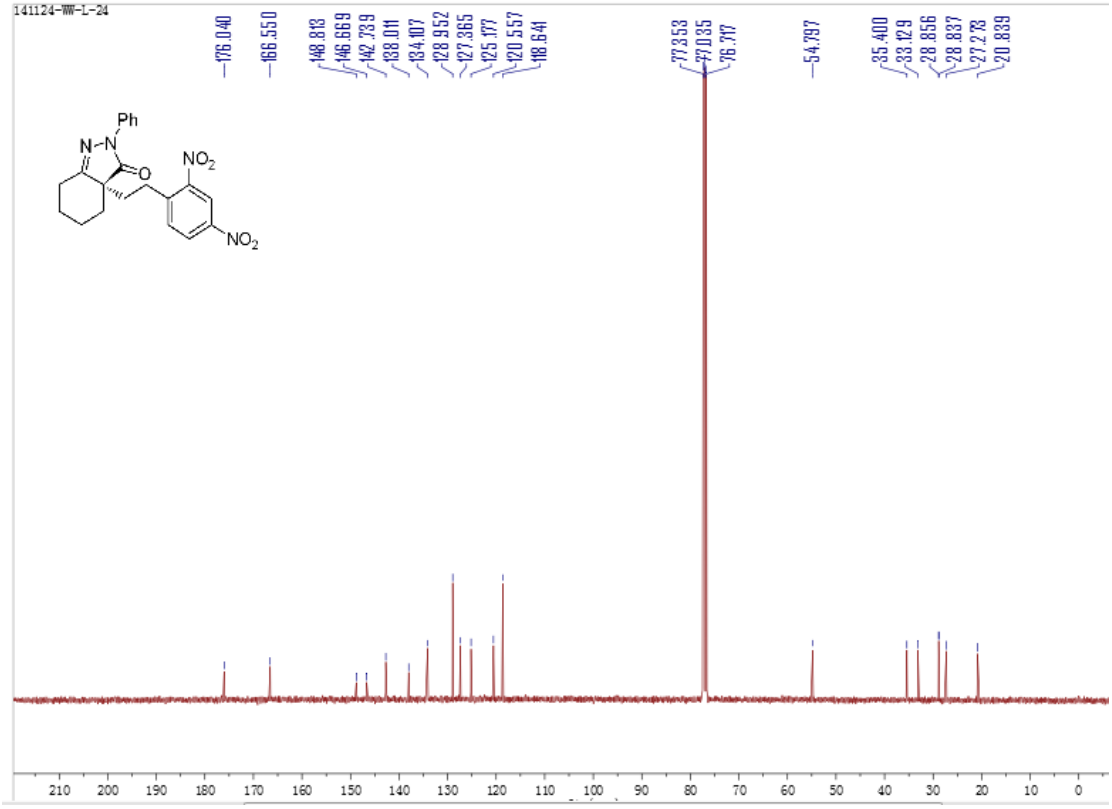
(*R*)-Ethyl 1-(4-(methylsulfonyl)-2-nitrophenethyl)-2-oxocyclohexanecarboxylate (3l)



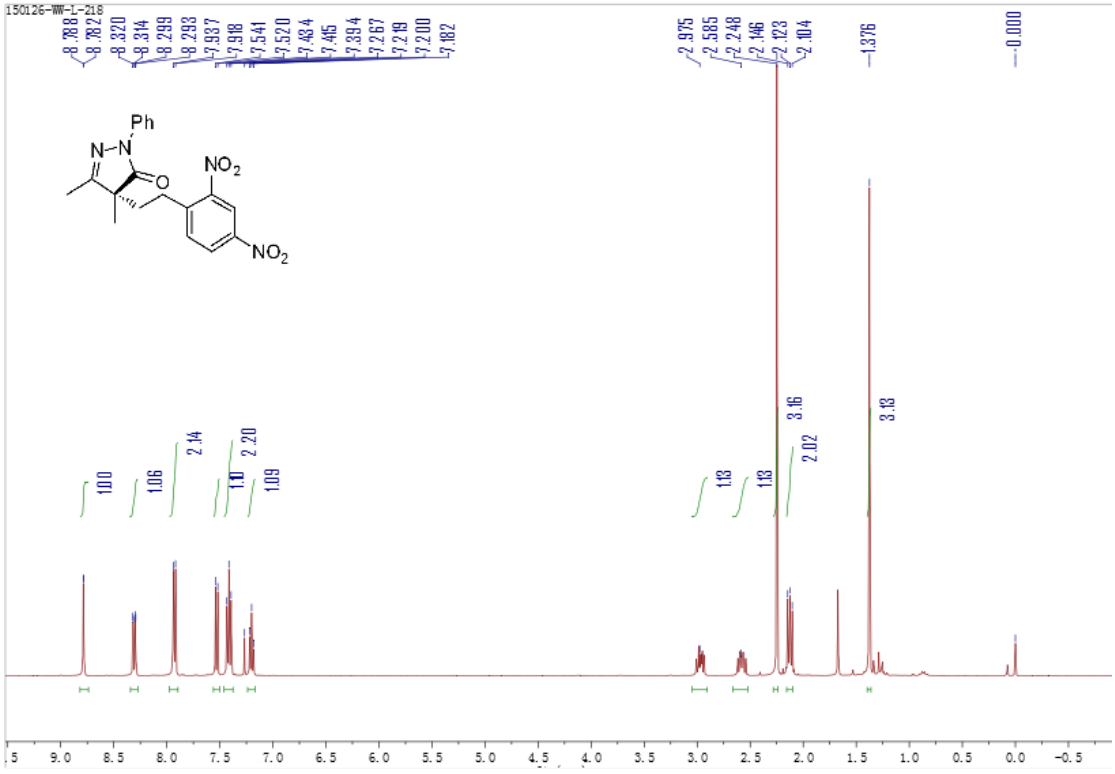


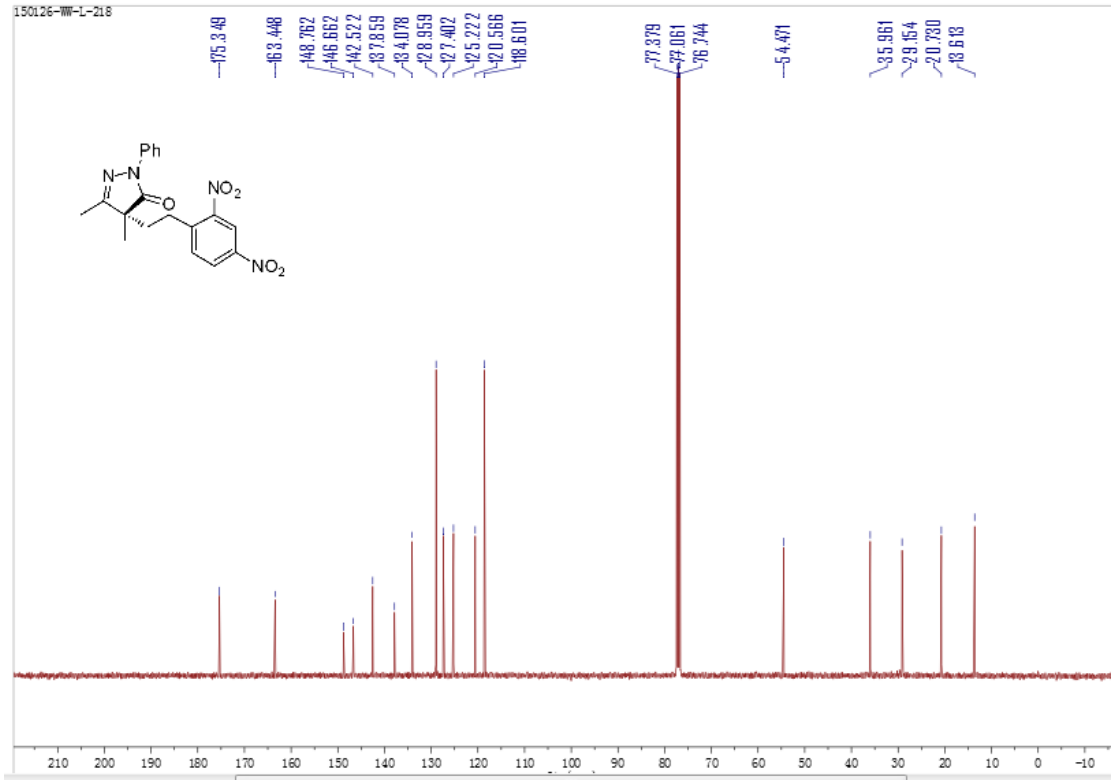
(*R*)-3a-(2,4-Dinitrophenethyl)-2-phenyl-4,5,6,7-tetrahydro-2H-indazol-3(3aH)-one (5a)





(*R*)-4-(2,4-Dinitrophenethyl)-3,4-dimethyl-1-phenyl-1H-pyrazol-5(4H)-one (5d)





9. Chiral HPLC analysis spectra

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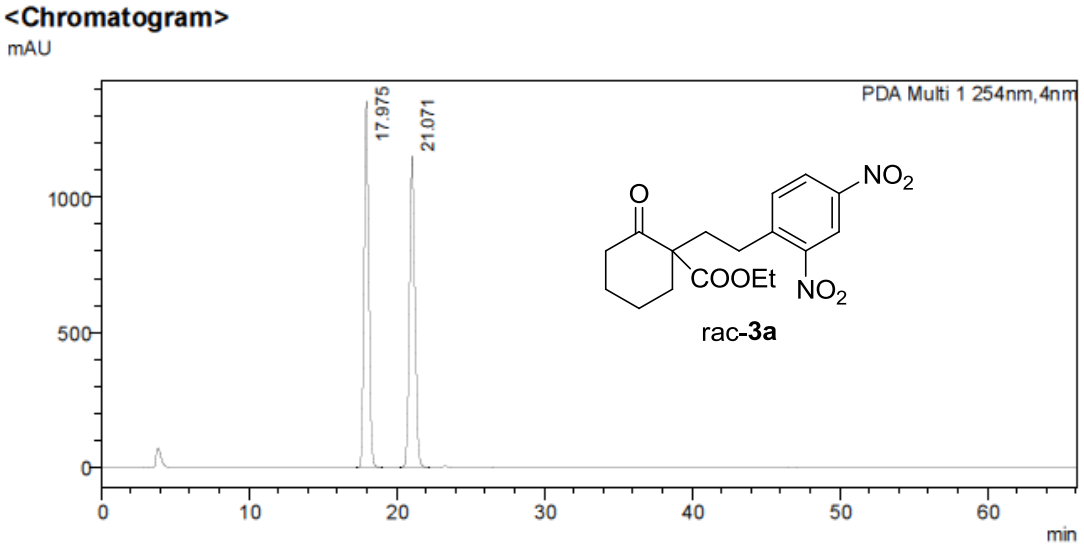

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.975	29262654	1352788	50.031	%		RT:17.975
2	21.071	29226919	1150531	49.969	%		RT:21.071
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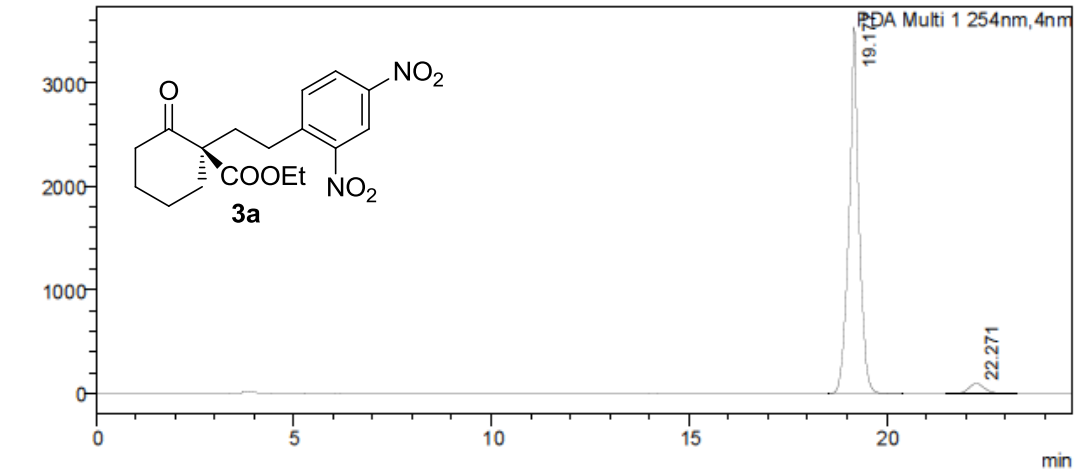

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.177	61375078	3195339	96.042	%		RT:19.177
2	22.271	2529643	94422	3.958	%		RT:22.271
Total		63904721	3289760				

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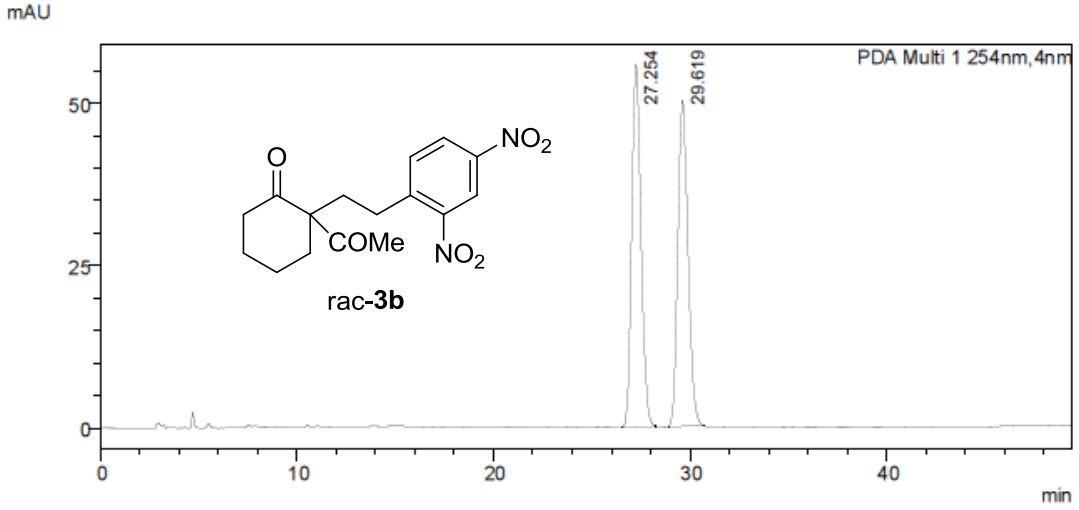

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PDA Ch1 254nm

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1	27.254	1805972	55661	50.184	%		RT:27.254
2	29.619	1792712	50174	49.816	%		RT:29.619
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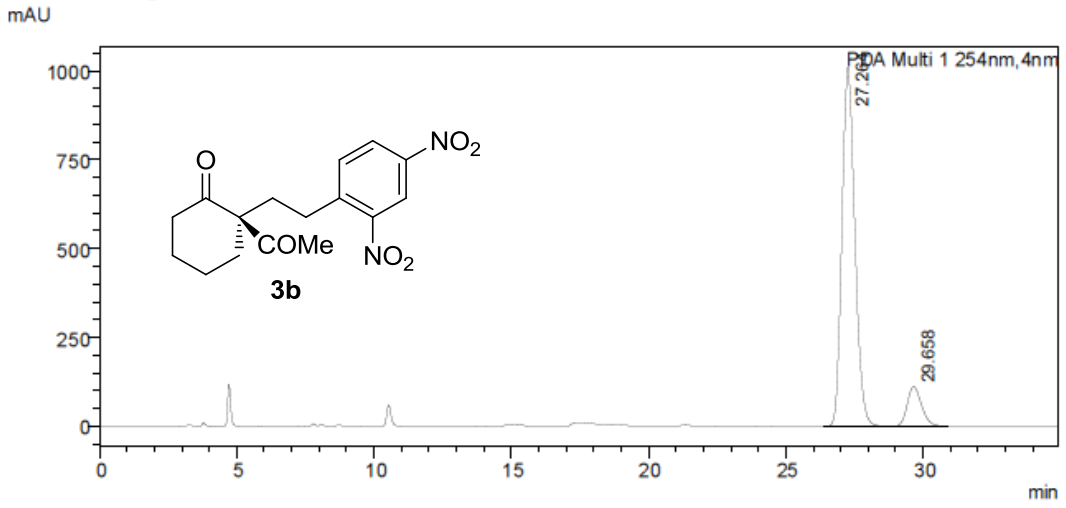

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PDA Ch1 254nm

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2	29.658	3988378	111043	10.783	%	V	RT:29.658
Total		36986521	1119566				

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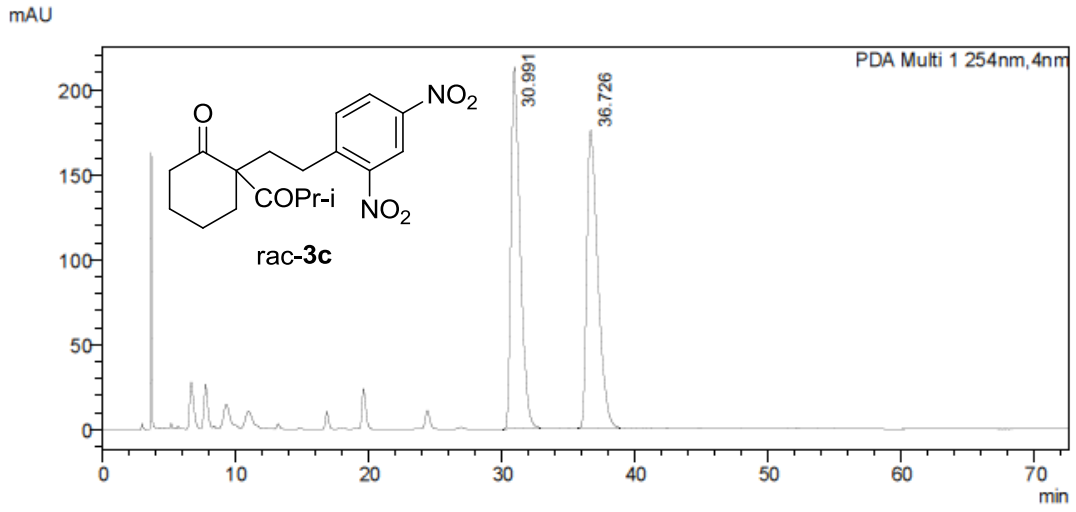

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PDA Ch1 254nm

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1	30.991	10074409	212460	50.019	%		RT:30.991
2	36.726	10066823	175228	49.981	%		RT:36.726
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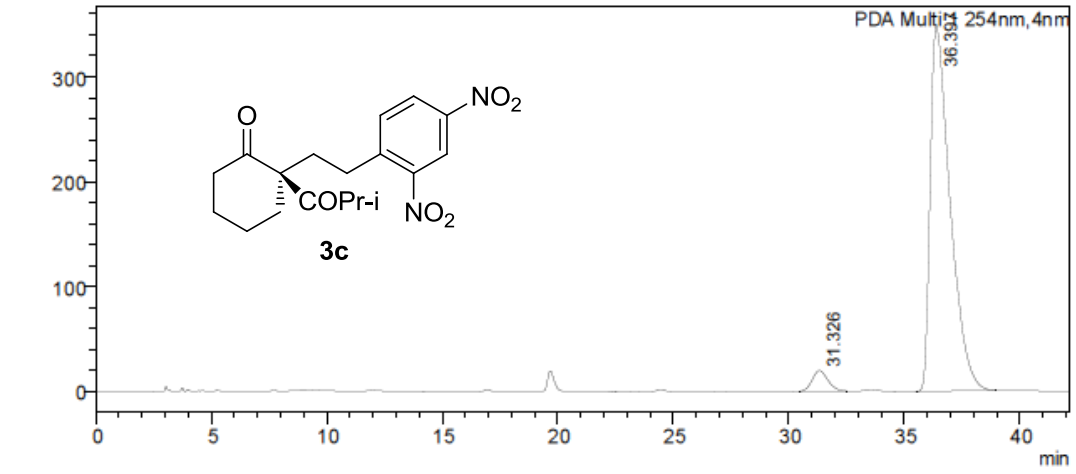

<Peak Table>

PDA Ch1 254nm

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1	31.326	908131	19562	4.182	%		RT:31.326
2	36.397	20804686	347031	95.818	%		RT:36.397
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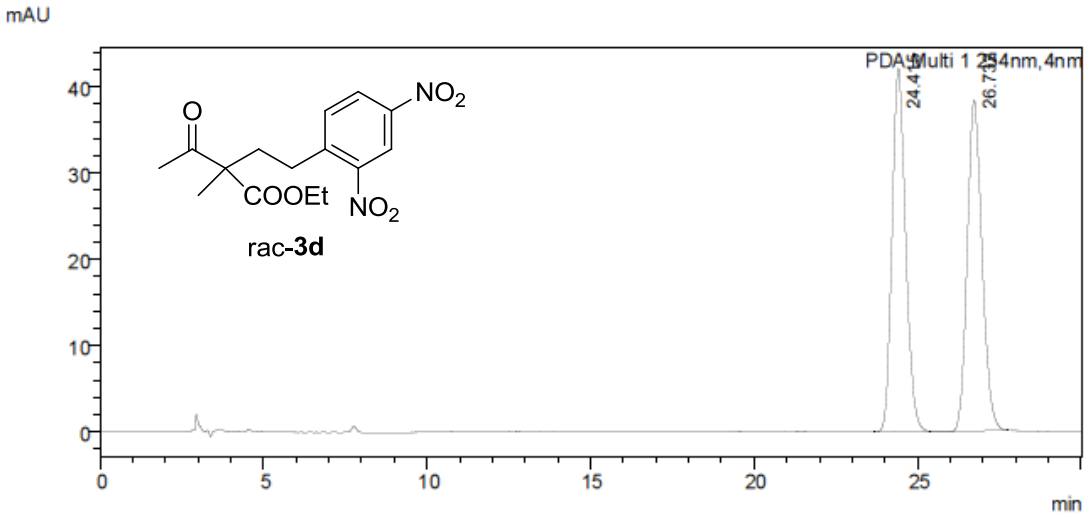

<Peak Table>

PDA Ch1 254nm

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1	24.415	1210181	41290	50.206	%		RT:24.415
2	26.732	1200240	37640	49.794	%	V	RT:26.732
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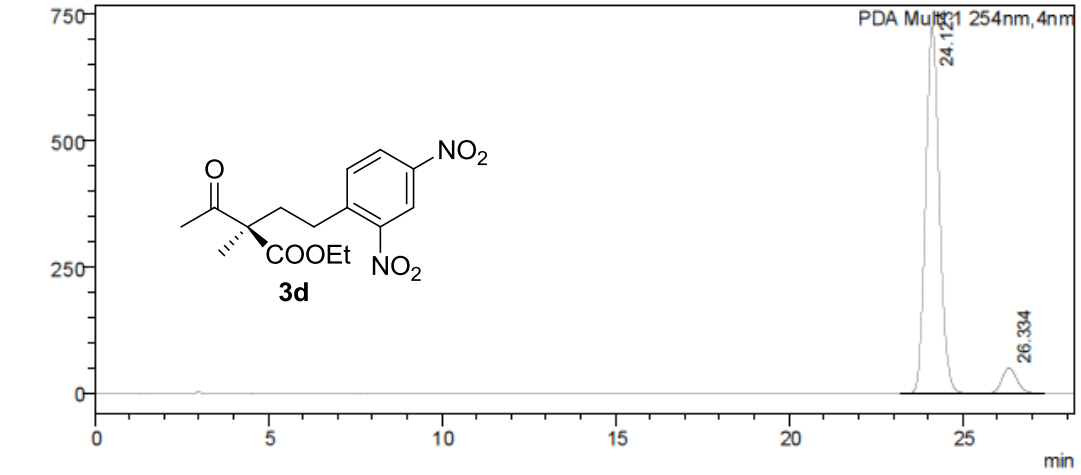

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PDA Ch1 254nm

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1	24.123	19911807	706685	92.931	%		RT:24.123
2	26.334	1514690	50382	7.069	%	V	RT:26.334
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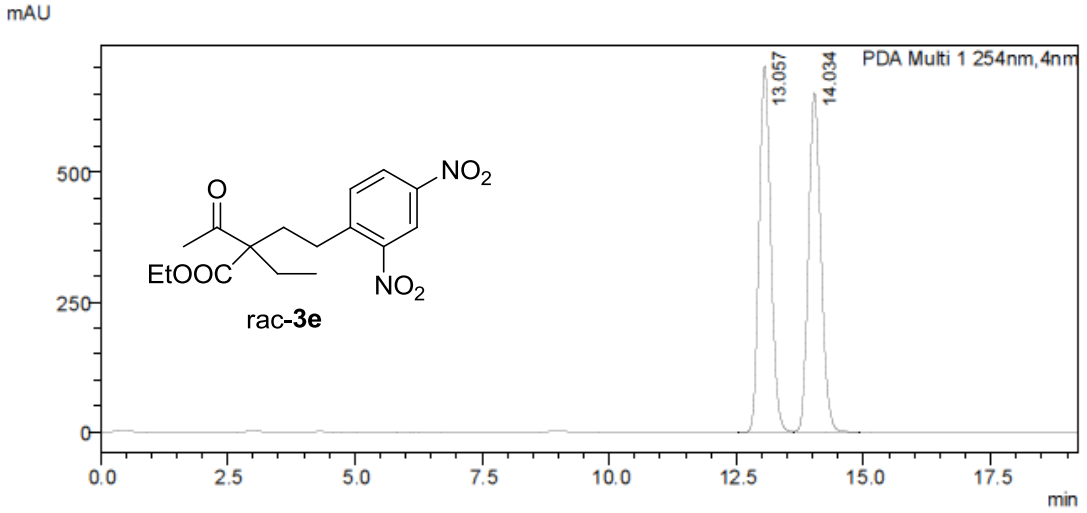

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PDA Ch1 254nm

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2	14.034	11116985	649991	49.900	%	V	RT:14.034
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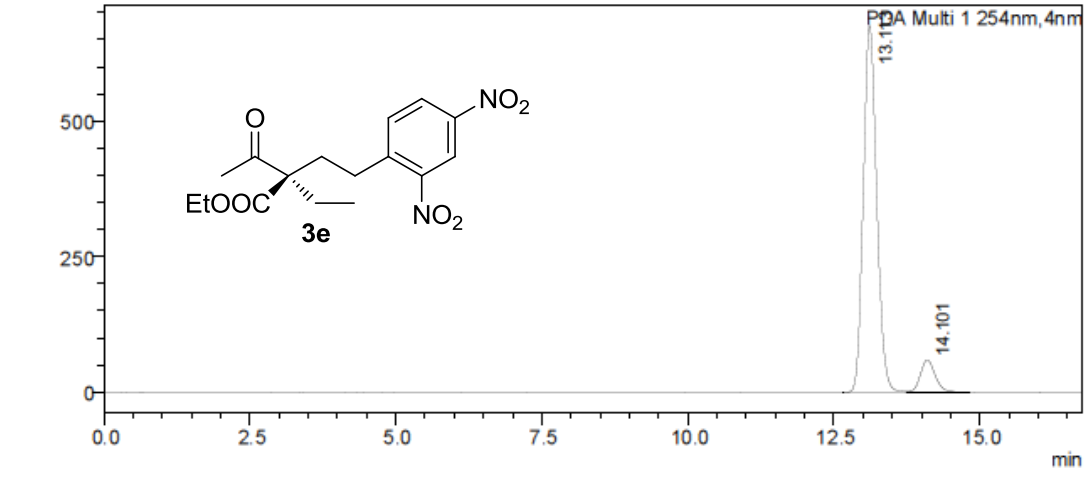

<Peak Table>

PDA Ch1 254nm

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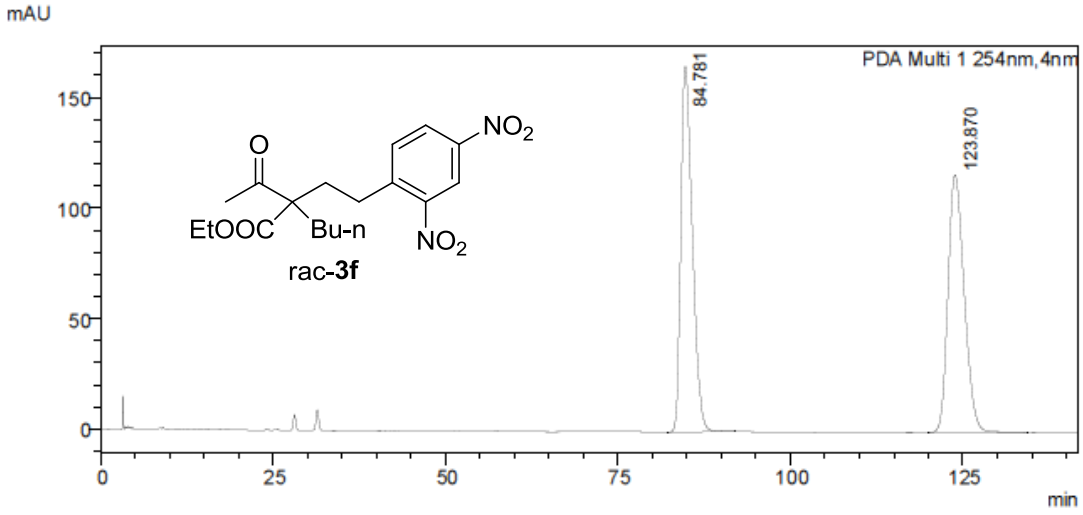

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	84.781	18945696	165241	50.010	%	S	RT:84.781
2	123.870	18938449	116341	49.990	%	S	RT:123.870
Total		37884145	281582				

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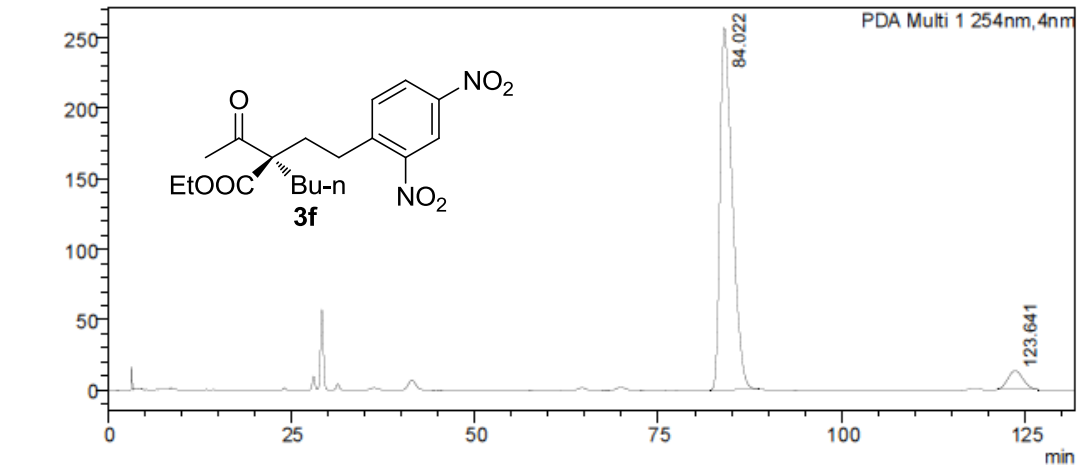

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PDA Ch1 254nm

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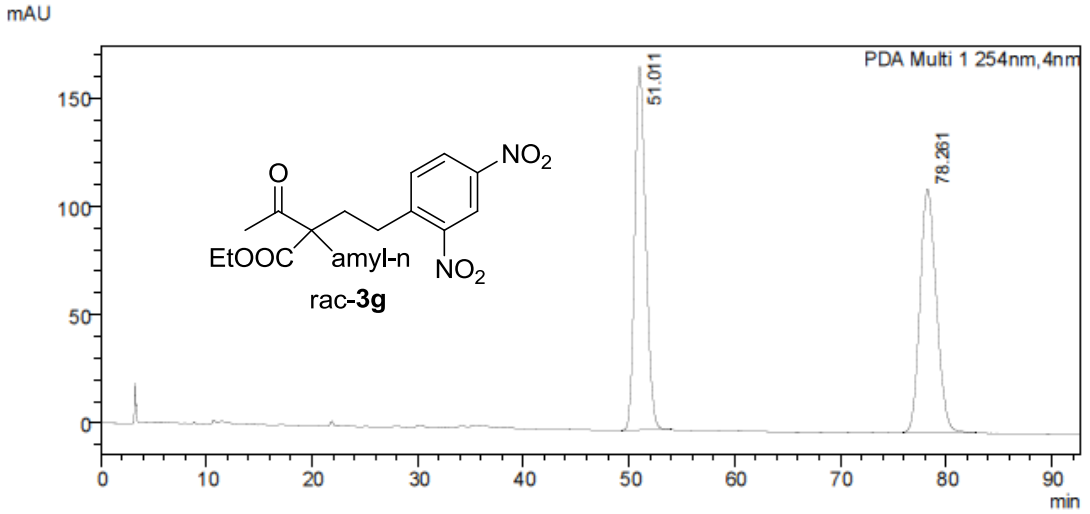

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PDA Ch1 254nm

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2	78.261	12079226	112405	50.058	%		RT:78.261
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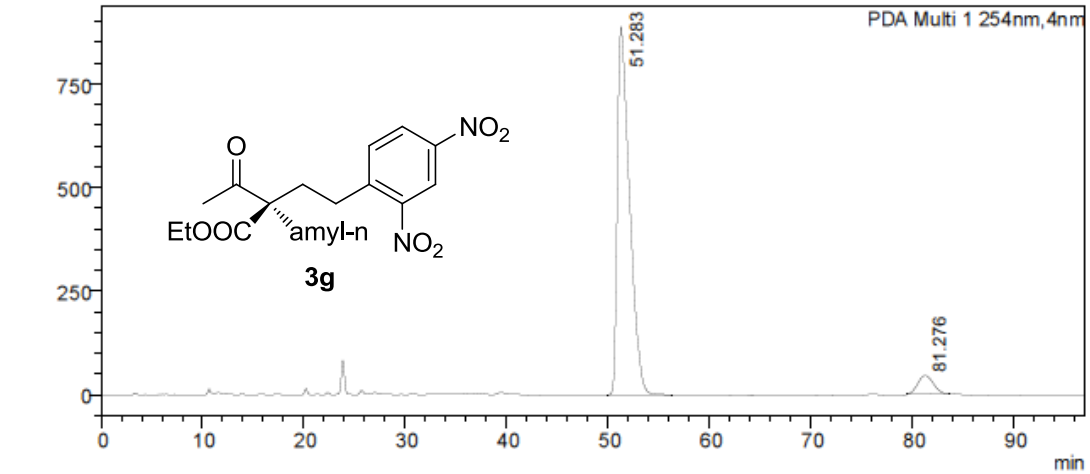

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PDA Ch1 254nm

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1	51.283	73435779	887767	93.808	%		RT:51.283
2	81.276	4846947	45093	6.192	%		RT:81.276
Total		78282726	932859				

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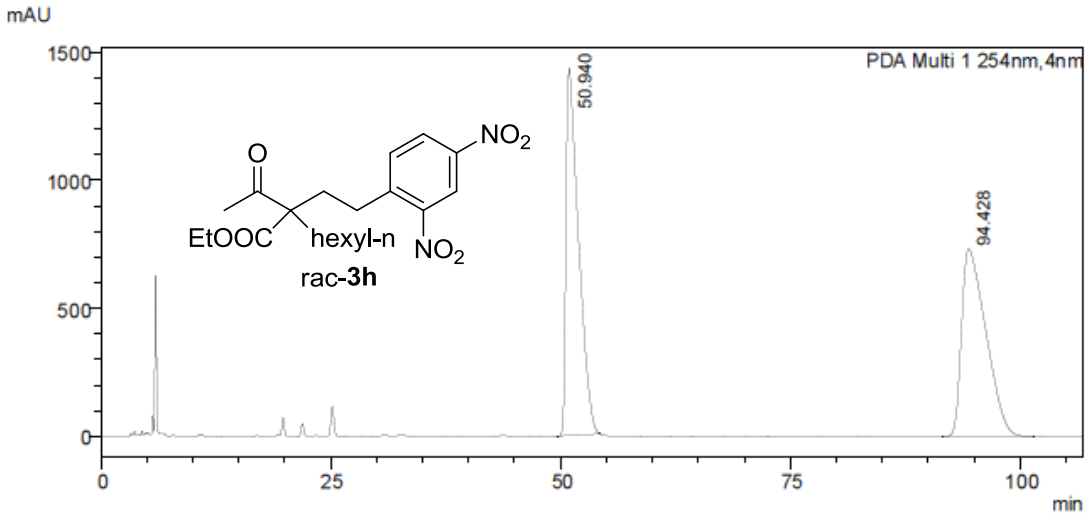
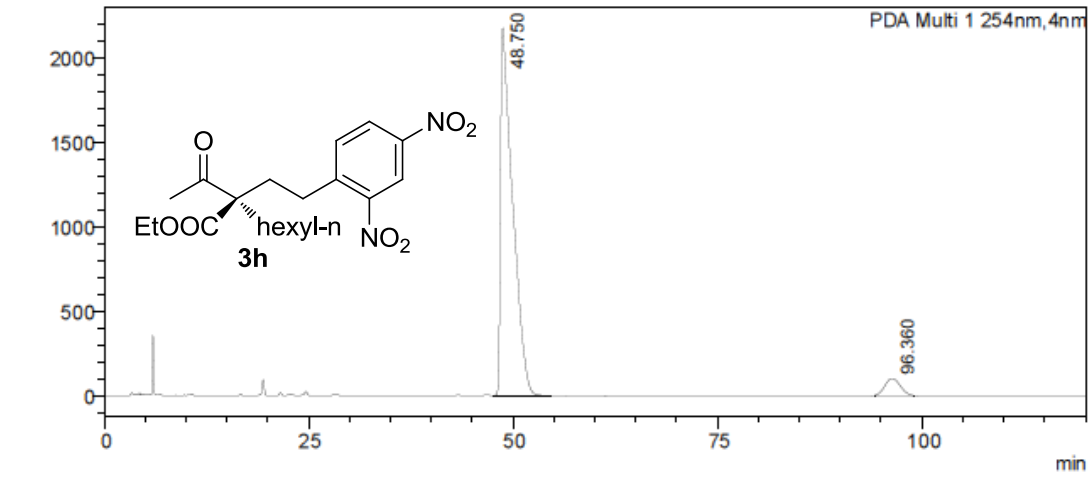


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	50.940	134543000	1434517	50.035	%		RT:50.940
2	94.428	134355215	732039	49.965	%		RT:94.428
Total		268898215	2166556				

<Chromatogram>

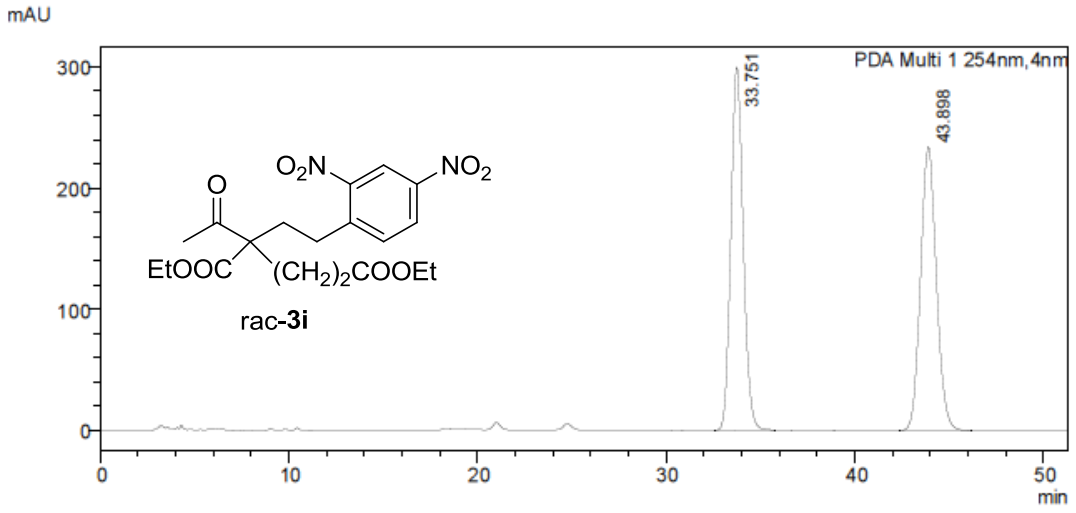


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	48.750	221396778	2176760	94.477	%		RT:48.750
2	96.360	12942524	100805	5.523	%		RT:96.360
Total		234339302	2277565				

<Chromatogram>

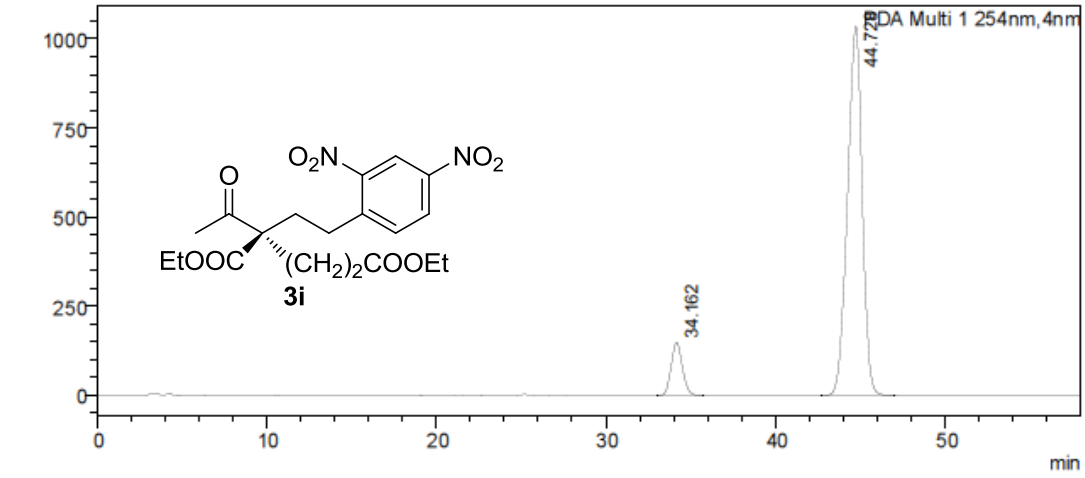


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	33.751	13565572	299421	49.991	%		RT:33.751
2	43.898	13570375	233825	50.009	%		RT:43.898
Total		27135946	533246				

<Chromatogram>

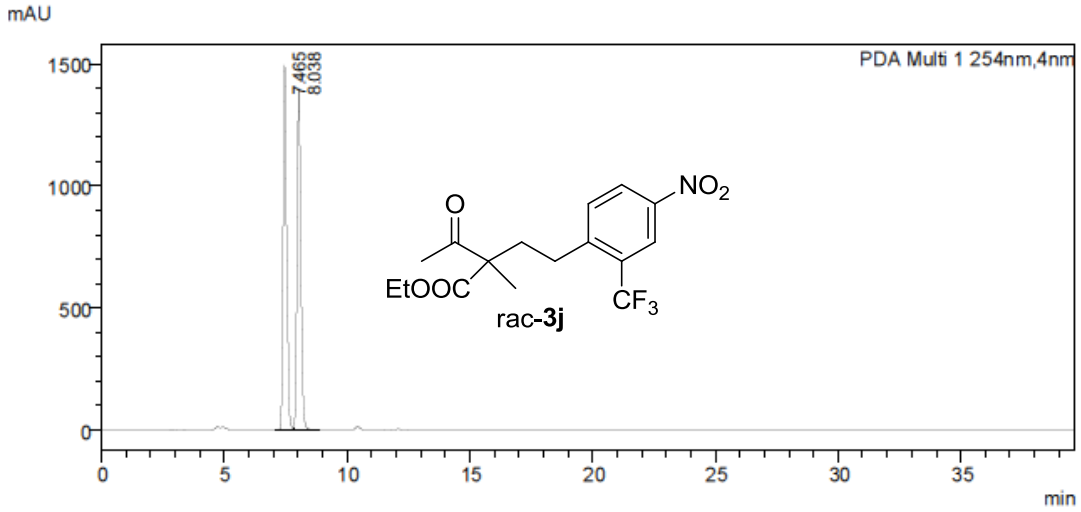


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.162	6743040	148282	9.799	%		RT:34.162
2	44.728	62071145	1034309	90.201	%		RT:44.728
Total		68814184	1182592				

<Chromatogram>

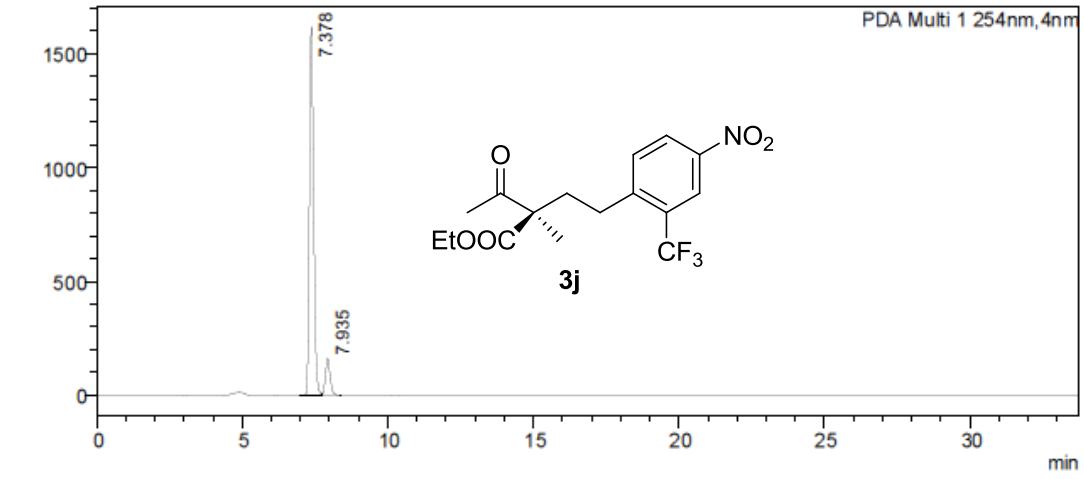


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.465	14791498	1450818	50.098	%		RT:7.465
2	8.038	14733773	1354266	49.902	%	V	RT:8.038
Total		29525271	2805085				

<Chromatogram>

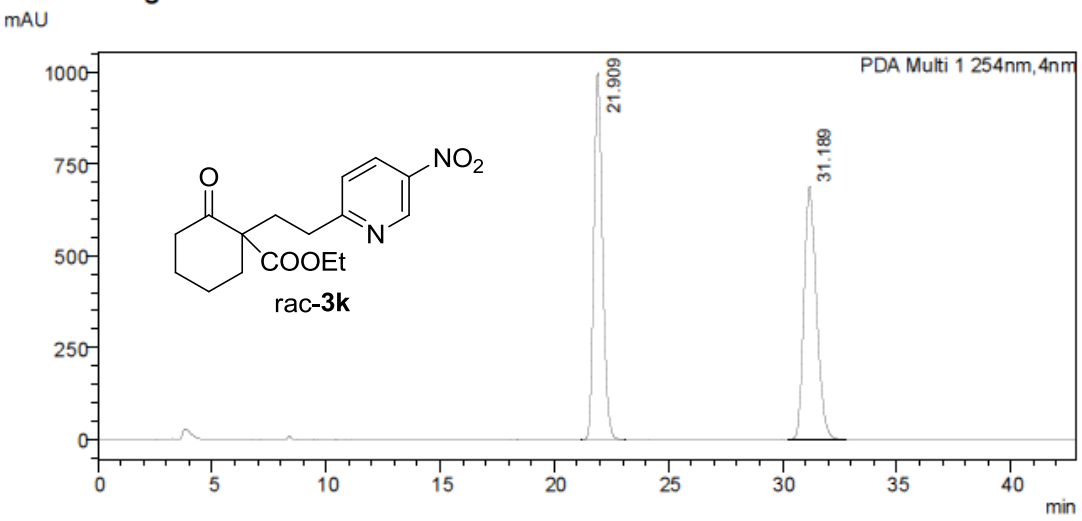


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.378	16205292	1599642	90.309	%		RT:7.378
2	7.935	1738955	158857	9.691	%	V	RT:7.935
Total		17944247	1758499				

<Chromatogram>

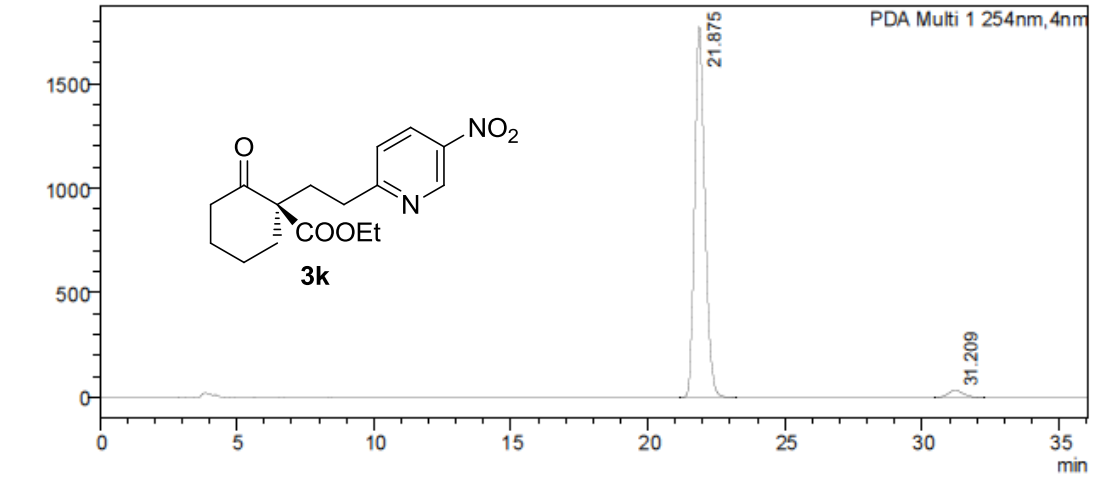


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.909	26360816	997589	50.207	%		RT:21.909
2	31.189	26143216	688633	49.793	%		RT:31.189
Total		52504033	1686222				

<Chromatogram>

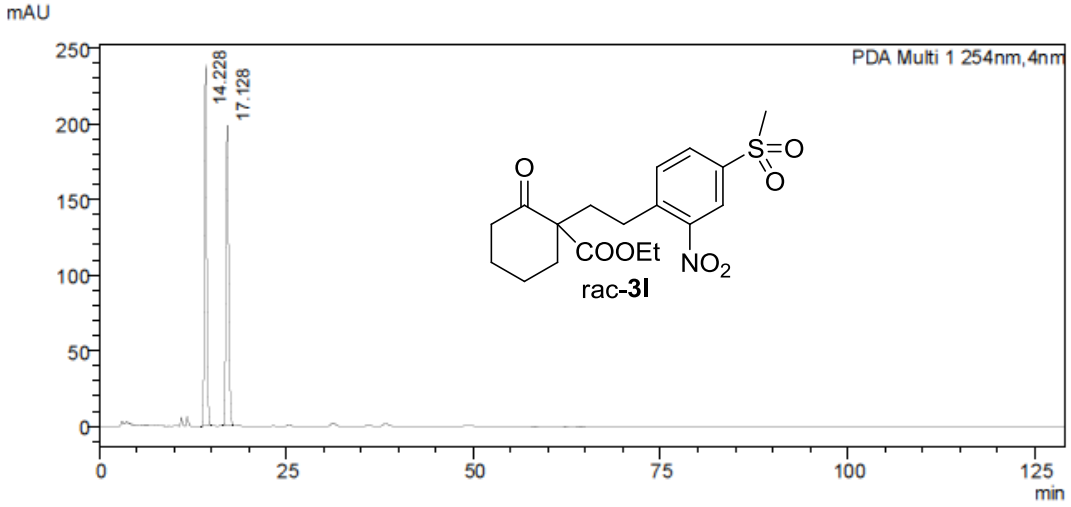


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.875	45536343	1769090	97.408	%		RT:21.875
2	31.209	1211892	32532	2.592	%		RT:31.209
Total		46748235	1801623				

<Chromatogram>

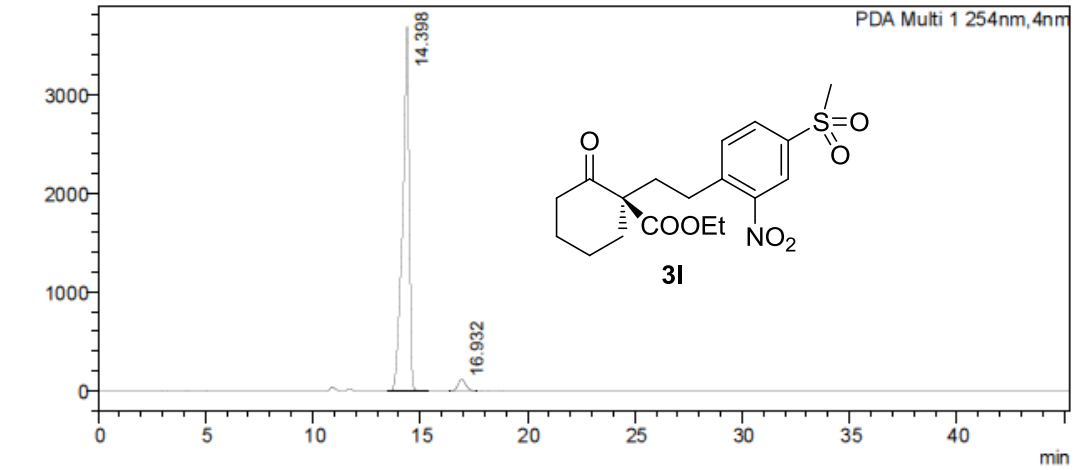


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.228	4976294	238153	50.092	%		RT:14.228
2	17.128	4958082	197339	49.908	%		RT:17.128
Total		9934376	435492				

<Chromatogram>

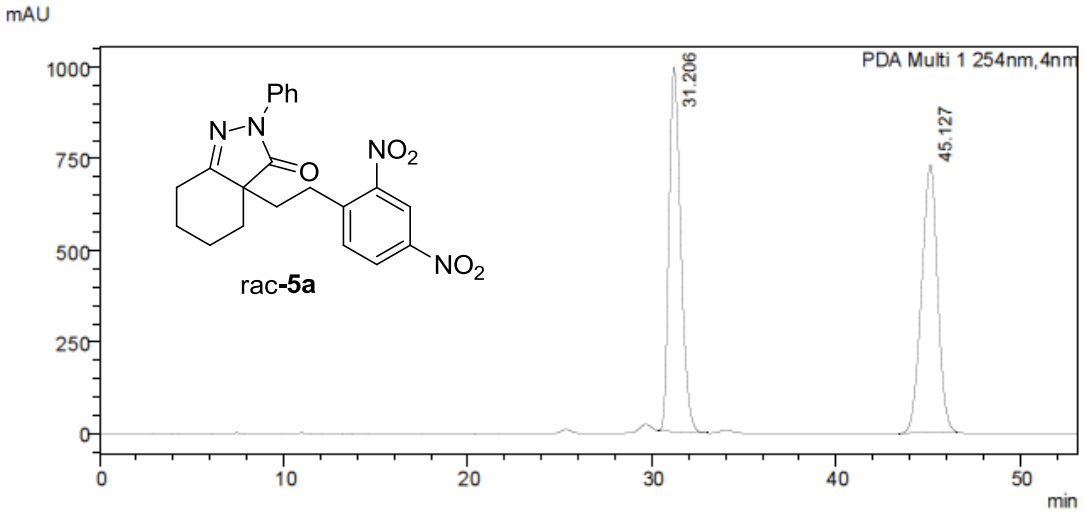


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.398	76662201	3673878	96.477	%		RT:14.398
2	16.932	2799685	115770	3.523	%		RT:16.932
Total		79461886	3789647				

<Chromatogram>

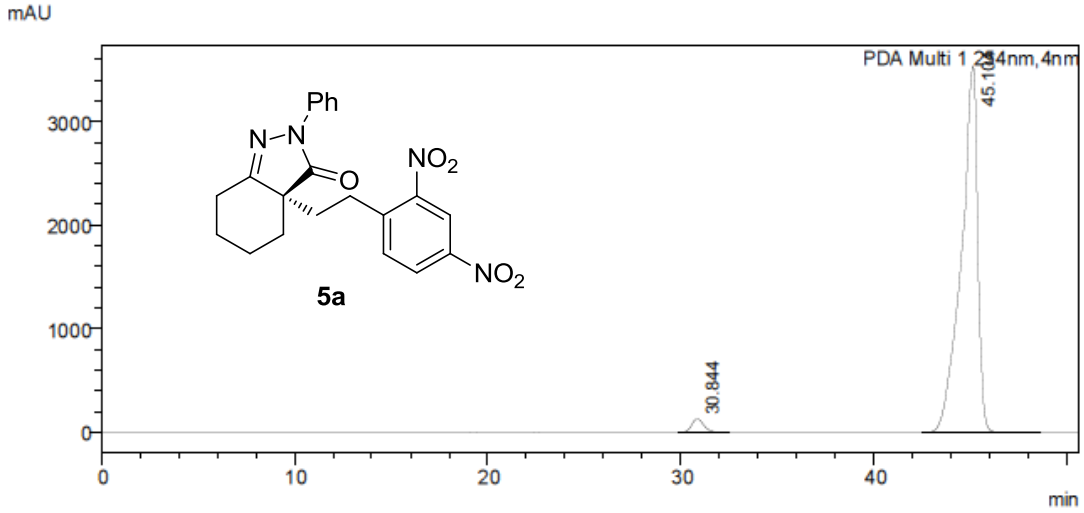


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.206	43893789	993139	49.940	%		RT:31.206
2	45.127	43999368	729715	50.060	%		RT:45.127
Total		87893157	1722854				

<Chromatogram>

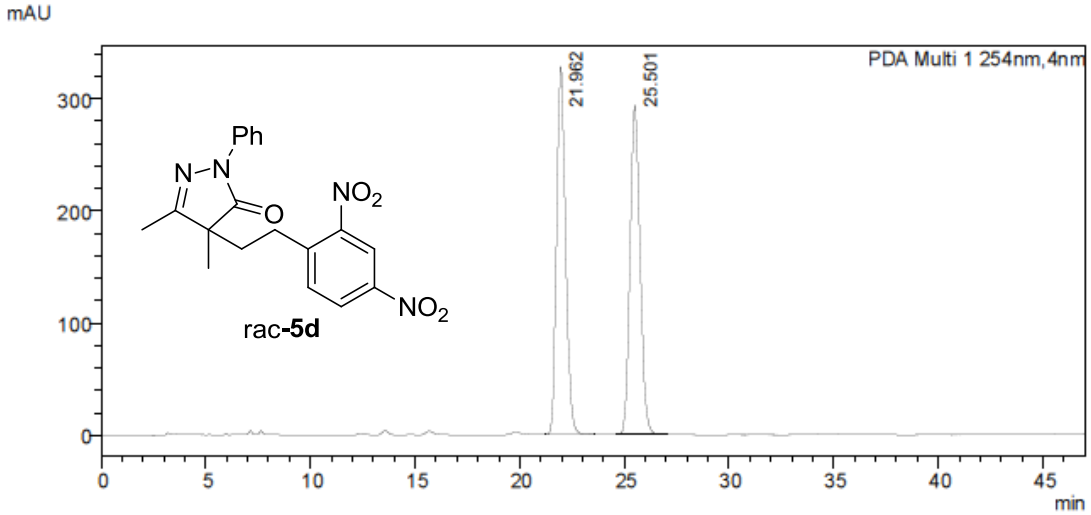


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.844	5577535	130175	2.629	%		RT:30.844
2	45.104	206614375	3536560	97.371	%		RT:45.104
Total		212191909	3666735				

<Chromatogram>

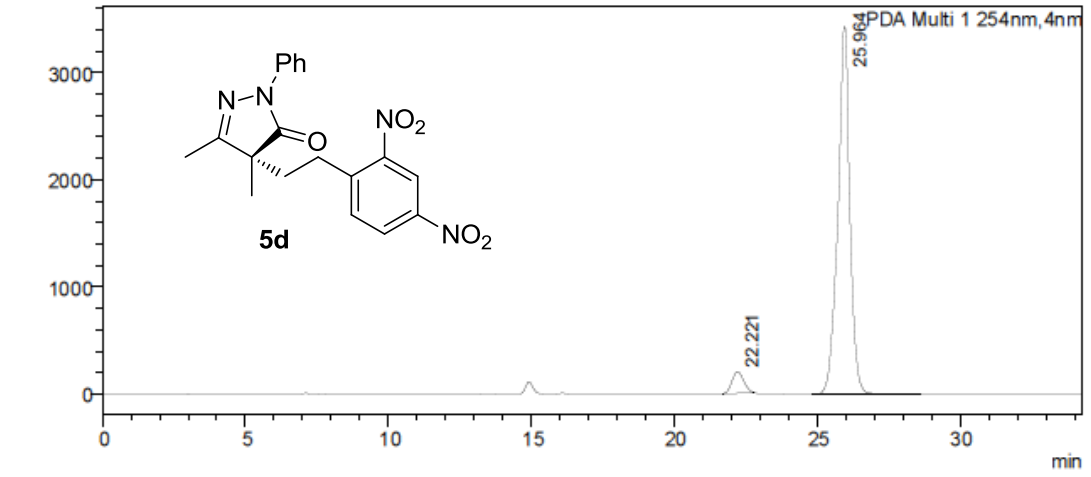


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.962	9720346	327929	50.172	%		RT:21.962
2	25.501	9653860	293423	49.828	%		RT:25.501
Total		19374207	621351				

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.221	5728296	202287	5.432	%		RT:22.221
2	25.964	99724805	3427340	94.568	%		RT:25.964
Total		105453101	3629627				