

Supporting Information

Electrochemical Synthesis of Polycyclic *N*-Heteroaromatics through Cascade Radical Cyclization of Diynes

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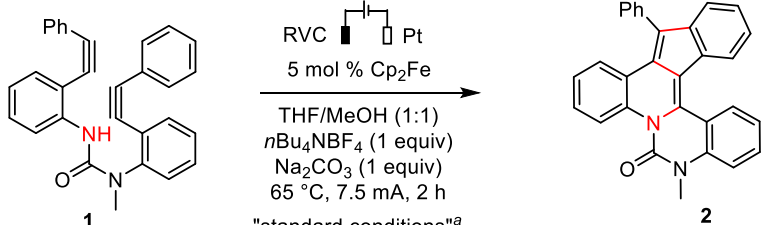
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1. General Information

Anhydrous dichloromethane and tetrahydrofuran were obtained by distillation under argon from calcium hydride and sodium/benzophenone, respectively. Flash column chromatography was performed with silica gel (230–400 mesh). NMR spectra were recorded on Bruker AV-400 and Bruker AV-500 instruments. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^1H and CDCl_3 (77.2 ppm) for ^{13}C . The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra (ESI HRMS) were recorded on a Micromass QTOF2 Quadruple/Time-of-Flight Tandem mass spectrometer by the instrumentation center of Department of Chemistry, Xiamen University. Cyclic voltammograms were obtained on a CHI 760E potentiostat. Infrared spectra (IR) were recorded on a Nicolet AVATER FTIR330 spectrometer.

2. Reaction Optimization

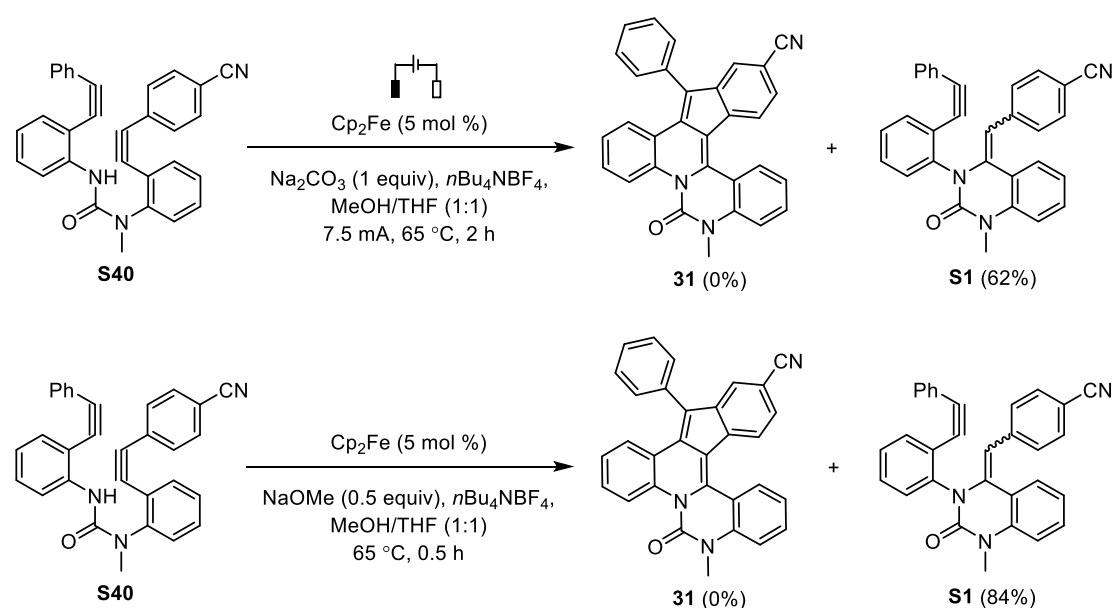
Table S1. Reaction optimization.

		
Entry	Deviation from standard conditions	Yield ^b
1	none	78 ^c
2	MeOH as solvent	37
3	no Cp_2Fe	6 (81)
4	no Na_2CO_3	14 (43)
5	Et_4NBF_4 as electrolyte	61
6	$n\text{Bu}_4\text{NPF}_6$ as electrolyte	72
7	Et_4NOTs as electrolyte	50
6	Pt plate (1 cm x 1 cm) as anode	35 (42)
7	Pt plate (1 cm x 1 cm) as anode, 2.5 mA, 6 h	33 (32)
8	Pt plate (1 cm x 1 cm) as anode, 5 mA, 3 h	31 (41)
9	Pt plate (1 cm x 1 cm) as anode, 10 mA, 1.5 h	21 (29)
10	graphite plate (1 cm x 1 cm) as anode	56 (28)
11	graphite plate (1 cm x 1 cm) as anode, 2.5 mA, 6 h	24 (28)
12	graphite plate (1 cm x 1 cm) as anode, 5 mA, 3 h	30 (32)
13	graphite plate (1 cm x 1 cm) as anode, 10 mA, 1.5 h	16 (25)
14	10 mA, 1.5 h	54
15	5 mA, 3 h	76
16	NaHCO_3 as base	70
17	Na_2HPO_4 as base	59
18	K_2CO_3 as base	35
19	KF as base	46
20	under air	74
21	room temperature	19 (45)

^aRVC anode (100 PPI, 1.2 cm x 1.2 cm x 0.6 cm), Pt plate cathode (1 cm x 1 cm), **1** (0.2 mmol), THF/MeOH (1:1, 6 mL). ^bYield determined by ^1H -NMR analysis using 1,3,5-trimethoxybenzene as the internal standard, unreacted **1** in parenthesis. ^cYield of isolated product.

The low conversion in the absence of Cp_2Fe was probably caused by competitive oxidation of the methanol solvent. Generation of amidyl radicals employing direct electrolysis has been demonstrated by Moeller in basic methanol solution (0.5 equiv of LiOMe) or by Waldvogel under neutral conditions in hexafluoroisopropanol (Ref. 15 of the manuscript). The diyne substrates are prone to base promoted cyclization (Scheme S1).¹ In addition, the desired nitrogen-doped PAH product is oxidized at potential lower than that of the diyne substrate (Scheme S2). Hence, indirect electrolysis was investigated for the cascade cyclization reactions. Our previous studies showed that ferrocene mediated amidyl radical reactions are efficient and selective.²

3. The Cyclization Reaction of **S40**



Scheme S1. The cyclization reaction of **S40**.

The reaction of **S40** under the standard electrolysis conditions afforded the monocyclization product **S1** as the only product in 62% yield (Scheme S1). In the absence of electricity, **S40** cyclized quickly to give **S1** in 84% yield when NaOMe was added. Base promoted alkyne hydroamidation has been reported by others¹ and observed in our previous studies.^{2b} During the electrolysis, methoxide is generated continuously at the cathode as a result of reduction of methanol solvent (Scheme S2). The electrochemically generated base promotes substrate oxidation.² The success of the electrochemical cyclization relies on the continuous generation of the requisite base to keep its concentration low avoiding base promoted hydroamidation. But for **S40** with a strong electron-accepting cyano group, base promoted ionic cyclization outcompetes the desired single electron transfer process.

4. Mechanistic Studies and Proposal

The cyclic voltammograms were recorded in an electrolyte of $n\text{Bu}_4\text{NBF}_4$ (0.1 M) in THF/MeOH (1:1) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire

auxiliary electrode and a SCE reference electrode. The scan rate was 100 mV/s. The CV studies suggested that ferrocene was an efficient mediator for the oxidation of diyne **1** in the presence of NaOMe (Figure S1). Consistent with our previous studies,² Na₂CO₃ did not promote oxidation of **1**.

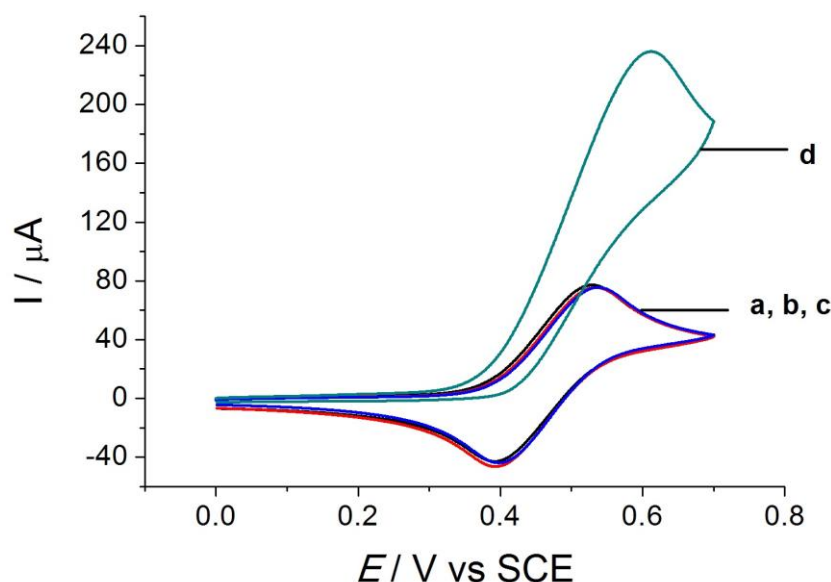
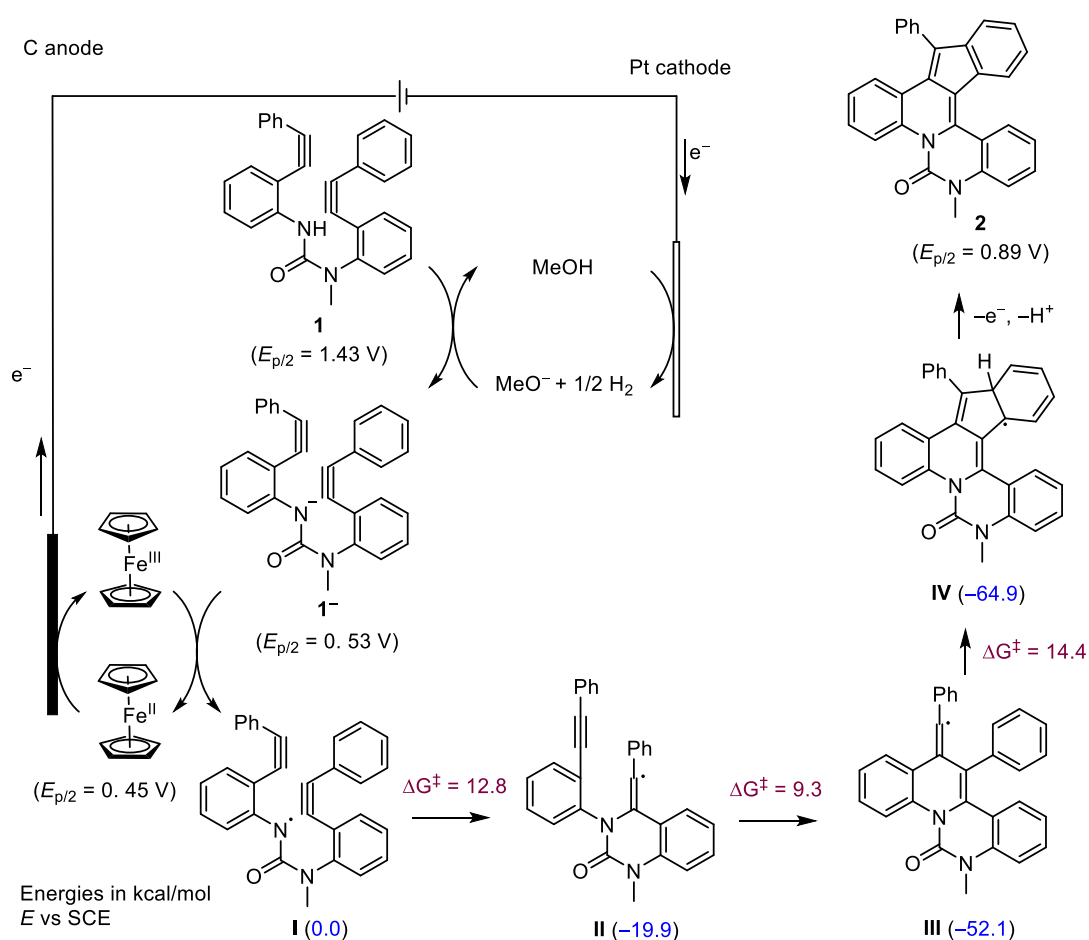


Figure S1. Cyclic voltammograms in THF/MeOH (1:1). a. Cp₂Fe (3 mM). b. Cp₂Fe (3 mM), **1** (12 mM). c. Cp₂Fe (3 mM), **1** (12 mM), Na₂CO₃ (12 mM). d. Cp₂Fe (3 mM), **1** (12 mM), NaOMe (12 mM).

The neutral diyne **1** ($E_{p/2} = 1.43$ V) was oxidized at a potential much higher than that of the product **2** ($E_{p/2} = 0.89$ V) and ferrocene ($E_{p/2} = 0.45$ V) (Scheme S2). Direct electrolysis of **1** might cause the overoxidation of the desired PAH product. Mechanistically, methoxide generated at the cathode deprotonated **1** to give its conjugate base **1**[−] ($E_{p/2} = 0.53$ V), which could be oxidized at a potential much lower than its neutral counterpart. Single electron transfer between ferrocenium generated at the anode and **1**[−] led to the regeneration of ferrocene and formation of nitrogen radical **I**. The latter underwent a cascade radical cyclization and homolytic aromatic C–H substitution to afford the PAH **2**. Since compounds such as **1** were prone to base-promoted hydroamidation reaction, it was essential to keep a low concentration of base. Fortunately, methoxide could be continuously generated at the cathode. The role of ferrocene as a mediator was confirmed by observing a catalytic current (Figure S1). Electron-transfer was observed when methoxide was present but not with Na₂CO₃.



Scheme S2. Mechanistic proposal. Potentials were measured in THF/MeOH (1:1) on a glassy carbon electrode.

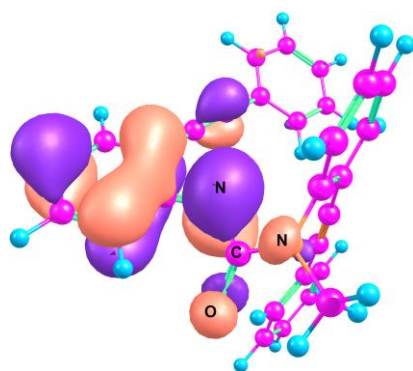


Figure S2. Radical orbital (single occupied natural orbital) of I.

The radical orbital of nitrogen conjugates with the phenyl ring probably because it is more stable when the radical is delocalized. The spin density of the amidyl nitrogen is 0.499 and the carbonyl oxygen only 0.055 with the rest spin densities residue mainly on the aryl ring linked to the nitrogen radical. The C(aryl)-N-C=O dihedral angle is 50°. The electron-withdrawing

ability of the carbonyl group increase the electrophilicity of the nitrogen radical and thus its reactivity toward alkyne addition.

5. General Procedure for the Electrolysis

A 10 mL three-necked round-bottomed flask (Figure S3) was charged with Cp_2Fe (0.01 mmol), the substrate (0.2 mmol), $n\text{Bu}_4\text{NBF}_4$ (0.2 mmol), and Na_2CO_3 (0.2 mmol). The flask was equipped with a condenser, a reticulated vitreous carbon (100 PPI, $\sim 65\text{ cm}^2\text{ cm}^{-3}$, 1.2 cm x 1.2 cm x 0.6 cm) anode and a platinum plate (1 cm x 1 cm) cathode and then flushed with argon. THF (3 mL) and MeOH (3 mL) were added. The electrolysis was carried out at 65 °C (internal temperature) using a constant current of 7.5 mA until complete consumption of the substrate (monitored by TLC or ^1H NMR). The reaction mixture was cooled to RT and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired product.

The 2.1-g scale electrolysis was conducted in a 250-mL beaker-type cell with two RVC anodes (100 PPI, 4.5 cm x 4 cm x 1.2 cm), a Pt plate cathode (3 cm x 3 cm), and a constant current of 187 mA (2 h, 2.8 *F*). The 10-g scale electrolysis was conducted in a 1 L beaker-type cell with two RVC anodes (100 PPI, 6.6 cm x 6.5 cm x 1.2 cm), a Pt plate cathode (5 cm x 5 cm), and a constant current of 900 mA (2.5 h, 3.5 *F*).

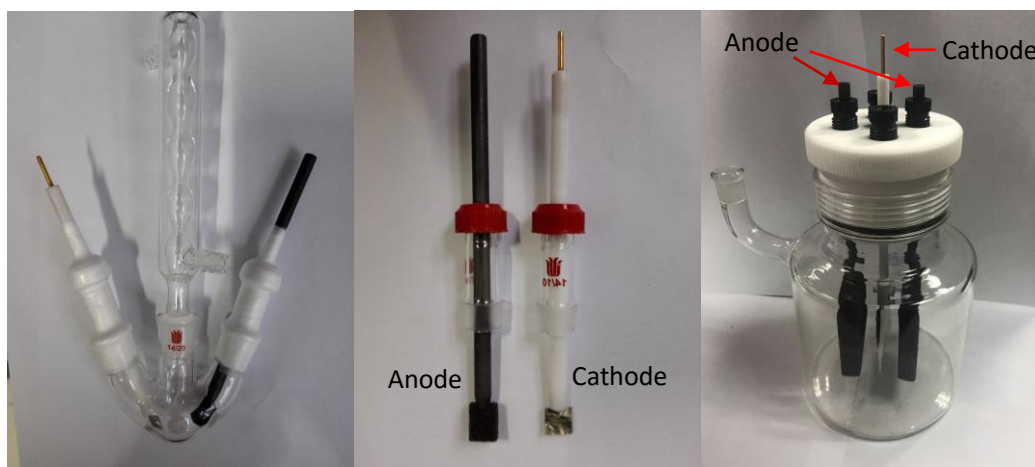
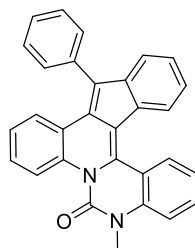


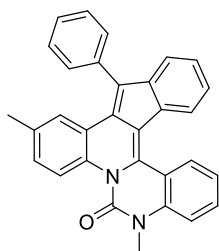
Figure S3. The electrolysis setup

6. Characterization Data for the Electrolysis Products

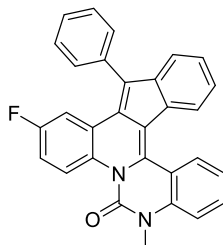


5-Methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5*H*)-one (2). Yield = 78%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (d, $J = 7.8$ Hz, 1H), 8.13 (d, $J = 7.8$ Hz,

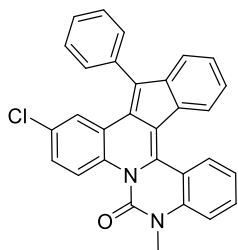
1H), 8.07 (d, $J = 8.5$ Hz, 1H), 7.63–7.50 (m, 6H), 7.48–7.43 (m, 1H), 7.40–7.35 (m, 1H), 7.34–7.25 (m, 3H), 7.21 (d, $J = 8.2$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.2, 145.3, 138.4, 136.6, 134.5, 133.0, 132.2, 130.6, 130.4, 130.0, 129.4, 129.2, 127.7, 127.3, 126.2, 125.9, 125.5, 124.9, 124.2, 123.8, 122.9, 122.8, 121.2, 120.3, 118.6, 114.0, 31.6; IR (neat, cm^{-1}): 2919, 1693, 1502, 1470, 1268, 1197, 1076, 751; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{20}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 447.1468, obsd 447.1469.



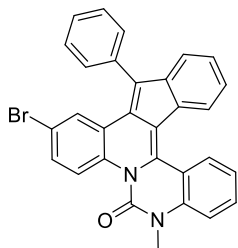
5,10-Dimethyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (3). Yield = 62%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 7.97 (d, $J = 8.5$ Hz, 1H), 7.63–7.57 (m, 3H), 7.53 (t, $J = 7.8$ Hz, 2H), 7.48–7.43 (m, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.37–7.34 (m, 1H), 7.33–7.27 (m, 2H), 7.21 (d, $J = 8.5$ Hz, 1H), 7.17–7.13 (m, 1H), 7.09 (dd, $J = 8.5, 2.0$ Hz, 1H), 3.59 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.1, 145.2, 138.4, 136.7, 135.0, 134.5, 132.1, 130.8, 130.6, 130.4, 130.0, 129.1, 129.0, 127.7, 127.4, 127.2, 126.0, 125.5, 124.7, 123.9, 123.6, 122.8, 122.6, 121.2, 120.3, 118.6, 113.9, 31.6, 21.3; IR (neat, cm^{-1}): 2919, 1692, 1612, 1461, 1377, 1196, 1132, 1076; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{22}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 461.1624, obsd 461.1627.



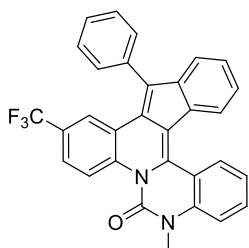
10-Fluoro-5-methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (4). Yield = 65%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.29 (d, $J = 7.8$ Hz, 1H), 8.15 (d, $J = 7.9$ Hz, 1H), 8.07 (dd, $J = 9.3, 5.3$ Hz, 1H), 7.68–7.45 (m, 6H), 7.41–7.37 (m, 1H), 7.36–7.29 (m, 2H), 7.26–7.16 (m, 3H), 7.02–6.94 (m, 1H), 3.61 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.7 (d, $J_{\text{C-F}} = 244.8$ Hz), 150.2, 145.0, 138.4, 135.9, 134.5, 132.3, 130.6, 130.4 (2C), 129.9, 129.4, 129.2 (d, $J = 2.5$ Hz), 128.1, 127.4, 126.7 (d, $J_{\text{C-F}} = 9.5$ Hz), 126.2 (d, $J_{\text{C-F}} = 8.8$ Hz), 125.2 (d, $J_{\text{C-F}} = 2.6$ Hz), 124.1, 123.0, 122.2, 121.3, 120.6, 118.5, 114.1, 113.8 (d, $J_{\text{C-F}} = 23.6$ Hz), 110.9 (d, $J_{\text{C-F}} = 24.1$ Hz), 31.7; ^{19}F NMR (471 MHz, CDCl_3) δ -115.1 (ddd, $J = 10.4, 7.8, 5.2$ Hz); IR (neat, cm^{-1}): 2900, 1689, 1603, 1475, 1269, 1132, 753; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{19}\text{FN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 465.1374, obsd 465.1385.



10-Chloro-5-methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (5). Yield = 64%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.14 (d, $J = 7.8$ Hz, 1H), 8.02 (d, $J = 9.0$ Hz, 1H), 7.63–7.60 (m, 1H), 7.59–7.54 (m, 4H), 7.52–7.47 (m, 2H), 7.41–7.38 (m, 1H), 7.35–7.29 (m, 2H), 7.24–7.16 (m, 3H), 3.59 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.0, 145.0, 138.3, 135.8, 134.4, 132.4, 131.4, 130.9, 130.6, 130.4 (2C), 129.8, 129.3, 128.2, 127.5, 126.4, 126.2, 125.6, 124.8, 124.7, 124.2, 123.1, 122.6, 121.3, 120.6, 118.4, 114.1, 31.6; IR (neat, cm^{-1}): 2919, 1691, 1603, 1464, 1196, 1132, 1076; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{19}\text{ClN}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 459.1259, obsd 459.1260.

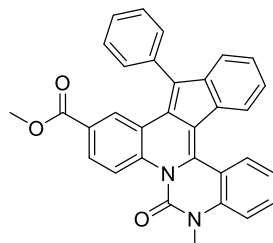


10-Bromo-5-methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (6). Yield = 71%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.25 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 7.95 (d, $J = 9.0$ Hz, 1H), 7.66 (d, $J = 2.4$ Hz, 1H), 7.62–7.54 (m, 5H), 7.51–7.47 (m, 1H), 7.41–7.39 (m, 1H), 7.36–7.28 (m, 3H), 7.22–7.15 (m, 2H), 3.58 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.0, 144.9, 138.3, 135.8, 134.4, 132.4, 131.8, 130.6, 130.4 (2C), 129.7, 129.3, 129.0, 128.2, 127.9, 127.5, 126.7, 125.8, 124.6, 124.2, 123.1, 122.7, 121.3, 120.6, 118.8, 118.4, 114.1, 31.6; IR (neat, cm^{-1}): 2920, 1681, 1601, 1469, 1372, 1132, 1077, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{20}\text{BrN}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 503.0754, 505.0733, obsd 503.0756, 505.0736.



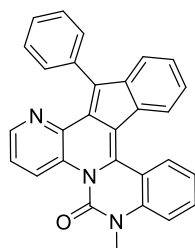
5-Methyl-12-phenyl-10-(trifluoromethyl)indeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (7). Yield = 64%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.28 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.17 (m, 2H), 7.84 (d, $J = 2.1$ Hz, 1H), 7.68–7.54 (m, 5H), 7.52–7.40 (m, 3H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.26–7.18 (m, 2H), 3.62 (s, 3H); ^{13}C NMR (126 MHz,

CDCl₃) δ 150.2, 145.0, 138.4, 135.7, 135.3, 134.3, 132.5, 131.0, 130.6, 130.4, 129.7, 129.4, 128.3, 127.7, 127.2 (q, J = 33.2 Hz), 125.1, 124.8 (2C), 124.3, 123.9 (q, J_{C-F} = 271.0 Hz), 123.2, 123.0, 122.6 (q, J = 4.1 Hz), 122.5 (q, J = 3.6 Hz), 121.4, 120.8, 118.5, 114.2, 31.7; ¹⁹F NMR (471 MHz, CDCl₃) δ -62.9; IR (neat, cm⁻¹): 2923, 1694, 1604, 1439, 1348, 1320, 1198, 1125, 1085, 753, 727; ESI HRMS m/z calcd for [C₃₁H₁₉F₃N₂ONa]⁺ (M+Na)⁺ 515.1342, obsd 515.1343.

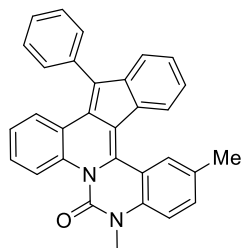


Methyl

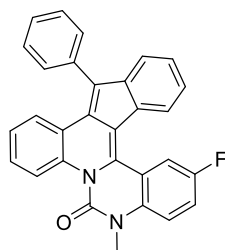
5-methyl-6-oxo-12-phenyl-5,6-dihydroindeno[1',2':3,4]quinolino[1,2-c]quinazoline-10-carboxylate (8). Yield = 62%; Red solid; ¹H NMR (500 MHz, CDCl₃) δ 8.32–8.21 (m, 2H), 8.13 (dd, J = 9.9, 8.3 Hz, 2H), 7.89 (dd, J = 8.8, 2.0 Hz, 1H), 7.65–7.55 (m, 5H), 7.54–7.48 (m, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.37–7.27 (m, 2H), 7.24–7.15 (m, 2H), 3.76 (s, 3H), 3.59 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.5, 150.1, 145.2, 138.3, 136.3, 136.0, 134.3, 132.4, 130.6 (2C), 130.3, 129.7, 129.4, 128.0, 127.5, 127.3, 126.7, 125.3, 124.7, 124.2, 124.1, 123.1, 122.9, 121.3, 120.6, 118.4, 114.1, 52.1, 31.6; IR (neat, cm⁻¹): 2920, 1722, 1698, 1603, 1437, 1270, 1197, 1132, 764; ESI HRMS m/z calcd for [C₃₂H₂₂N₂O₃Na]⁺ (M+Na)⁺ 505.1523, obsd 505.1523.



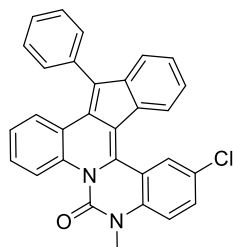
5-Methyl-12-phenylindeno[1',2':3,4][1,5]naphthyridino[1,2-c]quinazolin-6(5H)-one (9). Yield = 59%; Red solid; ¹H NMR (500 MHz, CDCl₃) δ 8.40 (dd, J = 8.5, 1.6 Hz, 1H), 8.36 (dd, J = 4.4, 1.6 Hz, 1H), 8.31 (dd, J = 7.7, 1.6 Hz, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.73–7.67 (m, 2H), 7.62 (m, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.44–7.39 (m, 1H), 7.39–7.34 (m, 1H), 7.31 (td, J = 7.5, 1.0 Hz, 1H), 7.24–7.18 (m, 3H), 3.60 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 150.1, 147.1, 144.9, 142.7, 138.3, 136.0, 133.5, 132.4, 132.1, 131.0, 130.7, 130.5, 129.4, 127.9 (2C), 127.5, 127.3, 125.9, 124.3, 123.7, 123.2, 121.5, 121.4, 120.7, 118.4, 114.1, 31.6; IR (neat, cm⁻¹): 2923, 1692, 1603, 1428, 1272, 1203, 754; ESI HRMS m/z calcd for [C₂₉H₁₉N₃ONa]⁺ (M+Na)⁺ 426.1601, obsd 426.1606.



2,5-Dimethyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (10). Yield = 64%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.17 (d, J = 7.9 Hz, 1H), 8.13 (d, J = 2.0 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.63–7.57 (m, 3H), 7.54 (t, J = 7.4 Hz, 2H), 7.47–7.37 (m, 3H), 7.32 (t, J = 7.4 Hz, 1H), 7.29–7.26 (m, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 3.59 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.2, 145.3, 136.7, 136.2, 134.9, 133.1, 132.9, 132.6, 130.8, 130.5, 130.0, 129.2 (2C), 127.7, 127.2, 126.2, 126.0, 125.5, 125.4, 124.9, 124.2, 123.7, 122.6, 121.0, 120.3, 118.5, 113.9, 31.6, 20.8; IR (neat, cm^{-1}): 2919, 1645, 1468, 1196, 1132, 1090; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{22}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 461.1624, obsd 461.1628.

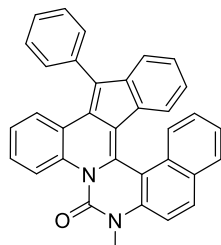


2-Fluoro-5-methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (11). Yield = 65%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.14 (d, J = 7.9 Hz, 1H), 8.05 (dd, J = 8.6, 1.2 Hz, 1H), 8.00 (dd, J = 8.6, 2.9 Hz, 1H), 7.61–7.52 (m, 5H), 7.49–7.44 (m, 1H), 7.38–7.26 (m, 4H), 7.22–7.16 (m, 2H), 7.06 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.4 (d, $J_{\text{C-F}}$ = 243.5 Hz), 150.1, 145.5, 136.4, 134.9 (d, $J_{\text{C-F}}$ = 2.2 Hz), 133.1 (d, $J_{\text{C-F}}$ = 2.6 Hz), 133.0, 130.1, 130.0, 129.9, 129.2, 127.9, 127.7, 126.4, 125.9, 125.6, 125.5, 124.8, 124.2, 124.1, 123.7, 121.2, 120.5, 120.1 (d, $J_{\text{C-F}}$ = 8.5 Hz), 119.0 (d, $J_{\text{C-F}}$ = 23.1 Hz), 116.8 (d, $J_{\text{C-F}}$ = 24.8 Hz), 115.5 (d, $J_{\text{C-F}}$ = 8.1 Hz), 31.9; ^{19}F NMR (471 MHz, CDCl_3) δ -119.6; IR (neat, cm^{-1}): 2920, 1693, 1614, 1462, 1197, 1132, 1077; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{19}\text{FN}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 443.1554, obsd 443.1559.



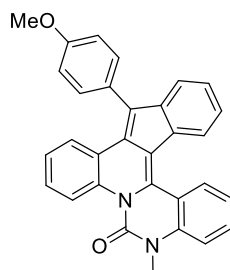
2-Chloro-5-methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (12). Yield = 61%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (d, J = 2.4 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.05 (dd, J = 8.4, 1.2 Hz, 1H), 7.61–7.52 (m, 6H), 7.49–7.45 (m, 1H), 7.38–7.33

(m, 2H), 7.28 (ddd, $J = 8.6, 7.2, 1.6$ Hz, 1H), 7.22 (ddd, $J = 8.2, 6.7, 1.6$ Hz, 1H), 7.16 (d, $J = 8.6$ Hz, 1H), 7.06 (ddd, $J = 8.4, 7.2, 1.2$ Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.1, 145.6, 137.1, 136.4, 132.9 (2C), 131.8, 130.2, 130.1, 129.9 (2C), 129.2, 128.4, 127.9, 127.7, 126.4, 125.8, 125.7, 125.5, 124.9, 124.3, 124.2, 123.7, 121.0, 120.6, 120.1, 115.4, 31.7; IR (neat, cm^{-1}): 2919, 1698, 1514, 1462, 1196, 1132, 1077; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{20}\text{ClN}_2\text{O}]^+ (\text{M}+\text{H})^+$ 459.1259, obsd 459.1264.



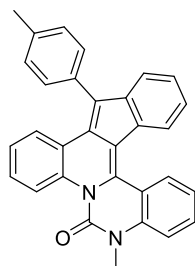
3-Methyl-10-phenylbenzo[f]indeno[1',2':3,4]quinolino[1,2-c]quinazolin-4(3H)-one (13).

Yield = 52%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.12 (d, $J = 8.9$ Hz, 1H), 8.05–7.91 (m, 3H), 7.71–7.43 (m, 8H), 7.38–7.29 (m, 3H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.11 (t, $J = 7.8$ Hz, 1H), 6.80 (t, $J = 7.5$ Hz, 1H), 6.37 (d, $J = 7.8$ Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.8, 145.0, 137.7, 136.3, 133.0, 131.1, 130.6, 130.1, 129.9 (2C), 129.3, 129.2, 128.7, 128.3, 127.8, 126.9, 126.8, 126.4, 126.1, 125.8, 125.7 (2C), 125.6, 125.5, 125.0, 123.9, 123.7, 120.2, 113.5, 112.5, 32.0; IR (neat, cm^{-1}): 2919, 1689, 1626, 1599, 1514, 1440, 1196, 1133, 1078, 751; ESI HRMS m/z calcd for $[\text{C}_{34}\text{H}_{22}\text{N}_2\text{ONa}]^+ (\text{M}+\text{Na})^+$ 497.1624, obsd 497.1627.

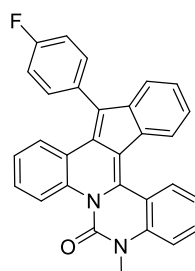


12-(4-Methoxyphenyl)-5-methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (14).

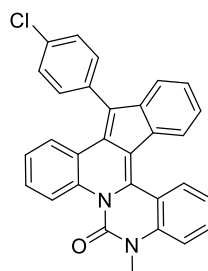
Yield = 61%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 8.06 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.66–7.59 (m, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.35–7.26 (m, 3H), 7.25–7.22 (m, 1H), 7.16 (ddd, $J = 8.2, 7.2, 1.3$ Hz, 1H), 7.11–7.05 (m, 3H), 3.93 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.3, 150.3, 145.5, 138.5, 134.2, 133.1, 132.1, 131.1, 130.6, 130.4, 129.3, 128.7, 127.3, 126.2, 125.8, 125.5, 125.4, 125.2, 124.2, 123.8, 123.0, 122.9, 121.2, 120.4, 118.8, 114.7, 114.0, 55.5, 31.6; IR (neat, cm^{-1}): 2921, 1688, 1606, 1508, 1270, 1197, 1132, 1076, 754; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{22}\text{N}_2\text{O}_2]^+ (\text{M}+\text{H})^+$ 455.1754, obsd 455.1753.



5-Methyl-12-(p-tolyl)indeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (15). Yield = 64%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.26 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 8.06 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.66–7.56 (m, 2H), 7.49 (d, $J = 7.5$ Hz, 2H), 7.40–7.25 (m, 6H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.17–7.12 (m, 1H), 7.07 (ddd, $J = 8.4, 7.1, 1.2$ Hz, 1H), 3.60 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.3, 145.4, 138.5, 137.4, 134.3, 133.5, 133.0, 132.1, 130.6, 130.4, 129.9, 129.8, 129.6, 127.2, 126.2, 125.8, 125.5, 125.4, 125.1, 124.2, 123.8, 123.0, 122.9, 121.1, 120.4, 118.7, 114.0, 31.6, 21.7; IR (neat, cm^{-1}): 2920, 1690, 1605, 1471, 1304, 1269, 1198, 1076, 753; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{22}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 461.1624, obsd 461.1624.

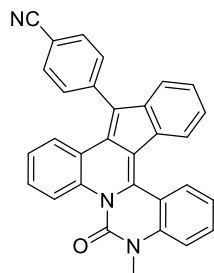


12-(4-Fluorophenyl)-5-methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (16). Yield = 72%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.26 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 8.08 (dd, $J = 8.6, 1.3$ Hz, 1H), 7.62–7.58 (m, 1H), 7.58–7.52 (m, 3H), 7.34–7.26 (m, 4H), 7.25–7.20 (m, 3H), 7.16 (ddd, $J = 8.2, 6.1, 2.3$ Hz, 1H), 7.08 (ddd, $J = 8.2, 7.1, 1.3$ Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.5 (d, $J_{\text{C-F}} = 246.6$ Hz), 150.1, 145.1, 138.4, 134.7, 133.1, 132.5 (d, $J_{\text{C-F}} = 3.3$ Hz), 132.3, 131.7 (d, $J_{\text{C-F}} = 7.9$ Hz), 130.6, 130.3, 128.1, 127.3, 126.3, 126.2, 125.5, 125.3, 124.8, 124.3, 123.9, 122.9, 122.6, 121.2, 120.1, 118.5, 116.3 (d, $J_{\text{C-F}} = 21.2$ Hz), 114.0, 31.6; ^{19}F NMR (471 MHz, CDCl_3) δ -114.3; IR (neat, cm^{-1}): 2920, 1693, 1605, 1505, 1471, 1268, 1221, 1130, 1075, 753; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{20}\text{FN}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 443.1554, obsd 443.1559.

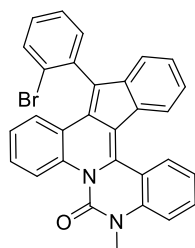


12-(4-Chlorophenyl)-5-methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (17). Yield = 68%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (dd, $J = 7.7, 1.6$ Hz, 1H), 8.14 (d,

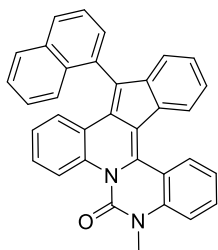
$J = 8.0$ Hz, 1H), 8.10 (d, $J = 8.6$, 1H), 7.66–7.49 (m, 6H), 7.37–7.27 (m, 4H), 7.25–7.21 (m, 1H), 7.17 (ddd, $J = 8.0$, 6.4, 2.1 Hz, 1H), 7.13–7.07 (m, 1H), 3.61 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.1, 144.9, 138.4, 135.2, 134.9, 133.5, 133.1, 132.3, 131.4, 130.6, 130.3, 129.5, 127.8, 127.3, 126.4, 126.3, 125.6, 125.3, 124.7, 124.3, 123.9, 123.0, 122.7, 121.2, 120.0, 118.5, 114.0, 31.6; IR (neat, cm^{-1}): 2920, 1692, 1605, 1472, 1326, 1269, 1198, 1076, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{19}\text{ClN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 481.1078, obsd 481.1074.



4-(5-Methyl-6-oxo-5,6-dihydroindeno[1',2':3,4]quinolino[1,2-c]quinazolin-12-yl)benzonitrile (18). Yield = 53%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.20 (dd, $J = 7.8$, 1.5 Hz, 1H), 8.12–8.02 (m, 2H), 7.74 (d, $J = 7.8$ Hz, 2H), 7.65 (d, $J = 7.8$ Hz, 2H), 7.56 (td, $J = 7.8$, 1.5 Hz, 1H), 7.40 (dd, $J = 8.2$, 1.5 Hz, 1H), 7.28–7.22 (m, 4H), 7.20–7.17 (m, 1H), 7.13–7.08 (m, 1H), 7.05–6.99 (m, 1H), 3.55 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.8, 144.0, 142.1, 138.3, 135.6, 133.1, 133.0, 132.6, 130.9, 130.6, 130.3, 127.4, 127.0, 126.8, 126.6, 125.7, 125.2, 124.4, 124.1 (2C), 123.1, 122.5, 121.3, 119.7, 119.2, 118.2, 114.1, 111.2, 31.7; IR (neat, cm^{-1}): 2921, 2214, 1694, 1600, 1442, 1302, 1266, 1196, 1133, 1076, 754; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{19}\text{N}_3\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 472.1420, obsd 472.1421.

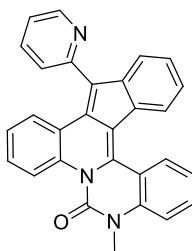


12-(2-Bromophenyl)-5-methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (19). Yield = 69%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.32 (dd, $J = 7.8$, 1.4 Hz, 1H), 8.15–8.11 (m, 2H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.60 (td, $J = 7.8$, 1.4 Hz, 1H), 7.49–7.43 (m, 2H), 7.37–7.28 (m, 5H), 7.23 (d, $J = 8.2$ Hz, 1H), 7.18–7.12 (m, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.2, 144.6, 138.3, 138.1, 135.1, 133.5, 132.9, 132.3, 132.2, 130.8, 130.0, 129.5, 128.2, 127.7, 127.2, 126.8, 126.3, 125.9, 125.1 (2C), 124.7, 124.1, 123.6, 123.0, 121.9, 121.3, 120.3, 118.5, 114.0, 31.7; IR (neat, cm^{-1}): 2920, 1636, 1458, 1354, 1268, 1131, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{20}\text{BrN}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 503.0754, 505.0733, obsd 503.0756, 505.0735.



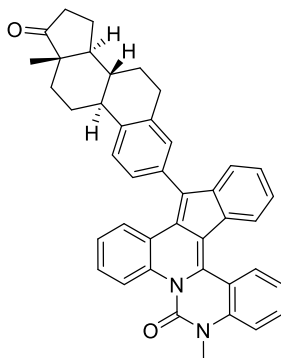
5-Methyl-12-(naphthalen-1-yl)indeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (20).

Yield = 71%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.37 (dd, $J = 7.7, 1.5$ Hz, 1H), 8.18 (d, $J = 7.7$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 8.02–7.96 (m, 2H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.67–7.60 (m, 3H), 7.50 (t, $J = 7.7$ Hz, 1H), 7.36–7.26 (m, 3H), 7.24–7.12 (m, 4H), 7.02 (d, $J = 7.7$ Hz, 1H), 6.85 (t, $J = 7.7$ Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.3, 146.2, 138.4, 134.8, 134.7, 134.3, 133.0, 132.3 (2C), 130.8, 130.3, 128.5, 128.3, 127.8, 127.5, 127.3, 127.2, 126.7, 126.4, 126.3, 126.2, 126.1, 125.7, 125.6, 124.8, 124.0, 123.6, 123.0, 122.4, 121.2, 120.7, 118.7, 114.0, 31.7; IR (neat, cm^{-1}): 2920, 1692, 1615, 1462, 1269, 1206, 1132, 1076, 752; ESI HRMS m/z calcd for $[\text{C}_{34}\text{H}_{23}\text{N}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 475.1805, obsd 475.1810.



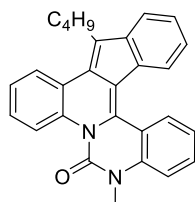
5-Methyl-12-(pyridin-2-yl)indeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (21).

Yield = 64%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.88 (d, $J = 4.7$ Hz, 1H), 8.29 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.13 (t, $J = 8.7$ Hz, 3H), 7.81 (td, $J = 7.8, 1.8$ Hz, 1H), 7.68–7.64 (m, 1H), 7.64–7.56 (m, 2H), 7.54 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.36–7.28 (m, 4H), 7.23 (d, $J = 8.2$ Hz, 1H), 7.18–7.14 (m, 1H), 7.10 (ddd, $J = 8.2, 7.1, 1.5$ Hz, 1H), 3.61 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 156.3, 150.5, 149.9, 144.4, 138.3, 136.7, 135.1, 133.2, 132.3, 130.8, 130.4, 127.6, 127.4, 126.6, 125.7, 125.5 (2C), 124.4, 124.2, 123.8, 123.0 (2C), 122.3, 121.1, 120.7, 118.5, 114.0, 31.6; IR (neat, cm^{-1}): 2920, 1693, 1605, 1462, 1355, 1198, 1132, 1076, 749; ESI HRMS m/z calcd for $[\text{C}_{29}\text{H}_{20}\text{N}_3\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 426.1601, obsd 426.1602.

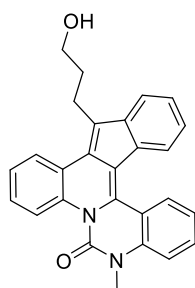


5-Methyl-12-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6

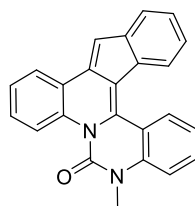
***H*-cyclopenta[*a*]phenanthren-3-yl]indeno[1',2':3,4]quinolino[1,2-*c*]quinazolin-6(5*H*)-one (22).** Yield = 74%; Red solid; ¹H NMR (500 MHz, CDCl₃) δ 8.26 (dd, *J* = 7.7, 1.5 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 8.06 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.60 (td, *J* = 7.9, 1.5 Hz, 1H), 7.45–7.36 (m, 3H), 7.34–7.26 (m, 4H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.17–7.13 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 3.60 (s, 3H), 3.02–2.92 (m, 2H), 2.57–2.49 (m, 2H), 2.21–2.01 (m, 4H), 1.78–1.62 (m, 3H), 1.59–1.50 (m, 3H), 0.99 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 221.1, 150.3, 145.3, 139.2, 138.5, 137.1, 134.2, 133.8, 133.0, 132.1, 130.6, 130.4, 130.3, 129.5, 127.3, 127.2, 126.2, 126.0, 125.7, 125.6, 125.4, 125.1, 124.2, 123.8, 123.0, 122.9, 121.1, 120.5, 118.7, 114.0, 50.8, 48.2, 44.8, 38.4, 36.1, 31.9, 31.6, 29.6, 26.8, 25.9, 21.8, 14.1; IR (neat, cm⁻¹): 2921, 1737, 1694, 1604, 1471, 1353, 1269, 1202, 1132, 1075, 754; ESI HRMS *m/z* calcd for [C₄₂H₃₇N₂O₂]⁺ (*M*+*H*)⁺ 601.2850, obsd 601.2849.



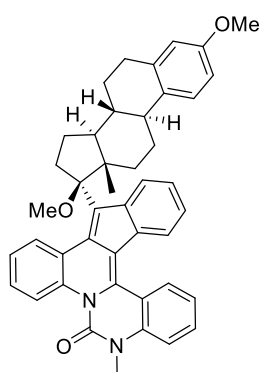
12-Butyl-5-methylindeno[1',2':3,4]quinolino[1,2-*c*]quinazolin-6(5*H*)-one (23). Yield = 54%; Red solid; ¹H NMR (500 MHz, CDCl₃) δ 8.22–8.01 (m, 4H), 7.62–7.52 (m, 2H), 7.44–7.33 (m, 3H), 7.29–7.25 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 3.56 (s, 3H), 3.15 (t, *J* = 8.0 Hz, 2H), 1.89–1.75 (m, 2H), 1.65–1.56 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 150.5, 145.4, 138.5, 132.9, 132.7, 131.9, 130.7, 130.5, 130.3, 127.1, 126.0, 125.9, 125.7, 125.2, 125.1, 124.4, 123.6, 123.2, 122.8, 121.1, 119.0, 118.9, 113.9, 31.5, 31.3, 26.5, 23.5, 14.3; IR (neat, cm⁻¹): 2921, 1689, 1604, 1470, 1261, 1196, 1133, 1094, 801, 754; ESI HRMS *m/z* calcd for [C₂₈H₂₄N₂ONa]⁺ (*M*+*Na*)⁺ 472.1420, obsd 472.1421.



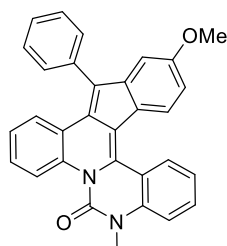
12-(3-Hydroxypropyl)-5-methylindeno[1',2':3,4]quinolino[1,2-*c*]quinazolin-6(5*H*)-one (24). Yield = 57%; Red solid; ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 7.9 Hz, 1H), 8.12–8.04 (m, 2H), 7.62–7.55 (m, 2H), 7.42–7.33 (m, 3H), 7.28–7.25 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 3.87–3.80 (m, 2H), 3.56 (s, 3H), 3.27 (t, *J* = 7.8 Hz, 2H), 2.14–2.05 (m, 2H), 1.53 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 150.4, 145.2, 138.5, 133.1, 132.7, 132.0, 130.7, 130.4, 129.0, 127.2, 126.0, 125.9, 125.8, 125.5, 125.1, 124.4, 123.6, 123.0, 122.8, 121.1, 118.9, 118.7, 113.9, 62.9, 31.9, 31.5, 22.9; IR (neat, cm⁻¹): 3446, 2925, 1622, 1458, 1356, 1271, 1132, 750; ESI HRMS *m/z* calcd for [C₂₇H₂₂N₂O₂Na]⁺ (*M*+*Na*)⁺ 429.1573, obsd 429.1570.



5-Methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (25). Yield = 32%; Yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, J = 8.3 Hz, 1H), 7.32 (t, J = 7.4 Hz, 2H), 7.25–7.14 (m, 4H), 7.02–6.90 (m, 3H), 6.66–6.56 (m, 2H), 6.13 (s, 1H), 3.45 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 151.4, 138.9, 137.8, 135.5, 135.2, 130.3, 129.3, 129.0, 128.2 (2C), 127.9, 127.8, 127.2, 127.0, 124.8, 123.0, 122.9, 122.0, 120.2, 113.4, 31.2; IR (neat, cm^{-1}): 2922, 1683, 1603, 1470, 1304, 1276, 1168, 1132, 1076, 754; ESI HRMS m/z calcd for $[\text{C}_{24}\text{H}_{17}\text{N}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 349.1335, obsd 349.1339.

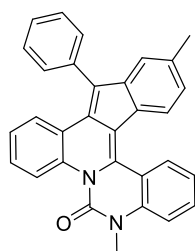


12-((8R,9S,13S,14S,17S)-3,17-Dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)-5-methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (26). Yield = 52%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 9.20 (s, 1H), 8.17 (dd, J = 7.8, 1.5 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 8.08–8.02 (m, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.62–7.57 (m, 1H), 7.40–7.34 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.26–7.22 (m, 2H), 7.08–7.01 (m, 2H), 6.64–6.58 (m, 2H), 3.74 (s, 3H), 3.59 (s, 3H), 3.13–3.02 (m, 1H), 2.97 (s, 3H), 2.91–2.79 (m, 2H), 2.41–2.32 (m, 1H), 2.30–2.19 (m, 2H), 2.12–1.94 (m, 4H), 1.91–1.82 (m, 1H), 1.54–1.45 (m, 2H), 1.42–1.33 (m, 1H), 1.29 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.5, 150.0, 145.1, 138.5, 138.0, 133.6, 133.0, 132.1, 131.6, 131.5, 131.1, 130.8, 126.6, 126.3 (2C), 125.3, 124.7, 123.8, 123.0, 122.8 (2C), 121.6, 120.4, 118.7, 114.0, 113.9, 111.5, 93.4, 55.3, 52.0, 51.9, 51.4, 43.0, 39.6, 34.8, 34.2, 31.6, 30.0, 27.8, 27.0, 25.7, 15.3; IR (neat, cm^{-1}): 2924, 1636, 1458, 1378, 1196, 1077, 756; ESI HRMS m/z calcd for $[\text{C}_{44}\text{H}_{42}\text{N}_2\text{O}_3\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$ 669.3088, obsd 669.3077.



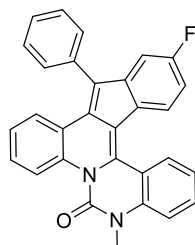
14-Methoxy-5-methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (27). Yield = 58%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.26 (dd, J = 7.7, 1.5 Hz, 1H),

8.08 (dd, $J = 8.5, 1.3$ Hz, 1H), 8.04 (d, $J = 8.5$ Hz, 1H), 7.62–7.52 (m, 6H), 7.48–7.44 (m, 1H), 7.33–7.26 (m, 2H), 7.23 (d, $J = 8.2$ Hz, 1H), 7.04 (ddd, $J = 8.2, 7.1, 1.3$ Hz, 1H), 6.87 (d, $J = 2.5$ Hz, 1H), 6.74 (dd, $J = 8.5, 2.5$ Hz, 1H), 3.80 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.9, 150.4, 147.2, 138.4, 136.6, 133.1, 132.8, 131.9, 130.4, 130.0, 129.3, 129.2, 127.8, 127.0, 126.2, 125.5, 125.4, 124.7, 124.2, 123.5, 122.9, 122.6, 122.2, 118.9, 114.0, 110.8, 104.6, 55.7, 31.6; IR (neat, cm^{-1}): 2921, 1669, 1604, 1511, 1462, 1251, 1091, 754; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{22}\text{N}_2\text{O}_2\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$ 477.1573, obsd 477.1578.



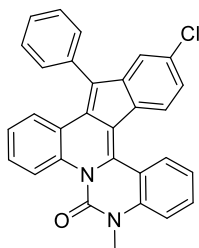
5,14-Dimethyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (28).

Yield = 80%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.25 (d, $J = 7.7$ Hz, 1H), 8.14–7.92 (m, 2H), 7.68–7.42 (m, 7H), 7.31–7.12 (m, 4H), 7.04 (t, $J = 7.7$ Hz, 1H), 6.97 (d, $J = 8.1$ Hz, 1H), 3.58 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.3, 145.7, 138.4, 137.4, 136.8, 133.7, 133.1, 132.0, 130.5, 130.0, 129.4, 129.2, 127.9, 127.7, 126.2, 126.1, 125.4 (2C), 125.0, 124.9, 124.2, 122.9, 122.8, 121.0, 120.7, 118.8, 113.9, 31.6, 21.9; IR (neat, cm^{-1}): 2920, 1688, 1608, 1460, 1304, 1270, 1207, 1078, 751; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{22}\text{N}_2\text{O}_2\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$ 461.1624, obsd 461.1624.



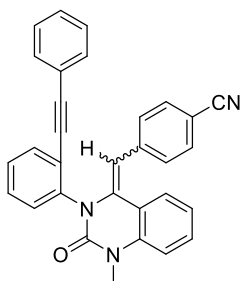
14-Fluoro-5-methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (29).

Yield = 69%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.22 (dd, $J = 7.8, 1.5$ Hz, 1H), 8.09 (dd, $J = 8.6, 1.3$ Hz, 1H), 8.06 (dd, $J = 8.6, 5.1$ Hz, 1H), 7.62–7.52 (m, 6H), 7.49–7.44 (m, 1H), 7.32–7.27 (m, 2H), 7.24–7.21 (m, 1H), 7.06 (m, 1H), 7.03 (dd, $J = 9.5, 2.5$ Hz, 1H), 6.84 (td, $J = 8.6, 2.5$ Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.9 (d, $J_{\text{C-F}} = 244.9$ Hz), 150.0, 147.3 (d, $J_{\text{C-F}} = 9.0$ Hz), 138.4, 136.2, 134.4 (d, $J_{\text{C-F}} = 1.7$ Hz), 133.1, 132.3, 130.4, 129.9, 129.3, 128.5 (d, $J_{\text{C-F}} = 3.3$ Hz), 127.9, 127.5, 126.5, 126.2 (d, $J_{\text{C-F}} = 2.2$ Hz), 125.5 (2C), 124.5, 124.2, 123.0, 122.3 (d, $J_{\text{C-F}} = 9.2$ Hz), 121.9, 118.4, 114.1, 110.7 (d, $J_{\text{C-F}} = 23.6$ Hz), 106.6 (d, $J_{\text{C-F}} = 23.4$ Hz), 31.6; ^{19}F NMR (471 MHz, CDCl_3) δ -114.3; IR (neat, cm^{-1}): 2921, 1694, 1599, 1460, 1196, 1131, 1076, ; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{19}\text{FN}_2\text{O}_2\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$ 465.1374, obsd 465.1378.

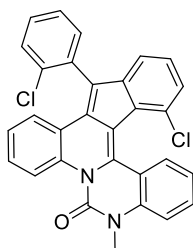


14-Chloro-5-methyl-12-phenylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (30).

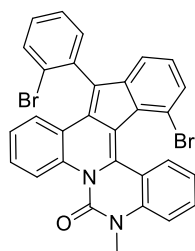
Yield = 60%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.21 (dd, J = 7.8, 1.5 Hz, 1H), 8.10 (dd, J = 8.5, 1.2 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.67–7.52 (m, 6H), 7.50–7.44 (m, 1H), 7.34–7.27 (m, 3H), 7.26–7.23 (m, 1H), 7.13–7.04 (m, 2H), 3.62 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.9, 146.7, 138.4, 136.1, 135.2, 133.1, 133.1, 132.5, 130.5, 129.9 (2C), 129.3 (2C), 128.5, 128.2, 128.0, 127.2, 126.6, 125.6, 125.5, 124.5, 124.2, 123.5, 123.0, 122.1, 121.7, 120.0, 118.3, 114.1, 31.7; IR (neat, cm^{-1}): 2921, 1694, 1604, 1442, 1302, 1266, 1197, 1132, 1076, 753; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{19}\text{ClN}_2\text{O}]^+ (\text{M}+\text{Na})^+$ 481.1078, obsd 481.1077.



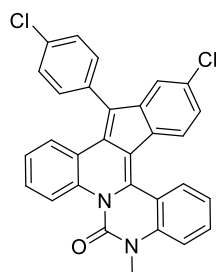
4-((1-Methyl-2-oxo-3-(2-(phenylethynyl)phenyl)-2,3-dihydroquinazolin-4(1H)-ylidene)methyl)benzonitrile (S1). Yield = 62%; Brown oil; ^1H NMR (500 MHz, CDCl_3) δ 7.71 (dd, J = 7.7, 1.6 Hz, 0.79 H), 7.65 (d, J = 7.7 Hz, 0.24 H), 7.54–7.35 (m, 5H), 7.25–6.92 (m, 10H), 6.78 (td, J = 7.7, 1.1 Hz, 1H), 6.34 (s, 0.24 H), 5.44 (s, 0.79 H), 3.48 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 151.9, 151.3, 142.7, 141.4, 141.2, 140.4, 139.6, 138.6, 138.0, 137.4, 133.6, 132.9, 132.3, 132.2, 131.7, 131.6, 131.1, 130.9, 130.8, 130.0 (3C), 129.6, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.0, 124.2, 123.3, 123.1, 123.0, 122.9, 122.1, 121.9, 121.5, 119.3, 119.2, 118.3, 113.9, 113.7, 109.7, 109.4, 108.1, 107.2, 95.4, 94.5, 86.7, 85.8, 31.2, 31.0; IR (neat, cm^{-1}): 2224, 1682, 1631, 1602, 1496, 1476, 1335, 1286, 912, 755; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{21}\text{N}_3\text{O}]^+ (\text{M}+\text{Na})^+$ 474.1577, obsd 474.1584.



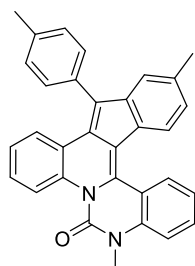
16-Chloro-12-(2-chlorophenyl)-5-methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (32). Yield = 60%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.31 (d, J = 8.6 Hz, 1H), 7.68–7.57 (m, 2H), 7.56–7.40 (m, 5H), 7.33–7.26 (m, 2H), 7.22–7.15 (m, 3H), 7.11–7.05 (m, 2H), 3.69 (s, 3H); IR (neat, cm^{-1}): 2920, 1694, 1605, 1451, 1407, 1265, 1197, 1145, 1086, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{19}\text{Cl}_2\text{N}_2\text{O}]^+ (\text{M}+\text{H})^+$ 515.0688, obsd 515.0694.



16-Bromo-12-(2-bromophenyl)-5-methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (33). Yield = 41%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.34 (d, J = 8.6 Hz, 1H), 7.87–7.81 (m, 1H), 7.62 (dd, J = 22.4, 7.8 Hz, 1H), 7.55–7.36 (m, 6H), 7.34–7.30 (m, 1H), 7.23–7.14 (m, 3H), 7.11–7.05 (m, 2H), 3.70 (s, 3H); IR (neat, cm^{-1}): 2922, 1693, 1605, 1459, 1264, 1197, 1084, 751; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{18}\text{Br}_2\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 602.9678, 604.9658, obsd 602.9687, 604.9666.

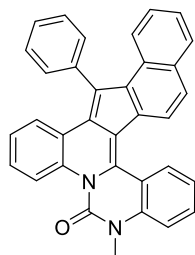


14-Chloro-12-(4-chlorophenyl)-5-methylindeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (34). Yield = 55%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.22 (dd, J = 7.7, 1.6 Hz, 1H), 8.13 (dd, J = 8.6, 1.1 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.68–7.62 (m, 1H), 7.59–7.48 (m, 5H), 7.35–7.30 (m, 2H), 7.29–7.26 (m, 2H), 7.14–7.09 (m, 2H), 3.63 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.9, 146.3, 138.4, 135.6, 134.6, 133.8, 133.2, 133.1, 132.6, 131.4, 130.6, 129.7, 128.5, 127.6, 126.8, 126.6, 125.8, 125.4, 124.3, 123.6, 123.1, 122.2, 121.5, 119.8, 118.2, 114.2, 31.7; IR (neat, cm^{-1}): 2919, 1693, 1635, 1454, 1268, 1152, 1077, 756; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{19}\text{Cl}_2\text{N}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 515.0688, obsd 515.0693.

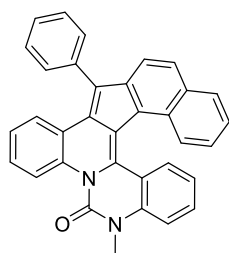


5,14-Dimethyl-12-(p-tolyl)indeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (35). Yield = 52%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.26 (d, J = 7.8, 1.4 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.63–7.56 (m, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.38–7.33 (m, 2H), 7.31–7.25 (m, 2H), 7.24–7.20 (m, 1H), 7.17 (s, 1H), 7.07–7.03 (m, 1H), 6.97 (d, J = 8.0 Hz, 1H), 3.60 (s, 3H), 2.50 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.4, 145.8, 138.4, 137.4, 133.6, 133.5, 133.1, 131.9, 130.5, 129.9, 129.8, 129.5, 127.9,

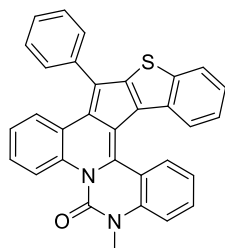
126.1, 125.5, 125.4, 125.1, 124.9, 124.2, 122.9 (2C), 121.0, 120.8, 118.9, 113.9, 31.6, 21.9, 21.7; IR (neat, cm^{-1}): 2924, 1681, 1603, 1473, 1371, 1266, 1108, 819, 754; ESI HRMS m/z calcd for $[\text{C}_{34}\text{H}_{24}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 499.1781, obsd 499.1784.



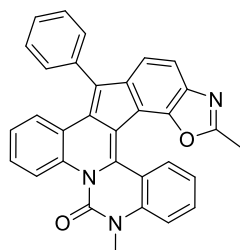
5-Methyl-12-phenylbenzo[4',5']indeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (36). Yield = 67%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.33 (d, J = 7.7 Hz, 1H), 8.24–8.14 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.68–7.51 (m, 8H), 7.39–7.25 (m, 5H), 7.16–7.11 (m, 1H), 7.06–7.01 (m, 1H), 3.65 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.9, 140.4, 140.0, 138.3, 136.7, 134.0, 132.5, 132.4, 131.7, 130.4, 130.3, 129.9, 129.0, 128.6, 128.1, 126.7, 125.9, 125.6, 125.4, 125.3, 125.1, 125.0 (2C), 124.8, 123.9, 123.7, 123.1, 121.7, 120.3, 118.6, 114.1, 31.8; IR (neat, cm^{-1}): 2919, 2849, 1696, 1603, 1468, 1350, 1267, 1187, 1132, 1096, 1077, 755; ESI HRMS m/z calcd for $[\text{C}_{34}\text{H}_{22}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 497.1624, obsd 497.1626.



5-Methyl-12-phenylbenzo[6',7']indeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (37). Yield = 75%; Black solid; ^1H NMR (500 MHz, CDCl_3) δ 8.38 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.77 (dd, J = 8.3, 2.9 Hz, 2H), 7.69–7.47 (m, 7H), 7.43 (d, J = 8.5 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 7.4 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.3, 145.6, 137.7, 137.4, 133.6, 133.2, 132.1, 131.9, 129.3, 129.2, 128.4, 128.3, 127.7, 127.4, 126.1, 125.7, 125.3, 125.2, 125.1, 124.2, 123.9, 123.5, 123.4, 123.2, 121.1, 120.7, 119.9, 113.9, 31.9; IR (neat, cm^{-1}): 2921, 1694, 1601, 1469, 1263, 1193, 1130, 1076, 754; ESI HRMS m/z calcd for $[\text{C}_{34}\text{H}_{22}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 497.1624, obsd 497.1622.



5-Methyl-12-phenylbenzo[4'',5'']thieno[2'',3'':4',5']cyclopenta[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (38). Yield = 82%; Black solid; ^1H NMR (500 MHz, CDCl_3) δ 8.35 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.81–7.71 (m, 3H), 7.62 (t, J = 8.0 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.32–7.25 (m, 2H), 7.23–7.19 (m, 1H), 7.16–7.10 (m, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.0, 149.7, 142.6, 137.7, 137.1, 135.8, 133.8, 133.2, 132.5, 132.4, 129.2 (2C), 127.9, 126.0, 125.6, 125.3, 124.9, 124.6, 124.5, 124.0, 123.9, 123.8, 123.7, 123.4, 122.3, 119.7, 118.7, 113.7, 31.9; IR (neat, cm^{-1}): 2918, 1696, 1603, 1460, 1264, 1195, 1180, 751; ESI HRMS m/z calcd for $[\text{C}_{32}\text{H}_{20}\text{N}_2\text{OSNa}]^+$ ($\text{M}+\text{Na}$) $^+$ 503.1189, obsd 503.1192.



5,16-Dimethyl-12-phenyloxazolo[4'',5'':6',7']indeno[1',2':3,4]quinolino[1,2-c]quinazolin-6(5H)-one (39). Yield = 72%; Red solid; ^1H NMR (500 MHz, CDCl_3) δ 8.18 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.67–7.53 (m, 7H), 7.51–7.46 (m, 1H), 7.33–7.27 (m, 2H), 7.24–7.20 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 3.67 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.5, 150.0, 145.1, 144.1, 139.3, 138.2, 136.9, 136.7, 133.1 (2C), 132.0, 130.2, 129.7, 129.3, 127.9, 126.2, 125.5, 125.4, 125.3, 124.4, 123.9, 122.2, 119.2, 119.0, 117.9, 117.2, 113.2, 112.8, 31.7, 14.5; IR (neat, cm^{-1}): 2920, 1693, 1603, 1470, 1418, 1267, 1132, 1098, 755; ESI HRMS m/z calcd for $[\text{C}_{32}\text{H}_{21}\text{N}_3\text{O}_2\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$ 502.1526, obsd 502.1530.

7. X-ray Crystallography

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of each compound (cyclohexane/ CH_2Cl_2) in a loosely capped vial.

Table S2. Crystal data and structure refinement for 37

Empirical formula	$\text{C}_{34}\text{H}_{22}\text{N}_2\text{O}$
Formula weight	474.54
Temperature/K	273.15
Crystal system	N/A
Space group	$\text{P2}_1/\text{n}$
$a/\text{\AA}$	14.833(5)
$b/\text{\AA}$	9.407(3)
$c/\text{\AA}$	15.704(5)

$\alpha/^\circ$	90.00
$\beta/^\circ$	94.506(5)
$\gamma/^\circ$	90.00
Volume/ $\text{\AA}^3$	2184.5(12)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.443
μ/mm^{-1}	0.087
F(000)	992.0
Crystal size/ mm^3	$0.2 \times 0.2 \times 0.1$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	3.64 to 52
Index ranges	$-18 \leq h \leq 17, -11 \leq k \leq 11, -19 \leq l \leq 19$
Reflections collected	13935
Independent reflections	4268 [$R_{\text{int}} = 0.0579$, $R_{\text{sigma}} = \text{N/A}$]
Data/restraints/parameters	4268/0/334
Goodness-of-fit on F^2	0.782
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1315$, $wR_2 = 0.3164$
Final R indexes [all data]	$R_1 = 0.1476$, $wR_2 = 0.3298$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.44/-0.39

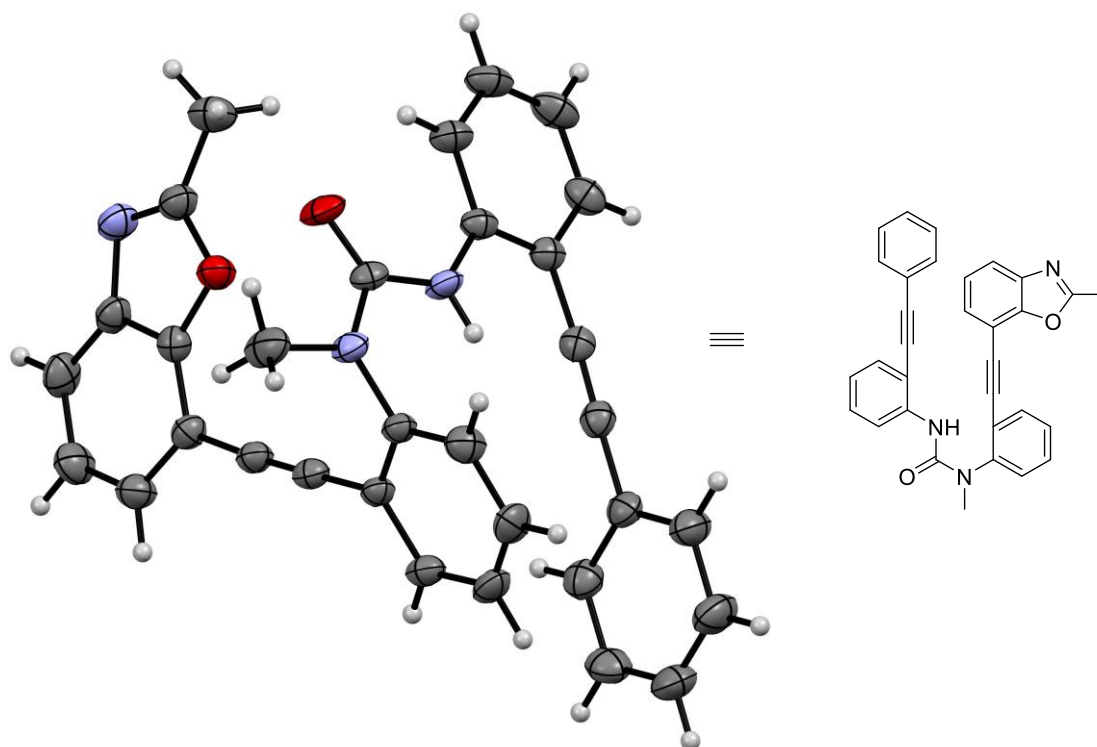


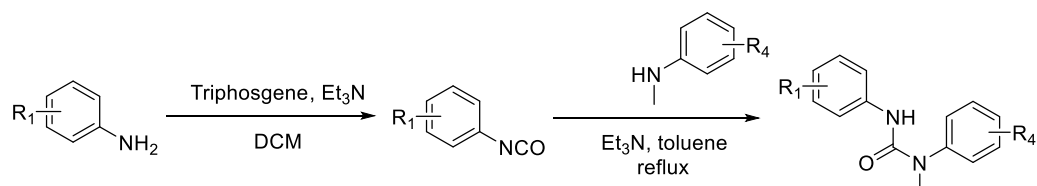
Figure S4. The ORTEP Representation for **39s** (CCDC 1546187). The urea **39s** existed in the (*cis,trans*)-conformation in the solid state.

Table S3. Crystal data and structure refinement for **39s**

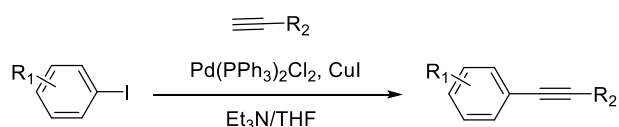
Empirical formula	C ₃₂ H ₂₃ N ₃ O ₂
Formula weight	481.53
Temperature/K	273.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	9.6225(17)
b/Å	23.534(4)
c/Å	11.696(2)
α /°	90
β /°	112.491(3)
γ /°	90
Volume/Å ³	2447.2(7)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.307
μ/mm^{-1}	0.083
F(000)	1008.0

Crystal size/mm ³	0.4 × 0.3 × 0.2
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.462 to 57.668
Index ranges	-12 ≤ h ≤ 12, -31 ≤ k ≤ 31, -15 ≤ l ≤ 15
Reflections collected	20229
Independent reflections	5881 [R_{int} = 0.0476, R_{sigma} = 0.0482]
Data/restraints/parameters	5881/0/336
Goodness-of-fit on F^2	1.177
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0777, wR_2 = 0.1684
Final R indexes [all data]	R_1 = 0.0905, wR_2 = 0.1760
Largest diff. peak/hole / e Å ⁻³	0.39/-0.30

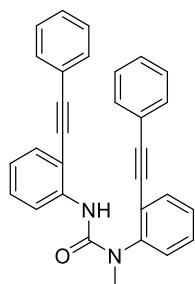
8. Synthesis and Characterization of Substrates



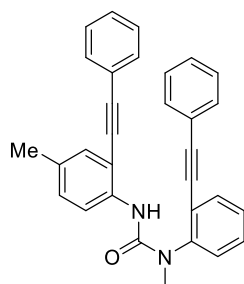
General procedure A for the synthesis of ureas: To a solution of triphosgene (2.0 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (8 mL) was added dropwise aniline (4.0 mmol, 2.0 equiv) and then Et₃N (4.0 mmol, 2.0 equiv) at 0 °C. The mixture was stirred at rt for 3 h. The solvent was then removed under reduced pressure. The residue was dissolved in toluene (6.0 mL) and treated with *N*-methyl-aniline (2.0 mmol, 1.0 equiv) and Et₃N (4.0 mmol, 2.0 equiv). The reaction mixture was heated to reflux and maintained at this temperature for 48 h. The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.



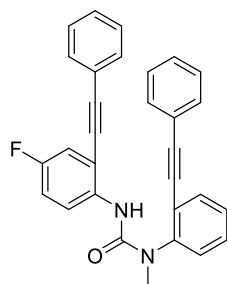
General procedure B for Sonogashira cross-coupling reaction: The corresponding iodobenzene (2.0 mmol, 1.0 equiv), CuI (5 mol %), and PdCl₂(PPh₃)₂ (2 mol %) were dissolved in Et₃N/THF (1:1, 10 mL) under a nitrogen atmosphere. The alkyne (3.0 mmol, 1.2 equiv) was added. The resulting mixture was stirred at rt for 2–12 h until complete consumption of the starting material (monitored by TLC) and then filtered through a pad of celite. The filtrate was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.



1-Methyl-1,3-bis(2-(phenylethynyl)phenyl)urea (1). The title compound was prepared starting from the known compound 2-(phenylethynyl)aniline³ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 79%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.39 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.50–7.46 (m, 2H), 7.37–7.26 (m, 10H), 7.22–7.18 (m, 2H), 7.15 (s, 1H), 7.09 (td, *J* = 7.7, 1.7 Hz, 1H), 6.94 (td, *J* = 7.7, 1.2 Hz, 1H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H), 3.38 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.2, 143.6, 140.8, 133.6, 132.0, 131.9, 131.7, 130.0, 129.8, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 123.2, 122.7, 122.4, 121.7, 118.1, 111.1, 95.4, 95.2, 85.1, 84.2, 36.8; IR (neat, cm⁻¹): 3376, 3060, 1683, 1578, 1516, 1449, 1305, 1142, 754; ESI HRMS *m/z* calcd for [C₃₀H₂₂N₂O₂Na]⁺ (*M*+Na)⁺ 449.1624, obsd 449.1628.

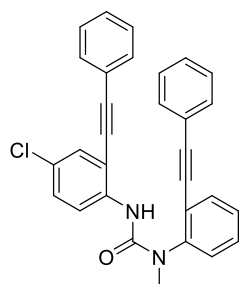


1-Methyl-3-(4-methyl-2-(phenylethynyl)phenyl)-1-(2-(phenylethynyl)phenyl)urea (S2). The title compound was prepared starting from the known compound 4-methyl-2-(phenylethynyl)aniline³ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 68%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, *J* = 8.6 Hz, 1H), 7.50–7.45 (m, 2H), 7.37–7.29 (m, 8H), 7.21–7.17 (m, 2H), 7.14–7.05 (m, 4H), 6.96 (td, *J* = 7.6, 1.3 Hz, 1H), 3.37 (s, 3H), 2.22 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.4, 143.7, 138.4, 133.6, 132.0, 131.9 (2C), 131.1, 130.6, 130.0, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 123.2, 122.8, 122.6, 118.2, 111.0, 95.4, 94.9, 85.1, 84.5, 36.8, 20.6; IR (neat, cm⁻¹): 3384, 2922, 1681, 1585, 1513, 1304, 1142, 755; ESI HRMS *m/z* calcd for [C₃₁H₂₄N₂O₂Na]⁺ (*M*+Na)⁺ 463.1781, obsd 463.1780.



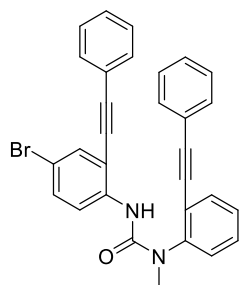
3-(4-Fluoro-2-(phenylethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S3).

The title compound was prepared starting from the known compound 4-fluoro-2-(phenylethynyl)aniline³ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 52%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.32 (dd, *J* = 9.2, 5.3 Hz, 1H), 7.52–7.43 (m, 2H), 7.42–7.28 (m, 8H), 7.23–7.18 (m, 2H), 7.11 (td, *J* = 7.7, 1.6 Hz, 1H), 7.06–6.94 (m, 4H), 3.37 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 157.3 (d, *J*_{C-F} = 241.3 Hz), 154.3, 143.5, 137.2 (d, *J*_{C-F} = 2.5 Hz), 133.6, 132.1, 131.9, 130.0, 129.1, 128.9, 128.8, 128.6, 128.4, 128.3, 123.2, 122.7, 122.0, 119.8 (d, *J*_{C-F} = 7.9 Hz), 117.7 (d, *J*_{C-F} = 24.0 Hz), 116.7 (d, *J*_{C-F} = 22.0 Hz), 112.4 (d, *J*_{C-F} = 9.5 Hz), 95.9, 95.5, 85.0, 83.3 (d, *J*_{C-F} = 3.1 Hz), 36.8; ¹⁹F NMR (471 MHz, CDCl₃) δ –121.6; IR (neat, cm^{–1}): 3457, 2948, 1681, 1581, 1518, 1494, 1421, 1335, 1302, 1257, 1197, 1133, 1089, 755, 689; ESI HRMS *m/z* calcd for [C₃₀H₂₁FN₂ONa]⁺ (*M*+Na)⁺ 467.1530, obsd 467.1530.



3-(4-Chloro-2-(phenylethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S4).

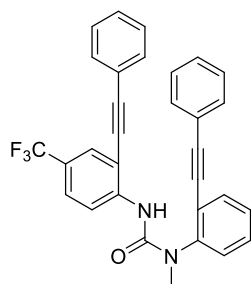
The title compound was prepared starting from the known compound 4-chloro-2-(phenylethynyl)aniline³ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 72%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 9.0 Hz, 1H), 7.49–7.44 (m, 2H), 7.40–7.30 (m, 8H), 7.30–7.27 (m, 1H), 7.24–7.21 (m, 1H), 7.21–7.17 (m, 2H), 7.14–7.09 (m, 2H), 6.96 (td, *J* = 7.6, 1.3 Hz, 1H), 3.37 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.1, 143.4, 139.5, 133.6, 132.1, 131.9, 131.0, 130.0, 129.7, 129.1, 129.0, 128.8, 128.6, 128.5, 128.3, 126.4, 123.2, 122.6, 122.0, 119.3, 112.6, 96.2, 95.5, 84.9, 83.0, 36.9; IR (neat, cm^{–1}): 3376, 2922, 1686, 1573, 1508, 1404, 1303, 1142, 755; ESI HRMS *m/z* calcd for [C₃₀H₂₁ClN₂ONa]⁺ (*M*+Na)⁺ 483.1235, obsd 483.1233.



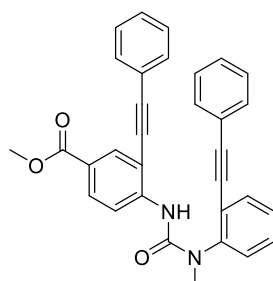
3-(4-Bromo-2-(phenylethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S5).

The title compound was prepared starting from the known compound 4-bromo-2-(phenylethynyl)aniline³ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 69%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.30 (d, *J* = 9.0 Hz, 1H), 7.50–7.42 (m, 3H), 7.40–7.29 (m, 9H), 7.21–7.16 (m, 2H), 7.14–7.08 (m, 2H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 3.37 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.1, 143.4, 139.9, 133.9, 133.6, 132.6, 132.1, 131.9, 130.0, 129.1, 129.0, 128.8, 128.6, 128.5, 128.3,

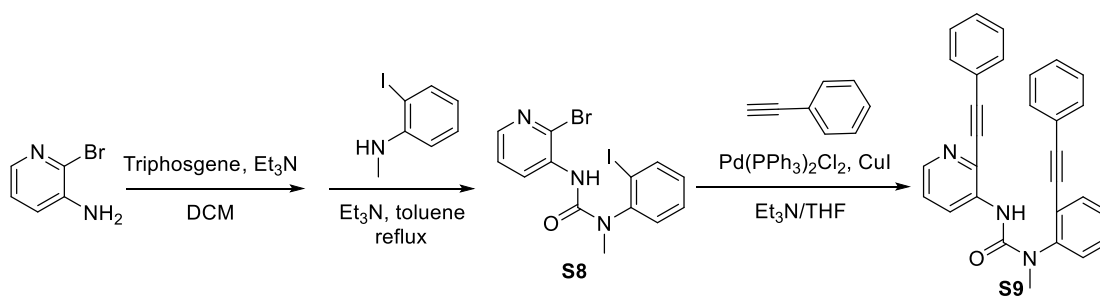
123.2, 122.6, 122.0, 119.6, 113.7, 113.0, 96.3, 95.6, 84.9, 82.8, 36.9; IR (neat, cm^{-1}): 3376, 2925, 1684, 1568, 1505, 1302, 1142, 755; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{BrN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 527.0729, 529.0709, obsd 527.0727, 529.0705.



1-Methyl-3-(2-(phenylethynyl)-4-(trifluoromethyl)phenyl)-1-(2-(phenylethynyl)phenyl)urea (S6). The title compound was prepared starting from the known compound 2-(phenylethynyl)-4-(trifluoromethyl)aniline³ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 53%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.54 (d, J = 8.8 Hz, 1H), 7.61–7.55 (m, 1H), 7.53–7.43 (m, 3H), 7.42–7.28 (m, 9H), 7.23–7.17 (m, 2H), 7.12 (td, J = 7.7, 1.6 Hz, 1H), 6.95 (td, J = 7.6, 1.3 Hz, 1H), 3.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.9, 143.5, 143.2, 133.7, 132.1, 131.9, 130.1, 129.2, 129.0, 128.8 (q, $J_{\text{C-F}}$ = 4.1 Hz), 128.7, 128.6 (2C), 128.3, 126.6 (q, $J_{\text{C-F}}$ = 3.6 Hz), 124.1 (q, $J_{\text{C-F}}$ = 271.0 Hz), 123.7 (q, $J_{\text{C-F}}$ = 33.2 Hz), 123.2, 122.6, 121.8, 117.7, 111.2, 96.4, 95.6, 84.8, 82.7, 36.9; ^{19}F NMR (471 MHz, CDCl_3) δ –62.1; IR (neat, cm^{-1}): 3369, 2948, 1691, 1586, 1522, 1423, 1332, 1268, 1122, 755; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{21}\text{F}_3\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 517.1498, obsd 517.1497.

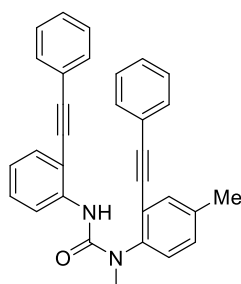


Methyl 4-(3-methyl-3-(2-(phenylethynyl)phenyl)ureido)-3-(phenylethynyl)benzoate (S7). The title compound was prepared starting from the known compound methyl 4-amino-3-(phenylethynyl)benzoate³ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 67%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.50 (d, J = 8.9 Hz, 1H), 8.03 (d, J = 2.1 Hz, 1H), 7.94 (dd, J = 8.9, 2.1 Hz, 1H), 7.50–7.44 (m, 2H), 7.44–7.28 (m, 9H), 7.23–7.17 (m, 2H), 7.16–7.10 (m, 1H), 6.99–6.92 (m, 1H), 3.86 (s, 3H), 3.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.4, 153.9, 144.5, 143.2, 133.7, 133.5, 132.1, 131.9, 131.3, 130.1, 129.0 (2C), 128.7, 128.6 (2C), 128.3, 123.3, 123.2, 122.6, 122.0, 117.2, 110.9, 95.9, 95.6, 84.8, 83.2, 52.2, 37.0; IR (neat, cm^{-1}): 3368, 2948, 1719, 1689, 1581, 1515, 1317, 1252, 1116, 755; ESI HRMS m/z calcd for $[\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$ 507.1679, obsd 507.1677.



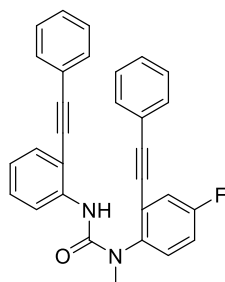
3-(2-Bromopyridin-3-yl)-1-(2-iodophenyl)-1-methylurea (S8). The title compound was prepared starting from 2-bromopyridin-3-amine and 2-iodo-*N*-methylaniline⁴ by following the General Procedure A. Yield = 75%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.60 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.96 (dd, *J* = 4.6, 1.8 Hz, 1H), 7.54 (td, *J* = 7.7, 1.4 Hz, 1H), 7.46 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.22 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H), 6.66 (s, 1H), 3.30 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 153.1, 143.8, 143.1, 141.1, 134.9, 132.7, 130.9, 130.8, 129.9, 127.2, 123.7, 100.3, 36.1; IR (neat, cm⁻¹): 3377, 3054, 2929, 1683, 1579, 1505, 1298, 742; ESI HRMS *m/z* calcd for [C₁₃H₁₁BrIN₃ONa]⁺ (*M*+Na)⁺ 453.9022, 455.9002, obsd 453.9029, 455.9009.

1-Methyl-1-(2-(phenylethynyl)phenyl)-3-(2-(phenylethynyl)pyridin-3-yl)urea (S9). The title compound was prepared starting from S8 and ethynylbenzene by following the General Procedure B. Yield = 75%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.70 (dd, *J* = 8.6, 1.4 Hz, 1H), 8.17 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.49–7.44 (m, 2H), 7.42–7.28 (m, 8H), 7.28–7.22 (m, 2H), 7.21–7.13 (m, 3H), 7.04–6.97 (m, 1H), 3.39 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.1, 143.4, 143.1, 138.1, 133.6, 132.2, 131.8, 131.1, 130.1, 129.3, 128.9, 128.6 (2C), 128.5, 128.2, 125.1, 123.7, 123.1, 122.5, 121.4, 95.5, 95.1, 84.8, 83.5, 36.8; IR (neat, cm⁻¹): 3375, 3056, 2922, 1684, 1571, 1508, 1291, 756; ESI HRMS *m/z* calcd for [C₂₉H₂₂N₃O]⁺ (*M*+H)⁺ 428.1757, obsd 428.1765.



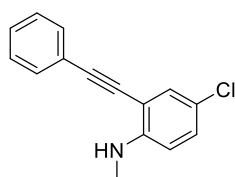
1-Methyl-1-(4-methyl-2-(phenylethynyl)phenyl)-3-(2-(phenylethynyl)phenyl)urea (S10). The title compound was prepared starting from the known compound 2-(phenylethynyl)aniline³ and *N*,4-dimethyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 57%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.39 (d, *J* = 8.5 Hz, 1H), 7.49–7.44 (m, 2H), 7.38–7.27 (m, 8H), 7.25–7.19 (m, 4H), 7.18 (d, *J* = 2.1 Hz, 1H), 6.94–6.87 (m, 2H), 3.36 (s, 3H), 2.03 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.4, 141.1, 140.8, 138.5, 134.2, 131.9 (2C), 131.8, 130.9, 129.8, 128.8, 128.6 (2C), 128.5, 128.3, 122.8 (2C), 122.7, 121.6, 118.1, 111.0, 95.2, 95.0, 85.3, 84.4, 36.8, 20.9; IR (neat, cm⁻¹): 3376, 2923, 1685, 1578, 1517, 1450, 1304, 1144, 755; ESI HRMS *m/z* calcd for [C₃₁H₂₅N₂O]⁺

(M+H)⁺ 441.1961, obsd 441.1960.

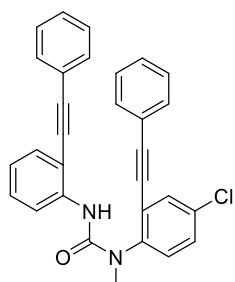


1-(4-Fluoro-2-(phenylethynyl)phenyl)-1-methyl-3-(2-(phenylethynyl)phenyl)urea (S11).

The title compound was prepared starting from the known compound 2-(phenylethynyl)aniline³ and 4-fluoro-*N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 57%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.37 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.49–7.45 (m, 2H), 7.39–7.27 (m, 9H), 7.24–7.21 (m, 2H), 7.14 (s, 1H), 7.00 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.91 (td, *J* = 7.7, 1.2 Hz, 1H), 6.76 (ddd, *J* = 8.6, 7.7, 3.0 Hz, 1H), 3.34 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 161.5 (d, *J*_{C-F} = 250.0 Hz), 154.2, 140.7, 139.8 (d, *J*_{C-F} = 3.2 Hz), 132.1, 131.8, 131.7, 130.6 (d, *J*_{C-F} = 9.2 Hz), 129.8, 129.3, 128.9, 128.6, 128.4, 125.2 (d, *J*_{C-F} = 10.5 Hz), 122.3 (d, *J*_{C-F} = 6.9 Hz), 121.9, 120.2, 120.0, 118.1, 117.2 (d, *J*_{C-F} = 22.7 Hz), 111.1, 96.5, 95.4, 84.1, 84.0 (d, *J*_{C-F} = 2.8 Hz), 36.9; ¹⁹F NMR (471 MHz, CDCl₃) δ -111.5; IR (neat, cm⁻¹): 3378, 2924, 1687, 1578, 1450, 1310, 1139, 754; ESI HRMS *m/z* calcd for [C₃₀H₂₁FN₂ONa]⁺ (M+Na)⁺ 467.1530, obsd 467.1534.



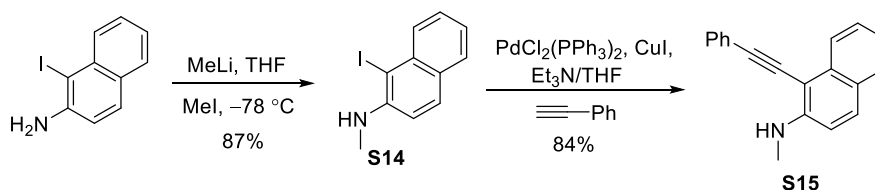
4-Chloro-*N*-methyl-2-(phenylethynyl)aniline (S12). The title compound was prepared starting from the known compound 4-chloro-2-iodo-*N*-methylaniline⁵ and ethynylbenzene by following the General Procedure B. Yield = 76%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 7.54–7.48 (m, 2H), 7.39–7.30 (m, 4H), 7.17 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.51 (d, *J* = 8.8 Hz, 1H), 4.66 (q, *J* = 5.2 Hz, 1H), 2.90 (d, *J* = 5.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 148.6, 131.7, 131.5, 130.0, 128.7, 128.6, 123.0, 120.8, 110.2, 108.8, 96.0, 84.9, 30.6; IR (neat, cm⁻¹): 3426, 1638, 1510, 1317, 1265, 754; ESI HRMS *m/z* calcd for [C₁₅H₁₃ClN]⁺ (M+H)⁺ 242.0731, obsd 242.0733.



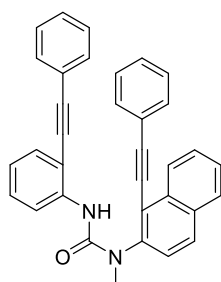
1-(4-Chloro-2-(phenylethynyl)phenyl)-1-methyl-3-(2-(phenylethynyl)phenyl)urea (S13).

The title compound was prepared starting from the known compound

2-(phenylethynyl)aniline and **S12** by following the General Procedure **A**. Yield = 61%; Pale yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 8.35 (dd, $J = 8.5, 1.2$ Hz, 1H), 7.49–7.44 (m, 2H), 7.40–7.36 (m, 3H), 7.36–7.28 (m, 6H), 7.25 (d, $J = 4.4$ Hz, 1H), 7.24–7.20 (m, 2H), 7.15 (s, 1H), 7.07 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.91 (td, $J = 7.6, 1.2$ Hz, 1H), 3.34 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.0, 142.3, 140.5, 134.2, 133.4, 132.0, 131.8, 131.7, 130.2, 130.1, 129.8, 129.3, 128.9, 128.6, 124.9, 122.3, 122.2, 122.0, 118.2, 111.2, 96.7, 95.6, 84.2, 83.9, 36.9; IR (neat, cm^{-1}): 3380, 2925, 1687, 1578, 1516, 1445, 1305, 1142, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{ClN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 483.1235, obsd 483.1235.

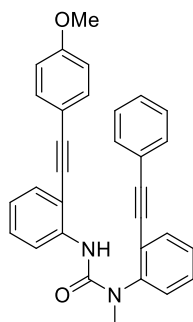


N-Methyl-1-(phenylethynyl)naphthalen-2-amine (S15). MeLi (6.3 mL, 1.6 M in THF solution, 10.0 mmol, 1.0 equiv) was added dropwise to a solution of the known compound 1-iodonaphthalen-2-amine⁶ (2.69 g, 10.0 mmol, 1.0 equiv) in dry THF (50 mL) at $-78\text{ }^\circ\text{C}$. The resulting mixture was stirred for 30 min before treating with MeI (0.69 mL, 11.0 mmol, 1.1 equiv). The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 2 h and then rt for 1 h. Water was added to quench the reaction. The reaction mixture was extracted with ethyl acetate (50 mL x 3). The combined organic solution was washed with brine, dried over anhydrous Na_2SO_4 , and filtered. The filtrate was concentrated reduced pressure and the residue (1.42 g, 5.0 mmol, 1.0 equiv) along with CuI (5 mol%) and $\text{PdCl}_2(\text{PPh}_3)_2$ (2 mol%) were dissolved in $\text{Et}_3\text{N}/\text{THF}$ (1:1, 25 mL) under a nitrogen atmosphere. The alkyne (0.82 mL, 7.5 mmol, 1.5 equiv) was added. The resulting reaction mixture was stirred at rt until complete consumption of the starting material (monitored by TLC) and then filtered through a pad of celite. The filtrate was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product **S15** as a yellow oil (1.08 g, 84% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.4$ Hz, 1H), 7.75–7.65 (m, 2H), 7.64–7.58 (m, 2H), 7.49–7.44 (m, 1H), 7.42–7.29 (m, 3H), 7.25–7.18 (m, 1H), 7.01 (d, $J = 9.0$ Hz, 1H), 5.02 (d, $J = 4.0$ Hz, 1H), 3.03 (d, $J = 4.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.3, 134.6, 131.6, 130.5, 128.6, 128.4, 128.2, 127.4, 126.7, 124.3, 123.9, 122.3, 112.1, 100.5, 98.9, 84.9, 30.7; IR (neat, cm^{-1}): 3414, 3053, 2917, 1617, 1571, 1514, 1307, 1171, 803, 775; ESI HRMS m/z calcd for $[\text{C}_{19}\text{H}_{15}\text{NNa}]^+$ ($\text{M}+\text{Na}$) $^+$ 280.1097, obsd 280.1101.

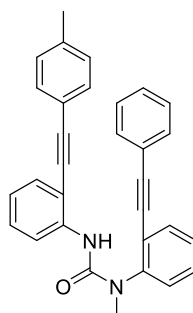


1-Methyl-1-(1-(phenylethynyl)naphthalen-2-yl)-3-(2-(phenylethynyl)phenyl)urea (S16). The title compound was prepared starting from the known compound

2-(phenylethynyl)aniline³ and **S15** by following the General Procedure **A**. Yield = 42%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.44 (d, *J* = 8.9 Hz, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 7.66–7.54 (m, 5H), 7.51–7.42 (m, 2H), 7.37–7.33 (m, 3H), 7.32–7.27 (m, 3H), 7.21–7.16 (m, 1H), 7.03–6.98 (m, 2H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H), 6.72–6.63 (m, 2H), 3.47 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.4, 142.1, 140.7, 134.0, 132.5, 132.0, 131.9, 131.3, 130.6, 129.8, 129.0, 128.6, 128.5, 128.3, 128.2, 127.8, 127.3, 126.7, 126.0, 122.9, 122.1, 121.8, 120.4, 118.2, 111.2, 101.0, 95.4, 84.1, 83.4, 36.9; IR (neat, cm⁻¹): 3380, 3059, 2965, 2927, 1721, 1682, 1579, 1515, 1490, 1445, 1320, 753; ESI HRMS *m/z* calcd for [C₃₄H₂₄N₂ONa]⁺ (M+Na)⁺ 499.1781, obsd 499.1791.

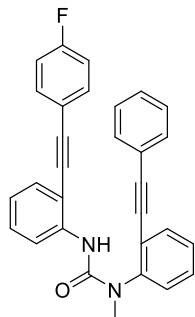


3-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S17). The title compound was prepared starting from the known compound 2-((4-methoxyphenyl)ethynyl)aniline⁷ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure **A**. Yield = 75%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.36 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.50–7.45 (m, 2H), 7.38 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.36–7.28 (m, 5H), 7.28–7.25 (m, 1H), 7.18–7.10 (m, 4H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H), 6.89 (td, *J* = 7.6, 1.2 Hz, 1H), 6.87–6.83 (m, 2H), 3.86 (s, 3H), 3.38 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 160.0, 154.3, 143.7, 140.7, 133.6, 133.5, 131.9, 131.7, 130.0, 129.5, 128.9, 128.5, 128.3, 123.2, 122.8, 121.7, 118.1, 114.7, 114.4, 113.8, 111.4, 95.4, 95.3, 85.1, 82.9, 55.5, 36.8; IR (neat, cm⁻¹): 3372, 2921, 1682, 1577, 1509, 1446, 1249, 1133, 754; ESI HRMS *m/z* calcd for [C₃₁H₂₄N₂O₂Na]⁺ (M+Na)⁺ 479.1730, obsd 479.1730.



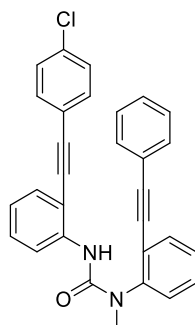
1-Methyl-1-(2-(phenylethynyl)phenyl)-3-(2-(*p*-tolylethynyl)phenyl)urea (S18). The title compound was prepared starting from the known compound 2-(*p*-tolylethynyl)aniline⁷ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure **A**. Yield = 63%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.52–7.45 (m, 2H), 7.40–7.22 (m, 7H), 7.20–7.03 (m, 6H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 3.38 (s, 3H), 2.40 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 154.3, 143.7, 140.7, 138.8, 133.6, 131.9

(2C), 131.7, 130.0, 129.6, 128.9, 128.8 (2C), 128.5, 128.4, 123.2, 122.7, 121.7, 119.4, 118.1, 111.3, 95.5, 95.4, 85.1, 83.6, 36.8, 21.7; IR (neat, cm^{-1}): 3375, 2948, 1683, 1577, 1517, 1447, 1335, 1305, 1196, 1133, 1093, 817, 754; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{24}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 463.1781, obsd 463.1783.



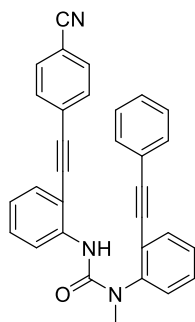
3-(2-((4-Fluorophenyl)ethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S19).

The title compound was prepared starting from the known compound 2-((4-fluorophenyl)ethynyl)aniline⁷ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 80%; Pale yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 8.38 (dd, J = 8.5, 1.2 Hz, 1H), 7.49–7.45 (m, 2H), 7.37 (dd, J = 7.8, 1.6 Hz, 1H), 7.35–7.27 (m, 6H), 7.20–7.11 (m, 4H), 7.05–6.97 (m, 3H), 6.90 (td, J = 7.5, 1.2 Hz, 1H), 3.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.8 (d, $J_{\text{C-F}}$ = 250.2 Hz), 154.2, 143.7, 140.8, 133.9 (d, $J_{\text{C-F}}$ = 8.2 Hz), 133.6, 131.9, 131.7, 129.9 (2C), 128.9 (2C), 128.5, 128.3, 123.3, 122.7, 121.8, 118.6 (d, $J_{\text{C-F}}$ = 3.6 Hz), 118.2, 115.5 (d, $J_{\text{C-F}}$ = 22.0 Hz), 110.9, 95.5, 94.1, 85.0, 84.0, 36.8; ^{19}F NMR (471 MHz, CDCl_3) δ -110.3; IR (neat, cm^{-1}): 3376, 2926, 1685, 1578, 1518, 1304, 1230, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{FN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 467.1530, obsd 467.1530.



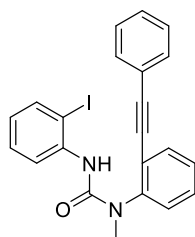
3-(2-((4-Chlorophenyl)ethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S20).

The title compound was prepared starting from the known compound 2-((4-chlorophenyl)ethynyl)aniline⁷ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 57%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.37 (d, J = 8.4 Hz, 1H), 7.51–7.43 (m, 2H), 7.41–7.27 (m, 9H), 7.20–7.07 (m, 4H), 7.02 (td, J = 7.5, 1.2 Hz, 1H), 6.90 (td, J = 7.5, 1.2 Hz, 1H), 3.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.2, 143.7, 140.8, 134.8, 133.6, 133.2, 131.9, 131.7, 130.1, 130.0, 129.0, 128.9, 128.6 (2C), 128.4, 123.3, 122.6, 121.8, 121.0, 118.2, 110.7, 95.6, 94.0, 85.3, 85.0, 36.9; IR (neat, cm^{-1}): 3379, 1684, 1577, 1517, 1489, 1447, 1304, 1089, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{ClN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 483.1235, obsd 483.1233.

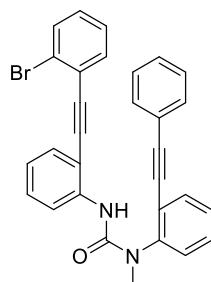


3-(2-((4-Cyanophenyl)ethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S21).

The title compound was prepared starting from the known compound 4-((2-aminophenyl)ethynyl)benzonitrile⁸ and *N*-methyl-2-(phenylethynyl)aniline by following the General Procedure A. Yield = 57%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, *J* = 8.9 Hz, 1H), 7.64–7.58 (m, 2H), 7.50–7.43 (m, 2H), 7.42–7.35 (m, 2H), 7.35–7.29 (m, 5H), 7.29–7.25 (m, 2H), 7.20 (td, *J* = 7.6, 1.5 Hz, 1H), 7.08–7.01 (m, 2H), 6.93 (td, *J* = 7.6, 1.2 Hz, 1H), 3.38 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.1, 143.8, 141.0, 133.6, 132.4, 131.9, (3C), 130.7, 130.0, 129.1, 129.0, 128.6, 128.4, 127.4, 123.4, 122.5, 122.0, 118.6, 118.5, 112.0, 110.1, 95.8, 93.4, 88.9, 84.8, 37.0; IR (neat, cm⁻¹): 3384, 3248, 2226, 1684, 1516, 1449, 1303, 1141, 755; ESI HRMS *m/z* calcd for [C₃₁H₂₁N₃O₂Na]⁺ (*M*+Na)⁺ 474.1577, obsd 499.1575.

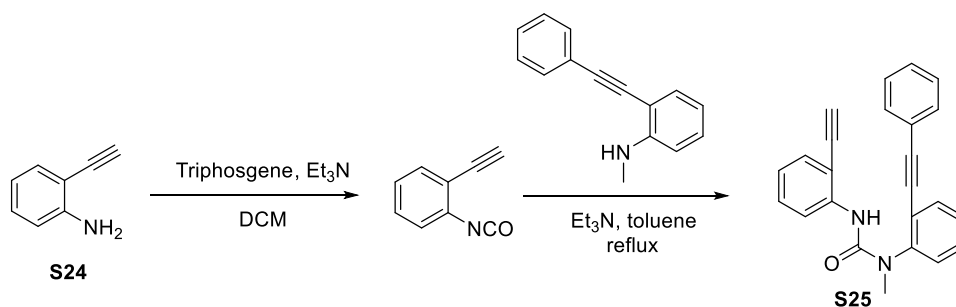


3-(2-(2-Iodophenyl)ethynyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S22). The title compound was prepared starting from the known compound 2-iodoaniline and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 88%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.24 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.68 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51–7.43 (m, 4H), 7.39 (td, *J* = 7.3, 1.8 Hz, 1H), 7.33–7.28 (m, 3H), 7.26–7.23 (m, 1H), 6.65 (td, *J* = 7.6, 1.6 Hz, 2H), 3.40 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.3, 143.5, 139.8, 138.6, 133.9, 131.9, 130.3, 129.5, 129.2, 128.9, 128.8, 128.5, 124.2, 123.8, 122.7, 120.2, 95.5, 89.0, 85.0, 36.5; IR (neat, cm⁻¹): 3376, 1683, 1521, 1431, 1299, 1148, 752; ESI HRMS *m/z* calcd for [C₂₂H₁₇IN₂O₂Na]⁺ (*M*+Na)⁺ 475.0278, obsd 475.0278.

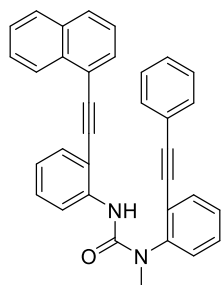


3-(2-((2-Bromophenyl)ethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S23).

The title compound was prepared starting from **S22** and the known compound 1-bromo-2-ethynylbenzene⁹ by following the General Procedure **B**. Yield = 72%; Yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.39 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.63–7.57 (m, 1H), 7.49–7.45 (m, 2H), 7.37–7.26 (m, 8H), 7.24–7.20 (m, 2H), 7.16 (s, 1H), 7.06 (td, *J* = 7.6, 1.6 Hz, 1H), 6.91 (td, *J* = 7.6, 1.1 Hz, 1H), 6.84 (td, *J* = 7.6, 1.1 Hz, 1H), 3.38 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.3, 143.6, 141.0, 133.8, 133.5, 132.5, 132.0, 131.8, 130.2, 129.9 (2C), 128.9 (2C), 128.5, 128.1, 126.9, 126.2, 124.9, 123.2, 122.8, 121.8, 118.2, 110.7, 95.4, 93.5, 88.8, 85.1, 36.8; IR (neat, cm⁻¹): 3374, 3060, 2921, 1683, 1578, 1518, 1445, 1305, 1143, 754; ESI HRMS *m/z* calcd for [C₃₀H₂₁BrN₂ONa]⁺ (*M*+Na)⁺ 527.0729, 529.0709, obsd 527.0727, 529.0706.

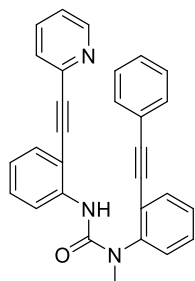


3-(2-Ethynylphenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S25). The title compound was prepared starting from the known compound 2-ethynylaniline **S24**^{2b} and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure **A**. Yield = 68%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.39 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.49–7.44 (m, 2H), 7.42–7.33 (m, 3H), 7.30–7.22 (m, 6H), 6.84 (td, *J* = 7.6, 1.2 Hz, 1H), 3.40 (s, 3H), 2.84 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 154.0, 143.6, 141.5, 133.6, 131.8, 131.5, 130.2, 130.0, 129.2, 128.8, 128.4, 123.6, 122.5, 121.4, 117.5, 109.6, 95.4, 84.9, 83.4, 78.9, 36.3; IR (neat, cm⁻¹): 3375, 2925, 1685, 1578, 1447, 1308, 1144, 755; ESI HRMS *m/z* calcd for [C₂₄H₁₈N₂ONa]⁺ (*M*+Na)⁺ 373.1311, obsd 373.1310.

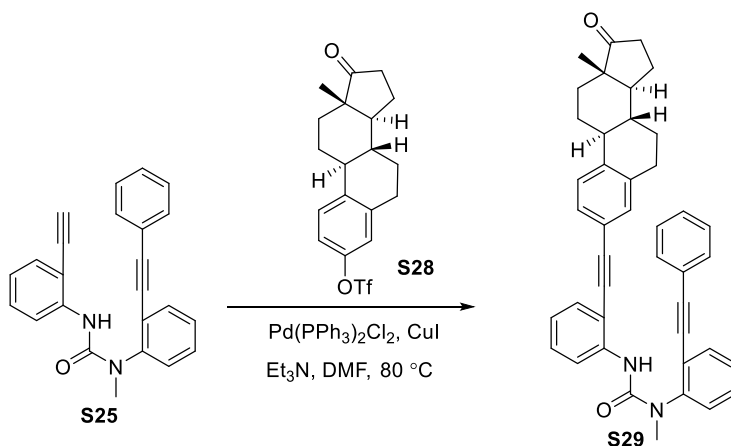


1-Methyl-3-(2-(naphthalen-1-ylethynyl)phenyl)-1-(2-(phenylethynyl)phenyl)urea (S26). The title compound was prepared starting from the known compound 1-iodonaphthalene and **S25** by following the General Procedure **B**. Yield = 79%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.47 (d, *J* = 8.5 Hz, 1H), 8.06 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.90–7.85 (m, 2H), 7.56–7.49 (m, 2H), 7.48–7.38 (m, 5H), 7.35–7.26 (m, 5H), 7.15 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.93 (td, *J* = 7.7, 1.3 Hz, 1H), 6.86 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.59 (td, *J* = 7.7, 1.6 Hz, 1H), 6.33 (td, *J* = 7.7, 1.3 Hz, 1H), 3.33 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.2, 143.2,

141.1, 133.5, 133.3, 133.2, 131.9, 131.6, 130.9, 130.0, 129.6, 129.2, 128.8, 128.5 (2C), 128.3, 127.8, 127.0, 126.6, 126.5, 125.1, 122.9, 122.8, 121.7, 120.1, 117.9, 111.0, 95.3, 93.2, 88.8, 85.1, 36.6; IR (neat, cm^{-1}): 3372, 2925, 1684, 1578, 1516, 1448, 1305, 1143, 754; ESI HRMS m/z calcd for $[\text{C}_{34}\text{H}_{25}\text{N}_2\text{O}]^+ (\text{M}+\text{H})^+$ 477.1961, obsd 477.1965.

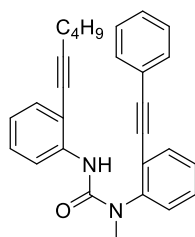


1-Methyl-1-(2-(phenylethynyl)phenyl)-3-(2-(pyridin-2-ylethynyl)phenyl)urea (S27). The title compound was prepared starting from the known compound 2-(pyridin-2-ylethynyl)aniline¹⁰ and *N*-methyl-2-(phenylethynyl)aniline⁴ by following the General Procedure A. Yield = 70%; Pale yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 8.61 (d, $J = 4.2$ Hz, 1H), 8.37 (d, $J = 8.5$ Hz, 1H), 7.65 (td, $J = 7.7, 1.9$ Hz, 1H), 7.50–7.45 (m, 2H), 7.41–7.36 (m, 3H), 7.33–7.26 (m, 5H), 7.18–7.11 (m, 3H), 6.97–6.88 (m, 2H), 3.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.2, 150.0, 143.7, 142.8, 141.1, 135.9, 133.6, 132.1, 131.9, 130.4, 130.0, 129.0, 128.9, 128.5, 128.1, 127.6, 123.3, 123.1, 122.7, 121.8, 118.3, 110.2, 95.5, 94.3, 85.0, 84.2, 36.8; IR (neat, cm^{-1}): 3378, 1685, 1580, 1517, 1447, 1305, 1142, 757; ESI HRMS m/z calcd for $[\text{C}_{29}\text{H}_{22}\text{N}_3\text{O}]^+ (\text{M}+\text{H})^+$ 428.1757, obsd 428.1754.

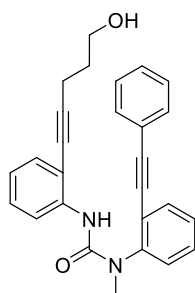


1-Methyl-3-(2-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)ethynyl)phenyl)-1-(2-(phenylethynyl)phenyl)urea (S29). To a mixture of **S25** (805 mg, 2.0 mmol, 1.0 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.2 mmol) and CuI (0.4 mmol) in DMF (20 mL) was added $i\text{Pr}_2\text{NH}$ (3.5 mL, 10.0 mmol, 5.0 equiv) and **S28**¹¹ (841 mg, 2.4 mmol, 1.2 equiv). The resulting reaction mixture was stirred at 100 °C for 12 h. The reaction was quenched with water and extracted with EtOAc (40 mL x 3). The combined organic solution was washed with brine, dried over anhydrous Na_2SO_4 , and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography to afford the product **S29** as a pale yellow solid (658 mg, 55% yield); ^1H NMR (500 MHz, CDCl_3) δ 8.35 (d, $J = 8.4$ Hz, 1H), 7.49–7.46 (m, 2H), 7.41 (dd, $J = 7.6, 1.6$

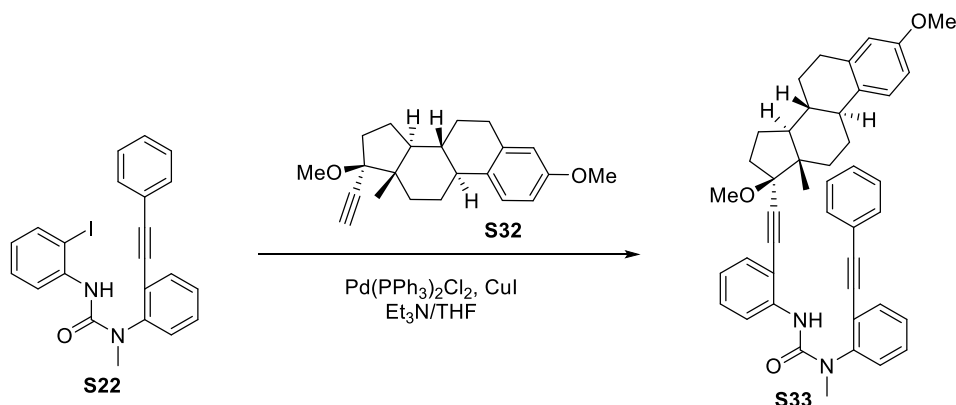
Hz, 1H), 7.36 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.33–7.30 (m, 4H), 7.29–7.26 (m, 1H), 7.25–7.22 (m, 1H), 7.19–7.14 (m, 2H), 7.03 (td, $J = 7.6, 1.3$ Hz, 1H), 7.00–6.95 (m, 2H), 6.89 (td, $J = 7.6, 1.3$ Hz, 1H), 3.38 (s, 3H), 2.93 (m, 2H), 2.57–2.43 (m, 2H), 2.36–2.32 (m, 1H), 2.20–2.00 (m, 4H), 1.68–1.47 (m, 6H), 0.95 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 220.7, 154.3, 143.8, 140.7, 140.6, 136.4, 133.6, 132.3, 131.9, 131.8, 130.0, 129.6, 129.4, 128.9 (2C), 128.5, 128.3, 125.2, 123.3, 122.7, 121.8, 119.8, 118.3, 111.4, 95.5 (2C), 85.1, 83.7, 50.7, 48.1, 44.7, 38.3, 36.9, 36.0, 31.8, 29.3, 26.6, 25.9, 21.8, 14.1; IR (neat, cm^{-1}): 3376, 2925, 1737, 1686, 1577, 1516, 1447, 1304, 1143, 755; ESI HRMS m/z calcd for $[\text{C}_{42}\text{H}_{39}\text{N}_2\text{O}_2]^+$ ($\text{M}+\text{H}$) $^+$ 603.3006, obsd 603.3016.



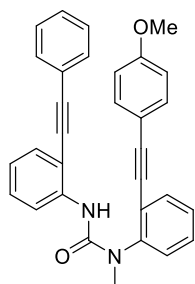
3-(2-(Hex-1-yn-1-yl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S30). The title compound was prepared starting from hex-1-yne and **S22** by following the General Procedure **B**. Yield = 67%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.34 (d, $J = 8.3$ Hz, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.52–7.28 (m, 8H), 7.24–7.12 (m, 3H), 6.83 (t, $J = 7.6$ Hz, 1H), 3.39 (s, 3H), 2.07–1.97 (m, 2H), 1.41–1.29 (m, 4H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 144.1, 140.7, 133.6, 132.0, 131.5, 129.9, 129.4, 128.9, 128.5, 128.3, 123.8, 122.7, 121.5, 117.6, 111.8, 96.8, 95.6, 85.0, 75.8, 36.8, 31.0, 22.2, 19.1, 13.8; IR (neat, cm^{-1}): 3372, 2929, 1684, 1518, 1448, 1307, 1144, 754; ESI HRMS m/z calcd for $[\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_2\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$ 429.1937, obsd 429.1939.



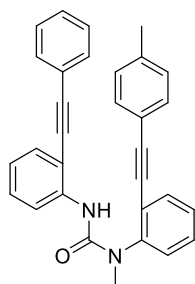
3-(2-(5-Hydroxypent-1-yn-1-yl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S31). The title compound was prepared starting from pent-4-yn-1-ol and **S22** by following the General Procedure **B**. Yield = 86%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.33 (dd, $J = 8.5, 1.2$ Hz, 1H), 7.67 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.48–7.45 (m, 2H), 7.45–7.36 (m, 3H), 7.32–7.27 (m, 3H), 7.23–7.17 (m, 2H), 7.12 (s, 1H), 6.82 (td, $J = 7.5, 1.2$ Hz, 1H), 3.68–3.62 (m, 2H), 3.38 (s, 3H), 2.15 (t, $J = 7.1$ Hz, 2H), 1.96 (s, 1H), 1.66–1.59 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 143.9, 140.6, 133.6, 131.9, 131.5, 130.0, 129.2, 129.0, 128.9, 128.5 (2C), 123.6, 122.6, 121.6, 117.7, 111.6, 95.9, 95.6, 84.9, 76.2, 61.5, 36.7, 31.5, 15.9; IR (neat, cm^{-1}): 3370, 2927, 1662, 1520, 1448, 1308, 755; ESI HRMS m/z calcd for $[\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_2\text{Na}]^+$ ($\text{M}+\text{Na}$) $^+$ 431.1730, obsd 431.1734.



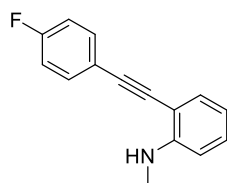
3-(2-(((8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-Dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)ethynyl)phenyl)-1-methyl-1-(2-(phenylethynyl)phenyl)urea (S33). The title compound was prepared starting from **S22** and **S32**¹² by following the General Procedure **B**. Yield = 76%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.53–7.47 (m, 2H), 7.44–7.30 (m, 7H), 7.26–7.23 (m, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.97 (s, 1H), 6.89 (td, *J* = 7.6, 1.2 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 3.75 (s, 3H), 3.41 (s, 3H), 3.16 (s, 3H), 2.86–2.74 (m, 2H), 2.31–2.22 (m, 1H), 2.16–2.09 (m, 1H), 1.91–1.60 (m, 7H), 1.47–1.26 (m, 4H), 0.85 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 157.6, 154.5, 144.0, 140.4, 138.0, 133.9, 132.7, 132.6, 131.9, 130.2, 129.6, 128.9, 128.8, 128.5, 128.4, 126.5, 123.1, 122.7, 121.9, 119.0, 113.9, 111.6, 111.4, 96.9, 95.5, 86.2, 85.3, 83.3, 55.3, 53.6, 49.8, 48.2, 43.6, 39.4, 37.5, 37.2, 34.7, 30.0, 27.3, 26.7, 22.9, 13.0; IR (neat, cm⁻¹): 3385, 3057, 1684, 1578, 1447, 1092, 756; ESI HRMS *m/z* calcd for [C₄₄H₄₄N₂O₃Na]⁺ (*M*+Na)⁺ 671.3244, obsd 671.3256.



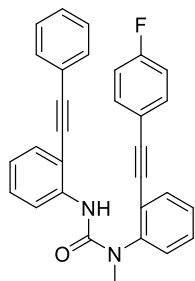
1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1-methyl-3-(2-(phenylethynyl)phenyl)urea (S34). The title compound was prepared starting from the known compound 2-(phenylethynyl)aniline³ and 2-((4-methoxyphenyl)ethynyl)-*N*-methylaniline¹² by following the General Procedure **A**. Yield = 64%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.38 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.44–7.39 (m, 2H), 7.36–7.26 (m, 7H), 7.22–7.18 (m, 2H), 7.07 (td, *J* = 7.7, 1.6 Hz, 1H), 6.95–6.88 (m, 2H), 6.86–6.81 (m, 2H), 3.80 (s, 3H), 3.37 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 160.1, 154.3, 143.3, 140.7, 133.5, 133.3, 132.0, 131.7, 129.8, 129.6, 128.8, 128.7, 128.3, 128.2, 123.5, 122.5, 121.7, 118.1, 114.9, 114.2, 111.0, 95.6, 95.2, 84.2, 83.9, 55.5, 36.8; IR (neat, cm⁻¹): 3375, 2919, 1682, 1578, 1513, 1450, 1250, 1133, 754; ESI HRMS *m/z* calcd for [C₃₁H₂₄N₂O₂Na]⁺ (*M*+Na)⁺ 479.1730, obsd 479.1733.



1-Methyl-3-(2-(phenylethynyl)phenyl)-1-(2-(*p*-tolylethynyl)phenyl)urea (S35). The title compound was prepared starting from the known compound 2-(phenylethynyl)aniline³ and *N*-methyl-2-(*p*-tolylethynyl)aniline¹³ by following the General Procedure **A**. Yield = 69%; White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, *J* = 8.5 Hz 1H), 7.39–7.26 (m, 9H), 7.22–7.17 (m, 2H), 7.17–7.05 (m, 4H), 6.96–6.87 (m, 2H), 3.37 (s, 3H), 2.34 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.3, 143.5, 140.8, 139.1, 133.5, 132.0, 131.8, 131.7, 129.8 (2C), 129.3, 128.8, 128.7, 128.3, 128.2, 123.4, 122.5, 121.7, 119.7, 118.2, 111.1, 95.7, 95.2, 84.5, 84.3, 36.8, 21.7; IR (neat, cm⁻¹): 3377, 3058, 2920, 2216, 1685, 1578, 1516, 1450, 1305, 1142, 754; ESI HRMS *m/z* calcd for [C₃₁H₂₄N₂ONa]⁺ (*M*+Na)⁺ 463.1781, obsd 463.1779.

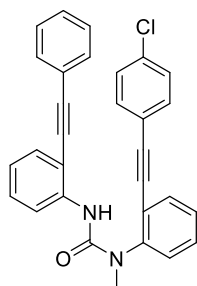


2-((4-Fluorophenyl)ethynyl)-*N*-methylaniline (S36). The title compound was prepared starting from 1-ethynyl-4-fluorobenzene and 2-iodo-*N*-methylaniline by following the General Procedure **B**. Yield = 84%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 7.52–7.43 (m, 2H), 7.35 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.25–7.19 (m, 1H), 7.06–6.97 (m, 2H), 6.65 (td, *J* = 7.6, 1.1 Hz, 1H), 6.59 (dd, *J* = 8.3, 1.1 Hz, 1H), 4.63 (s, 1H), 2.89 (d, *J* = 4.8 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.5 (d, *J*_{C-F} = 249.4 Hz), 149.9, 133.5 (d, *J*_{C-F} = 8.3 Hz), 132.2, 130.3, 119.6 (d, *J*_{C-F} = 3.6 Hz), 116.4, 115.8 (d, *J*_{C-F} = 22.2 Hz), 109.2, 107.2, 93.9, 85.9 (d, *J*_{C-F} = 1.4 Hz), 30.4; ¹⁹F NMR (471 MHz, CDCl₃) δ -111.0; IR (neat, cm⁻¹): 3422, 2914, 1603, 1504, 1320, 1230, 834, 746; ESI HRMS *m/z* calcd for [C₁₅H₁₃FN]⁺ (*M*+H)⁺ 226.1027, obsd 226.1027.



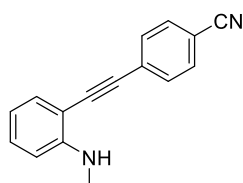
1-(2-((4-Fluorophenyl)ethynyl)phenyl)-1-methyl-3-(2-(phenylethynyl)phenyl)urea (S37). The title compound was prepared starting from the known compound 2-(phenylethynyl)aniline³ and **S36** by following the General Procedure **A**. Yield = 69%; Pale yellow solid; ¹H NMR (500 MHz, CDCl₃) δ 8.37 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.47–7.42 (m, 2H),

7.37–7.26 (m, 7H), 7.22–7.18 (m, 2H), 7.15 (s, 1H), 7.11 (td, $J = 7.7, 1.6$ Hz, 1H), 7.03–6.98 (m, 2H), 6.95 (td, $J = 7.6, 1.2$ Hz, 1H), 6.90 (td, $J = 7.6, 1.2$ Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.9 (d, $J_{\text{C-F}} = 250.3$ Hz), 154.3, 143.7, 140.8, 133.9 (d, $J_{\text{C-F}} = 8.5$ Hz), 133.5, 132.0, 131.7, 130.1, 129.8, 128.8 (2C), 128.4, 128.2, 123.1, 122.5, 121.8, 118.8 (d, $J_{\text{C-F}} = 3.5$ Hz), 118.1, 115.9 (d, $J_{\text{C-F}} = 22.2$ Hz), 111.1, 95.3, 94.3, 84.8 (d, $J_{\text{C-F}} = 1.6$ Hz), 84.2, 36.9; ^{19}F NMR (471 MHz, CDCl_3) δ -110.1; IR (neat, cm^{-1}): 3377, 2919, 1681, 1579, 1510, 1451, 1196, 1132, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{FN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 467.1530, obsd 467.1528.

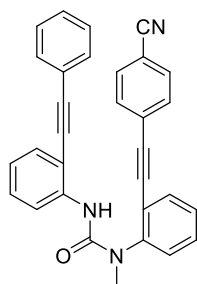


1-(2-((4-Chlorophenyl)ethynyl)phenyl)-1-methyl-3-(2-(phenylethynyl)phenyl)urea (S38).

The title compound was prepared starting from 2-(phenylethynyl)aniline and 2-((4-chlorophenyl)ethynyl)-*N*-methylaniline¹³ by following the General Procedure A. Yield = 68%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.42–8.32 (m, 1H), 7.40–7.24 (m, 11H), 7.20–7.08 (m, 4H), 6.94 (td, $J = 7.7, 1.3$ Hz, 1H), 6.89 (td, $J = 7.7, 1.3$ Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 143.7, 140.7, 134.9, 133.5, 133.1, 132.0, 131.7, 130.2, 129.8, 128.8 (2C), 128.7, 128.4, 128.2, 122.9, 122.4, 121.8, 121.2, 118.1, 111.1, 95.3, 94.2, 86.0, 84.2, 36.9; IR (neat, cm^{-1}): 3376, 3061, 1685, 1578, 1517, 1450, 1305, 1091, 754; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{ClN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 483.1235, obsd 483.1234.

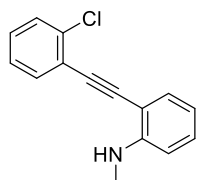


4-((2-(Methylamino)phenyl)ethynyl)benzonitrile (S39). The title compound was prepared starting from 4-iodobenzonitrile and 2-ethynyl-*N*-methylaniline by following the General Procedure B. Yield = 86%; Brown oil; ^1H NMR (500 MHz, CDCl_3) δ 7.64–7.60 (m, 2H), 7.60–7.55 (m, 2H), 7.36 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.28 (ddd, $J = 8.5, 7.5, 1.6$ Hz, 1H), 6.67 (t, $J = 7.5$ Hz, 1H), 6.63 (d, $J = 8.5$ Hz, 1H), 4.63 (d, $J = 5.2$ Hz, 1H), 2.94 (d, $J = 5.2$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.2, 132.6, 132.2, 132.0, 131.2, 128.5, 118.7, 116.6, 111.4, 109.4, 106.3, 93.6, 91.0, 30.5; IR (neat, cm^{-1}): 3394, 2917, 2227, 2205, 1598, 1514, 1462, 1321, 1169, 838; ESI HRMS m/z calcd for $[\text{C}_{16}\text{H}_{13}\text{N}_2]^+$ ($\text{M}+\text{H}$) $^+$ 233.1073, obsd 233.1075.

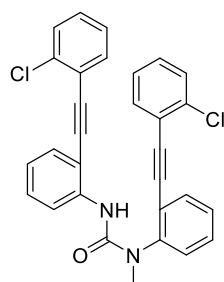


1-(2-((4-Cyanophenyl)ethynyl)phenyl)-1-methyl-3-(2-(phenylethynyl)phenyl)urea (S40).

The title compound was prepared starting from 2-(phenylethynyl)aniline and **S39** by following the General Procedure **A**. Yield = 86%; Brown solid; ^1H NMR (500 MHz, CDCl_3) δ 8.35 (d, J = 8.5 Hz, 1H), 7.62–7.55 (m, 2H), 7.55–7.50 (m, 2H), 7.40–7.27 (m, 7H), 7.21–7.11 (m, 4H), 6.98 (td, J = 7.6, 1.3 Hz, 1H), 6.91 (td, J = 7.6, 1.3 Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 144.1, 140.7, 133.8, 132.4, 132.2, 132.0, 131.8, 131.0, 129.9, 128.9, 128.8, 128.5, 128.3, 127.6, 122.4, 122.3, 122.0, 118.6, 118.1, 112.1, 111.1, 95.3, 93.4, 89.2, 84.2, 37.0; IR (neat, cm^{-1}): 3451, 2083, 1636, 1517, 1446, 1305, 1133, 752; ESI HRMS m/z calcd for $[\text{C}_{31}\text{H}_{21}\text{N}_3\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 474.1577, obsd 474.1584.

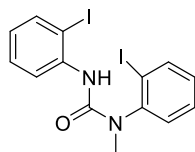


2-((2-Chlorophenyl)ethynyl)-N-methylaniline (S41). The title compound was prepared starting from 1-chloro-2-iodobenzene and 2-ethynyl-N-methylaniline by following the General Procedure **B**. Yield = 88%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.55–7.50 (m, 1H), 7.42–7.36 (m, 2H), 7.26–7.18 (m, 3H), 6.64 (td, J = 7.5, 1.1 Hz, 1H), 6.59 (dd, J = 8.3, 1.1 Hz, 1H), 5.02 (q, J = 5.4 Hz, 1H), 2.91 (d, J = 5.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.4, 135.1, 132.8, 132.0, 130.7, 129.3, 129.1, 126.7, 123.5, 116.1, 109.1, 106.8, 92.1, 92.0, 30.4; IR (neat, cm^{-1}): 3415, 3070, 2910, 2817, 2207, 1603, 1579, 1513, 1321, 1287, 1169, 1052, 746; ESI HRMS m/z calcd for $[\text{C}_{15}\text{H}_{13}\text{ClN}]^+$ ($\text{M}+\text{H}$) $^+$ 242.0731, obsd 242.0733.

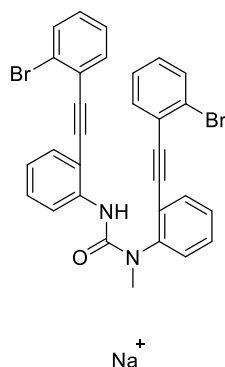


1,3-Bis(2-((2-chlorophenyl)ethynyl)phenyl)-1-methylurea (S42). The title compound was prepared starting from the known compound 2-((2-chlorophenyl)ethynyl)aniline¹⁴ and **S41** by following the General Procedure **A**. Yield = 55%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.38 (dd, J = 8.5, 1.2 Hz, 1H), 7.50 (dd, J = 7.6, 1.8 Hz, 1H), 7.42–7.28 (m, 7H), 7.26–7.18 (m, 4H), 7.14 (s, 1H), 7.09 (td, J = 7.6, 1.8 Hz, 1H), 6.91 (td, J = 7.6, 1.2 Hz, 1H), 6.85 (td, J = 7.6, 1.2 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.1, 143.6, 141.0, 136.4, 136.1, 133.9, 133.8 (2C), 131.7, 130.3, 130.2, 129.9, 129.8, 129.4, 129.3, 129.0, 128.1, 126.6,

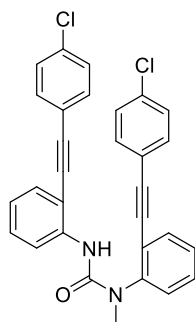
126.4, 122.9, 122.8, 122.7, 121.8, 118.2, 110.7, 91.8, 91.7, 90.1, 89.4, 36.9; IR (neat, cm^{-1}): 3375, 2925, 1625, 1578, 1519, 1446, 1305, 1097, 753; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{21}\text{Cl}_2\text{N}_2\text{O}]^+$ ($\text{M}+\text{H}$) $^+$ 495.1025, obsd 495.1031.



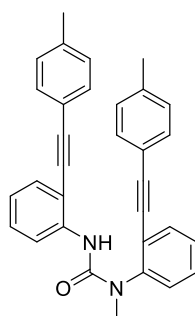
1,3-Bis(2-iodophenyl)-1-methylurea (S43). The title compound was prepared starting from 2-iodoaniline and 2-iodo-*N*-methylaniline by following the General Procedure A. Yield = 83%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.25 (dd, $J = 8.3, 1.5$ Hz, 1H), 8.02 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.61 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.52 (td, $J = 7.6, 1.5$ Hz, 1H), 7.49–7.45 (m, 1H), 7.32–7.27 (m, 1H), 7.14 (td, $J = 7.7, 1.6$ Hz, 1H), 6.70 (td, $J = 7.7, 1.6$ Hz, 1H), 6.47 (s, 1H), 3.29 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.5, 144.4, 141.0, 139.6, 138.6, 130.8, 130.6, 130.2, 129.3, 124.4, 120.2, 100.9, 89.0, 36.1; IR (neat, cm^{-1}): 3375, 2918, 1682, 1517, 1430, 1297, 748; ESI HRMS m/z calcd for $[\text{C}_{14}\text{H}_{12}\text{I}_2\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 500.8931, obsd 500.8936.



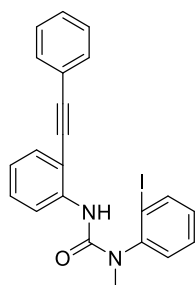
1,3-Bis(2-((2-bromophenyl)ethynyl)phenyl)-1-methylurea (S44). The title compound was prepared starting from the known compound 1-bromo-2-ethynylbenzene and **S43** by following the General Procedure B. Yield = 58%; Yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 8.38 (dd, $J = 8.5, 1.2$ Hz, 1H), 7.62–7.55 (m, 2H), 7.49 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.38–7.28 (m, 5H), 7.28–7.25 (m, 1H), 7.25–7.21 (m, 2H), 7.19–7.13 (m, 2H), 7.10 (td, $J = 7.7, 1.6$ Hz, 1H), 6.91 (td, $J = 7.6, 1.2$ Hz, 1H), 6.85 (td, $J = 7.6, 1.2$ Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.1, 143.5, 141.0, 133.9 (3C), 132.6, 132.4, 131.7, 130.3, 130.2, 130.0, 129.9, 129.0, 128.1, 127.2, 126.9, 126.2, 125.6, 125.1, 124.9, 122.9, 121.8, 118.2, 110.7, 93.6, 93.5, 89.5, 88.8, 37.0; IR (neat, cm^{-1}): 3375, 2925, 1683, 1578, 1519, 1445, 1305, 753; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{20}\text{Br}_2\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 606.9814, 604.9835, obsd 606.9819, 604.9841.



1,3-Bis(2-((4-chlorophenyl)ethynyl)phenyl)-1-methylurea (S45). The title compound was prepared starting from the known compound 1-chloro-4-ethynylbenzene and **S43** by following the General Procedure **B**. Yield = 64%; Pale yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 8.35 (d, J = 8.6 Hz, 1H), 7.40–7.34 (m, 4H), 7.32–7.27 (m, 6H), 7.18 (td, J = 7.6, 1.6 Hz, 1H), 7.13–7.07 (m, 3H), 7.03 (td, J = 7.6, 1.2 Hz, 1H), 6.91 (td, J = 7.6, 1.2 Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 143.8, 140.7, 135.1, 134.8, 133.6, 133.2, 133.1, 131.8, 130.2, 130.1, 128.9, 128.6, 128.4, 123.0, 121.9, 121.1, 121.0, 118.2, 110.8, 94.4, 94.1, 85.9, 85.3, 37.0; IR (neat, cm^{-1}): 3379, 3065, 2926, 1684, 1578, 1305, 1090, 755; ESI HRMS m/z calcd for $[\text{C}_{30}\text{H}_{20}\text{Cl}_2\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 517.0845, obsd 517.0843.

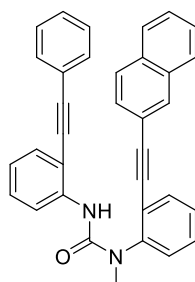


1-Methyl-1,3-bis(2-(p-tolyethynyl)phenyl)urea (S46). The title compound was prepared starting from the known compound 1-ethynyl-4-methylbenzene and **S43** by following the General Procedure **B**. Yield = 81%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.40–8.32 (m, 1H), 7.40–7.24 (m, 6H), 7.17–7.06 (m, 8H), 6.97 (t, J = 7.6 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 3.37 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 143.6, 140.7, 139.1, 138.8, 133.5, 131.9, 131.8, 131.7, 129.8, 129.6, 129.3, 128.9, 128.8, 128.3, 123.4, 121.7, 119.7, 119.5, 118.2, 111.3, 95.7, 95.5, 84.5, 83.6, 36.8, 21.7 (2C); IR (neat, cm^{-1}): 3376, 3028, 2919, 1684, 1578, 1517, 1448, 1334, 1304, 816, 753; ESI HRMS m/z calcd for $[\text{C}_{32}\text{H}_{26}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 477.1937, obsd 477.1938.



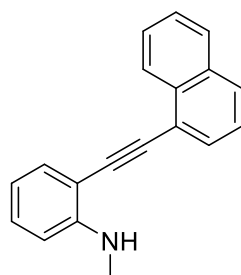
1-(2-Iodophenyl)-1-methyl-3-(2-(phenylethynyl)phenyl)urea (S47). The title compound was prepared starting from the known compound 2-(phenylethynyl)aniline and

2-iodo-*N*-methylaniline by following the General Procedure **A**. Yield = 76%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.38 (d, J = 8.4 Hz, 1H), 7.56 (dd, J = 7.9, 1.4 Hz, 1H), 7.43–7.27 (m, 6H), 7.25–7.19 (m, 2H), 7.15 (td, J = 7.6, 1.4 Hz, 1H), 6.99–6.86 (m, 2H), 6.61 (td, J = 7.6, 1.4 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.5, 144.4, 140.7, 140.6, 132.1, 131.7, 130.3, 130.1, 129.9, 129.6, 128.9, 128.2, 122.4, 122.0, 118.2, 111.1, 100.1, 95.2, 84.1, 36.4; IR (neat, cm^{-1}): 3375, 2921, 1683, 1578, 1517, 1490, 1450, 1304, 754, 690; ESI HRMS m/z calcd for $[\text{C}_{22}\text{H}_{17}\text{IN}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 475.0278, obsd 475.0278.

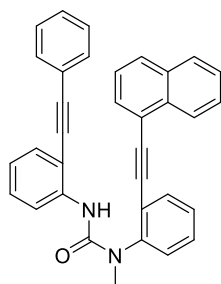


1-Methyl-1-(2-(naphthalen-2-ylethynyl)phenyl)-3-(2-(phenylethynyl)phenyl)urea (S48).

The title compound was prepared starting from 2-ethynynaphthalene and **S47** by following the General Procedure **B**. Yield = 76%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.43 (d, J = 8.5 Hz, 1H), 7.96 (s, 1H), 7.80–7.73 (m, 3H), 7.53–7.44 (m, 3H), 7.41–7.26 (m, 8H), 7.23–7.18 (m, 3H), 7.10 (t, J = 7.8 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 3.42 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 143.7, 140.8, 133.7, 133.1, 133.0, 132.0 (2C), 131.7, 130.0, 129.8, 128.8, 128.7, 128.4, 128.3, 128.2, 128.0, 127.9, 127.0, 126.7, 123.2, 122.4, 121.8, 120.0, 118.1, 111.1, 95.8, 95.3, 85.4, 84.3, 36.9; IR (neat, cm^{-1}): 3381, 3057, 1682, 1578, 1516, 1490, 1445, 1321, 1143, 753; ESI HRMS m/z calcd for $[\text{C}_{34}\text{H}_{24}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 499.1781, obsd 499.1774.

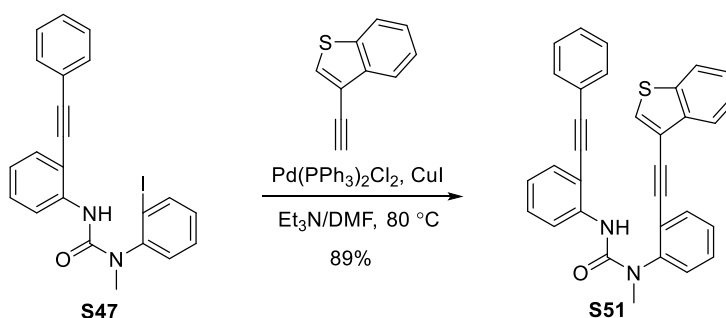


***N*-Methyl-2-(naphthalen-1-ylethynyl)aniline (S49).** The title compound was prepared starting from 1-ethynynaphthalene and 2-iodo-*N*-methylaniline by following the General Procedure **B**. Yield = 82%; Yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 8.42 (d, J = 8.3 Hz, 1H), 7.88–7.81 (m, 2H), 7.74 (dd, J = 7.1, 1.1 Hz, 1H), 7.61–7.56 (m, 1H), 7.54–7.42 (m, 3H), 7.30–7.25 (m, 1H), 6.71 (td, J = 7.5, 1.1 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 4.80 (s, 1H), 2.94 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.1, 133.4, 133.3, 132.4, 130.4 (2C), 128.9, 128.5, 127.0, 126.6, 126.3, 125.5, 121.2, 116.5, 109.3, 107.7, 93.1, 91.1, 30.6; IR (neat, cm^{-1}): 3376, 3061, 1685, 1578, 1517, 1450, 1305, 1091, 754; ESI HRMS m/z calcd for $[\text{C}_{19}\text{H}_{15}\text{NNa}]^+$ ($\text{M}+\text{Na}$) $^+$ 483.1235, obsd 483.1234.



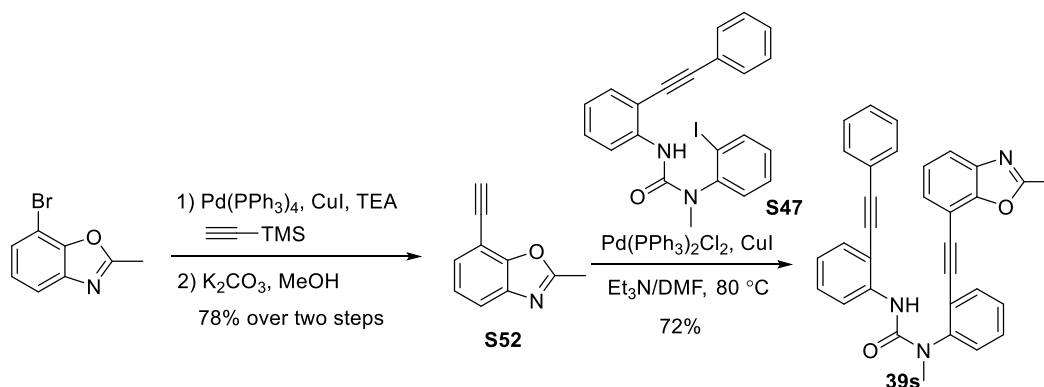
1-Methyl-1-(2-(naphthalen-1-ylethynyl)phenyl)-3-(2-(phenylethynyl)phenyl)urea (S50).

The title compound was prepared starting from the known compound 2-(phenylethynyl)aniline and **S49** by following the General Procedure **A**. Yield = 68%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.42 (d, J = 8.4 Hz, 1H), 8.37–8.30 (m, 1H), 7.87–7.79 (m, 2H), 7.72 (d, J = 7.1 Hz, 1H), 7.55–7.27 (m, 11H), 7.25–7.20 (m, 3H), 7.14 (td, J = 7.6, 1.6 Hz, 1H), 6.99 (td, J = 7.6, 1.2 Hz, 1H), 6.90 (td, J = 7.6, 1.2 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.2, 143.4, 140.8, 133.9, 133.3, 132.1, 131.7, 131.1, 130.2, 129.8, 129.4, 129.0, 128.8, 128.5, 128.4, 128.2, 127.3, 126.7, 126.3, 125.4, 123.4, 122.5, 121.8, 120.4, 118.3, 111.2, 95.3, 93.5, 89.9, 84.3, 36.9; IR (neat, cm^{-1}): 3372, 1683, 1578, 1515, 1448, 1304, 1134, 753; ESI HRMS m/z calcd for $[\text{C}_{34}\text{H}_{24}\text{N}_2\text{ONa}]^+$ ($\text{M}+\text{Na}$) $^+$ 499.1781, obsd 499.1780.



1-(2-(Benzo[b]thiophen-3-ylethynyl)phenyl)-1-methyl-3-(2-(phenylethynyl)phenyl)urea (S51).

To a mixture of **S47** (452 mg, 1.0 mmol, 1.0 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.05 mmol) and CuI (0.1 mmol) in DMF (2 mL) and Et_3N (6 mL) was added the known compound 3-ethynylbenzo[b]thiophene¹⁵ (190 mg, 1.2 mmol, 1.2 equiv). The resulting reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with water and extracted with EtOAc (40 mL x 3). The combined organic solution was washed with brine, dried over anhydrous Na_2SO_4 , and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography to afford the product **S51** as brown solid (429 mg, 89% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.41 (d, J = 8.5 Hz, 1H), 7.98–7.91 (m, 1H), 7.85–7.78 (m, 1H), 7.66 (s, 1H), 7.42–7.27 (m, 9H), 7.23–7.18 (m, 3H), 7.13 (td, J = 7.7, 1.6 Hz, 1H), 6.97 (td, J = 7.6, 1.3 Hz, 1H), 6.90 (td, J = 7.6, 1.3 Hz, 1H), 3.41 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.2, 143.5, 140.8, 139.0, 138.9, 133.8, 132.1, 131.7, 131.2, 130.1, 129.8, 128.9, 128.8, 128.5, 128.2, 125.3, 125.2, 123.3, 123.2, 122.7, 122.5, 121.8, 118.2, 118.0, 111.2, 95.3, 89.0, 87.5, 84.3, 36.9; IR (neat, cm^{-1}): 3374, 3059, 2920, 1683, 1578, 1516, 1450, 1305, 1142, 753; ESI HRMS m/z calcd for $[\text{C}_{32}\text{H}_{22}\text{N}_2\text{OSNa}]^+$ ($\text{M}+\text{Na}$) $^+$ 505.1345, obsd 505.1348.

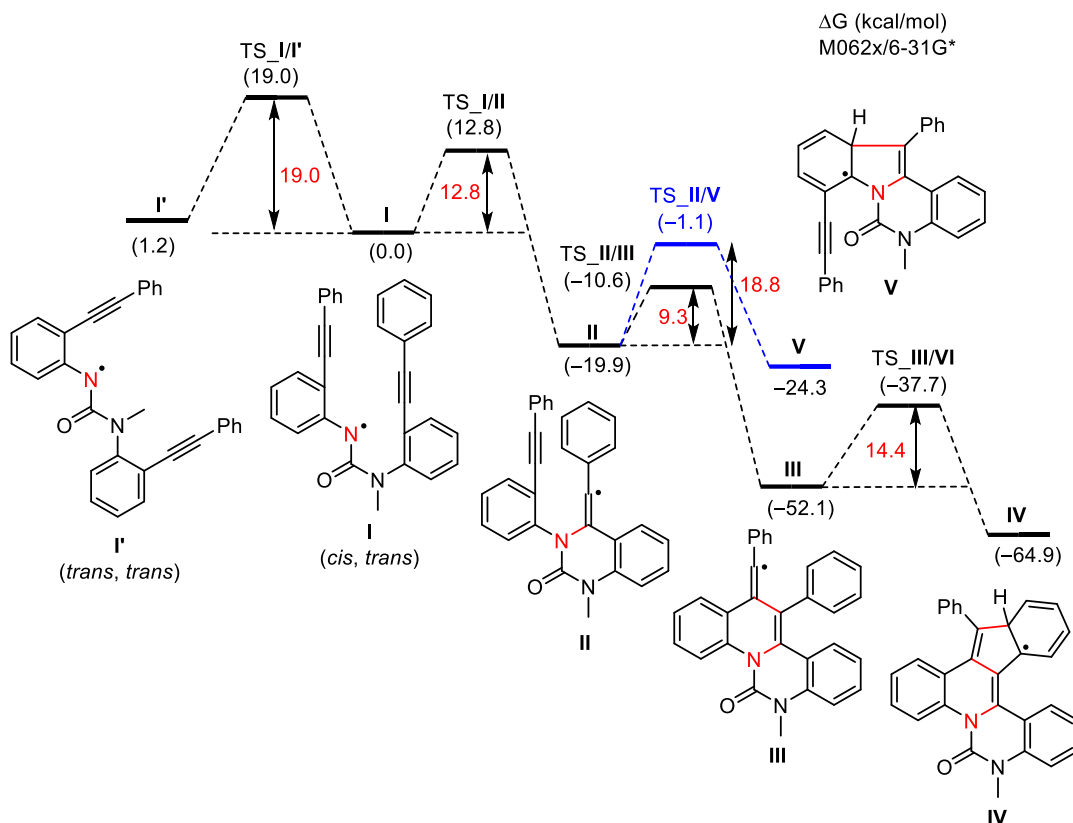


7-Ethynyl-2-methylbenzo[d]oxazole (S52). To a mixture of the known compound 7-bromo-2-methylbenzo[d]oxazole¹⁶ (2.11 g, 10.0 mmol, 1.0 equiv), Pd(PPh₃)₄ (577 mg, 0.5 mmol, 0.05 equiv) and CuI (190 mg, 1.0 mmol, 0.1 equiv) in Et₃N (40 mL) was added ethynyltrimethylsilane (2.1 mL, 15.0 mmol, 1.5 equiv). The resulting reaction mixture was stirred at 50 °C for 6 h before quenching with water. The reaction mixture was extracted with EtOAc (40 mL x 3). The combined organic solution was washed with brine, dried over anhydrous Na₂SO₄, and filtered. The filtrate was concentrated under reduced pressure and the residue was dissolved in MeOH (40 mL). K₂CO₃ (3.45 g, 25.0 mmol, 2.5 equiv) was added. The resulting mixture was stirred at 40 °C for 2 h before addition of water. The reaction mixture was extracted with EtOAc (40 mL x 3). The combined organic solution was washed with brine, dried over anhydrous Na₂SO₄, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography to afford the product **S52** as a white solid (1.23 g, 78% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 3.41 (s, 1H), 2.68 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 164.4, 151.7, 141.7, 128.7, 124.2, 120.6, 105.6, 82.2, 77.5, 14.7; IR (neat, cm⁻¹): 3209, 2918, 1603, 1572, 1418, 1272, 1259, 1179; ESI HRMS *m/z* calcd for [C₁₀H₈NO]⁺ (*M*+H)⁺ 158.0600, obsd 158.0601.

1-Methyl-1-(2-((2-methylbenzo[d]oxazol-7-yl)ethynyl)phenyl)-3-(2-(phenylethynyl)phenyl)urea (39s). To a mixture of **S47** (452 mg, 1.0 mmol, 1.0 equiv), Pd(PPh₃)₂Cl₂ (0.05 mmol) and CuI (0.1 mmol) in DMF (2 mL) and Et₃N (6 mL) was added **S52** (188 mg, 1.2 mmol, 1.2 equiv). The resulting reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched with water and extracted with EtOAc (40 mL x 3). The combined organic solution was washed with brine, dried over anhydrous Na₂SO₄, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography to afford the product **39s** as a white solid (346 mg, 72% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.37 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.43–7.30 (m, 7H), 7.29–7.21 (m, 5H), 7.19–7.13 (m, 2H), 6.98 (td, *J* = 7.6, 1.3 Hz, 1H), 6.90 (td, *J* = 7.6, 1.3 Hz, 1H), 3.42 (s, 3H), 2.61 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 164.5, 154.1, 151.2, 143.8, 141.7, 140.8, 133.8, 132.0, 131.7, 130.5, 129.7, 129.0, 128.7, 128.4, 128.2, 128.1, 124.3, 122.7, 122.5, 121.8, 120.4, 118.2, 111.1, 106.3, 95.3, 89.8, 88.9, 84.2, 36.8, 14.6; IR (neat, cm⁻¹): 3377, 1683, 1578, 1516, 1447, 1275, 1196, 1133, 1077, 764, 751; ESI HRMS *m/z* calcd for [C₃₂H₂₃N₃O₂Na]⁺ (*M*+Na)⁺ 481.1078, obsd 481.1074.

9. Computational Studies.

Computational methods: All geometries were optimized in the gas phase using M06-2X/6-31G* as implemented in the Gaussian 09 suite of programs.¹⁷ All stationary points were verified as minima or first-order saddle points by vibrational frequency analysis. All discussed energies are Gibbs free energies in gas phase (ΔG) at 298 K.



Molecular Geometries and Energies

M06-2x 6-31G* cartesian coordinates and energies in Hartree

I

C	1.081508	-4.180262	-3.104394
C	2.210996	-4.065223	-2.269971
C	2.233973	-3.155823	-1.241161
C	1.102733	-2.307781	-0.992086
C	-0.041230	-2.429173	-1.874469
C	-0.028059	-3.368959	-2.906197
N	0.981176	-1.444652	0.005227
C	2.061113	-1.145558	0.840001
N	1.687444	-1.023409	2.157665
C	0.314255	-0.911576	2.535019
C	-0.423764	0.235162	2.176529
O	3.209746	-0.953350	0.459692
C	-0.271965	-1.899599	3.314402

C	-1.593432	-1.769985	3.736344
C	-2.332343	-0.647356	3.373443
C	-1.752883	0.350165	2.597110
C	2.671081	-0.493755	3.093314
C	-1.152117	-1.571764	-1.676053
C	0.214671	1.232972	1.378728
C	0.849169	2.002091	0.689072
C	1.647231	2.854193	-0.138473
C	-2.081457	-0.813060	-1.497424
C	2.894580	2.392084	-0.586789
C	3.680977	3.207091	-1.391858
C	3.236872	4.476541	-1.757489
C	1.997264	4.935282	-1.315913
C	1.202858	4.130511	-0.508406
C	-3.133719	0.122607	-1.256708
C	-2.842017	1.334366	-0.611033
C	-3.857584	2.249836	-0.364567
C	-5.166449	1.969906	-0.754684
C	-5.459293	0.769679	-1.399397
C	-4.450241	-0.151147	-1.653486
H	1.080502	-4.904179	-3.913083
H	3.071981	-4.702699	-2.445302
H	3.104759	-3.048232	-0.605896
H	-0.894287	-3.448467	-3.554343
H	0.318080	-2.772072	3.578216
H	-2.046053	-2.549334	4.341227
H	-3.364458	-0.547406	3.693668
H	-2.325184	1.225169	2.306269
H	3.660576	-0.825911	2.781389
H	2.648280	0.603544	3.101206
H	2.447948	-0.867179	4.094937
H	3.224186	1.395749	-0.302462
H	4.644421	2.846957	-1.738908
H	3.855322	5.107777	-2.388269
H	1.648692	5.922769	-1.602135
H	0.236360	4.479167	-0.158346
H	-1.816412	1.540329	-0.317008
H	-3.626494	3.187770	0.131839
H	-5.956948	2.688393	-0.560662
H	-6.477471	0.551041	-1.706091
H	-4.668484	-1.088746	-2.154442

Energies (0K) = -1339.88350446

Energies (0K) + ZPE = -1339.456568

Enthalpies (298K) = -1339.427759

Free Energies (298K) = -1339.519626

TS_I/I'

C	4.855097	3.507695	-0.628585
C	5.352762	2.232499	-0.293936
C	4.508072	1.241027	0.141559
C	3.104930	1.492728	0.283981
C	2.605639	2.792850	-0.112788
C	3.497536	3.779038	-0.543785
N	2.197601	0.629923	0.740764
C	2.521758	-0.629023	1.193520
N	1.429334	-1.533359	0.957428
C	1.652599	-2.613520	0.075287
C	0.533683	-3.176699	-0.585339
O	3.515746	-0.939927	1.821135
C	2.925432	-3.111770	-0.217416
C	3.090650	-4.139372	-1.141539
C	1.990002	-4.708454	-1.775387
C	0.718870	-4.228441	-1.490734
C	0.705363	-1.800682	2.204386
C	1.206605	3.004912	-0.124580
C	-0.781878	-2.658893	-0.367359
C	-1.900210	-2.235585	-0.167981
C	-3.213058	-1.734370	0.106861
C	-0.000963	3.100386	-0.201835
C	-3.468170	-1.048251	1.304219
C	-4.744923	-0.575448	1.581750
C	-5.781010	-0.775864	0.671133
C	-5.534235	-1.452232	-0.522749
C	-4.260108	-1.930681	-0.806374
C	-1.422205	3.090533	-0.332742
C	-2.081141	1.854896	-0.444126
C	-3.458626	1.818633	-0.618875
C	-4.188745	3.005458	-0.663054
C	-3.540650	4.233550	-0.539651
C	-2.161569	4.281261	-0.381079
H	5.537683	4.278988	-0.970766
H	6.416713	2.034661	-0.377125
H	4.890227	0.269599	0.428280
H	3.107521	4.749061	-0.832606
H	3.784033	-2.702235	0.301741
H	4.090269	-4.508544	-1.350411
H	2.120083	-5.515774	-2.488333
H	-0.154180	-4.647209	-1.981029

H	0.341875	-0.848784	2.603530
H	-0.152292	-2.440691	1.998150
H	1.356887	-2.280265	2.946760
H	-2.654750	-0.888513	2.005149
H	-4.930502	-0.042929	2.509195
H	-6.777327	-0.404242	0.889901
H	-6.337254	-1.608650	-1.236409
H	-4.060370	-2.458930	-1.732962
H	-1.497693	0.938765	-0.402166
H	-3.962030	0.862313	-0.722475
H	-5.266085	2.971600	-0.795168
H	-4.111326	5.156468	-0.572705
H	-1.645053	5.231700	-0.293667

Energies (0K) = -1339.85517256

Energies (0K) + ZPE = -1339.428760

Enthalpies (298K) = -1339.400898

Free Energies (298K) = -1339.489360

I'

C	0.513639	3.557551	1.792542
C	-0.740297	2.946955	1.976979
C	-0.901559	1.597608	1.774514
C	0.206188	0.779897	1.361803
C	1.490117	1.430444	1.182176
C	1.614403	2.802101	1.403550
N	0.153493	-0.514362	1.072082
C	-1.054505	-1.210202	1.218253
N	-1.270018	-2.116811	0.193846
C	-0.435534	-2.162370	-1.002783
O	-1.818207	-1.111583	2.162783
C	-2.620655	-2.547980	0.022529
C	2.606514	0.668939	0.749942
C	3.570654	0.036706	0.371278
C	-2.995558	-3.851941	0.311332
C	-4.309830	-4.264020	0.100649
C	-5.251902	-3.367016	-0.396651
C	-4.885239	-2.057936	-0.688226
C	-3.567051	-1.636397	-0.487435
C	-3.143392	-0.300472	-0.777264
C	-2.684289	0.800290	-0.995255
C	4.686625	-0.737789	-0.070585
C	4.562084	-2.128473	-0.212323
C	5.644395	-2.883945	-0.643921
C	6.858348	-2.265595	-0.938574

C	6.988528	-0.885087	-0.799505
C	5.911332	-0.121966	-0.367967
C	-2.107532	2.094258	-1.203993
C	-0.736545	2.208246	-1.481337
C	-0.154249	3.462146	-1.610140
C	-0.928725	4.612558	-1.467080
C	-2.292113	4.504665	-1.200070
C	-2.882920	3.253356	-1.069301
H	0.623022	4.626062	1.949022
H	-1.593247	3.550659	2.270178
H	-1.863854	1.121371	1.913905
H	2.582074	3.270535	1.257222
H	0.595163	-1.941211	-0.727547
H	-0.497475	-3.166594	-1.429705
H	-0.771614	-1.436533	-1.755247
H	-2.249545	-4.530903	0.711826
H	-4.598345	-5.284361	0.332574
H	-6.276616	-3.686957	-0.556633
H	-5.611580	-1.351554	-1.076380
H	3.612549	-2.598370	0.023326
H	5.541619	-3.959432	-0.750151
H	7.702883	-2.859415	-1.274170
H	7.933631	-0.401811	-1.026697
H	6.003592	0.953516	-0.255850
H	-0.136242	1.306630	-1.566721
H	0.909706	3.540902	-1.811789
H	-0.470486	5.591914	-1.566150
H	-2.897617	5.399516	-1.092383
H	-3.941885	3.159738	-0.851210

Energies (0K) = -1339.88310509

Energies (0K) + ZPE = -1339.455678

Enthalpies (298K) = -1339.427206

Free Energies (298K) = -1339.517729

TS_I/II

C	-3.346445	-2.061873	-1.901322
C	-3.746903	-0.723320	-1.868532
C	-2.833635	0.282377	-1.594120
C	-1.478130	-0.028171	-1.352056
C	-1.084959	-1.400662	-1.357729
C	-2.022996	-2.396838	-1.645541
N	-0.491512	0.862354	-1.007762
C	-0.254897	0.875399	1.054822
C	-1.306058	0.444682	1.538762

C	-0.617191	2.221817	-1.270150
N	0.426079	2.970177	-0.722242
C	1.406987	2.431284	0.136456
C	1.083005	1.402819	1.043811
C	2.714799	2.924844	0.137373
C	3.663799	2.431290	1.028685
C	3.334200	1.423295	1.929605
C	2.045144	0.905220	1.924508
C	-2.585608	-0.147035	1.661607
C	0.266094	-1.728425	-1.046722
C	1.426145	-1.947185	-0.770719
O	-1.461166	2.755071	-1.974673
C	0.374761	4.408387	-0.960699
C	-2.711945	-1.548171	1.612617
C	-3.969819	-2.131288	1.629435
C	-5.112739	-1.334206	1.702141
C	-4.995257	0.054757	1.769978
C	-3.743481	0.650112	1.754571
C	2.814940	-2.096611	-0.469509
C	3.628083	-0.952947	-0.439245
C	4.980062	-1.068539	-0.142794
C	5.536637	-2.319018	0.119762
C	4.733991	-3.458638	0.087054
C	3.379688	-3.352001	-0.203928
H	-4.069924	-2.842226	-2.116481
H	-4.785517	-0.465336	-2.051262
H	-3.141523	1.319261	-1.573111
H	-1.700435	-3.433099	-1.654161
H	3.002870	3.691085	-0.573531
H	4.671414	2.835304	1.005271
H	4.076587	1.028619	2.615065
H	1.762745	0.102523	2.597785
H	-0.103201	4.581430	-1.922528
H	-0.206308	4.911802	-0.179571
H	1.379040	4.828086	-0.974392
H	-1.814039	-2.153413	1.537080
H	-4.062747	-3.211559	1.574725
H	-6.095620	-1.795385	1.709795
H	-5.885486	0.673161	1.827947
H	-3.638423	1.729591	1.792081
H	3.180669	0.015023	-0.647466
H	5.599026	-0.176454	-0.116641
H	6.594446	-2.406954	0.348388
H	5.166310	-4.433891	0.288934

H 2.747834 -4.233974 -0.229242
 Energies (0K) = -1339.86850670
 Energies (0K) + ZPE = -1339.441551
 Enthalpies (298K) = -1339.414684
 Free Energies (298K) = -1339.499290

II

C	-4.152214	-0.048486	2.692305
C	-4.583102	-0.853239	1.640390
C	-3.673039	-1.311562	0.692011
C	-2.331205	-0.974362	0.801688
C	-1.878619	-0.179567	1.873383
C	-2.808955	0.286379	2.809582
N	-1.378229	-1.410094	-0.167877
C	-0.728924	-0.415279	-0.950247
C	-1.279900	0.765908	-1.144920
C	-1.138985	-2.769649	-0.292928
N	-0.038301	-3.112885	-1.071642
C	0.927284	-2.175932	-1.461208
C	0.605046	-0.809602	-1.441712
C	2.202687	-2.573272	-1.881325
C	3.132755	-1.619210	-2.281703
C	2.812097	-0.264298	-2.269144
C	1.550102	0.131954	-1.844849
C	-1.253255	2.137778	-1.416018
C	-0.486132	0.124869	1.990664
C	0.705844	0.343487	2.015810
O	-1.838495	-3.606044	0.245060
C	0.227453	-4.532349	-1.238092
C	-0.593946	3.023854	-0.523120
C	-0.586040	4.386782	-0.767998
C	-1.231553	4.908649	-1.891539
C	-1.890415	4.050868	-2.775555
C	-1.909053	2.685400	-2.546431
C	2.115872	0.593072	2.006425
C	2.961357	-0.209967	1.225779
C	4.327189	0.041516	1.196630
C	4.865299	1.087996	1.942960
C	4.030320	1.887114	2.722035
C	2.662703	1.644534	2.755869
H	-4.863405	0.315760	3.426702
H	-5.630958	-1.121744	1.552887
H	-3.986981	-1.941839	-0.132235
H	-2.460444	0.902254	3.631948

H	2.473865	-3.622078	-1.891976
H	4.117058	-1.944777	-2.604113
H	3.541544	0.478081	-2.574872
H	1.286197	1.184842	-1.808507
H	-0.683033	-5.072987	-0.991922
H	0.512519	-4.730177	-2.274816
H	1.030090	-4.868728	-0.571651
H	-0.099565	2.605721	0.349614
H	-0.073430	5.052335	-0.079831
H	-1.222667	5.978043	-2.076732
H	-2.391668	4.455727	-3.649569
H	-2.421355	2.014100	-3.228119
H	2.535607	-1.020884	0.641406
H	4.970421	-0.581969	0.582960
H	5.933249	1.281856	1.917860
H	4.446875	2.702755	3.305092
H	2.005722	2.262591	3.359564

Energies (0K) = -1339.92099034

Energies (0K) + ZPE = -1339.491246

Enthalpies (298K) = -1339.463699

Free Energies (298K) = -1339.551302

TS_II/III

C	1.311196	4.666492	-1.362982
C	2.597089	4.125416	-1.347147
C	2.806941	2.841846	-0.867858
C	1.741511	2.079523	-0.384164
C	0.448356	2.622100	-0.381399
C	0.248846	3.917632	-0.886517
N	1.994332	0.749753	0.061034
C	1.160423	-0.332287	-0.368078
C	-0.093890	-0.139365	-0.738366
C	3.014686	0.567372	0.992137
N	3.338905	-0.751761	1.282969
C	2.936825	-1.821174	0.471841
C	1.848003	-1.640178	-0.393696
C	3.583918	-3.059774	0.521008
C	3.148742	-4.102669	-0.289229
C	2.077989	-3.924218	-1.159873
C	1.435949	-2.692753	-1.210022
O	3.586959	1.499381	1.524097
C	4.356043	-0.962750	2.300171
C	-0.690182	1.905655	0.130674
C	-1.272781	-0.868761	-1.082589

C	-1.776646	1.662580	0.642695
C	-1.910118	-0.689409	-2.324881
C	-3.113392	-1.327750	-2.597394
C	-3.710361	-2.145196	-1.637382
C	-3.091832	-2.328930	-0.400897
C	-1.887987	-1.697760	-0.122032
C	-3.008564	1.097974	1.079528
C	-4.071669	0.966489	0.170282
C	-5.247342	0.340710	0.559629
C	-5.382422	-0.157433	1.855080
C	-4.334791	-0.021741	2.765350
C	-3.154370	0.603587	2.386462
H	1.141156	5.668166	-1.744317
H	3.438697	4.702083	-1.717342
H	3.803063	2.415486	-0.852581
H	-0.759549	4.317939	-0.883680
H	4.429068	-3.212199	1.181323
H	3.660890	-5.058662	-0.241110
H	1.746871	-4.735714	-1.798978
H	0.603693	-2.534495	-1.888322
H	4.417366	-0.061468	2.904823
H	4.070941	-1.813467	2.924091
H	5.337258	-1.156367	1.851299
H	-1.450838	-0.035934	-3.060777
H	-3.592450	-1.182740	-3.561226
H	-4.656109	-2.634056	-1.850656
H	-3.558398	-2.954207	0.354395
H	-1.407784	-1.822315	0.844093
H	-3.944186	1.328527	-0.844892
H	-6.057323	0.229176	-0.154721
H	-6.302039	-0.650315	2.155366
H	-4.438878	-0.408032	3.774648
H	-2.330786	0.706237	3.085666

Energies (0K) = -1339.90873790

Energies (0K) + ZPE = -1339.479241

Enthalpies (298K) = -1339.452583

Free Energies (298K) = -1339.536527

III

C	-1.245994	4.238576	-1.205842
C	0.105119	4.586464	-1.177046
C	1.062968	3.662355	-0.790144
C	0.673354	2.373259	-0.408901
C	-0.676552	2.010190	-0.449760

C	-1.625830	2.954385	-0.853821
N	1.635563	1.393757	-0.036853
C	1.300421	0.017002	-0.165835
C	0.008794	-0.385486	-0.151491
C	2.739082	1.777059	0.732921
N	3.661486	0.772575	0.990467
C	3.673488	-0.425397	0.265803
C	2.482959	-0.843202	-0.346728
C	4.832031	-1.199141	0.150037
C	4.806101	-2.371226	-0.595878
C	3.641404	-2.770197	-1.246507
C	2.490136	-2.003463	-1.125207
O	2.890246	2.905579	1.157765
C	4.805497	1.134001	1.812510
C	-1.072696	0.621776	-0.101648
C	-0.395625	-1.816048	-0.137936
C	-2.318011	0.294701	0.179981
C	-1.302929	-2.309498	-1.081747
C	-1.690661	-3.645442	-1.059118
C	-1.186795	-4.502648	-0.083707
C	-0.297027	-4.015806	0.871019
C	0.093029	-2.681244	0.845637
C	-3.679613	0.171061	0.374312
C	-4.547815	-0.077059	-0.728827
C	-5.908623	-0.220456	-0.534226
C	-6.458786	-0.126964	0.747840
C	-5.623042	0.114028	1.842881
C	-4.259199	0.259902	1.672667
H	-1.993454	4.962517	-1.514236
H	0.418410	5.584248	-1.467292
H	2.109023	3.934789	-0.768920
H	-2.670063	2.655623	-0.888402
H	5.753695	-0.882693	0.623430
H	5.710979	-2.964904	-0.681161
H	3.629625	-3.671598	-1.849550
H	1.581974	-2.303372	-1.635859
H	4.526066	1.990704	2.420630
H	5.065858	0.288669	2.453640
H	5.672132	1.404087	1.198198
H	-1.696290	-1.638315	-1.840495
H	-2.389757	-4.017057	-1.802074
H	-1.492295	-5.544324	-0.063345
H	0.090668	-4.676246	1.640638
H	0.787411	-2.297641	1.587732

H	-4.118312	-0.148960	-1.723456
H	-6.554101	-0.407677	-1.387371
H	-7.528067	-0.241379	0.892572
H	-6.047218	0.189180	2.839730
H	-3.608707	0.446499	2.520748

Energies (0K) = -1339.97988873

Energies (0K) + ZPE = -1339.547500

Enthalpies (298K) = -1339.522087

Free Energies (298K) = -1339.602678

TS_II/V

C	0.192299	4.487231	-0.352798
C	1.513240	4.362115	-0.807841
C	2.059588	3.101899	-1.050103
C	1.273663	1.974224	-0.893704
C	-0.109170	2.066194	-0.511926
C	-0.611714	3.376062	-0.221736
N	1.798758	0.673625	-0.728478
C	1.281301	0.055220	0.452347
C	0.273151	0.698552	1.037245
C	2.858044	0.212238	-1.487841
N	3.385933	-1.010145	-1.098508
C	3.000113	-1.682131	0.069051
C	1.964600	-1.172002	0.873404
C	3.644011	-2.865283	0.451150
C	3.271798	-3.522494	1.616489
C	2.256845	-3.014156	2.422322
C	1.612103	-1.844866	2.046025
C	-0.760314	0.541646	2.009688
C	-1.082725	1.114094	-0.998963
C	-1.967595	0.367745	-1.354184
O	3.281043	0.834200	-2.444952
C	4.453254	-1.555383	-1.923202
C	-1.714001	-0.491519	1.886060
C	-2.767959	-0.587246	2.784978
C	-2.901578	0.344506	3.815180
C	-1.972398	1.377368	3.941399
C	-0.915951	1.482013	3.046658
C	-3.029825	-0.525118	-1.709696
C	-2.992240	-1.267208	-2.897986
C	-4.034715	-2.131151	-3.212863
C	-5.123120	-2.263383	-2.353152
C	-5.165947	-1.527641	-1.170509
C	-4.127272	-0.664207	-0.846215

H	-0.213502	5.470997	-0.137808
H	2.130192	5.245394	-0.935684
H	3.099947	2.985626	-1.328451
H	-1.657496	3.467791	0.052209
H	4.442084	-3.273297	-0.155498
H	3.786099	-4.437095	1.894470
H	1.969887	-3.523615	3.335842
H	0.820199	-1.434284	2.663998
H	4.574494	-0.899708	-2.781429
H	5.392271	-1.598015	-1.361535
H	4.190071	-2.562057	-2.261130
H	-1.609205	-1.206752	1.074934
H	-3.492664	-1.389374	2.677526
H	-3.728414	0.268145	4.514497
H	-2.077555	2.107269	4.738313
H	-0.196717	2.291333	3.129596
H	-2.143247	-1.157223	-3.564896
H	-3.998353	-2.702841	-4.135113
H	-5.936130	-2.937400	-2.604662
H	-6.012336	-1.626695	-0.497619
H	-4.145707	-0.090066	0.075311

Energies (0K) = -1339.89190817

Energies (0K) + ZPE = -1339.463211

Enthalpies (298K) = -1339.436412

Free Energies (298K) = -1339.521415

V

C	1.228201	-0.495146	3.797106
C	0.819396	-1.855257	3.667046
C	-0.006475	-2.265187	2.602571
C	-0.258158	-1.363962	1.602616
C	0.520424	-0.071430	1.466290
C	1.020704	0.409467	2.807427
N	-1.260542	-1.331099	0.625852
C	-1.387049	-0.001865	0.128772
C	-0.453882	0.807110	0.678379
C	-2.208681	-2.328961	0.469497
N	-3.276423	-2.010467	-0.359926
C	-3.347699	-0.827856	-1.106899
C	-2.408438	0.199630	-0.893056
C	-4.341695	-0.658754	-2.079299
C	-4.383208	0.499630	-2.843887
C	-3.428646	1.498545	-2.668958
C	-2.446487	1.339049	-1.703291

C	-0.303134	2.267543	0.589770
C	1.712287	-0.321212	0.605821
C	2.688137	-0.506714	-0.085735
O	-2.110836	-3.404754	1.028503
C	-4.287153	-3.040753	-0.545215
C	0.948248	2.858746	0.368624
C	1.079750	4.244341	0.341455
C	-0.030179	5.061380	0.535469
C	-1.277471	4.483928	0.767863
C	-1.410489	3.101611	0.804473
C	3.849691	-0.715836	-0.901017
C	3.739301	-1.335363	-2.153591
C	4.868640	-1.525987	-2.940235
C	6.117405	-1.102032	-2.490541
C	6.233811	-0.486015	-1.246158
C	5.109313	-0.293499	-0.453487
H	1.684682	-0.174647	4.729360
H	1.039231	-2.556779	4.463706
H	-0.497100	-3.228267	2.613513
H	1.311077	1.451788	2.893660
H	-5.077966	-1.433831	-2.250244
H	-5.160446	0.611121	-3.593338
H	-3.443672	2.390863	-3.285105
H	-1.687757	2.101384	-1.571497
H	-4.080247	-3.838841	0.162926
H	-5.280019	-2.624518	-0.353635
H	-4.253237	-3.441603	-1.563855
H	1.815309	2.224983	0.205903
H	2.055667	4.685990	0.163591
H	0.075815	6.141585	0.512795
H	-2.146974	5.112490	0.935644
H	-2.378712	2.649637	1.003033
H	2.763244	-1.662351	-2.496809
H	4.773302	-2.006634	-3.909054
H	6.997736	-1.252219	-3.107980
H	7.204812	-0.154626	-0.891313
H	5.191914	0.182576	0.518319

Energies (0K) = -1339.93077520

Energies (0K) + ZPE = -1339.499695

Enthalpies (298K) = -1339.472911

Free Energies (298K) = -1339.558383

TS_III/IV

C	-1.531325	4.022820	-0.859680
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C	-0.212133	4.473978	-0.880743
C	0.833827	3.601019	-0.625996
C	0.574060	2.258255	-0.326007
C	-0.749522	1.787089	-0.333359
C	-1.788405	2.686932	-0.603384
N	1.647955	1.351919	-0.077404
C	1.426646	-0.046700	-0.236274
C	0.170223	-0.540442	-0.218671
C	2.760518	1.802183	0.645196
N	3.788470	0.882377	0.807091
C	3.841999	-0.322776	0.099360
C	2.651276	-0.827342	-0.442343
C	5.038059	-1.028854	-0.060795
C	5.044344	-2.224107	-0.770135
C	3.872315	-2.716938	-1.338880
C	2.686467	-2.012486	-1.180739
O	2.840300	2.923023	1.108675
C	4.949662	1.324687	1.563397
C	-1.006025	0.344894	-0.159376
C	-0.277156	-1.940975	-0.094296
C	-1.551944	-2.194763	-0.687554
C	-2.186152	-0.279201	-0.083139
C	0.233047	-2.828745	0.845035
C	-0.480320	-3.975807	1.196429
C	-1.734246	-4.228574	0.626638
C	-2.255967	-3.369166	-0.323693
H	-1.770310	-1.765578	-1.664605
C	-3.589069	-0.061685	0.081665
C	-4.522345	-0.586261	-0.834227
C	-5.884684	-0.410514	-0.634826
C	-6.350354	0.282893	0.481471
C	-5.438315	0.800375	1.401752
C	-4.074580	0.625975	1.213520
H	-2.350400	4.705202	-1.062790
H	0.008427	5.512708	-1.105585
H	1.853830	3.956767	-0.644958
H	-2.807153	2.313881	-0.624272
H	5.962418	-0.644530	0.353221
H	5.978877	-2.763146	-0.890255
H	3.883336	-3.638243	-1.911075
H	1.768807	-2.378433	-1.628313
H	4.652327	2.175510	2.170808
H	5.292796	0.508560	2.203936
H	5.765630	1.630336	0.898406

H	1.172220	-2.596242	1.339641
H	-0.072645	-4.657923	1.935534
H	-2.287152	-5.117930	0.913970
H	-3.203818	-3.591704	-0.804859
H	-4.163532	-1.127173	-1.705644
H	-6.589371	-0.817024	-1.354096
H	-7.416440	0.416190	0.635712
H	-5.793542	1.338913	2.275348
H	-3.361080	1.021024	1.930585

Energies (0K) = -1339.95637709

Energies (0K) + ZPE = -1339.524459

Enthalpies (298K) = -1339.499042

Free Energies (298K) = -1339.579716

IV

C	-1.675709	3.805687	-1.102554
C	-0.402022	4.346916	-0.928806
C	0.653636	3.542465	-0.531304
C	0.440853	2.183567	-0.270167
C	-0.843032	1.628445	-0.418516
C	-1.882613	2.458187	-0.863665
N	1.535675	1.329334	0.048640
C	1.442056	-0.061358	-0.225069
C	0.195859	-0.652030	-0.245724
C	2.595807	1.818434	0.821585
N	3.689077	0.970090	0.942720
C	3.859513	-0.155003	0.129797
C	2.718152	-0.708865	-0.474835
C	5.112153	-0.738634	-0.073597
C	5.229310	-1.853185	-0.897785
C	4.111044	-2.382203	-1.538962
C	2.866313	-1.802666	-1.333532
O	2.573979	2.907237	1.361028
C	4.792196	1.438271	1.767165
C	-1.016100	0.185511	-0.213516
C	-0.215366	-2.015400	-0.155945
C	-1.719104	-2.043875	-0.251895
C	-2.128336	-0.588221	-0.123036
C	0.470329	-3.185391	0.215445
C	-0.227570	-4.266117	0.709676
C	-1.646300	-4.186201	0.960561
C	-2.363602	-3.108660	0.584326
H	-1.975147	-2.312990	-1.304660
C	-3.541387	-0.213211	0.031851

C	-4.544840	-0.884709	-0.680281
C	-5.885998	-0.561059	-0.499192
C	-6.250276	0.432486	0.404878
C	-5.263095	1.097328	1.131313
C	-3.924118	0.774020	0.952088
H	-2.497687	4.428844	-1.439735
H	-0.221319	5.399022	-1.125216
H	1.643563	3.961037	-0.420298
H	-2.860881	2.024458	-1.034277
H	5.995399	-0.321175	0.394812
H	6.207423	-2.298094	-1.050834
H	4.210104	-3.233063	-2.204574
H	1.986741	-2.187540	-1.840206
H	4.408965	2.196912	2.444938
H	5.195486	0.596947	2.335963
H	5.588441	1.877501	1.155316
H	1.554724	-3.215728	0.207482
H	0.311570	-5.157201	1.014075
H	-2.125696	-4.998794	1.499053
H	-3.426405	-3.027650	0.796230
H	-4.269457	-1.659679	-1.391600
H	-6.647834	-1.086902	-1.066794
H	-7.296616	0.683263	0.548847
H	-5.538914	1.865327	1.847803
H	-3.154093	1.284472	1.524102

Energies (0K) = -1340.00183318

Energies (0K) + ZPE = -1339.568957

Enthalpies (298K) = -1339.543641

Free Energies (298K) = -1339.623007

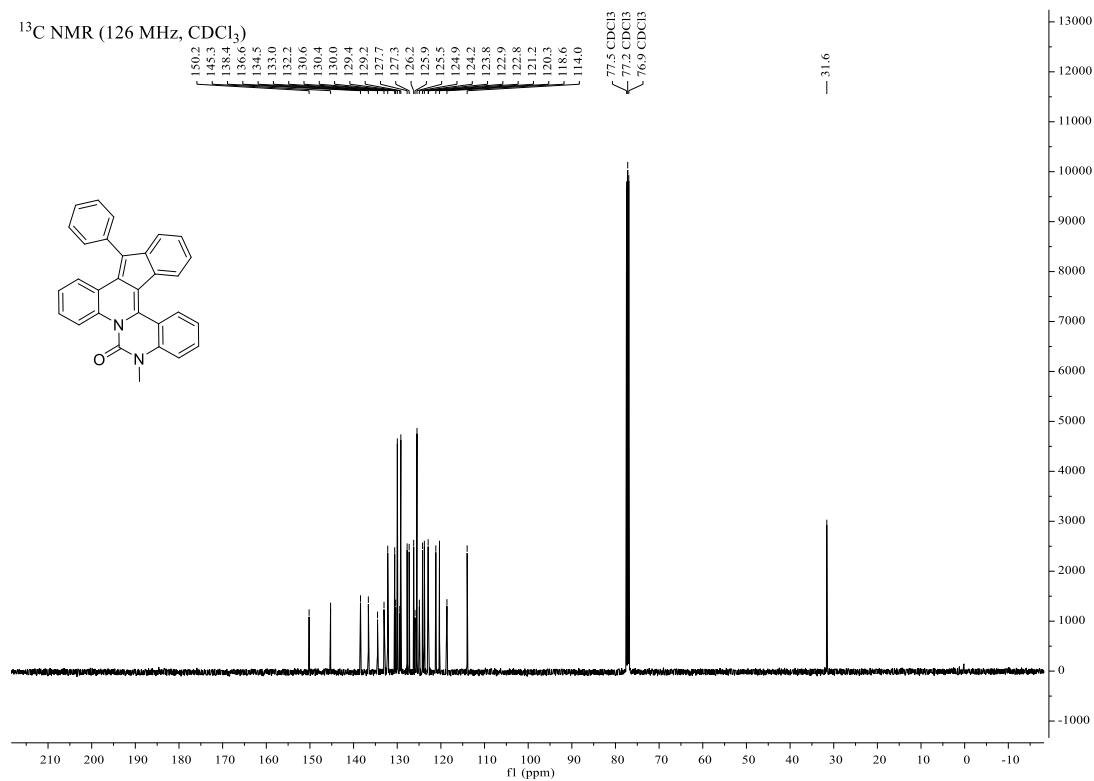
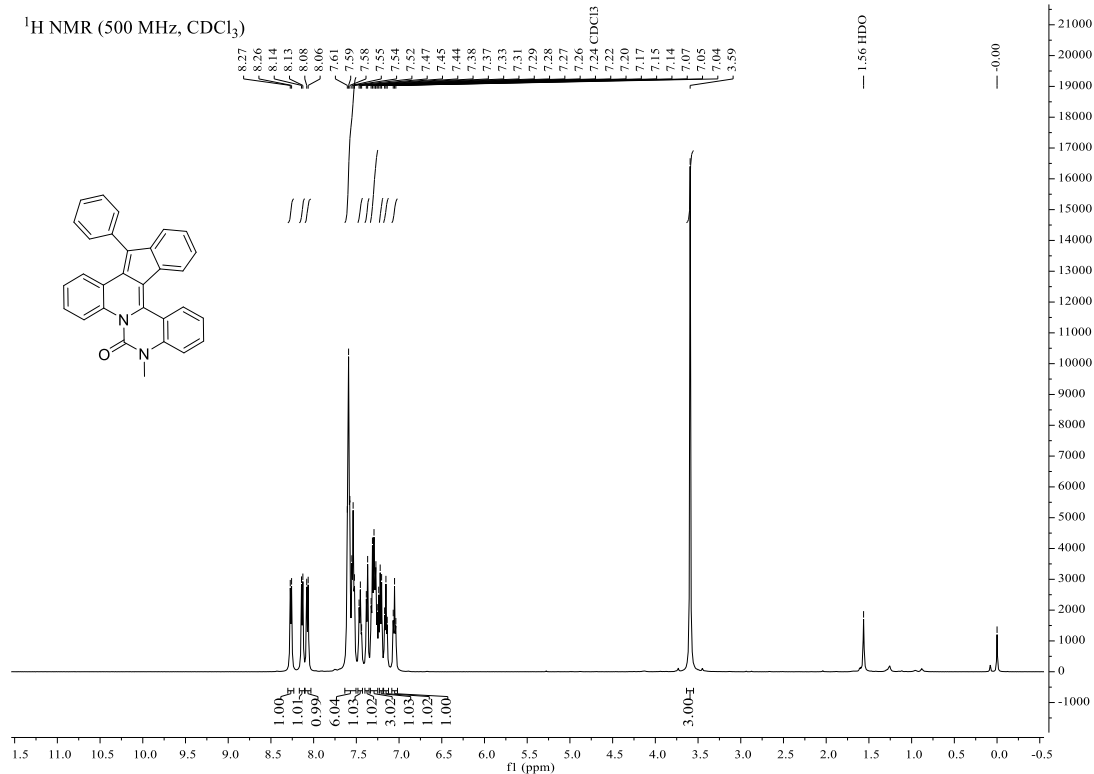
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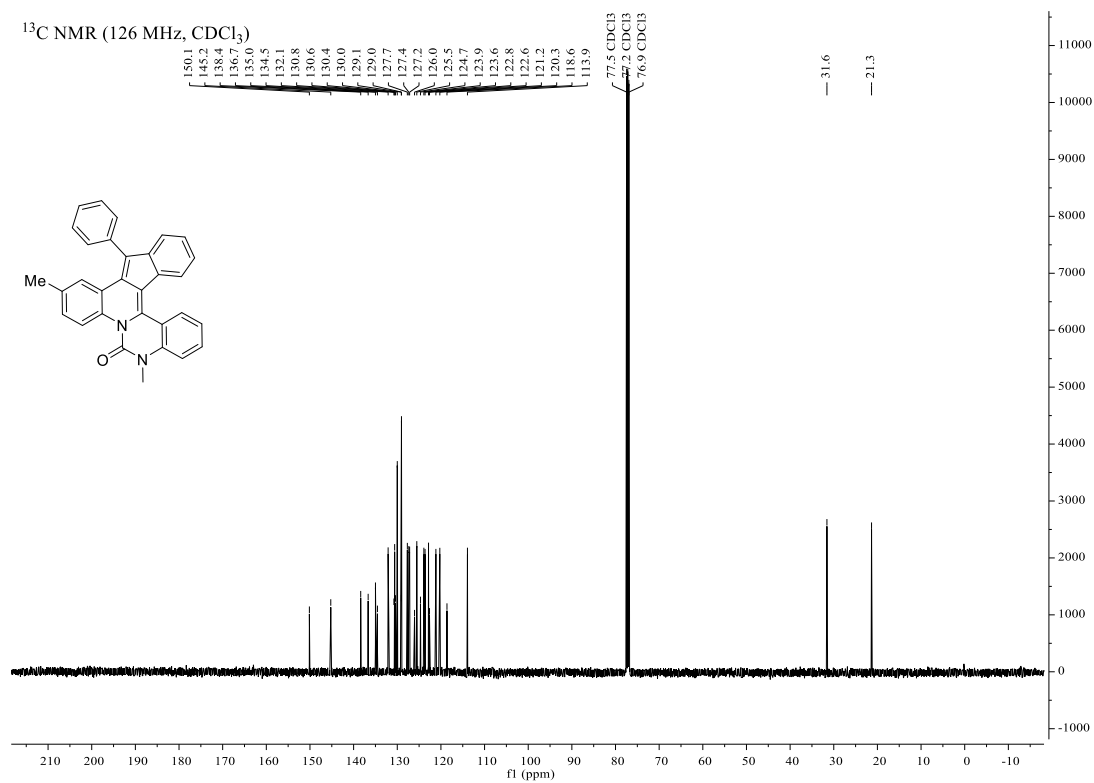
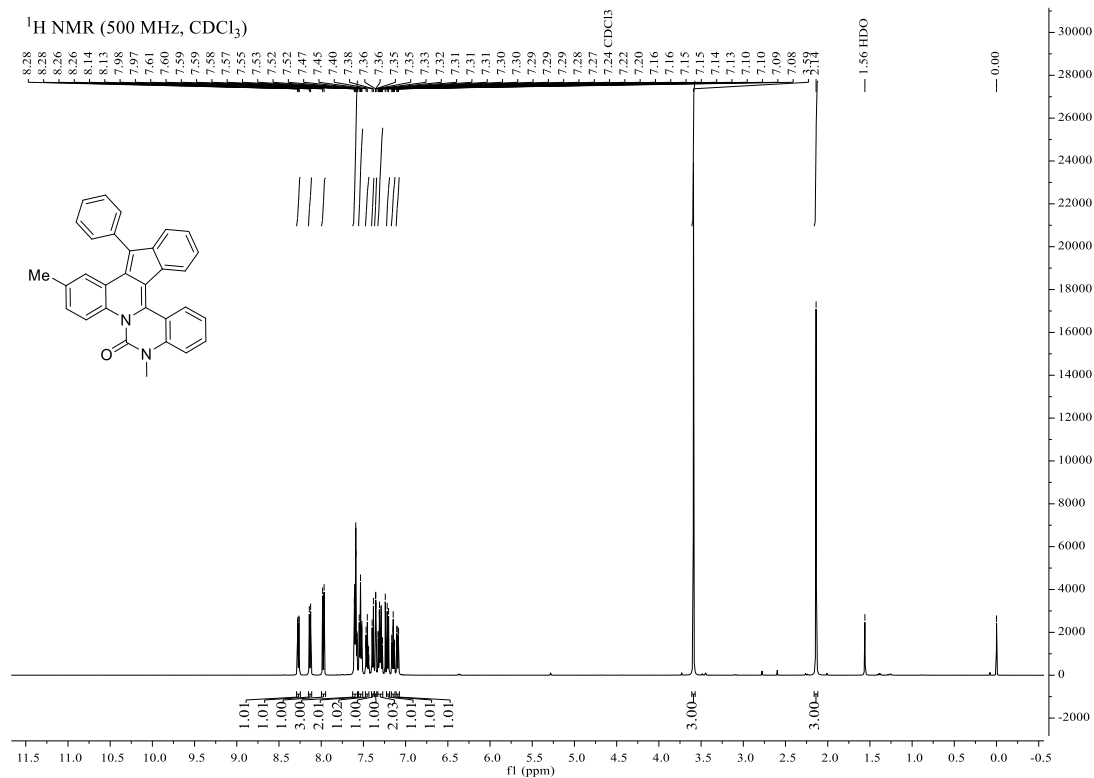
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11. NMR Spectra for New Compounds

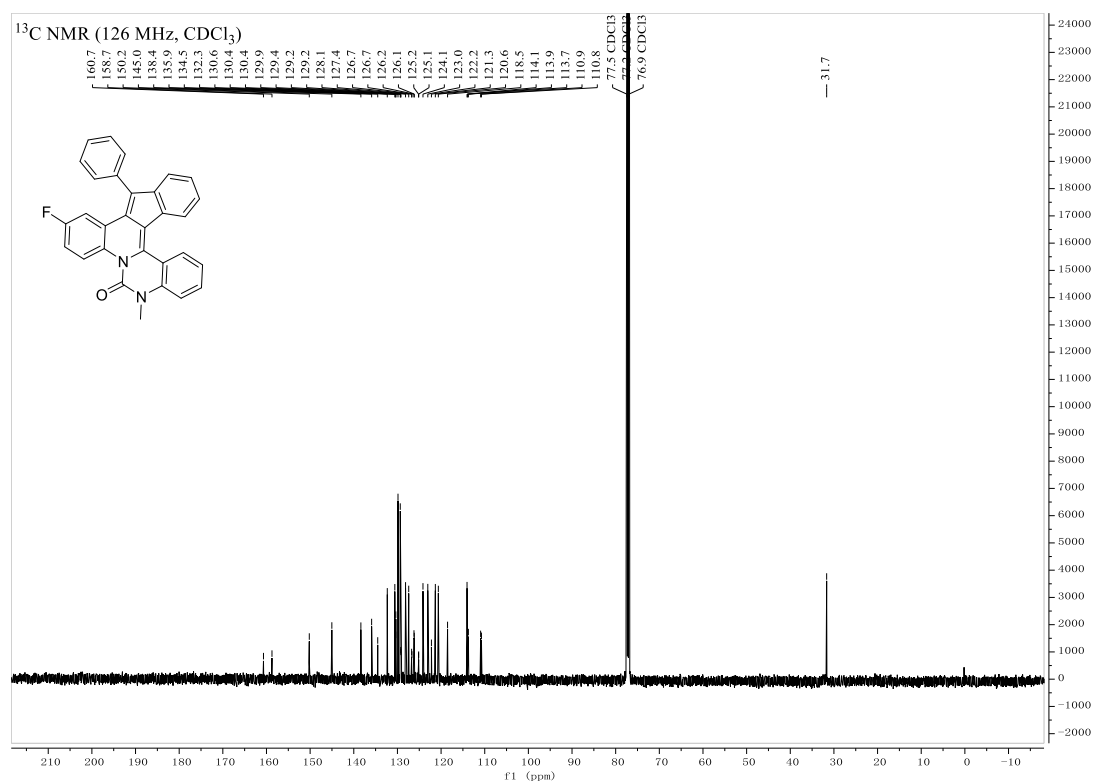
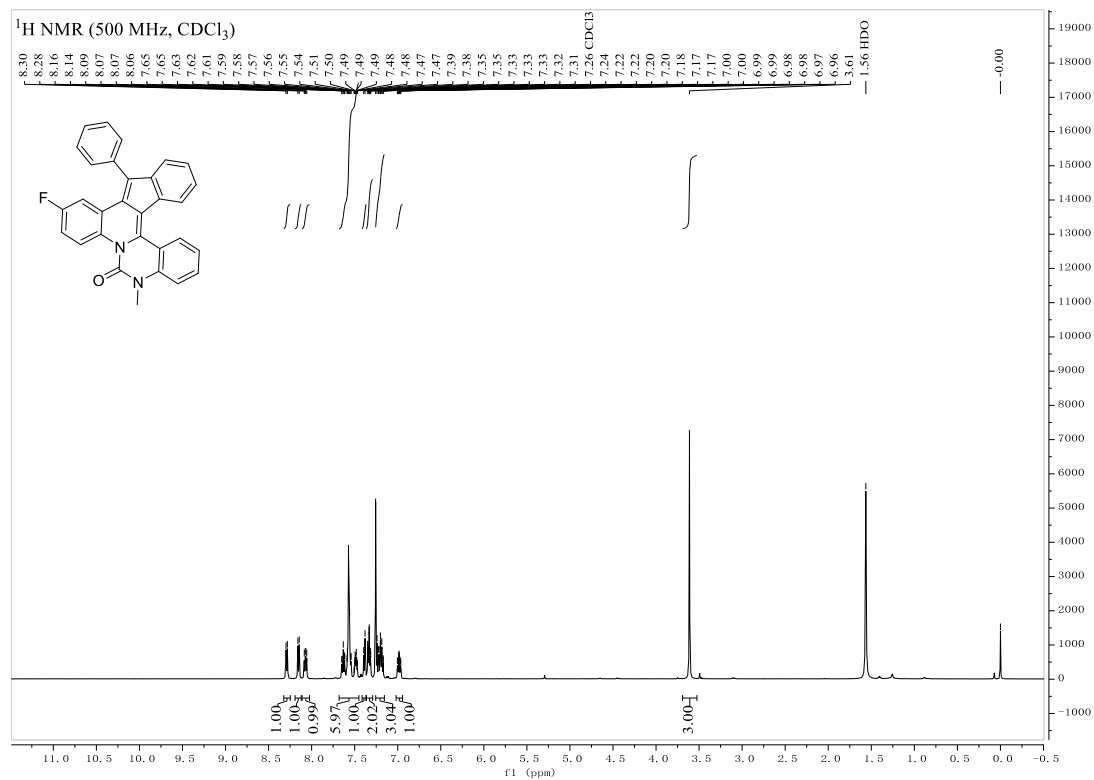
Compound 2



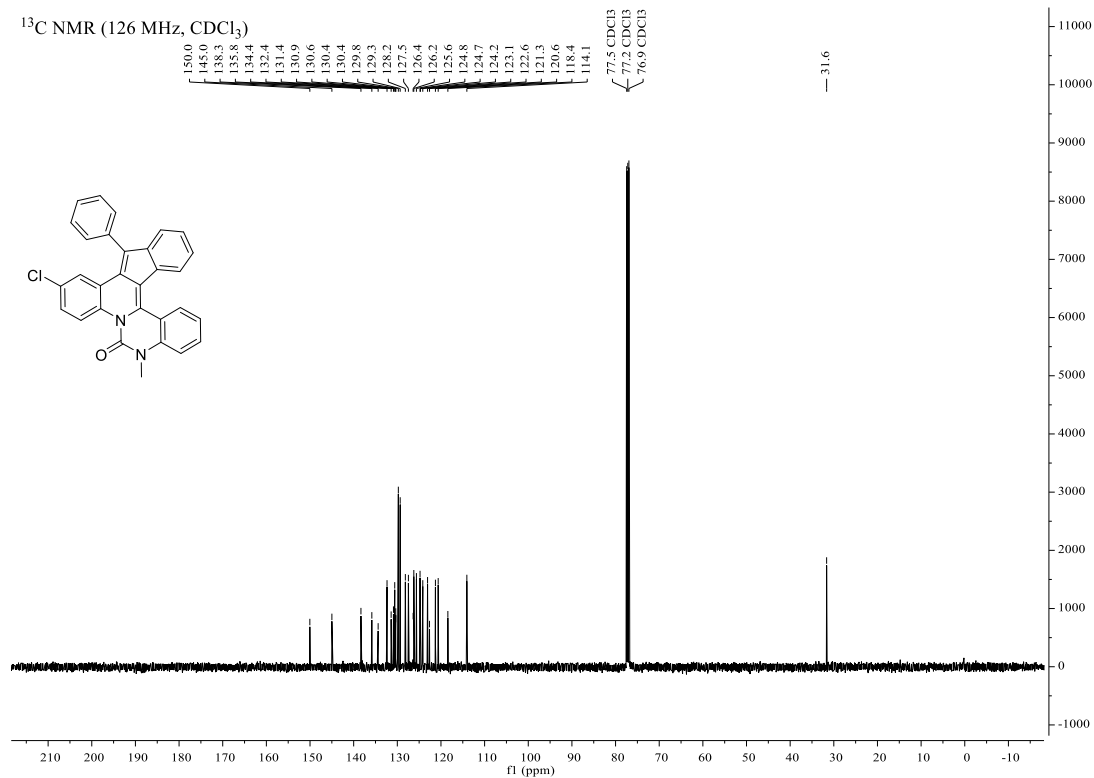
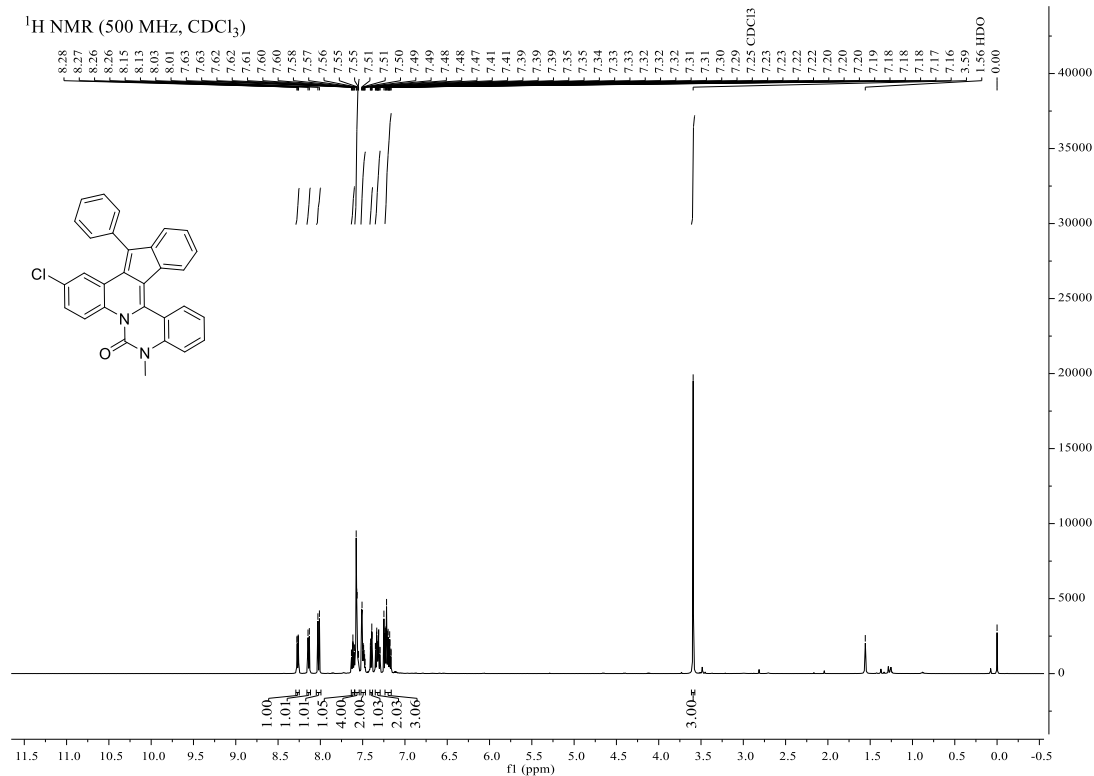
Compound 3



Compound 4



Compound 5

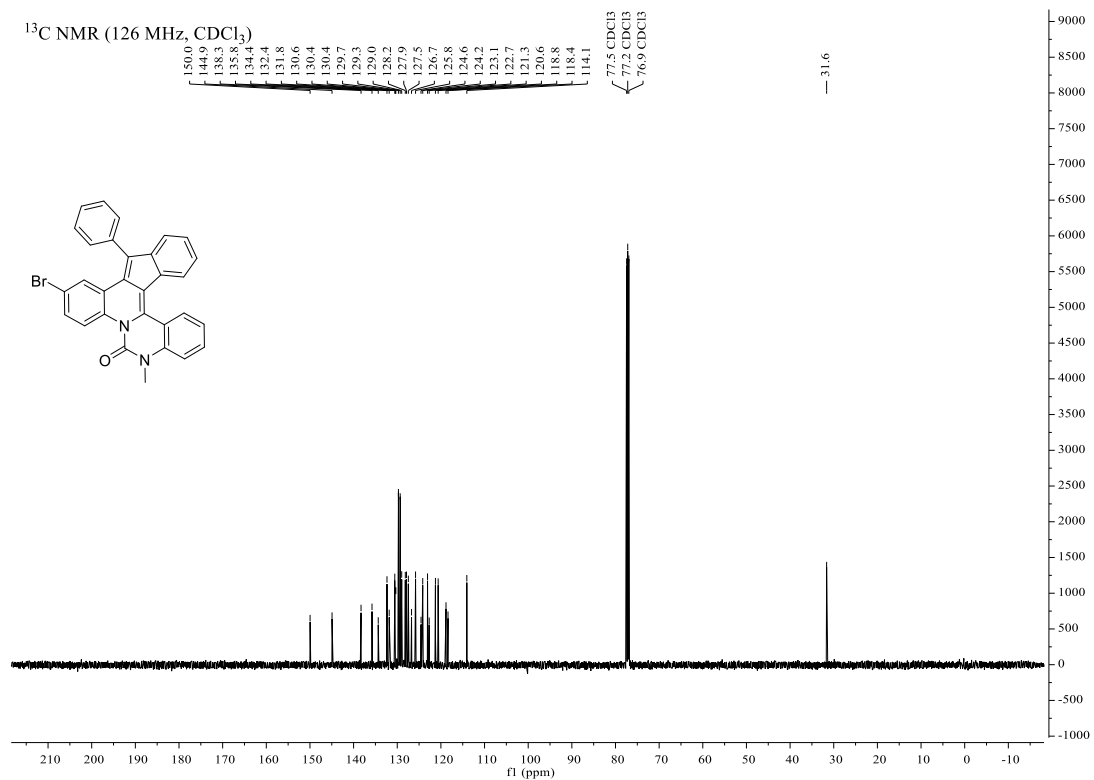


¹H NMR (500 MHz, CDCl₃)

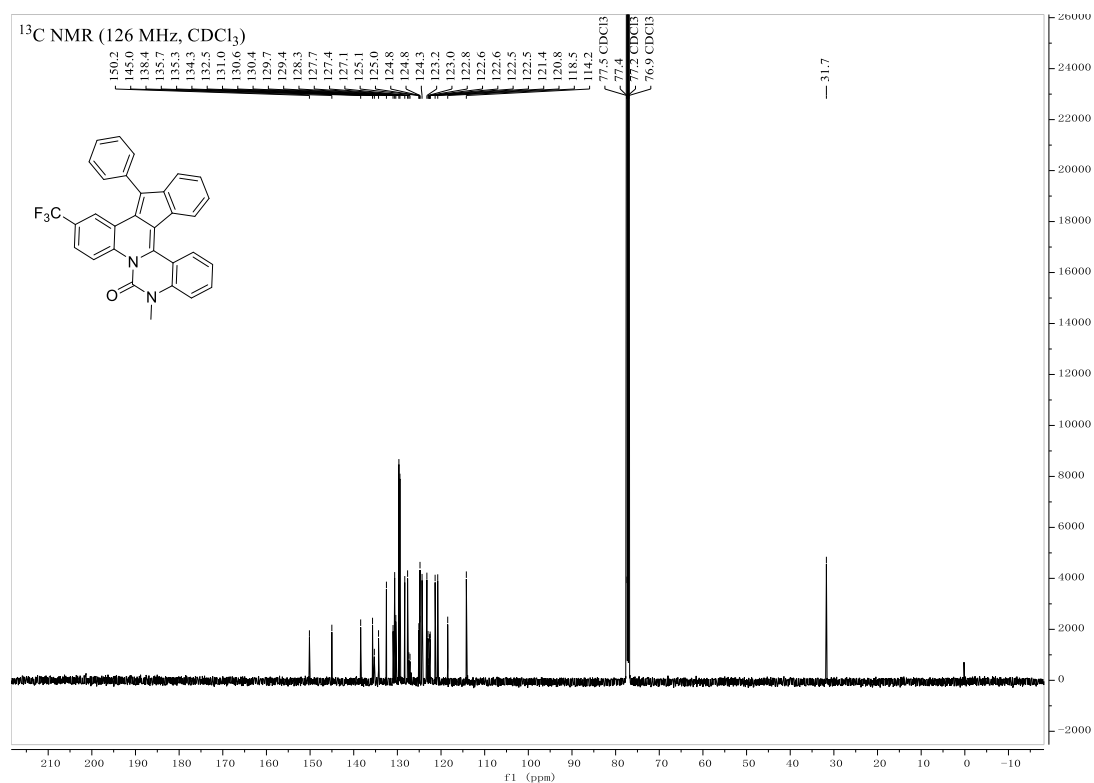
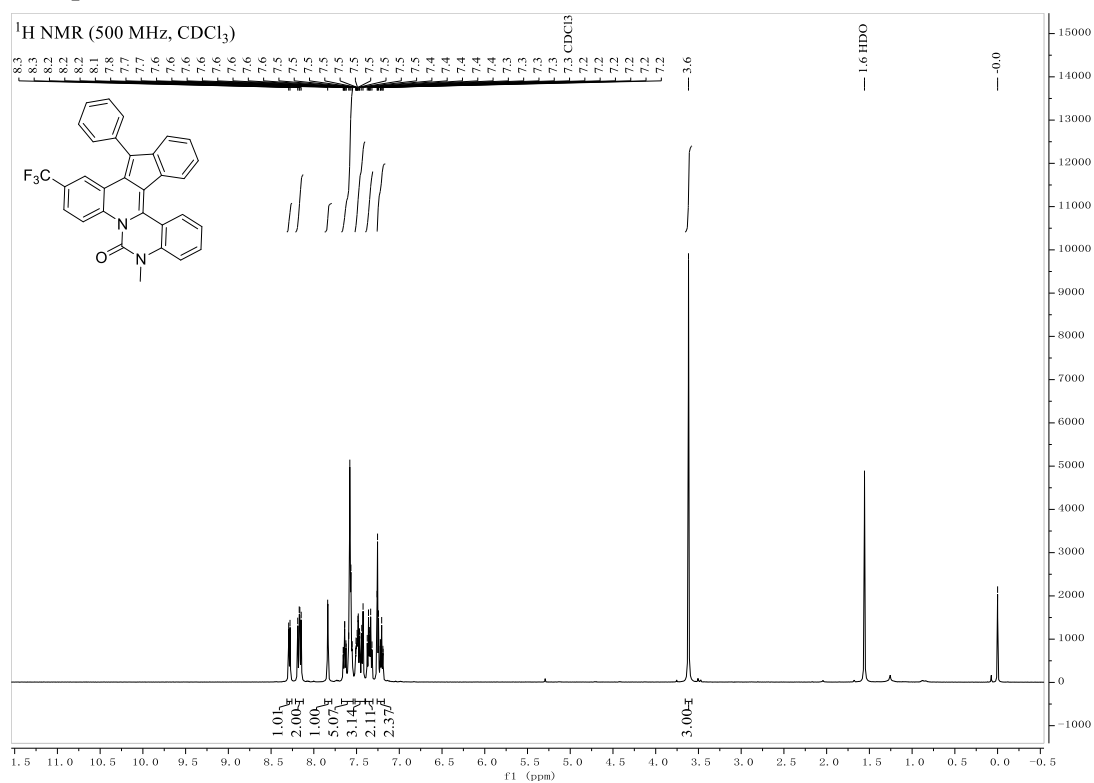
Chemical structure: CN1CCCC1c2nc3ccccc3c4c2c5ccccc5c4Br

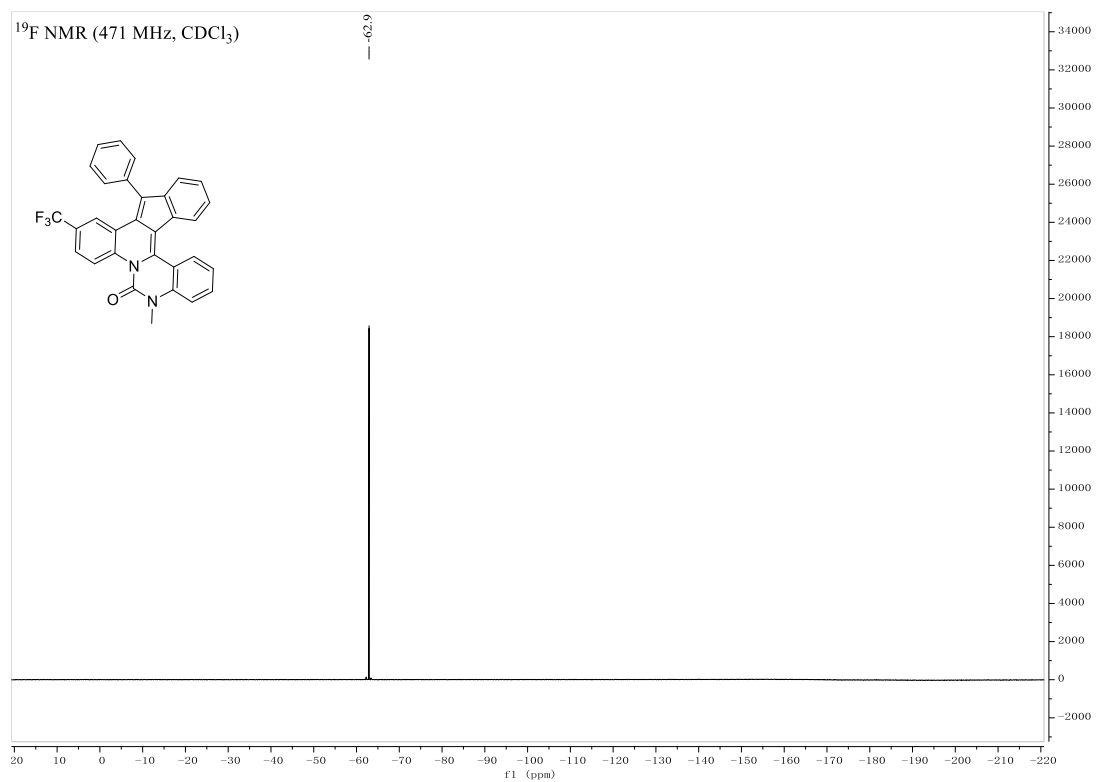
Peak list (ppm): 8.26, 8.26, 8.26, 8.24, 8.24, 8.24, 8.14, 8.14, 8.12, 8.12, 7.96, 7.96, 7.94, 7.66, 7.66, 7.62, 7.62, 7.61, 7.61, 7.60, 7.60, 7.60, 7.60, 7.59, 7.59, 7.58, 7.57, 7.57, 7.56, 7.56, 7.55, 7.55, 7.50, 7.50, 7.50, 7.49, 7.49, 7.48, 7.48, 7.47, 7.47, 7.41, 7.41, 7.41, 7.39, 7.39, 7.39, 7.39, 7.35, 7.35, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.32, 7.31, 7.31, 7.31, 7.29, 7.29, 7.29, 7.28, 7.28, 7.24 CDCl₃, 7.24 CDCl₃, 7.21, 7.21, 7.20, 7.20, 7.19, 7.19, 7.18, 7.18, 7.17, 7.17, 7.16, 7.16, 3.58, 0.00.

Integration values: 1.01, 1.02, 1.00, 1.00, 5.03, 1.04, 1.04, 3.02, 2.04, 3.00.

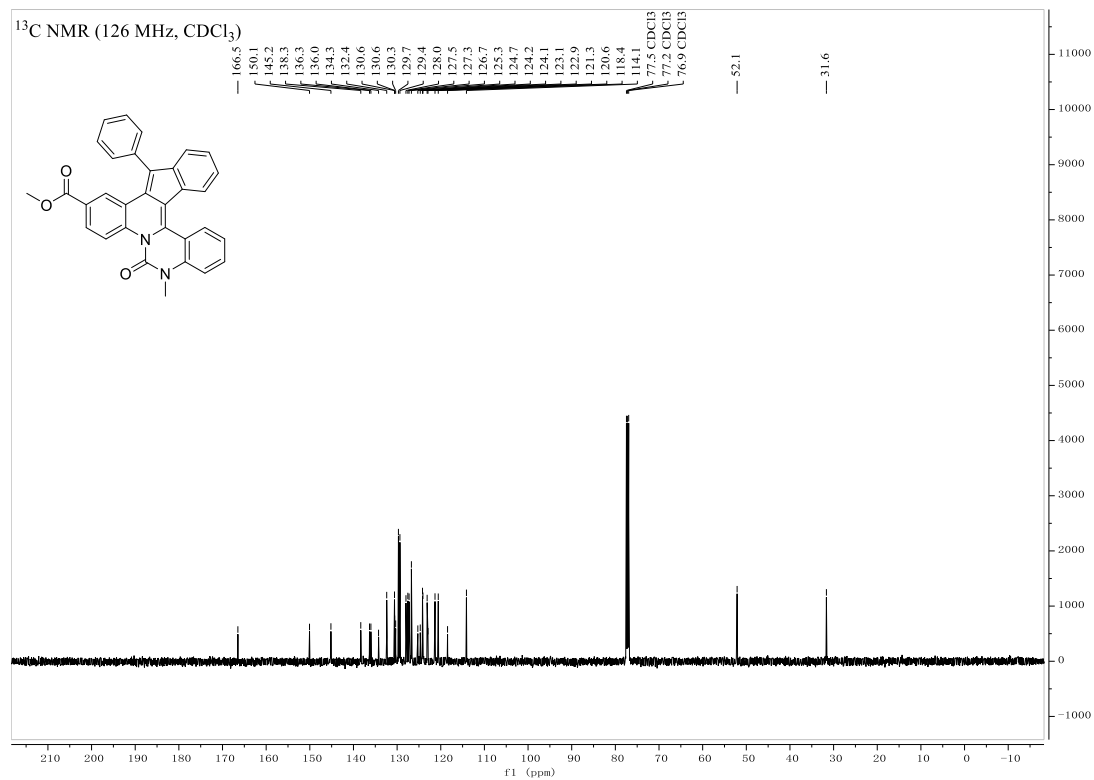
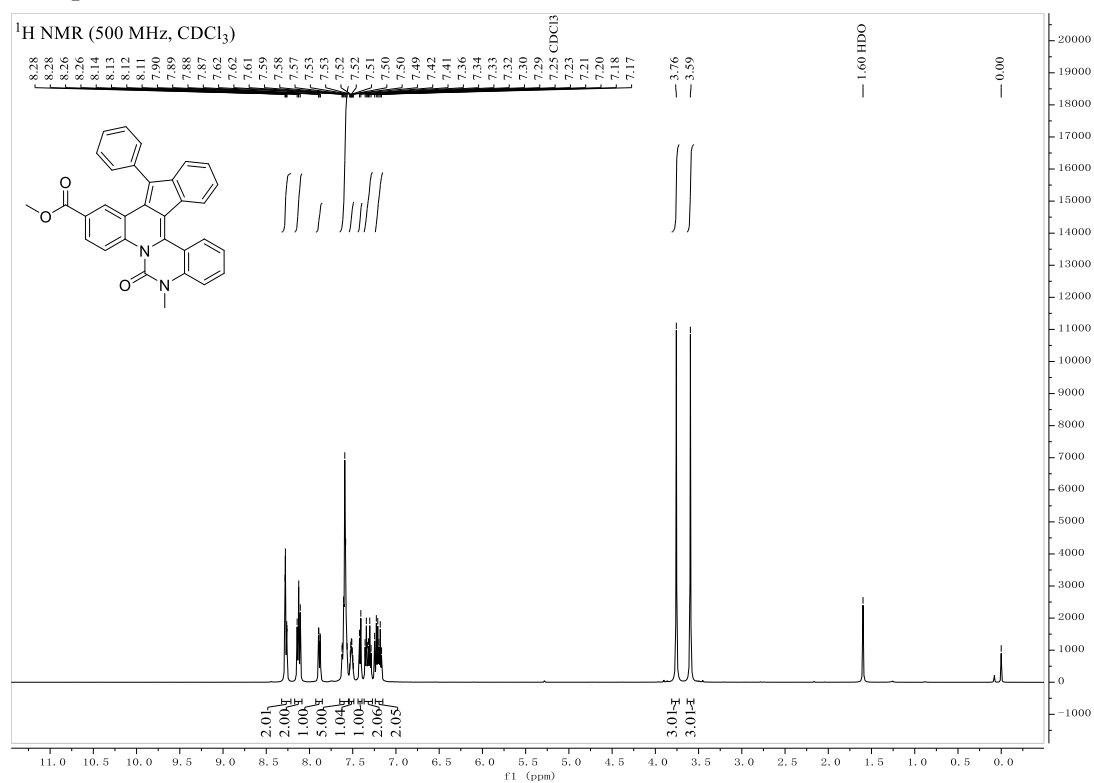


Compound 7



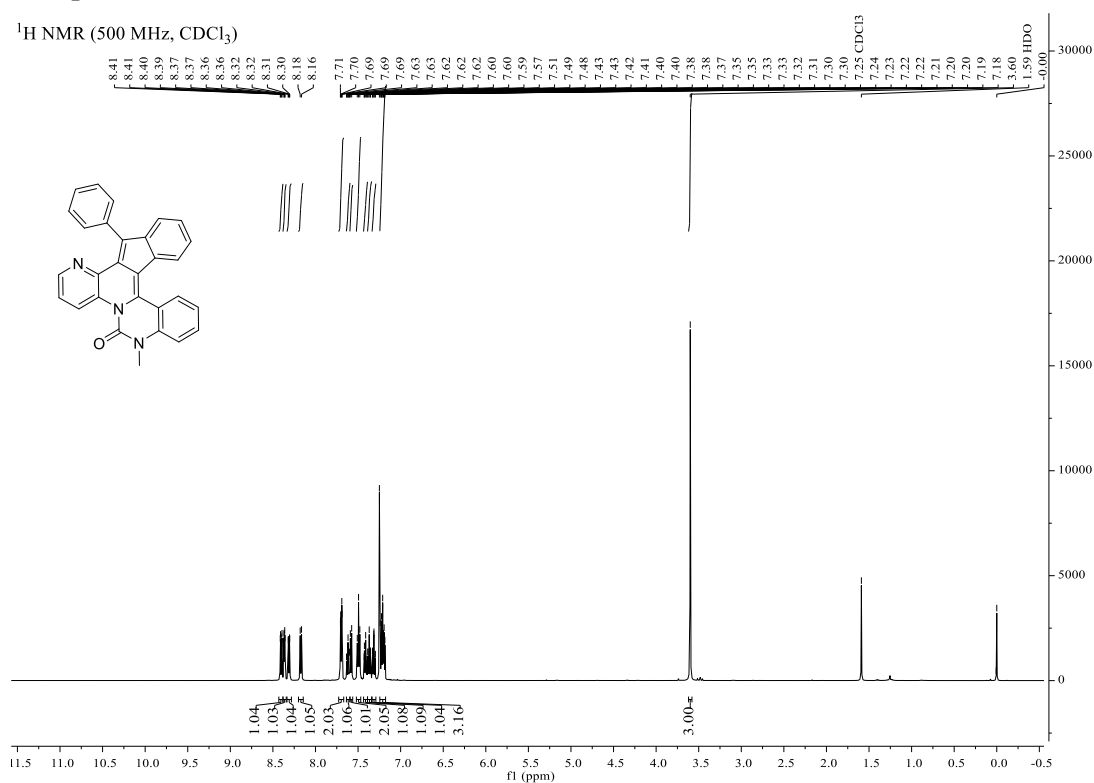


Compound 8

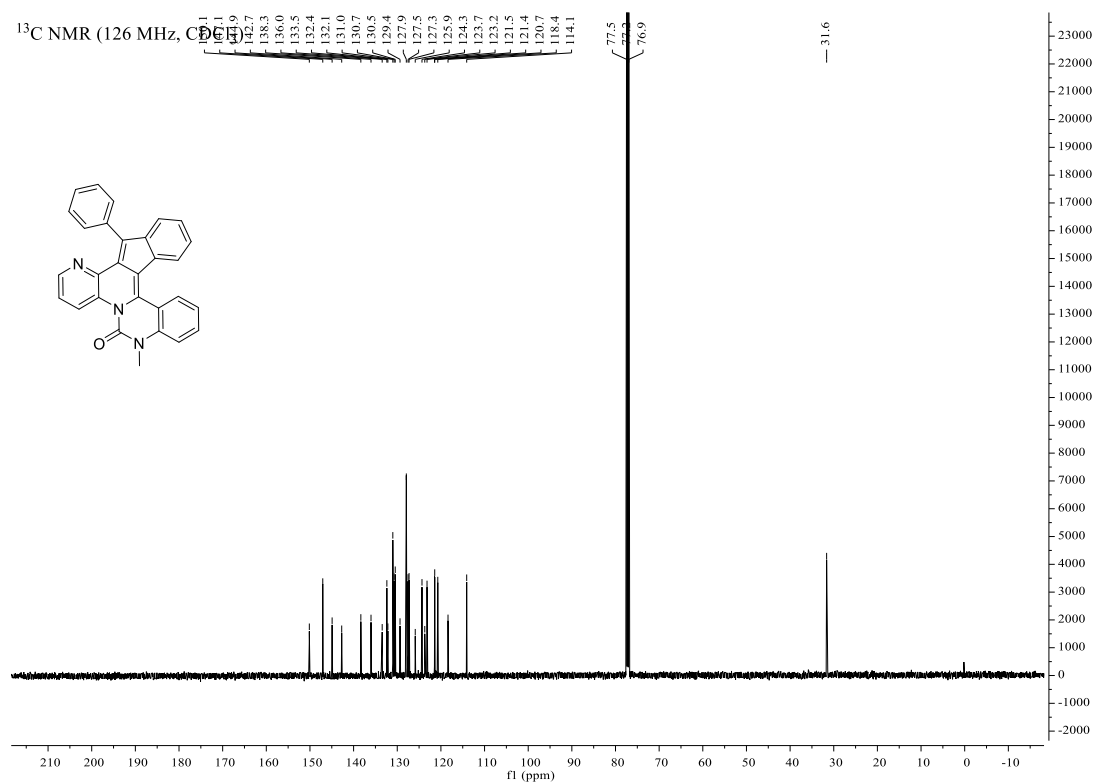


Compound 9

¹H NMR (500 MHz, CDCl₃)

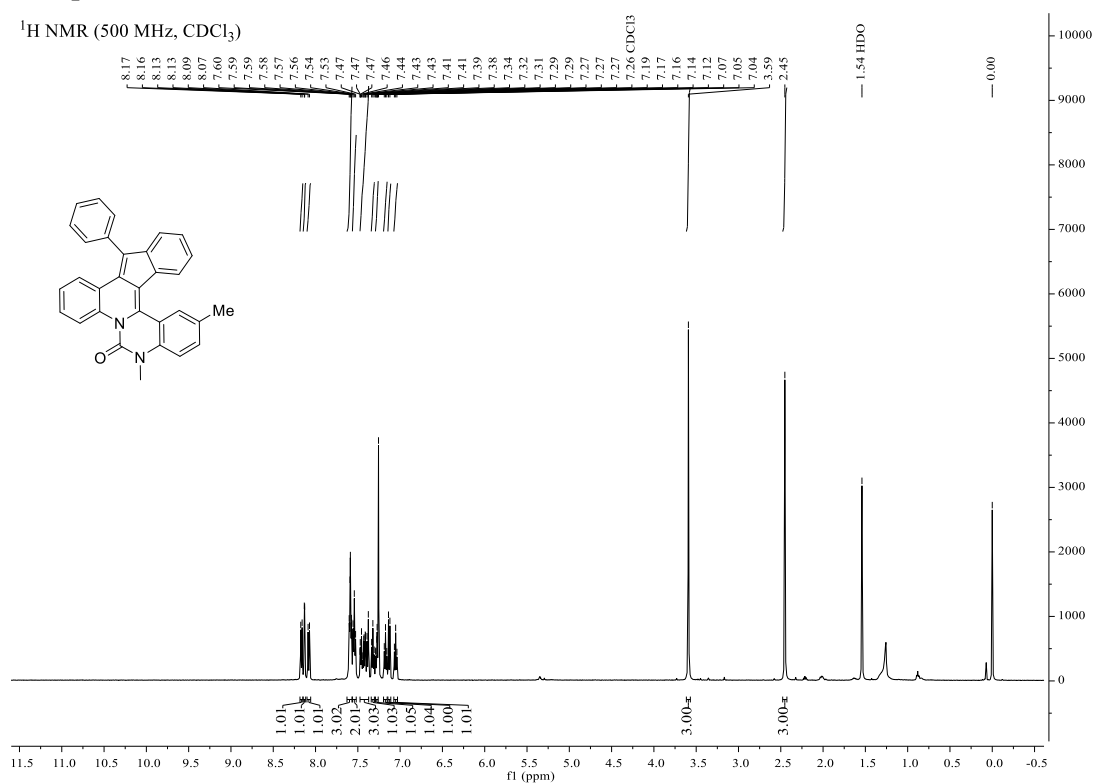


¹³C NMR (126 MHz, CDCl₃)

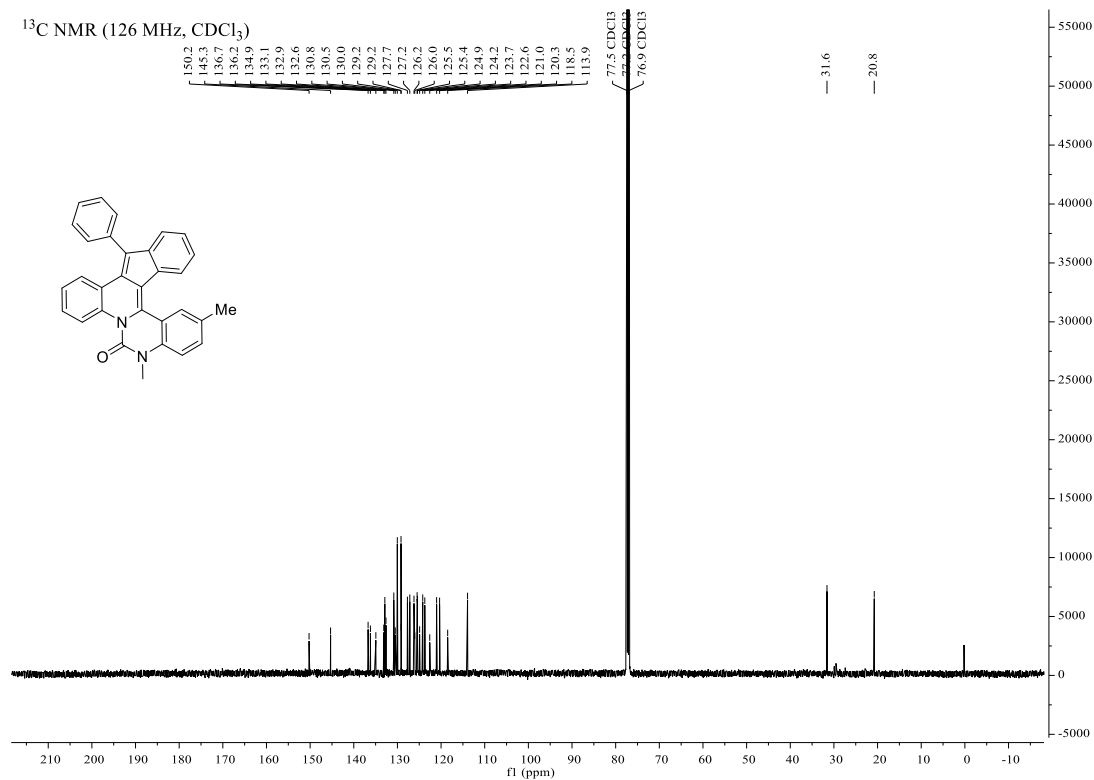


Compound 10

¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)

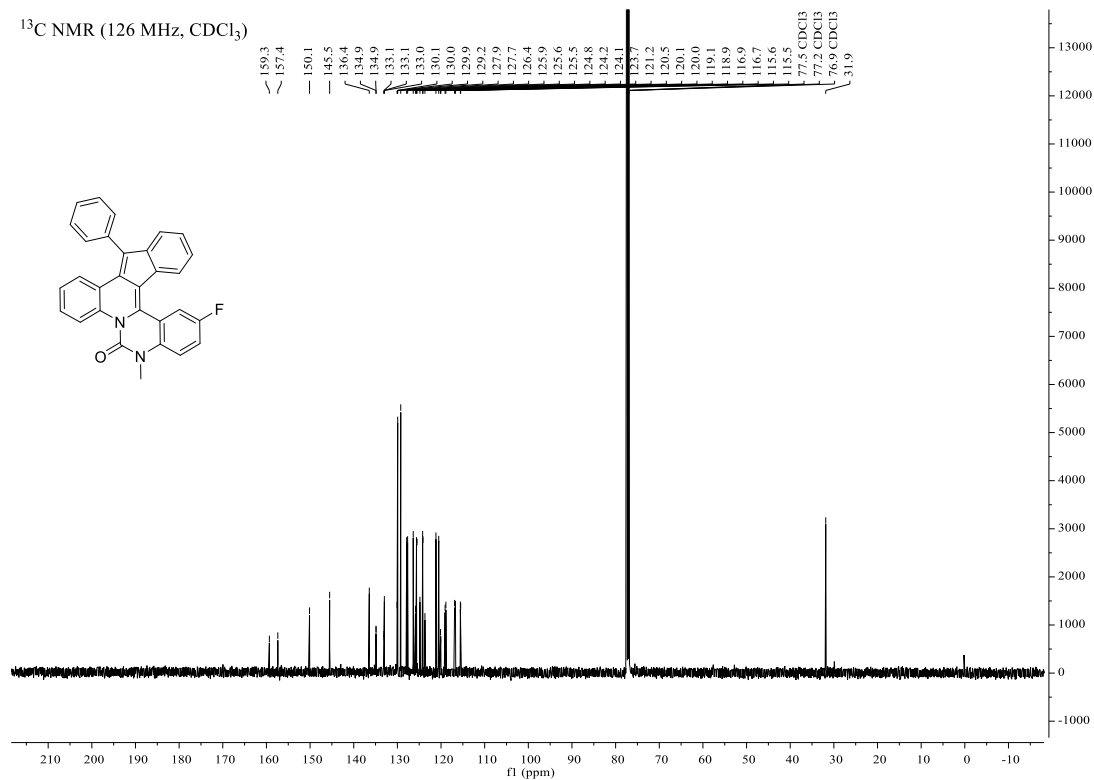


¹H NMR (500 MHz, CDCl₃)

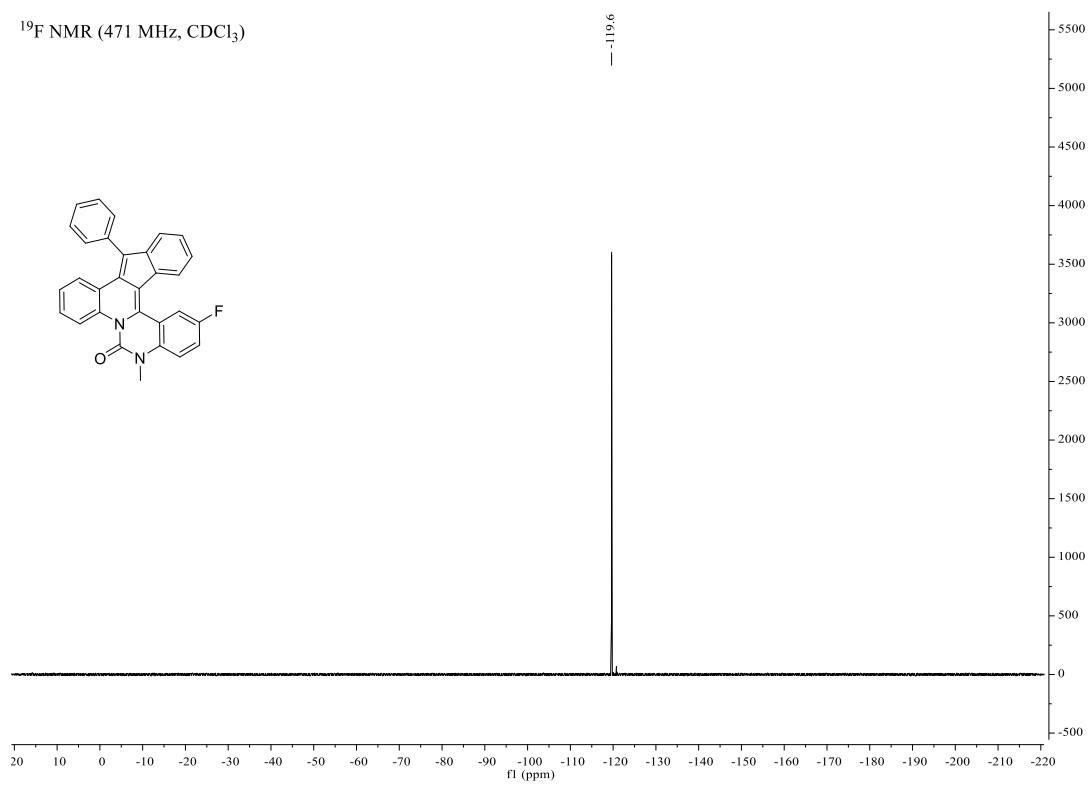
Chemical structure: CN1C(=O)c2c(c3ccccc3c4c2c(c5ccccc5)cc4c6ccccc6F)ccccc16

Peak list (ppm): 8.15, 8.13, 8.06, 8.06, 8.04, 8.04, 8.01, 8.01, 7.99, 7.99, 7.96, 7.96, 7.90, 7.88, 7.88, 7.85, 7.85, 7.56, 7.56, 7.54, 7.53, 7.48, 7.48, 7.47, 7.47, 7.46, 7.46, 7.38, 7.38, 7.36, 7.36, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.32, 7.31, 7.31, 7.30, 7.30, 7.29, 7.29, 7.28, 7.28, 7.28, 7.26, 7.26, 7.25 (CDCl₃), 7.22, 7.22, 7.20, 7.20, 7.19, 7.19, 7.18, 7.18, 7.16, 7.16, 7.08, 7.08, 7.07, 7.07, 7.06, 7.06, 7.04, 7.04, 1.55 (H₂O), 1.359, 0.00.

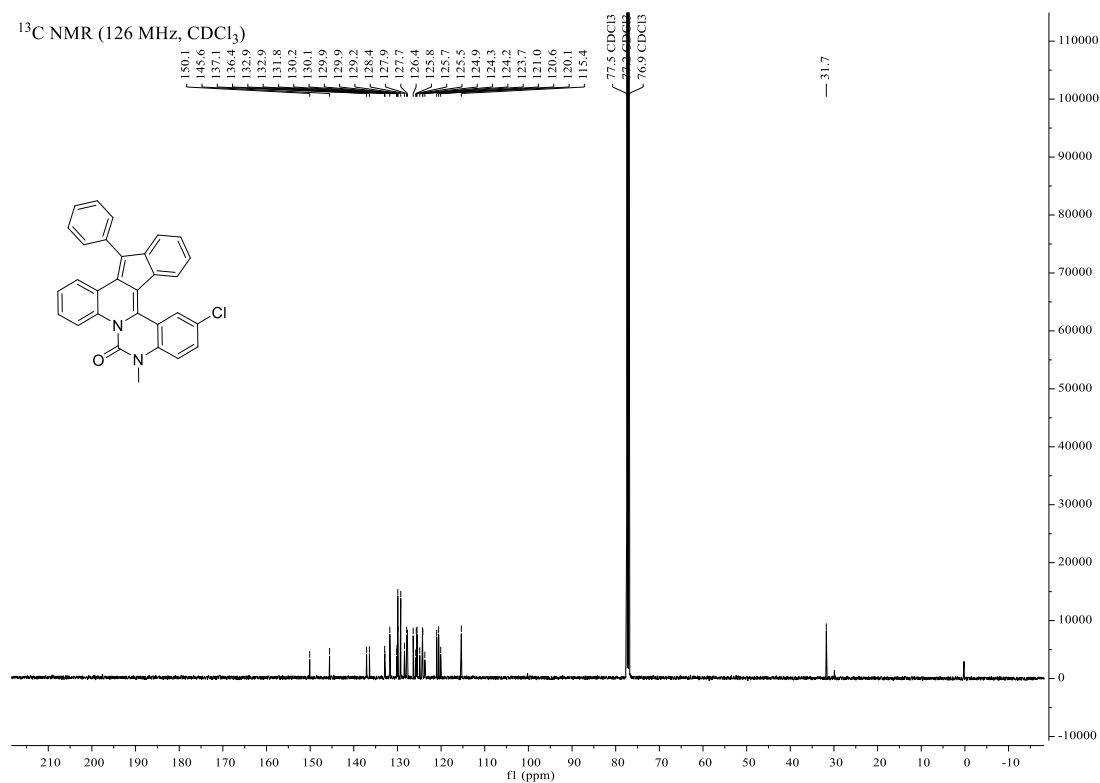
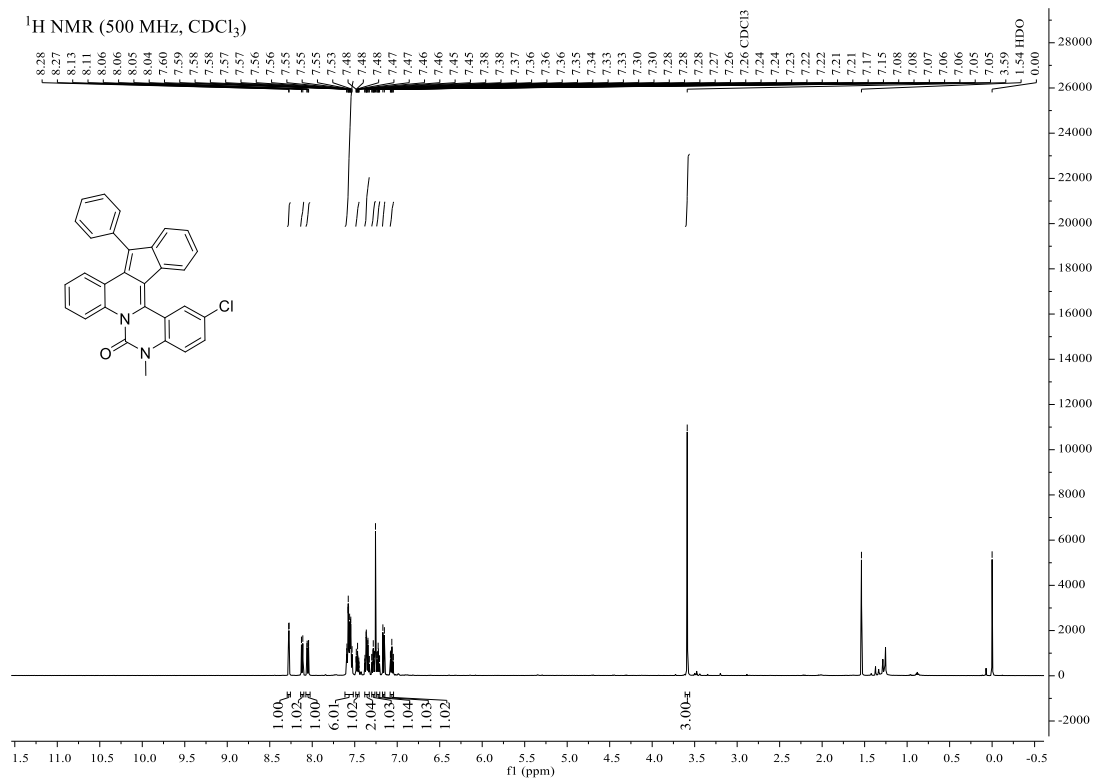
Integration values: 1.02, 1.00, 1.00, 5.02, 1.01, 1.01, 4.07, 2.02, 1.03, 3.00.



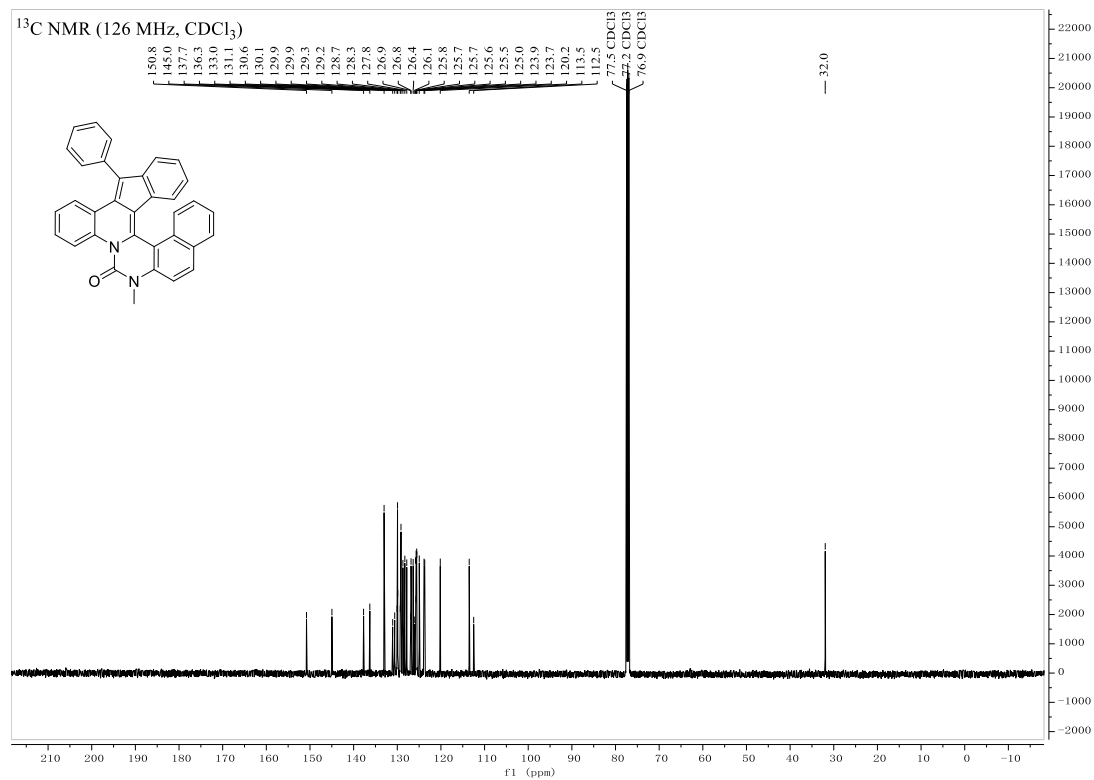
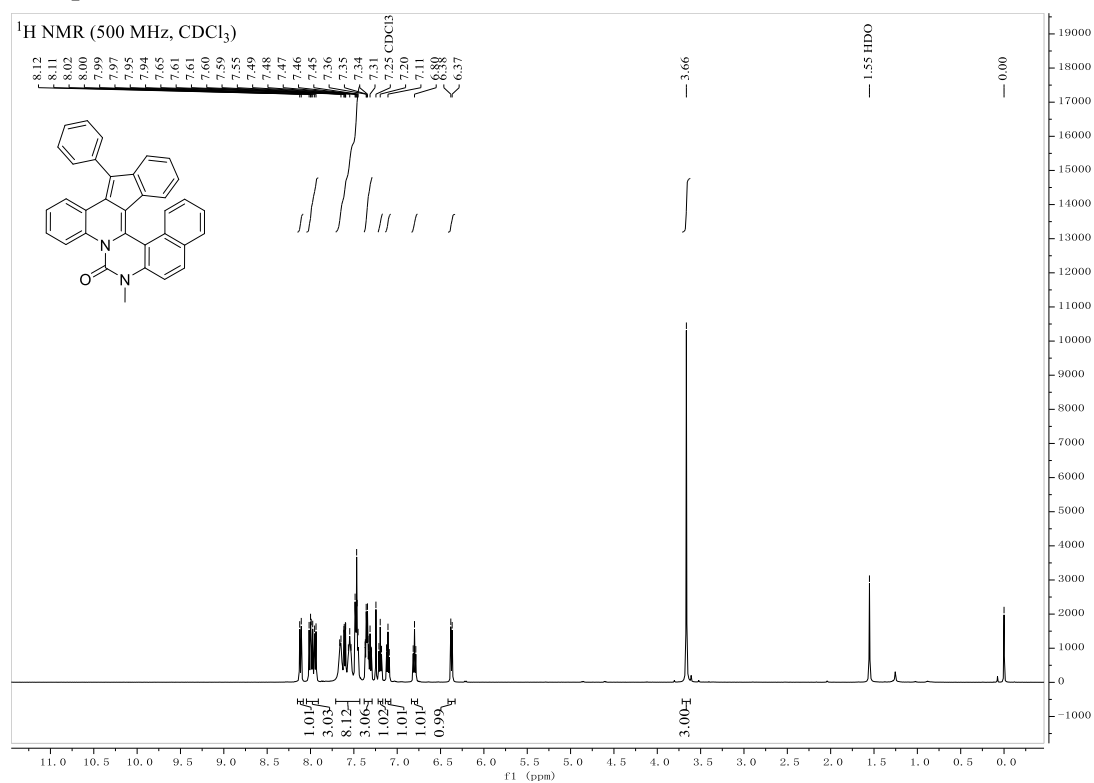
^{19}F NMR (471 MHz, CDCl_3)



Compound 12



Compound 13

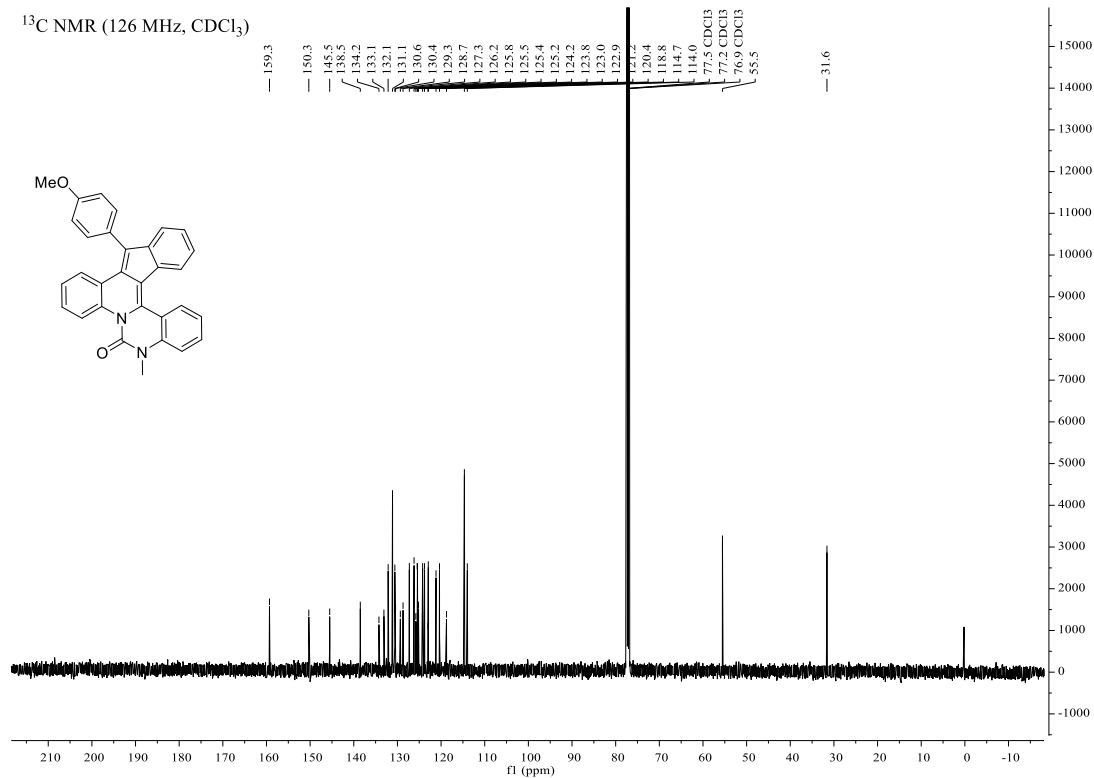


¹H NMR (500 MHz, CDCl₃)

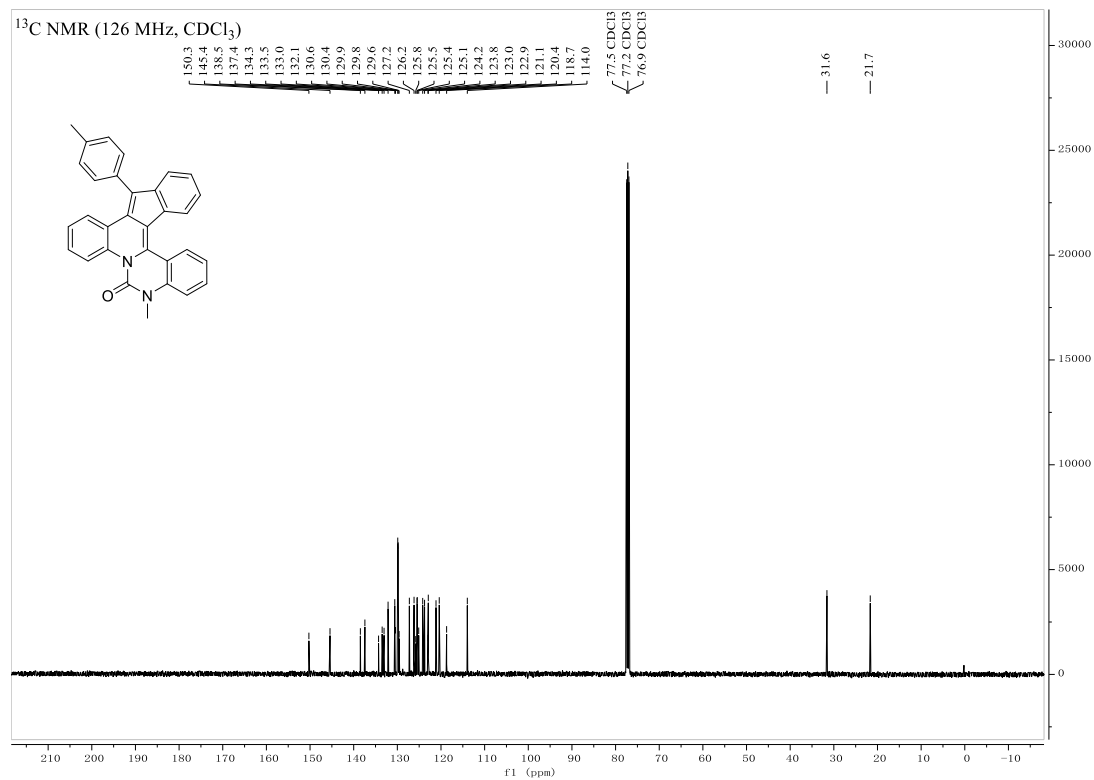
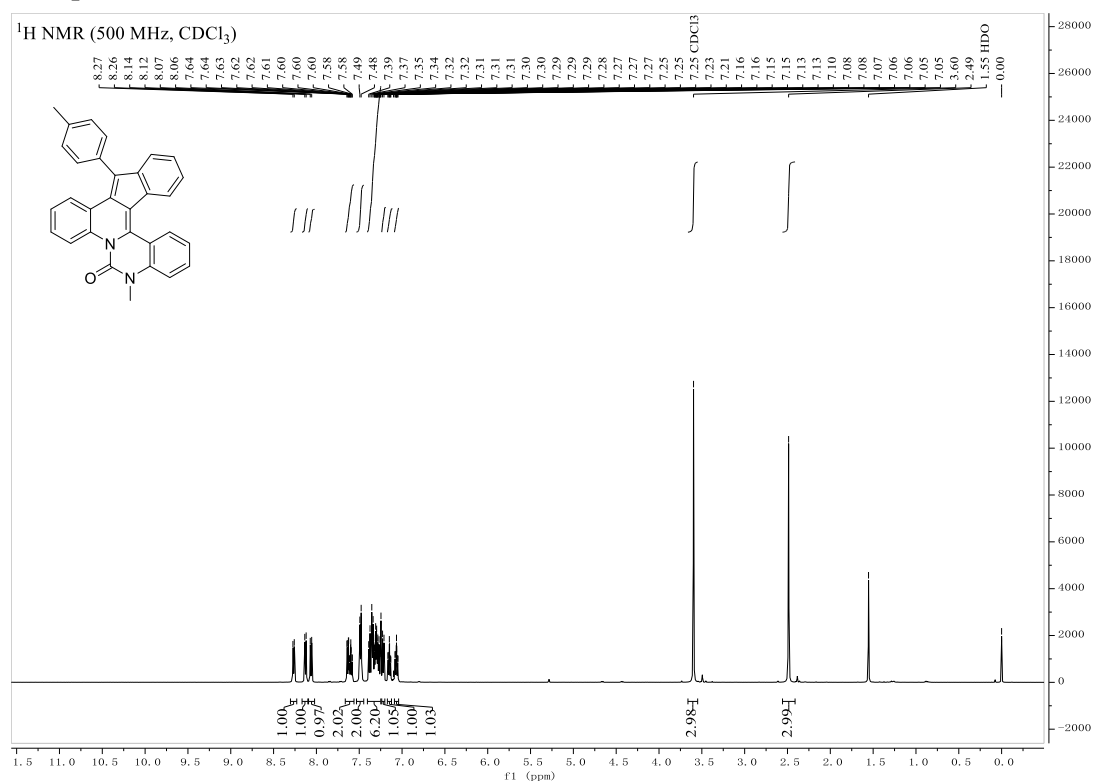
Chemical structure of compound 10 is shown in the top left corner.

The spectrum displays peaks from 0.00 to 8.28 ppm. Integration values are provided below the baseline: 1.01, 1.02, 1.00, 2.03, 1.01, 1.01, 3.02, 1.02, 1.03, 3.02, 3.01, and 3.00.

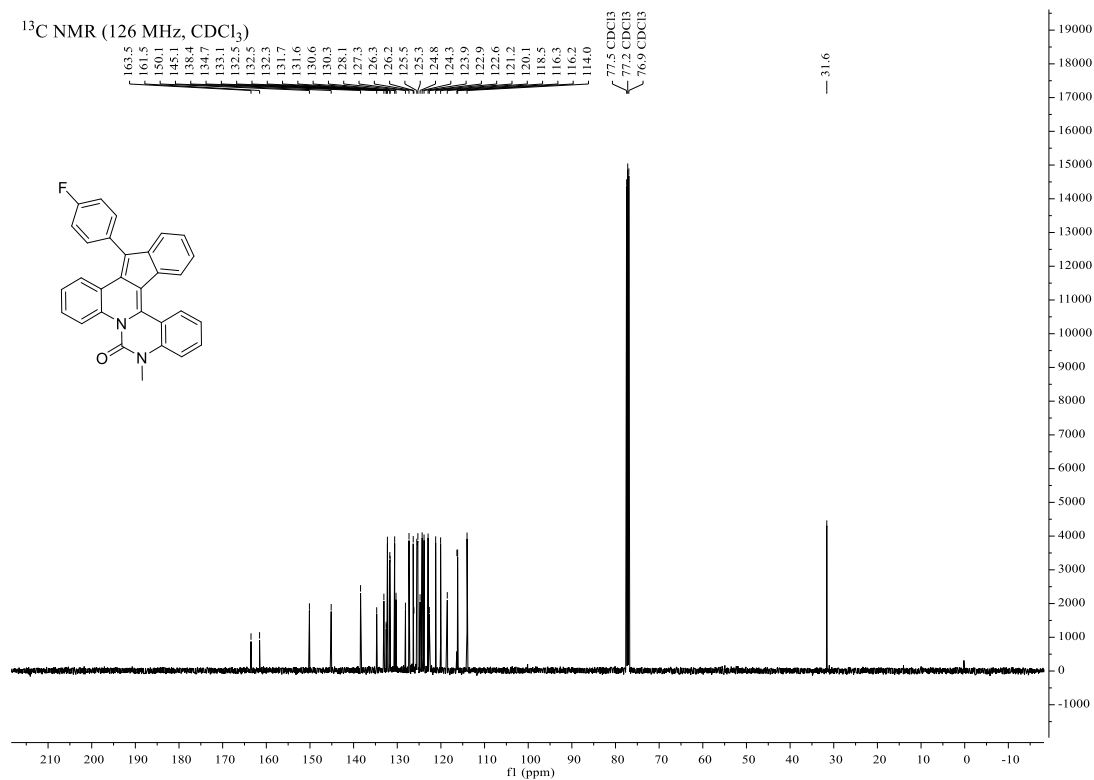
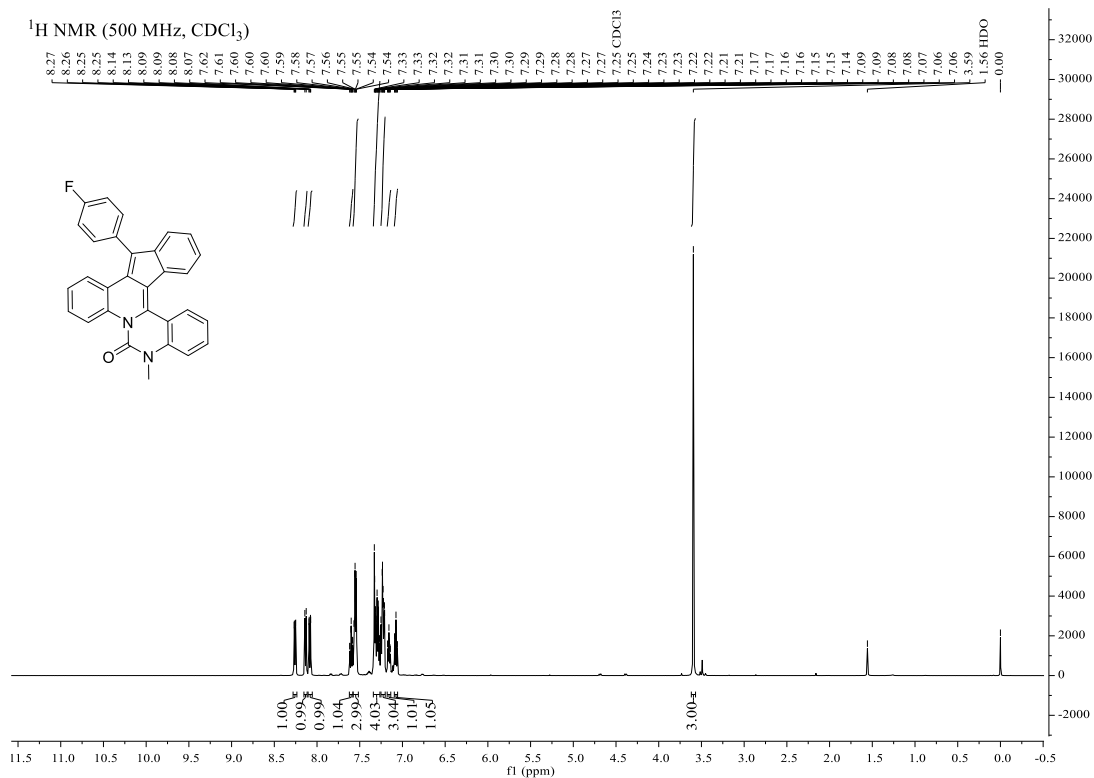
The x-axis is labeled 'f1 (ppm)' and the y-axis is labeled 'Intensity'.



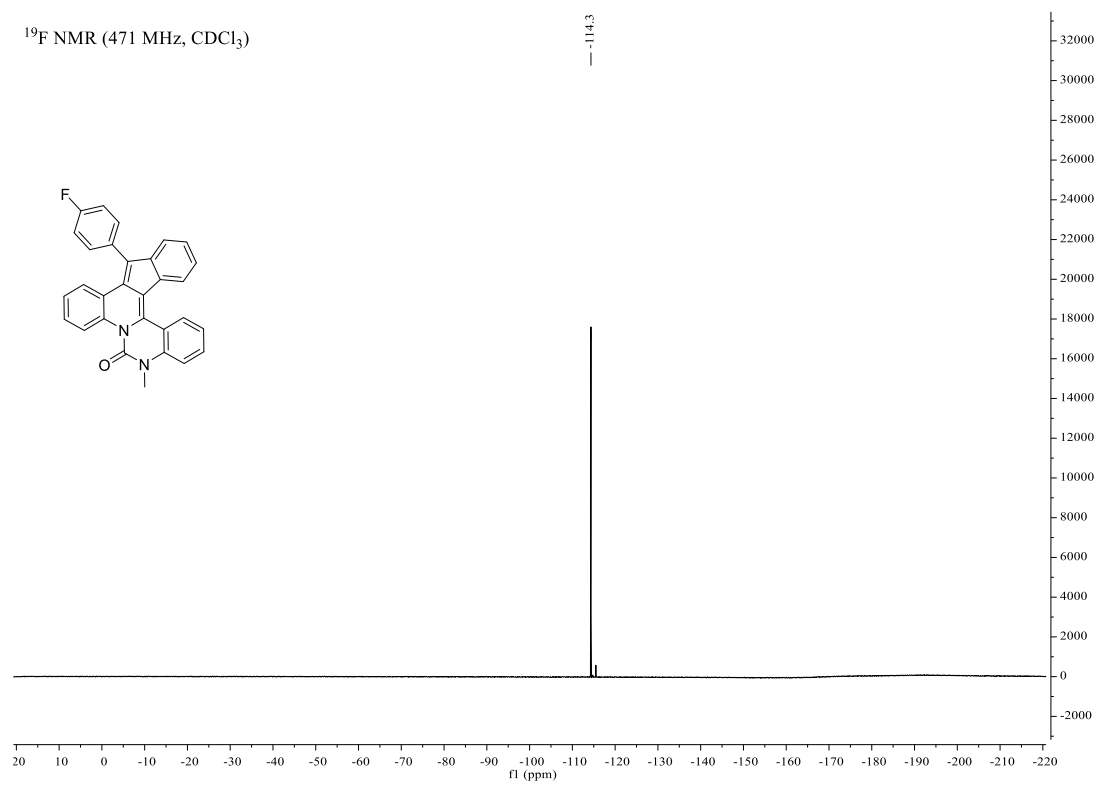
Compound 15



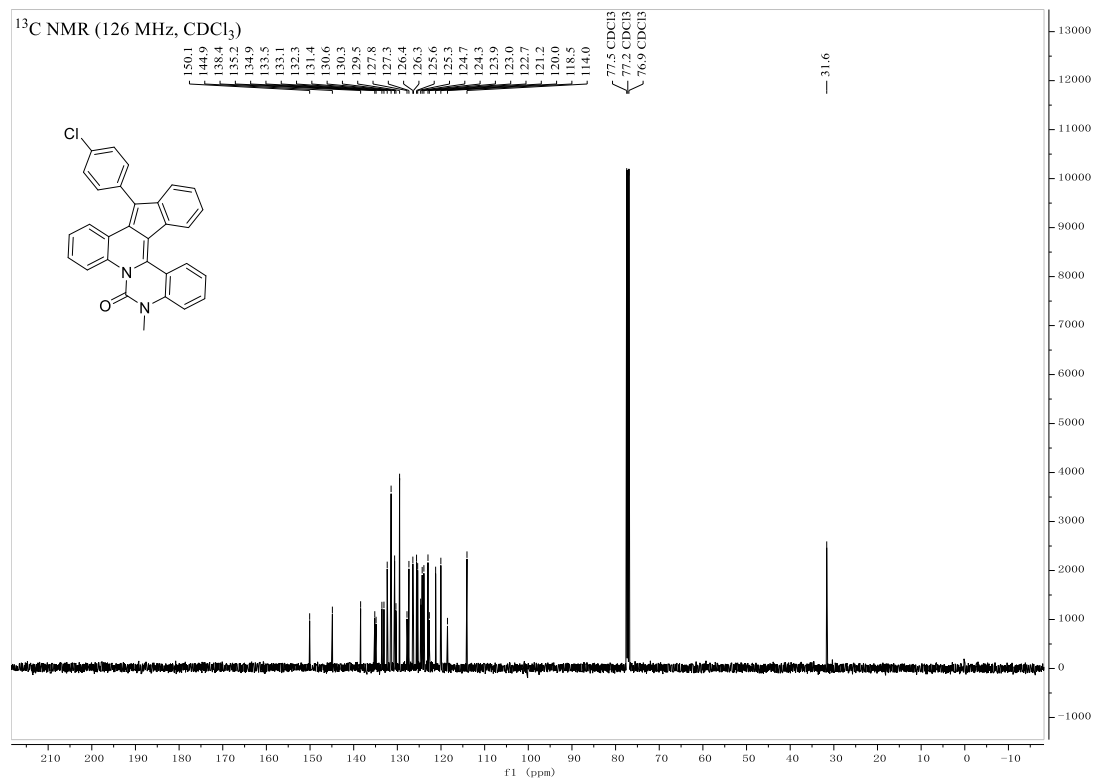
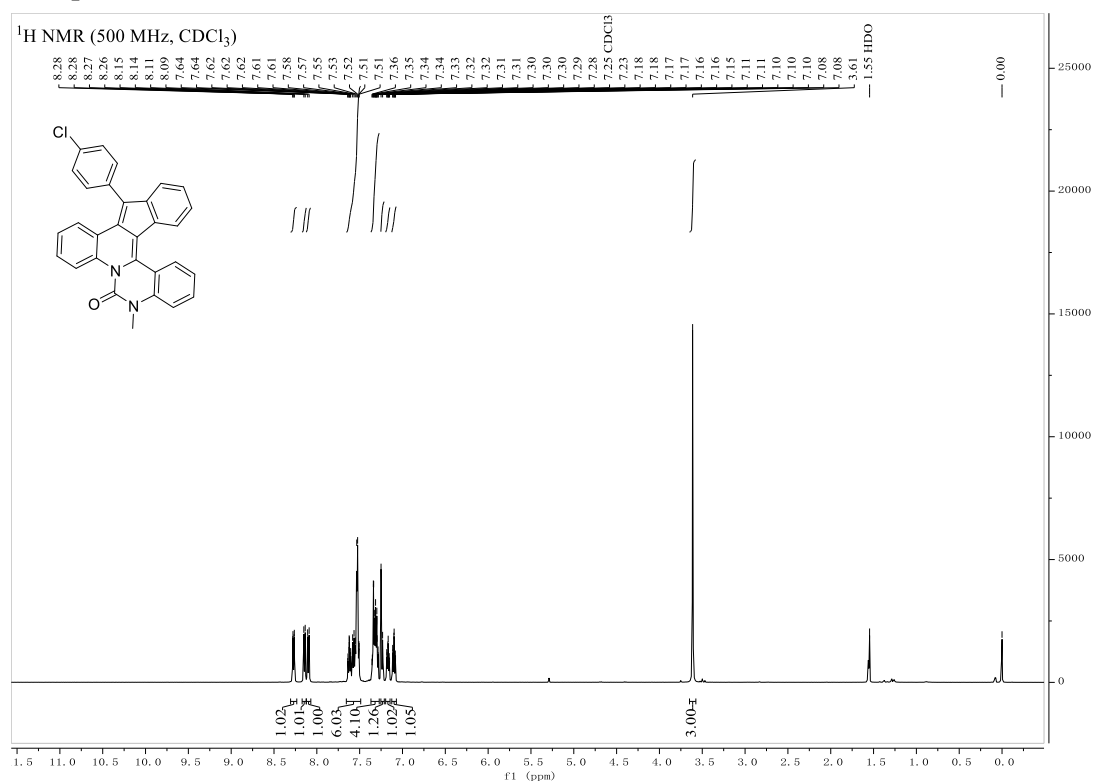
Compound 16



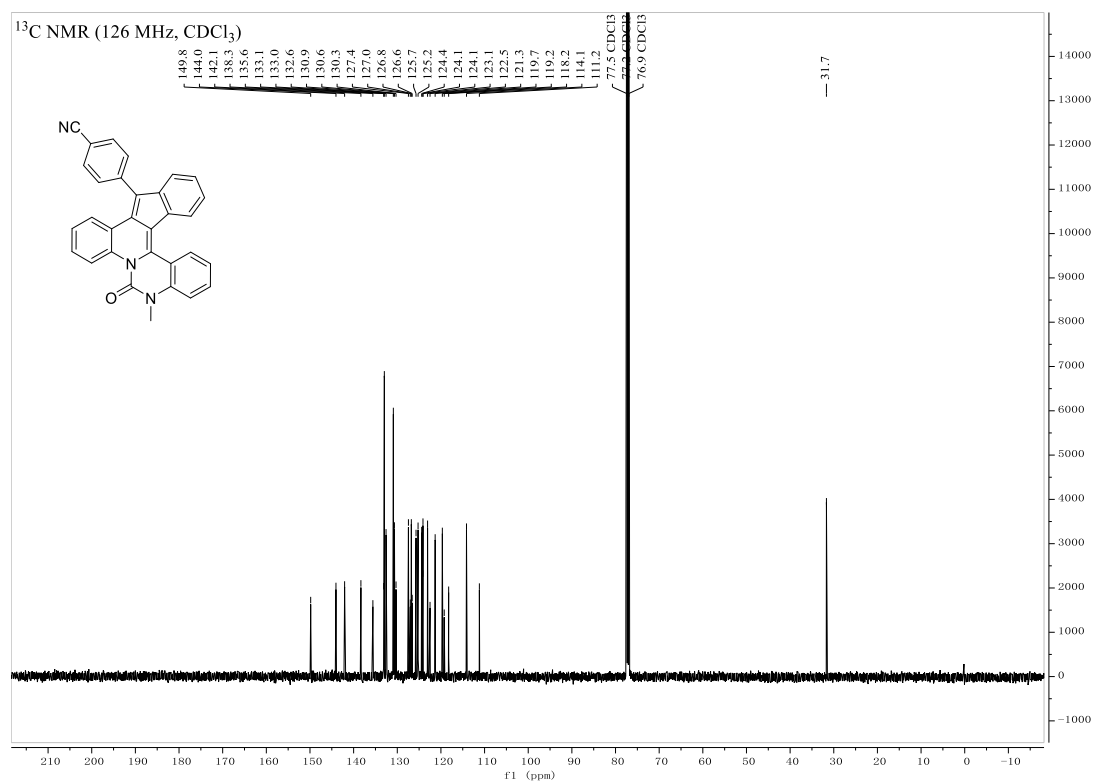
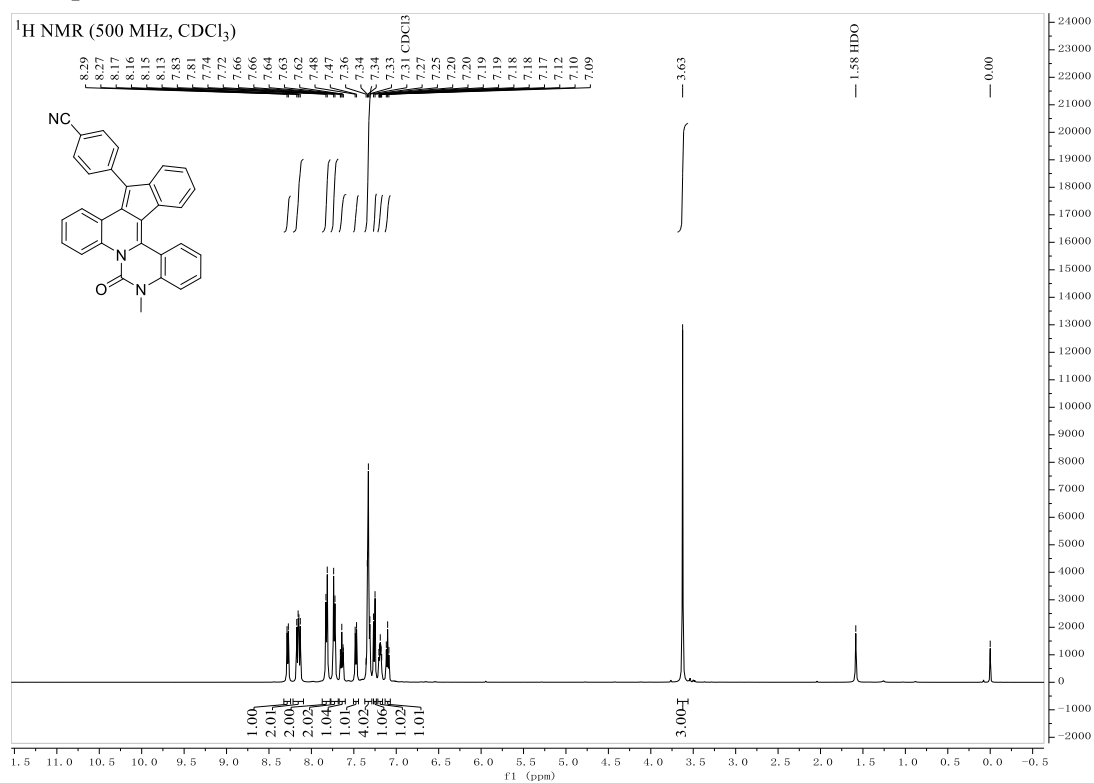
^{19}F NMR (471 MHz, CDCl_3)



Compound 17

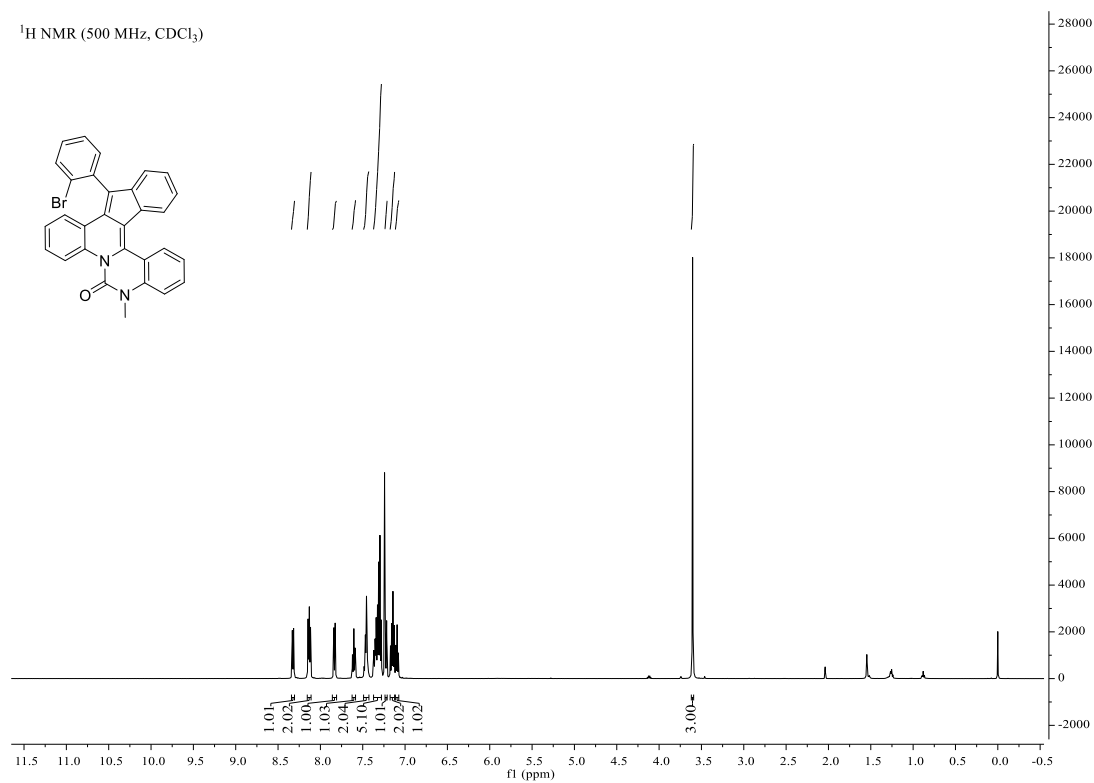


Compound 18

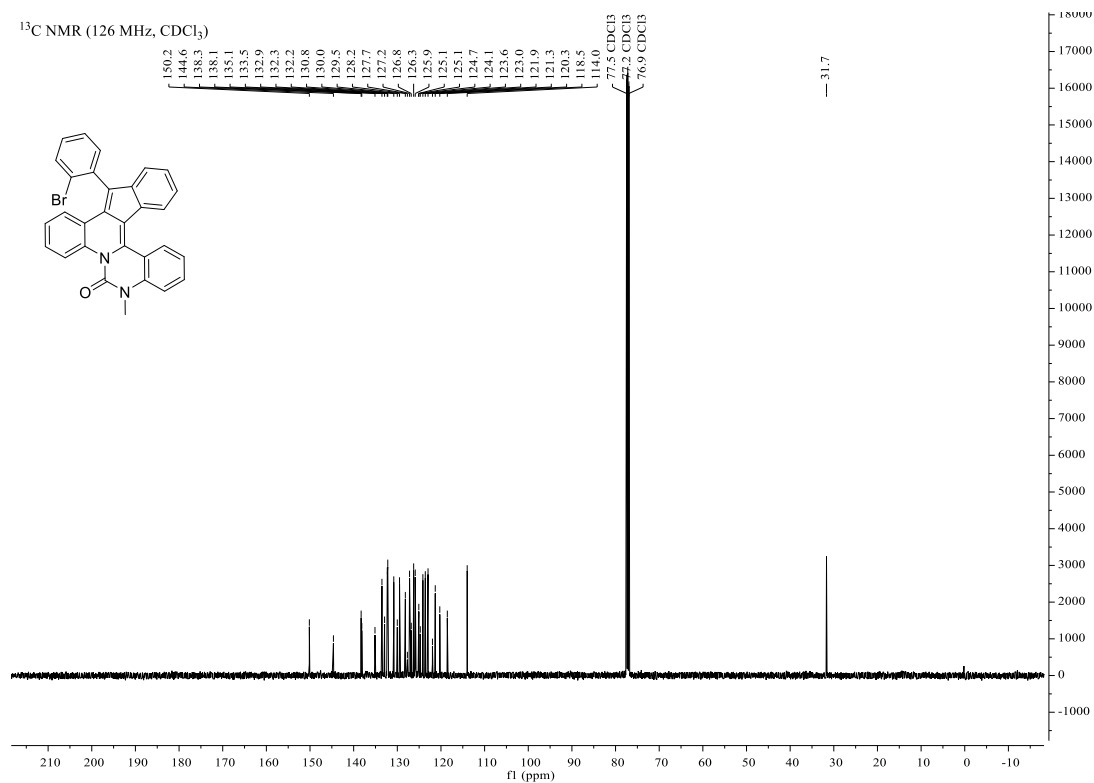


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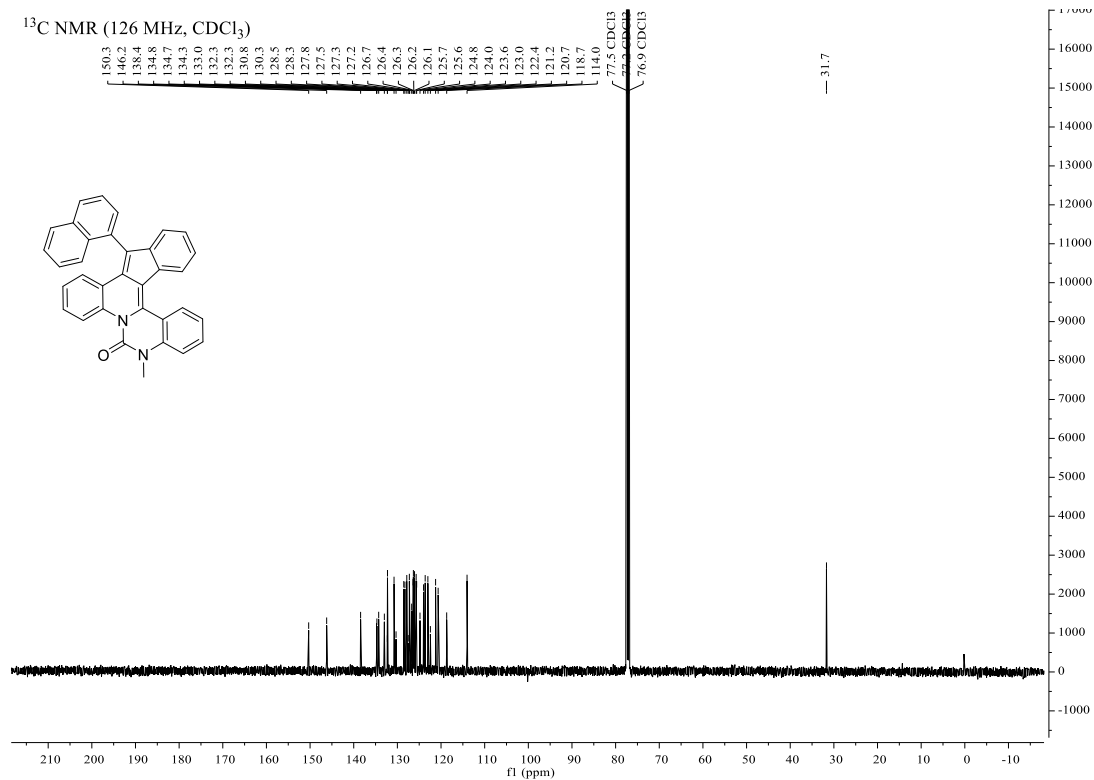
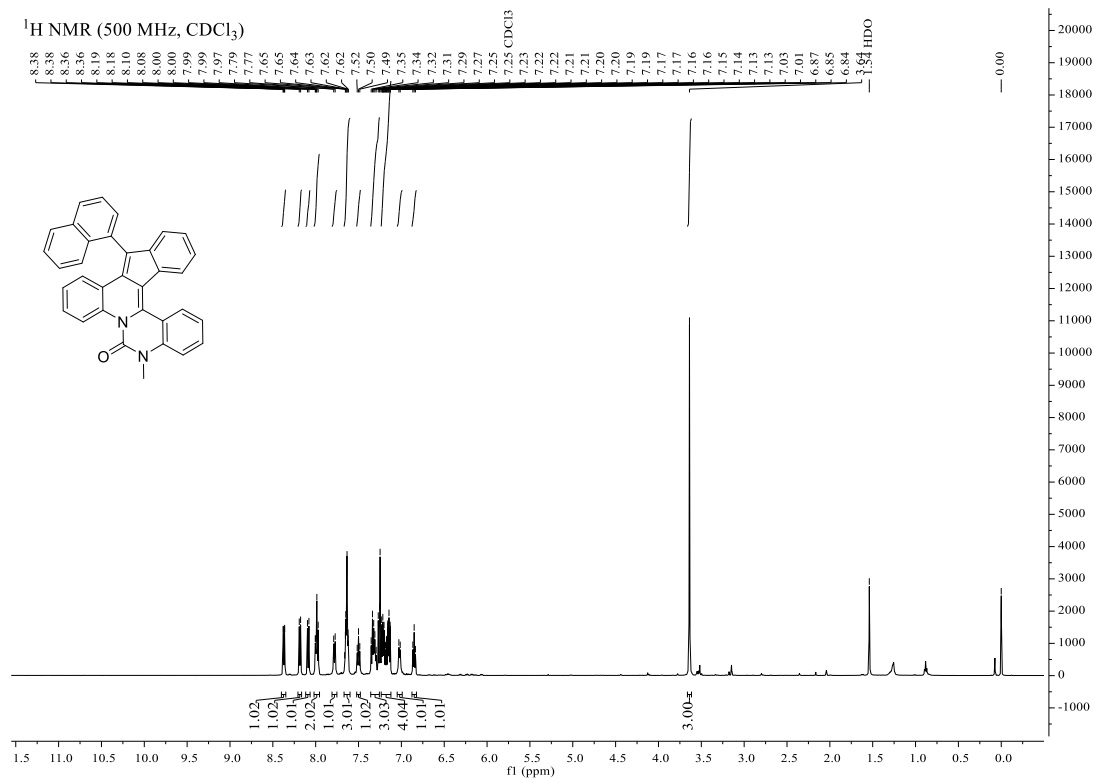
^1H NMR (500 MHz, CDCl_3)



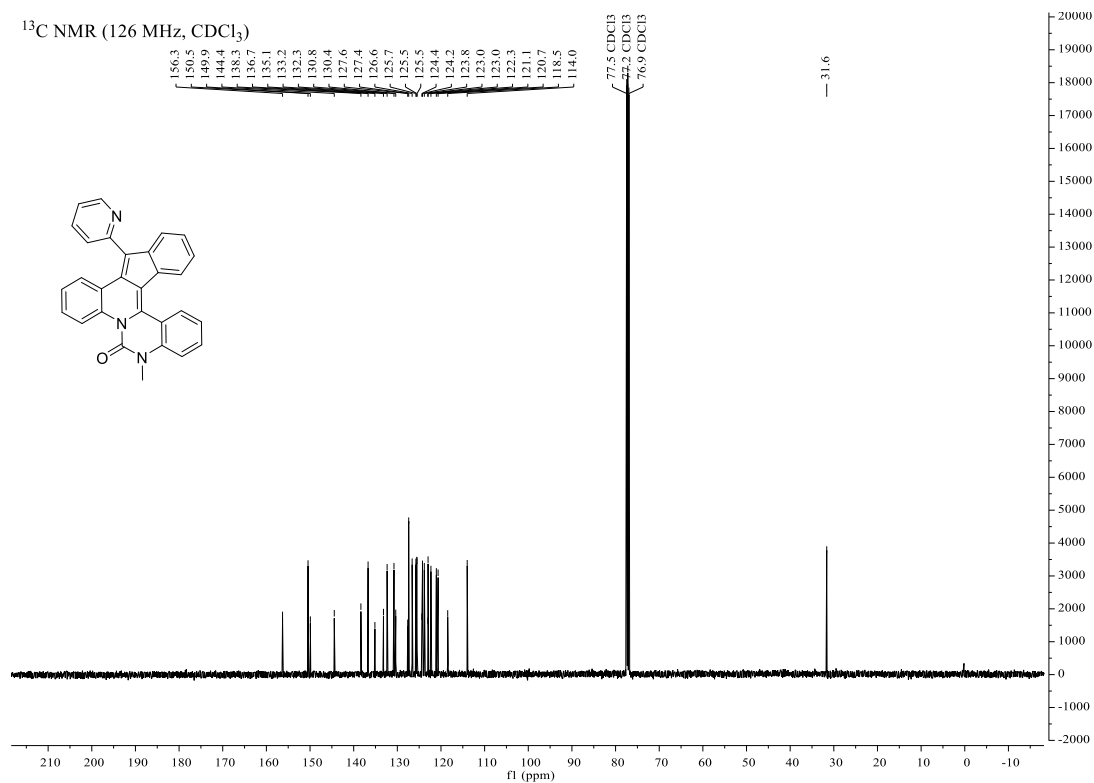
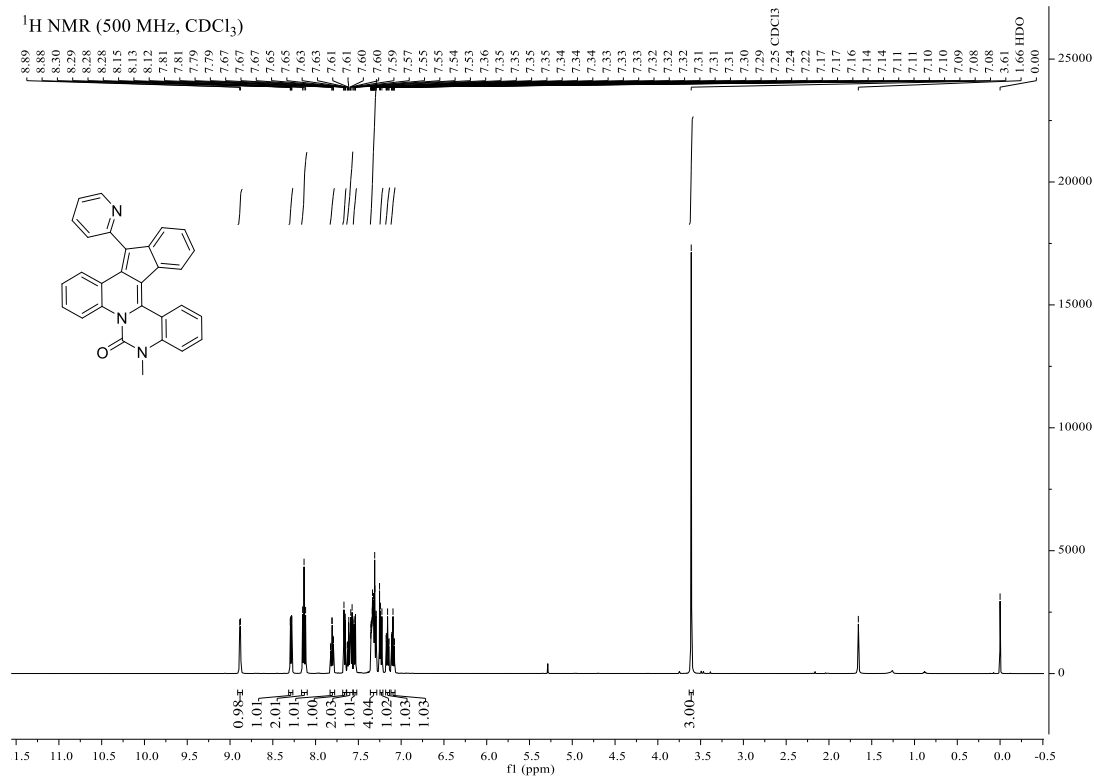
^{13}C NMR (126 MHz, CDCl_3)



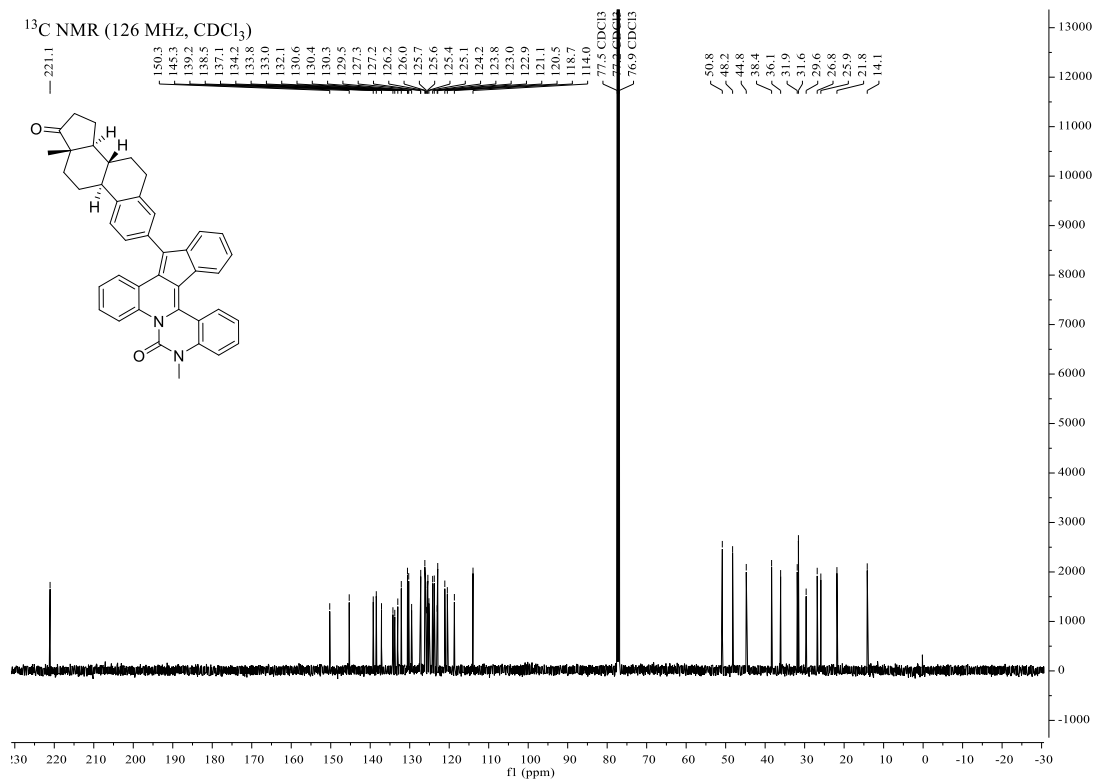
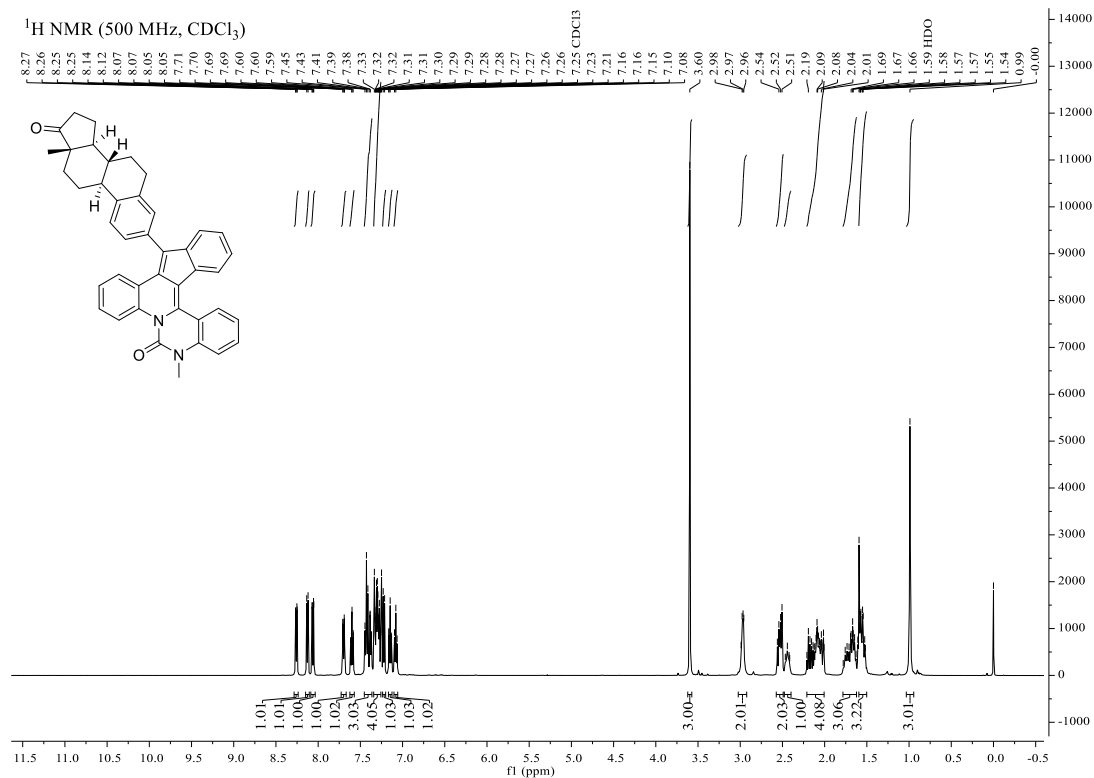
Compound 20



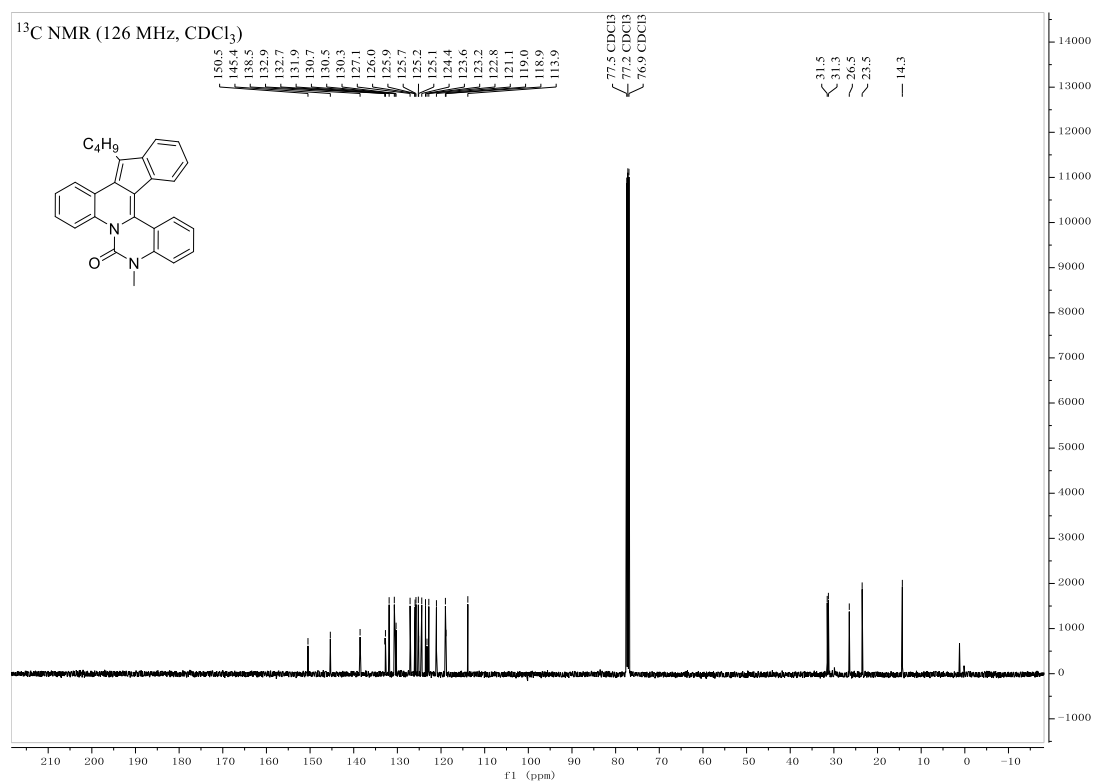
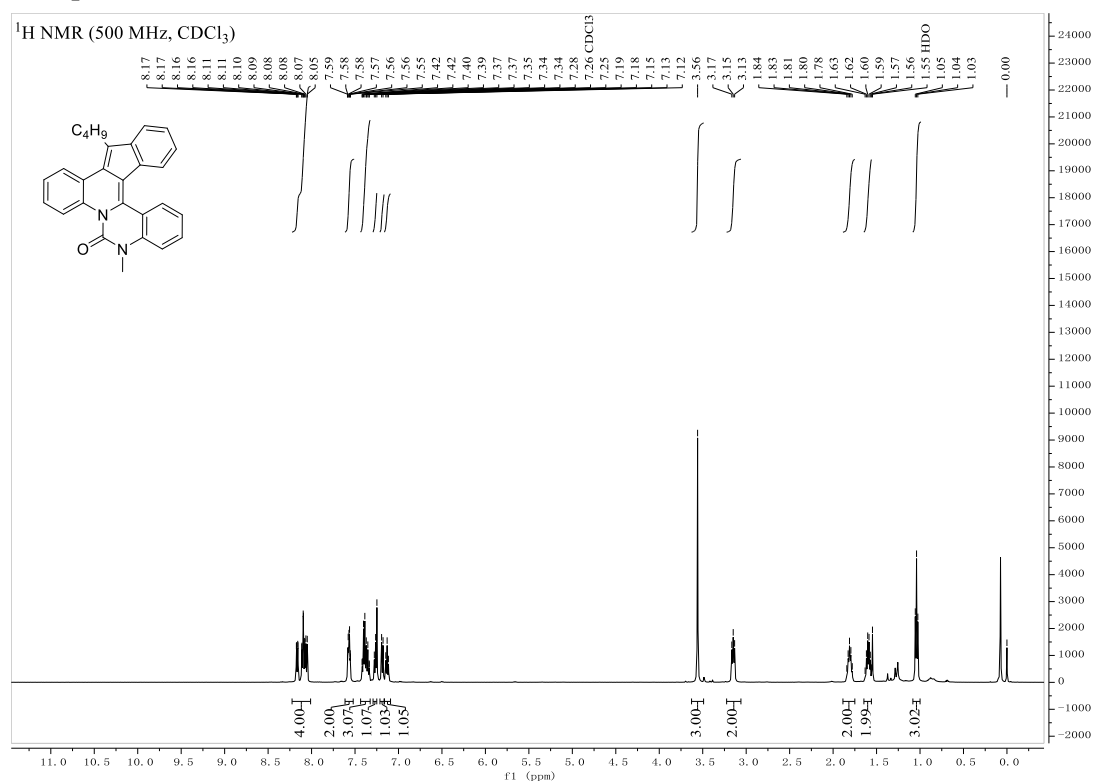
Compound 21



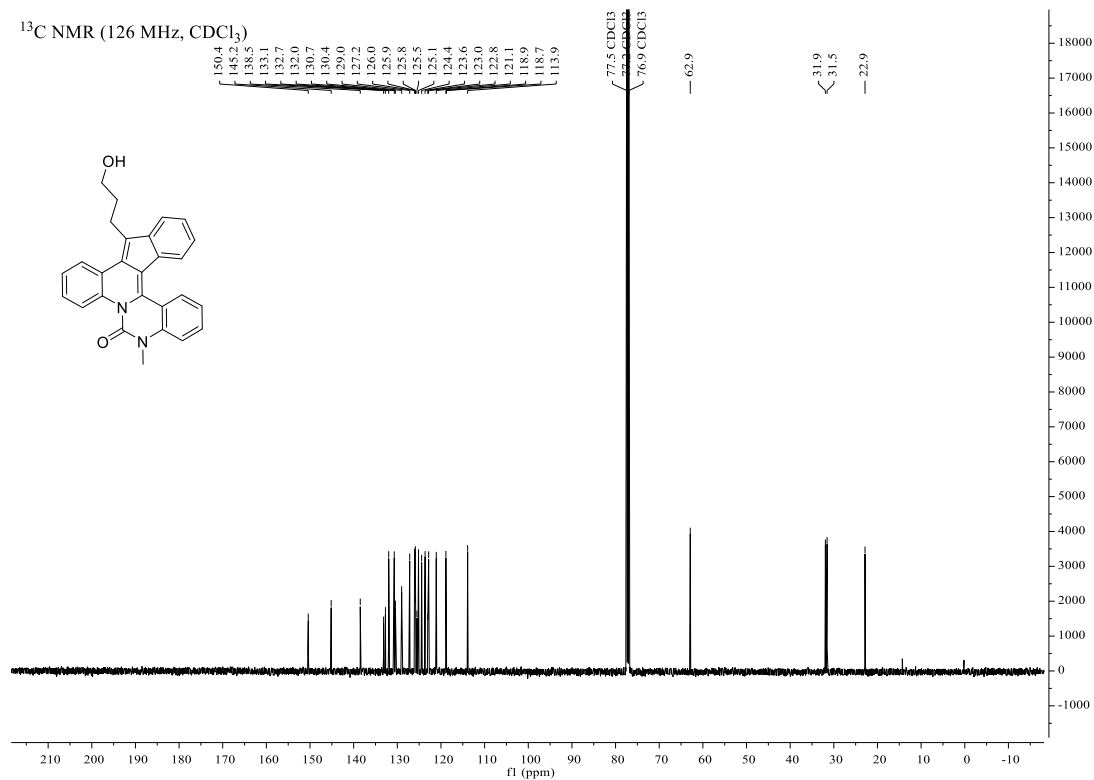
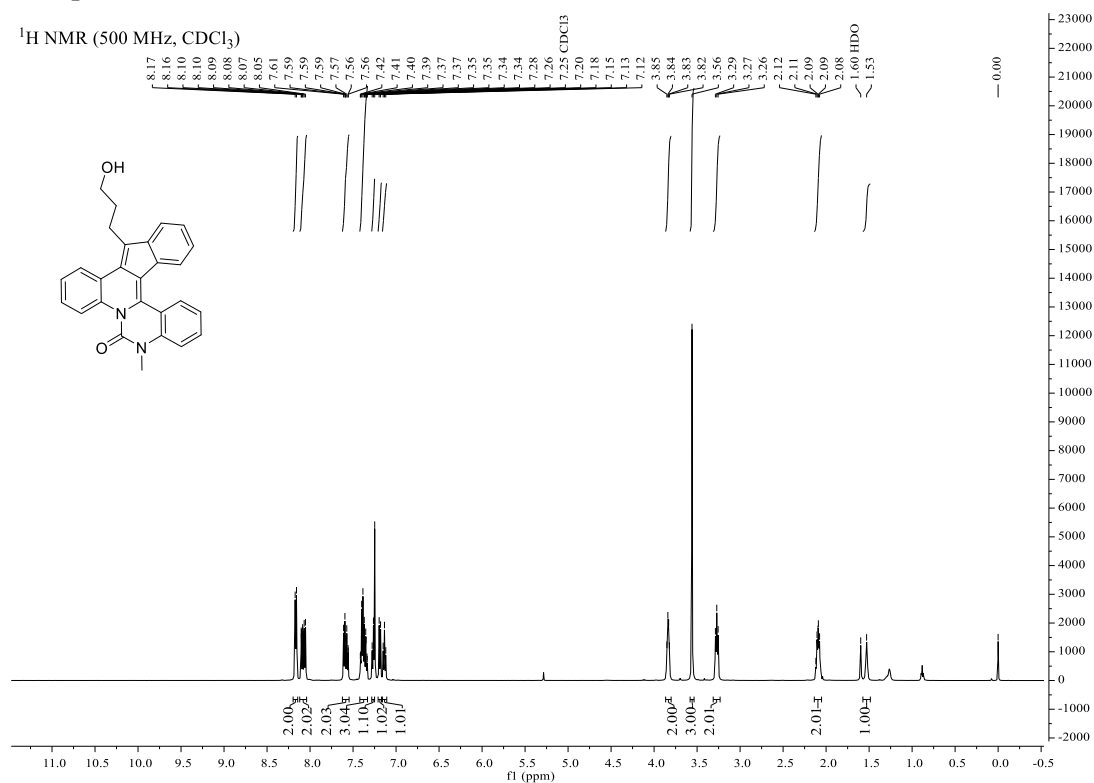
Compound 22



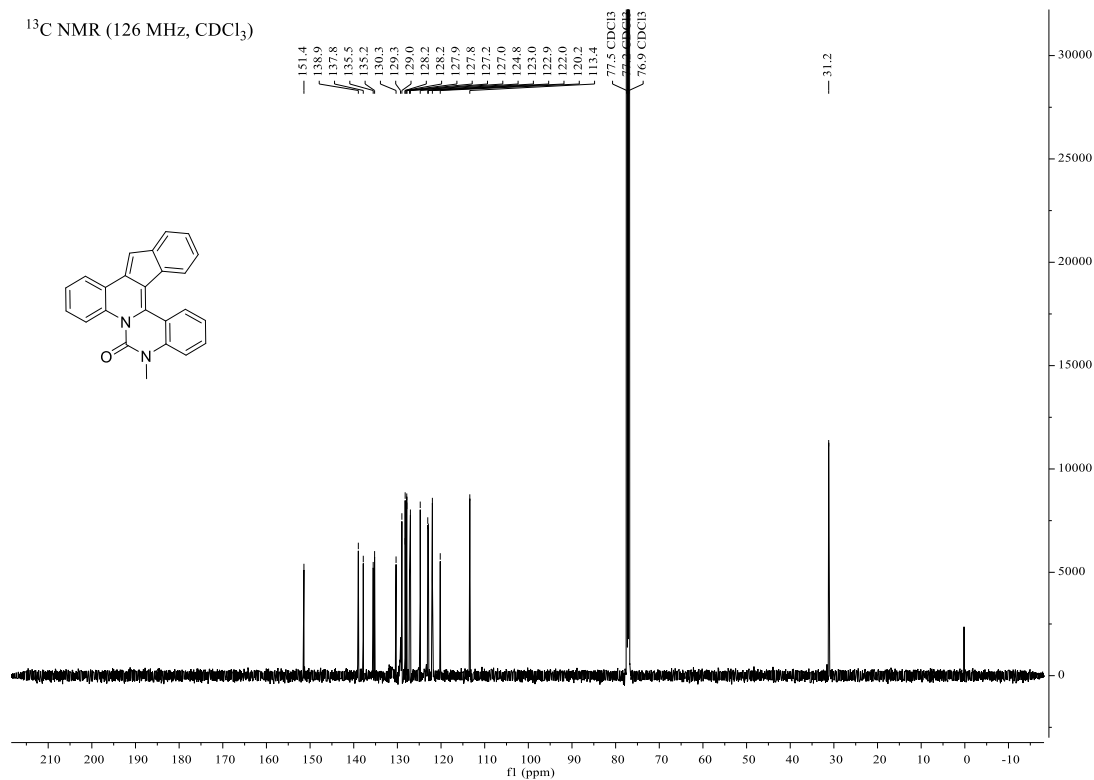
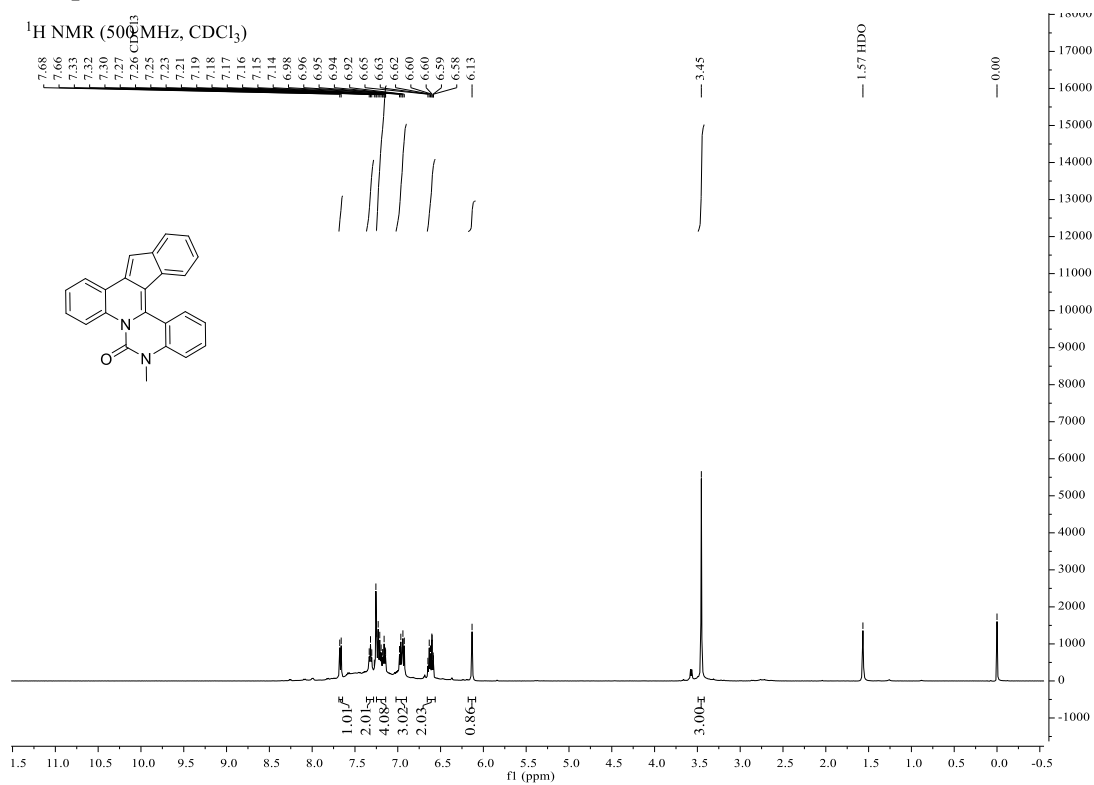
Compound 23



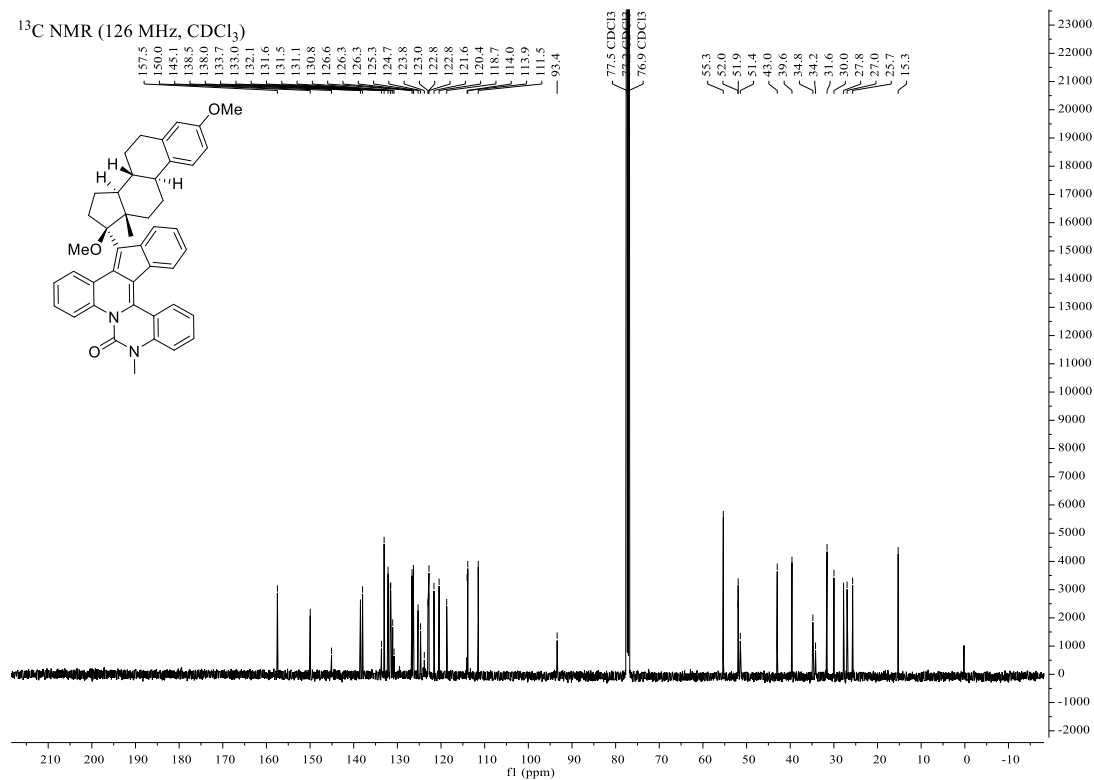
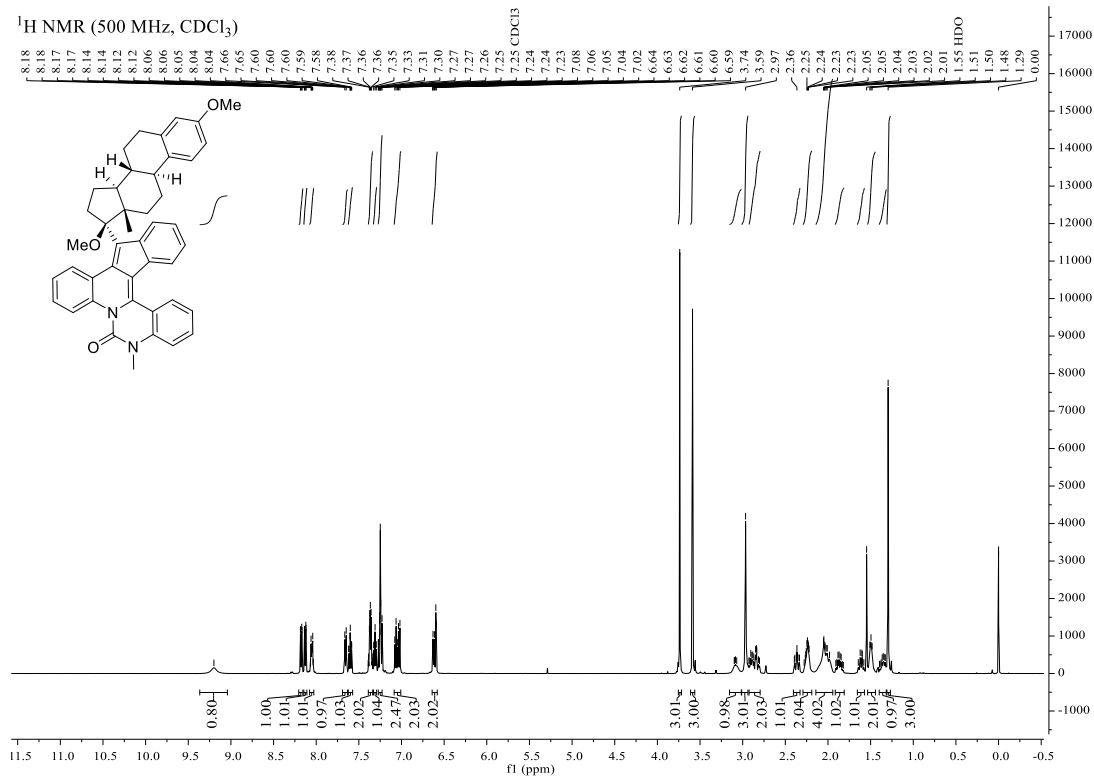
Compound 24



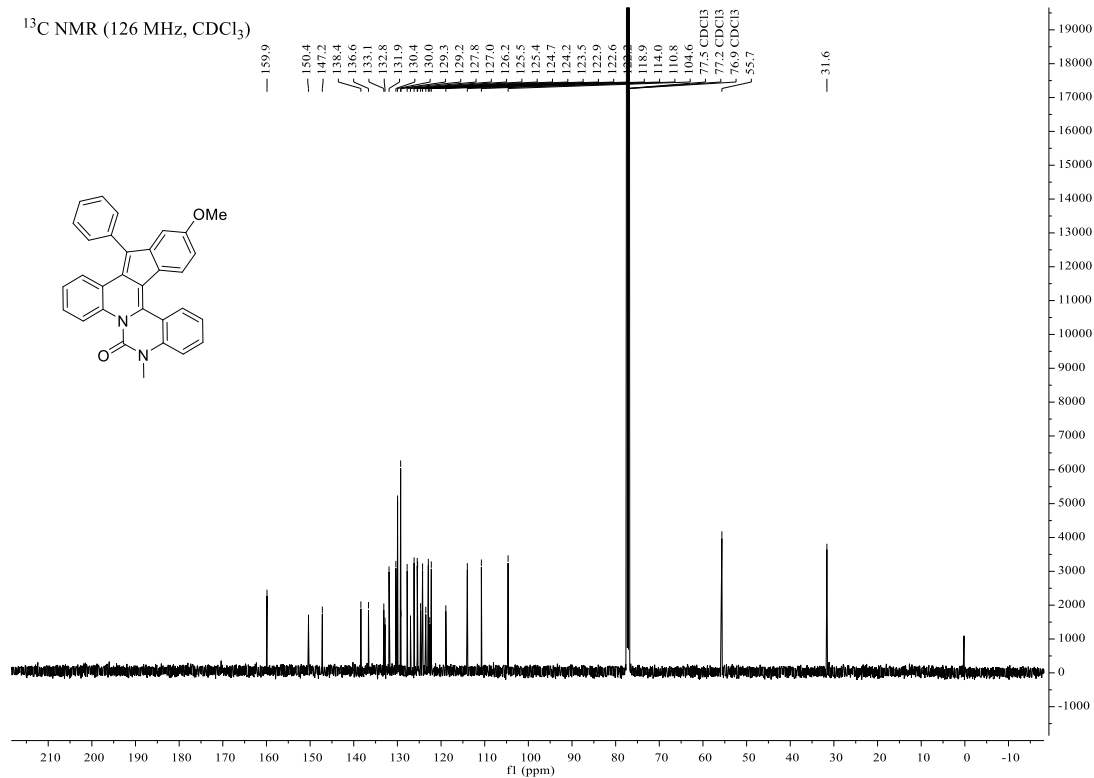
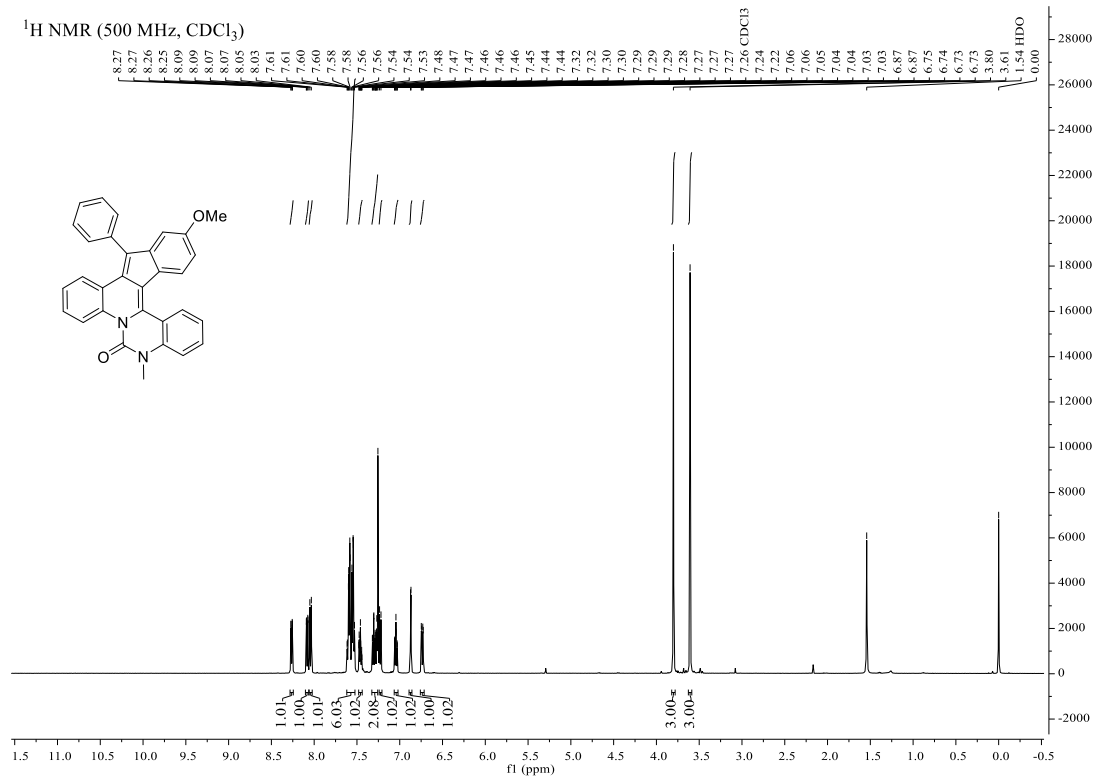
Compound 25



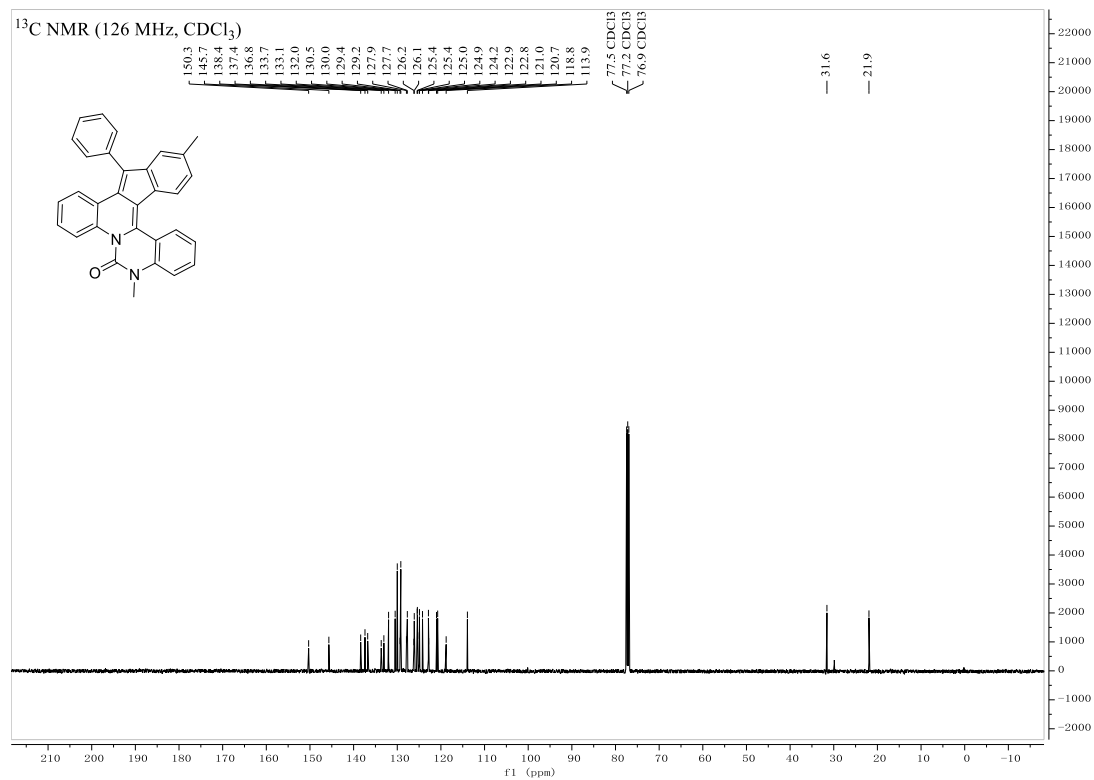
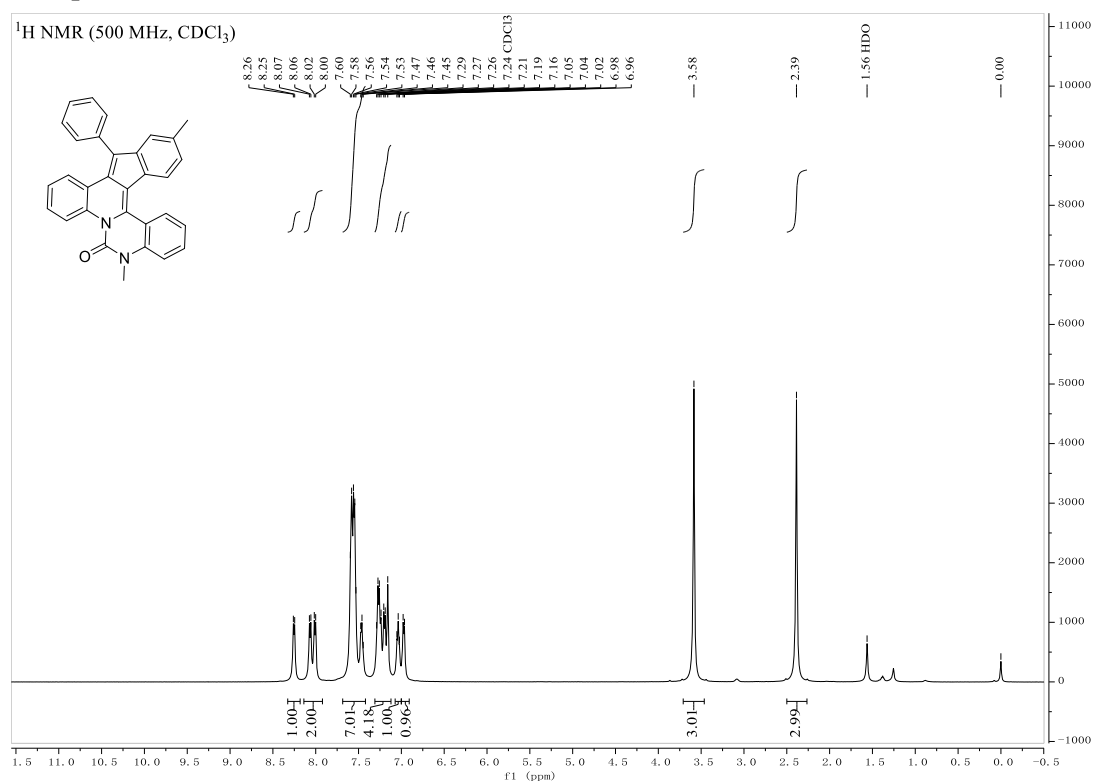
Compound 26



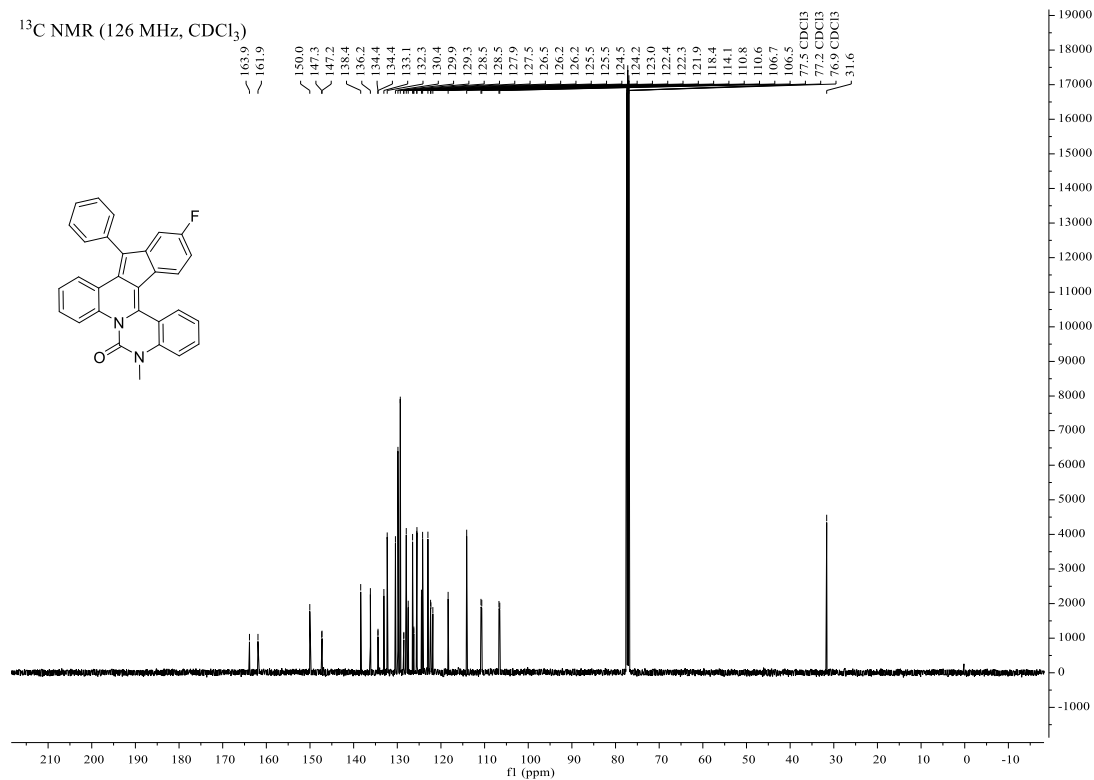
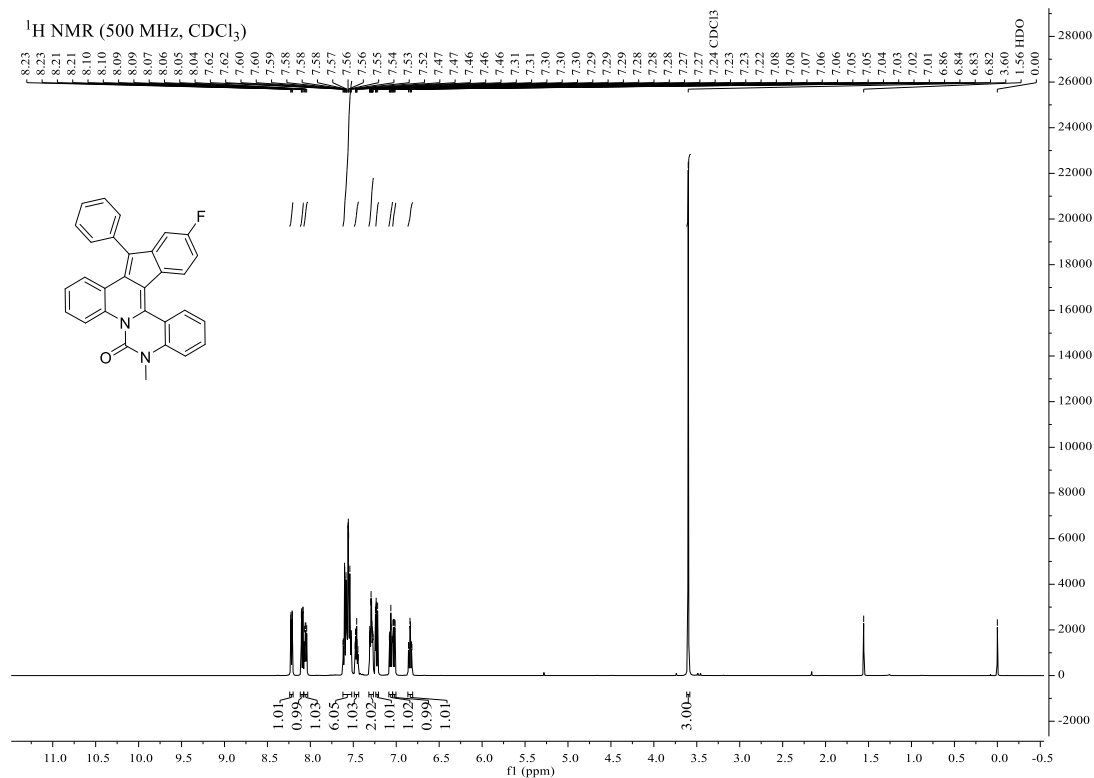
Compound 27



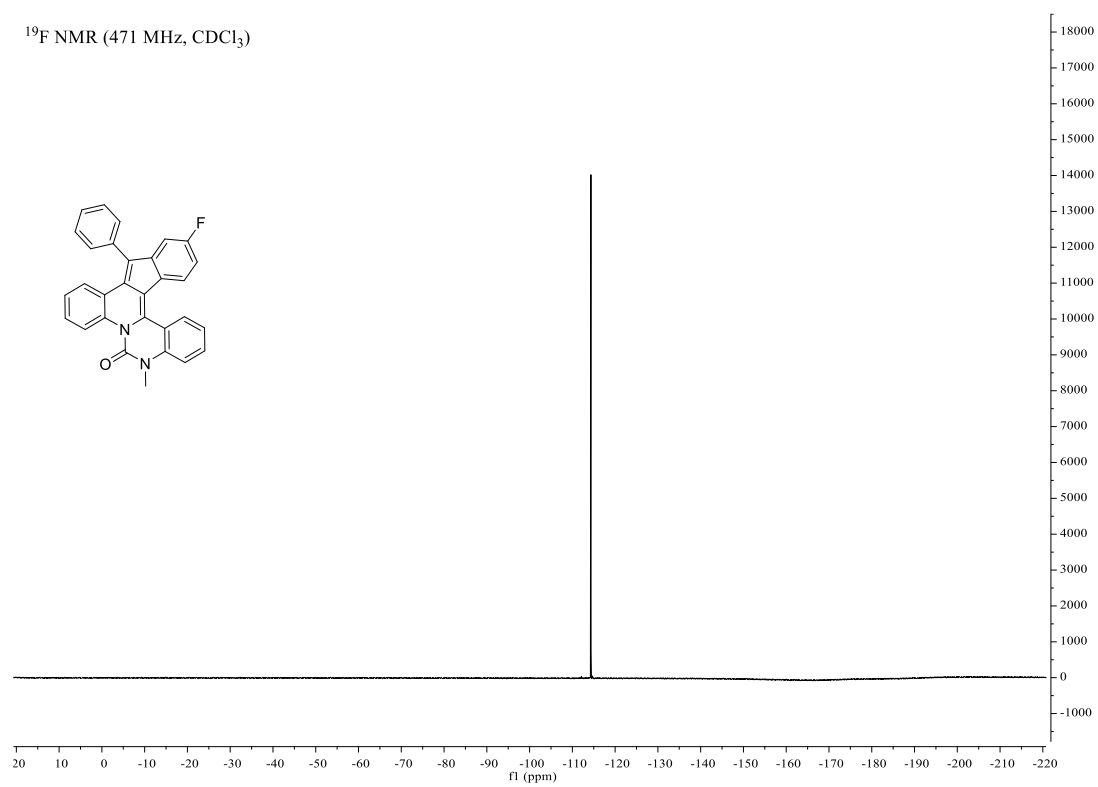
Compound 28



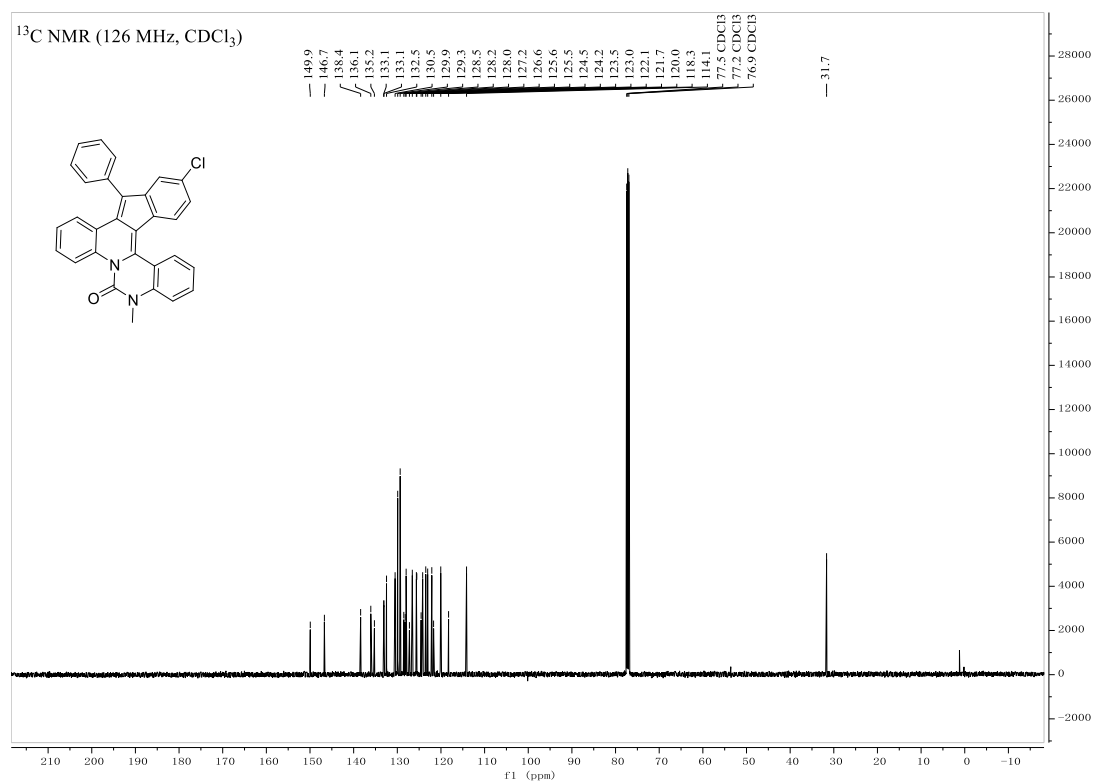
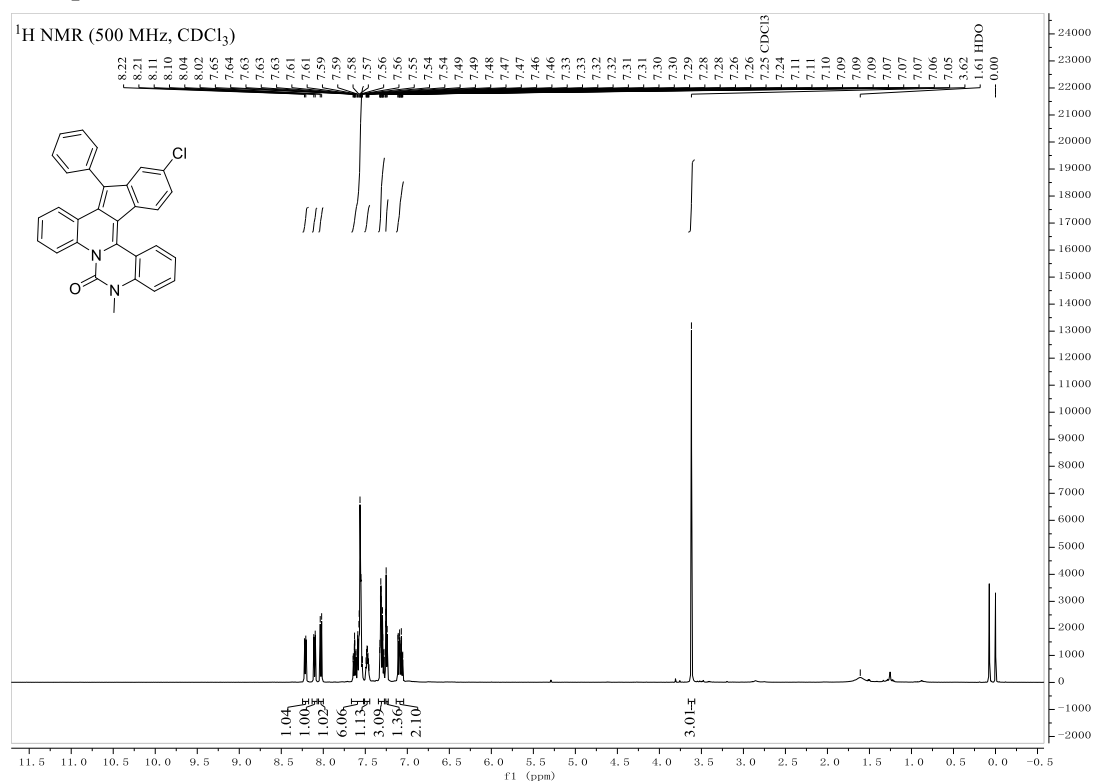
Compound 29



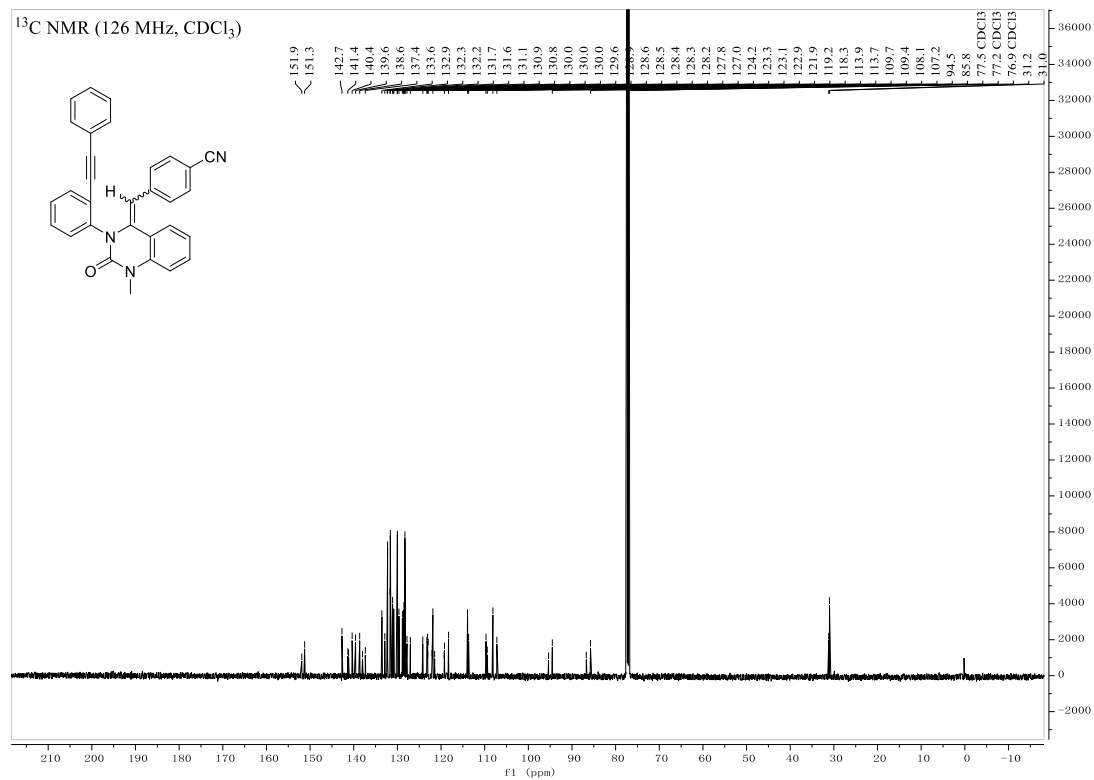
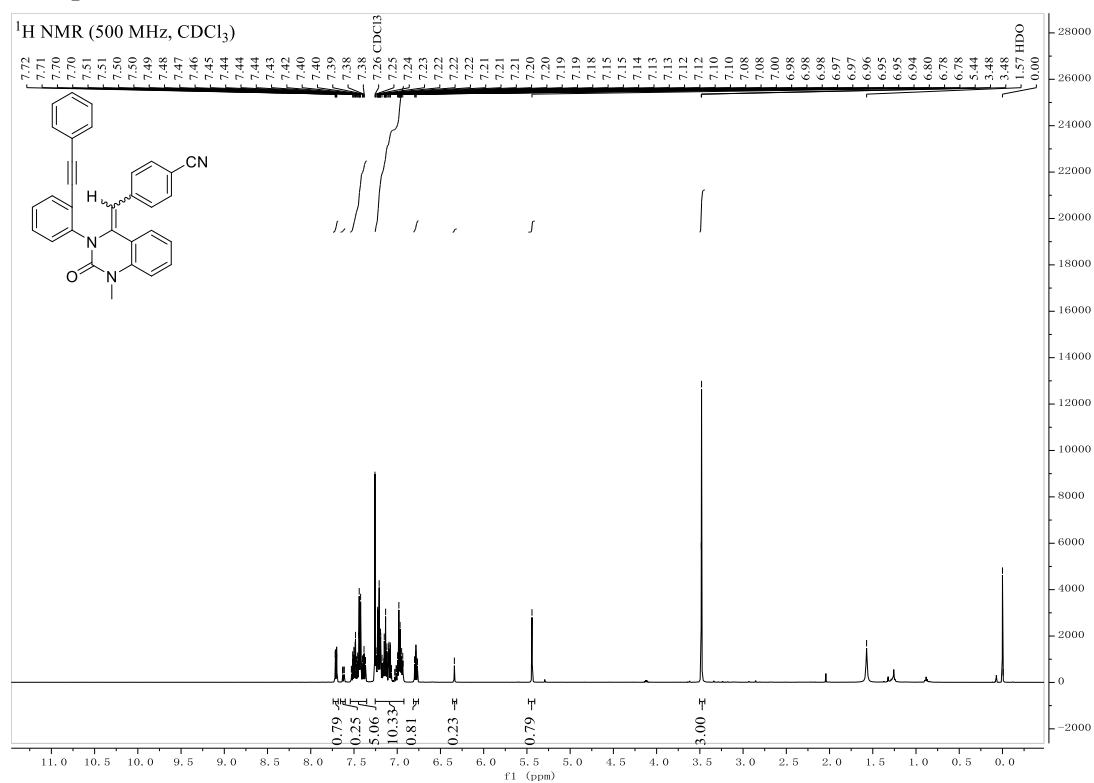
^{19}F NMR (471 MHz, CDCl_3)



Compound 30

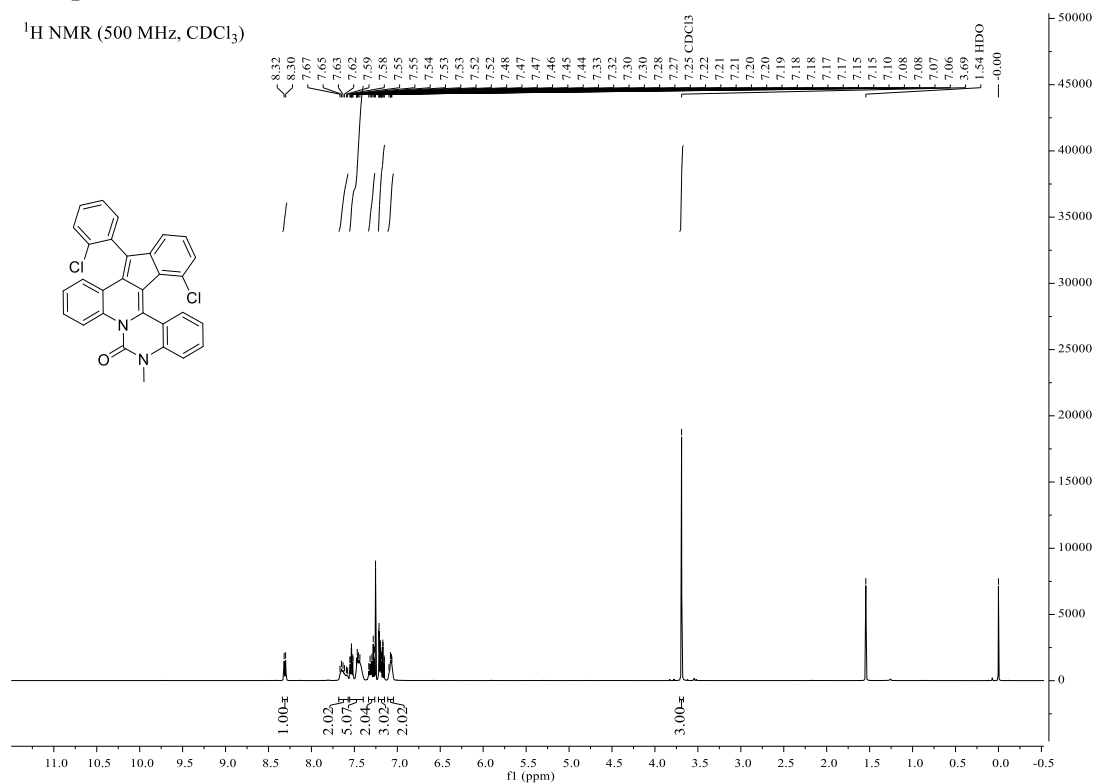


Compound S1

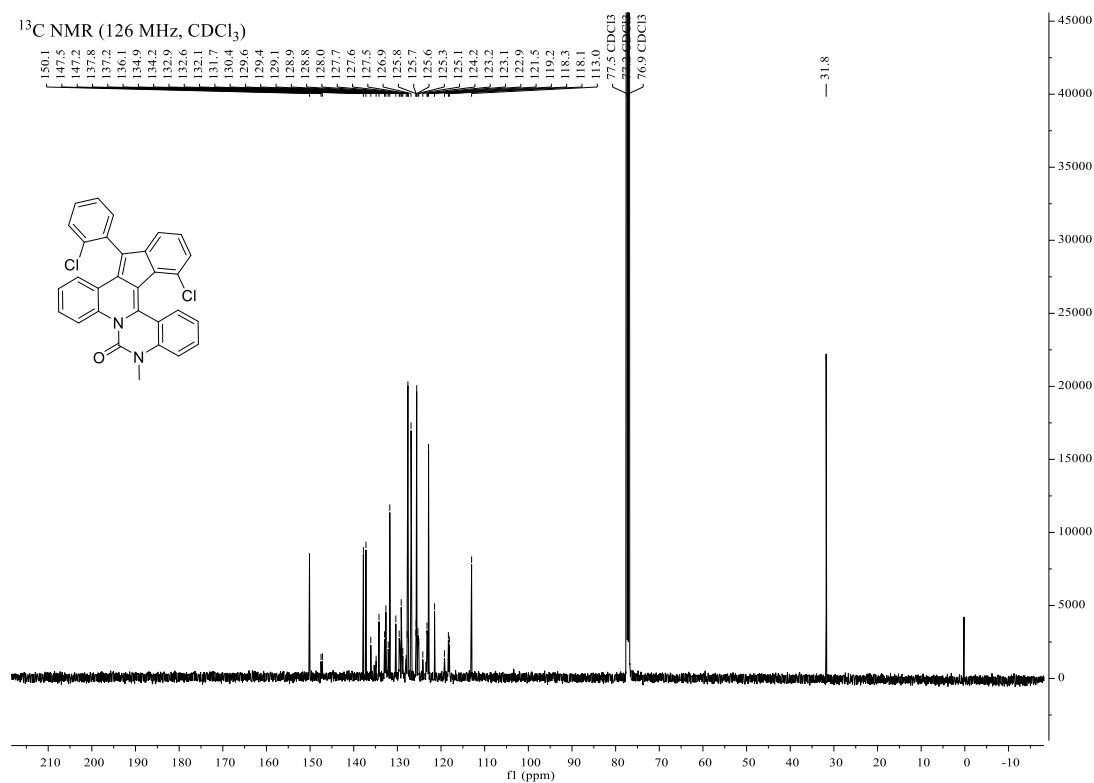


Compound 32

^1H NMR (500 MHz, CDCl_3)

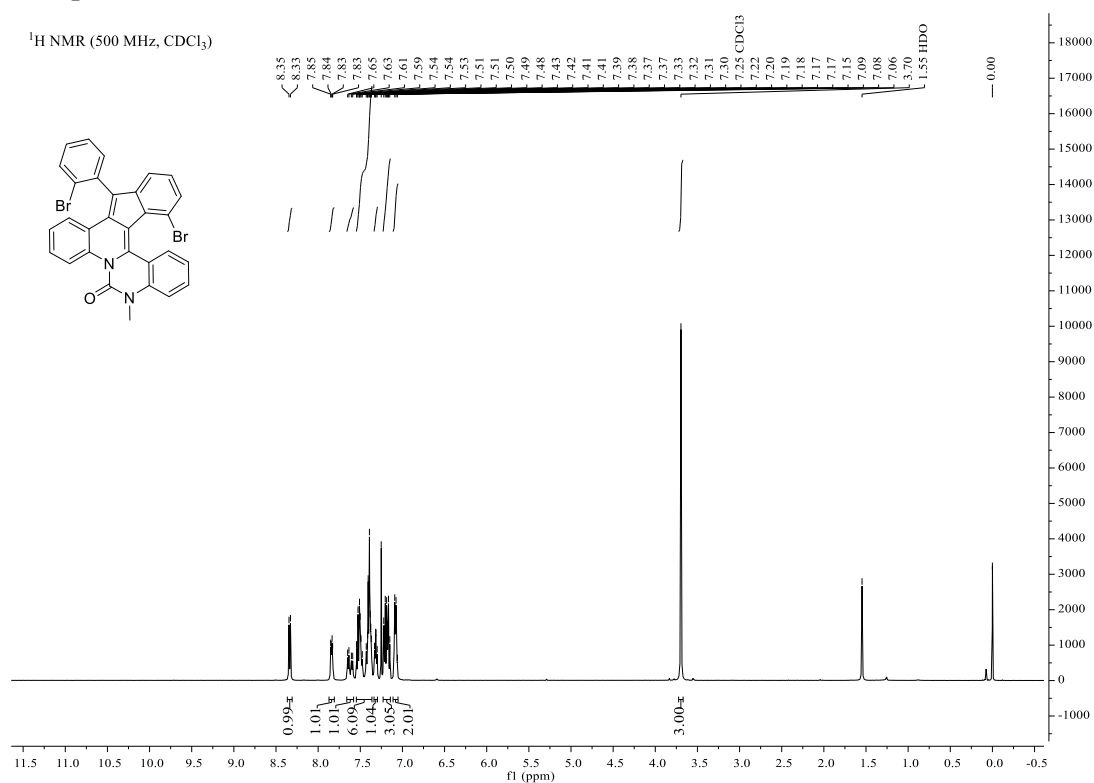


^{13}C NMR (126 MHz, CDCl_3)

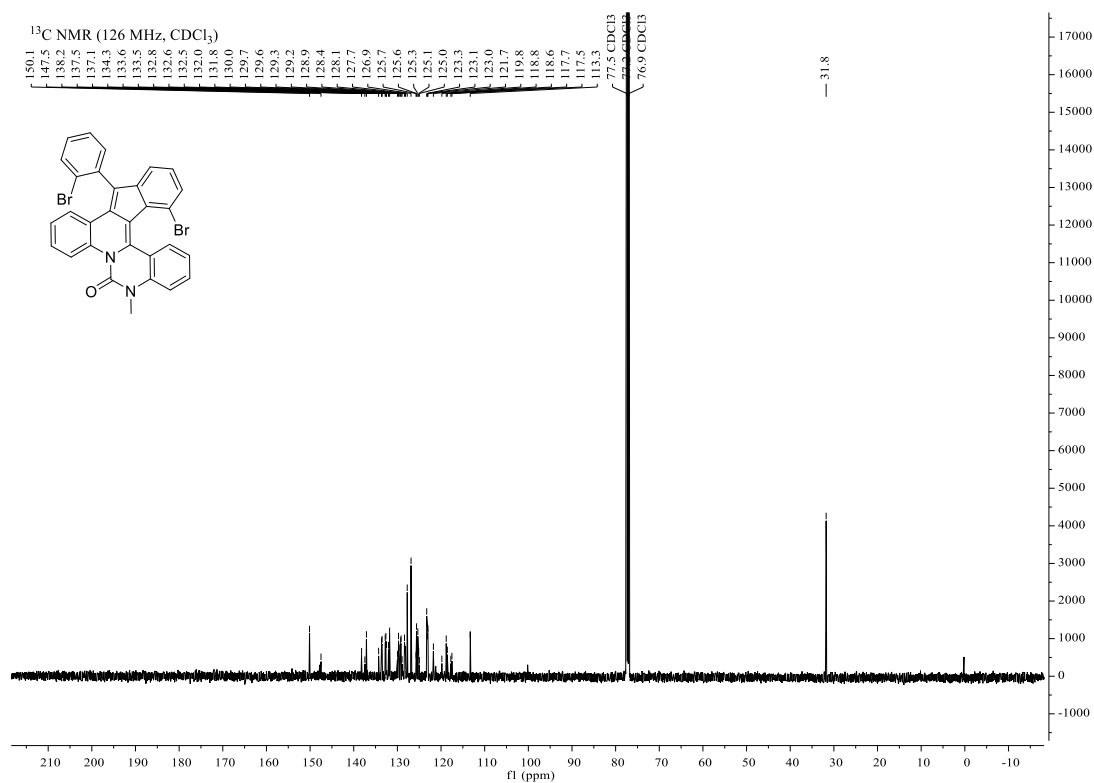


Compound 33

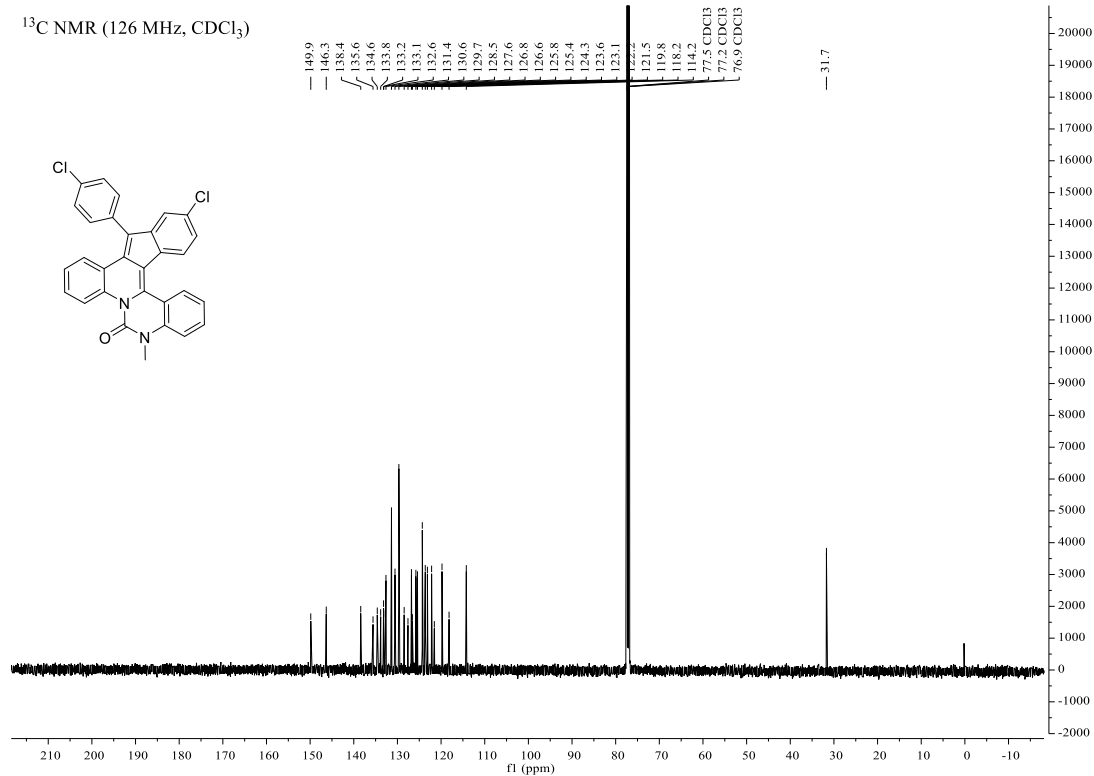
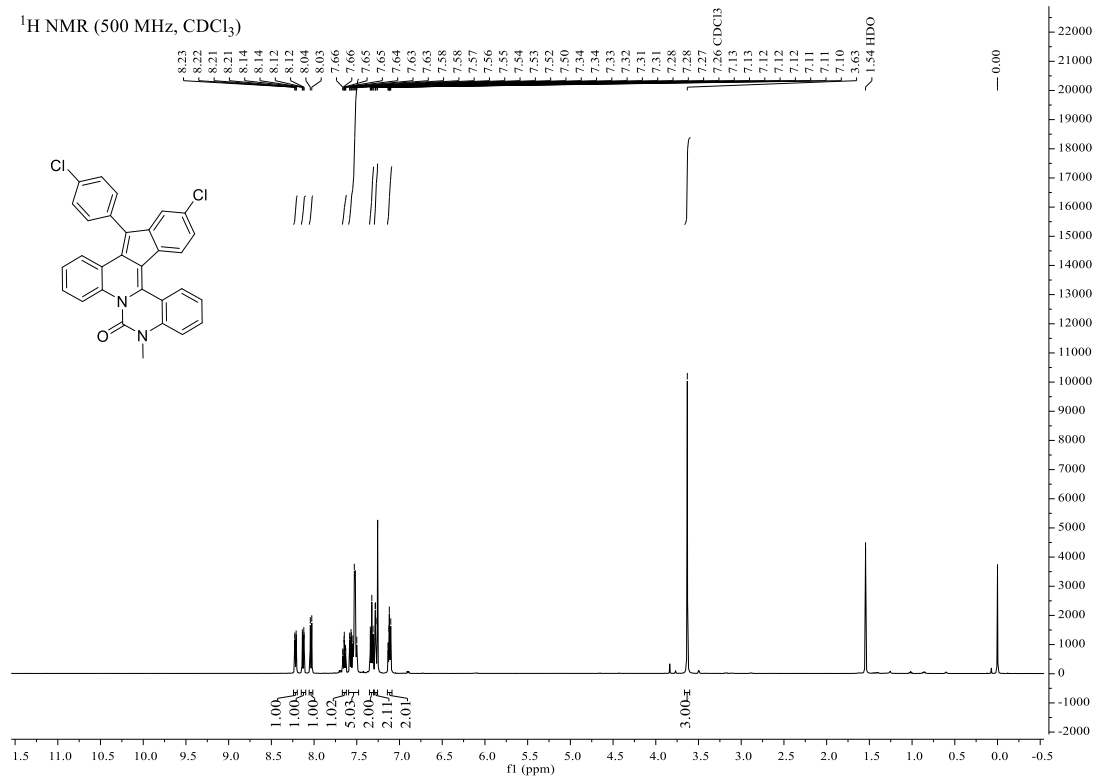
¹H NMR (500 MHz, CDCl₃)



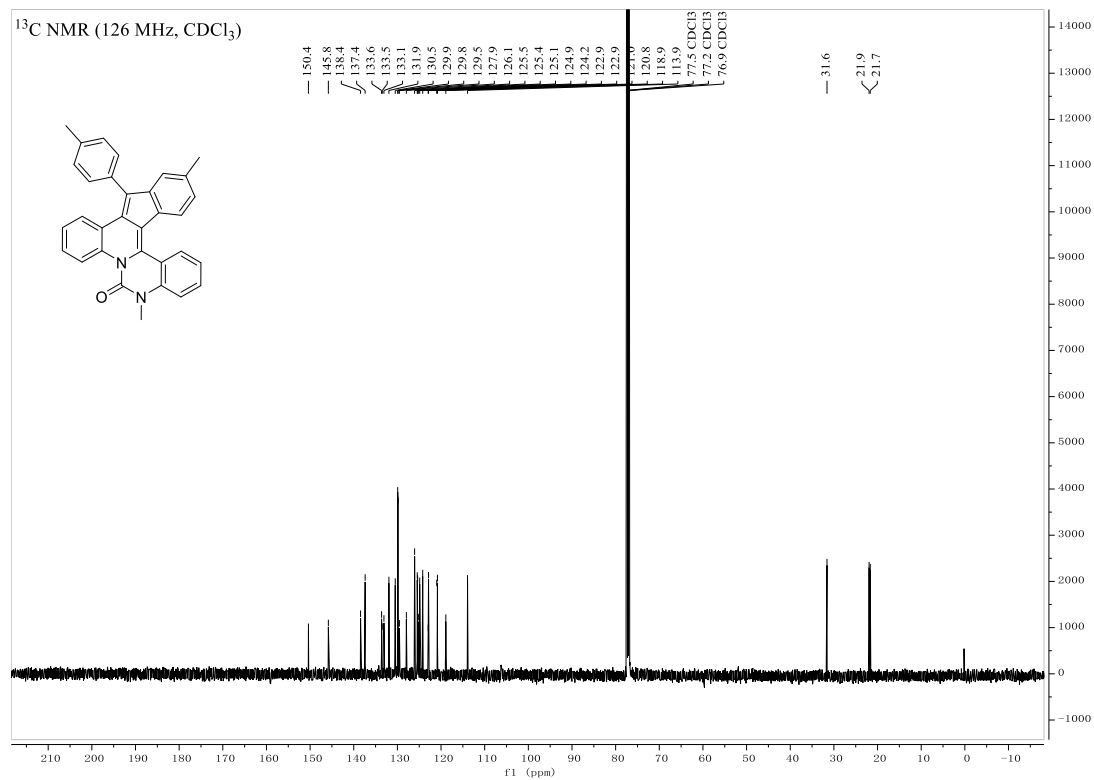
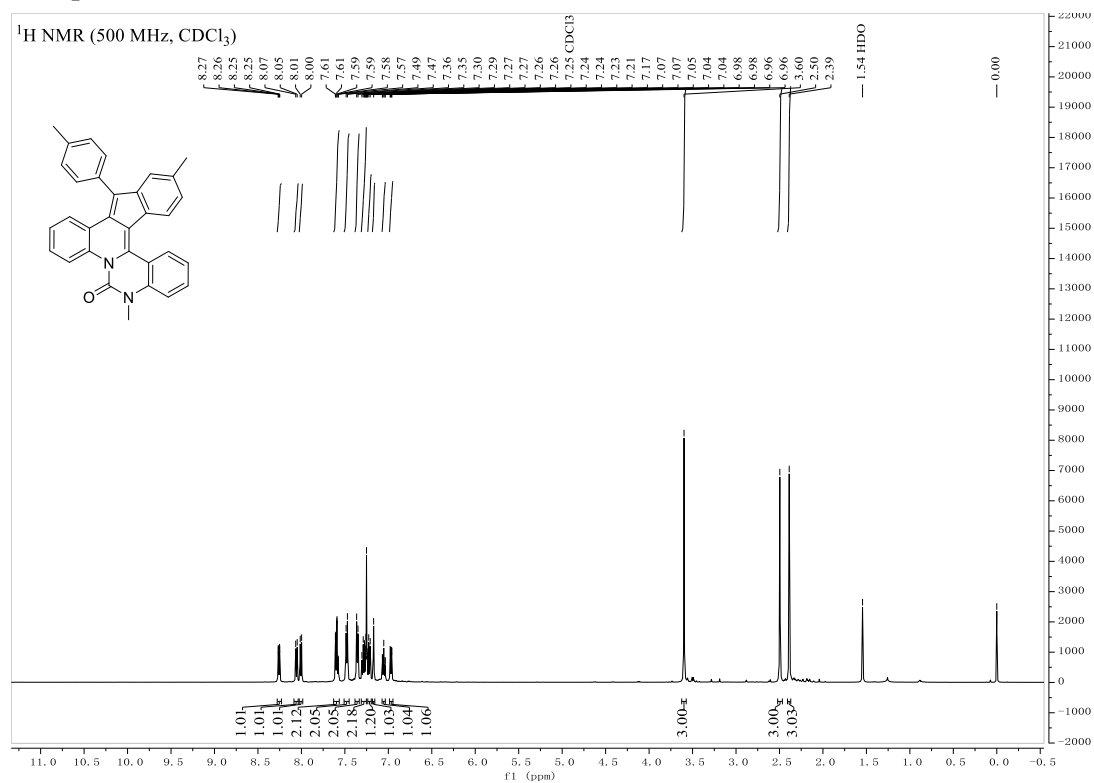
¹³C NMR (126 MHz, CDCl₃)



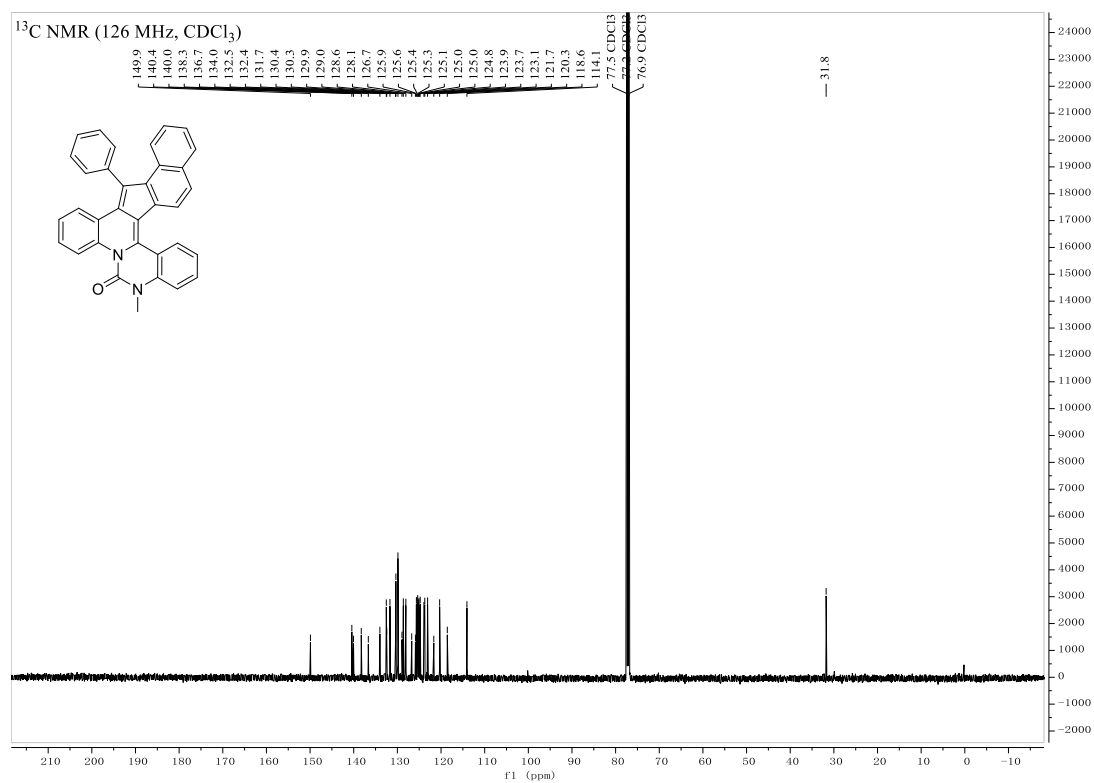
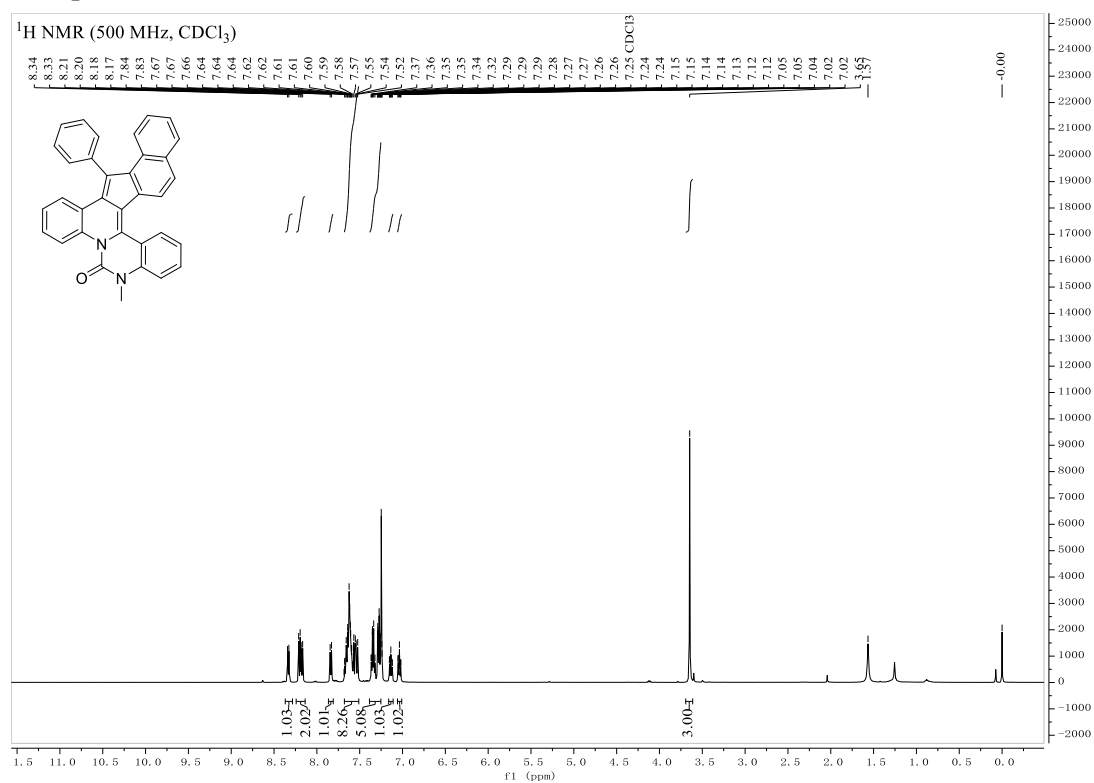
Compound 34



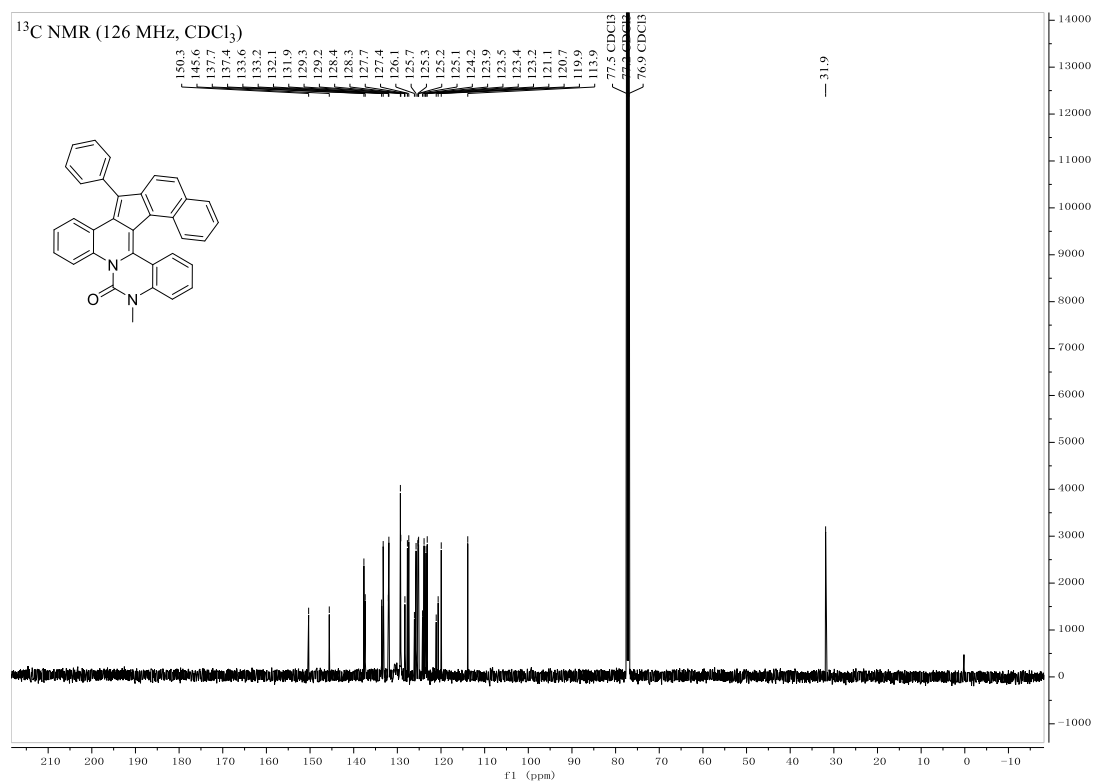
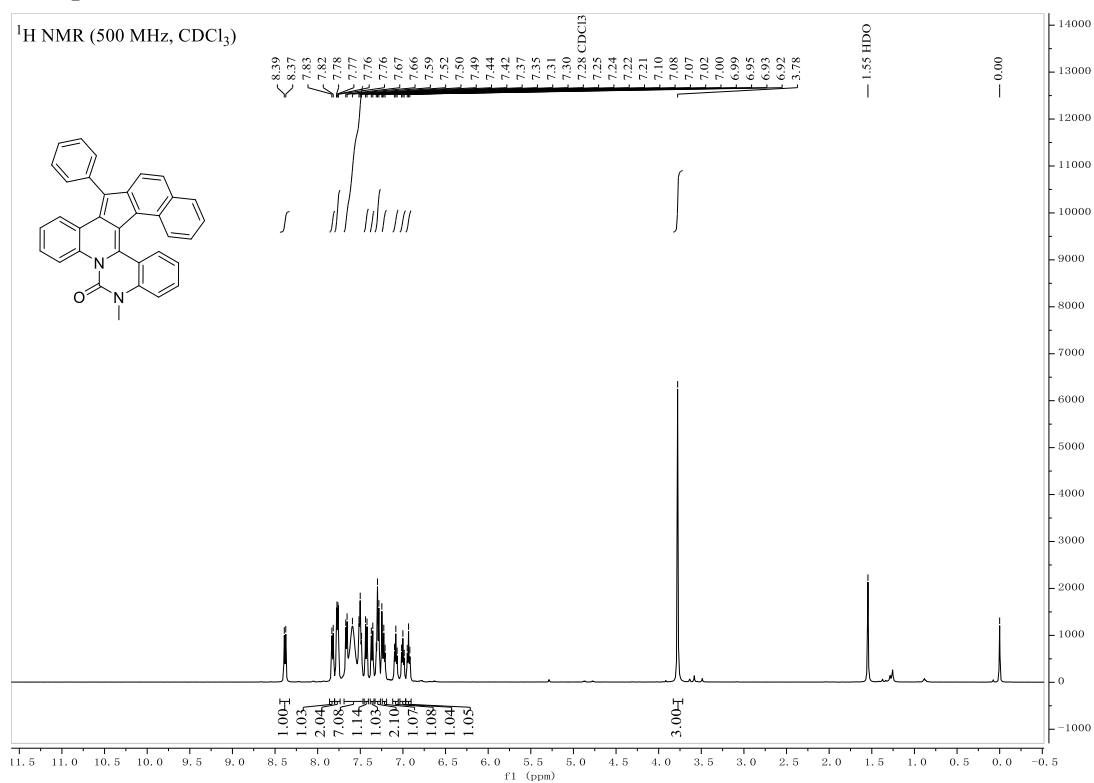
Compound 35



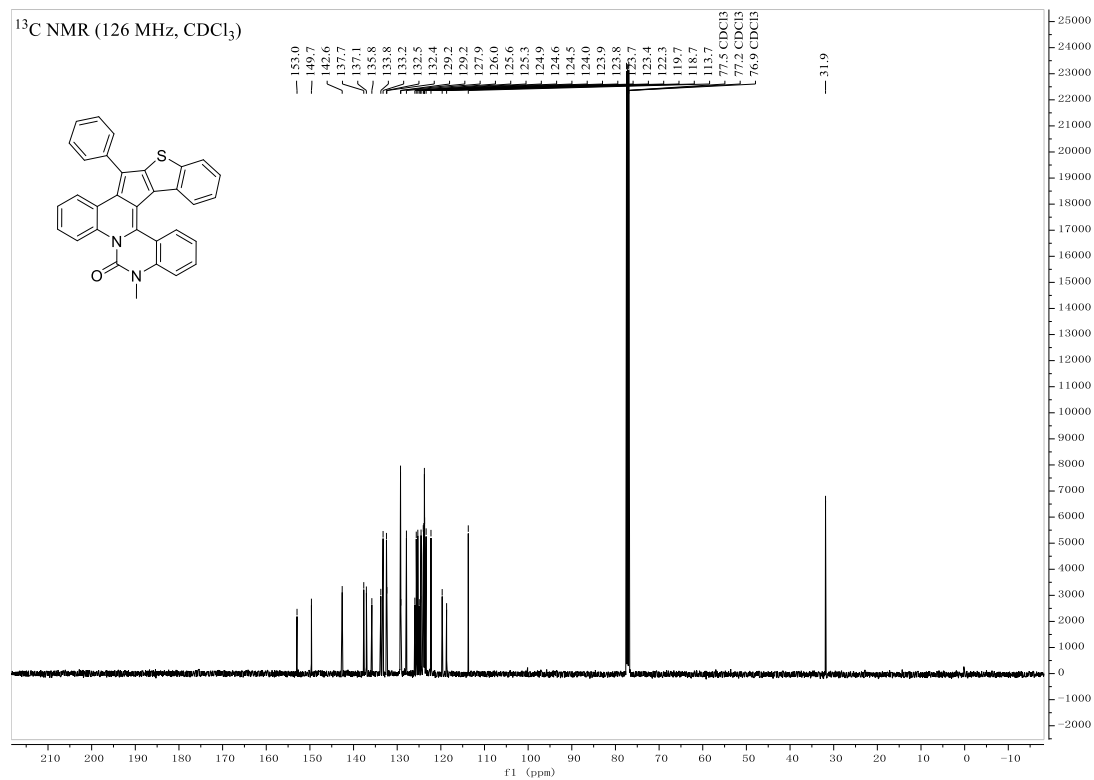
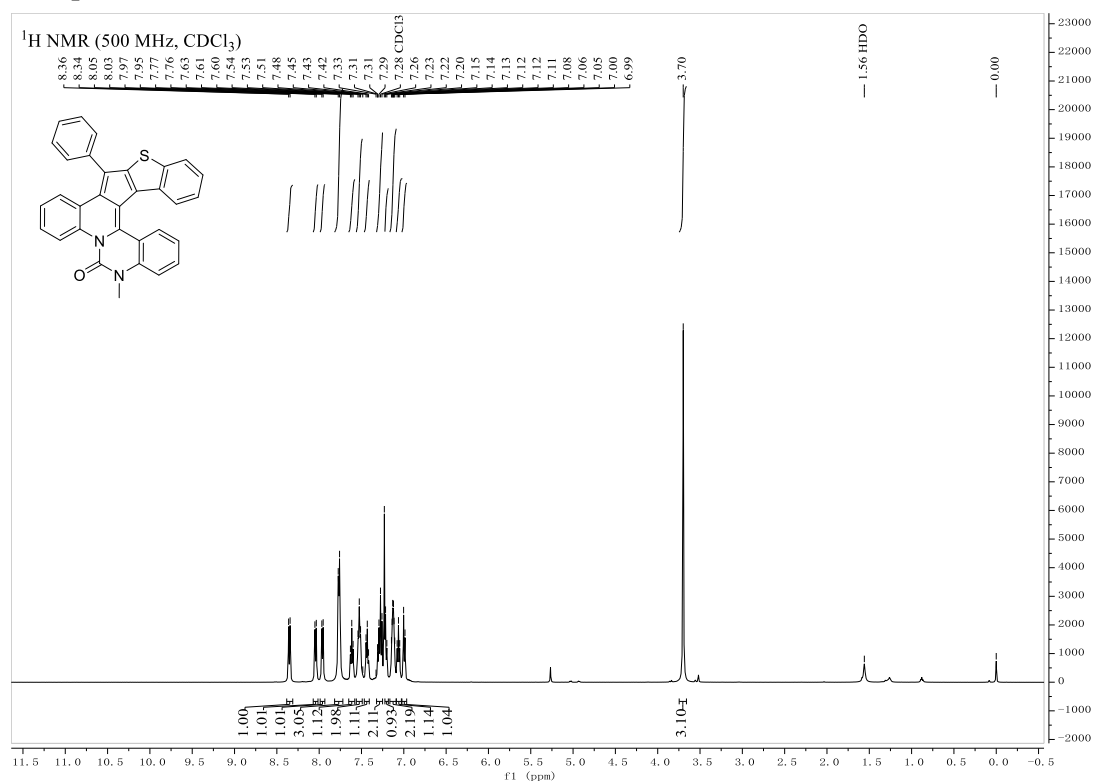
Compound 36



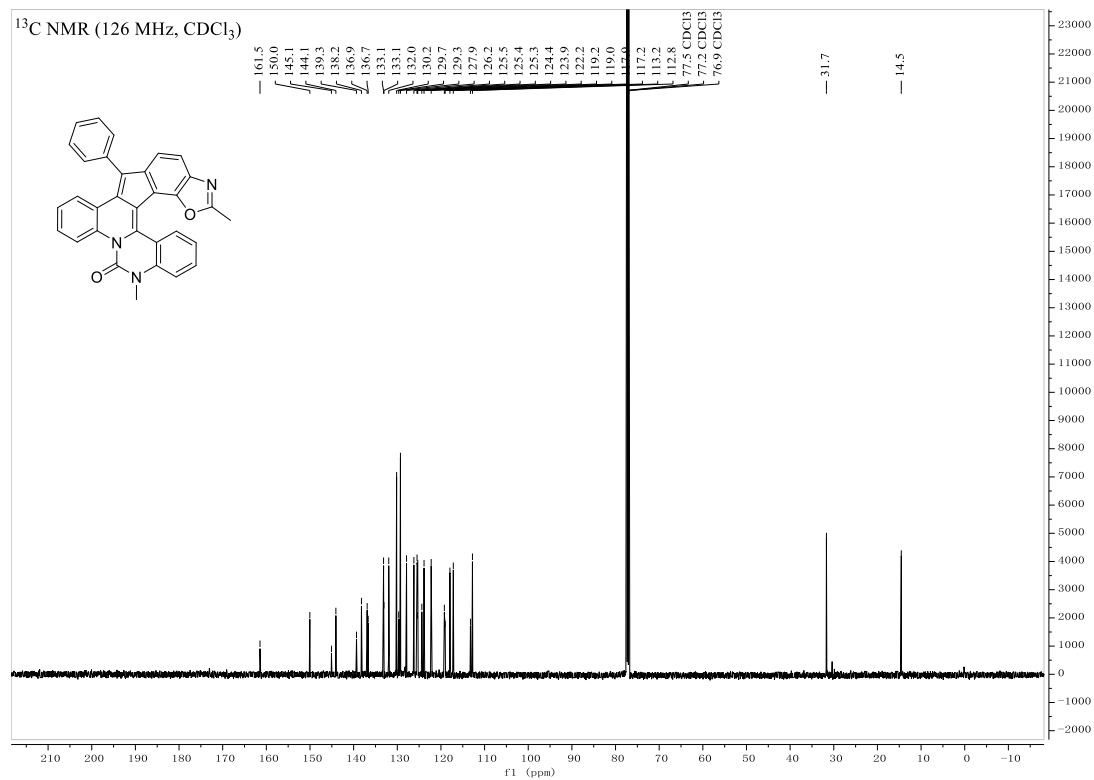
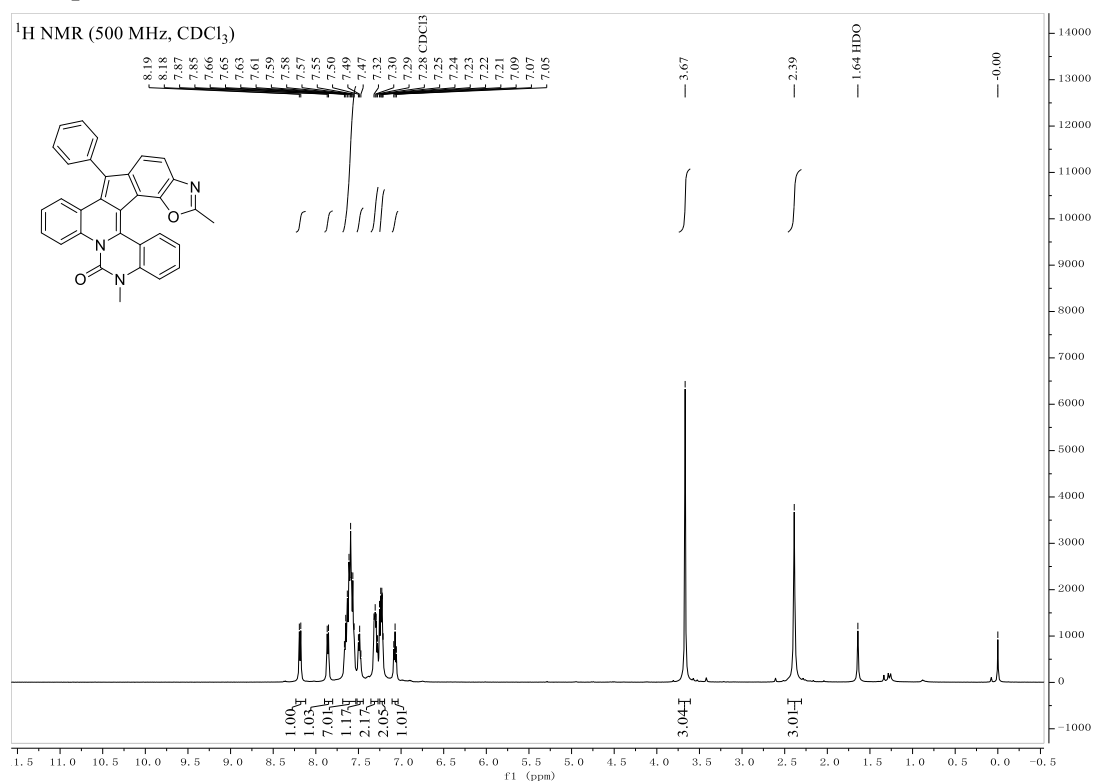
Compound 37



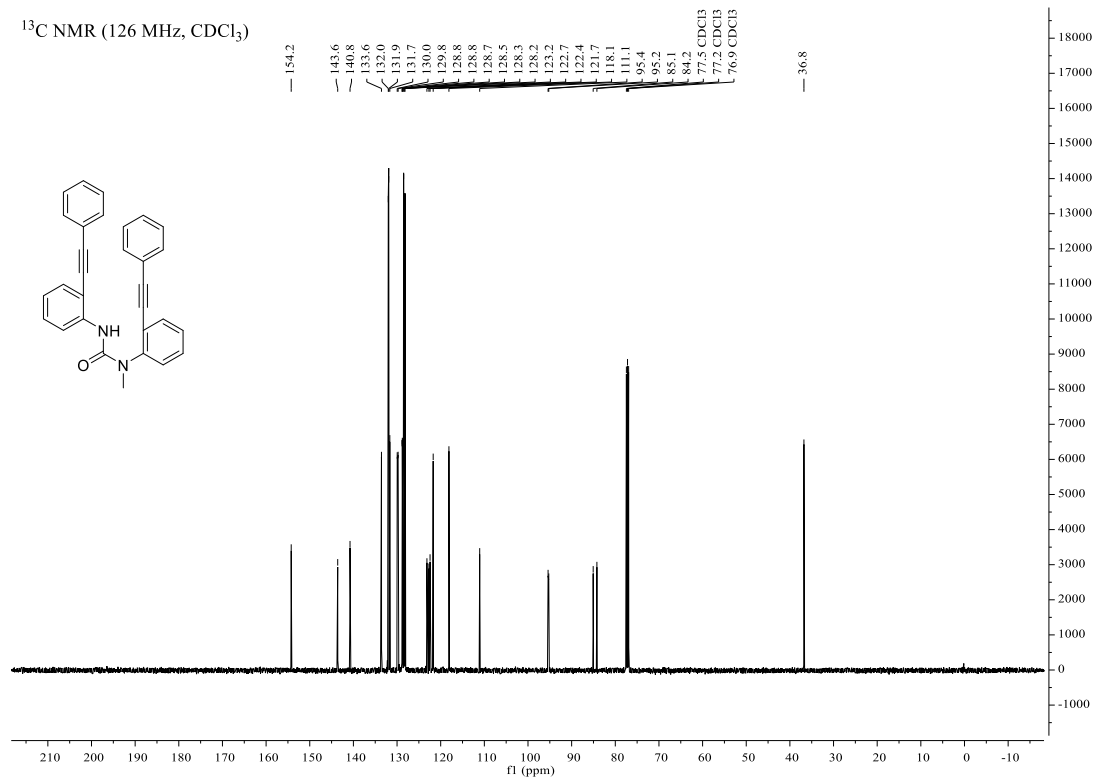
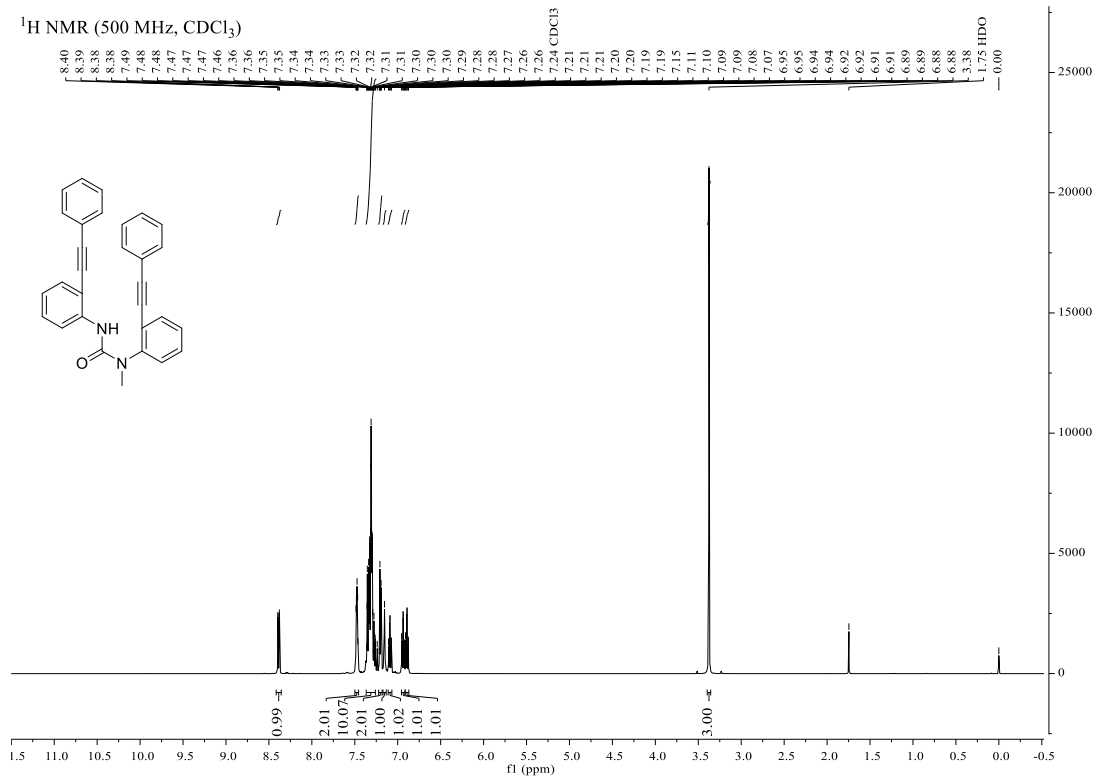
Compound 38



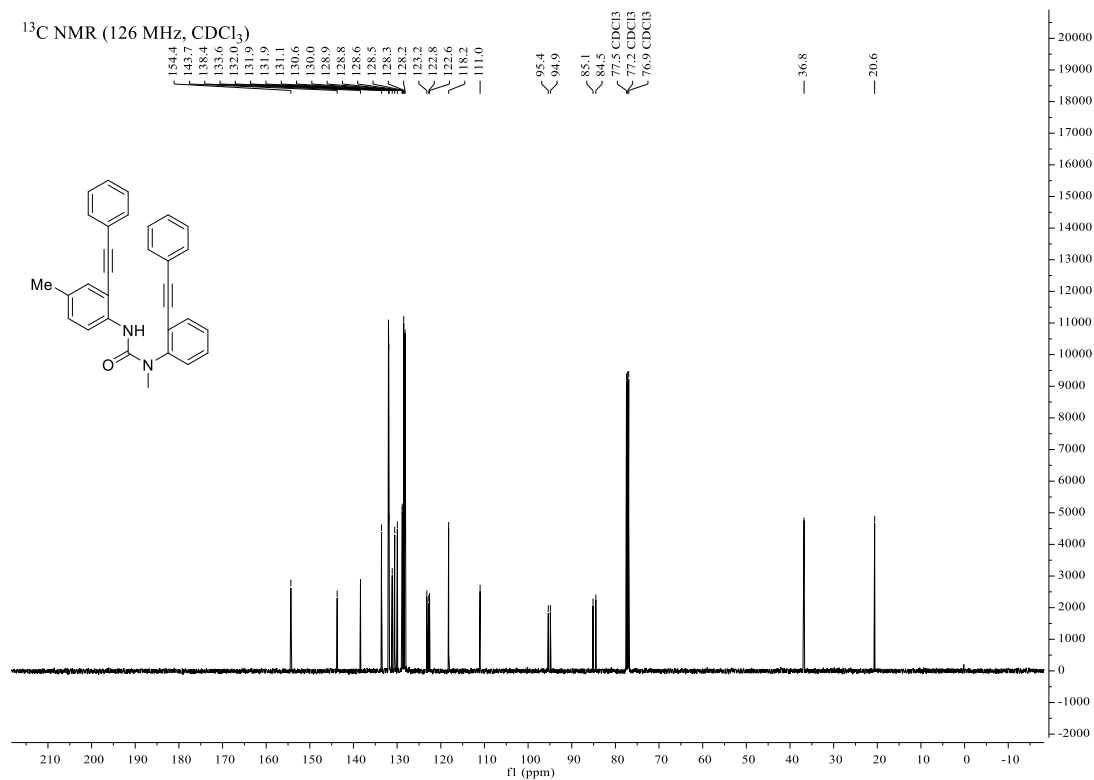
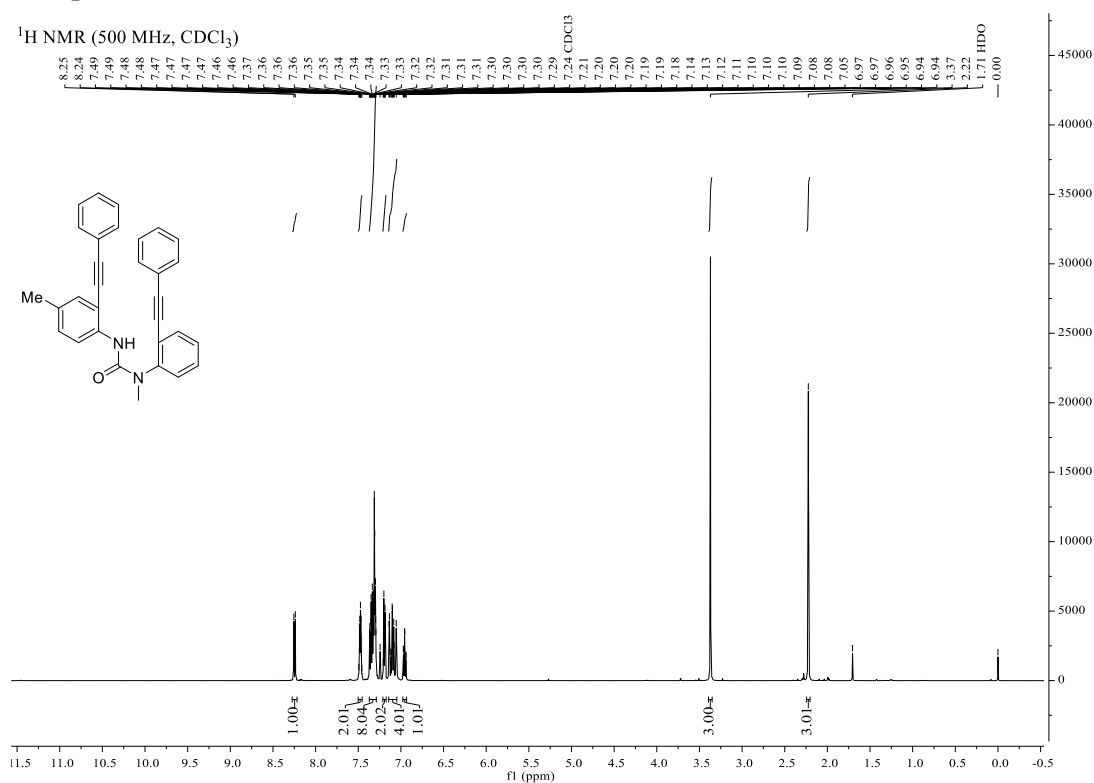
Compound 39



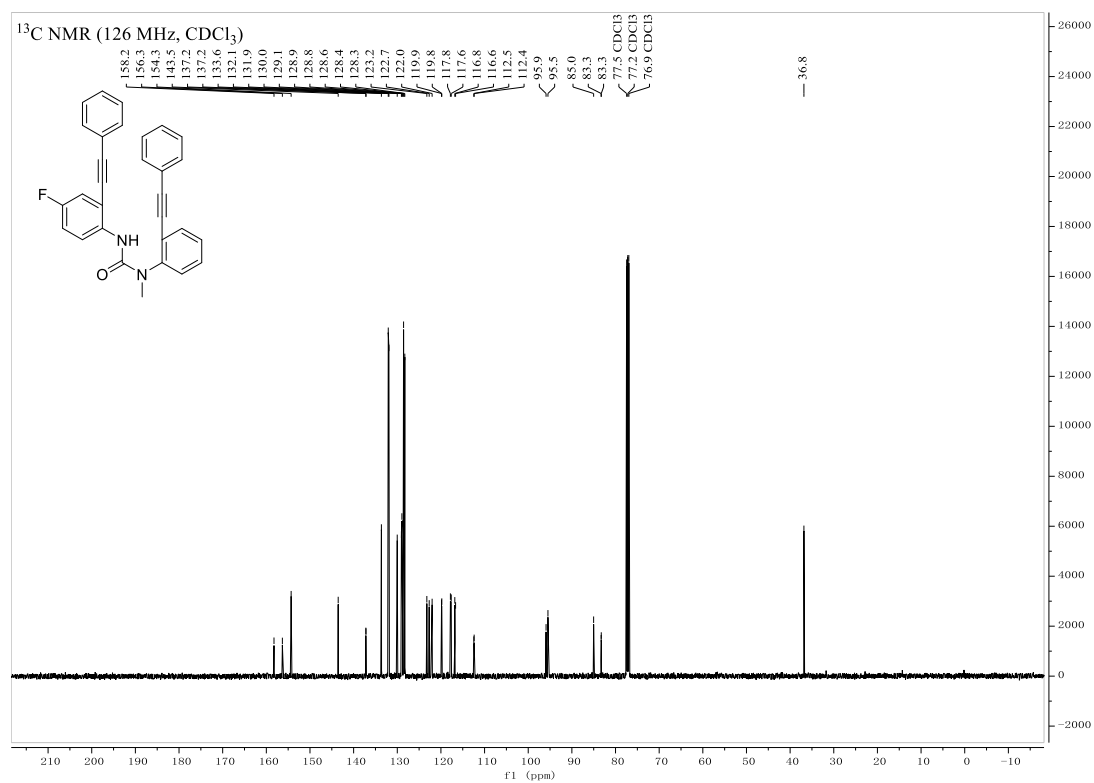
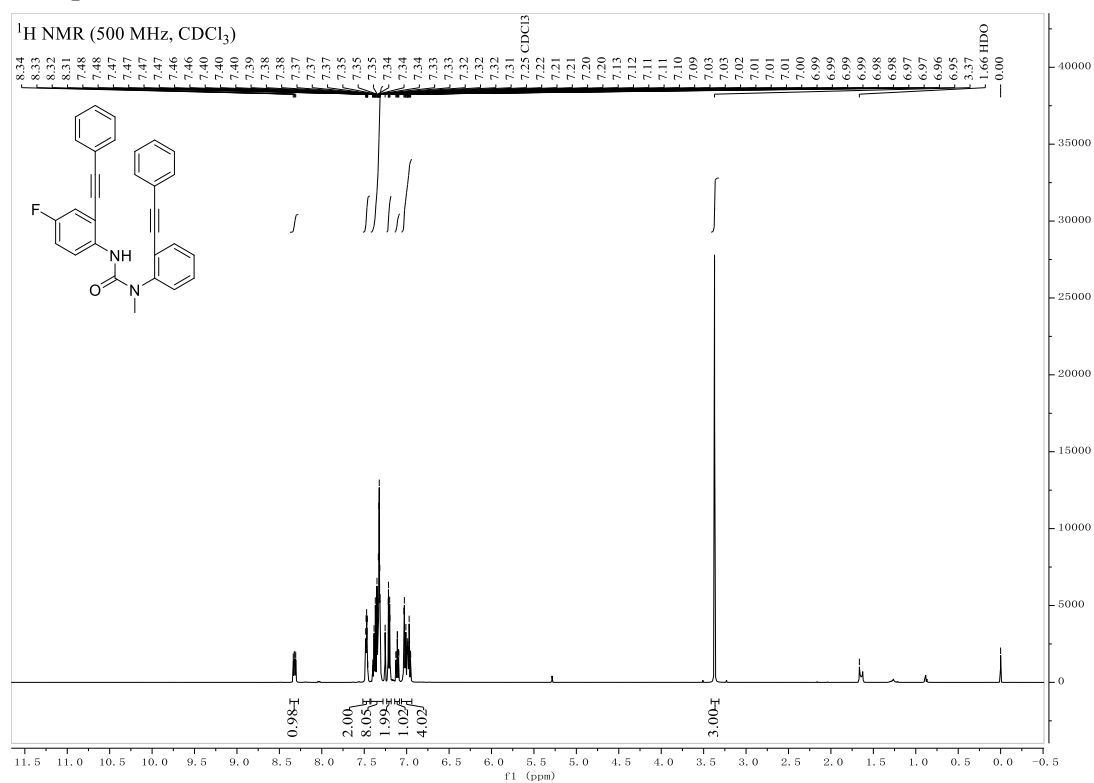
Compound 1

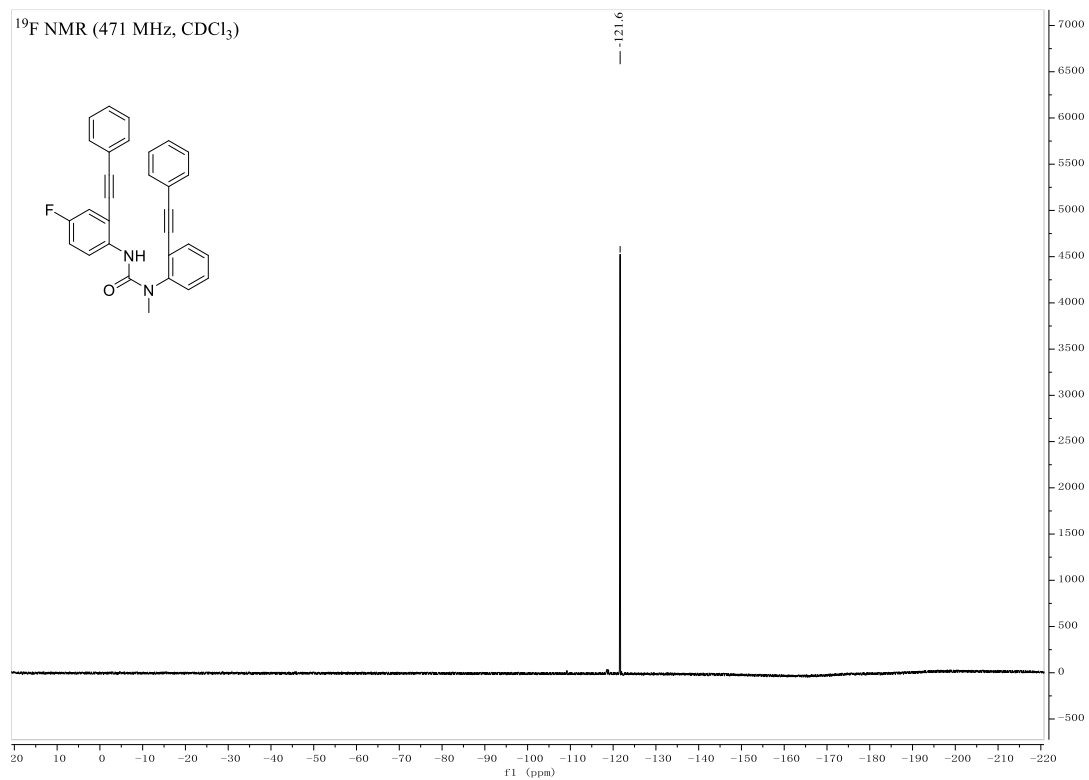


Compound S2

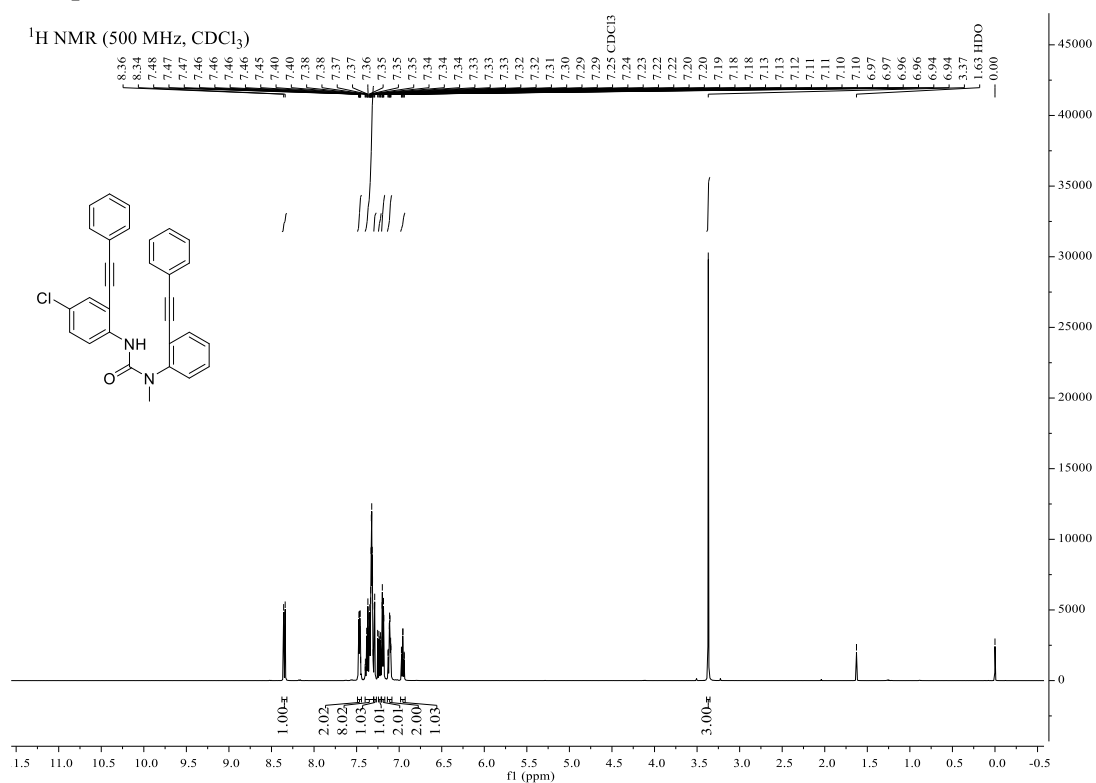


Compound S3

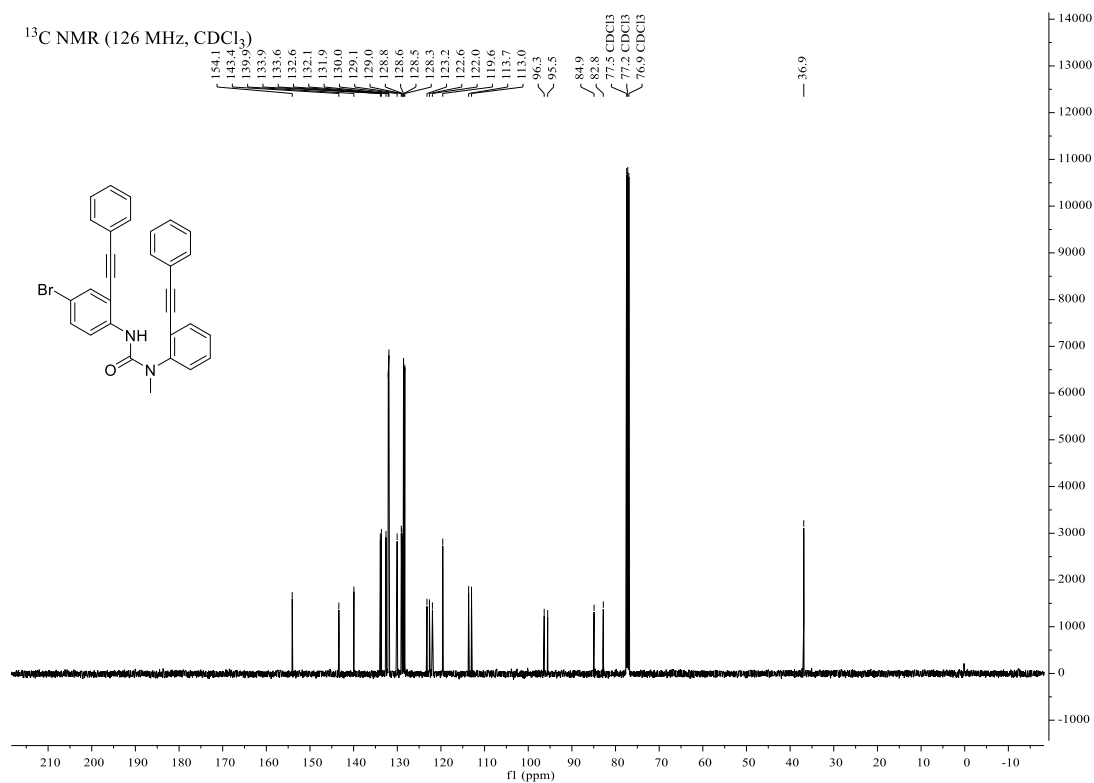
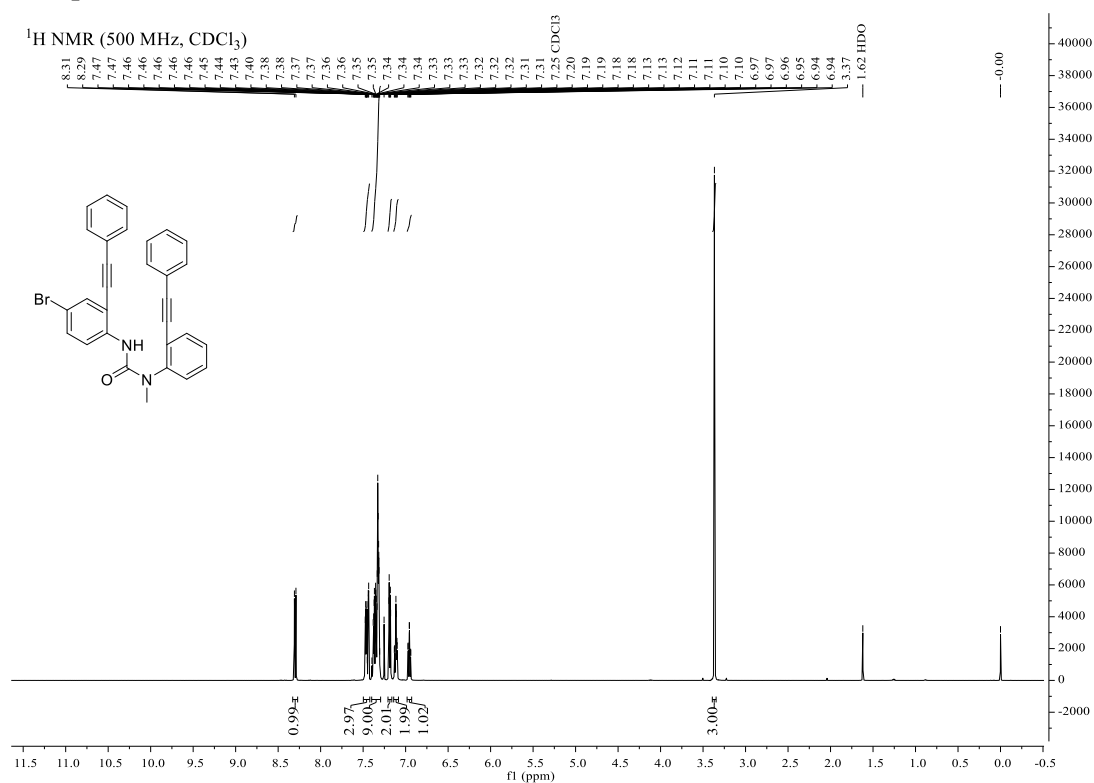




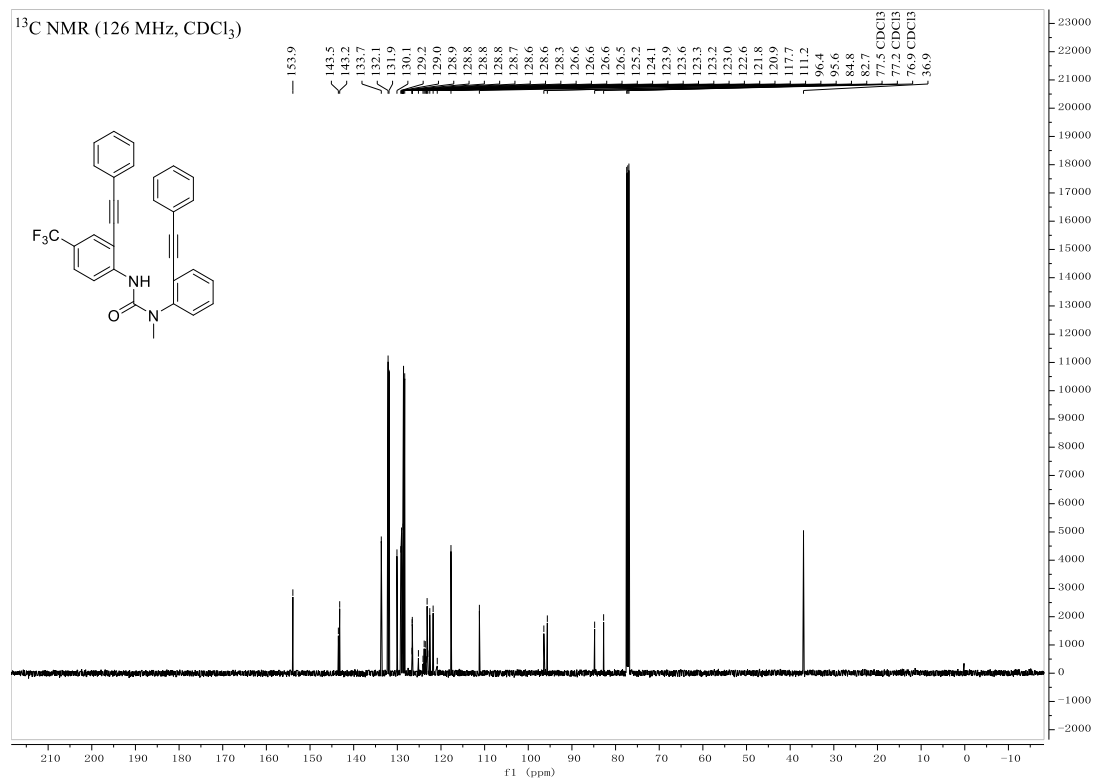
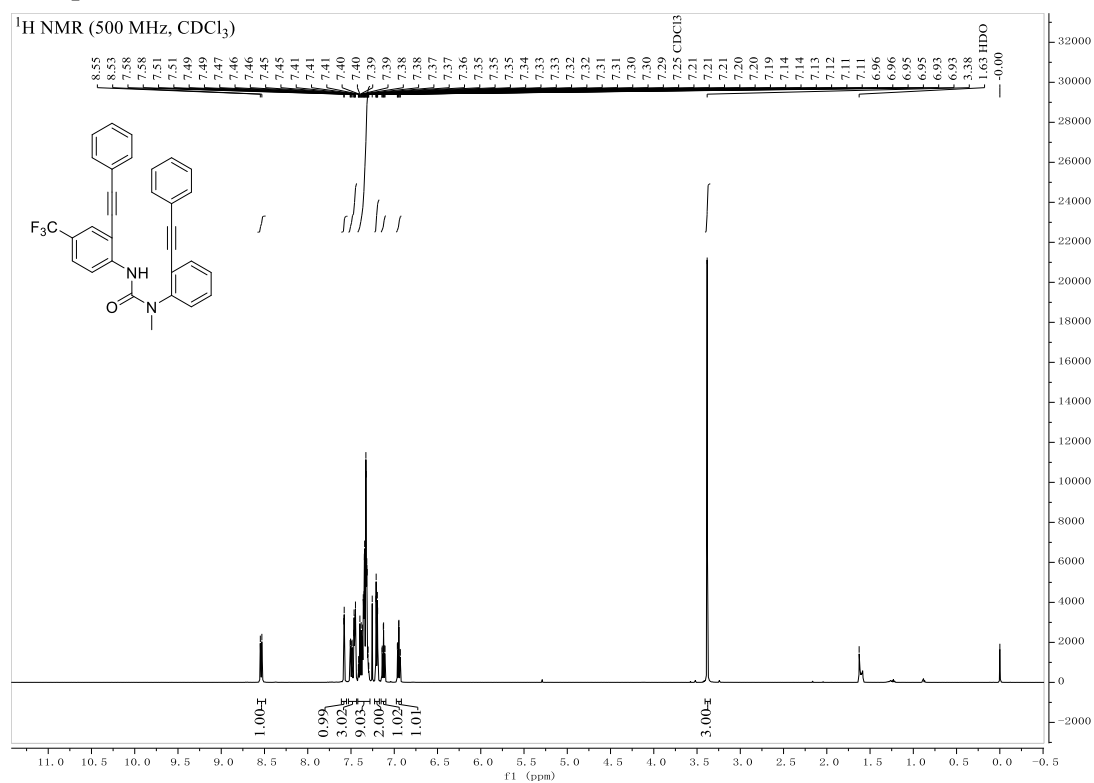
Compound S4

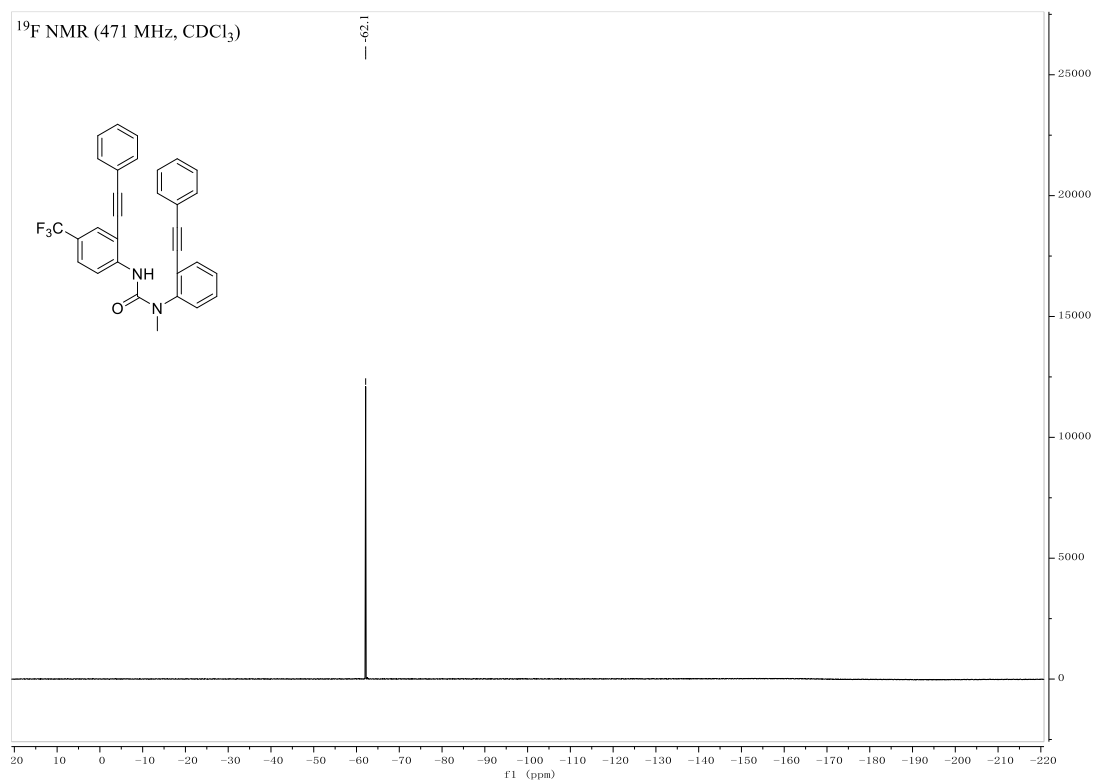


Compound S5

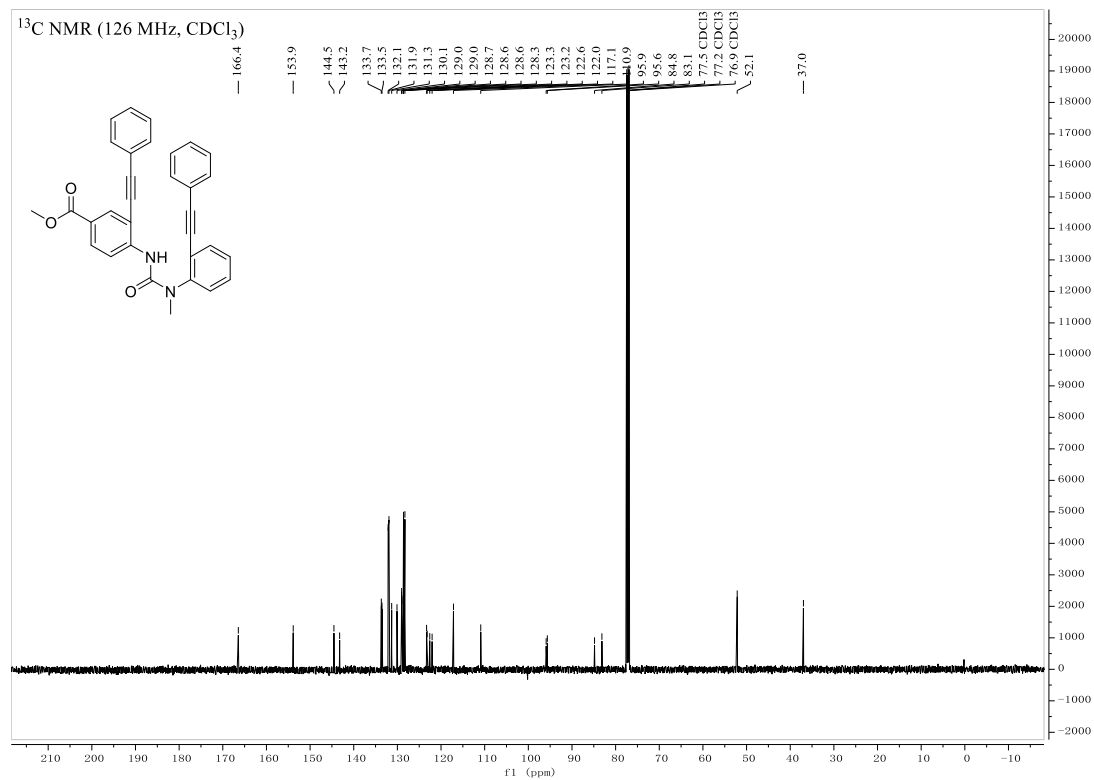
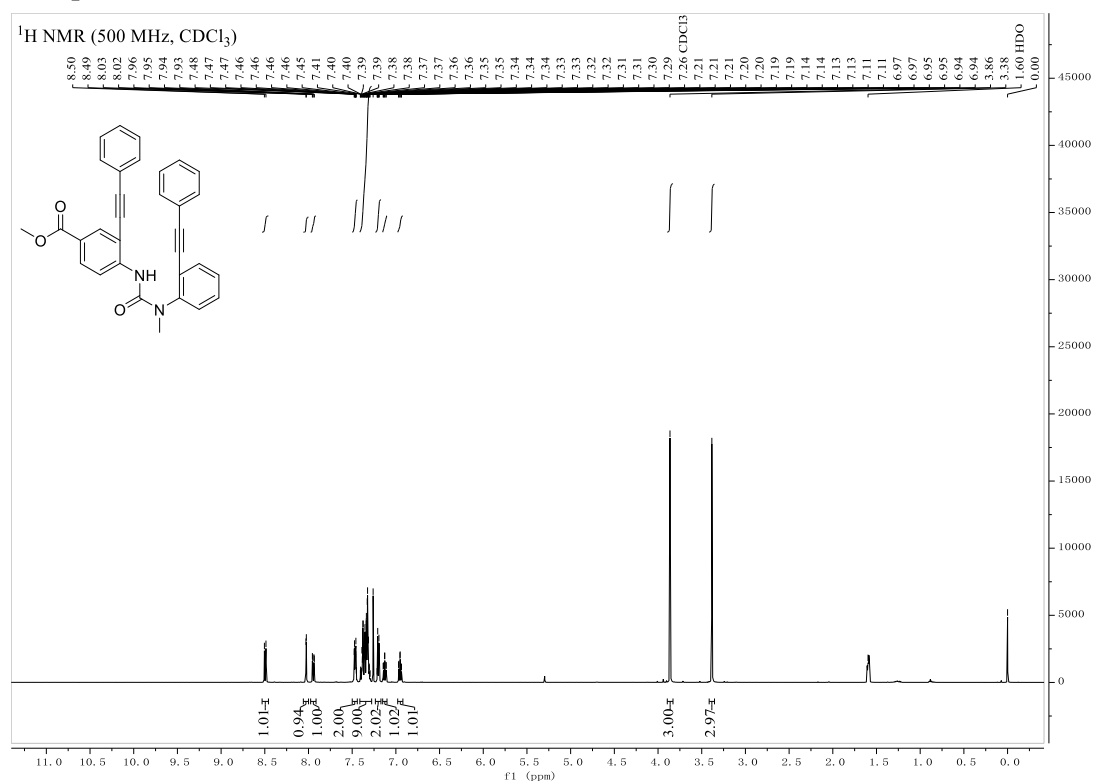


Compound S6

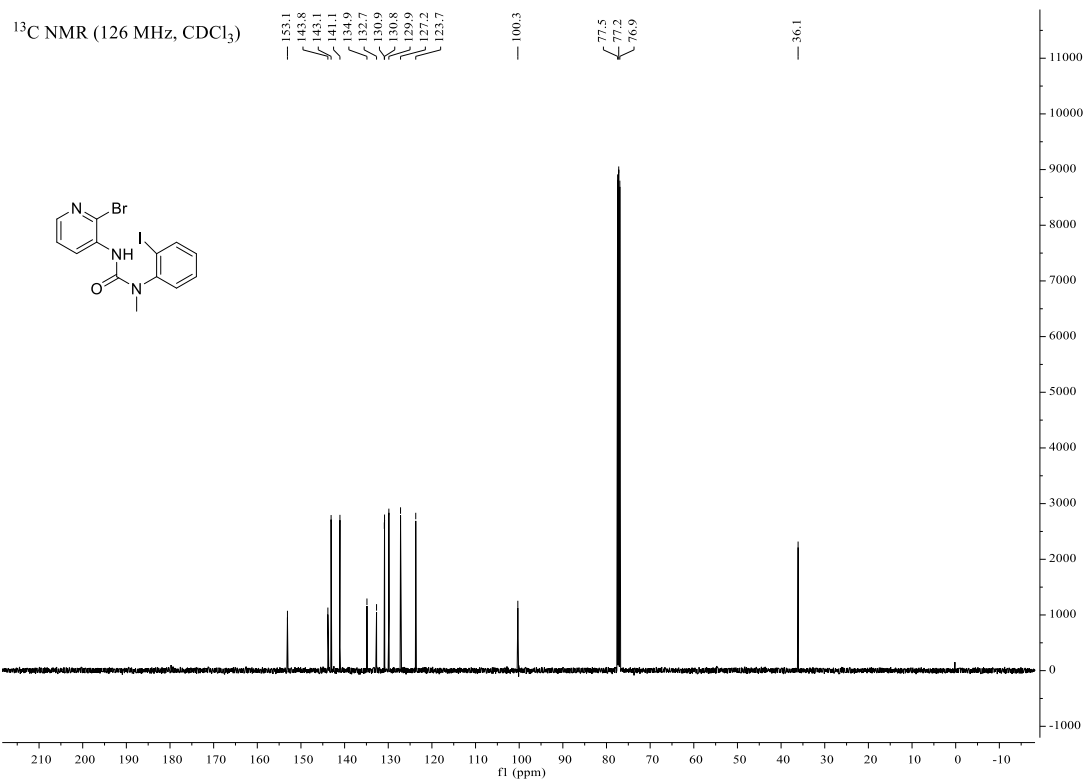
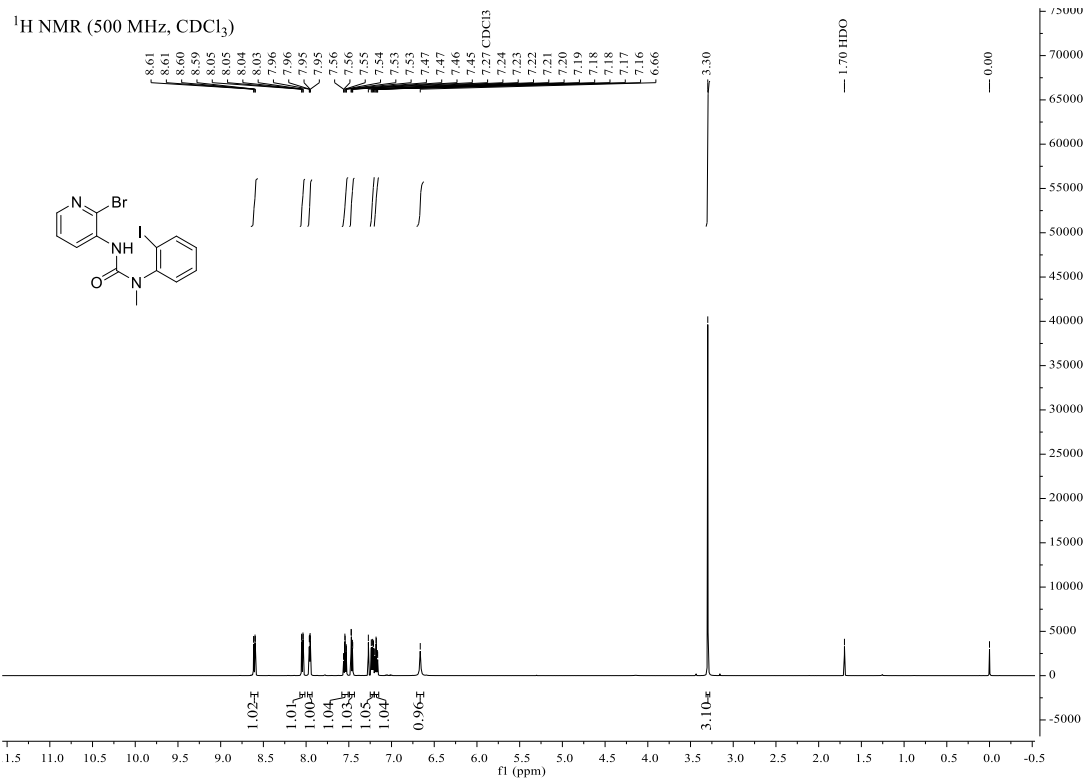




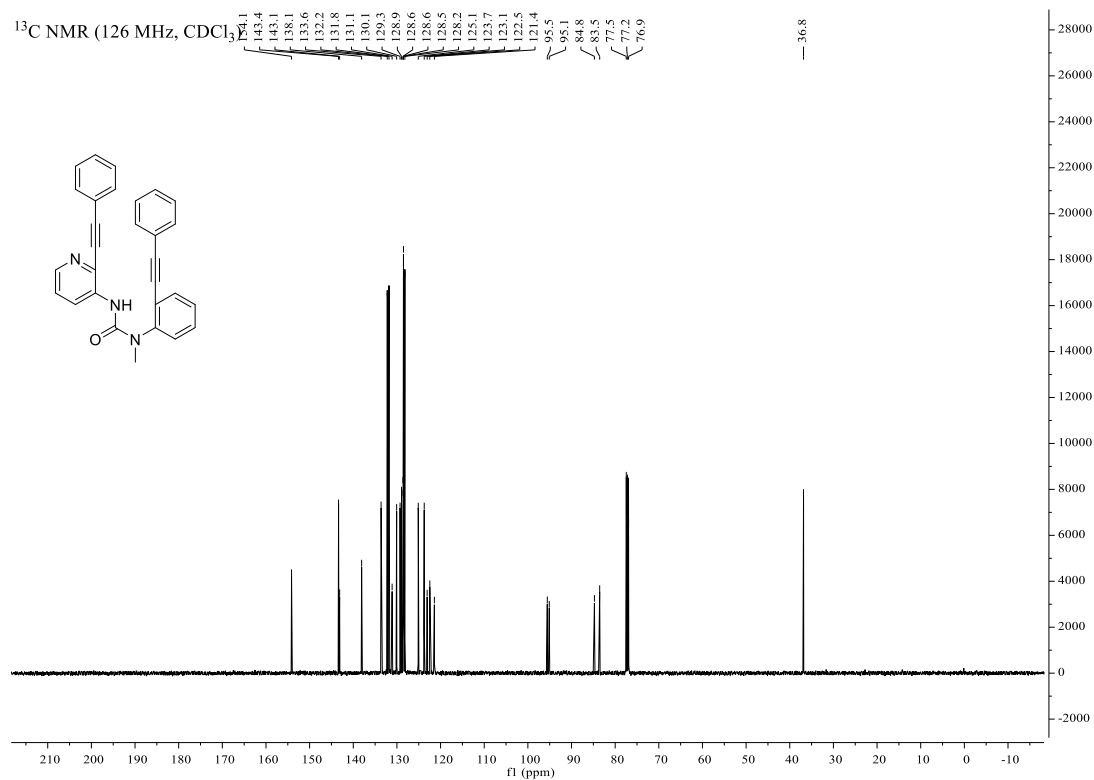
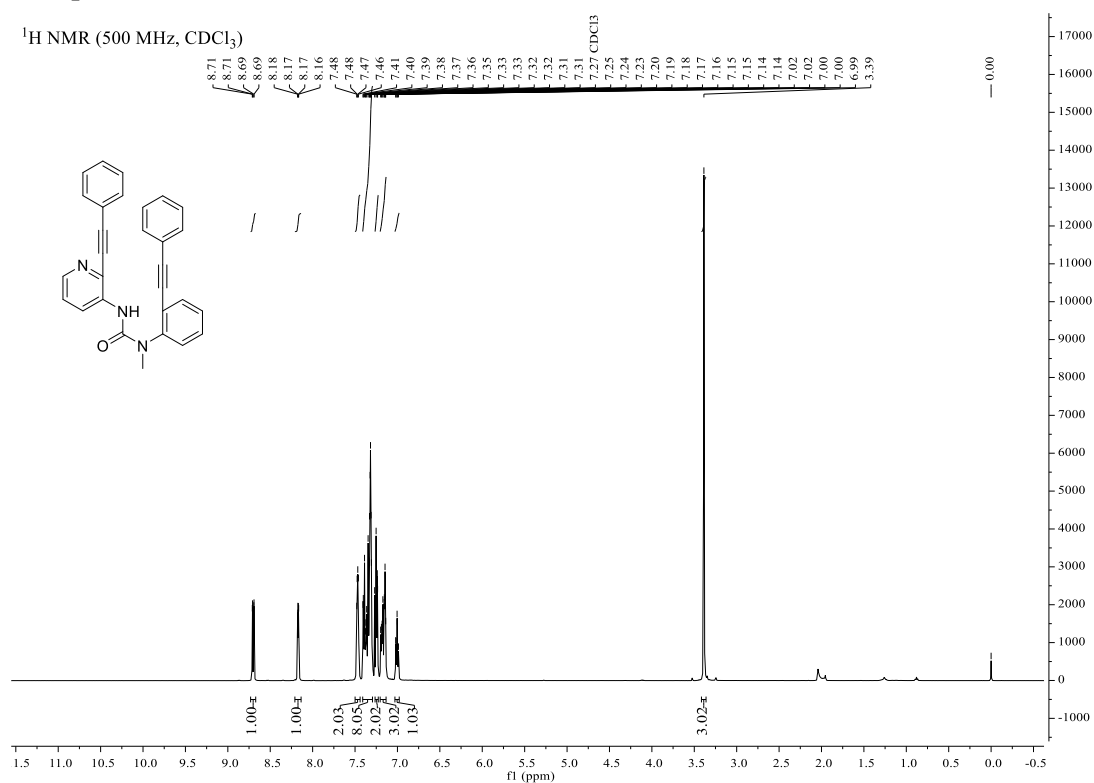
Compound S7



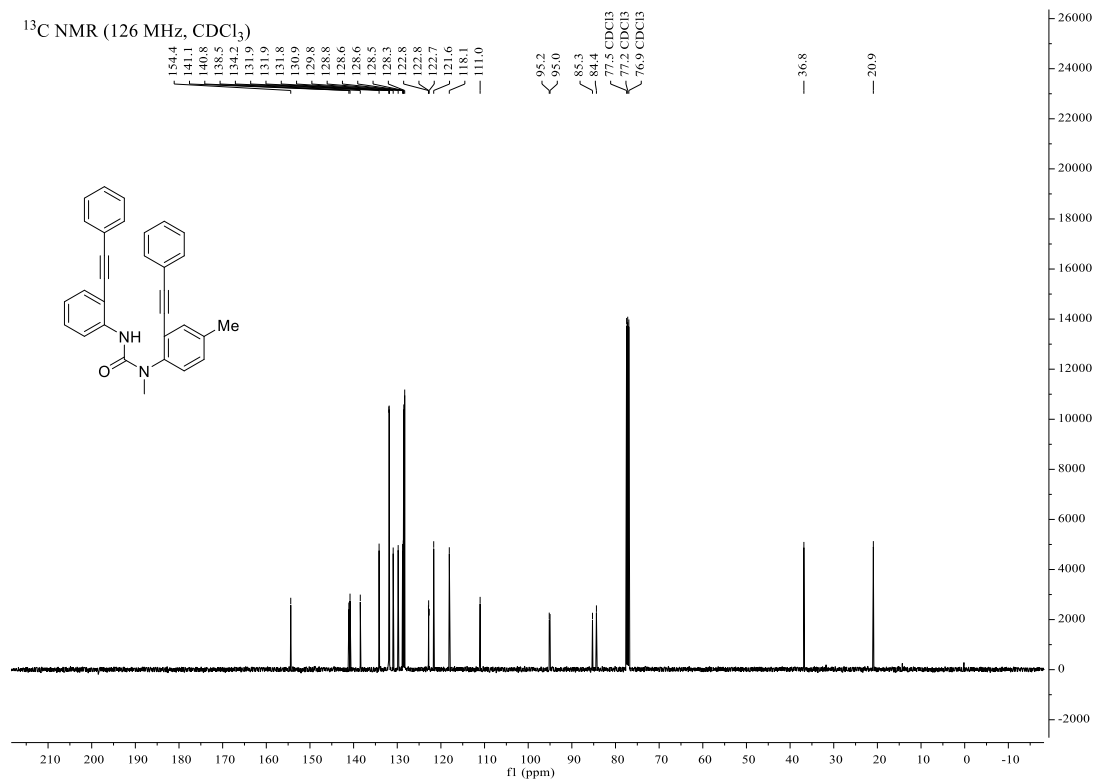
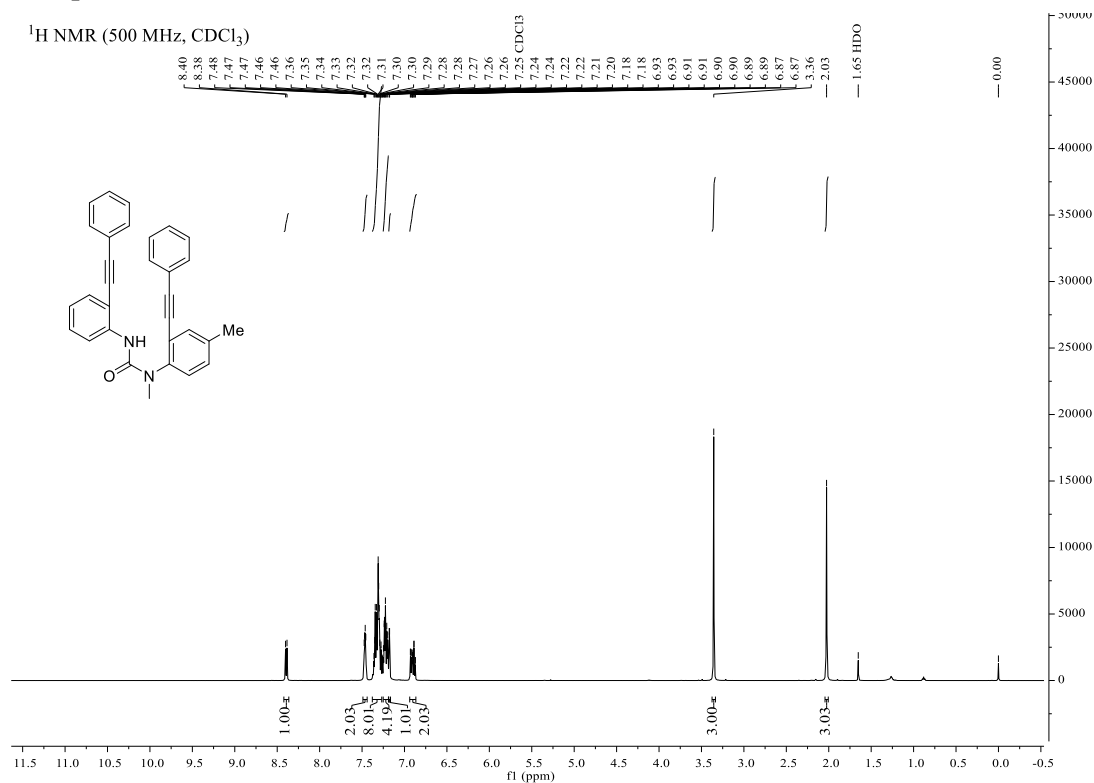
Compound S8



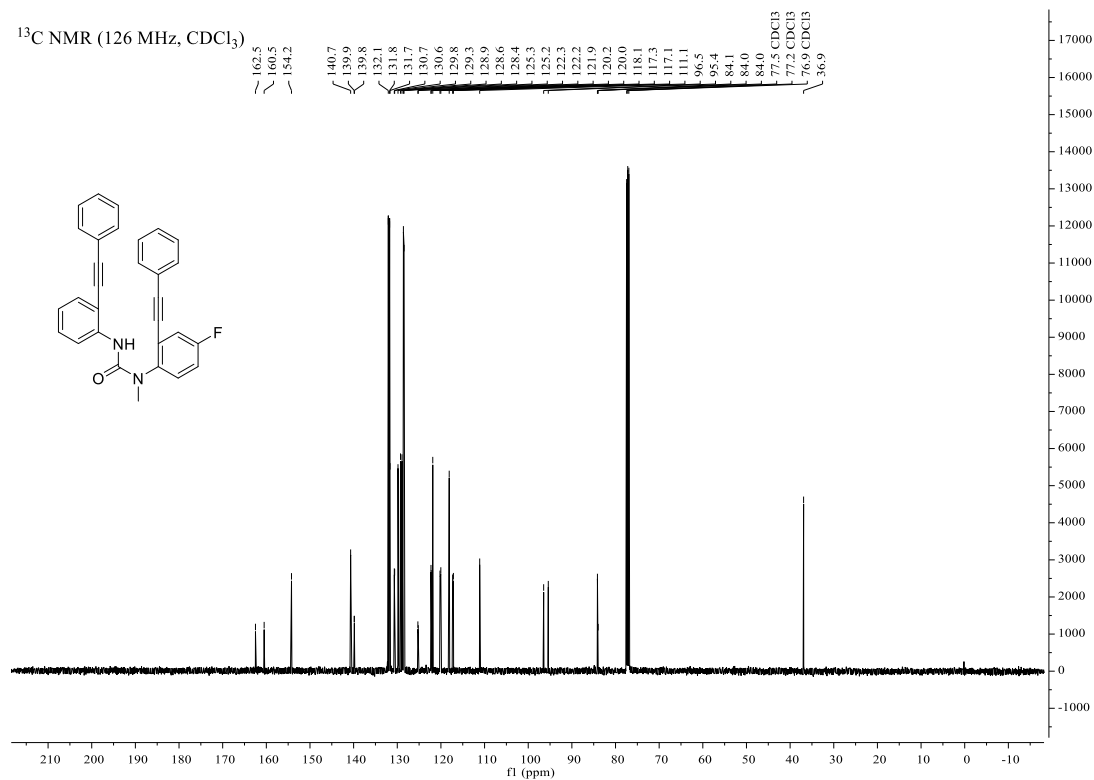
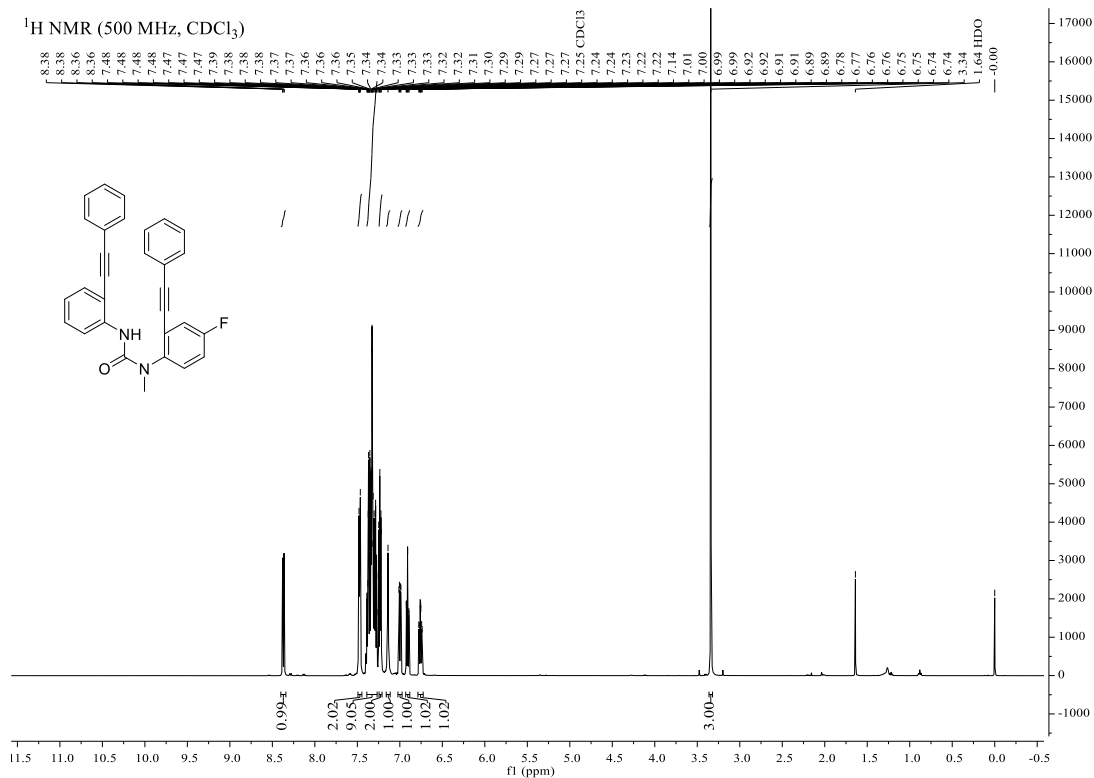
Compound S9



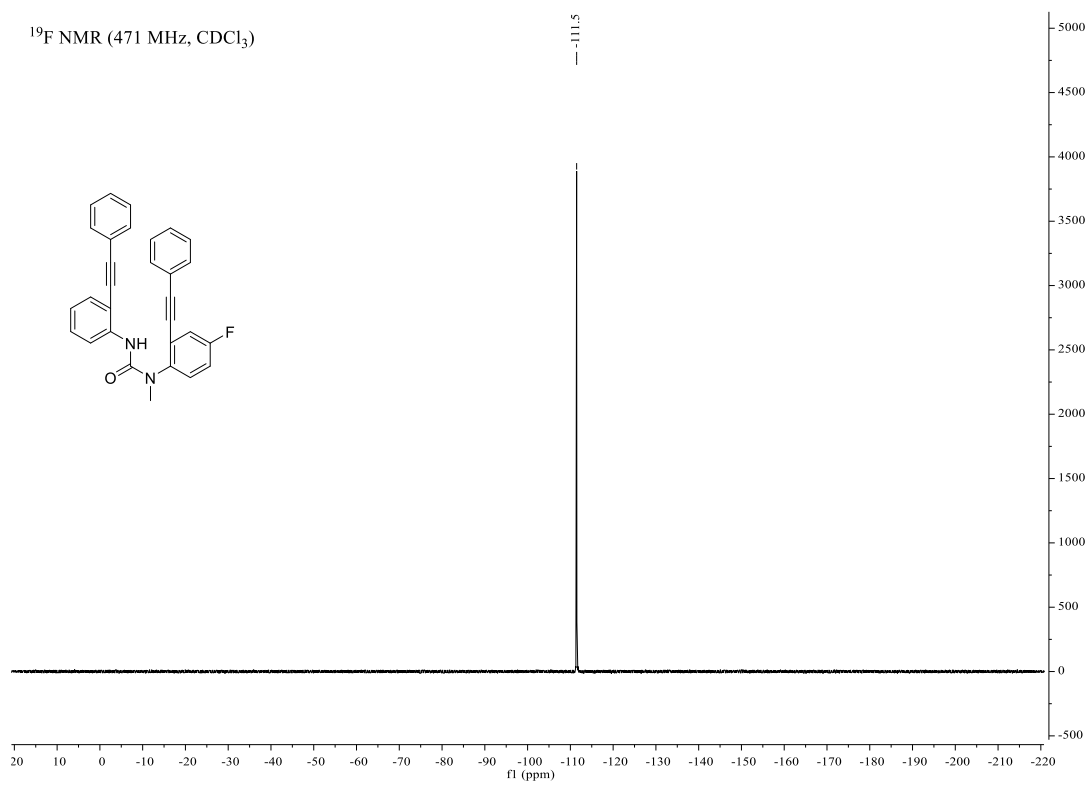
Compound S10



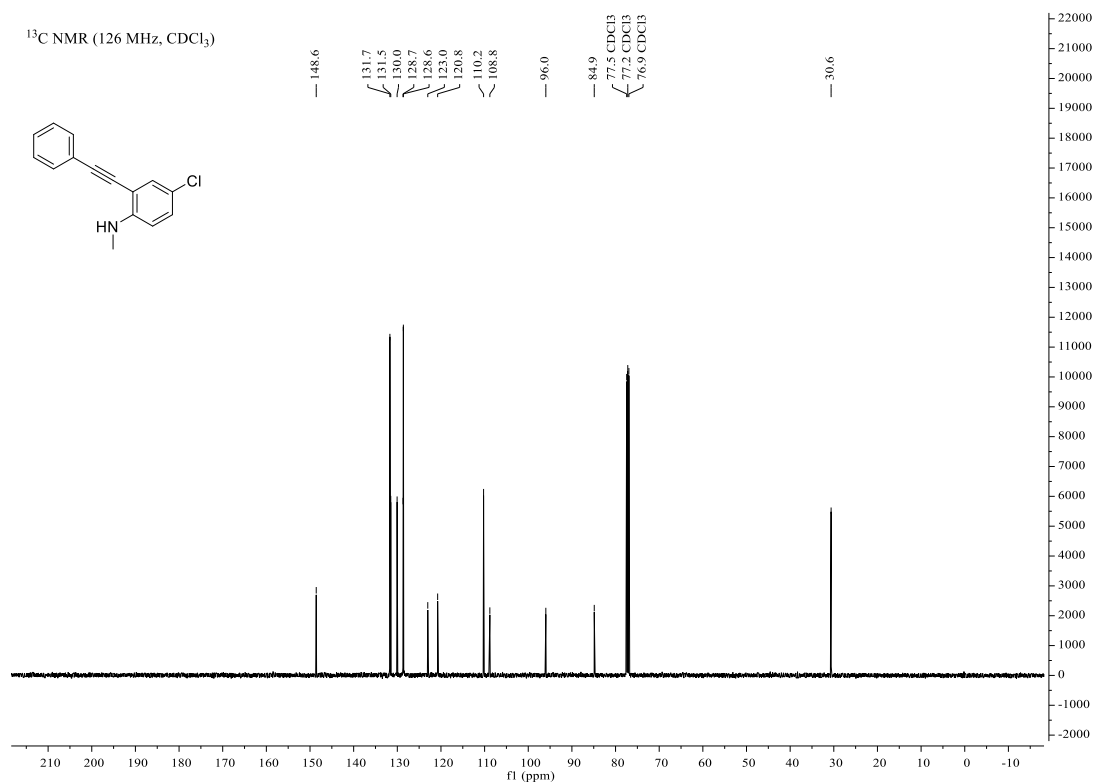
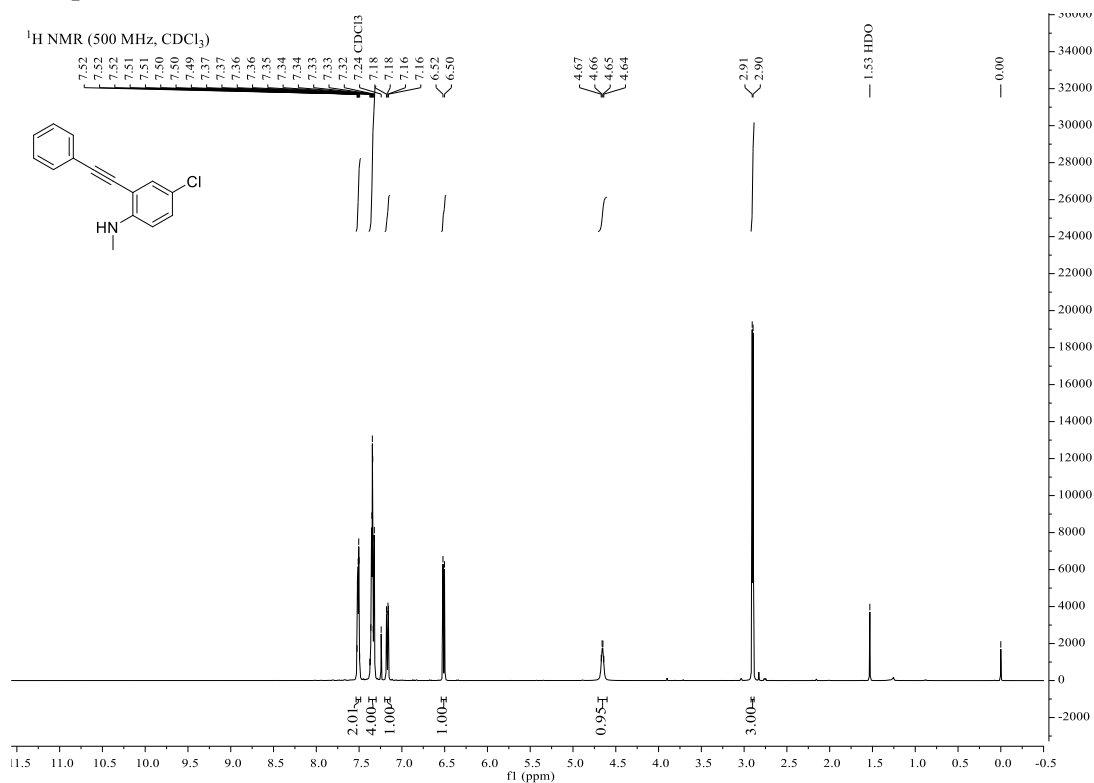
Compound S11



¹⁹F NMR (471 MHz, CDCl₃)



Compound S12

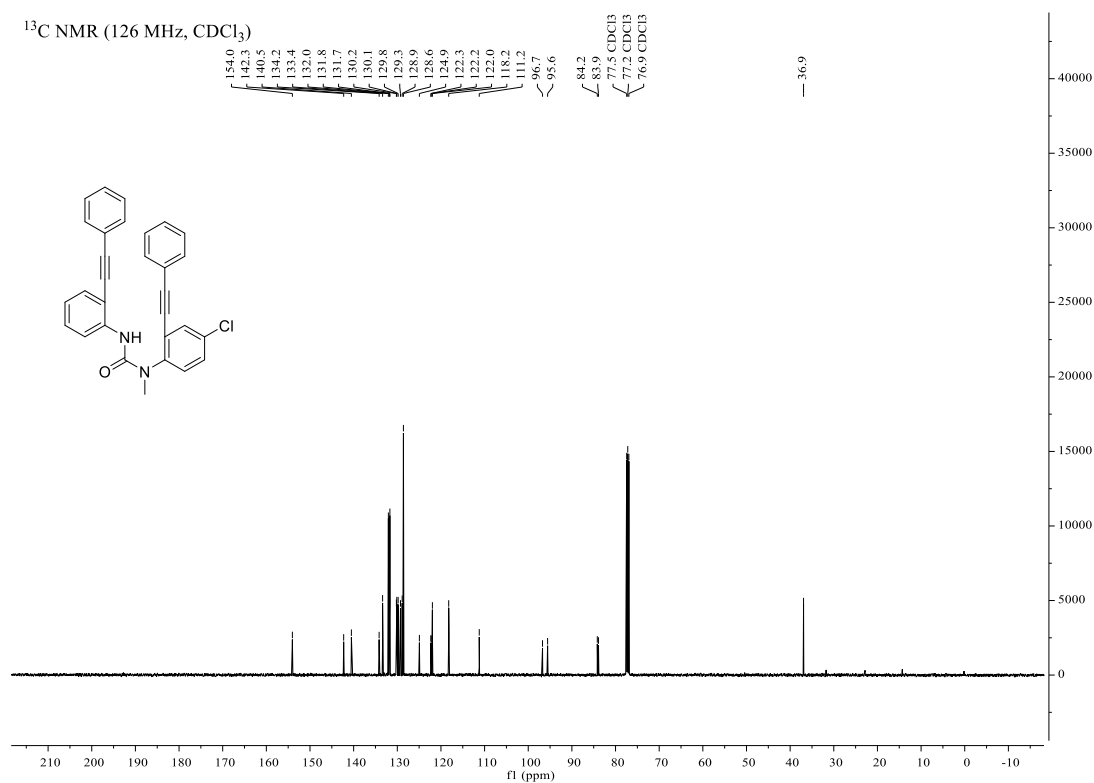


¹H NMR (500 MHz, CDCl₃)

Chemical structure of compound 10: CN(C(=O)Nc1ccccc1)C2=CC=C(C=C2)C#Cc3ccccc3

Chemical shifts (ppm): 8.36, 8.36, 8.34, 8.34, 7.47, 7.47, 7.47, 7.46, 7.46, 7.38, 7.38, 7.38, 7.37, 7.37, 7.36, 7.35, 7.35, 7.34, 7.34, 7.34, 7.33, 7.33, 7.33, 7.32, 7.32, 7.31, 7.31, 7.30, 7.30, 7.29, 7.28, 7.28, 7.27, 7.27, 7.26, 7.26, 7.25, 7.25, 7.23, 7.23, 7.22, 7.22, 7.21, 7.21, 7.15, 7.15, 7.08, 7.08, 7.07, 7.06, 6.93, 6.93, 6.91, 6.91, 6.90, 6.90, 3.34, 1.62 H₂O, 0.00.

Integration values: 1.00, 2.02, 3.01, 6.07, 0.99, 2.03, 1.00, 1.02, 1.03, 3.00.

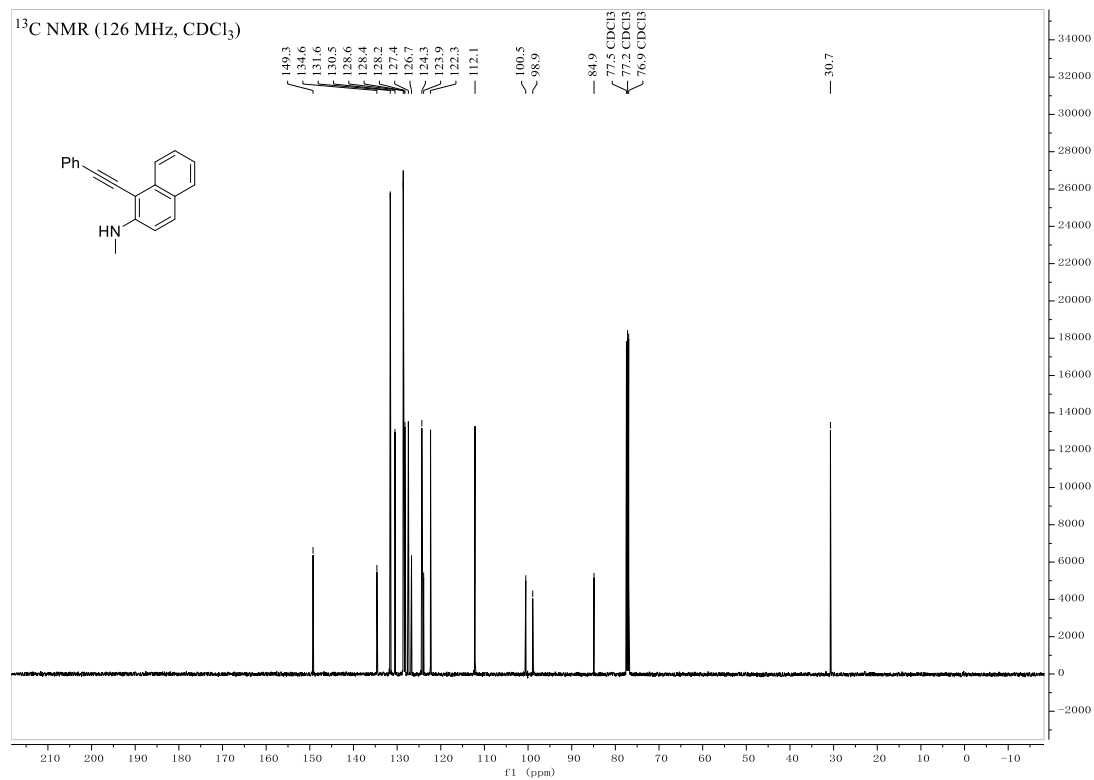


¹H NMR (500 MHz, CDCl₃)

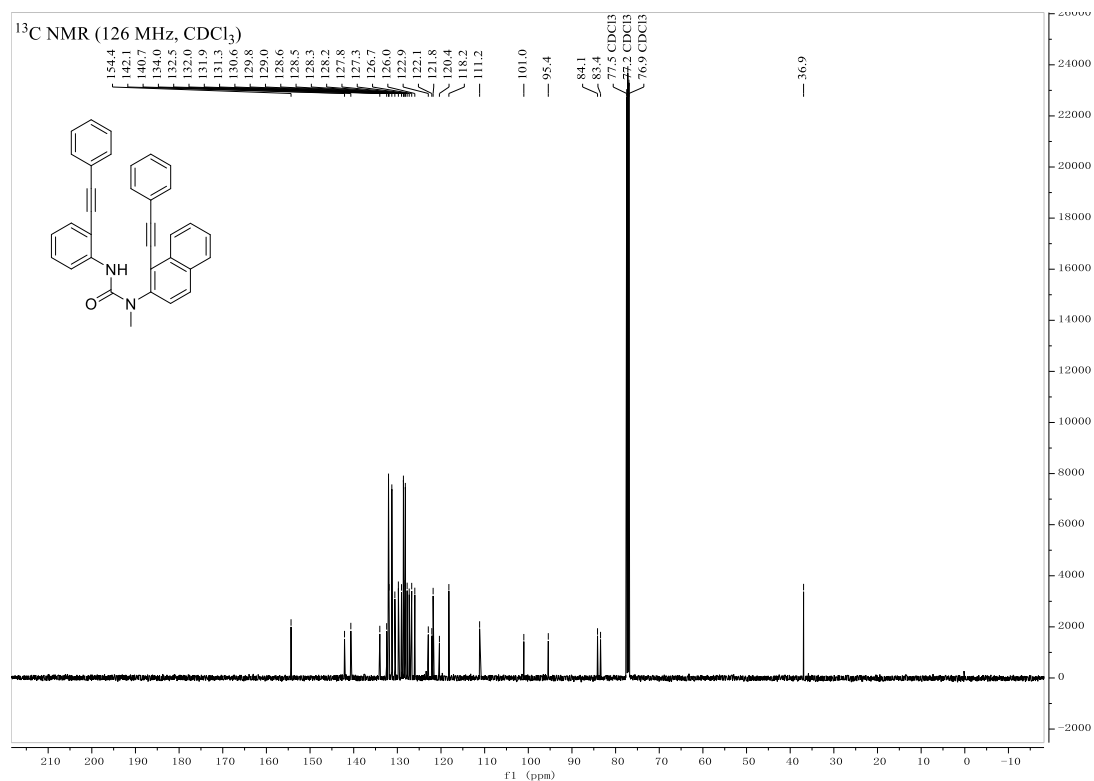
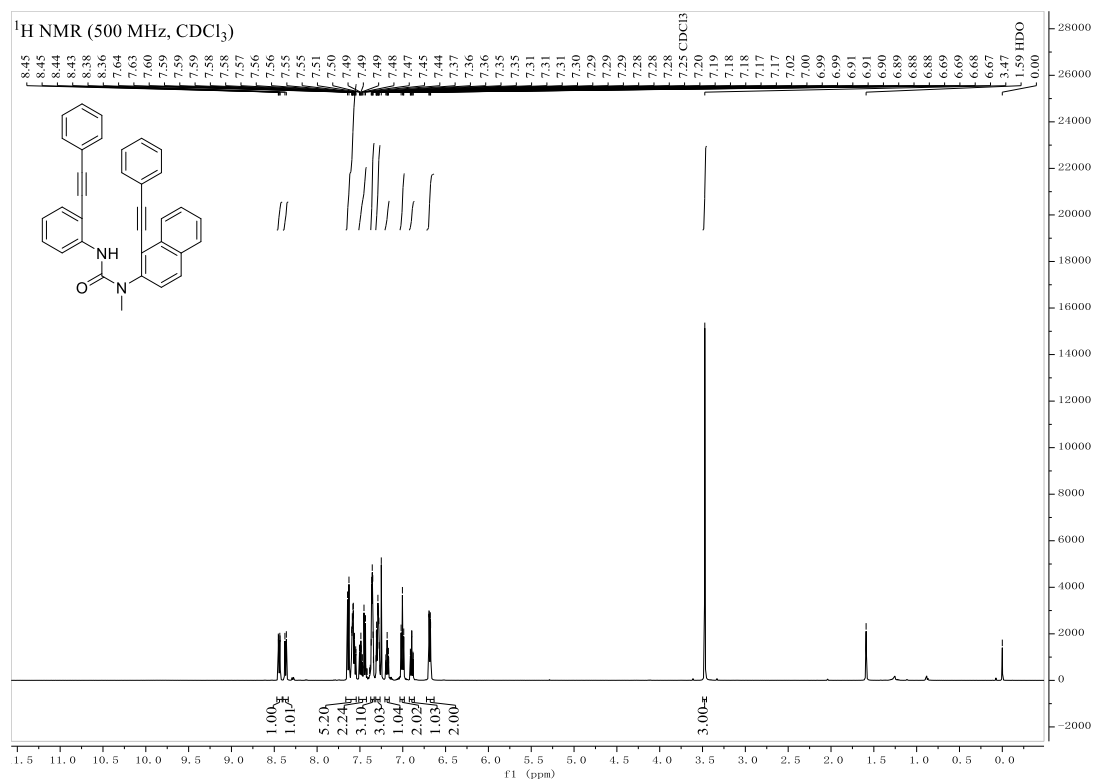
Chemical structure: C1CCN(C1)C2=CC=CC=C2C#CC3=CC=CC=C3

Peak list (ppm): 8.16, 8.15, 7.73, 7.71, 7.69, 7.68, 7.67, 7.62, 7.61, 7.61, 7.60, 7.60, 7.48, 7.47, 7.46, 7.46, 7.45, 7.39, 7.39, 7.38, 7.37, 7.37, 7.36, 7.34, 7.34, 7.33, 7.32, 7.32, 7.31, 7.31, 7.31, 7.31, 7.22, 7.22, 7.21, 7.20, 7.02, 7.00, 5.03, 5.02, 3.04, 3.03, 1.48 H₂O, 0.00.

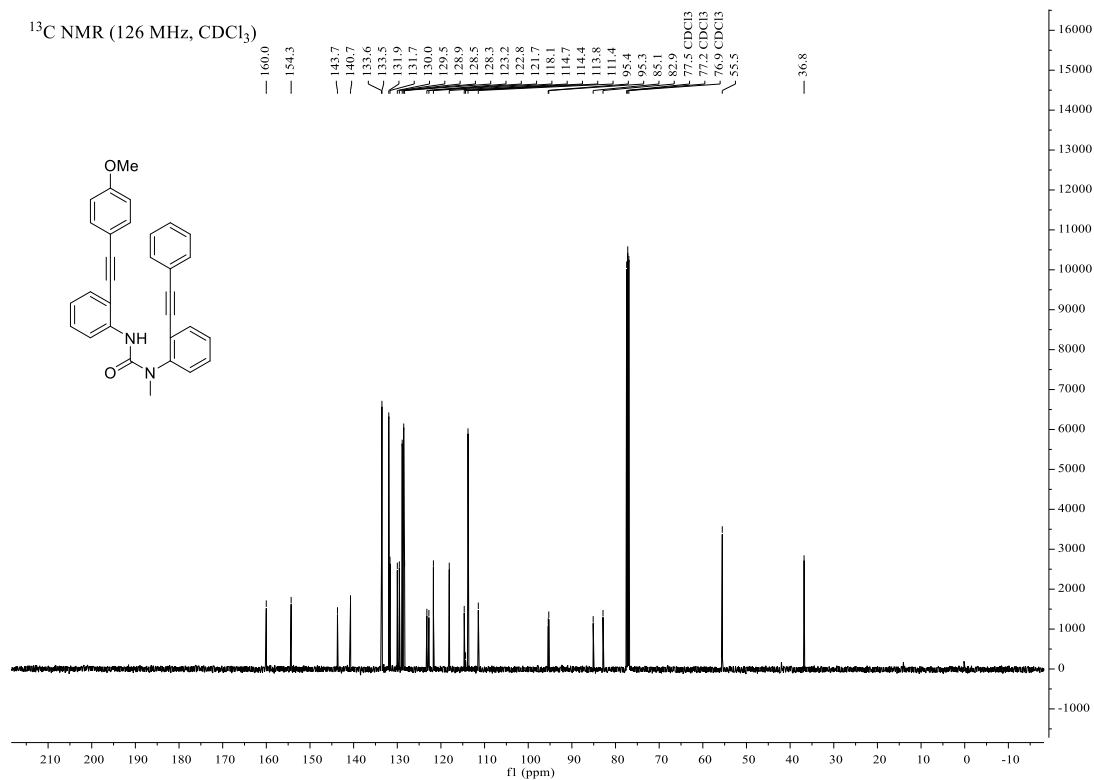
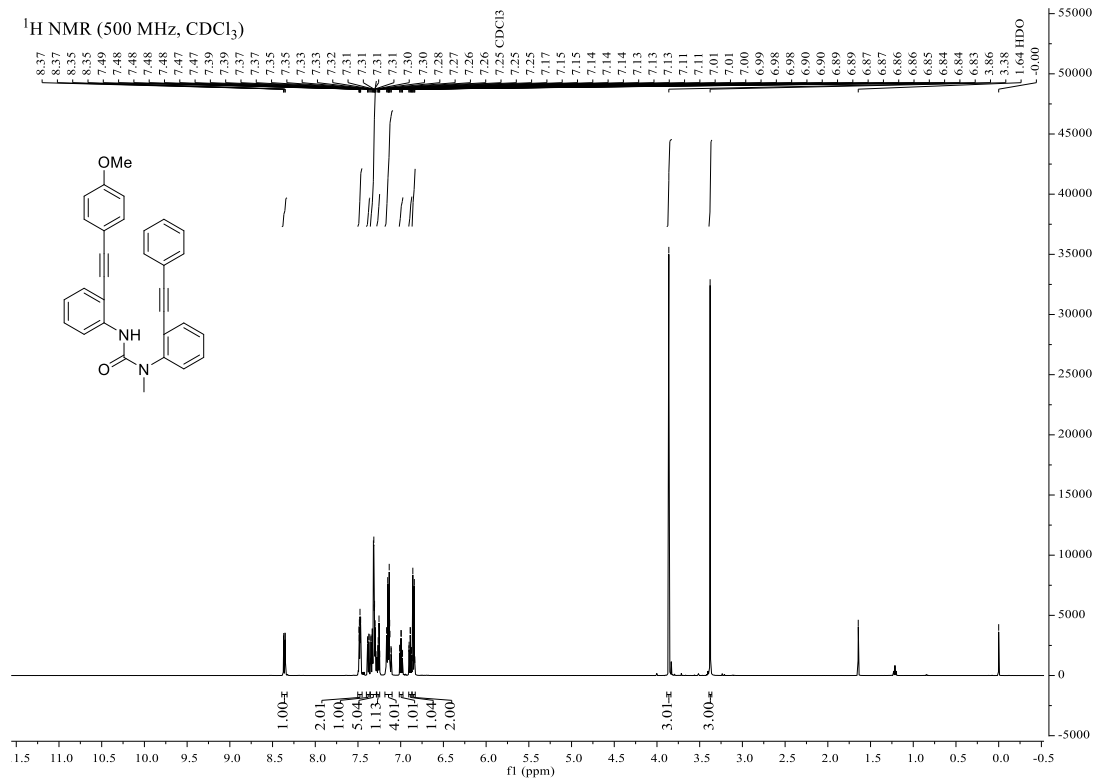
Integration values: 0.96, 2.00, 1.97, 1.01, 3.00, 1.18, 1.00, 1.00, 3.01.



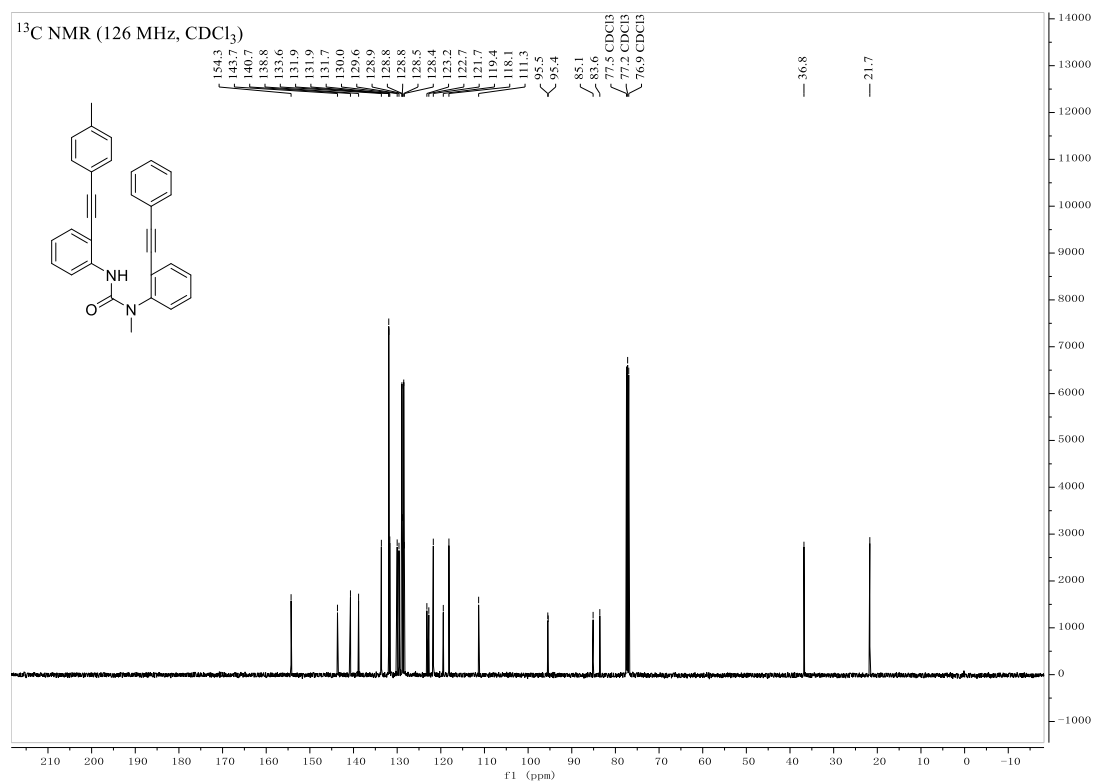
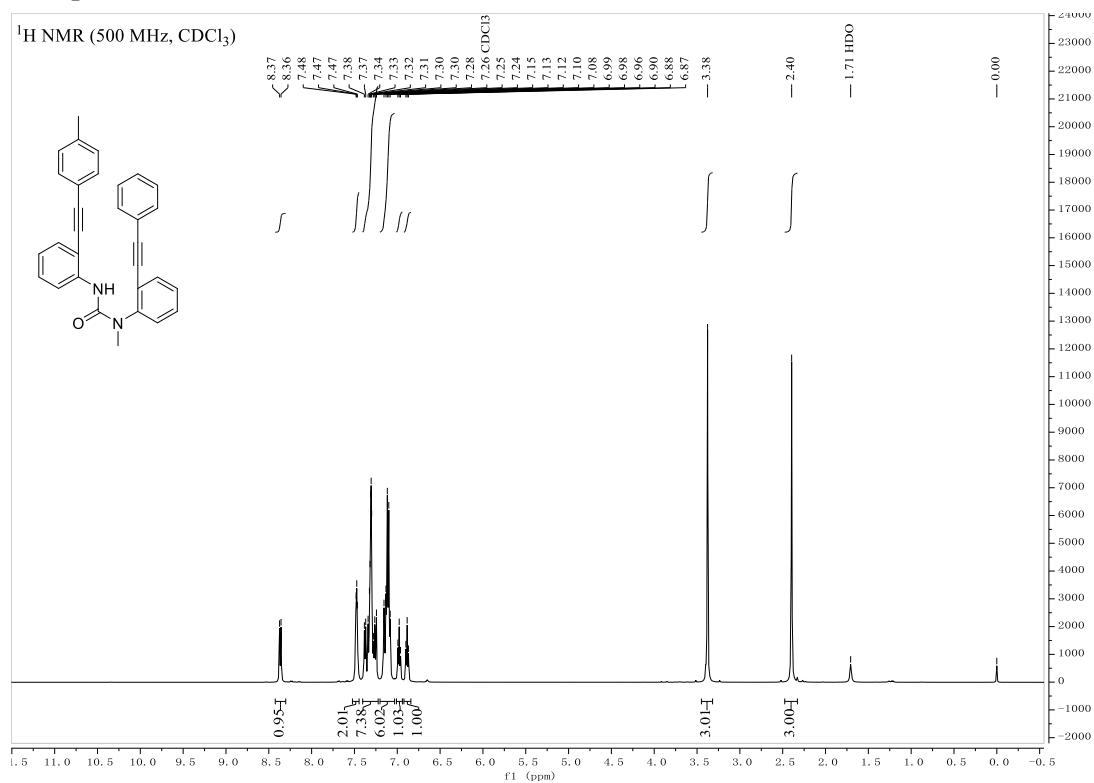
Compound S16



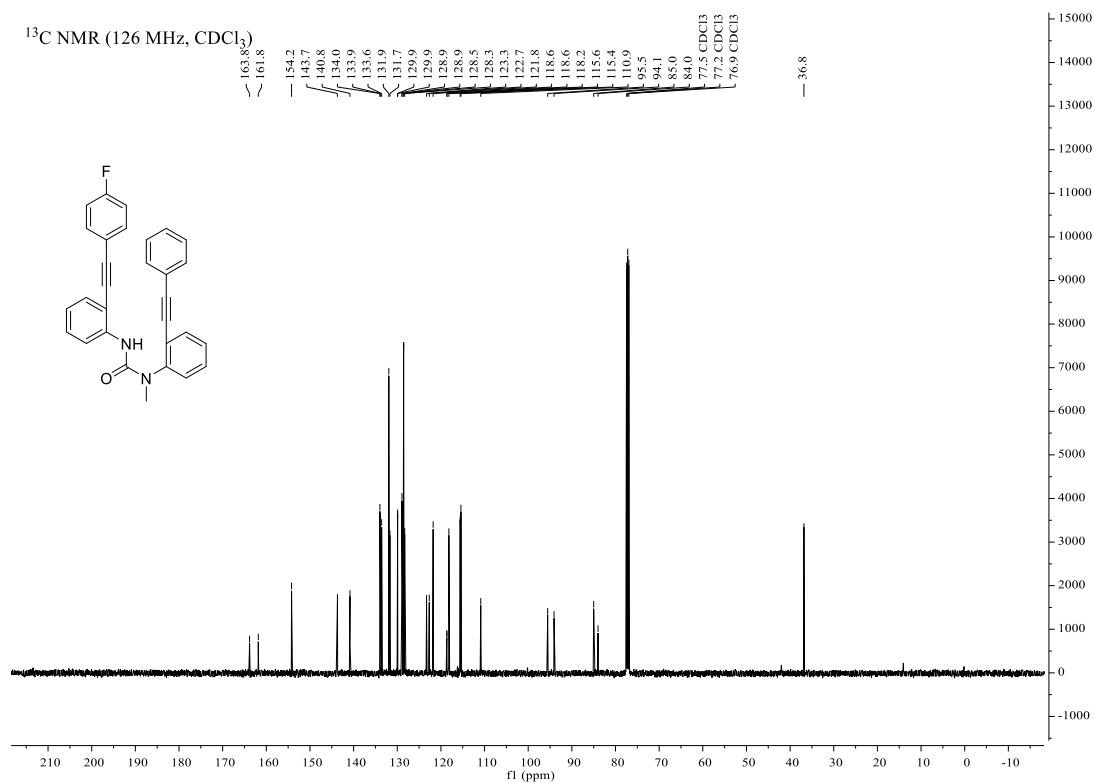
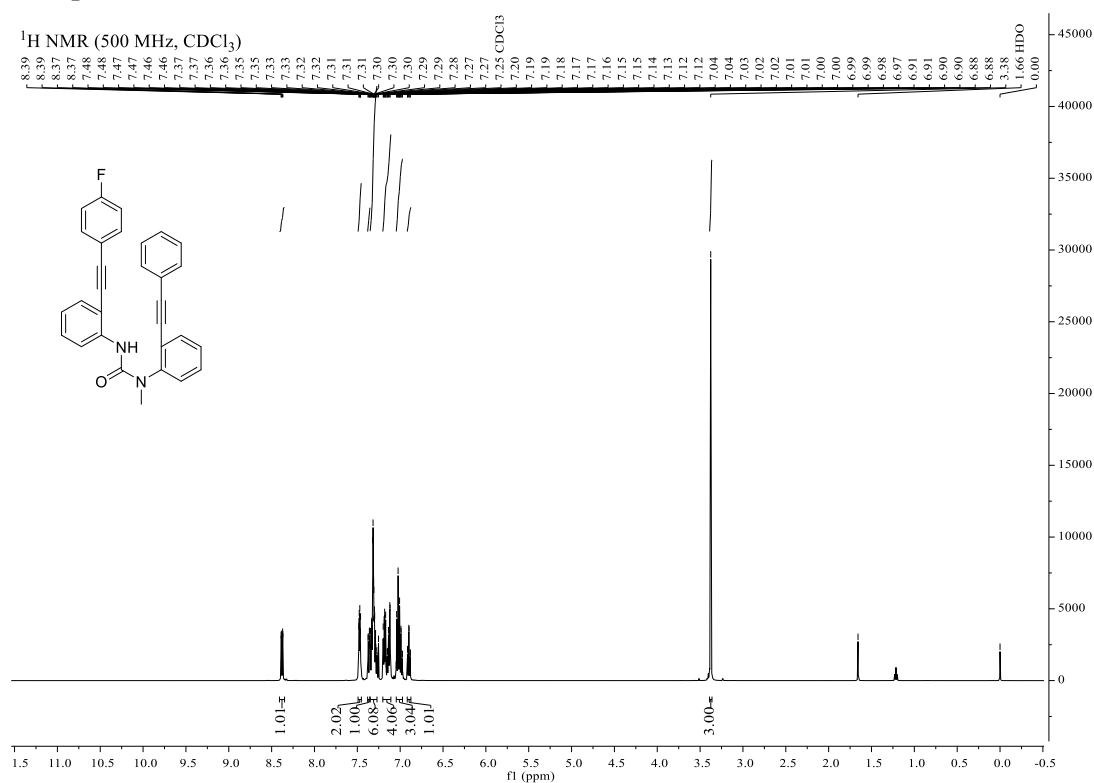
Compound S17



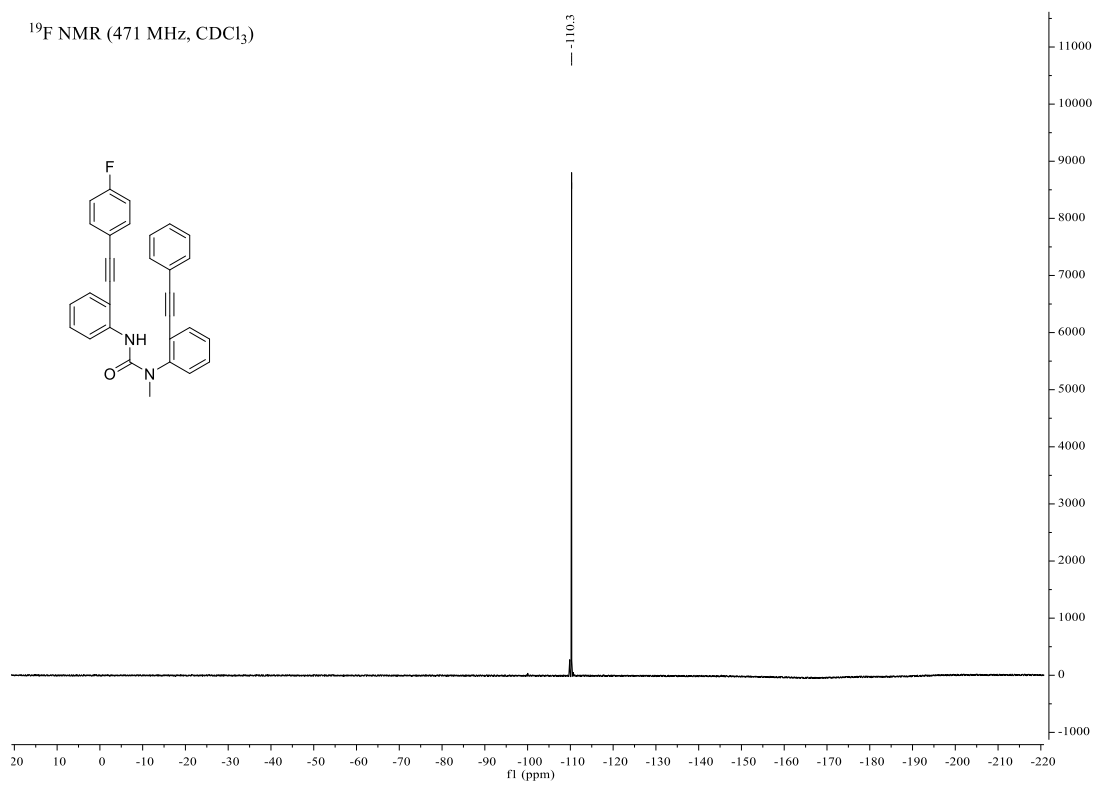
Compound S18



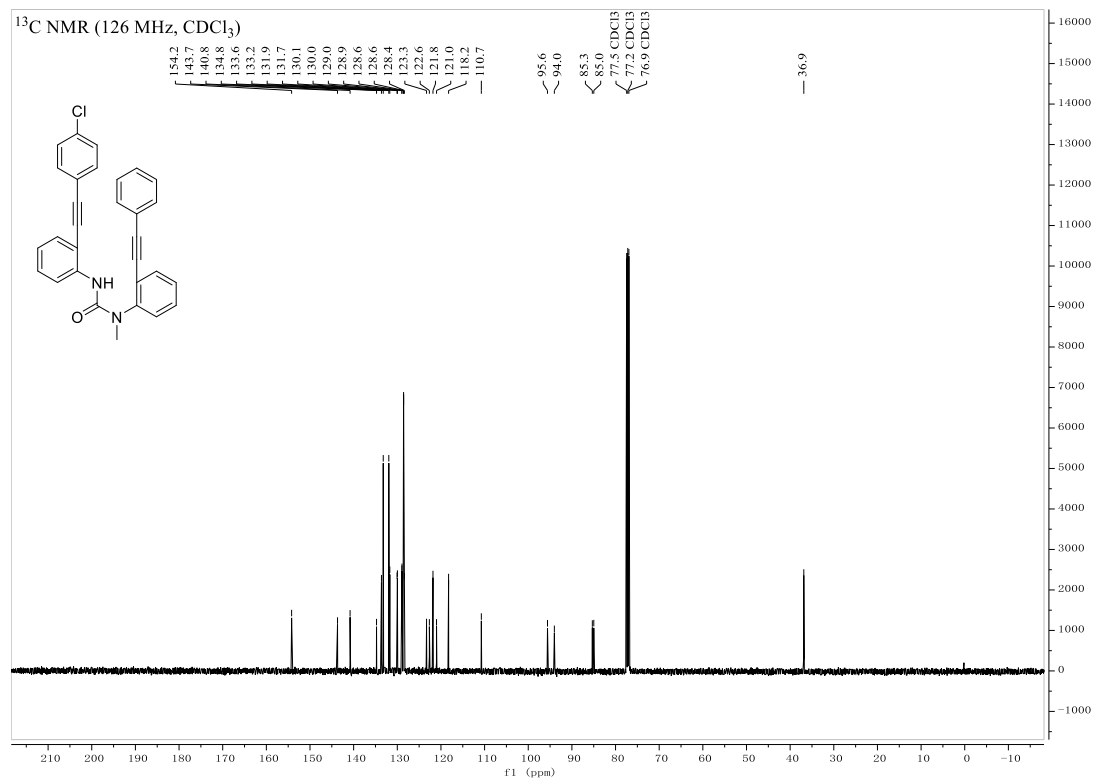
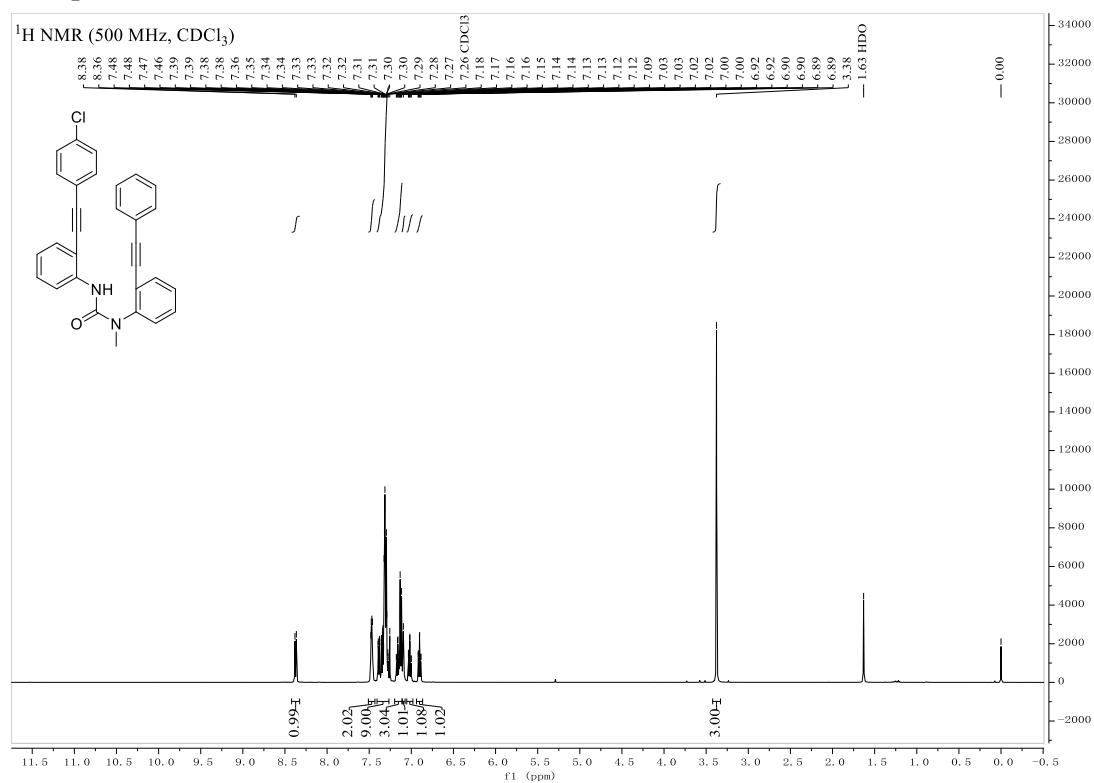
Compound S19



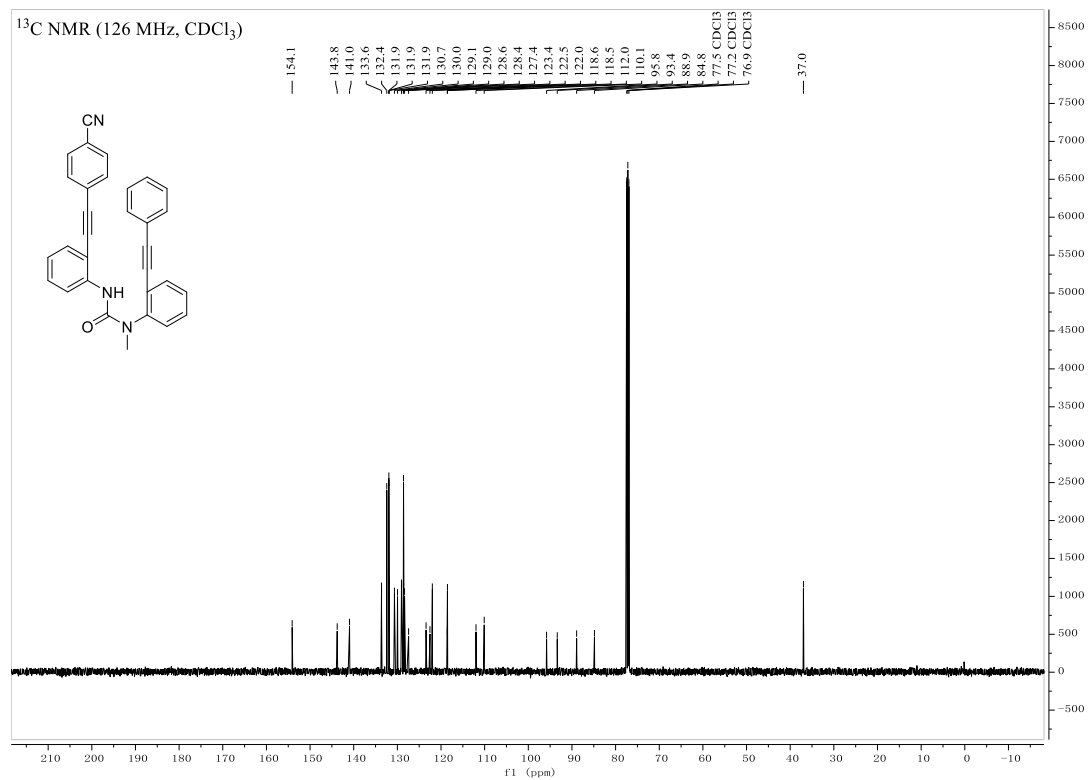
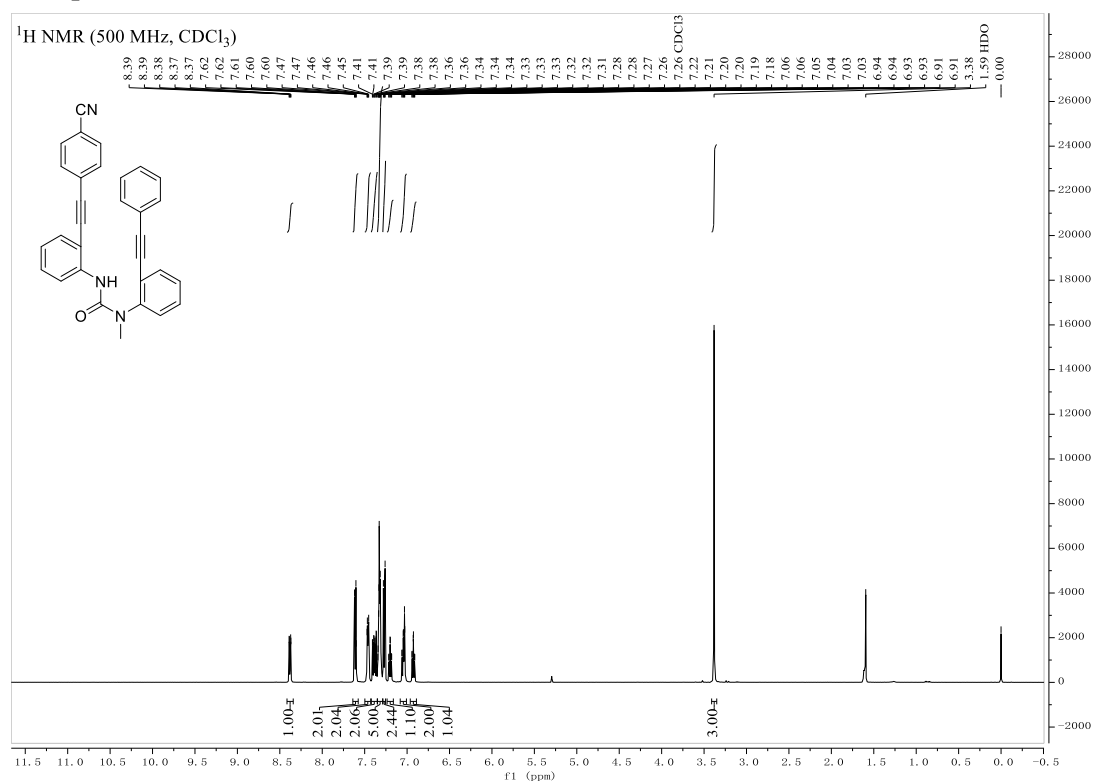
^{19}F NMR (471 MHz, CDCl_3)



Compound S20

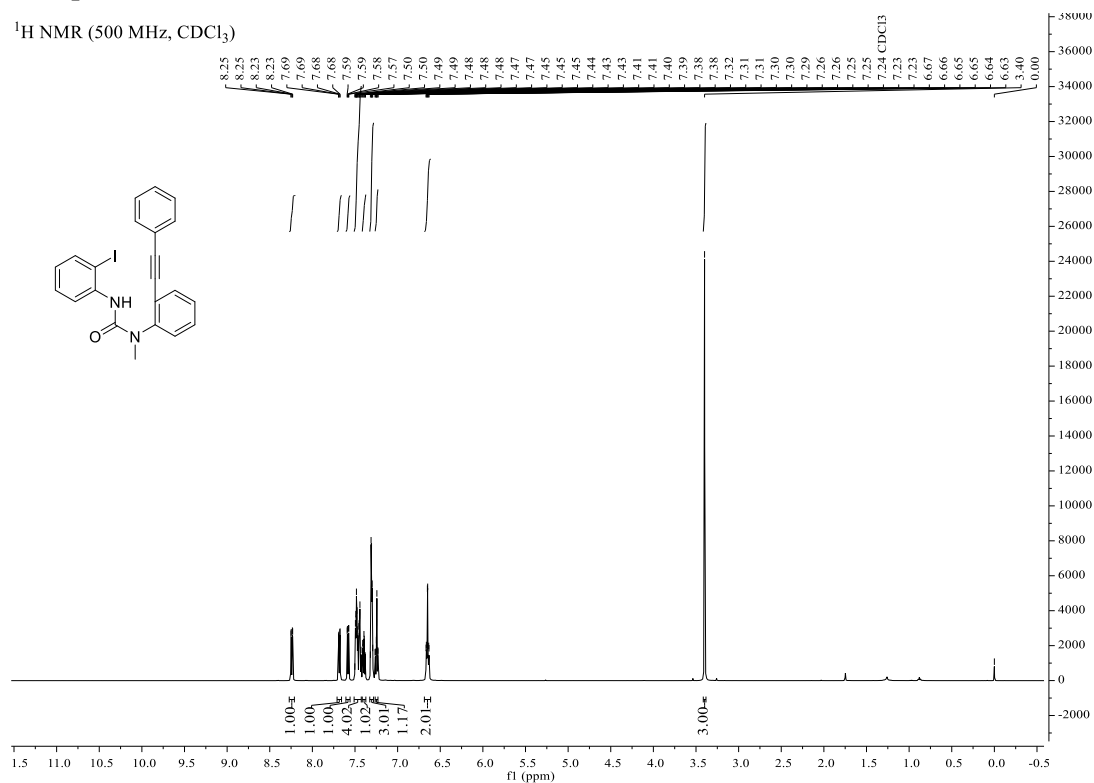


Compound S21

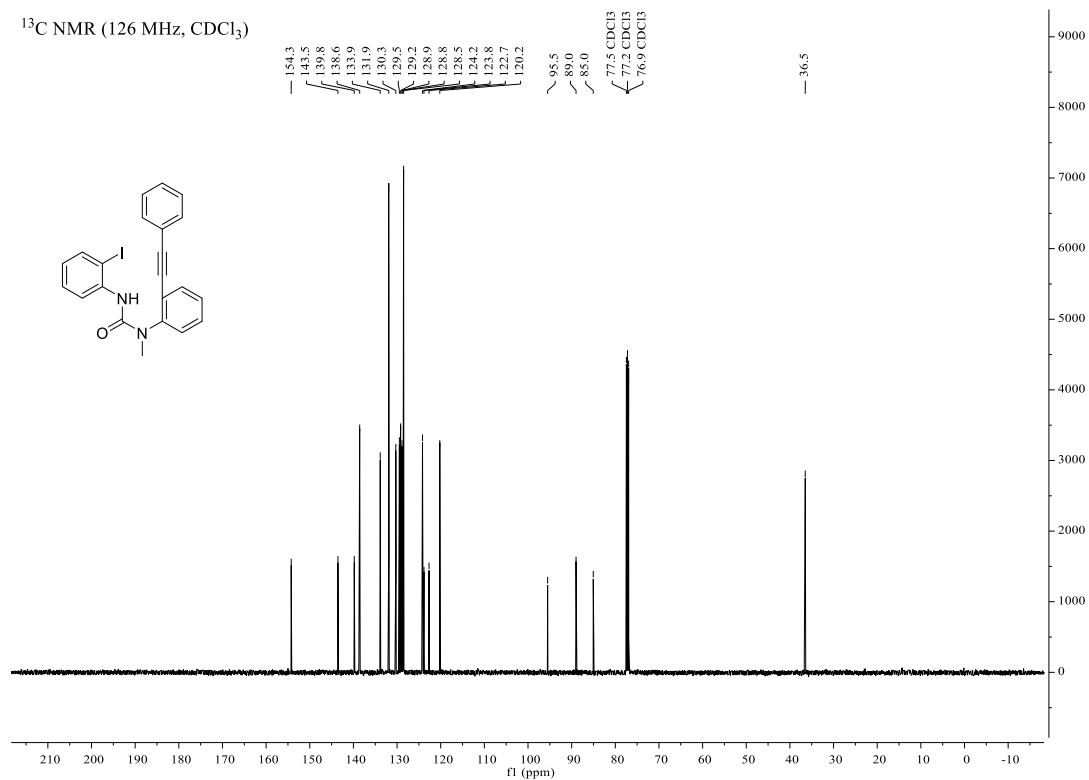


Compound S22

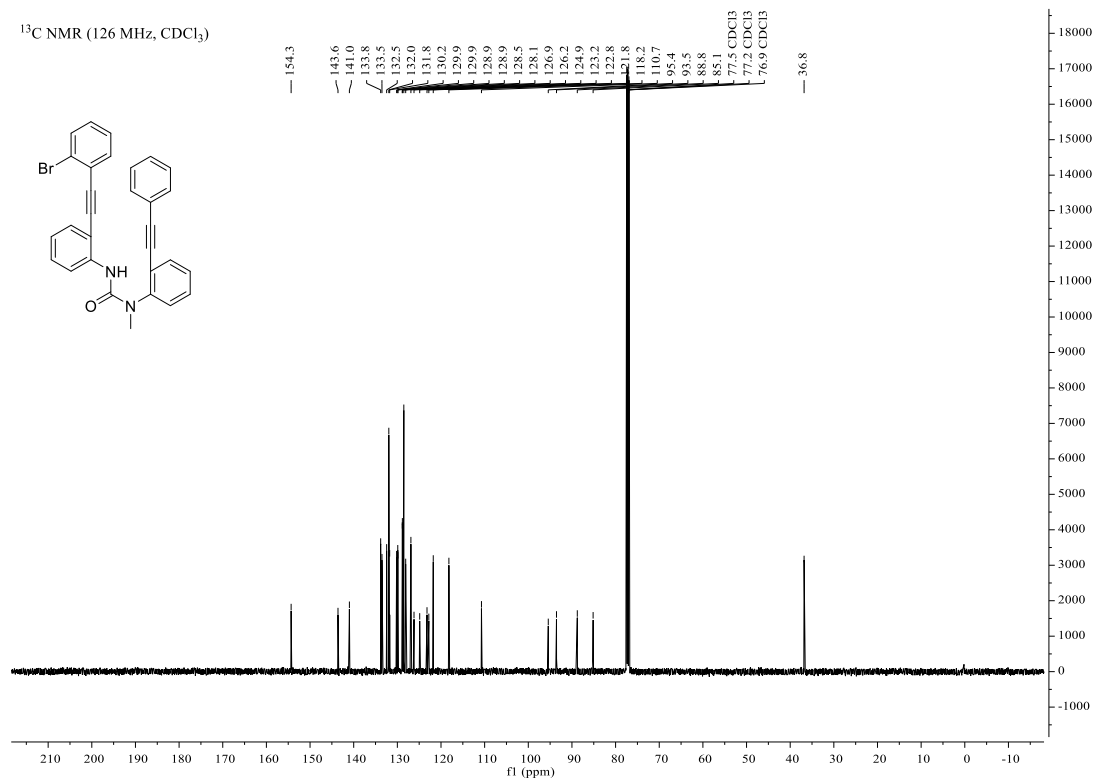
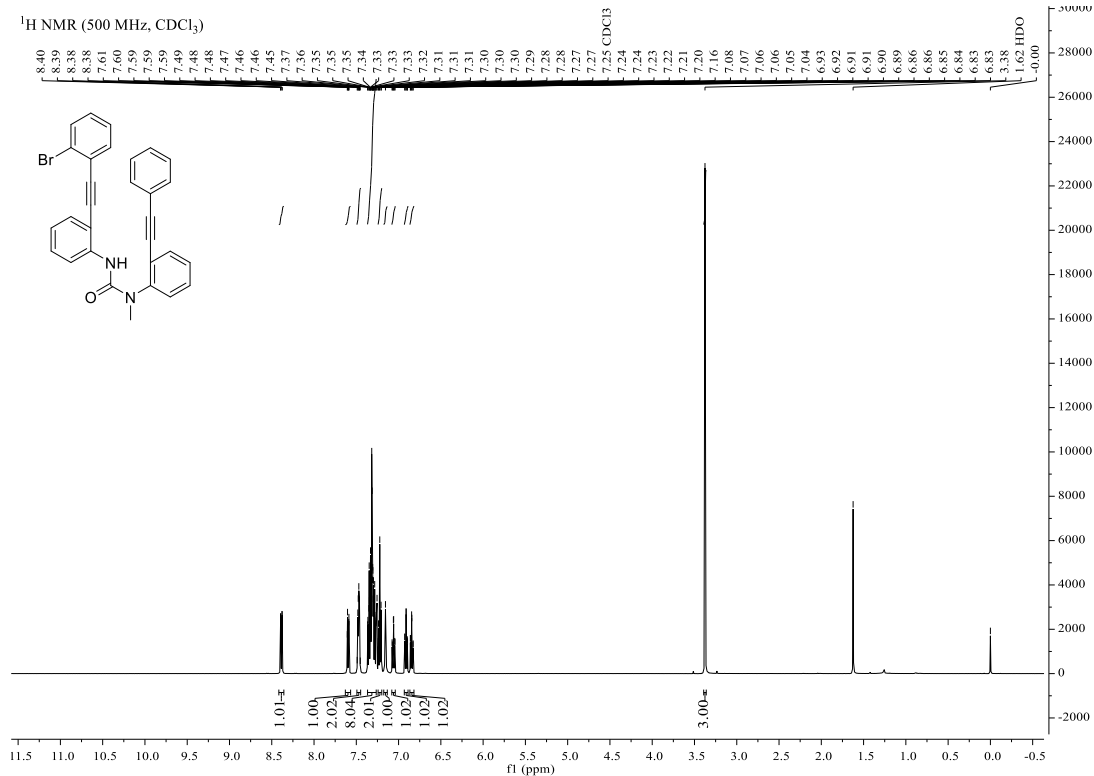
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)



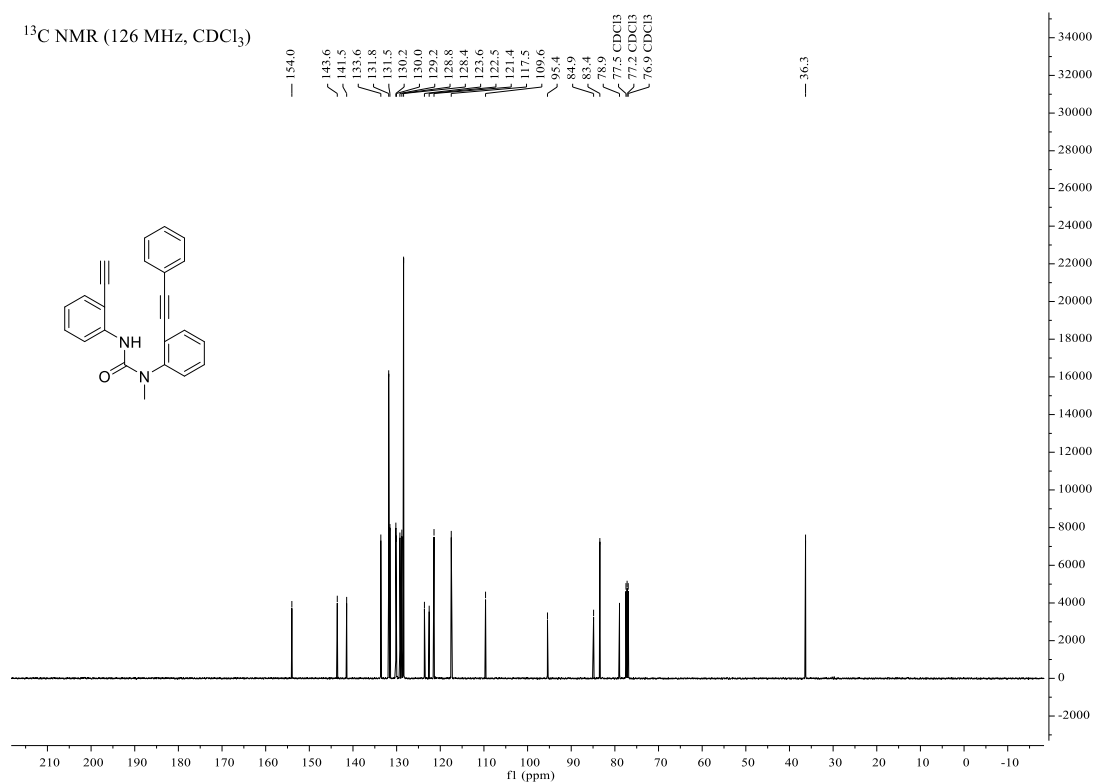
Compound S23



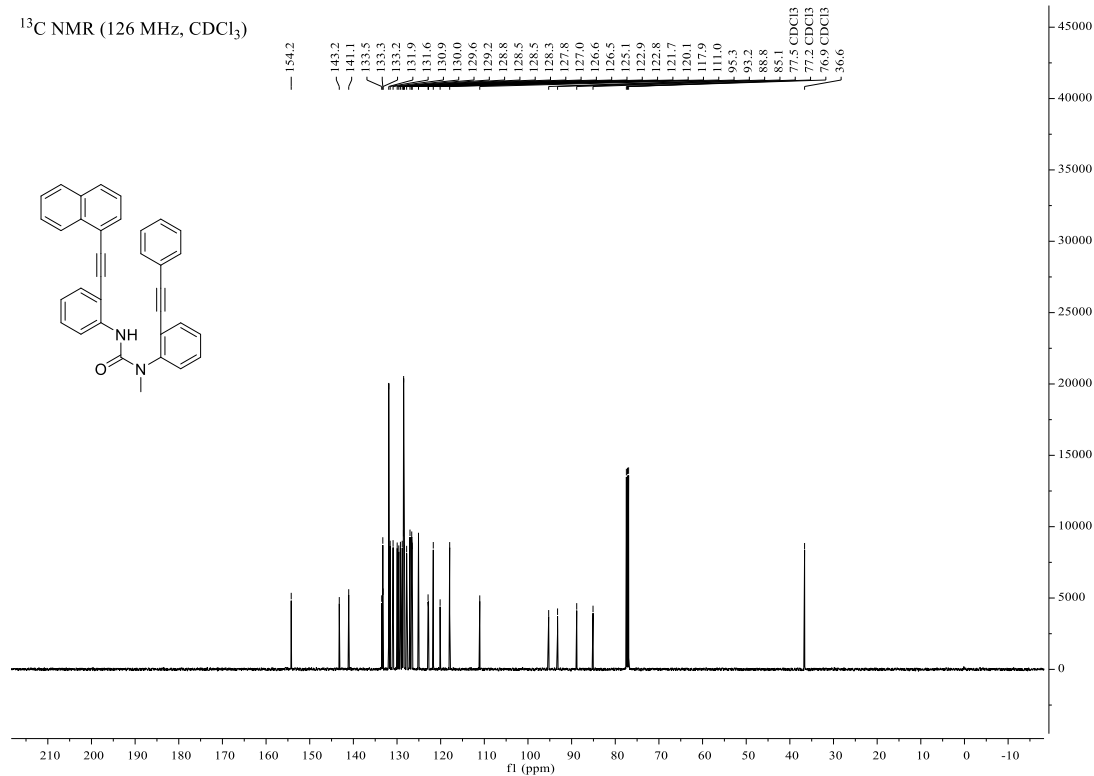
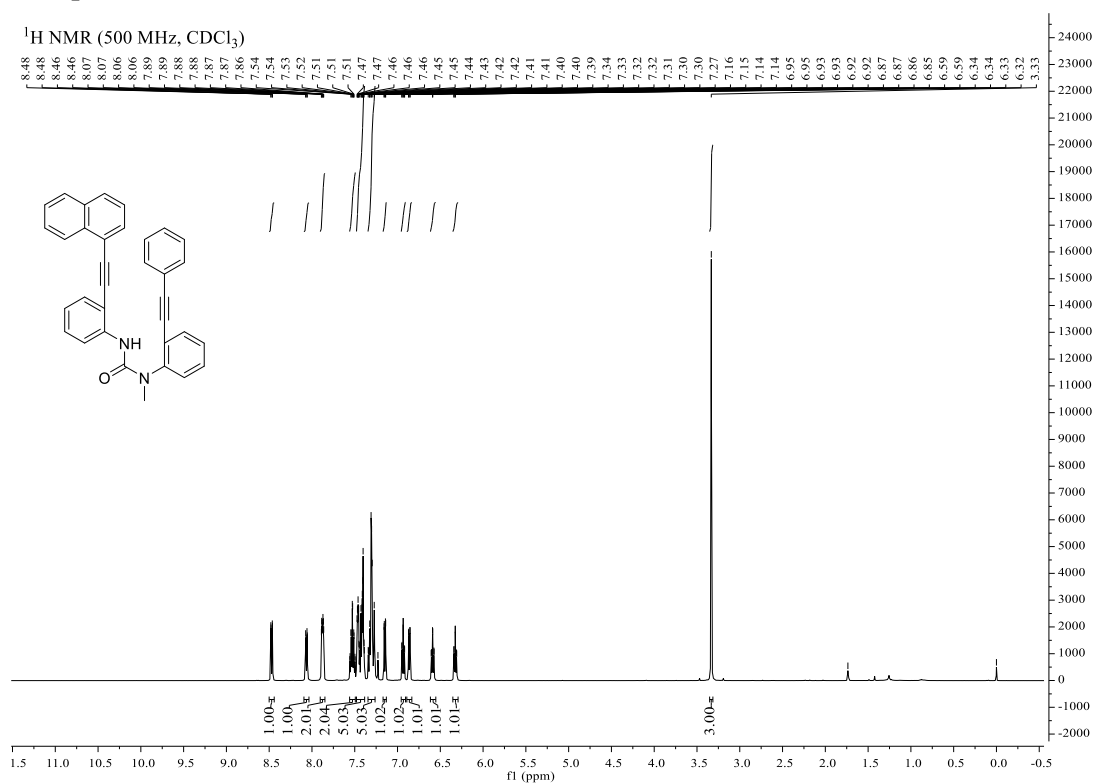
¹H NMR (500 MHz, CDCl₃)

Chemical structure: CC(=O)N(c1ccccc1)C#Cc2ccccc2

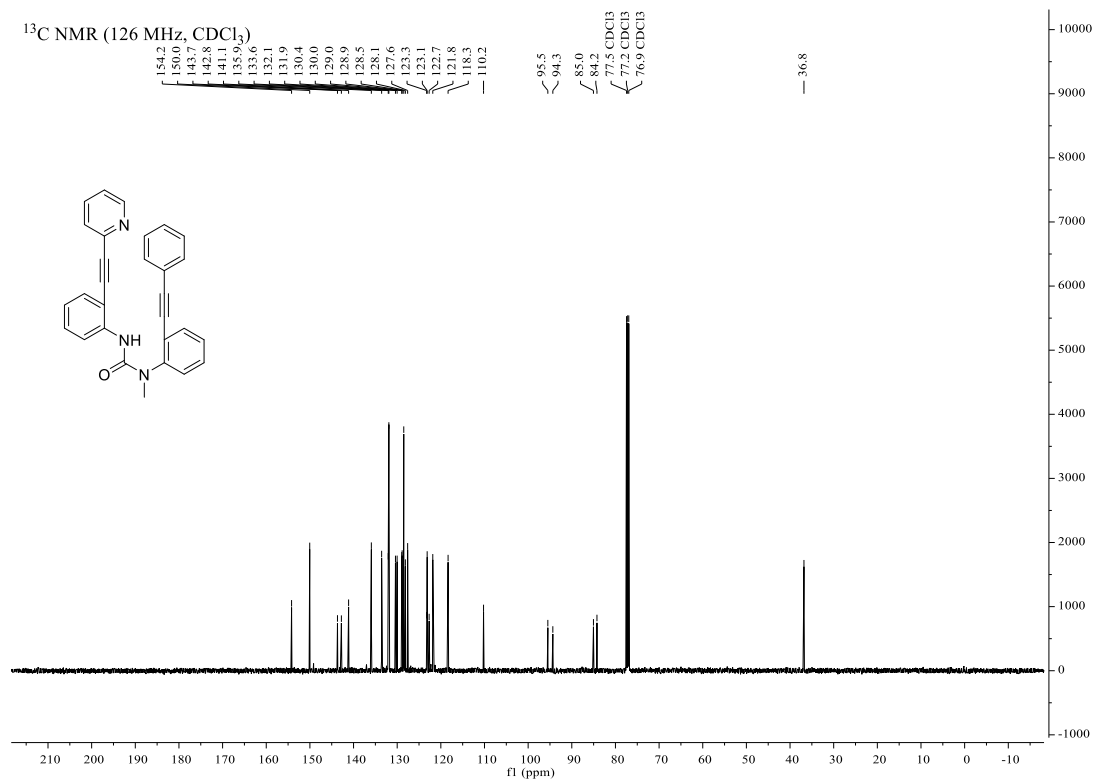
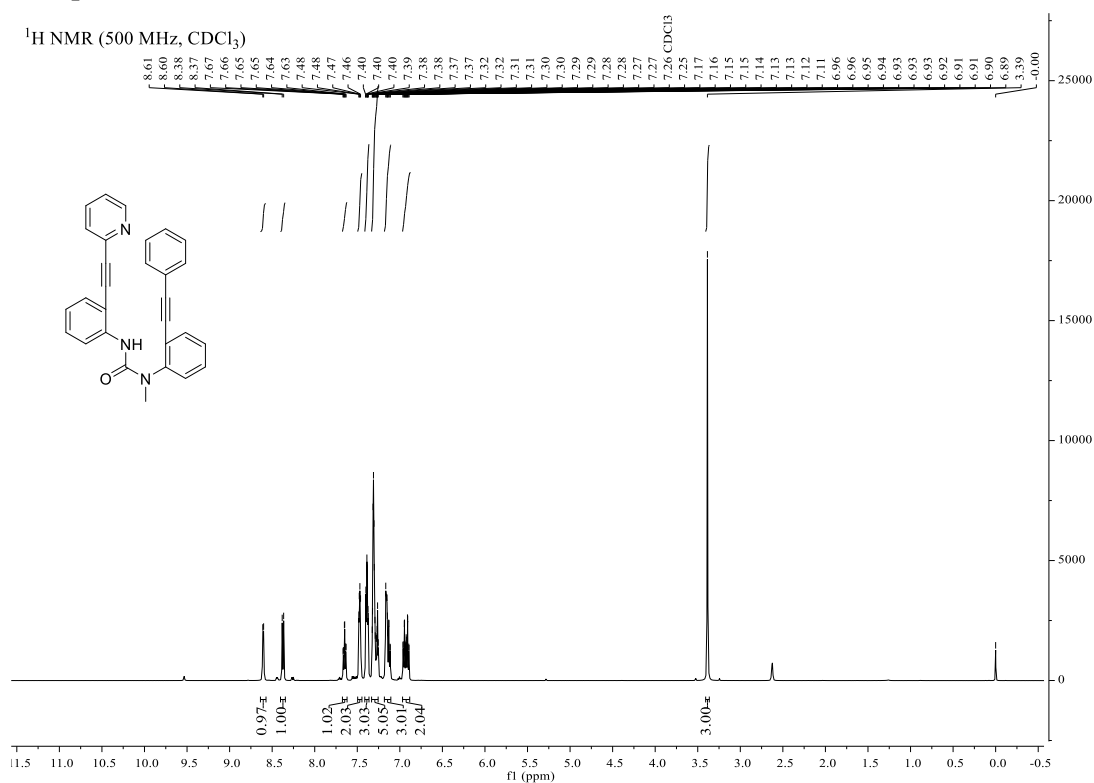
Peak list (ppm): 8.40, 8.39, 8.38, 8.36, 8.35, 8.34, 8.33, 8.32, 8.31, 8.30, 8.29, 8.28, 8.27, 8.26, 8.25, 8.24, 8.23, 8.22, 8.21, 8.20, 8.19, 8.18, 8.17, 8.16, 8.15, 8.14, 8.13, 8.12, 8.11, 8.10, 8.09, 8.08, 8.07, 8.06, 8.05, 8.04, 8.03, 8.02, 8.01, 8.00, 7.99, 7.98, 7.97, 7.96, 7.95, 7.94, 7.93, 7.92, 7.91, 7.90, 7.89, 7.88, 7.87, 7.86, 7.85, 7.84, 7.83, 7.82, 7.81, 7.80, 7.79, 7.78, 7.77, 7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1



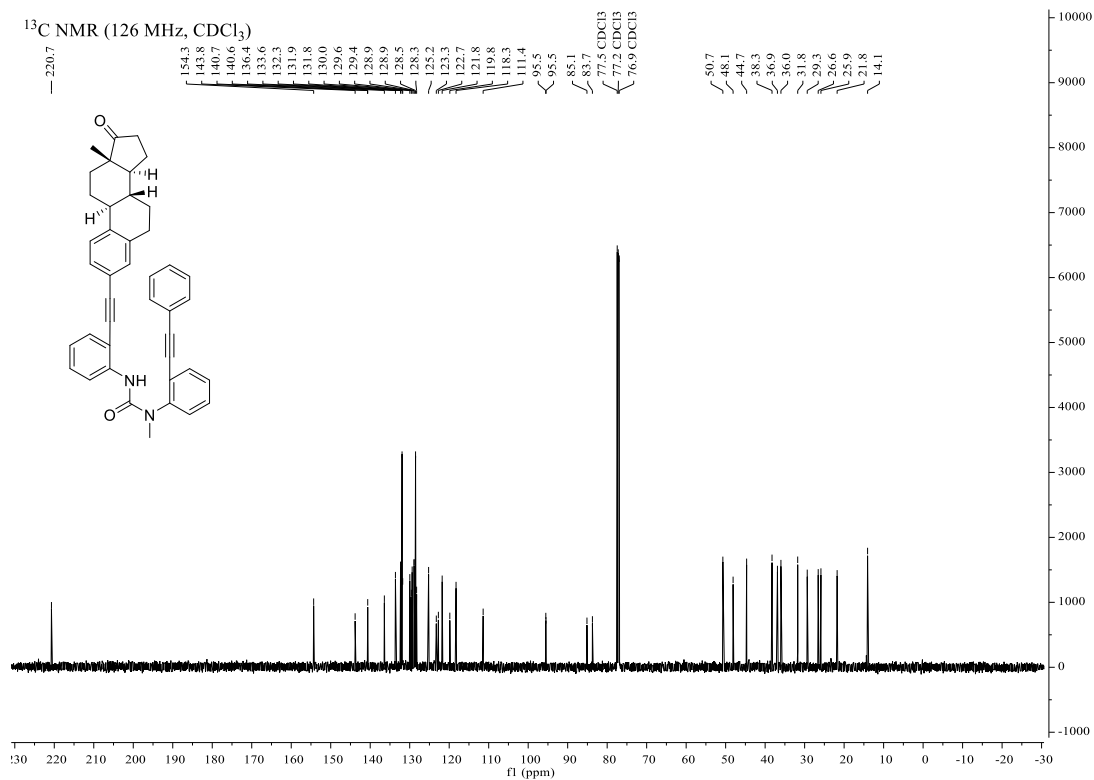
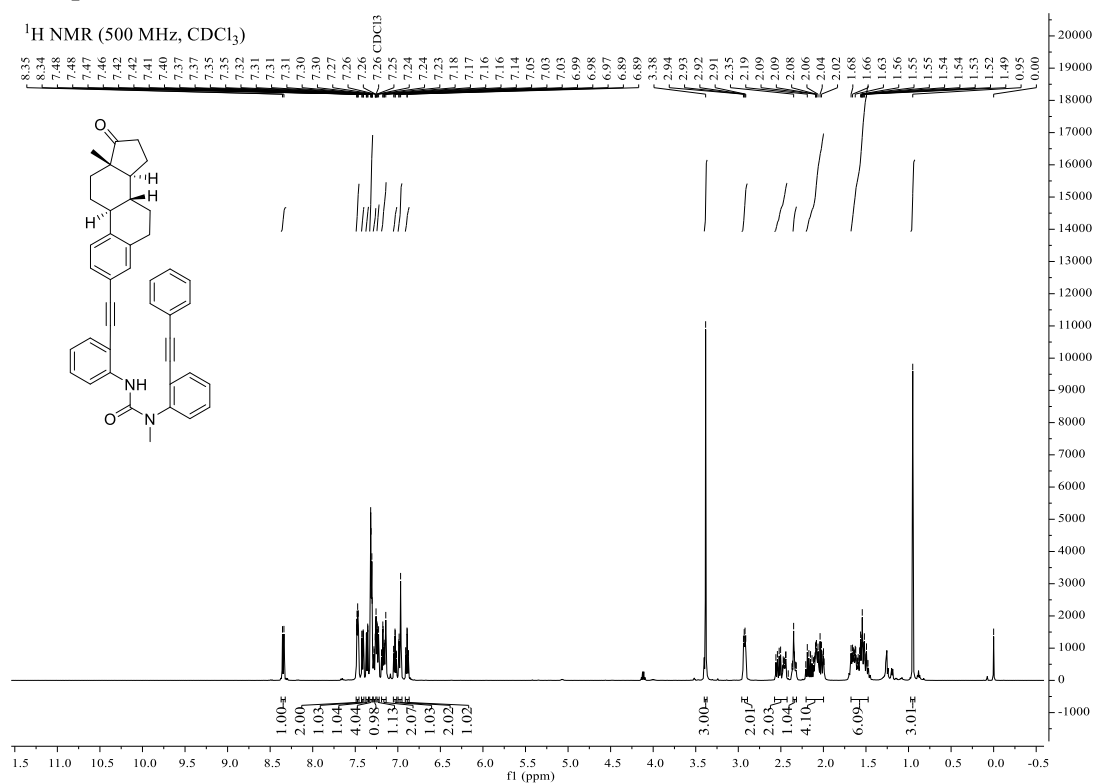
Compound S26



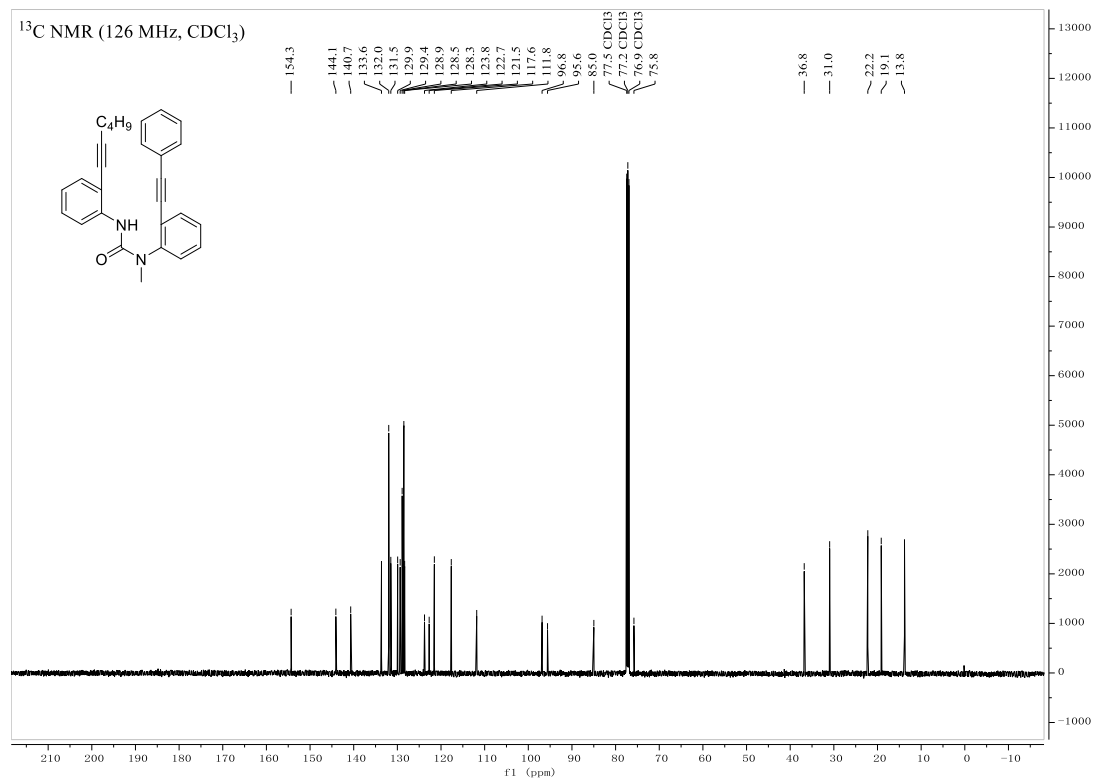
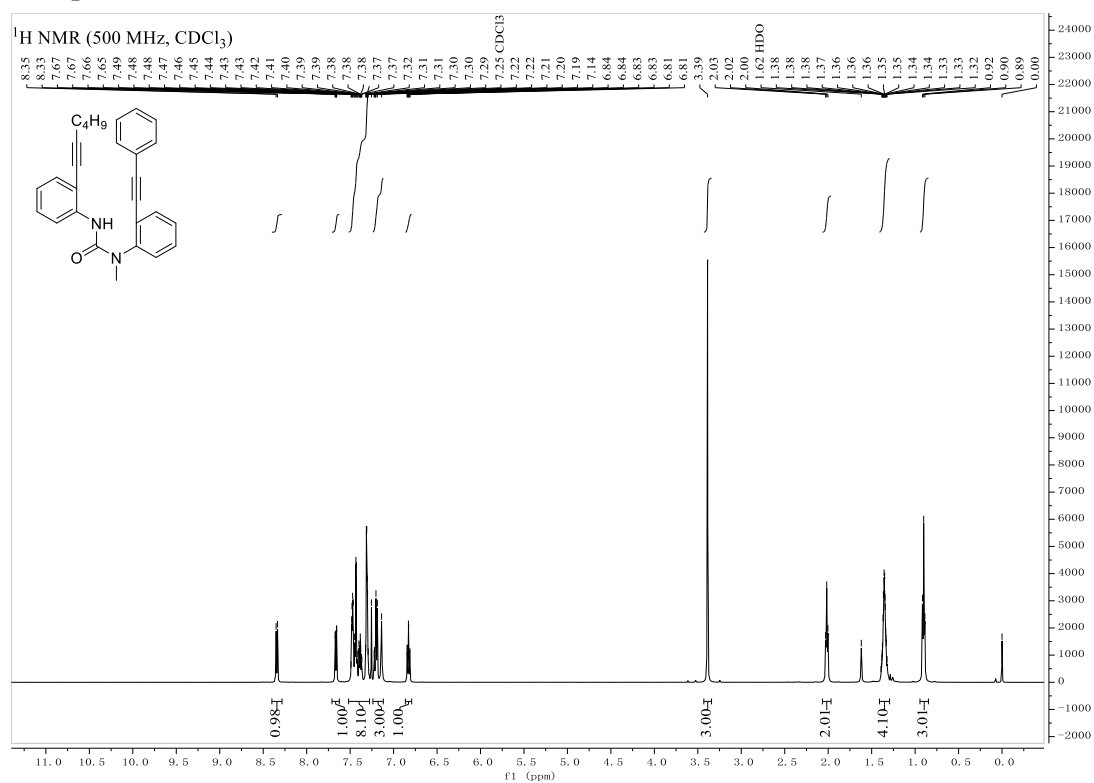
Compound S27



Compound S29

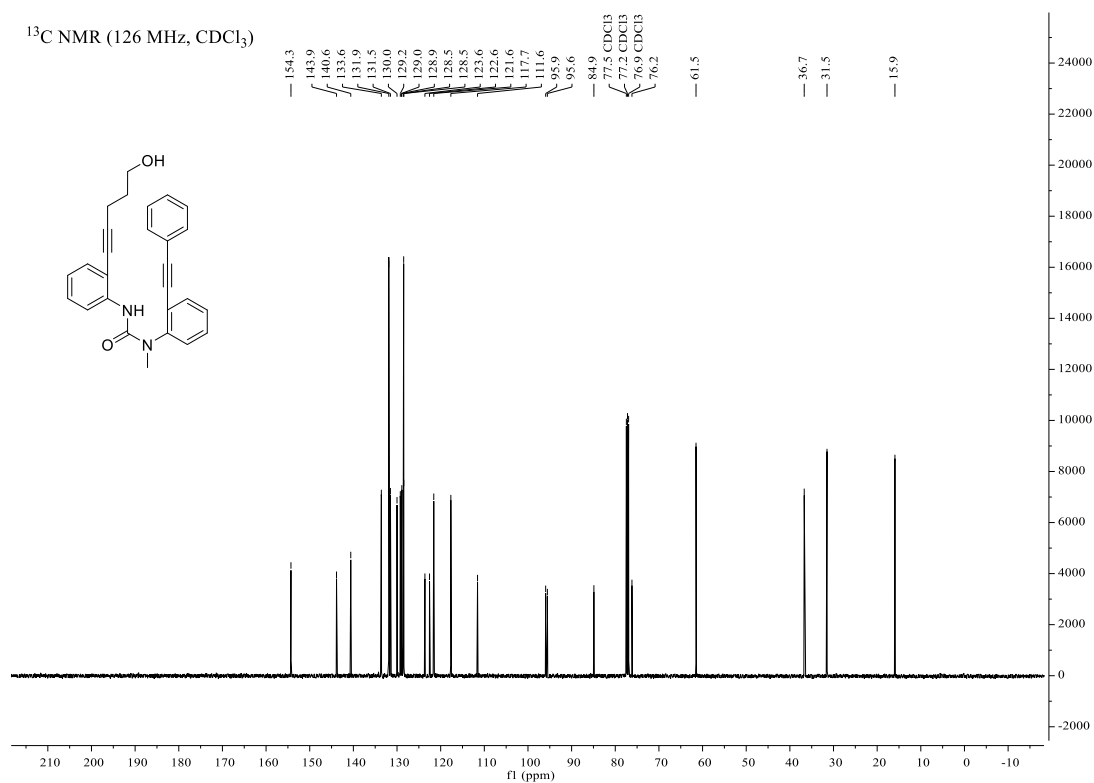


Compound S30

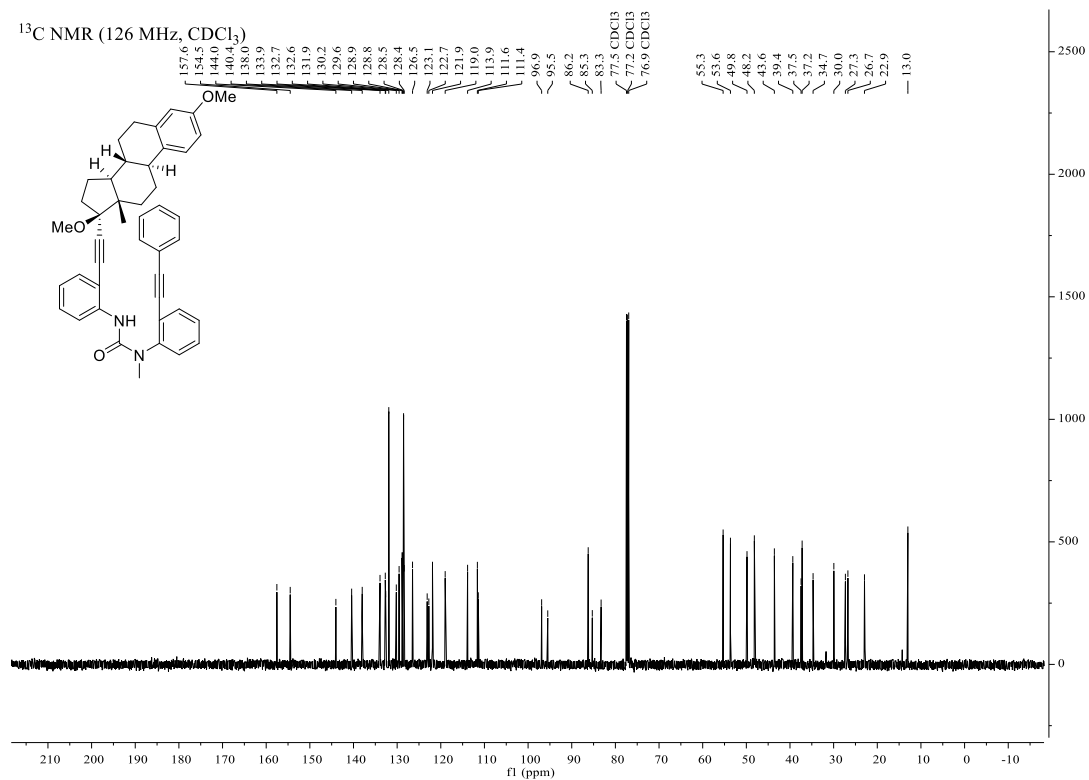
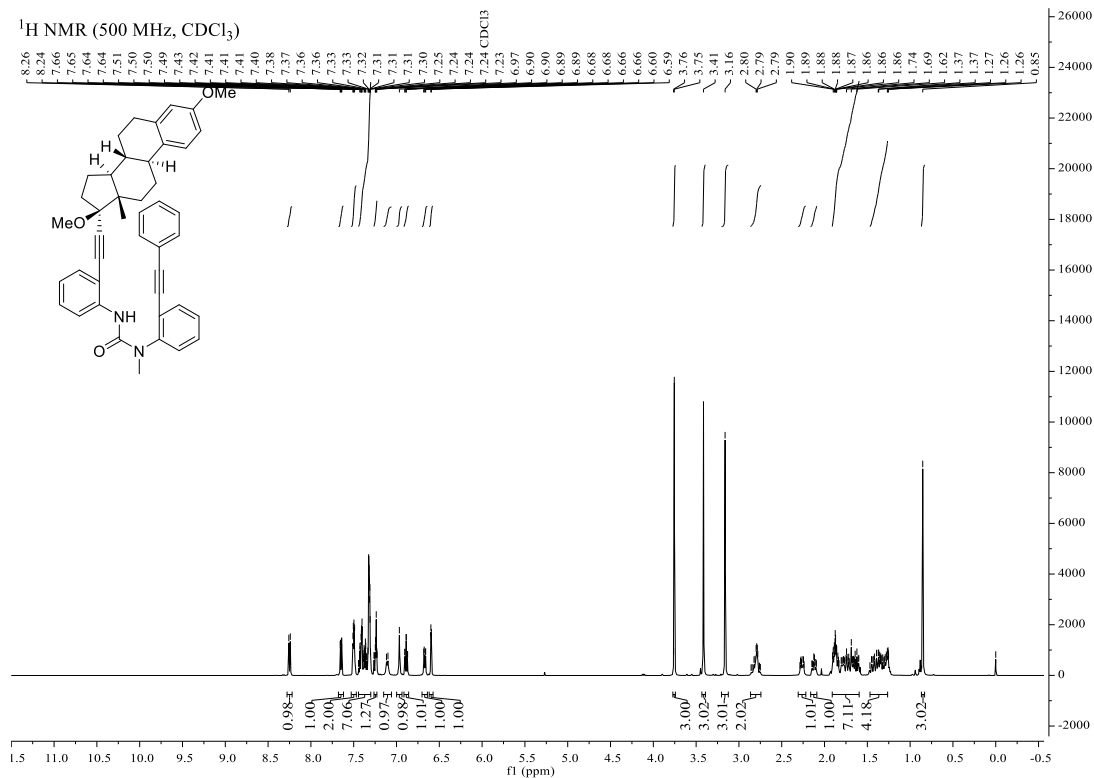


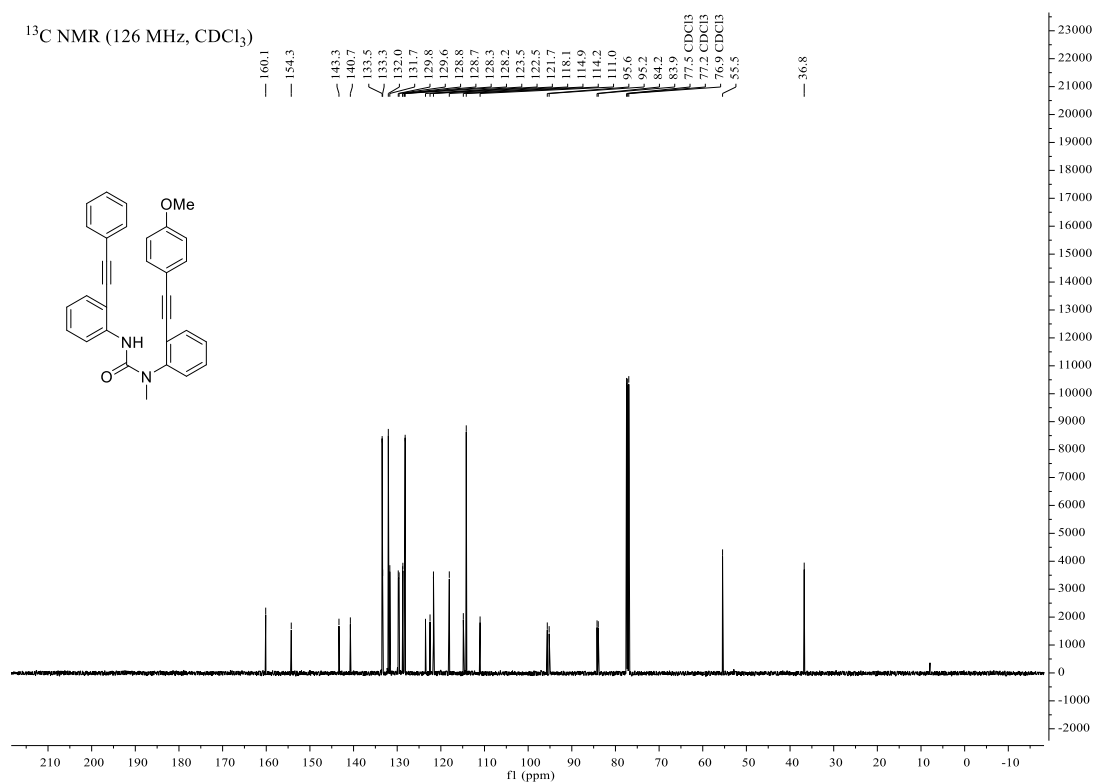
¹H NMR (500 MHz, CDCl₃) spectrum of compound 10. The chemical structure of 10 is shown in the top left. The spectrum displays peaks corresponding to the structure, with integration values indicated below the baseline.

Chemical Shift (ppm)	Integration
10.1	1.00
7.4-7.5	1.01, 2.03, 3.01, 3.02, 2.04, 1.00, 1.01
3.5	2.02, 3.00
2.0	2.01, 1.01, 2.04

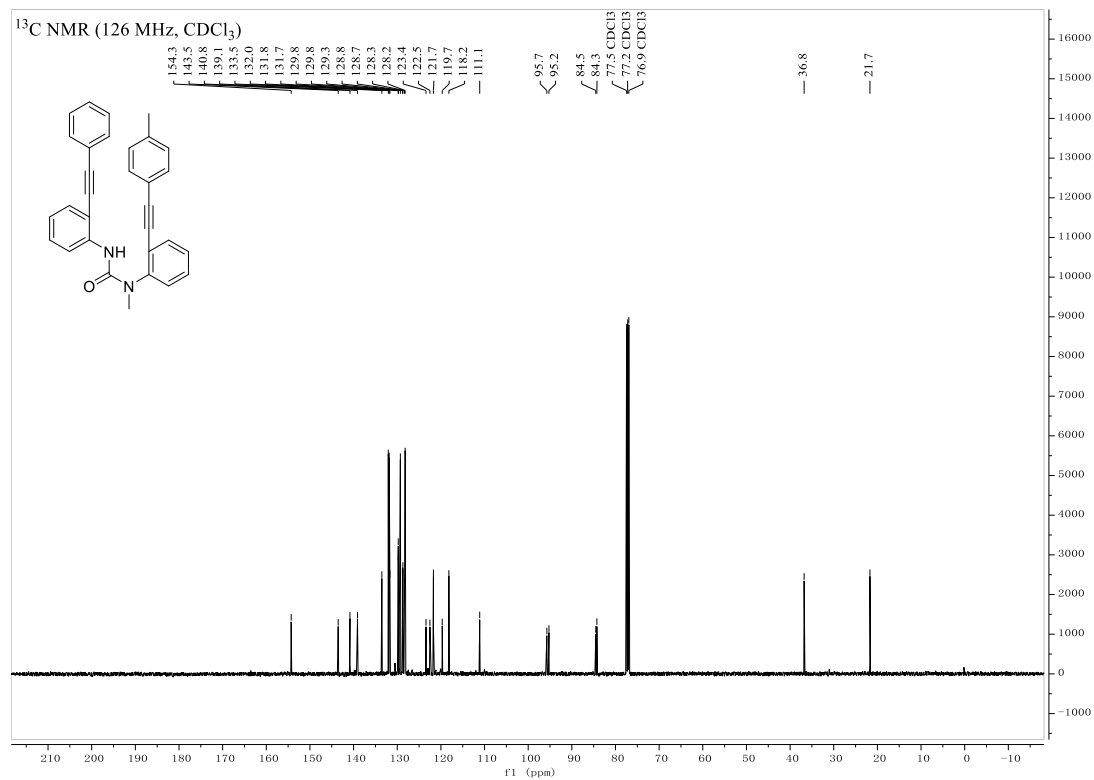
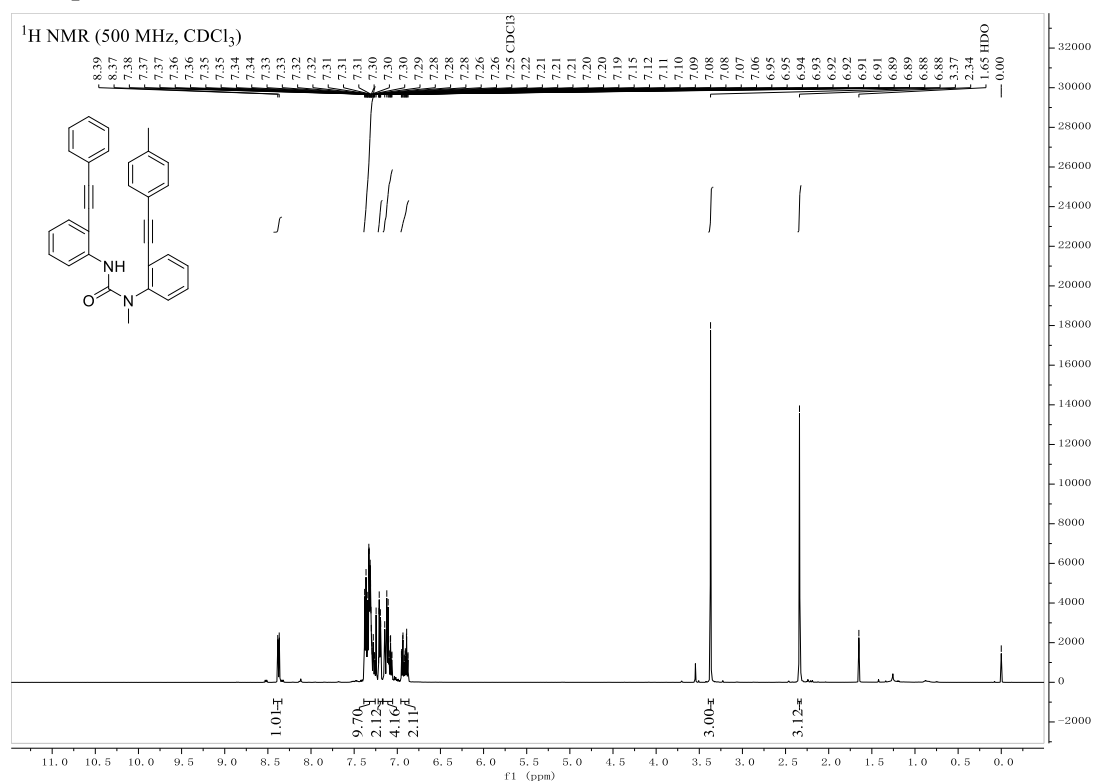


Compound S33

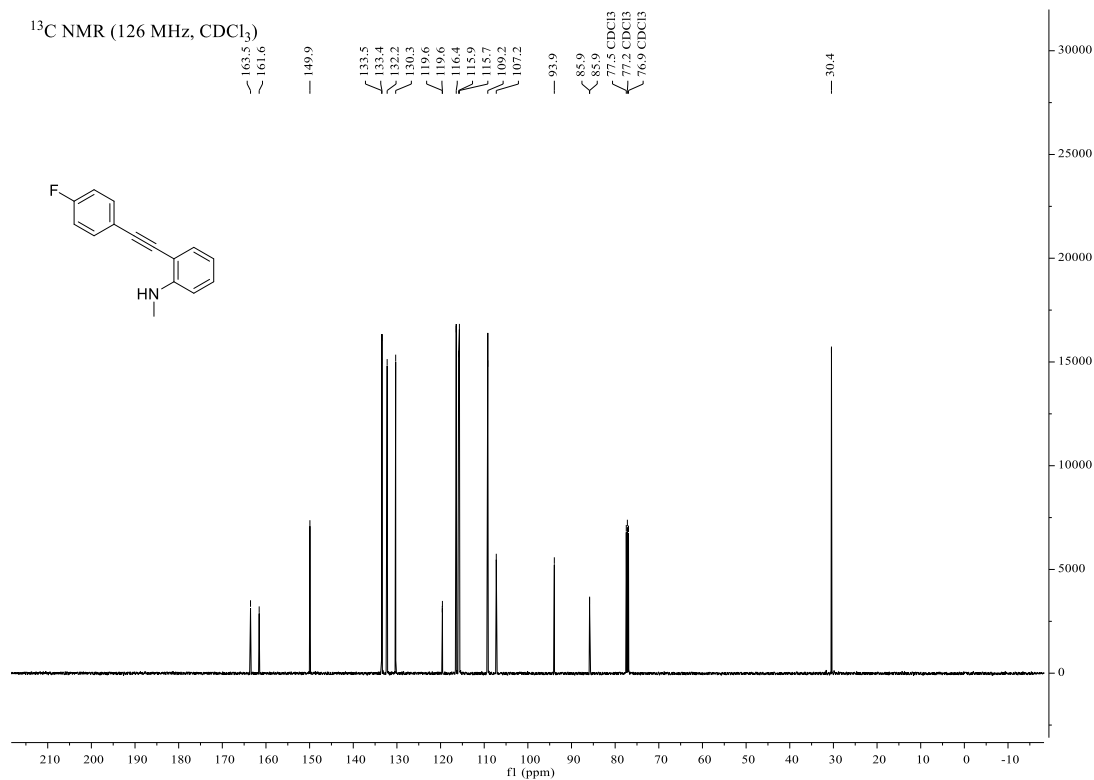
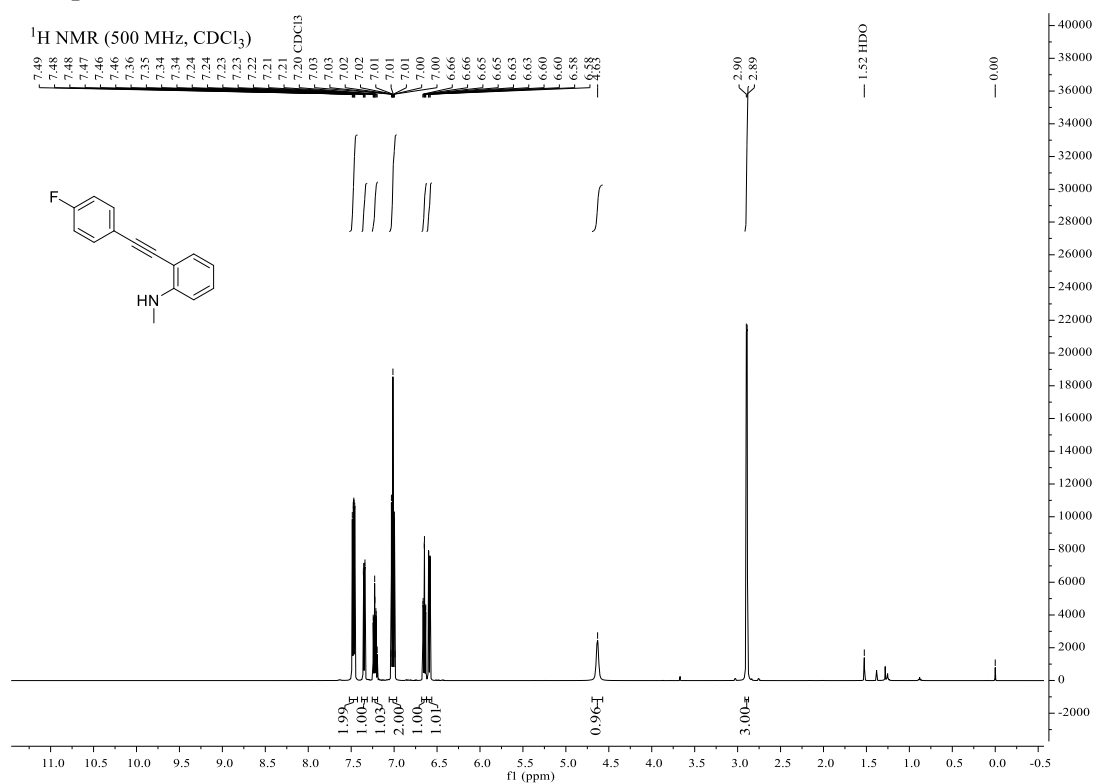




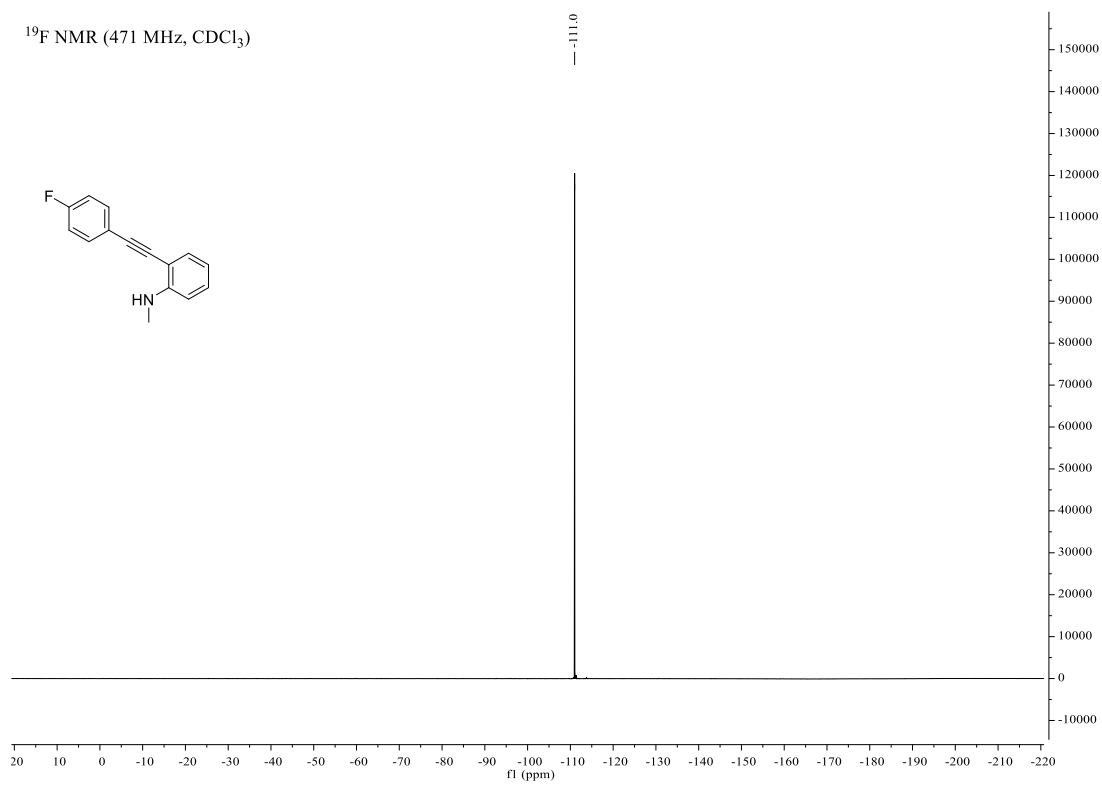
Compound S35



Compound S36



^{19}F NMR (471 MHz, CDCl_3)

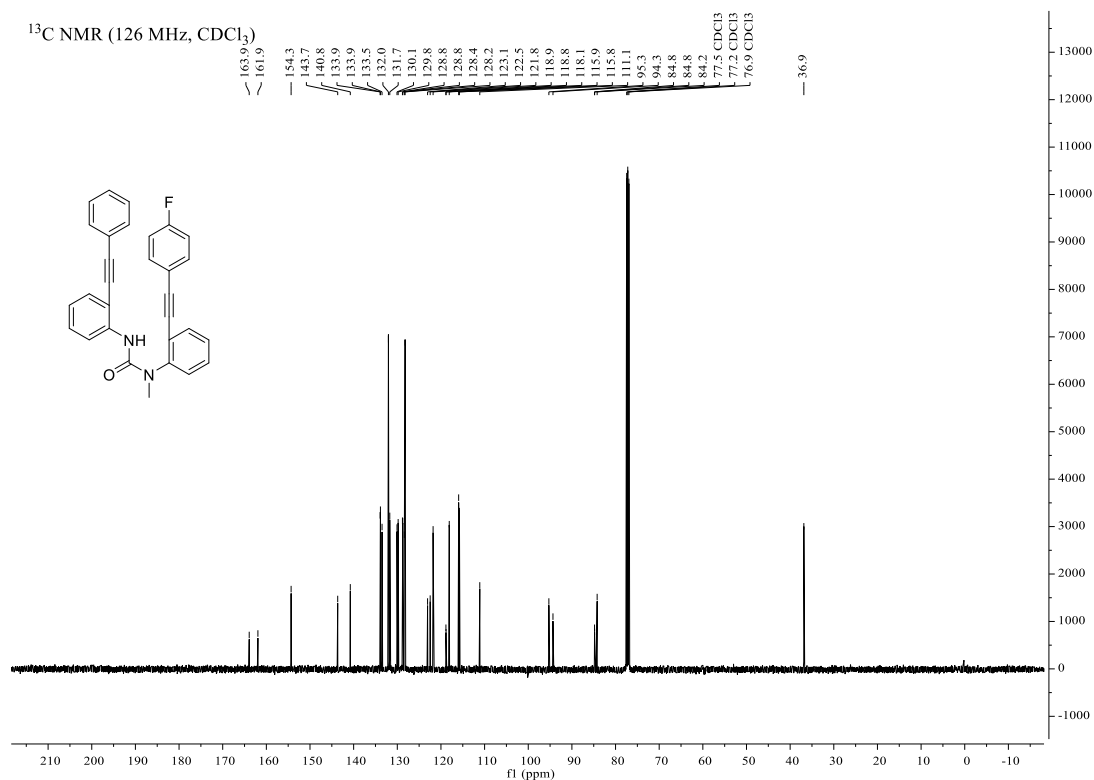


¹H NMR (500 MHz, CDCl₃)

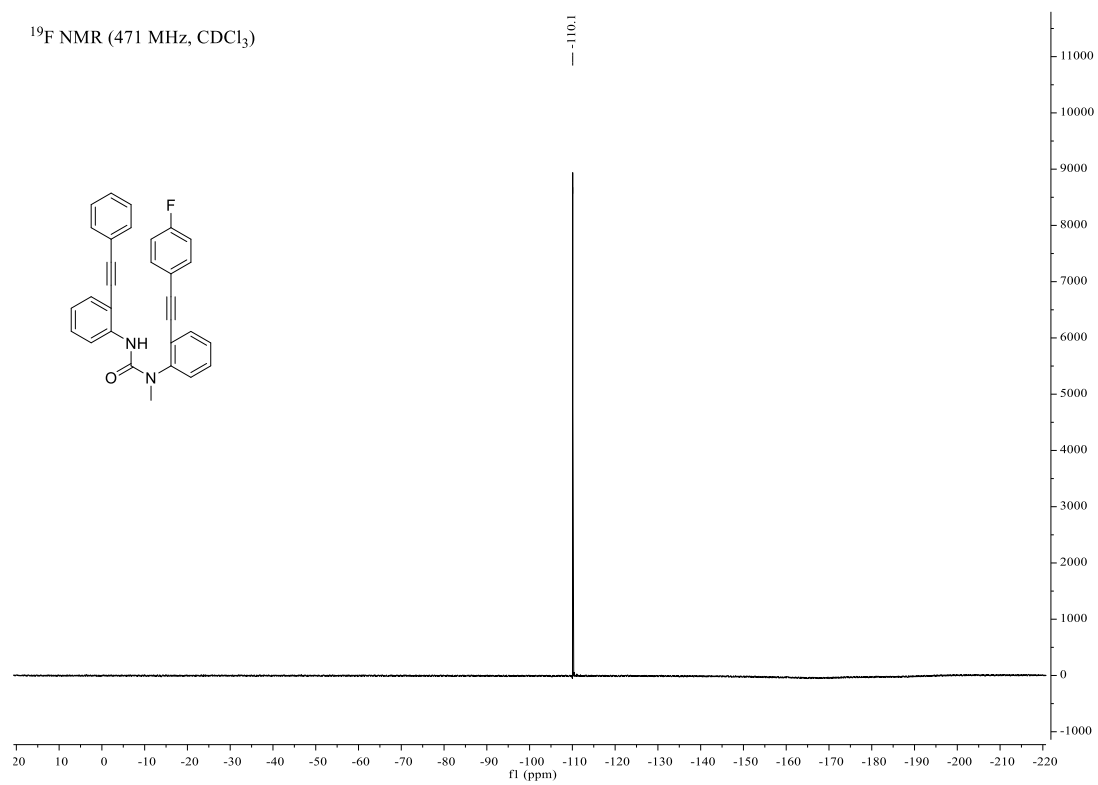
Chemical structure of compound 10: CN(C(=O)Nc1ccccc1)C#Cc2cc(F)ccc2C#Cc3ccccc3

Peak list (ppm): 8.38, 8.36, 8.36, 7.46, 7.45, 7.45, 7.44, 7.44, 7.43, 7.43, 7.38, 7.38, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.32, 7.32, 7.32, 7.31, 7.31, 7.31, 7.30, 7.30, 7.30, 7.30, 7.28, 7.28, 7.28, 7.26, 7.26, 7.25 CDCl₃, 7.21, 7.20, 7.20, 7.19, 7.19, 7.19, 7.15, 7.15, 7.13, 7.12, 7.11, 7.11, 7.10, 7.09, 7.02, 7.02, 7.01, 7.00, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.95, 6.94, 6.92, 6.92, 6.90, 6.90, 6.89, 6.89, 3.36, 1.64 H₂O, 0.00.

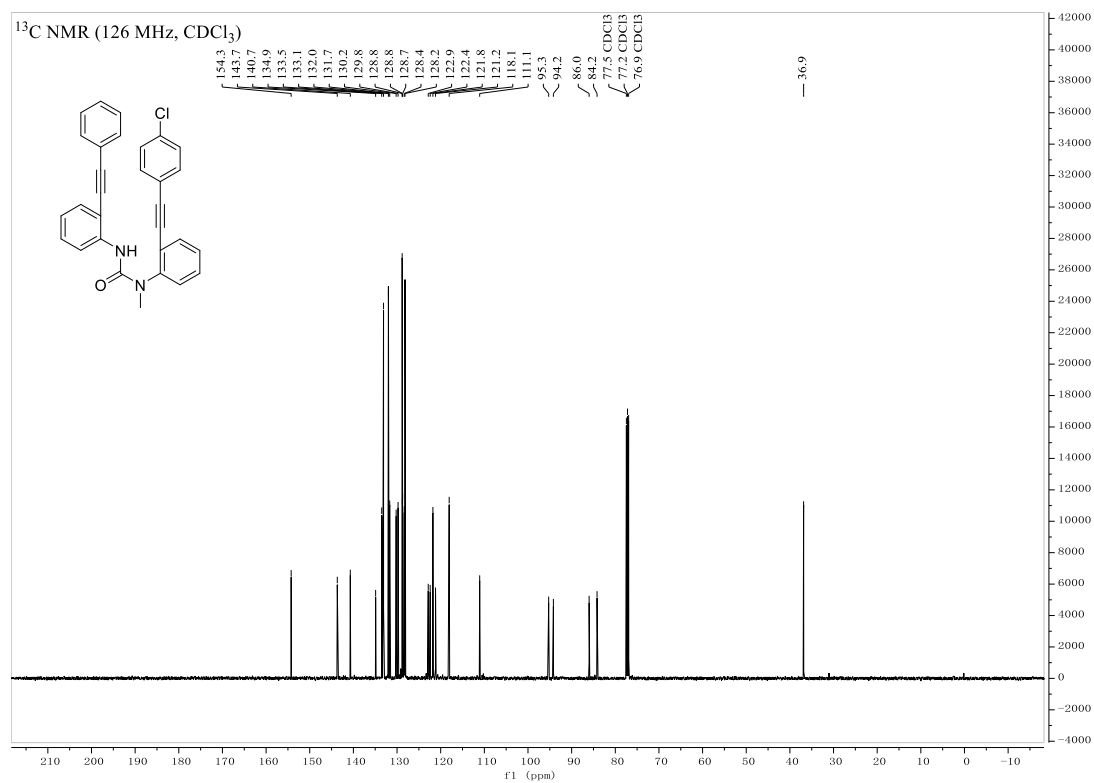
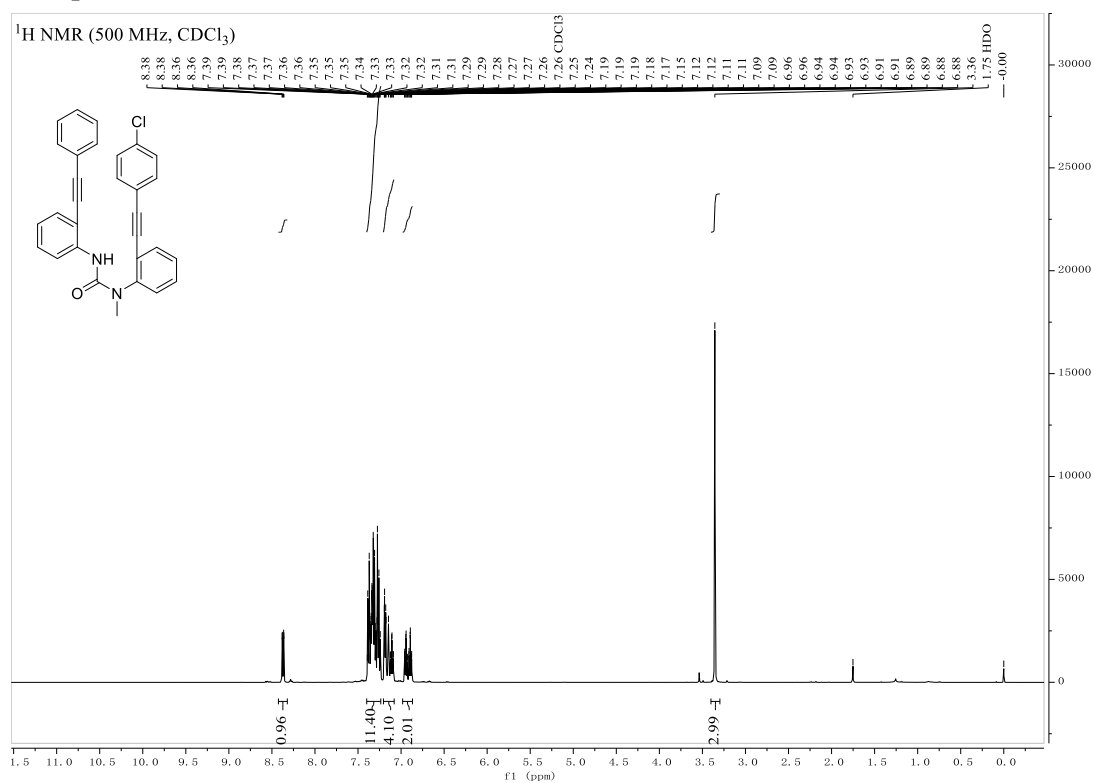
Integration values: 1.00, 2.00, 7.06, 1.00, 1.01, 1.04, 2.02, 1.02, 1.00, 3.00.



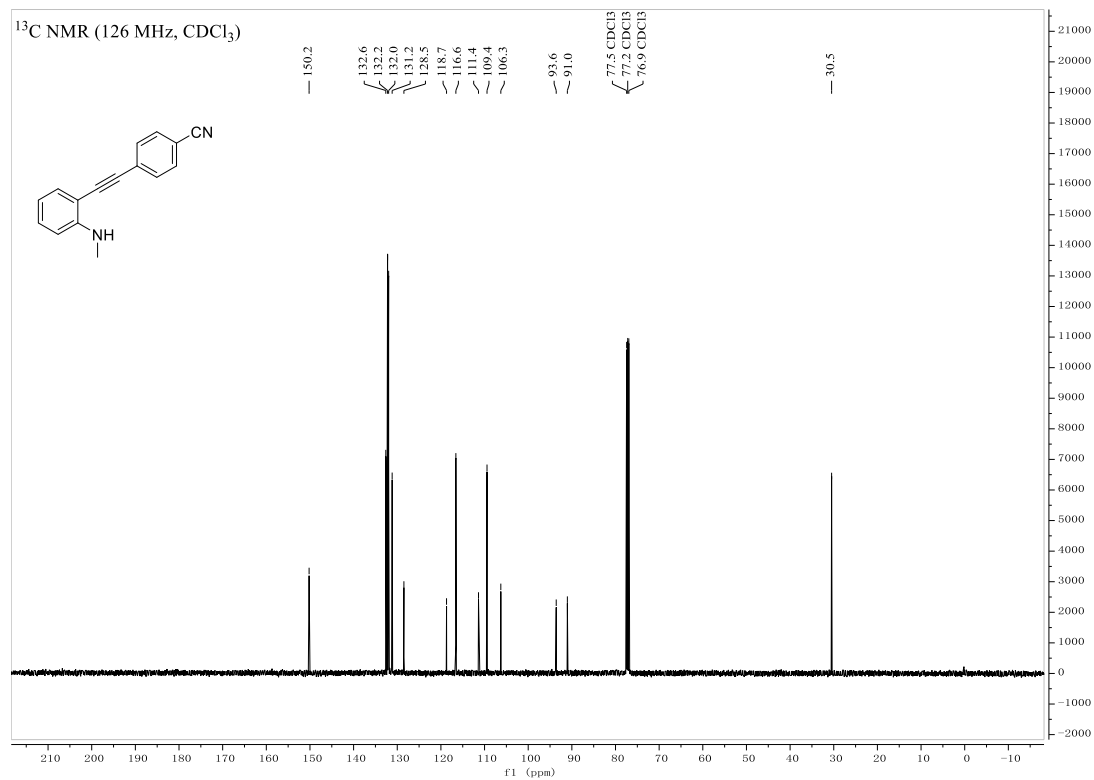
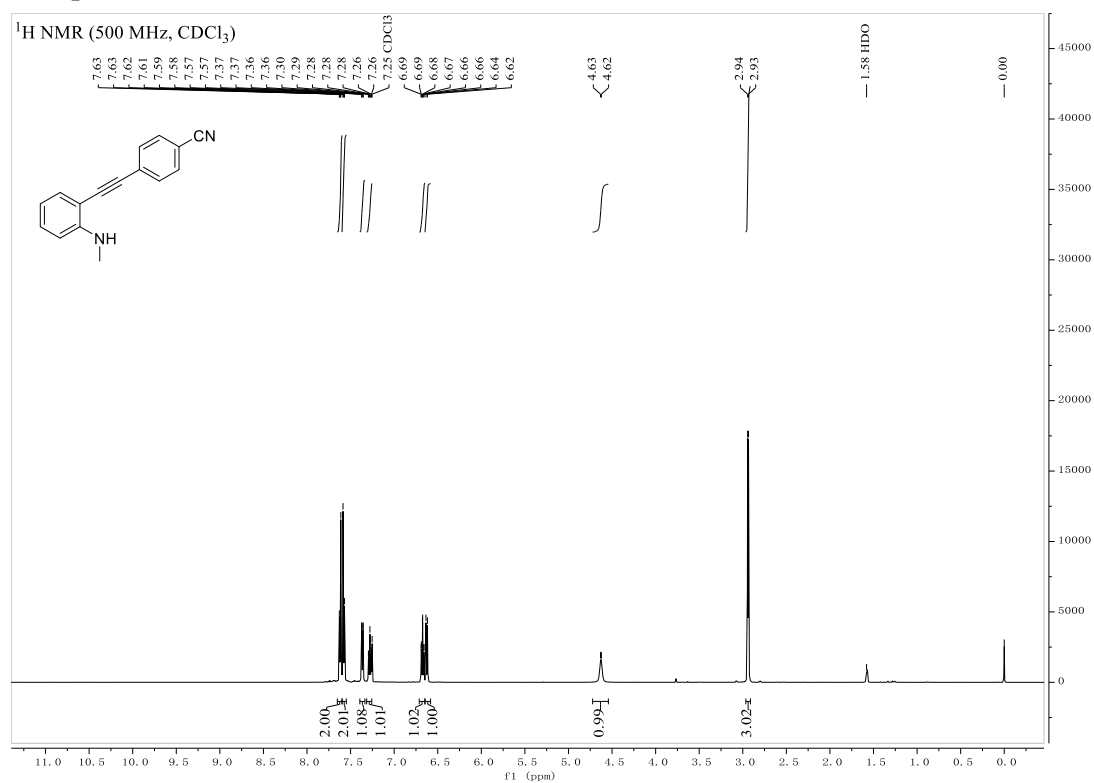
¹⁹F NMR (471 MHz, CDCl₃)



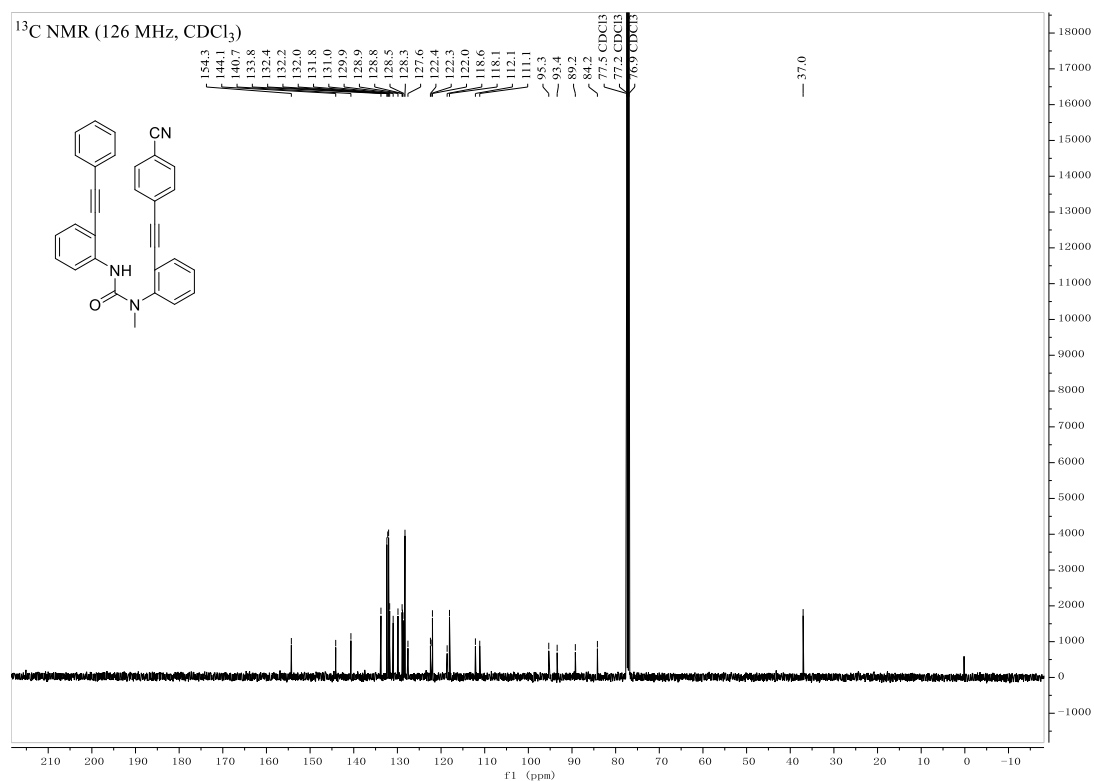
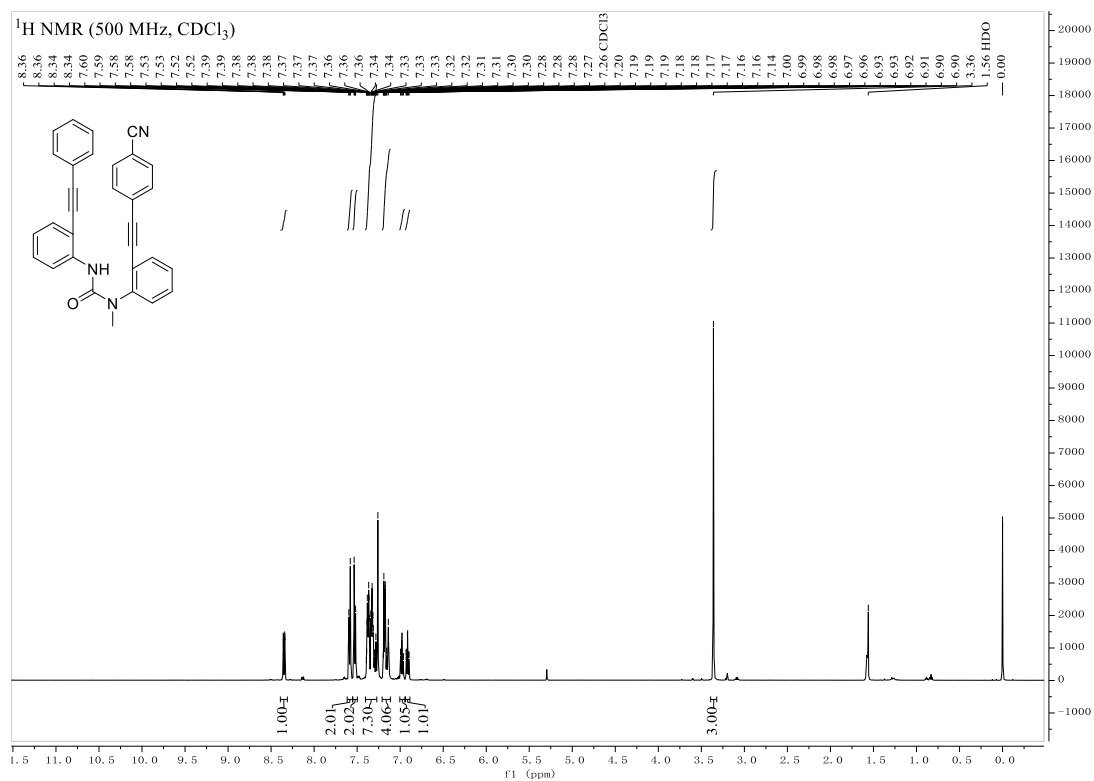
Compound S38



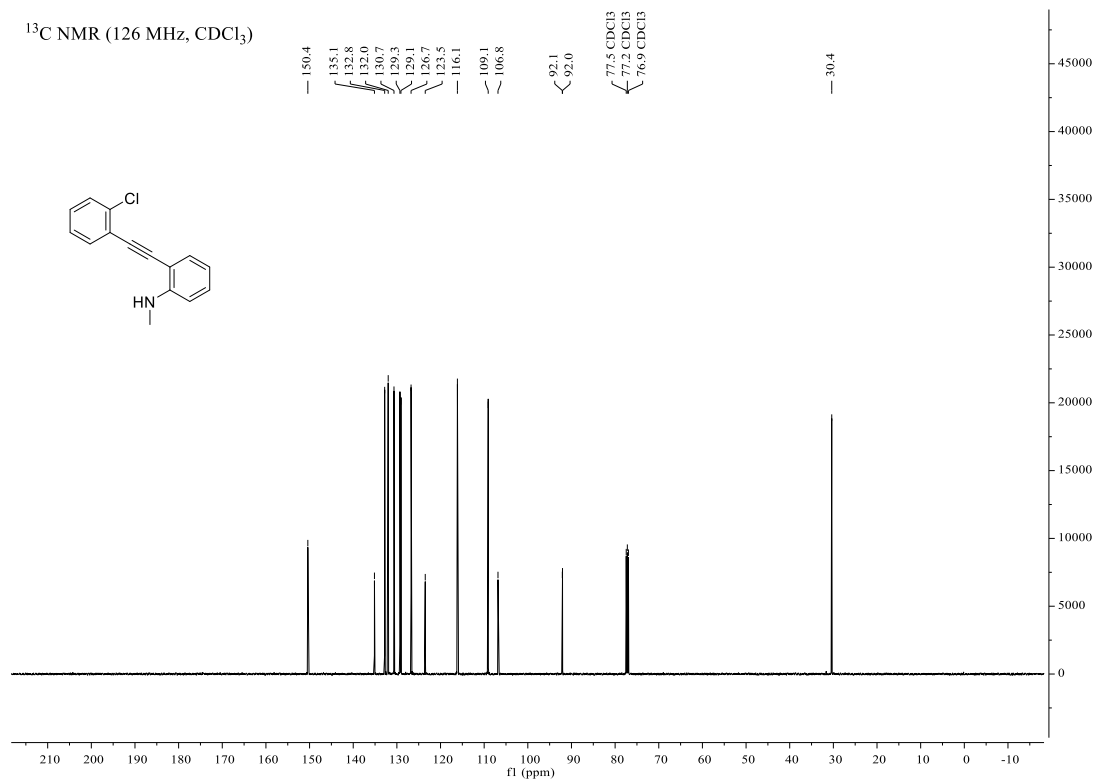
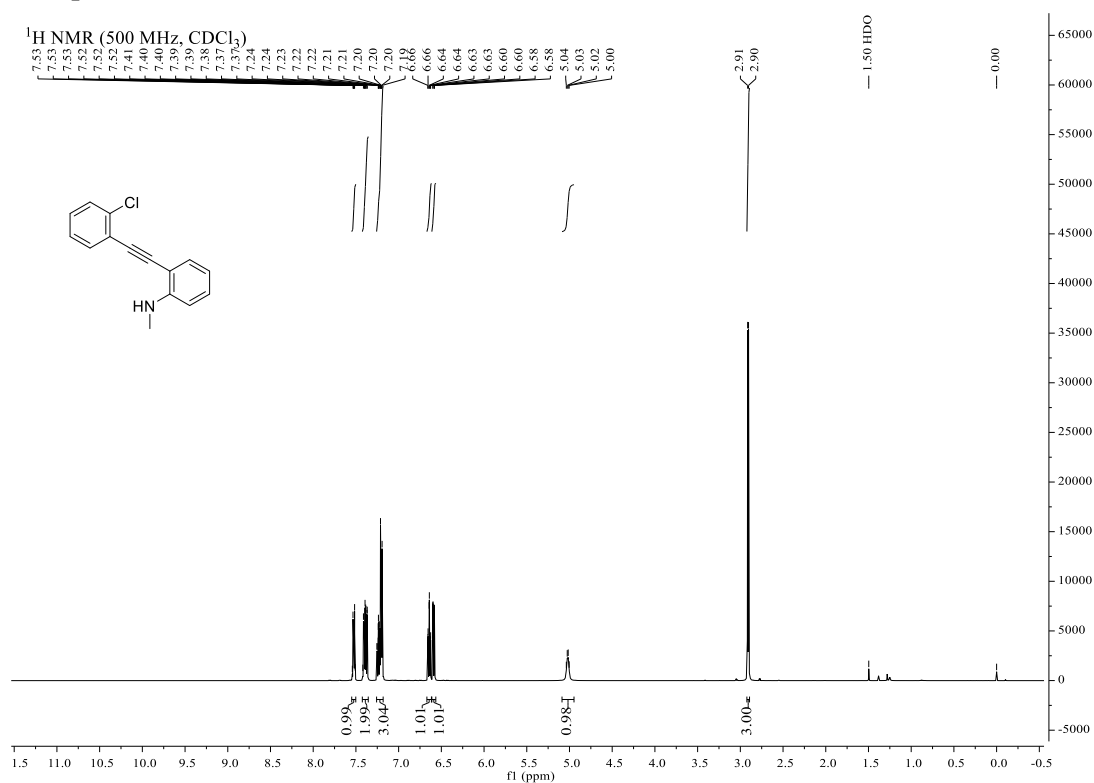
Compound S39



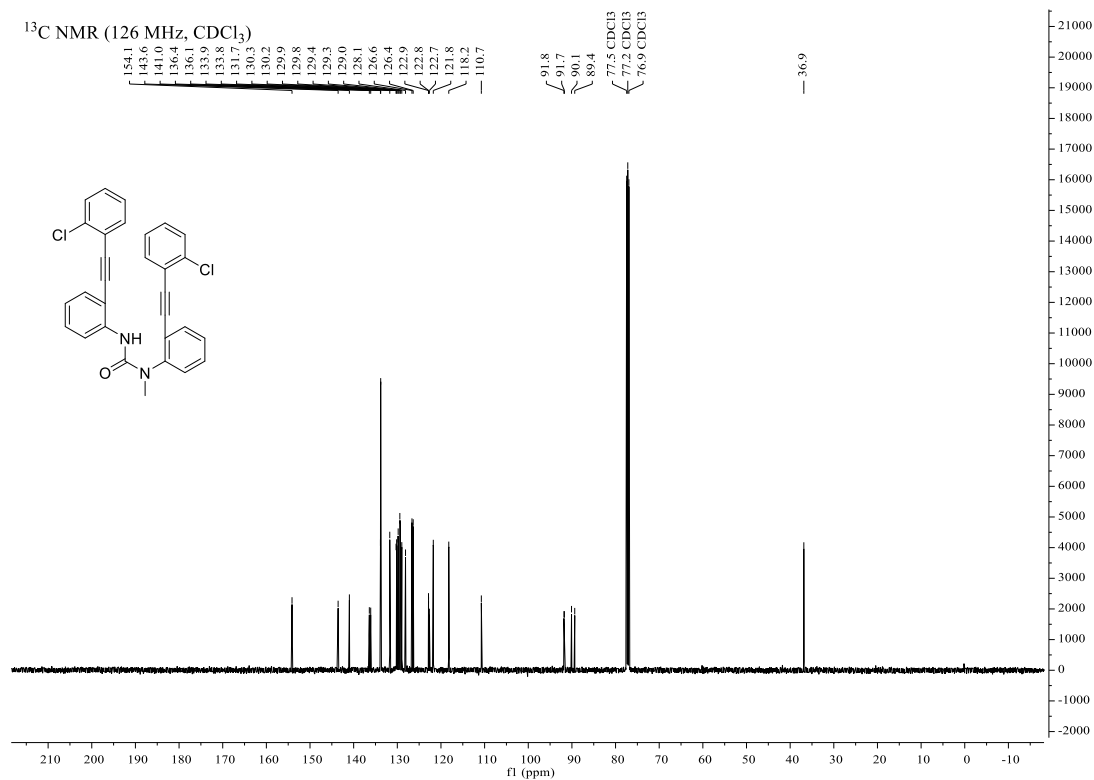
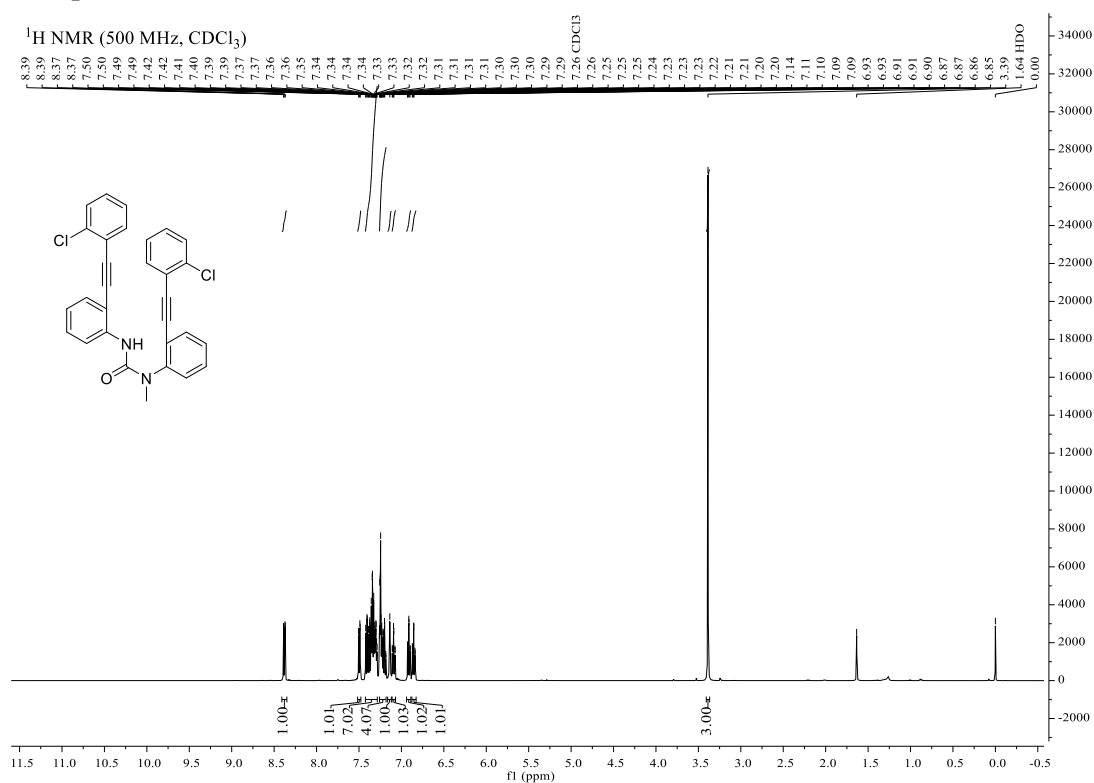
Compound S40



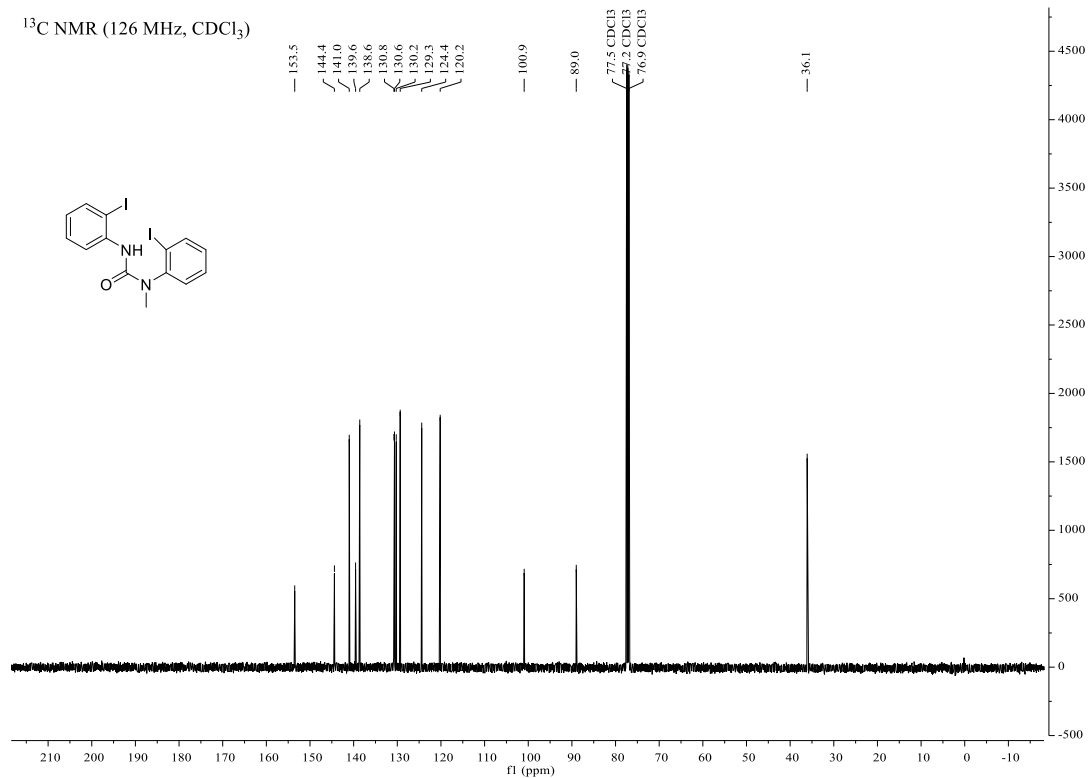
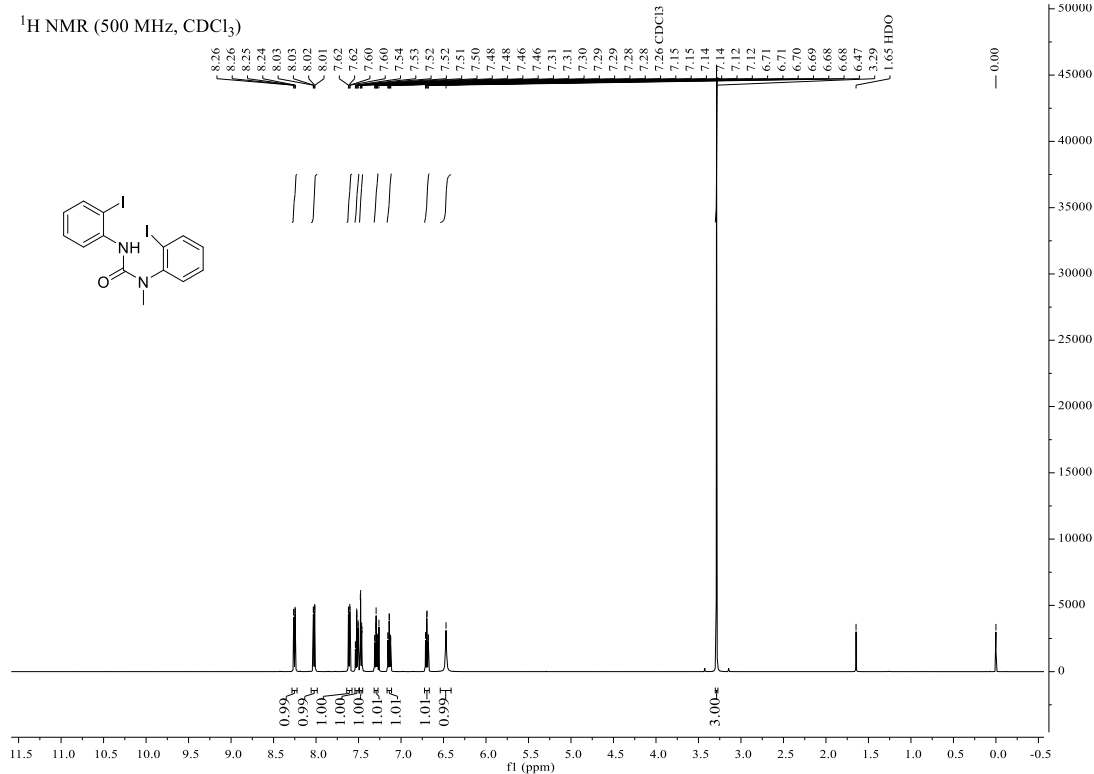
Compound S41



Compound S42

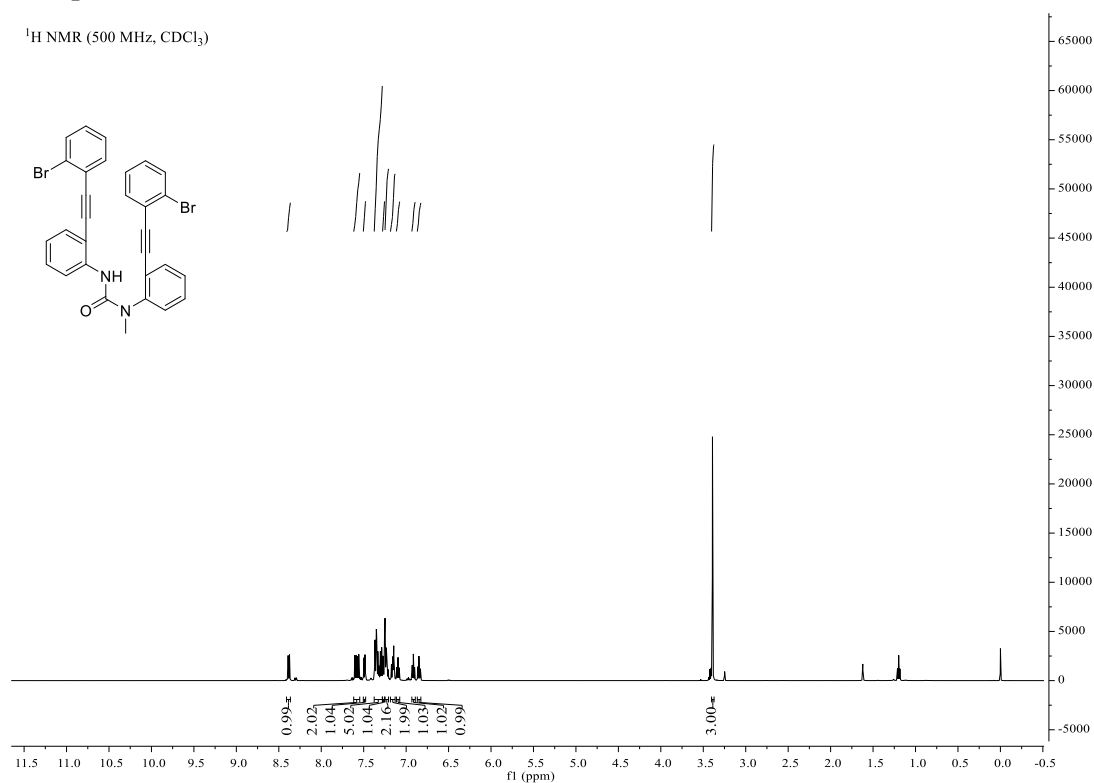


Compound S43

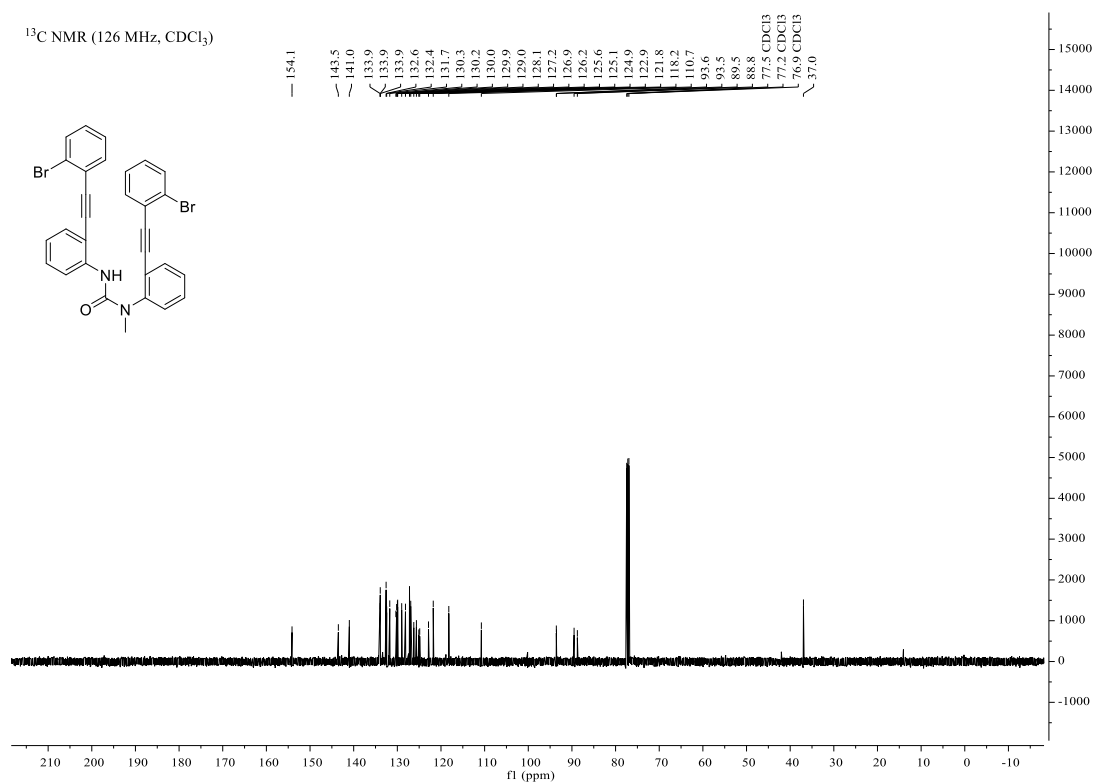


Compound S44

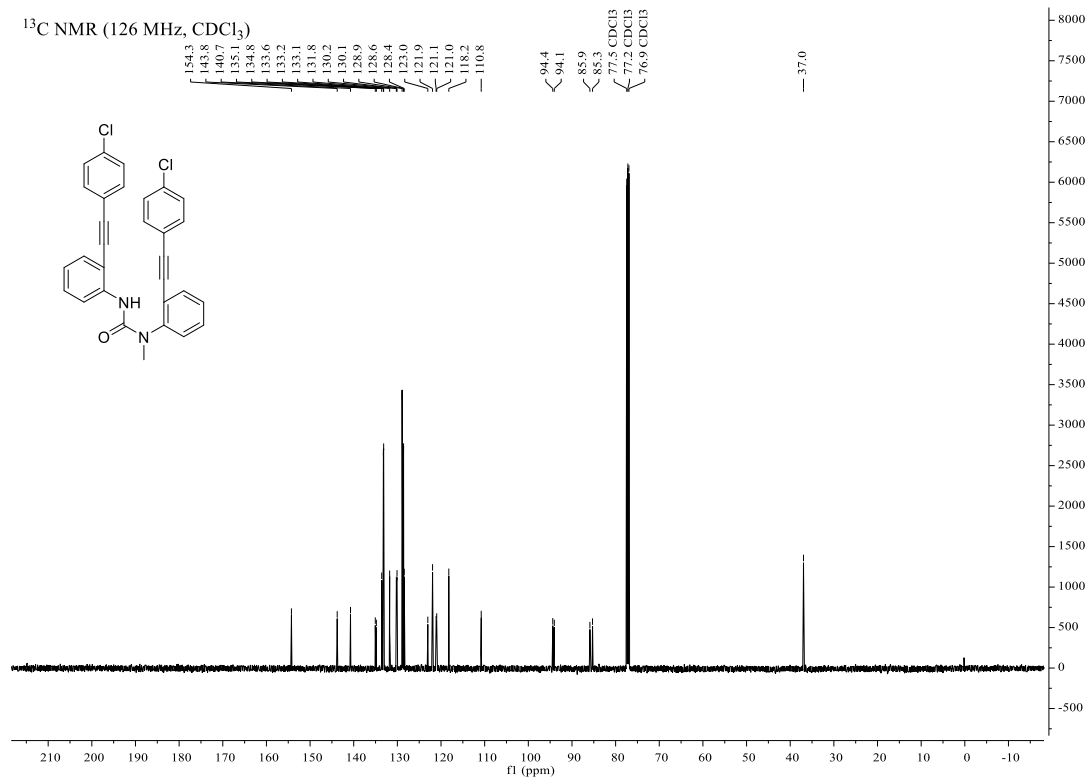
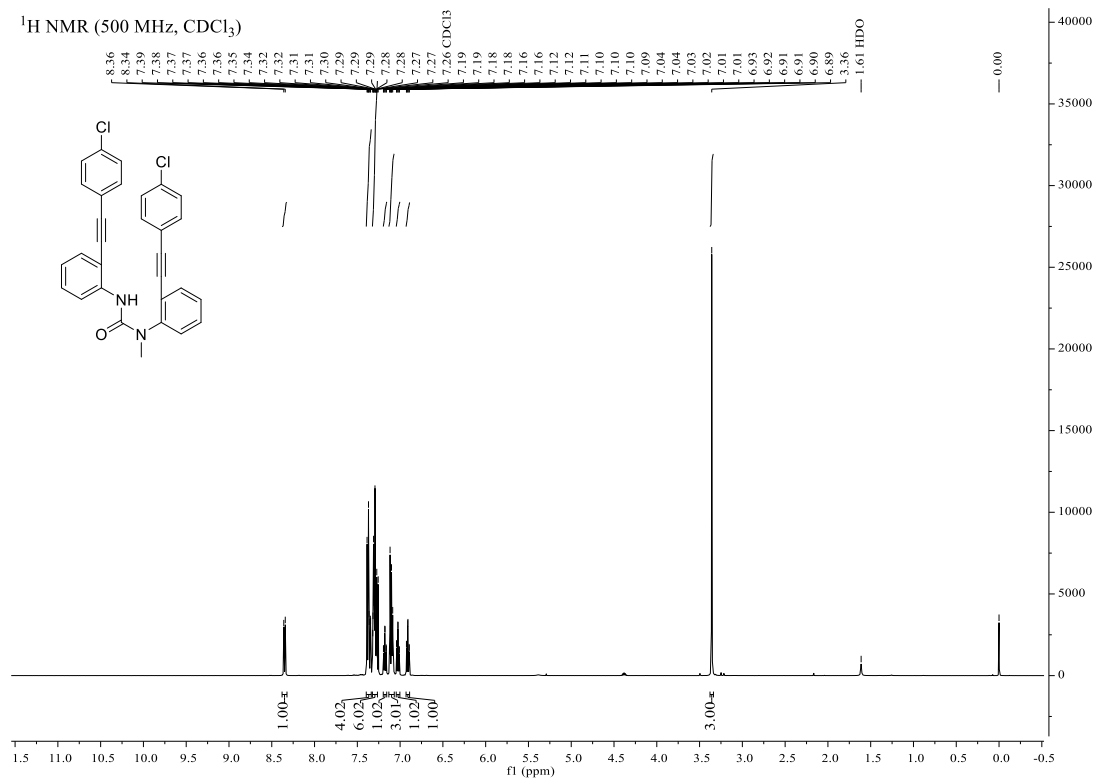
^1H NMR (500 MHz, CDCl_3)



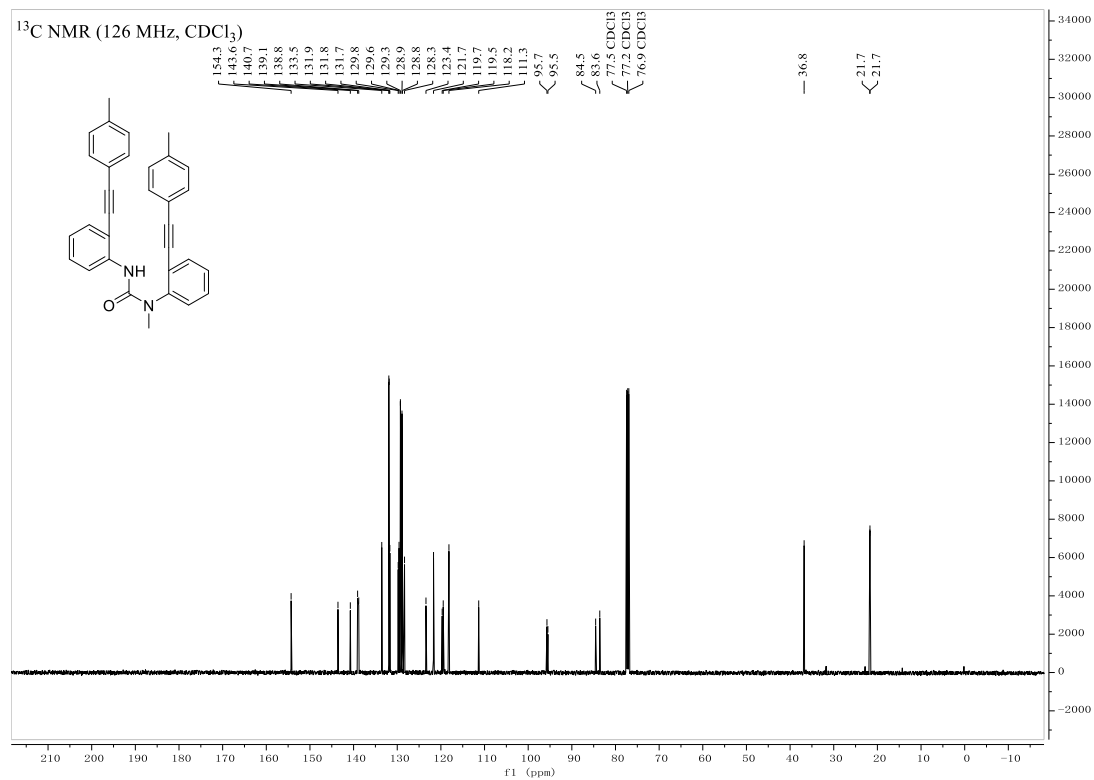
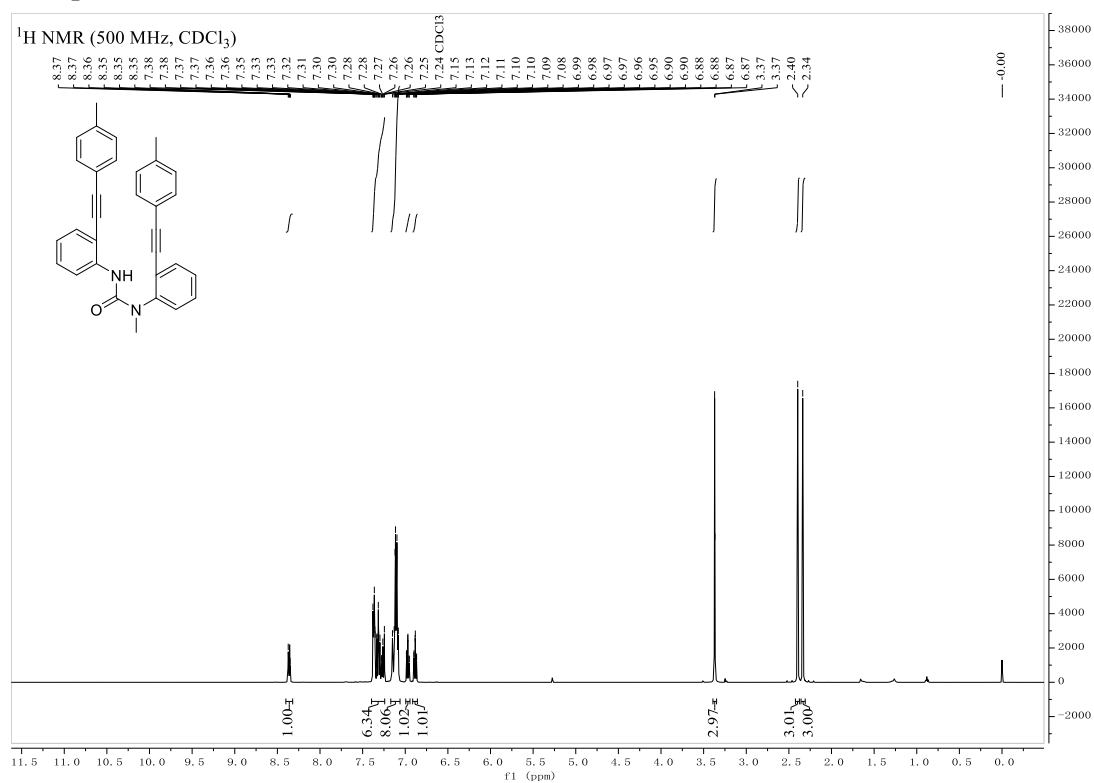
^{13}C NMR (126 MHz, CDCl_3)



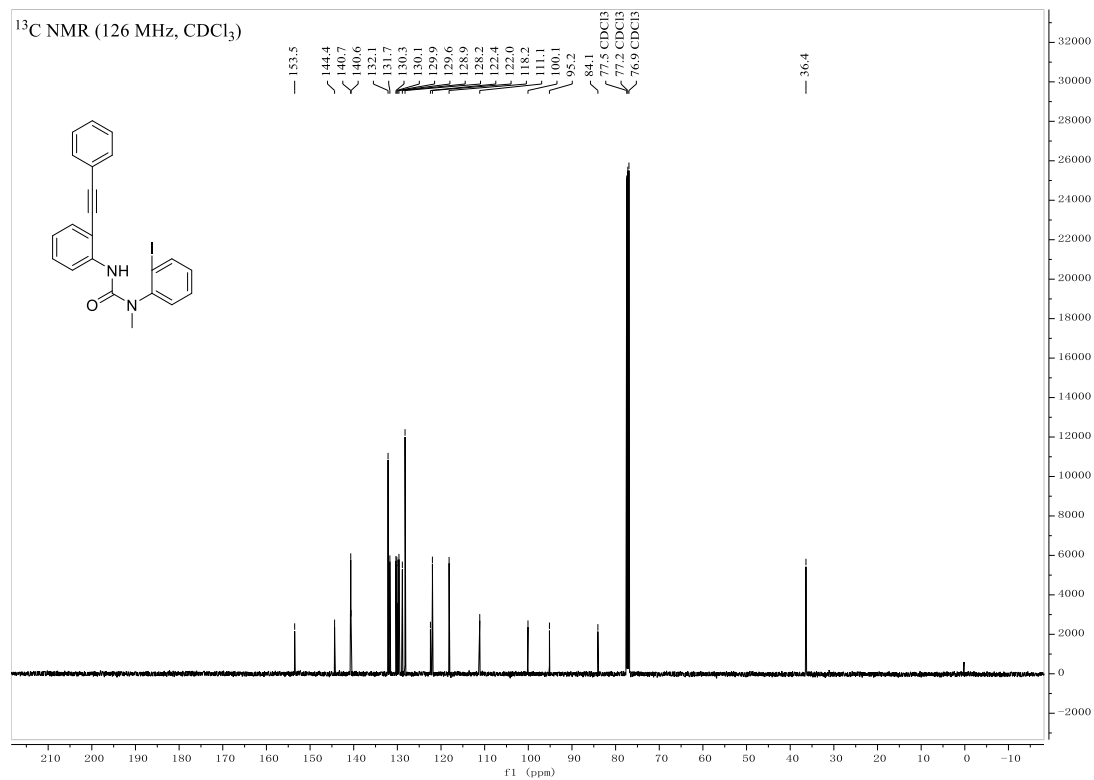
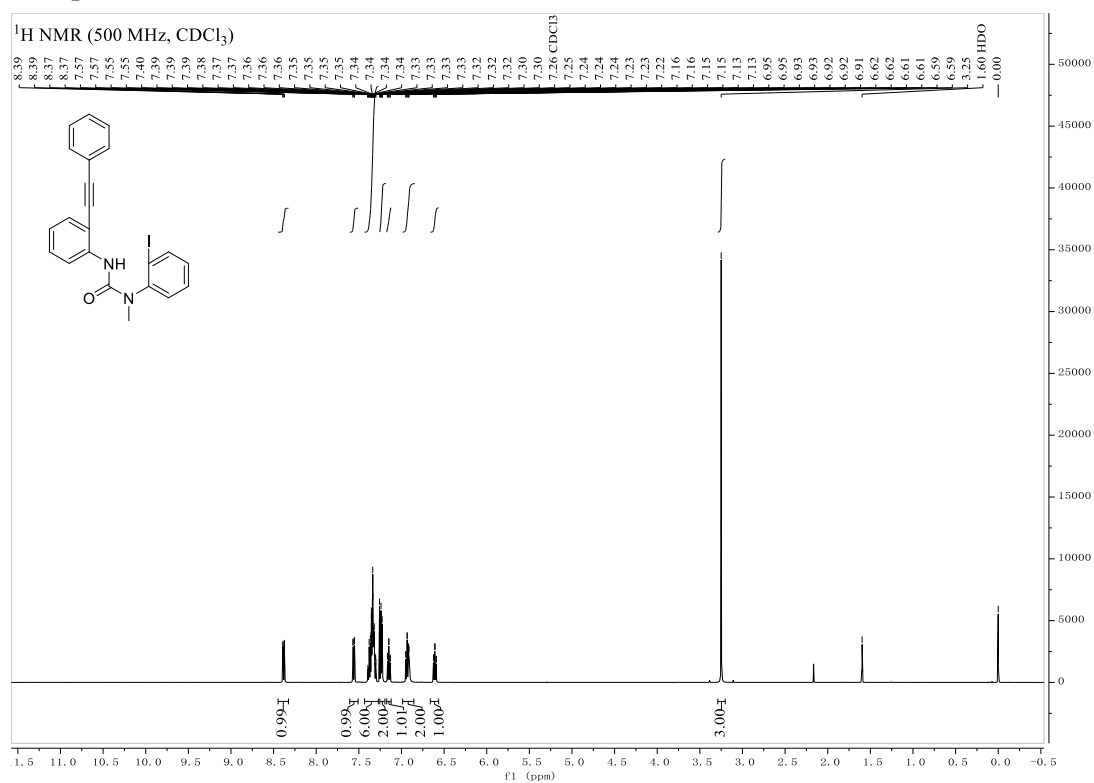
Compound S45



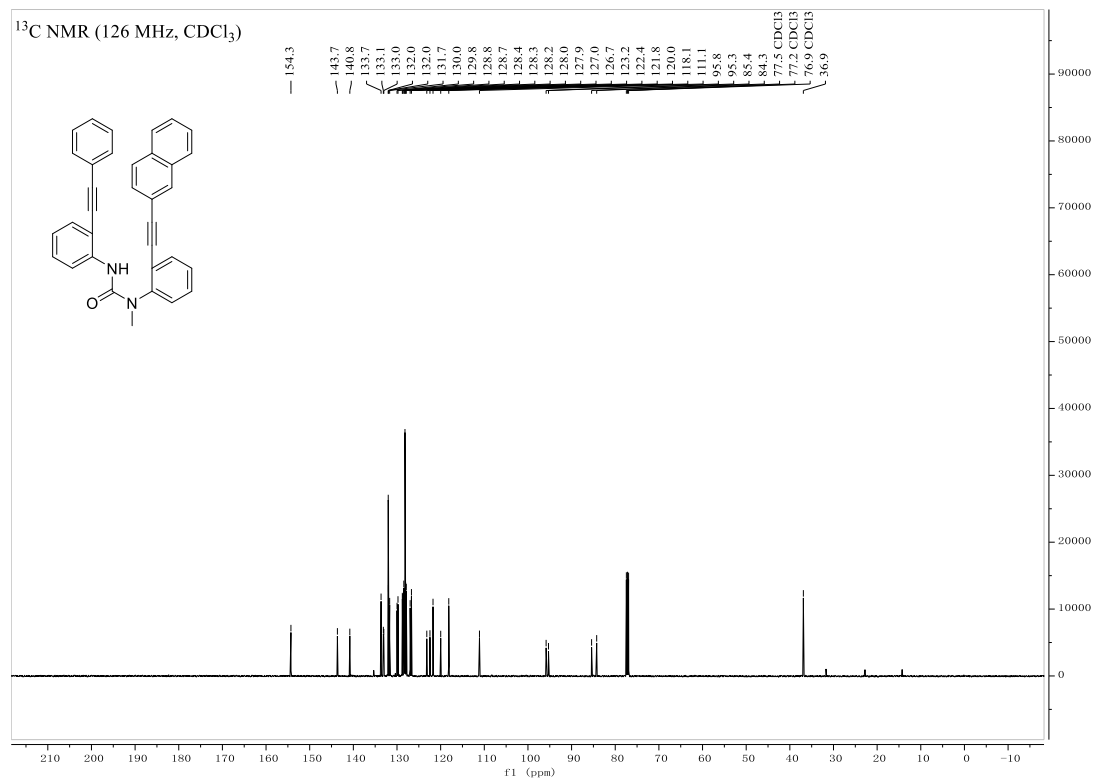
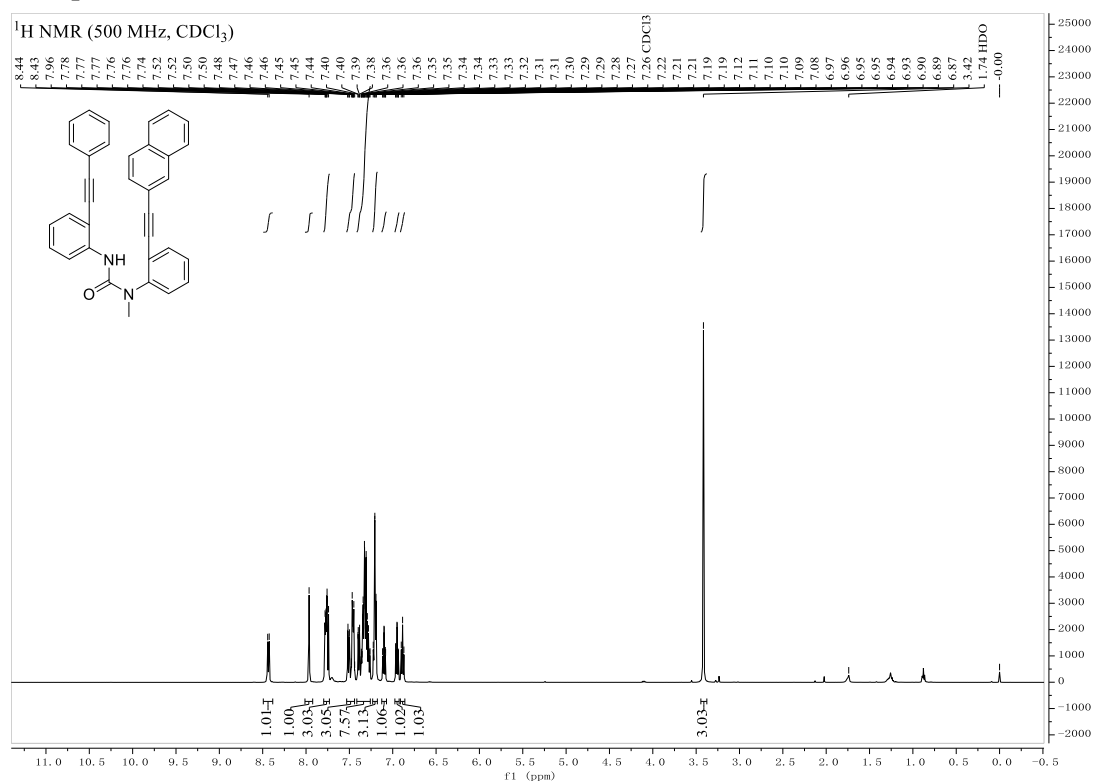
Compound S46



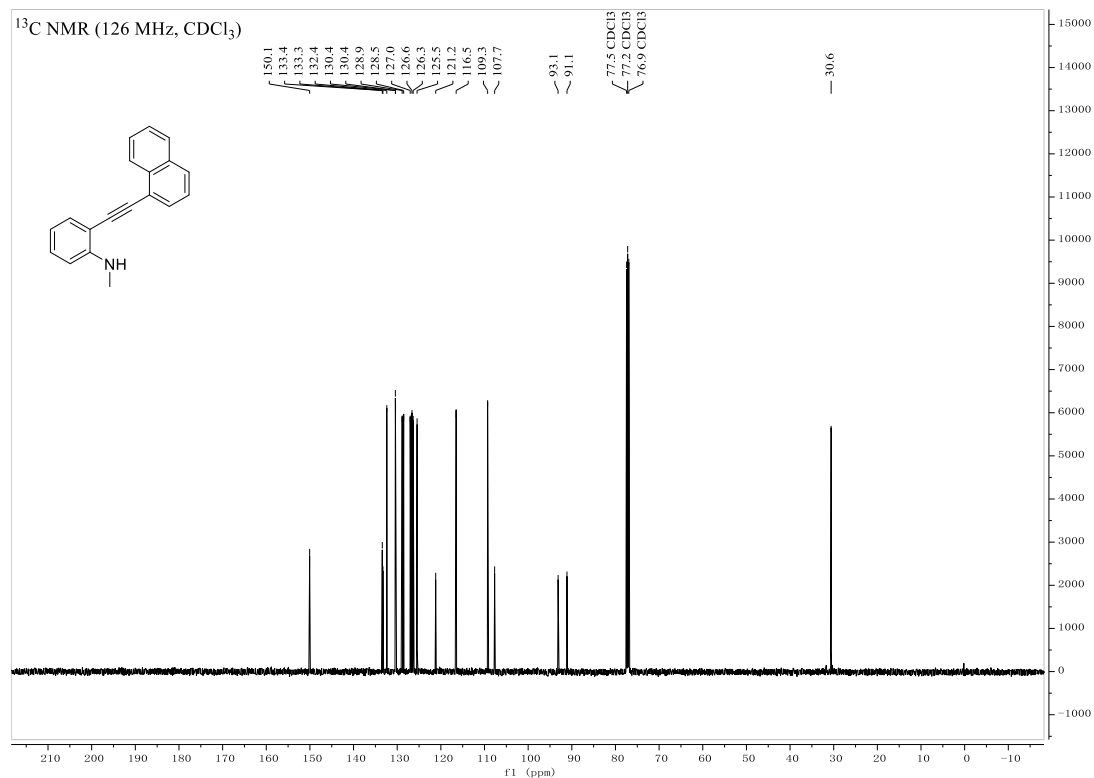
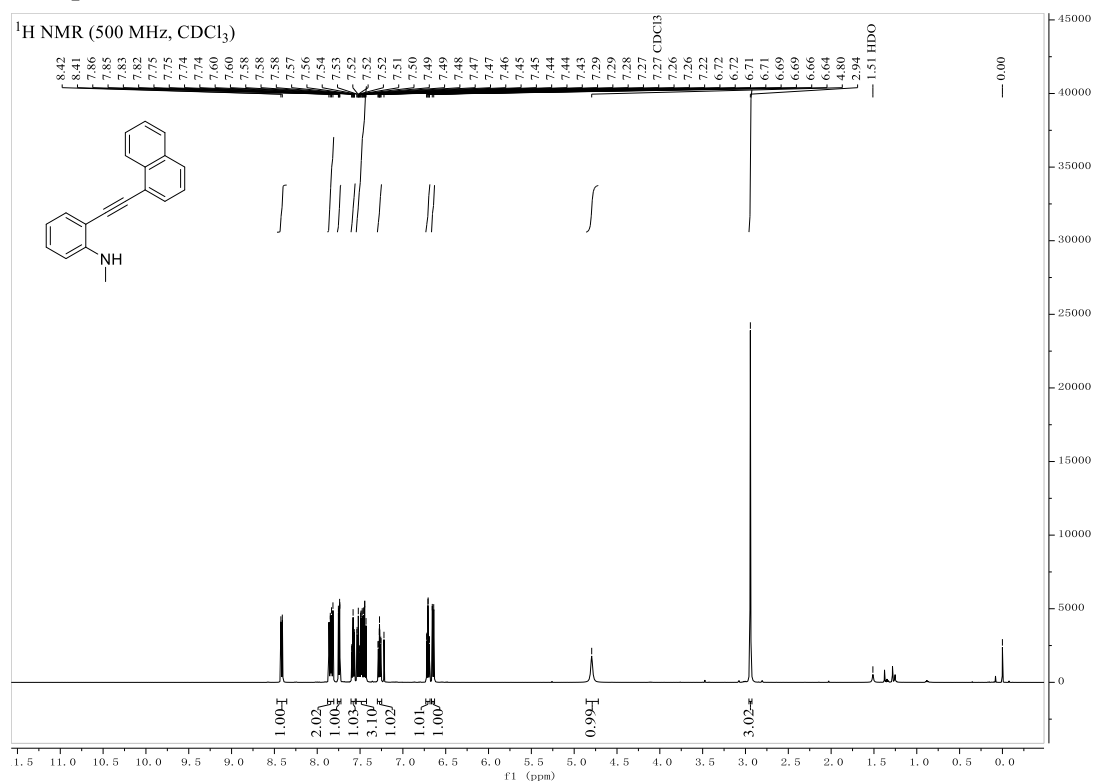
Compound S47



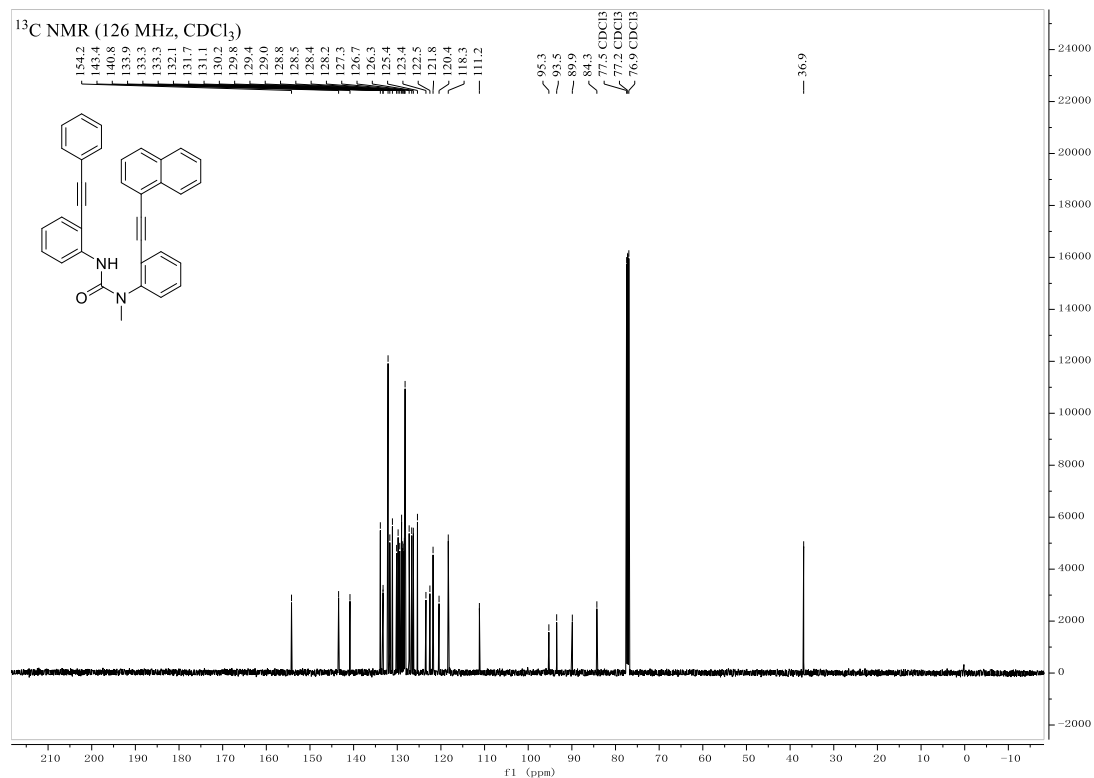
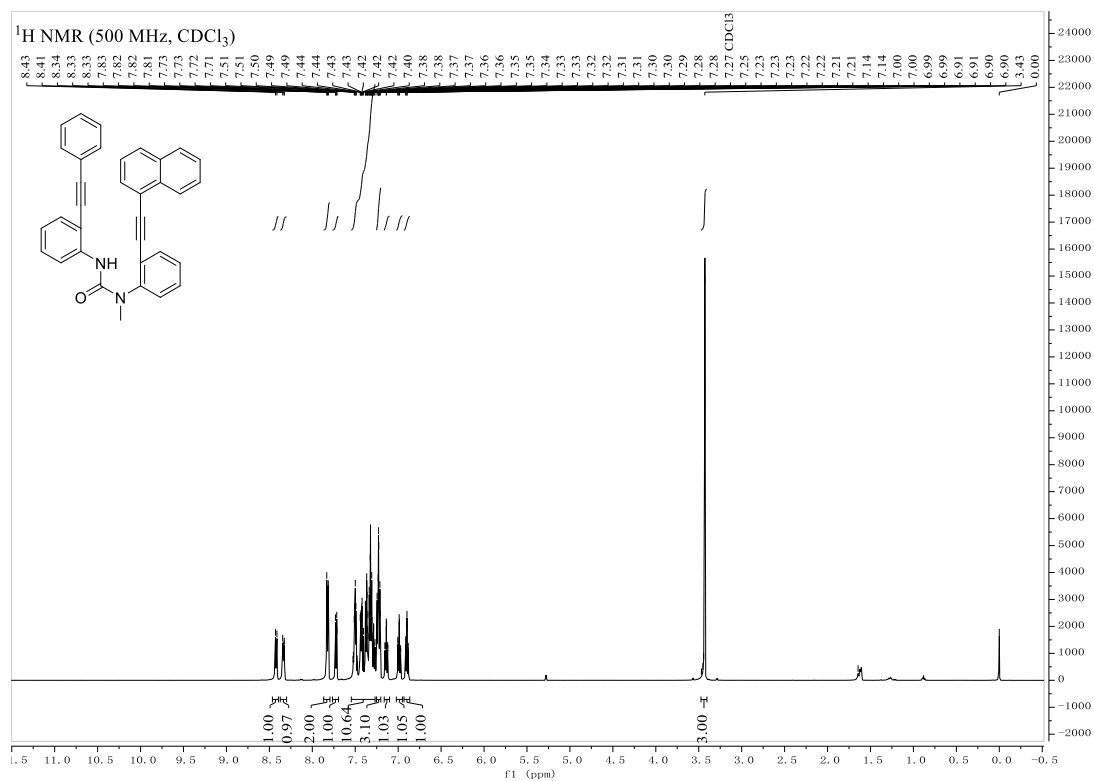
Compound S48



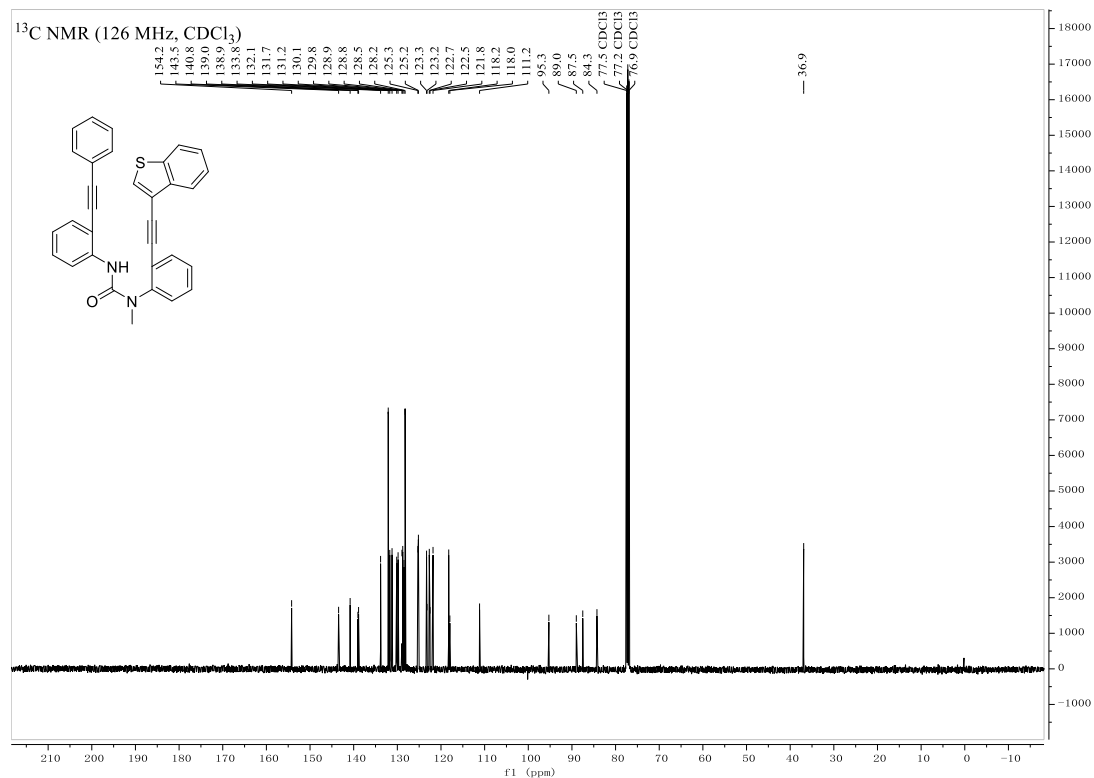
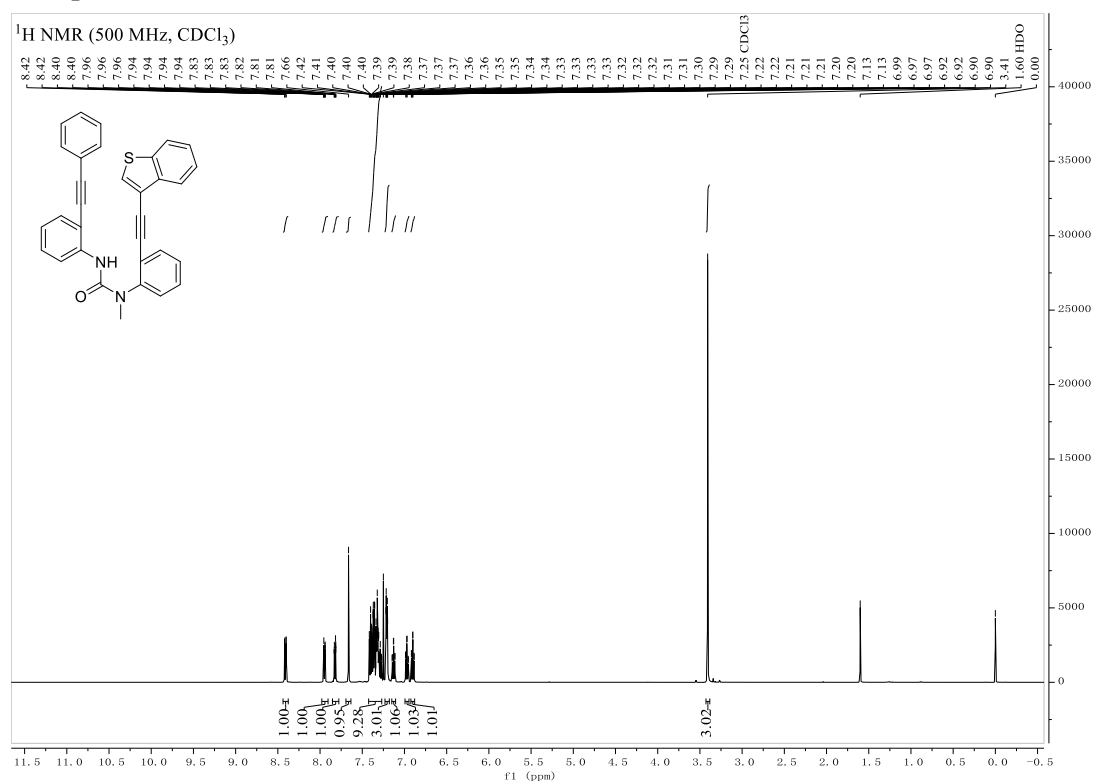
Compound S49



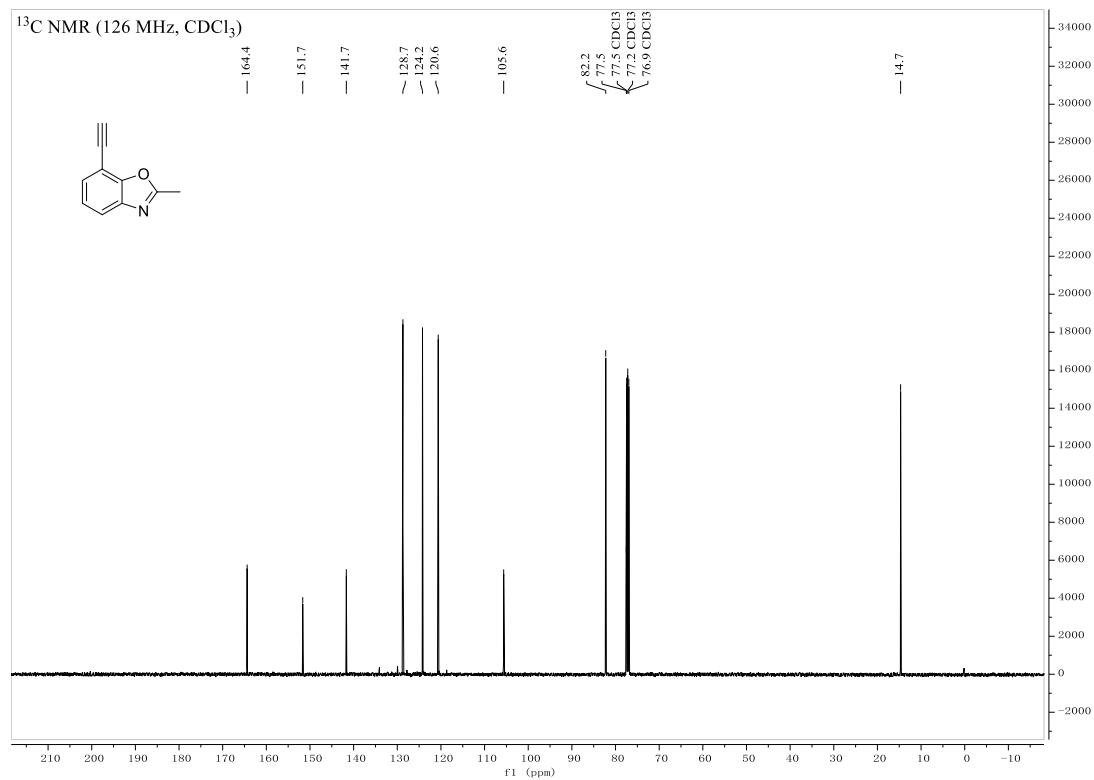
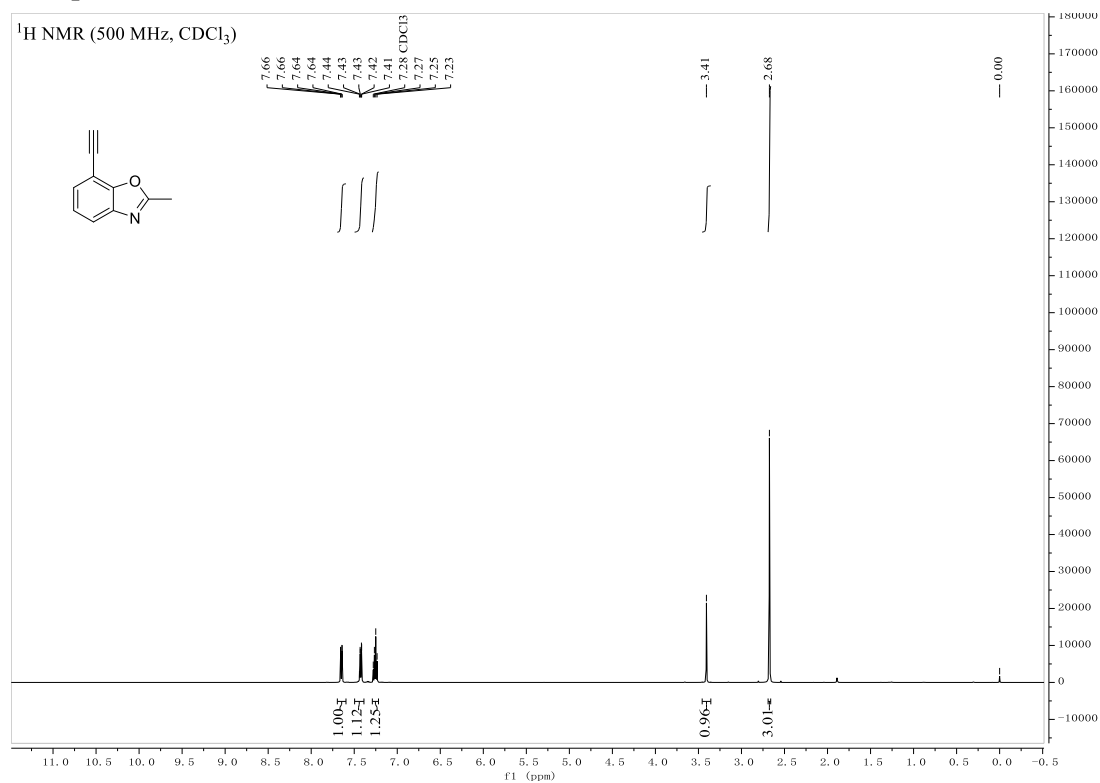
Compound S50



Compound S51



Compound S52



Compound 39s

