Electronic supplementary information

Hypervalent Iodine(III)-Promoted N-Incorporation into N-Aryl Vinylogous Carbamates to Quinoxaline diesters: Access to 1, 4, 5, 8 Tetraazaphenanthrene

A. Sagar, Shinde Vidyacharan, Anand H. Shinde and Duddu S. Sharada*

Table of Contents

General Considerations …… (S2)

Methods for vinylogous carbamates preparation includes GP-I and GP-II ……. (S3-S4)

General procedure (GP-III) for the synthesis of (**2a-2j**, **2z**, **2aa** and **2ab**)…….. (S5)

Substrate scope of halogen substituted vinylogous carbamates …….. (S5)

General procedure (GP-IV) for the synthesis of (**2k-2x**) and optimizations ……. (S5-S7)

X-ray crystal structure data of compound (**2h**)……. (S7-S8)

Spectral data of all compounds (**1d-1f**, **1h**, **1p**, **1w**, **1x, 1y and 1ab)**, **2a-2j**, **2k-1**, **2k-2**,

2l-2r, **2r-1**, **2r-2**, **2s**, **2t-1**, **2t-2**, **2u**, **2v**, **2w-1**, **2w-2**, **2x-1**, **2x-2**, **2y-2**, **2z-2 and 2ab..** (S9-S26)

Copies of ^{1}H, ^{13}C NMR spectra of all compounds (**1d-1f, 1h, 1p, 1w, 1x, 1y and 1ab**), **2a-2j, 2k-1, 2k-2, 2l-2r, 2r-1, 2r-2, 2s, 2t-1, 2t-2, 2u, 2v, 2w-1, 2w-2, 2x-1, 2x-2, 2y-2, 2z-2 and 2ab**

…….. (S28-S65)

References **…….** (S66)

General Considerations

IR spectra were recorded on a FTIR spectrophotometer. ^{1}H NMR spectra were recorded on 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the 1HNMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s. = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Hyper valent iodine reagents (PIFA and PIDA) were purchased from Sigma Aldrich. All dry solvents were used THF were dried over sodium metal and CH_3CN, DMF, DCE, DCM, HFIP, TFE which are commercial available from sigma Aldrich.

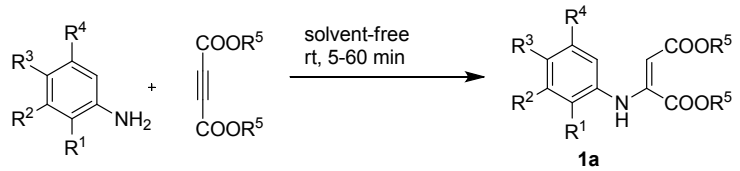
All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. Reactions were generally run under argon, nitrogen and oxygen atmosphere wherever necessary. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 ˚C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

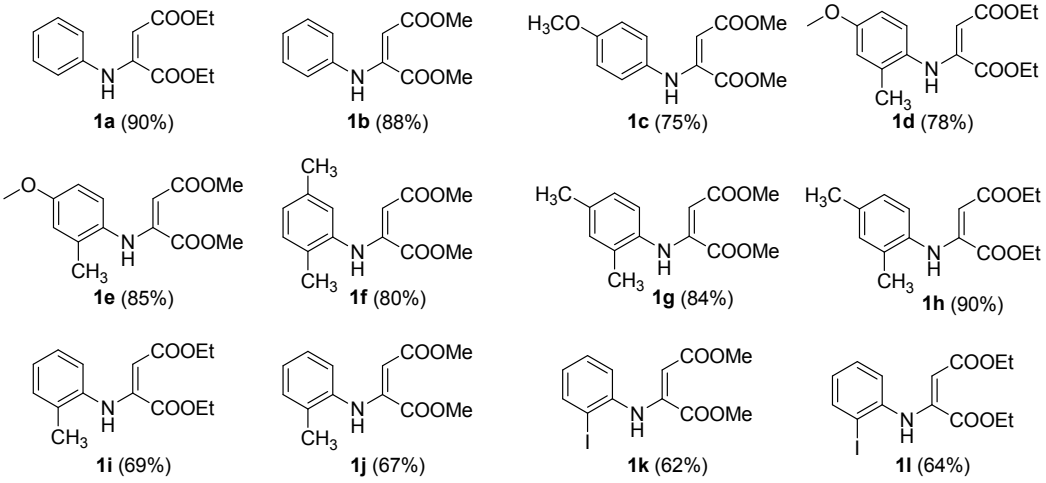
A) The requisite precursors have been synthesized by using literature procedures[1,2]

I) General Procedure (GP-I) for the synthesis of (1a-1y) and 1ab

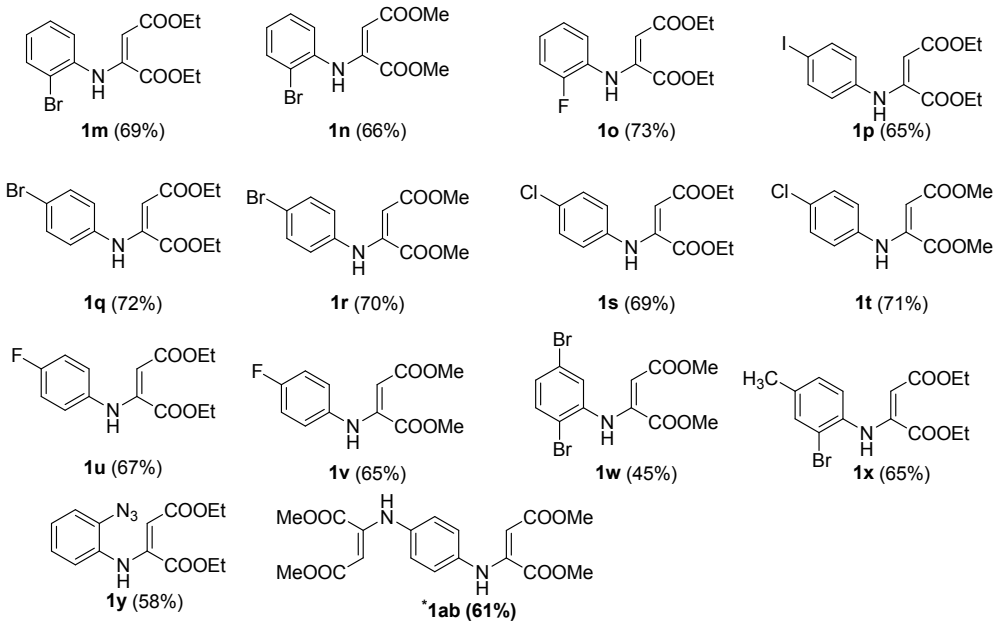
Amine (1 mmol) was taken in a dried round bottom flask, and dialkyl acetylenedicarboxylate (1 mmol) was then added slowly with thorough mixing to form a homogeneous paste. Then, the reaction mixture was stirred (if required) at room temperature for 5−60 min and then filtered through a short silica gel column using petroleum ether/ethyl acetate (9.8:0.2 to 9.6:0.4) as eluent to furnish the dialkyl-2-(phenylamino)maleate **1a-1y**. All the unknown compounds (**1d-1f**, **1h**, **1p**, **1w-1y**) were confirmed by FTIR, 1H NMR, 13CNMR and HR-MS Spectral analyses. Compounds **1a-1c**, **1g, 1i-1o** and **1q-1v** were prepared using the literature reported reaction conditons.[1]

Following vinylogous carbamates used as a starting materials for the synthesis of quinoxalines





Contd.

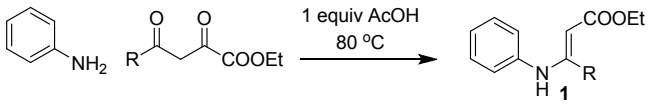


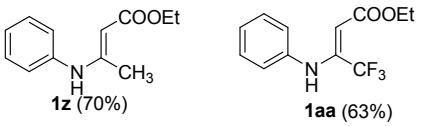
---

*compound **1ab** was prepared by using two equivalents of dimethyl acetylene dicarboxylate.

II) General procedure (GP-II) for the synthesis of 1z and 1aa

A mixture of alkyl acetoacetate (1 mmol) and aniline (1 mmol) refluxed in acetic acid (1 mmol) at 80 °C for 3 h. The Progress of the reaction was monitored by TLC till the reaction is completed. The reaction mixture was quenched by addition of saturated solution of $NaHCO_3$ and dried (Na_2SO_4), and concentrated in vacuo. The residue was purified through a silica gel column using petroleum ether/ethyl acetate (9.8:0.2 to 9.9:0.1) as eluent to give the pure product **1z** and **1aa**. Compounds **1z** and **1aa** were known in the literature.[2]

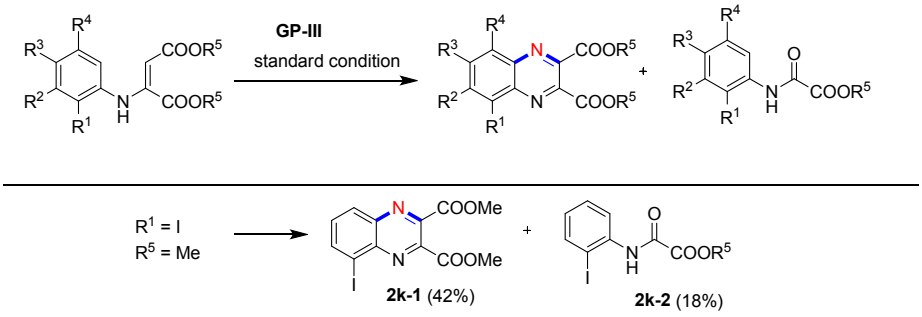




III) General procedure (GP-III) for the synthesis of (2a-2j, 2z and 2aa)

To a cold (0 °C), magnetically stirred solution of *N*-aryl vinylogous carbamates **1a-1j, 1z** and **1aa** (0.19 mmol) and NaN_3 (0.38 mmol) in DCE (3 mL) was added PIDA (0.38 mmol) portions wise for 20 min and the resulting mixture was stirred at room temperature (27 °C) for 4-6 h. Progress of the reaction was monitored by TLC until the reaction is completed. The reaction mixture was quenched by addition of aq $Na_2S_2O_3$ (1.0 M, 5 mL) solution and extracted with EtOAc (3 × 10 mL). The organic layer was washed with saturated solution of $NaHCO_3$ and dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate (8.5:1.5 to 9.5:0.5) as eluent furnished the quinoxalines **2a-2j, 2z,** and **2aa**. All the compounds (**2a-2j, 2z-2**) were confirmed by FTIR, 1H NMR, 13CNMR and HR-MS Spectral analyses. Among all **2a-2c** and **2j** were known.

Scheme 1 substrate scope of halogen substituted vinylogous carbamates with "2 equiv of NaN_3"

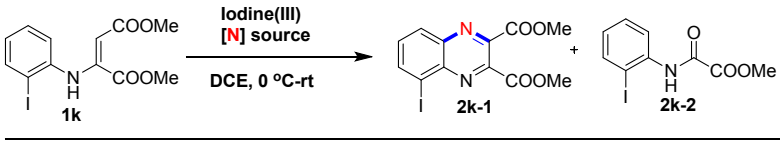


IV) General procedure (GP-IV) for the synthesis of (2k-2x) and 2ab

To a cold (0 °C), magnetically stirred solution of *N*-aryl vinylogous carbamates **1k-1x** (0.19 mmol) and NaN_3 (0.76 mmol) in DCE (3 mL) was added PIDA (0.38 mmol) portions wise for 20 min and the resulting mixture was stirred at room temperature (28 °C) for 4-6 h. Progress of the reaction was monitored by TLC until the reaction is completed. The reaction mixture was

quenched by addition of aq $Na_2S_2O_3$ (1.0 M, 5 mL) solution and extracted with EtOAc (3 × 10 mL). The organic layer was washed with saturated solution of $NaHCO_3$ and dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate (8.5:1.5 to 9.5:0.5) as eluent furnished the quinoxalines **2k-2x**. All the compounds (**2k-2x**) and **2ab** were confirmed by FTIR, 1H NMR, 13CNMR and HR-MS Spectral analyses. In the case of **2r-1**, **2w-1**, **2x-1** we have found minute quantity of corresponding alkyl *N*-aryloxamates **2r-2**, **2w-2**, **2x-2** respectively in the 1H NMR spectra and we have included those in the spectral data. Among all the compounds **2r-1**, **2t-1**, **2v** were known.

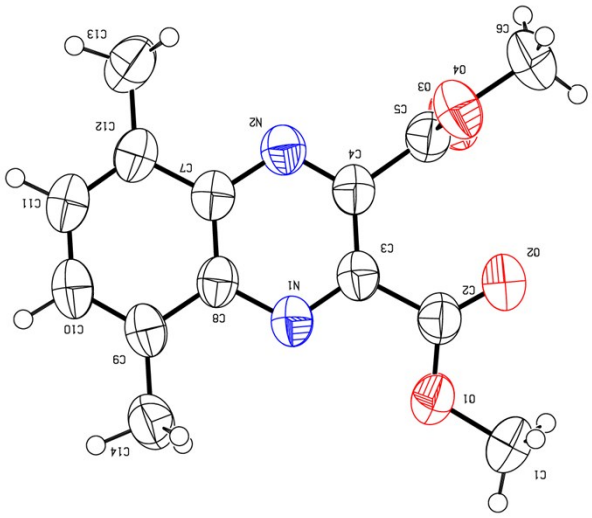
Table 1 Optimization condition for the synthesis of halo substituted quinoxalines[a]



entry	Iodine(III) (equiv)	[N] source	solvent	yield (%) 2k-1/2k-2
1	PIDA (2.0)	NaN_3 (2.0)	DCE	42/18
2	PIDA (2.0)	NaN_3 (2.5)	DCE	45/16
3	PIDA (2.0)	NaN_3 (3.0)	DCE	50/10
4	PIDA (2.0)	NaN_3 (3.5)	DCE	55/4
5	**PIDA (2.0)**	**NaN_3 (4.0)**	**DCE**	**58/0**
6	PIDA (2.0)	NaN_3 (4.5)	DCE	58/0

[a]Yield of isolated products after column chromatography.

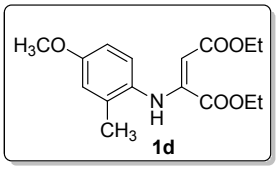
Table 2. Single X-ray crystal structure of **2h** (ORTEP diagram) and thermal ellipsoids are drawn at 25% probability level CCDC 994876.



Identification code	exp_6045
Empirical formula	$C_{14}H_{16}N_2O_4$
Formula weight	274.28
Temperature/K	296(1)
Crystal system	triclinic
Space group	P-1
a/Å	8.2596(12)
b/Å	8.9504(13)
c/Å	10.0044(15)
α/°	75.628(13)
β/°	72.518(13)
γ/°	85.932(12)

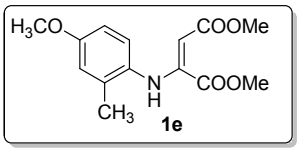
Volume/$Å^3$	683.35(18)
Z	2
$\rho_{calc}g/cm^3$	1.3329
μ/mm^{-1}	0.828
F(000)	289.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.54 to 144.1
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-12 \leq l \leq 9$
Reflections collected	5187
Independent reflections	2577 [$R_{int} = 0.0227$, $R_{sigma} = 0.0334$]
Data/restraints/parameters	2577/0/184
Goodness-of-fit on F^2	1.113
Final R indexes [I> = 2σ (I)]	$R_1 = 0.0630$, $wR_2 = 0.1780$
Final R indexes [all data]	$R_1 = 0.0977$, $wR_2 = 0.2209$
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.28

Spectral data of all compounds **(1d-1f, 1h, 1p, 1w, 1x, 1y and 1ab), 2a-2j, 2k-1, 2k-2, 2l-2r, 2r-1, 2r-2, 2s, 2t-1, 2t-2, 2u, 2v, 2w-1, 2w-2, 2x-1, 2x-2, 2y-2, 2z-2** and **1ab**



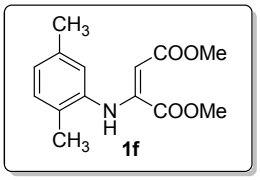
Diethyl 2-((4-methoxy-2-methylphenyl)amino)maleate (1d)

Yellow viscous oil; (78%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3274, 2980, 2936, 1734, 1661, 1606, 1505, 1466, 1367, 1256, 1199, 1140, 1039, 860, 803, 776; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 9.36 (s, 1H), 6.77-6.72 (m, 2H), 6.62 (dd, 1H, J_a = 8.6 and J_b = 2.7 Hz), 5.27 (s, 1H), 4.18 (q, 2H, J = 7.2 Hz), 4.06 (q, 2H, J = 7.3 Hz), 3.75 (s, 1H), 2.3 (s, 3H). 1.29 (t, 3H, J = 7.1 Hz), 1.04 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.1, 164.3, 157.3, 150.6, 134.0, 132.3, 124.5, 116.0, 111.2, 90.9, 61.7, 59.7, 55.4, 18.2, 14.4, 13.7; HR-MS (ESI+) m/z calculated for $[C_{16}H_{22}NO_5]^+ = [M+H]^+$: 308.1492; found: 308.1507.



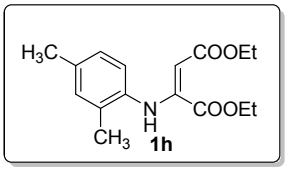
Dimethyl 2-((4-methoxy-2-methylphenyl)amino)maleate (1e)

Yellow viscous oil; (85%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3273, 2952, 2839, 1740, 1667, 1610, 1507, 1436, 1276, 1215, 1144, 1036, 807, 777; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 9.39 (br s, 1H), 6.74-6.72 (m, 2H), 8.52 (dd, 1H, J_a = 8.6 and J_b = 2.7 Hz), 5.29 (s, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H), 2.3 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.4, 164.7, 157.2, 150.1, 133.3, 132.1, 124.0, 116.1, 111.4, 90.7, 55.3, 52.6, 51.1, 18.2; HR-MS (ESI+) m/z calculated for $[C_{14}H_{17}NNaO_5]^+ = [M+Na]^+$: 302.0999; found: 302.1012.



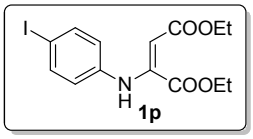
Dimethyl 2-((2,5-dimethylphenyl)amino)maleate (1f)

Yellow solid; (80%); mp 64−66 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3270, 2951, 1741, 1668, 1612, 1435, 1385, 1275, 1215, 1187, 1147, 1069, 1031, 798, 773; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.55 (br s, 1H), 7.00-6.93 (m, 2H), 6.63 (d, 1H, *J* = 7.3 Hz), 5.36 (s, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 2.3 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.3, 164.9, 149.4, 138.9, 137.8, 129.3, 126.8, 125.6, 119.7, 92.1, 52.7, 51.1, 20.5, 13.8; HR-MS (ESI+) m/z calculated for $[C_{14}H_{17}NNaO_4]^+$ = $[M+Na]^+$: 286.1050; found: 286.1061.



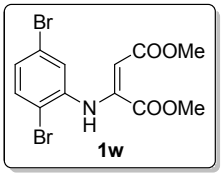
Diethyl 2-((2,4-dimethylphenyl)amino)maleate (1h)

Yellow viscous oil; (90%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3272, 2980, 1738, 1665, 1608, 1511, 1449, 1368, 1274, 1207, 1147, 1039, 813, 776; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.47 (br s, 1H), 6.99 (s, 1H), 6.88 (d, 1H, *J* = 8.3 Hz), 6.68 (d, 1H, *J* = 7.8 Hz), 5.33 (s, 1H), 4.19 (q, 2H, *J* = 7.3 Hz), 4.13 (q, 2H, *J* = 7.3 Hz), 2.3 (s, 3H), 2.27 (s, 3H), 1.30 (t, 3H, *J* = 7.1 Hz), 1.07 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.0, 164.4, 149.8, 136.5, 134.6, 131.3, 130.8, 126.9, 122.2, 91.8, 61.8, 59.8, 20.8, 17.8, 14.4, 13.6; HR-MS (ESI+) m/z calculated for $[C_{16}H_{21}NNaO_4]^+$ = $[M+Na]^+$: 314.1363; found: 314.1378.



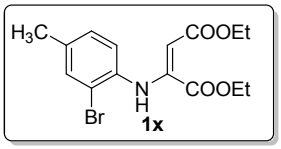
Diethyl 2-((4-iodophenyl)amino)maleate (**1p**)

Yellow viscous oil; (65%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3273, 2980, 2933, 1733, 1666, 1611, 1586, 1491, 1392, 1366, 1267, 1203, 1139, 1095, 1037, 1006, 858, 815, 779; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 9.59 (br s, 1H), 7.55 (d, 2H, J = 8.8 Hz), 6.65 (d, 2H, J = 8.8 Hz), 5.43 (s, 1H), 4.21-4.14 (m, 4H), 1.29 (t, 3H, J = 7.1 Hz), 1.14 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.4, 164.0, 147.5, 140.2, 138.0, 122.7, 95.3, 87.4, 62.2, 60.1, 14.3, 13.8; HR-MS (ESI+) m/z calculated for $[C_{14}H_{17}INO_4]^+ = [M+H]^+$: 390.0197; found: 390.0212.



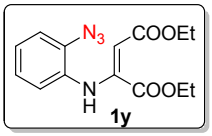
Dimethyl 2-((2,5-dibromophenyl)amino)maleate (**1w**)

Yellow solid; (45%); mp 120−122 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3357, 2954, 2924, 2118, 1739, 1579, 1509, 1437, 1401, 1259, 1231, 1159, 1082, 1023, 875, 801, 756; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 9.72 (br s, 1H), 7.41 (d, 1H, J = 8.8 Hz), 7.04 (dd, 1H, J_a = 8.8 and J_b = 2 Hz), 6.86 (d, 1H, J = 2 Hz), 5.63 (s, 1H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.3, 164.0, 145.6, 140.0, 134.0, 127.5, 123.5, 121.0, 114.1, 97.7, 53.0, 51.6; HR-MS (ESI+) m/z calculated for $[C_{12}H_{12}Br_2NO_4]^+ = [M+H]^+$: 391.9128; found: 391.9139.



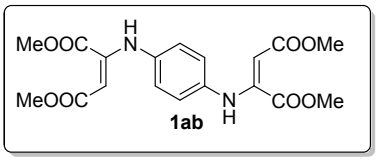
Diethyl 2-((2-bromo-4-methylphenyl)amino)maleate (1x)

Yellow viscous oil; (65%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3271, 2985, 2940, 1717, 1671, 1611, 1368, 1234, 1206, 1094, 1035, 856, 746, 673; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.65 (br s, 1H), 7.37 (s, 1H), 6.98 (d, 1H, *J* = 7.8 Hz), 6.7 (d, 1H, *J* = 8.3 Hz), 5.47 (s, 1H), 4.21 (q, 2H, *J* = 7.3 Hz), 4.16 (q, 2H, *J* = 7.24 Hz), 2.28 (s, 3H), 1.3 (t, 3H, *J* =7.1 Hz), 1.12 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.3, 164.0, 147.4, 136.3, 135.3, 133.3, 128.4, 121.7, 116.1, 95.0, 62.1, 60.1, 20.5, 14.4, 13.7; HR-MS (ESI+) m/z calculated for $[C_{15}H_{18}BrKNO_4]^+$ = $[M+K]^+$: 394.0051; found: 394.0052.



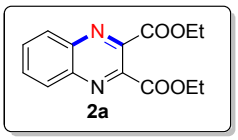
Diethyl 2-((2-azidophenyl)amino)maleate (1y)

Yellow viscous oil; (58%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2982, 2935, 2126, 2105, 1734, 1668, 1611, 1505, 1449, 1367, 1264, 1203, 1139, 1093, 1037, 748; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.58 (br s, 1H), 7.14-7.07 (m, 2H), 7.03-6.99 (m, 1H), 6.78 (d, 1H, *J* = 7.8 Hz), 5.47 (s, 1H), (q, 2H, *J* = 7.1 Hz), 4.16 (q, 2H, *J* = 7.34 Hz), 1.31-1.29 (m, 3H), 1.15 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.4, 164.0, 147.2, 131.7, 131.1, 124.9, 124.8, 121.4, 118.7, 95.0, 62.1, 60.1, 14.3, 13.7; HR-MS (ESI+) m/z calculated for $[C_{14}H_{17}N_4O_4]^+$ = $[M+H]^+$: 305.1244; found: 305.1246.



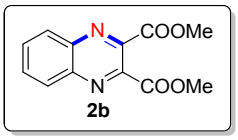
(*E*)-tetramethyl 2,2'-(1,4-phenylenebis(azanediyl))dimaleate (1ab)

Yellow solid; (61%); mp 116-118; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3277, 2965, 1737, 1668, 1602, 1518, 1435, 1390, 1268, 1206, 1182, 1139, 1030, 977, 850, 777; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.89 (br s, 1H), 7.50-7.46 (m, 2H), 7.35-7.25 (m, 2H), 7.09-7.08 (m, 1H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 168.9, 138.0, 128.9, 124.3, 120.1, 24.0.; HR-MS (ESI+) m/z calculated for $[C_{18}H_{20}KN_2O_4]^+ = [M+K]^+$: 431.0851; found: 431.0872.



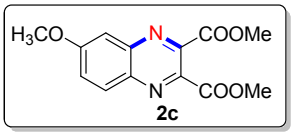
Diethyl quinoxaline-2,3-dicarboxylate (2a)[3]

White solid; (78%); mp 128−130 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2981, 2925, 1745, 1726, 1550, 1510, 1468, 1410, 1370, 1328, 1231, 1182, 1113, 1061, 1017, 860, 767; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.27 (dd, 2H, J_a = 9.84 and J_b = 2.96 Hz), 7.93 (dd, 2H, J_a = 9.84 and J_b = 2.96), 4.56 (q, 4H, J = 7 Hz), 1.48 (t, 6H, J = 7.1, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.8, 144.2, 141.4, 132.5, 129.9, 62.9, 14.1; HR-MS (ESI+) m/z calculated for $[C_{14}H_{15}N_2O_4]^+ = [M+H]^+$: 275.1026; found: 275.1027.



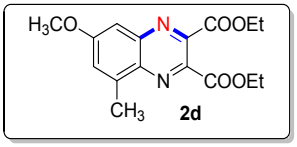
Dimethyl quinoxaline-2,3-dicarboxylate (2b)[4]

White solid; (72%); mp 122−124 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2008, 2953, 1720, 1551, 1444, 1400, 1325, 1288, 1230, 1191, 1165, 1114, 1063, 952, 851, 766, 596; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.27 (dd, 2H, J_a = 6.4 and J_b = 3.4 Hz), 7.95 (dd, 2H, J_a = 6.4 and J_b = 3.4 Hz), 4.1 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.2, 143.8, 141.4, 132.7, 129.9, 53.6; HR-MS (ESI+) m/z calculated for $[C_{12}H_{11}N_2O_4]^+ = [M+H]^+$: 247.0713; found: 247.0714.



Dimethyl 6-methoxyquinoxaline-2,3-dicarboxylate (2c)[5]

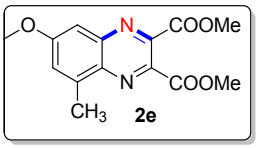
White solid; (67%); mp 96−98 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3008, 2954, 1743, 1726, 1617, 1492, 1442, 1414, 1308, 1215, 1176, 1142, 1122, 1067, 1019, 859, 837, 787; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.11 (d, 1H, J = 9.3 Hz), 7.55 (dd, 1H, J_a = 9.3 and J_b = 2.9 Hz),7.48 (d, 1H, J = 2.4 Hz), 4.07 (s, 3H), 4.06 (s, 3H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.6, 163.1, 144.7, 143.6, 140.4, 137.8, 130.9, 126.8, 114.5, 106.6, 56.2, 53.2, 53.5; HR-MS (ESI+) m/z calculated for $[C_{13}H_{13}N_2O_5]^+ = [M+H]^+$: 277.0819; found: 277.0815.



Diethyl 7-methoxy-5-methylquinoxaline-2,3-dicarboxylate (2d)

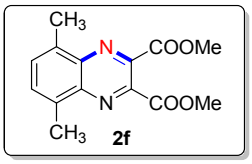
Brown solid; (80%); mp 80−82 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2954, 1741, 1716, 1615, 1508, 1442, 1404, 1306, 1286, 1225, 1171, 1096, 1056, 853. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.37 (s, 1H), 7.33 (d, 1H, J = 2.9 Hz), 4.56 (q, 4H, J = 7 Hz), 3.95 (s, 3H), 2.78 (s,

3H), 1.45 (t, 6H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.3, 165.2, 162.5, 143.9, 143.8, 140.5, 139.9, 137.5, 125.7, 104.6, 63.0, 55.9, 29.7, 17.1, 14.2. 14.1; HR-MS (ESI+) m/z calculated for $[C_{16}H_{22}N_3O_5]^+ = [M+NH_4]^+$: 336.1554; found: 336.1564.



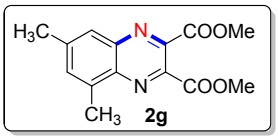
Dimethyl 7-methoxy-5-methylquinoxaline-2,3-dicarboxylate (2e)

White solid; (75%); mp 106−108 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2983, 2925, 1740, 1716, 1614, 1454, 1409, 1341, 1285, 1212, 1174, 1142, 1096, 1056, 1021, 841; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.37 (s, 1H), 7.32 (d, 1H, J = 2.4 Hz), 4.07 (s, 3H), 4.06 (s, 3H), 3.95 (s, 3H), 2.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.8, 165.6, 162.6, 143.8, 143.3, 140.3, 139.9, 137.6, 126.0, 104.5, 55.9, 53.5, 53.3, 17.1; HR-MS (ESI+) m/z calculated for $[C_{14}H_{15}N_2O_5]^+ = [M+H]^+$: 291.0975; found: 291.0962.



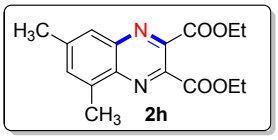
Dimethyl 5,8-dimethylquinoxaline-2,3-dicarboxylate (2f)

White solid; (65%); mp 128−130 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2984, 2928, 1784, 1720, 1692, 1661, 1549, 1530, 1483, 1450, 1385, 1318, 1289, 1259, 1162, 1095 ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.63 (s, 2H), 4.07 (s, 6H), 2.78 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.8, 142.1, 140.9, 136.1, 132.1, 53.3, 17.0; HR-MS (ESI+) m/z calculated for $[C_{14}H_{15}N_2O_4]^+ = [M+H]^+$: 275.1026; found: 275.1019.



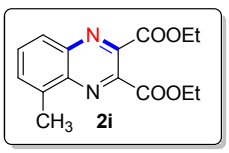
Dimethyl 5,7-dimethylquinoxaline-2,3-dicarboxylate (2g)

White solid; (68%); mp 96−98 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2955, 2924, 1718, 1616, 1441, 1305, 1284, 1243, 1220, 1165, 1139, 1093, 1050, 964, 857, 788; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.85 (s, 1H), 7.6 (s, 1H), 4.07 (s, 3H), 4.06 (s, 3H), 2.85 (s, 3H), 2.59 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 143.4, 142.7, 142.4, 141.8, 138.0, 135.1, 126.4, 53.5, 53.2, 22.1, 17.0; HR-MS (ESI+) m/z calculated for $[C_{14}H_{15}N_2O_4]^+ = [M+H]^+$: 275.1026; found: 275.1023.



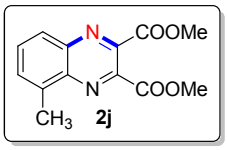
Diethyl 5,7-dimethylquinoxaline-2,3-dicarboxylate (2h)

Yellow solid; (64%); mp 60−63 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2982, 2932, 1743, 1721, 1619, 1465, 1407, 1372, 1342, 1303, 1240, 1215, 1168, 1139, 1050, 1018, 860. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.84 (s, 1H), 7.58 (s, 1H), 4.56 (q, 4H, J = 7.1 Hz), 2.8 (s, 3H), 2.58 (s, 3H), 1.46 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.4, 165.1, 143.2, 143.1, 142.6, 141.8, 134.8, 126.4, 62.7, 62.5, 22.1, 17.0, 14.1, 14.0; HR-MS (ESI+) m/z calculated for $[C_{16}H_{19}N_2O_4]^+ = [M+H]^+$: 303.1339; found: 303.1334. 4.56 (q, 4H, J = 7 Hz), 1.48 (t, 6H, J = 7.1, 6H)



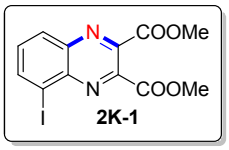
Diethyl 5-methylquinoxaline-2,3-dicarboxylate (2i)

Brown oil; (62%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2958, 2925, 1727, 1574, 1464, 1372, 1335, 1275, 1228, 118, 1135, 1090, 1018, 858, 802, 764; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.07 (d, 1H, J = 8.3 Hz), 7.80-7.82 (m, 2H), 4.50 (q, 4H, J = 7.2 Hz), 2.83 (s, 3H), 1.46 (t, 6H, J = 7.1); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.3, 164.8, 143.6, 140.7, 132.4, 132.1, 130.6, 127.7, 125.9, 121.6, 62.8, 62.6, 17.1, 14.1, 14.0; HR-MS (ESI+) m/z calculated for $[C_{15}H_{17}N_2O_4]^+$ = $[M+H]^+$: 289.1183; found: 289.1183.



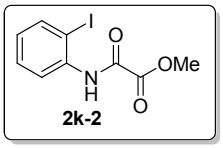
Dimethyl 5-methylquinoxaline-2,3-dicarboxylate (2j)[5]

White solid; (61%); mp 140−142 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2956, 1744, 1723, 1571, 1447, 1395, 1307, 1284, 1250, 1225, 166, 1134, 1096, 1034, 870, 800, 778; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.08 (d, 1H, J = 8.3 Hz), 7.82-7.73 (m, 2H), 4.08 (s, 3H), 4.07 (s, 3H), 2.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.8, 165.2, 143.5, 142.4, 141.5, 140.8, 138.7, 132.6, 132.3, 127.7, 53.6, 53.4, 17.1; HR-MS (ESI+) m/z calculated for $[C_{13}H_{13}N_2O_4]^+$ = $[M+H]^+$: 261.0870; found: 261.0866.



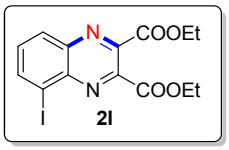
Dimethyl 5-iodoquinoxaline-2,3-dicarboxylate (2k-1)

White solid; (51%); mp 100−102 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2953, 2924, 2852, 175, 1543, 1442, 1391, 1333, 1277, 1232, 1202, 1163, 122, 1065, 802, 762; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.52 (dd, 1H, J_a = 7.3 and J_b = 1 Hz), 8.24-8.25 (m, 1H), 7.65 (t, 1H, J = 8.1 Hz), 4.1 (s, 3H), 4.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.8, 164.5, 145.1, 144.0, 143.0, 141.9, 141.4, 133.5, 130.6, 102.6, 53.8, 53.6; HR-MS (ESI+) m/z calculated for $[C_{12}H_{10}IN_2O_4]^+$ = $[M+H]^+$: 372.9650; found: 372.9673.



Methyl 2-((2-iodophenyl)amino)-2-oxoacetate (2k-2)

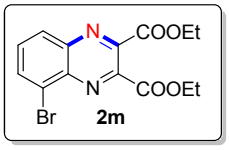
White solid; (18%); mp 100−102 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3324, 2961, 1729, 1703, 1581, 1527, 1433, 1316, 1289, 1168, 1014, 975, 744, 659. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 9.34 (br s), 8.33 (dd, 1H, J_a = 8.3 and J_b = 1.5 Hz), 7.83 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 7.42-7.38 (m, 1H), 6.93 (td, 1H, J_a = 7.2 and J_b = 1.2 Hz), 4.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 161.1, 153.7, 139.2, 137.0, 129.5, 127.1, 121.4, 89.7, 54.2; HR-MS (ESI+) m/z calculated for $[C_9H_8INNaO_3]^+$ = $[M+H]^+$: 327.9441; found: 327.9448.



Diethyl 5-iodoquinoxaline-2,3-dicarboxylate (2l)

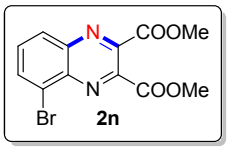
White solid; (59%); mp 110−112 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2982, 2932, 1724, 1541, 1467, 1445, 1407, 1329, 1299, 1274, 1226, 1198, 1174, 1119, 1062, 2026, 801, 762; ^1H

NMR ($CDCl_3$, 400 MHz): δ_H = 8.50 (dd, 1H, J_a = 7.3 and J_b = 1 Hz), 8.23 (dd, 1H, J_a = 8.3 and J_b = 1 Hz),7.63 (t, 1H, J = 8.1 Hz), 4.55 (q, 4H, J = 7.2 Hz), 1.47 (t, 6H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.3, 145.3, 144.5, 142.8, 141.8, 141.3, 133.3, 130.6, 102.6, 63.1, 62.9, 14.1, 14.1; HR-MS (ESI+) m/z calculated for $[C_{14}H_{14}IN_2O_4]^+$ = $[M+H]^+$: 400.9993; found: 400.9997.



Diethyl 5-bromoquinoxaline-2,3-dicarboxylate (2m)

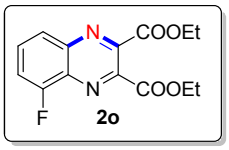
Brown solid; (61%); mp 90−92 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2982, 2932, 1746, 1727, 1661, 1549, 1513, 1469, 1451, 1389, 1335, 1300, 1227, 1176, 1122, 1064; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.23 (d, 2H, J = 7.8 Hz), 7.79-7.75 (m, 1H), 4.58 (q, 4H, J = 7.3 Hz), 1.47 (t, 6H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.5, 164.3, 145.1, 144.4, 142.3, 139.3, 135.9, 132.5, 129.6, 124.8, 63.1, 62.9, 14.1, 14.1; HR-MS (ESI+) m/z calculated for $[C_{14}H_{13}BrN_2NaO_4]^+$ = $[M+Na]^+$: 374.9951; found: 374.9948.



Dimethyl 5-bromoquinoxaline-2,3-dicarboxylate (2n)

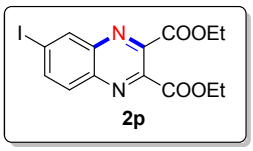
Brown solid; (58%); mp 128−130 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2954, 1728, 1547, 1442, 1391, 1334, 1301, 1277, 1231, 1201, 1164, 1123, 1066, 862, 762; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.22 (dd, 2H, J_a = 7.3 and J_b = 5.9 Hz), 7.78 (t, 1H, J = 8.1 Hz), 4.09 (s, 6H); ^{13}C

NMR ($CDCl_3$, 100 MHz): 164.9, 164.6, 144.7, 144.0, 142.3, 139.4, 136.1, 132.7, 129.6, 124.8, 53.7, 53.6; HR-MS (ESI+) m/z calculated for $[C_{12}H_{10}BrN_2O_4]^+$ = $[M+H]^+$: 324.9818; found: 324.9819.



Diethyl 5-fluoroquinoxaline-2,3-dicarboxylate (2o)

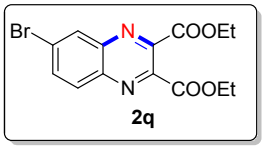
Yellow viscous oil; (57%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3062, 2975, 2931, 1737, 1719, 1567, 1479, 1412, 1391, 1337, 1281, 1226, 1172, 1138, 1005, 808, 761; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.08 (d, 1H, J = 8.8 Hz), 7.88 (td, 1H, J_a = 8.1 and J_b = 5.4 Hz), 7.63-7.26 (m, 1H), 4.55 (q, 4H, J = 7.2 Hz), 1.47 (t, 6H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.4, 164.3, 158.5, 155.9, 144.9, 142.1, 132.1, 132.0, 125.7, 125.6, 116.3, 63.1, 63.0, 14.1; HR-MS (ESI+) m/z calculated for $[C_{14}H_{14}FN_2O_4]^+$ = $[M+H]^+$: 293.0932; found: 293.0933.



Dimethyl 6-iodoquinoxaline-2,3-dicarboxylate (2p)

Yellow viscous oil; (61%);IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2981, 2924, 1723, 1591, 1469, 1409, 1329, 1295, 1211, 1151, 1119, 1061, 1016, 918, 831; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.68 (d, 1H, J = 1.5 Hz), 8.15 (dd, 1H, J_a = 8.8 and J_b = 2Hz), 7.95 (d, 1H, J = 8.8 Hz), 4.54 (q, 4H, J = 7.3 Hz), 1.46 (t, 6, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.5, 144.9, 144.3, 141.9,

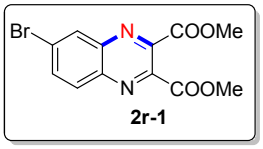
141.4, 140.5, 138.8, 137.9, 130.8, 117.3, 99.3, 63.1, 63.0, 14.1; HR-MS (ESI+) m/z calculated for $[C_{14}H_{14}IN_2O_4]^+ = [M+H]^+$: 400.9993; found: 400.9994.



2q

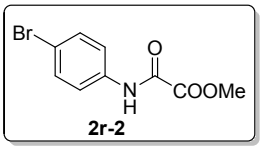
Diethyl 6-bromoquinoxaline-2,3-dicarboxylate (**2q**)

Brown solid; (64%); mp 78−80 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2985, 2927, 1741, 1512, 1292, 1258, 1225, 1159, 1094, 1013, 841; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.43 (d, 1H, J = 2 Hz), 8.11 (d, 1H, J = 8.8 Hz), 7.98 (dd, 1H, J_a = 9.3 and J_b = 2 Hz), 4.54 (q, 4H, J = 7 Hz), 1.46 (t, 6H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.5, 164.4, 145.2, 144.1, 141.8, 140.1, 136.1, 132.1, 131.0, 127.1, 63.0, 14.1; HR-MS (ESI+) m/z calculated for $[C_{14}H_{14}BrN_2O_4]^+ = [M+H]^+$: 353.0131; found: 353.0145.



2r-1

+



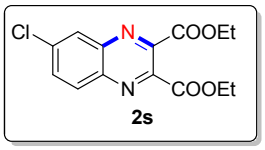
2r-2

Dimethyl 6-bromoquinoxaline-2,3-dicarboxylate (**2r-1**)[5] and

Methyl 2-((4-bromophenyl)amino)-2-oxoacetate (2r-2)

White solid; (58%); mp 116−118 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2954, 1732, 1598, 1475, 1441, 1336, 1299, 1222, 1151, 1122, 1067, 920, 837, 804; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.42 (d, 1H, J = 2 Hz), 8.11-8.09 (m, 1H), 7.99 (dd, 1H, J_a = 8.8 and J_b = 2 Hz), 7.7 (d, 0.74H, J = 8.8 Hz), 7.40-7.37 (m, 1.2 H), 4.08 (s, 6H), 4.0 (s, 0.64H).; ^{13}C NMR ($CDCl_3$, 100 MHz): 164.9, 164.8, 144.8, 143.7, 141.9, 140.1, 136.4, 132.9, 132.7, 132.0, 132.1, 132.0, 131.1, 127.4,

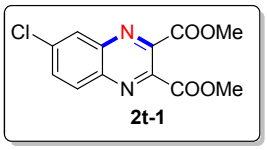
127.0, 125.9, 53.7; HR-MS (ESI+) m/z calculated for $[C_{12}H_{19}BrN_2NaO_4]^+ = [M+Na]^+$: 346.9638; found: 346.9638, and HR-MS (ESI+) m/z calculated for $[C_9H_8BrNNaO_3]^+ = [M+Na]^+$: 279.9580; found: 279.9582



2s

Diethyl 6-chloroquinoxaline-2,3-dicarboxylate (2s)

Brown solid; (61%); mp 118−120 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3332, 2956, 2921, 2852, 1700, 1595, 1543, 1492, 1402, 1298, 1176, 1081, 1013, 965, 849, 824, 711; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.25 (s, 1H), 8.2 (d, 1H, J = 8.8 Hz), 7.87-7.86 (m, 1H), 4.55 (q, 4H, J = 7.3 Hz), 1.47 (t, 6H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.6, 164.4, 145.2, 144.0, 141.7, 140.0, 138.8, 133.6, 131.1, 128.7, 63.1, 14.1, 14.0; HR-MS (ESI+) m/z calculated for $[C_{14}H_{14}ClN_2O_4]^+ = [M+H]^+$: 309.0637; found: 309.0651.

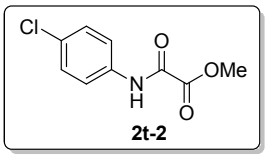


2t-1

Dimethyl 6-chloroquinoxaline-2,3-dicarboxylate (2t-1)[5]

Brown solid; (61%); mp 120−122 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2954, 1728, 2602, 1551, 1440, 1397, 1336, 1297, 1218, 1148, 1119, 1062, 929, 837, 804, 770. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.22 (d, 1H, J = 2 Hz), 8.18 (d, 1H, J = 8.8 Hz), 7.86 (dd, 1H, J_a = 8.8 and J_b = 2 Hz), 4.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.9, 164.8, 144.9, 143.5, 141.7, 139.9,

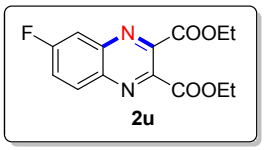
139.1, 133.8, 131.0, 128.6, 53.7; HR-MS (ESI+) m/z calculated for $[C_{12}H_{10}ClN_2O_4]^+ = [M+H]^+$: 281.0324; found: 281.0323.



2t-2

Methyl 2-((4-chlorophenyl)amino)-2-oxoacetate (2t-2)

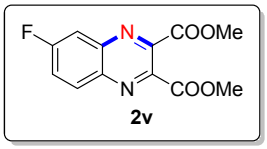
Brown white solid; (15%); mp 78−80 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3346, 2953, 2919, 1743, 1685, 1598, 1547, 1492, 1404, 1298, 1166, 1086, 837, 681; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.80 (br s, 1H), 7.60 (d, 2H, J = 8.8 Hz), 7.34 (d, 2H, J = 8.8 Hz), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 161.3, 153.6, 134.8, 130.8, 129.4, 121.1, 54.2; HR-MS (ESI+) m/z calculated for $[C_9H_{12}ClN_2O_3]^+ = [M+NH_4]^+$: 231.0531; found: 231.0526.



2u

Diethyl 6-fluoroquinoxaline-2,3-dicarboxylate (2u)

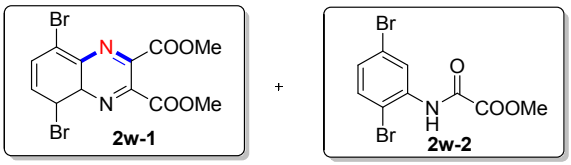
Viscous oil; (62%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2984, 2928, 1744, 1621, 1490, 1299, 1224, 1188, 1112, 1063, 1017841. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.27 (dd, 1H, J_a = 9.3 and J_b = 5.4 Hz), 7.86 (dd, 1H, J_a = 8.8 and J_b = 2.4 Hz), 7.72-7.67 (m, 1H), 4.56 (q, 4H, J = 7.1 Hz), 1.47 (m, 6H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.9, 164.7, 145.6, 143.6, 132.5, 132.4, 123.5, 123.3, 123.3, 116.4, 113.7, 113.5, 63.2, 14.3; HR-MS (ESI+) m/z calculated for $[C_{14}H_{14}FN_2O_4]^+ = [M+H]^+$: 293.0932; found: 293.0932.



2v

Dimethyl 6-fluoroquinoxaline-2,3-dicarboxylate (2v)[5]

Viscous oil; (70 mg, 64%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3363, 2956, 2119, 1733, 1621, 1484, 1442, 1345, 1289, 1233, 1167, 1140, 1100, 797, 760; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.27 (dd, 1H, J_a = 9.3 and J_b = 5.9 Hz), 7.86 (dd, 1H, J_a = 8.8 and J_b = 2.4 Hz), 7.74-7.76 (m, 1H), 4.085 (s, 3H), 4.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.8, 163.1, 145.1, 142.8, 142.6, 138.7, 132.3, 123.6, 123.3, 113.5, 113.3, 53.7; HR-MS (ESI+) m/z calculated for $[C_{12}H_{10}FN_2O_4]^+ = [M+H]^+$: 265.0619; found: 265.0630.

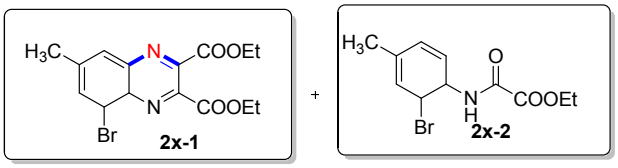


2w-1 + 2w-2

Dimethyl 5,8-dibromoquinoxaline-2,3-dicarboxylate (2w-1) and

Methyl 2-((3,6-dibromocyclohexa-2,4-dien-1-yl)amino)-2-oxoacetate (2w-2)

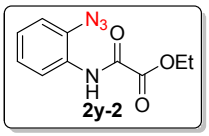
Brown solid; (70 mg, 57%); mp 190−192 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3008, 2952, 1745, 1724, 1533, 1455, 1439, 1388, 1282, 1227, 1192, 1154, 1066, 913, 797; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 10.36 (br s, 0.08H), 8.50 (d, 0.09H, J = 2.4 Hz), 8.09 (s, 2H), 7.4 (d, 0.11, J = 8.8 Hz), 7.11 (dd, 0.10H, J_a = 8.3 and J_b = 2.4 Hz), 4.1 (s, 6H), 3.89 (s, 0.41H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.4, 144.8, 140.2, 135.9, 124.4, 53.7; HR-MS (ESI+) m/z calculated for $[C_{12}H_{11}Br_2N_2O_4]^+ = [M+H]^+$: 404.9080; found: 404.9086 and HR-MS (ESI+) m/z calculated for $[C_9H_8Br_2NO_3]^+ = [M+H]^+$: 335.8865; found: 335.8872.



Diethyl 5-bromo-7-methylquinoxaline-2,3-dicarboxylate (**2x-1**) and

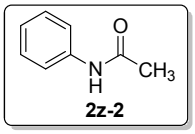
Methyl 2-((6-bromo-4-methylcyclohexa-2,4-dien-1-yl)amino)-2-oxoacetate (2x-2)

Brown solid; (48%); mp 82−84 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 2982, 2929, 1744, 1726, 1543, 1464, 1409, 1369, 1338, 1298, 1222, 1208, 1164, 1138, 1065, 1016, 855, 780; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 8.01 (d, 1H, J = 1.5 Hz), 7.98 (s, 1H), 7.59 (s, 0.12H), 7.33 (s, 0.31H), 4.54 (q, 4H, J = 7 Hz), 4.43 (q, 0.32, J = 7.3 Hz), 2.62 (s, 3H), 2.47 (s, 0.41H), 1.46 (t, 6H, J_a = 7.1 Hz), 1.36 (t, 0.66H, J = 7.2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.5, 154.4, 144.6, 144.0, 142.2, 138.1, 137.8, 128.5, 124.2, 63.0, 62.8, 21.8, 14.1, 14.1; HR-MS (ESI+) m/z calculated for $[C_{15}H_{17}BrN_2NaO_4]^+ = [M+H]^+$: 391.0264; found: 391.0262 and HR-MS (ESI+) m/z calculated for $[C_{11}H_{14}BrNNaO_3]^+ = [M+H]^+$: 310.0049; found: 310.0054



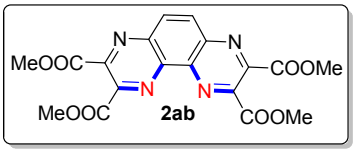
Ethyl 2-((2-azidophenyl)amino)-2-oxoacetate (2y-2)

Viscous solid; (23%); IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3366, 2924, 2853, 2130, 1713, 1598, 1530, 1478, 1452, 1294, 1175, 1017, 751; ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 9.28 (br s, 1H), 8.42-8.39 (m, 1H), 7.22-7.18 (m, 3H), 4.43 (q, 2H, J = 7.3 Hz), 1.44 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 161.0, 154.9, 129.8, 128.9, 125.7, 125.6, 120.8, 117.8, 63.8, 29.7; HR-MS (ESI+) m/z calculated for $[C_{10}H_{11}N_4O_3]^+ = [M+H]^+$: 235.0826; found: 235.0830.



_N_-phenylacetamide (2z)

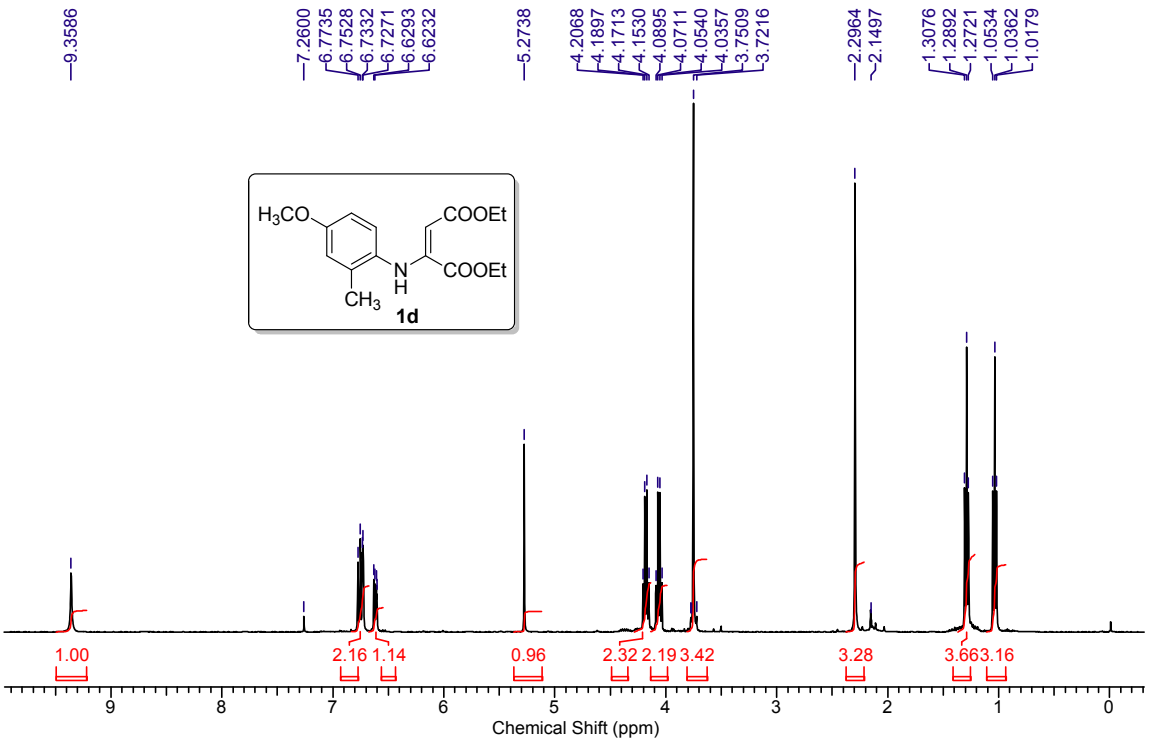
Brown solid; (35%); mp 111−113 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3305, 3197, 2954, 2922, 2852, 1733, 1666, 1598, 1542, 1497, 1440, 1370, 1316, 1260, 1078, 1030, 753, 692; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.89 (br s, 1H), 7.50-7.46 (m, 2H), 7.35-7.25 (m, 2H), 7.09-7.08 (m, 1H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 168.9, 138.0, 128.9, 124.3, 120.1, 24.0; HR-MS (ESI+) m/z calculated for $[C_8H_{10}NO]^+ = [M+H]^+$: 136.0757; found: 136.0745.



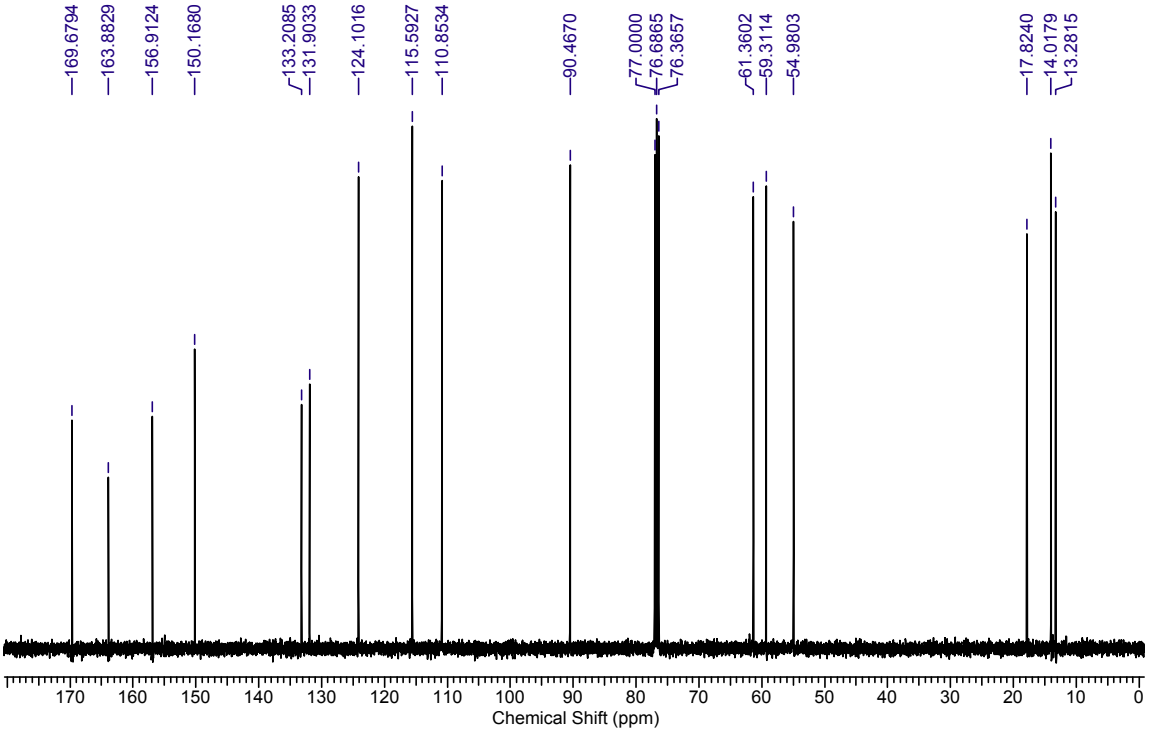
Tetramethyl pyrazino[2,3-*g*]quinoxaline-2,3,7,8-tetracarboxylate (2ab)

Light yellow solid; (52%); mp 118−120 ˚C; IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3252, 2956, 1820, 1732, 1625, 1548, 1516, 1445, 1369, 1287, 1248, 1200, 1164, 1110, 1055, 848, 797, 670 ; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.55 (s, 2H), 4.13 (s, 6H), 4.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.6, 164.4, 146.7, 144.3, 144.2, 139.3, 133.8, 53.9, 53.8; HR-MS (ESI+) m/z calculated for $[C_{18}H_{14}N4NaO_8]^+ = [M+Na]^+$: 437.0704; found: 437.0690.

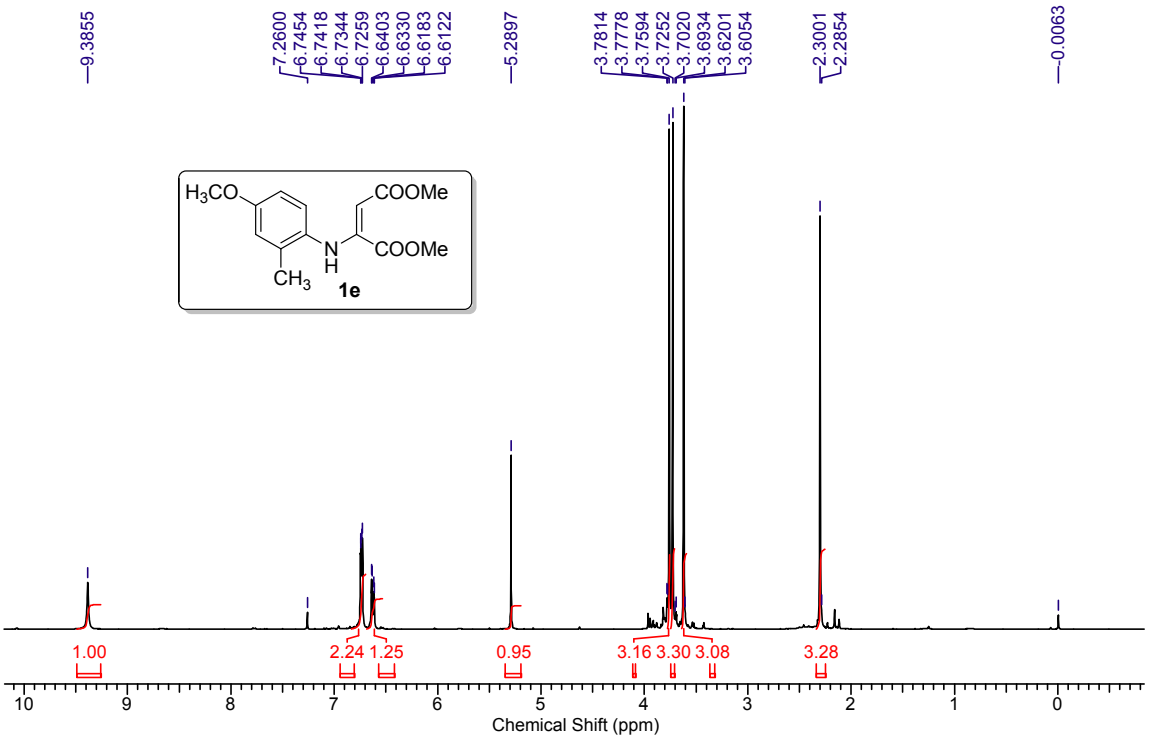
Copies of ^{1}H, ^{13}C NMR spectra of all compounds (**1d-1f, 1h, 1p, 1w, 1x and 1y**), (**2a-2j, 2k-1, 2k-2, 2l-2r, 2r-1, 2r-2, 2s, 2t-1, 2t-2, 2u, 2v, 2w-1, 2w-2, 2x-1, 2x-2, 2y-2 and 2z-2**)



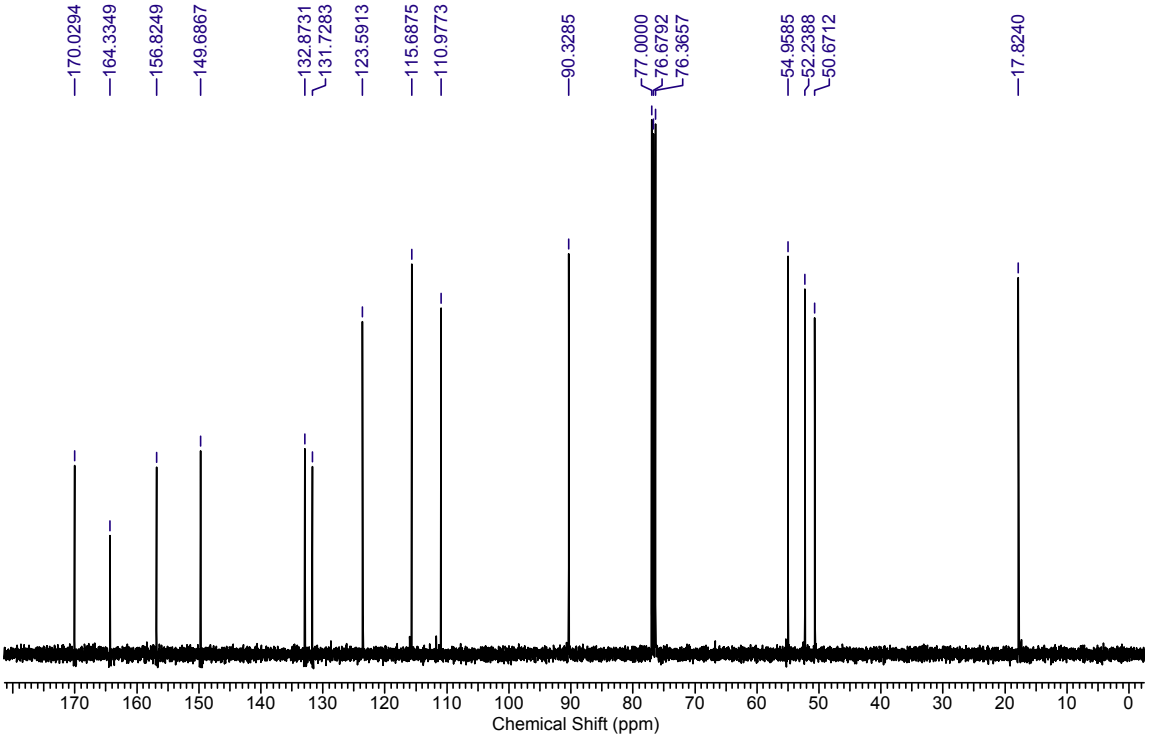
^{1}H NMR (400 MHz) spectrum of compound **1d** in $CDCl_3$



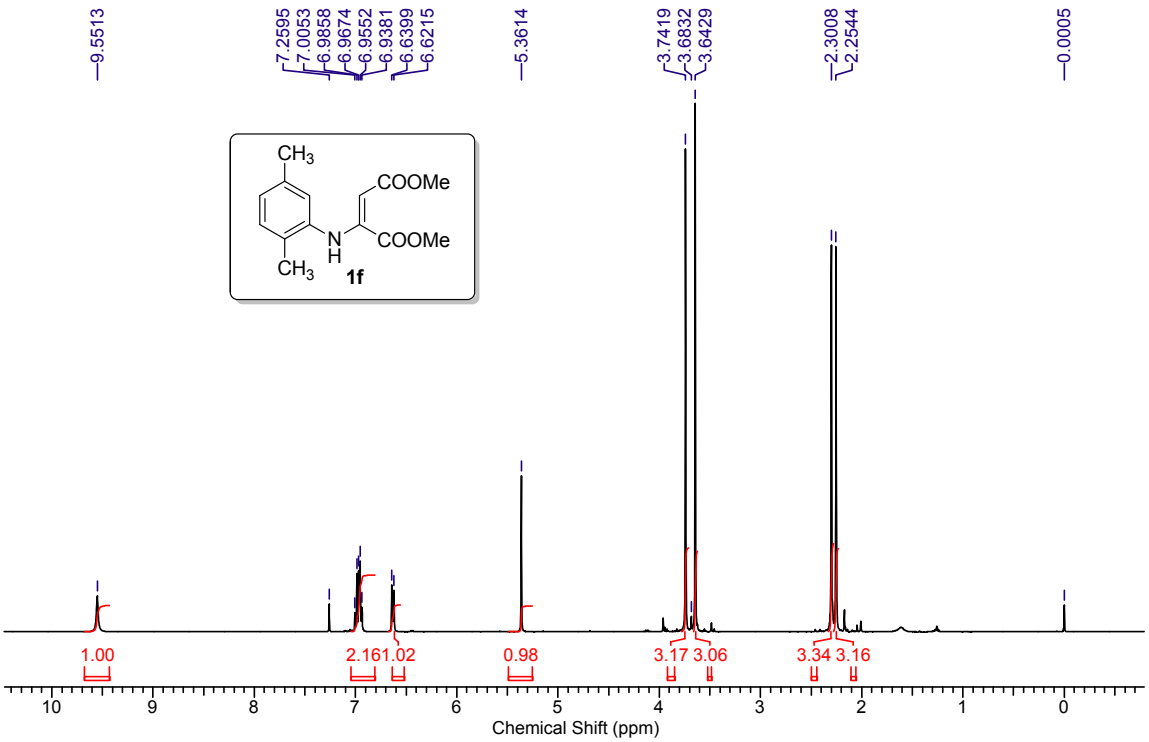
^{13}C NMR (100 MHz) spectrum of compound **1d** in $CDCl_3$



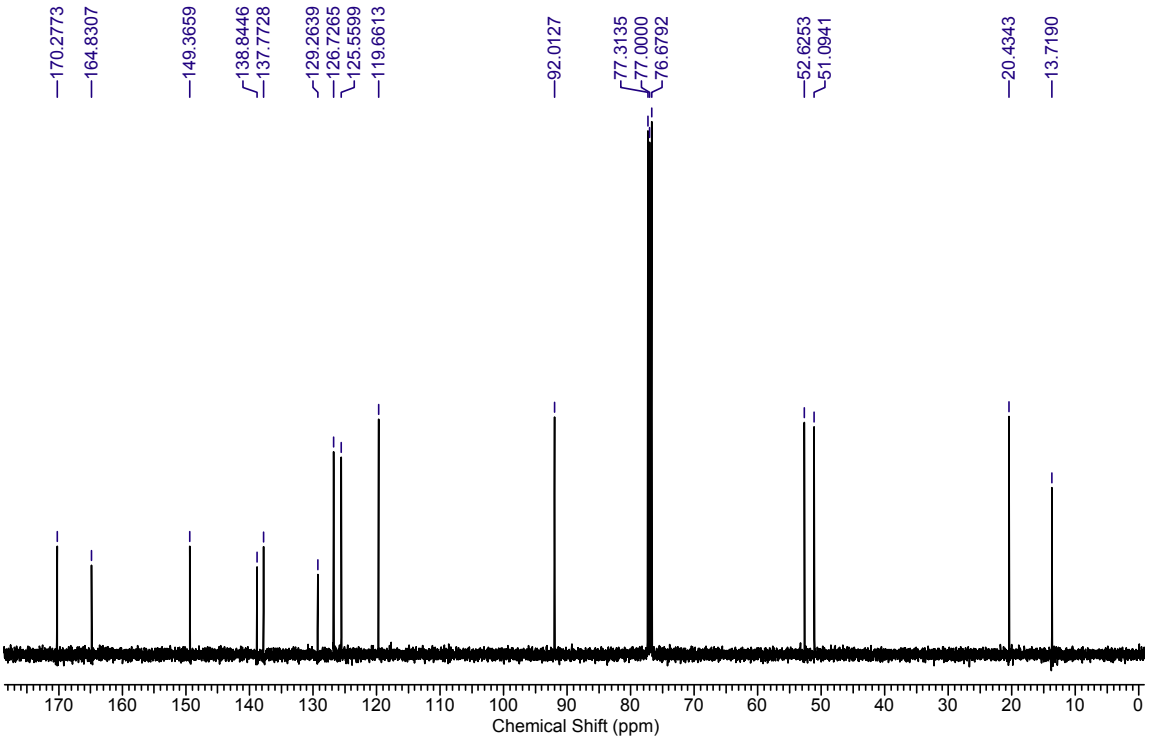
^{1}H NMR (400 MHz) spectrum of compound **1e** in $CDCl_3$



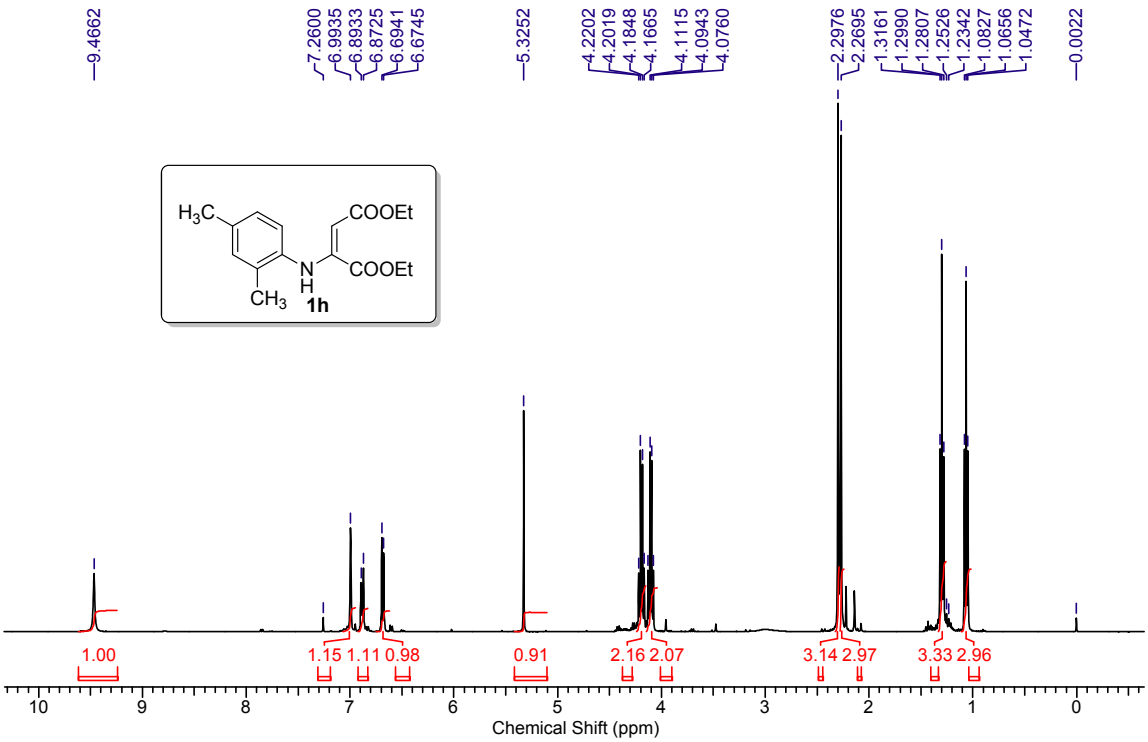
^{13}C NMR (100 MHz) spectrum of compound **1e** in $CDCl_3$



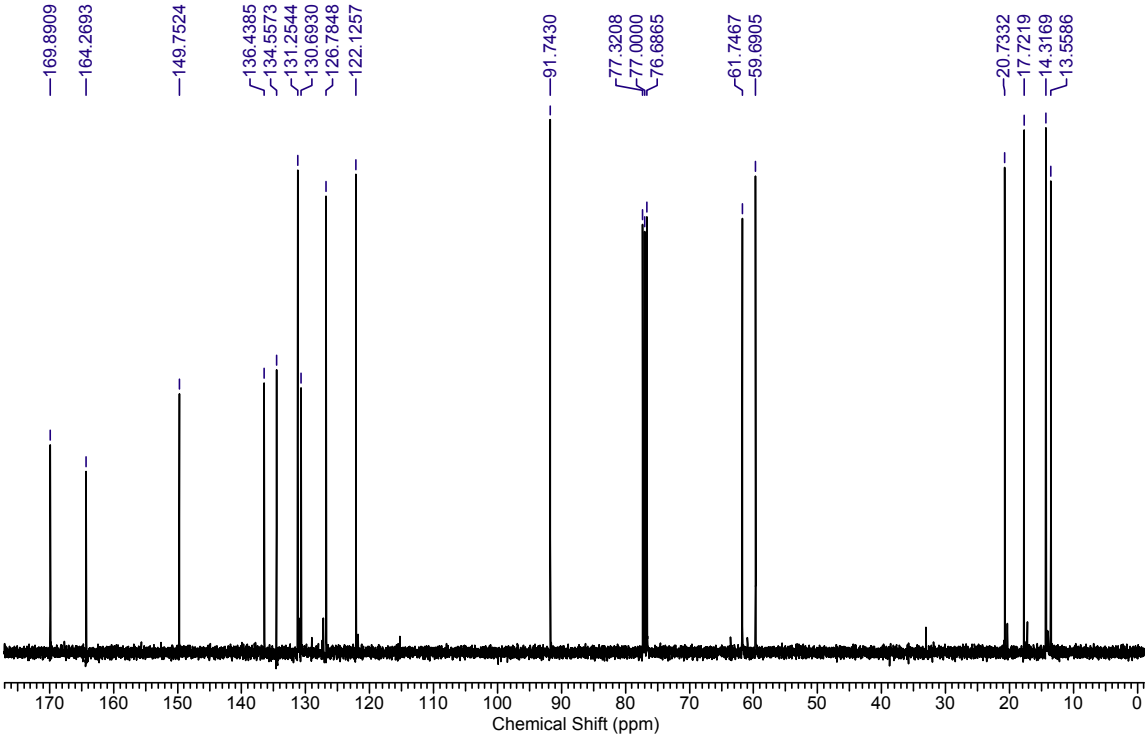
^{1}H NMR (400 MHz) spectrum of compound **1f** in $CDCl_3$



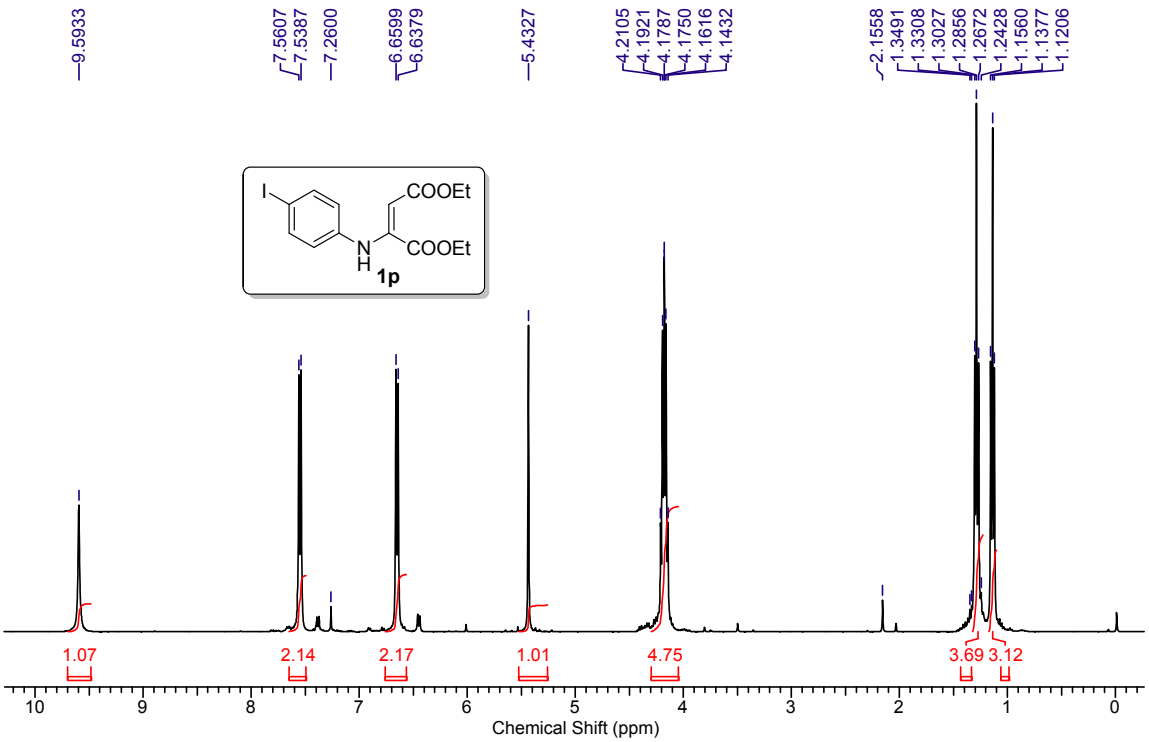
^{13}C NMR (100 MHz) spectrum of compound **1f** in $CDCl_3$



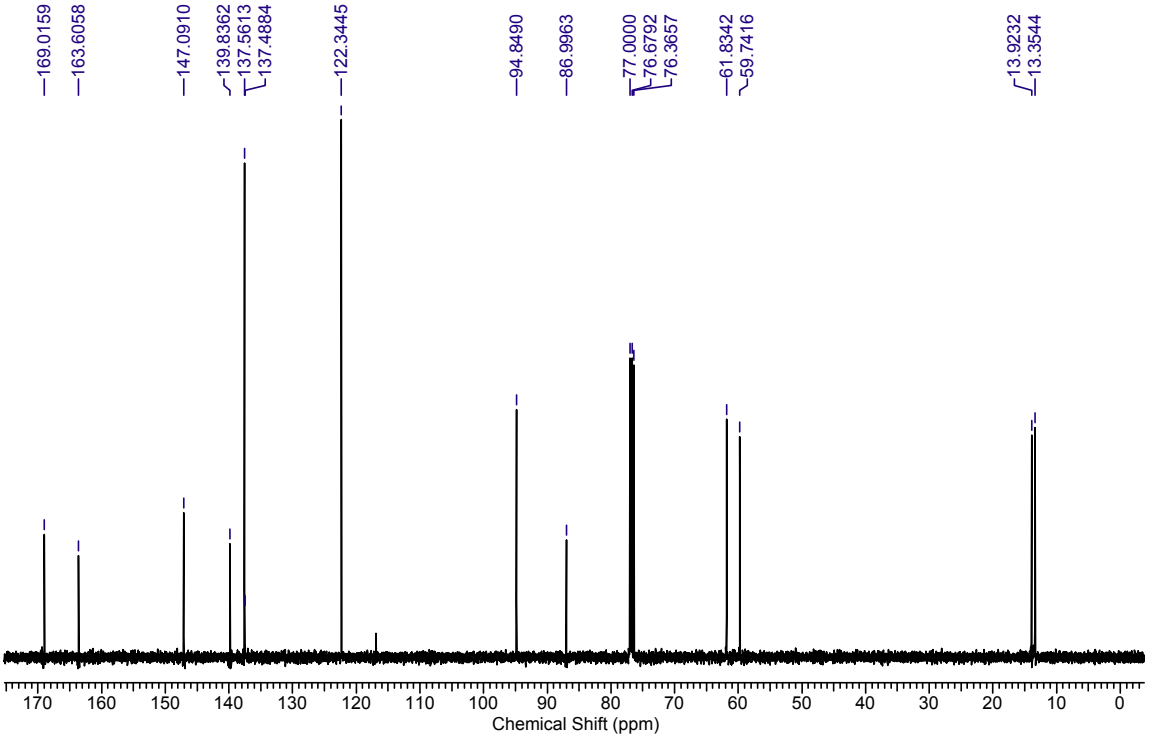
^{1}H NMR (400 MHz) spectrum of compound **1h** in $CDCl_3$



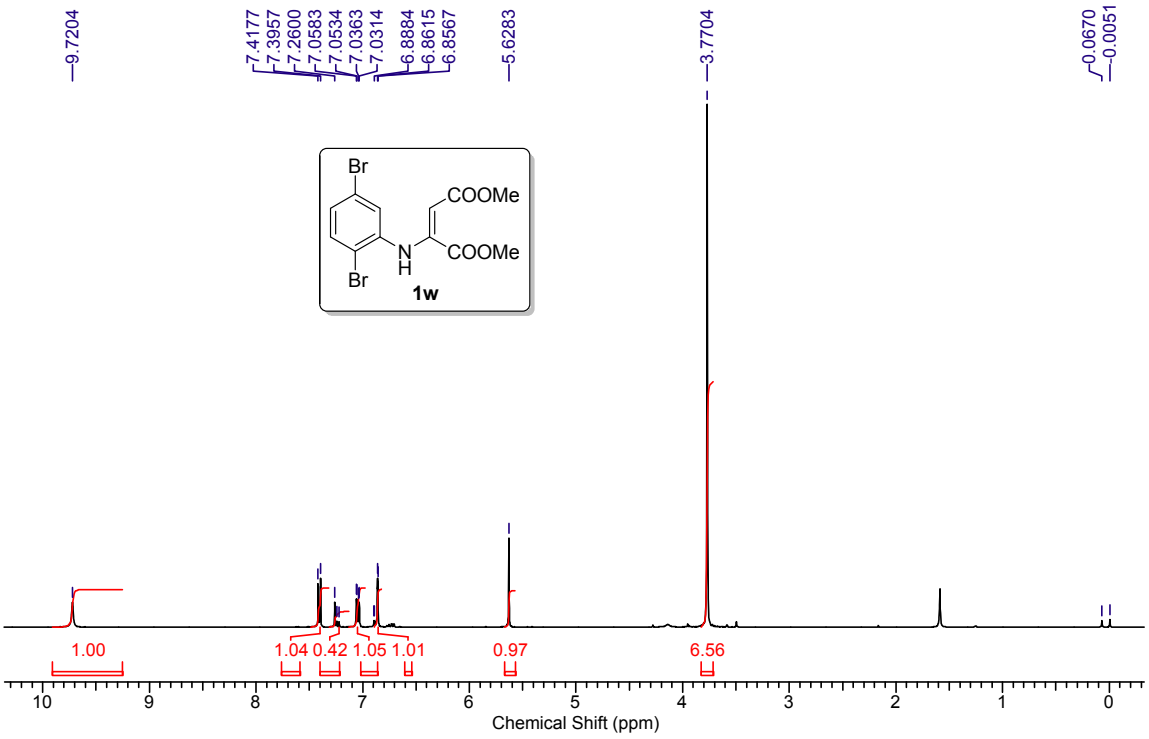
^{13}C NMR (100 MHz) spectrum of compound **1h** in $CDCl_3$



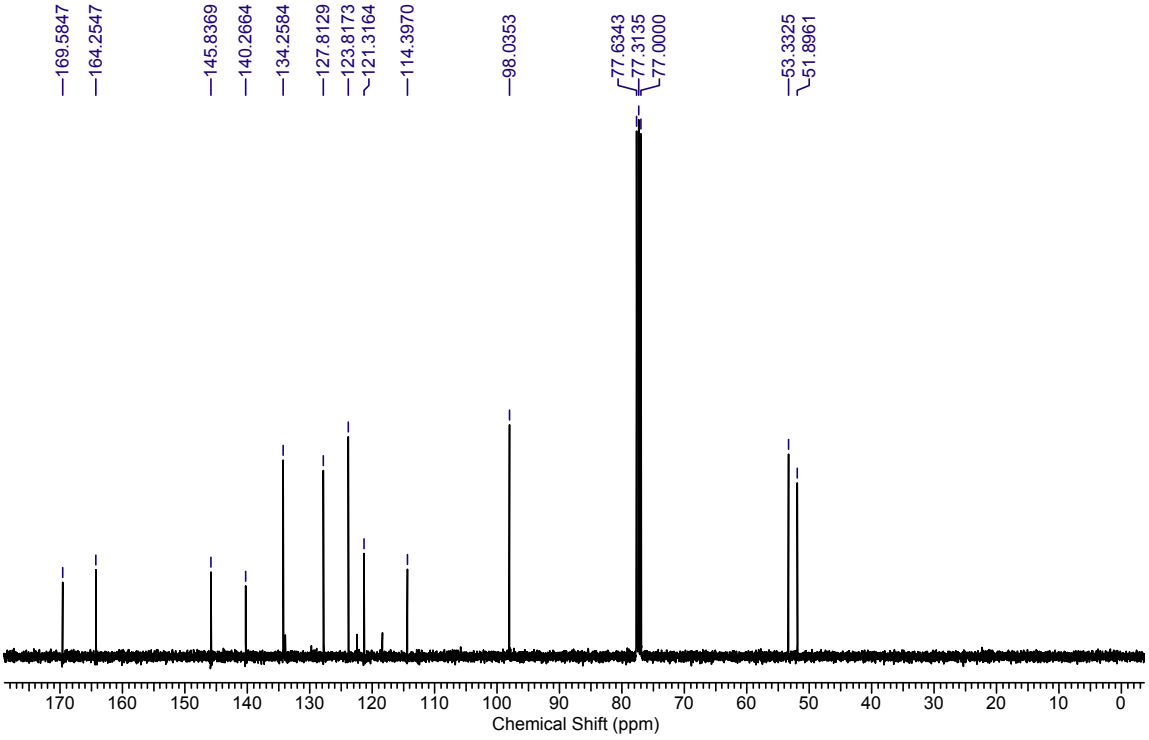
^{1}H NMR (400 MHz) spectrum of compound **1p** in $CDCl_3$



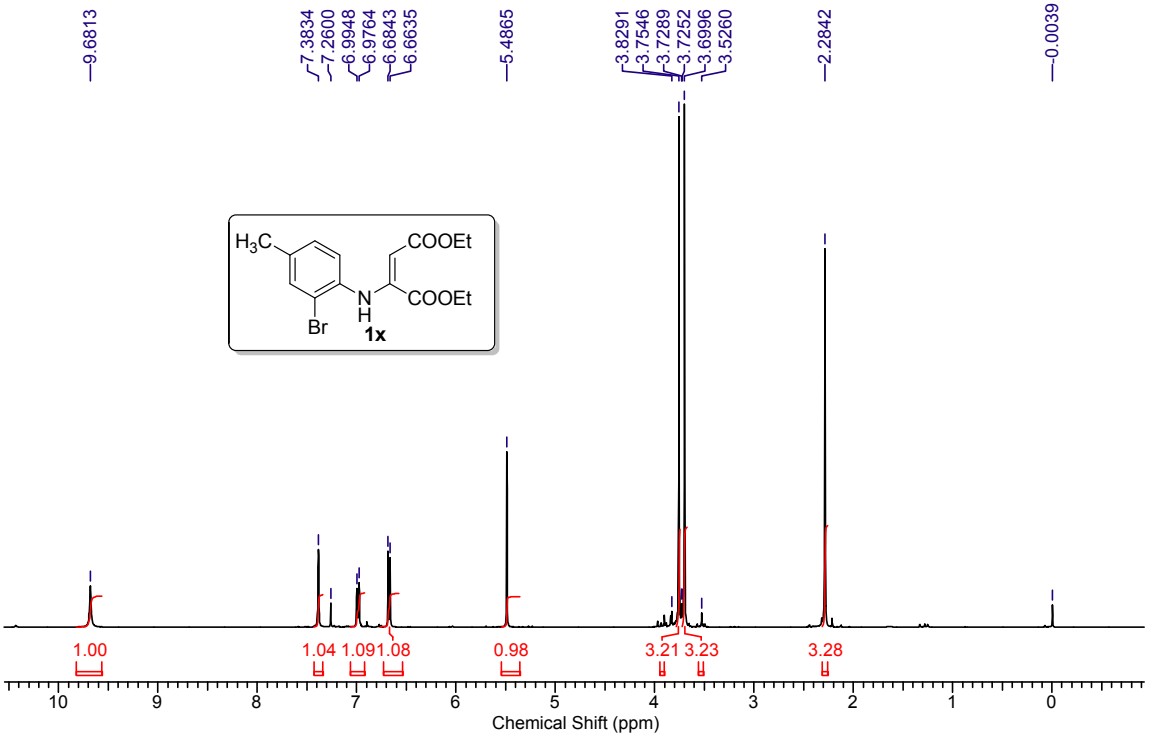
^{13}C NMR (100 MHz) spectrum of compound **1p** in $CDCl_3$



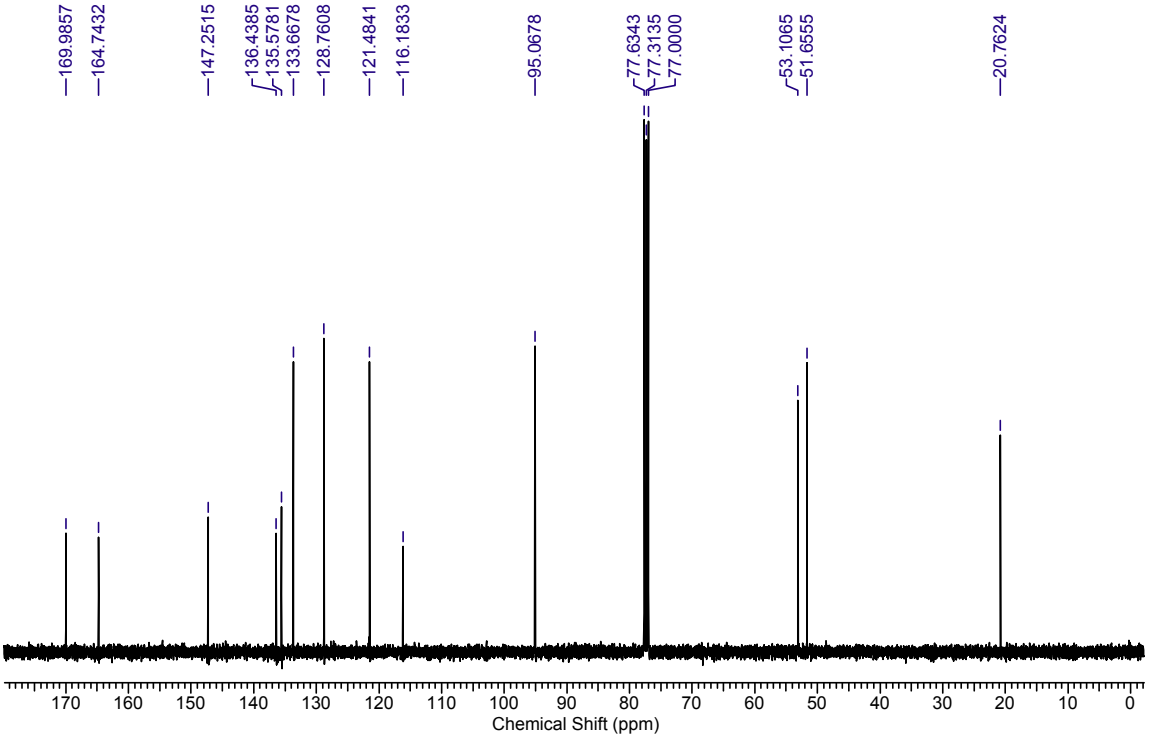
^{1}H NMR (400 MHz) spectrum of compound **1w** in $CDCl_3$



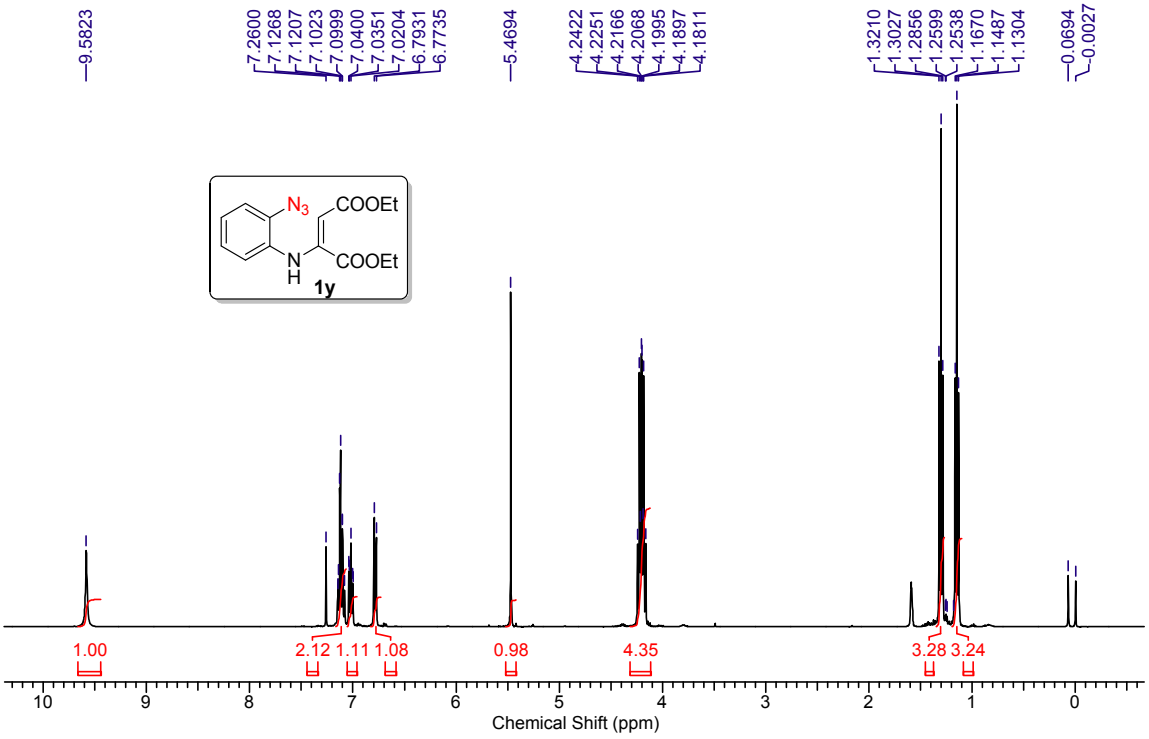
^{13}C NMR (100 MHz) spectrum of compound **1w** in $CDCl_3$



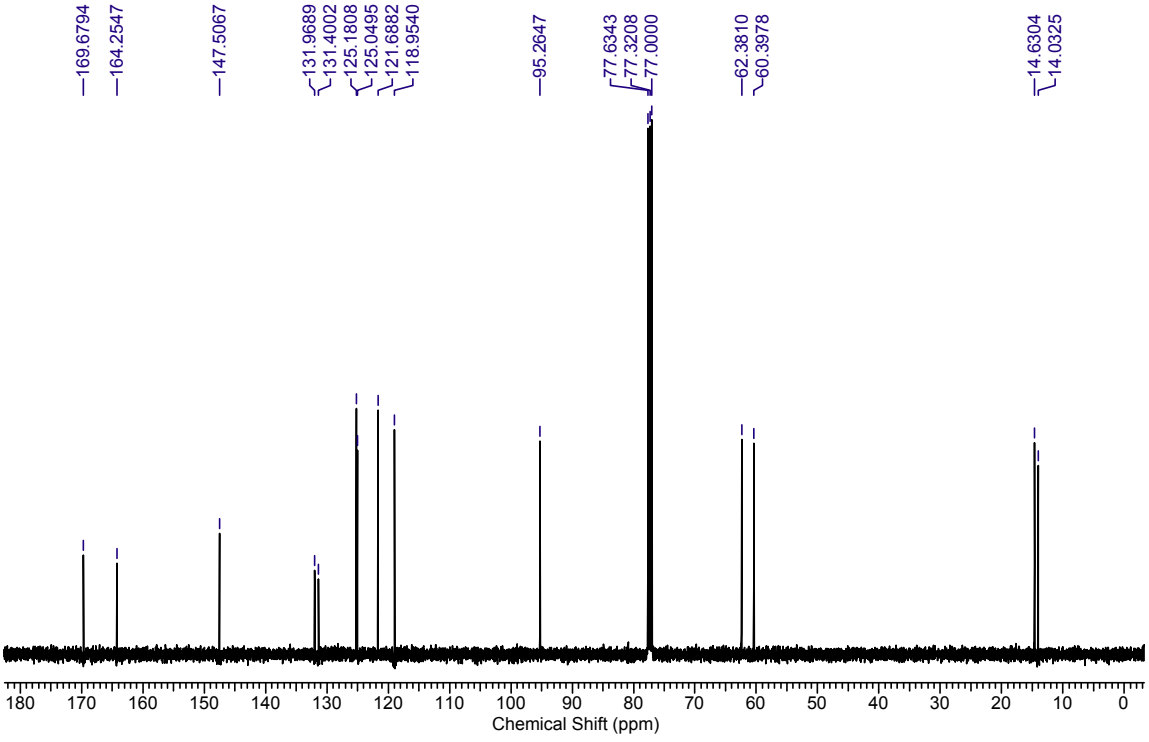
^{1}H NMR (400 MHz) spectrum of compound **1x** in $CDCl_3$



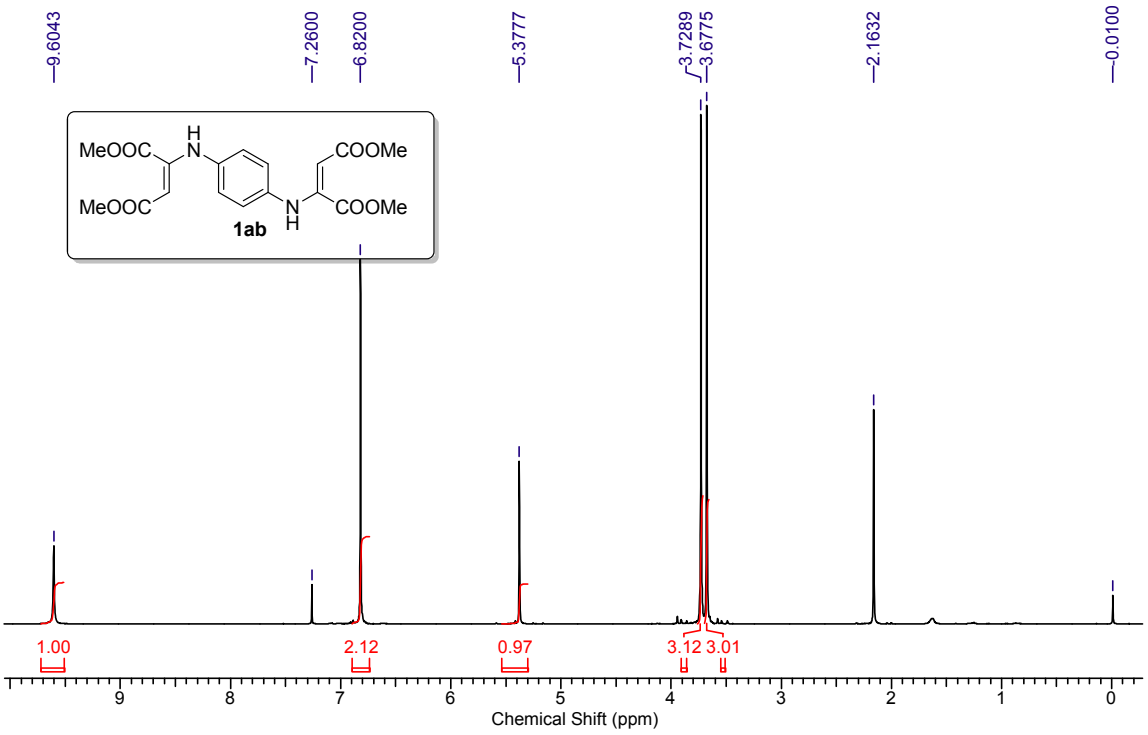
^{13}C NMR (100 MHz) spectrum of compound **1x** in $CDCl_3$



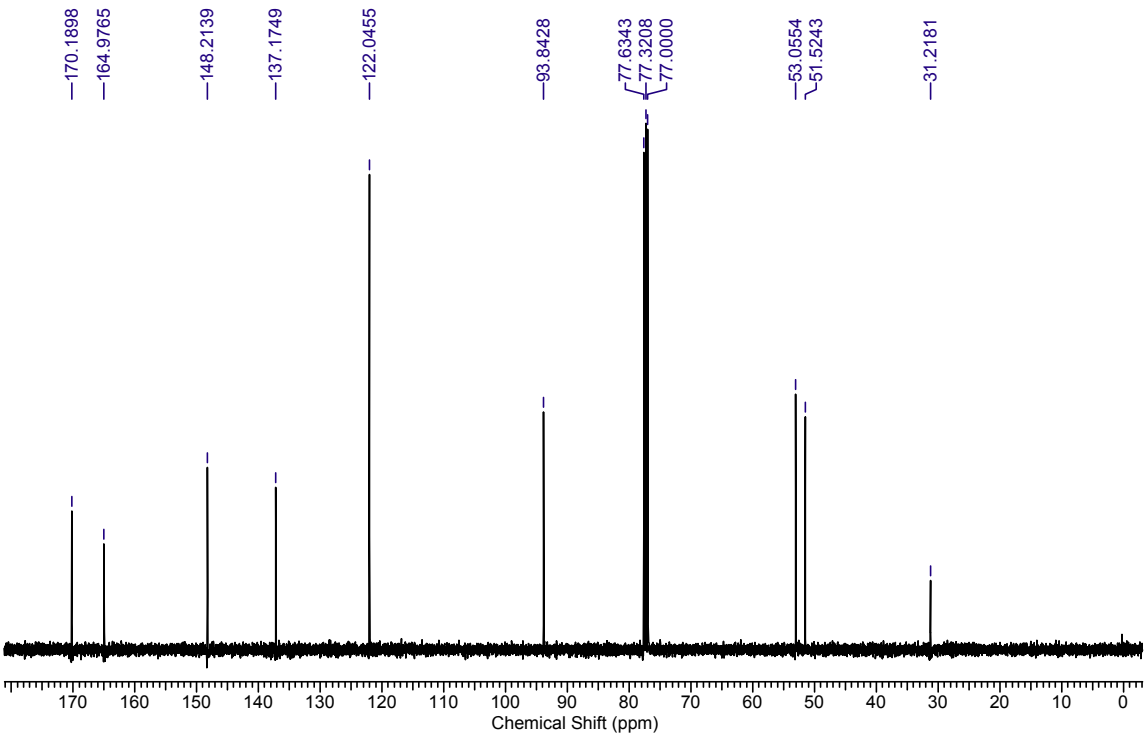
^{1}H NMR (400 MHz) spectrum of compound **1y** in $CDCl_3$



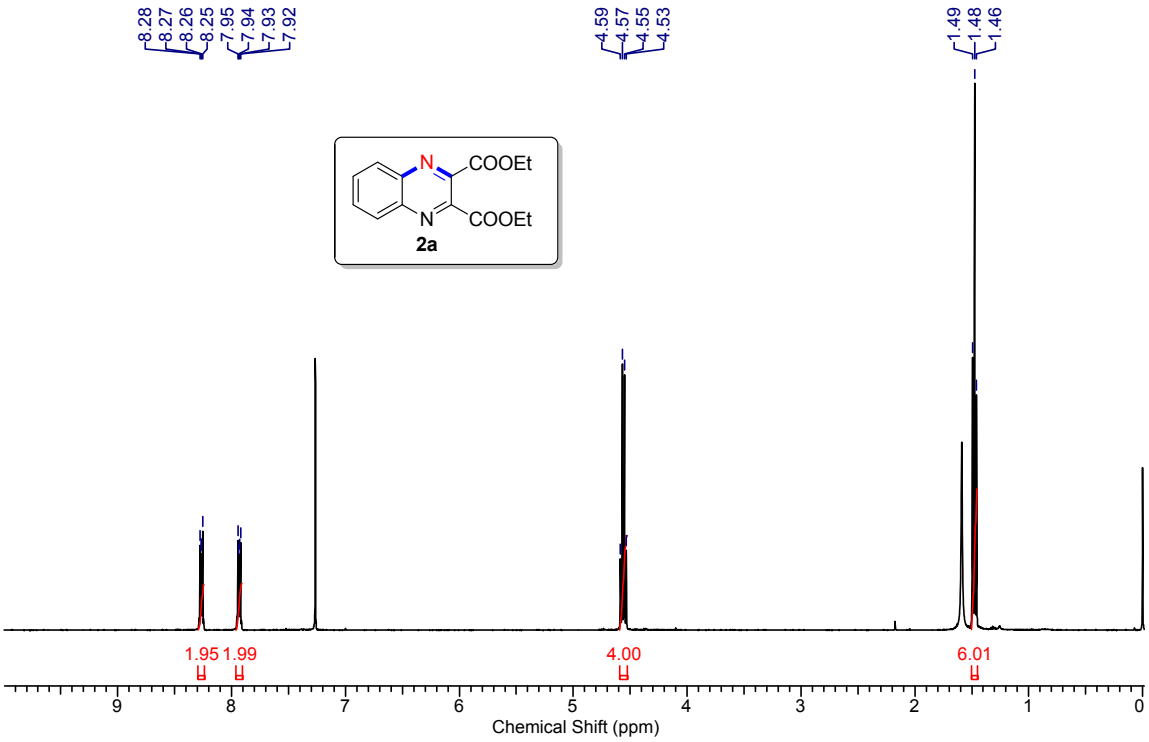
^{13}C NMR (100 MHz) spectrum of compound **1y** in $CDCl_3$



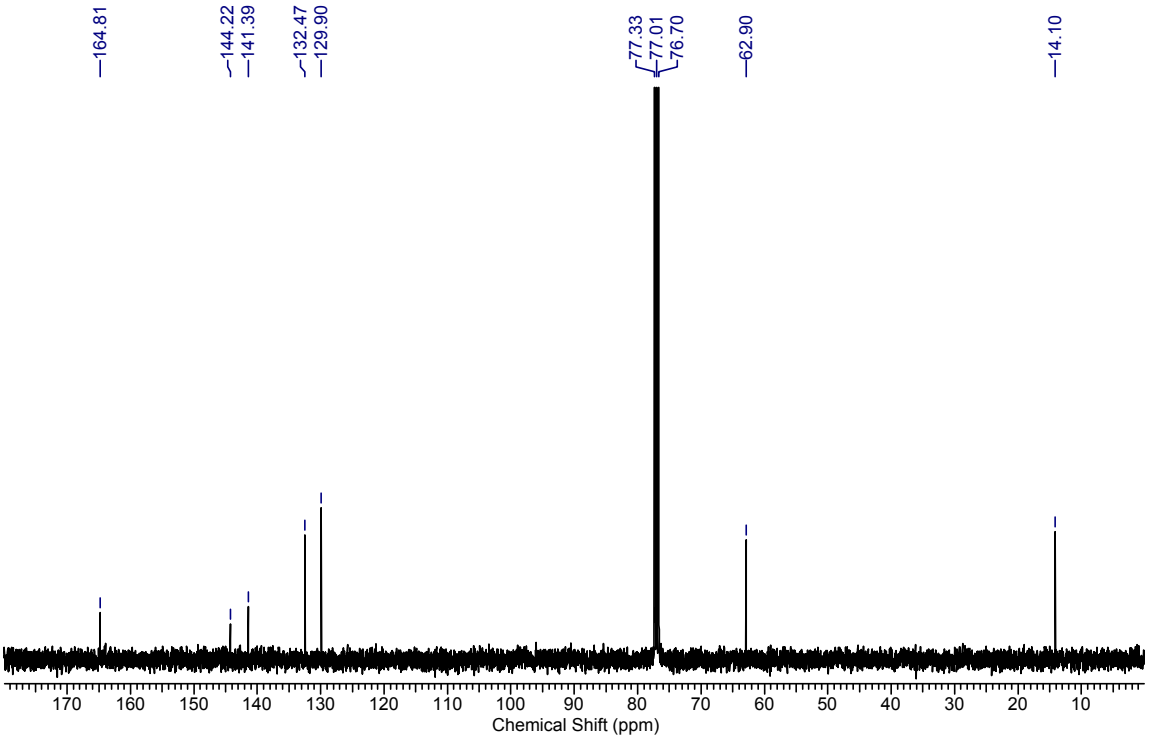
^{1}H NMR (400 MHz) spectrum of compound **1ab** in $CDCl_3$



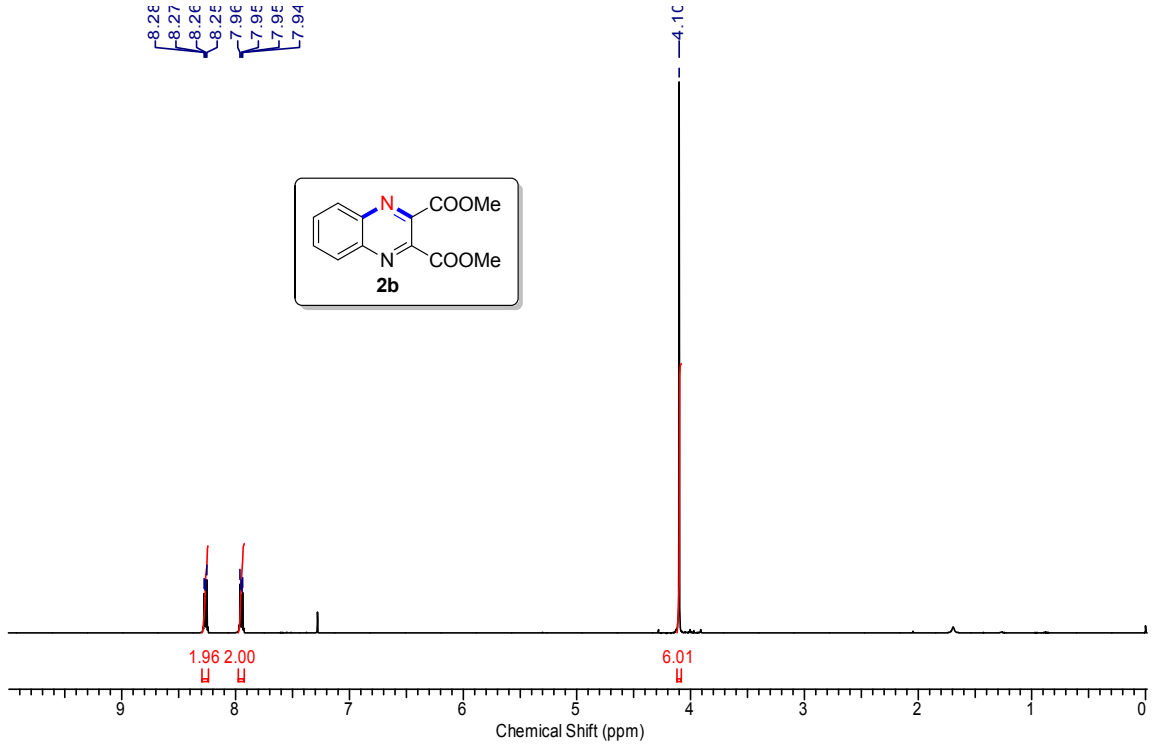
^{13}C NMR (100 MHz) spectrum of compound **1ab** in $CDCl_3$



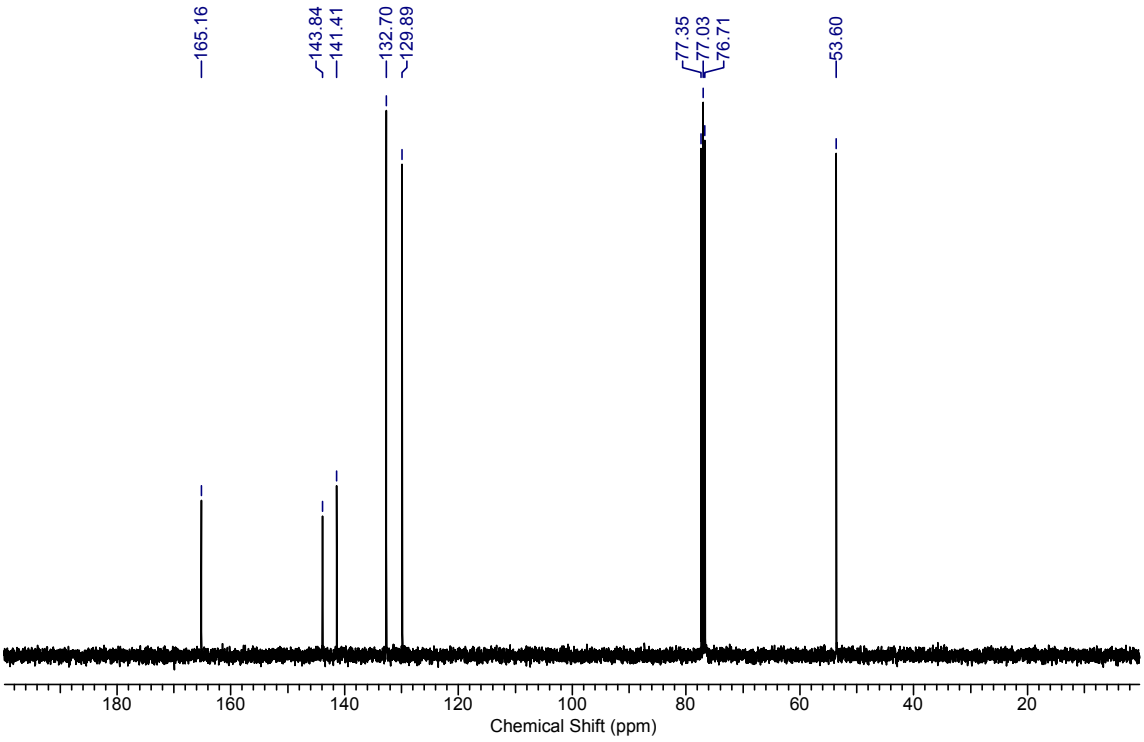
^{1}H NMR (400 MHz) spectrum of compound **2a** in $CDCl_3$



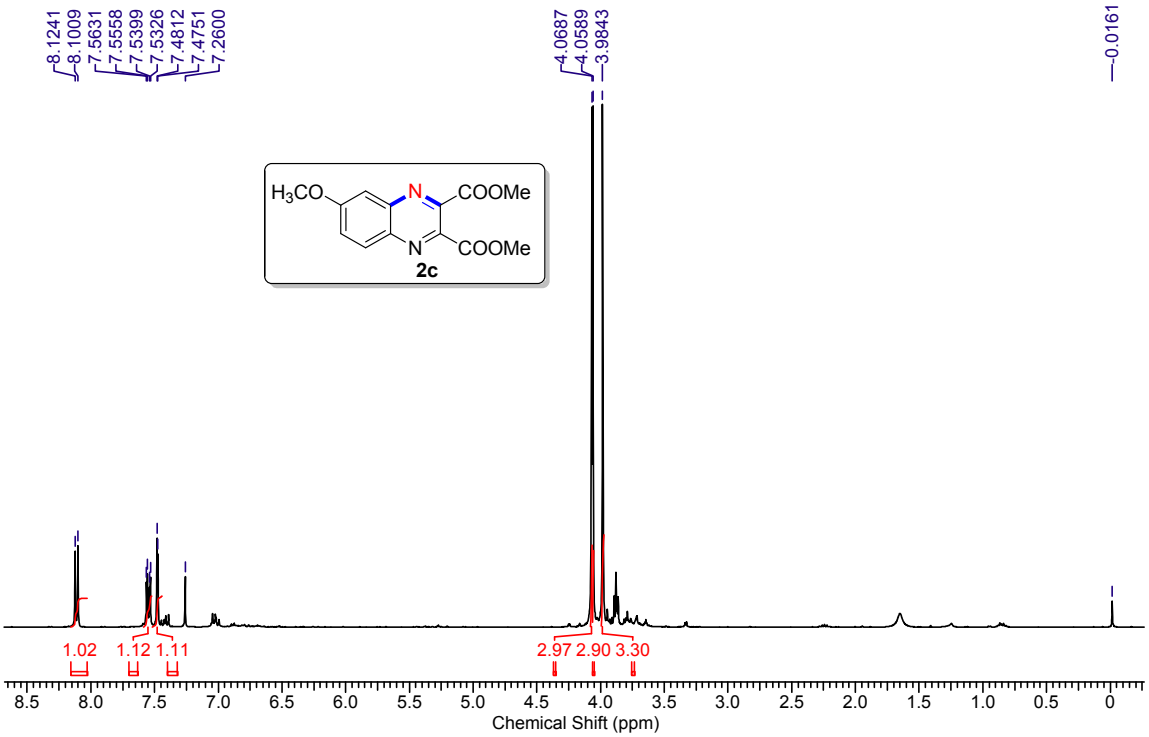
^{13}C NMR (100 MHz) spectrum of compound **2a** in $CDCl_3$



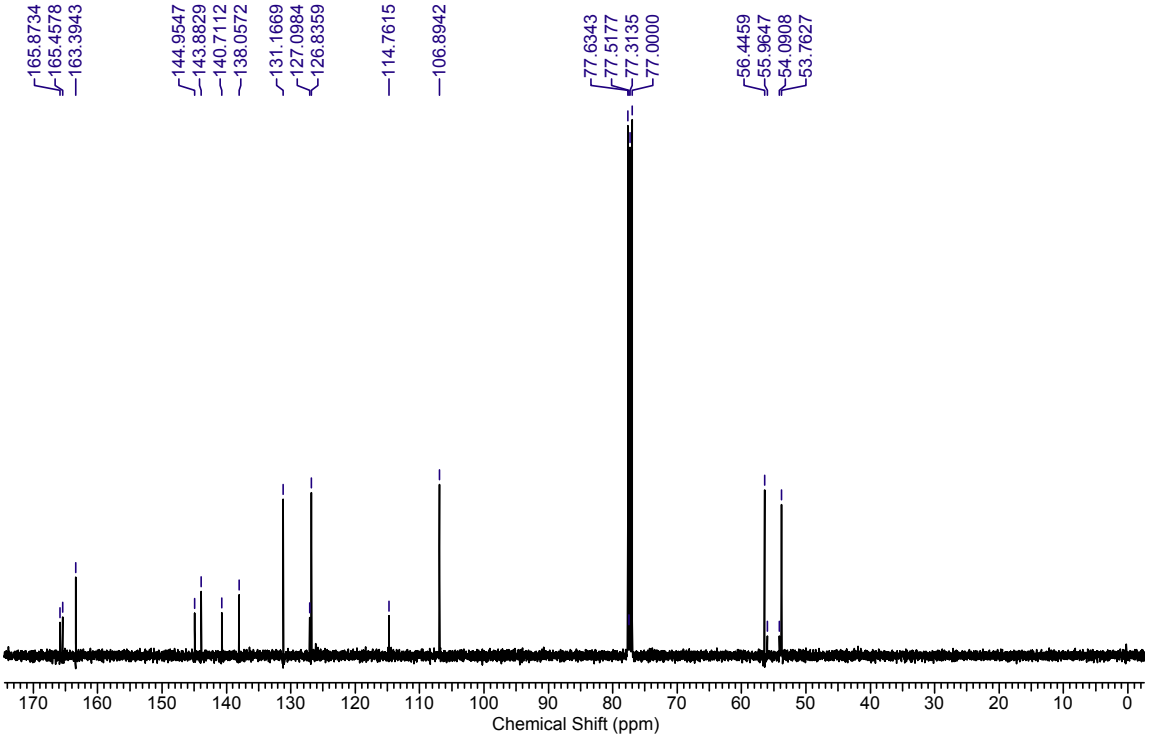
^{1}H NMR (400 MHz) spectrum of compound **2b** in $CDCl_3$



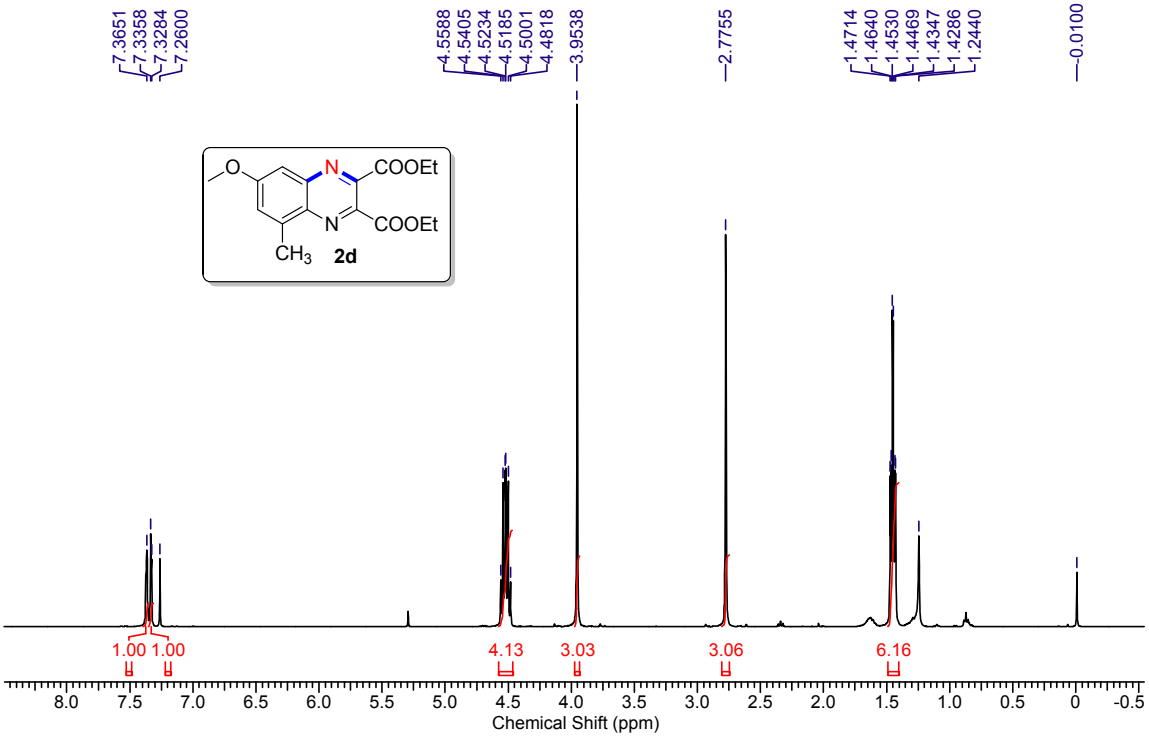
^{13}C NMR (100 MHz) spectrum of compound **2b** in $CDCl_3$



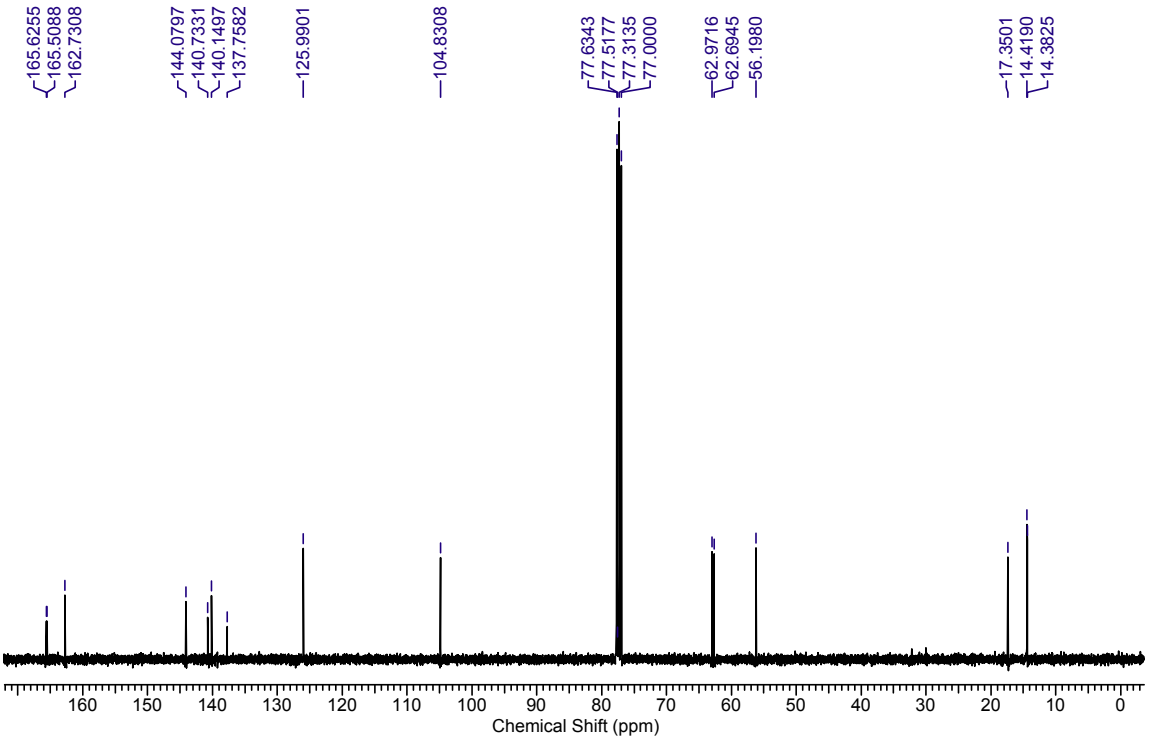
^{1}H NMR (400 MHz) spectrum of compound **2c** in $CDCl_3$



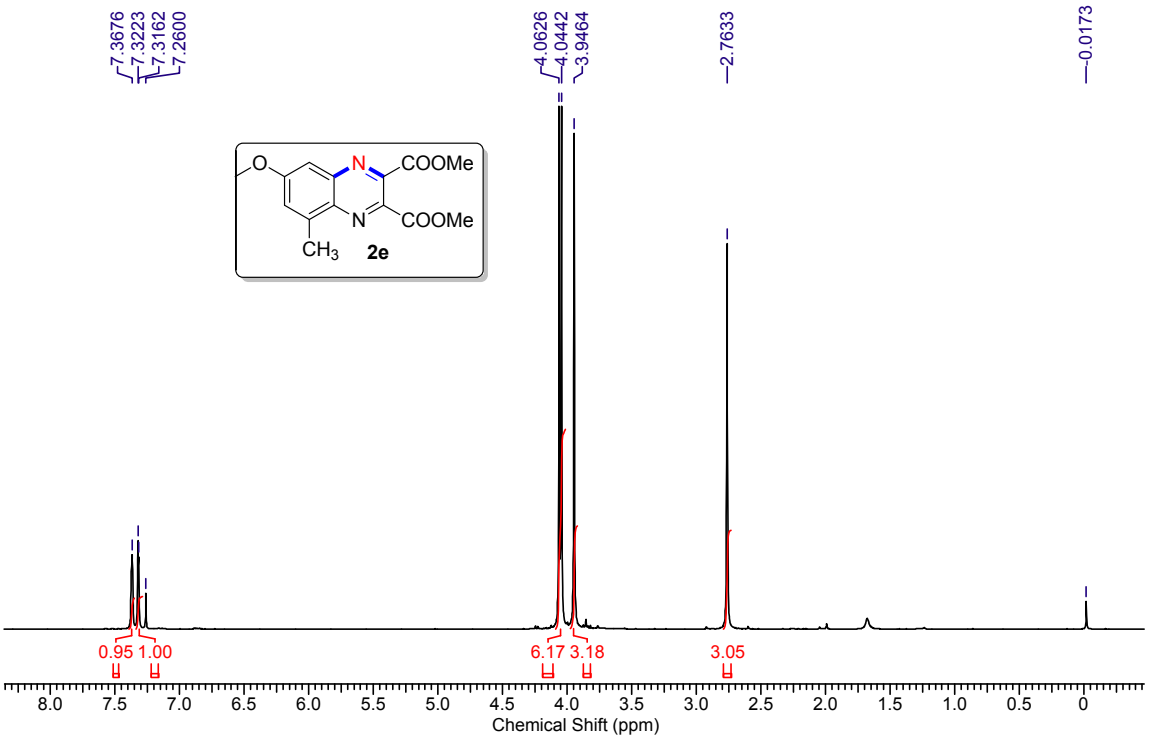
^{13}C NMR (100 MHz) spectrum of compound **2c** in $CDCl_3$



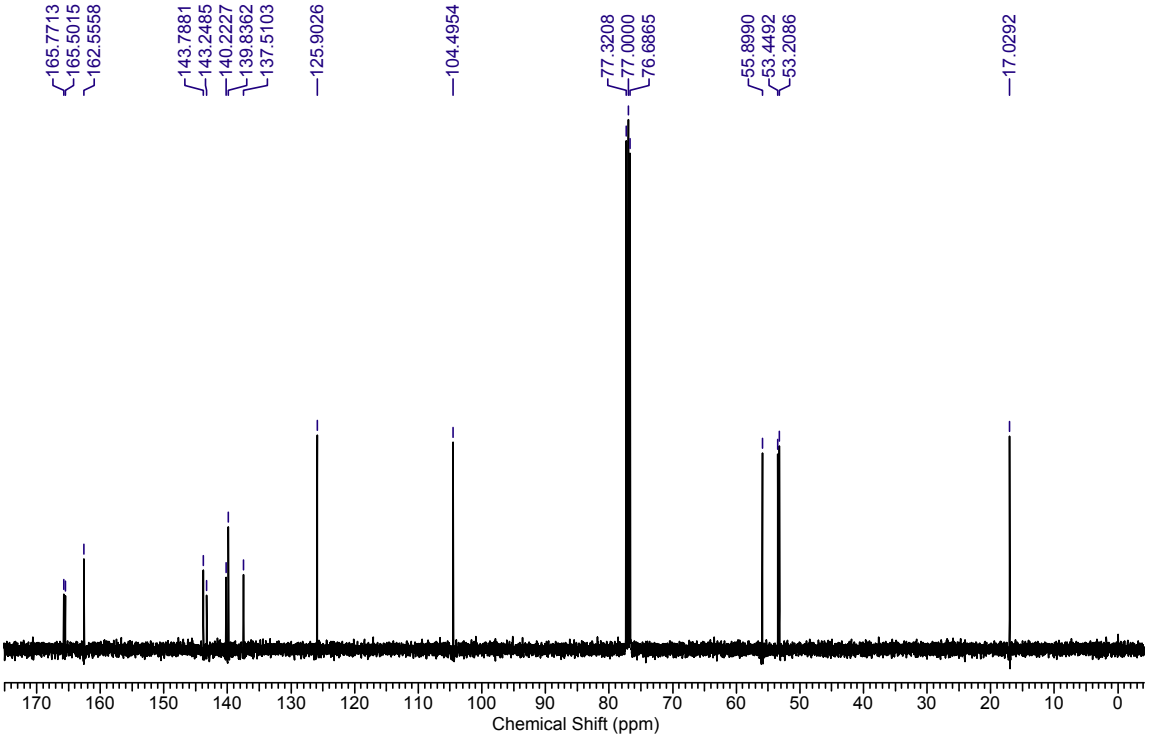
^{1}H NMR (400 MHz) spectrum of compound **2d** in $CDCl_3$



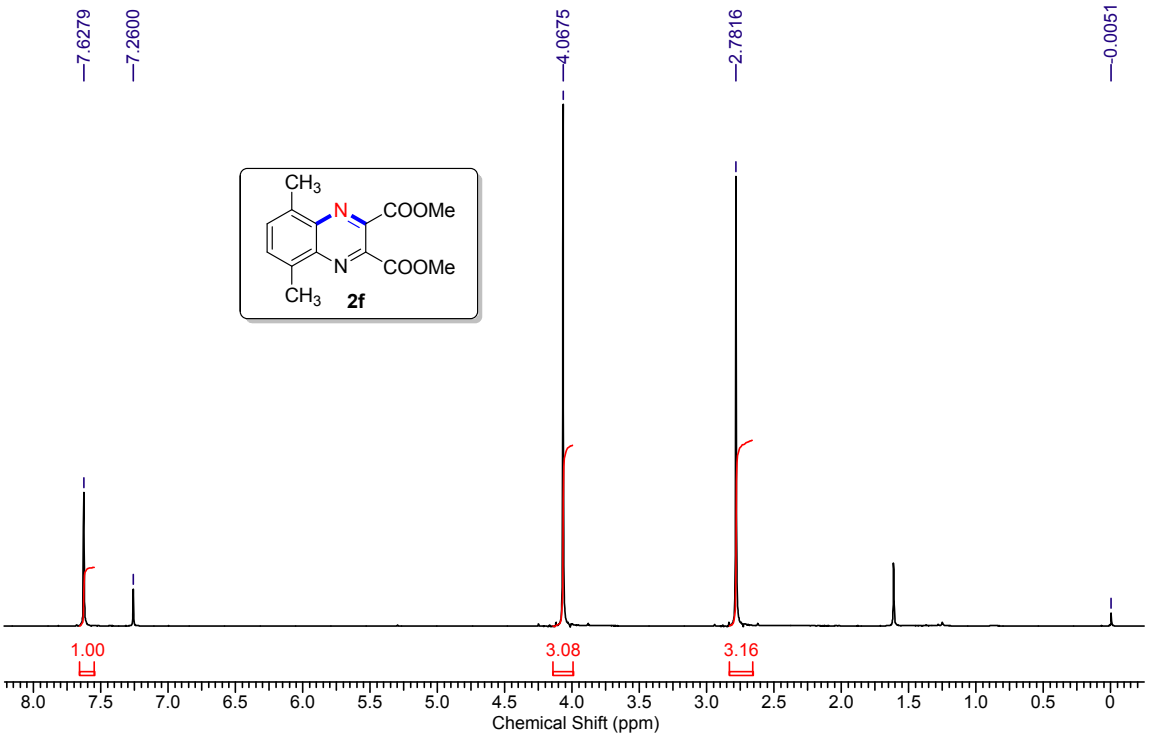
^{13}C NMR (100 MHz) spectrum of compound **2d** in $CDCl_3$



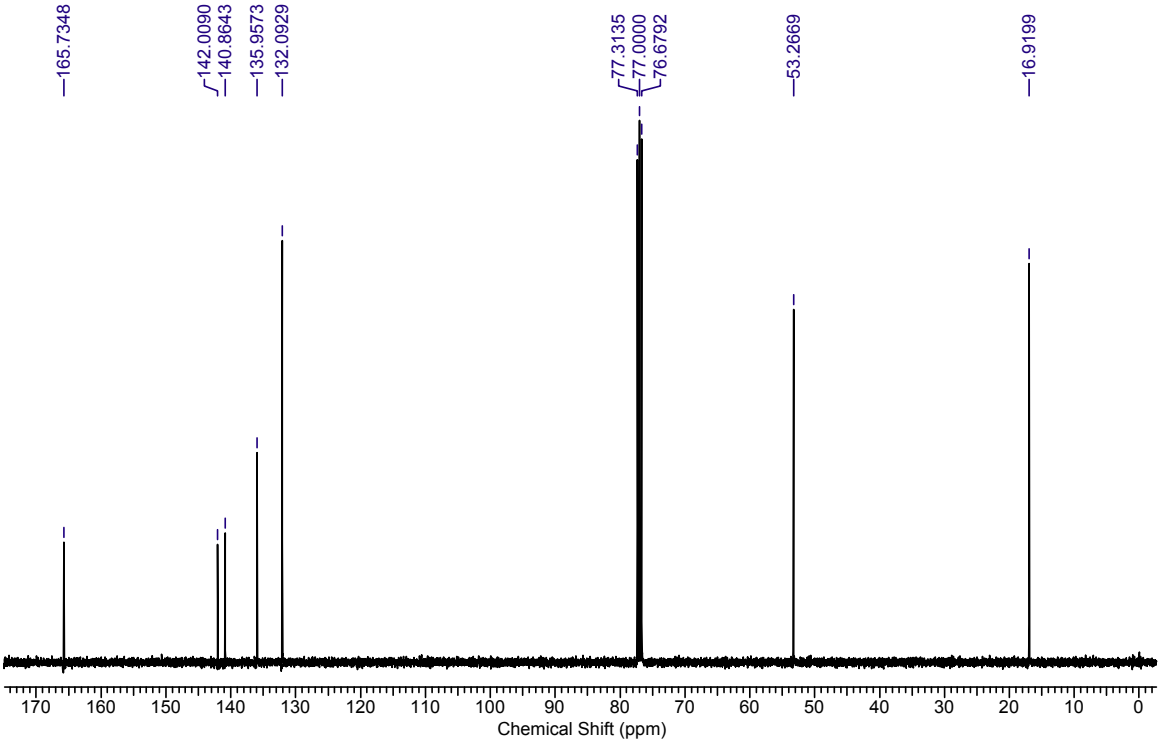
^{1}H NMR (400 MHz) spectrum of compound **2e** in $CDCl_3$



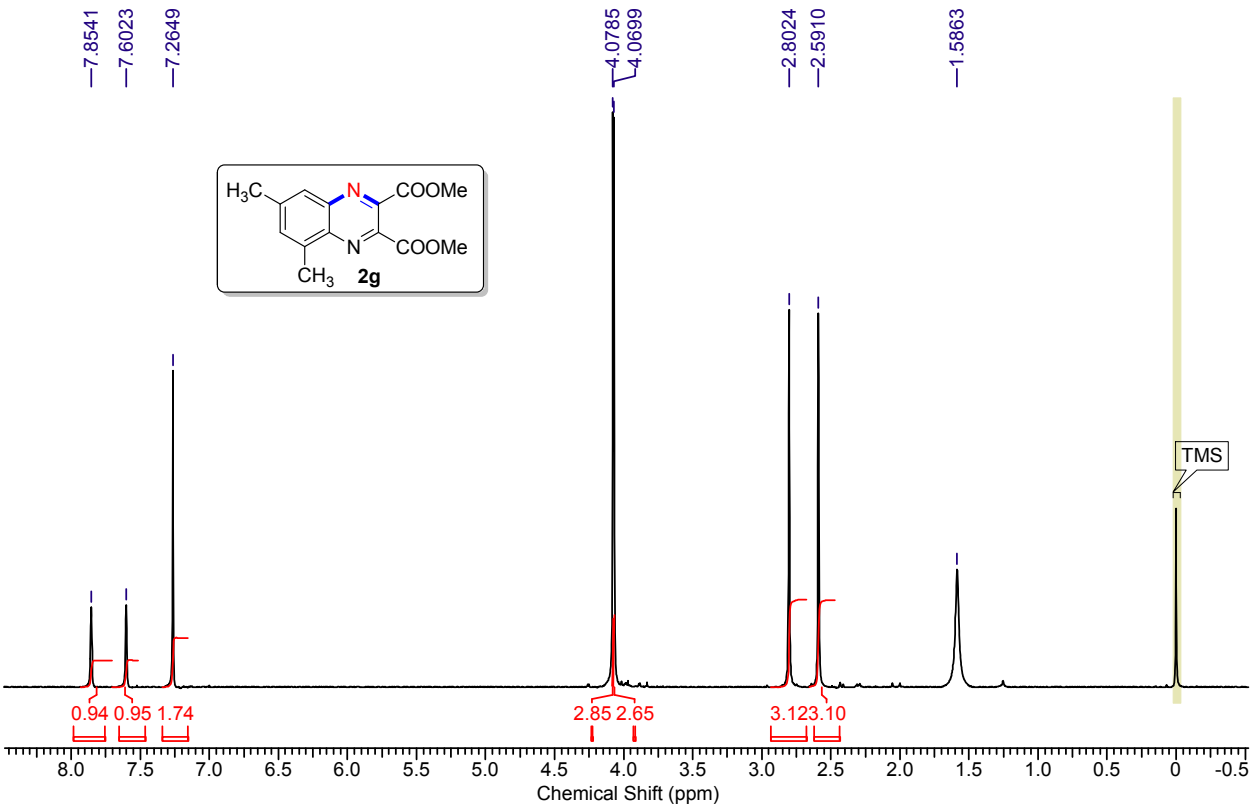
^{13}C NMR (100 MHz) spectrum of compound **2e** in $CDCl_3$



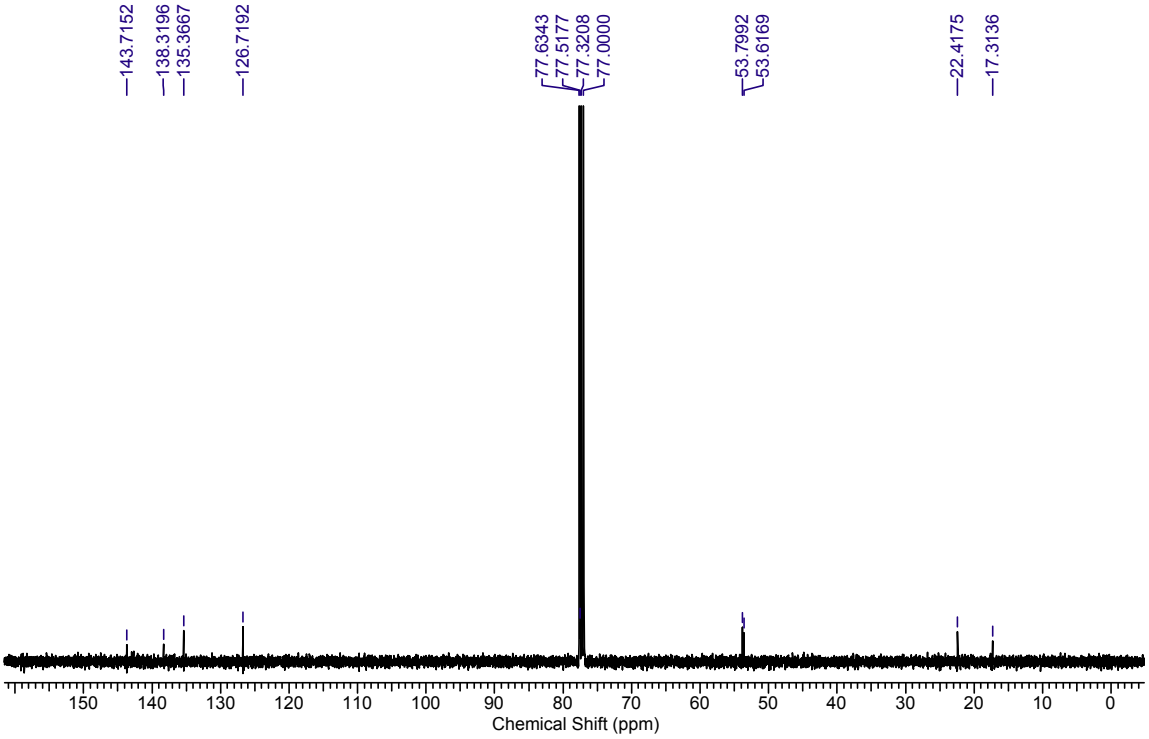
^{1}H NMR (400 MHz) spectrum of compound **2f** in $CDCl_3$



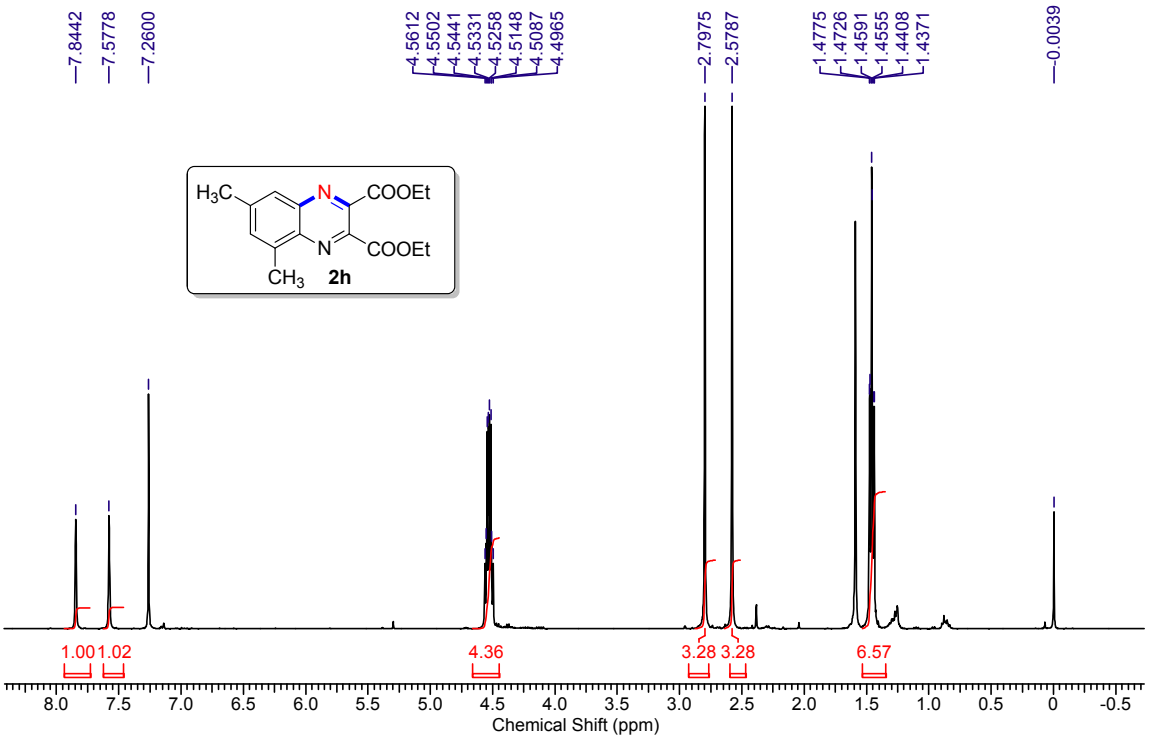
^{13}C NMR (100 MHz) spectrum of compound **2f** in $CDCl_3$



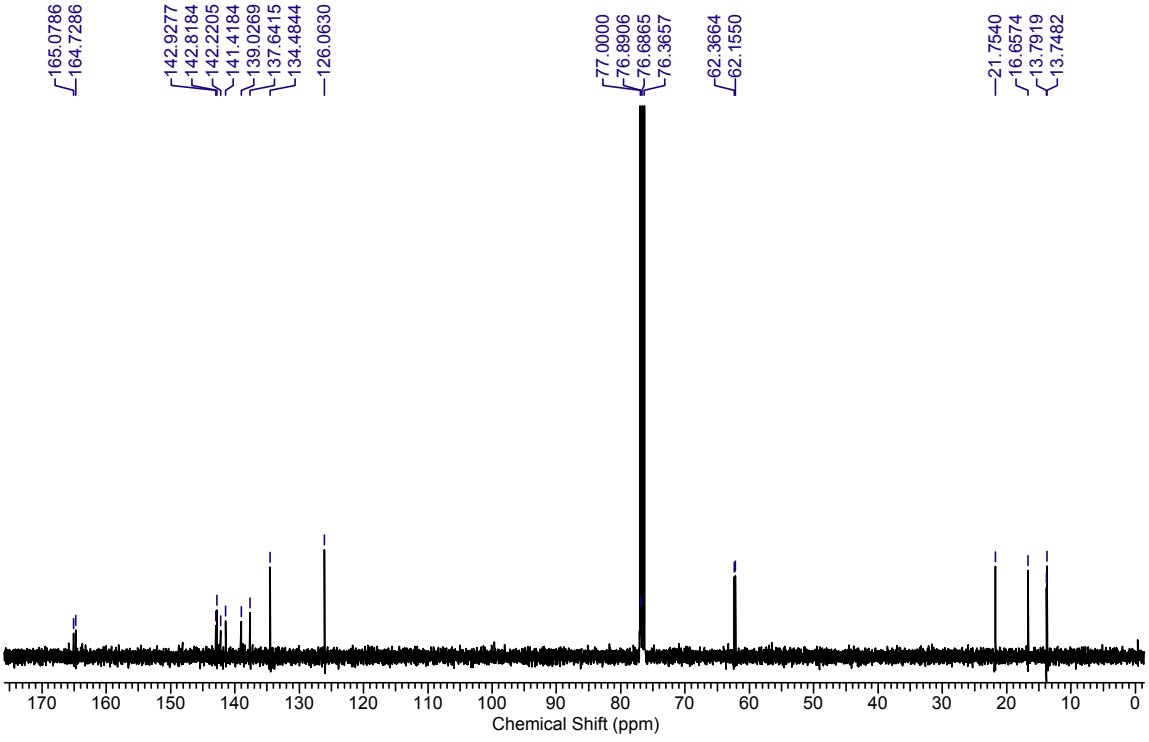
^{1}H NMR (400 MHz) spectrum of compound **2g** in $CDCl_3$



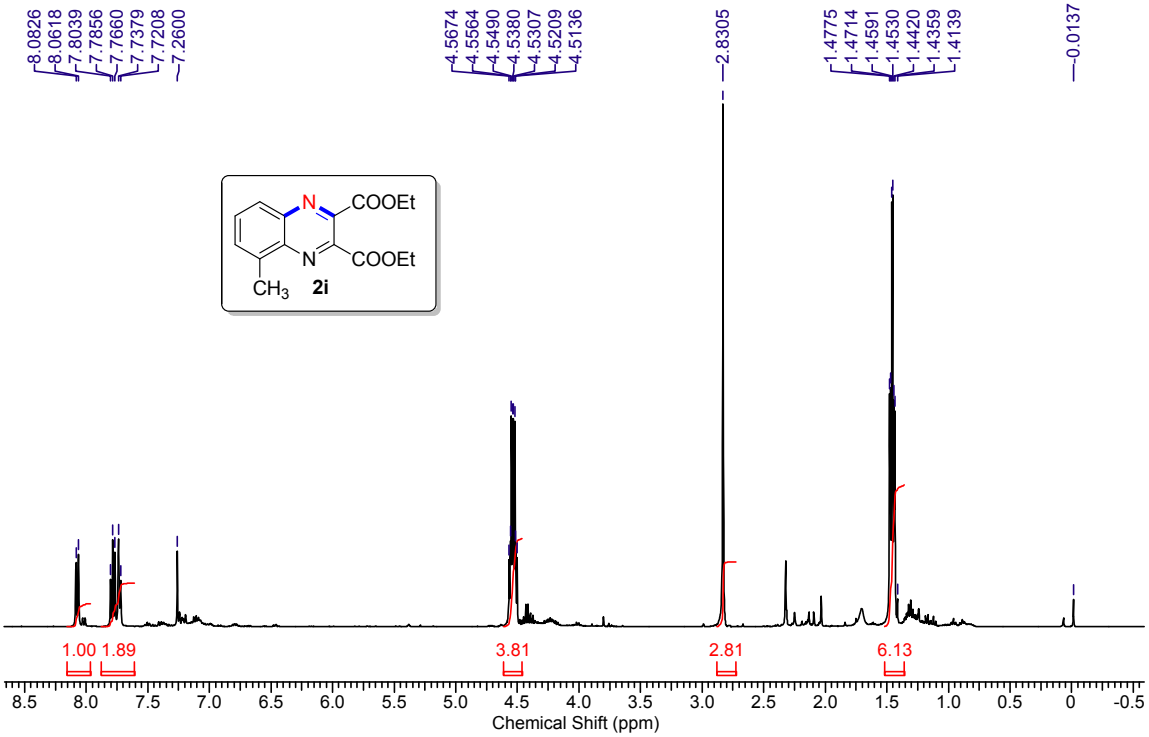
^{13}C NMR (100 MHz) spectrum of compound **2g** in $CDCl_3$



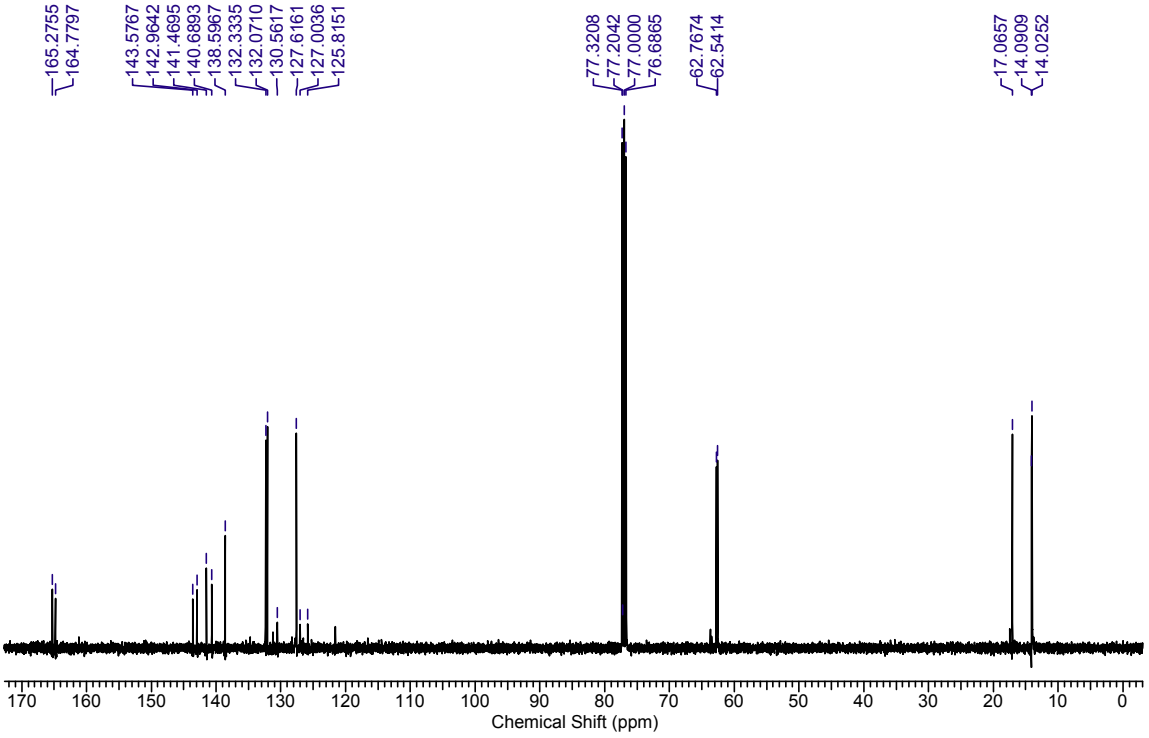
^{1}H NMR (400 MHz) spectrum of compound **2h** in $CDCl_3$



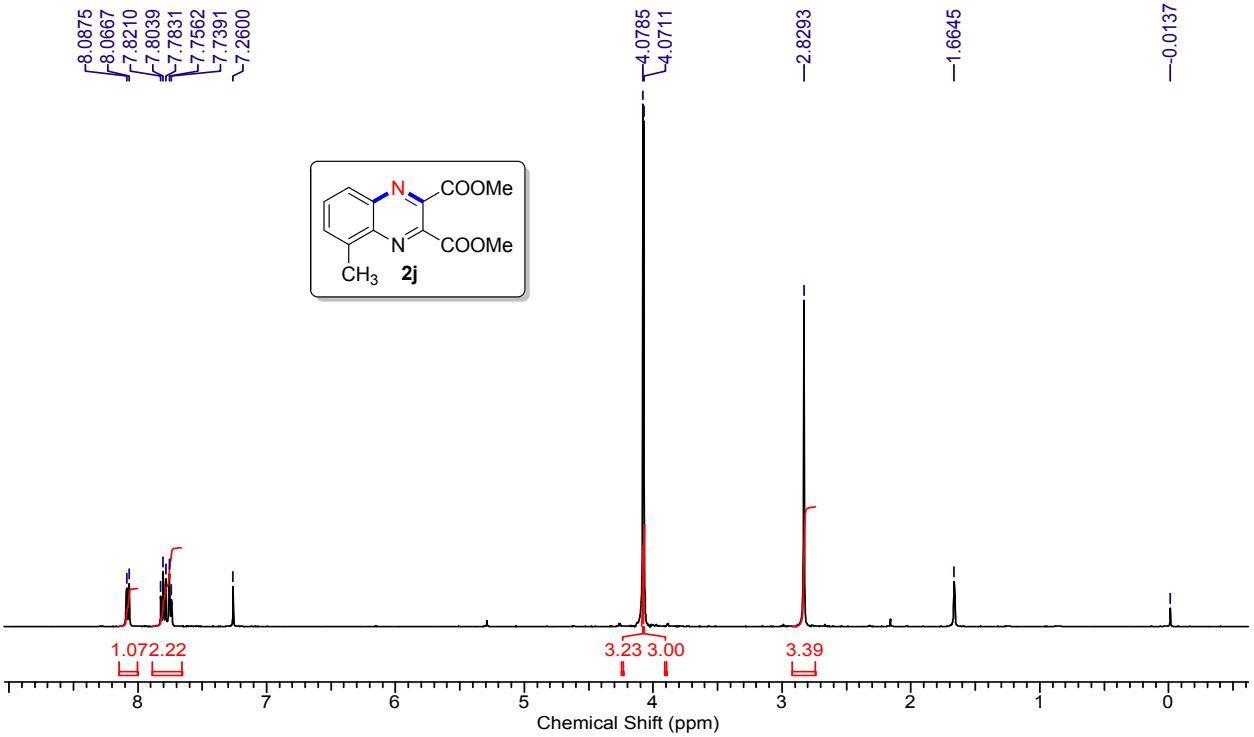
^{13}C NMR (100 MHz) spectrum of compound **2h** in $CDCl_3$



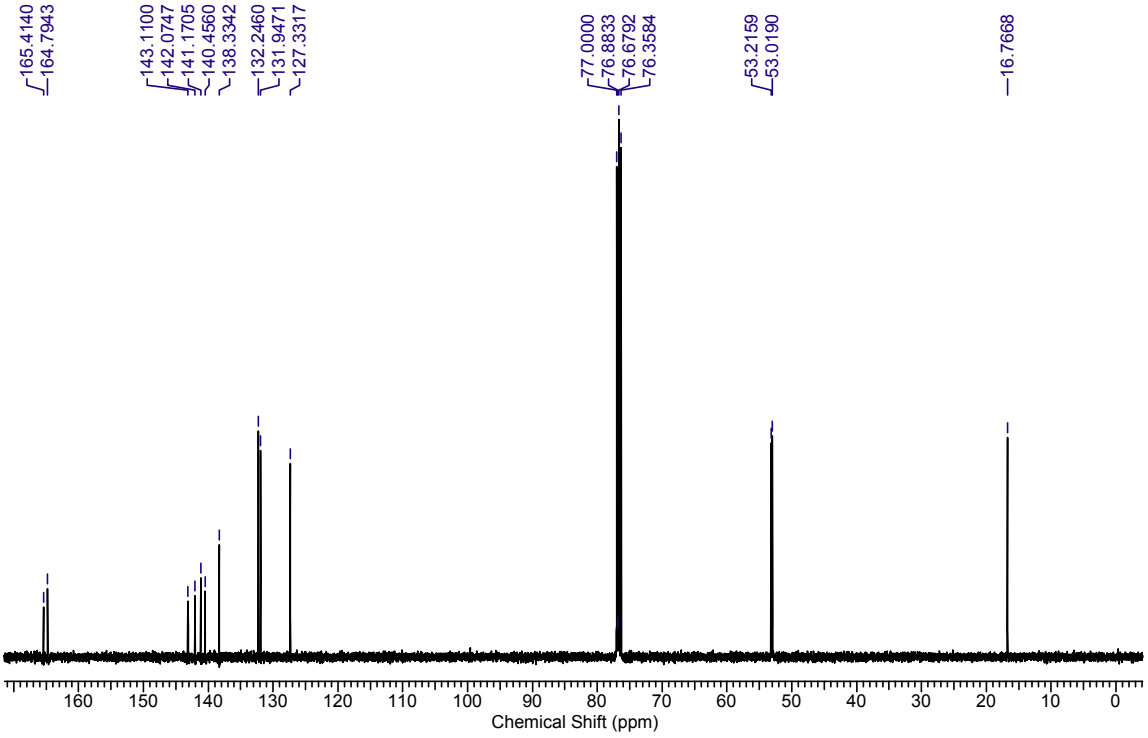
^{1}H NMR (400 MHz) spectrum of compound **2i** in $CDCl_3$



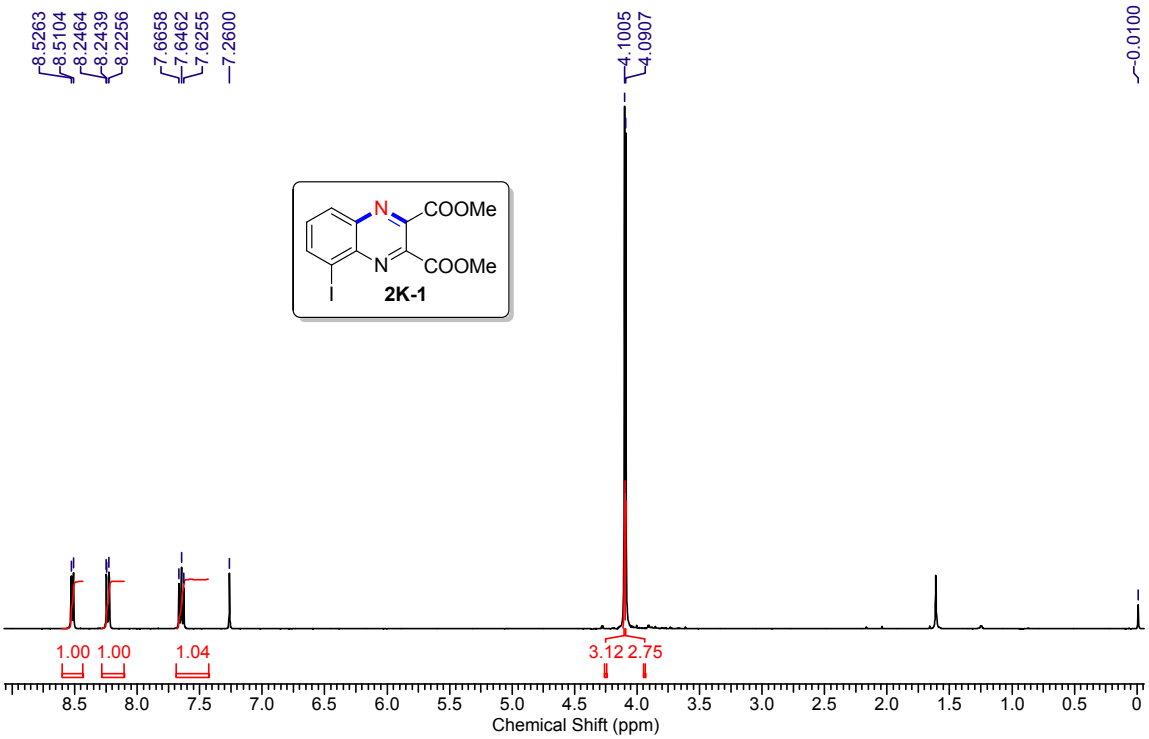
^{13}C NMR (100 MHz) spectrum of compound **2i** in $CDCl_3$



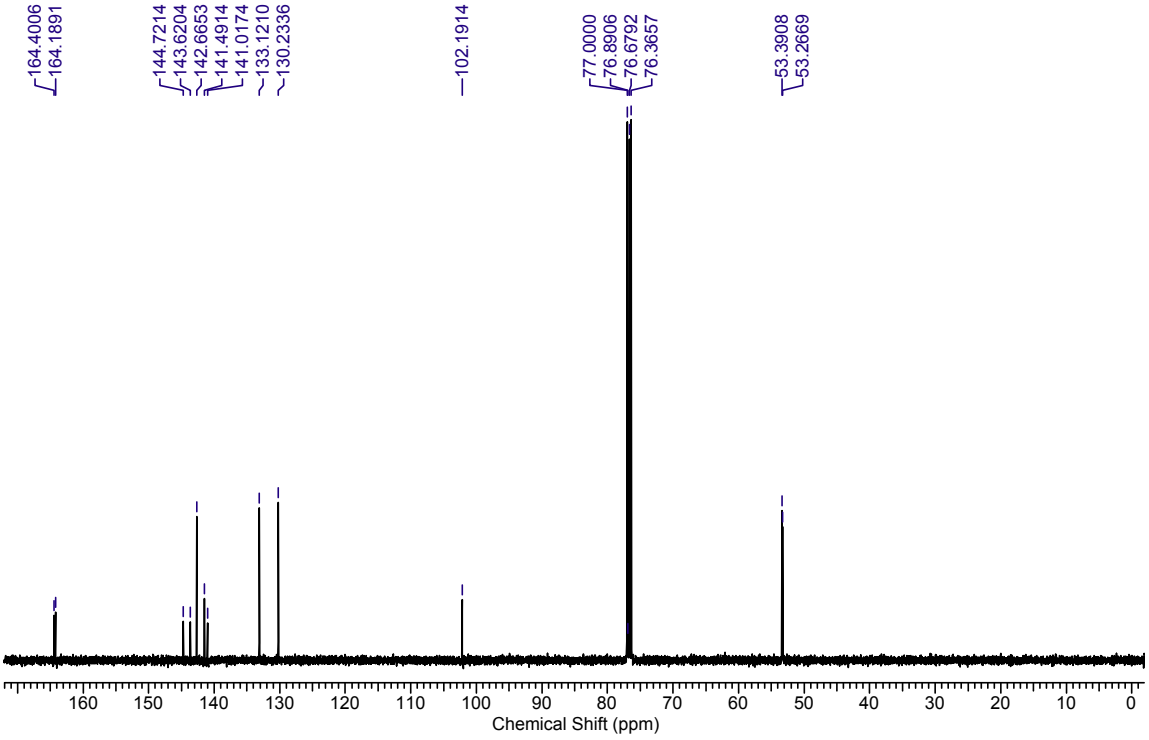
^{1}H NMR (400 MHz) spectrum of compound **2j** in $CDCl_3$



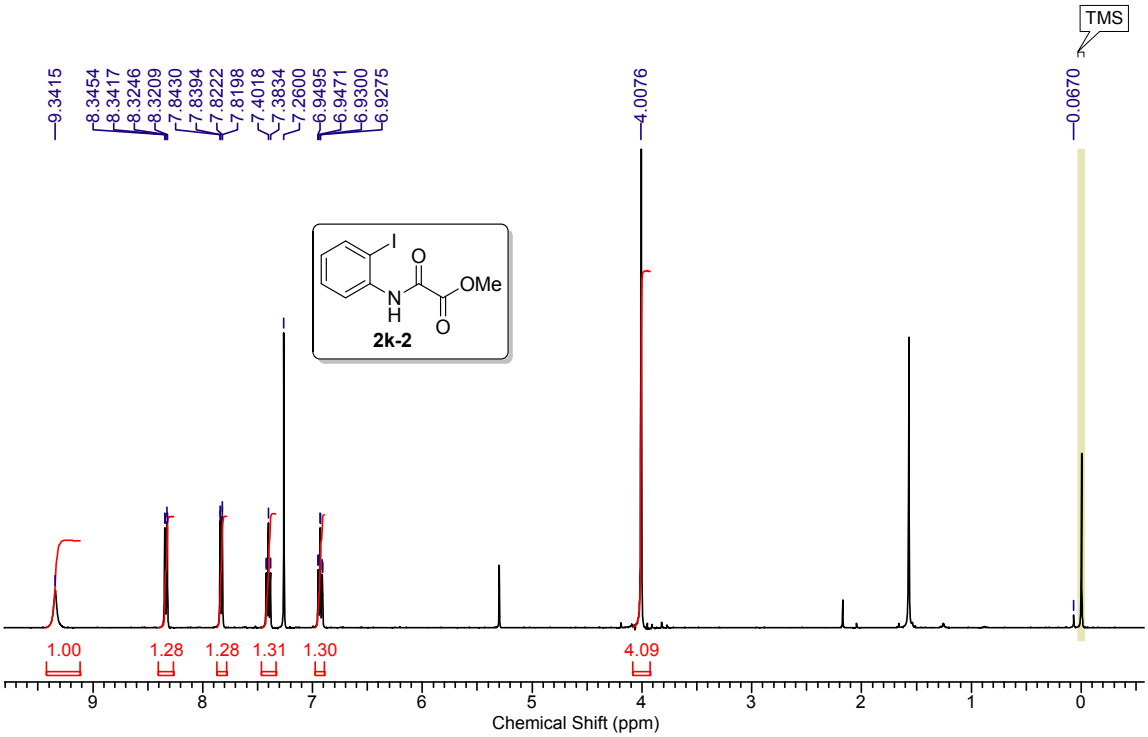
^{13}C NMR (100 MHz) spectrum of compound **2j** in $CDCl_3$



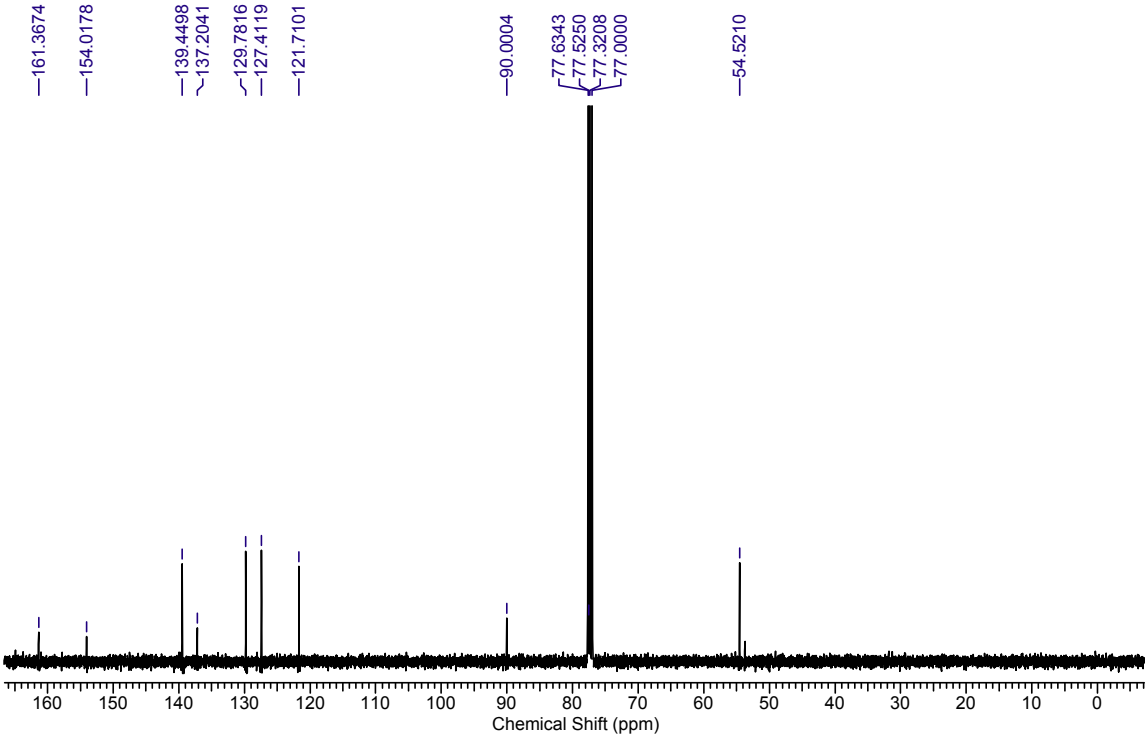
^{1}H NMR (400 MHz) spectrum of compound **2k-1** in $CDCl_3$



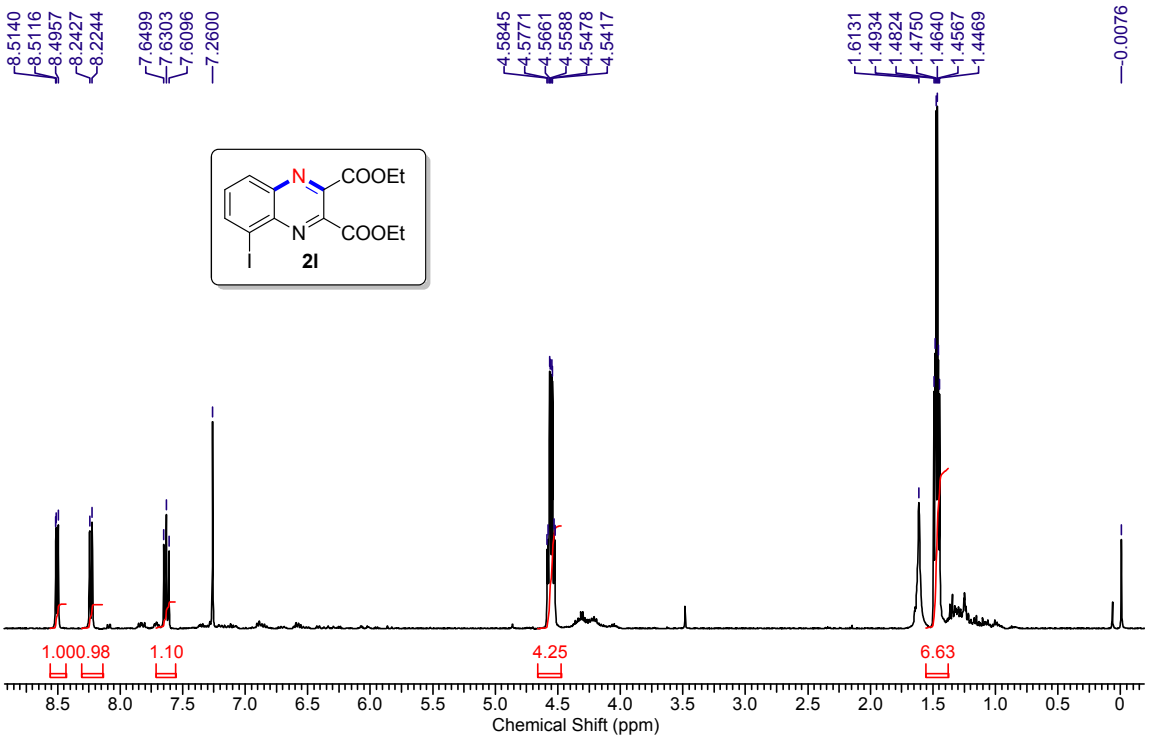
^{13}C NMR (100 MHz) spectrum of compound **2k-1** in $CDCl_3$



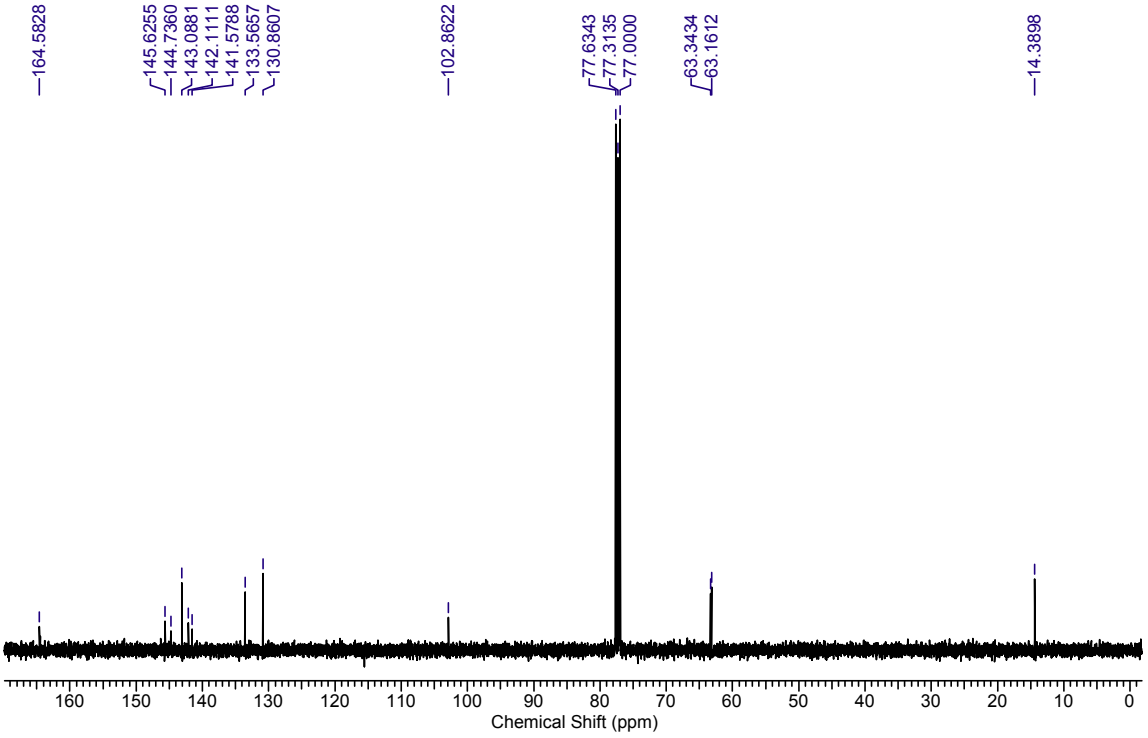
^{1}H NMR (400 MHz) spectrum of compound **2k-2** in $CDCl_3$



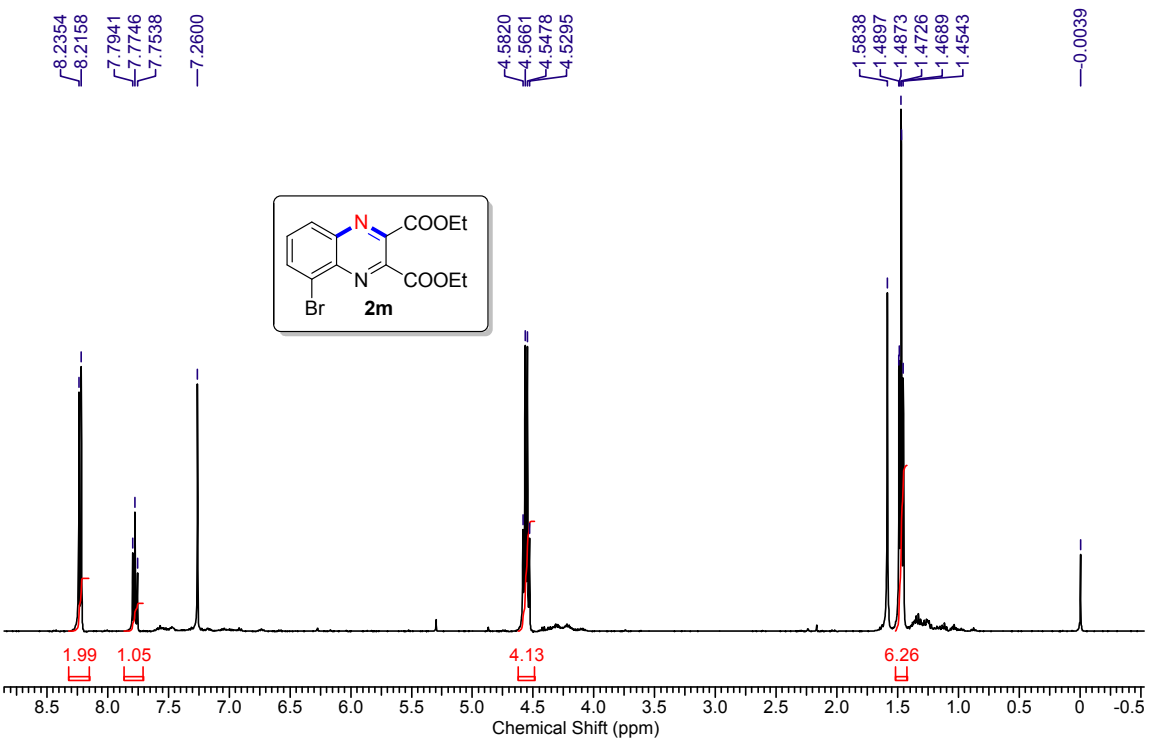
^{13}C NMR (100 MHz) spectrum of compound **2k-2** in $CDCl_3$



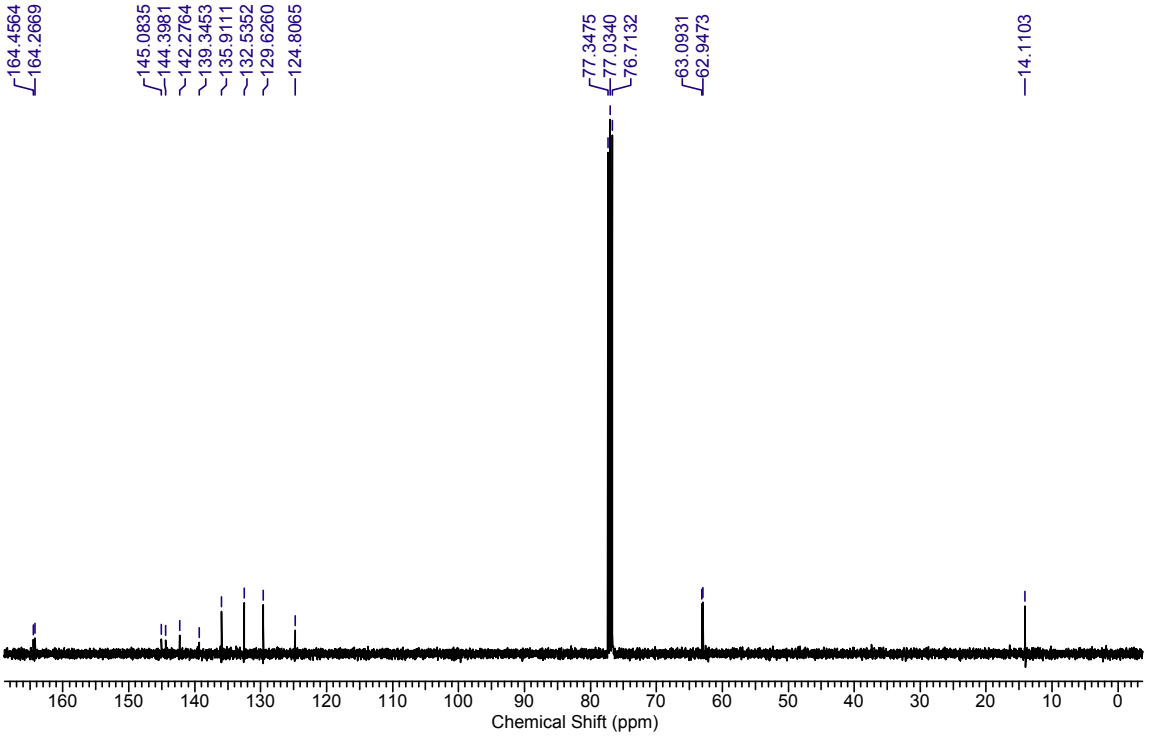
^{1}H NMR (400 MHz) spectrum of compound **2l** in $CDCl_3$



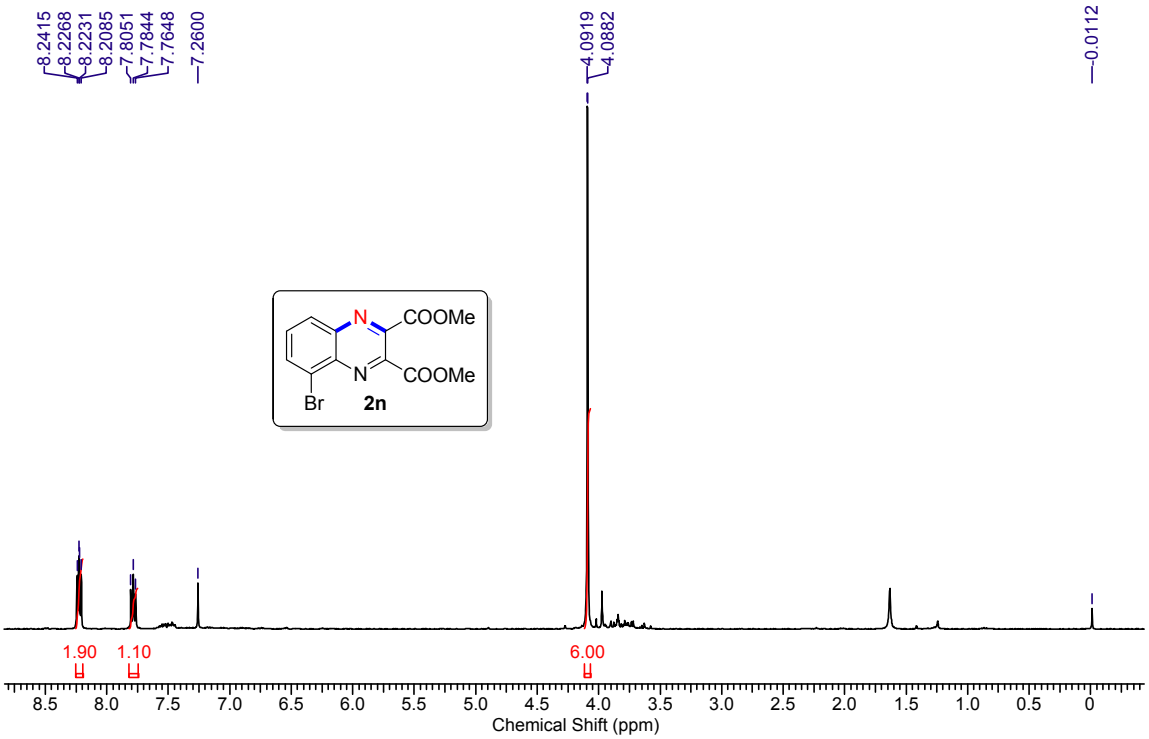
^{13}C NMR (100 MHz) spectrum of compound **2l** in $CDCl_3$



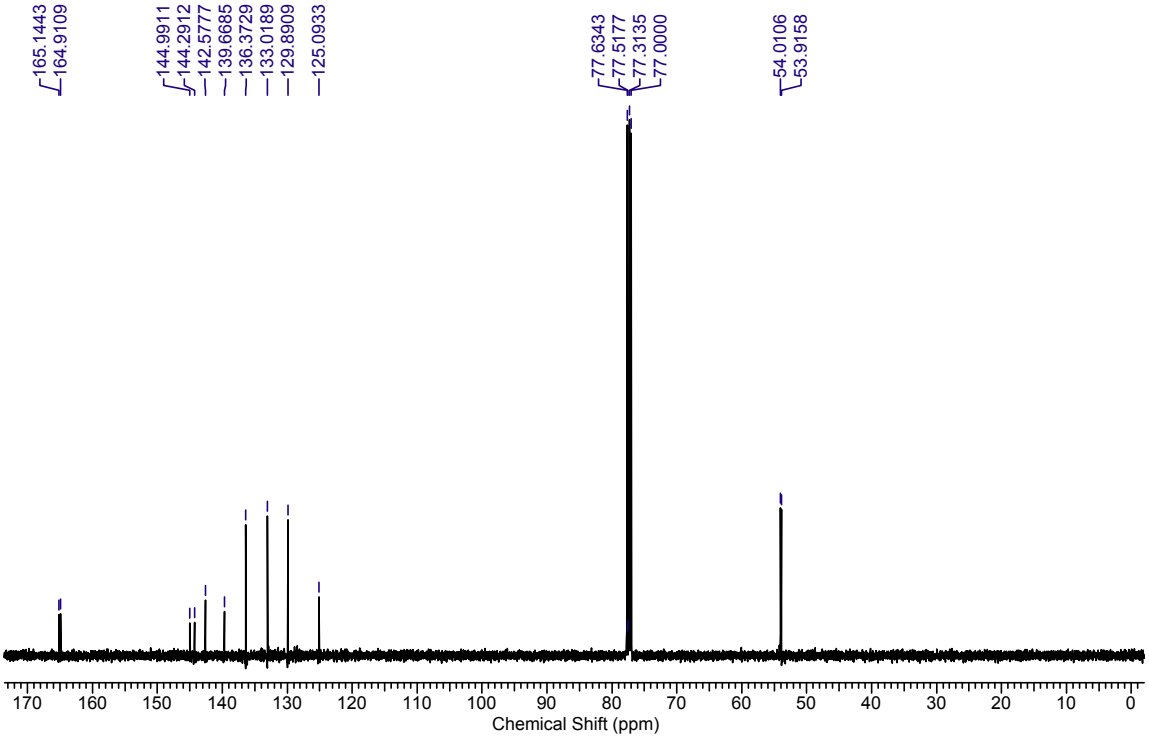
^{1}H NMR (400 MHz) spectrum of compound **2m** in $CDCl_3$



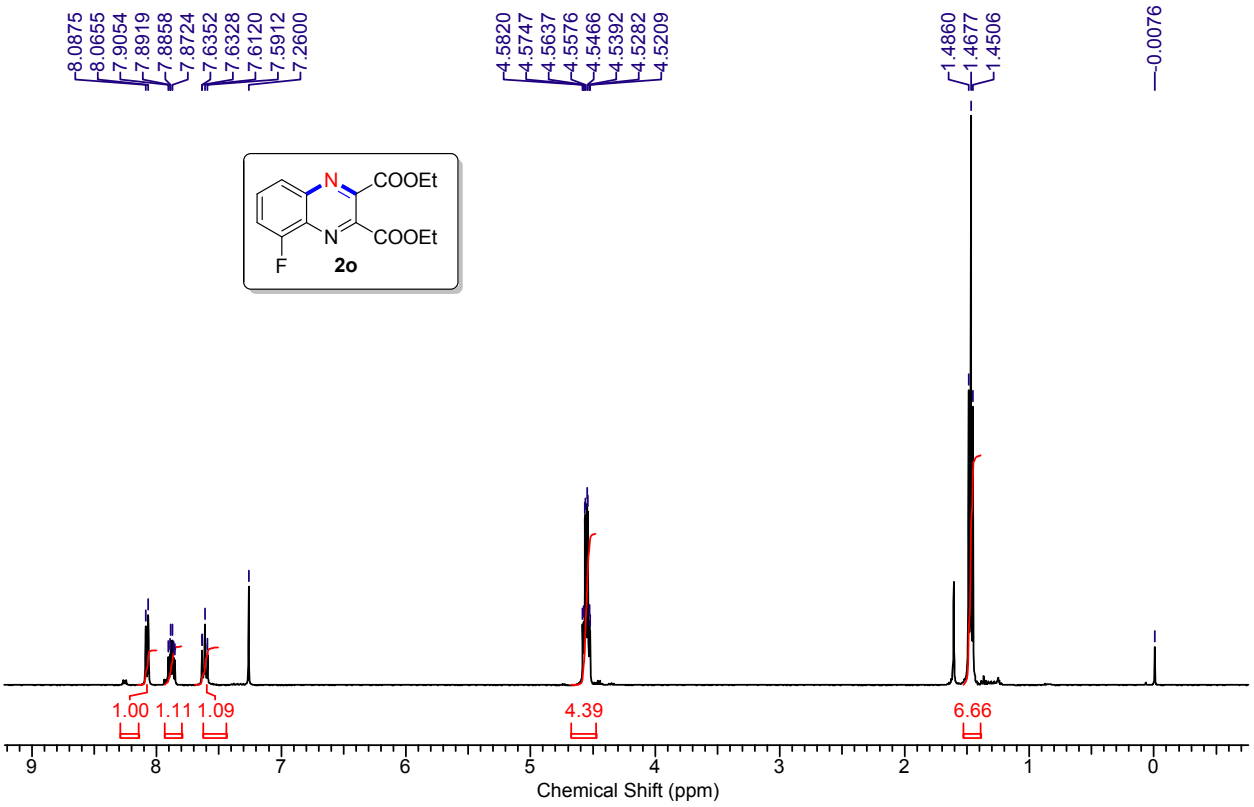
^{13}C NMR (100 MHz) spectrum of compound **2m** in $CDCl_3$



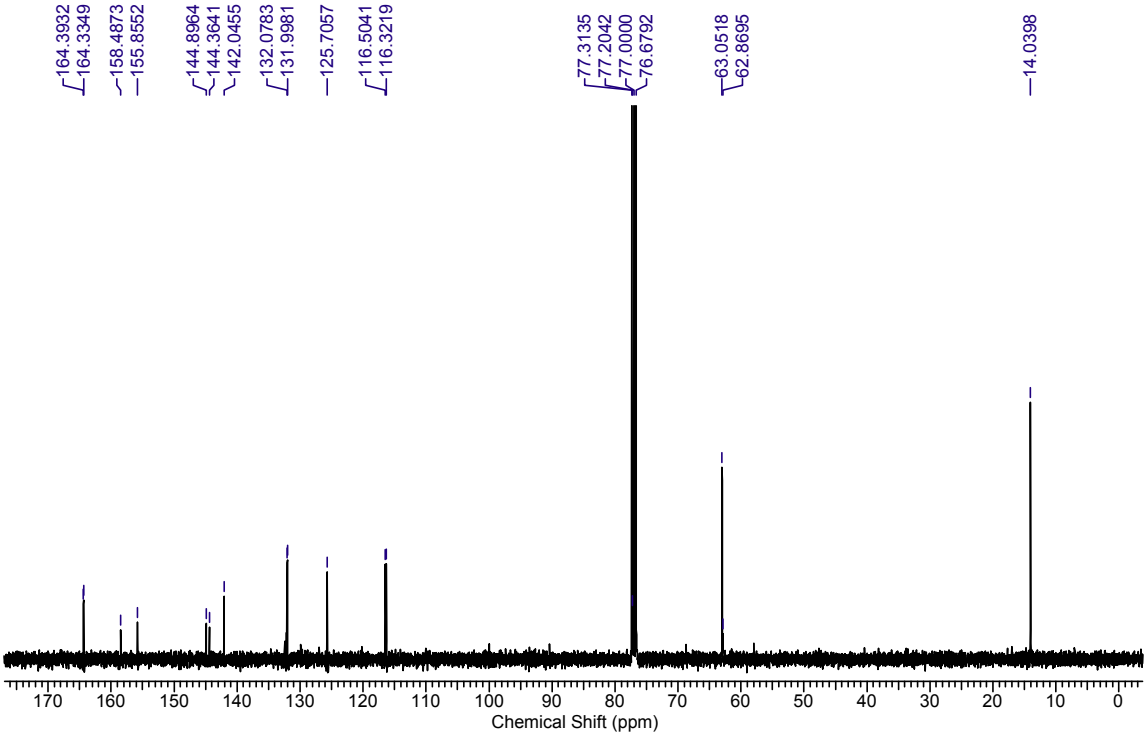
^{1}H NMR (400 MHz) spectrum of compound **2n** in $CDCl_3$



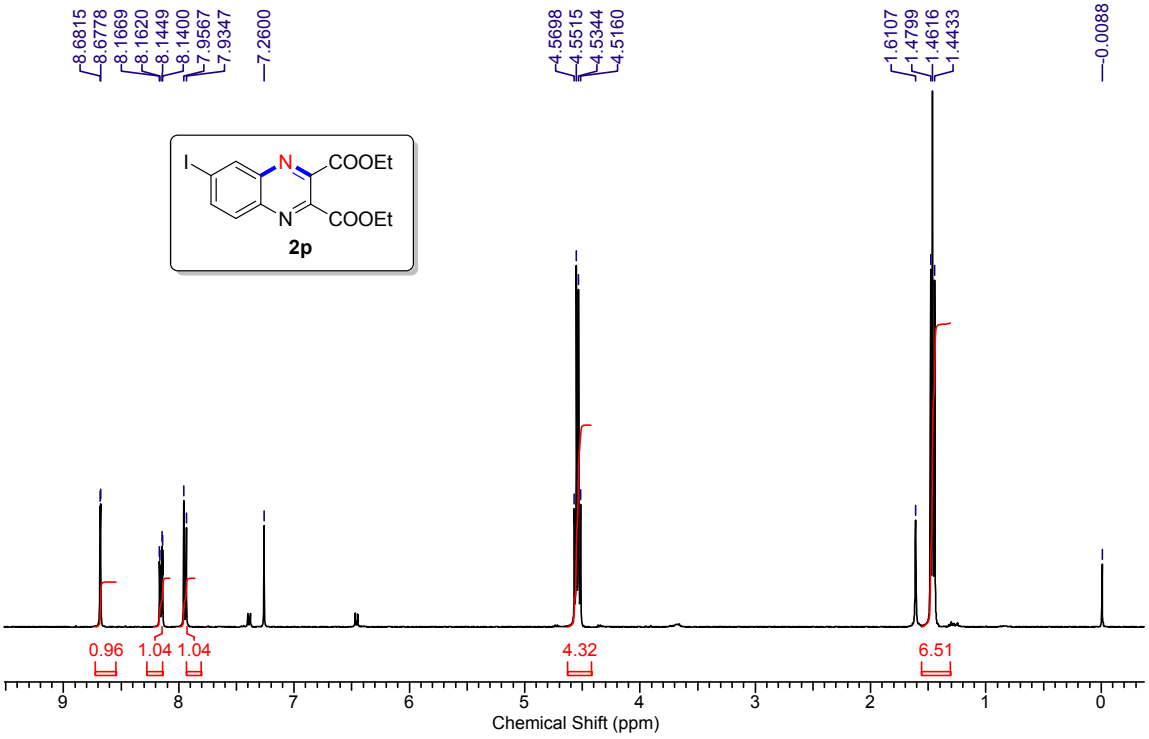
^{13}C NMR (100 MHz) spectrum of compound **2n** in $CDCl_3$



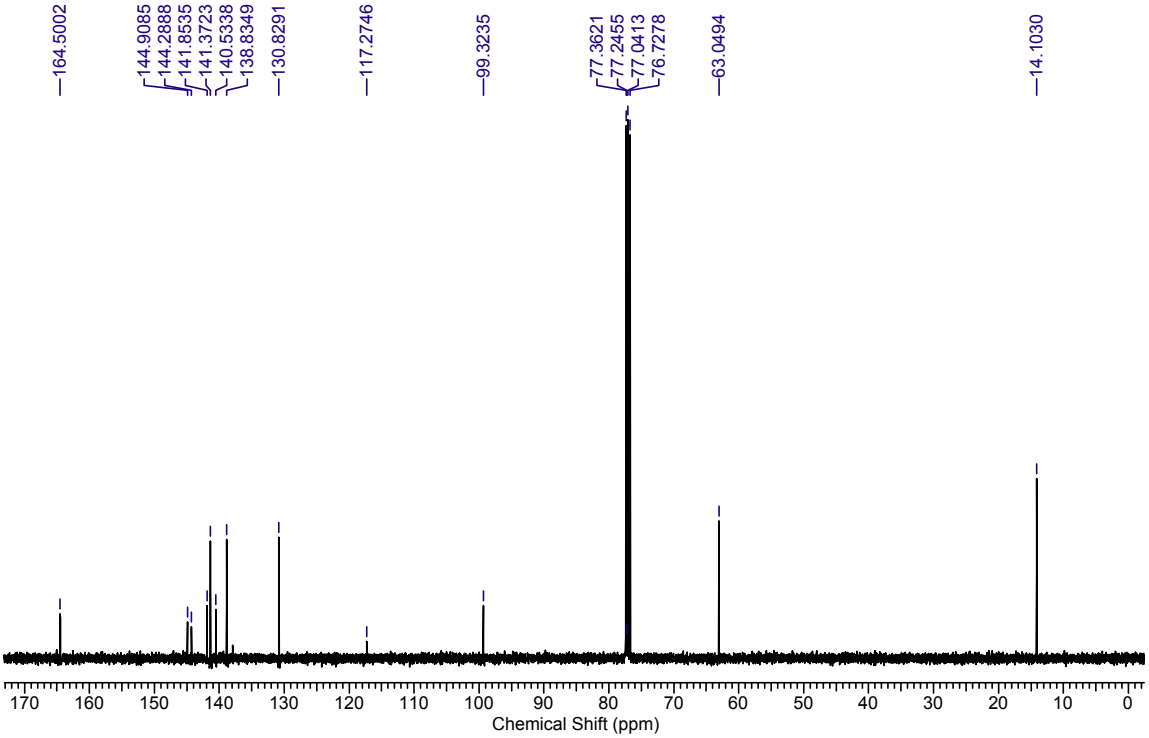
^{1}H NMR (400 MHz) spectrum of compound **2o** in $CDCl_3$



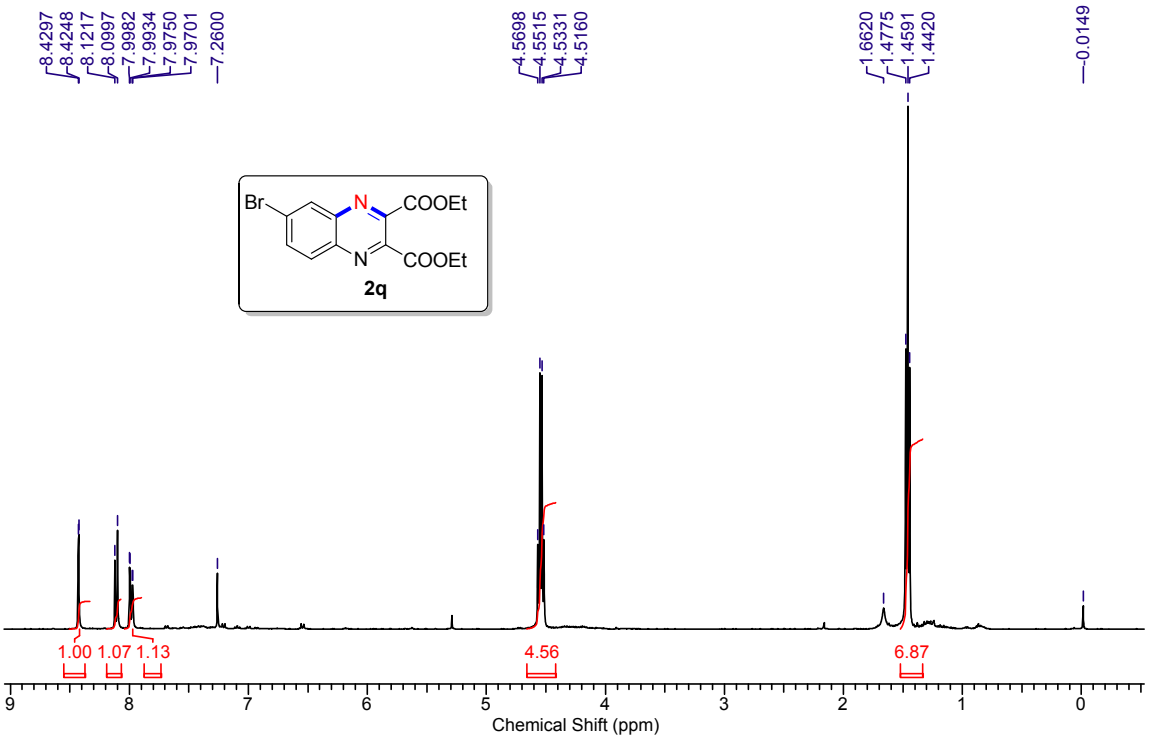
^{13}C NMR (100 MHz) spectrum of compound **2o** in $CDCl_3$



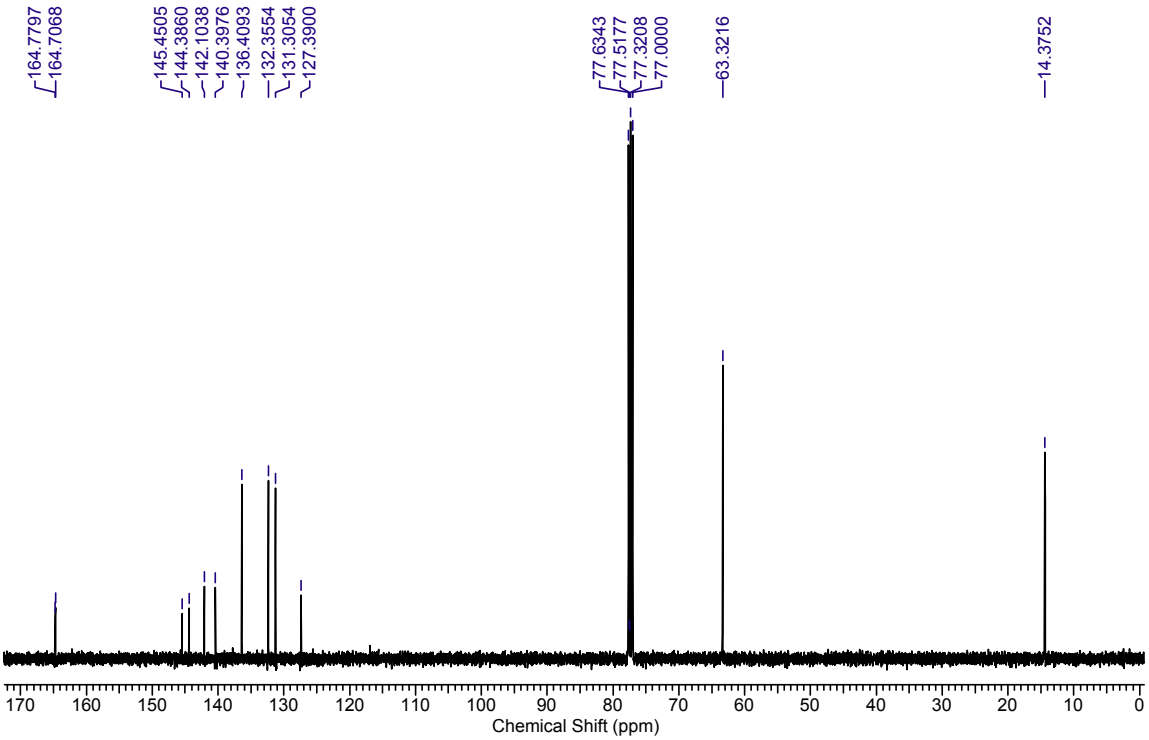
^{1}H NMR (400 MHz) spectrum of compound **2p** in $CDCl_3$



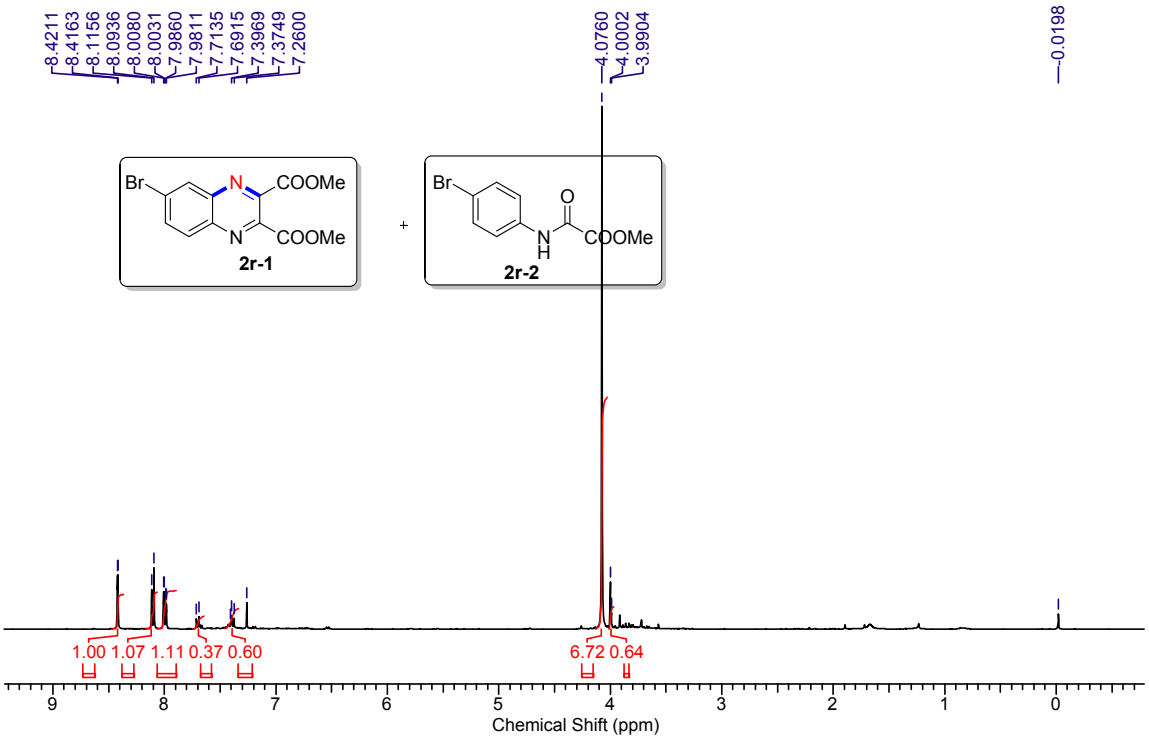
^{13}C NMR (100 MHz) spectrum of compound **2p** in $CDCl_3$



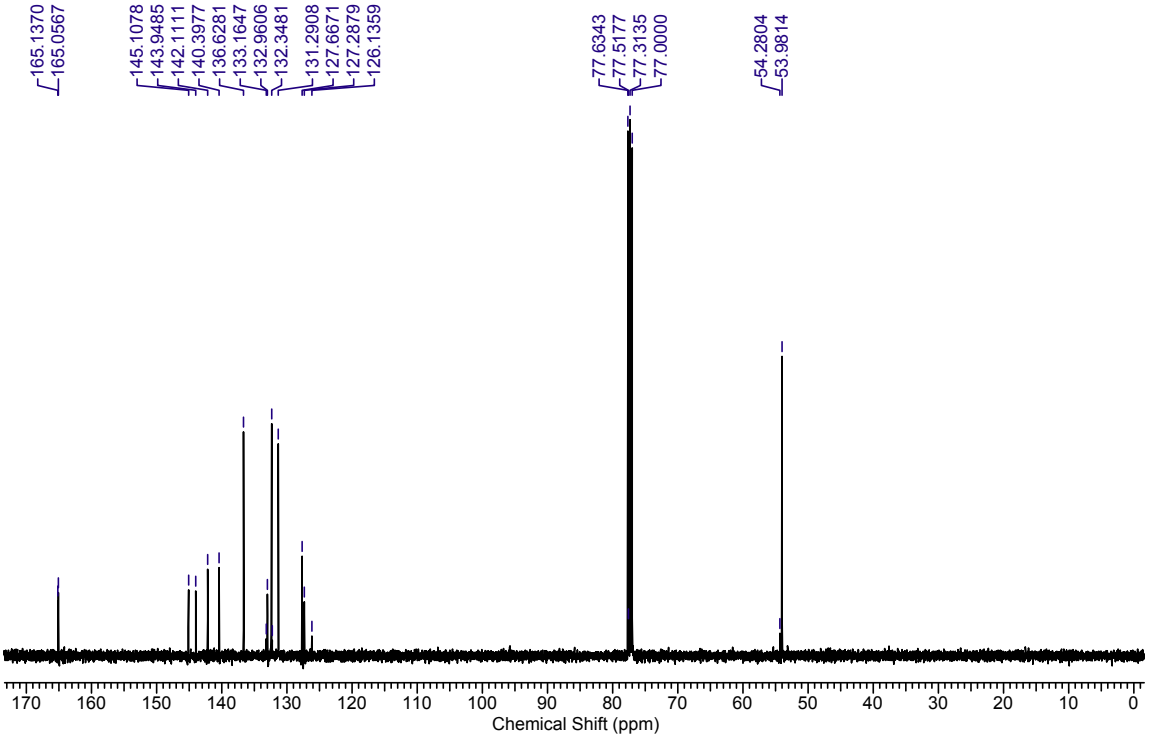
^{1}H NMR (400 MHz) spectrum of compound **2q** in $CDCl_3$



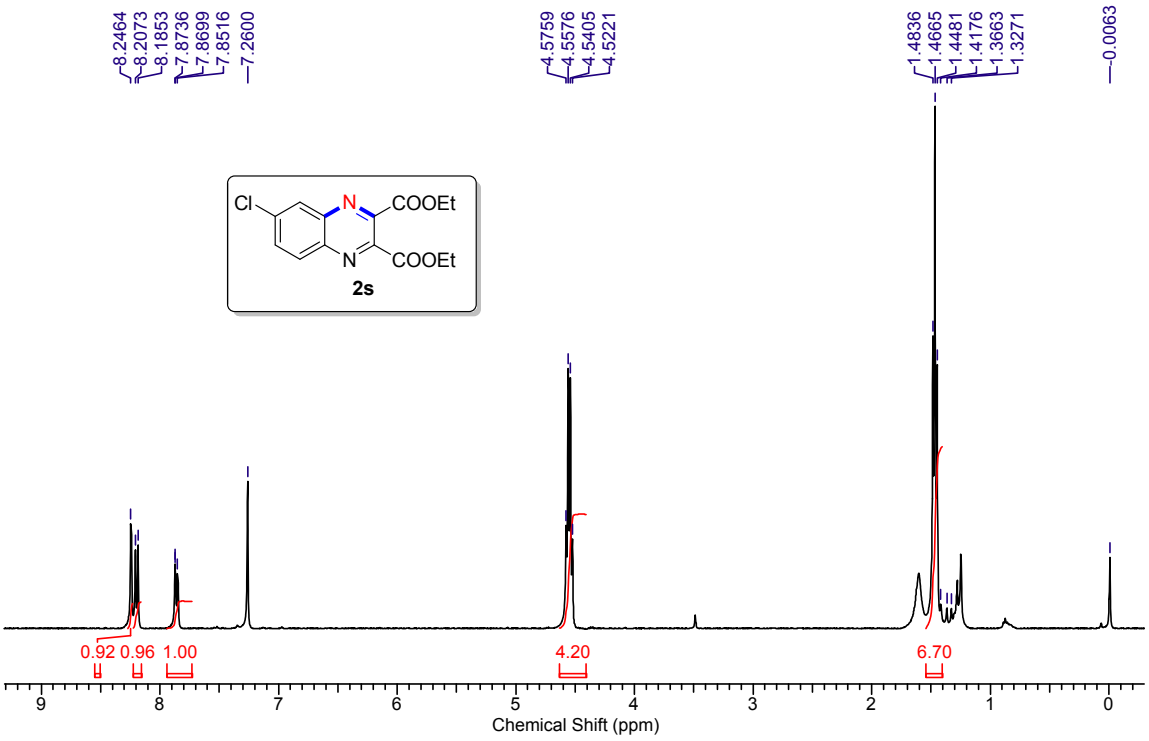
^{13}C NMR (100 MHz) spectrum of compound **2q** in $CDCl_3$



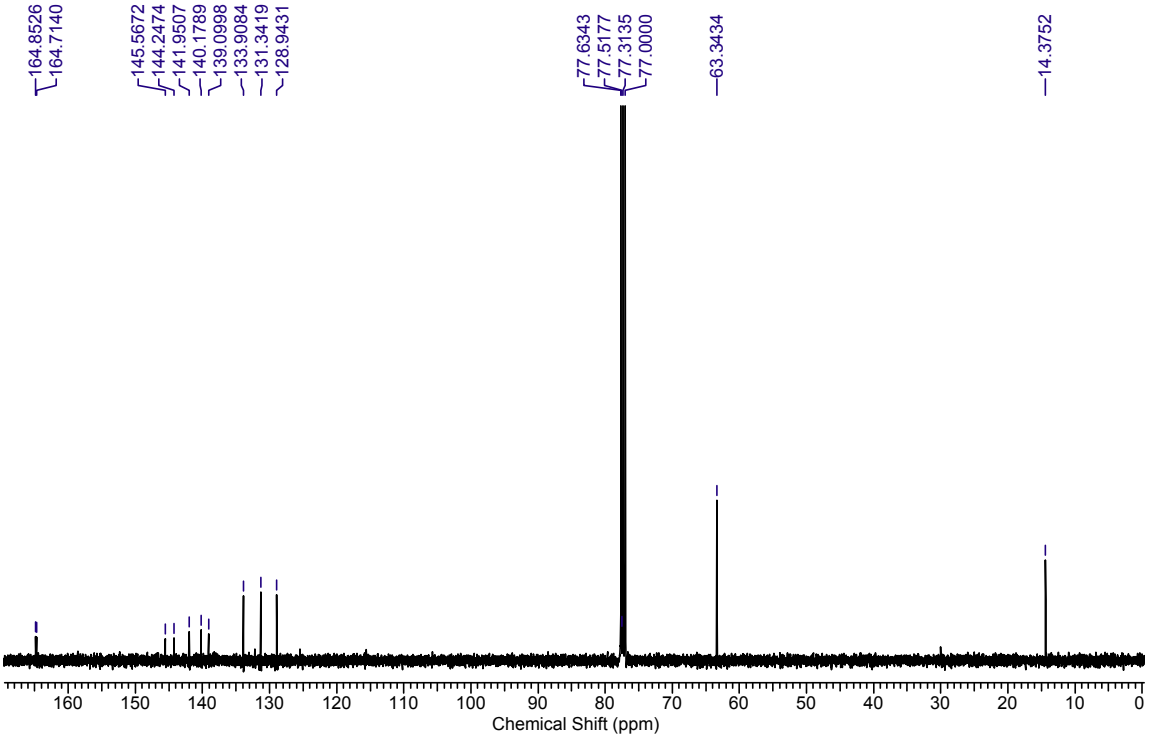
^{1}H NMR (400 MHz) spectrum of compound **2r-1**/**2r-2** in $CDCl_3$



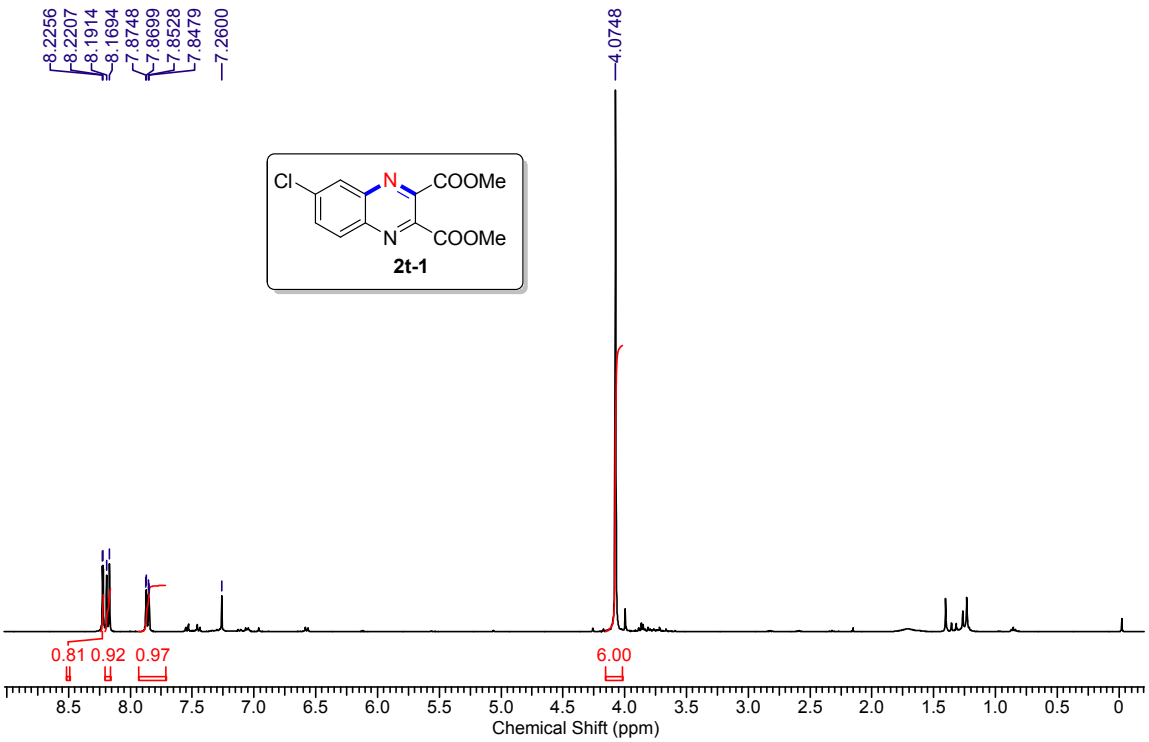
^{13}C NMR (100 MHz) spectrum of compound **2r-1**/**2r-2** in $CDCl_3$



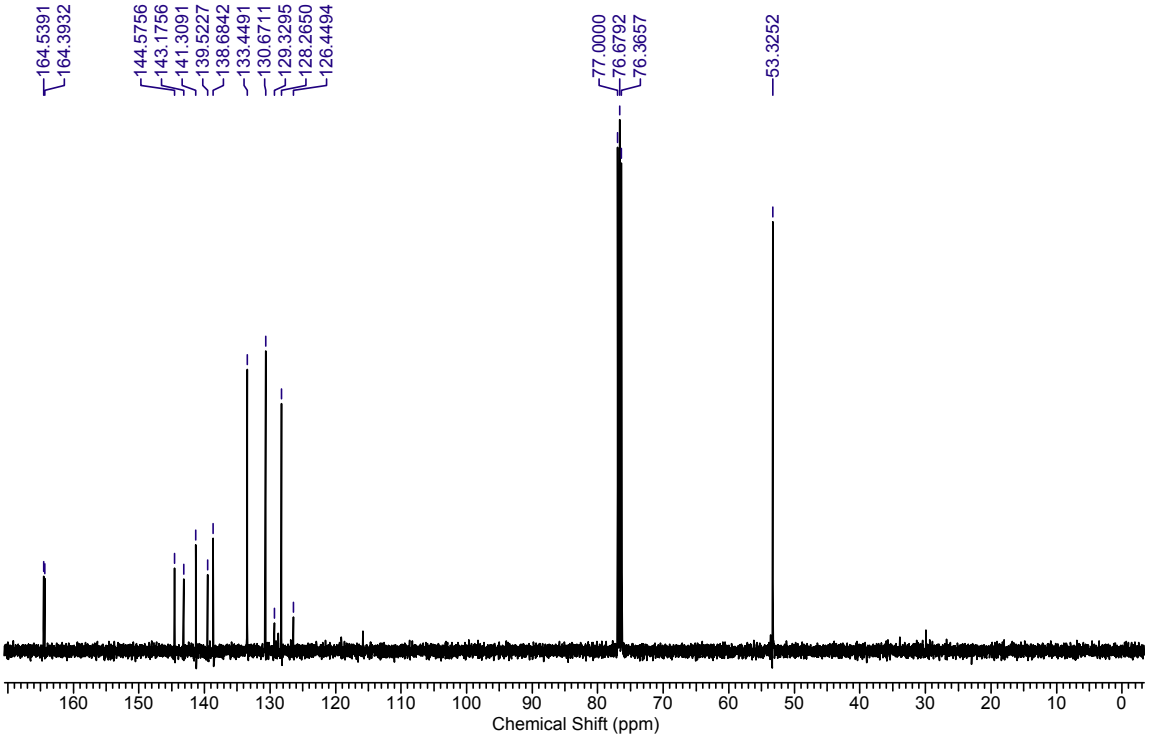
^{1}H NMR (400 MHz) spectrum of compound **2s** in $CDCl_3$



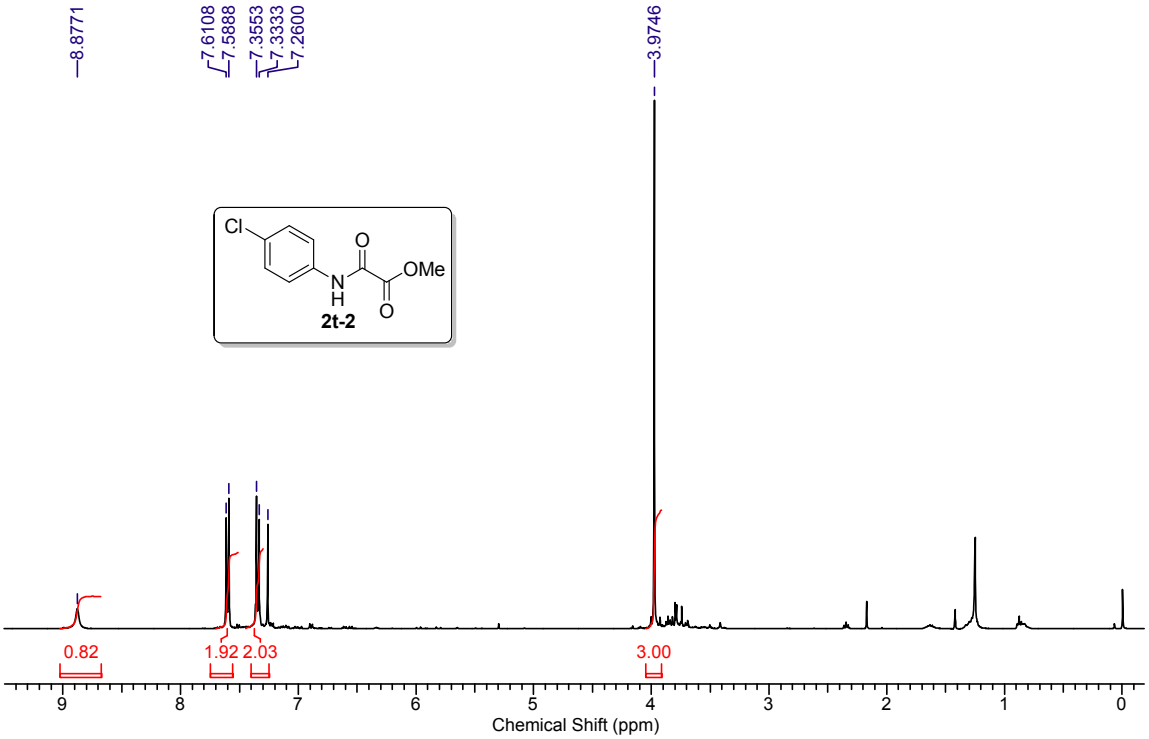
^{13}C NMR (100 MHz) spectrum of compound **2s** in $CDCl_3$



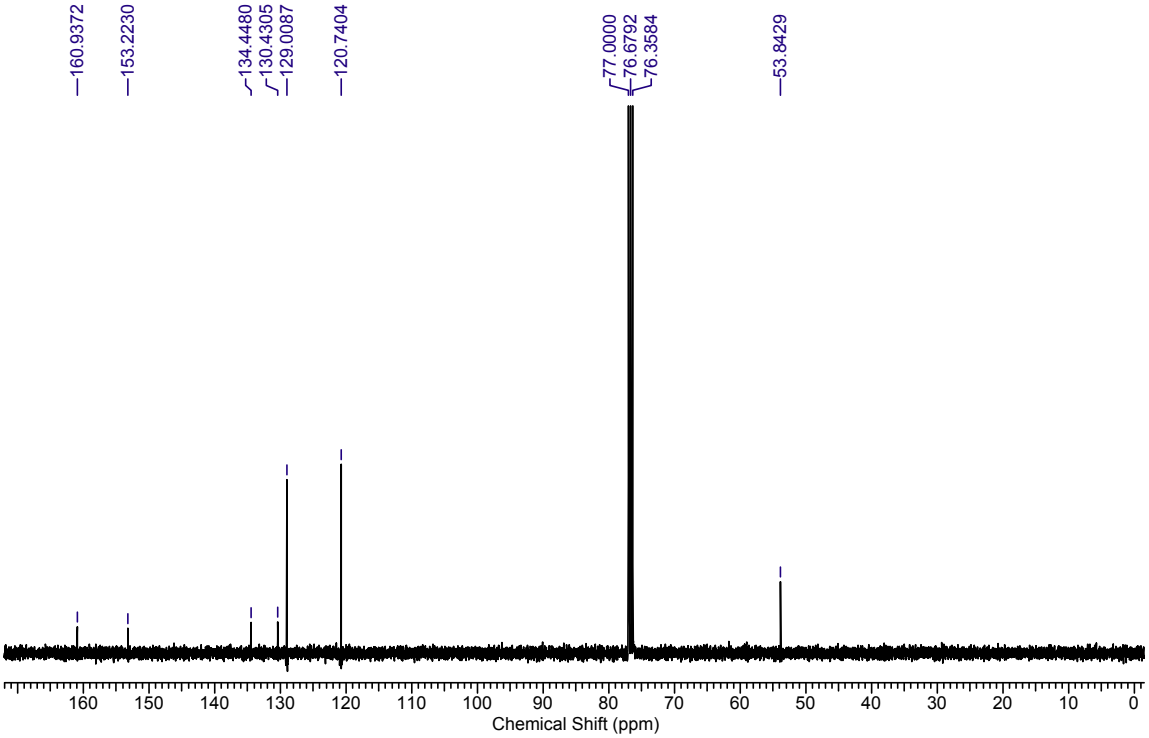
^{1}H NMR (400 MHz) spectrum of compound **2t-1** in $CDCl_3$



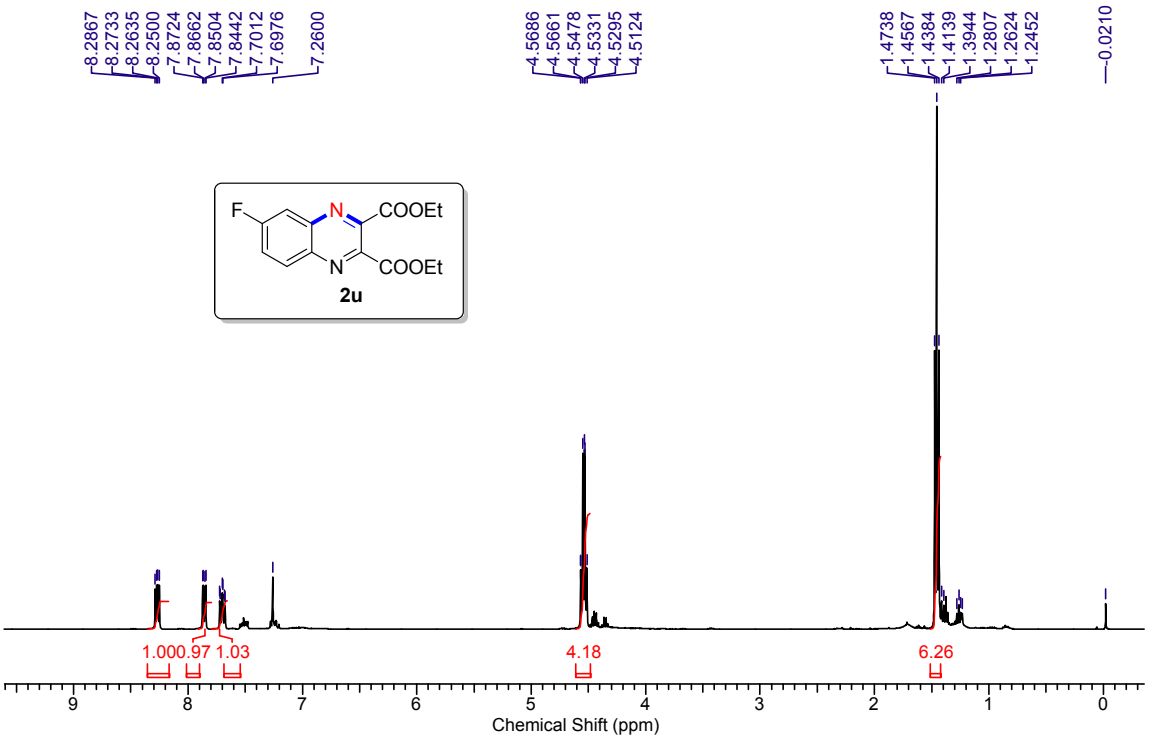
^{13}C NMR (100 MHz) spectrum of compound **2t-1** in $CDCl_3$



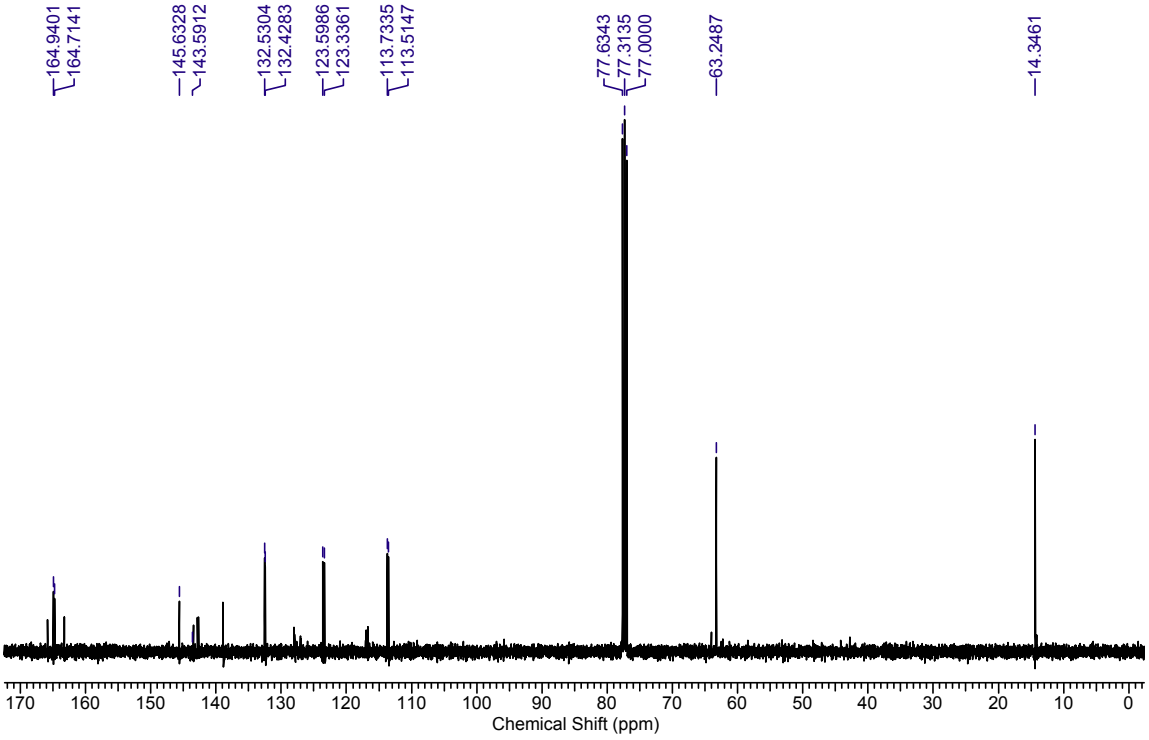
^{1}H NMR (400 MHz) spectrum of compound **2t-2** in $CDCl_3$



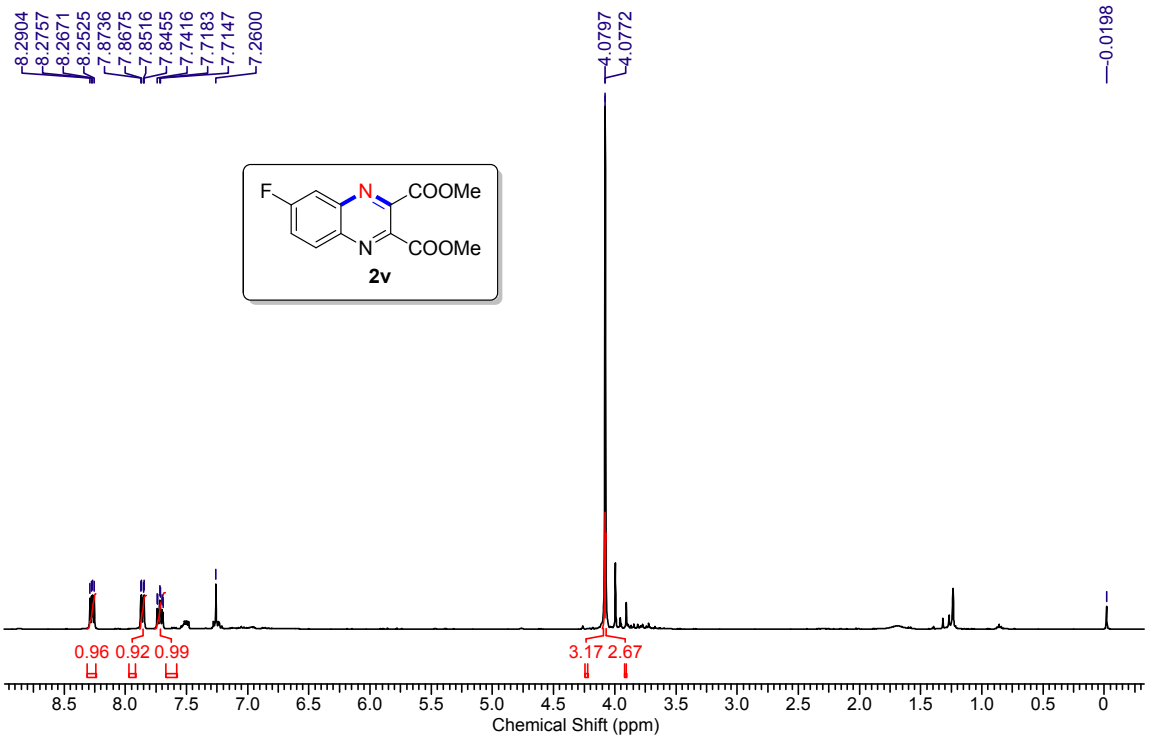
^{13}C NMR (100 MHz) spectrum of compound **2t-2** in $CDCl_3$



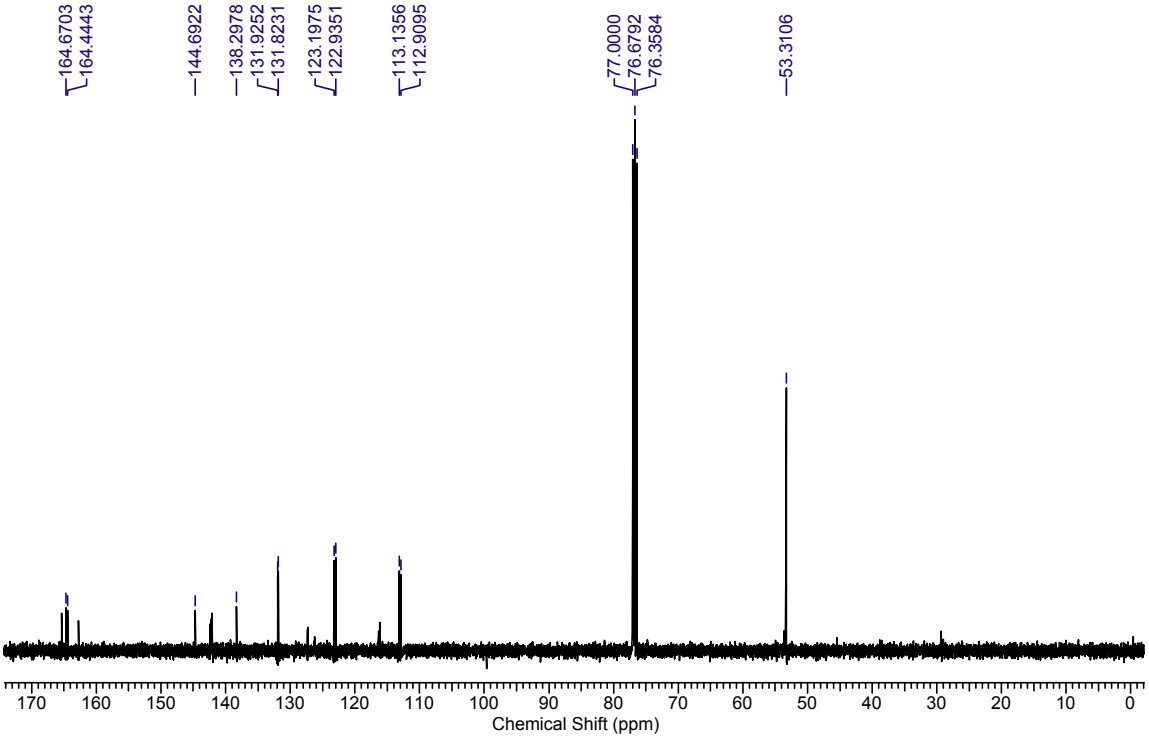
^{1}H NMR (400 MHz) spectrum of compound **2u** in $CDCl_3$



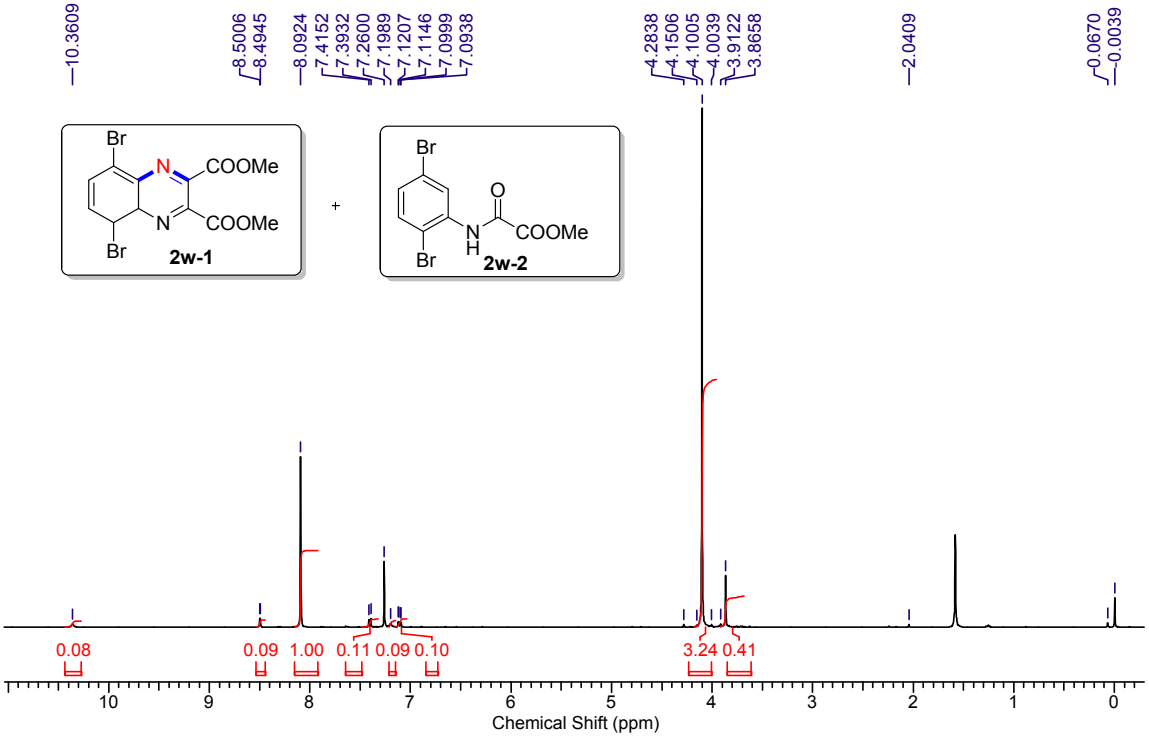
^{13}C NMR (100 MHz) spectrum of compound **2u** in $CDCl_3$



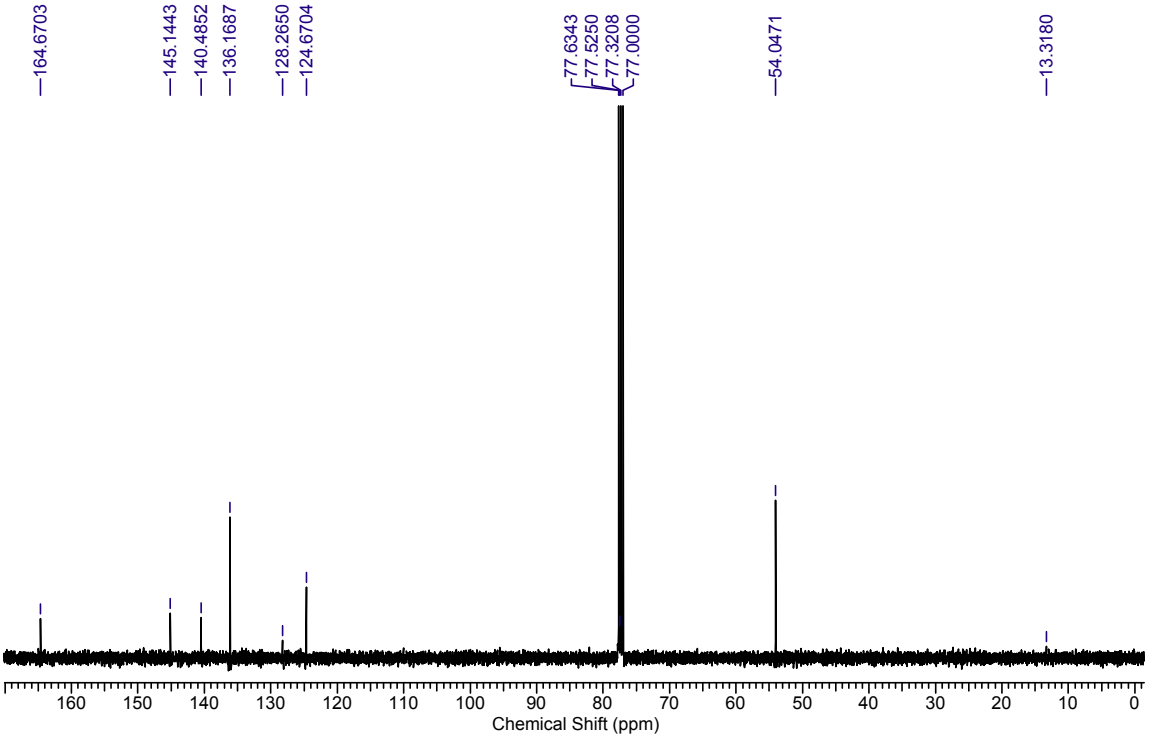
^{1}H NMR (400 MHz) spectrum of compound **2v** in $CDCl_3$



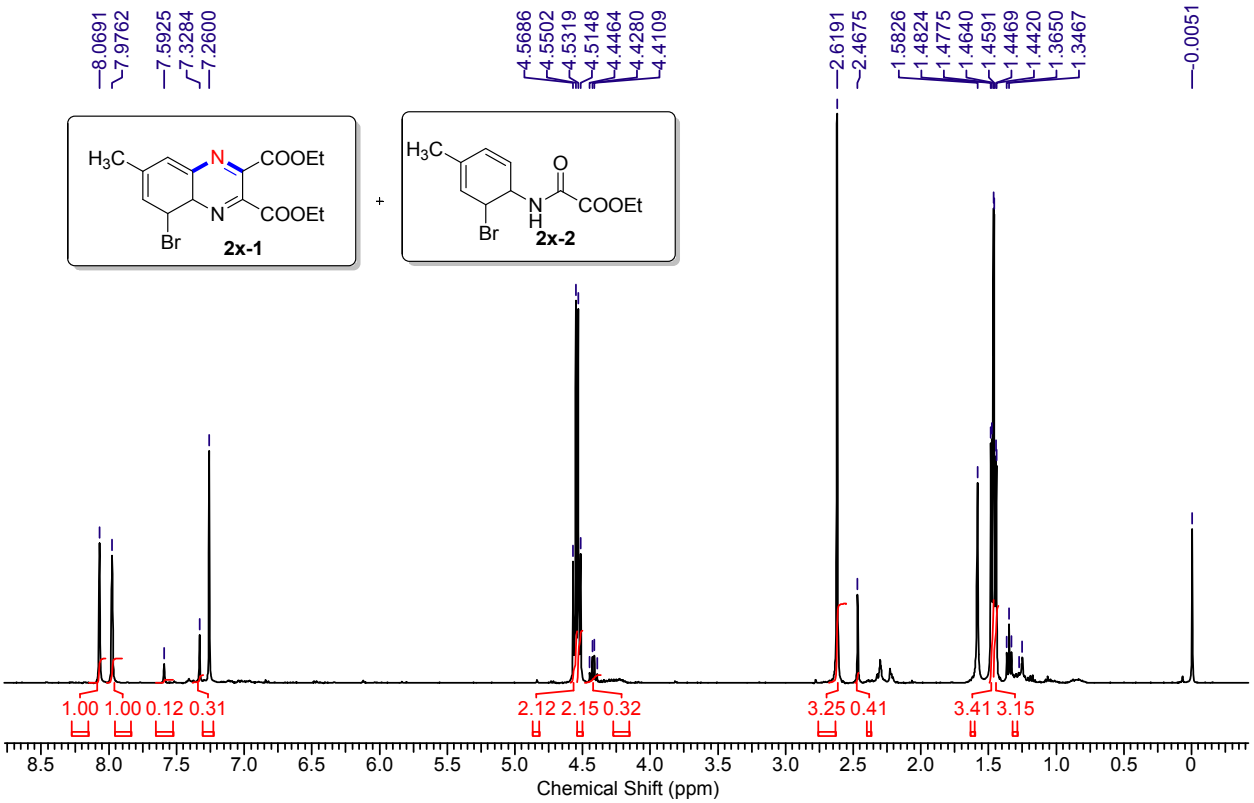
^{13}C NMR (100 MHz) spectrum of compound **2v** in $CDCl_3$



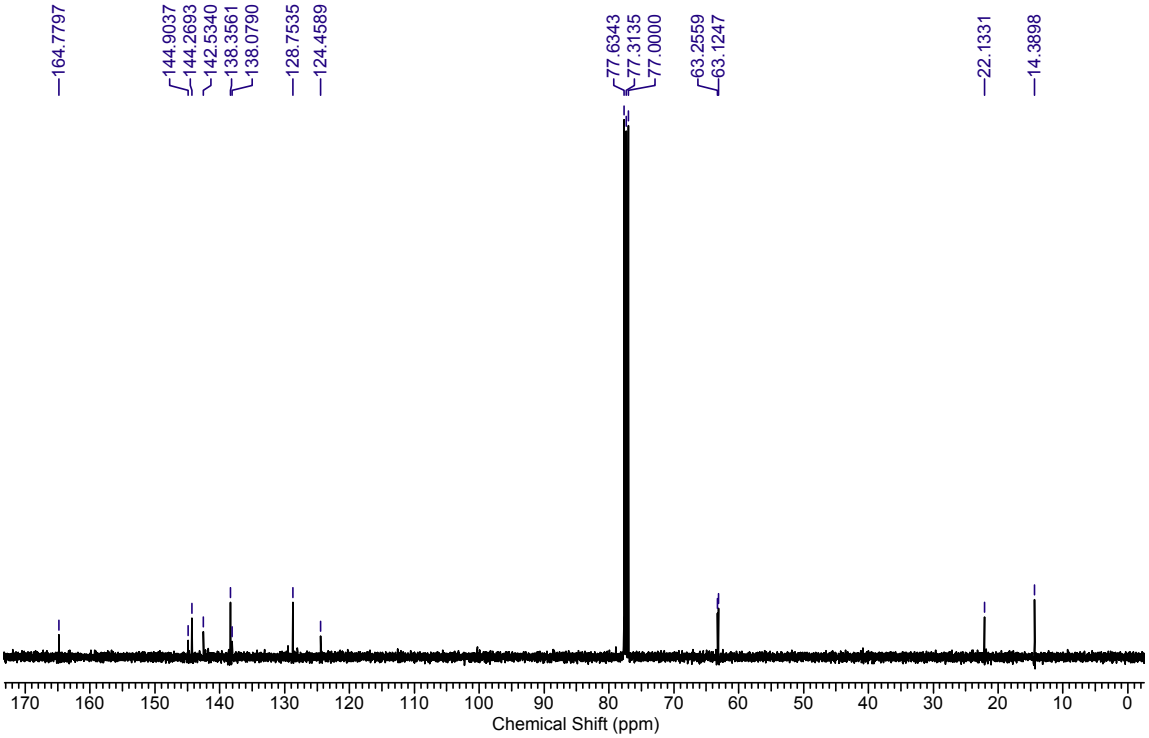
^{1}H NMR (400 MHz) spectrum of compound **2w-1/2w-2** in $CDCl_3$



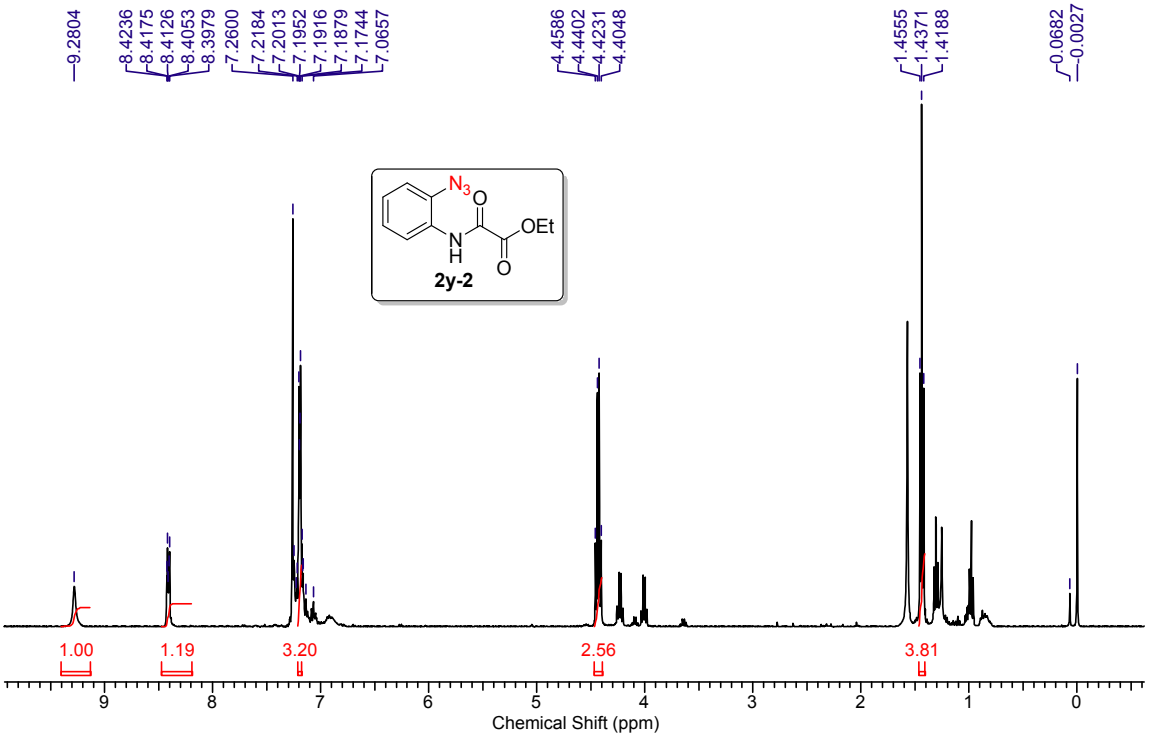
^{13}C NMR (100 MHz) spectrum of compound **2w-1/2w-2** in $CDCl_3$



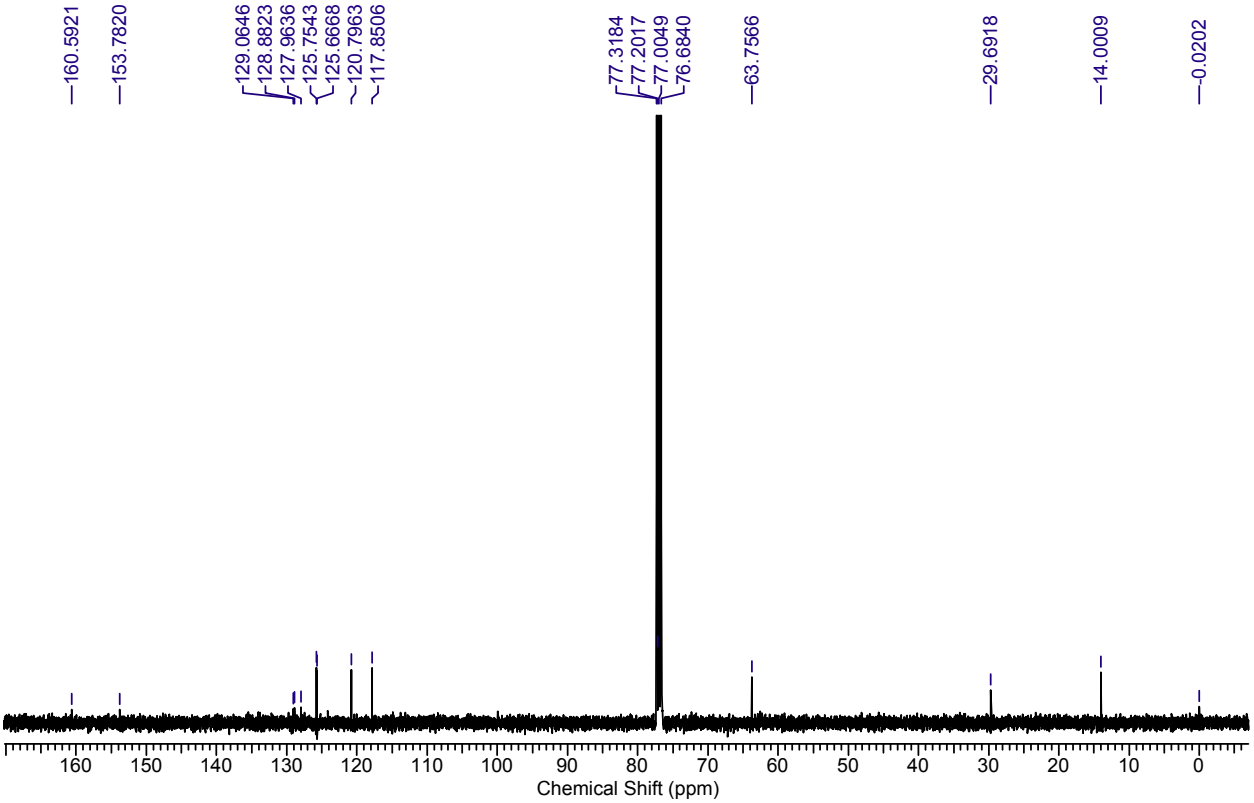
^{1}H NMR (400 MHz) spectrum of compound **2x-1/2x-2** in $CDCl_3$



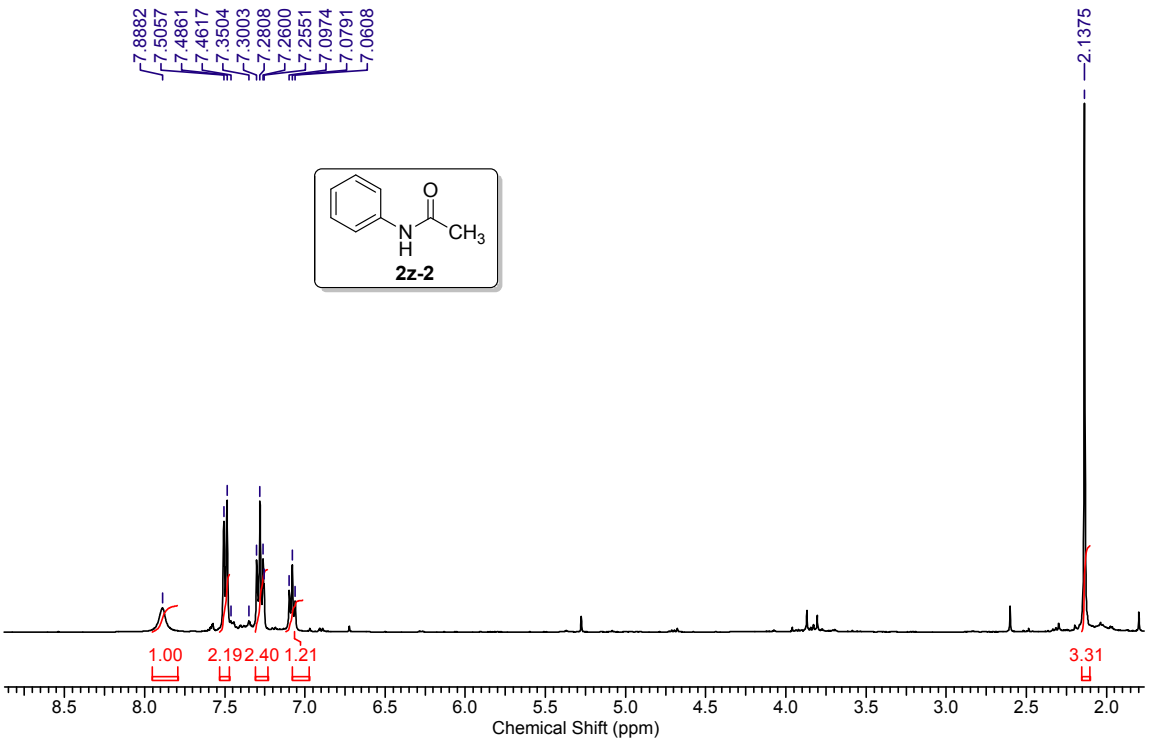
^{13}C NMR (100 MHz) spectrum of compound **2x-1/2x-2** in $CDCl_3$



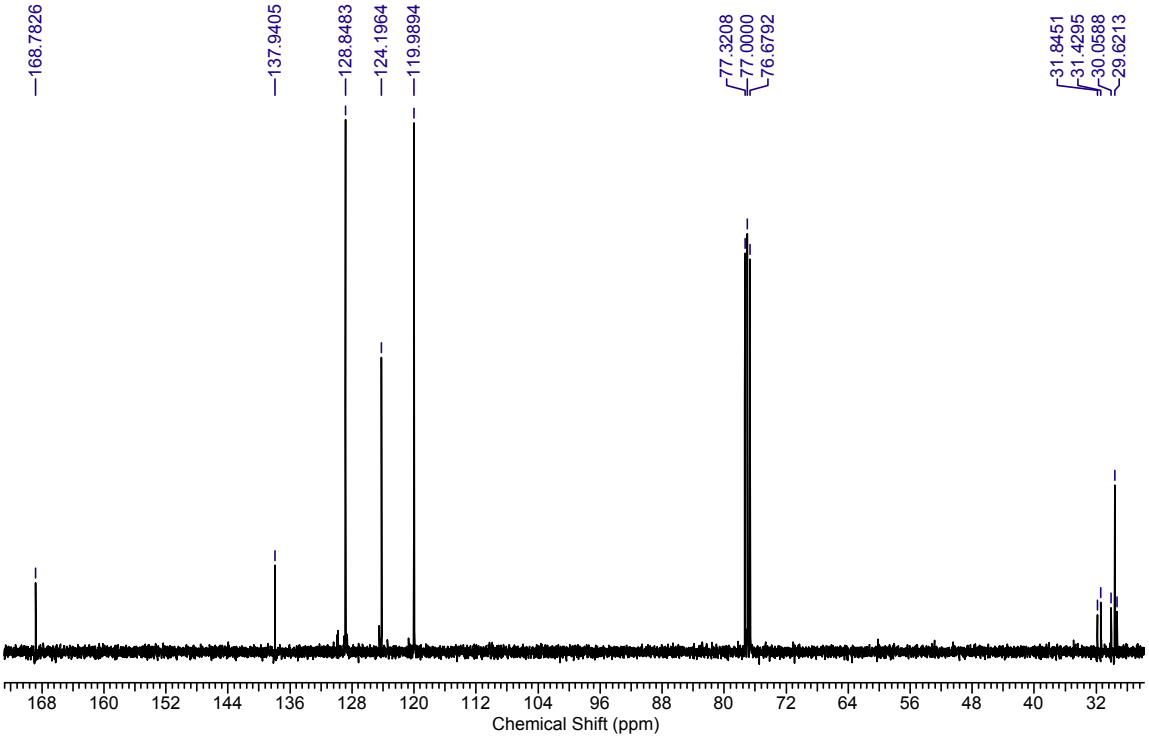
^{1}H NMR (400 MHz) spectrum of compound **2y-2** in $CDCl_3$



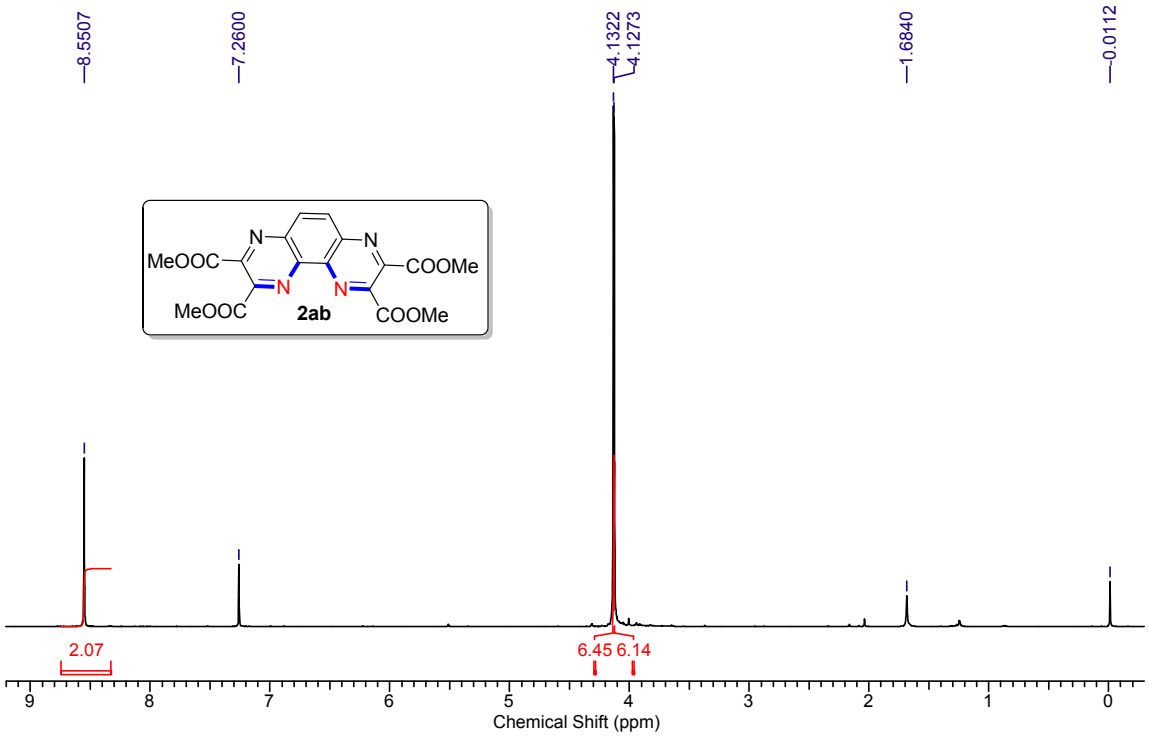
^{13}C NMR (100 MHz) spectrum of compound **2y-2** in $CDCl_3$



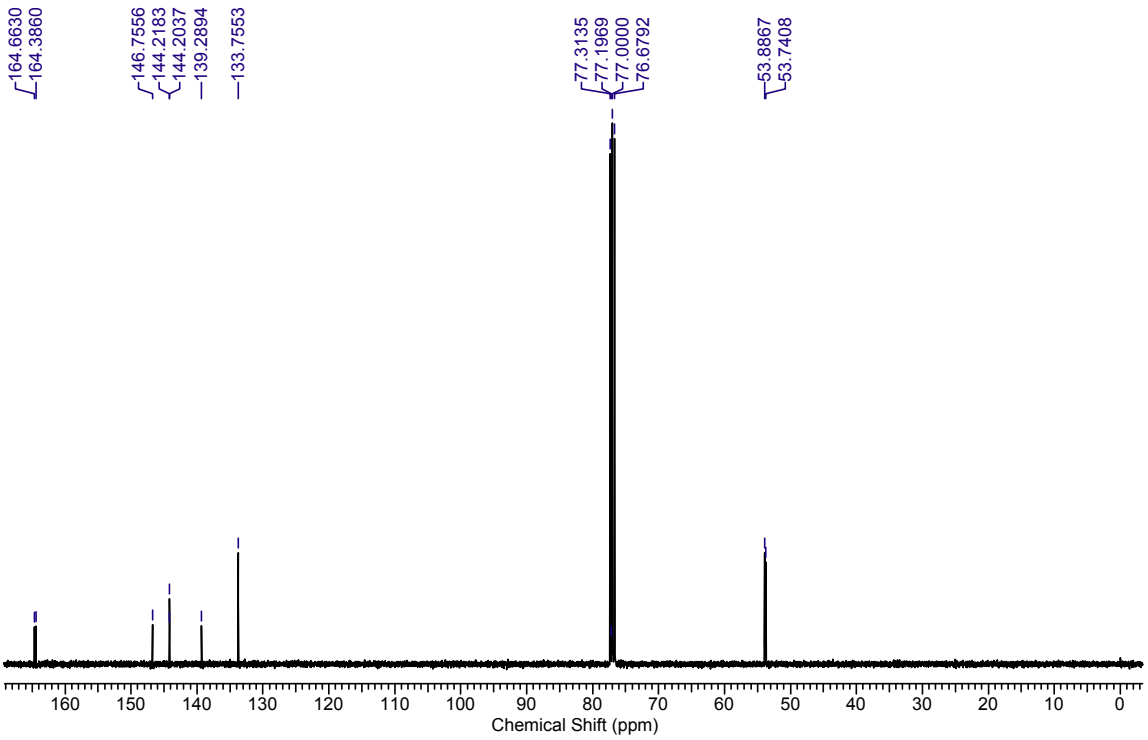
^{1}H NMR (400 MHz) spectrum of compound **2z-2** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound **2z-2** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of compound **2ab** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound **2ab** in $CDCl_3$

References:

1. (a) Choudhary, G.; Peddinti, R. *Green Chem*. **2011**, *13*, 3290. (b) Ramanathan, D.; Pitchumani, K. *Eur*. *J*. *Org*. *Chem*. **2015**, 463. (c) Thorwirth, R.; Stolle, A. *Synlett*. **2011**, *15*, 2200. (d) Ziyaei-Halimehjani, A.; R. Saidi, M. *Tetrahedron Lett*. **2008**, *49*, 1244. (e) Kah Toh, K.; Sanjaya, S.; Sahnoun, S.; Yee Chong, S.; Chiba, S. O*rg. Lett*, **2012**, *14*, 2290. (f) Weiße, M.; Zille, M.; Jacob, K.; Schmidt, R.; Stolle, A. *Chem*. *Eur*. *J*. **2015**, *21*, 6511**. (g)** Zewge, D.; Chen, C-y.; Deer, C.; G. Dormer, P.; L. Hughes, J. D. *Org*. *Chem*. **2007**, *72*, 4276.
2. Dai, Q.; Yang, W.; Zhang, X. *Org. Lett*, **2005**, *7*, 5343.
3. M Chiurato, M.; Boulahjara, R.; Routiera, S.;Troinb, Y.; Guillaumeta, G.; *Tetrahedron* **2010**, *66*, 4647.
4. Teresa M. V. D.; Melo, P.; Lopes, C S. J.; António M. d'A.; Gonsalves, R.; Beja, A.M.; Paixão, J. A.; Silva, M. R.; da Veiga, L. A. *J. Org. Chem*. **2002**, *67*, 66.
5. Okumura, S.; Takeda, Y.; Kiyokawa, K.; Minakata, S. *Chem. Commun.* 2013, *49*, 9266.