Supportting Information

Photocatalytic C-H amination of electron-rich arenes by fused quinoline-based photocatalysts

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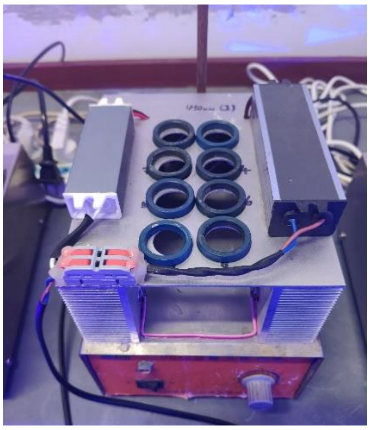
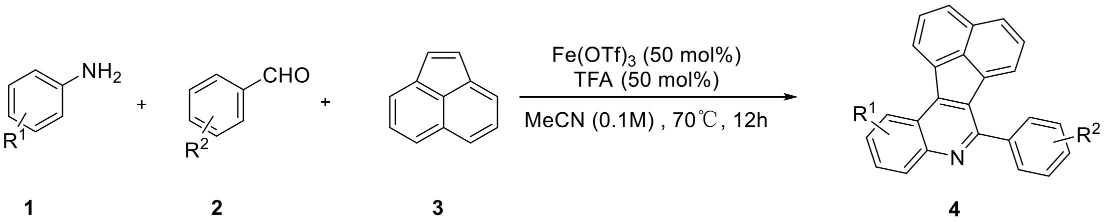
1. General information

Aldehydes, acenaphthylene, amine, and arene were obtained from the commercial sources or synthesized following literature procedures. Solvents were obtained from Sigma-Aldrich, Alfa-Aesar, Oakwood, and Acros and used directly without further purification. Analytical thin-layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light. 'H NMR was recorded on Bruker instrument (500MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet, br = broad. Coupling constants, J, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker instrument (126 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to either the center line of a triplet at 77.0 ppm of chloroform-d or referenced to the center line of a septet at 39.52 ppm of DMSO-d_6. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).



2. Synthesis of fused quinoline-based photocatalysts



General Proceduce 1. Standard reaction conditions

Prepare a clean pressure-resistant tube, mark it and place a suitable magnetic stirring bar inside. Add amine (0.2 mmol, 1.0 equiv.) and aldehyde (0.24 mmol, 1.2 equiv.) in 2 ml of acetonitrile. Add $Fe(OTf)_3$ (0.5 equiv., 0.25 mmol) and TFA (0.5 equiv., 0.25 mmol) in sequence. Then seal it, place the reaction flask on a magnetic stirrer, adjust to an appropriate speed, and stir at room temperature for 30 minutes. After stirring at room temperature, monitor the reaction progress. Then add acenaphthylene (0.3 mmol, 1.5 equiv.), tighten the pressure-resistant tube cap, and place it on a heating magnetic stirrer to react at 80°C for 12 hours. Track the reaction progress using thin-layer chromatography (TLC). Evaporate most of the acetonitrile solvent under reduced pressure,then add 2 ml of water to quench the reaction. Extract with DCM (3 × 4 ml), dry the organic phase with anhydrous Na_2SO_4, and purify the product through column chromatography (dichloromethane/tetrahydrofuran from 80:1 to 40:1) with silica gel to obtain pure fused quinoline-based photocatalysts. Calculate the yield after drying.

3. Reaction optimization of Povarov reaction

Initial Reaction Attempt: At the outset, 4-Methylaniline, p-methoxybenzaldehyde, and acenaphthylene were selected as the starting materials. Based on a literature review,[1] boron trifluoride diethyl etherate was chosen as the acid catalyst and acetonitrile as the solvent. The reaction was conducted at 70 °C to investigate its feasibility.

Results and Analysis: After 12 hours of reaction, thin-layer chromatography indicated the formation of a yellow fluorescent spot. Structural confirmation of the target product was achieved through NMR, HRMS and single-crystal X-ray diffraction analysis. However, the isolated yield of the target product was very low, only 21%. Further efforts were then directed toward screening the reaction components and optimizing the reaction conditions to improve the product yield.

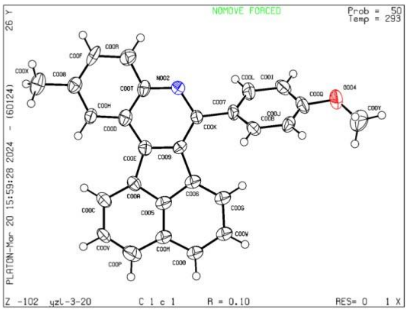


Figure 1: X-ray crystallography of **4a**

Lewis acid investigation

Optimization Procedure (**Table 1**): To a 15 mL pressure-resistant tube equipped with a clean stir bar were added 4-Methylaniline (0.20 mmol) and p-methoxybenzaldehyde (1.2 equiv., 0.24 mmol), followed by the addition of MeCN (2 mL). The lewis acid (0.3 equiv., 0.06 mmol) was then added slowly. The mixture was stirred at room temperature for 30 minutes. Subsequently, acenaphthylene (1.2 equiv., 0.24 mmol) was added, and the reaction was maintained at 70 °C for 12 hours. Upon completion, the mixture was extracted successively three times with DCM and water. The combined organic phases were dried over Na_2SO_4, adsorbed onto silica gel, and concentrated under reduced pressure. The crude product was purified by column chromatography using DCM/THF (50:1, v/v) as the eluent to afford the corresponding product.

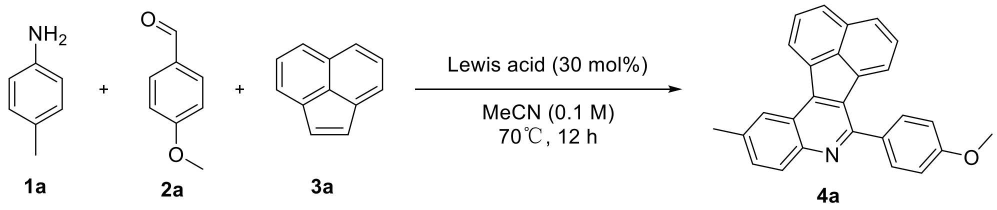


Table 1. Screening of the lewis acid

Entry	Lewis acid	Yield of **4a**
1	$BF_3 \cdot OEt_2$	21%
2	$FeCl_3$	18%
3	$AlCl_3$	23%
4	$CuCl_2$	16%
5	$Zn(OTf)_2$	52%
6	$Ag(OTf)_2$	0
7	$Fe(OTf)_2$	54%
8	$Fe(OTf)_3$	59%
9	$Cu(OTf)_2$	41%
10	$Ni(OTf)_2$	0
11	LiOTf	5%
12	$Sc(OTf)_2$	49%

Protonic acid investigation

Optimization Procedure (**Table 2**): To a 15 mL pressure-resistant tube equipped with a clean stir bar were added 4-Methylaniline (0.20 mmol) and p-methoxybenzaldehyde (1.2 equiv., 0.24 mmol), followed by the addition of MeCN (2 mL). $Fe(OTf)_3$ (0.3 equiv., 0.06 mmol) and Protonic acid (0.3 equiv., 0.06 mmol) was then added slowly. The mixture was stirred at room temperature for 30 minutes. Subsequently, acenaphthylene (1.2 equiv., 0.24 mmol) was added, and the reaction was maintained at 70 °C for 12 hours. Upon completion, the mixture was extracted successively three times with DCM and water. The combined organic phases were dried over Na_2SO_4, adsorbed onto silica gel, and concentrated under reduced pressure. The crude product was purified by column chromatography using DCM/THF (50:1, v/v) as the eluent to afford the corresponding product.

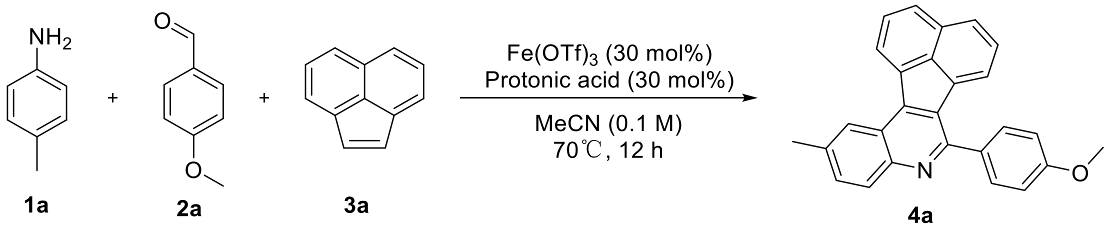


Table 2. Screening of the Protonic acid

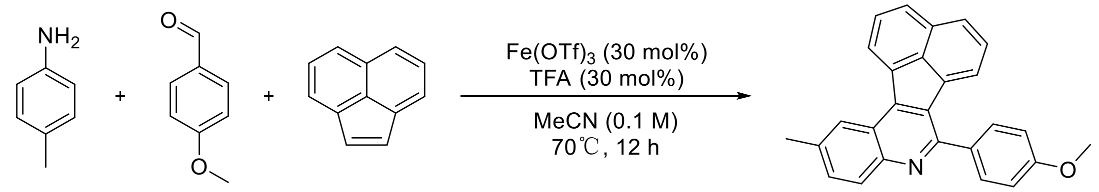
Entry	Acid	Yield of **4a**
1	TFA	76%
2	AcOH	59%

Table 2. (Continued) Screening of the Protonic acid

Entry	Acid	Yield of **4a**
3	TfOH	41%
4	MsOH	39%
5	H_2SO_4	24%
6	HBF_4	65%

Solvent investigation

Optimization Procedure (**Table 3**): To a 15 mL pressure-resistant tube equipped with a clean stir bar were added 4-Methylaniline (0.20 mmol) and p-methoxybenzaldehyde (1.2 equiv., 0.24 mmol), followed by the addition of solvent (2 ml). $Fe(OTf)_3$ (0.3 equiv., 0.06 mmol) and TFA (0.3 equiv., 0.06 mmol) was then added slowly. The mixture was stirred at room temperature for 30 minutes. Subsequently, acenaphthylene (1.2 equiv., 0.24 mmol) was added, and the reaction was maintained at 70 °C for 12 hours. Upon completion, the mixture was extracted successively three times with DCM and water. The combined organic phases were dried over Na_2SO_4, adsorbed onto silica gel, and concentrated under reduced pressure. The crude product was purified by column chromatography using DCM/THF (50:1, v/v) as the eluent to afford the corresponding product.



1a **2a** **3a** **4a**

Table 3. Screening of the solvent

Entry	Solvent	Yield of **4a**
1	MeCN	76%
2	DMSO	32%
3	DMF	49%
4	1, 4-dioxane	34%
5	DCM	32%
6	TFE	36%
7	THF	trace
8 [a]	MeCN	71%
9 [b]	MeCN	63%

[a] MeCN (2.5 ml); [b] MeCN (1 ml).

Other Conditions Investigation

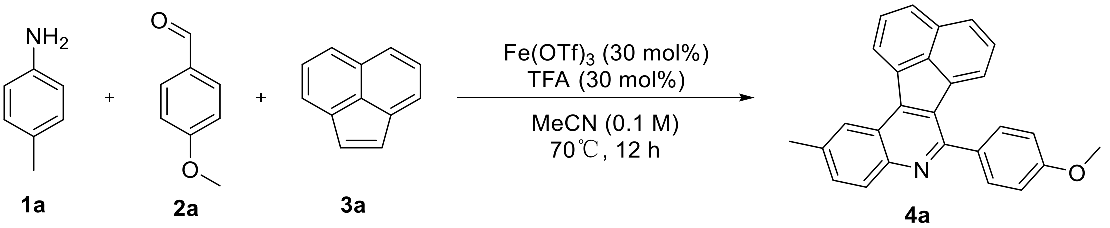


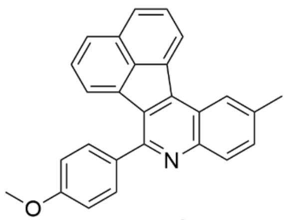
Table 4. Screening of other Conditions

Entry	Variation from the “standard conditions”	Yield of **4a**
1	Fe(OTf)$_3$ 50 mol%	81%
2	Fe(OTf)$_3$ 50 mol%; TFA 50 mol%	86%
3	**3a** 1.2 equiv.	78%
4	**3a** 2.0 equiv.	85%
5	React for 50 °C	71%
6	React for 90 °C	81%
7	React for 70 °C at 6 h	73%
8	React for 70 °C at 24 h	86%
9	N$_2$ atmosphere	86%

3.1 Characterization of fused quinoline-based photocatalysts

Note: Compounds **4a**–**4d**, **4e**, and **4f** exhibited poor solubility, and no satisfactory **^{13}C NMR** spectra could be obtained.

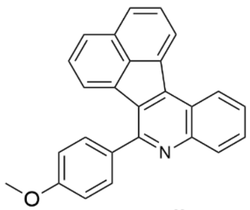
6-(4-methoxyphenyl)-2-methylacenaphtho[1,2-c] quinoline (4a)



4a

Compound 4a was synthesised by following ***General Procedure 1*** and was purified by column chromatography eluted with dichloromethane/tetrahydrofuran to provide **4a** as yellow solid (64.2 mg, 86% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.32 (d, J = 7.3 Hz, 1H), 8.95 (s, 1H), 8.44 (d, J = 8.1 Hz, 1H), 8.38 (d, J = 8.2 Hz, 2H), 8.21 (dd, J = 11.7, 8.4 Hz, 2H), 8.16 (d, J = 8.2 Hz, 2H), 8.04 (t, J = 7.7 Hz, 1H), 7.99 (d, J = 10.5 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 4.00 (s, 3H), 2.74 (s, 3H). **HRMS** (ESI): m/z calculated for $C_{27}H_{20}NO^+$ $[M+H]^+$ 374.1500, found 374.1505.

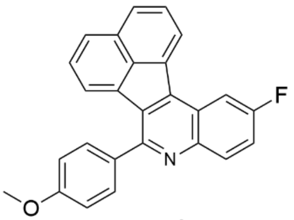
6-(4-methoxyphenyl)acenaphtho[1,2-c] quinoline (4b)



4b

Compound 4b was synthesised by following ***General Procedure 1*** and was purified by column chromatography eluted with dichloromethane/tetrahydrofuran to provide **4b** as yellow solid (57.4 mg, 80% yield). **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.74 (d, J = 8.2 Hz, 1H), 8.63 (d, J = 7.0 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.50 (m, J = 15.0, 7.1 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 3.98 (s, 3H). **HRMS** (ESI): m/z calculated for $C_{26}H_{18}NO^+$ $[M+H]^+$ 360.1344, found 360.1358.

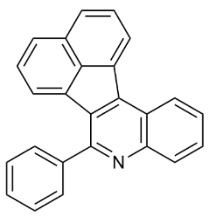
2-fluoro-6-(4-methoxyphenyl)acenaphtho[1,2-c] quinoline (4c)



4c

Compound 4c was synthesised by following ***General Procedure 1*** and was purified by column chromatography eluted with dichloromethane/tetrahydrofuran to provide **4c** as yellow solid (59.5 mg, 79% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.52 (d, J = 7.2 Hz, 1H), 8.26 (dd, J = 9.8, 2.7 Hz, 1H), 8.22 (dd, J = 9.3, 5.6 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.82 – 7.74 (m, 3H), 7.52 (d, J = 7.0 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.14 (d, J = 8.9 Hz, 2H), 3.96 (s, 3H). **HRMS** (ESI): m/z calculated for $C_{26}H_{17}FNO^+$ $[M+H]^+$ 378.1249, found 378.1255.

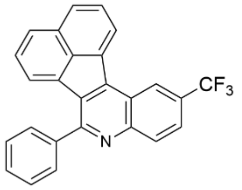
6-phenylacenaphtho[1,2-c] quinoline (4d)



4d

Compound 4d was synthesised by following ***General Procedure 1*** and was purified by column chromatography eluted with dichloromethane/tetrahydrofuran to provide **4d** as yellow solid (43.4 mg, 66% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.17 (dd, J = 15.9, 7.8 Hz, 2H), 8.40 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 8.2 Hz, 1H), 8.11 (t, J = 7.7 Hz, 1H), 7.98 (d, J = 7.2 Hz, 4H), 7.86 (d, J = 7.2 Hz, 1H), 7.82 (t, J = 7.2 Hz, 2H), 7.65 (t, J = 7.7 Hz, 1H), 7.27 (d, J = 7.1 Hz, 1H). **HRMS** (ESI): m/z calculated for $C_{25}H_{16}N^+$ $[M+H]^+$ 330.1238, found 330.1241.

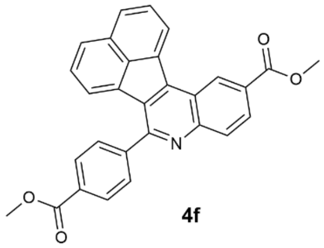
6-phenyl-2-(trifluoromethyl)acenaphtho[1,2-c] quinoline (4e)



4e

Compound 4e was synthesised by following ***General Procedure 1*** and was purified by column chromatography eluted with dichloromethane/tetrahydrofuran to provide **4e** as yellow solid (42.1mg, 53% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.01 (s, 1H), 8.63 (d, J = 7.1 Hz, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.87 – 7.81 (m, 3H), 7.63 (m, 3H), 7.48 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 7.0 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.58, 148.84, 143.54, 140.24, 134.57, 134.52, 131.76, 131.74, 130.76, 130.29, 129.82, 129.34, 128.98, 128.75, 128.40, 128.27, 128.25, 126.64, 125.57, 124.59, 124.57, 123.64, 122.04, 122.01. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.22. **HRMS** (ESI): m/z calculated for $C_{25}H_{16}N^+$ $[M+H]^+$ 398.1112, found 398.1120.

Methyl-6-(4-(methoxycarbonyl)phenyl)acenaphtho[1,2-c]quinoline-2-carboxylate (4f)

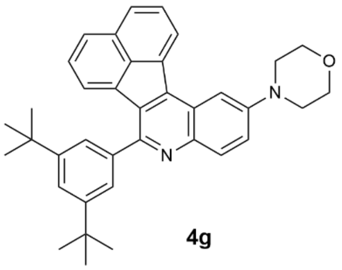


4f

Compound 4f was synthesised by following ***General Procedure 1*** and was purified by column chromatography eluted with dichloromethane/tetrahydrofuran to provide **4f** as a yellow solid (69.4 mg, 78% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.54 (s, 1H), 8.80 (d, J = 7.0 Hz, 1H), 8.36 – 8.32 (m, 2H), 8.29 (d, J =

8.7 Hz, 1H), 8.11 (d, J = 8.1 Hz, 2H), 7.98 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H), 4.11 (s, 3H), 4.05 (s, 3H). **HRMS** (ESI): m/z calculated for $C_{29}H_{20}NO_4^+$ [M+H]$^+$ 446.1348, found 446.1355.

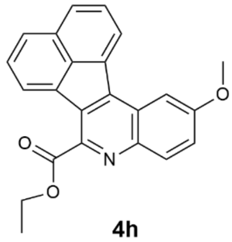
4-(6-(3,5-di-tert-butylphenyl)acenaphtho[1,2-c]quinolin-2-yl)morpholine (4g)



4g

Compound 4g was synthesised by following ***General Procedure 1*** and was purified by column chromatography eluted with dichloromethane/tetrahydrofuran to provide **4g** as a yellow solid (85.3 mg, 81% yield). ^{1}**H NMR** (500 MHz, Chloroform-d) δ 8.46 (d, J = 7.0 Hz, 1H), 8.16 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.87 (s, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.67 (s, 2H), 7.62 (s, 1H), 7.50 (dd, J = 9.4, 2.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.0 Hz, 1H), 4.05 – 3.96 (m, 4H), 3.47 – 3.39 (m, 4H), 1.42 (s, 18H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 155.07, 150.76, 149.68, 144.12, 140.99, 139.83, 135.86, 135.78, 131.98, 131.53, 130.25, 129.73, 128.97, 127.92, 127.88, 127.50, 125.56, 124.92, 123.50, 122.53, 121.55, 105.34, 66.93, 49.45, 35.11, 31.58. **HRMS** (ESI): m/z calculated for $C_{37}H_{39}N_2O^+$ [M+H]$^+$ 527.3018, found 527.3022.

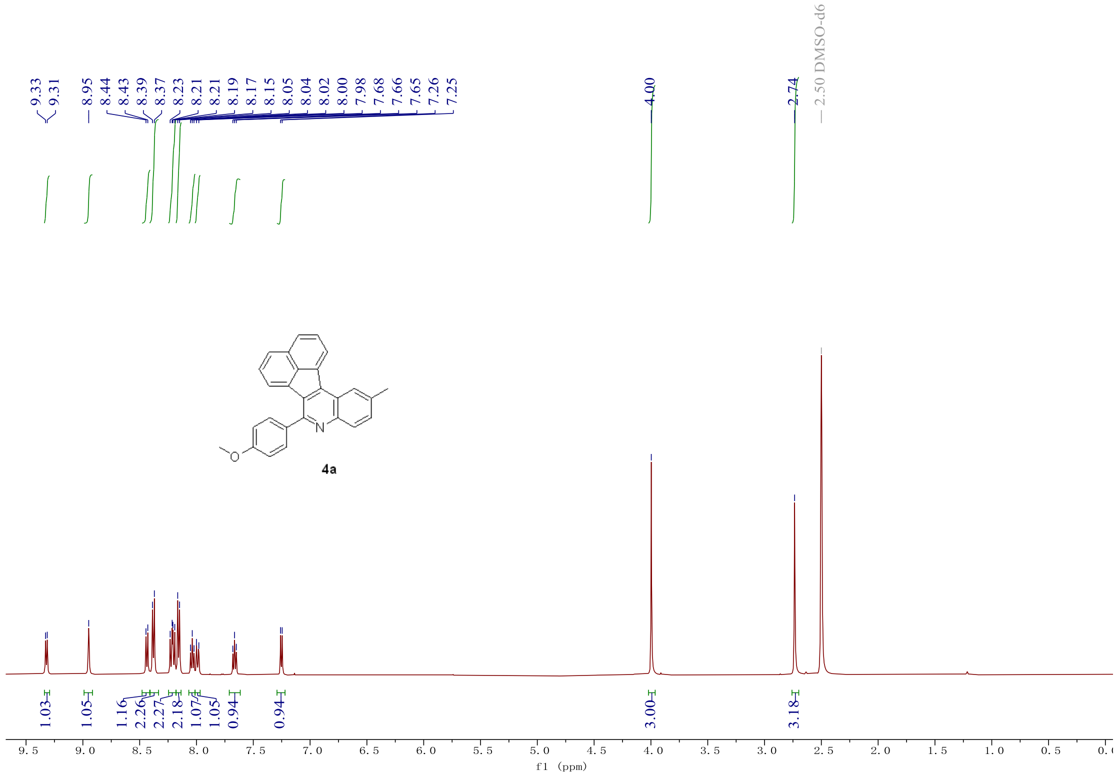
Ethyl-2-methoxyacenaphtho[1,2-c]quinoline-6-carboxylate (4h)



4h

Compound 4h was synthesised by following **General Procedure 1** and was purified by column chromatography eluted with dichloromethane/tetrahydrofuran to provide **4h** as yellow solid (48.2 mg, 68% yield). ^{1}**H NMR**(500 MHz, Chloroform-*d*) δ 8.57 (d, J = 7.2 Hz, 1H), 8.29 (d, J = 7.2 Hz, 1H), 8.16 (d, J = 9.2 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.73 (s, 1H), 7.66 (d, J = 4.3 Hz, 2H), 7.38 (d, J = 9.3 Hz, 1H), 4.72 (q, J = 7.2 Hz, 2H), 4.05 (s, 3H), 1.61 (t, J = 7.1 Hz, 3H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 167.17, 159.55, 143.23, 142.72, 142.15, 134.55, 133.67, 132.62, 131.93, 130.12, 129.62, 129.42, 128.41, 128.27, 127.59, 127.08, 127.05, 125.43, 122.21, 101.69, 62.15, 55.57, 14.45. **HRMS** (ESI): m/z calculated for $C_{23}H_{18}NO_3^+$ [M+H]$^+$ 356.1242, found 356.1249.

3.2 NMR data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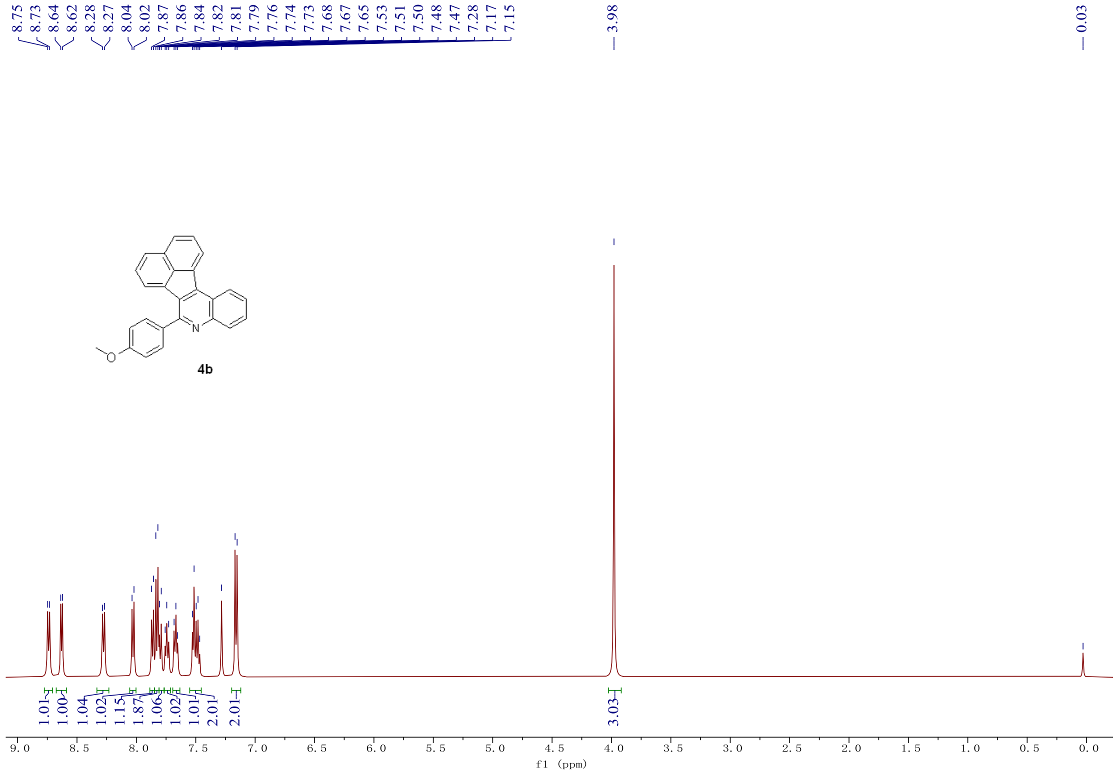
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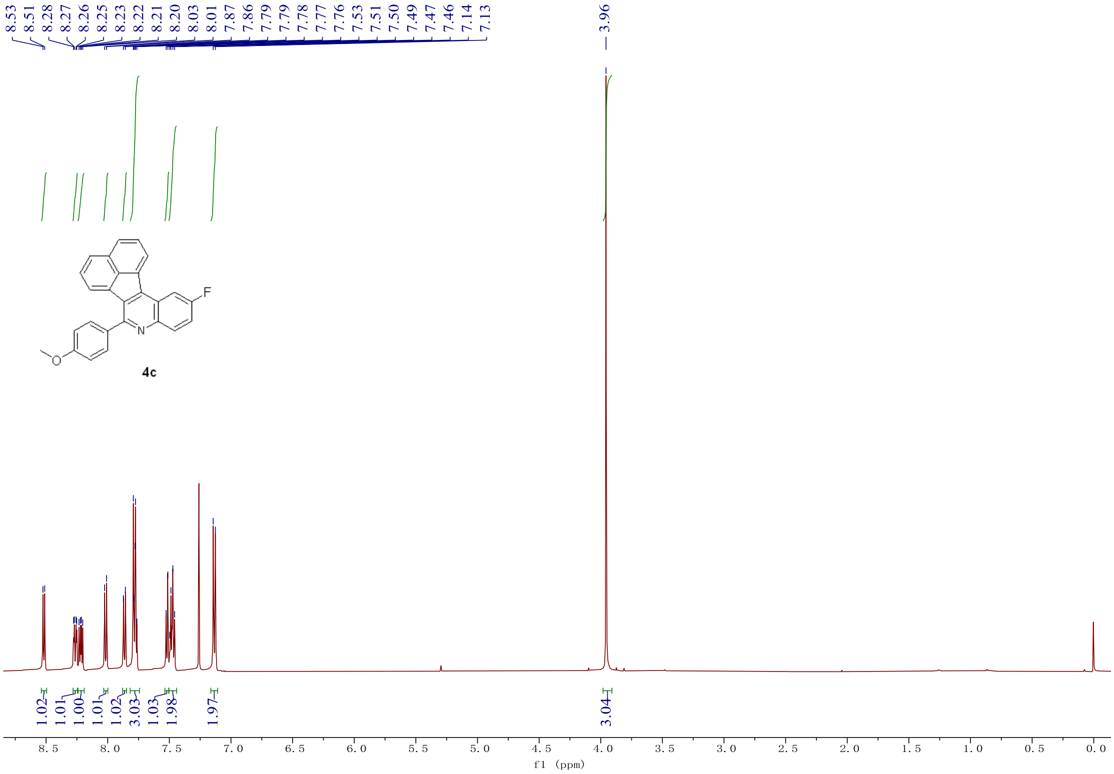
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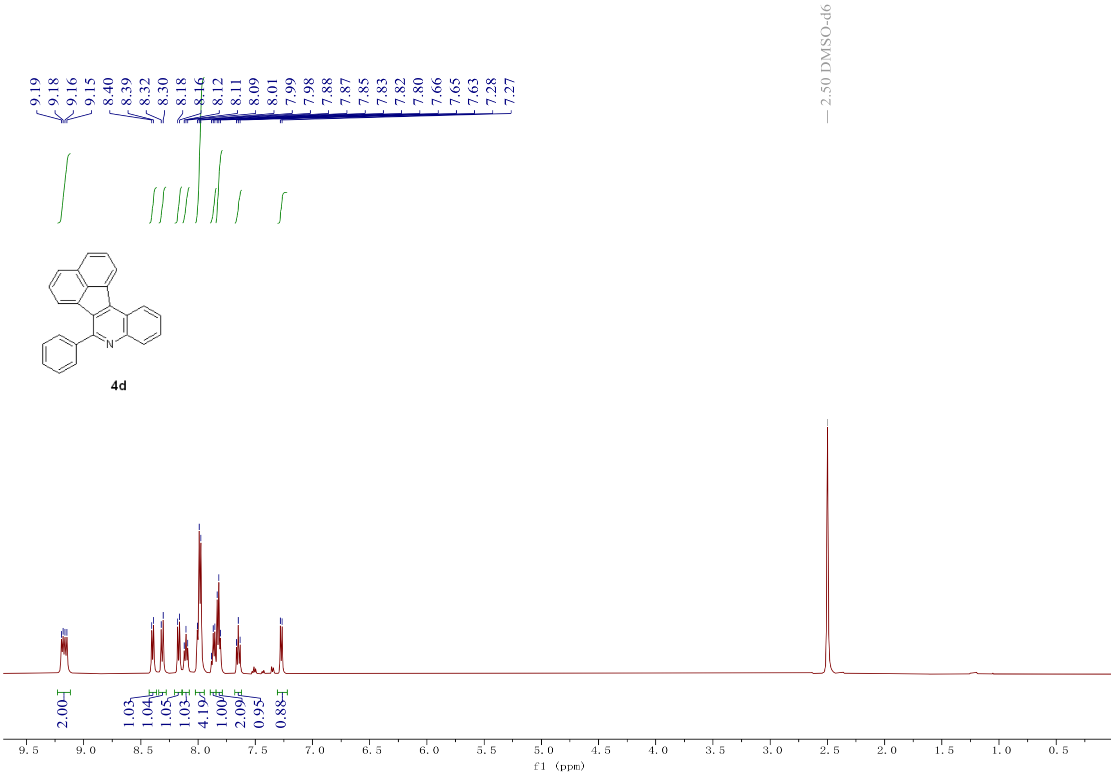
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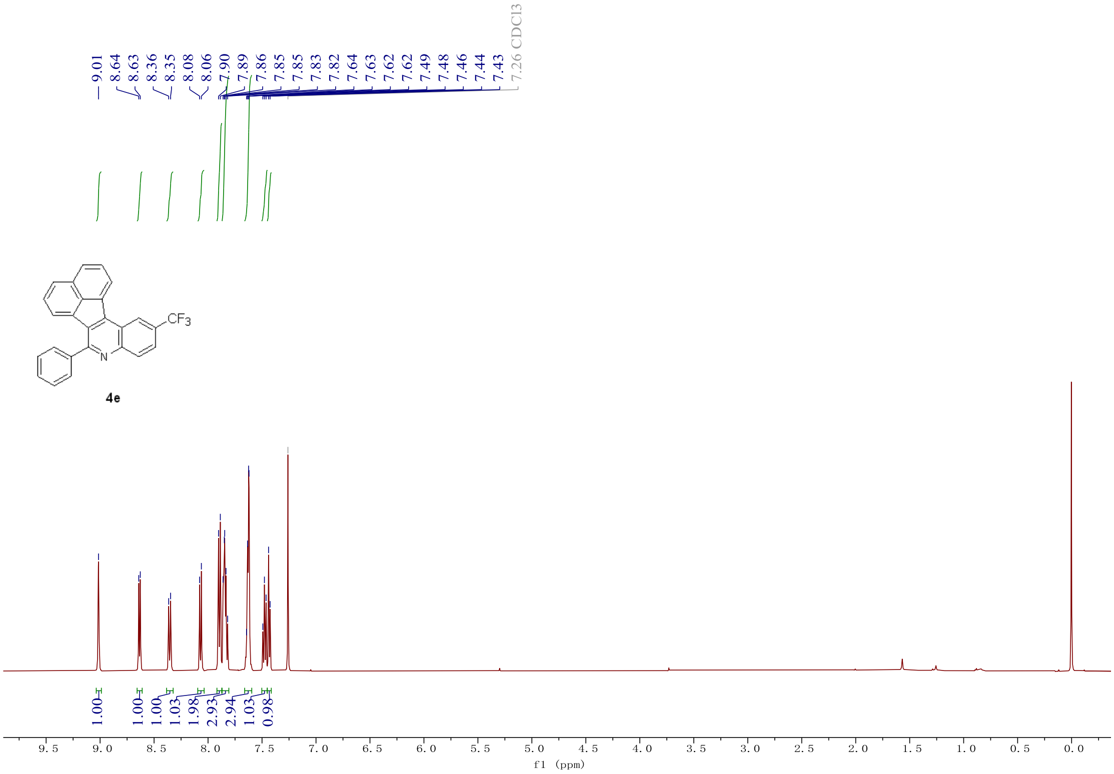
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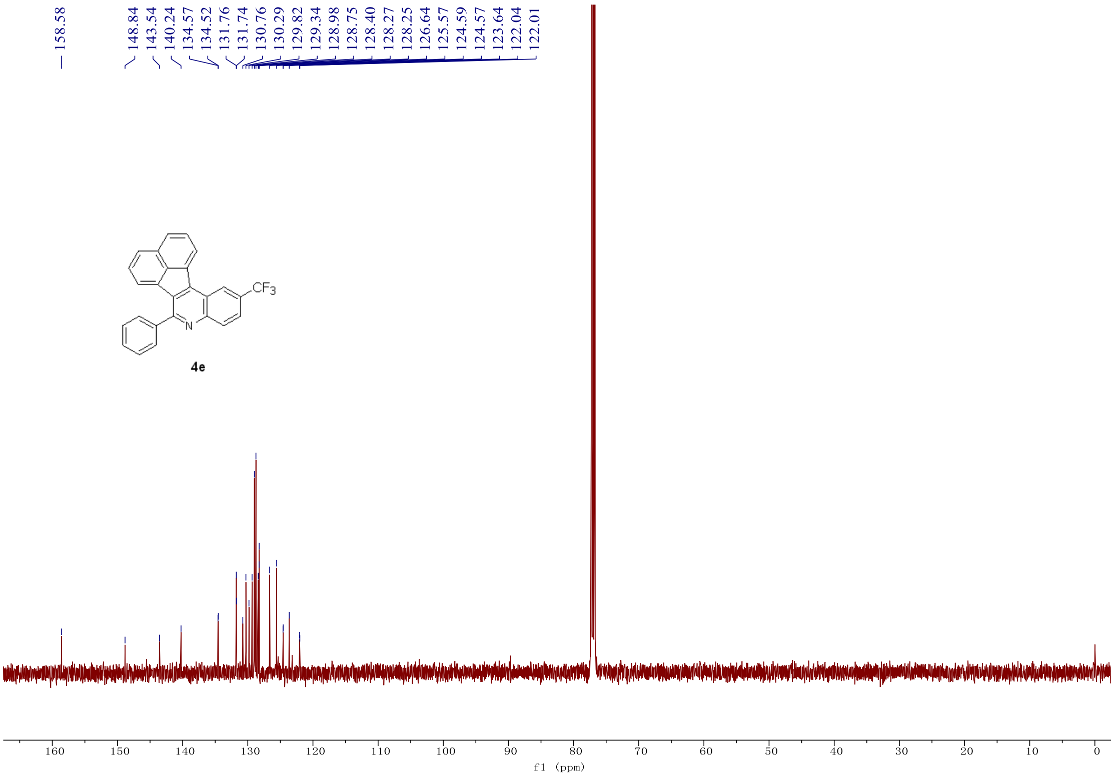
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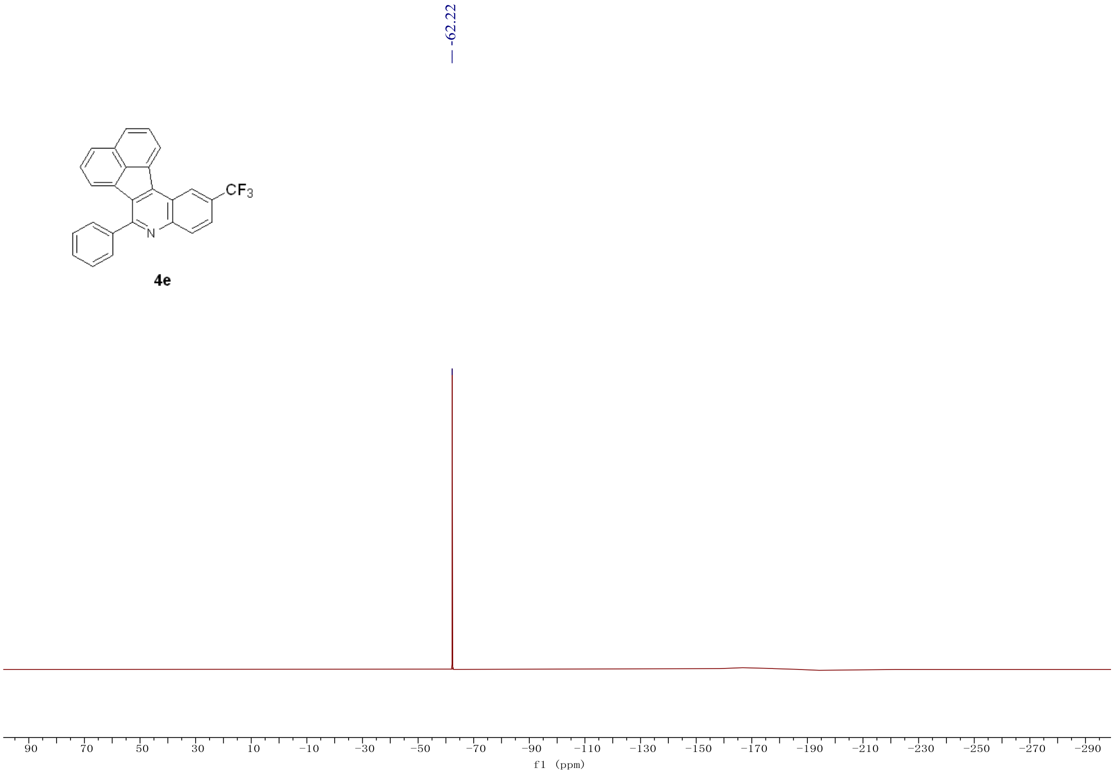
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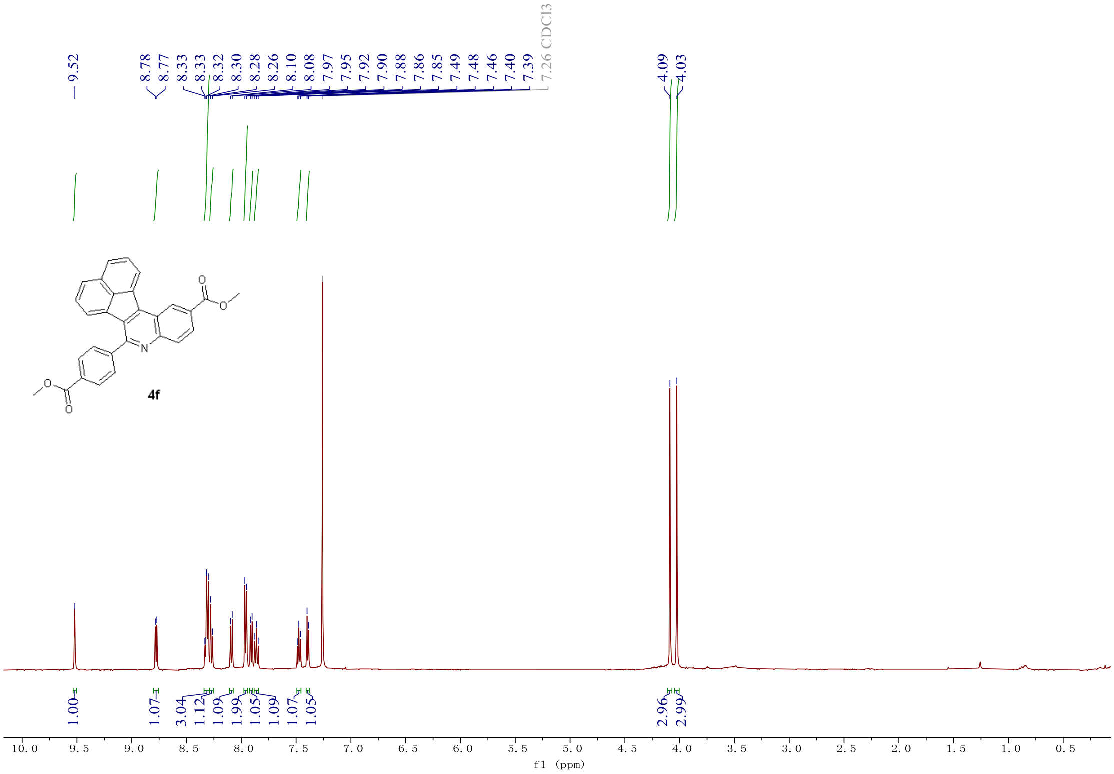
4e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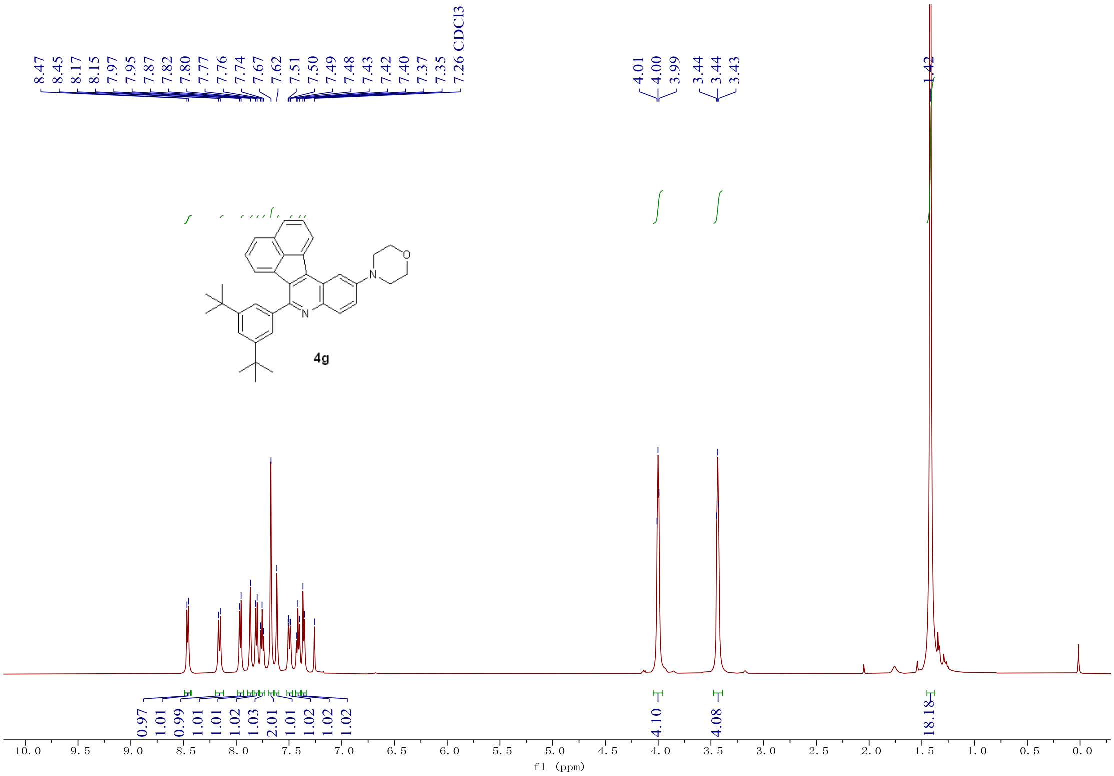
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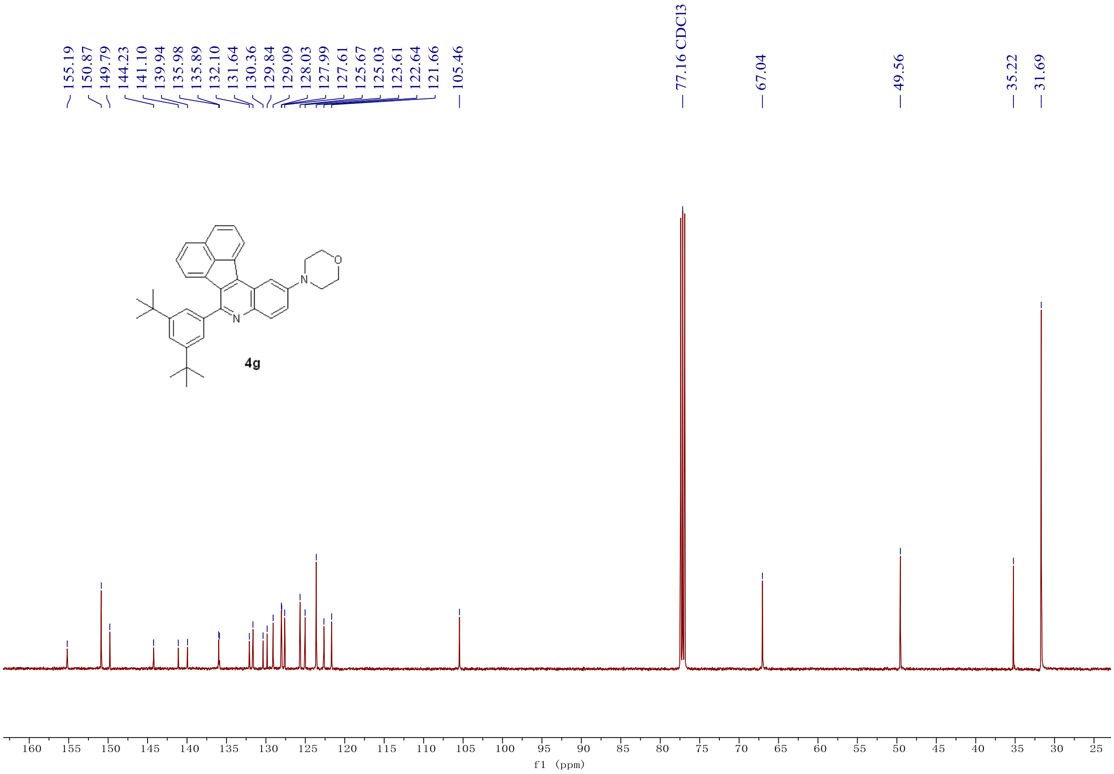
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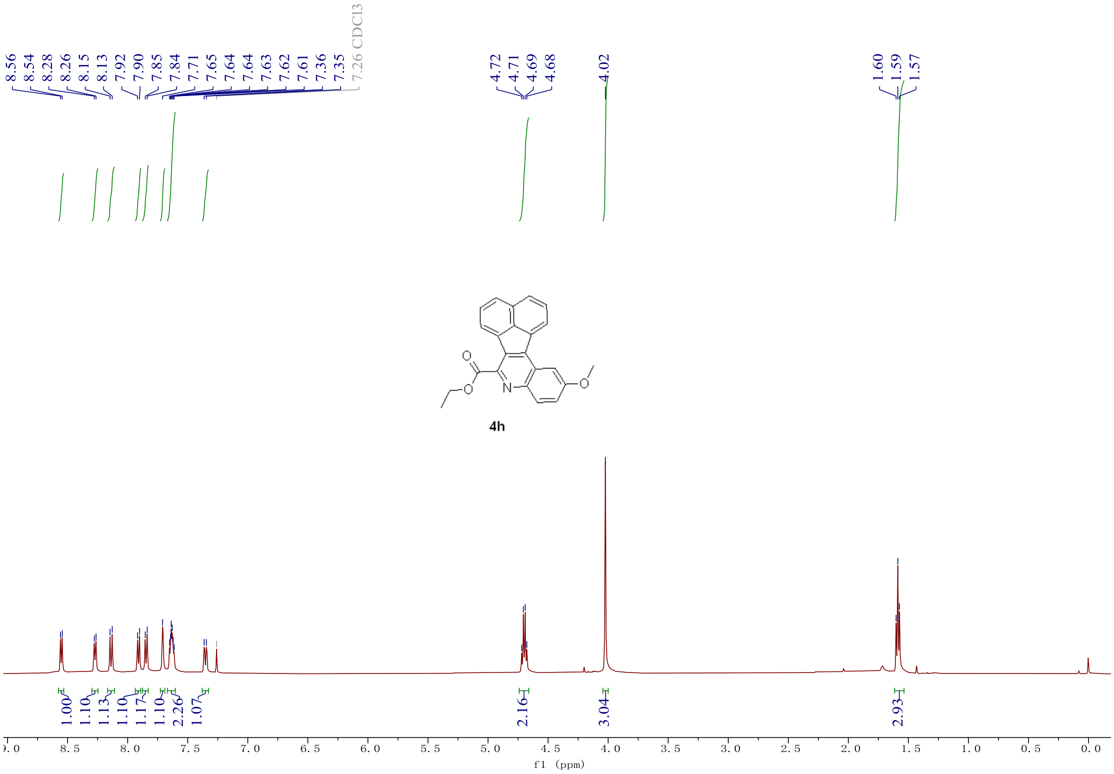
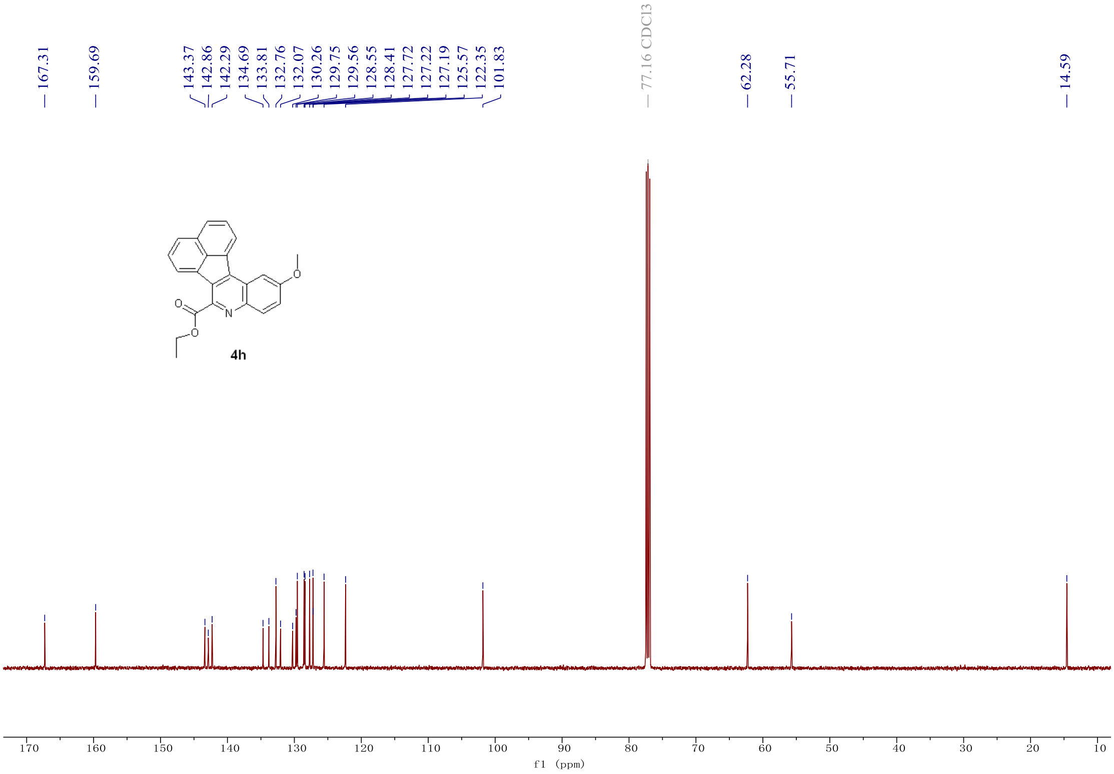




4. Reaction optimization of C(sp^2)-H amination

Optimization Procedure (**Table 5**): Biphenyl (30.8 mg, 0.2 mmol, 1.0 equiv.), **4e** and HBF$_4$ were weighed into a 10 mL vial equipped with a stir bar. Solvent (4.0 mL, 0.05 M) was added, followed by pyrazole. The mixture was sparged with O_2 for 10 minutes, after which the clear reaction vial was placed in a 450 nm photoreactor and stirred at an appropriate rate for 48 hours.

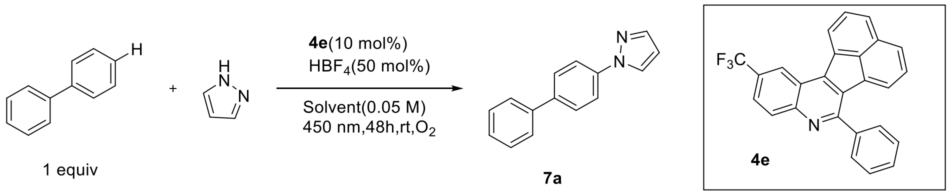


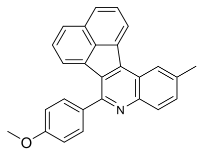
Table 5 Screening of other Conditions

Entry	**4e** (mol%)	HBF_4 (mol%)	Pyrazole (eq)	Solvent	Yield[a](%)
1	5	50	5	DCE:MeCN = 2:1	50
2	**10**	**50**	**5**	DCE:MeCN = 2:1	**75**
3	20	50	5	DCE:MeCN = 2:1	77
4	10	10	5	DCE:MeCN = 2:1	50
5	10	25	5	DCE:MeCN = 2:1	68
6	10	75	5	DCE:MeCN = 2:1	75
7	10	50	2.5	DCE:MeCN = 2:1	54
8	10	50	7.5	DCE:MeCN = 2:1	75
9	10	50	5	DCE	58
10	10	50	5	MeCN	68
11	10	50	5	DCE:MeCN = 1:1	74
12	10	50	5	DCE:MeCN = 1:2	70
13	\	50	5	DCE:MeCN = 2:1	0
14	10	\	5	DCE:MeCN = 2:1	36
15[b]	10	50	5	DCE:MeCN = 2:1	32
16[c]	10	50	5	DCE:MeCN = 2:1	0
17[d]	10	50	5	DCE:MeCN = 2:1	58

[a]Isolated yield. [b]Reaction performed with prior N_2 sparging. [c]Reaction performed in the dark (no light). [d]Reaction time: 24 h.

4.1 Photocatalysts investigation

Optimization Procedure (**Table 6**): Biphenyl (30.8 mg, 0.2 mmol, 1.0 equiv.), Fused quinoline-based photocatalyst (0.02 mmol, 0.10 equiv.), and HBF_4 (8.7 mg, 0.1 mmol, 0.5 equiv.) were weighed into a 10 mL vial equipped with a stir bar. The solvent of DCE/MeCN (2:1v/v, 4.0 mL, 0.05 M) was added, followed by pyrazole (68 mg, 1 mmol, 5.0 equiv.). The mixture was sparged with O_2 for 10 minutes, after which the clear reaction vial was placed in a 450 nm photoreactor and stirred at an appropriate rate for 48 hours.



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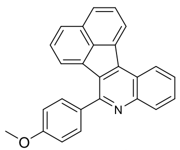

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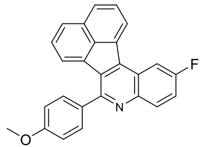

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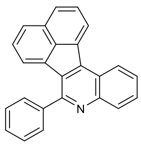

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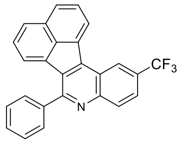

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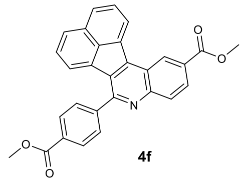

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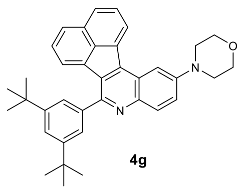
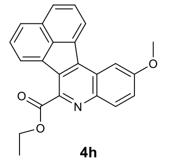


4g



4h

Table 6. Screening of fused quinoline-based photocatalysts

Entry	Photocatalyst	Yield[a](%)
1	4a	58
2	4b	60
3	4c	65
4	4d	68
5	**4e**	**75**
6	4f	65
7	4g	60
8	4h	64

[a]Isolated yield.

4.2 Acid investigation

Optimization Procedure (**Table 7**): Biphenyl (30.8 mg, 0.2 mmol, 1.0 equiv.), **4e** (7.96 mg, 0.02 mmol, 0.10 equiv.), and **Acid** (0.1 mmol, 0.5 equiv.) were weighed into a 10 mL vial equipped with a stir bar. The solvent of DCE/MeCN (2:1v/v, 4.0 mL, 0.05 M) was added, followed by pyrazole (68 mg, 1 mmol, 5.0 equiv.). The mixture was sparged with O_2 for 10 minutes, after which the clear reaction vial was placed in a 450 nm photoreactor and stirred at an appropriate rate for 48 hours.

Table 7. Screening of acid

Entry	Acid	Yield[a] (%)
1	**HBF_4**	**75**
2	TfOH	55
3	TsOH	46
4	HPF_6	50
5	H_2SO_4	63
6	AcOH	40
7	$AgBF_4$	45
8	$NaBF_4$	47

[a]Isolated yield.

4.3 Light source investigation

Optimization Procedure (**Table 8**): Biphenyl (30.8 mg, 0.2 mmol, 1.0 equiv.), **4e** (7.96 mg, 0.02 mmol, 0.10 equiv.), and HBF_4 (0.1 mmol, 0.5 equiv.) were weighed into a 10 mL vial equipped with a stir bar. The solvent of DCE/MeCN (2:1v/v, 4.0 mL, 0.05 M) was added, followed by pyrazole (68 mg, 1 mmol, 5.0 equiv.). The mixture was sparged with O_2 for 10 minutes, after which the clear reaction vial was placed in photoreactors equipped with different wavelength light sources and stirred at an appropriate rate for 48 hours.

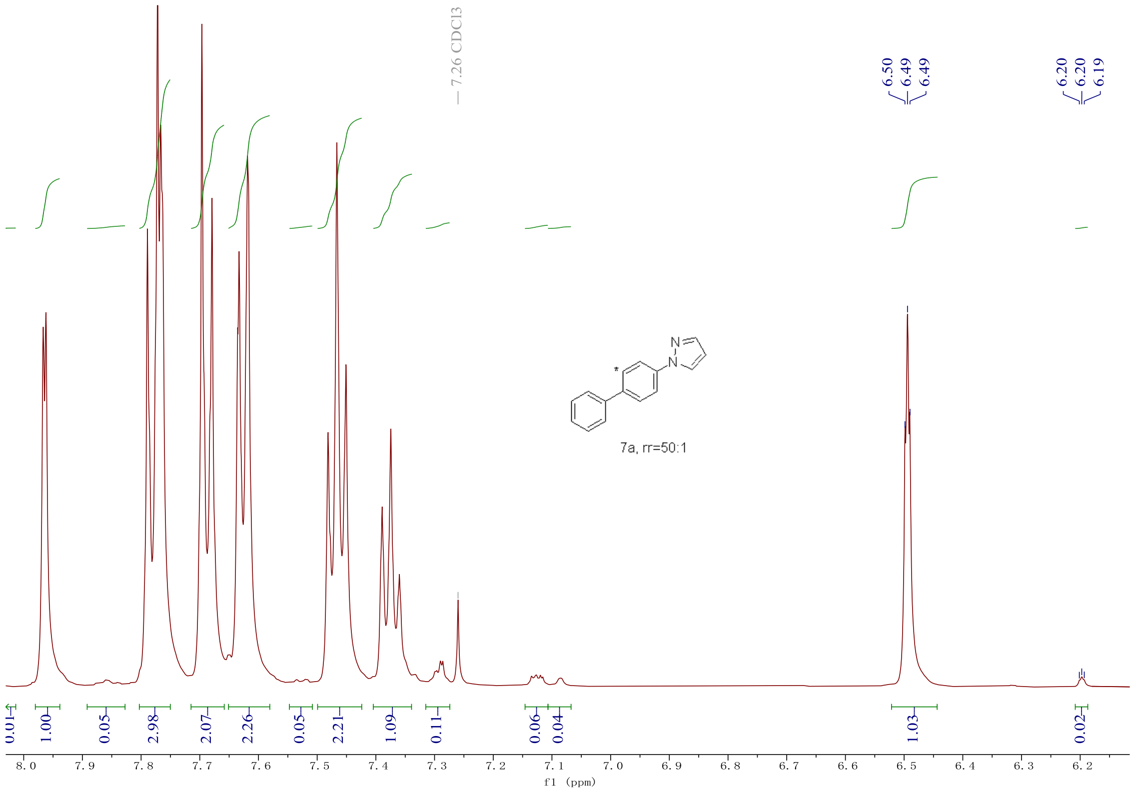
Table 8. Screening of light source

Entry	light source	Yield[a] (%)
1	450 nm	**75**
2	380 nm	79
3	Red light	NR
4	Green light	NR

[a]Isolated yield.

Note: Considering that blue light has lower energy consumption and results in a milder reaction, we ultimately selected blue light despite the slightly higher yield under purple light.

4.4 ^{1}H NMR of the crude product for 7a



Under the optimized conditions for the reaction between biphenyl and pyrazole, **^{1}H NMR** analysis showed that the ratio of para-product (**7a**) to ortho-product was 50:1

5. Competition between fused quinoline-based photocatalysts and nitrogen nucleophiles

We investigated whether nitrogen nucleophiles (one of the reaction substrates) could competitively bind with HBF_4 in the presence of the fused quinoline-based photocatalyst (A), thereby inhibiting the formation of the active photocatalyst PC (B). Qualitative tests and UV-Vis spectroscopic experiments were conducted.[2]

5.1 Qualitative tests

In a mixed solvent of MeCN:DCE = 1:2, the fused quinoline-based photocatalyst (A) was combined with HBF_4 to generate photocatalyst **PC** (B) *in situ*. The solution color changed from pale yellow (A) to bright yellow (B). Subsequently, various nitrogen nucleophiles (5 equiv.) were separately added to the solution of B (**PC**). As shown in **Figure 2**, nitrogen nucleophiles with pKaH lower than that of the fused quinoline-based photocatalyst maintained the bright yellow color of B, whereas those with pKaH higher than that of the photocatalyst caused the color of solution B to fade. These results indicate that the latter class of nitrogen nucleophiles can competitively suppress the formation of the active photocatalyst PC.

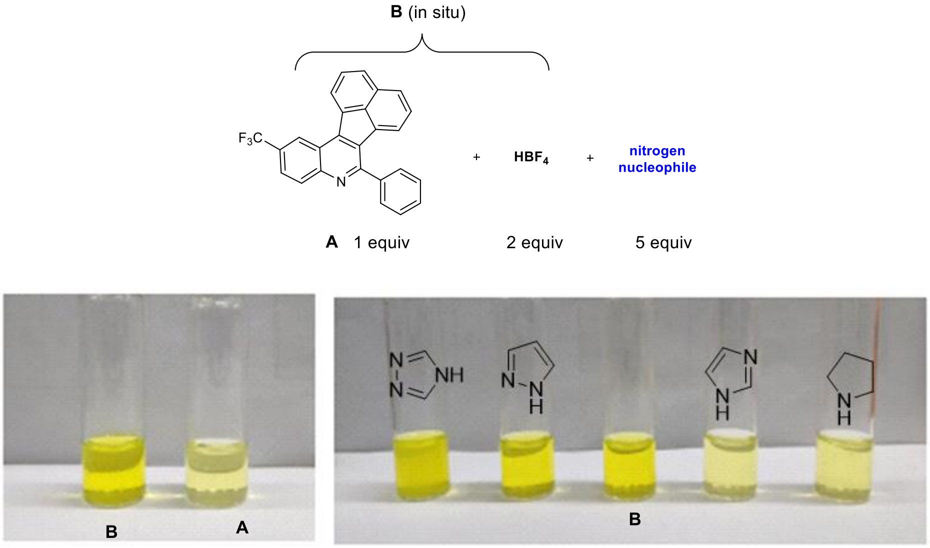


Figure 2: Qualitative Tests

5.2 UV-vis spectroscopy

UV-vis measurements were obtained on a Shimadzu UV-1900i UV-vis spectrophotometer using a 3.5 mL (1 cm path length) cuvette. Processing of UV-vis data: the generated data was plotted Using Origin. All samples were prepared using stock solutions.

Sample prepared in DCE:MeCN=2:1

1. **4e (A)**
2. **B** = **4e** (1 equiv.) + HBF_4 (1 equiv.)
3. **B** + Pyrazole (5 equiv.)
4. **B** + Imidazole (5 equiv.)
5. **B** + Pyrrolidine (5 equiv.)

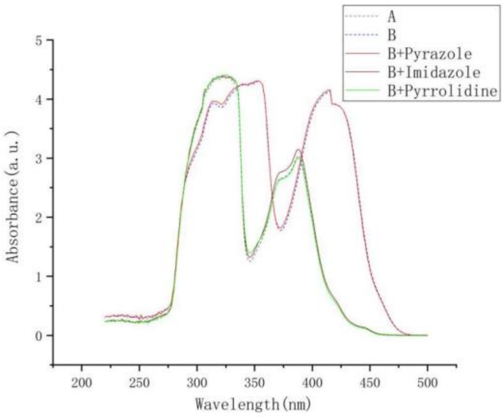


Figure 3: UV-vis Spectroscopy of samples 1-5

Consistent with the qualitative observations, the addition of pyrazole to solution B resulted in little change in absorbance, whereas the introduction of imidazole or pyrrolidine restored the absorbance to a level identical to that of A. This indicates that nitrogen nucleophiles with a higher pKaH than the fused quinoline-based photocatalyst competitively inhibit the formation of the active photocatalyst PC.

6. Characterization of *in situ* photocatalyst

6.1 UV-vis spectroscopic analysis

UV-vis measurements were obtained on a Shimadzu UV-1900i UV-vis spectrophotometer using a 3.5 mL (1 cm path length) cuvette. Processing of UV-vis data: the generated data was plotted Using Origin. All samples were prepared using stock solutions.

Sample prepared in DCE:MeCN=2:1

1. **A**=**4e (**0.25 mM**)**
2. **A** + HBF_4 (0.25 mM)
3. **A** + HBF_4(0.5 mM)
4. **A** + HBF_4(1.25 mM)

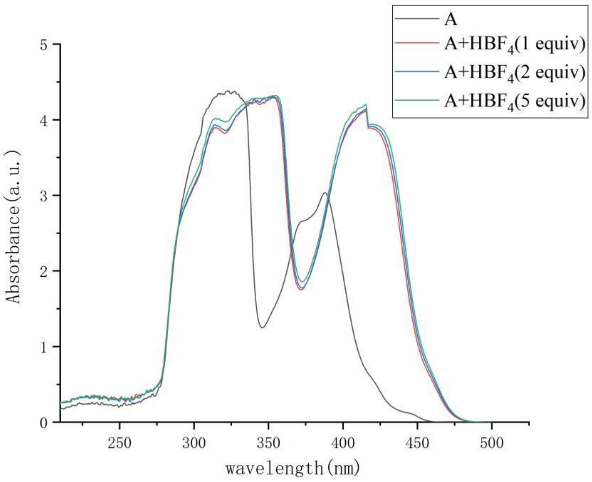


Figure 4: Effect of HBF_4 equivalents on the *in situ* Formation of B

The addition of HBF_4 to a resulted in a redshift of the UV-Vis absorption spectrum. One equivalent of HBF_4 was sufficient for the complete protonation of the fused quinoline-based photocatalyst to generate B *in situ*.

6.2 Emission spectrum of B (PC)

Parameters:
Excitation wavelength: 244 nm.
Emission collection: 200-800 nm.

In DCE:MeCN = 2:1(anhydrous):
B (PC) = **4e** (0.012 mM) + HBF_4 (0.012 mM)

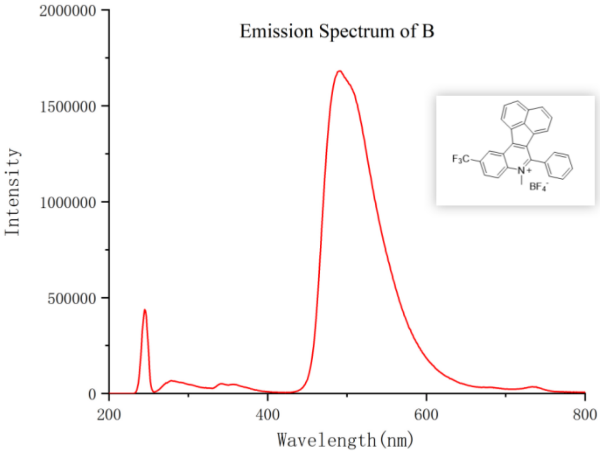
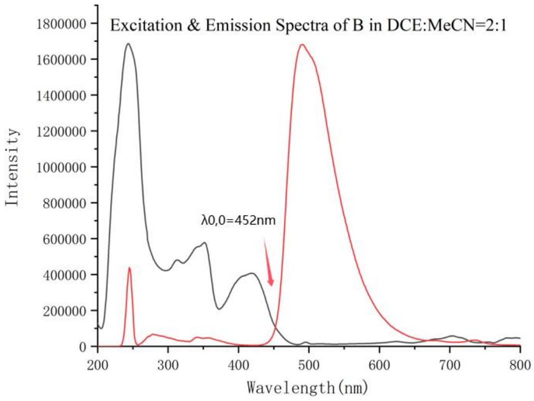
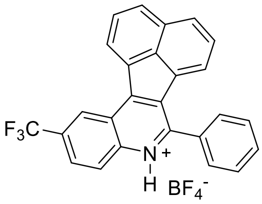


Figure 5: Emission spectrum of B in DCE:MeCN = 2:1. The maximum emission intensity was observed at λ_{max} = 490 nm. Excitation wavelength = 244 nm. Note: a solvent blank was subtracted from the spectrum.

6.3 Calculation of excited-state energy for B (PC)

The excited state energy ($E_{0,0}$) is the wavelength (energy) at which the excitation (absorption) and emission spectra intersect.





B (PC)

Figure 6: Excitation and emission spectra of B (**PC**)

$\lambda_{0,0}$ = 452nm

$$E_{0,0} = 1240/\lambda_{0,0} = 2.73V$$

6.4 Calculation of E^*_{red} of B (PC)

Cyclic voltammetry was performed on a Biologic VSP potentiostat (using EC-Lab software) with a three-electrode setup: working (glassy carbon), reference (Ag/AgCl in 3 M NaCl), counter (platinum wire). A 0.1 M solution of n-Bu_4NPF_6, in DCE:MeCN=2:1, was prepared inside of a nitrogenfilled glovebox. Concentration of **B** (1.5 mM **4e** and 1.5 mM HBF_4) in DCE:MeCN=2:1, with 0.1 M n-Bu_4NPF_6 (5 mL) as the supporting electrolyte. Each experiment was run under an atmosphere of nitrogen outside of the glovebox and utilized a scan rate of 20 mV/s. The working electrode (glassy carbon) was polished between each experiment. Reduction potentials were experimentally referenced to Ag/AgCl and converted to a Saturated Calomel Electrode (SCE) reference by subtracting 0.030 V from the measured potential. Note, each voltammogram was corrected by subtracting the background current of the n-Bu4NPF6 electrolyte from that of **B (PC)**.

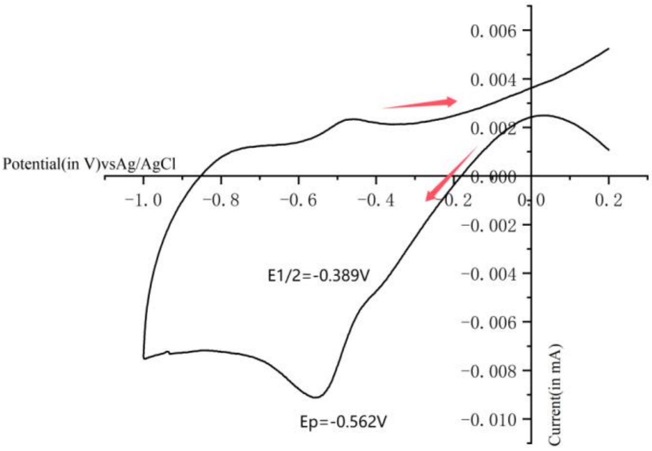


Figure 7: Cyclic voltammogram and measured reduction potential of **B** (**PC**) in DCE:MeCN = 2:1.

$$E_{red,1/2} = E_{1/2} = -0.389V \textbf{ vs Ag/AgCl}$$

$$\mathbf{E_{red,1/2} = -0.419V\ vs\ SCE}$$

B (PC) exhibits an irreversible CV in DCE:MeCN=2:1. This is not completely uncommon for organic photocatalysts.

The excited state reduction potential of **B (PC)** was calculated by adding the excited state energy ($E_{0,0}$) and the ground state reduction potential (determined by CV).

$$\mathbf{E^*_{red} = E_{red,1/2}+E_{0,0}}$$

$$\mathbf{E^*_{red} = 2.73V+(-0.419V) = 2.31V\ vs\ SCE}$$

7. Control experiments

To gain a deeper insight into the mechanism of this cascade oxidative cyclization, several control experiments were conducted. The desired product was not detected when 2.5 equivalents of

TEMPO or 1,1-diphenylethylene was added. As shown, the radical scavenger shuts down the reaction, which may indicate a single-electron-transfer process.

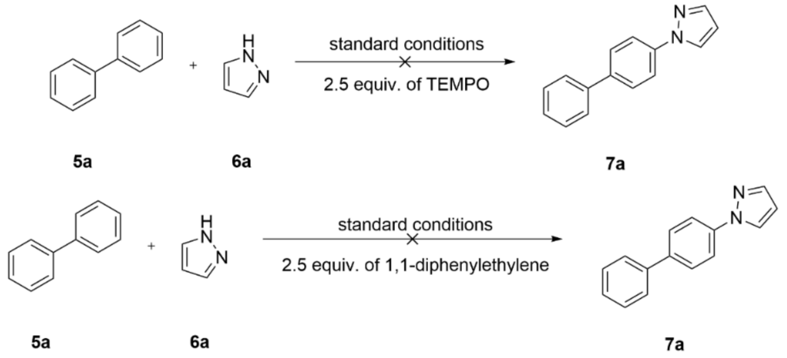


Figure 8: Control experiments

8. H_2O_2 detection experiment

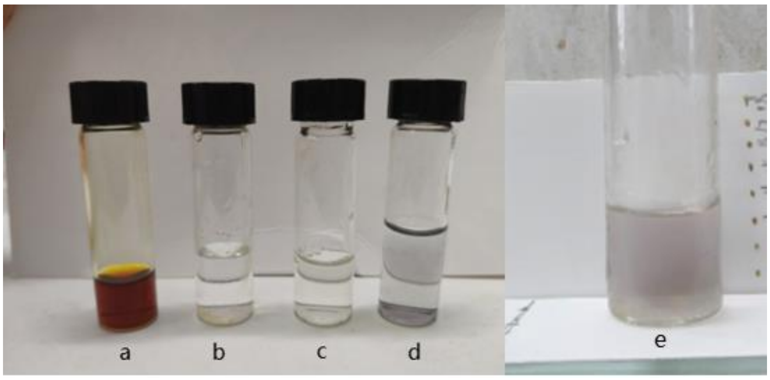


Figure 9: H_2O_2 detection experiment: (a) Reaction mixture after completion, (b) Portion of the aqueous extract, (c) Freshly prepared KI-starch solution, (d) and (e) Appearance of blue-purple color due to the formation of I_2-starch complex (H_2O_2 detected).

Biphenyl, 4e and HBF_4 were weighed into a 10 mL vial equipped with a stir bar. The solvent of DCE/MeCN (2:1v/v) was added, followed by pyrazole. The mixture was sparged with O_2 for 10 minutes, after which the clear reaction vial was placed in a 450 nm photoreactor and stirred at an appropriate rate for 48 hours. After completion, the reaction mixture was poured into a 50 mL separatory funnel and dichloromethane (10 ml) was added. Then, this organic phase was extracted with distilled water (10 ml). To a portion of this aqueous extract (Figure 9b), the freshly prepared KI-starch solution (Figure 9c) was added and stirred vigorously. The solution developed a color due to the formation of an iodine-starch complex. The observed color was a blue-purple indicating the presence of H_2O_2, which is attributed to the use of corn starch (which has a high amylopectin content).

9. Gram-scale reaction

Insufficient light penetration depth, reduced oxygen diffusion efficiency, and decreased radical formation efficiency were identified as major barriers to maintaining high conversion at larger volumes. It has been demonstrated that tempo assists in the aerobic oxidation of radical intermediates under photocatalytic conditions.[3] Therefore, the originally optimized reaction was scaled to 1 g of the biphenyl substrate with the addition of 20 mol% tempo. Extending the reaction time to 72 h afforded 0.9 g of the desired product 7a (0.9 g, 59% isolated yield).

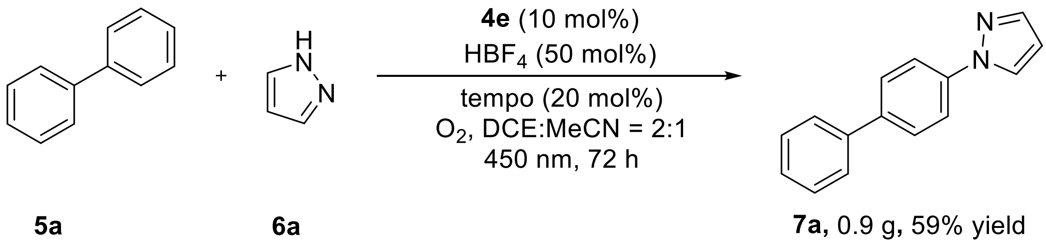
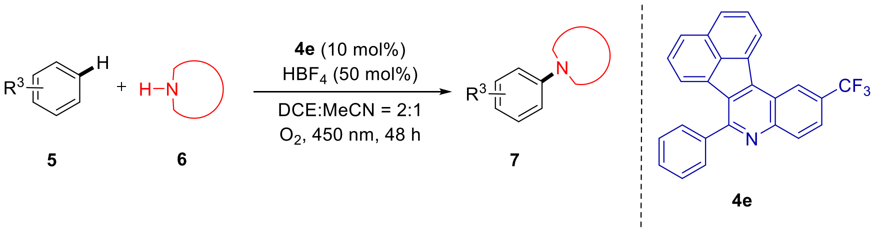


Figure 10: Gram-scale reaction

10. General procedure for C(sp^2)–H amination

Yields are calculated with respect to the arene source as the limiting reagent (1.0 equiv.). Reagents were handled on the benchtop without exclusion of air or moisture.

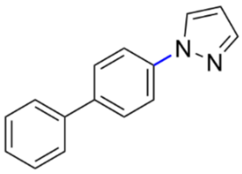


General Proceduce 2. Standard Reaction Conditions

In a 10 mL reaction vial equipped with a suitable magnetic stir bar, aromatic substrate (0.20 mmol, 1.0 equiv.) and **4e** (7.96 mg, 0.02 mmol, 0.10 equiv.) were added sequentially. Then, the solvent of DCE/MeCN (2:1v/v, 4.0 mL, 0.05 M) and HBF$_4$ (8.7 mg, 0.1 mmol, 0.5 equiv.) were introduced, followed by the amine (0.5 mmol, 5.0 equiv.). After bubbling oxygen through the mixture for 10 minutes, the clear reaction vial was placed in a 450 nm photoreactor and stirred at an appropriate speed for 48 hours. Upon completion, most of the solvent was removed under reduced pressure. The mixture was extracted with ethyl acetate (3 × 4 ml), and the combined organic layers were dried over anhydrous Na_2SO_4. Purification by column chromatography on silica gel (eluent: hexane/ethyl acetate, gradient from 40:1 to 1:1) afforded the amination product. The yield was determined after drying.

11. Characterization of C(sp^2)-H amination products

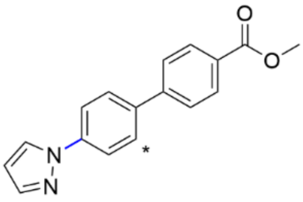
1-([1,1'-biphenyl]-4-yl)-1H-pyrazole (7a)



7a

Compound 7a was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) as a white solid (75% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.76 (s, 1H), 7.74 (s, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.46 (s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.24, 140.17, 139.47, 139.38, 128.96, 128.12, 127.58, 127.03, 126.76, 119.50, 107.78.

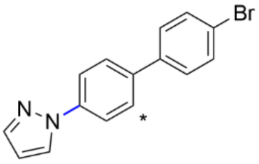
Methyl-4'-(1H-pyrazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (7b)



7b

Compound 7b was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford a **mixture of two regioisomers** as a white solid (45% yield). Analysis of the isolated product by ^{1}H NMR spectroscopy determined the **para isomer (7b) to ortho isomer (7b') ratio** to be **20:1**. The spectral data provided below correspond to the major isomer **(7b)** as shown. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.98 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.76 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 6.50 (s, 1H), 3.94 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.04, 144.60, 141.50, 140.18, 138.13, 130.34, 129.26, 128.40, 126.96, 126.83, 119.60, 108.04, 52.25. **HRMS** (ESI): m/z calculated for $C_{17}H_{15}N_2O_2^+$ $[M+H]^+$ 279.1089, found 279.1095.

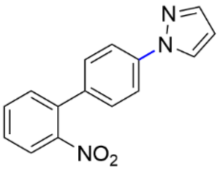
1-(4'-bromo-[1,1'-biphenyl]-4-yl)-1H-pyrazole (7c)



7c

Compound 7c was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford a **mixture of two regioisomers** as a white solid (48% yield). Analysis of the isolated product by ^{1}H NMR spectroscopy determined the **para isomer (7c) to ortho isomer (7c') ratio** to be **10:1**. The spectral data provided below correspond to the major isomer **(7c)** as shown. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.78 (s, 1H), 7.76 (d, *J* = 5.3 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.50 (t, *J* = 2.1 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.43, 139.85, 139.21, 138.23, 132.15, 128.68, 128.03, 126.82, 121.93, 119.68, 107.97. **HRMS** (ESI): m/z calculated for $C_{15}H_{12}BrN_2^+$ $[M+H]^+$ 299.0139, found 299.0145.

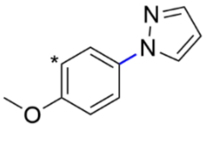
1-(2'-nitro-[1,1'-biphenyl]-4-yl)-1H-pyrazole (7d)



7d

Compound 7d was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7d** as a yellow oil (24% yield) which is a known compound.[4] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.77 (s, 1H), 7.75 (d, *J* = 6.9 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 6.4 Hz, 2H), 6.49 (s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.39, 141.52, 140.22, 135.60, 135.56, 132.52, 132.05, 129.24, 128.55, 126.88, 124.36, 119.40, 108.05, 108.03.

1-(4-methoxyphenyl)-1H-pyrazole (7e)

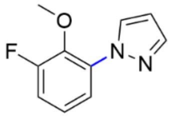


7e

Compound 7e was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford a **mixture of two regioisomers** as a yellow oil (66% yield) which is a known compound.[2] Analysis of the isolated product by ^{1}H NMR spectroscopy determined the **para isomer (7e) to ortho isomer (7e') ratio** to be **2.7:1**. The spectral data provided below correspond to the major isomer **(7e)** as shown. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.69 (s, 1H), 7.59 (d, *J* = 7.3

Hz, 2H), 6.97 (d, *J* = 7.4 Hz, 2H), 6.43 (s, 1H), 3.83 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.34, 151.44, 140.71, 140.16, 134.14, 131.66, 129.86, 128.13, 126.93, 125.40, 121.27, 121.01, 114.62, 112.38, 107.27, 106.26, 56.03, 55.65.

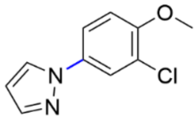
1-(3-fluoro-2-methoxyphenyl)-1H-pyrazole (7f)



7f

Compound 7f was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7f** as a yellow oil (36% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 2.5 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.48 (dd, *J* = 12.0, 2.6 Hz, 1H), 7.38 (m, *J* = 8.8, 2.6, 1.5 Hz, 1H), 7.02 (t, *J* = 8.9 Hz, 1H), 6.45 (t, *J* = 2.1 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.65, 151.68, 146.51, 146.42, 141.15, 134.23, 126.88, 114.86, 114.15, 108.77, 108.58, 107.77, 56.83. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -132.36 (q, *J* = 9.8 Hz). **HRMS** (ESI): m/z calculated for $C_{10}H_{10}FN_2O^+$ [M+H]$^+$ 193.0732, found 193.0736.

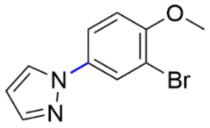
1-(3-chloro-4-methoxyphenyl)-1H-pyrazole (7g)



7g

Compound 7g was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7g** as a yellow oil (64% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 2.5 Hz, 1H), 7.74 (d, *J* = 2.7 Hz, 1H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.54 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.45 (t, *J* = 2.1 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.80, 134.29, 126.92, 123.33, 121.87, 118.73, 112.51, 107.77, 56.60.

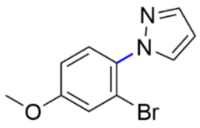
1-(3-chloro-4-methoxyphenyl)-1H-pyrazole (7h)



7h

Compound 7h was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7h** as a yellow oil (45% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 2.7 Hz, 1H), 7.82 (d, *J* = 2.4 Hz, 1H), 7.70 (s, 1H), 7.59 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.45 (t, *J* = 2.1 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.79, 141.17, 134.67, 126.93, 124.88, 119.55, 112.34, 107.75, 56.76.

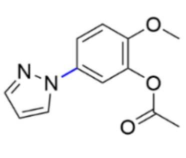
1-(2-bromo-4-methoxyphenyl)-1H-pyrazole (7i)



7i

Compound 7i was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7i** as a yellow oil (40% yield) which is a known compound.[3] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.69 (s, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.20 (s, 1H), 6.93 (d, *J* = 8.9 Hz, 1H), 6.44 (s, 1H), 3.84 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.97, 140.64, 133.34, 131.62, 129.14, 120.02, 118.53, 114.01, 106.34, 55.99.

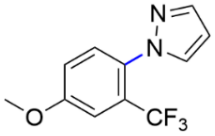
2-methoxy-5-(1H-pyrazol-1-yl)phenyl acetate (7j)



7j

Compound 7j was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7j** as a yellow oil (33% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.68 (s, 1H), 7.51 (d, *J* = 6.1 Hz, 1H), 7.43 (s, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.43 (s, 1H), 3.86 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.80, 150.00, 141.01, 140.33, 134.09, 126.90, 117.55, 112.98, 107.60, 56.42, 20.73.

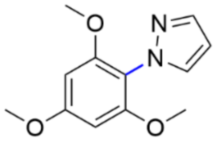
1-(4-methoxy-2-(trifluoromethyl)phenyl)-1H-pyrazole (7k)



7k

Compound 7k was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7k** as a yellow oil (25% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.25 (s, 1H), 7.12 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.42 (t, *J* = 2.1 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.70, 140.88, 132.10, 131.73, 130.87, 127.75, 127.50, 124.01, 121.84, 117.57, 112.75, 112.71, 112.67, 112.63, 106.63, 106.60, 56.05, 56.01. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -59.81.

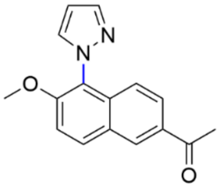
1-(2,4,6-trimethoxyphenyl)-1H-pyrazole (7l)



7l

Compound 7l was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7l** as a white solid (70% yield) which is a known compound.[5] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.60 (s, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.26 (s, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 6.42 (s, 1H), 3.90 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.70, 140.88, 132.10, 131.73, 130.87, 127.75, 127.50, 124.01, 121.84, 117.57, 112.75, 112.71, 112.67, 112.63, 106.63, 106.60, 56.05, 56.01.

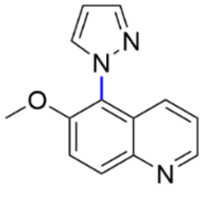
1-(6-methoxy-5-(1H-pyrazol-1-yl)naphthalen-2-yl)ethan-1-one (7m)



7m

Compound 7m was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7m** as a white solid (70% yield) which is a known compound.[5] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.86 (s, 1H), 7.65 (s, 1H), 7.38 (d, *J* = 9.1 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 6.55 (s, 1H), 3.87 (s, 3H), 2.62 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 197.32, 154.45, 140.57, 134.26, 132.91, 132.36, 129.95, 127.52, 125.67, 123.01, 122.55, 114.10, 106.11, 106.08, 56.63, 56.58, 26.43, 26.38.

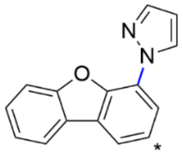
6-methoxy-5-(1H-pyrazol-1-yl)quinoline (7n)



7n

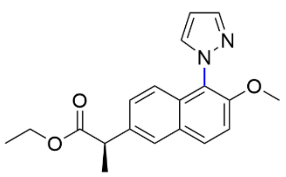
Compound 7n was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7n** as a white solid (63% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.83 – 8.76 (m, 1H), 8.22 (d, *J* = 9.4 Hz, 1H), 7.86 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 9.4 Hz, 1H), 7.33 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.55 (s, 1H), 3.89 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.37, 148.82, 143.37, 140.75, 133.10, 131.97, 130.93, 127.21, 122.39, 116.72, 106.22, 106.19, 56.90, 56.86.

1-(dibenzo[b,d]furan-4-yl)-1H-pyrazole (7o)


7o

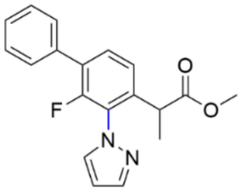
Compound 7o was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford a **mixture of two regioisomers** as a white solid (58% yield) which is a known compound.[2] Analysis of the isolated product by 1H NMR spectroscopy determined the **ortho isomer (7o) to para isomer (7o') ratio** to be **10:1**. The spectral data provided below correspond to the major isomer **(7o)** as shown. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.63 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 8.17 (s, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.80 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.58 (s, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 156.07, 155.93, 141.17, 139.23, 128.13, 127.34, 123.29, 123.13, 121.78, 121.46, 120.98, 113.87, 111.54, 108.07, 101.81.

Ethyl-(R)-2-(6-methoxy-5-(1H-pyrazol-1-yl) naphthalen-2-yl) propanoate (7p)


7p

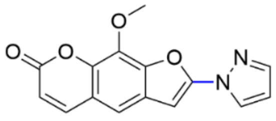
Compound 7p was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7p** as a white solid (55% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 9.1 Hz, 1H), 7.86 (s, 1H), 7.73 (s, 1H), 7.65 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 9.1 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.54 (s, 1H), 4.17 – 4.04 (m, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.82 (t, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 174.44, 152.51, 140.58, 136.76, 133.00, 131.35, 130.57, 128.91, 127.88, 125.87, 123.14, 122.66, 113.89, 106.02, 60.89, 56.88, 45.44, 18.52, 14.17. **HRMS** (ESI): m/z calculated for $C_{19}H_{21}N_2O_3^+$ [M+H]$^+$ 325.1507, found 325.1512.

methyl 2-(2-fluoro-3-(1H-pyrazol-1-yl)-[1,1'-biphenyl]-4-yl)propanoate (7q)


7q

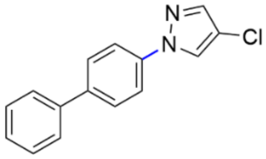
Compound 7q was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7q** as a white solid (30% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.6 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.74 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.19 – 7.11 (m, 2H), 6.48 (s, 1H), 3.77 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 174.40, 160.85, 158.87, 142.31, 142.25, 141.31, 139.71, 133.70, 130.66, 130.03, 126.76, 123.75, 119.20, 115.56, 115.38, 107.83, 52.23, 45.04, 18.49. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -117.23 – -117.39 (m). **HRMS** (ESI): m/z calculated for $C_{19}H_{18}FN_2O_2^+$ [M+H]$^+$ 325.1308, found 325.1352.

9-methoxy-2-(1H-pyrazol-1-yl)-7H-furo[3,2-g]chromen-7-one (7r)


7r

Compound 7r was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7r** as a white solid (34% yield).**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.77 (d, *J* = 13.9 Hz, 2H), 7.70 (s, 1H), 6.71 (s, 1H), 6.58 (s, 1H), 6.37 (d, *J* = 9.8 Hz, 1H), 4.33 (s, 3H).^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 159.69, 147.39, 147.28, 143.17, 141.83, 140.09, 133.12, 132.09, 123.26, 123.20, 115.76, 112.77, 107.60, 105.03, 61.62, 61.59. **HRMS** (ESI): m/z calculated for $C_{15}H_{10}N_2NaO_4^+$ $[M+Na]^+$ 305.0541, found 305.0548.

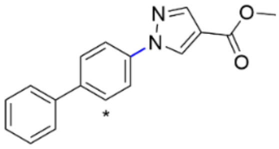
1-([1,1'-biphenyl]-4-yl)-4-chloro-1H-pyrazole (7s)



7s

Compound 7s was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7s** as a white solid (59% yield) which is a known compound.[2] ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.75 – 7.65 (m, 5H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 140.06, 140.02, 139.69, 138.99, 129.04, 128.27, 127.77, 127.10, 124.89, 119.33, 112.62.

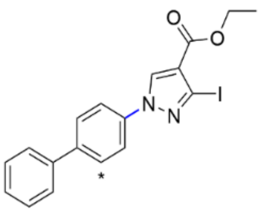
Methyl-1-([1,1'-biphenyl]-4-yl)-1H-pyrazole-4-carboxylate (7t)



7t

Compound 7t was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford a **mixture of two regioisomers** as a white solid (40% yield). Analysis of the isolated product by 1H NMR spectroscopy determined the **para isomer (7t) to ortho isomer (7t') ratio** to be **18:1**. The spectral data provided below correspond to the major isomer **(7t)** as shown. ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.13 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 7.0 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 3.89 (s, 3H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 163.36, 142.38, 140.69, 139.92, 138.63, 130.10, 129.07, 128.36, 127.90, 127.15, 119.99, 116.76, 51.75, 51.71. **HRMS** (ESI): m/z calculated for $C_{17}H_{15}N_2O_2{}^+$ $[M+H]^+$ 279.1089, found 279.1092.

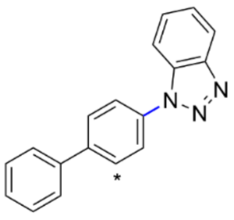
Ethyl-1-([1,1'-biphenyl]-4-yl)-3-iodo-1H-pyrazole-4-carboxylate (7u)



7u

Compound 7u was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford a **mixture of two regioisomers** as a white solid (35% yield). Analysis of the isolated product by 1H NMR spectroscopy determined the **para isomer (7u) to ortho isomer (7u') ratio** to be **21:1**. The spectral data provided below correspond to the major isomer **(7u)** as shown. ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 141.06, 139.74, 137.97, 131.53, 129.06, 128.29, 127.96, 127.13, 119.85, 119.59, 100.08, 60.83, 14.45. **HRMS** (ESI): m/z calculated for $C_{18}H_{15}IN_2NaO_2{}^+$ $[M+Na]^+$ 441.0076, found 441.0083.

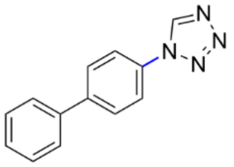
1-([1,1'-biphenyl]-4-yl)-1H-benzo[d][1,2,3]triazole (7v)



7v

Compound 7v was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford a **mixture of two regioisomers** as a white solid (57% yield) which is a known compound. Analysis of the isolated product by 1H NMR spectroscopy determined the **para isomer (7v) to ortho isomer (7v') ratio** to be **10:1**. The spectral data provided below correspond to the major isomer **(7v)** as shown. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.43 (t, *J* = 7.2 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 146.63, 141.67, 139.81, 132.35, 131.35, 130.31, 129.07, 128.52, 128.36, 128.01, 127.20, 124.49, 123.11, 120.41, 110.49. **HRMS** (ESI): m/z calculated for $C_{18}H_{13}N_3{}^+$ $[M+H]^+$ 272.1143, found 272.1182.

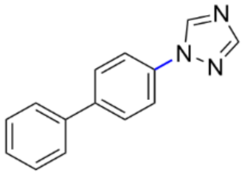
1-([1,1'-biphenyl]-4-yl)-1H-tetrazole (7w)



7w

Compound 7w was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7w** as a white solid (30% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.05 (s, 1H), 7.79 (s, 4H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143.34, 140.56, 139.31, 132.97, 131.02, 129.25, 128.92, 128.49, 127.29, 121.68.

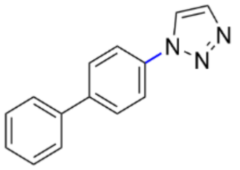
1-([1,1'-biphenyl]-4-yl)-1H-1,2,4-triazole (7x)



7x

Compound 7x was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7x** as a white solid (52% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.13 (s, 1H), 7.74 (q, *J* = 8.7 Hz, 4H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.77, 141.37, 140.94, 139.77, 136.22, 129.09, 128.50, 128.02, 127.17, 120.47.

1-([1,1'-biphenyl]-4-yl)-1H-1,2,3-triazole (7y)



7y

Compound 7y was synthesised by following ***General Procedure 2*** and was purified by column chromatography (eluent: hexane/EtOAc) to afford **7y** as a white solid (84% yield) which is a known compound.[2] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.86 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.85, 139.67, 136.21, 134.59, 129.08, 128.44, 128.06, 127.15, 121.76, 121.01.

12. References

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Okram, R. Singh and O. Singh, *ChemistrySelect*, 2025, **10**; (c) P. Mohinuddin, R. Dada, A. Almansour, N. Arumugam and S. Yaragorla, *Tetrahedron Lett.*, 2019, **60**, 1043–1048.

2 (a) D. S. Brandes, M. R. Lasky, A. V. R. D. Lisboa, E.-C. Liu, M. S. Remy and M. S. Sanford, *Org. Lett.,* 2025, **27**, 10011–10015; (b) M. R. Lasky, E.-C. Liu, M. S. Remy and M. S. Sanford, *J. Am. Chem. Soc.*, 2024, **146**, 14799–14806.

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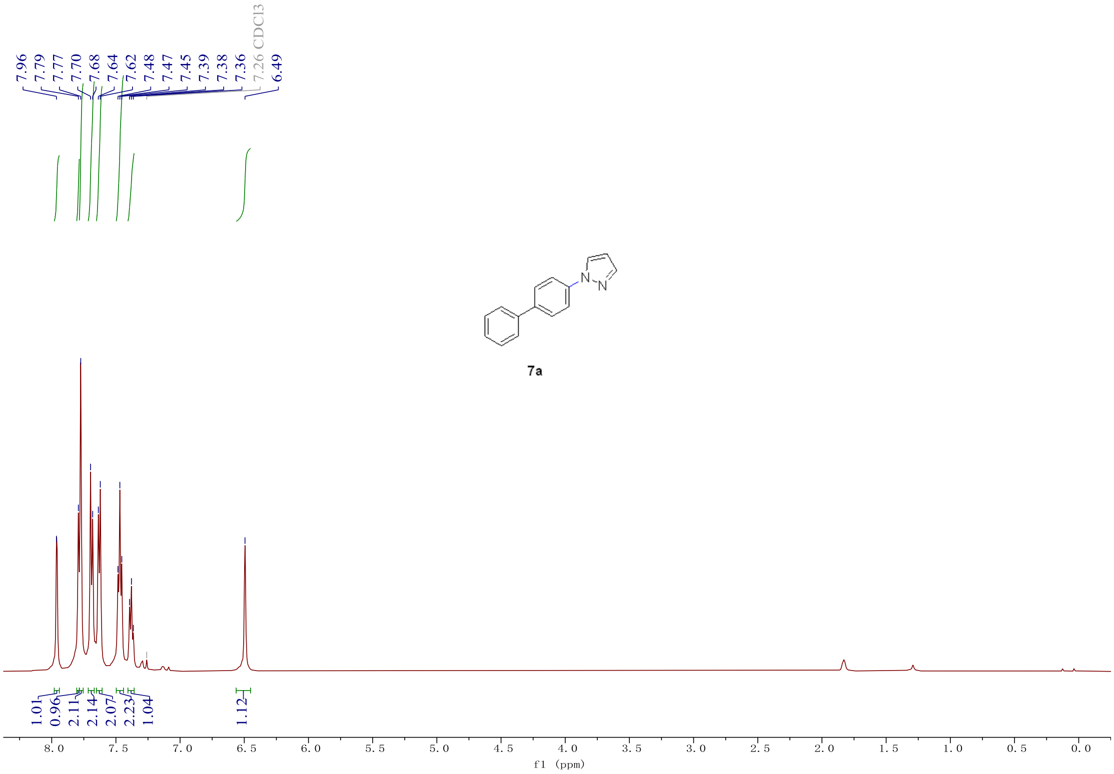
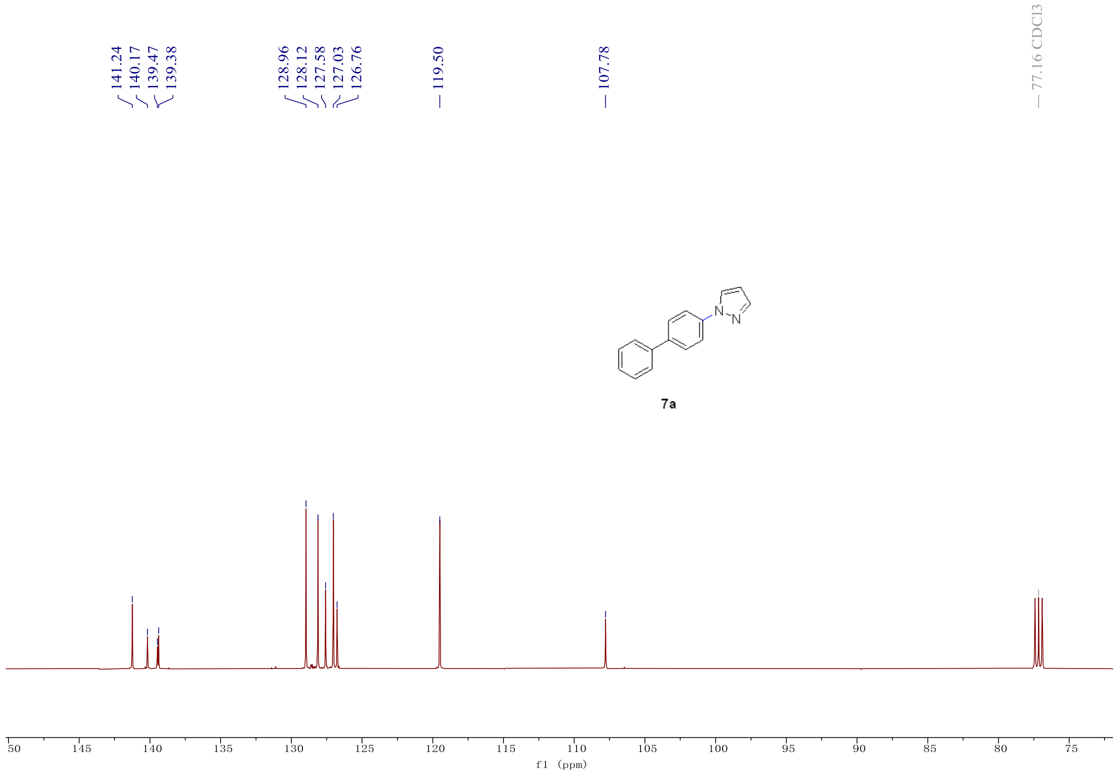
5 M. Zheng, I. Ghosh, B. König and X. Wang, *ChemCatChem*, 2018, **11**, 703–706

13. NMR data




7a

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140.17
139.47
139.38
128.96
128.12
127.58
127.03
126.76
119.50
107.78
77.16 CDCl3
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50
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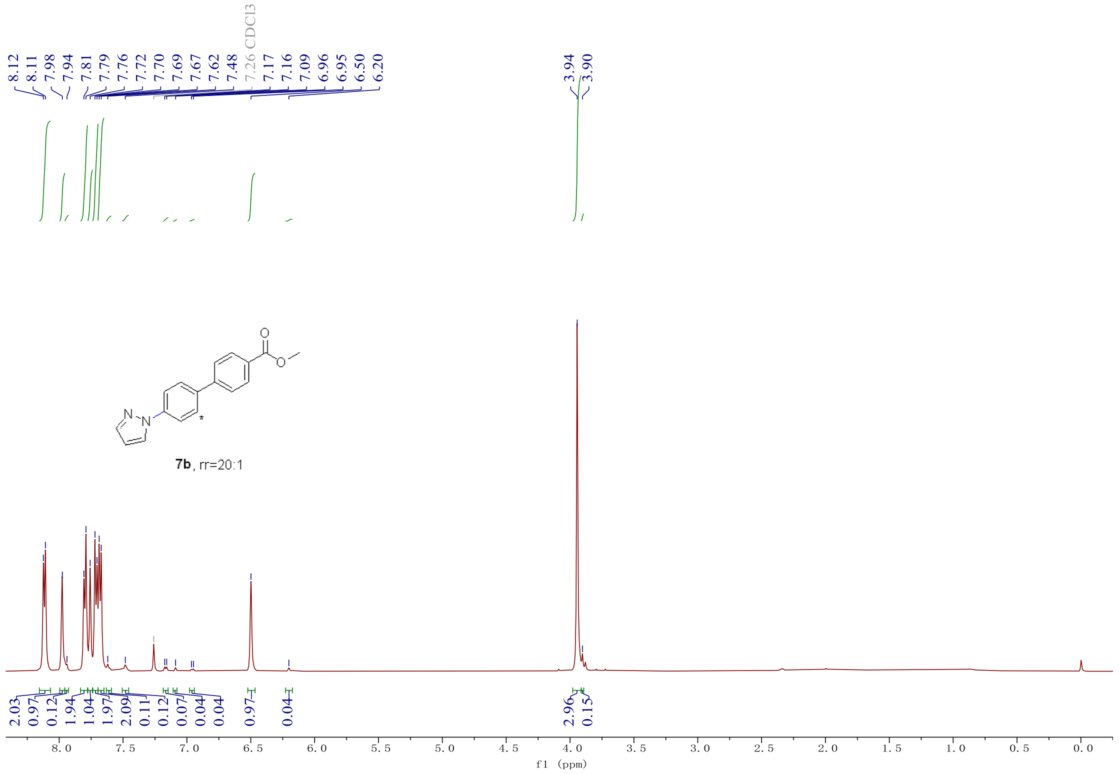
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)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7.67
7.62
7.48
7.26 CDCl3
7.17
7.16
7.09
6.96
6.95
6.50
6.20
3.94
3.90
O
O
N
N
*
2.03
0.97
0.12
1.94
1.04
1.97
2.09
0.11
0.12
0.07
0.04
0.04
0.97
0.04
2.96
0.15
8.0
7.5
7.0
6.5
6.0
5.5
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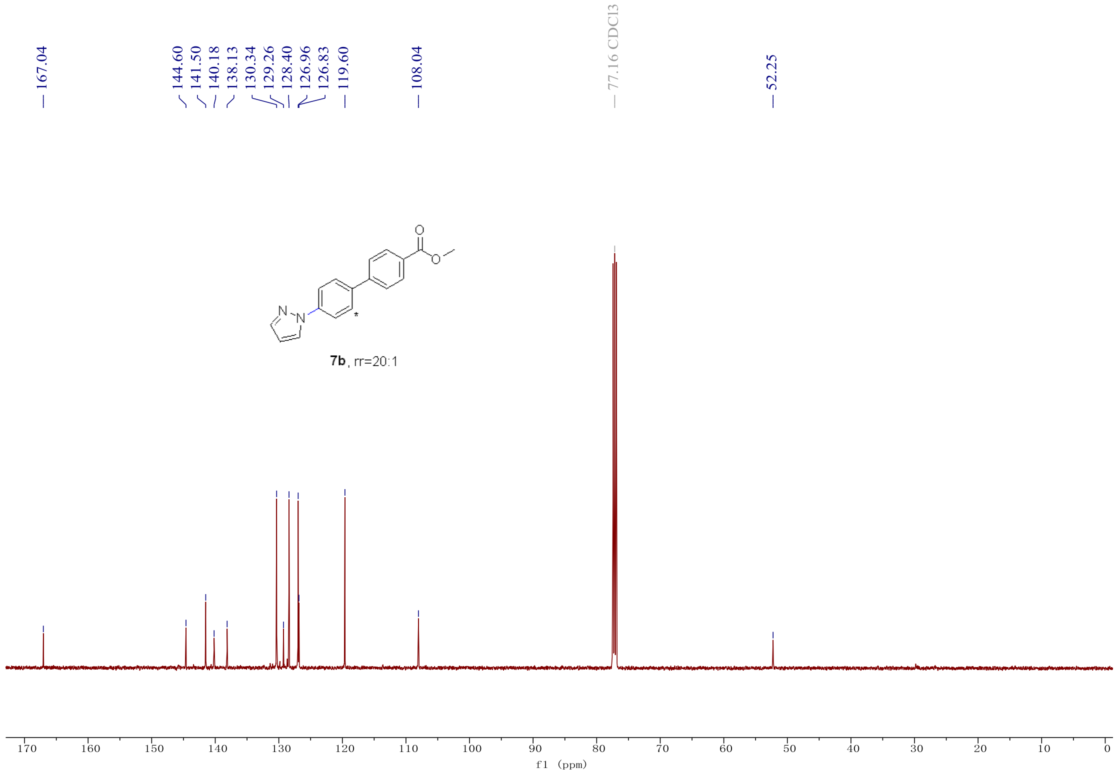
f1 (ppm)



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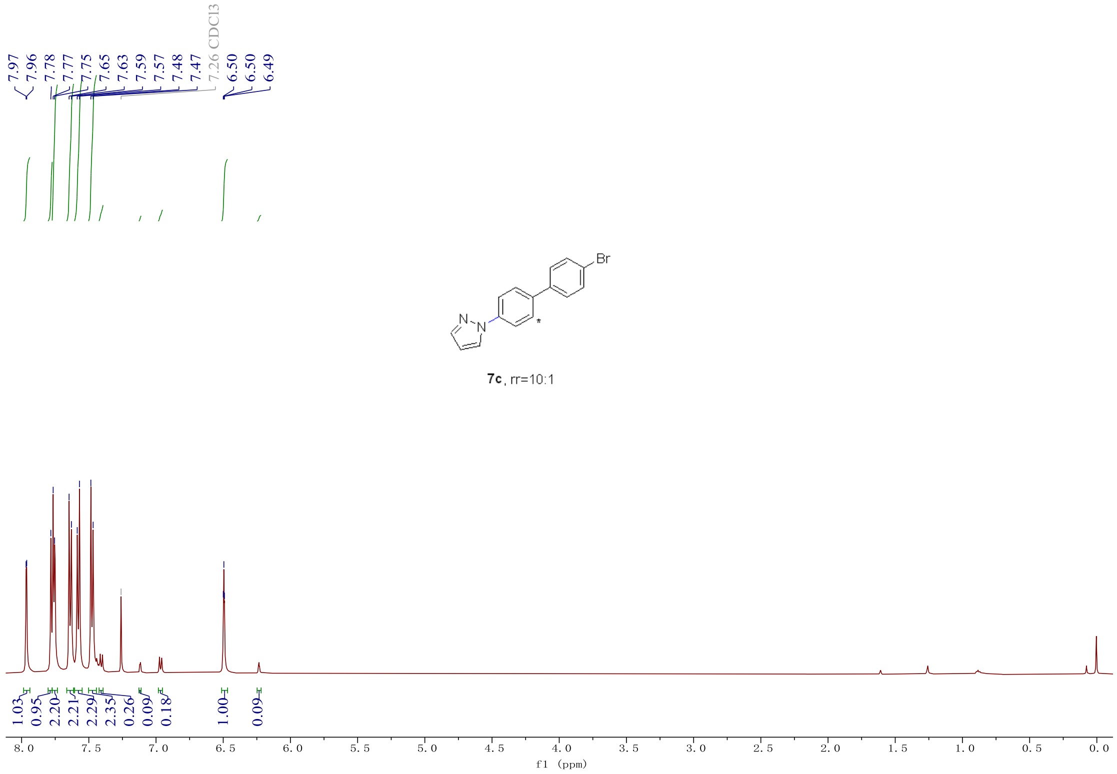

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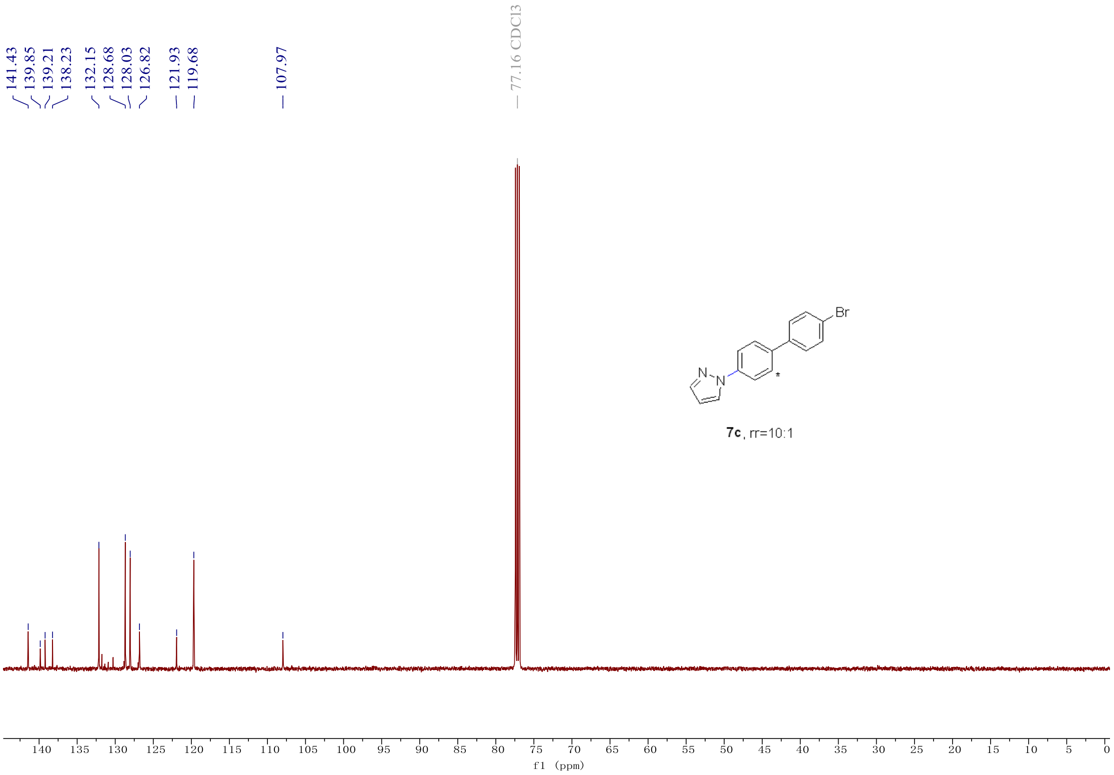
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N
N
Br
*
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
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45
40
35
30
25
20
15
10
5
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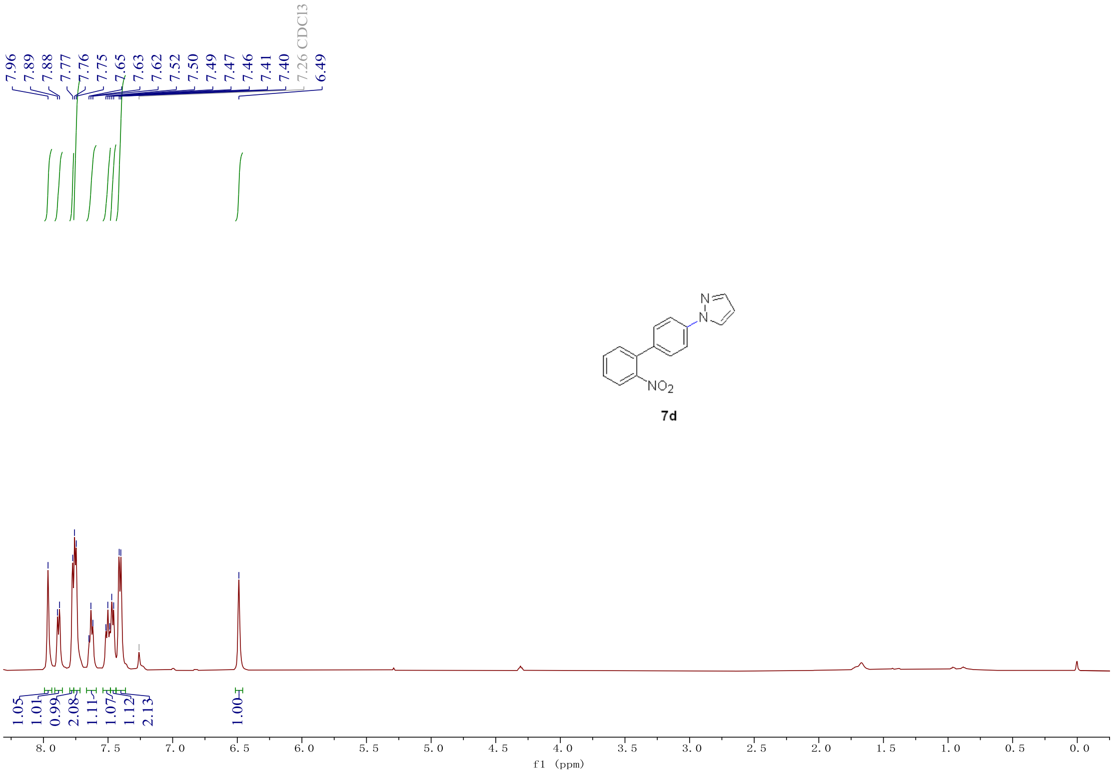
f1 (ppm)

7c, rr=10:1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2.08
1.11
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2.13
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5.0
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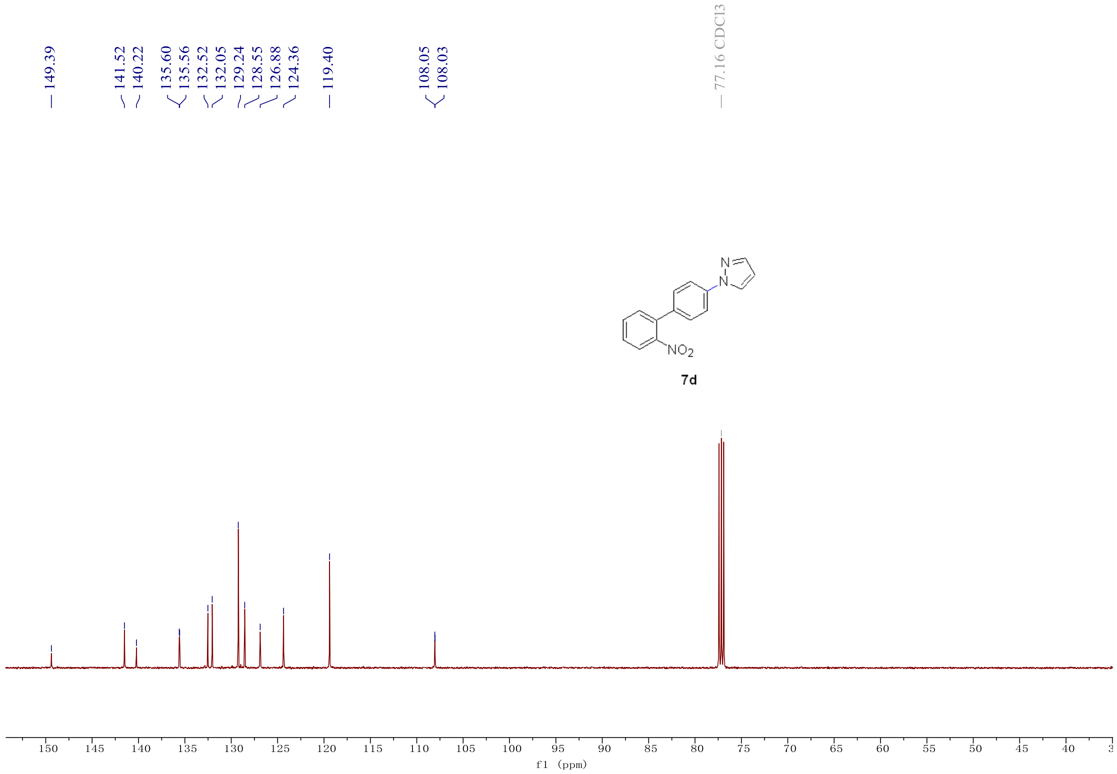
f1 (ppm)

7d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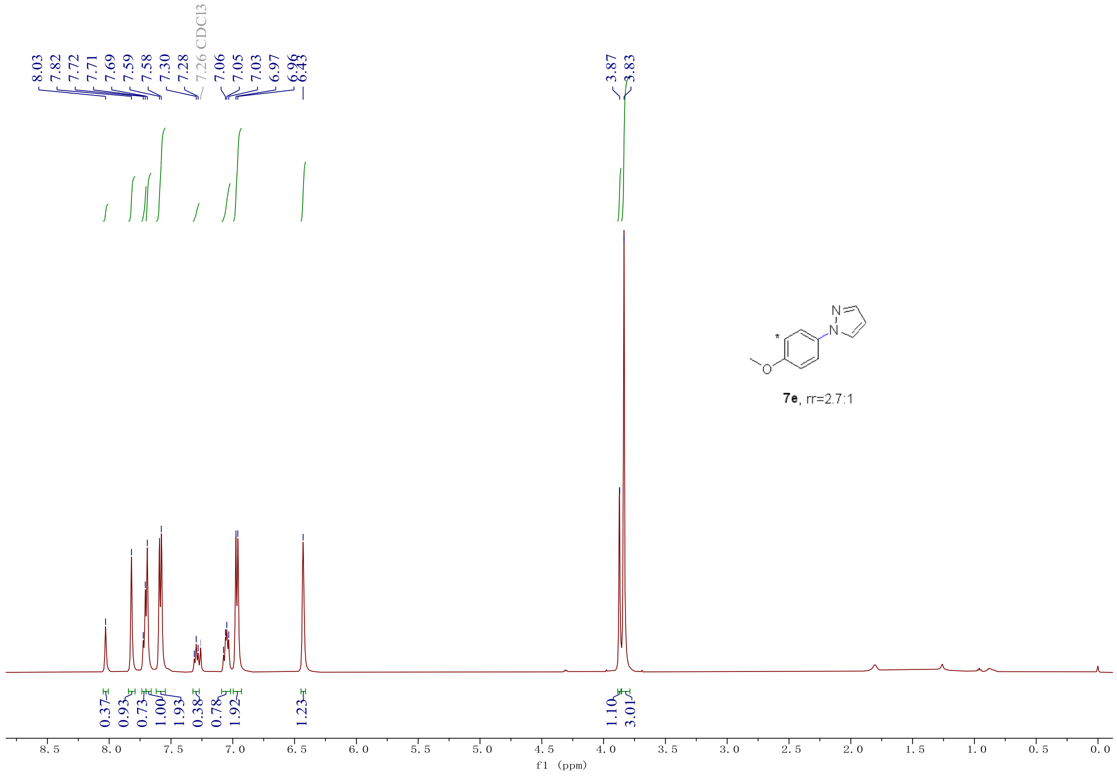
f1 (ppm)

7d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7.03
6.97
6.96
6.43
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3.83
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O
*
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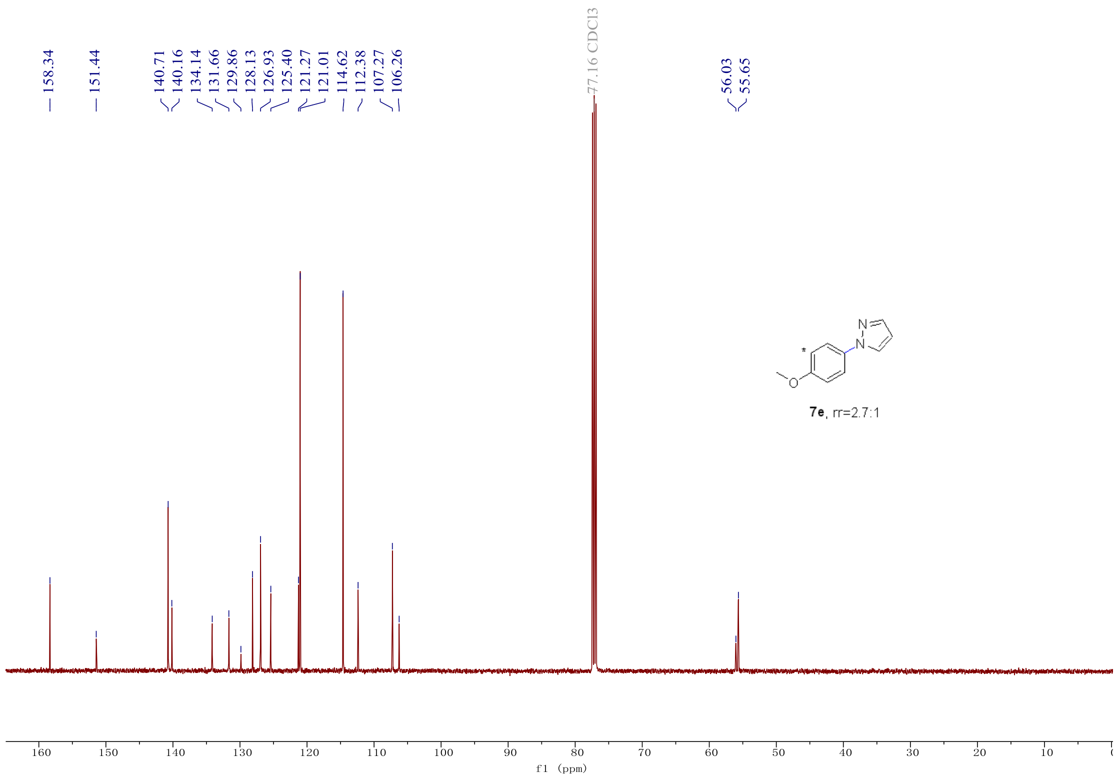
0.93
0.73
1.00
1.93
0.38
0.78
1.92
1.23
1.10
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

7e, rr=2.7:1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112.38
107.27
106.26
77.16 CDCl3
56.03
55.65
N
N
*
O
7e, rr=2.7:1
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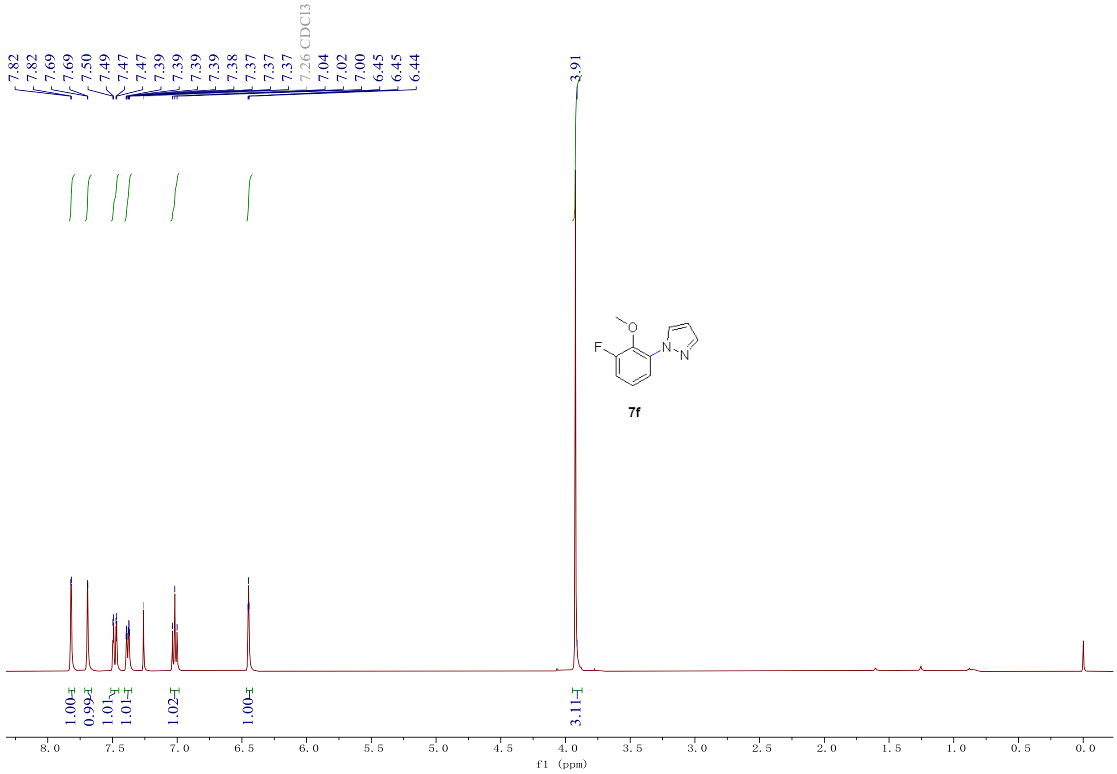
20
10
f1 (ppm)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7.02
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3.91
O
F
N
N
7f
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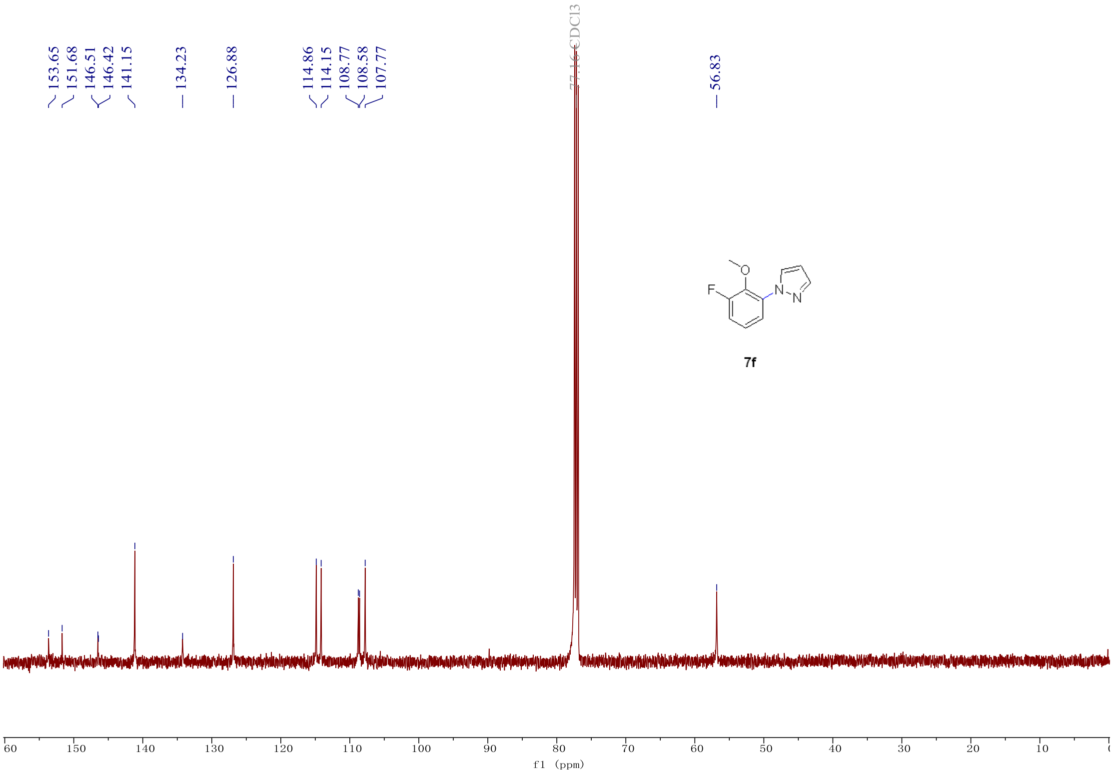
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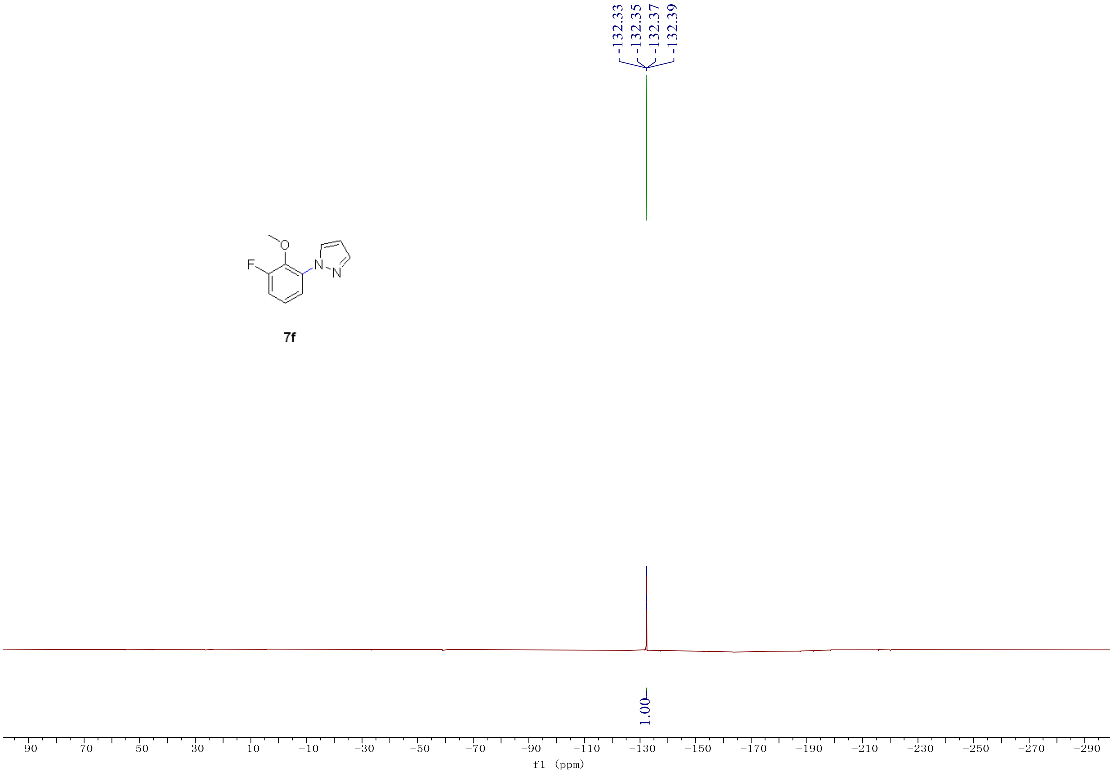
7f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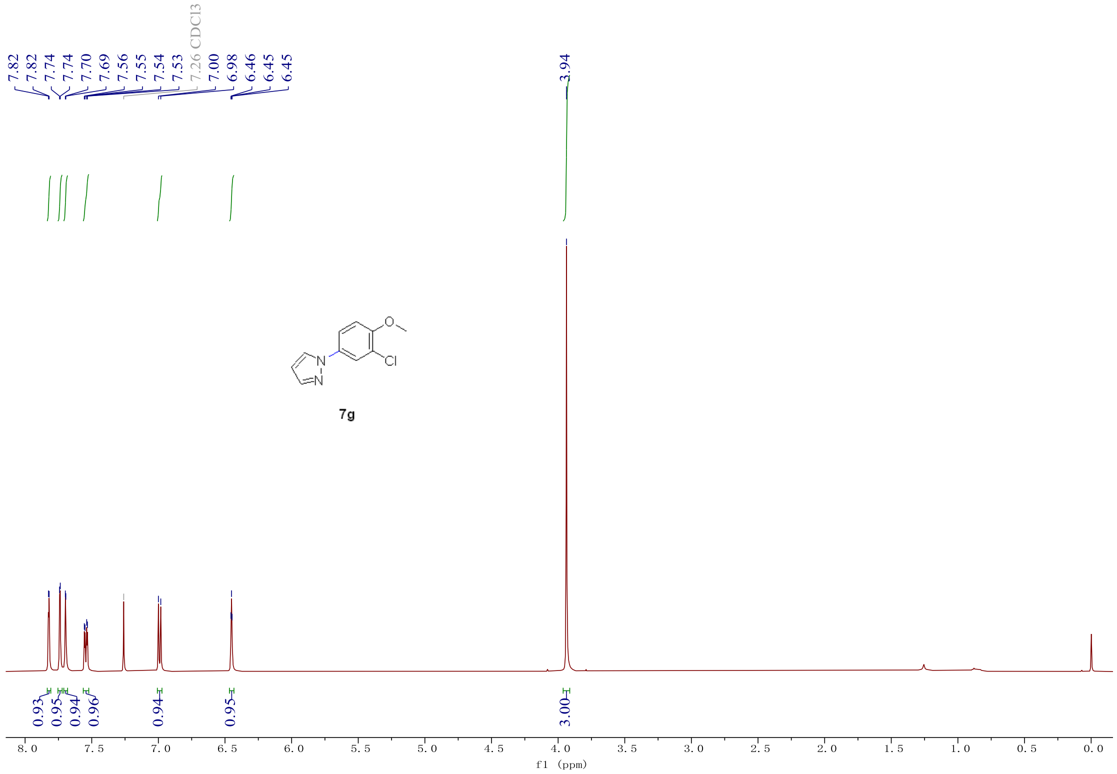
f1 (ppm)

7f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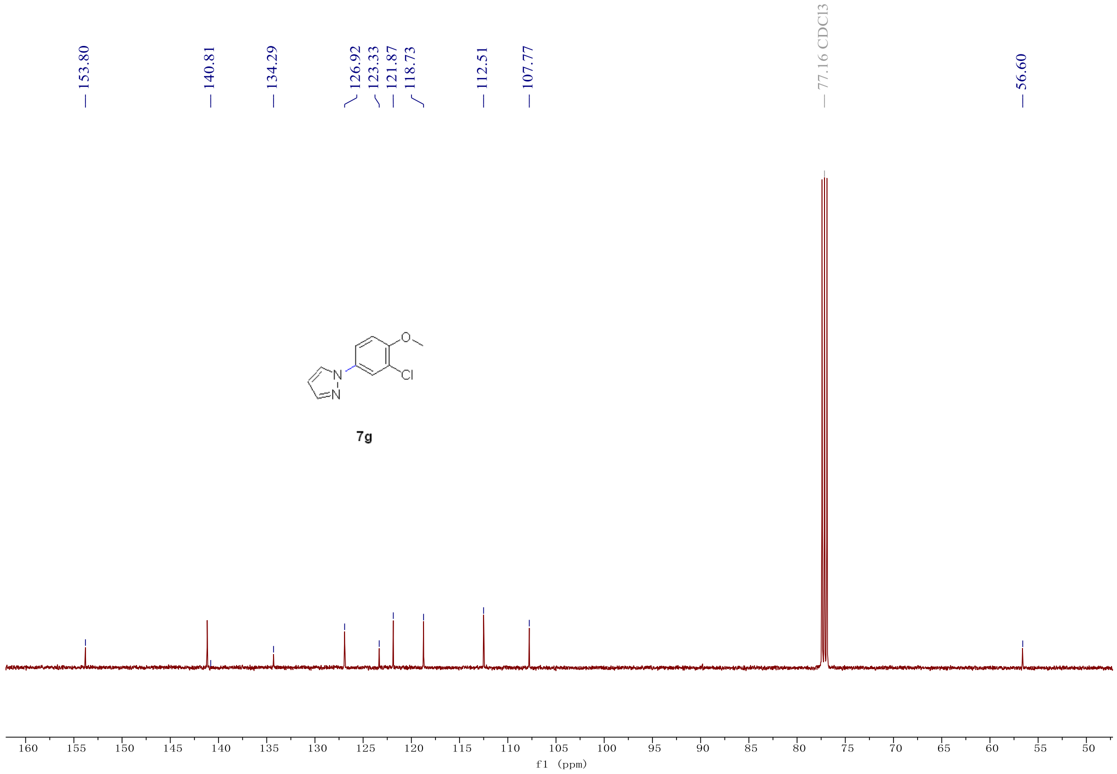
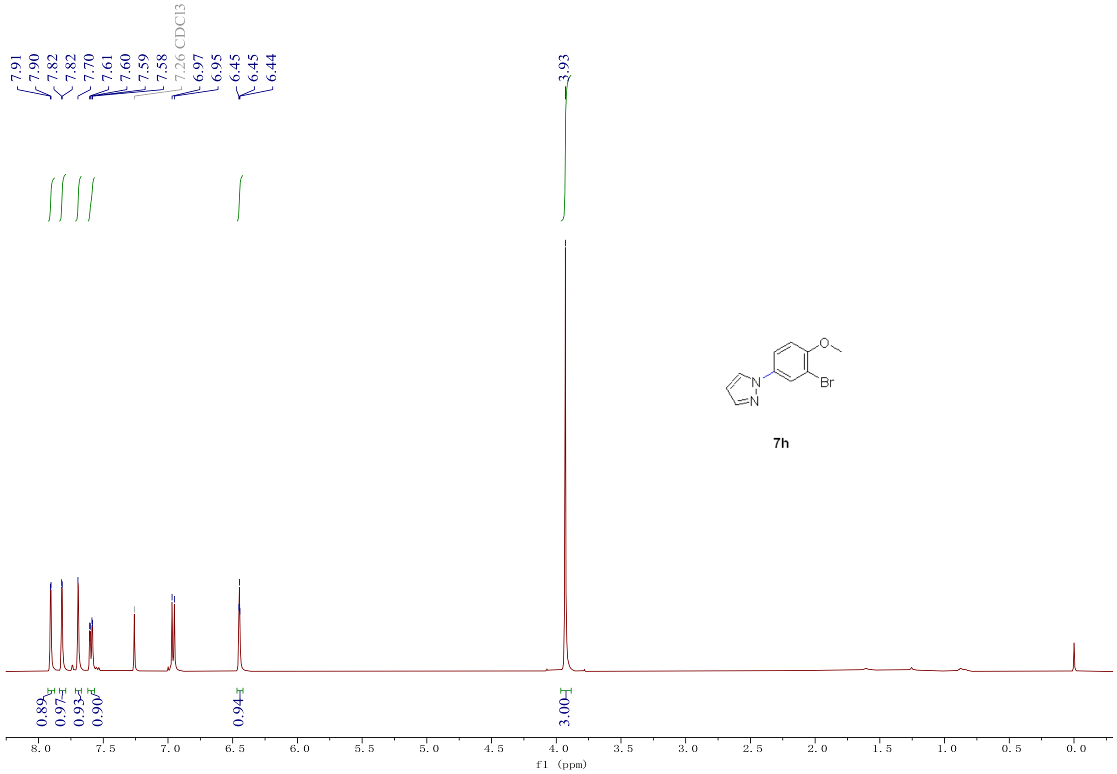
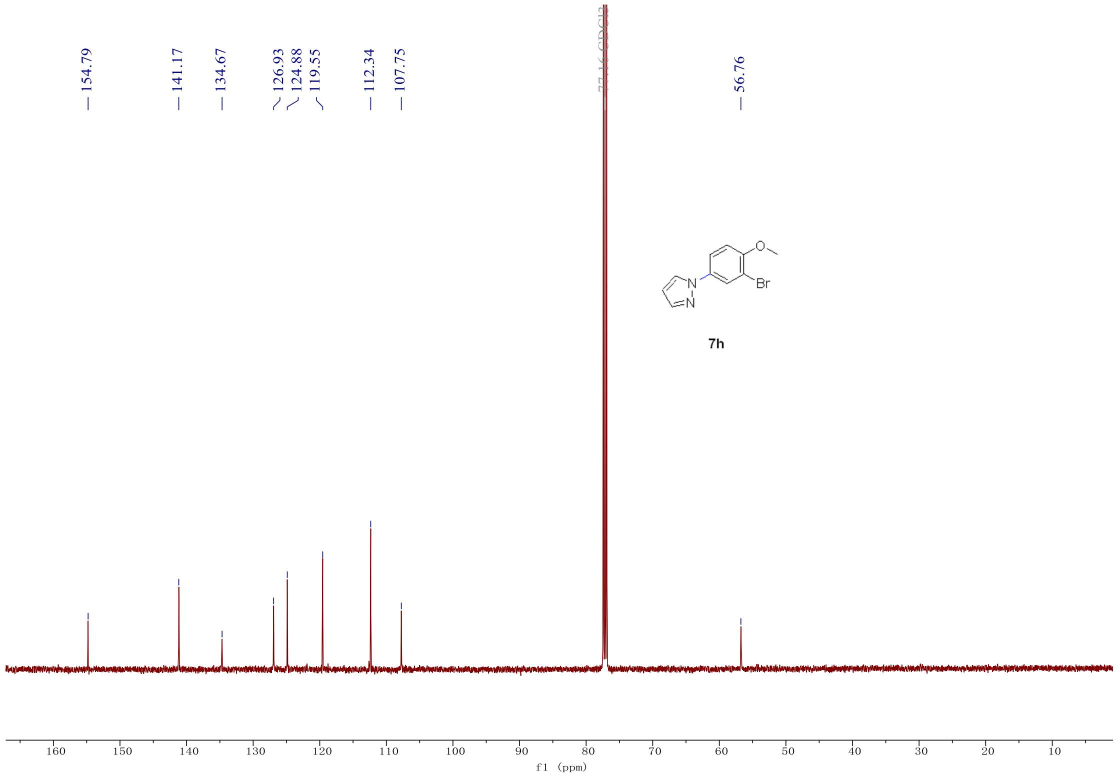
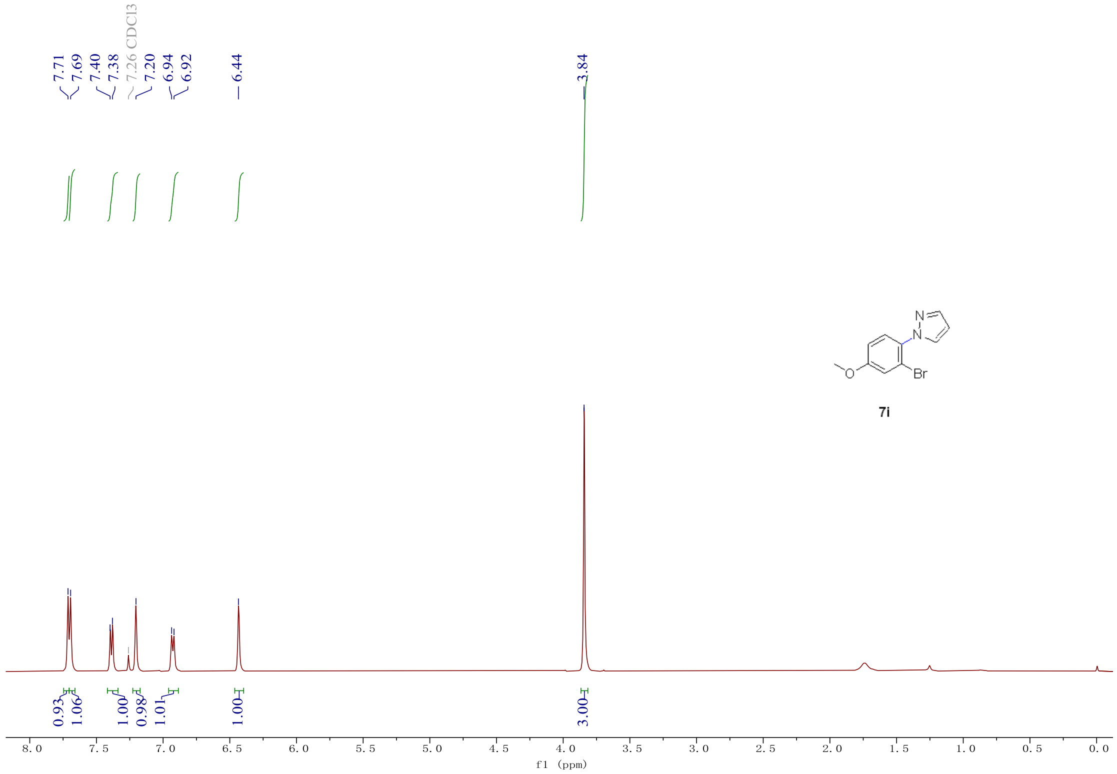
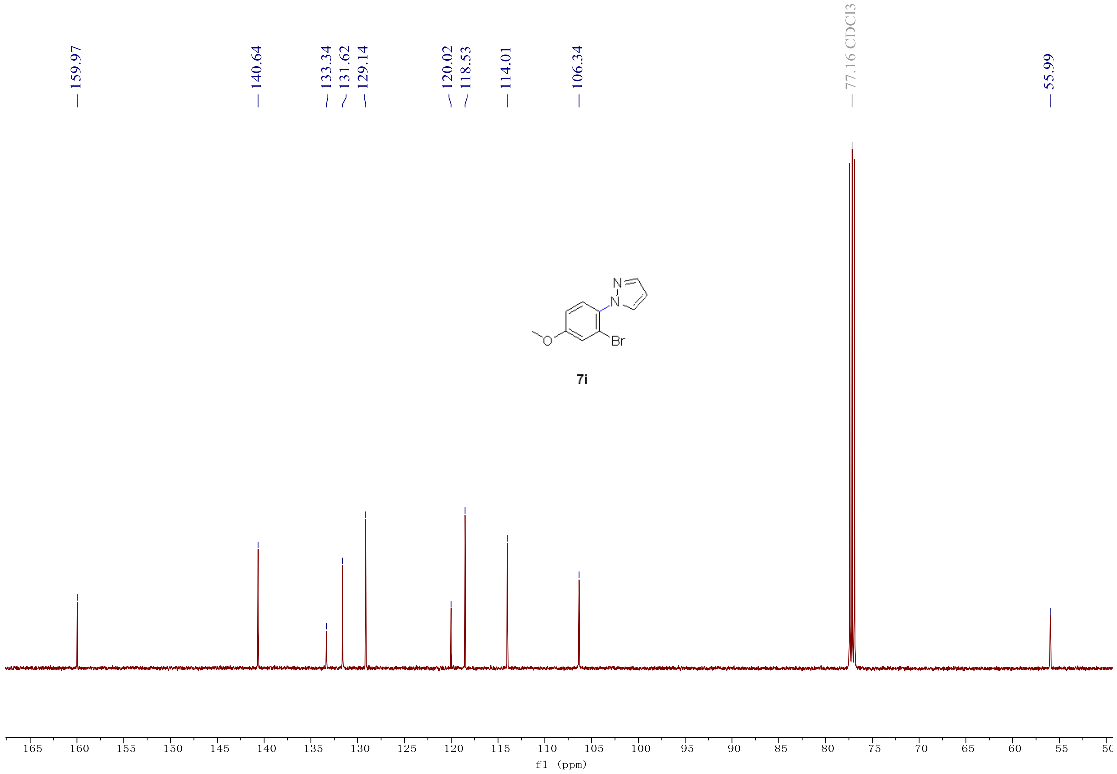
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

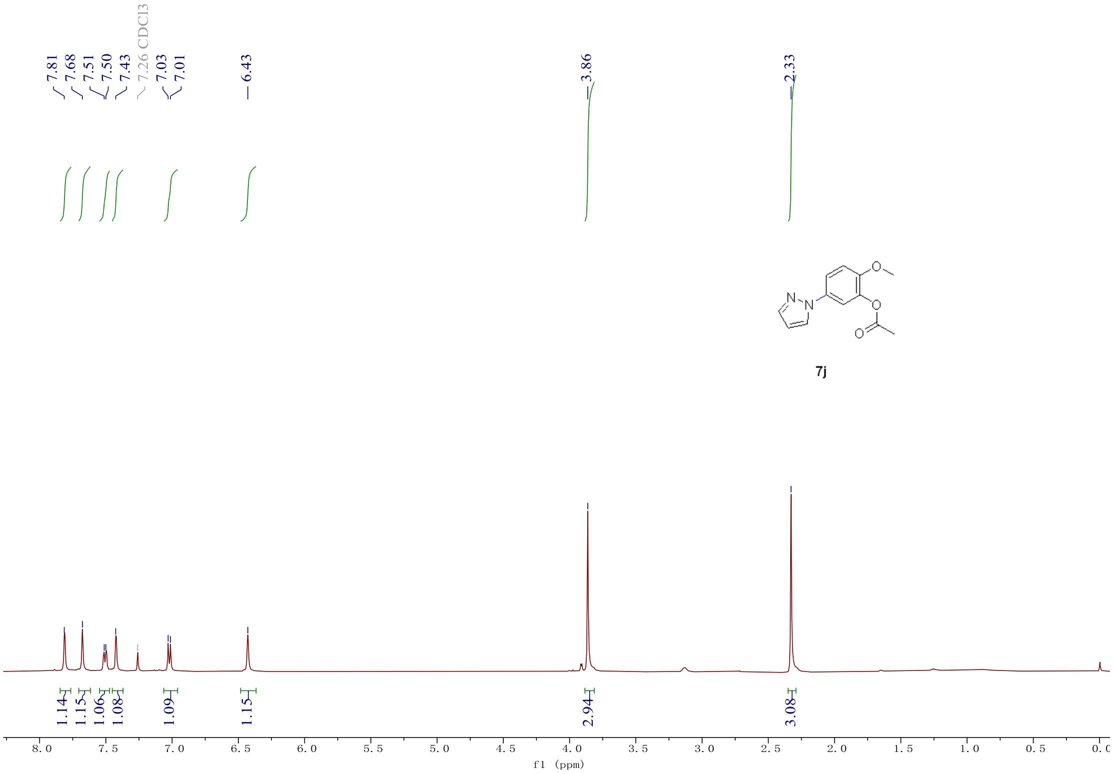

153.80
140.81
134.29
126.92
123.33
121.87
118.73
112.51
107.77
77.16 CDCl3
56.60
N
N
O
Cl
7g
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
f1 (ppm)

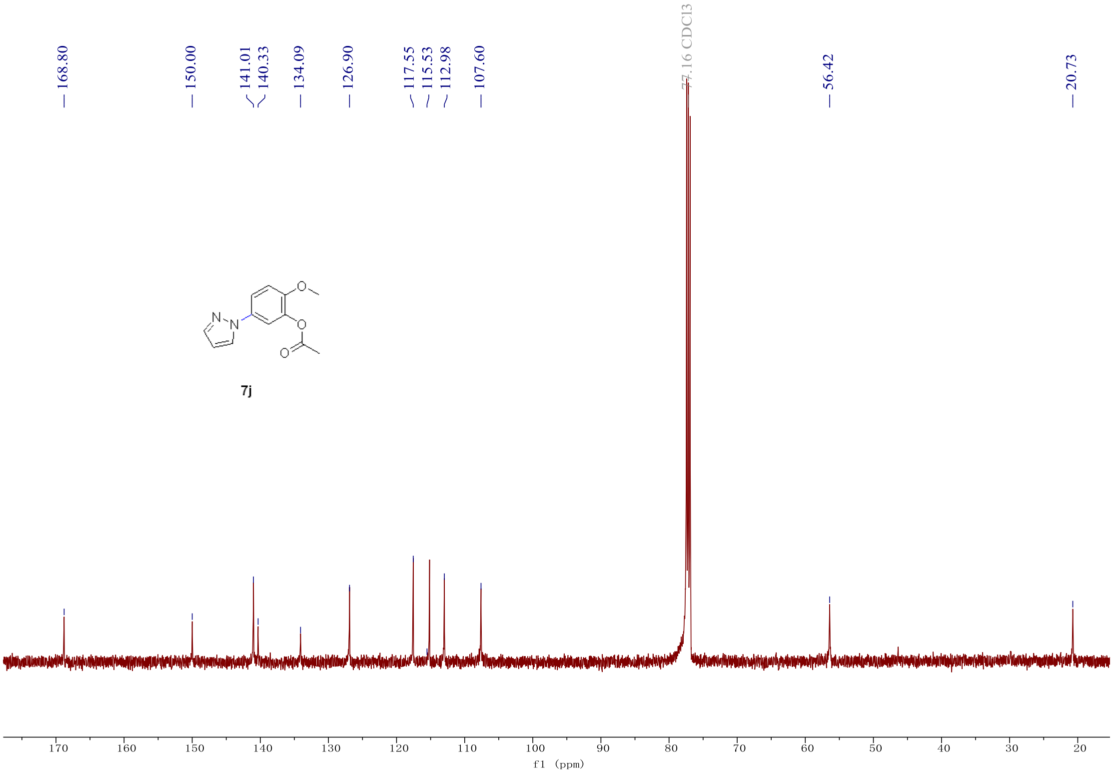

7.91
7.90
7.82
7.82
7.70
7.61
7.60
7.59
7.58
7.26 CDCl3
6.97
6.95
6.45
6.45
6.44
3.93
N
N
O
Br
7h
0.89
0.97
0.93
0.90
0.94
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

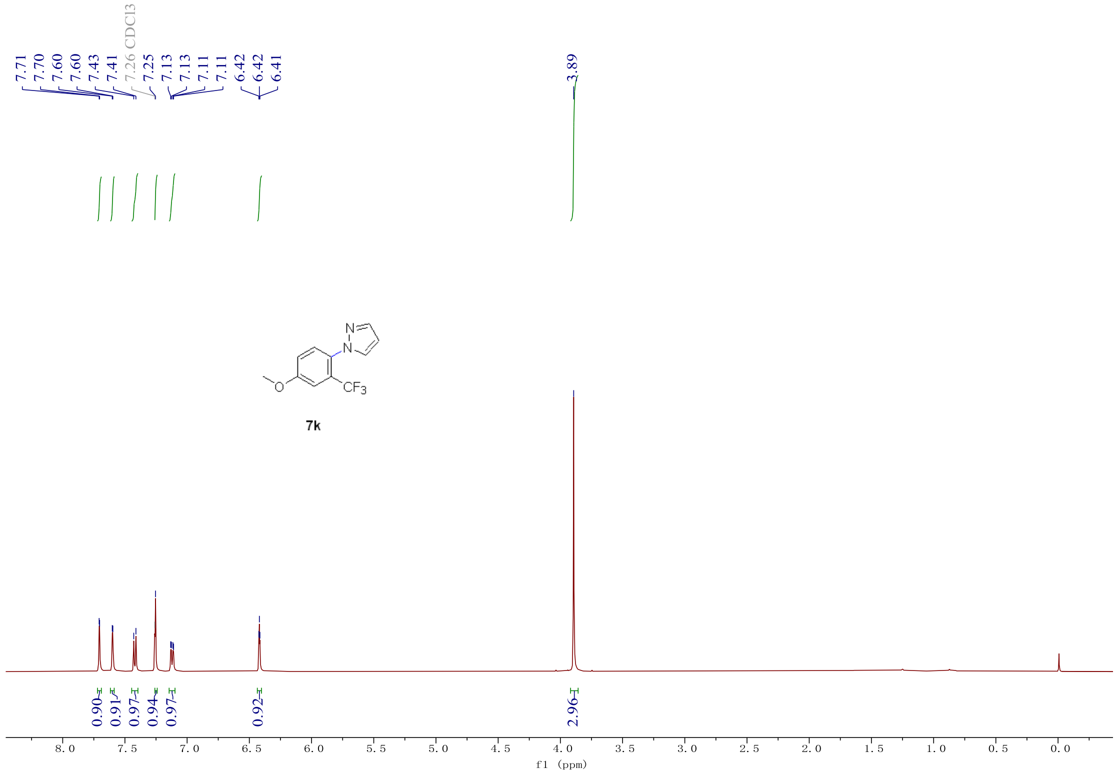

154.79
141.17
134.67
126.93
124.88
119.55
112.34
107.75
77.16 CDCl3
56.76
N
N
O
Br
7h
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

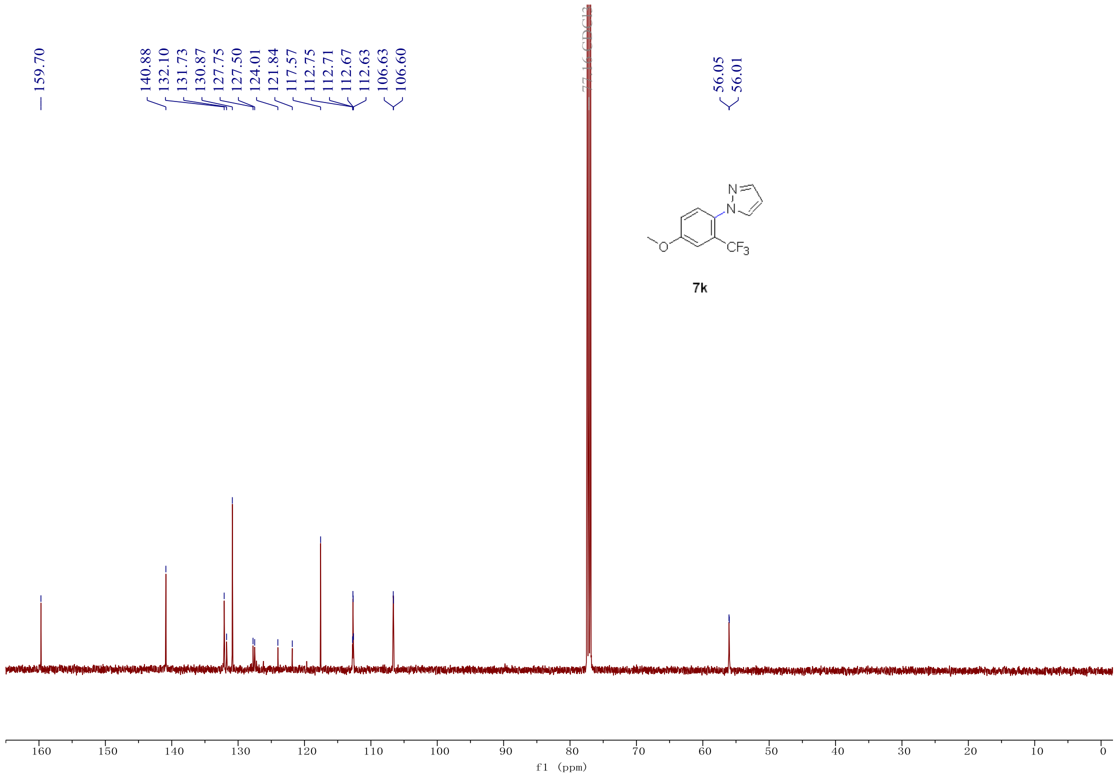

7.71
7.69
7.40
7.38
7.26 CDCl3
7.20
6.94
6.92
6.44
3.84
N
N
O
Br
7i
0.93
1.06
1.00
0.98
1.01
1.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

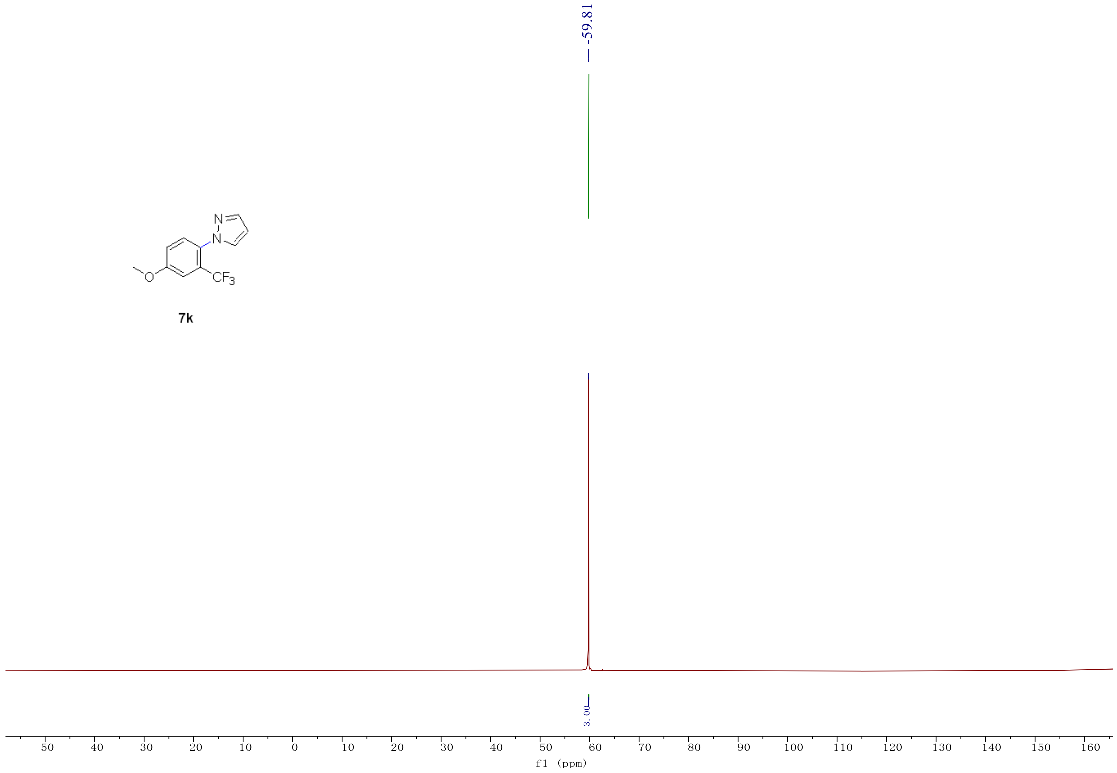

159.97
140.64
133.34
131.62
129.14
120.02
118.53
114.01
106.34
77.16 CDCl3
55.99
N
N
O
Br
7i
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
f1 (ppm)


7.81
7.68
7.51
7.50
7.43
7.26 CDCl3
7.03
7.01
6.43
3.86
2.33
7j
1.14
1.15
1.06
1.08
1.09
1.15
2.94
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

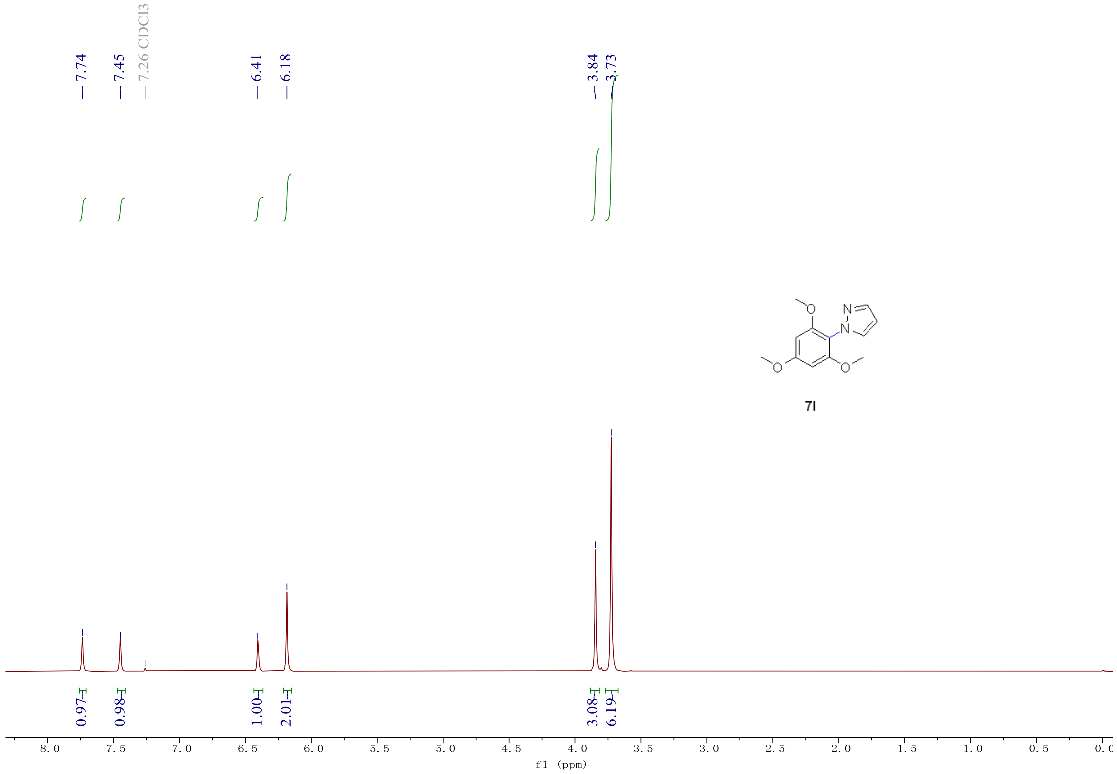

168.80
150.00
141.01
140.33
134.09
126.90
117.55
115.53
112.98
107.60
77.16 CDCl3
56.42
20.73
7j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.71
7.70
7.60
7.60
7.43
7.41
7.26 CDCl3
7.25
7.13
7.13
7.11
7.11
6.42
6.42
6.41
3.89
N
N
O
CF3
7k
0.90
0.91
0.97
0.94
0.97
0.92
2.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

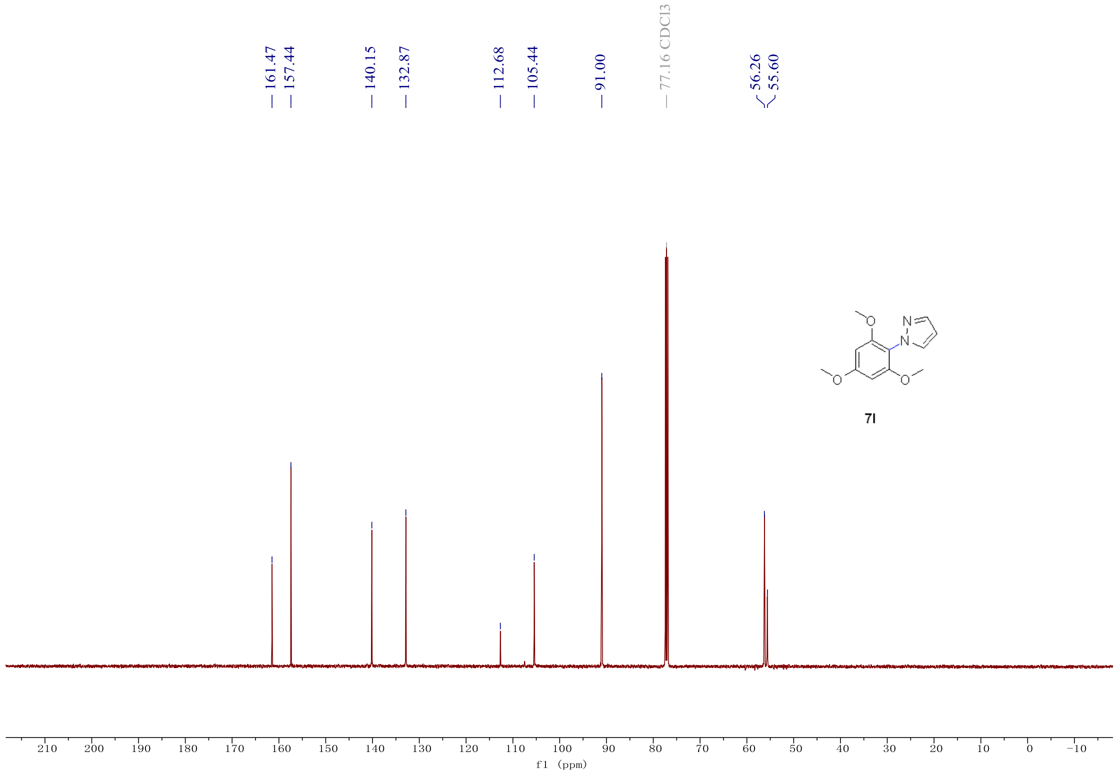

159.70
140.88
132.10
131.73
130.87
127.75
127.50
124.01
121.84
117.57
112.75
112.71
112.67
112.63
106.63
106.60
77.16 CDCl3
56.05
56.01
N
N
O
CF3
7k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-59.81
3.00
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
f1 (ppm)
N
N
O
CF3

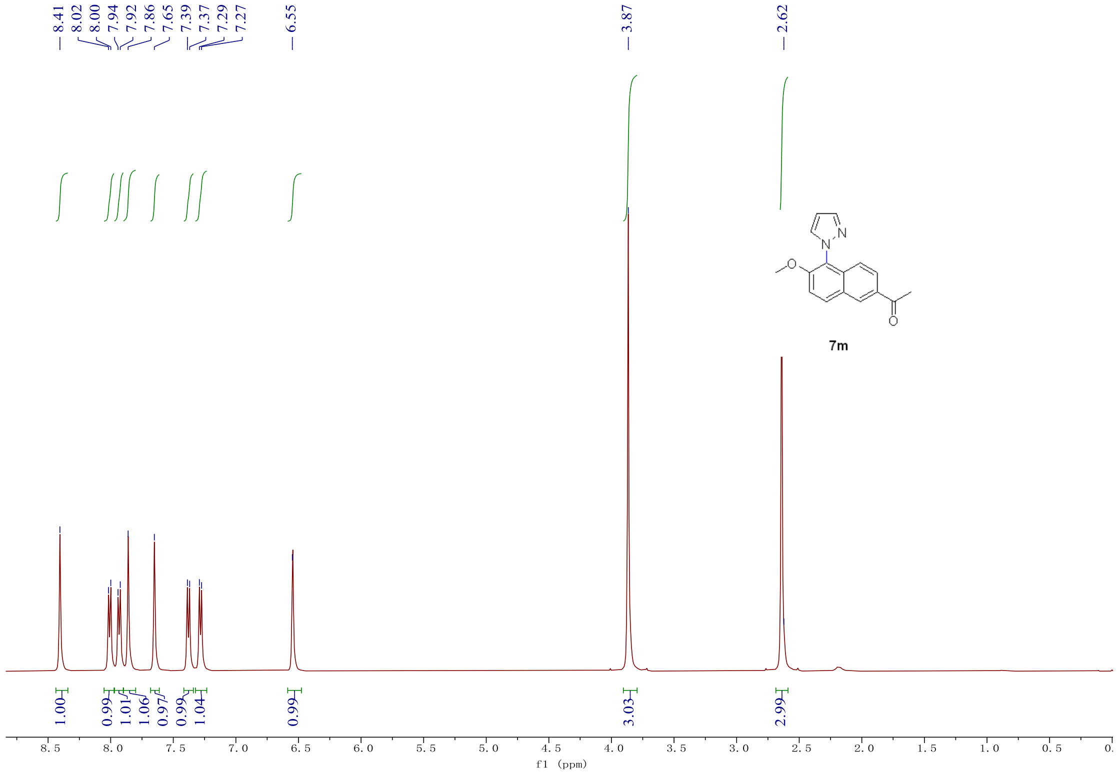
7k


7.74
7.45
7.26 CDCl3
6.41
6.18
3.84
3.73
0.97
0.98
1.00
2.01
3.08
6.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
N
N
O
O

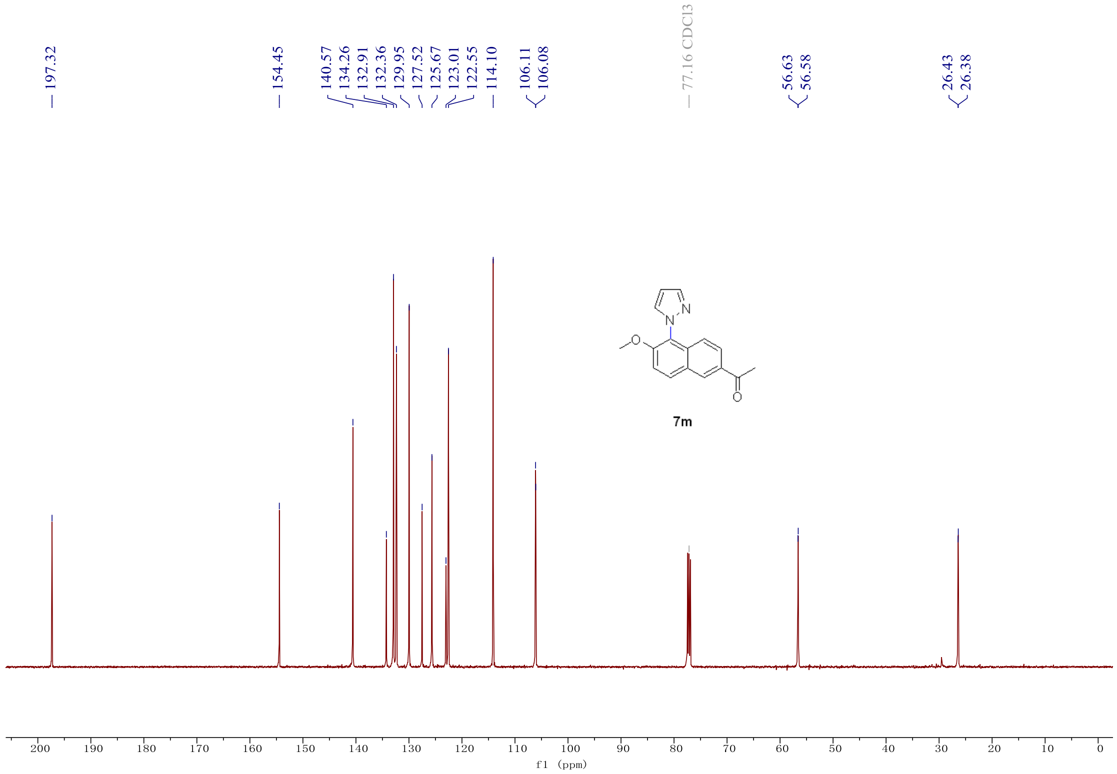
7l



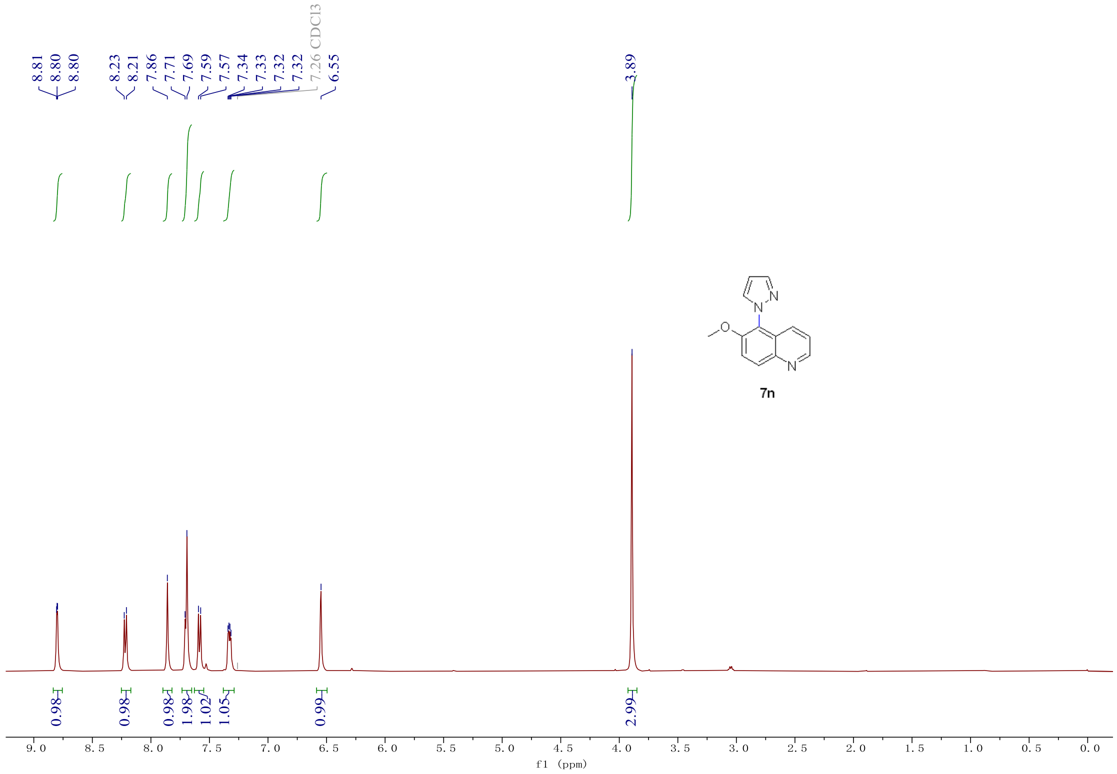
161.47
157.44
140.15
132.87
112.68
105.44
91.00
77.16 CDCl3
56.26
55.60
N
N
O
O
O
7l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



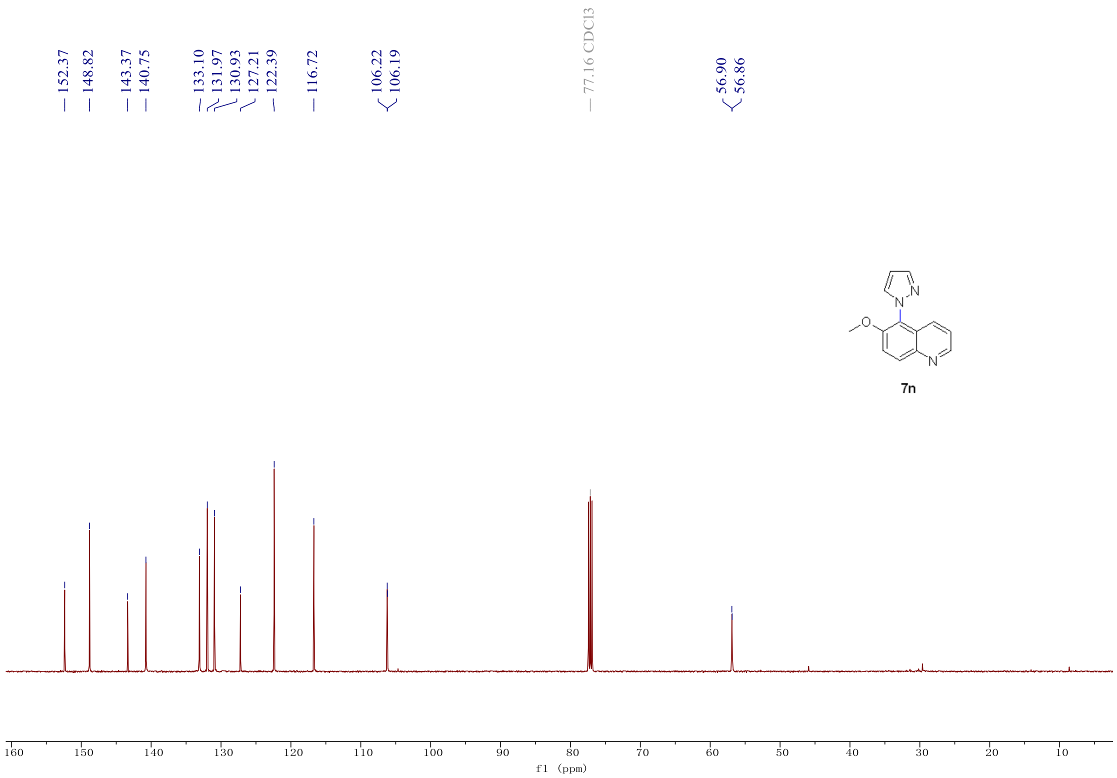
8.41
8.02
8.00
7.94
7.92
7.86
7.65
7.39
7.37
7.29
7.27
6.55
3.87
2.62
N
N
O
O
7m
1.00
0.99
1.01
1.06
0.97
0.99
1.04
0.99
3.03
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


197.32
154.45
140.57
134.26
132.91
132.36
129.95
127.52
125.67
123.01
122.55
114.10
106.11
106.08
77.16 CDCl3
56.63
56.58
26.43
26.38
O
N
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

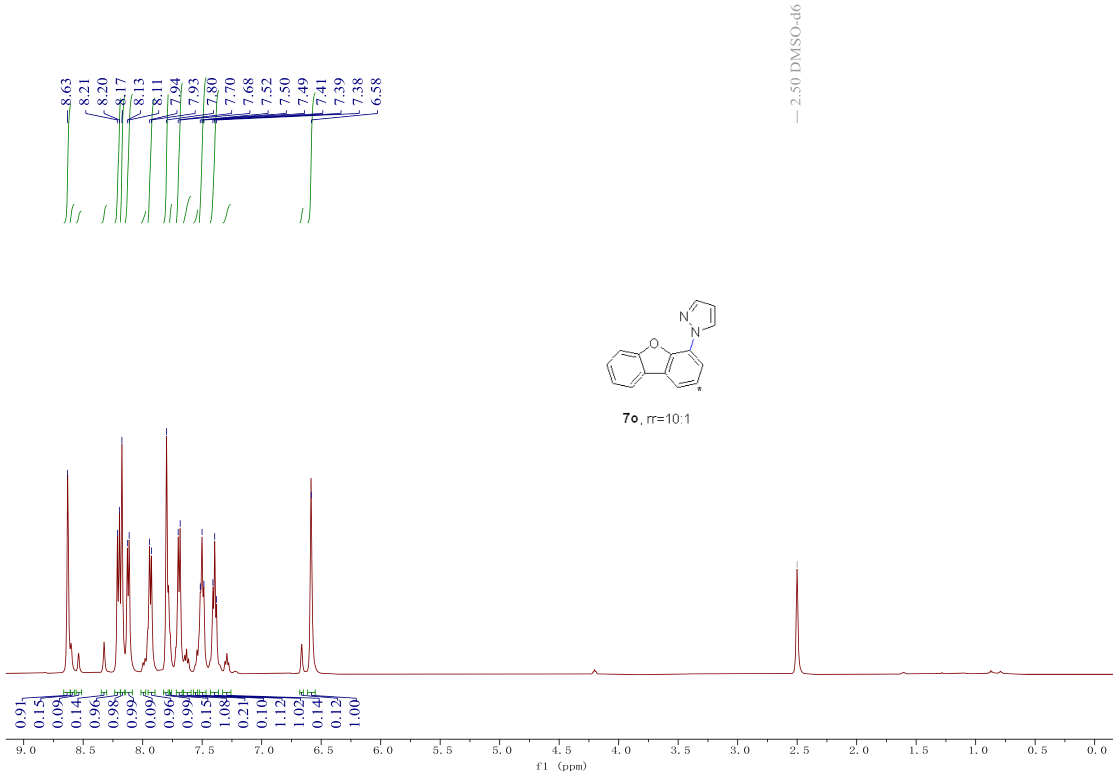
7m


8.81
8.80
8.80
8.23
8.21
7.86
7.71
7.69
7.59
7.57
7.34
7.33
7.32
7.32
7.26 CDCl3
6.55
3.89
O
N
N
N
0.98
0.98
0.98
1.98
1.02
1.05
0.99
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

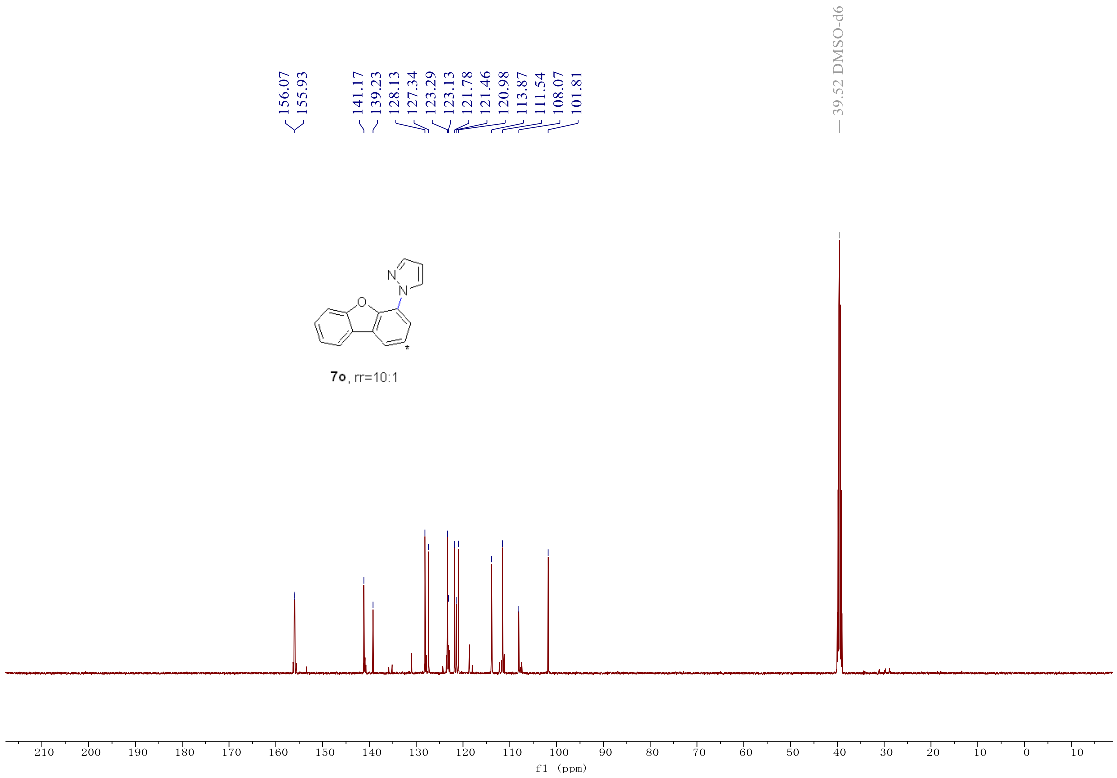
7n


152.37
148.82
143.37
140.75
133.10
131.97
130.93
127.21
122.39
116.72
106.22
106.19
77.16 CDCl3
56.90
56.86
N
N
O
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

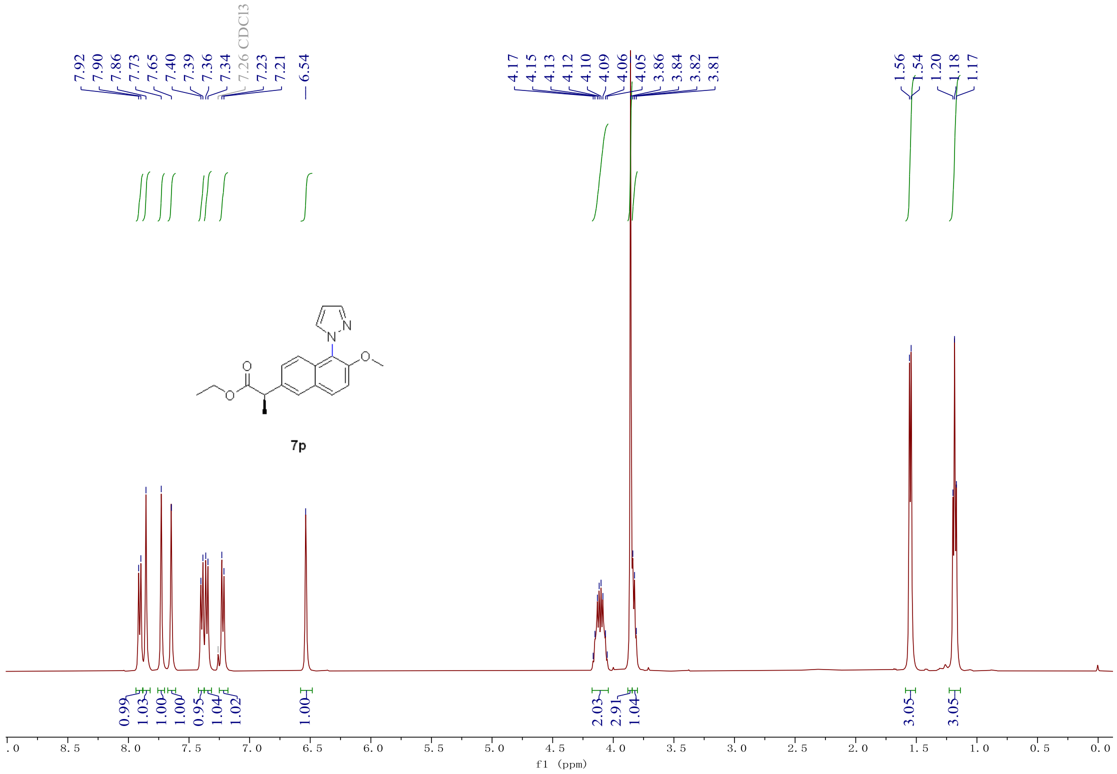
7n


8.63
8.21
8.20
8.17
8.13
8.11
7.94
7.93
7.80
7.70
7.68
7.52
7.50
7.49
7.41
7.39
7.38
6.58
2.50 DMSO-d6
N
N
O
*
0.91
0.15
0.09
0.14
0.96
0.98
0.99
0.09
0.96
0.99
0.15
1.08
0.21
0.10
1.12
1.02
0.14
0.12
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

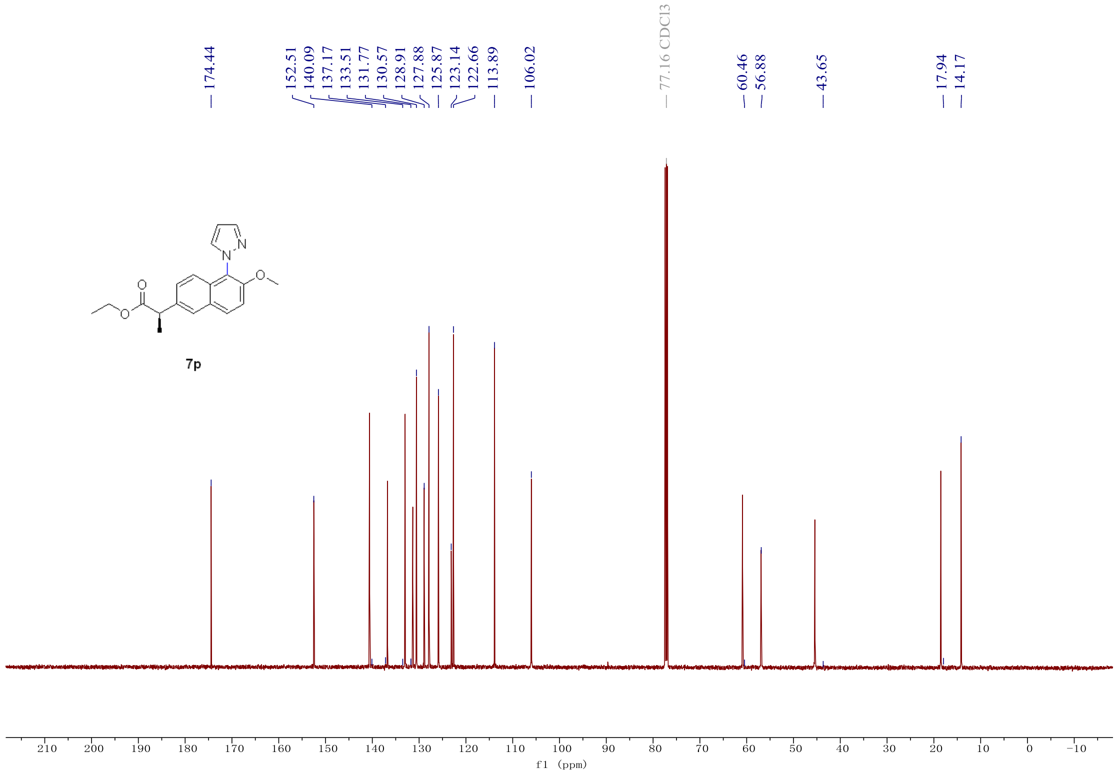
7o, rr=10:1


156.07
155.93
141.17
139.23
128.13
127.34
123.29
123.13
121.78
121.46
120.98
113.87
111.54
108.07
101.81
39.52 DMSO-d6
N
N
O
*
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

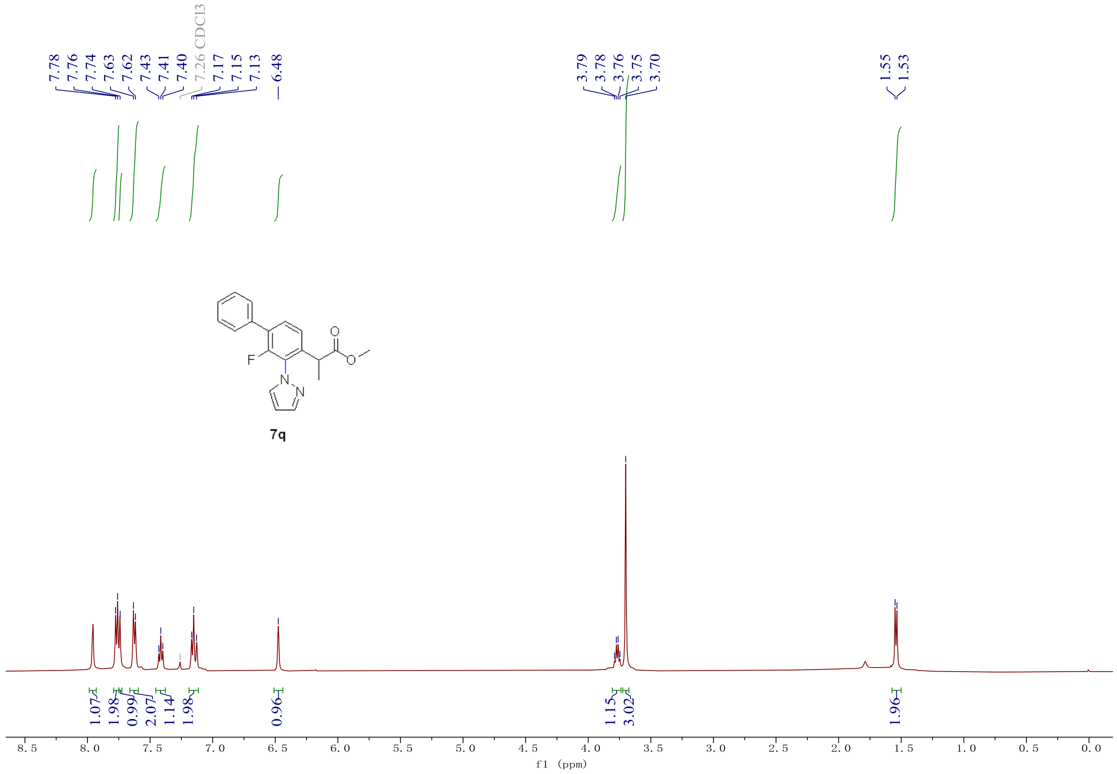
7o, rr=10:1


7.92
7.90
7.86
7.73
7.65
7.40
7.39
7.36
7.34
7.26 CDCl3
7.23
7.21
6.54
4.17
4.15
4.13
4.12
4.10
4.09
4.06
4.05
3.86
3.84
3.82
3.81
1.56
1.54
1.20
1.18
1.17
N
N
O
O
O
0.99
1.03
1.00
1.00
0.95
1.04
1.02
1.00
2.03
2.91
1.04
3.05
3.05
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

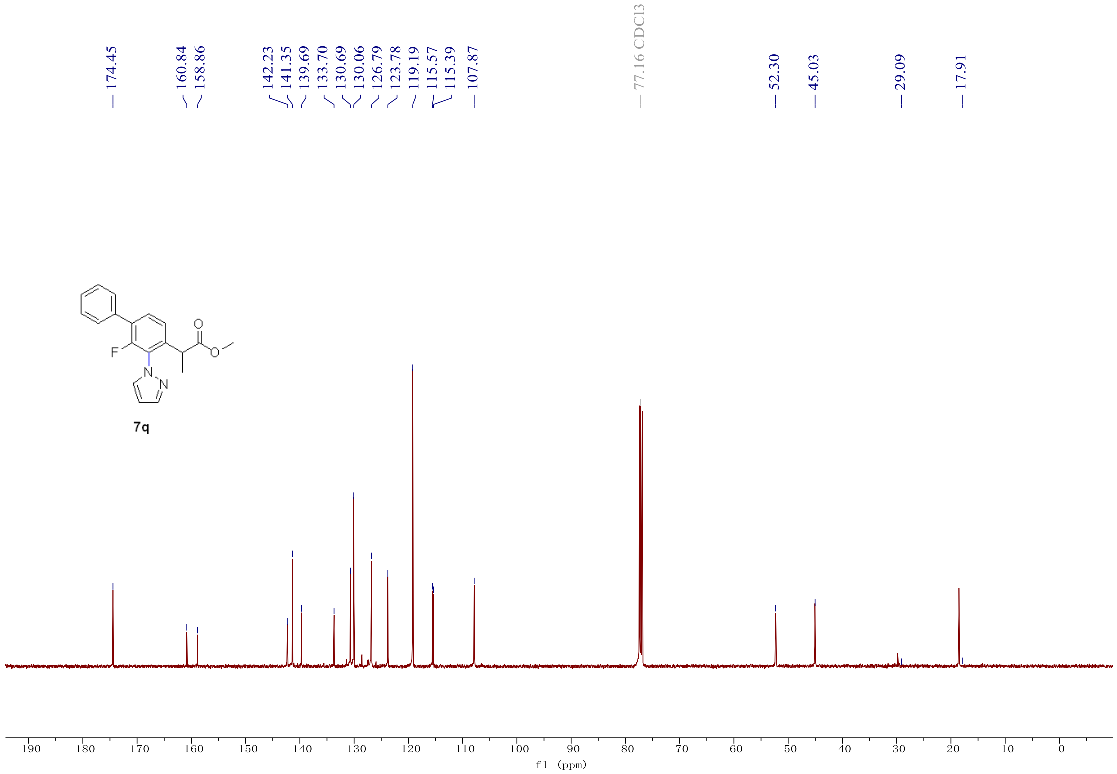
7p


7p

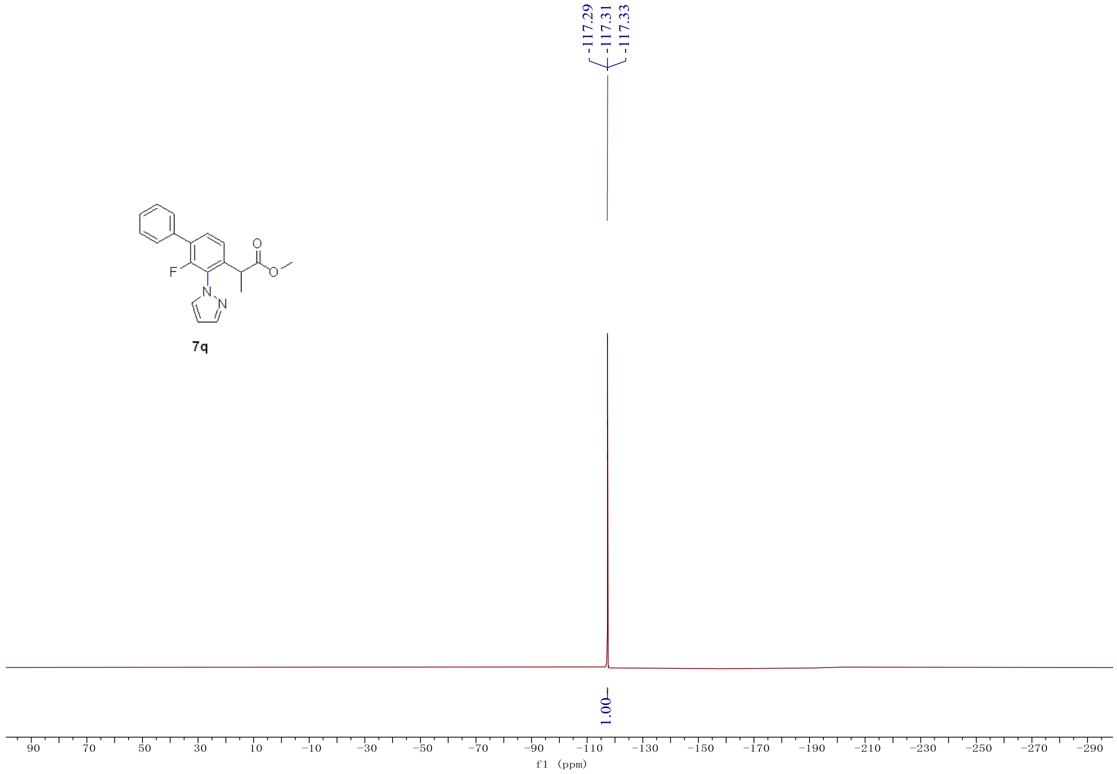
174.44
152.51
140.09
137.17
133.51
131.77
130.57
128.91
127.88
125.87
123.14
122.66
113.89
106.02
77.16 CDCl3
60.46
56.88
43.65
17.94
14.17
N
N
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7q

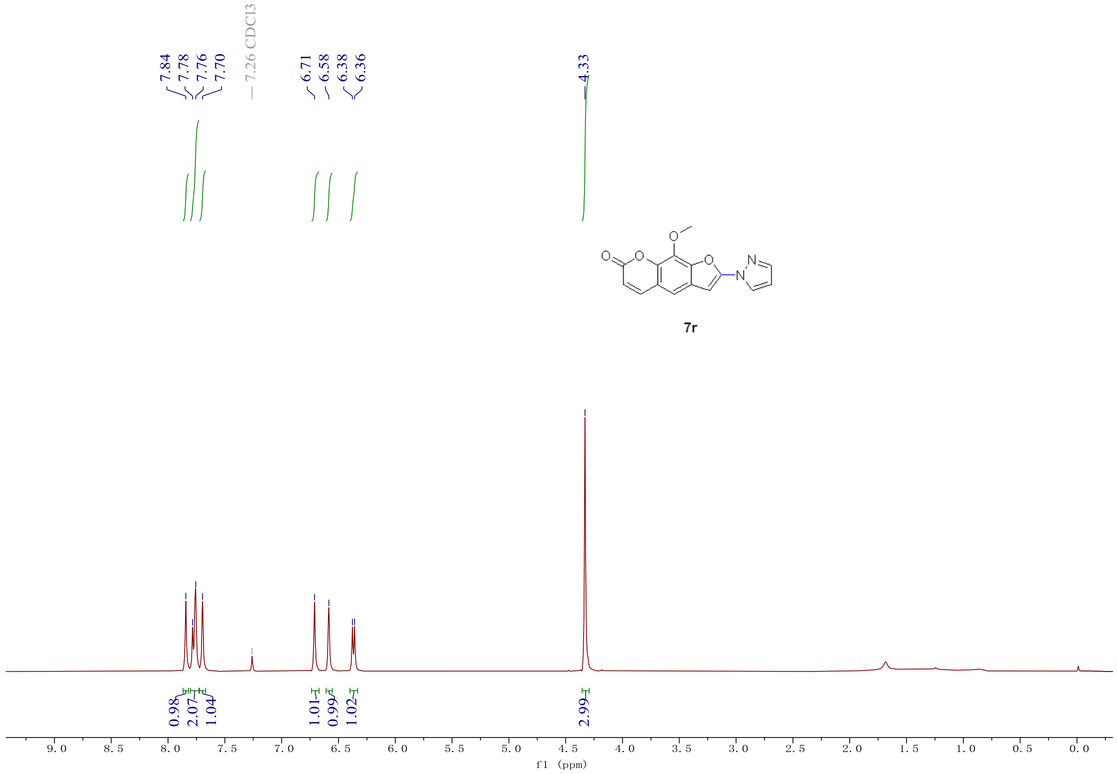
7.78
7.76
7.74
7.63
7.62
7.43
7.41
7.40
7.26 CDCl3
7.17
7.15
7.13
6.48
3.79
3.78
3.76
3.75
3.70
1.55
1.53
F
N
N
O
O
1.07
1.98
0.99
2.07
1.14
1.98
0.96
1.15
3.02
1.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

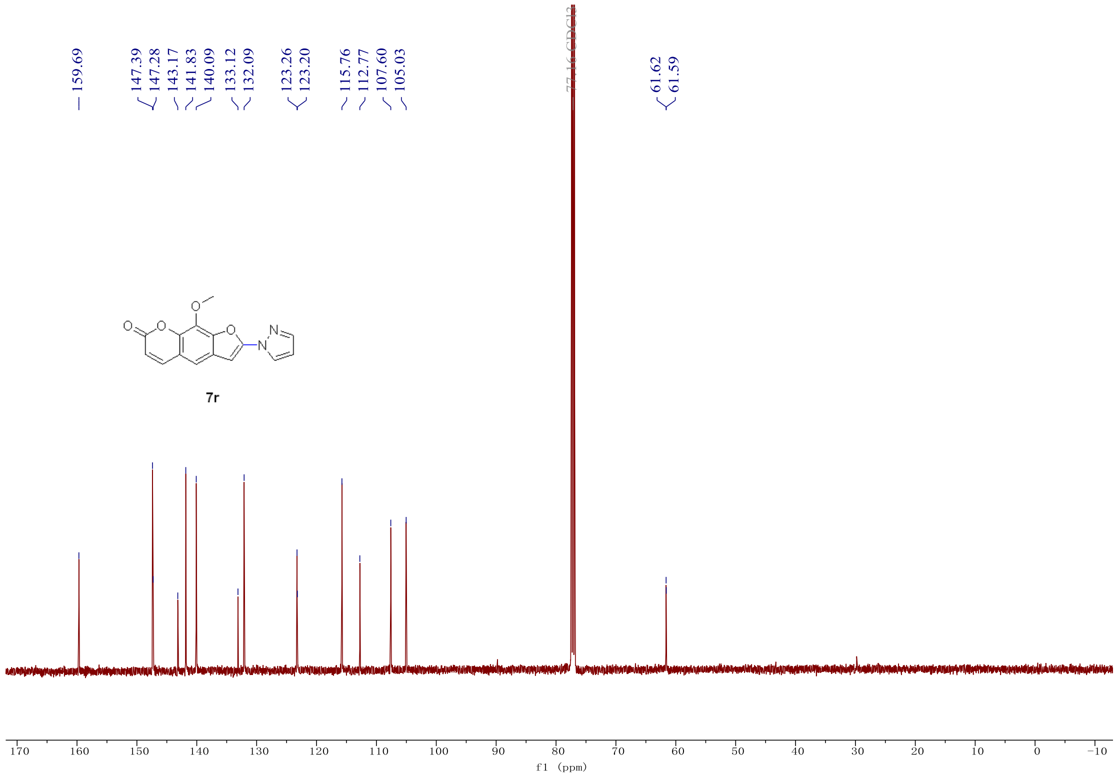


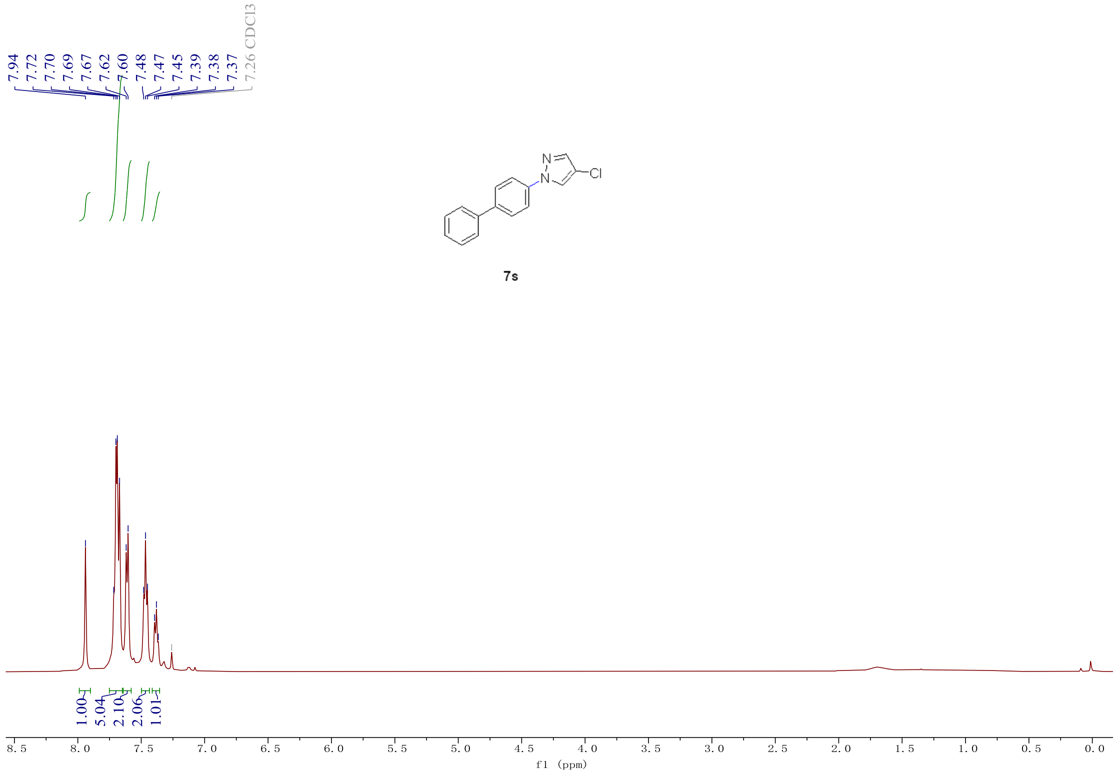
174.45
160.84
158.86
142.23
141.35
139.69
133.70
130.69
130.06
126.79
123.78
119.19
115.57
115.39
107.87
77.16 CDCl3
52.30
45.03
29.09
17.91
F
N
N
O
O
7q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



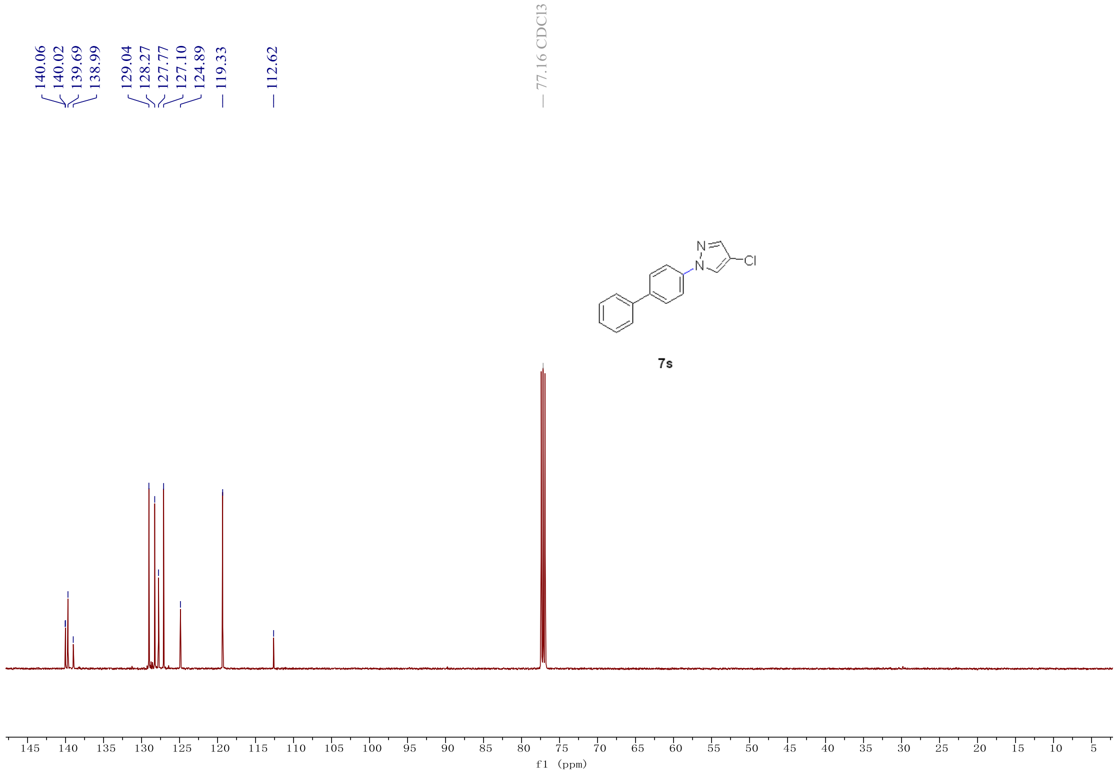
-117.29
-117.31
-117.33
F
N
N
O
O
7q
1.00
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
−250
−270
−290
f1 (ppm)


7.84
7.78
7.76
7.70
7.26 CDCl3
6.71
6.58
6.38
6.36
4.33
7r
0.98
2.07
1.04
1.01
0.99
1.02
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

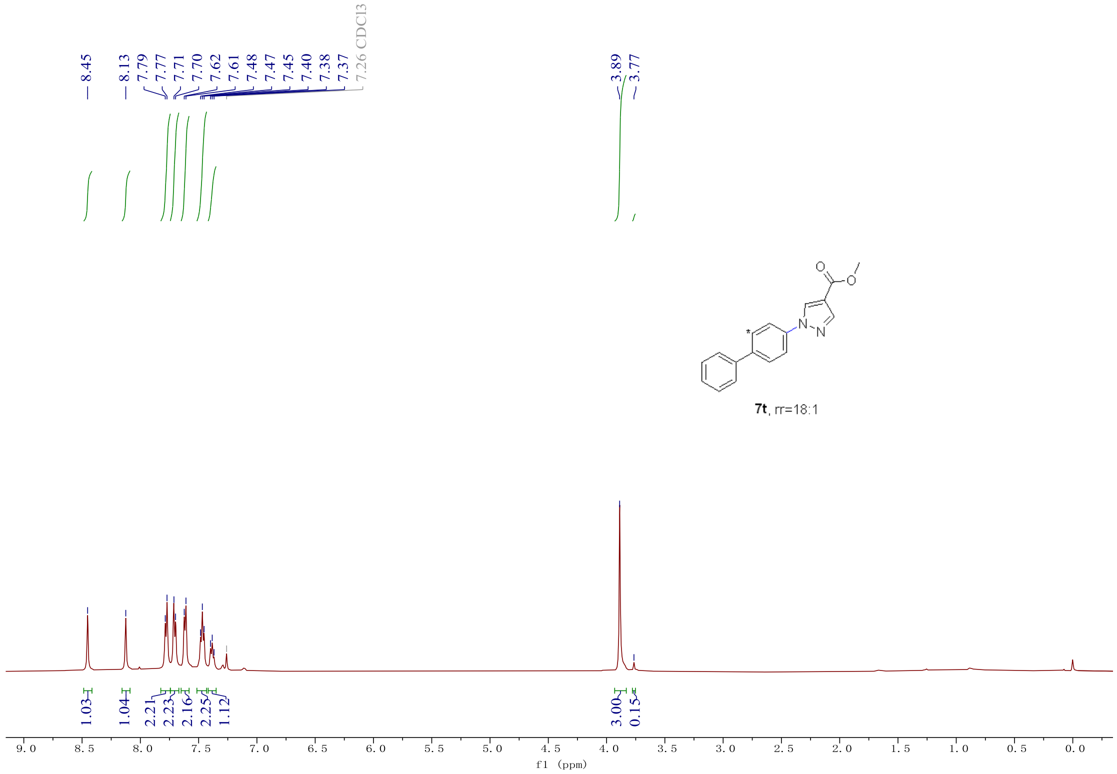

159.69
147.39
147.28
143.17
141.83
140.09
133.12
132.09
123.26
123.20
115.76
112.77
107.60
105.03
77.16 CDCl3
61.62
61.59
7r
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

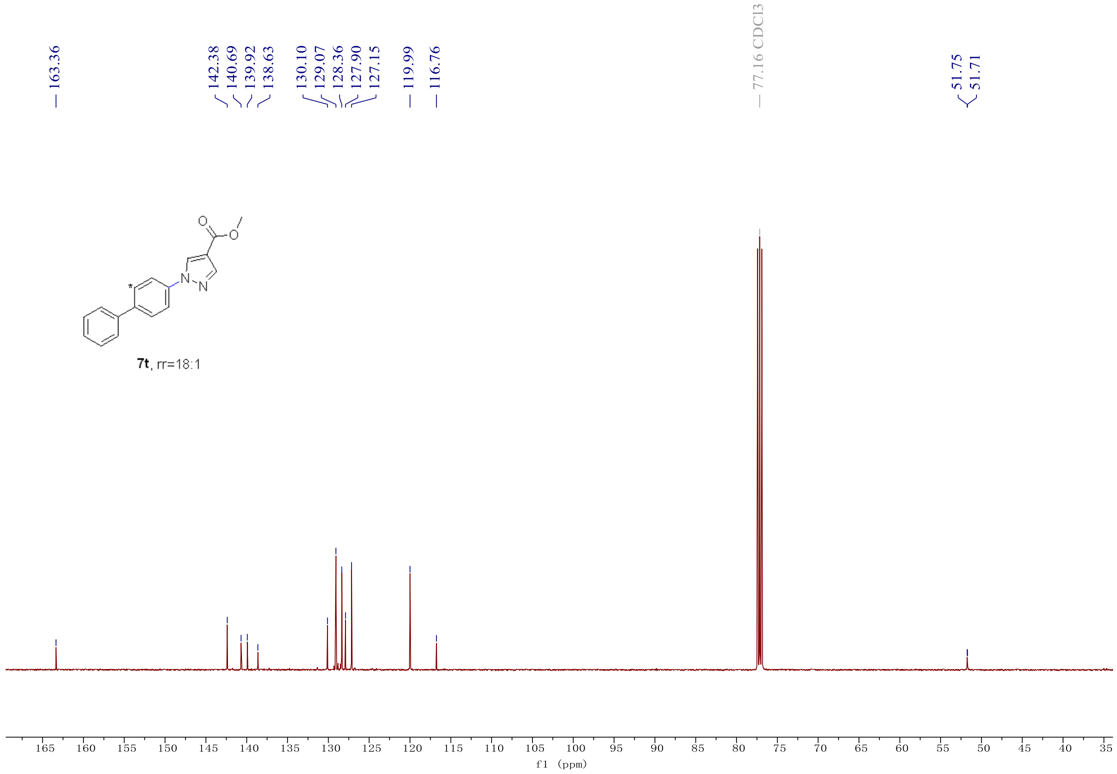

7.94
7.72
7.70
7.69
7.67
7.62
7.60
7.48
7.47
7.45
7.39
7.38
7.37
7.26 CDCl3
N
N
Cl
1.00
5.04
2.10
2.06
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

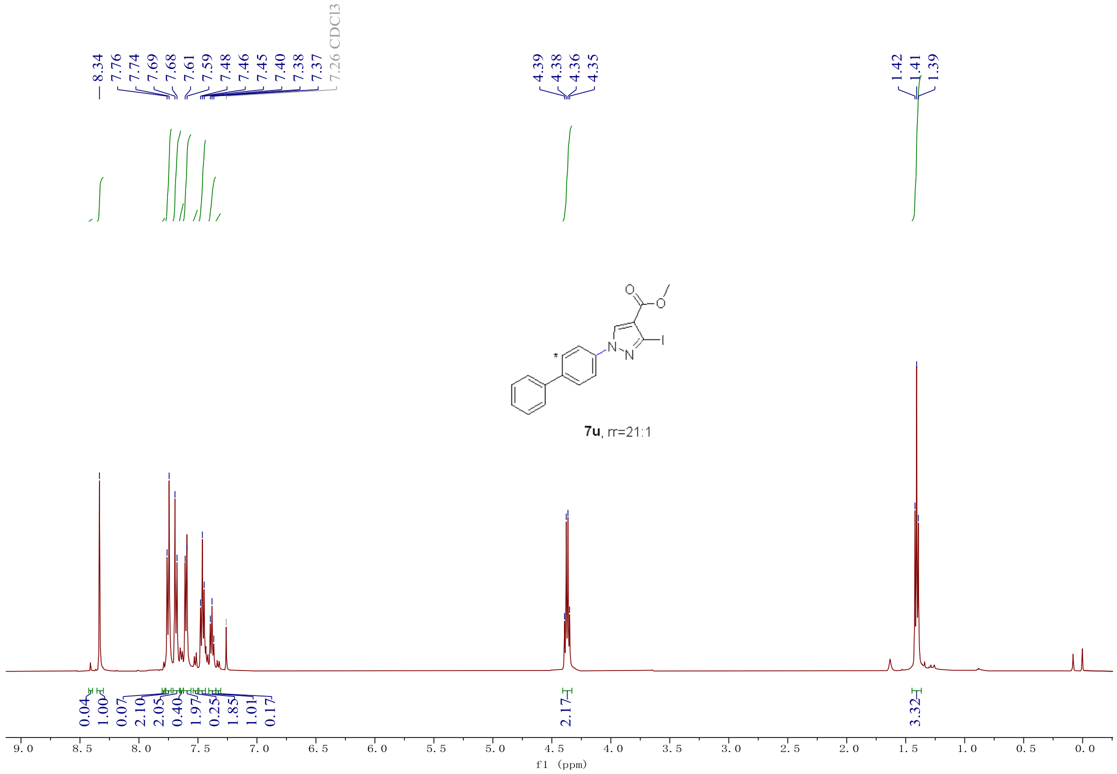
7s


140.06
140.02
139.69
138.99
129.04
128.27
127.77
127.10
124.89
119.33
112.62
77.16 CDCl3
N
N
Cl
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

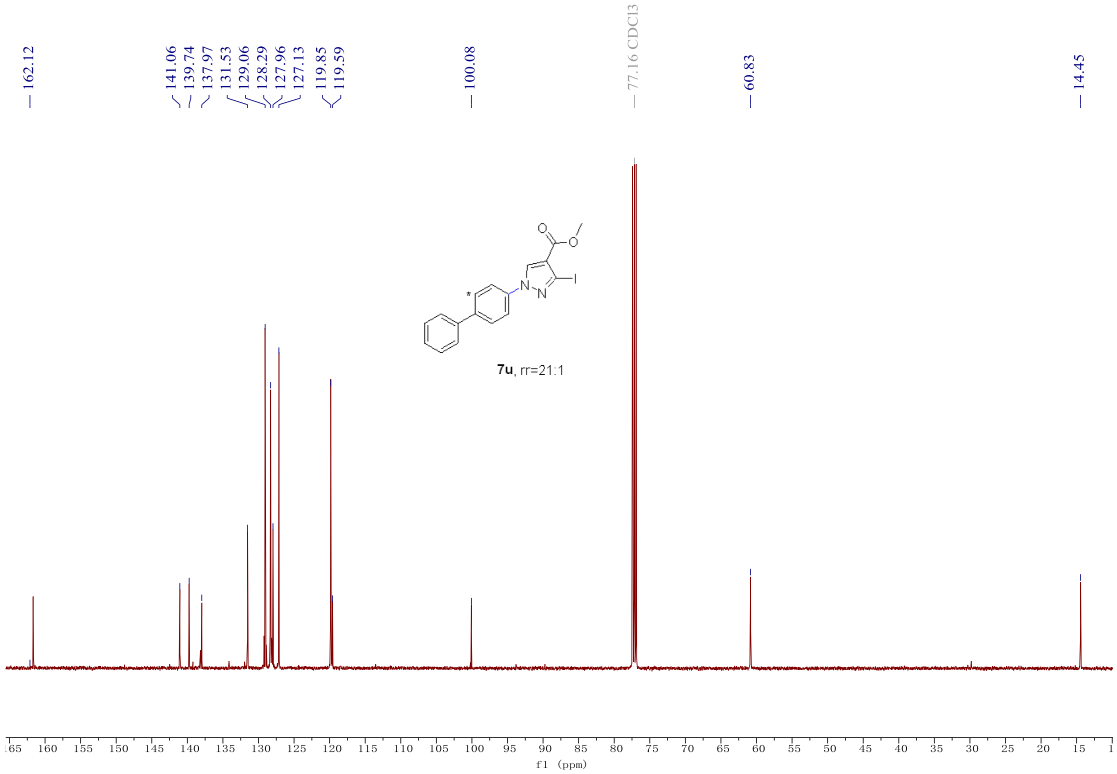
7s


8.45
8.13
7.79
7.77
7.71
7.70
7.62
7.61
7.48
7.47
7.45
7.40
7.38
7.37
7.26 CDCl3
3.89
3.77
7t, rr=18:1
1.03
1.04
2.21
2.23
2.16
2.25
1.12
3.00
0.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

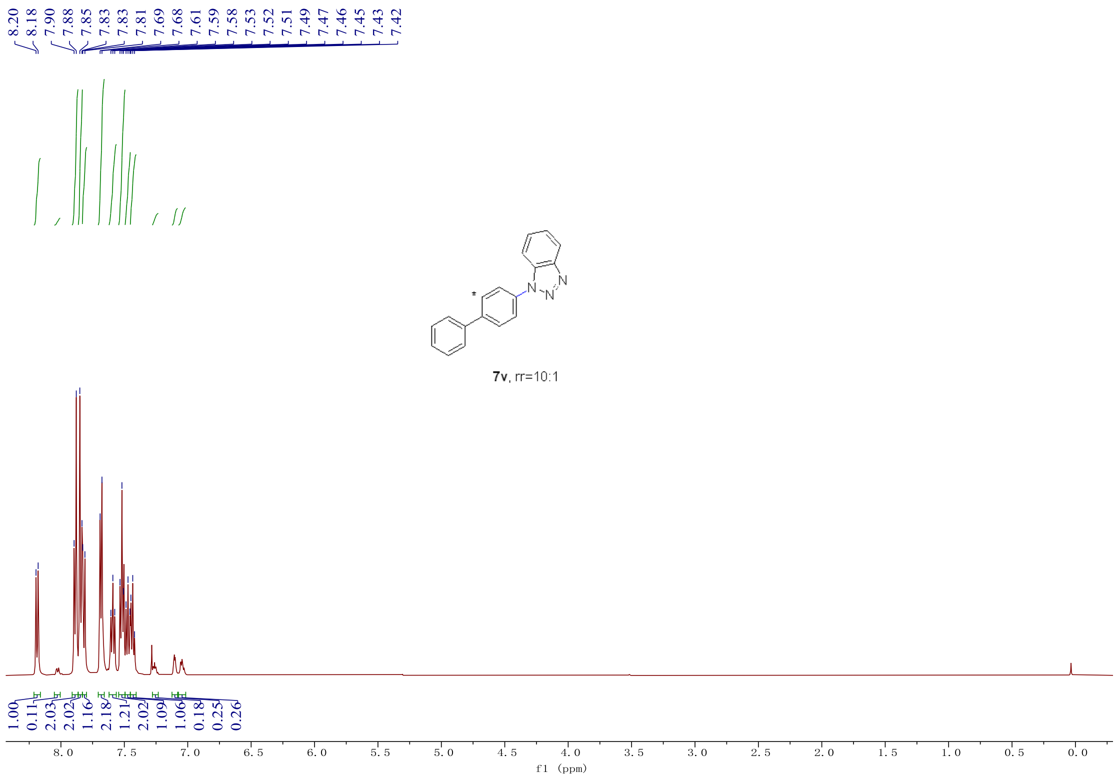

163.36
142.38
140.69
139.92
138.63
130.10
129.07
128.36
127.90
127.15
119.99
116.76
77.16 CDCl3
51.75
51.71
7t, rr=18:1
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)

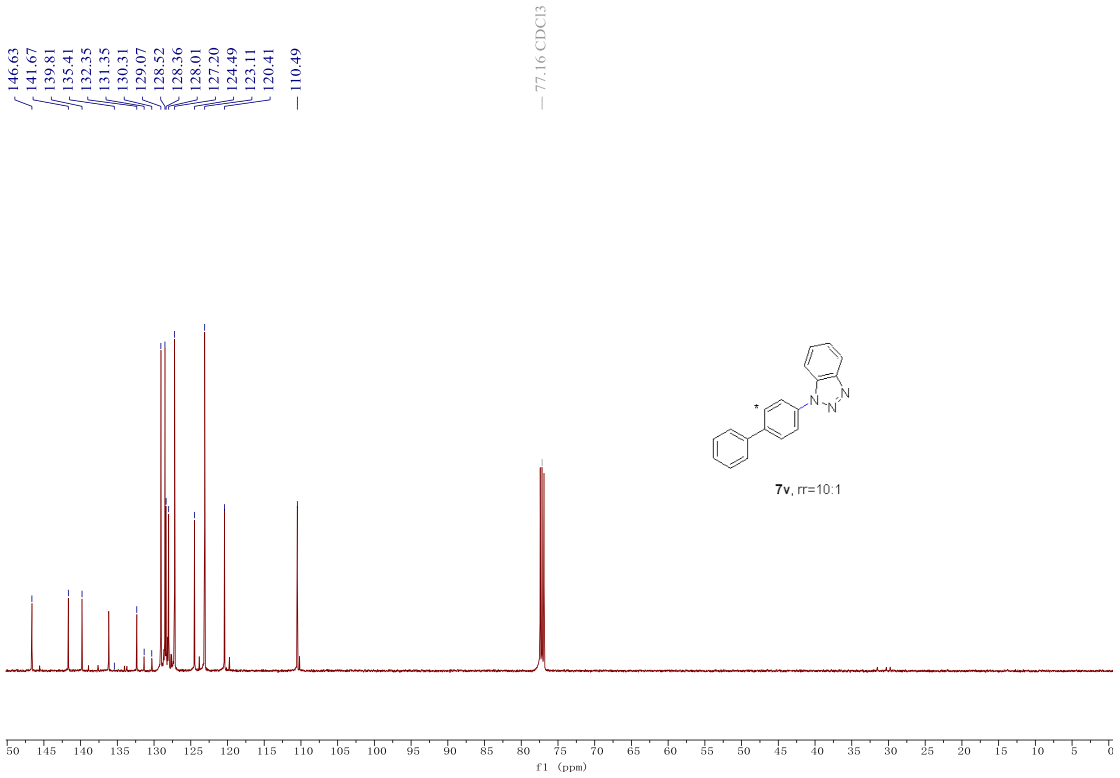


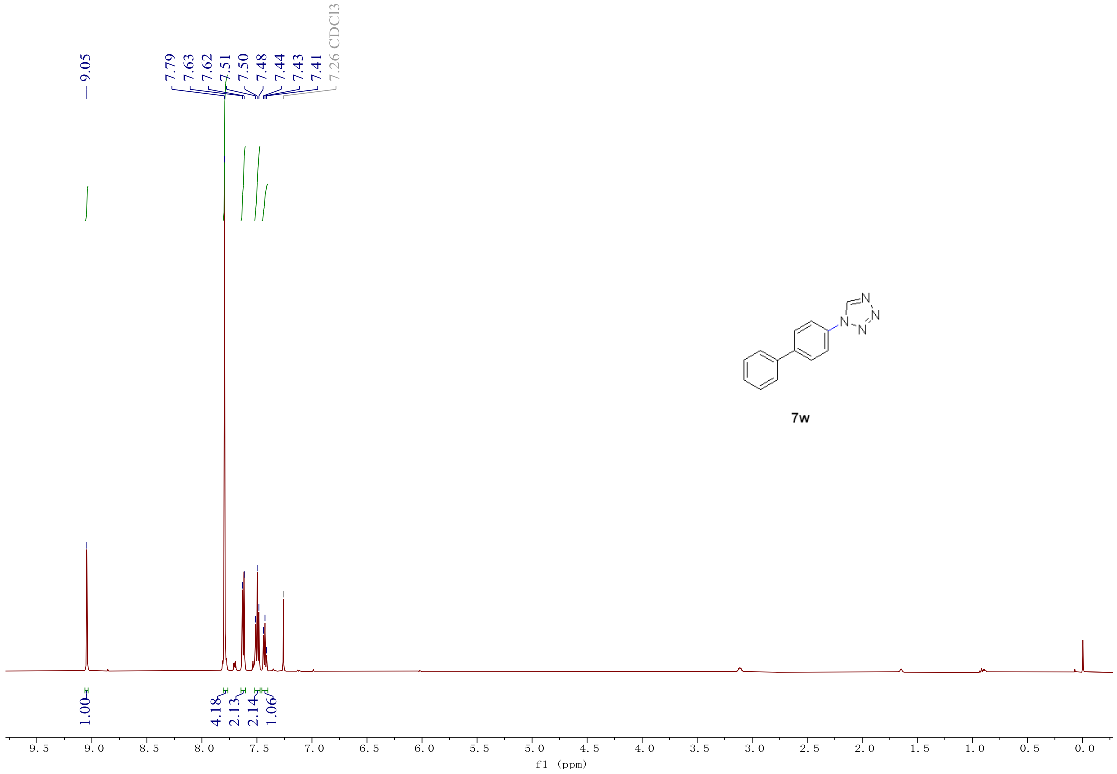
7u, rr=21:1

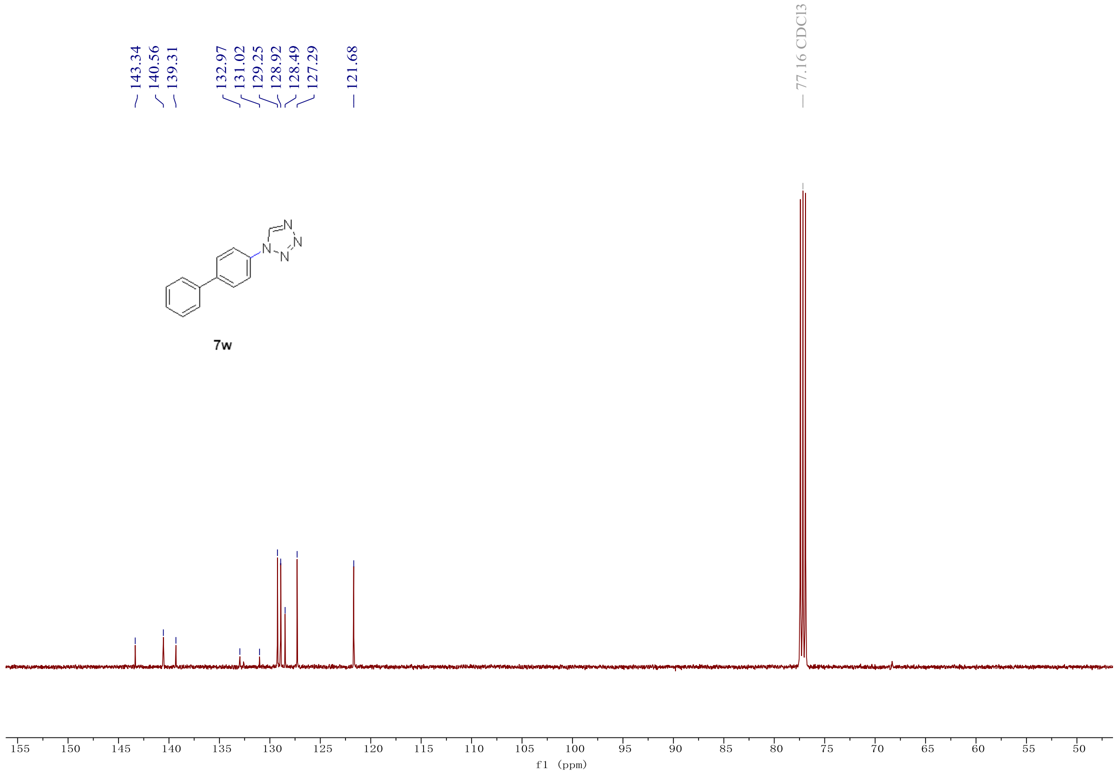


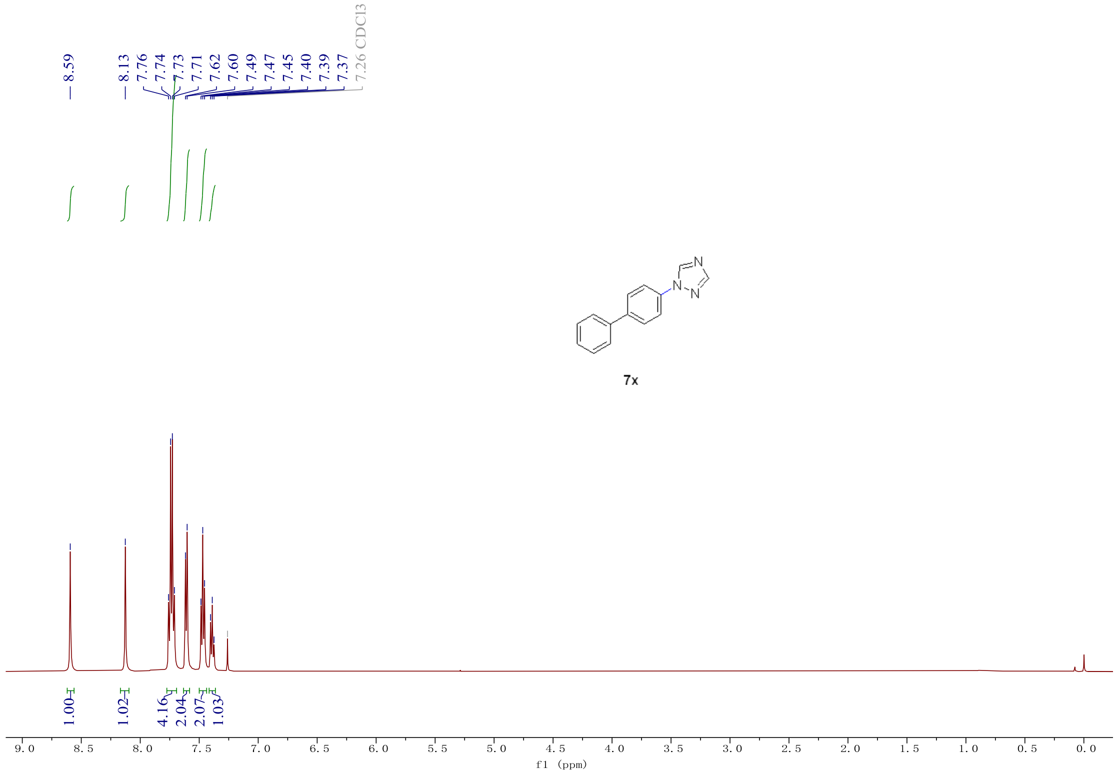
7u, rr=21:1


8.20
8.18
7.90
7.88
7.85
7.83
7.83
7.81
7.69
7.68
7.61
7.59
7.58
7.53
7.52
7.51
7.49
7.47
7.46
7.45
7.43
7.42
7v, rr=10:1
1.00
0.11
2.03
2.02
1.16
2.18
1.21
2.02
1.09
1.06
0.18
0.25
0.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

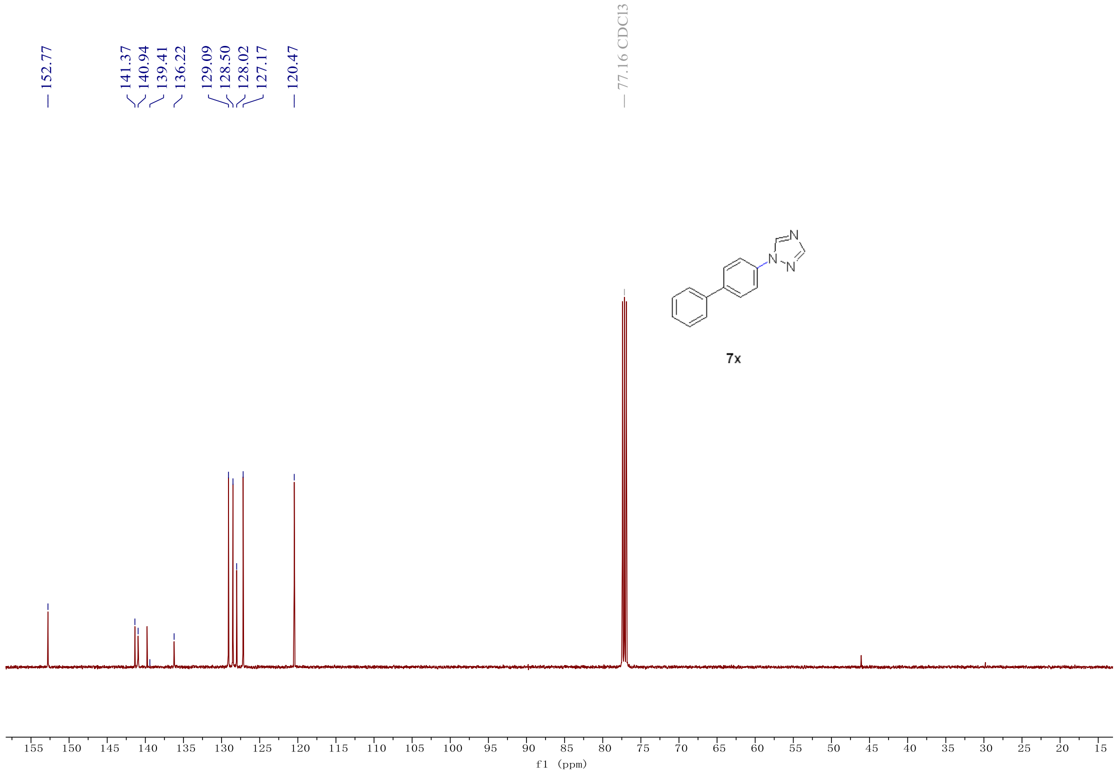

146.63
141.67
139.81
135.41
132.35
131.35
130.31
129.07
128.52
128.36
128.01
127.20
124.49
123.11
120.41
110.49
77.16 CDCl3
7v, rr=10:1
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


9.05
7.79
7.63
7.62
7.51
7.50
7.48
7.44
7.43
7.41
7.26 CDCl3
N
N
N
N
7w
1.00
4.18
2.13
2.14
1.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

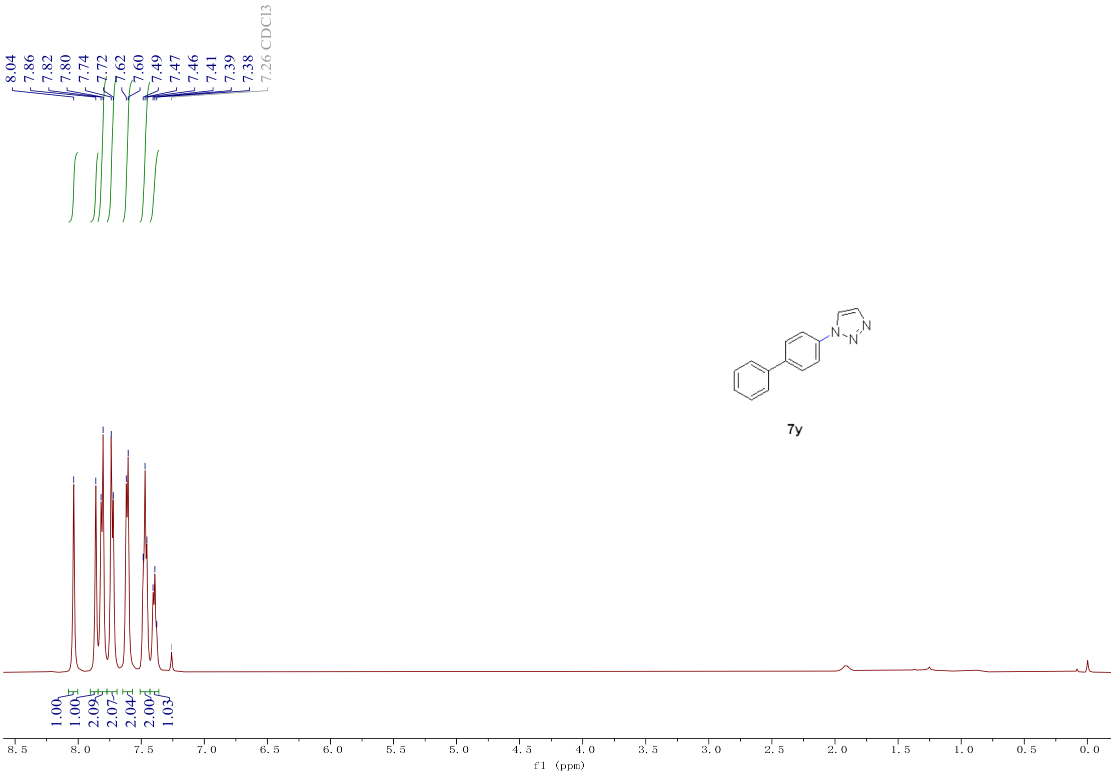

143.34
140.56
139.31
132.97
131.02
129.25
128.92
128.49
127.29
121.68
77.16 CDCl3
N
N
N
N
7w
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
f1 (ppm)

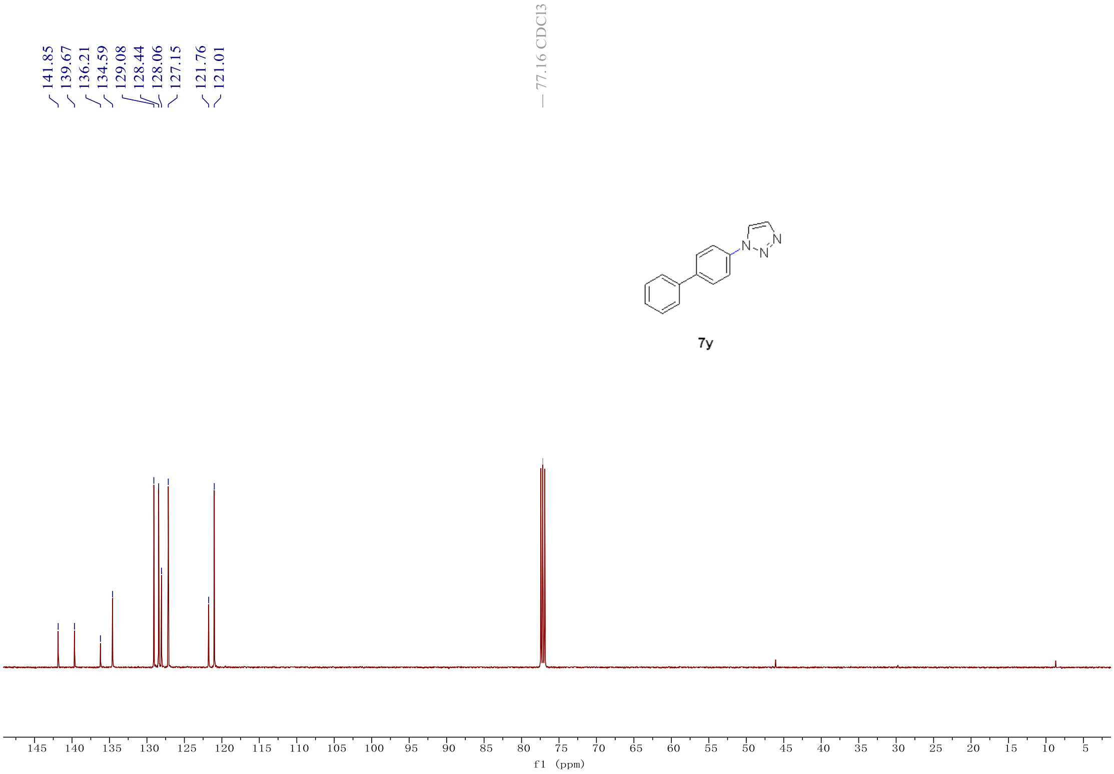

8.59
8.13
7.76
7.74
7.73
7.71
7.62
7.60
7.49
7.47
7.45
7.40
7.39
7.37
7.26 CDCl3
1.00
1.02
4.16
2.04
2.07
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
N
N
N

7x


152.77
141.37
140.94
139.41
136.22
129.09
128.50
128.02
127.17
120.47
77.16 CDCl3
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)
N
N
N

7x


8.04
7.86
7.82
7.80
7.74
7.72
7.62
7.60
7.49
7.47
7.46
7.41
7.39
7.38
7.26 CDCl3
N
N
N
7y
1.00
1.00
2.09
2.07
2.04
2.00
1.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.85
139.67
136.21
134.59
129.08
128.44
128.06
127.15
121.76
121.01
77.16 CDCl3
N
N
N
7y
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)