Electronic Supplementary Information

Achieving Visible-Light-Excited Organic Room-Temperature Phosphorescence by Manipulating p-π Conjugation

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General Information

Materials: naphthalene-1-thiol, naphthalene-2-thiol, 2-bromoacetic acid, 3-bromopropanoic acid, ethyl 4-bromobutanoate, were purchased from Adamas, Aladdin, or Energy. All solvents were obtained commercially and used as supplied without further purification.

Instruments: ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 spectrometer. The electronic spray ionization (ESI) high-resolution mass spectra were tested on a Waters LCT Premier XE spectrometer. The UV-Vis absorption spectra were obtained on a PerkinElmer Lambda 950 spectrophotometer and a Cary 60 (Agilent Technologies) spectrophotometer. Fluorescence, phosphorescence, and lifetime of delayed emission spectra were recorded on an Agilent Cary Eclipse spectrophotometer. Phosphorescence mode: Delay time = 0.1 ms, Gate time = 2.0 ms. Photoluminescence

spectra were recorded on HORIBA FluoroMax-4 spectrometer. Fluorescence lifetimes were measured on Edinburgh Instruments Fluorescence Spectrometer (FLS1000). Absolute PL quantum yields were measured by using an integrating sphere on a spectrometer C11347-11 (Hamamatsu, Japan). Powder X-ray diffraction (XRD) was performed on Bruker D8 Venture diffractometer with a PHOTON 100 CMOS area detector, using Mo-K radiation from an Incoatec IμS microsource with focusing mirrors.

The preparation of crystals and films: The crystals were obtained by slow evaporation of methanol solution of compounds. The THF solution (3 mL) of phosphor (3mg) was added to the aqueous solution (30 mL) of PVA (1.0 g) under vigorous stirring. Then the solvent was evaporated under vacuum to obtain the PVA film contained desired phosphor.

1. Photophysical spectra

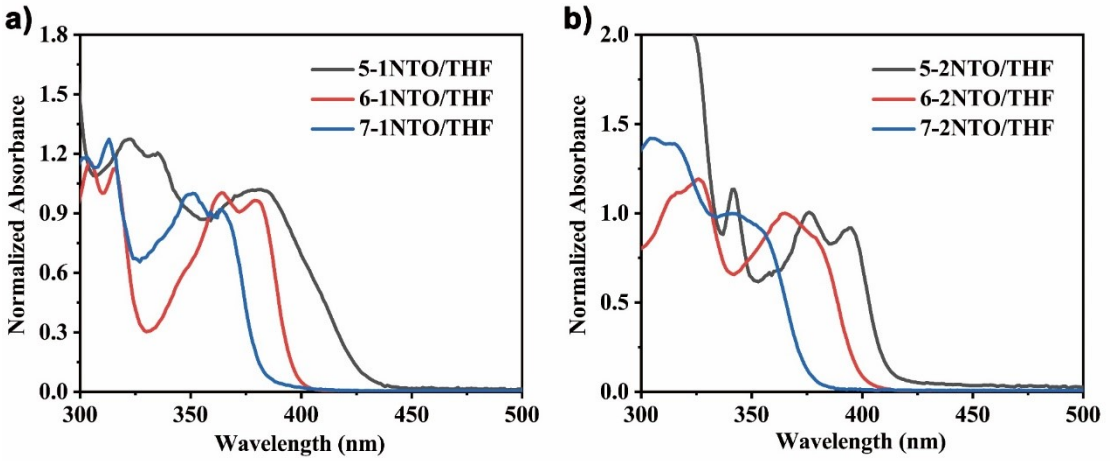


Fig. S1. Absorption spectra of **n-1NTO** and **n-2NTO** groups molecule in THF solution (5×10^{-5} M).

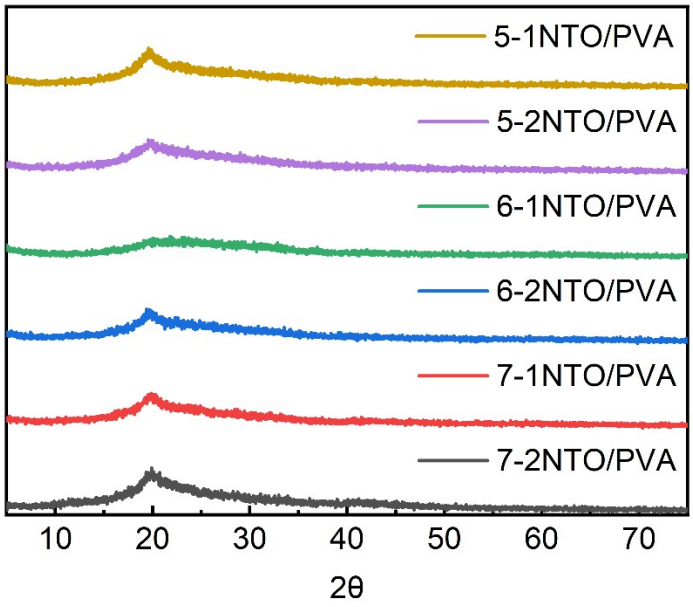


Fig. S2. XRD spectra of the films.

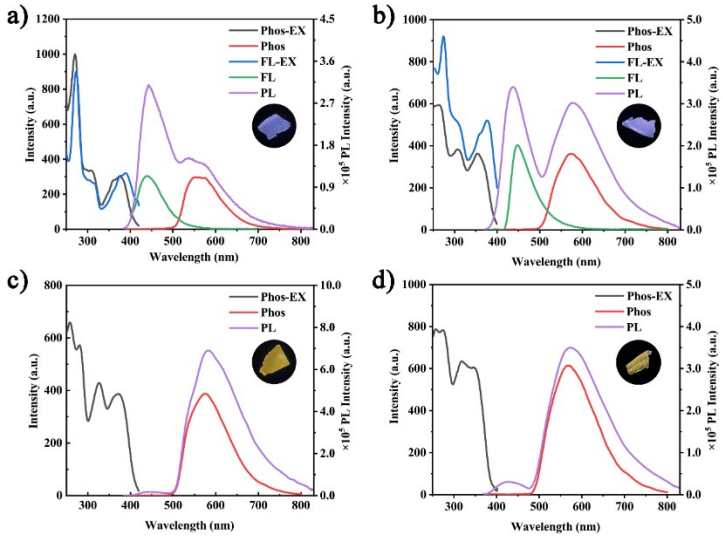


Fig. S3. The excitation (black line for phosphorescence, blue line for fluorescence), phosphorescence (red line), fluorescence (green line) and photoluminescence (purple) spectra of **6-1NTO/PVA** (a), **7-1NTO/PVA** (b), **6-2NTO/PVA** (c), **7-2NTO/PVA** (d). Inset: the photographs of the films upon excitation by 365nm light source.

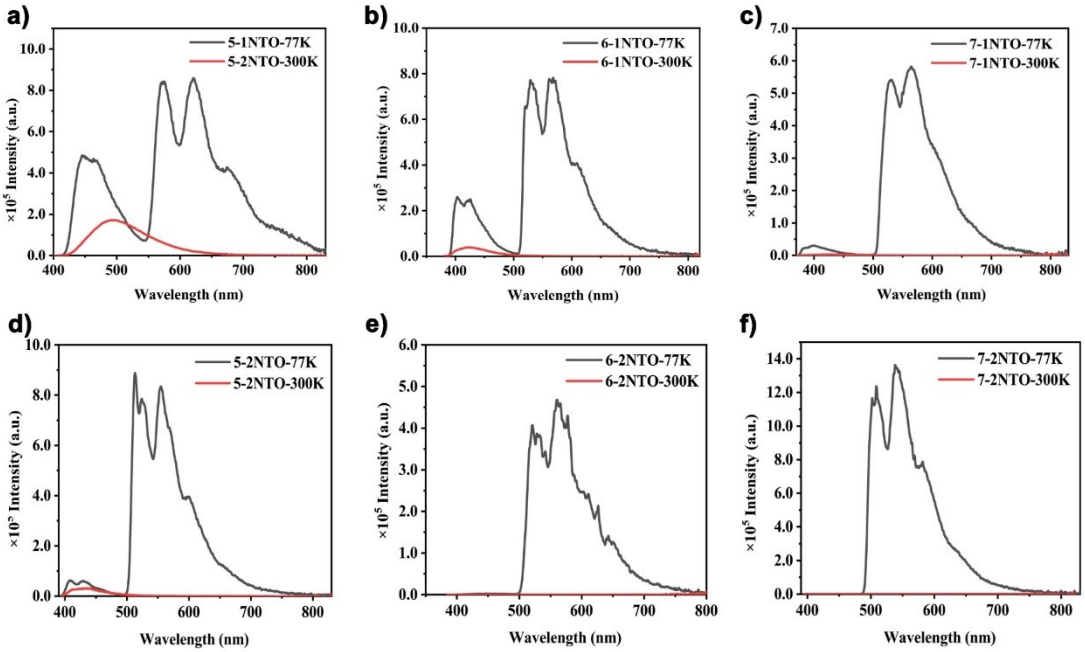


Fig. S4. PL spectra of the six molecules in 2-methyl tetrahydrofuran solutions (5×10^{-5} mol/L) at 77 K (black line) and 300 K (red line).

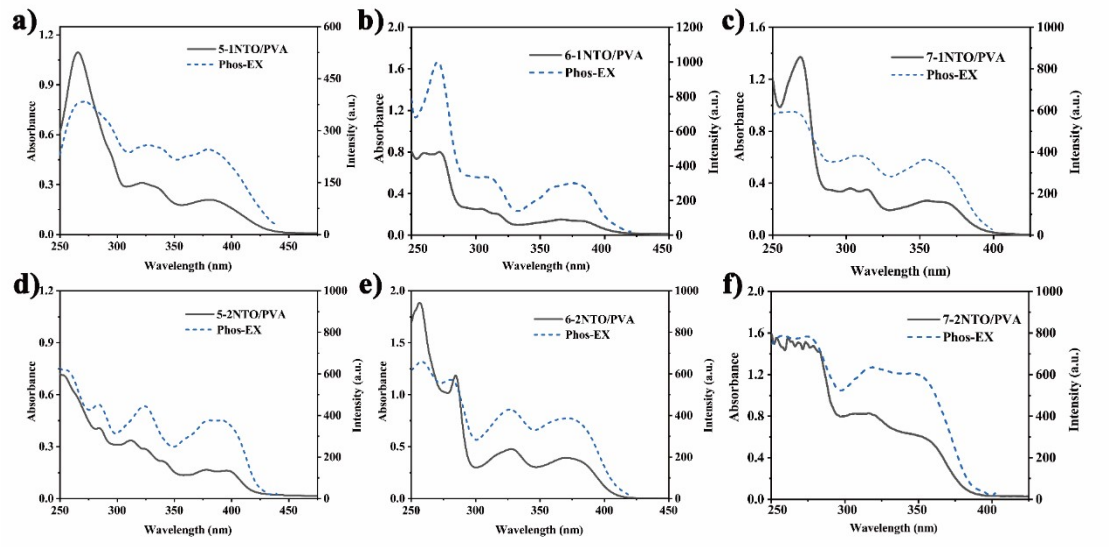


Fig. S5. Absorption and excitation spectra of the obtained films.

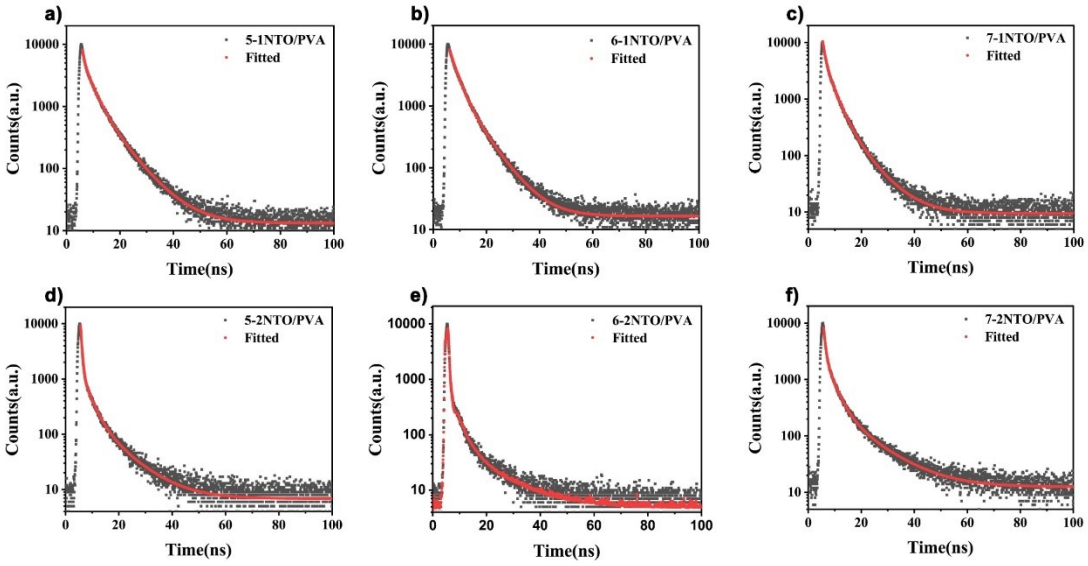


Fig. S6. Lifetime decay spectra of fluorescence of the six molecules in films.

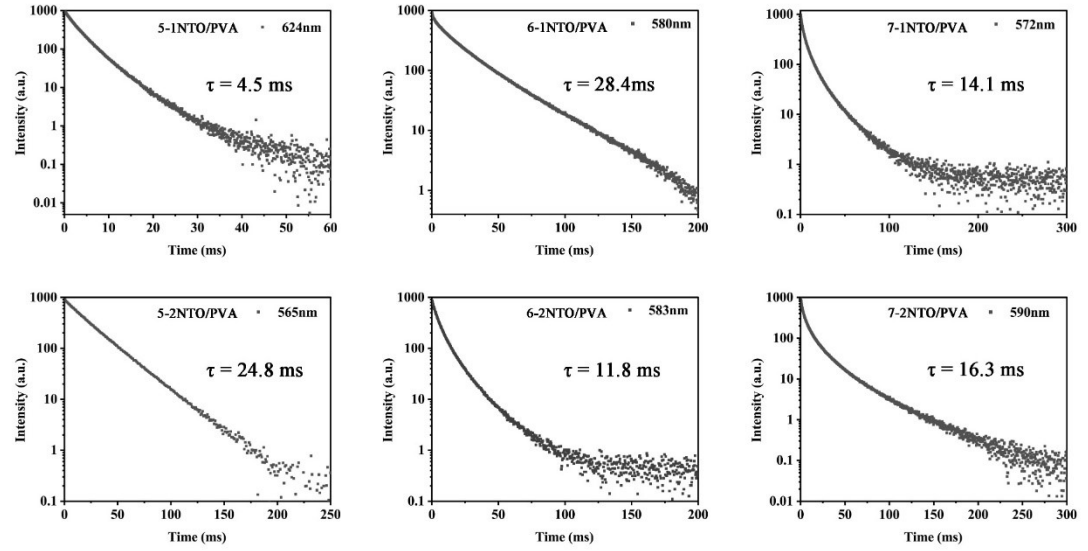


Fig. S7. Lifetime decay spectra phosphorescence of the six molecules in films.

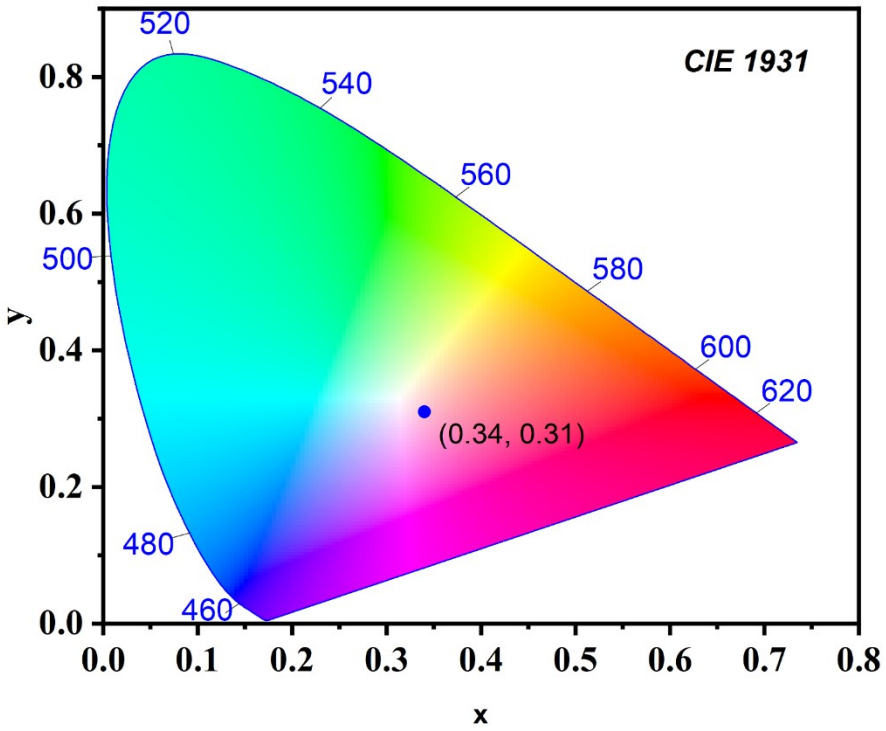


Fig. S8. CIE coordinate of the phosphorescence of 7-1NTO/PVA under 365 UV light.

Table S1. The singlet and triplet excited states transition configurations (%) of molecules in gas phase revealed by Natural transition orbitals (NTOs) calculation.

Compound	S_1	T_1	T_2	T_3
5-1NTO	(π, π*) 94.0%	(π, π*) 94.7%	(π, π*) 86.1%	(n, π*) 99.0%
6-1NTO	(π, π*) 92.4%	(π, π*) 94.3%	(n, π*) 85.5%	(π, π*) 77.7%
7-1NTO	(π, π*) 94.8%	(π, π*) 92.1%	(n, π*) 85.6%	-
5-2NTO	(π, π*) 94.8%	(π, π*) 93.0%	(π, π*) 90.5%	(n, π*) 96.9%
6-2NTO	(π, π*) 94.0%	(π, π*) 93.5%	(n, π*) 90.9%	(n, π*) 92.1%
7-2NTO	(π, π*) 92.5%	(π, π*) 90.5%	(n, π*) 90.8%	(n, π*) 85.3%

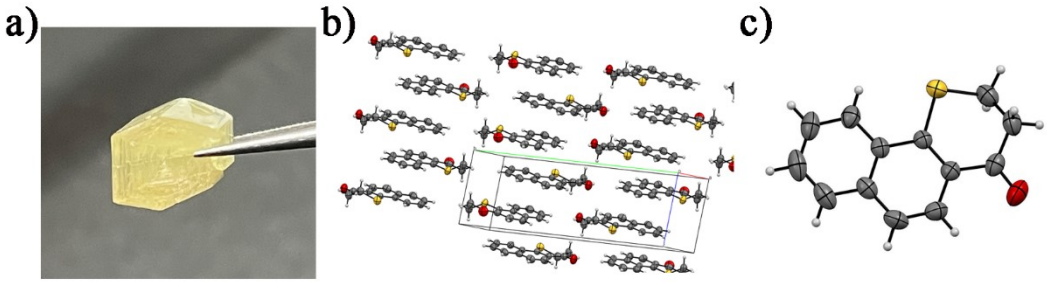
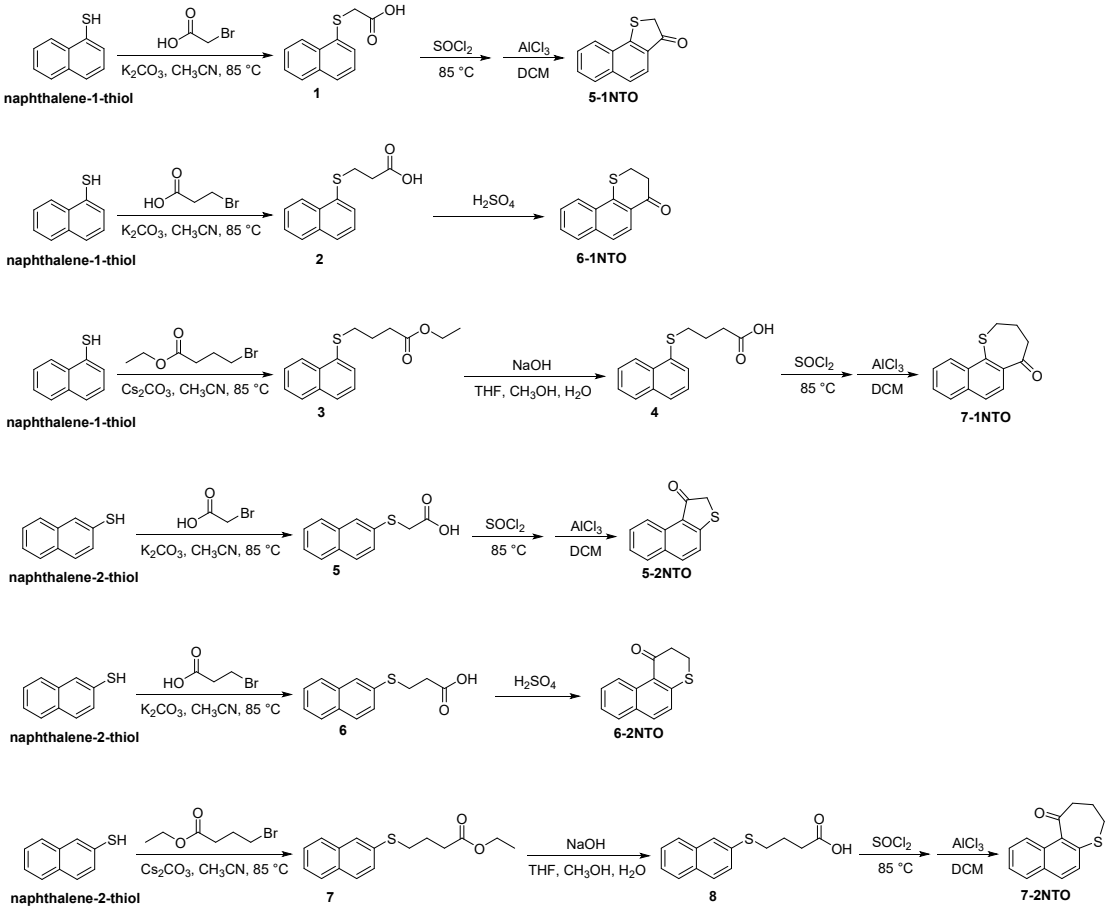


Fig. S9. The picture and single-crystal X-ray diffraction structure of **6-1NTO**.

Table S2. Single crystal data of **6-1NTO**.

Name	**6-1NTO**
Formula	$C_{13}H_{10}OS$
Wavelength	1.54178 Å
Space group	P 1 21/c 1
Cell Lengths (Å)	a = 7.3300(12) b = 20.189(3) c = 6.9841(12)
Cell Angles (°)	α= 90 β= 101.016(6) γ= 90
Volume(Å^3)	1014.5(3)
Z	12
Density (Mg/m^3)	1.475
F (000)	456.0
h_{max}, k_{max}, l_{max}	8, 24, 8
max. and min. transmission	0.328 and 0.753
CCDC	2095161

2. Synthesis of target compounds



Scheme S1. Synthesis route of the compounds.

Six target molecules were synthesized via short and straightforward syntheses. First, carbonic chains of different lengths with a carboxyl group at the end were added to the thionaphthol, and then the acylation of naphthalene was realized by different cyclization methods. Detailed synthetic route was described in the Scheme S1.

General procedure for the synthesis of compound **1**, **2, 5** and **6.**

Synthesis of compound 1

K_2CO_3 (18.7 mmol, 2.6 g) was added to the solution of naphthalene-1-thiol (6.2 mmol, 1.0 g) in acetonitrile and stirred at reflux temperature for 1 h. Then 2-bromoacetic acid (6.9 mmol, 1.0 g) was added into the system and the mixture was

brought to reflux after stirring for about 12 h. After the reaction was completed, the precipitate was filtered off and washed with ethyl acetate, the filtrate was concentrated by a rotary evaporator. The crude product was purified by the silica gel column chromatography with eluent petroleum ether (PE): ethyl acetate (EA)= 5/1, providing the desired product **1** as a white solid (1.2 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.61 – 7.48 (m, 2H), 7.44 – 7.38 (m, 1H), 3.70 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.03, 134.03, 132.99, 131.18, 130.50, 128.93, 128.76, 126.93, 126.45, 125.67, 124.84, 36.81.

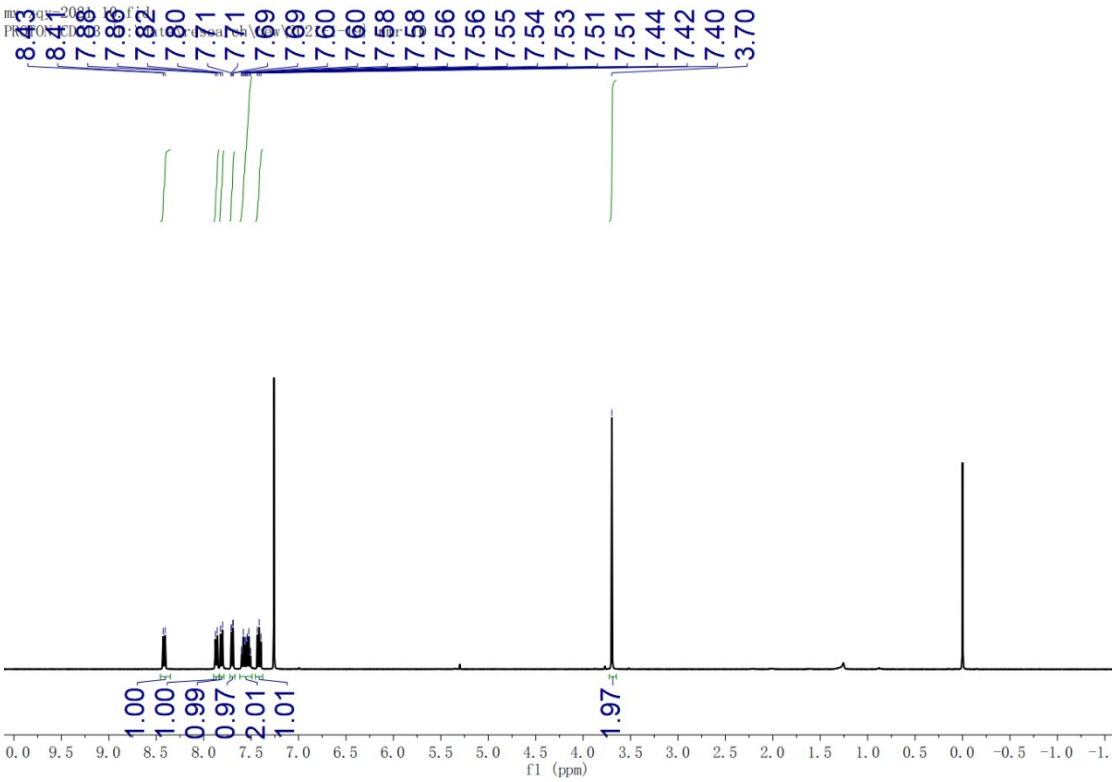


Fig. S10. ^{1}H NMR spectra of compound **1** in $CDCl_3$.

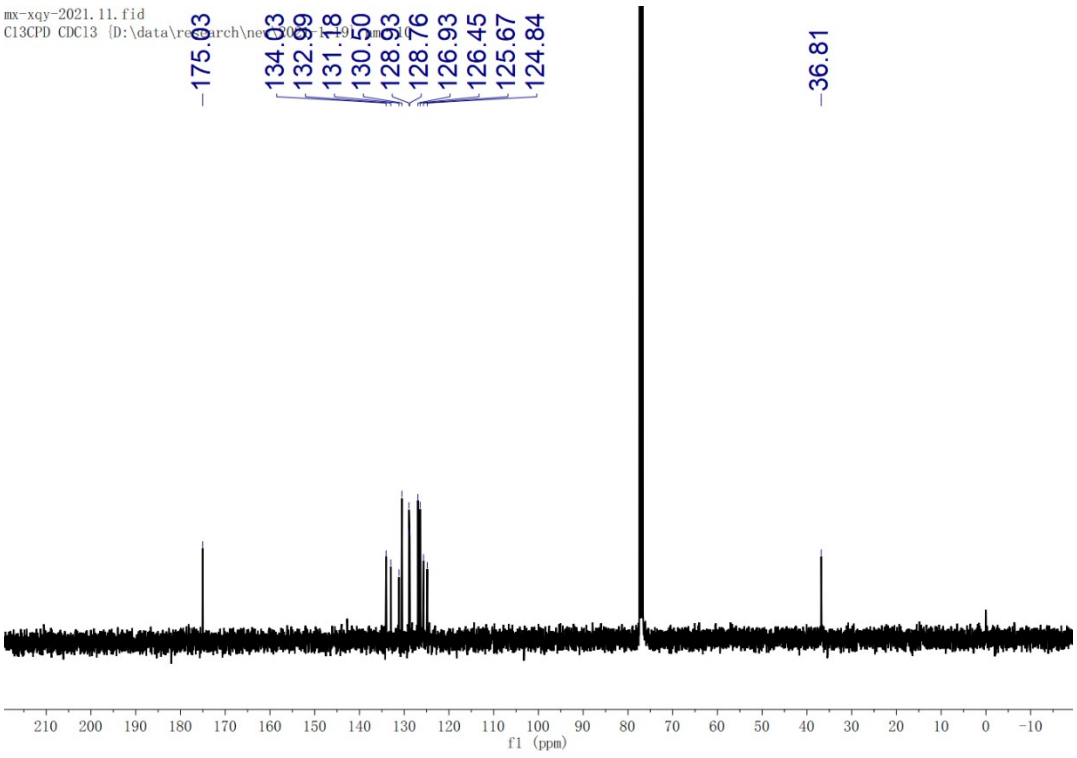


Fig. S11. ^{13}C NMR spectra of compound **1** in $CDCl_3$.

Synthesis of compound 2

Compound **2** was synthesized by the same way with compound **1**, just changed the raw material 2-bromoacetic acid to 3-bromopropanoic acid. Finally got target compound as white solid (83% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.66 (dd, J = 7.2, 0.9 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.47 – 7.40 (m, 1H), 3.20 (t, J = 7.3 Hz, 2H), 2.66 (t, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.88, 134.08, 133.42, 131.79, 130.25, 128.67, 128.34, 126.73, 126.37, 125.57, 125.20, 34.21, 29.21.

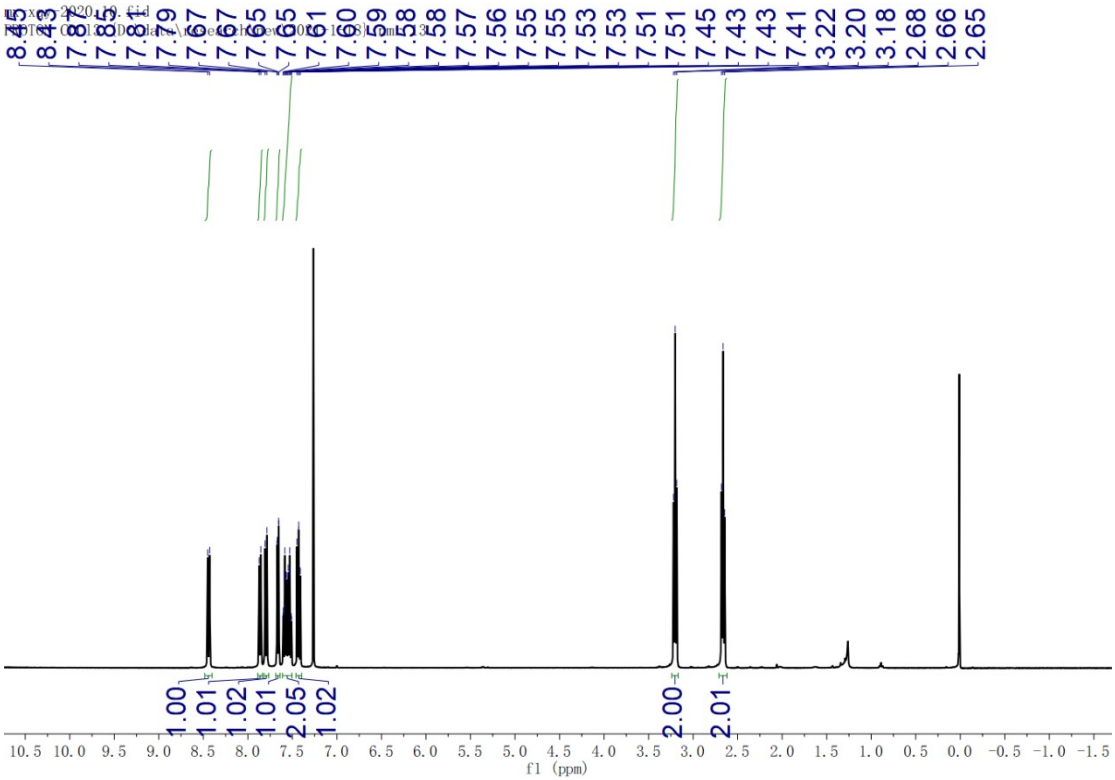


Fig. S12. ^{1}H NMR spectra of compound **2** in $CDCl_3$.

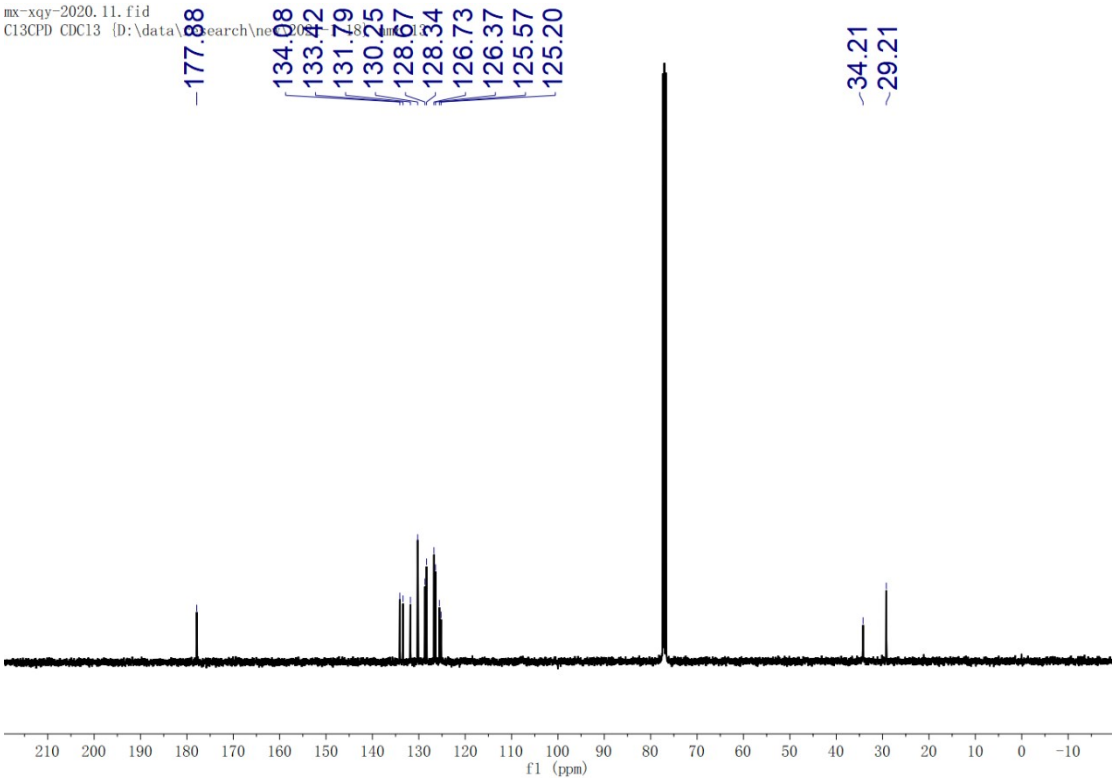


Fig. S13. ^{13}C NMR spectra of compound **2** in $CDCl_3$.

Synthesis of compound 5

Compound **5** was synthesized by the same way with compound **1**, just changed the raw material naphthalene-1-thiol to naphthalene-2-thiol. Finally got target compound as white solid (69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.77 (d, *J* = 8.5 Hz, 3H), 7.53 – 7.42 (m, 3H), 3.76 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.67, 133.65, 132.24, 131.79, 128.85, 128.45, 127.74, 127.47, 127.39, 126.74, 126.28, 36.50.

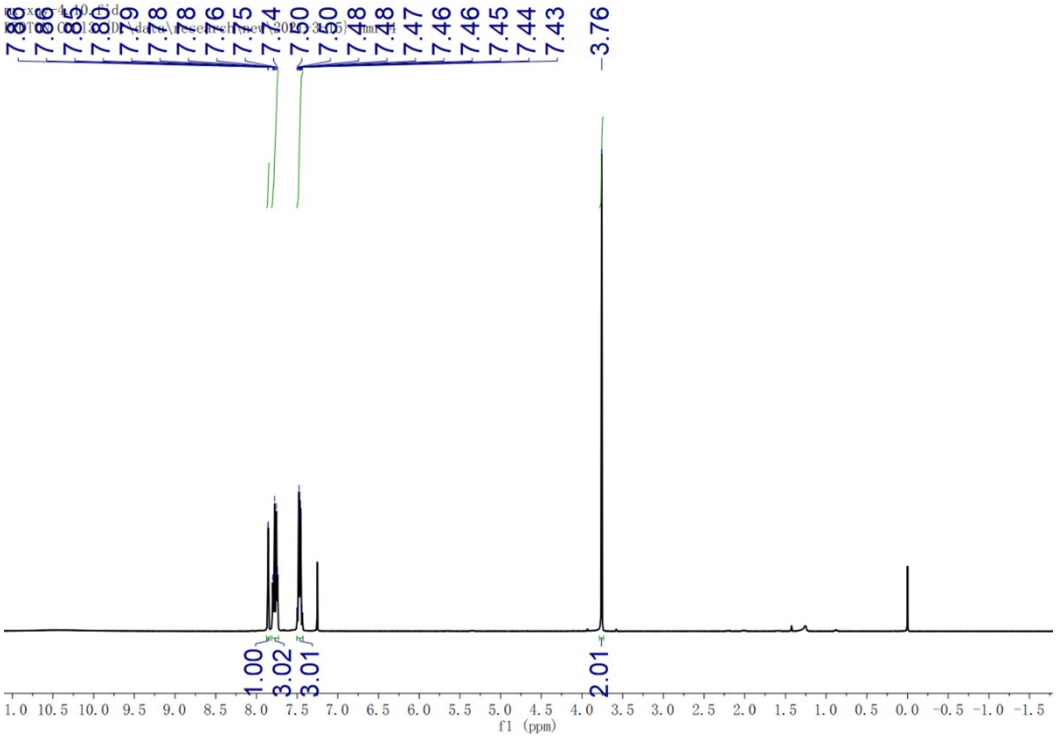


Fig. S14. ^{1}H NMR spectra of compound **5** in $CDCl_3$.

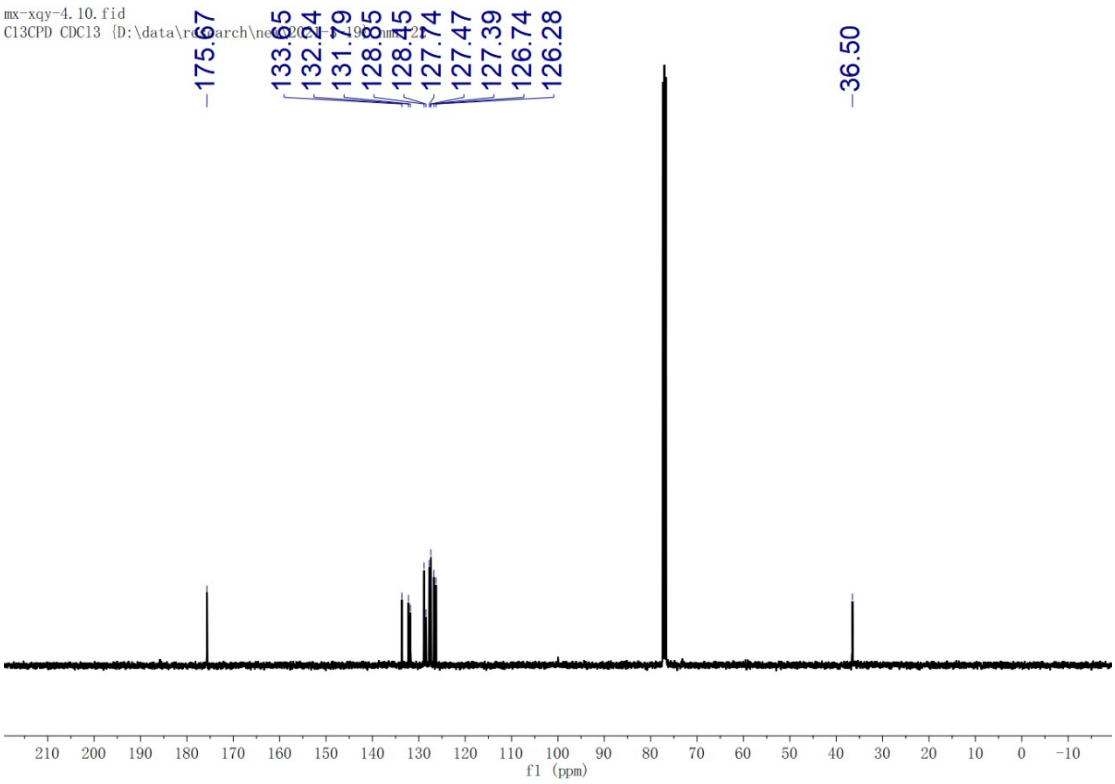


Fig. S15. ^{13}C NMR spectra of compound **5** in $CDCl_3$.

Synthesis of compound 6

Compound **6** was synthesized by the same way with compound **2**, just changed the raw material naphthalene-1-thiol to naphthalene-2-thiol. Finally got target compound as white solid (81% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 15.9, 7.6 Hz, 4H), 7.56 – 7.41 (m, 3H), 3.25 (t, J = 7.3 Hz, 2H), 2.71 (t, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.48, 133.72, 132.31, 132.10, 128.73, 128.51, 128.01, 127.74, 127.24, 126.68, 126.05, 34.11, 28.68.

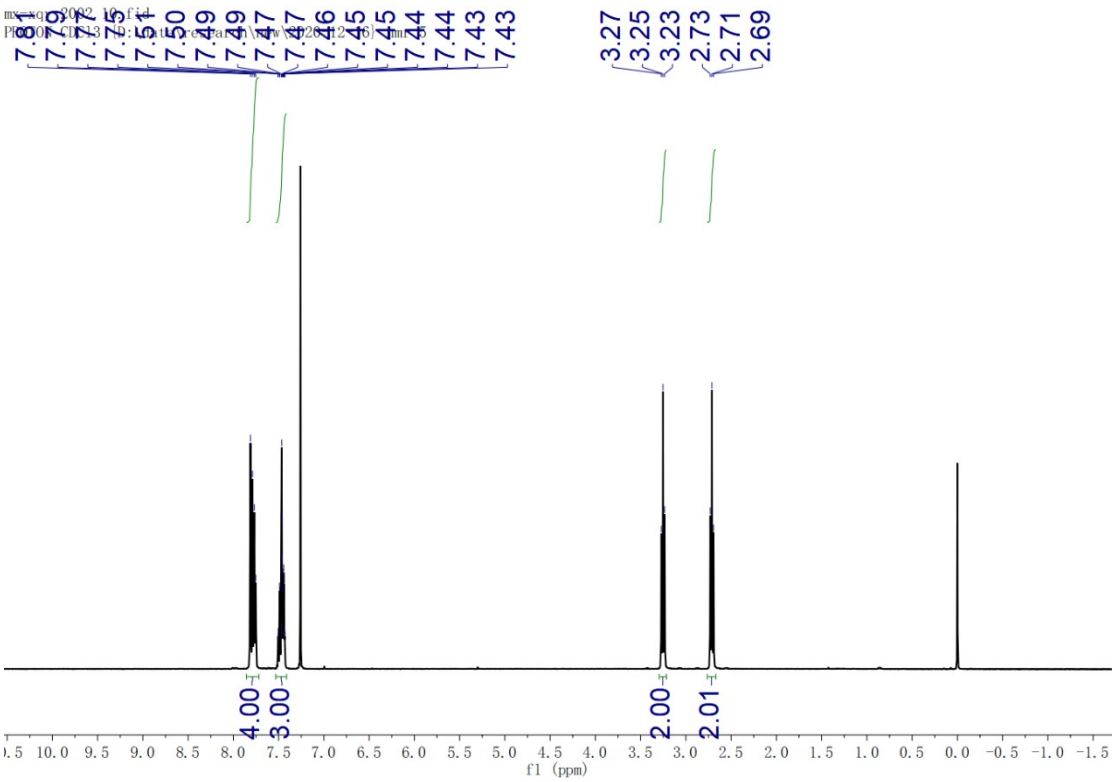


Fig. S16. ^{1}H NMR spectra of compound **6** in $CDCl_3$.

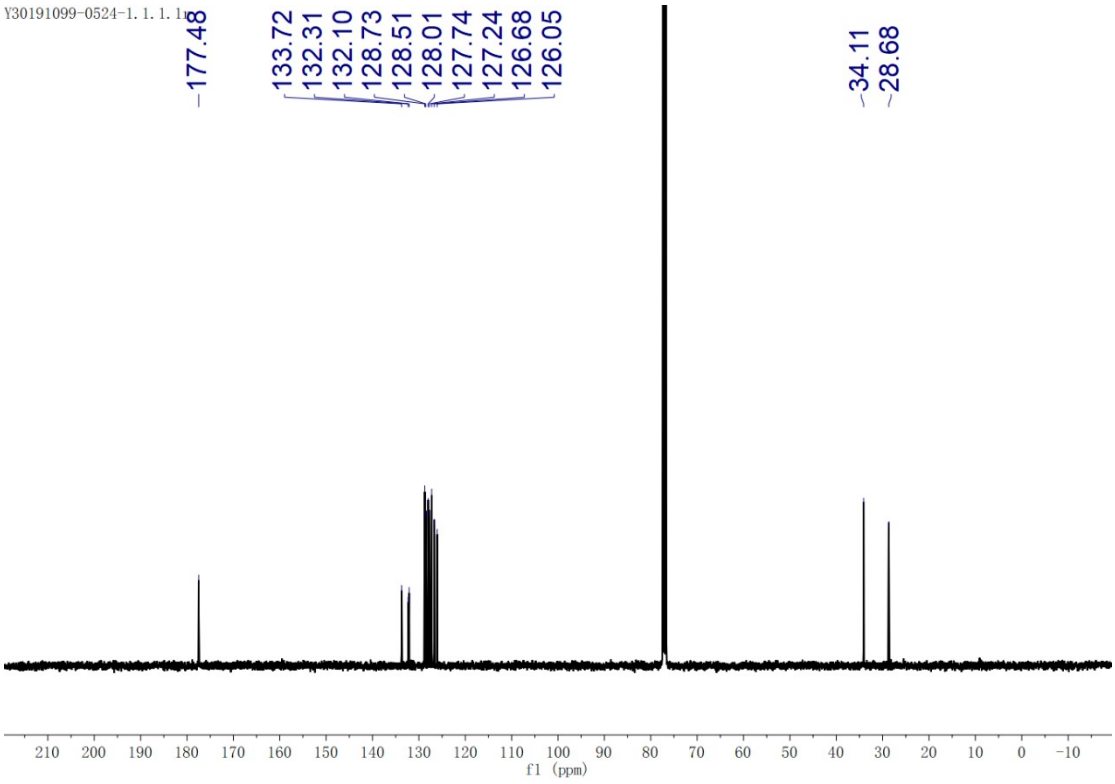


Fig. S17. ^{13}C NMR spectra of compound **6** in $CDCl_3$.

2.1 General procedure for the synthesis of compound **3**, **4**, **7** and **8**.

Synthesis of compound 3

Cs_2CO_3 (15.0 mmol, 4.9 g) was added to the solution of naphthalene-1-thiol (5.0 mmol, 0.8 g) in acetonitrile and stirred at reflux temperature for 1h. Then ethyl 4-bromobutanoate (5.5 mmol, 1.1 g) was added into the system and the mixture was brought to reflux after stirring for about 8h. After the reaction was completed, the precipitate was filtered off and washed with ethyl acetate, the filtrate was concentrated by a rotary evaporator. The crude product was purified by the column chromatography with eluent PE/EA= 10/1, providing the desired product **3** as faint yellow oil. (0.7 g, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.64 – 7.48 (m, 3H), 7.45 – 7.38 (m, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.03 (t, J = 7.2 Hz, 2H), 2.48 (t, J = 7.3 Hz, 2H), 2.05 – 1.92 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.99, 133.96, 133.14, 133.01, 128.60, 128.31, 127.33, 126.42, 126.23, 125.58, 125.03, 60.46, 33.51, 33.02, 24.40, 14.27. HRMS (ESI+) (m/z): $[M+Na]^+$ calc. for $[C_{16}H_{18}O_2SNa]^+$, 297.0925; found, 297.0938.

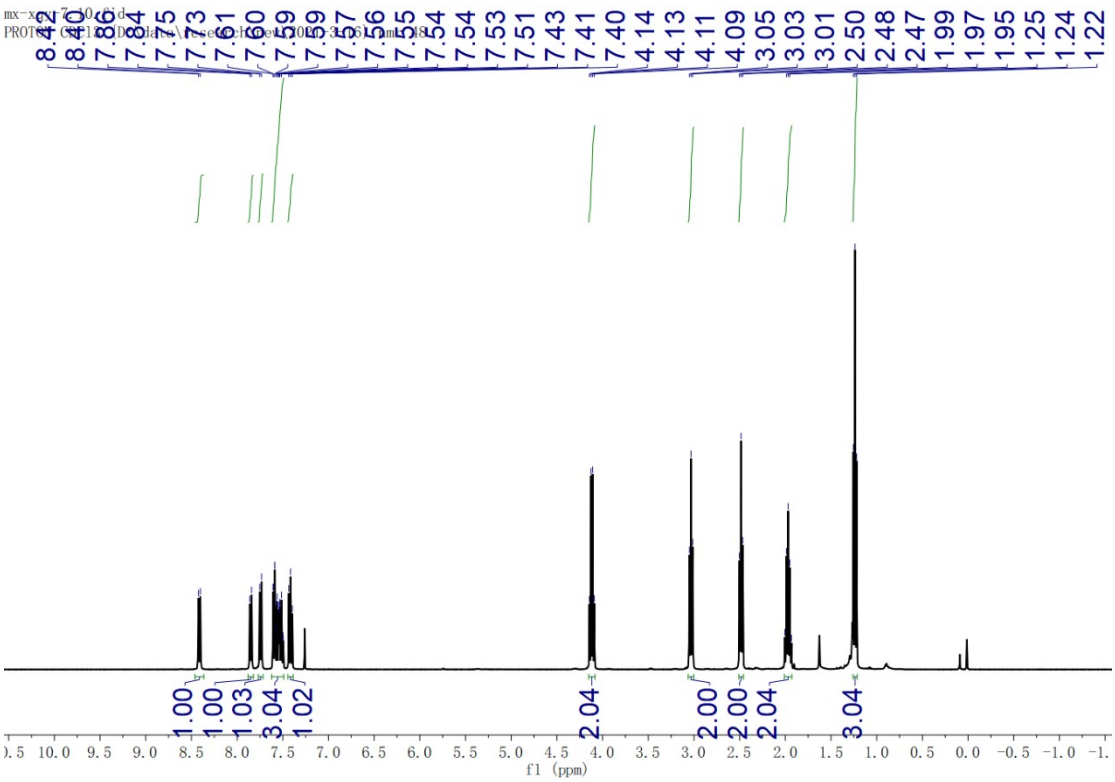


Fig. S18. ^{1}H NMR spectra of compound **3** in $CDCl_3$.

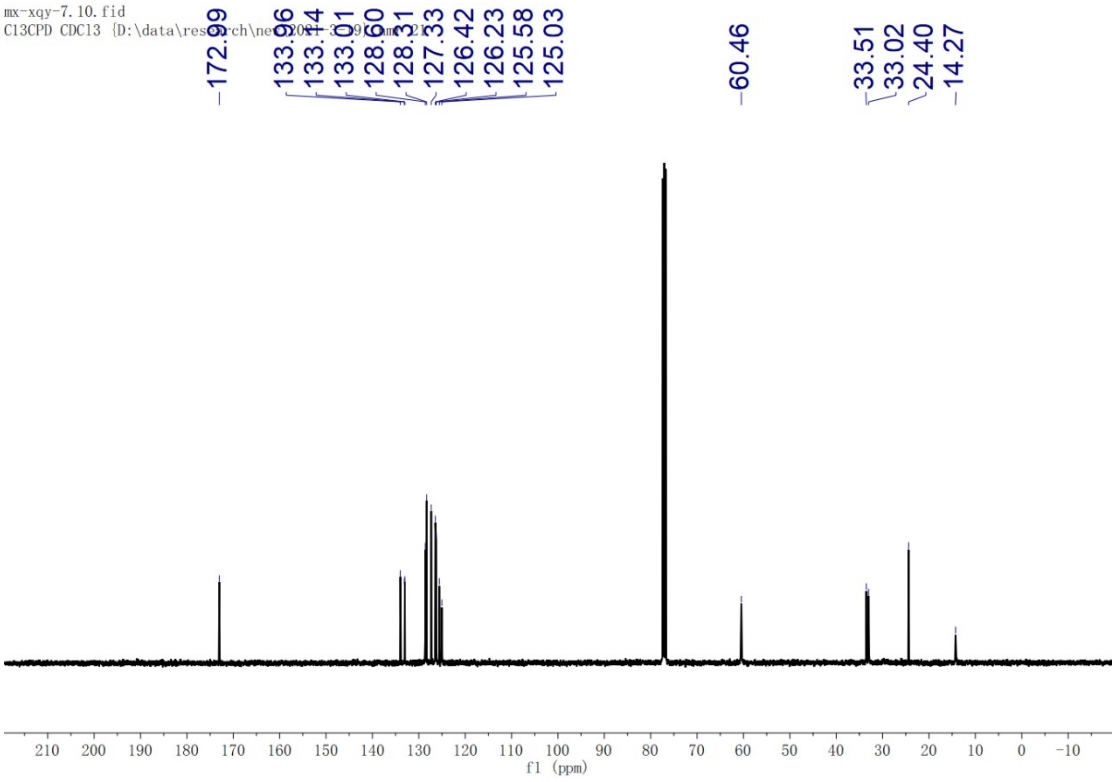


Fig. S19. ^{13}C NMR spectra of compound **3** in $CDCl_3$.

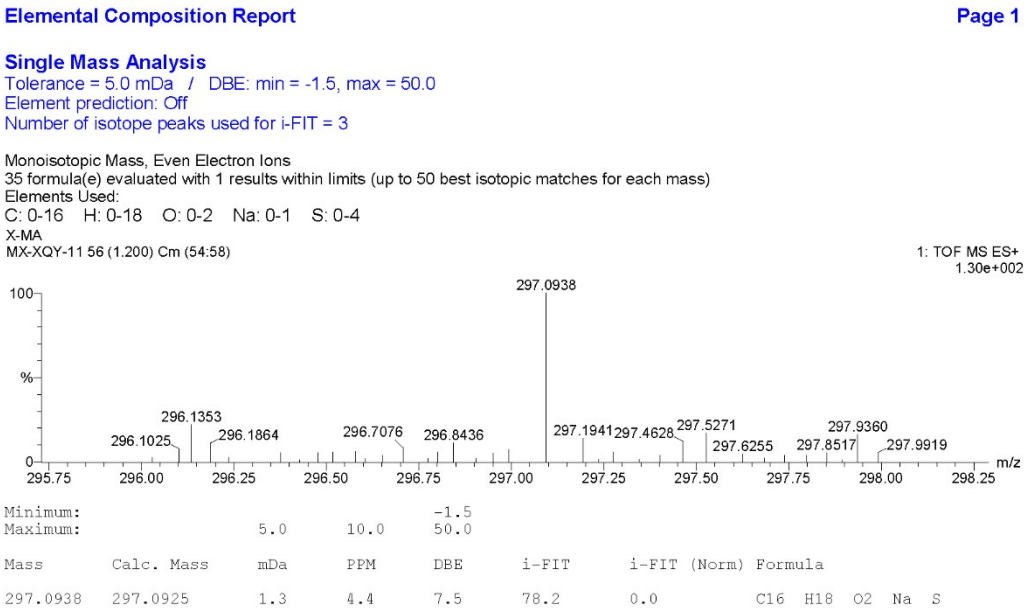


Fig. S20. HRMS spectra of compound **3**.

Synthesis of compound 4

NaOH (4.3 mmol, 0.2 g) aqueous solution (10 mL) was added to the THF and MeOH mixed solution of compound **3** (2.2 mmol, 0.6 g) and stirred at room temperature for 8 h. After the reaction was completed, the mixture was neutralized by HCl until pH adjusted to 5.0. Then the mixed solution was extracted with ethyl acetate and the organic phase was washed with water, dried by Mg_2SO_4, and then concentrated over the rotatory evaporator. The crude product compound **4** was used for the step without further purification.

Synthesis of compound 7

Compound **7** was synthesized by the same way with compound **3**, just changed the raw material naphthalene-1-thiol to naphthalene-2-thiol. Finally got target compound as colorless oil (63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 4H), 7.54 – 7.39 (m, 3H), 4.14 (q, J = 7.1 Hz, 2H), 3.08 (t, J = 7.2 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H),

2.10 – 1.95 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.98, 133.80, 133.65, 131.76, 128.47, 127.73, 127.36, 127.08, 126.94, 126.58, 125.67, 60.50, 32.94, 32.78, 24.36, 14.31.

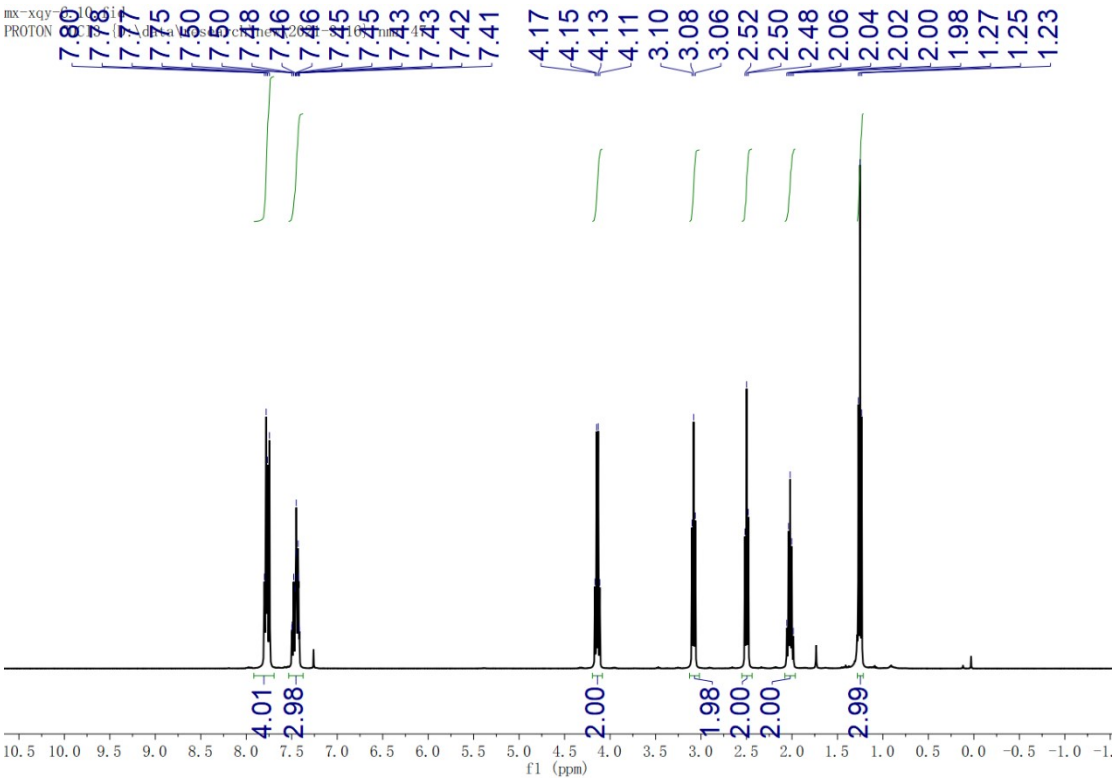


Fig. S21. ^{1}H NMR spectra of compound **7** in $CDCl_3$.

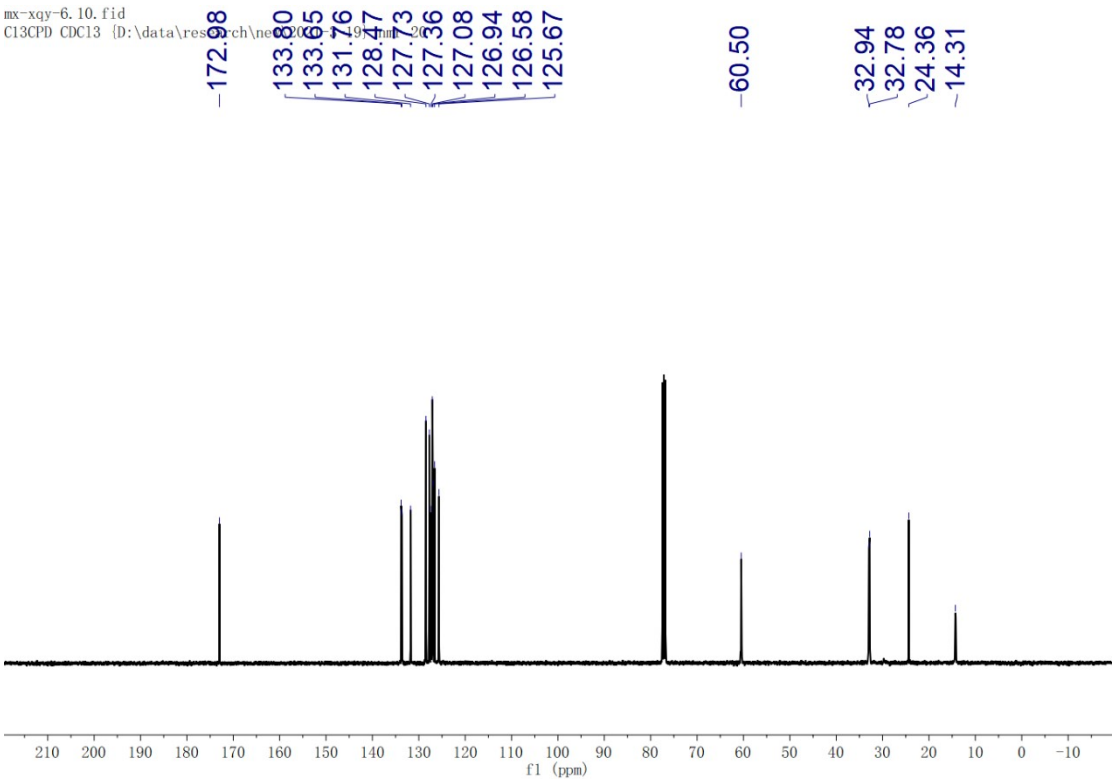


Fig. S22. ^{13}C NMR spectra of compound **7** in $CDCl_3$.

Synthesis of compound 8

Compound **8** was synthesized by the same way with compound **4**, just changed the raw material compound **3** to compound **7**. The crude product was used for the step without further purification.

2.2 General procedure for the synthesis of compound **5-1NTO**, **7-1NTO**, **5-2NTO** and **7-2NTO.**

Synthesis of compound 5-1NTO

The $SOCl_2$ solution of compound **1** (0.4 g, 1.8 mmol) was heated to reflux for 1h. After cooling down to room temperature, $SOCl_2$ was removed in vacuo. Then dichloromethane (10 mL) and $AlCl_3$ (0.5 g, 3.6 mmol) were added to the system in ice bath and stirred at 0 ^oC for 2h. After the reaction was completed, the mixture was

dropped into ice water and then extracted with dichloromethane for three times. The combined organic phase was washed with brine, dried by magnesium sulfate and evaporated in vacuo, the crude product was purified by silica gel column chromatography with PE/EA = 15/1 to give target product **5-1NTO** (0.2 g, 37% yield) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 7.2 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.61 (t, J = 7.7 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.61, 135.24, 133.84, 130.07, 129.22, 128.49, 127.36, 126.55, 126.05, 125.91, 125.81, 36.00. HRMS (ESI+) (m/z): $[M+H]^+$ calc. for $[C_{12}H_9OS]^+$, 201.0374; found, 201.0374.

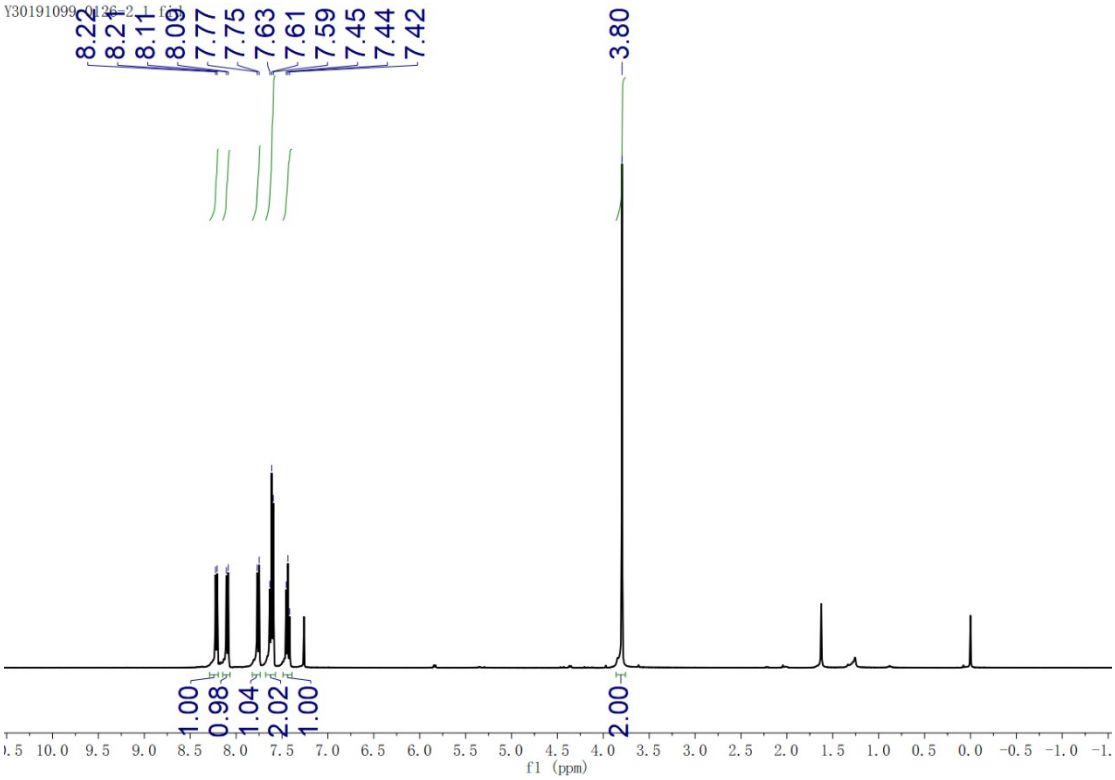


Fig. S23. ^{1}H NMR spectra of compound **5-1NTO** in $CDCl_3$.

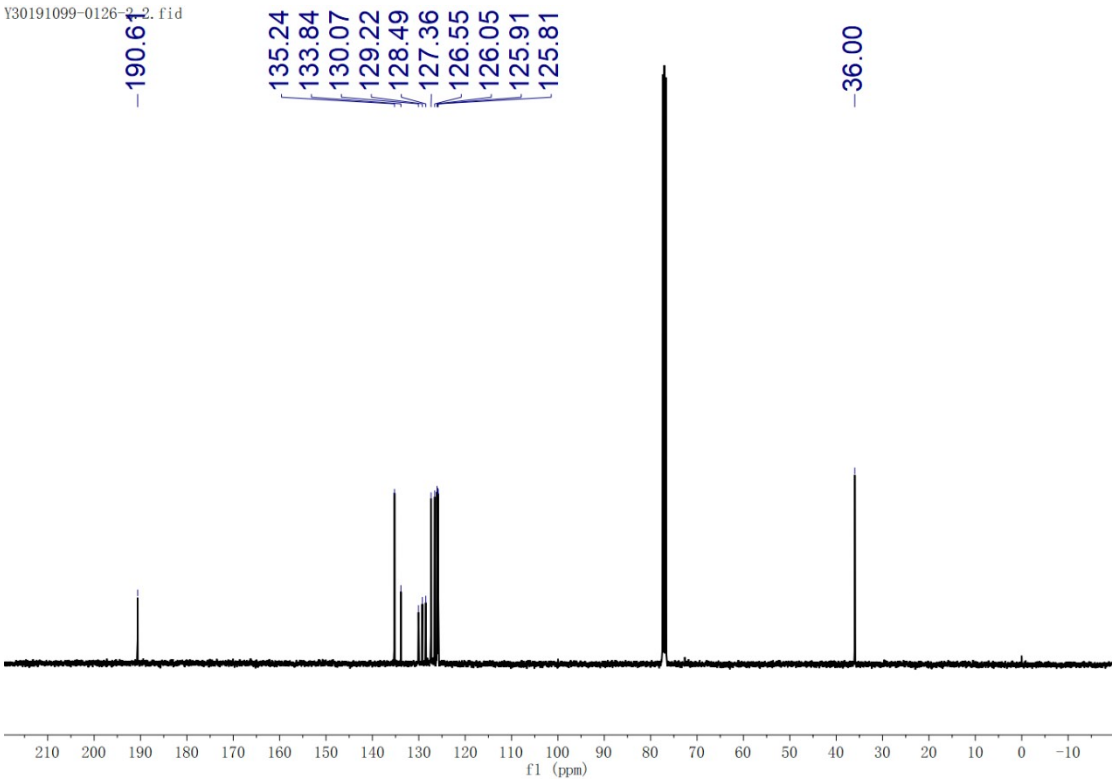


Fig. S24. ^{13}C NMR spectra of compound **5-1NTO** in $CDCl_3$.

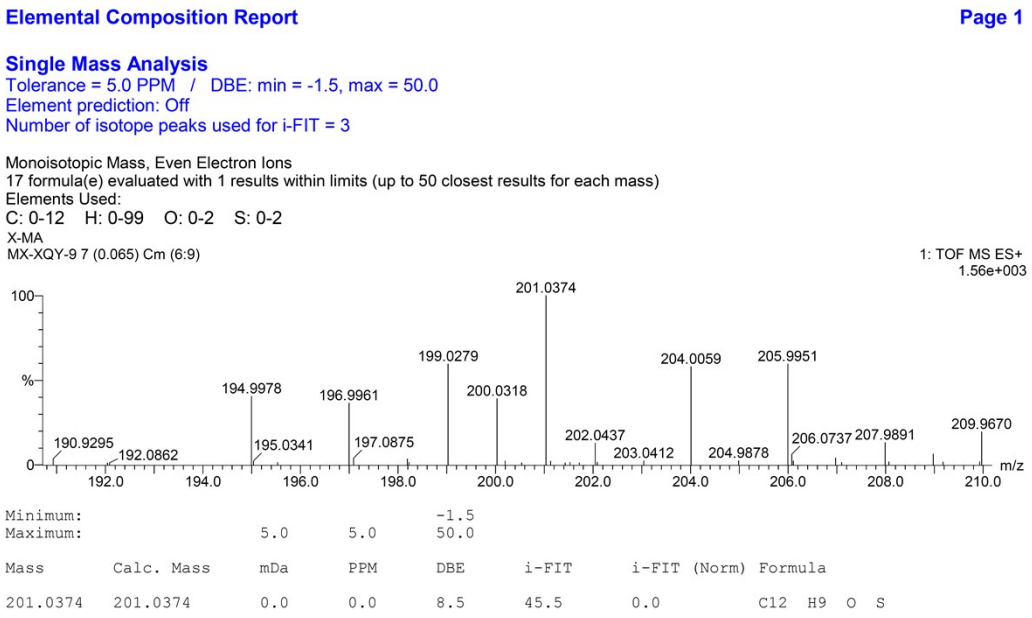


Fig. S25. HRMS spectra of compound **5-1NTO**.

Synthesis of compound 7-1NTO [1]

Compound **7-1NTO** was synthesized by the same way with compound **5-1NTO**,

just changed the raw material compound **1** to compound **4**. Finally got target compound as colorless oil (17% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.47 (m, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.62 – 7.55 (m, 2H), 3.15 (dt, *J* = 14.7, 6.8 Hz, 4H), 2.42-2.33 (m, *J* = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.54, 143.17, 135.52, 134.10, 132.07, 128.36, 128.26, 126.84, 126.17, 125.95, 125.79, 40.68, 35.71, 30.43.

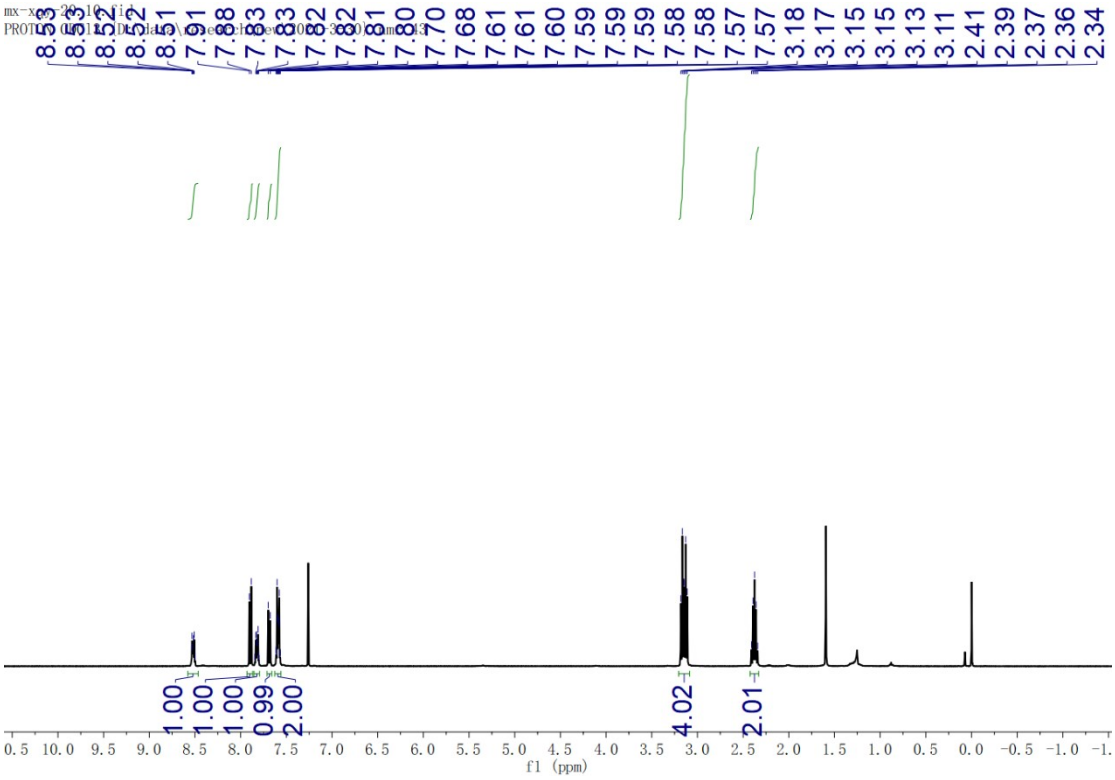


Fig. S26. ^{1}H NMR spectra of compound **7-1NTO** in $CDCl_3$.

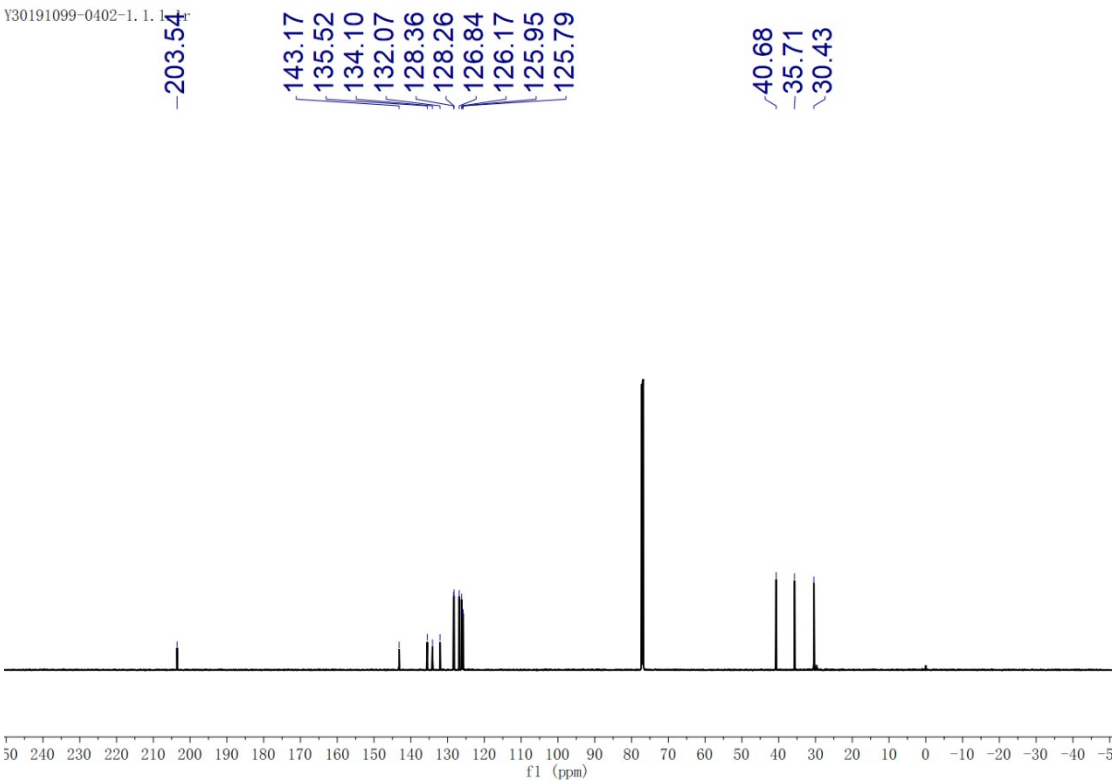


Fig. S27. ^{13}C NMR spectra of compound **7-1NTO** in $CDCl_3$.

Synthesis of compound 5-2NTO [2]

Compound **5-2NTO** was synthesized by the same way with compound **5-1NTO**, just changed the raw material compound **1** to compound **5**. Finally got target compound as yellow solid (23% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.71 - 7.65 (m, 1H), 7.56 – 7.50 (m, 1H), 7.47 (d, J = 8.7 Hz, 1H), 3.92 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.45, 159.76, 136.76, 131.15, 131.10, 129.75, 128.36, 126.30, 123.63, 122.55, 122.45, 40.01.

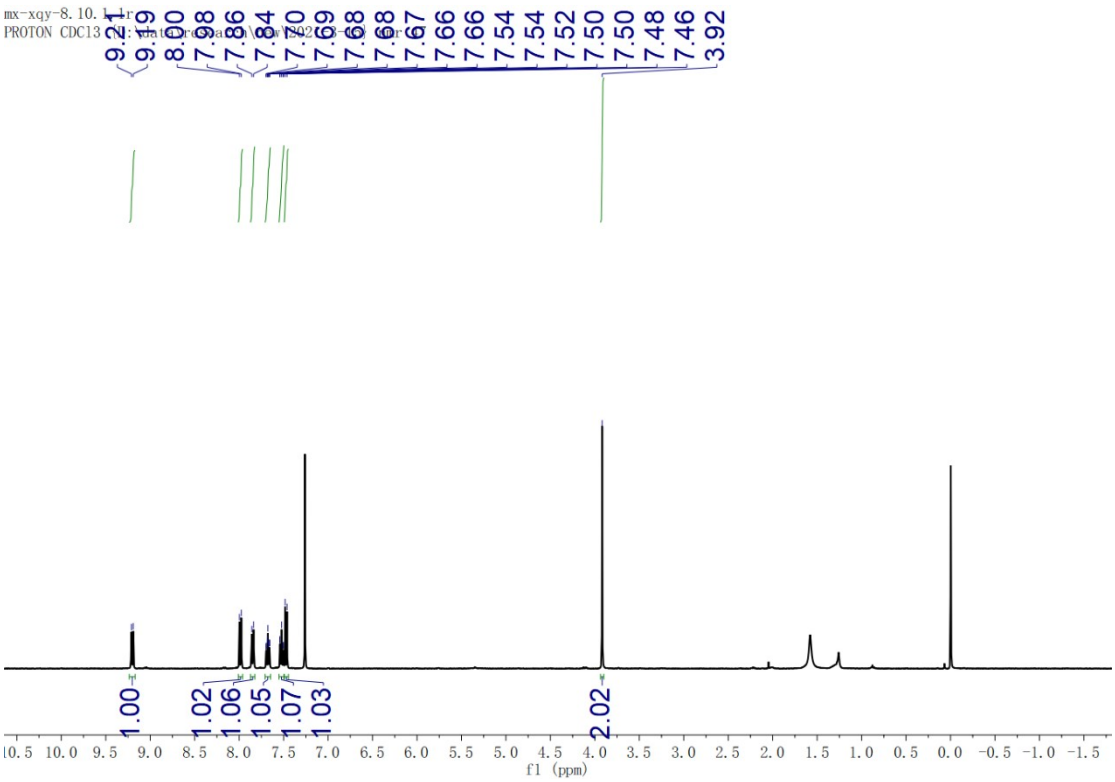


Fig. S28. ^{1}H NMR spectra of compound **5-2NTO** in $CDCl_3$.

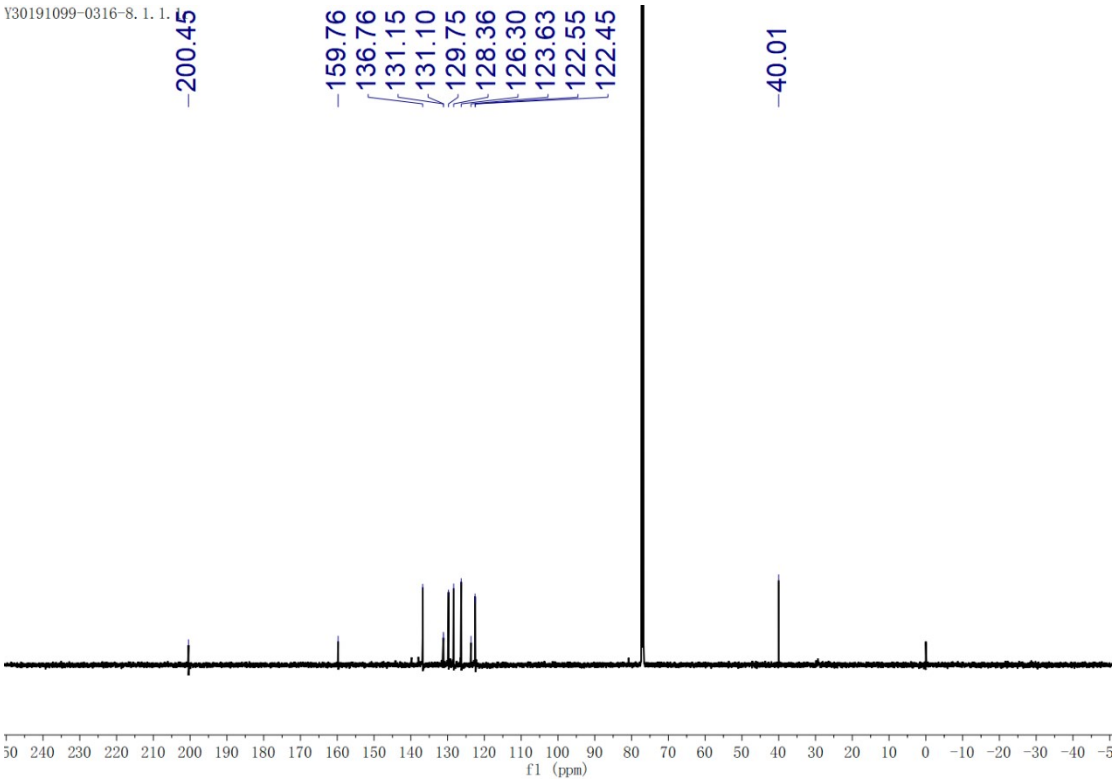


Fig. S29. ^{13}C NMR spectra of compound **5-2NTO** in $CDCl_3$.

Synthesis of compound 7-2NTO [3]

Compound **7-2NTO** was synthesized by the same way with compound **5-1NTO**, just changed the raw material compound **1** to compound **8**. Finally got target compound as colorless oil (27% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.50-7.42 (m, 2H), 3.10 – 2.98 (m, 4H), 2.38 - 2.26 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.69, 136.48, 136.40, 132.30, 130.63, 130.23, 128.20, 128.04, 128.00, 126.07, 124.58, 41.71, 33.43, 29.88.

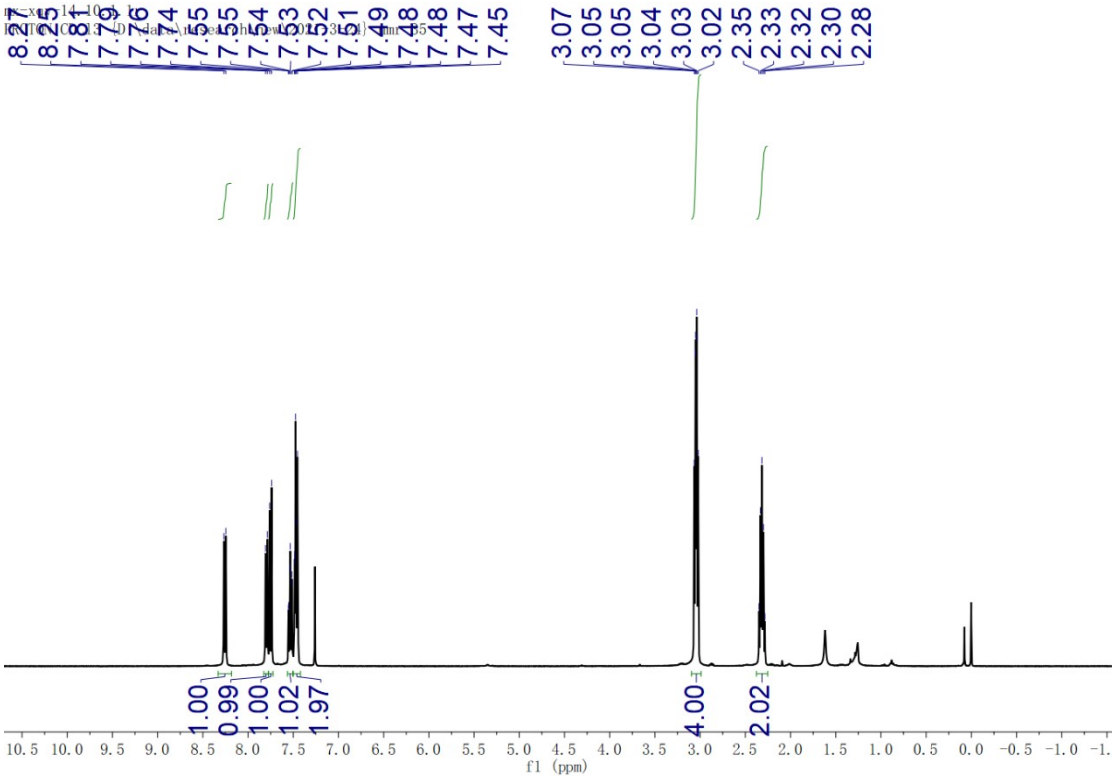


Fig. S30. ^{1}H NMR spectra of compound **7-2NTO** in $CDCl_3$.

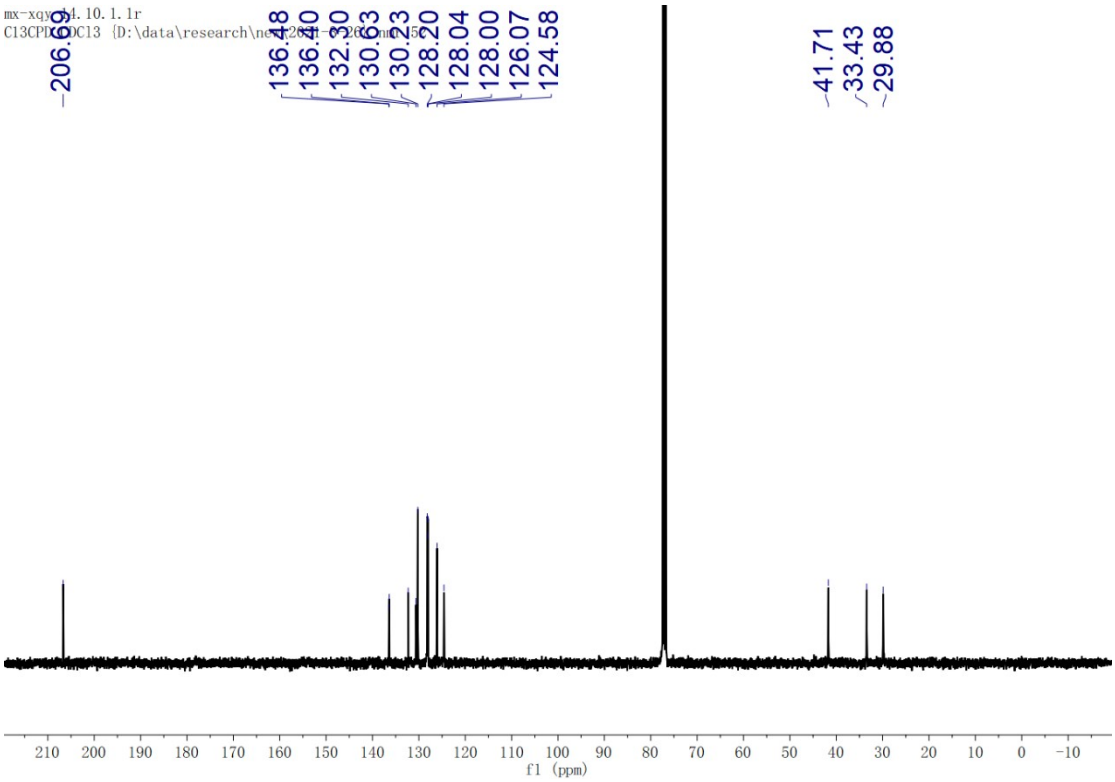


Fig. S31. ^{13}C NMR spectra of compound **7-2NTO** in $CDCl_3$.

2.3 General procedure for the synthesis of compound **6-1NTO** and **6-2NTO.**

Synthesis of compound 6-1NTO [4]

Compound **2** (2.2 mmol, 0.5 g) was added to 2 mL concentrated H_2SO_4 under ice bath. After the reaction was completed, the mixture was doped into vast cold sodium carbonate aqueous solution and then extracted with DCM for three times. The combined organic phase was washed with brine, dried by magnesium sulfate, and concentrated over the rotatory evaporator. The crude product was purified by the silica gel column chromatography with eluent PE: EA = 15: 1 to obtain **6-1NTO** as yellow solid (0.2 g, 38% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.68 – 7.51 (m, 4H), 3.42 – 3.34 (m, 2H), 3.11 – 3.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.13, 143.06, 135.15, 130.42, 129.09, 128.57, 128.16, 126.76, 125.40, 124.84, 124.13, 38.81, 26.35.

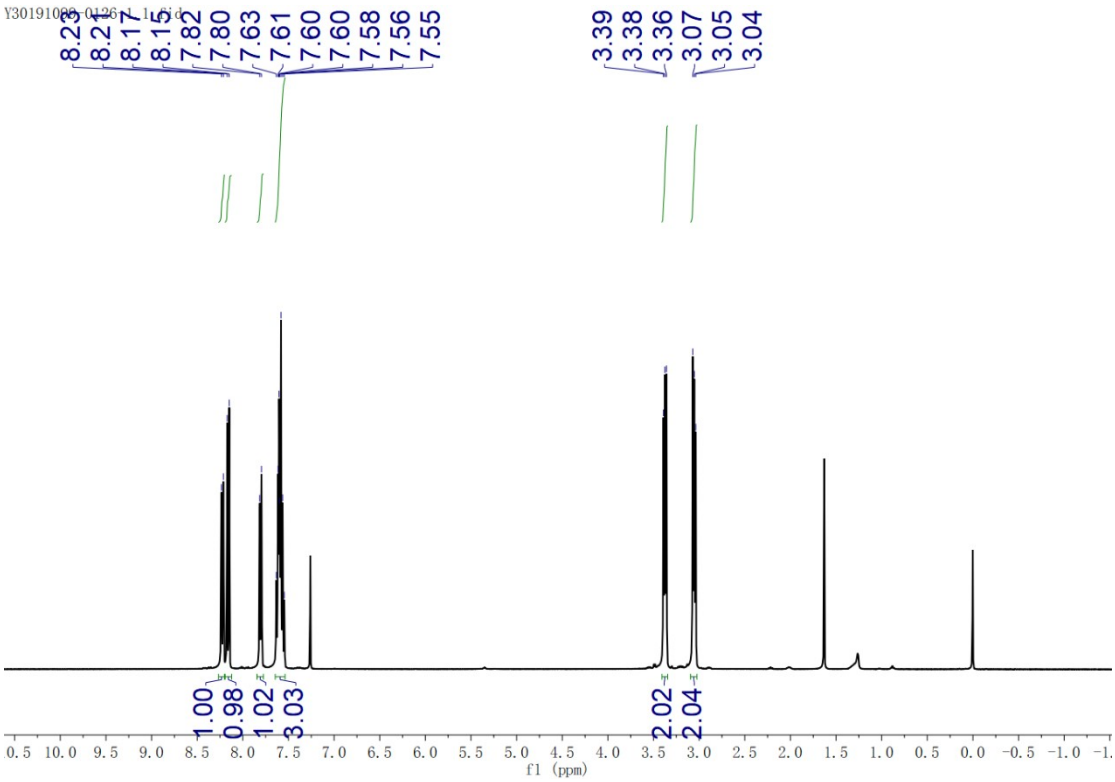


Fig. S32. ^{1}H NMR spectra of compound **6-1NTO** in $CDCl_3$.

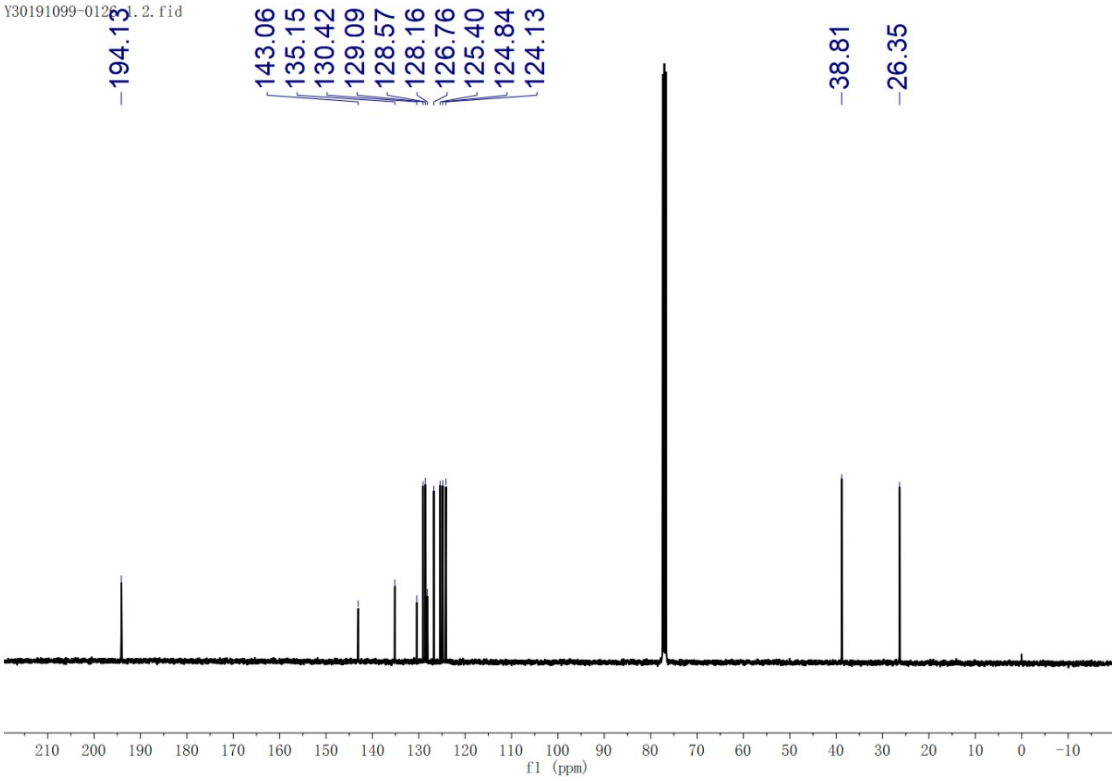


Fig. S33. ^{13}C NMR spectra of compound **6-1NTO** in $CDCl_3$.

Synthesis of compound 6-2NTO [5]

Compound **6-2NTO** was synthesized by the same way with compound **6-1NTO**, just changed the raw material compound **2** to compound **6**. Finally got target compound as yellow oil (39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.64 - 7.57 (m, 1H), 7.49 – 7.41 (m, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 3.34 – 3.26 (m, 2H), 3.15 – 3.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.18, 145.18, 133.63, 132.49, 131.79, 129.19, 128.46, 126.11, 125.69, 125.66, 125.41, 41.32, 26.38.

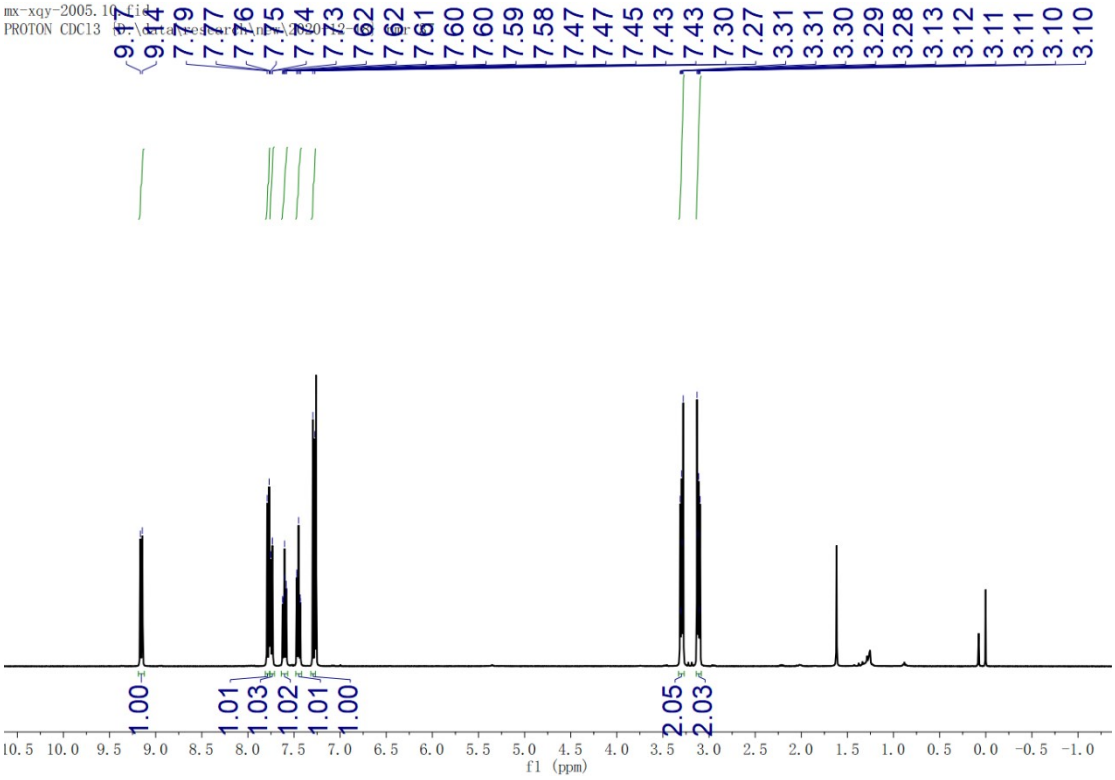


Fig. S34. ^{1}H NMR spectra of compound **6-2NTO** in $CDCl_3$.

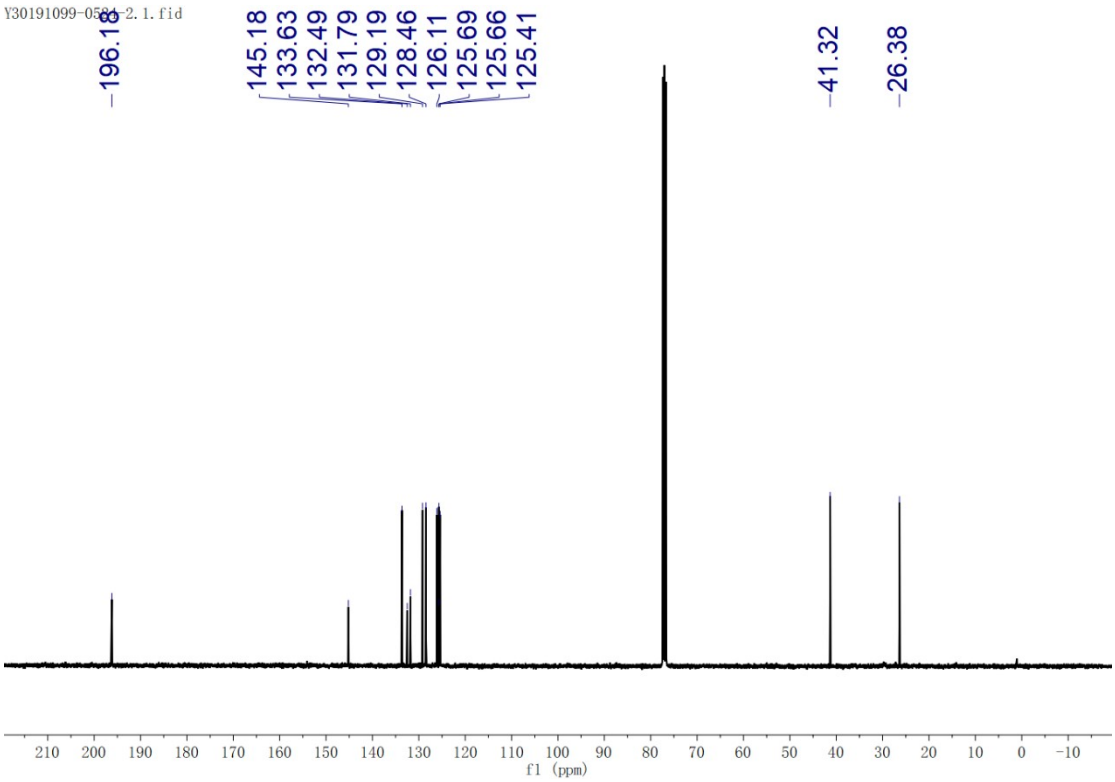


Fig. S35. ^{13}C NMR spectra of compound **6-2NTO** in $CDCl_3$.

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