Cobalt(II)-Catalyzed Hydroarylation of 1,3-Diynes and Internal Alkynes with Picolinamides Promoted by Alcohol

Yuan Gao,[a‡] Mengfan Zhang,[a‡] Chaoyu Wang,[a] Zhen Yang,[a] Xianqiang Huang,[b] Ruokun Feng[a*] and Chenze Qi [a]

[a]Zhejiang Key Laboratory of Alternative Technologies for Fine Chemicals Process, Department of Chemistry, Shaoxing University, Shaoxing 312000, China

[b]Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry & Chemical Engineering, Liaocheng University, Liaocheng 252059, China

Fax: +86-575-88345681; Tel: +86-575-88345681

E-mail: fengshenghm@usx.edu.cn

Supporting Information

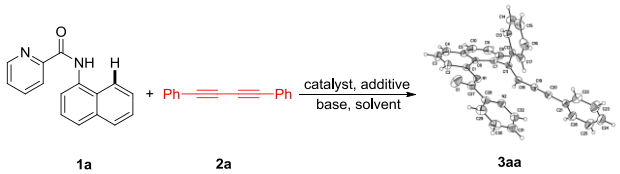
Content

General The reagents and solvents were purchased from common commercial sources and used without additional purification, if there is no special version. The starting materials of *N*-(naphthalen-1-yl)picolinamide were prepared according to the known methods. [1] NMR spectra were recorded for ^{1}H NMR at 400 MHz, and ^{13}C NMR at 100 MHz using TMS as internal standard. The following abbreviations were used to describe peak patterns where appropriate: singlet (s), doublet (d), triplet (t), quintuplet(q), multiplet (m), doublet of doublet (dd), broad resonances (br). Mass spectroscopy data of the products were collected on Xevo G2-XS QTof(Waters).

Optimization of the reaction conditions

Initially, we explored the reaction of *N*-(naphthalen-1-yl)picolinamide (1a) and 1,4-diphenylbuta-1,3-diyne (2a) in the presence of $Co(OAc)_2$ (30 mol%), KOAc (2.0 equiv.). As we expected, the desired product (3aa) was obtained in 60% yield (Table S1, entry 1) and the structure of 3aa was further confirmed by X-ray crystallography. After a screening of other cobalt catalysts, $Co(OAc)_2 \cdot 4H_2O$ showed a good catalytic activity, generating 3aa in 85% yield (Table S1, entries 1-8). It was noteworthy that when Co(II) was employed as a catalyst, the reaction yield was higher than that of Co(0) and Co(III). Furthermore, among the bases examined, such as KOAc, CsOAc, NaOPiv, $KHCO_3$, Cs_2CO_3 and K_2CO_3, KOAc gave the best result (Table S1, entries 9-13). Different solvents, such as MeOH and *i*-BuOH were failed to give a better yield than TFE and no desired product was achieved when DCE and PhF were applied as the solvents (Table S1, entries 14-17). The reaction was less active when additives, such as PivOH and H_2O were added (Table S1, entries 18 and 19). The yield was reduced to 73% when the reaction was deal with N_2 (Table S1, entry 20). The introduction of oxidants, such as Ag_2CO_3 and O_2, significantly reduced the reaction yield (Table S1, entries 21 and 22). The reaction yield was reduced to 68%, when 0.2 equivalent $Co(OAc)_2 \cdot 4H_2O$ was used (Table S1, entry 23). Finally, the optimized reaction conditions were obtained: $Co(OAc)_2 \cdot 4H_2O$ (30 mol%), KOAc (2.0 equiv.) in TFE (2.0 mL) at 100 ^{o}C for 12 h.

Table S1. Optimization of the reaction conditions[a]



1a 2a 3aa

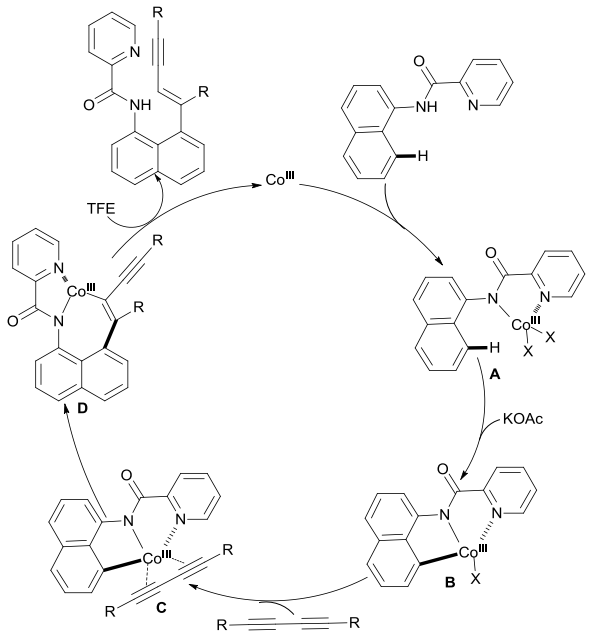
entry	catalyst	base	solvent	yield (%)[b]
1	$Co(OAc)_2$	KOAc	TFE	60
2	$CoBr_2$	KOAc	TFE	62
3	$CoCl_2$	KOAc	TFE	64
4	CoF_2	KOAc	TFE	55
5	$Co(OAc)_2 \cdot 4H_2O$	KOAc	TFE	85
6	$CoCO_3 \cdot xH_2O$	KOAc	TFE	58
7	$Co_2(CO)_8$	KOAc	TFE	57
8	$Cp^*Co(CO)I_2$	KOAc	TFE	26
9	$Co(OAc)_2 \cdot 4H_2O$	CsOAc	TFE	20
10	$Co(OAc)_2 \cdot 4H_2O$	NaOPiv	TFE	59
11	$Co(OAc)_2 \cdot 4H_2O$	$KHCO_3$	TFE	46
12	$Co(OAc)_2 \cdot 4H_2O$	Cs_2CO_3	TFE	30
13	$Co(OAc)_2 \cdot 4H_2O$	K_2CO_3	TFE	NR
14	$Co(OAc)_2 \cdot 4H_2O$	KOAc	MeOH	56
15	$Co(OAc)_2 \cdot 4H_2O$	KOAc	*i*-BuOH	65
16	$Co(OAc)_2 \cdot 4H_2O$	KOAc	DCE	NR
17	$Co(OAc)_2 \cdot 4H_2O$	KOAc	PhF	NR
18	$Co(OAc)_2 \cdot 4H_2O$	KOAc	TFE	24[c]
19	$Co(OAc)_2 \cdot 4H_2O$	KOAc	TFE	61[d]
20	$Co(OAc)_2 \cdot 4H_2O$	KOAc	TFE	73[e]
21	$Co(OAc)_2 \cdot 4H_2O$	KOAc	TFE	41[f]
22	$Co(OAc)_2 \cdot 4H_2O$	KOAc	TFE	53[g]
23	$Co(OAc)_2 \cdot 4H_2O$	KOAc	TFE	68[h]

[a]Reaction conditions unless otherwise specified: 1a (0.1 mmol), 2a (0.2 mmol),

catalyst (30 mol%), base (2.0 equiv.), additive (2.0 equiv.), solvent (2 mL), 100 ^{o}C for 12 h. [b]Isolated yield. [c]PivOH (2.0 equiv.) was added. [d]H_2O (2.0 equiv.) was added. [e]The reaction was carried out under N_2. [f]Ag_2CO_3 (2.0 equiv.) was added as the oxidant. [g]The reaction was carried out under O_2. [h]$Co(OAc)_2 \cdot 4H_2O$ (20 mol%) was used.

Possible reaction mechanism

Based on the control experiments and previous reports, a possible reaction mechanism was proposed as shown in **Scheme S1**. Initially, a Co(III) species was furnished under the standard reaction condition, followed by the coordination of **1a**, obtaining a Co(III) intermediate **A**. Subsequently, intermediate **A** underwent a concerted metalation deprotonation (CDC) process to produce the intermediate **B**. Then intermediate **B** coordinated with the 1,3-diyne, which after insertion lead to the intermediate **D**. The desired product was achieved by the protonolysis of intermediate **D** and accompanied with the formation of Co(III) species to fulfill the catalytic cycle. Trifluoroethanol may promote the last protonolysis step.



Scheme S1. Proposed Mechanism

Experimental Procedures

General Procedure for Preparation of products 3 and 4

A 25 mL sealed tube with a magnetic stir bar was charged with $Co(OAc)_2 \cdot 4H_2O$ (30 mol%), KOAc (2.0 equiv.), **1** (0.1 mmol), **2** (0.2 mmol), TFE (2 mL). Then the sealed tube was sealed and heated to 100 ^oC with stirring for 12 h. After cooling down, EtOAc (20 mL) and H_2O (20 mL) were added, and then theaqueous phase was extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 10 mL) and dried over anhydrous Na_2SO_4. Then the residue was concentrated and purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

General Procedure for Preparation of products 6

A 25 mL sealed tube with a magnetic stir bar was charged with **3ah** (0.1 mmol), NaOH (2 mmol), MeOH (1 mL). Then the sealed tube was sealed and heated to 100 ^oC with stirring for 12 h. After cooling down, the mixture was concentrated, and then the residue was extracted with EA and water. The organic layer was collected and dried over Na_2SO_4. After concentrated in vacuum and the residue was purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

General Procedure for Preparation of products 7

A 25 mL Schlenk tube with a magnetic stir bar was charged with **3ak** (0.2 mmol), K_2CO_3 (0.3 mmol). The reaction vessel was evacuated and filled with argon three times and then MeOH (1 mL) was added under argon atmosphere. Then the sealed tube was sealed and stirredat room temperature for 1 h. Finally, EtOAc (10 mL) was added to the mixture. After concentrated the organic layer in vacuum and the residue was purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding product in 87% yield.

General Procedure for Preparation of products 8

The CuI (5 mol%) and $NiCl_2 \cdot 6H_2O$ (5 mol%)were dissolved in THF (4 mL) and TMEDA (20 mol%), and the solution was stirred for 2 min at room temperature. **7**

(0.1 mmol**)** was added subsequently and the reaction mixture was stirred under air for 24 hours at room temperature. After cooling down, the mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel to afford pure **8** in 46% yield.

Control experiment

Scheme 5a: A 25 mL sealed tube with a magnetic stir bar was charged with $Co(OAc)_2•4H_2O$ (30 mol%), KOAc (2.0 equiv.), **1** (0.1 mmol), **2** (0.2 mmol), TEMPO (2.0 equiv.), TFE (2 mL). Then the sealed tube was sealed and heated to 100 ^oC with stirring for 12 h. After cooling down, EtOAc (20 mL) and H_2O (20 mL) were added, and then the aqueous phase was extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 10 mL) and dried over anhydrous Na_2SO_4. Then the residue was concentrated and purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

Scheme 5b: A 25 mL sealed tube with a magnetic stir bar was charged with $Co(OAc)_2•4H_2O$ (30 mol%), KOAc (2.0 equiv.), **1a** (0.1 mmol), or *d*-1a (0.1 mmol), **2a** (0.2 mmol), TFE (2 mL). Then the sealed tube was sealed and heated to 100 ^oC with stirring for 2 h. After cooling down, EtOAc (20 mL) and H_2O (20 mL) were added, and then the aqueous phase was extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 10 mL) and dried over anhydrous Na_2SO_4. Then the residue was concentrated and purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

Scheme 5c: A 25 mL sealed tube with a magnetic stir bar was charged with $Co(OAc)_2•4H_2O$ (30 mol%), KOAc (2.0 equiv.), **1a** (0.05 mmol), and *d*-1a (0.05 mmol), **2a** (0.2 mmol), TFE (2 mL). Then the sealed tube was sealed and heated to 100 ^oC with stirring for 2 h. After cooling down, EtOAc (20 mL) and H_2O (20 mL) were added, and then theaqueous phase was extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 10 mL) and dried over anhydrous Na_2SO_4. Then the residue was concentrated and purified by flash column

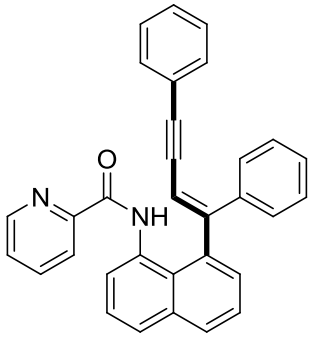
chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

Scheme 5d: A 25 mL sealed tube with a magnetic stir bar was charged with $Co(OAc)_2$ (30 mol%), KOAc (2.0 equiv.), *d*-**1** (0.1 mmol), **2** (0.2 mmol), TFE (2 mL). Then the sealed tube was sealed and heated to 100^{o}C with stirring for 12 h. After cooling down, EtOAc (20 mL) and H_2O (20 mL) were added, and then the aqueous phase was extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 10 mL) and dried over anhydrous Na_2SO_4. Then the residue was concentrated and purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

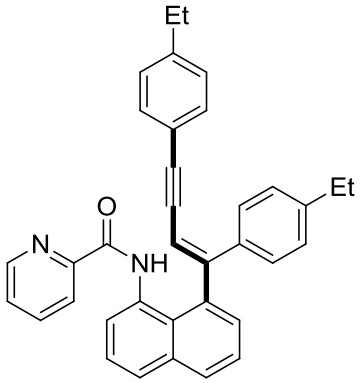
Scheme 5e: A 25 mL sealed tube with a magnetic stir bar was charged with $Co(OAc)_2$ (30 mol%), KOAc (2.0 equiv.), **1** (0.1 mmol), **2** (0.2 mmol), D_2O (4 equiv.), TFE (2 mL). Then the sealed tube was sealed and heated to 100^{o}C with stirring for 12 h. After cooling down, EtOAc (20 mL) and H_2O (20 mL) were added, and then the aqueous phase was extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 10 mL) and dried over anhydrous Na_2SO_4. Then the residue was concentrated and purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

Scheme 5f: A 25 mL sealed tube with a magnetic stir bar was charged with $Co(OAc)_2$•$4H_2O$ (30 mol%), KOAc (2.0 equiv.), **1** (0.1 mmol), **2** (0.2 mmol), CD_3OD (2 mL). Then the sealed tube was sealed and heated to 100 ^{o}C with stirring for 4 h. After cooling down, EtOAc (20 mL) and H_2O (20 mL) were added, and then the aqueous phase was extracted with EtOAc two times. The combined organic layer was washed with saturated NaCl (3 × 10 mL) and dried over anhydrous Na_2SO_4. Then the residue was concentrated and purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

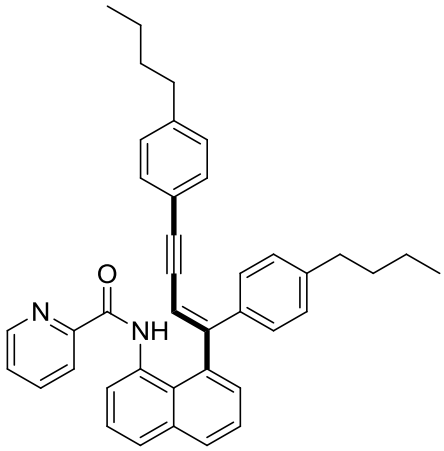
Characterization data of the products



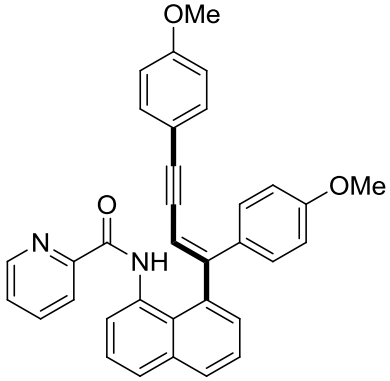
(*E*)-*N*-(8-(1,4-diphenylbut-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3aa) yellow solid (39 mg, 85% yield); mp (^{o}C): 143–144; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.34 (s, 1H), 7.06–7.10 (m, 2H), 7.14–7.18 (m, 1H), 7.29–7.33 (m, 1H), 7.38–7.40(m, 3H), 7.41–7.45 (m, 5H), 7.52–7.60 (m, 2H), 7.77–7.83 (m, 2H), 7.94–7.97 (m, 1H), 8.11–8.14 (m, 1H), 8.23–8.25 (m, 1H), 8.55–8.57 (m, 1H), 10.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 89.2, 94.9, 108.7, 122.2, 122.4, 123.6, 125.2, 126.1 (2C), 126.3, 127.5, 128.3, 128.4 (2C), 128.6, 129.5, 130.4, 131.3, 133.0, 135.4, 137.1, 137.3, 138.5, 148.0, 150.2, 151.7, 162.3.IR *v* 2958, 1687, 1525, 1495, 1265cm^{-1}; HRMS (ESI):*m/z* Calcd for $C_{32}H_{22}N_2O[M + H]^+$, 451.1805, Found 451.1808.



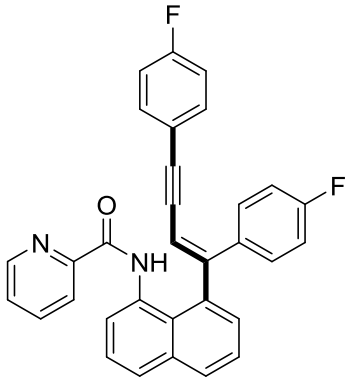
(*E*)-*N*-(8-(1,4-bis(4-ethylphenyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide(3ab) yellow solid (40 mg, 79% yield); mp (^{o}C): 120–121; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (t, 3H, *J* = 8.0 Hz); 1.23 (t, 3H, *J* = 8.0 Hz); 2.47 (q, 2H, *J* = 16.0 Hz); 2.64 (q, 2H, *J* = 16.0 Hz); 6.22 (s, 1H), 6.81–6.84 (m, 2H), 7.15–7.23 (m, 4H), 7.31–7.34 (m, 5H), 7.41–7.51(m, 2H), 7.67–7.71 (m, 2H), 7.83–7.85 (m, 1H), 8.03–8.05 (m, 1H), 8.19–8.21 (m, 1H), 8.54 (d, 1H, *J* = 8.0 Hz); 10.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.4 (2C), 28.6, 28.9, 89.0, 95.3, 108.2, 121.0, 122.2, 122.4, 125.3, 126.1 (2C), 126.2, 126.3, 127.0, 128.1, 128.7, 129.5, 130.4, 131.3, 133.2, 135.4, 136.1, 137.1, 137.6, 144.6, 144.8, 148.2, 150.3, 151.2, 162.4. IR *v* 2925, 1683, 1523, 1433, 1262 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{36}H_{30}N_2O[M + H]^+$, 507.2431, Found 507.2430.



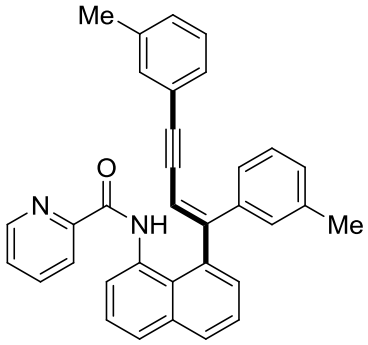
(*E*)-*N*-(8-(1,4-bis(4-butylphenyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3ac) yellow solid (46 mg, 81% yield); mp (^{o}C): 127–128; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.91–0.95 (m, 3H), 0.98–1.02 (m, 3H), 1.27–1.34 (m, 2H), 1.40–1.44 (m, 2H),1.51–1.55 (m, 2H), 1.66–1.70 (m, 2H),2.51 (t, 2H, *J* = 8.0 Hz), 2.69 (t, 2H, *J* = 8.0 Hz), 6.27 (s, 1H), 6.86–6.89(m, 2H), 7.21–7.23(m, 2H), 7.28–7.32 (m, 1H), 7.37–7.43 (m, 4H), 7.50–7.60 (m, 2H), 7.76–7.82 (m, 2H), 7.93 (d, 1H, *J* = 8.0 Hz), 8.09 (d, 1H, *J* = 8.0 Hz), 8.24 (d, 1H, *J* = 8.0 Hz), 8.58–8.59 (m, 1H), 10.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 14.1, 22.3, 22.4, 33.4, 33.5, 35.4, 35.7, 89.0, 95.4, 108.1, 121.0, 122.2, 122.5, 125.2, 126.0, 126.1, 126.3 (2C), 127.6, 128.6 (2C), 129.4, 130.3, 131.2, 133.1, 135.4, 136.0, 137.1, 137.6, 143.3, 143.5, 148.2, 150.3, 151.2, 162.3 .IR *v* 2929, 1687, 1523, 1499, 1262 cm^{-1}; HRMS (ESI):*m/z* Calcd for $C_{40}H_{38}N_2O[M + H]^+$, 563.3057, Found 563.3061.



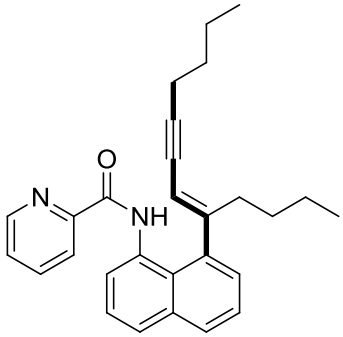
(*E*)-*N*-(8-(1,4-bis(4-methoxyphenyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinam (3ad) yellow solid (42 mg, 83% yield); mp (^{o}C): 181–182; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.70 (s, 3H), 3.87 (s, 3H), 6.22 (s, 1H), 6.55–6.57 (m, 2H), 6.91–6.94 (m, 2H), 7.28–7.37 (m, 6H), 7.50–7.56 (m, 2H), 7.77–7.80 (m, 2H), 7.92–7.93 (m, 1H),8.11 (d, 1H, *J* = 8.0 Hz), 8.25 (d, 1H, *J* = 8.0 Hz), 8.61–8.62 (m, 1H), 10.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 55.1, 55.4, 88.4, 94.7, 107.1, 112.8, 114.2, 115.9, 122.2, 125.2, 126.0, 126.1, 126.2, 129.4, 130.1, 130.3, 131.5, 132.7, 133.1, 135.4, 137.1, 137.7, 148.2, 150.3, 159.3, 159.6, 162.3. IR *v* 2925, 1684, 1508, 1495, 1291 cm^{-1}; HRMS (ESI):*m/z* Calcd for $C_{34}H_{26}N_2O_3[M + H]^+$, 511.2016, Found 511.2021.



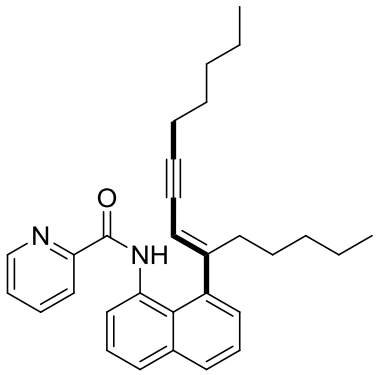
(E)-*N*-(8-(1,4-bis(4-fluorophenyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamid e (3ae) yellow solid (31 mg, 64% yield); mp (^{o}C): 168–169; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.27 (s, 1H), 6.71–6.76 (m, 2H), 7.05–7.10 (m, 2H), 7.31–7.41 (m, 6H), 7.50–7.58 (m, 2H), 7.79–7.83 (m, 2H), 7.93–7.95 (m, 1H), 8.13 (d, 1H, *J* = 8.0 Hz), 8.20 (d, 1H, *J* = 8.0 Hz), 8.54 (d, 1H, *J* = 4.0 Hz), 10.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 88.6, 93.7, 108.2, 114.4, 114.6, 115.8, 116.0, 119.5, 119.6, 122.3, 122.6, 125.2, 126.0, 126.1, 126.3, 126.4, 129.7, 130.4, 130.5, 130.6, 132.9, 133.1 (2C), 134.8, 135.4, 137.0, 137.3, 147.9, 150.2, 150.8, 161.1, 161.3, 162.1, 163.8. IR *v* 2926, 1735, 1690, 1488, 1273 cm^{-1}; HRMS (ESI):*m/z* Calcd for $C_{32}H_{20}F_2N_2O$[M + H]$^{+}$, 487.1616, Found 487.1620.



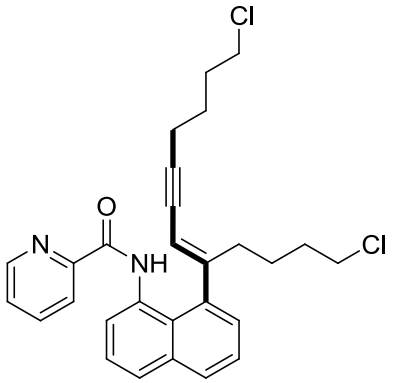
(*E*)-*N*-(8-(1,4-di-m-tolylbut-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3af) yellow solid (35 mg, 73% yield); mp (^{o}C):121–122; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.08 (s, 3H), 2.40 (s, 3H), 6.34 (s, 1H), 6.92–6.98 (m, 3H), 7.19–7.32 (m, 5H), 7.44–7.60 (m, 4H), 7.79–7.83 (m, 2H), 7.93–7.96 (m, 2H), 8.14–8.23 (m, 2H), 8.62–8.63 (m, 1H),10.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 21.5, 89.2, 95.2, 108.6, 122.1, 122.5, 123.6, 125.2, 126.0, 126.1 (2C), 126.2, 126.3, 127.6, 128.4 (2C), 129.1, 129.2, 129.3, 129.5, 130.4, 132.0, 133.1, 135.4, 136.6, 137.2, 137.5, 138.1, 138.5, 148.2, 150.4, 151.9, 162.3. IR *v* 3056, 2922, 1686, 1495, 1265 cm^{-1}; HRMS (ESI):*m/z* Calcd for $C_{34}H_{26}N_2O$[M + H]$^{+}$,479.2118, Found 479.2118.



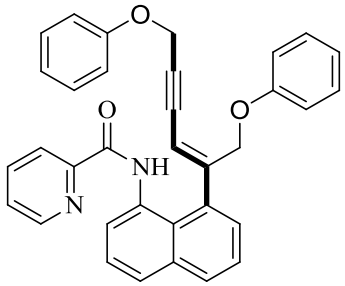
(*E*)-*N*-(8-(dodec-5-en-7-yn-5-yl)naphthalen-1-yl)picolinamide (3ag) yellow solid (31 mg, 75% yield); mp (^{o}C): 77–78; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.72–0.75 (m, 3H), 0.91–0.94 (m, 3H), 1.10–1.28 (m, 4H), 1.38–1.53 (m, 4H),2.10–2.17 (m, 1H), 2.36–2.41 (m, 2H), 2.73–2.80 (m, 1H),5.89 (s, 1H), 7.17–7.19(m, 1H), 7.41 (t, 1H, *J* = 8.0 Hz), 7.47–7.49 (m, 1H), 7.56 (t, 1H, *J* = 8.0 Hz), 7.72–7.74 (m, 1H), 7.81–7.83(m, 1H), 7.90–7.95(m, 1H), 8.34 (d, 1H, *J* = 8.0 Hz), 8.45 (d, 1H, *J* = 8.0 Hz), 8.77 (d, 1H, *J* = 8.0 Hz), 10.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 13.6, 13.9, 19.4, 21.9, 22.6, 29.7, 31.0, 35.5, 78.7, 94.6, 110.1, 121.2, 122.3, 124.7, 125.0, 125.9, 126.0 (2C), 128.9 (2C), 133.2, 135.4, 137.3, 137.7, 148.4, 150.2, 156.2, 162.5.IR *v* 2960, 2931, 1689, 1528, 1265 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{28}H_{30}N_2O[M + H]^+$, 411.2431, Found 411.2439.



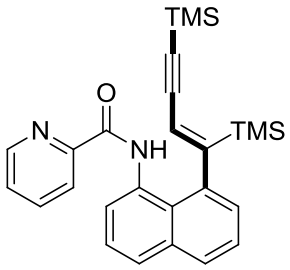
(*E*)-*N*-(8-(tetradec-6-en-8-yn-6-yl)naphthalen-1-yl)picolinamide (3ah) yellow solid (33 mg, 77% yield); mp (^{o}C): 71–72; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.73–0.78 (m, 3H), 0.89–0.93 (m, 3H), 1.06–1.19 (m, 5H), 1.22–1.41 (m, 5H),1.50–1.57 (m, 2H), 2.11–2.18 (m, 1H), 2.36–2.40 (m, 2H),2.73–2.80 (m, 1H), 5.90 (s, 1H), 7.17–7.19(m, 1H), 7.40 (t, 1H, *J* = 8.0 Hz), 7.45–7.48 (m, 1H), 7.55 (t, 1H, *J* = 8.0 Hz), 7.71–7.73(m, 1H), 7.79–7.81(m, 1H), 7.88–7.92(m, 1H), 8.34 (d, 1H, *J* = 8.0 Hz), 8.47 (d, 1H, *J* = 8.0 Hz), 8.76–8.77 (d, 1H, *J* = 8.0 Hz), 10.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0 (2C), 19.7, 22.3, 22.4, 27.2, 28.6, 31.1, 31.6, 35.7, 78.7, 94.7, 110.2, 121.1, 122.3, 124.6, 125.0, 125.9, 126.0 (2C), 128.9 (2C), 133.2, 135.4, 137.3, 137.7, 148.4, 150.2, 156.2, 162.5.IR *v* 2930, 2055, 1688, 1494, 1265 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{30}H_{34}N_2O[M + H]^+$, 439.2744, Found 439.2744.



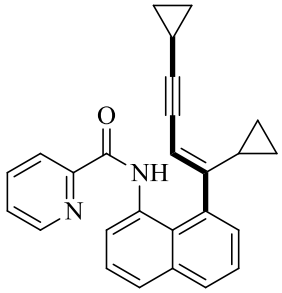
(*E*)-*N*-(8-(1,12-dichlorododec-5-en-7-yn-5-yl)naphthalen-1-yl)picolinamide (3ai) yellow solid (35 mg, 74% yield); mp (^{o}C): 68–69; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.25–1.41 (m, 2H), 1.56–1.69 (m, 4H), 1.82–1.89 (m, 2H), 2.13–2.20 (m, 1H),2.39–2.42 (m, 2H), 2.71–2.78 (m, 1H), 3.32–3.39 (m, 2H), 3.53–3.56 (m, 2H), 5.91 (s, 1H), 7.15–7.17(m, 1H), 7.39 (d, 1H, *J* = 8.0 Hz), 7.47–7.50 (m, 1H), 7.54 (t, 1H, *J* = 8.0 Hz), 7.21 (d, 1H, *J* = 8.0 Hz), 7.80 (d, 1H, *J* = 8.0 Hz), 7.89–7.93 (m, 1H), 8.33 (d, 1H, J = 8.0 Hz), 8.41 (d, 1H, J = 8.0 Hz), 8.73 (d, 1H, J = 4.0 Hz), 10.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 19.1, 24.8, 26.1, 31.6, 32.1, 34.8, 44.6, 44.8, 93.9, 110.4, 121.5, 122.4, 124.7, 125.1, 126.0, 126.1, 128.9, 129.2, 133.1, 135.4, 137.1, 137.5, 148.4, 150.0, 155.5, 162.4.IR *v* 2956, 2923, 2852, 1729, 1657, 1631, 1468 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{28}H_{28}Cl_2N_2O[M + H]^+$, 479.1651, Found 479.1649.



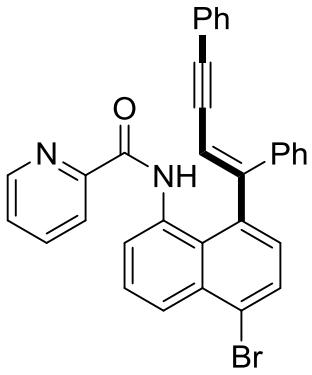
(*Z*)-*N*-(8-(1,6-diphenoxyhex-2-en-4-yn-2-yl)naphthalen-1-yl)picolinamide (3aj): Dark liquid (27 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.76 (s, 1H), 8.30 (s, 1H), 8.30 (s, 1H), 8.17 (d, 1H, *J* = 8.0 Hz), 7.81–7.90 (m, 3H), 7.61 (t, 1H, *J* = 8.0 Hz), 7.44 (t, 1H, *J* = 7.6 Hz), 7.25–7.35 (m, 4H), 7.19 (t, 1H, *J* = 8.0 Hz), 7.04 (t, 1H, *J* = 8.0 Hz), 6.90–6.96 (m, 3H), 6.69 (d, 1H, *J* = 8.0 Hz), 5.84 (s, 1H), 5.00 (dd, 1H, *J* = 56, 12 Hz), 4.65–4.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 158.3, 157.6, 151.9, 148.1, 137.2, 135.2, 134.5, 132.6, 129.6, 129.5, 129.2, 128.6, 126.9, 126.8, 126.2, 125.9, 124.9, 124.0, 122.5, 121.5, 121.0, 114.8, 111.0, 90.2, 83.2, 69.4, 56.2.IR *v* 2961, 2359, 2341, 1683, 1598, 1495, 907 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{34}H_{26}N_2O_3[M + H]^+$, 511.2016, Found 511.2021.



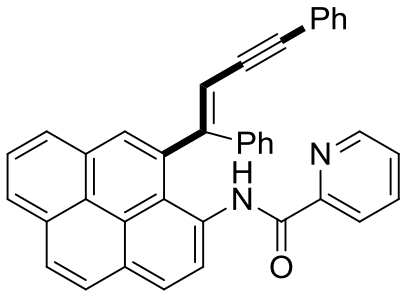
(*E*)-*N*-(8-(1,4-bis(trimethylsilyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3ak) yellow solid (30 mg, 67% yield); mp (^{o}C): 123–124; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ -0.21 (s, 9H), 0.23 (s, 9H), 6.63 (s, 1H), 6.95–6.97(m, 1H), 7.38–7.42(m, 1H), 7.46–7.54 (m, 2H), 7.66–7.76 (m, 2H),7.91–7.95 (m, 1H),8.33 (d, 1H, *J* = 8.0 Hz), 8.54 (d, 1H, *J* = 8.0 Hz), 8.82–8.83 (m, 1H),10.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ-2.1, -0.2, 99.7, 105.3, 119.4, 120.7, 122.4, 124.7, 125.3, 125.6, 126.1 (2C), 126.6, 128.1, 134.2, 135.0, 137.5, 140.1, 148.6, 150.2, 162.5, 163.2.IR *v* 2958, 2112, 1679, 1495, 1262 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{26}H_{30}N_2OSi_2[M + H]^+$, 443.1969, Found 443.1967.



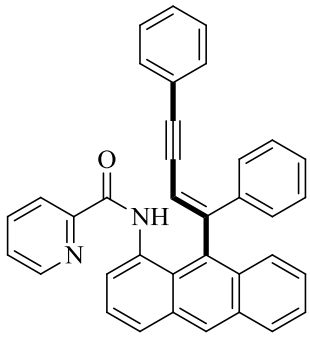
(*E*)-*N*-(8-(1,4-dicyclopropylbut-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3al): yellow liquid (14 mg, 36% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.97 (s, 1 H), 8.84–8.92 (m, 1 H), 8.35 (d, 1 H, *J* = 4.0 Hz), 8.25 (d,1 H, *J* = 8.0 Hz), 7.93–7.97 (m, 1 H), 7.83 (d, 1 H, *J* = 8.0 Hz), 7.74 (d, 1 H, *J* = 8.0 Hz), 7.52–7.58 (m, 2 H), 7.39 (t, 1 H, *J* = 8.0 Hz), 7.03–7.05 (m, 1 H), 5.71 (m, 1 H), 2.27–2.32 (m, 1 H), 1.44–1.49 (m, 1 H), 0.86–0.92 (m, 2 H), 0.66–0.78 (m, 3 H), 0.48–0.55 (m, 1 H), 0.32–0.37 (m, 1 H), 0.08–0.15 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 162.8, 156.2, 150.4, 148.3, 137.3, 134.9, 133.0, 129.9, 129.2, 126.5, 126.3, 126.0, 125.8, 124.6, 122.9, 122.3, 109.5, 97.4, 74.0, 29.7, 17.1, 8.7, 5.8, 5.4, 0.6.IR *v* 2922, 2359, 2342, 1684, 1522, 1496, 907 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{26}H_{22}N_2O[M + H]^+$, 379.1805, Found 379.1810.



(*E*)-*N*-(5-bromo-8-(1,4-diphenylbut-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3ba) white solid (33 mg, 63% yield); mp (^{o}C): 175–176; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.27 (s, 1H), 7.01–7.05(m, 2H), 7.10–7.14(m, 1H), 7.24–7.28 (m, 2H), 7.31–7.36 (m, 7H), 7.63 (t, 1H, *J* = 8.0 Hz), 7.72–7.77 (m, 1H), 7.82 (d, 1H, *J* = 8.0 Hz), 8.07 (d, 1H, *J* = 8.0 Hz), 8.20 (d, 1H, *J* = 8.0 Hz), 8.24–8.26 (m, 1H), 8.50–8.51 (m, 1H), 10.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 89.0, 95.2, 108.8, 122.3, 123.5 (2C), 124.2, 125.5, 126.2, 127.5 (2C), 127.6, 128.4, 128.5, 128.6 (2C), 129.6, 130.4, 131.3, 133.4 (2C), 137.2, 137.5, 138.2, 148.0, 150.0, 151.0, 162.3. IR *v* 3047, 2925, 1687, 1519, 1397 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{32}H_{21}BrN_2O[M + H]^+$, 529.0910, Found 529.0913.

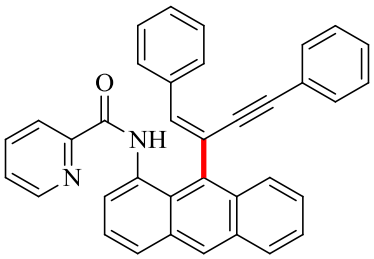


(*E*)-*N*-(10-(1,4-diphenylbut-1-en-3-yn-1-yl)pyren-1-yl)picolinamide (3ca) yellow solid (39 mg, 76% yield); mp (^{o}C): 153–154; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ6.62 (s, 1H), 7.01–7.05 (m, 2H), 7.14–7.17 (m, 1H), 7.36–7.43 (m, 4H), 7.44–7.48 (m, 4H), 7.84–7.88 (m, 1H),8.03–8.12 (m, 4H), 8.17–8.20 (m, 2H), 8.23–8.26 (m, 2H), 8.69–8.72 (m, 2H), 10.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 89.3, 94.9, 106.5, 122.3, 122.6, 123.2, 123.7, 124.8, 124.9, 125.7, 126.2, 126.4 (3C), 126.5, 127.6, 127.8, 128.4, 128.5, 128.6, 129.1, 130.4, 131.3, 131.4, 131.8 (2C), 136.5, 137.3, 138.0, 148.2, 150.4, 152.2, 162.2. IR *v* 2925, 2851, 1691, 1507, 1274 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{38}H_{24}N_2O[M + H]^+$, 525.1961, Found 525.1959.

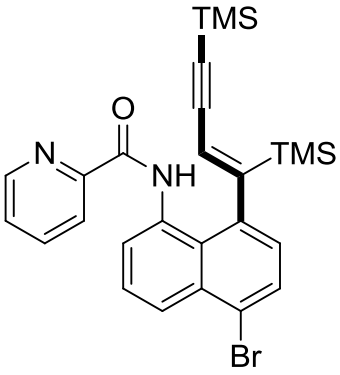


(*E*)-*N*-(9-(1,4-diphenylbut-1-en-3-yn-1-yl)anthracen-1-yl)picolinamide (3da): yellow solid (11 mg, 21% yield) : mp (℃): 186-189; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.82 (s, 1H), 8.59 (s, 1H), 8.42 (d, 1H, *J* = 4.0 Hz), 8.01–8.09 (m, 5H), 7.66–7.73 (m, 3H), 7.56–7.60 (m, 1H), 7.39–7.51 (m, 7H), 7.22–7.26 (m, 1H), 7.08–7.15 (m, 3H), 6.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 162.8, 150.1, 149.2, 147.9, 138.8, 137.0, 133.6, 133.0, 132.4, 131.6, 131.4, 131.1, 128.7, 128.6, 128.5, 128.1, 127.8, 127.5, 126.7, 126.4, 125.9 (2C), 125.6 (2C), 125.0, 124.2, 123.7,

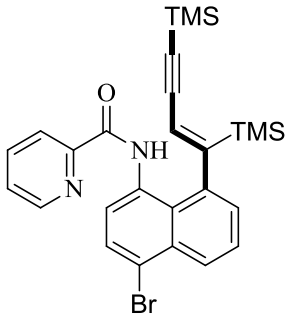
122.2, 110.5, 96.2, 89.2. IR *v* 2923, 1684, 1506, 907 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{36}H_{24}N_2O[M + H]^+$, 501.1961, Found 501.1960.



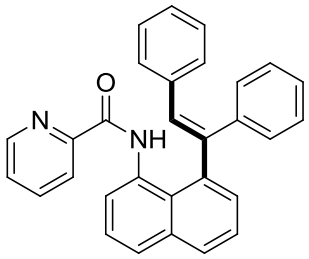
(*E*)-*N*-(9-(1,4-diphenylbut-1-en-3-yn-2-yl)anthracen-1-yl)picolinamide (3d'a): yellow soild (22 mg, 43% yield) : mp (℃): 204-205; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 10.78 (s, 1H), 8.64 (s, 1H), 8.60 (d, 1H, *J* = 4.0 Hz), 8.06–8.08 (m, 3H), 7.98–8.01 (m, 2H), 7.77–7.81 (m, 1H), 7.58 (t, 1H, *J* = 8.0 Hz), 7.56–7.60 (m, 1H), 7.43–7.49 (m, 2H), 7.35–7.39 (m, 1H), 7.13–7.16 (m, 2H), 6.98–7.07 (m, 7H), 6.55–6.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 162.4, 151.8, 150.2, 147.6, 138.7, 137.1, 133.1, 132.4, 131.3, 131.2, 130.9, 130.8, 128.5 (2C), 128.3, 128.2, 127.9, 127.6, 126.3 (2C), 126.0, 125.9, 125.5, 124.8, 123.7, 122.9, 122.3, 109.4, 97.5, 88.2. IR *v* 2922, 1683, 1506, 907 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{36}H_{24}N_2O[M + H]^+$, 501.1961, Found 501.1958.



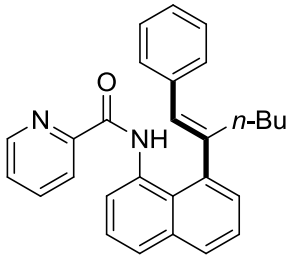
(*Z*)-*N*-(8-(1,4-bis(trimethylsilyl)but-1-en-3-yn-1-yl)-5-bromonaphthalen-1-yl)pico linamide (3bk) yellow solid (26 mg, 51% yield) : mp (℃): 153-154; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 10.91 (s, 1H), 8.78 (d, 1H, *J* = 4.0 Hz), 8.57 (d, 1H, *J* = 8.0 Hz), 8.30 (d, 1H, *J* = 8.0 Hz), 8.13 (d, 1H, *J* = 8.0 Hz), 7.89–7.93 (m, 1H), 7.71 (d, 1H, *J* = 8.0 Hz), 7.61 (t, 1H, *J* = 8.0 Hz), 7.45–7.48 (m, 1H), 6.78 (d, 1H, *J* = 8.0 Hz), 6.59 (s, 1H), 0.19 (s, 9H), -0.24 (s, 9H); ^{13}C NMR (100 MHz,$CDCl_3$, TMS) δ 162.4, 162.3, 150.1, 148.6, 140.3, 137.5, 134.7, 132.9, 129.7, 127.5, 125.9, 124.6, 122.4, 120.7, 120.2, 105.0, 100.3, -0.26, -2.12. IR *v* 2959, 1687, 1519, 1490, 1265, 1249, 843 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{26}H_{29}BrN_2OSi_2[M + H]^+$, 521.1075, Found 521.1082.



(*Z*)-*N*-(8-(1,4-bis(trimethylsilyl)but-1-en-3-yn-1-yl)-5-bromonaphthalen-1-yl)pico linamide (3ck) yellow solid (20 mg, 38% yield) : mp (℃): 205-206; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.92 (s, 1H), 8.79 (d, 1H, *J* = 4.0 Hz), 8.57 (d, 1H, *J* = 8.0 Hz), 8.30 (d, 1H, *J* = 8.0 Hz), 8.14 (d, 1H, *J* = 8.0 Hz), 7.90–7.94 (m, 1H), 7.72 (d, 1H, *J* = 8.0 Hz), 7.62 (t, 1H, *J* = 8.0 Hz), 7.46–7.49 (m, 1H), 6.79 (d, 1H, *J* = 8.0 Hz), 6.60 (s, 1H), 0.19 (s, 9H), -0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 162.5, 162.3, 150.1, 148.6, 140.4, 137.5, 134.7, 133.0, 129.7, 127.5, 126.0, 124.6, 122.5, 120.7, 120.2, 105.0, 100.3. IR *v* 2958, 1688, 1519, 1490, 1248, 842 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{26}H_{29}BrN_2OSi_2[M + H]^+$, 521.1075, Found 521.1082.

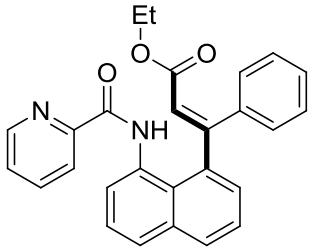


(*E*)-*N*-(8-(1,2-diphenylvinyl)naphthalen-1-yl)picolinamide (4a) yellow solid (29 mg, 70% yield); mp (^{o}C): 124–125; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.94 (s, 1H), 7.01–7.02(m, 4H), 7.10–7.18(m, 6H), 7.32–7.36 (m, 1H), 7.45–7.56 (m, 3H), 7.76–7.83 (m, 2H),7.88–7.90 (m, 1H),8.17 (d, 1H, *J* = 8.0 Hz), 8.22–8.23 (m, 1H),8.35 (d, 1H, *J* = 8.0 Hz), 10.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 121.5, 122.5, 125.0, 125.2, 125.9, 126.0, 127.0, 127.5, 127.8, 127.9, 129.0, 129.5, 129.7, 130.7, 131.0, 133.4, 135.7, 137.1, 137.2, 139.4 (2C), 142.8, 147.8, 150.5, 162.3. IR *v* 2921, 2843, 1683, 1519, 1495 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{30}H_{22}N_2O[M + H]^+$, 427.1805, Found 427.1808.

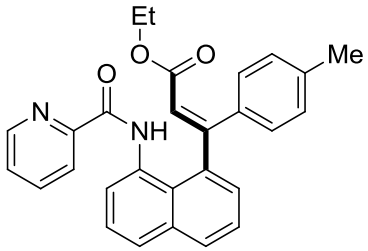


(*E*)-*N*-(8-(1-phenylhex-1-en-1-yl)naphthalen-1-yl)picolinamide (4b') yellow solid (17 mg, 41% yield); mp (^{o}C): 124–125; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ

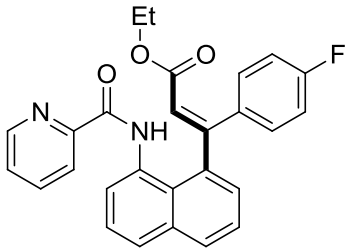
0.75–0.79(m, 3H), 1.14–1.27(m, 2H), 1.39–1.45(m, 2H), 2.27–2.35 (m, 1H), 2.85–2.92(m, 1H), 6.81 (s, 1H), 7.13–7.16 (m, 1H), 7.19–7.20 (m, 1H), 7.18–7.34 (m, 2H), 7.40–7.42 (m, 4H), 7.45–7.49 (m, 1H), 7.57–7.60 (m, 1H), 7.75–7.78 (m, 2H), 7.85–7.87 (m, 1H), 8.23–8.25 (m, 1H), 8.51–8.54 (m, 1H), 11.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 13.9, 22.9, 29.9, 33.9, 121.1, 122.1, 124.4, 125.0, 125.8, 125.9, 126.1, 126.6, 128.4, 128.6, 129.1, 129.4, 129.9, 133.3, 135.5, 137.0, 138.0, 140.0, 146.7, 147.8, 149.9, 162.7. IR *v* 2962, 2929, 1683, 1519, 1486 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{28}H_{26}N_2O[M + H]^+$,407.2118, Found 407.2115.



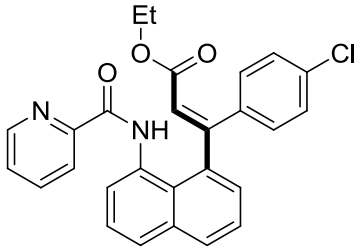
(*E*)-ethyl 3-phenyl-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4c) yellow solid (23 mg, 54% yield); mp (^{o}C): 135–136; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (t, 3H, *J* = 8.0 Hz), 4.00–4.10 (m, 2H), 6.37 (s, 1H), 7.02–7.10 (m, 4H), 7.17–7.19 (m, 1H), 7.40–7.42 (m, 2H), 7.46–7.49 (m, 3H), 7.74–7.77 (m, 1H), 7.89–7.92 (m, 2H), 8.25–8.30 (m, 2H), 8.54–8.56 (m, 1H), 10.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 60.1, 119.8, 121.9, 122.4, 124.9, 125.1, 126.2, 126.3, 126.4, 127.3, 128.8, 129.6, 130.0, 130.4, 133.0, 135.5, 137.3, 137.5, 137.8, 148.1, 150.2, 157.0, 162.3, 165.9. IR *v* 2962, 2925, 1687, 1523, 1491 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{27}H_{22}N_2O_3[M + H]^+$, 423.1703, Found 423.1704.



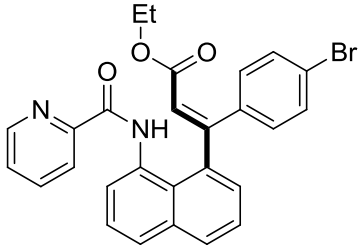
(*E*)-ethyl 3-(8-(picolinamido)naphthalen-1-yl)-3-(*p*-tolyl)acrylate (4d) yellow solid (25 mg, 58% yield); mp (^{o}C): 128–129; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (t, 3H, *J* = 8.0 Hz), 2.20 (s, 2H), 3.98–4.10 (m, 2H), 6.30 (s, 1H), 6.82–6.88(m, 4H), 7.36–7.38(m, 1H), 7.44–7.48 (m, 3H), 7.71–7.73 (m, 1H), 7.86–7.91 (m, 2H), 8.21–8.26 (m, 2H), 8.52–8.54 (m, 1H), 10.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.1, 21.3, 60.0, 119.0, 121.8, 122.4, 124.8, 125.2, 126.1, 126.3 (2C), 128.0, 129.6, 129.9, 130.3, 133.0, 134.8, 135.5, 137.4, 137.6, 138.9, 148.1, 150.3, 157.3, 162.3, 166.0. IR *v* 2921, 2851, 1683, 1519, 1458 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{28}H_{24}N_2O_3[M + H]^+$, 437.1860, Found 437.1862.



(*E*)-ethyl 3-(4-fluorophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4e) yellow solid (30 mg, 68% yield); mp (^{o}C): 136–137; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.14 (t, 3H, *J* = 8.0 Hz), 4.00–4.11 (m, 2H), 6.35 (s, 1H), 6.72 (t, 2H, *J* = 8.0 Hz), 6.97–7.00 (m, 2H), 7.35–7.37 (m, 1H), 7.43–7.50 (m, 3H), 7.70–7.72 (m, 1H), 7.86–7.90 (m, 2H), 8.22–8.26 (m, 2H), 8.53–8.54 (m, 1H), 10.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.1, 60.2, 114.2, 114.4, 119.6, 122.0, 122.5, 124.9, 125.1, 126.2, 126.4, 126.5, 130.1, 130.4, 131.7, 131.8, 132.9, 133.7, 135.5, 137.2, 137.6, 148.1, 150.1, 156.1, 161.6, 162.2, 164.0, 165.8. IR *ν* 2923, 1719, 1681, 1523, 1270 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{27}H_{21}FN_2O_3[M + H]^+$, 441.1609, Found 441.1610.

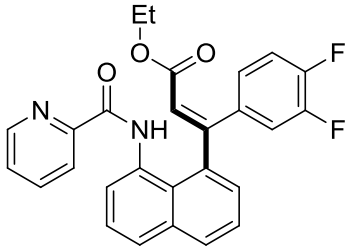


(*E*)-ethyl 3-(4-chlorophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4f) yellow solid (28 mg, 61% yield); mp (^{o}C): 117–118; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (t, 3H, *J* = 8.0 Hz), 3.98–4.09 (m, 2H), 6.35 (s, 1H), 6.92–6.95(m, 2H), 6.99–7.02 (m, 2H), 7.34–7.36 (m, 1H), 7.45–7.51 (m, 3H), 7.72–7.74 (m, 1H), 7.88–7.92 (m, 2H), 8.24 (d, 2H, *J* = 8.0 Hz), 8.51–8.53 (m, 1H), 10.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.1, 60.2, 120.0, 122.1, 122.5, 124.9, 125.1, 126.3, 126.4, 126.5, 127.5, 130.2, 130.4, 131.0, 132.8, 134.8, 135.5, 136.1, 136.9, 137.6, 148.1, 150.1, 155.9, 162.2, 165.7. IR *ν* 2921, 1723, 1687, 1527, 1495 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{27}H_{21}ClN_2O_3[M + H]^+$, 457.1313, Found 457.1315.

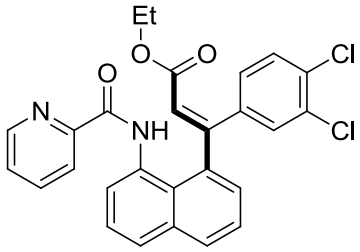


(*E*)-ethyl 3-(4-bromophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4g) yellow solid (28 mg, 56% yield); mp (^{o}C):146–147; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (t, 3H, *J* = 8.0 Hz), 3.98–4.09 (m, 2H), 6.35 (s, 1H), 6.85–6.89(m, 2H), 7.15–7.18(m, 2H), 7.33–7.35 (m, 1H), 7.43–7.50 (m, 3H), 7.70–7.72 (m, 1H), 7.86–7.90 (m, 2H), 8.24 (d, 2H, *J* = 8.0 Hz), 8.51–8.52 (m, 1H), 10.60 (s, 1H); ^{13}C

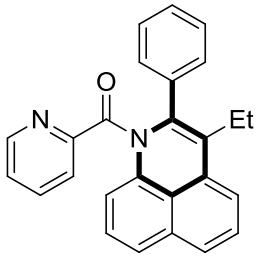
NMR (100 MHz, $CDCl_3$, TMS) δ 14.1, 60.2, 120.1, 122.1, 122.5, 123.3, 124.9, 125.1, 126.3, 126.4, 126.5, 130.2, 130.4, 130.5, 131.3, 132.8, 135.5, 136.6, 136.8, 137.6, 148.1, 150.1, 156.0, 162.2, 165.7. IR *v*2917, 1719, 1687, 1520, 1495 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{27}H_{21}BrN_2O_3[M + H]^+$, 501.0808, Found 501.0806.



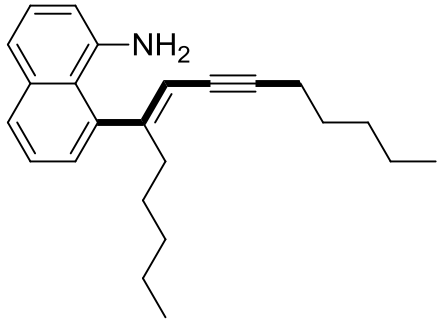
(*E*)-ethyl 3-(3,4-difluorophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4h) yellow solid (32 mg, 71% yield); mp (°C): 135–136; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.15 (t, 3H, *J* = 8.0 Hz), 3.99–4.13 (m, 2H), 6.37 (s, 1H), 6.62–6.65(m, 1H), 6.76–6.88(m, 2H), 7.36–7.38 (m, 1H), 7.46–7.52 (m, 3H), 7.73–7.75 (m, 1H), 7.89–7.94 (m, 2H), 8.16–8.18 (m, 1H),8.23–8.26 (m, 1H),10.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 60.3, 116.0, 116.2, 118.9, 119.1, 120.3, 122.6, 124.9, 125.3, 126.2, 126.3, 126.5, 126.7, 130.4, 130.5, 132.7, 134.4, 134.5, 135.6, 136.5, 137.7, 148.1, 150.0, 154.7, 162.3, 165.6. IR *v* 2917, 2855, 1687, 1523, 1278 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{27}H_{20}F_2N_2O_3[M + H]^+$, 459.1515, Found 459.1518.



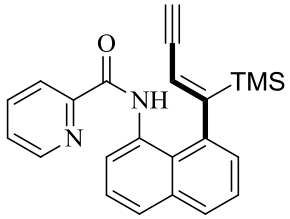
(*E*)-ethyl 3-(3,4-dichlorophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4i) yellow solid (31 mg, 63% yield); mp (°C): 128–129; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.12 (t, 3H, *J* = 8.0 Hz), 3.96–4.11(m, 2H), 6.37 (s, 1H), 6.69–6.71 (m, 1H), 7.09 (d, 1H, *J* = 8.0 Hz), 7.14 (m, 1H), 7.35–7.37 (m, 1H), 7.46–7.52 (m, 3H), 7.73–7.76 (m, 1H), 7.89–7.94 (m, 2H), 8.14–8.17 (m, 1H), 8.25–8.27 (m, 1H), 8.57–8.58 (m, 1H), 10.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 60.4, 120.8, 122.7 (2C), 125.0, 125.3, 126.5, 125.6, 126.7, 128.8, 129.3, 130.5, 130.6, 131.3, 131.5, 132.6, 132.8, 135.6, 136.2, 137.6, 137.7, 148.1, 149.9, 154.3, 162.3, 165.5. IR *v* 2917, 2851, 1715, 1691, 1486 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{27}H_{20}Cl_2N_2O_3[M + H]^+$, 491.0924, Found 491.0921.



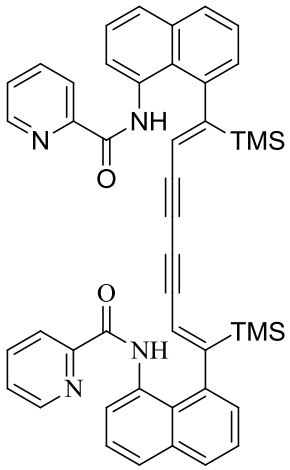
(2-ethyl-3-phenyl-1H-benzo[*de*]quinolin-1-yl)(pyridin-2-yl)methanone (5) yellow liquid (13 mg, 35% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.18 (t, 3H, *J* = 8.0 Hz), 2.48 (q, 2H, *J* = 12.0 Hz), 6.94–6.96 (m, 2H), 7.04–7.09 (m, 4H), 7.17–7.20 (m, 1H), 7.34–7.36 (m, 1H), 7.41–7.48 (m, 3H), 7.53–7.55 (m, 1H), 7.60–7.62 (m, 1H), 8.36 (d, 1H, *J* = 8.0 Hz), 8.45–8.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ14.1, 21.8, 112.6, 117.7, 122.3, 123.9, 124.3, 124.8, 125.1, 126.6, 126.7, 127.1, 128.0, 129.5, 130.8, 134.2, 135.9, 136.6, 136.9, 139.1, 148.2, 155.0, 170.5. IR *v* 2930, 1713, 1643, 1532, 1451 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{26}H_{20}N_2O[M + H]^+$, 377.1648, Found 377.1646.



(E)-8-(tetradec-6-en-8-yn-6-yl)naphthalen-1-amine (6) yellow liquid (26 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.84–0.88 (m, 3H), 0.95–0.99 (m, 3H), 1.29–1.32 (m, 4H), 1.37–1.43 (m, 4H),1.45–1.51 (m, 2H), 1.63–1.66 (m, 2H), 2.44–2.47 (m, 2H), 2.50–2.54 (m, 1H), 3.04–3.09 (m, 1H), 5.72 (s, 1H), 6.69–6.72(m, 1H), 7.01 (d, 1H, *J* = 8.0 Hz), 7.28–7.29 (m, 2H), 7.31–7.35 (m, 1H), 7.71 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 19.7, 22.3, 22.4, 27.1, 31.1, 31.8, 36.4, 77.8, 95.2, 109.1, 110.9, 118.7, 120.8, 124.6, 126.4, 126.7, 128.6, 135.8, 138.4, 143.9, 157.9. IR *v* 2918, 1668, 1536, 1487 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{24}H_{31}N[M + H]^+$, 334.2529, Found 334.2561.

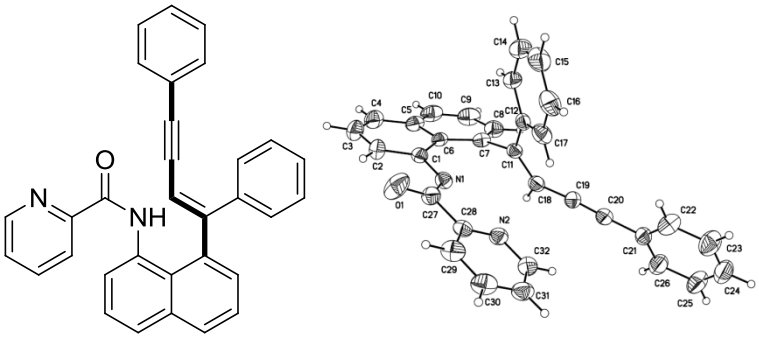


(*Z*)-*N*-(8-(1-(trimethylsilyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide(7) yellow solid (64 mg, 87% yield); mp (^{o}C): 147–148; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 8.83 (d, 1H, *J* = 4.0 Hz), 8.54 (d, 1H, *J* = 8.0 Hz), 8.35 (d, 1H, *J* = 8.0 Hz), 7.92–7.96 (m, 1H), 7.77 (d, 1H, *J* = 8.0 Hz), 7.69 (d, 1H, *J* = 8.0 Hz), 7.507.56 (m, 2H), 7.42 (d, 1H, *J* = 8.0 Hz), 6.97–6.99 (m, 1H), 6.62 (d, 1H, *J* = 4.0 Hz), 3.25 (d, 1H, *J* = 4.0 Hz), -0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 163.9, 162.5, 150.3, 148.4, 140.0, 137.4, 135.1, 134.2, 128.1, 126.6, 126.2, 126.0, 125.6, 125.2, 124.7, 122.5, 119.7, 83.5, 82.5, -1.96. IR *v* 3296, 2958, 1683, 1586, 1494, 1265, 1248, 842 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{23}H_{22}N_2OSi[M + H]^+$, 371.1574, Found 371.1577.

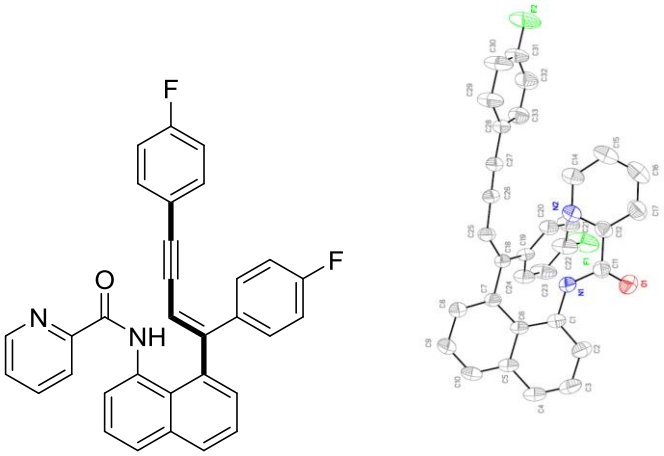


***N*,*N*'-(((1*Z*,7*Z*)-1,8-bis(trimethylsilyl)octa-1,7-dien-3,5-diyne-1,8-diyl)bis(naphthalene-8,1-diyl))dipicolinamide (8)** yellow solid (34 mg, 46% yield); mp (^{o}C): 138–139; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.91 (s, 1H), 8.73 (d, 1H, *J* = 4.0 Hz), 8.47 (d, 1H, *J* = 8.0 Hz), 8.31 (d, 1H, *J* = 8.0 Hz), 7.93 (t, 1H, *J* = 8.0 Hz), 7.74 (d, 1H, *J* = 8.0 Hz), 7.66 (d, 1H, *J* = 8.0 Hz), 7.49–7.54 (m, 2H), 7.38 (t, 1H, *J* = 8.0 Hz), 6.92 (d, 1H, *J* = 8.0 Hz), 6.72 (s, 1H), -0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 164.9, 162.5, 150.2, 148.7, 139.6, 137.5, 135.0, 134.1, 128.2, 126.6, 126.3, 126.1, 125.7, 125.2, 124.7, 122.5, 120.6, 119.2, 94.3, -2.0. IR *ν* 2924, 1679, 1524, 1495, 1246, 906 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{46}H_{42}N_4O_2Si_2[M + H]^+$, 739.2919, Found 739.2921.

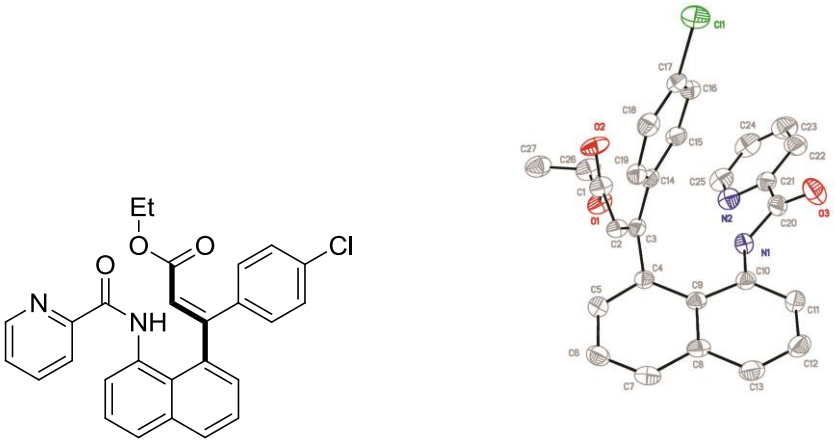
X-ray crystallography of 3aa



X-ray crystallography of 3ae



X-ray crystallography of 4f

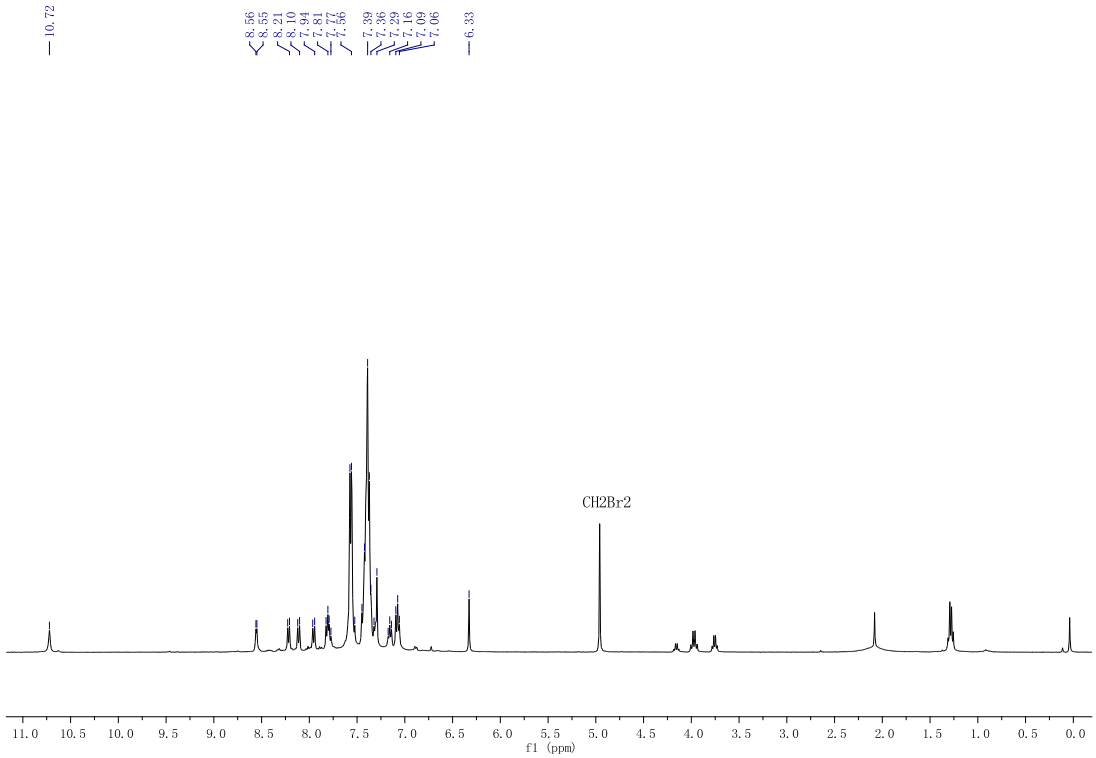


References

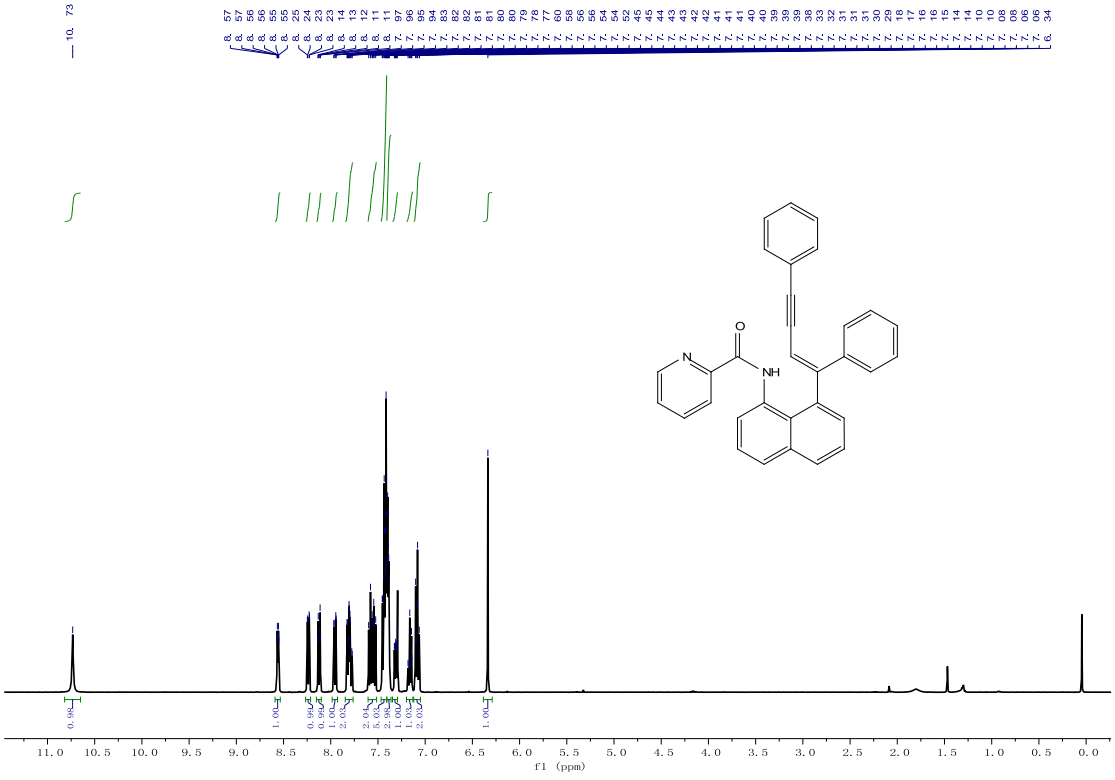
1.(a) Moseley, J. D.; Lenden, P. *Tetrahedron***2007**, *63*, 4120; (b) Perkowski, A. J.; Cruz, C. L.; Nicewicz, D. A. *J. Am. Chem. Soc*.**2015**, *137*, 15684. (c) Zhao Y, Xie Y.; Xia, C. Huang, H. *Adv. Synth. Catal*.**2014**, *356*, 2471.

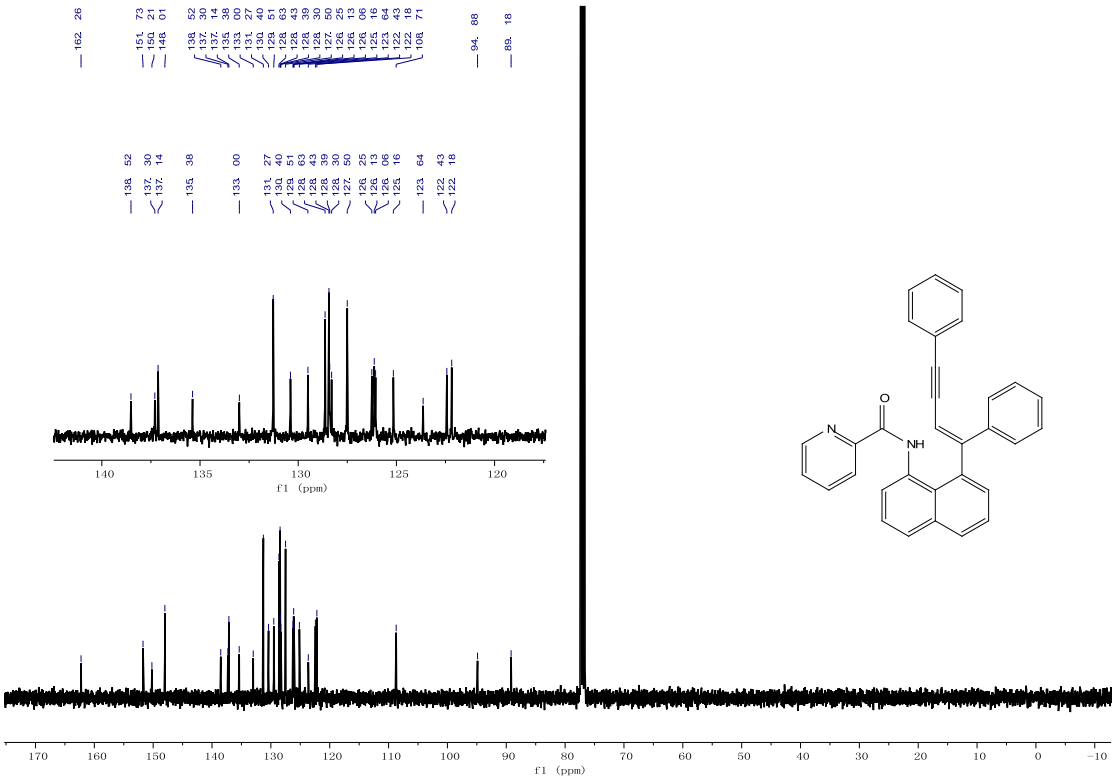
^{1}H NMR and ^{13}C NMR spectra

The crude ^{1}H NMR spectrum of 3aa



(*E*)-*N*-(8-(1,4-diphenylbut-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3aa)

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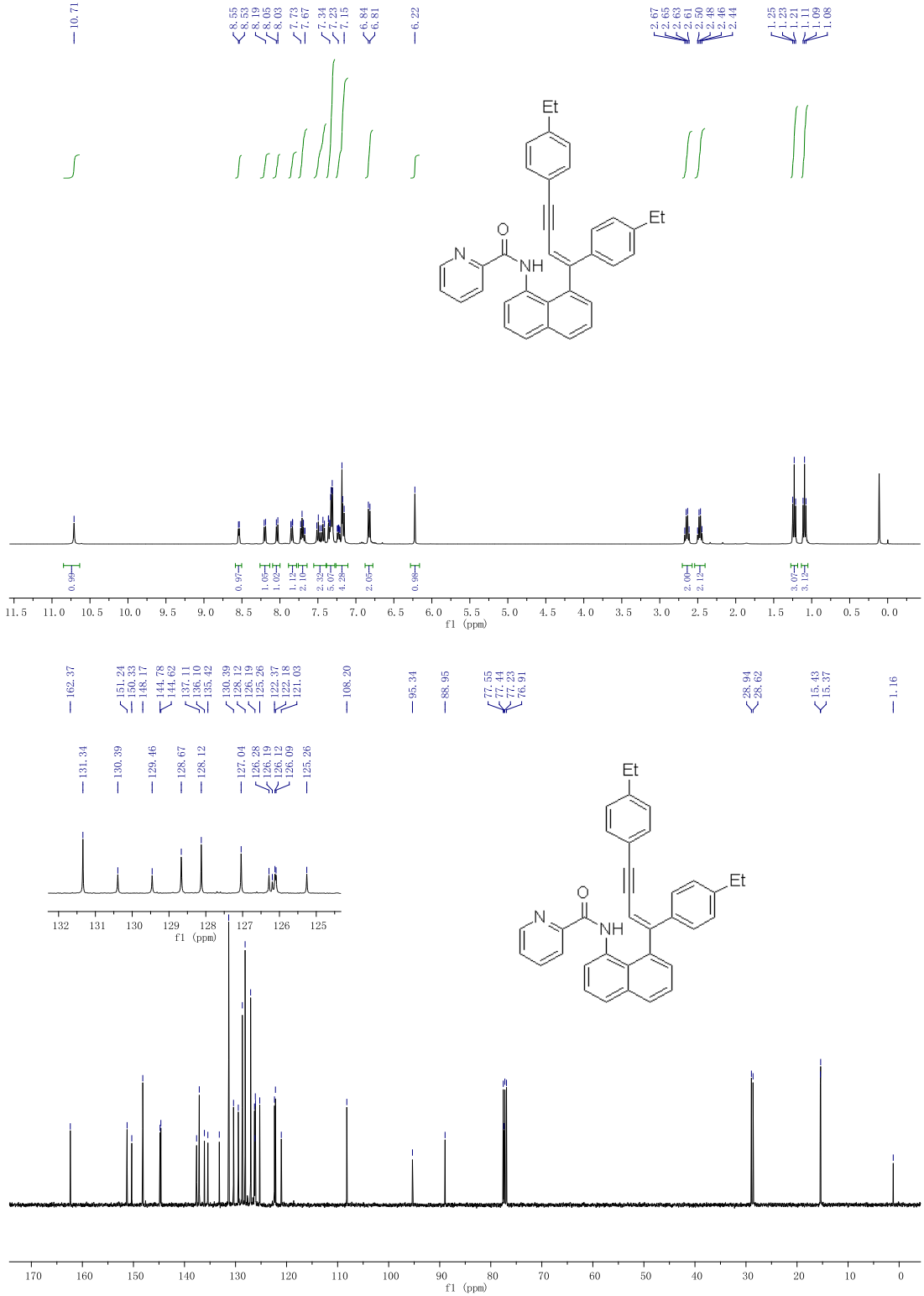
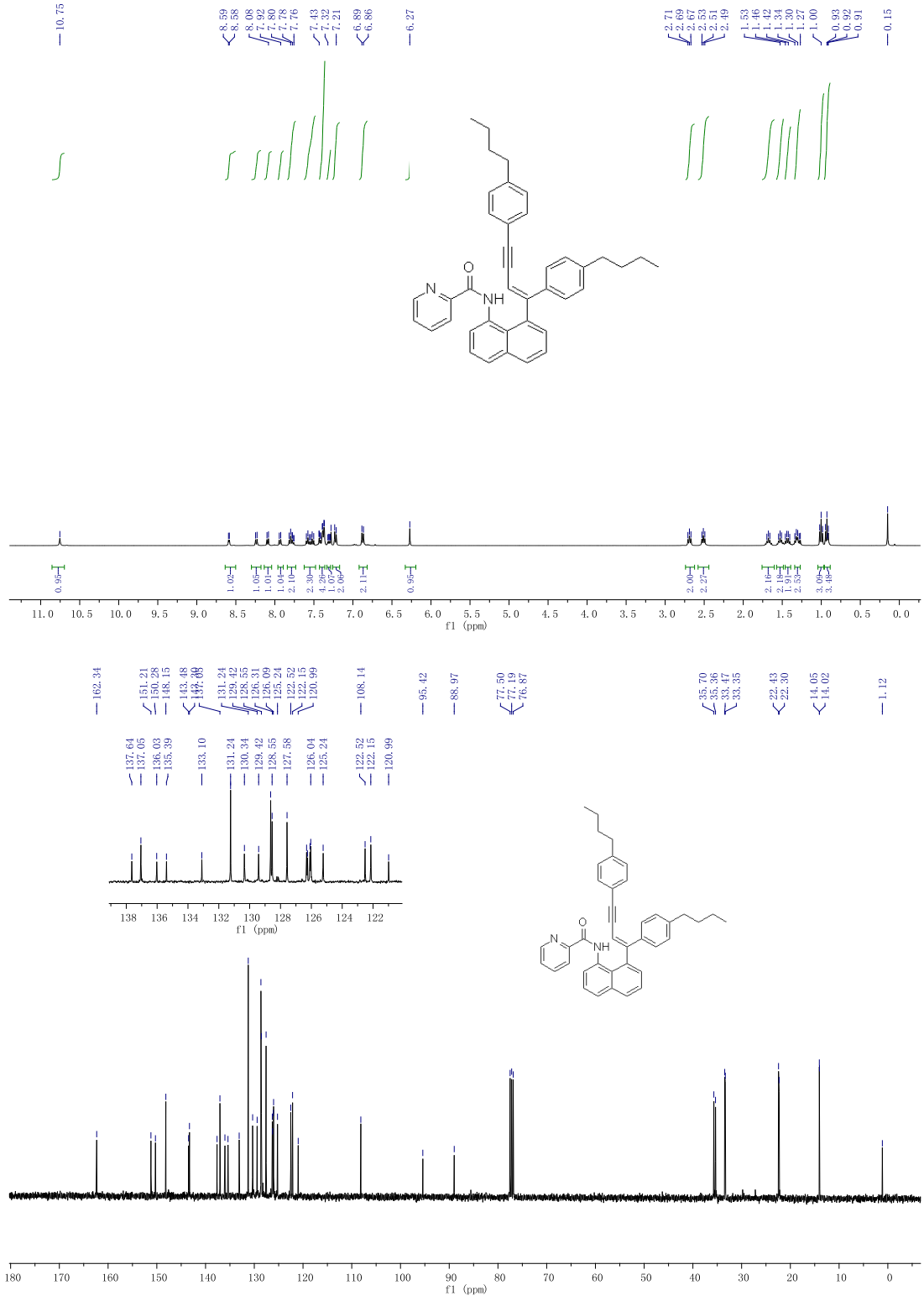
128.43
128.39
128.30
127.50
126.25
126.13
126.06
125.16
123.64
122.43
122.18
108.71
94.88
89.18
140
135
130
125
120
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
O
N
NH

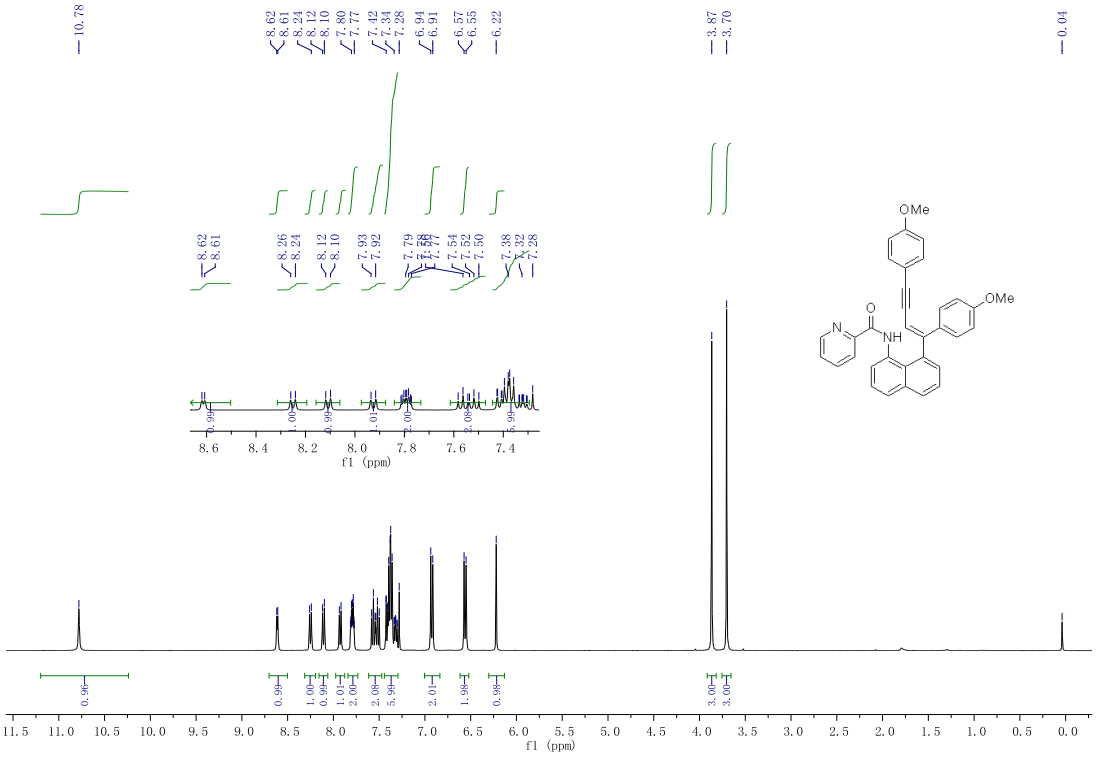
(*E*)-*N*-(8-(1,4-bis(4-ethylphenyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3ab)

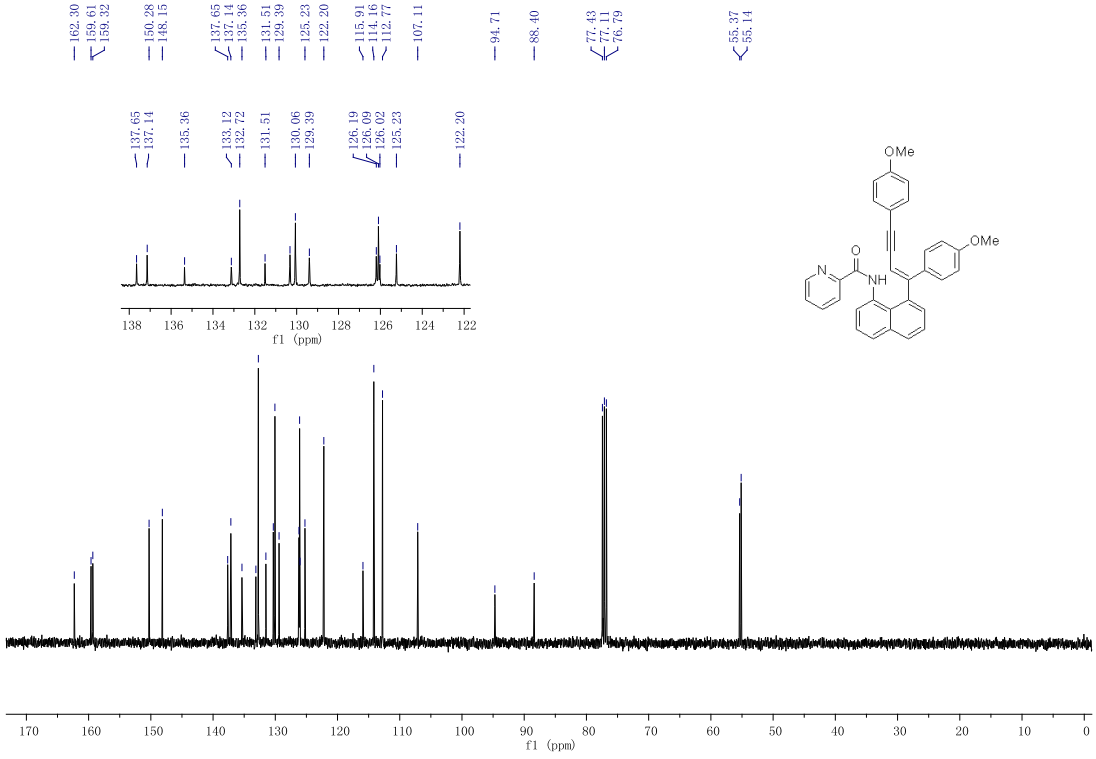


(*E*)-*N*-(8-(1,4-bis(4-butylphenyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3ac)

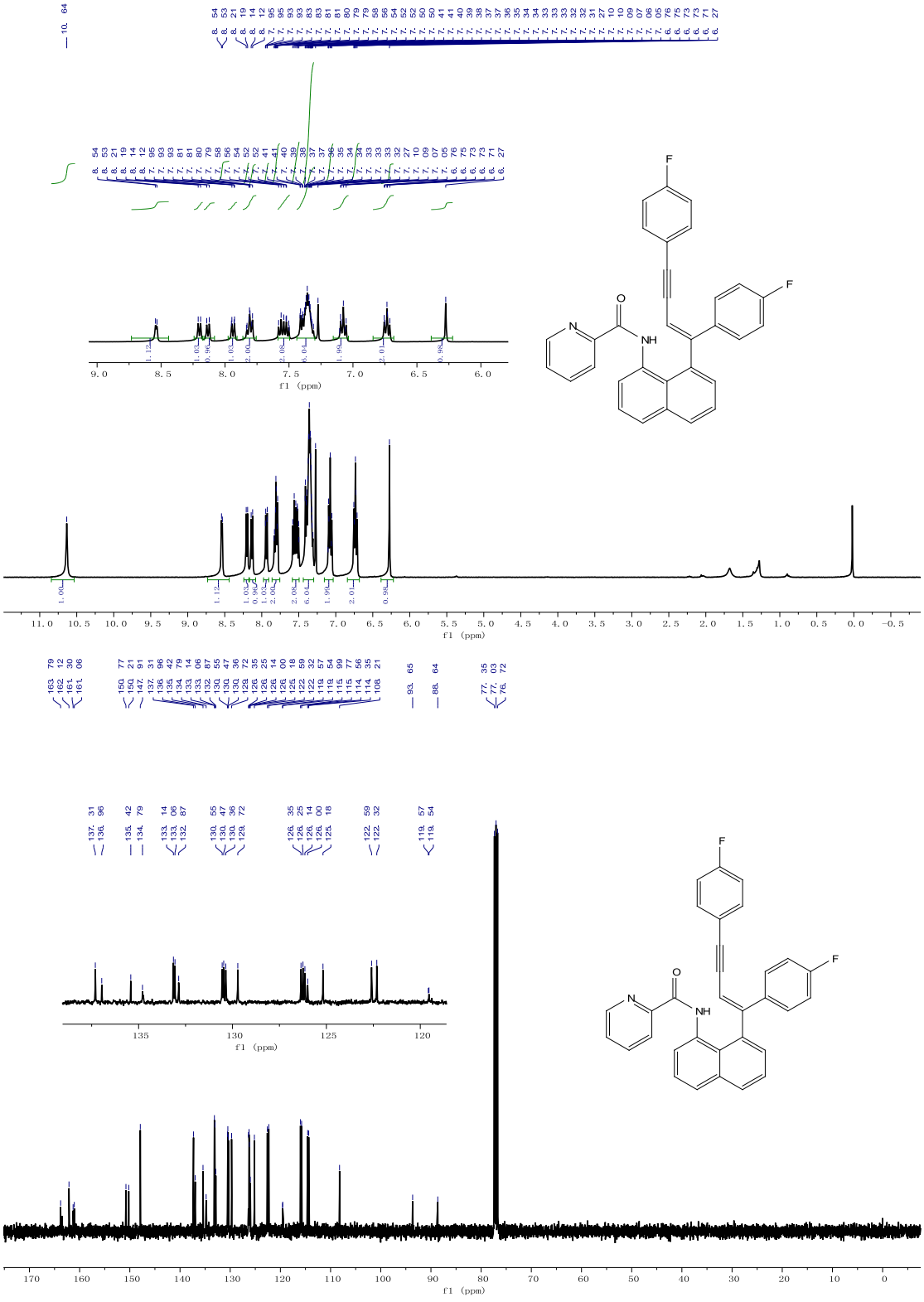


(*E*)-*N*-(8-(1,4-bis(4-methoxyphenyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinam (3ad)

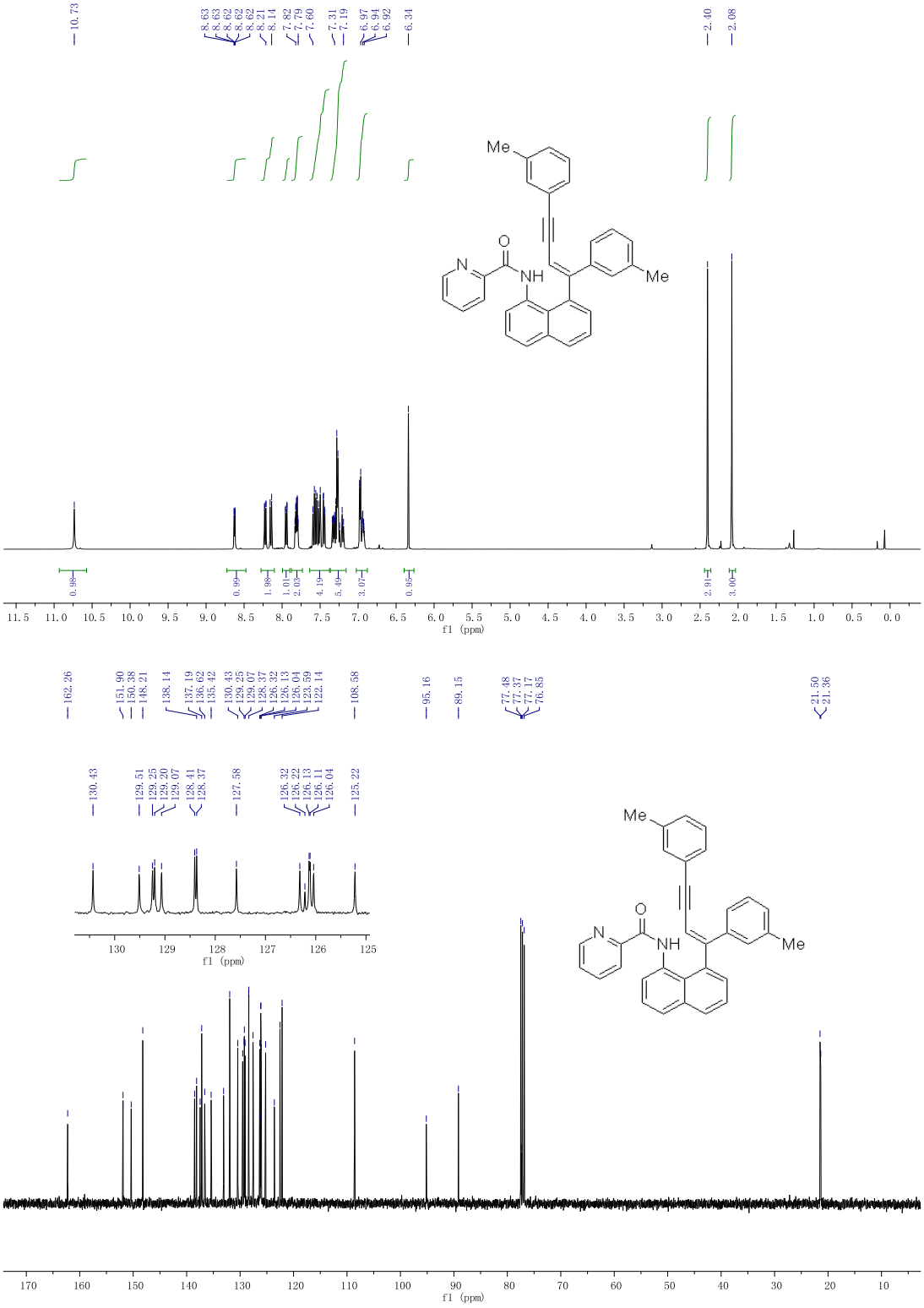




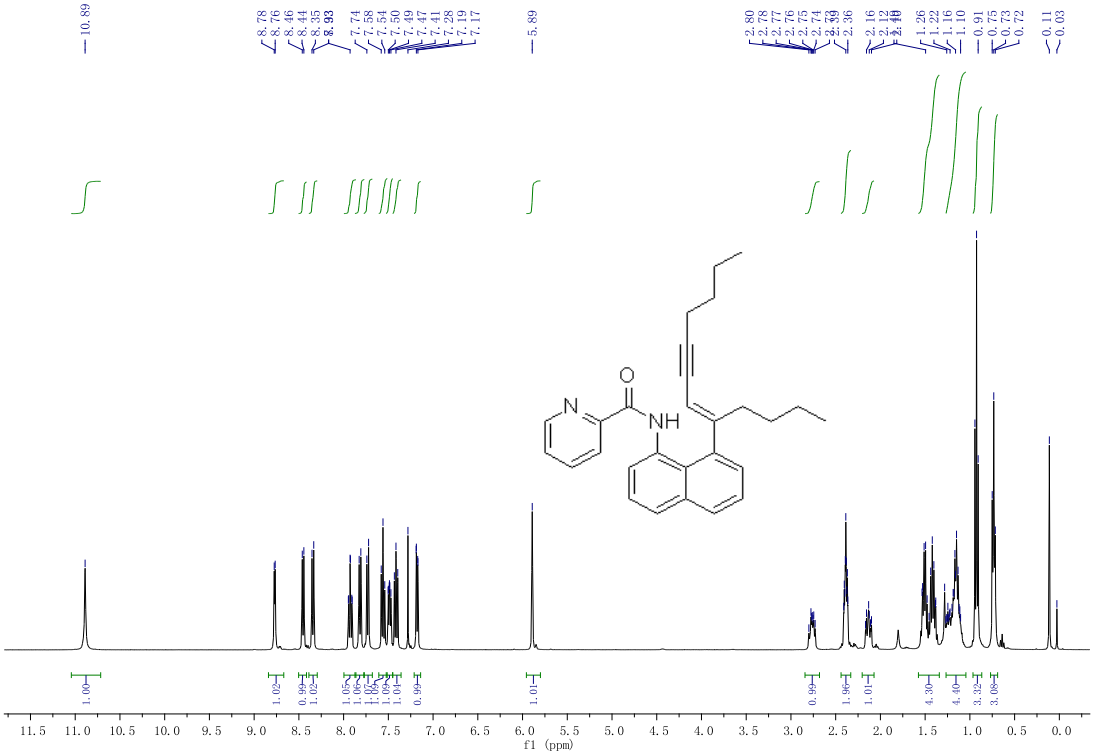
(E)-*N*-(8-(1,4-bis(4-fluorophenyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3ae)

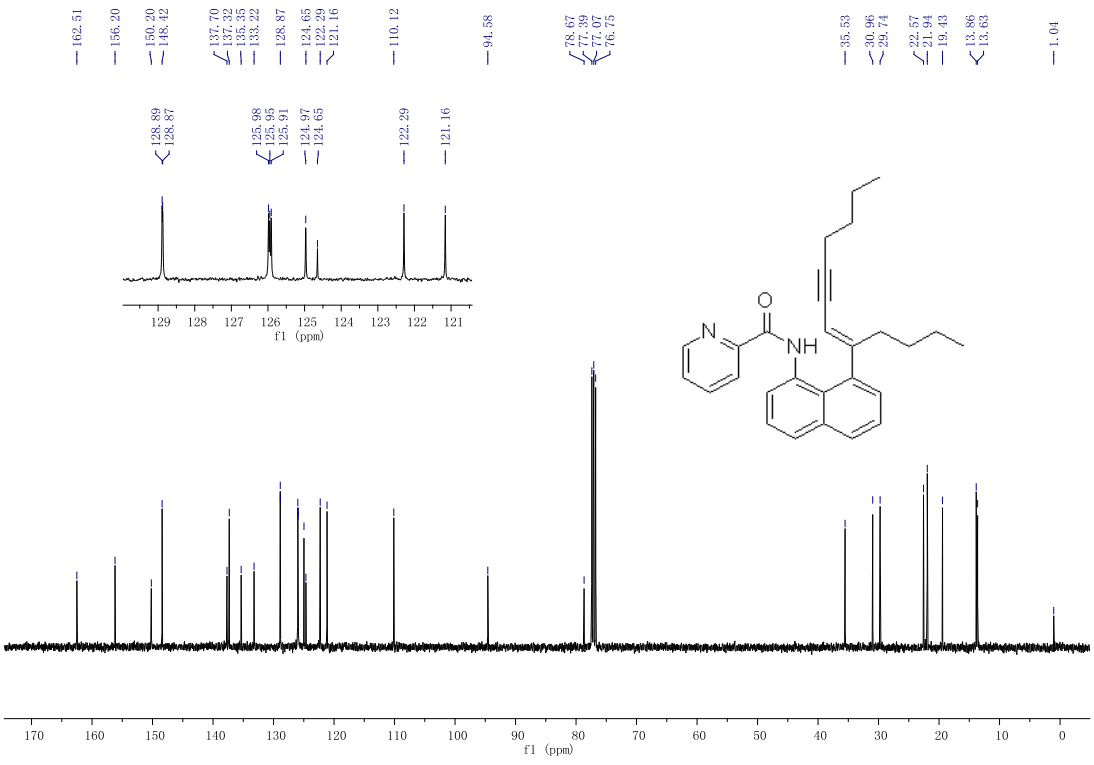


(*E*)-*N*-(8-(1,4-di-m-tolylbut-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3af)

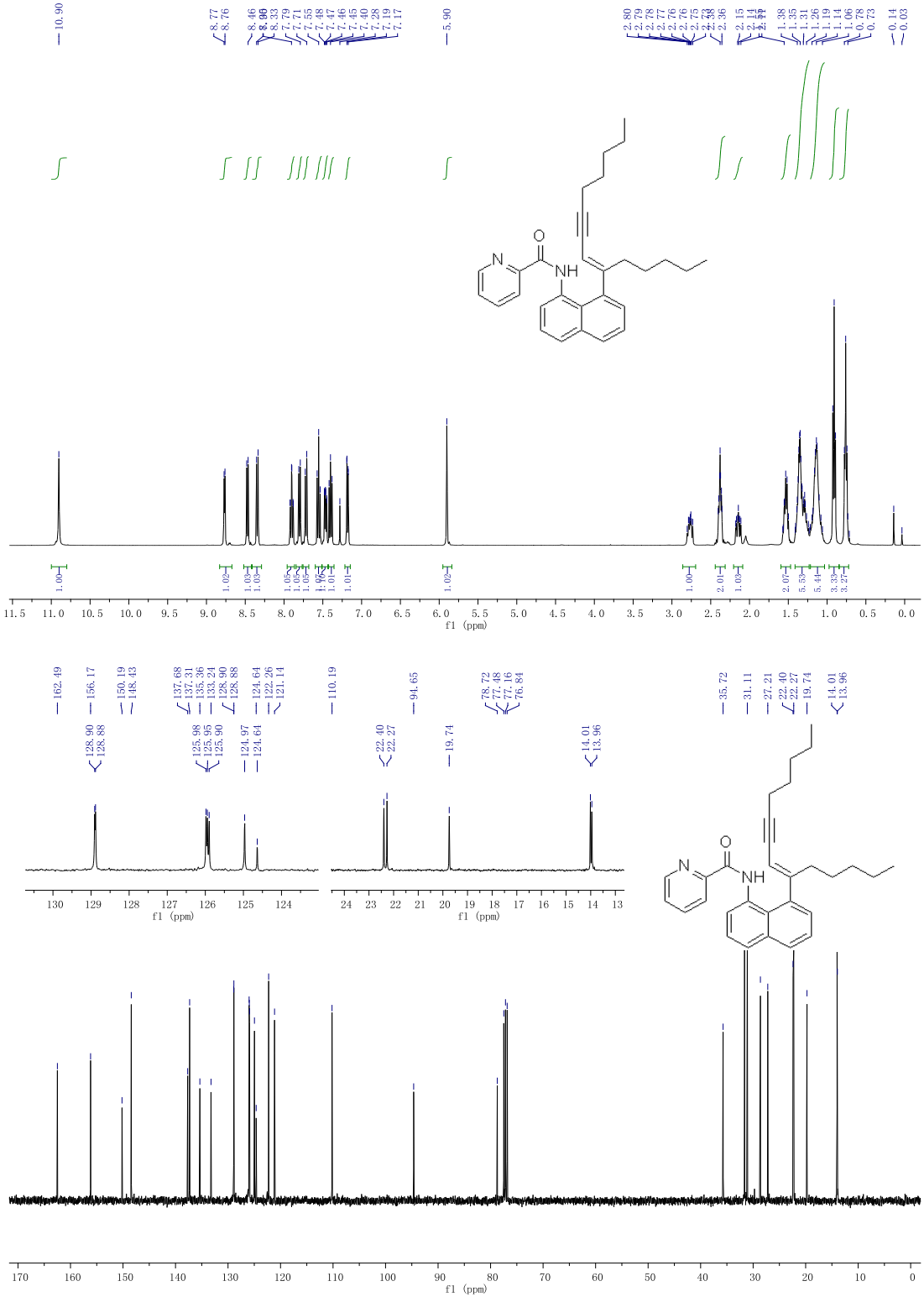


(*E*)-*N*-(8-(dodec-5-en-7-yn-5-yl)naphthalen-1-yl)picolinamide (3ag)

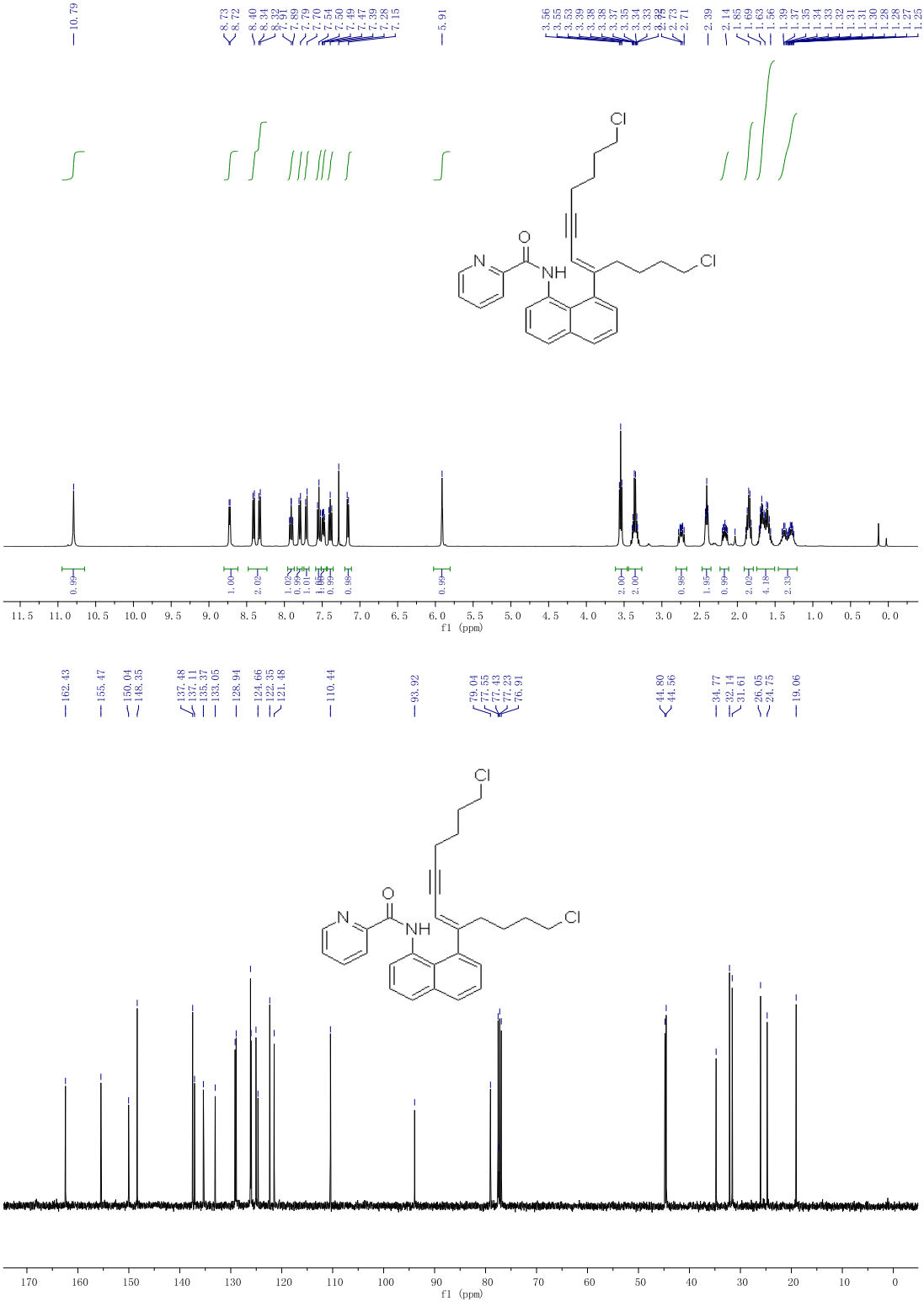




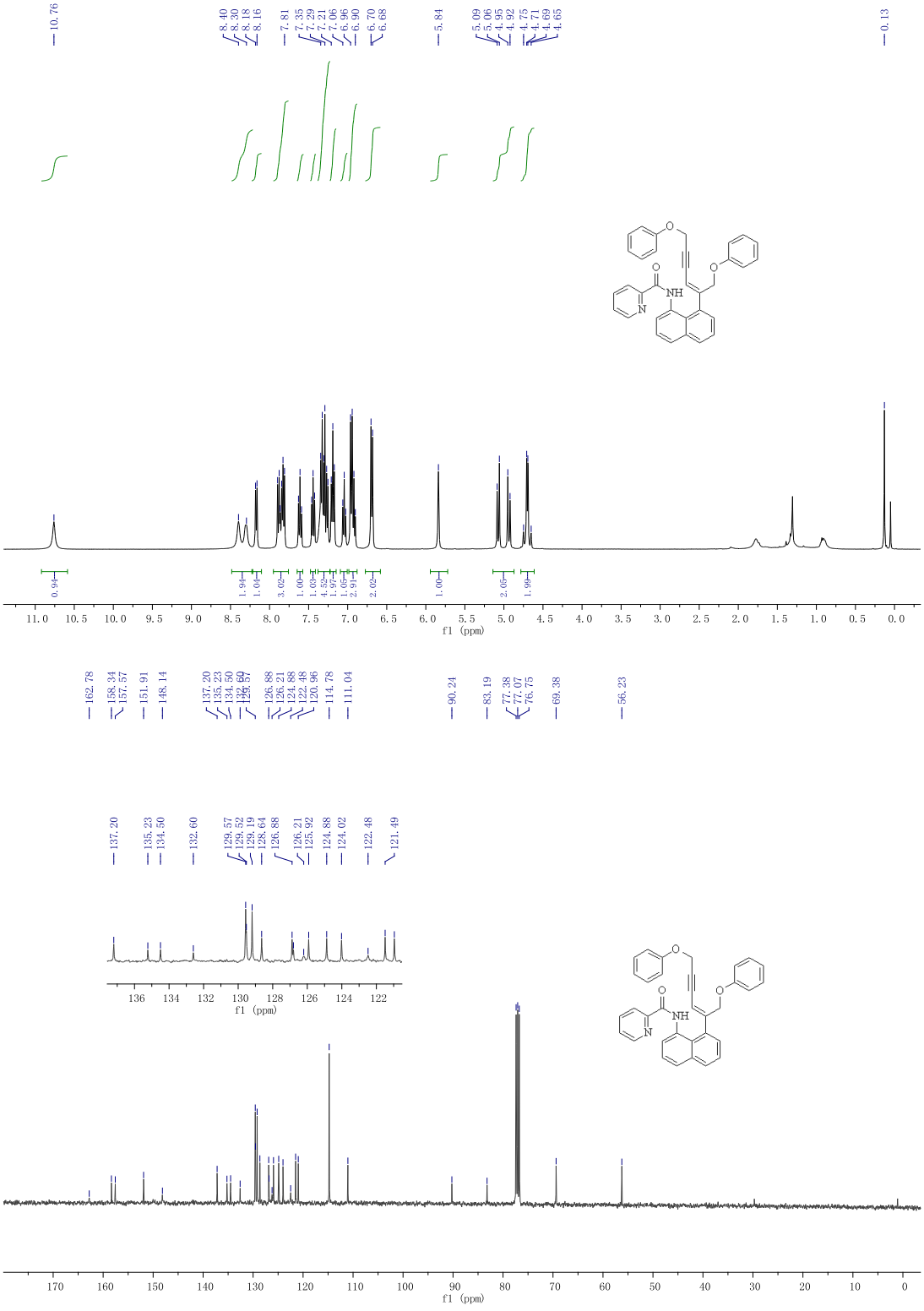
(*E*)-*N*-(8-(tetradec-6-en-8-yn-6-yl)naphthalen-1-yl)picolinamide (3ah)



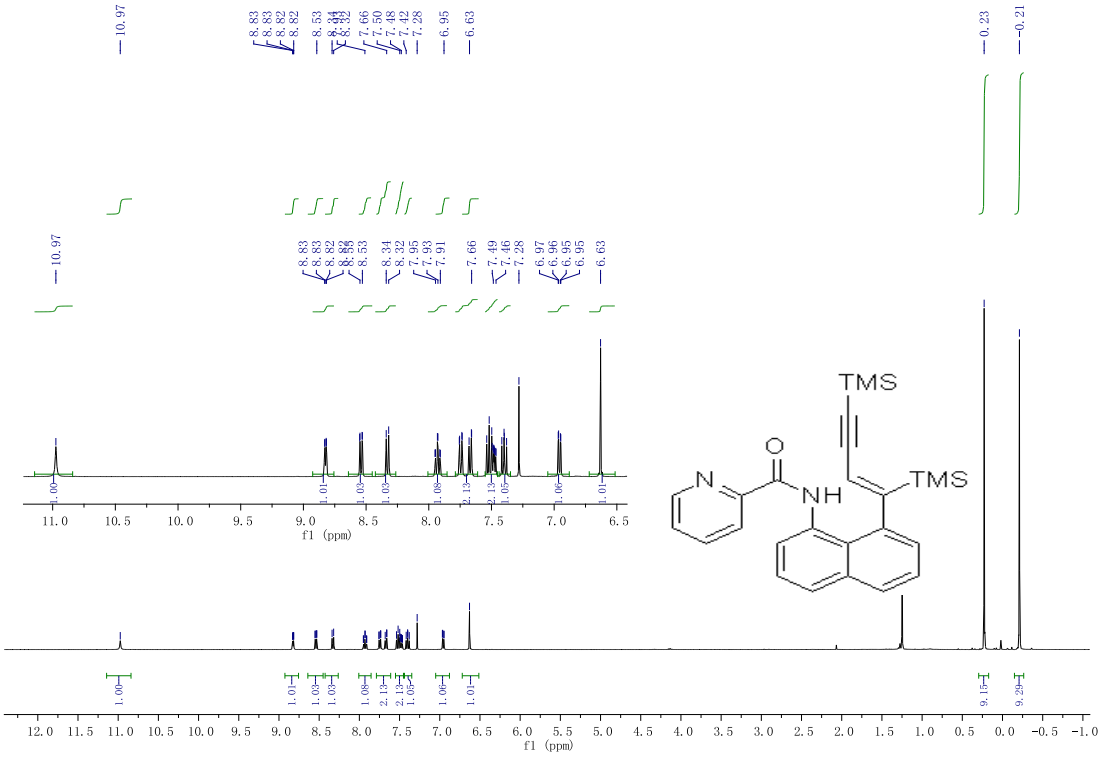
(*E*)-*N*-(8-(1,12-dichlorododec-5-en-7-yn-5-yl)naphthalen-1-yl)picolinamide (3ai)

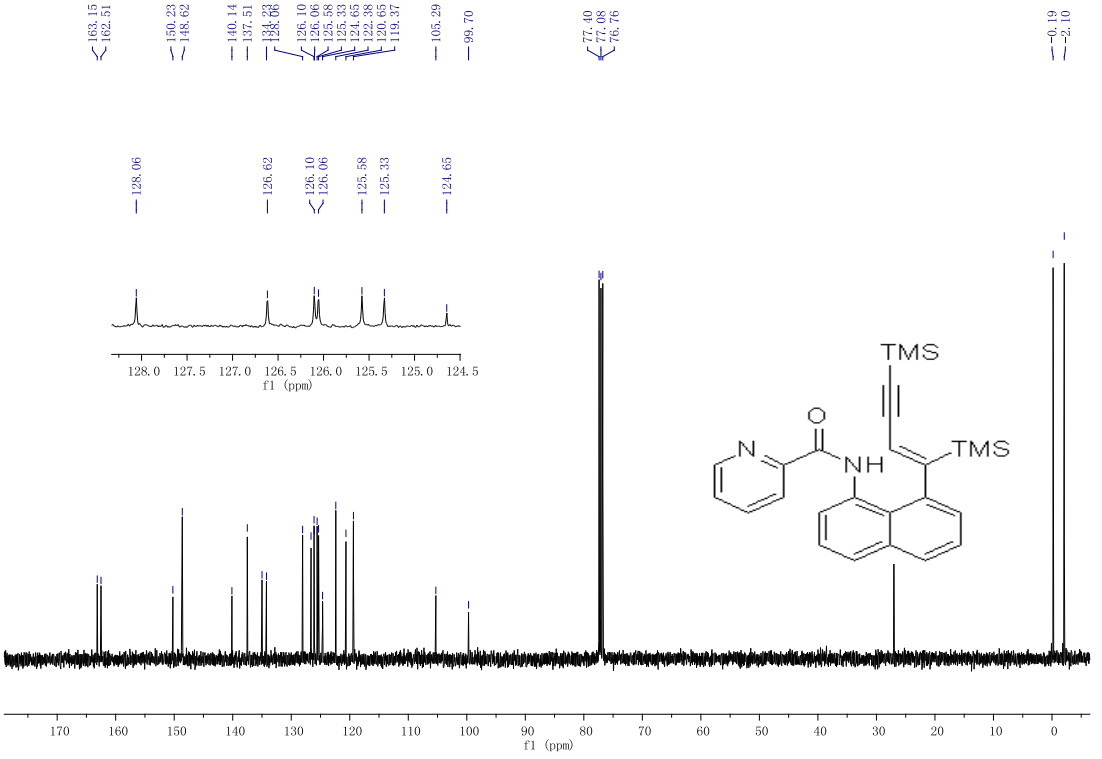


(*Z*)-*N*-(8-(1,6-diphenoxyhex-2-en-4-yn-2-yl)naphthalen-1-yl)picolinamide (3aj)

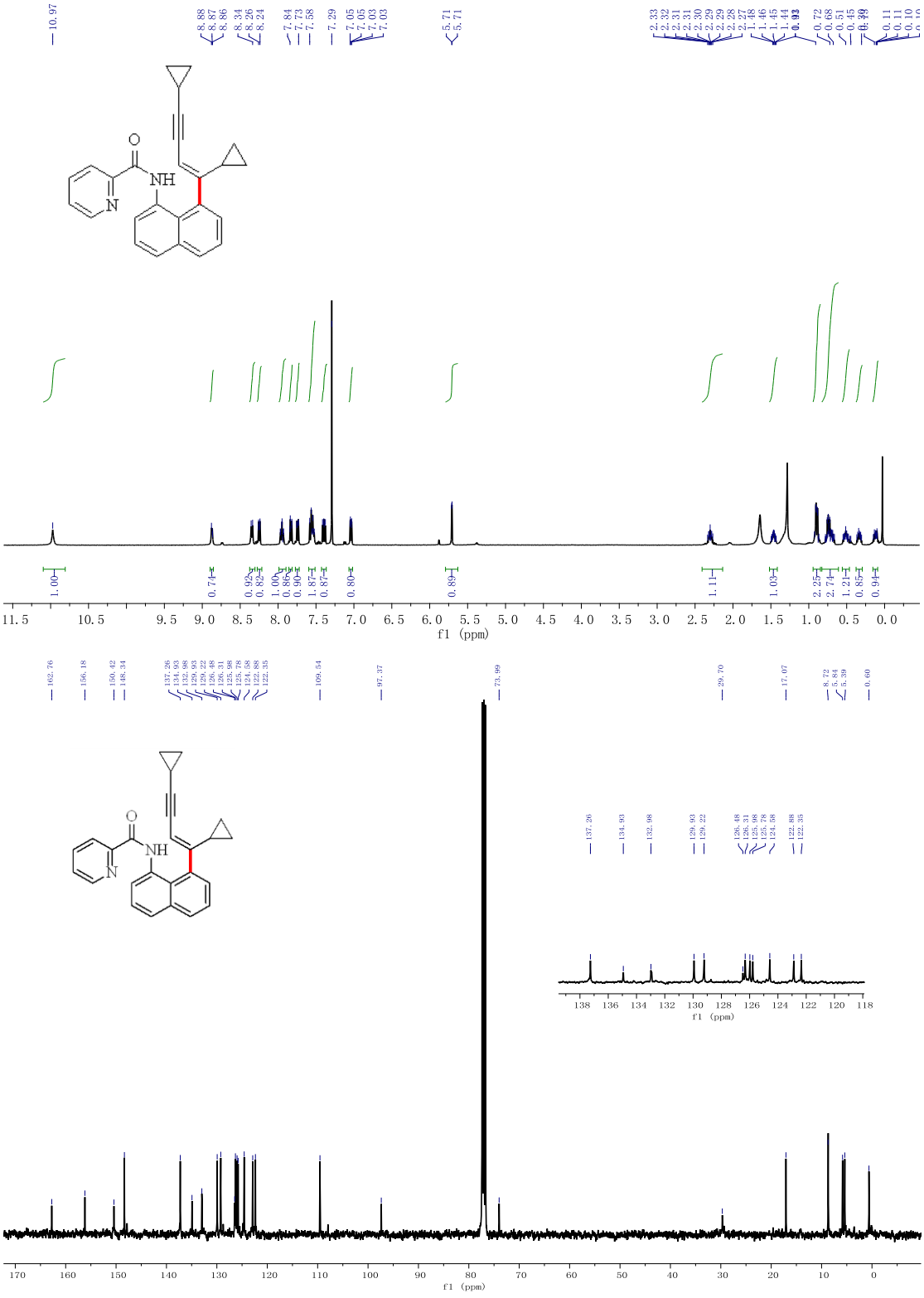


(*E*)-*N*-(8-(1,4-bis(trimethylsilyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3ak)

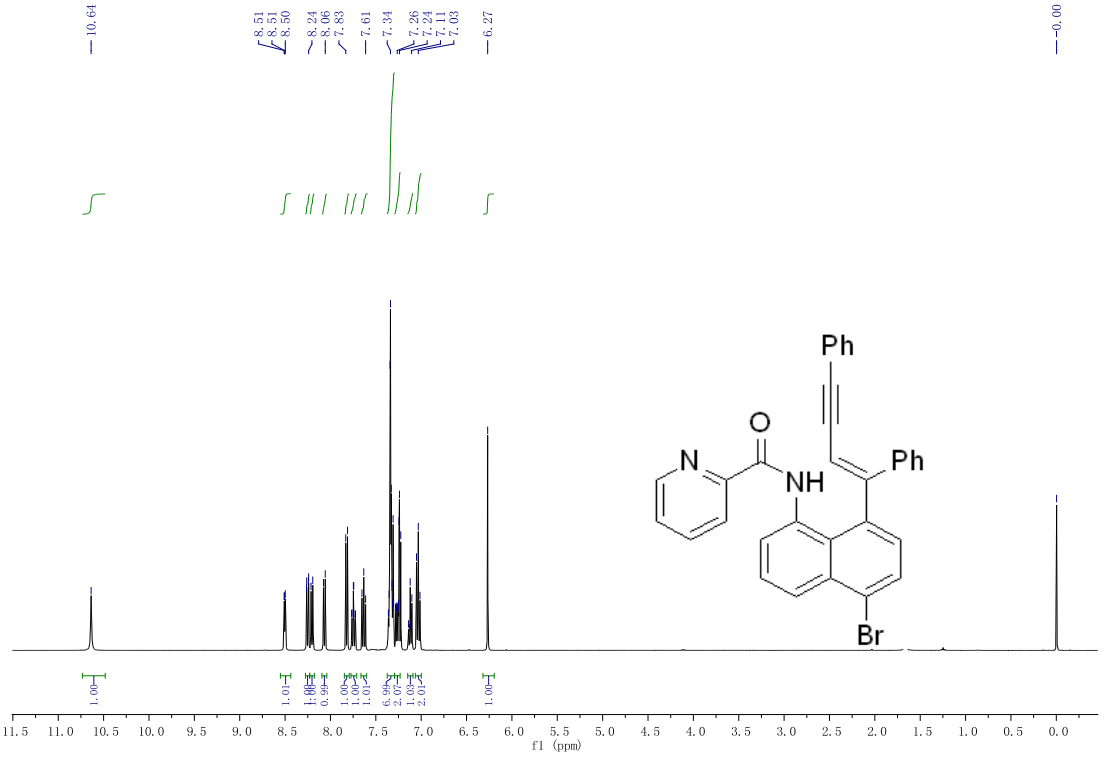


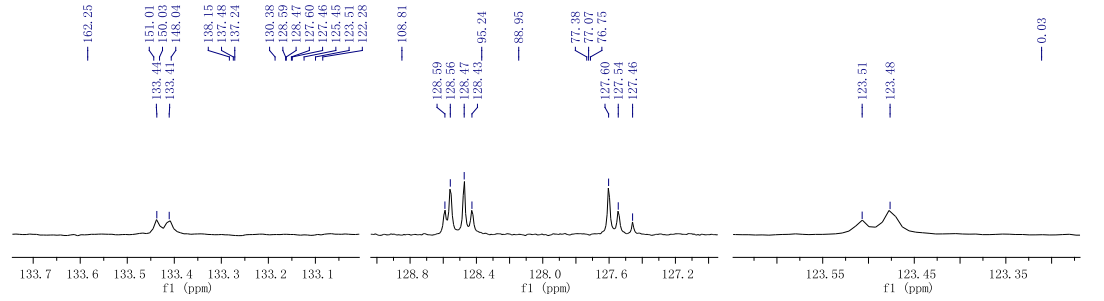


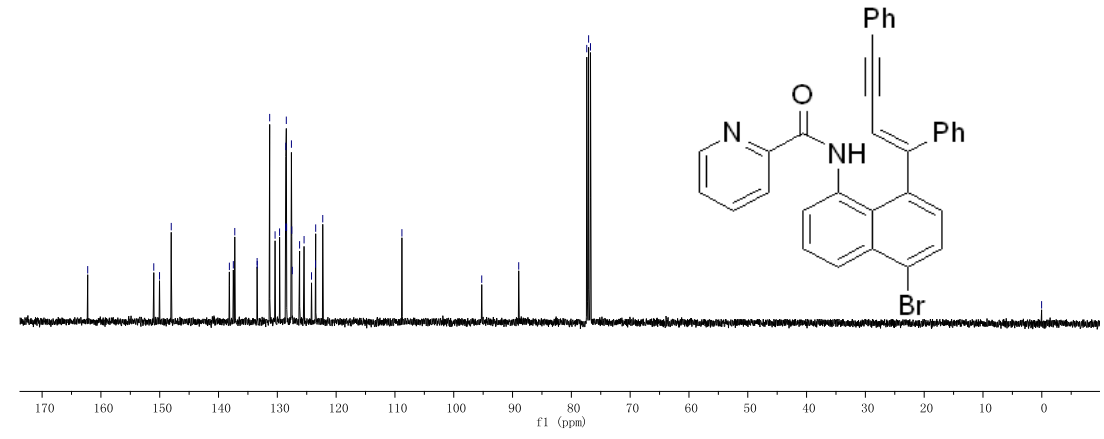
(*E*)-*N*-(8-(1,4-dicyclopropylbut-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3al)



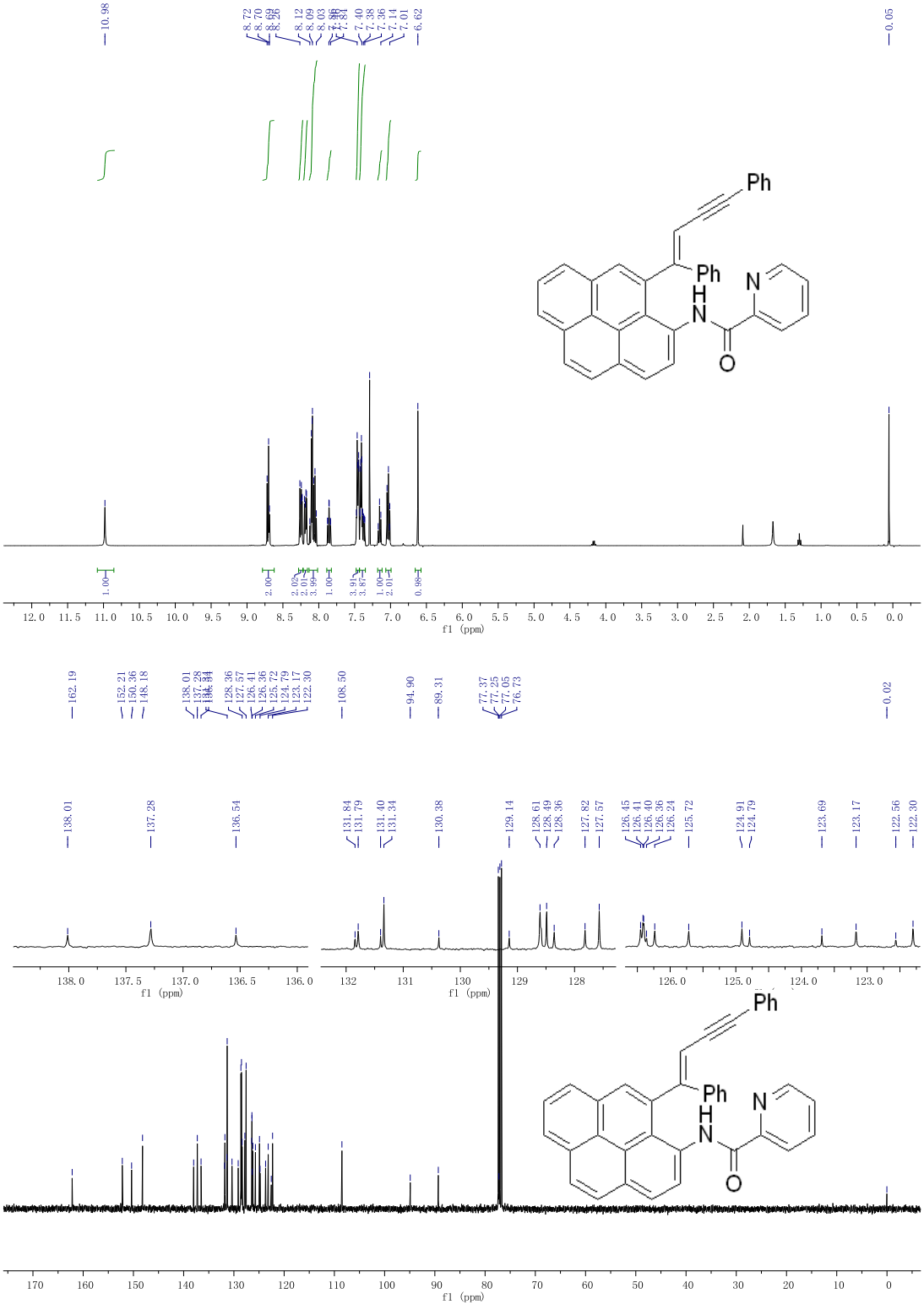
(*E*)-*N*-(5-bromo-8-(1,4-diphenylbut-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide (3ba)



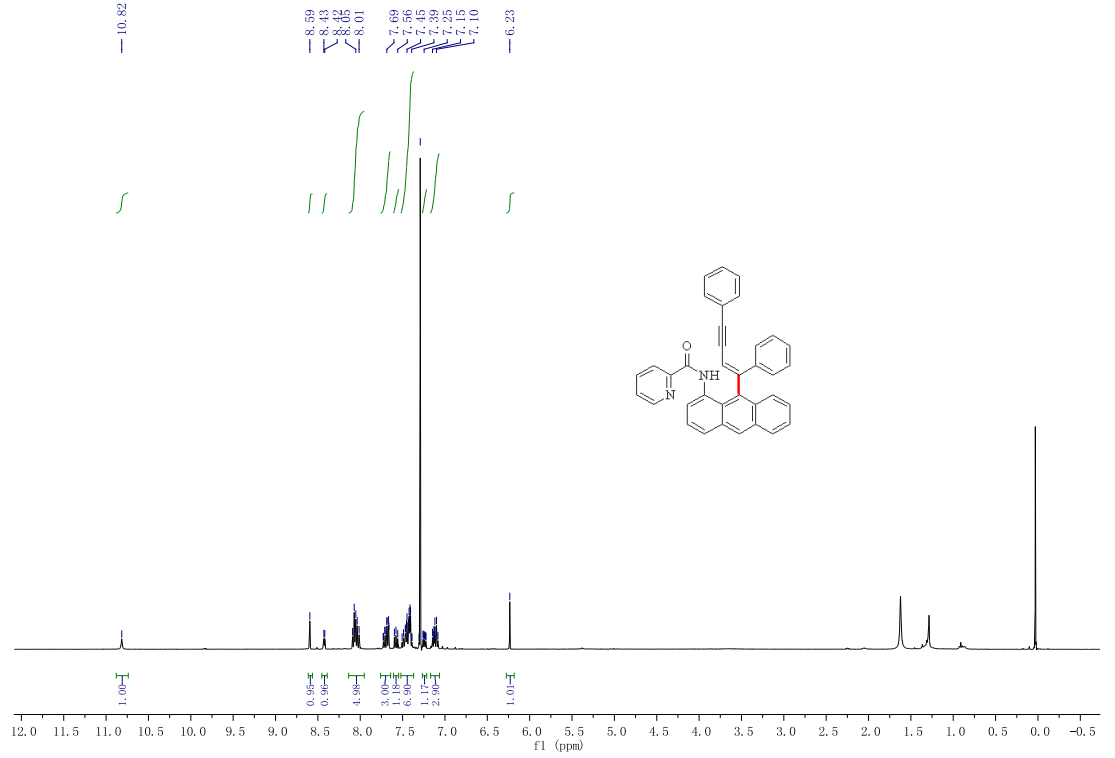


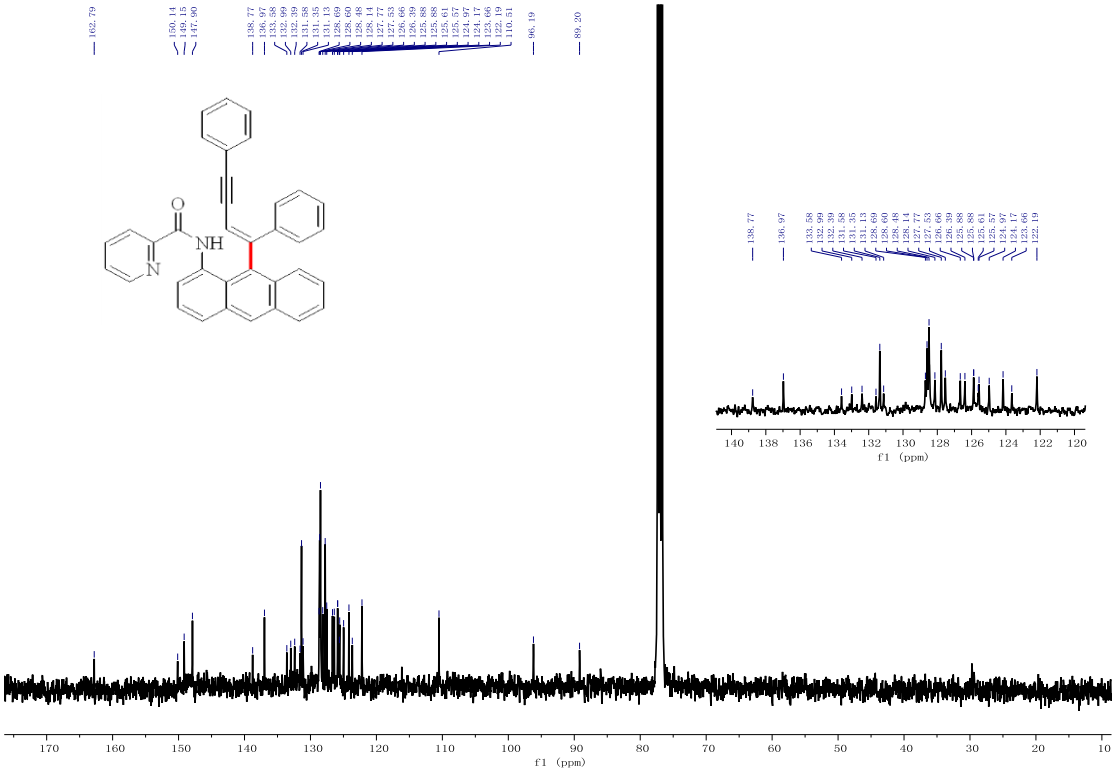


(*E*)-*N*-(10-(1,4-diphenylbut-1-en-3-yn-1-yl)pyren-1-yl)picolinamide (3ca)

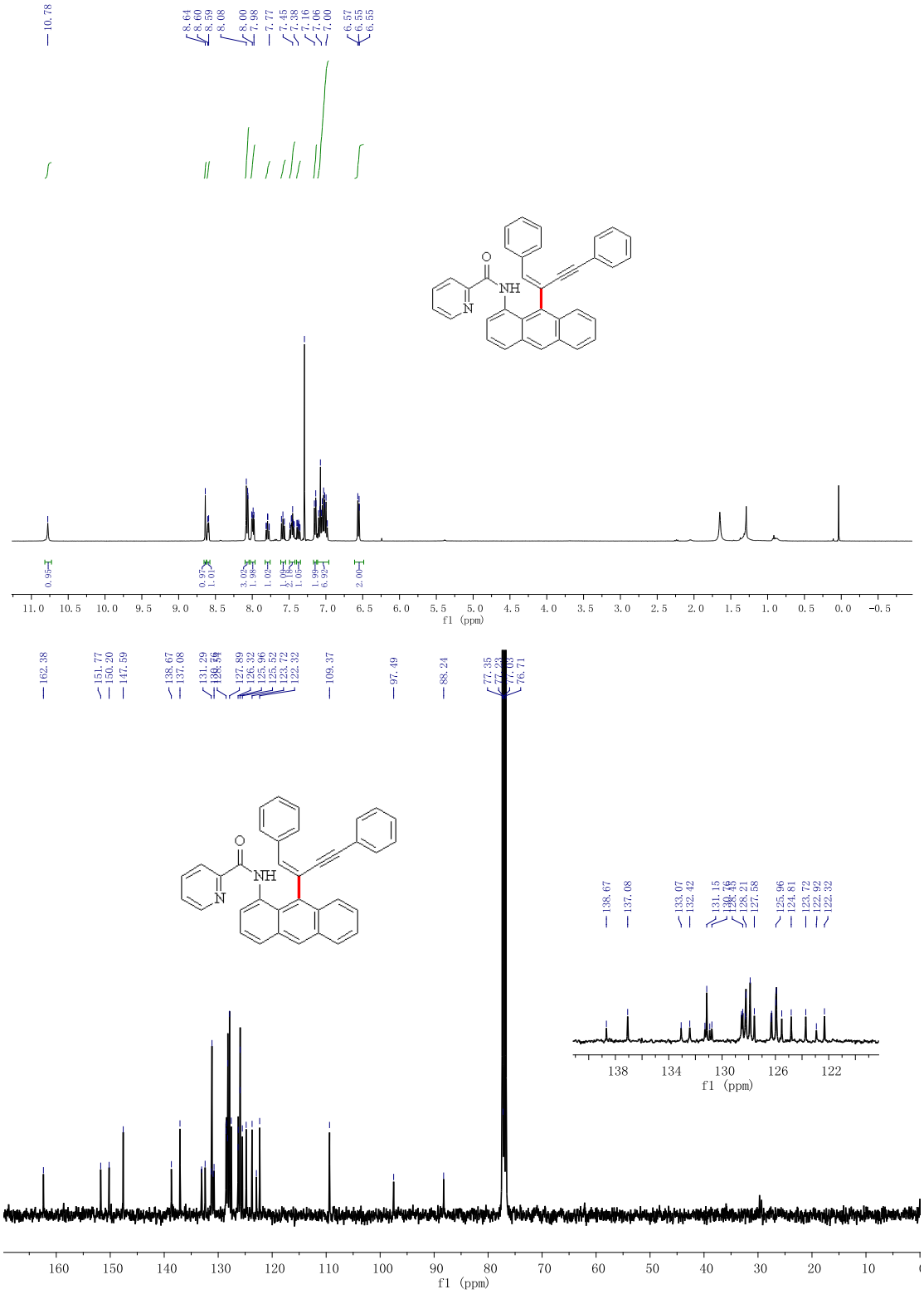


(*E*)-*N*-(9-(1,4-diphenylbut-1-en-3-yn-1-yl)anthracen-1-yl)picolinamide (3da)

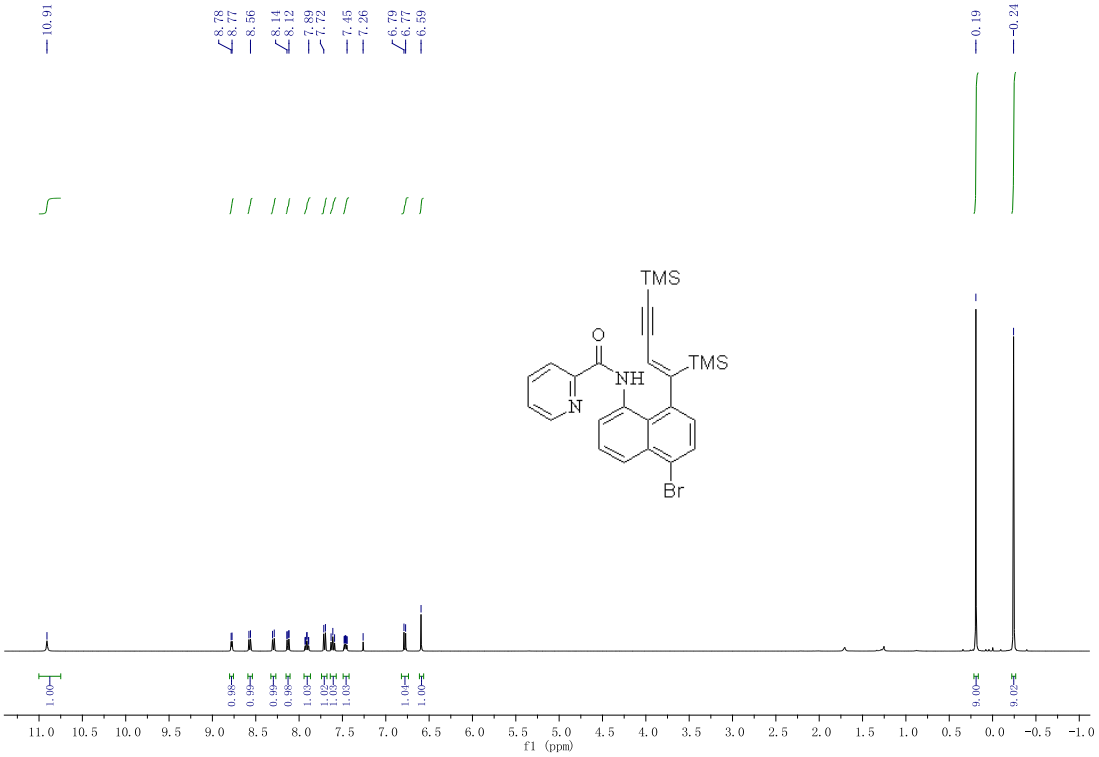


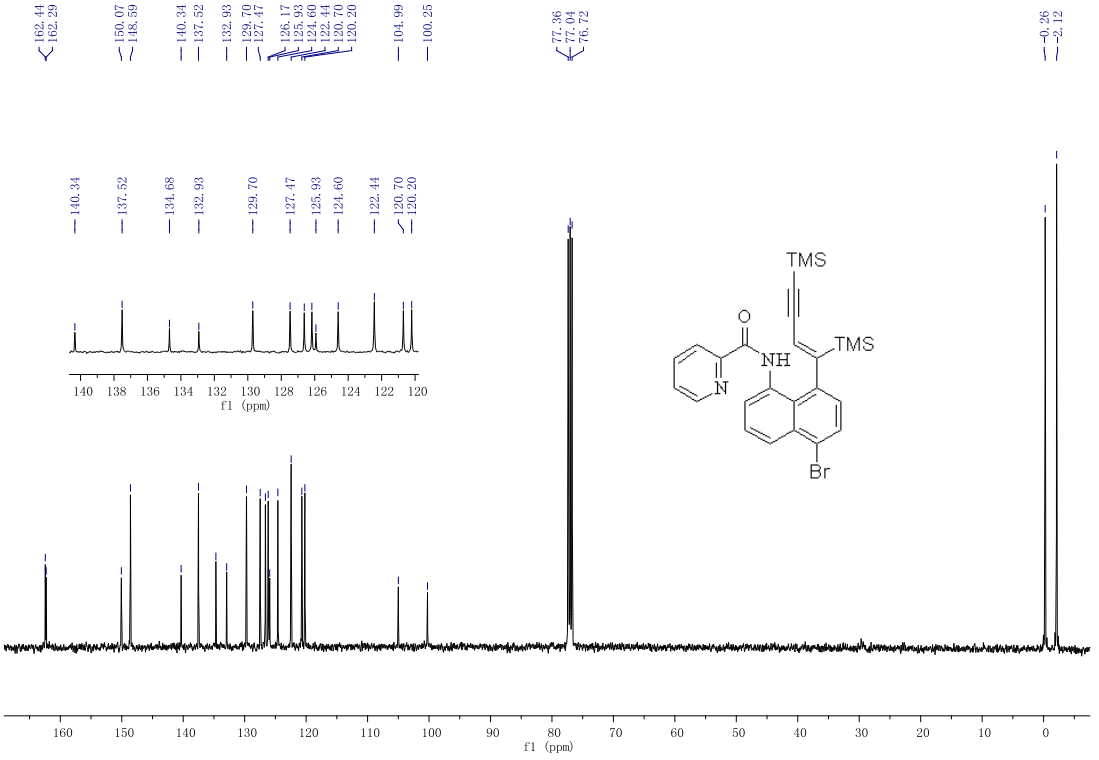


(*E*)-*N*-(9-(1,4-diphenylbut-1-en-3-yn-2-yl)anthracen-1-yl)picolinamide (3d'a)

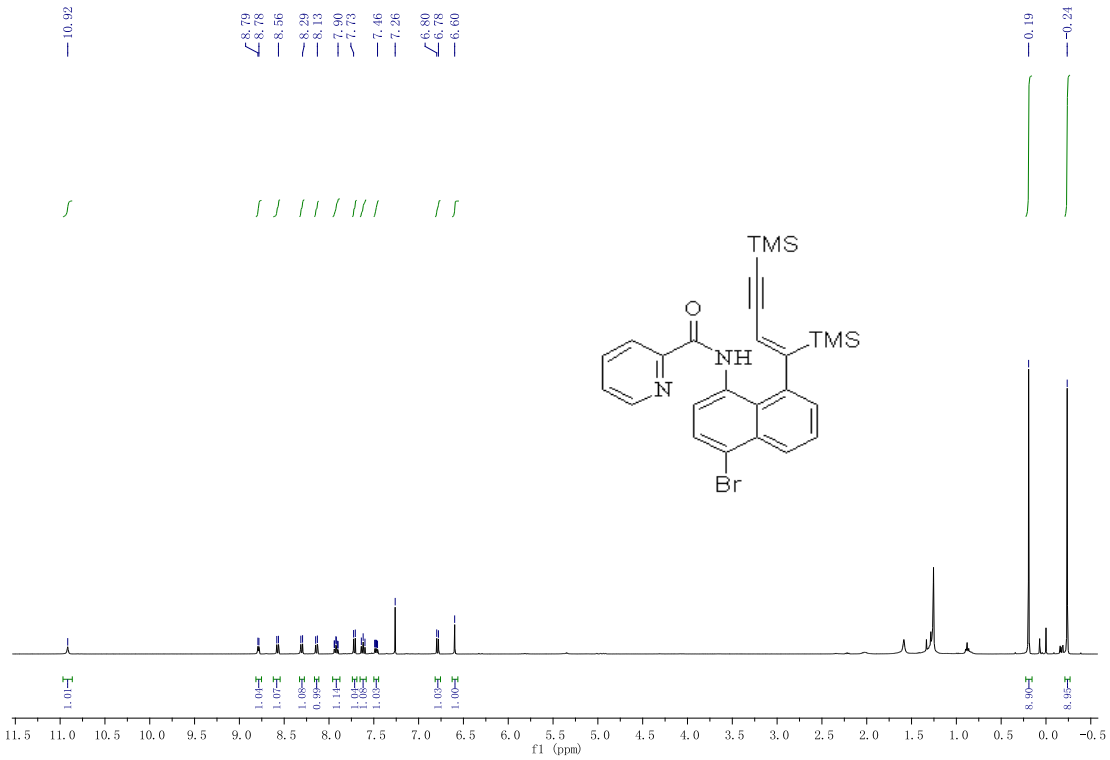


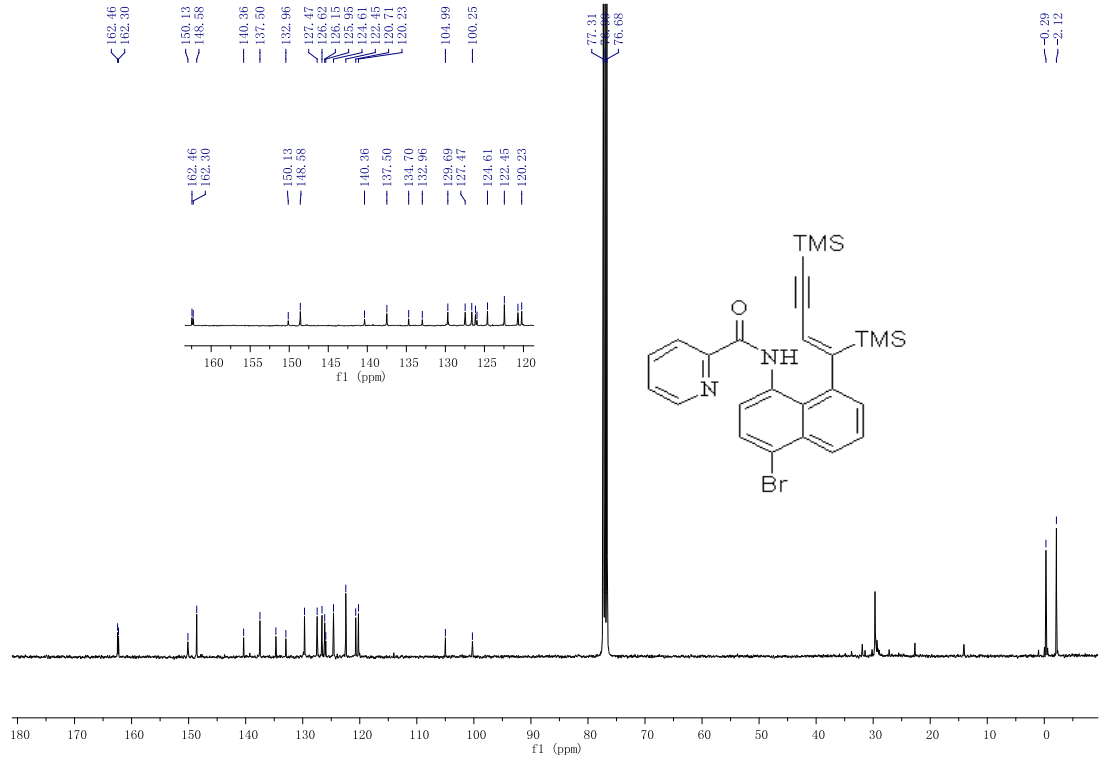
(*Z*)-*N*-(8-(1,4-bis(trimethylsilyl)but-1-en-3-yn-1-yl)-5-bromonaphthalen-1-yl)picolinamide (3bk)



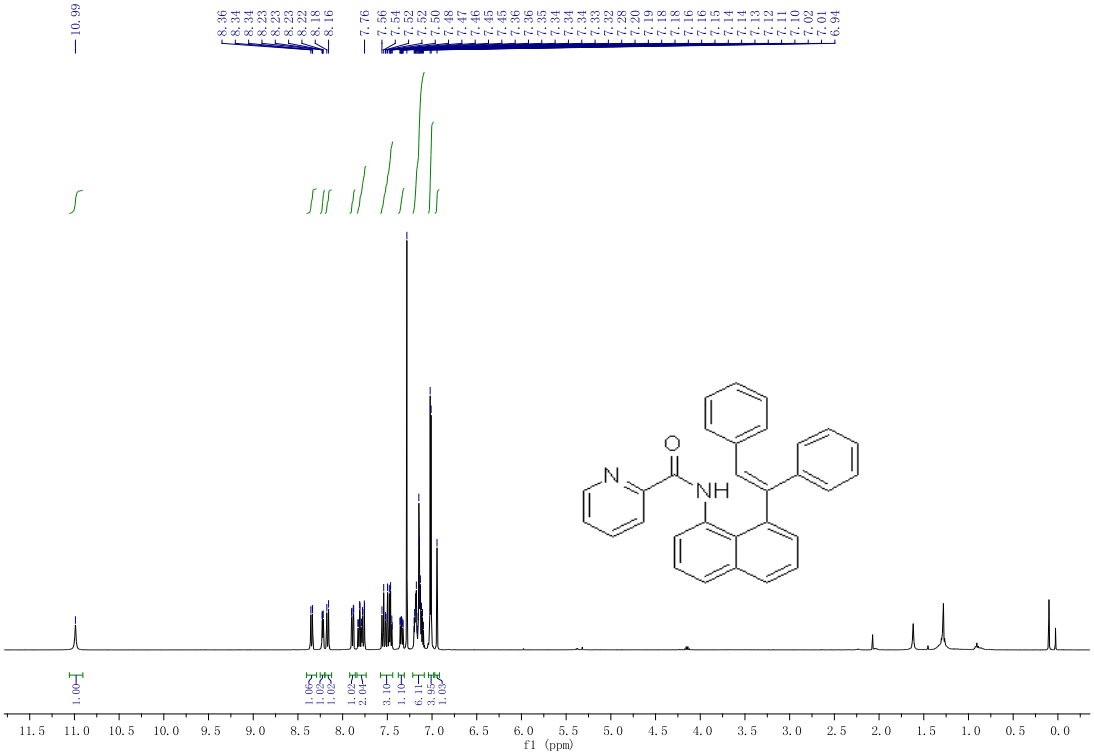


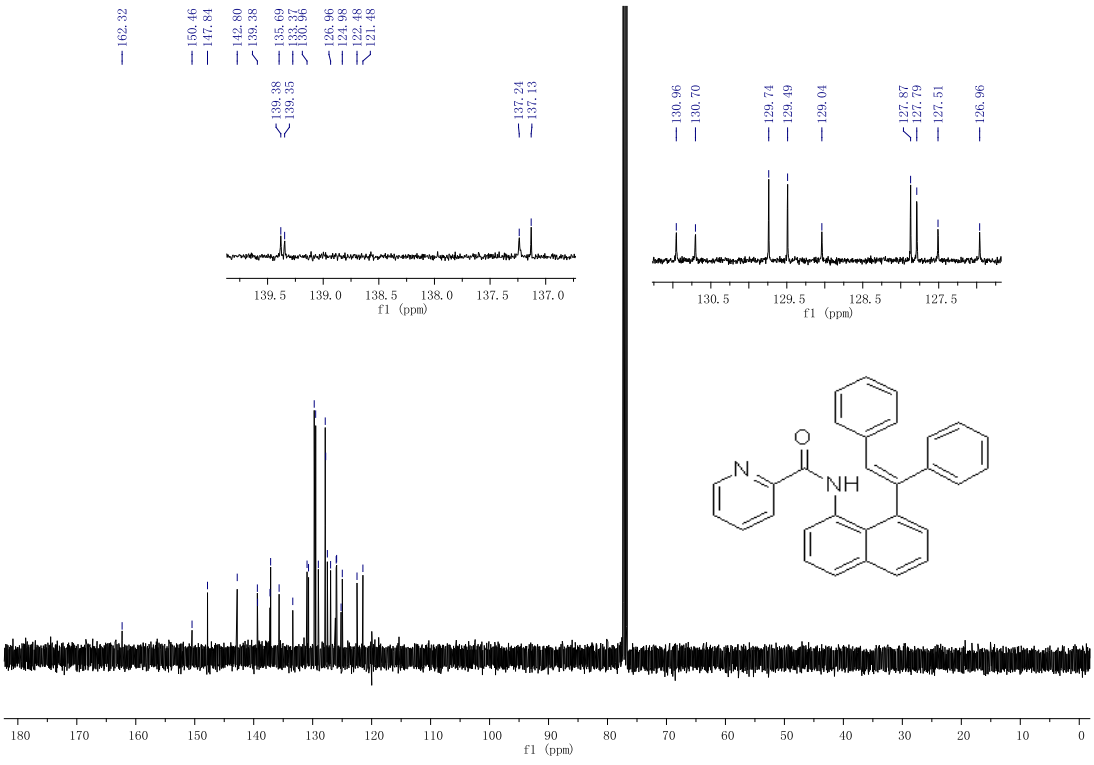
(*Z*)-*N*-(8-(1,4-bis(trimethylsilyl)but-1-en-3-yn-1-yl)-5-bromonaphthalen-1-yl)picolinamide (3ck)



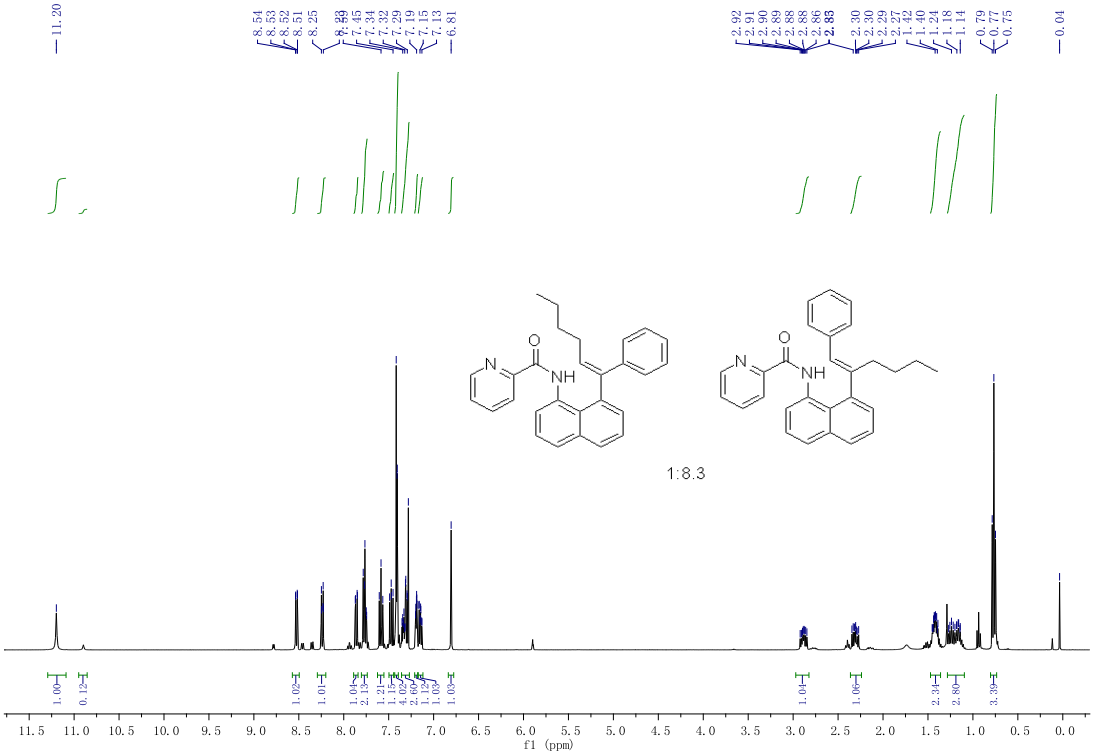


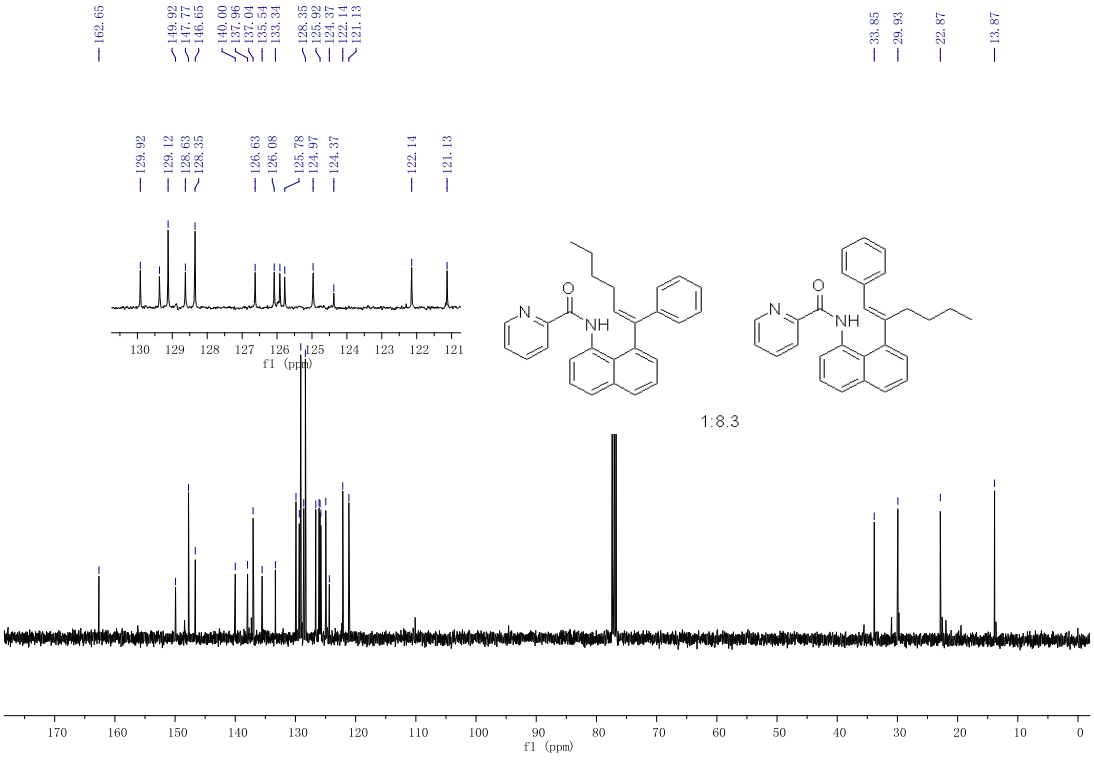
(*E*)-*N*-(8-(1,2-diphenylvinyl)naphthalen-1-yl)picolinamide (4a)



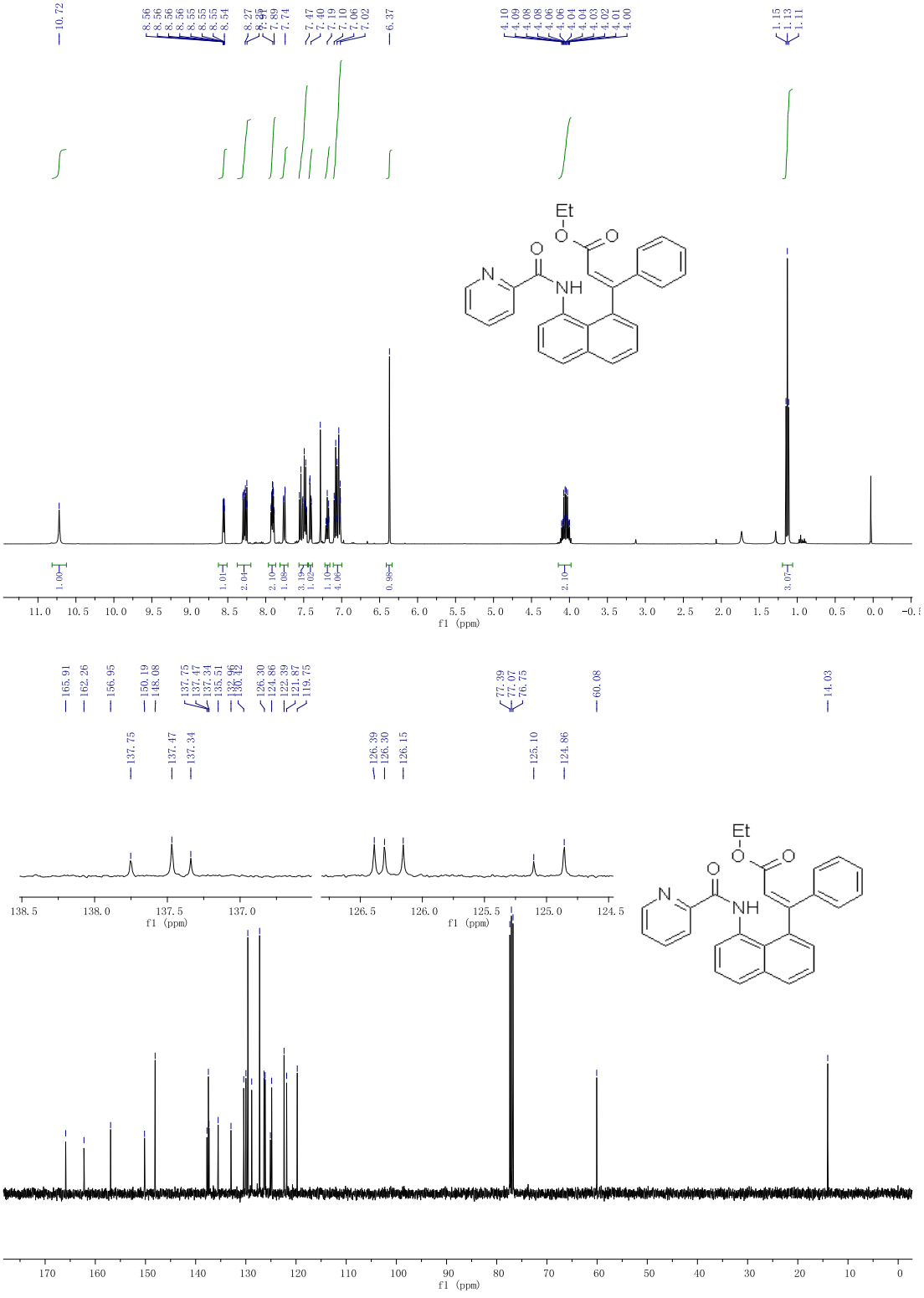


(*E*)-*N*-(8-(1-phenylhex-1-en-1-yl)naphthalen-1-yl)picolinamide (4b')

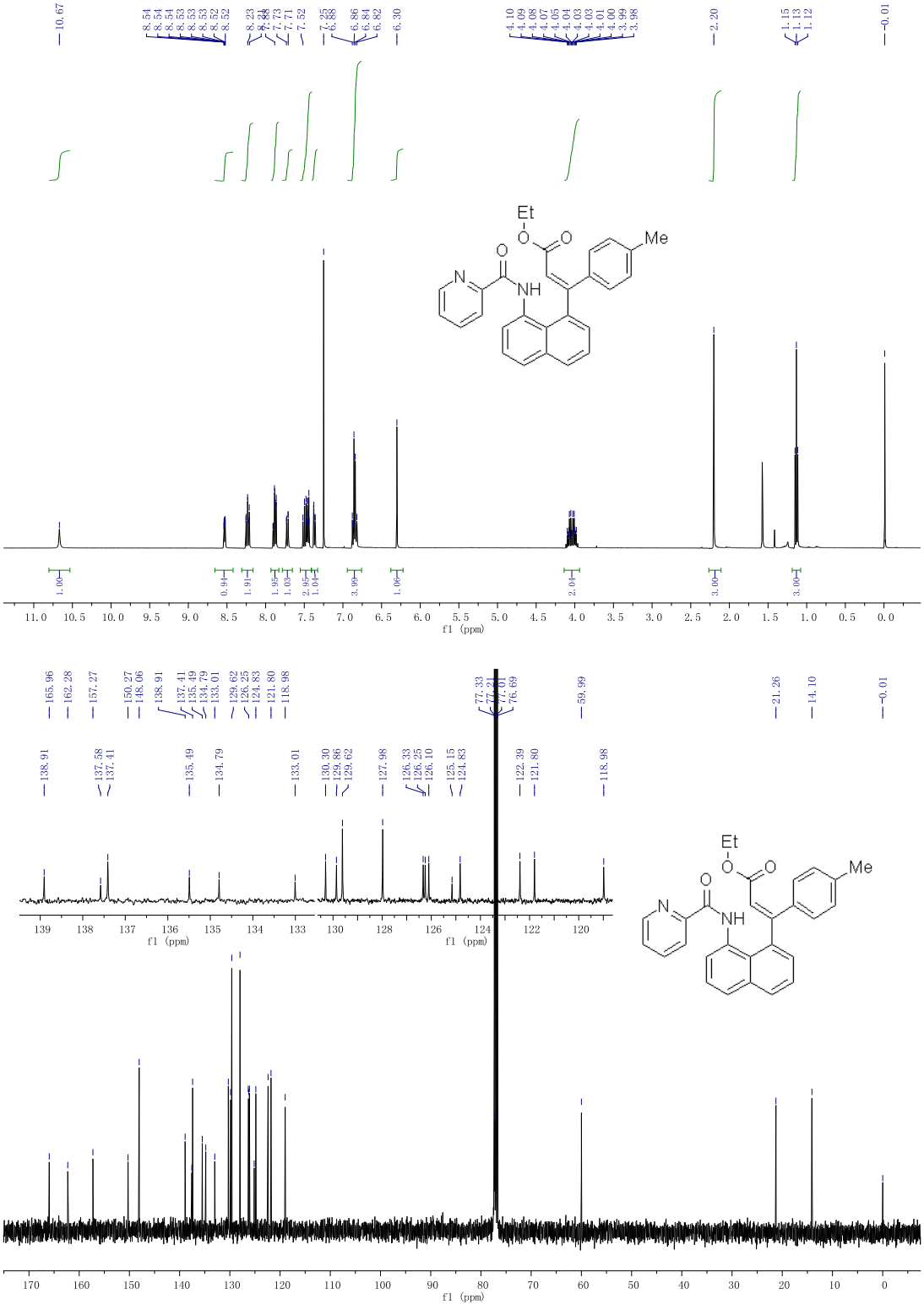




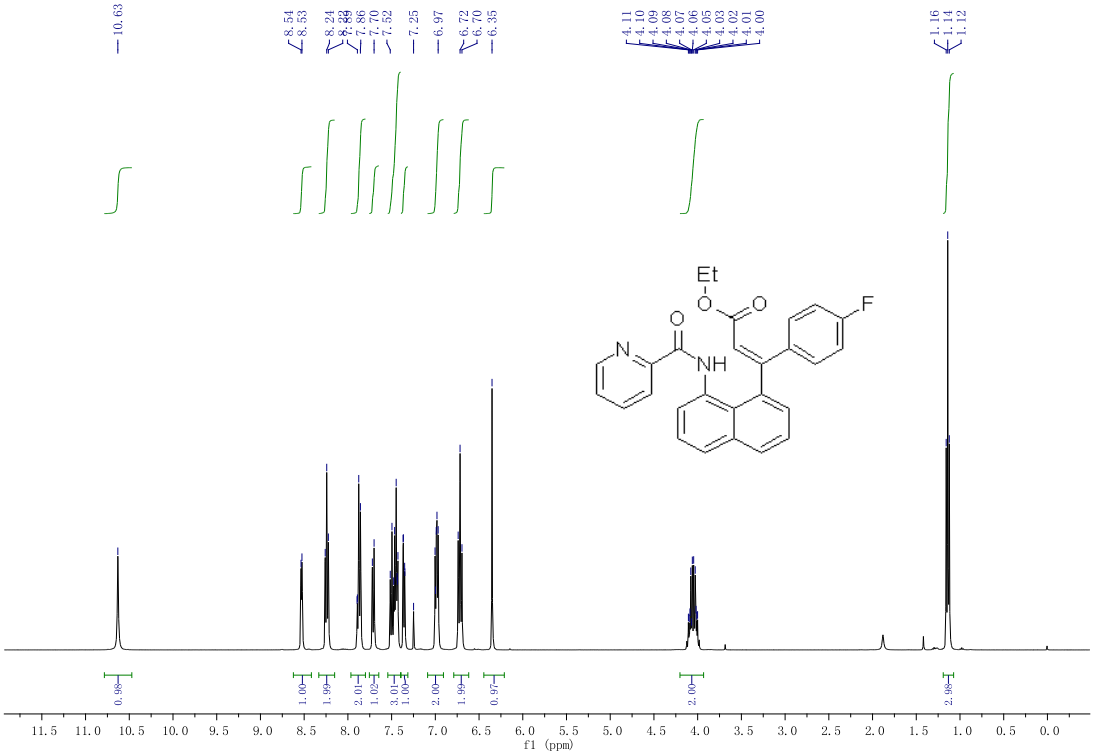
(*E*)-ethyl 3-phenyl-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4c)

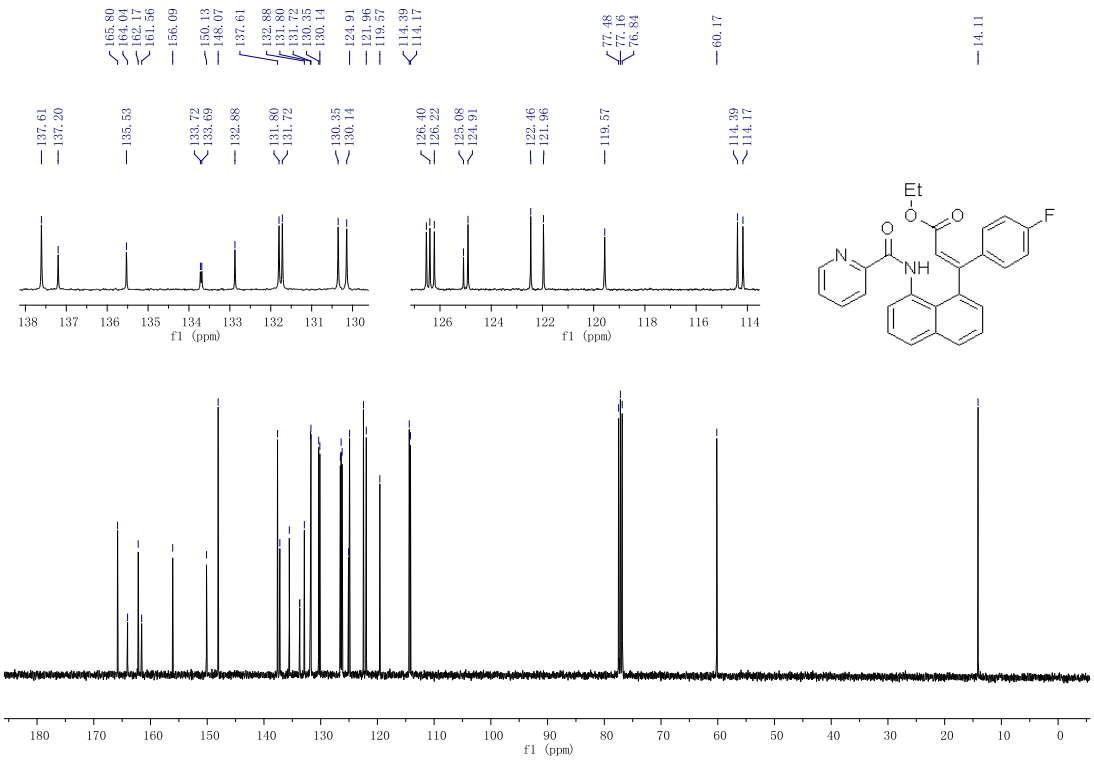


(*E*)-ethyl 3-(8-(picolinamido)naphthalen-1-yl)-3-(*p*-tolyl)acrylate (4d)

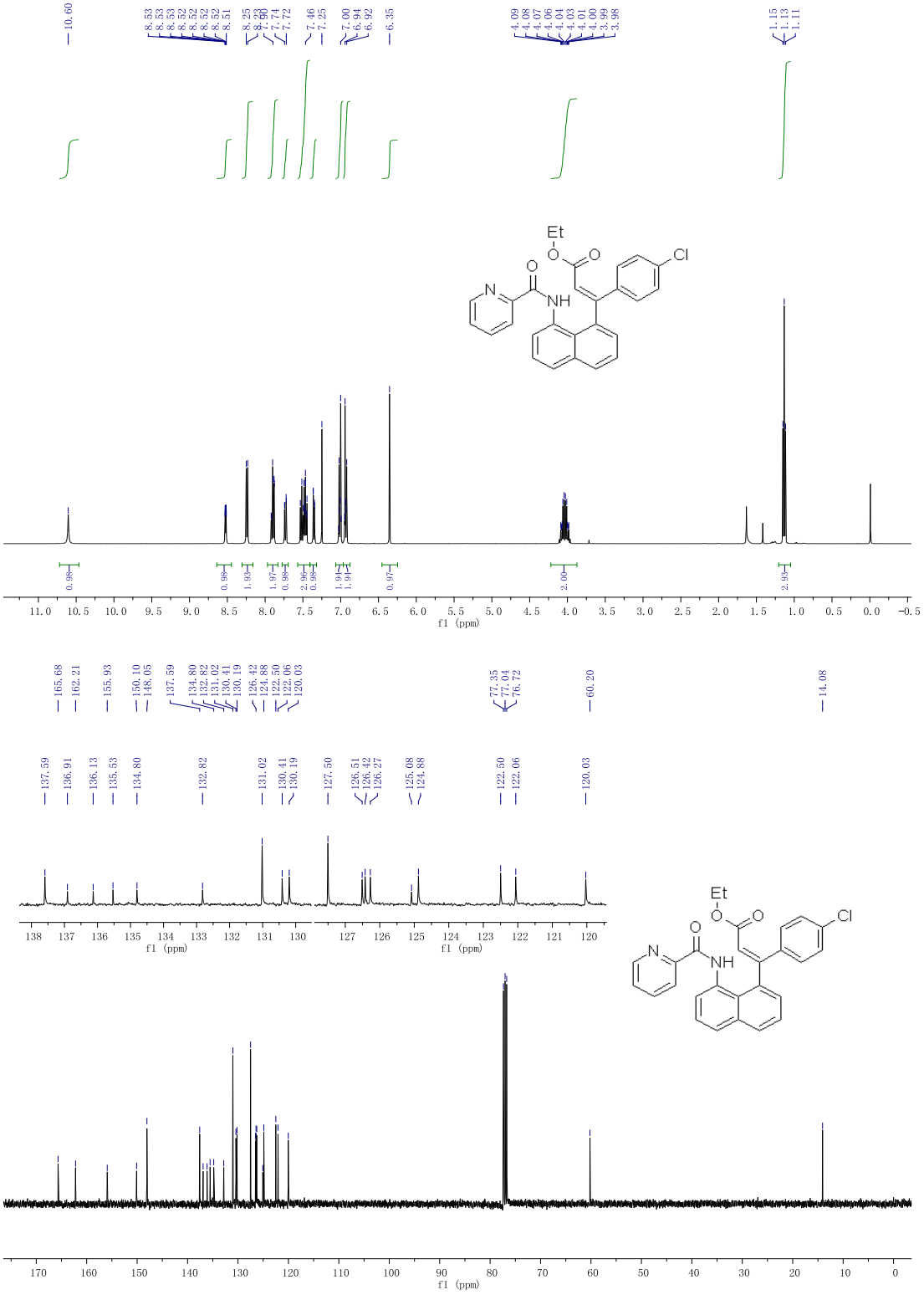


(*E*)-ethyl3-(4-fluorophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4e)

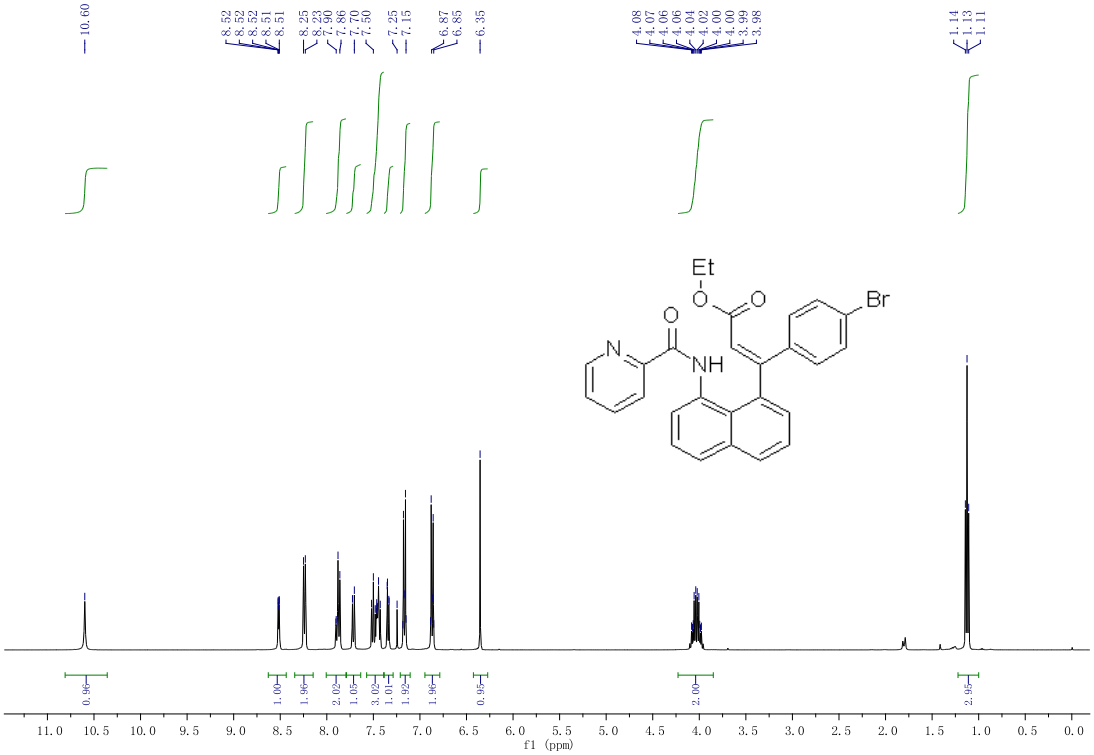


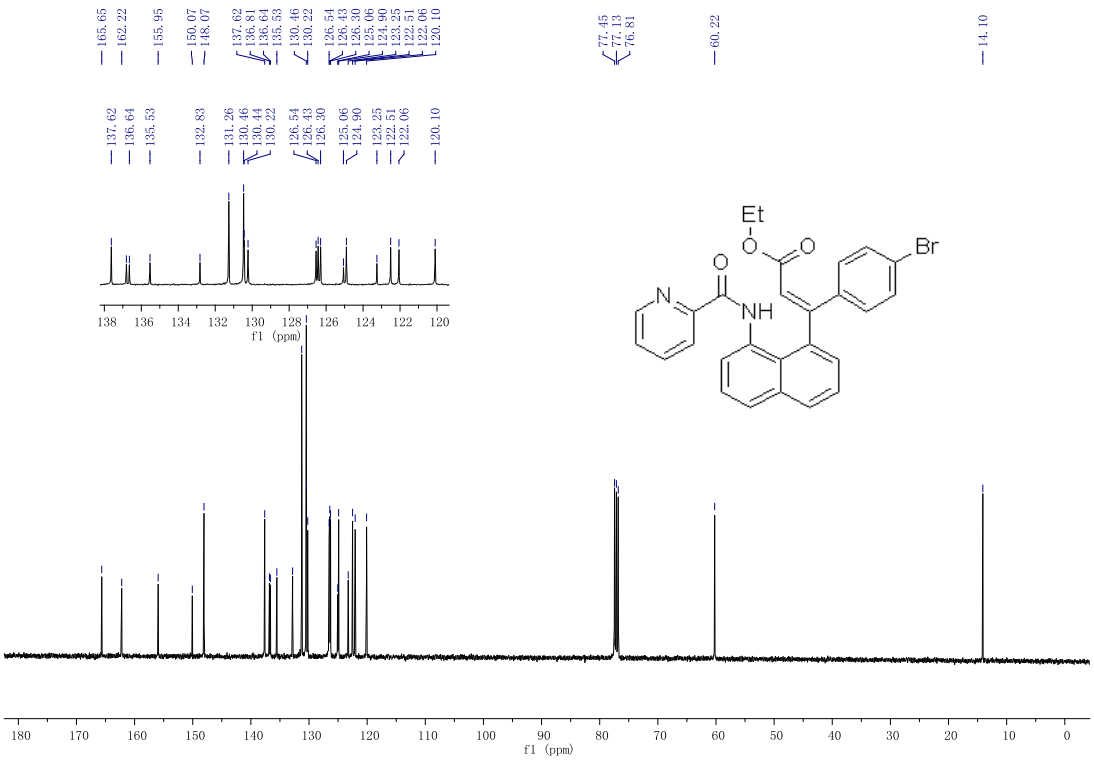


(*E*)-ethyl3-(4-chlorophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4f)

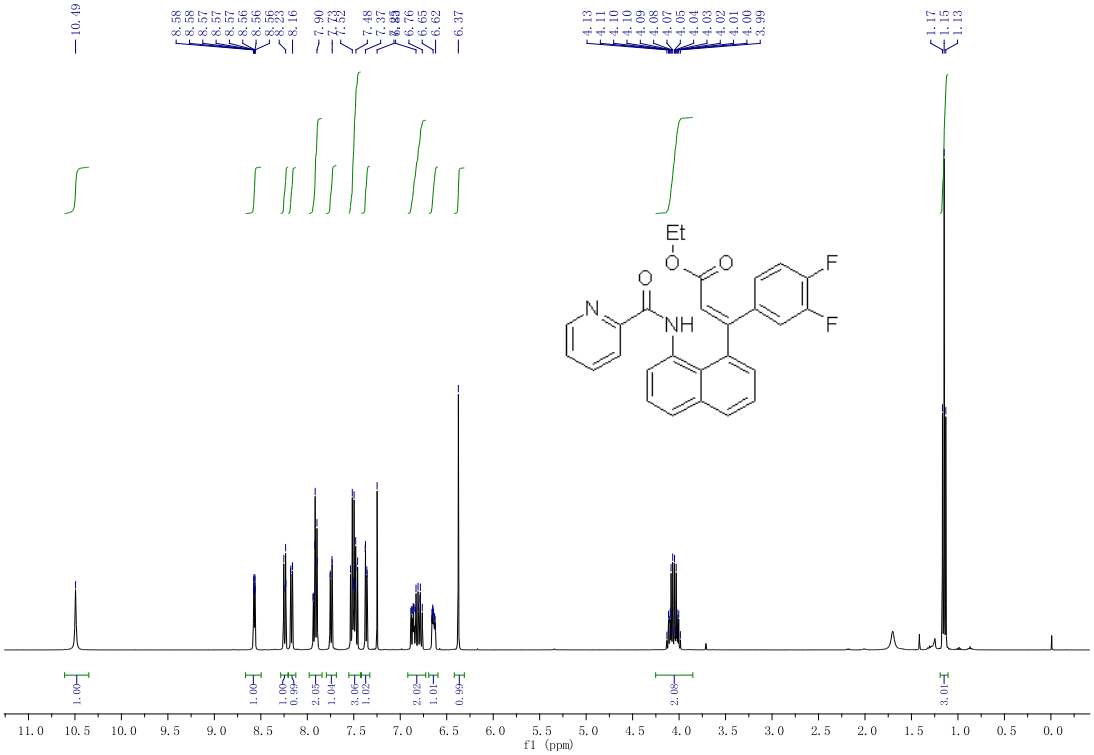


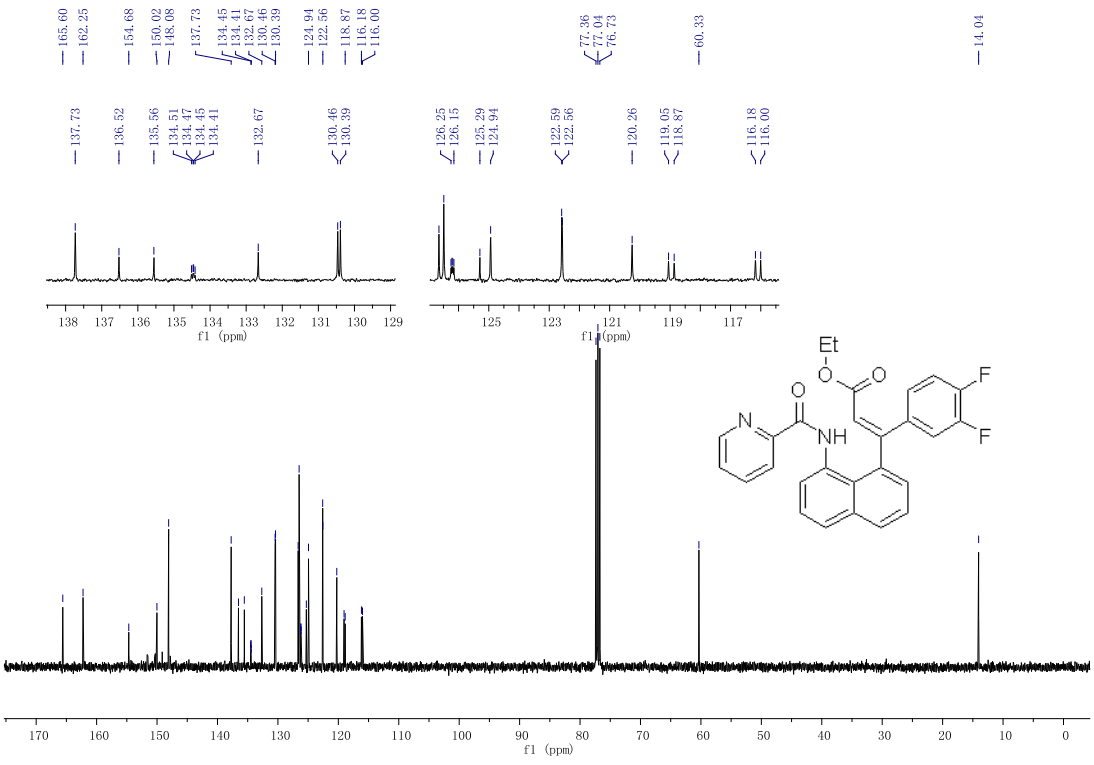
(*E*)-ethyl3-(4-bromophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4g)



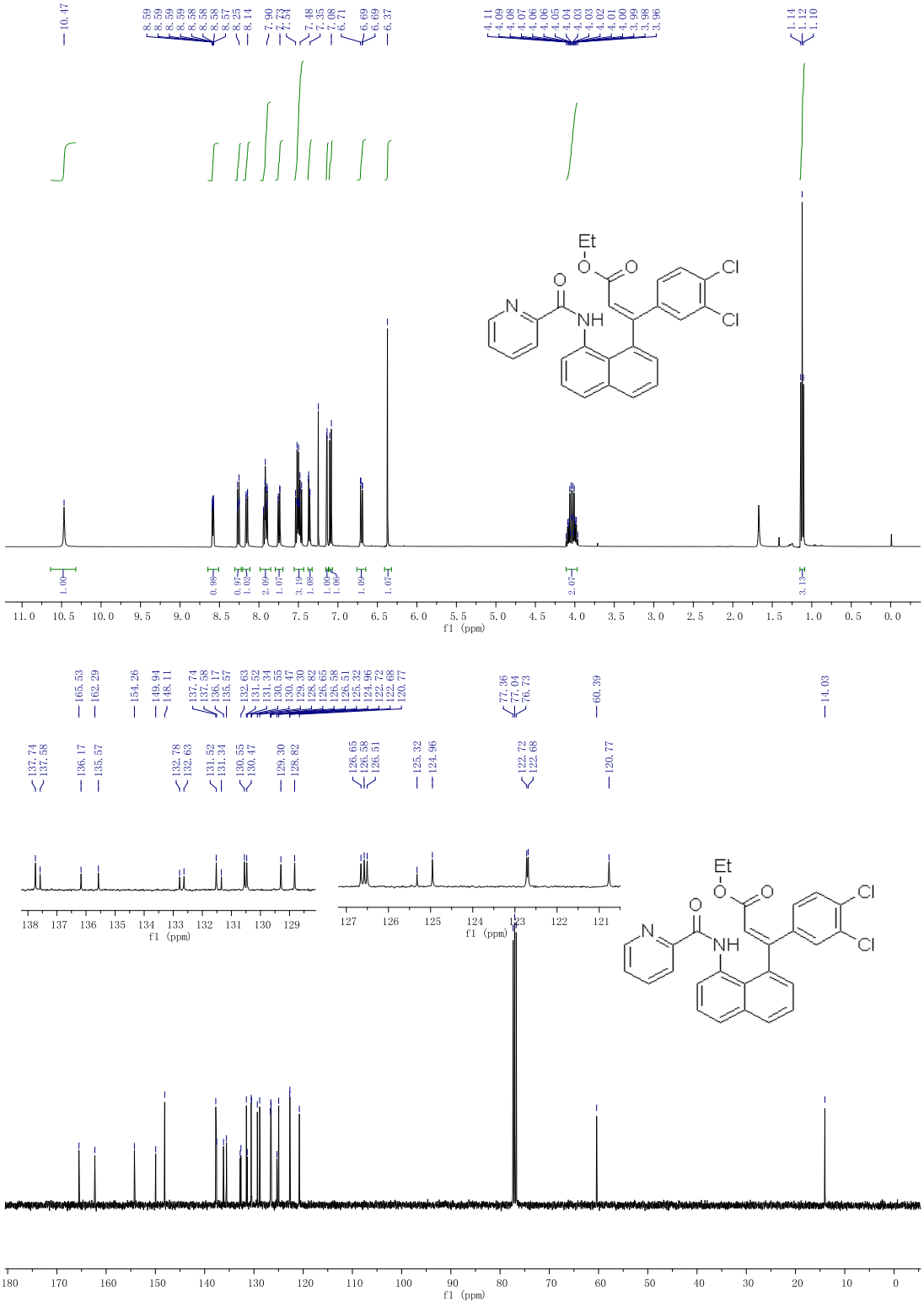


(*E*)-ethyl3-(3,4-difluorophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4h)

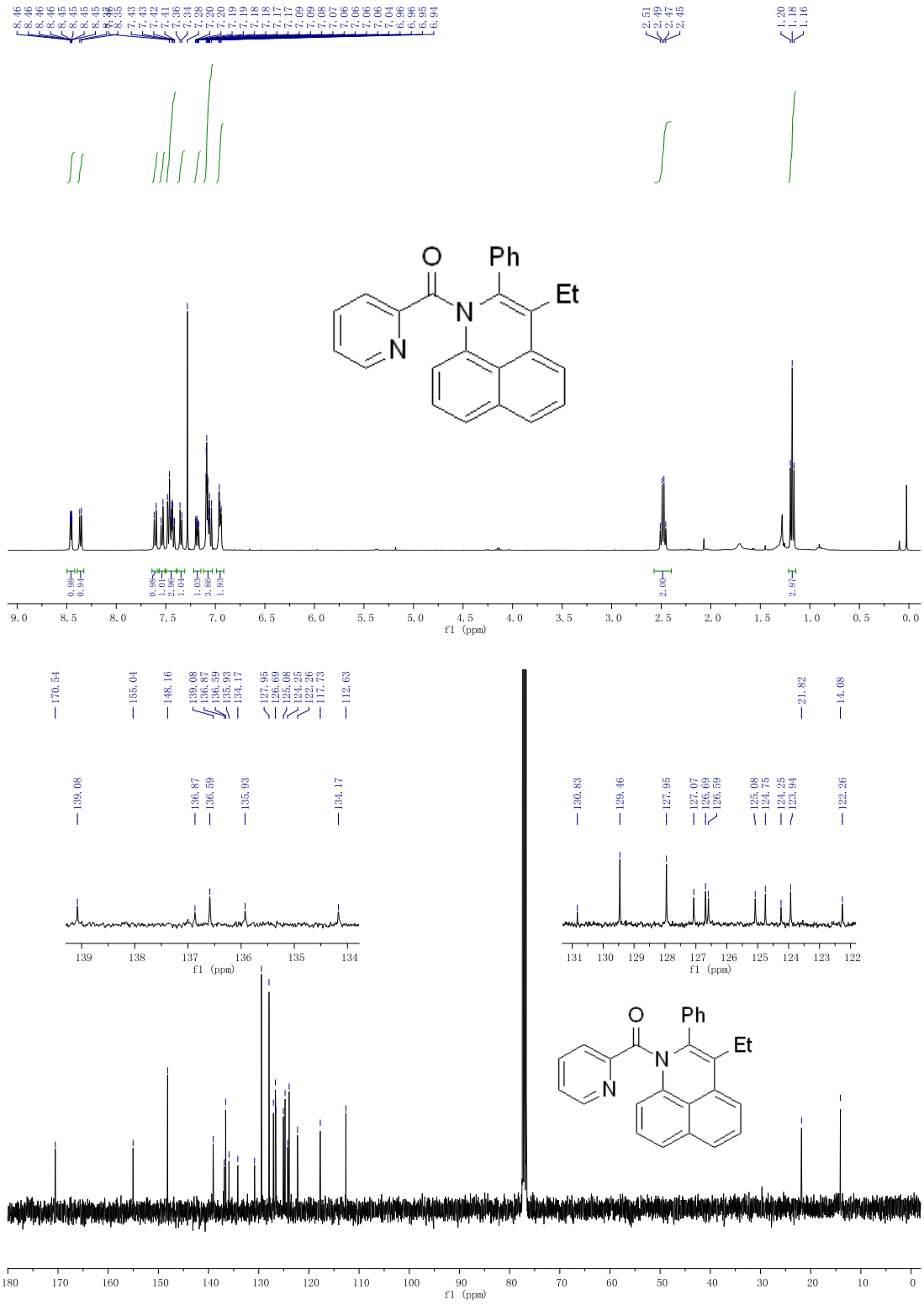




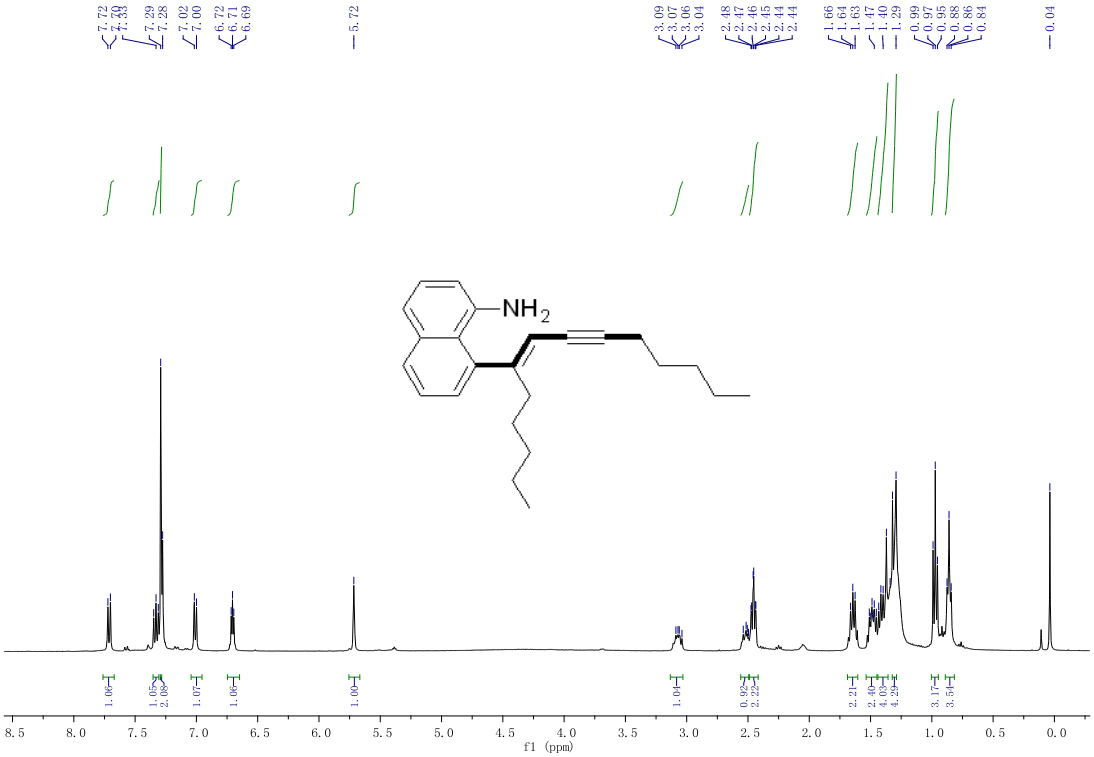
(*E*)-ethyl3-(3,4-dichlorophenyl)-3-(8-(picolinamido)naphthalen-1-yl)acrylate (4i)

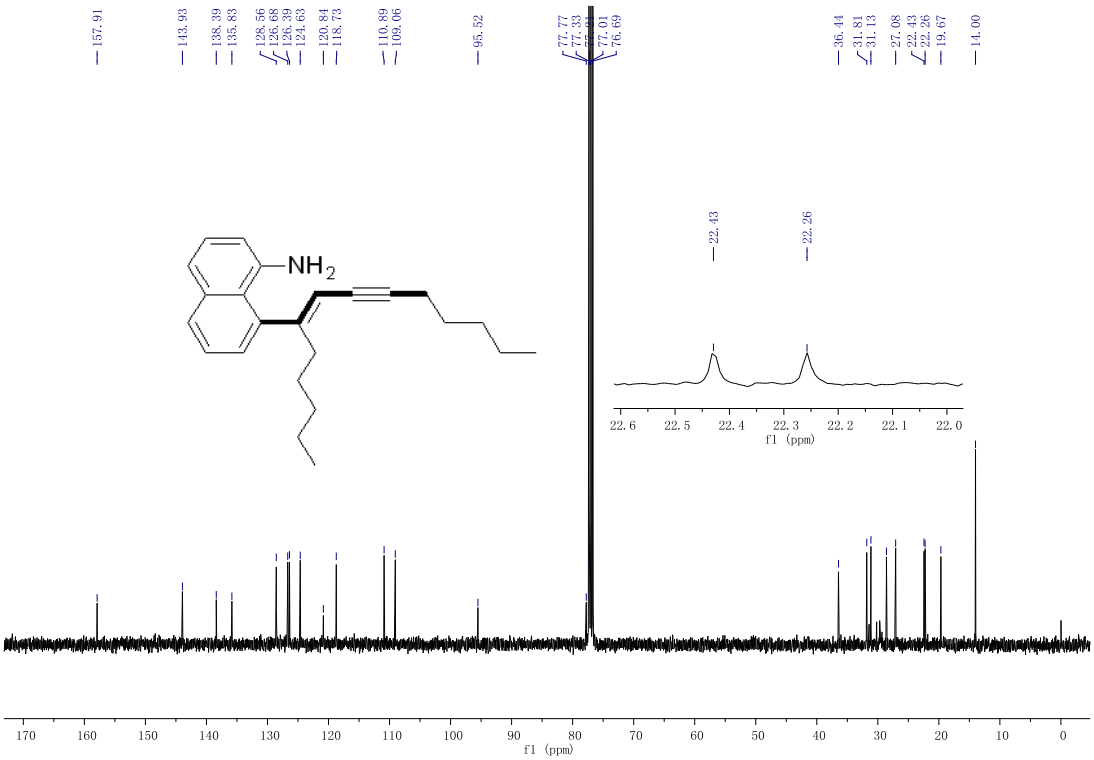


(2-ethyl-3-phenyl-1H-benzo[*de*]quinolin-1-yl)(pyridin-2-yl)methanone (5)

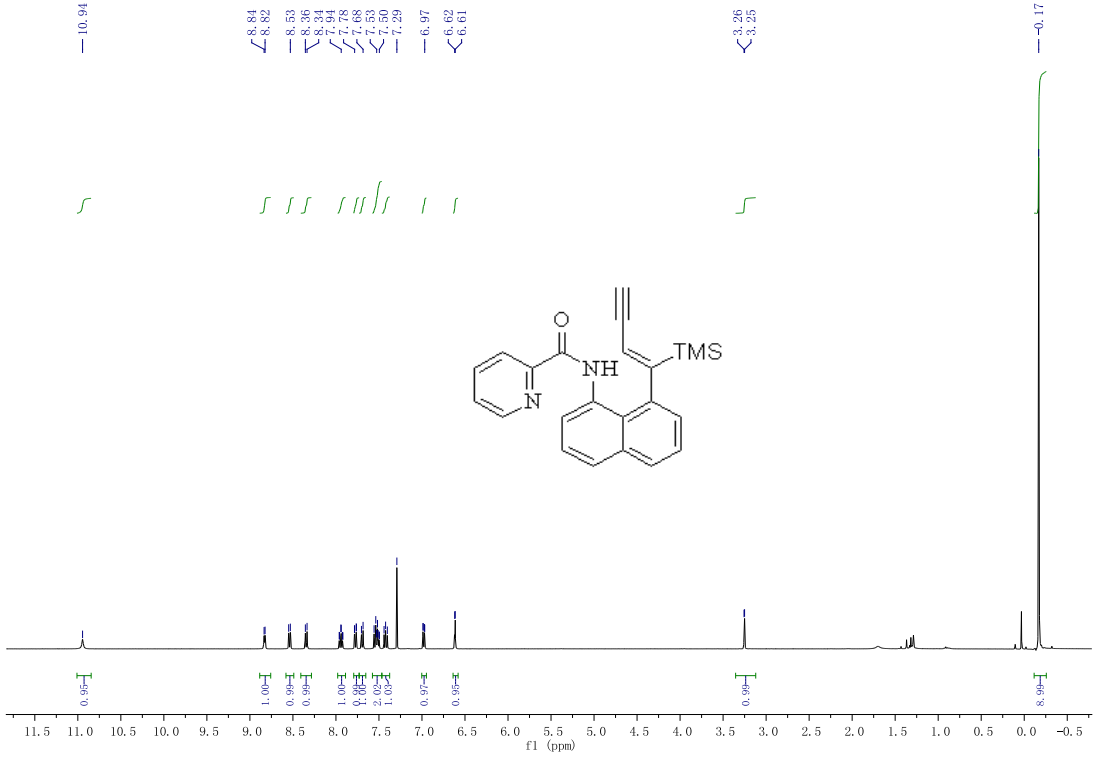


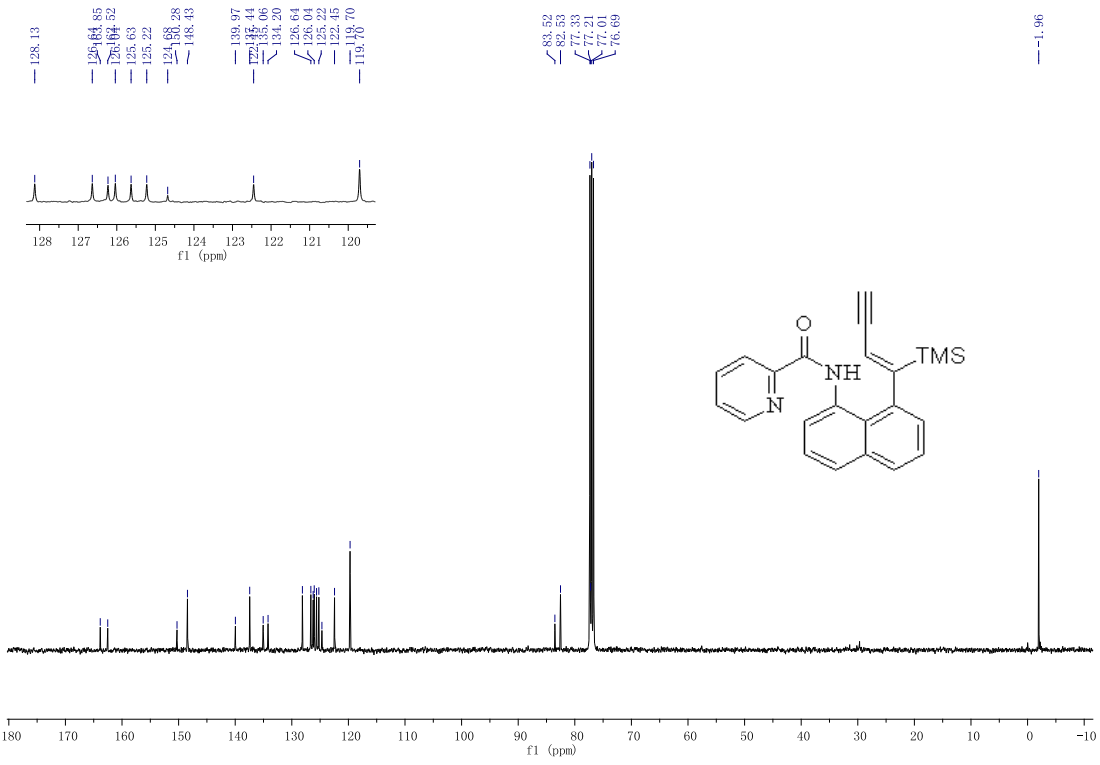
(*E*)-8-(tetradec-6-en-8-yn-6-yl)naphthalen-1-amine (6)



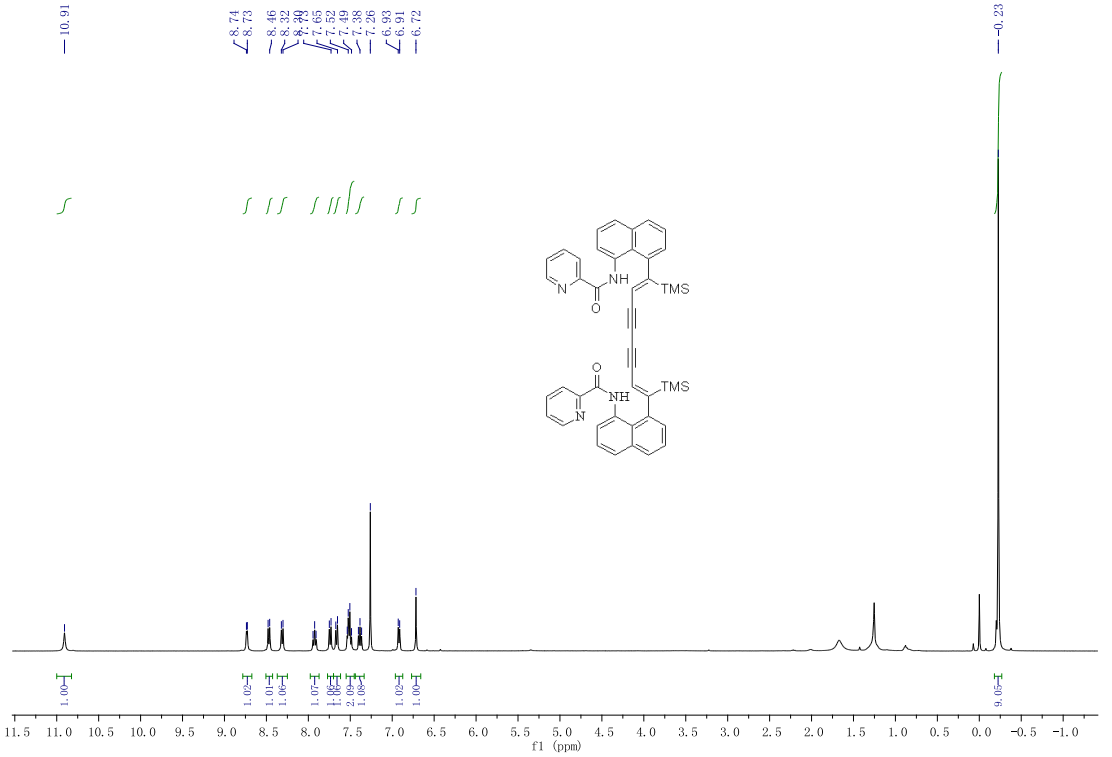


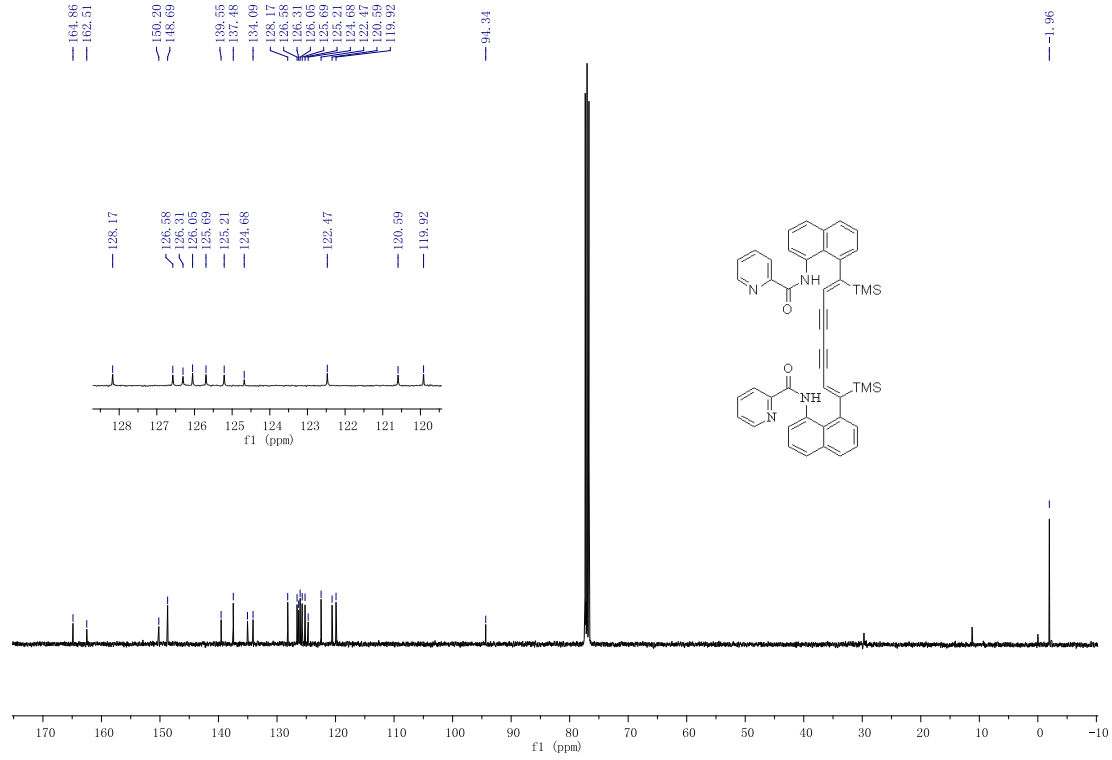
(*Z*)-*N*-(8-(1-(trimethylsilyl)but-1-en-3-yn-1-yl)naphthalen-1-yl)picolinamide(7)





***N*,*N*'-(((1*Z*,7*Z*)-1,8-bis(trimethylsilyl)octa-1,7-dien-3,5-diyne-1,8-diyl)bis(naphthalene-8,1-diyl))dipicolinamide (8)**





The deuterium labeled experiment