Supporting Information

Substrate-controlled Synthesis of Spirocyclopropylpyrazolones and Bicyclic 4,5-Dihydropyrazoles from 1,2-Diaza-1,3-dienes with Sulfur Ylides

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I. General Information

All solvents were purified according to standard methods. Melting points were recorded on a BüCHI B-540 melting point apparatus. NMR spectra were recorded for ^{1}H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. For ^{1}H NMR, tetramethylsilane (TMS) served as internal standard (δ = 0) and data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hz and integration. For ^{13}C NMR, $CDCl_3$ (δ =77.26) or DMSO-D_6 (δ =39.6) was used as internal standard and spectra were obtained with complete proton decoupling. HRMS data were obtained on an Agilent 1290 HPLC-6224 Time of Flight Mass Spectrometer. The X-ray diffraction measurements were carried out on a Rigaku RAXIS-RAPID single-crystal diffractometer. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. 1, 2-diaza-1, 3-dienes (DDs) and sulfur ylides were synthesized according to literature procedure. [1, 2]

References:

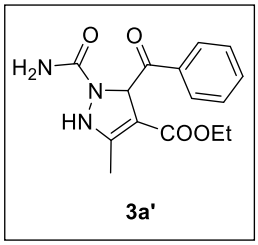
1. (a) Preti, L.; Attanasi, O. A.; Caselli, E.; Favi, G.; Ori, C.; Davoli, P.; Felluga, F.; Prati, F., *Eur. J. Org. Chem.* **2010**, *22*, 4312. (b) Attanasi, O. A.; Crescentini, L. D.; Favi, G.; Fillippone, P.; Golobič, A.; Lillini, S.; Mantellini, F., *Synlett.* **2006**, *17*, 2735. (c) Hatcher, J. M.; Coltart, D. M., *J. Am. Chem. Soc.* **2010**, *132*, 4546.
2. Sabounchei, S. J.; Ahmadianpoor, M.; Yousefi, A.; Bayat, M.; Sedghi, A.; Bagherjeri, F. A.; Gable, R. W., *RSC Adv.* **2016**, *6*, 28308.

II. General Procedure of 3

General Procedure of **3a-3s**: A mixture of linear 1,2-diaza-1,3-dienes (DDs) (0.5 mmol, 1.0 equiv) and sulfur ylides (1.0 mmol, 2.0 equiv) were stirred in 5 mL DCE at 25 ^{o}C for 12 hours. After the completeness of the reaction (monitored by TLC), the reaction mixture was then concentrated and purified by chromatography (silica gel, 40-63 μm) to afford **3a-3s** as desired products (**3a** was carried out when 1 mmol (or 5.5 mmol) DDs and 2 mmol (or 11 mmol) sulfur ylide were used).

General Procedure of **3a'**: A mixture of linear 1,2-diaza-1,3-dienes (DDs) (0.5 mmol, 1.0 equiv) and sulfur ylides (0.5 mmol, 1.0 equiv) were stirred in 5 mL EtOAc at 25 ^{o}C for 12 hours. After the completeness of the reaction (monitored by TLC), the reaction mixture was then concentrated and purified by chromatography (silica gel, 40-63 μm) to afford **3a'** as desired products.

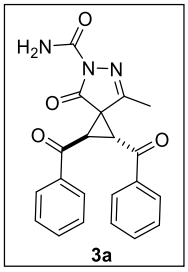
III. Characterization Data of 3



3a'

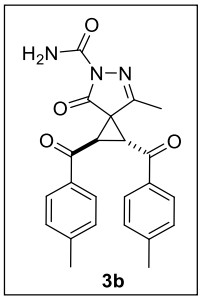
Ethyl 3-benzoyl-2-carbamoyl-5-methyl-2,3-dihydro-*1*H-pyrazole-4-carboxylate (**3a'**)

Purified by column chromatography (silica gel, Pe : EA = 1 :1) to afford **3a'** as a white solid. 47mg. 31% yield. m.p.: 235.1–236.7 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 10.06 (s, 1H), 8.18–8.02 (m, 2H), 7.68 (d, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 7.42 (s, 1H), 6.77 (s, 1H), 5.81 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.15 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 188.69, 167.50, 156.55, 148.06, 142.88, 137.39, 134.11, 129.36, 129.00, 121.87, 61.09, 14.40, 12.49. HRMS (ESI): m/z calcd for $C_{15}H_{18}N_3O_4^+$ $[M+H]^+$: 304.1292, found: 304.1294.



Trans-1,2-dibenzoyl-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3a**)

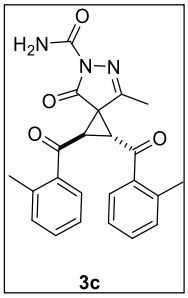
Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3a** as a white solid. 278 mg, 74% yield (the yield of **3a** was 68% when 5.5 mmol of DDs and 11 mmol of sulfur ylide were carried out). m.p.: 166.3–168.6 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.03 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.74 (t, J = 7.4 Hz, 1H), 7.69 (t, J = 7.4 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H), 7.57–7.54 (m, 3H), 7.11 (s, 1H), 4.82 (d, J = 8.8 Hz, 1H), 4.25 (d, J = 8.8 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, DMSO-D_6) δ 191.27, 189.85, 169.39, 156.38, 149.31, 135.89, 135.50, 135.06, 134.81, 129.69, 129.56, 129.11, 128.76, 44.06, 40.87, 40.41, 15.23. HRMS (ESI): m/z calcd for $C_{21}H_{18}N_3O_4^+$ $[M+H]^+$: 376.1292, found: 376.1296.



Trans-7-methyl-1,2-bis(4-methylbenzoyl)-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carb oxamide (**3b**)

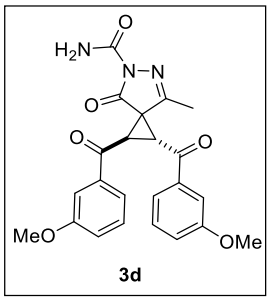
Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3b** as a white solid. 157 mg, 78% yield. m.p.: 166.5–167.2 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.91 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.52 (s, 1H), 7.41 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 7.09 (s, 1H), 4.74 (d, J = 8.8 Hz, 1H), 4.18 (d, J = 8.8 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 191.71, 189.28, 169.41, 156.39, 149.31, 145.82, 145.43, 133.51 (m,

1H), 133.17, 130.24, 130.08, 129.17, 128.85, 44.02, 40.87, 39.75, 21.77, 21.73, 15.16). HRMS (ESI): m/z calcd for $C_{23}H_{22}N_3O_4^+$ $[M+H]^+$: 404.1605, found: 404.1607.



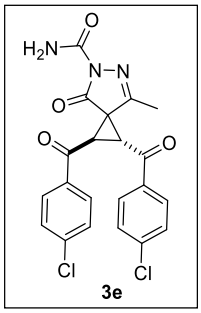
Trans-7-methyl-1,2-bis(2-methylbenzoyl)-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3c**)

Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3c** as a white solid. 127 mg, 63% yield. m.p.: 149.4–151.1 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.86 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.57–7.48 (m, 3H), 7.44–7.33 (m, 4H), 7.09 (s, 1H), 4.79 (d, J = 8.7 Hz, 1H), 4.01 (d, J = 8.7 Hz, 1H), 2.53 (s, 3H), 2.50 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 193.60, 192.26, 169.65, 156.43, 149.31, 139.88, 139.53, 135.76, 135.17, 133.57, 133.28, 132.77, 132.66, 130.74, 130.39, 126.92, 126.65, 45.23, 43.51, 42.01, 21.76, 21.73, 15.38. HRMS (ESI): m/z calcd for $C_{23}H_{22}N_3O_4^+$ $[M+H]^+$: 404.1605, found: 404.1610.



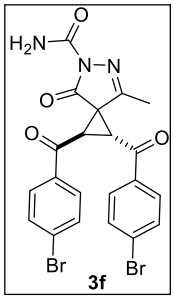
Trans-1,2-bis(3-methoxybenzoyl)-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3d**)

Purified by column chromatography (silica gel, DCM : MeOH = 50 :1) to afford **3d** as a white solid. 174 mg, 80% yield. m.p.: 158.7–159.3 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.60 (d, J = 7.6 Hz, 1H), 7.55–7.46 (m, 4H), 7.39 (d, J = 7.6 Hz, 1H), 7.35–7.28 (m, 2H), 7.26 (dd, J = 8.1, 2.0 Hz, 1H), 7.09 (s, 1H), 4.78 (d, J = 8.8 Hz, 1H), 4.21 (d, J = 8.8 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125MHz, DMSO–D_6) δ 191.04, 189.68, 169.38, 160.04, 159.88, 156.47, 149.28, 137.22, 136.83, 130.92, 130.77, 121.59, 121.19, 121.13, 121.01, 113.42, 112.99, 55.87, 55.74, 44.06, 41.18, 40.27, 15.18. HRMS (ESI): m/z calcd for $C_{23}H_{22}N_3O_6^+$ $[M+H]^+$: 436.1503, found: 436.1507.



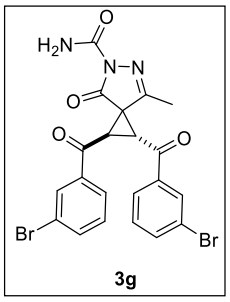
Trans-1,2-bis(4-chlorobenzoyl)-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carb oxamide (**3e**)

Purified by column chromatography (silica gel, DCM : MeOH = 50 :1) to afford **3e** as a white solid. 198 mg, 89% yield. m.p.: 172.6–173.7 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.01 (d, J = 8.6 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.52 (s, 1H), 7.07 (s, 1H), 4.79 (d, J = 8.7 Hz, 1H), 4.23 (d, J = 8.7 Hz, 1H), 1.97 (s, 3H).^{13}C NMR (125 MHz, DMSO-D_6) δ 190.33 (s, 1H), 188.92, 169.23, 156.10, 149.29, 140.01, 139.74, 134.62, 134.25, 131.01, 130.61, 129.81, 129.72, 44.07, 40.62, 40.31, 15.23. HRMS (ESI): m/z calcd for $C_{21}H_{16}Cl_2N_3O_4^+$ $[M+H]^+$: 444.0512, found: 444.0518.



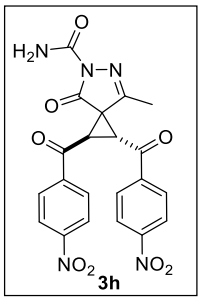
Trans-1,2-bis(4-bromobenzoyl)-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carb oxamide (**3f**)

Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3f** as a white solid. 219 mg, 82% yield. m.p.: 168.4–168.6 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.93 (d, J = 8.6 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H), 7.81–7.77 (m, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.53 (s, 1H), 7.08 (s, 1H), 4.79 (d, J = 8.7 Hz, 1H), 4.22 (d, J = 8.7 Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 190.56, 189.15, 169.21, 156.07, 149.27, 134.92, 134.55, 132.76, 132.68, 131.05, 130.66, 129.33, 129.04, 44.05, 40.27, 39.46, 15.23. HRMS (ESI): m/z calcd for $C_{21}H_{16}Br_2N_3O_4^+$ $[M+H]^+$: 531.9502, found: 531.9500.



Trans-1,2-bis(3-bromobenzoyl)-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carb oxamide (**3g**)

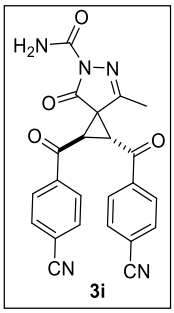
Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3g** as a white solid.227 mg, 85% yield. m.p.: 183.4–184.3 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.15 (s, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 6.2 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.60–7.52 (m, 3H), 7.09 (s, 1H), 4.84 (d, J = 8.7 Hz, 1H), 4.26 (d, J = 8.7 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 190.28, 188.92, 169.20, 156.13, 149.25, 137.88, 137.52, 137.40, 137.36, 131.87, 131.84, 131.54, 131.12, 128.25, 127.87, 44.14, 40.64, 39.65, 15.31. HRMS (ESI): m/z calcd for $C_{21}H_{16}Br_2N_3O_4^+$ $[M+H]^+$: 531.9502, found: 531.9506.



3h

Trans-7-methyl-1,2-bis(4-nitrobenzoyl)-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carbo xamide (**3h**)

Purified by column chromatography (silica gel, DCM : MeOH = 50 :1) to afford **3h** as a yellow solid.161 mg, 69% yield. m.p.: 171.8–173.2 ℃. ^{1}H NMR (500 MHz, DMSO –D_6) δ 8.41 (d, J = 8.7 Hz, 2H), 8.37 (d, J = 8.7 Hz, 2H), 8.24 (d, J = 8.7 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 7.52 (s, 1H), 7.06 (s, 1H), 4.94 (d, J = 8.6 Hz, 1H), 4.34 (d, J = 8.6 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D6) δ 190.63, 189.08, 169.05, 155.78, 151.04, 150.98, 149.25, 140.38, 139.87, 130.64, 130.23, 124.67, 44.35, 40.70, 39.59, 15.36. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_5O_8^+$ $[M+H]^+$: 466.0993, found: 466.0997.

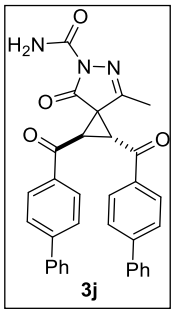


3i

Trans-1,2-bis(4-cyanobenzoyl)-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carb oxamide (**3i**)

Purified by column chromatography (silica gel, DCM : MeOH = 50 :1) to afford **3i** as a white solid.181mg. 85% yield. m.p.: 193.4–195.2 ℃.^{1}H NMR (500 MHz, DMSO –D_6) δ 8.15 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.3 Hz, 2H), 7.53 (s, 1H), 7.06 (s, 1H), 4.88 (d, J = 8.7 Hz, 1H), 4.30 (d, J = 8.7 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 190.79, 189.32, 169.08, 155.90, 149.25, 138.96, 138.47, 133.60, 129.73, 129.32, 118.44, 118.40,

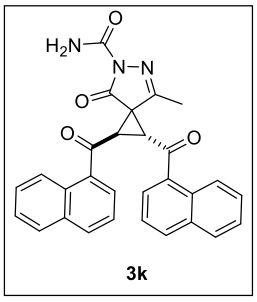
116.69, 116.61, 44.22, 40.54, 39.48, 15.33. HRMS (ESI): m/z calcd for $C_{23}H_{16}N_5O_4^+$ $[M+H]^+$: 426.1197, found: 426.1201.



3j

Trans-1,2-di([1,1'-biphenyl]-4-carbonyl)-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3j**)

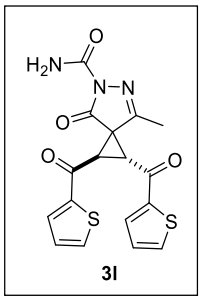
Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3j** as a white solid. 229 mg. 87% yield. m.p.: 164.7–167.1 °C. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.12 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 6.0 Hz, 4H), 7.88 (d, J = 8.0 Hz, 2H), 7.77 (t, J = 6.9 Hz, 4H), 7.61–7.43 (m, 7H), 7.14 (s, 1H), 4.87 (d, J = 8.6 Hz, 1H), 4.33 (d, J = 8.6 Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 190.76, 189.31, 169.46, 156.40, 149.35, 146.31, 146.01, 139.04, 134.74, 134.39, 129.86, 129.64, 129.60, 129.53, 129.19, 129.12, 127.83, 127.68, 127.57, 127.56, 44.15, 41.00, 39.50, 15.28. HRMS (ESI): m/z calcd for $C_{33}H_{26}N_3O_4^+$ $[M+H]^+$: 528.1918, found: 528.1924.



3k

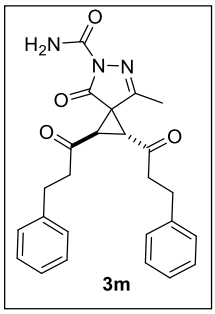
Trans-1,2-di(1-naphthoyl)-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3k**)

Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3k** as a light yellow solid. 207 mg, 87% yield. m.p.: 168.9–169.7 °C. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.93 (d, J = 8.6 Hz, 1H), 8.86 (d, J = 8.6 Hz, 1H), 8.33–8.19 (m, 3H), 8.14–8.00 (m, 3H), 7.78 – 7.60 (m, 6H), 7.50 (s, 1H), 7.07 (s, 1H), 5.07 (d, J = 8.7 Hz, 1H), 4.32 (d, J = 8.7 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 193.69, 192.42, 169.72, 156.47, 149.35, 135.32, 135.15, 134.08, 134.05, 132.86, 132.27, 131.82 , 131.45, 130.40, 130.20, 129.37, 129.33, 129.18, 129.10, 127.32, 127.22, 126.07, 125.66, 125.53, 125.32, 45.78, 43.90, 42.35, 15.53. HRMS (ESI): m/z calcd for $C_{29}H_{22}N_3O_4^+$ $[M+H]^+$: 476.1605, found: 476.1607.



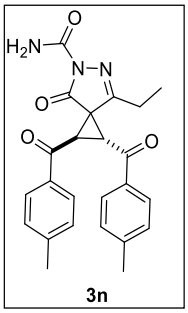
Trans-7-methyl-4-oxo-1,2-di(thiophene-2-carbonyl)-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3l**)

Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3l** as a white solid. 99 mg, 51% yield. m.p.: 165.7–167.3 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.17 (dd, J = 4.9, 1.1 Hz, 1H), 8.10 (dd, J = 4.9, 1.1 Hz, 1H), 8.00 (dd, J = 3.8, 1.1 Hz, 1H), 7.70 (dd, J = 3.8, 1.1 Hz, 1H), 7.54 (s, 1H), 7.32 (dd, J = 4.9, 3.9 Hz, 1H), 7.27 (dd, J = 4.9, 3.8 Hz, 1H), 7.12 (s, 1H), 4.74 (d, J = 8.6 Hz, 1H), 4.18 (d, J = 8.6 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 182.55, 181.23, 168.20, 155.15, 148.25, 141.52, 141.19, 136.58, 135.73, 134.86, 133.73, 128.82, 128.49, 43.07, 39.78, 39.17, 14.09. HRMS (ESI): m/z calcd for $C_{17}H_{14}N_3O_4S_2^+$ $[M+H]^+$: 388.0420, found: 388.0422.



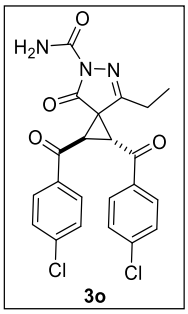
Trans-7-methyl-4-oxo-1,2-bis(3-phenylpropanoyl)-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3m**)

Purified by column chromatography (silica gel, DCM : MeOH = 40 :1) to afford **3m** as a white solid. 126 mg. 58% yield. m.p.: 131.7–133.2 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.55 (s, 1H), 7.21 (dq, J = 24.6, 7.0 Hz, 11H), 3.83 (d, J = 8.9 Hz, 1H), 3.51 (d, J = 8.9 Hz, 1H), 3.12 (t, J = 7.1 Hz, 2H), 3.02–2.93 (m, 1H), 2.82–2.71 (m, 5H), 1.73 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 201.86, 199.73, 169.96, 156.26, 149.56, 141.09, 141.00, 128.74, 128.70, 128.69, 128.66, 44.72, 44.21, 43.85, 42.27, 41.05, 29.14, 29.06, 15.04. HRMS (ESI): m/z calcd for $C_{25}H_{26}N_3O_4^+$ $[M+H]^+$: 432.1918, found: 432.1926.



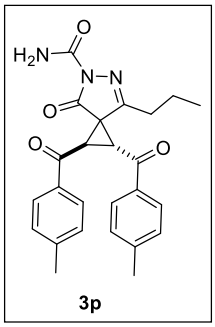
Trans-7-ethyl-1,2-bis(4-methylbenzoyl)-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3n**)

Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3n** as a white solid. 167 mg. 80% yield. m.p.: 180.4–181.8 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.89 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.54 (s, 1H), 7.40 (d, J = 7.7 Hz, 2H), 7.35 (d, J = 7.7 Hz, 2H), 7.10 (s, 1H), 4.70 (d, J = 8.7 Hz, 1H), 4.15 (d, J = 8.7 Hz, 1H), 2.48–2.43 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 1.95 (dd, J = 17.5, 7.4 Hz, 1H), 1.09 (t, J = 7.0 Hz, 4H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 190.72, 189.35, 169.58, 159.99, 149.39, 145.83, 145.37, 133.49, 133.23, 130.24, 130.07, 129.17, 128.80, 43.88, 41.06, 39.51, 21.77, 21.71, 21.63, 9.94. HRMS (ESI): m/z calcd for $C_{24}H_{24}N_3O_4^+$ $[M+H]^+$: 418.1761, found: 418.1755.



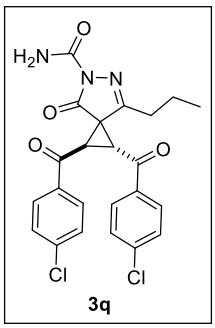
Trans-1,2-bis(4-chlorobenzoyl)-7-ethyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene-5-carboxamide (**3o**)

Purified by column chromatography (silica gel, DCM : MeOH = 50:1) to afford **3o** as a white solid. 197 mg, 86% yield. m.p.: 134.6–136.1 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.04–7.96 (m, 2H), 7.85–7.76 (m, 2H), 7.72–7.66 (m, 2H), 7.66 – 7.62 (m, 2H), 7.55 (s, 1H), 7.09 (s, 1H), 4.77 (d, J = 8.7 Hz, 1H), 4.20 (d, J = 8.7 Hz, 1H), 2.48–2.41 (m, 1H), 1.95 (dq, J = 17.7, 7.2 Hz, 1H), 1.11 (d, J = 7.3 Hz, 3H). ^{13}C NMR (125MHz, DMSO–D_6) δ 190.35, 189.02, 169.40, 159.69, 149.36, 140.02, 139.69, 134.92, 134.30, 131.01, 130.57, 129.82, 129.73, 43.89, 40.81, 39.36, 21.70, 9.89. HRMS (ESI): m/z calcd for $C_{22}H_{18}Cl_2N_3O_4^+$ $[M+H]^+$: 458.0669, found: 458.0671.



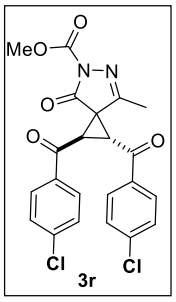
Trans-1,2-bis(4-methylbenzoyl)-4-oxo-7-propyl-5,6-diazaspiro[2.4]hept-6-ene-5-carb oxamide (**3p**)

Purified by column chromatography (silica gel, Pe : EA = 2:1) to afford **3p** as a white solid. 177 mg. 82% yield. m.p.: 181.8–182.4 ℃. ^{1}H NMR (500 MHz, DMSO –D_6) δ 7.89 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.54 (s, 1H), 7.40 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.10 (s, 1H), 4.71 (d, J = 8.8 Hz, 1H), 4.14 (d, J = 8.8 Hz, 1H), 2.47 – 2.41 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 1.94 (ddd, J = 17.0, 8.7, 6.0 Hz, 1H), 1.65 (dd, J = 14.4, 7.1 Hz, 1H), 1.60–1.49 (m, 1H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125MHz, DMSO–D_6) δ 190.70, 189.37, 169.48, 158.88, 149.37, 145.82, 145.39, 133.53, 133.25, 130.23, 130.04, 129.16, 128.77, 43.90, 41.12, 29.87, 21.77, 21.70, 18.74, 14.00. HRMS (ESI): m/z calcd for $C_{25}H_{26}N_3O_4^+$ $[M+H]^+$: 432.1918, found: 432.1918.



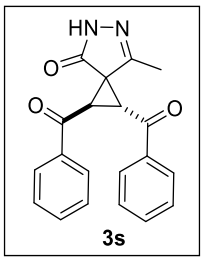
Trans-1,2-bis(4-chlorobenzoyl)-4-oxo-7-propyl-5,6-diazaspiro[2.4]hept-6-ene-5-carb oxamide (**3q**)

Purified by column chromatography (silica gel, DCM : MeOH = 50:1) to afford **3q** as a white solid.189mg, 80% yield. m.p.: 177.8–179.7 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.00 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.55 (s, 1H), 7.08 (s, 1H), 4.78 (d, J = 8.7 Hz, 1H), 4.20 (d, J = 8.7 Hz, 1H), 2.39 (ddd, J = 16.9, 8.9, 6.1 Hz, 1H), 1.93 (ddd, J = 17.0, 8.8, 6.0 Hz, 1H), 1.60 (dtd, J = 16.0, 14.6, 7.2 Hz, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 190.34, 189.04, 169.30, 158.61, 149.34, 140.02, 139.69, 134.61, 134.32, 131.00, 130.53, 129.81, 129.70, 43.89, 40.89, 39.33, 29.95, 18.71, 14.03. HRMS (ESI): m/z calcd for $C_{23}H_{20}Cl_2N_3O_4^+$ $[M+H]^+$: 472.0825, found: 472.0830



Trans-methyl-1,2-bis(4-chlorobenzoyl)-7-methyl-4-oxo-5,6-diazaspiro[2.4]hept-6-ene -5-carboxylate (**3r**)

Purified by column chromatography (silica gel, DCM : MeOH = 50 :1) to afford **3r** as a light yellow solid. m.p.: 224.8–225.7 ℃. 64 mg. 28% yield. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.02 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H),4.79 (d, J = 8.7 Hz, 1H), 4.21 (d, J = 8.7 Hz, 1H), 3.77 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 190.36, 188.83, 167.35, 157.18, 149.08, 140.02, 139.74, 134.58, 134.22, 131.05, 130.66, 129.79, 129.75, 54.15, 43.48, 40.64, 39.37, 15.28. HRMS (ESI): m/z calcd for $C_{22}H_{17}Cl_2N_2O_5^+$ $[M+H]^+$: 459.0509, found: 459.0513.



Trans-4-methyl-7-oxo-5,6-diazaspiro[2.4]hept-4-ene-1,2-diyl)bis(phenylmethanone)(**3s**)

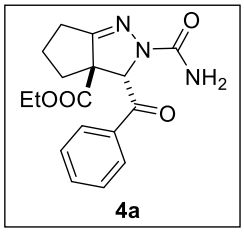
Purified by column chromatography (silica gel, Pe : EtOAc = 3 :1) to afford **3s** as a white solid. m.p.: 192.3–193.3 ℃. 42 mg. 25% yield in the reaction of 2-(dimethyl-λ^4-sulfanylidene)-1-phenylethan-1-one and tert-butyl-2-(4-ethoxy-4-oxobut-2-en-2-yl)diazene-1-carboxylate (55 mg. 33% yield in the reaction of 2-(dimethyl-λ^4-sulfanylidene)-1-phenylethan-1-one and ethyl 3-(acetyldiazenyl)but-2-enoate). ^{1}H NMR (500 MHz, DMSO–D_6) δ 11.40 (s, 1H), 7.96 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 7.5 Hz, 2H), 7.73 (t, J = 7.3 Hz, 1H), 7.66 (t, J = 7.3 Hz, 1H), 7.61 (t, J = 7.6 Hz, 2H), 7.54 (t, J = 7.6 Hz, 2H), 4.56 (d, J = 8.3 Hz, 1H), 3.99 (d, J = 8.3 Hz, 1H), 1.86 (s, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 191.9, 190.57, 171.28, 154.84, 136.08, 135.87, 134.93, 134.42, 129.71, 129.39, 128.80, 128.66, 42.61, 39.19, 37.85, 15.08. HRMS (ESI): m/z calcd for $C_{20}H_{17}N_2O_3^+$ $[M+H]^+$: 333.1234, found: 333.1236.

IV. General Procedure of 4

A mixture of cyclic 1, 2-diaza-1, 3-dienes (DDs) (0.5 mmol, 1.0 equiv) and sulfur ylides (0.5 mmol, 1.0 equiv) were stirred in 5 mL DCE at 65 ºC for 4 hours. After the

completeness of the reaction (monitored by TLC), the reaction mixture was then concentrated and purified by chromatography (silica gel, 40-63 μm) to afford **4a**-**4n** as desired products (**4i** was carried out when 1 mmol cyclic DDs and 1 mmol sulfur ylide was used).

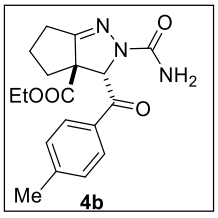
V. Characterization Data of 4



4a

Trans-ethyl-3-benzoyl-2-carbamoyl-2,4,5,6-tetrahydrocyclopenta[c]pyrazole-3a(3*H*)-carboxylate (**4a**)

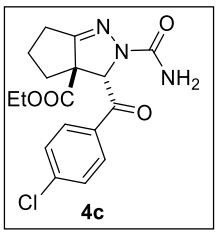
Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4a** as a white solid. 147 mg, 89% yield. m.p.: 174.7–176.1 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.04 (d, J = 8.5 Hz, 2H), 7.74 (dd, J = 16.3, 8.9 Hz, 1H), 7.60 (t, J = 7.8 Hz, 2H), 6.48 (s, 2H), 6.04 (s, 1H), 4.38–4.12 (m, 2H), 2.57–2.52 (m, 1H), 2.31 (m, 1H), 2.14–1.92 (m, 2H), 1.79 (ddd, J = 12.7, 6.9, 1.8 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.261.22 (m, 1H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 192.76, 170.93, 162.58, 155.58, 135.00 134.74, 129.62, 128.69, 67.45, 67.24, 62.68, 29.92, 25.84, 22.30, 14.29. HRMS (ESI): m/z calcd for $C_{17}H_{20}N_3O_4^+$ $[M+H]^+$: 330.1448, found:330.1452.



4b

Trans-ethyl-2-carbamoyl-3-(4-methylbenzoyl)-2,4,5,6-tetrahydrocyclopenta[c] pyrazole-3a (3*H*)-carboxylate (**4b**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4b** as a white solid. 158 mg. 92% yield. m.p.: 223.1–223.9 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.93 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 6.45 (s, 2H), 6.01 (s, 1H), 4.38–4.17 (m, 2H), 2.56–2.49 (m, 1H), 2.37–2.26 (m, 1H), 2.08–1.92 (m, 2H), 1.76 (ddd, J = 12.7, 6.9, 1.8 Hz, 1H), 1.28 (d, J = 7.1 Hz, 3H), 1.26–1.19 (m, 1H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 192.14, 170.99, 162.56, 155.59, 145.35, 132.54, 130.14, 128.80, 67.45, 67.20, 62.65, 29.92, 25.84, 22.31, 21.70 14.29. HRMS (ESI): m/z calcd for $C_{18}H_{22}N_3O_4^+$ $[M+H]^+$: 344.1605, found: 344.1602.

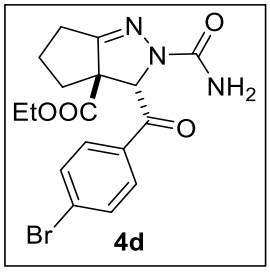


4c

Trans-ethyl-2-carbamoyl-3-(4-chlorobenzoyl)-2,4,5,6-tetrahydrocyclopenta

[c]pyrazole-3a (3*H*)-carboxylate (**4c**)

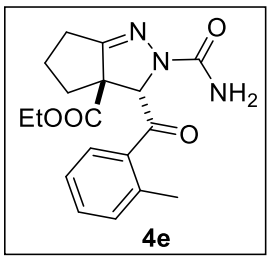
Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4c** as a white solid. 173 mg. 95% yield. m.p.: 168.7–170.1 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.05 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 6.49 (s, 2H), 6.03 (s, 1H), 4.42 – 4.12 (m, 2H), 2.52 (ddd, J = 8.3, 6.9, 3.2 Hz, 1H), 2.32 (dd, J = 16.5, 8.6 Hz, 1H), 2.08–1.94 (m, 2H), 1.84–1.73 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.26–1.17 (m, 1H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 191.96, 170.82, 162.59, 155.54, 139.81, 133.63, 130.60, 129.82, 67.44, 67.11, 62.72, 29.90, 25.83, 22.24, 14.27. HRMS (ESI): m/z calcd for $C_{17}H_{19}ClN_3O_4^+$ $[M+H]^+$: 364.1059, found: 364.1061.



4d

Trans-ethyl-3-(4-bromobenzoyl)-2-carbamoyl-2,4,5,6-tetrahydrocyclopenta[c] pyrazole-3a(3*H*)-carboxylate (**4d**)

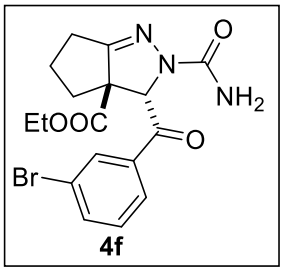
Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4d** as a white solid. 198 mg, 97% yield. m.p.: 198.0–199.1 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.96 (d, J = 8.6 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H), 6.49 (s, 2H), 6.02 (s, 1H), 4.38–4.15 (m, 2H), 2.60–2.51 (m, 1H), 2.40–2.23 (m, 1H), 2.10–1.95 (m, 2H), 1.86–1.73 (m, 1H), 1.28 (d, J = 7.1 Hz, 3H), 1.26–1.20 (m, 1H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 192.20, 170.81, 162.58, 155.53, 133.95, 132.79, 130.65, 129.09, 67.43, 67.08, 62.72, 29.89, 25.83, 22.24, 14.28. HRMS (ESI): m/z calcd for $C_{17}H_{19}BrN_3O_4^+$ $[M+H]^+$: 408.0553, found: 408.0555.



4e

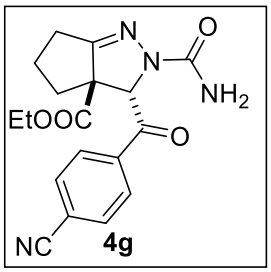
Trans-ethyl-2-carbamoyl-3-(2-methylbenzoyl)-2,4,5,6-tetrahydrocyclopenta [c]pyrazole-3a(3*H*)-carboxylate (**4e**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4e** as a white solid.151 mg. 88% yield. m.p.: 170.4–171.8 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 7.97 (d, J = 7.2 Hz, 1H), 7.53 (td, J = 7.5, 1.1 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 6.49 (s, 2H), 5.85 (s, 1H), 4.37–4.09 (m, 2H), 2.60–2.51 (m, 1H), 2.45 (s, 3H), 2.38–2.28 (m, 1H), 2.14–1.97 (m, 2H), 1.88 (ddd, J = 12.7, 6.9, 2.4 Hz, 1H), 1.42 (dt, J = 12.8, 9.5 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 195.96, 171.01, 162.36, 155.68, 139.66, 134.84, 133.16, 132.81, 129.81, 126.58, 68.51, 67.86, 62.60, 29.53, 25.71, 22.34, 21.60, 14.26. HRMS (ESI): m/z calcd for $C_{18}H_{22}N_3O_4^+$ $[M+H]^+$: 344.1605, found: 344.1609.



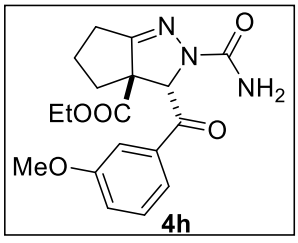
Trans-ethyl-carbamoyl-3-(3-bromobenzoyl)-2-carbamoyl-2,4,5,6-tetrahydrocyclopent a[c]pyrazole-3a(3*H*)-carboxylate (**4f**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4f** as a white solid. 190 mg. 93% yield. m.p.: 165.9–167.3 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.19 (s, 1H), 8.04 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.9 Hz, 1H), 6.50 (s, 2H), 6.04 (s, 1H), 4.27 (dtt, J = 14.3, 10.7, 7.1 Hz, 2H), 2.55 –2.53 (m, 1H), 2.38–2.27 (m, 1H), 2.10–1.94 (m, 2H), 1.86–1.71 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.24 (d, J = 10.1 Hz, 1H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 191.92, 170.79, 162.60, 155.51, 137.41, 136.88, 131.92, 131.25, 127.73, 122.98, 67.44, 67.01, 62.75, 29.99, 25.80, 22.22, 16.43. HRMS (ESI): m/z calcd for $C_{17}H_{19}BrN_3O_4^+$ $[M+H]^+$: 408.0553, found: 408.0556.



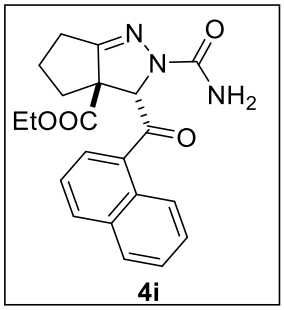
Trans-ethyl-2- carbamoyl-3-(4-cyanobenzoyl)-2,4,5,6-tetrahydrocyclopenta [c] pyrazole-3a(3*H*)-carboxylate (**4g**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4g** as a white solid. 170 mg. 96% yield. m.p.: 196.1–197.5 ℃.^{1}H NMR (500 MHz, DMSO–D_6) δ 8.19 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.3 Hz, 2H), 6.53 (s, 2H), 6.10 (s, 1H), 4.35–4.20 (m, 2H), 2.55 (d, J = 4.9 Hz, 1H), 2.39–2.29 (m, 1H), 2.08–1.95 (m, 2H), 1.86–1.72 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.24 (dd, J = 12.7, 10.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 192.63, 170.67, 162.58, 155.49, 138.02, 133.71, 129.30, 118.41, 116.69, 67.44, 67.17, 62.77, 29.86, 25.81, 22.18, 14.26. HRMS (ESI): m/z calcd for $C_{18}H_{19}N_4O_4^+$ $[M+H]^+$: 355.1401, found: 355.1404.



Trans-ethyl-2-carbamoyl-3-(3-methoxybenzoyl)-2, 4, 5, 6-tetrahydrocyclopenta [c] pyrazole-3a(3*H*)-carboxylate (**4h**)

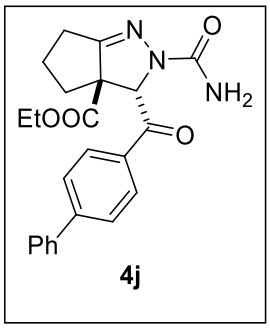
Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4h** as a white solid.White solid, 167 mg. 93% yield. m.p.: 153.6–154.9 ℃.^{1}H NMR (500 MHz, DMSO–D_6) δ 7.63 (d, J = 7.7 Hz, 1H), 7.52 (dd, J = 14.1, 5.9 Hz, 2H), 7.29 (dd, J = 8.1, 2.1 Hz, 1H), 6.49 (s, 2H), 6.02 (s, 1H), 4.27 (dddd, J = 24.9, 10.7, 7.1, 3.6 Hz, 2H), 2.58–2.52 (m, 1H), 2.36–2.27 (m, 1H), 2.02 (t, J = 10.3 Hz,3H), 1.85–1.75 (m, 1H). ^{13}C NMR (125MHz, DMSO–D_6) δ 192.43, 171.02, 162.63, 160.06, 155.59, 136.23, 130.81, 121.08, 120.95, 113.04, 67.50, 67.45, 62.72, 55.85, 30.07, 25.87, 22.32, 14.30. HRMS (ESI): m/z calcd for $C_{18}H_{22}N_3O_5^+$ $[M+H]^+$: 360.1554, found: 360.1556.



4i

Trans-ethyl-3-(1-naphthoyl)-2-carbamoyl-2,4,5,6-tetrahydrocyclopenta[c]pyrazole-3a (3*H*)-carboxylate (**4i**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4i** as a white solid.364 mg. 96% yield. m.p.: 190.5–191.7 ℃.^{1}H NMR (500 MHz, DMSO–D_6) δ 8.72 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 6.8 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.11–8.01 (m, 1H), 7.73–7.58 (m, 3H), 6.57 (s, 2H), 6.05 (s, 1H), 4.33–4.11 (m, 2H), 2.66–2.51 (m, 1H), 2.45–2.33 (m, 1H), 2.12–1.96 (m, 2H), 1.84 (ddd, J = 12.6, 6.2, 3.1 Hz, 1H), 1.53 (dt, J = 12.8, 9.5 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 196.33, 170.97, 162.42, 155.77, 134.73, 134.13, 132.31, 130.26, 130.22, 129.26, 128.91, 127.18, 125.74, 125.23, 68.91, 68.13, 62.61, 29.48, 25.70, 22.37, 14.26. HRMS (ESI): m/z calcd for $C_{21}H_{22}N_3O_4^+$ $[M+H]^+$: 380.1605, found: 380.1611.

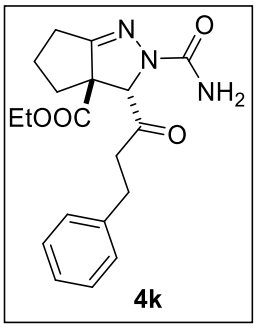


4j

Trans-ethyl-3-([1,1'-biphenyl]-4-carbonyl)-2-carbamoyl-2,4,5,6-tetrahydrocyclopenta [c]pyrazole-3a (3*H*) -carboxylate (**4j**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4j** as a white solid. 192 mg. 95% yield. m.p.: 163.1–164.7 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.13 (d, J = 7.4 Hz, 2H), 7.91 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 6.8 Hz, 2H), 7.52 (d, J = 7.4 Hz, 2H), 7.45 (d, J = 6.6 Hz, 1H), 6.50 (s, 2H), 6.08 (s, 1H), 4.45–4.11 (m, 2H), 2.52 (s, 1H), 2.41–2.27 (m, 1H), 2.00 (d, J = 16.5 Hz, 2H), 1.84 (d,

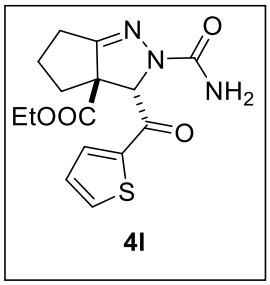
J = 10.9 Hz, 1H), 1.29 (t, *J* = 6.2 Hz, 3H), 1.22–1.03 (m,1H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 192.35, 171.01, 162.61, 155.61, 145.99, 139.06, 133.77, 129.62, 129.44, 129.13, 127.77, 127.57, 67.51, 67.26, 62.71, 29.96, 25.88, 22.34, 14.33. HRMS (ESI): m/z calcd for $C_{23}H_{24}N_3O_4^+$ $[M+H]^+$: 406.1761, found: 406.1764.



4k

Trans-ethyl-2-carbamoyl-3-(3-phenylpropanoyl)-2,4,5,6-tetrahydrocyclopenta[c] pyrazole-3a(3*H*)-carboxylate (**4k**)

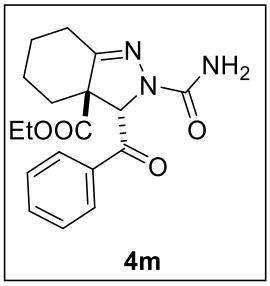
Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4k** as a white solid. 136 mg. 76% yield. m.p.: 90.8–92.8 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.6, 6.5 Hz, 2H), 7.22–7.17 (m, 3H), 5.34 (s, 3H), 5.23 (s, 1H), 4.28–4.18 (m, 2H), 2.95–2.79 (m, 4H), 2.58–2.51 (m, 1H), 2.38–2.29 (m, 1H), 2.15–2.07 (m, 1H), 1.96 (dddd, *J* = 24.4, 17.6, 8.8, 3.9 Hz, 2H), 1.30 (d, *J* = 7.1 Hz, 3H), 1.27–1.21 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.90, 170.55, 163.35, 155.35, 140.67, 128.63, 128.45, 126.21, 69.39, 67.61, 62.46, 42.82, 28.80, 28.76, 25.45, 22.14, 14.07. HRMS (ESI): m/z calcd for $C_{19}H_{24}N_3O_4^+$ $[M+H]^+$: 358.1761, found: 358.1764.



4l

Trans-ethyl-2-carbamoyl-3-(thiophene-2-carbonyl)-2,4,5,6-tetrahydrocyclopenta[c]py razole-3a(3*H*)-carboxylate (**4l**)

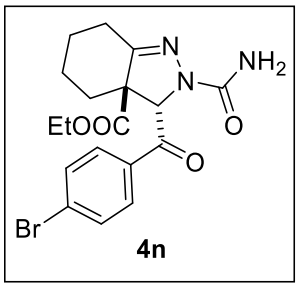
Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4l** as a white solid. 146 mg. 87% yield. m.p.: 194.2–196.1 ℃. ^{1}H NMR (500 MHz, DMSO–D_6) δ 8.14 (dd, *J* = 4.9, 0.8 Hz, 1H), 8.09 – 8.04 (m, 1H), 7.33 (dd, *J* = 4.8, 3.9 Hz, 1H), 6.49 (s, 2H), 5.91 (s, 1H), 4.32–4.18 (m, 2H), 2.52 (ddd, *J* = 9.0, 6.6, 3.8 Hz, 1H), 2.38–2.26 (m, 1H), 2.02 (ddd, *J* = 11.8, 9.0, 3.3 Hz, 2H), 1.82 (ddd, *J* = 12.7, 6.2, 2.8 Hz, 1H), 1.37–1.30 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO–D_6) δ 185.98, 170.86, 162.63, 155.49, 141.49, 137.19, 134.62, 129.72, 67.78, 67.66, 62.68, 29.79, 25.71, 22.28, 14.30. HRMS (ESI): m/z calcd for $C_{15}H_{18}N_3O_4S^+$ $[M+H]^+$: 336.1013, found: 336.1017.



4m

Trans-ethyl-3-benzoyl-2-carbamoyl-2,3,4,5,6,7-hexahydro-3a*H*-indazole-3a-carboxyl ate (**4m**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4m** as a white solid. 55 mg, 32% yield. m.p.: 150.0–151.7 ℃. ^{1} HNMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.49 (d, J = 7.8 Hz, 2H), 5.98 (s, 1H), 5.30 (s, 2H), 4.34 (ddq, J = 45.3, 10.8, 7.1 Hz, 2H), 2.68 (d, J = 14.0 Hz, 1H), 2.52–2.40 (m, 1H), 2.14–2.07 (m, 1H), 1.92 (s, 1H), 1.68–1.57 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.36–1.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.86, 171.50, 155.04, 154.04, 135.57, 134.00, 128.90, 128.80, 66.26, 62.51, 62.05, 32.75, 26.49, 25.25, 22.06, 14.18. HRMS (ESI): m/z calcd for $C_{18}H_{22}N_3O_4^+$ $[M+H]^+$: 344.1605, found: 344.1609.



4n

Trans-ethyl-3-(4-bromobenzoyl)-2-carbamoyl-2,3,4,5,6,7-hexahydro-3a*H*-indazole-3a -carboxylate (**4n**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **4n** as a white solid. 86 mg, 41% yield. m.p.: 199.0–200.2 ℃.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 5.91 (s, 1H), 5.36 (s, 2H), 4.33 (ddq, J = 45.3, 10.7, 7.1 Hz, 2H), 2.67 (d, J = 13.5 Hz, 1H), 2.47 (dt, J = 20.4, 10.2 Hz, 1H), 2.06 (d, J = 6.3 Hz, 1H), 1.93 (d, J = 7.3 Hz, 1H), 1.68–1.56(m, 2H), 1.37 (d, J = 7.1 Hz, 3H), 1.32 (d, J = 7.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.11, 171.51, 154.86, 154.04, 134.30, 132.19, 130.37, 129.50, 66.15, 62.63, 62.08, 32.30, 26.47, 25.25, 22.01, 14.17. HRMS (ESI): m/z calcd for $C_{18}H_{21}BrN_3O_4^+$ $[M+H]^+$: 422.0710, found: 422.0708.

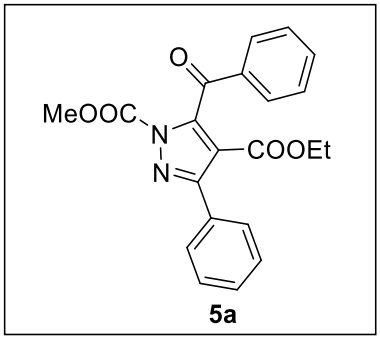
VI. General Procedure of 5

General Procedure of **5a**: A mixture of ethyl-3-(carbamoyldiazenyl)-3-phenylacrylate (0.5 mmol, 1.0 equiv) and benzoyl-sulfur ylides (0.5 mmol, 1.0 equiv) were stirred in 5 mL DCE at 25 ºC for 12 hours. After the completeness of the reaction (monitored by TLC), the reaction mixture was then concentrated and purified by chromatography (silica gel, 40-63μm) to afford the desired products.

General Procedure of **5b**-**5d**: A mixture of α-halogeno ketohydrazones (0.5 mmol,

1.0 equiv), sulfur ylides (0.5 mmol, 1.0 equiv) and trimethylamine (0.5 mmol, 1.0 equiv) were stirred in 5 mL DCE at 25 °C for 12 hours. After the completeness of the reaction (monitored by TLC), the reaction mixture was then concentrated and purified by chromatography (silica gel, 40-63μm) to afford the desired products **5b-5d**.

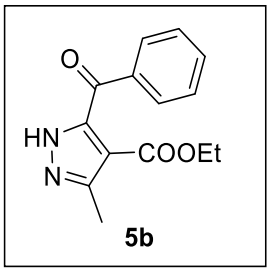
VII. Characterization Data of 5



4-ethyl-1-methyl 5-benzoyl-3-phenyl-1*H*-pyrazole-1,4-dicarboxylate (**5a**)

Purified by column chromatography (silica gel, Pe : EA = 5 :1) to afford **5a** as a white solid. 147 mg. 78% yield. m.p.: 133.6–135.2 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.7 Hz, 2H), 7.79 (dd, J = 6.1, 2.5 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.47–7.41 (m, 3H), 4.01 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 0.83 (d, J = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.70, 161.00, 155.71, 149.11, 146.99, 135.93, 134.21, 130.36, 129.64, 129.59, 129.05, 128.92, 128.02, 115.09, 61.17, 55.77, 13.21.

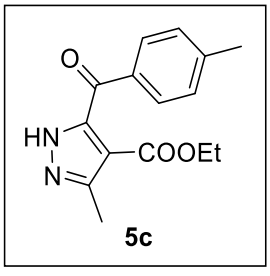
HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_5^+$ $[M+H]^+$: 379.1288, found: 379.1290.



Ethyl-5-benzoyl-3-methyl-1*H*-pyrazole-4-carboxylate (**5b**)

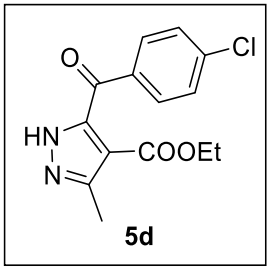
Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **5b** as a light yellow sticky solid. 163 mg. 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.4 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.7 Hz, 2H), 3.90 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 0.82 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.01, 162.92, 150.79, 145.61, 137.31, 133.59, 129.72, 128.46, 110.97, 60.25, 13.53, 10.90.

HRMS (ESI): m/z calcd for $C_{14}H_{15}N_2O_3^+$ $[M+H]^+$: 259.1077, found: 259.1086.



Ethyl-3-methyl-5-(4-methylbenzoyl)-1*H*-pyrazole-4-carboxylate (**5c**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **5c** as a light yellow sticky solid.. 101 mg, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.92 (d, J = 7.1 Hz, 2H), 2.39 (s, 3H), 2.34 (d, J = 5.2 Hz, 3H), 0.85 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.56, 161.94, 149.91, 144.51, 143.56, 133.65, 128.88, 128.58, 128.14, 125.27, 109.85, 59.19, 20.72, 12.55, 9.95. HRMS (ESI): m/z calcd for $C_{15}H_{17}N_2O_3^+$ $[M+H]^+$: 273.1234, found: 273.1235.



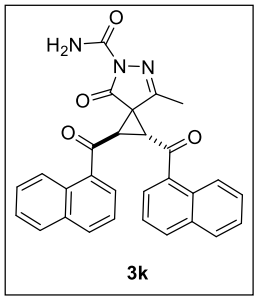
5d

Ethyl-5-(4-chlorobenzoyl)-3-methyl-1*H*-pyrazole-4-carboxylate (**5d**)

Purified by column chromatography (silica gel, Pe : EA = 4 :1) to afford **5d** as a a light yellow sticky solid. 106 mg, 72% yield. m.p.: 87.9 – 88.7 ℃.^{1}H NMR (500 MHz, $CDCl_3$) δ 12.37 (s, 1H), 7.78 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 4.01 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 0.95 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.64, 162.77, 140.13, 135.45, 131.10, 128.81, 111.07, 60.41, 13.67, 11.05. HRMS (ESI): m/z calcd for $C_{14}H_{14}ClN_2O_3^+$ $[M+H]^+$: 293.0687, found: 293.0685.

VIII. *X*-ray Crystallography Data of 3k and 4i

Single crystals of compound **3k** was measured on a Rigaku RAXIS-RAPID single-crystal diffractometer. The recrystallization solvent of **3k** was MeOH/DCM (volume ratio 1:1). (CCDC No. 1842437)



3k

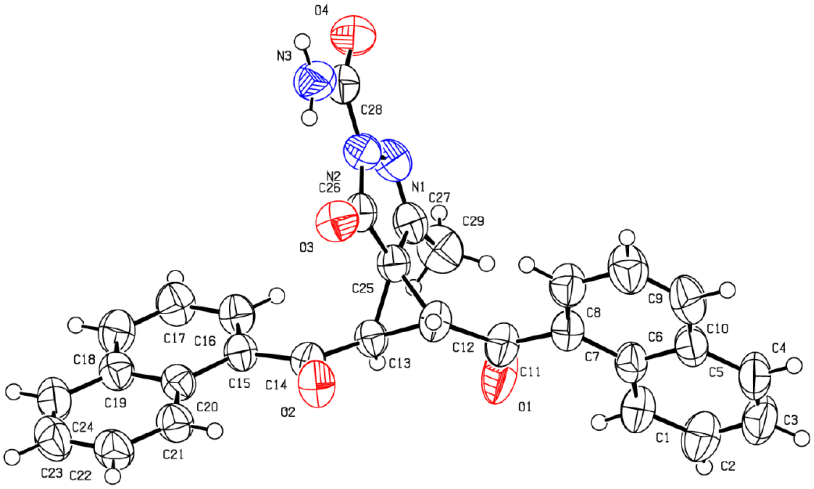


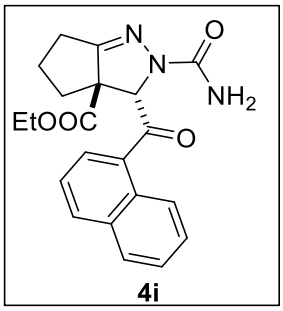
Figure S1 X-ray crystallography of **3k**.

Table S1 X-ray crystallography data of **3k**.

Formula moiety	$C_{29}H_{21}N_3O_4$
Formula sum	$C_{29}H_{21}N_3O_4$
Formula weight	475.49
Temperature	110 K
Crystal system	monoclinic
Space group	P1 21/c1
Unit cell dimensions	a= 18.8826 (8) Å
	b= 13.2600 (5) Å
	c= 9.2363 (9) Å
	alpha=90 deg.
	beta = 90.076（4） deg.
	gamma = 90 deg.
Volume	2312.61 (17) $Å^3$
Z	4
Calculated density	1.366 g/cm^3
Absorption coefficient	0.753 mm^{-1}
F(000)	992

Crystal size	0.48 × 0.38 × 0.2 mm
Theta range for data collection	3.3302 to 66.9151 deg
Reflections collected / unique	3555 / 4085 [R(int) = 0.0660]
Data / restraints / parameters	4085/ 0 / 326
Goodness-of-fit on F2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0660, wR2 = 0.1810
R indices (all data)	R1 = 0.0744, wR2 = 0.1970

Single crystals of compound **4i** was measured on a Rigaku RAXIS-RAPID single-crystal diffractometer. The recrystallization solvent of **4i** was MeOH/DCM (volume ratio 1:1). (CCDC No. 1842438)



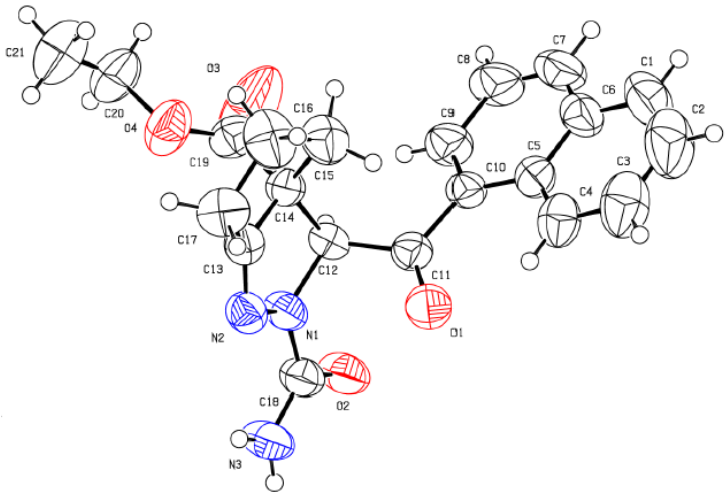


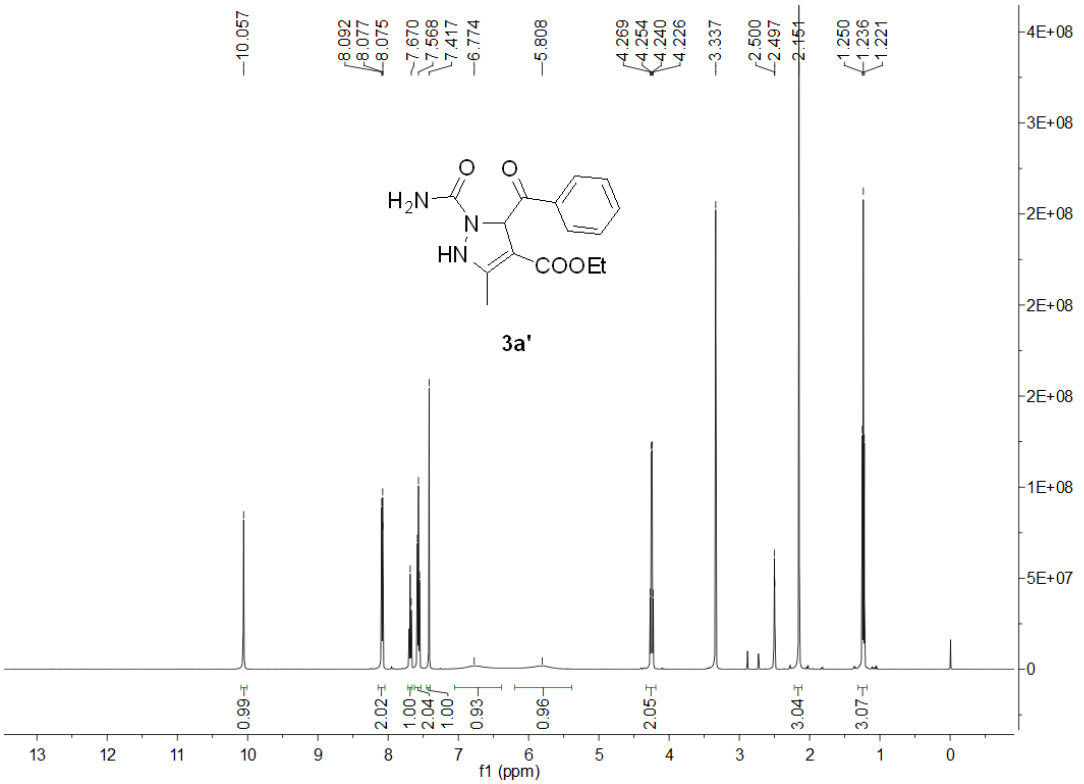
Figure S2 X-ray crystallography of **4i**.

Table S2 X-ray crystallography data of **4i**.

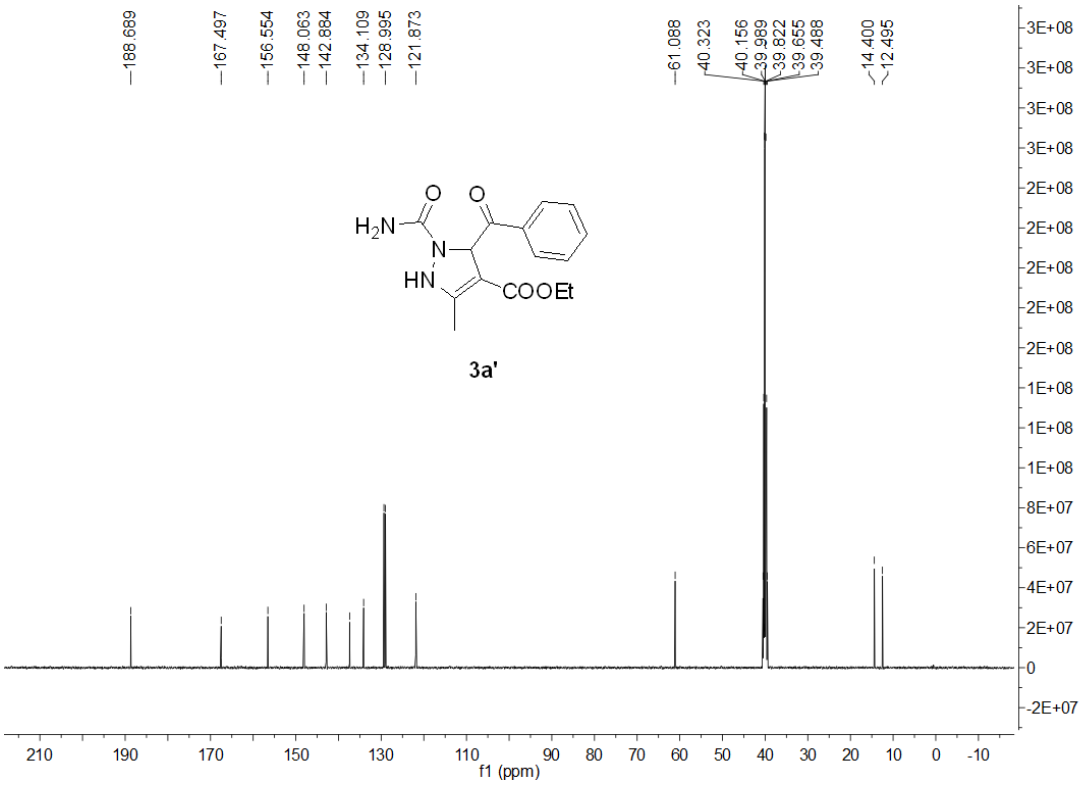
Formula moiety	$C_{21}H_{21}N_3O_4$
Formula sum	$C_{21}H_{21}N_3O_4$
Formula weight	379.41

Temperature	293.15 K
Crystal system	monoclinic
Space group	C 12/c1
Unit cell dimensions	a= 24.860 (3) Å
	b= 10. 591 (2) Å
	c= 15.0502 (19) Å
	alpha=90 deg.
	beta = 105.338（13） deg.
	gamma = 90 deg.
Volume	3821.5 (10) $Å^3$
Z	8
Calculated density	1.319 g/cm^3
Absorption coefficient	0.093 mm^{-1}
F(000)	1600
Crystal size	0.46 × 0.39 × 0.36 mm
Theta range for data collection	3.1990 to 29.3537 deg
Reflections collected / unique	2089 / 3490 [R(int) = 0.0569]
Data / restraints / parameters	3490/ 0 / 254
Goodness-of-fit on F2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1359
R indices (all data)	R1 = 0.1016, wR2 = 0.1691

IX. ^{1}H NMR and ^{13}C NMR Spectra of Final Products



3a'



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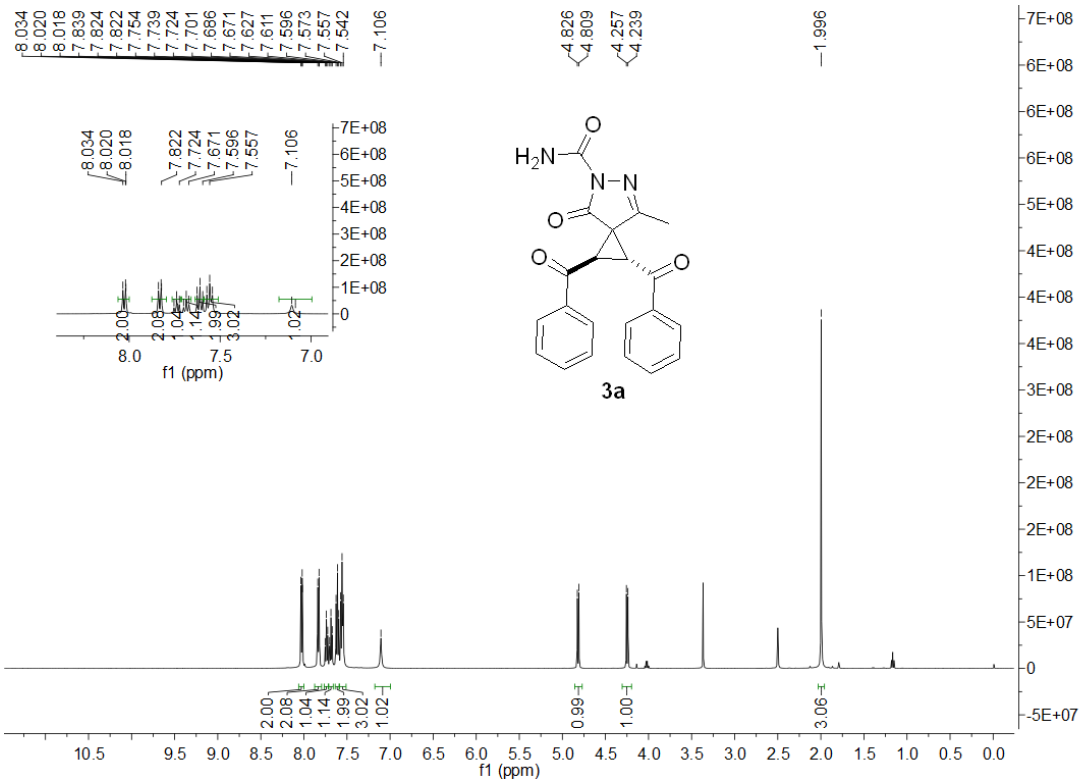
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7.724
7.701
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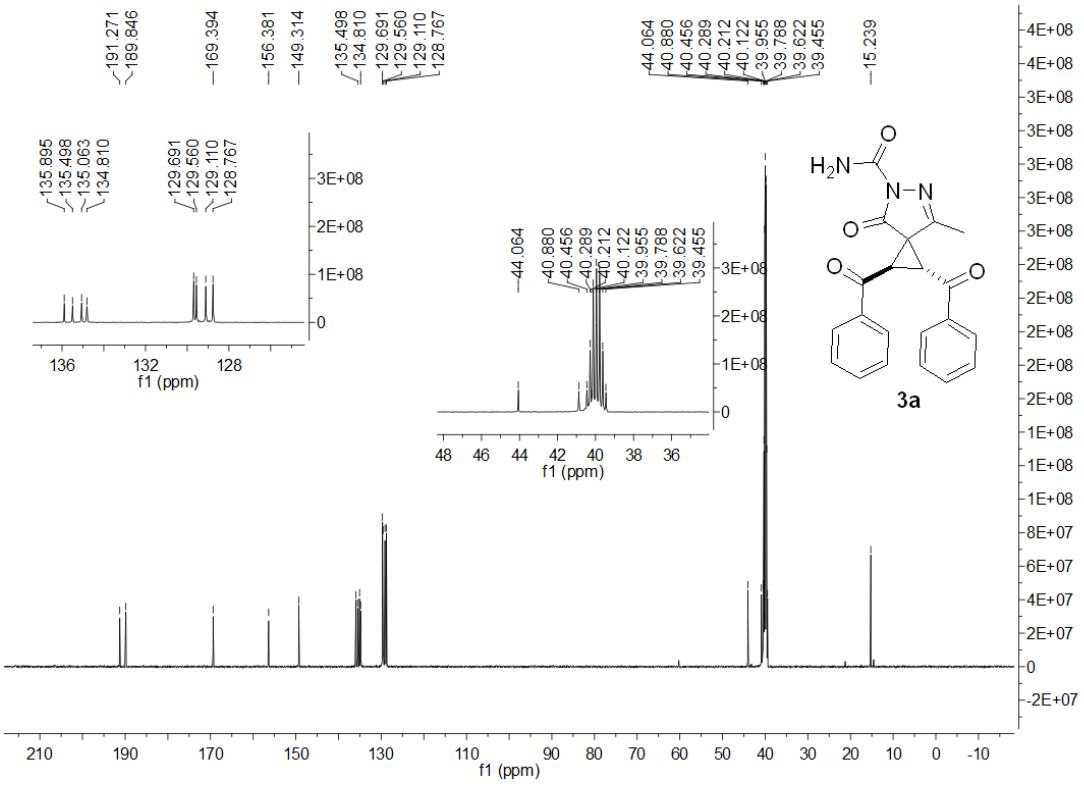
7.671
7.627
7.611
7.596
7.573
7.557
7.542
7.106
4.826
4.809
4.257
4.239
1.996
f1 (ppm)
3a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169.394
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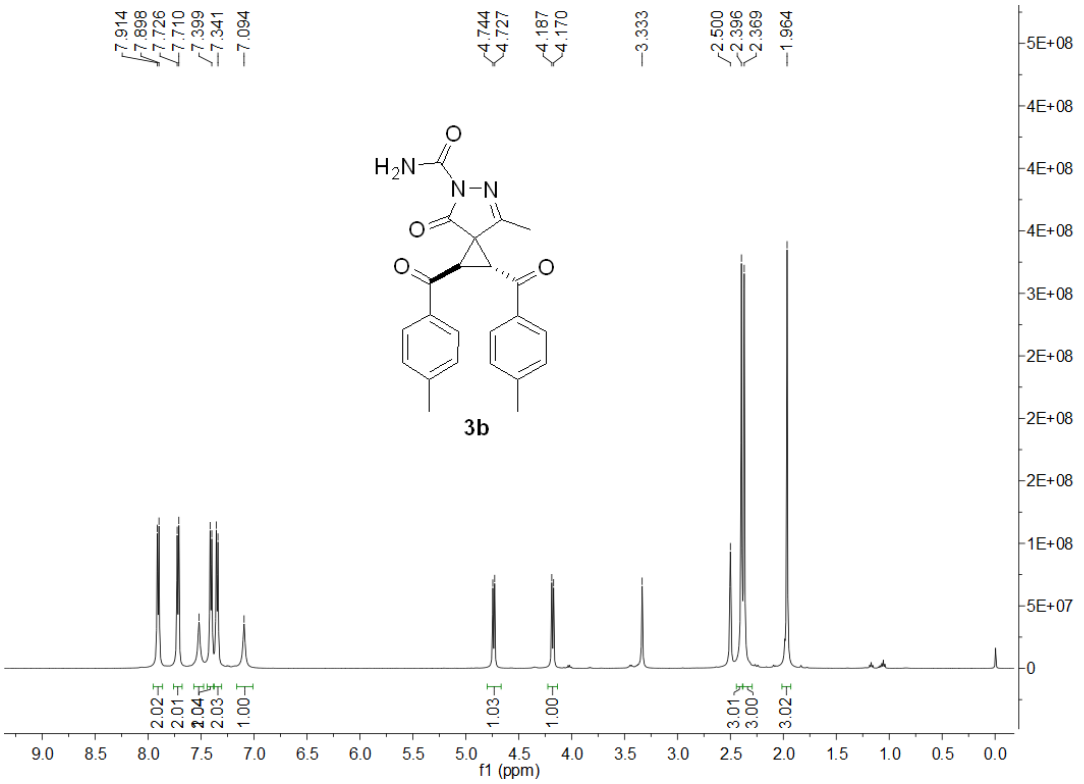
135.498
134.810
129.691
129.560
129.110
128.767
44.064
40.880
40.456
40.289
40.212
40.122
39.955
39.788
39.622
39.455
15.239
f1 (ppm)
3a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7.726
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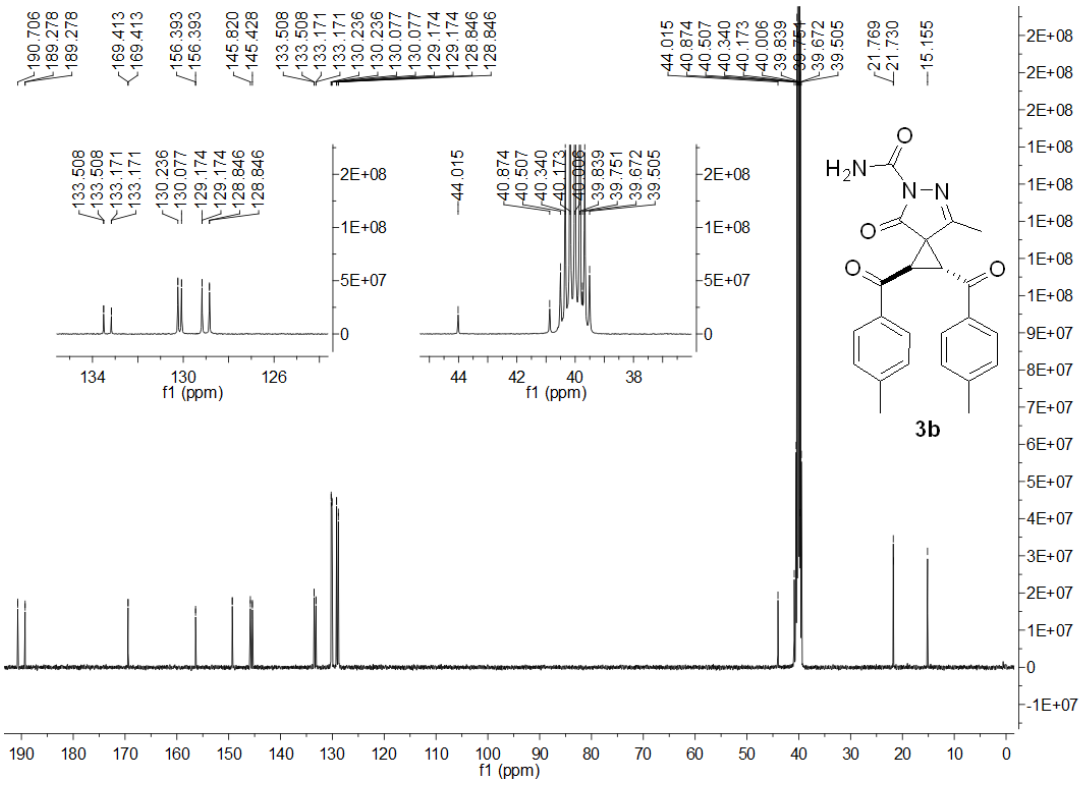
7.399
7.341
7.094
4.744
4.727
4.187
4.170
3.333
2.500
2.396
2.369
1.964
3b
f1 (ppm)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145.820
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133.508
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133.171
130.236
130.236
130.077
130.077
129.174
129.174
128.846
128.846
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40.874
40.507
40.340
40.173
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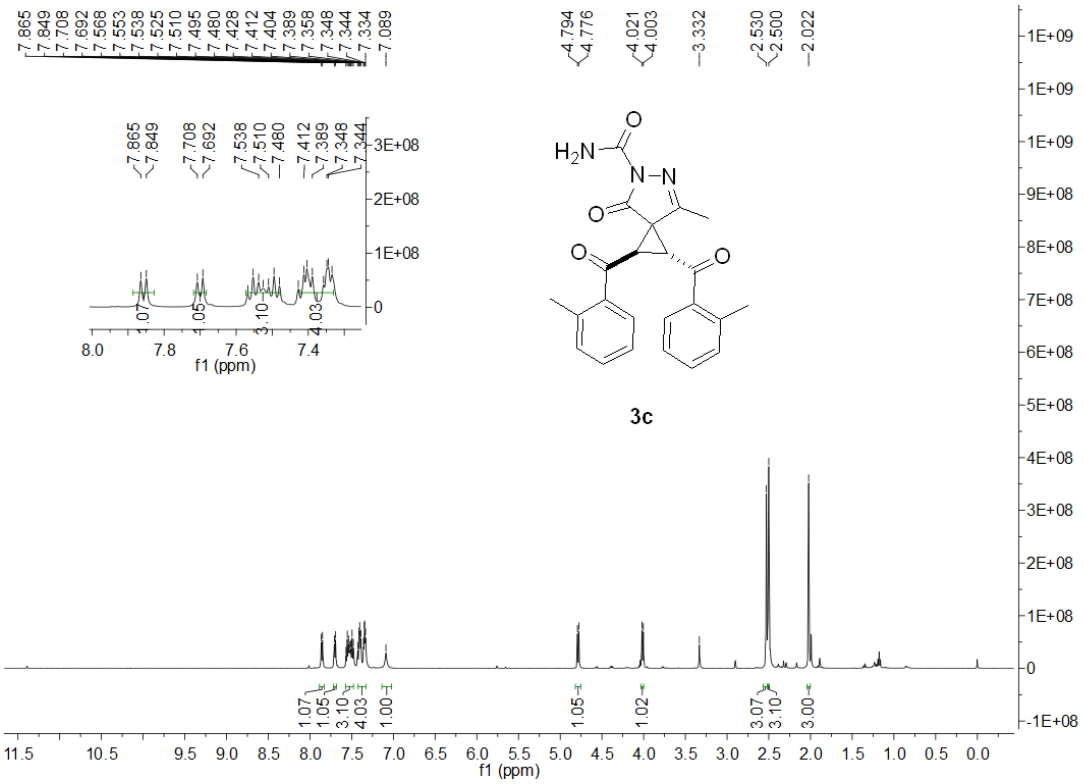
39.751
39.672
39.505
21.769
21.730
15.155
3b
f1 (ppm)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7.553
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7.525
7.510
7.495
7.480
7.428
7.412
7.404
7.389
7.358
7.348
7.344
7.334
7.089
4.794
4.776
4.021
4.003
3.332
2.530
2.500
2.022
f1 (ppm)
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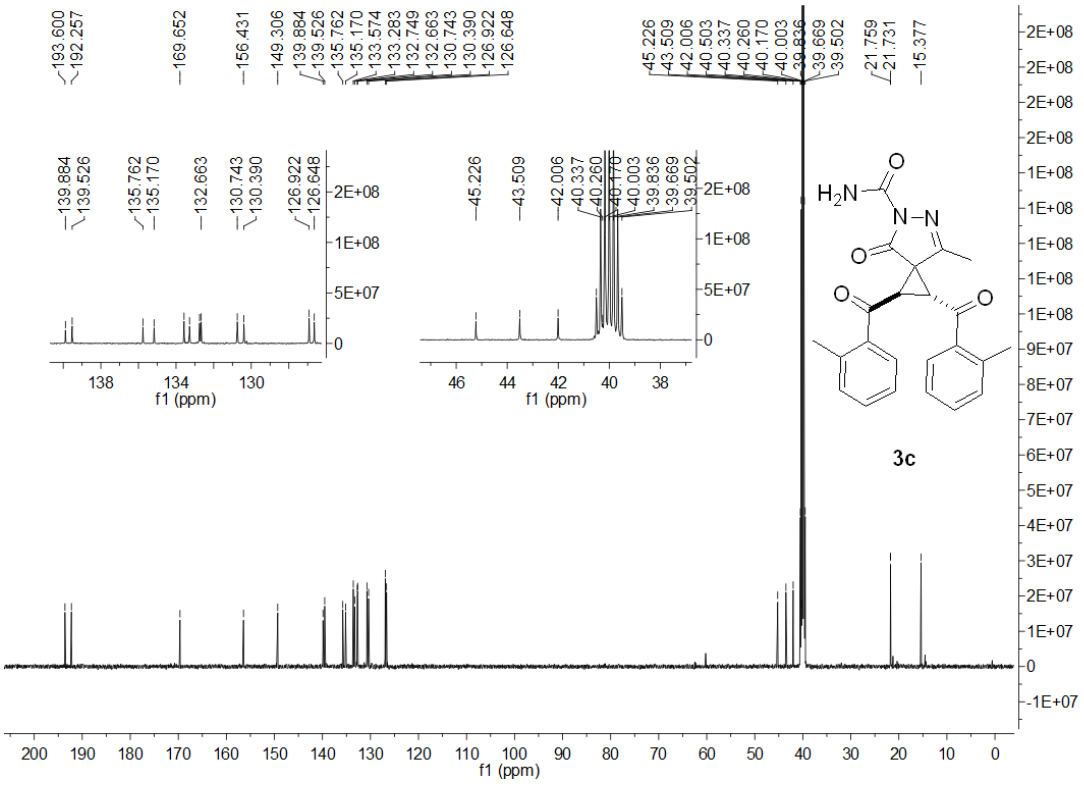
1.05
3.10
4.03
1.00
1.05
1.02
3.07
3.10
3.00

3c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133.283
132.749
132.663
130.743
130.390
126.922
126.648
45.226
43.509
42.006
40.503
40.337
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40.170
40.003
39.836
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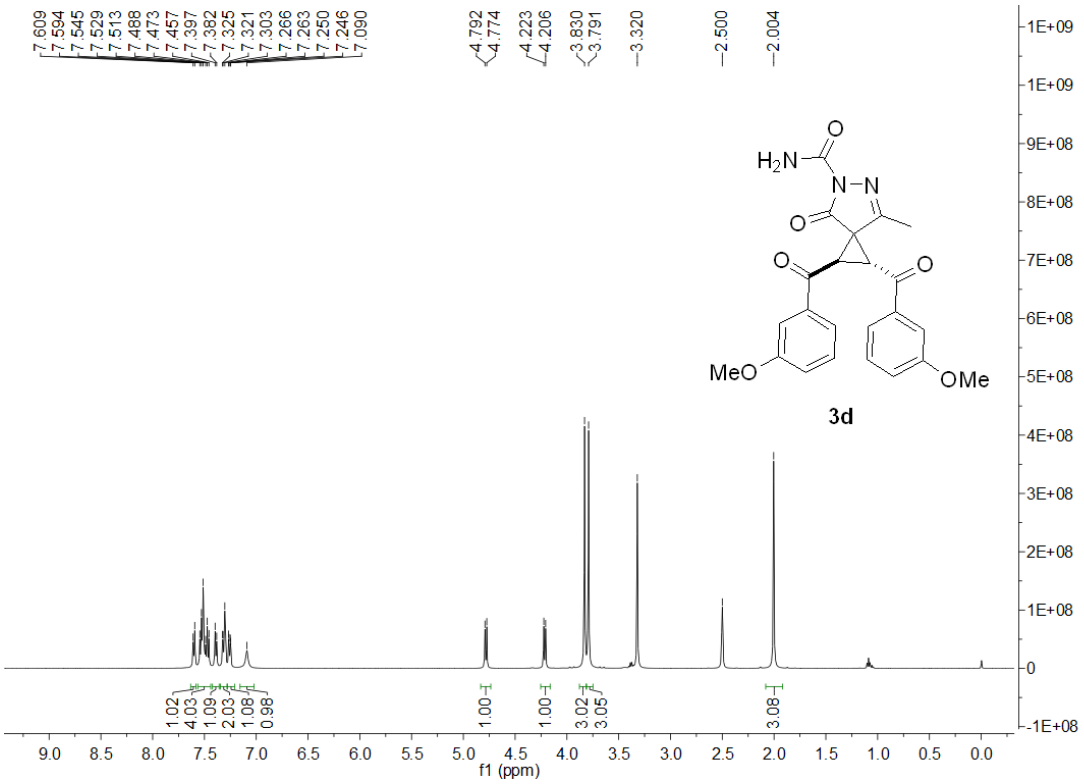
21.731
15.377
f1 (ppm)

3c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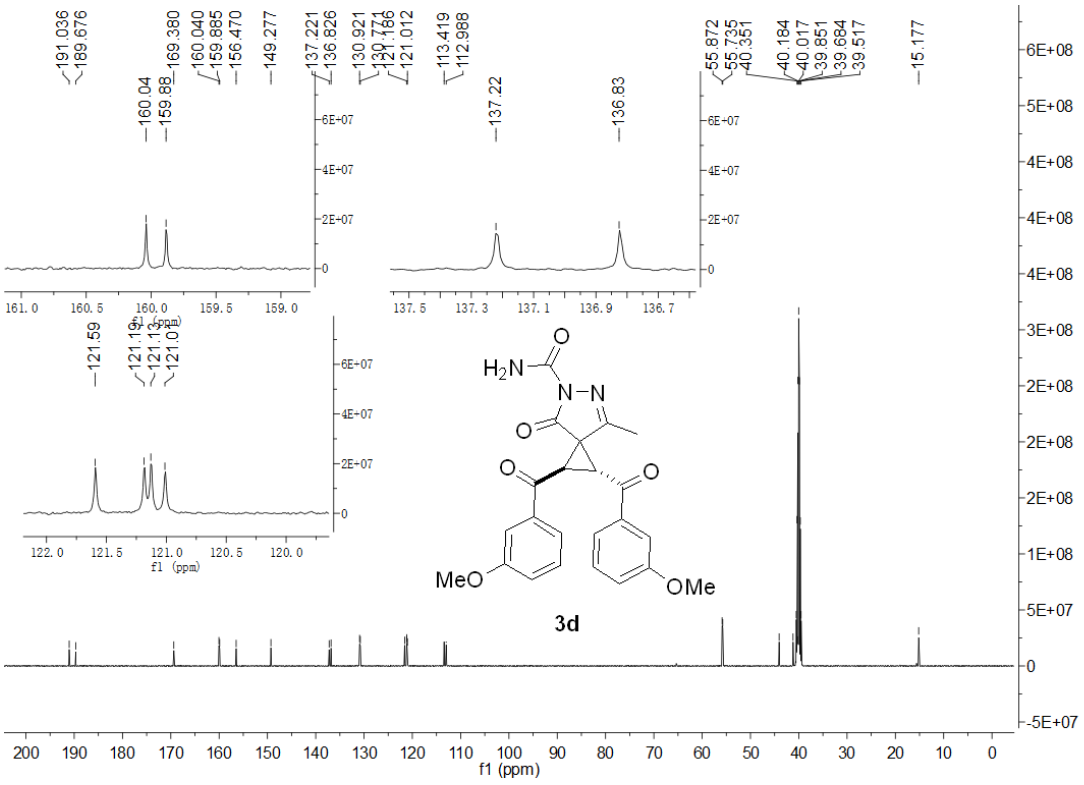
7.513
7.488
7.473
7.457
7.397
7.382
7.325
7.321
7.303
7.266
7.263
7.250
7.246
7.090
4.792
4.774
4.223
4.206
3.830
3.791
3.320
2.500
2.004
1.02
4.03
1.09
2.03
1.08
0.98
1.00
1.00
3.02
3.05
3.08
f1 (ppm)
3d


191.036
189.676
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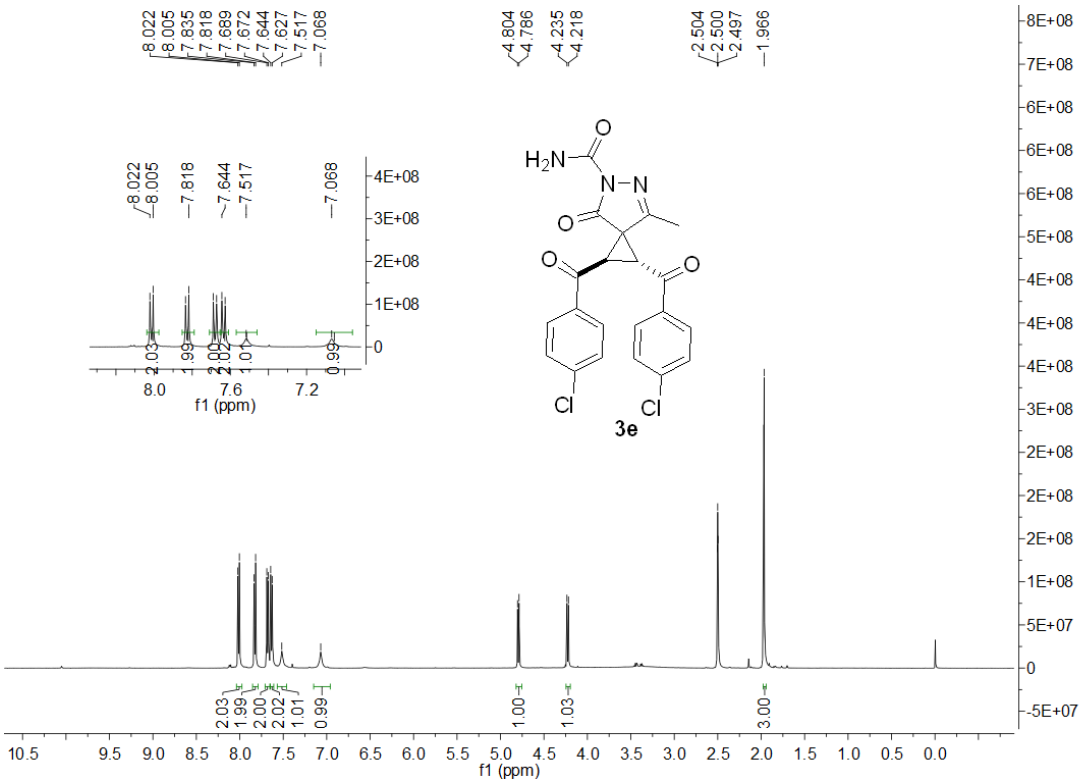
159.88
169.380
160.040
159.885
156.470
149.277
137.221
136.826
130.921
130.771
121.186
121.012
113.419
112.988
137.22
136.83
55.872
55.735
40.351
40.184
40.017
39.851
39.684
39.517
15.177
121.59
121.19
121.13
121.07
f1 (ppm)
3d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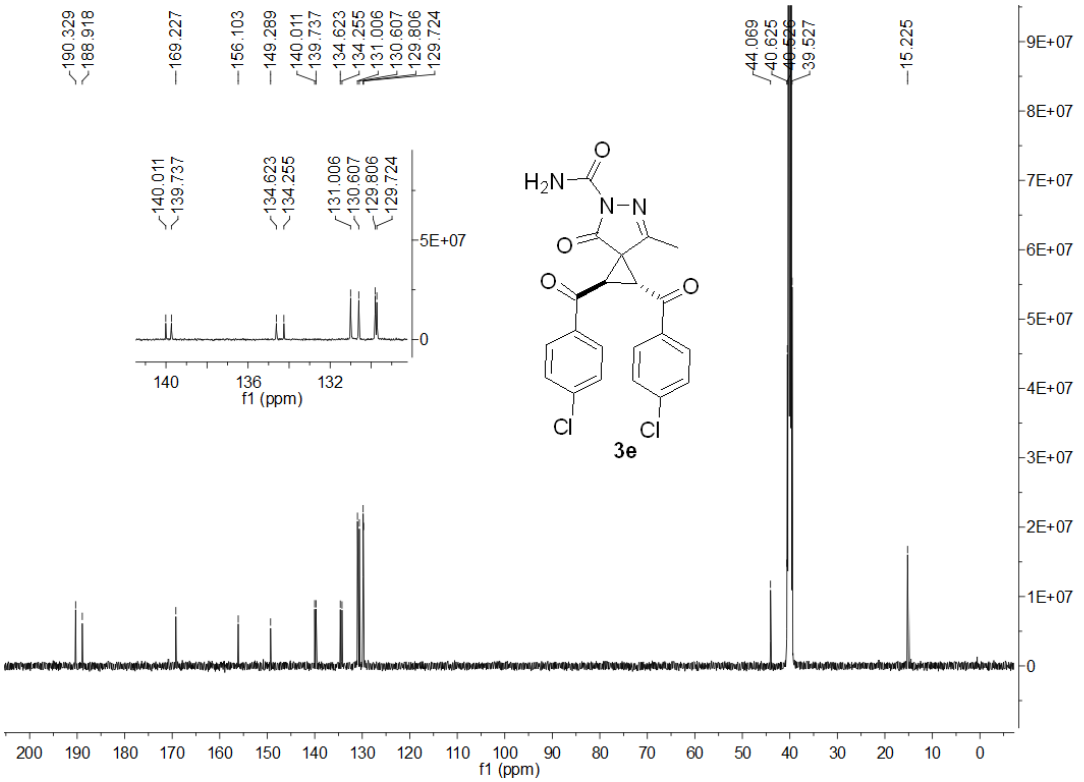
8.005
7.835
7.818
7.689
7.672
7.644
7.627
7.517
7.068
4.804
4.786
4.235
4.218
2.504
2.500
2.497
1.966
H2N
N–N
O
Cl
Cl
3e
f1 (ppm)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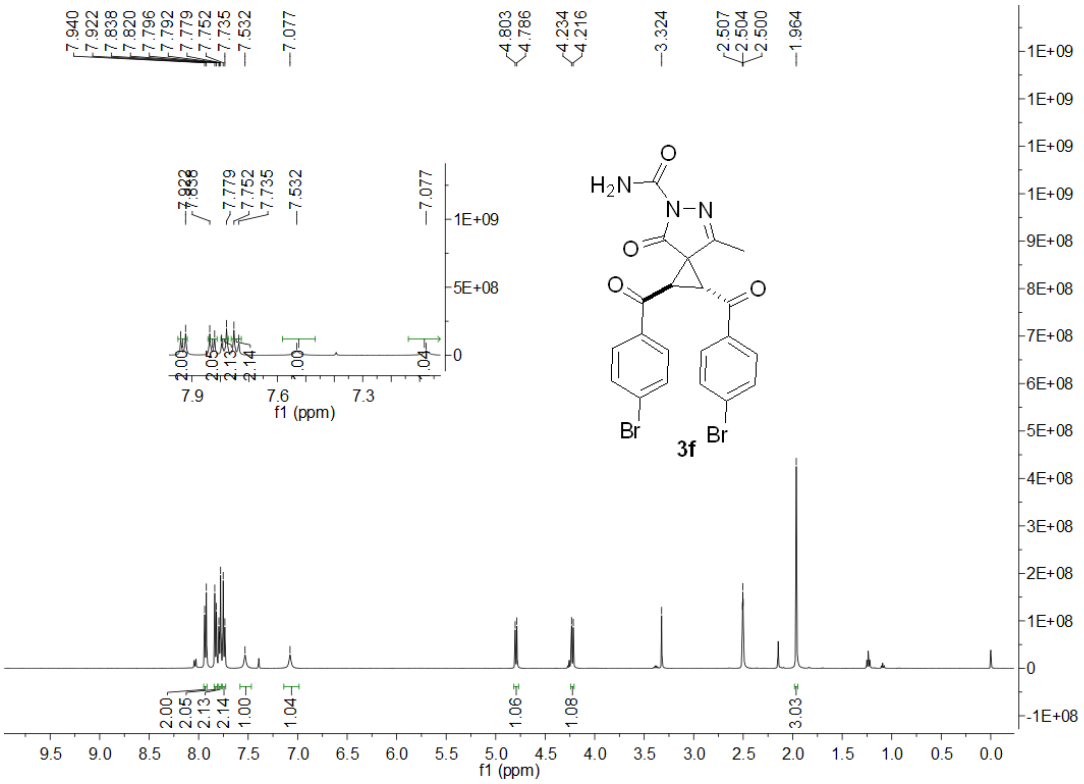
188.918
169.227
156.103
149.289
140.011
139.737
134.623
134.255
131.006
130.607
129.806
129.724
44.069
40.625
39.527
15.225
H2N
N–N
O
Cl
Cl
3e
f1 (ppm)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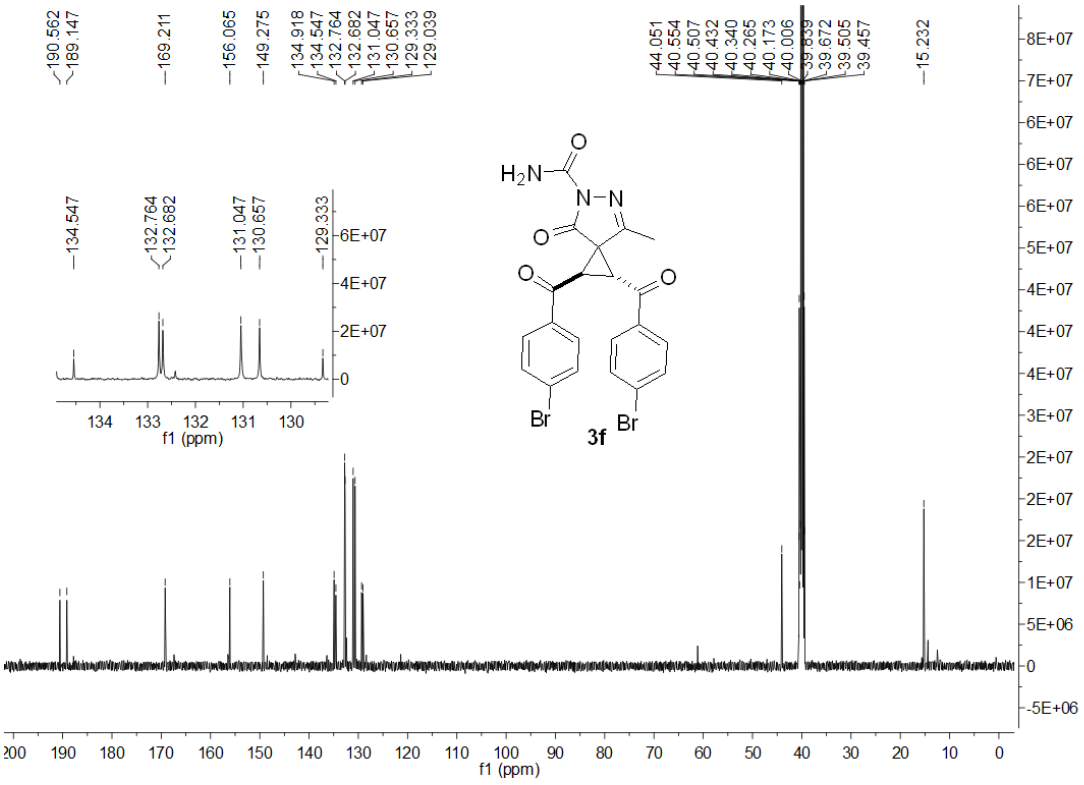
7.838
7.820
7.796
7.792
7.779
7.752
7.735
7.532
7.077
4.803
4.786
4.234
4.216
3.324
2.507
2.504
2.500
1.964
H2N
N–N
O
Br
Br
3f
f1 (ppm)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169.211
156.065
149.275
134.918
134.547
132.764
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131.047
130.657
129.333
129.039
44.051
40.554
40.507
40.432
40.340
40.265
40.173
40.006
39.839
39.672
39.505
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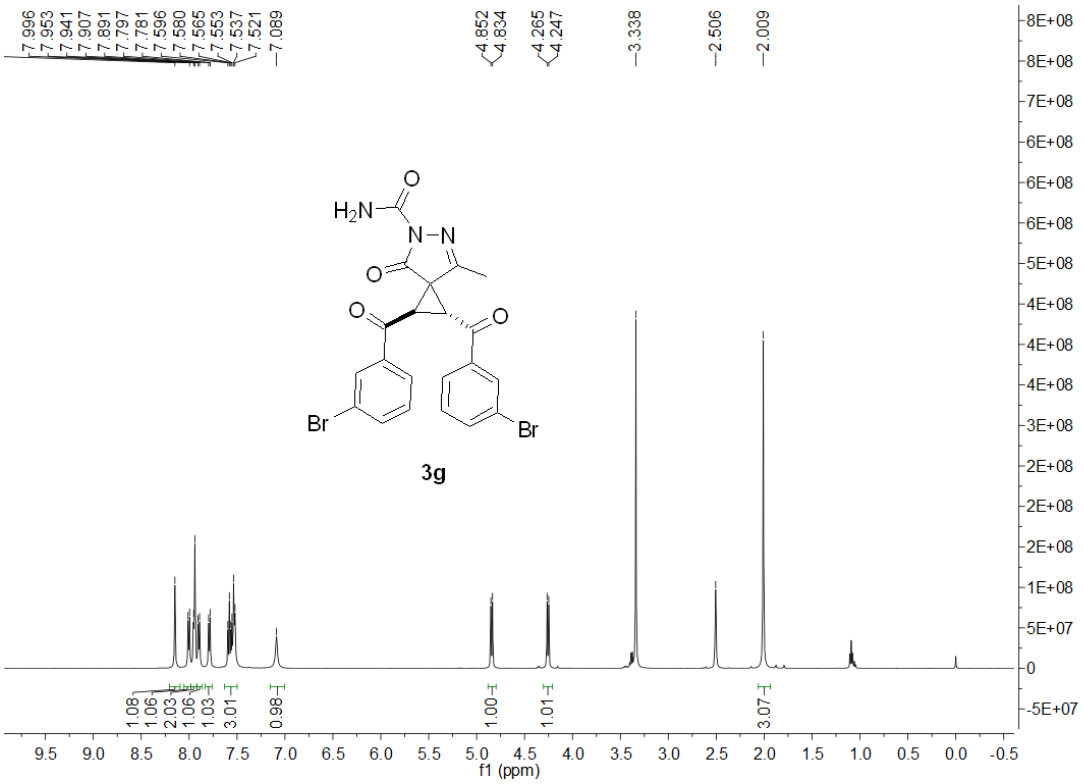
15.232
H2N
N–N
O
Br
Br
3f
f1 (ppm)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7.797
7.781
7.596
7.580
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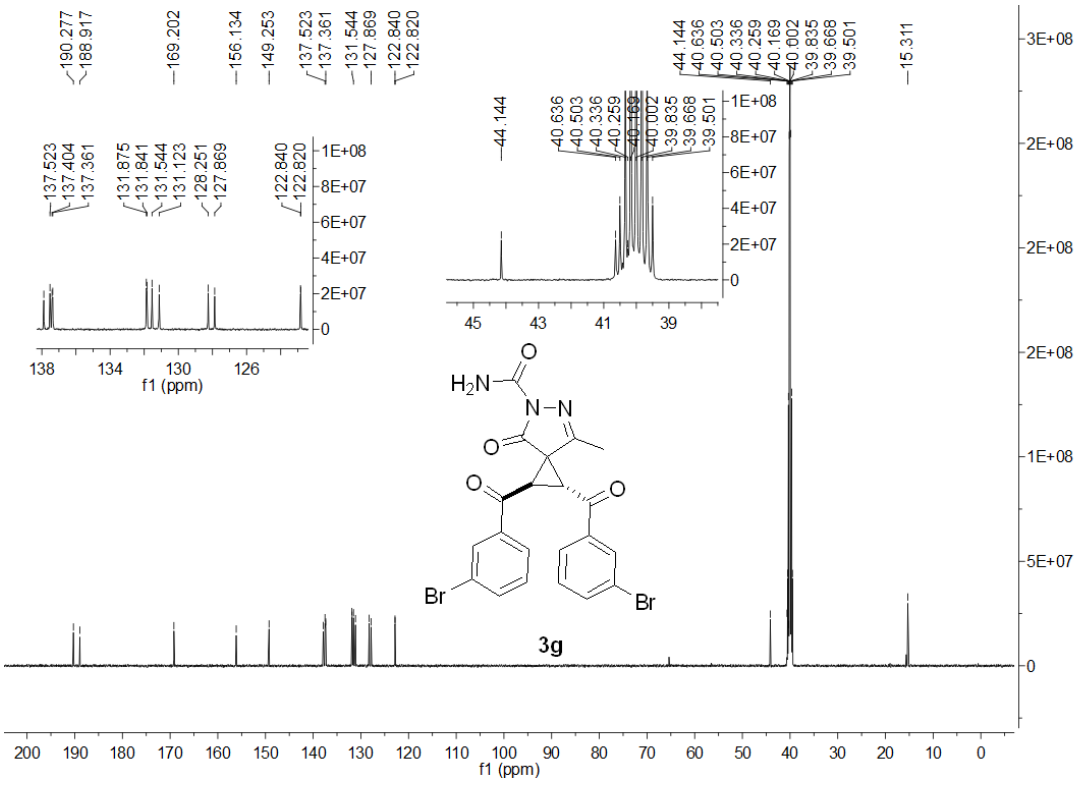
7.553
7.537
7.521
7.089
4.852
4.834
4.265
4.247
3.338
2.506
2.009
3g
1.08
1.06
2.03
1.06
1.03
3.01
0.98
1.00
1.01
3.07
f1 (ppm)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137.361
131.544
127.869
122.840
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40.259
40.169
40.002
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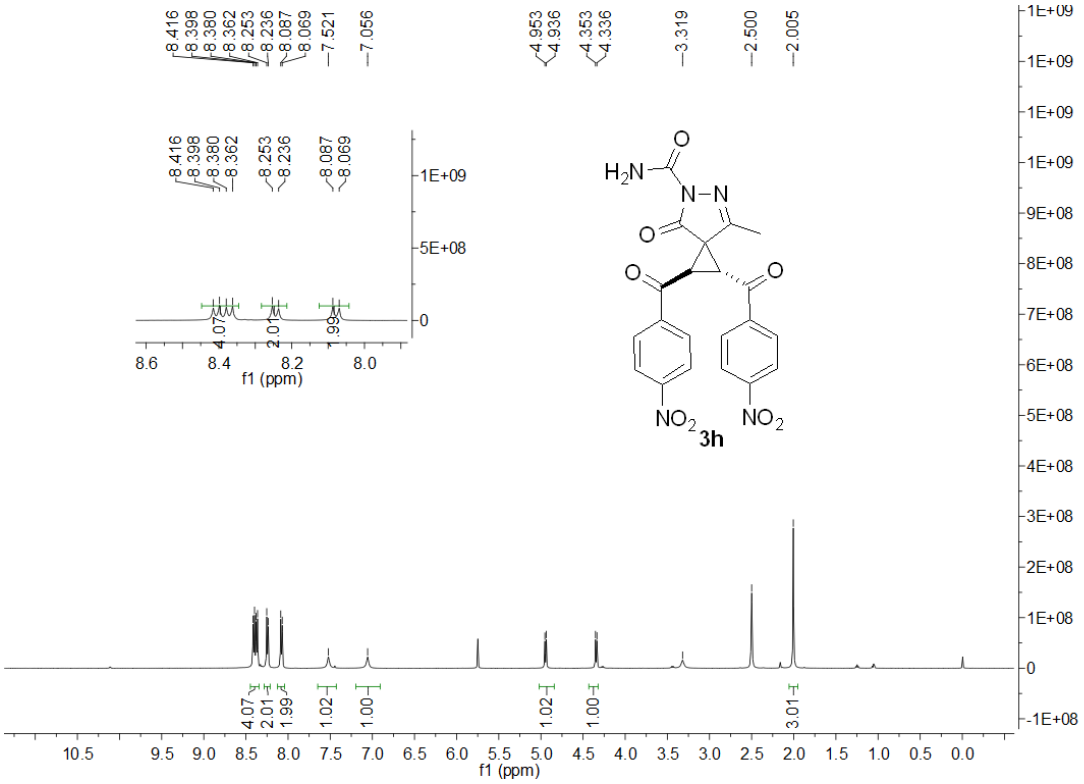
39.668
39.501
15.311
3g
f1 (ppm)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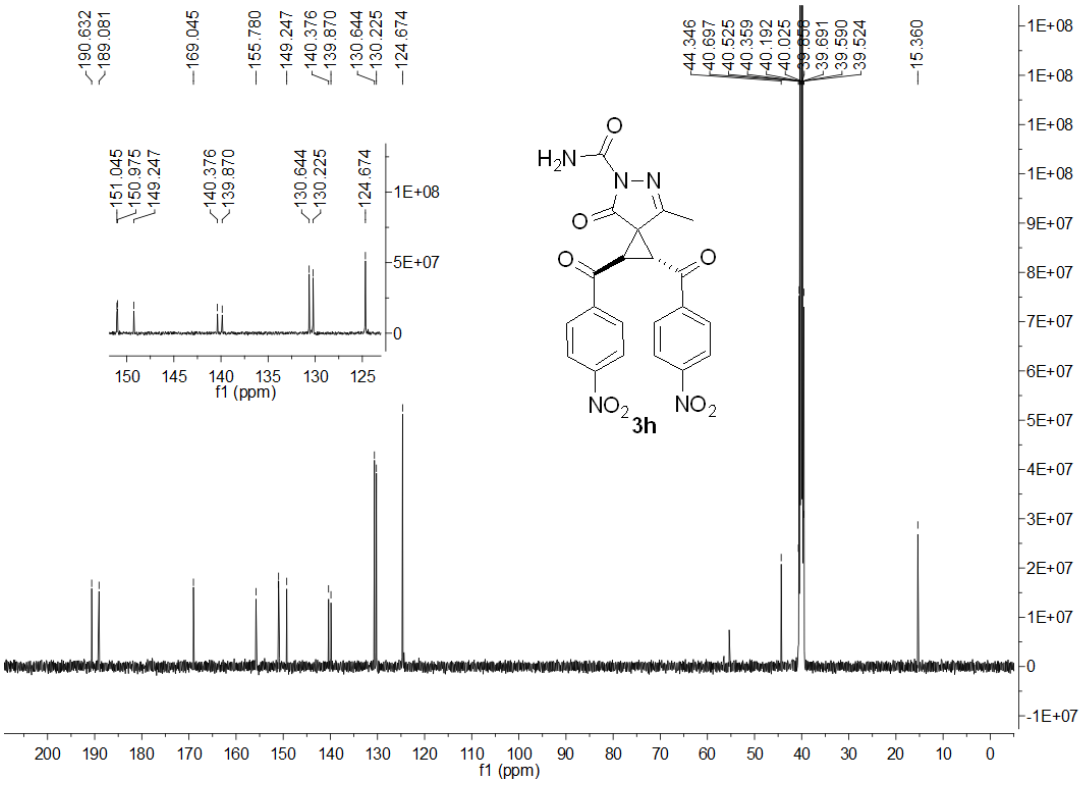
8.253
8.236
8.087
8.069
7.521
7.056
4.953
4.936
4.353
4.336
3.319
2.500
2.005
f1 (ppm)
3h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139.870
130.644
130.225
124.674
44.346
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40.192
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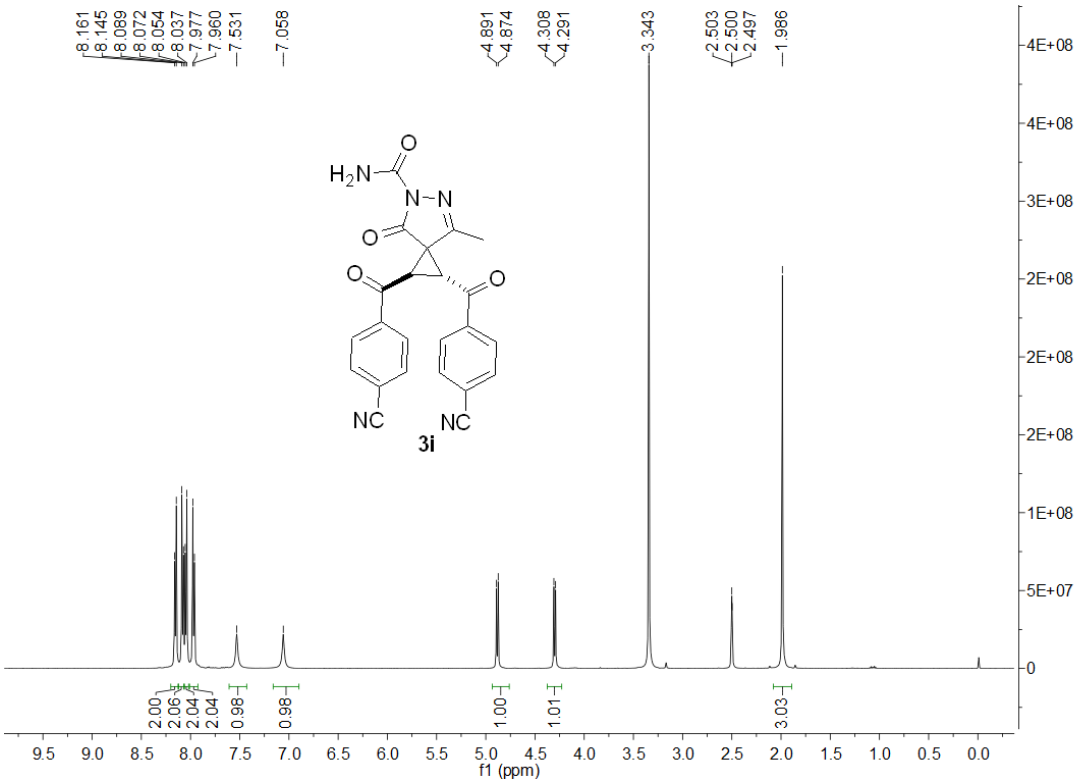
39.524
15.360
f1 (ppm)
3h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7.531
7.058
4.891
4.874
4.308
4.291
3.343
2.503
2.500
2.497
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3i
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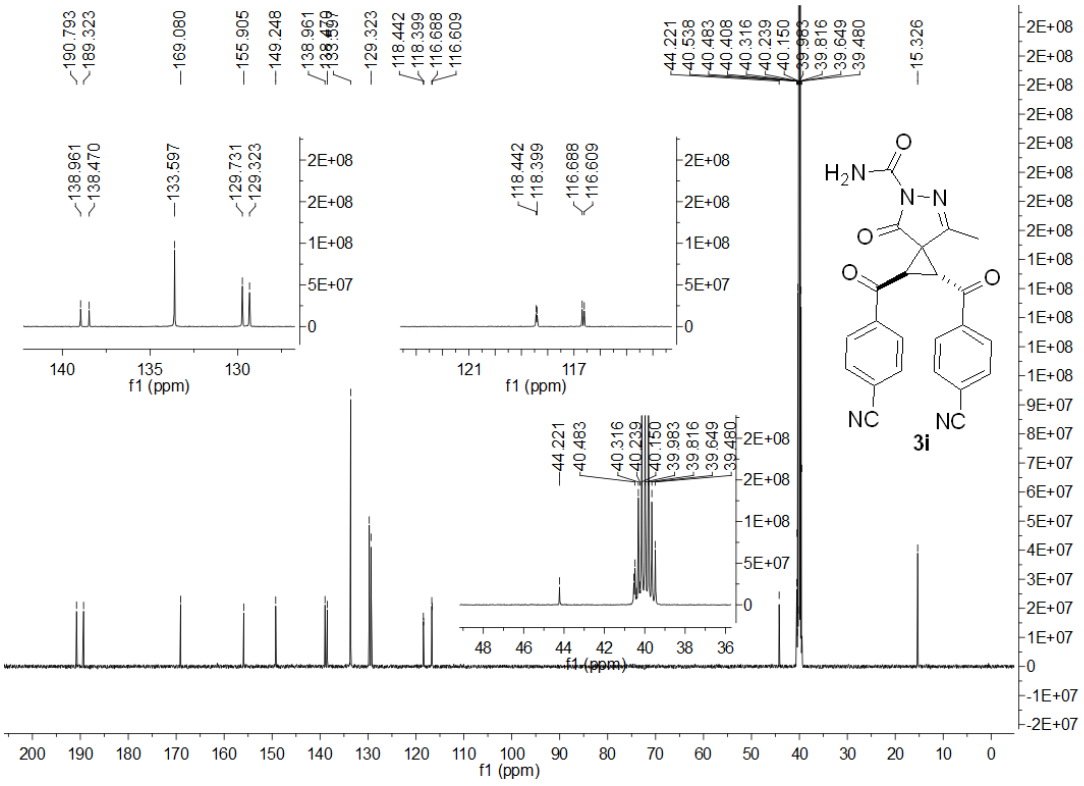
2.06
2.04
2.04
0.98
0.98
1.00
1.01
3.03
f1 (ppm)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40.408
40.316
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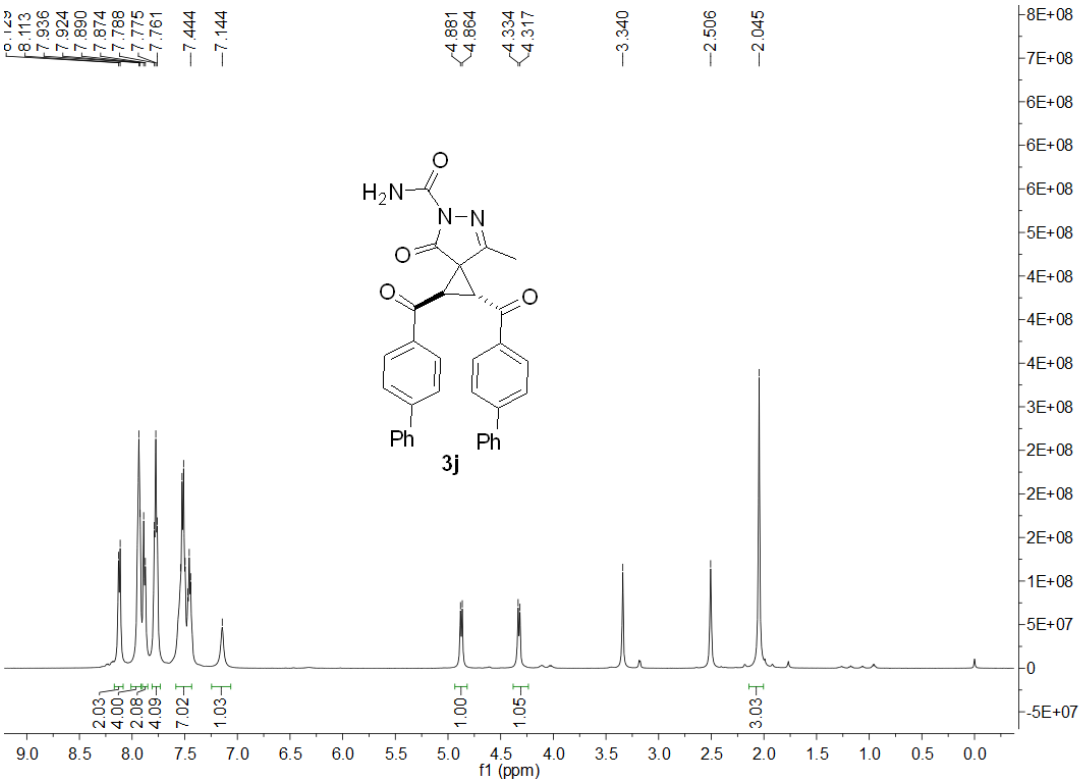
129.731
129.323
3i
f1 (ppm)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4.864
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4.317
3.340
2.506
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2.08
4.09
7.02
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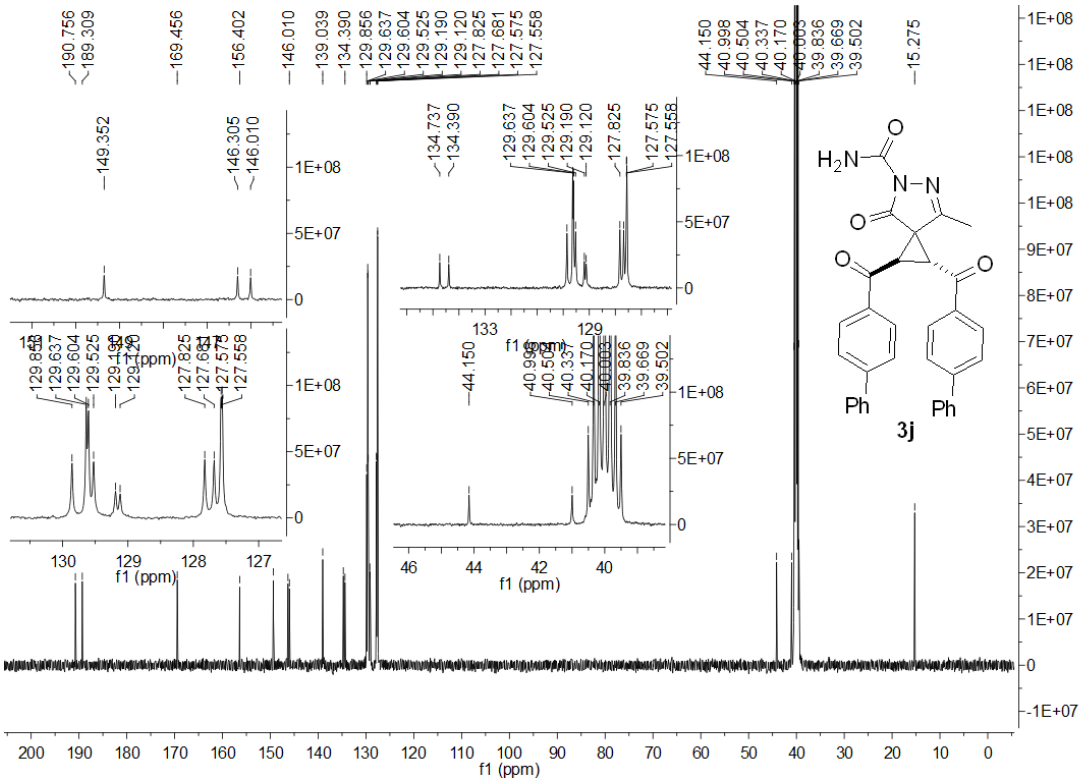
1.00
1.05
3.03
f1 (ppm)
3j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127.825
127.681
127.575
127.558
44.150
40.998
40.504
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39.836
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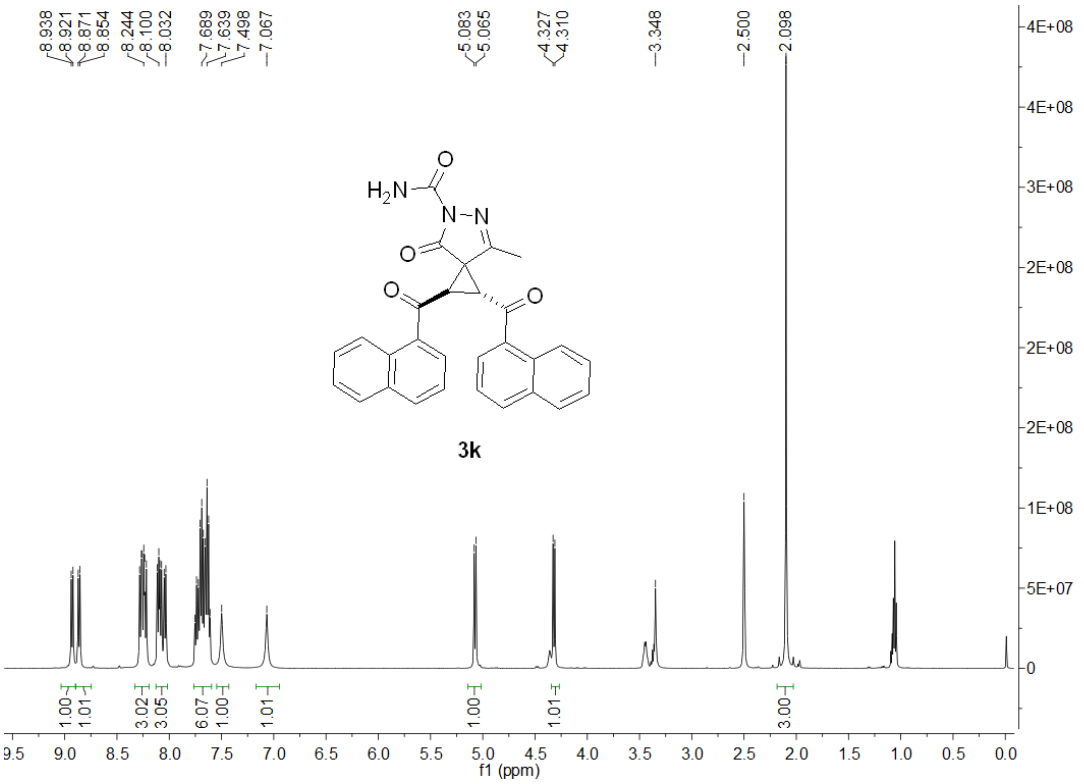
146.010
f1 (ppm)
3j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7.067
5.083
5.065
4.327
4.310
3.348
2.500
2.098
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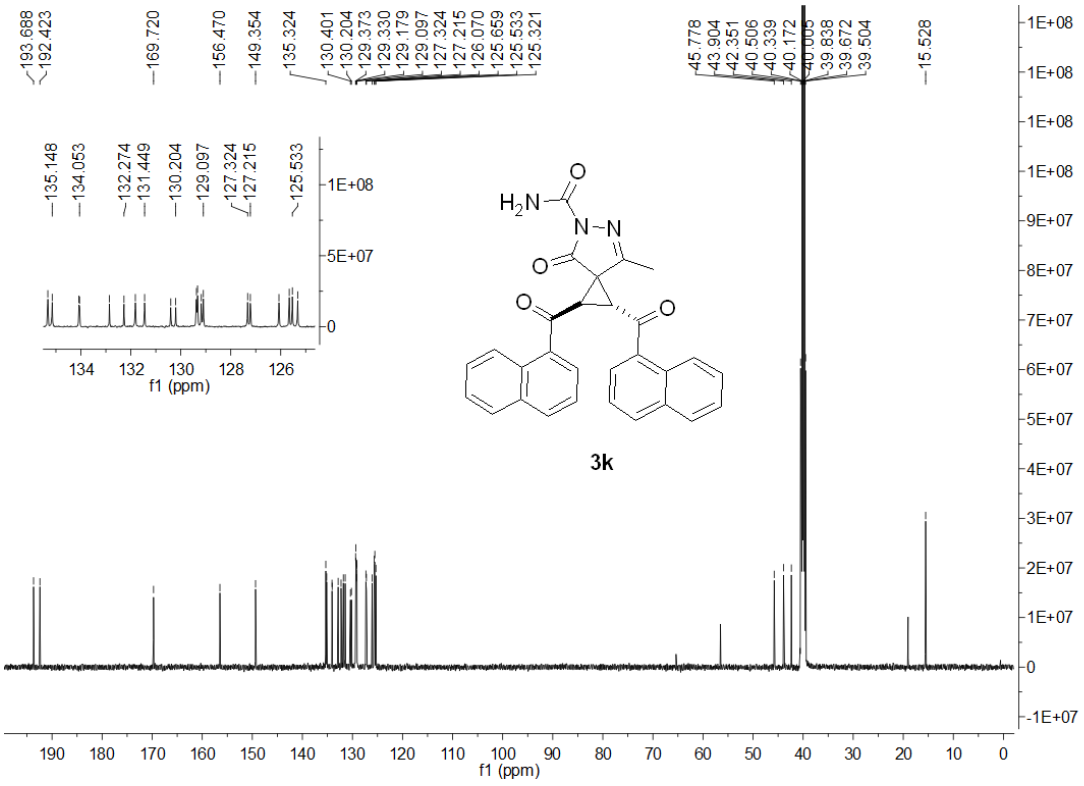
1.00
1.01
3.00
f1 (ppm)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127.215
126.070
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125.533
125.321
45.778
43.904
42.351
40.506
40.339
40.172
39.838
39.672
39.504
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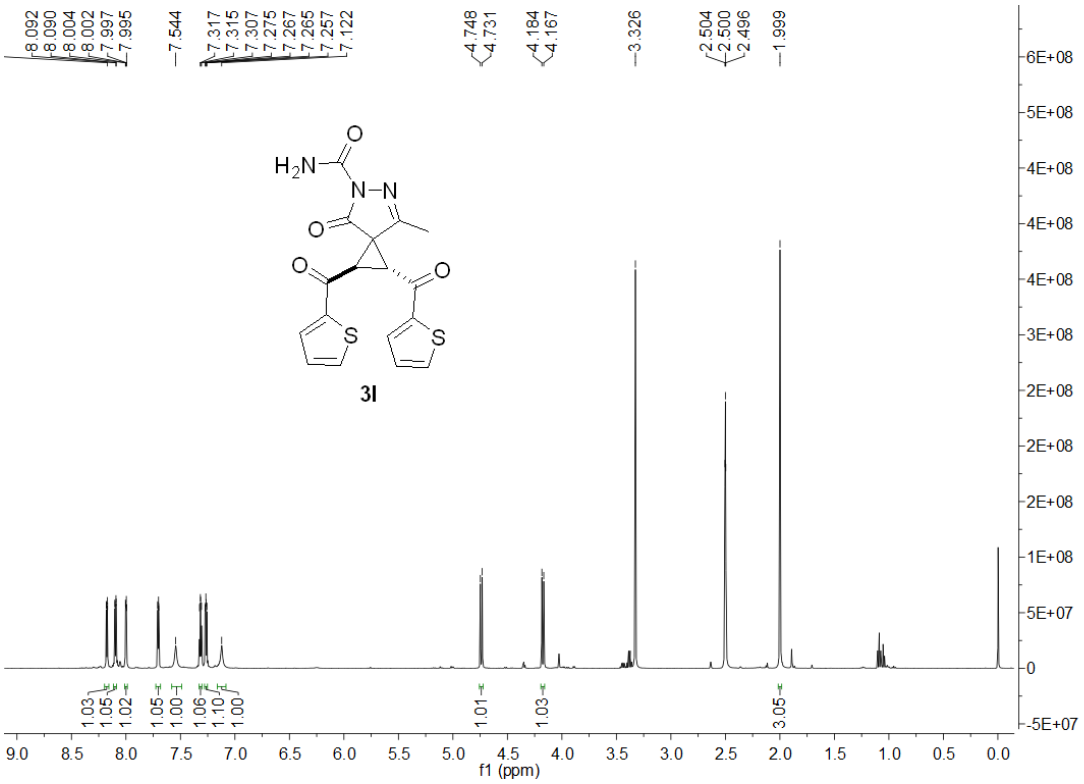
3k
f1 (ppm)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7.257
7.122
4.748
4.731
4.184
4.167
3.326
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2.500
2.496
1.999
3I
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1.01
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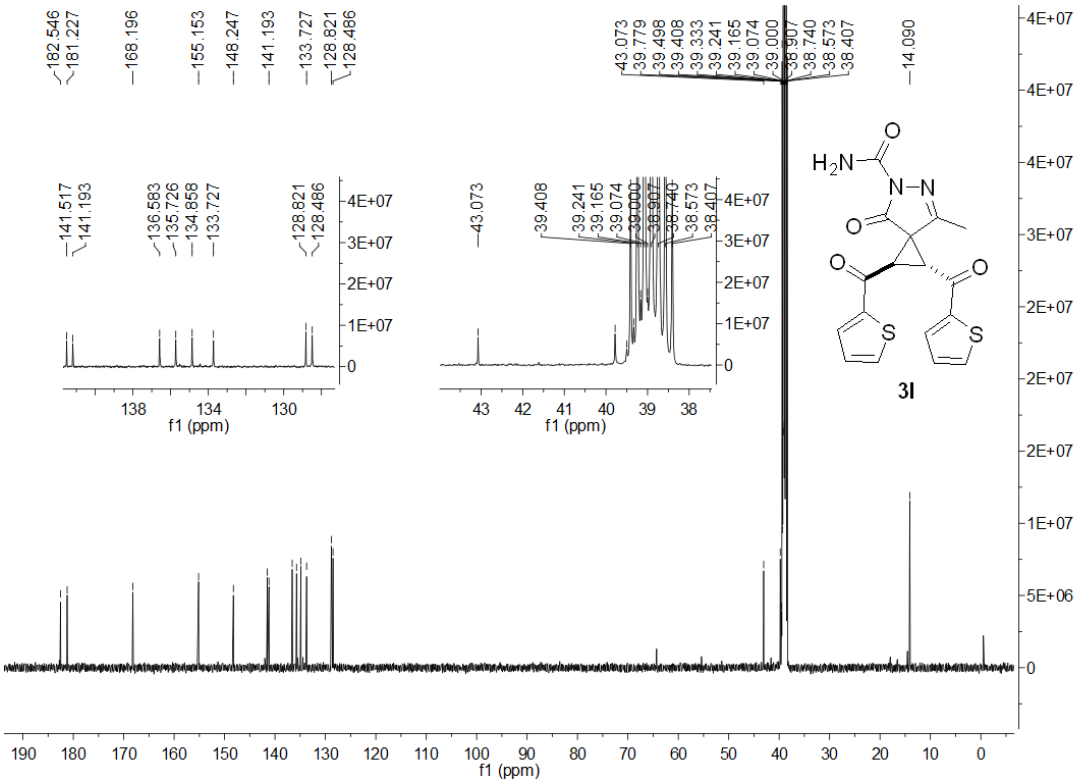
3.05
f1 (ppm)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39.779
39.498
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39.333
39.241
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39.074
39.000
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38.740
38.573
38.407
14.090
141.517
141.193
136.583
135.726
134.858
133.727
128.821
128.486
43.073
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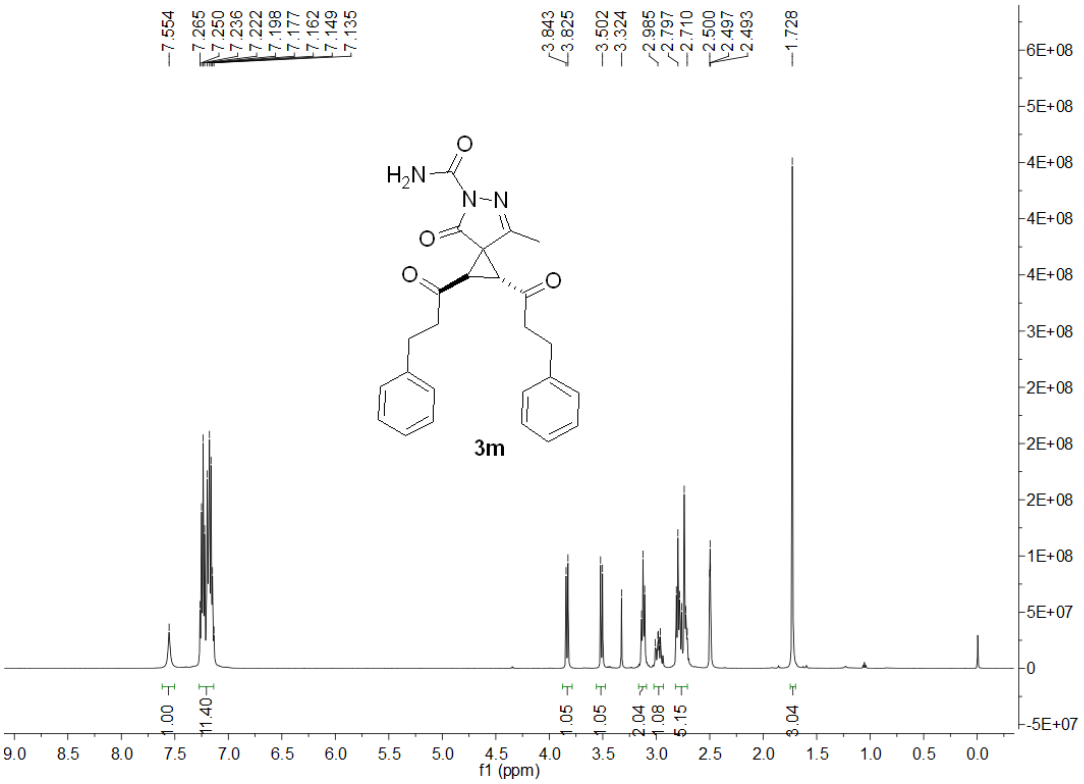
38.407
3I
f1 (ppm)
f1 (ppm)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3.324
2.985
2.797
2.710
2.500
2.497
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3m
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1.05
2.04
1.08
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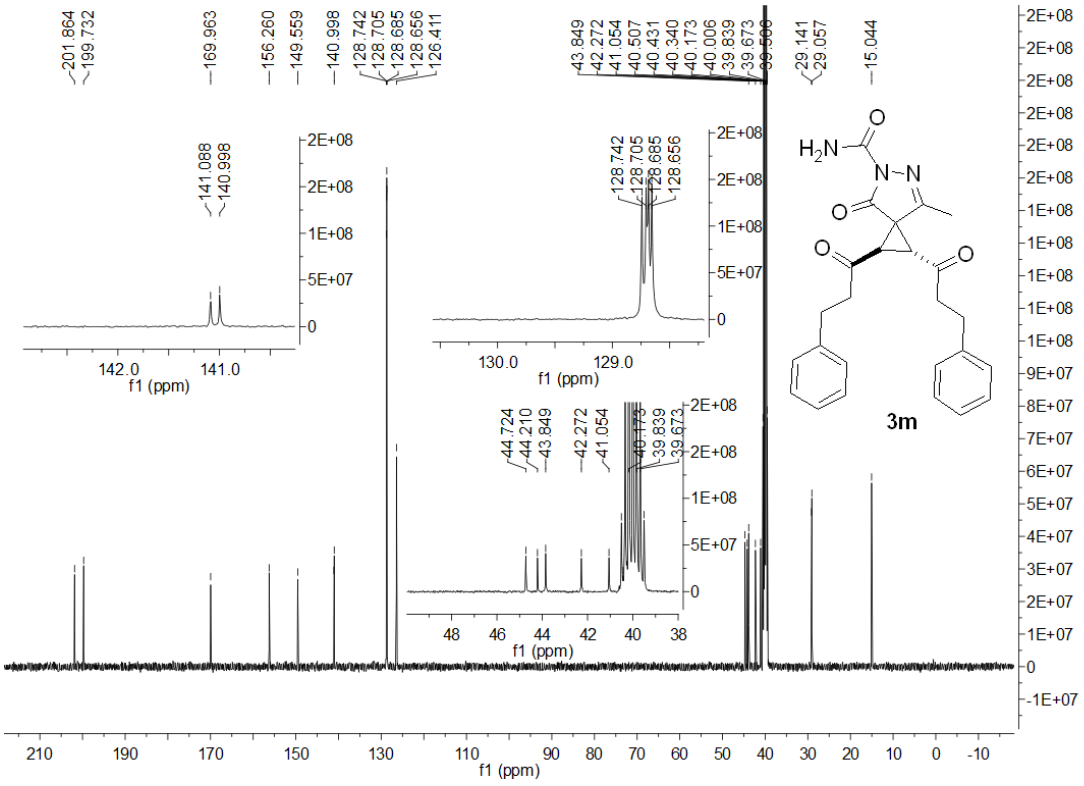
3.04
f1 (ppm)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42.272
41.054
40.507
40.431
40.340
40.173
40.006
39.839
39.673
39.506
29.141
29.057
15.044
141.088
140.998
128.742
128.705
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44.724
44.210
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42.272
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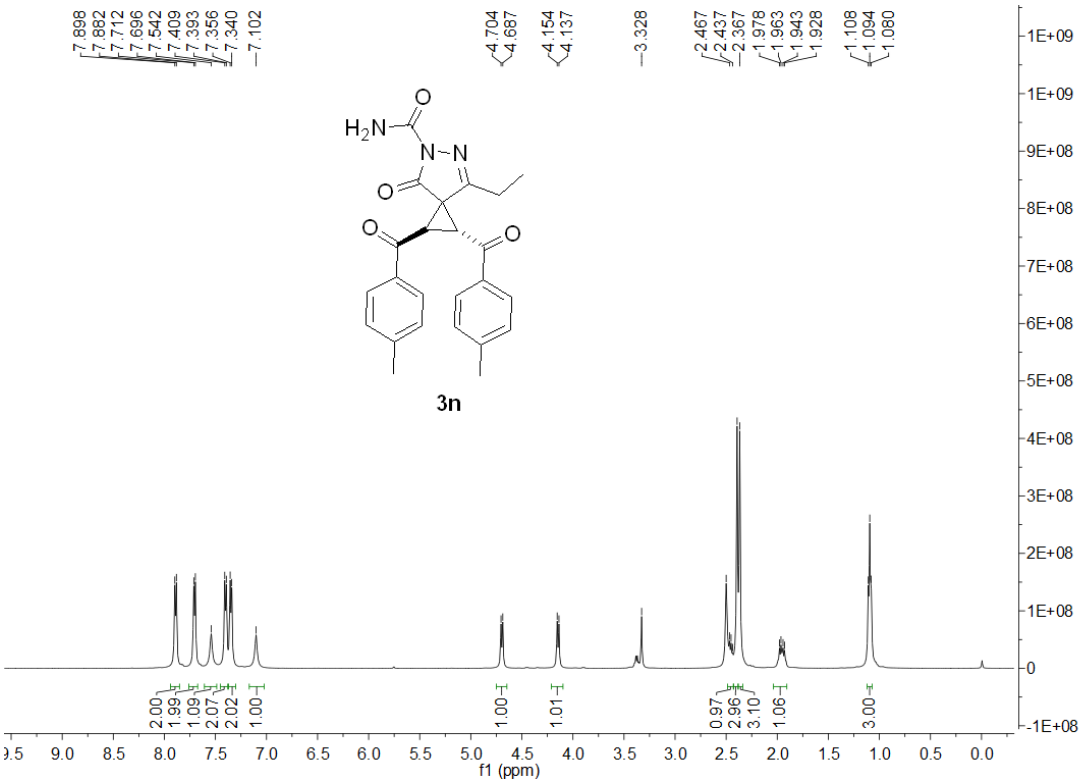
39.839
39.673
3m
f1 (ppm)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7.356
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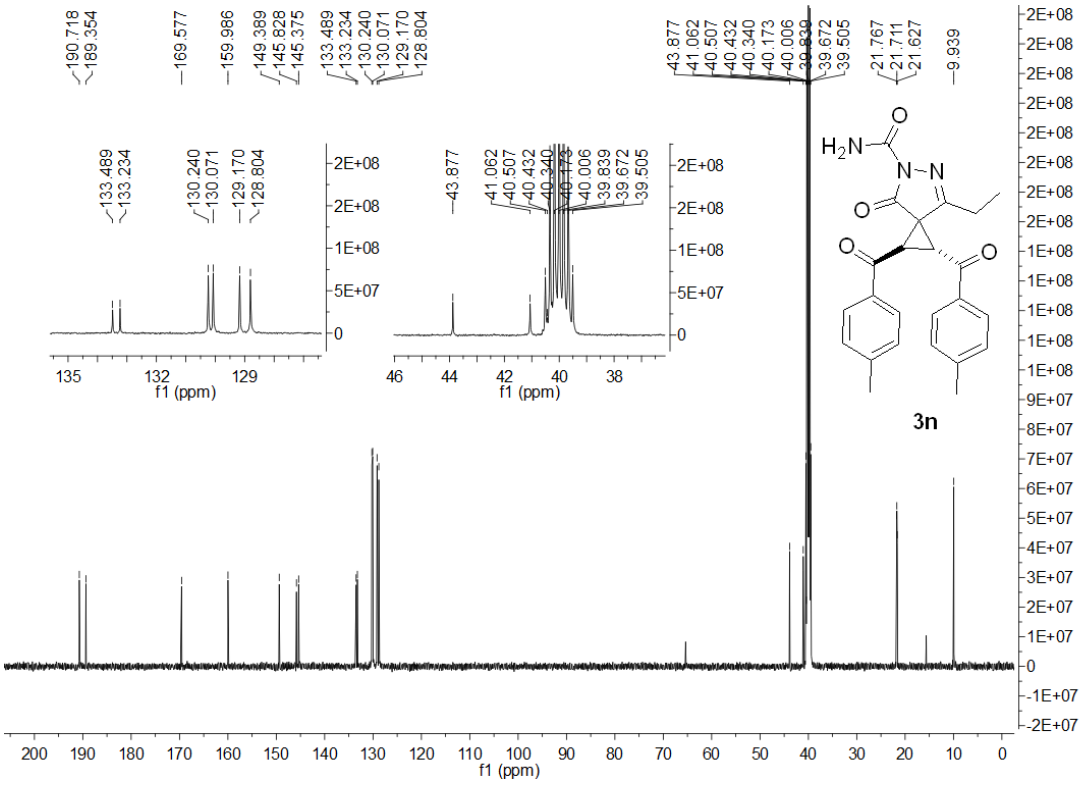
4.154
4.137
3.328
2.467
2.437
2.367
1.978
1.963
1.943
1.928
1.108
1.094
1.080
3n
f1 (ppm)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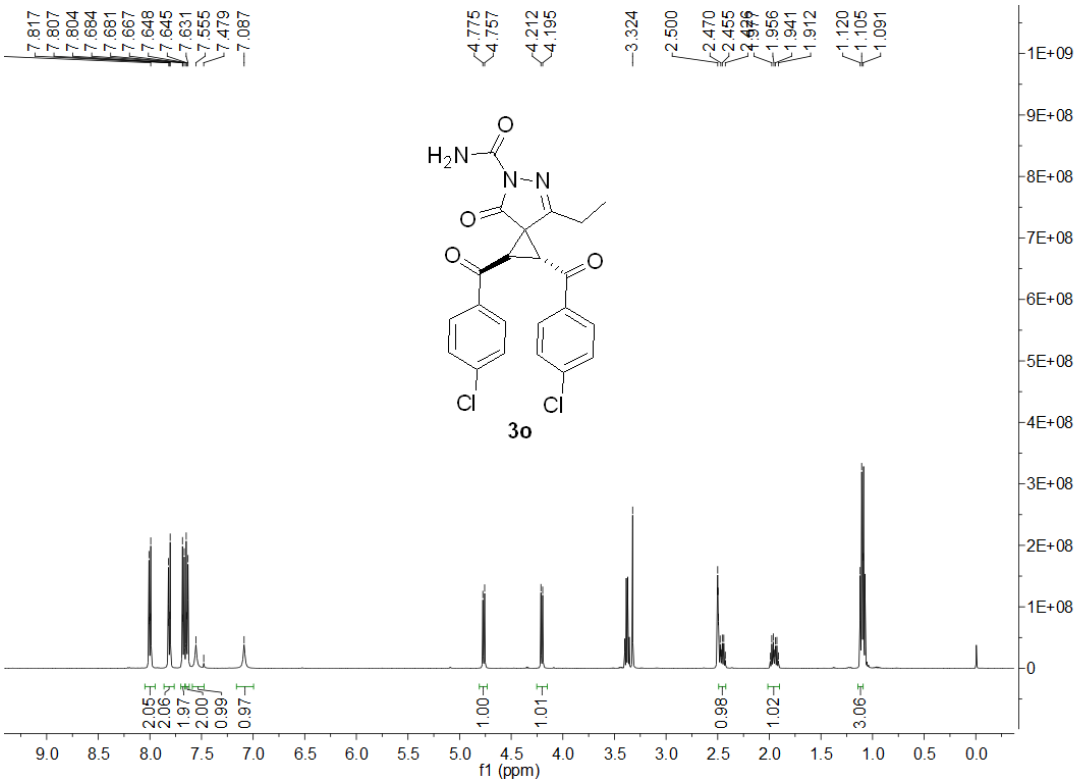
169.577
159.986
149.389
145.828
145.375
133.489
133.234
130.240
130.071
129.170
128.804
43.877
41.062
40.507
40.432
40.340
40.173
40.006
39.839
39.672
39.505
21.767
21.711
21.627
9.939
3n
f1 (ppm)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7.804
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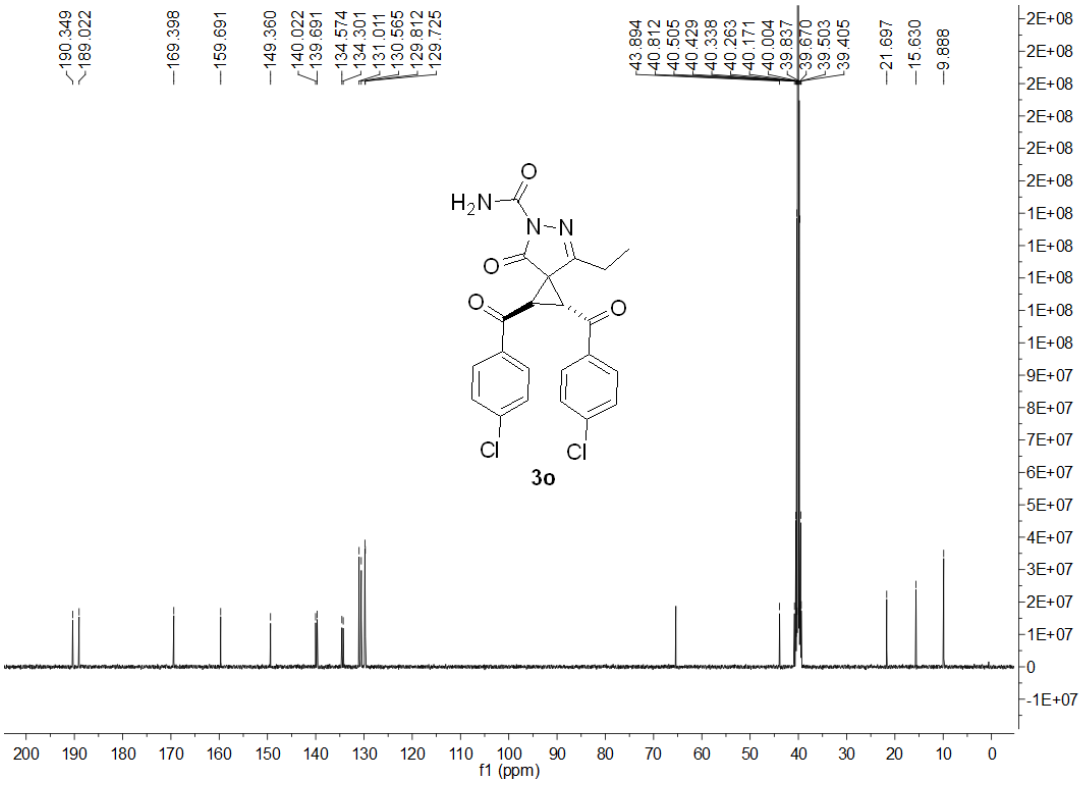
7.667
7.648
7.645
7.631
7.555
7.479
7.087
4.775
4.757
4.212
4.195
3.324
2.500
2.470
2.455
1.956
1.941
1.912
1.120
1.105
1.091
3o
2.05
2.06
1.97
2.00
0.99
0.97
1.00
1.01
0.98
1.02
3.06
f1 (ppm)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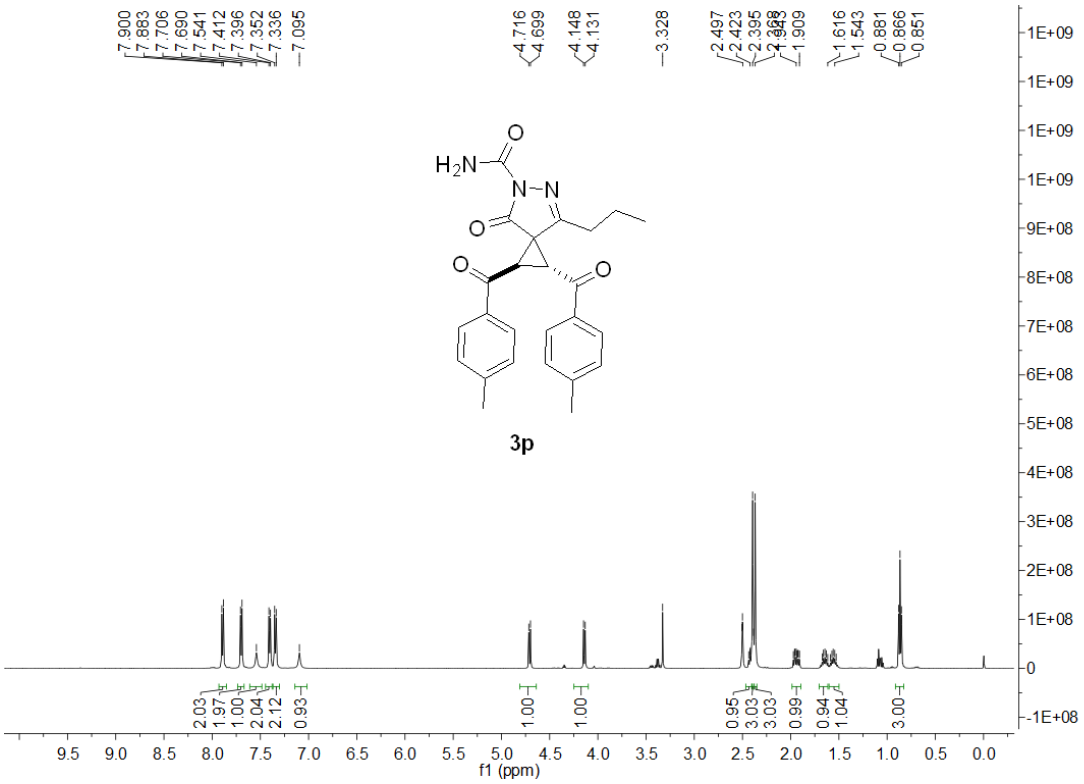
189.022
169.398
159.691
149.360
140.022
139.691
134.574
134.301
131.011
130.565
129.812
129.725
43.894
40.812
40.505
40.429
40.338
40.263
40.171
40.004
39.837
39.670
39.503
39.405
21.697
15.630
9.888
3o
f1 (ppm)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7.706
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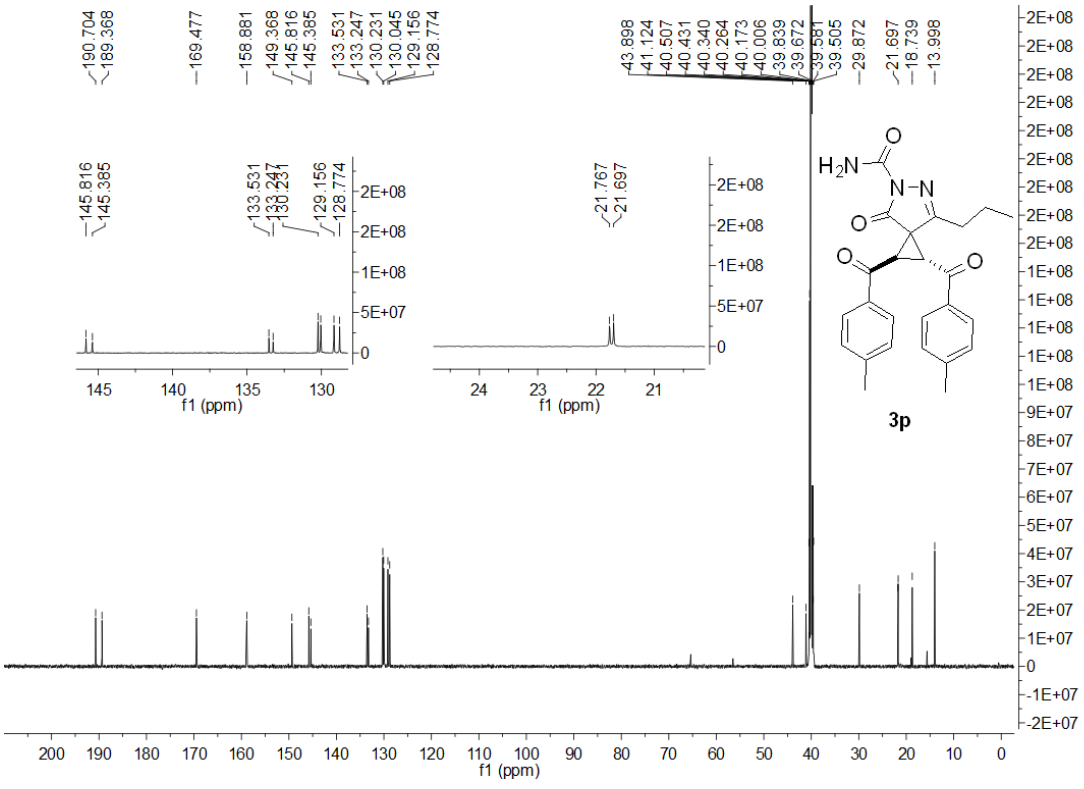
7.541
7.412
7.396
7.352
7.336
7.095
4.716
4.699
4.148
4.131
3.328
2.497
2.423
2.395
1.909
1.616
1.543
0.881
0.866
0.851
3p
f1 (ppm)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169.477
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149.368
145.816
145.385
133.531
133.247
130.231
130.045
129.156
128.774
43.898
41.124
40.507
40.431
40.340
40.264
40.173
40.006
39.839
39.672
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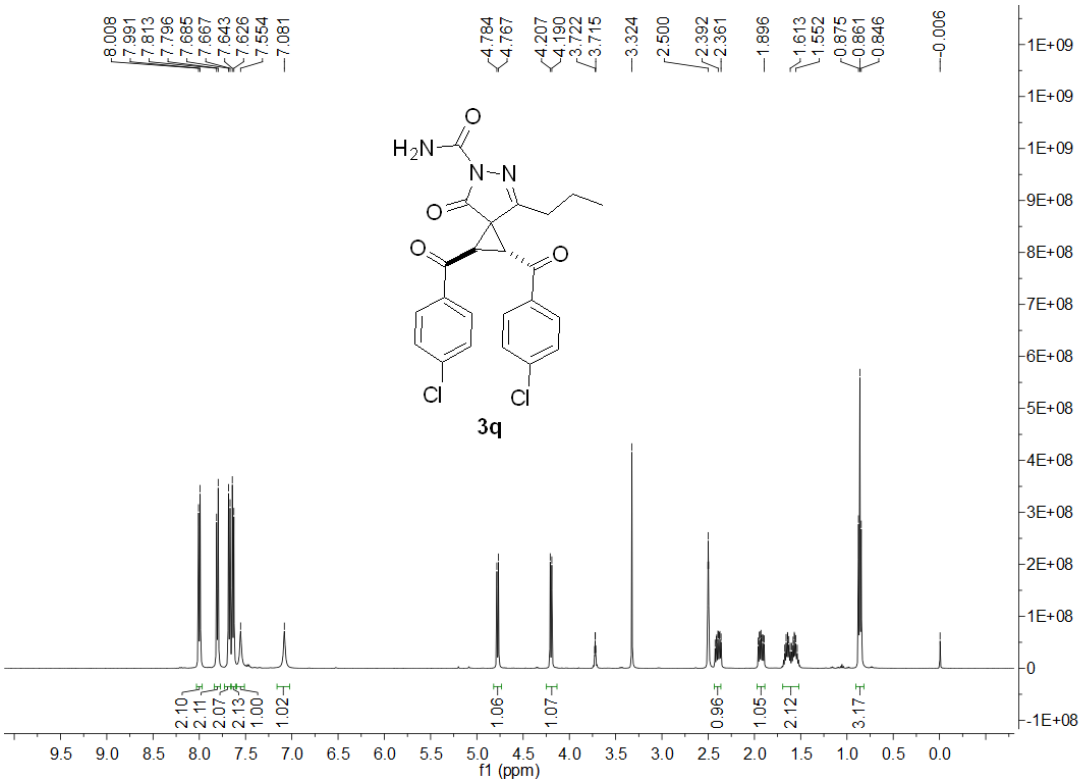
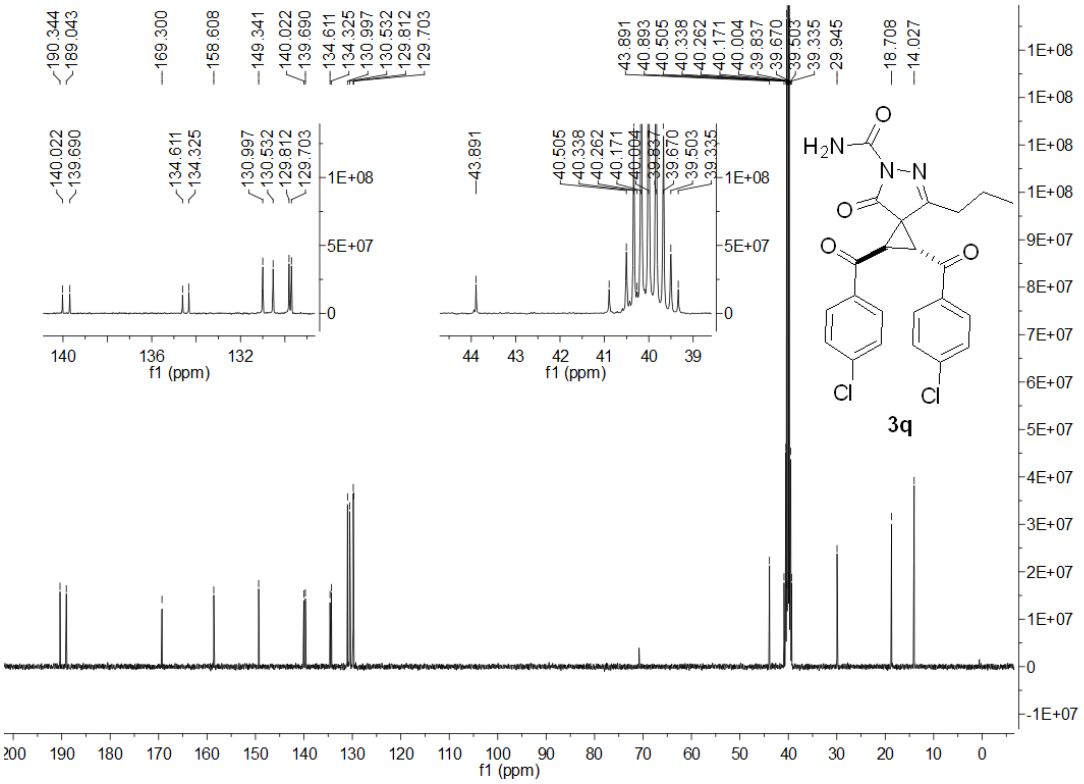
39.505
29.872
21.697
18.739
13.998
21.767
21.697
3p
f1 (ppm)


8.008
7.991
7.813
7.796
7.685
7.667
7.643
7.626
7.554
7.081
4.784
4.767
4.207
4.190
3.722
3.715
3.324
2.500
2.392
2.361
1.896
1.613
1.552
0.875
0.861
0.846
0.006
3q
f1 (ppm)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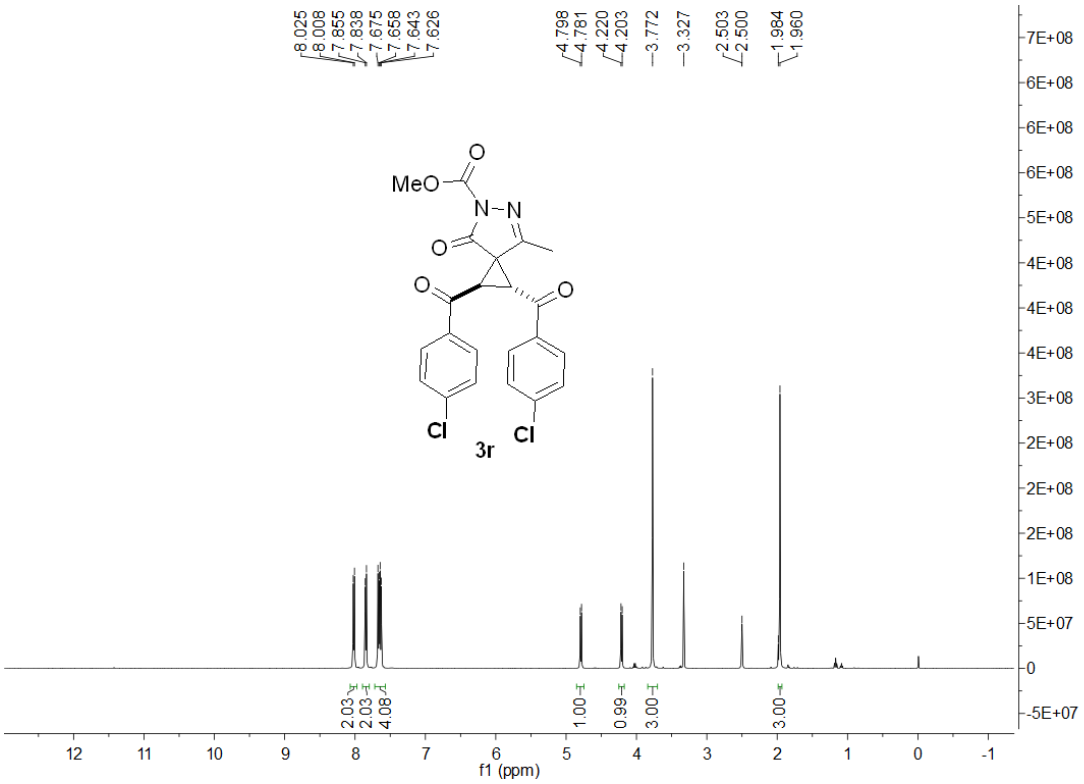
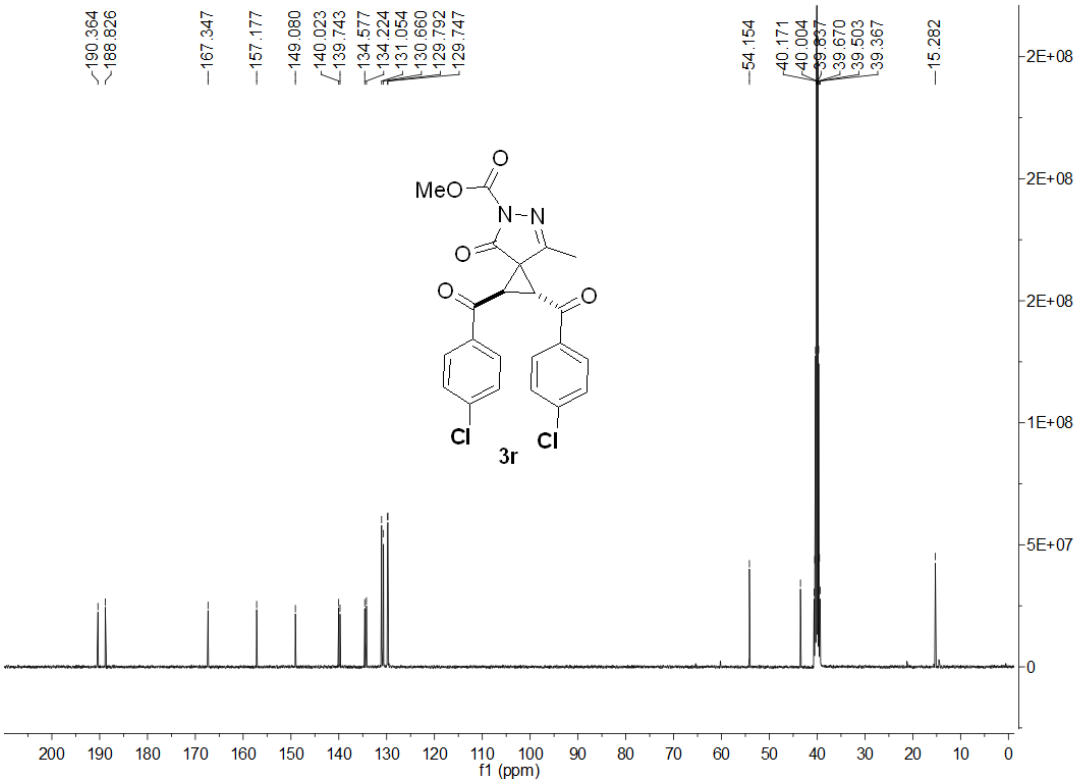
169.300
158.608
149.341
140.022
139.690
134.611
134.325
130.997
130.532
129.812
129.703
43.891
40.893
40.505
40.338
40.262
40.171
40.004
39.837
39.670
39.503
39.335
29.945
18.708
14.027
3q
f1 (ppm)


8.025
8.008
7.855
7.838
7.675
7.658
7.643
7.626
4.798
4.781
4.220
4.203
3.772
3.327
2.503
2.500
1.984
1.960
MeO
N-N
O
Cl
Cl
3r
2.03
2.03
4.08
1.00
0.99
3.00
3.00
f1 (ppm)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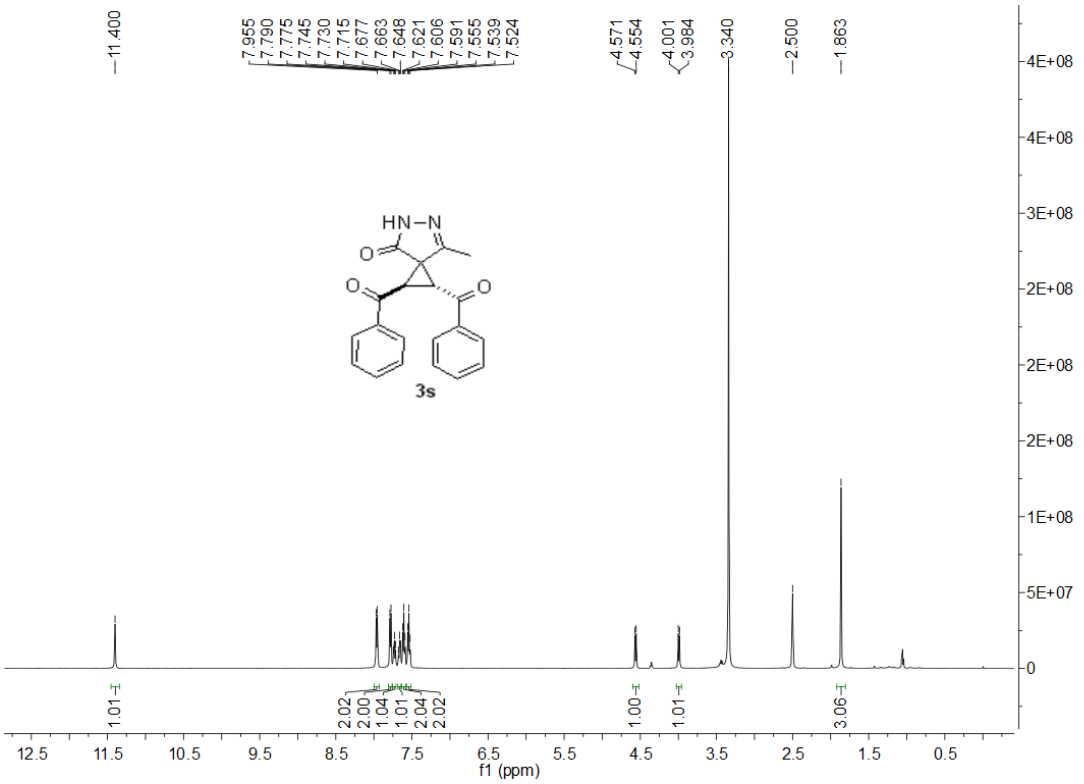
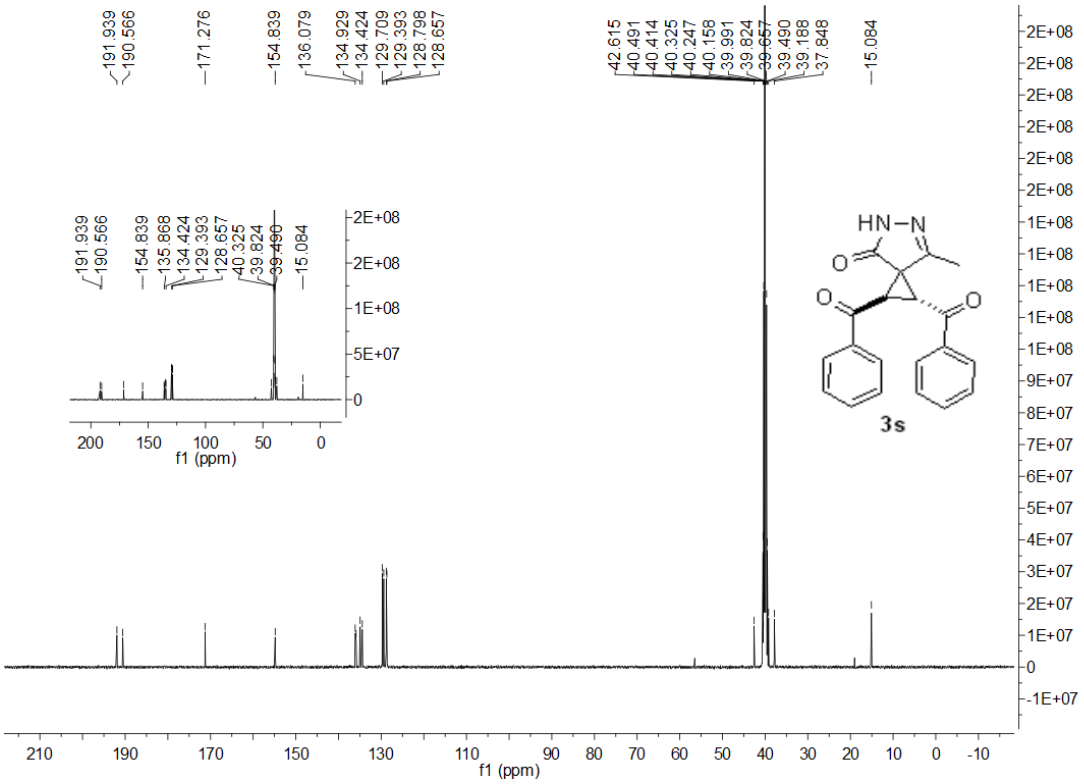
149.080
140.023
139.743
134.577
134.224
131.054
130.660
129.792
129.747
54.154
40.171
40.004
39.837
39.670
39.503
39.367
15.282
MeO
N-N
O
Cl
Cl
3r
f1 (ppm)


11.400
7.955
7.790
7.775
7.745
7.730
7.715
7.677
7.663
7.648
7.621
7.606
7.591
7.555
7.539
7.524
4.571
4.554
4.001
3.984
3.340
2.500
1.863
HN−N
O
O
O
3s
1.01
2.02
2.00
1.04
1.01
2.04
2.02
1.00
1.01
3.06
f1 (ppm)


191.939
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154.839
136.079
134.929
134.424
129.709
129.393
128.798
128.657
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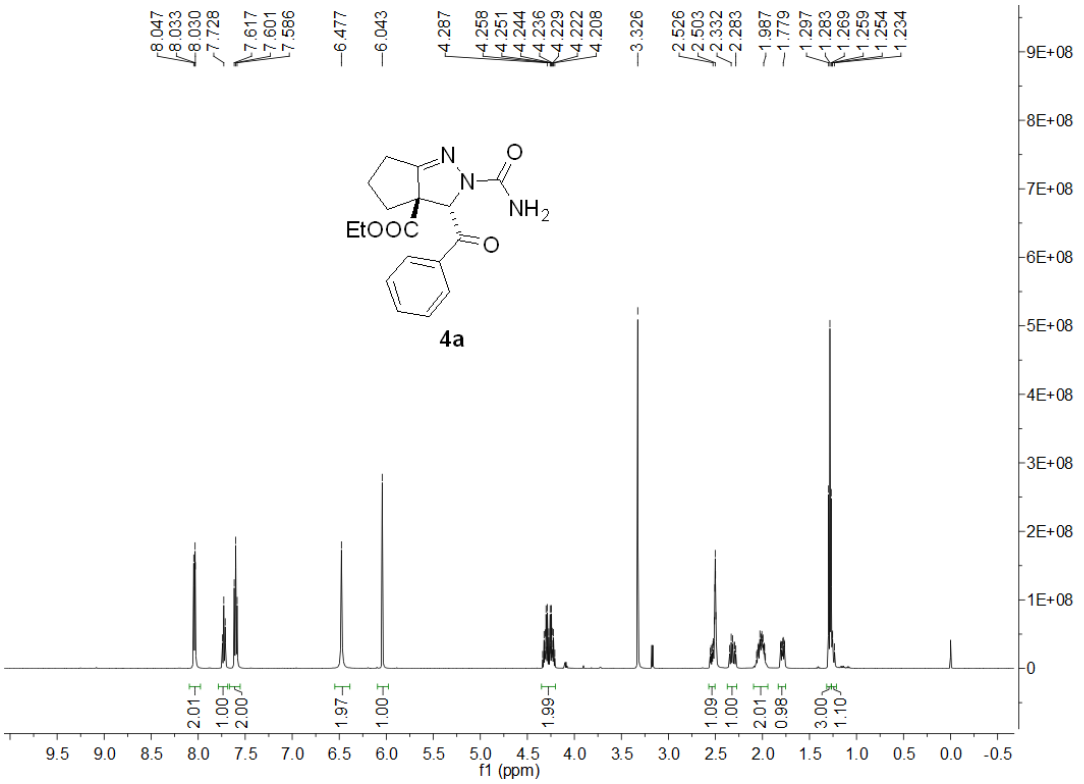
40.491
40.414
40.325
40.247
40.158
39.991
39.824
39.657
39.490
39.188
37.848
15.084
HN−N
O
O
O
3s
f1 (ppm)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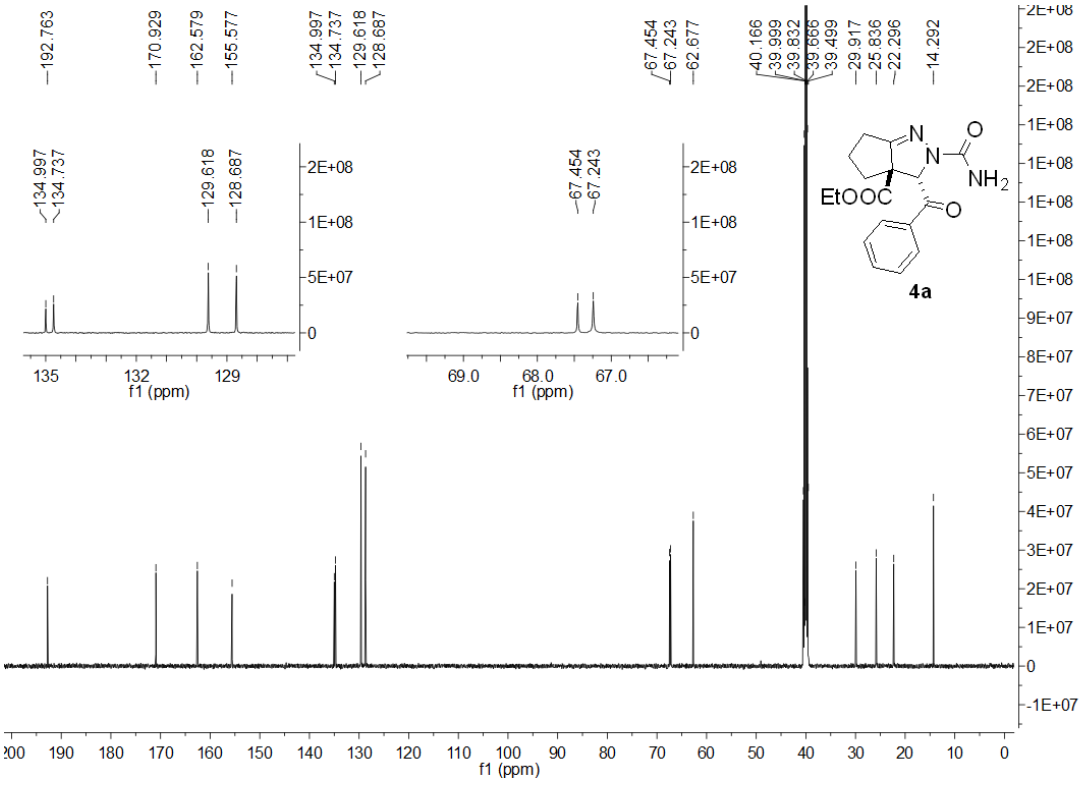
8.030
7.728
7.617
7.601
7.586
6.477
6.043
4.287
4.258
4.251
4.244
4.236
4.229
4.222
4.208
3.326
2.526
2.503
2.332
2.283
1.987
1.779
1.297
1.283
1.269
1.259
1.254
1.234
EtOOC
NH2
4a
f1 (ppm)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134.997
134.737
129.618
128.687
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67.243
62.677
40.166
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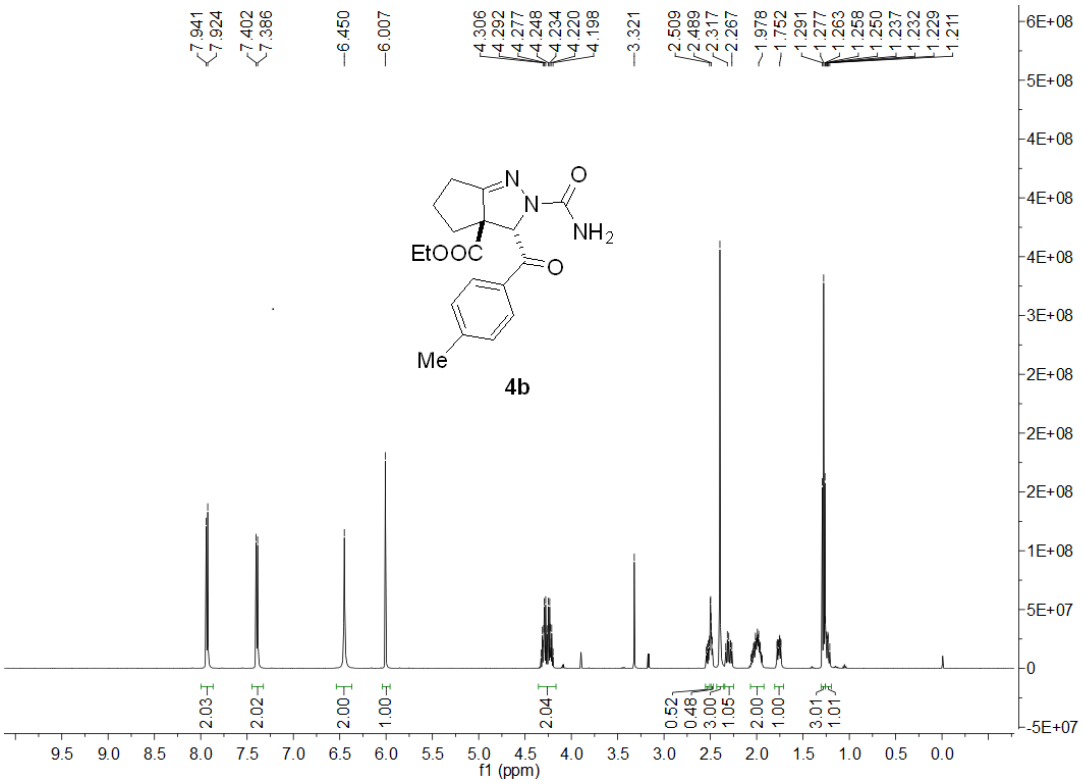
39.832
39.666
39.499
29.917
25.836
22.296
14.292
EtOOC
NH2
4a
f1 (ppm)


7.941
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7.402
7.386
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6.007
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4.292
4.277
4.248
4.234
4.220
4.198
3.321
2.509
2.489
2.317
2.267
1.978
1.752
1.291
1.277
1.263
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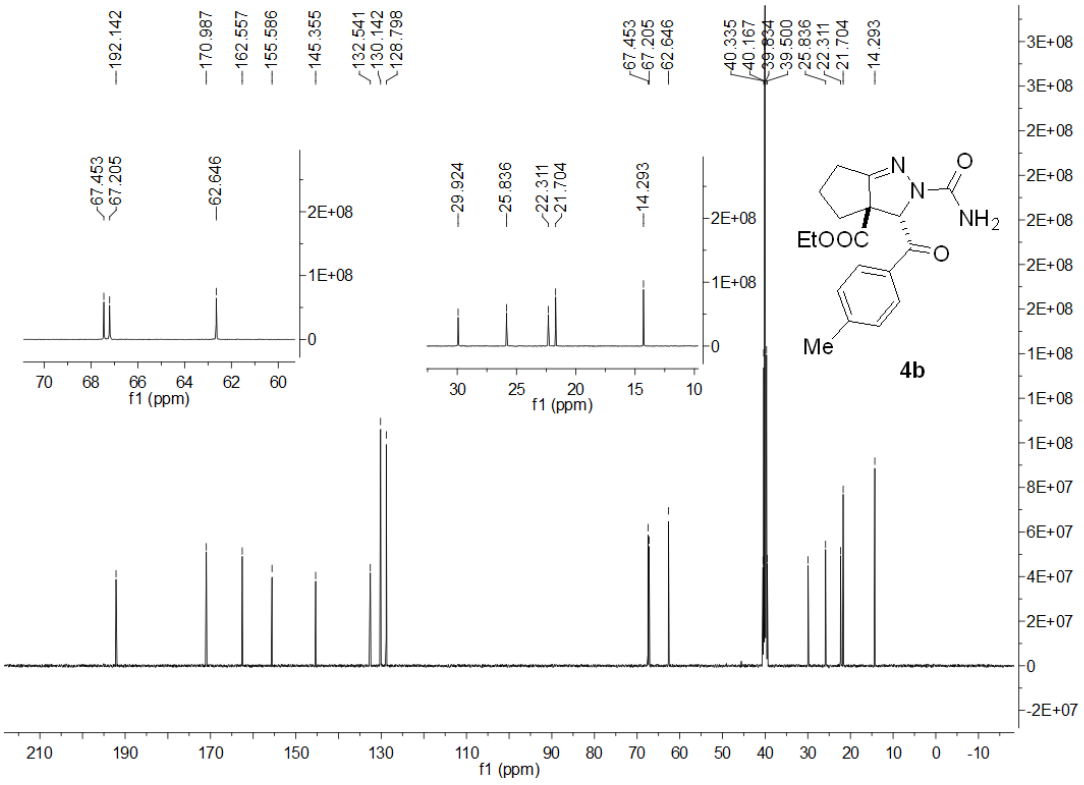
1.250
1.237
1.232
1.229
1.211
EtOOC
NH2
Me
4b
f1 (ppm)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130.142
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67.205
62.646
40.335
40.167
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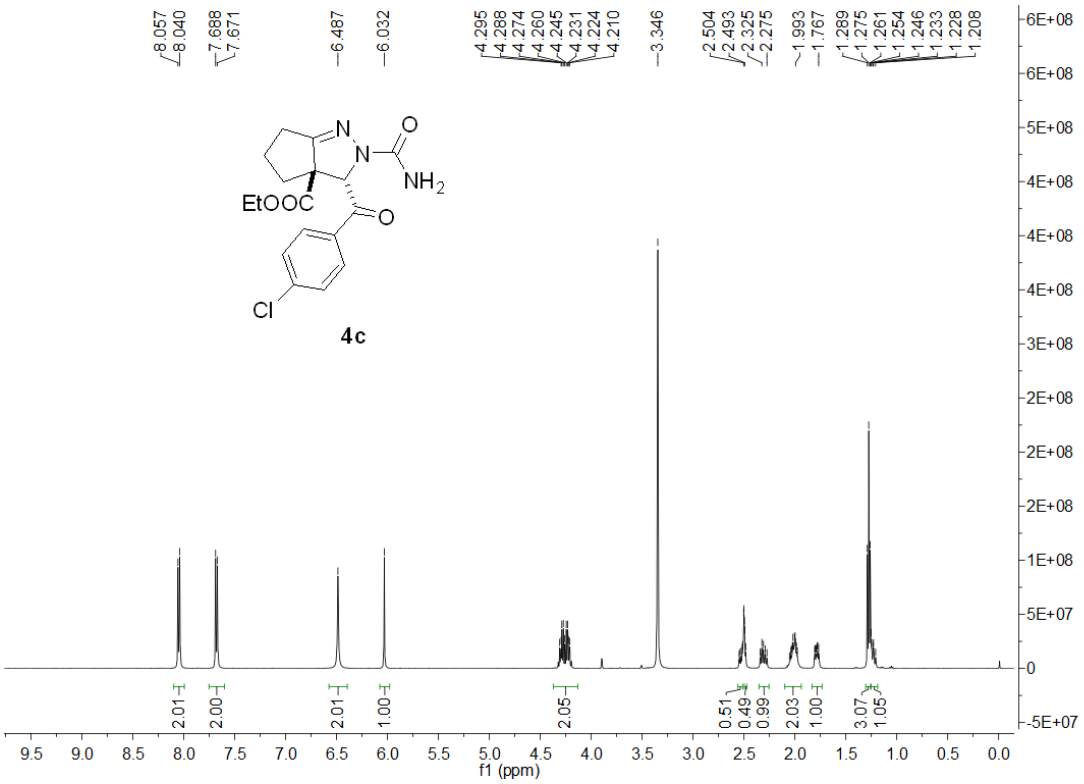
29.924
EtOOC
NH2
Me
4b
f1 (ppm)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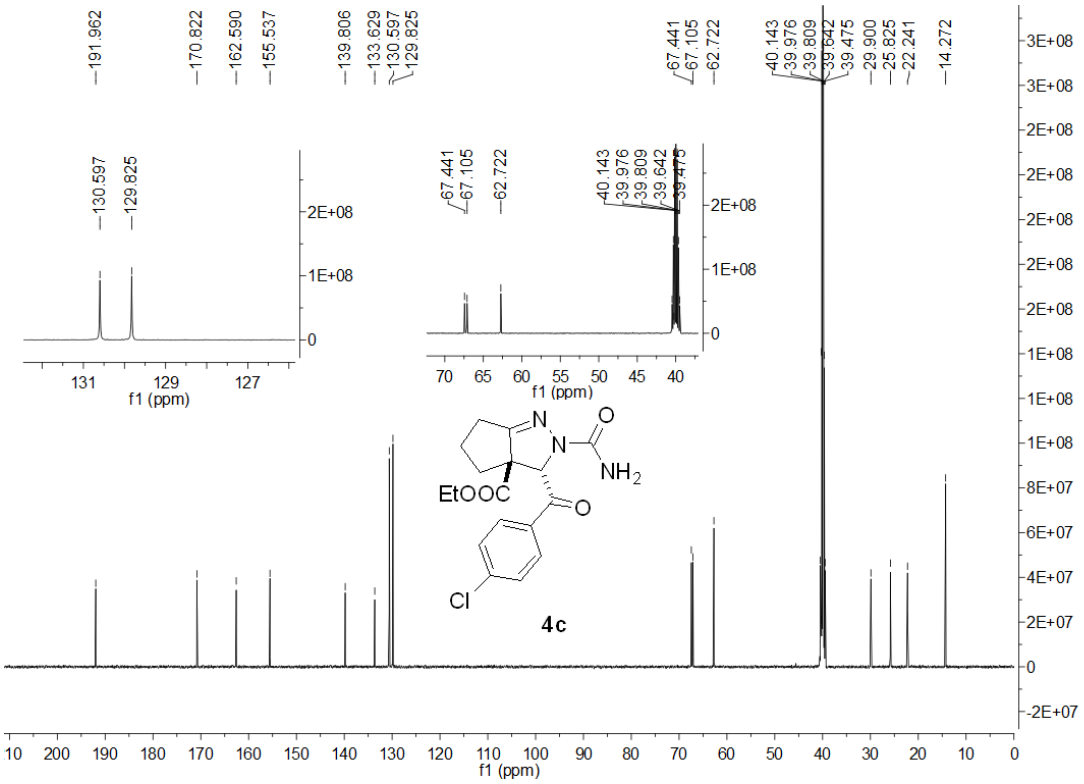
8.040
7.688
7.671
6.487
6.032
4.295
4.288
4.274
4.260
4.245
4.231
4.224
4.210
3.346
2.504
2.493
2.325
2.275
1.993
1.767
1.289
1.275
1.261
1.254
1.246
1.233
1.228
1.208
EtOOC
NH2
Cl
4c
f1 (ppm)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39.976
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EtOOC
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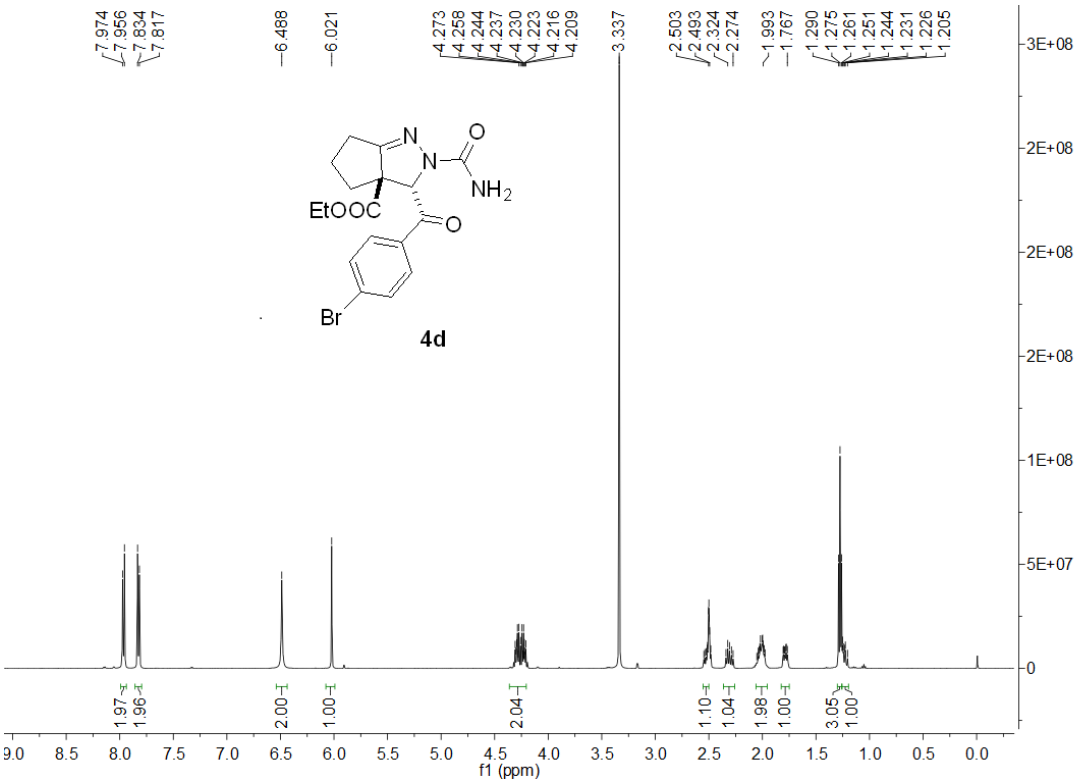
Cl
4c
f1 (ppm)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4.237
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4.223
4.216
4.209
3.337
2.503
2.493
2.324
2.274
1.993
1.767
1.290
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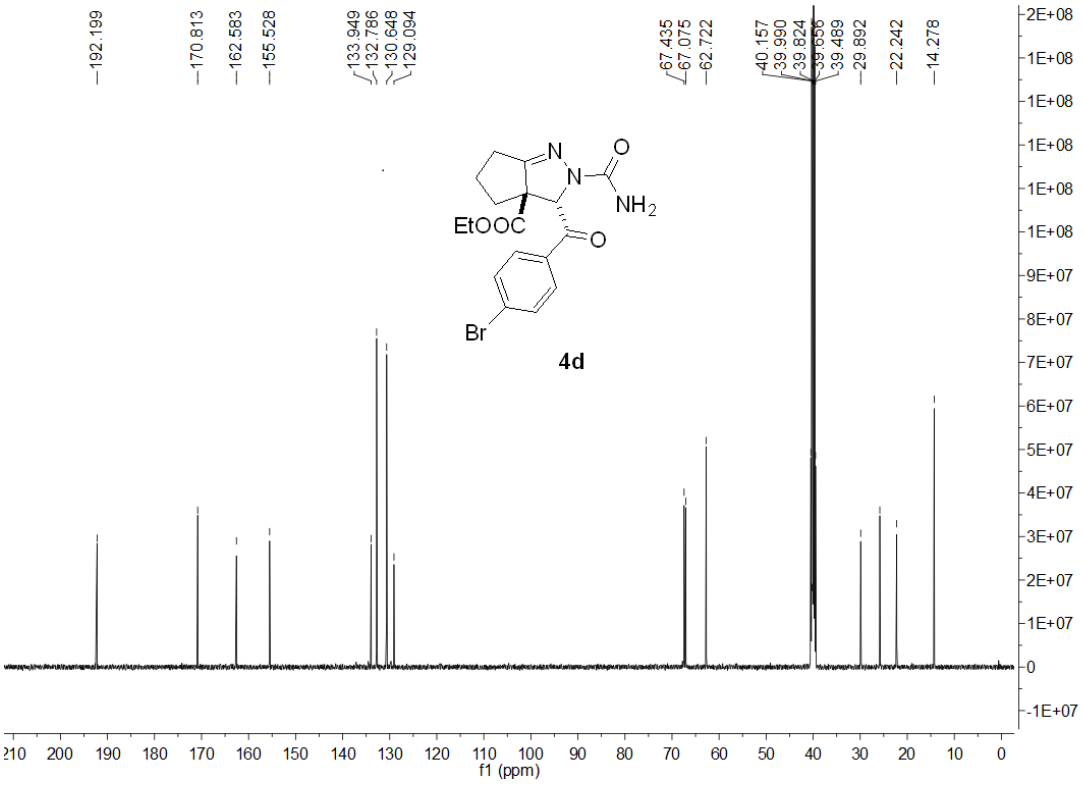
1.251
1.244
1.231
1.226
1.205
EtOOC
NH2
Br
4d
f1 (ppm)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67.075
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40.157
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29.892
22.242
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EtOOC
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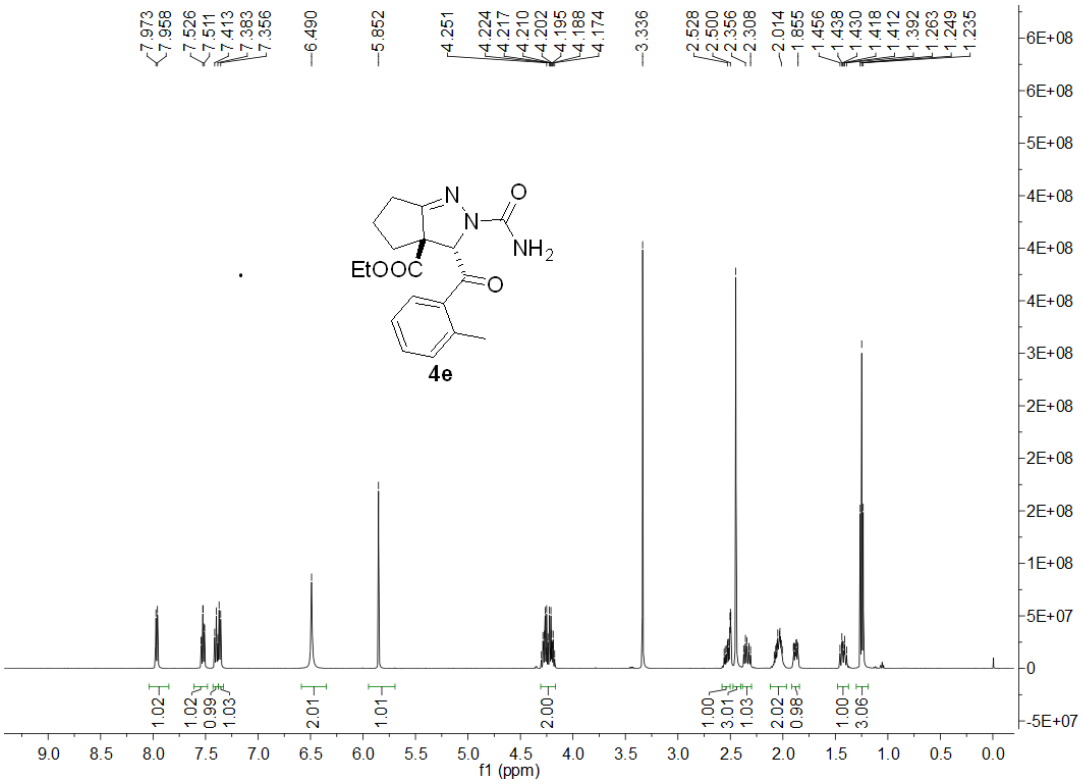
Br
4d
f1 (ppm)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4.210
4.202
4.195
4.188
4.174
3.336
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2.500
2.356
2.308
2.014
1.855
1.456
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1.412
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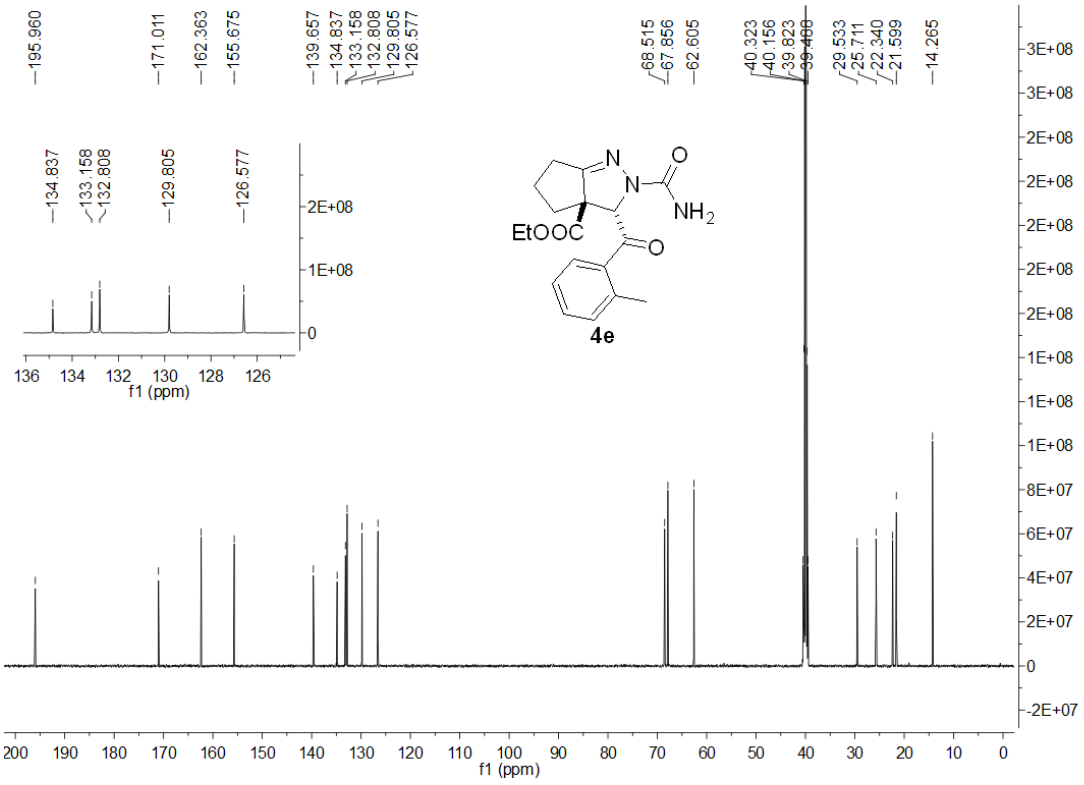
1.249
1.235
EtOOC
NH2
4e
f1 (ppm)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62.605
40.323
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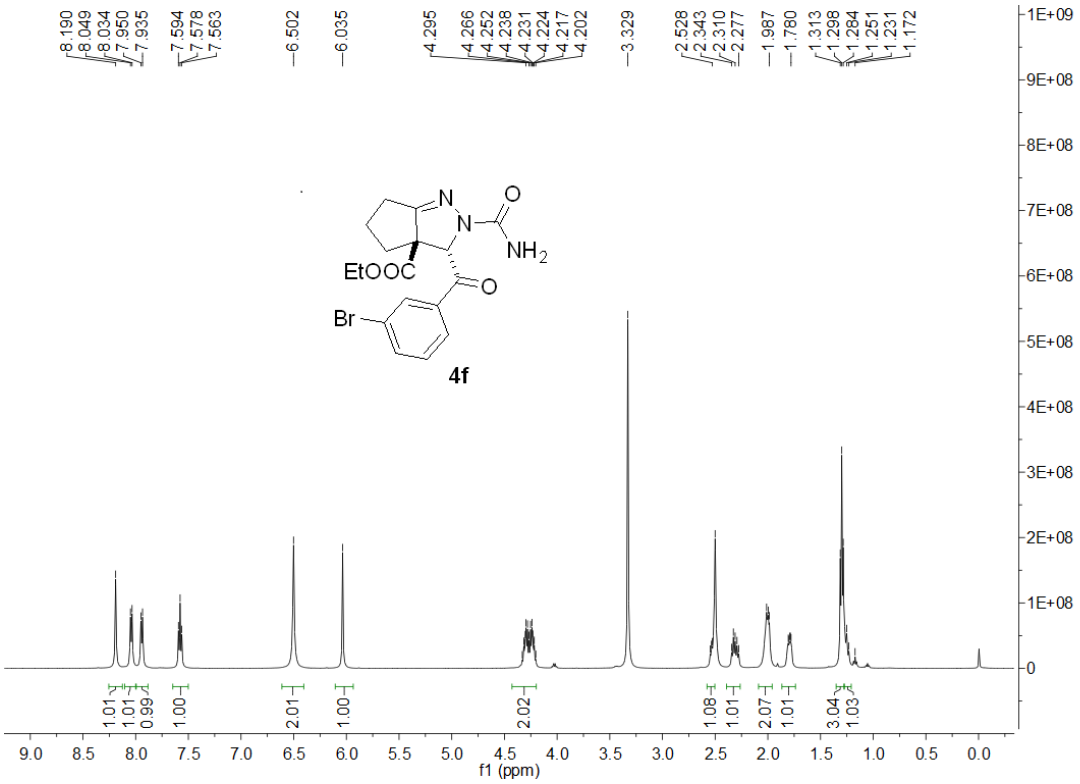
39.490
29.533
25.711
22.340
21.599
14.265
EtOOC
NH2
4e
f1 (ppm)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7.563
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4.252
4.238
4.231
4.224
4.217
4.202
3.329
2.528
2.343
2.310
2.277
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1.298
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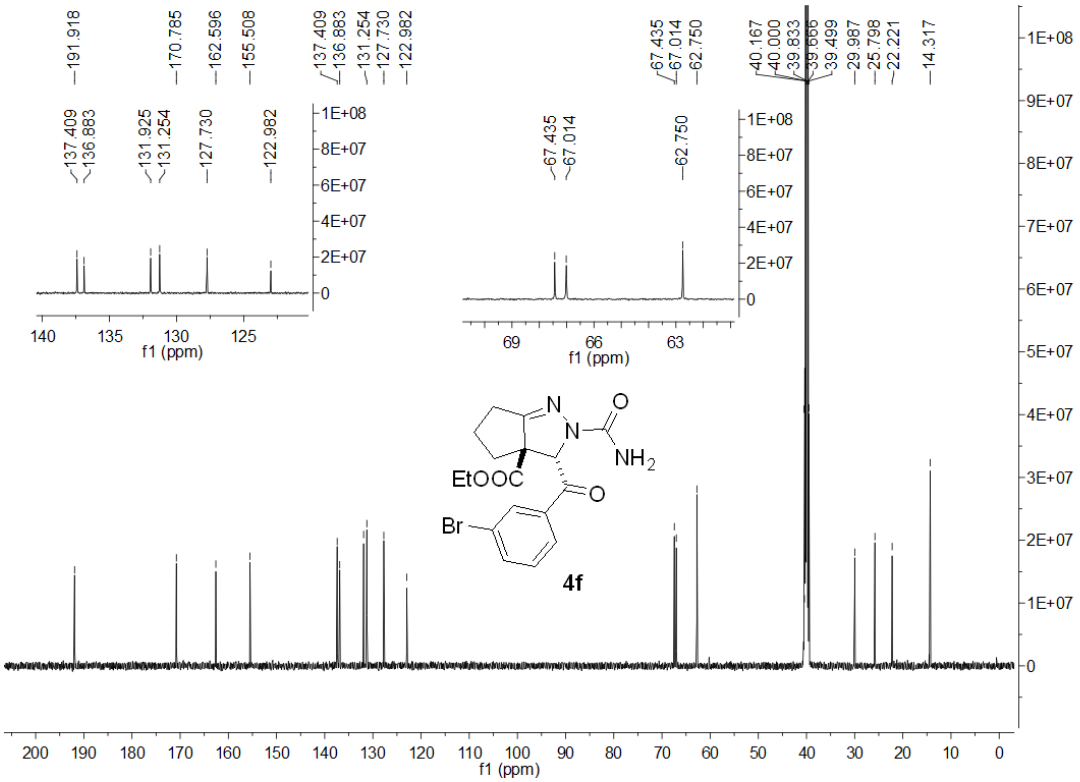
1.172
EtOOC
Br
4f
f1 (ppm)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127.730
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40.167
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39.499
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14.317
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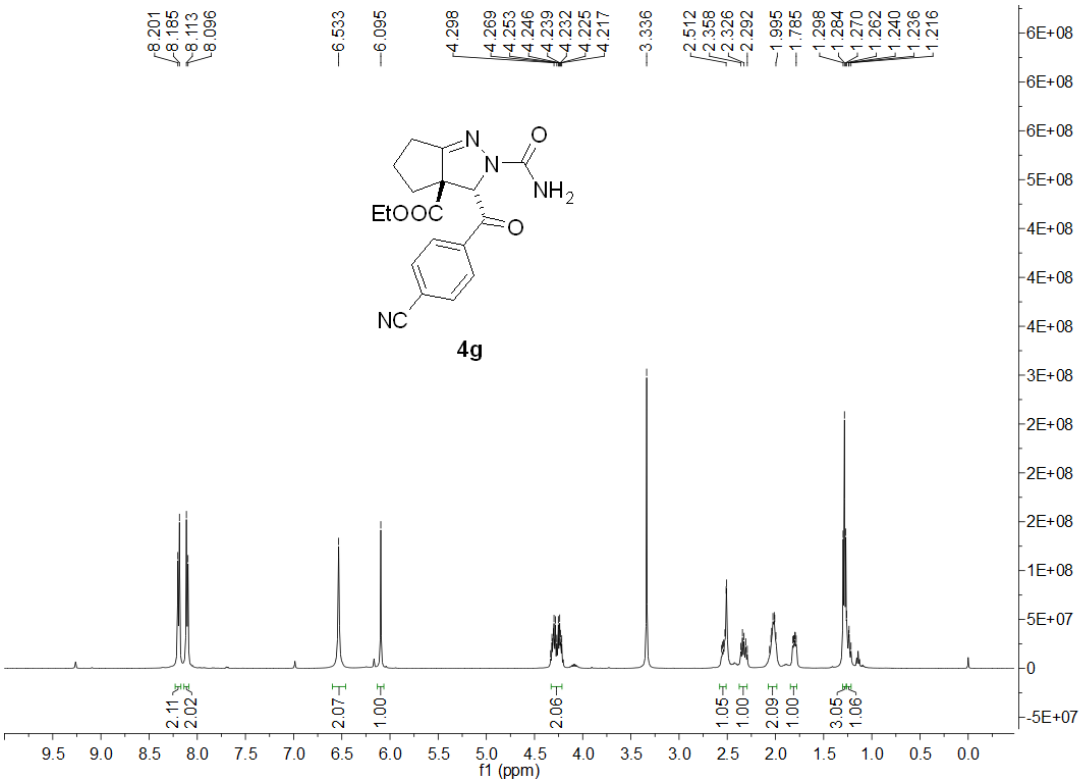
Br
4f
f1 (ppm)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4.239
4.232
4.225
4.217
3.336
2.512
2.358
2.326
2.292
1.995
1.785
1.298
1.284
1.270
1.262
1.240
1.236
1.216
EtOOC
NC
4g
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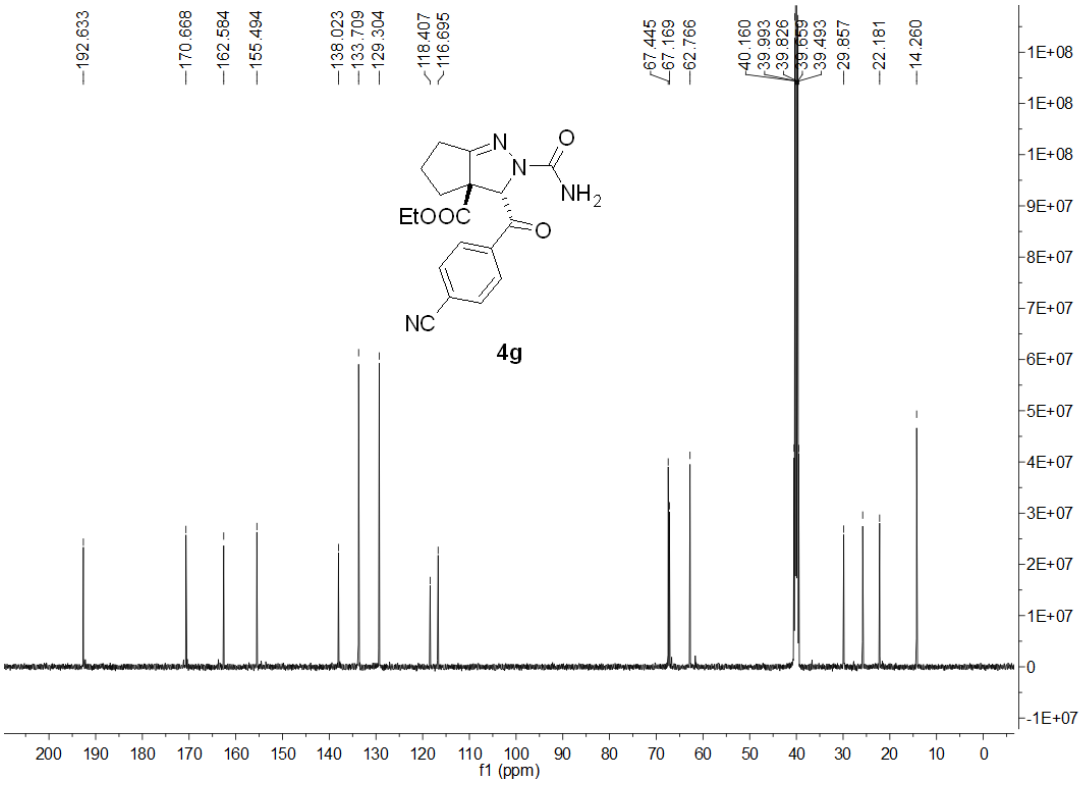
1.00
2.06
1.05
1.00
2.09
1.00
3.05
1.06
f1 (ppm)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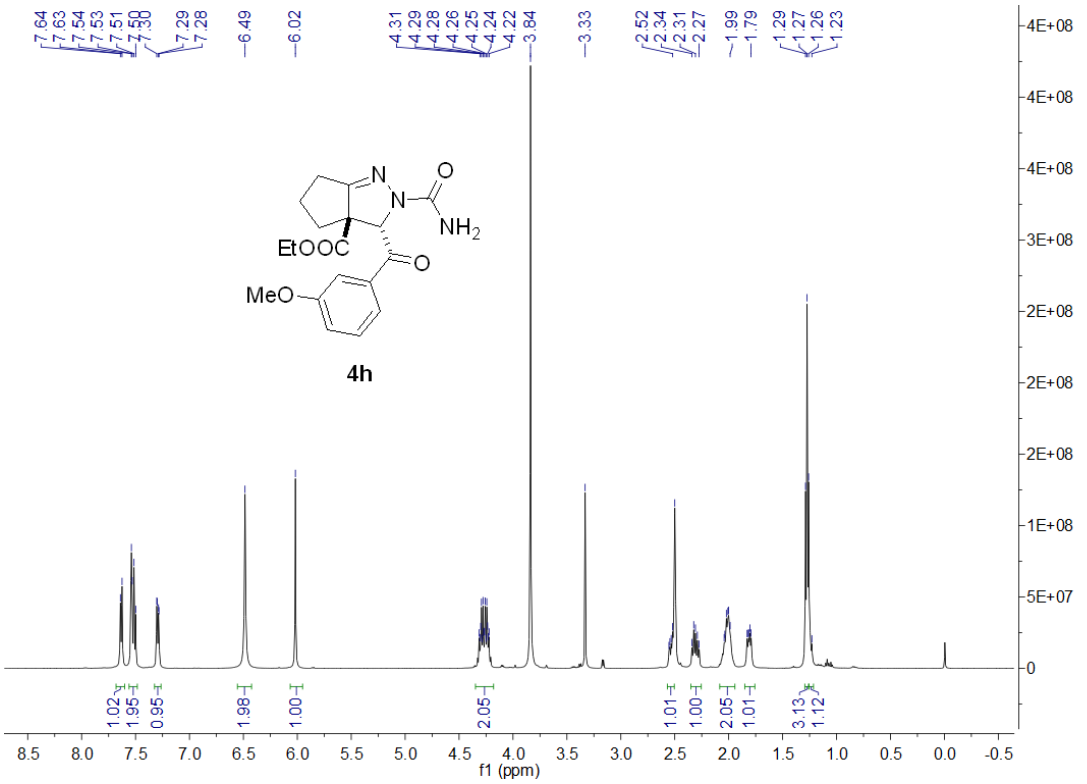
14.260
EtOOC
NC
4g
f1 (ppm)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7.30
7.29
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4.29
4.28
4.26
4.25
4.24
4.22
3.84
3.33
2.52
2.34
2.31
2.27
1.99
1.79
1.29
1.27
1.26
1.23
N
O
N
NH2
EtOOC
O
MeO
4h
1.02
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0.95
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1.00
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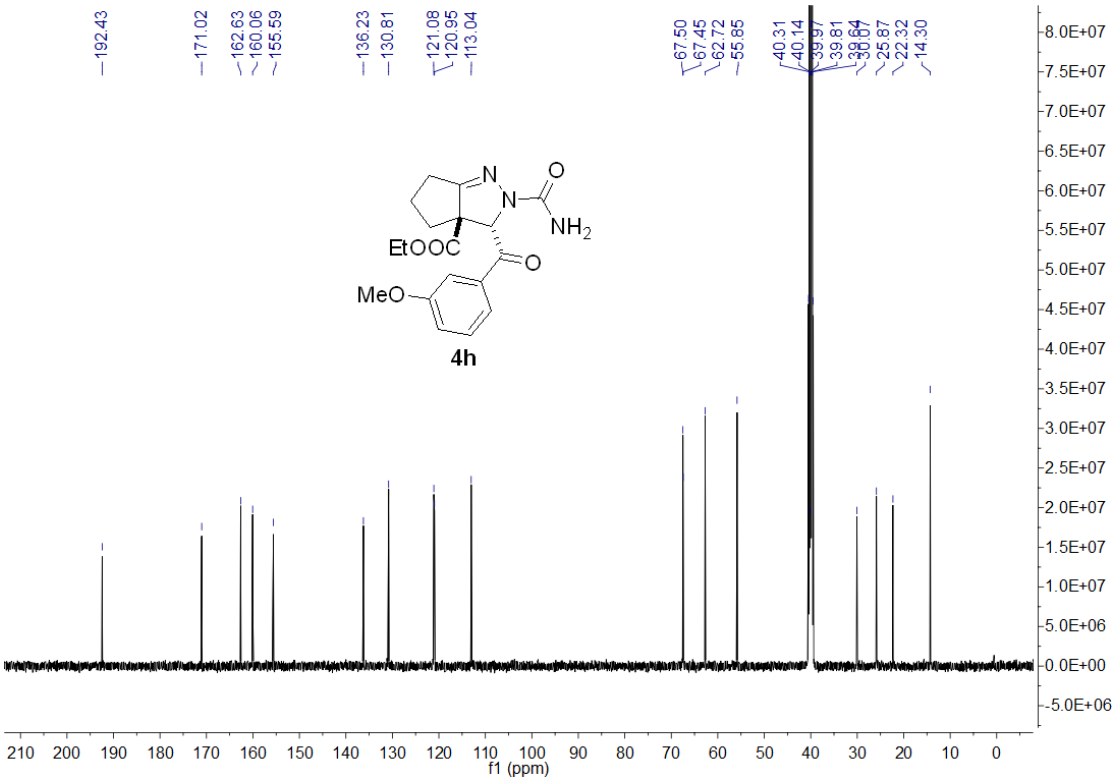
1.01
1.00
2.05
1.01
3.13
1.12
f1 (ppm)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67.45
62.72
55.85
40.31
40.14
39.97
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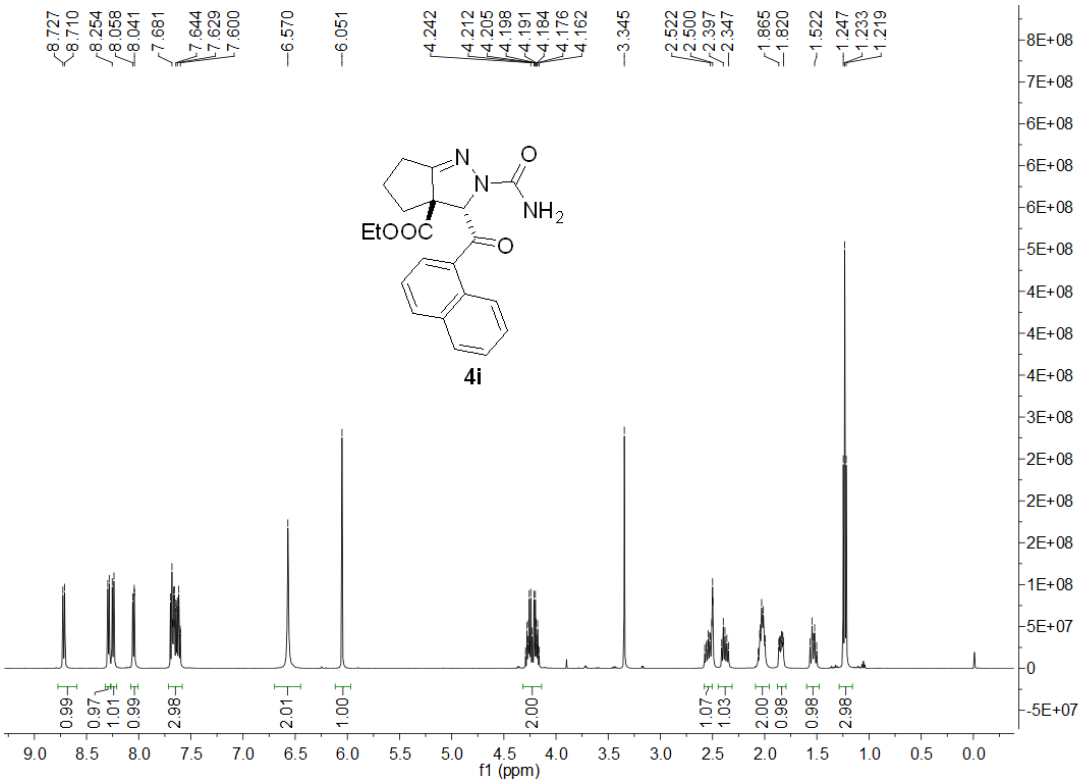
22.32
14.30
N
O
N
NH2
EtOOC
O
MeO
4h
f1 (ppm)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7.644
7.629
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4.205
4.198
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4.184
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2.347
1.865
1.820
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1.247
1.233
1.219
N
N
O
NH2
EtOOC
O
4i
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2.98
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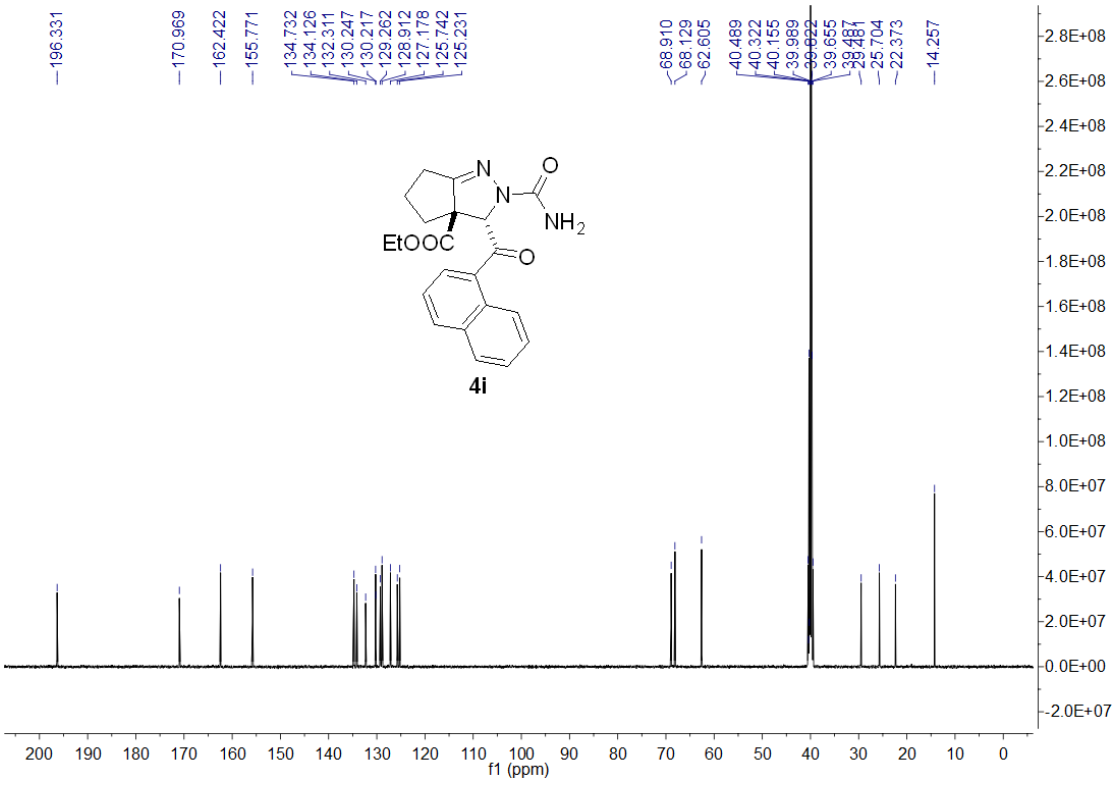
1.00
2.00
1.07
1.03
2.00
0.98
0.98
2.98
f1 (ppm)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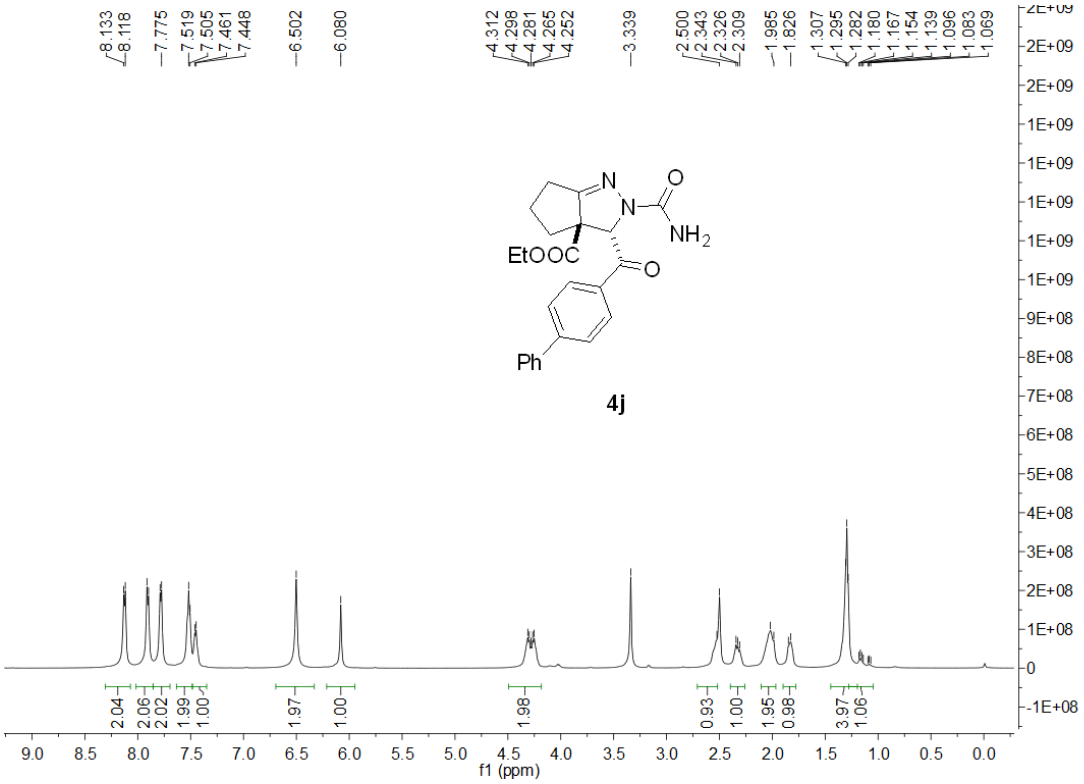
162.422
155.771
134.732
134.126
132.311
130.247
130.217
129.262
128.912
127.178
125.742
125.231
68.910
68.129
62.605
40.489
40.322
40.155
39.989
39.822
39.655
39.487
29.481
25.704
22.373
14.257
N
N
O
NH2
EtOOC
O
4i
f1 (ppm)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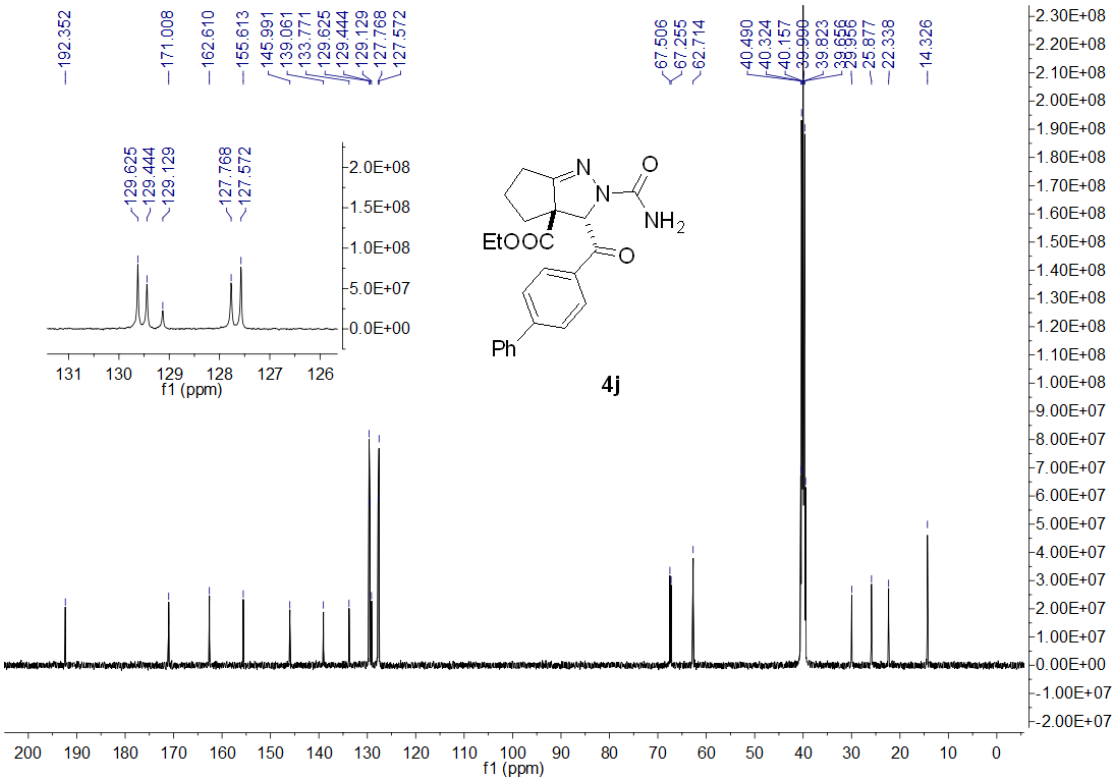
8.118
7.775
7.519
7.505
7.461
7.448
6.502
6.080
4.312
4.298
4.281
4.265
4.252
3.339
2.500
2.343
2.326
2.309
1.985
1.826
1.307
1.295
1.282
1.180
1.167
1.154
1.139
1.096
1.083
1.069
N
O
N
NH2
EtOOC
O
Ph
4j
2.04
2.06
2.02
1.99
1.00
1.97
1.00
1.98
0.93
1.00
1.95
0.98
3.97
1.06
f1 (ppm)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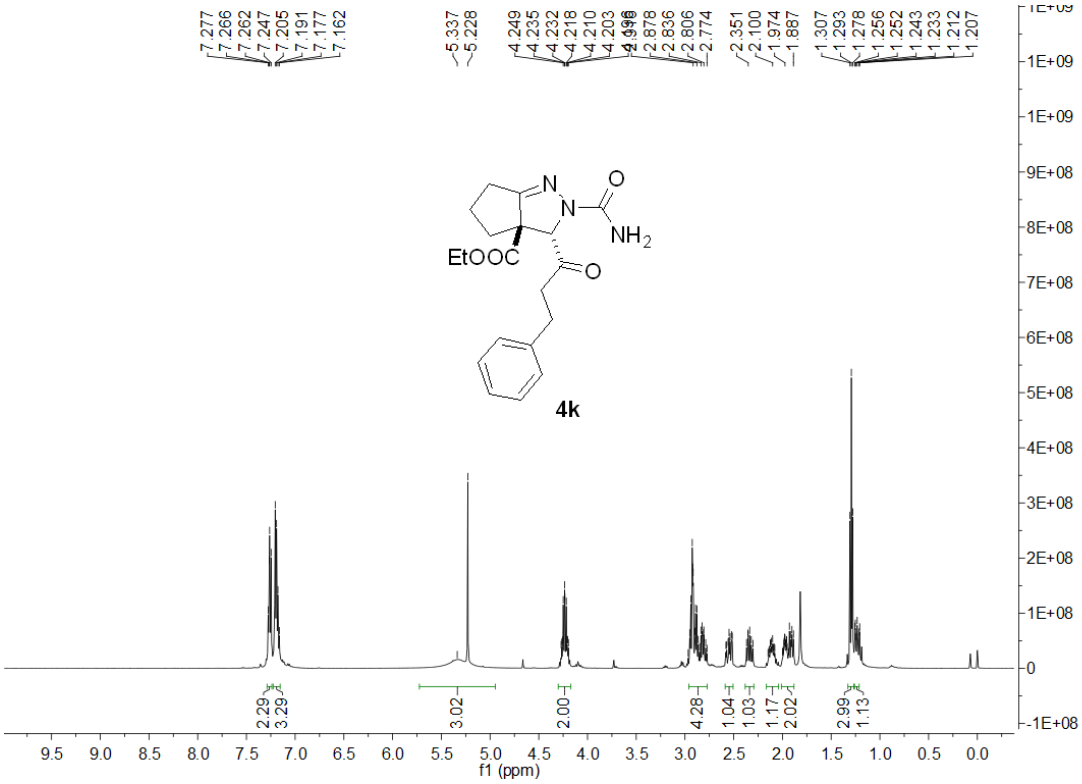
171.008
162.610
155.613
145.991
139.061
133.771
129.625
129.444
129.129
127.768
127.572
67.506
67.255
62.714
40.490
40.324
40.157
39.990
39.823
39.656
25.877
22.338
14.326
N
O
N
NH2
EtOOC
O
Ph
4j
f1 (ppm)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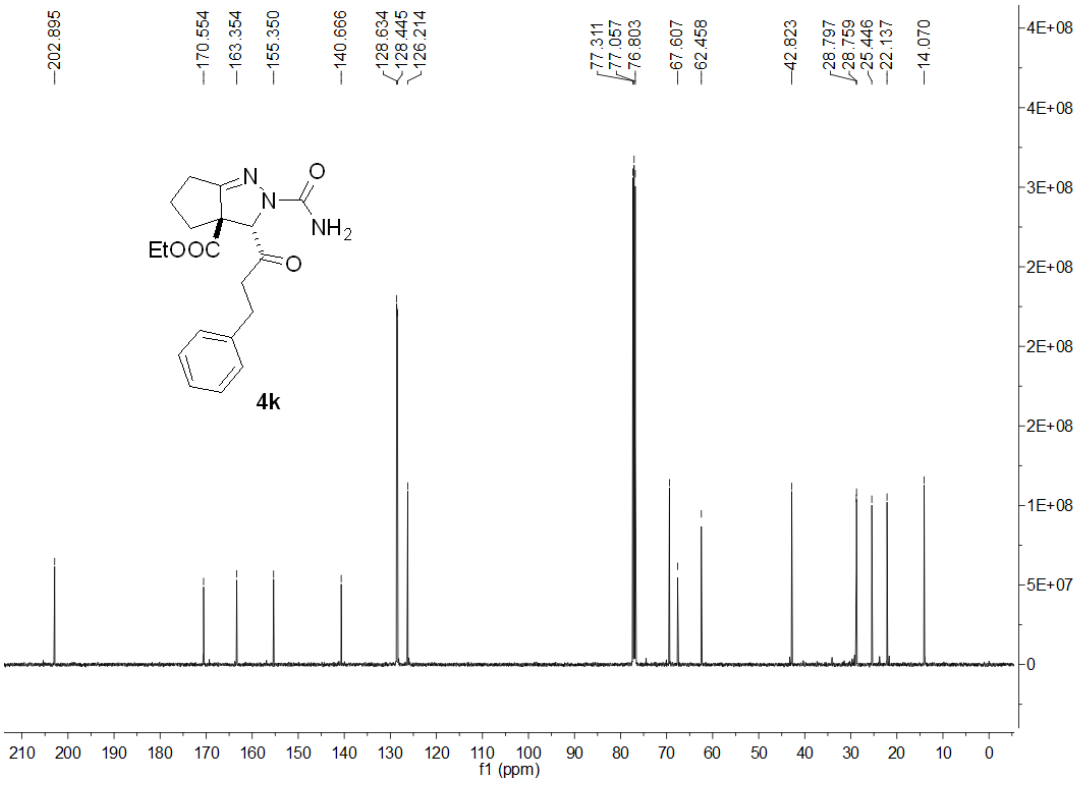
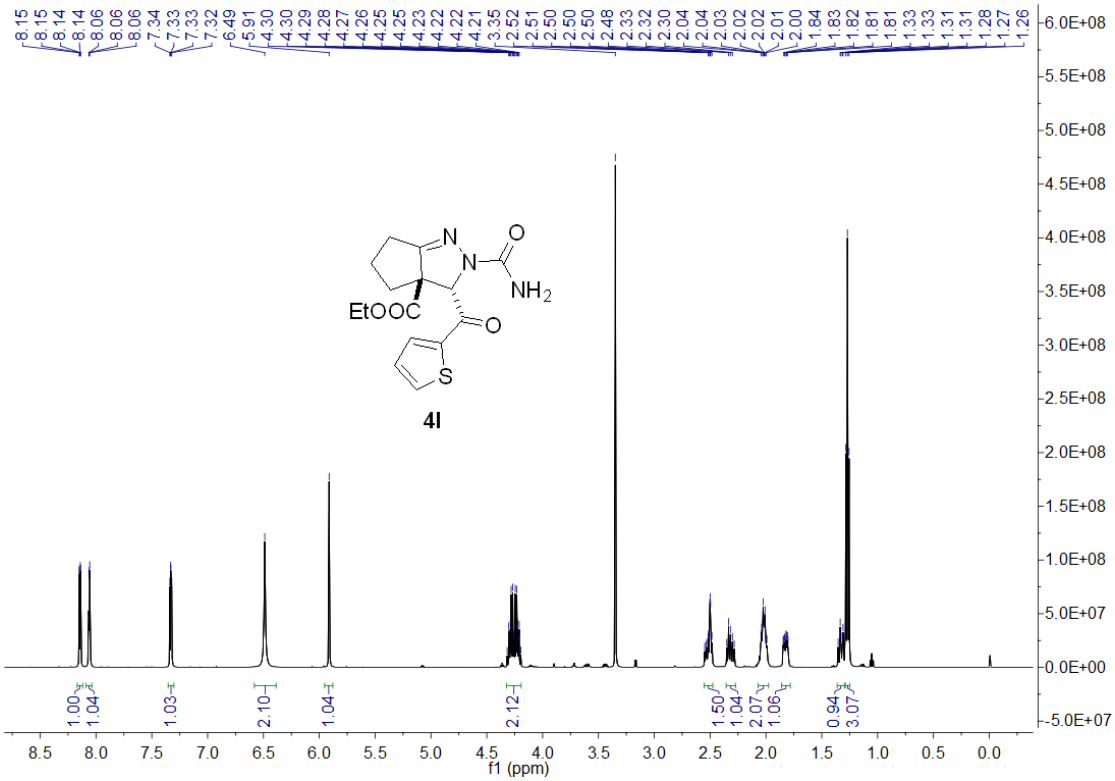
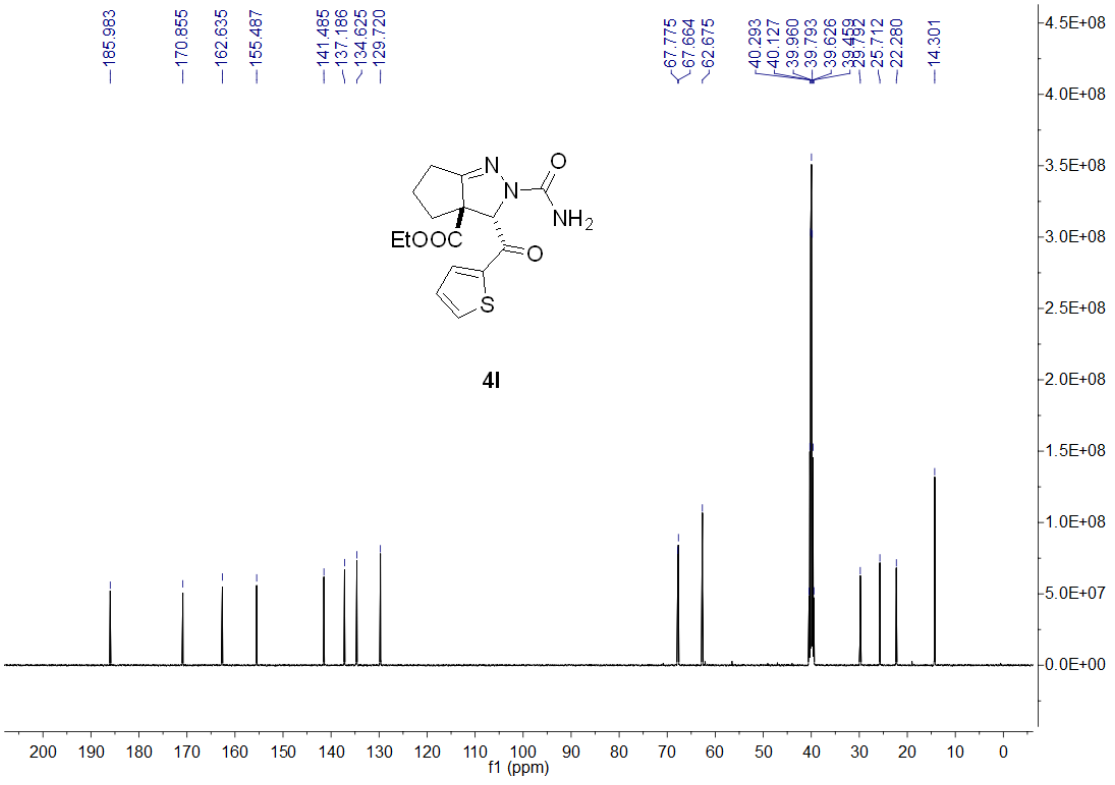
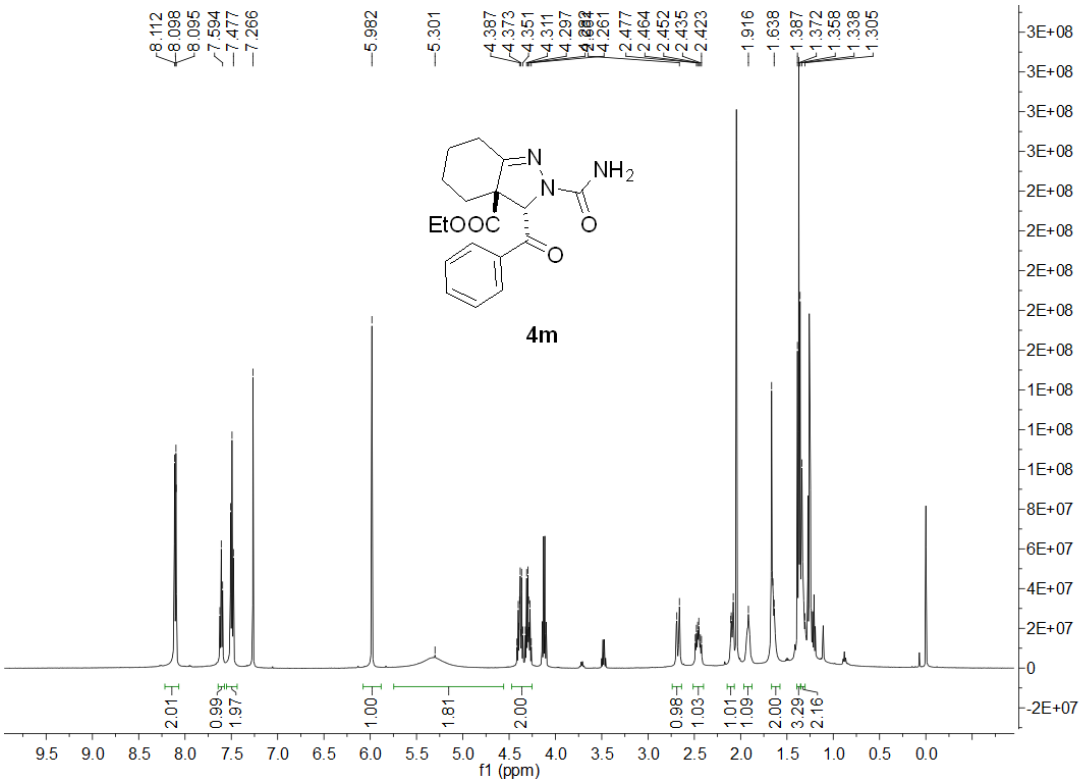
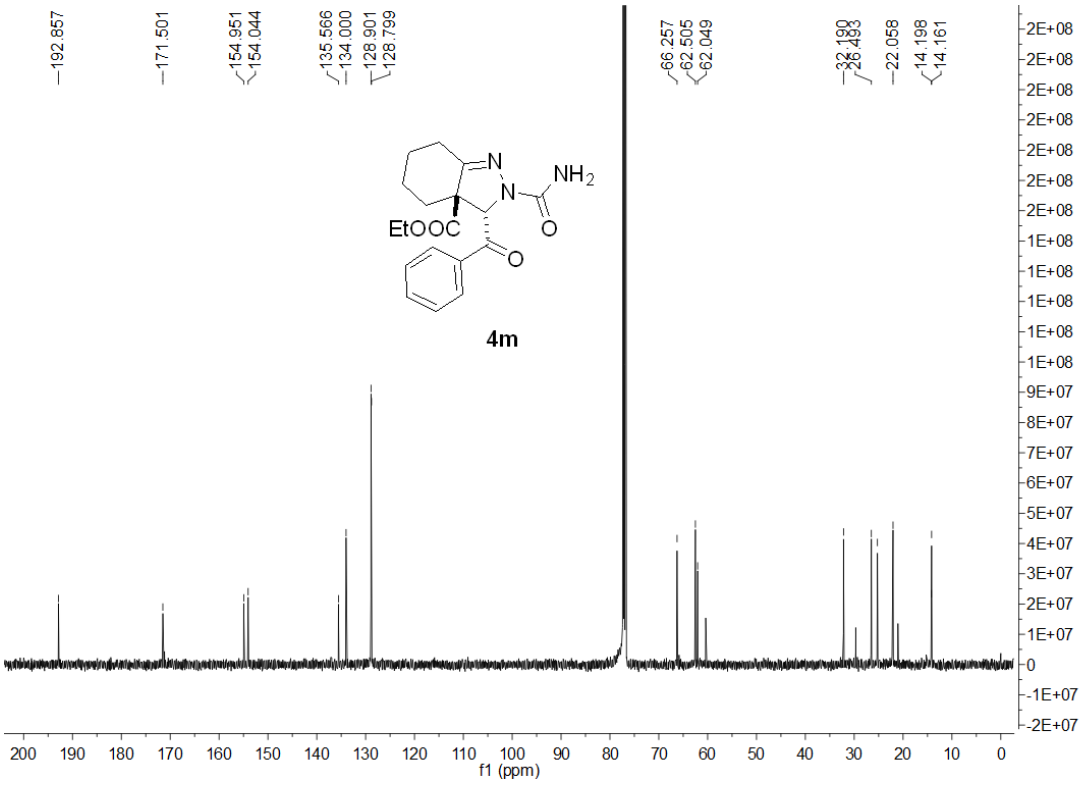
7.266
7.262
7.247
7.205
7.191
7.177
7.162
5.337
5.228
4.249
4.235
4.232
4.218
4.210
4.203
2.878
2.836
2.806
2.774
2.351
2.100
1.974
1.887
1.307
1.293
1.278
1.256
1.252
1.243
1.233
1.212
1.207
EtOOC
O
N
N
O
NH2
4k
2.29
3.29
3.02
2.00
4.28
1.04
1.03
1.17
2.02
2.99
1.13
f1 (ppm)

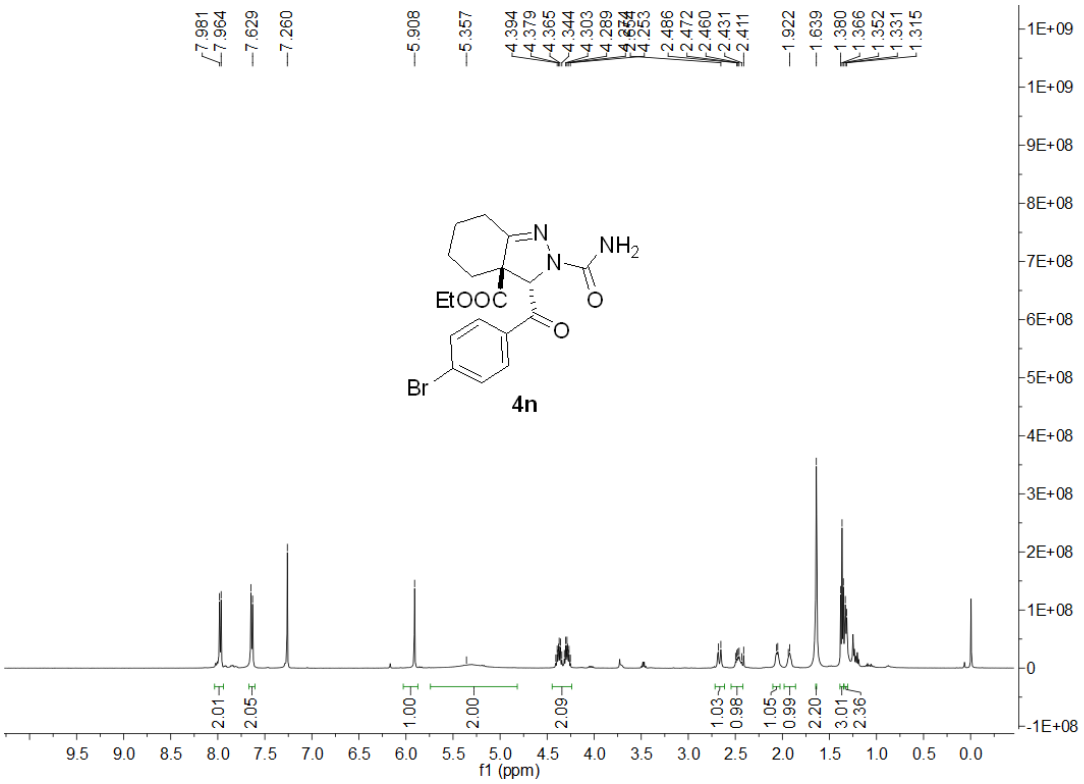

202.895
170.554
163.354
155.350
140.666
128.634
128.445
126.214
77.311
77.057
76.803
67.607
62.458
42.823
28.797
28.759
25.446
22.137
14.070
EtOOC
O
N
N
O
NH2
4k
f1 (ppm)

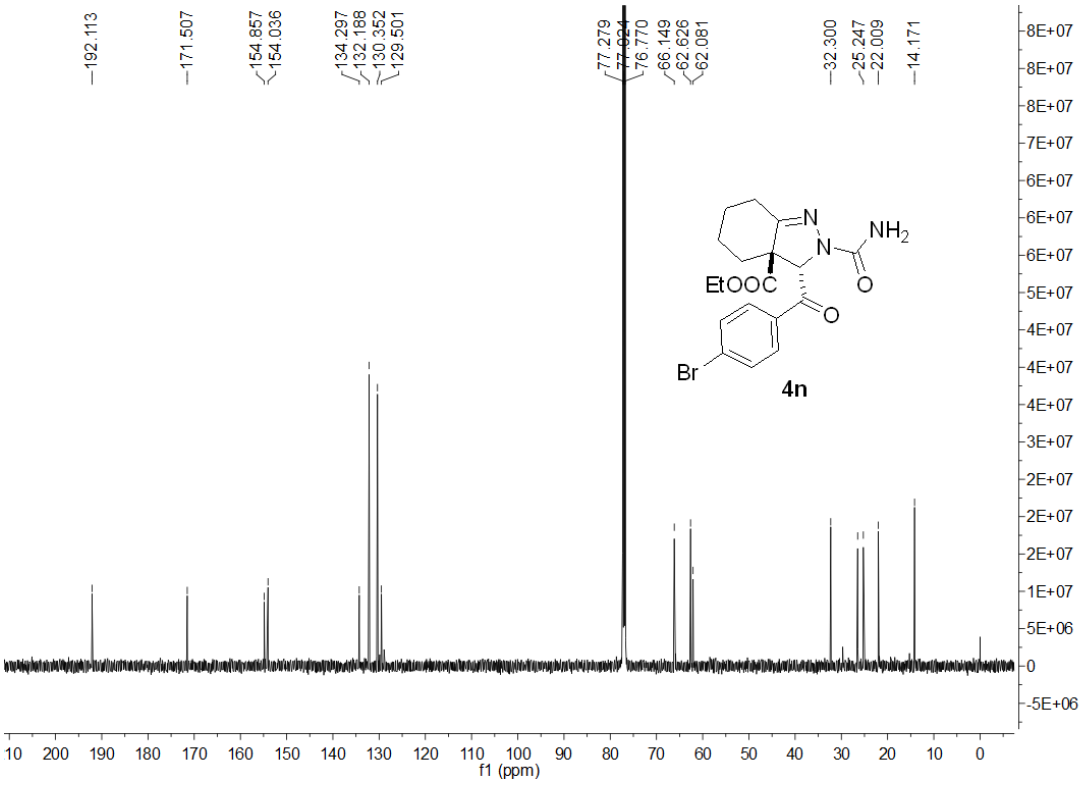

8.15 8.15 8.14 8.14 8.06 8.06 8.06 8.06 7.34 7.33 7.33 7.32 6.49 5.91 4.30 4.30 4.29 4.28 4.27 4.26 4.25 4.25 4.23 4.22 4.22 4.21 3.35 2.52 2.51 2.50 2.50 2.50 2.48 2.33 2.32 2.30 2.04 2.04 2.03 2.02 2.02 2.01 2.00 1.84 1.83 1.82 1.81 1.81 1.33 1.33 1.31 1.31 1.28 1.27 1.26
EtOOC
NH2
4l
1.00 1.04 1.03 2.10 1.04 2.12 1.50 1.04 2.07 1.06 0.94 3.07
f1 (ppm)

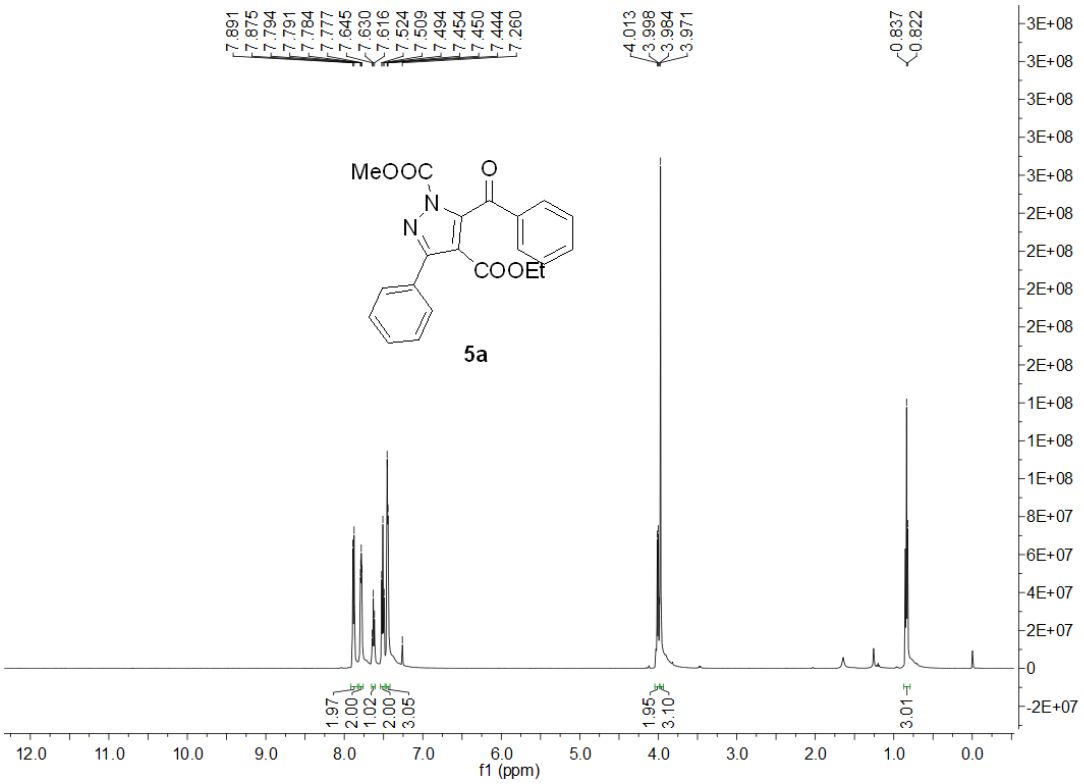

185.983 170.855 162.635 155.487 141.485 137.186 134.625 129.720 67.775 67.664 62.675 40.293 40.127 39.960 39.793 39.626 25.712 22.280 14.301
EtOOC
NH2
4l
f1 (ppm)

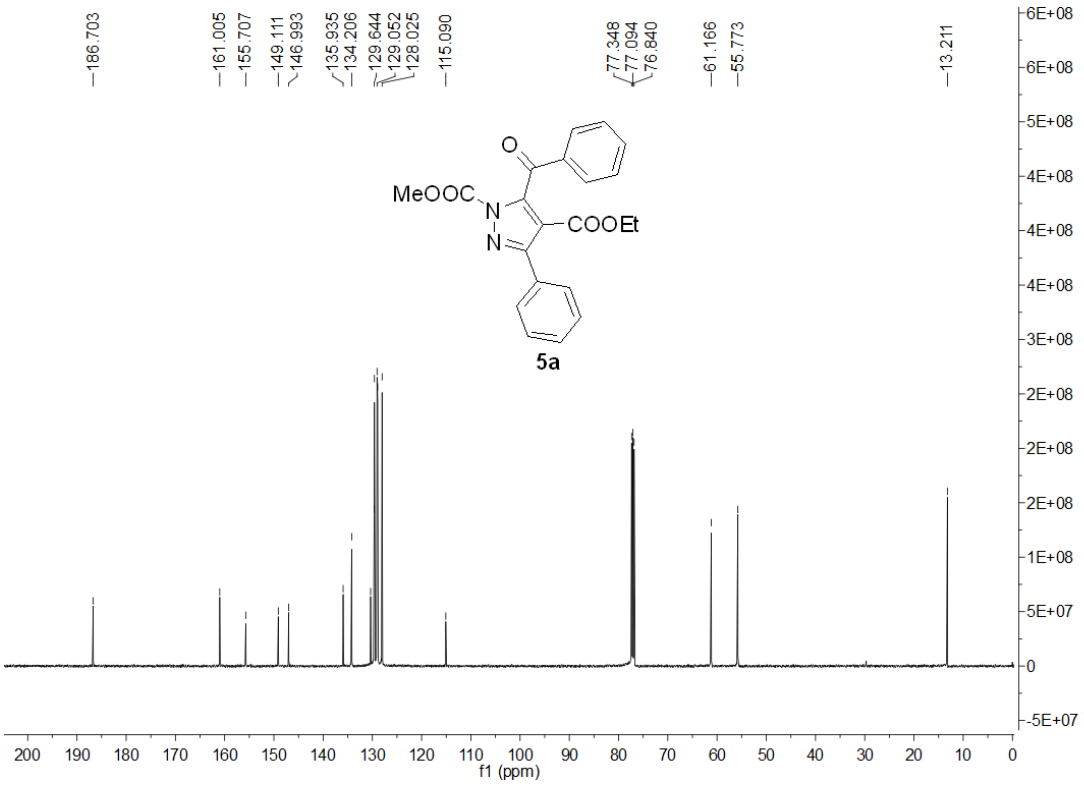

8.112
8.098
8.095
7.594
7.477
7.266
5.982
5.301
4.387
4.373
4.351
4.311
4.297
4.261
2.477
2.464
2.452
2.435
2.423
1.916
1.638
1.387
1.372
1.358
1.338
1.305
N
N
NH2
O
EtOOC
O
4m
2.01
0.99
1.97
1.00
1.81
2.00
0.98
1.03
1.01
1.09
2.00
3.29
2.16
f1 (ppm)

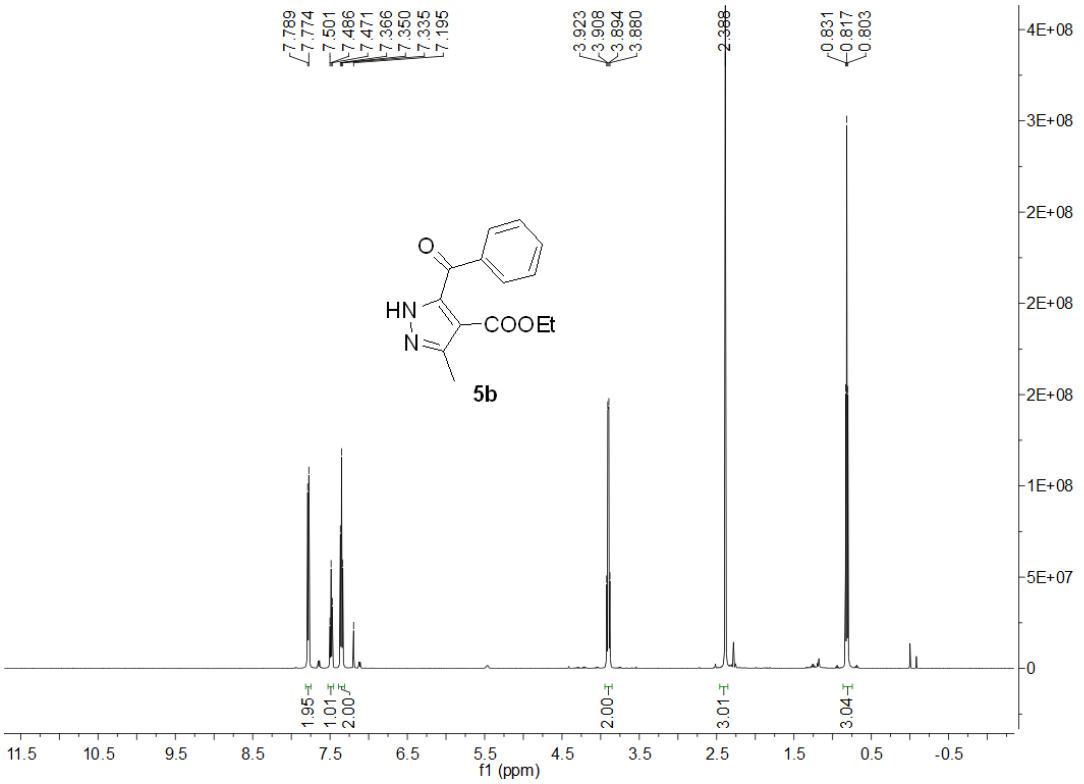

192.857
171.501
154.951
154.044
135.566
134.000
128.901
128.799
66.257
62.505
62.049
32.190
26.493
22.058
14.198
14.161
N
N
NH2
O
EtOOC
O
4m
f1 (ppm)

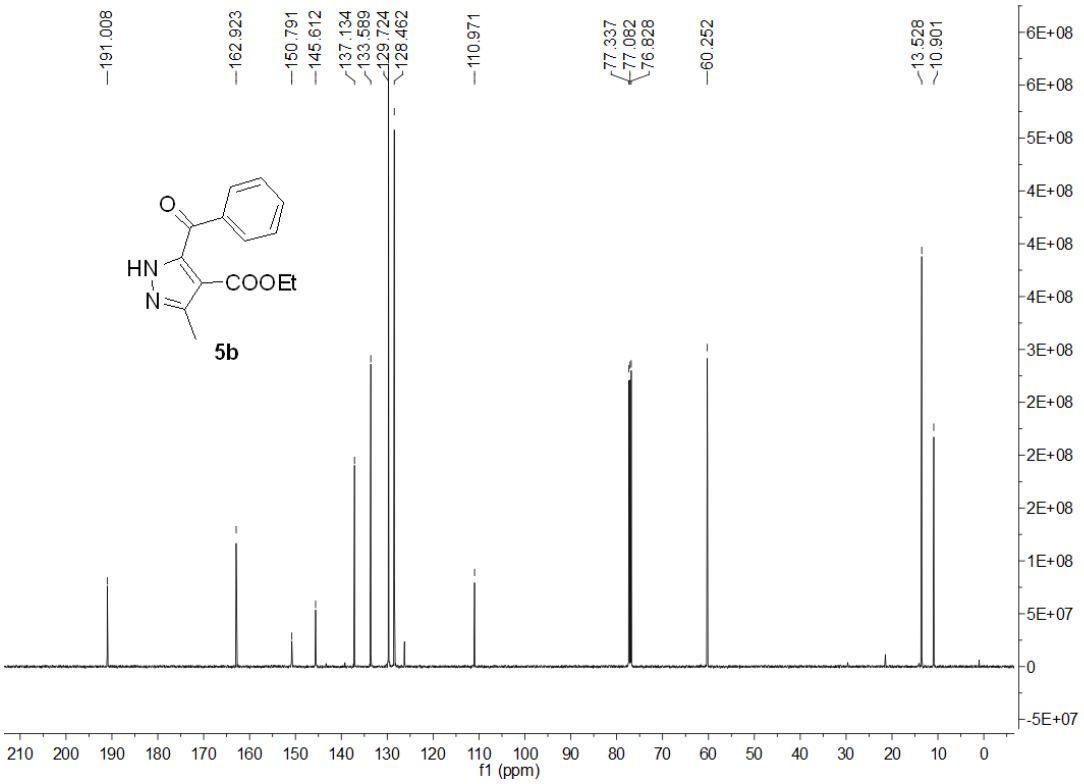

7.981
7.964
7.629
7.260
5.908
5.357
4.394
4.379
4.365
4.344
4.303
4.289
4.254
4.253
2.486
2.472
2.460
2.431
2.411
1.922
1.639
1.380
1.366
1.352
1.331
1.315
EtOOC
NH2
O
Br
4n
2.01
2.05
1.00
2.00
2.09
1.03
0.98
1.05
0.99
2.20
3.01
2.36
f1 (ppm)

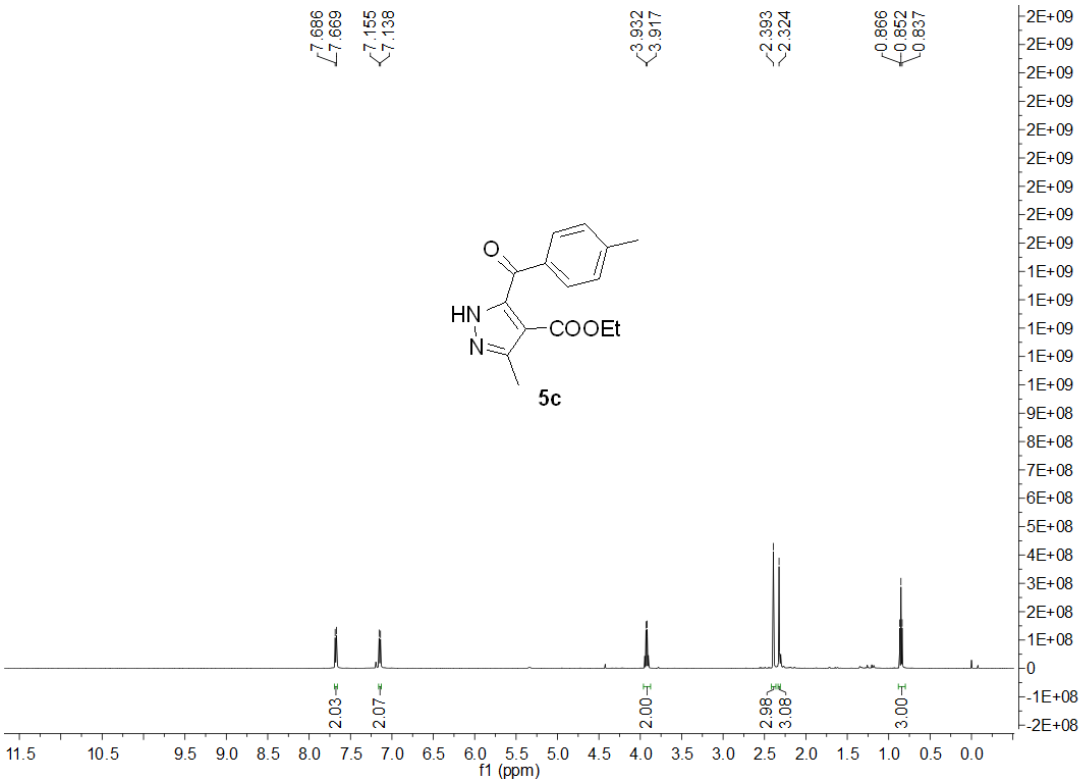

192.113
171.507
154.857
154.036
134.297
132.188
130.352
129.501
77.279
77.024
76.770
66.149
62.626
62.081
32.300
25.247
22.009
14.171
EtOOC
NH2
O
Br
4n
f1 (ppm)

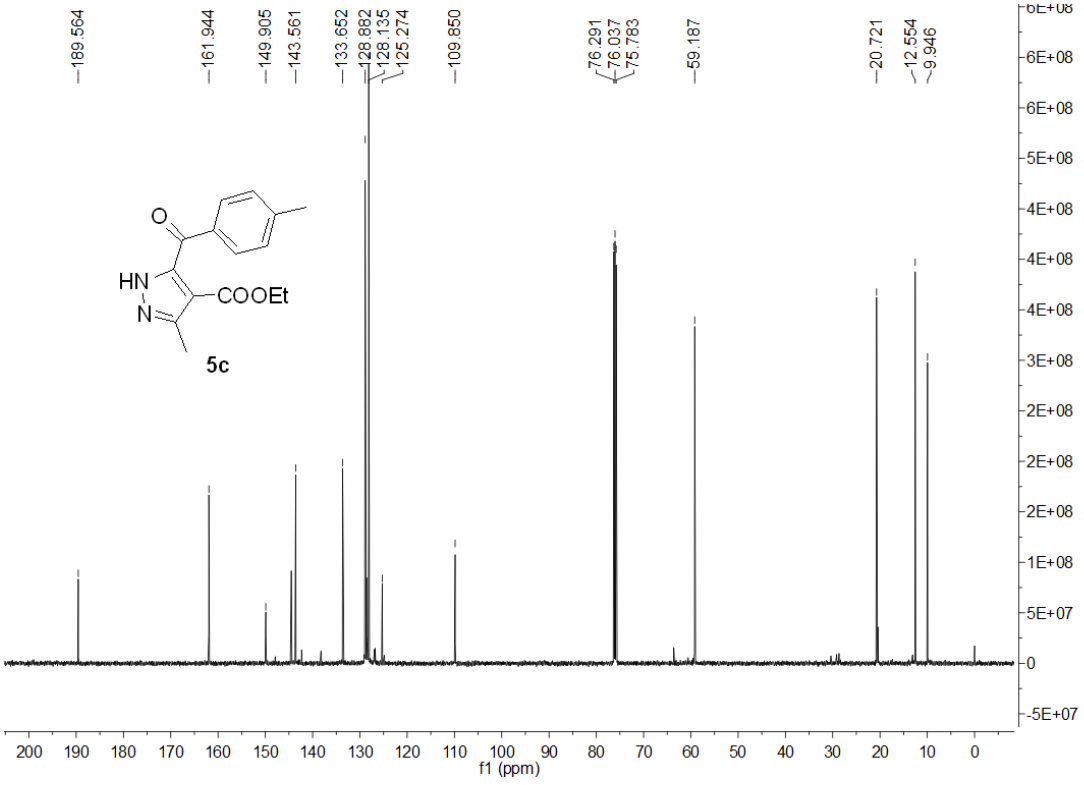

7.891
7.875
7.794
7.791
7.784
7.777
7.645
7.630
7.616
7.524
7.509
7.494
7.454
7.450
7.444
7.260
4.013
3.998
3.984
3.971
0.837
0.822
MeOOC
O
N
N
COOEt
5a
1.97
2.00
1.02
2.00
3.05
1.95
3.10
3.01
f1 (ppm)

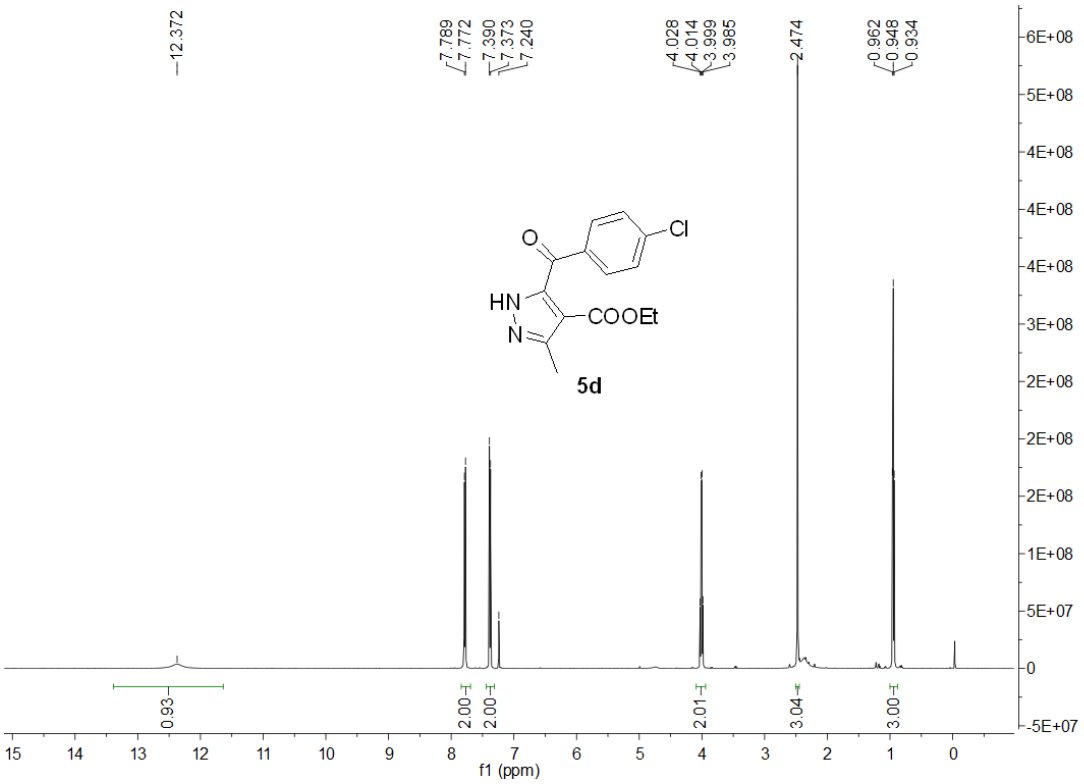

186.703
161.005
155.707
149.111
146.993
135.935
134.206
129.644
129.052
128.025
115.090
77.348
77.094
76.840
61.166
55.773
13.211
O
MeOOC
N
N
COOEt
5a
f1 (ppm)

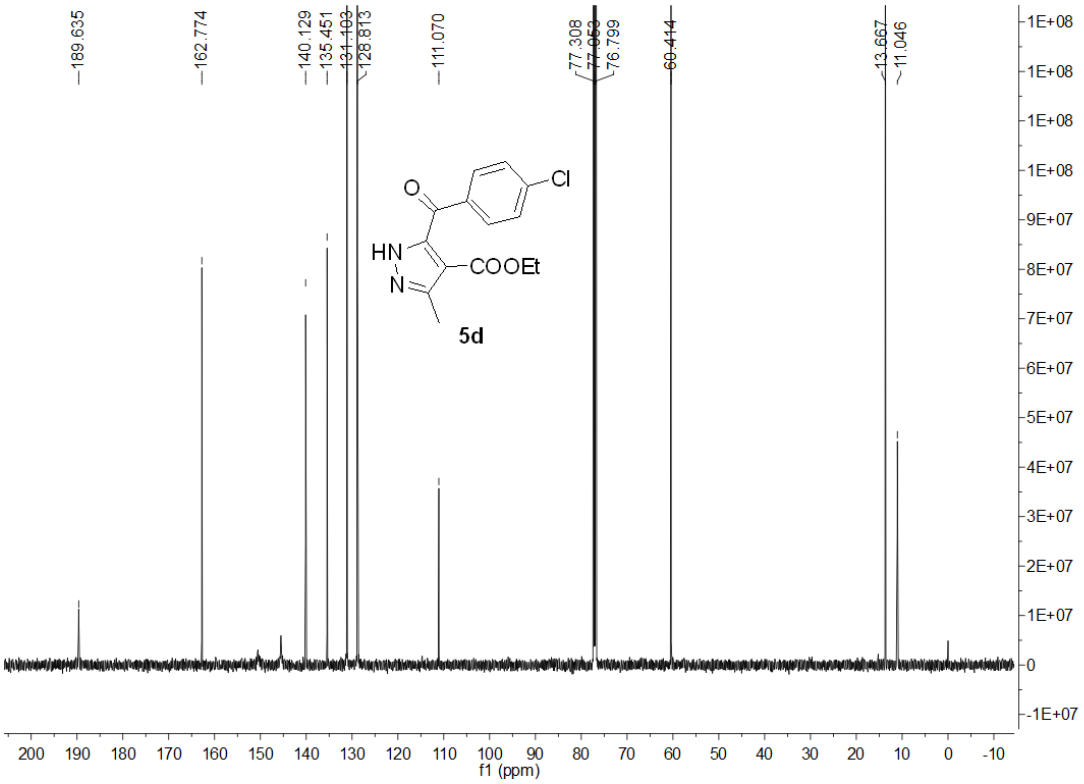

7.789
7.774
7.501
7.486
7.471
7.366
7.350
7.335
7.195
3.923
3.908
3.894
3.880
2.388
0.831
0.817
0.803
O
HN
N
COOEt
5b
1.95
1.01
2.00
2.00
3.01
3.04
f1 (ppm)


191.008
162.923
150.791
145.612
137.134
133.589
129.724
128.462
110.971
77.337
77.082
76.828
60.252
13.528
10.901
O
HN
N
COOEt
5b
f1 (ppm)


7.686
7.669
7.155
7.138
3.932
3.917
2.393
2.324
0.866
0.852
0.837
O
HN
N
COOEt
5c
2.03
2.07
2.00
2.98
3.08
3.00
f1 (ppm)


189.564
161.944
149.905
143.561
133.652
128.882
128.135
125.274
109.850
76.291
76.037
75.783
59.187
20.721
12.554
9.946
O
HN
N
COOEt
5c
f1 (ppm)


12.372
7.789
7.772
7.390
7.373
7.240
4.028
4.014
3.999
3.985
2.474
0.962
0.948
0.934
O
Cl
HN
N
COOEt
5d
0.93
2.00
2.00
2.01
3.04
3.00
f1 (ppm)


189.635
162.774
140.129
135.451
131.103
128.813
111.070
77.308
77.066
76.799
60.414
13.667
11.046
O
Cl
HN
N
COOEt
5d
f1 (ppm)