SUPPORTING INFORMATION

EnT Catalysis-Enabled, Radical-Relayed Cascade Cyclization to Access Multisubstituted Cyclohexane/Cyclohexene

Mei Xiang,[1,#] Cong Huang,[1,#] Jie *Gao,[1] Kai Chen,[1,2] Zhen-Zhen Xie,[*,3] Hua Yang,[*,1,2]*

[1]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China

[2]Xiangjiang Laboratory, Changsha 410205, P. R. China

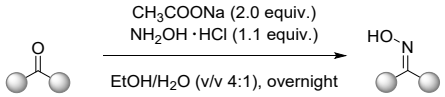
[3]School of Chemical Engineering, Xiangtan University, Xiangtan 411105, P. R. China

Table of Contents

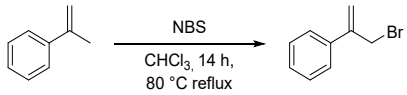
1. General information

Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and used without further purification. The light source used for illuminating the reaction vessel consists of purple LEDs (λ_{max} = 380-385 nm) were purchased from Taobao (https://gpiled.taobao.com/, manufacture: Shenzhen Star Sources Lighting Technology Co., Ltd.). The reaction is carried out in a sealed tube. ^{1}H NMR spectra were recorded with Bruker AVANCE III 400 or 500 MHz spectrometer. The chemical shifts were recorded in *ppm* with reference to tetramethyl silane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, dd = double doublet, dt = double triplet, td = triple doublet), coupling constants (Hz), integration. ^{13}C{^{1}H} NMR at 101 or 126 MHz and ^{19}F{^{1}H} NMR at 376 or 471 MHz were collected with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES^{+} mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200 - 300 mesh). All fluorescence measurements were recorded using a Hitachi FL-7000 Fluorometer. Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected.

2. Procedures for the synthesis of bifunctional reagents 1a-1c, 1d and alkenes 2 (Scheme S1-S3).

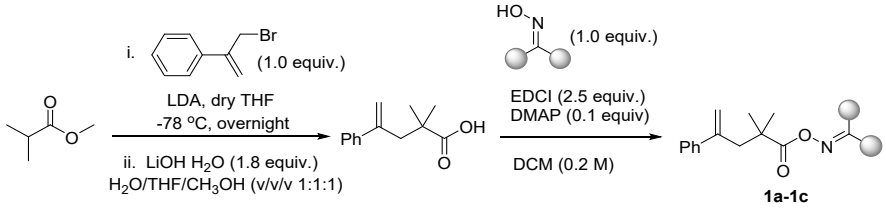


Dissolve aromatic ketone (50.0 mmol, 1.0 equiv.) in the mixed solvent of EtOH/H_2O (v/v, 4:1, 125 mL) in a 250 mL round bottom flask equipped with a condenser. Then, add hydroxylamine hydrochloride (55.0 mmol, 1.1 equiv.) and NaOAc (100.0 mmol, 2.0 equiv.) in one portion. Reflux the reaction mixture overnight and monitor the consumption of the starting material by TLC. Cool the reaction solution to room temperature and concentrate under reduced pressure to remove ethanol. Dilute the solid with water (100.0 mL) and extract with ethyl acetate (80×3 mL). Dry over anhydrous $MgSO_4$. And obtain benzophenone oxime by evaporating the solvent.



The synthesis of this compound was adapted from a literature procedure for a similar substrate.[1]

A mixture of α-methylstyrene (30.00 mmol, 1.0 equiv.) and N-bromosuccinimide (33 mmol, 1.15 equiv.) in chloroform (4.5 mL) was stirred at reflux for 16 hours. Then, Dilute the solid with water (10.0 mL) and extract with ethyl acetate (10×3 mL). The filtrate was concentrated at reduced pressure and purified by flash chromatography on silica gel (100% hexanes) to obtain 4.76 g of product as a colorless oil (81% yield)

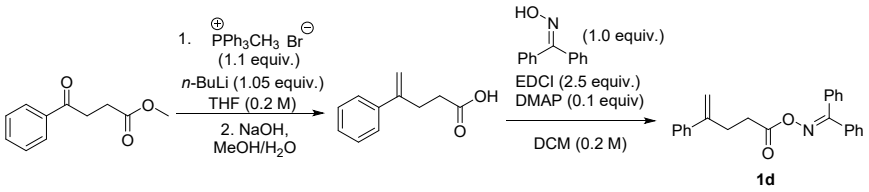


Scheme S1. synthesis of bifunctional reagents **1a-1c**

The synthesis of this compound was adapted from a literature procedure for a similar substrate.[2-3]

To a flame-dried 250 mL round bottom flask stir-bar was added anhydrous THF (20 mL) under an atmosphere of Ar. The flask was cooled to -78 ˚C and LDA (20 mL, 2.0 M in THF/ethylbenzene/heptane, 50 mmol) was added. To the LDA solution was then added dropwise methyl isobutyrate (5 mL, 43.5 mmol). The reaction was stirred for 1.5 h at –78 ˚C, then warmed to –40 ˚C and maintained for 1 h. To the reaction was then added dropwise a solution of (3- bromoprop-1-en-2-yl)benzene (5.75 mL, 39.95 mmol) in anhydrous THF (7.5 mL). The reaction was then allowed warm to room temperature overnight with stirring. The reaction was then concentrated in vacuo. To the resulting oily solid was added lithium hydroxide monohydrate (3 g, 71.5 mmol), methanol (30 mL), THF (30 mL), and H_2O (30 mL). The hydrolysis reaction was stirred for 48 h at room temperature. The reaction was then transferred to a 500 mL separatory funnel, washing the flask with ethyl acetate, and diluted with 75 mL 2 N NaOH solution and 75 mL of additional ethyl acetate. The funnel was shaken and the layers were separated. The aqueous layer was washed twice with 75 mL ethyl acetate. The aqueous layer was then acidified with 75 mL 4 N HCl solution and extracted twice with 75 mL ethyl acetate. The organic extracts were then combined and dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the carboxylic acid as an off-white crystalline solid (8.15 g, 85%).

Ketoxime from previous step (30 mmol) and aliphatic carboxylic acid (30 mmol) were dissolved in CH_2Cl_2 (150 mL). The reaction bath is lowered to 0 °C in a low-temperature stirring reaction bath. Then, EDCI (2.5 equiv.) and DMAP (10 mol%, 3 mmol) was added sequentially. The mixture was stirred at room temperature under argon atmosphere until the reaction was complete as monitored by TLC analysis. The mixture was diluted with distilled water and the CH_2Cl_2 layer was separated, dried over anhydrous Na_2SO_4 and concentrated. The crude mass was purified by flash column chromatography using petroleum ether/ethyl acetate (EtOAc) (v/v, 24:1) as eluent to afford the desired products (65%-80% yield).



Scheme S2. synthesis of bifunctional reagents **1d**

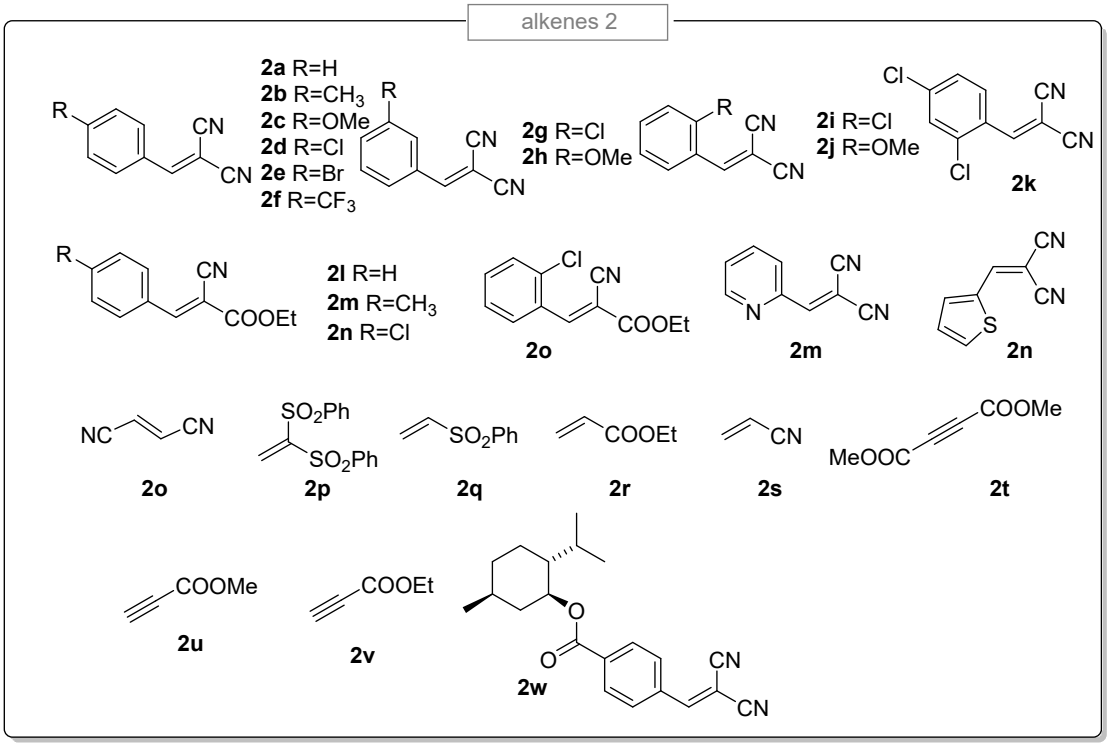
The synthesis of this compound was adapted from a literature procedure for a similar substrate.[4]

Methyl triphenylphosphonium bromide (980 mg, 2.8 mmol) was suspended in THF (15 mL) at -5 °C, n-BuLi (1 M in THF, 2.7 mL, 2.7 mmol) was added, and after 30 min the ylide sokution was lowered to -78 °C. 4-Oxo-4-phenylbutyric acid methyl ester (500 mg, 2.6 mmol) was added and the reaction mixture allowed to warm to room temperature and heated to reflux for 40 h. The reaction was quenched with saturated aqueous NH_4Cl solution (20 mL) and extracted with EtOAc (2 × 50 mL). The combined extracts were washed with water (2 × 60 mL), brine (80 mL), dried over $MgSO_4$ and concentrated to give a light brown oil oil. The oil was purified by chromatography (8 : 2, PE : CH_2Cl_2) to give the desired olefin (460 mg, 93%) as a pale yellow oil.

To a stirred solution of the above ester (528 mg, 2.8 mmol) in MeOH (20 mL) at 0 °C was added NaOH (560 mg, 14.0 mmol) in water (20 mL). The reaction mixture was allowed to warm to room temperature and stirred for a further 18 h. The solution was acidified aqueous HCl solution (1 M) and extracted with Et_2O (2 × 20 mL). The organic layers were combined, washed with water (30 mL), brine (30 mL), dried over $MgSO_4$ and concentrated to give acid (450 mg, 92%) as off white crystals:

Ketoxime from previous step (3 mmol) and aliphatic carboxylic acid (3 mmol) were dissolved in DCM (15 mL). The reaction bath is lowered to 0 °C in a low-temperature stirring reaction bath. Then, EDCI (2.5 equiv.) and DMAP (10 mol%, 0.3 mmol) was added sequentially. The mixture was stirred at room temperature under argon atmosphere until the reaction was complete as monitored by TLC analysis. The mixture was diluted with distilled water and the DCM layer was separated, dried over anhydrous Na_2SO_4 and concentrated. The crude mass was purified by flash column chromatography using petroleum ether/ethyl acetate (EtOAc) (v/v, 24:1) as eluent to

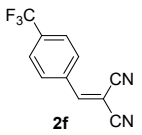
afford the desired products (75% yield).



Scheme S3. Alkene substrates in this work

Alkene **2a-2n**, **2w**[5] and alkene **2p**[6] were synthesized according to reported literature procedures. And other alkenes **2o** and **2q – 2v** were purchased from commercial suppliers (https://www.energy-chemical.com/front/index.htm) and used without further purification.

All alkenes **2a -2e** and **2g – 2w** shown in Scheme S2 are known compounds.

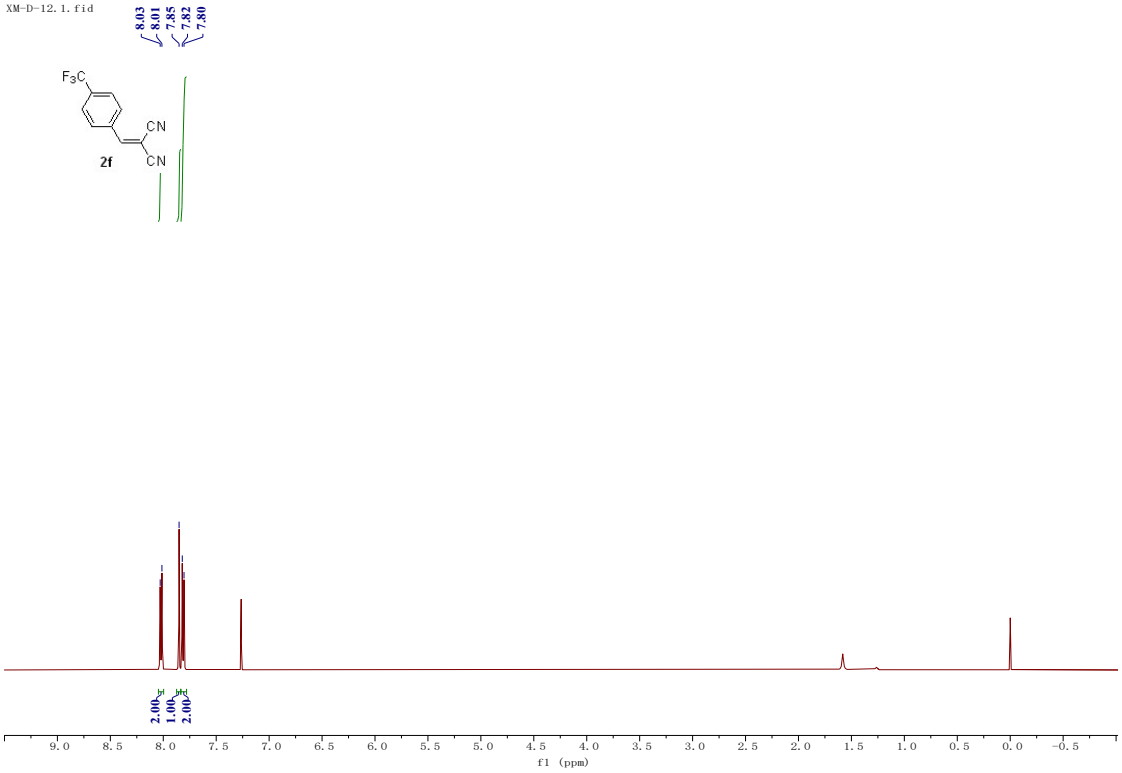


^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.85 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H).

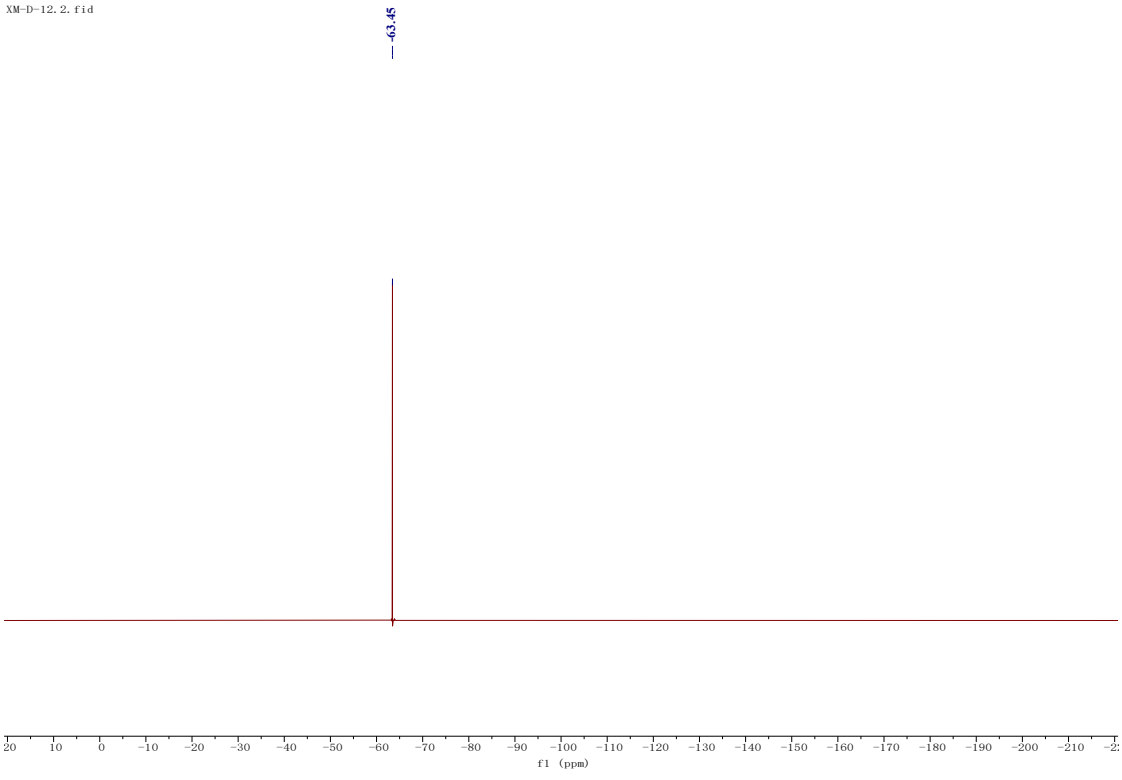
^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.45.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.1, 135.3 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 133.7, 130.8, 126.6 (q, $^{4}J_{C\text{-}F}$ = 3.7 Hz), 123.1 (q, $^{1}J_{C\text{-}F}$ = 273.0 Hz), 113.0, 111.9, 86.0.

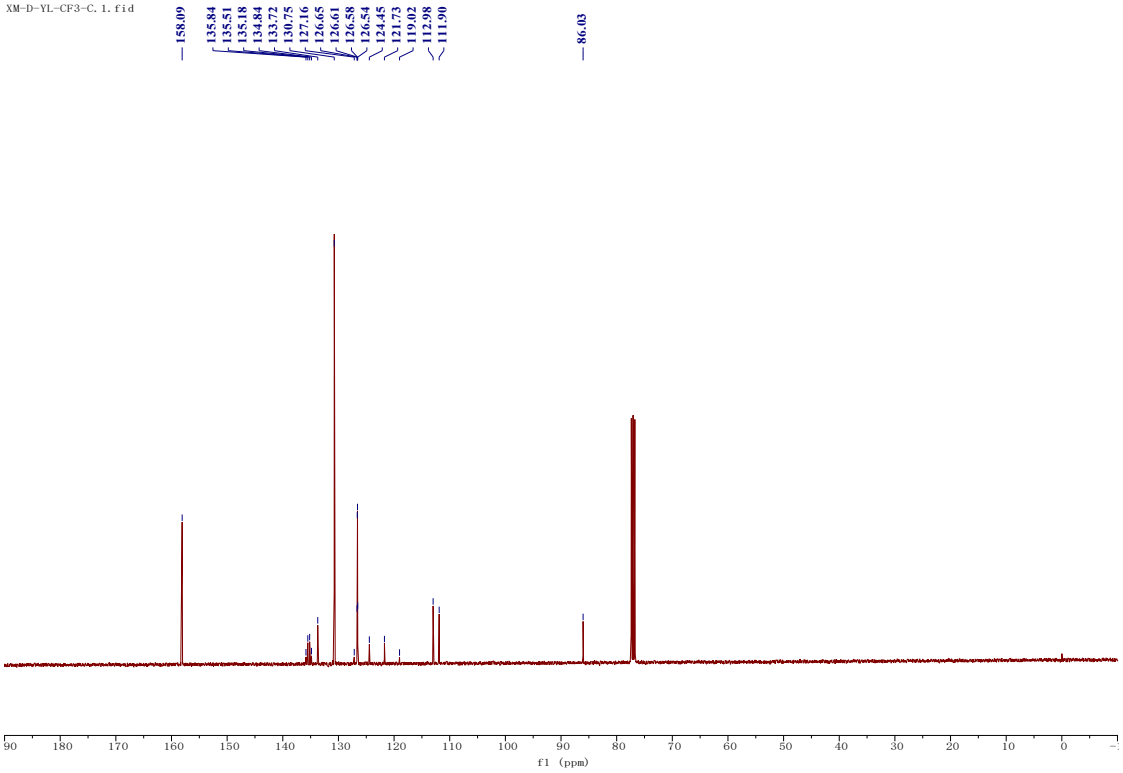
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of product 2f



^{19}F NMR (471 MHz, $CDCl_3$) spectrum of product 2f



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 2f



3. Experimental details for the preparation of compounds 3-31

3.1 Photoreaction set-up (Figure S1)

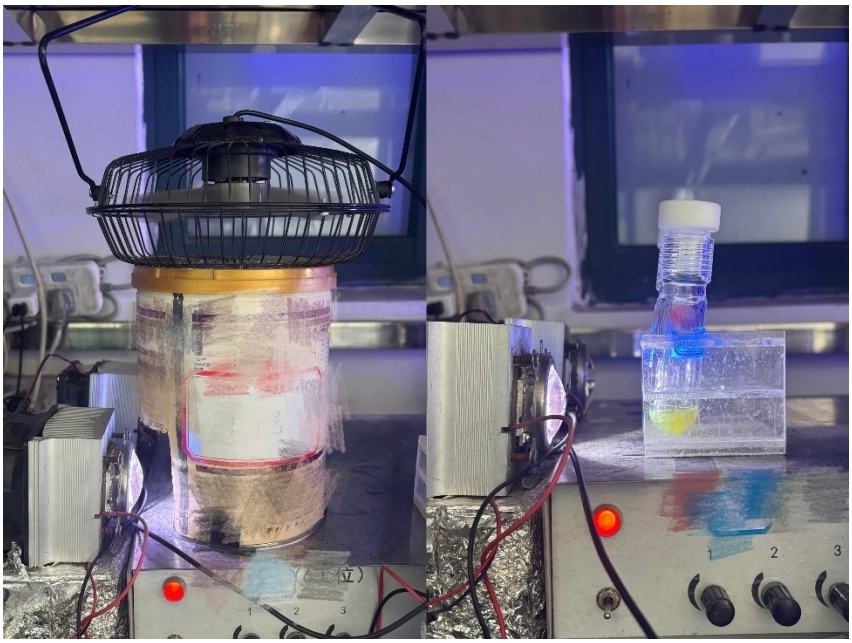
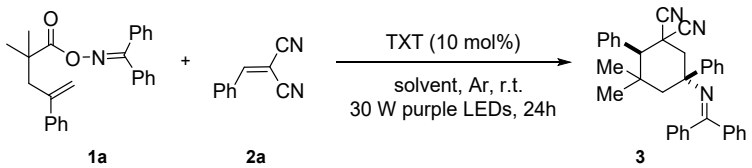


Figure S1. The set-up for the reaction (photographed by Mei Xiang)

The light source used for illuminating the reaction vessel (commercial supplier: Synthware) consists of purple LEDs (λ_{max}= 380-385 nm) purchased from Taobao (https://gpiled.taobao.com). The whole process of the reaction and the measured reaction temperature varied between 25 - 37 °C.

3.2 Detailed optimization of reaction conditions

Table S1. Optimization of reaction conditions I[a]



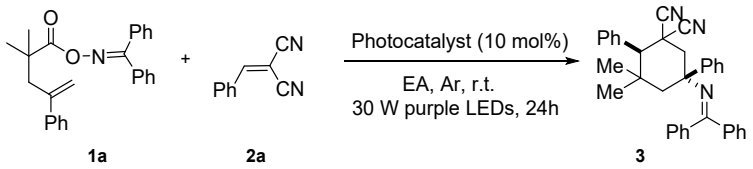
1a 2a 3

Entry	PC (10mol%)	Solvent (0.1M)	LEDs	Yield (%)
1	TXT	EtOAc	405 nm	79
2	TXT	MeCN	405 nm	65
3	TXT	DMF	405 nm	31
4	TXT	DMSO	405 nm	57
5	TXT	DCM	405 nm	57
6	TXT	MeOH	405 nm	trace

7	TXT	Acetone	405 nm	54
8	TXT	THF	405 nm	41
9	TXT	DCE	405 nm	74

[a]Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2a** (0.1 mmol, 1.0 equiv.), TXT (2 mg, 10 mol%), Solvent (1.0 mL) under Ar at r.t. for 24 h, 405 nm LEDs, isolated yield.

Table S2. Optimization of reaction conditions II[a]

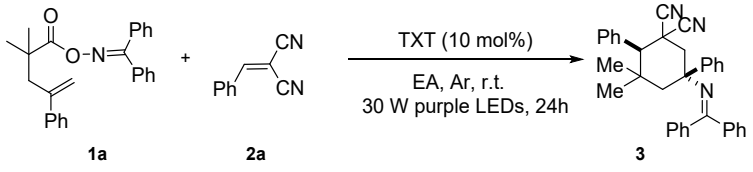


1a 2a 3

Entry	PC	Solvent (0.1M)	LEDs	Yield (%)
1	$[Ir(dF(CF_2)ppy)_2(dtbbpy)](PF_6)$	EA	405 nm	58
2	$Ir(ppy)_3$	EA	405 nm	N.R.
3	$Ir(ppy)_2dtbbpyPF_6$	EA	405 nm	N.R.
4	4CZIPN	EA	405 nm	Trace
5	Benzophenone	EA	365 nm	60
6	-	EA	365 nm	49
7	TXT	EA	-	N.R.
[b]8	TXT	EA	405 nm	Trace
9	-	EA	405 nm	N.R.

[a]Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2a** (0.1 mmol, 1.0 equiv.), **EA** (1.0 mL), PC (10mol%) under Ar at r.t. for 24 h, 405 nm or 365 nm LEDs, isolated yield. [b]in air.

Table S3. Optimization of reaction conditions III[a]



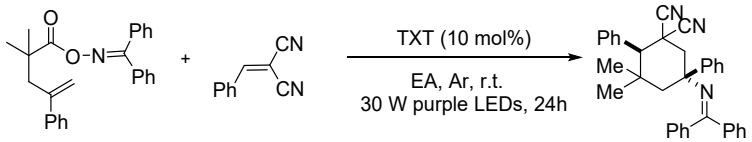
1a 2a 3

Entry	PC	Solvent	1a (equiv.)	2a (equiv.)	Yield (%)
1	TXT	EA	2.0	1.0	63

2	TXT	EA	3.0	1.0	70
3	TXT	EA	1.0	1.5	74
4	TXT	EA	1.0	2.0	79
5	TXT	EA	1.0	3.0	42

[a]Reaction conditions: **1a**, **2a**, TXT (2 mg, 10mol%), Solvent (1.0 mL) under Ar at r.t. for 24 h, 405 nm LEDs, EA (2 mL) isolated yield.

Table S4. Optimization of reaction conditions IV[a]

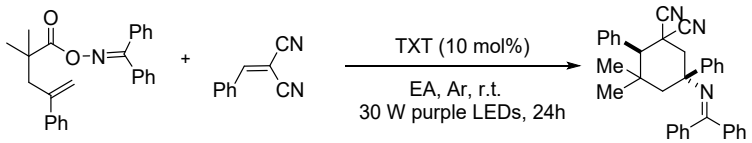


1a **2a** **3**

Entry	PC	Solvent	LEDs	Yield (%)
1	TXT	EA (0.5 mL)	405 nm	Trace
2	TXT	EA (1.5 mL)	405 nm	50
3	TXT	EA (2.0 mL)	405 nm	71

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), TXT (2 mg, 10 mol%), EA (2 mL) under Ar at r.t. for 24 h, 405 nm LEDs, isolated yield.

Table S5. Optimization of reaction conditions V[a]

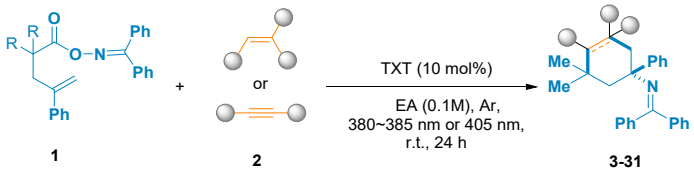


1a **2a** **3**

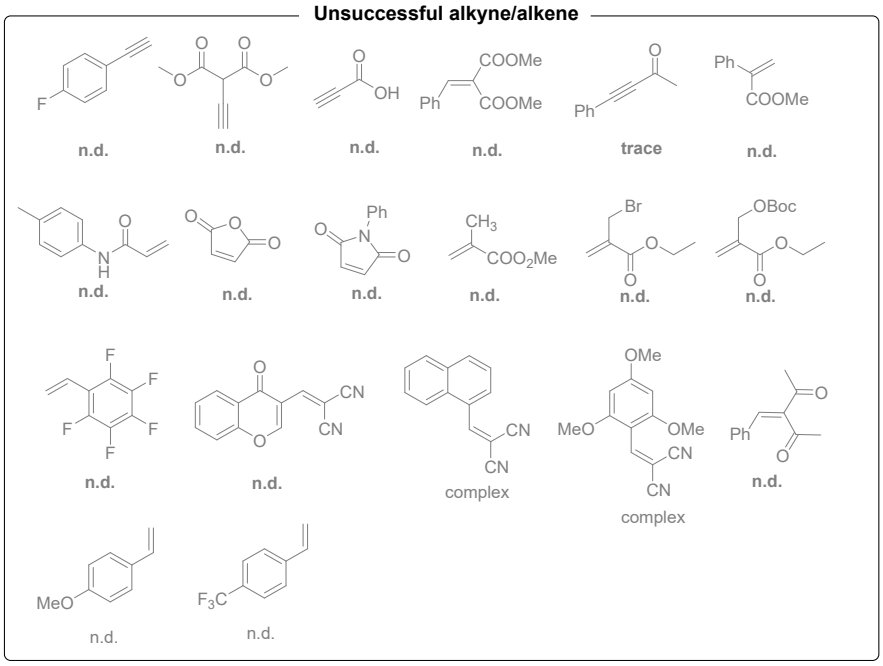
Entry	PC (10mol%)	Solvent (0.1M)	LEDs	Yield (%)
1	TXT	EA	365 nm	70
2	TXT	EA	395 nm	75
3	TXT	EA	380~385 nm	60

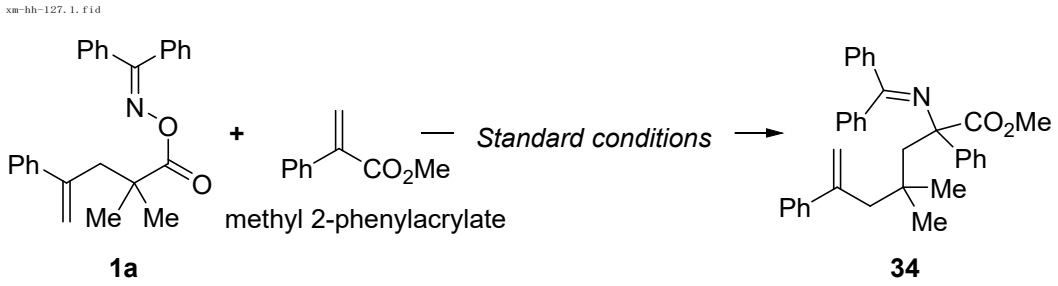
[a]Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.) **2a** (0.1 mmol, 1.0 equiv.), TXT (2 mg, 10mol%), EA (2 mL) under Ar at r.t. for 24 h, 365 nm or 395 nm LEDs, isolated yield.

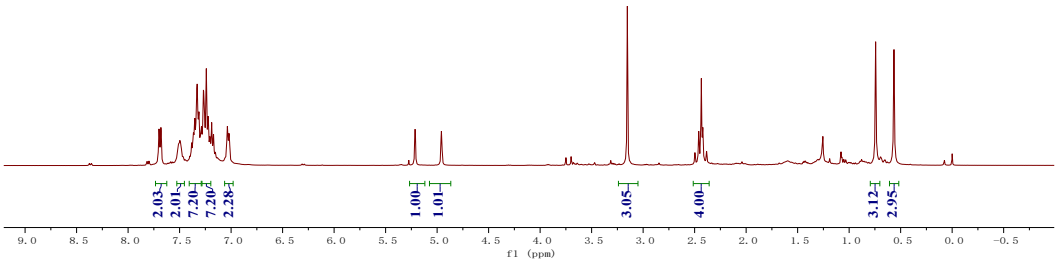
3.3 General procedure for the preparation of compounds 3-31



To an oven-dried 20 mL quartz flask equipped with a magnetic stirring bar was added bifunctional reagent **1** (0.2 mmol, 1.0 equiv.), alkene **2** (0.4 mmol, 2.0 equiv.), EA (2.0 mL), and TXT (10 mol%). The reaction tube was evacuated and backfilled with argon three times before light irradiation. The reaction mixture was stirred at ambient temperature (*note: the reaction temperature ranges from 25 to 37°C*) under irradiation of 30 W purple LEDs (distance app. 3 cm) for specific time. After completion, the solvent was removed under reduced pressure, and the resulting residue was then purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (9:1 to 1:1) as the eluent to afford the desired products **3-31.**







^{1}H NMR of product **34**

※ Notes:

For the reaction between alkenes and the bifunctional reagents, benzophenone was consistently observed as a main by-product. n.d. means the desired product was not detected. Complex means only rendered fairly complex reaction, and the corresponding desired products was unable to be isolated.

3.2 Scale-up reaction

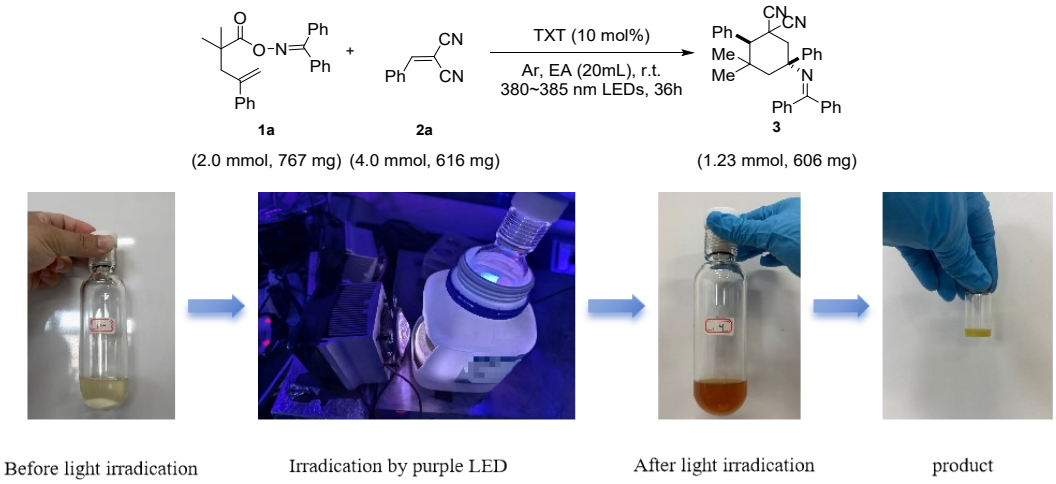
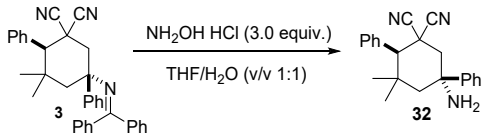


Figure S2. Process of scale-up reaction for the synthesis of compound **3**

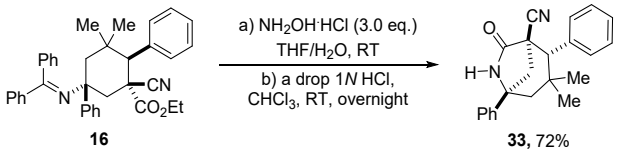
(Photographed by Mei Xiang)

To an oven-dried 120 mL schlenk flask equipped with a magnetic stirring bar was charged with bifunctional reagent **1a** (2.0 mmol, 1.0 equiv.), alkenes **2a** (4.0 mmol, 2.0 equiv.), EA (20 mL, 0.1 M) and TXT (10 mol%). The flask was evacuated and backfilled with Ar three times before light irradiation. After that, the tube was stirred at ambient temperature (note: the reaction temperature ranges from 25 to 40°C) under irradiation of 380~385 nm LEDs for 36 h. The solvent was removed under reduced pressure, and then the resulting residue was purified by flash chromatography on silica gel with a mixture of ethyl acetate and petroleum ether (PE/EA=99:1) as the eluent to afford the desired product **3** of 606 mg in 62% yield.

3.3 Procedure for further transformations of product 3, 16



Charge an oven-dried 25 mL round bottomed flask equipped with a stir bar with vicinal diamines **3** (0.2 mmol, 1.0 equiv., 98.6 mg). Take up 6 mL of 50 percent aqueous tetrahydrofuran by syringe. Add the mixture to the reaction flask under air. Add $NH_2OH{\cdot}HCl$ (0.6 mmol, 3.0 equiv., 41.7 mg) to the solution. Stir the reaction mixture for 12 hours at room temperature. After the reaction was completed (monitored by TLC), evaporate the THF under reduced pressure to leave an aqueous solution. Treat the remaining residue with 1N aqueous HCl until pH = 1 is reached. Extract the aqueous phase with ether, then adjust the water phase to pH = 10 with 1N aqueous NaOH. Extract the aqueous phase with ethyl acetate (3 ✂ 5 mL). Concentrate the combined organic layers in vacuo afforded the product (27.0 mg, 41% yield). This product was sufficiently pure as determined by NMR without further purification.



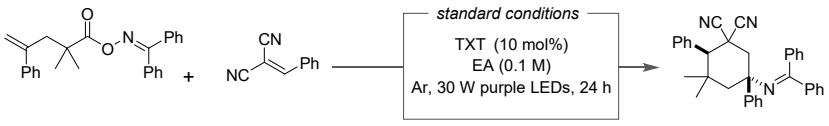
Charge an oven-dried 25 mL round bottomed flask equipped with a stir bar with vicinal diamines **16** (0.2 mmol, 1.0 equiv., 98.6 mg). Take up 6 mL of 50 percent aqueous tetrahydrofuran by syringe. Add the mixture to the reaction flask under air. Add $NH_2OH{\cdot}HCl$ (0.6 mmol, 3.0 equiv., 41.7 mg) to the solution. Stir the reaction

mixture for 24 hours at room temperature. After the reaction was completed (monitored by TLC), evaporate the THF under reduced pressure to leave an aqueous solution. Treat the remaining residue with 1N aqueous HCl until pH = 1 is reached. Extract the aqueous phase with ether, then adjust the water phase to pH = 10 with 1N aqueous NaOH. Extract the aqueous phase with ethyl acetate (3 ✕ 5 mL). Concentrate the combined organic layers in vacuo afforded white solid. Then chloroform (1 mL) and one drop of 1 M aqueous HCl were added, and the mixture was stirred at ambient temperature overnight; reaction progress was monitored periodically by TLC. Extract the aqueous phase with ethyl acetate (3 ✕ 5 mL), Concentrate the combined organic layers in vacuo, and then the resulting residue was purified by flash chromatography on silica gel with a mixture of ethyl acetate and petroleum ether (PE/EA=79:21) as the eluent to afford the desired product **33** of 47.3 mg in 72% yield.

4 Mechanistic studies

4.1 Trapping experiment

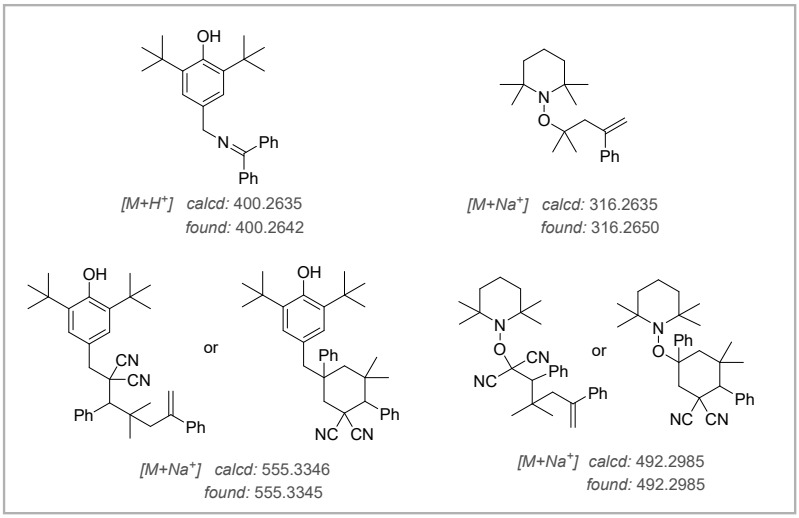
Radical trapping experiments between **1a** and **2a** were conducted under standard conditions with trapping agents (BHT or TEMPO) to catch the possible radicals. Interestingly, the yield of product **3** was effectively suppressed when BHT or TEMPO was employed as the radical scavenger. ESI-MS analysis of the crude reaction mixture was performed, and the corresponding radical captured products were supported by HRMS (Figure S3). HRMS (EI): $C_{21}H_{34}NO^+$, $[M+H]^+$ calcd: 316.2635, found: 316.2650 (TEMPO-adduct); $C_{31}H_{39}N_3NaO^+$, $[M+Na]^+$ calcd: 492.2985 found: 492.2985 (TEMPO-adduct); $C_{28}H_{34}NO^+$, $[M+H]^+$ calcd: 400.2635, found: 400.2642 (BHT-adduct); $C_{37}H_{44}N_2NaO^+$, $[M+Na]^+$ calcd: 555.3346, found: 555.3345 (BHT-adduct).



1a 1.0 equiv. **2a** 2.0 equiv. **3**

deviation from standard conditions	*yield*
adding TEMPO (3.0 equiv)	*trace*
adding BHT (3.0 equiv)	trace

detected by ESI-HRMS

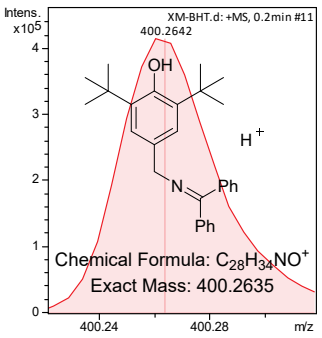


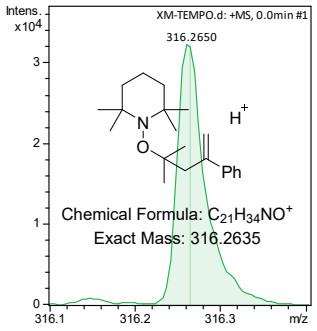
[M+H⁺] calcd: 400.2635 *found:* 400.2642

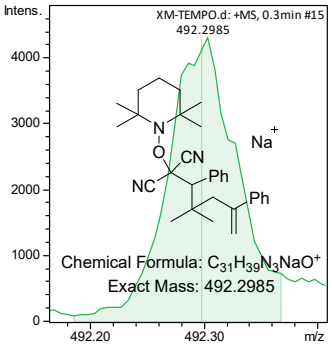
[M+Na⁺] calcd: 316.2635 *found:* 316.2650

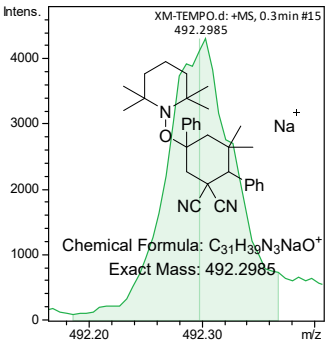
[M+Na⁺] calcd: 555.3346 *found:* 555.3345

[M+Na⁺] calcd: 492.2985 *found:* 492.2985









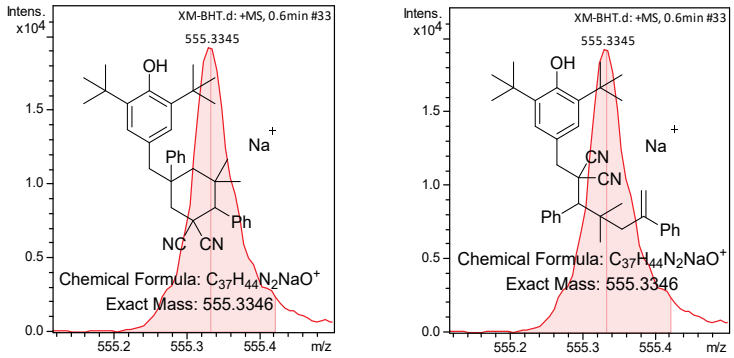


Figure S3. Crude ESI-MS analysis of the radical trapping experiments

4.2 Time profile of the transformation with the light on/off over time

General procedure was set up with **1a** (0.5 mmol, 1.0 equiv.) in a 1.0 mmol scale according to General procedure 3.2, and **2a** (1.0 mmol) was added as an internal standard to determine the NMR yield. The reaction was placed in light or dark in every alternative 2 h. After being irradiated with 30 W purple LEDs for 2 h, an aliquot (0.9 mL) from the reaction mixture was transferred into an oven-dried 25 mL round bottom flask. The solvent was removed under reduced pressure and the resulting residue was dissolved by 0.5 mL $CDCl_3$, and the yield of the product **3** was determined by ^1H NMR. Then, the reaction mixture was stirred with light-off for 2 h. All of the following yields were analyzed at the identical way after a 2 h light-on or light-off.

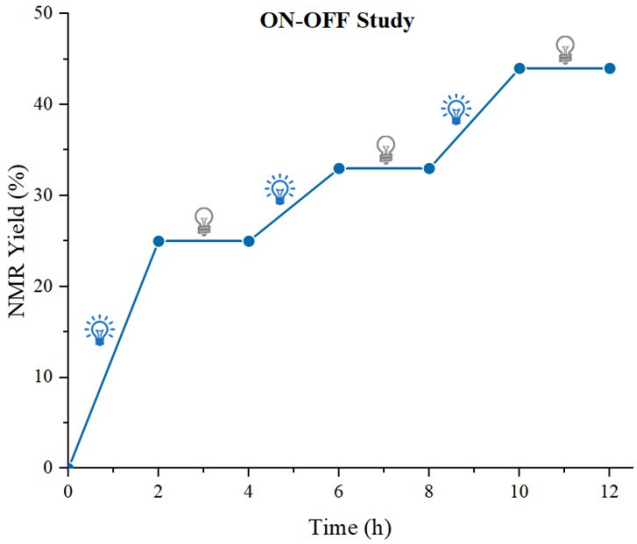


Figure S4. Time profile with the light On/Off over time

4.3 Emission quenching experiments (Stern-Volmer Studies) (Figure S5)

All fluorescence measurements were recorded using a Hitachi FL-7000 Fluorometer. Quenching studies were conducted in EtOAc. All [Ir(dF(CF_3)ppy)$_2$dtbpy] PF_6 solutions (concentration of 1×10^{-4} M) were excited at 368 nm and the emission intensity was collected at 483 nm. Five measurements were made at different concentrations using the corresponding quenching agent. (Note: Ir-F was used in place of TXT in this analysis, due to similarity in their region of emission/absorption, and the emission spectra of TXT having secondary emission peaks.)

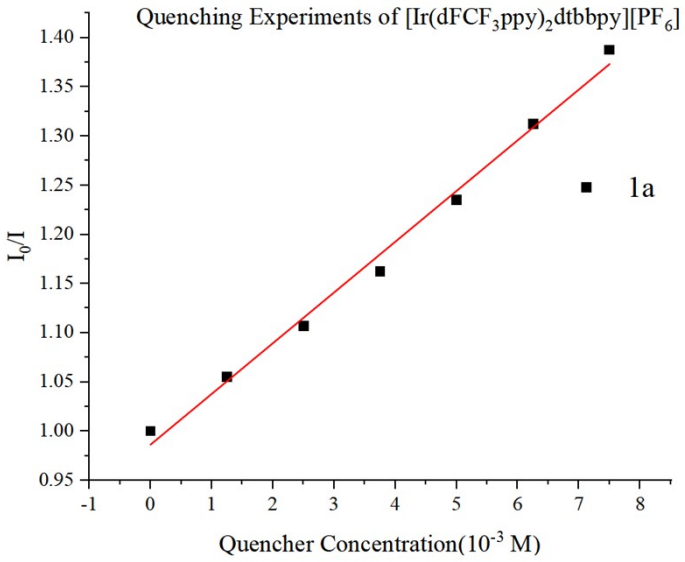
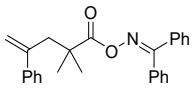


Figure S5. Stern-Volmer fluorescence quenching studies

5. Characterization Data of Compounds 1a, 1b, 1c, 1d, and 3-33



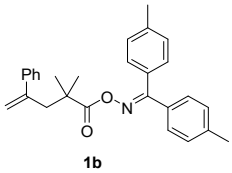
1a

1a: white solid;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 (d, J = 7.9 Hz, 2H), 7.46 – 7.42 (m, 4H), 7.34 (t, J = 7.6 Hz, 3H), 7.26 – 7.21 (m, 6H), 5.22 (s, 1H), 4.98 (s, 1H), 2.66 (s, 2H), 0.98 (s, 6H);

^{13}C NMR (100 MHz, Chloroform-d) δ 174.1, 165.0, 145.4, 142.4, 134.6, 132.9, 130.9, 129.4, 129.0, 128.6, 128.4, 128.2, 128.1, 127.3, 126.5, 117.1, 44.8, 42.8, 25.1;

HRMS (ESI): $C_{26}H_{25}KNO_2^+$, $[M+K]^+$, Calcd 422.1517, Found 422.1518.



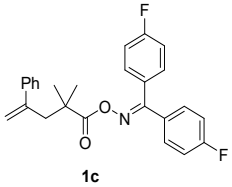
1b

1b: white solid;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.46 (d, J = 8.2 Hz, 2H), 7.26 – 7.21 (m, 7H), 7.18 – 7.14 (m, 4H), 5.22 (d, J = 1.6 Hz, 1H), 4.99 (d, J = 1.5 Hz, 1H), 2.68 (s, 2H), 2.42 (s, 3H), 2.36 (s, 3H), 1.00 (s, 6H);

^{13}C NMR (100 MHz, Chloroform-d) δ 174.3, 165.1, 145.4, 142.4, 141.1, 139.4, 132.1, 130.0, 129.1, 129.0, 128.8, 128.7, 128.2, 127.2, 126.5, 117.1, 44.8, 42.8, 25.2, 21.5, 21.5;

HRMS (ESI): $C_{28}H_{30}NO_2^+$, $[M+H]^+$, Calcd 412.2271, Found 412.2279.



1c

1c: white solid;

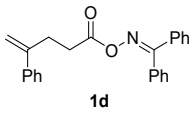
^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.52 (m, 2H), 7.29 – 7.21 (m, 7H), 7.14 (t, J = 8.5 Hz, 2H), 7.05 (t, J = 8.5 Hz, 2H), 5.24 (s, 1H), 5.00 (s, 1H), 2.69 (s, 2H), 1.01

(s, 6H);

^{19}F NMR (376 MHz, Chloroform-d) δ -108.85, -110.06;

^{13}C NMR (100 MHz, Chloroform-d) δ 174.0, 164.5 (d, $^{1}J_{C\text{-}F}$ = 252.2 Hz), 163.2 (d, $^{1}J_{C\text{-}F}$ = 250.4 Hz), 162.8, 145.3, 142.2, 131.1 (d, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 130.9 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 130.7 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 128.4 (d, $^{4}J_{C\text{-}F}$ = 3.7 Hz), 128.2, 127.4, 126.5, 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 115.4 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 45.0, 42.8, 25.2;

HRMS (ESI): $C_{26}H_{23}F_2KNO_2^+$, $[M+K]^+$, Calcd 458.1328, Found 458.1339.



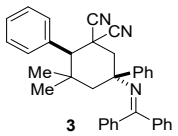
1d

1d, white solid;

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 2H), 7.47 – 7.39 (m, 4H), 7.38 – 7.25 (m, 9H), 5.29 (d, *J* = 0.9 Hz, 1H), 5.04 (d, *J* = 1.2 Hz, 1H), 2.83 – 2.76 (m, 2H), 2.53 – 2.46 (m, 2H);

^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.5, 165.0, 146.4, 140.3, 134.7, 132.6, 130.9, 129.6, 129.1, 128.8, 128.4, 128.4, 128.2, 127.6, 126.1, 113.0, 32.0, 30.2;

HRMS (ESI): $C_{24}H_{21}NNaO_2^+$, $[M+Na]^+$, Calcd 378.1465, Found 378.1473.



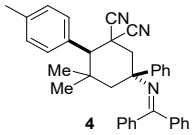
3

3 yellow oil, 77.9 mg, 79% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.29 (m, 6H), 7.17 – 7.08 (m, 4H), 7.07 – 7.01 (m, 4H), 6.49 (d, *J* = 7.3 Hz, 2H), 3.62 (s, 1H), 3.31 (d, *J* = 14.5 Hz, 1H), 2.89 (d, *J* = 14.5 Hz, 1H), 2.50 – 2.39 (m, 2H), 1.30 (s, 3H), 0.99 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 160.0, 146.6, 140.7, 137.9, 136.8, 134.7, 130.8, 130.4, 129.7, 128.8, 128.6, 128.3, 128.1, 127.5, 127.3, 127.3, 127.1, 126.1, 117.8, 117.1, 61.9, 55.9, 47.3, 46.0, 35.6, 34.9, 32.8.

HRMS (ESI): $C_{35}H_{32}N_3^+$, $[M+H]^+$, Calcd 494.2591, Found 494.2597;

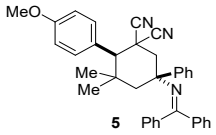


4 yellow oil, 50 mg, 49% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, J = 7.6 Hz, 2H), 7.53 – 7.43 (m, 1H), 7.40 – 7.37 (m, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.19 – 7.13 (m, 4H), 7.11 – 7.08 (m, 1H), 7.07 – 6.99 (m, 4H), 6.49 (d, J = 7.5 Hz, 2H), 3.56 (s, 1H), 3.35 – 3.26 (m, 1H), 2.95 – 2.84 (m, 1H), 2.54 – 2.41 (m, 2H), 2.33 (s, 3H), 1.30 (s, 3H), 0.97 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.3, 130.1, 129.5, 128.3, 128.1, 127.4, 127.4, 127.1, 126.2, 117.9, 117.1, 55.7, 35.8, 34.9, 32.8, 21.1;

HRMS (ESI): $C_{36}H_{34}N_3^+$, $[M+H]^+$, Calcd 508.2747, Found 508.2754.

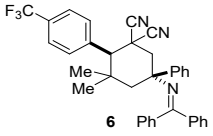


5 yellow oil, 66.8 mg, 64% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 2H), 7.38 – 7.35 (m, 1H), 7.36 – 7.28 (m, 4H), 7.17 – 7.08 (m, 4H), 7.06 – 7.01 (m, 4H), 6.89 – 6.85 (m, 2H), 6.52 – 6.46 (m, 2H), 3.79 (s, 3H), 3.58 (s, 1H), 3.28 (dd, J = 14.5, 1.3 Hz, 1H), 2.87 (d, J = 14.5 Hz, 1H), 2.46 – 2.39 (m, 2H), 1.28 (s, 3H), 0.98 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.5, 159.6, 140.7, 137.9, 130.4, 128.6, 128.3, 128.1, 127.4, 127.3, 127.2, 127.0, 126.1, 117.9, 117.2, 114.1, 61.9, 55.2, 55.2, 35.9, 35.0, 32.8, 29.7;

HRMS (ESI): $C_{36}H_{33}KN_3O^+$, $[M+K]^+$, Calcd 562.2255, Found 562.2258.



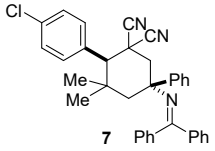
6 yellow oil, 57.3 mg, 51% yield (EA/PE = 1%);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 4H), 7.60 – 7.55 (m, 2H), 7.41 – 7.36 (m, 1H), 7.34 – 7.30 (m, 2H), 7.18 – 7.13 (m, 2H), 7.11 – 7.08 (m, 2H), 7.06 – 7.00 (m, 4H), 6.52 – 6.47 (m, 2H), 3.78 (s, 1H), 3.35 (d, *J* = 14.6 Hz, 1H), 2.93 (d, *J* = 14.6 Hz, 1H), 2.48 (s, 2H), 1.25 (s, 3H), 1.02 (s, 3H);

^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.1, 168.8, 158.1, 146.1, 140.6, 137.8, 132.5, 130.6, 130.1, 130.0, 128.6, 128.4, 128.2, 127.5, 127.4, 127.2, 127.2, 126.2, 125.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.0, 122.9, 117.3, 117.0, 86.1, 62.0, 55.5, 47.9, 46.5, 35.2, 35.0, 32.8;

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.77;

HRMS (ESI): $C_{36}H_{31}F_3N_3^+$, $[M+H]^+$, Calcd 562.2465, Found 562.2467.



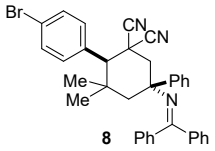
7

7 yellow oil, 82.3 mg, 78% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.58 (m, 2H), 7.40 – 7.30 (m, 7H), 7.19 – 7.12 (m, 2H), 7.12 – 7.07 (m, 2H), 7.07 – 6.99 (m, 4H), 6.49 (d, *J* = 7.1 Hz, 2H), 3.65 (s, 1H), 3.32 (d, *J* = 14.5 Hz, 1H), 2.89 (d, *J* = 14.5 Hz, 1H), 2.45 (s, 2H), 1.25 (s, 3H), 1.00 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.7, 140.5, 137.8, 135.1, 134. 7, 130.5, 129.0, 128.6, 128.3, 128.2, 127.5, 127.3, 127.2, 127.1, 126.1, 117.5, 117.0, 61.9, 55.2, 47.7, 46.2, 35.4, 34.9, 32.8;

HRMS (ESI): $C_{35}H_{31}ClN_3^+$, $[M+H]^+$, Calcd 528.2201, Found 528.2214.



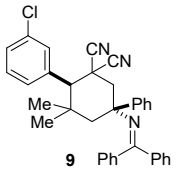
8

8 white solid, 97.1 mg, 85% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.73 (m, 1H), 7.71 – 7.67 (m, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.35 – 7.30 (m, 3H), 7.15 – 7.08 (m, 3H), 7.06 – 6.99 (m, 4H), 6.49 (d, *J* = 7.5 Hz, 2H), 3.64 (s, 1H), 3.31 (d, *J* = 14.6 Hz, 1H), 2.89 (d, *J* = 14.5 Hz, 1H), 2.44 (s, 2H), 1.24 (s, 3H), 1.00 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.7, 158.4, 146.2, 140.6, 137.8, 135.6, 133.1, 132.0, 131.8, 130.5, 129.9, 129.7, 128.5, 128.3, 128.1, 127.5, 127.3, 127.3, 127.1, 126.1, 122.9, 117.4, 117.0, 113.5, 112.4, 83.6, 61.9, 55.3, 47.8, 46.3, 35.4, 34.9, 32.8;

HRMS (ESI): $C_{35}H_{31}BrN_3^+$, $[M+H]^+$, Calcd 572.1696, Found 572.1697.



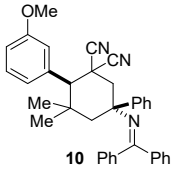
9

9 yellow solid, 52.5 mg, 50% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.83 – 7.80 (m, 1H), 7.70 (s, 1H), 7.63 – 7.56 (m, 3H), 7.50 – 7.46 (m, 1H), 7.41 – 7.36 (m, 2H), 7.34 – 7.31 (m, 3H), 7.15 – 7.09 (m, 3H), 7.04 – 7.00 (m, 3H), 6.49 (d, *J* = 7.5 Hz, 2H), 3.63 (s, 1H), 3.32 (d, *J* = 14.6 Hz, 1H), 2.89 (d, *J* = 14.3 Hz, 1H), 2.45 (s, 2H), 1.27 (s, 3H), 1.01 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 168.7, 158.3, 146.3, 140.6, 138.7, 137.8, 135.8, 134.6, 134.4, 132.4, 130.9, 130.5, 130.5, 130.0, 128.9, 128.6, 128.4, 128.2, 127.5, 127.3, 127.3, 127.1, 126.1, 117.4, 116.9, 113.2, 112.1, 84.7, 61.9, 55.5, 47.6, 46.3, 35.3, 34.9, 32.8;

HRMS (ESI): $C_{35}H_{31}ClN_3^+$, $[M+H]^+$, Calcd 528.2201, Found 528.2201.



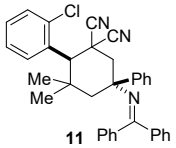
10

10 yellow oil, 45.1 mg, 43% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.63 – 7.59 (m, 2H), 7.46 – 7.40 (m, 2H), 7.35 – 7.31 (m, 2H), 7.19 – 7.11 (m, 3H), 7.11 – 7.09 (m, 1H), 7.07 – 7.02 (m, 4H), 6.99 – 6.94 (m, 2H), 6.90 – 6.87 (m, 1H), 6.49 (d, *J* = 7.5 Hz, 2H), 3.78 (s, 3H), 3.57 (s, 1H), 3.31 (d, *J* = 14.6 Hz, 1H), 2.91 (d, *J* = 14.5 Hz, 1H), 2.51 – 2.41 (m, 2H), 1.30 (s, 3H), 1.00 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.5, 159.6, 146.6, 140.7, 138.2, 137.9, 130.4, 129.7, 128.6, 128.3, 128.1, 127.4, 127.3, 127.2, 127.0, 126.1, 117.8, 117.1, 113.6, 82.2, 61.9, 55.9, 55.2, 47.3, 46.0, 35.5, 34.9, 32.8;

HRMS (ESI): $C_{36}H_{33}KN_3O^+$, $[M+K]^+$, Calcd 562.2255, Found 562.2258.



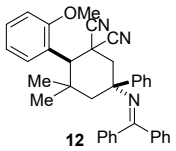
11

11 yellow oil, 45.2 mg, 43% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 1H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.31 – 7.27 (m, 1H), 7.21 – 7.19 (m, 2H), 7.11 – 7.05 (m, 2H), 7.04 – 7.00 (m, 2H), 6.99 – 6.93 (m, 4H), 6.43 (d, *J* = 7.5 Hz, 2H), 4.67 (s, 1H), 3.29 (d, *J* = 14.6 Hz, 1H), 2.85 (d, *J* = 14.4 Hz, 1H), 2.41 (s, 2H), 1.19 (s, 3H), 0.99 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.8, 168.5, 146.0, 140.3, 137.7, 136.3, 135.9, 134.2, 132.5, 130.3, 130.2, 130.2, 129.3, 129.1, 128.7, 128.5, 128.1, 127.7, 127.2, 127.0, 126.8, 126.7, 125.9, 116.9, 116.9, 113.7, 81.5, 61.8, 47.8, 46.6, 35.3, 34.9, 31.9, 27.7;

HRMS (ESI): $C_{35}H_{31}ClN_3^+$, $[M+H]^+$, Calcd 528.2201, Found 528.2208.



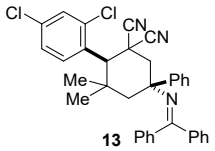
12

12 yellow oil, 45 mg, 43% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.64 (m, 2H), 7.59 – 7.55 (m, 1H), 7.37 – 7.30 (m, 4H), 7.17 – 7.09 (m, 4H), 7.06 – 7.01 (m, 4H), 6.97 – 6.92 (m, 2H), 6.51 – 6.47 (m, 2H), 4.69 (s, 1H), 3.82 (s, 3H), 3.32 (d, J = 14.5 Hz, 1H), 2.87 (d, J = 14.4 Hz, 1H), 2.45 (s, 2H), 1.24 (s, 3H), 1.03 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-d) δ 168.3, 158.1, 140.7, 137.9, 130.3, 129.3, 128.7, 128.2, 128.0, 127.4, 127.3, 127.2, 126.9, 126.2, 125.5, 120.5, 117.9, 117.6, 111.3, 62.0, 55.8, 43.0, 35.4, 35.0, 32.3, 29.7;

HRMS (ESI): $C_{36}H_{33}KN_3O^+$, $[M+K]^+$, Calcd 562.2255, Found 562.2256.



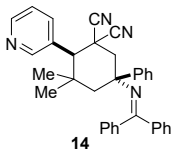
13

13 white solid, 42.8 mg, 38% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.52 – 7.50 (m, 1H), 7.45 (dd, *J* = 14.1, 7.4 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.32 – 7.29 (m, 2H), 7.16 – 7.13 (m, 1H), 7.12 – 7.10 (m, 1H), 7.09 – 7.04 (m, 3H), 7.03 – 6.99 (m, 2H), 6.51 (d, *J* = 7.5 Hz, 2H), 4.75 (s, 1H), 3.37 (d, *J* = 14.5 Hz, 1H), 2.92 (d, *J* = 14.4 Hz, 1H), 2.53 – 2.43 (m, 2H), 1.21 (s, 3H), 1.08 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.0, 168.9, 146.0, 140.4, 137.8, 137.3, 136.1, 134.9, 132.9, 132.7, 130.6, 130.4, 130.3, 130.2, 128.9, 128.7, 128.3, 128.0, 127.5, 127.4, 127.3, 127.3, 127.1, 126.1, 117.1, 116.8, 113.9, 62.0, 47.6, 47.1, 35.6, 35.0, 32.1, 27.6;

HRMS (ESI): $C_{35}H_{30}Cl_2N_3^+$, $[M+H]^+$, Calcd 562.1811, Found 562.1810.



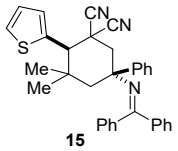
14

14 yellow oil, 49.9 mg, 51% yield (EA/PE = 15%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (s, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.39 – 7.36 (m, 1H), 7.35 – 7.30 (m, 3H), 7.18 – 7.09 (m, 4H), 7.06 – 7.00 (m, 4H), 6.50 (d, *J* = 7.5 Hz, 2H), 3.75 (s, 1H), 3.35 (d, *J* = 14.4 Hz, 1H), 2.88 (d, *J* = 14.6 Hz, 1H), 2.52 – 2.41 (m, 2H), 1.26 (s, 3H), 1.03 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.9, 145.0, 146.1, 140.5, 137.7, 130.6, 128.5, 128.4, 128.2, 127.5, 127.3, 127.2, 127.2, 126.1, 117.2, 116.9, 61.9, 53.3, 47.8, 46.1, 35.3, 34.9, 32.7;

HRMS (ESI): $C_{34}H_{31}N_4^+$, $[M+H]^+$, Calcd 495.2543, Found 495.2543.



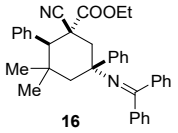
15

15 yellow oil, 19.8 mg, 20% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 2H), 7.50 – 7.42 (m, 3H), 7.37 – 7.30 (m, 3H), 7.16 – 7.12 (m, 3H), 7.09 – 7.04 (m, 3H), 7.03 – 7.01 (m, 2H), 6.45 (d, *J* = 7.5 Hz, 2H), 3.95 (s, 1H), 3.30 – 3.23 (m, 1H), 2.72 (d, *J* = 14.5 Hz, 1H), 2.44 – 2.32 (m, 2H), 1.53 (s, 3H), 0.92 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.0, 140.7, 138.1, 137.9, 136.1, 132.7, 130.4, 128.9, 128.8, 128.4, 128.0, 127.5, 127.4, 127.3, 127.1, 125.8, 125.7, 117.9, 116.3, 113.9, 61.5, 51.9, 43.7, 36.1, 35.0, 31.6, 29.7;

HRMS (ESI): $C_{33}H_{30}N_3S^+$, $[M+H]^+$, Calcd 500.2155, Found 500.2160.



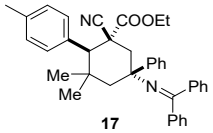
16

16 yellow oil, 43.2 mg, 40% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.53 – 7.43 (m, 2H), 7.38 – 7.26 (m, 6H), 7.18 – 7.14 (m, 1H), 7.11 – 7.02 (m, 7H), 6.52 (d, *J* = 7.4 Hz, 2H), 3.97 – 3.90 (m, 2H), 3.63 (s, 1H), 3.19 (d, *J* = 14.5 Hz, 1H), 2.94 (d, *J* = 14.4 Hz, 1H), 2.73 (d, *J* = 14.1 Hz, 1H), 2.41 (d, *J* = 14.3 Hz, 1H), 1.08 (s, 3H), 1.01 (s, 3H), 0.90 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.4, 166.7, 138.3, 136.73, 130.1, 128.3, 128.0, 127.9, 127.8, 127.5, 127.4, 127.4, 127.1, 127.0, 126.6, 121.4, 62.7, 55.4, 50.2, 48.1, 47.3, 34.9, 32.9, 29.7, 25.4, 13.5;

HRMS (ESI): $C_{37}H_{37}N_2O_2^+$, $[M+H]^+$, Calcd 541.2850, Found 541.2849.



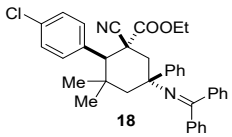
17

17 yellow oil, 45.9 mg, 41% yield (EA/PE = 3%);

^{1}H NMR (400 MHz, Chloroform-d) δ 7.59 – 7.55 (m, 2H), 7.36 – 7.28 (m, 4H), 7.17 – 7.02 (m, 11H), 6.57 – 6.43 (m, 2H), 3.99 – 3.91 (m, 2H), 3.57 (s, 1H), 3.16 (d, J = 14.5 Hz, 1H), 2.94 (d, J = 14.5 Hz, 1H), 2.72 (d, J = 14.3 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.30 (s, 3H), 1.06 (s, 3H), 0.99 (s, 3H), 0.93 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-d) δ 169.4, 166.6, 137.1, 133.6, 130.1, 128.5, 128.3, 128.0, 127.7, 127.4, 127.1, 127.0, 126.5, 121.4, 62.7, 55.0, 50.3, 48.2, 47.1, 34.9, 33.0, 25.4, 21.0, 13.6;

HRMS (ESI): $C_{38}H_{39}N_2O_2^+$, $[M+H]^+$, Calcd 555.3006, Found 555.3013.



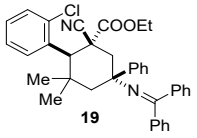
18

18 yellow oil, 58.1 mg, 51% yield (EA/PE = 3%);

^{1}H NMR (400 MHz, Chloroform-d) δ 7.59 – 7.55 (m, 2H), 7.39 – 7.24 (m, 7H), 7.18 – 7.14 (m, 1H), 7.09 – 7.02 (m, 7H), 6.55 – 6.49 (m, 2H), 4.01 – 3.95 (m, 2H), 3.64 (s, 1H), 3.15 (d, J = 14.5 Hz, 1H), 2.93 (d, J = 14.5 Hz, 1H), 2.71 (d, J = 14.3 Hz, 1H), 2.45 – 2.38 (m, 1H), 1.05 (s, 3H), 1.01 – 0.96 (m, 6H);

^{13}C NMR (100 MHz, Chloroform-d) δ 169.2, 166.8, 135.3, 133.5, 130.1, 128.2, 128.1, 127.8, 127.4, 127.3, 126.9, 126.6, 121.2, 62.9, 54.5, 50.1, 47.9, 34.8, 32.9, 25.3, 13.6;

HRMS (ESI): $C_{37}H_{36}ClN_2O_2^+$, $[M+H]^+$, Calcd 575.2460, Found 575.2466.



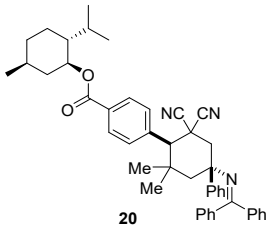
19

19 yellow oil, 49.7 mg, 43% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.27 (m, 2H), 7.21 – 7.12 (m, 3H), 7.08 – 7.00 (m, 7H), 6.54 (d, J = 7.4 Hz, 2H), 4.70 (s, 1H), 4.04 – 3.91 (m, 2H), 3.37 (d, J = 14.4 Hz, 1H), 2.91 (d, J = 14.3 Hz, 1H), 2.72 (d, J = 14.2 Hz, 1H), 2.45 (d, J = 14.1 Hz, 1H), 1.14 (s, 3H), 1.08 (s, 3H), 0.97 (t, J = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-d) δ 168.9, 166.8, 146.3, 140.9, 138.3, 136.4, 135.1, 130.6, 130.1, 129.9, 128.54, 128.47, 127.89, 127.85, 127.3, 127.1, 126.7, 126.5, 126.3, 121.6, 62.9, 62.8, 49.1, 48.6, 48.3, 47.4, 36.0, 32.1, 26.0, 13.5;

HRMS (ESI): $C_{37}H_{36}ClN_2O_2^+$, $[M+H]^+$, Calcd 575.2460, Found 575.2466.



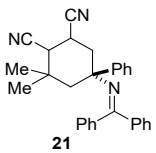
20

20 yellow oil, 63.6 mg, 47% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.65 – 7.58 (m, 2H), 7.55 – 7.47 (m, 2H), 7.42 – 7.36 (m, 1H), 7.35 – 7.29 (m, 2H), 7.18 – 7.09 (m, 4H), 7.07 – 7.00 (m, 4H), 6.49 (d, J = 7.4 Hz, 2H), 4.97 – 4.89 (m, 1H), 3.74 (d, J = 4.4 Hz, 1H), 3.40 – 3.30 (m, 1H), 2.91 (d, J = 14.4 Hz, 1H), 2.46 (s, 2H), 2.14 – 2.09 (m, 1H), 2.00 – 1.94 (m, 1H), 1.78 – 1.68 (m, 3H), 1.60 – 1.49 (m, 3H), 1.27 (d, J = 11.6 Hz, 4H), 1.01 (d, J = 2.6 Hz, 3H), 0.93 – 0.91 (m, 6H), 0.79 (d, J = 6.9 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 165.5, 158.7, 146.3, 141.5, 140.6, 137.8, 131.1, 130.5, 130.4, 129.9, 128.6, 128.4, 128.1, 127.5, 127.3, 127.3, 127.1, 126.1, 117.5, 117.0, 116.9, 85.2, 75.1, 61.9, 55.7, 55.7, 47.3, 47.2, 41.0, 35.2, 35.0, 34.3, 32.7, 31.5, 29.7, 26.4, 23.6, 23.5, 22.1, 22.0, 20.9, 20.8, 16.6, 16.4;

HRMS (ESI): $C_{46}H_{49}KN_3O_2^+$, $[M+K]^+$, Calcd 714.3456, Found 714.3477.



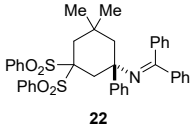
21

21 yellow oil, 15.8 mg, 19% yield (EA/PE = 3%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.54 (m, 2H), 7.54 – 7.41 (m, 1H), 7.37 – 7.33 (m, 1H), 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.16 – 7.02 (m, 5H), 6.94 (s, 2H), 6.44 (s, 1H), 3.38 – 3.24 (m, 1H), 2.70 (d, J = 4.3 Hz, 1H), 2.59 – 2.45 (m, 2H), 2.31 (d, J = 14.5 Hz, 1H), 1.68 – 1.55 (m, 1H), 1.40 (s, 3H), 0.67 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.0, 132.5, 130.3, 130.1, 128.5, 128.4, 128.3, 128.0, 127.5, 127.4, 126.9, 126.1, 119.2, 117.4, 61.2, 49.9, 41.7, 34.3, 29.7, 26.5;

HRMS (ESI): $C_{29}H_{28}N_3^+$, $[M+H]^+$, Calcd 418.2278, Found 418.2277.



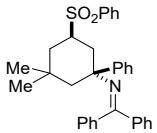
22

22 yellow solid, 75.2 mg, 58% yield (EA/PE = 8%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.12 (m, 2H), 7.83 – 7.75 (m, 3H), 7.65 – 7.59 (m, 3H), 7.50 – 7.43 (m, 3H), 7.29 – 7.25 (m, 1H), 7.21 – 7.17 (m, 3H), 7.11 – 7.02 (m, 4H), 7.00 – 6.93 (m, 4H), 6.44 – 6.31 (m, 2H), 3.70 (d, *J* = 16.5 Hz, 1H), 2.92 (d, *J* = 16.6 Hz, 1H), 2.63 (d, *J* = 2.6 Hz, 2H), 2.41 (d, *J* = 13.8 Hz, 1H), 2.15 – 2.07 (m, 1H), 1.23 (s, 3H), 1.06 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.5, 149.7, 141.0, 138.3, 137.8, 136.8, 134.5, 134.2, 132.5, 132.2, 131.8, 130.1, 129.7, 128.8, 128.4, 128.4, 128.0, 127.9, 127.4, 127.1, 126.8, 126.4, 126.3, 92.2, 63.7, 42.5, 41.8, 36.4, 33.2, 32.8, 30.5;

HRMS (ESI): $C_{39}H_{38}NO_4S_2^+$, $[M+H]^+$, Calcd 648.2237, Found 648.2257.



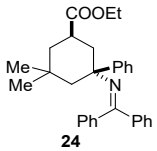
23

23 yellow oil, 62.1 mg, 62% yield (EA/PE = 4%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.75 (m, 3H), 7.75 – 7.69 (m, 1H), 7.64 – 7.58 (m, 2H), 7.46 – 7.42 (m, 2H), 7.34 – 7.19 (m, 4H), 7.17 – 6.88 (m, 6H), 6.75 (s, 2H), 3.37 (tt, *J* = 13.0, 3.0 Hz, 1H), 2.74 – 2.60 (m, 2H), 2.18 (d, *J* = 14.2 Hz, 1H), 1.84 – 1.78 (m, 1H), 1.61 (t, 1H), 1.42 (t, *J* = 12.7 Hz, 1H), 1.02 (s, 3H), 0.20 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.7, 144.3, 141.4, 138.4, 137.3, 133.7, 129.9, 129.2, 129.0, 128.0, 128.0, 127.9, 127.4, 127.2, 127.1, 126.9, 126.2, 63.0, 58.9, 55.3, 37.0, 33.9, 33.2, 31.9, 25.7;

HRMS (ESI): $C_{33}H_{33}KNO_2S^+$, $[M+K]^+$, Calcd 546.1864, Found 546.1868.



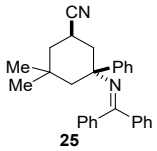
24

24 yellow oil, 20.8 mg, 24% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.75 (m, 2H), 7.62 – 7.57 (m, 1H), 7.55 – 7.44 (m, 4H), 7.32 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 7.18 – 7.12 (m, 1H), 7.05 – 6.99 (m, 5H), 4.18 – 4.09 (m, 2H), 2.81 – 2.55 (m, 3H), 2.24 (d, *J* = 13.9 Hz, 1H), 1.71 (t, *J* = 13.3 Hz, 1H), 1.61 – 1.52 (m, 1H), 1.40 (t, *J* = 12.7 Hz, 1H), 1.27 – 1.24 (m, 3H), 0.99 (s, 3H), 0.23 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.9, 166.3, 145.4, 141.8, 138.8, 137.6, 132.5, 130.1, 129.6, 128.3, 128.0, 127.9, 127.7, 127.5, 127.3, 127.2, 126.8, 125.9, 63.0, 60.3, 55.6, 41.4, 38.0, 35.9, 34.1, 31.6, 29.7, 25.7, 14.3;

HRMS (ESI): $C_{30}H_{34}NO_2^+$, $[M+H]^+$, Calcd 440.2584, Found 440.2598.



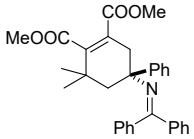
25

25 yellow oil, 18.6 mg, 24% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.49 (m, 2H), 7.34 – 7.30 (m, 1H), 7.29 – 7.21 (m, 3H), 7.19 – 7.14 (m, 1H), 7.08 – 7.00 (m, 4H), 6.97 – 6.90 (m, 2H), 6.44 (s, 2H), 2.96 – 2.87 (m, 1H), 2.64 – 2.49 (m, 2H), 2.31 – 2.21 (m, 1H), 2.06 – 1.93 (m, 1H), 1.66 – 1.59 (m, 2H), 1.07 (s, 3H), 0.32 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.4, 145.0, 141.3, 138.4, 132.5, 130.1, 123.0, 128.3, 128.2, 128.1, 128.0, 127.4, 127.4, 127.1, 126.7, 126.4, 122.9, 62.1, 54.0, 41.7, 37.1, 32.9, 31.5, 26.6, 23.4;

HRMS (ESI): $C_{28}H_{28}N_2Na^+$, $[M+Na]^+$, Calcd 415.2145, Found 415.2147.



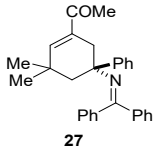
26

26 yellow oil, 26.1 mg, 27% yield (EA/PE = 5%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.30 – 7.25 (m, 3H), 7.17 – 7.14 (m, 1H), 7.10 – 6.99 (m, 7H), 6.53 (d, *J* = 7.5 Hz, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 2.79 (s, 2H), 2.51 (d, *J* = 13.5 Hz, 1H), 2.36 (d, *J* = 13.6 Hz, 1H), 1.30 (s, 3H), 0.75 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.2, 148.8, 147.0, 141.1, 138.6, 132.4, 130.1, 129.9, 128.3, 128.0, 127.9, 127.5, 127.2, 127.2, 126.6, 126.4, 126.2, 61.5, 52.8, 52.1, 51.8, 36.6, 35.9, 29.8, 28.6;

HRMS (ESI): $C_{31}H_{32}NO_4^+$, $[M+H]^+$, Calcd 482.2326, Found 482.2330.



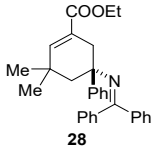
27

27 yellow oil, 25.6 mg, 32% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.35 – 7.24 (m, 4H), 7.17 – 7.11 (m, 1H), 7.08 – 6.95 (m, 5H), 6.93 – 6.84 (m, 2H), 6.55 – 6.48 (m, 2H), 2.82 (d, *J* = 17.2 Hz, 1H), 2.59 (d, *J* = 17.2 Hz, 1H), 2.46 (d, *J* = 13.5 Hz, 1H), 2.37 (d, *J* = 14.6 Hz, 1H), 2.32 (s, 3H), 1.23 (s, 3H), 0.59 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 149.6, 134.8, 132.5, 130.1, 128.3, 128.2, 127.9, 127.7, 127.5, 127.2, 127.0, 126.1, 51.8, 34.4, 33.4, 31.3, 29.7, 29.0, 25.7;

HRMS (ESI): $C_{29}H_{29}KNO^+$, $[M+K]^+$, Calcd 446.1881, Found 446.1883.



28

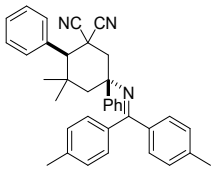
28 yellow oil, 13.1 mg, 15% yield (EA/PE = 2%);

^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 – 7.74 (m, 1H), 7.58 – 7.52 (m, 2H), 7.52 – 7.46 (m, 1H), 7.34 – 7.30 (m, 1H), 7.29 – 7.27 (m, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.09 –

7.00 (m, 5H), 6.98 – 6.93 (m, 2H), 6.68 (s, 1H), 6.51 (s, 1H), 4.26 – 4.13 (m, 2H), 2.80 (d, J = 17.3 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.40 (q, J = 13.6 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.18 (s, 3H), 0.55 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.0, 148.3, 147.3, 141.4, 138.7, 137.6, 132.5, 130.1, 129.7, 128.3, 128.2, 127.9, 127.7, 127.6, 127.2, 127.0, 127.0, 126.1, 125.6, 62.5, 60.5, 51.9, 34.6, 34.1, 31.1, 28.8, 14.3;

HRMS (ESI): $C_{30}H_{32}NO_2^+$, $[M+H]^+$, Calcd 438.2428, Found 438.2428.



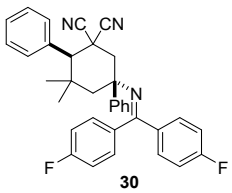
29

29 yellow solid, 51.6 mg, 50% yield (EA/PE = 1%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.50 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.32 (m, 3H), 7.14 – 7.08 (m, 5H), 7.07 – 7.02 (m, 2H), 6.86 – 6.80 (m, 2H), 6.35 (d, *J* = 7.6 Hz, 2H), 3.61 (s, 1H), 3.29 (d, *J* = 14.5 Hz, 1H), 2.86 (d, *J* = 14.6 Hz, 1H), 2.43 (s, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 1.29 (s, 3H), 0.98 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.7, 147.1, 140.6, 138.4, 136.9, 135.1, 128.8, 128.7, 128.6, 128.5, 128.2, 128.0, 127.3, 126.9, 126.1, 117.8, 117.2, 61.8, 55.9, 47.5, 45.9, 35.6, 34.9, 32.8, 21.3, 21.2;

HRMS (ESI): $C_{37}H_{36}N_3^+$, $[M+H]^+$, Calcd 522.2904, Found 522.2928.



30

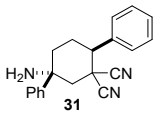
30 yellow solid, 55.7 mg, 53% yield (EA/PE = 4%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.40 – 7.33 (m, 5H), 7.20 – 7.12 (m, 3H), 7.07 – 6.97 (m, 4H), 6.75 (t, *J* = 8.5 Hz, 2H), 6.50 – 6.39 (m, 2H), 3.61 (s, 1H), 3.30 (d, *J* = 14.5 Hz, 1H), 2.88 – 2.81 (m, 1H), 2.49 – 2.33 (m, 2H), 1.32 (s, 3H), 0.98 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.13, -113.16;

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.5 (d, $^{1}J_{C\text{-}F}$= 251.6 Hz), 161.8 (d, $^{1}J_{C\text{-}F}$ = 248.4 Hz), 146.7, 136.7 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 133.5 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 130.7 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 129.1 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 128.8, 128.7, 128.5, 127.3, 126.0, 117.9, 116.9, 115.1 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 114.7 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 61.9, 55.9, 47.1, 45.7, 35.5, 34.9, 32.7;

HRMS (ESI): $C_{35}H_{29}F_2N_3Na^+$, $[M+Na]^+$, Calcd 552.2222, Found 552.2221.



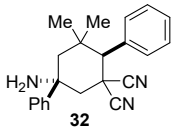
31

31 white solid, 36 mg, 39% yield (EA/PE = 5%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.39 (m, 3H), 7.38 – 7.27 (m, 8H), 7.21 – 7.12 (m, 4H), 7.11 – 7.03 (m, 3H), 6.46 (s, 2H), 3.69 – 3.56 (m, 1H), 3.25 – 3.08 (m, 2H), 2.75 – 2.62 (m, 1H), 2.48 – 2.36 (m, 1H), 2.05 – 1.90 (m, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.2, 141.7, 140.8, 138.0, 137.1, 130.3, 128.9, 128.8, 128.4, 128.4, 128.2, 128.0, 127.7, 127.5, 127.4, 127.4, 127.4, 116.0, 112.3, 61.5, 50.4, 49.9, 39.0, 33.0, 26.1;

HRMS (ESI): $C_{33}H_{28}N_3^+$, $[M+H]^+$, Calcd 466.2278, Found 466.2285.



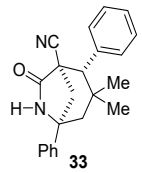
32

32 white solid, 26.8 mg, 41% yield;

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.50 (m, 2H), 7.42 – 7.36 (m, 5H), 7.36 – 7.33 (m, 1H), 7.33 – 7.28 (m, 1H), 7.27 – 7.25 (m, 1H), 5.92 (s, 2H), 3.07 – 2.98 (m, 2H), 2.36 – 2.30 (m, 1H), 2.04 – 2.00 (m, 1H), 1.92 – 1.87 (m, 1H), 1.38 (s, 3H), 0.86 (s, 3H);

^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.9, 138.6, 132.9, 128.9, 128.8, 128.6, 127.8, 127.3, 125.3, 118.8, 71.0, 53.4, 52.4, 46.2, 44.6, 36.2, 34.1, 33.2;

HRMS (ESI): $C_{22}H_{24}N_3^+$, $[M+H]^+$, Calcd 330.1965, Found 330.1968.



33

33 white solid, 47.3 mg, 72% yield (EA/PE = 21%);

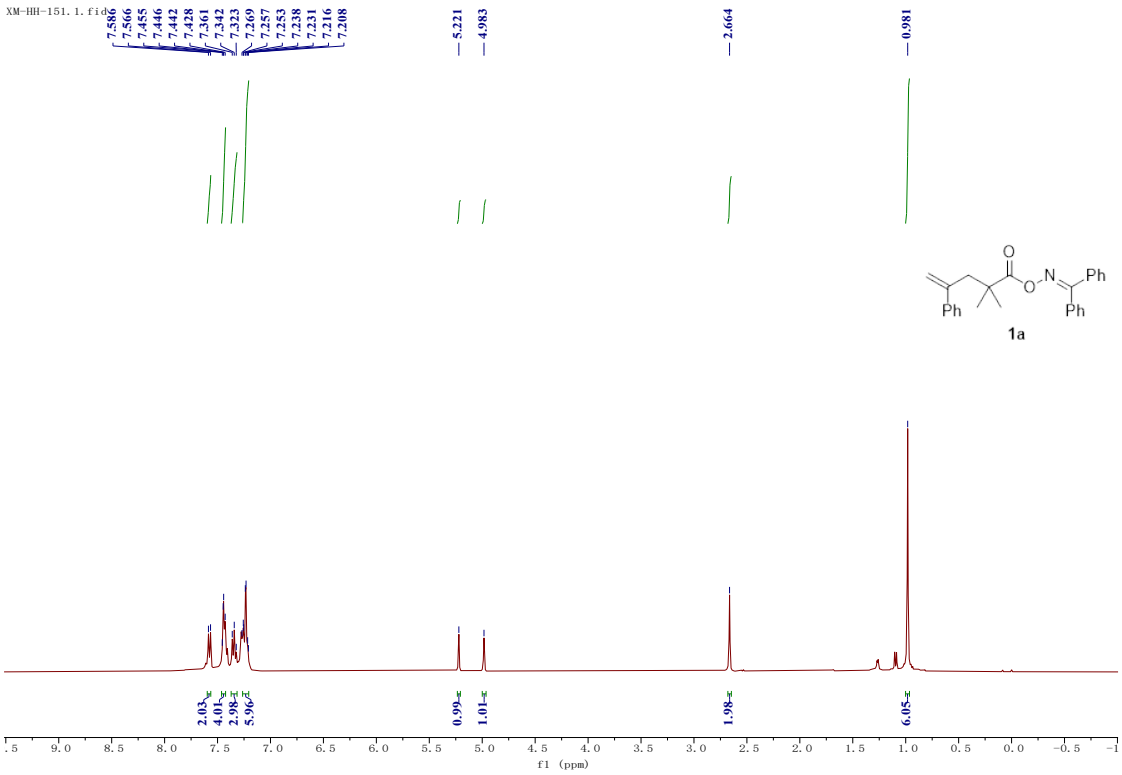
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.76 – 7.68 (m, 1H), 7.64 – 7.57 (m, 2H), 7.47 – 7.25 (m, 7H), 3.11 (s, 1H), 3.08 – 3.00 (m, 1H), 2.32 – 2.23 (m, 2H), 1.84 – 1.75 (m, 1H), 1.34 (s, 3H), 0.78 (s, 3H);

^{13}C NMR (100 MHz, DMSO-d_6) δ 171.8, 143.0, 139.3, 133.1, 129.6, 128.9, 128.7, 128.3, 128.0, 127.8, 125.7, 119.1, 61.9, 53.2, 50.7, 46.1, 42.0, 36.1, 33.8, 33.0;

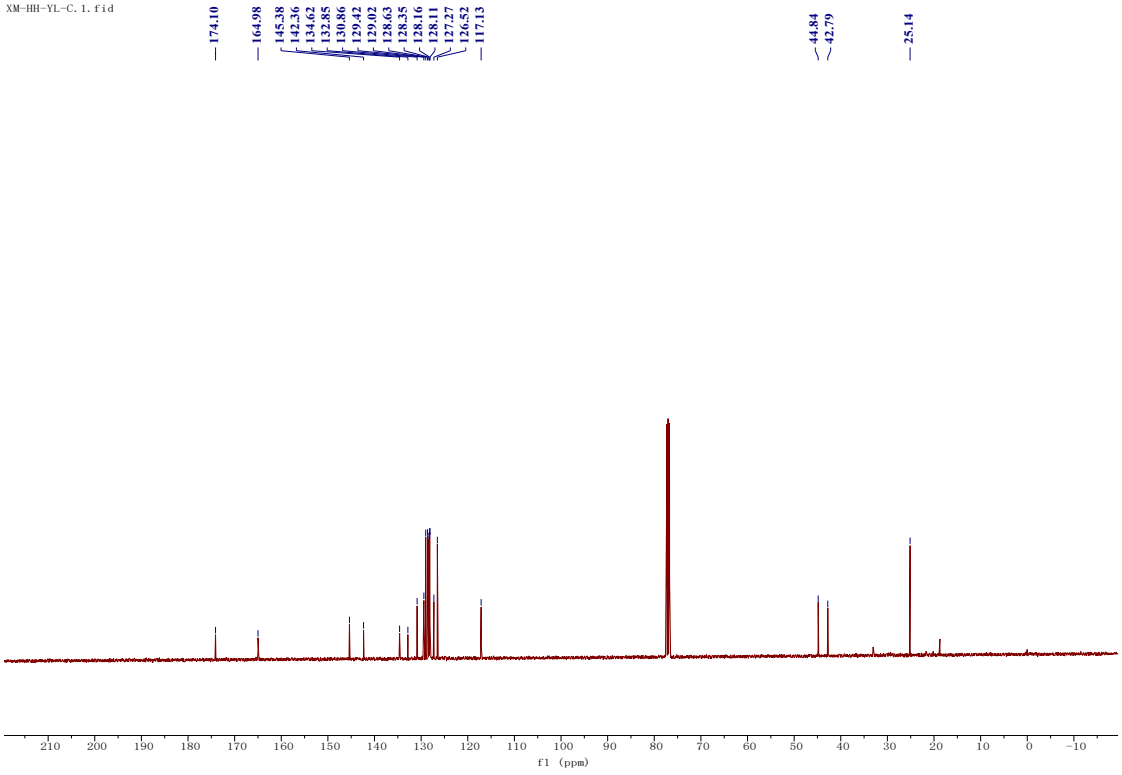
HRMS (ESI): $C_{22}H_{22}N_2NaO^+$, $[M+Na]^+$, Calcd 353.1624, Found 353.1633.

6. NMR Spectra of Compounds 1a, 1b, 1c, 1d and 3-33.

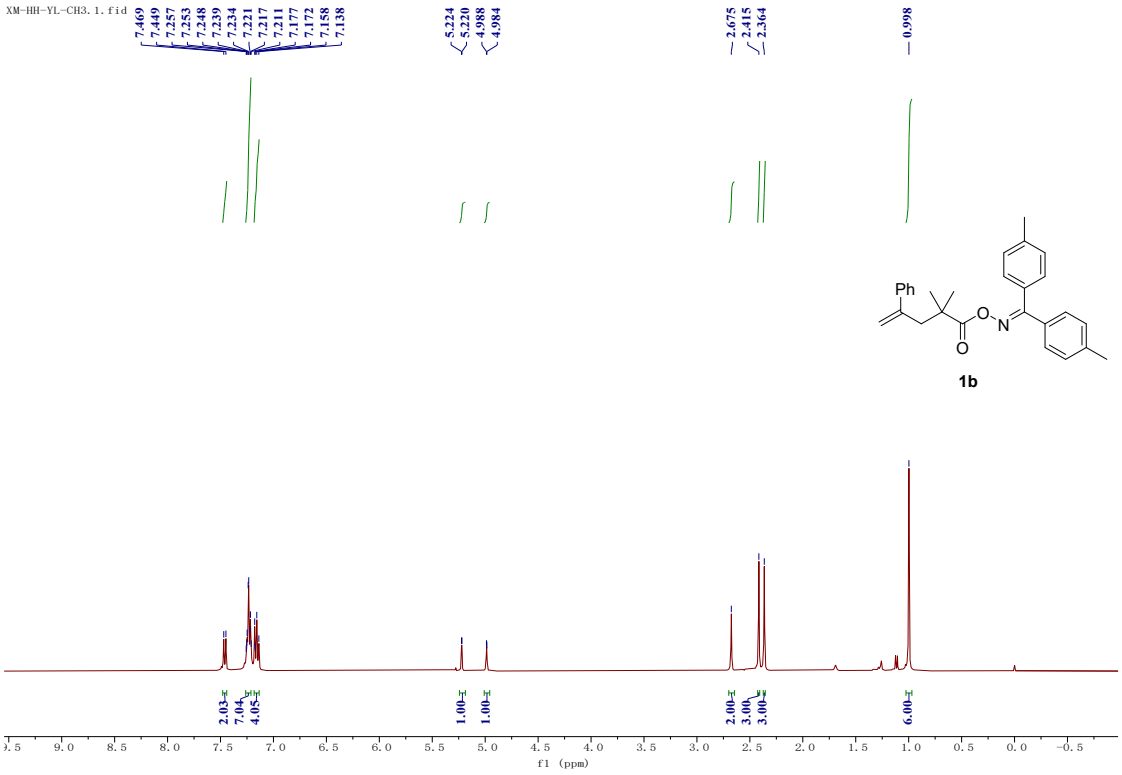
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 1a



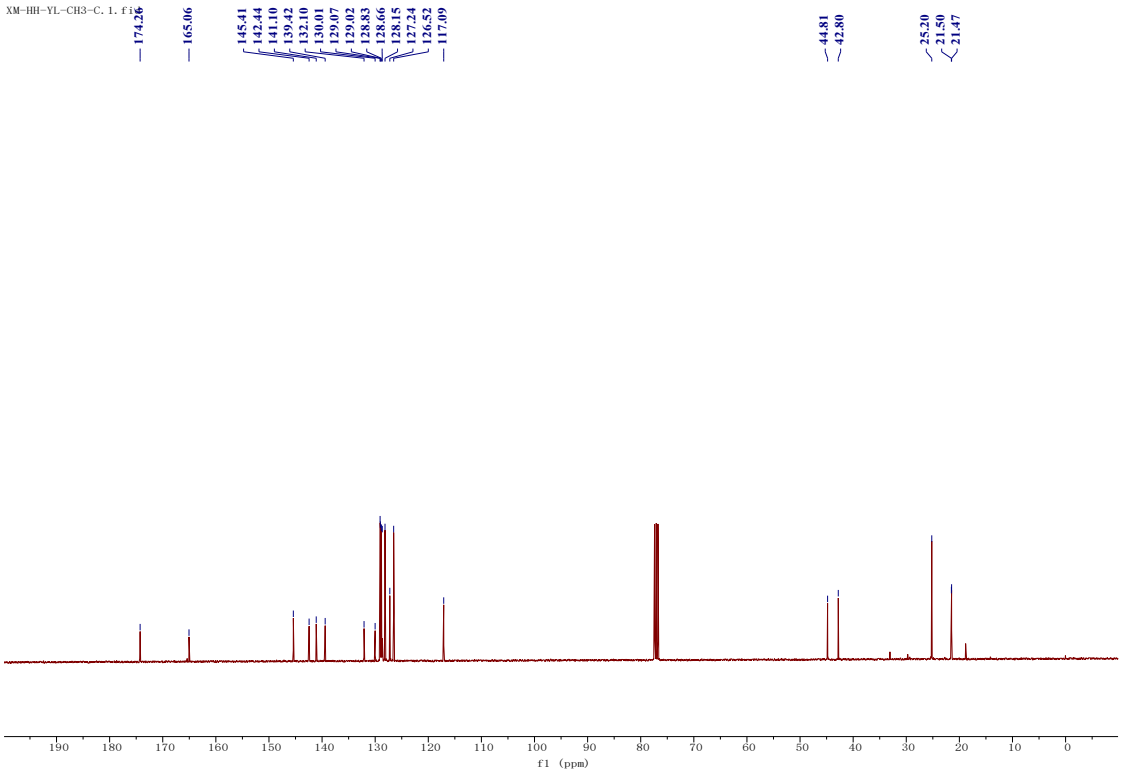
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 1a



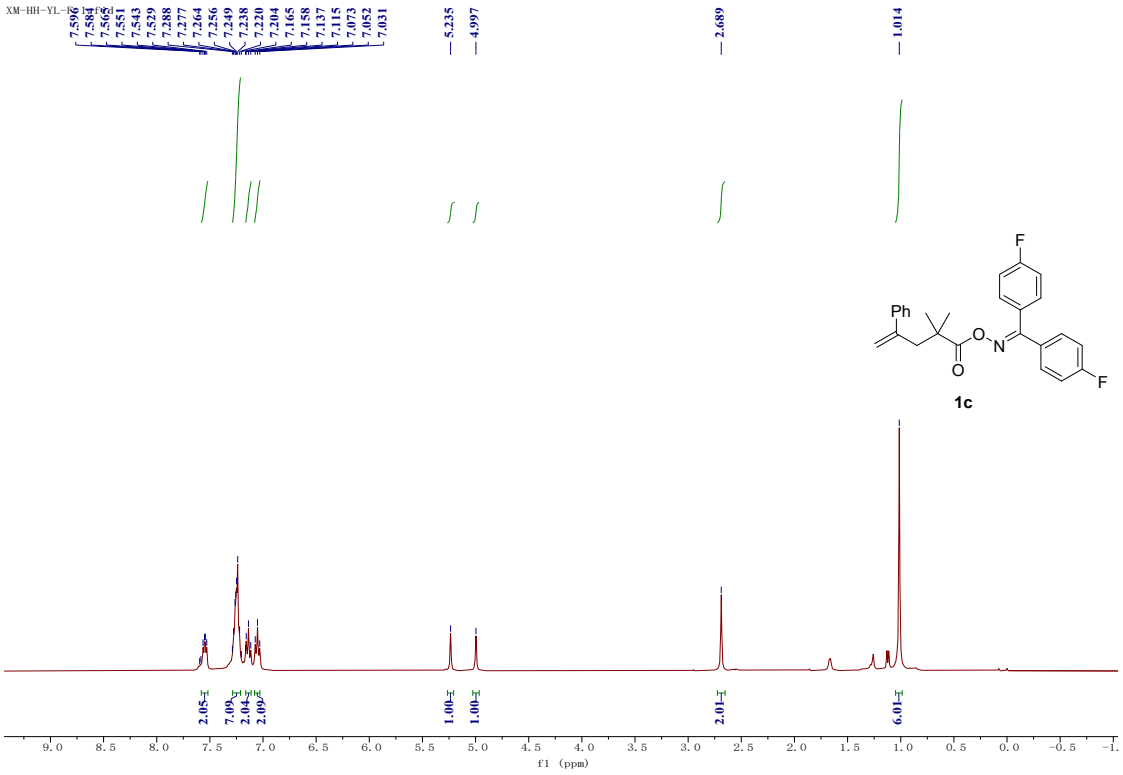
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 1b



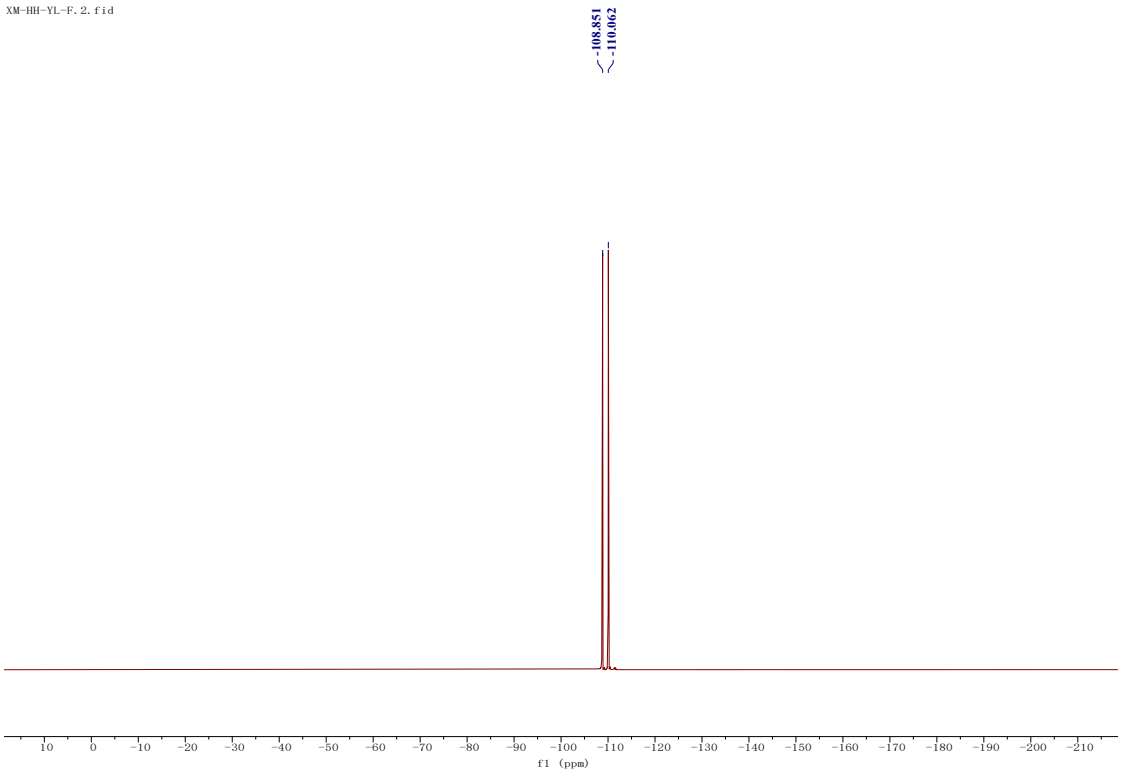
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 1b



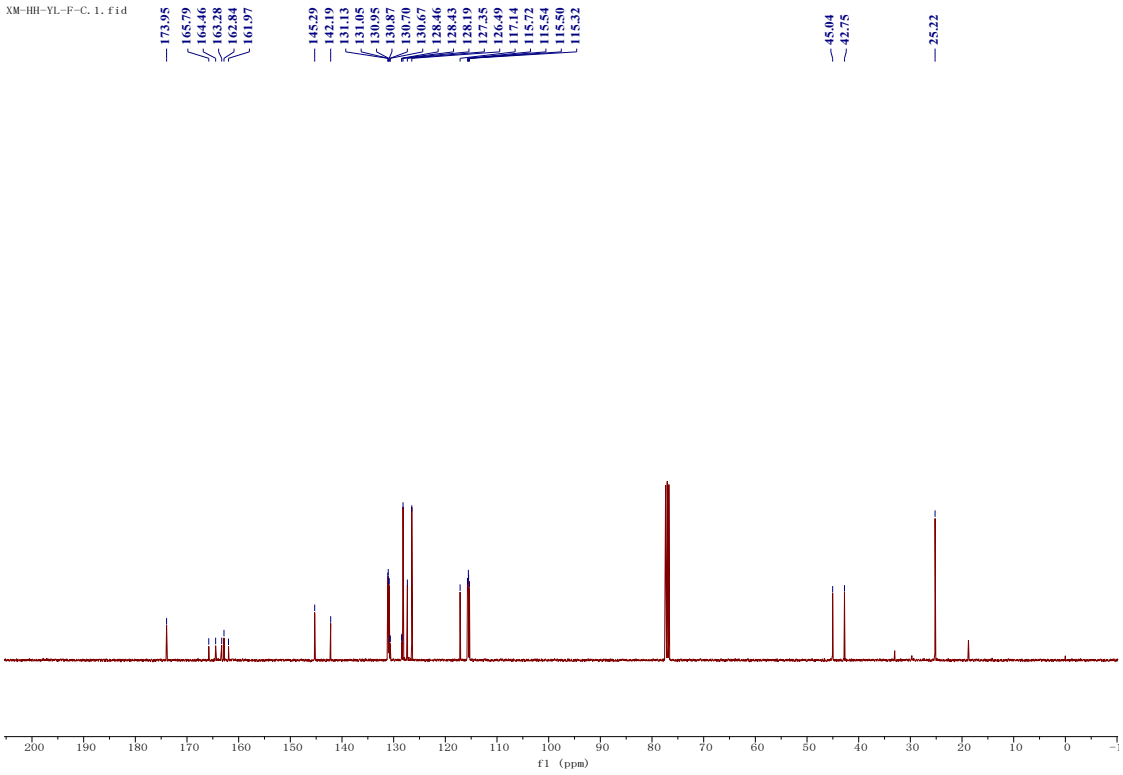
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 1c



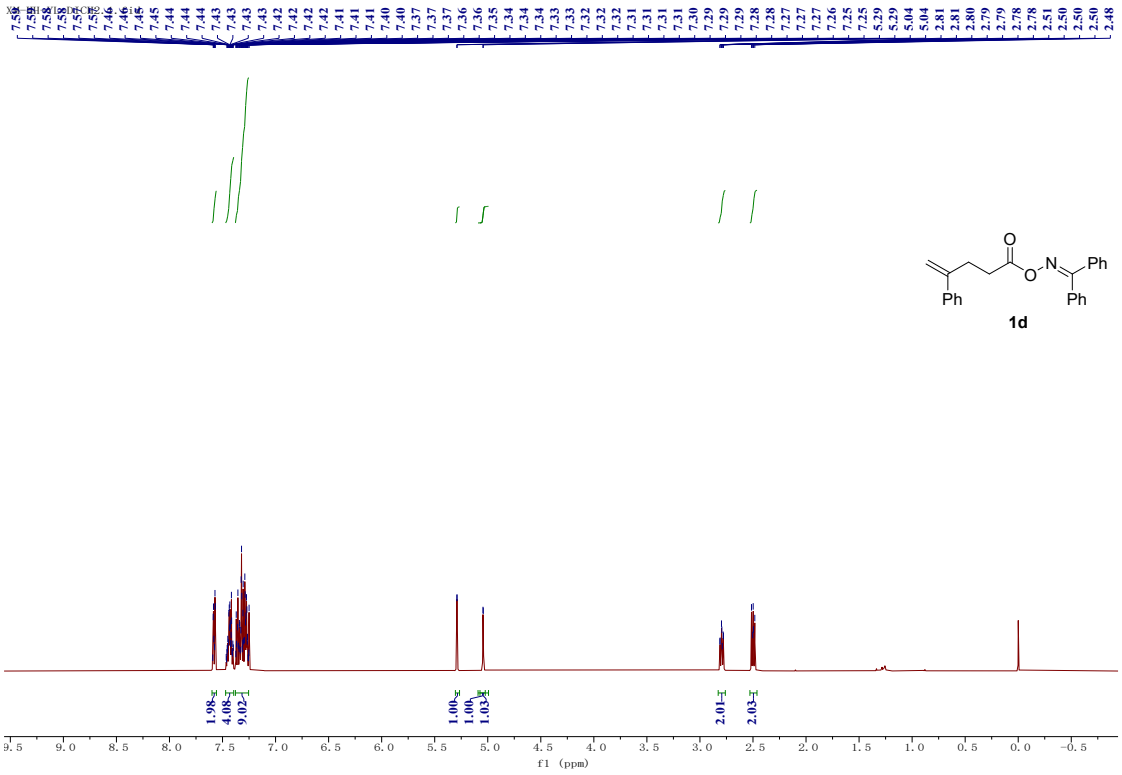
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 1c



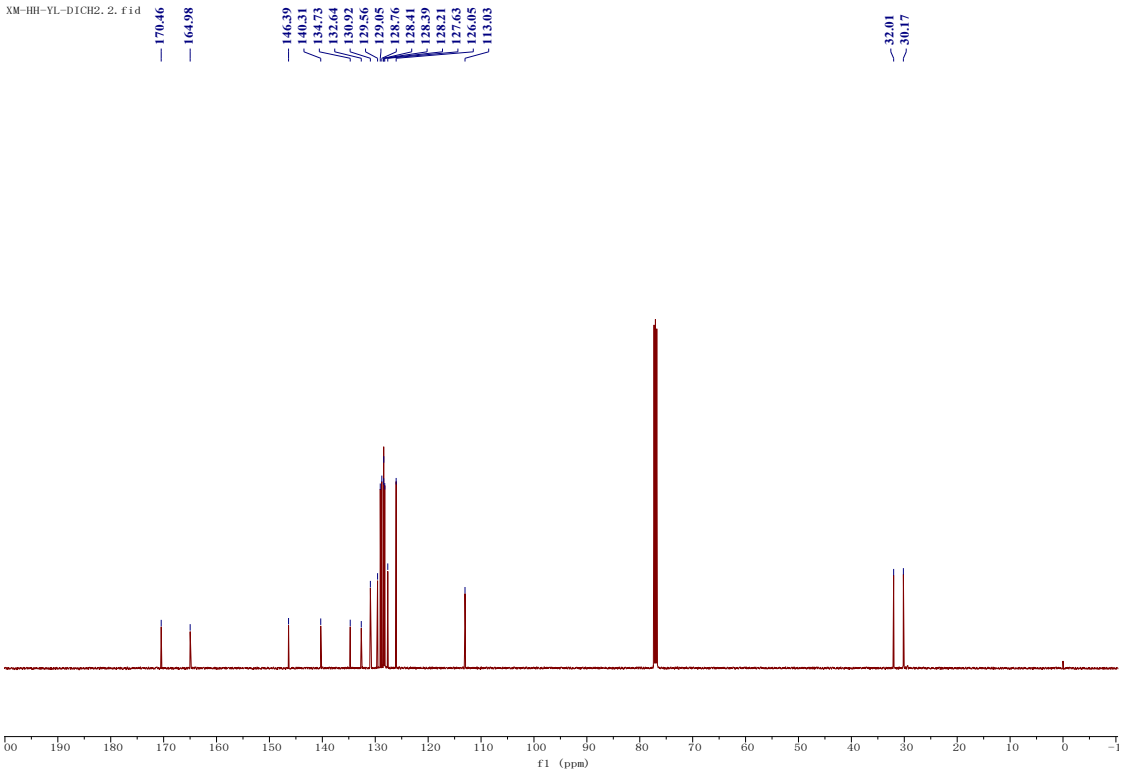
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 1c



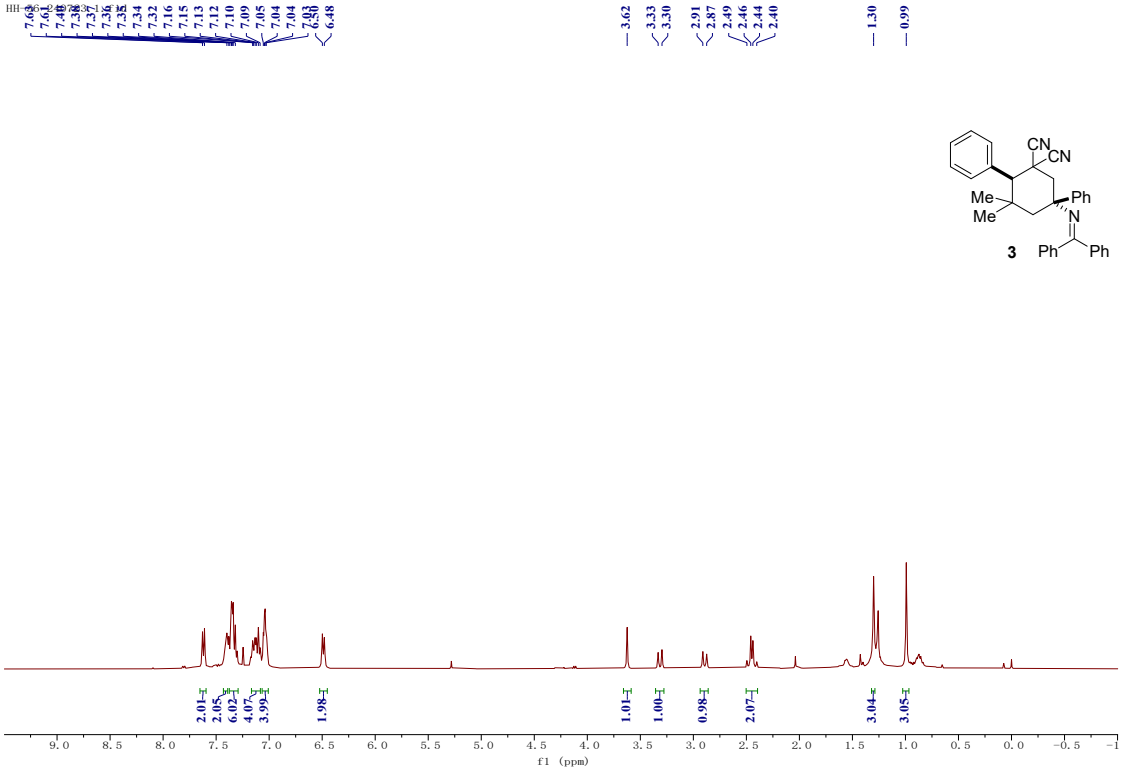
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of product 1d



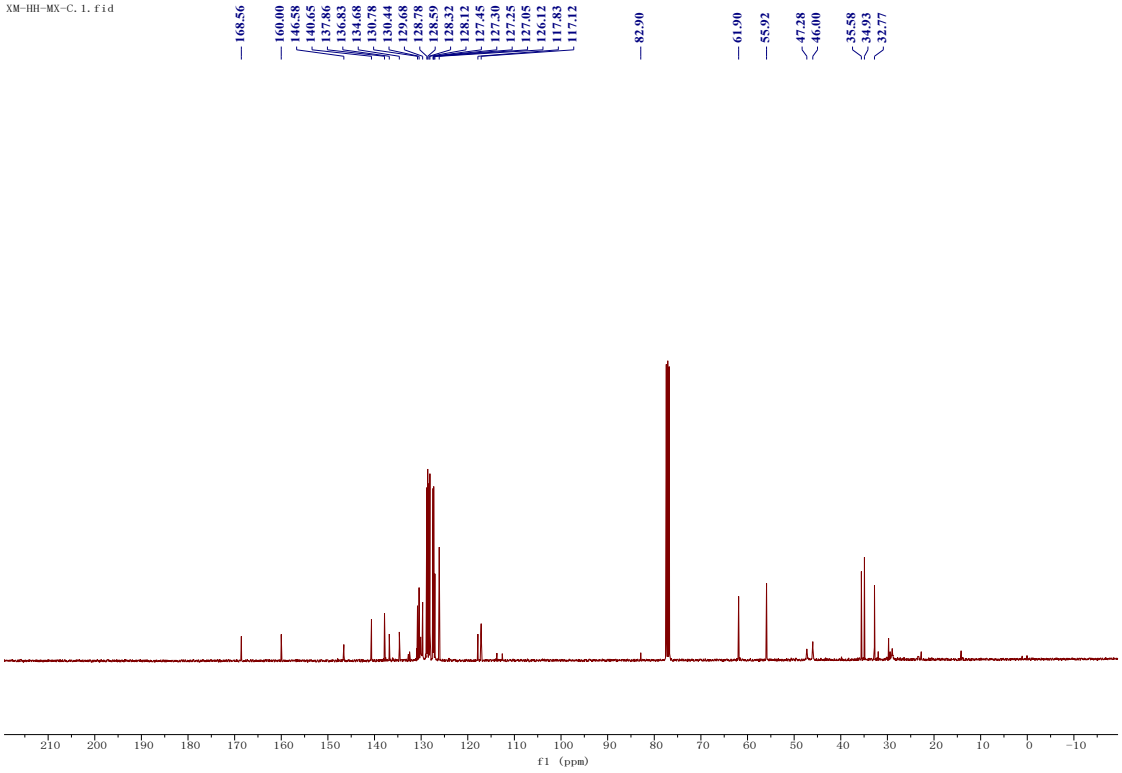
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of product 1d



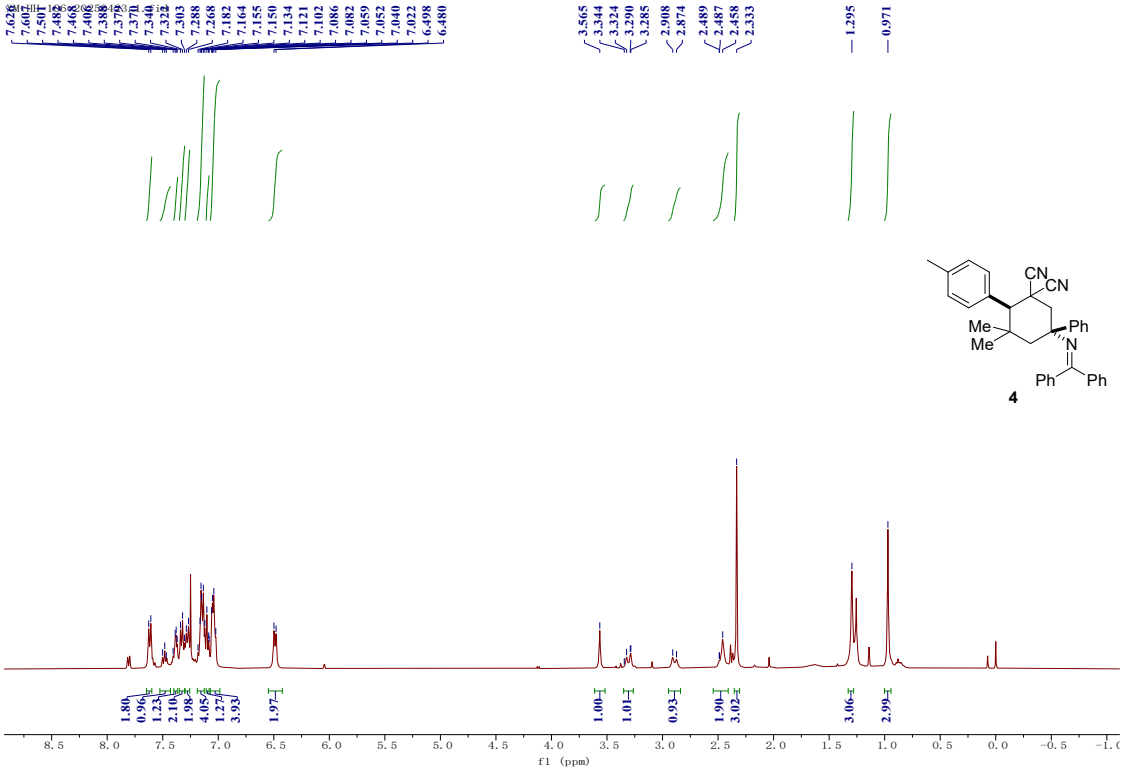
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 3



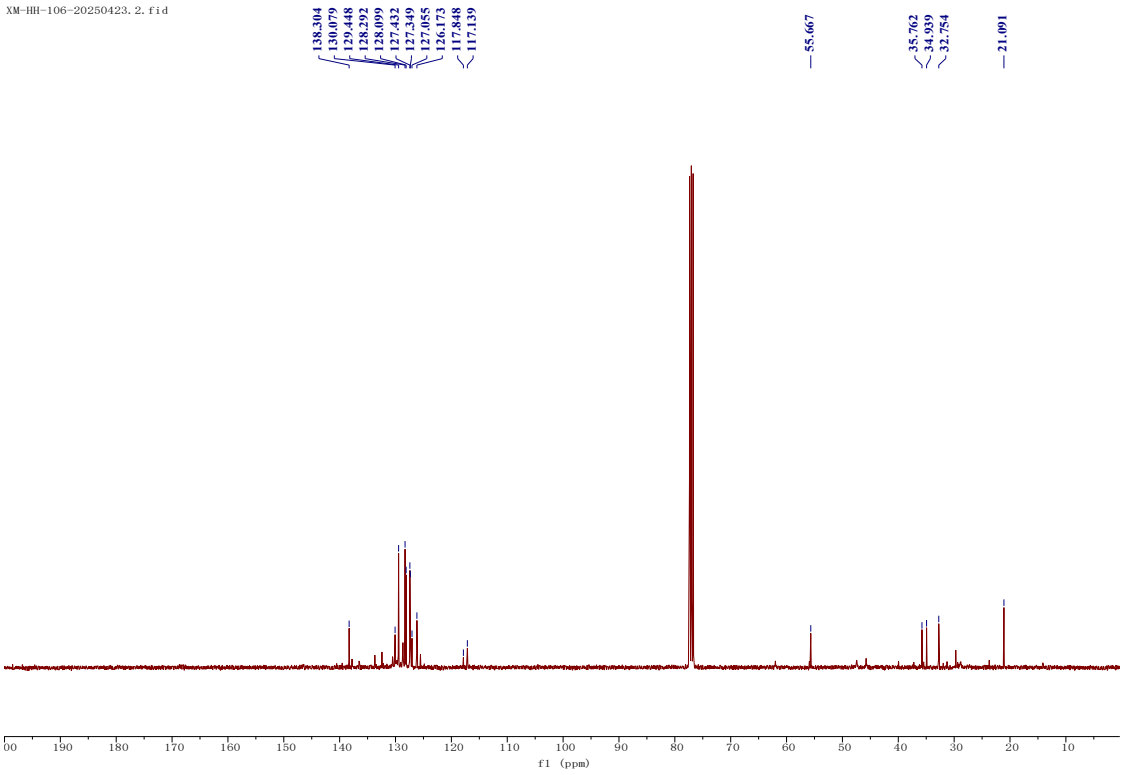
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3



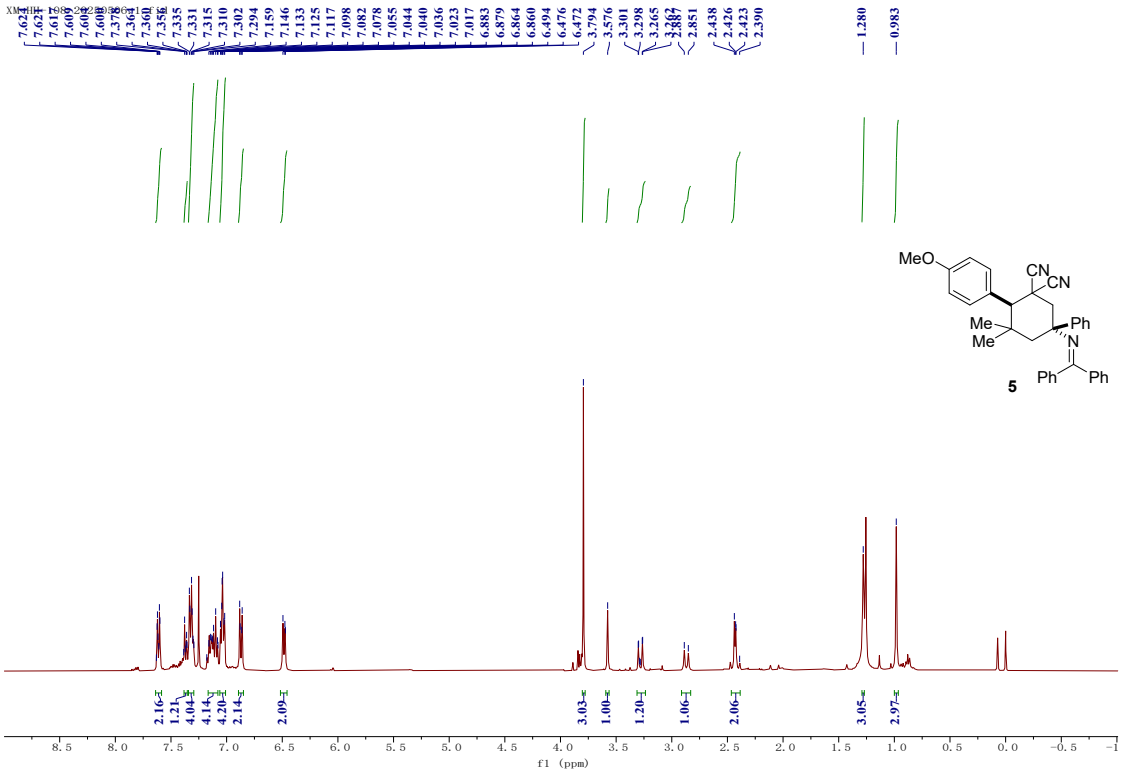
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 4



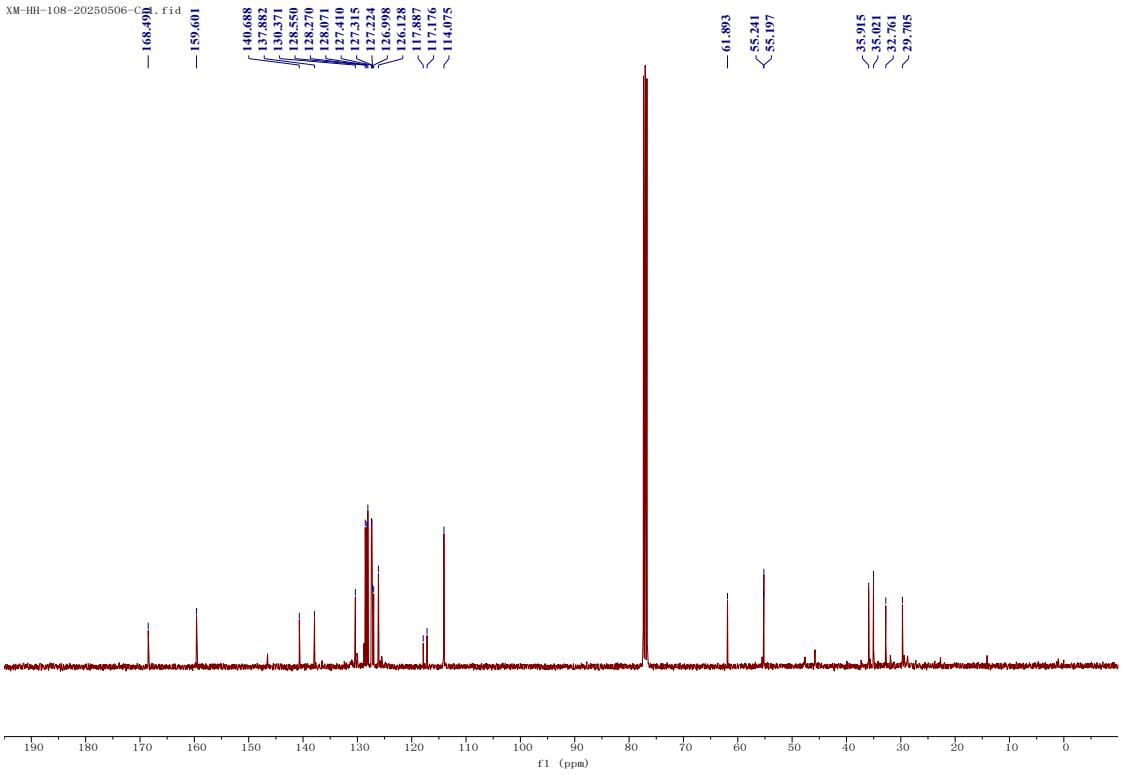
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4



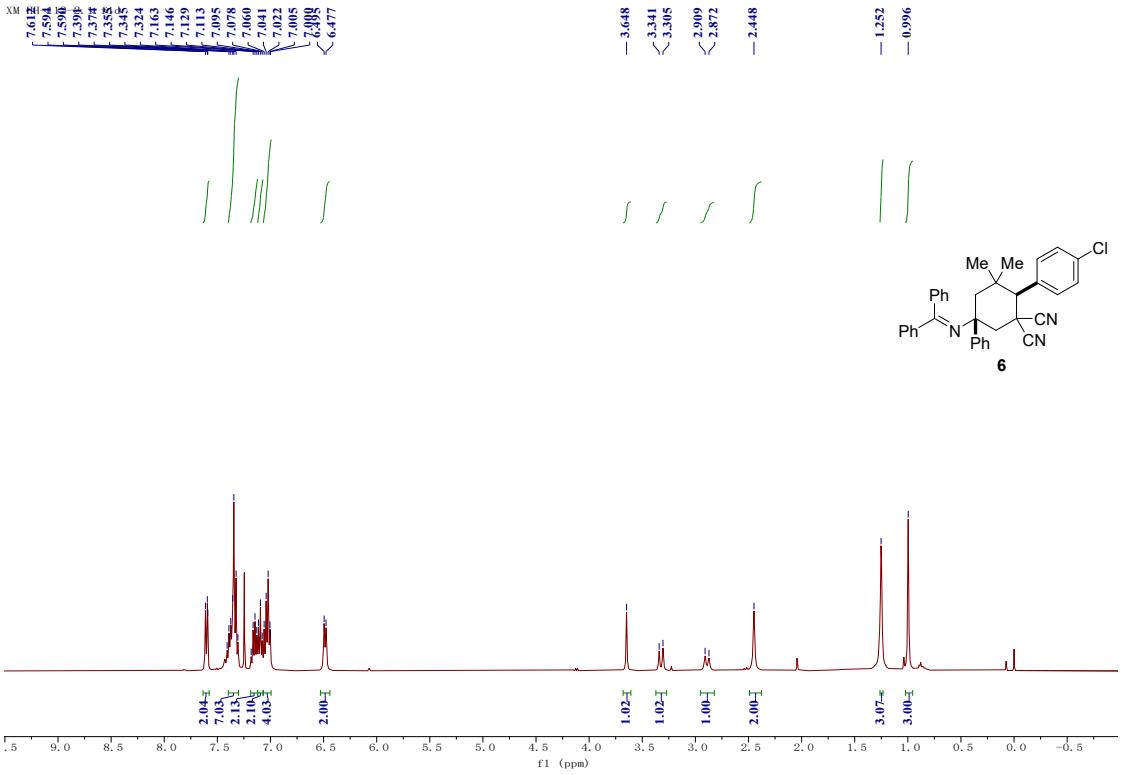
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 5



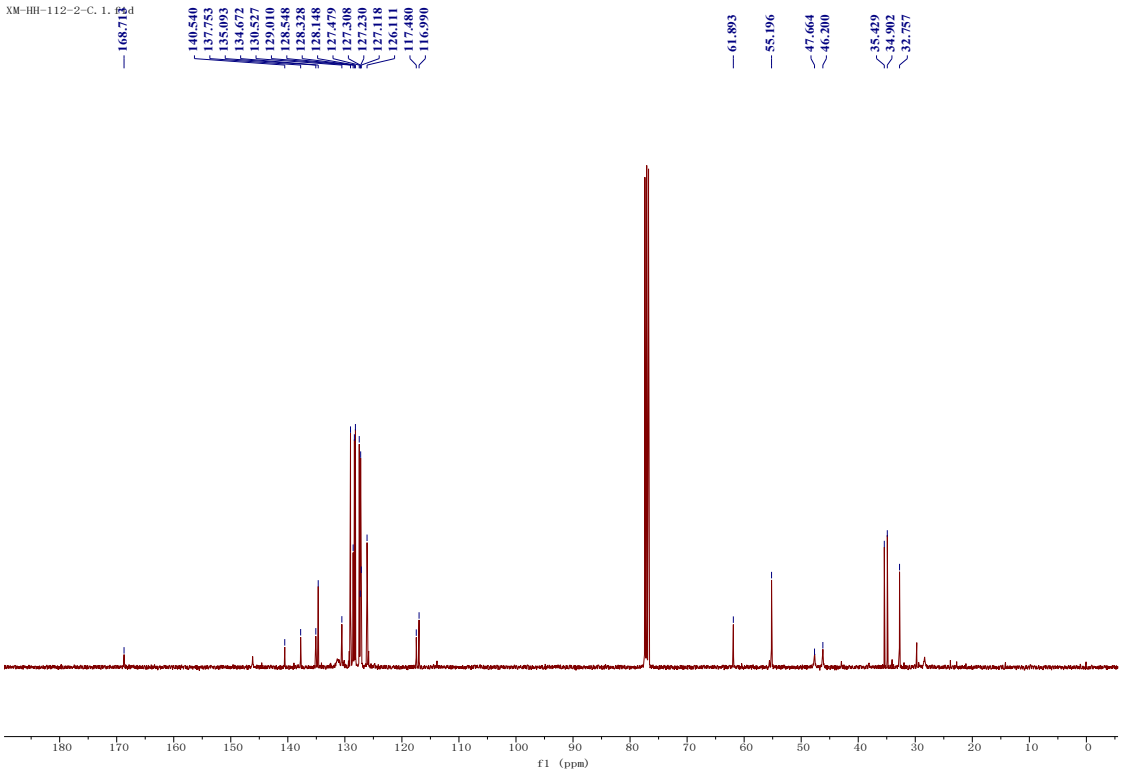
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 5



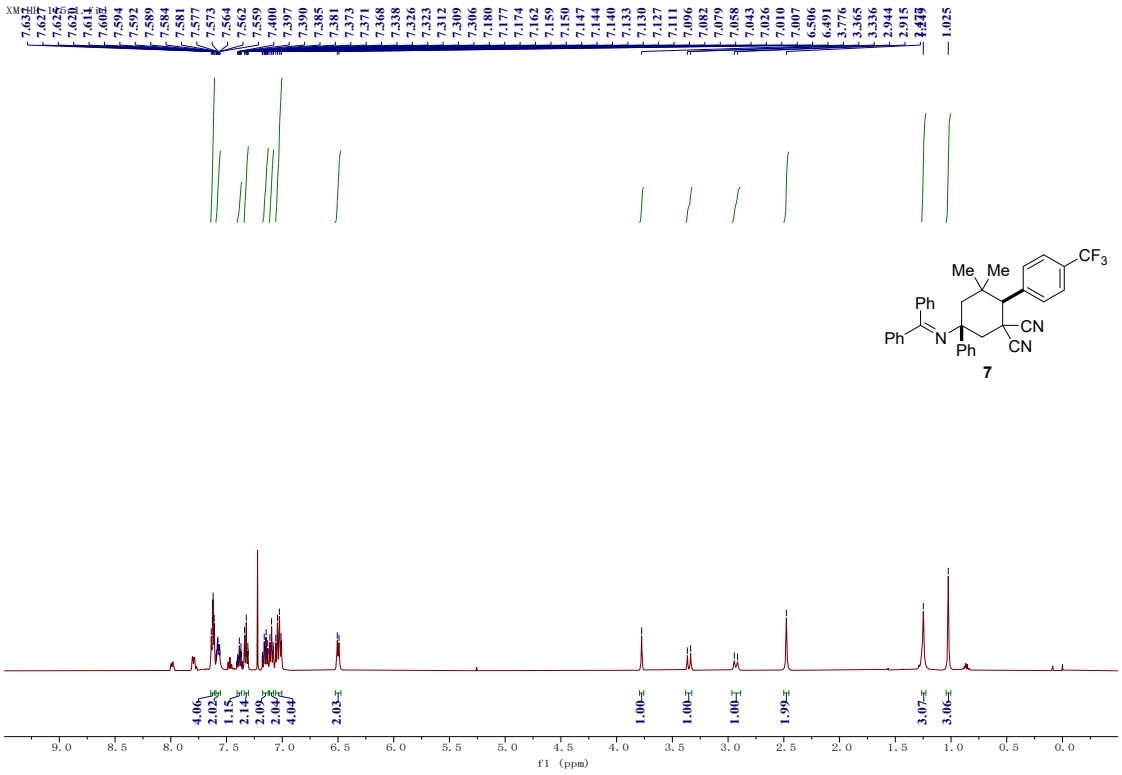
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 6



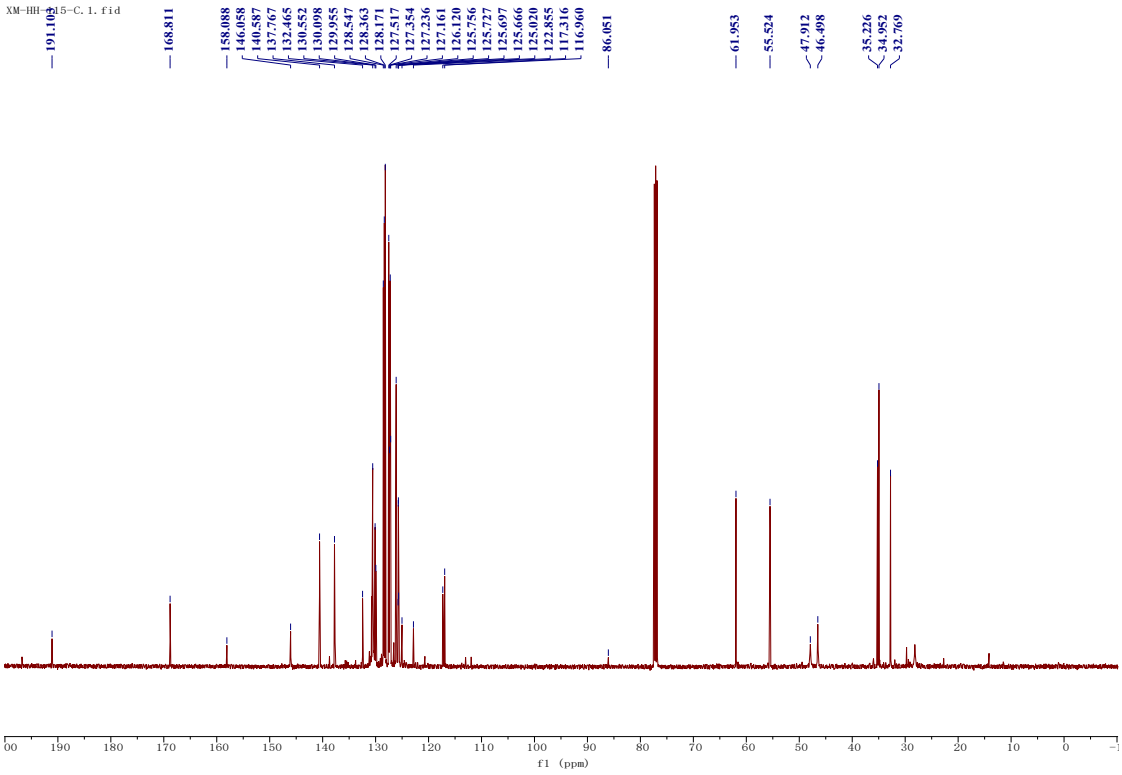
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6



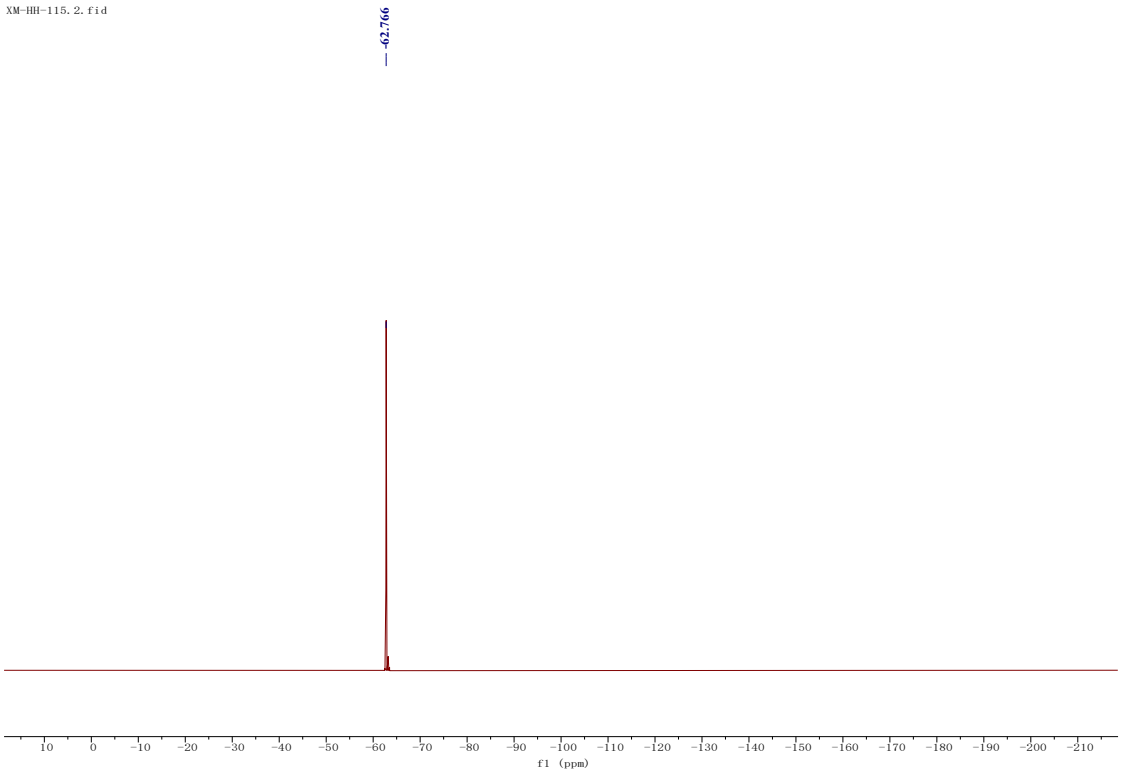
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of product 7



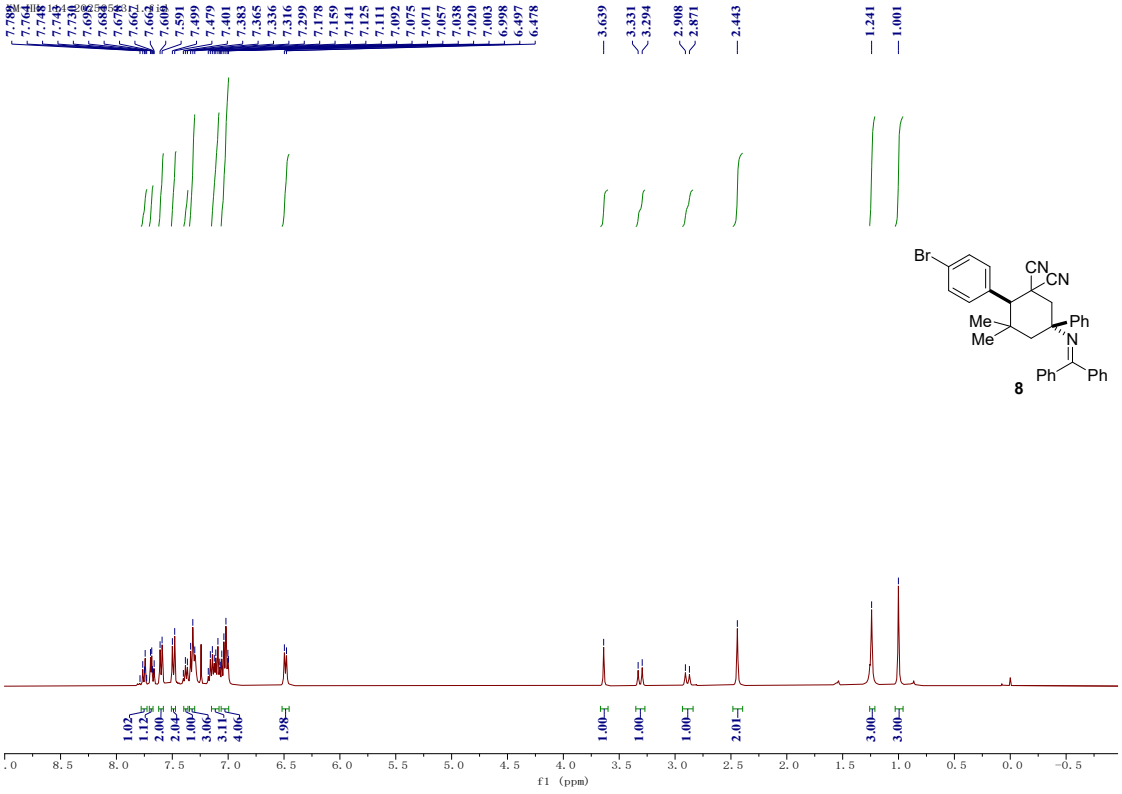
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of product 7



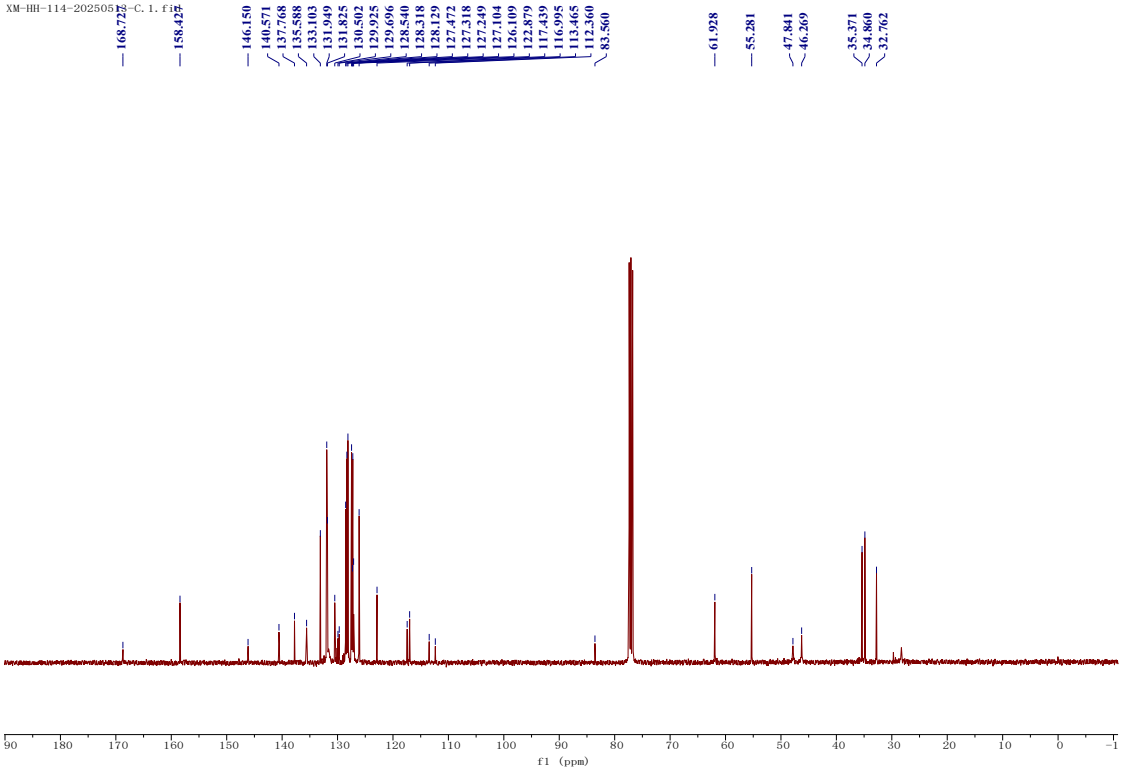
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 7



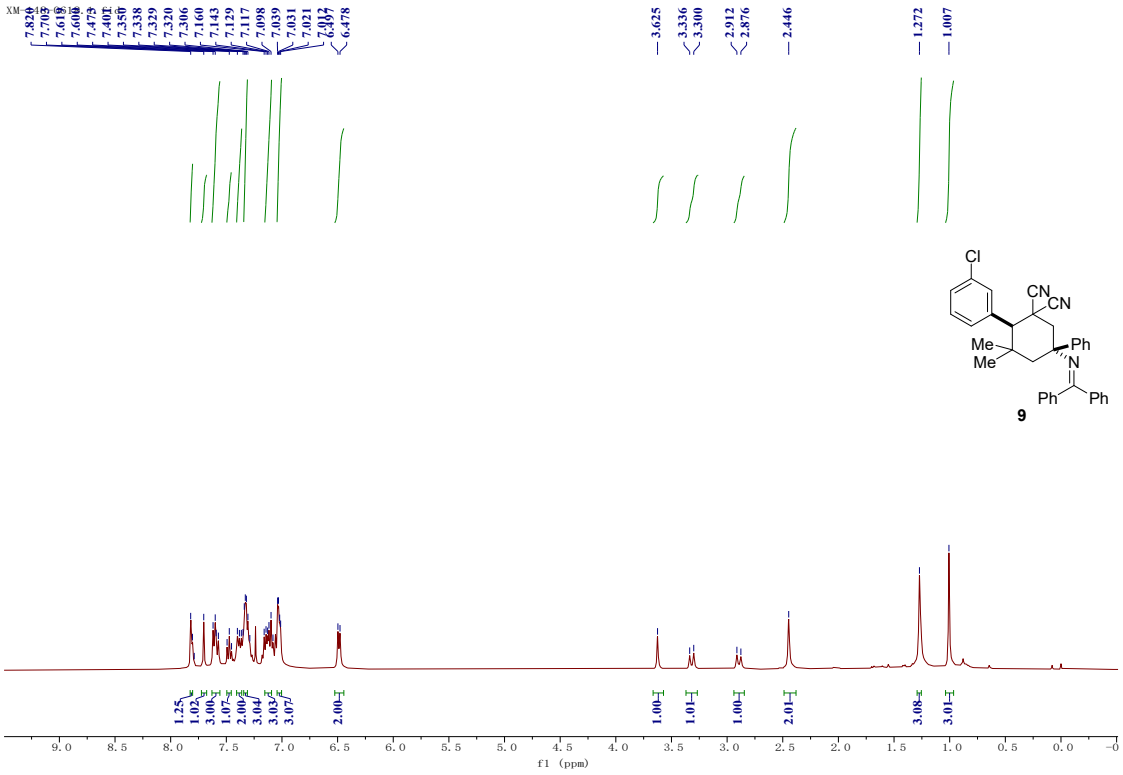
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 8



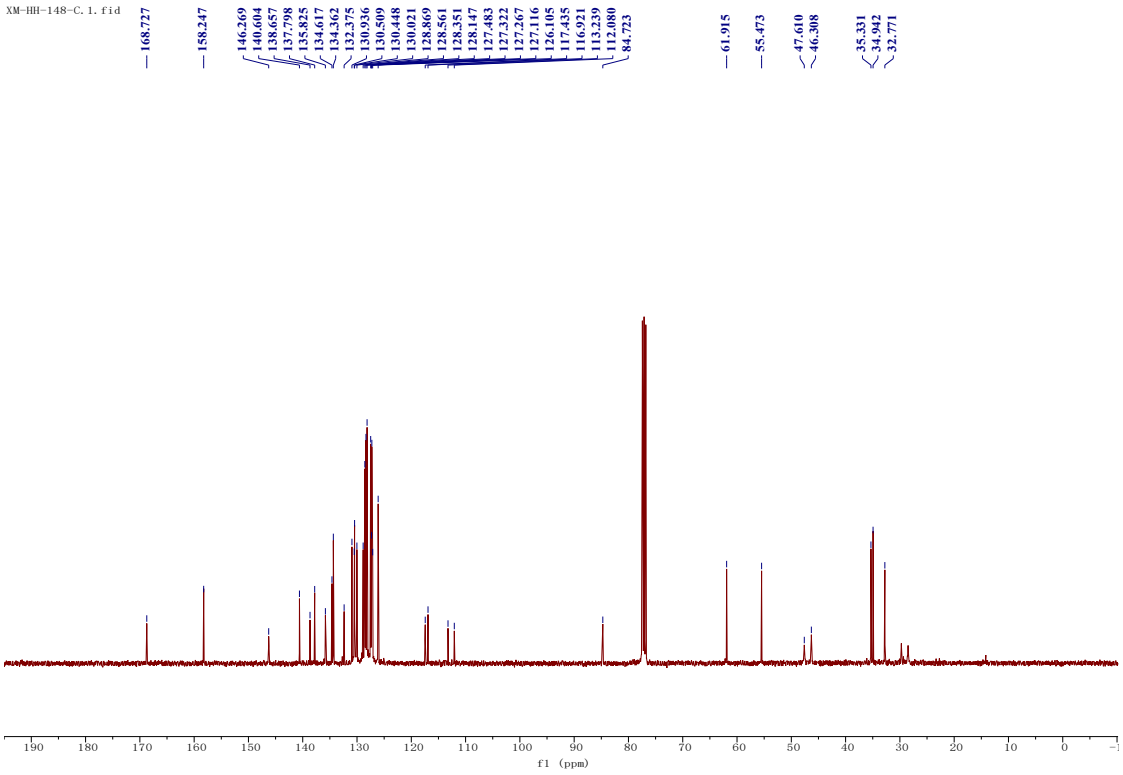
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 8



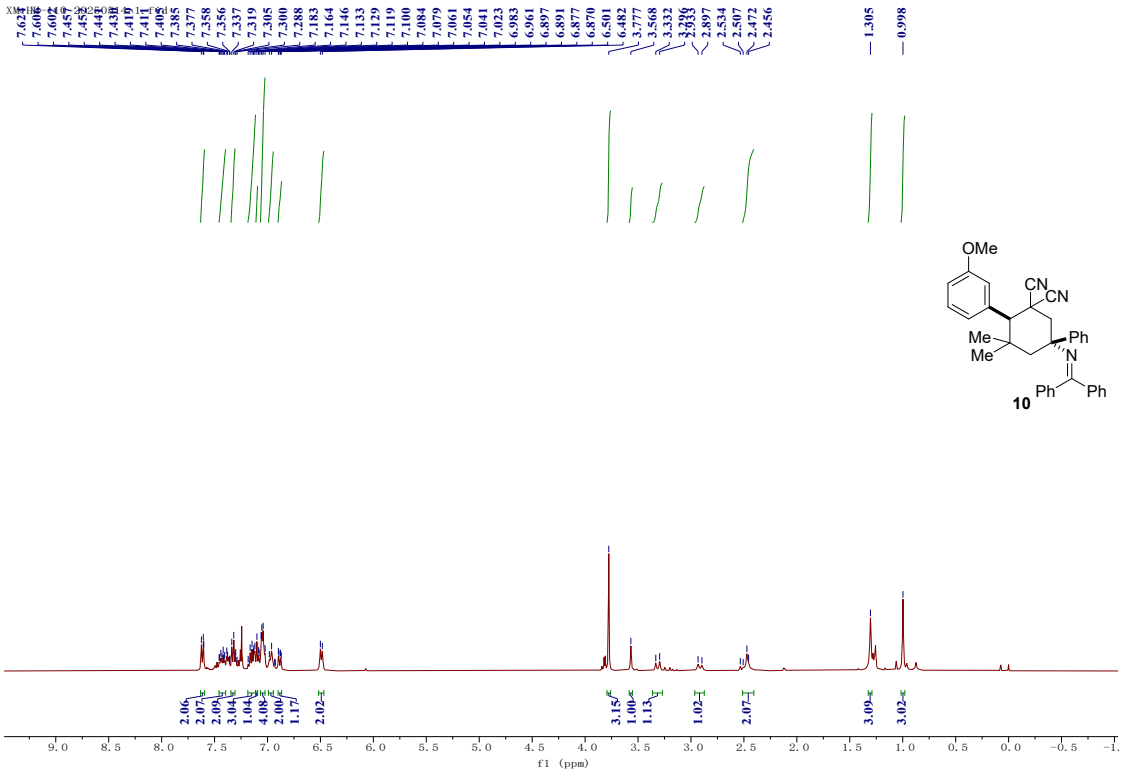
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 9



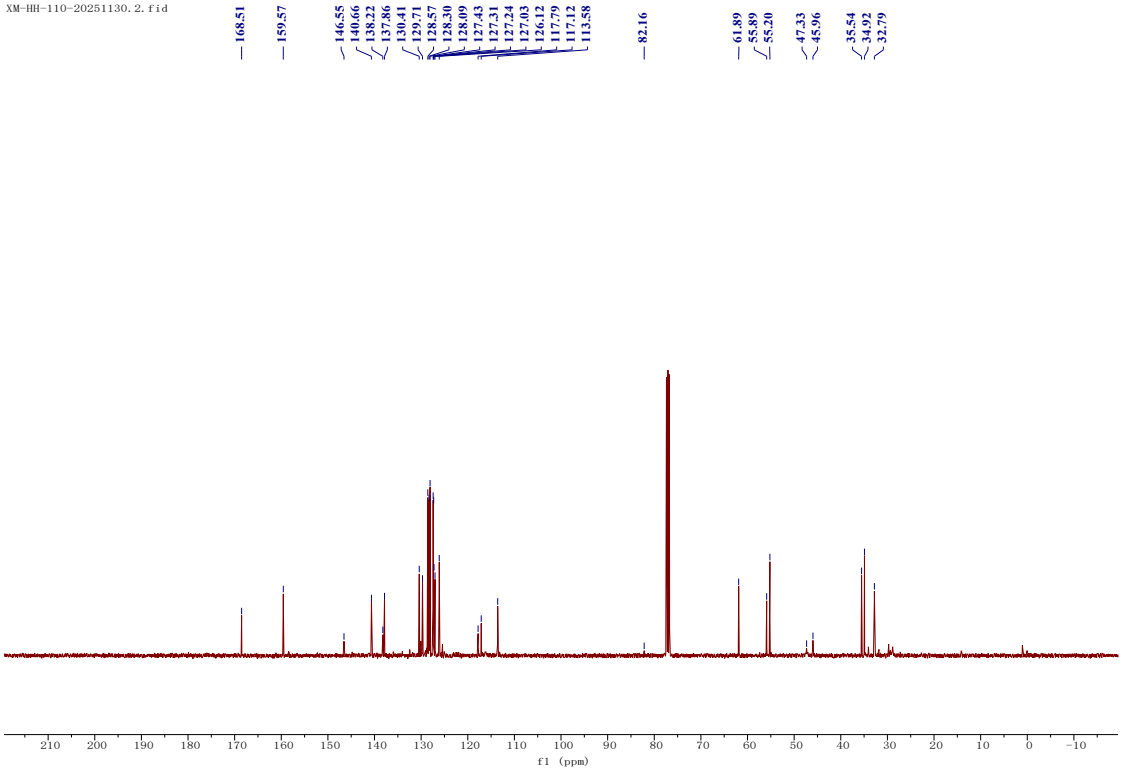
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 9



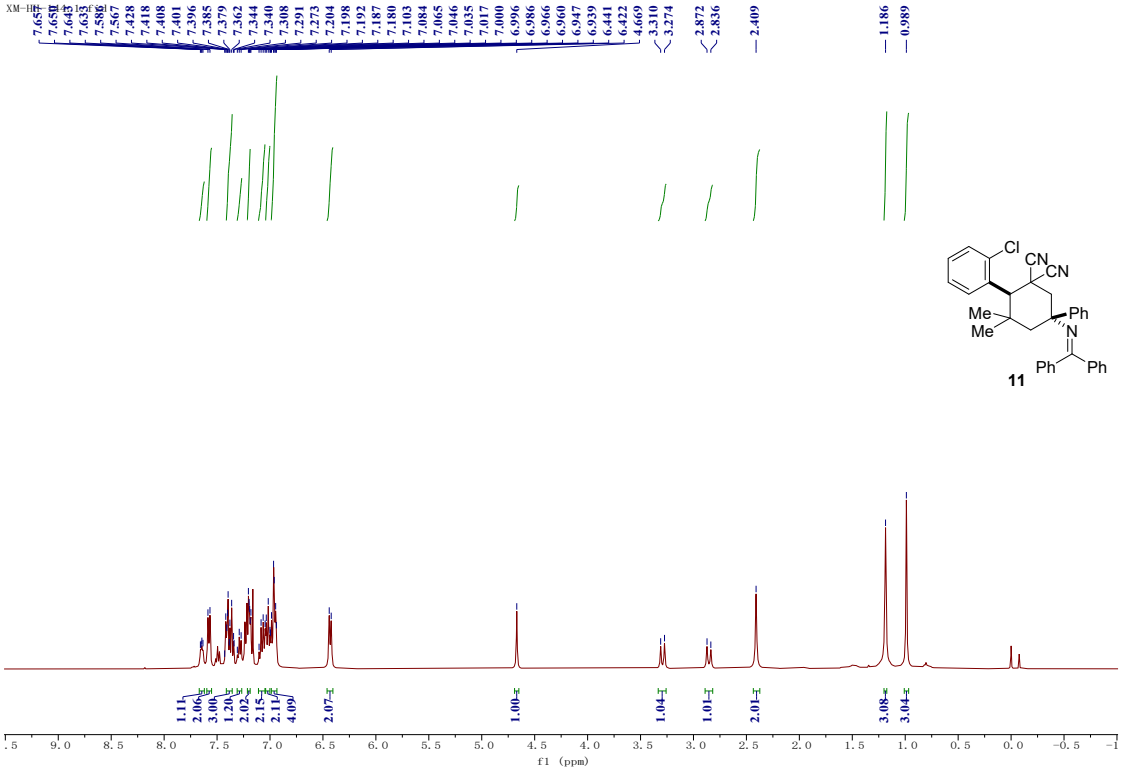
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 10



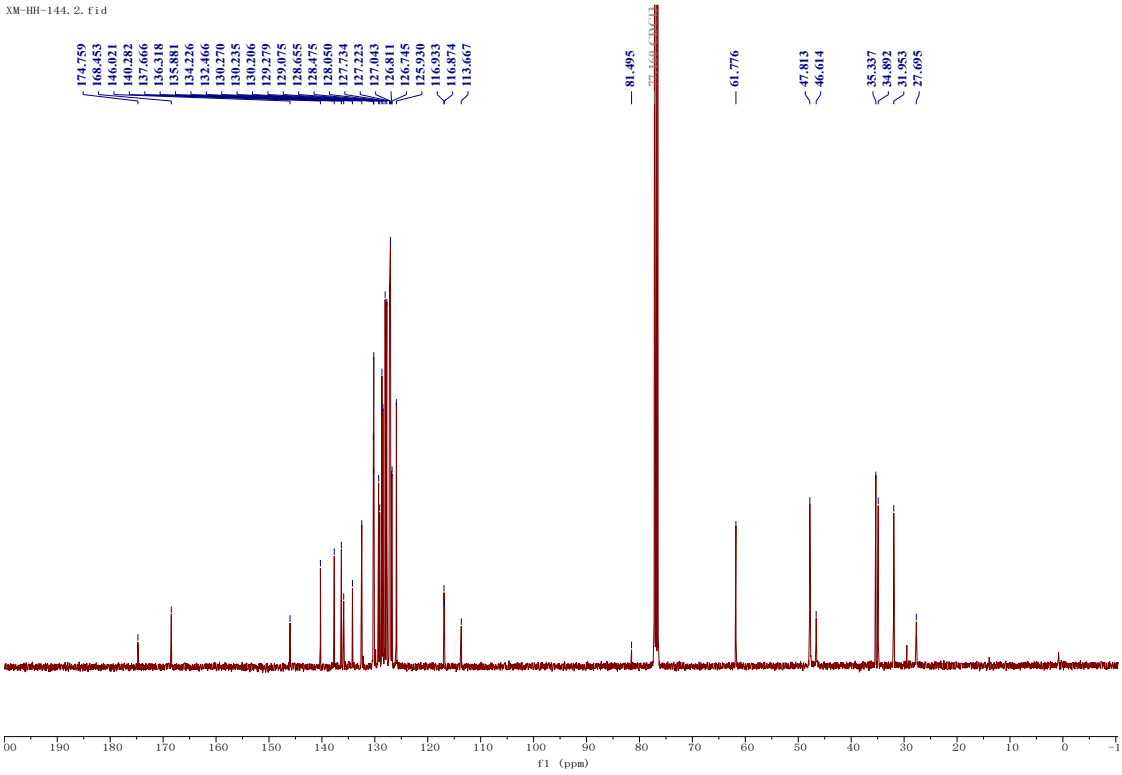
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 10



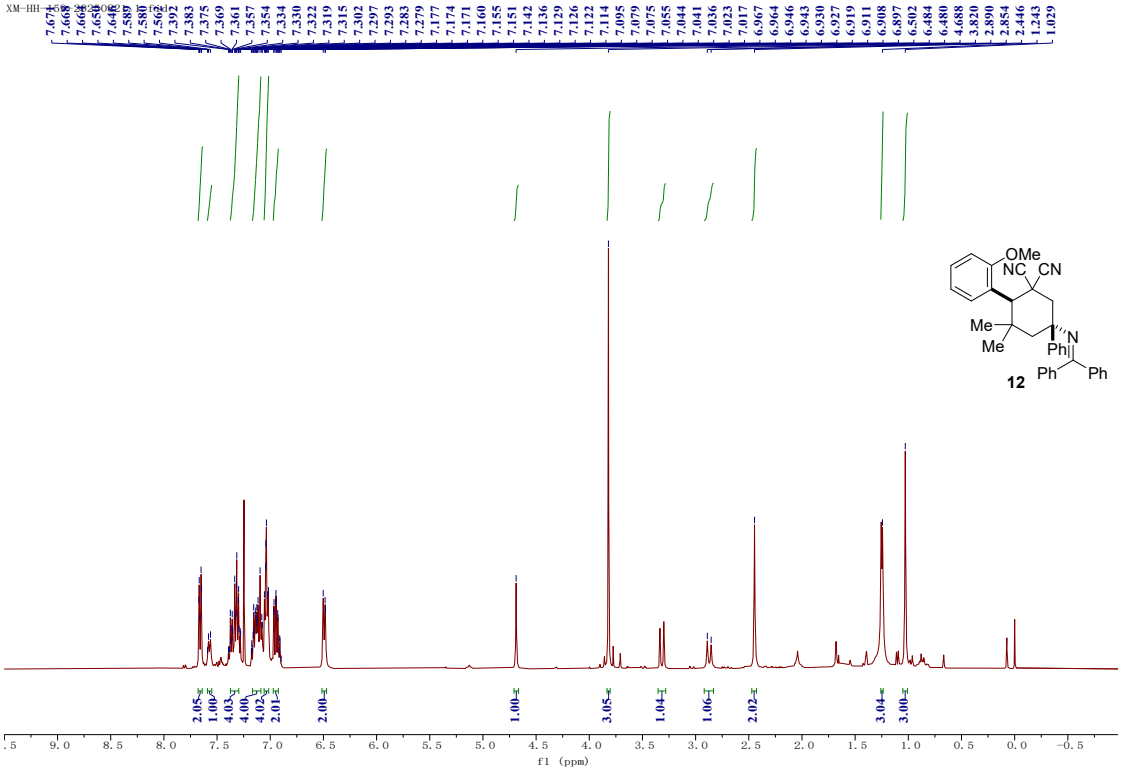
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 11



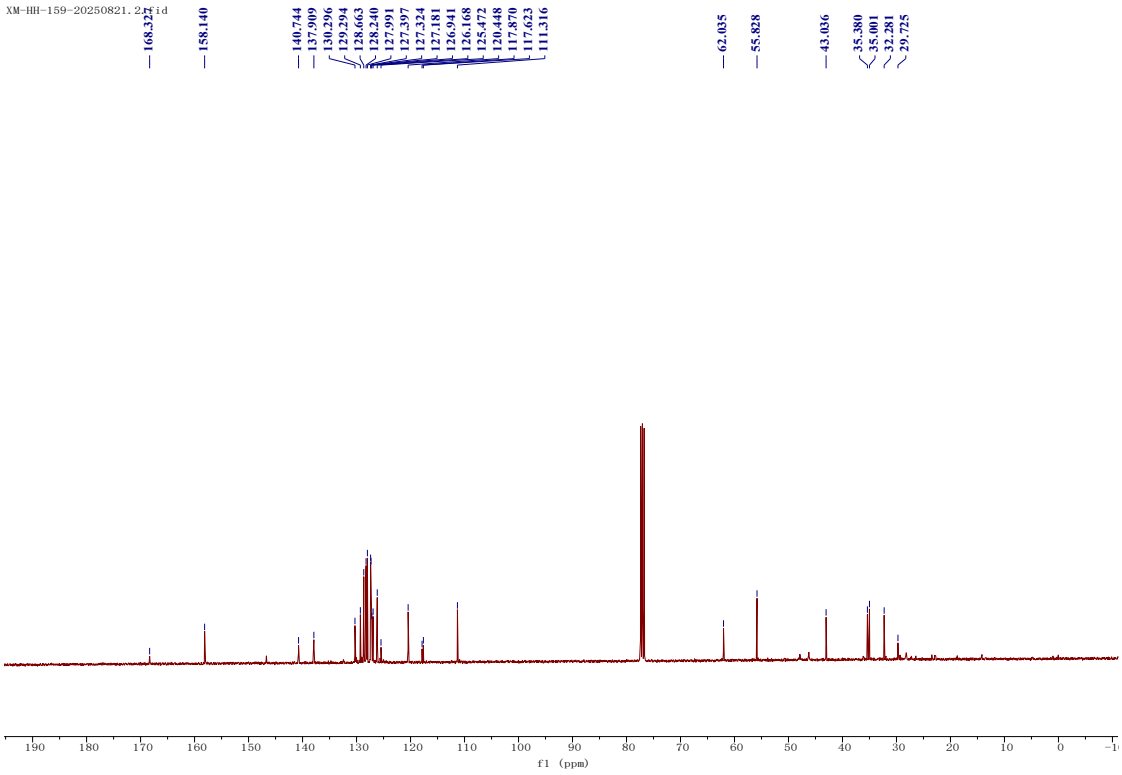
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 11



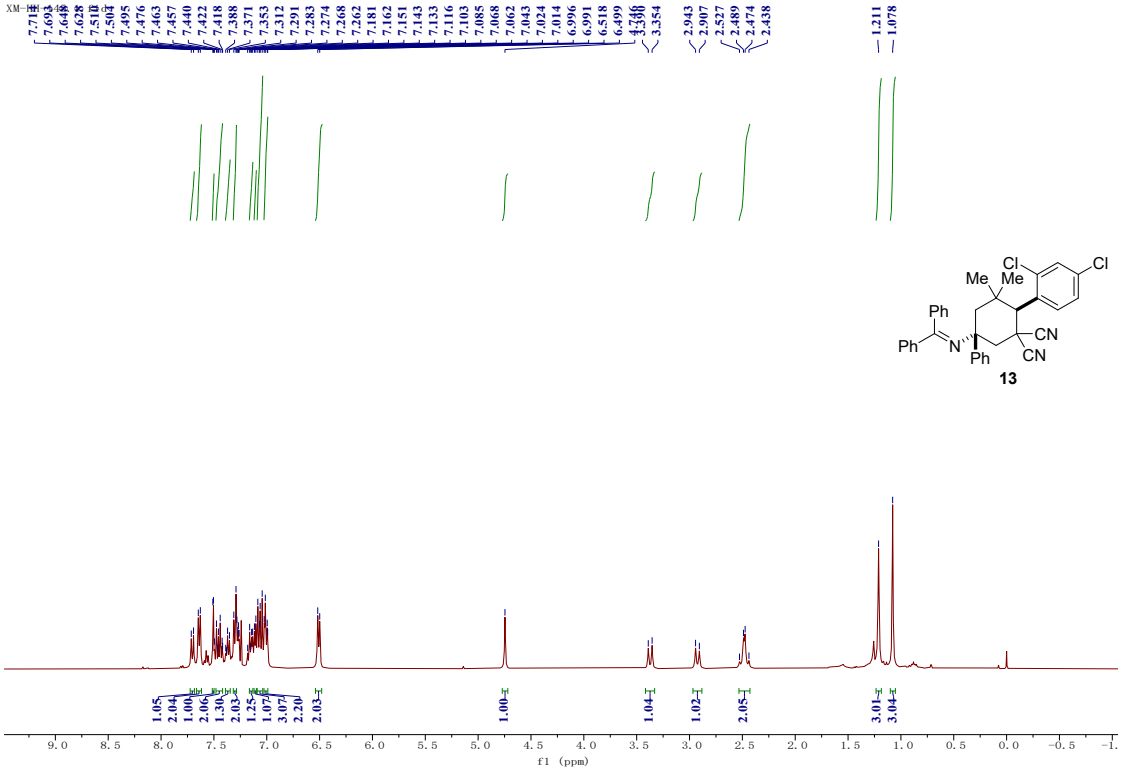
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 12



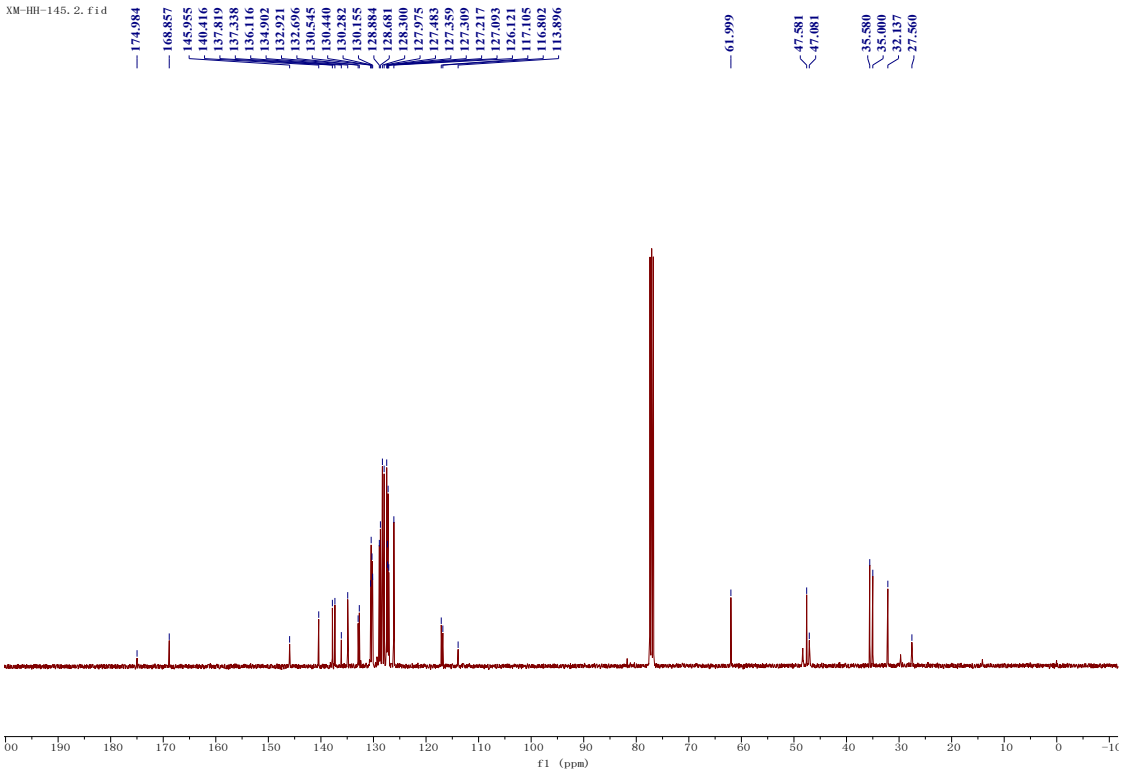
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 12



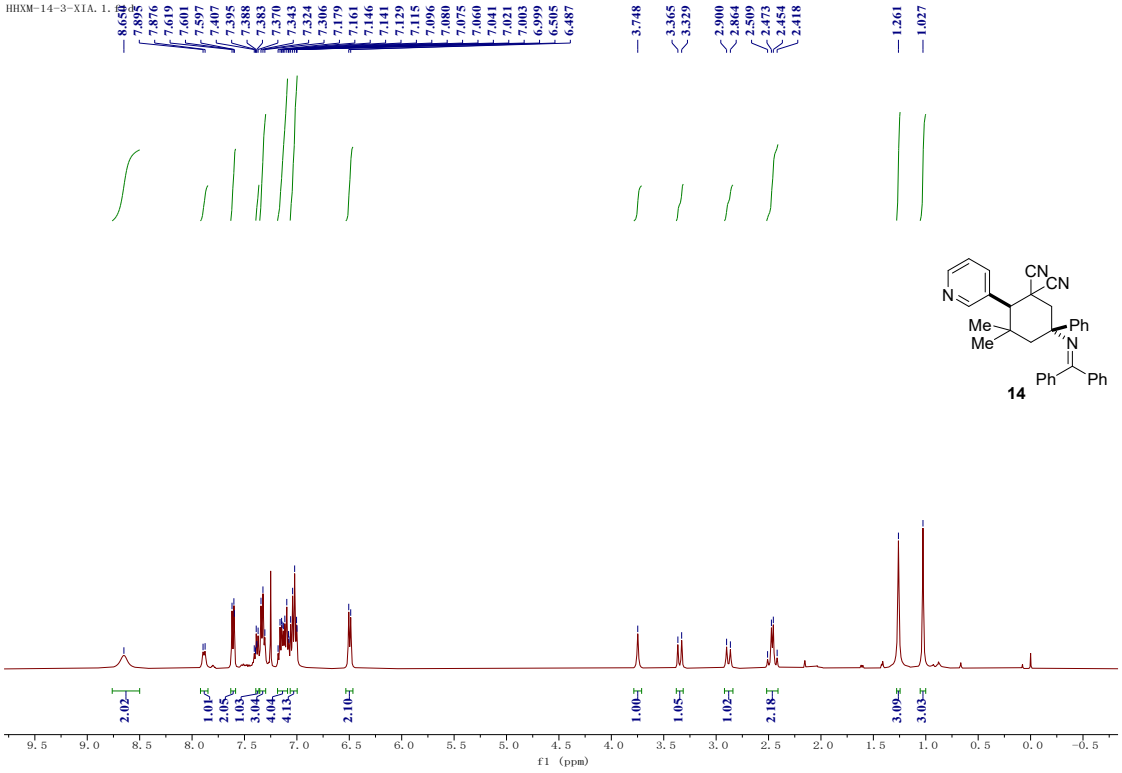
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 13



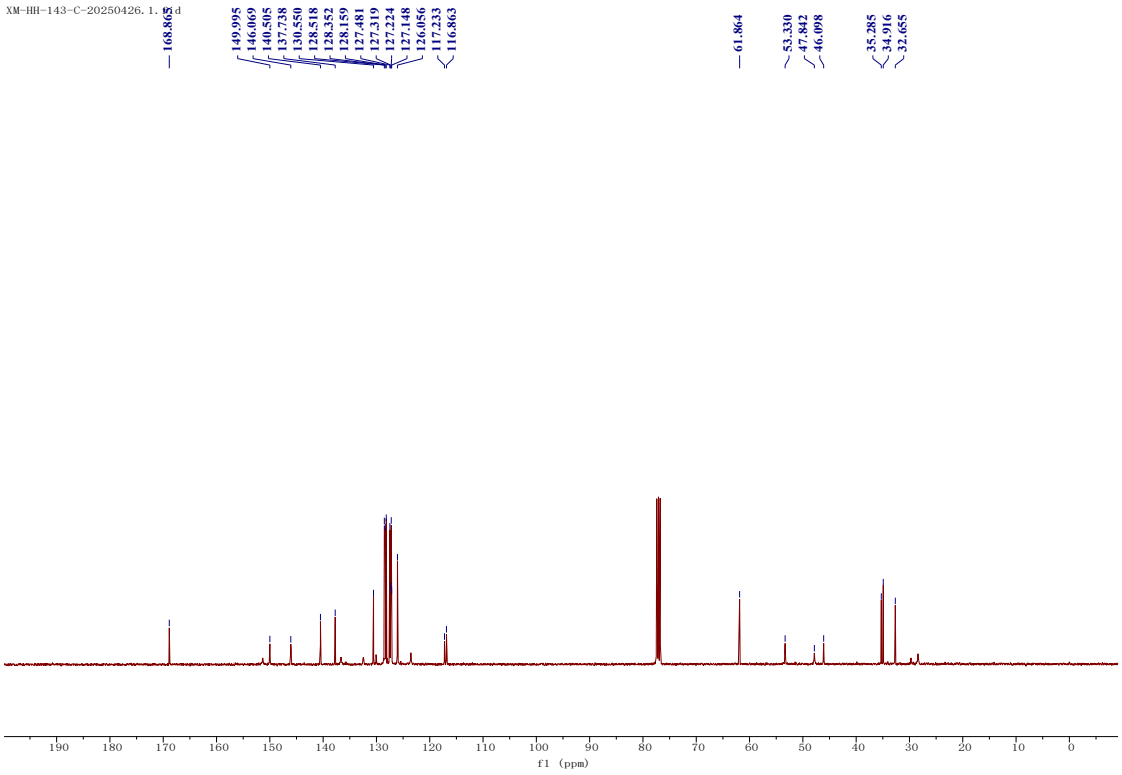
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 13



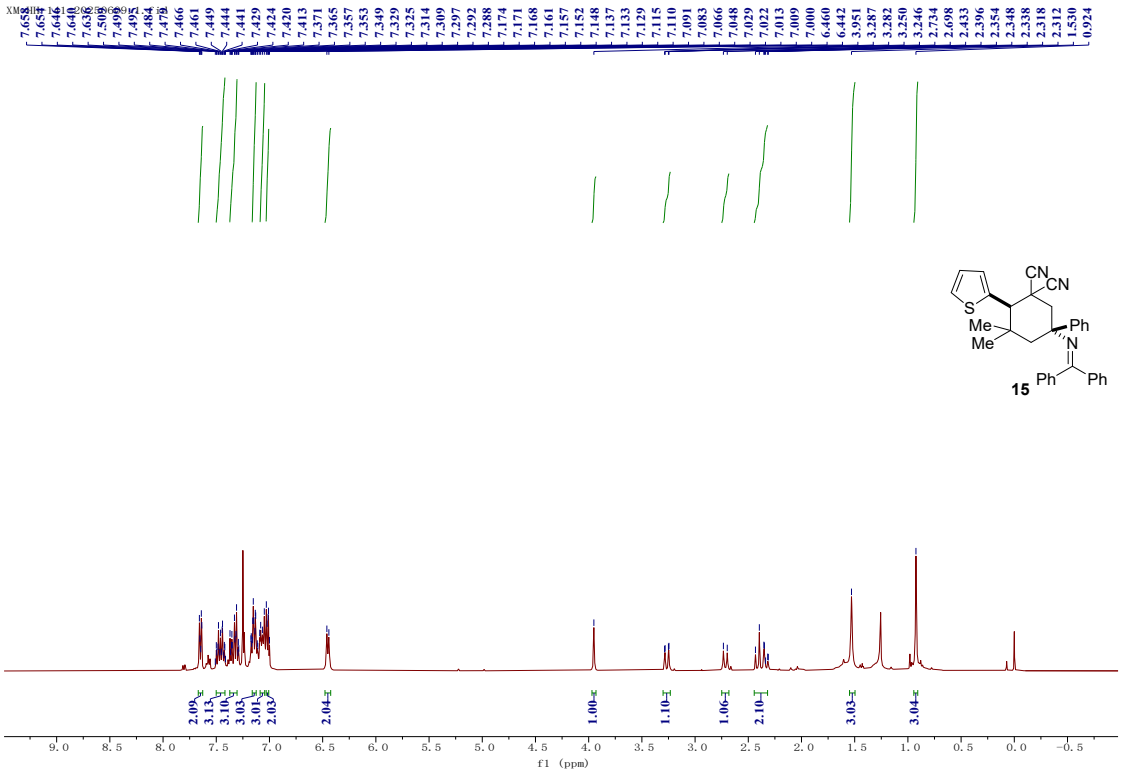
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 14



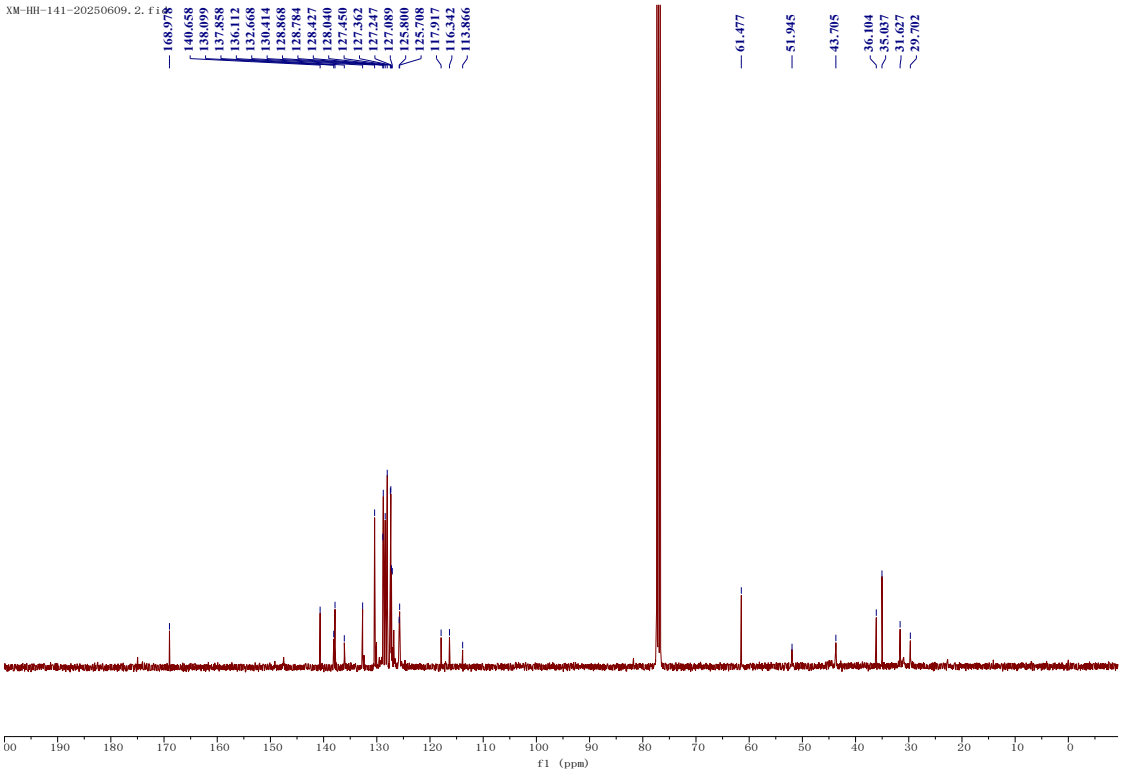
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 14



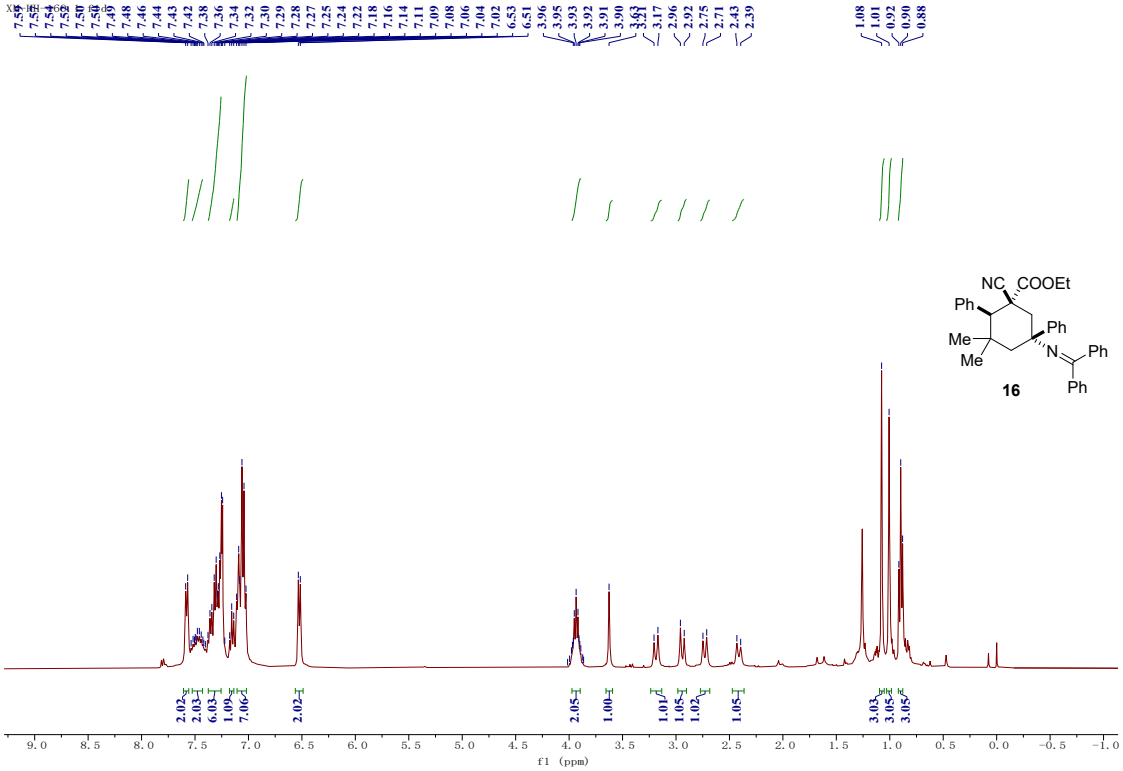
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 15



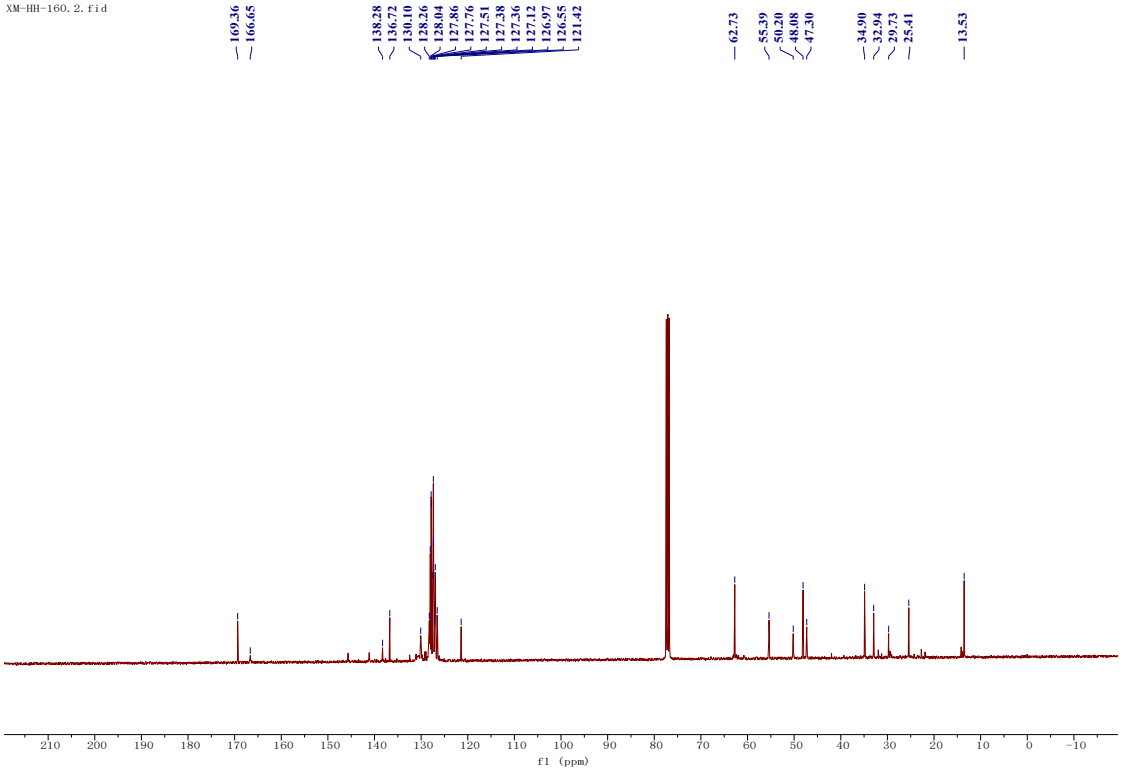
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 15



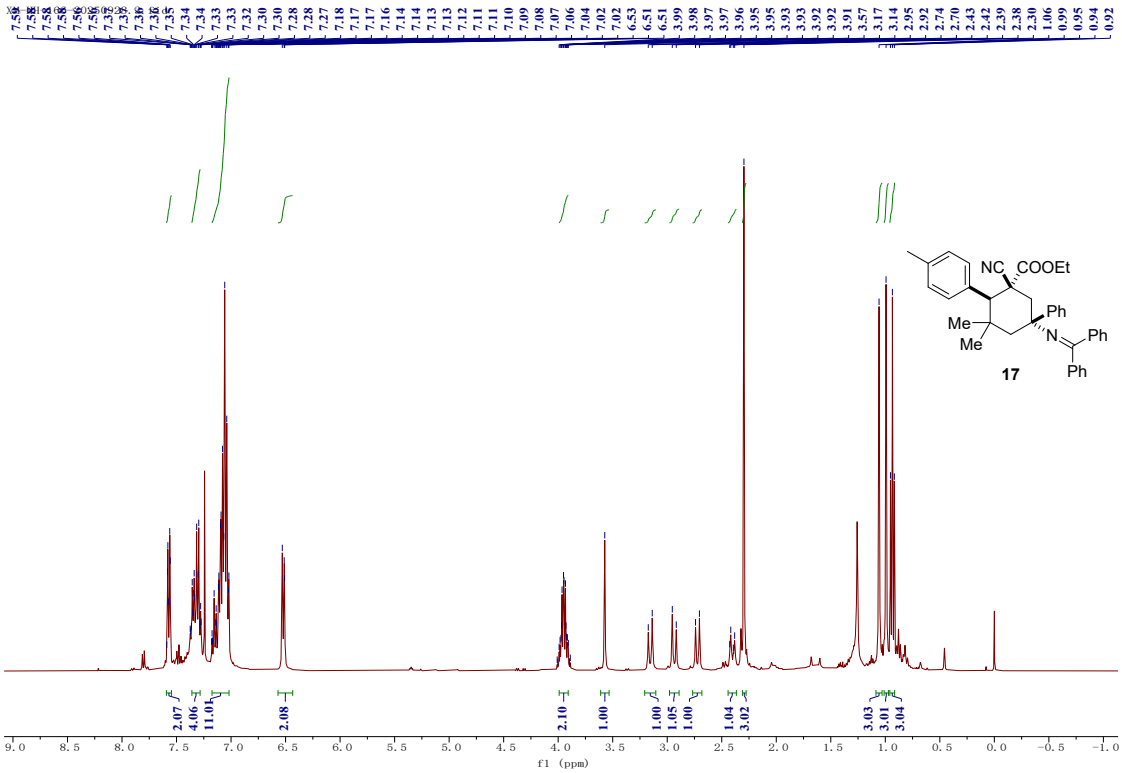
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 16



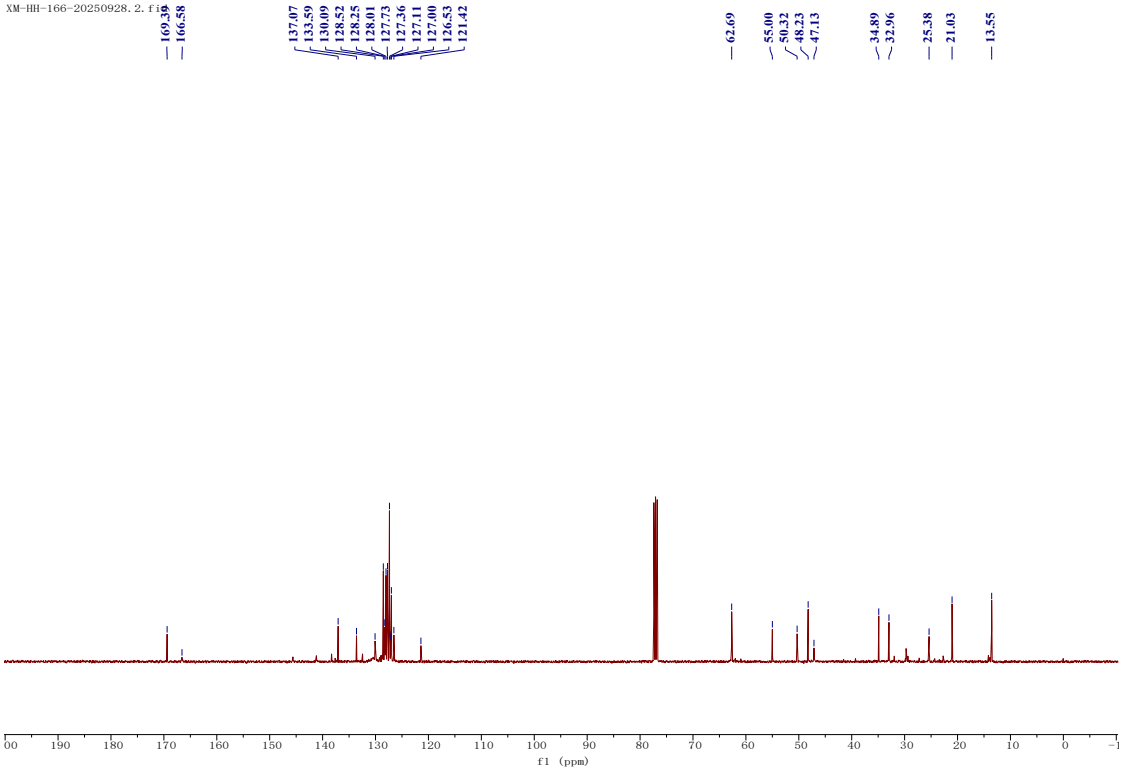
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 16



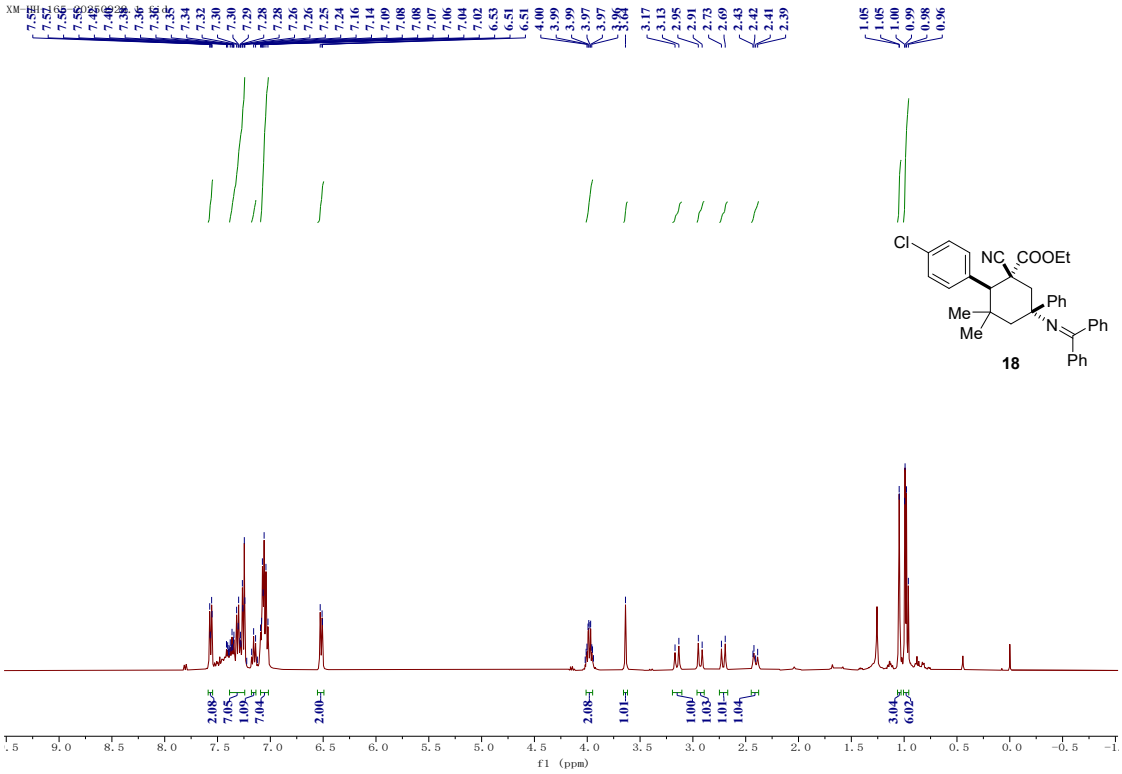
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 17



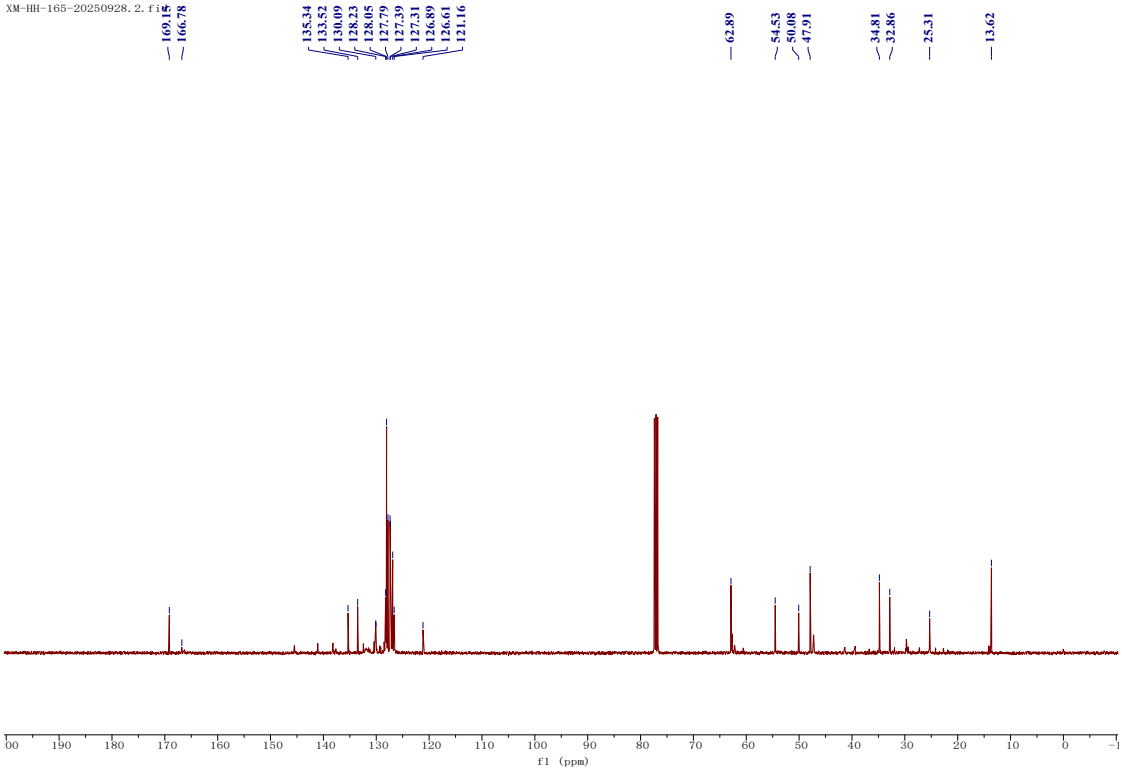
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 17



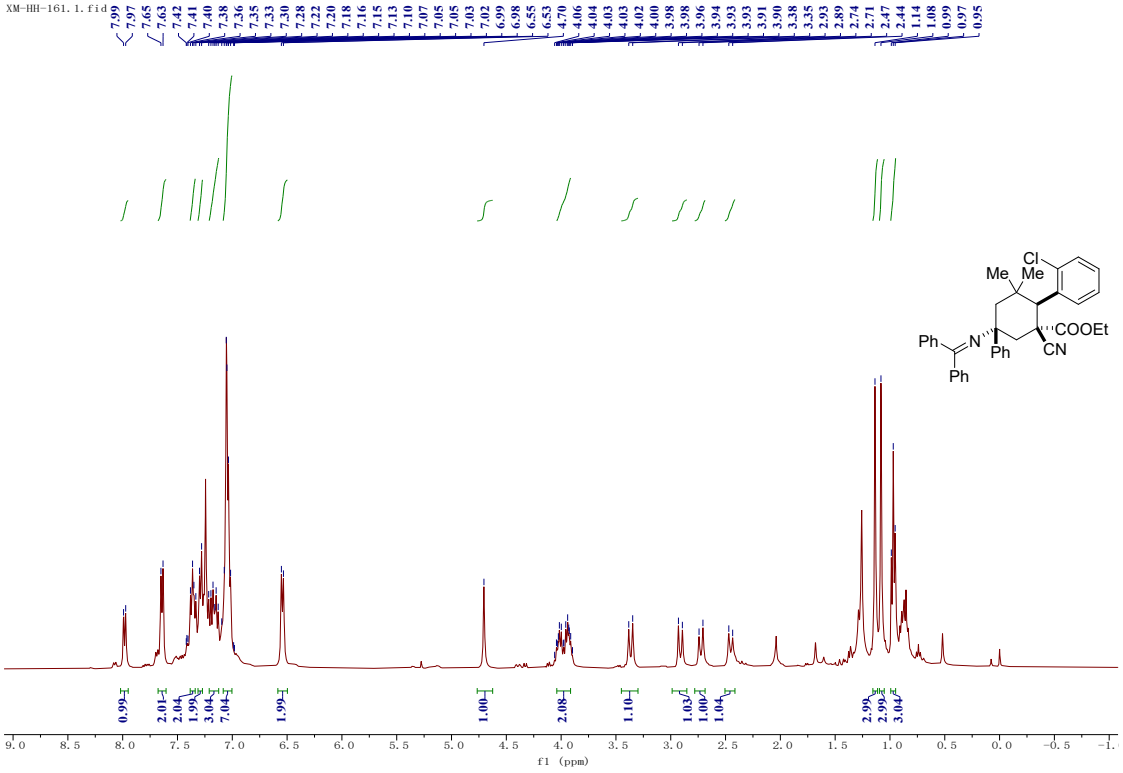
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 18



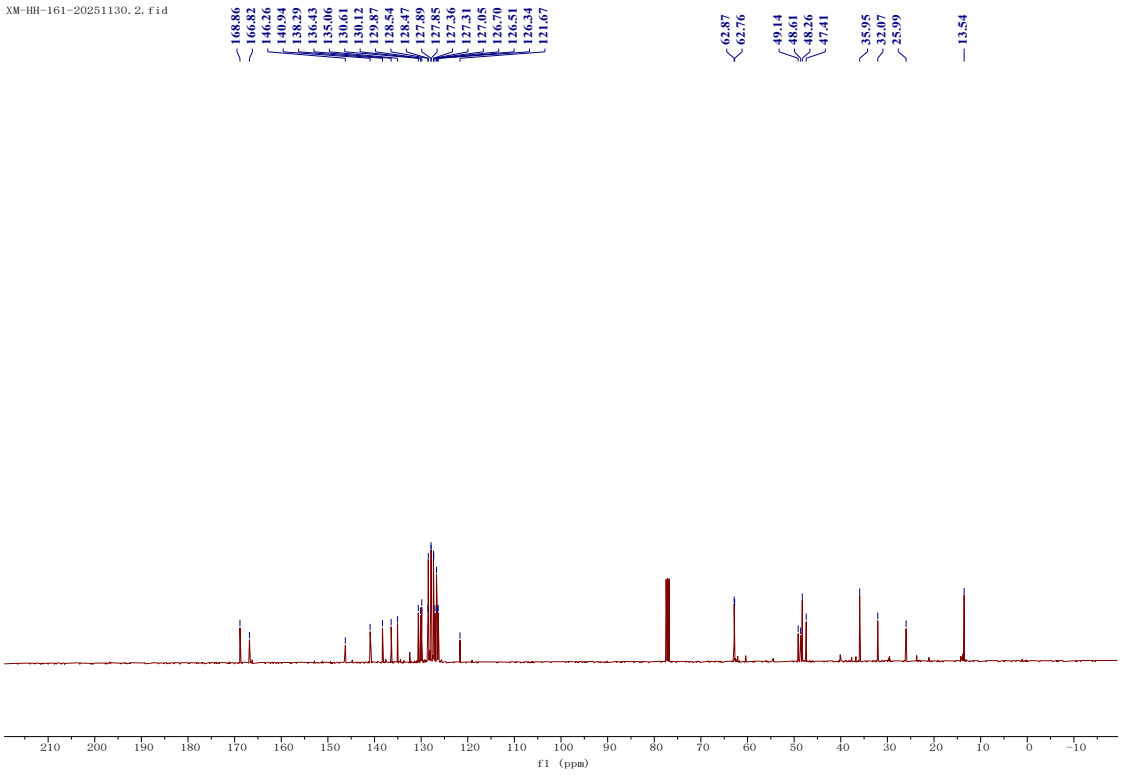
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 18



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 19

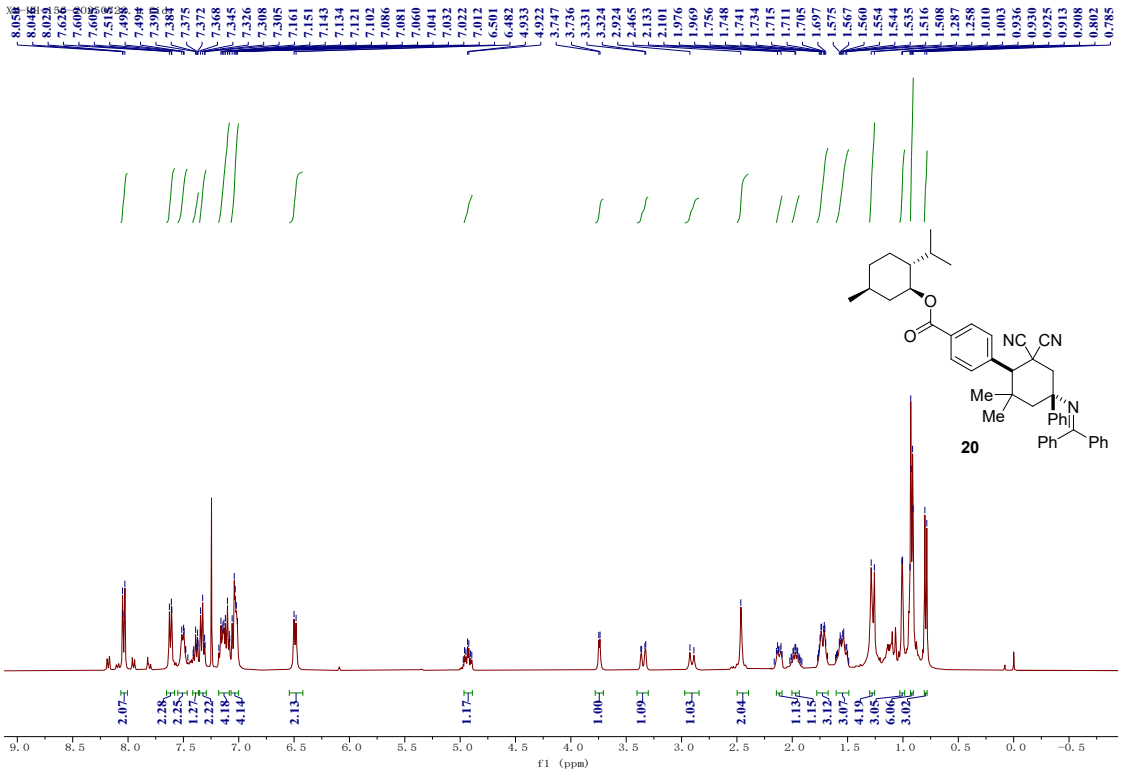


^{13}C NMR (126 MHz, $CDCl_3$) spectrum of product 19

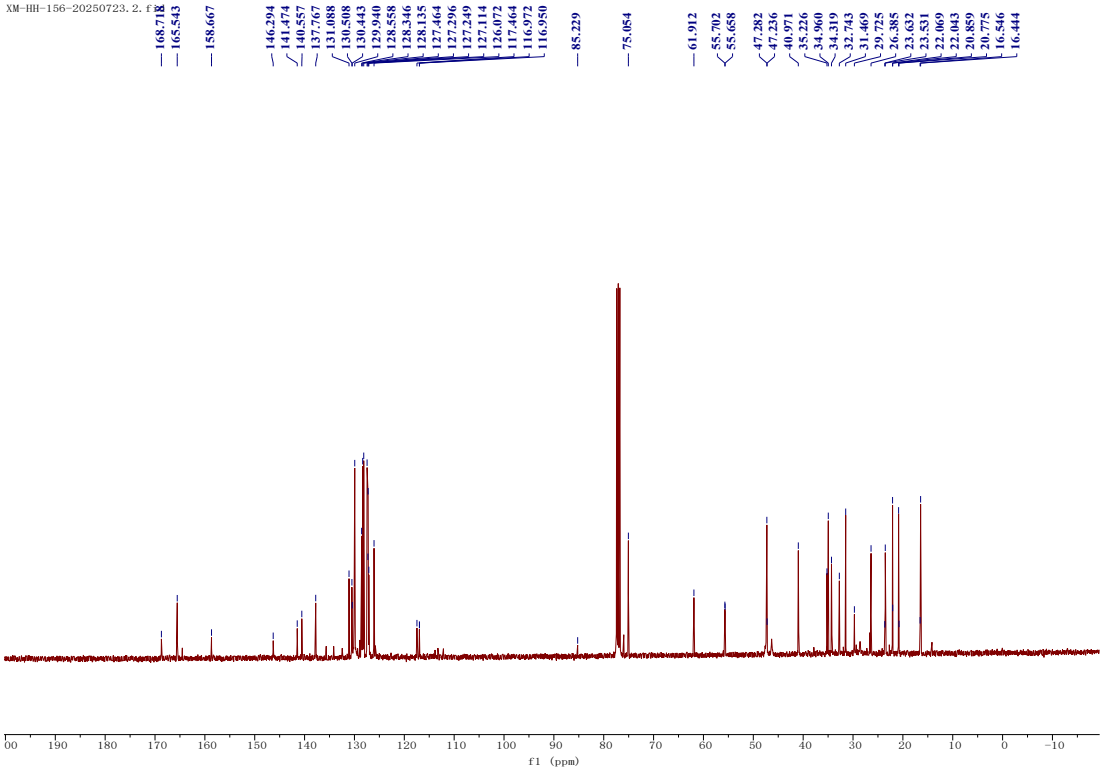


k

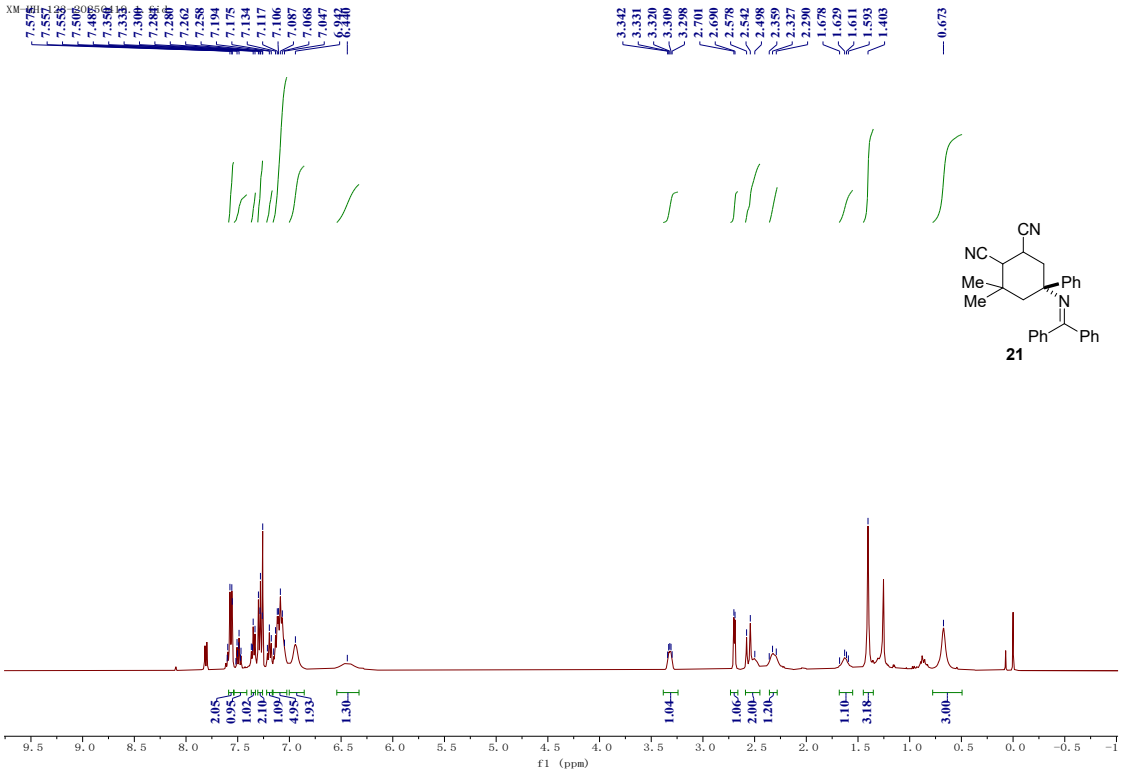
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 20



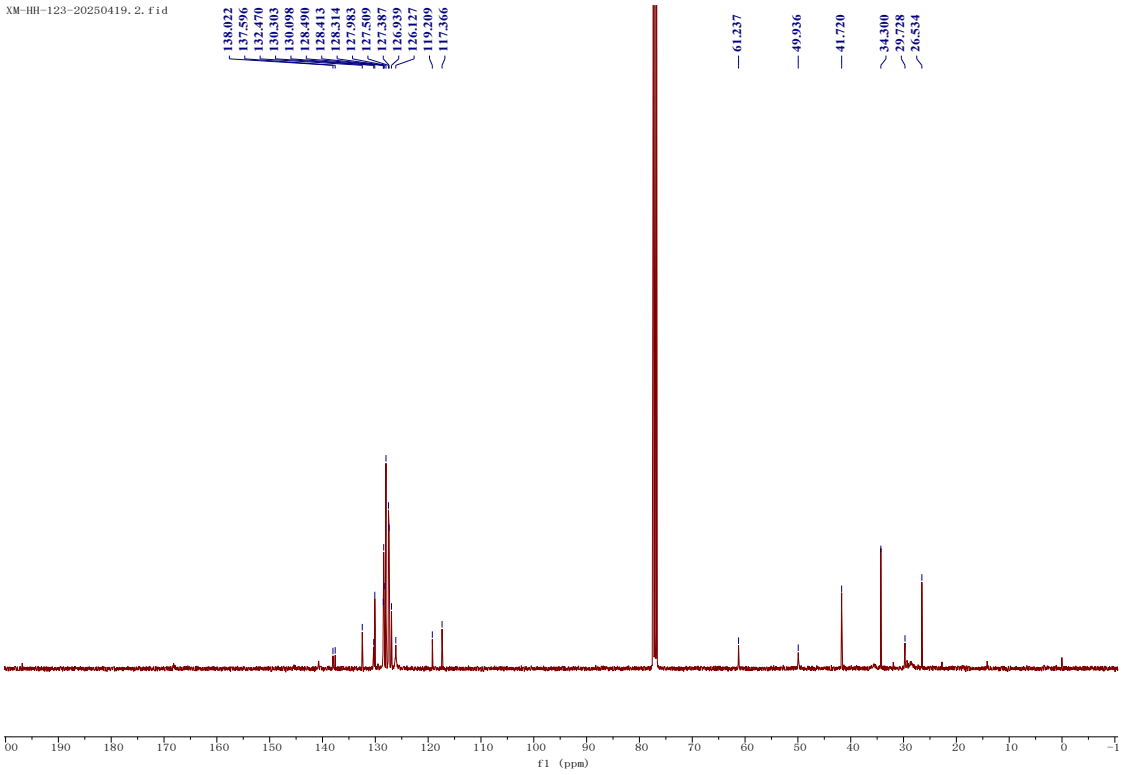
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 20



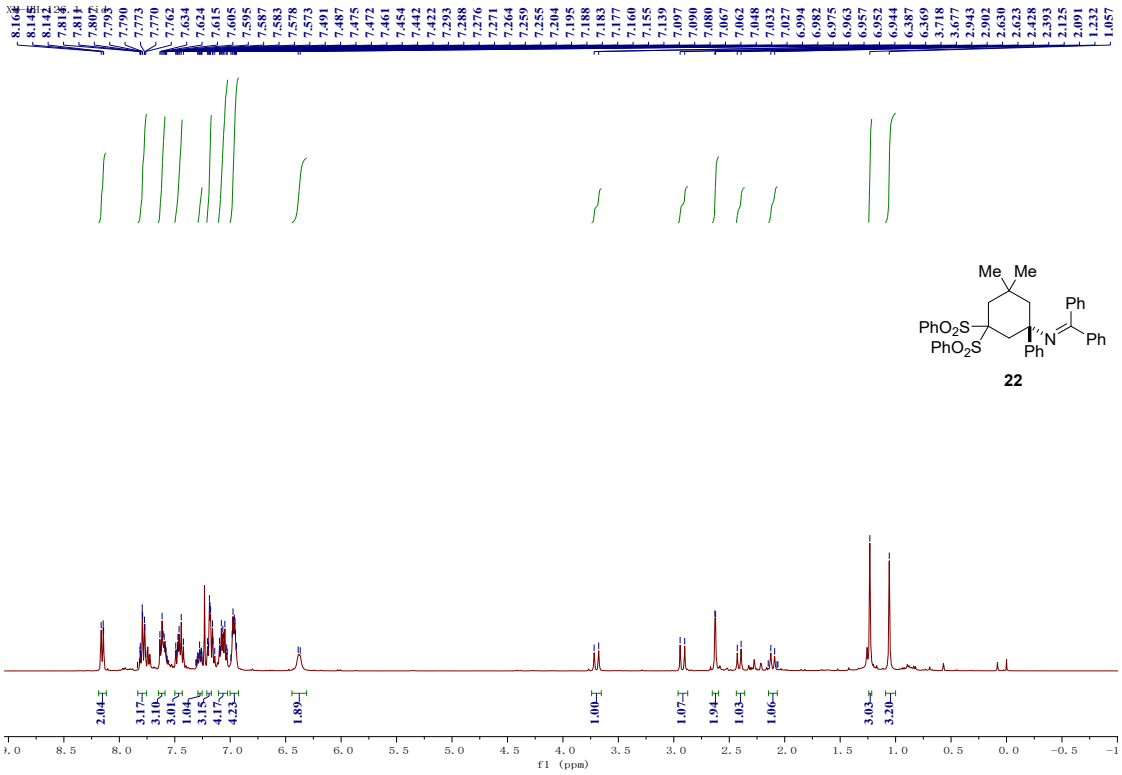
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 21



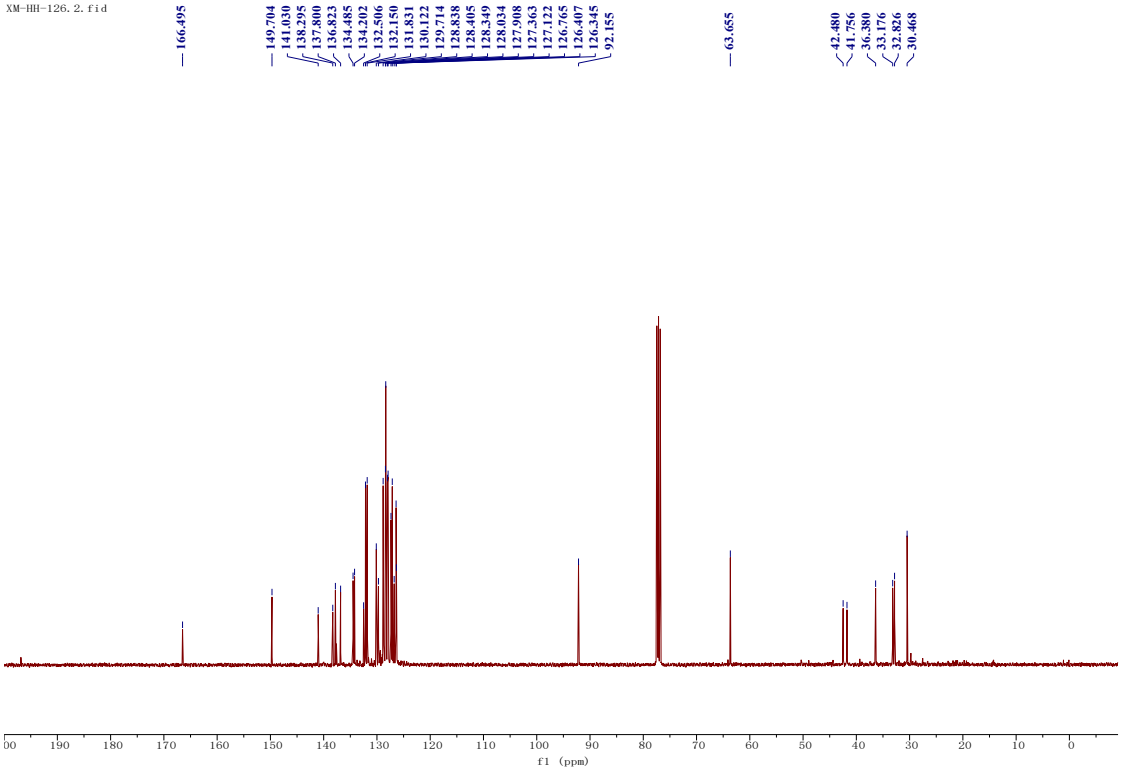
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 21



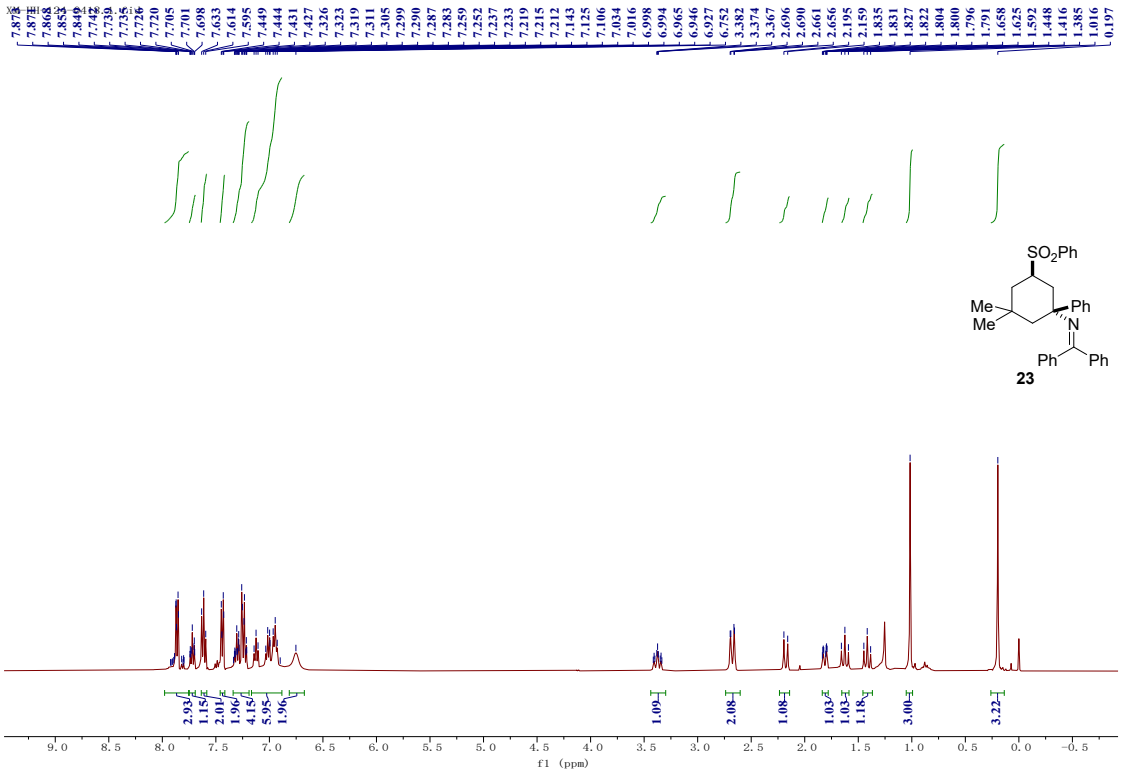
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 22



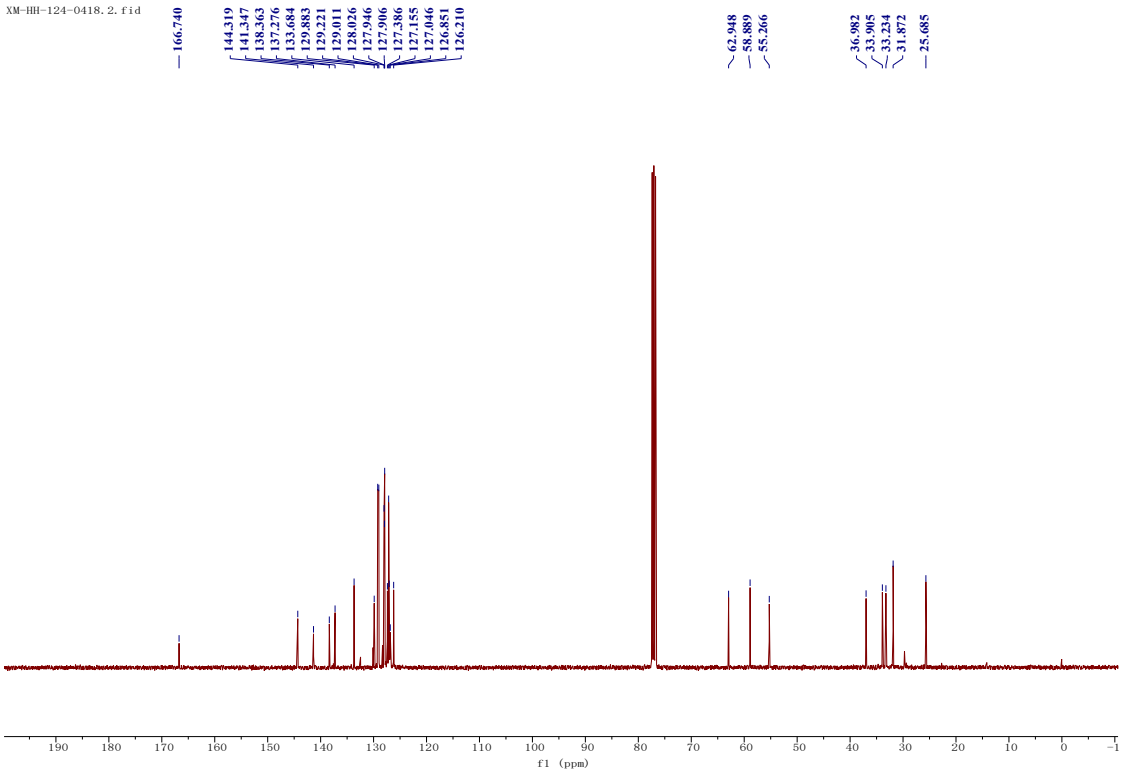
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 22



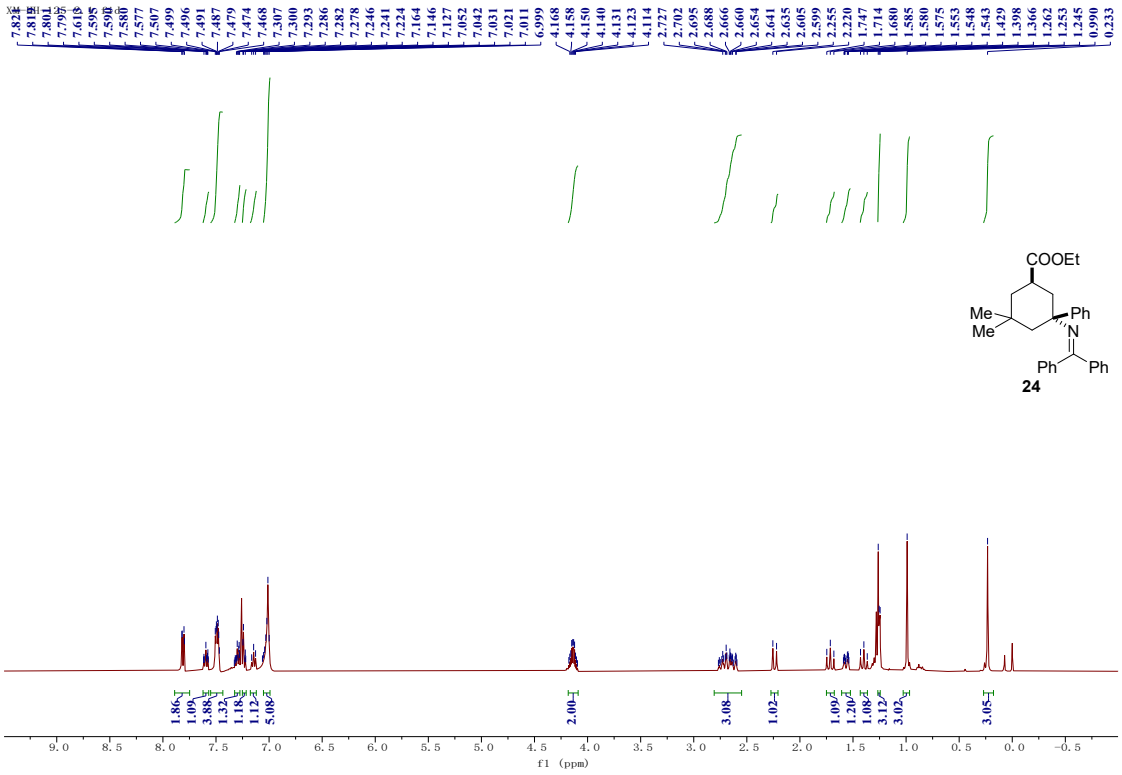
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 23



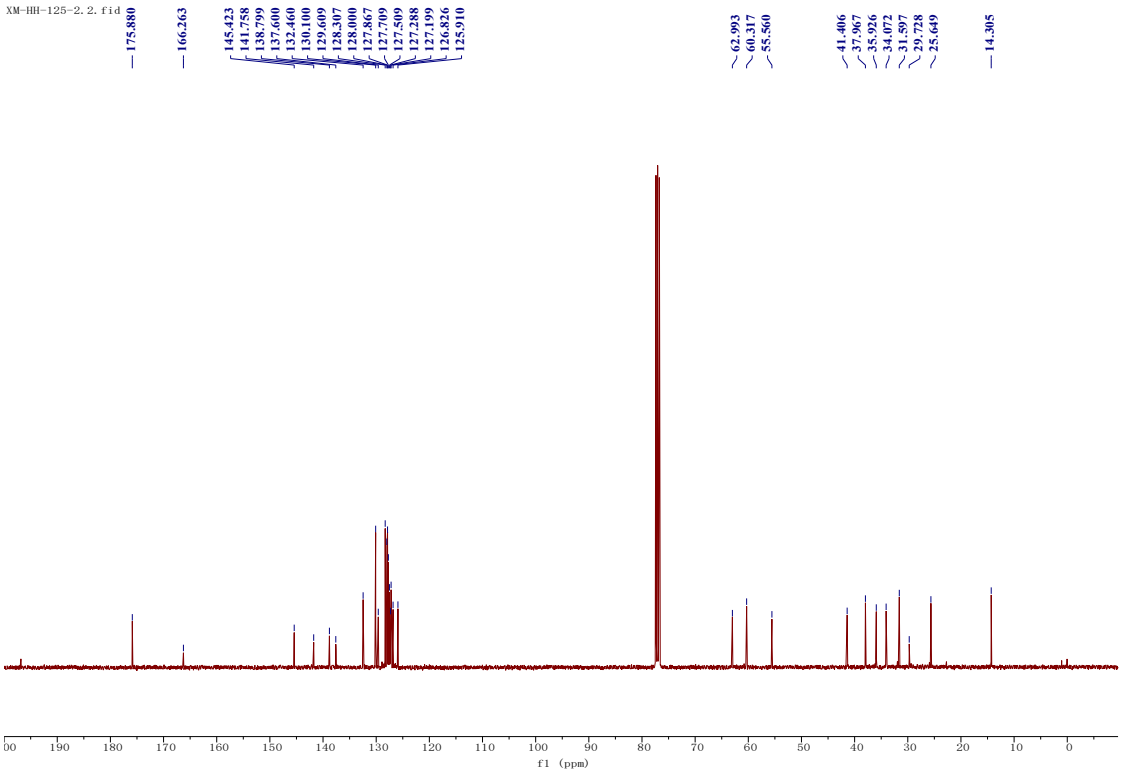
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 23



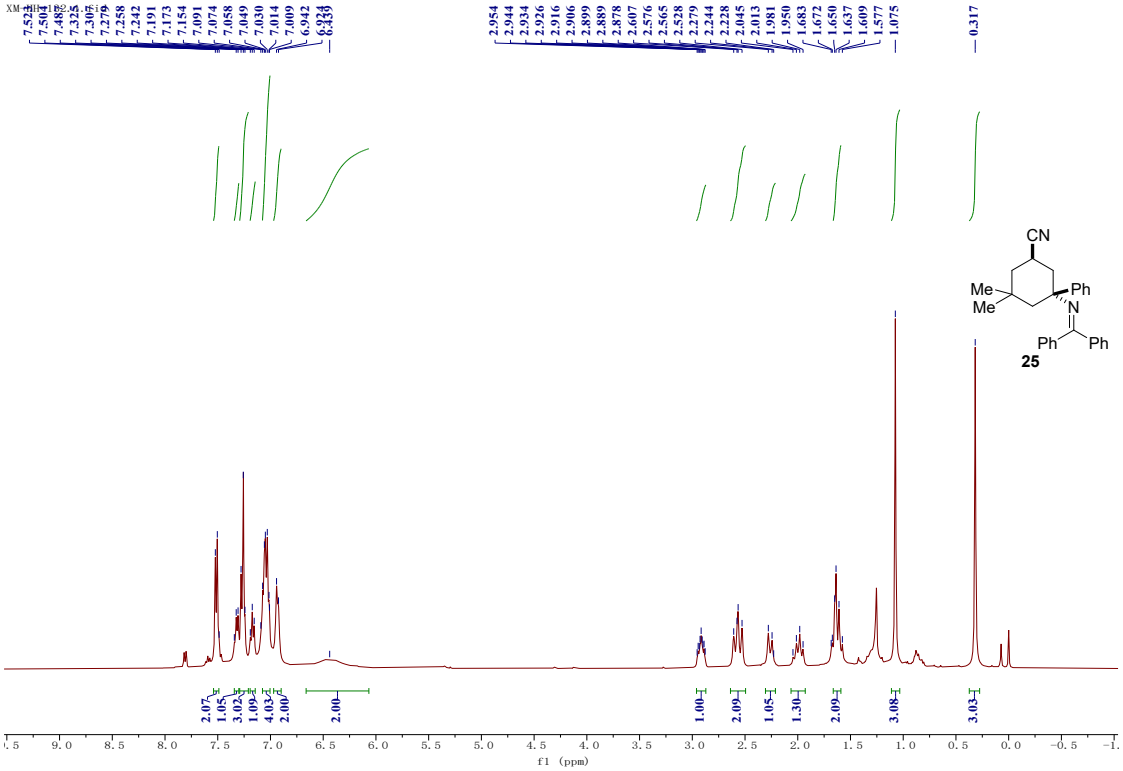
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 24



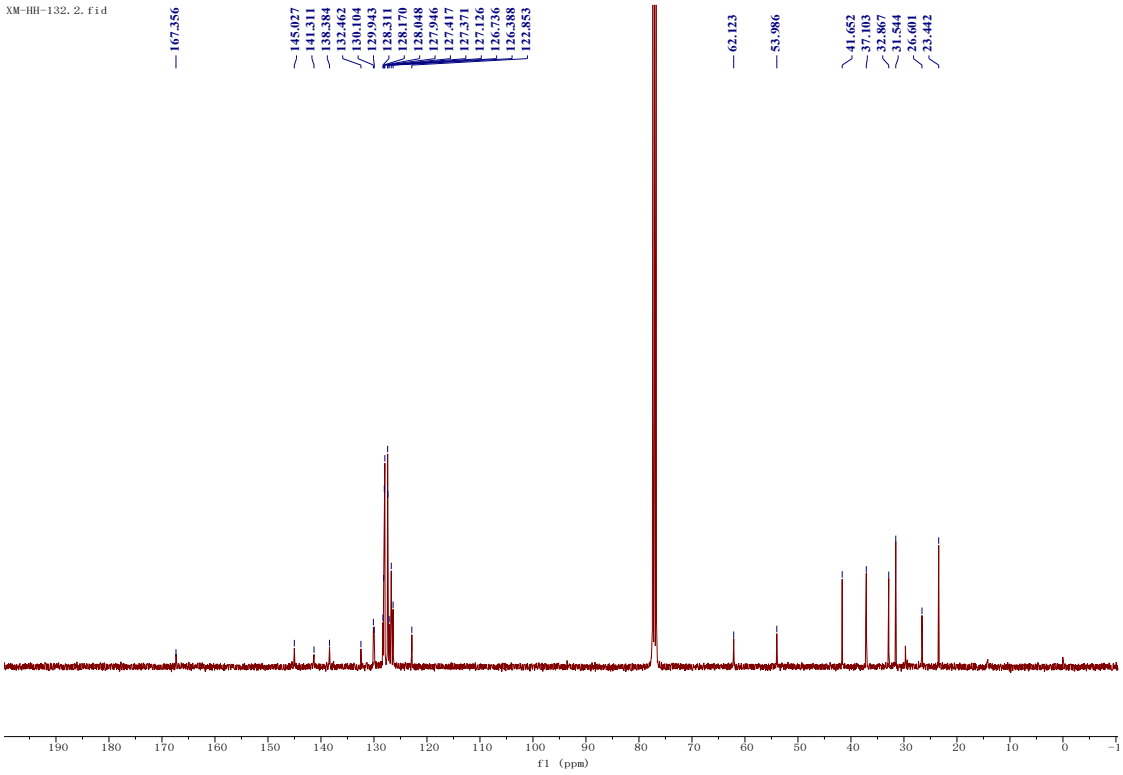
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 24



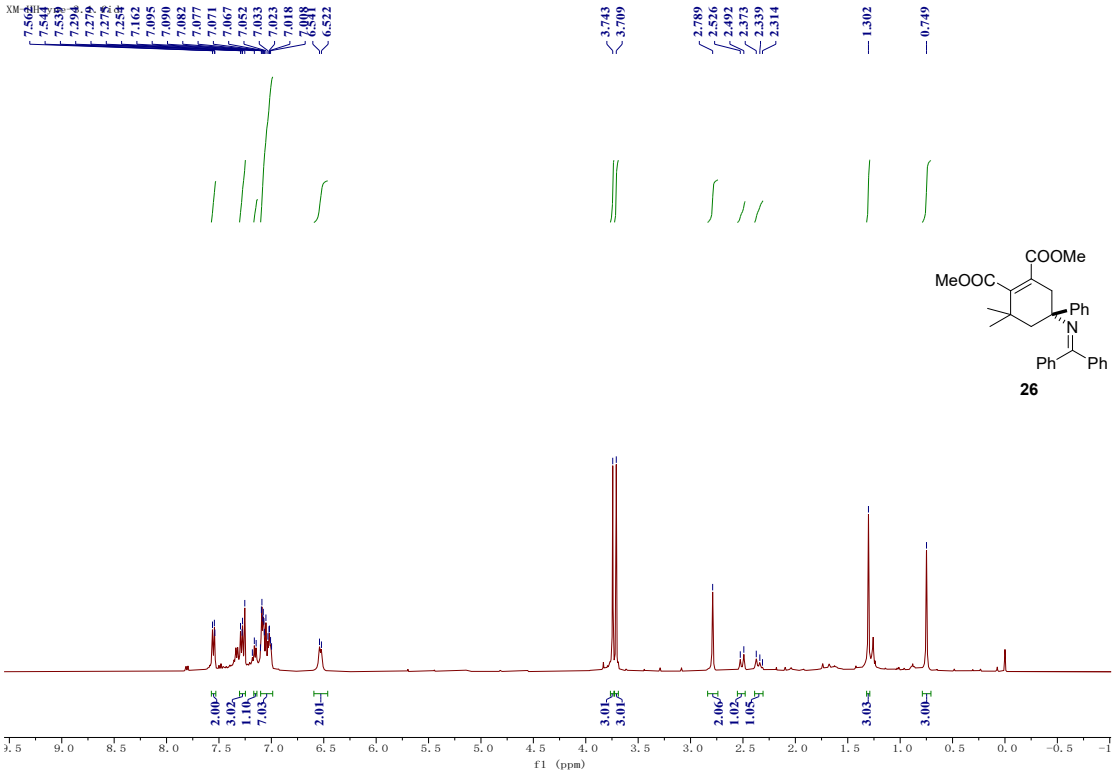
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 25



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 25

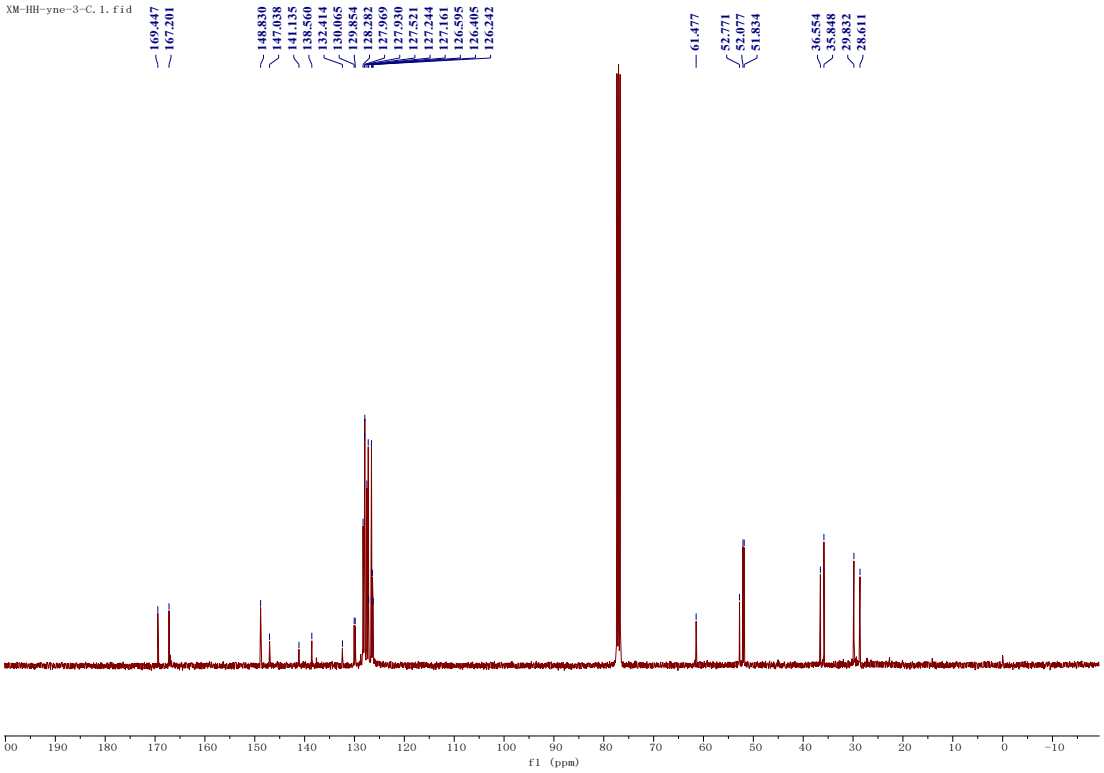


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 26

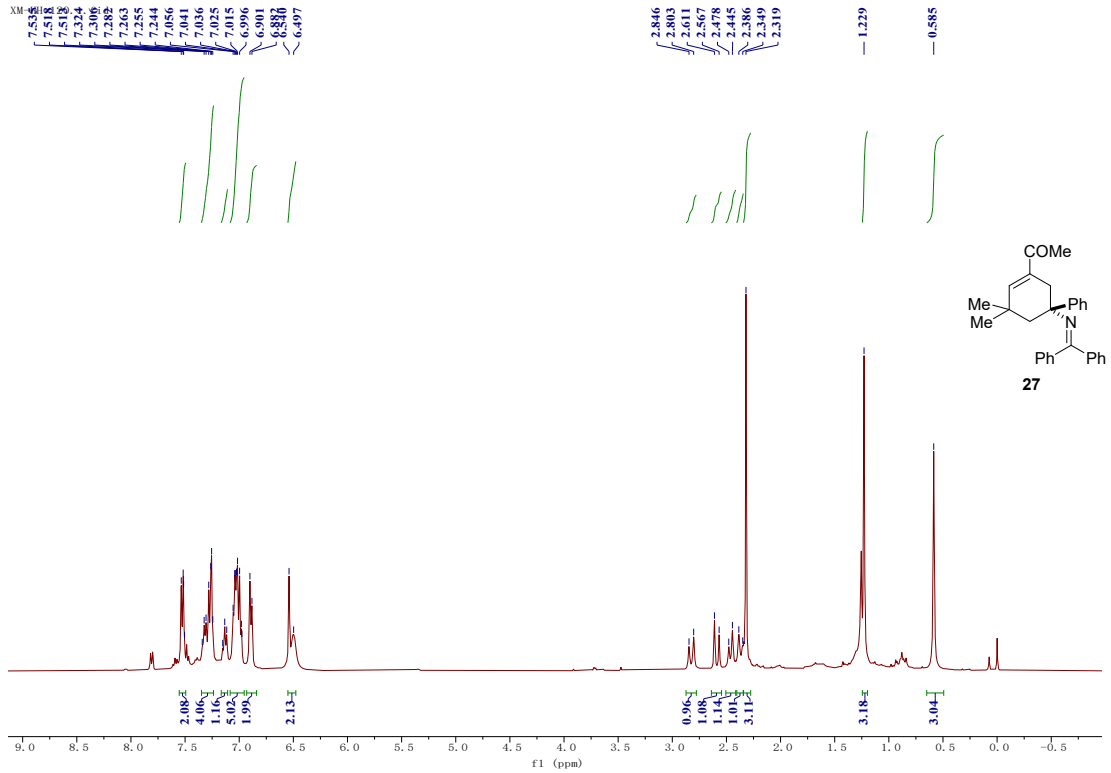


26

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 26

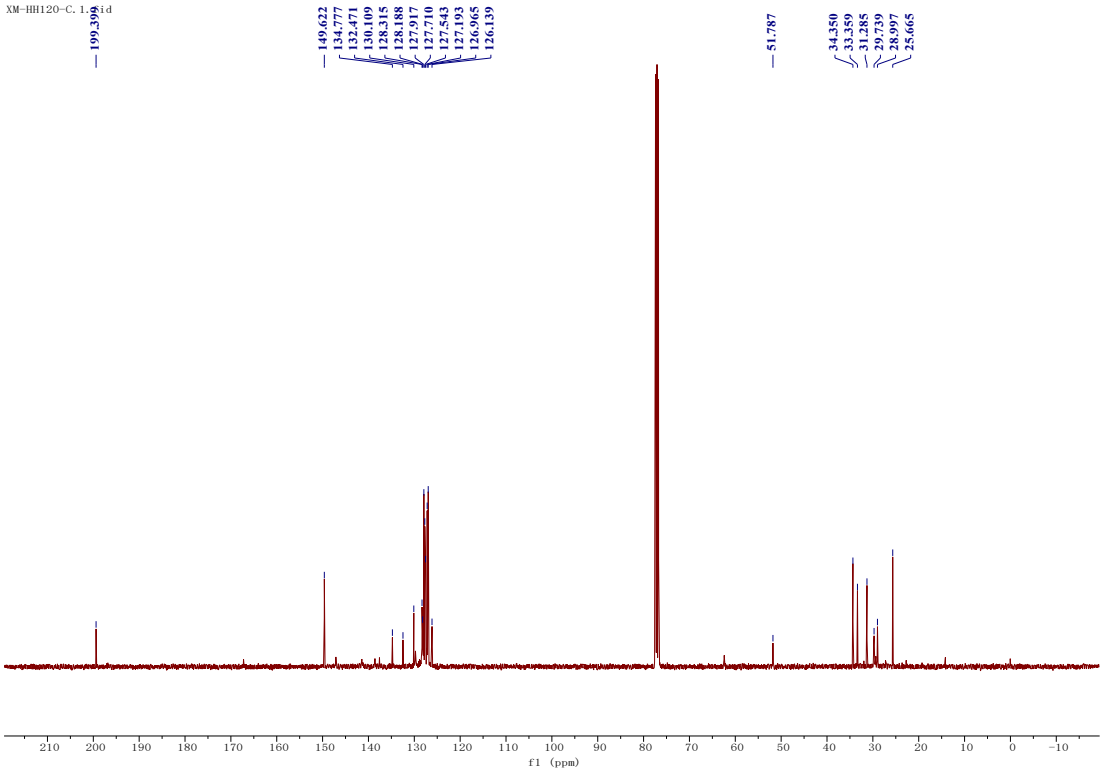


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 27

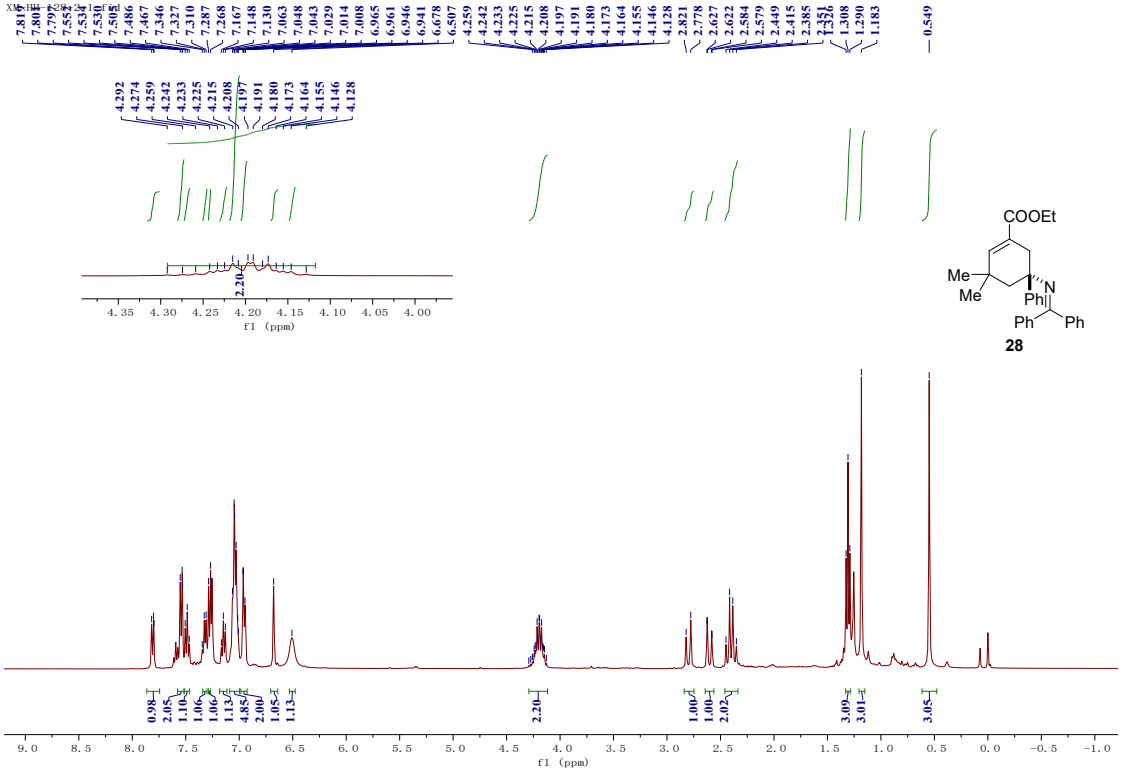


27

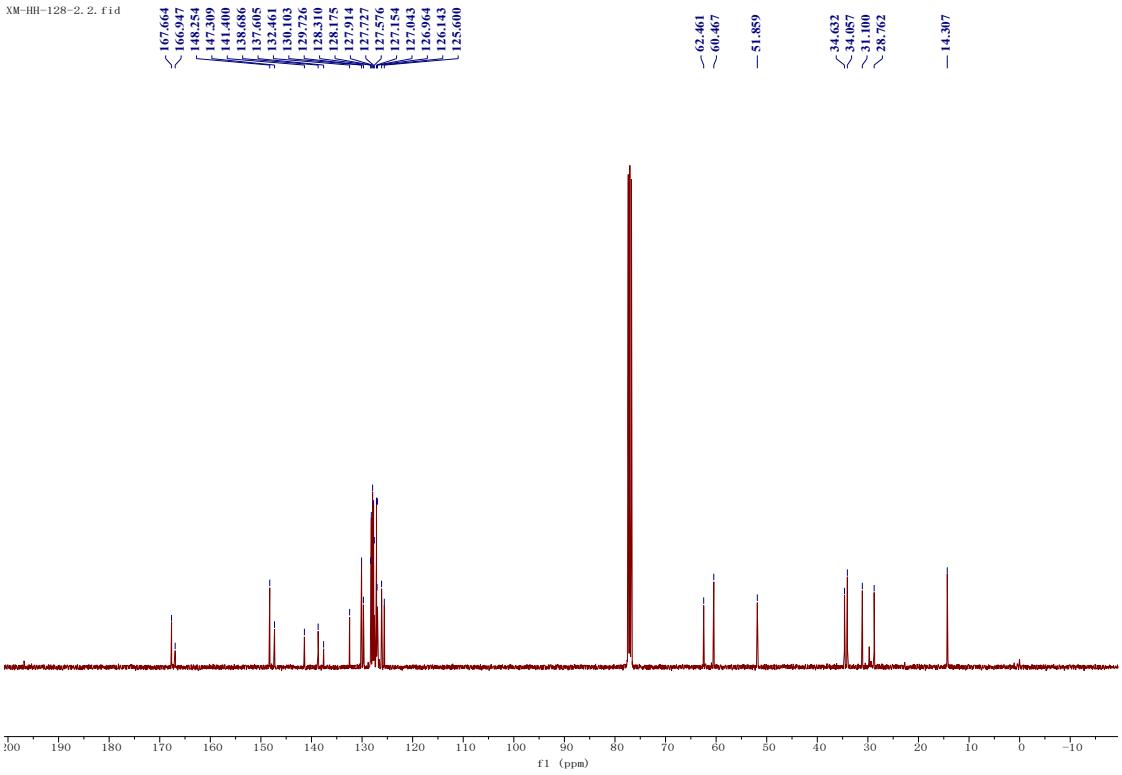
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 27



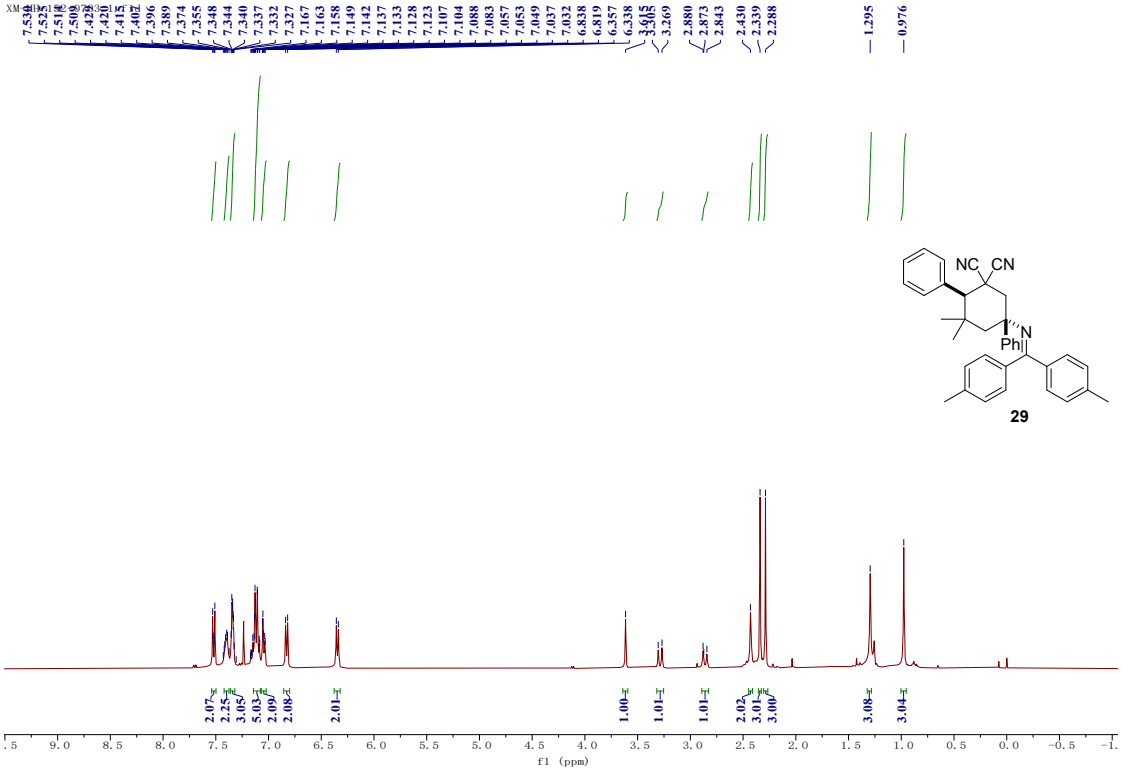
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 28



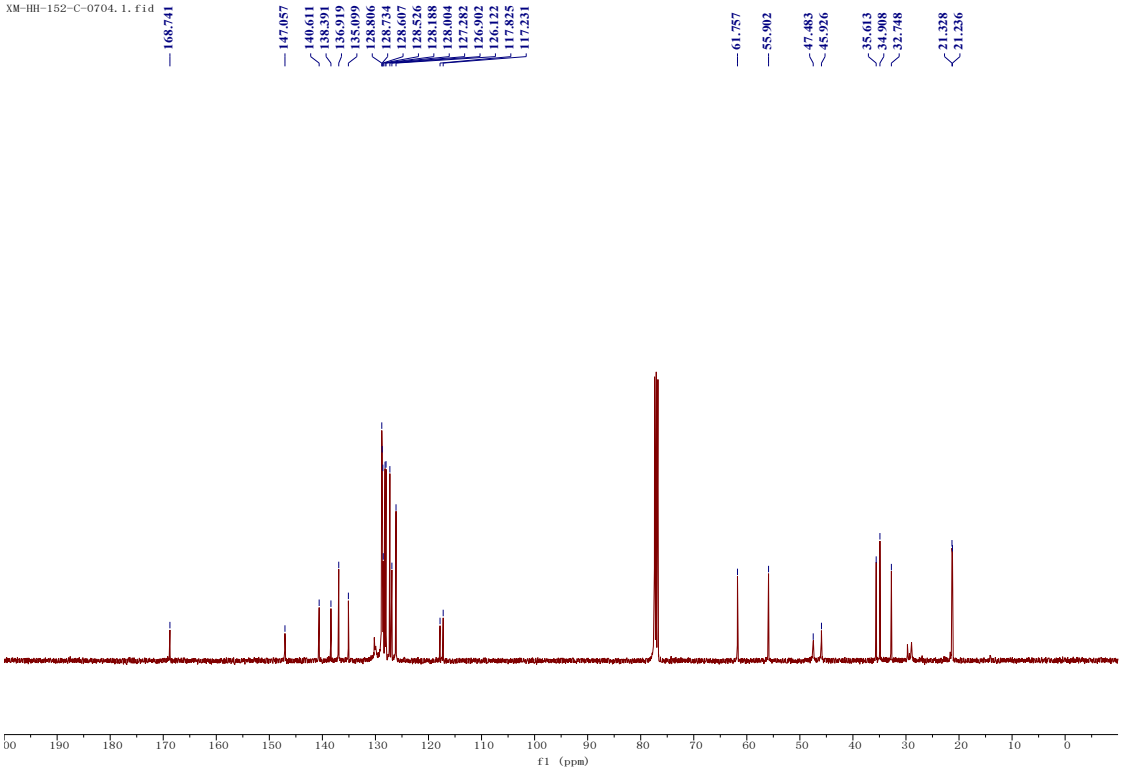
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 28



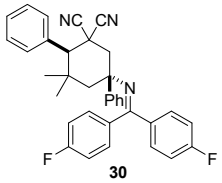
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 29



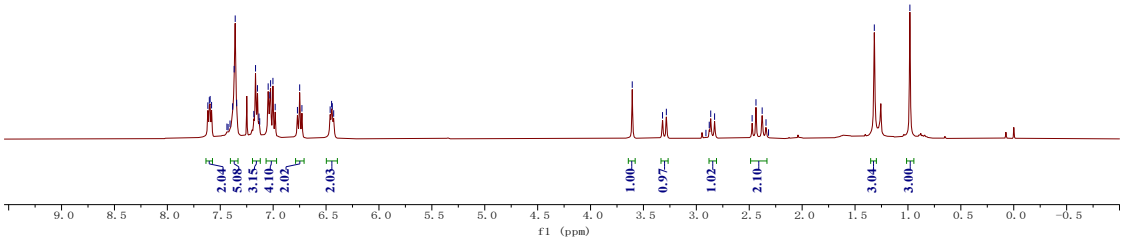
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 29



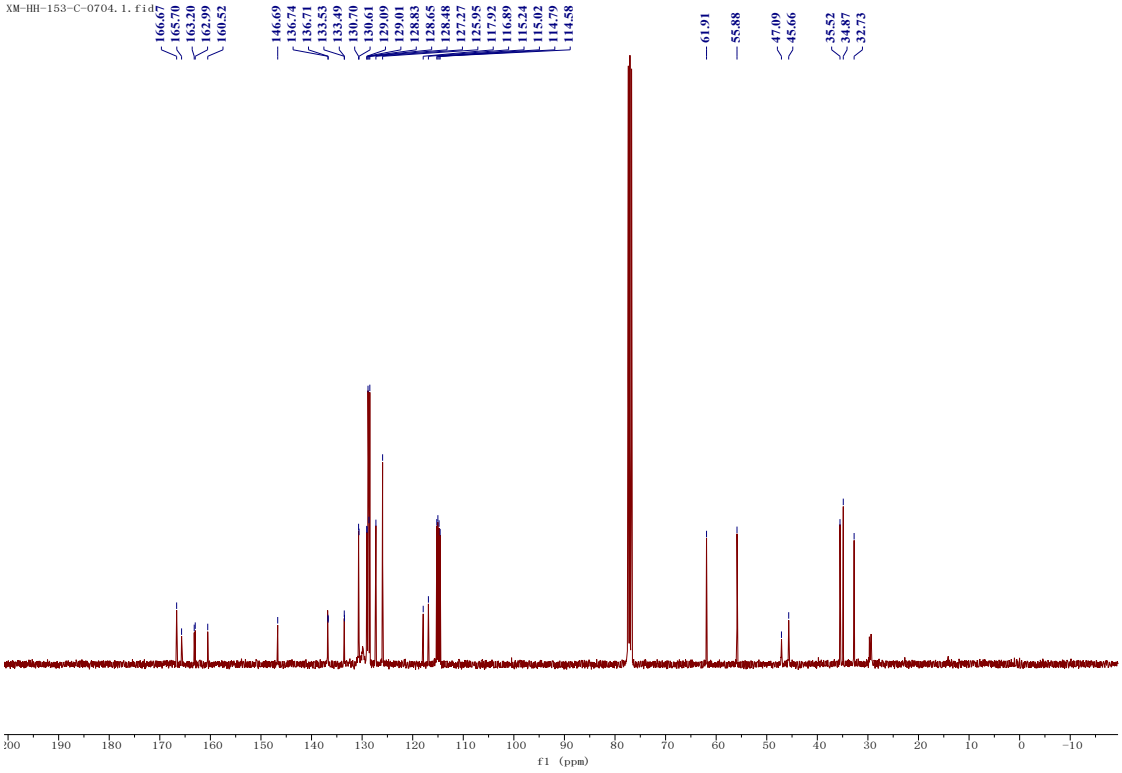
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 30



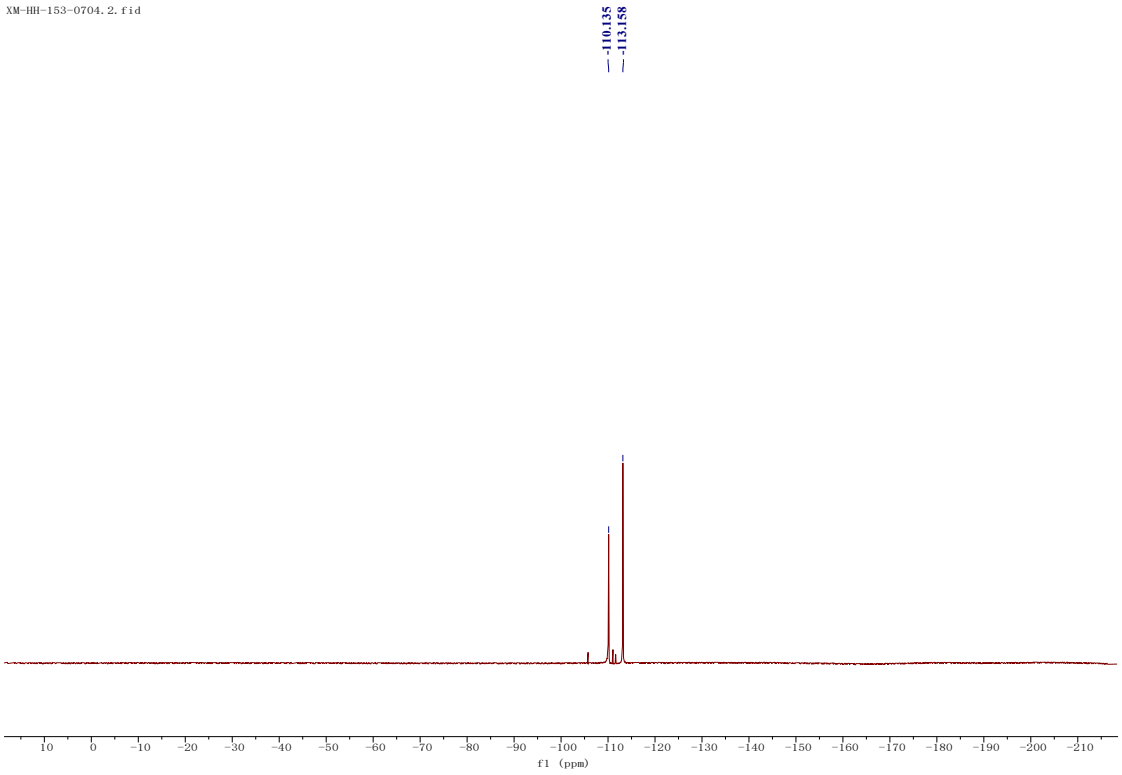
30



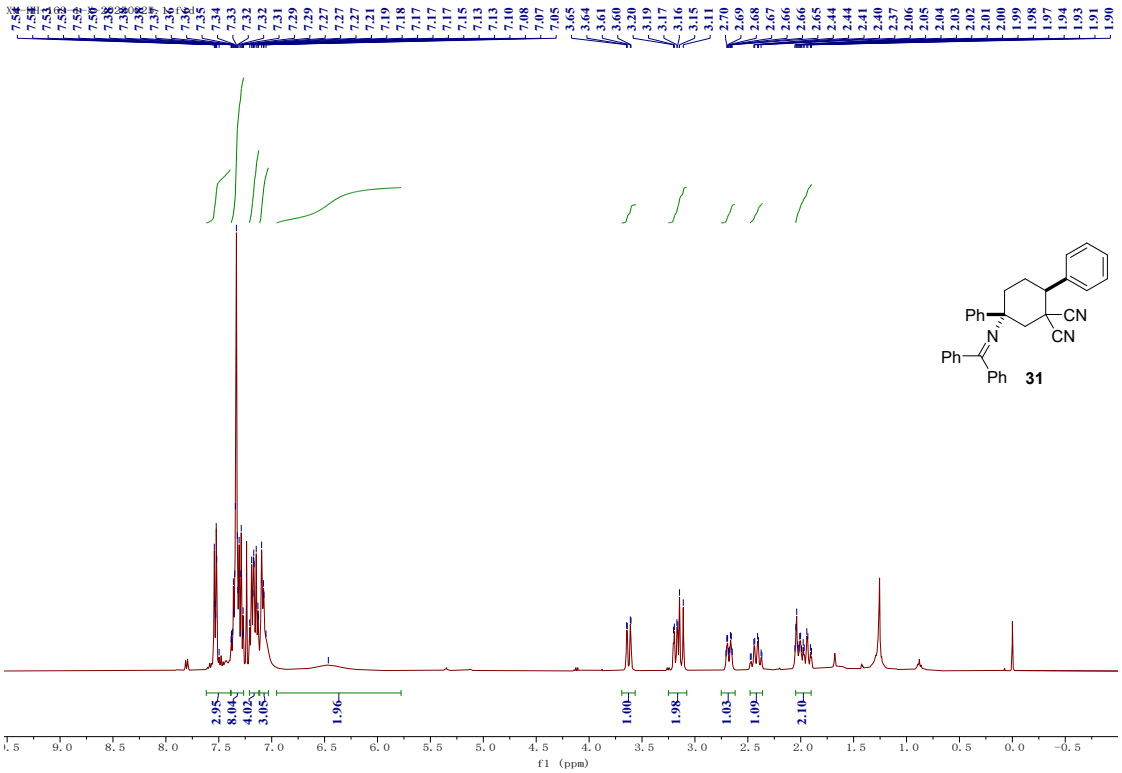
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 30



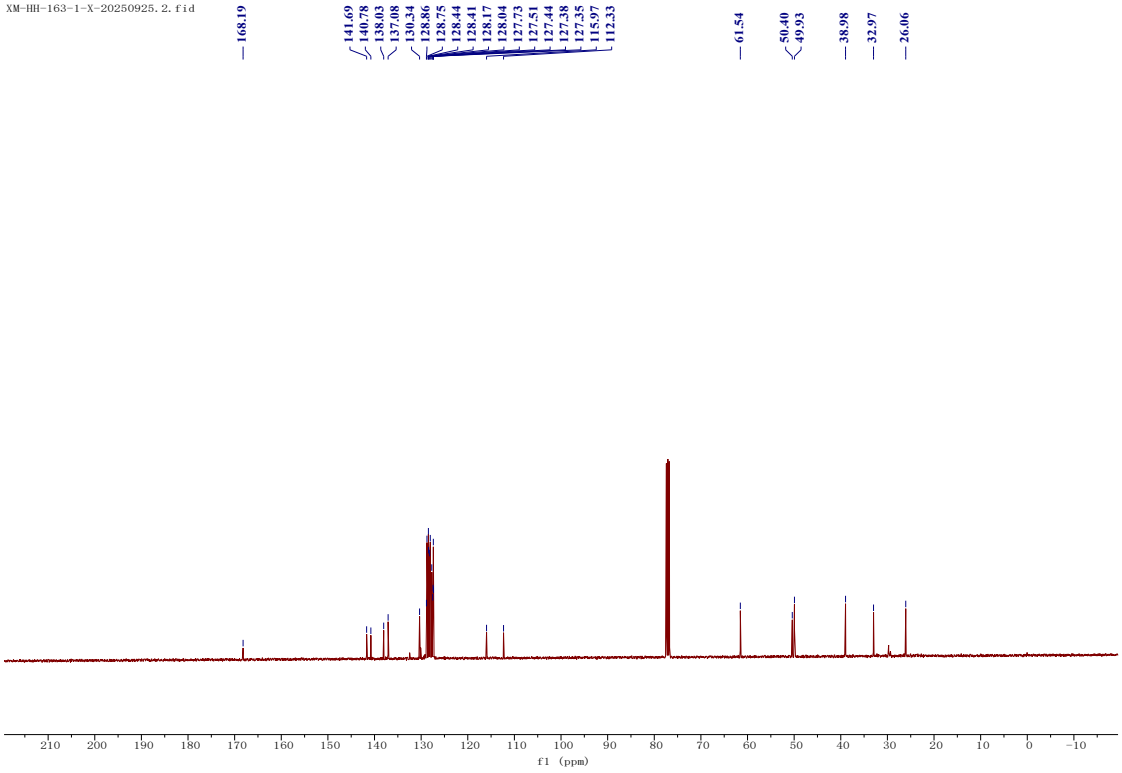
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 30



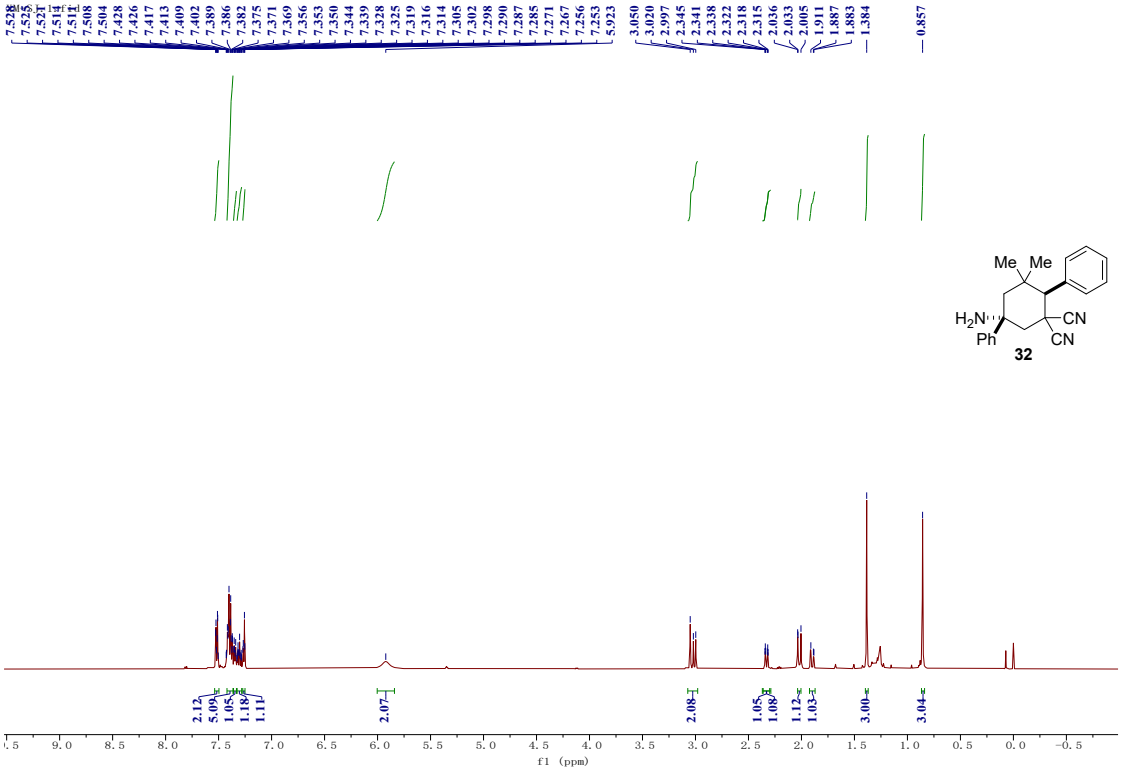
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product 31



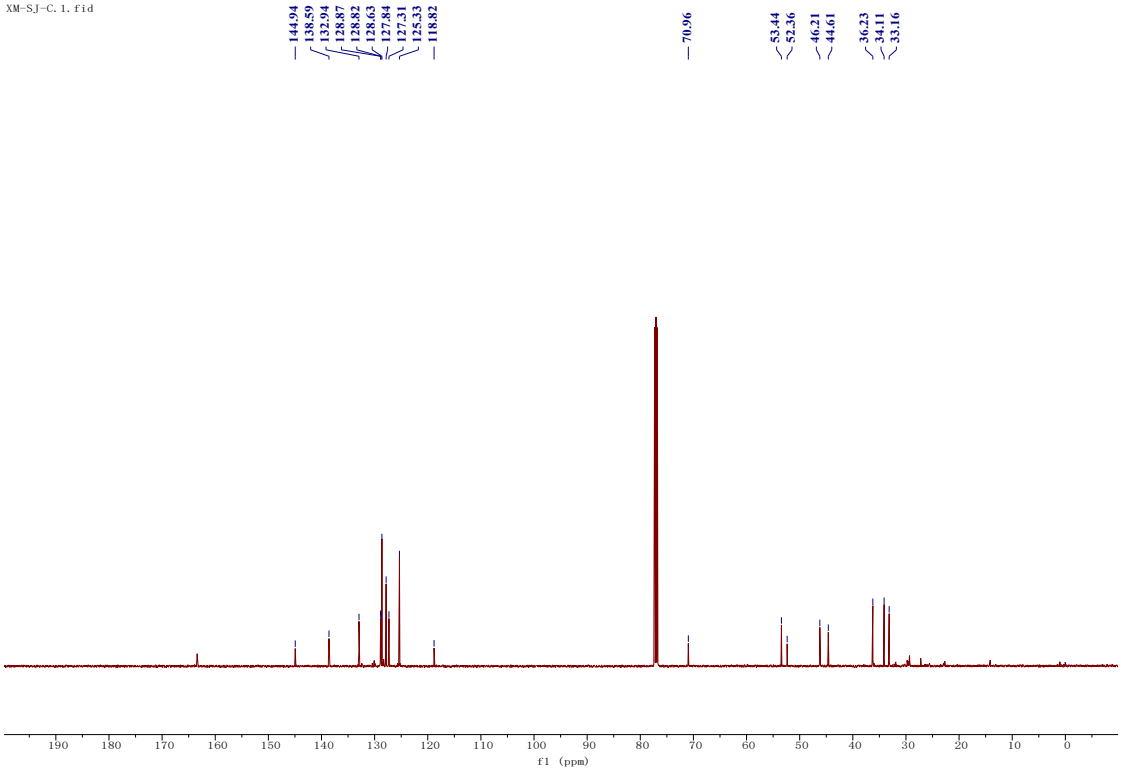
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 31



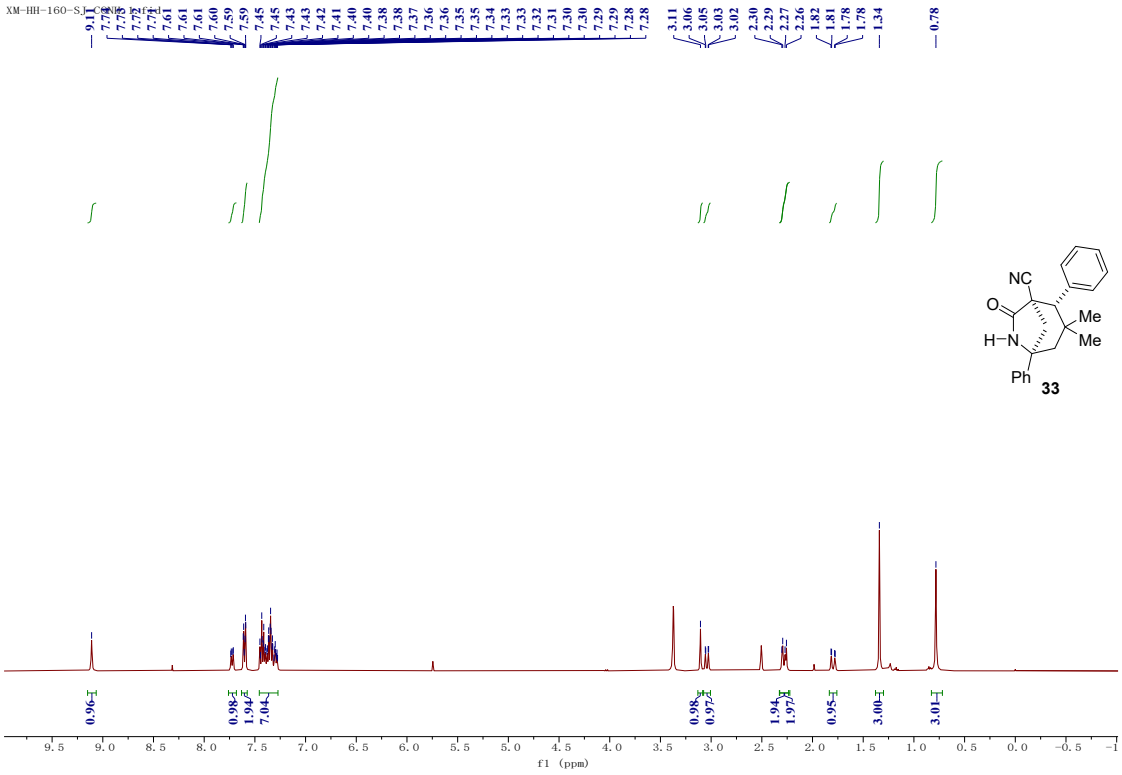
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of product 32



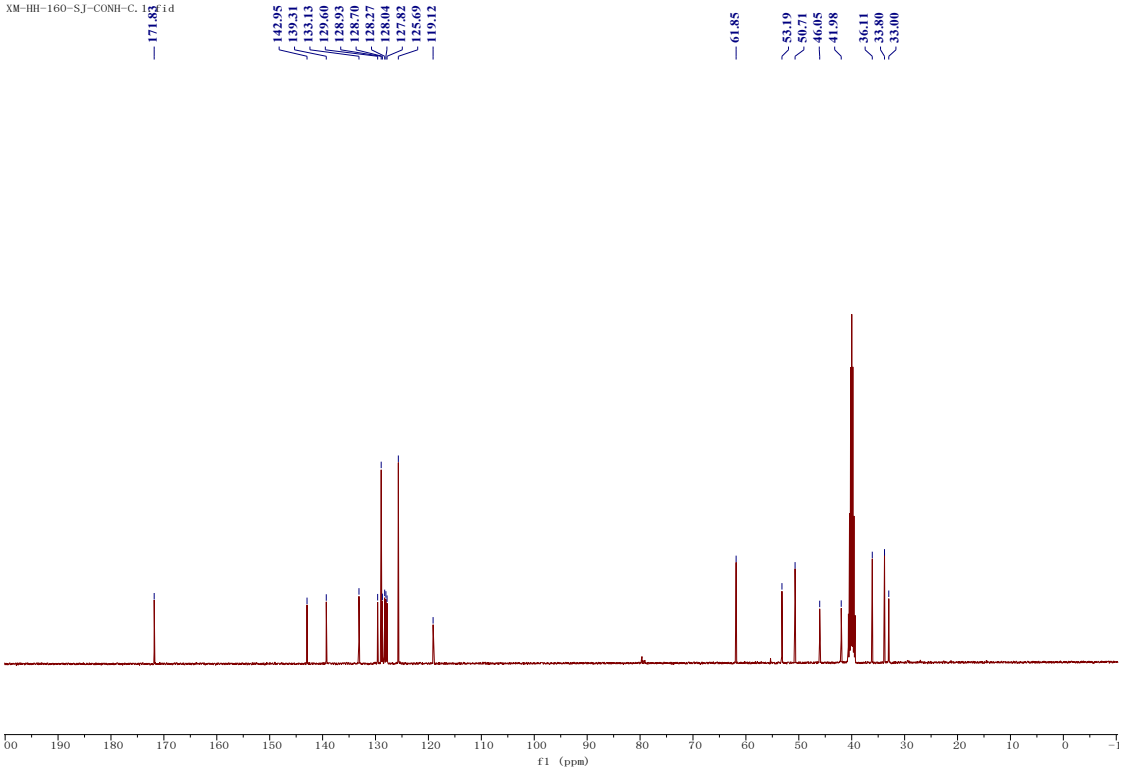
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of product 32



^{1}H NMR (400 MHz, DMSO-d_6) spectrum of product 33



^{13}C NMR (100 MHz, DMSO-d_6) spectrum of product 33



7. X-ray Crystallographic Data of Compounds

7.1 Data of Compound 8 (CCDC: 2480481)

Crystal sample preparation and crystal structure determination

To a 10 mL vial, the corresponding samples (25.0 mg) were dissolved in 2.0 mL CH_2Cl_2, and then 1.0 mL *n*-hexane was slowly dropwise into the above solution. The vial, which was not screwed down, was carefully set in a clean place at room temperature, and wait for the crystals to precipitate. The crystals were confirmed by X-ray crystallographic.

All the measurements were obtained on a BRUKER Single Crystal X-Ray Diffractometer, Germany (model of the instrument –AXS D8 Quest System).

Specification: D8 QUEST, Photon 100 CMOS Detector, Horizontal Goniometer, Fixed Chi stage, Goniometer head manual, Ceramic Tube KFF Mo-2K-90c, two pinhole collimator (0.3/17 m rad, 0.6/17 m rad), Head turned by 90°, APEX2 w. SHELXTL S/W, Video microscope SCD, Cryostream-700plus extended range low temperature.

X-ray crystallographic analysis of compound **8** (CCDC:2480481) showing the thermal ellipsoids at 50% probability level.

```
Bond precision:   C-C = 0.0081 A          Wavelength=0.71076

Cell:             a=14.7393(5)     b=8.7872(3)         c=22.5044(8)
                  alpha=90         beta=89.995(1)      gamma=90
Temperature:      296 K

                 Calculated                Reported
Volume           2914.71(17)               2914.71(17)
Space group      P 21                      P 1 21 1
Hall group       P 2yb                     P 2yb
Moiety formula   C35 H30 Br N3             2(C35 H30 Br N3)
Sum formula      C35 H30 Br N3             C70 H60 Br2 N6
Mr               572.52                    1145.06
Dx,g cm-3        1.305                     1.305
Z                4                         2
Mu (mm-1)        1.438                     1.438
F000             1184.0                    1184.0
F000'            1183.21
h,k,lmax         17,10,26                  17,10,26
Nref             10331[ 5536]              10020
Tmin,Tmax                                  0.641,0.745
Tmin'

Correction method= # Reported T Limits: Tmin=0.641 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.81/0.97        Theta(max)= 25.037

R(reflections)= 0.0406( 6315)                    wR2(reflections)=
                                                 0.0818( 10020)
S = 0.996                  Npar= 708
```

7.2 Data of Compound 22 (CCDC: 2480483)

Crystal sample preparation and crystal structure determination

To a 10 mL vial, the corresponding samples (25.0 mg) were dissolved in 2.0 mL CH_2Cl_2, and then 1.0 mL *n*-hexane was slowly dropwise into the above solution. The vial, which was not screwed down, was carefully set in a clean place at room temperature, and wait for the crystals to precipitate. The crystals were confirmed by X-ray crystallographic.

All the measurements were obtained on a BRUKER Single Crystal X-Ray Diffractometer, Germany (model of the instrument –AXS D8 Quest System).

Specification: D8 QUEST, Photon 100 CMOS Detector, Horizontal Goniometer, Fixed Chi stage, Goniometer head manual, Ceramic Tube KFF Mo-2K-90c, two pinhole collimator (0.3/17 m rad, 0.6/17 m rad), Head turned by 90°, APEX2 w. SHELXTL S/W, Video microscope SCD, Cryostream-700plus extended range low temperature.

X-ray crystallographic analysis of compound **22** (CCDC:2480483) showing the thermal ellipsoids at 50% probability level.

```
Bond precision:   C-C = 0.0060 A          Wavelength=0.71076

Cell:          a=11.1879(6)       b=12.0483(6)     c=16.9670(8)
               alpha=109.200(1)   beta=98.081(1)   gamma=104.655(1)
Temperature:   296 K

                Calculated                  Reported
Volume          2025.94(18)                 2025.94(18)
Space group     P -1                        P -1
Hall group      -P 1                        -P 1
Moiety formula  C39 H37 N O4 S2 [+ solvent] C39 H37 N O4 S2
Sum formula     C39 H37 N O4 S2 [+ solvent] C39 H37 N O4 S2
Mr              647.82                      647.81
Dx,g cm-3       1.062                       1.062
Z               2                           2
Mu (mm-1)       0.166                       0.166
F000            684.0                       684.0
F000'           684.77
h,k,lmax        13,14,20                    13,14,20
Nref            7147                        7040
Tmin,Tmax                                   0.634,0.745
Tmin'

Correction method= # Reported T Limits: Tmin=0.634 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.985          Theta(max)= 25.007

R(reflections)= 0.0573( 4742)                wR2(reflections)=
                                             0.1472( 7040)
S = 1.048                 Npar= 418
```

8. References

[1] Rigotti, T.; Bach, T. Bicyclo [2. 1. 1] Hexanes by Visible Light-Driven Intramolecular Crossed [2 + 2] Photocycloadditions. *Org. Lett.* **2022**, *24*, 8821–8825.

[2] Gorin, C. F.; Beh, E. S.; Bui, Q. M.; Dick, G. R.; Kanan, M. W. Interfacial Electric Field Effects on a Carbene Reaction Catalyzed by Rh Porphyrins. *J. Am. Chem. Soc.* **2013**, *135*, 11257– 11265.

[3] Zheng, Y.; Wang, Z. J.; Ye, Z. P.; Tang, K.; Xie, Z. Z.; Xiao, J. A.; Xiang, H. Y.; Chen, K.; Chen, X. Q.; Yang, H. Regioselective Access to Vicinal Diamines by Metal-Free Photosensitized Amidylimination of Alkenes with Oxime Esters. *Angew. Chem., Int. Ed.* **2022**, *61*, e202212292.

[4] Braddock, D. C.; Cansell, G.; Hermitage, S. A. Ortho-Substituted Iodobenzenes as Novel Organocatalysts for Bromination of Alkenes. *Chem. Commun.*, **2006**, *23*, 2483-2485.

[5] Liu, Q.; Ai, H. M. Sodium Benzoate as a Green, Efficient, and Recyclable Catalyst for Knoevenagel Condensation. *Synthetic Communications*, **2012**, *42*, 3004–3010.

[6] Wu, W. Q.; Xie, P. P.; Wang, L. Y.; Gou, B. B.; Lin, Y.; Hu, L. W.; Zheng, C., You, S. L.; Shi, H. Chiral Bis(binaphthyl) Cyclopentadienyl Ligands for Rhodium-Catalyzed Desymmetrization of Diarylmethanes via Selective Arene Coordination. *J. Am. Chem. Soc.* **2024**, *146*, 26630– 26638.