Electronic Supplementary Information

Phosphine-Catalyzed [3+2] Cycloaddition of Phthalazinium Dicyanomethanides with Allenoates: Highly Efficient Synthesis of 1,2,3,10b-Tetrahydropyrrolo[2,1-a]phthalazine Derivatives

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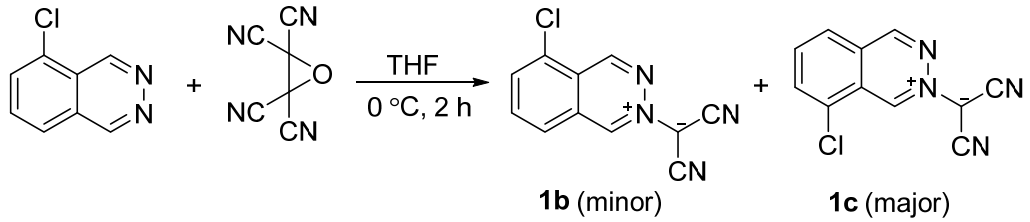
General Information

All reactions were performed under N_2 atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 using a 300 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on a Perkin-Elmer 343 polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. Melting points were determined on a Stuard SMP3 melting apparatus. X-ray crystallographic data were collected using a MM007HF Saturn724+.

Preparation of Azomethine Ylides 1 and 4

Phthalazinium dicyanomethanides 1[1]. Phthalazine or phthalazine derivative[2,3] (14.58 mmol) was added to a solution of TCNEO[4] (4.86 mmol) in THF (50 mL) at 0 °C. The reaction was stirred at this temperature during 2 h. Then, the formed solid was filtrated and washed with cold THF (3 × 25 mL) to give the product in nearly quantitative yield.

By HPLC analysis, the ratio of two isomers was, **1b** : **1c** = 33 : 67.



Isoquinolinium-2-dicyanomethanide 1g[1]. Isoquinoline (2.77 g, 21.4 mmol) was added to a solution of TCNEO[4] (6.00 g, 41.6 mmol) in THF (50 mL) at 0 ºC. The reaction was stirred at 4 ºC during 20 h. Then, the solvent was evaporated and the formed solid was recrystalized in EtOH (3.23 g, 78%).

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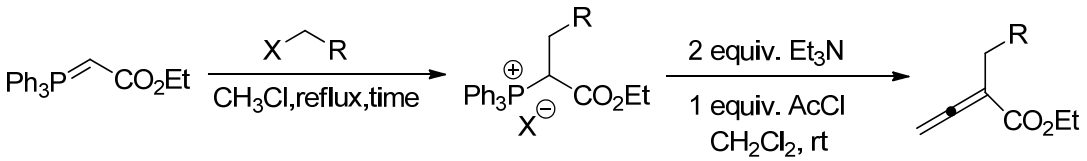
[1] Naiara, F.; Luisa, C.; Jose, L. V.; Dolores, B.; Efraim, R. *Chem. Commun.* **2011**, *47*, 12313.
[2] Simon, N. K.; Hermann, A. W. *Org. Lett.* **2012**, *14*, 3268.
[3] Timothy, J. M.; Yunus, E. T.; Noumaan, A. S.; Christopher, M.; Chintan, S. S.; Viresh, H. R.; Sergey, A. K. *Angew. Chem. Int. Ed.* **2013**, *52*, 13576.
[4] Linn, W. J.; Webster, O. W.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 3651.

Pyridazinium dicyanomethanide 4[4]. A solutionof pyridazine (0.98 mL, 7.0 mmol) in ethyl acetate (20 mL) was cooled to below 0 °C in an ice-bath. This was treated dropwise with a cooled ethyl acetate solution (5 mL) of TCNEO[4] (1.0 g, 7.0 mmol). The yellow product precipitated from the solution and was collected in three crops as the 1,3-dipole gradually separated from the solution (0.69 g, 70%).

Preparation of Allenoates 2[5]



The pertinent alkyl halide (1.0-1.2 equiv) was added to a stirred solution of (carbethoxymethylene)triphenylphosphorane 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 ^1H 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 in 50–85% yield.

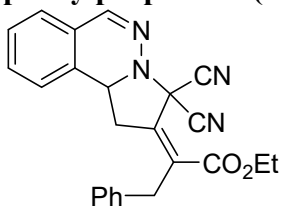
General Procedure for the [3+2] Cycloaddition Reactions of Azomethine Ylides and Allenoates

Under a nitrogen atmosphere, to a stirred solution of Ylides 1 (0.1 mmol, 1.0 equiv) and catalyst PMe_3 (0.02 mmol, 20 mol %) in DCM (1 mL) was added Allenoate 2 (0.15 mmol, 1.5 equiv) via a syringe. Then the reaction solution was vigorously stirred at room temperature and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to furnish the corresponding product.

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

Characterization Data for the [3+2] Cycloaddition Products 3, 5 and 6

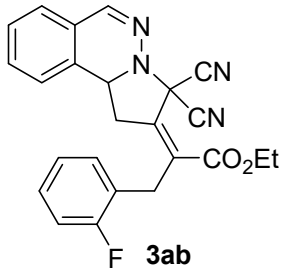
(Z)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-phenylpropanoate(3aa)



3aa

Prepared according to the general procedure as described above in 95% yield (37.7 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 145 – 147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.50 (td, *J* = 7.4, 1.5 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.39 – 7.31 (m, 3H), 7.30 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 4.54 – 4.23 (m, 3H), 3.90 (q, *J* = 15.4 Hz, 2H), 3.36 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.04 (ddd, *J* = 16.4, 10.2, 1.4 Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 146.4, 140.8, 136.4, 134.3, 133.4, 132.2, 129.0, 128.9, 128.0, 127.0, 126.3, 125.1, 123.4, 112.7, 111.4, 62.5, 59.3, 54.4, 36.0, 33.1, 13.8; IR (film) ν_{max} 577, 600, 666, 702, 722, 739, 763, 883, 940, 1032, 1074, 1109, 1144, 1210, 1300, 1369, 1454, 1495, 1562, 1604, 1712, 2984, 3030 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{20}N_4O_2Na^+$ $[M+Na]^+$ 419.1478, found 419.1479.

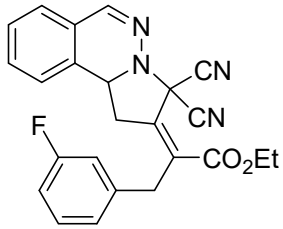
(Z)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-(2-fluorophenyl)propanoate (3ab)



3ab

Prepared according to the general procedure as described above in 91%yield (37.7 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 143 – 145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.37 – 7.34 (m, 1H), 7.32 – 7.17 (m, 2H), 7.17 – 7.10 (m, 2H), 7.10 – 7.01 (m, 1H), 4.56 – 4.18 (m, 3H), 3.88 (dd, *J* = 43.5, 15.4 Hz, 2H), 3.44 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.06 (ddd, *J* = 16.5, 10.2, 1.5 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 161.0 (d, *J* = 245.6 Hz), 146.4, 141.0, 133.5, 133.1, 132.2, 130.0 (d, *J* = 4.1 Hz), 128.9 (d, *J* = 8.2 Hz), 128.9, 126.3, 125.1, 124.6 (d, *J* = 3.5 Hz), 123.4, 123.4 (d, *J* = 15.3 Hz), 115.6 (d, *J* = 22.0 Hz), 112.6, 111.3, 62.5, 59.3, 54.4, 32.9 (d, *J* = 3.0 Hz), 29.6, 13.8; IR (film) ν_{max} 522, 580, 600, 666, 758, 798, 870, 883, 935, 1031, 1101, 1143, 1233, 1264, 1292, 1369, 1454, 1491, 1585, 1659, 1713, 2352, 2853, 2924 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}FN_4O_2Na^+$ $[M+Na]^+$ 437.1384, found 437.1385.

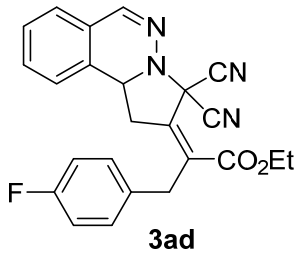
(*Z*)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-(3-fluorophenyl)propanoate (3ac)



3ac

Prepared according to the general procedure as described above in 96%yield (39.8 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 155 – 156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.51 (td, *J* = 7.4, 1.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.38 – 7.25 (m, 2H), 7.13 – 7.11 (m, 1H), 7.00 – 6.91 (m, 3H), 4.54 – 4.17 (m,3H), 3.88 (q, *J* = 15.8 Hz, 2H), 3.35 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.05 (ddd, *J* = 16.5, 10.2, 1.3 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 163.1 (d, *J* = 246.9 Hz), 146.5, 141.3, 138.9 (d, *J* = 7.2 Hz), 133.5 (d, *J* = 24.0 Hz), 132.2, 130.5 (d, *J* = 8.4 Hz), 128.9, 126.3, 125.1, 123.4 (d, *J* = 2.9 Hz), 123.4, 115.1 (d, *J* = 21.8 Hz), 114.1 (d, *J* = 21.0 Hz), 112.6, 111.2, 62.7, 59.3, 54.4, 35.7 (d, *J* = 1.5 Hz), 33.1, 13.8; IR (film) ν_{max} 520, 581, 600, 666, 686, 723, 737, 802, 866, 883, 945, 1032, 1109, 1143, 1209, 1265, 1299, 1370, 1452, 1488, 1563, 1590, 1614, 1713, 2810, 2965 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}FN_4O_2Na^+$ $[M+Na]^+$ 437.1384, found 437.1385.

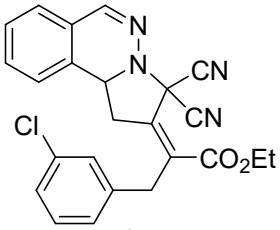
(*Z*)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-(4-fluorophenyl)propanoate (3ad)



3ad

Prepared according to the general procedure as described above in 99%yield (41.0 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 168 – 169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.37 – 7.34(m, 1H), 7.31 – 7.20 (m, 3H), 7.14 – 7.11(m, 1H), 7.09 – 7.01 (m, 1H), 4.53 – 4.20 (m, 3H), 3.97 – 3.71 (m, 2H), 3.35 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.05 (ddd, *J* = 16.4, 10.2, 1.3 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 146.5, 139.9 (d, *J* = 216.4 Hz), 134.7, 133.4 (d, *J* = 19.2 Hz), 132.2, 130.3, 128.9, 128.4, 127.3, 126.3, 125.9, 125.1, 123.4, 112.6, 111.2, 62.7, 59.3, 54.4, 35.7, 33.2, 13.8; IR (film) ν_{max} 668, 677, 724, 738, 772, 794, 883, 918, 944, 1034, 1108, 1142, 1221, 1263, 1296, 1368, 1430, 1474, 1575, 1597, 1658, 1708, 2350, 2357, 2964 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}FN_4O_2Na^+$ $[M+Na]^+$ 437.1384, found 437.1385.

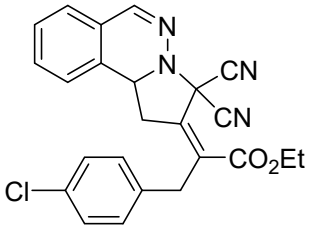
(Z)-Ethyl 3-(3-chlorophenyl)-2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)propanoate (3ae)



3ae

Prepared according to the general procedure as described above in 98%yield (42.2 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 160 – 162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.51 (td, *J* = 7.4, 1.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.34 – 7.37 (m, 1H), 7.30 – 7.15 (m, 3H), 7.15 – 7.11 (m, 1H), 7.10 – 6.96 (m, 1H), 4.58 – 4.14 (m, 3H), 3.85 (q, *J* = 15.5 Hz, 2H), 3.35 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.04 (ddd, *J* = 16.4, 10.2, 1.3 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 146.3, 141.2, 138.3, 134.5, 133.4, 133.1, 132.0, 130.1, 128.8, 128.3, 127.1, 126.2, 125.7, 124.9, 123.2, 112.4, 111.1, 62.5, 59.1, 54.2, 35.5, 33.0, 13.7; IR (film) ν_{max} 494, 579, 600, 649, 680, 733, 762, 884, 912, 1032, 1078, 1109, 1144, 1210, 1299, 1370, 1454, 1475, 1509, 1574, 1597, 1713, 2256, 2935, 2984 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}ClN_4O_2Na^+$ $[M+Na]^+$ 453.1089, found 453.1090.

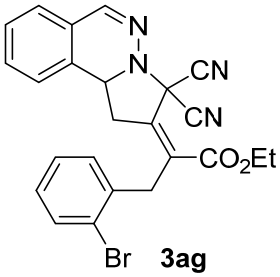
(Z)-Ethyl 3-(4-chlorophenyl)-2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)propanoate (3af)



3af

Prepared according to the general procedure as described above in 95%yield (40.9 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 95 – 96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.50 (td, *J* = 7.4, 1.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.36 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.15 – 7.10 (m, 3H), 4.60 – 4.11 (m, 3H), 3.85 (q, *J* = 15.6 Hz, 2H), 3.34 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.03 (ddd, *J* = 16.4, 10.2, 1.2 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 146.5, 141.1, 134.9, 133.8, 133.3, 132.9, 132.2, 129.3, 129.1, 128.9, 126.3, 125.1, 123.4, 112.6, 111.3, 62.6, 59.3, 54.4, 35.4, 33.1, 13.8; IR (film) ν_{max} 704, 737, 762, 804, 865, 883, 912, 1016, 1031, 1108, 1144, 1209, 1235, 1263, 1288, 1369, 1408, 1454, 1491, 1712, 2964 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}ClN_4O_2Na^+$ $[M+Na]^+$ 453.1089, found 453.1090.

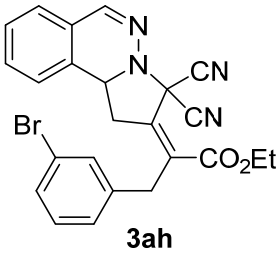
(Z)-Ethyl 3-(2-bromophenyl)-2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)propanoate (3ag)



3ag

Prepared according to the general procedure as described above in 96%yield (45.6 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 173 – 175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.63 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.50 (td, *J* = 7.4, 1.6 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.36 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H), 7.16 (td, *J* = 7.7, 1.6 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 4.50 – 4.25 (m, 3H), 4.13 – 3.79 (m, 2H), 3.31 (dd, *J* = 16.5, 5.9 Hz, 1H), 2.98 (ddd, *J* = 16.5, 10.2, 1.5 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 146.5, 141.7, 136.0, 133.4, 133.4, 133.1, 132.2, 128.9, 128.7, 128.6, 128.1, 126.3, 125.1, 124.6, 123.4, 112.5, 111.2, 62.6, 59.3, 54.4, 36.4, 33.1, 13.8; IR (film) ν_{max} 757, 884, 1029, 1109, 1146, 1209, 1235, 1264, 1300, 1369, 1442, 1469, 1565, 1610, 1713, 2353, 2984 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}BrN_4O_2Na^+$ $[M+Na]^+$ 497.0584, found 497.0584.

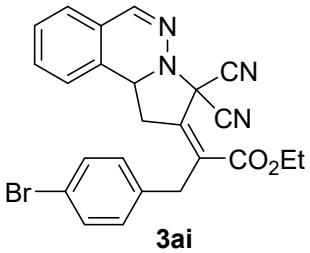
(Z)-Ethyl 3-(3-bromophenyl)-2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)propanoate (3ah)



3ah

Prepared according to the general procedure as described above in 98%yield (46.6 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 150 – 152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.51 (td, *J* = 7.4, 1.5 Hz, 1H), 7.47 – 7.33 (m, 4H), 7.23 – 7.18 (m, 1H), 7.14 – 7.09 (m, 2H), 4.55 – 4.13 (m, 3H), 3.85 (q, *J* = 15.4 Hz, 2H), 3.35 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.05 (ddd, *J* = 16.4, 10.2, 1.4 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 146.5, 141.3, 138.7, 133.6, 133.3, 132.2, 131.4, 130.5, 130.2, 129.0, 126.3, 126.3, 125.1, 123.4, 122.9, 112.5, 111.2, 62.7, 59.3, 54.4, 35.6, 33.2, 13.8; IR (film) ν_{max} 724, 738, 772, 883, 917, 1032, 1072, 1108, 1142, 1209, 1264, 1298, 1368, 1426, 1454, 1474, 1569, 1594, 1658, 1710, 2353, 2927 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}BrN_4O_2Na^+$ $[M+Na]^+$ 497.0584, found 497.0584.

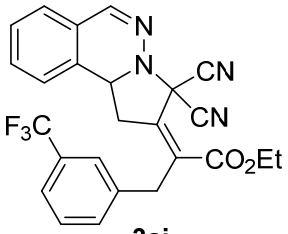
(Z)-Ethyl 3-(4-bromophenyl)-2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)propanoate (3ai)



3ai

Prepared according to the general procedure as described above in 99%yield (47.1 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 123 – 125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.37 – 7.34 (m, 1H), 7.13 – 7.07 (m, 3H), 4.50 – 4.22 (m, 3H), 3.83 (q, *J* = 15.7 Hz, 2H), 3.34 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.03 (ddd, *J* = 16.4, 10.2, 1.3 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 146.5, 141.2, 135.5, 133.8, 133.3, 132.2, 132.0, 129.7, 129.0, 126.4, 125.1, 123.4, 120.9, 112.6, 111.3, 62.7, 59.3, 54.4, 35.5, 33.1, 13.9; IR (film) ν_{max} 703, 737, 762, 802, 865, 883, 912, 934, 1012, 1031, 1072, 1109, 1145, 1209, 1235, 1264, 1288, 1302, 1369, 1404, 1454, 1488, 1563, 1610, 1658, 1713, 2938, 2983 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}BrN_4O_2Na^+$ $[M+Na]^+$ 497.0584, found 497.0584.

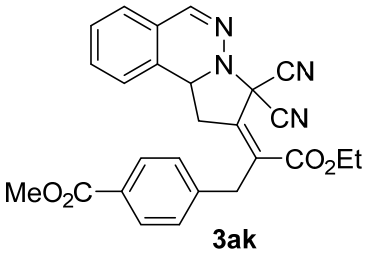
(Z)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-(3-(trifluoromethyl)phenyl)propanoate (3aj)



3aj

Prepared according to the general procedure as described above in 96%yield (44.6 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 144 – 145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.57 – 7.40 (m, 5H), 7.35 – 7.37(m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 4.50 – 4.25 (m, 3H), 3.94 (q, *J* = 15.6 Hz, 2H), 3.38 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.06 (ddd, *J* = 16.3, 10.2, 0.9 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 146.5, 141.5, 137.5, 133.5, 133.3, 132.2, 131.2 (q, *J* = 32.2 Hz), 131.0, 129.6, 129.0, 126.4, 125.3 (q, *J* = 3.8 Hz), 125.1, 124.0 (q, *J* = 272.4 Hz), 123.9 (q, *J* = 3.8 Hz), 123.4, 112.5, 111.2, 62.7, 59.3, 54.4, 35.8, 33.2, 13.7; IR (film) ν_{max} 573, 701, 739, 765, 791, 883, 1032, 1074, 1120, 1212, 1236, 1266, 1302, 1332, 1370, 1451, 1564, 1710, 2964 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{19}F_3N_4O_2Na^+$ $[M+Na]^+$ 487.1352, found 487.1354.

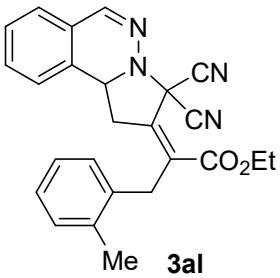
(Z)-Methyl 4-(2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-ethoxy-3-oxopropyl)benzoate (3ak)



3ak

Prepared according to the general procedure as described above in 99%yield (45.0 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 168 – 170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.92 (m, 2H), 7.80 (s, 1H), 7.49 (td, *J* = 7.4, 1.6 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.36 – 7.33 (m, 1H), 7.28 – 7.26 (m, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 4.50 – 4.17 (m, 3H), 4.08 – 3.76 (m, 5H), 3.34 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.03 (ddd, *J* = 16.5, 10.2, 1.2 Hz, 1H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 164.3, 146.5, 141.8, 141.5, 133.5, 133.3, 132.2, 130.2, 129.0, 128.9, 128.0, 126.3, 125.1, 123.4, 112.6, 111.2, 62.6, 59.3, 54.4, 52.1, 36.0, 33.2, 13.8; IR (film) ν_{max} 706, 724, 737, 761, 811, 866, 884, 914, 938, 965, 1021, 1109, 1145, 1209, 1235, 1284, 1370, 1416, 1435, 1563, 1611, 1716, 2956, 2986 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{22}N_4O_4Na^+$ $[M+Na]^+$ 477.1533, found 477.1535.

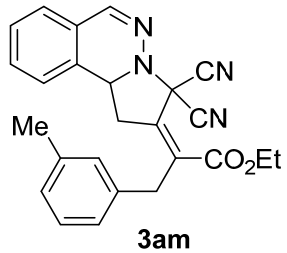
(Z)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-(o-tolyl)propanoate (3al)



3al

Prepared according to the general procedure as described above in 99%yield (40.6 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 155 – 156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.49 (td, *J* = 7.4, 1.6 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.38 – 7.35 (m, 1H), 7.27 – 7.13 (m, 3H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.02 – 6.96 (m, 1H), 4.66 – 4.22 (m, 3H), 4.09 – 3.59 (m, 2H), 3.24 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.00 (ddd, *J* = 16.4, 10.2, 1.5 Hz, 1H), 2.40 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 146.4, 140.6, 136.4, 134.6, 134.1, 133.4, 132.2, 130.6, 128.9, 127.0, 126.6, 126.3, 125.1, 123.4, 112.7, 111.4, 62.5, 59.3, 54.4, 33.4, 32.9, 19.8, 13.8; IR (film) ν_{max} 724, 755, 801, 882, 906, 932, 1027, 1107, 1144, 1220, 1262, 1299, 1369, 1453, 1491, 1712, 2351, 2963 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}N_4O_2Na^+$ $[M+Na]^+$ 433.1635, found 433.1640.

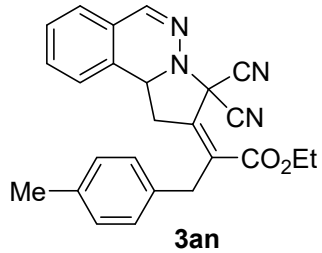
(Z)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-(m-tolyl)propanoate (3am)



3am

Prepared according to the general procedure as described above in 98%yield (40.2 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 135 – 136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.37 – 7.34 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.16 – 6.96 (m, 4H), 4.61 – 4.22 (m, 3H), 3.86 (dd, *J* = 37.8, 15.6 Hz, 2H), 3.36 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.05 (ddd, *J* = 16.5, 10.2, 1.4 Hz, 1H), 2.36 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 146.4, 140.6, 138.6, 136.3, 134.3, 133.5, 132.2, 128.9, 128.8, 127.8, 126.3, 125.1, 124.9, 123.4, 112.7, 111.4, 62.5, 59.3, 54.4, 35.9, 33.1, 21.5, 13.9; IR (film) ν_{max} 723, 737, 763, 866, 883, 919, 941, 1032, 1072, 1109, 1144, 1209, 1235, 1267, 1298, 1369, 1454, 1490, 1562, 1607, 1658, 1712, 2927, 2983 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}N_4O_2Na^+$ $[M+Na]^+$ 433.1635, found 433.1640.

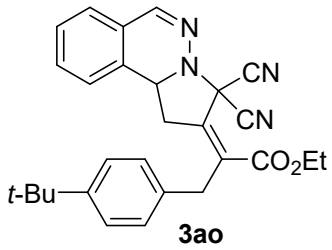
(Z)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-(p-tolyl)propanoate (3an)



3an

Prepared according to the general procedure as described above in 98%yield (40.2 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 163 – 165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.50 (td, *J* = 7.4, 1.5 Hz, 1H), 7.43 (tdd, *J* = 7.5, 1.3, 0.7 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.17 – 7.08 (m, 5H), 4.59 – 4.27 (m, 3H), 3.85 (dd, *J* = 37.7, 15.4 Hz, 2H), 3.35 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.04 (ddd, *J* = 16.4, 10.2, 1.4 Hz, 1H), 2.34 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 146.4, 140.5, 136.6, 134.5, 133.5, 133.3, 132.2, 129.6, 128.9, 127.8, 126.3, 125.1, 123.4, 112.7, 111.4, 62.5, 59.3, 54.4, 35.6, 33.0, 21.0, 13.9; IR (film) ν_{max} 479, 578, 598, 666, 724, 737, 762, 792, 865, 883, 911, 934, 1033, 1072, 1109, 1144, 1209, 1234, 1266, 1294, 1369, 1454, 1514, 1562, 1610, 1657, 1712, 2926, 2984 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}N_4O_2Na^+$ $[M+Na]^+$ 433.1635, found 433.1640.

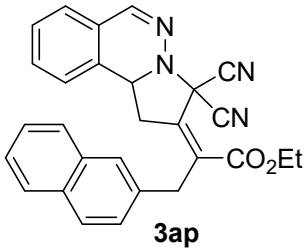
(*Z*)-Ethyl 3-(4-(tert-butyl)phenyl)-2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)propanoate (3ao)



3ao

Prepared according to the general procedure as described above in 92%yield (41.6 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a yellow semi-solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.50 (td, *J* = 7.4, 1.5 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.40 – 7.32 (m, 3H), 7.15 – 7.11 (m, 3H), 4.55 – 4.29 (m, 3H), 3.87 (dd, *J* = 41.3, 15.5 Hz, 2H), 3.37 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.06 (ddd, *J* = 16.4, 10.2, 1.2 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 149.9, 146.4, 140.5, 134.4, 133.5, 133.3, 132.2, 128.9, 127.6, 126.3, 125.9, 125.1, 123.4, 112.7, 111.4, 62.5, 59.3, 54.4, 35.4, 34.5, 33.1, 31.4, 13.8; IR (film) ν_{max} 578, 666, 738, 762, 812, 865, 883, 936, 1032, 1109, 1144, 1208, 1265, 1296, 1368, 1454, 1514, 1714, 2869, 2964 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{28}N_4O_2Na^+$ $[M+Na]^+$ 475.2104, found 475.2107.

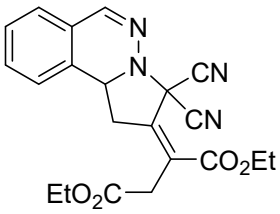
(*Z*)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-(naphthalen-2-yl)propanoate (3ap)



3ap

Prepared according to the general procedure as described above in 97%yield (43.3 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a yellow solid. mp = 65 – 66 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 4H), 7.63 (s, 1H), 7.53 – 7.45 (m, 3H), 7.44 – 7.39 (m, 1H), 7.37 – 7.32 (m, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 4.51 – 4.30 (m, 3H), 4.05 (dd, *J* = 41.4, 15.6 Hz, 2H), 3.39 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.06 (ddd, *J* = 16.5, 10.2, 1.4 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 146.4, 141.0, 134.2, 134.0, 133.5, 133.4, 132.4, 132.2, 128.9, 128.8, 127.7, 126.4, 126.4, 126.3, 126.3, 125.9, 125.1, 123.4, 112.7, 111.4, 62.6, 59.4, 54.4, 36.1, 33.1, 13.9; IR (film) ν_{max} 475, 738, 800, 817, 862, 883, 918, 939, 1032, 1109, 1144, 1220, 1265, 1290, 1369, 1454, 1508, 1562, 1601, 1711, 2983, 3054 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}N_4O_2Na^+$ $[M+Na]^+$ 469.1635, found 469.1636.

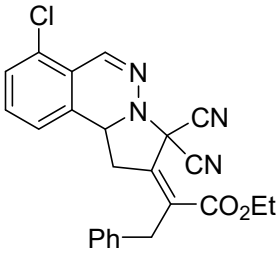
(Z)-Diethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)succinate (3aq)



3aq

Prepared according to the general procedure as described above in 94%yield (36.9 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 133 – 135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.50 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.34 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 4.54 – 4.29 (m, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.55 (dt, *J* = 51.7, 9.0 Hz, 2H), 3.33 (dd, *J* = 16.3, 5.8 Hz, 1H), 3.05 (ddd, *J* = 16.2, 10.2, 0.6 Hz, 1H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 163.8, 146.4, 142.5, 133.3, 132.2, 129.0, 128.9, 126.3, 125.1, 123.4, 112.4, 111.0, 62.7, 61.6, 59.1, 54.3, 36.1, 33.2, 14.1, 13.9; IR (film) ν_{max} 581, 665, 763, 884, 918, 944, 1032, 1110, 1146, 1196, 1296, 1334, 1370, 1454, 1562, 1732, 2985 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_4O_4Na^+$ $[M+Na]^+$ 415.1377, found 415.1380.

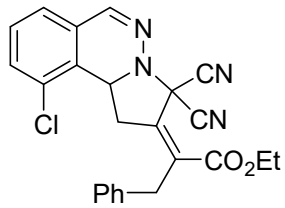
(Z)-Ethyl 2-(7-chloro-3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-phenylpropanoate (3ba)



3ba

Prepared according to the general procedure as described above in 93%yield (40.1 mg). It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. mp = 49 – 50°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.46 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.36 – 7.31 (m, 2H), 7.31 – 7.24 (m, 2H), 7.24 – 7.18 (m, 2H), 4.63 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.51 – 4.23 (m, 2H), 4.00 – 3.80 (m, 2H), 3.71 (dd, *J* = 17.0, 5.6 Hz, 1H), 3.25 (dd, *J* = 17.0, 10.4 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 145.3, 140.5, 136.5, 134.1, 133.3, 131.1, 131.0, 130.2, 128.9, 128.1, 127.3, 127.0, 125.4, 112.4, 111.4, 62.5, 59.5, 54.6, 36.1, 35.4, 13.8; IR (film) ν_{max} 667, 701, 738, 778, 800, 862, 918, 938, 963, 1030, 1095, 1131, 1153, 1197, 1223, 1239, 1266, 1299, 1369, 1452, 1495, 1558, 1603, 1658, 1712, 2356, 2985, 3030 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}ClN_4O_2Na^+$ $[M+Na]^+$ 453.1089, found 453.1090.

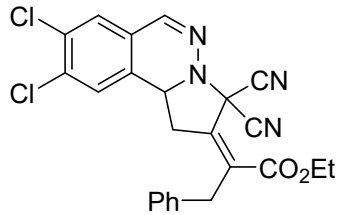
(*Z*)-Ethyl 2-(10-chloro-3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-phenylpropanoate (3ca)



3ca

Prepared according to the general procedure as described above in 94%yield (40.5 mg). It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. mp = 157 – 158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 7.21 – 7.18 (m, 2H), 7.05 – 7.00 (m, 1H), 4.55 – 4.21 (m, 3H), 3.89 (q, *J* = 15.8 Hz, 2H), 3.36 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.04 (ddd, *J* = 16.4, 10.2, 1.3 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 142.9, 140.3, 136.3, 135.5, 134.5, 133.0, 132.5, 130.0, 129.0, 127.9, 127.0, 122.7, 122.1, 112.5, 111.2, 62.6, 59.2, 54.3, 35.9, 33.0, 13.8; IR (film) ν_{max} 599, 683, 703, 745, 783, 878, 926, 969, 1031, 1077, 1136, 1157, 1208, 1230, 1288, 1369, 1446, 1495, 1555, 1601, 1657, 1712, 2984, 3030 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{19}ClN_4O_2Na^+$ $[M+Na]^+$ 453.1089, found 453.1090.

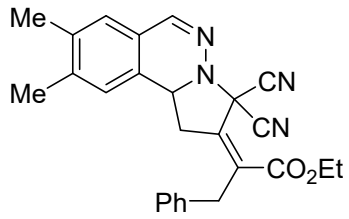
(*Z*)-Ethyl 2-(8,9-dichloro-3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-phenylpropanoate (3da)



3da

Prepared according to the general procedure as described above in 95%yield (44.2 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 173 – 175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.42 (s, 1H), 7.40 – 7.31 (m, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.18 (m, 3H), 4.50 – 4.27 (m, 3H), 3.89 (dd, *J* = 43.5, 15.5 Hz, 2H), 3.33 (dd, *J* = 16.3, 5.9 Hz, 1H), 3.03 (ddd, *J* = 16.4, 10.2, 1.2 Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 144.0, 139.7, 136.2, 136.0, 134.8, 133.3, 132.8, 129.0, 127.9, 127.1, 125.8, 124.7, 112.4, 111.1, 62.7, 59.1, 53.8, 35.9, 32.8, 13.8; IR (film) ν_{max} 583, 619, 647, 673, 700, 734, 792, 910, 974, 1031, 1078, 1126, 1209, 1237, 1303, 1370, 1453, 1478, 1495, 1543, 1604, 1712, 2255, 2984, 3031 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{18}Cl_2N_4O_2Na^+$ $[M+Na]^+$ 487.0699, found 487.0701.

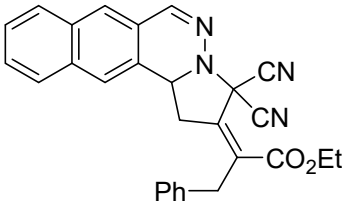
(Z)-Ethyl 2-(3,3-dicyano-8,9-dimethyl-1,10b-dihydropyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-phenylpropanoate (3ea)



3ea

Prepared according to the general procedure as described above in 98%yield (41.6 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a white solid. mp = 151 – 153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 2H), 7.12 (s, 1H), 6.88 (s, 1H), 4.49 – 4.24 (m, 3H), 3.90 (dd, *J* = 40.3, 15.7 Hz, 2H), 3.33 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.02 (ddd, *J* = 16.4, 10.2, 1.4 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 146.6, 141.5, 141.1, 137.3, 136.5, 134.1, 131.1, 128.9, 127.9, 127.5, 127.0, 124.6, 123.0, 112.8, 111.4, 62.4, 59.4, 54.3, 35.9, 33.2, 20.1, 19.5, 13.8; IR (film) ν_{max} 701, 739, 804, 866, 908, 1030, 1072, 1094, 1138, 1214, 1264, 1304, 1369, 1453, 1495, 1553, 1603, 1622, 1657, 1713, 2980, 3028 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{24}N_4O_2Na^+$ $[M+Na]^+$ 447.1791, found 447.1791.

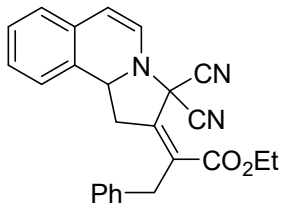
(Z)-Ethyl 2-(3,3-dicyano-1,12b-dihydrobenzo[g]pyrrolo[2,1-*a*]phthalazin-2(3*H*)-ylidene)-3-phenylpropanoate (3fa)



3fa

Prepared according to the general procedure as described above in 99%yield (44.2 mg). It was purified by flash chromatography (16% EtOAc/PE) to afford a red solid. mp = 83 – 85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 3H), 7.65 (s, 1H), 7.62 – 7.52 (m, 2H), 7.42 – 7.33 (m, 3H), 7.32 – 7.28 (m, 1H), 7.26 – 7.23 (m, 2H), 4.54 – 4.25 (m, 3H), 3.92 (dd, *J* = 47.9, 15.8 Hz, 2H), 3.38 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.02 (ddd, *J* = 16.5, 10.3, 1.4 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 146.4, 140.7, 136.5, 134.6, 134.2, 132.7, 130.7, 129.1, 129.0, 128.3, 128.0, 127.8, 127.3, 127.0, 126.8, 122.6, 122.5, 112.9, 111.4, 62.5, 59.6, 55.0, 36.0, 33.1, 13.9; IR (film) ν_{max} 477, 580, 616, 639, 701, 751, 806, 867, 911, 1031, 1075, 1108, 1137, 1221, 1302, 1328, 1368, 1453, 1495, 1566, 1604, 1657, 1712, 2931, 2983, 3029 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}N_4O_2Na^+$ $[M+Na]^+$ 469.1635, found 469.1638.

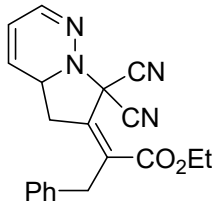
(Z)-Ethyl 2-(3,3-dicyano-1,10b-dihydropyrrolo[2,1-*a*]isoquinolin-2(3*H*)-ylidene)-3-phenylpropanoate (3ga)



3ga

Prepared according to the general procedure as described above in 88%yield (34.8 mg). It was purified by flash chromatography (5% EtOAc/PE) to afford a white solid. mp = 112 – 114 °C; ^{1}H NMR (300 MHz, DMSO) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.16 (m, 5H), 7.14 – 7.08 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.02 (d, *J* = 7.6 Hz, 1H), 4.54 (dd, *J* = 9.8, 5.5 Hz, 1H), 4.27 – 4.10 (m, 2H), 3.84 (s, 2H), 3.72 (dd, *J* = 17.1, 5.7 Hz, 1H), 3.17 (dd, *J* = 17.2, 10.0 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO) δ 165.0, 144.1, 137.5, 132.8, 131.5, 130.8, 129.6, 128.9, 128.5, 127.6, 126.9, 124.7, 124.6, 112.8, 112.2, 110.1, 62.1, 57.5, 56.4, 36.1, 35.1, 13.9; IR (film) ν_{max} 566, 636, 702, 737, 771, 865, 939, 1031, 1077, 1098, 1210, 1257, 1299, 1368, 1408, 1456, 1494, 1566, 1622, 1710, 2930, 2983, 3028 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{20}N_3O_2^-$ $[M-H]^-$ 394.1561, found 394.1562.

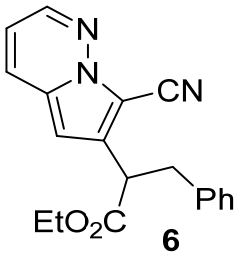
(Z)-Ethyl 2-(7,7-dicyano-4a,5-dihydropyrrolo[1,2-*b*]pyridazin-6(7*H*)-ylidene)-3-phenylpropanoate (5)



5

Prepared according to the general procedure as described above in 78%yield (27.0 mg). It was purified by flash chromatography (9% EtOAc/Petroleum ether containing 1% Et_3N) to afford a white solid. mp = 110 – 111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 3H), 7.28 – 7.22 (m, 1H), 7.19 – 7.12 (m, 2H), 6.18 (dt, *J* = 9.6, 1.9 Hz, 1H), 6.01 (dt, *J* = 9.6, 2.7 Hz, 1H), 4.49 – 4.26 (m, 2H), 4.01 (ddt, *J* = 10.3, 5.8, 2.3 Hz, 1H), 3.81 (dd, *J* = 35.3, 15.4 Hz, 2H),3.02 (dd, *J* = 16.5, 5.8 Hz, 1H), 2.81 (ddd, *J* = 16.5, 10.1, 1.4 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 143.9, 140.6, 136.4, 134.3, 130.4, 128.9, 127.9, 127.0, 120.5, 112.5, 111.2, 62.5, 58.6, 51.6, 35.8, 33.9, 13.8; IR (film) ν_{max} 511, 568, 649, 700, 738, 833, 914, 1026, 1091, 1152, 1234, 1294, 1369, 1396, 1454, 1495, 1542, 1603, 1712, 2255, 2984, 3030 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{18}N_4O_2Na^+$ $[M+Na]^+$ 369.1322, found 369.1323.

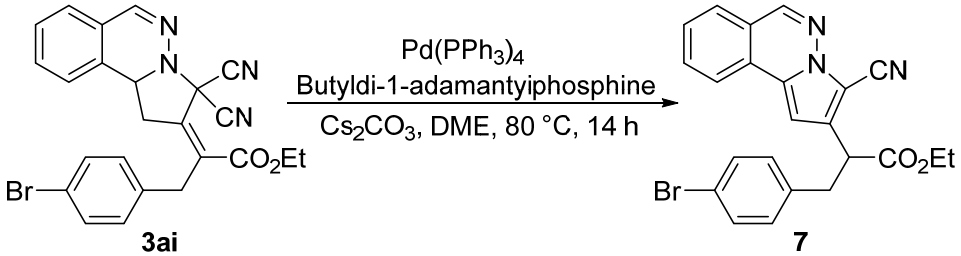
Ethyl 2-(7-cyanopyrrolo[1,2-*b*]pyridazin-6-yl)-3-phenylpropanoate (6)



6

Prepared according to the general procedure as described above in 19%yield (6.1 mg). It was purified by flash chromatography (9% EtOAc/Petroleum ether containing 1% Et_3N) to afford a white solid. mp = 90 – 92 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 4.5, 1.7 Hz, 1H), 7.77 (dd, *J* = 9.1, 1.7 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.25 – 7.23 (m, 1H), 7.23 – 7.15 (m, 3H), 6.82 (dd, *J* = 9.1, 4.5 Hz, 1H), 6.62 (s, 1H), 4.32 – 4.20 (m, 1H), 4.20 – 4.03 (m, 2H), 3.48 (dd, *J* = 13.7, 8.4 Hz, 1H), 3.18 (dd, *J* = 13.7, 7.4 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 143.1, 137.7, 133.6, 129.7, 128.7, 128.3, 126.9, 126.6, 114.2, 111.7, 100.1, 100.0, 61.1, 45.8, 39.5, 13.9; IR (film) ν_{max} 513, 700, 749, 800, 1029, 1096, 1152, 1215, 1295, 1324, 1370, 1443, 1496, 1539, 1604, 1732, 2216, 2928, 2962, 3029 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{17}N_3O_2Na^+$ $[M+Na]^+$ 342.1213, found 342.1211.

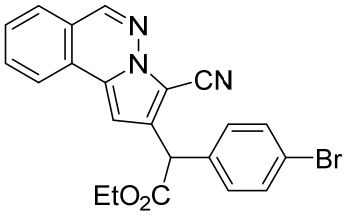
Transformations of the product 3ai



3ai **7**

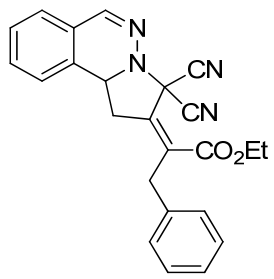
Under argon atmosphere, the compound **3ai** (47.5 mg, 0.1 mmol), Cs_2CO_3 (0.2 mmol), $Pd(Ph_3P)_4$ (0.005 mmol) and butyldi-1-adamantylphosphine (0.006 mmol) were added sequentially to a dry tube. After adding DME (1.0 mL) to the reaction system, the reaction mixture was stirred at 80 °C for 14 h. Then, the reaction mixture was subjected to flash column chromatography (9% EtOAc/PE) to afford the product **7** in 78% yield (34.9 mg).

Ethyl 9-(4-bromophenyl)-8-cyano-12,12a-dihydroazepino[2,1-*a*]phthalazine-10-carboxylate (7)

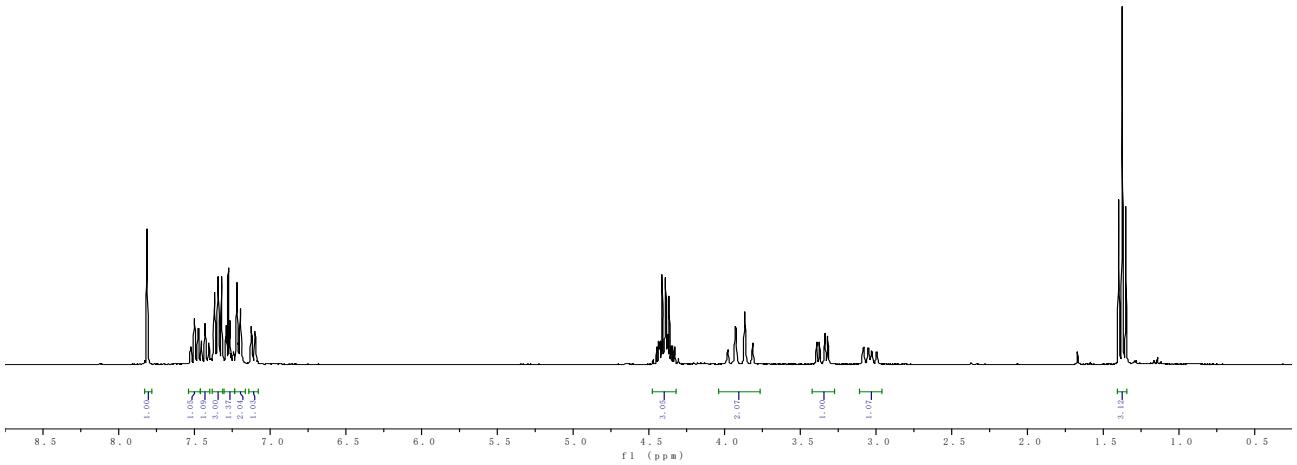


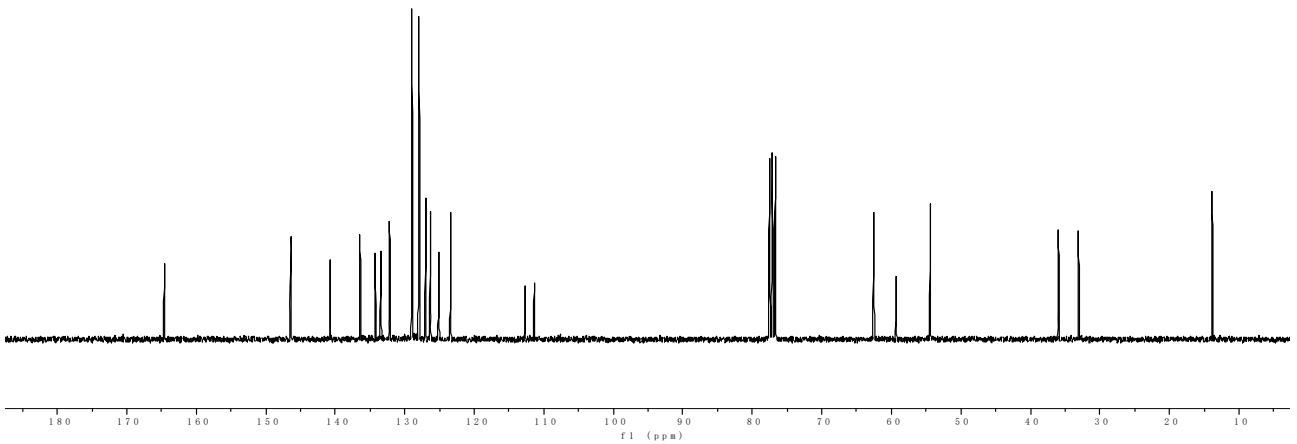
7

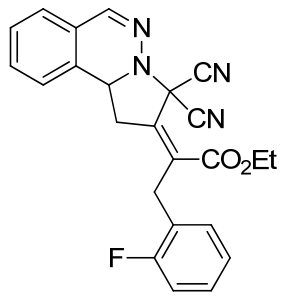
A white solid. mp = 151 – 153 °C; ^{1}H NMR (300 MHz, DMSO) δ 8.93 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.93 (t, *J* = 7.7 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.34 (s, 1H), 7.23 – 7.12 (m, 2H), 4.17 (t, *J* = 7.9 Hz, 1H), 4.14 – 3.99 (m, 2H), 3.42 (dd, *J* = 13.6, 7.5 Hz, 1H), 3.19 (dd, *J* = 13.7, 8.4 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO) δ 171.5, 146.5, 137.9, 134.0, 132.3, 131.4, 131.4, 129.2, 129.0, 127.3, 126.1, 122.8, 120.7, 119.9, 112.3, 100.3, 99.8, 61.2, 45.5, 37.4, 14.2; IR (film) ν_{max} 584, 760, 806, 1012, 1072, 1098, 1153, 1204, 1329, 1431, 1489, 1535, 1624, 1732, 2216, 2982 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{18}BrN_3O_2Na^+$ $[M+Na]^+$ 472.0457, found 472.0456.



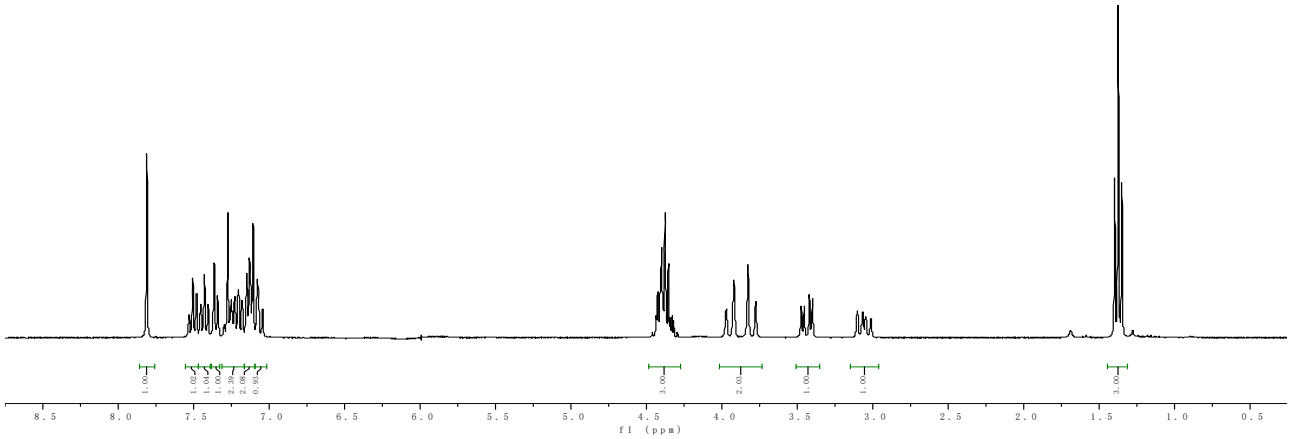
3aa

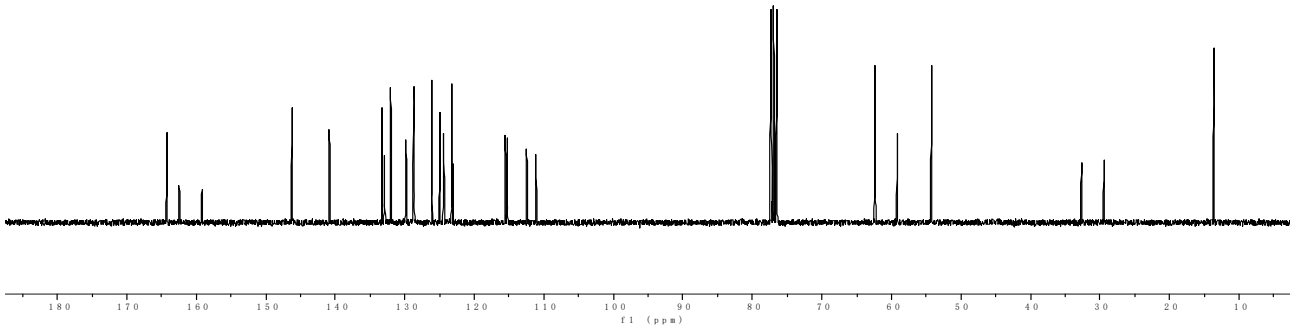


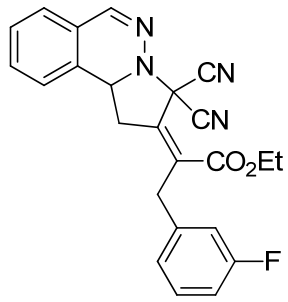




3ab







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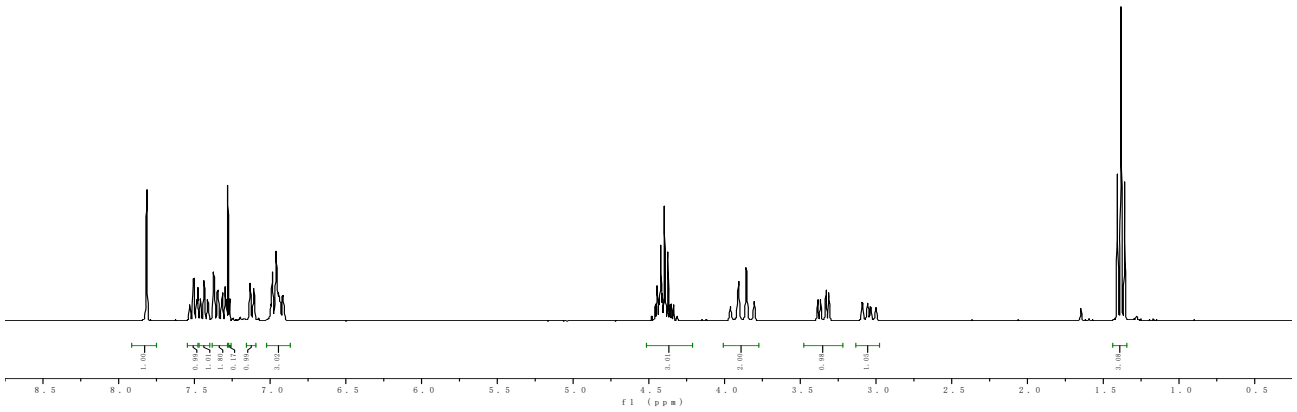

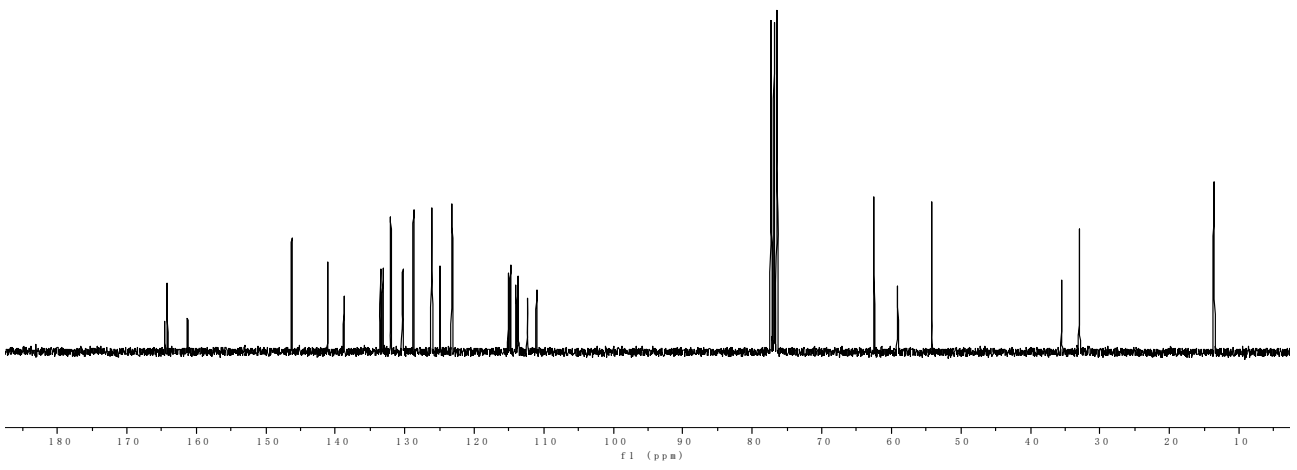

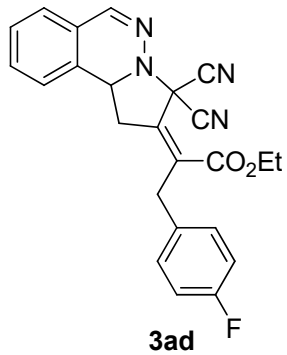

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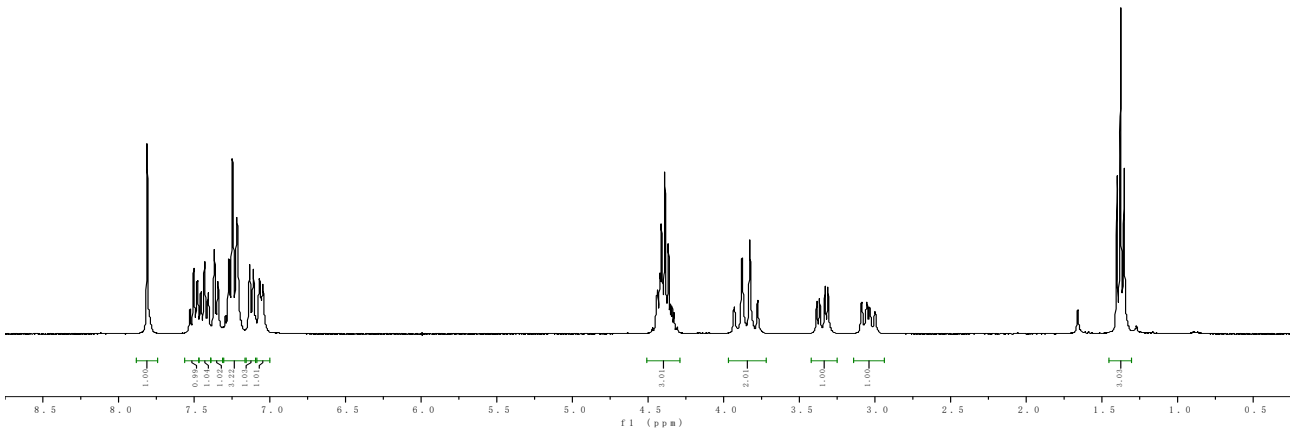

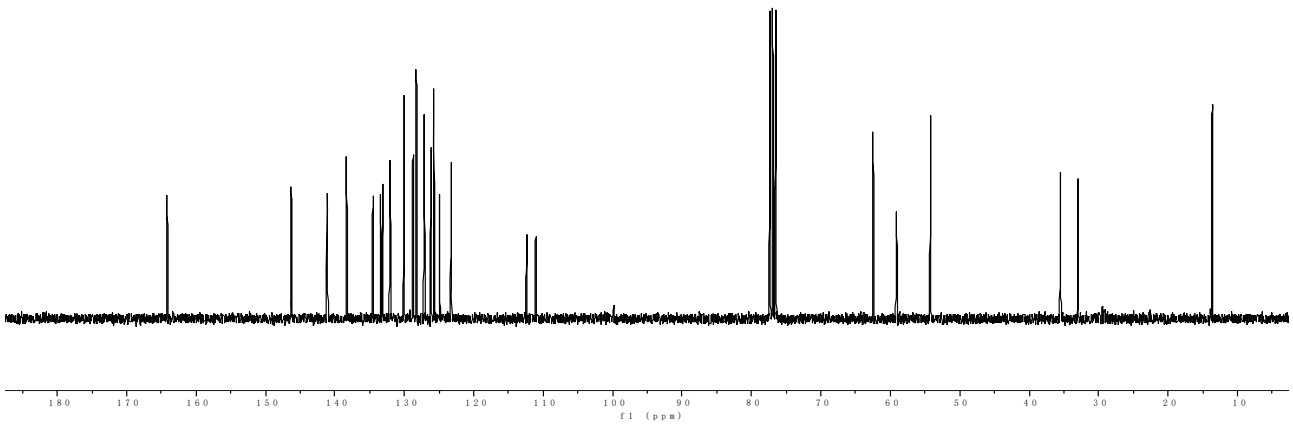

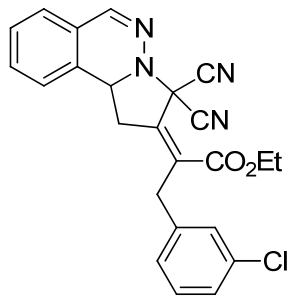

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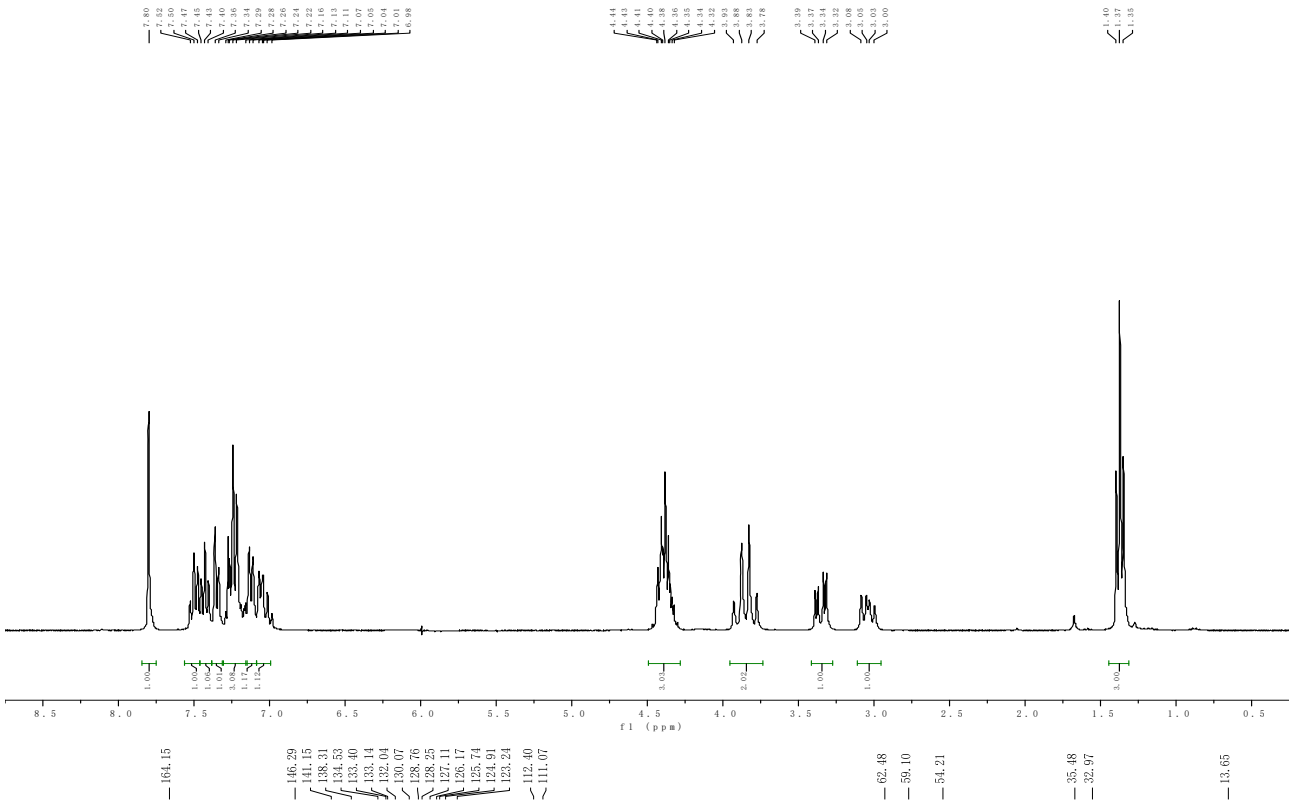

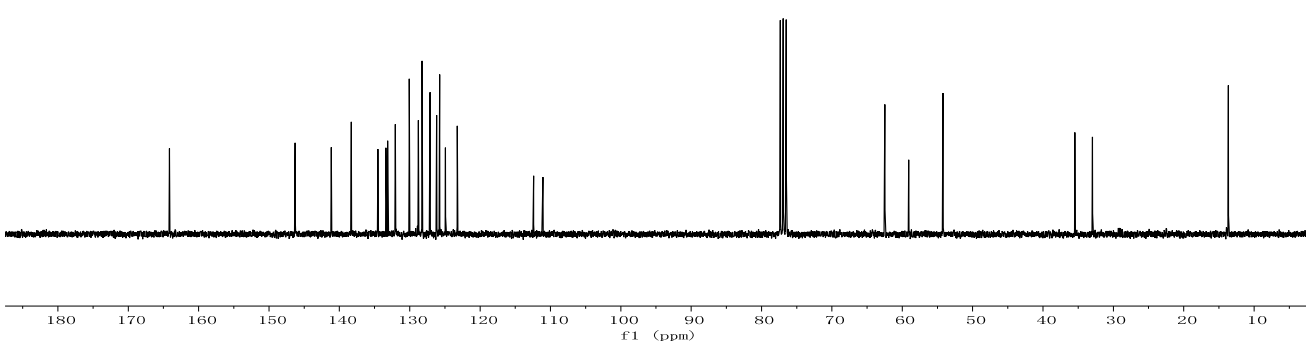

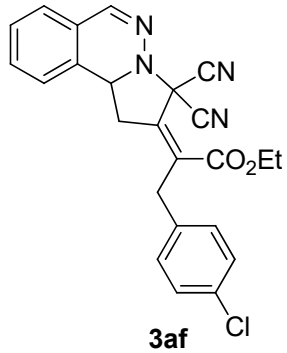

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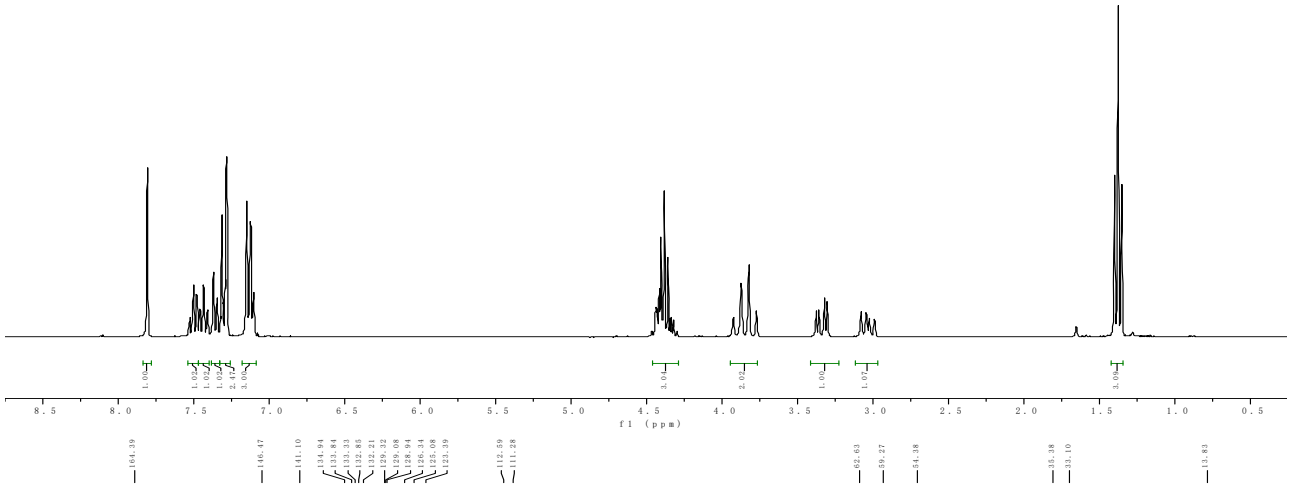

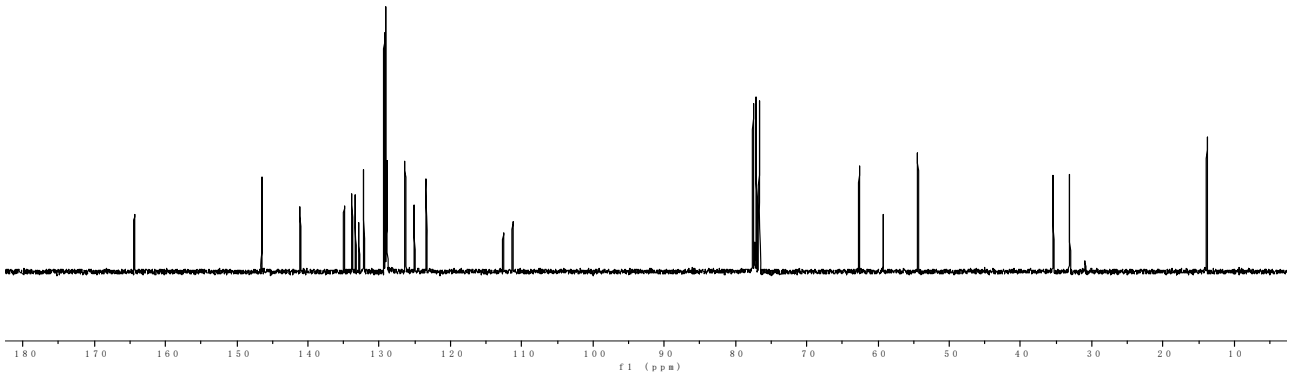

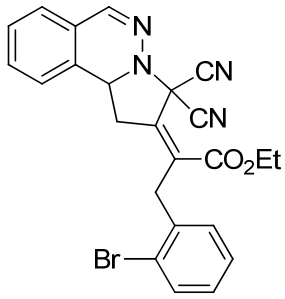

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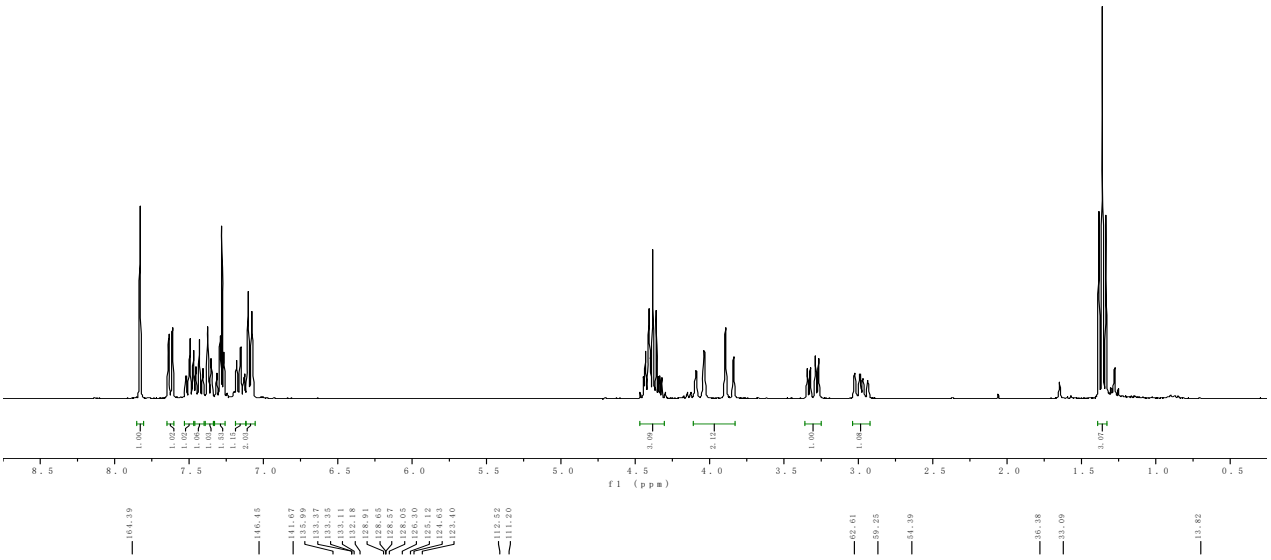
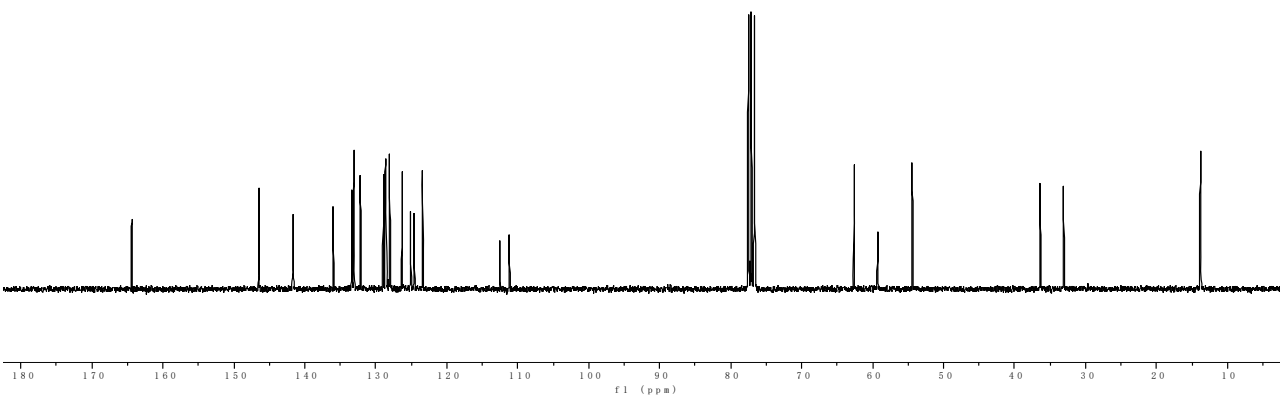
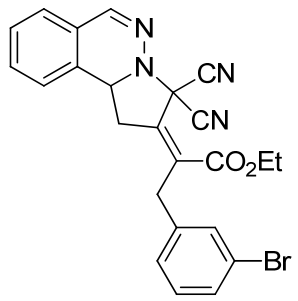
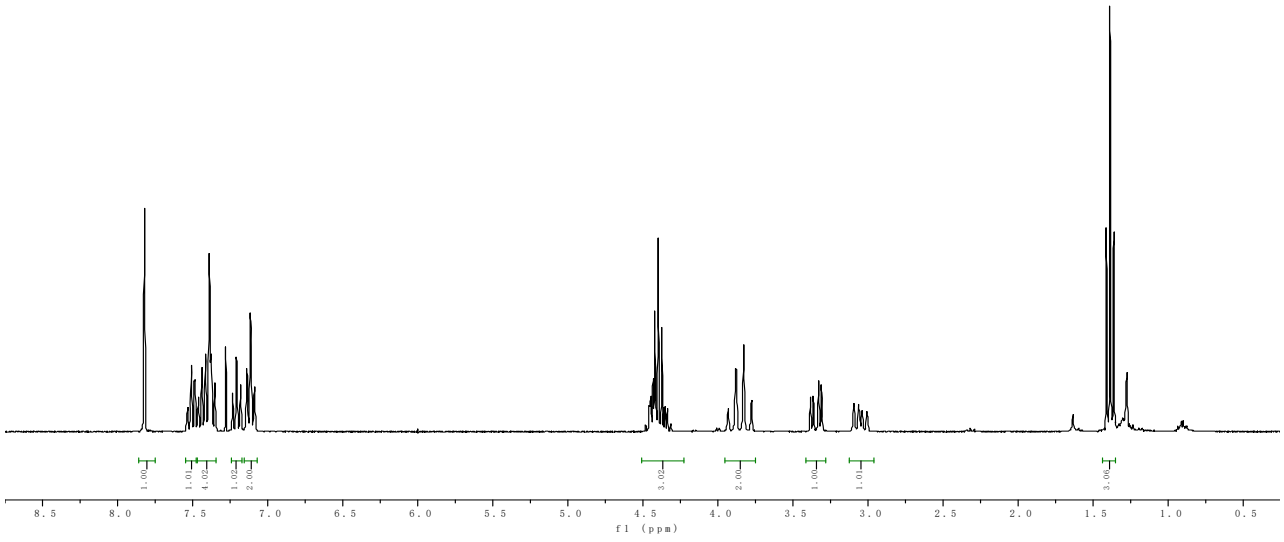
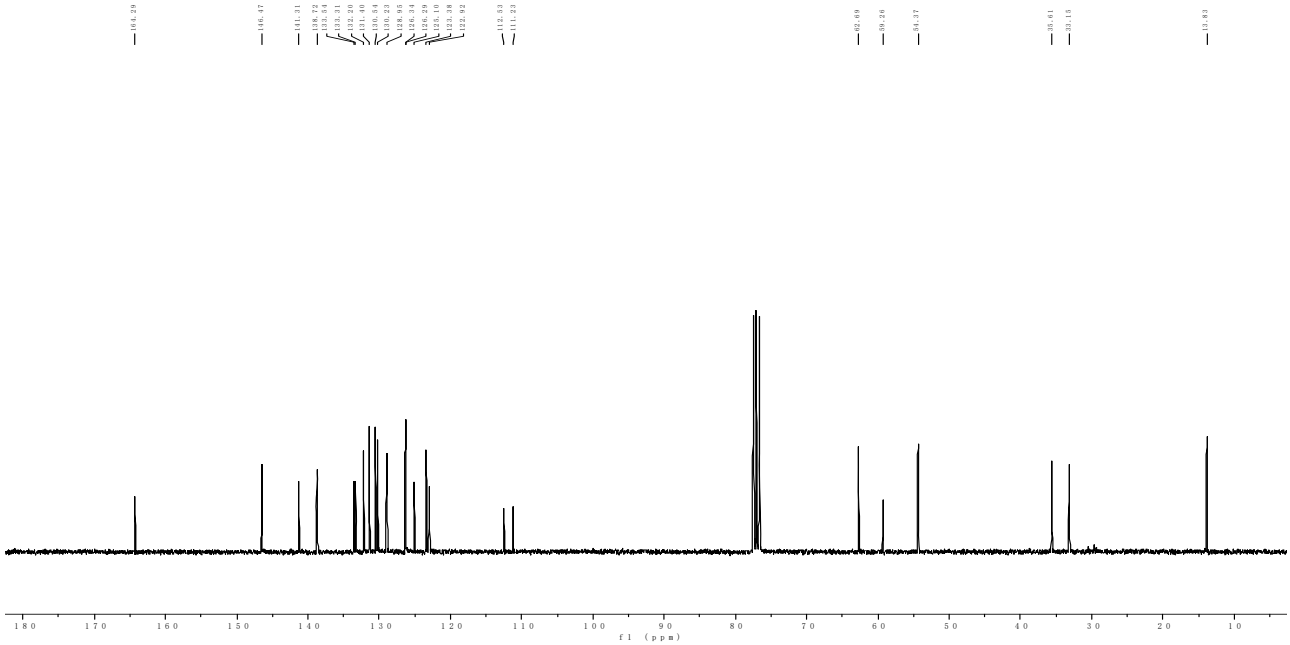


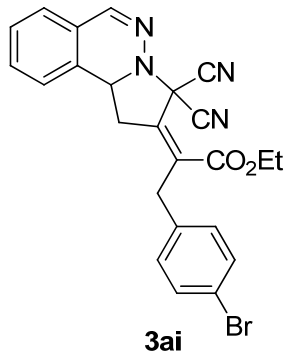




3ah







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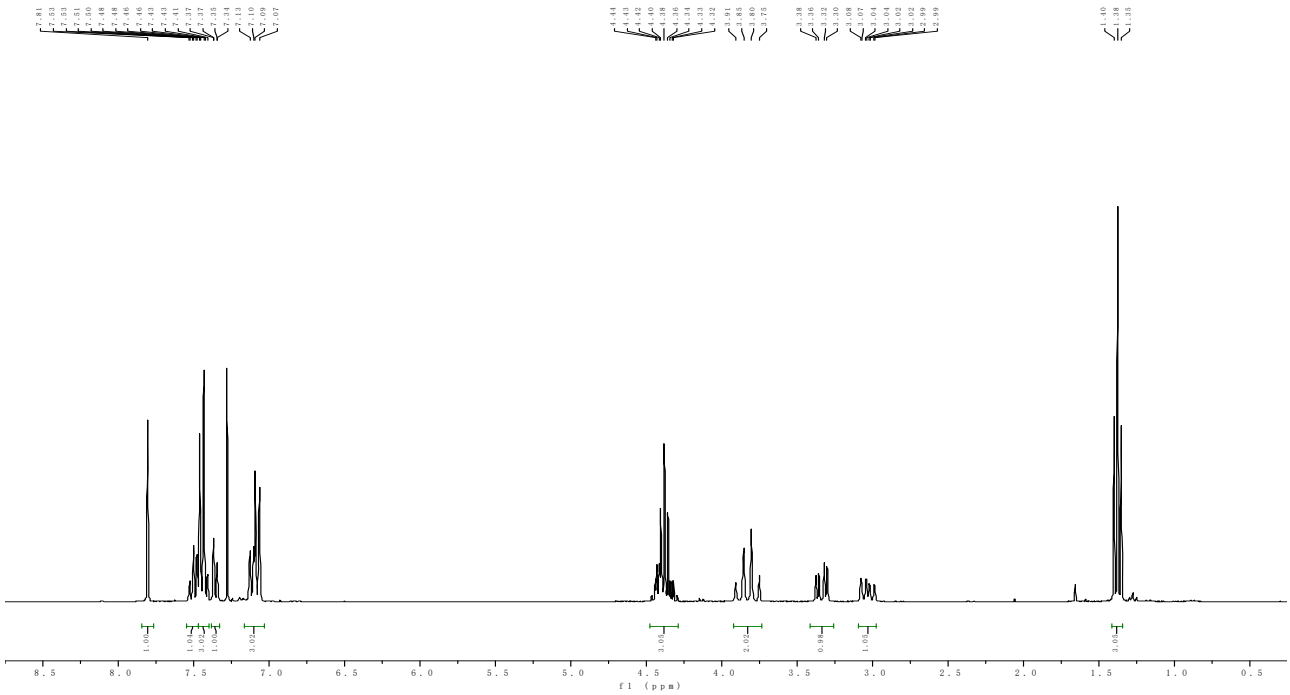

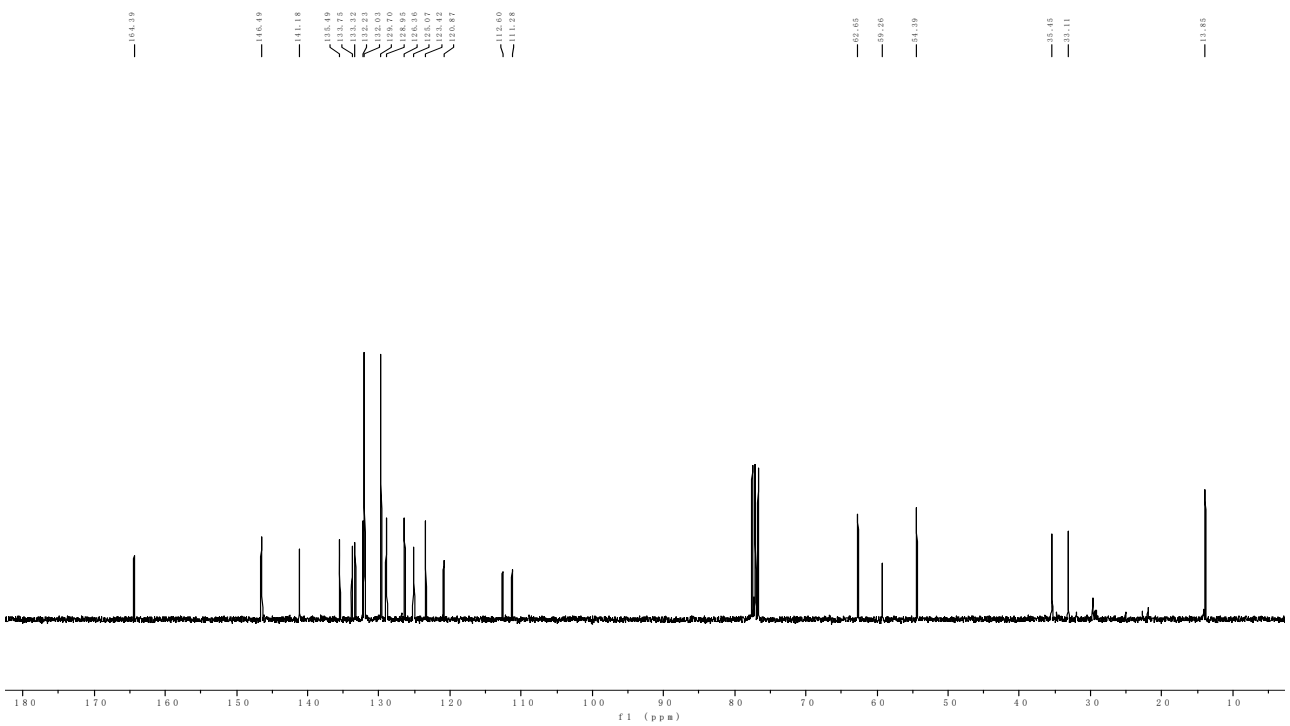

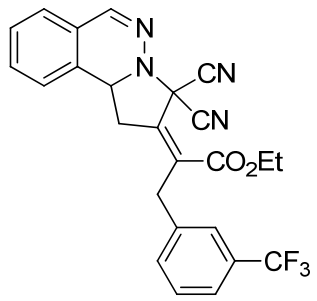

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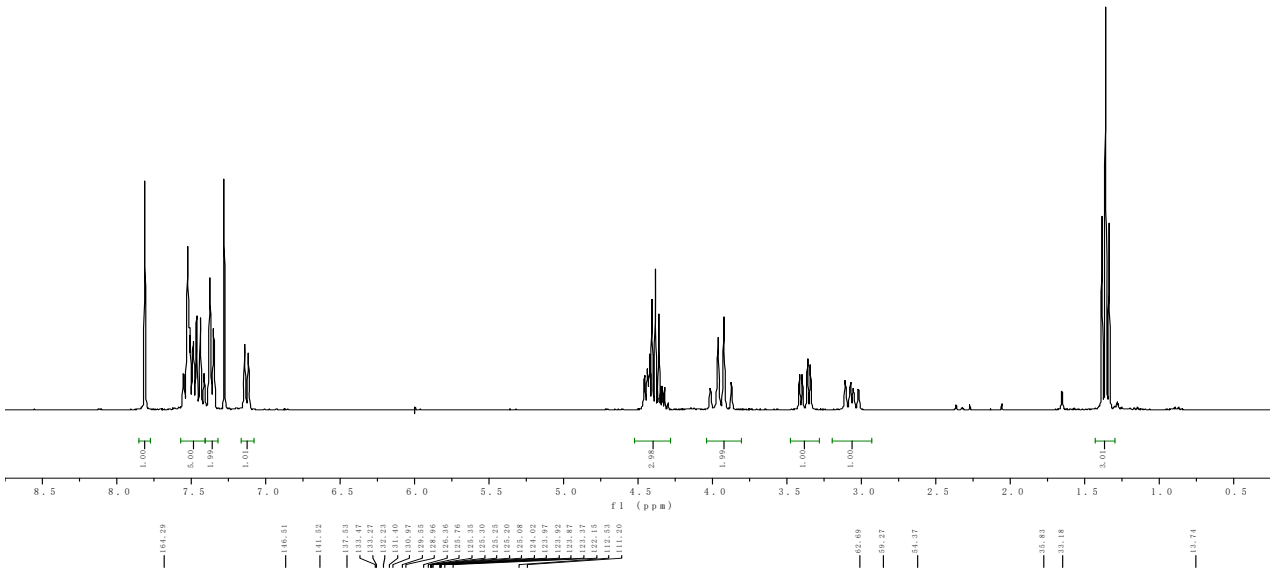

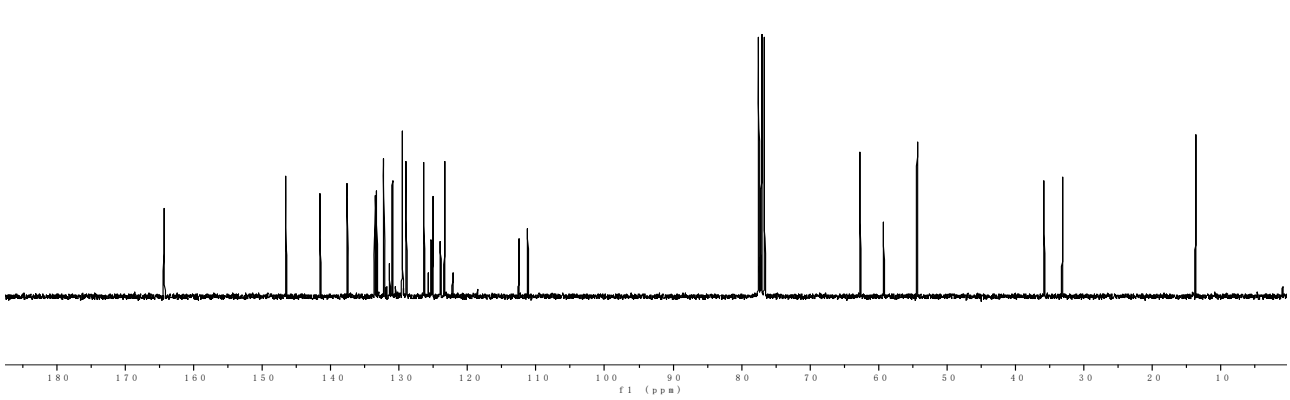

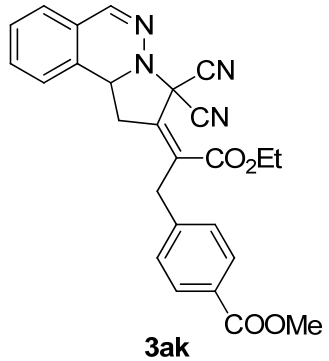

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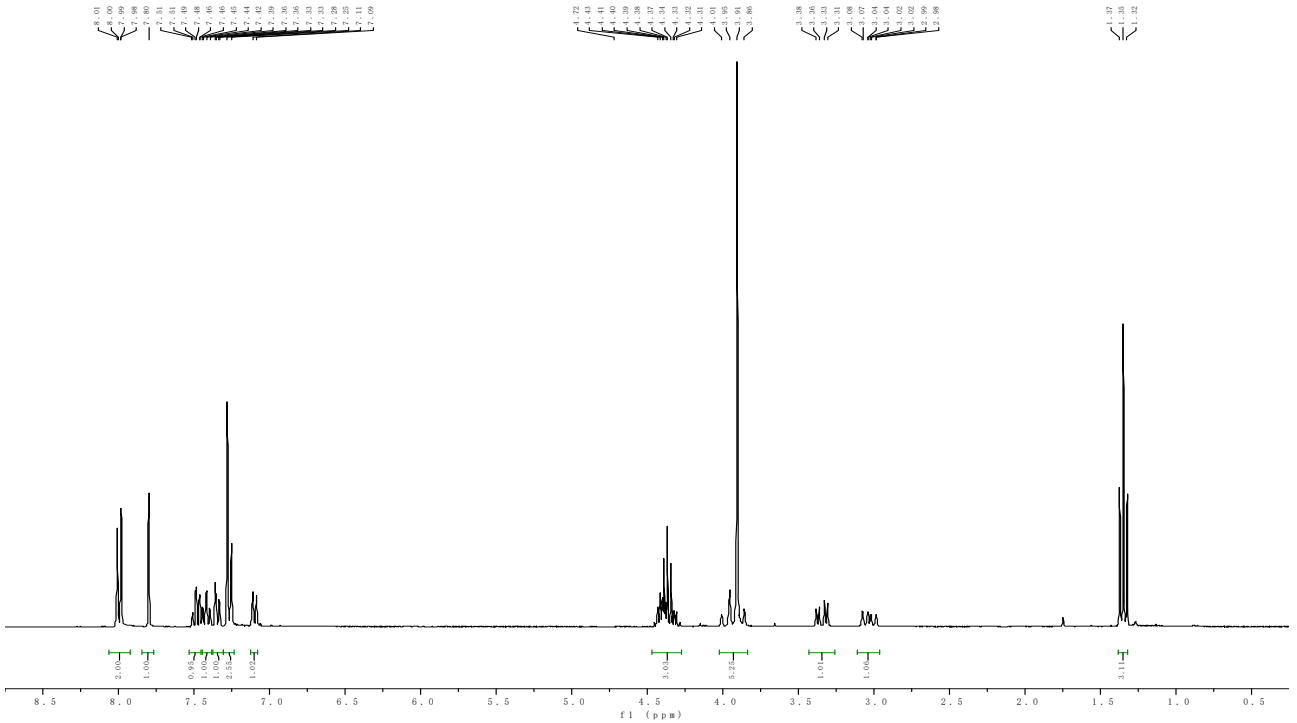

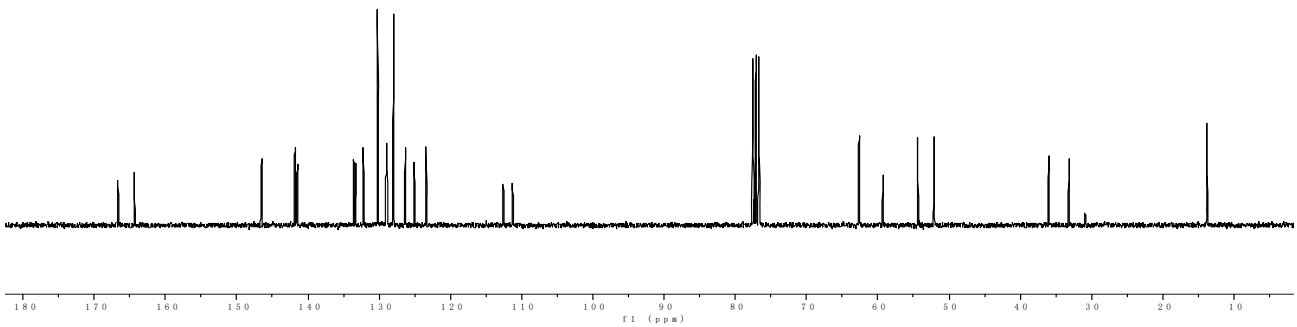

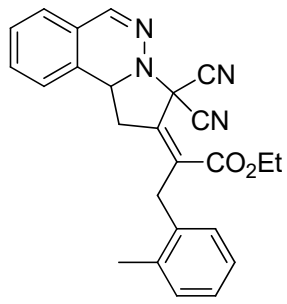

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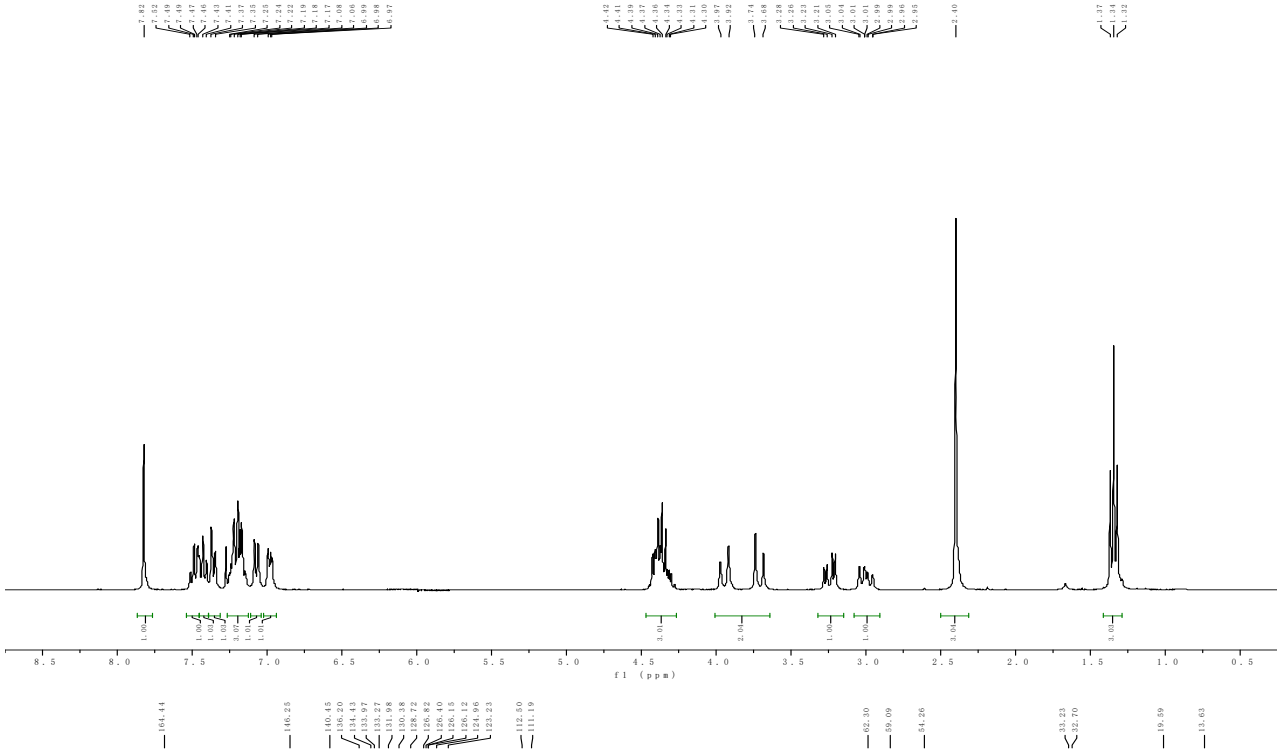

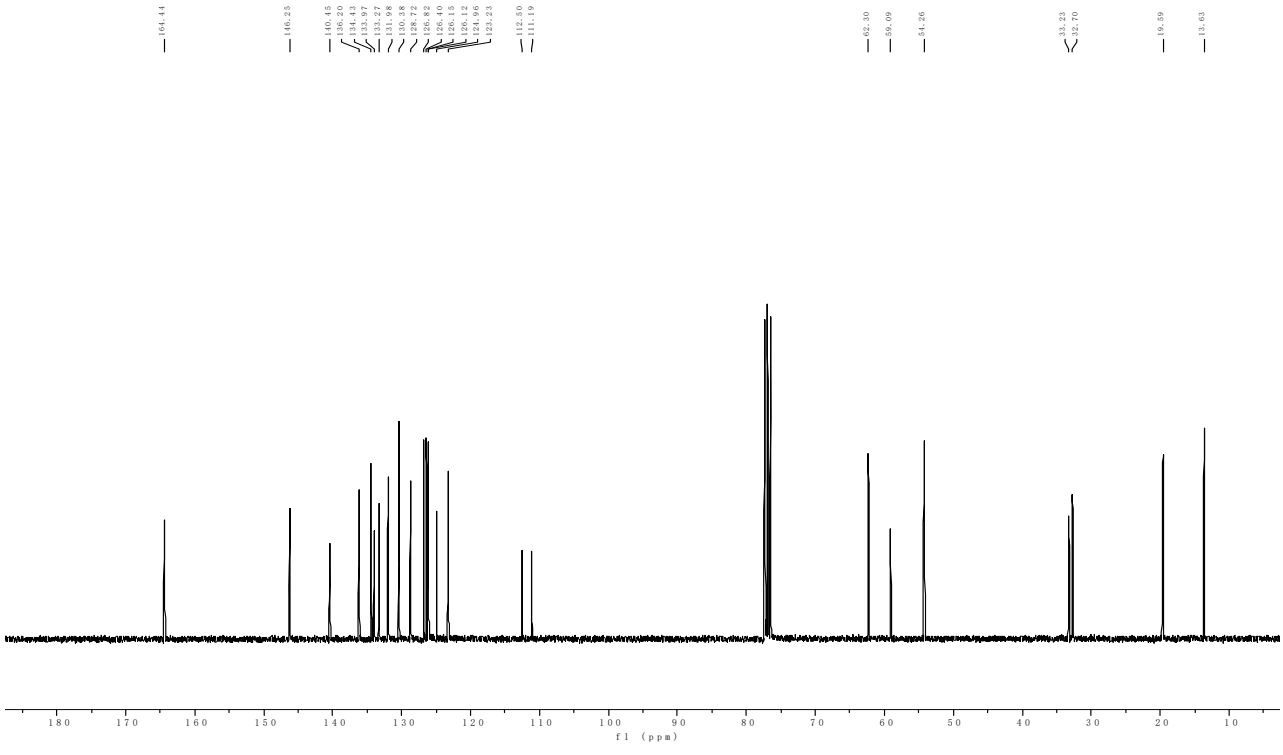

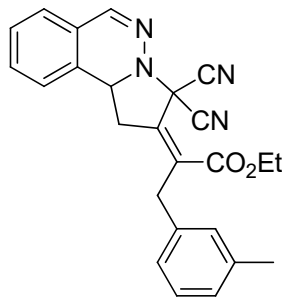

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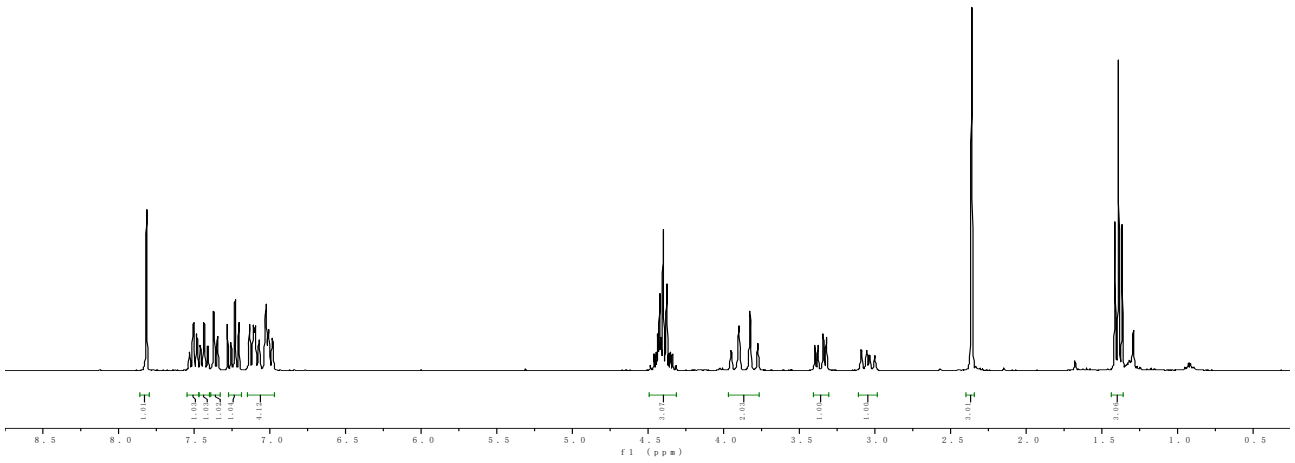

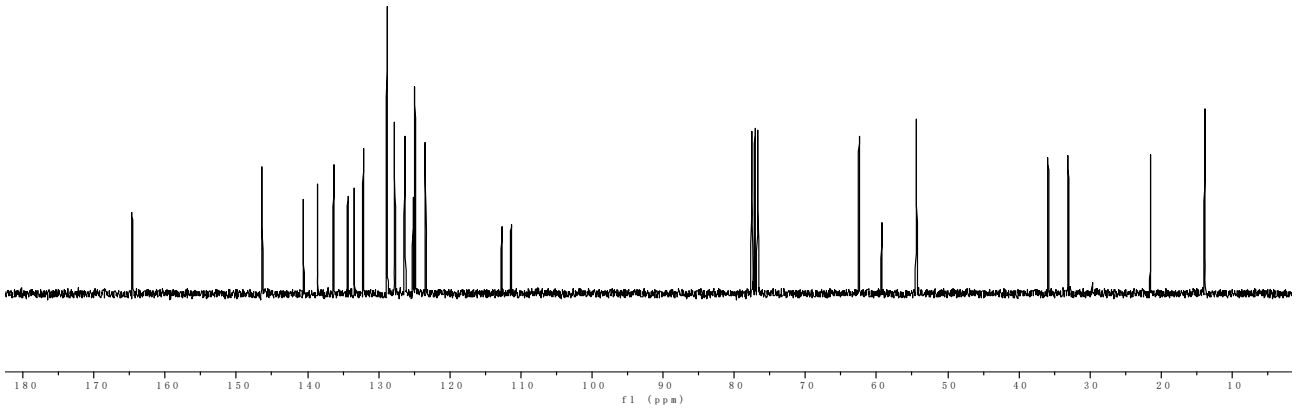

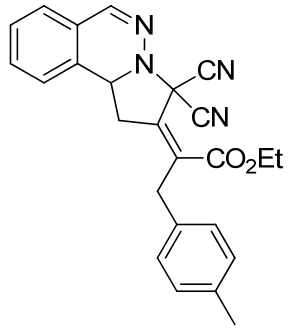

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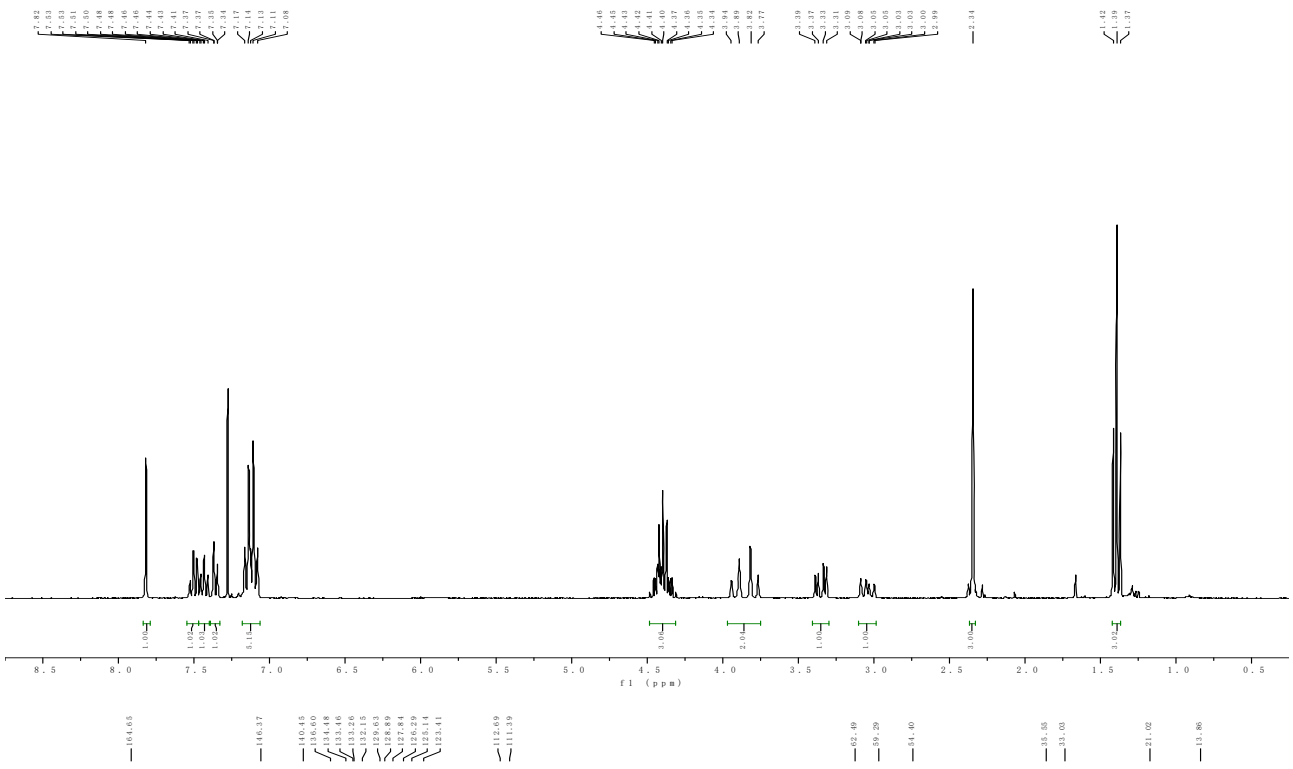

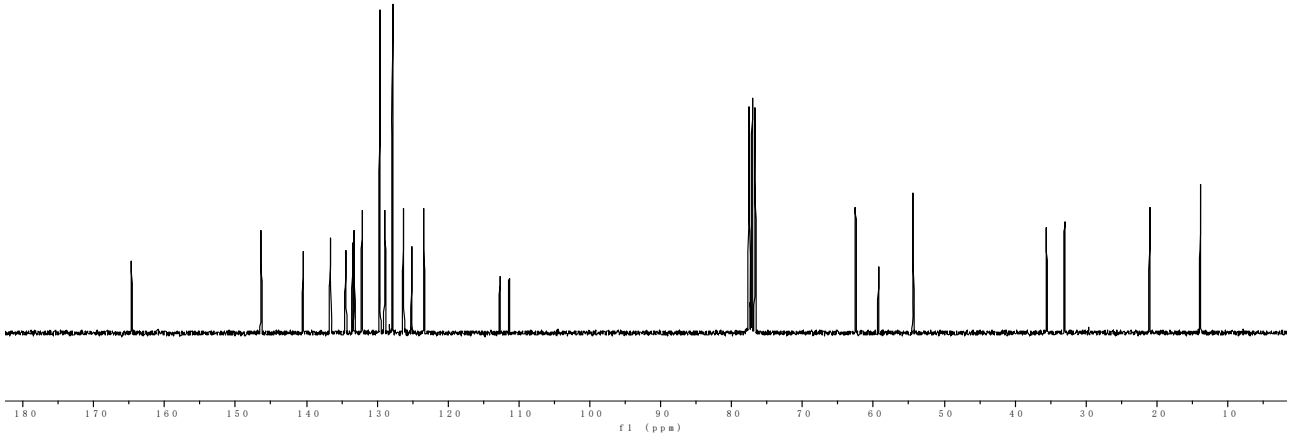

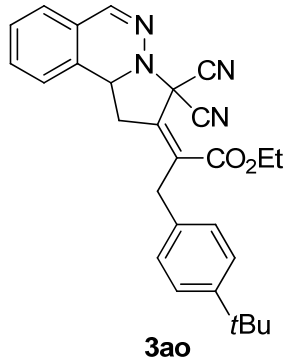

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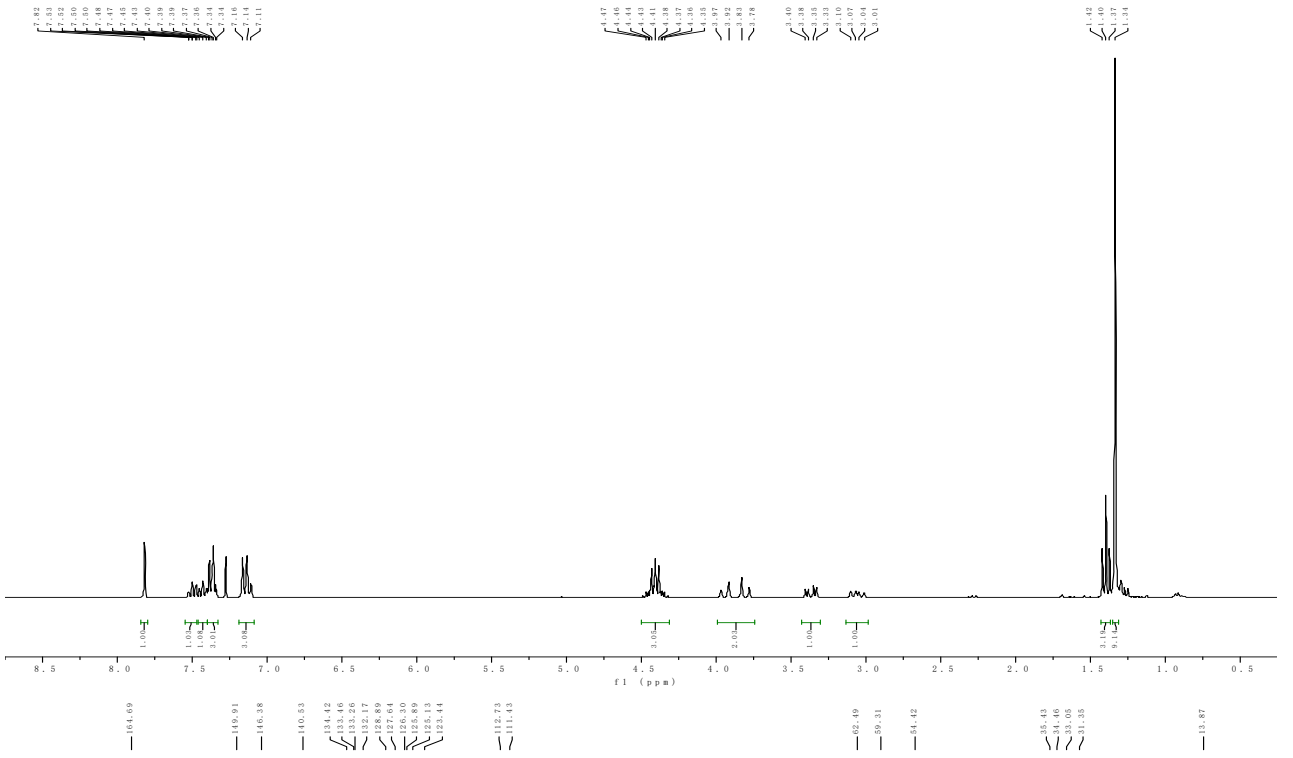

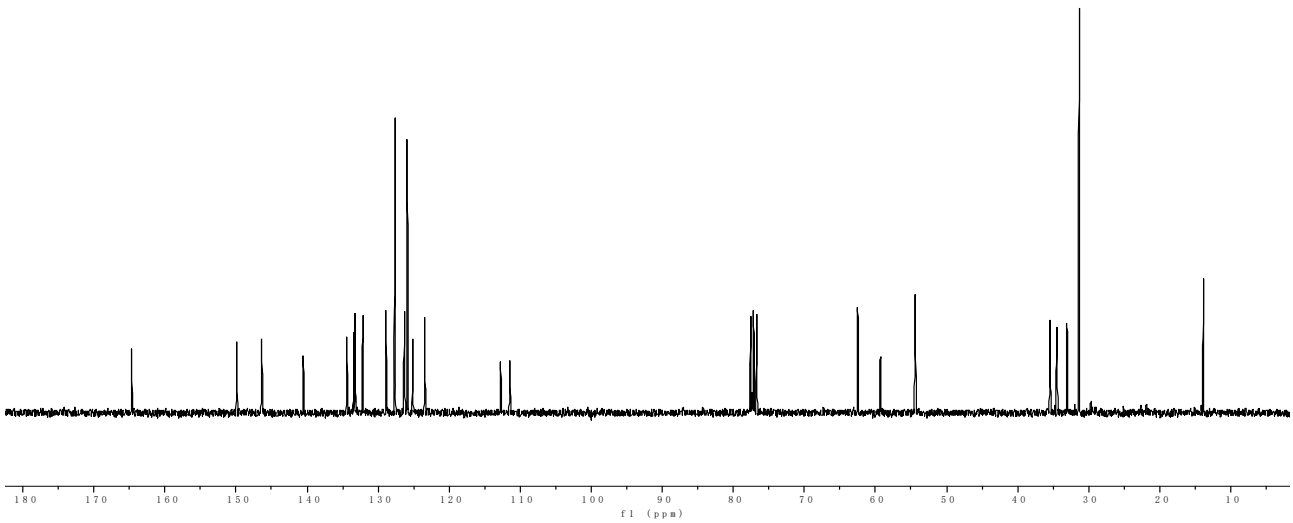

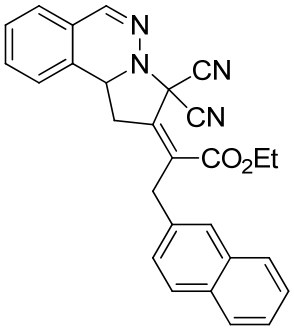
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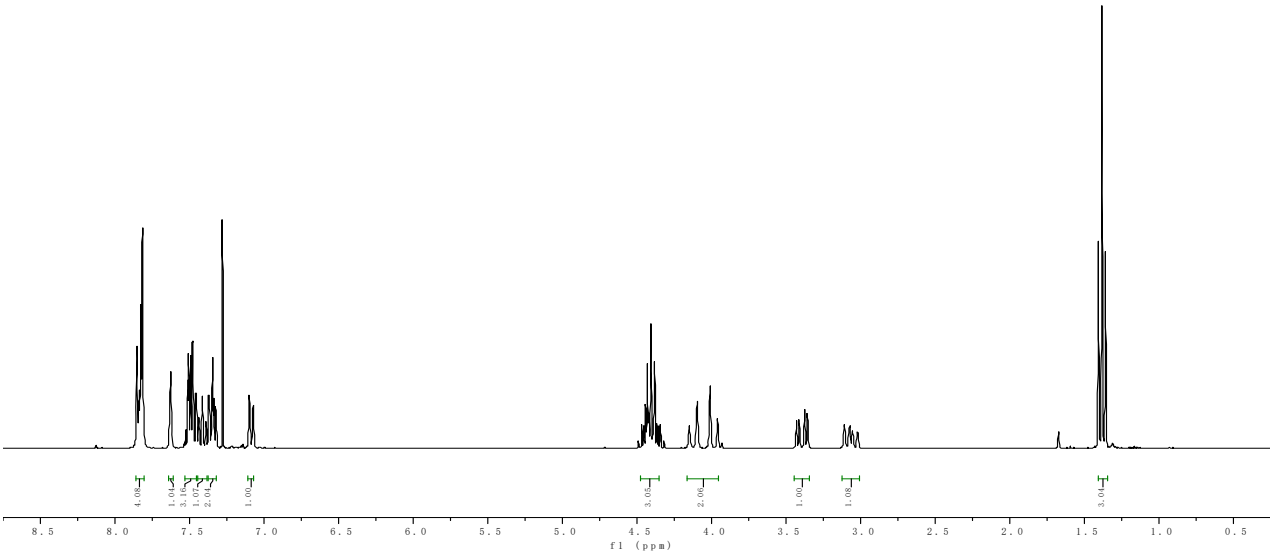
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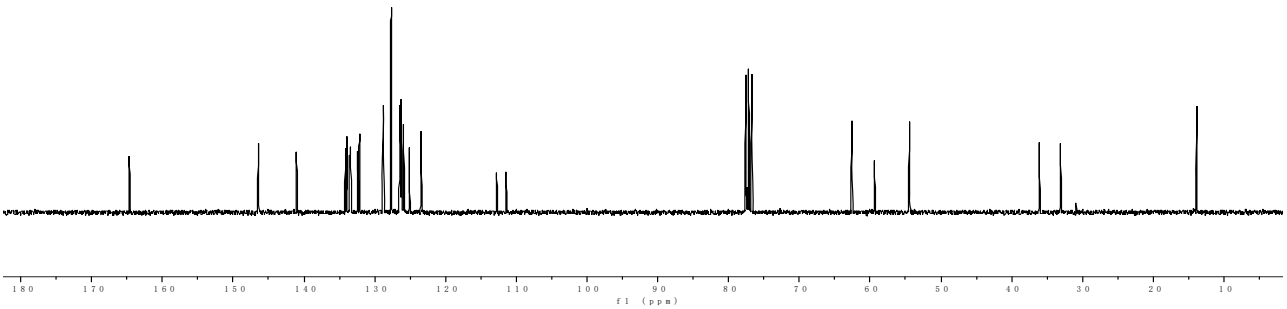
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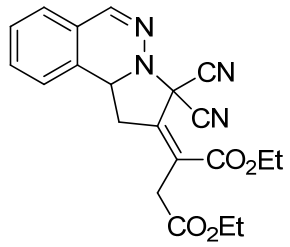

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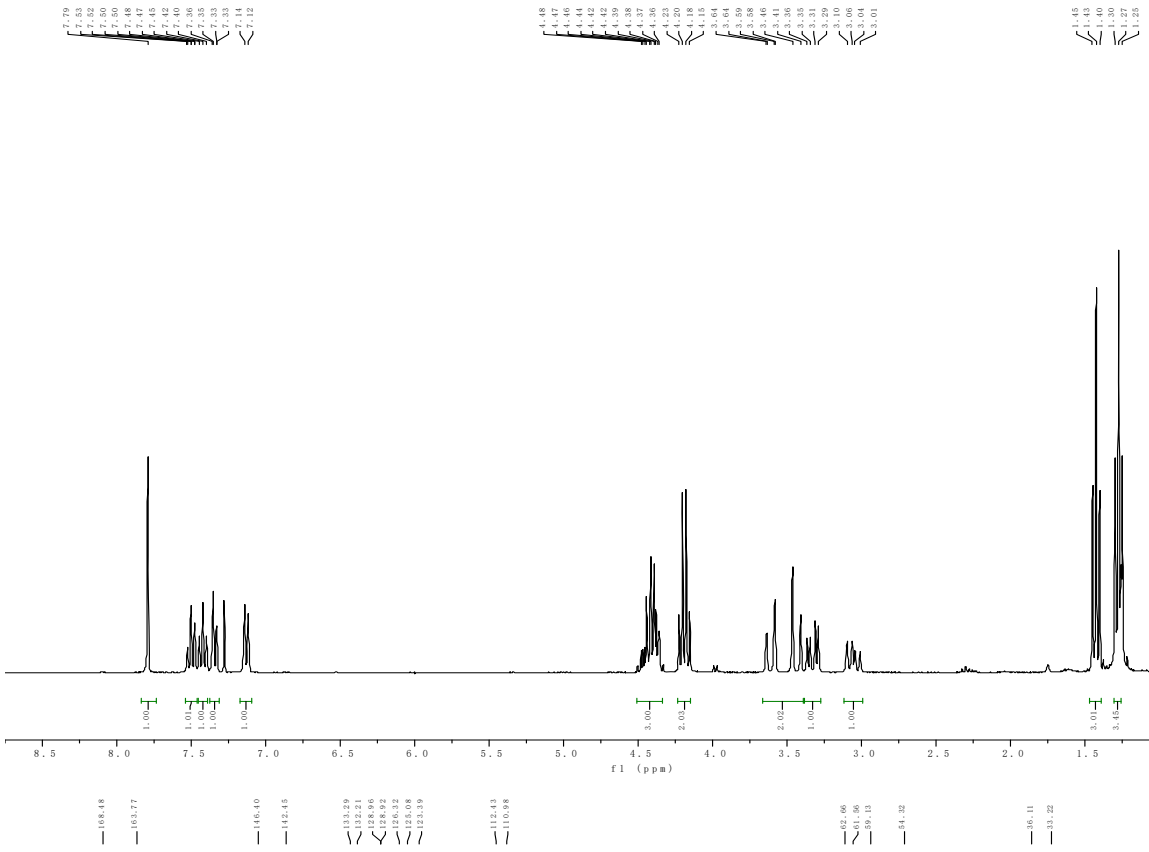

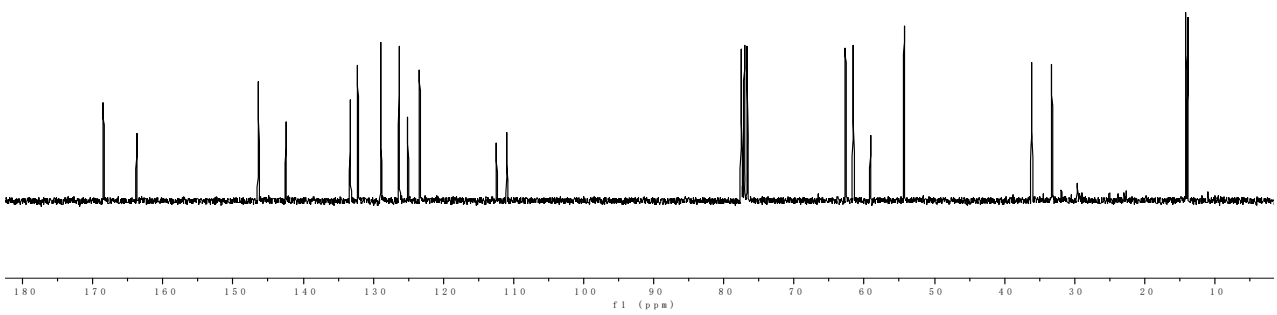

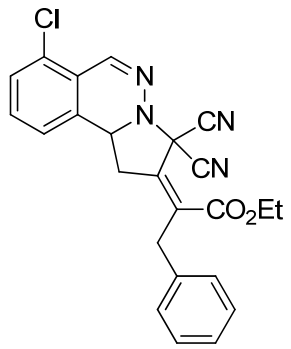

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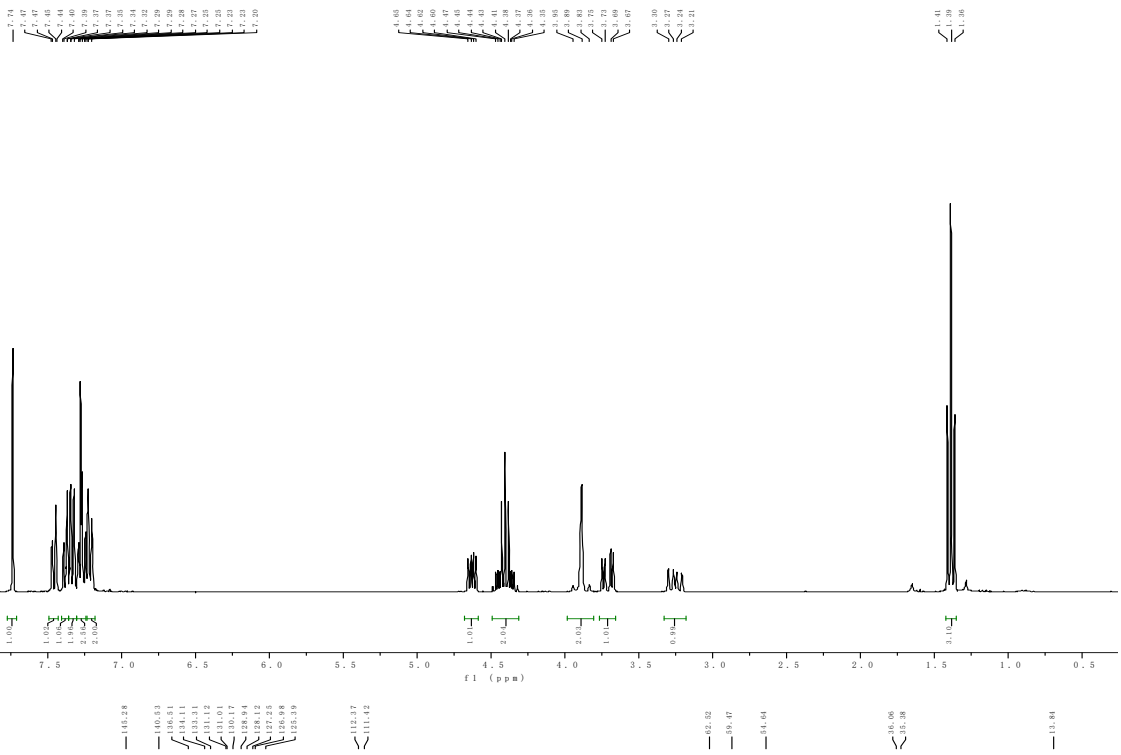

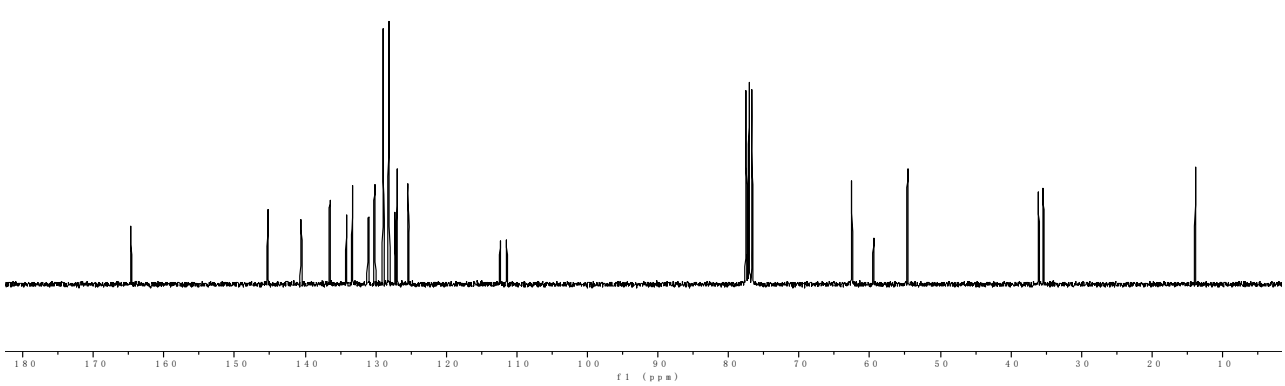

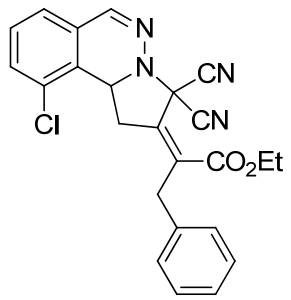

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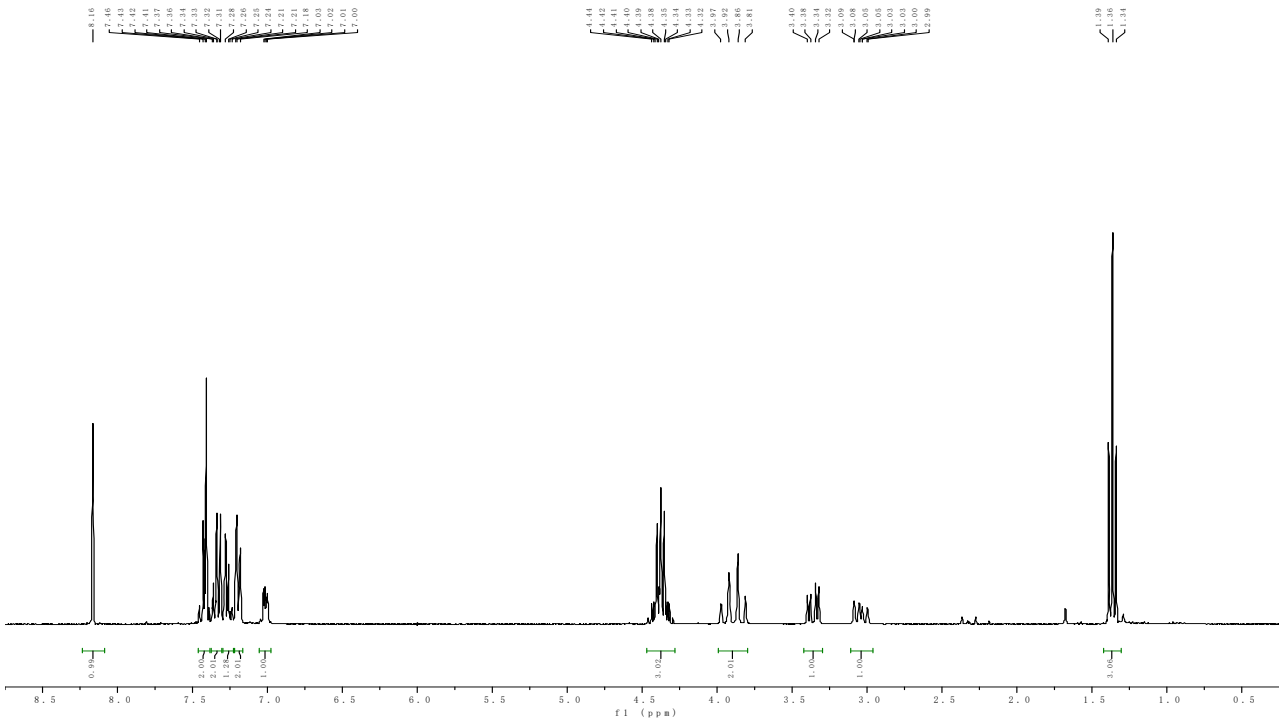

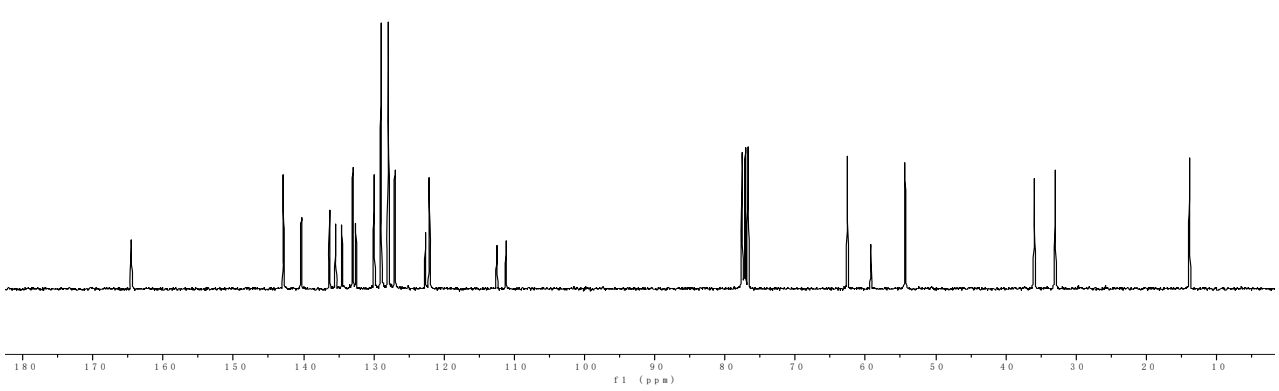

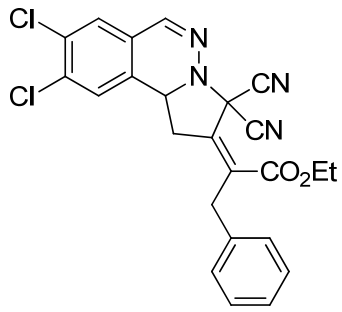

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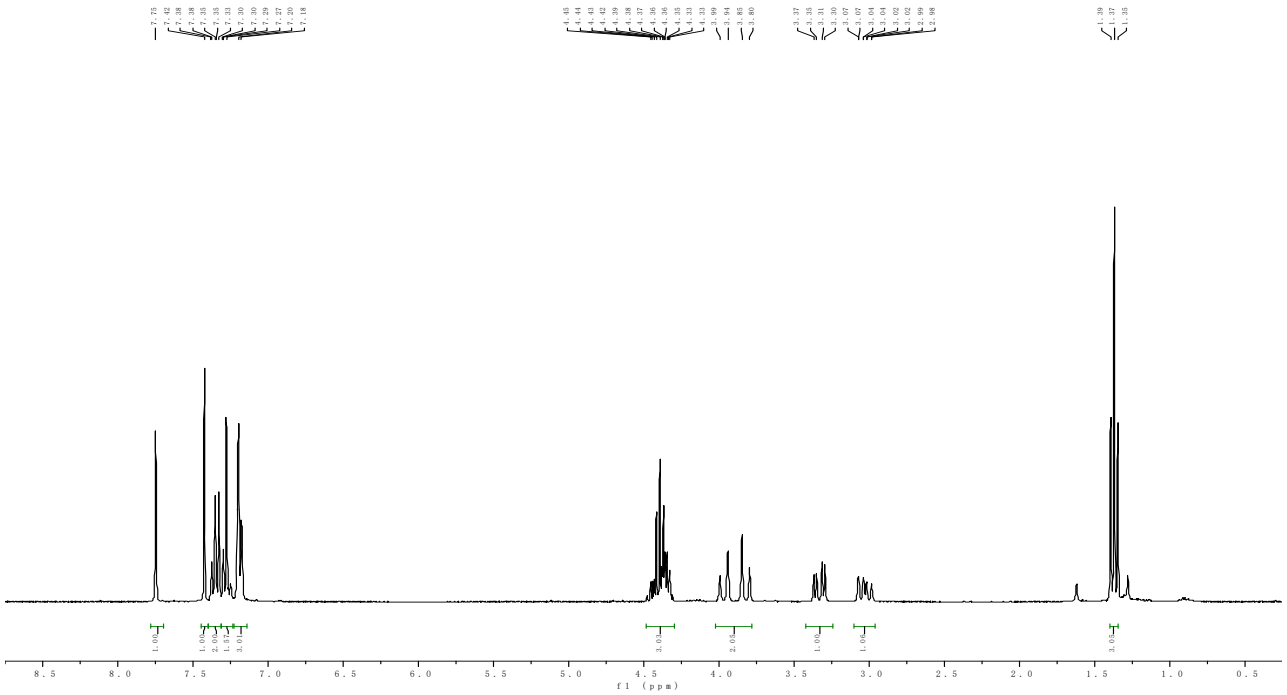

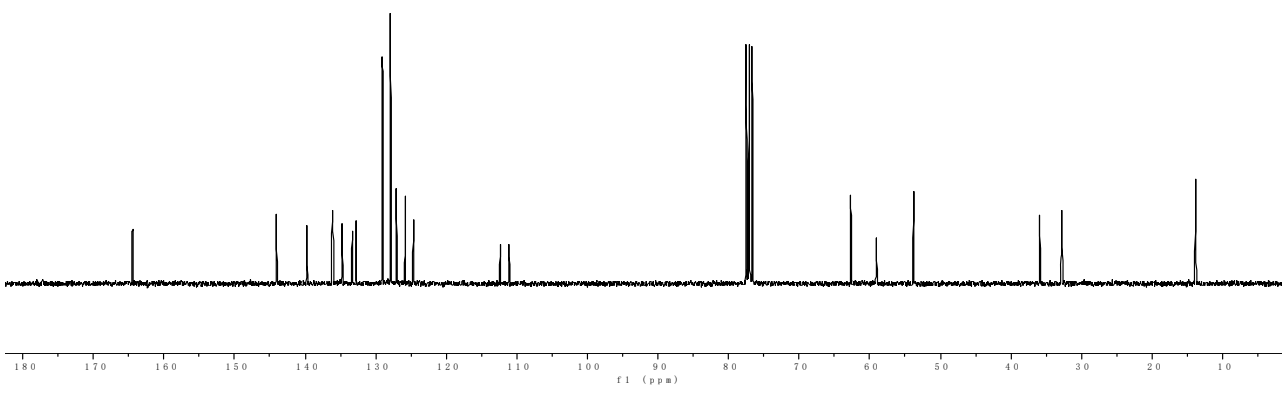

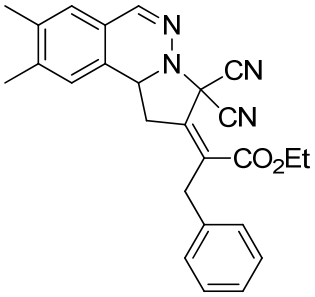

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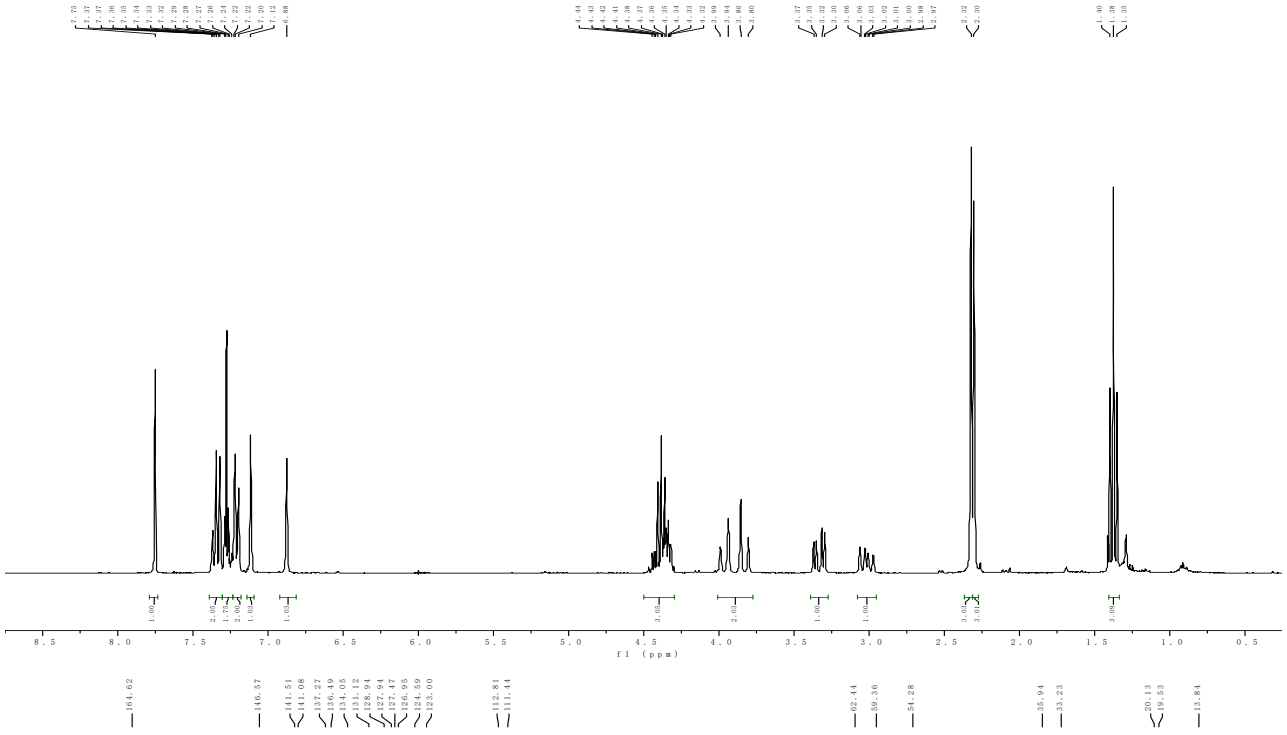

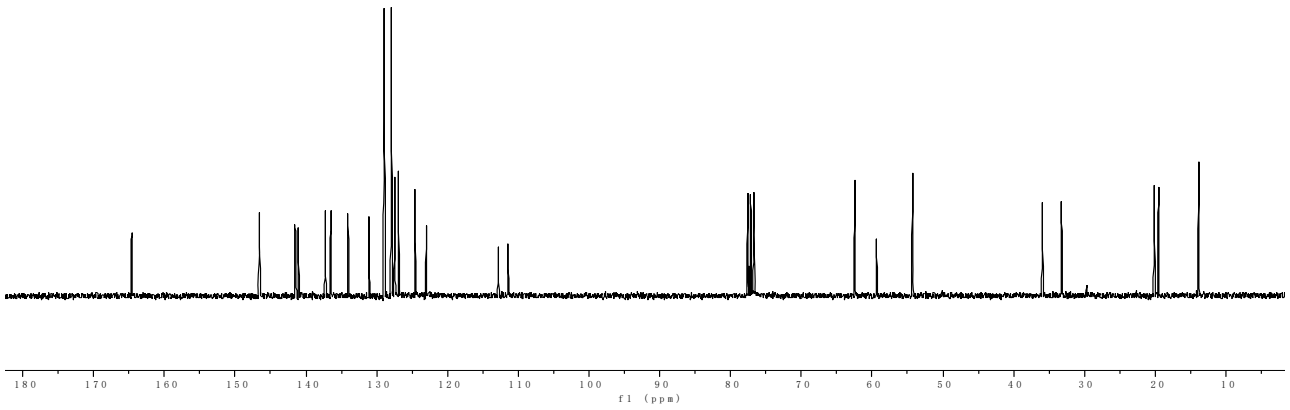

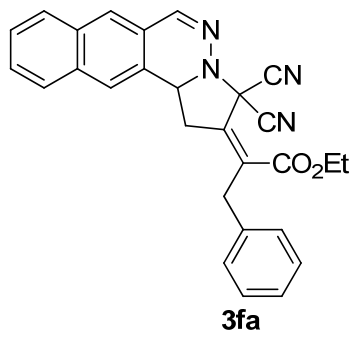

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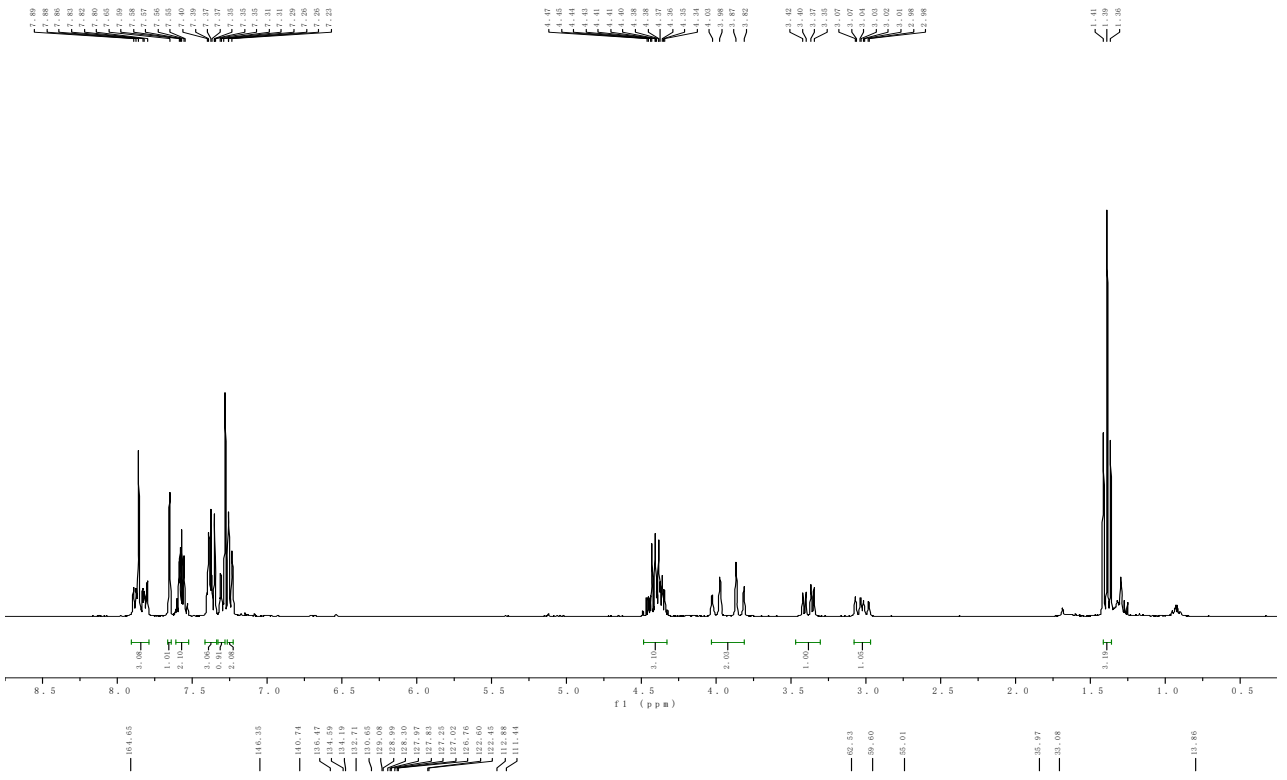

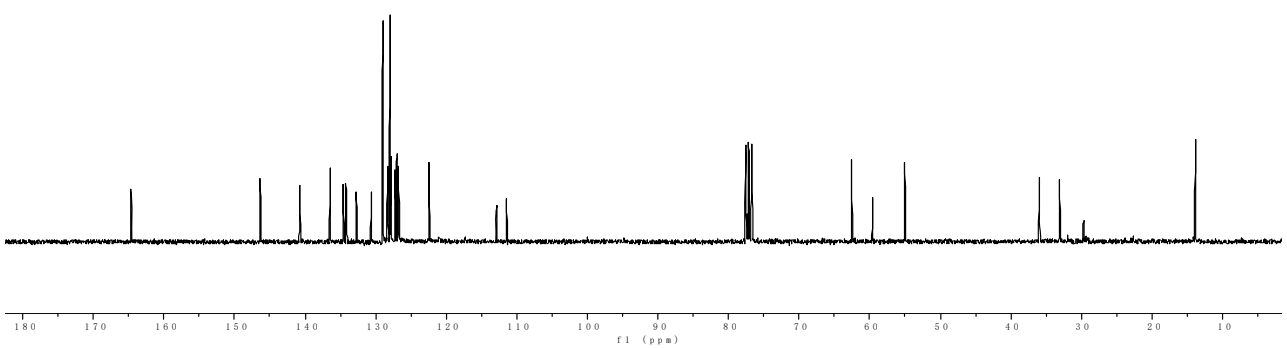

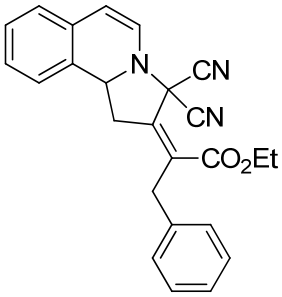

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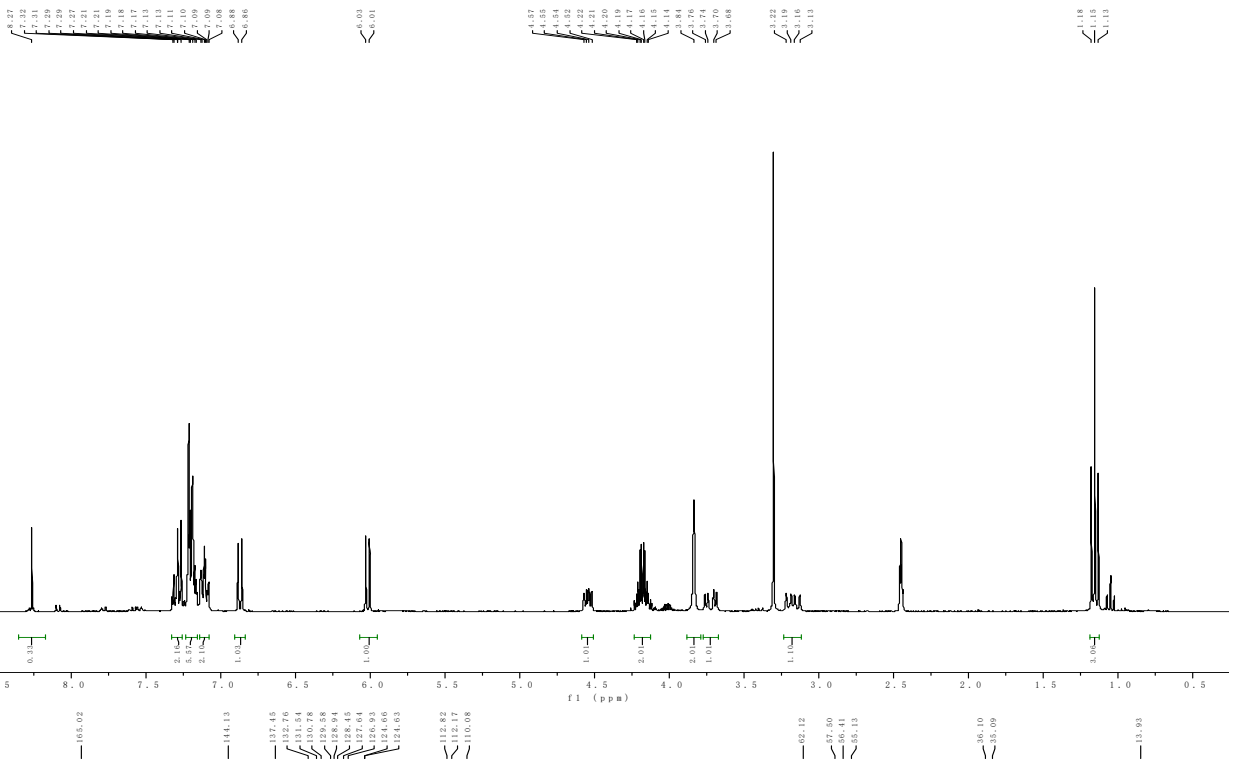

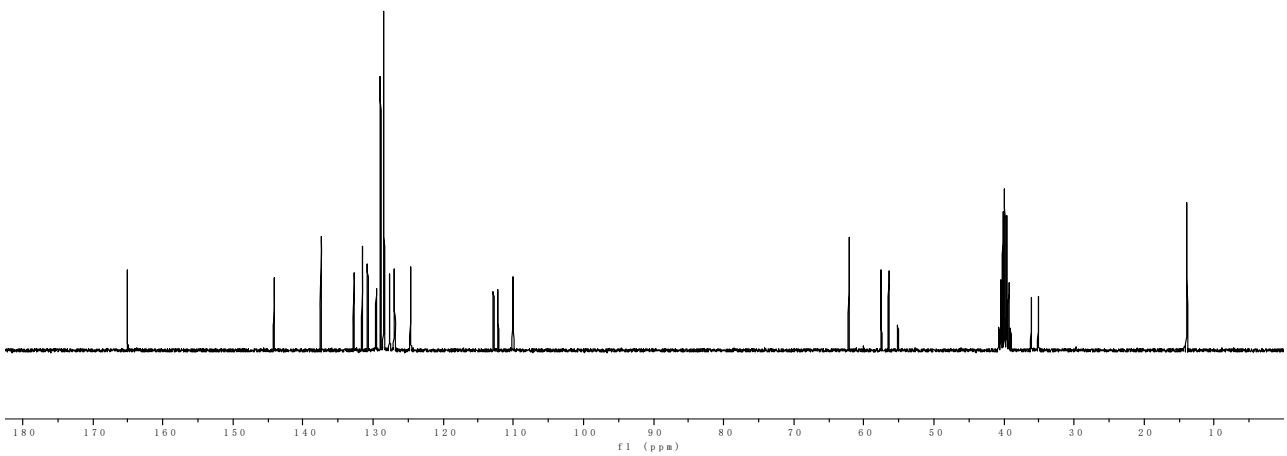

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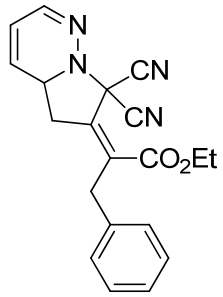

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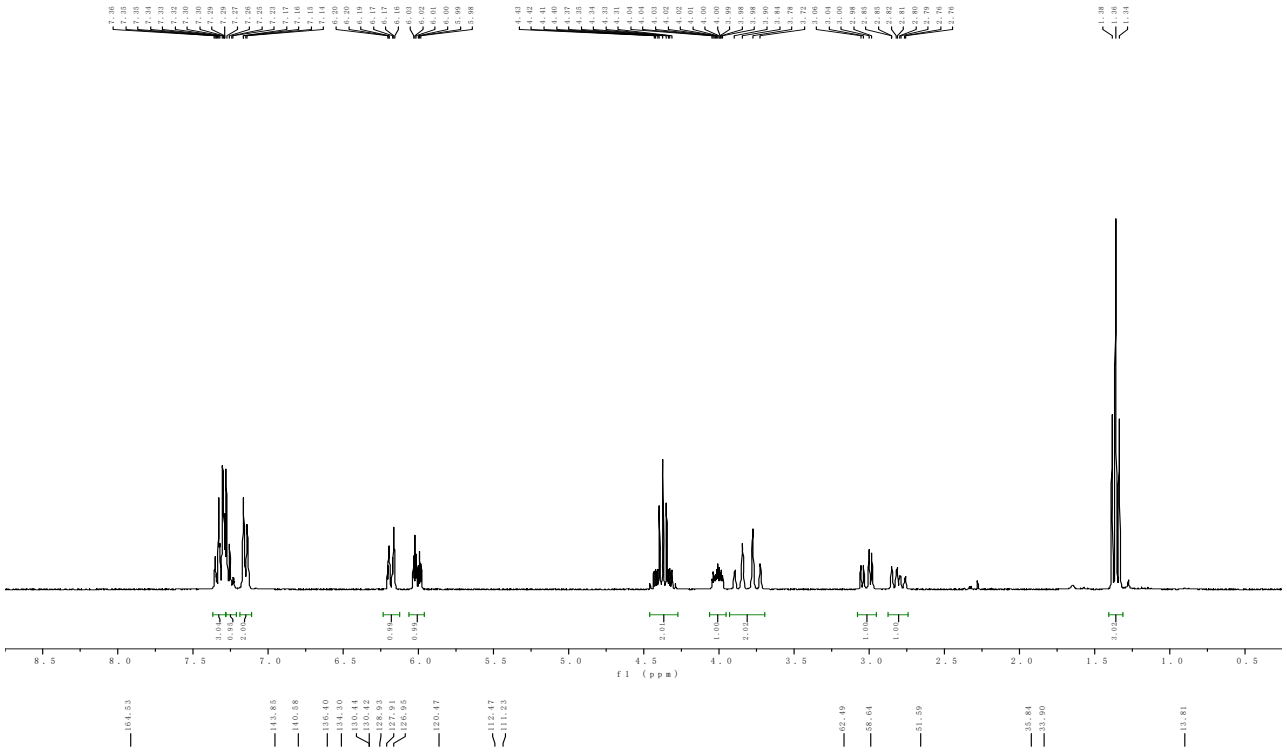

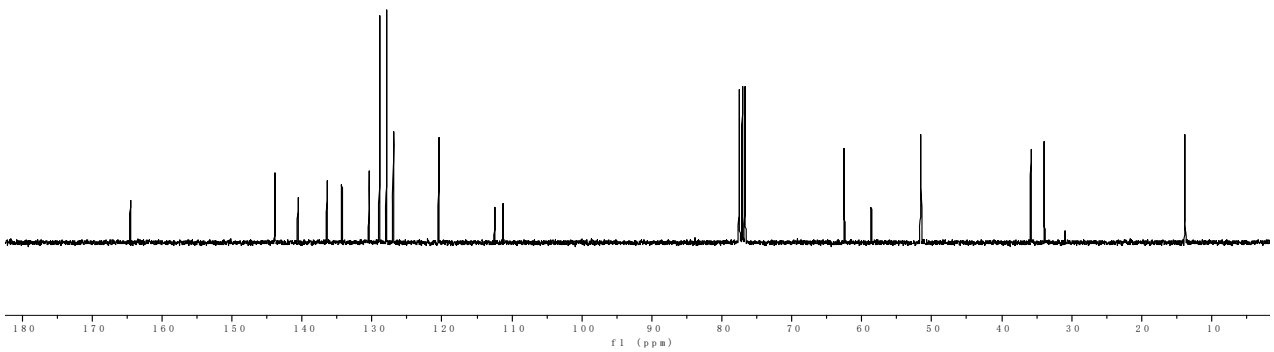

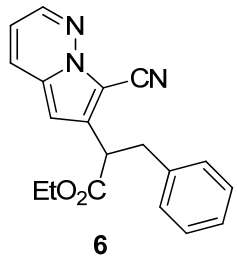

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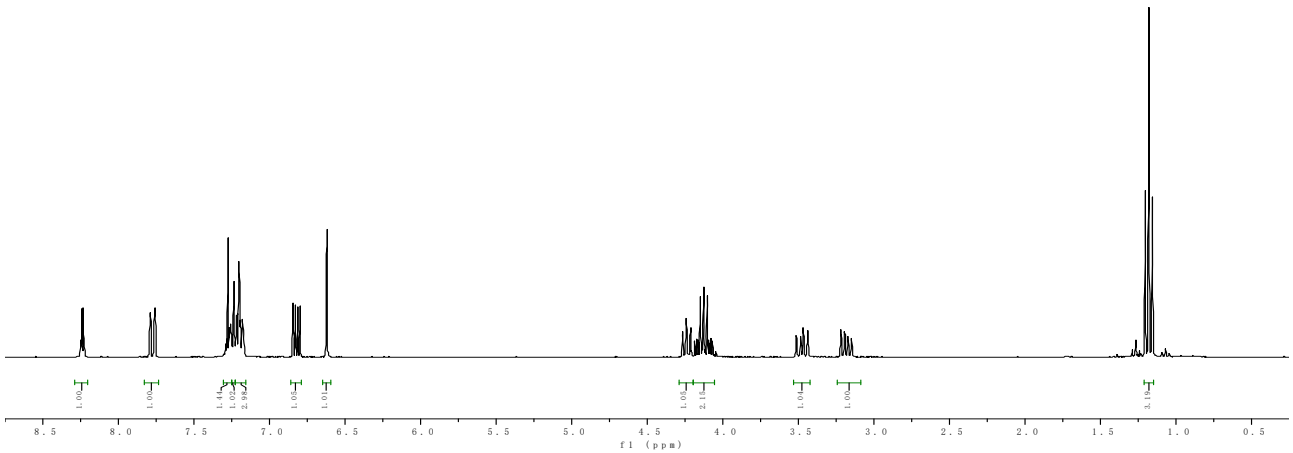

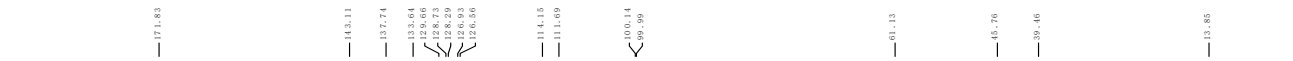

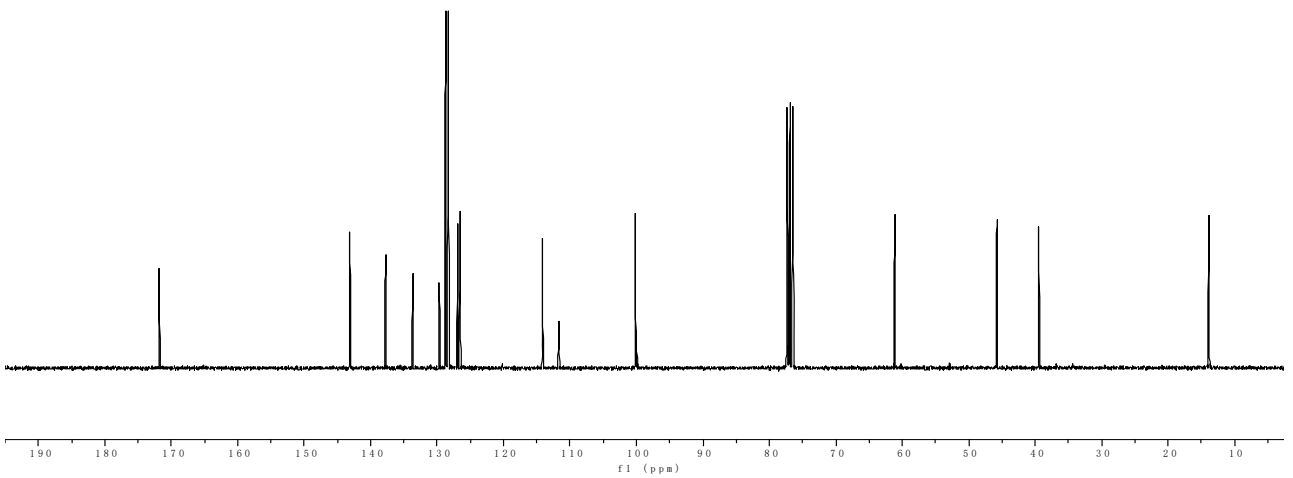

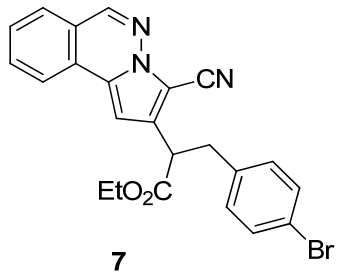

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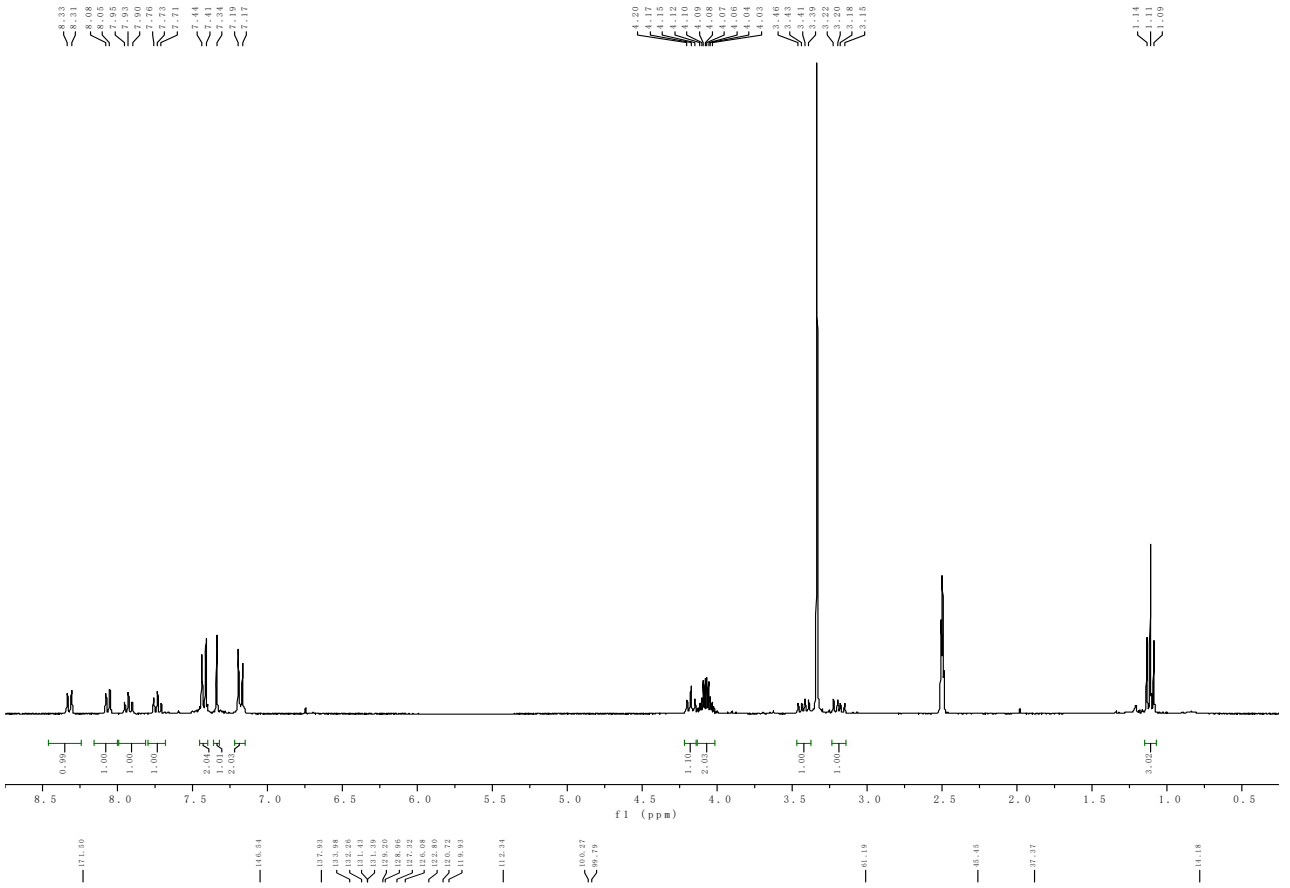
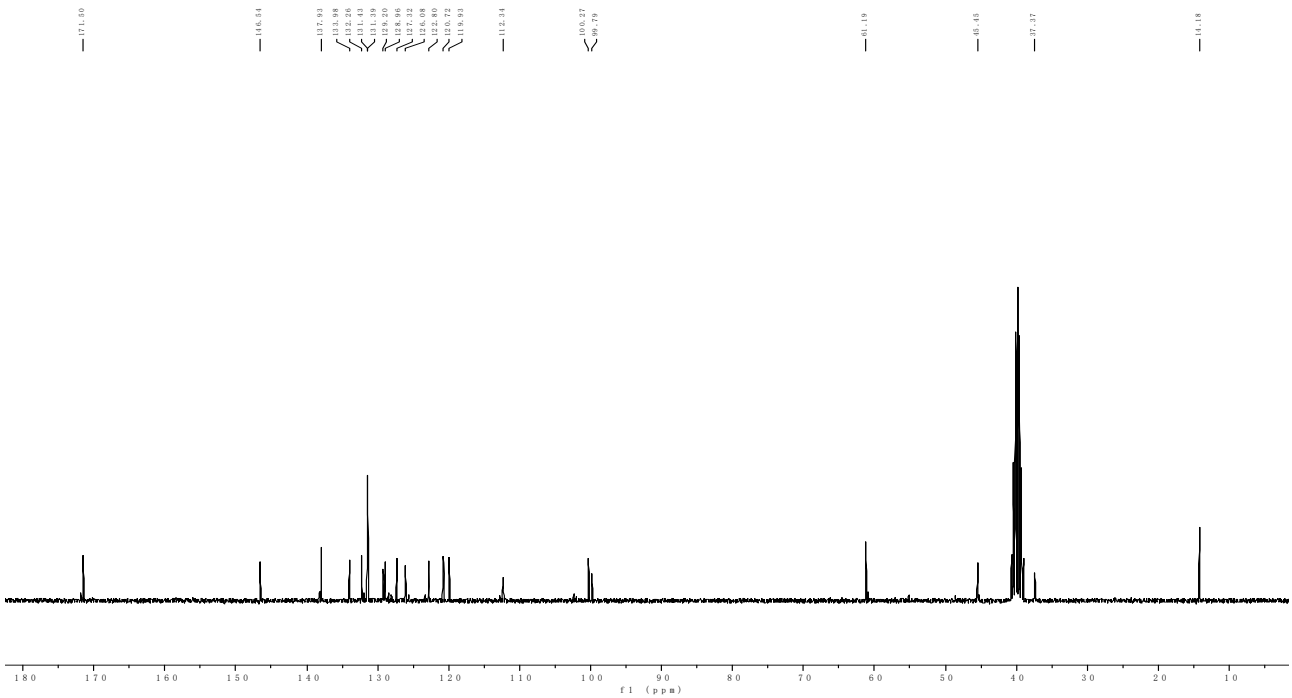
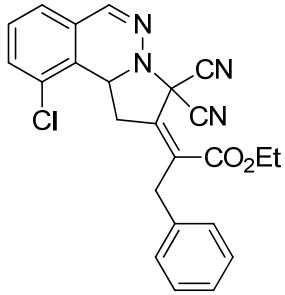
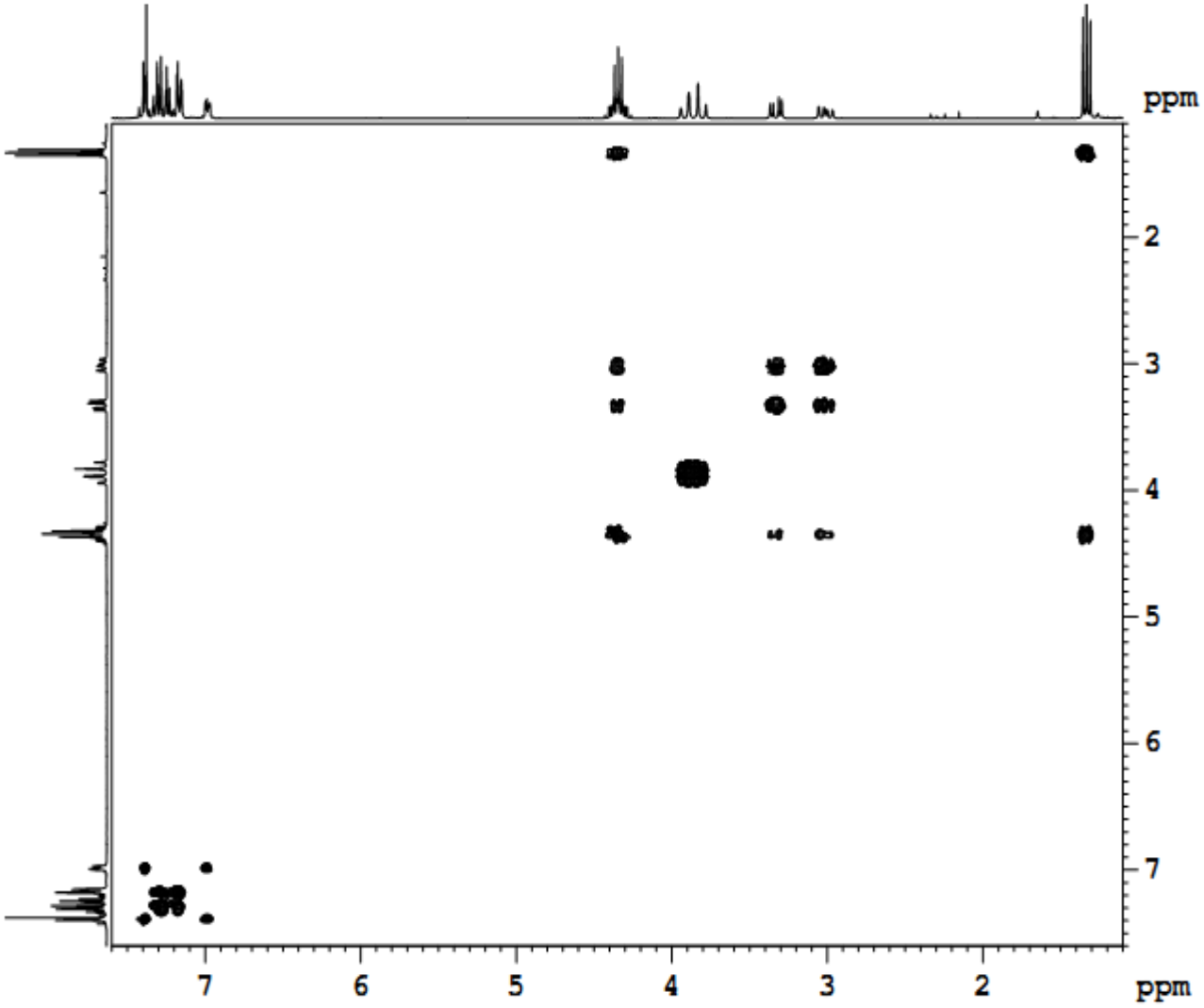




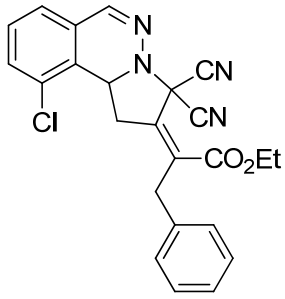
2D NMR COSY of 3ca



3ca



2D NMR HSQC of 3ca



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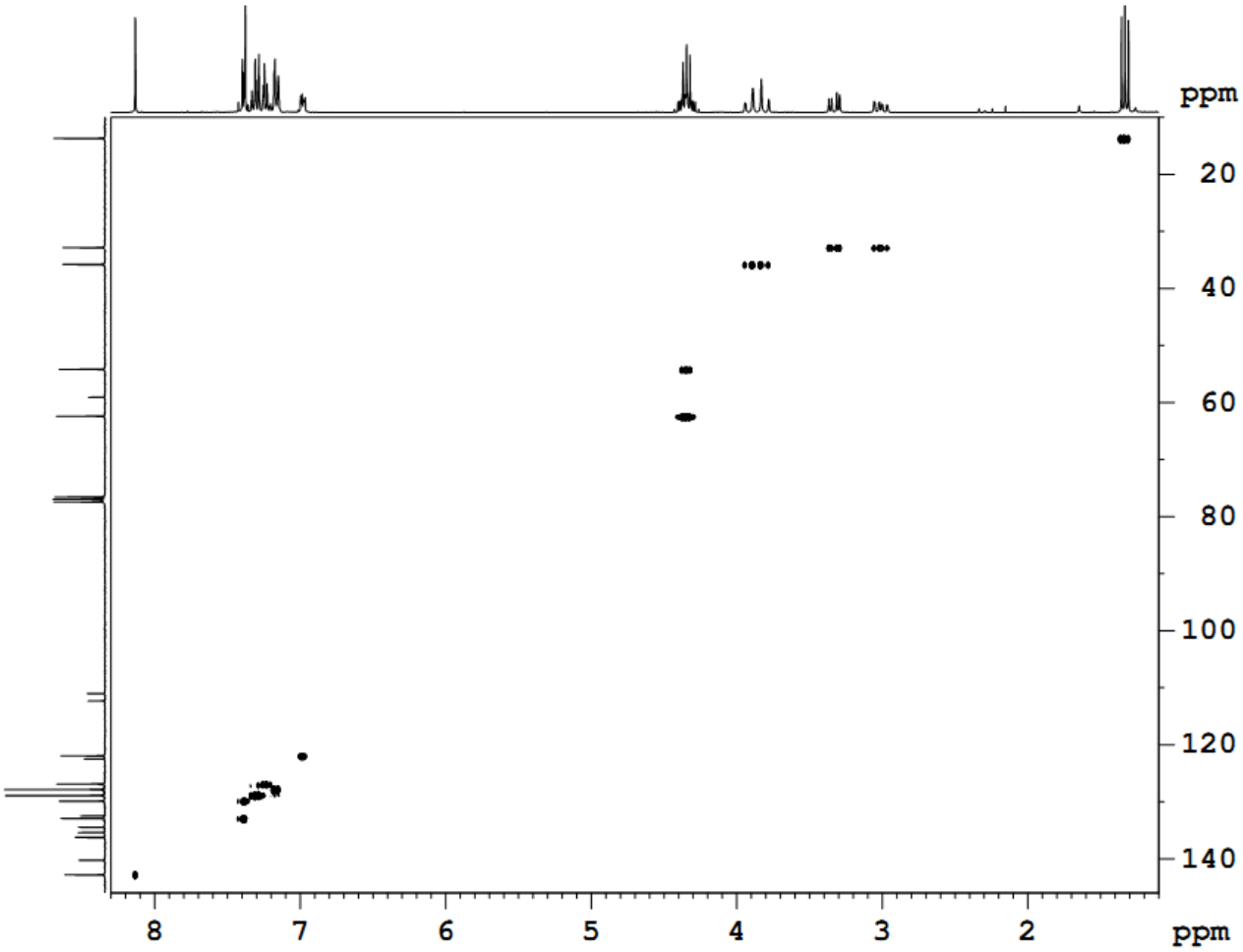
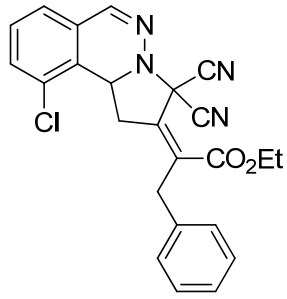


2D NMR HMBC of 3ca



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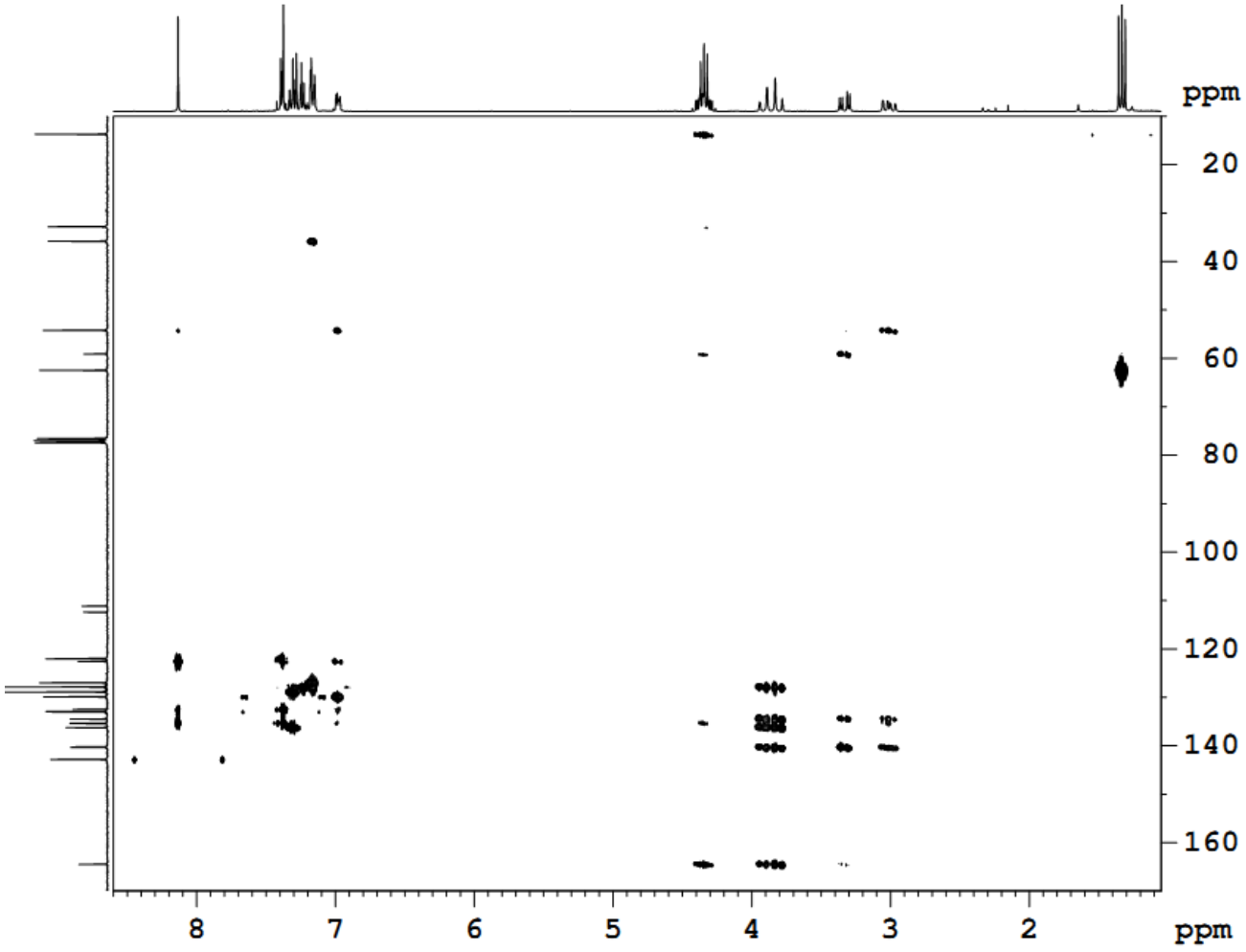
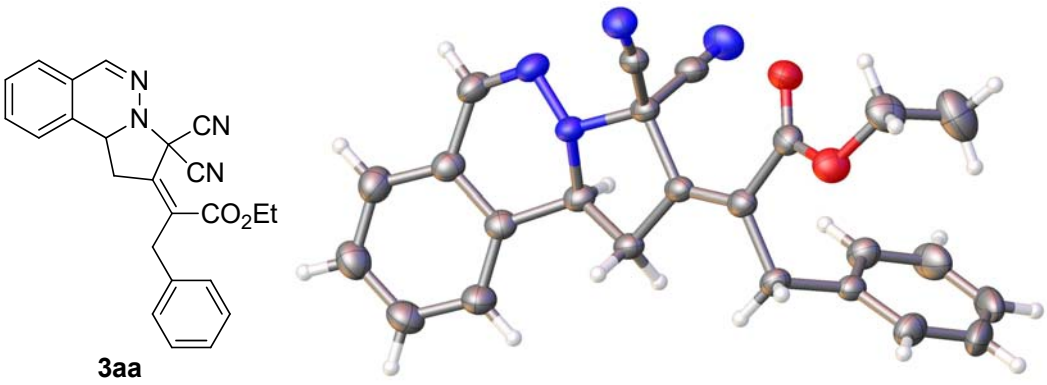


X-Ray Crystallography Data

Crystallographic data for **3aa**, **3ga**, **6**, **7** and **3aa'** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1455366, 1455369, 1455370, 1455373 and 1465124. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

X-Ray Crystallography Data of **3aa**



3aa

Table 1. Crystal data and structure refinement for **3aa.**

Identification code	3aa	
Empirical formula	$C_{24}H_{20}N_4O_2$	
Formula weight	396.44	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 n 1	
Unit cell dimensions	a = 11.285(2) Å	a= 90°
	b = 14.466(3) Å	b= 112.20(3)°
	c = 13.528(3) Å	g = 90°
Volume	2044.9(8) $Å^3$	
Z	4	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	832	
Crystal size	0.53 x 0.14 x 0.12 mm^3	
Theta range for data collection	2.012 to 27.489°	
Index ranges	-13<=h<=14, -18<=k<=18, -17<=l<=17	
Reflections collected	24275	
Independent reflections	8978 [R(int) = 0.0419]	

Completeness to theta = 26.000°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7145
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8978 / 2 / 543
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1012
R indices (all data)	R1 = 0.0477, wR2 = 0.1027
Absolute structure parameter	0.7(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.328 and -0.343 e.Å^{-3}

Table 2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	-3751(2)	-2177(2)	-2583(2)	44(1)
O2	-5679(2)	-2866(2)	-3183(2)	43(1)
N1	-2737(2)	1173(2)	-2808(2)	36(1)
N2	-3865(2)	682(2)	-3377(2)	29(1)
N3	-3710(3)	-410(2)	-1168(2)	40(1)
N4	-1719(3)	-978(2)	-3337(2)	48(1)
C1	-5658(3)	2107(2)	-5676(2)	43(1)
C2	-5790(3)	3051(2)	-5857(3)	47(1)
C3	-4919(3)	3661(2)	-5170(3)	47(1)
C4	-3903(3)	3324(2)	-4294(2)	44(1)
C5	-3770(3)	2383(2)	-4102(2)	36(1)
C6	-4653(3)	1768(2)	-4802(2)	33(1)
C7	-4370(3)	763(2)	-4548(2)	31(1)
C8	-2727(3)	1988(2)	-3178(2)	38(1)
C9	-5465(3)	69(2)	-4855(2)	31(1)
C10	-4985(2)	-684(2)	-4019(2)	28(1)
C11	-3774(2)	-301(2)	-3118(2)	29(1)
C12	-3738(3)	-405(2)	-2016(2)	31(1)
C13	-2604(3)	-718(2)	-3208(2)	35(1)
C14	-5468(3)	-1528(2)	-4060(2)	31(1)
C15	-4853(3)	-2217(2)	-3186(2)	35(1)
C16	-5186(4)	-3647(2)	-2460(3)	52(1)

C17	-4724(5)	-4363(3)	-3000(4)	74(1)
C18	-6592(3)	-1876(2)	-5012(2)	32(1)
C19	-6200(2)	-2659(2)	-5570(2)	28(1)
C20	-5052(3)	-2633(2)	-5709(2)	8(1)
C21	-4715(4)	-3327(3)	-6262(3)	53(1)
C22	-5542(4)	-4059(2)	-6676(3)	56(1)
C23	-6668(4)	-4102(2)	-6525(3)	55(1)
C24	-7009(3)	-3408(2)	-5979(2)	42(1)
O3	-1574(2)	-3812(2)	-6176(2)	53(1)
O4	-1052(3)	-2938(2)	-7302(2)	73(1)
N5	1443(2)	-4349(2)	-2340(2)	35(1)
N6	1288(2)	-3581(2)	-3005(2)	32(1)
N7	1053(3)	-4924(2)	-5093(3)	56(1)
N8	-1840(3)	-4200(2)	-3829(3)	57(1)
C25	2256(3)	-2511(2)	-1594(2)	36(1)
C26	2788(3)	-1648(2)	-1261(2)	45(1)
C27	3784(4)	-1556(3)	-272(3)	54(1)
C28	4234(4)	-2321(3)	378(3)	52(1)
C29	3720(3)	-3182(2)	41(2)	45(1)
C30	2729(3)	-3292(2)	-959(2)	36(1)
C31	2162(3)	-4185(2)	-1360(2)	38(1)
C32	1112(3)	-2681(2)	-2601(2)	33(1)
C33	905(3)	-2070(2)	-3570(2)	30(1)
C34	199(3)	-2699(2)	-4506(2)	30(1)
C35	270(3)	-3690(2)	-4060(2)	31(1)
C36	683(3)	-4394(2)	-4653(2)	38(1)
C37	-958(3)	-3976(2)	-3974(2)	36(1)
C38	-330(3)	-2453(2)	-5532(2)	33(1)
C39	-1047(3)	-3149(2)	-6357(2)	38(1)
C40	-1873(8)	-3503(3)	-8205(3)	121(3)
C41	-2518(6)	-2982(4)	-9068(5)	121(3)
C42	-270(3)	-1481(2)	-5919(2)	37(1)
C43	-1562(3)	-1091(2)	-6596(2)	30(1)
C44	-2555(3)	-1074(2)	-6225(2)	41(1)
C45	-3758(3)	-745(2)	-6870(3)	46(1)
C46	-3981(3)	-430(2)	-7880(2)	41(1)
C47	-3010(3)	-442(2)	-8260(2)	39(1)
C48	-1815(3)	-773(2)	-7624(2)	36(1)

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

O1-C15	1.205(4)
O2-C15	1.325(4)
O2-C16	1.460(4)
N1-N2	1.406(3)
N1-C8	1.283(4)
N2-C7	1.472(3)
N2-C11	1.459(3)
N3-C12	1.135(4)
N4-C13	1.140(4)
C1-H1	0.9300
C1-C2	1.385(4)
C1-C6	1.383(4)
C2-H2	0.9300
C2-C3	1.384(5)
C3-H3	0.9300
C3-C4	1.390(5)
C4-H4	0.9300
C4-C5	1.384(4)
C5-C6	1.403(4)
C5-C8	1.470(4)
C6-C7	1.501(4)
C7-H7	0.9800
C7-C9	1.523(4)
C8-H8	0.9300
C9-H9A	0.9700
C9-H9B	0.9700
C9-C10	1.515(4)
C10-C11	1.550(3)
C10-C14	1.330(4)
C11-C12	1.484(4)
C11-C13	1.498(4)
C14-C15	1.500(4)
C14-C18	1.512(4)
C16-H16A	0.9700
C16-H16B	0.9700
C16-C17	1.471(6)

C17-H17A	0.9600
C17-H17B	0.9600
C17-H17C	0.9600
C18-H18A	0.9700
C18-H18B	0.9700
C18-C19	1.517(4)
C19-C20	1.378(4)
C19-C24	1.390(4)
C20-H20	0.9300
C20-C21	1.388(4)
C21-H21	0.9300
C21-C22	1.382(6)
C22-H22	0.9300
C22-C23	1.362(6)
C23-H23	0.9300
C23-C24	1.384(5)
C24-H24	0.9300
O3-C39	1.202(4)
O4-C39	1.312(4)
O4-C40	1.471(5)
N5-N6	1.398(3)
N5-C31	1.288(4)
N6-C32	1.455(3)
N6-C35	1.464(3)
N7-C36	1.142(4)
N8-C37	1.133(4)
C25-C26	1.385(4)
C25-C30	1.397(4)
C25-C32	1.501(4)
C26-H26	0.9300
C26-C27	1.391(5)
C27-H27	0.9300
C27-C28	1.384(5)
C28-H28	0.9300
C28-C29	1.378(5)
C29-H29	0.9300
C29-C30	1.401(4)
C30-C31	1.454(4)

C31-H31	0.9300
C32-H32	0.9800
C32-C33	1.525(4)
C33-H33A	0.9700
C33-H33B	0.9700
C33-C34	1.518(4)
C34-C35	1.546(3)
C34-C38	1.335(4)
C35-C36	1.476(4)
C35-C37	1.493(4)
C38-C39	1.494(4)
C38-C42	1.510(4)
C40-H40A	0.9700
C40-H40B	0.9700
C40-C41	1.349(7)
C41-H41A	0.9600
C41-H41B	0.9600
C41-H41C	0.9600
C42-H42A	0.9700
C42-H42B	0.9700
C42-C43	1.508(4)
C43-C44	1.390(4)
C43-C48	1.387(4)
C44-H44	0.9300
C44-C45	1.391(5)
C45-H45	0.9300
C45-C46	1.371(5)
C46-H46	0.9300
C46-C47	1.376(5)
C47-H47	0.9300
C47-C48	1.382(4)
C48-H48	0.9300

C15-O2-C16	117.4(3)
C8-N1-N2	113.0(2)
N1-N2-C7	116.8(2)
N1-N2-C11	113.2(2)
C11-N2-C7	107.37(19)

C2-C1-H1	120.0
C6-C1-H1	120.0
C6-C1-C2	120.0(3)
C1-C2-H2	119.7
C3-C2-C1	120.5(3)
C3-C2-H2	119.7
C2-C3-H3	120.1
C2-C3-C4	119.8(3)
C4-C3-H3	120.1
C3-C4-H4	120.0
C5-C4-C3	120.1(3)
C5-C4-H4	120.0
C4-C5-C6	119.9(3)
C4-C5-C8	122.5(3)
C6-C5-C8	117.7(3)
C1-C6-C5	119.8(3)
C1-C6-C7	125.1(3)
C5-C6-C7	115.1(2)
N2-C7-C6	106.6(2)
N2-C7-H7	109.7
N2-C7-C9	100.7(2)
C6-C7-H7	109.7
C6-C7-C9	119.7(2)
C9-C7-H7	109.7
N1-C8-C5	124.5(3)
N1-C8-H8	117.8
C5-C8-H8	117.8
C7-C9-H9A	110.9
C7-C9-H9B	110.9
H9A-C9-H9B	108.9
C10-C9-C7	104.2(2)
C10-C9-H9A	110.9
C10-C9-H9B	110.9
C9-C10-C11	106.9(2)
C14-C10-C9	127.2(2)
C14-C10-C11	125.9(2)
N2-C11-C10	101.4(2)
N2-C11-C12	108.2(2)

N2-C11-C13	111.0(2)
C12-C11-C10	115.8(2)
C12-C11-C13	110.5(2)
C13-C11-C10	109.5(2)
N3-C12-C11	174.5(3)
N4-C13-C11	174.2(3)
C10-C14-C15	121.1(2)
C10-C14-C18	122.7(2)
C15-C14-C18	116.0(2)
O1-C15-O2	125.4(3)
O1-C15-C14	123.6(3)
O2-C15-C14	111.0(2)
O2-C16-H16A	109.8
O2-C16-H16B	109.8
O2-C16-C17	109.3(3)
H16A-C16-H16B	108.3
C17-C16-H16A	109.8
C17-C16-H16B	109.8
C16-C17-H17A	109.5
C16-C17-H17B	109.5
C16-C17-H17C	109.5
H17A-C17-H17B	109.5
H17A-C17-H17C	109.5
H17B-C17-H17C	109.5
C14-C18-H18A	109.4
C14-C18-H18B	109.4
C14-C18-C19	111.3(2)
H18A-C18-H18B	108.0
C19-C18-H18A	109.4
C19-C18-H18B	109.4
C20-C19-C18	120.9(2)
C20-C19-C24	118.5(3)
C24-C19-C18	120.6(3)
C19-C20-H20	119.5
C19-C20-C21	121.1(3)
C21-C20-H20	119.5
C20-C21-H21	120.3
C22-C21-C20	119.5(3)

C22-C21-H21	120.3
C21-C22-H22	120.0
C23-C22-C21	120.0(3)
C23-C22-H22	120.0
C22-C23-H23	119.7
C22-C23-C24	120.6(3)
C24-C23-H23	119.7
C19-C24-H24	119.8
C23-C24-C19	120.3(3)
C23-C24-H24	119.8
C39-O4-C40	116.7(3)
C31-N5-N6	113.1(2)
N5-N6-C32	118.1(2)
N5-N6-C35	113.8(2)
C32-N6-C35	107.2(2)
C26-C25-C30	120.7(3)
C26-C25-C32	124.1(3)
C30-C25-C32	115.1(2)
C25-C26-H26	120.3
C25-C26-C27	119.5(3)
C27-C26-H26	120.3
C26-C27-H27	119.9
C28-C27-C26	120.2(3)
C28-C27-H27	119.9
C27-C28-H28	119.8
C29-C28-C27	120.4(3)
C29-C28-H28	119.8
C28-C29-H29	119.9
C28-C29-C30	120.3(3)
C30-C29-H29	119.9
C25-C30-C29	118.9(3)
C25-C30-C31	118.5(3)
C29-C30-C31	122.6(3)
N5-C31-C30	124.4(3)
N5-C31-H31	117.8
C30-C31-H31	117.8
N6-C32-C25	107.2(2)
N6-C32-H32	109.6

N6-C32-C33	101.2(2)
C25-C32-H32	109.6
C25-C32-C33	119.0(2)
C33-C32-H32	109.6
C32-C33-H33A	111.1
C32-C33-H33B	111.1
H33A-C33-H33B	109.1
C34-C33-C32	103.4(2)
C34-C33-H33A	111.1
C34-C33-H33B	111.1
C33-C34-C35	107.3(2)
C38-C34-C33	126.5(2)
C38-C34-C35	126.1(2)
N6-C35-C34	100.7(2)
N6-C35-C36	108.2(2)
N6-C35-C37	111.3(2)
C36-C35-C34	114.1(2)
C36-C35-C37	110.2(2)
C37-C35-C34	112.0(2)
N7-C36-C35	177.2(4)
N8-C37-C35	174.9(3)
C34-C38-C39	120.0(2)
C34-C38-C42	123.2(3)
C39-C38-C42	116.8(2)
O3-C39-O4	124.3(3)
O3-C39-C38	123.8(3)
O4-C39-C38	111.9(3)
O4-C40-H40A	109.2
O4-C40-H40B	109.2
H40A-C40-H40B	107.9
C41-C40-O4	111.9(4)
C41-C40-H40A	109.2
C41-C40-H40B	109.2
C40-C41-H41A	109.5
C40-C41-H41B	109.5
C40-C41-H41C	109.5
H41A-C41-H41B	109.5
H41A-C41-H41C	109.5

H41B-C41-H41C	109.5
C38-C42-H42A	108.9
C38-C42-H42B	108.9
H42A-C42-H42B	107.7
C43-C42-C38	113.6(2)
C43-C42-H42A	108.9
C43-C42-H42B	108.9
C44-C43-C42	120.9(2)
C48-C43-C42	121.2(3)
C48-C43-C44	117.8(3)
C43-C44-H44	119.7
C43-C44-C45	120.6(3)
C45-C44-H44	119.7
C44-C45-H45	119.8
C46-C45-C44	120.4(3)
C46-C45-H45	119.8
C45-C46-H46	120.1
C45-C46-C47	119.7(3)
C47-C46-H46	120.1
C46-C47-H47	120.0
C46-C47-C48	119.9(3)
C48-C47-H47	120.0
C43-C48-H48	119.3
C47-C48-C43	121.5(3)
C47-C48-H48	119.3

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	41(1)	40(1)	41(1)	3(1)	3(1)	4(1)
O2	46(1)	46(1)	38(1)	6(1)	16(1)	-2(1)
N1	37(1)	38(1)	26(1)	-4(1)	6(1)	-6(1)

N2	30(1)	31(1)	22(1)	-1(1)	5(1)	-1(1)
N3	44(2)	43(1)	29(1)	-1(1)	10(1)	2(1)
N4	36(2)	59(2)	49(2)	0(1)	16(1)	10(1)
C1	45(2)	42(2)	33(2)	2(1)	5(1)	2(1)
C2	50(2)	47(2)	39(2)	11(1)	10(1)	7(2)
C3	58(2)	40(2)	46(2)	8(1)	21(2)	6(2)
C4	55(2)	38(2)	37(2)	1(1)	16(1)	-5(1)
C5	38(2)	38(2)	29(1)	1(1)	12(1)	-3(1)
C6	37(2)	36(1)	24(1)	1(1)	12(1)	1(1)
C7	30(1)	37(1)	23(1)	-2(1)	7(1)	0(1)
C8	42(2)	38(2)	29(1)	-3(1)	8(1)	-9(1)
C9	28(1)	34(1)	26(1)	-2(1)	5(1)	2(1)
C10	27(1)	33(1)	22(1)	-4(1)	6(1)	4(1)
C11	27(1)	33(1)	23(1)	-3(1)	6(1)	4(1)
C12	31(1)	31(1)	26(1)	-2(1)	6(1)	3(1)
C13	31(2)	41(2)	26(1)	-2(1)	4(1)	1(1)
C14	29(1)	34(1)	27(1)	-4(1)	8(1)	4(1)
C15	40(2)	34(1)	28(1)	-4(1)	11(1)	3(1)
C16	60(2)	50(2)	45(2)	14(2)	21(2)	1(2)
C17	83(3)	53(2)	93(3)	21(2)	43(3)	18(2)
C18	27(1)	35(1)	31(1)	-4(1)	7(1)	-2(1)
C19	29(1)	29(1)	23(1)	2(1)	5(1)	-1(1)
C20	34(2)	41(2)	37(2)	-4(1)	12(1)	-1(1)
C21	48(2)	66(2)	46(2)	-7(2)	18(2)	19(2)
C22	72(3)	44(2)	40(2)	-8(1)	8(2)	26(2)
C23	72(3)	28(2)	49(2)	-8(1)	4(2)	-2(2)
C24	46(2)	35(2)	39(2)	-1(1)	11(1)	-9(1)
O3	60(2)	46(1)	40(1)	-3(1)	5(1)	-23(1)
O4	141(3)	40(1)	33(1)	-3(1)	26(2)	-20(2)
N5	44(2)	26(1)	34(1)	7(1)	13(1)	2(1)
N6	36(1)	25(1)	30(1)	3(1)	7(1)	1(1)
N7	80(2)	37(2)	53(2)	-4(1)	28(2)	5(1)
N8	48(2)	63(2)	58(2)	12(2)	18(2)	-9(1)
C25	38(2)	36(2)	32(1)	0(1)	11(1)	2(1)
C26	54(2)	36(2)	36(2)	-2(1)	6(2)	-4(1)
C27	56(2)	47(2)	46(2)	-9(2)	6(2)	-12(2)
C28	47(2)	58(2)	36(2)	-6(2)	0(1)	-4(2)
C29	45(2)	48(2)	34(2)	3(1)	7(1)	9(1)

C30	38(2)	36(2)	30(1)	1(1)	10(1)	4(1)
C31	47(2)	32(1)	31(1)	7(1)	10(1)	8(1)
C32	35(2)	29(1)	34(1)	1(1)	13(1)	2(1)
C33	34(2)	23(1)	31(1)	1(1)	11(1)	-1(1)
C34	30(1)	25(1)	33(1)	2(1)	9(1)	-1(1)
C35	33(2)	24(1)	31(1)	3(1)	7(1)	-2(1)
C36	49(2)	26(1)	34(2)	4(1)	11(1)	-3(1)
C37	39(2)	33(1)	34(1)	3(1)	11(1)	-6(1)
C38	32(2)	30(1)	31(1)	5(1)	6(1)	-1(1)
C39	41(2)	32(2)	34(2)	5(1)	4(1)	2(1)
C40	251(8)	45(2)	34(2)	-12(2)	18(3)	-30(3)
C41	93(4)	77(3)	118(5)	-33(3)	-45(3)	6(3)
C42	40(2)	29(1)	34(2)	6(1)	6(1)	-4(1)
C43	35(2)	24(1)	27(1)	0(1)	8(1)	-4(1)
C44	53(2)	38(2)	33(2)	4(1)	18(1)	3(1)
C45	48(2)	43(2)	52(2)	-1(1)	24(2)	4(1)
C46	39(2)	32(1)	41(2)	-4(1)	2(1)	5(1)
C47	47(2)	36(2)	28(1)	2(1)	7(1)	4(1)
C48	40(2)	34(1)	31(1)	4(1)	13(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3aa**.

	x	y	z	U(eq)
H1	-6245	1702	-6142	51
H2	-6468	3277	-6444	56
H3	-5014	4294	-5295	57
H4	-3311	3732	-3835	52
H7	-3723	554	-4818	37
H8	-2011	2355	-2838	46
H9A	-6235	353	-4836	37
H9B	-5646	-176	-5564	37
H16A	-5857	-3898	-2256	62
H16B	-4490	-3444	-1819	62
H17A	-5393	-4522	-3666	111

H17B	-4478	-4903	-2554	111
H17C	-3998	-4133	-3130	111
H18A	-6941	-1373	-5512	38
H18B	-7257	-2091	-4777	38
H20	-4494	-2142	-5428	45
H21	-3939	-3299	-6354	64
H22	-5329	-4522	-7056	67
H23	-7212	-4602	-6792	66
H24	-7783	-3443	-5886	50
H26	2481	-1134	-1695	54
H27	4149	-979	-46	65
H28	4887	-2252	1045	62
H29	4032	-3694	479	53
H31	2329	-4671	-877	46
H32	335	-2686	-2441	39
H33A	395	-1531	-3567	36
H33B	1715	-1868	-3591	36
H40A	-1348	-3948	-8391	145
H40B	-2479	-3843	-7993	145
H41A	-2824	-3368	-9691	181
H41B	-1959	-2518	-9156	181
H41C	-3231	-2691	-8971	181
H42A	125	-1082	-5306	44
H42B	270	-1479	-6332	44
H44	-2413	-1284	-5540	49
H45	-4416	-740	-6614	55
H46	-4786	-207	-8306	49
H47	-3156	-229	-8945	47
H48	-1167	-784	-7890	43

Table 6. Torsion angles [°] for **3aa**.

N1-N2-C7-C6	-60.4(3)
N1-N2-C7-C9	174.0(2)
N1-N2-C11-C10	-167.6(2)
N1-N2-C11-C12	70.1(3)
N1-N2-C11-C13	-51.3(3)

N2-N1-C8-C5	-0.4(4)
N2-C7-C9-C10	-34.0(3)
C1-C2-C3-C4	0.1(5)
C1-C6-C7-N2	-145.1(3)
C1-C6-C7-C9	-32.0(4)
C2-C1-C6-C5	-0.1(5)
C2-C1-C6-C7	-176.9(3)
C2-C3-C4-C5	-0.7(5)
C3-C4-C5-C6	0.8(5)
C3-C4-C5-C8	-179.0(3)
C4-C5-C6-C1	-0.5(4)
C4-C5-C6-C7	176.7(3)
C4-C5-C8-N1	161.0(3)
C5-C6-C7-N2	37.9(3)
C5-C6-C7-C9	151.0(3)
C6-C1-C2-C3	0.2(5)
C6-C5-C8-N1	-18.7(5)
C6-C7-C9-C10	-150.3(2)
C7-N2-C11-C10	-37.2(3)
C7-N2-C11-C12	-159.5(2)
C7-N2-C11-C13	79.1(3)
C7-C9-C10-C11	12.7(3)
C7-C9-C10-C14	-164.8(3)
C8-N1-N2-C7	41.9(3)
C8-N1-N2-C11	167.4(2)
C8-C5-C6-C1	179.3(3)
C8-C5-C6-C7	-3.5(4)
C9-C10-C11-N2	13.9(3)
C9-C10-C11-C12	130.8(2)
C9-C10-C11-C13	-103.5(2)
C9-C10-C14-C15	177.5(3)
C9-C10-C14-C18	2.1(4)
C10-C14-C15-O1	-22.1(4)
C10-C14-C15-O2	158.6(3)
C10-C14-C18-C19	113.9(3)
C11-N2-C7-C6	171.2(2)
C11-N2-C7-C9	45.6(3)
C11-C10-C14-C15	0.5(4)

C11-C10-C14-C18	-174.9(2)
C14-C10-C11-N2	-168.6(3)
C14-C10-C11-C12	-51.7(4)
C14-C10-C11-C13	74.0(3)
C14-C18-C19-C20	-40.4(4)
C14-C18-C19-C24	141.5(3)
C15-O2-C16-C17	-87.6(4)
C15-C14-C18-C19	-61.6(3)
C16-O2-C15-O1	-6.3(4)
C16-O2-C15-C14	172.9(2)
C18-C14-C15-O1	153.5(3)
C18-C14-C15-O2	-25.8(3)
C18-C19-C20-C21	-177.0(3)
C18-C19-C24-C23	177.4(3)
C19-C20-C21-C22	-0.3(5)
C20-C19-C24-C23	-0.8(4)
C20-C21-C22-C23	-1.0(5)
C21-C22-C23-C24	1.3(5)
C22-C23-C24-C19	-0.4(5)
C24-C19-C20-C21	1.2(4)
N5-N6-C32-C25	57.8(3)
N5-N6-C32-C33	-176.8(2)
N5-N6-C35-C34	171.1(2)
N5-N6-C35-C36	-68.9(3)
N5-N6-C35-C37	52.3(3)
N6-N5-C31-C30	2.0(4)
N6-C32-C33-C34	33.9(3)
C25-C26-C27-C28	-0.5(6)
C25-C30-C31-N5	15.2(5)
C25-C32-C33-C34	150.9(2)

C26-C25-C30-C29	2.5(5)
C26-C25-C30-C31	-178.2(3)
C26-C25-C32-N6	146.6(3)
C26-C25-C32-C33	32.8(4)
C26-C27-C28-C29	1.5(6)
C27-C28-C29-C30	-0.5(6)
C28-C29-C30-C25	-1.5(5)
C28-C29-C30-C31	179.2(3)
C29-C30-C31-N5	-165.5(3)
C30-C25-C26-C27	-1.5(5)
C30-C25-C32-N6	-36.9(3)
C30-C25-C32-C33	-150.7(3)
C31-N5-N6-C32	-40.7(4)
C31-N5-N6-C35	-167.7(3)
C32-N6-C35-C34	38.7(3)
C32-N6-C35-C36	158.6(2)
C32-N6-C35-C37	-80.2(3)
C32-C25-C26-C27	174.8(3)
C32-C25-C30-C29	-174.2(3)
C32-C25-C30-C31	5.1(4)
C32-C33-C34-C35	-11.4(3)
C32-C33-C34-C38	171.7(3)
C33-C34-C35-N6	-15.3(3)
C33-C34-C35-C36	-131.0(3)
C33-C34-C35-C37	103.0(3)
C33-C34-C38-C39	-177.2(3)
C33-C34-C38-C42	1.5(5)
C34-C38-C39-O3	27.0(5)
C34-C38-C39-O4	-154.2(3)
C34-C38-C42-C43	-127.1(3)

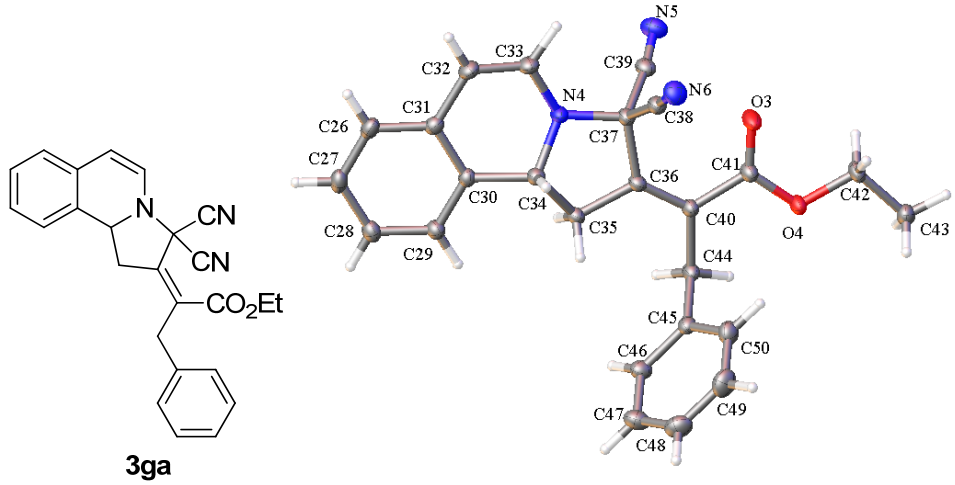
C35-N6-C32-C25	-172.1(2)
C35-N6-C32-C33	-46.7(3)
C35-C34-C38-C39	6.5(5)
C35-C34-C38-C42	-174.9(3)
C38-C34-C35-N6	161.6(3)
C38-C34-C35-C36	46.0(4)
C38-C34-C35-C37	-80.0(4)
C38-C42-C43-C44	54.0(4)
C38-C42-C43-C48	-123.2(3)
C39-O4-C40-C41	137.1(6)
C39-C38-C42-C43	51.6(4)
C40-O4-C39-O3	6.7(6)
C40-O4-C39-C38	-172.0(4)
C42-C38-C39-O3	-151.7(3)
C42-C38-C39-O4	27.0(4)
C42-C43-C44-C45	-177.5(3)
C42-C43-C48-C47	177.9(3)
C43-C44-C45-C46	-0.3(5)
C44-C43-C48-C47	0.6(4)
C44-C45-C46-C47	0.4(5)
C45-C46-C47-C48	0.0(5)
C46-C47-C48-C43	-0.5(4)
C48-C43-C44-C45	-0.2(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3aa** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-Ray Crystallography Data of 3ga



3ga

Table 1. Crystal data and structure refinement for **3ga**.

Identification code	**3ga**	
Empirical formula	$C_{25}H_{21}N_3O2$	
Formula weight	395.45	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 16.156(3) Å	a= 90°
	b = 10.118(2) Å	b= 105.14(3)°
	c = 25.816(5) Å	g = 90°
Volume	4073.8(15) $Å^3$	
Z	4	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	1660	
Crystal size	0.21 x 0.19 x 0.07 mm^3	
Theta range for data collection	1.306 to 27.480°	
Index ranges	-20<=h<=20, -13<=k<=13, -33<=l<=33	
Reflections collected	28360	
Independent reflections	9274 [R(int) = 0.0542]	
Completeness to theta = 26.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7639	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9274 / 0 / 565	

Goodness-of-fit on F^2	1.162
Final R indices [I>2sigma(I)]	R1 = 0.0704, wR2 = 0.1499
R indices (all data)	R1 = 0.0835, wR2 = 0.1583
Extinction coefficient	n/a
Largest diff. peak and hole	0.421 and -0.210 e.$Å^{-3}$

Table 2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3ga**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	1760(1)	2624(1)	1537(1)	46(1)
O2	1951(1)	492(1)	1372(1)	38(1)
N1	-556(1)	4018(2)	1740(1)	52(1)
N2	1429(1)	4348(2)	2487(1)	51(1)
N3	393(1)	4442(2)	732(1)	52(1)
C1	-2747(1)	5148(2)	2173(1)	43(1)
C2	-3280(2)	4201(3)	2298(1)	48(1)
C3	-3083(1)	2879(2)	2284(1)	42(1)
C4	-2355(1)	2490(2)	2137(1)	37(1)
C5	-1820(1)	3434(2)	2006(1)	36(1)
C6	-2010(1)	4782(2)	2026(1)	35(1)
C7	-1428(1)	5743(2)	1893(1)	40(1)
C8	-731(1)	5361(2)	1757(1)	38(1)
C10	-733(1)	1768(2)	1781(1)	33(1)
C11	118(1)	2008(2)	1661(1)	33(1)
C12	240(1)	3532(2)	1651(1)	36(1)
C13	962(1)	3970(2)	2106(1)	37(1)
C14	351(1)	4022(2)	1132(1)	36(1)
C15	673(1)	1084(2)	1592(1)	32(1)
C16	1505(1)	1493(2)	1499(1)	34(1)
C17	2792(1)	862(2)	1304(1)	42(1)
C18	3195(2)	-347(2)	1147(1)	55(1)
C19	472(1)	-372(2)	1629(1)	33(1)
C20	-174(1)	-913(2)	1140(1)	32(1)
C21	-979(1)	-1311(2)	1172(1)	39(1)
C22	-1576(2)	-1818(2)	732(1)	49(1)
C23	-1374(2)	-1947(2)	250(1)	54(1)

C24	-574(2)	-1558(3)	209(1)	56(1)
C25	25(2)	-1038(2)	650(1)	46(1)
C9	-897(3)	3063(4)	2010(2)	26(1)
O3	3465(1)	3799(1)	1028(1)	50(1)
O4	3177(1)	5930(1)	1141(1)	35(1)
N4	5684(1)	2704(2)	584(1)	33(1)
N5	3635(1)	2189(2)	12(1)	50(1)
N6	5005(1)	1820(2)	1673(1)	49(1)
C26	7994(1)	1962(2)	223(1)	39(1)
C27	8488(1)	3012(2)	130(1)	41(1)
C28	8265(1)	4292(2)	215(1)	38(1)
C29	7552(1)	4531(2)	406(1)	34(1)
C30	7062(1)	3490(2)	507(1)	30(1)
C31	7269(1)	2184(2)	407(1)	32(1)
C32	6703(1)	1118(2)	482(1)	38(1)
C33	5942(1)	1385(2)	561(1)	38(1)
C34	6358(1)	3672(2)	784(1)	32(1)
C35	5863(1)	4952(2)	709(1)	31(1)
C36	5014(1)	4583(2)	806(1)	30(1)
C37	4940(1)	3056(2)	768(1)	31(1)
C38	4950(1)	2408(2)	1289(1)	34(1)
C39	4168(1)	2590(2)	356(1)	35(1)
C40	4446(1)	5444(2)	899(1)	31(1)
C41	3652(1)	4954(2)	1025(1)	35(1)
C42	2384(1)	5510(2)	1261(1)	40(1)
C43	1922(1)	6736(2)	1355(1)	40(1)
C44	4596(1)	6917(2)	870(1)	33(1)
C45	5233(1)	7507(2)	1352(1)	32(1)
C46	5926(1)	8228(2)	1281(1)	39(1)
C47	6510(2)	8804(2)	1709(1)	49(1)
C48	6408(2)	8671(3)	2219(1)	54(1)
C49	5729(2)	7960(3)	2297(1)	56(1)
C50	5143(2)	7379(2)	1869(1)	45(1)
C9A	-1172(3)	3096(4)	1682(3)	31(1)

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

O1-C16	1.211(2)
O2-C16	1.331(2)
O2-C17	1.465(2)
N1-C8	1.391(3)
N1-C12	1.449(3)
N1-C9	1.386(4)
N1-C9A	1.344(4)
N2-C13	1.138(3)
N3-C14	1.135(3)
C1-C2	1.382(3)
C1-C6	1.392(3)
C2-C3	1.378(3)
C3-C4	1.384(3)
C4-C5	1.387(3)
C5-C6	1.402(3)
C5-C9	1.537(4)
C5-C9A	1.540(5)
C6-C7	1.454(3)
C7-C8	1.322(3)
C10-C11	1.507(3)
C10-C9	1.490(4)
C10-C9A	1.510(4)
C11-C12	1.555(3)
C11-C15	1.339(3)
C12-C13	1.491(3)
C12-C14	1.482(3)
C15-C16	1.486(3)
C15-C19	1.517(3)
C17-C18	1.490(3)
C19-C20	1.514(3)
C20-C21	1.385(3)
C20-C25	1.390(3)
C21-C22	1.382(3)
C22-C23	1.372(4)
C23-C24	1.381(4)
C24-C25	1.390(3)

O3-C41	1.207(2)
O4-C41	1.333(2)
O4-C42	1.457(2)
N4-C33	1.404(2)
N4-C34	1.456(2)
N4-C37	1.447(3)
N5-C39	1.138(3)
N6-C38	1.139(3)
C26-C27	1.387(3)
C26-C31	1.391(3)
C27-C28	1.377(3)
C28-C29	1.387(3)
C29-C30	1.382(3)
C30-C31	1.403(3)
C30-C34	1.505(3)
C31-C32	1.460(3)
C32-C33	1.326(3)
C34-C35	1.507(3)
C35-C36	1.504(3)
C36-C37	1.551(3)
C36-C40	1.331(3)
C37-C38	1.493(3)
C37-C39	1.488(3)
C40-C41	1.489(3)
C40-C44	1.515(3)
C42-C43	1.500(3)
C44-C45	1.515(3)
C45-C46	1.387(3)
C45-C50	1.386(3)
C46-C47	1.381(3)
C47-C48	1.374(4)
C48-C49	1.370(4)
C49-C50	1.385(3)

C16-O2-C17	114.45(15)
C8-N1-C12	122.23(17)
C9-N1-C8	123.6(2)
C9-N1-C12	109.2(2)

C9A-N1-C8	122.0(2)
C9A-N1-C12	114.1(2)
C2-C1-C6	120.6(2)
C3-C2-C1	120.4(2)
C2-C3-C4	120.1(2)
C3-C4-C5	119.9(2)
C4-C5-C6	120.4(2)
C4-C5-C9	119.7(2)
C4-C5-C9A	122.3(2)
C6-C5-C9	117.2(2)
C6-C5-C9A	114.9(2)
C1-C6-C5	118.6(2)
C1-C6-C7	122.57(19)
C5-C6-C7	118.83(19)
C8-C7-C6	120.96(19)
C7-C8-N1	119.3(2)
C11-C10-C9A	103.6(2)
C9-C10-C11	101.9(2)
C10-C11-C12	106.83(16)
C15-C11-C10	126.37(18)
C15-C11-C12	126.77(18)
N1-C12-C11	102.32(15)
N1-C12-C13	108.50(19)
N1-C12-C14	110.56(18)
C13-C12-C11	110.98(17)
C14-C12-C11	113.10(18)
C14-C12-C13	110.99(17)
N2-C13-C12	170.7(2)
N3-C14-C12	175.9(2)
C11-C15-C16	119.52(17)
C11-C15-C19	120.58(18)
C16-C15-C19	119.86(17)
O1-C16-O2	123.05(19)
O1-C16-C15	123.49(18)
O2-C16-C15	113.46(16)
O2-C17-C18	107.98(17)
C20-C19-C15	114.26(16)
C21-C20-C19	120.50(19)

C21-C20-C25	118.2(2)
C25-C20-C19	121.28(19)
C22-C21-C20	121.5(2)
C23-C22-C21	120.0(2)
C22-C23-C24	119.4(2)
C23-C24-C25	120.8(2)
C20-C25-C24	120.1(2)
N1-C9-C5	109.9(3)
N1-C9-C10	106.2(3)
C10-C9-C5	119.0(3)
C41-O4-C42	114.93(15)
C33-N4-C34	116.84(16)
C33-N4-C37	121.95(16)
C37-N4-C34	109.04(15)
C27-C26-C31	120.6(2)
C28-C27-C26	120.4(2)
C27-C28-C29	119.8(2)
C30-C29-C28	120.24(19)
C29-C30-C31	120.42(18)
C29-C30-C34	122.49(17)
C31-C30-C34	116.71(17)
C26-C31-C30	118.55(19)
C26-C31-C32	122.53(18)
C30-C31-C32	118.89(18)
C33-C32-C31	120.53(18)
C32-C33-N4	119.89(19)
N4-C34-C30	109.70(16)
N4-C34-C35	102.10(15)
C30-C34-C35	119.08(17)
C36-C35-C34	104.03(15)
C35-C36-C37	107.13(16)
C40-C36-C35	124.70(17)
C40-C36-C37	128.17(18)
N4-C37-C36	102.09(15)
N4-C37-C38	111.93(16)
N4-C37-C39	107.43(17)
C38-C37-C36	113.40(17)
C39-C37-C36	113.43(16)

C39-C37-C38	108.36(16)
N6-C38-C37	173.3(2)
N5-C39-C37	173.0(2)
C36-C40-C41	119.68(17)
C36-C40-C44	120.51(18)
C41-C40-C44	119.81(17)
O3-C41-O4	123.78(19)
O3-C41-C40	123.75(18)
O4-C41-C40	112.47(16)
O4-C42-C43	107.18(16)
C45-C44-C40	115.48(17)
C46-C45-C44	119.89(18)
C50-C45-C44	122.30(19)
C50-C45-C46	117.8(2)
C47-C46-C45	121.6(2)
C48-C47-C46	119.8(2)
C49-C48-C47	119.6(2)
C48-C49-C50	120.7(2)
C49-C50-C45	120.6(2)
N1-C9A-C5	112.0(3)
N1-C9A-C10	107.3(3)
C10-C9A-C5	117.5(3)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	36(1)	27(1)	81(1)	-8(1)	26(1)	-6(1)
O2	27(1)	29(1)	60(1)	-6(1)	18(1)	-2(1)
N1	42(1)	22(1)	106(2)	7(1)	43(1)	4(1)
N2	62(1)	38(1)	52(1)	-7(1)	13(1)	4(1)
N3	39(1)	63(1)	51(1)	4(1)	5(1)	-9(1)
C1	42(1)	46(1)	42(1)	-1(1)	12(1)	14(1)

C2	38(1)	65(2)	45(1)	6(1)	19(1)	13(1)
C3	33(1)	55(1)	41(1)	10(1)	11(1)	3(1)
C4	31(1)	40(1)	41(1)	5(1)	10(1)	3(1)
C5	32(1)	35(1)	46(1)	0(1)	16(1)	3(1)
C6	35(1)	34(1)	36(1)	0(1)	8(1)	6(1)
C7	43(1)	27(1)	52(1)	-1(1)	16(1)	5(1)
C8	38(1)	24(1)	53(1)	2(1)	14(1)	2(1)
C10	30(1)	26(1)	47(1)	4(1)	17(1)	1(1)
C11	28(1)	26(1)	46(1)	0(1)	12(1)	-3(1)
C12	30(1)	24(1)	59(1)	0(1)	18(1)	-1(1)
C13	43(1)	24(1)	47(1)	1(1)	19(1)	2(1)
C14	29(1)	31(1)	49(1)	-1(1)	7(1)	-6(1)
C15	26(1)	27(1)	44(1)	-3(1)	9(1)	-3(1)
C16	28(1)	27(1)	46(1)	-2(1)	10(1)	0(1)
C17	29(1)	37(1)	64(1)	-6(1)	22(1)	-5(1)
C18	40(1)	45(1)	89(2)	-15(1)	31(1)	-4(1)
C19	30(1)	24(1)	46(1)	0(1)	11(1)	0(1)
C20	35(1)	19(1)	43(1)	0(1)	11(1)	2(1)
C21	38(1)	28(1)	52(1)	0(1)	11(1)	-6(1)
C22	41(1)	36(1)	65(2)	0(1)	4(1)	-9(1)
C23	54(2)	39(1)	57(2)	-8(1)	-8(1)	3(1)
C24	67(2)	56(2)	43(1)	-8(1)	12(1)	14(1)
C25	42(1)	45(1)	52(1)	-2(1)	17(1)	5(1)
C9	24(2)	28(2)	23(3)	-1(2)	3(2)	-1(1)
O3	41(1)	29(1)	91(1)	3(1)	34(1)	-1(1)
O4	26(1)	31(1)	53(1)	1(1)	17(1)	0(1)
N4	30(1)	24(1)	48(1)	-2(1)	16(1)	-2(1)
N5	44(1)	41(1)	57(1)	0(1)	2(1)	-7(1)
N6	53(1)	49(1)	49(1)	7(1)	18(1)	-1(1)
C26	35(1)	41(1)	40(1)	-10(1)	10(1)	6(1)
C27	30(1)	55(1)	39(1)	-7(1)	12(1)	3(1)
C28	29(1)	44(1)	41(1)	0(1)	10(1)	-2(1)
C29	28(1)	32(1)	40(1)	0(1)	10(1)	-1(1)
C30	26(1)	32(1)	31(1)	-2(1)	8(1)	2(1)
C31	32(1)	31(1)	33(1)	-3(1)	6(1)	2(1)
C32	40(1)	25(1)	51(1)	-3(1)	14(1)	4(1)
C33	39(1)	24(1)	51(1)	-2(1)	14(1)	-1(1)
C34	31(1)	28(1)	40(1)	-2(1)	12(1)	-2(1)

C35	27(1)	26(1)	39(1)	-1(1)	10(1)	-3(1)
C36	28(1)	25(1)	37(1)	2(1)	9(1)	-3(1)
C37	27(1)	26(1)	42(1)	1(1)	12(1)	-2(1)
C38	32(1)	29(1)	44(1)	-1(1)	13(1)	-2(1)
C39	34(1)	27(1)	46(1)	3(1)	11(1)	-3(1)
C40	25(1)	27(1)	42(1)	-1(1)	11(1)	-1(1)
C41	27(1)	30(1)	50(1)	2(1)	13(1)	0(1)
C42	30(1)	37(1)	57(1)	5(1)	21(1)	-2(1)
C43	36(1)	40(1)	49(1)	-5(1)	19(1)	-2(1)
C44	28(1)	25(1)	47(1)	2(1)	14(1)	1(1)
C45	33(1)	25(1)	41(1)	-1(1)	14(1)	2(1)
C46	44(1)	32(1)	41(1)	-1(1)	13(1)	-6(1)
C47	48(1)	42(1)	55(1)	-2(1)	8(1)	-12(1)
C48	60(2)	50(1)	48(1)	-10(1)	3(1)	-2(1)
C49	66(2)	67(2)	40(1)	-2(1)	21(1)	7(1)
C50	47(1)	47(1)	47(1)	1(1)	22(1)	1(1)
C9A	25(2)	25(2)	40(4)	2(2)	4(2)	1(2)

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

	x	y	z	U(eq)
H1	-2883	6039	2186	52
H2	-3773	4457	2393	57
H3	-3441	2247	2373	51
H4	-2224	1597	2126	45
H7	-1549	6640	1903	48
H8	-318(18)	5970(30)	1683(11)	64(8)
H10	-723(19)	1210(30)	1996(12)	73(10)
H17A	3149	1218	1636	50
H17B	2729	1531	1027	50
H18A	2851	-669	810	83
H18B	3237	-1015	1417	83
H18C	3759	-137	1114	83
H19A	1000	-871	1683	40

H19B	254	-509	1941	40
H21	-1121	-1235	1497	47
H22	-2114	-2072	763	59
H23	-1772	-2294	-46	65
H24	-435	-1645	-117	67
H25	560	-773	616	55
H9	-558	3078	2385	31
H26	8148	1102	162	46
H27	8973	2851	10	49
H28	8591	4994	145	45
H29	7403	5394	466	40
H32	6878	244	475	46
H33	5481(15)	700(20)	593(9)	48(7)
H34	6597	3523	1169	39
H35A	6154	5611	965	37
H35B	5788	5293	349	37
H42A	2509	4953	1578	47
H42B	2033	5012	963	47
H43A	1788	7267	1036	61
H43B	2281	7231	1646	61
H43C	1402	6495	1445	61
H44A	4795	7093	553	39
H44B	4052	7366	824	39
H46	5998	8326	938	46
H47	6971	9280	1653	59
H48	6796	9062	2508	65
H49	5661	7866	2642	68
H50	4686	6899	1928	54
H9A	-1492	3110	1303	37

Table 6. Torsion angles [°] for **3ga**.

C1-C2-C3-C4	-0.8(3)
C1-C6-C7-C8	179.7(2)
C2-C1-C6-C5	0.2(3)
C2-C1-C6-C7	-179.7(2)
C2-C3-C4-C5	0.3(3)

C3-C4-C5-C6	0.5(3)
C3-C4-C5-C9	161.6(3)
C3-C4-C5-C9A	-161.0(3)
C4-C5-C6-C1	-0.7(3)
C4-C5-C6-C7	179.2(2)
C4-C5-C9-N1	164.7(3)
C4-C5-C9-C10	42.0(5)
C4-C5-C9A-N1	-161.0(3)
C4-C5-C9A-C10	-36.1(5)
C5-C6-C7-C8	-0.2(3)
C6-C1-C2-C3	0.5(3)
C6-C5-C9-N1	-33.6(4)
C6-C5-C9-C10	-156.3(3)
C6-C5-C9A-N1	36.6(5)
C6-C5-C9A-C10	161.5(3)
C6-C7-C8-N1	0.3(4)
C8-N1-C12-C11	-179.4(2)
C8-N1-C12-C13	63.2(3)
C8-N1-C12-C14	-58.7(3)
C8-N1-C9-C5	36.2(5)
C8-N1-C9-C10	166.2(2)
C8-N1-C9A-C5	-39.5(6)
C8-N1-C9A-C10	-169.9(3)
C10-C11-C12-N1	-2.5(2)
C10-C11-C12-C13	113.07(19)
C10-C11-C12-C14	-121.44(19)
C10-C11-C15-C16	-177.4(2)
C10-C11-C15-C19	0.4(3)
C11-C10-C9-N1	34.2(4)
C11-C10-C9-C5	158.7(3)
C11-C10-C9A-N1	-23.8(4)
C11-C10-C9A-C5	-151.0(3)
C11-C15-C16-O1	8.2(3)
C11-C15-C16-O2	-172.32(19)
C11-C15-C19-C20	76.4(3)
C12-N1-C8-C7	-173.3(2)
C12-N1-C9-C5	-168.5(2)
C12-N1-C9-C10	-38.5(4)

C12-N1-C9A-C5	154.7(3)
C12-N1-C9A-C10	24.4(5)
C12-C11-C15-C16	0.5(3)
C12-C11-C15-C19	178.3(2)
C15-C11-C12-N1	179.3(2)
C15-C11-C12-C13	-65.1(3)
C15-C11-C12-C14	60.4(3)
C15-C19-C20-C21	-112.2(2)
C15-C19-C20-C25	68.5(2)
C16-O2-C17-C18	-178.2(2)
C16-C15-C19-C20	-105.9(2)
C17-O2-C16-O1	2.3(3)
C17-O2-C16-C15	-177.20(18)
C19-C15-C16-O1	-169.6(2)
C19-C15-C16-O2	9.9(3)
C19-C20-C21-C22	-179.44(19)
C19-C20-C25-C24	178.9(2)
C20-C21-C22-C23	0.5(3)
C21-C20-C25-C24	-0.4(3)
C21-C22-C23-C24	-0.5(4)
C22-C23-C24-C25	-0.1(4)
C23-C24-C25-C20	0.5(4)
C25-C20-C21-C22	-0.1(3)
C9-N1-C8-C7	-21.1(4)
C9-N1-C12-C11	24.9(3)
C9-N1-C12-C13	-92.5(3)
C9-N1-C12-C14	145.6(3)
C9-N1-C9A-C5	65.0(5)
C9-N1-C9A-C10	-65.4(4)
C9-C5-C6-C1	-162.3(3)
C9-C5-C6-C7	17.6(4)
C9-C5-C9A-N1	-65.5(5)
C9-C5-C9A-C10	59.4(4)
C9-C10-C11-C12	-18.3(3)
C9-C10-C11-C15	159.9(3)
C9-C10-C9A-N1	67.0(4)
C9-C10-C9A-C5	-60.2(5)
N4-C34-C35-C36	33.7(2)

C26-C27-C28-C29	1.4(3)
C26-C31-C32-C33	-167.4(2)
C27-C26-C31-C30	-1.4(3)
C27-C26-C31-C32	176.5(2)
C27-C28-C29-C30	-0.5(3)
C28-C29-C30-C31	-1.3(3)
C28-C29-C30-C34	171.36(19)
C29-C30-C31-C26	2.2(3)
C29-C30-C31-C32	-175.73(19)
C29-C30-C34-N4	148.48(18)
C29-C30-C34-C35	31.5(3)
C30-C31-C32-C33	10.5(3)
C30-C34-C35-C36	154.65(17)
C31-C26-C27-C28	-0.4(3)
C31-C30-C34-N4	-38.6(2)
C31-C30-C34-C35	-155.56(18)
C31-C32-C33-N4	-1.4(3)
C33-N4-C34-C30	48.3(2)
C33-N4-C34-C35	175.52(18)
C33-N4-C37-C36	171.23(18)
C33-N4-C37-C38	49.6(3)
C33-N4-C37-C39	-69.2(2)
C34-N4-C33-C32	-29.8(3)
C34-N4-C37-C36	30.1(2)
C34-N4-C37-C38	-91.47(19)
C34-N4-C37-C39	149.70(16)
C34-C30-C31-C26	-170.86(18)
C34-C30-C31-C32	11.2(3)

C34-C35-C36-C37	-16.4(2)
C34-C35-C36-C40	164.4(2)
C35-C36-C37-N4	-7.4(2)
C35-C36-C37-C38	113.23(19)
C35-C36-C37-C39	-122.61(18)
C35-C36-C40-C41	-175.95(18)
C35-C36-C40-C44	4.9(3)
C36-C40-C41-O3	-3.2(3)
C36-C40-C41-O4	176.02(18)
C36-C40-C44-C45	-77.8(3)
C37-N4-C33-C32	-168.1(2)
C37-N4-C34-C30	-168.36(16)
C37-N4-C34-C35	-41.2(2)
C37-C36-C40-C41	5.0(3)
C37-C36-C40-C44	-174.13(19)
C40-C36-C37-N4	171.8(2)
C40-C36-C37-C38	-67.6(3)
C40-C36-C37-C39	56.6(3)
C40-C44-C45-C46	125.5(2)
C40-C44-C45-C50	-55.9(3)
C41-O4-C42-C43	-177.45(18)
C41-C40-C44-C45	103.1(2)
C42-O4-C41-O3	-1.6(3)
C42-O4-C41-C40	179.16(17)
C44-C40-C41-O3	176.0(2)
C44-C40-C41-O4	-4.8(3)
C44-C45-C46-C47	178.7(2)
C44-C45-C50-C49	-178.5(2)

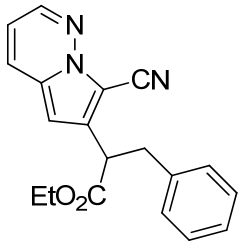
C45-C46-C47-C48	-0.3(4)
C46-C45-C50-C49	0.1(3)
C46-C47-C48-C49	0.5(4)
C47-C48-C49-C50	-0.3(4)
C48-C49-C50-C45	0.0(4)
C50-C45-C46-C47	0.0(3)
C9A-N1-C8-C7	22.1(5)
C9A-N1-C12-C11	-13.7(4)
C9A-N1-C12-C13	-131.1(4)
C9A-N1-C12-C14	107.0(4)
C9A-N1-C9-C5	-63.5(4)
C9A-N1-C9-C10	66.5(4)
C9A-C5-C6-C1	162.1(3)
C9A-C5-C6-C7	-18.0(4)
C9A-C5-C9-N1	60.4(4)
C9A-C5-C9-C10	-62.3(4)
C9A-C10-C11-C12	15.3(3)
C9A-C10-C11-C15	-166.5(3)
C9A-C10-C9-N1	-62.6(4)
C9A-C10-C9-C5	61.9(5)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mx3423 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-Ray Crystallography Data of 6



6

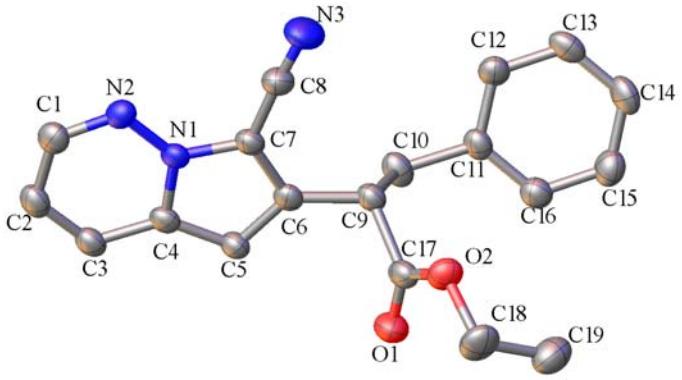


Table 1. Crystal data and structure refinement for **6**

Identification code	**6**	
Empirical formula	$C_{19}H_{17}N_3O_2$	
Formula weight	319.35	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.427(5) Å	a= 83.90(3)°
	b = 8.87(5) Å	b= 89.32(3)°
	c = 11.531(7) Å	g = 71.399(19)°
Volume	812(5) $Å^3$	
Z	2	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	336	
Crystal size	0.29 x 0.21 x 0.06 mm^3	
Theta range for data collection	2.858 to 27.452°	
Index ranges	-10<=h<=10, -11<=k<=11, -14<=l<=14	
Reflections collected	6873	
Independent reflections	3614 [R(int) = 0.0619]	
Completeness to theta = 26.000°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.4197	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3614 / 0 / 218	
Goodness-of-fit on F^2	1.112	
Final R indices [I>2sigma(I)]	R1 = 0.0943, wR2 = 0.2530	
R indices (all data)	R1 = 0.1078, wR2 = 0.2690	

Extinction coefficient	n/a
Largest diff. peak and hole	0.384 and -0.369 e.Å^{-3}

Table 2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	5890(3)	6364(2)	6824(2)	49(1)
O2	6000(3)	5314(2)	8701(2)	41(1)
N1	10236(3)	1011(2)	6263(2)	29(1)
N2	11539(3)	-380(3)	6337(2)	35(1)
N3	8528(4)	-696(3)	8654(3)	60(1)
C1	12694(3)	-404(3)	5565(3)	37(1)
C2	12650(3)	866(3)	4697(2)	38(1)
C3	11329(3)	2240(3)	4639(2)	35(1)
C4	10050(3)	2354(3)	5461(2)	31(1)
C5	8559(3)	3506(3)	5710(2)	31(1)
C6	7835(3)	2868(3)	6662(2)	30(1)
C7	8900(3)	1313(3)	6991(2)	30(1)
C8	8737(4)	173(3)	7904(3)	39(1)
C9	6215(3)	3566(3)	7259(2)	30(1)
C10	4696(3)	3575(4)	6521(2)	38(1)
C11	3159(3)	3726(3)	7253(2)	33(1)
C12	2905(3)	2341(3)	7799(2)	36(1)
C13	1556(4)	2436(4)	8519(3)	41(1)
C14	443(3)	3900(4)	8712(3)	43(1)
C15	684(4)	5277(4)	8180(3)	44(1)
C16	2034(3)	5193(3)	7446(2)	37(1)
C17	6011(3)	5251(3)	7550(2)	34(1)
C18	5829(4)	6833(4)	9130(3)	54(1)
C19	4027(5)	7835(4)	9170(3)	56(1)

Table 3. Bond lengths [Å] and angles [°] for **6**.

O1-C17	1.203(5)
O2-C17	1.333(4)
O2-C18	1.448(8)
N1-N2	1.360(5)
N1-C4	1.396(6)
N1-C7	1.370(3)
N2-C1	1.308(4)
N3-C8	1.147(5)
C1-H1	0.9300
C1-C2	1.417(6)
C2-H2	0.9300
C2-C3	1.359(6)
C3-H3	0.9300
C3-C4	1.413(4)
C4-C5	1.392(5)
C5-H5	0.9300
C5-C6	1.403(4)
C6-C7	1.399(7)
C6-C9	1.500(4)
C7-C8	1.417(5)
C9-H9	0.9800
C9-C10	1.544(4)
C9-C17	1.522(9)
C10-H10A	0.9700
C10-H10B	0.9700
C10-C11	1.515(4)
C11-C12	1.396(7)
C11-C16	1.383(7)
C12-H12	0.9300
C12-C13	1.386(4)
C13-H13	0.9300
C13-C14	1.376(7)
C14-H14	0.9300
C14-C15	1.380(7)
C15-H15	0.9300
C15-C16	1.397(4)

C16-H16	0.9300
C18-H18A	0.9700
C18-H18B	0.9700
C18-C19	1.498(5)
C19-H19A	0.9600
C19-H19B	0.9600
C19-H19C	0.9600

C17-O2-C18	118.4(3)
N2-N1-C4	126.2(3)
N2-N1-C7	124.5(2)
C7-N1-C4	109.2(2)
C1-N2-N1	114.4(3)
N2-C1-H1	117.5
N2-C1-C2	125.1(3)
C2-C1-H1	117.5
C1-C2-H2	120.4
C3-C2-C1	119.3(3)
C3-C2-H2	120.4
C2-C3-H3	120.8
C2-C3-C4	118.5(3)
C4-C3-H3	120.8
N1-C4-C3	116.5(2)
C5-C4-N1	107.0(3)
C5-C4-C3	136.5(3)
C4-C5-H5	125.8
C4-C5-C6	108.4(3)
C6-C5-H5	125.8
C5-C6-C9	130.7(3)
C7-C6-C5	107.2(3)
C7-C6-C9	122.1(2)
N1-C7-C6	108.2(2)
N1-C7-C8	122.5(3)
C6-C7-C8	129.3(3)
N3-C8-C7	176.5(3)
C6-C9-H9	107.9
C6-C9-C10	111.8(2)
C6-C9-C17	111.3(2)

C10-C9-H9	107.9
C17-C9-H9	107.9
C17-C9-C10	110.0(2)
C9-C10-H10A	109.2
C9-C10-H10B	109.2
H10A-C10-H10B	107.9
C11-C10-C9	111.9(2)
C11-C10-H10A	109.2
C11-C10-H10B	109.2
C12-C11-C10	119.1(3)
C16-C11-C10	122.3(3)
C16-C11-C12	118.5(4)
C11-C12-H12	119.6
C13-C12-C11	120.7(3)
C13-C12-H12	119.6
C12-C13-H13	119.7
C14-C13-C12	120.5(3)
C14-C13-H13	119.7
C13-C14-H14	120.4
C13-C14-C15	119.3(4)
C15-C14-H14	120.4
C14-C15-H15	119.7
C14-C15-C16	120.7(3)
C16-C15-H15	119.7
C11-C16-C15	120.3(3)
C11-C16-H16	119.8
C15-C16-H16	119.8
O1-C17-O2	125.3(3)
O1-C17-C9	123.5(4)
O2-C17-C9	111.2(2)
O2-C18-H18A	109.4
O2-C18-H18B	109.4
O2-C18-C19	111.4(3)
H18A-C18-H18B	108.0
C19-C18-H18A	109.4
C19-C18-H18B	109.4
C18-C19-H19A	109.5
C18-C19-H19B	109.5

C18-C19-H19C	109.5
H19A-C19-H19B	109.5
H19A-C19-H19C	109.5
H19B-C19-H19C	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	51(1)	37(1)	59(1)	-1(1)	14(1)	-18(1)
O2	43(1)	38(1)	47(1)	-13(1)	-1(1)	-17(1)
N1	25(1)	28(1)	40(1)	-5(1)	2(1)	-14(1)
N2	28(1)	31(1)	47(1)	-9(1)	0(1)	-10(1)
N3	78(2)	44(2)	61(2)	2(1)	20(2)	-27(2)
C1	28(1)	40(1)	48(2)	-10(1)	0(1)	-16(1)
C2	31(1)	46(2)	42(1)	-10(1)	6(1)	-21(1)
C3	33(1)	40(1)	39(1)	-6(1)	4(1)	-21(1)
C4	30(1)	33(1)	36(1)	-5(1)	0(1)	-18(1)
C5	28(1)	31(1)	38(1)	-3(1)	3(1)	-14(1)
C6	27(1)	31(1)	36(1)	-8(1)	1(1)	-16(1)
C7	30(1)	31(1)	34(1)	-5(1)	2(1)	-16(1)
C8	42(2)	32(1)	44(2)	-5(1)	6(1)	-16(1)
C9	28(1)	32(1)	34(1)	-4(1)	2(1)	-15(1)
C10	33(1)	52(2)	37(1)	-9(1)	2(1)	-22(1)
C11	27(1)	42(1)	37(1)	-9(1)	2(1)	-18(1)
C12	35(1)	36(1)	42(1)	-12(1)	2(1)	-17(1)
C13	39(2)	51(2)	43(2)	-2(1)	-2(1)	-30(1)
C14	27(1)	61(2)	46(2)	-7(1)	5(1)	-21(1)
C15	32(1)	46(2)	52(2)	-13(1)	3(1)	-9(1)
C16	37(1)	38(1)	41(1)	-6(1)	2(1)	-17(1)
C17	25(1)	33(1)	48(2)	-3(1)	2(1)	-13(1)
C18	54(2)	49(2)	69(2)	-29(2)	-1(2)	-22(2)
C19	64(2)	43(2)	56(2)	-9(2)	3(2)	-10(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **6**.

	x	y	z	U(eq)
H1	13617	-1327	5589	45
H2	13516	761	4173	45
H3	11268	3086	4072	42
H5	8117	4524	5313	38
H9	6237	2893	7994	36
H10A	4448	4462	5909	46
H10B	4974	2591	6152	46
H12	3649	1344	7678	43
H13	1402	1503	8875	49
H14	-462	3961	9195	51
H15	-59	6270	8311	52
H16	2176	6129	7085	45
H18A	6424	7408	8627	65
H18B	6330	6643	9907	65
H19A	3547	8082	8395	83
H19B	3950	8811	9492	83
H19C	3429	7256	9650	83

Table 6. Torsion angles [°] for **6**.

N1-N2-C1-C2	-0.7(4)
N1-C4-C5-C6	0.0(3)
N2-N1-C4-C3	1.1(4)
N2-N1-C4-C5	-179.0(2)
N2-N1-C7-C6	179.0(2)
N2-N1-C7-C8	-0.7(4)
N2-C1-C2-C3	0.4(4)
C1-C2-C3-C4	0.6(4)
C2-C3-C4-N1	-1.3(4)
C2-C3-C4-C5	178.8(3)
C3-C4-C5-C6	179.9(3)
C4-N1-N2-C1	-0.1(3)
C4-N1-C7-C6	-0.1(3)
C4-N1-C7-C8	-179.8(2)

C4-C5-C6-C7	-0.1(3)
C4-C5-C6-C9	-177.7(2)
C5-C6-C7-N1	0.1(3)
C5-C6-C7-C8	179.7(3)
C5-C6-C9-C10	74.3(4)
C5-C6-C9-C17	-49.1(4)
C6-C9-C10-C11	160.4(2)
C6-C9-C17-O1	64.3(3)
C6-C9-C17-O2	-115.2(2)
C7-N1-N2-C1	-179.0(2)
C7-N1-C4-C3	-179.9(2)
C7-N1-C4-C5	0.0(3)
C7-C6-C9-C10	-103.0(4)
C7-C6-C9-C17	133.6(3)
C9-C6-C7-N1	178.0(2)
C9-C6-C7-C8	-2.4(4)
C9-C10-C11-C12	-88.1(3)
C9-C10-C11-C16	88.8(3)
C10-C9-C17-O1	-60.2(3)
C10-C9-C17-O2	120.3(2)
C10-C11-C12-C13	177.0(2)
C10-C11-C16-C15	-176.4(2)
C11-C12-C13-C14	-0.2(4)
C12-C11-C16-C15	0.5(4)
C12-C13-C14-C15	-0.1(4)
C13-C14-C15-C16	0.5(4)
C14-C15-C16-C11	-0.7(4)
C16-C11-C12-C13	-0.1(4)
C17-O2-C18-C19	84.8(3)
C17-C9-C10-C11	-75.4(3)
C18-O2-C17-O1	0.0(4)
C18-O2-C17-C9	179.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **6** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-Ray Crystallography Data of **7**

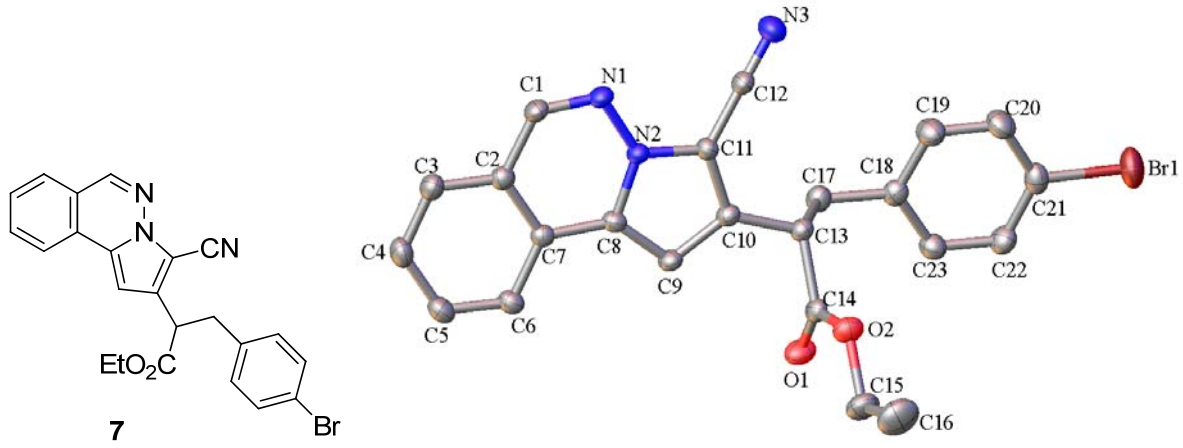


Table 1. Crystal data and structure refinement for **7**.

Identification code	**7**	
Empirical formula	C_{23} H_{18} Br N_3 O_2	
Formula weight	448.31	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.234(3) Å	a= 74.328(11)°
	b = 10.079(3) Å	b= 87.518(14)°
	c = 11.771(4) Å	g = 72.598(10)°
Volume	1005.7(5) $Å^3$	
Z	2	
Density (calculated)	1.480 Mg/m^3	
Absorption coefficient	2.068 mm^{-1}	
F(000)	456	
Crystal size	0.48 x 0.46 x 0.05 mm^3	
Theta range for data collection	1.798 to 27.510°	
Index ranges	-12<=h<=12, -13<=k<=13, -15<=l<=15	
Reflections collected	12571	
Independent reflections	4584 [R(int) = 0.0414]	
Completeness to theta = 26.000°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.4524	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4584 / 0 / 263	
Goodness-of-fit on F^2	1.084	

Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.0915
R indices (all data)	R1 = 0.0448, wR2 = 0.0964
Extinction coefficient	n/a
Largest diff. peak and hole	0.701 and -0.738 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br1	3229(1)	8878(1)	10259(1)	46(1)
O1	8862(2)	5627(2)	6307(2)	35(1)
O2	9232(2)	3944(2)	8047(1)	32(1)
N1	6354(2)	592(2)	5206(2)	25(1)
N2	6961(2)	1617(2)	5369(2)	21(1)
N3	4009(2)	2249(2)	7285(2)	39(1)
C1	6992(2)	-22(2)	4398(2)	27(1)
C2	8234(2)	285(2)	3706(2)	24(1)
C3	8830(2)	-428(2)	2842(2)	29(1)
C4	10031(3)	-126(2)	2207(2)	32(1)
C5	10658(2)	885(2)	2431(2)	31(1)
C6	10084(2)	1609(2)	3274(2)	26(1)
C7	8852(2)	1321(2)	3919(2)	21(1)
C8	8155(2)	2035(2)	4797(2)	22(1)
C9	8368(2)	3100(2)	5259(2)	24(1)
C10	7298(2)	3315(2)	6127(2)	22(1)
C11	6429(2)	2391(2)	6180(2)	22(1)
C12	5103(2)	2289(2)	6800(2)	25(1)
C13	7030(2)	4328(2)	6908(2)	23(1)
C14	8465(2)	4721(2)	7037(2)	24(1)
C15	10651(3)	4222(3)	8235(2)	40(1)
C16	11328(4)	3257(3)	9400(3)	56(1)
C17	5689(2)	5705(2)	6430(2)	27(1)
C18	5119(2)	6482(2)	7370(2)	26(1)
C19	4070(3)	6057(3)	8161(2)	35(1)
C20	3519(3)	6747(3)	9032(2)	37(1)
C21	4027(3)	7876(2)	9112(2)	31(1)
C22	5078(3)	8313(2)	8351(2)	31(1)
C23	5614(2)	7612(2)	7483(2)	30(1)

Table 3. Bond lengths [Å] and angles [°] for **7**.

Br1-C21	1.896(2)
O1-C14	1.207(3)
O2-C14	1.329(3)
O2-C15	1.457(3)
N1-N2	1.371(2)
N1-C1	1.298(3)
N2-C8	1.381(2)
N2-C11	1.377(2)
N3-C12	1.145(3)
C1-H1	0.9300
C1-C2	1.439(3)
C2-C3	1.401(3)
C2-C7	1.412(3)
C3-H3	0.9300
C3-C4	1.374(3)
C4-H4	0.9300
C4-C5	1.399(3)
C5-H5	0.9300
C5-C6	1.383(3)
C6-H6	0.9300
C6-C7	1.400(3)
C7-C8	1.437(3)
C8-C9	1.392(3)
C9-H9	0.9300
C9-C10	1.404(3)
C10-C11	1.388(3)
C10-C13	1.512(3)
C11-C12	1.414(3)
C13-H13	0.9800
C13-C14	1.516(3)
C13-C17	1.545(3)
C15-H15A	0.9700
C15-H15B	0.9700
C15-C16	1.486(4)
C16-H16A	0.9600
C16-H16B	0.9600

C16-H16C	0.9600
C17-H17A	0.9700
C17-H17B	0.9700
C17-C18	1.511(3)
C18-C19	1.393(3)
C18-C23	1.387(3)
C19-H19	0.9300
C19-C20	1.387(3)
C20-H20	0.9300
C20-C21	1.380(3)
C21-C22	1.382(3)
C22-H22	0.9300
C22-C23	1.387(3)
C23-H23	0.9300

C14-O2-C15	115.77(17)
C1-N1-N2	114.19(16)
N1-N2-C8	127.83(16)
N1-N2-C11	122.68(16)
C11-N2-C8	109.48(16)
N1-C1-H1	117.1
N1-C1-C2	125.71(18)
C2-C1-H1	117.1
C3-C2-C1	121.24(19)
C3-C2-C7	120.31(19)
C7-C2-C1	118.45(18)
C2-C3-H3	120.1
C4-C3-C2	119.9(2)
C4-C3-H3	120.1
C3-C4-H4	120.1
C3-C4-C5	119.8(2)
C5-C4-H4	120.1
C4-C5-H5	119.3
C6-C5-C4	121.4(2)
C6-C5-H5	119.3
C5-C6-H6	120.3
C5-C6-C7	119.4(2)
C7-C6-H6	120.3

C2-C7-C8	117.07(17)
C6-C7-C2	119.24(18)
C6-C7-C8	123.68(18)
N2-C8-C7	116.72(17)
N2-C8-C9	107.21(17)
C9-C8-C7	136.07(18)
C8-C9-H9	126.0
C8-C9-C10	107.97(17)
C10-C9-H9	126.0
C9-C10-C13	130.31(17)
C11-C10-C9	107.53(17)
C11-C10-C13	122.17(18)
N2-C11-C10	107.80(17)
N2-C11-C12	121.20(17)
C10-C11-C12	130.57(19)
N3-C12-C11	177.9(2)
C10-C13-H13	108.2
C10-C13-C14	109.98(16)
C10-C13-C17	111.87(17)
C14-C13-H13	108.2
C14-C13-C17	110.39(16)
C17-C13-H13	108.2
O1-C14-O2	124.19(19)
O1-C14-C13	124.0(2)
O2-C14-C13	111.85(17)
O2-C15-H15A	110.2
O2-C15-H15B	110.2
O2-C15-C16	107.5(2)
H15A-C15-H15B	108.5
C16-C15-H15A	110.2
C16-C15-H15B	110.2
C15-C16-H16A	109.5
C15-C16-H16B	109.5
C15-C16-H16C	109.5
H16A-C16-H16B	109.5
H16A-C16-H16C	109.5
H16B-C16-H16C	109.5
C13-C17-H17A	109.3
C13-C17-H17B	109.3
H17A-C17-H17B	108.0

C18-C17-C13	111.51(18)
C18-C17-H17A	109.3
C18-C17-H17B	109.3
C19-C18-C17	119.82(19)
C23-C18-C17	122.07(19)
C23-C18-C19	118.1(2)
C18-C19-H19	119.3
C20-C19-C18	121.4(2)
C20-C19-H19	119.3
C19-C20-H20	120.5
C21-C20-C19	118.9(2)
C21-C20-H20	120.5
C20-C21-Br1	119.51(18)
C20-C21-C22	121.1(2)
C22-C21-Br1	119.32(17)
C21-C22-H22	120.5
C21-C22-C23	119.1(2)
C23-C22-H22	120.5
C18-C23-H23	119.3
C22-C23-C18	121.3(2)
C22-C23-H23	119.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... \quad + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br1	56(1)	49(1)	35(1)	-21(1)	10(1)	-8(1)
O1	39(1)	38(1)	35(1)	-6(1)	1(1)	-24(1)
O2	28(1)	32(1)	34(1)	-5(1)	-4(1)	-10(1)
N1	24(1)	26(1)	31(1)	-12(1)	4(1)	-14(1)
N2	19(1)	21(1)	26(1)	-9(1)	3(1)	-9(1)
N3	33(1)	49(1)	44(1)	-22(1)	14(1)	-20(1)
C1	26(1)	29(1)	33(1)	-14(1)	4(1)	-14(1)
C2	22(1)	24(1)	26(1)	-6(1)	0(1)	-6(1)

C3	28(1)	30(1)	32(1)	-14(1)	2(1)	-9(1)
C4	30(1)	36(1)	31(1)	-16(1)	6(1)	-7(1)
C5	27(1)	35(1)	31(1)	-9(1)	9(1)	-11(1)
C6	22(1)	27(1)	29(1)	-7(1)	4(1)	-8(1)
C7	20(1)	20(1)	23(1)	-4(1)	0(1)	-6(1)
C8	19(1)	21(1)	25(1)	-5(1)	2(1)	-7(1)
C9	22(1)	22(1)	30(1)	-10(1)	3(1)	-11(1)
C10	21(1)	20(1)	26(1)	-6(1)	0(1)	-7(1)
C11	20(1)	23(1)	25(1)	-9(1)	4(1)	-8(1)
C12	26(1)	27(1)	29(1)	-13(1)	4(1)	-12(1)
C13	22(1)	23(1)	26(1)	-9(1)	2(1)	-9(1)
C14	24(1)	23(1)	30(1)	-14(1)	4(1)	-8(1)
C15	28(1)	46(1)	48(2)	-14(1)	-7(1)	-13(1)
C16	47(2)	56(2)	59(2)	-7(2)	-20(1)	-12(1)
C17	25(1)	26(1)	31(1)	-10(1)	-1(1)	-5(1)
C18	23(1)	22(1)	30(1)	-7(1)	-2(1)	-3(1)
C19	35(1)	31(1)	45(1)	-14(1)	9(1)	-15(1)
C20	37(1)	40(1)	38(1)	-11(1)	12(1)	-16(1)
C21	32(1)	30(1)	29(1)	-11(1)	1(1)	-3(1)
C22	34(1)	26(1)	37(1)	-12(1)	2(1)	-10(1)
C23	28(1)	28(1)	34(1)	-9(1)	5(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7**.

	x	y	z	U(eq)
H1	6612	-720	4254	32
H3	8414	-1105	2699	34
H4	10425	-593	1629	38
H5	11479	1075	2004	37
H6	10512	2281	3410	31
H9	9091	3584	5033	28
H13	6784	3822	7693	27
H15A	10459	5224	8229	47
H15B	11339	4025	7614	47
H16A	11537	2268	9389	84
H16B	10628	3447	10006	84

H16C	12256	3432	9558	84
H17A	6013	6348	5767	33
H17B	4868	5445	6149	33
H19	3733	5295	8103	42
H20	2819	6454	9554	45
H22	5422	9068	8419	38
H23	6320	7906	6967	36

Table 6. Torsion angles [°] for **7**.

Br1-C21-C22-C23	-177.50(17)
N1-N2-C8-C7	0.2(3)
N1-N2-C8-C9	-179.72(18)
N1-N2-C11-C10	179.38(17)
N1-N2-C11-C12	-7.4(3)
N1-C1-C2-C3	-179.2(2)
N1-C1-C2-C7	1.1(3)
N2-N1-C1-C2	0.4(3)
N2-C8-C9-C10	0.5(2)
C1-N1-N2-C8	-1.1(3)
C1-N1-N2-C11	179.52(19)
C1-C2-C3-C4	-179.1(2)
C1-C2-C7-C6	178.55(19)
C1-C2-C7-C8	-1.9(3)
C2-C3-C4-C5	0.4(3)
C2-C7-C8-N2	1.3(3)
C2-C7-C8-C9	-178.8(2)
C3-C2-C7-C6	-1.2(3)
C3-C2-C7-C8	178.38(18)
C3-C4-C5-C6	-0.8(4)
C4-C5-C6-C7	0.2(3)
C5-C6-C7-C2	0.8(3)
C5-C6-C7-C8	-178.7(2)
C6-C7-C8-N2	-179.18(18)
C6-C7-C8-C9	0.8(4)
C7-C2-C3-C4	0.6(3)
C7-C8-C9-C10	-179.4(2)
C8-N2-C11-C10	-0.1(2)

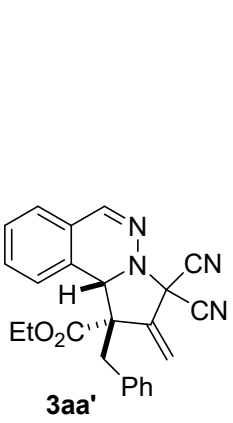
C8-N2-C11-C12	173.10(19)
C8-C9-C10-C11	-0.6(2)
C8-C9-C10-C13	179.5(2)
C9-C10-C11-N2	0.4(2)
C9-C10-C11-C12	-171.9(2)
C9-C10-C13-C14	-23.5(3)
C9-C10-C13-C17	99.6(2)
C10-C13-C14-O1	80.3(2)
C10-C13-C14-O2	-99.4(2)
C10-C13-C17-C18	162.58(17)
C11-N2-C8-C7	179.68(17)
C11-N2-C8-C9	-0.3(2)
C11-C10-C13-C14	156.63(19)
C11-C10-C13-C17	-80.3(2)
C13-C10-C11-N2	-179.65(17)
C13-C10-C11-C12	8.0(3)
C13-C17-C18-C19	-84.4(2)
C13-C17-C18-C23	95.1(2)
C14-O2-C15-C16	180.0(2)
C14-C13-C17-C18	-74.6(2)
C15-O2-C14-O1	-1.2(3)
C15-O2-C14-C13	178.52(18)
C17-C13-C14-O1	-43.6(3)
C17-C13-C14-O2	136.70(18)
C17-C18-C19-C20	-179.8(2)
C17-C18-C23-C22	180.0(2)
C18-C19-C20-C21	-0.1(4)
C19-C18-C23-C22	-0.5(3)
C19-C20-C21-Br1	177.64(19)
C19-C20-C21-C22	-0.6(4)
C20-C21-C22-C23	0.8(4)
C21-C22-C23-C18	-0.2(3)
C23-C18-C19-C20	0.7(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for sa4017 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-Ray Crystallography Data of 3aa'



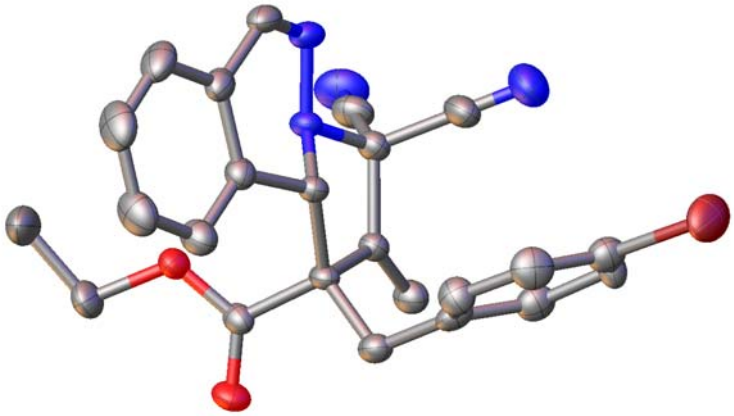


Table 1. Crystal data and structure refinement for **3aa'**.

Identification code	**3aa'**	
Empirical formula	C24 H19 Br N4 O2	
Formula weight	475.34	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.775(2) Å	a= 90°.
	b = 16.891(3) Å	b= 93.444(3)°.
	c = 14.538(4) Å	g = 90°.
Volume	2150.9(9) $Å^3$	
Z	4	
Density (calculated)	1.468 Mg/m^3	
Absorption coefficient	1.940 mm^{-1}	
F(000)	968	
Crystal size	0.266 x 0.188 x 0.159 mm^3	
Theta range for data collection	2.412 to 27.477°.	
Index ranges	-11<=h<=11, -21<=k<=21, -18<=l<=18	
Reflections collected	15229	
Independent reflections	4899 [R(int) = 0.0368]	
Completeness to theta = 26.000°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7571	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4899 / 306 / 366
Goodness-of-fit on F^2	1.184
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1064
R indices (all data)	R1 = 0.0622, wR2 = 0.1130
Extinction coefficient	n/a
Largest diff. peak and hole	0.291 and -0.261 e.Å^{-3}

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

	x	y	z	U(eq)
Br1	5206(6)	6543(1)	10145(1)	56(1)
O1	5260(2)	3698(1)	4930(1)	38(1)
O2	4222(10)	2688(7)	5618(7)	32(1)
N1	2357(2)	3156(1)	7136(1)	26(1)
N2	1717(2)	2776(1)	7880(1)	32(1)
N3	777(3)	4786(2)	8148(2)	60(1)
N4	-1060(3)	3471(2)	5862(2)	55(1)
C1	4194(2)	3915(1)	6398(1)	24(1)
C2	2586(2)	4250(1)	6181(1)	25(1)
C3	1474(2)	3834(1)	6801(2)	29(1)
C4	3950(2)	3427(1)	7276(1)	24(1)
C5	4931(3)	2729(1)	7552(1)	27(1)
C6	6440(3)	2622(2)	7347(2)	37(1)
C7	7264(3)	1988(2)	7719(2)	47(1)
C8	6601(4)	1459(2)	8299(2)	50(1)
C9	5100(4)	1557(1)	8506(2)	44(1)
C10	4243(3)	2188(1)	8132(1)	30(1)
C11	2653(3)	2314(1)	8334(2)	33(1)
C12	4583(2)	3425(1)	5551(1)	26(1)
C13	4699(10)	2156(4)	4889(5)	39(2)
C14	4261(13)	1336(4)	5143(6)	71(2)

C15	5420(3)	4576(1)	6533(2)	29(1)
C16	5400(3)	5035(1)	7419(2)	30(1)
C17	6348(17)	4903(9)	8218(11)	34(2)
C18	6284(11)	5358(7)	9008(6)	40(2)
C19	5207(11)	5930(7)	9045(8)	34(2)
C20	4208(12)	6103(7)	8341(7)	31(2)
C21	4410(20)	5659(12)	7548(14)	34(3)
C22	2175(3)	4798(1)	5570(2)	32(1)
C23	1061(3)	4379(2)	7561(2)	39(1)
C24	46(3)	3598(2)	6283(2)	37(1)
O2A	3792(18)	2703(14)	5518(14)	33(3)
C13A	4075(19)	2143(9)	4777(9)	41(3)
C14A	5110(30)	1516(10)	5150(9)	78(5)
Br1A	5792(15)	6431(5)	10125(2)	80(2)
C20A	4546(18)	5992(11)	8353(13)	40(3)
C19A	5671(15)	5838(10)	9039(11)	30(3)
C18A	6739(15)	5257(9)	8875(10)	35(2)
C17A	6610(19)	4857(11)	8041(11)	35(3)
C21A	4270(30)	5600(16)	7517(16)	33(3)

Table 3. Bond lengths [Å] and angles [°] for **3aa'**.

Br1-C19	1.906(12)
O1-C12	1.202(3)
O2-C12	1.290(12)
O2-C13	1.470(13)
N1-N2	1.403(2)
N1-C3	1.451(3)
N1-C4	1.473(3)
N2-C11	1.287(3)
N3-C23	1.136(3)
N4-C24	1.136(3)
C1-C2	1.535(3)
C1-C4	1.546(3)
C1-C12	1.539(3)
C1-C15	1.556(3)
C2-C3	1.537(3)

C2-C22	1.318(3)
C3-C23	1.498(3)
C3-C24	1.478(3)
C4-C5	1.500(3)
C5-C6	1.386(3)
C5-C10	1.404(3)
C6-C7	1.384(3)
C7-C8	1.380(4)
C8-C9	1.379(4)
C9-C10	1.396(3)
C10-C11	1.459(3)
C12-O2A	1.40(2)
C13-C14	1.490(10)
C15-C16	1.505(3)
C16-C17	1.405(9)
C16-C21	1.385(10)
C16-C17A	1.386(9)
C16-C21A	1.391(10)
C17-C18	1.39(2)
C18-C19	1.356(10)
C19-C20	1.339(10)
C20-C21	1.396(13)
O2A-C13A	1.47(2)
C13A-C14A	1.48(2)
Br1A-C19A	1.867(16)
C20A-C19A	1.386(9)
C20A-C21A	1.392(10)
C19A-C18A	1.387(9)
C18A-C17A	1.387(10)

C12-O2-C13	117.0(8)
N2-N1-C3	112.91(16)
N2-N1-C4	117.11(17)
C3-N1-C4	106.54(16)
C11-N2-N1	113.62(18)
C2-C1-C4	101.27(15)
C2-C1-C12	106.23(16)
C2-C1-C15	112.40(17)

C4-C1-C15	114.10(17)
C12-C1-C4	115.00(16)
C12-C1-C15	107.56(16)
C1-C2-C3	108.59(17)
C22-C2-C1	127.43(19)
C22-C2-C3	124.0(2)
N1-C3-C2	102.29(16)
N1-C3-C23	112.68(19)
N1-C3-C24	112.17(19)
C23-C3-C2	109.99(18)
C24-C3-C2	111.90(18)
C24-C3-C23	107.81(19)
N1-C4-C1	103.19(16)
N1-C4-C5	108.53(17)
C5-C4-C1	122.28(17)
C6-C5-C4	125.8(2)
C6-C5-C10	119.7(2)
C10-C5-C4	114.25(19)
C7-C6-C5	120.0(2)
C8-C7-C6	120.6(3)
C9-C8-C7	120.0(2)
C8-C9-C10	120.3(2)
C5-C10-C11	118.5(2)
C9-C10-C5	119.3(2)
C9-C10-C11	122.1(2)
N2-C11-C10	124.99(19)
O1-C12-O2	124.1(5)
O1-C12-C1	122.62(19)
O1-C12-O2A	125.0(9)
O2-C12-C1	113.0(5)
O2A-C12-C1	111.2(9)
O2-C13-C14	107.5(7)
C16-C15-C1	115.71(17)
C17-C16-C15	126.0(8)
C21-C16-C15	123.1(8)
C21-C16-C17	110.8(13)
C17A-C16-C15	113.5(8)
C17A-C16-C21A	127.3(11)

C21A-C16-C15	119.1(8)
C18-C17-C16	123.0(12)
C19-C18-C17	119.4(9)
C18-C19-Br1	117.1(8)
C20-C19-Br1	119.3(7)
C20-C19-C18	123.5(10)
C19-C20-C21	113.9(10)
C16-C21-C20	129.2(13)
N3-C23-C3	178.4(3)
N4-C24-C3	175.1(3)
C12-O2A-C13A	118.7(14)
O2A-C13A-C14A	108.7(12)
C19A-C20A-C21A	128.3(15)
C20A-C19A-Br1A	120.6(11)
C20A-C19A-C18A	117.9(13)
C18A-C19A-Br1A	121.4(10)
C17A-C18A-C19A	118.3(14)
C16-C17A-C18A	118.9(13)
C16-C21A-C20A	109.0(14)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br1	90(1)	49(1)	30(1)	-10(1)	2(1)	-12(1)
O1	48(1)	40(1)	29(1)	4(1)	18(1)	-1(1)
O2	40(4)	29(2)	27(2)	-4(2)	12(3)	-4(3)
N1	26(1)	27(1)	28(1)	4(1)	9(1)	-1(1)
N2	37(1)	30(1)	31(1)	2(1)	12(1)	-8(1)
N3	77(2)	51(1)	55(2)	-4(1)	30(1)	7(1)
N4	33(1)	71(2)	61(2)	11(1)	1(1)	-3(1)
C1	26(1)	23(1)	23(1)	4(1)	8(1)	1(1)
C2	25(1)	25(1)	27(1)	0(1)	6(1)	0(1)

C3	26(1)	30(1)	32(1)	2(1)	8(1)	2(1)
C4	24(1)	24(1)	24(1)	1(1)	7(1)	-1(1)
C5	33(1)	26(1)	23(1)	1(1)	4(1)	2(1)
C6	38(1)	37(1)	35(1)	6(1)	7(1)	7(1)
C7	45(2)	51(2)	45(1)	5(1)	5(1)	20(1)
C8	65(2)	40(1)	46(2)	7(1)	1(1)	24(1)
C9	69(2)	27(1)	35(1)	7(1)	4(1)	5(1)
C10	44(1)	24(1)	24(1)	-1(1)	6(1)	0(1)
C11	44(1)	28(1)	28(1)	2(1)	12(1)	-8(1)
C12	29(1)	27(1)	24(1)	4(1)	5(1)	6(1)
C13	51(4)	35(2)	31(2)	-9(2)	13(3)	0(3)
C14	102(6)	37(3)	80(4)	-20(2)	54(4)	-17(3)
C15	27(1)	28(1)	32(1)	5(1)	7(1)	-1(1)
C16	30(1)	26(1)	33(1)	6(1)	2(1)	-8(1)
C17	34(4)	35(3)	33(4)	3(3)	-2(3)	5(3)
C18	38(4)	49(4)	33(3)	0(3)	-9(3)	-2(4)
C19	33(4)	34(3)	34(3)	1(2)	0(3)	-4(3)
C20	33(4)	30(3)	30(2)	-6(2)	3(2)	6(3)
C21	32(4)	35(5)	35(4)	1(3)	-3(3)	-5(4)
C22	31(1)	32(1)	33(1)	4(1)	5(1)	4(1)
C23	41(1)	37(1)	42(1)	5(1)	19(1)	6(1)
C24	26(1)	45(1)	42(1)	6(1)	8(1)	1(1)
O2A	39(6)	30(3)	31(5)	-8(3)	14(5)	-7(5)
C13A	49(6)	44(4)	32(4)	-13(3)	18(5)	-7(5)
C14A	119(11)	65(8)	51(6)	-13(5)	8(7)	53(8)
Br1A	121(4)	80(2)	38(1)	-19(1)	6(1)	-45(2)
C20A	36(6)	34(5)	51(5)	-6(4)	9(4)	0(4)
C19A	29(6)	34(5)	25(3)	0(3)	-7(4)	-12(5)
C18A	31(5)	35(4)	39(5)	2(3)	-8(4)	-1(4)
C17A	31(4)	39(4)	35(5)	0(4)	3(4)	-9(4)
C21A	40(6)	34(5)	25(5)	-7(4)	-1(4)	-9(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3aa'**.

	x	y	z	U(eq)

H4	3995	3796	7798	28
H6	6899	2977	6961	44
H7	8275	1918	7577	56
H8	7167	1038	8549	60
H9	4656	1200	8897	52
H11	2287	2039	8829	40
H13A	5794	2190	4838	47
H13B	4196	2302	4301	47
H14A	4664	1220	5757	106
H14B	4668	967	4720	106
H14C	3168	1292	5116	106
H15A	6420	4337	6499	35
H15B	5285	4946	6024	35
H17	7052	4491	8216	41
H18	6973	5271	9509	48
H20	3449	6484	8377	37
H21	3790	5801	7032	41
H22A	2901	5027	5212	38
H22B	1160	4957	5497	38
H13C	4534	2416	4276	49
H13D	3120	1910	4540	49
H14D	4690	1277	5676	118
H14E	6090	1744	5331	118
H14F	5240	1121	4686	118
H20A	3895	6411	8464	48
H18A	7521	5138	9314	42
H17A	7325	4476	7901	42
H21A	3452	5699	7093	39

Table 6. Torsion angles [°] for **3aa'**.

Br1-C19-C20-C21	174.7(14)
O1-C12-O2A-C13A	15.2(16)
O2-C12-O2A-C13A	-78(4)
N1-N2-C11-C10	1.0(3)
N1-C4-C5-C6	148.4(2)

N1-C4-C5-C10	-37.3(2)
N2-N1-C3-C2	166.57(16)
N2-N1-C3-C23	48.5(2)
N2-N1-C3-C24	-73.4(2)
N2-N1-C4-C1	-171.92(16)
N2-N1-C4-C5	57.0(2)
C1-C2-C3-N1	-15.2(2)
C1-C2-C3-C23	104.7(2)
C1-C2-C3-C24	-135.48(19)
C1-C4-C5-C6	28.7(3)
C1-C4-C5-C10	-157.07(19)
C1-C12-O2A-C13A	-177.3(10)
C1-C15-C16-C17	98.3(9)
C1-C15-C16-C21	-81.7(14)
C1-C15-C16-C17A	107.7(10)
C1-C15-C16-C21A	-75.4(18)
C2-C1-C4-N1	31.82(19)
C2-C1-C4-C5	154.11(19)
C2-C1-C12-O1	93.1(2)
C2-C1-C12-O2	-92.3(5)
C2-C1-C12-O2A	-74.8(8)
C2-C1-C15-C16	73.4(2)
C3-N1-N2-C11	-163.04(19)
C3-N1-C4-C1	-44.47(19)
C3-N1-C4-C5	-175.54(16)
C4-N1-N2-C11	-38.7(3)
C4-N1-C3-C2	36.7(2)
C4-N1-C3-C23	-81.4(2)
C4-N1-C3-C24	156.73(18)
C4-C1-C2-C3	-10.3(2)
C4-C1-C2-C22	170.0(2)
C4-C1-C12-O1	-155.8(2)
C4-C1-C12-O2	18.8(5)
C4-C1-C12-O2A	36.3(8)
C4-C1-C15-C16	-41.1(2)
C4-C5-C6-C7	173.6(2)
C4-C5-C10-C9	-173.8(2)
C4-C5-C10-C11	5.4(3)

C5-C6-C7-C8	-0.4(4)
C5-C10-C11-N2	15.6(3)
C6-C5-C10-C9	0.9(3)
C6-C5-C10-C11	-179.9(2)
C6-C7-C8-C9	0.5(4)
C7-C8-C9-C10	0.0(4)
C8-C9-C10-C5	-0.8(4)
C8-C9-C10-C11	-179.9(2)
C9-C10-C11-N2	-165.2(2)
C10-C5-C6-C7	-0.3(4)
C12-O2-C13-C14	176.1(10)
C12-C1-C2-C3	110.16(18)
C12-C1-C2-C22	-69.5(3)
C12-C1-C4-N1	-82.2(2)
C12-C1-C4-C5	40.1(3)
C12-C1-C15-C16	-169.99(18)
C12-O2A-C13A-C14A	101(2)
C13-O2-C12-O1	0.9(8)
C13-O2-C12-C1	-173.6(4)
C13-O2-C12-O2A	100(5)
C15-C1-C2-C3	-132.46(18)
C15-C1-C2-C22	47.8(3)
C15-C1-C4-N1	152.81(17)
C15-C1-C4-C5	-84.9(2)
C15-C1-C12-O1	-27.5(3)
C15-C1-C12-O2	147.1(5)
C15-C1-C12-O2A	164.6(8)
C15-C16-C17-C18	179.0(8)
C15-C16-C21-C20	176.0(18)
C15-C16-C17A-C18A	178.4(13)
C15-C16-C21A-C20A	-175.1(16)
C16-C17-C18-C19	3.9(18)
C17-C16-C21-C20	-4(3)
C17-C16-C17A-C18A	-32(4)

C17-C16-C21A-C20A	11(3)
C17-C18-C19-Br1	-179.0(9)
C17-C18-C19-C20	-2.0(16)
C18-C19-C20-C21	-2(2)
C19-C20-C21-C16	6(3)
C21-C16-C17-C18	-1.1(18)
C21-C16-C17A-C18A	8(2)
C21-C16-C21A-C20A	-47(16)
C22-C2-C3-N1	164.5(2)
C22-C2-C3-C23	-75.6(3)
C22-C2-C3-C24	44.2(3)
Br1A-C19A-C18A-C17A	-177.8(13)
C20A-C19A-C18A-C17A	-1(2)
C19A-C20A-C21A-C16	-5(4)
C19A-C18A-C17A-C16	-2(2)
C17A-C16-C17-C18	144(6)
C17A-C16-C21-C20	-14(3)
C17A-C16-C21A-C20A	1(4)
C21A-C16-C17-C18	-7(2)
C21A-C16-C21-C20	121(20)
C21A-C16-C17A-C18A	2(3)
C21A-C20A-C19A-Br1A	-178(2)
C21A-C20A-C19A-C18A	5(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3aa'** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)