*Electronic Supplementary Information*

# Indium-Mediated Annulation of 2-Azidoaryl Aldehydes with Propargyl Bromides to [1,2,3]Triazolo-[1,5-*a*]Quinolines

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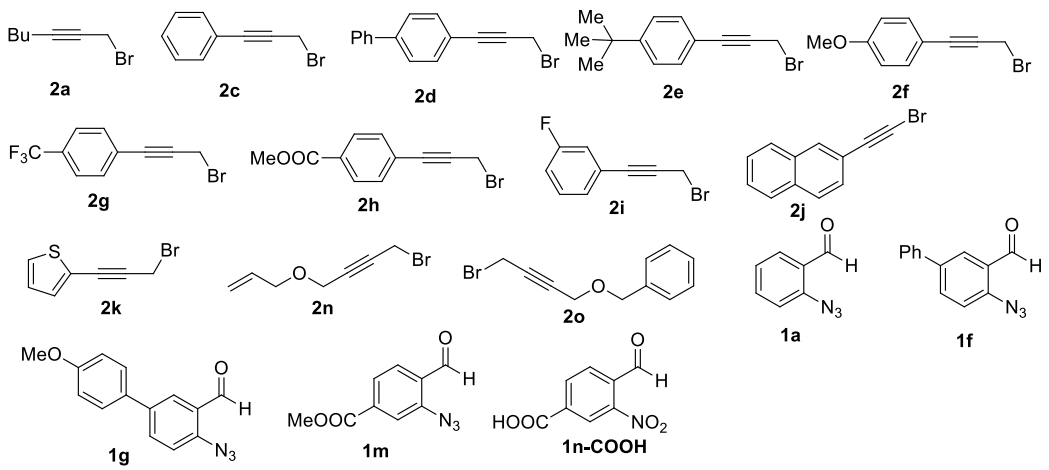
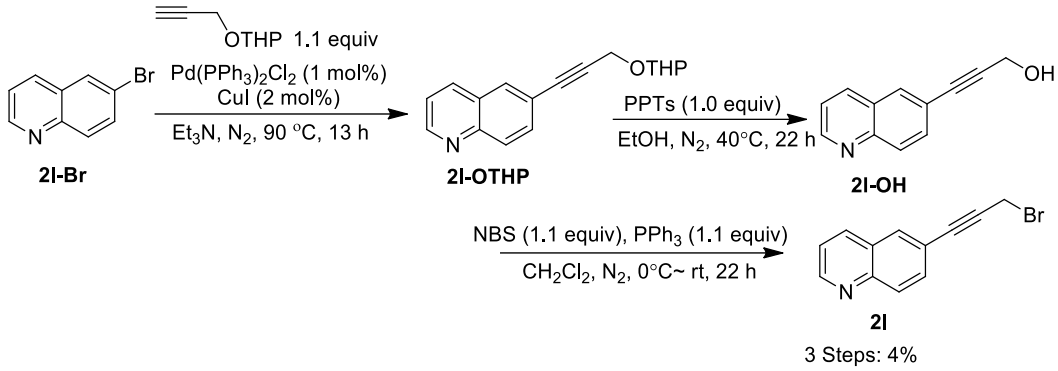
**Materials**: DME, MTBE, 1,4-Dioxane, and THF were distilled from Na/benzophenone before use. DCE, DMA, and DMSO were distilled from $CaH_2$ and stored with 4 Å molecular sieve. MeCN, DCM, MeOH, and DMF were purchased from Energy Chemical and used without purification. Anhydrous In and LiI compounds were purchased from Energy Chemical and used without purification. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. Infrared spectra were recorded on a Nicolet iS5 using neat thin film technique. High-resolution mass spectra (HRSM) were obtained on a Waters I-Class VION IMS QTof and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$, $[M-OH]^+$, $[M-H]^-$ or $[M]^+$. $^1H$ NMR spectra were recorded on a Bruker-400 MHz spectrometer, $^{13}C$ NMR spectra were recorded at 101 MHz, and $^{19}F$ NMR spectra were recorded at 376 MHz. All spectra were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ = 7.26 ppm ($^1H$) and 77.00 ppm ($^{13}C$). Coupling constants were reported in Hertz (Hz). Data for NMR spectra were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration.

The propargyl bromides **2b** and **2p** were purchased from Energy Chemical. The compounds, including **2a**,[1] **2c**,[2-4] **2d**,[2-4] **2e**,[2-4] **2f**,[5] **2g**,[2-4] **2h**,[2-4] **2i**,[5] **2j**,[2-4] **2k**,[2-4] **2n**,[6] **2o**[6], **1a**,[7] **1f**,[7] **1g**,[7] **1m**,[8] and **1o-COOH**,[9] were known and prepared according to the known literature.



**General Procedure for Preparation of 2l and 2m**



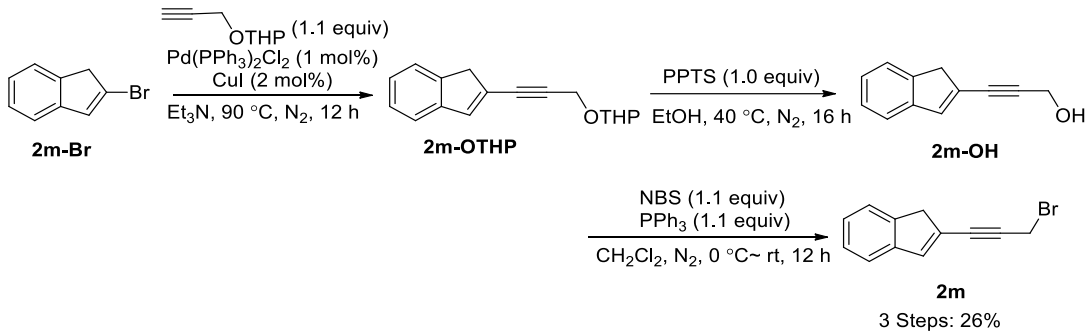

**Typical Procedure 1:** To a dried flask with condenser were added $Pd_2(PPh_3)_2Cl_2$ (0.0945 g, 0.13 mmol), CuI (0.0385 g, 0.20 mmol), 6-Bromoquinoline **2l-Br** (2.0503 g, 9.86 mmol), $Et_3N$ (30 mL), and tetrahydro-2-(2-propynyloxy)-2*H*-pyran (1.50 mL, *d* = 0.997 g/mL, 10.7 mmol) under $N_2$. The resulting solutions were then warmed to 90 ℃ for 13 h. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered through celite. Evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) afforded **2l-OTHP** (2.4304 g), which was used for next step directly.

To a solution of **2l-OTHP** (2.4302 g, 9.10 mmol) in ethanol (36 mL) was added pyridinium *p*-toluenesulfonate (2.1485 g, 8.56 mmol). The resulting mixture was stirred at 55 °C for 13 h. Evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1 to 2/1) afford **2l-OH** (0.3563 g), which was used for next step directly.

To a flask were added **2l-OH** (0.3563 g, 1.95 mmol), NBS (0.3815 g, 2.14 mmol), DCM (9 mL), and a solution of $PPh_3$ (0.5582g, 2.13 mmol) in DCM (5 mL) at 0 °C. The resulting mixture was allowed to warm up to rt and stirred for 22 h. Evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1) to afford **2l** (0.1057 g, 4% for 3 steps): Pink solid. mp. 84.7-85.3 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, $J_1$ = 4.3 Hz, $J_2$ = 1.6 Hz, 1 H, Ar-H), 8.09 (d, $J$ = 7.9 Hz, 1 H, Ar-H), 8.04 (d, $J$ = 8.7 Hz, 1 H, Ar-H), 7.93 (d, $J$ = 1.5 Hz, 1 H, Ar-H), 7.70 (dd, $J_1$ = 8.7 Hz, $J_2$ = 1.8 Hz, 1 H, Ar-H), 7.41 (dd, $J_1$ = 8.3 Hz, $J_2$ = 4.3 Hz, 1 H), 4.20 (s, 2 H, $CH_2$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.1, 147.6, 135.8, 132.0, 131.7,

129.5, 127.8, 121.8, 120.4, 86.1, 85.4, 15.0. IR ν (neat, $cm^{-1}$) 2989, 2937, 2214, 1587, 1566, 1493, 1424. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_9BrN$ 245.9913; found 245.9901.

**2m** was prepared according to Typical Procedure 1.

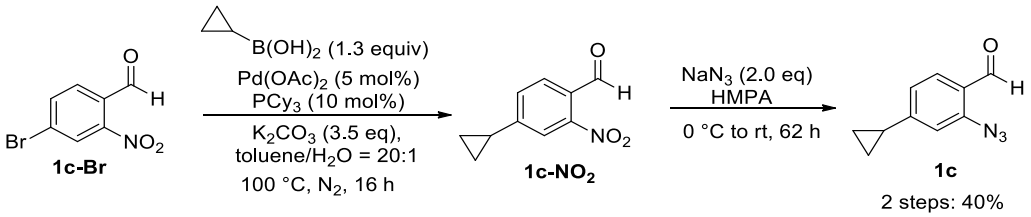



The reaction of **2o-Br** (1.5698 g, 8.05 mmol), $Pd_2(PPh_3)_2Cl_2$ (0.0703 g, 0.10 mmol), CuI (0.0304 g, 0.20 mmol), and tetrahydro-2-(2-propynyloxy)-2*H*-pyran (1.23 mL, *d* = 0.997 g/mL, 1.232 g, 8.8 mmol) in $Et_3N$ (24 mL) afforded **2o-OTHP** (1.9429 g) (eluent: petroleum ether/ethyl acetate = 15/1), which was used for next step directly.

The reaction of **2o-OTHP** (1.9429 g, 7.65 mmol) and pyridinium p-toluenesulfonate (1.9200 g, 7.65 mmol) in EtOH (30 mL) afforded **2o-OH** (1.0543 g) (eluent: petroleum ether/ethyl acetate = 8/1 to 4/1), which was used for next step directly.

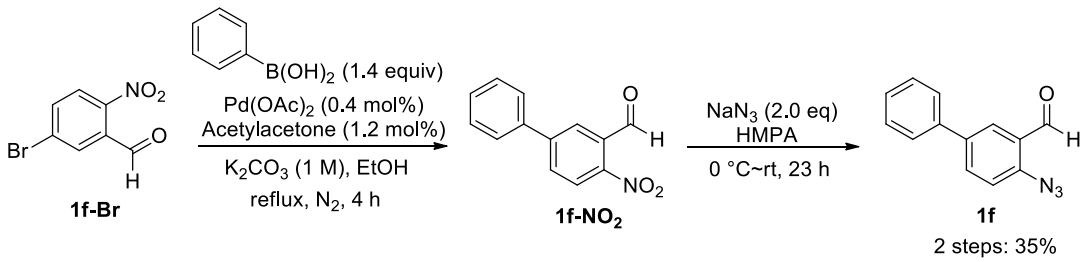
The reaction of **2o-OH** (1.0500 g, 6.18 mmol), NBS (1.2167 g, 6.84 mmol), and $PPh_3$ (1.7868 g, 6.82 mmol) in DCM (25 mL) afforded **2o** (0.3731 g, 26% for 3 steps) (eluent: petroleum ether/ethyl acetate = 30/1 for the first round and petroleum ether/ethyl acetate = 50/1 for second round): yellow solid. mp. 53.8-55.7 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, $J_1$ = 12.7 Hz, $J_2$ = 7.1 Hz, 2 H, Ar-H), 7.30 (t, *J* = 6.9 Hz, 1 H, Ar-H), 7.28-7.23 (m, 1 H, Ar-H), 7.13(s, 1 H), 4.20 (s, 2 H, $CH_2$), 3.53 (s, 2 H, $CH_2$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.6, 142.9, 138.8, 126.8, 126.1, 126.0, 123.6, 121.6, 88.8, 84.0, 42.4, 15.7. IR ν (neat, $cm^{-1}$) 3067, 2919, 2222, 2202, 1458, 1388, 1201. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{10}Br$ 232.9960; found 232.9958.

**General Procedure for Preparation of 2-Azidoaryl Aldehydes**



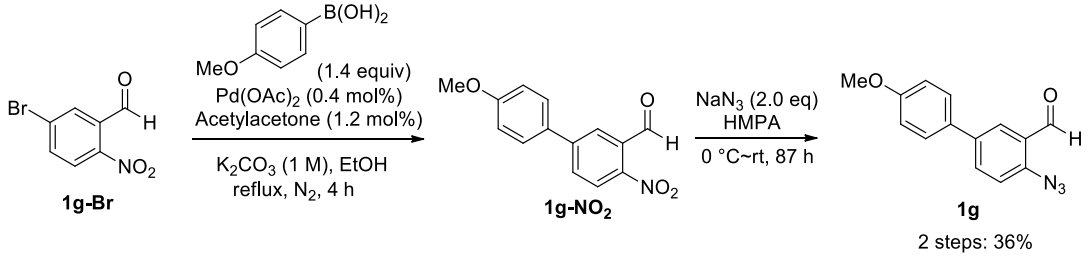

To an oven-dried flask were added **1c-Br** (0.7008 g, 3.04 mmol), cyclopropylboronic acid (0.3411 g, 3.96 mmol), $K_3PO_4$ (2.2590 g, 10.65 mmol), toluene (14 mL), $H_2O$ (0.7 mL), a solution of $PCy_3$ (0.0855 g, 0.30 mmol) in toluene (0.4 mL), and $Pd(OAc)_2$ (0.0344 g, 0.15 mmol) under $N_2$. The resulting mixture was heated at 100 °C for 16 h and then cooled to rt. Evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded **1c-NO2** (0.4700 g) as a brown solid, which was used for next step directly.

**Typical Procedure 2:** To a stirring solution of **1c-NO2** (0.4700 g, 2.46 mmol) in HMPA (8 mL) was added $NaN_3$ (0.3203 g, 4.92 mmol) at 0 ℃. The resulting mixture was stirred at room temperature for 13 h, then poured over ice, and extracted with DCM (20 mL × 3). The organic layer was washed with $H_2O$ (50 mL × 2), brine (15 mL), and dried over anhydrous $Na_2SO_4$. Filtration, evaporation, and flash chromatography on silica gel afforded **1c** (0.2298 g, 40% for 2 steps) (eluent: petroleum ether/ethyl acetate = 50/1 to 20/1): white solid. mp: 68.7-69.7 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1 H, CHO), 7.76 (d, *J* = 8.1 Hz, 1 H, Ar-H), 6.92 (s, 1 H, Ar-H), 6.85 (d, *J* = 8.1 Hz, 1 H, Ar-H), 2.03-1.89 (m, 1 H, CH), 1.18-1.06 (m, 2 H, $CH_2$), 0.88-0.75 (m, 2 H, $CH_2$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.1, 153.6, 142.8, 129.1, 124.7, 121.8, 115.9, 16.1, 10.7. IR (neat, $cm^{-1}$) 3008, 2119, 1682, 1600, 1566, 1432, 1395, 1316, 1280, 1208. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{10}H_{10}NO$ 160.0757; found 160.0746.



To an oven-dried flask were added **1f-Br** (0.4995 g, 2.17 mmol), EtOH (3 mL), $K_2CO_3$ (1.0 M aqueous solution, 3 mL, 3.00 mmol), phenylboronic acid (0.3715 g, 3.04 mmol), $Pd(OAc)_2$ (0.0021 g, 0.0087 mmol), and acetylacetone (2.7 μL, $d$ = 0.975 g/mL, 2.6 mg) under $N_2$. The resulting mixture was heated to reflux for 28 h and then cooled to rt. $H_2O$ (10 mL) was added and the aqueous layer was extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with $H_2O$ (30 mL) and dried over anhydrous $Na_2SO_4$. Evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 22/1 to 20/1) afforded **1f-NO2** (0.2673 g) as an ocher solid, which was used for next step directly.

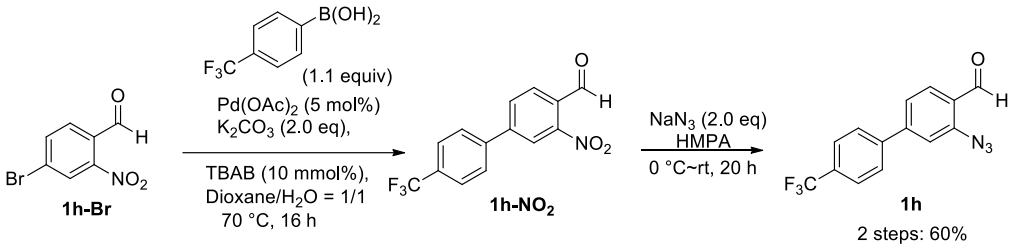
Following Typical Procedure 2, the reaction of **1f-NO2** (0.2673 g, 1.17 mmol), and $NaN_3$ (0.1544 g, 2.36 mmol) in HMPA (8.0 mL) afforded **1f** (0.1696 g, 35% for two steps) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 86.6-87.3 °C (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1 H, CHO), 8.12 (s, 1 H, Ar-H), 7.86 (d, $J$ = 8.3 Hz, 1 H, Ar-H), 7.59 (d, $J$ = 7.4 Hz, 2 H, Ar-H), 7.46 (t, $J$ = 7.4 Hz, 2 H, Ar-H), 7.32-7.42 (m, 2 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.6, 141.9, 138.8, 138.0, 133.8, 129.0, 128.0, 127.2, 127.1, 126.8, 119.6. IR (neat, cm$^{-1}$) 2922, 2852, 2125, 1684, 1477, 1456. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{13}H_{10}NO$ 196.0757; found 196.0743.




To an oven-dried flask were added **1g-Br** (0.5005 g, 2.17 mmol), methoxyphenylboronic acid (0.4683 g, 3.04 mmol), $Pd(OAc)_2$ (0.0022 g, 0.0087 mmol), acetylacetone (2.7 μL, $d$ = 0.975 g/mL, 2.6 mg), and $K_2CO_3$ (1.0 M aqueous solution, 3 mL, 3.0 mmol) under $N_2$. The resulting mixture was heated to reflux for 4 h and then cooled to rt. $H_2O$ (10 mL) was added and the aqueous layer was extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with $H_2O$ (30 mL) and dried over anhydrous $Na_2SO_4$. Evaporation and flash chromatography on silica gel

(eluent: petroleum ether/ethyl acetate = 30/1 to 14/1) afforded **1g-NO2** (0.3221 g) as an tan solid, which was used for next step directly.

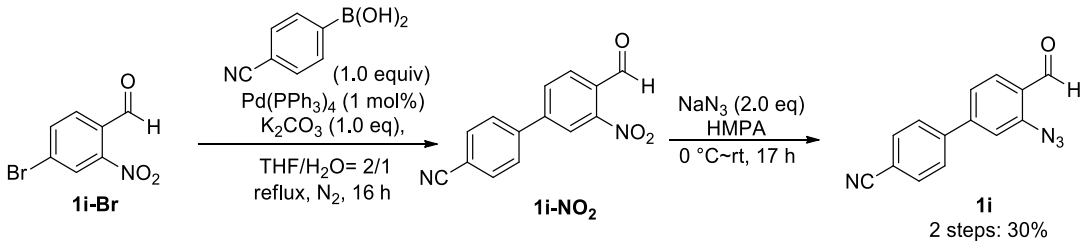
Following Typical Procedure 2, the reaction of **1g-NO2** (0.3221 g, 1.25 mmol), and $NaN_3$ (0.1650 g, 2.51 mmol) in HMPA (8.0 mL) afforded **1g** (0.1960 g, 36% for two steps) (eluent: petroleum ether/ethyl acetate = 10/1): light yellow solid. mp: 89.2-90.3 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1 H, CHO), 8.07 (d, $J$ = 2.2 Hz, 1 H, Ar-H), 7.81 (dd, $J_1$ = 8.0 Hz, $J_2$ = 2.3 Hz, 1 H, Ar-H), 7.56-7.51 (m, 2 H, Ar-H), 7.33 (d, $J$ = 8.4 Hz, 1 H, Ar-H), 7.02-6.96 (m, 2 H, Ar-H), 3.86 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.6, 159.6, 141.2, 137.7, 133.4, 131.2, 127.9, 127.0, 126.6, 119.5, 114.4, 55.3. IR (neat, cm$^{-1}$) 2923, 2127, 1684, 1481, 1457, 1247. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{14}H_{12}NO_2$ 226.0863; found 226.0851.




To an oven-dried flask were added **1h-Br** (0.5000 g, 2.17 mmol), $Pd(OAc)_2$ (0.0246 g, 0.11 mmol), 4-trifluoromethylphenylboronic acid (0.4542 g, 2.39 mmol), TBAB (0.7005 g, 2.17 mmol), $K_2CO_3$ (0.7509 g, 5.43 mmol), 1,4-dioxane (3.5 mL), and $H_2O$ (3.5 mL) under $N_2$. The resulting mixture was heated to 70 ℃ for 16 h and then cooled to rt. The aqueous layer was extracted with ethyl acetate (EA) (50 mL × 2) and dried over anhydrous $MgSO_4$. Evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1) afforded **1h-NO2** (0.4725 g) as a light green solid solid, which was used for next step directly.

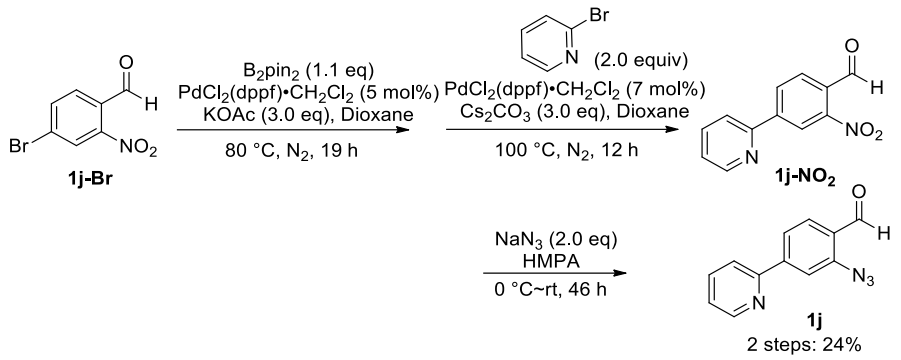
Following Typical Procedure 2, the reaction of **1h-NO2** (0.4725 g, 1.60 mmol), and $NaN_3$ (0.2095 g, 3.20 mmol) in HMPA (5.0 mL) afforded **1h** (0.3811 g, 60% for two steps). (eluent: petroleum ether/ethyl acetate = 10/1): white solid. mp: 109.4-110.2 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1 H, CHO), 7.99 (d, $J$ = 8.0 Hz, 1 H, Ar-H), 7.75 (q, $J$ = 8.5 Hz, 4 H, Ar-H), 7.53-7.38 (m, 2 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.0, 146.9, 143.4, 142.4, 130.9 (q, $^2J_{C\text{-}F}$ = 33.3 Hz), 129.7, 127.7,

126.3, 126.1 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 124.0, 123.9 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz), 117.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.7. IR (neat, $cm^{-1}$) 2119, 1686, 1600, 1322, 1295, 1070. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{14}H_9F_3NO$ 264.0631; found 264.0626.




To an oven-dried flask were added **1i-Br** (0.5004 g, 2.17 mmol), *p*-cyanophenylboronic acid (0.3192 g, 2.17 mmol), $Pd(PPh_3)_4$ (0.0250 g, 0.0217 mmol), $K_2CO_3$ (0.3010 g, 2.17 mmol), THF (17 mL), and $H_2O$ (8.7 mL) under $N_2$. The resulting mixture was heated to reflux for 16 h and then cooled to rt. $H_2O$ (10 mL) was added and the aqueous layer was extracted with ethyl acetate (30 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$. Evaporation and flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1 to 5/1 to 2/1) afforded **1i-NO₂** (0.4599 g) as a white solid, which was used for next step directly.

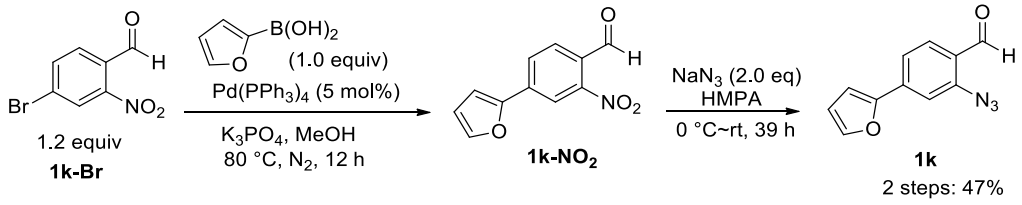
Following Typical Procedure 2, the reaction of **1i-NO₂** (0.4599 g, 1.83 mmol), and $NaN_3$ (0.2373 g, 3.65 mmol) in HMPA (5.0 mL) afforded **1i** (0.1638 g, 30% for two steps) (petroleum ether/ethyl acetate = 20/1 to 10/1 to 5/1): white solid. mp: 148.5-150.1 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1 H, CHO), 8.00 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.84-7.76 (m, 2 H, Ar-H), 7.76-7.68 (m, 2 H, Ar-H), 7.46-7.40 (m, 2 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.0, 146.2, 143.5, 143.3, 132.9, 130.0, 128.0, 126.5, 124.0, 118.3, 117.7, 112.6. IR (neat, $cm^{-1}$) 2120, 1684, 1634, 1603, 1396, 1264. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{14}H_9N_2O$ 221.0709; found 221.0697.




To an oven-dried flask were added **1j-Br** (1.0064 g, 4.35 mmol), Bis(pinacolato)diboron (1.2162 g, 4.78 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.1780 g, 0.22 mmol), KOAc (1.2795 g, 13.04 mmol), and 1,4-dioxane (16 mL) under $N_2$. The resulting mixture was heat to 80 ℃ for 16 h, cooled to rt, and concentrated.

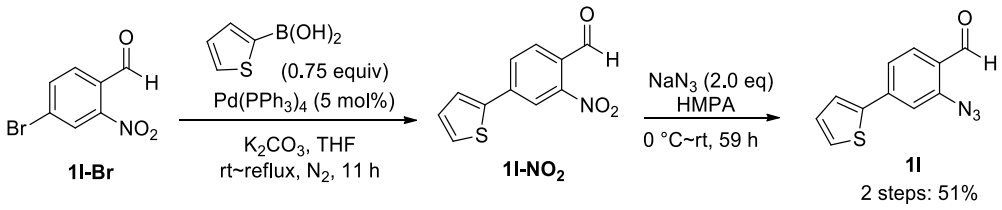
To the crude product afforded above were added $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.2485 g, 0.3 mmol), $Cs_2CO_3$ (4.2573 g, 13.0 mmol), 2-bromopyridine (0.83 mL, *d* = 1.657 g/mL, 8.7 mmol), and 1,4-dioxane (16 mL) under $N_2$. The resulting mixture was heated to 100 ℃ for 12 h and then cooled to rt. Filtration through celite, evaporation, and flash chromatography on silica gel afforded **1j-NO2** (0.4263 g) (eluent: petroleum ether/ethyl acetate = 10/1 to 5/1) as a yellow/green solid, which was used for next step directly.

Following Typical Procedure 2, the reaction of **1j-NO2** (0.4263 g, 1.87 mmol), and $NaN_3$ (0.2431 g, 3.74 mmol) in HMPA (8.0 mL) afforded **1j** (0.2365 g, 24% for two steps) (eluent: petroleum ether/ethyl acetate = 10/1 to 5/1): yellow solid. mp: 117.5-117.9 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1 H, CHO), 8.72 (d, *J* = 8.0 Hz, 1 H, Py), 8.00 (s, 1 H, Ar-H), 7.94 (d, *J* = 8.1 Hz, 1 H, Ar-H), 7.86-7.70 (m, 3 H, Ar-H), 7.35-7.29 (m, 1 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.3, 154.6, 149.9, 145.9, 143.4, 137.0, 129.3, 126.6, 123.6, 122.9, 121.0, 117.5. IR (neat, $cm^{-1}$) 2130, 1684, 1602, 1586, 1561, 1440, 1395, 1307, 1281, 1264. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{12}H_9N_2O$ 197.0709; found 197.0703.



To an oven-dried flask were added **1k-Br** (0.5029 g, 2.17 mmol), 2-furan boronic acid (0.2105 g, 1.81 mmol), $K_3PO_4$ (0.4618 g, 2.17 mol), $Pd(PPh_3)_4$ (0.1051 g, 0.0906 mmol), and MeOH (15 mL) under $N_2$. The resulting mixture was heated to 80 ℃ for 12 h, filtered through celite, and concentrated. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded **1k-NO₂** (0.2840 g) as a yellow solid, which was used for next step directly.

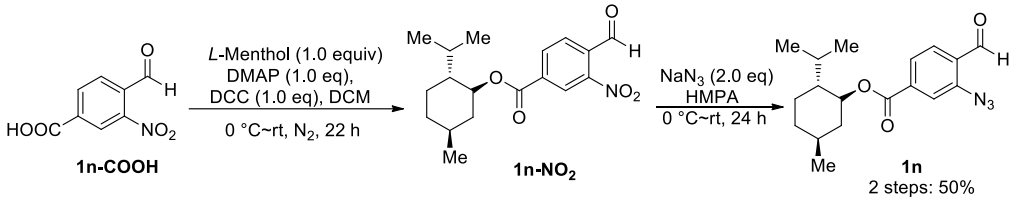
Following Typical Procedure 2, **1k-NO₂** (0.2840 g, 1.31 mmol), and $NaN_3$ (0.1720 g, 2.62 mmol) in HMPA (8.0 mL) afforded **1k** (0.2174 g, 47% for two steps) (eluent: petroleum ether/ethyl acetate = 20/1): light yellow solid. mp: 96.1-96.6 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1 H, CHO), 7.87 (d, *J* = 8.2 Hz, 1 H, Ar-H), 7.56 (s, 1 H, Ar-H), 7.50 (s, 1 H, Ar-H), 7.46 (d, *J* = 8.2 Hz, 1 H, Ar-H), 6.86 (s, 1 H, Ar-H), 6.54 (s, 1 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 187.8, 151.7, 144.0, 143.5, 137.1, 129.5, 125.3, 120.0, 113.3, 112.4, 108.9. IR (neat, $cm^{-1}$) 2880, 2110, 1690, 1601, 1393, 1262. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{11}H_8NO$ 186.0550; found 186.0541.




To an oven-dried flask were added **1l-Br** (0.4588 g, 1.99 mmol), THF (15 mL), and $Pd(PPh_3)_4$ (0.1154 g, 0.0997 mmol). After stirring at room temperature for 30 min under $N_2$, 2-thiopheneboronic acid (0.1918 g, 1.50 mmol) and $K_2CO_3$ (0.5506 g, 4.00 mmol) were added. The resulting mixture was stirred at room temperature for additional 30 min and was then heated to 80 ℃ for 11 h. Cooling, evaporation and fash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1) afforded **1l-NO₂** (0.3916 g) as a yellow solid, which was used for next step directly.

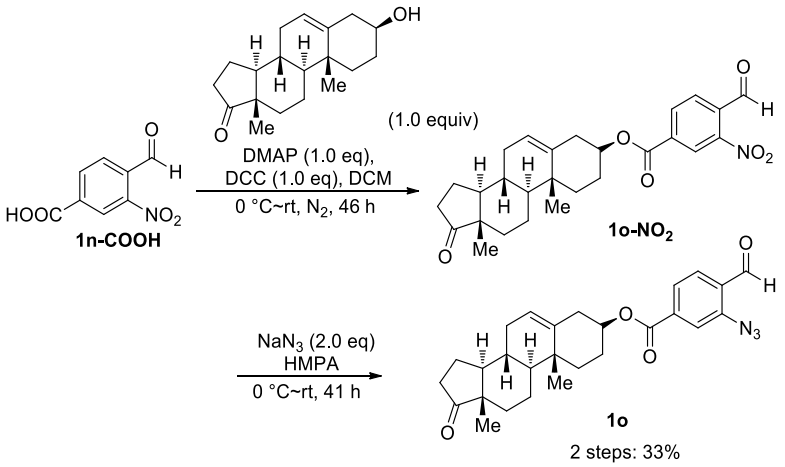
Following Typical Procedure 2, **1l-NO₂** (0.3916 g, 1.7 mmol), and $NaN_3$ (0.2189 g, 3.4 mmol) in HMPA (5.0 mL) afforded **1l** (0.2310 g, 51% for two steps) (eluent: petroleum ether/ethyl acetate = 10/1): yellow solid. mp: 107.4-108.0 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 1 H, CHO), 7.89 (d, *J* =

8.1 Hz, 1 H, Ar-H), 7.50-7.40 (m, 4 H, Ar-H), 7.15 (t, $J$ = 4.3 Hz, 1 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 187.8, 143.5, 141.7, 141.3, 129.7, 128.6, 127.5, 125.6, 122.3, 115.5. IR (neat, $cm^{-1}$) 2120, 1684, 1634, 1603, 1396, 1264. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{11}H_8NOS$ 202.0321; found 202.0312.



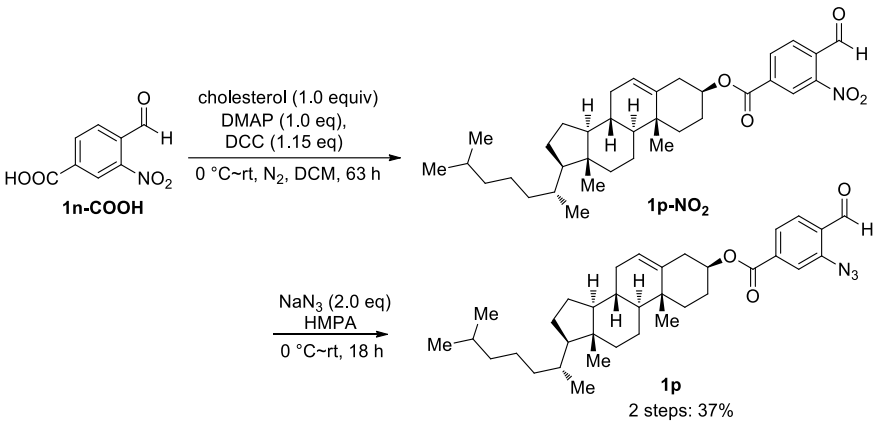

**Typical Procedure 3**: To an oven-dried flask were added **1n-COOH** (0.7427 g, 3.81 mmol), DMAP (0.4690 g, 3.81 mmol), (L)-menthol (0.5984 g, 3.81 mmol), DCM (20 mL), and DCC (0.7863 g, 3.81 mmol) at 0 ℃ under $N_2$. The resulting mixture was stirred at room temperature for 22 h and diluted with DCM (30 mL). The organic layer was washed with 10% HCl twice, $NaHCO_3$ saturated aqueous solution, and $H_2O$. The combined organic layer was dried over anhydrous $Na_2SO_4$, filtered, and evaporated. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded **1n-NO₂** (0.7693 g) as a yellow solid, which was used for next step directly.

Following Typical Procedure 2, the reaction of **1n-NO₂** (0.7693 g, 2.31 mmol), and $NaN_3$ (0.3009 g, 4.62 mmol) in HMPA (10.0 mL) afforded **1n** (0.6216 g, 50% for two steps) (eluent: petroleum ether/ethyl acetate = 50/1): white solid. mp: 89.0-89.7 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1 H, CHO), 7.96-7.91 (m, 2 H, Ar-H), 7.83 (d, $J$ = 8.1 Hz, 1 H, Ar-H), 4.97 (td, $J_1$ = 10.8, $J_2$ = 3.8 Hz, 1 H, CH), 2.11 (d, $J$ = 12.0 Hz, 1 H, CH), 1.97-1.84 (m, 1 H, CH), 1.74 (d, $J$ = 8.0 Hz, 2 H, $CH_2$), 1.58 (t, $J$ = 11.0 Hz, 2 H, $CH_2$), 1.14 (q, $J$ = 11.8 Hz, 2 H, $CH_2$), 0.98-0.87 (m, 7 H, $CH_3$ × 2 and CH), 0.80 (d, $J$ = 8.0 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.1, 164.3, 143.0, 136.9, 129.2, 129.0, 125.5, 120.2, 76.1, 47.1, 40.8, 34.2, 31.4, 26.6, 23.6, 22.0, 20.7, 16.5. IR (neat, $cm^{-1}$) 2955, 2928, 2869, 2125, 1721, 1697, 1572, 1290. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{18}H_{24}NO_3$ 302.1751; found 302.1745.




Following Typical Procedure 3, the reaction of **1n-COOH** (0.6776 g, 3.47 mmol), DMAP (0.4274 g, 3.47 mmol), dehydroepiandrosterone (1.0000 g, 3.47 mmol), and DCC (0.7160 g, 3.47 mmol) in DCM (20 mL) afforded **1o-$NO_2$** (0.8553 g) (eluent: petroleum ether/ethyl acetate = 5/1 to 2/1) as a yellow solid, which was used for next step directly.

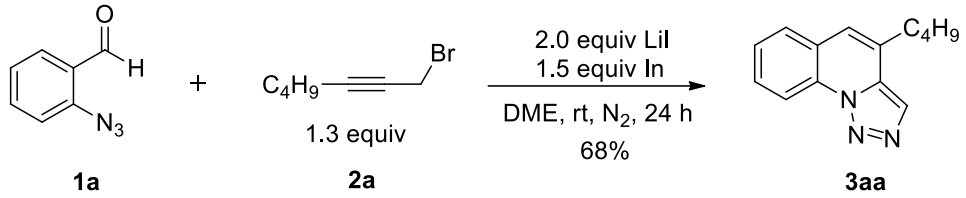
Following Typical Procedure 2, the reaction of **1o-$NO_2$** (0.8553 g, 1.84 mmol), and $NaN_3$ (0.2397 g, 3.67 mmol) in HMPA (10.0 mL) afforded **1o** (0.5226 g, 33% for two steps) (eluent: petroleum ether/ethyl acetate = 5/1): white solid. mp: 151.8-152.9 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1 H, CHO), 7.97-7.90 (m, 2 H, Ar-H), 7.85 (d, *J* = 8.4 Hz, 1 H, Ar-H), 5.47 (d, *J* = 4.5 Hz, 1 H, CH), 4.99-4.77 (m, 1 H, CH), 2.57-2.41 (m, 3 H, $CH_3$), 2.22-1.66 (m, 11 H), 1.61-1.46 (m, 2 H, $CH_2$), 1.36-1.26 (m, 3 H, $CH_3$), 1.11 (s, 3 H, $CH_3$), 0.90 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.1, 164.1, 143.0, 139.5, 136.8, 129.2, 129.0, 125.5, 122.3, 120.2, 75.5, 51.6, 50.1, 47.5, 38.0, 36.8, 36.7, 35.8, 31.4, 31.3, 30.7, 27.7, 21.8, 20.3, 19.3, 13.5. IR (neat, $cm^{-1}$) 2945, 2856, 2126, 1737, 1694, 1571, 1488, 1412, 1272. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{27}H_{32}NO_4$ 434.2326; found 434.2319.



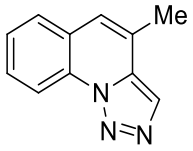

Following Typical Procedure 3, the reaction of **1n-COOH** (0.7092 g, 3.64 mmol), DMAP (0.4436 g, 3.64 mmol), Cholesterol (1.4092 g, 3.64 mmol), and DCC (0.8664 g, 4.18 mmol) in DCM (20 mL) afforded **1p-NO2** (0.8749 g) (eluent: petroleum ether/ethyl acetate = 20/1) as a yellow solid, which was used for next step directly.

Following Typical Procedure 2, the reaction of **1p-NO2** (0.8749 g, 1.55 mmol), and $NaN_3$ (0.2017 g, 3.10 mmol) in HMPA (8 mL) afforded **1p** (0.7620 g, 37% for two steps) (eluent: petroleum ether/ethyl acetate = 20/1): white powder solid. mp: 129.4-131.6 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1 H, CHO), 7.95-7.93 (m, 1 H, Ar-H), 7.93 (s, 1 H, Ar-H), 7.85 (d, *J* = 8.2 Hz, 1 H, Ar-H), 5.43 (d, *J* = 4.7 Hz, 1 H), 4.98-4.81 (m, 1 H, CH), 2.52-2.44 (m, 2 H, $CH_2$), 2.06-1.90 (m, 4 H), 1.90-1.70 (m, 2 H, $CH_2$), 1.63-1.56 (m, 1 H, CH), 1.55-1.42 (m, 4 H), 1.41-1.30 (m, 3 H), 1.27-0.90 (m, 14 H), 0.92 (d, *J* = 8.0 Hz, 3 H, $CH_3$), 0.86 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 7 H), 0.69 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.2, 164.1 143.0, 139.2, 136.9, 129.2, 129.0, 125.6, 123.1, 120.2, 75.8, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.0, 36.9, 36.6, 36.1, 35.8, 31.9, 31.8, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.8. IR (neat, $cm^{-1}$) 2935, 2866, 2125, 1721, 1695, 1572, 1467, 1413, 1289. HRMS (ESI) m/z: $[M+H-N_2]^+$ Calcd for $C_{35}H_{50}NO_3$ 532.3785; found 532.3786.

**Synthesis of [1,2,3]Triazolo-[1,5-*a*]Quinolines**



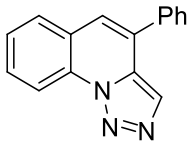

**Typical Procedure 4:** To a Schlenk tube were added In powder (0.0865 g, 0.75 mmol), LiI (0.1348 g, 1.01 mmol), and a premixed solution of **1a** (0.0738 g, 0.50 mmol) and **2a** (0.1139 g, 0.65 mmol) in DME (5 mL). The resulting mixture was stirred at room temperature for 24 h. Filtration through celite, evaporation, and flash chromatography on silica gel afforded **3aa** (0.0763 g, 68%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 104.1-105.6 ℃ (DCM/Hexane). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.12 (s, 1 H, Ar-H), 7.79 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.70 (t, *J* = 7.2 Hz, 1 H, Ar-H), 7.58 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.29 (s, 1 H, Ar-H), 2.90 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 1.86-1.70 (m, 2 H, $CH_2$), 1.55-1.38 (m, 2 H, $CH_2$), 0.98 (t, *J* = 7.4 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.1, 130.7, 129.7, 128.9, 127.9, 127.0, 126.5, 124.4, 123.6, 116.1, 32.2, 30.8, 22.4, 13.8. IR ν (neat, $cm^{-1}$) 2952, 1613, 1541, 1460, 1451, 1471, 1203. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}N_3$ 226.1339; found 226.1331.




**3ab**

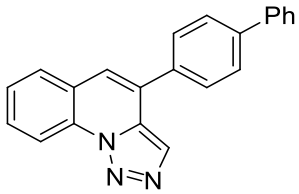
Following Typical Procedure 5, the reaction of In powder (0.0873 g, 0.76 mmol), LiI (0.1343 g, 1.00 mmol), **1a** (0.0738 g, 0.50 mmol), and **2b** (57 μL, *d* = 1.519 g/mL, 0.65 mmol) in DME (5 mL) afforded **3ab** (0.0580 g, 63%) (eluent: petroleum ether/ethyl acetate = 10/1 to 5/1 to 3/1): yellow solid. mp: 177.6-178.7 ℃ (DCM/Hexane). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.75 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.68 (t, *J* = 7.7 Hz, 1 H, Ar-H), 7.56 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.25 (s, 1 H, Ar-H), 2.56 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.5, 130.6, 128.9, 127.7, 127.0, 126.6, 124.9, 124.6, 124.5, 116.2, 18.2. IR ν (neat, $cm^{-1}$) 2954, 1616, 1468, 1432, 1265. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}N_3$ 184.0869;

found 184.0859.



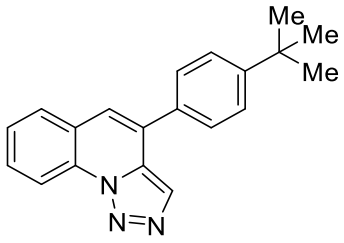

**3ac**

Following Typical Procedure 4, the reaction of In powder (0.0865 g, 0.75 mmol), LiI (0.1349 g, 1.01 mmol), **1a** (0.0738 g, 0.50 mmol), and **2c** (0.1279 g, 0.66 mmol) in DME (5 mL) afforded **3ac** (0.0785 g, 64%) (eluent: petroleum ether/ethyl acetate = 30/1 to 20/1): yellow solid. mp: 127.9-128.5 ℃ (DCM/Hexane). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.4 Hz, 1 H, Ar-H), 8.21 (s, 1 H, Ar-H), 7.87 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.77-7.68 (m, 3 H, Ar-H), 7.65-7.45 (m, 5 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 136.7, 132.1, 130.9, 129.7, 129.6, 129.2, 129.1, 128.5, 127.9, 127.7, 127.3, 124.6, 124.3, 116.3. IR ν (neat, $cm^{-1}$) 2922, 2853, 1607, 1458, 1376. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}N_3$ 246.1026; found 246.1019.



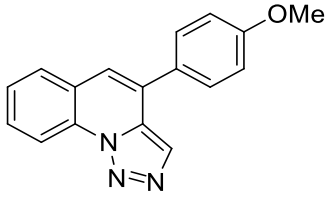

**3ad**

Following Typical Procedure 4, the reaction of In powder (0.0873 g, 0.76 mmol), LiI (0.1343 g, 1.00 mmol), **1a** (0.0734 g, 0.50 mmol), and **2d** (0.1767 g, 0.65 mmol) in DME (5 mL) afforded **3ad** (0.0701g, 63%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1 to 5/1): yellow solid. mp: 116.2-117.8 ℃ (DCM/Hexane). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.27 (s, 1 H, Ar-H), 7.88 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.82-7.71 (m, 5 H, Ar-H), 7.67 (d, *J* = 7.4 Hz, 2 H, Ar-H), 7.64-7.55 (m, 2 H, Ar-H), 7.49 (t, *J* = 7.4 Hz, 2 H, Ar-H), 7.40 (t, *J* = 7.1 Hz, 1 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.9, 140.1, 135.5, 132.0, 130.9, 129.7, 129.1, 128.9, 128.5, 128.1, 127.9, 127.79, 127.75, 127.3, 127.1, 124.5, 124.3, 116.3. IR ν (neat, $cm^{-1}$) 3037, 2923, 1607, 1487, 1408. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{16}N_3$ 322.1339; found 322.1330.



**3ae**

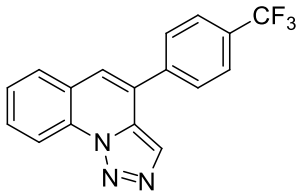
Following Typical Procedure 4, the reaction of In powder (0.0873 g, 0.76 mmol), LiI (0.1352 g, 1.01 mmol), **1a** (0.0736 g, 0.50 mmol), and **2e** (0.1894 g, 0.75 mmol) in DME (5 mL) afforded **3ae** (0.0859 g, 57%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1 to 5/1): yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.26 (s, 1 H, Ar-H), 7.89 (d, *J* = 7.7 Hz, 1 H, Ar-H), 7.76 (t, *J* = 7.2 Hz, 1 H, Ar-H), 7.68 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.62 (d, *J* = 7.3 Hz, 1 H, Ar-H), 7.60-7.52 (m, 3 H, Ar-H), 1.41 (s, 9 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.3, 133.7, 132.1, 130.8, 129.53, 129.45, 128.5, 128.0, 127.4, 127.2, 126.1, 124.4, 124.2, 116.2, 34.8, 31.3. IR ν (neat, $cm^{-1}$) 2959, 2924, 1607, 1458, 1363. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}N_3$ 302.1652; found 302.1652.



**3af**

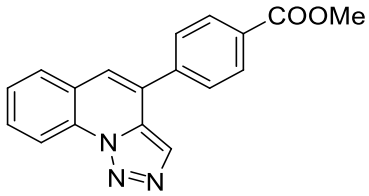
Following Typical Procedure 4, the reaction of In powder (0.0865 g, 0.75 mmol), LiI (0.1344 g, 1.00 mmol), **1a** (0.0732 g, 0.50 mmol), and **2f** (0.1390 g, 0.62 mmol) in DME (5 mL) afforded **3af** (0.0794 g, 58%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1 to 5/1 to 3/1): yellow solid. mp: 146.1-147.8 ℃ (DCM/Hexane). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.20 (s, 1 H, Ar-H), 7.84 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.71 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.65 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.59 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.47 (s, 1 H, Ar-H), 7.06 (d, *J* = 8.7 Hz, 2 H, Ar-H), 3.89 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 160.3, 132.2, 130.7, 129.4, 129.2, 129.03, 128.95, 128.4, 127.9, 127.2, 124.5, 123.7, 116.2, 114.5, 55.4. IR ν (neat, $cm^{-1}$) 2927,

1607, 1512, 1269, 1178, 1031. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}N_3O$ 276.1131; found 276.1126.



**3ag**

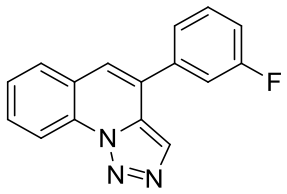
Following Typical Procedure 4, the reaction of In powder (0.0866 g, 0.75 mmol), LiI (0.1351 g, 1.01 mmol), **1a** (0.0731 g, 0.50 mmol), and **2g** (0.1727 g, 0.66 mmol) in DME (5 mL) afforded **3ag** (0.0932 g, 60%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 184.7-185.6 ℃ (DCM / Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, $J$ = 8.3 Hz, 1 H, Ar-H), 8.18 (s, 1 H, Ar-H), 7.90 (d, $J$ = 7.8 Hz, 1 H, Ar-H), 7.87-7.73 (m, 5 H, Ar-H), 7.63 (t, $J$ = 7.2 Hz, 1 H, Ar-H), 7.58 (s, 1 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.2, 131.5, 131.1, 131.0 (C-F, q, $^2J_{C\text{-}F}$ = 32.9 Hz), 130.3, 128.7, 128.1, 128.0, 127.6, 127.5, 126.2 (C-F, q, $^3J_{C\text{-}F}$ = 3.7 Hz), 125.5, 124.0, 123.9 (C-F, q, $^1J_{C\text{-}F}$ = 273.3 Hz), 116.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.6. IR ν (neat, $cm^{-1}$) 1608, 1413, 1331, 1174, 1101. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{11}F_3N_3$ 314.0900; found 314.0894.



**3ah**

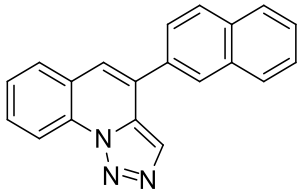
Following Typical Procedure 4, the reaction of In powder (0.0873 g, 0.76 mmol), LiI (0.1349 g, 1.01 mmol), **1a** (0.0739 g, 0.50 mmol), and **2h** (0.1643 g, 0.65 mmol) in DME (5 mL) at 60 ℃ afforded **3ah** (0.0609 g, 40%) (eluent: petroleum ether/ethyl acetate = 10/1 to 4/1 to 2/1): yellow solid. mp: 197.1-198.2 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, $J$ = 8.3 Hz, 1 H, Ar-H), 8.25-8.13 (m, 3 H, Ar-H), 7.87 (d, $J$ = 7.9 Hz, 1 H, Ar-H), 7.81-7.71 (m, 3 H, Ar-H), 7.65-7.53 (m, 2 H, Ar-H), 3.96 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.4, 140.9, 131.5, 131.0, 130.5, 130.4, 130.2, 128.7, 128.4, 127.7, 127.4, 125.3, 124.0, 116.3, 52.3. IR ν (neat, $cm^{-1}$)

2951, 1725, 1608, 1432, 1282, 1105. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}N_3O_2$ 304.1081; found 304.1079.



**3ai**

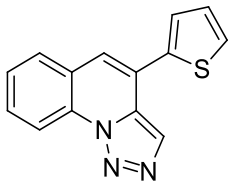
Following Typical Procedure 4, the reaction of In powder (0.0863 g, 0.75 mmol), LiI (0.1349 g, 1.01 mmol), **1a** (0.0738 g, 0.50 mmol), and **2i** (0.1394 g, 0.65 mmol) in DME (5 mL) afforded **3ai** (0.0643 g, 49%) (eluent: petroleum ether/ethyl acetate = 30/1 to 10/1 to 5/1): yellow solid. mp: 176.7-177.7 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.22 (s, 1 H, Ar-H), 7.91 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.79 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.64 (t, *J* = 7.2 Hz, 1 H, Ar-H), 7.57 (s, 1 H, Ar-H), 7.55-7.50 (m, 2 H, Ar-H), 7.43 (d, *J* = 9.6 Hz, 1 H, Ar-H), 7.24-7.16 (m, 1 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, $^1J_{C\text{-}F}$ = 247.5 Hz), 138.71 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 131.7, 131.0, 130.8 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 130.1, 128.6, 128.2 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 127.7, 127.4, 125.0, 124.0, 123.4 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 116.3, 116.0 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 114.8 (d, $^2J_{C\text{-}F}$ = 22.5 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.6. IR ν (neat, $cm^{-1}$) 2923, 2853, 1614, 1463, 1242, 1209. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{11}FN_3$ 264.0932; found 264.0920.



**3aj**

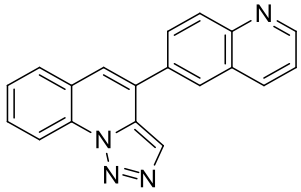
Following Typical Procedure 4, the reaction of In powder (0.0863 g, 0.75 mmol), LiI (0.1340 g, 1.00 mmol), **1a** (0.0734 g, 0.50 mmol), and **2j** (0.1790 g, 0.73 mmol) in DME (5 mL) afforded **3aj** (0.1008 g, 68%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 138.6-140.7 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.30 (s, 1 H, Ar-H), 8.21 (s, 1 H, Ar-H), 8.03 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.98-7.91 (m, 3 H, Ar-H), 7.85-7.76 (m, 2 H, Ar-H), 7.70-7.62 (m, 2 H, Ar-H), 7.62-7.56 (m, 2 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.9, 133.30,

133.28, 132.1, 130.8, 129.7, 129.4, 128.9, 128.5, 128.2, 127.9, 127.7, 127.3, 127.0, 126.82, 126.80, 125.2, 124.8, 124.3, 116.2. IR ν (neat, $cm^{-1}$) 3054, 2922, 2851, 1559, 1465, 1273. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{14}N_3$ 296.1182; found 296.1174.



**3ak**

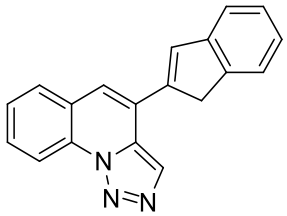
Following Typical Procedure 4, the reaction of In powder (0.0863 g, 0.75 mmol), LiI (0.1341 g, 1.00 mmol), **1a** (0.0730 g, 0.50 mmol), and **2k** (0.1310 g, 0.65 mmol) in DME (5 mL) afforded **3ak** (0.0610 g, 49%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 156.2-157.0 °C (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.40 (s, 1 H, Ar-H), 7.80 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.69 (t, *J* = 8.4 Hz, 1 H, Ar-H), 7.60 (s, 1 H, Ar-H), 7.58-7.52 (m, 2 H, Ar-H), 7.44 (d, *J* = 4.2 Hz, 1 H, Ar-H), 7.19 (dd, $J_1$ = 5.1 Hz, $J_2$ = 3.7 Hz, 1 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.5, 131.0, 130.7, 129.8, 128.4, 128.1, 128.0, 127.3, 126.5, 126.1, 123.9, 123.4, 122.6, 116.2. IR ν (neat, $cm^{-1}$) 2923, 2853, 1599, 1458, 1376, 1268. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{10}N_3S$ 252.0590; found 252.0583.



**3al**

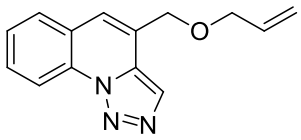
Following Typical Procedure 4, the reaction of In powder (0.0874 g, 0.76 mmol), LiI (0.1352 g, 1.01 mmol), **1a** (0.0734 g, 0.50 mmol), and **2l** (0.1650 g, 0.67 mmol) in DME (5 mL) afforded **3al** (0.0465 g, 31%) (eluent: petroleum ether/ethyl acetate = 5/1 to 2/1 to 1/2): yellow solid. mp: 195.5-199.1 °C (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 2.9 Hz, 1 H, Ar-H), 8.79 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.25 (t, *J* = 7.8 Hz, 3 H, Ar-H), 8.14 (s, 1 H, Ar-H), 8.02 (dd, $J_1$ = 8.7, $J_2$ = 1.6 Hz, 1 H, Ar-H), 7.89 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.75 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.68-7.56 (m, 2 H, Ar-H), 7.49 (dd, $J_1$ = 8.2, $J_2$ = 4.2 Hz, 1 H, Ar-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.2, 148.1, 136.3, 134.7, 131.9, 130.9, 130.5, 130.0, 128.9, 128.6, 128.3, 127.8, 127.4, 126.8,

125.3, 124.1, 121.9, 116.3. IR ν (neat, $cm^{-1}$) 2922, 2852, 1541, 1498, 1465, 1377. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{13}N_4$ 297.1135; found 297.1128.



**3am**

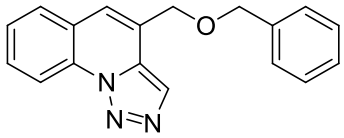
Following Typical Procedure 4, the reaction of In powder (0.0865 g, 0.75 mmol), LiI (0.1345 g, 1.00 mmol), **1a** (0.0734 g, 0.50 mmol), and **2m** (0.1603 g, 0.69 mmol) in DME (5 mL) afforded **3am** (0.0503 g, 36%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 211.4-213.1 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.44 (s, 1 H, Ar-H), 7.80 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.67 (t, *J* = 7.7 Hz, 1 H, Ar-H), 7.61-7.47 (m, 4 H, Ar-H), 7.45 (s, 1 H, Ar-H), 7.34 (t, *J* = 7.3 Hz, 1 H, Ar-H), 7.29 (d, *J* = 7.5 Hz, 1 H, Ar-H), 3.92 (s, 2 H, $CH_2$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.3, 141.2, 131.4, 130.8, 130.7, 129.8, 128.3, 127.9, 128.6, 125.6, 127.3, 127.0, 126.0, 124.3, 124.0, 123.7, 123.1, 121.8, 116.2, 39.5. IR ν (neat, $cm^{-1}$) 2922, 2853, 1605, 1458, 1377. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{14}N_3$ 284.1182; found 284.1169.



**3an**

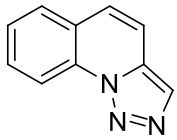
Following Typical Procedure 4, the reaction of In powder (0.0874 g, 0.76 mmol), LiI (0.1351 g, 1.01 mmol), **1a** (0.0739 g, 0.50 mmol), and **2n** (0.1311 g, 0.69 mmol) in DME (5 mL) afforded **3an** (0.0689 g, 58%) (eluent: petroleum ether/ethyl acetate = 10/1): orange oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.4 Hz, 1 H, Ar-H), 8.17 (s, 1 H, Ar-H), 7.80 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.71 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.57 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.47 (s, 1 H, Ar-H), 6.07-5.88 (m, 1 H, CH=), 5.34 (dd, $J_1$ = 17.2 Hz, $J_2$ = 1.5 Hz, 1 H, one proton of $CH_2$=), 5.25 (d, *J* = 10.4 Hz, 1 H, one proton of $CH_2$=), 4.75 (s, 2 H, $CH_2$), 4.11 (d, *J* = 5.6 Hz, 2 H, $CH_2$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.9, 131.2, 129.7, 128.3, 127.1, 126.7, 125.8, 124.0, 123.7, 117.9, 116.1,

71.5, 68.7. IR ν (neat, $cm^{-1}$) 2922, 2853, 1619, 1546, 1462. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}N_3O$ 240.1131; found 240.1124.



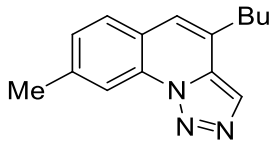
**3ao**

Following Typical Procedure 4, the reaction of In powder (0.0865 g, 0.75 mmol), LiI (0.1348 g, 1.01 mmol), **1a** (0.0735 g, 0.50 mmol), and **2o** (0.1603 g, 0.69 mmol) in DME (5 mL) afforded **3ao** (0.0613 g, 42%) (eluent: petroleum ether/ethyl acetate = 10/1 to 5/1): yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.18 (s, 1 H, Ar-H), 7.85 (d, *J* = 7.8 Hz,1 H, Ar-H), 7.76 (t, *J* = 7.2 Hz, 1 H, Ar-H), 7.61 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.53 (s, 1 H, Ar-H), 7.42-7.30 (m, 5 H, Ar-H), 4.81 (s, 2 H, $CH_2$), 4.66 (s, 2 H, $CH_2$). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 137.3, 131.2, 129.8, 128.5, 128.4, 128.0, 127.9, 127.1, 126.8, 125.8, 124.3, 123.7, 116.2, 72.7, 68.8. IR ν (neat, $cm^{-1}$) 3059, 2856, 1619, 1462, 1382. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}N_3O$ 290.1288; found 290.1280.



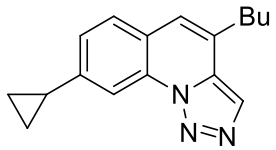
**3ap**

Following Typical Procedure 4, the reaction of In powder (0.0865 g, 0.75 mmol), LiI (0.1353 g, 1.01 mmol), **1a** (0.0738 g, 0.50 mmol), and **2p** (0.0779 g, 0.69 mmol) in DME (5 mL) afforded **3ap** (0.0186 g, 22 %). (petroleum ether/ethyl acetate = 10/1 to 3/1): yellow solid. mp: 73.5-74.7 °C (DCM/Hexane). $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.81 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.73 (t, *J* = 8.3 Hz, 1 H, Ar-H), 7.58 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.54-7.46 (m, 2 H, Ar-H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 131.8, 131.7, 130.0, 128.5, 127.6, 127.0, 126.6, 123.8, 116.2, 114.7. IR ν (neat, $cm^{-1}$) 3069, 1617, 1468, 1458, 1285. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_3$ 170.0713; found 170.0701.



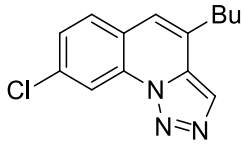

**3ba**

Following Typical Procedure 4, the reaction of **1b** (0.0809 g, 0.50 mmol), **2a** (0.1136 g, 0.65 mmol), In (0.0865 g, 0.75 mmol), and LiI (0.1346 g, 1.00 mmol) in DME (5 mL) afforded **3ba** (0.0635 g, 53%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 87.2-88.3 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.66 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.38 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.23 (s, 1 H, Ar-H), 2.94-2.80 (m, 2 H, $CH_2$), 2.59 (s, 3 H, $CH_3$), 1.72-1.79 (m, 2 H, $CH_2$), 1.39-1.48 (m, 2 H, $CH_2$), 0.97 (t, *J* = 7.2 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.7, 133.2, 130.6, 128.5, 128.5, 127.6, 126.3, 123.5, 122.2, 116.0, 32.1, 30.8, 22.4, 21.8, 13.8. IR (neat, $cm^{-1}$) 3057, 2954, 2927, 2859, 1626, 1540, 1468, 1456. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}N_3$ 240.1495; found 240.1489.



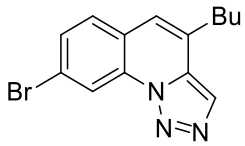

**3ca**

Following Typical Procedure 4, the reaction of **1c** (0.0938 g, 0.50 mmol), **2a** (0.1132 g, 0.65 mmol), In (0.0868 g, 0.75 mmol), and LiI (0.1365 g, 1.00 mmol) in DME (5 mL) afforded **3ca** (0.0479 g, 36%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 56.8-58.6 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.66 (d, *J* = 8.2 Hz, 1 H, Ar-H), 7.30 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.5 Hz, 1 H, Ar-H), 7.23 (s, 1 H, Ar-H), 2.87 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 2.16-2.10 (m, 1 H, CH), 1.80-1.73 (m, 2 H, $CH_2$), 1.49-1.39 (m, 2 H, $CH_2$), 1.16-1.10 (m, 2 H, $CH_2$), 0.97 (t, *J* = 7.3 Hz, 3 H, $CH_3$), 0.93-0.89 (m, 2 H, $CH_2$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 146.4, 133.3, 130.8, 128.3, 127.6, 126.4, 125.3, 123.5, 122.2, 112.2, 32.2, 30.9, 22.4, 16.0, 13.9, 10.5. IR (neat, $cm^{-1}$) 2952, 2927, 2867, 1625. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}N_3$ 266.1652; found 266.1646.



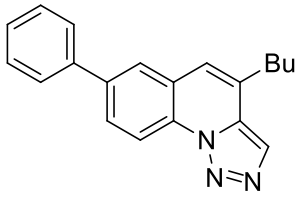

**3da**

Following Typical Procedure 4, the reaction of **1d** (0.0911 g, 0.50 mmol), **2a** (0.1137 g, 0.65 mmol), In (0.0866 g, 0.75 mmol), and LiI (0.1340 g, 1.00 mmol) in DME (5 mL) afforded **3da** (0.0572 g, 44%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): white solid. mp: 89.1-92.6 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, $J$ = 1.8 Hz, 1 H, Ar-H), 8.09 (s, 1 H, Ar-H), 7.67 (d, $J$ = 8.5 Hz, 1 H, Ar-H), 7.48 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1 H, Ar-H), 7.20 (s, 1 H, Ar-H), 2.85 (t, $J$ = 7.7 Hz, 2H), 1.72-1.79 (m, 2 H, $CH_2$), 1.48-1.39 (m, 2 H, $CH_2$), 0.97 (t, $J$ = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 134.8, 133.2, 130.9, 130.1, 129.0, 127.6, 126.6, 122.8, 122.8, 116.1, 32.2, 30.7, 22.4, 13.8. IR (neat, $cm^{-1}$) 2954, 2924, 2853, 1652, 1609, 1456. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}ClN_3$ 260.0949; found 260.0943.



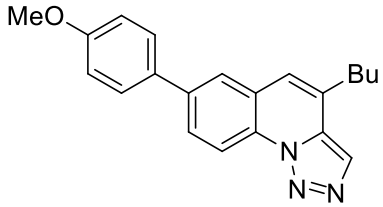

**3ea**

Following Typical Procedure 4, the reaction of **1e** (0.1132 g, 0.50 mmol), **2a** (0.1140 g, 0.65 mmol), In (0.0873 g, 0.75 mmol), and LiI (0.1351 g, 1.00 mmol) in DME (5 mL) afforded **3ea** (0.0685 g, 45%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): white solid. mp: 106.2-106.7 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 7.66-7.60 (m, 2 H, Ar-H), 7.20 (s, 1 H, Ar-H), 2.85 (t, $J$ = 7.7 Hz, 2 H, $CH_2$), 1.80-1.72 (m, 2 H, $CH_2$), 1.49-1.40 (m, 2 H, $CH_2$), 0.97 (t, $J$ = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.2, 131.1, 130.4, 130.3, 129.1, 126.7, 123.1, 122.9, 122.6, 119.2, 32.2, 30.7, 22.4, 13.8. IR (neat, $cm^{-1}$) 3099, 2957, 2930, 2867, 1606, 1558, 1463. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}BrN_3$ 304.0444; found 304.0439.




**3fa**

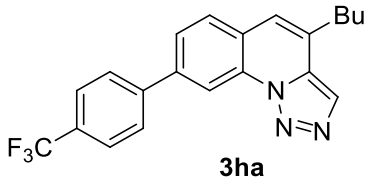
Following Typical Procedure 4, the reaction of **1f** (0.1114 g, 0.50 mmol), **2a** (0.1134 g, 0.65 mmol), In (0.0864 g, 0.75 mmol), and LiI (0.1348 g, 1.00 mmol) in DME (5 mL) afforded **3fa** (0.0806 g, 54 %) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 94.8-99.6 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.6 Hz, 1 H, Ar-H), 8.12 (s, 1 H, Ar-H), 8.00-7.87 (m, 2 H, Ar-H), 7.69 (d, *J* = 7.7 Hz, 2 H, Ar-H), 7.50 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.41 (t, *J* = 7.3 Hz, 1 H, Ar-H), 7.32 (s, 1 H, Ar-H), 2.90 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 1.83-1.76 (m, 2 H, $CH_2$), 1.51-1.42 (m, 2 H, $CH_2$), 0.99 (t, *J* = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.1, 139.8, 133.1, 130.1, 129.9, 129.0, 128.1, 127.9, 127.2, 126.6, 125.9, 124.8, 123.7, 116.6, 32.2, 30.8, 22.4, 13.8. IR (neat, $cm^{-1}$) 3060, 2955, 2929, 2869, 1652, 1577. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}N_3$ 302.1652; found 302.1647.




**3ga**

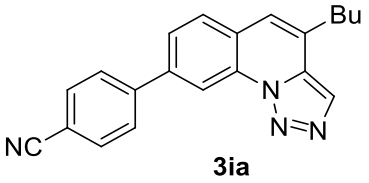
Following Typical Procedure 4, the reaction of **1g** (0.1269 g, 0.50 mmol), **2a** (0.1131 g, 0.65 mmol), In (0.0868 g, 0.75 mmol), and LiI (0.1364 g, 1.00 mmol) in DME (5 mL) afforded **3ga** (0.0907 g, 55 %) (eluent: petroleum ether/ethyl acetate = 20/1 to 5/1): yellow solid. mp: 125.5-126.4 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.6 Hz, 1 H, Ar-H), 8.12 (s, 1 H, Ar-H), 7.92-7.88 (m, *J* = 8.7 Hz, 2 H, Ar-H), 7.63 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.31 (s, 1 H, Ar-H), 7.04 (d, *J* = 8.0 Hz, 2 H, Ar-H), 3.88 (s, 3 H, OMe), 2.90 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 1.81-1.77 (m, 2 H, $CH_2$), 1.49-1.44 (m, 2 H, $CH_2$), 0.99 (t, *J* = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.6, 139.7, 133.0, 132.2, 130.0, 129.5, 128.3, 127.8, 126.5, 125.2, 124.8, 123.7, 116.5, 114.4,

55.4, 32.2, 30.8, 22.4, 13.8. IR (neat, $cm^{-1}$) 3043, 2953, 2930, 2868, 2832, 1606, 1516, 1473, 1248. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}N_3O$ 332.1757; found 332.1756.




**3ha**

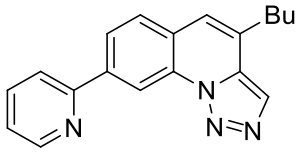
Following Typical Procedure 4, the reaction of **1h** (0.1454 g, 0.50 mmol), **2a** (0.1141 g, 0.65 mmol), In (0.0870 g, 0.75 mmol), and LiI (0.1346 g, 1.00 mmol) in DME (5 mL) afforded **3ha** (0.1035 g, 56%) (eluent: petroleum ether/ethyl acetate = 20/1 to 5/1): yellow solid. mp: 113.5-113.8 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1 H, Ar-H), 8.15 (s, 1 H, Ar-H), 7.88 (d, $J$ = 8.2 Hz, 3 H, Ar-H), 7.82 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1 H, Ar-H), 7.77 (d, $J$ = 8.2 Hz, 2 H, Ar-H), 7.31 (s, 1 H, Ar-H), 2.85 (t, $J$ = 7.7 Hz, 2 H, $CH_2$), 1.84-1.76 (m, 2 H, $CH_2$), 1.52-1.42(m, 2 H, $CH_2$), 0.97 (t, $J$ = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.0, 140.2, 133.3, 131.0, 130.3, 130.1 (q, $^2J_{C\text{-}F}$ = 33.3 Hz), 128.6, 127.7, 126.8, 125.9 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.09 (q, $^1J_{C\text{-}F}$ = 273.7 Hz), 124.08, 123.1, 114.4, 32.3, 30.8, 22.4, 13.8. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.5. IR (neat, $cm^{-1}$) 2959, 2932, 2873, 1615, 1325, 1123. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}F_3N_3$ 370.1526; found 370.1525.




**3ia**

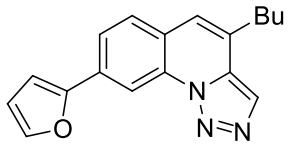
Following Typical Procedure 4, the reaction of **1i** (0.1244 g, 0.50 mmol), **2a** (0.1152 g, 0.65 mmol), In (0.0867 g, 0.75 mmol), and LiI (0.1362 g, 1.00 mmol) in DME (5 mL) afforded **3ia** (0.0860 g, 53%) (eluent: petroleum ether/ethyl acetate = 5/1 to 3/1): yellow solid. mp: 179.1-180.8 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1 H, Ar-H), 8.16 (s, 1 H, Ar-H), 7.94-7.83 (m, 3 H, Ar-H), 7.83-7.79 (m, 3 H, Ar-H), 7.32 (s, 1 H, Ar-H), 2.92 (t, $J$ = 7.3 Hz, 2 H, $CH_2$), 1.84-1.77 (m, 2 H, $CH_2$), 1.52-1.43(m, 2 H, $CH_2$), 1.00 (t, $J$ = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ

144.0, 139.7, 133.3, 132.8, 131.1, 130.8, 128.7, 128.0, 126.9, 125.9, 124.5, 123.1, 118.6, 114.6, 111.9, 32.3, 30.8, 22.4, 13.9. IR (neat, $cm^{-1}$) 2923, 2853, 2225, 1605, 1457, 1376. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}N_4$ 327.1604; found 327.1602.




**3ja**

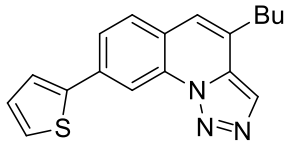
Following typical procedure 4, the reaction of **1j** (0.1116 g, 0.50 mmol), **2a** (0.1137 g, 0.65 mmol), In (0.0866 g, 0.75 mmol), and LiI (0.1352 g, 1.00 mmol) in DME (5 mL) afforded **3ja** (0.0791 g, 53 %) (eluent: petroleum ether/ethyl acetate = 10/1 to 2/1): light yellow solid. mp: 97.1-99.4 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1 H, Ar-H), 8.72 (ddd, $J_1$ = 4.6 Hz, $J_2$ = 1.6 Hz, $J_3$ = 0.8 Hz, 1 H, Ar-H), 8.32-8.27 (m, 1 H, Ar-H), 8.13 (s, 1 H, Ar-H), 7.96-7.91 (m, 1 H, Ar-H), 7.85-7.76 (m, 2 H, Ar-H), 7.29-7.20 (m, 2 H, Ar-H, included the residue $CHCl_3$), 2.85 (t, $J$ = 7.9 Hz, 2 H, $CH_2$), 1.80-1.70 (m, 2 H, $CH_2$), 1.48-1.36 (m, 2 H, $CH_2$), 0.94 (t, $J$ = 7.4 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.8, 149.9, 140.0, 137.0, 133.3, 131.0, 130.3, 128.3, 126.7, 125.7, 124.8, 123.3, 122.9, 121.0, 114.1, 32.3, 30.8, 22.5, 13.9. IR (neat, $cm^{-1}$) 2956, 2923, 2853, 1661, 1622, 1586, 1463. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_4$ 303.1604; found 303.1600.




**3ka**

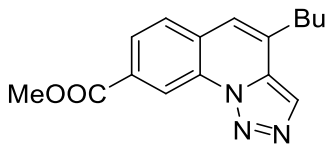
Following Typical Procedure 4, the reaction of **1k** (0.1064 g, 0.50 mmol), **2a** (0.1144 g, 0.65 mmol), In (0.0866 g, 0.75 mmol), and LiI (0.1350 g, 1.00 mmol) in DME (5 mL) afforded **3ka** (0.1001 g, 69 %) (eluent: petroleum ether/ethyl acetate = 10/1 to 5/1): yellow solid. mp: 116.0-116.7 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1 H, Ar-H), 8.07 (s, 1 H, Ar-H), 7.85-7.75 (m, 1 H, Ar-H), 7.69 (d, $J$ = 8.3 Hz,

1 H, Ar-H), 7.54 (d, $J$ = 1.0 Hz, 1 H, Ar-H), 7.18 (s, 1 H, Ar-H), 6.87 (d, $J$ = 2.9 Hz, 1 H, Ar-H), 6.53 (dd, $J_1$ = 3.4 Hz, $J_2$ = 1.8 Hz, 1 H, Ar-H), 2.82 (t, $J$ = 7.5 Hz, 2 H, $CH_2$), 1.78-1.70 (m, 2 H, $CH_2$), 1.48-1.38 (m, 2 H, $CH_2$), 0.97 (t, $J$ = 7.4 Hz, 2 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.7, 143.1, 133.3, 131.2, 130.9, 129.3, 128.2, 126.5, 123.2, 122.5, 112.1, 110.5, 107.2, 32.1, 30.7, 22.4, 13.8. IR (neat, $cm^{-1}$) 3161, 3090, 2961, 2929, 2867, 2355, 1623, 1557, 1504. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}N_3O$ 292.1444; found 292.1444.




**3la**

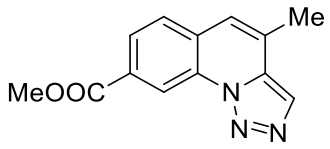
Following Typical Procedure 4, the reaction of **3l** (0.1146 g, 0.50 mmol), **2a** (0.1140 g, 0.65 mmol), In (0.0862 g, 0.75 mmol), and LiI (0.1347 g, 1.00 mmol) in DME (5 mL) afforded **3la** (0.0825 g, 54 %) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 88.8-89.4 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1 H, Ar-H), 8.10 (s, 1 H, Ar-H), 7.80-7.70 (m, 2 H, Ar-H), 7.54 (d, $J$ = 8.3 Hz, 1 H, Ar-H), 7.38 (d, $J$ = 1.0 Hz, 1 H, Ar-H), 7.22 (s, 1 H, Ar-H), 7.17-7.12 (m, 1 H, Ar-H), 2.86 (t, $J$ = 7.5 Hz, 2 H, $CH_2$), 1.81-1.68 (m, 2 H, $CH_2$), 1.51-1.38 (m, 2 H, $CH_2$), 0.98 (t, $J$ = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.8, 135.0, 133.3, 130.9, 129.4, 128.4, 128.3, 126.6, 126.2, 124.7, 124.5, 123.4, 123.2 112.3, 32.2, 30.8, 22.4, 13.8. IR (neat, $cm^{-1}$) 3106, 2955, 2928, 2868, 1621, 1565, 1445. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}N_3S$ 308.1216; found 308.1217.




**3ma**

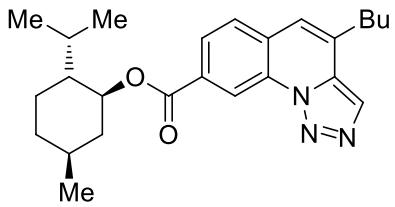
Following Typical Procedure 4, the reaction of **1m** (0.1027 g, 0.50 mmol), **2a** (0.1141 g, 0.65 mmol), In (0.0863 g, 0.75 mmol), and LiI (0.1342 g, 1.00 mmol) in DME (5

mL) afforded **3ma** (0.0927 g, 65%) (eluent: petroleum ether/ethyl acetate = 20/1 to 5/1): yellow solid. mp: 101.4-102.2 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, *J* = 4.0 Hz, 1 H, Ar-H), 8.20-8.14 (m, 1 H, Ar-H), 8.11 (s, 1 H, Ar-H), 7.80 (dd, $J_1$ = 8.3 Hz, $J_2$ = 2.1 Hz, 1 H, Ar-H), 7.23-7.21 (m, 1 H, Ar-H), 3.98 (s, 3 H, $CH_3$), 2.87 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 1.77-1.72 (m, 2 H, $CH_2$), 1.46-1.41 (m, 2 H, $CH_2$), 0.95 (t, *J* = 7.4 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.9, 133.1, 132.5, 130.2, 127.9, 127,6, 127.4, 127.0, 122.9, 117.8, 76.7, 52.5, 32.3, 30.7, 22.4, 13.8. IR (neat, $cm^{-1}$) 2954, 2931, 2870, 1723, 1485, 1290, 1271. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}N_3O_2$ 284.1394; found 284.1389.




**3mb**

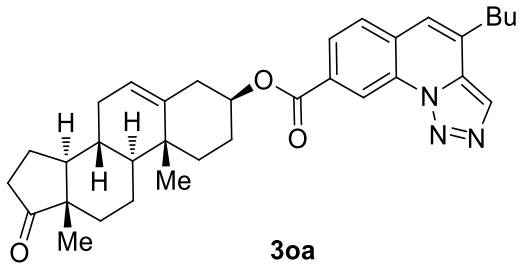
Following Typical Procedure 4, the reaction of **1m** (0.1030 g, 0.50 mmol), **2b** (0.0875 g, 0.65 mmol), In (0.0864 g, 0.75 mmol), and LiI (0.1346 g, 1.00 mmol) in DME (5 mL) afforded **3mb** (0.0702 mg, 58%) (eluent: petroleum ether/ethyl acetate = 10/1 to 2/1): yellow solid. mp: 101.4-102.2 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, CDCl3) δ 9.36 (s, 1 H, Ar-H), 8.17 (d, *J* = 8.3 Hz, 1 H, Ar-H), 8.11 (s, 1 H, Ar-H), 7.78 (d, *J* = 8.3 Hz, 1 H, Ar-H), 4.00 (s, 3 H, $CH_3$), 2.57 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, CDCl3) δ 165.9, 133.5, 130.2, 130.1, 127.8, 127.7, 127.6, 127.4, 127.1, 124.0, 117.8, 52.5, 18.3. IR (neat, $cm^{-1}$) 3032, 2944, 1721, 1613, 1435, 1274, 1260. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}N_3O_2$ 242.0924; found 242.0918.




**3na**

Following typical procedure 4, the reaction of **1n** (0.1653 g, 0.50 mmol), **2a** (0.1132 g, 0.65 mmol), In (0.0869 g, 0.75 mmol), and LiI (0.1350 g, 1.00 mmol) in DME (5

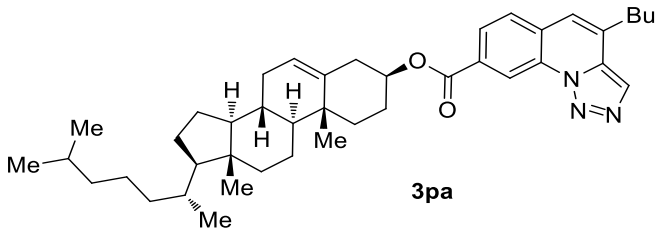
mL) afforded **3na** (0.1296 g, 63%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): bright yellow solid. mp: 94.3-96.9 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1 H, Ar-H), 8.21 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1 H, Ar-H), 8.15 (s, 1 H, Ar-H), 7.83 (d, $J$ = 8.3 Hz, 1 H, Ar-H), 7.30 (s, 1 H, Ar-H), 5.03 (td, $J_1$ = 12.0 Hz, $J_2$ = 4.4 Hz, 1 H, CH), 2.90 (t, $J$ = 7.6 Hz, 2 H, $CH_2$), 2.15 (d, $J$ = 11.7 Hz, 1 H, CH), 2.04-1.95 (m, 1 H, CH), 1.82-1.56 (m, 7 H), 1.50-1.41 (m, 2 H, $CH_2$), 1.22-1.08 (m, 2 H, $CH_2$), 1.00-0.90 (m, 10 H), 0.81 (d, $J$ = 6.9 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.0, 133.2, 132.3, 131.0, 130.2, 127.9, 127.5, 127.6, 127.0, 123.0, 117.6, 75.6, 47.0, 40.9, 34.2, 32.3, 31.5, 30.7, 26.4, 23.5, 22.4, 22.0, 20.8, 16.4, 13.8. IR (neat, $cm^{-1}$) 2955, 2928, 2869, 1714, 1446, 1270, 1258. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{34}N_3O_2$ 408.2646; found 408.2643.




**3oa**

Following typical procedure 4, the reaction of **1o** (0.2303 g, 0.50 mmol), **2a** (0.1141 g, 0.65 mmol), In (0.0867 g, 0.75 mmol), and LiI (0.1340 g, 1.00 mmol) in DME (5 mL) afforded **3oa** (0.1607 g, 60%) (eluent: petroleum ether/ethyl acetate = 5/1 to 2/1): light yellow solid. mp: 163.1-164.9 ℃ (hexane/chloroform). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1 H, Ar-H), 8.22 (d, $J$ = 8.2 Hz, 1 H, Ar-H), 8.15 (s, 1 H, Ar-H), 7.83 (d, $J$ = 8.3 Hz, 1 H, Ar-H), 7.30 (s, 1 H, Ar-H), 5.47 (d, $J$ = 4.9 Hz, 1 H), 5.00-4.91 (m, 1 H), 2.91 (t, $J$ = 7.6 Hz, 2 H, $CH_2$), 2.60-2.40 (m, 3 H, $CH_2$), 2.14-1.94 (m, 6 H), 1.88-1.72 (m, 4 H), 1.57-1.43 (m, 4 H), 1.33-1.28 (m, 3 H), 1.24 (s, 3 H, $CH_3$), 1.12 (s, 3 H, $CH_3$), 0.98 (t, $J$ = 7.3 Hz, 3 H, $CH_3$), 0.90 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.9, 139.8, 133.2, 132.4, 130.9, 130.2, 127.9, 127.6, 127.5, 127.0, 123.1, 122.1, 117.7, 75.1, 51.7, 50.1, 47.5, 38.1, 36.9, 36.8, 35.8, 32.3, 31.4, 31.4, 30.8, 30.7, 27.8, 22.4, 21.9, 20.3, 19.4, 14.1, 13.8, 13.5. IR (neat, $cm^{-1}$) 2932, 2856, 1737, 1715, 1441,

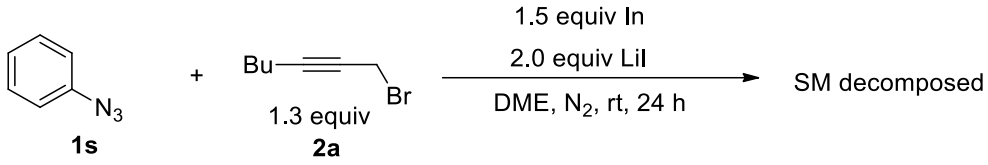
1290, 1269, 1255, 1110. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{42}N_3O_3$ 540.3221.; found 540.3225.



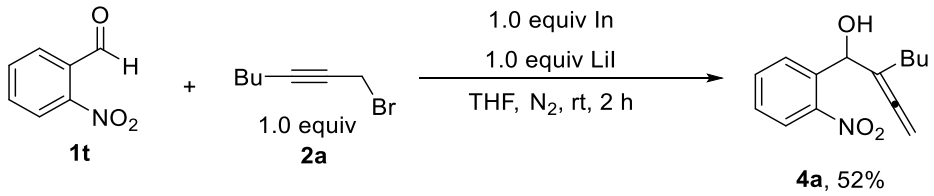

**3pa**

Following typical procedure 4, the reaction of **1p** (0.2804 g, 0.50 mmol), **2a** (0.1139 g, 0.65 mmol), In (0.0867 g, 0.75 mmol), and LiI (0.1344 g, 1.00 mmol) in DME (5 mL) afforded **3pa** (0.1672 g, 52%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow solid. mp: 220.9-221.8 ℃ (hexane/chloroform). $^1$H NMR (400 MHz, CDCl3) 1H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1 H, Ar-H), 8.22 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1 H, Ar-H), 8.16 (s, 1 H, Ar-H), 7.83 (d, $J$ = 8.3 Hz, 1 H, Ar-H), 7.30 (s, 1 H, Ar-H), 5.44 (d, $J$ = 4.9 Hz, 1 H, CH), 5.00-4.91 (m, 1 H, CH), 2.91 (t, $J$ = 7.5 Hz, 2 H, $CH_2$), 2.59-2.47 (m, 2 H, $CH_2$), 2.05-1.93 (m, 4 H), 1.88-1.76 (m, 4 H), 1.64-1.42 (m, 9 H), 1.37-1.11 (m, 9 H), 1.10 (s, 3 H, $CH_3$), 1.09-0.95 (m, 7 H), 0.92 (d, $J$ = 6.5 Hz, 3 H), 0.86 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.8 Hz, 6 H), 0.69 (s, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.8, 139.5, 133.2, 132.3, 131.0, 130.2, 127.9, 127.6, 127.5, 127.0, 123.0, 122.9, 117.7, 75.3, 56.6, 56.1, 50.0, 42.2, 39.7, 39.5, 38.1, 37.0, 36.6, 36.1, 35.8, 32.3, 31.9, 31.8, 30.7, 28.2, 28.0, 27.8, 24.2, 23.8, 22.8, 22.5, 22.4, 21.0, 19.3, 18.7, 13.8, 11.8. IR (neat, $cm^{-1}$) 2949, 2867, 1718, 747. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{60}N_3O_2$ 638.4680; found 638.4697.

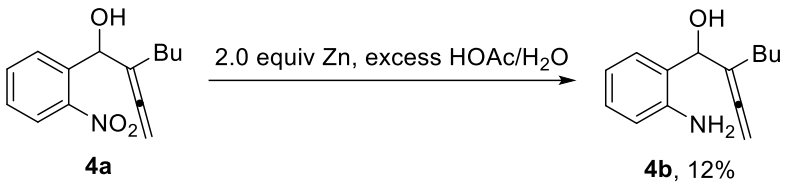
**Mechanistic studies**



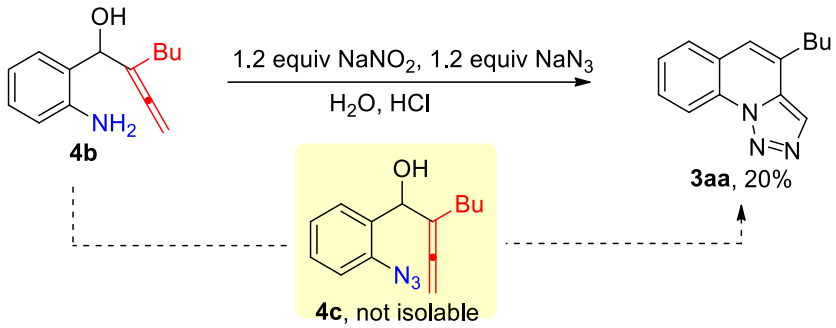

To a Schlenk tube were added In (0.0342 g, 0.3 mmol), LiI (0.0540 g, 0.4 mmol), and a premixed solution of **1s** (0.0235 g, 0.2 mmol) and **2a** (0.0480 g, 0.27 mmol) in DME (2 mL). The resulting mixture was stirred at room temperature for 24 h to afford a complicated mixture.




To a Schlenk tube were added In (0.0580 g, 0.5 mmol), LiI (0.0671 g, 0.5 mmol), THF (2 mL), **2a** (0.0869 g, 0.5 mmol). After stirring for 30 min at room temperature under nitrogen atmosphere, **1t** (0.0756 g, 0.5 mmol) was added to the resulting mixture and stirring for additional 2 h. The reaction mixture was quenched with saturated $NaHCO_3$ (20 mL). The aqueous layer was extracted with EA (3 × 20 mL) and the combined organic layers were dried over $Na_2SO_4$. Evaporation and flash chromatography on silica gel afforded **4a** (0.0642 g, 52%) (eluent: petroleum ether/ethyl acetate = 20/1 to 10/1): yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 1 H, Ar-H), 7.75 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.62 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.42 (t, *J* = 7.7 Hz, 1 H, Ar-H), 5.79-5.72 (m, 1 H, CH), 4.80-4.70 (m, 2 H, $=CH_2$), 2.59 (d, *J* = 6.3 Hz, 1 H, OH), 2.08-1.95 (m, 2 H, $CH_2$), 1.49-1.24 (m, 4 H, $CH_2$ × 2), 0.87 (t, *J* = 7.2 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 205.0, 148.4, 137.3, 133.0, 128.8, 128.3, 124.3, 107.1, 79.4, 70.4, 29.5, 28.8, 22.3, 13.9. IR ν (neat, $cm^{-1}$) 3389, 2957, 2929, 2871, 1956, 1646, 1558. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}NO_3$ 248.1281; found 248.1288.



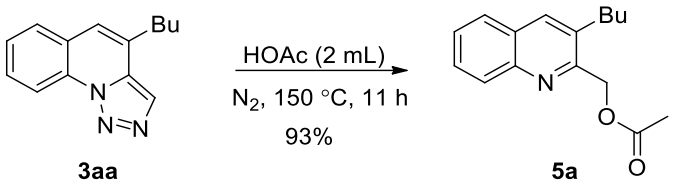

To a Schlenk tube were added **4a** (0.2208 g, 0.89 mmol), AcOH (2.7 mL), $H_2O$ (0.3 mL), Zn (0.1159 g, 1.78 mmol). The resulting mixture was stirred at room temperature for 9 h. After quenching with saturated $NaHCO_3$ (20 mL), the aqueous layer was extracted with EA (3 × 10 mL) and the combined organic layers were dried over $Na_2SO_4$. Evaporation and flash chromatography on silica gel afforded **4b** (0.0235 g, 12%) (eluent: petroleum ether/ethyl acetate/$Et_3N$ = 100/5/1): yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.16-7.07 (m, 2 H, Ar-H), 6.74 (dd, $J_1$ = 7.9 Hz, $J_2$ = 7.0 Hz, 1 H, Ar-H), 6.66 (d, $J$ = 7.8 Hz, 1 H, Ar-H), 5.11 (t, $J$ = 3.0 Hz, 1 H, CH), 5.06-4.90 (m, 2 H, $=CH_2$), 4.07 (s, 2 H, $NH_2$), 1.95-1.75 (m, 2 H, $CH_2$), 1.45-1.36 (m, 2 H, $CH_2$), 1.35-1.25 (m, 2 H, $CH_2$), 0.85 (t, $J$ = 7.3 Hz, 3 H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 203.9, 145.2, 128.8, 128.5, 125.0, 118.1, 116.8, 106.7, 79.9, 73.1, 29.7, 28.1, 22.3, 13.9. IR ν (neat, $cm^{-1}$) 3381, 2954, 2925, 2856, 1954, 1617, 1457. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}NO$ 218.1539; found 218.1532.




To a stirring solution of **4b** (0.0210 g, 0.1 mmol) in $H_2O$ (0.1 mL) was added conc. HCl (25 μL), a solution of $NaNO_2$ (0.0080 g, 0.1 mmol) in $H_2O$ (0.1 mL), and a solution of $NaN_3$ (0.0089 g, 0.12 mmol) in $H_2O$ (0.1 mL). The resulting mixture was stirred at 0 °C for 15 min and room temperature for another 12 h. After quenching with saturated $NaHCO_3$ (5 mL), the aqueous layer was extracted with EA (5 mL × 3) and the combined

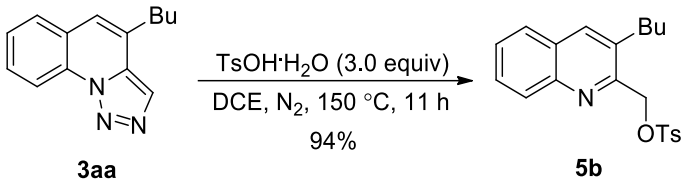
organic layers were dried over $Na_2SO_4$. While no **4c** was observed, 20% of **3aa** was determined by the crude $^1H$ NMR using mesitylene as the internal standard.

**Synthetic Potentials of the Products**




**3aa** **5a**

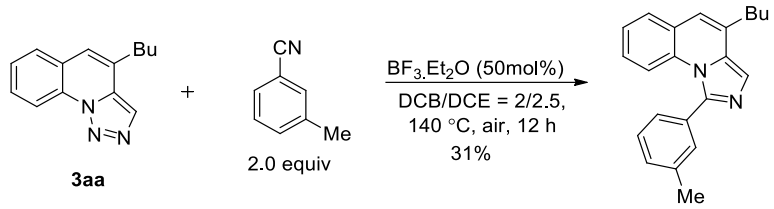
To a Schlenk tube were added **3aa** (0.0451 g, 0.2 mmol) and acetic acid (2 mL) under $N_2$. The resulting mixture was heated at 150 ℃ for 11 h.[10] After cooling to room temperature, excess acetic acid was distilled off and the residue mixture was neutralized with a saturated aqueous solution of $NaHCO_3$. The aqueous phase was extracted with DCM and dried over anhydrous $Na_2SO_4$. Flash chromatography on silica gel afforded the product **5a** (0.0482 g, 93%) (eluent: petroleum ether/ethyl acetate = 10/1): yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.94 (s, 1 H, Ar-H), 7.75 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.69-7.61 (m, 1 H, Ar-H), 7.52 (t, *J* = 7.5 Hz, 1 H, Ar-H), 5.42 (s, 2 H, $CH_2$), 2.80 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 2.17 (s, 3 H, $CH_3$), 1.75-1.63 (m, 2 H, $CH_2$), 1.51-1.40 (m, 2 H, $CH_2$), 0.97 (t, *J* = 7.3 Hz, 3 H, $CH_3$). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.7, 154.3, 146.2, 135.6, 134.2, 129.1, 128.8, 128.1, 126.9, 126.8, 65.9, 32.6, 31.3, 22.6, 20.9, 13.9. IR (neat, $cm^{-1}$) 2956, 2870, 1742, 1621, 1233, 1031, 751. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}NO_2$ 258.1489; found 258.1492.



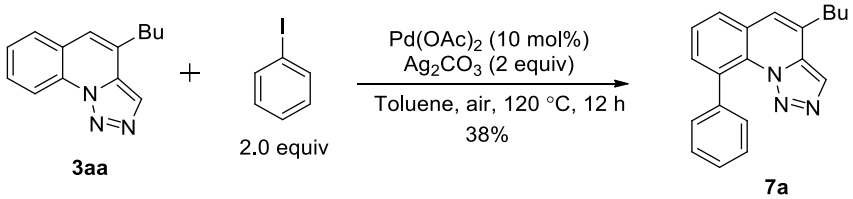

**3aa** **5b**

To a Schlenk tube were added **3aa** (0.0458 g, 0.2 mmol), $TsOH·H_2O$ (0.1141 g, 0.6 mmol), and DCE (2 mL) under $N_2$. The resulting solution was then warmed to 150 ℃ for 11 h. Evaporation and flash chromatography on silica gel afforded the product **5b** (0.0695 g, 94%) (eluent: DCM/MeOH = 20/1): white solid. mp. 118.3-119.8 ℃ (DCM/Hexane). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 1 H, Ar-H), 7.92

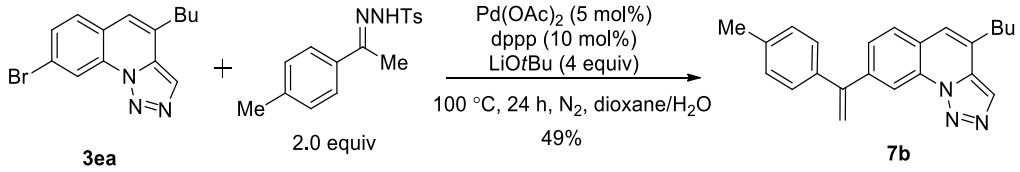
(s, 1 H, Ar-H), 7.84-7.79 (m, 2 H, Ar-H), 7.74 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.67-7.61 (m, 1 H, Ar-H), 7.56-7.49 (m, 1 H, Ar-H), 7.27 (d, *J* = 8.7 Hz, 2 H, Ar-H, overlapped with residue $CHCl_3$), 5.38 (s, 2 H, $CH_2$), 2.81 (t, *J* = 7.76 Hz, 2 H, $CH_2$), 2.39 (s, 3 H, $CH_3$), 1.70-1.61 (m, 2 H, $CH_2$), 1.47-1.37 (m, 2 H, $CH_2$), 0.97 (t, *J* = 7.3 Hz, 3 H, $CH_3$). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 151.7, 145.9, 144.8, 135.9, 135.0, 132.8, 129.7, 129.0, 128.9, 128.3, 128.1, 127.2, 126.9, 72.1, 32.6, 31.0, 22.50, 21.50, 13.9. IR (neat, $cm^{-1}$) 2956, 2928, 1597, 1362, 1188, 1175, 947; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}NO_3S$ 370.1471; found 370.1473.




To a 4 mL vial were added **3aa** (0.0415 g, 0.18 mmol), *m*-tolunitrile (48 μL, *d* = 0.976 g/mL, 0.4 mmol), $BF_3 \cdot Et_2O$ (12 μL, *d* = 1.15 g/mL, 0.1 mmol), dichlorobenzene (DCB) (0.2 mL), and dichloroethane (DCE) (0.25 mL) under air.[11] The resulting mixture was then warmed to 140 ℃ for 12 h. Evaporation and flash chromatography on silica gel afforded the product **6** (0.0178 g, 31%) (petroleum ether/ethyl acetate = 10/1 to 5/1 to 3/1): yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.03-7.94 (m, 2 H, Ar-H), 7.94-7.85 (m, 2 H, Ar-H), 7.84-7.76 (m, 2 H, Ar-H), 7.76-7.65 (m, 2 H, Ar-H), 7.64 (s, 1 H, Ar-H), 7.58-7.48 (m, 1 H, Ar-H), 3.19 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 2.81 (s, 3 H, $CH_3$), 2.25-2.11 (m, 2 H, $CH_2$), 1.93-1.79 (m, 2 H, $CH_2$), 1.38 (t, *J* = 7.3 Hz, 3 H, $CH_3$). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 142.3, 138.8, 132.6, 131.5, 131.1, 130.4, 130.2, 128.7, 128.1, 126.6, 126.1, 125.4, 119.7, 119.4, 117.3, 31.6, 30.8, 22.6, 21.4, 13.9. IR (neat, $cm^{-1}$) 2954, 2927, 1607, 1476, 1368, 790, 755. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2$ 315.1856; found 315.1857.

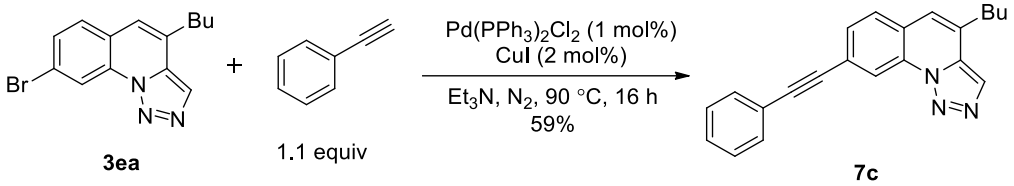


To a 4 mL vial were added **3aa** (0.0458 g, 0.2 mmol), iodobenzene (45 μL, *d* = 1.83 g/mL, 0.4 mmol), $Pd(OAc)_2$ (0.0051 g, 0.02 mmol), $Ag_2CO_3$ (0.1113 g, 0.4 mmol), and toluene (1 mL) under $N_2$.[12] The vial was sealed and the resulting mixture was heated at 120 °C for 12 h. Evaporation and flash chromatography on silica gel afforded the product **7a** (0.0235 g, 38%) (petroleum ether/ethyl acetate = 15/1): yellow solid. mp: 126.8-128.3 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.77 (d, *J* = 7.0 Hz, 1 H, Ar-H), 7.73-7.67 (m, 1 H, Ar-H), 7.62-7.55 (m, 3 H, Ar-H), 7.52-7.45 (m, 3 H, Ar-H), 7.26 (s, 1 H, Ar-H), 2.69 (t, *J* = 7.8 Hz, 2 H, $CH_2$), 1.35-1.23 (m, 2 H, $CH_2$), 1.09-0.98 (m, 2 H, $CH_2$), 0.67 (t, *J* = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.2, 132.4, 131.0, 130.5, 129.3, 129.0, 128.5, 128.1, 127.6, 127.0, 124.3, 116.2, 32.2, 31.7, 22.2, 13.6. IR (neat, $cm^{-1}$) 2954, 2856, 1609, 1641, 1163, 778, 756, 702. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}N_3$ 302.1652; found 302.1655.

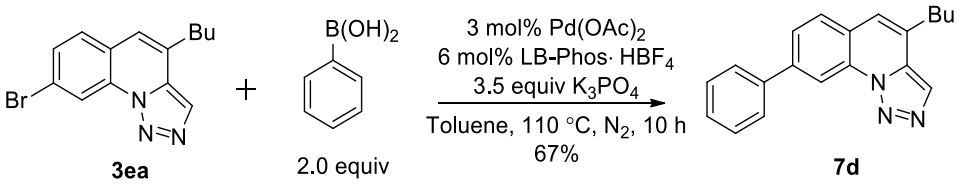



To a Schlenk tube were added **3ea** (0.0607 mg, 0.2 mmol), *N*-tosylhydrazone (0.1213 g, 0.4 mmol), $Pd(OAc)_2$ (0.0023 g, 0.01 mmol), dppp (0.0083 g, 0.02 mmol), *t*-LiOBu (0.0642 g, 0.8 mmol), dioxane (2.0 mL), and $H_2O$ (200 μL). The mixture was heated at 100 °C for 24 h.[13] Evaporation and flash chromatography on silica gel afforded the product **7b** (0.0334 g, 49%) (eluent: petroleum ether/ethyl acetate = 30/1 to 20/1): white solid. mp. 123.6-125.2 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1 H, Ar-H), 8.11 (s, 1 H, Ar-H), 7.72 (d, *J* = 8.3 Hz, 1 H, Ar-H), 7.53 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.4 Hz, 1 H, Ar-H), 7.32-7.22 (m, 3 H, Ar-H), 7.17 (d, *J* = 7.9 Hz, 2 H, Ar-H), 5.61 (d, *J* = 15.7 Hz, 2 H, $CH_2$), 2.88 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 2.38 (s, 3 H, $CH_3$), 1.83-1.72 (m, 2 H, $CH_2$), 1.53-1.38 (m, 2 H, $CH_2$), 0.98 (t, *J* = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.9, 142.7, 137.9, 137.9, 133.2, 130.6, 129.6, 129.1, 128.1, 127.5, 127.3, 126.6, 123.8, 123.3, 115.7, 115.5, 32.2, 30.8, 22.4, 21.2, 13.8. IR (neat, $cm^{-1}$) 2955, 2928, 1608, 1561, 1439, 892, 825. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}N_3$

342.1965; found 342.1966.




To a reaction tube were added **3ea** (0.1029 g, 0.34 mmol), $Pd_2(PPh_3)_2Cl_2$ (0.0029 g, 0.004 mmol), CuI (0.0017g, 0.008 mmol), dry $Et_3N$ (1.2 mL), and phenylacetylene (48 μL, *d* = 0.93 g/mL, 0.44 mmol) under $N_2$.[14] The resulting solution was stirred at 90 ℃ for 16 h. Then the mixtures were allowed to cool to room temperature, and filtered through celite. Evaporation and flash chromatography on silica gel afforded the product **7c** (0.0661 g, 59%) (eluent: petroleum ether to petroleum ether/ethyl acetate = 20/1): yellow solid. mp. 119.2-120.5 ℃ (DCM/Hexane). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1 H, Ar-H), 8.13 (s, 1 H, Ar-H), 7.75 (d, *J* = 8.2 Hz, 1 H, Ar-H), 7.68 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.4 Hz, 1 H, Ar-H), 7.64-7.56 (m, 2 H, Ar-H), 7.43-7.36 (m, 3 H, Ar-H), 7.26 (s, 1 H, Ar-H, overlapped with residue $CHCl_3$), 2.90 (t, *J* = 7.7 Hz, 2 H, $CH_2$), 1.84-1.73 (m, 2 H, $CH_2$), 1.52-1.40 (m, 2 H, $CH_2$), 0.99 (t, *J* = 7.4 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.2, 131.8, 130.5, 129.9, 128.8, 128.4, 127.8, 126.7, 124.0, 123.9, 123.2, 122.6, 119.1, 91.9, 88.6, 32.3, 30.8, 22.4, 13.9. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.2, 131.8, 130.5, 129.9, 128.8, 128.4, 127.8, 126.7, 124.0, 123.9, 123.2, 122.6, 119.1, 91.9, 88.6, 32.3, 30.8, 22.4, 13.9. IR (neat, $cm^{-1}$) 3058, 2955, 2928, 2869, 2214, 1618, 1560, 1442. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3$ 326.1652; found 362.1652.




To a dried Schlenk tube were added $K_3PO_4$ (0.1489 g, 0.7 mmol), $Pd(OAc)_2$ (0.0019 g, 0.006 mmol), LB-Phos·$BF_4$ (0.0053 g, 0.012 mmol), phenylboronic acid (0.0493 g, 0.4 mmol), and toluene (0.5 mL) sequentially under a nitrogen atmosphere at room temperature.[15] After stirring for 5 min at room temperature, **3ea** (64.4 mg, 0.20 mmol) and toluene (0.5 mL) were added in 5 min under a nitrogen atmosphere. The resulting

mixture was then stirred for 10 h at 110 ℃. Evaporation and flash column chromatography on silica gel gave the product **7d** (0.0401 g, 67%) (eluent: petroleum ether to petroleum ether/ethyl acetate = 20/1): yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1 H, Ar-H), 8.13 (s, 1 H, Ar-H), 7.88-7.72 (m, 4 H, Ar-H), 7.51 (t, *J* = 7.5 Hz, 2 H, Ar-H), 7.42 (t, *J* = 7.3 Hz, 1 H, Ar-H), 7.27 (s, 1 H, Ar-H), 2.88 (t, *J* = 7.6 Hz, 2 H, $CH_2$), 1.84-1.72 (m, 2 H, $CH_2$), 1.57-1.37 (m, 2 H, $CH_2$), 0.98 (t, *J* = 7.3 Hz, 3 H, $CH_3$). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.9, 139.5, 133.3, 131.0, 129.6, 129.0, 128.3, 128.2, 127.4, 126.6, 126.0, 123.4, 123.3, 114.1, 32.2, 30.8, 22.4, 13.9. IR (neat, $cm^{-1}$) 2955, 2928, 1653, 1474, 1432. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}N_3$ 302.1652; found 302.1655.

**X-ray Crystallography of 3ab**

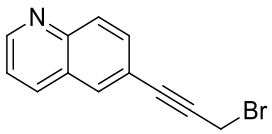
Crystal data for $C_{11}H_9N_3$, *M* = 183.21, orthorhombic, space group Pccn, final R indices [I > 2σ(I)], $R_1$ = 0.0328, $wR_2$ = 0.0826; R indices (all data), $R_1$ = 0.0432, $wR_2$ = 0.0901; *a* = 14.159(3) Å, *b* = 17.002(4) Å, *c* = 7.4730(16) Å, α = β = γ = 90°, *V* = 1799.0(7) $Å^3$, *T* = 296(2) K, *Z* = 8, reflection collected/unique 15648 / 1593 ($R_{int}$ = 0.027), number of observations [>2σ(I)] 1305, parameters: 128. CCDC 2078447 contains supplementary crystallographic data for structure of **3ab**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

## References:


1. T. Kippo, T. Fukuyama, and I. Ryu, Regioselective Radical Bromoallylation of Allenes Leading to 2-Bromo-Substituted 1,5-Dienes, *Org. Lett.,* 2011, **13**, 3864-3867.
2. A. Smeyanov and A. Schmidt, $K_3PO_4$-KOH Mixture as Efficient Reagent for the Deprotection of 4-Aryl-2-methyl-3-butyn-2-ols to Terminal Acetylenes, *Synth. Commun.,* 2013, **43**, 2809-2816.
3. C. Borie, S. Mondal, T. Arif, M. Briand, H. Lingua, F. Dumur, D. Gigmes, P. Stocker, B. Barbarat, V. Robert, C. Nicoletti, D. Olive, M. Maresca, and Nechab, M. Enediynes Bearing Polyfluoroaryl Sulfoxide as New Antiproliferative Agents with Dual Targeting of Microtubules and DNA, *Eur. J. Med. Chem.,* 2018, **148**, 306-313.
4. Y. Hayashi, D. Sakamoto, and D. Okamura, One-Pot Synthesis of (*S*)-Baclofen via Aldol Condensation of Acetaldehyde with Diphenylprolinol Silyl Ether Mediated Asymmetric Michael Reaction as a Key Step, *Org. Lett*., 2016, **18**, 4-7.
5. (a) B. M. Trost, A. Breder, B. M. O'Keefe, M. Rao, and A. W. Franz, Propargyl Alcohols as Beta-oxocarbenoid Precursors for the Ruthenium-catalyzed Cyclopropanation of Unactivated Olefins by Redox Isomerization. *J. Am. Chem. Soc.,* 2011, **133**, 4766-4769; (b) R. C. Lloyd, M. C. Lloyd, M. E. B. Smith, K. E. Holt, J. P. Swift, P. A. Keene, S. J. C. Taylor, and R. McCague, Use of hydrolases for the synthesis of cyclic amino acids, *Tetrahedron,* 2004, **60**, 717-728.
6. R. Ballesteros-Garrido, F. R. Leroux, R. Ballesteros, B. Abarca, and F. Colobert, The Deprotonative Metalation of [1,2,3]Triazolo[1,5-*a*]quinoline. Synthesis of 8-Haloquinolin-2-carboxaldehydes. *Tetrahedron*, 2009, **65**, 4410-4417.
7. J. S. Benjamin, L. Sheng, and G. D. Tom, $Rh_2$(II)-Catalyzed Nitro-Group Migration Reactions: Selective Synthesis of 3-Nitroindoles from β-Nitro Styryl Azides, *J. Am. Chem. Soc.,* 2011, **133**, 4702-4705.
8. A. A. Gayan, J. S. James, and F. M. Stephen, Novel Substituted Triazolo Benzodiazepine Scaffolds to Explore Chemical Space, *Tetrahedron Lett*., 2021, **66**, 152828.
9. T. Khuloud, C. Ting, and P. Evangelos, Structureeactivity relationship study of 4EGI-1, small molecule eIF4E/eIF4G proteineprotein interaction inhibitors, *Eur. J. Med. Chem.*, 2014, **77**, 361-377.
10. R. Ballesteros-Garrido, F. R. Leroux, R. Ballesteros, B. Abarca, and F. Colobert, The Deprotonative Metalation of [1,2,3]Triazolo[1,5-*a*]quinoline. Synthesis of 8-Haloquinolin-2-carboxaldehydes, *Tetrahedron,* 2009, **65**, 4410-4417.
11. A. Joshi, R. Semwal, E. Suresh, and S. Adimurthy, Pd-Catalyzed Regioselective Synthesis of 2,6-Disubstituted Pyridines through Denitrogenation of Pyridotriazoles and 3,8-Diarylation of Imidazo[1,2-*a*]pyridines, *Chem. Commun.,* 2019, **55**, 10888-10891.
12. D. Lamaa, H.-P. Lin, T. Bzeih, P. Retailleau, M. Alami, and A. Hamze, TBAB-Catalyzed $C_{sp3}$−N Bond Formation by Coupling Pyridotriazoles with Anilines: A New Route to (2-Pyridyl)alkylamines, *Eur. J. Org. Chem.,* 2019, **2019**, 2602-2611.
13. J. Panteleev, R. Y. Huang, and M. Lautens, Addition of Arylboronic Acids to Arypropargyl Alcohols en Route to Indenes and Quinolines, *Org. Lett.,* 2011, **13**, 5314-5317.
14. Z.-H. Shang, Z.-X. Zhang, W.-Z. Weng, Y.-F. Wang, T.-W. Cheng, Q.-Y. Zhang, L.-Q. Song, T.-Q. Shao, K.-X. Liu, and Y.-P. Zhu, A Metal- and Azide-free Oxidative Coupling Reaction for the Synthesis of [1,2,3]Triazolo[1,5-*a*]quinolines and Their Application to Construct C−C and

C−P Bonds, 2-Cyclopropylquinolines and Imidazo[1,5-*a*]quinolines, *Adv. Synth. Catal.,* 2021, **363**, 490-496.

15. (a) B. Lü, C. Fu, and S. Ma, Application of a Readily Available and Air Stable Monophosphine $HBF_4$ Salt for the Suzuki Coupling Reaction of Aryl or 1-Alkenyl Chlorides, *Tetrahedron Lett.,* 2010, **51**, 1284-1286; (b) B. Lü, C. Fu, and S. Ma, Application of Dicyclohexyl-(S)-trimethoxyphenyl Phosphine·$HBF_4$ salt for the Highly Selective Suzuki Coupling of the C−Cl Bond in Beta-Chlorobutenolides over the More Reactive Allylic C−O bond, *Chem. Eur. J.,* 2010, **16**, 6434-6437; (c) R. Zeng, S. Wu, C. Fu, and S. Ma, Room-temperature Synthesis of Trisubstituted Allenylsilanes via Regioselective C−H functionalization, *J. Am. Chem. Soc.,* 2013, **135**, 18284-18287.




**2l**

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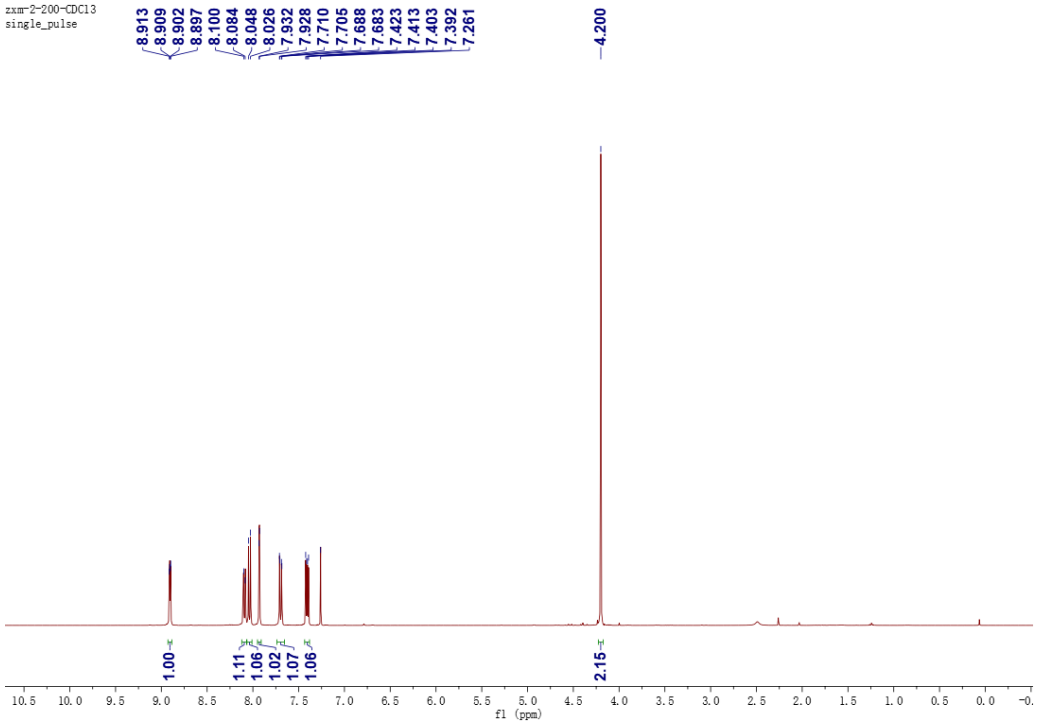


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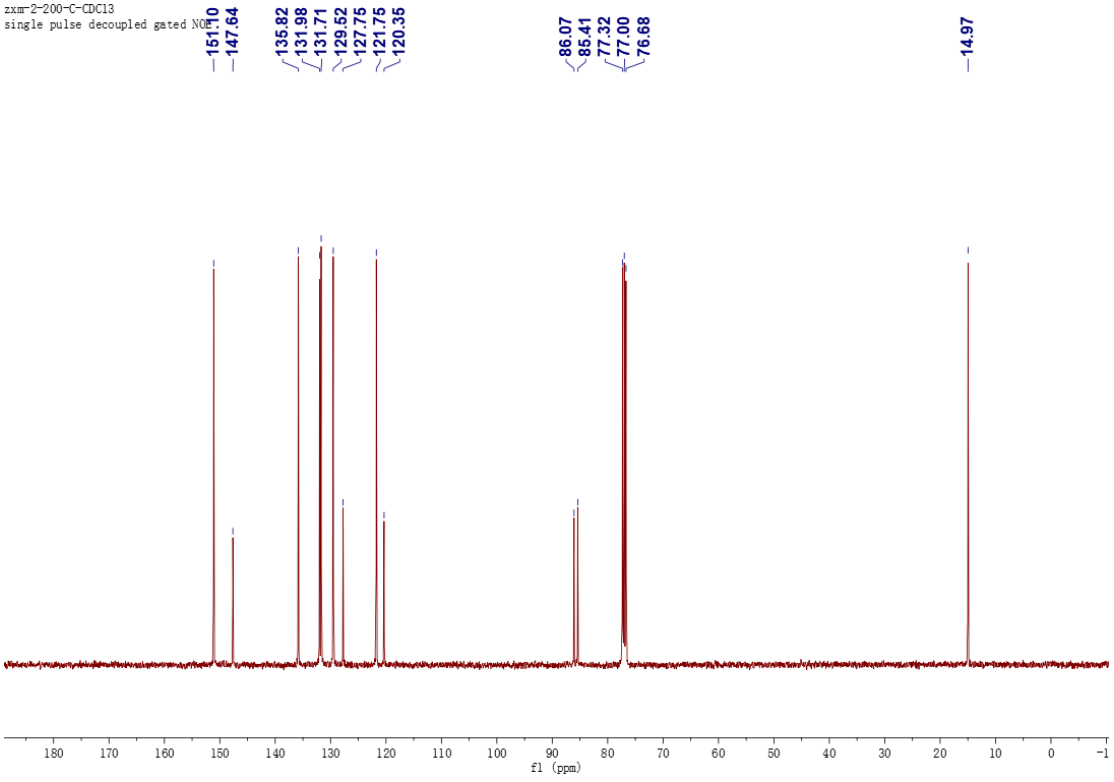

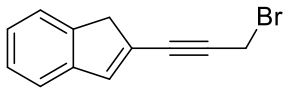


**2m**

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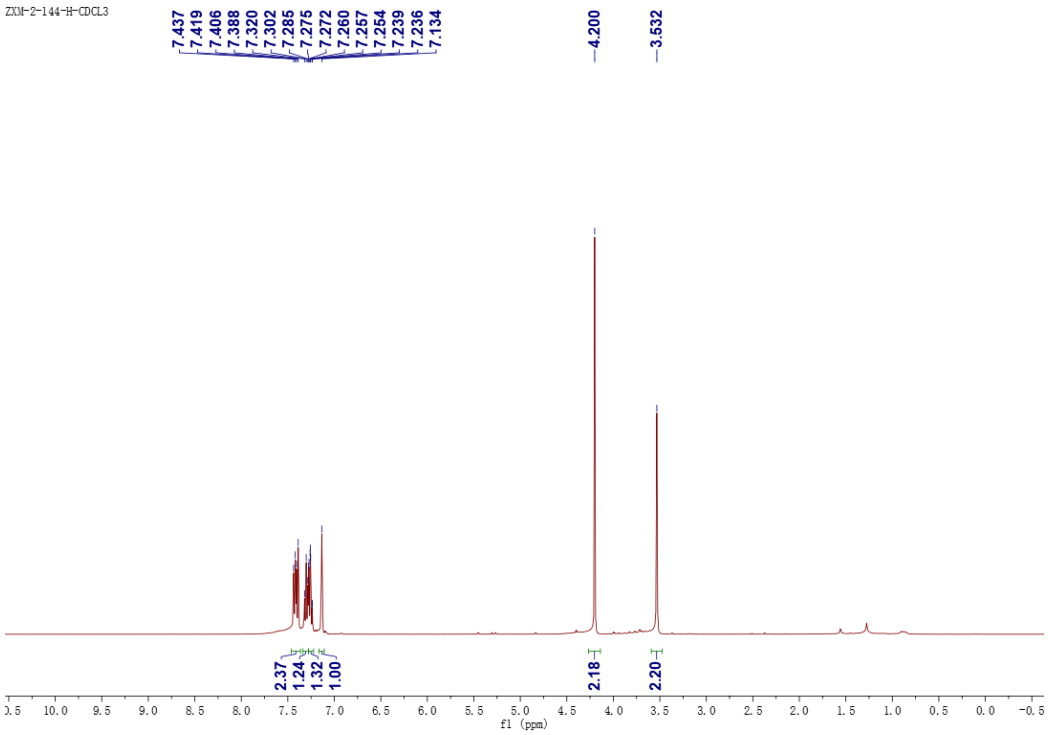


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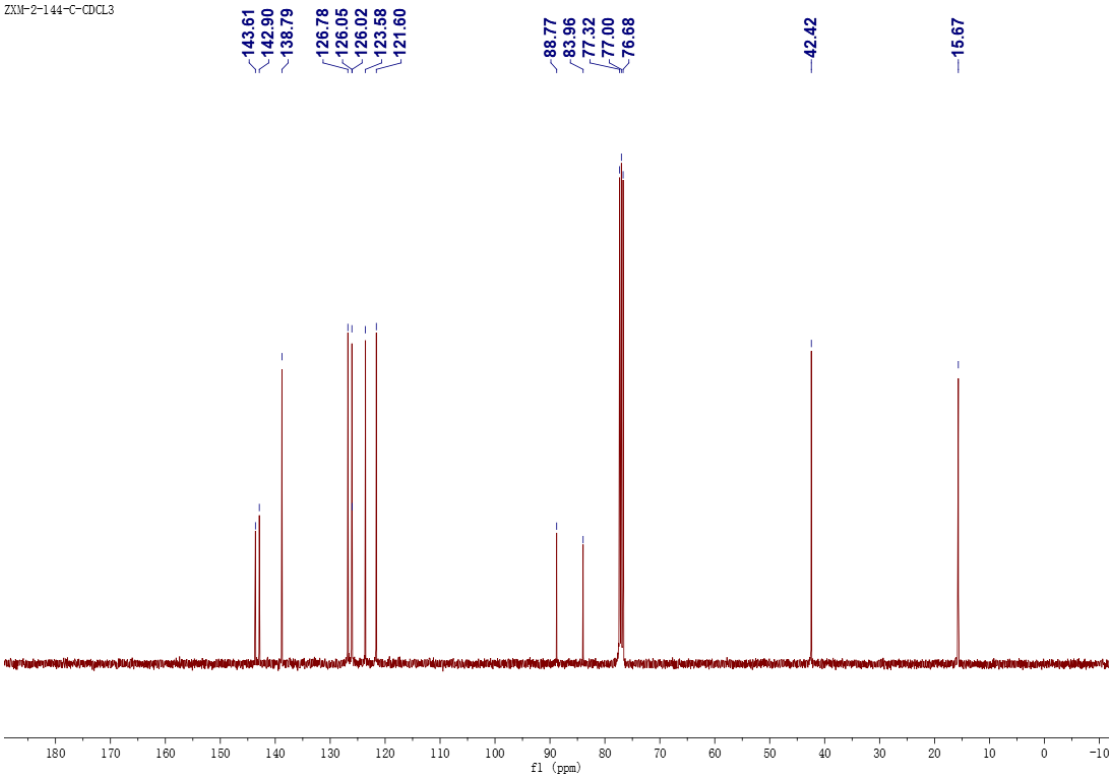

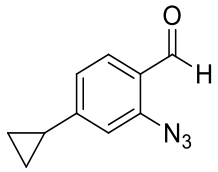


**1c**

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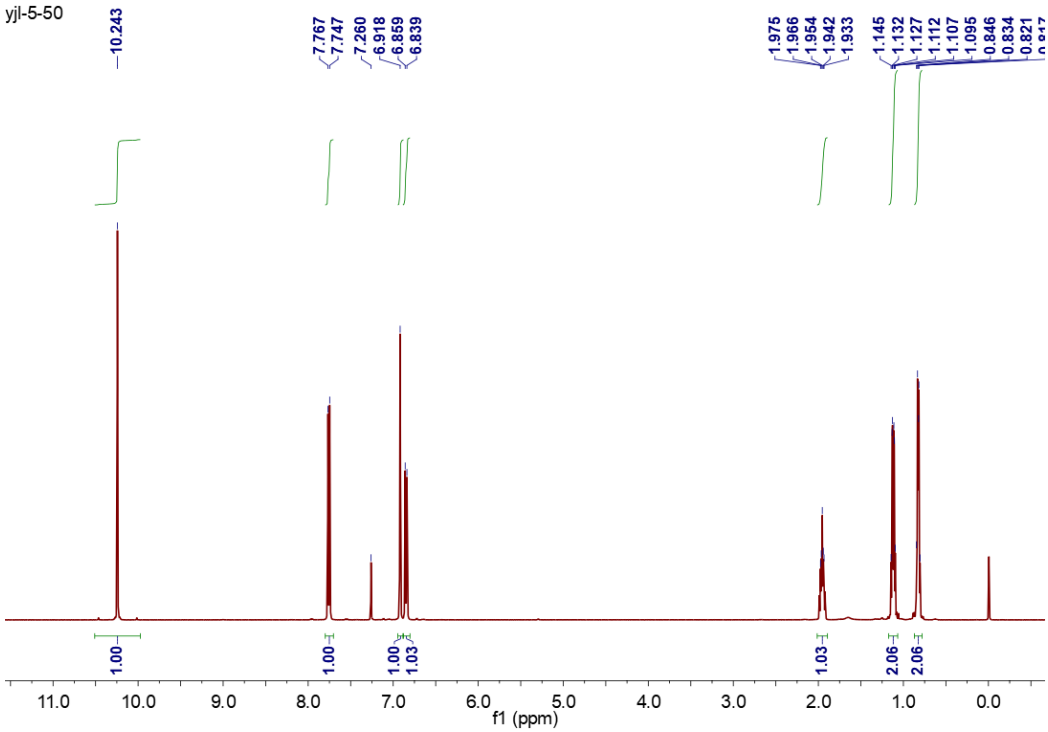
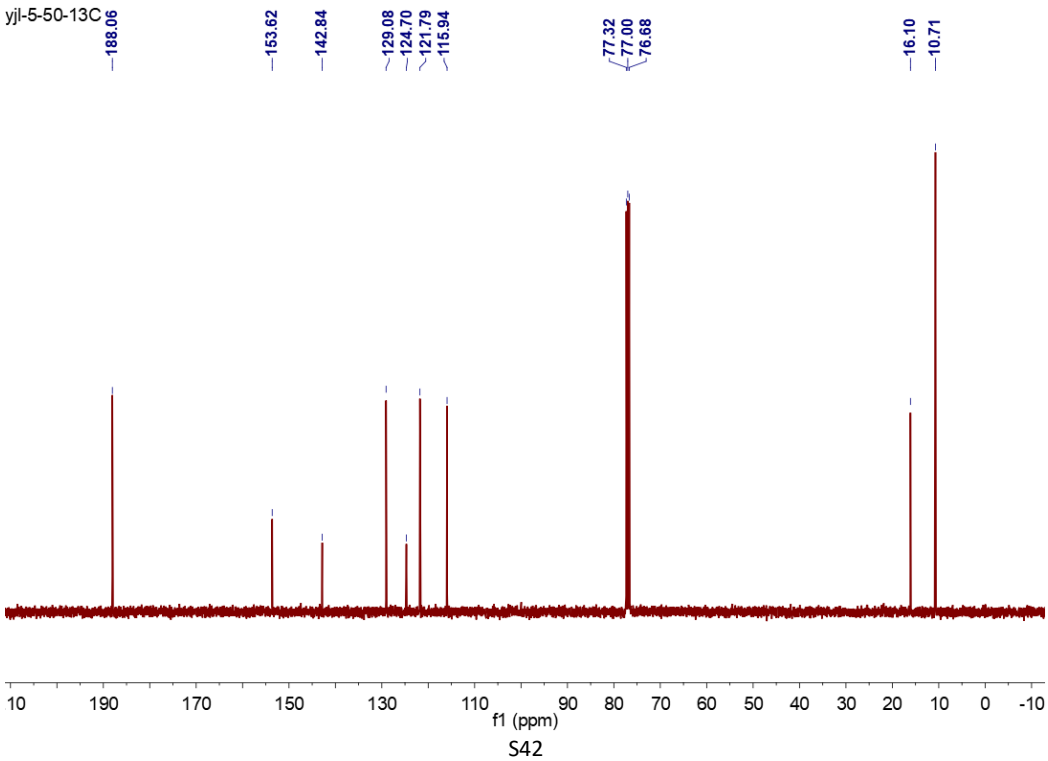
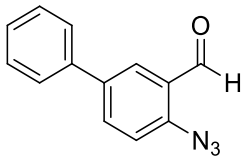


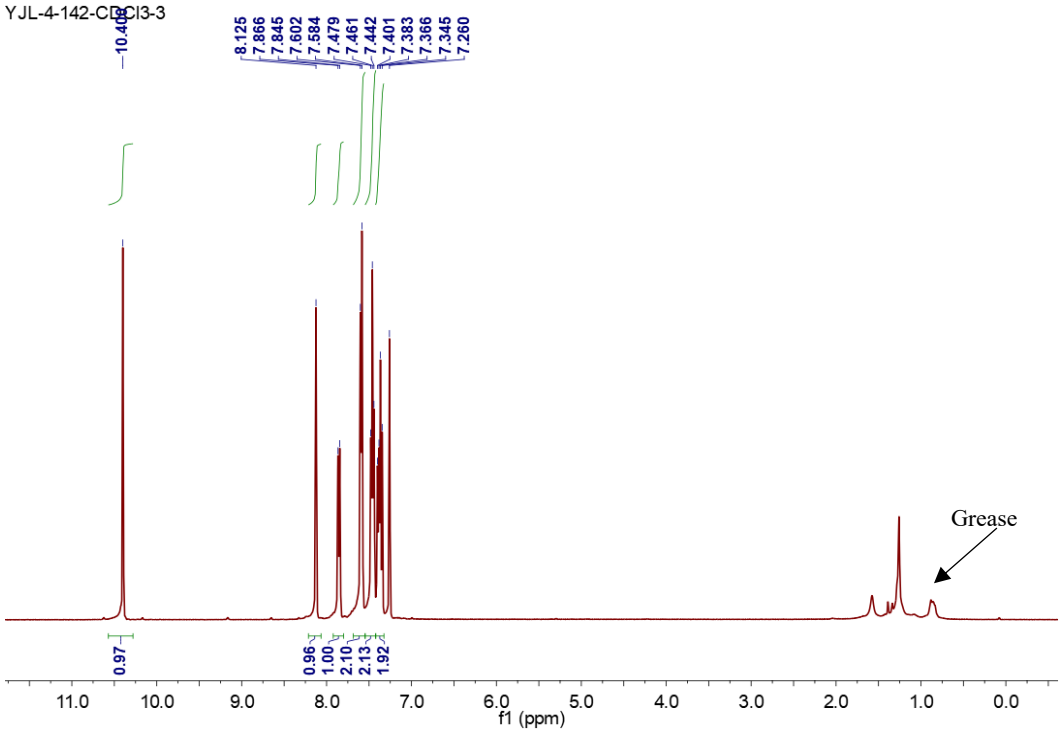

$^{13}$C NMR Spectrum of **1c:**



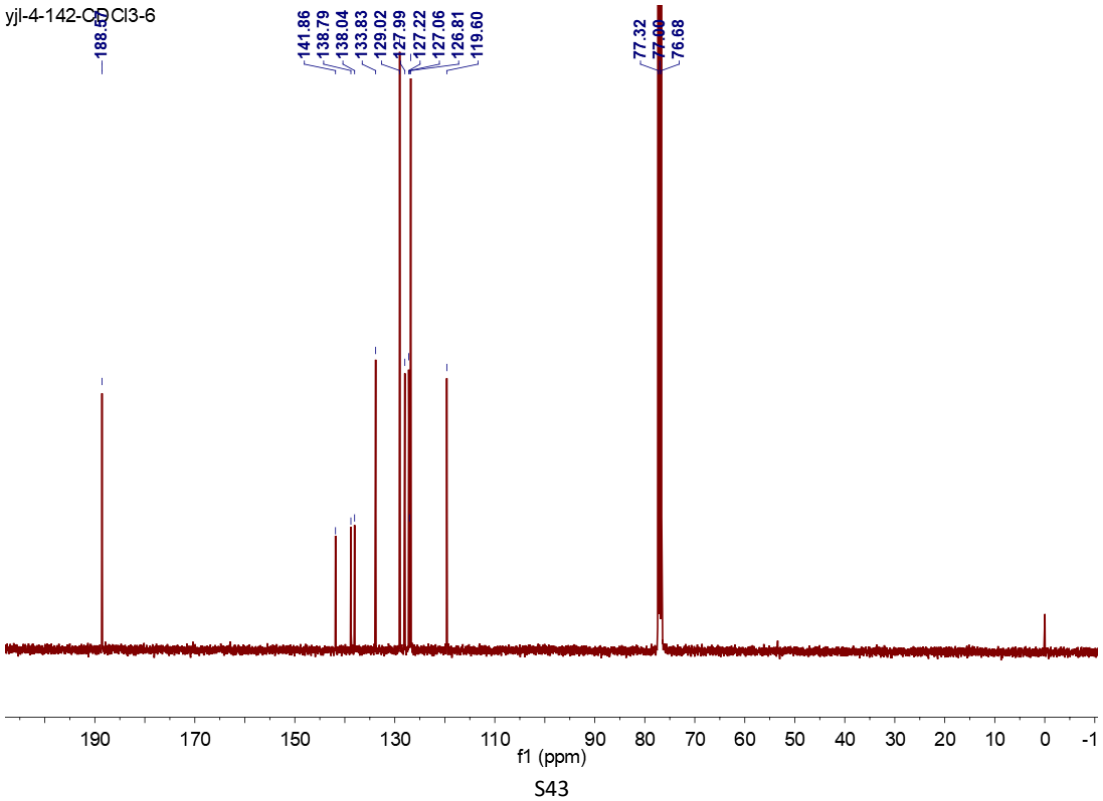


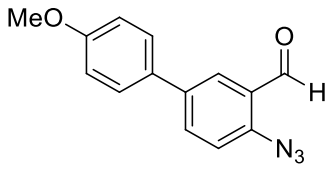

**1f**

$^{1}$H NMR Spectrum of **1f:**




$^{13}$C NMR Spectrum of **1f:**






**1g**

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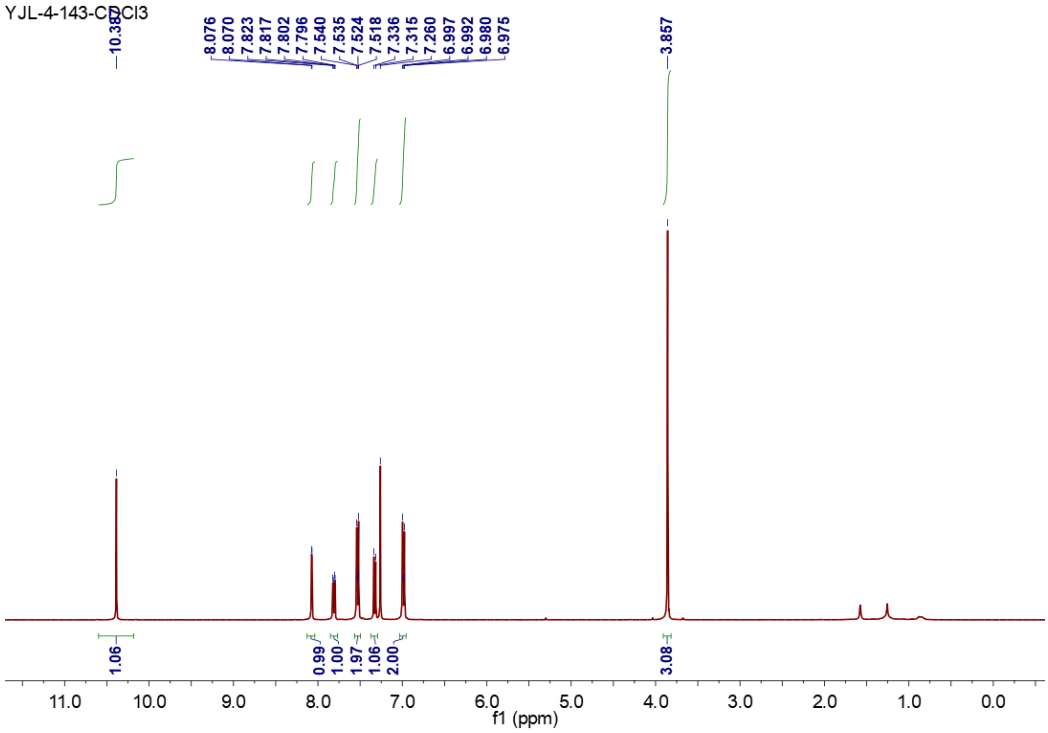


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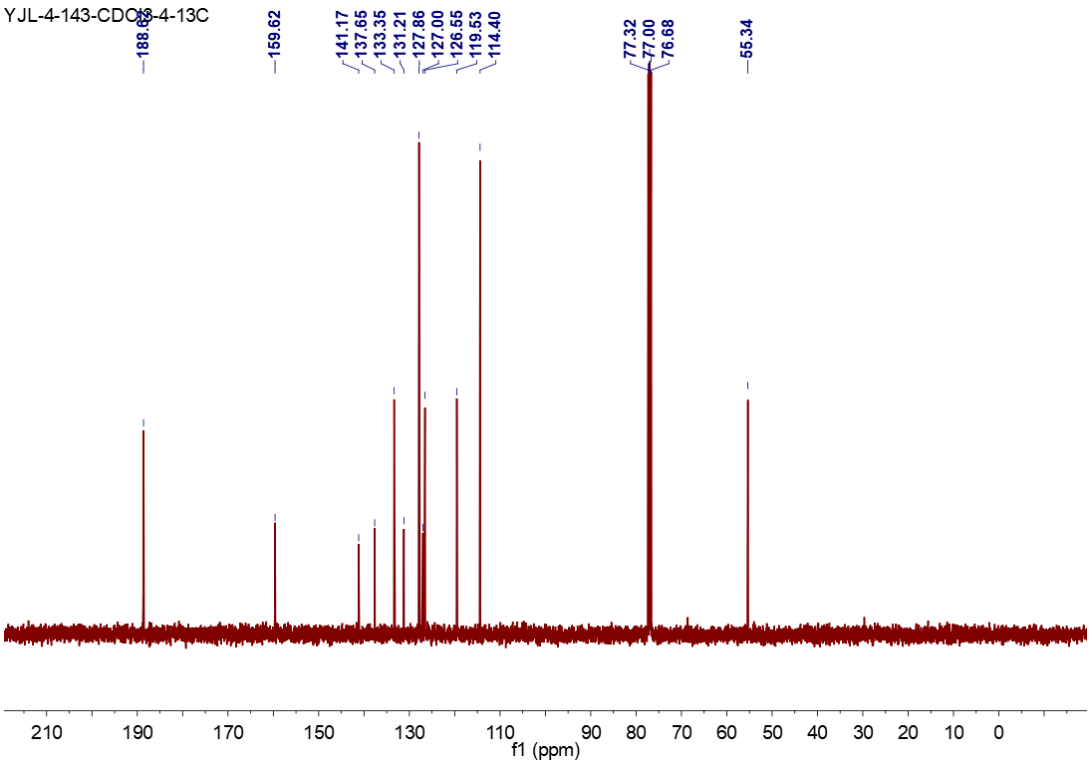

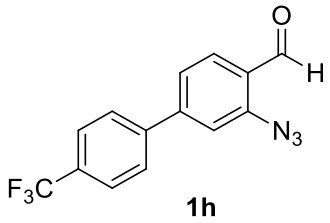


**1h**

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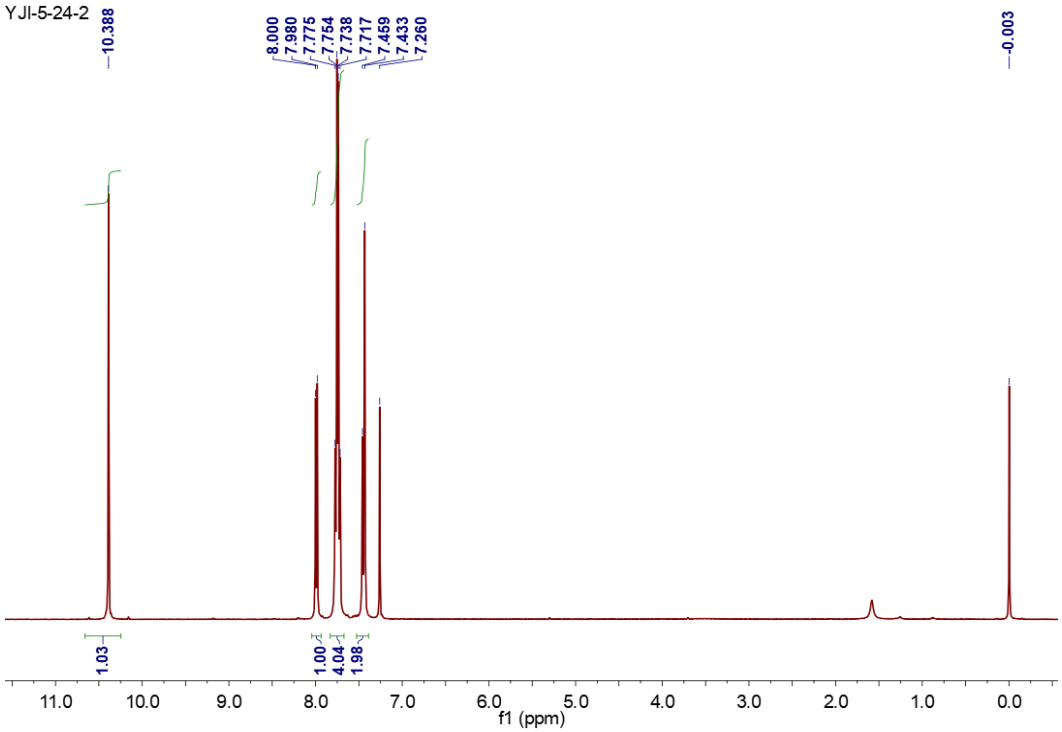


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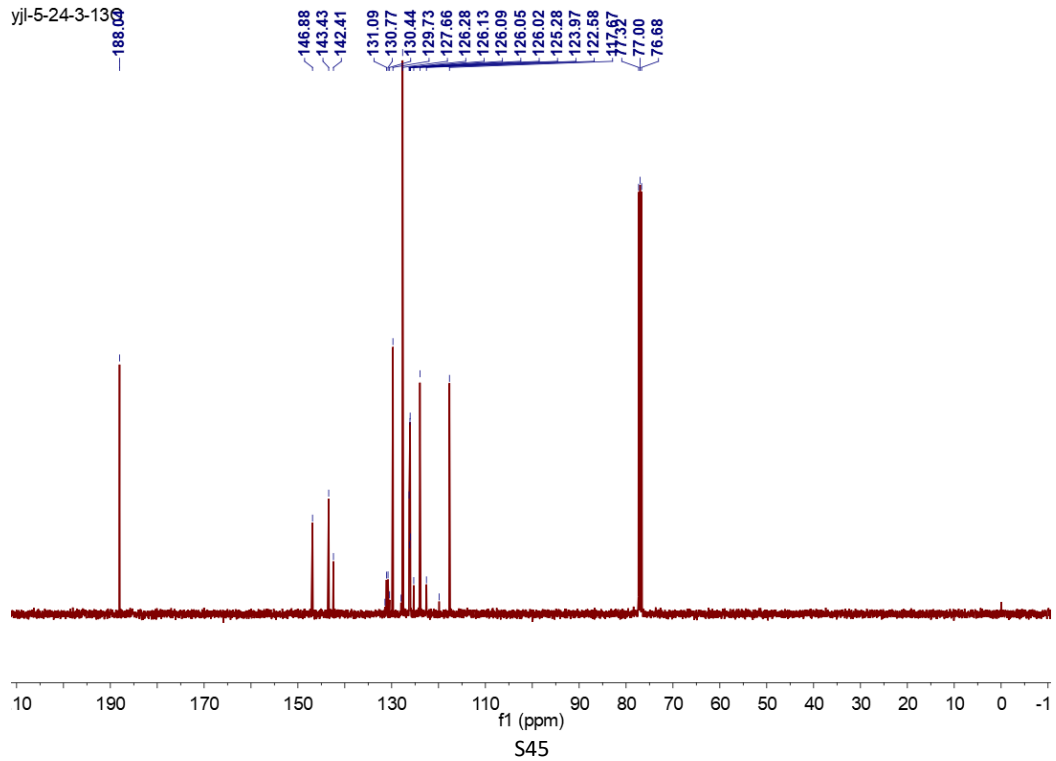

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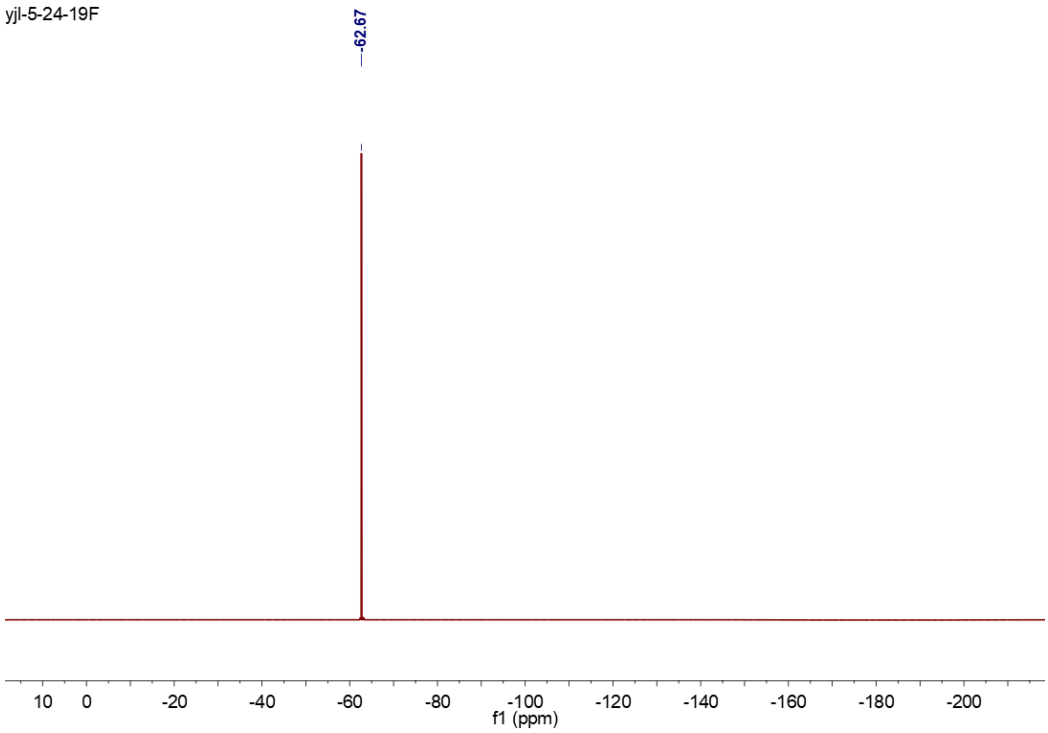
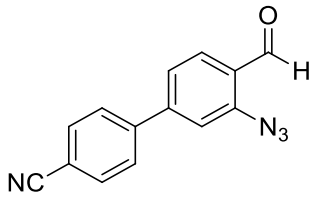
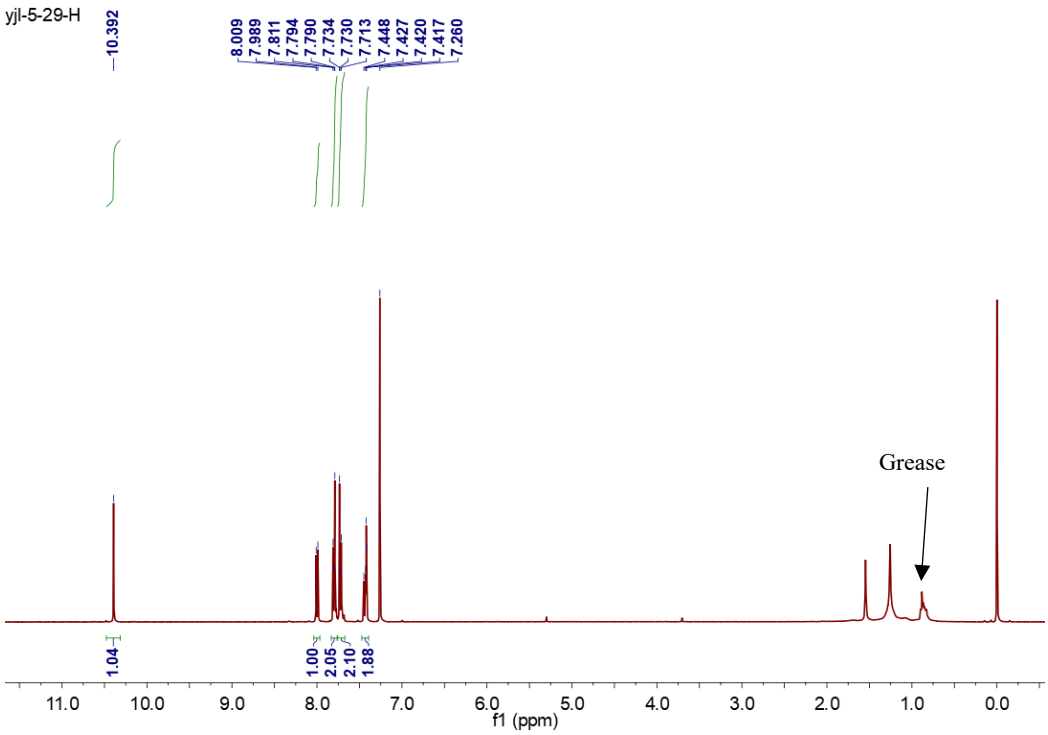



**1i**

$^{1}$H NMR Spectrum of **1i:**



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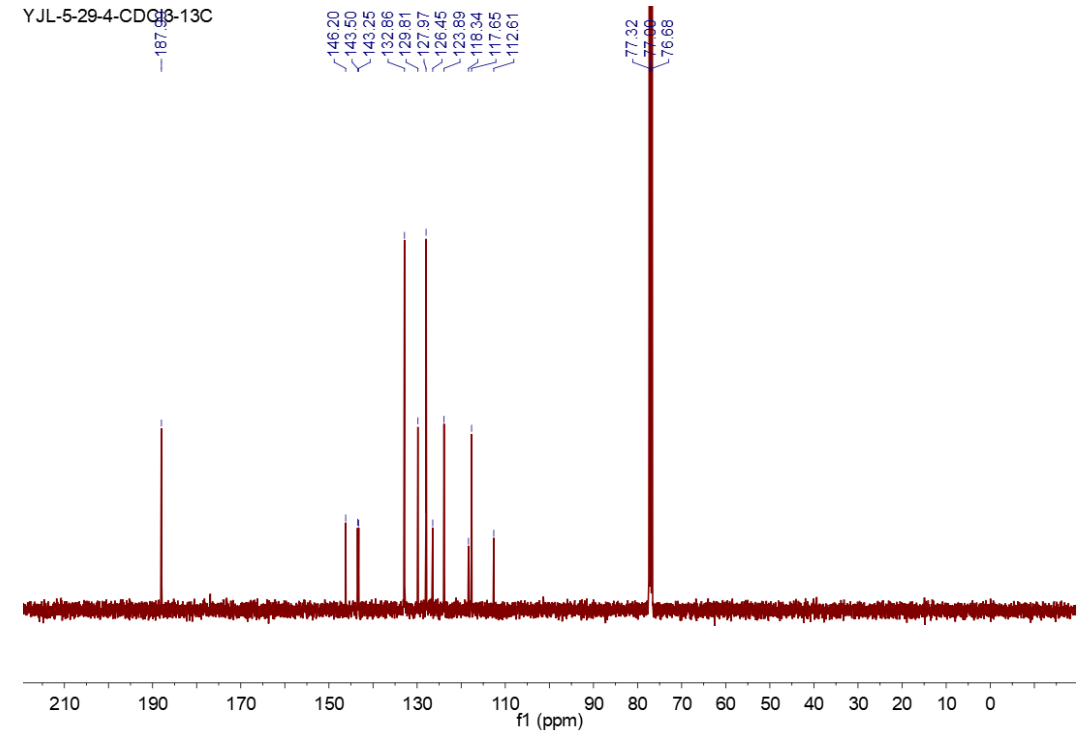


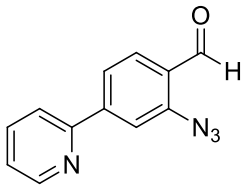


**1j**

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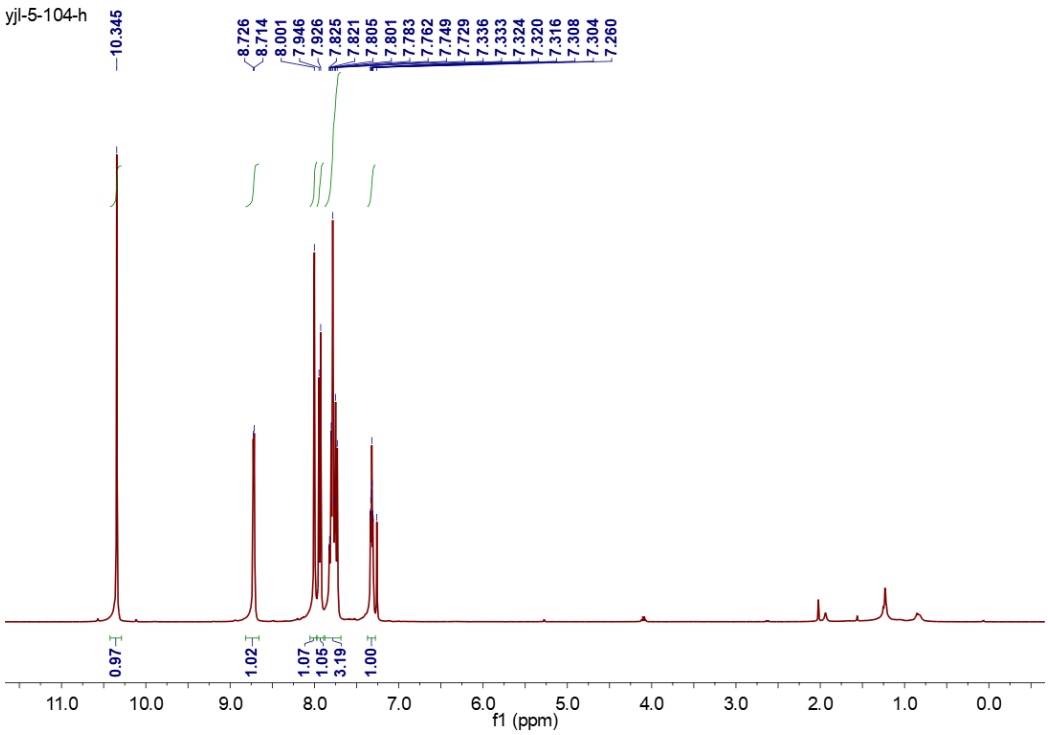

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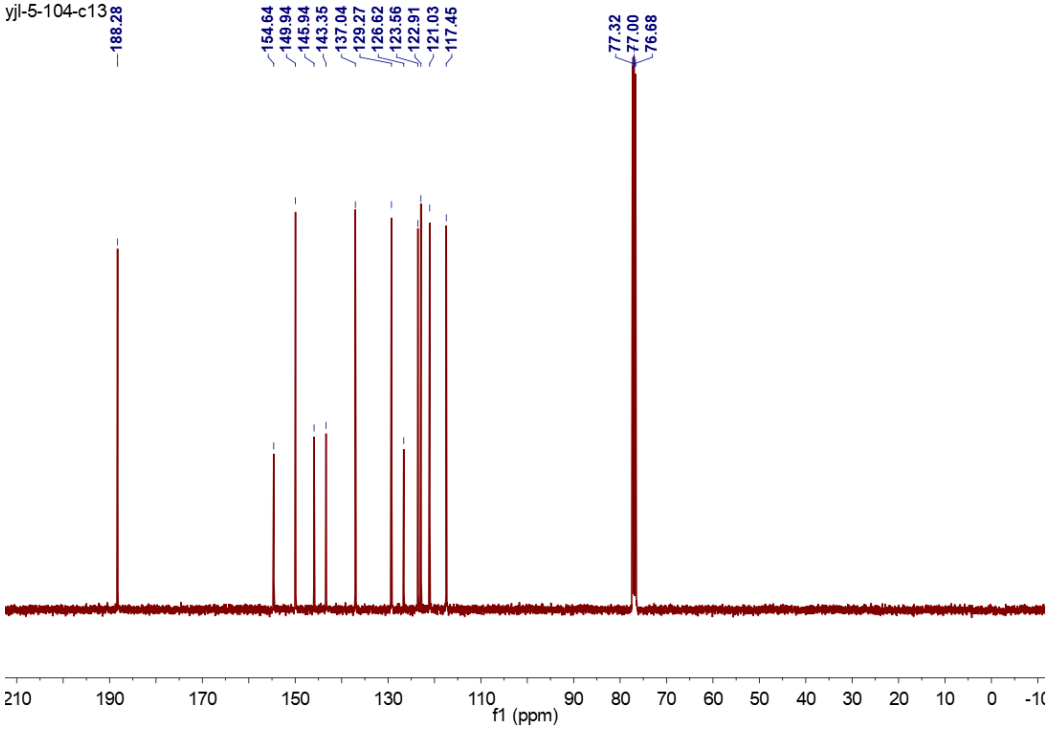


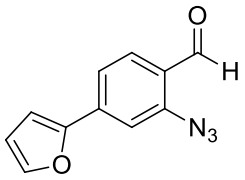


**1k**

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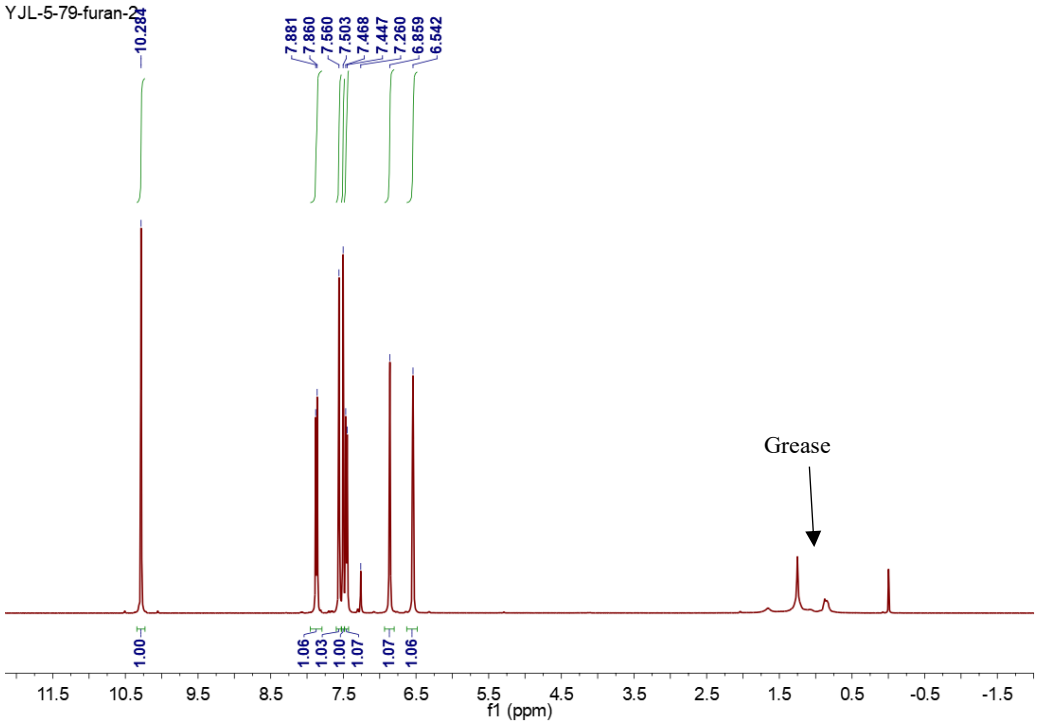

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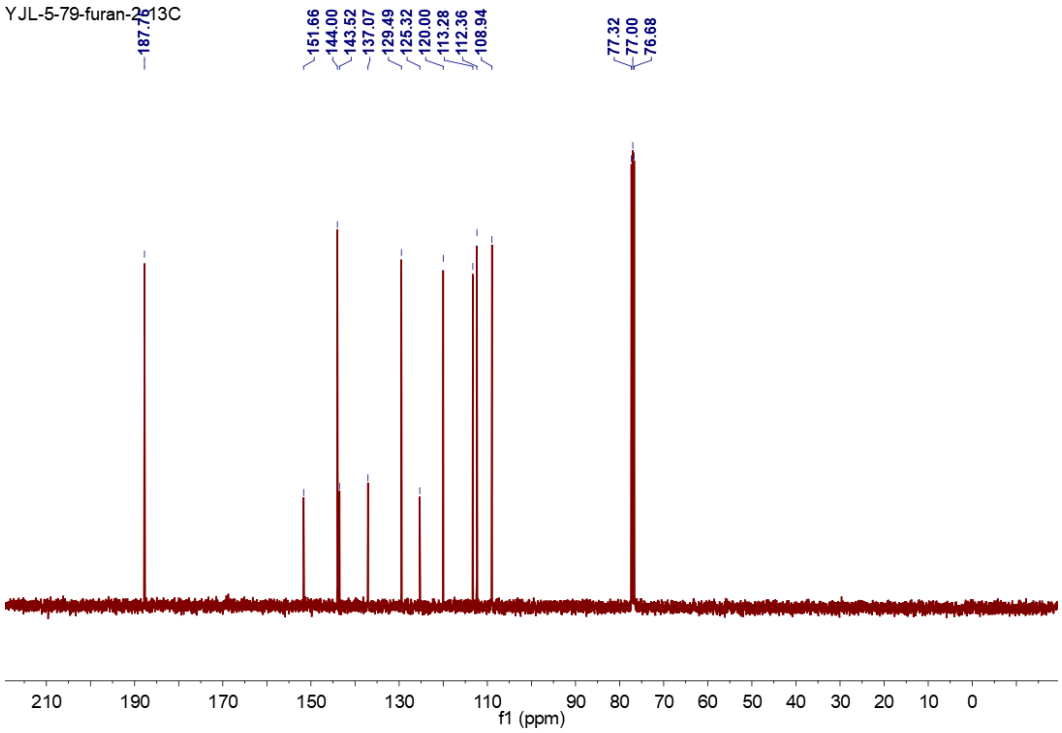


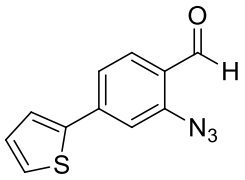


**1l**

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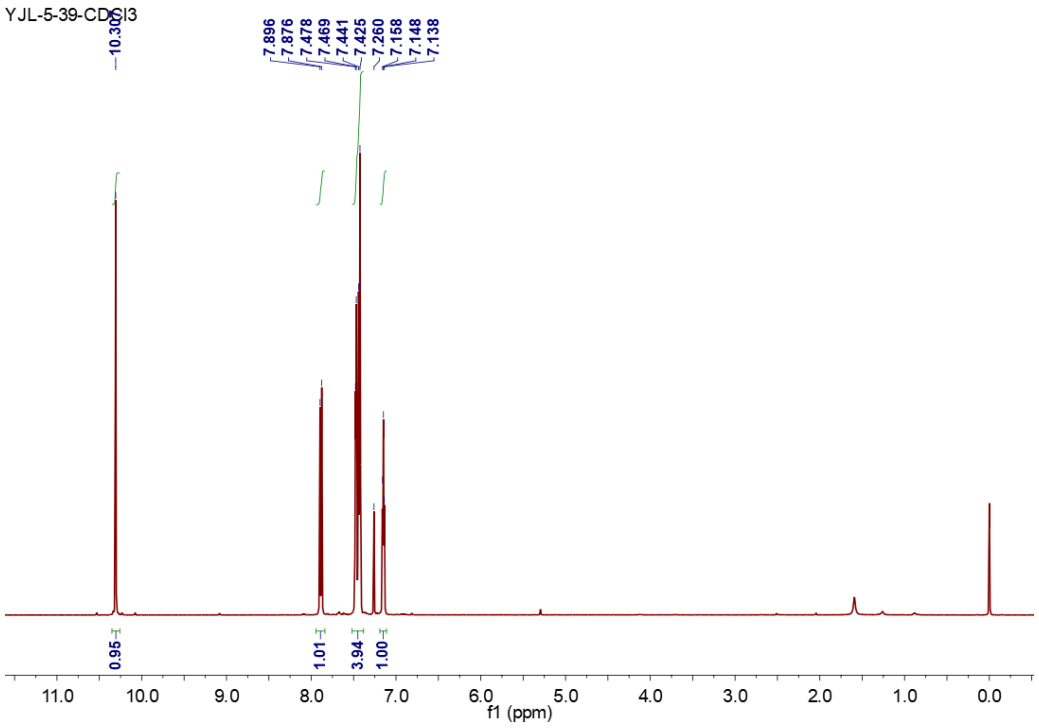

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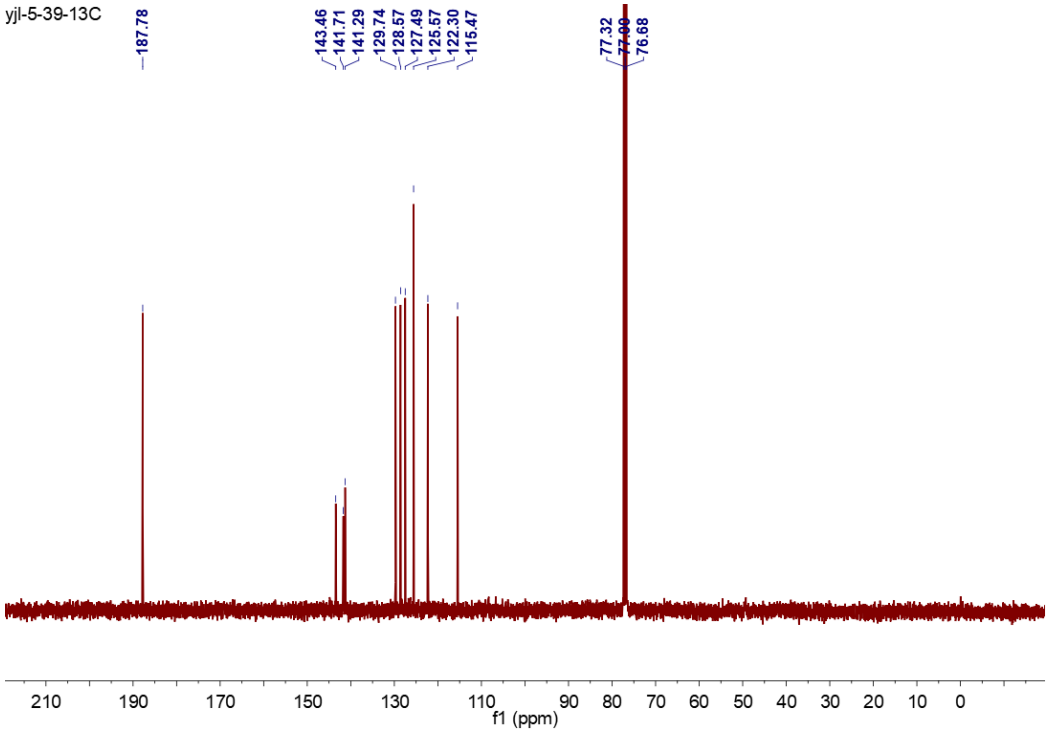


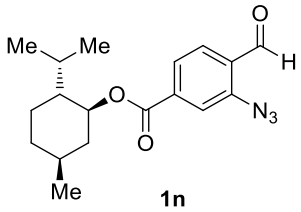


**1n**

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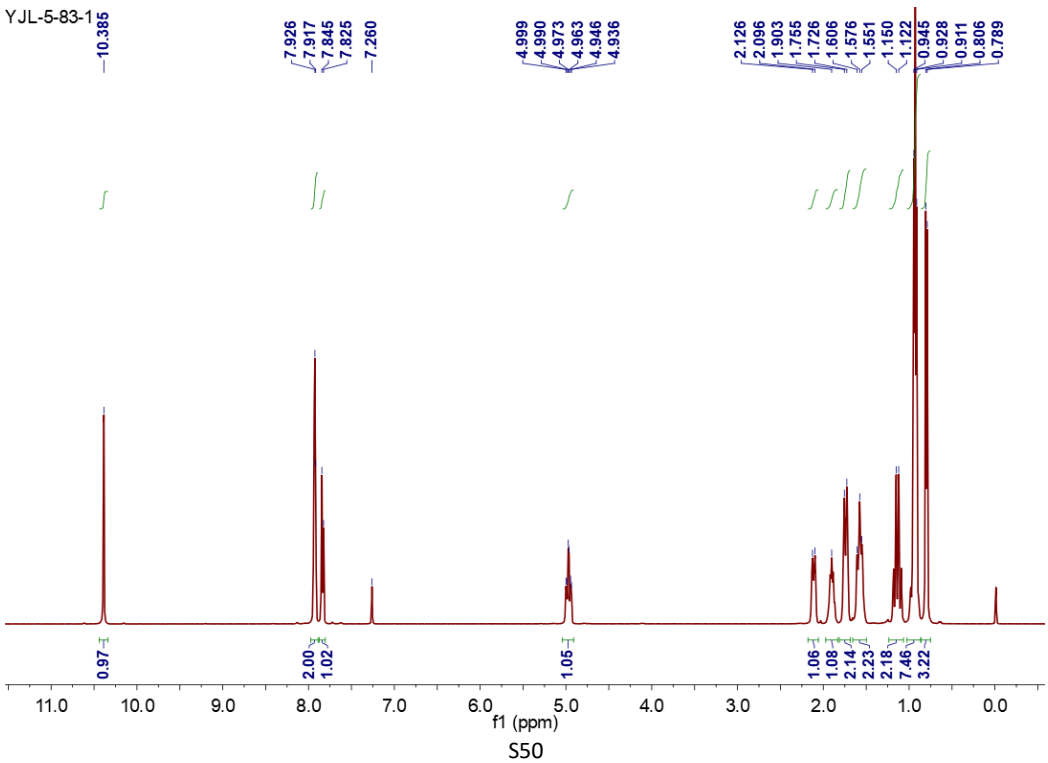

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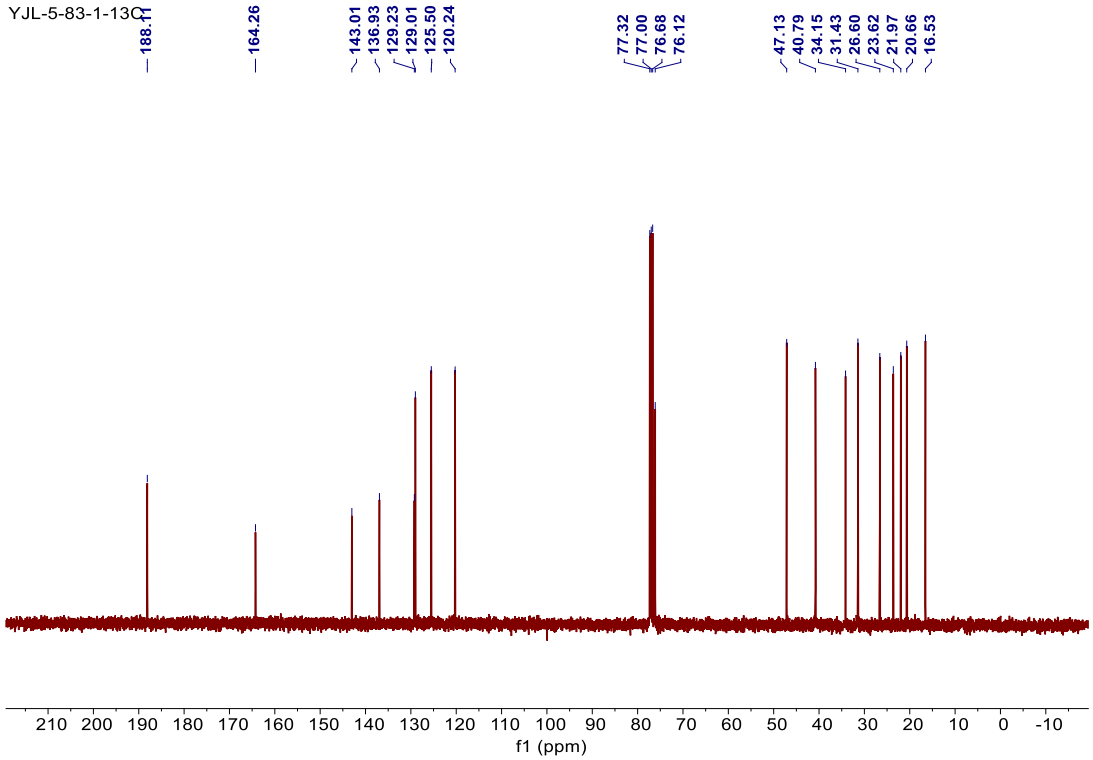


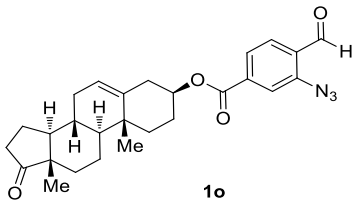


**1o**

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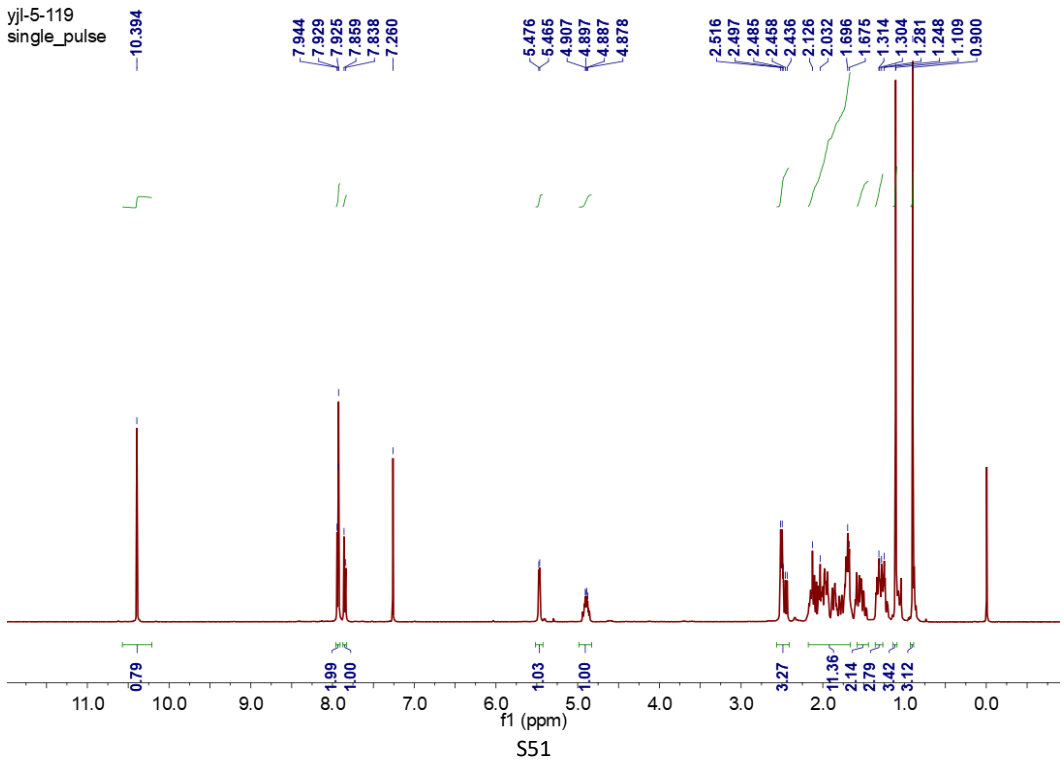

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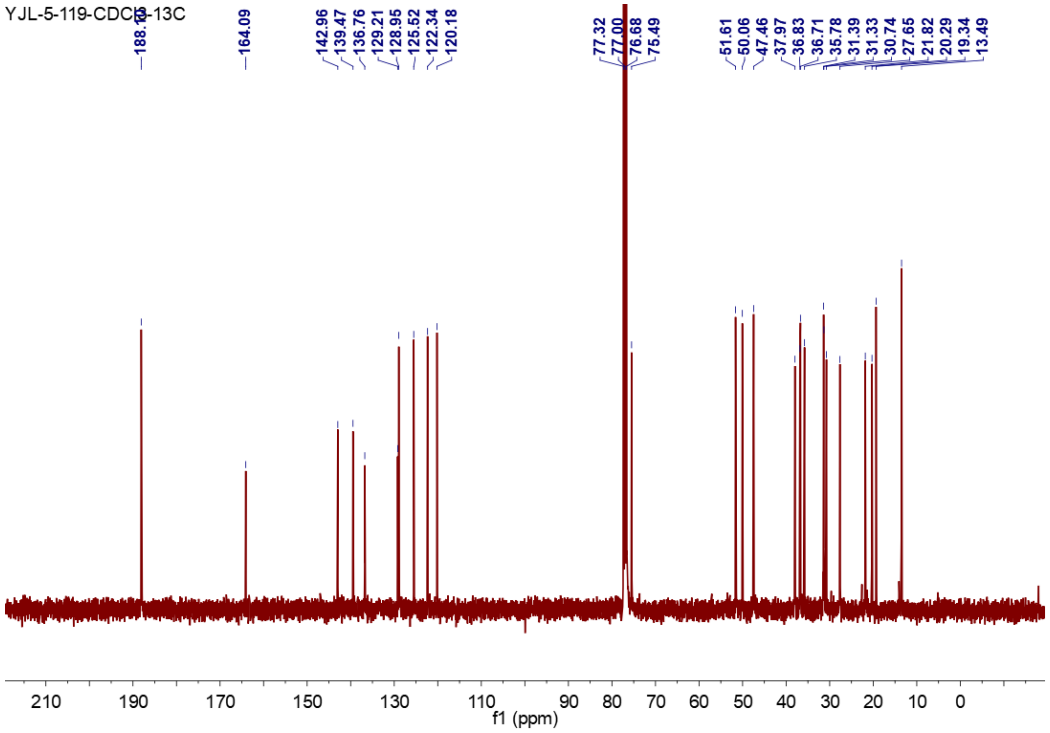


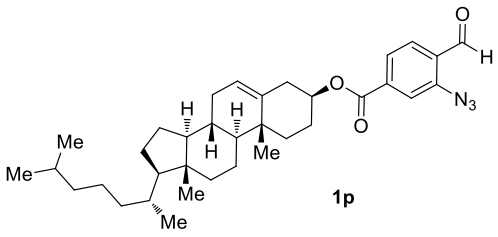


**1p**

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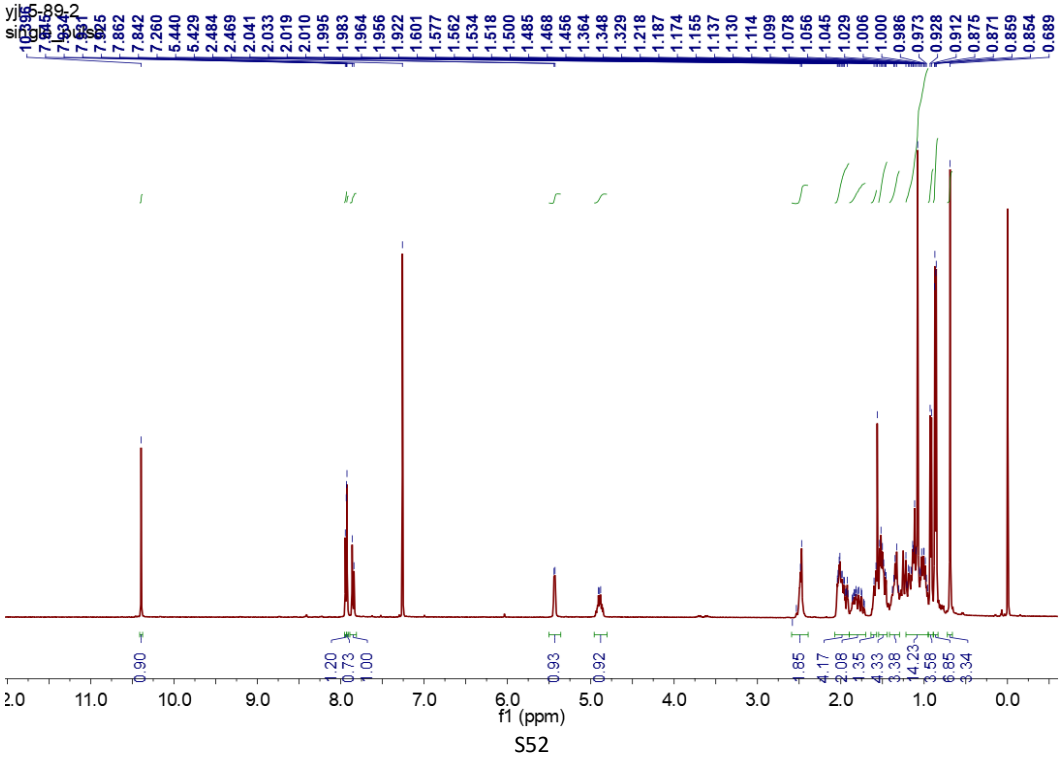

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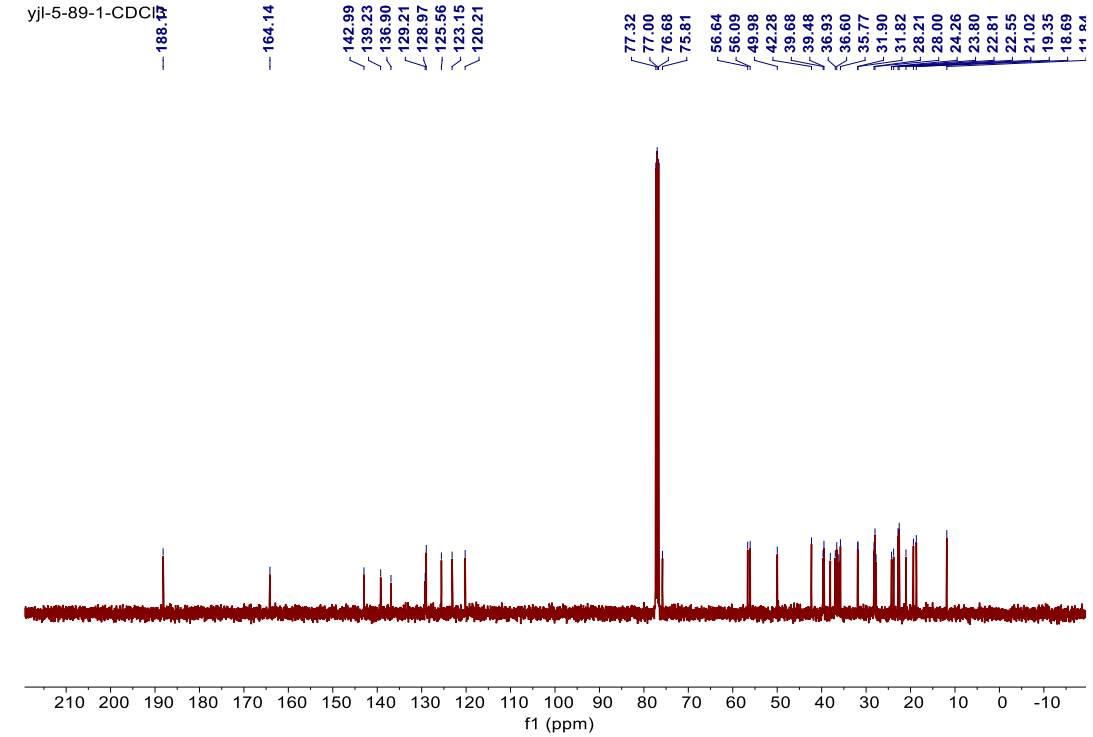


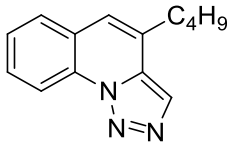


**3aa**

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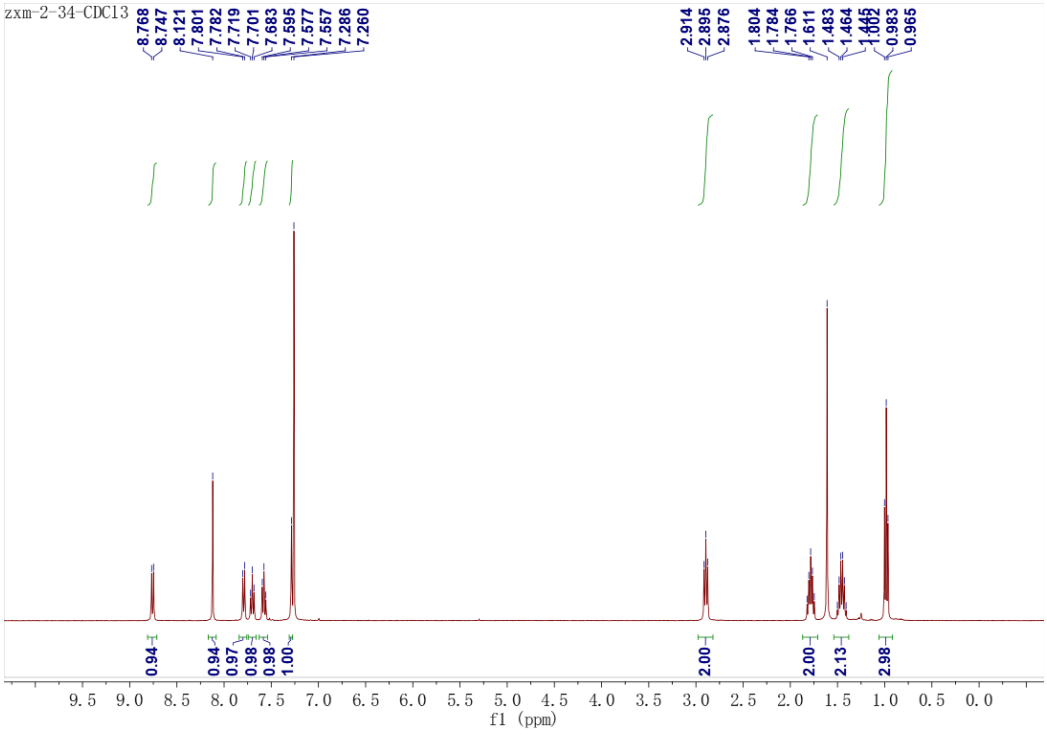

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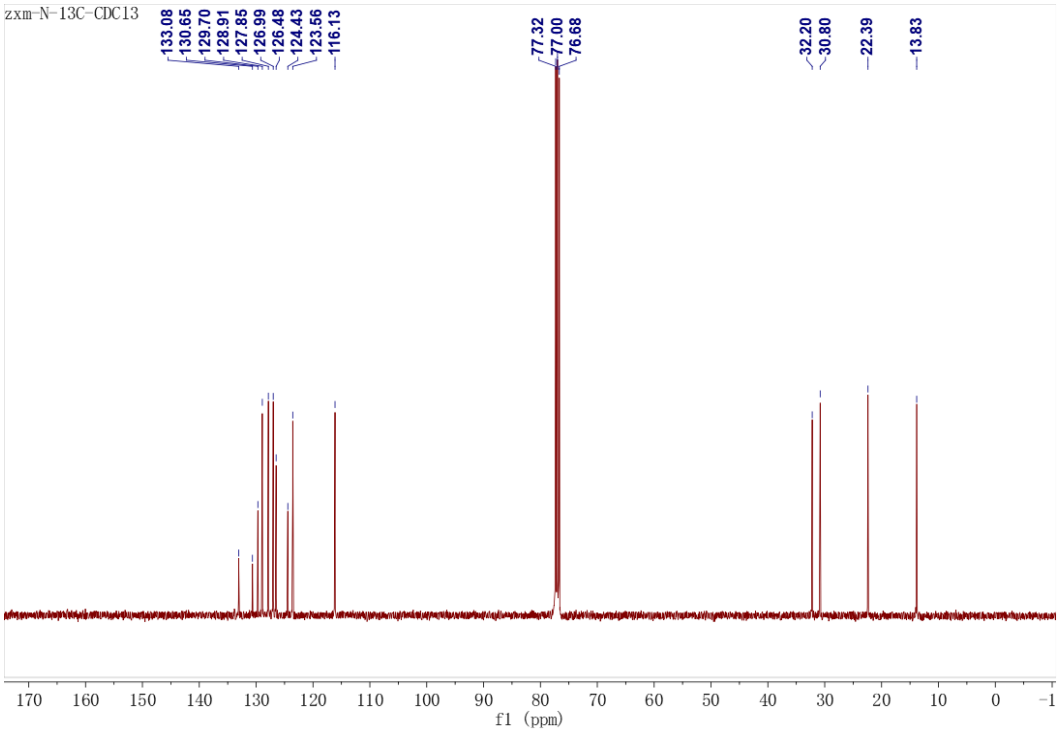


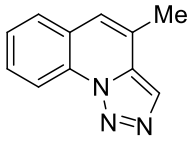


**3ab**

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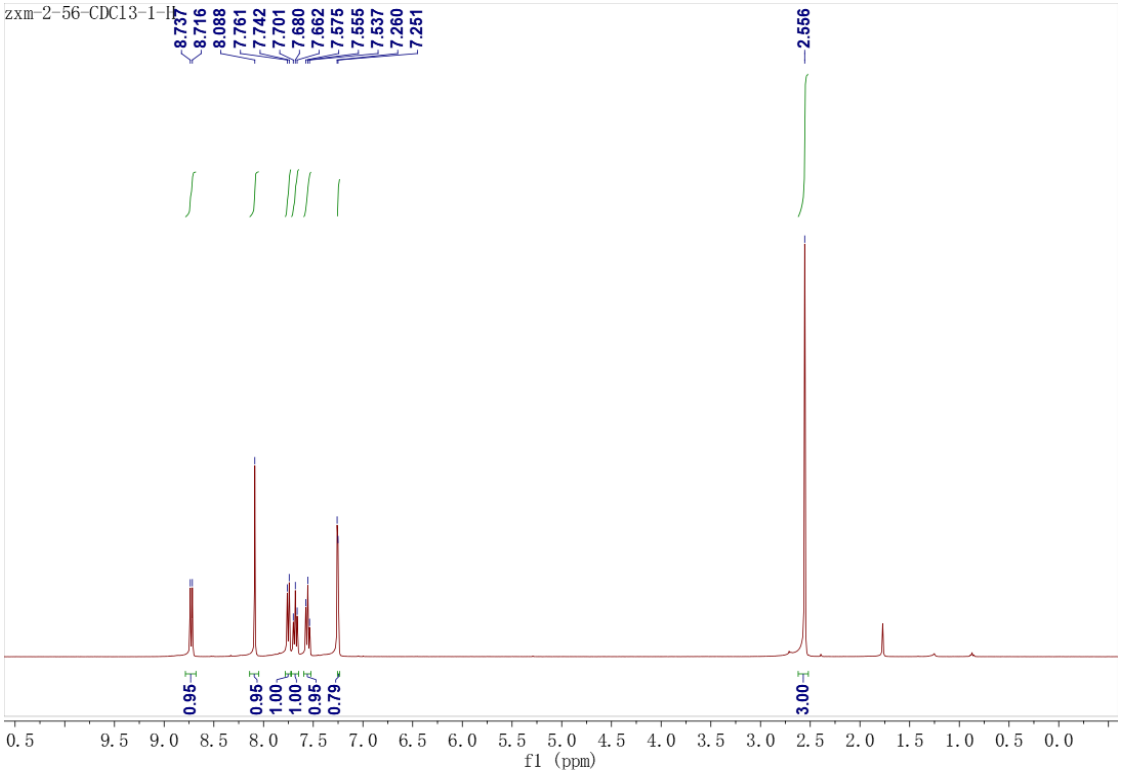

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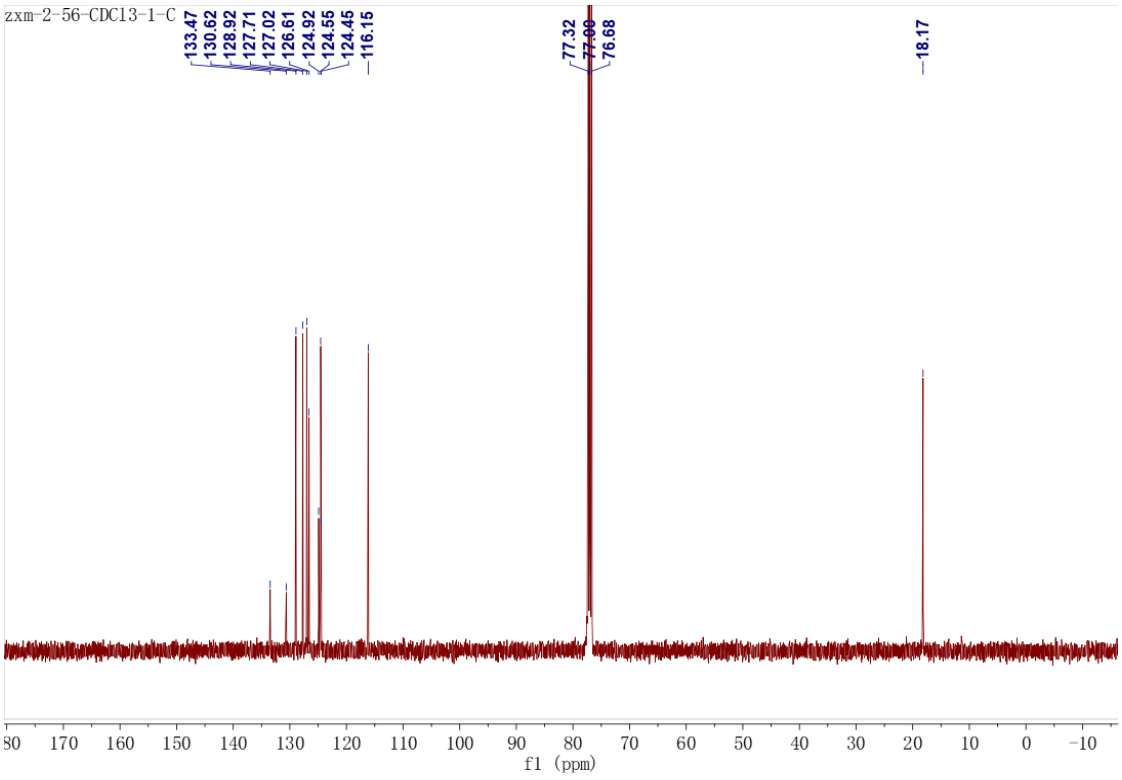
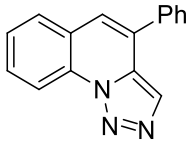
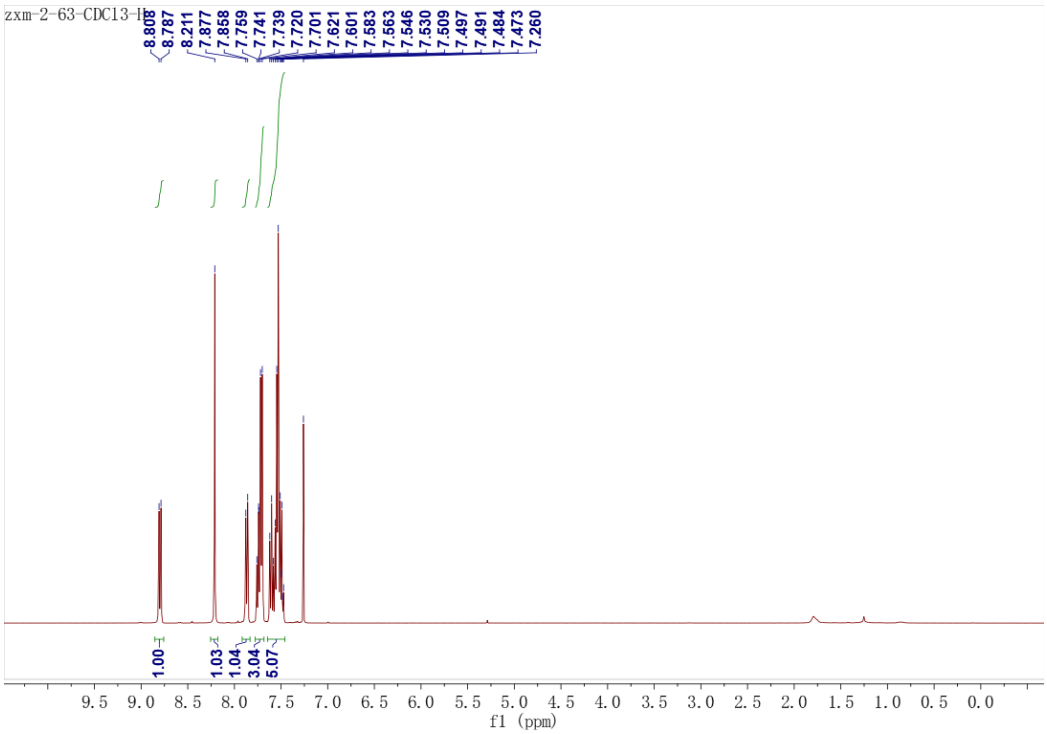


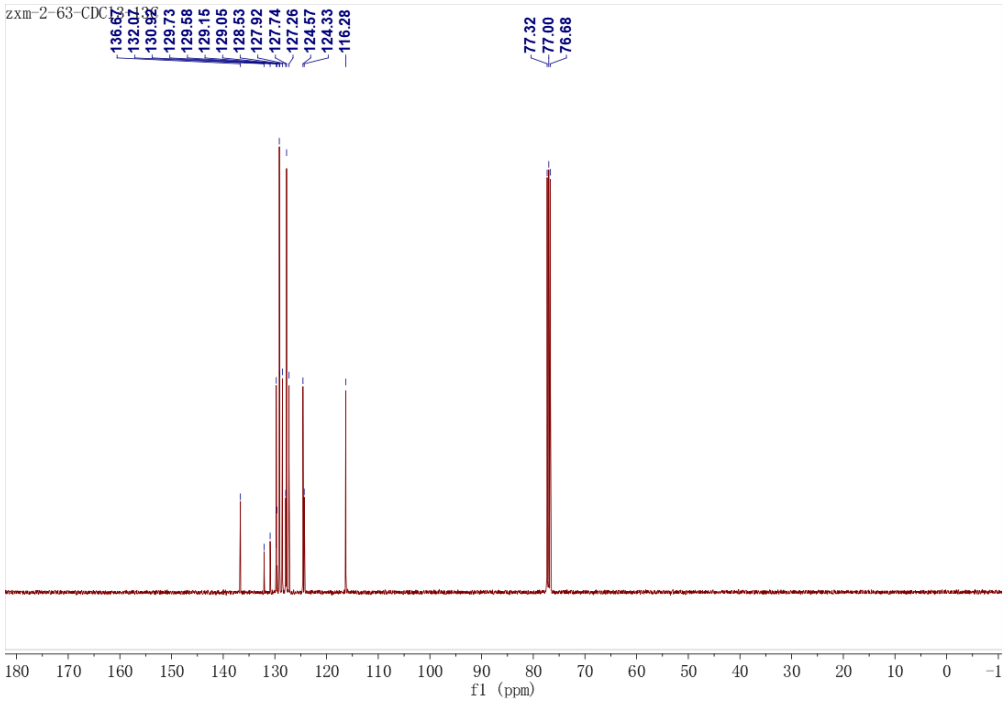



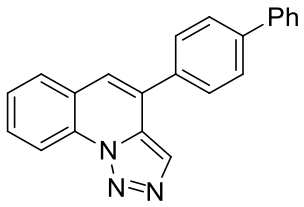

**3ac**

$^{1}$H NMR Spectrum of **3ac:**



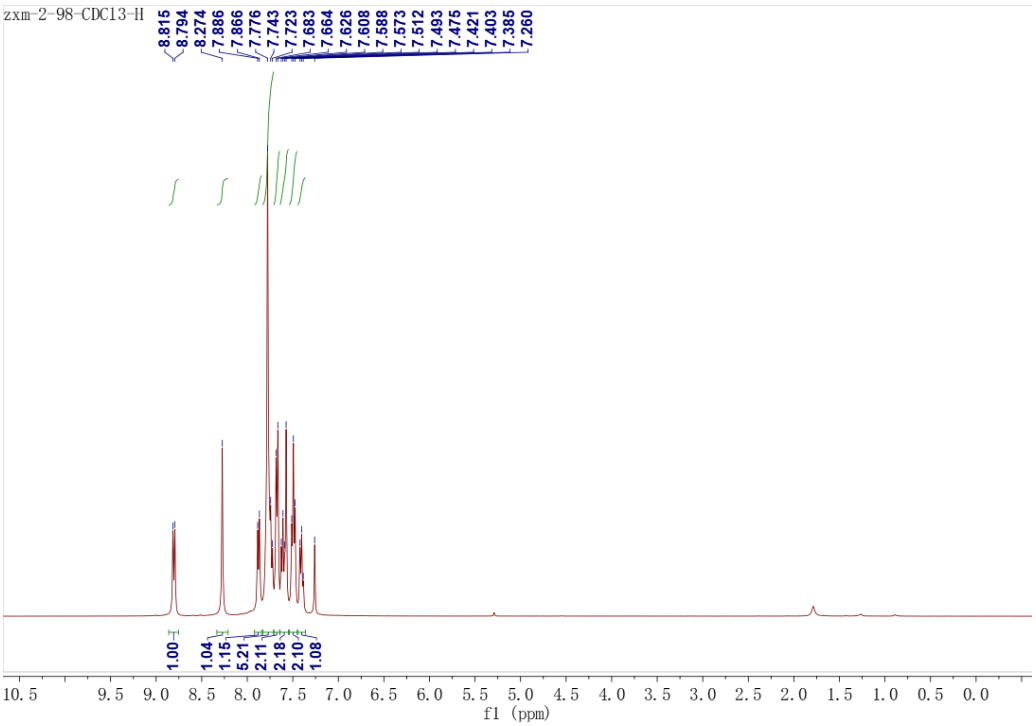
$^{13}$C NMR Spectrum of **3ac:**



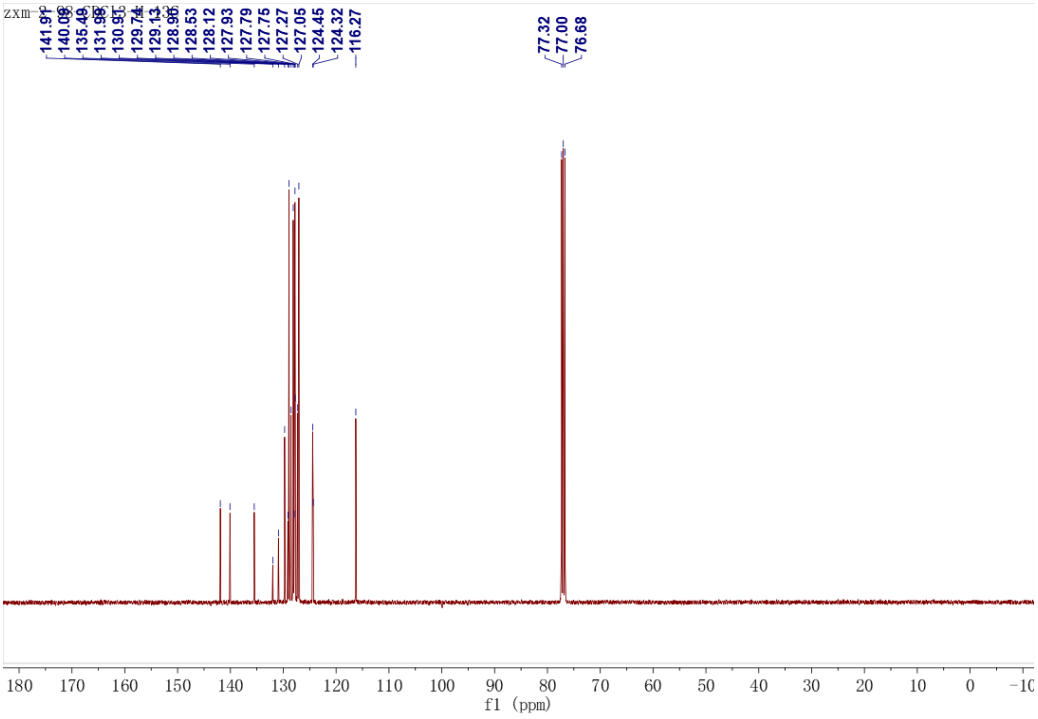



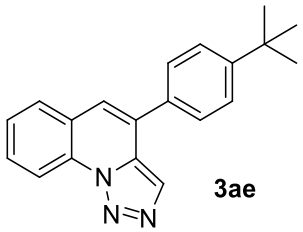

**3ad**

$^{1}$H NMR Spectrum of **3ad:**



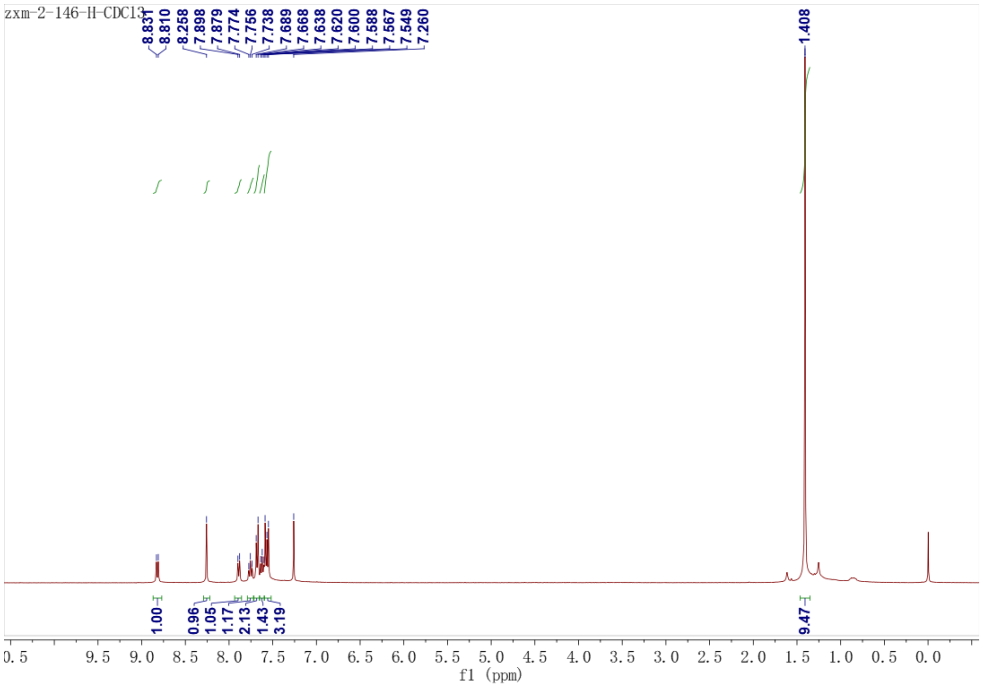
$^{13}$C NMR Spectrum of **3ad:**



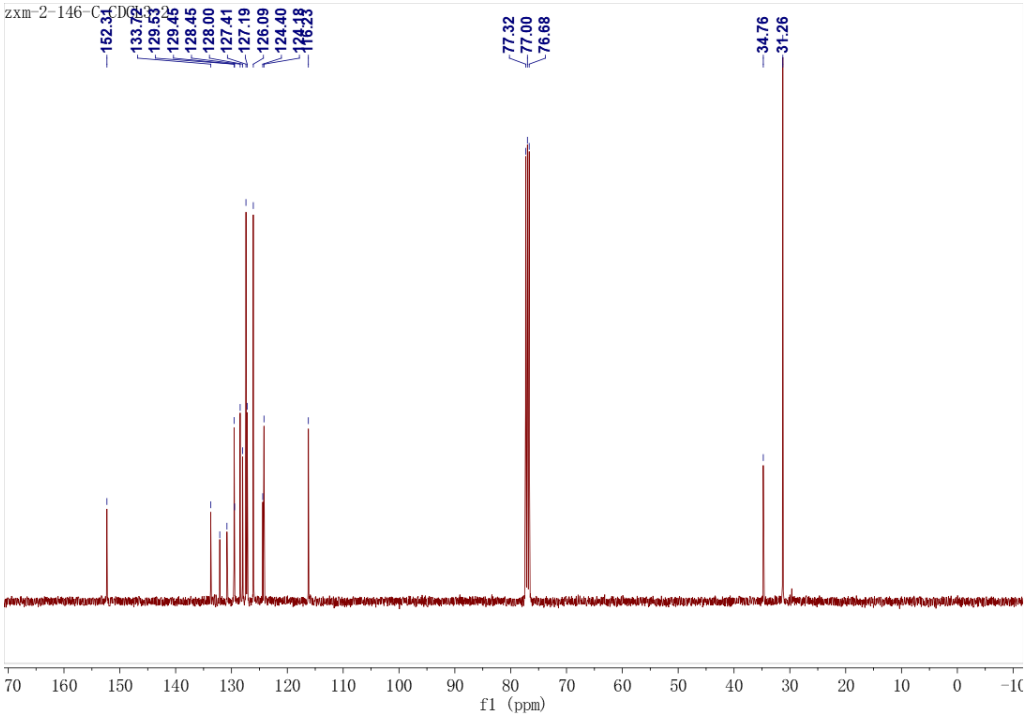



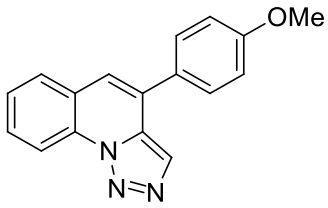

**3ae**

$^{1}$H NMR Spectrum of **3ae:**



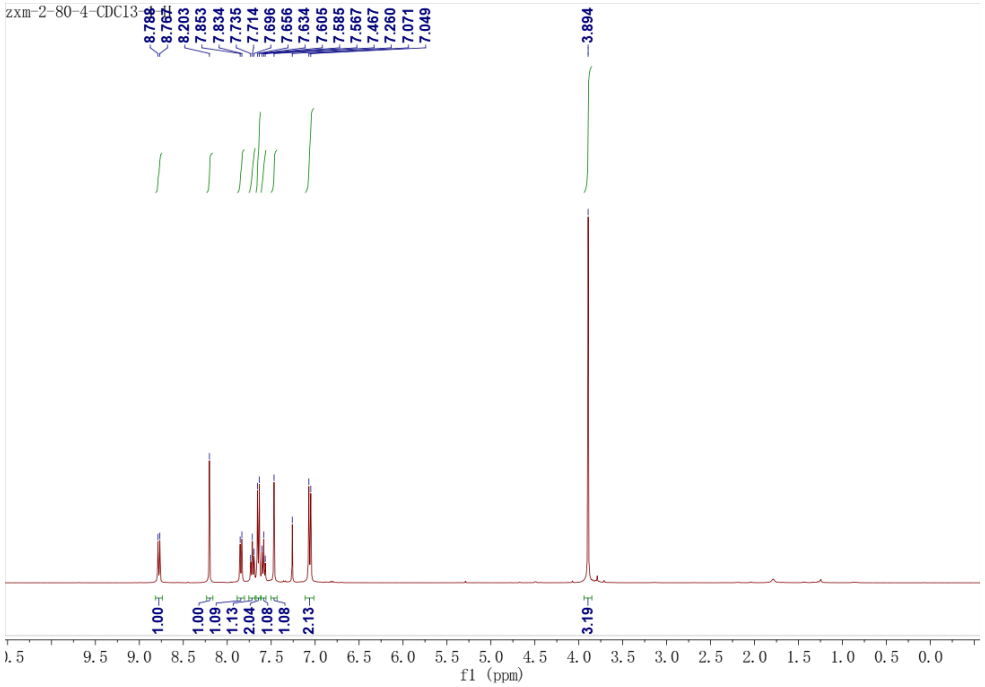
$^{13}$C NMR Spectrum of **3ae:**



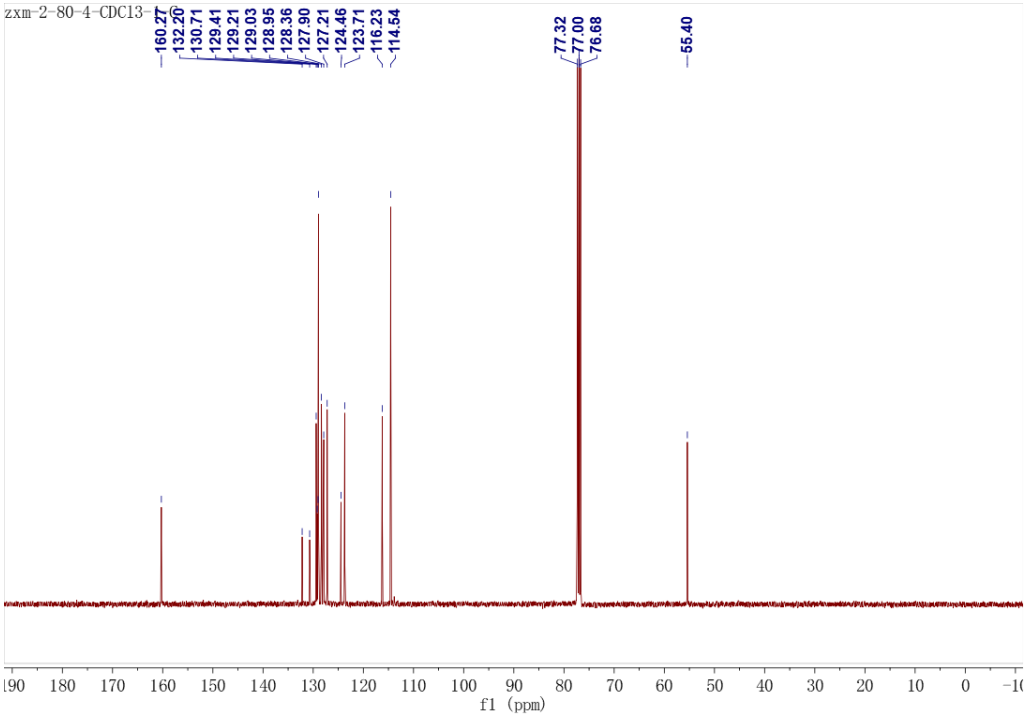



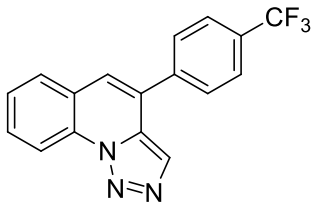

**3af**

$^{1}$H NMR Spectrum of **3af:**



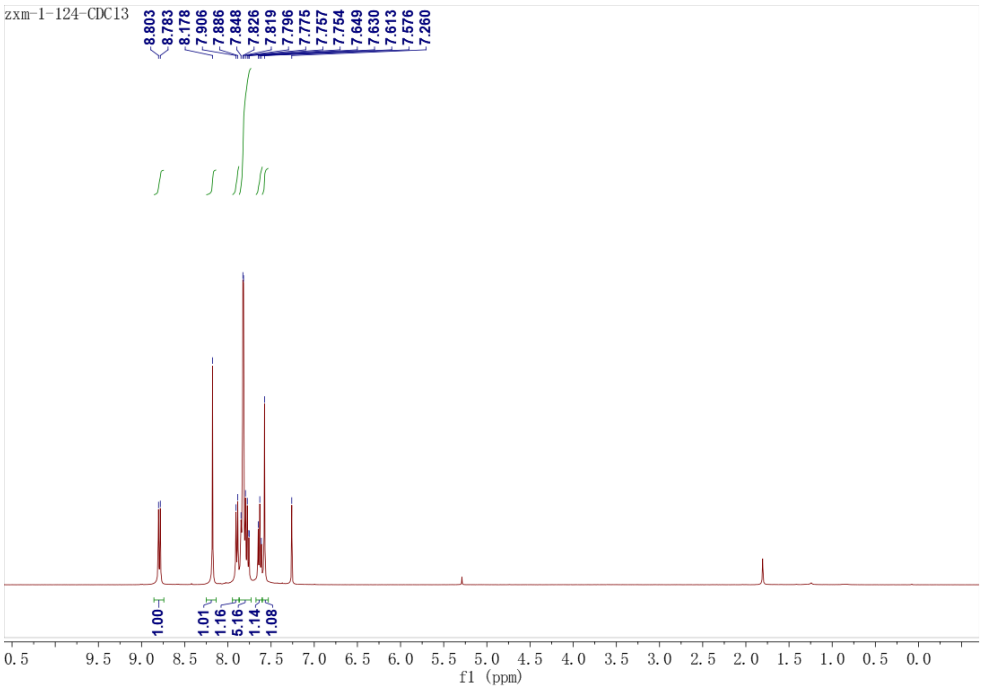
$^{13}$C NMR Spectrum of **3af:**



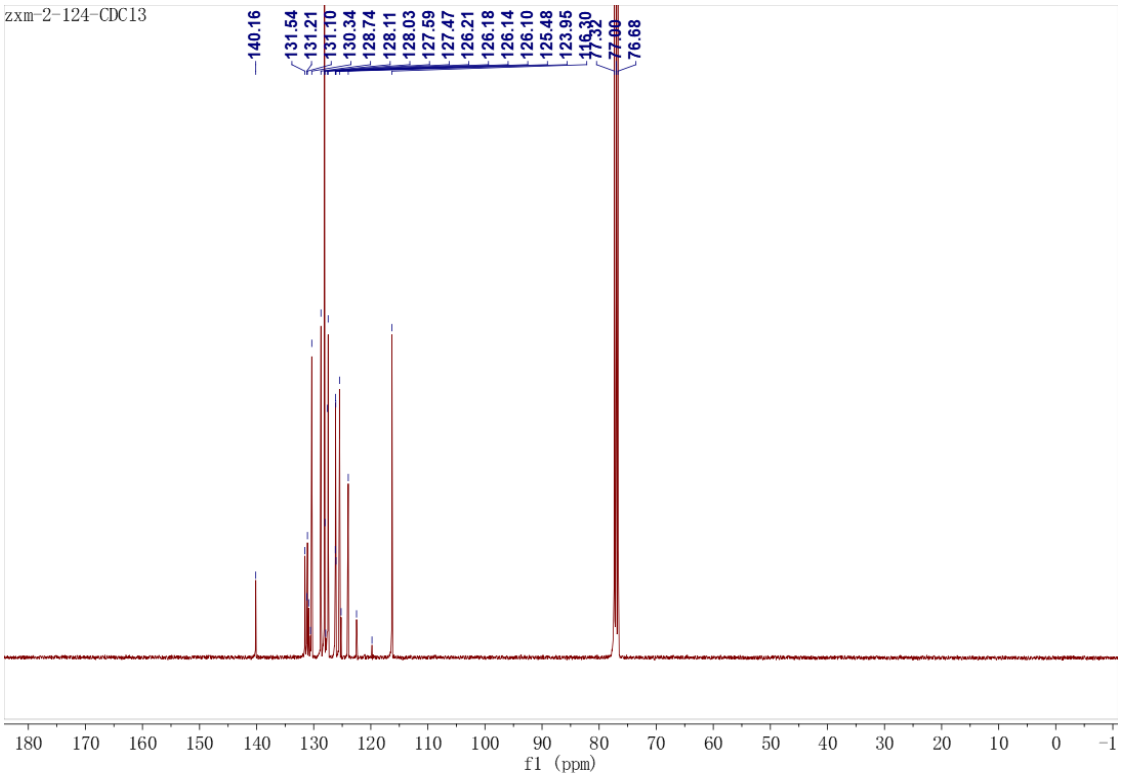




**3ag**

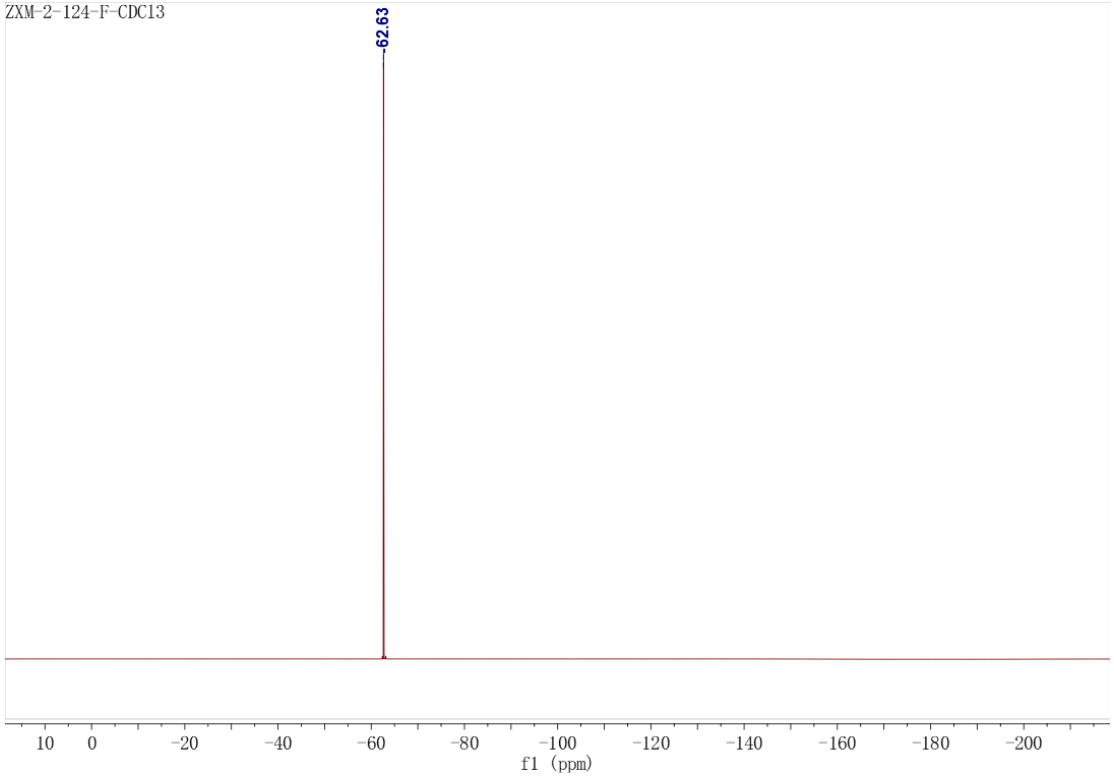
$^{1}$H NMR Spectrum of **3ag:**

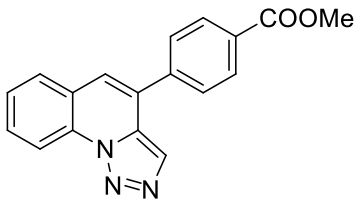


$^{13}$C NMR Spectrum of **3ag:**



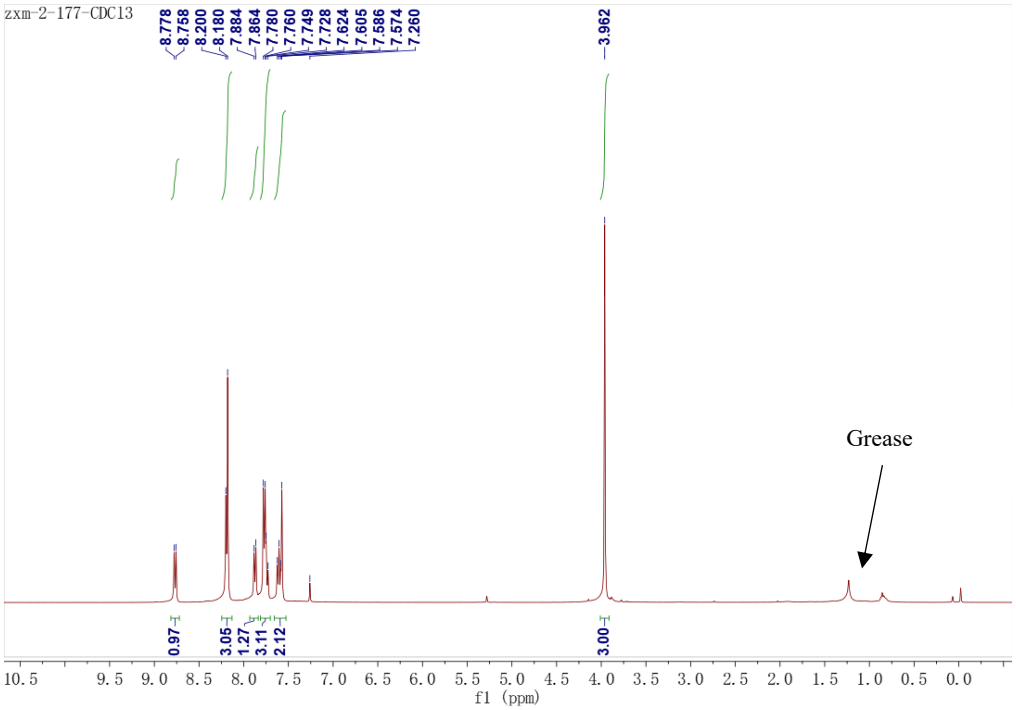

$^{19}$F NMR Spectrum of **3ag:**



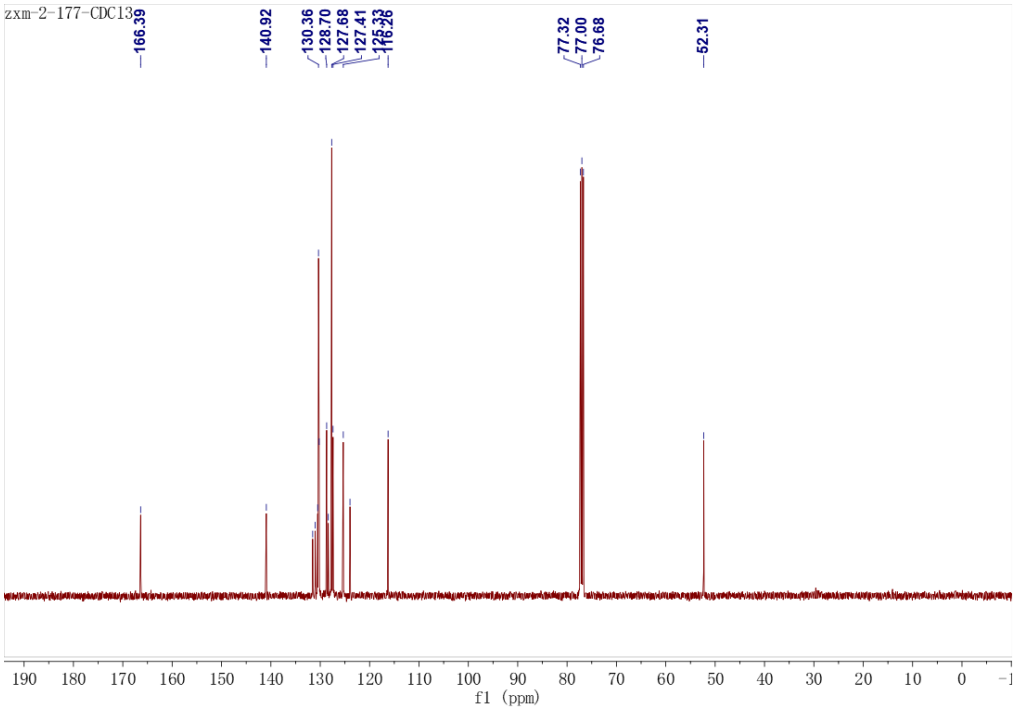


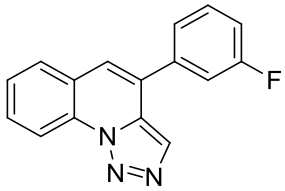

**3ah**

$^{1}$H NMR Spectrum of **3ah:**



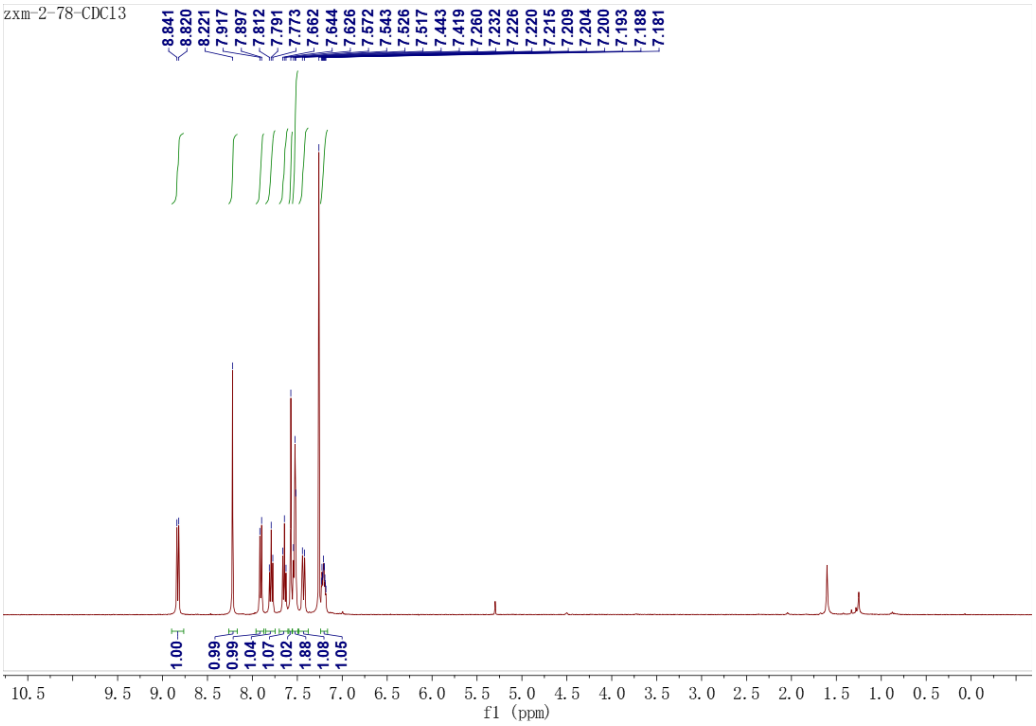

$^{13}$C NMR Spectrum of **3ah:**



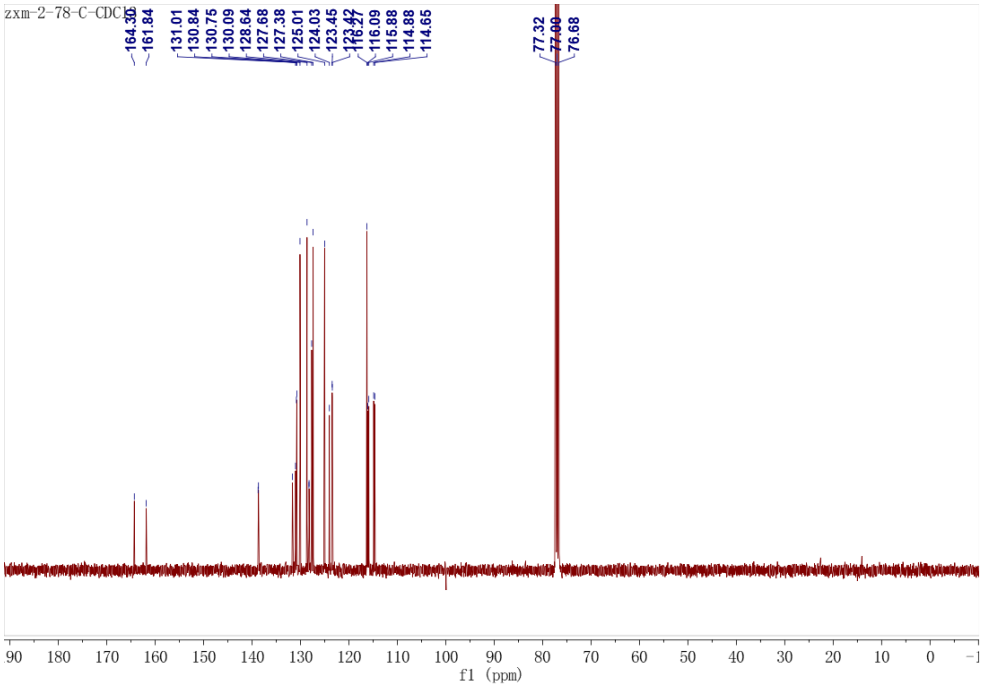



**3ai**

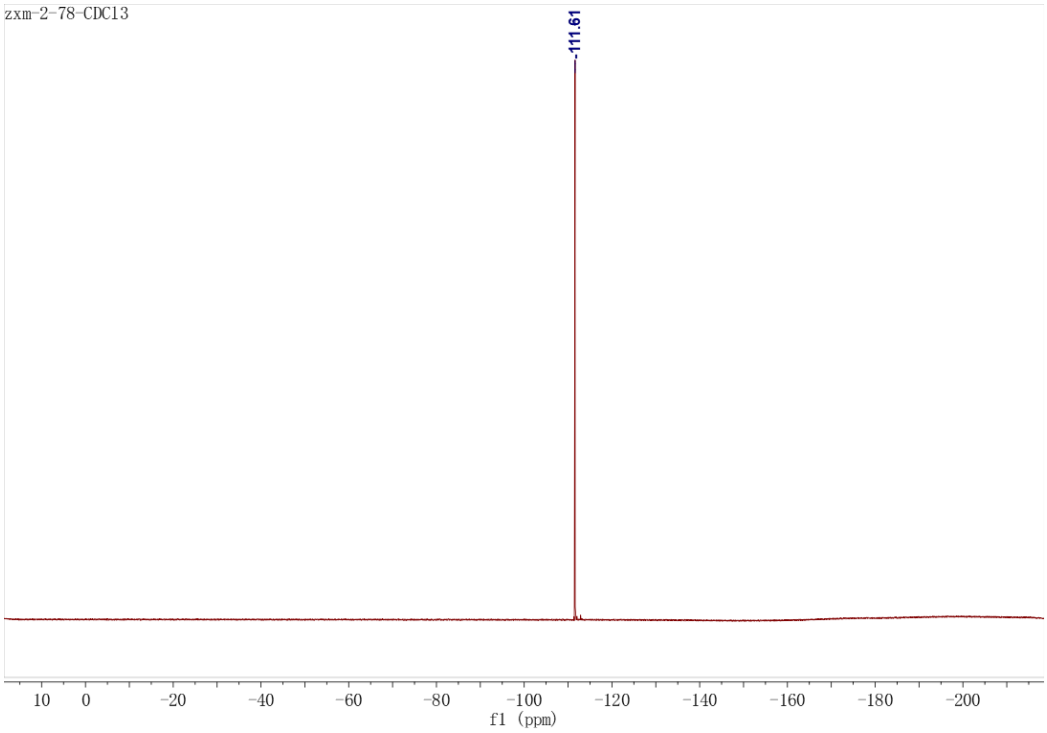
$^{1}$H NMR Spectrum of **3ai:**

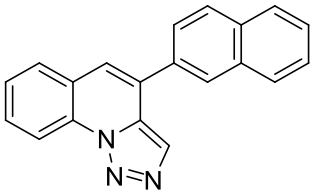



$^{13}$C NMR Spectrum of **3ai:**



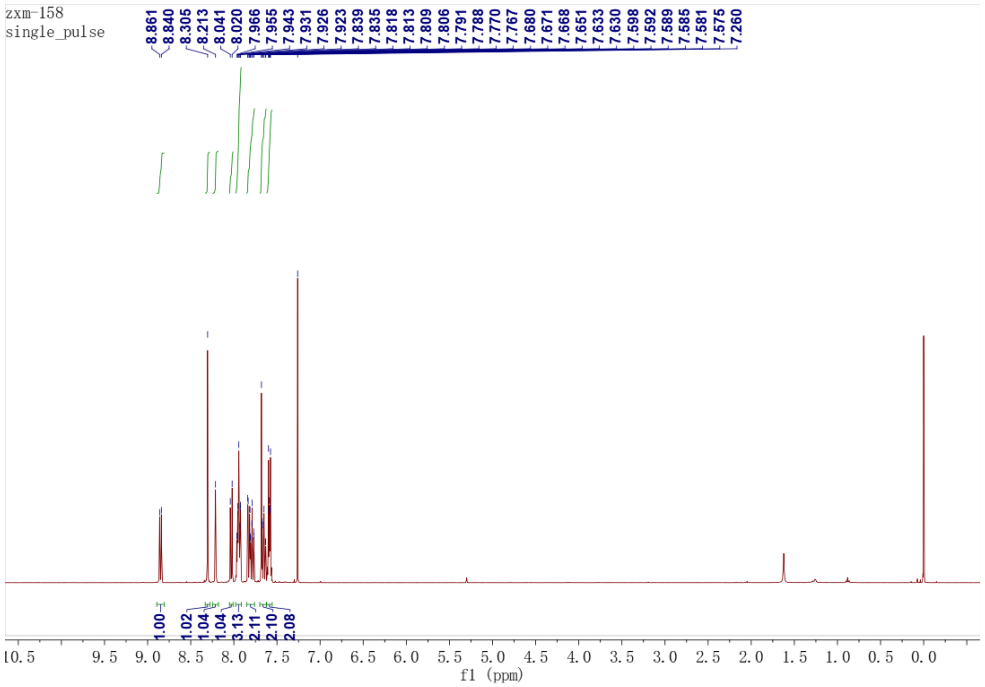
$^{19}$F NMR Spectrum of **3ai:**



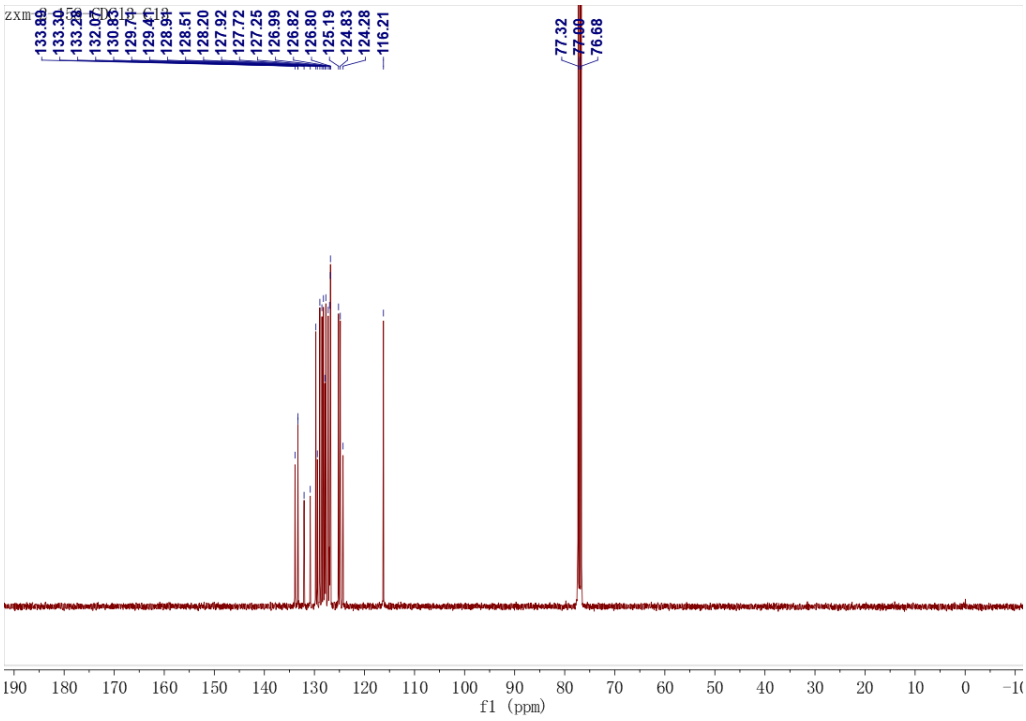



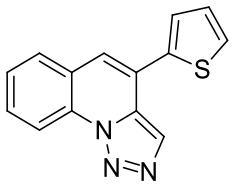
**3aj**

$^{1}$H NMR Spectrum of **3aj:**



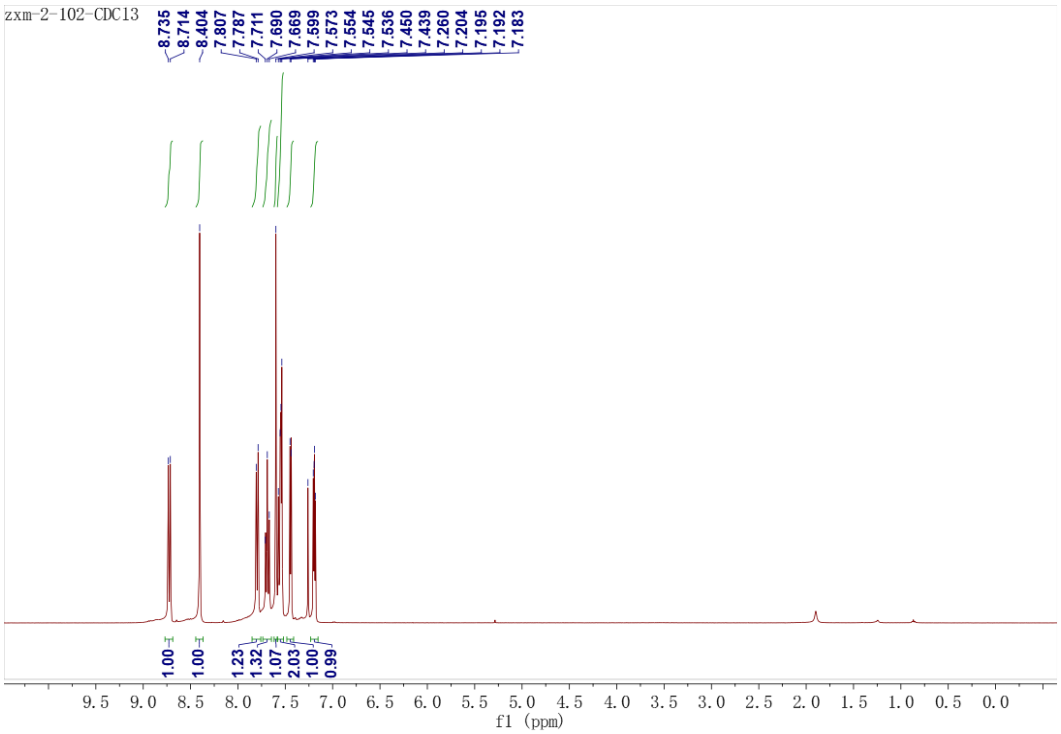
$^{13}$C NMR Spectrum of **3aj:**



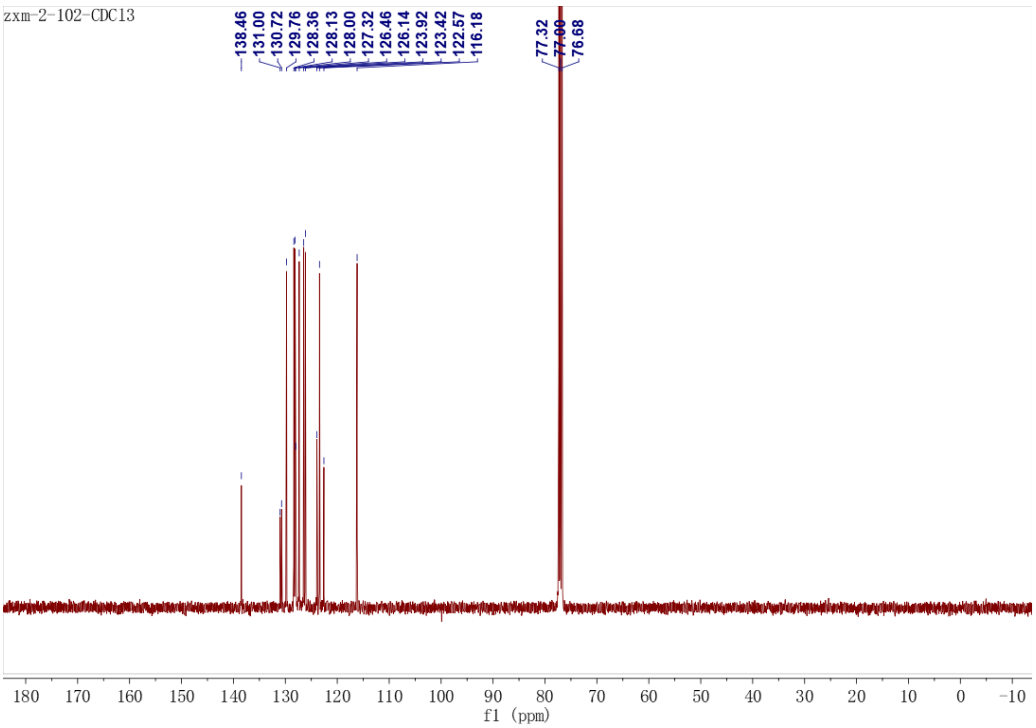



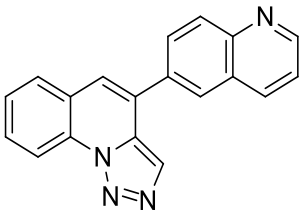

**3ak**

$^{1}$H NMR Spectrum of **3ak:**



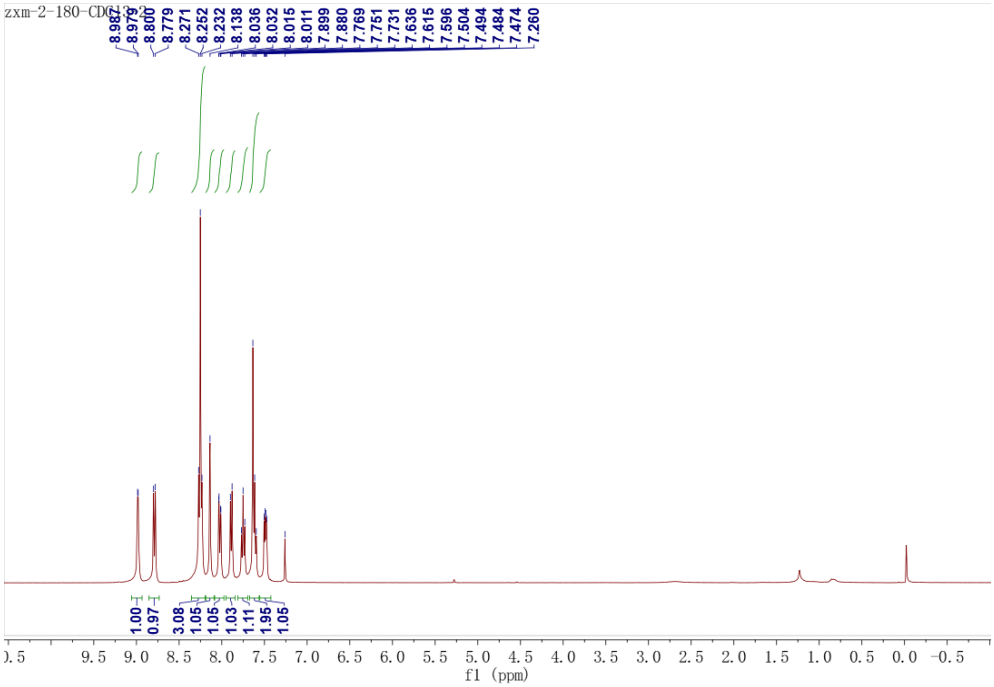
$^{13}$C NMR Spectrum of **3ak:**



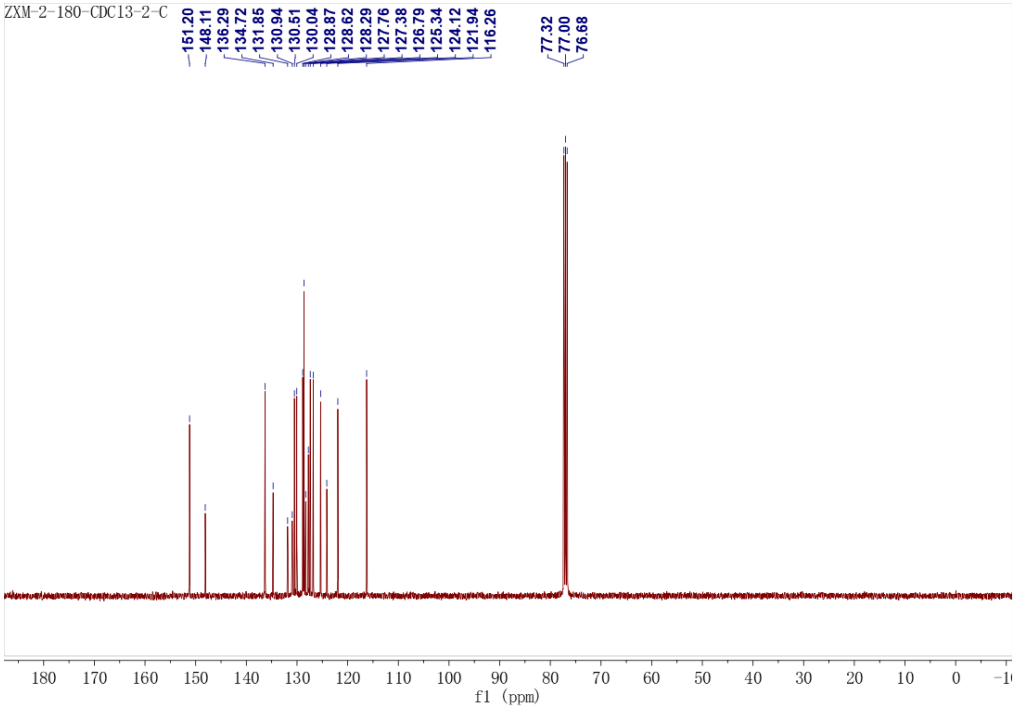



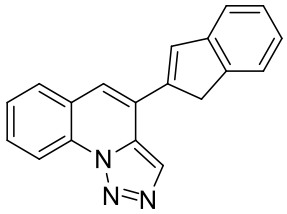

**3al**

$^{1}$H NMR Spectrum of **3al:**



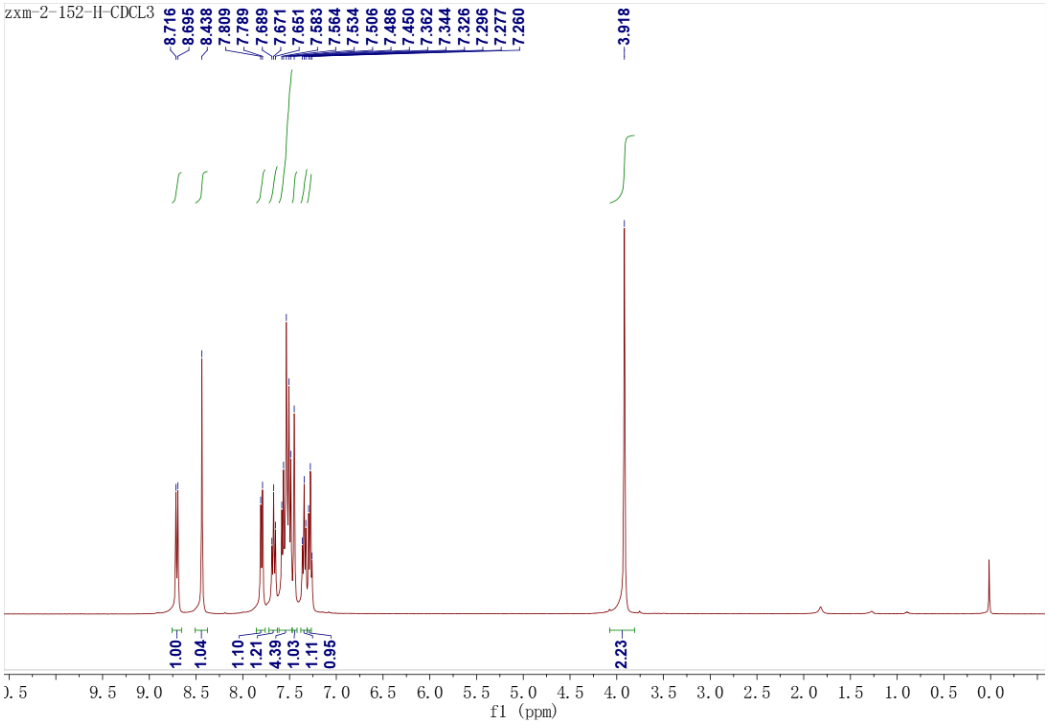
$^{13}$C NMR Spectrum of **3al:**



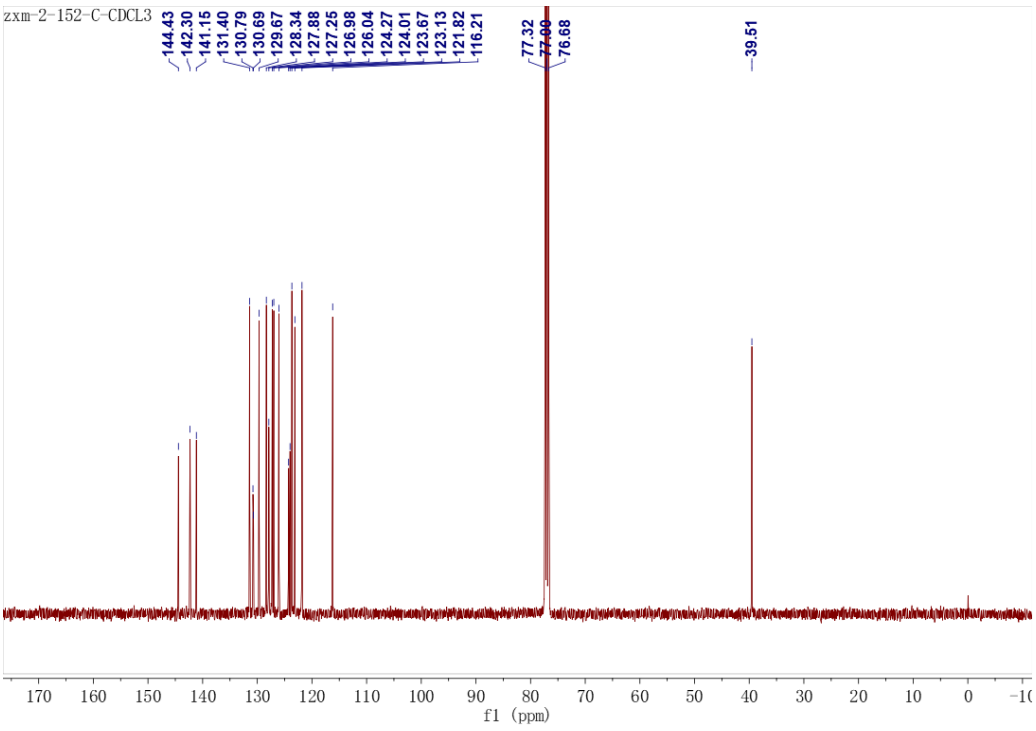



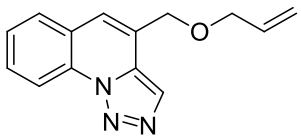
**3am**

$^{1}$H NMR Spectrum of **3am:**



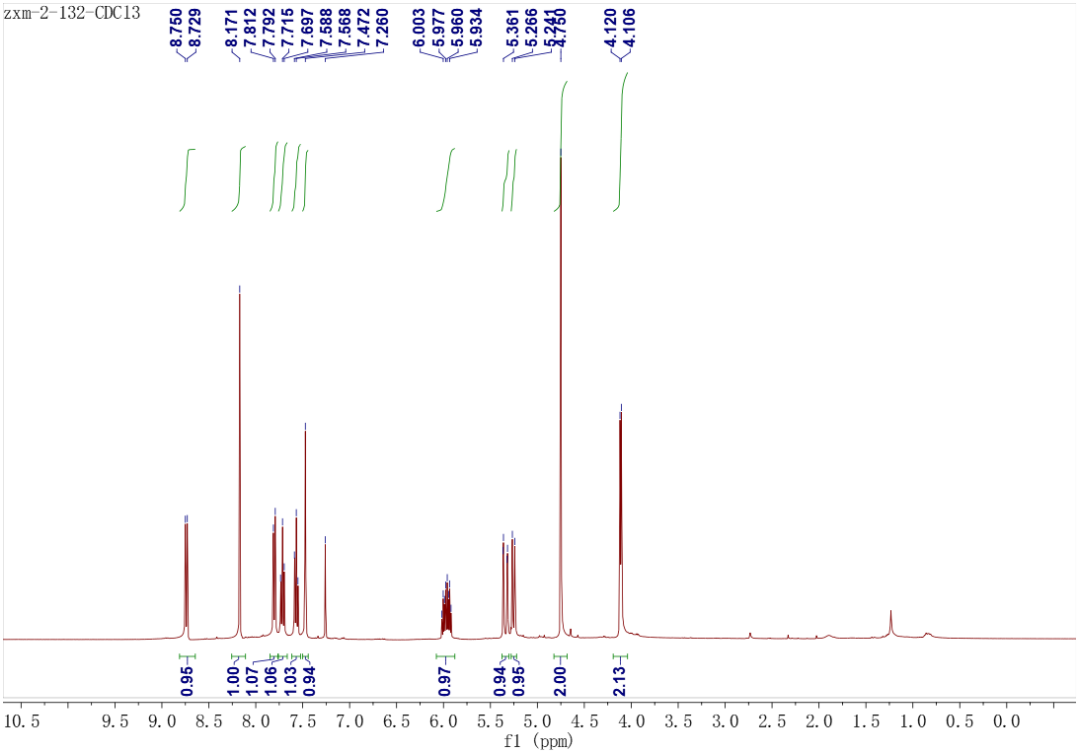
$^{13}$C NMR Spectrum of **3am:**



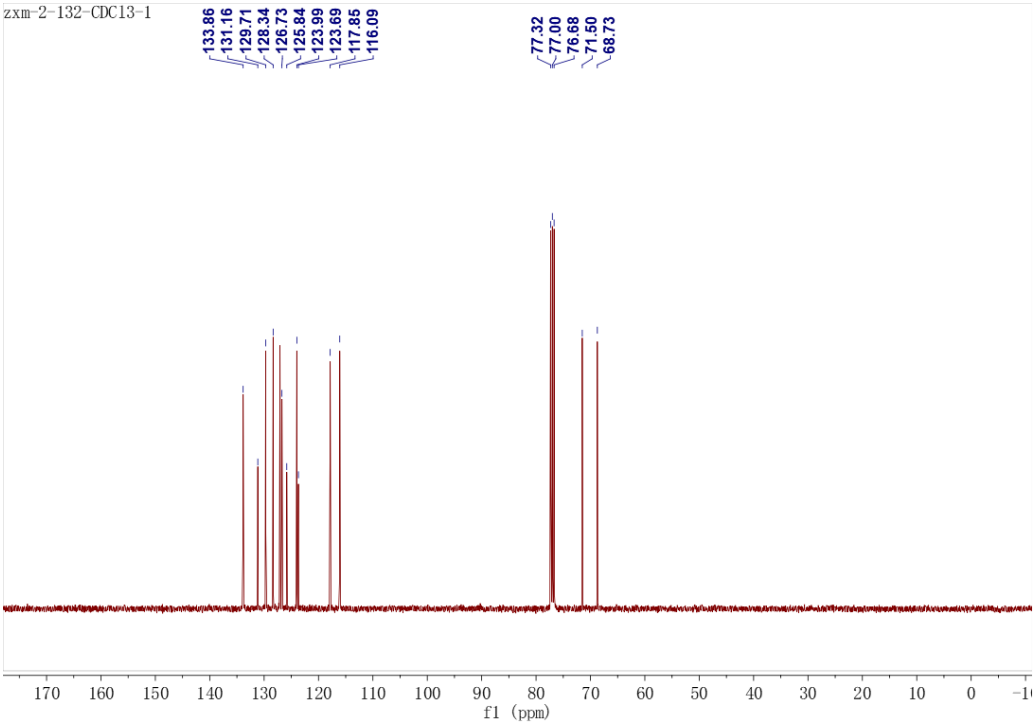



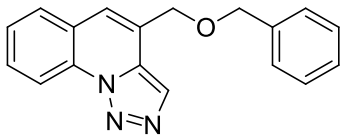

**3an**

$^{1}$H NMR Spectrum of **3an:**



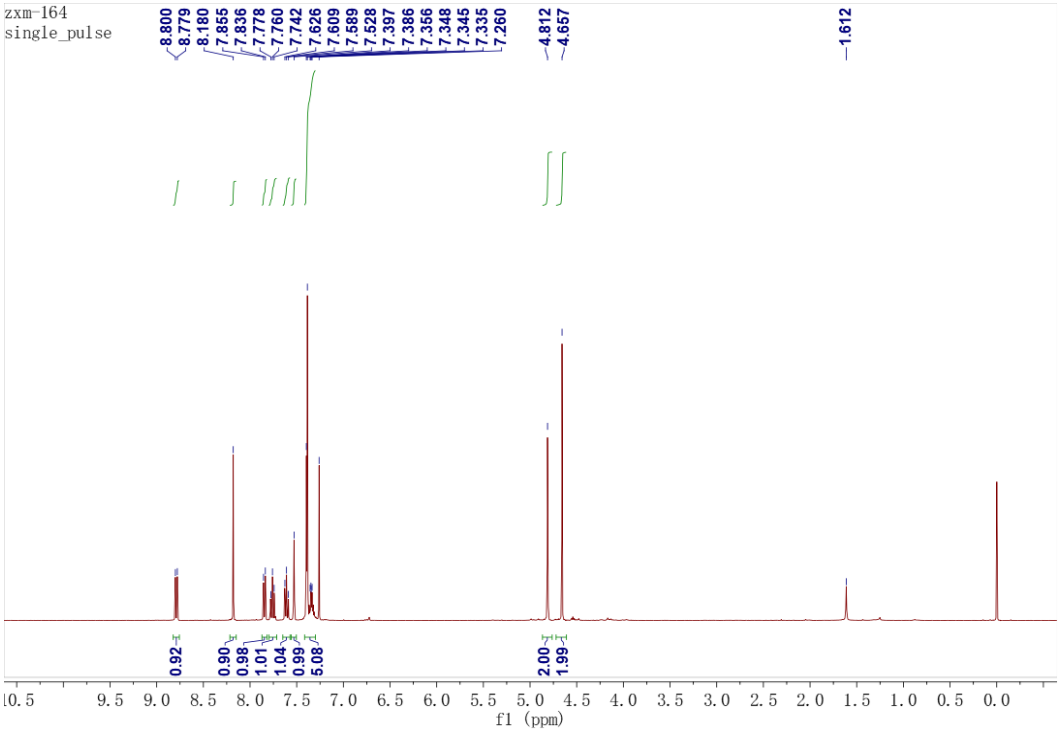
$^{13}$C NMR Spectrum of **3an:**



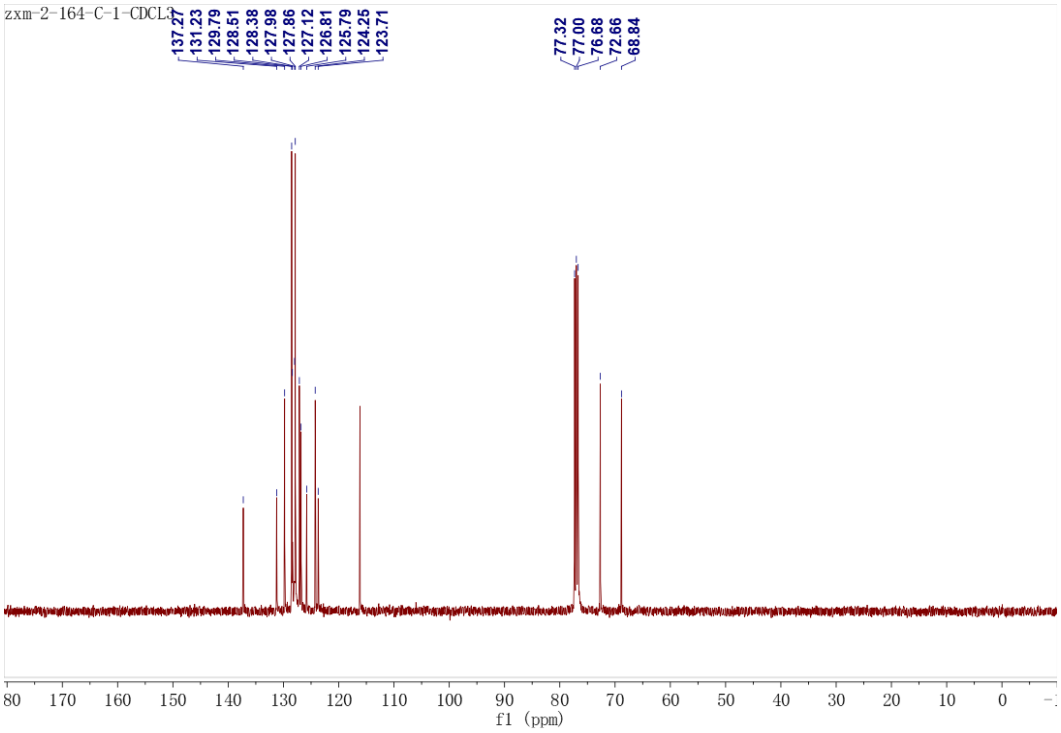



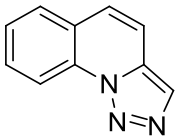
**3ao**

$^{1}$H NMR Spectrum of **3ao:**



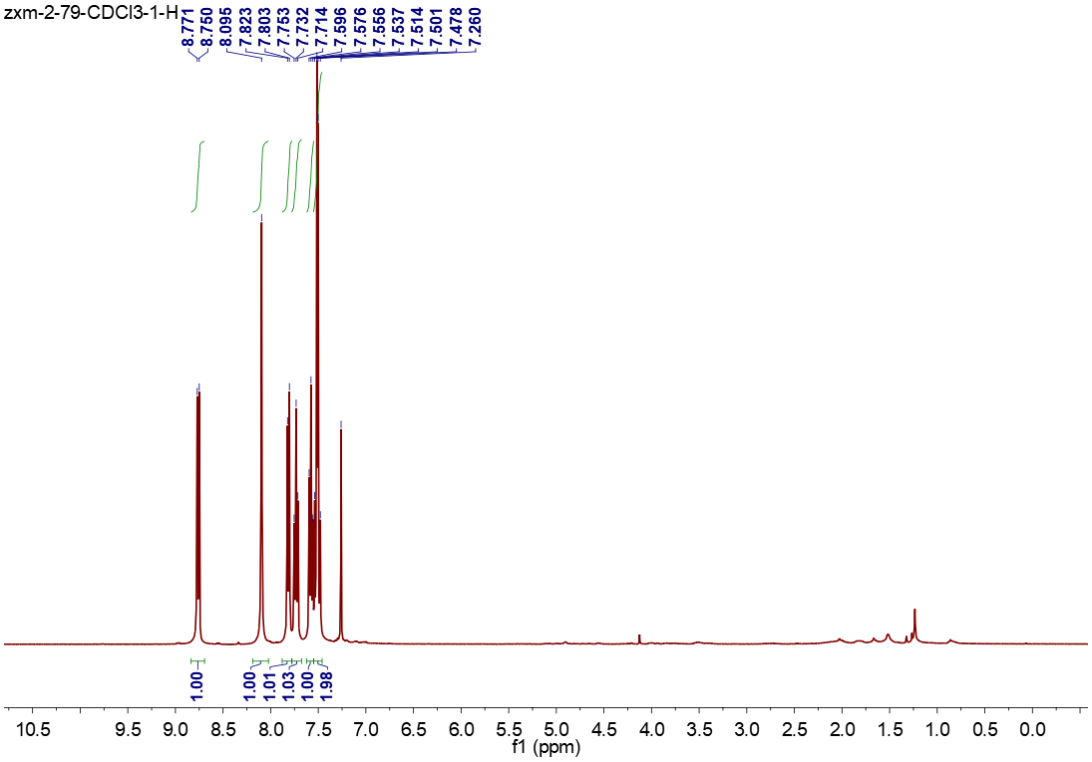
$^{13}$C NMR Spectrum of **3ao:**



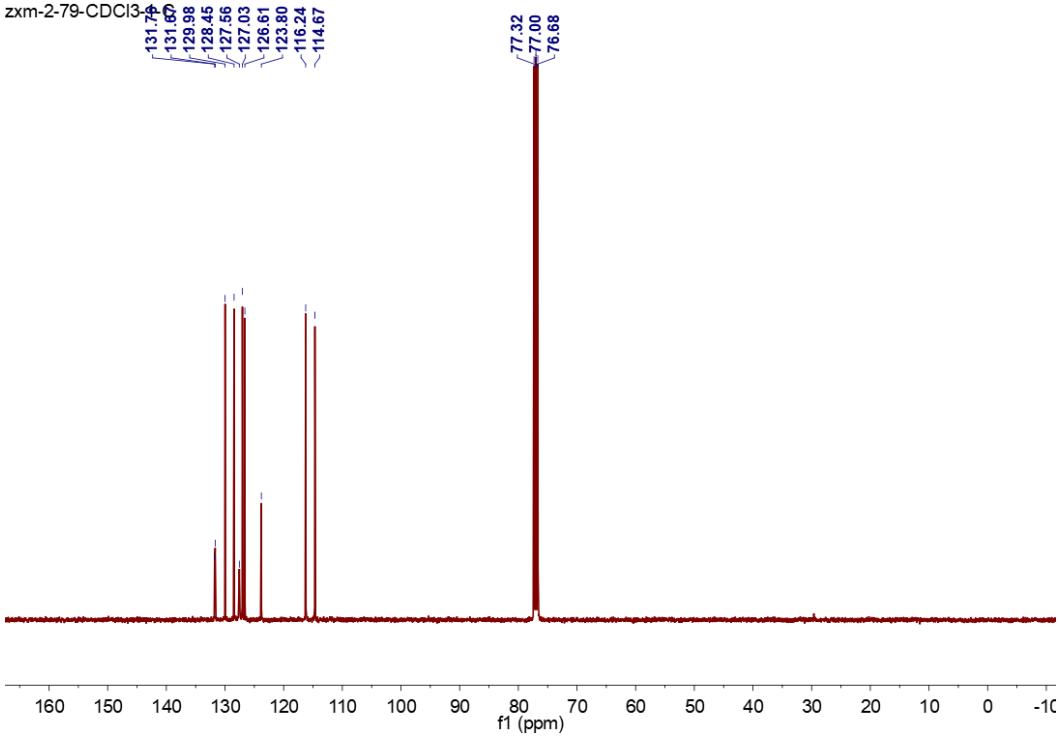



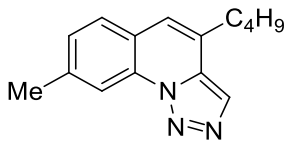
**3ap**

$^{1}$H NMR Spectrum of **3ap:**



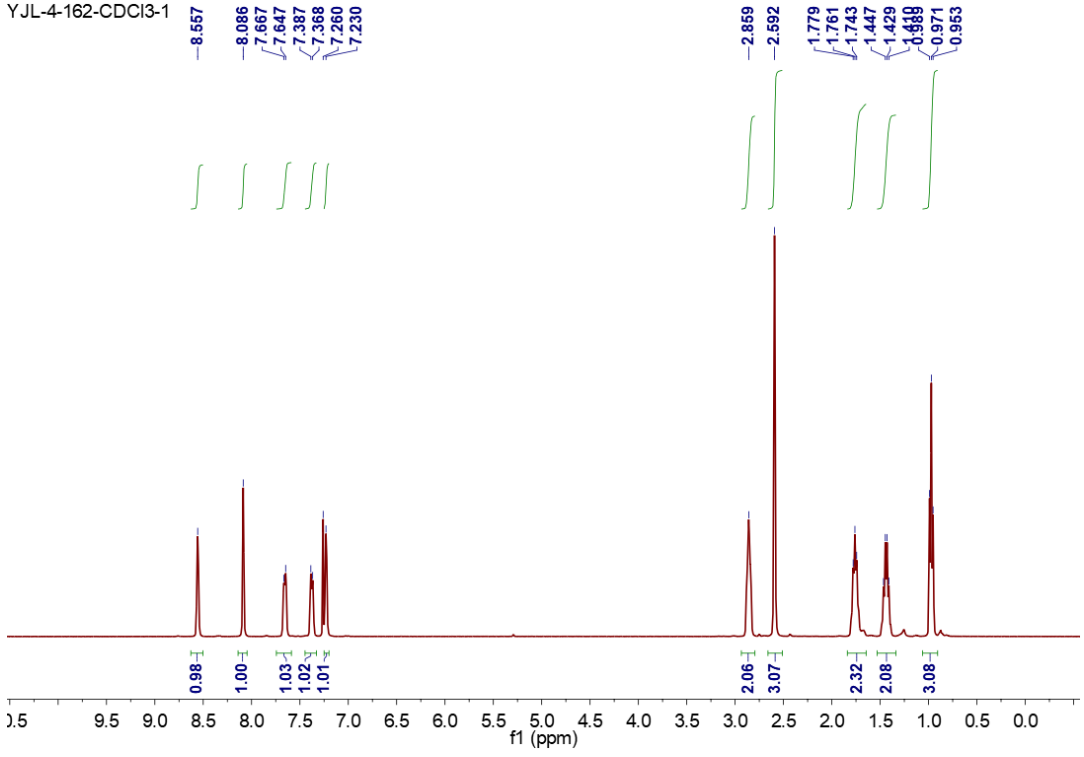
$^{13}$C NMR Spectrum of **3ap:**



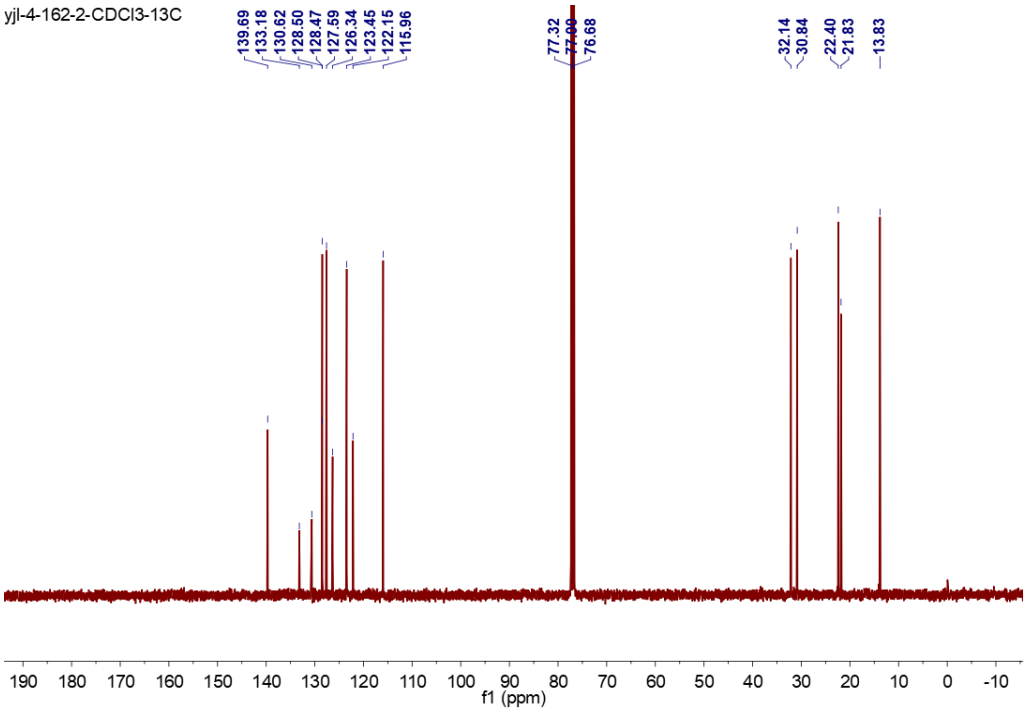



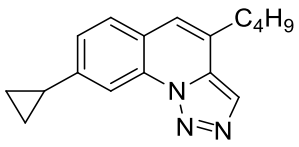

**3ba**

$^{1}$H NMR Spectrum of **3ba:**



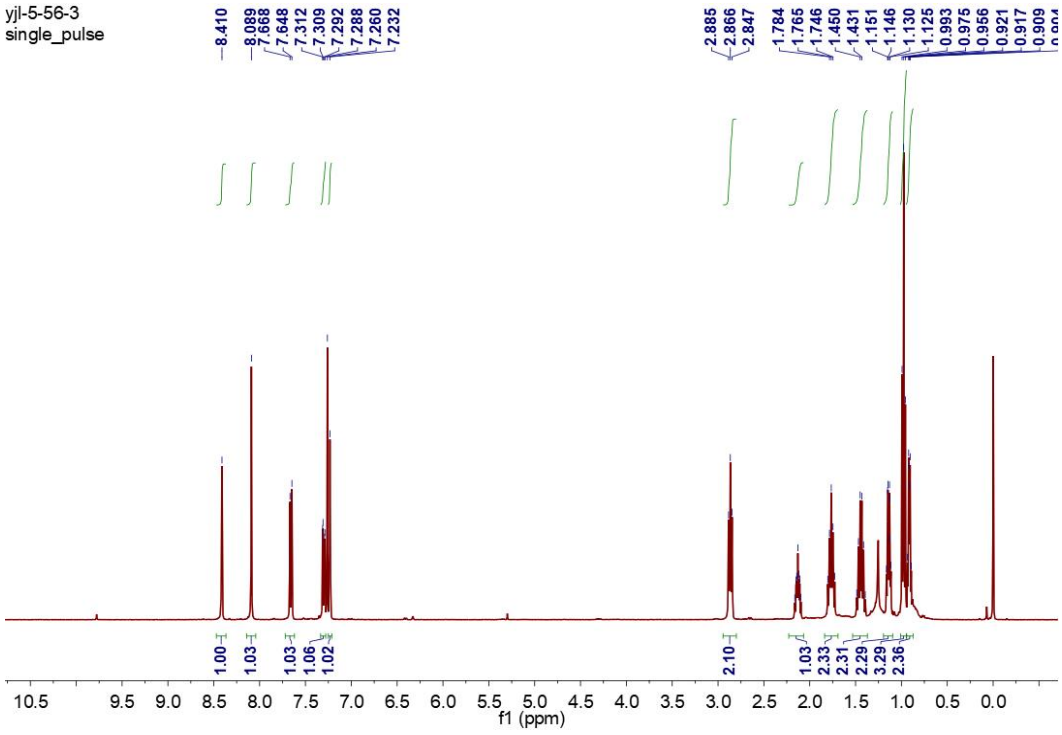
$^{13}$C NMR Spectrum of **3ba:**



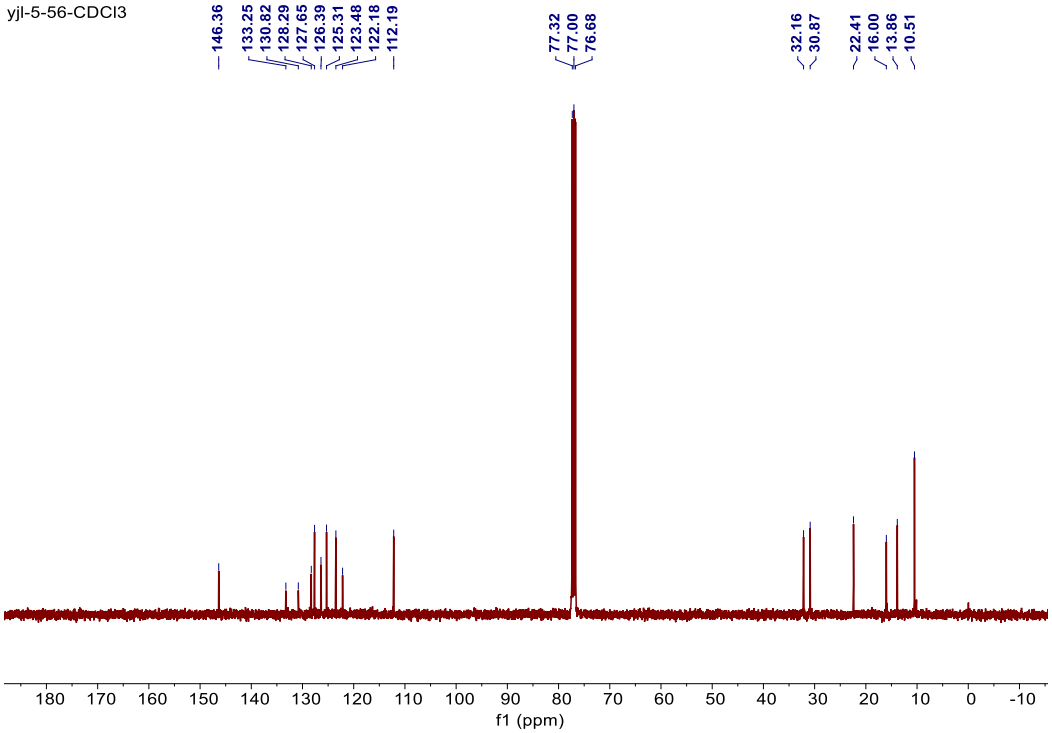



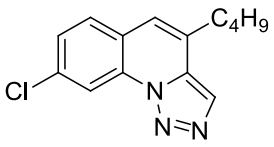

**3ca**

$^{1}$H NMR Spectrum of **3ca:**



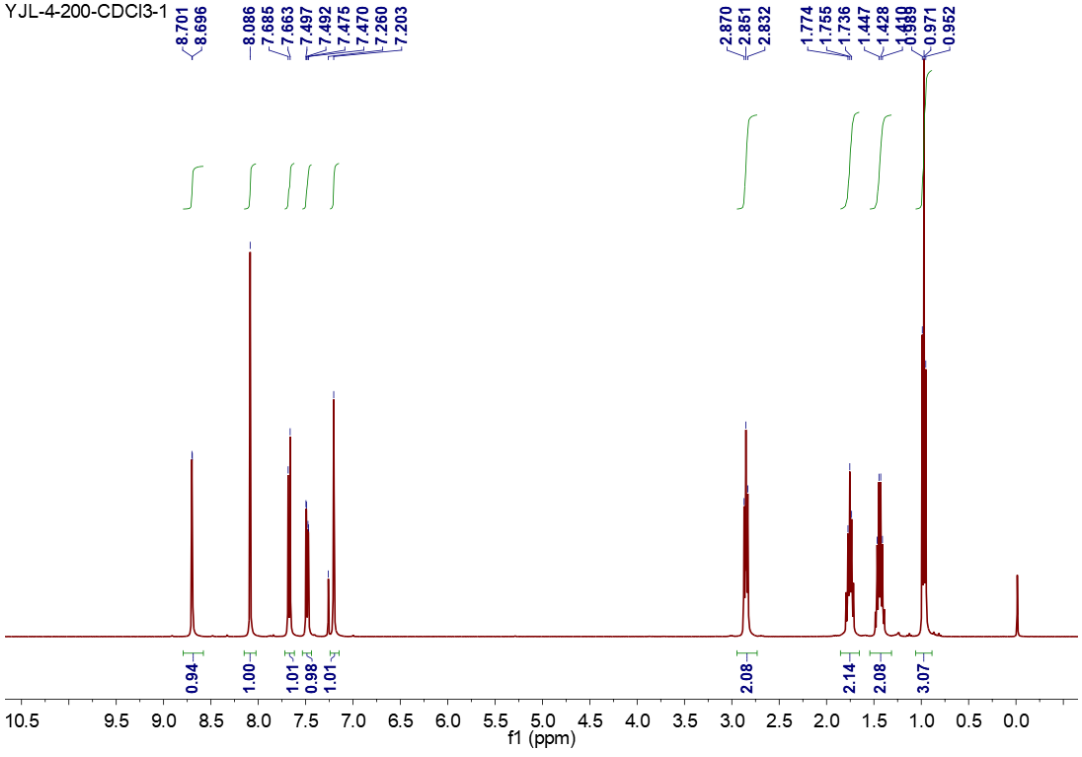
$^{13}$C NMR Spectrum of **3ca:**



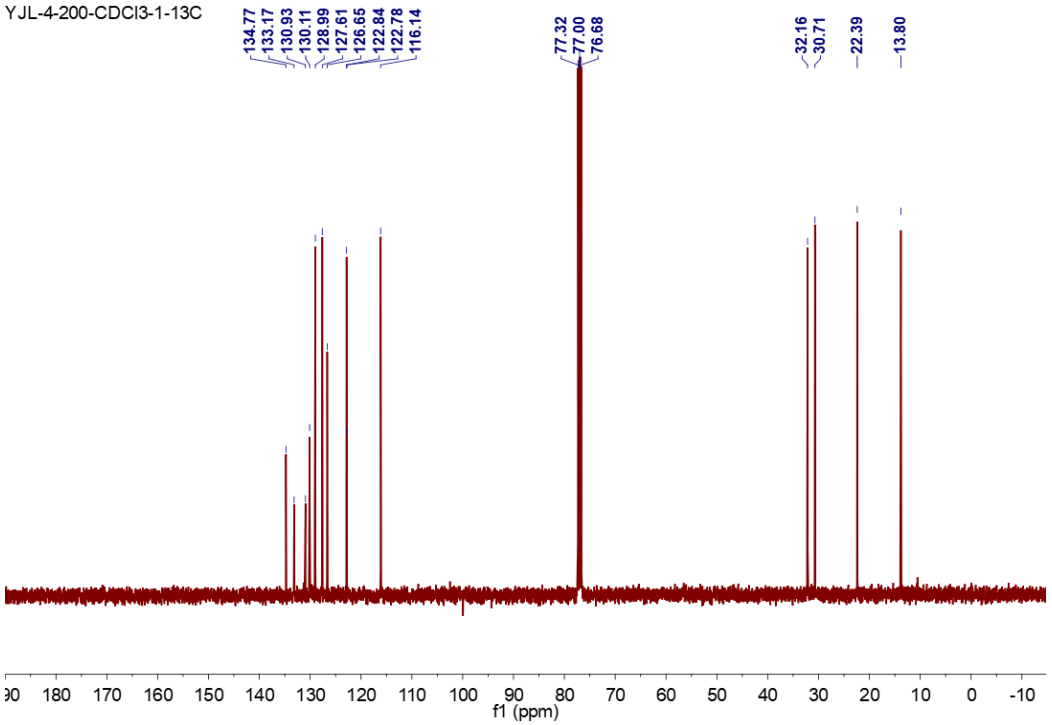



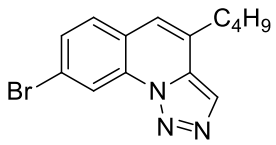

**3da**

$^{1}$H NMR Spectrum of **3da:**



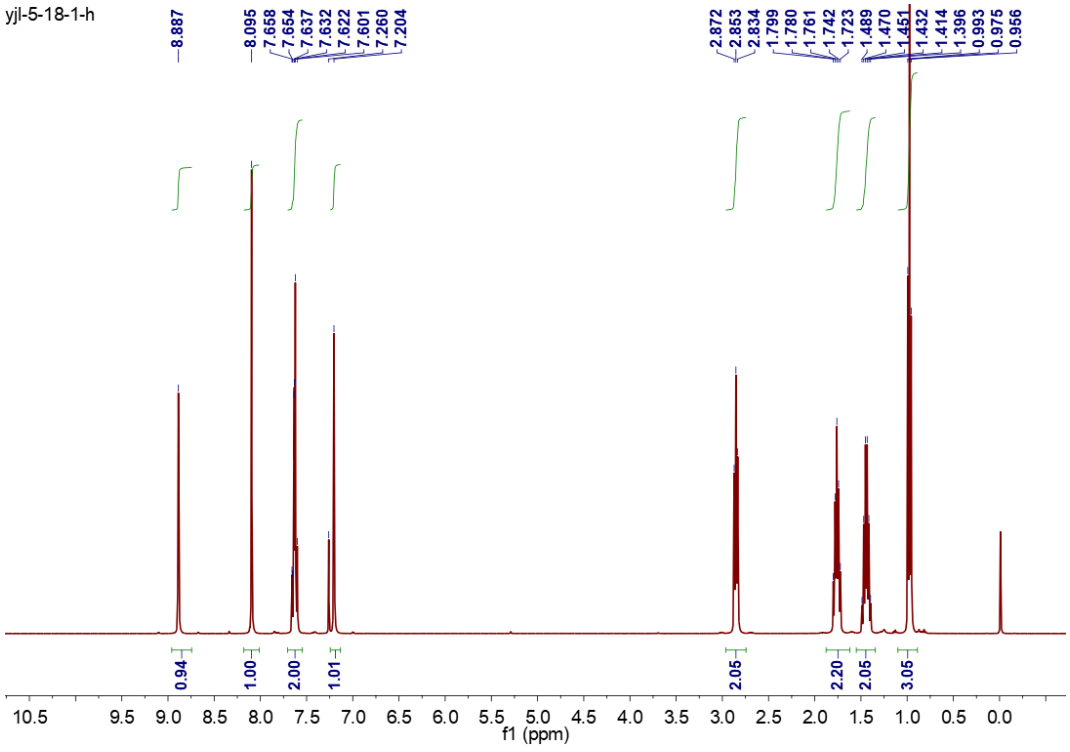
$^{13}$C NMR Spectrum of **3da:**



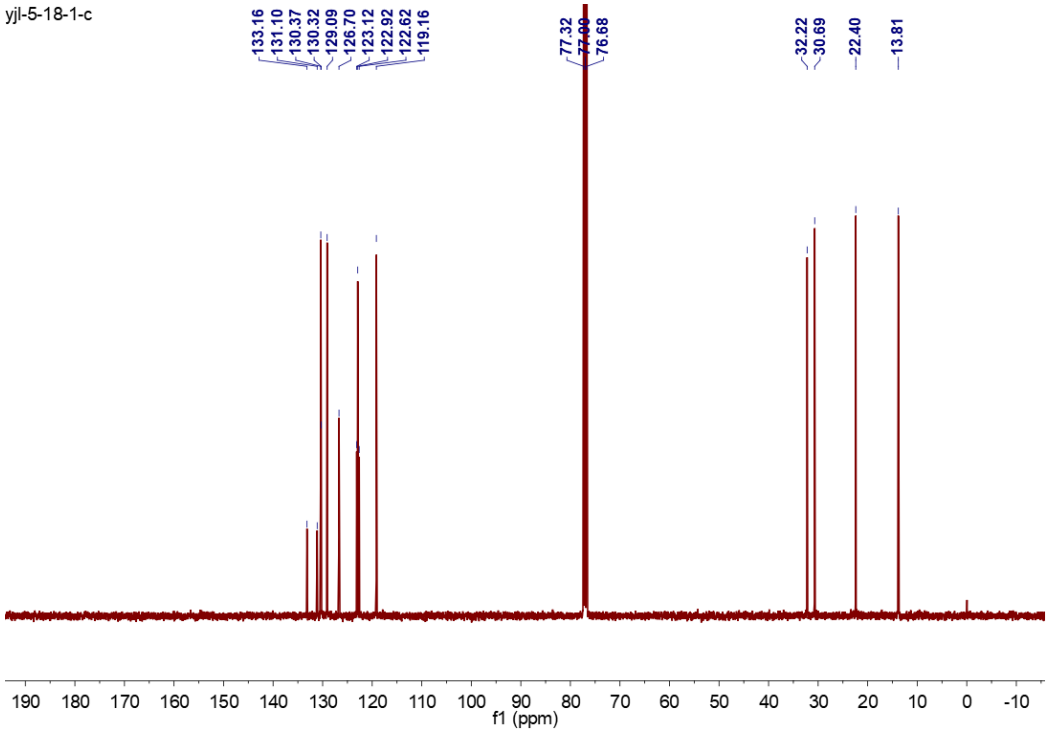



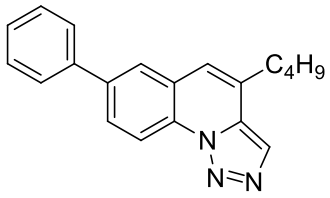

**3ea**

$^{1}$H NMR Spectrum of **3ea:**



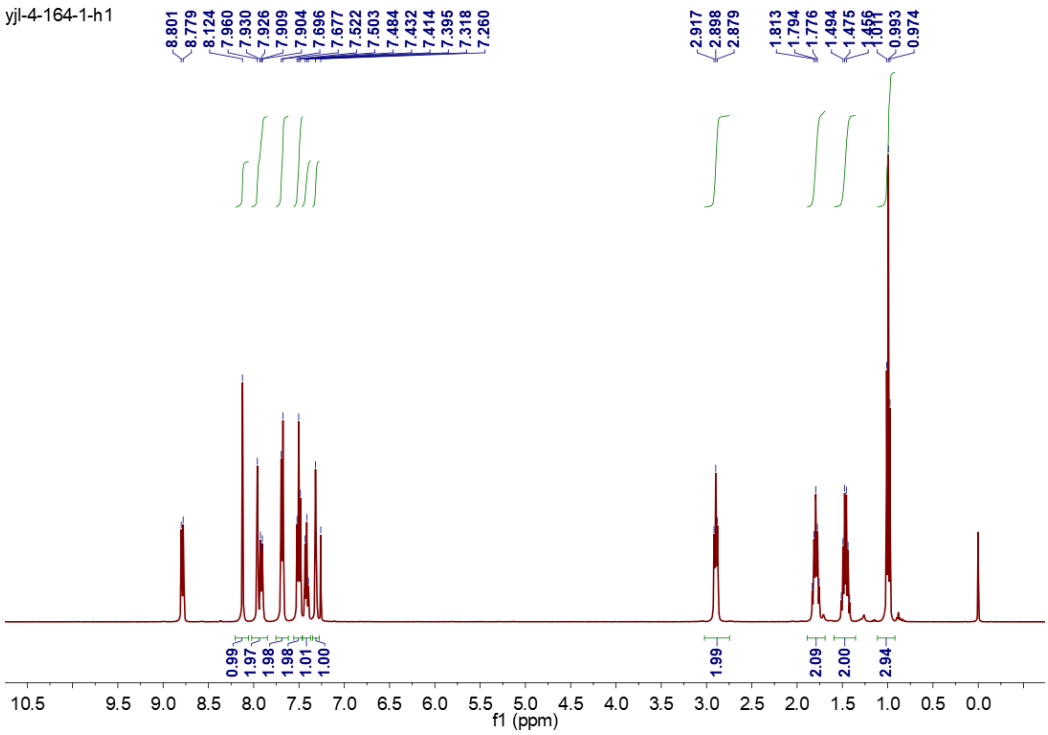
$^{13}$C NMR Spectrum of **3ea:**



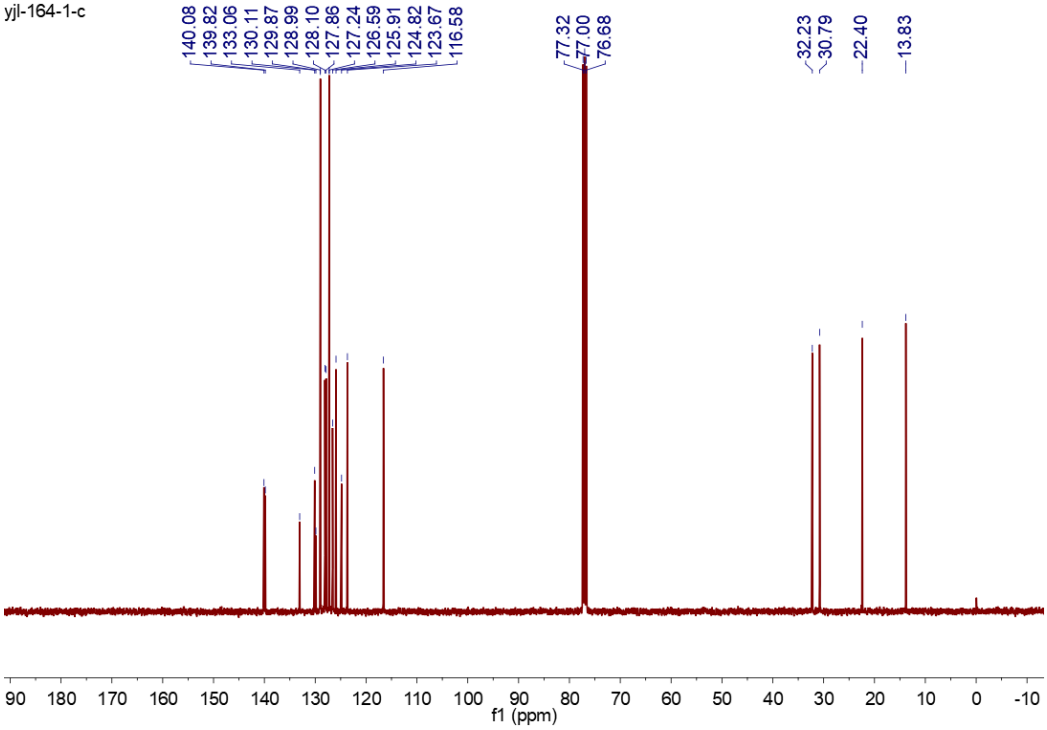



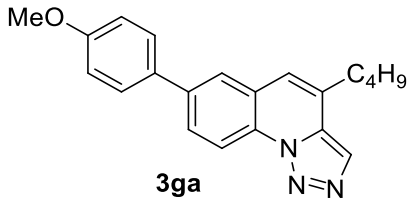

**3fa**

$^{1}$H NMR Spectrum of **3fa:**



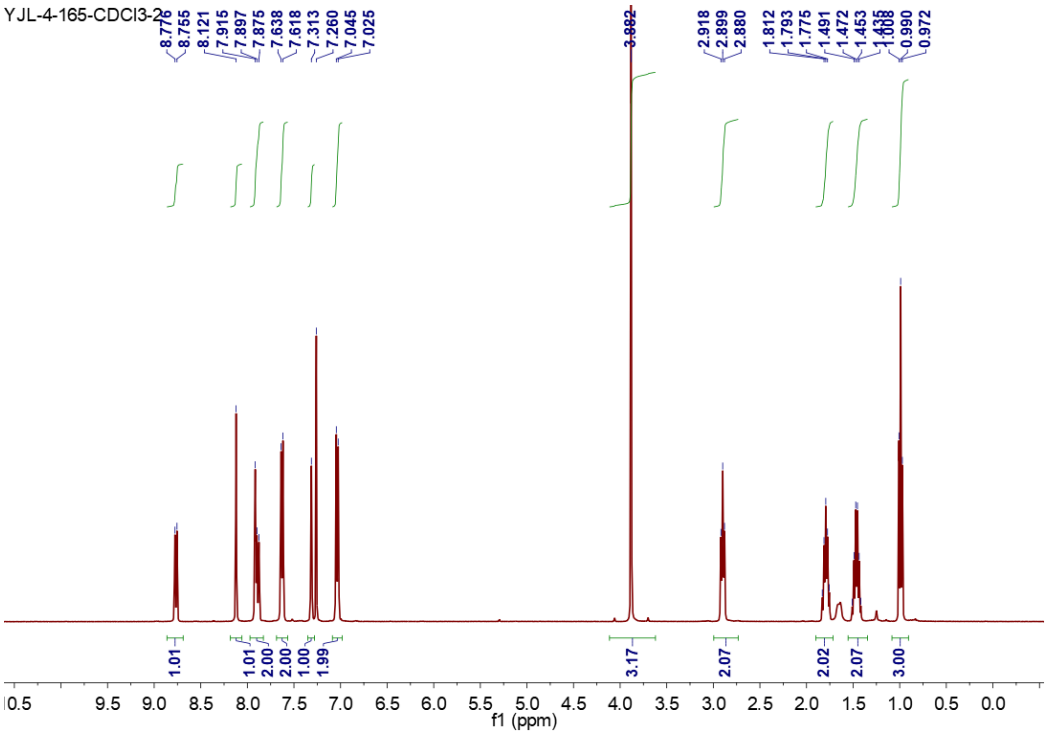
$^{13}$C NMR Spectrum of **3fa:**



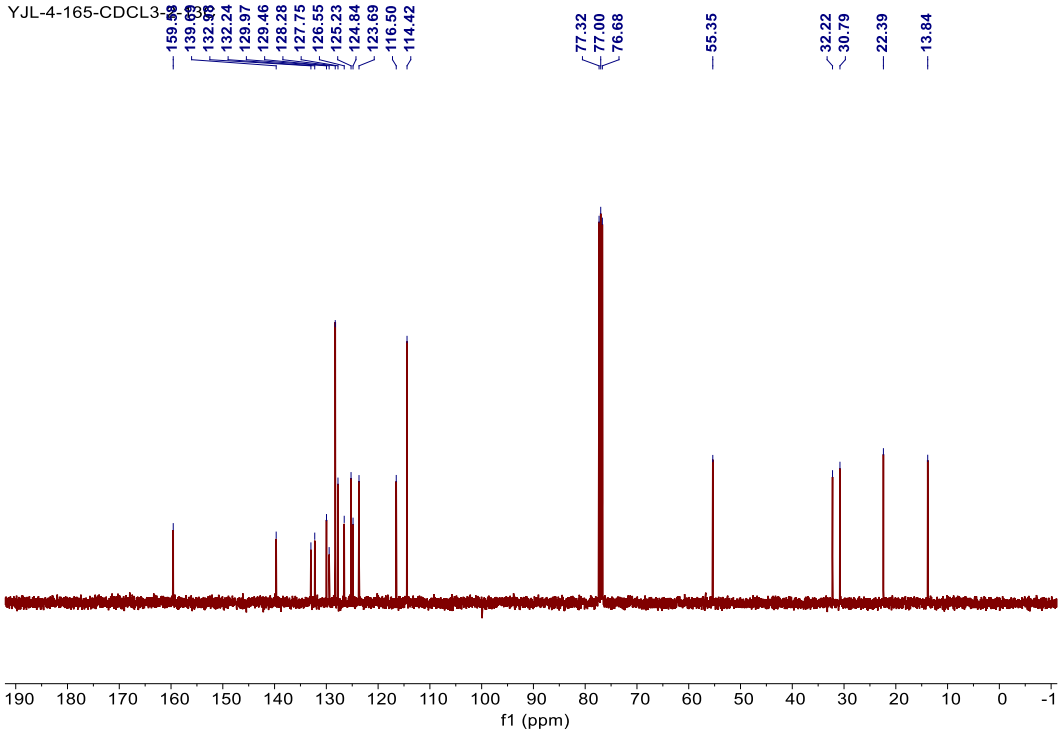



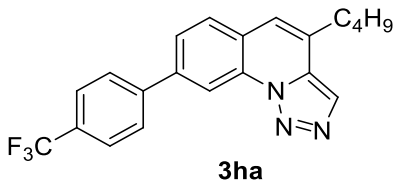

**3ga**

$^{1}$H NMR Spectrum of **3ga:**



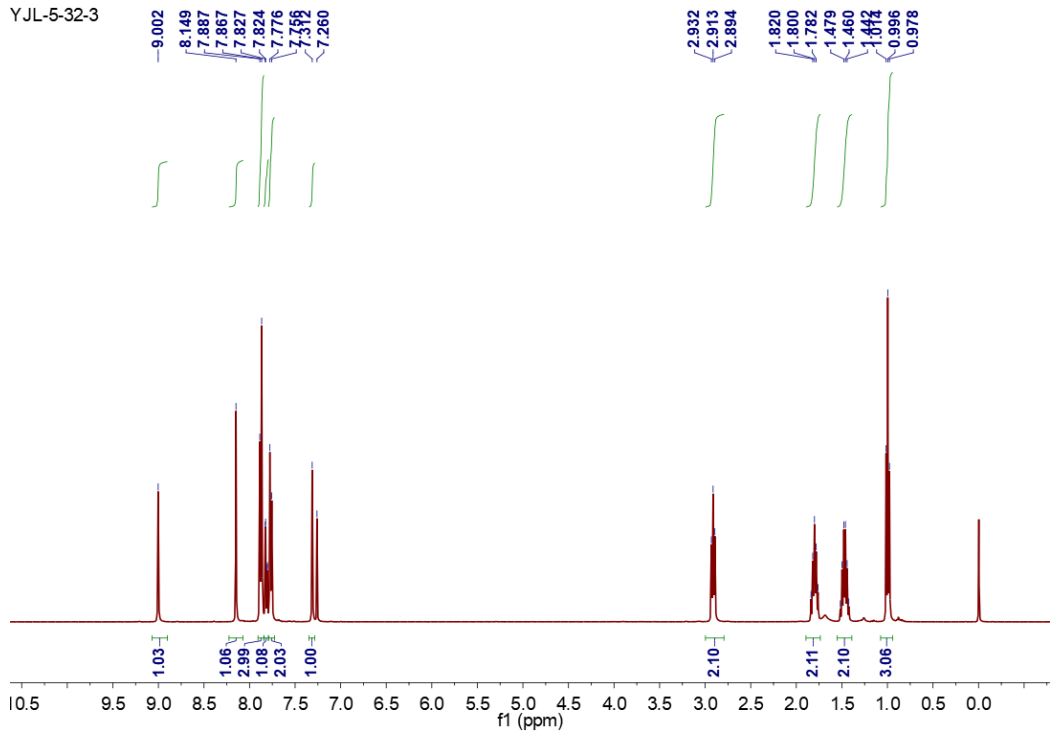
$^{13}$C NMR Spectrum of **3ga:**



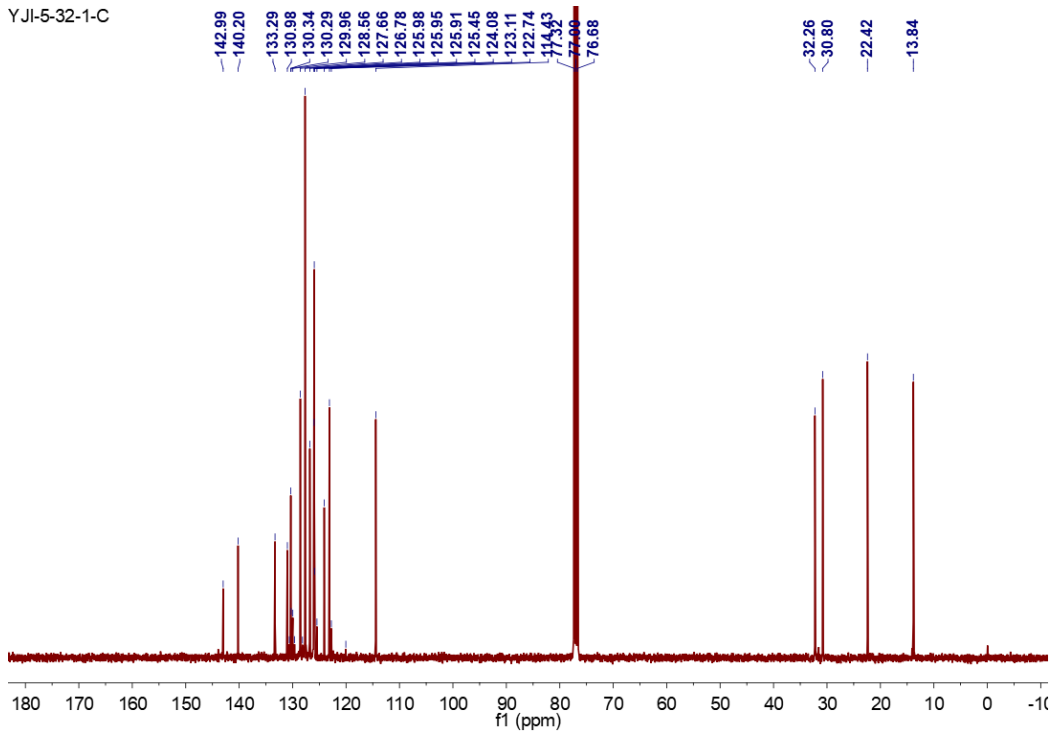




**3ha**

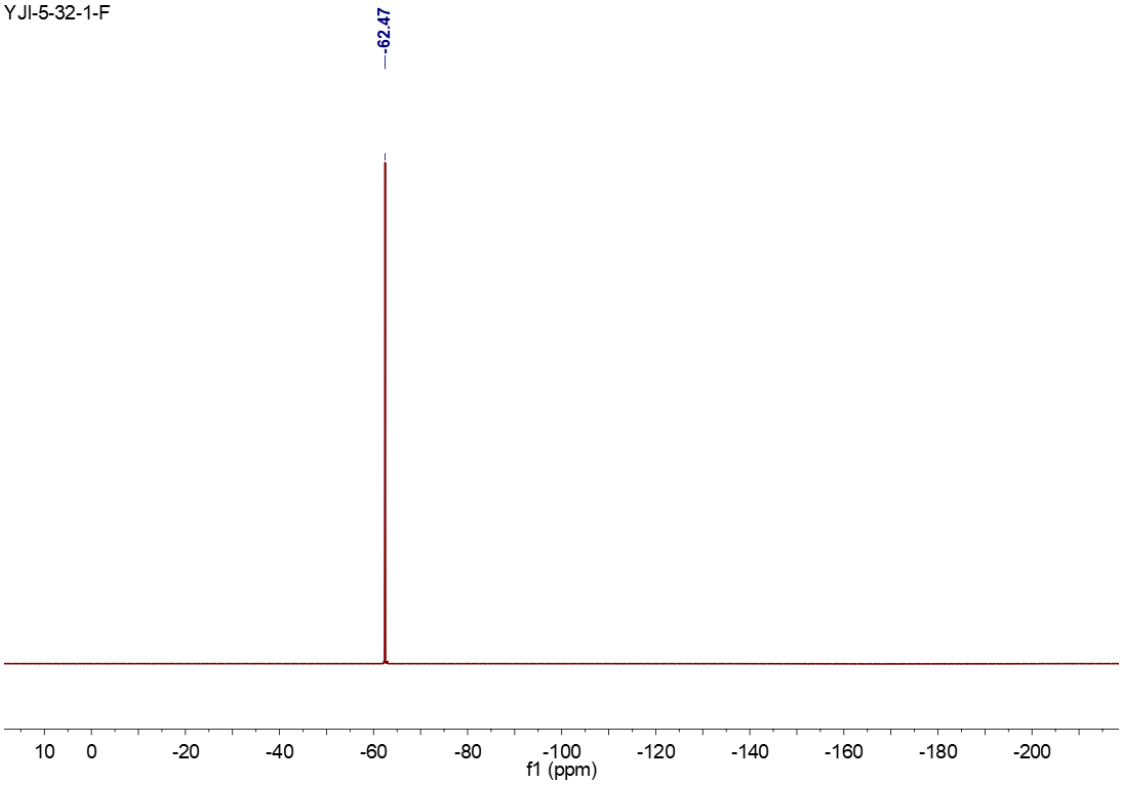
$^{1}$H NMR Spectrum of **3ha:**

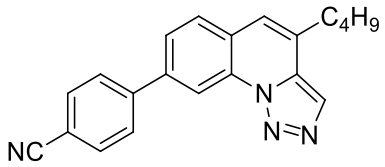


$^{13}$C NMR Spectrum of **3ha:**



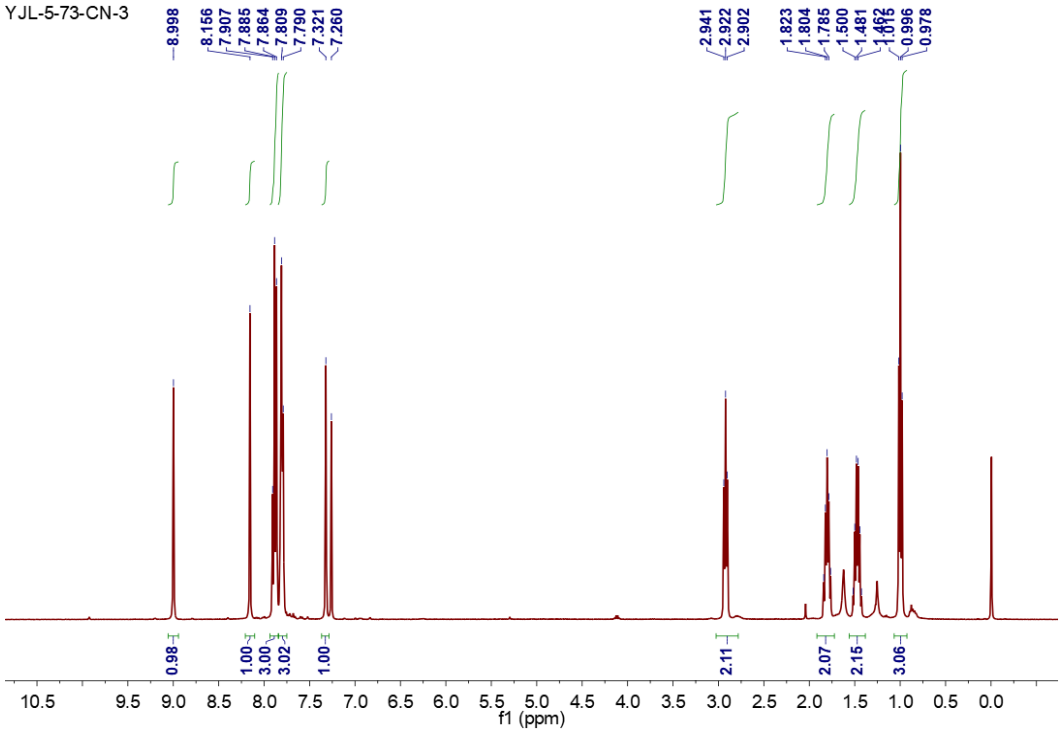

$^{19}$F NMR Spectrum of **3ha:**



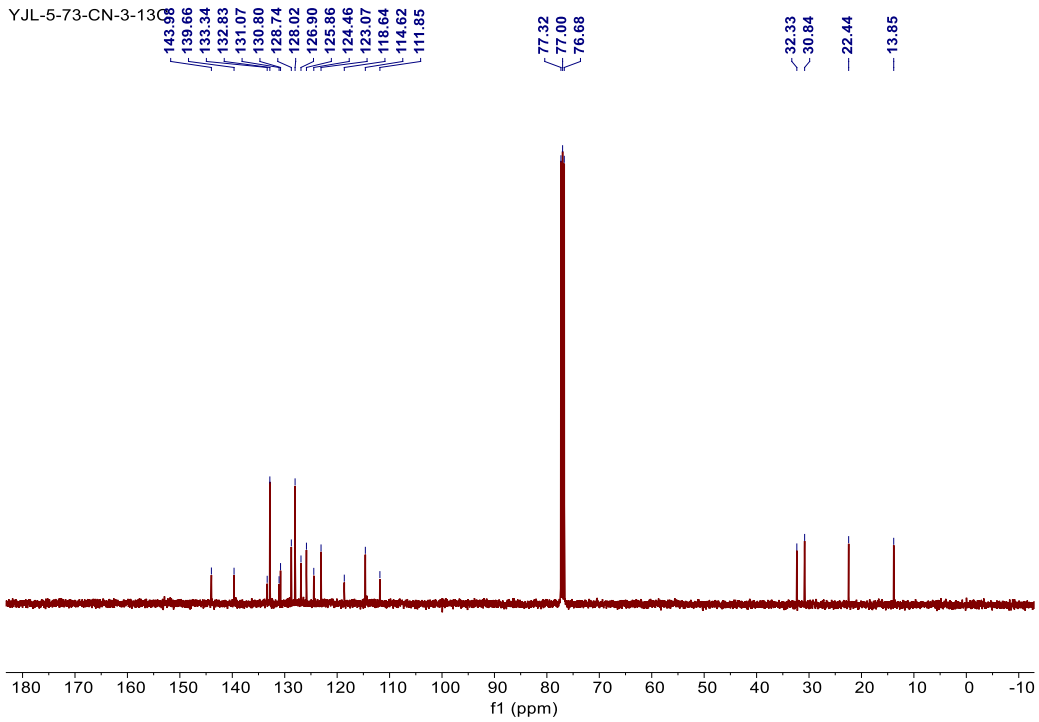


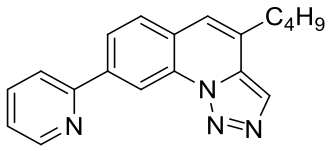

**3ia**

$^{1}$H NMR Spectrum of **3ia:**



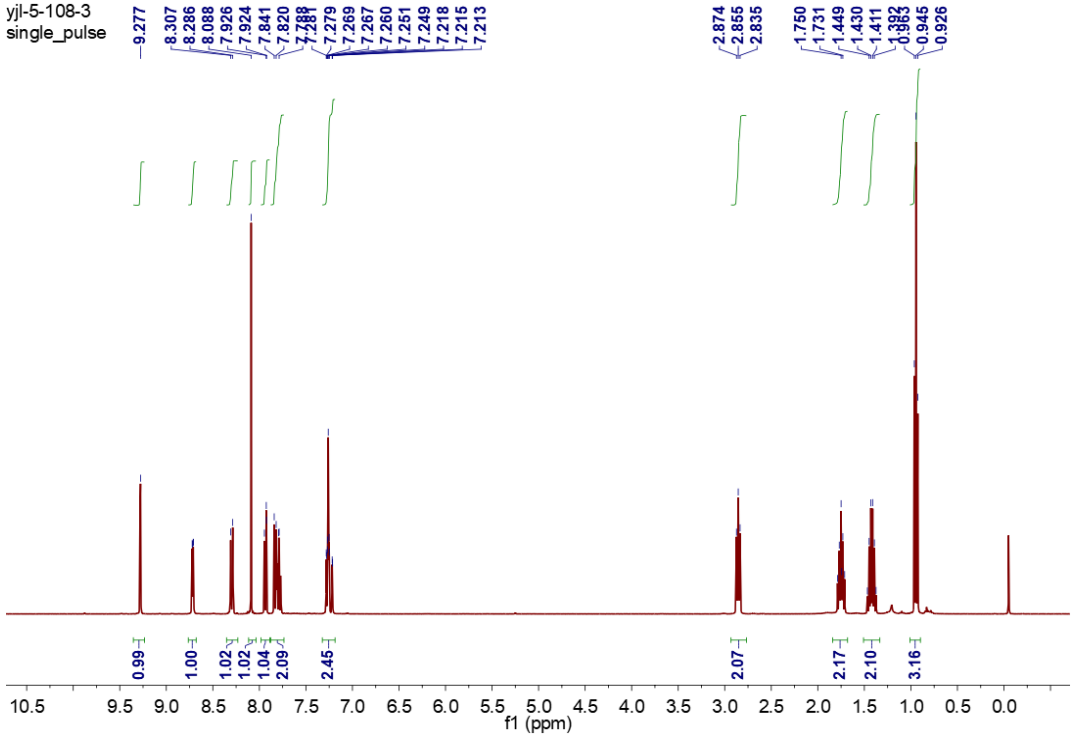

$^{13}$C NMR Spectrum of **3ia:**



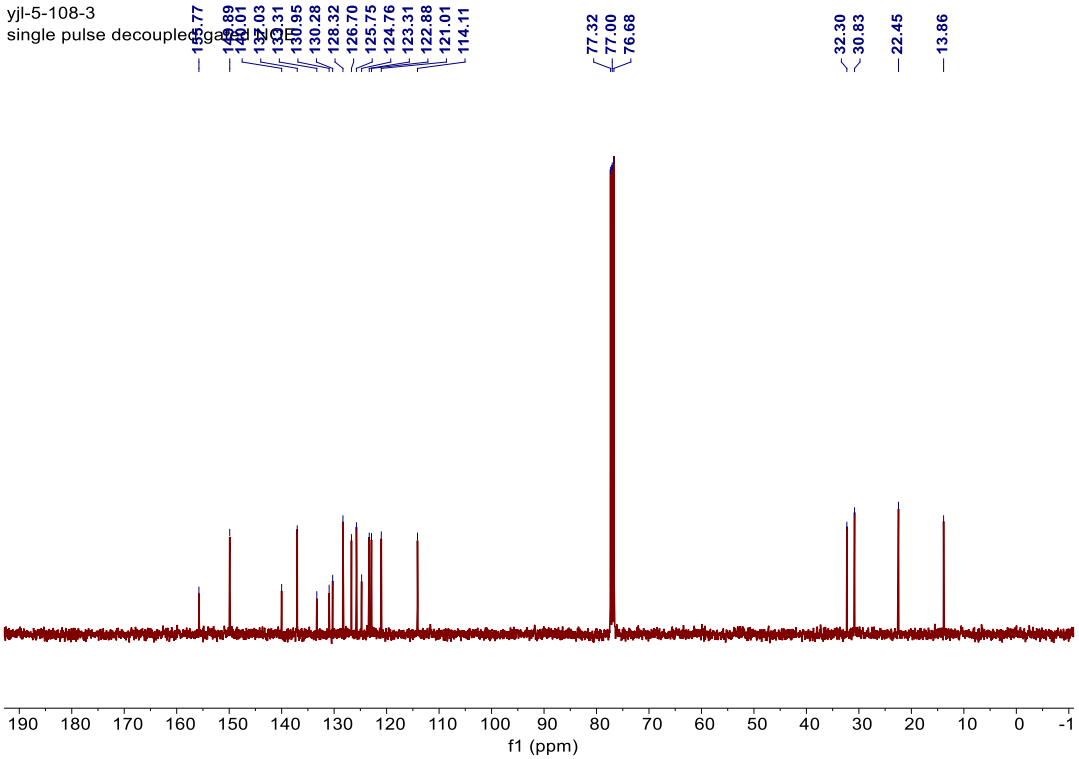


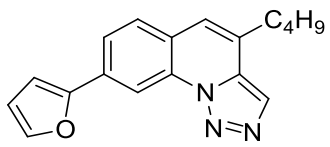

**3ja**

$^{1}$H NMR Spectrum of **3ja:**



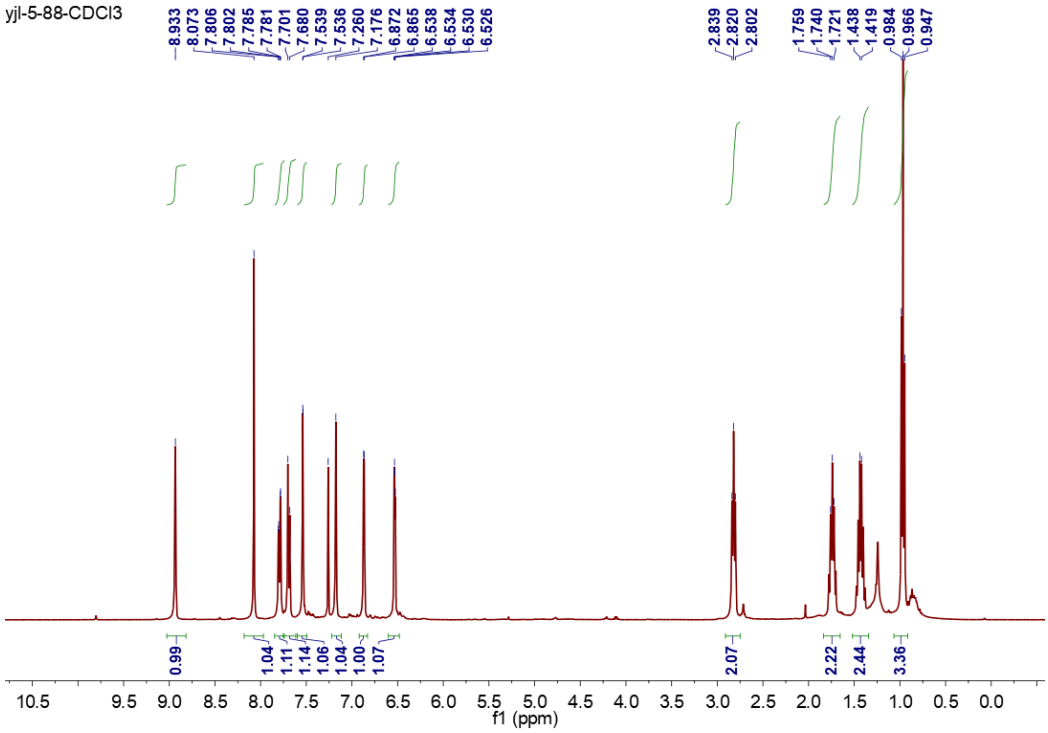

$^{13}$C NMR Spectrum of **3ja:**



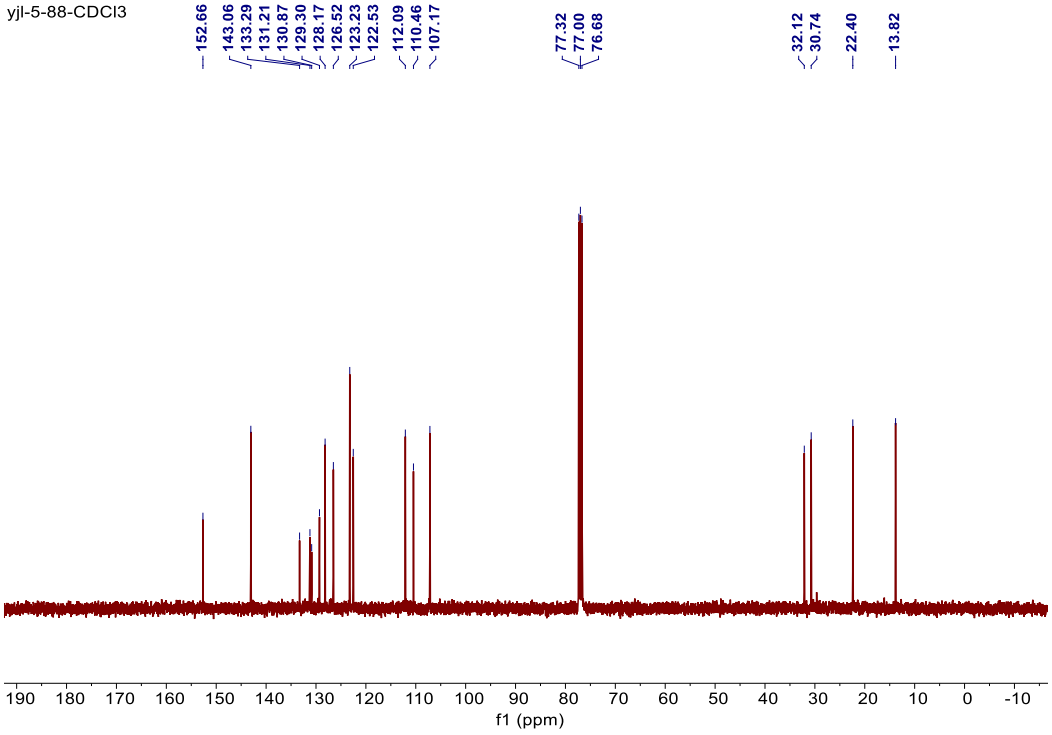


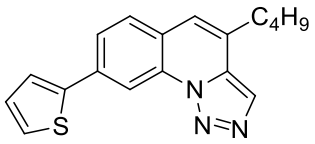

**3ka**

$^{1}$H NMR Spectrum of **3ka:**



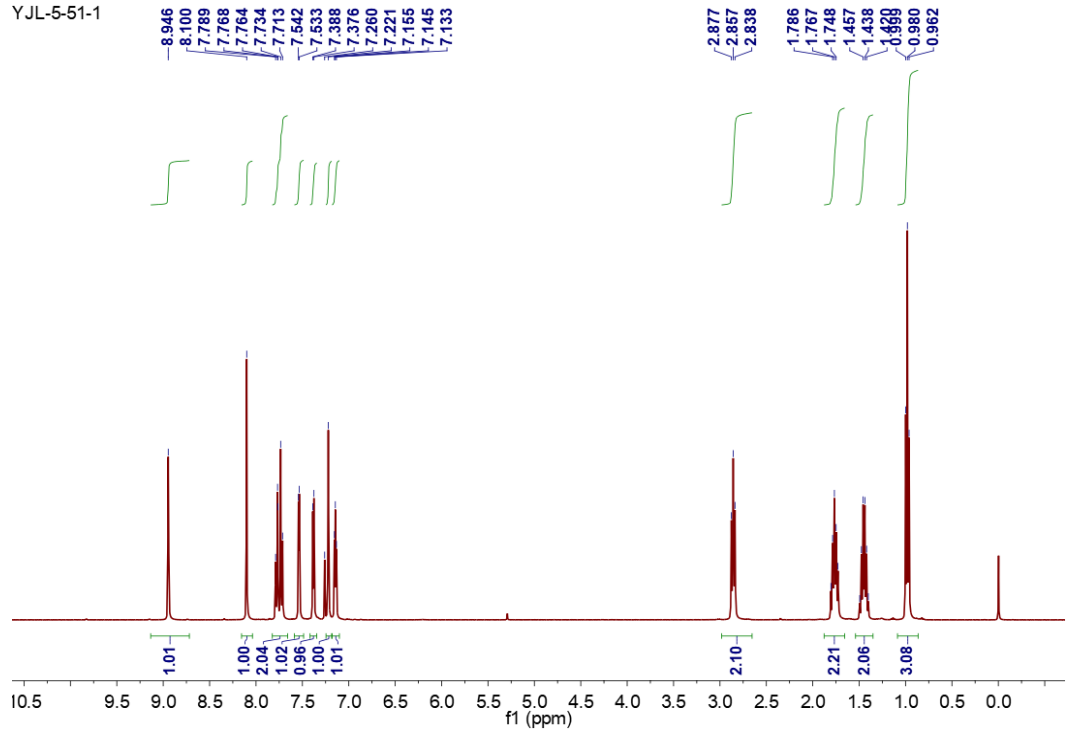

$^{13}$C NMR Spectrum of **3ka:**



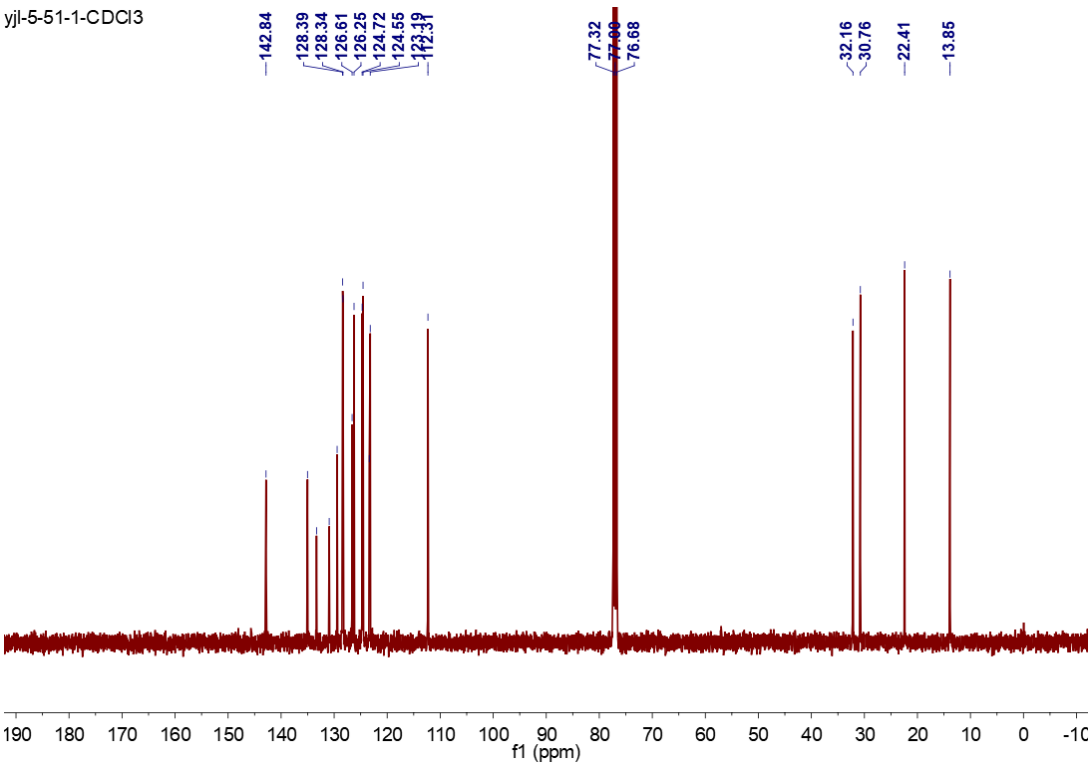


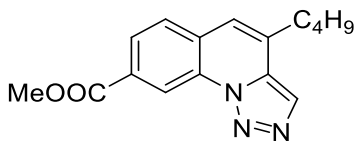

**3la**

$^{1}$H NMR Spectrum of **3la:**



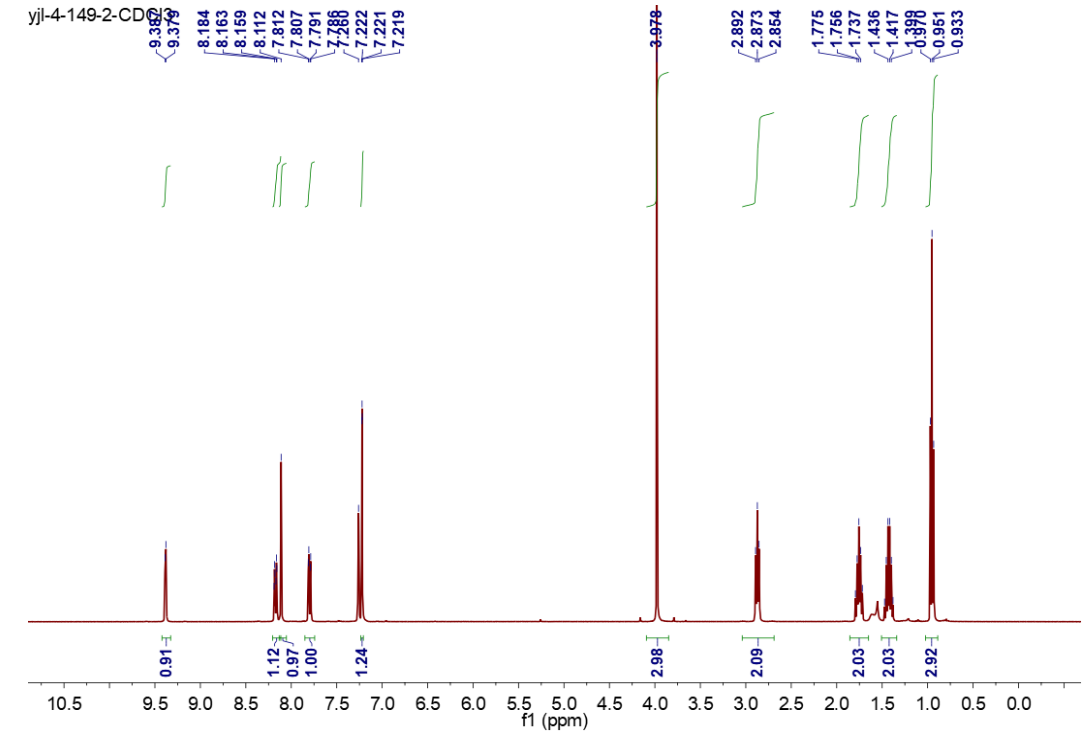

$^{13}$C NMR Spectrum of **3la:**



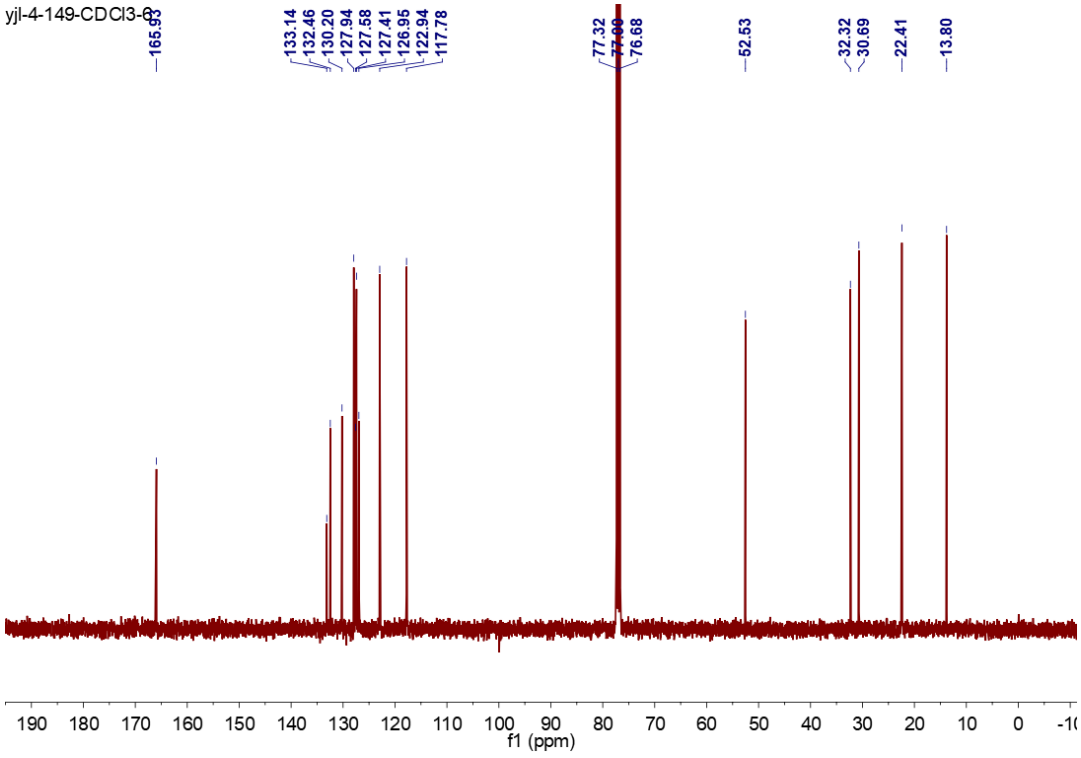


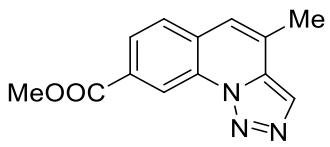

**3ma**

$^{1}$H NMR Spectrum of **3ma:**



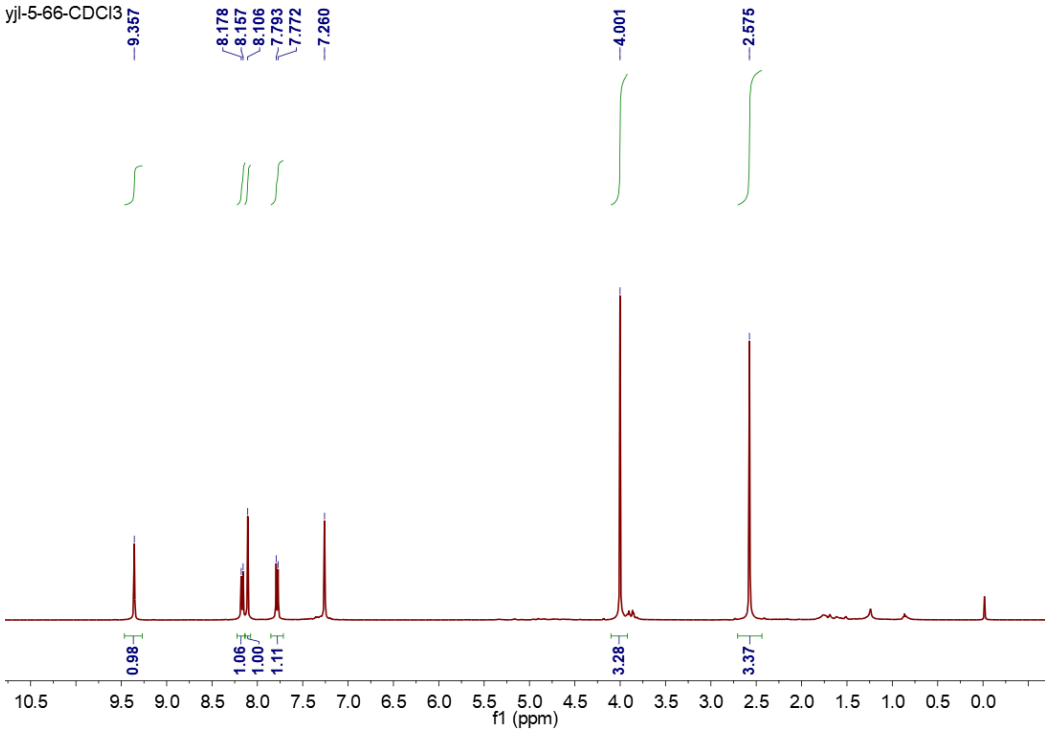

$^{13}$C NMR Spectrum of **3ma:**



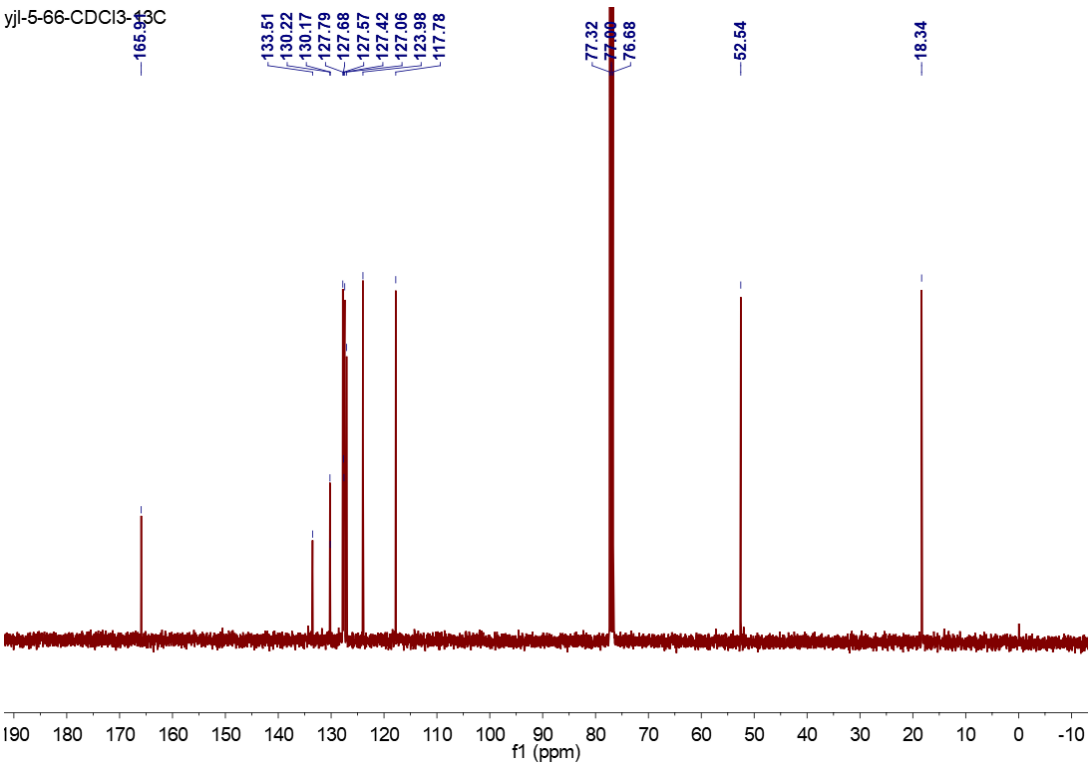


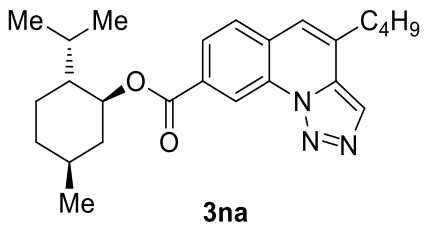

**3mb**

$^{1}$H NMR Spectrum of **3mb:**



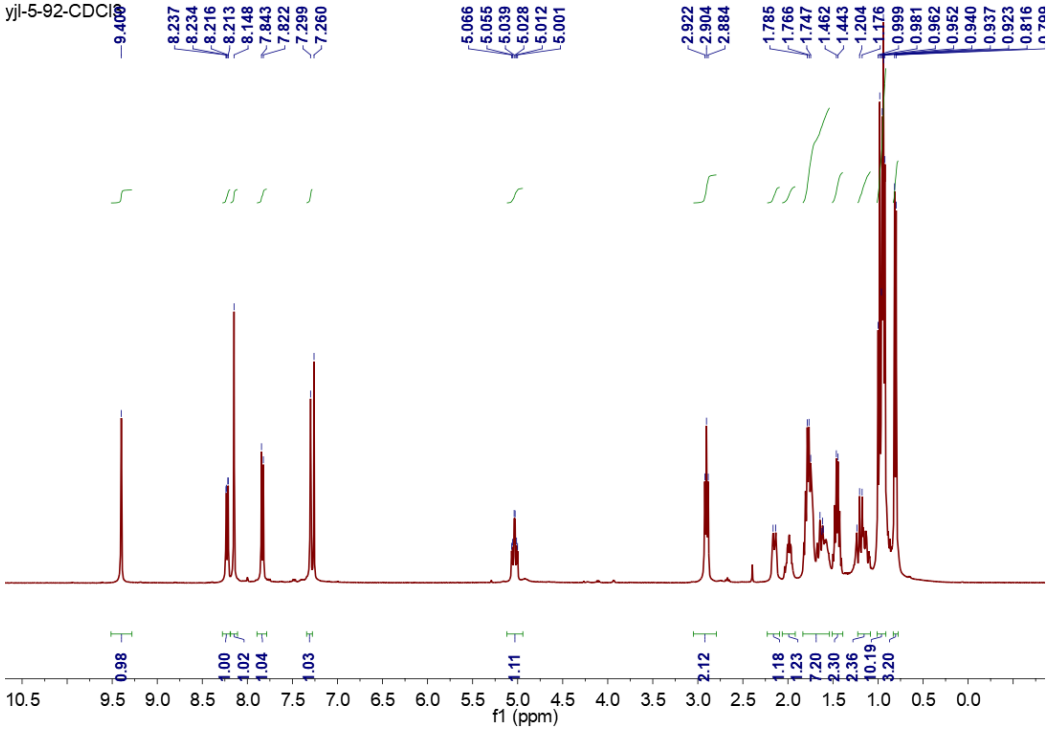

$^{13}$C NMR Spectrum of **3mb:**



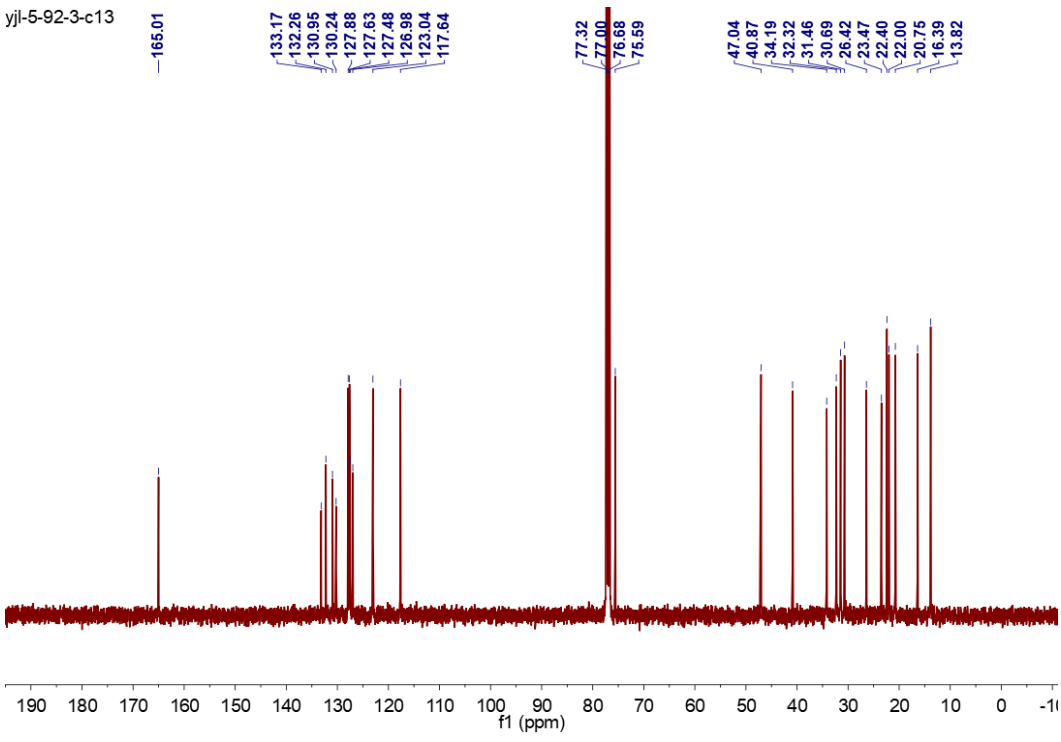


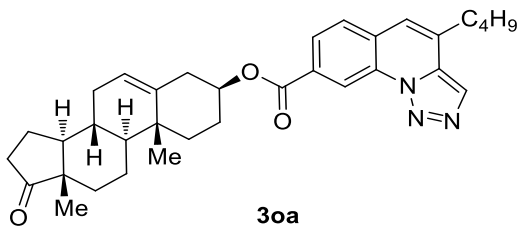

**3na**

$^{1}$H NMR Spectrum of **3na:**



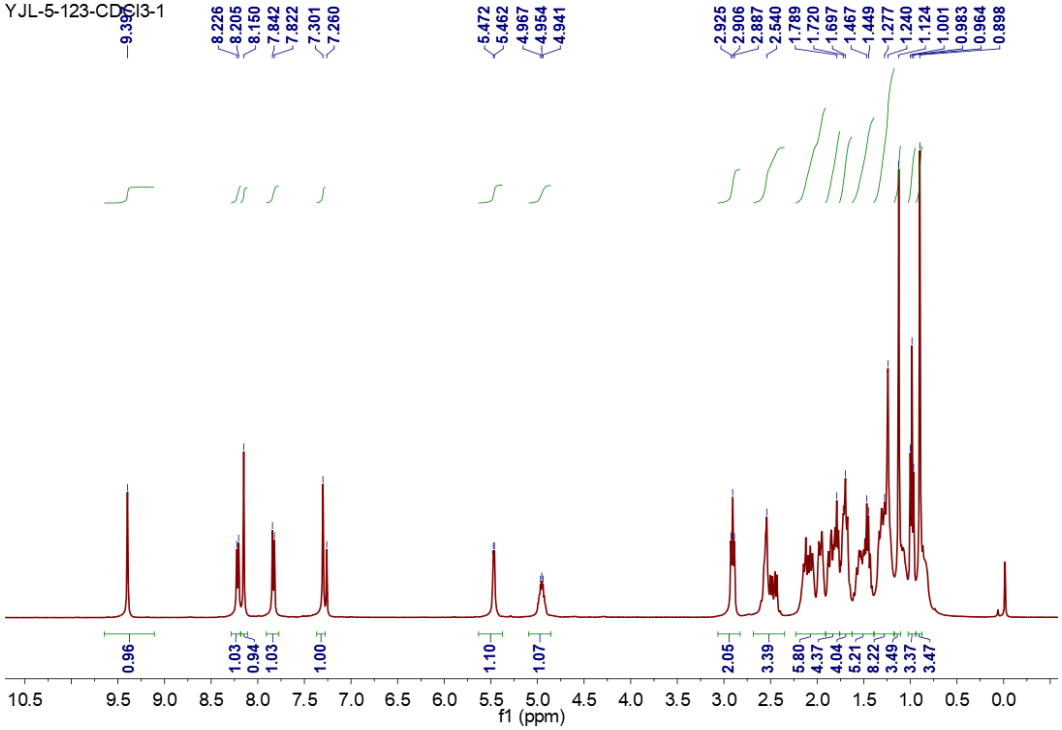

$^{13}$C NMR Spectrum of **3na:**



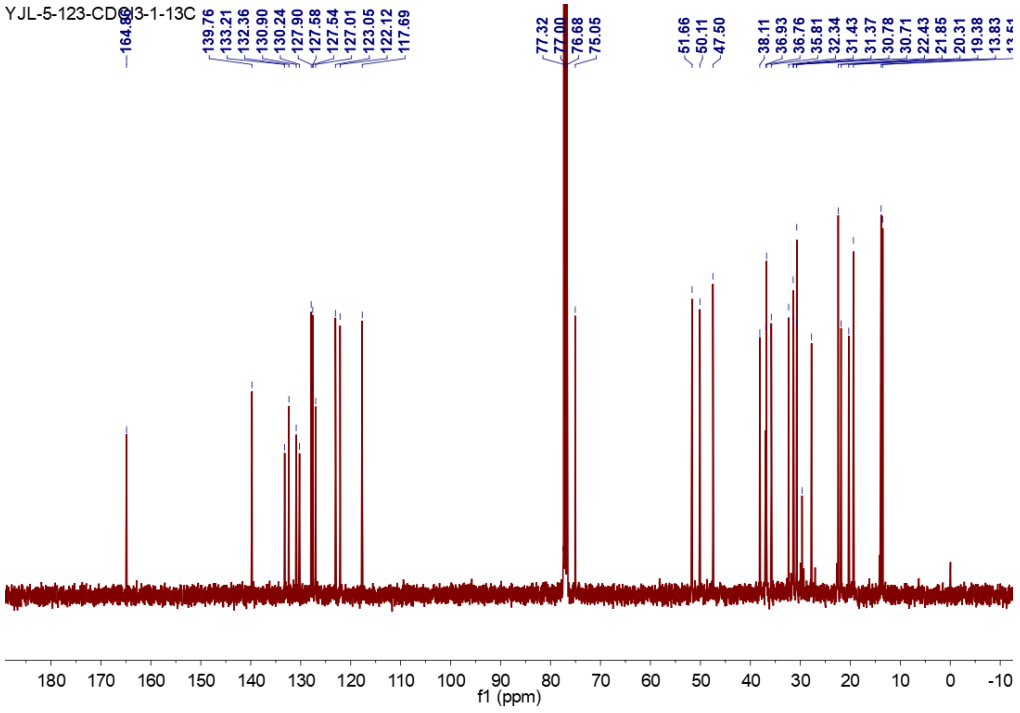


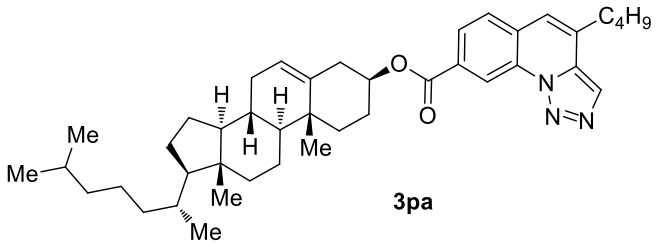

**3oa**

$^{1}$H NMR Spectrum of **3oa:**



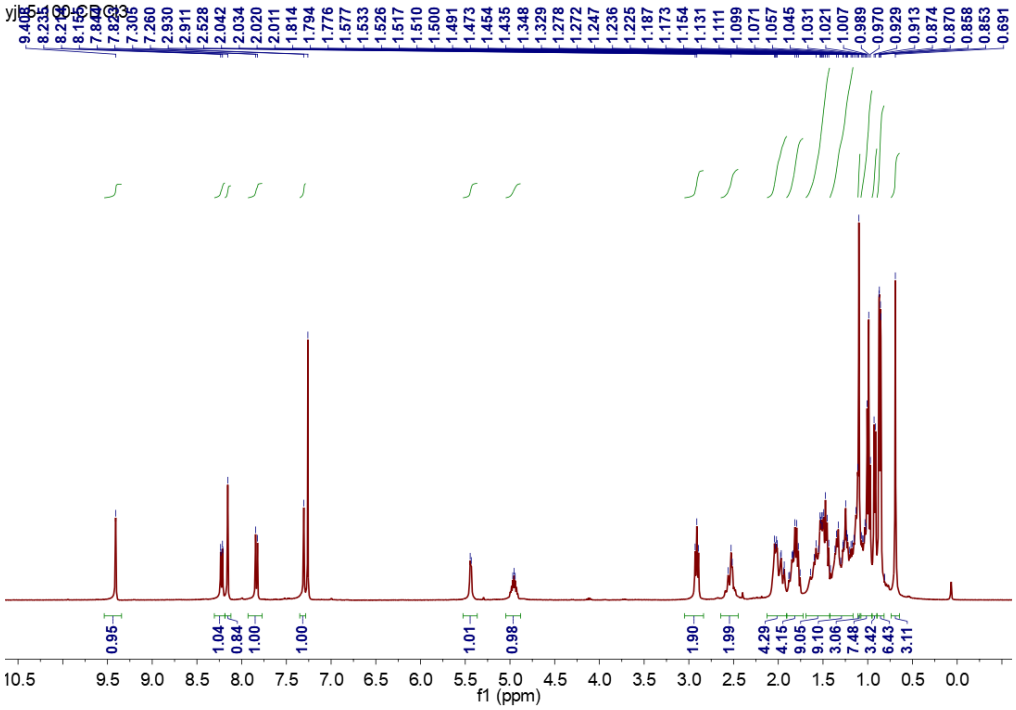

$^{13}$C NMR Spectrum of **3oa:**



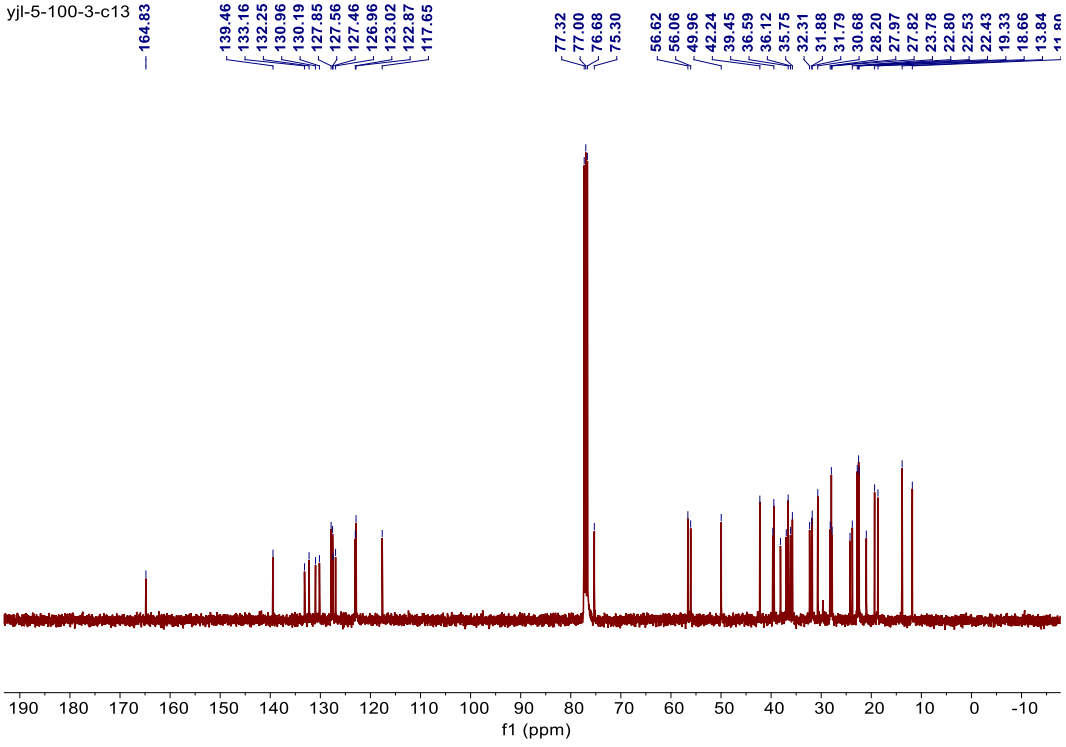


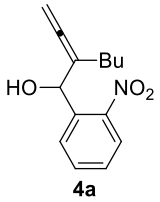

**3pa**

$^{1}$H NMR Spectrum of **3pa:**



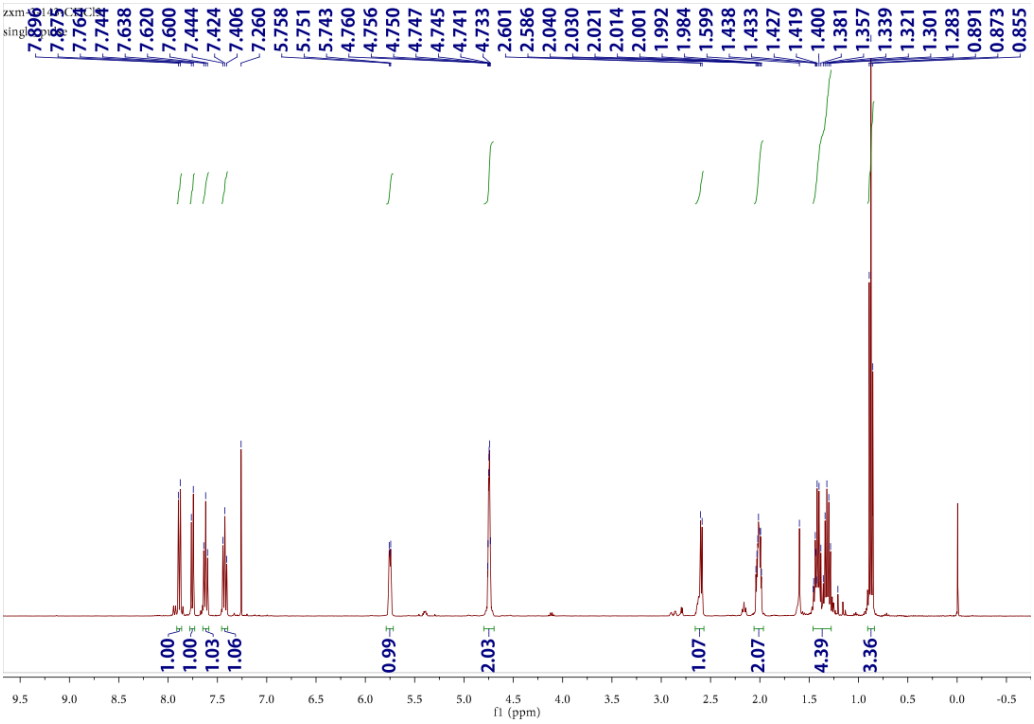

$^{13}$C NMR Spectrum of **3pa:**



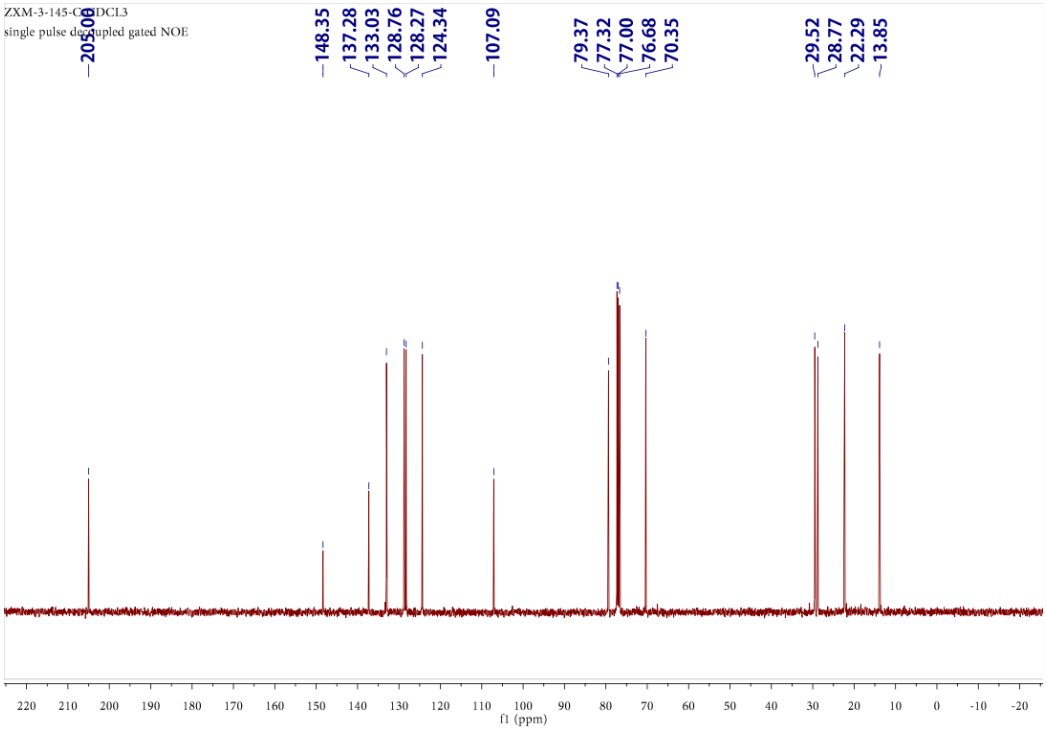


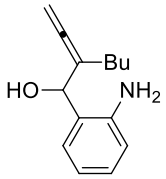

**4a**

$^{1}$H NMR Spectrum of **4a:**



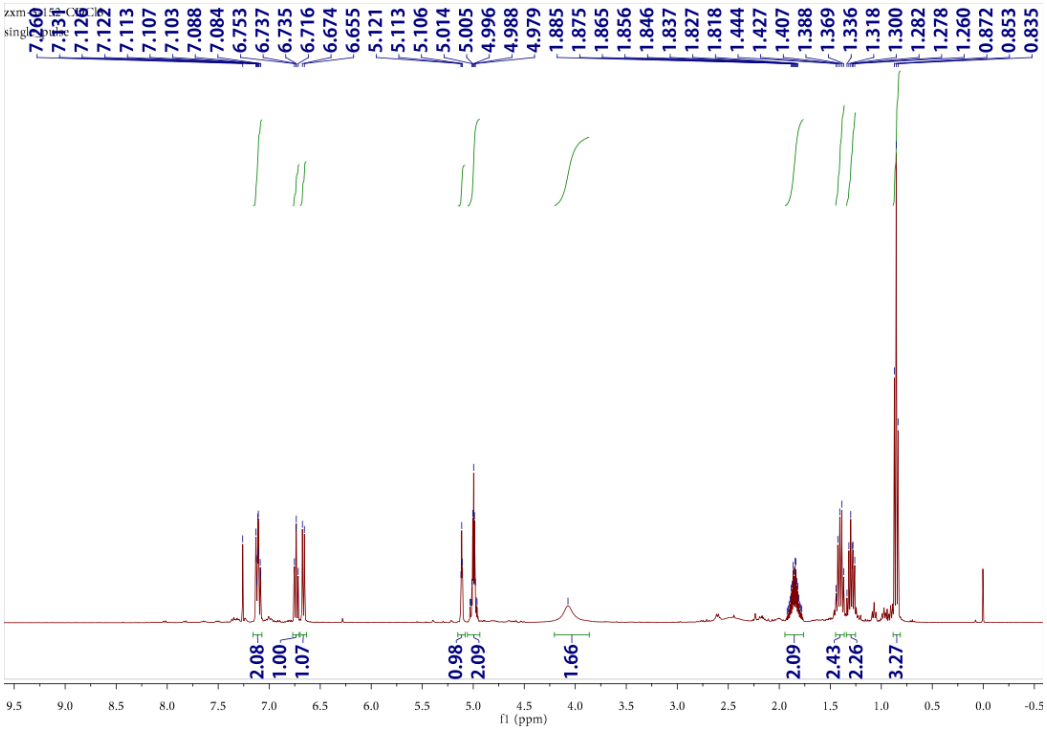

$^{13}$C NMR Spectrum of **4a:**



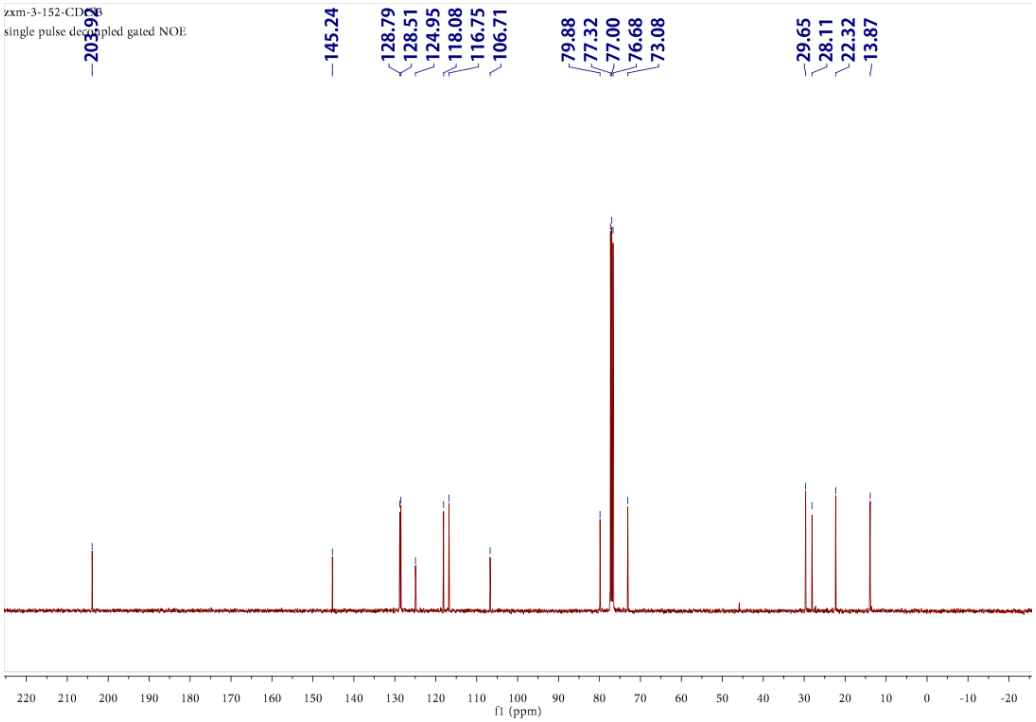


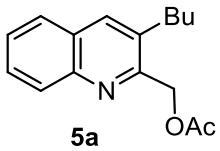

**4b**

$^{1}$H NMR Spectrum of **4b:**



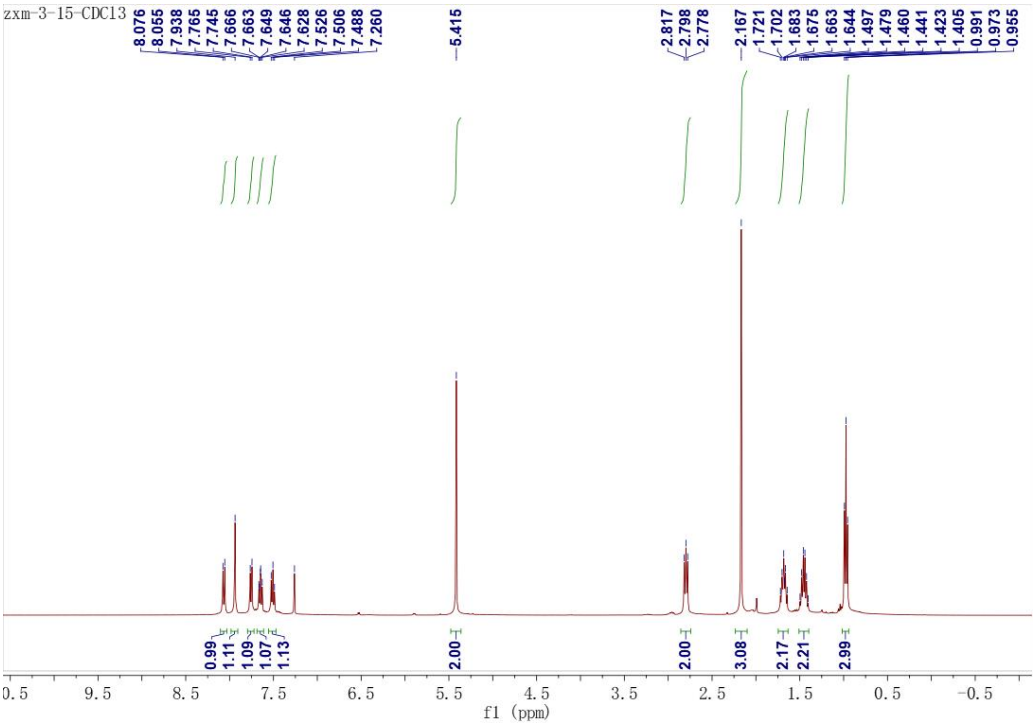

$^{13}$C NMR Spectrum of **4b:**



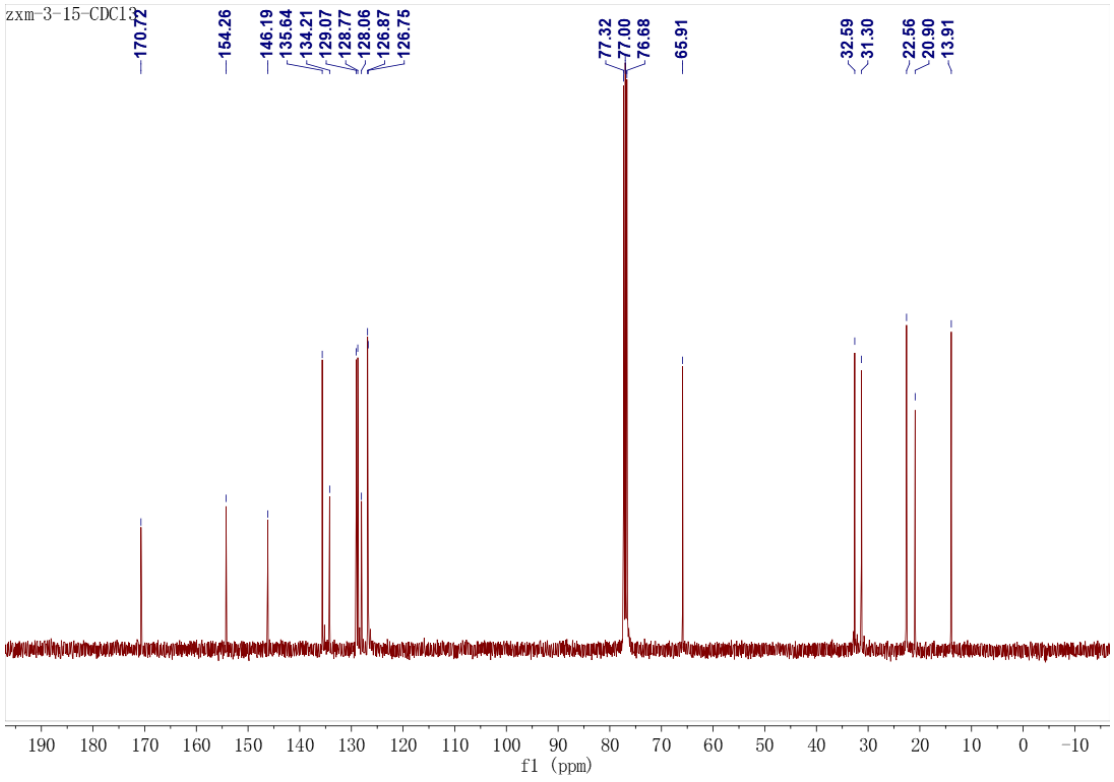


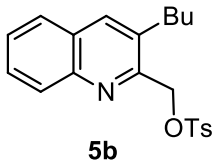

**5a**

$^{1}$H NMR Spectrum of **5a:**



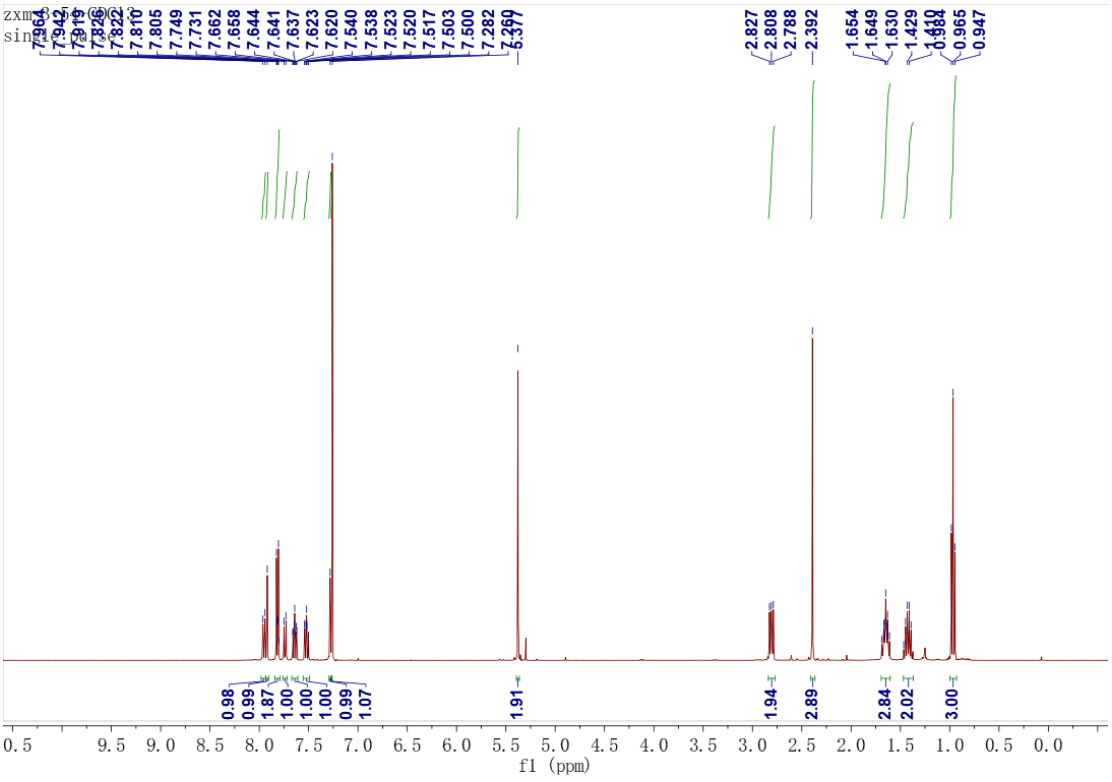

$^{13}$C NMR Spectrum of **5a:**



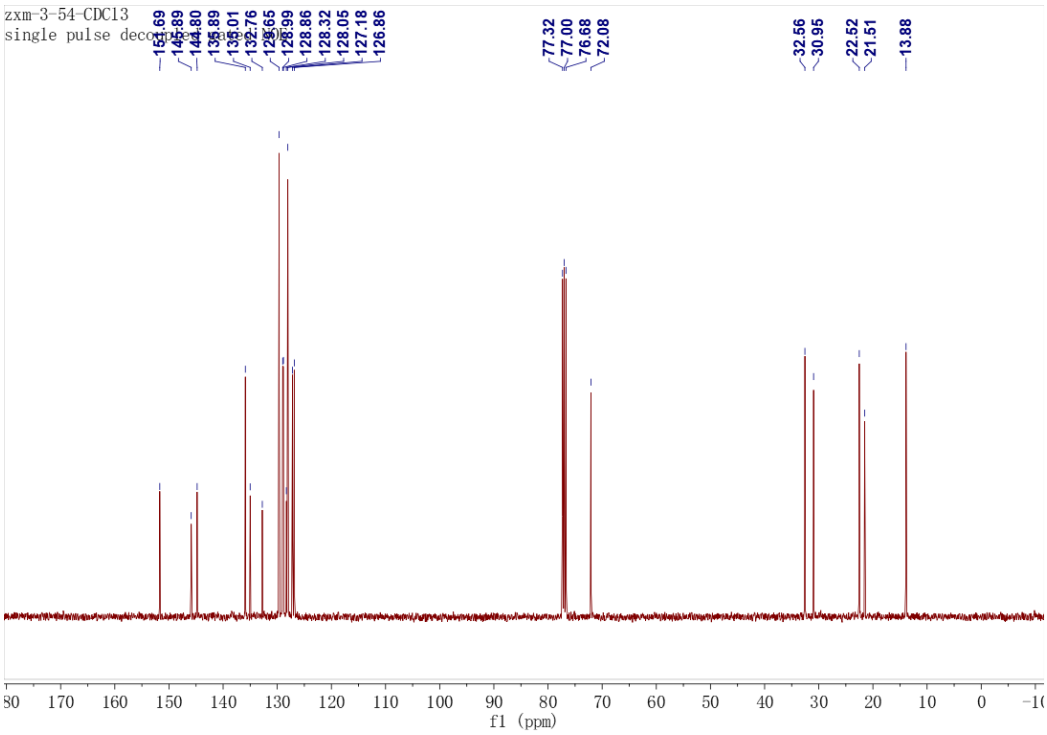


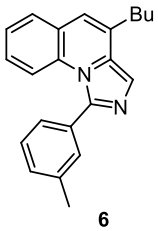

**5b**

$^{1}$H NMR Spectrum of **5b**：



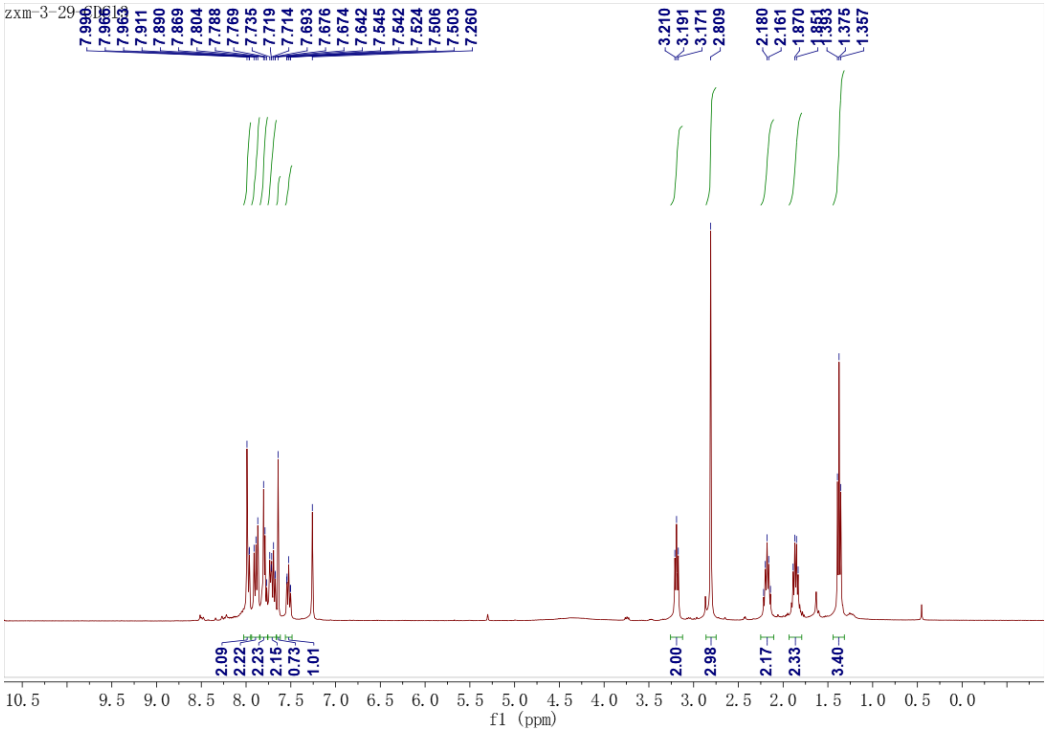

$^{13}$C NMR Spectrum of **5b**：



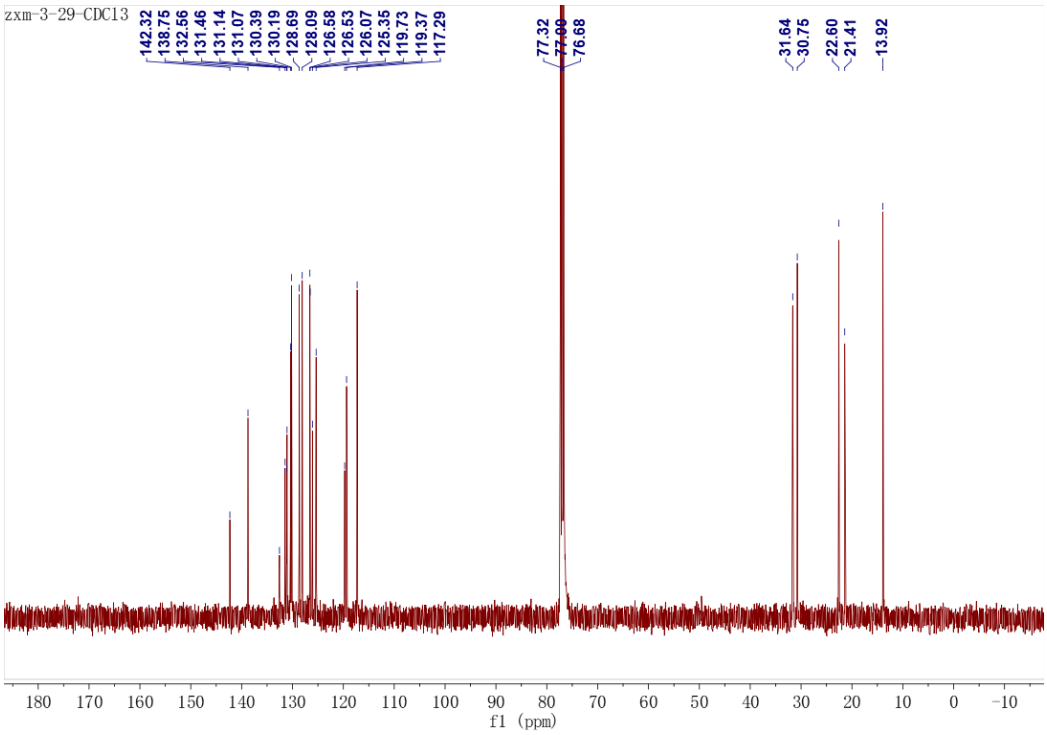


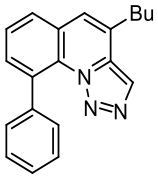

**6**

$^{1}$H NMR Spectrum of **6**:



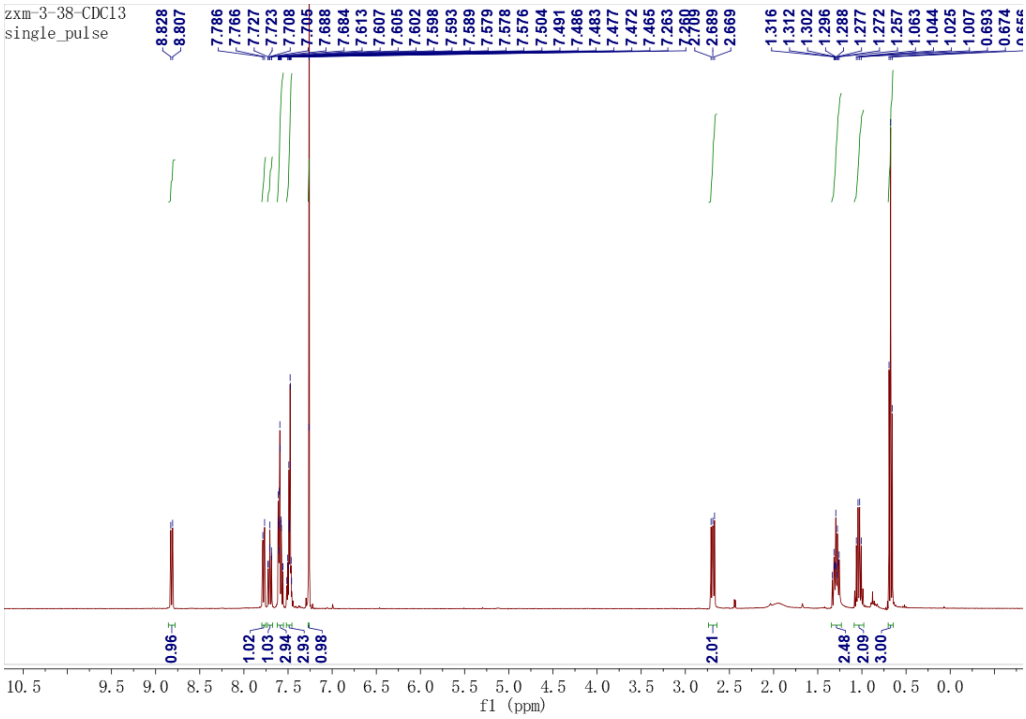

$^{13}$C NMR Spectrum of **6**:



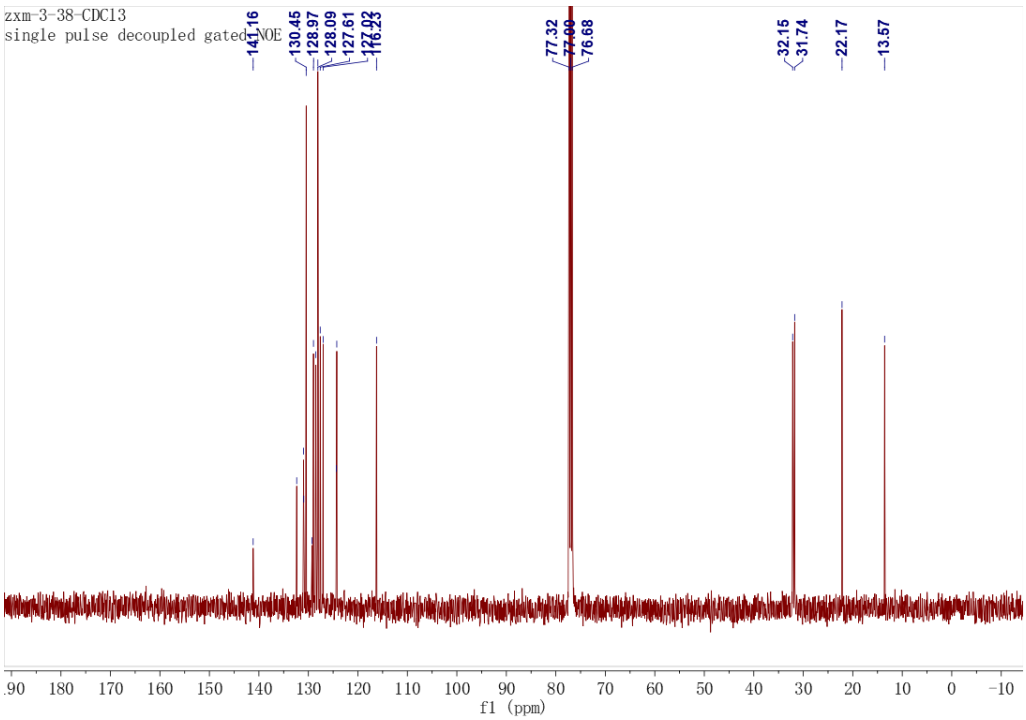


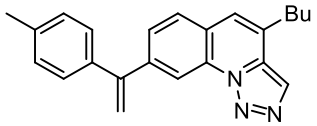

**7a**

$^{1}$H NMR Spectrum of **7a**：



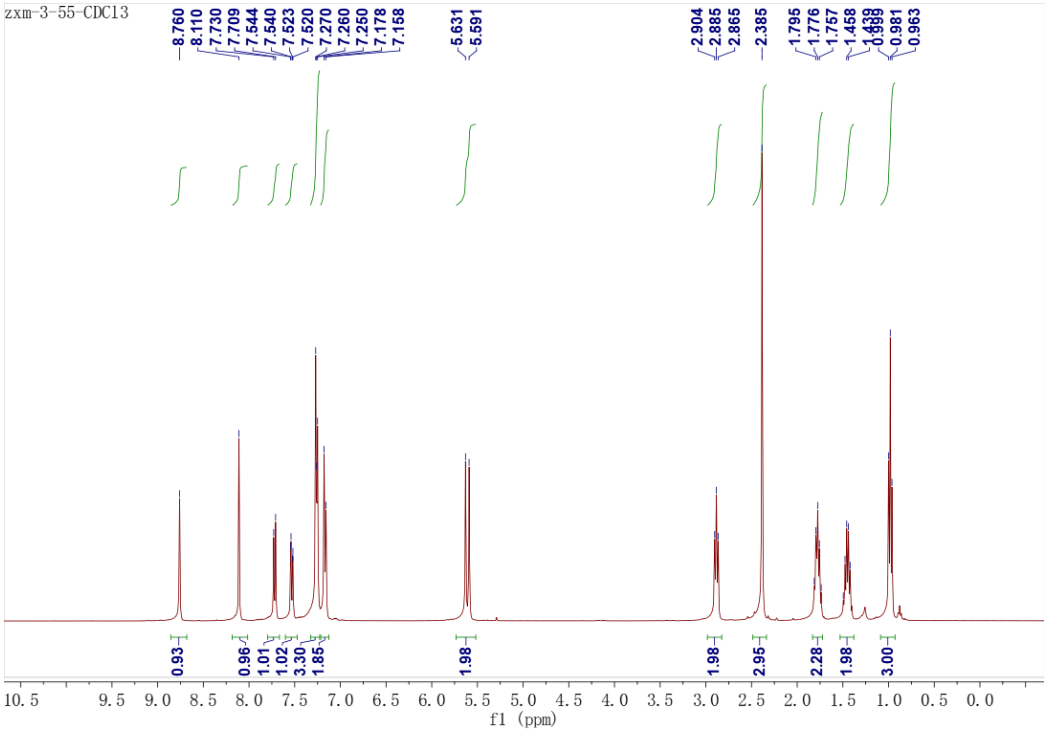

$^{13}$C NMR Spectrum of **7a:**



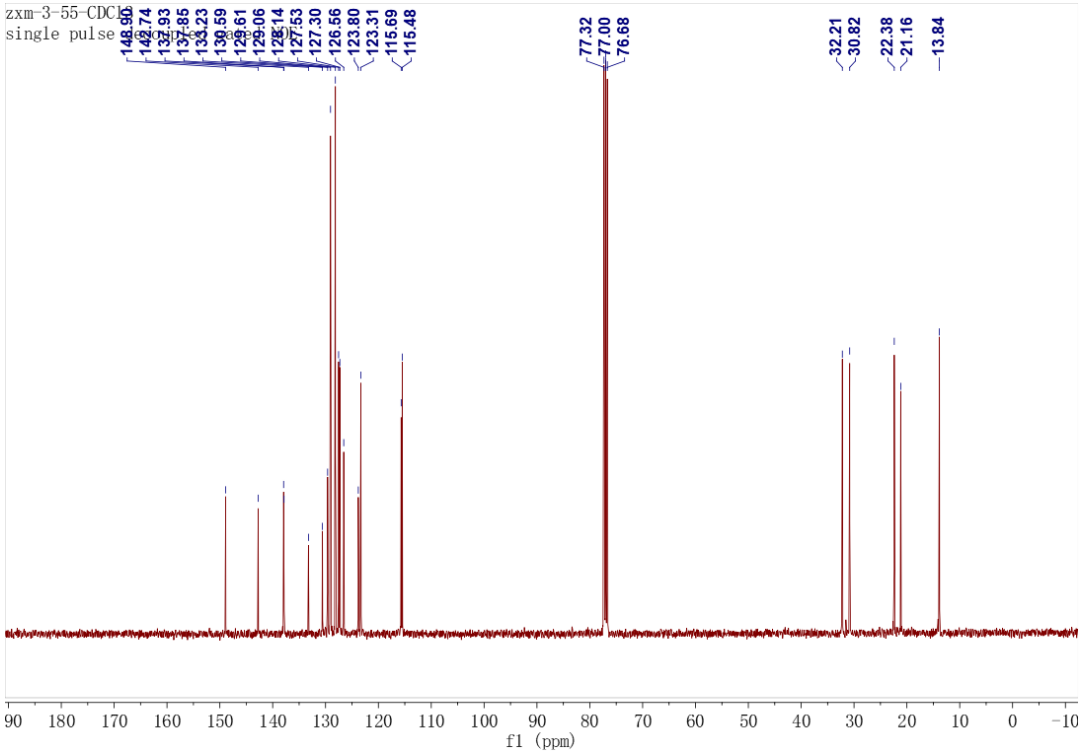


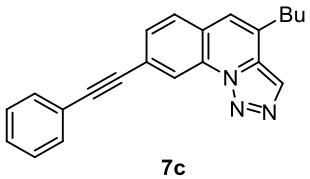

**7b**

$^{1}$H NMR Spectrum of **7b:**



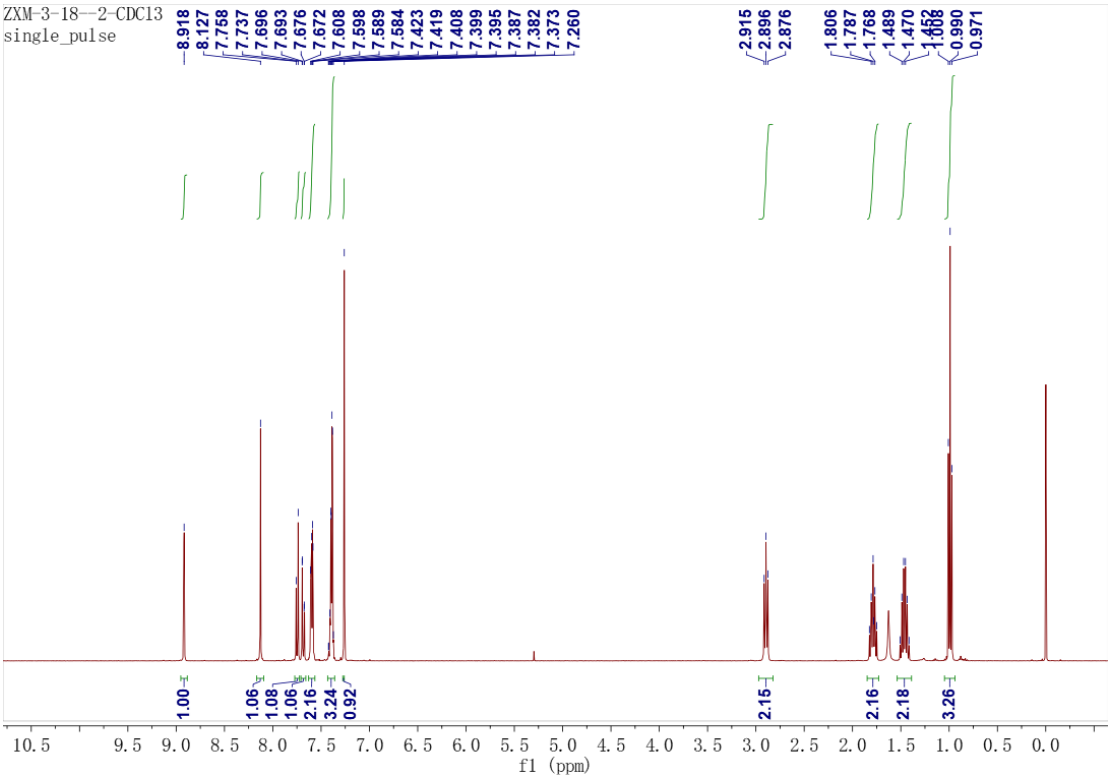

$^{13}$C NMR Spectrum of **7b:**



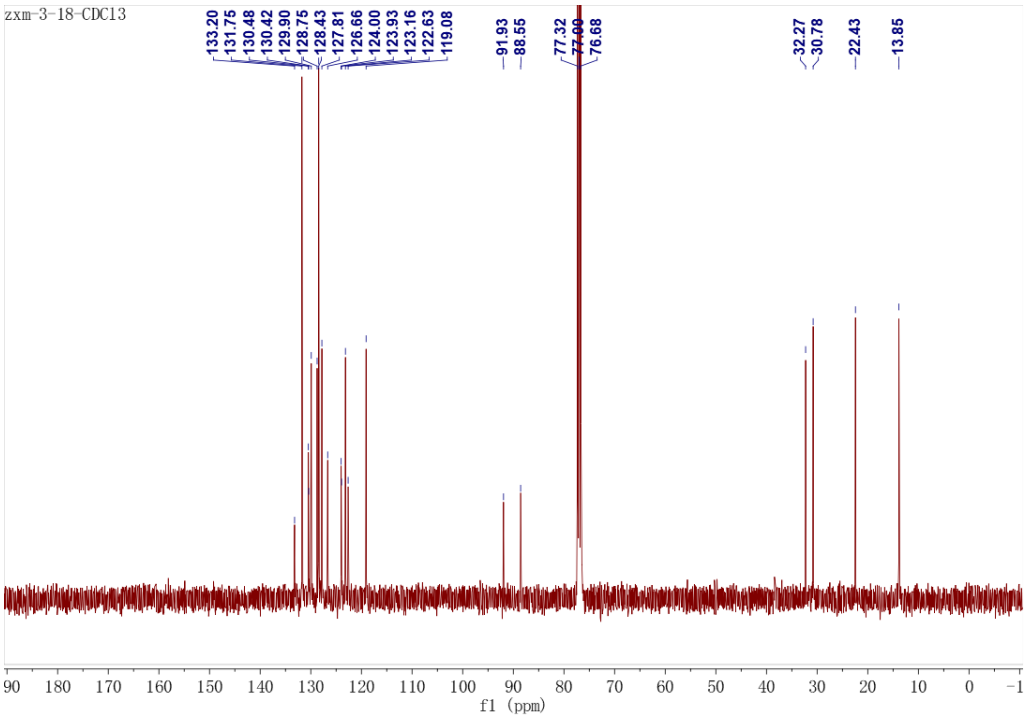


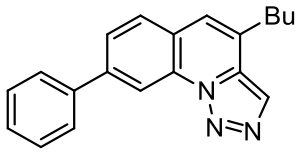

**7c**

$^{1}$H NMR Spectrum of **7c:**



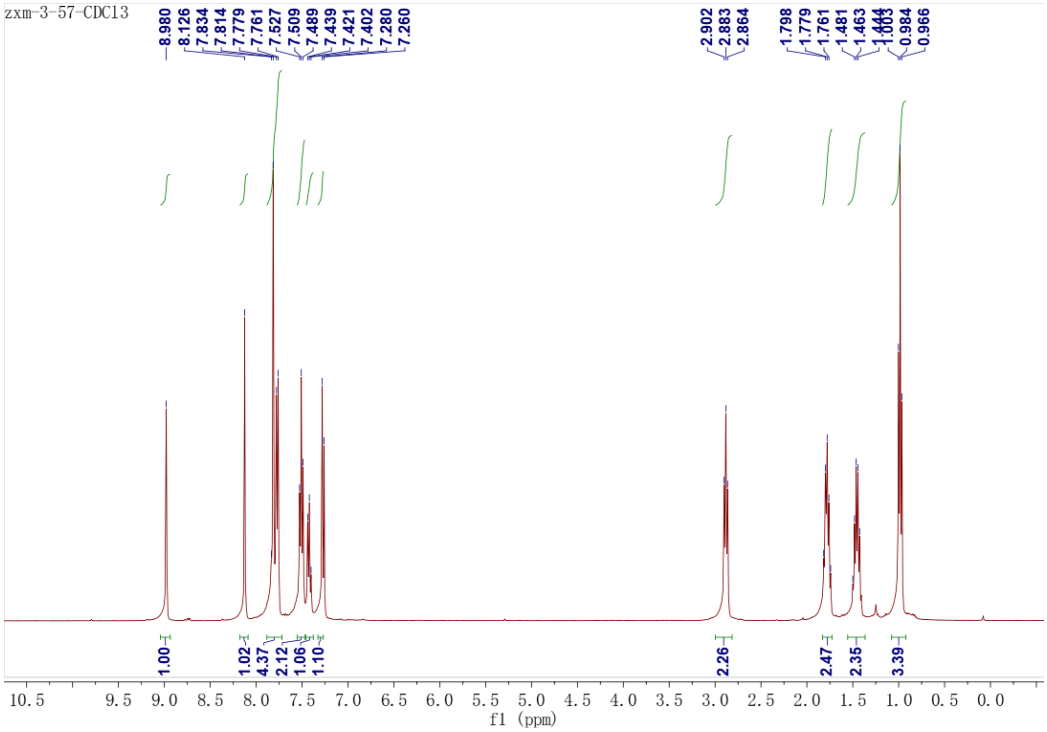

$^{13}$C NMR Spectrum of **7c:**






**7d**

$^{1}$H NMR Spectrum of **7d:**




$^{13}$C NMR Spectrum of **7d:**