

Supporting Information

Copper-Catalyzed Oxidative Direct C3-cyanoarylation of Quinoxalin-2(1*H*)-ones *via* Denitrogenative Ring-Opening of 3- Aminoindazoles

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1 General information

All chemicals were commercially available and used as received without further. Column chromatography was performed using 300-400 mesh silica. Nuclear magnetic resonance spectra were recorded on Bruker Avance 400 MHz spectrometer. ^1H NMR spectra are recorded in parts per million from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane. ^{19}F NMR spectra were recorded in parts per million with fluorobenzene as external standard. High resolution mass spectra (HR MS) was performed using a Thermo Scientific Q Exactive Hybrid Quadrupole-Orbitrap mass spectrometer equipped with an EASY Spray nanospray source operated in positive ion mode. IR spectra were recorded on WQF-510 Fourier transform infrared spectrophotometer. Melting points were measured on an XT4A microscopic apparatus uncorrected.

2 Screening the reaction conditions

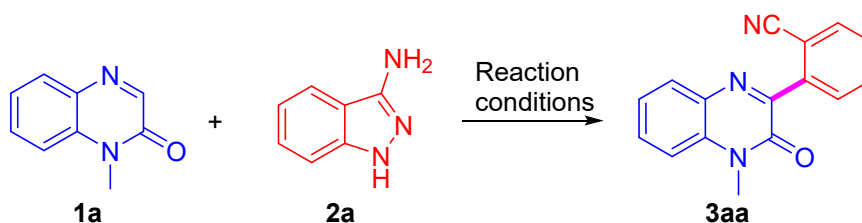


Table S1 Screening the molar ratio of **1a** and **2a**^a

Entry	the molar ratio of 1a and 2a	Yields (%) ^b
1	1 : 1.0	45
2	1 : 1.2	50
3	1 : 1.5	56
4	1 : 2.0	56

^a Reaction conditions: 1-methyl quinoxalin-2(1H)-ones **1a** (0.2 mmol), 3-aminoindazole **2a**, $\text{Cu}(\text{OAc})_2$ (0.03 mmol, 5.43 mg), TBPB (0.5 mmol, 97.0 mg), and MeCN (2 mL), heated in oil bath at 120 °C for 2.0 h under air.

^b Isolated yield.

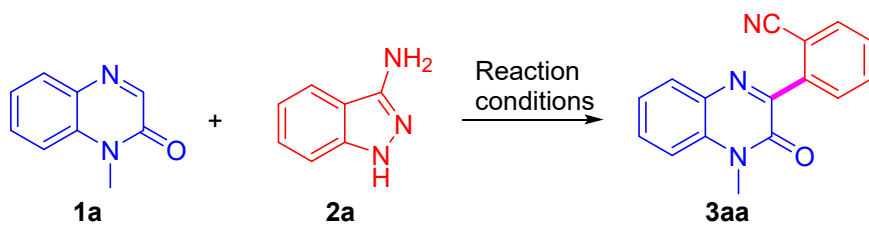


Table S2 Screening the reaction temperature ^a

Entry	the reaction temperature (°C)	Yields (%) ^b
1	60	40
2	80	51
3	100	63
4	120	57

^a Reaction conditions: 1-methyl quinoxalin-2(1H)-ones **1a** (0.2 mmol, 32.0 mg), 3-aminoindazole **2a** (0.3 mmol, 39.9 mg), Cu(OAc)₂ (0.03 mmol, 5.43 mg), TBPB (0.5 mmol, 97.0 mg), and MeCN (2 mL), heated at 120 °C for 2.0 h under air.

^b Isolated yield.

3 Copies of spectra of products

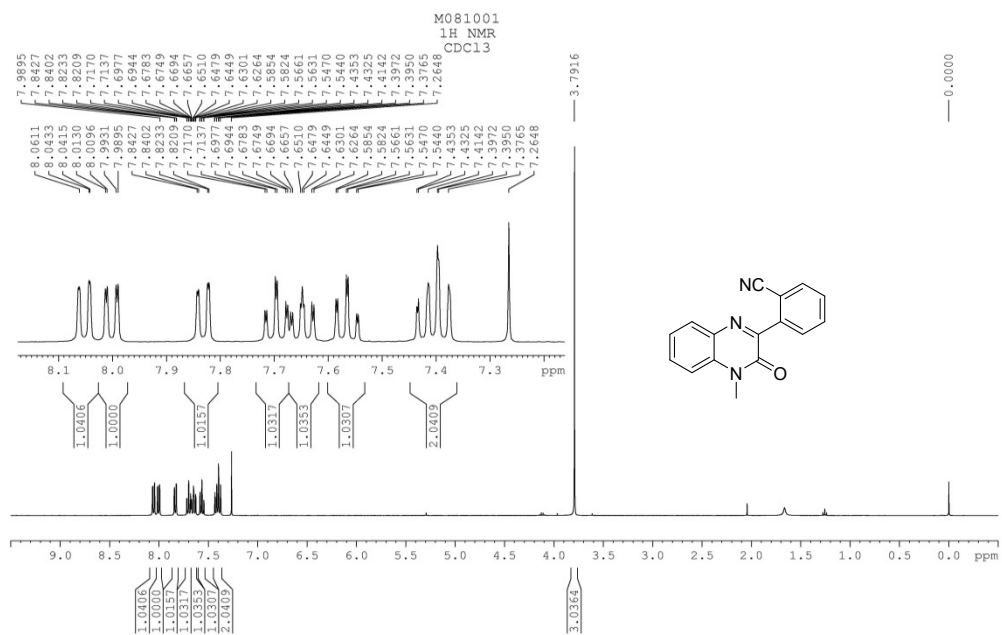


Fig. 1 ¹H NMR spectrum of compound 3aa

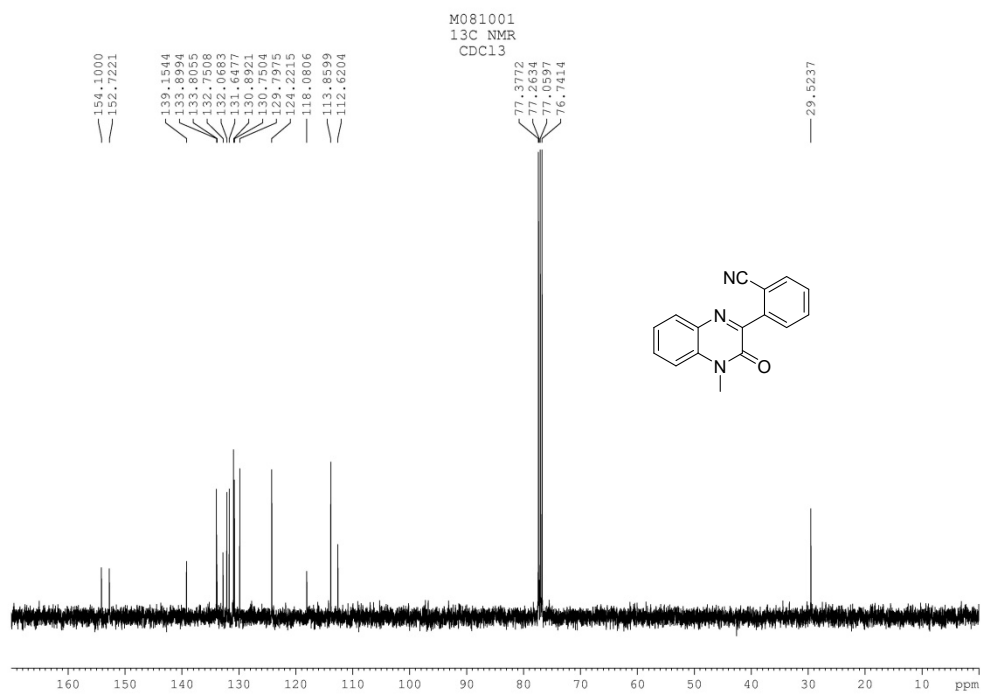


Fig. 2 ¹³C NMR spectrum of compound 3aa

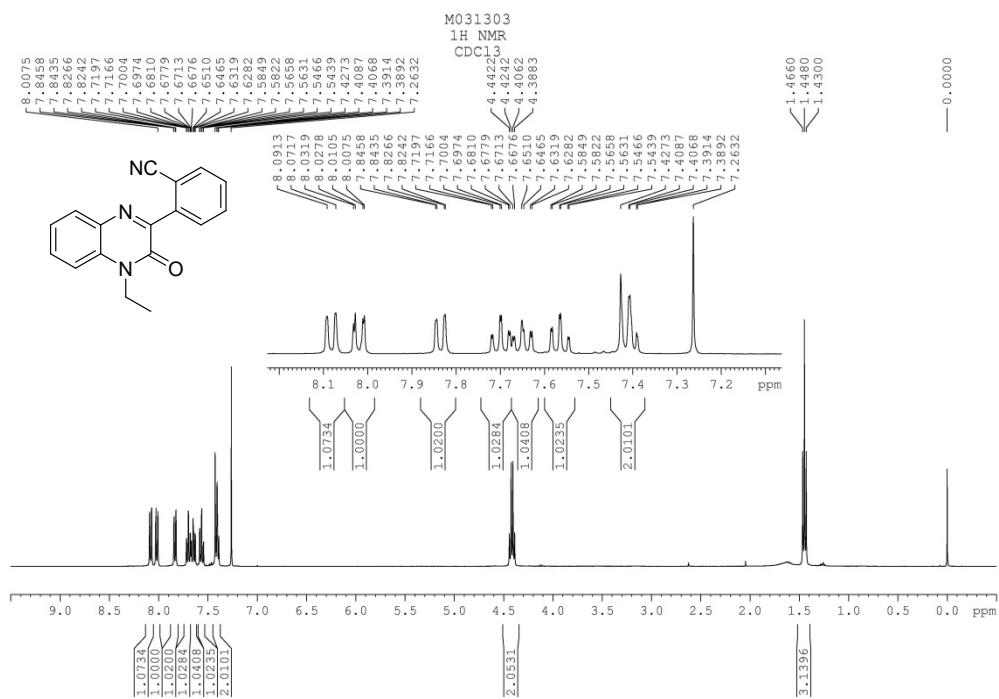


Fig. 3 ¹H NMR spectrum of compound 3ba

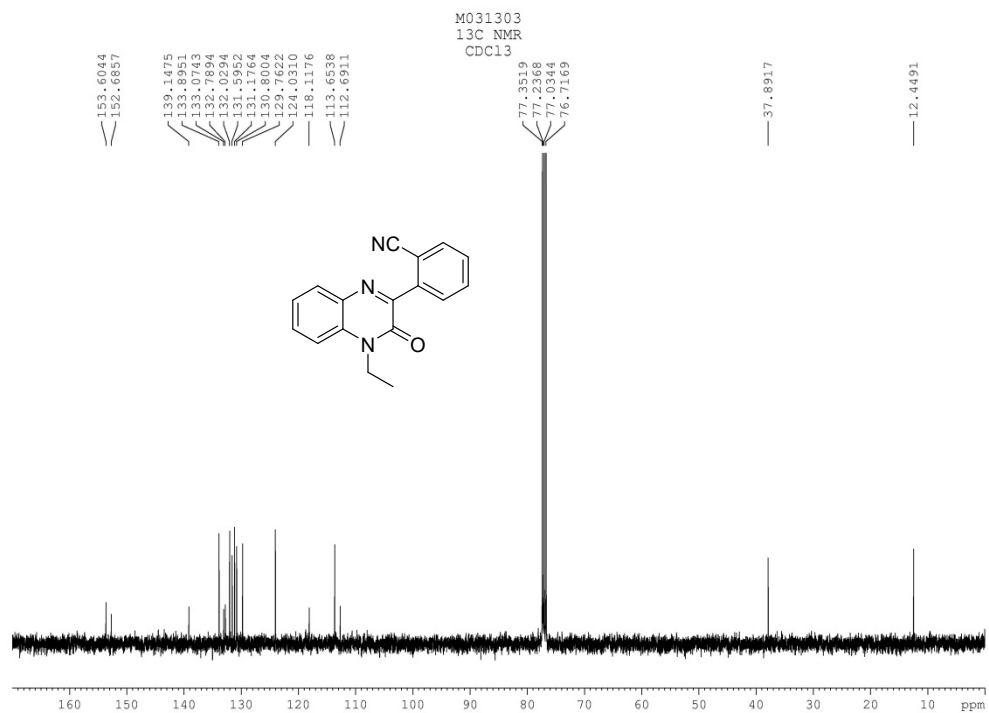


Fig. 4 ¹³C NMR spectrum of compound 3ba

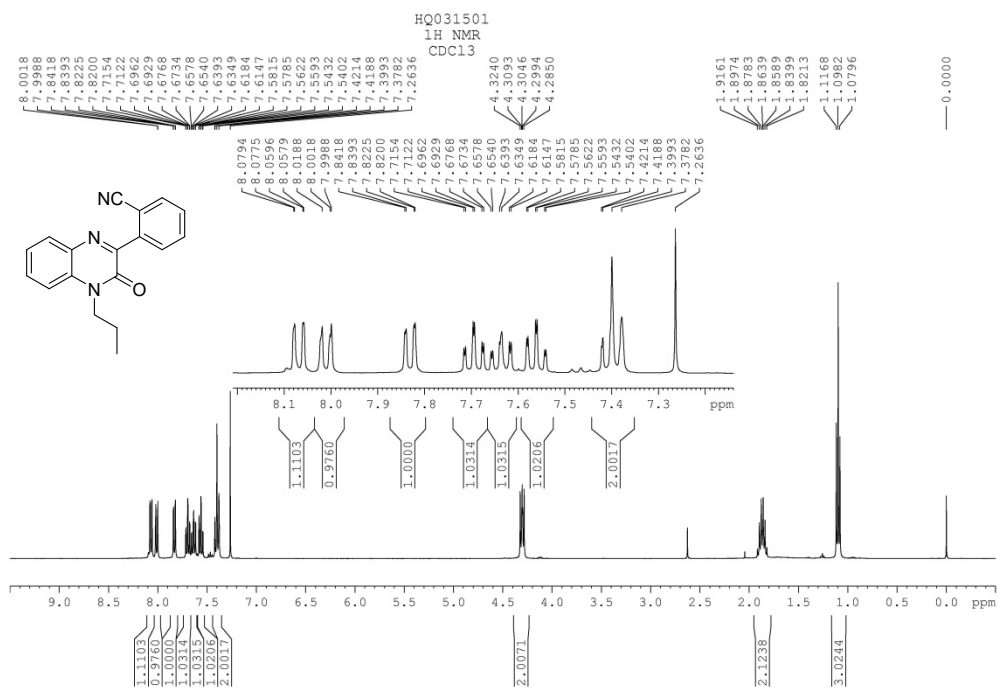


Fig. 5 ¹H NMR spectrum of compound 3ca

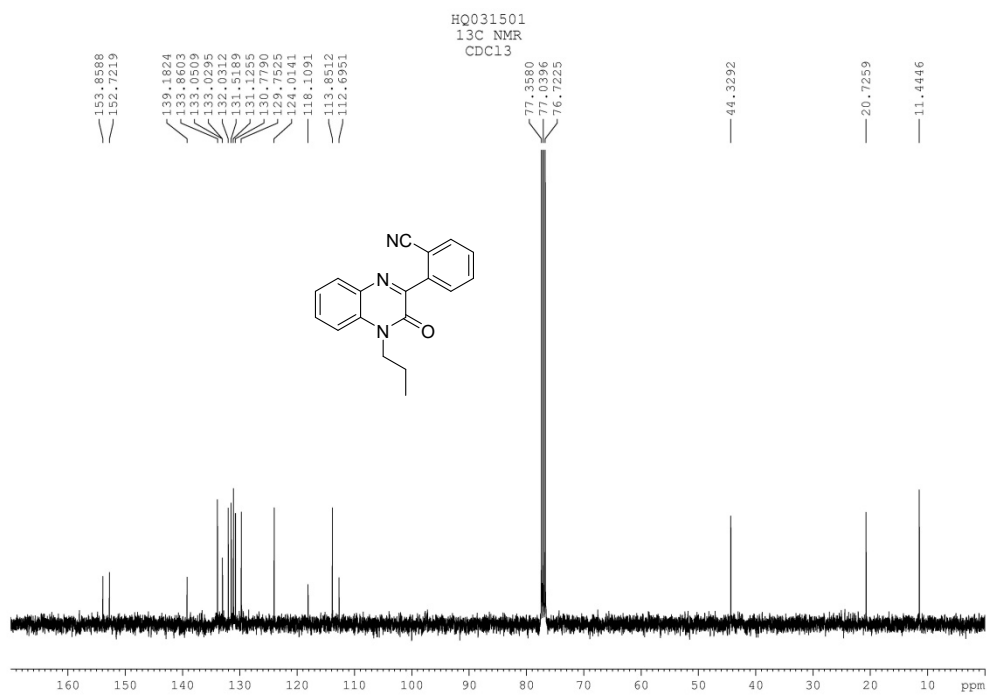


Fig. 6 ¹³C NMR spectrum of compound 3ca

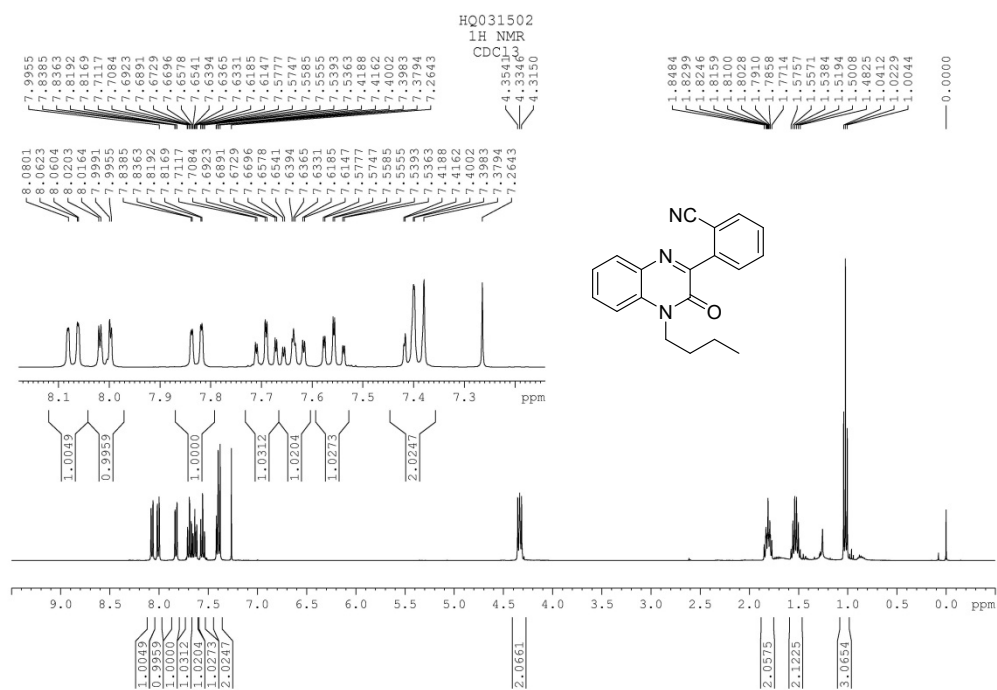


Fig. 7 ¹H NMR spectrum of compound 3da

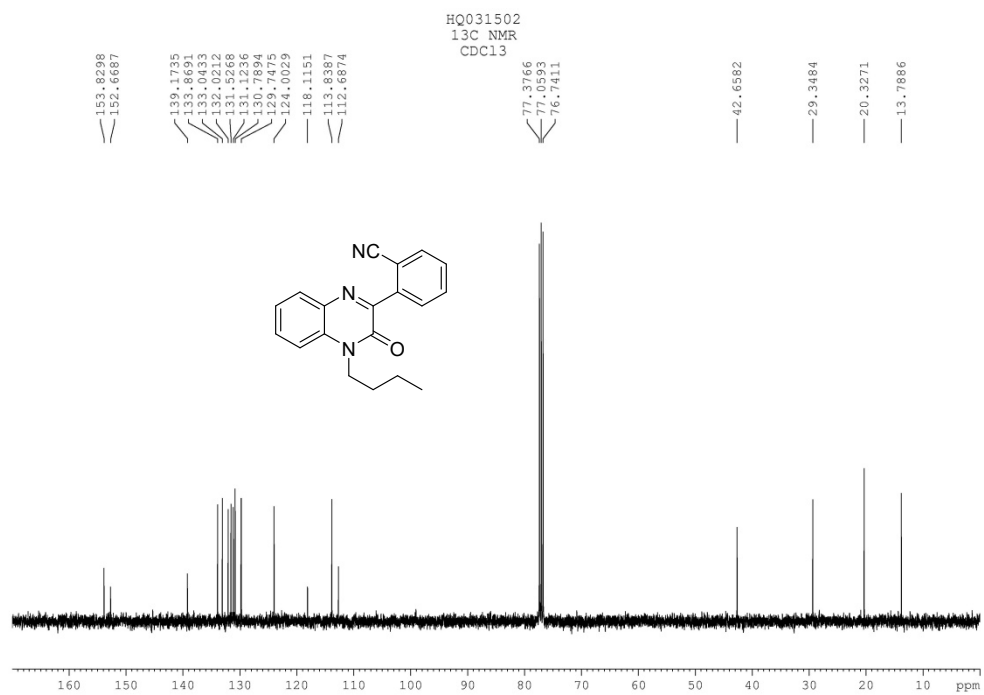


Fig. 8 ¹³C NMR spectrum of compound 3da

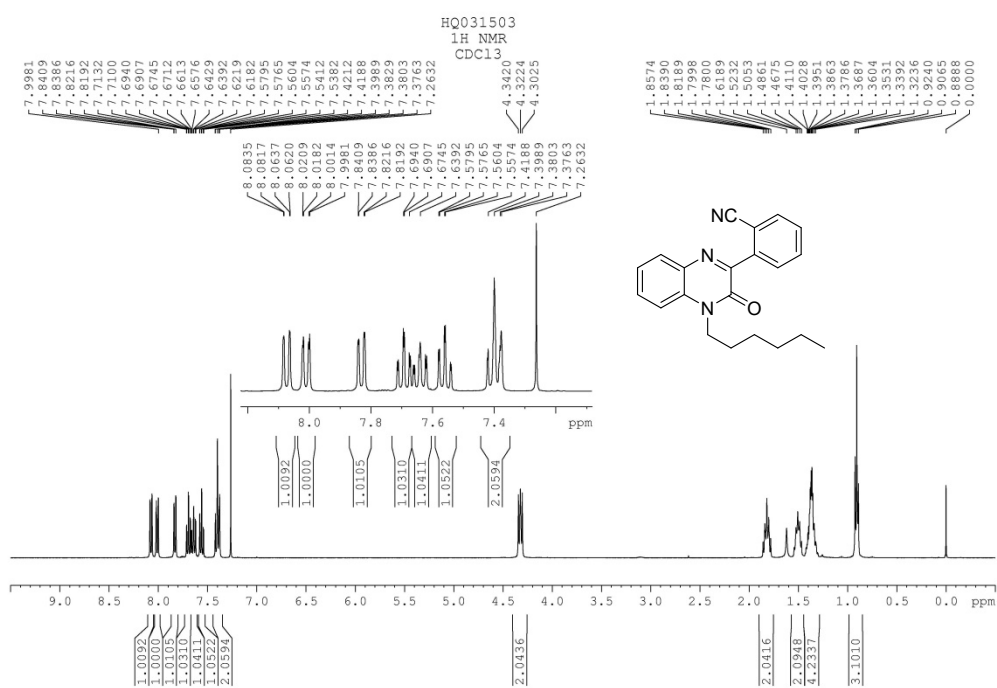


Fig. 9 ¹H NMR spectrum of compound 3ea

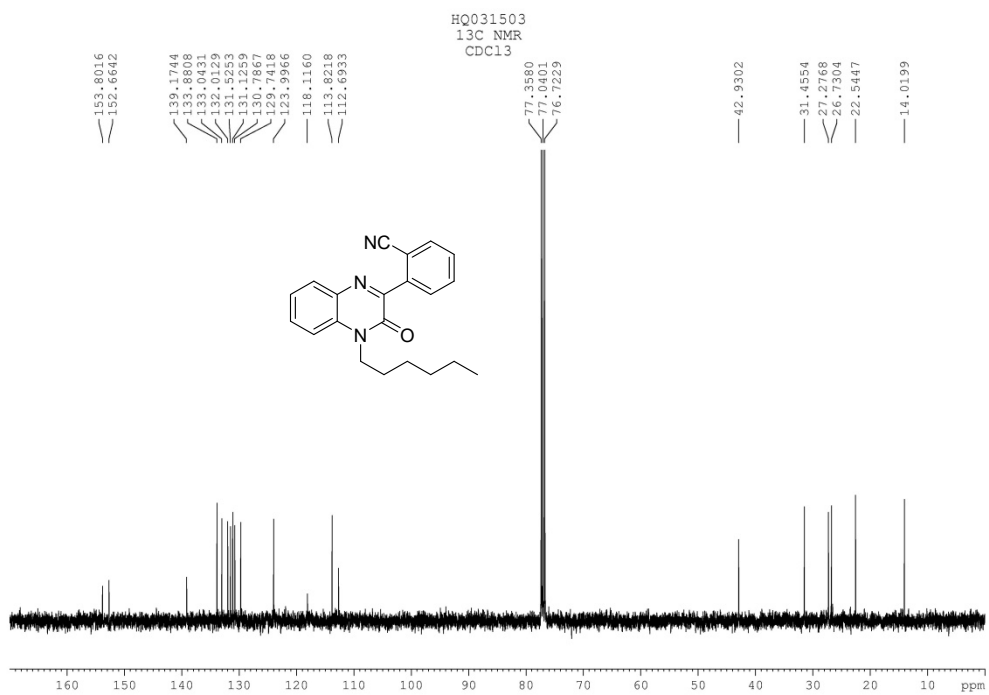


Fig. 10 ¹³C NMR spectrum of compound 3ea

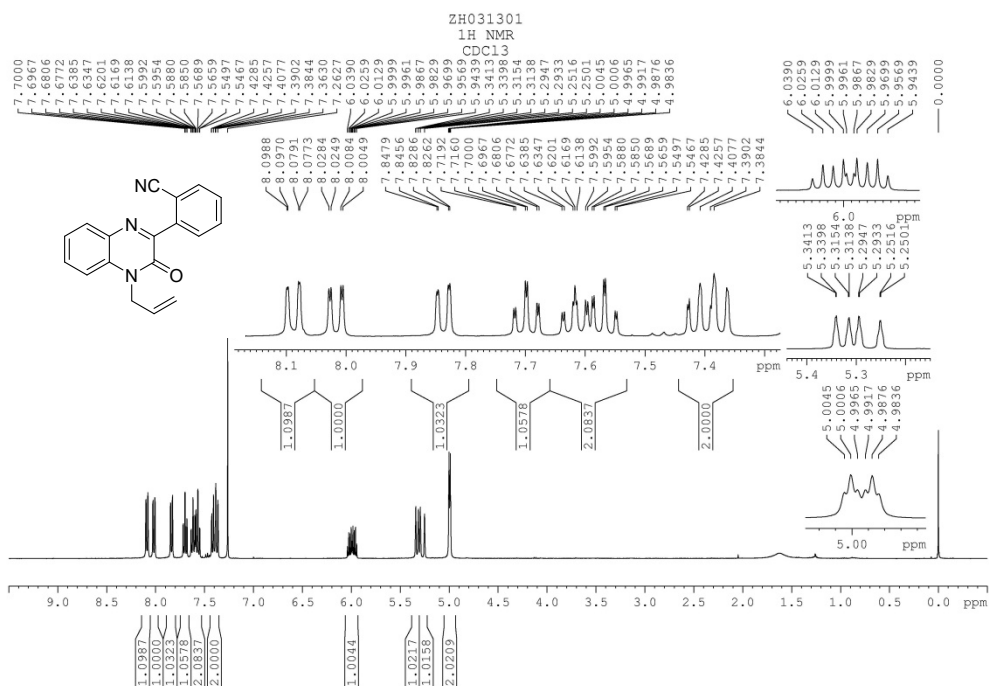


Fig. 11 ^1H NMR spectrum of compound 3fa

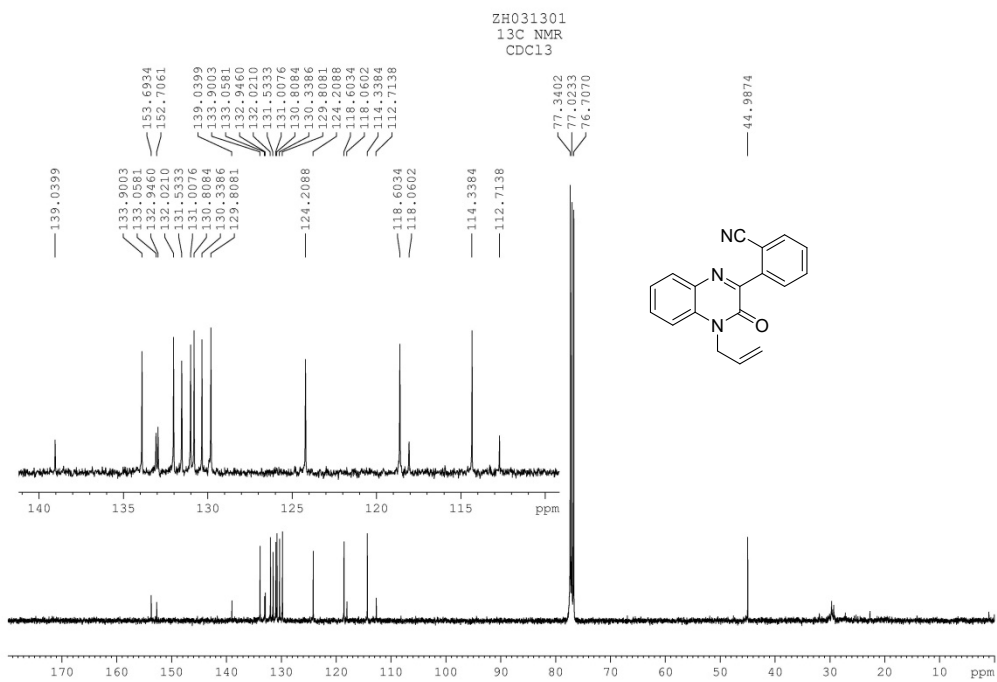


Fig. 12 ^{13}C NMR spectrum of compound 3fa

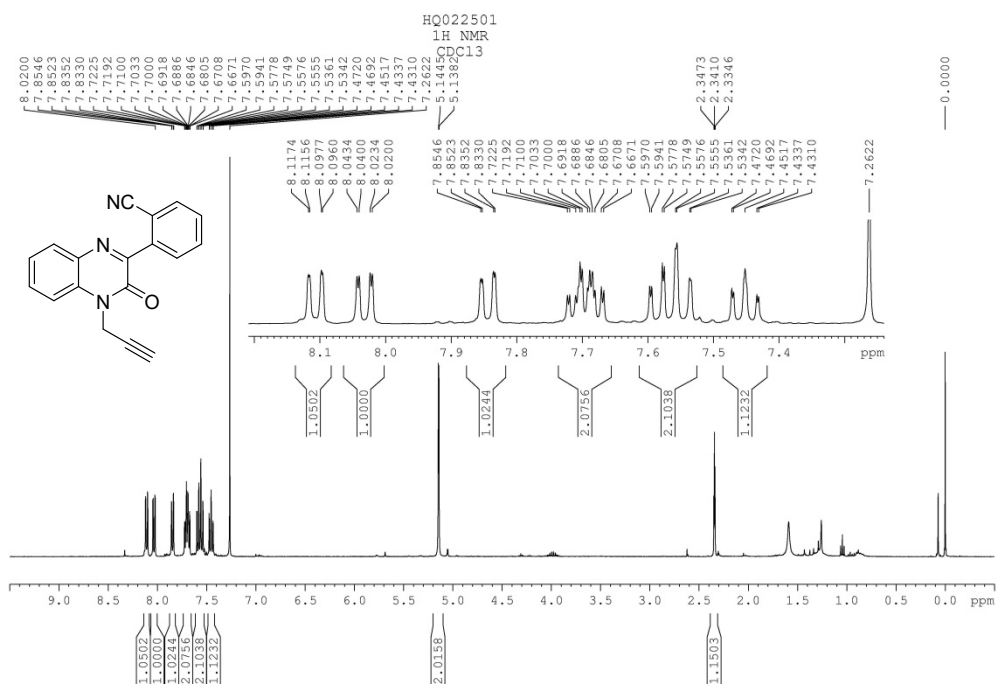


Fig. 13 ^1H NMR spectrum of compound 3ga

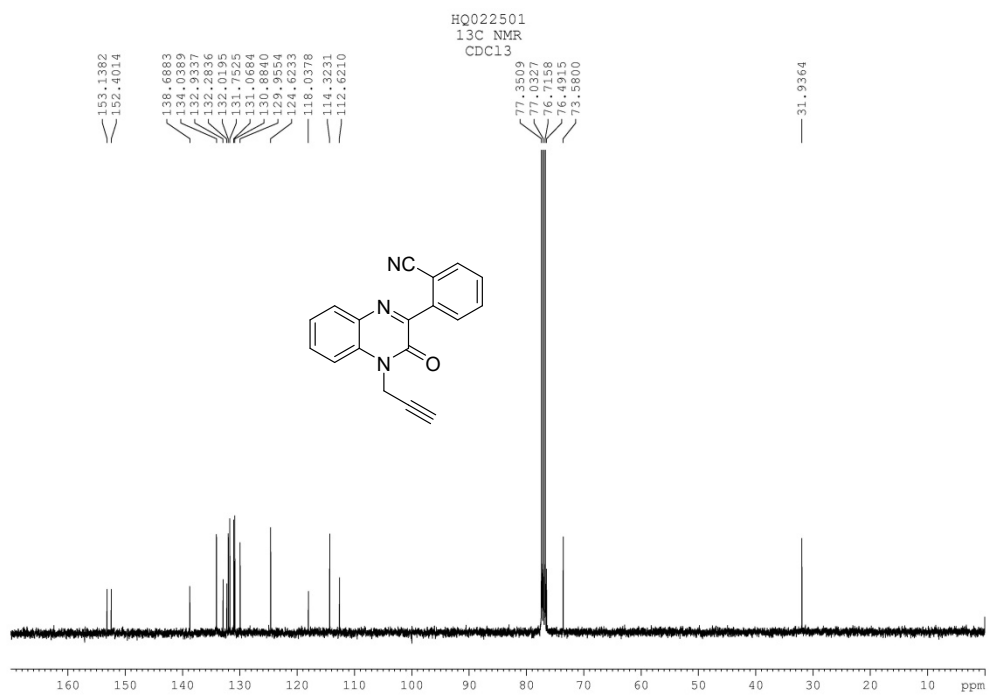


Fig. 14 ^{13}C NMR spectrum of compound 3ga

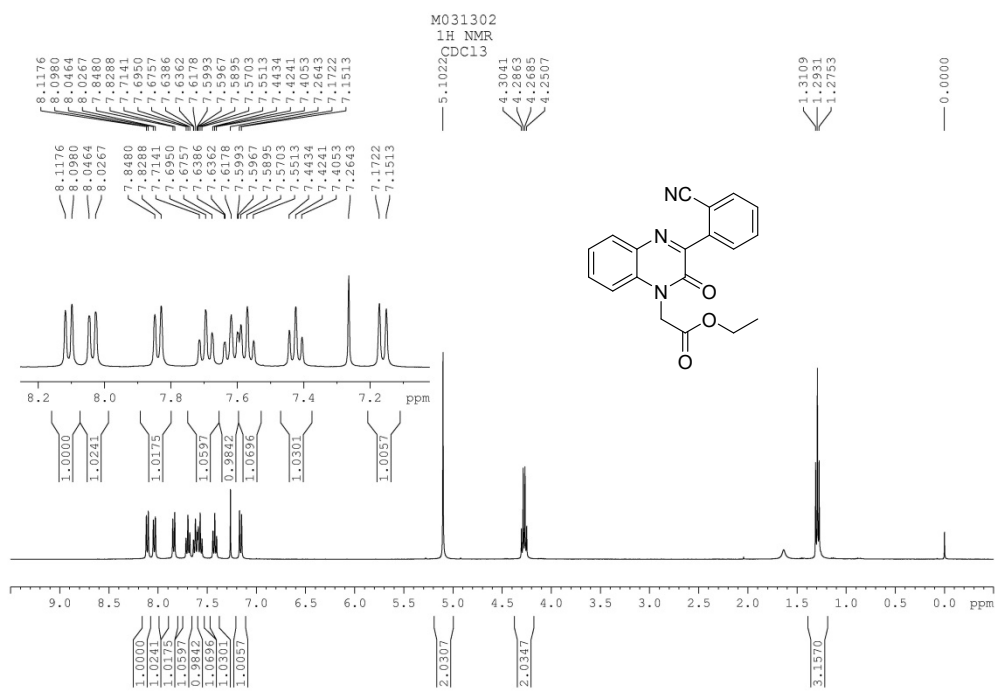


Fig. 15 ¹H NMR spectrum of compound 3ha

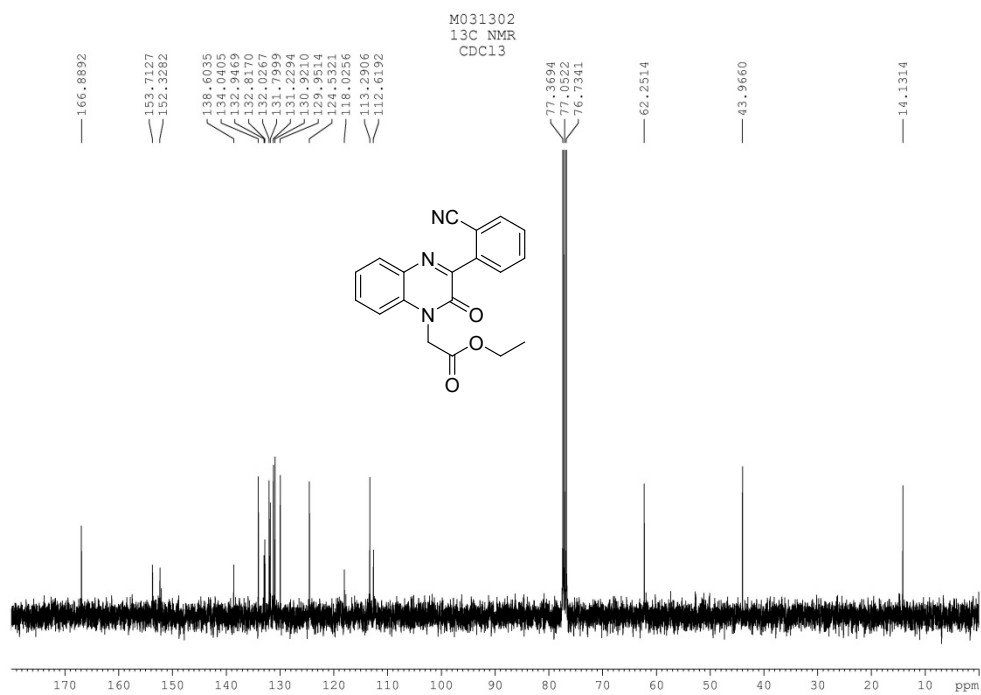


Fig. 16 ¹³C NMR spectrum of compound 3ha

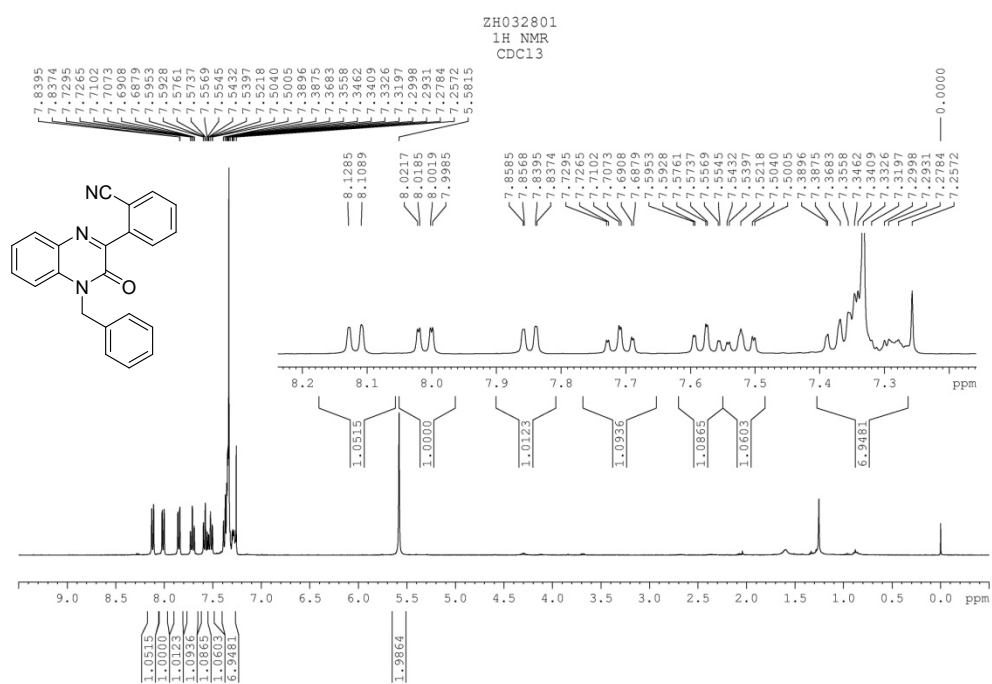


Fig. 17 ¹H NMR spectrum of compound 3ia

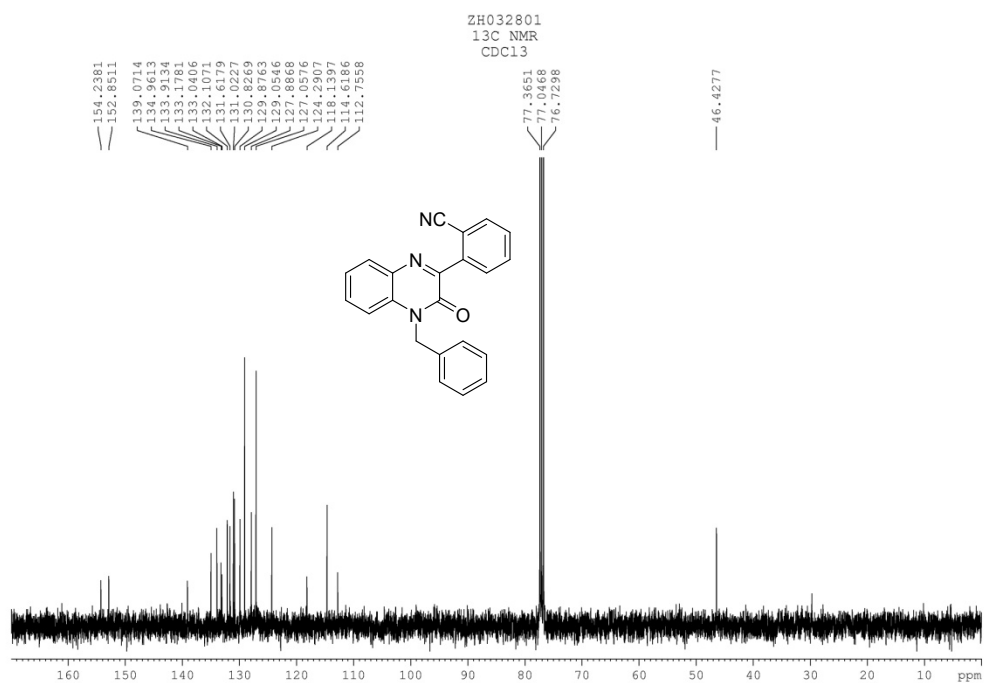


Fig. 18 ¹³C NMR spectrum of compound 3ia

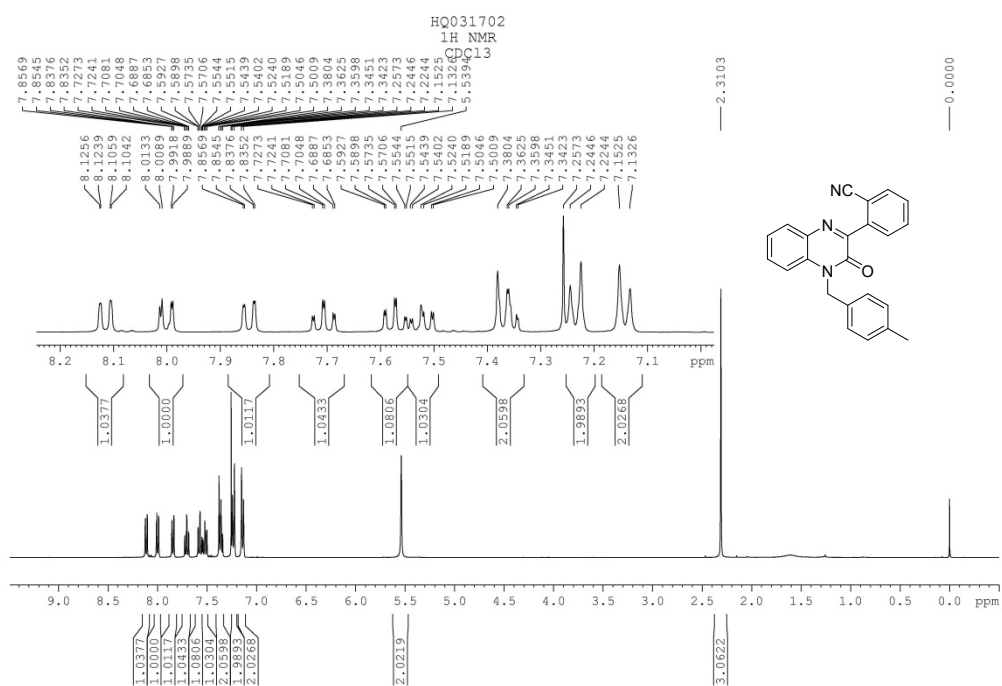


Fig. 19 ¹H NMR spectrum of compound 3ja

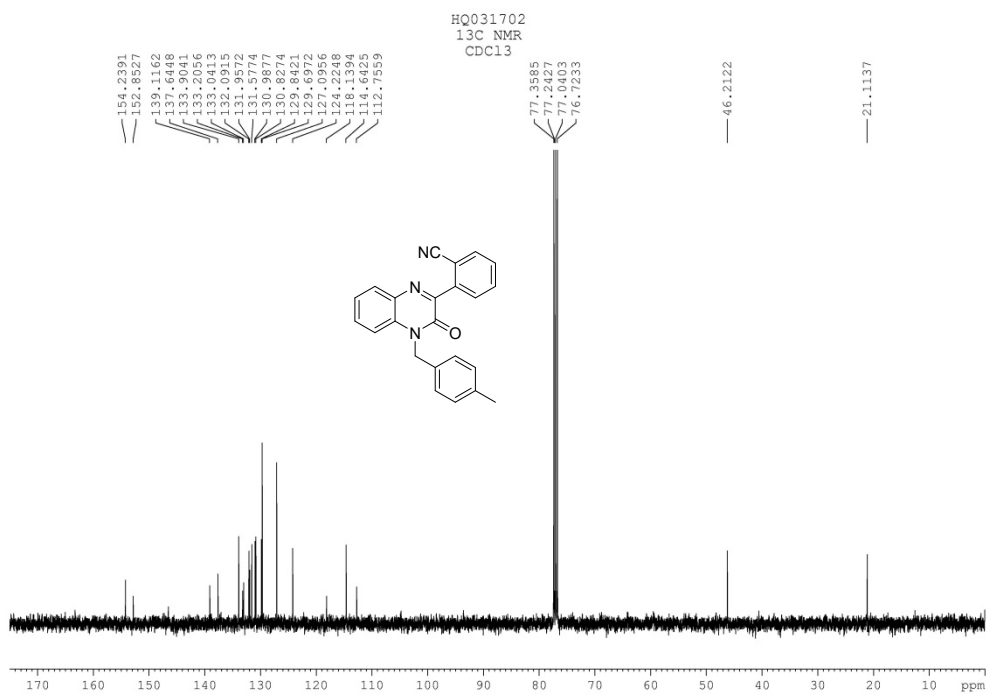


Fig. 20 ¹³C NMR spectrum of compound 3ja

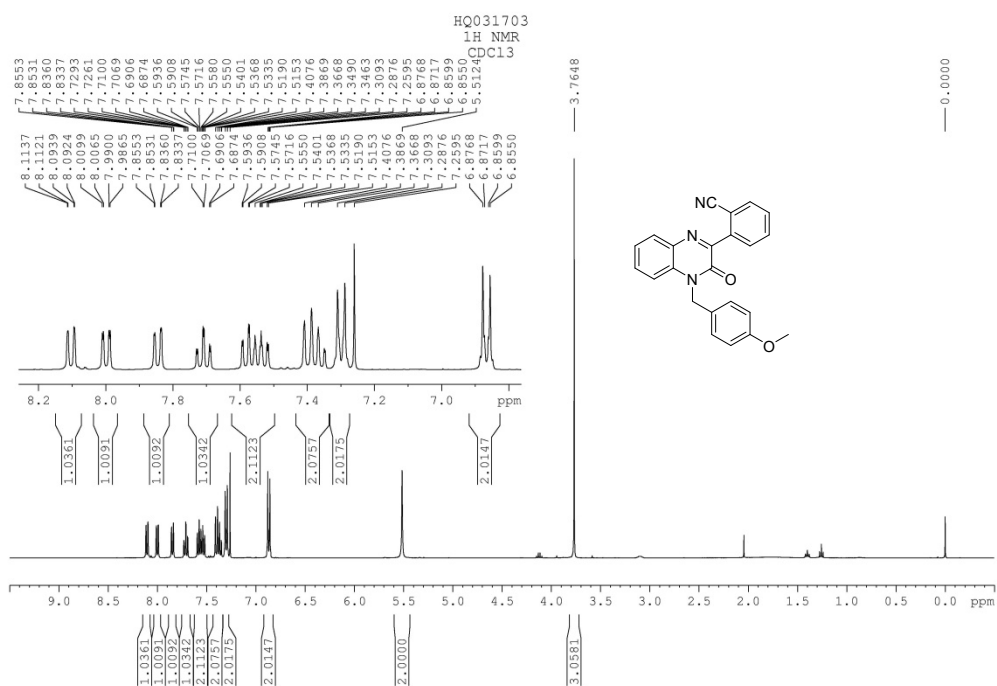


Fig. 21 ¹H NMR spectrum of compound 3ka

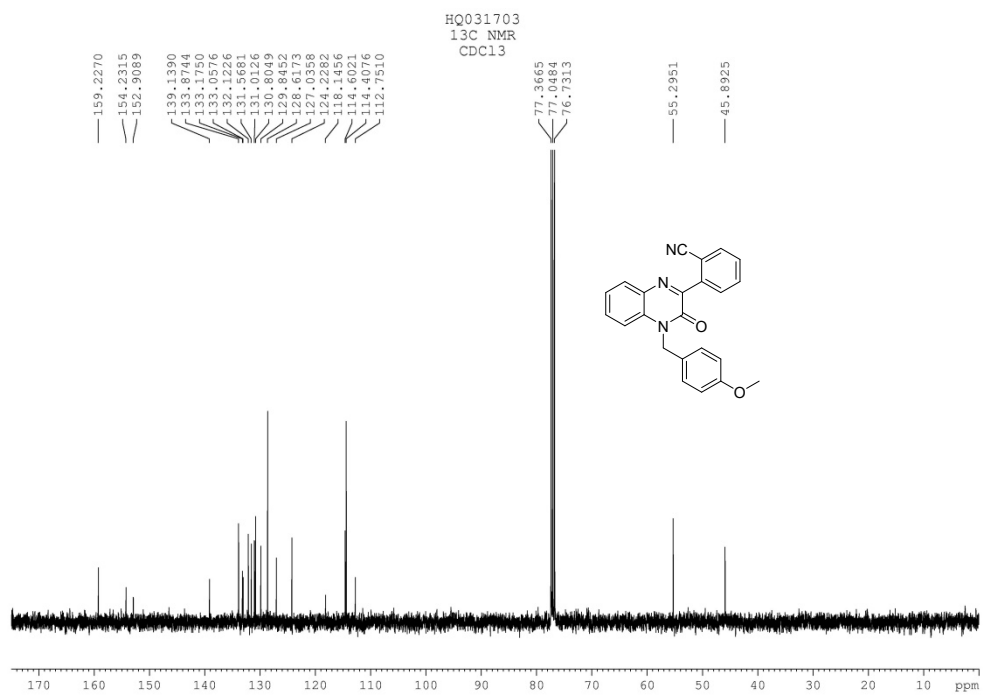


Fig. 22 ¹³C NMR spectrum of compound 3ka

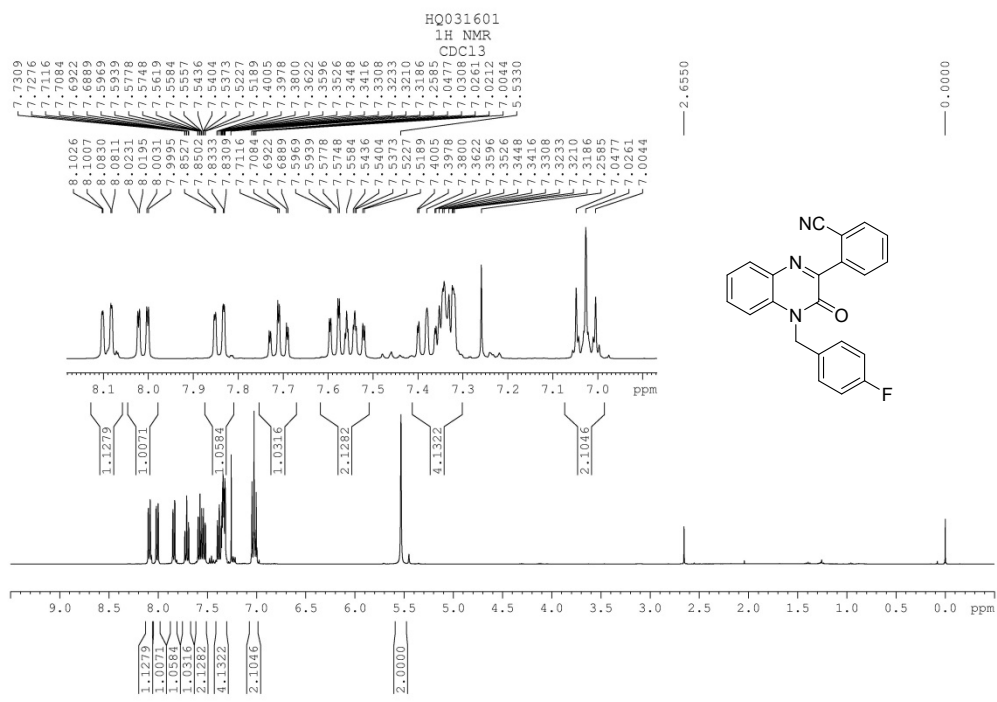


Fig. 23 ¹H NMR spectrum of compound 3la

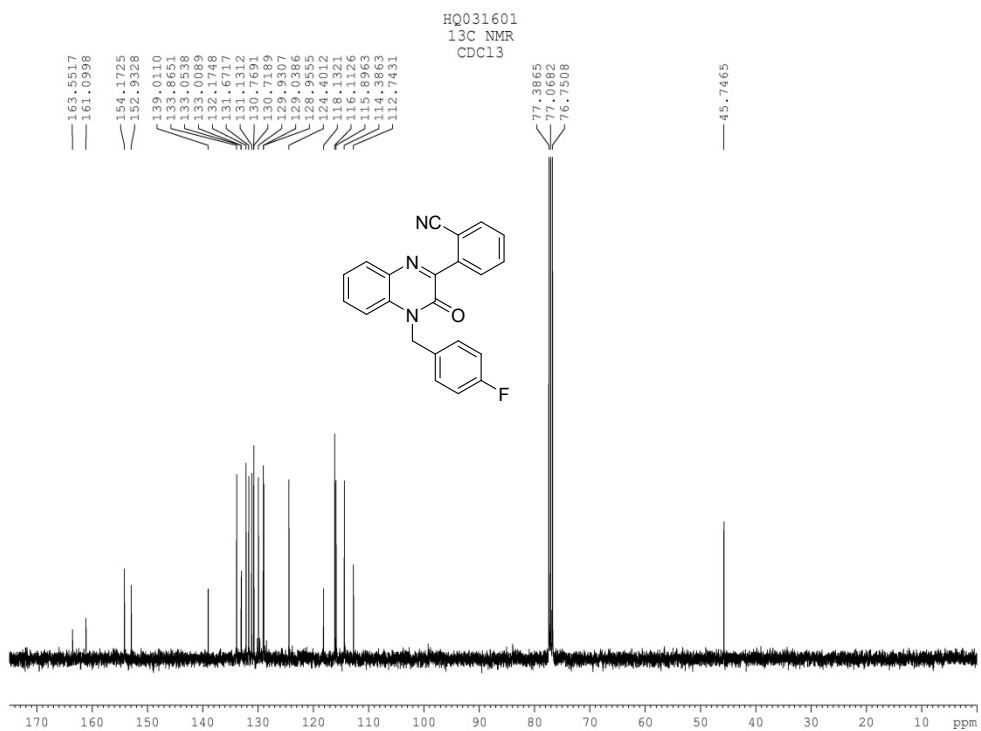


Fig. 24 ¹³C NMR spectrum of compound 3la

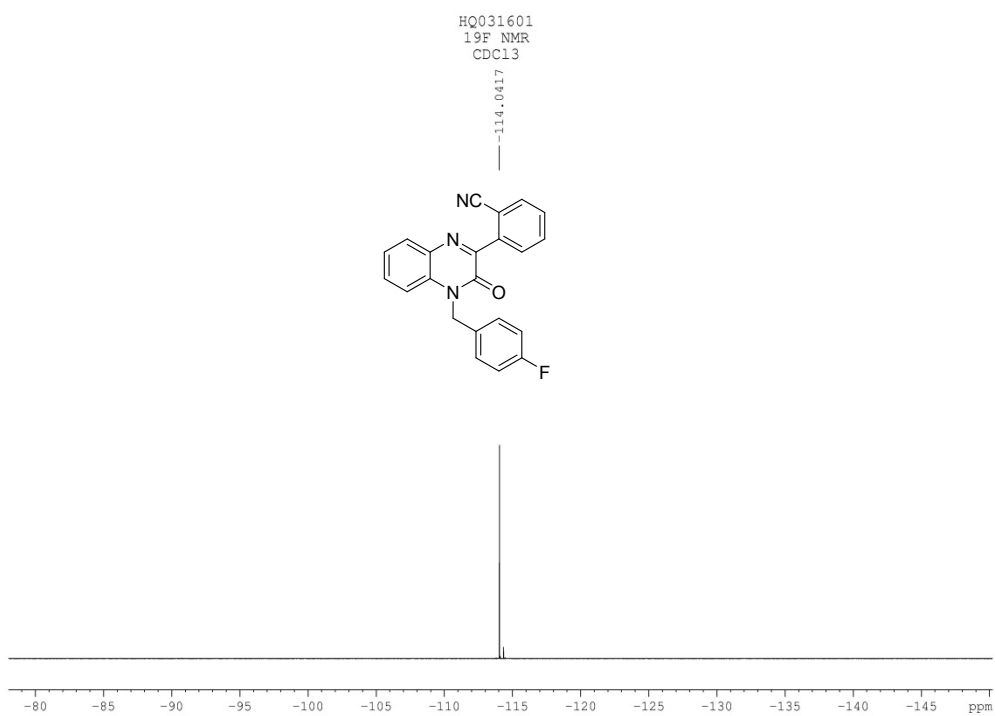


Fig. 25 ¹⁹F NMR spectrum of compound 3la

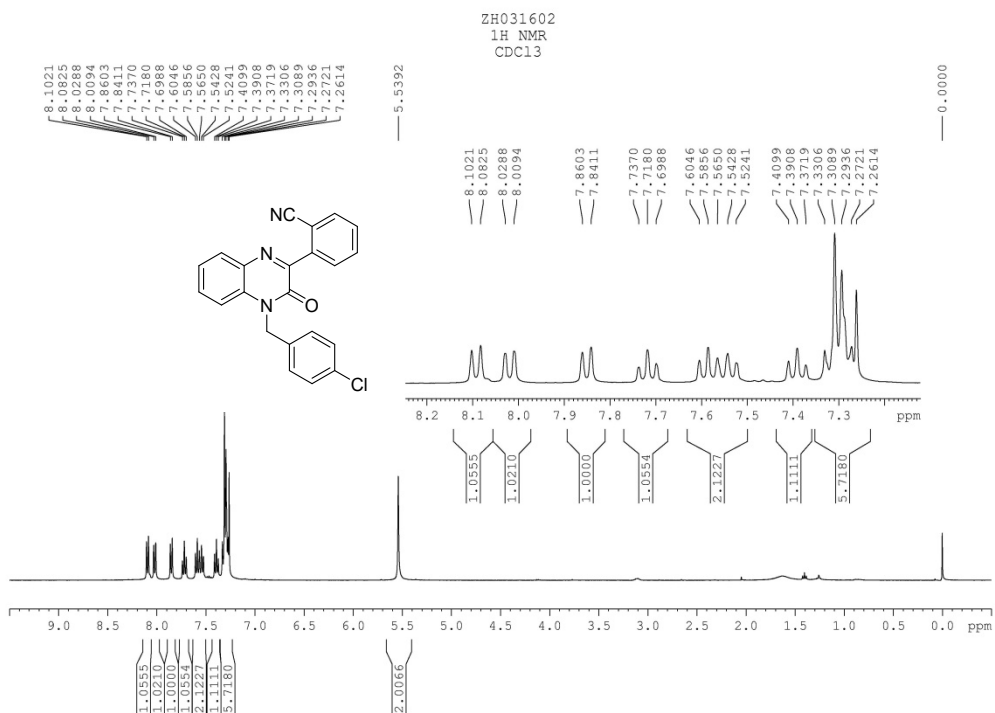


Fig. 26 ¹H NMR spectrum of compound 3ma

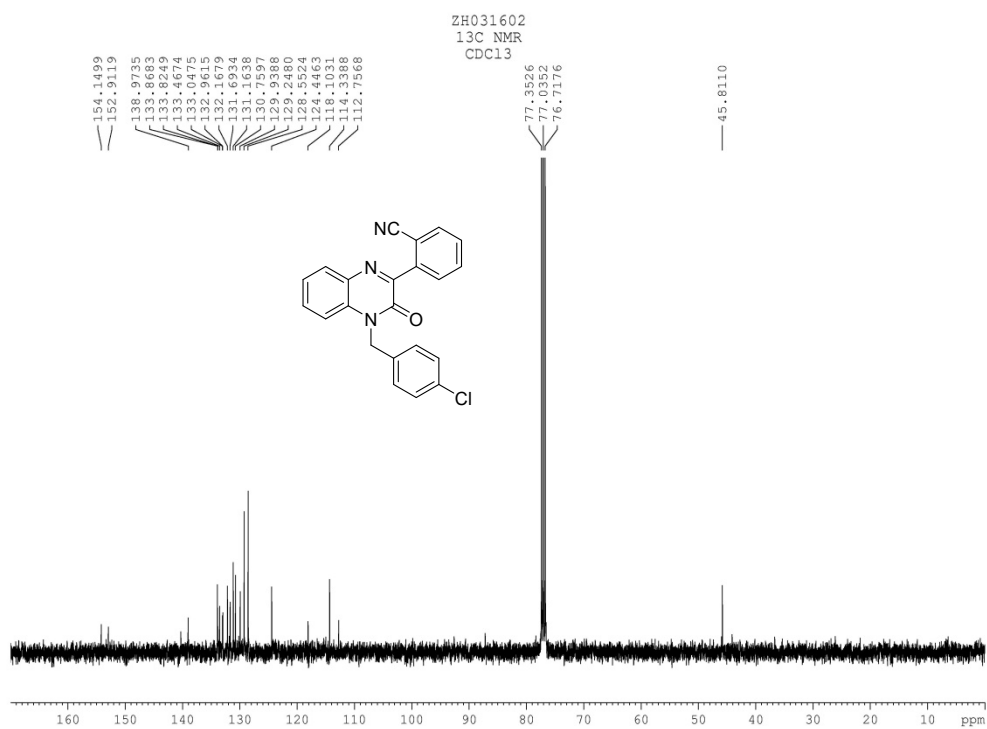


Fig. 27 ¹³C NMR spectrum of compound 3ma

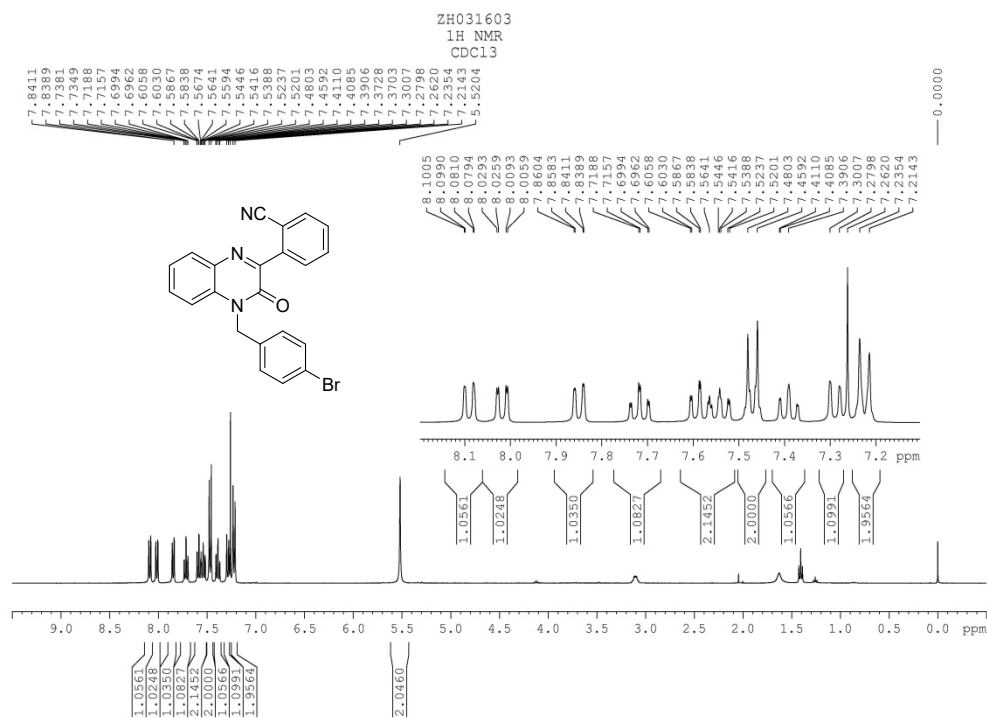


Fig. 28 ¹H NMR spectrum of compound 3na

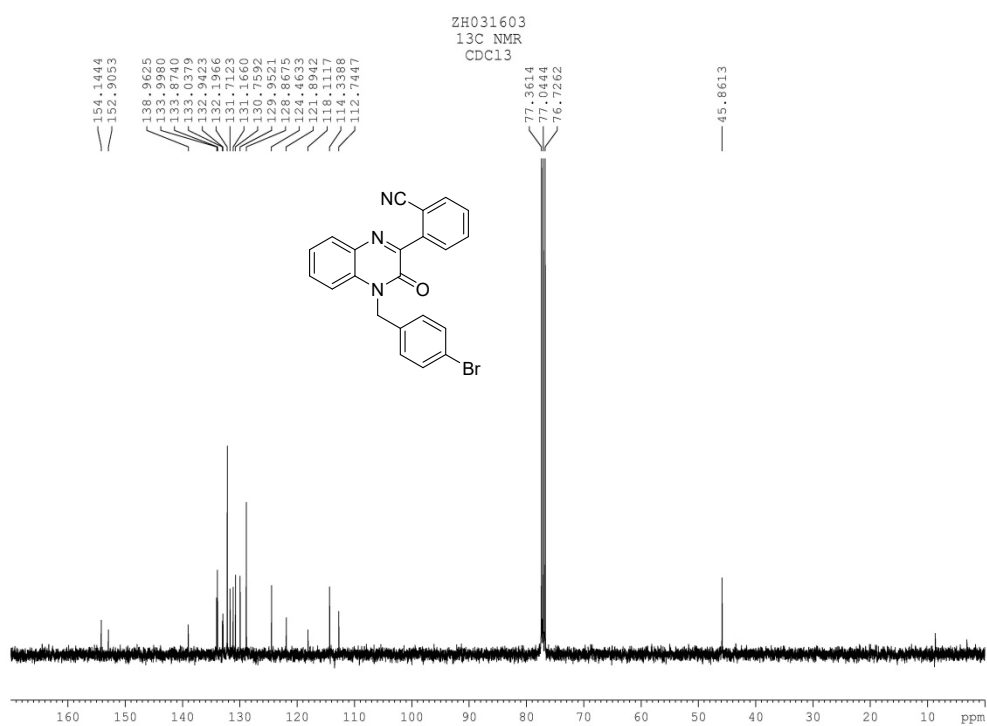


Fig. 29 ¹³C NMR spectrum of compound 3na

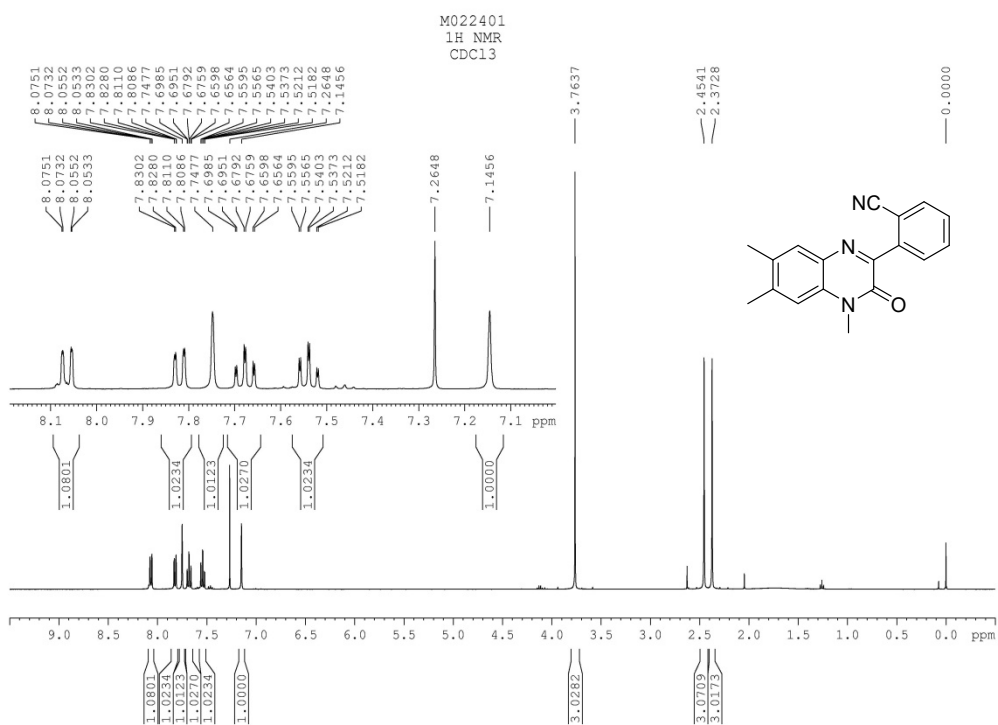


Fig. 30 ¹H NMR spectrum of compound 3oa

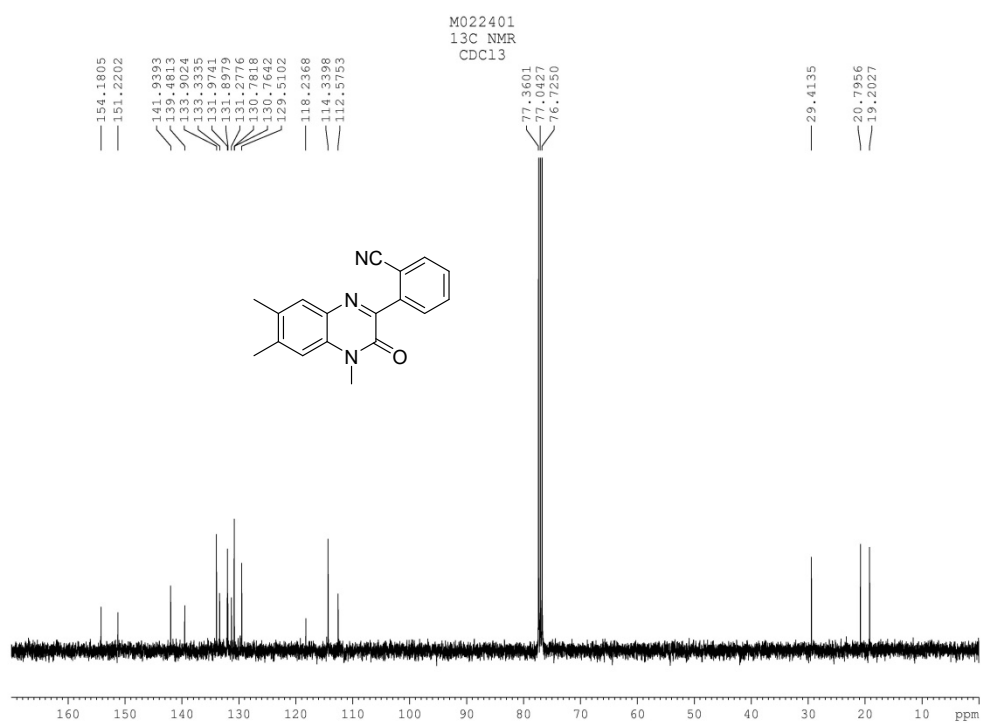


Fig. 31 ¹³C NMR spectrum of compound 30a

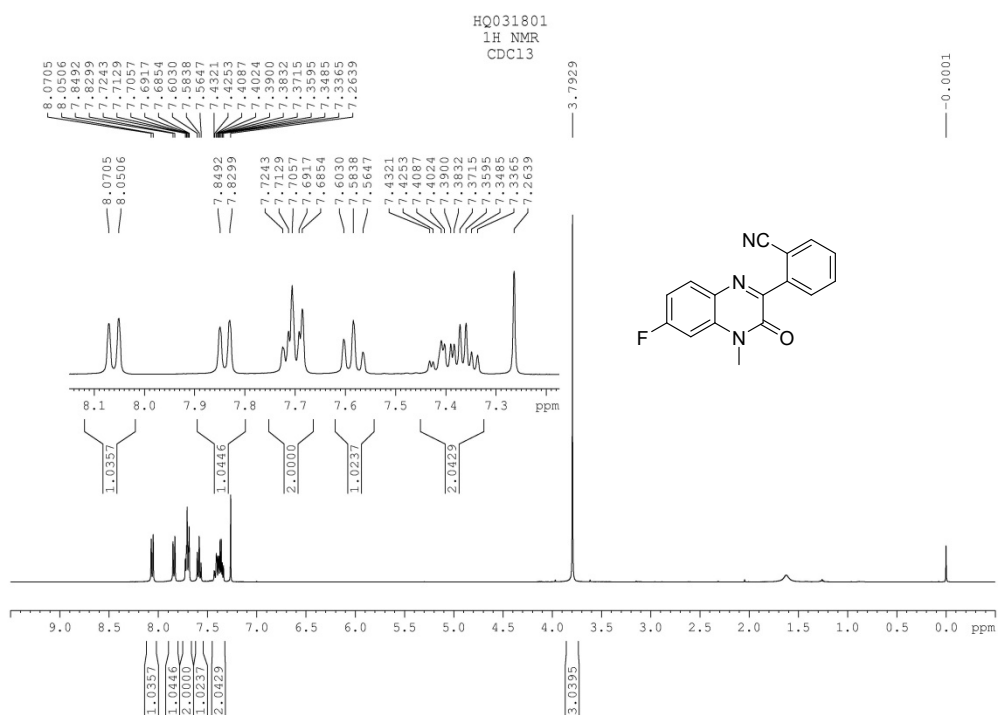


Fig. 32 ¹H NMR spectrum of compound 30a

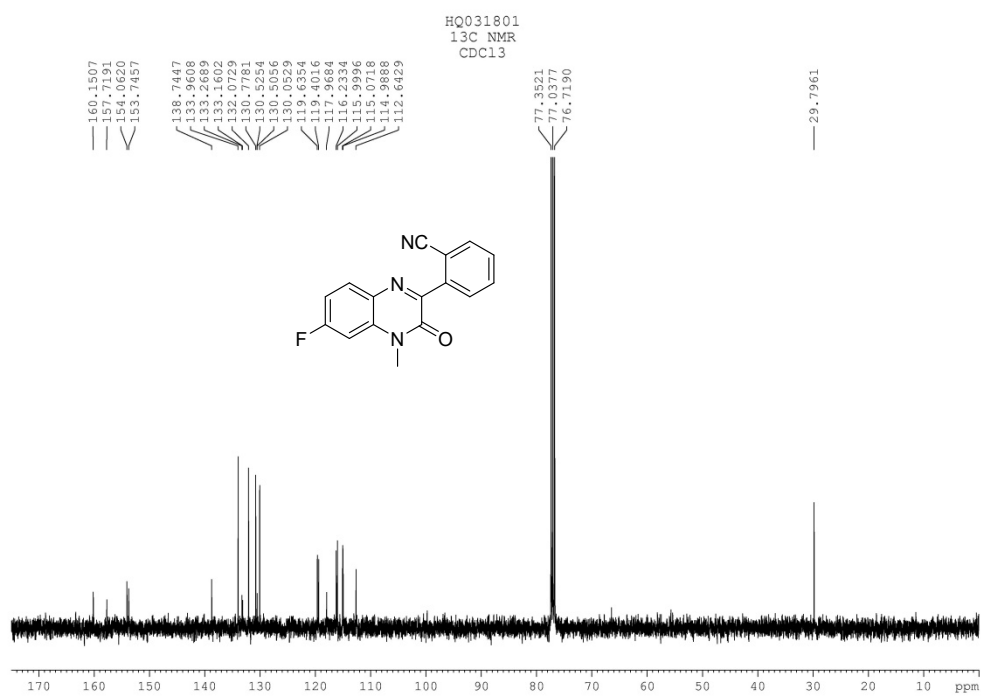


Fig. 33 ¹³C NMR spectrum of compound 3pa

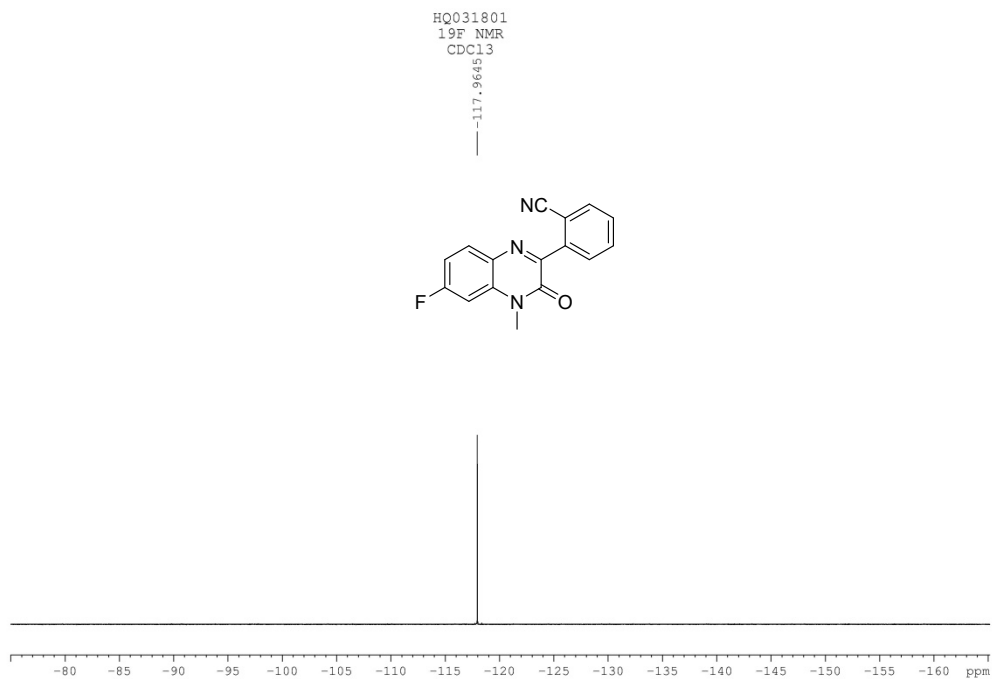


Fig. 34 ¹⁹F NMR spectrum of compound 3pa

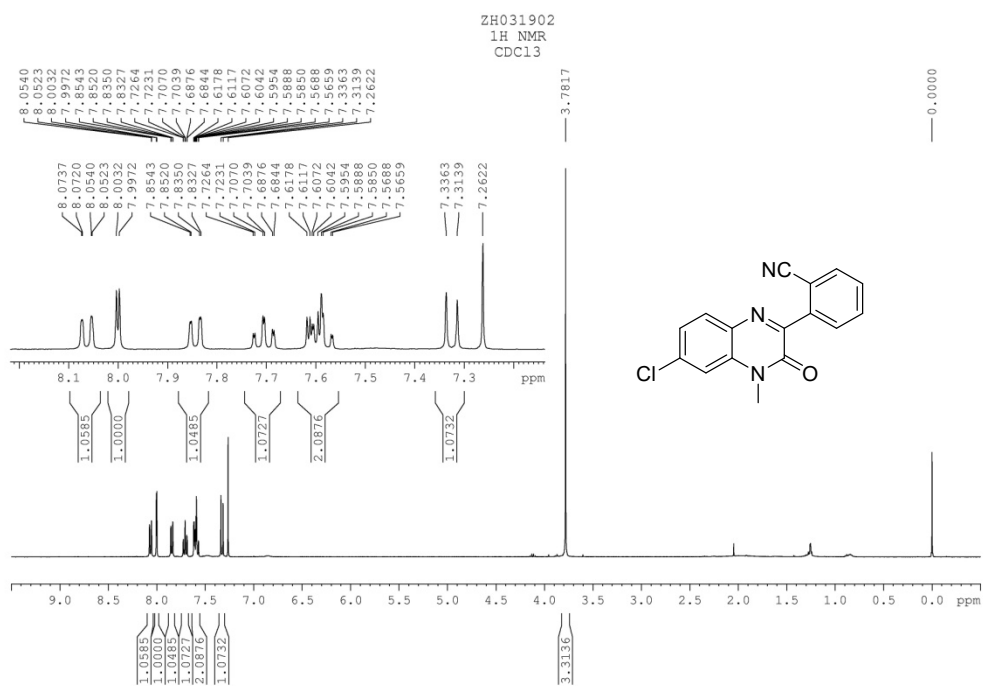


Fig. 35 ¹H NMR spectrum of compound 3qa

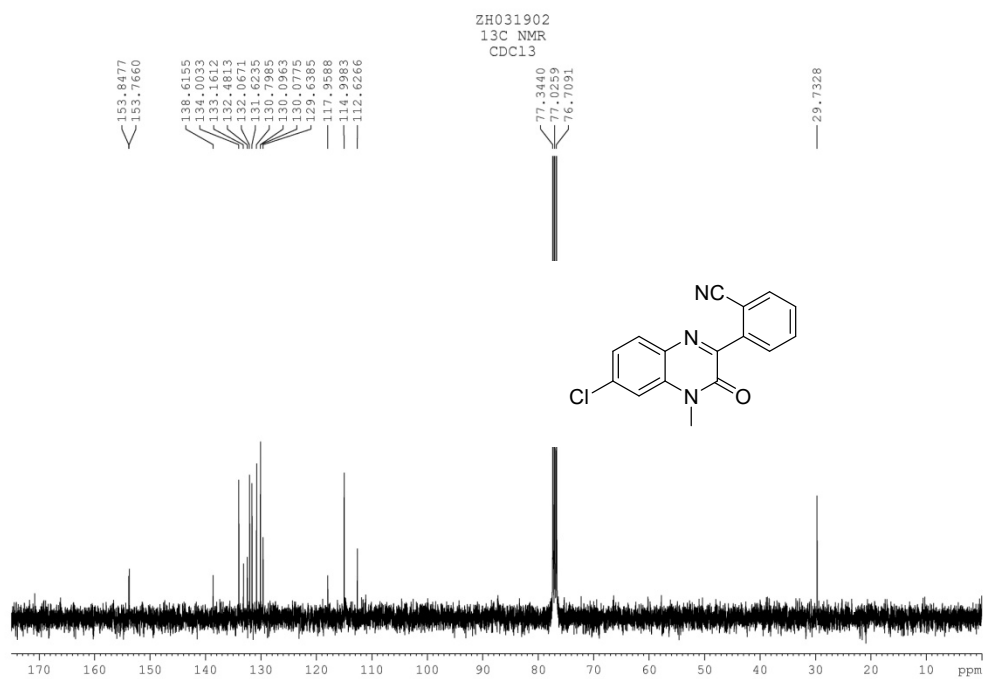


Fig. 36 ¹³C NMR spectrum of compound 3qa

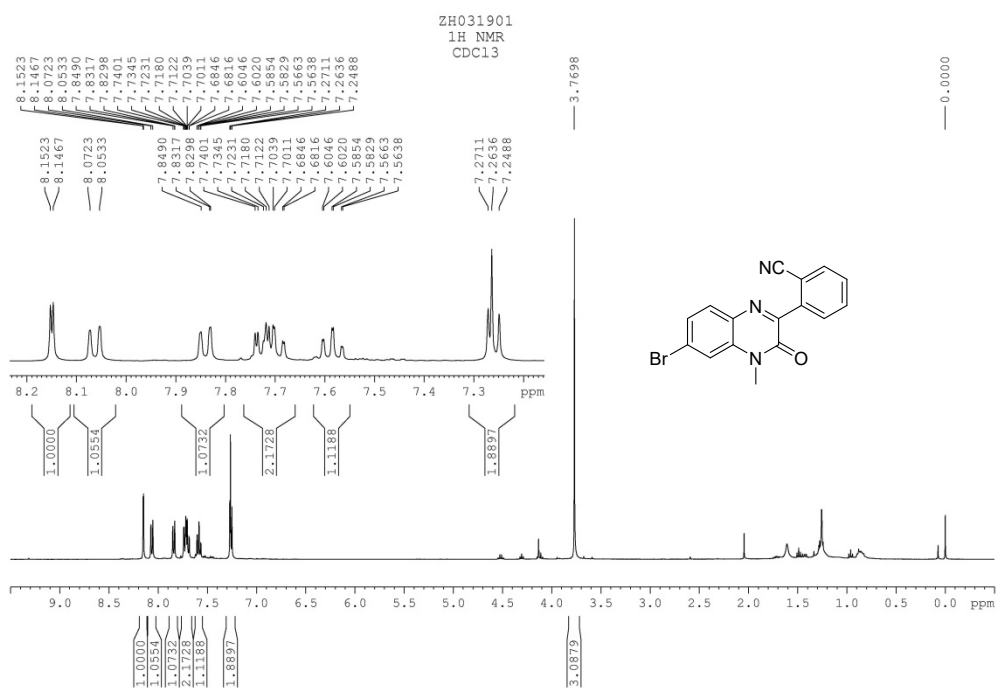


Fig. 37 ¹H NMR spectrum of compound 3ra

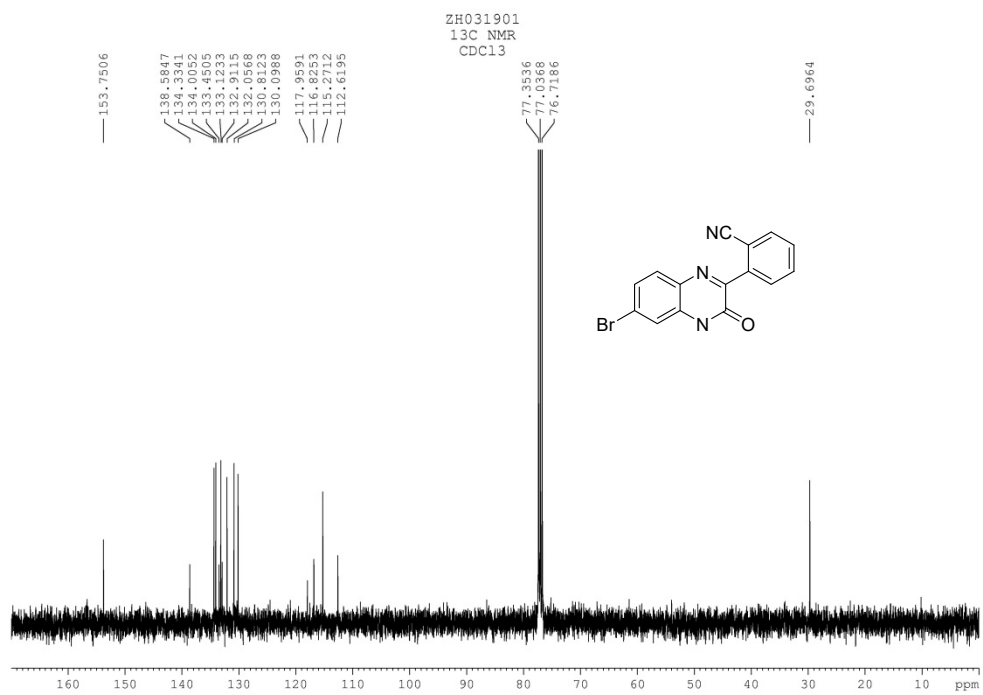


Fig. 38 ¹³C NMR spectrum of compound 3ra

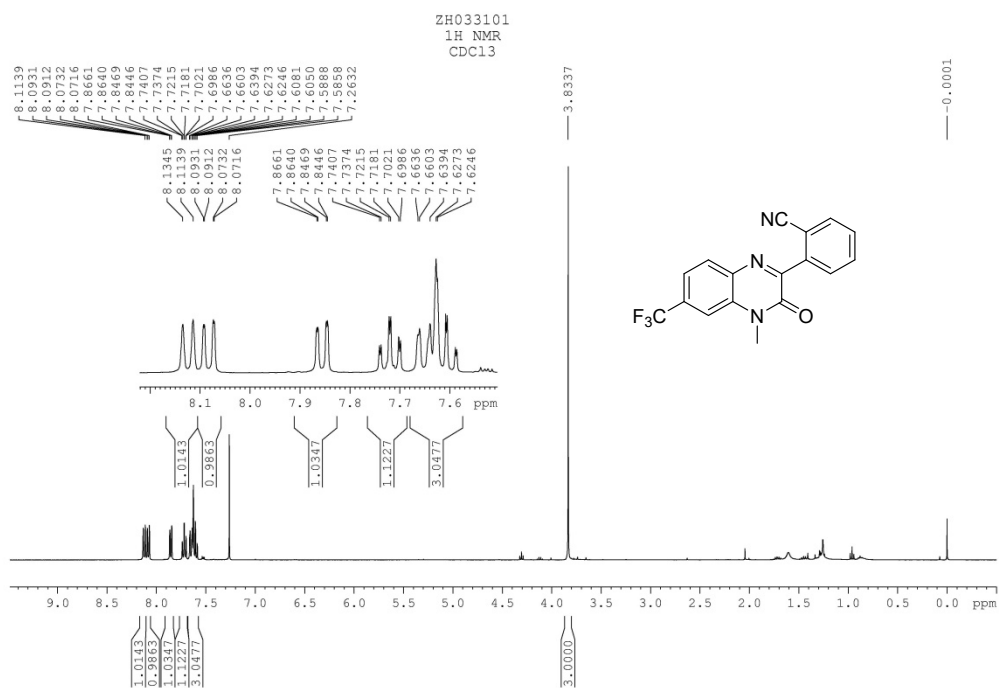


Fig. 39 ¹H NMR spectrum of compound 3sa

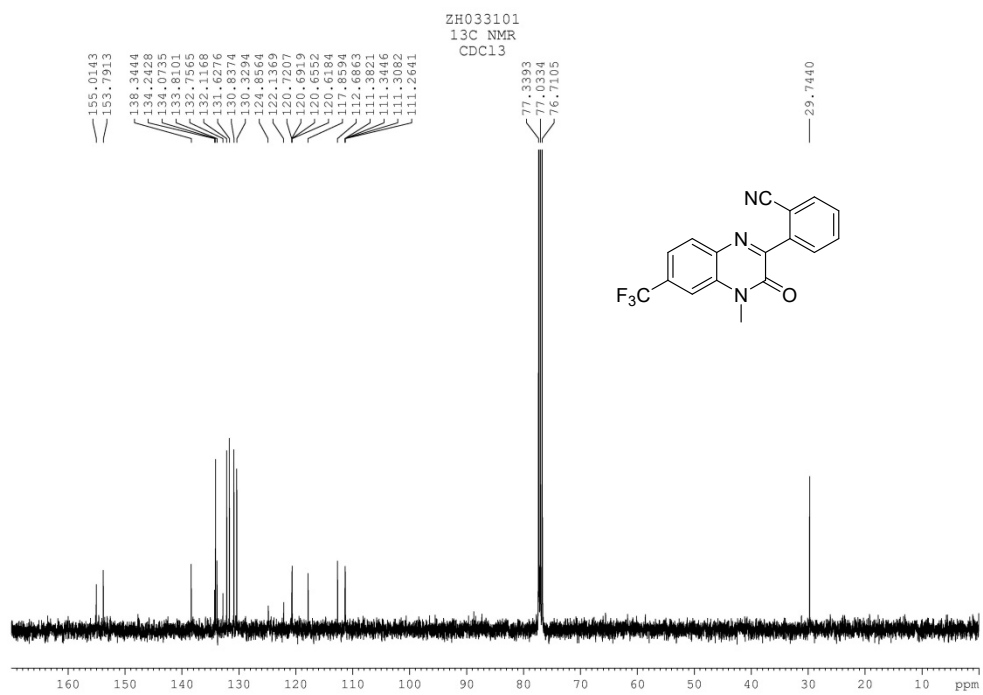


Fig. 40 ¹³C NMR spectrum of compound 3sa

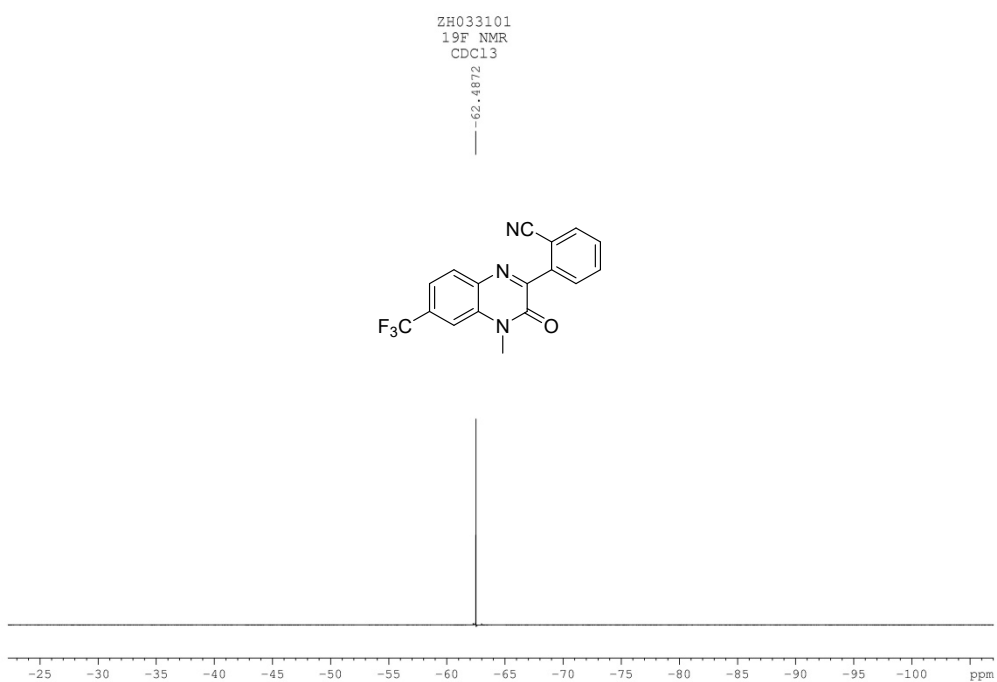


Fig. 41 ¹⁹F NMR spectrum of compound 3sa

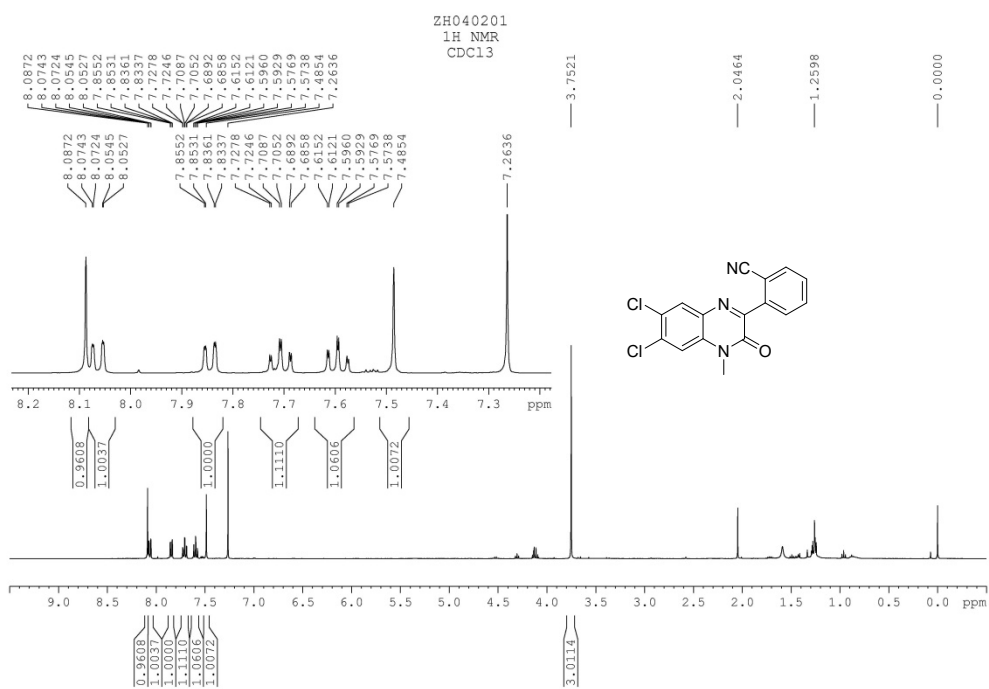


Fig. 42 ¹H NMR spectrum of compound 3ta

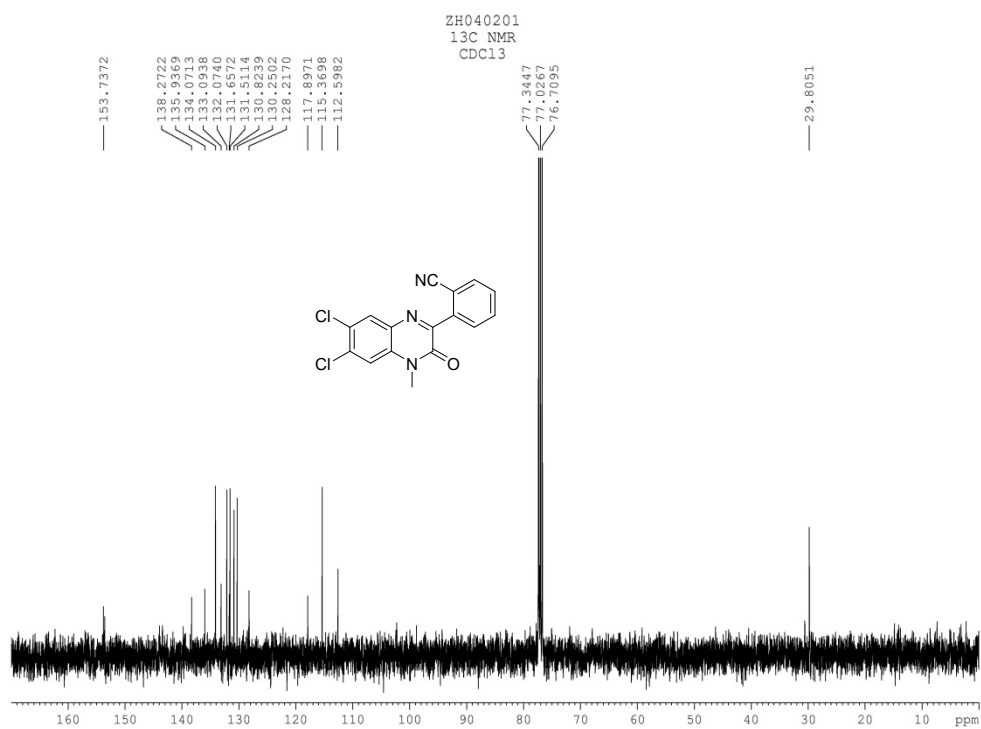


Fig. 43 ¹³C NMR spectrum of compound 3ta

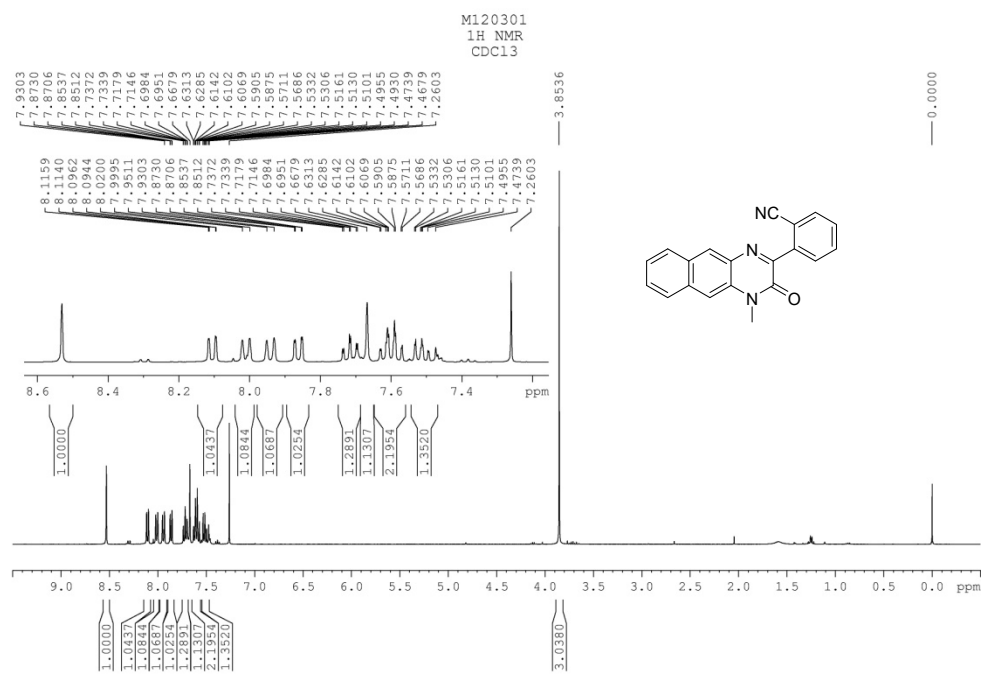


Fig. 44 ¹H NMR spectrum of compound 3ua

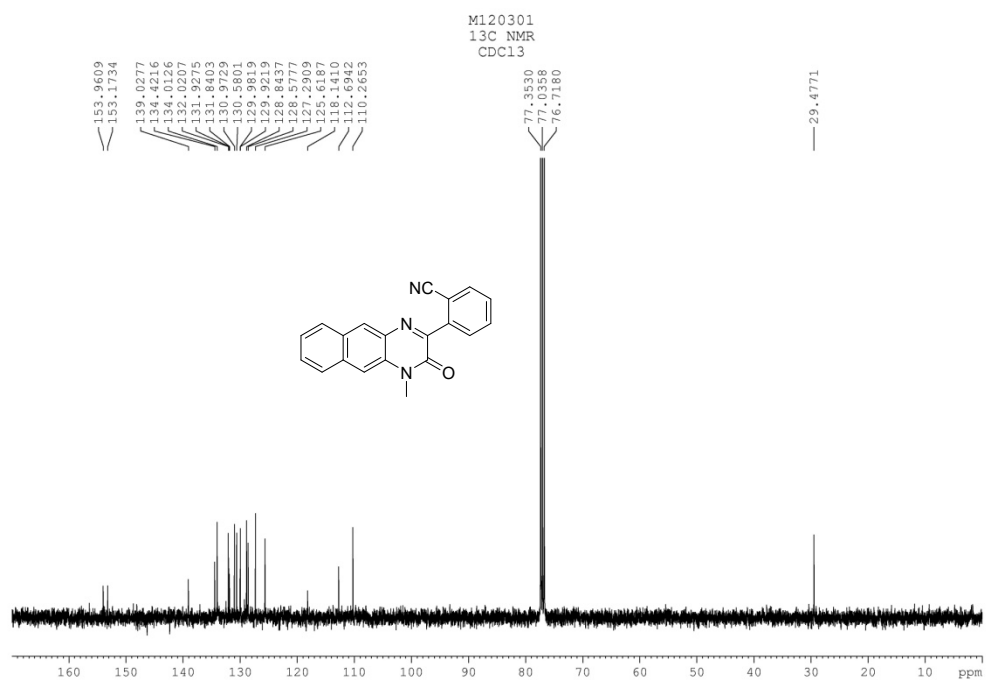


Fig. 45 ¹³C NMR spectrum of compound **3ua**

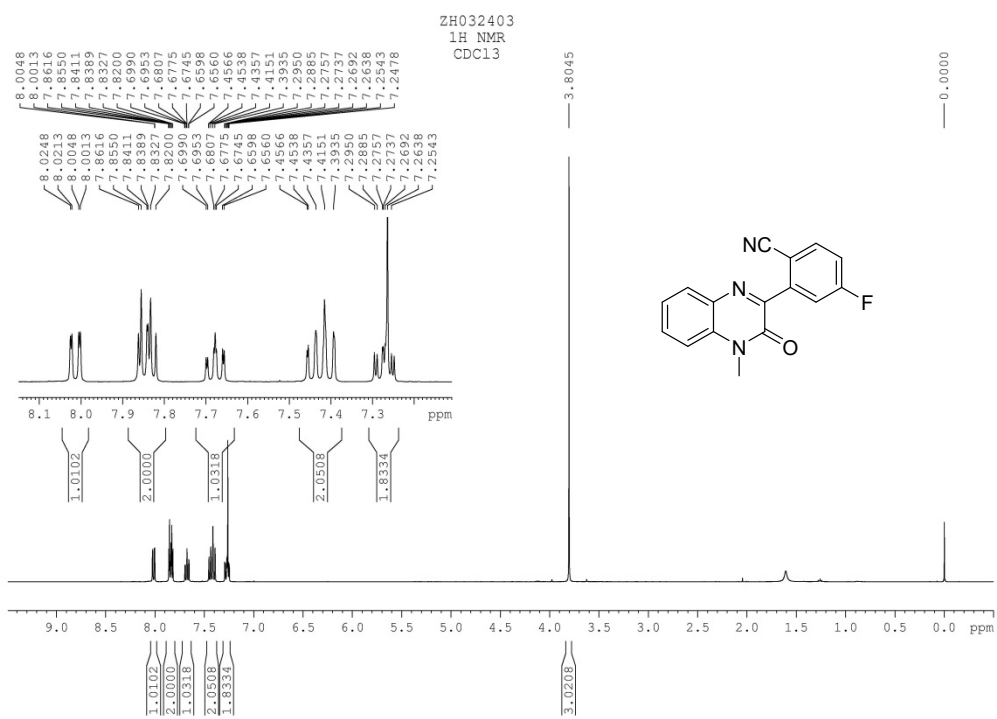


Fig. 46 ¹H NMR spectrum of compound **3ab**

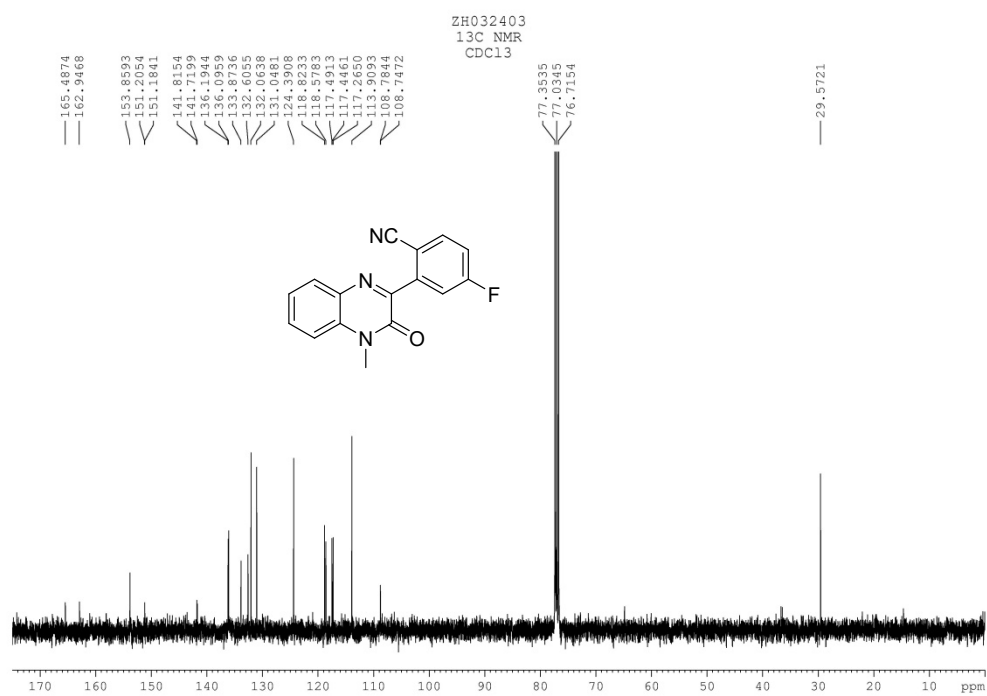


Fig. 47 ¹³C NMR spectrum of compound 3ab

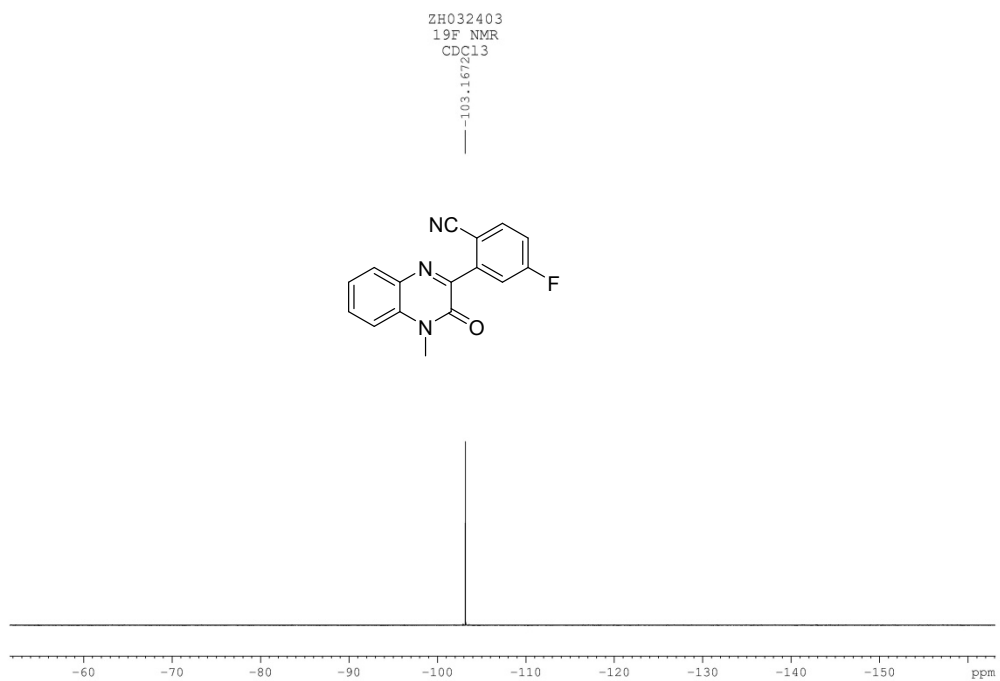


Fig. 48 ¹⁹F NMR spectrum of compound 3ab

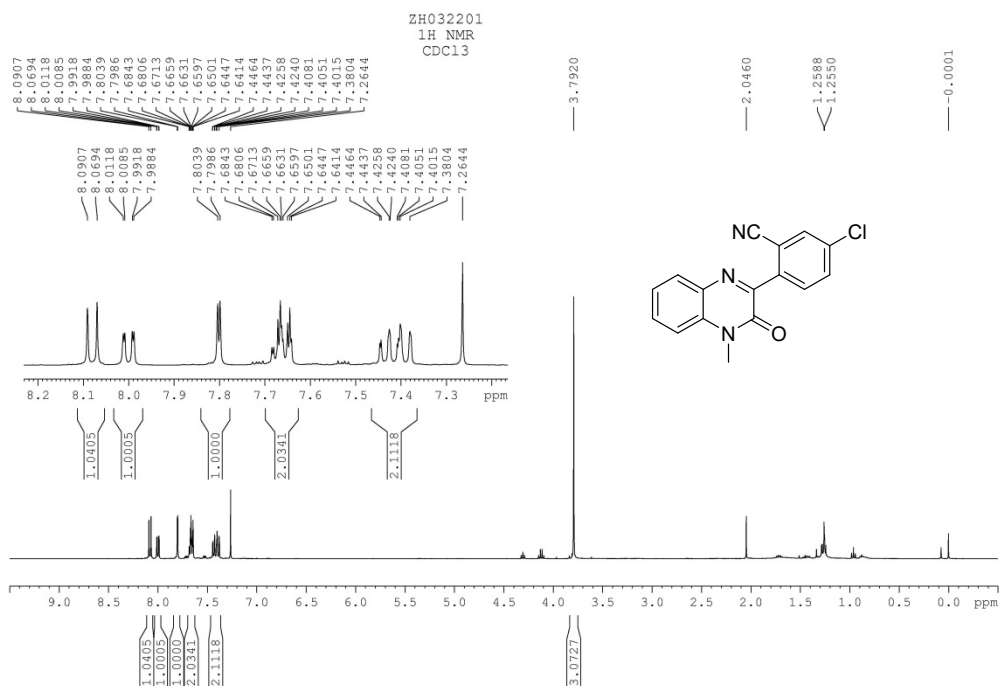


Fig. 49 ¹H NMR spectrum of compound 3ac

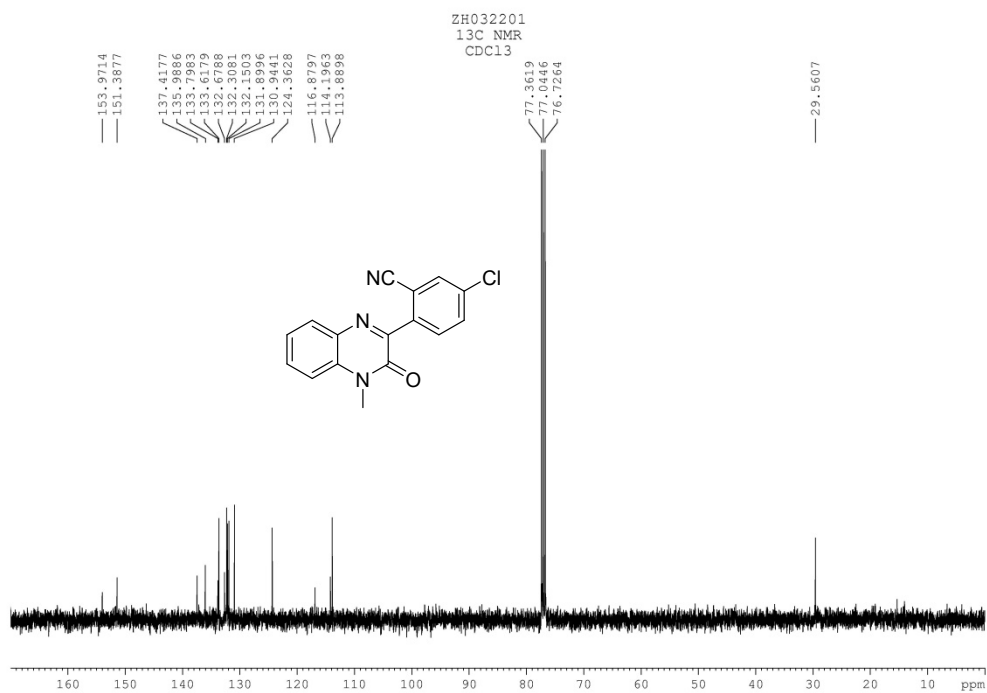


Fig. 50 ¹³C NMR spectrum of compound 3ac

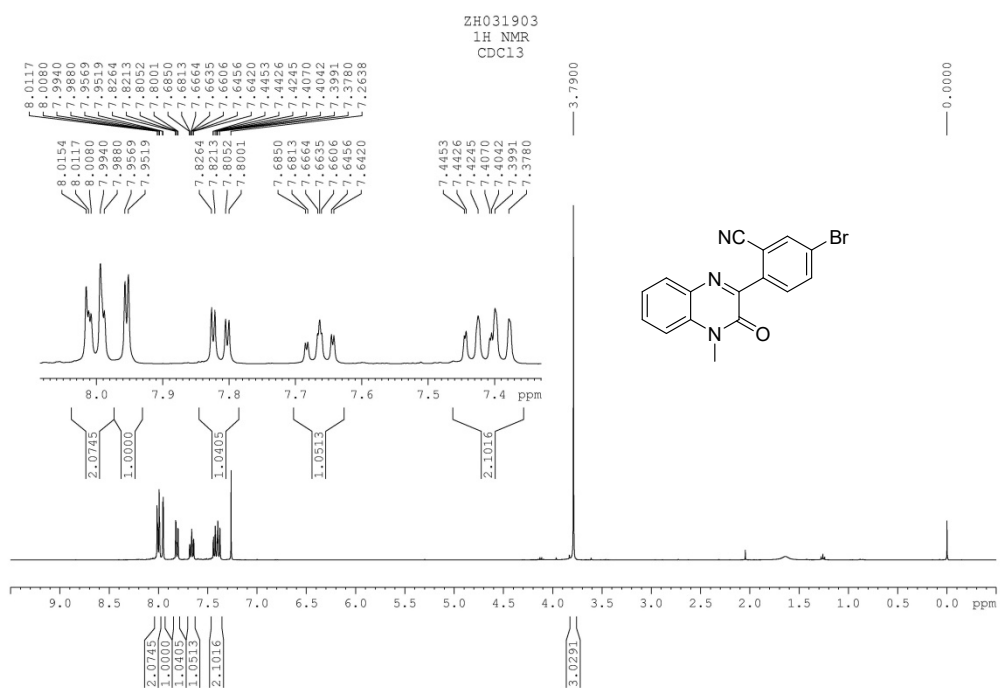


Fig. 51 ¹H NMR spectrum of compound 3ad

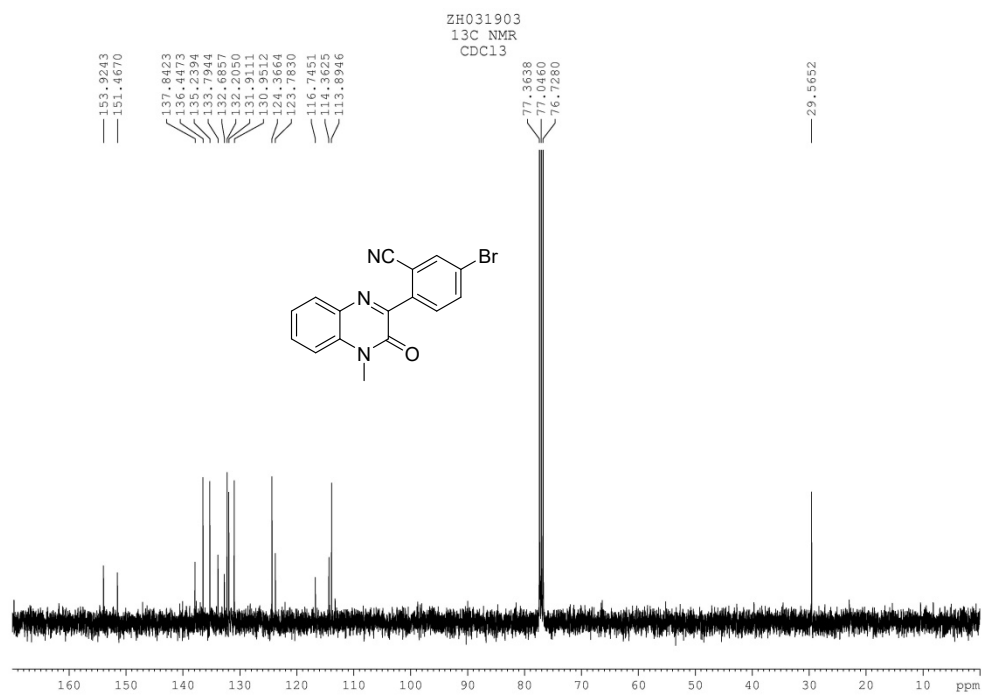


Fig. 52 ¹³C NMR spectrum of compound 3ad

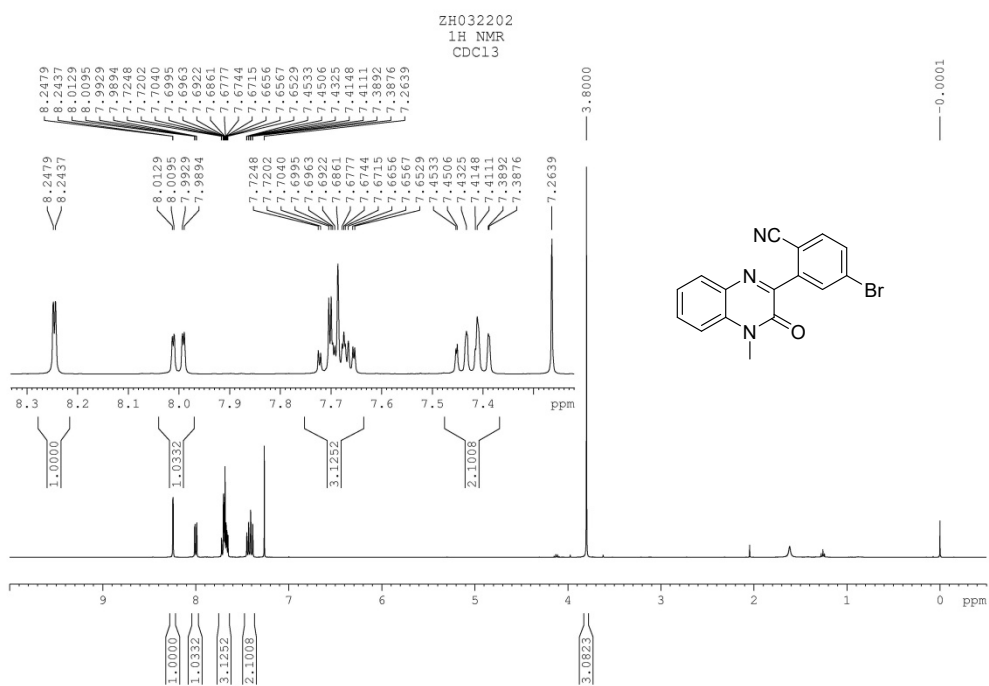


Fig. 53 ¹H NMR spectrum of compound 3ae

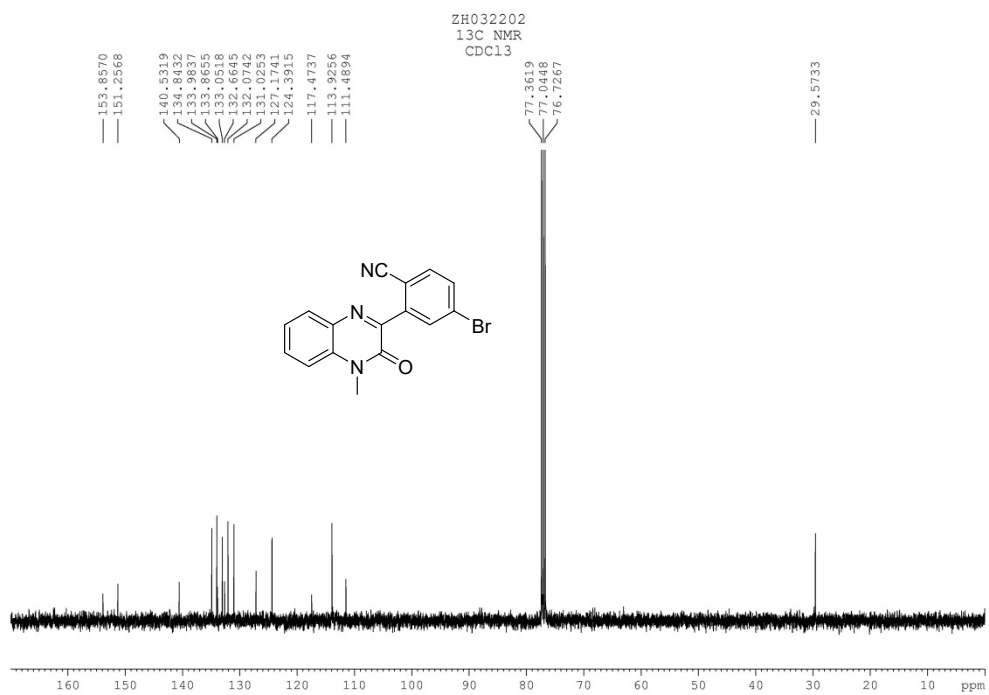


Fig. 54 ¹³C NMR spectrum of compound 3ae

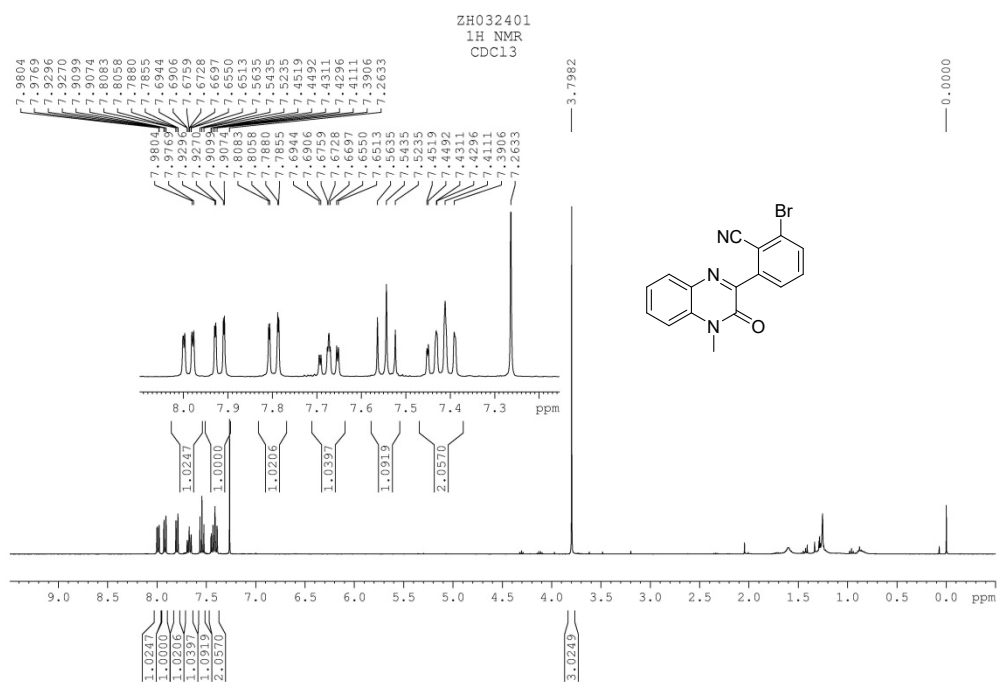


Fig. 55 ¹H NMR spectrum of compound 3af

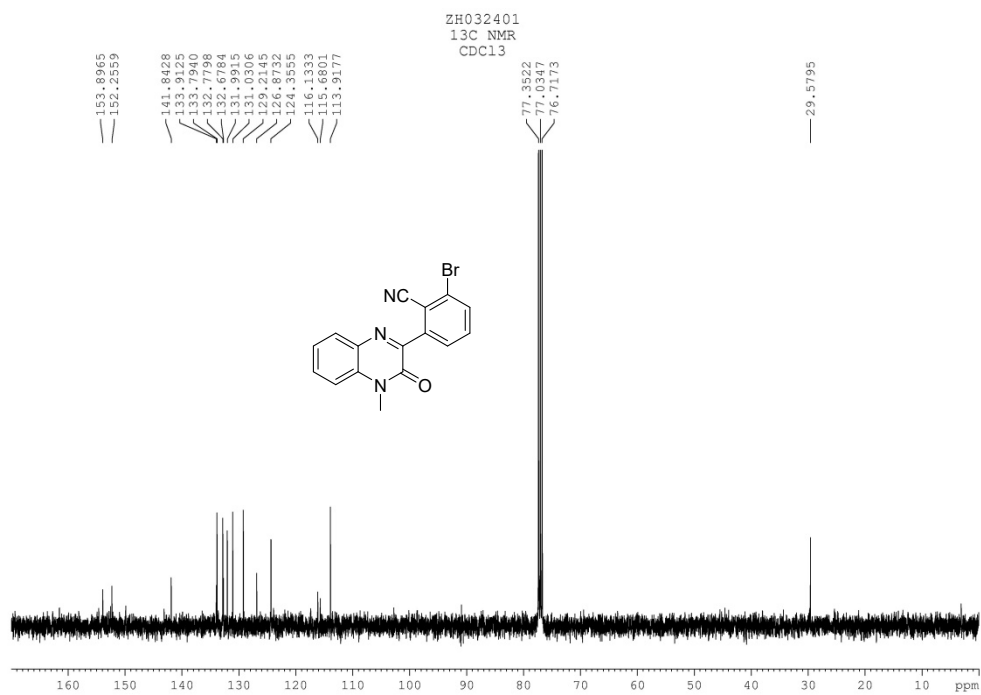


Fig. 56 ¹³C NMR spectrum of compound 3af

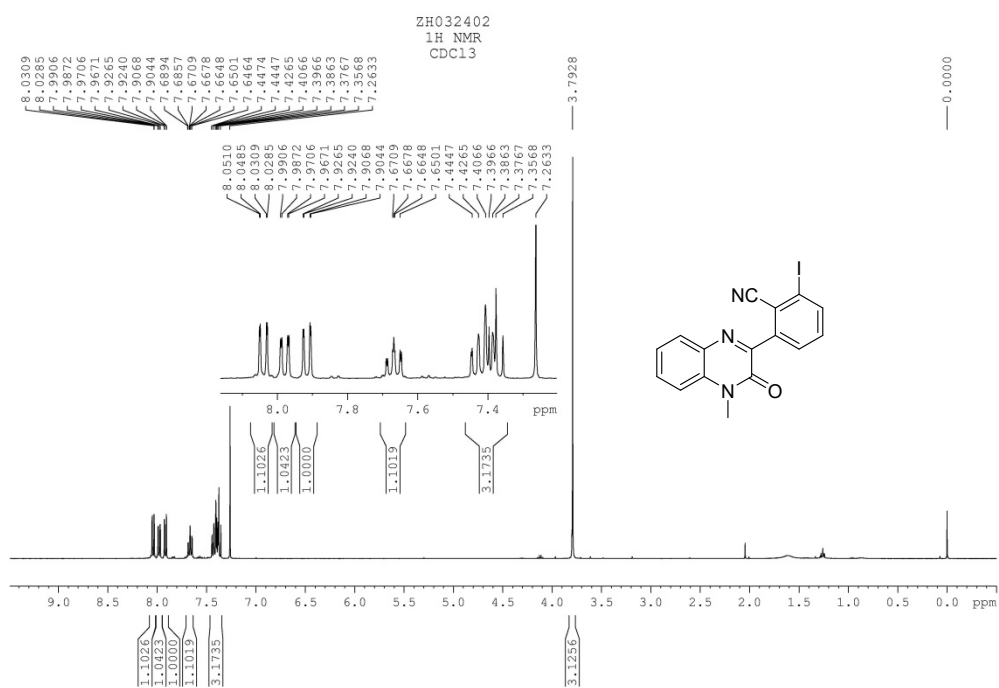


Fig. 57 ¹H NMR spectrum of compound **3ag**

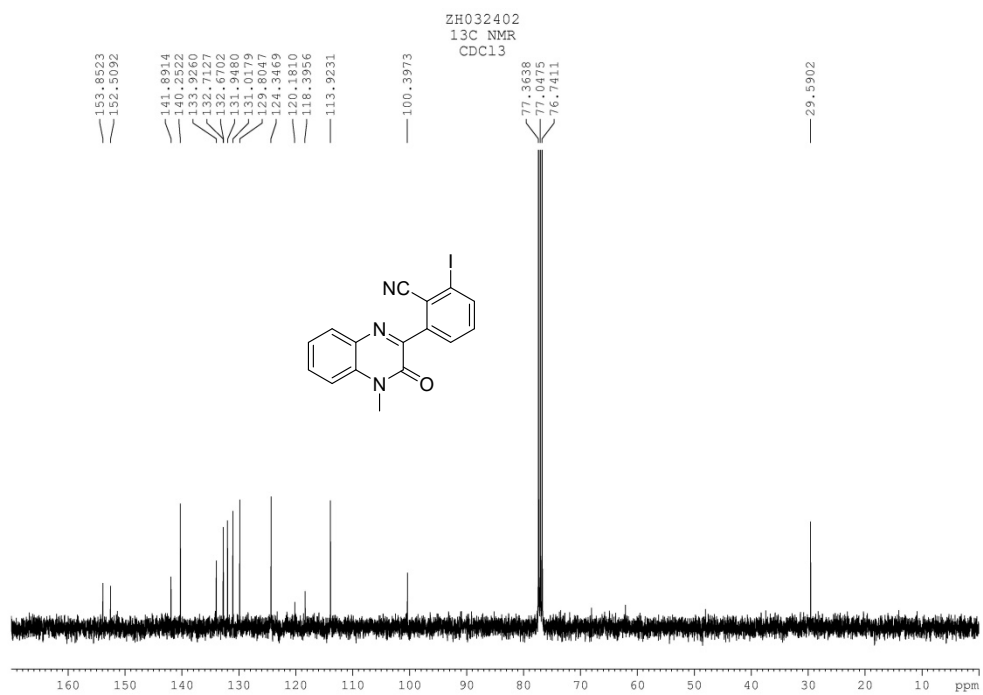


Fig. 58 ¹³C NMR spectrum of compound **3ag**



Fig. 59 ¹H NMR spectrum of compound 3ah

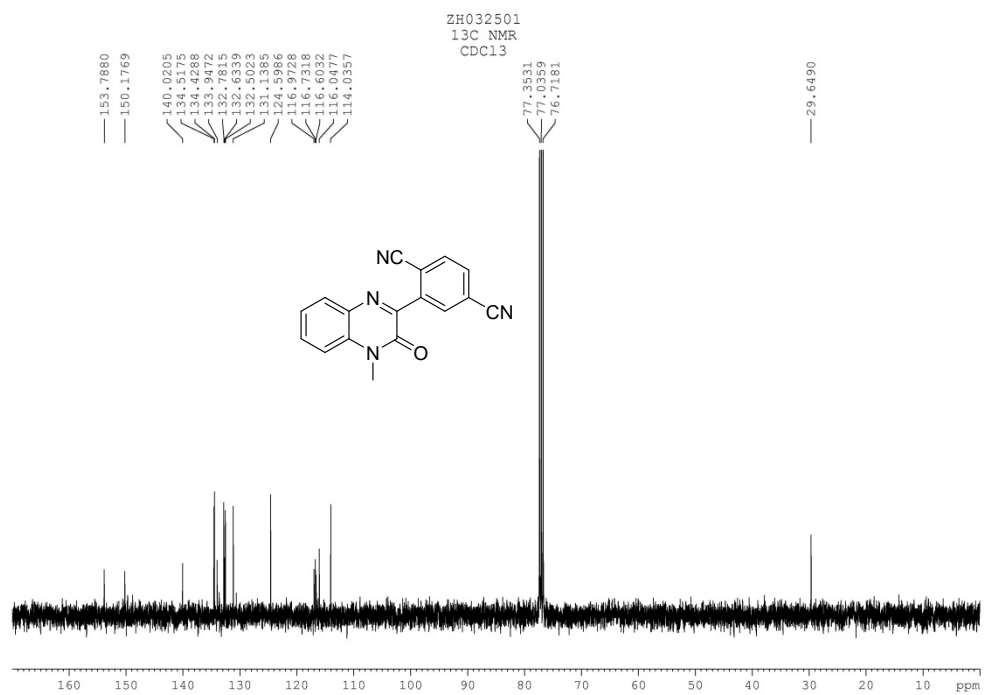


Fig. 60 ¹³C NMR spectrum of compound 3ah

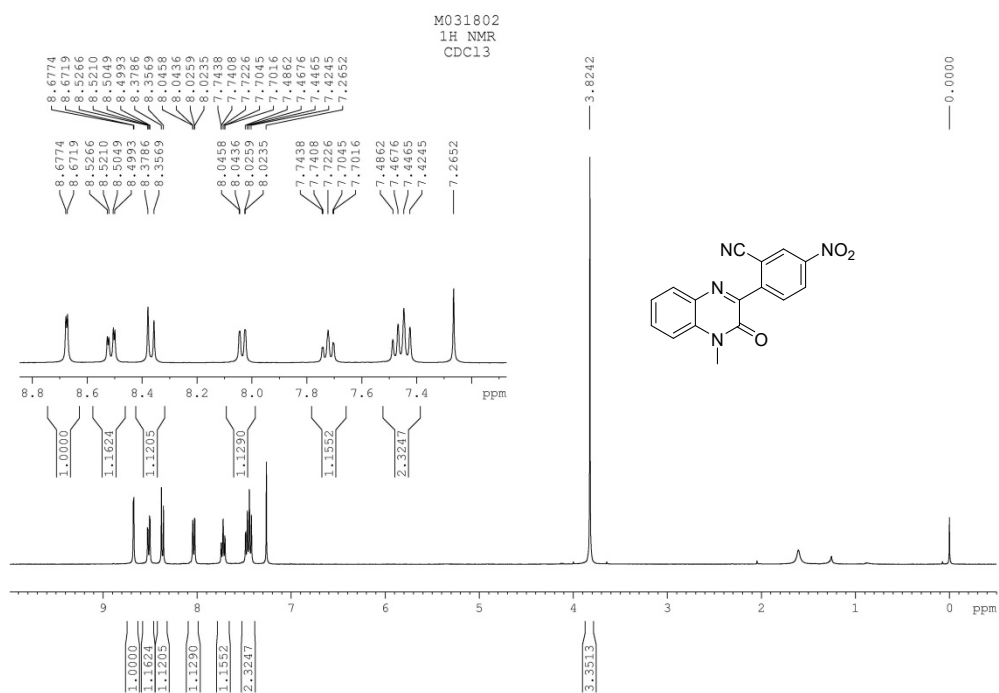


Fig. 61 ^1H NMR spectrum of compound 3ai

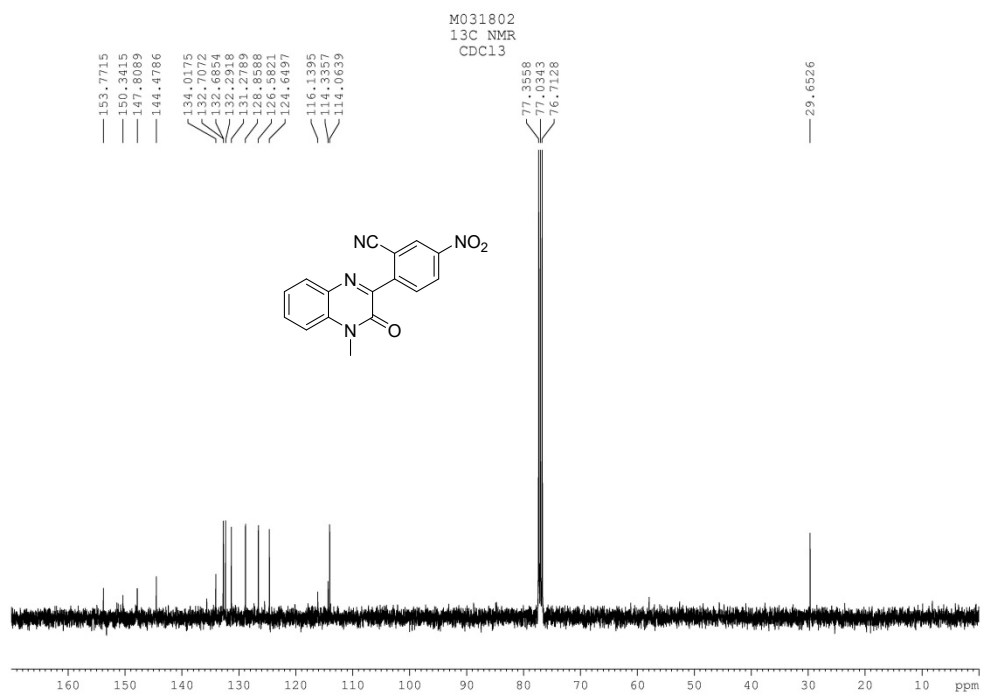


Fig. 62 ^{13}C NMR spectrum of compound 3ai

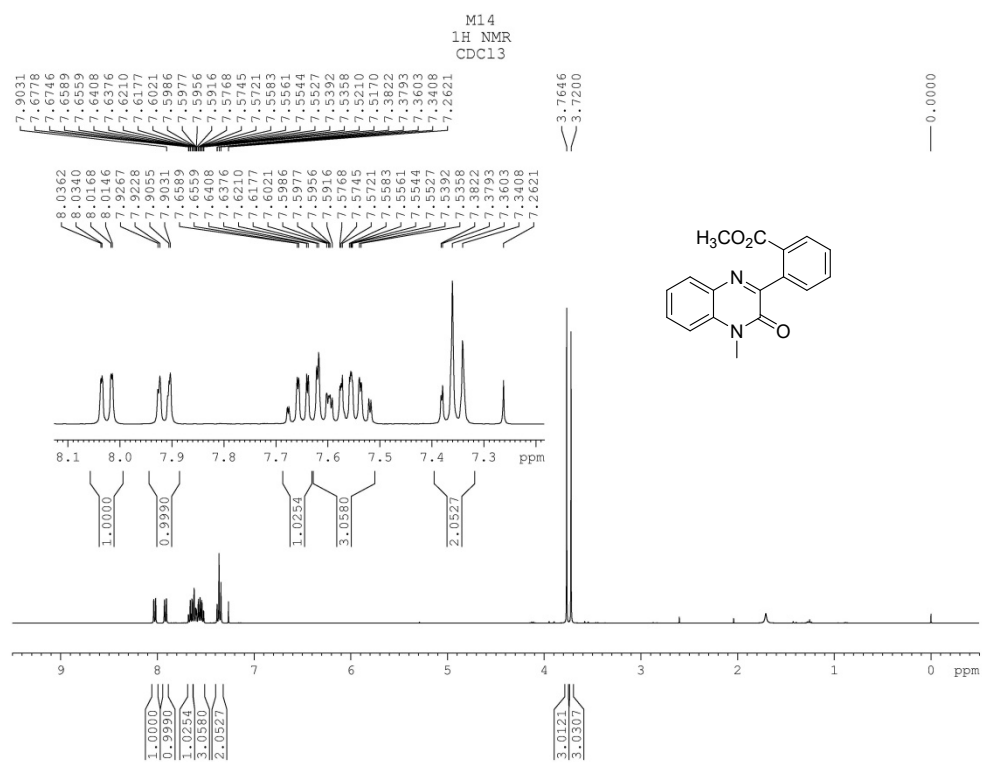


Fig. 63 ¹H NMR spectrum of compound 4

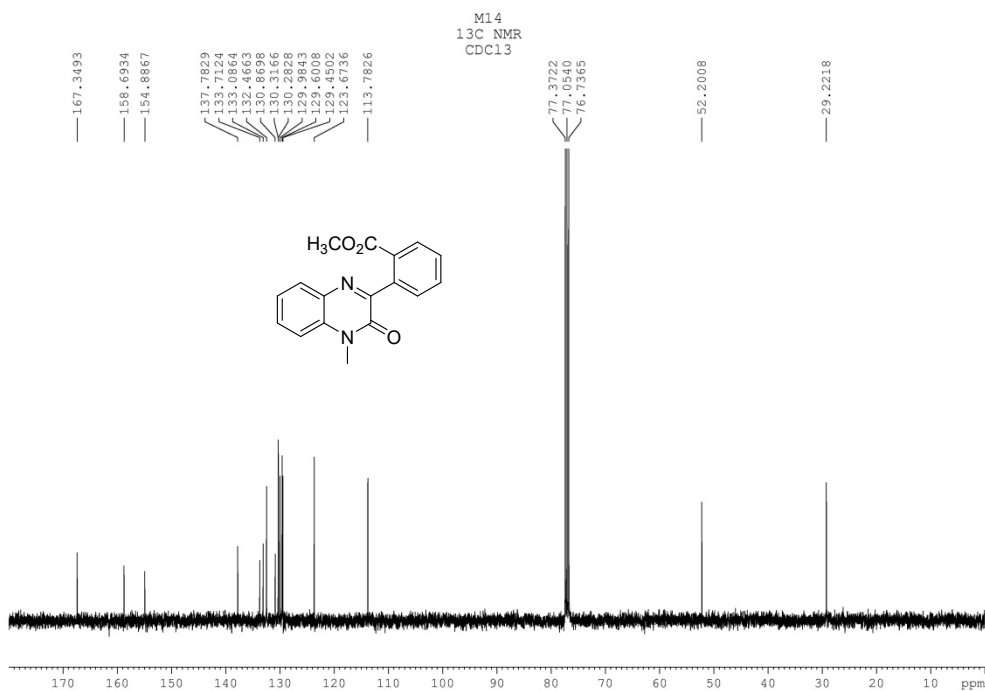


Fig. 64 ¹³C NMR spectrum of compound 4

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T: FTMS + p ESI/Full ms [0.0000-600.0000]

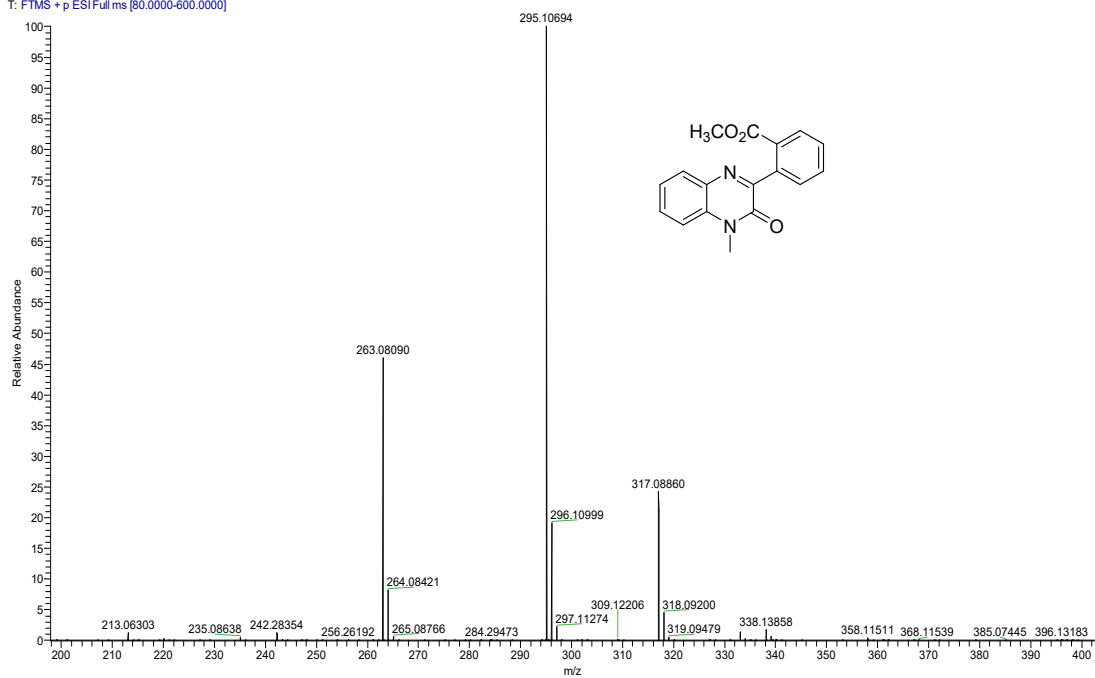


Fig. 65 HR MS spectrum of compound 4

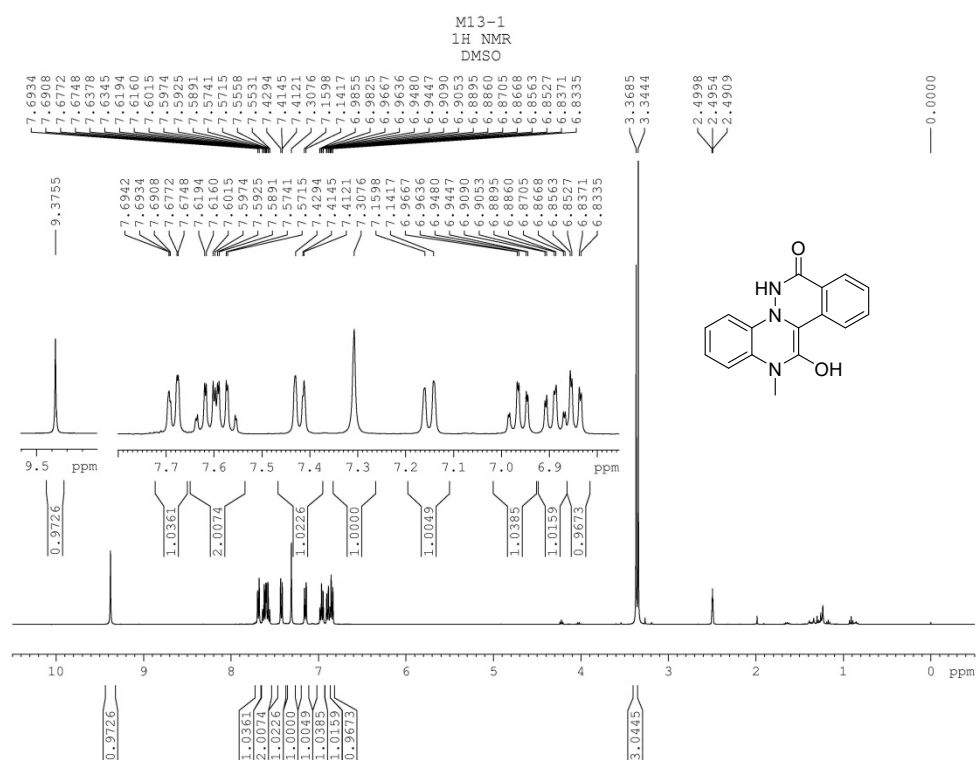


Fig. 66 ¹H NMR spectrum of compound 5

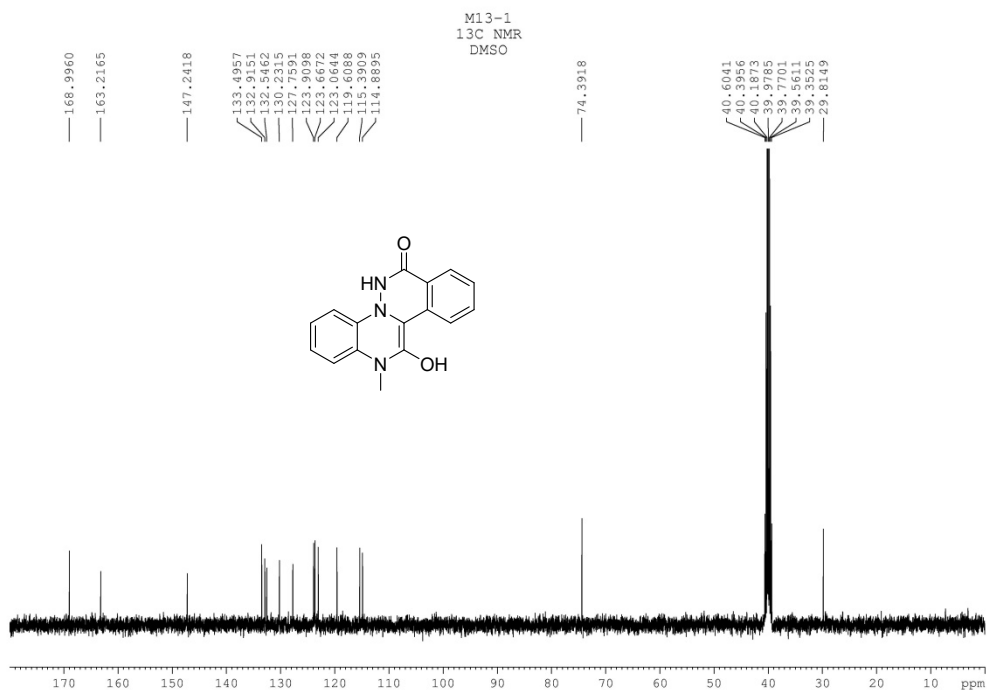


Fig. 67 ¹³C NMR spectrum of compound 5

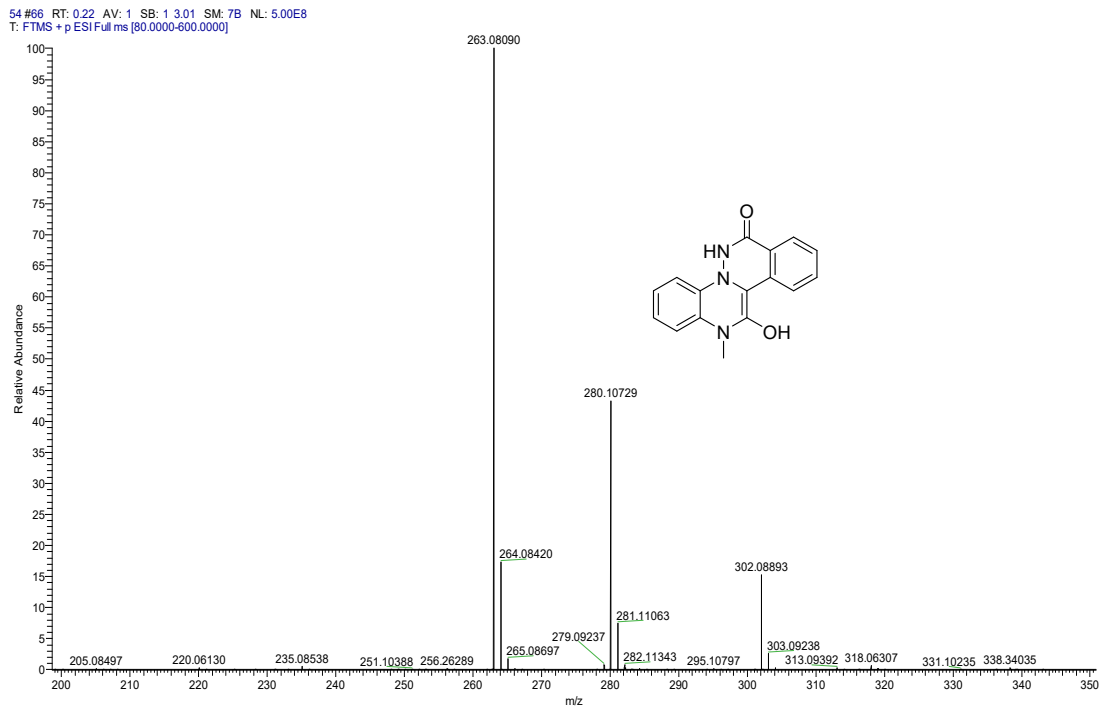


Fig. 68 HR MS spectrum of compound 5

4 D₂O deuterium substitution experiment of product 5

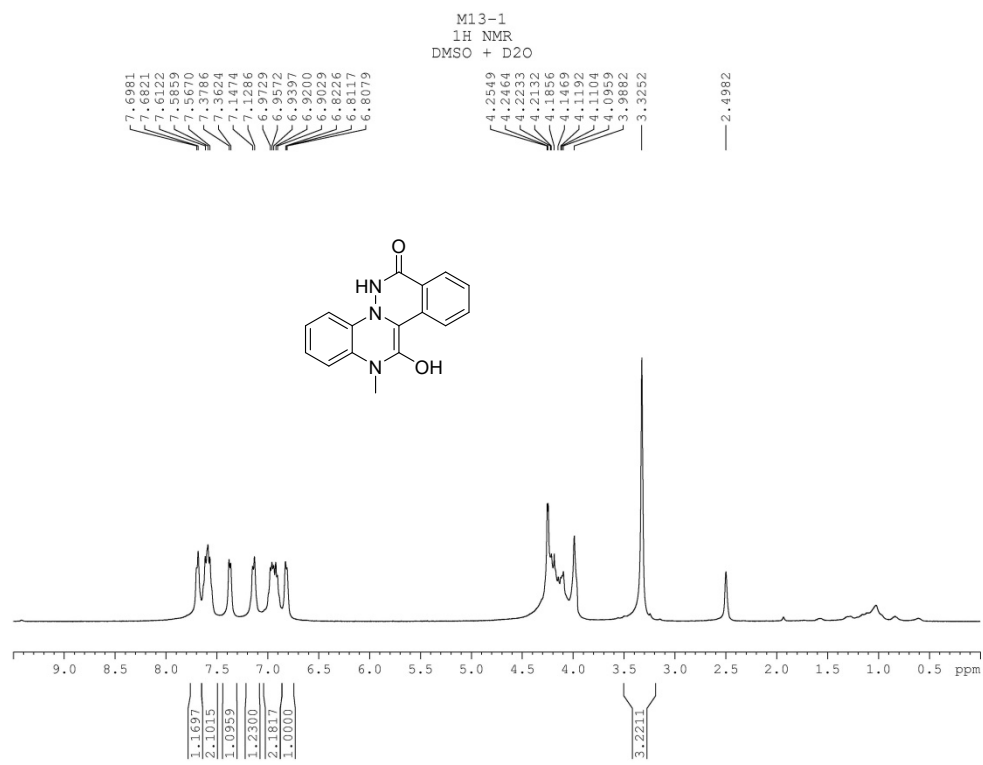


Fig. 69 ¹H NMR spectrum of compound 5 (D₂O + DMSO as co-solvent)

5 HR MS spectrum of the adduct 6

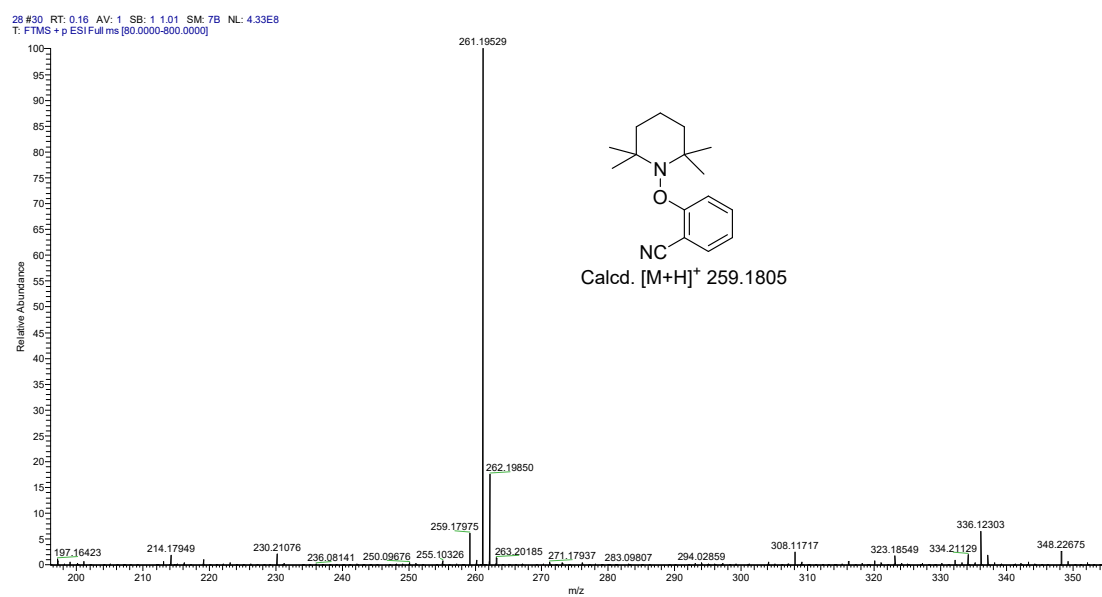


Fig. 70 HR MS spectrum of the adduct 6

6 HR MS spectrum of the adduct 7

30 #27 RT: 0.14 AV: 1 SB: 1.1.01 SM: 7B NL: 1.72E7
T: FTMS +p ESI Fullms [80.0000-800.0000]

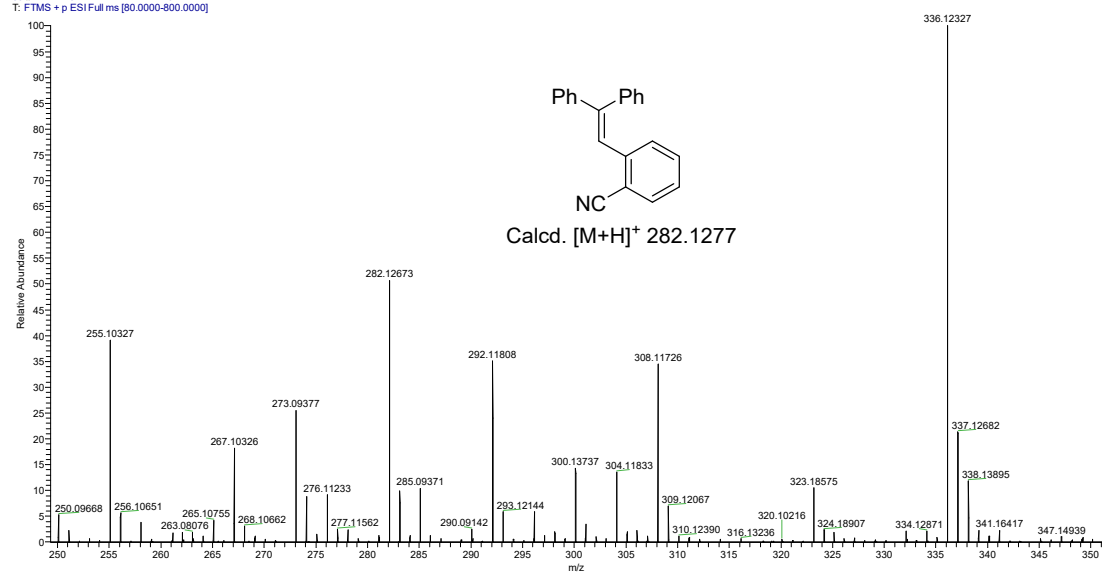


Fig. 71 HR MS spectrum of the adduct 7