CuI-mediated benzannulation of (*ortho*-arylethynyl)phenylenaminones to assemble *α*-aminonaphthalene derivatives

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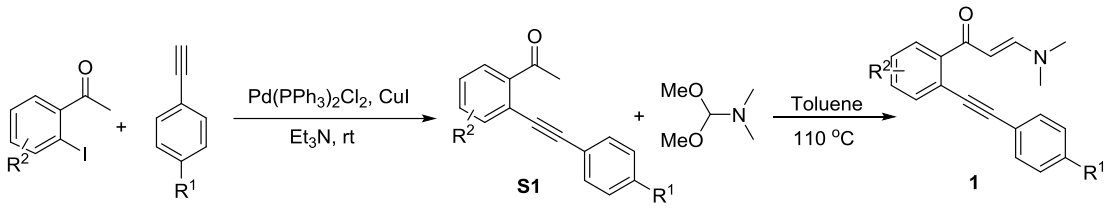
1. General information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in *ppm* relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *br s* = broad singlet, *p* = quintet, *h* = sextet, *hept* = septet, *m* = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample. Emission intensities were recorded using Perkin-Elemer LS 55 fluorescence spectrometer. Column chromatography was carried out on silica gel (200-300 mesh).

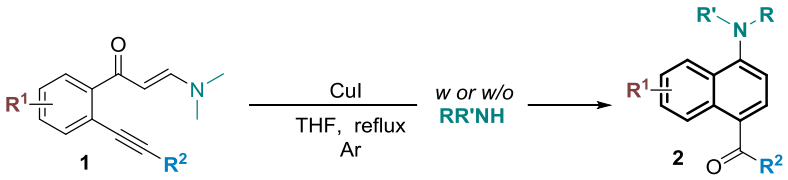
2. General procedure: synthesis of compounds 1



Step 1: To a stirred solution of *o*-iodoacetophenone (5.0 mmol, 1.0 equiv) and terminal aromatic alkynes (1.2 equiv) in Et_3N (30 mL) was added $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%). The resulted mixture was stirred at room temperature for 8 h. After the separation of ammonium salt by filtration and the removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 40 / 1) to afford the corresponding **S1** in yields ranging from 75% to 99%.[1]

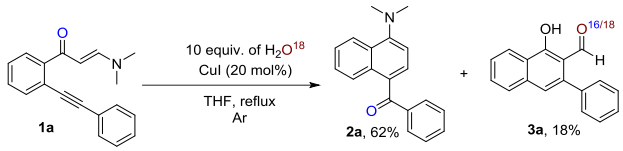
Step 2: To a stirred solution of ketone **S1** (5.0 mmol, 1.0 equiv.) in toluene (5 mL), 1,1-dimethoxy *N*,*N*-dimethylmethanamine (7.0 mmol, 1.4 equiv.) was added and stirred at 110 °C. After completion of the reaction (monitored by TLC), it was quenched with water, extracted with ethyl acetate and dried with anhydrous Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 1 / 1) to afford the corresponding compounds **1** in yields ranging from 70% to 80%.[2]

3. General procedure: synthesis of compounds 2



To a mixture of compound **1** (1 equiv.), CuI (20 mmol %) in THF was (or not) added amines (3 equiv.) under nitrogen. Then the reaction was heated to reflux for 8 h. When the reaction was complete, the solvent was removed in vacuum, and the crude product was eluted on silica gel with petroleum ether/ethyl acetate (1/20) to give the corresponding products **2**.

4. Labelling experiments

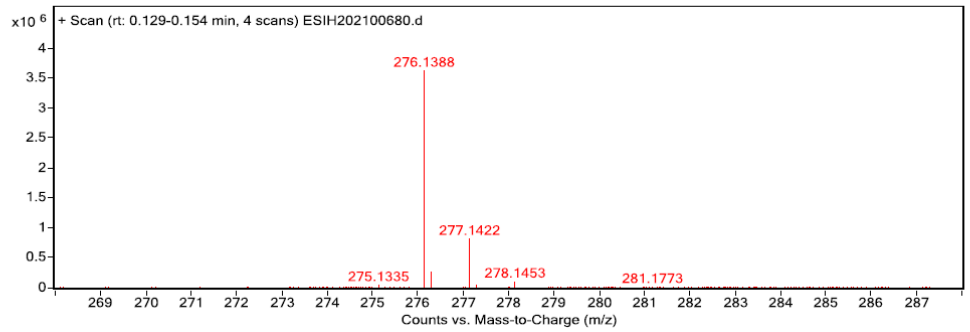


Qualitative Analysis Report

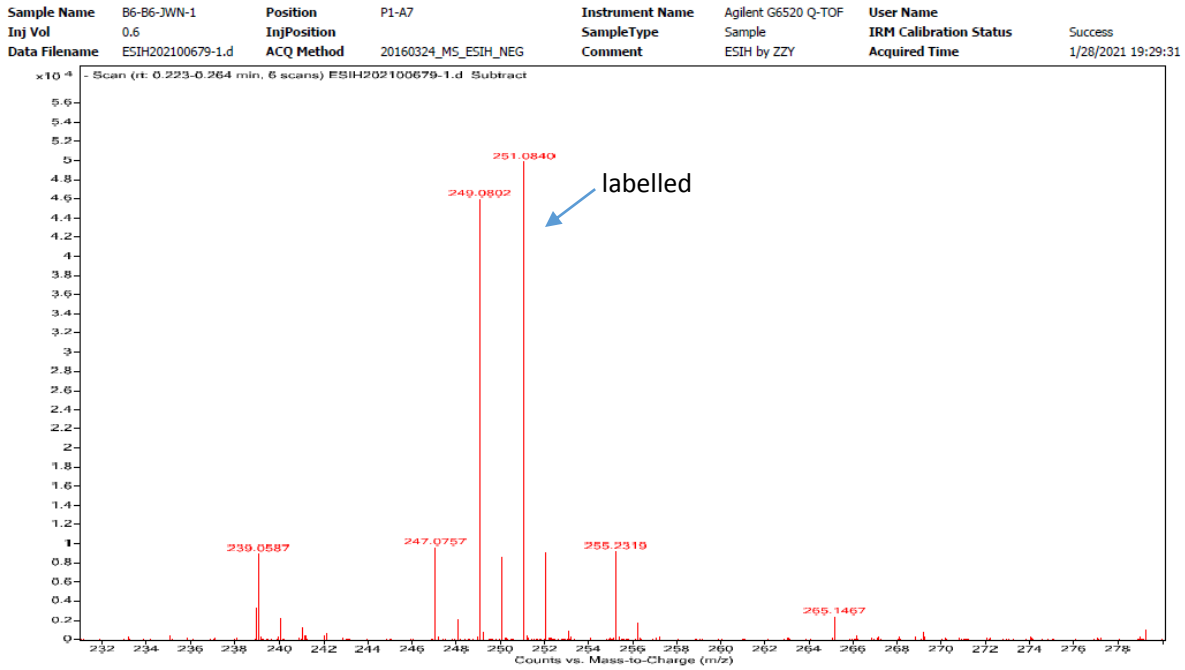
Data Filename	ESIH202100680.d	**Sample Name**	B6-B6-JWN-2
Sample ID		**Position**	P1-A8
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	1/28/2021 18:04:57	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

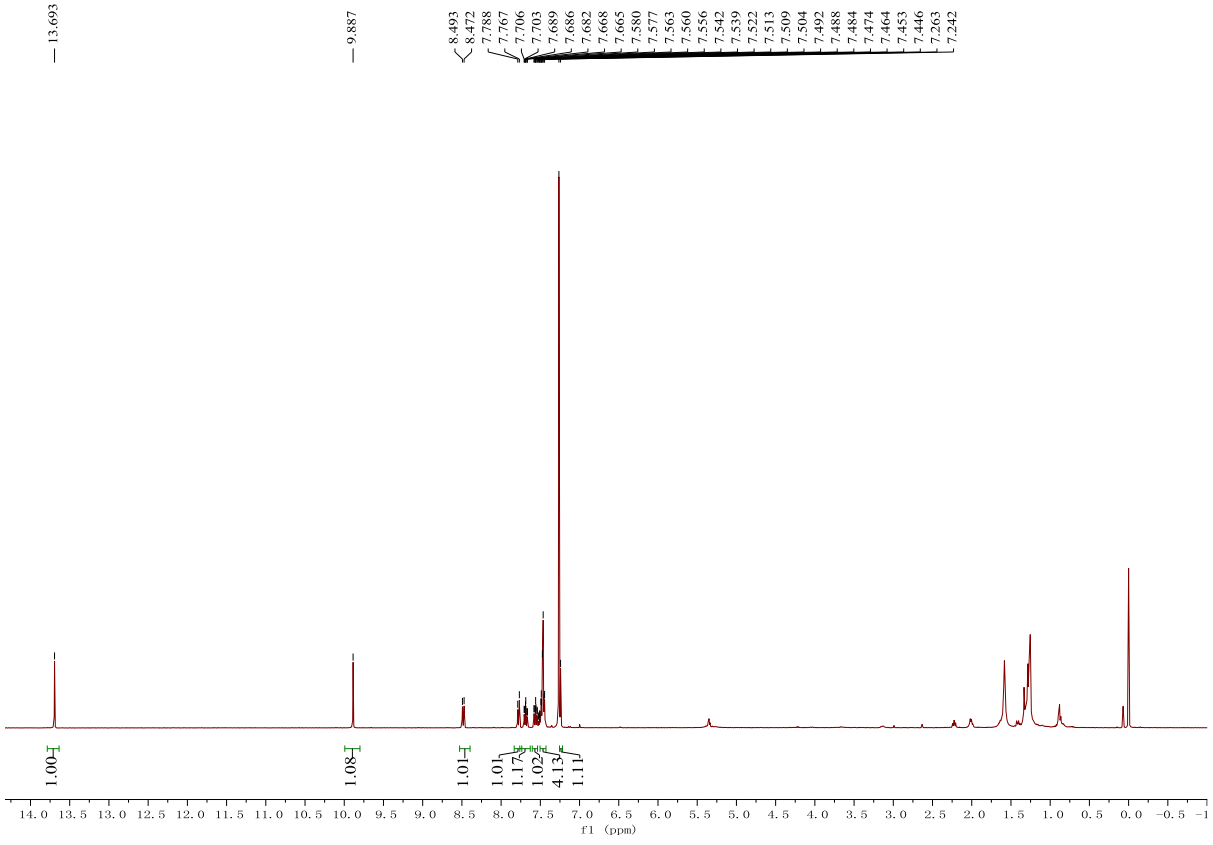
Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



HRMS of **2a**

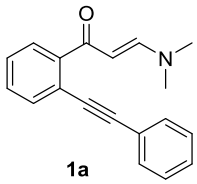


HRMS of 3**a**



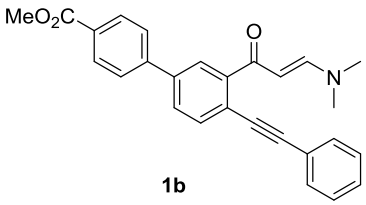
^{1}H NMR of **3a**

5. Characterization data of compounds



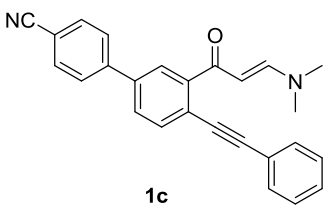
1a

(*E*)-3-(dimethylamino)-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one **1a**: purple oil;
IR (neat)*v* 3047, 2913, 1544, 1421, 758, 695 cm^{-1};
^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.53 (m, 3H), 7.51 – 7.43 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 3H), 5.72 (d, *J* = 12.5 Hz, 1H), 3.08 (s, 3H), 2.81 (s, 3H);
^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.1, 154.3, 144.6, 132.8, 131.4, 129.0, 128.3, 128.2, 128.1, 123.4, 120.5, 97.1, 93.7, 88.9, 44.9, 37.1;
HRMS (ESI): $C_{19}H_{18}NO^+$ [M+H] $^+$ 276.1383, found 276.1389.



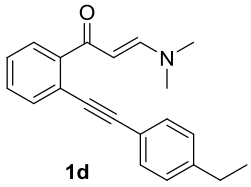
1b

Methyl-(*E*)-3'-(3-(dimethylamino)acryloyl)-4'-(phenylethynyl)-[1,1'-biphenyl]-4-carboxylate **1b**: purple oil;
IR (neat) *v* 2915, 1636, 1543, 1272, 759, 695 cm^{-1};
^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.89 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.62 (m, 3H), 7.50 – 7.48 (m, 2H), 7.37 – 7.30 (m, 3H), 5.78 (d, *J* = 11.7 Hz, 1H), 3.94 (s, 3H), 3.10 (s, 3H), 2.82 (s, 3H);
^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.6, 166.9, 154.4, 145.2, 144.3, 139.6, 133.4, 131.5, 130.2, 129.3, 128.4, 128.3, 127.6, 127.0, 126.9, 123.4, 120.4, 97.1, 94.9, 88.7, 52.2, 45.0, 37.2;
HRMS (ESI): $C_{27}H_{24}NO_3^+$ [M+H]$^+$410.1751, found 410.1755.



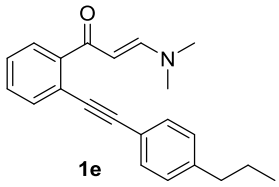
1c

(*E*)-3'-(3-(dimethylamino)acryloyl)-4'-(phenylethynyl)-[1,1'-biphenyl]-4-carbonitrile **1c**: purple oil;
IR (neat) *v* 2918, 1545, 1064, 723, 758, 541 cm^{-1};
^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.66 (s, 5H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.28 – 7.19 (s, 3H), 5.72 (d, J = 9.9 Hz, 1H), 3.05 (s, 3H), 2.76 (s, 3H);
^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.3, 145.3, 144.4, 138.7, 133.6, 132.7, 131.5, 128.6, 128.4, 127.6, 127.0, 123.2, 120.9, 118.9, 111.2, 96.7, 95.3, 88.5, 45.1, 37.3;
HRMS (ESI): $C_{26}H_{21}N_2O^+$ [M+H]$^+$377.1648, found 377.1653.



1d

(*E*)-3-(dimethylamino)-1-(2-((4-ethylphenyl)ethynyl)phenyl)prop-2-en-1-one **1d**: purple oil;
IR (neat) *v* 2922, 1543, 1064, 1062, 759, 539 cm^{-1};
^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.62 (m, 1H), 7.61 – 746 (m, 3H), 7.40 – 7.33 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 5.74 (d, *J* = 12.2 Hz, 1H), 3.07 (s, 3H), 2.80 (s, 3H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H);
^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.4, 154.1, 144.7, 132.8, 132.1, 131.9, 131.4, 129.0, 128.5, 128.0, 127.9, 120.7, 97.3, 94.0, 88.2, 44.9, 37.2, 28.8, 15.4;
HRMS (ESI): $C_{21}H_{22}NO^+$ [M+Na]$^+$326.1515, found 326.1518.



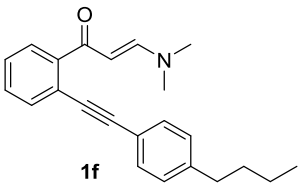
1e

(*E*)-3-(dimethylamino)-1-(2-((4-propylphenyl)ethynyl)phenyl)prop-2-en-1-one **1e**: purple oil;
IR (neat) *v* 2922, 1545, 1064, 1030, 760, 540 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.64 (m, 1H), 7.62 – 7.52 (m, 2H), 7.49 –7.46 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 5.74 (d, *J* = 12.4 Hz, 1H), 3.08 (s, 3H), 2.81 (s, 3H), 2.64 – 2.36 (m, 2H), 1.64 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.4, 154.5, 144.4, 143.2, 132.8, 132.1, 132.0, 131.3, 129.0, 128.6, 128.5, 128.1, 120.7, 97.2, 94.0, 88.3, 44.9, 38.0, 37.2, 24.3, 13.8;

HRMS (ESI): $C_{22}H_{24}NO^+$ $[M+H]^+$318.1852, found 318.1852.



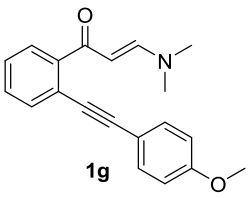
(*E*)-1-(2-((4-butylphenyl)ethynyl)phenyl)-3-(dimethylamino)prop-2-en-1-one **1f**: purple oil;

IR (neat) *v* 2921, 1638, 1551, 1422, 1064, 762 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.34 (m, 3H), 7.30 – 7.25 (m, 4H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.66 (d, *J* = 12.3 Hz, 1H), 2.99 (s, 3H), 2.72 (s, 3H), 2.63 – 2.41 (m, 2H), 1.51 (p, *J* = 7.5 Hz, 2H), 1.27 (p, *J* = 7.3 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.3, 154.3, 144.4, 143.4, 132.8, 131.3, 129.0, 128.4, 128.1, 128.0, 120.8, 120.6, 97.3, 94.0, 88.3, 45.0, 37.2, 35.6, 33.4, 22.3, 14.0;

HRMS (ESI): $C_{23}H_{26}NO^+$ $[M+H]^+$332.2009, found 332.2012.



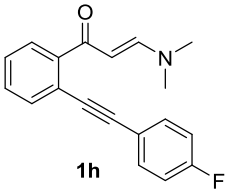
(*E*)-3-(dimethylamino)-1-(2-((4-methoxyphenyl)ethynyl)phenyl)prop-2-en-1-one **1g**: purple oil;

IR (neat) *v* 2909, 1543, 1243, 1028, 761, 533 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.51 (m, 3H), 7.44 – 7.38 (m, 2H), 7.37 – 7.30 (m, 2H), 6.89 – 6.77 (m, 2H), 5.74 (d, *J* = 12.4 Hz, 1H), 3.82 (s, 3H), 3.08 (s, 3H), 2.81 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.5, 159.6, 154.2, 144.3, 132.9, 132.6, 129.0, 128.1, 127.9, 120.9, 115.7, 113.9, 97.3, 93.8, 87.6, 55.3, 45.0, 37.2;

HRMS (ESI): $C_{20}H_{20}NO_2^+$ $[M+H]^+$306.1489, found 306.1499.



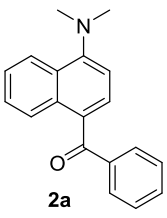
(*E*)-3-(dimethylamino)-1-(2-((4-fluorophenyl)ethynyl)phenyl)prop-2-en-1-one **1h**: purple oil;

IR (neat) *v* 2917, 1537, 1224, 1066, 762, 537 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.23 (m, 7H), 6.94 (t, *J* = 8.7 Hz, 2H), 5.59 (d, *J* = 12.5 Hz, 1H), 3.01 (s, 3H), 2.74 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.3, 162.5 (d, $^1J_{C\text{-}F}$ = 249.5 Hz), 154.5, 144.5, 133.3, 132.8, 132.1, 132.0, 129.1, 128.5 (d, $^3J_{C\text{-}F}$ = 12.1 Hz), 128.1, 120.4, 119.6, 115.58 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 97.1, 92.5, 88.5, 45.0, 37.2;

HRMS (ESI): $C_{19}H_{17}FNO^+$ $[M+H]^+$294.1289, found 294.1301.



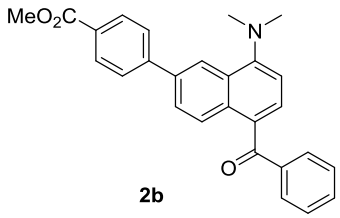
(4-(Dimethylamino)naphthalen-1-yl)(phenyl)methanone **2a**:yellow oil (48 mg, yield 88%);

IR (neat) *v* 2844, 1570, 1276, 1201, 719, 640 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 – 8.32 (m, 1H), 8.28 – 8.18 (m, 1H), 7.86 – 7.75 (m, 2H), 7.56 – 7.43 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 2.92 (s, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.5, 154.4, 139.4, 133.1, 132.6, 130.6, 130.4, 129.7, 128.5, 128.3, 127.3, 126.5, 125.5, 124.9, 111.5, 44.9;

HRMS (ESI): $C_{19}H_{18}NO^+$ $[M+Na]^+$298.1202, found 298.1213.



2b

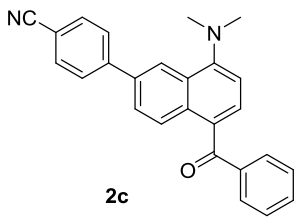
Methyl 4-(5-benzoyl-8-(dimethylamino)naphthalen-2-yl)benzoate **2b**: yellow oil (61 mg, yield 75%);

IR (neat) *v* 2854, 1720, 1224, 1104, 706, 444 cm^{-1};

^1H NMR (400 MHz, DMSO-d_6) δ 8.47 (s, 1H), 8.34 (d, *J* = 8.9 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 2H), 8.00 – 7.86 (m, 3H), 7.76 (d, *J* = 7.3 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 2.95 (s, 6H);

^{13}C NMR (100 MHz, DMSO-d_6) δ 197.0, 166.6, 154.8, 144.8, 139.1, 136.1, 133.5, 132.5, 131.7, 130.5, 130.2, 129.11, 129.06, 128.7, 128.1, 127.7, 127.3, 126.7, 123.3, 112.8, 52.7, 45.0;

HRMS (ESI): $C_{27}H_{23}KNO_3^+$ $[M+K]^+$448.1310, found 448.1339.



2c

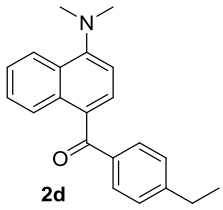
4-(5-Benzoyl-8-(dimethylamino)naphthalen-2-yl)benzonitrile **2c**: yellow oil (53 mg, yield 60%);

IR (neat) *v* 2933 , 1244, 1224, 1055, 812, 688 cm^{-1};

^1H NMR (400 MHz, DMSO-d_6) δ 8.46 (s, 1H), 8.38 – 8.23 (m, 1H), 7.99 – 7.90 (m, 5H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.60 – 7.43 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 1H), 2.96 (s, 6H);

^{13}C NMR (100 MHz, DMSO-d6) δ 196.7, 154.8, 144.8, 139.1, 135.5, 133.4, 133.3, 132.7, 131.8, 130.3, 129.0, 128.7, 128.3, 128.1, 127.4, 126.6, 123.5, 119.3, 112.8, 110.7, 45.0;

HRMS (ESI): $C_{26}H_{21}N_2O^+$ $[M+H]^+$ 377.1648, found 377.1632.



2d

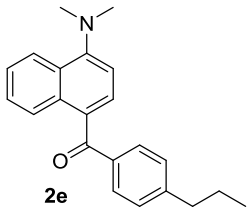
(4-(Dimethylamino)naphthalen-1-yl)(4-ethylphenyl)methanone **2d**: yellow oil (40 mg, yield 67%);

IR (neat) *v* 2922, 1638, 1351, 1066, 759, 539 cm^{-1};

^1H NMR (400 MHz, DMSO-d_6) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.48 (m, 3H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 1H), 2.93 (s, 6H), 2.70 (q, *J* = 7.4 Hz, 2H), 1.23 (d, *J* = 73 Hz, 3H);

^{13}C NMR (100 MHz, DMSO-d_6) δ 196.7, 154.1, 149.9, 136.8, 132.7, 130.5, 130.3, 129.6, 128.5, 128.1, 127.6, 126.3, 125.9, 125.1, 112.2, 44.9, 28.7, 15.6;

HRMS (ESI): $C_{21}H_{21}NNaO^+$ $[M+Na]^+$326.1515, found 326.1551.



2e

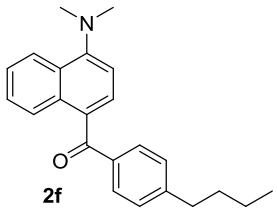
(4-(Dimethylamino)naphthalen-1-yl)(4-propylphenyl)methanone **2e**: yellow oil (51 mg, yield 81%);

IR (neat) *v* 2931, 1570, 1177, 1047, 834, 767 cm^{-1};

^1H NMR (400 MHz, Chloroform-*d*) δ 8.33 – 8.18 (m, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.46 (m, 3H), 7.30 – 7.19 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 2.98 (s, 6H), 2.70 – 2.54 (m, 2H), 1.68 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.4, 154.1, 148.1, 136.8, 133.0, 130.5, 130.3, 129.9, 128.5, 128.4, 127.1, 126.4, 125.4, 124.7, 111.5, 44.9, 38.1, 24.3, 13.8;

HRMS (ESI): $C_{22}H_{24}NO^+$ $[M+H]^+$318.1852, found 318.1852.



2f

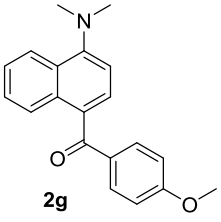
(4-Butylphenyl)(4-(dimethylamino)naphthalen-1-yl)methanone **2f**: yellow oil (44 mg, yield 67%);

IR (neat) *v*3183, 2923, 1430, 1055, 784 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 – 8.12 (m, 2H), 7.86 – 7.73 (m, 2H), 7.64 – 7.43 (m, 3H), 7.29 – 7.20 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 2.97 (s, 6H), 2.75 – 2.64 (m, 2H), 1.71 – 1.55 (m, 2H), 1.42 – 1.32 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.4, 154.1, 148.4, 136.8, 133.0, 130.6, 130.3, 129.9, 128.5, 128.3, 127.1, 126.4, 125.4, 124.7, 111.5, 44.9, 35.8, 33.3, 22.4, 13.9;

HRMS (ESI): $C_{23}H_{26}NO^+$ $[M+H]^+$332.2009, found 332.2012.



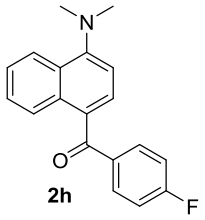
(4-(Dimethylamino)naphthalen-1-yl)(4-methoxyphenyl)methanone **2g**: yellow oil (40 mg, yield 66%);

IR (neat) *v* 2835, 1537, 1163, 1021, 769, 584 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 8.23 (m, 1H), 8.21 – 8.16 (m, 1H), 7.90 – 7.81 (m, 2H), 7.55 – 7.42 (m, 3H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.95 – 6.86 (m, 2H), 3.87 (s, 3H), 2.96 (s, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.5, 163.4, 153.8, 132.9, 132.7, 131.9, 130.7, 129.1, 128.5, 126.9, 126.4, 125.4, 124.7, 113.5, 111.7, 55.5, 44.9;

HRMS (ESI): $C_{20}H_{20}NO_2^+$ $[M+H]^+$306.1489, found 306.1499.



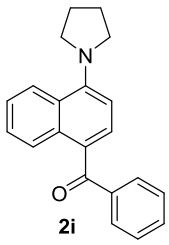
(4-(Dimethylamino)naphthalen-1-yl)(4-fluorophenyl)methanone **2h**: yellow oil (35 mg, yield 60%);

IR (neat) *v* 2837, 1570, 1146, 844, 767, 581 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 – 8.11 (m, 2H), 7.85 – 7.73 (m, 2H), 7.50 – 7.32 (m, 3H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 2.89 (s, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.0, 164.5 (d, $^1J_{C\text{-}F}$ = 254.2 Hz), 153.4, 134.5 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 131.9, 131.8 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 129.2, 128.5, 127.4, 126.2, 125.2, 124.4, 123.8, 114.3 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 110.4, 43.8;

HRMS (ESI): $C_{19}H_{17}FNO^+$ $[M+H]^+$294.1289, found 294.1273.



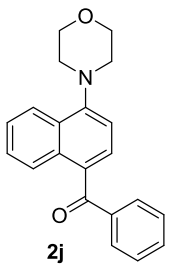
Phenyl(4-(pyrrolidin-1-yl)naphthalen-1-yl)methanone **2i**: yellow oil (43 mg, yield 71%);

IR (neat) *v* 3692, 2928, 1561, 1249, 1055, 723 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.37 – 7.31 (m, 3H), 6.63 (d, *J* = 8.2 Hz, 1H), 3.46 (t, *J* = 6.4 Hz, 4H), 1.93 (t, *J* = 6.4 Hz, 4H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.0, 151.6, 140.2, 133.8, 132.7, 131.9, 130.2, 128.1, 127.2, 126.6, 126.3, 126.1, 125.3, 124.0, 107.0, 52.8, 25.6;

HRMS (ESI): calculated $C_{21}H_{20}NO^+$ $[M+H]^+$ 302.1539, found 302.1538.



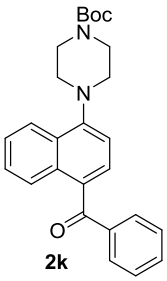
(4-Morpholinonaphthalen-1-yl)(phenyl)methanone **2j**: yellow oil (20 mg, yield 31%);

IR (neat) *v* 2846, 1574, 1113, 1063, 860, 771 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.68 (t, *J* = 7.1 Hz, 1H), 7.57 (p, *J* = 7.9, 7.4 Hz, 5H), 7.18 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 4H), 3.13 (s, 4H);

^{13}C NMR (100 MHz, DMSO-d_6) δ 197.2 152.8, 138.9, 133.6, 132.5, 130.6, 130.3, 130.6, 129.1, 128.3, 127.8, 126.5, 126.3, 124.6, 113.3, 66.9, 53.4;

HRMS (ESI): $C_{21}H_{19}KNO_2^+$ [M+K]$^+$ 356.1047, found 356.1098.



2k

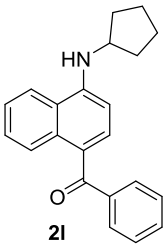
Tert-butyl 4-(4-benzoylnaphthalen-1-yl)piperazine-1-carboxylate **2k**: yellow oil (21.7 mg, yield 26%);

IR (neat) *v* 2837, 1588, 1570, 1047, 767, 581 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.65 – 7.50 (m, 5H), 7.18 (d, *J* = 7.8 Hz, 1H), 3.65 (s, 4H), 3.08 (s, 4H), 1.45 (s, 9H);

^{13}C NMR (100 MHz, DMSO-d_6) δ 197.1, 154.4, 152.7, 138.9, 133.6, 132.5, 130.8, 130.3, 130.2, 129.1, 128.4, 127.8, 126.6, 126.3, 124.5, 113.7, 79.5, 52.9, 28.6;

HRMS (ESI): $C_{26}H_{29}N_2O_3^+$ [M+H]$^+$ 417.2173, found 417.2173.



2l

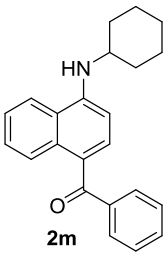
(4-(Cyclopentylamino)naphthalen-1-yl)(phenyl)methanone **2l**: yellow oil (14.1 mg, yield 22%);

IR (neat) *v* 2921, 1567, 1525, 1249, 697 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.78 (m, 3H), 7.68 – 7.39 (m, 6H), 6.53 (d, *J* = 8.3 Hz, 1H), 4.95 (s, 1H), 4.09 – 3.83 (m, 1H), 2.17 (dq, *J* = 12.3, 7.2 Hz, 2H), 1.90 – 1.57 (m, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.0, 146.8, 140.7, 134.7, 133.1, 131.6, 130.1, 128.0, 127.7, 127.2, 125.2, 123.0, 122.8, 119.5, 102.2, 54.5, 33.6, 24.3;

HRMS (ESI): $C_{22}H_{22}NO^+$ [M+H]$^+$ 316.1696, found 316.1201.



2m

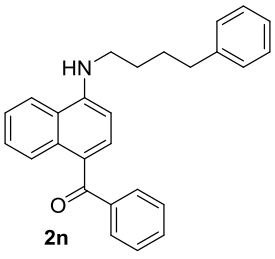
(4-(Cyclohexylamino)naphthalen-1-yl)(phenyl)methanone **2m**: yellow oil (14.3 mg, yield 23%);

IR (neat) *v* 2922, 1564, 1272, 1245, 754, 701 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.78 (m, 3H), 7.65 – 7.35 (m, 6H), 6.51 (d, *J* = 8.3 Hz, 1H), 4.90 (s, 1H), 3.55 (s, 1H), 2.29 – 2.09 (m, 2H), 1.92 – 1.78 (m, 2H), 1.78 – 1.59 (m, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.9, 146.2, 140.7, 135.0, 133.4, 131.6, 130.1, 128.0, 127.7, 127.2, 125.1, 122.7, 122.6, 119.5, 101.5, 51.5, 33.0, 25.8, 24.9;

HRMS (ESI): $C_{23}H_{24}NO^+$ [M+H] $^+$ 330.1852, found 330.1826.



2n

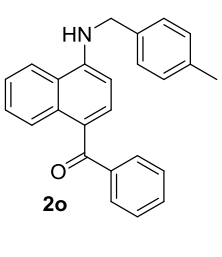
Phenyl(4-((4-phenylbutyl)amino)naphthalen-1-yl)methanone **2n**: yellow oil (11.8 mg, yield 23%);

IR (neat) *v* 3690, 3636, 3390, 2922, 1056, 722 cm^{-1};

1H NMR (400 MHz, Chloroform-d) δ 8.67 (d, *J* = 8.5 Hz, 1H), 7.78 – 7.66 (m, 3H), 7.57 – 7.32 (m, 6H), 7.28 – 7.18 (m, 2H), 7.16 – 7.07 (m, 3H), 6.40 (d, *J* = 8.2 Hz, 1H), 4.81 (s, 1H), 3.28 (t, *J* = 6.6 Hz, 2H), 2.64 (t, *J* = 6.7 Hz, 2H), 1.76 (p, *J* = 6.4 Hz, 4H);

^{13}C NMR (100 MHz, Chloroform-d) δ 197.1, 147.2, 141.9, 140.6, 134.7, 133.1, 131.7, 130.1, 128.4, 128.3, 128.1, 127.7, 127.2, 126.0, 125.3, 123.3, 122.7, 119.6, 101.2, 43.6, 35.6, 28.9, 28.7;

HRMS (ESI): $C_{27}H_{26}NO^+$ [M+H]$^+$380.2009, found 380.2012.



2o

(4-((4-Methylbenzyl)amino)naphthalen-1-yl)(phenyl)methanone **2o**: yellow oil (25 mg,

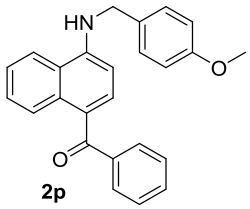
yield 34%);

IR (neat) *v* 3203, 2919, 1658, 1386, 1239, 1061, 688 cm^{-1};

^1H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 8.5 Hz, 1H), 7.81 – 7.68 (m, 3H), 7.53 – 7.31 (m, 6H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.43 (d, *J* = 8.2 Hz, 1H), 5.19 (s, 1H), 4.42 (s, 2H), 2.28 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 146.9, 140.5, 137.5, 135.0, 134.5, 133.0, 131.8, 130.2, 129.6, 128.1, 127.8, 127.6, 127.1, 125.4, 123.8, 122.8, 119.7, 101.9, 47.9, 21.2;

HRMS (ESI): $C_{25}H_{21}KNO^+$ $[M+K]^+$390.1255, found 390.1330.



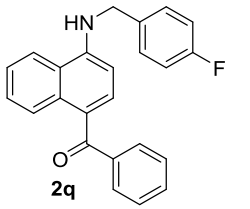
(4-((4-Methoxybenzyl)amino)naphthalen-1-yl)(phenyl)methanone **2p**: yellow solid (39 mg, yield 53%), m.p. 59 – 60 ℃;

IR (neat) *v* 3726, 3391, 2932, 1235, 1054, 723 cm^{-1};

^1H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 9.3 Hz, 1H), 7.83 – 7.62 (m, 3H), 7.53 – 7.39 (m, 4H), 7.39 – 7.33 (m, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 8.2 Hz, 1H), 5.14 (s, 1H), 4.40 (s, 2H), 3.74 (s, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 159.2, 146.9, 140.5, 134.4, 133.0, 131.8, 130.2, 130.0, 129.0, 128.1, 127.8, 127.1, 125.4, 123.8, 122.8, 119.7, 114.3, 101.8, 55.4, 47.7;

HRMS (ESI): $C_{25}H_{22}FNO^+$ $[M+H]^+$ 368.1645, found 368.1679.



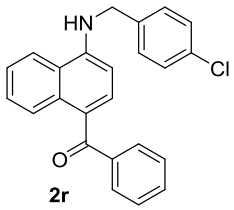
(4-((4-Fluorobenzyl)amino)naphthalen-1-yl)(phenyl)methanone **2q**: yellow solid (21 mg, yield 30%), m.p. 89 – 91 ℃;

IR (neat) *v* 3775, 3367, 2922, 1233, 1044, 789 cm^{-1};

^1H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.63 – 7.49 (m, 4H), 7.48 – 7.34 (m, 4H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.49 (d, *J* = 8.2 Hz, 1H), 5.27 (s, 1H), 4.54 (s, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 162.3 (d, $^1J_{C-F}$ = 246.0 Hz), 146.6, 140.3, 134.0, 133.7 (d, $^4J_{C-F}$ = 3.3 Hz), 132.9, 131.9, 130.1, 129.2 (d, $^3J_{C-F}$ = 8.1 Hz), 128.1, 127.8, 127.2, 125.5, 124.3, 122.9, 119.6, 115.8 (d, $^2J_{C-F}$ = 21.5 Hz), 102.0, 47.5;

HRMS (ESI): $C_{24}H_{18}FNNaO^+$ $[M+Na]^+$ 378.1256, found 378.1294.



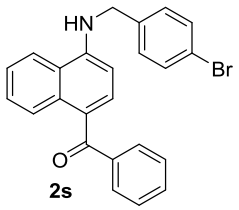
(4-((4-Chlorobenzyl)amino)naphthalen-1-yl)(phenyl)methanone**2r**: yellow oil (39 mg, yield 30%);

IR (neat) *v* 3395, 2936, 1537, 1260, 1056, 737 cm^{-1};

^1H NMR (400 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.60 – 7.37 (m, 8H), 7.28 – 7.19 (m, 2H), 6.42 (d, *J* = 8.1 Hz, 1H), 5.38 (s, 1H), 4.52 (s, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 146.5, 140.3, 136.6, 133.9, 133.4, 132.9, 131.9, 130.1, 129.0, 128.8, 128.1, 127.8, 127.2, 125.5, 124.4, 122.9, 119.6, 102.1, 47.4;

HRMS (ESI): $C_{24}H_{18}ClNNaO^+$ $[M+Na]^+$ 416.0645, found 416.0614.



(4-((4-Bromobenzyl)amino)naphthalen-1-yl)(phenyl)methanone **2s**: yellow solid (25 mg, yield 30%), m.p. 49 – 51 ℃;

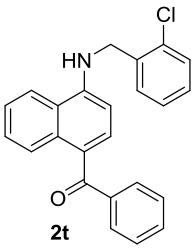
IR (neat) *v* 3727, 3390, 2921, 1242, 1056, 756 cm^{-1};

^1H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.31 (m, 7H), 7.25 – 7.12 (m, 3H), 6.37 (d, *J* = 8.1 Hz,

1H), 5.26 (s, 1H), 4.46 (d, *J* = 4.9 Hz, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 146.4, 140.3, 137.1, 134.0, 132.9, 132.0, 131.9, 130.2, 129.1, 128.1, 127.8, 127.2, 125.6, 124.3, 122.9, 121.5, 119.6, 102.1, 47.4;

HRMS (ESI): $C_{24}H_{18}NO^+$ $[M+H]^+$ 416.0645, found 416.0614.



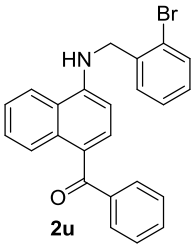
(4-((2-chlorobenzyl)amino)naphthalen-1-yl)(phenyl)methanone **2t**: yellow oil (32.7 mg, yield 44%);

IR (neat) *v* 3395, 1528, 1248, 751, 702, 461 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.84 – 7.72 (m, 2H), 7.61 – 7.48 (m, 4H), 7.47 – 7.35 (m, 4H), 7.25 – 7.19 (m, 2H), 6.45 (d, *J* = 8.2 Hz, 1H), 5.45 (s, 1H), 4.68 (d, *J* = 5.2 Hz, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 146.5, 140.3, 135.3, 134.1, 133.5, 133.0, 131.8, 130.1, 129.8, 129.0, 128.9, 128.1, 127.8, 127.2, 127.1, 125.5, 124.3, 122.9, 119.7, 102.1, 45.7;

HRMS (ESI): $C_{24}H_{18}ClNNaO^+$ $[M+Na]^+$394.0969, found 394.0995.



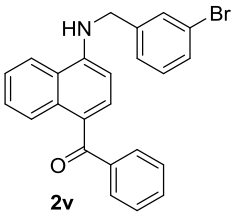
(4-((2-Bromobenzyl)amino)naphthalen-1-yl)(phenyl)methanone **2u**: yellow solid (42.7 mg, yield 51%), m.p. 109 – 111 ℃;

IR (neat) *v* 3395, 1528, 1438, 1240, 706, 461 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.51 (m, 5H), 7.46 – 7.36 (m, 3H), 7.31 – 7.23 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 5.49 (s, 1H), 4.65 (d, *J* = 5.3 Hz, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 146.4, 140.3, 136.8, 134.2, 133.1, 132.9, 131.9, 130.2, 129.2, 129.1, 128.1, 127.8, 127.7, 127.2, 125.5, 124.2, 123.5, 122.9, 119.7, 102.1, 48.2;

HRMS (ESI): $C_{24}H_{19}BrNO^+$ $[M+H]^+$416.0645, found 416.0629.



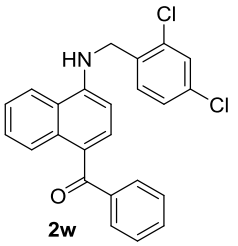
(4-((3-Bromobenzyl)amino)naphthalen-1-yl)(phenyl)methanone **2v**: yellow solid (42.7 mg, yield 51%), m.p. 94 – 96℃;

IR (neat) *v* 3363, 2921, 1518, 1223, 1051, 687 cm^{-1} ;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.49 (m, 5H), 7.44 (t, *J* = 7.6 Hz, 3H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 5.35 (s, 1H), 4.56 (d, *J* = 5.1 Hz, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.2, 146.4, 140.6, 140.2, 134.0, 132.9, 131.9, 130.8, 130.5, 130.4, 130.2, 128.1, 127.8, 127.2, 126.0, 125.6, 124.5, 123.0, 122.9, 119.7, 102.2, 47.5;

HRMS (ESI-TOF): $C_{24}H_{18}BrKNO^+$ $[M+H]^+$454.0203, found 454.0233.



(4-((2,4-Dichlorobenzyl)amino)naphthalen-1-yl)(phenyl)methanone **2w**: yellow oil (38.2 mg, yield 47%);

IR (neat) *v* 3361, 2926, 1418, 1242, 1064, 719 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 2H), 7.53 – 7.44 (m, 4H), 7.38 – 7.34 (m, 3H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.11 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.30 (d, *J* = 8.2 Hz, 1H), 5.39 (s, 1H), 4.57 (d, *J* = 4.2 Hz, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.1, 146.1, 140.2, 134.0, 133.9, 133.8, 133.0, 131.9, 130.2, 129.6, 129.6, 128.1, 127.8, 127.4, 127.2, 125.6, 124.6, 122.9, 119.6, 102.2, 45.2;

HRMS (ESI-TOF): $C_{24}H_{18}Cl_2NO^+$ $[M+H]^+$405.0687, found 405.0719.

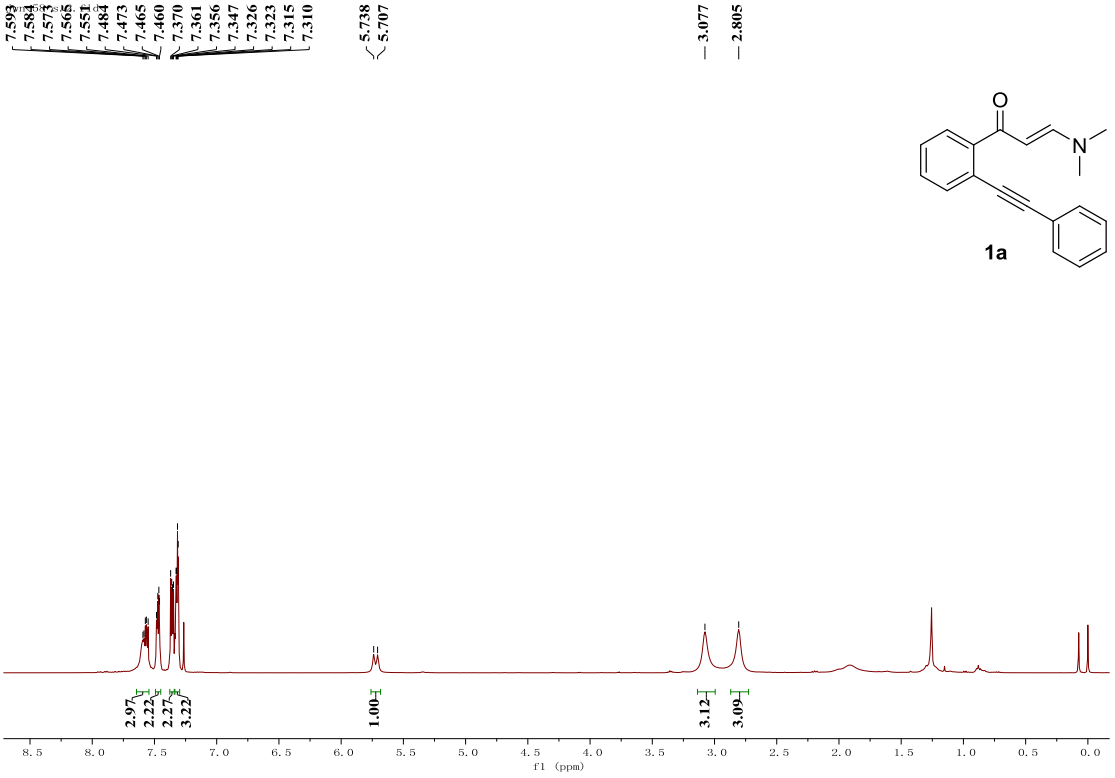
References

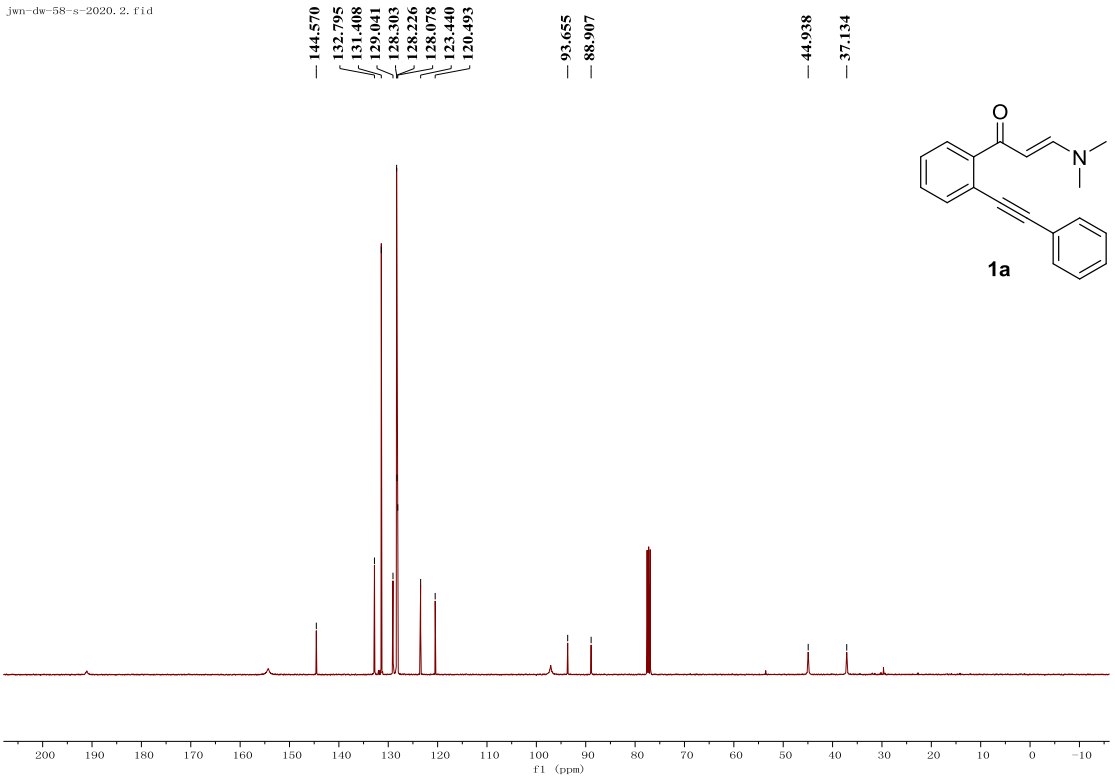
(1) Liu-Zhu Yu, Yin Wei, Min Shi, Synthesis of Polysubstituted Polycyclic Aromatic Hydrocarbons by Gold-Catalyzed Cyclization–Oxidation of Alkylidenecyclopropane-Containing 1,5-Enynes**,** *ACS Catal.* 2017, **7**, 4242−4247.

(2) Xiaoyu Liang, Pan Guo, Wenjie Yang, Meng Li, Chengzhou Jiang, Wangbin Sun, Teck-Peng Loh and Yaojia Jiang, Stereoselective Synthesis of Trifluoromethyl-substituted 2*H*-Furan-amines from Enaminones, *Chem. Commun.*, 2020, **56**, 2043—2046.

6. Copies of NMR Spectra

Product 1a:^{1}H NMR.





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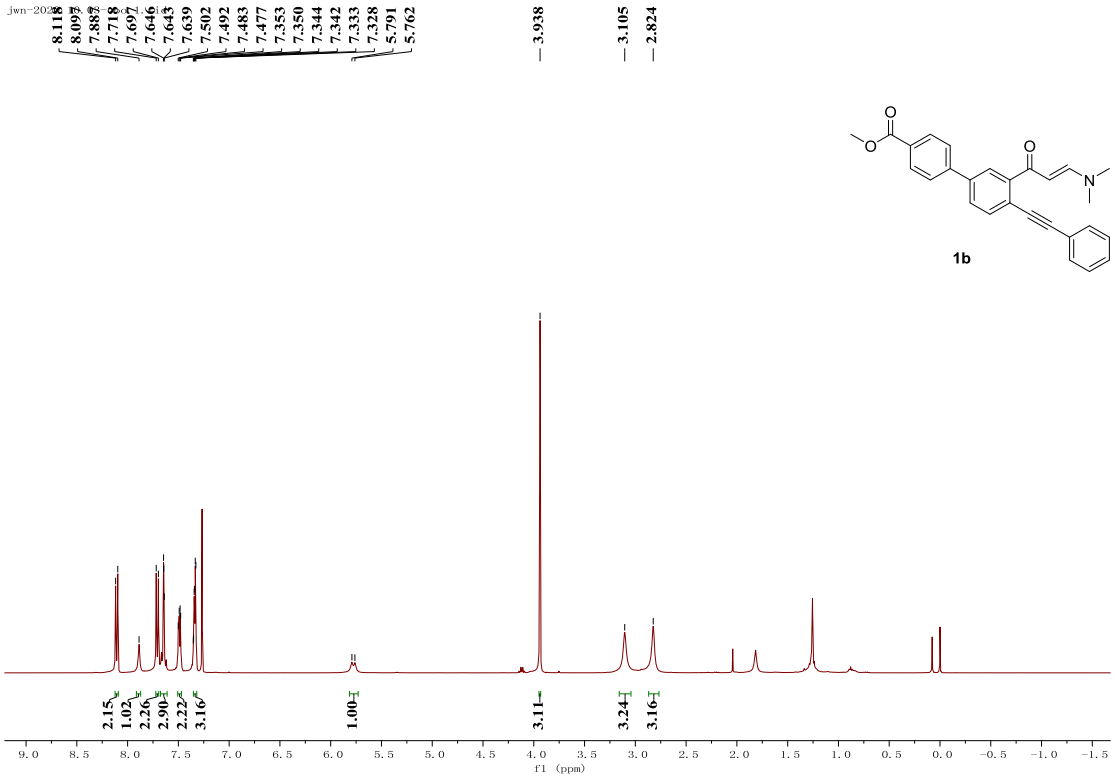

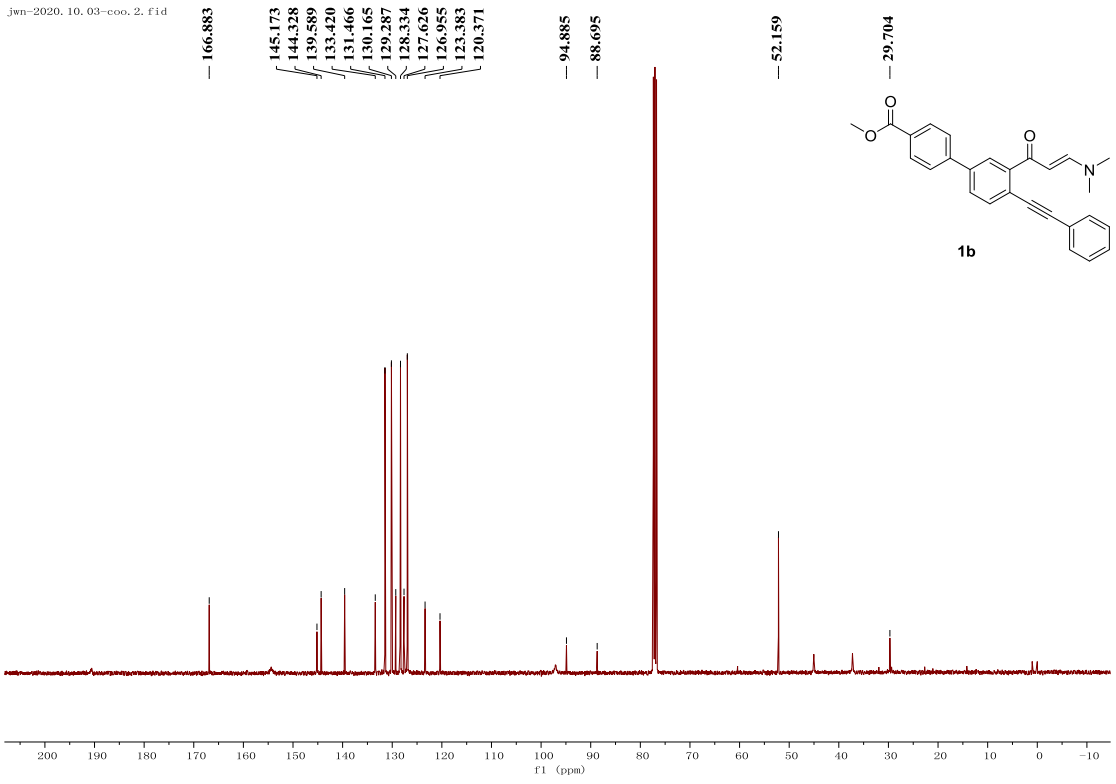

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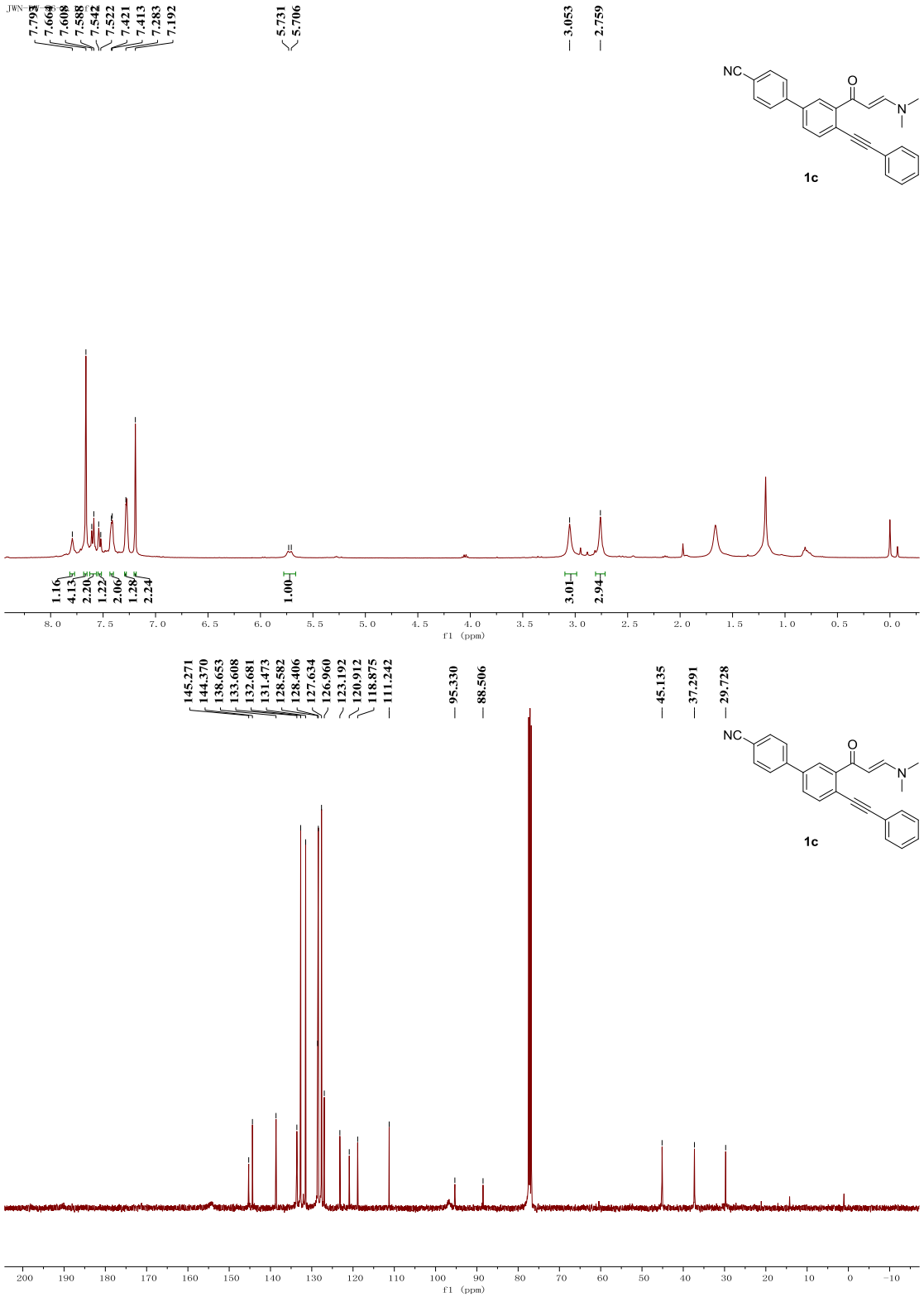

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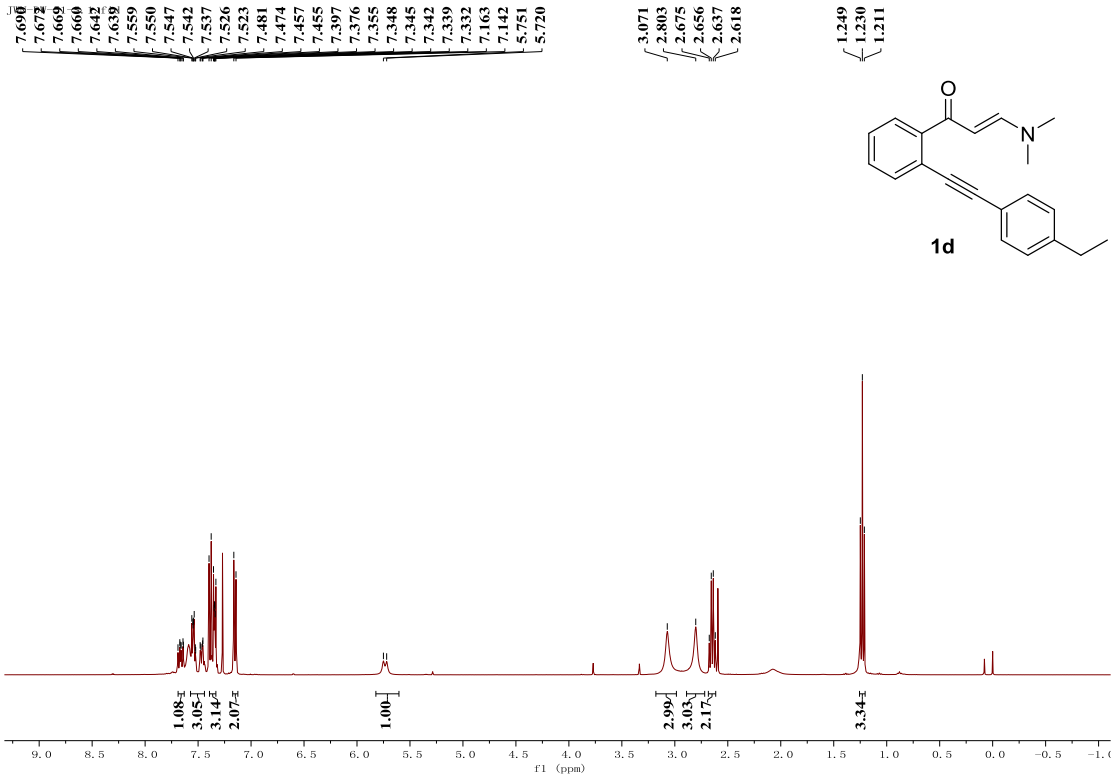

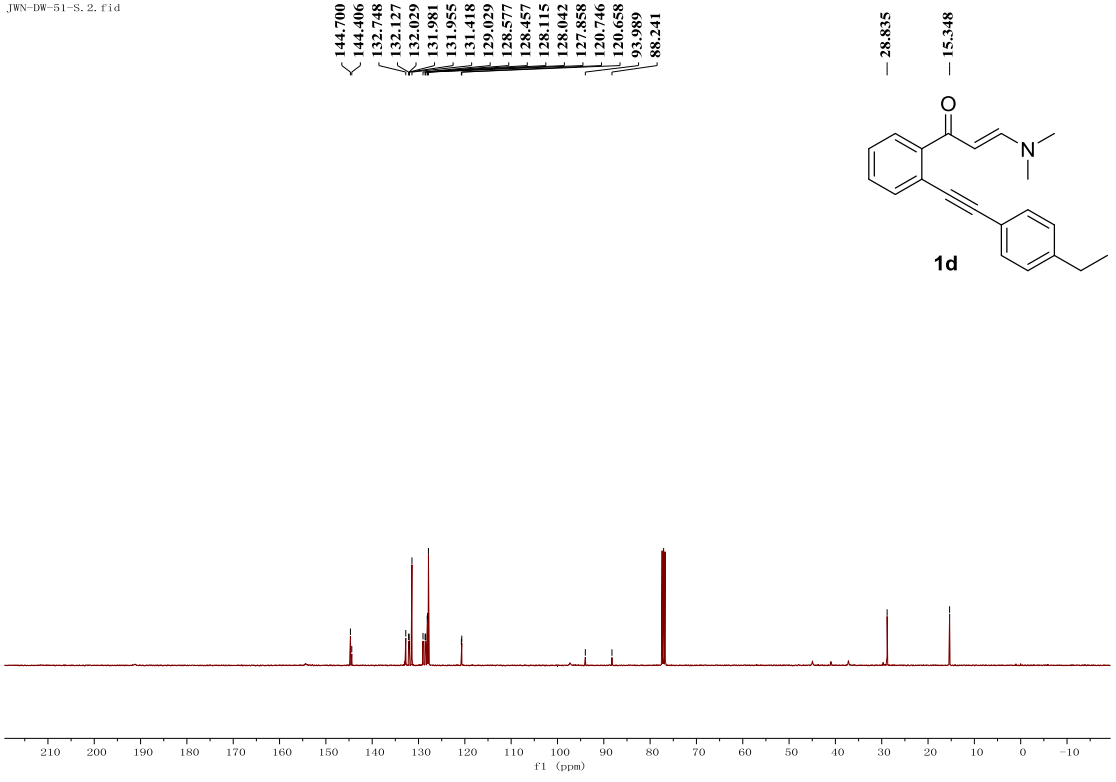

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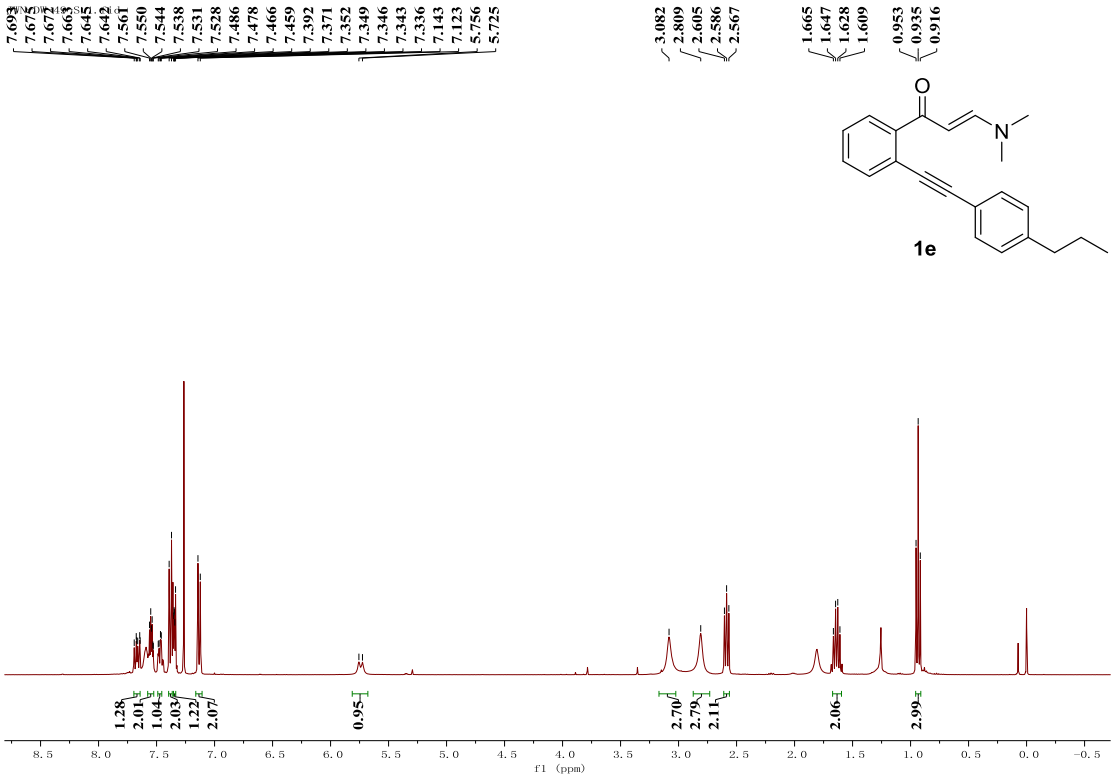

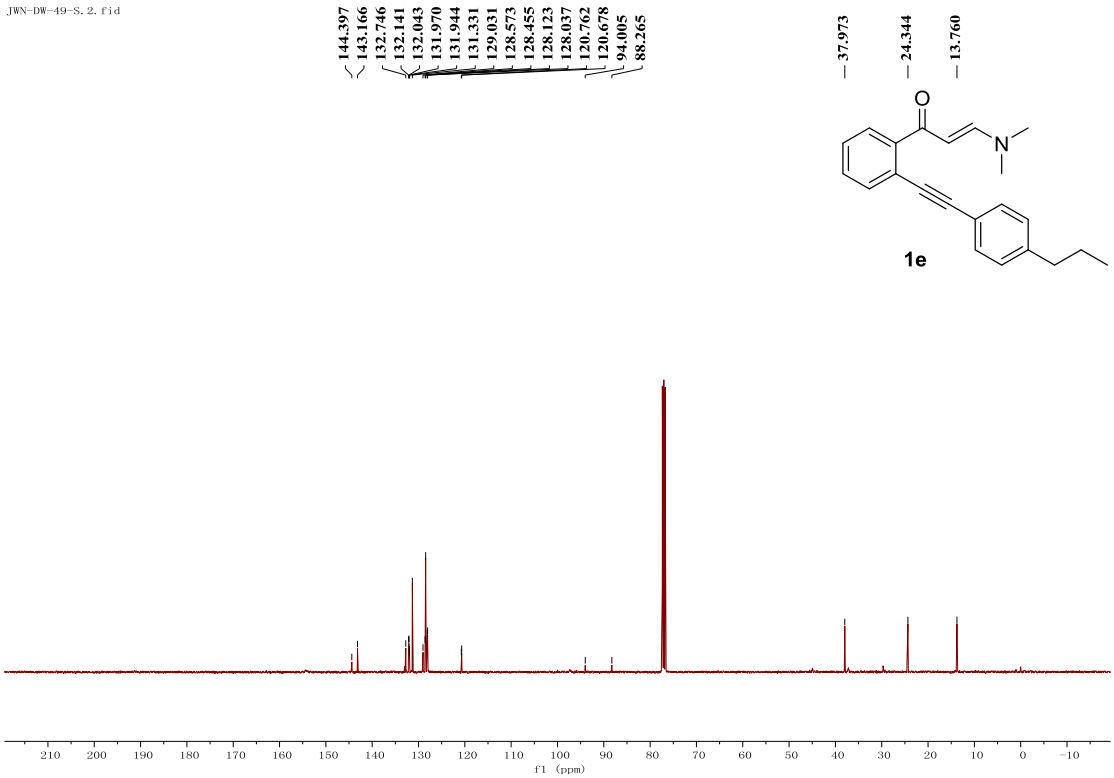

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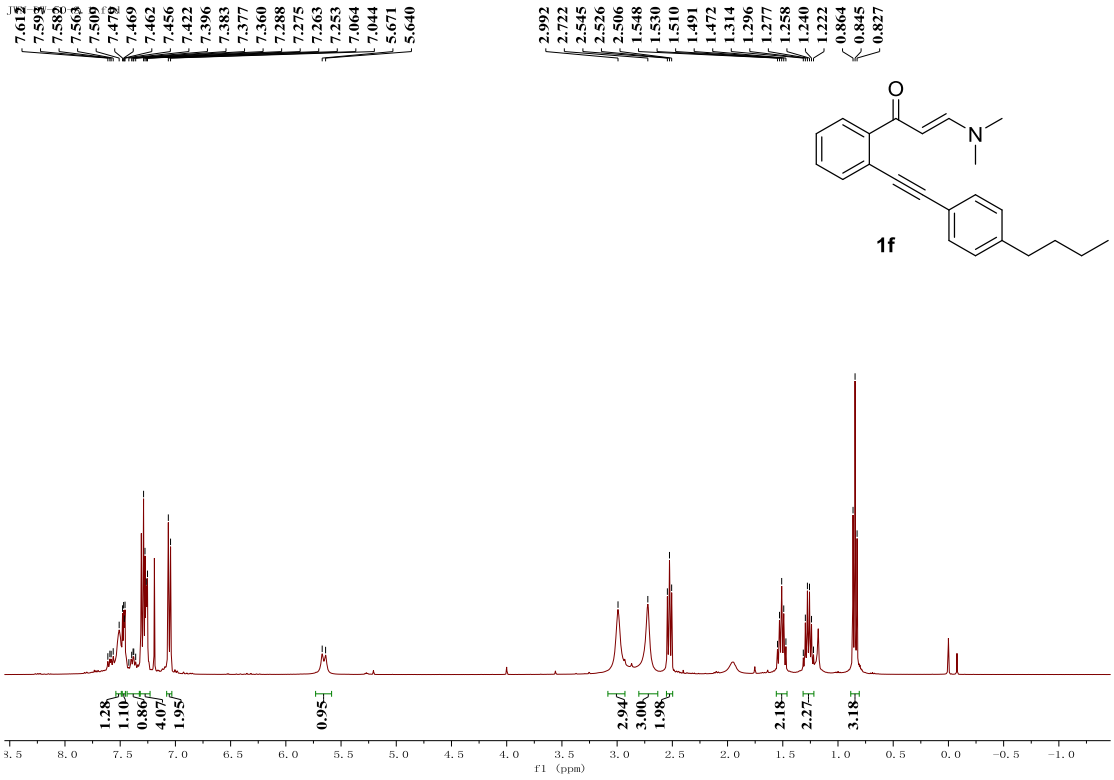

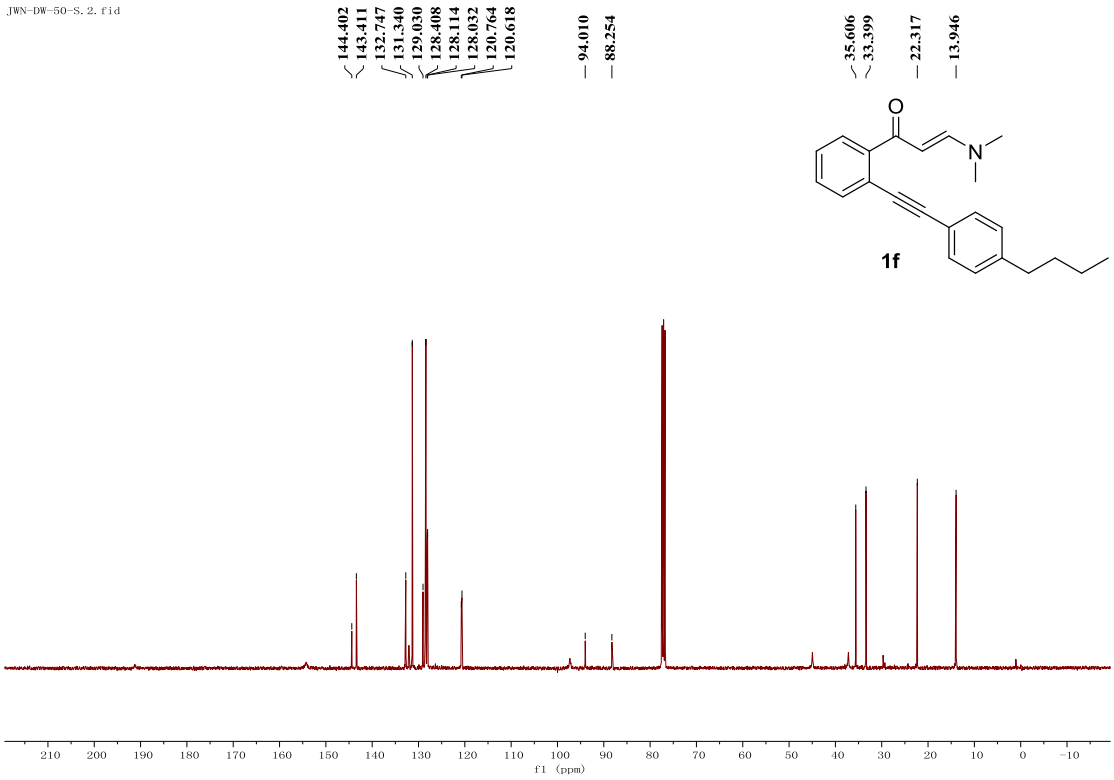

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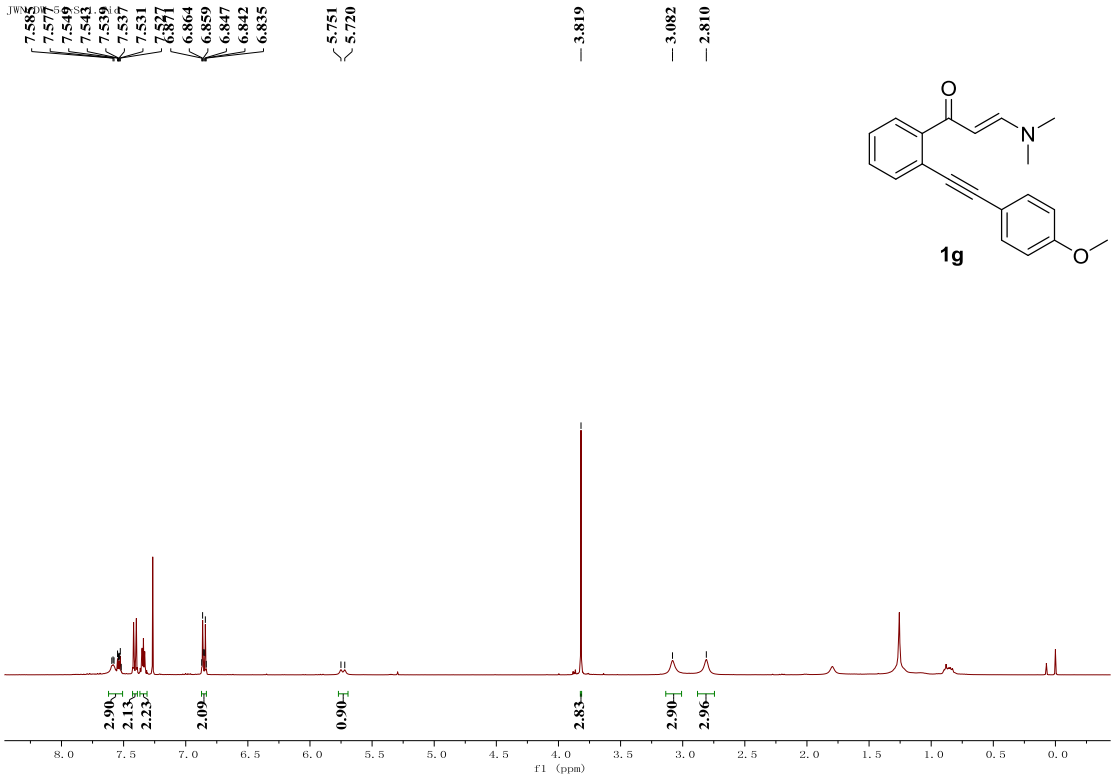
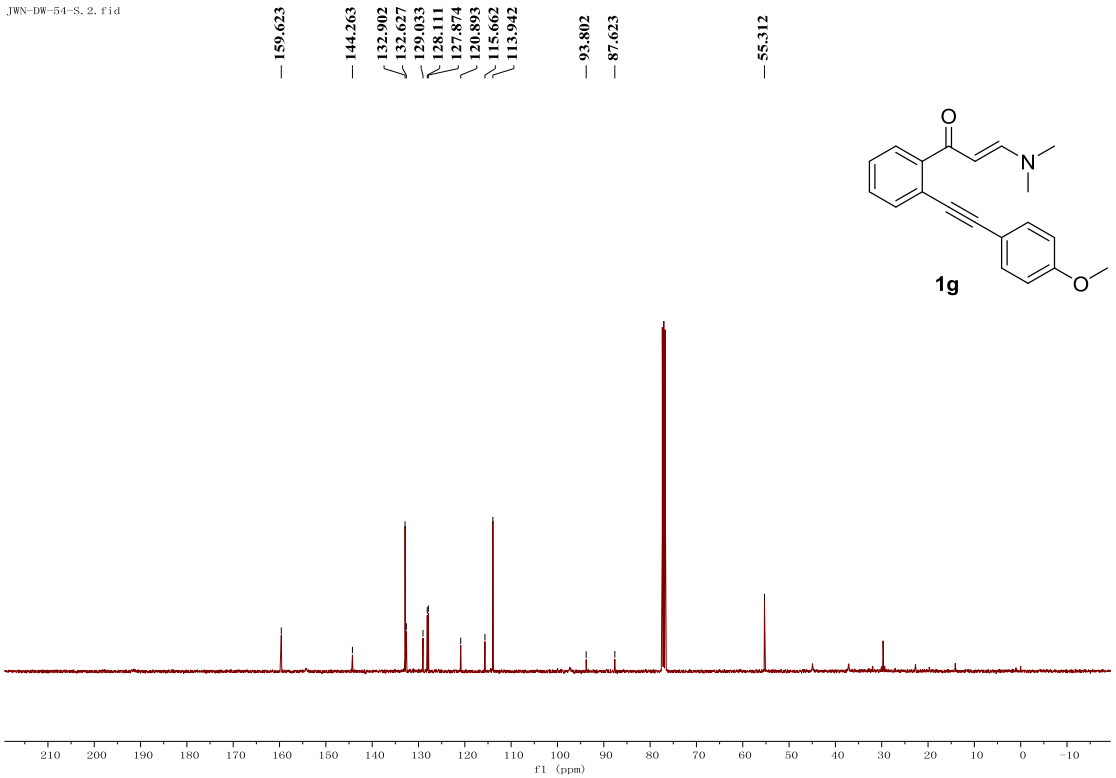
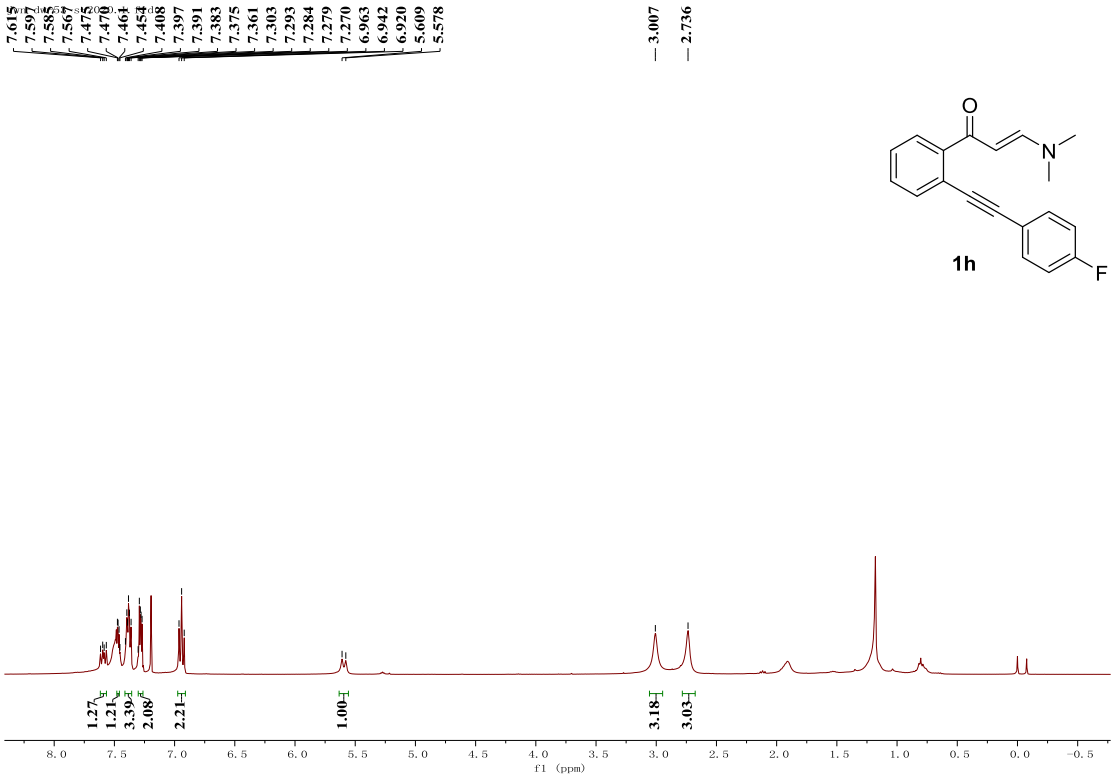
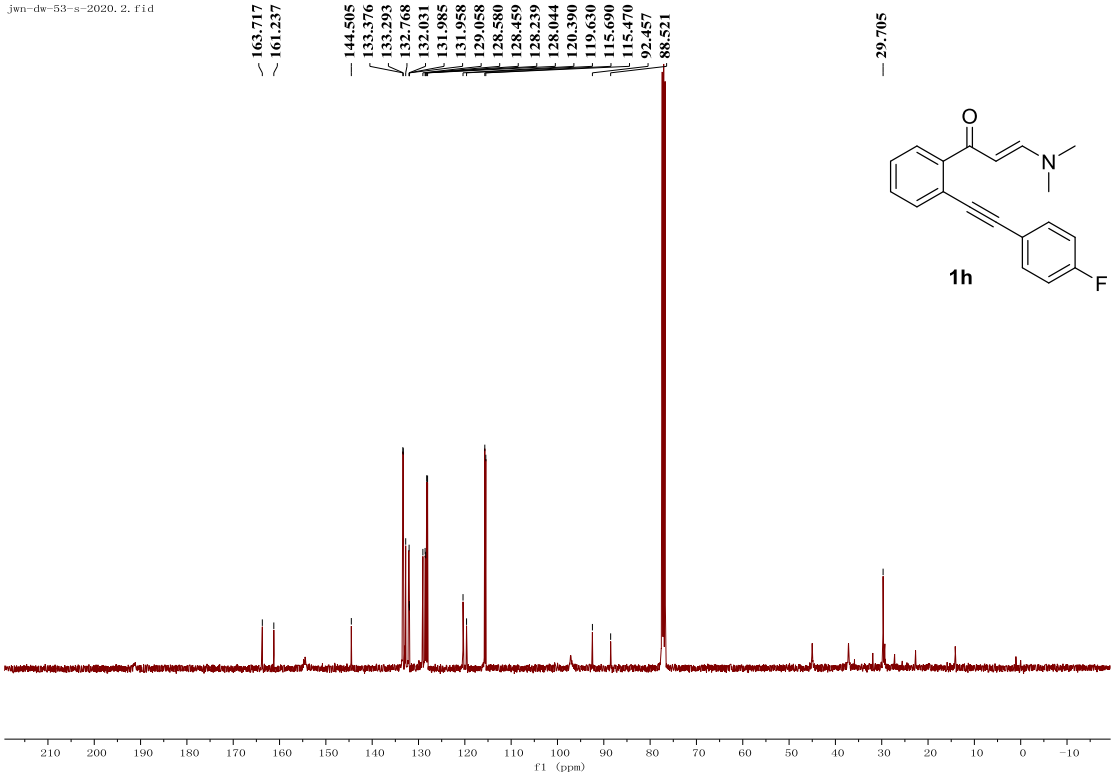


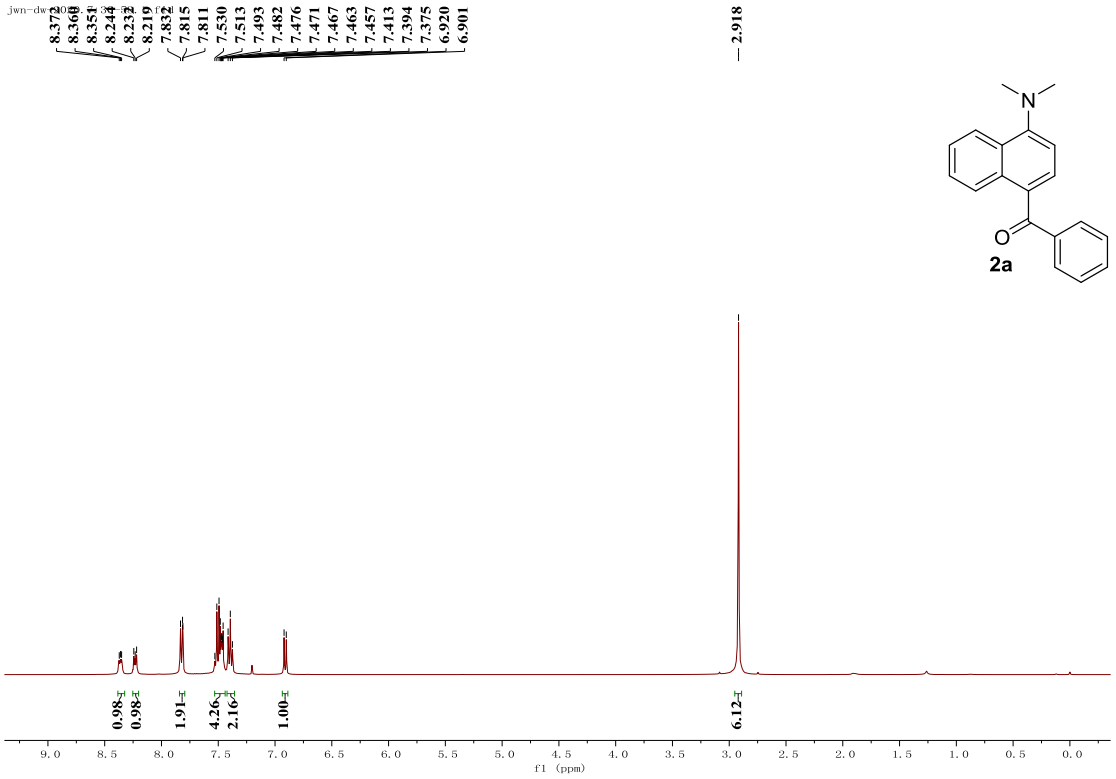


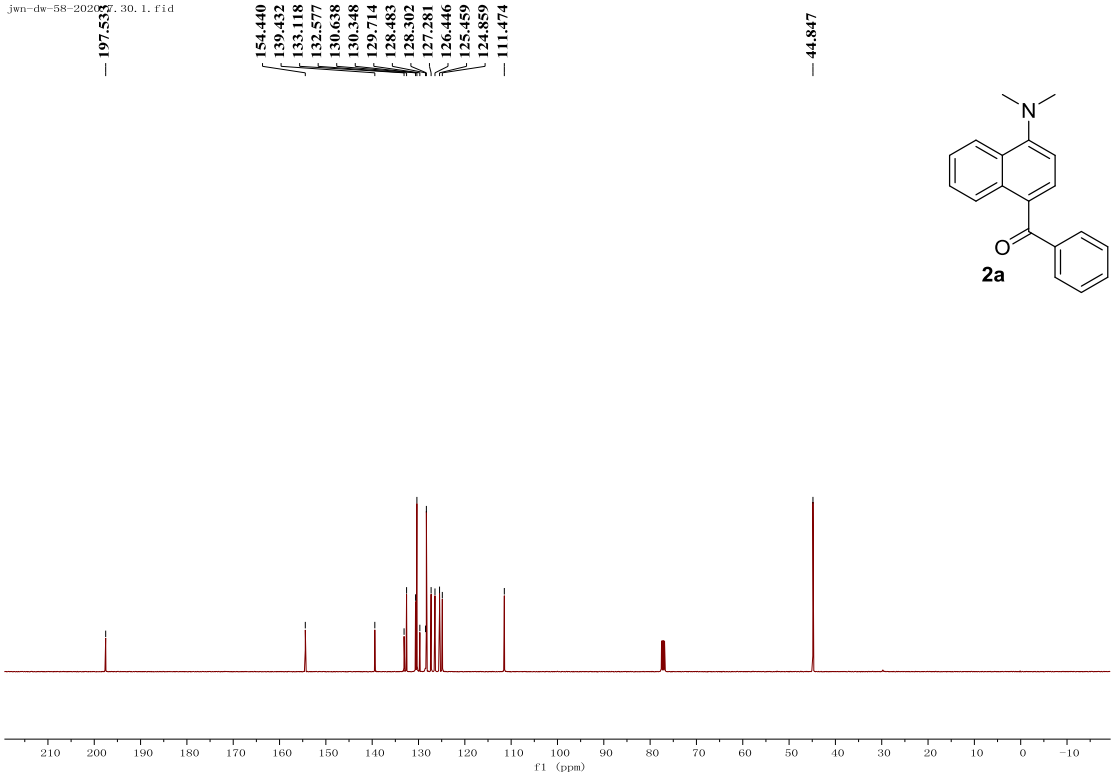
Product 1h:^{1}H NMR.





Product 2a:^{1}H NMR.





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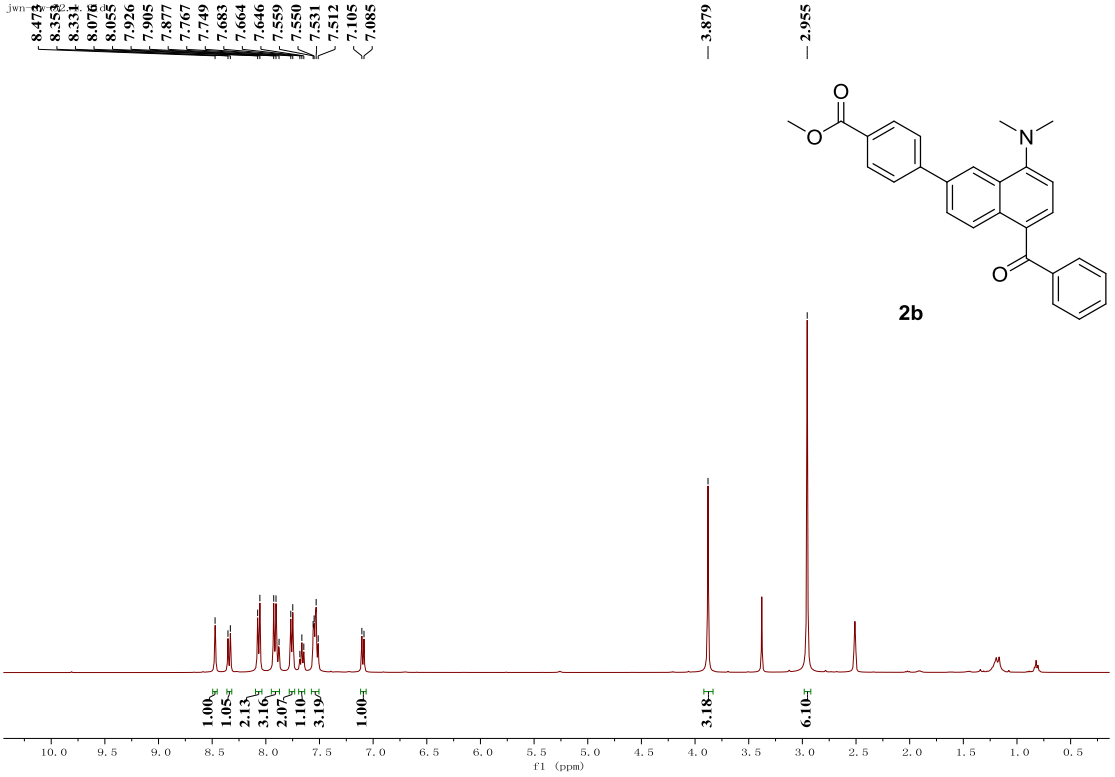

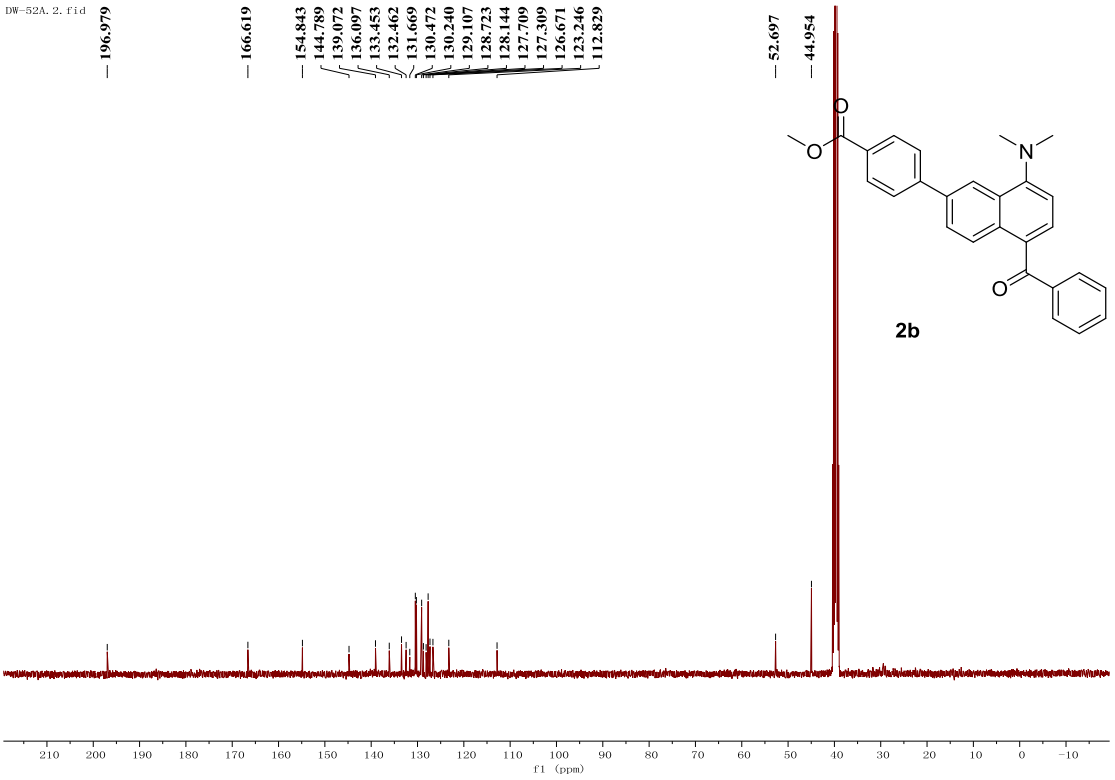

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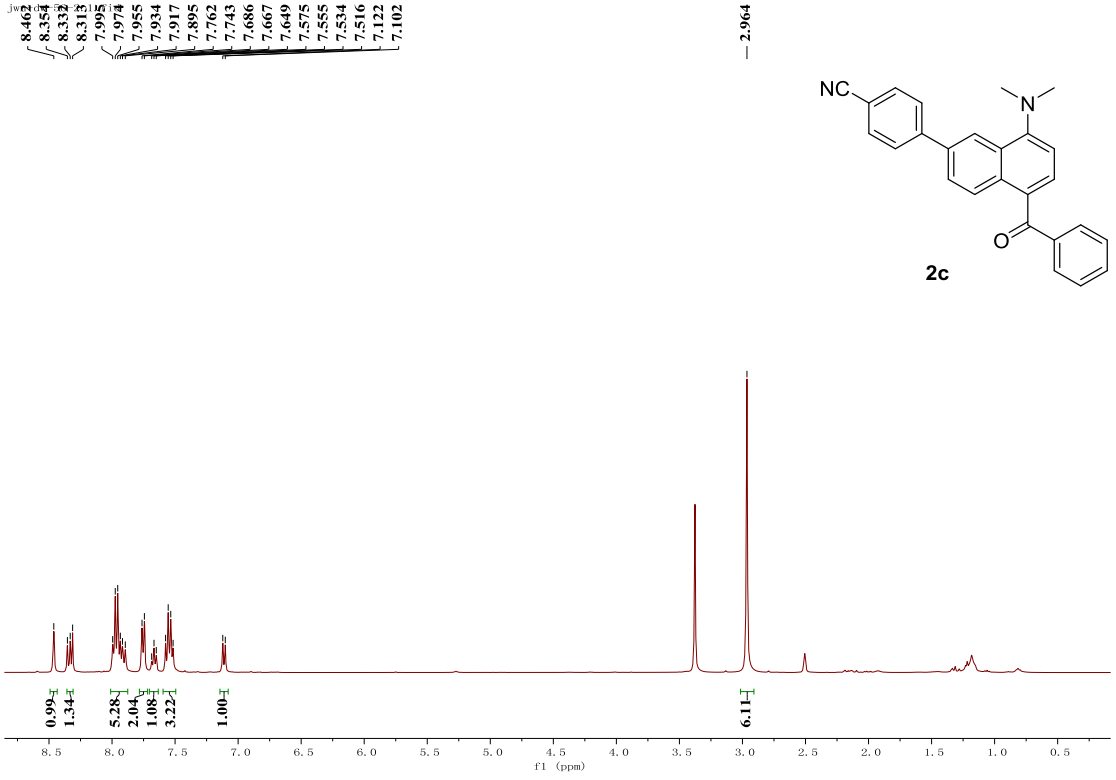

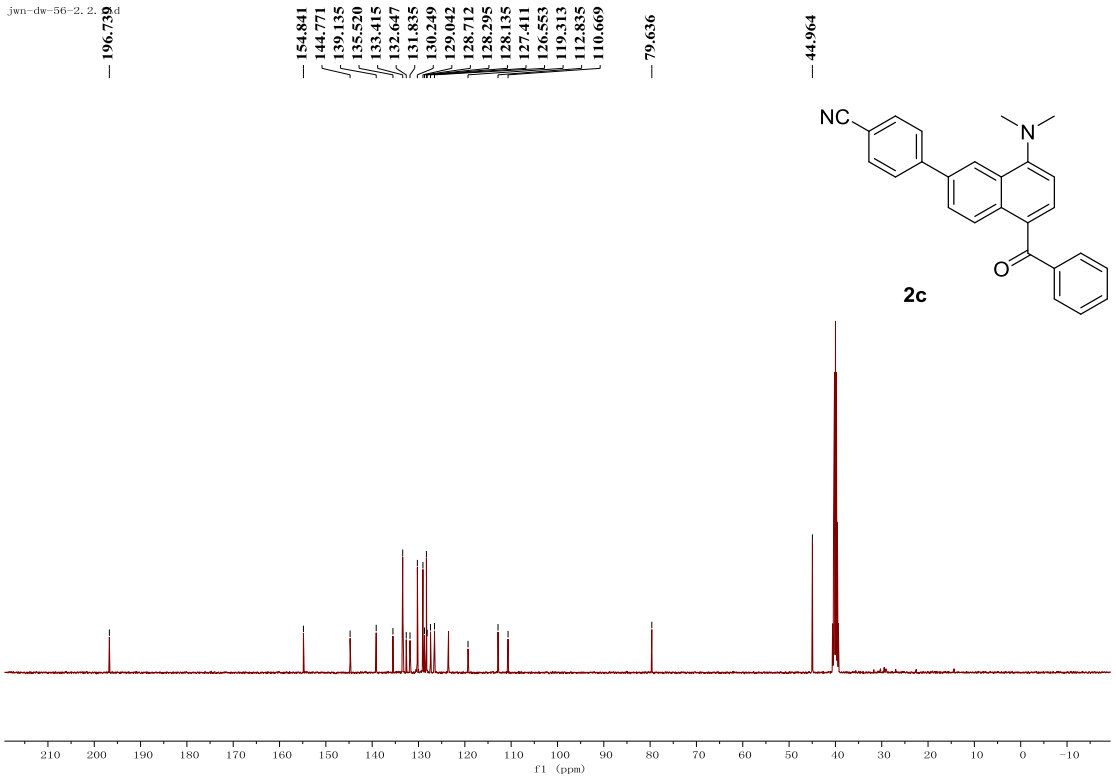

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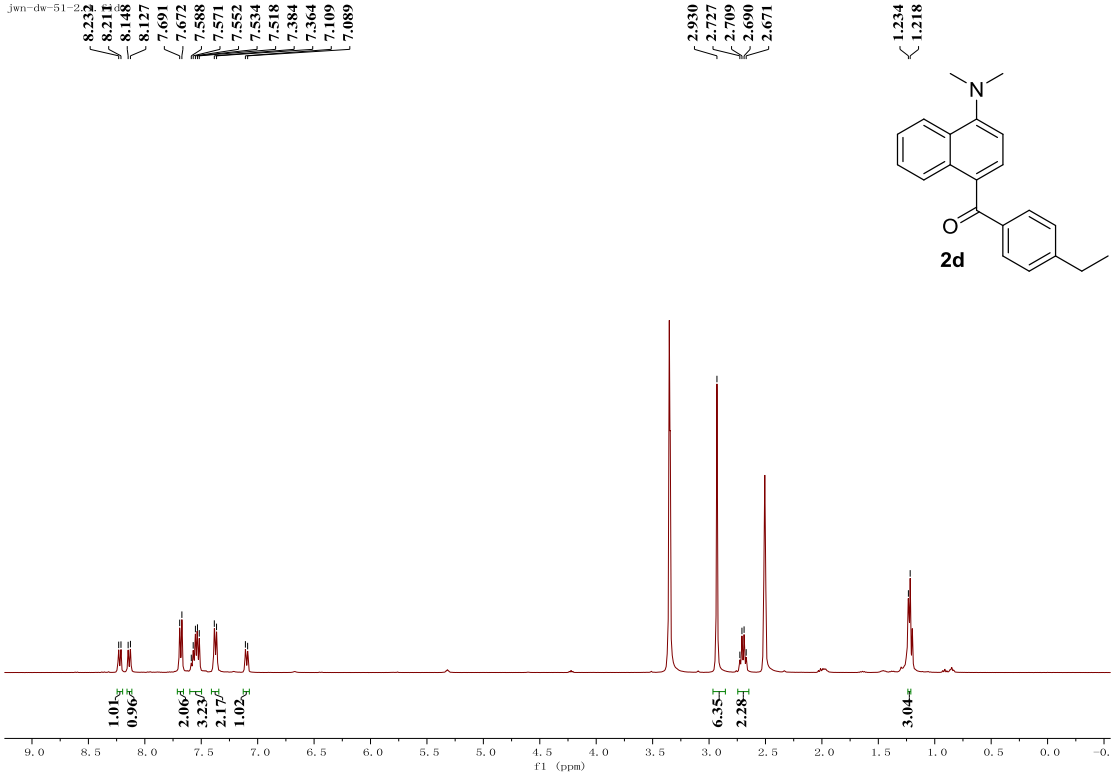

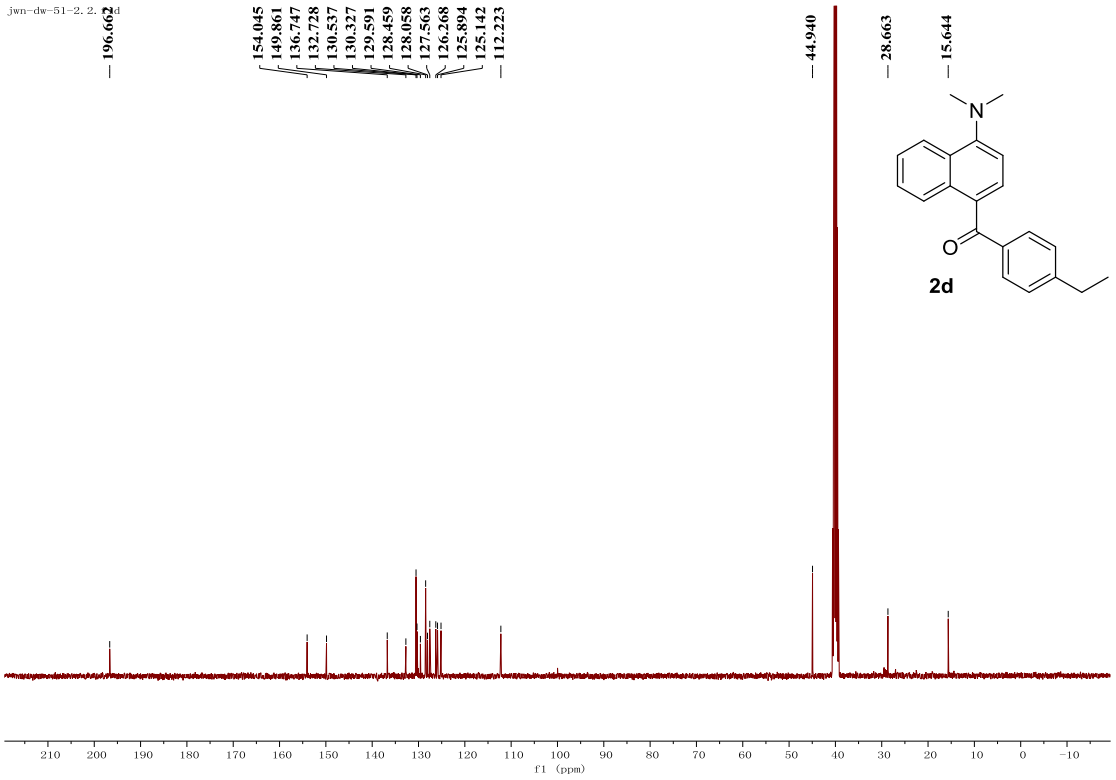

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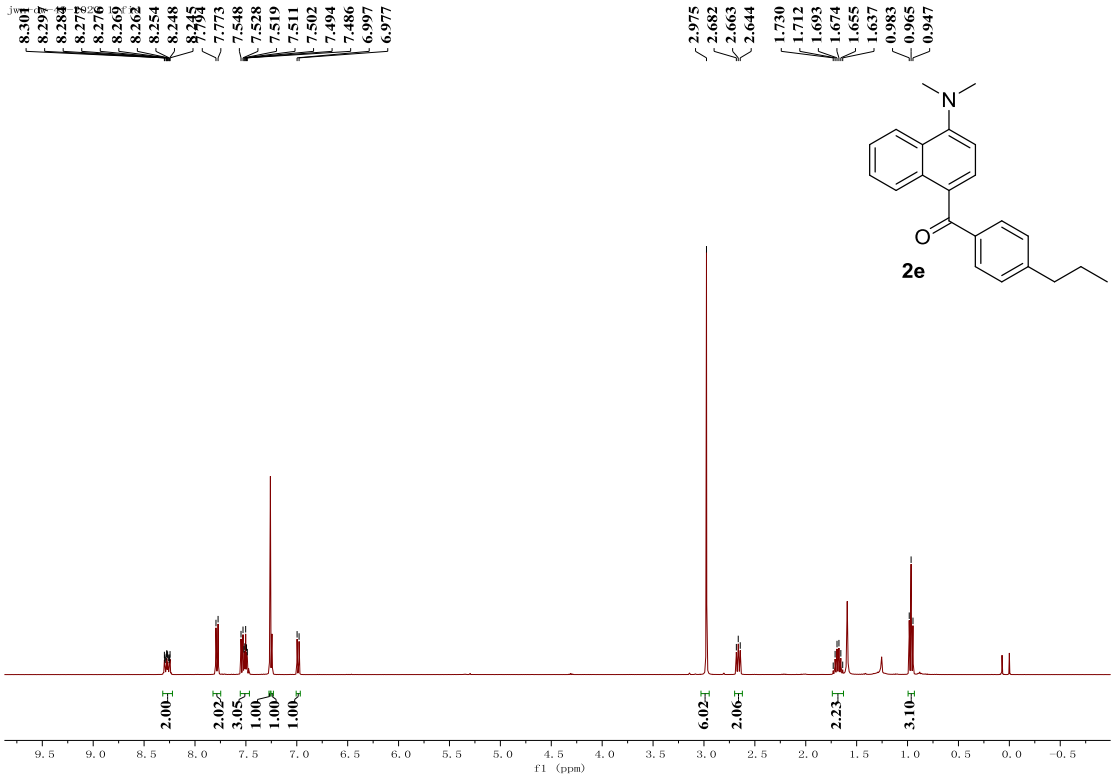

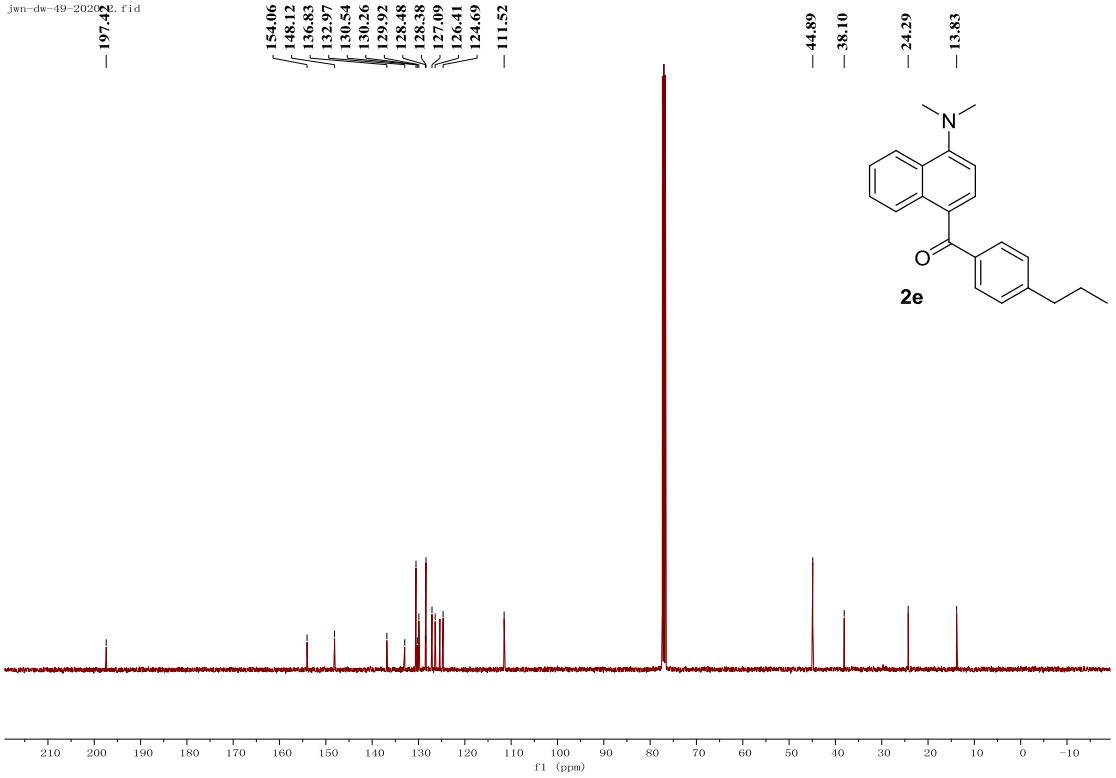

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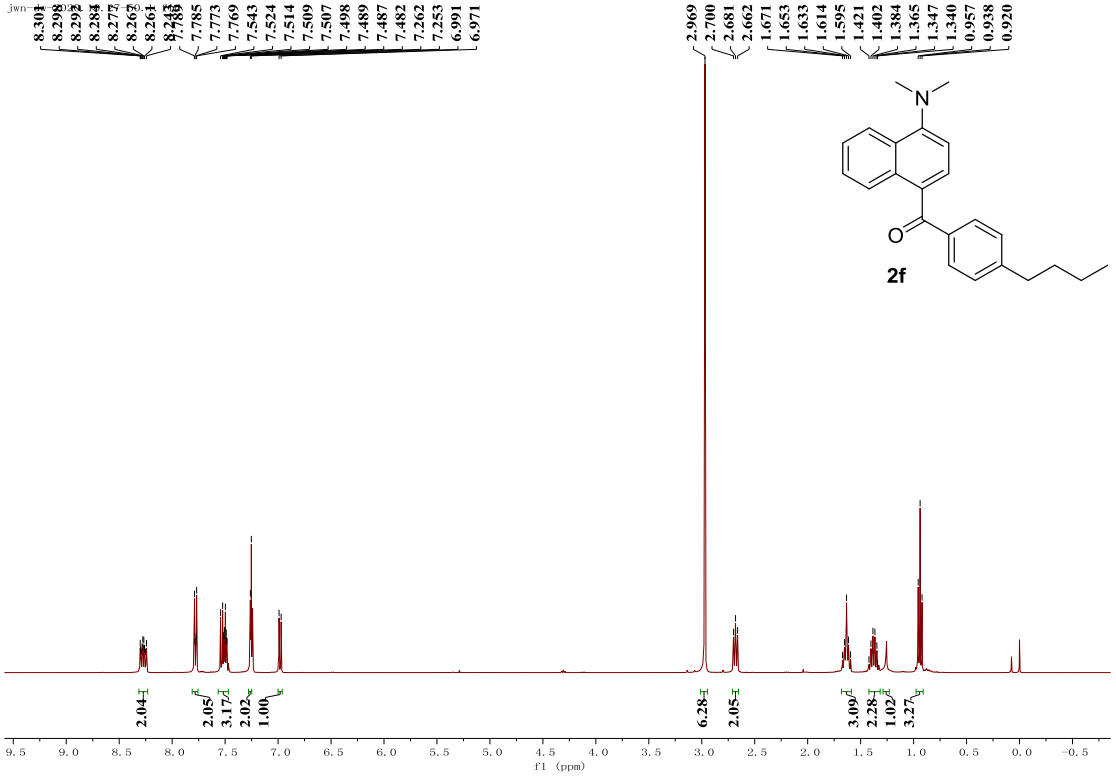

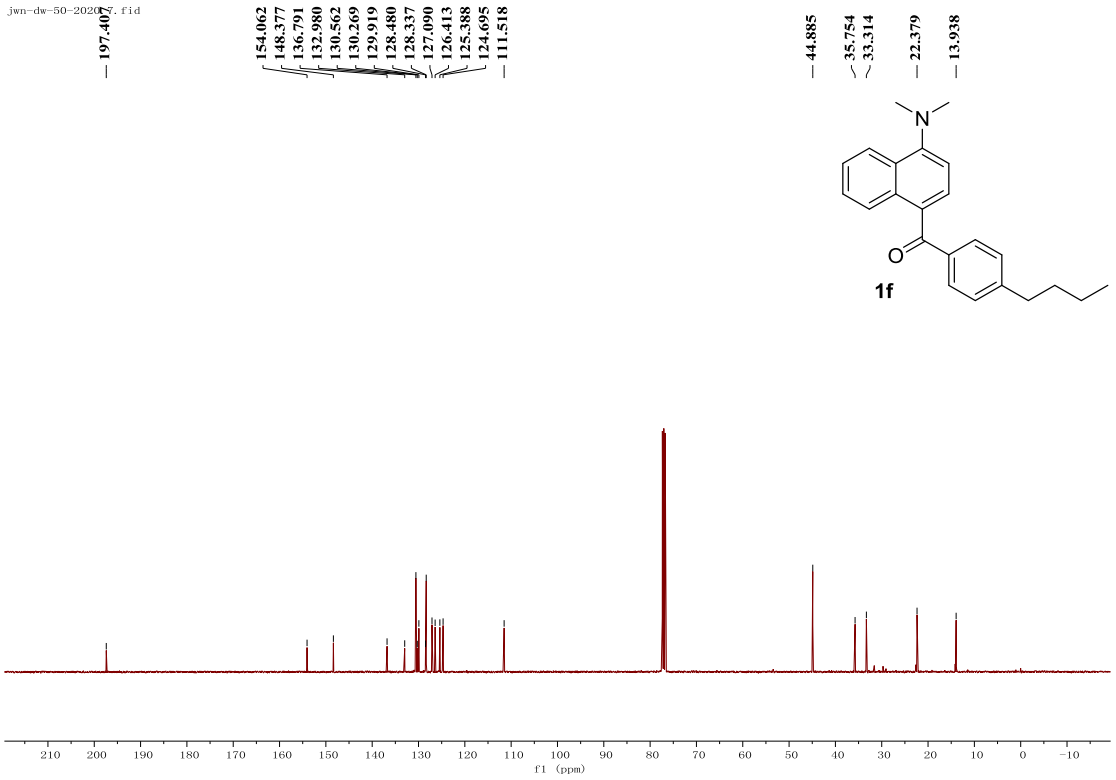

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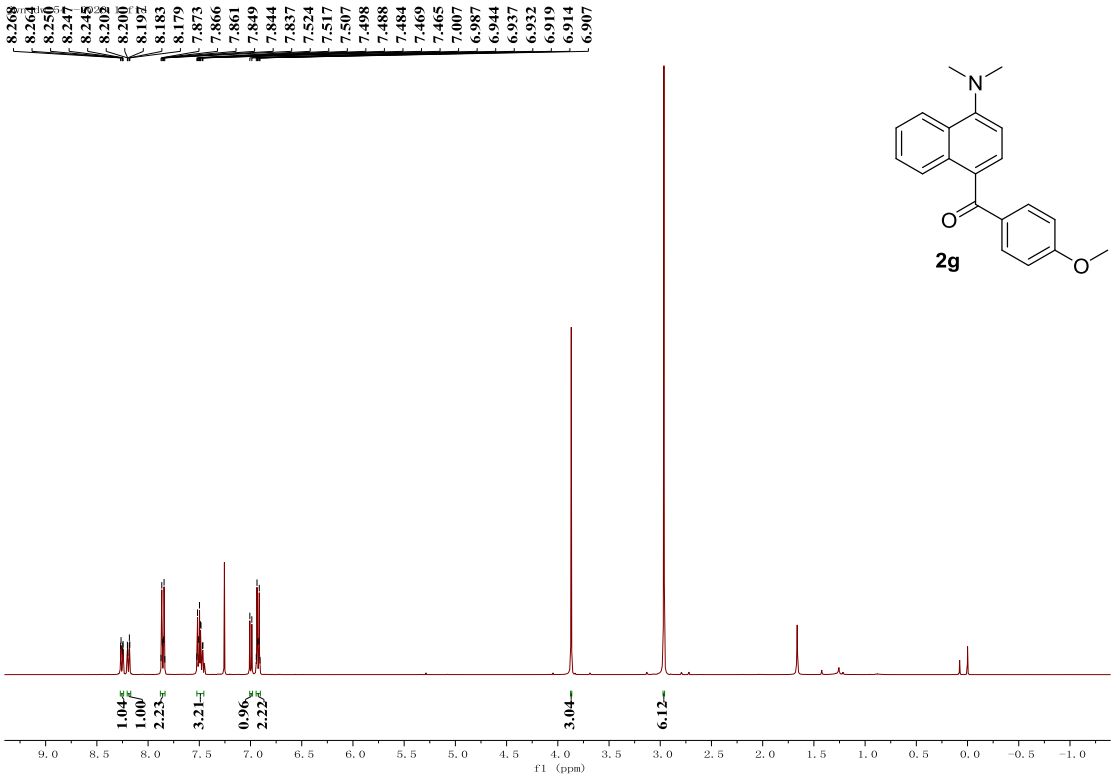

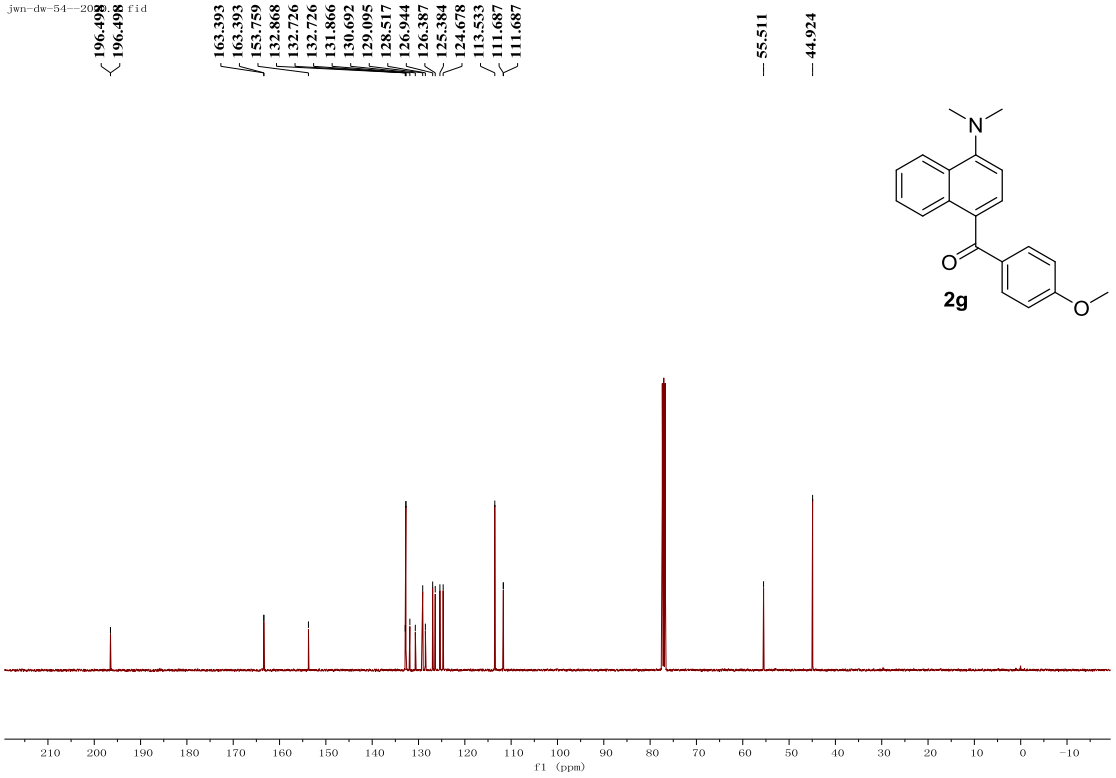

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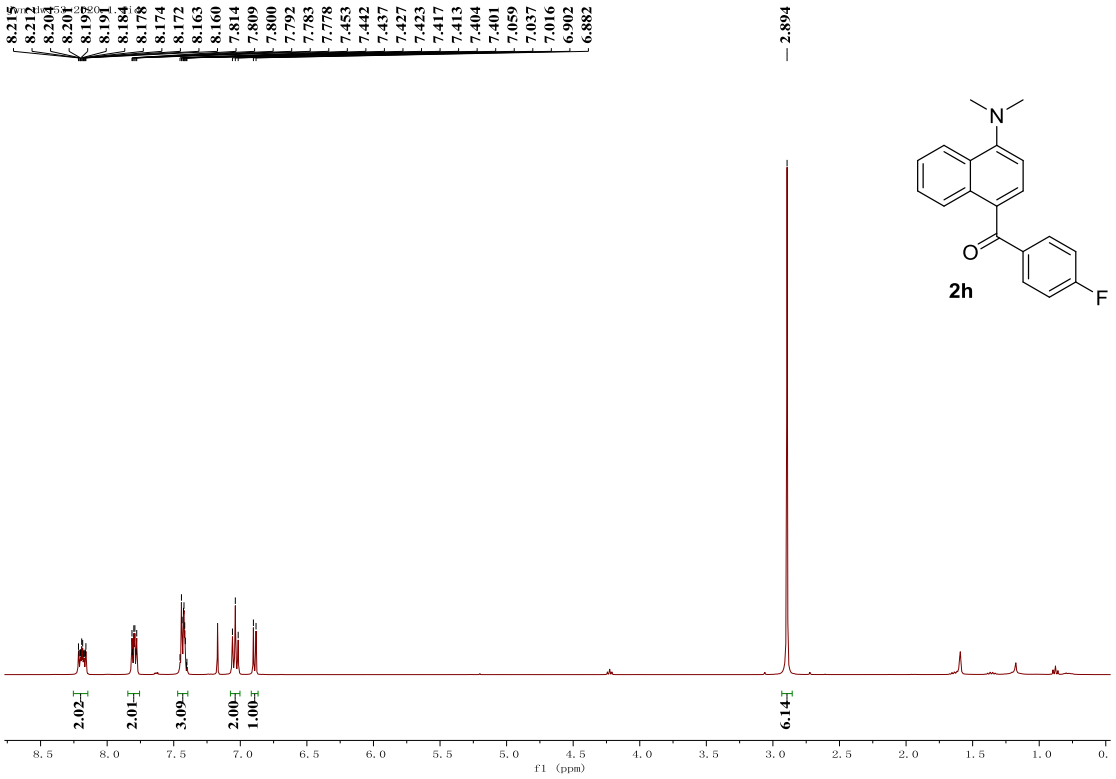
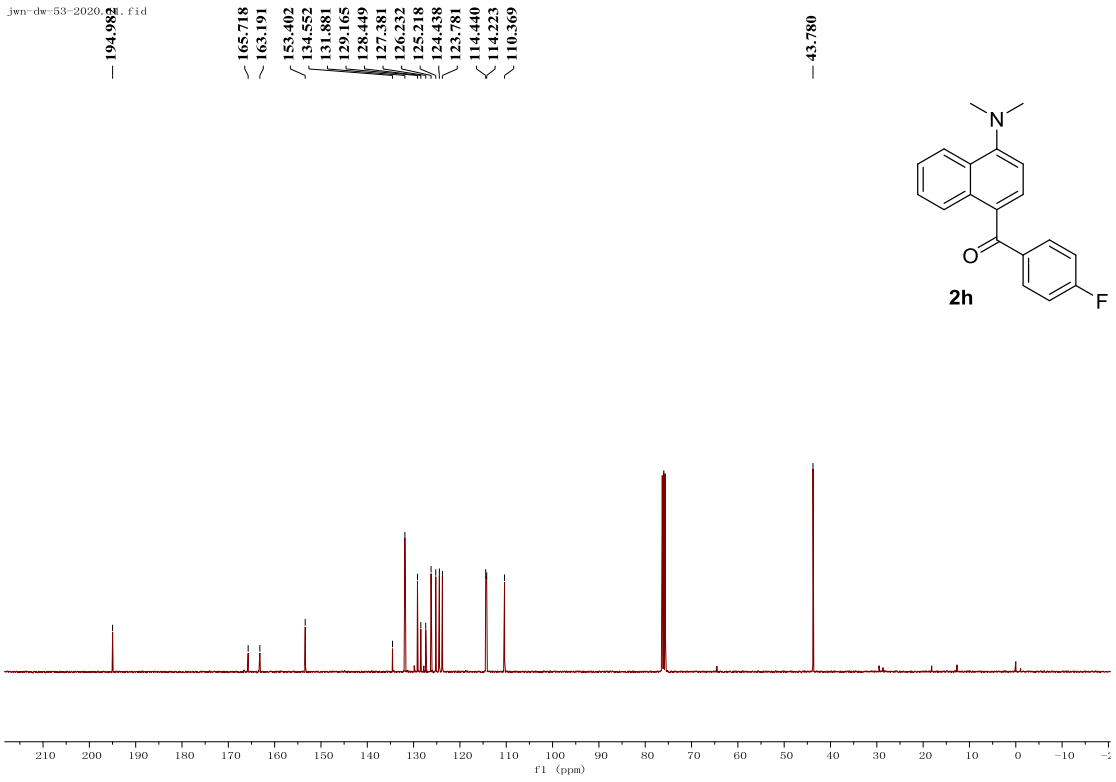
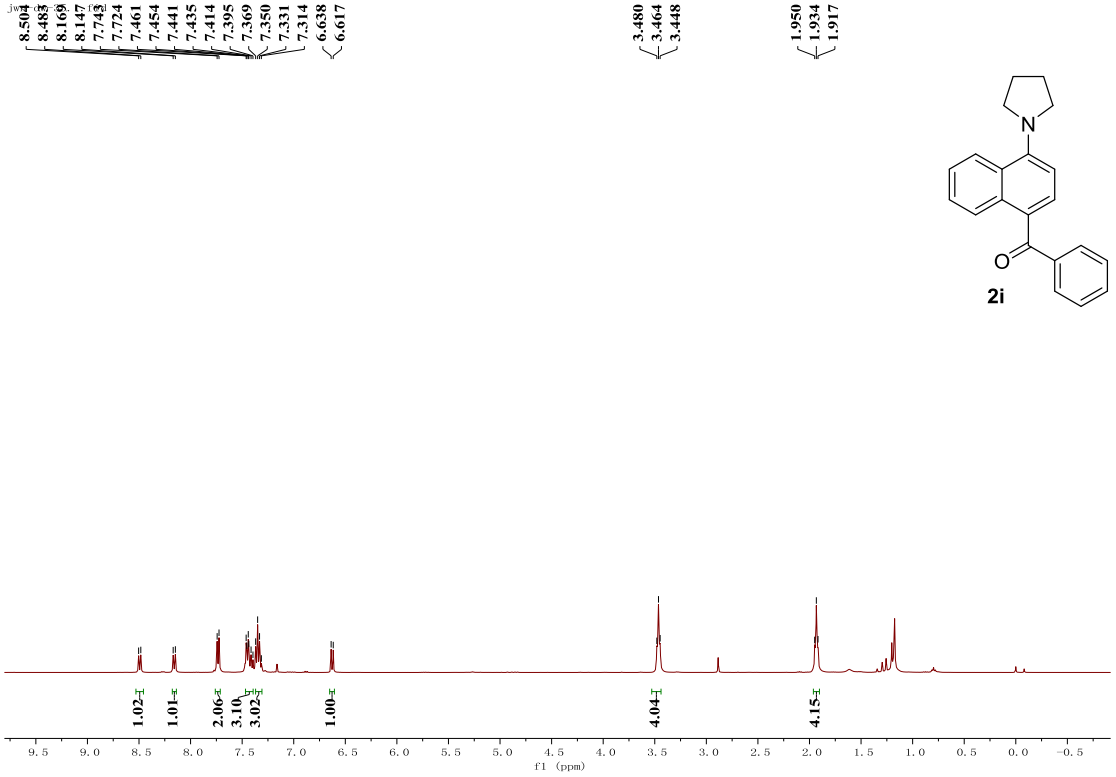
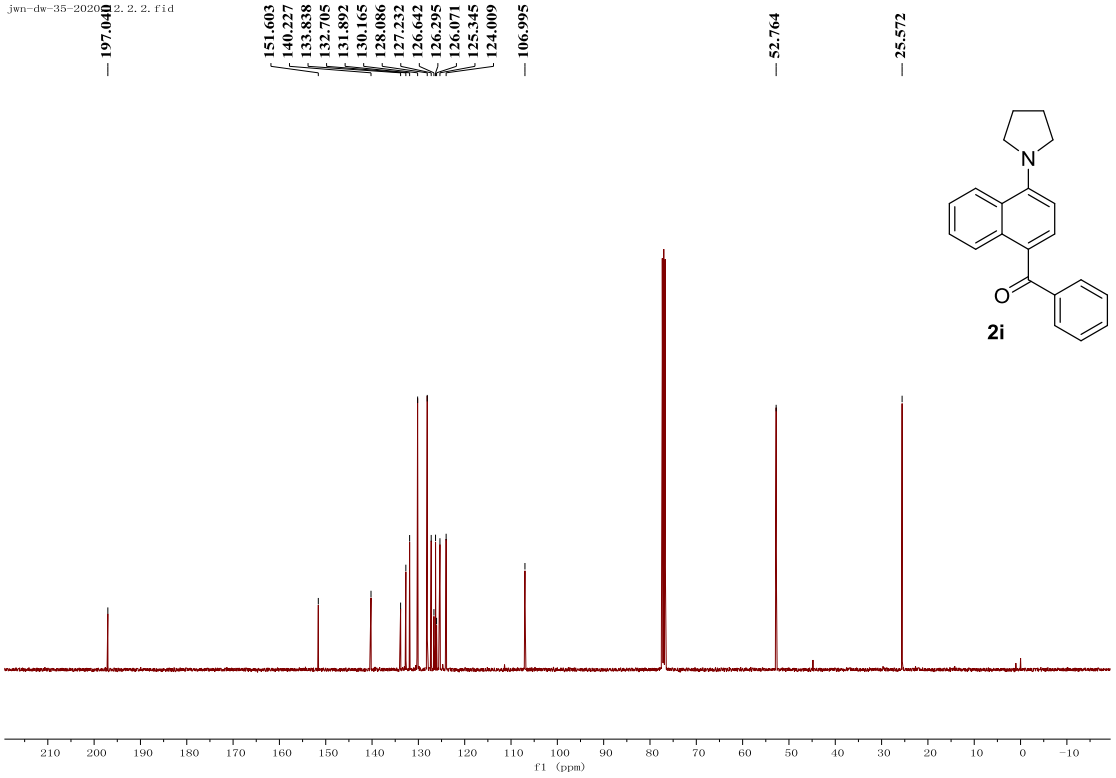




Product 2i:^{1}H NMR.





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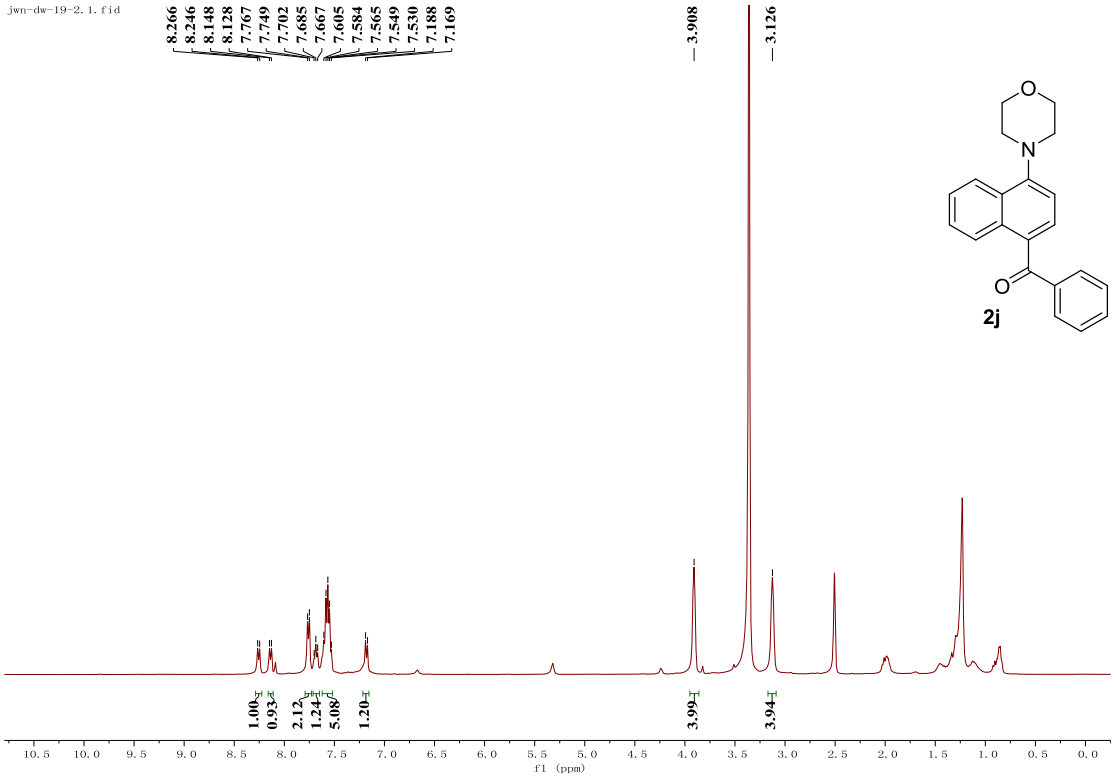

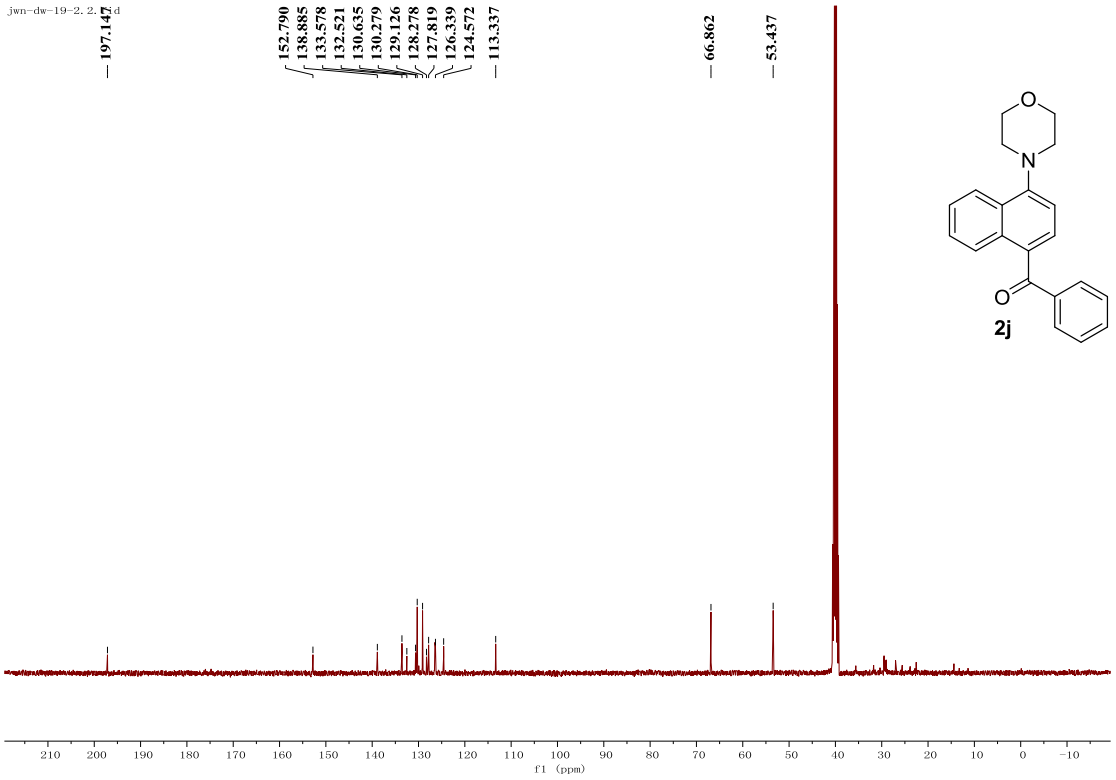

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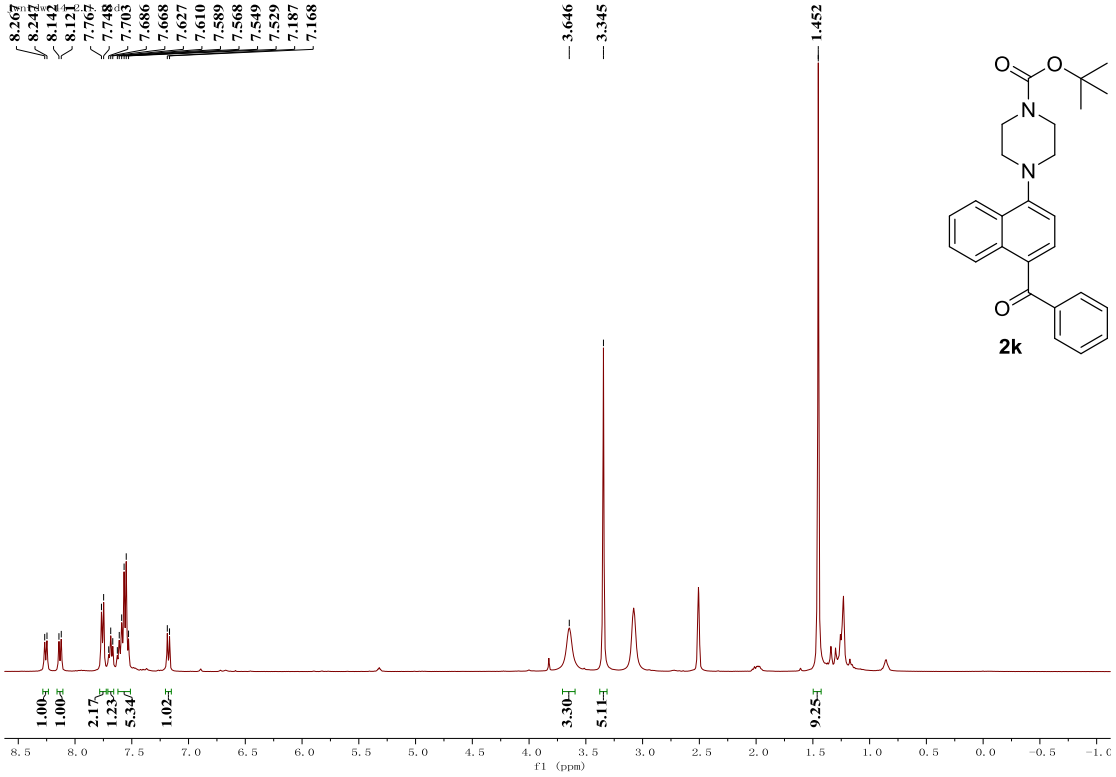

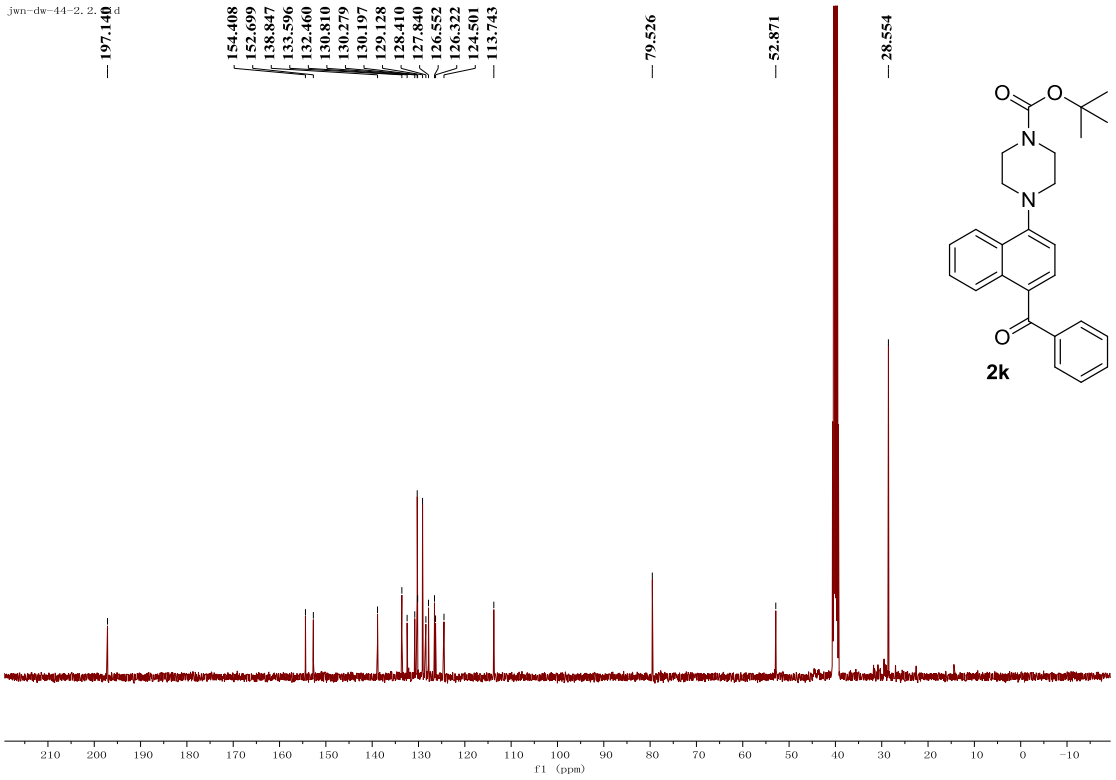

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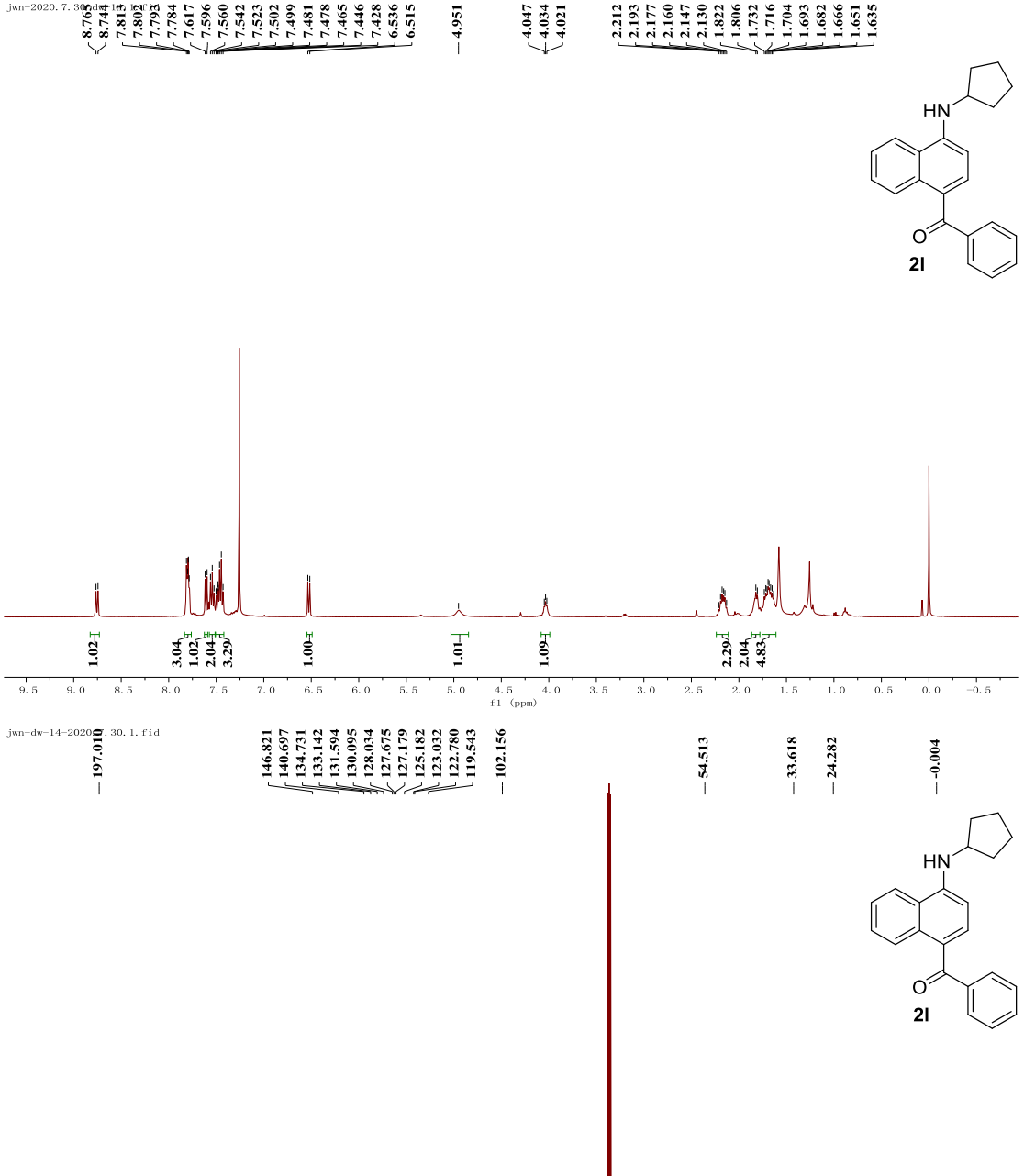

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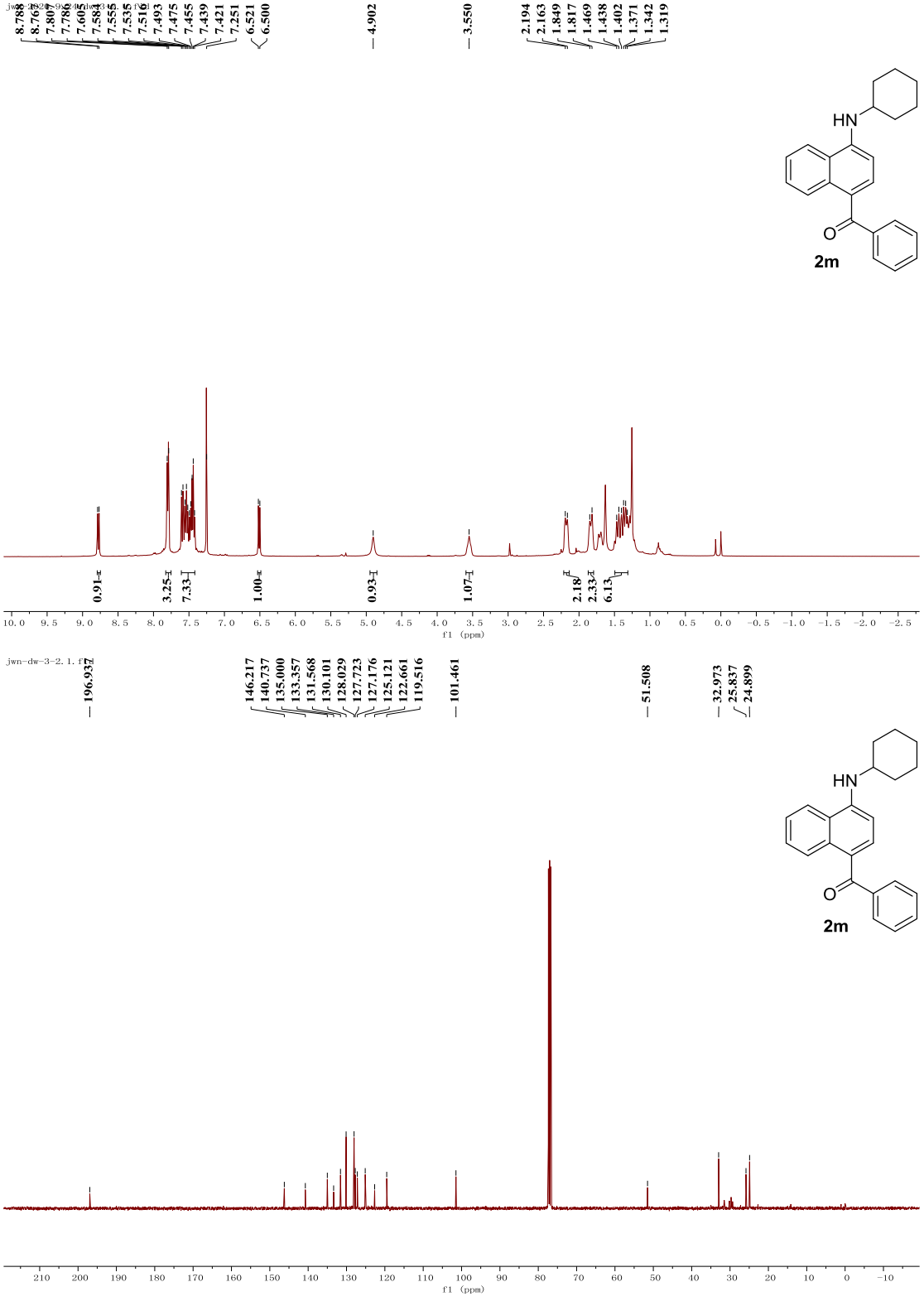

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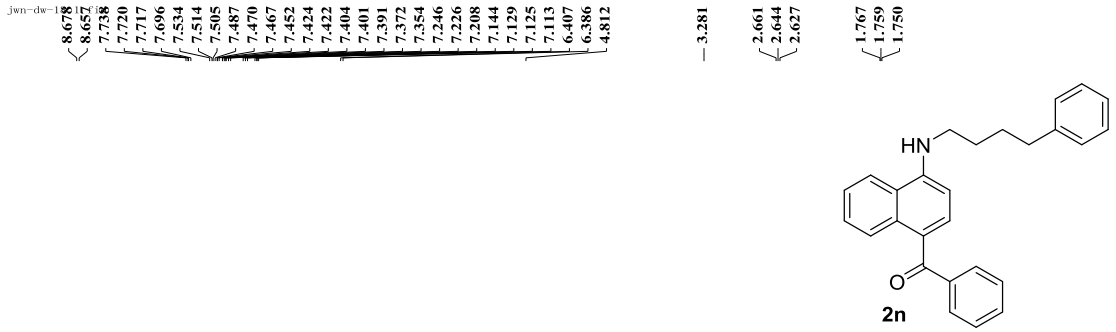

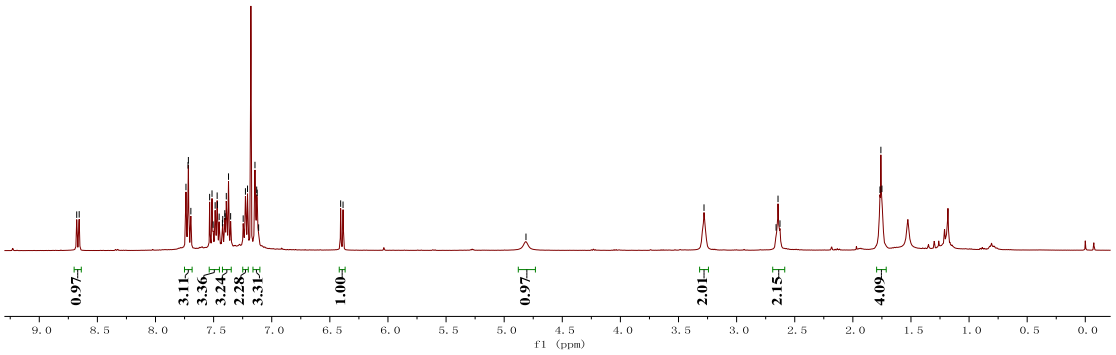

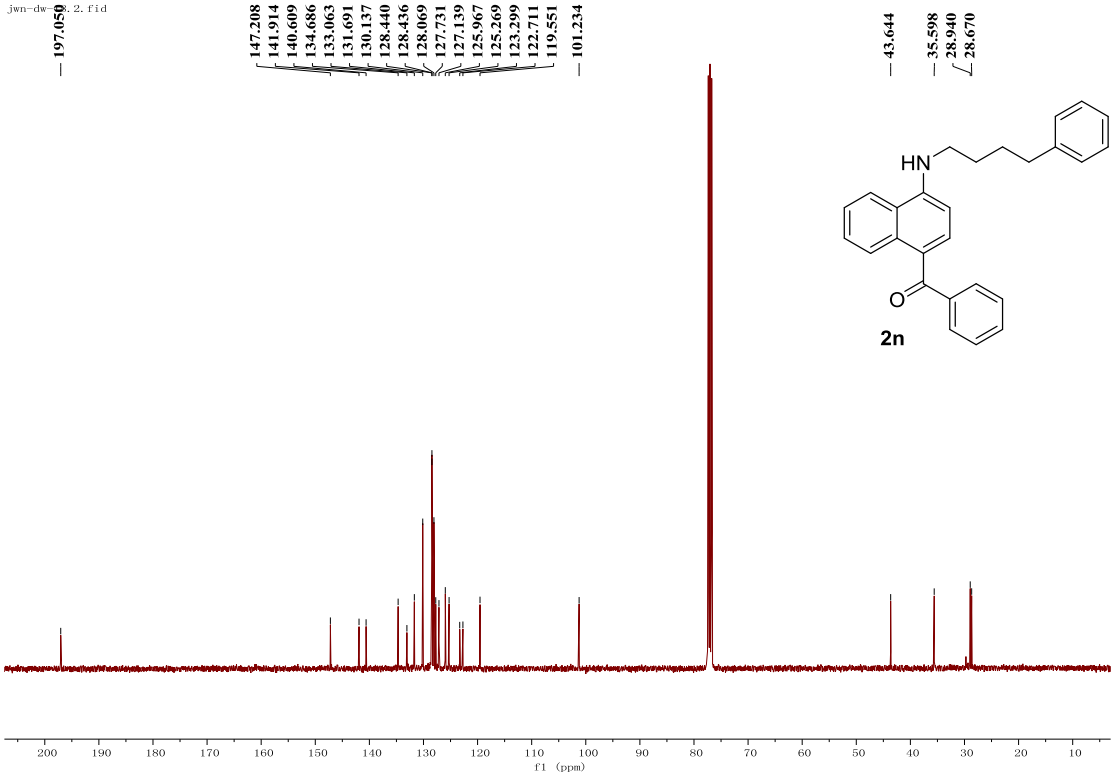

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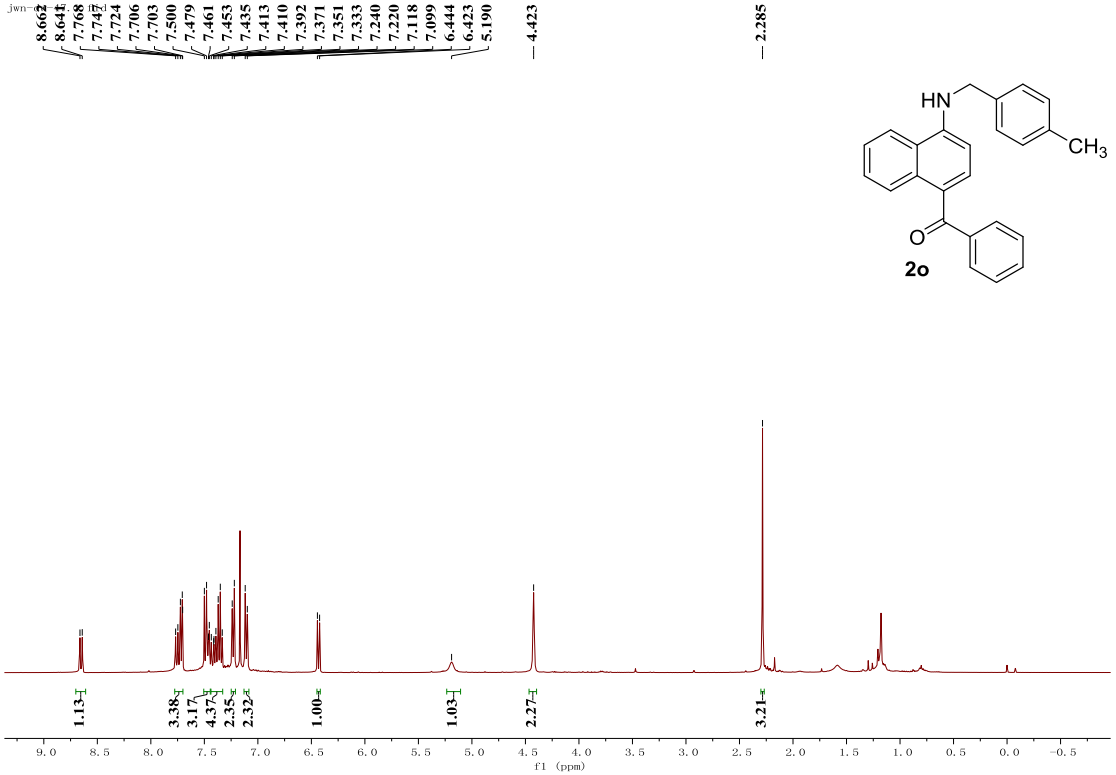

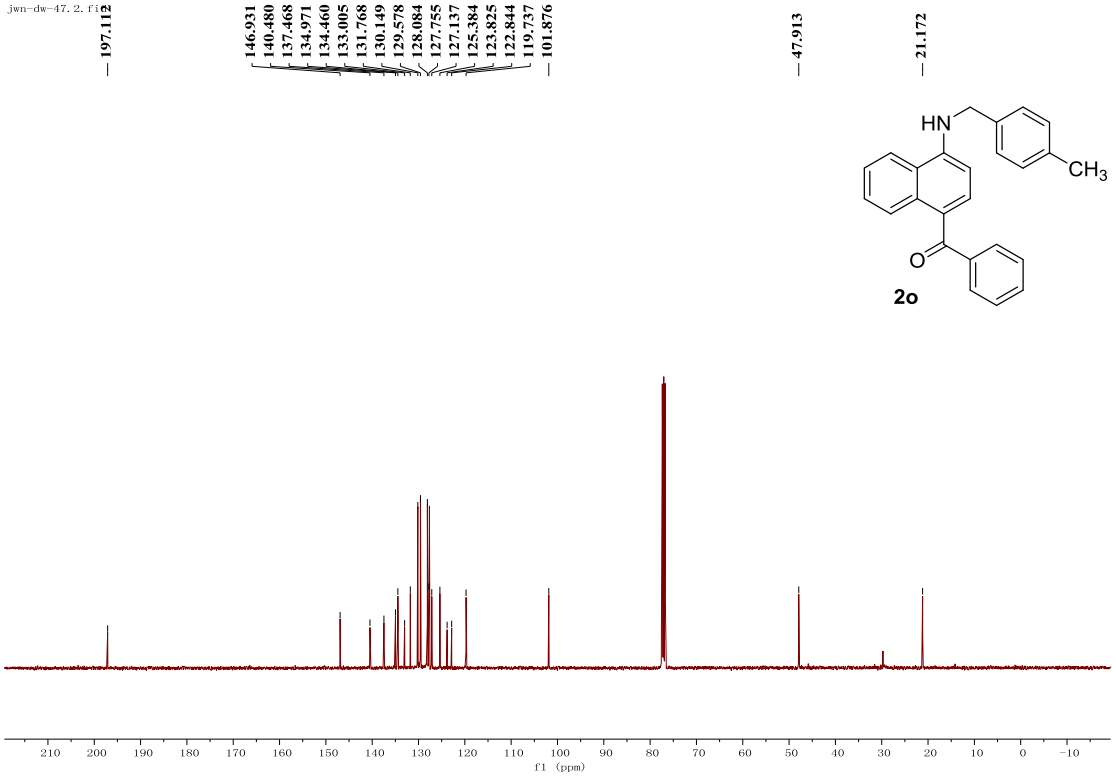

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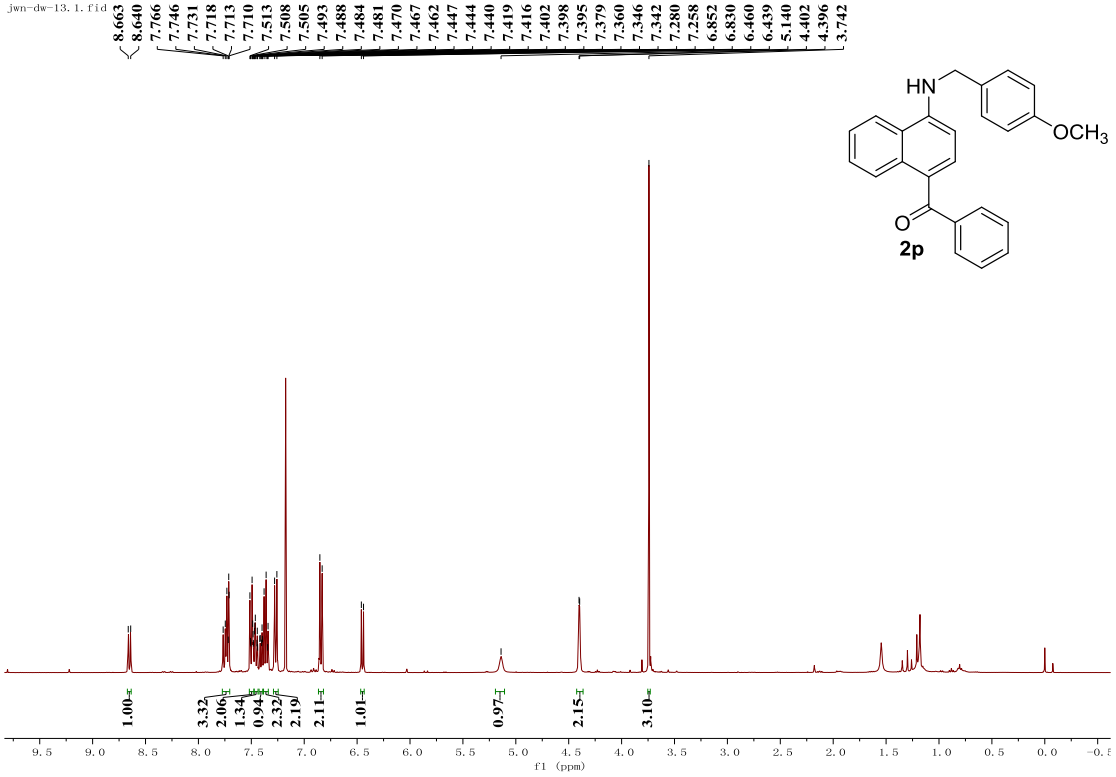

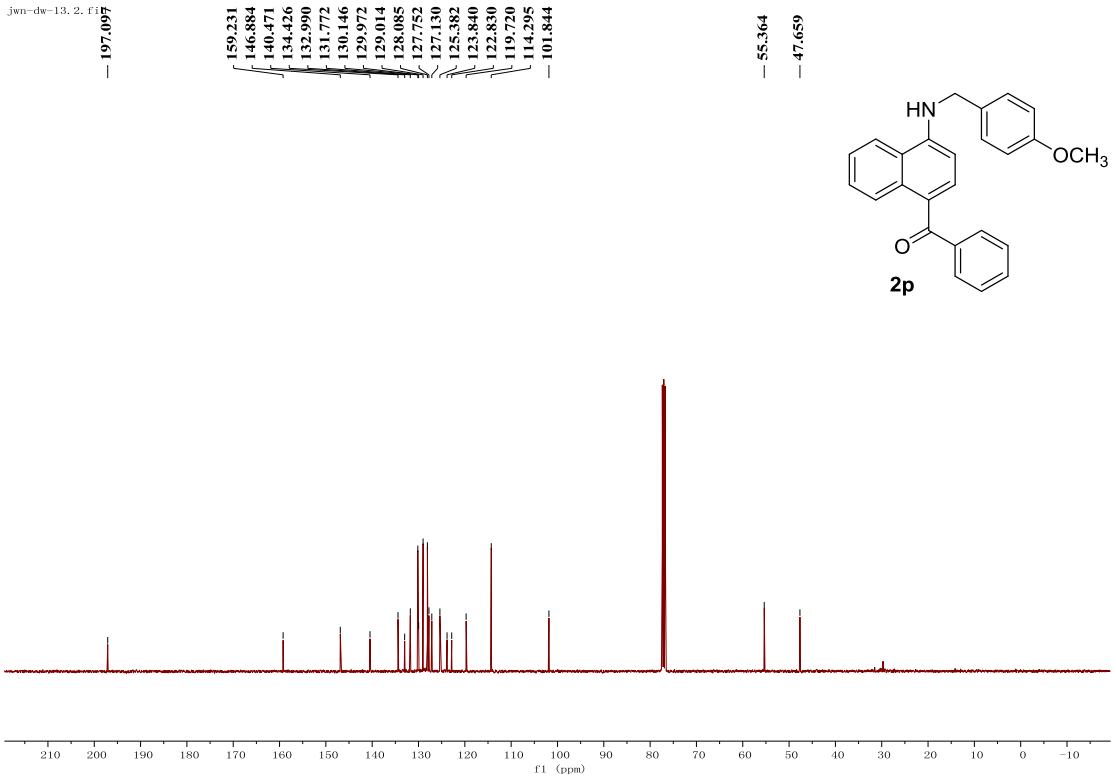

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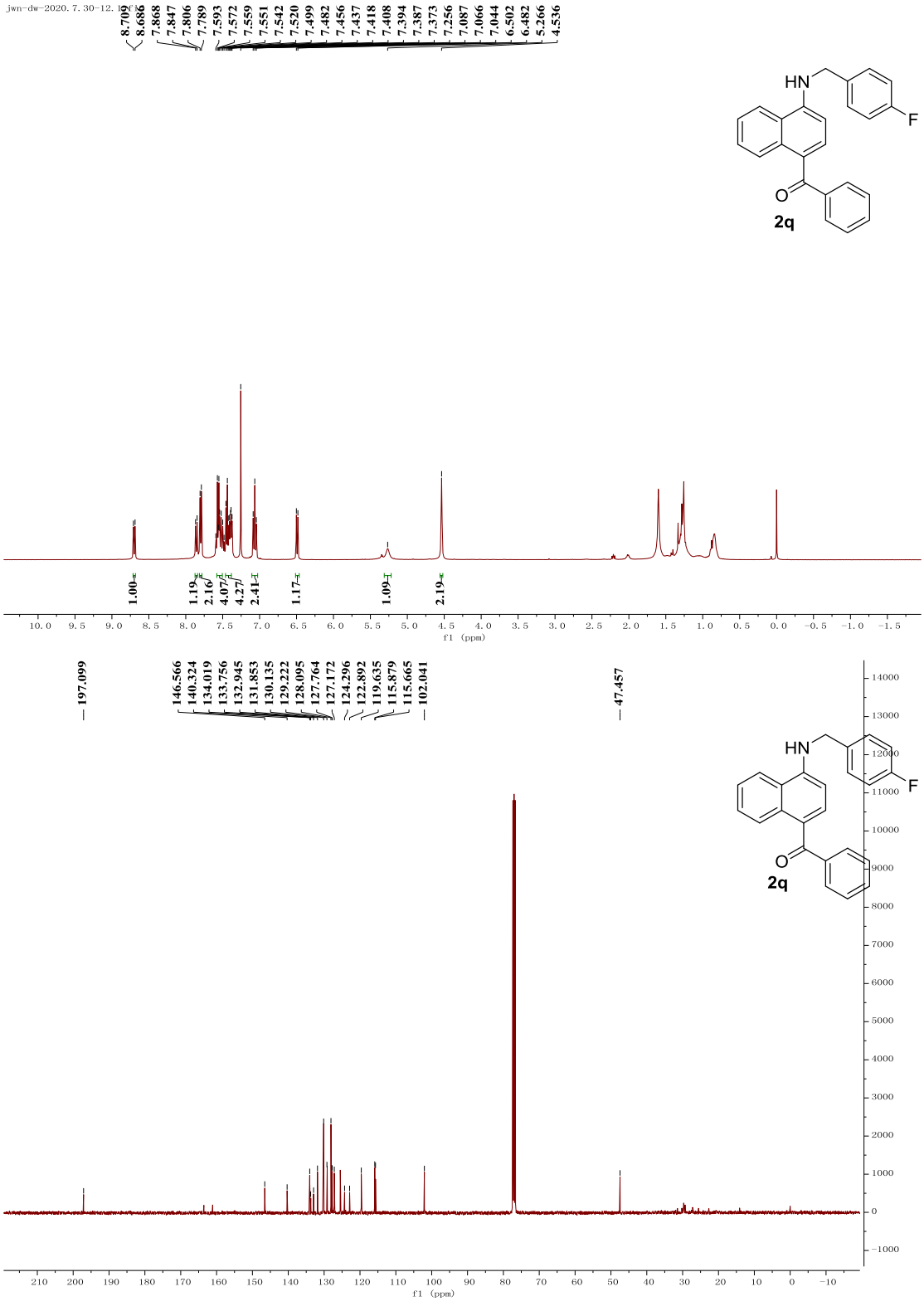
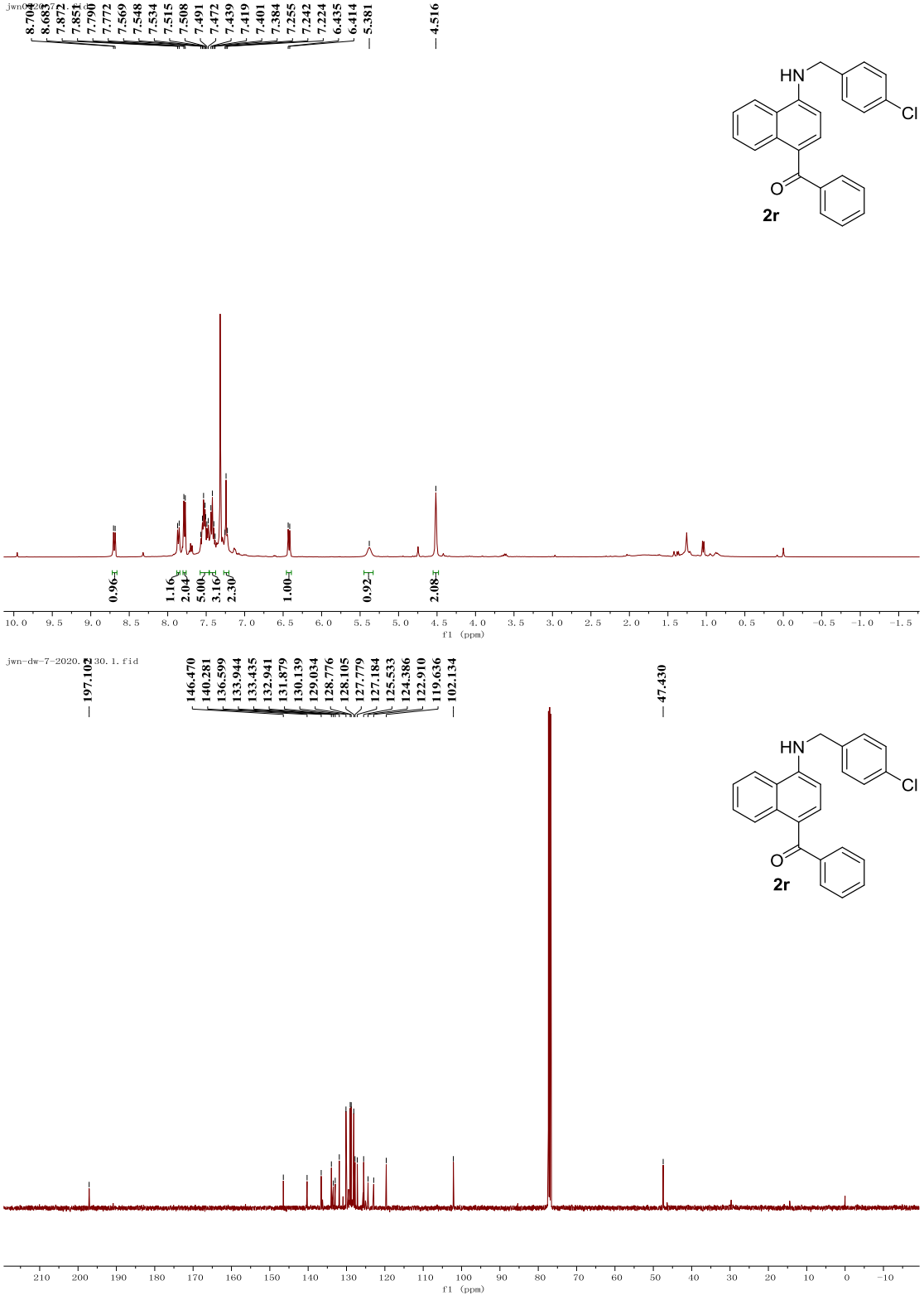
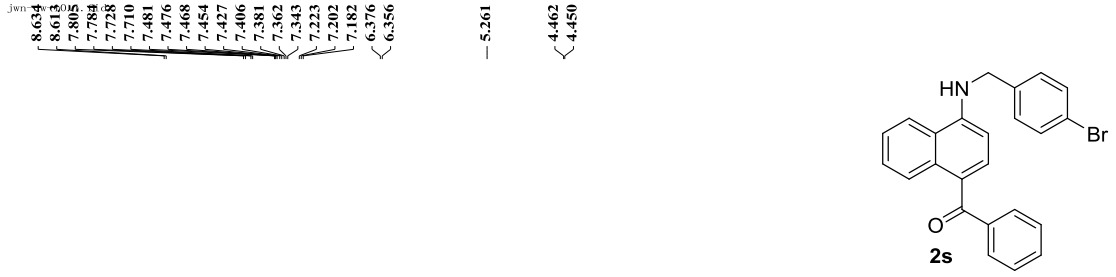
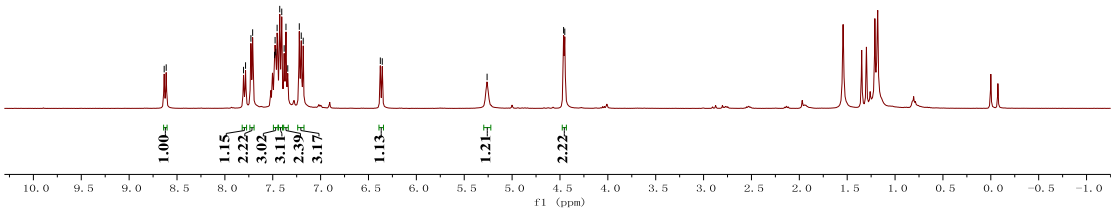


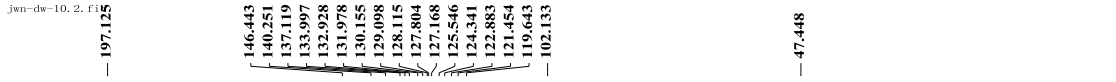
Product 2r:^{1}H NMR.

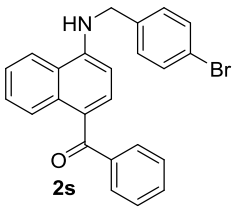


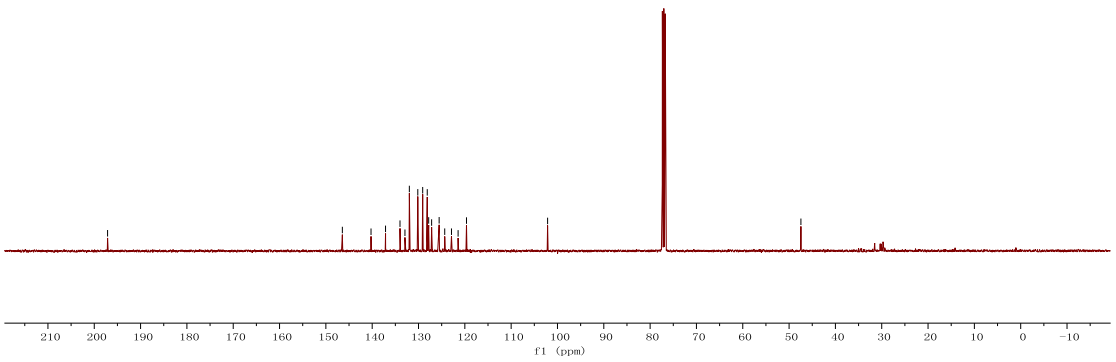
Product 2s:^{1}H NMR.



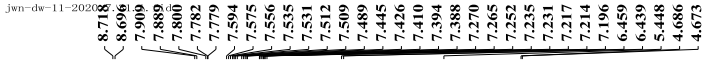


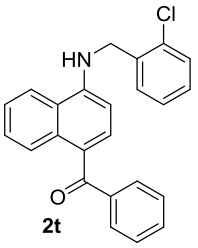


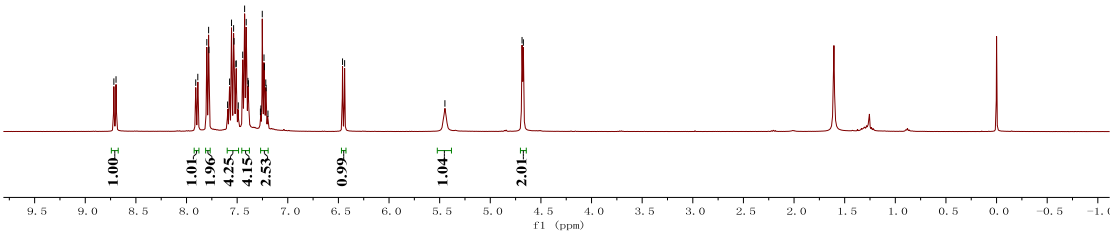


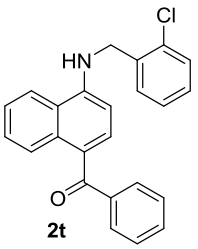


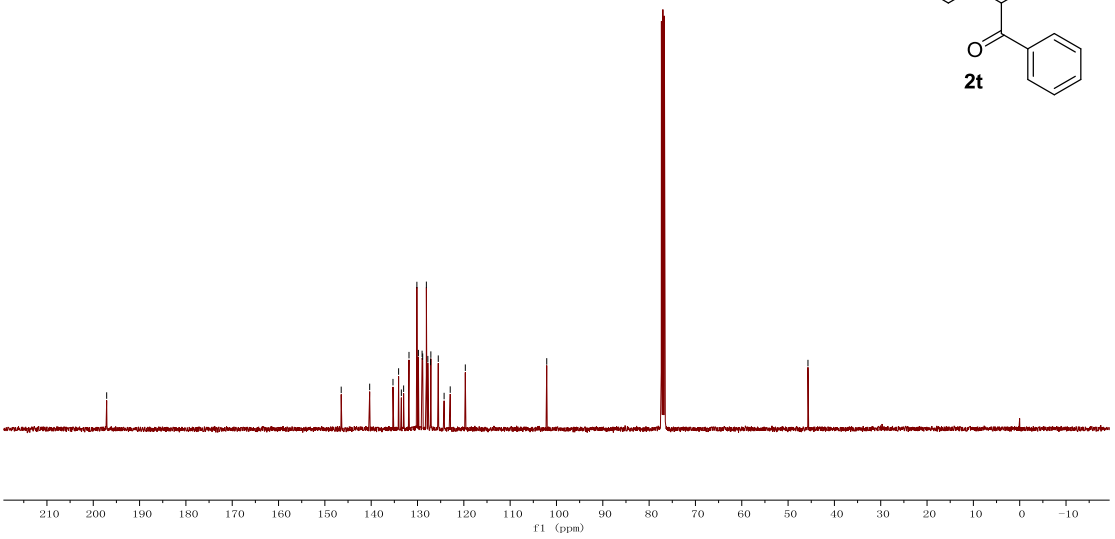
Product 2t:^{1}H NMR.



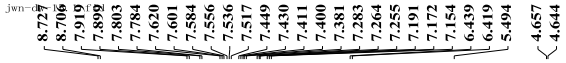


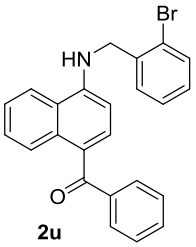






Product 2u:^{1}H NMR.





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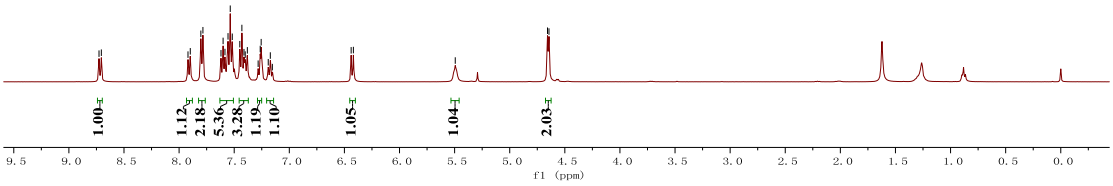

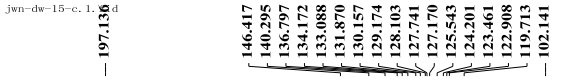

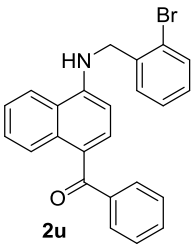

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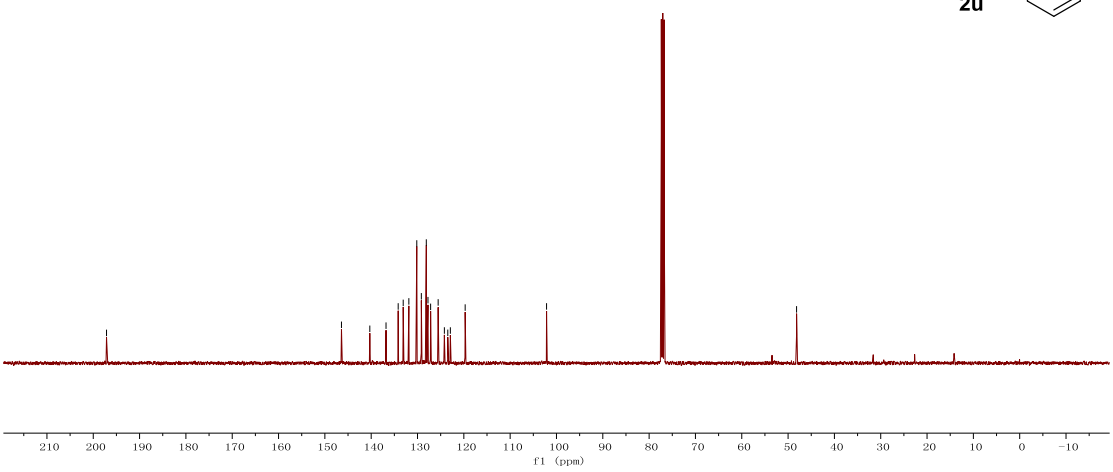
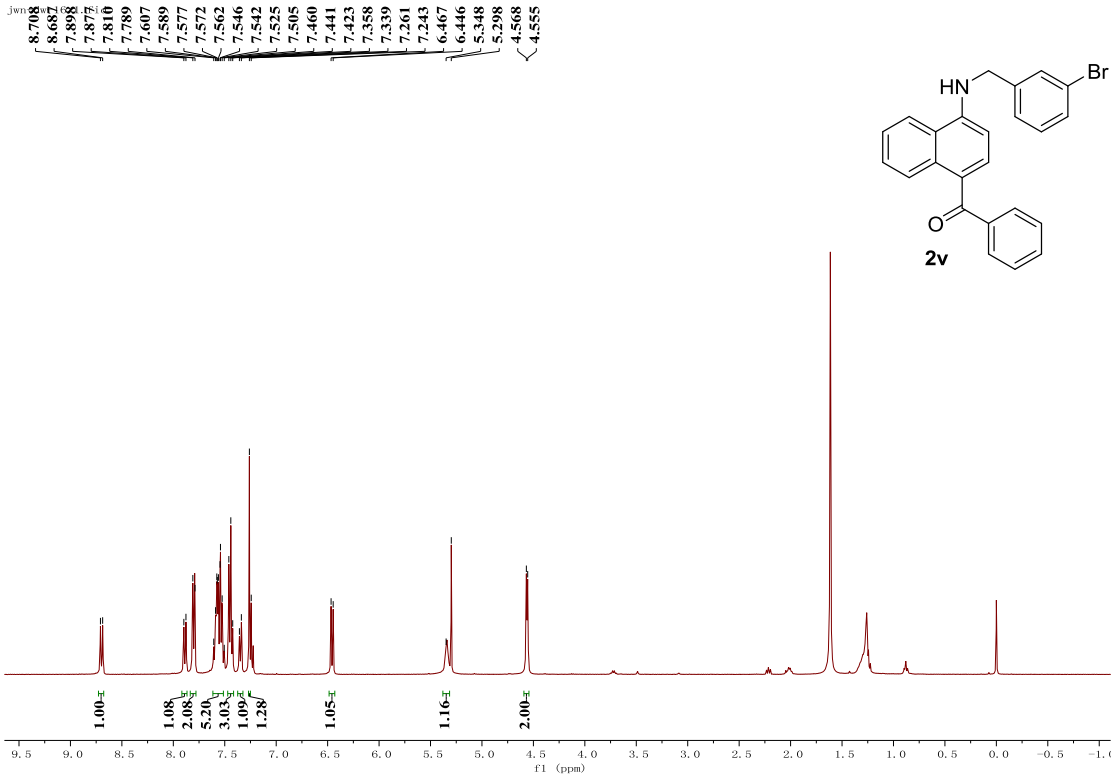
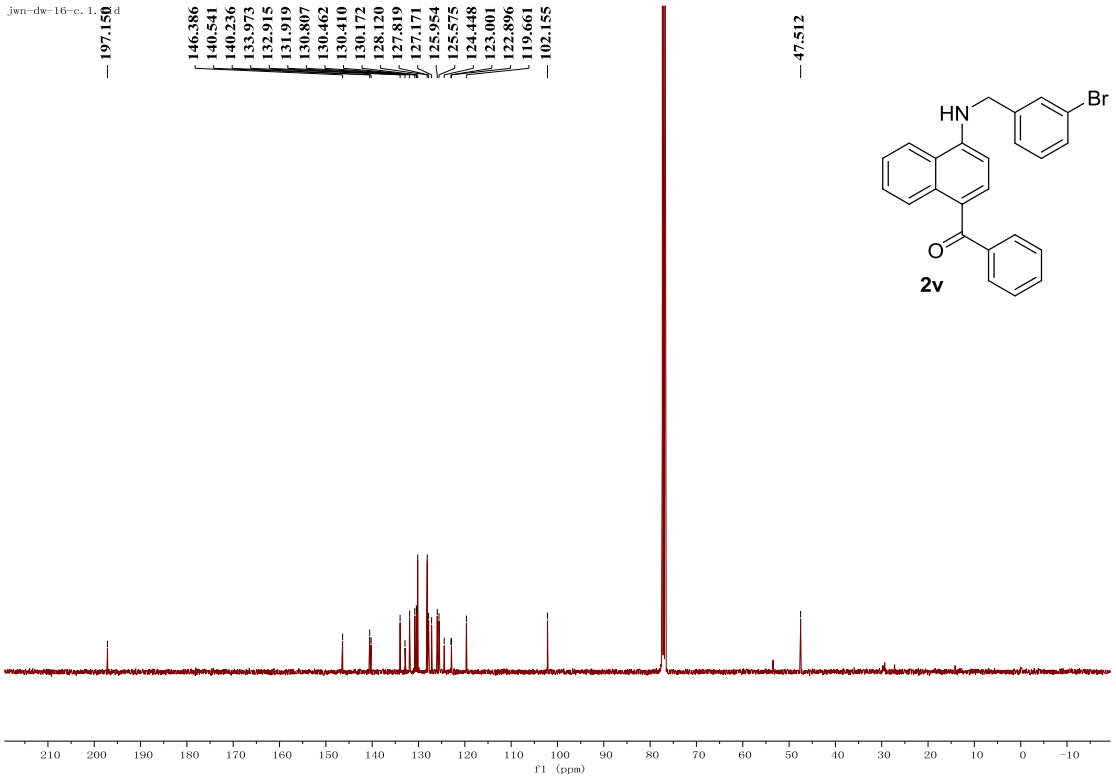


Product 2v:^{1}H NMR.





Product 2w:^{1}H NMR.