Supporting Information

Chemo-selective Control of Ritter-type Reaction by Coordinatively Unsaturated Inorganic Salt Hydrates

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1. General Methods

All reactions were conducted in oven or flame-dried glassware unless otherwise noted. Acetonitrile (CH_3CN) was distilled over calcium hydride (CaH_2) under a nitrogen atmosphere. All reactions were monitored by thin-layer chromatography (TLC), which was performed on percolated aluminum sheets of silica gel 60 (GF254). Chromatography was carried on flash silica gel (300-400 mesh). NMR spectra were recorded on a Bruker IMPACT-II 400, 500 or 600 spectrometers operating at 400 MHz or 600 MHz for ^{1}H NMR, 101 MHz, 126 MHz or 151 for MHz ^{13}C NMR, and 376 MHz for ^{19}F NMR, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker FTICRMS 7TSOLARIX spectrometer (ESI). All other reagents were obtained from commercial sources and used without further purification unless indicated otherwise. ESI-MS spectra and HPLC spectra were recorded on a ShimadzuLC-20AP. The water contents were determined by a Karl Fischer titrator (ZDJ-2S, Beijing Xianqu Weifeng Technology Development Co., Ltd.).

2. Materials

Inorganic salt hydrates $HCOOLi•2H_2O$, $LiOAc•2H_2O$, $Na_2CO_3•10H_2O$, $NaOAc•3H_2O$, $NaOAc•H_2O$, $K_2C_2O_4•H_2O$, $MgSO_4•7H_2O$, $MgSO_4•H_2O$, $Mg(OAc)_2•4H_2O$, $Mg(OAc)_2•H_2O$, $Mg_3(PO_4)_2•5H_2O$, $MgCl_2•6H_2O$, $CaBr•H_2O$, $Ca(C_2O_4)_2•H_2O$, $SrCl_2•6H_2O$, $BaCl_2•2H_2O$, and $Cu(OAc)_2•H_2O$ were purchased from Tianjin Xiensi Biochemical Technology Co., Ltd. (Tianjin, China).

$LiSO_4•H_2O$, $Na_2CO_3•H_2O$, $K_2CO_3•1.5H_2O$, $MgSO_4•2H_2O$, $Mg_3(PO_4)_2•4H_2O$, $CaCl_2•5H_2O$, $CaSO_4•2H_2O$, $CaSO_4•H_2O$, $SrCl_2•5H_2O$, and $SrOAc•1/2H_2O$ were purchased from Alfa Aesar Co. Inc (USA).

$LiI•3H_2O$, $LiCl•H_2O$, $Mg_5(CO_3)_4(OH)_2•5H_2O$, $CaBr•2H_2O$, $Ca(OAc)_2•2H_2O$, $Cu(COOCF_3)_2•H_2O$, $CuCl_2•2H_2O$, $Cu(NO_3)_2•3H_2O$, $CuSO_4•5H_2O$, $Fe_2(SO_4)_3•H_2O$, $FeCl_3•6H_2O$, $Ni(OAc)_2•H_2O$, and $Mn(OAc)_2•H_2O$ were purchased from Energy Chemical Co., Ltd. (Shanghai, China).

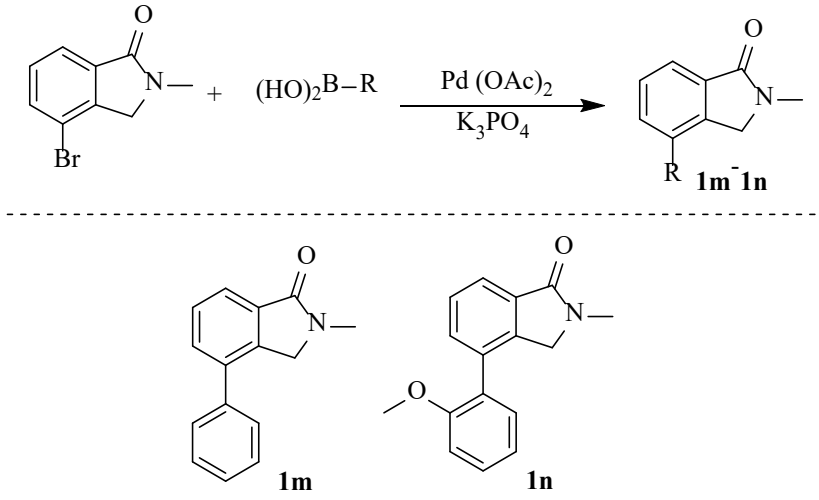
Na_2SO_4•$10H_2O$, $NaHSO_4$•H_2O, Na_2HPO_4•$12H_2O$, Na_3PO_4•$12H_2O$, K_3PO_4•$3H_2O$, $BeSO_4$•$4H_2O$, $CaCl_2$•$2H_2O$, and $FeCl_2$•$4H_2O$ were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China).

K_2HPO_4•$3H_2O$, KF•$2H_2O$, $MgHPO_4$•$3H_2O$, $Ni(OAc)_2$•$4H_2O$, and $NiCl_2$•$6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). $CaCl_2$•$6H_2O$, $CaSO_4$•$1/2H_2O$, and $Ca(HSO_4)$•$2H_2O$ were purchased from Acros Organics Co., Ltd. (USA).

Inorganic salt hydrates Na_2SO_4•$2H_2O$,[1] Na_2HPO_4•$8H_2O$,[2] Na_3PO_4•$8H_2O$,[3] $BeSO_4$•$2H_2O$,[4] $MgSO_4$•$6H_2O$,[5] $MgSO_4$•$5H_2O$,[5] $MgSO_4$•$4H_2O$,[5] $MgSO_4$•$3H_2O$,[5] $MgCl_2$•$5H_2O$,[6] $Cu(NO_3)_2$•$2H_2O$,[7] $CuSO_4$•$2H_2O$,[8] and $NiCl_2$•$4H_2O$[9] were prepared according to the reported literature.

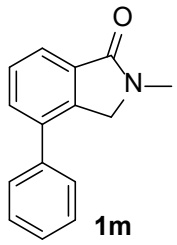
3. General Information for Starting materials

Starting materials **1a**-**1l** and **1p**-**1v** were prepared according to our reported procedure and the spectroscopic data were consistent with the reported values.[10] **1m** and **1n** were synthesized as following procedures:



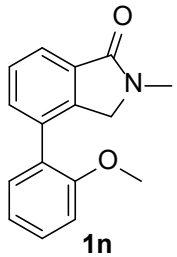
To a mixture of 4-bromo-2-methylisoindolin-1-one (1 mmol), arylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol) and $Pd(PPh_3)_4$ (2 mol %) was charged degassed toluene (6 mL) and MeOH (2 mL). The mixture was pumped and refilled with nitrogen three times

and stirred at 80°C for 24 h. After the reaction, 10 mL H_2O was poured into the mixture, which was then extracted three times with 10 mL CH_2Cl_2. The organic layer was separated, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1) to provide the coupling products.



1m

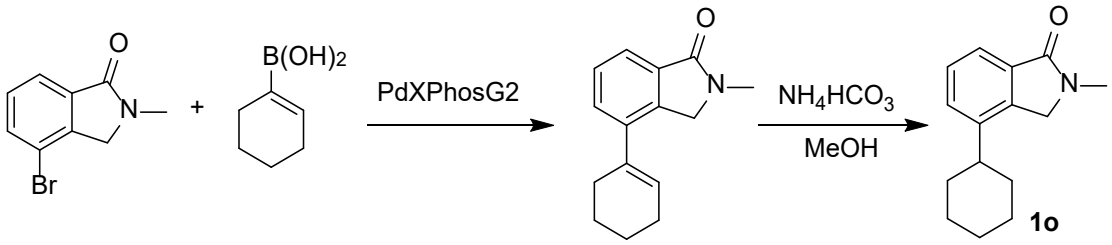
Compound 1m: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.79 (m, 1H), 7.61-7.56 (m, 2H), 7.53-7.47 (m, 4H), 7.46-7.41 (m, 1H), 4.47 (s, 2H), 3.22 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.7, 139.4, 137.8, 136.9, 135.7, 133.6, 131.3, 130.0, 129.1, 128.3, 122.0, 51.9, 29.4; **ESI-MS** (ESI+) calcd for $C_{15}H_{14}NO$ $[M+H]^+$: 224.10; found: 224.10.



1n

Compound 1n: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.84 (m, 1H), 7.57-7.51 (m, 1H), 7.51-7.46 (m, 1H), 7.46-7.40 (m, 1H), 7.28-7.24 (m, 1H), 7.11-7.02 (m, 2H), 4.28 (s, 2H), 3.82 (s, 3H), 3.19 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 139.7, 138.1, 136.9, 135.6, 133.0, 132.0, 130.4, 128.9, 128.2, 128.1, 125.9, 122.4, 51.7, 29.4, 19.9; **ESI-MS** (ESI+) calcd for $C_{16}H_{16}NO_2$ $[M+H]^+$: 254.11; found: 254.10.

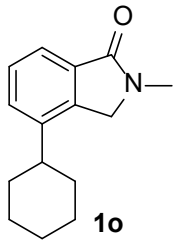
Synthesis of 1o



1o

To a Schlenk tube was added cyclohex-1-en-1-ylboronic acid (1 mmol), 4-bromo-2-methylisoindolin-1-one (1 mmol), PdXPhosG2 (1% mmol), Pd/C (0.12 mmol) and K_3PO_4 (3 mmol). The tube was purged with nitrogen, then 1,4-dioxane and water (vol: vol = 4:1) were added. The reaction mixture was stirred at 80°C for 4 h, followed by the addition of NH_4HCO_3 in MeOH (1.25 M) (10 equiv.). Following this, the reaction was stirred for 16 h at room temperature. After the reaction was completed, 15 mL H_2O

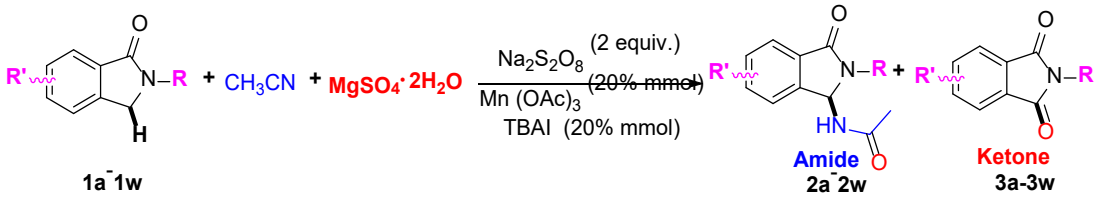
was poured into the mixture, which was then extracted three times with 15 mL EtOAc. The organic phases were combined and dried over anhydrous Na_2SO_4. After the removal of the solvent under reduced pressure, the crude mixture was purified by column chromatography on silica gel (petroleum ether /EtOAc = 4:1) to give the **1o** as a white solid.



1o

Compound 1o: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.53-7.36 (m, 3H), 4.47 (s, 2H), 3.03 (s, 3H), 2.33-2.27 (m, 1H), 2.19-2.12 (m, 1H), 1.81-1.56 (m, 5H), 1.50-1.17 (m, 4H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.0, 142.7, 133.4, 132.8, 128.7, 128.6, 127.7, 52.2, 33.2, 29.3, 28.5, 26.0, 25.6; **ESI-MS** (ESI+) calcd for $C_{15}H_{20}NO$ $[M+H]^+$: 230.15; found: 230.20.

4. General Procedure for products 2a-2w



1a-1w **2a-2w** **3a-3w**

Isoindolinone derivatives (1 mmol), $Na_2S_2O_8$ (2 mmol), $MgSO_4$•$2H_2O$ (1 mmol), $Mn(OAc)_3$ (replaced with $CuSO_4$ in the preparation of *N*-phenylisoindolinone derivatives) (20% mmol), TBAI (20% mmol) and distilled CH_3CN were introduced into a Schlenk tube. Then, the tube was fitted with a rubber septum. After evacuation and N_2 backfill three times, the mixture was stirred at 90°C for 36 h. After the reaction, suction filtration to remove insolubles, then the crude mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 8:1) to give the ketone products **3a-3w**, then hexane/EtOAc = 2:1 to give the amide products **2a-2w**.

5. Determination of Water Content by Karl Fischer Titration

The KF titration was carried out with a Karl Fischer titrator ZDJ-2S from Beijing

Xianqu Weifeng Technology Development Co., Ltd., using the Karl Fischer Reagents (without pyridine, 3-5 mg H_2O/mL), purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). The polarising current for bipotentiometric end-point determination was 28 μA. The end-point criterion was the drift stabilization (30 g H_2O min^{-1}). The water content was calculated as described by Scaccia,[11] and the measurement was corrected for the baseline drift, defined as the residual or penetrating water that the apparatus removes per minute. Samples were analyzed three times each.

5.1 Preparation of Samples

Water or hydrates and distilled CH_3CN (4 mL) were introduced into a Schlenk tube. Then, the tube was fitted with a rubber septum. After evacuation and N_2 backfill three times, the mixture was stirred at 90ºC for a certain time.

5.2 Procedure

The baseline drift was at first measured under certain conditions as follows. 30 mL MeOH was added to the titration vessel and pre-titrated to dryness. Then, the dried solvent was kept in the vessel (without sample) for 1 h under stirring and subsequently titrated with a stop-delay time of 60 s. The baseline drift, in μg H_2O/mL, was calculated from the KF reagent volume added to the working medium to keep the vessel dry during the chosen time and take into account the water equivalent of the reagent.

The Karl Fischer Reagents were calibrated by 10 μL H_2O and got the F value of Fisher's test solution.

Then, an accurately weighed sample was introduced into the titration vessel and kept vigorously stirring. After reaching the endpoint, took a reading of the water content of samples. The values of water content were based on the average of three runs.

6. Chromatographic Conditions

Analyses were performed with a Shimadzu LC-20AP HPLC instrument equipped with a binary gradient pump, an autosampler, a column oven, and diode-array detection. An Agilent ZORBAX Eclipse Plus C18 column (2.1 mm × 150 mm, 3.5 μm) was used as

the stationary phase. The composition of mobile phases was acetic acid in water (0.5%, v/v) (A) and methanol (B). The method's base composition of 30% B was initialized and the linear gradient from 30 to 50% of B was applied from 0 to 13 min. From 13 to 15 min, the linear gradient from 50 to 95%. From 15 to 18 min, the composition of B was kept at 95%. The flow rate was 0.2 mL min^{-1}, and the temperature of the column oven was 30°C. The detection wavelength was 254 nm.

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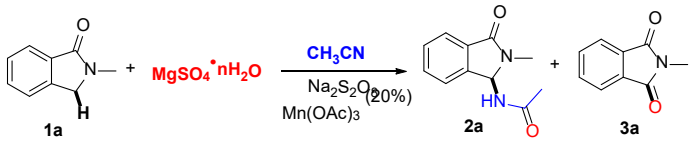
7. Optimization Experiments

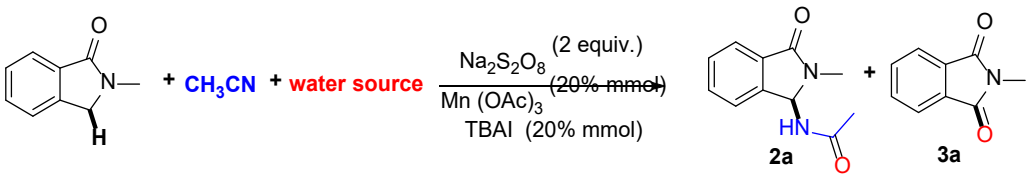
Table S1: Screening of Equivalents of Oxidants[a]



Entry	Oxidant	Equiv.	Conv. (%)	Yield (**2a**)	Yield (**3a**)
1	/	/	7	0	0
2	$Na_2S_2O_8$	1	30	5	15
3	$Na_2S_2O_8$	1.5	51	23	17
4	$Na_2S_2O_8$	2	92	68	21
5	$Na_2S_2O_8$	3	100	26	45
6[b]	$Na_2S_2O_8$	2	9	3	9

[a]Reaction conditions: 2-methylisoindolin-1-one (1 mmol), $Na_2S_2O_8$, $MgSO_4$•$2H_2O$ (2 mmol), $Mn(OAc)_3$ (20% mmol), TBAI (20% mmol) and CH_3CN (4 mL) at 90°C for 36 h under N_2 atmosphere. [b]The absence of $Mn(OAc)_3$.

Table S2: Screening of Water Sources[a]



Entry	X•nH$_2$O	Water Content (wt%) (N = 3)[b]	Conv. (%)	Yield[c] (**2a**)	Yield (**3a**)
1	HCOOLi•2H$_2$O	0.819 ± 0.015	1	n.d.	n.d.
2	LiSO$_4$•H$_2$O	0.586 ± 0.014	25	6	17
3	LiI•3H$_2$O	0.593 ± 0.009	50	38	11
4	LiCl•H$_2$O	0.789 ± 0.012	74	7	48
5	LiOAc•2H$_2$O	0.848 ± 0.014	83	18	53
6	Na$_2$SO$_4$•10H$_2$O	0.685 ± 0.011	66	36	27
7	Na$_2$SO$_4$•2H$_2$O	0.575 ± 0.011	55	35	15
8	NaHSO$_4$•H$_2$O	0.432 ± 0.013	69	46	20
9	Na$_2$CO$_3$•10H$_2$O	0.769 ± 0.003	61	n.d.	36
10	Na$_2$CO$_3$•H$_2$O	0.184 ± 0.010	50	13	35
11	NaOAc•3H$_2$O	0.476 ± 0.011	67	13	48
12	NaOAc•H$_2$O	0.134 ± 0.012	53	8	35
13	Na$_2$HPO$_4$•12H$_2$O	0.829±0.019	78	7	53
14	Na$_2$HPO$_4$•8H$_2$O	0.573 ± 0.021	56	33	23
15	Na$_3$PO$_4$•12H$_2$O	0.839 ± 0.003	91	24	51
16	Na$_3$PO$_4$•8H$_2$O	0.725 ± 0.015	77	31	28
17	K$_2$HPO$_4$•3H$_2$O	0.795 ± 0.018	81	n.d.	53
18	K$_3$PO$_4$•3H$_2$O	0.042 ± 0.015	83	16	49
19	K$_2$C$_2$O$_4$•H$_2$O	0.795 ± 0.014	33	n.d.	25
20	KF•2H$_2$O	0.823 ± 0.016	78	15	45
21	K$_2$CO$_3$•1.5H$_2$O	0.440 ± 0.014	85	18	48

22	$BeSO_4•4H_2O$	0.548 ± 0.011	77	11	32
23	$BeSO_4•2H_2O$	0.222 ± 0.013	68	22	16
24	$MgSO_4•7H_2O$	0.625 ± 0.010	96	46	41
25	$MgSO_4•6H_2O$	0.506 ± 0.009	95	52	37
26	$MgSO_4•5H_2O$	0.479 ± 0.008	95	55	32
27	$MgSO_4•4H_2O$	0.441 ± 0.010	93	62	29
28	$MgSO_4•3H_2O$	0.306 ± 0.016	93	67	24
29	$MgSO_4•2H_2O$	0.219 ± 0.013	92	68	21
30	$MgSO_4•H_2O$	0.152 ± 0.010	57	33	18
31	$Mg(OAc)_2•4H_2O$	0.779 ± 0.012	65	n.d.	43
32	$Mg(OAc)_2•H_2O$	0.268 ± 0.009	65	8	36
33	$MgHPO_4•3H_2O$	0.222 ± 0.013	100	18	42
34	$Mg_3(PO_4)_2•5H_2O$	0.158 ± 0.014	90	14	18
35	$Mg_3(PO_4)_2•4H_2O$	0.105 ± 0.022	74	16	15
36	$Mg_5(CO_3)_4(OH)_2•5H_2O$	0.177 ± 0.010	80	n.d.	21
37	$MgCl_2•6H_2O$	0.403 ± 0.011	77	23	26
38	$MgCl_2•5H_2O$	0.189 ± 0.015	71	32	30
39	$CaCl_2•6H_2O$	0.602 ± 0.011	56	n.d.	35
40	$CaCl_2•5H_2O$	0.338 ± 0.017	37	n.d.	25
41	$CaCl_2•2H_2O$	0.295 ± 0.012	31	n.d.	19
42	$CaBr•2H_2O$	0.587 ± 0.017	94	55	7
43	$CaBr•H_2O$	0.548 ± 0.011	80	50	n.d.
44	$CaSO_4•2H_2O$	0.288 ± 0.018	65	n.d.	37
45	$CaSO_4•H_2O$	0.189 ± 0.019	69	39	26
46	$CaSO_4•1/2H_2O$	0.115 ± 0.011	65	39	24
47	$Ca(HSO_4)•2H_2O$	0.200 ± 0.010	73	7	26

48	$Ca(OAc)_2•H_2O$	0.214 ± 0.011	50	n.d.	29
49	$Ca(C_2O_4)_2•2H_2O$	0.109 ± 0.016	38	n.d.	19
50	$SrCl_2•6H_2O$	0.796 ± 0.009	70	24	36
51	$SrCl_2•5H_2O$	0.303 ± 0.008	59	25	19
52	$SrOAc•1/2H_2O$	0.638 ± 0.022	64	8	44
53	$BaCl_2•2H_2O$	0.767 ± 0.012	56	n.d.	38
54	$Cu(COOCF_3)_2•H_2O$	0.012 ± 0	66	26	18
55	$CuCl_2•2H_2O$	0.664 ± 0.011	73	35	26
56	$Cu(NO_3)_2•3H_2O$	0.839 ± 0.010	75	21	42
57	$Cu(NO_3)_2•2H_2O$	0.678 ± 0.020	73	26	40
58	$CuSO_4•5H_2O$	0.647 ± 0.019	84	35	39
59	$CuSO_4•2H_2O$	0.415 ± 0.007	66	40	21
60	$Cu(OAc)_2•H_2O$	0.580 ± 0.012	51	6	26
61	$Fe_2(SO_4)_3•H_2O$	0.588 ± 0.017	67	26	31
62	$FeCl_3•6H_2O$	0.598 ± 0.013	39	n.d.	17
63	$FeCl_2•4H_2O$	0.516 ± 0.021	31	13	15
64	$Ni(OAc)_2•4H_2O$	0.645 ± 0.014	69	16	24
65	$Ni(OAc)_2•H_2O$	0.422 ± 0.021	52	n.d.	48
66	$NiCl_2•6H_2O$	0.732 ± 0.016	65	17	19
67	$NiCl_2•4H_2O$	0.662 ± 0.012	50	25	22
68	$Mn(OAc)_2•H_2O$	0.758 ± 0.049	99	7	54

[a]Reaction conditions: 2-methylisoindolin-1-one (1 mmol), $Na_2S_2O_8$ (2 mmol), water source (2 mmol, take $MgSO_4•7H_2O$ as example, 2/7 mmol was weighed), $Mn(OAc)_3$ (20% mmol), TBAI (20% mmol) and CH_3CN (4 mL) at 90°C for 36 h under N_2 atmosphere. [b]The water contents were measured at 12 hours. [c]Yield detected by HPLC based on three runs of each reaction.

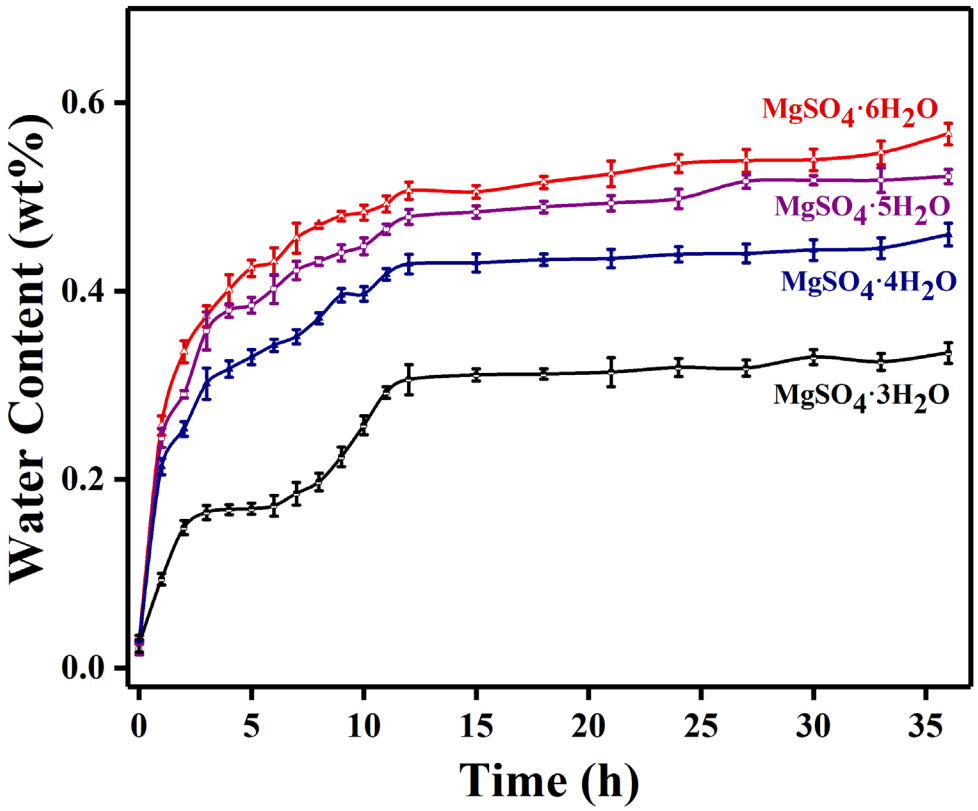
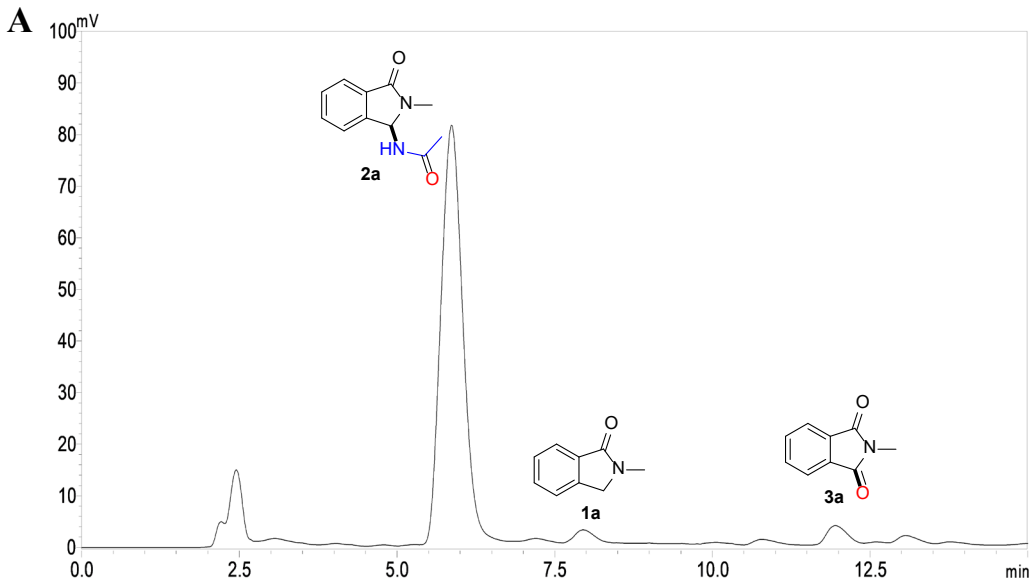


Figure S1. The water content of $MgSO_4$ hydrates as a function of time.



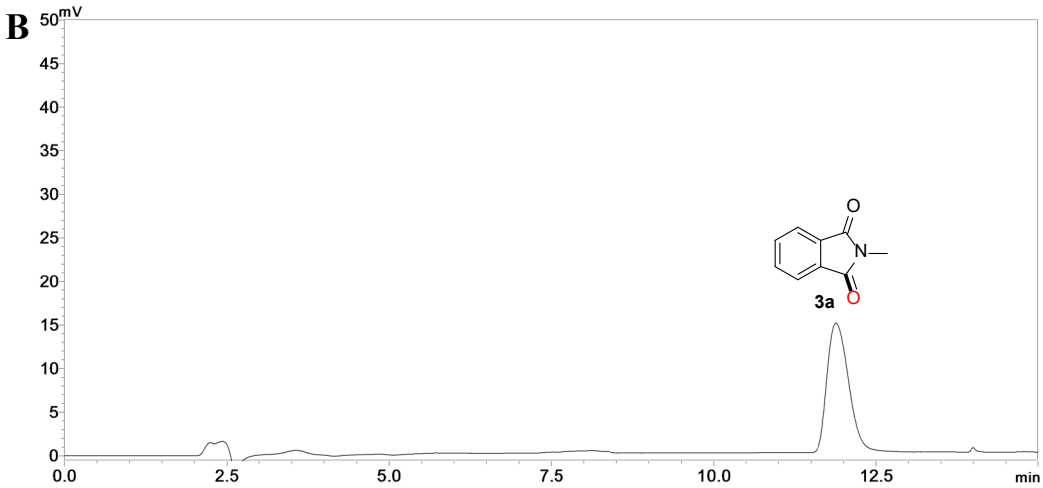
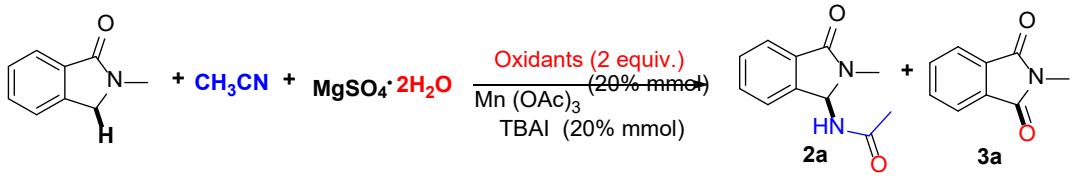


Figure S2. HPLC spectra of the use of 1 equivalent of $MgSO_4 \cdot 2H_2O$ (A); HPLC spectra of the use of 8 equivalents of free-water (B).

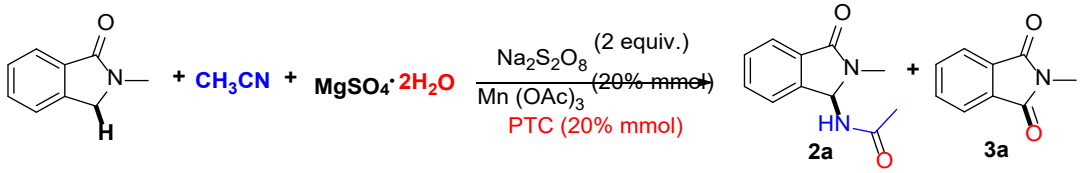
Table S3: Screening of Oxidants[a]



Entry	Oxidants	Conv. (%)	Yield[b] (**2a**)	Yield (**3a**)
1	/	11	n.d.	n.d.
2	$Na_2S_2O_8$	92	68	21
3	$K_2S_2O_8$	55	19	34
4	$(NH_4)_2S_2O_8$	61	26	30
5	$^tBuOO^tBu$	100	n.d.	69
6	TBHP	82	n.d.	54
7	DDQ	43	n.d.	n.d.
8	I_2	0	n.d.	n.d.
9	$Ce(NH_4)_2(NO_3)_6$	65	48	16
10	$KMnO_4$	99	n.d.	86
11	m-CPBA	34	15	n.d.

[a]Reaction conditions: 2-methylisoindolin-1-one (1 mmol), Oxidants (2 mmol), $Mn(OAc)_3$ (20% mmol), TBAI (20% mmol), $MgSO_4$•$2H_2O$ (1 mmol) and CH_3CN (4 mL) at 90°C for 36 h under N_2 atmosphere. [b]Yield detected by HPLC based on three runs of each reaction.

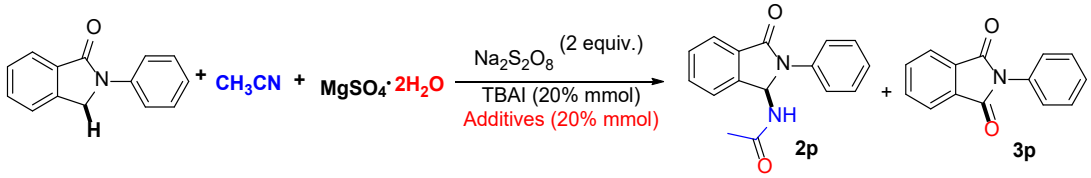
Table S4: Screening of PTCs[a]



Entry	PTCs	Conv. (%)	Yield[b] (**2a**)	Yield (**3a**)
1	/	40	11	10
2	TBAI	92	68	21
3	TBAB	100	0	84
4	TBAC	91	18	49
5	TBAF	92	22	41
6	TEAB	99	n.d.	69
7	TEAI	40	8	22
8	18-crown-6	82	n.d.	52
9	TBAHS	42	n.d.	35
10	TEBAC	47	n.d.	37
11	TPPB	100	18	71
12	PTMA	92	53	15
13	BTAI	96	57	36

[a]Reaction conditions: 2-methylisoindolin-1-one (1 mmol), $Na_2S_2O_8$ (2 mmol), $Mn(OAc)_3$ (20% mmol), PTCs (20% mmol), $MgSO_4$•$2H_2O$ (1 mmol) and CH_3CN (4 mL) at 90°C for 36 h under N_2 atmosphere. [b]Yield detected by HPLC based on three runs of each reaction. TBAI: Tetrabutylammonium Iodide; TBAB: Tetrabutylammonium Bromide; TBAC: Tetrabutylammonium Chloride; TBAF: Tetrabutylammonium Fluoride; TEAB: Tetraethylammonium Bromide; TEAI: Tetraethylammonium Iodide; TBAHS: Tetrabutylammonium Hydrogen Sulfate; TEBAC: Benzyltriethylammonium Chloride; TPPB: Tetraphenylphosphonium Bromide; PTMA: Phenyltrimethylammonium Iodide. BTAI: Benzyltriethylammonium Iodide.

Table S5: Screening of Additives for *N*-phenylisoindolinone[a]

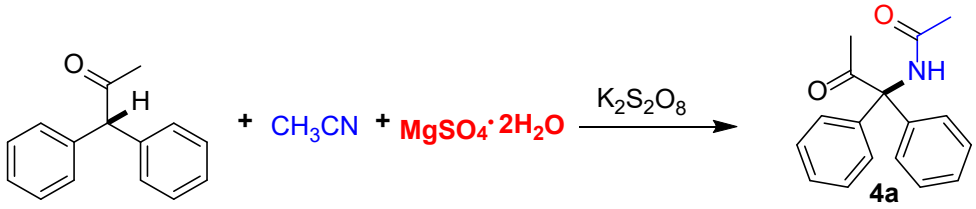


Entry	Additives	Conv. (%)	Yield[b] (**2p**)	Yield (**3p**)
1	/	21	6	11
2	$Mn(OAc)_3$	79	37	31
3	CuBr	95	61	23
4	$AgNO_3$	100	44	49
5	$Cu(OAc)_2$	81	32	35
6	CuI	55	20	29
7	AgOTf	78	36	18
8	$Mn(OAc)_2$	47	23	15
9	$Fe(OAc)_2$	47	17	21
10	$Cu(CN)_4Ph_4PF_6$	39	n.d.	22
11	$CuBr_2$	68	31	32
12	$FeCl_3$	26	n.d.	11
13	$CuSO_4$	100	65	23
14	$(CF_3SO_2)_3Sc$	48	14	18
15	CuCN	100	42	38

[a]Reaction conditions: 2-phenylisoindolin-1-one (1 mmol), $Na_2S_2O_8$ (2 mmol), Additives (20% mmol), TBAI (20% mmol), $MgSO_4$•$2H_2O$ (1 mmol) and CH_3CN (4 mL) at 90°C for 36 h under N_2 atmosphere. [b]Yield detected by HPLC based on three runs of each reaction.

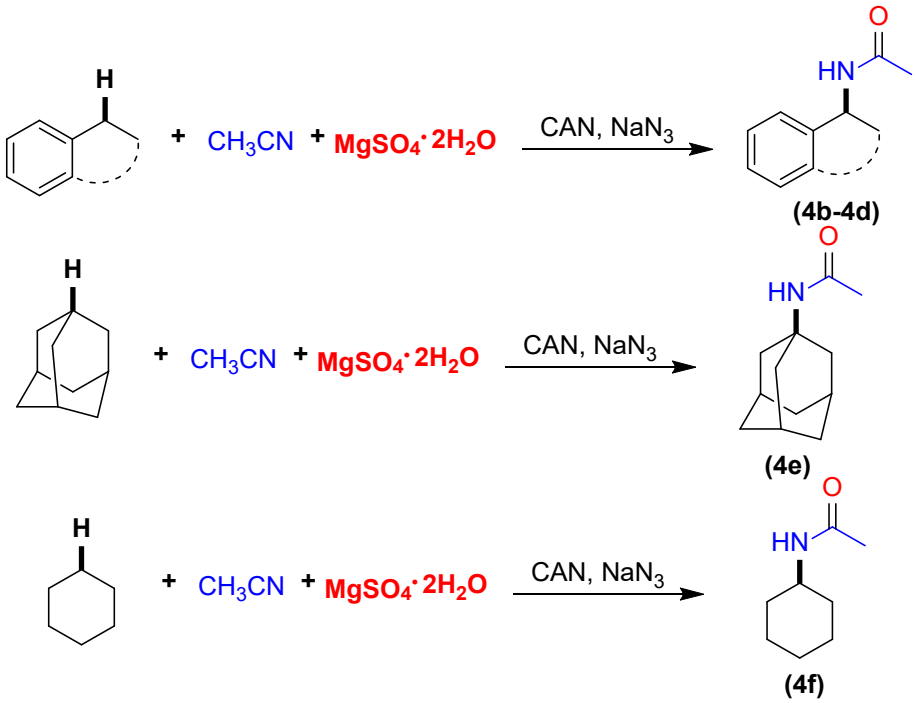
8. Gram-scale preparation of 4a-4o

8.1 Synthesis of 4a



1,1-diphenylpropan-2-one (10 mmol), $MgSO_4$•$2H_2O$ (10 mmol), $Na_2S_2O_8$ (20 mmol), $Cu(OTf_3)_2$ (1 mmol) and distilled CH_3CN (30 mL) were introduced into a Schlenk tube. Then, the tube was fitted with a rubber septum. After evacuation and N_2 backfill three times, the mixture was stirred at 90°C overnight. After the reaction was completed, suction filtration to remove insolubles, then the crude mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to give pure product **4a** (1.55 g, 58%).

8.2 Synthesis of 4b-4f



A deoxygenated solution of CAN (2.3 equiv.) in acetonitrile (30 mL) was added dropwise to a solution of substrates (1 equiv.), sodium azide (1.5 equiv.) and

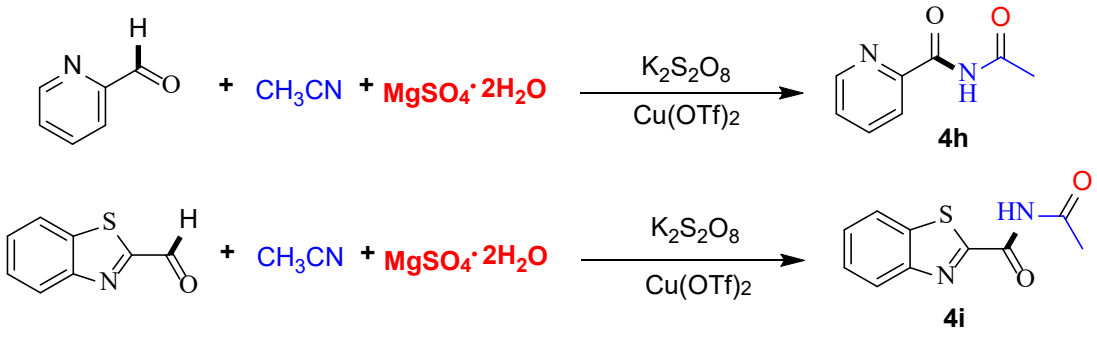
$MgSO_4$•$2H_2O$ (1 equiv.) in acetonitrile (20 mL) stirred at 0ºC under N_2 atmosphere. After the reaction was completed, the solvent was removed and the residue diluted with water (40 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic extract was washed with water, brine and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was subjected to column chromatography on silica gel, using petroleum ether-EtOAc (8:1-2:1) as eluent to give pure product **4b**-**4f**.

8.3 Synthesis of 4g

4g

Naphthalen-2-ol (10 mmol), 4-nitrobenzaldehyde (10 mmol), $MgSO_4$•$2H_2O$ (10 mmol), $Ce(SO_4)_2$ (10 mmol) and distilled CH_3CN (40 mL) were introduced into a Schlenk tube. Then, the tube was fitted with a rubber septum. After evacuation and N_2 backfill three times, the mixture was stirred at 85ºC for 16 h. After the reaction was completed, 50 mL H_2O was poured into the mixture, which was then extracted three times with 50 mL EtOAc. The organic phases were combined and dried over anhydrous Na_2SO_4. After the removal of the solvent under reduced pressure, the crude mixture was purified by column chromatography on silica gel (petroleum ether /EtOAc = 2:1) to give the **4g** as a white solid (1.58 g, 47%).

8.4 Synthesis of 4h and 4i

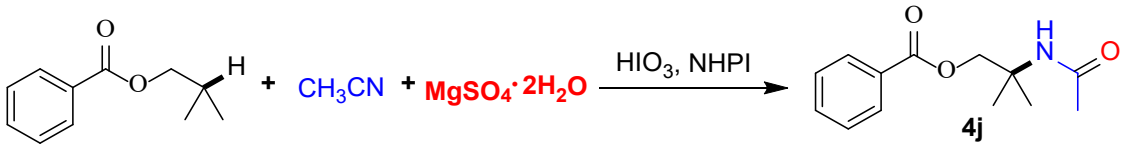


4h

4i

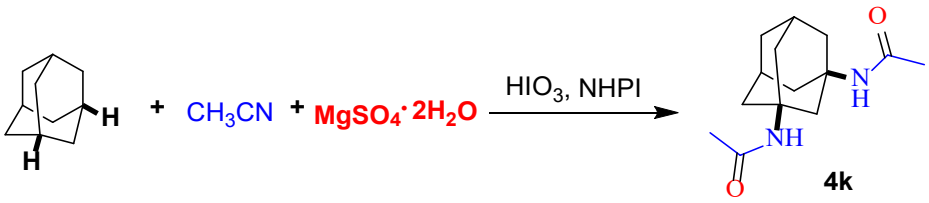
N-heteroaryl aldehydes (10 mmol), $MgSO_4 \cdot 2H_2O$ (10 mmol), $K_2S_2O_8$ (10 mmol), $Cu(OTf)_2$ (2 mmol), and distilled CH_3CN (40 mL) were added to a 75 mL reaction tube. Then the reaction mixture was stirred at 90ºC for 6 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (50 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether-EtOAc (10:1-6:1) as eluent to give pure product **4h** (1.15 g, 70% yield) and **4i** (1.34 g, 61% yield).

8.5 Synthesis of 4j



An oven-dried 75 mL Schlenk tube containing a magnetic stir bar was charged with isobutyl benzoate (10 mmol), $MgSO_4 \cdot 2H_2O$ (10 mmol), HIO_3 (20 mmol), NHPI (4 mmol), and distilled CH_3CN (40 mL). The Schlenk tube was purged with N_2 and sealed with a screw cap. The reaction mixture was stirred at 80°C for 24 h. After the reaction, suction filtration to remove insolubles, then the crude mixture was purified by flash column chromatography on silica gel (petroleum ether /EtOAc = 7:3) gave the product **4j** as a white solid (1.67 g, 71% yield).

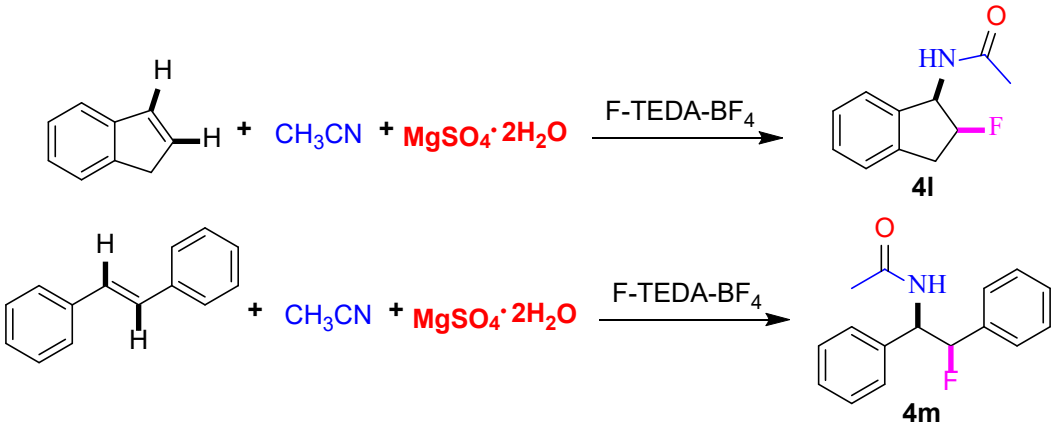
8.6 Synthesis of 4k



An oven-dried 75 mL Schlenk tube containing a magnetic stir bar was charged with adamantine (10 mmol), $MgSO_4 \cdot 2H_2O$ (10 mmol), HIO_3 (12 mmol), NHPI (2 mmol), and distilled CH_3CN (40 mL). The Schlenk tube was purged with N_2 and sealed with a screw cap. The reaction mixture was stirred at 80°C for 24 h. After the reaction, suction filtration to remove insolubles, then the crude mixture was purified by flash column chromatography on silica gel (petroleum ether /EtOAc = 6:4 then MeOH) gave the

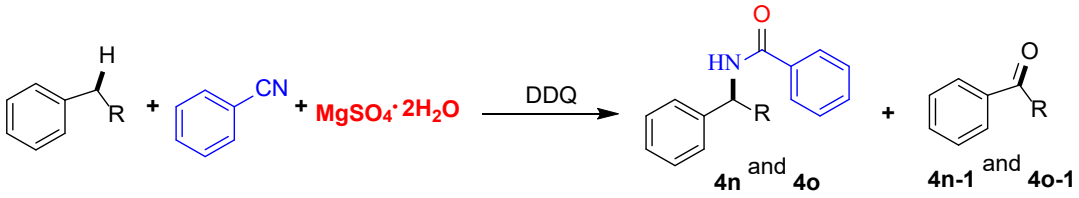
product **4k** as a white solid (1.45 g, 58% yield).

8.7 Synthesis of 4l and 4m



Alkenes (10 mmol), $MgSO_4$•$2H_2O$ (10 mmol), F-TEDA-BF_4 (20 mmol), and distilled CH_3CN (40 mL) were introduced into a Schlenk tube. Then, the tube was fitted with a rubber septum. After evacuation and N_2 backfill three times, the mixture was stirred at 90°C for 24 h. 50 mL H_2O was poured into the mixture, which was then extracted three times with 50 mL EtOAc. The organic phases were combined and dried over anhydrous Na_2SO_4. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether-EtOAc (8:1-4:1) as eluent to give pure product **4l** (1.12 g, 58% yield) and **4m** (1.37 g, 53% yield).

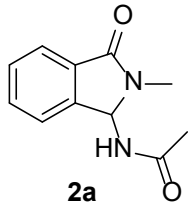
8.8 Synthesis of 4n and 4o



Diphenylmethane or 1,2,3,4-tetrahydronaphthalene (10 mmol), $MgSO_4$•$2H_2O$ or H_2O (10 mmol), benzonitrile (200 mmol), DDQ (1.2 mmol), and distilled 1,2-dichloroethane (30 mL) were introduced into a Schlenk tube. After evacuation and N_2 backfill three times, the mixture was stirred at 90°C for 24 h. 50 mL H_2O was poured into the mixture, which was then extracted three times with 50 mL dichloromethane. The organic phases were combined and dried over anhydrous Na_2SO_4. After the removal of the solvent

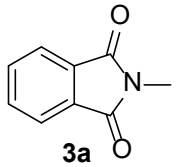
under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 50:1) to give the ketone products **4n-1** and **4o-1**, then petroleum ether /EtOAc = 4:1 to give the amide products as a white solid (1.12 g, 39% yield for **4n** and 0.89 g, 35% yield for **4o**).

9. Characterization Data of Products



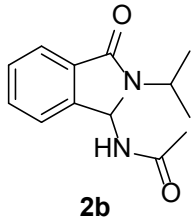
2a

Compound 2a: pale yellow solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.61 (d, J = 9.2 Hz, 1H), 7.71-7.66 (m, 1H), 7.66-7.60 (m, 1H), 7.58-7.51 (m, 2H), 6.33 (d, J = 9.2 Hz, 1H), 2.88 (s, 3H), 1.96 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.3, 167.7, 142.5, 132.1, 131.7, 129.4, 123.0, 122.9, 65.1, 26.5, 23.3; **HRMS** (ESI+) calcd for $C_{11}H_{13}N_2O_2$ $[M+H]^+$: 205.0899; found: 205.0898.



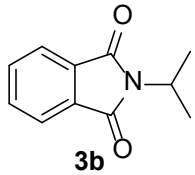
3a

Compound 3a: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.20-8.06 (m, 4H), 3.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 133.9, 132.2, 123.2, 23.9; **HRMS (ESI+)** calcd for $C_9H_8NO_2$ $[M+H]^+$: 162.0477; found: 162.0502.



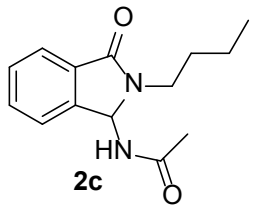
2b

Compound 2b: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 1H), 7.59-7.54 (m, 1H), 7.52-7.45 (m, 2H), 6.68 (d, J = 9.9 Hz, 1H), 5.90-5.83 (m, 1H), 4.46-4.36 (m, 1H), 2.12 (s, 3H), 1.43 (d, J = 6.9 Hz, 3H), 1.38 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.5, 167.7, 143.1, 132.2, 132.1, 129.4, 123.0, 122.8, 62.6, 44.3, 23.4, 20.9, 20.4; **HRMS (ESI+)** calcd for $C_{13}H_{17}N_2O_2$ $[M+H]^+$: 233.1212; found: 233.1201.



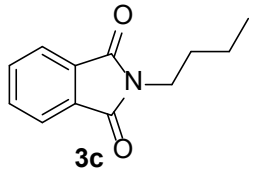
3b

Compound 3b: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.78 (m, 2H), 7.75-7.67 (m, 2H), 4.55 (q, J = 6.8 Hz, 1H), 1.54-1.46 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 133.7, 132.1, 123.0, 43.0, 20.1; **HRMS (ESI+)** calcd for $C_{11}H_{12}NO_2$ $[M+H]^+$: 190.0790; found: 190.0852.



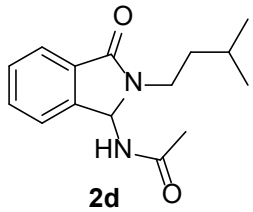
2c

Compound 2c: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.62 (d, J = 8.6 Hz, 1H), 7.78-7.61 (m, 2H), 7.58-7.51 (m, 2H), 6.43-6.38 (m, 1H), 3.66-3.57 (m, 1H), 3.11-3.02 (m, 1H), 1.94 (s, 3H), 1.61-1.49 (m, 2H), 1.33-1.18 (m, 2H), 0.88 (td, J = 7.3, 2.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 167.6, 142.8, 132.1, 131.8, 129.4, 123.1, 63.1, 39.1, 30.1, 30.0, 20.1, 20.0, 13.6; **HRMS (ESI+)** calcd for $C_{14}H_{19}N_2O_2$ $[M+H]^+$: 247.1368; found: 247.1370.



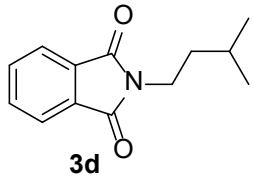
3c

Compound 3c: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.84 (m, 2H), 7.74-7.71 (m, 2H), 3.71 (t, J = 12.8 Hz, 2H), 1.73-1.64 (m, 2H), 1.45-1.35 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 133.8, 132.2, 123.1, 37.8, 30.6, 20.1, 13.6; **HRMS (ESI+)** calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$: 204.0946; found: 204.0969.



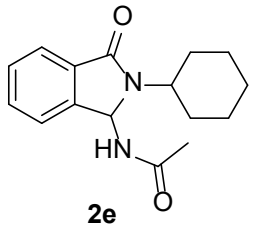
2d

Compound 2d: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.62 (d, J = 9.3 Hz, 1H), 7.70-7.67 (m, 1H), 7.67-7.64 (m, 1H), 7.59-7.52 (m, 2H), 6.41 (d, J = 9.3 Hz, 1H), 3.70-3.60 (m, 1H), 3.13-3.04 (m, 1H), 1.95 (s, 3H), 1.57-1.42 (m, 3H), 0.89 (dd, J = 6.3, 1.7 Hz, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.0, 166.7, 143.7, 132.6, 132.4, 129.7, 123.8, 122.9, 63.2, 37.8, 37.0, 25.8, 23.1, 23.0, 22.6; **HRMS (ESI+)** calcd for $C_{15}H_{21}N_2O_2$ $[M+H]^+$: 261.1525; found: 261.1527.



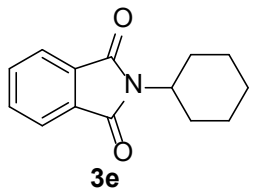
3d

Compound 3d: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.83 (m, 2H), 7.78-7.68 (m, 2H), 3.79-3.67 (m, 2H), 1.71-1.52 (m, 3H), 1.06-0.93 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 133.8, 132.2, 123.1, 37.3, 36.5, 25.9, 22.4; **HRMS (ESI+)** calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$: 218.1103; found: 218.1135.



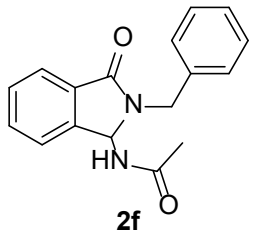
2e

Compound 2e: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.65 (m, 1H), 7.58-7.52 (m, 1H), 7.48-7.43 (m, 2H), 6.67 (d, *J* = 9.8 Hz, 1H), 6.02 (d, *J* = 10.3 Hz, 1H), 4.05-3.93 (m, 1H), 2.13 (s, 3H), 1.97-1.61 (m,7H), 1.47-1.32 (m, 2H), 1.29-1.13 (m, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.3, 166.9, 144.3, 132.5, 129.6, 123.5, 122.8, 63.0, 52.2, 31.3, 30.5, 26.2, 26.1, 25.6, 23.3; **HRMS (ESI+)** calcd for $C_{16}H_{21}N_2O_2$ $[M+H]^+$: 273.1525; found: 273.1527.



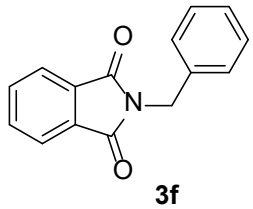
3e

Compound 3e: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.71-7.67 (m, 2H), 4.15-4.06 (m, 1H), 2.28-2.14 (m, 2H), 1.95-1.81 (m, 2H), 1.79-1.64 (m, 3H), 1.46-1.20 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 133.7, 132.1, 123.0, 50.9, 29.9, 26.0, 25.1; **HRMS (ESI+)** calcd for $C_{14}H_{16}NO_2$ $[M+H]^+$: 230.1103; found: 230.1135.



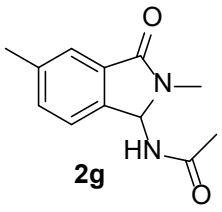
2f

Compound 2f: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.64 (d, *J* = 9.2 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.69-7.63 (m, 1H), 7.61-7.56 (m, 1H), 7.53 (d, *J* = 7.1 Hz, 1H), 7.35-7.22 (m, 5H), 6.35 (d, *J* = 9.2 Hz, 1H), 4.77 (d, *J* = 15.3 Hz, 1H), 4.33 (d, *J* = 15.3 Hz, 1H), 1.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.0, 167.6, 142.8, 137.1, 132.3, 131.7, 129.5, 128.6, 128.4, 127.6, 123.3, 123.2, 63.6, 43.9, 23.2; **HRMS (ESI+)** calcd for $C_{17}H_{17}N_2O_2$ $[M+H]^+$: 281.1212; found: 281.1220.



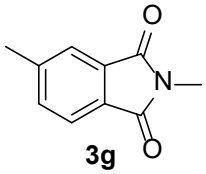
3f

Compound 3f: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 2H), 7.73-7.67 (m, 2H), 7.45-7.40 (m, 2H), 7.33-7.22 (m, 3H), 4.84 (s, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.2, 137.1, 135.0, 132.0, 129.0, 127.9, 127.8, 123.7, 41.3; **HRMS (ESI+)** calcd for $C_{15}H_{11}NO_2Na$ $[M+Na]^+$: 260.0790; found: 260.0752.



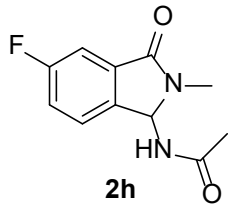
2g

Compound 2g: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.54 (d, J = 9.1 Hz, 1H), 7.48-7.45 (m, 1H), 7.44-7.35 (m, 2H), 6.25 (d, J = 9.1 Hz, 1H), 2.84 (s, 3H), 2.38 (s, 3H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 167.8, 143.0, 142.9, 130.2, 129.2, 123.5, 122.7, 65.0, 26.5, 23.3, 21.8; **HRMS (ESI+)** calcd for $C_{12}H_{15}N_2O_2$ $[M+H]^+$: 219.1055; found: 219.1050.



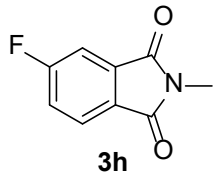
3g

Compound 3g: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.69 (m, 1H), 7.65-7.62 (m, 1H), 7.51-7.46 (m, 1H), 3.18-3.14 (m, 3H), 2.50 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 168.5, 145.1, 134.4, 132.6, 129.6, 123.7, 123.1, 23.9, 22.0; **HRMS (ESI+)** calcd for $C_{10}H_{10}NO_2$ $[M+H]^+$: 176.0633; found: 176.0656.



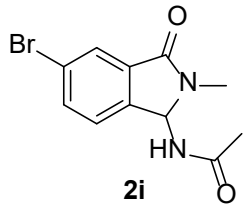
2h

Compound 2h: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.61 (d, J = 9.1 Hz, 1H), 7.62-7.57 (m, 1H), 7.52-7.44 (m, 2H), 6.32 (d, J = 9.1 Hz, 1H), 2.89 (s, 3H), 1.96 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.6 (d, $J_{C\text{-}F}$ = 3.78 Hz), 163.8, 161.8, 136.3 (d, $J_{C\text{-}F}$ = 1.26 Hz), 134.9 (d, $J_{C\text{-}F}$ = 8.82 Hz), 124.0 (d, $J_{C\text{-}F}$ = 8.82 Hz), 118.6 (d, $J_{C\text{-}F}$ = 23.94 Hz), 110.3 (d, $J_{C\text{-}F}$ = 22.68 Hz), 51.6, 29.6; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -112.16 – -112.17 (m); **HRMS (ESI+)** calcd for $C_{11}H_{12}FN_2O_2$ $[M+H]^+$: 223.0805; found: 223.0802.



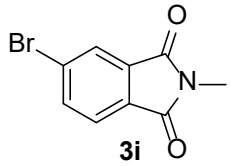
3h

Compound 3h: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.94-7.90 (m, 1H), 7.77-7.73 (m, 1H), 7.63-7.59 (m, 1H), 3.03 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5 (d, $J_{C\text{-}F}$ = 22.4 Hz), 167.0 (d, $J_{C\text{-}F}$ = 2.83 Hz), 165.0, 135.1 (d, $J_{C\text{-}F}$ = 9.57 Hz), 128.0 (d, $J_{C\text{-}F}$ = 2.83 Hz), 125.5 (d, $J_{C\text{-}F}$ = 9.39 Hz), 120.8, 120.7, 111.1 (d, $J_{C\text{-}F}$ = 2.83 Hz), 24.2; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -103.5 – -103.6 (m); **HRMS (ESI+)** calcd for $C_9H_7FNO_2$ $[M+H]^+$: 180.0383; found: 180.0405.



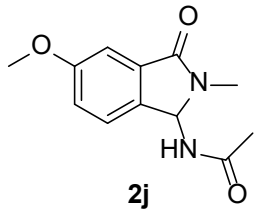
2i

Compound 2i: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.68 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 9.7 Hz, 1H), 6.23-6.20 (m, 1H), 3.03 (s, 3H), 2.20 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 166.3, 141.2, 135.3, 133.4, 125.9, 124.5, 123.7, 64.9, 26.6, 23.2; **HRMS (ESI+)** calcd for $C_{11}H_{12}BrN_2O_2$ $[M+H]^+$: 283.0004; found: 283.0004.



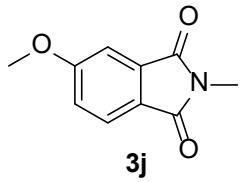
3i

Compound 3i: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.93 (m, 1H), 7.87-7.73 (m, 1H), 7.72-7.69 (m, 1H), 3.18 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 166.4, 138.7, 134.8, 134.4, 129.8, 122.2, 118.4, 24.2; **HRMS (ESI+)** calcd for $C_9H_7BrNO_2$ $[M+H]^+$: 239.9582; found: 239.9604.



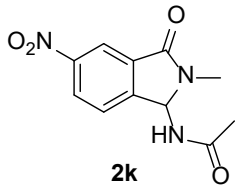
2j

Compound 2j: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.54 (d, *J* = 9.1 Hz, 1H), 7.50-7.36 (m, 1H), 7.21-7.12 (m, 2H), 6.25 (d, *J* = 9.2 Hz, 1H), 3.83 (s, 3H), 2.87 (s, 3H), 1.94 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 167.6, 160.8, 134.3, 133.2, 123.8, 119.7, 106.0, 64.7, 55.5, 26.7, 23.3; **HRMS (ESI+)** calcd for $C_{12}H_{15}N_2O_3$ $[M+H]^+$: 235.1004; found: 235.1022.



3j

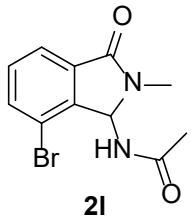
Compound 3j: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 1H), 7.31-7.30 (m, 1H), 7.14-7.11 (m, 1H), 3.90 (s, 3H), 3.14 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 164.6, 134.8, 124.8, 124.1, 119.5, 108.1, 56.1, 23.9; **HRMS (ESI+)** calcd for $C_{10}H_{10}NO_3$ $[M+H]^+$: 192.0582; found: 192.0615.



2k

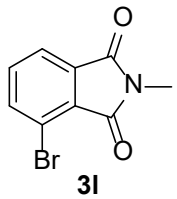
Compound 2k: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.72 (d, *J* = 8.9 Hz, 1H), 8.51-8.45 (m, 1H), 8.34 (d, *J* = 2.1 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 8.9 Hz, 1H), 2.93 (s,

3H), 1.97 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.1, 164.8, 149.9, 149.1, 134.1, 127.5, 125.5, 117.7, 65.2, 27.0, 23.1; **HRMS (ESI+)** calcd for $C_{11}H_{12}N_3O_4$ $[M+H]^+$: 250.0750; found: 250.0772.



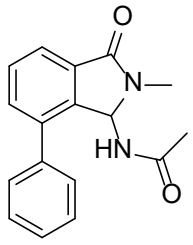
2l

Compound 2l: pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.66 (m, 1H), 7.62-7.58 (m, 1H), 7.39-7.33 (m, 1H), 6.43 (d, J = 9.8 Hz, 1H), 6.27 (d, J = 9.9 Hz, 1H), 2.99 (s, 3H), 2.19 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.0, 166.1, 140.9, 135.6, 134.6, 131.3, 122.1, 117.9, 65.3, 26.5, 23.1; **HRMS (ESI+)** calcd for $C_{11}H_{12}BrN_2O_2$ $[M+H]^+$: 283.0004; found: 283.0008.



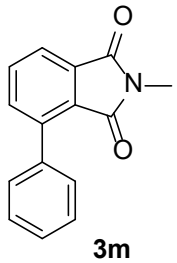
3l

Compound 3l: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.57-7.50 (m, 1H), 3.18 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.1, 136.9, 133.9, 130.7, 128.8, 126.6, 124.6, 24.2; **HRMS (ESI+)** calcd for $C_9H_7BrNO_2$ $[M+H]^+$: 239.9582; found: 239.9601.



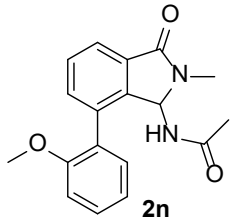
2m

Compound 2m: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.13 (d, J = 9.4 Hz, 1H), 7.72-7.68 (m, 1H), 7.67-7.60 (m, 2H), 7.48-7.44 (m, 2H), 7.43-7.34 (m, 3H), 6.70 (d, J = 9.4 Hz, 1H), 2.86 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.4, 166.4, 140.4, 138.1, 138.0, 133.6, 132.7, 130.3, 128.7, 128.6, 128.0, 122.0, 64.7, 26.6, 22.3; **HRMS (ESI+)** calcd for $C_{17}H_{16}N_2O_2Na$ $[M+Na]^+$: 303.1212; found: 303.1246.



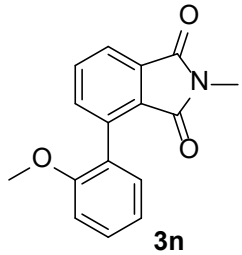
3m

Compound 3m: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.86 (m, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.68-7.65 (m, 1H), 7.60-7.56 (m, 2H), 7.52-7.47 (m, 3H), 3.14 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 168.0, 141.0, 136.2, 135.9, 133.7, 133.4, 129.4, 128.7, 128.1, 127.6, 122.1, 23.9; **HRMS (ESI+)** calcd for $C_{15}H_{12}NO_2$ $[M+H]^+$: 238.0790; found: 238.0822.



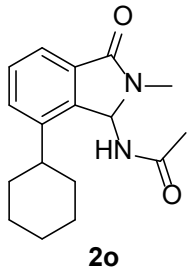
2n

Compound 2n: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.01 (d, J = 9.6 Hz, 1H, major), 7.96 (d, J = 9.6 Hz, 0.1H, minor), 7.68-7.54 (m, 4H, major), 7.52-7.48 (m, 0.5H, minor), 7.48-7.43 (m, 1.1H, major 1H, minor 0.1H), 7.42-7.38 (m, 1H, major), 6.99-6.95 (m, 0.1H, minor), 6.84 (d, J = 8.8 Hz, 1H, major), 6.36-6.32 (m, 0.1H, minor), 6.30-6.22 (m, 1H, major), 3.69 (s, 0.3H, minor), 3.67 (s, 3H, major), 2.79 (s, 3.3H, major 3H, minor 0.3H), 1.38 (s, 3H, major), 1.28 (s, 0.3H, minor); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.2, 170.2, 166.9, 166.6, 156.4, 156.2, 143.8, 141.8, 138.8, 138.2, 133.9, 133.6, 133.5, 132.7, 132.6, 132.5, 130.1, 129.8, 129.4, 123.9, 123.0, 122.4, 121.9, 120.5, 114.3, 65.0, 64.9, 55.9, 26.8, 26.5, 23.2, 22.3; **HRMS (ESI+)** calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$: 311.1317; found: 311.1320.



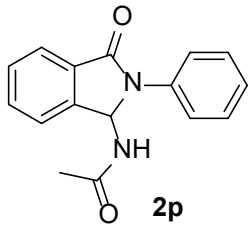
3n

Compound 3n: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84-7.79 (m, 1H), 7.76-7.65 (m, 1H), 7.61-7.56 (m, 1H), 7.45-7.38 (m, 1H), 7.25-7.20 (m, 1H), 7.07-6.97 (m, 2H), 3.74 (s, 3H), 3.10 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 156.8, 136.8, 136.4, 133.3, 132.7, 130.6, 130.2, 125.7, 121.9, 120.4, 110.8, 55.5, 23.8; **HRMS (ESI+)** calcd for $C_{16}H_{14}NO_3$ $[M+H]^+$: 268.0895; found: 268.0923.

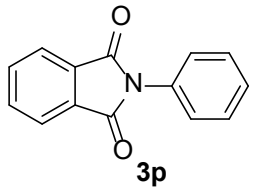


2o

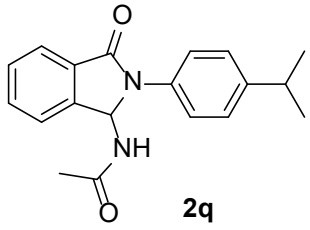
Compound 2o: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.54 (d, J = 10.8 Hz, 1H), 7.55-7.41 (m, 3H), 6.39 (d, J = 10.5 Hz, 1H), 2.82 (s, 3H), 2.58-2.49 (m, 1H), 1.89 (s, 3H), 1.80-1.63 (m, 5H), 1.51-1.16 (m, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.3, 166.9, 144.0, 140.5, 132.7, 130.1, 129.7, 120.5, 64.1, 34.2, 33.0, 27.0, 26.3, 26.0, 23.6, 22.9, 14.0; **HRMS (ESI+)** calcd for $C_{17}H_{22}N_2O_2Na$ $[M+Na]^+$: 309.1681; found: 309.1643.



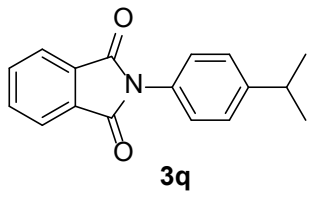
Compound 2p: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.4 Hz, 1H), 7.75-7.69 (m, 2H), 7.69-7.65 (m, 1H), 7.62-7.56 (m, 2H), 7.48-7.41 (m, 2H), 7.31-7.22 (m, 2H), 5.81 (d, *J* = 10.2 Hz, 1H), 2.02 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.4, 166.2, 143.7, 137.1, 133.4, 132.0, 130.0, 129.1, 125.4, 123.7, 123.5, 123.0, 64.4, 23.0; **HRMS (ESI+)** calcd for $C_{16}H_{15}N_2O_2$ $[M+H]^+$: 267.1055; found: 267.1058.



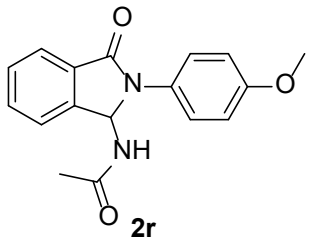
Compound 3p: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.96-7.91 (m, 2H), 7.90-7.86 (m, 2H), 7.53-7.47 (m, 2H), 7.44-7.38 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 134.4, 131.8, 131.7, 129.1, 128.1, 126.6, 123.8; **HRMS (ESI+)** calcd for $C_{14}H_{10}NO_2$ $[M+H]^+$: 224.0633; found: 224.0777.



Compound 2q: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.72 (d, *J* = 9.5 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.75-7.69 (m, 1H), 7.65-7.59 (m, 1H), 7.59-7.54 (m, 3H), 7.32-7.28 (m, 2H), 7.08 (d, *J* = 9.4 Hz, 1H), 2.95-2.87 (m, 1H), 1.81 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.1, 166.5, 146.0, 143.5, 134.4, 133.5, 131.7, 130.1, 127.0, 123.6, 123.5, 123.4, 64.6, 33.4, 24.3, 24.2, 23.0; **HRMS (ESI+)** calcd for $C_{19}H_{21}N_2O_2$ $[M+H]^+$: 309.1525; found: 309.1524.

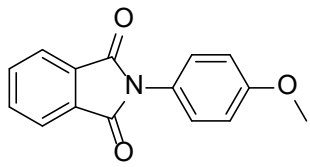


Compound 3q: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.84-7.79 (m, 2H), 7.41-7.35 (m, 4H), 3.05-2.94 (m, 1H), 1.31 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4, 148.9, 134.3, 131.8, 129.2, 127.2, 126.4, 123.7, 33.9, 23.9; **HRMS (ESI+)** calcd for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1103; found: 266.1125.



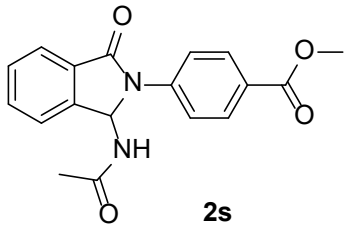
2r

Compound 2r: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) 8.73-8.64 (m, 1.8H, major 1H, minor 0.8H), 8.07-7.87 (m, 0.8H, minor), 7.81-7.75 (m, 1.8H, major 1H, minor 0.8H), 7.74-7.66 (m, 2H, major), 7.71-7.66 (m, 1.6H, minor), 7.58-7.51 (m, 3H, major), 7.51-7.46 (m, 2.6H, major 1H, minor 1.6H), 7.26-7.12 (m, 0.8H, minor), 7.12-7.03 (m, 3.6H, major 2H, minor 1.6H), 3.95-3.90 (m, 2.4 H, minor), 3.85 (s, 3H, major), 1.88 (s, 2.4 H, minor), 1.86 (s, 3H, major); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 170.7, 166.5, 157.3, 142.2, 142.0, 133.8, 132.9, 132.7, 131.7, 129.9, 129.8, 128.8, 124.1, 123.6, 123.6, 123.4, 123.1, 114.2, 110.6, 64.4, 64.3, 56.6, 55.4, 23.3; **HRMS (ESI+)** calcd for $C_{17}H_{17}N_2O_3$ $[M+H]^+$: 297.1161; found: 297.1157.



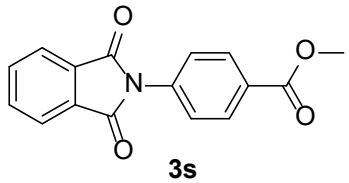
3r

Compound 3r: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2H), 7.81-7.60 (m, 2H), 7.37-7.32 (m, 2H), 7.04-7.00 (m, 2H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 159.3, 134.3, 131.8, 128.0, 124.3, 123.7, 114.5, 55.5; **HRMS (ESI+)** calcd for$C_{15}H_{12}NO_3$ $[M+H]^+$: 254.0739; found: 254.0761.



2s

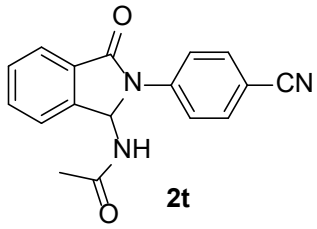
Compound 2s: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.78 (d, J = 9.2 Hz, 1H), 8.02-7.97 (m, 2H), 7.88-7.81 (m, 3H), 7.77-7.71 (m, 1H), 7.66-7.56 (m, 2H), 7.21 (d, J = 9.4 Hz, 1H), 3.84 (s, 3H), 1.80 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.2, 166.8, 166.4, 143.3, 141.2, 134.1, 131.2, 130.4, 130.3, 125.9, 123.8, 123.7, 121.8, 64.3, 52.6, 22.9; **HRMS (ESI+)** calcd for $C_{18}H_{16}N_2O_4Na$ $[M+Na]^+$: 347.1110; found: 347.1084.



3s

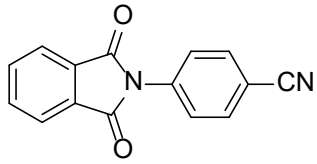
Compound 3s: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20-8.16 (m, 2H), 7.99-7.95 (m, 2H), 7.84-7.79 (m, 2H), 7.61-7.58 (m, 2H), 3.95 (s, 3H); **^{13}C NMR** (101 MHz,

$CDCl_3$) δ 166.8, 166.3, 135.9, 134.7, 131.6, 130.4, 129.3, 125.9, 123.9, 52.3; **HRMS (ESI+)** calcd for $C_{16}H_{12}NO_4$ $[M+H]^+$: 282.0688; found: 282.0721.



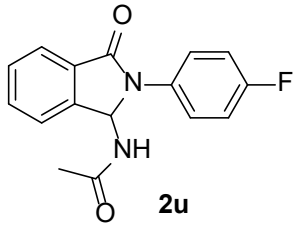
2t

Compound 2t: pale yellow solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.81 (d, J = 9.6 Hz, 1H), 7.94-7.90 (m, 4H), 7.88-7.84 (m, 1H), 7.80-7.75 (m, 1H), 7.68-7.59 (m, 2H), 7.23 (d, J = 9.5 Hz, 1H), 1.84 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.7, 166.8, 143.6, 141.3, 134.1, 133.4, 131.2, 130.2, 123.8, 123.7, 121.9, 119.3, 106.9, 64.2, 23.0; **HRMS (ESI+)** calcd for $C_{17}H_{14}N_3O_2$ $[M+H]^+$: 292.1008; found: 292.1012.



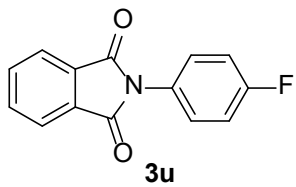
3t

Compound 3t: pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.96 (m, 2H), 7.86-7.83 (m, 2H), 7.82-7.79 (m, 2H), 7.70-7.67 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 135.9, 134.9, 132.9, 131.4, 126.5, 124.1, 118.3, 111.3; **HRMS (ESI+)** calcd for $C_{15}H_8N_2O_2Na$ $[M+Na]^+$: 271.0586; found: 271.0528.



2u

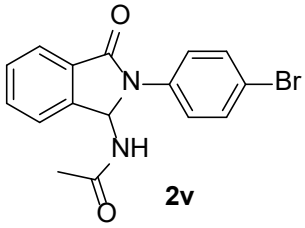
Compound 2u: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.74 (d, J = 9.5 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.76-7.70 (m, 1H), 7.68-7.62 (m, 3H), 7.62-7.57 (m, 1H), 7.32-7.25 (m, 2H), 7.10 (d, J = 9.5 Hz, 1H), 1.80 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.5, 166.3, 159.9 (d, $J_{C\text{-}F}$ = 243.21 Hz), 143.7, 133.4, 133.3 (d, $J_{C\text{-}F}$ = 3.03 Hz), 131.9, 130.0, 125.6 (d, $J_{C\text{-}F}$ = 8.08 Hz), 123.7, 123.5, 116.0, 115.8, 64.8, 23.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.05 – -117.12 (m); **HRMS (ESI+)** calcd for $C_{16}H_{14}FN_2O_2$ $[M+H]^+$: 285.0961; found: 285.1006.



3u

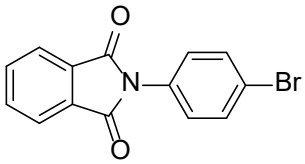
Compound 3u: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.94 (m, 2H), 7.83-7.78 (m, 2H), 7.51-7.39 (m, 2H), 7.23-7.17 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2,

161.9 (d, $J_{C\text{-}F}$ = 249.07 Hz), 134.5, 131.6, 128.4, 127.6 (d, $J_{C\text{-}F}$ = 3.13 Hz), 123.8, 116.1 (d, $J_{C\text{-}F}$ = 22.93 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.88 - -112.99 (m); **HRMS (ESI+)** calcd for $C_{14}H_9FNO_2$ $[M+H]^+$: 242.0539; found: 242.0561.



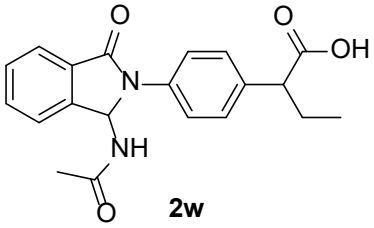
2v

Compound 2v: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84-7.81 (m, 1H), 7.70-7.65 (m, 1H), 7.62-7.56 (m, 4H), 7.55-7.50 (m, 2H), 7.23 (d, *J* = 10.1 Hz, 1H), 6.02 (d, *J* = 10.1 Hz, 1H), 2.04 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 166.5, 142.0, 135.2, 133.2, 132.0, 131.3, 130.0, 123.7, 123.2, 123.1, 118.4, 63.8, 23.2; **HRMS (ESI+)** calcd for $C_{16}H_{14}BrN_2O_2$ $[M+H]^+$: 345.0160; found: 345.0145.



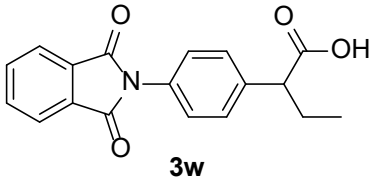
3v

Compound 3v: white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.93 (m, 2H), 7.82-7.77 (m, 2H), 7.64-7.61 (m, 2H), 7.37-7.32 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 134.6, 132.3, 131.6, 130.8, 128.0, 123.9, 121.8; **HRMS (ESI+)** calcd for $C_{14}H_8BrNO_2Na$ $[M+Na]^+$: 323.9738; found: 323.9680.



2w

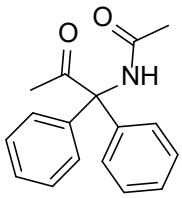
Compound 2w: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.35 (s, 1H), 8.71 (d, *J* = 9.4 Hz, 1H), 7.81-7.76 (m, 1H), 7.73-7.68 (m, 1H), 7.63-7.53 (m, 4H), 7.33-7.28 (m, 2H), 7.09 (d, *J* = 9.3 Hz, 1H), 3.41 (t, *J* = 7.6 Hz, 1H), 2.02-1.88 (m, 1H), 1.79 (s, 3H), 1.72-1.59 (m, 1H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 175.9, 171.9, 167.0, 143.2, 137.3, 135.2, 133.7, 131.3, 130.2, 128.6, 123.8, 123.6, 123.5, 64.9, 52.6, 26.4, 22.8, 12.3; **HRMS (ESI+)** calcd for $C_{20}H_{19}N_2O_4$ $[M-H]^+$: 351.1423; found: 351.1391.



3w

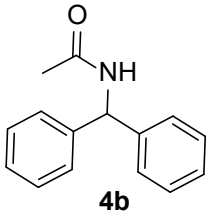
Compound 3w: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.43 (s, 1H), 7.95-7.91 (m, 2H), 7.89-7.85 (m, 2H), 7.43-7.34 (m, 4H), 3.47 (t, *J* = 7.6 Hz,

1H), 2.02-1.91 (m, 1H), 1.73-1.62 (m, 1H), 0.83 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 175.1, 167.5, 140.0, 135.2, 132.0, 131.0, 128.7, 127.8, 123.9, 52.7, 26.6, 12.6; **HRMS (ESI+)** calcd for $C_{18}H_{14}NO_4$ $[M-H]^+$: 308.1001; found: 308.1035.



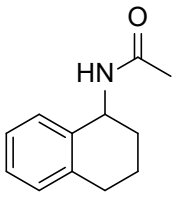
4a

Compound 4a: white solid; **^{1}H NMR** (400 MHz, MeOD) δ 7.39-7.34 (m, 4H), 7.34-7.24 (m, 6H), 2.04 (s, 3H), 1.99 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 202.3, 170.7, 141.0, 128.6, 128.3, 127.7, 72.8, 25.8, 23.0; **HRMS (ESI+)** calcd for $C_{17}H_{16}NO_2$ $[M-H]^+$: 266.1259; found: 266.1213.



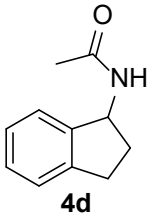
4b

Compound 4b: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.81 (d, J = 8.7 Hz, 1H), 7.36-7.30 (m, 4H), 7.30-7.21 (m, 6H), 6.11 (d, J = 8.7 Hz, 1H), 1.93 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 141.5, 128.7, 127.5, 127.4, 57.0, 23.3; **HRMS (ESI+)** calcd for $C_{15}H_{14}NO$ $[M-H]^+$: 224.1154; found: 224.1109.



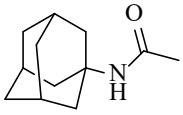
4c

Compound 4c: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.23 (d, J = 8.7 Hz, 1H), 7.20-7.12 (m, 3H), 7.11-7.06 (m, 1H), 4.96 (t, J = 7.4 Hz, 1H), 2.85-2.60 (m, 2H), 1.93-1.80 (m, 5H), 1.78-1.60 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.9, 138.1, 137.5, 129.1, 128.7, 127.1, 126.3, 46.7, 30.4, 29.3, 23.2, 20.4; **HRMS (ESI+)** calcd for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1154; found: 190.1183.



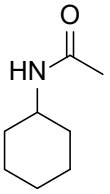
4d

Compound 4d: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.23 (d, J = 8.3 Hz, 1H), 7.31-7.08 (m, 4H), 5.26 (dd, J = 8.0, 16.0 Hz, 1H), 2.96-2.88 (m, 1H), 2.83-2.74 (m, 1H), 2.41-2.32 (m, 1H), 1.87 (s, 3H), 1.74-1.69 (m, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 169.4, 144.6, 143.3, 127.8, 126.8, 124.9, 124.4, 54.0, 33.5, 30.2, 23.1; **HRMS (ESI+)** calcd for $C_{11}H_{14}NO$ $[M+H]^+$: 176.0997; found: 176.1033.



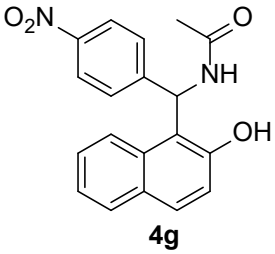
4e

Compound 4e: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.29 (s, 1H), 2.02-1.96 (m, 3H), 1.92-1.88 (m, 6H), 1.73 (s, 3H), 1.63-1.58 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 51.9, 41.6, 36.4, 29.4, 24.7; **HRMS (ESI+)** calcd for $C_{12}H_{20}NO$ $[M+H]^+$: 194.1467; found: 194.1496.



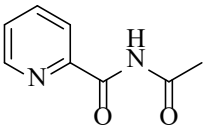
4f

Compound 4f: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.65 (d, J = 7.4 Hz, 1H), 3.50-3.38 (m, 1H), 1.72 (s, 3H), 1.70-1.58 (m, 4H), 1.55-1.46 (m, 1H), 1.26-1.13 (m, 2H), 1.11-1.00 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 48.4, 33.1, 25.5, 24.8, 23.4; **HRMS (ESI+)** calcd for $C_8H_{15}NONa$ $[M+Na]^+$: 164.1154; found: 164.1098.



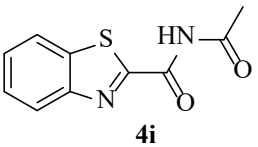
4g

Compound 4g: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.12 (s, 1H), 8.57 (d, J = 7.7 Hz, 1H), 8.15-8.10 (m, 2H), 7.84-7.76 (m, 3H), 7.41-7.35 (m, 3H), 7.30-7.25 (m, 1H), 7.23-7.20 (m, 1H), 7.18-7.14 (m, 1H), 2.01 (s, 3H); **^{13}C NMR** (101 MHz, MeOD) δ 171.8, 153.4, 150.1, 146.6, 132.5, 130.0, 129.0, 128.5, 126.9, 126.7, 122.8, 122.6, 122.0, 117.7, 117.5, 48.8, 21.3; **HRMS (ESI+)** calcd for $C_{19}H_{17}N_2O_4$ $[M+H]^+$: 337.1110; found: 337.1132.



4h

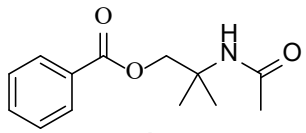
Compound 4h: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.61 (s, 1H), 8.70-8.68 (m, 1H), 8.14-8.10 (m, 1H), 8.08-8.03 (m, 1H), 7.72-7.67 (m, 1H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 162.9, 148.4, 148.1, 137.8, 127.6, 123.2, 25.4; **HRMS (ESI+)** calcd for $C_8H_9N_2O_2$ $[M+H]^+$: 165.0586; found: 165.0614.



4i

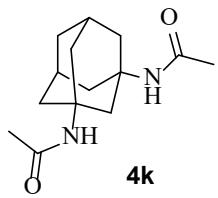
Compound 4i: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.18 (s, 1H), 8.29-8.24 (m, 1H), 8.23-8.16 (m, 1H), 7.69-7.58 (m, 2H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 161.4, 158.4, 152.4, 137.8, 127.8, 127.4, 125.1, 122.5, 25.5; **HRMS (ESI+)** calcd for

$C_{10}H_8N_2O_2SNa$ $[M+Na]^+$: 243.0306; found: 243. 0255.



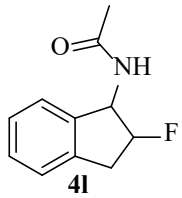
4j

Compound 4j: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.01-7.99 (m, 1H), 7.99-7.97 (m, 1H), 7.70-7.64 (m, 2H), 7.57-7.52 (m, 2H), 4.36 (s, 2H), 1.78 (s, 3H), 1.31 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 166.5, 133.17, 130.0, 129.6, 128.5, 69.6, 53.7, 24.4, 24.1; **HRMS (ESI+)** calcd for $C_{13}H_{18}NO_3$ $[M+H]^+$: 236.1208; found: 236.1234.



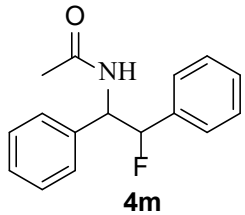
4k

Compound 4k: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.35 (s, 2H), 2.11-2.08 (m, 2H), 2.07-2.02 (m, 2H), 1.85-1.72 (m, 8H), 1.70 (s, 6H), 1.48-1.44 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 53.0, 44.8, 40.4, 35.2, 29.8, 24.5; **HRMS (ESI+)** calcd for $C_{14}H_{23}N_2O_2$ $[M+H]^+$: 251.1681; found: 251.1713.



4l

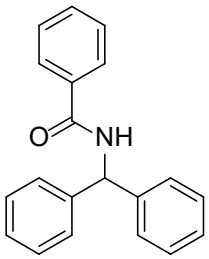
Compound 4l: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.31 (d, J = 8.7 Hz, 1H), 7.29-7.25 (m, 1H), 7.24-7.20 (m, 2H), 7.18-7.14 (m, 1H), 5.46-5.15 (m, 2H), 3.26-3.10 (m, 1H), 3.09-2.98 (m, 1H), 1.94 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 139.9, 138.8, 128.3, 127.4, 125.1, 123.9, 95.0 (d, $J_{C\text{-}F}$ = 181.90 Hz), 56.8 (d, $J_{C\text{-}F}$ = 16.87 Hz), 37.9 (d, $J_{C\text{-}F}$ = 22.32 Hz), 23.3; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -193.30 - -193.47 (m); **HRMS (ESI+)** calcd for $C_{11}H_{13}FNO$ $[M+H]^+$: 194.0903; found: 194.0931.



4m

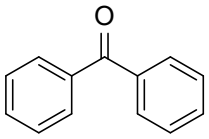
Compound 4m: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.73 (d, J = 9.3 Hz, 1H, major), 8.61 (d, J = 9.3 Hz, 0.2H, minor), 7.41-7.17 (m, 12H, major 10H, minor 2H), 5.84-5.57 (m, 1.2H, major 1H, minor 0.2H), 5.37-5.15 (m, 1.2H, major 1H, minor 0.2H), 1.82 (s, 3H, major), 1.74 (s, 0.6H, minor); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 138.4, 136.7 (d, $J_{C\text{-}F}$ = 20.40 Hz), 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.3, 125.7, 125.6, 125.5, 95.3 (d, $J_{C\text{-}F}$ = 21.51 Hz), 58.0 (d, $J_{C\text{-}F}$ = 21.21 Hz), 57.1 (d,

$J_{C\text{-}F}$ = 21.01 Hz), 23.4, 23.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -190.4 - 190.6 (m, major), -193.9 - -194.1 (m, minor); **HRMS (ESI+)** calcd for $C_{16}H_{17}FNO$ $[M+H]^+$: 258.1216; found: 258.1247.



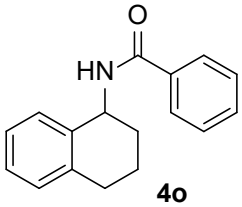
4n

Compound 4n: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.28 (d, J = 8.8 Hz, 1H), 7.95-7.90 (m, 2H), 7.56-7.50 (m, 1H), 7.49-7.43 (m, 2H), 7.40-7.31 (m, 8H), 7.29-7.33 (m, 2H), 6.40 (d, J = 8.8 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 166.4, 142.8, 134.8, 131.8, 128.8, 128.7, 128.1, 128.0, 127.5, 56.8; **HRMS (ESI+)** calcd for $C_{20}H_{18}NO$ $[M+H]^+$: 288.1310; found: 288.1352.



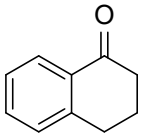
4n-1

Compound 4n-1: white solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82-7.80 (m, 2H), 7.80-7.78 (m, 2H), 7.60-7.56 (m, 2H), 7.50-7.46 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.8, 137.7, 132.5, 130.2, 128.3; **ESI-MS** (ESI+) calcd for $C_{13}H_{10}O$ $[M+H]^+$: 183.07; found: 183.20.[12]



4o

Compound 4o: white solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.77 (d, J = 6.4 Hz, 1H), 7.93-7.88 (m, 2H), 7.54-7.48 (m, 1H), 7.47-7.41 (m, 2H), 7.20-7.08 (m, 4H), 5.29-5.20 (m, 1H), 2.84-2.69 (m, 2H), 2.03-1.90 (m, 2H), 1.87-1.69 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 166.4, 138.2, 137.7, 135.0, 131.6, 129.2, 128.7, 128.2, 127.9, 127.1, 126.3, 47.7, 30.4, 29.4, 21.0; **HRMS (ESI+)** calcd for $C_{17}H_{17}NONa$ $[M+Na]^+$: 274.1310; found: 274.1252.



4o-1

Compound 4o-1: pale yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06-7.98 (m, 1H), 7.47-7.44 (m, 1H), 7.31-7.27 (m, 1H), 7.25-7.22 (m, 1H), 2.98-2.94(m, 2H), 2.67-2.63 (m, 2H), 2.16-2.10 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.4, 144.6, 133.5, 132.7, 128.9, 127.2, 126.7, 39.2, 29.8,

23.4; **ESI-MS** (ESI+) calcd for $C_{10}H_{10}O$ $[M+H]^+$: 147.07; found: 147.05.[12]

10. ^{1}H, ^{13}C, and ^{19}F NMR Spectra of Products

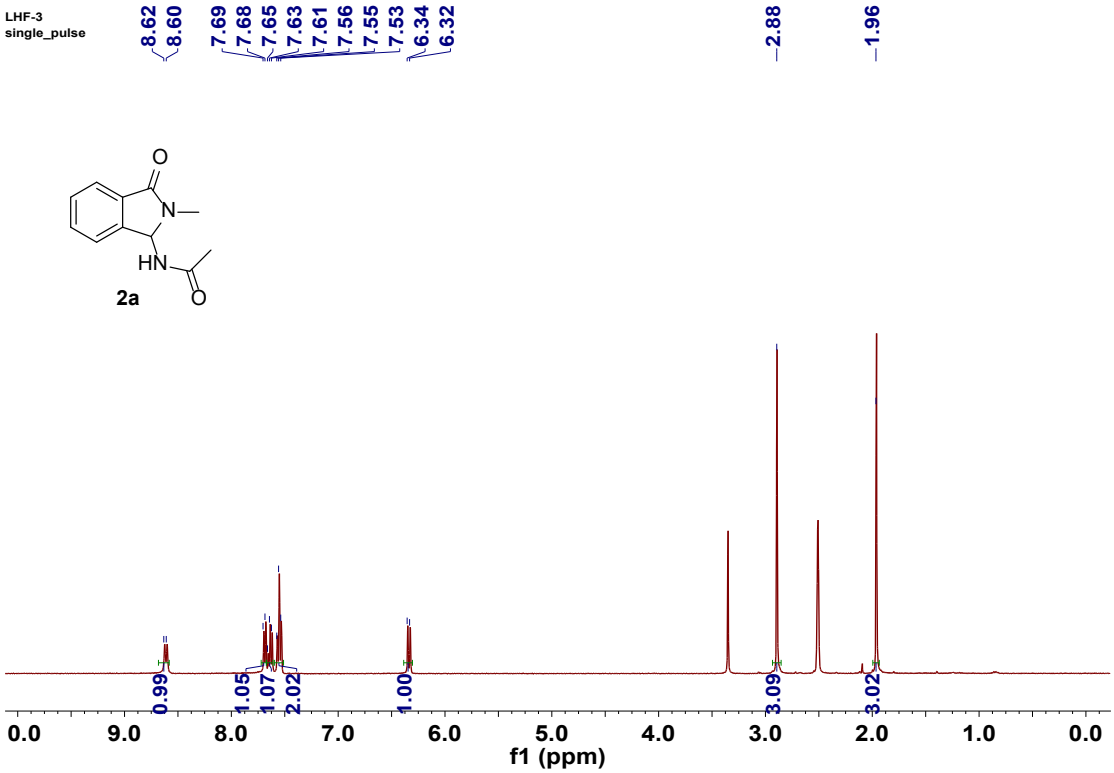


Figure S3. ^{1}H NMR spectrum of compound **2a** (400 MHz, solvent: DMSO-d_6)

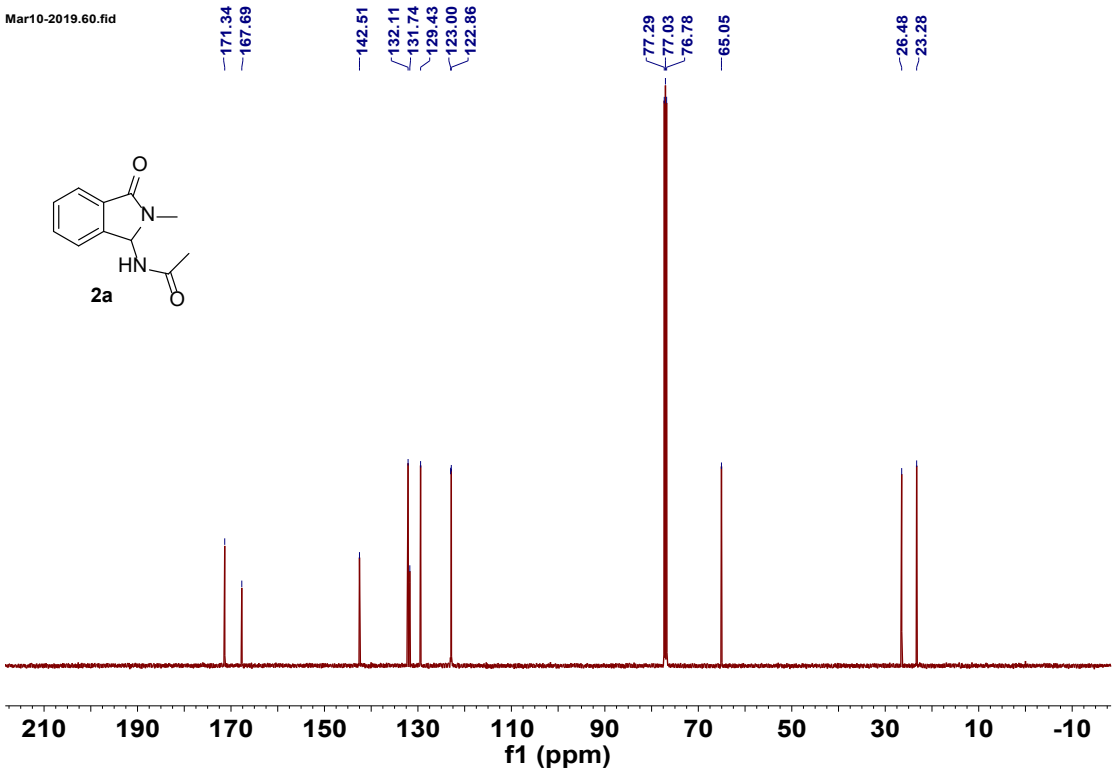


Figure S4. ^{13}C NMR spectrum of compound **2a** (126 MHz, solvent: $CDCl_3$)

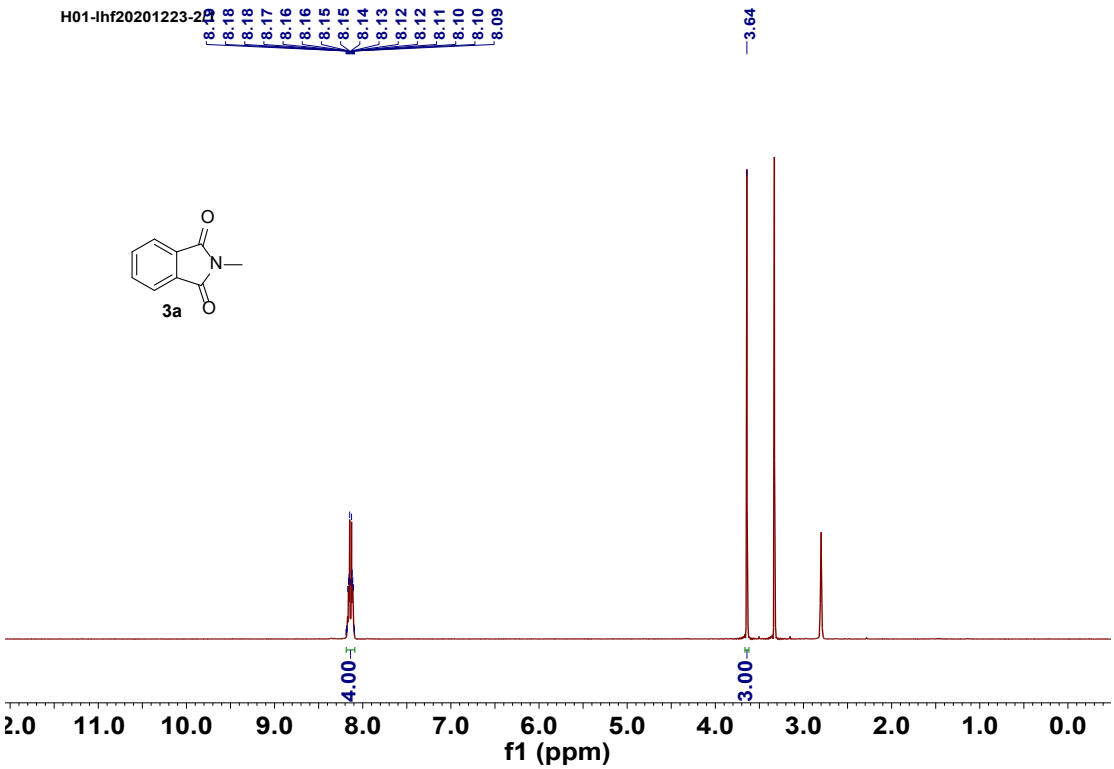


Figure S5. ^{1}H NMR spectrum of compound **3a** (400 MHz, solvent: DMSO-d_6)

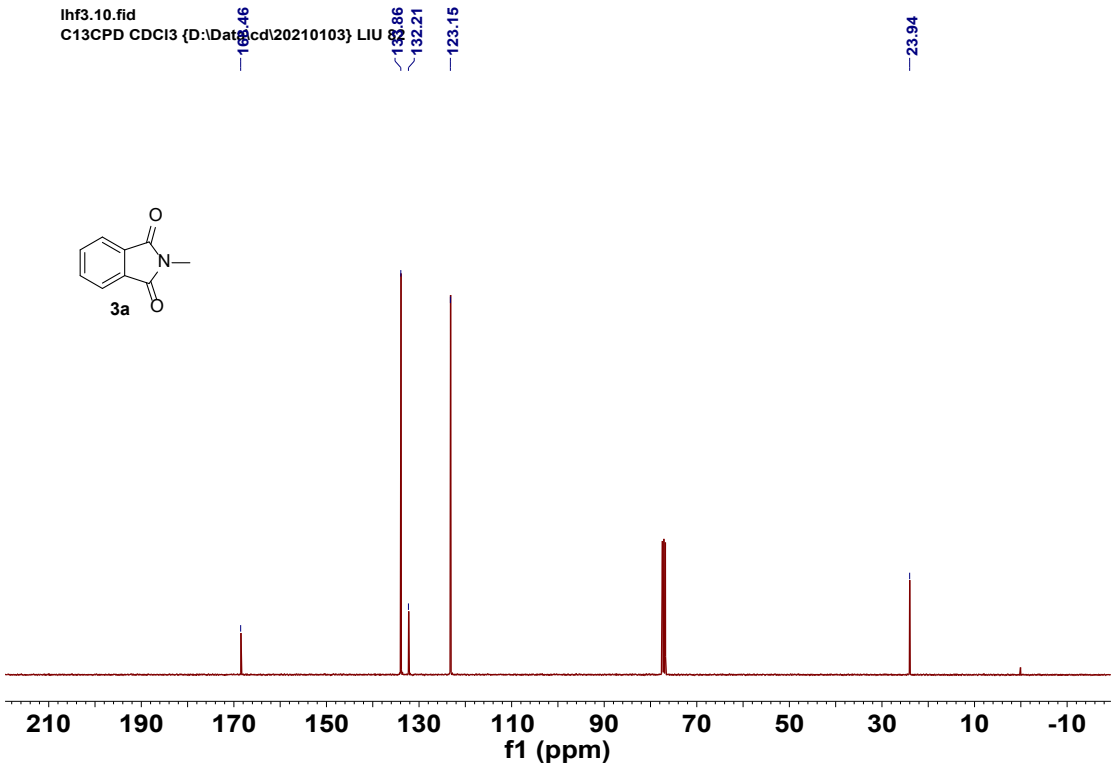


Figure S6. ^{13}C NMR spectrum of compound **3a** (101 MHz, solvent: $CDCl_3$)

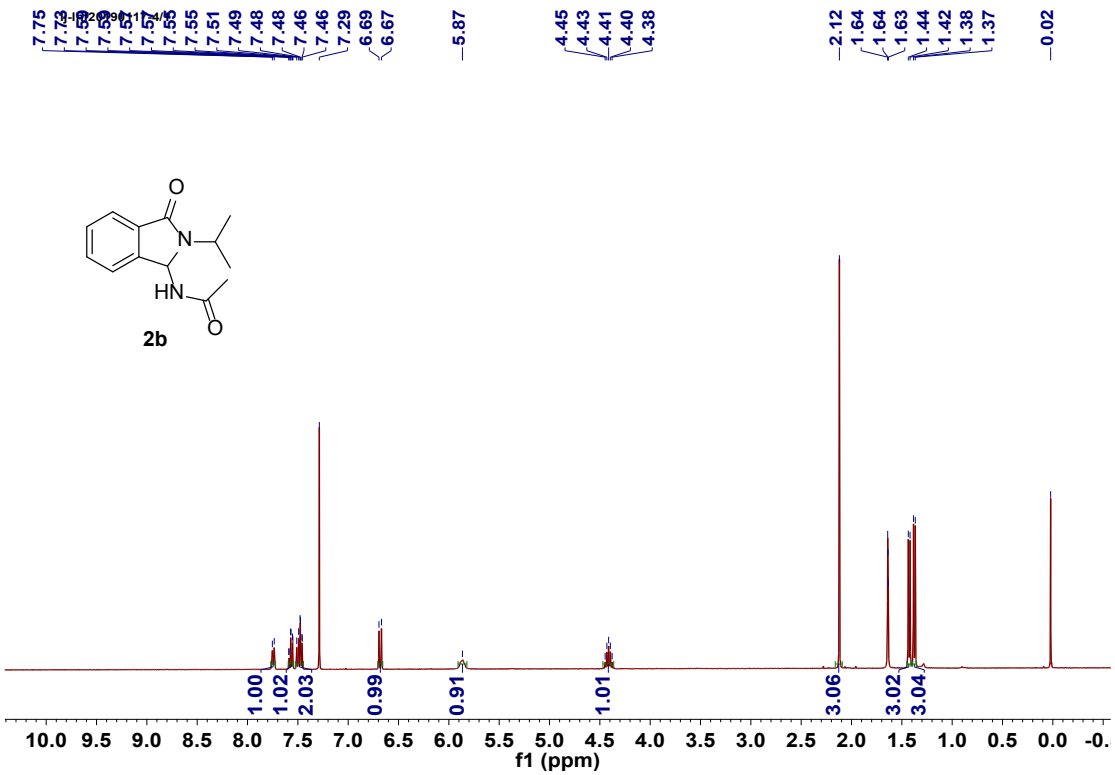


Figure S7. ^{1}H NMR spectrum of compound **2b** (400 MHz, solvent: $CDCl_3$)

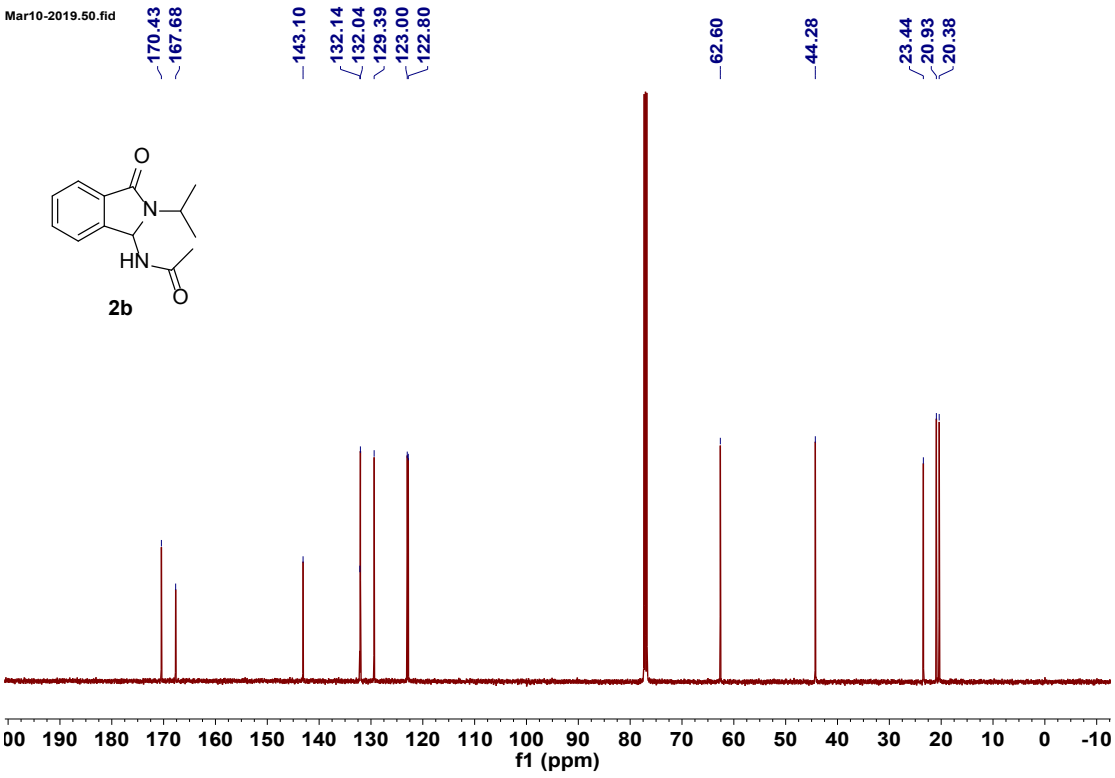


Figure S8. ^{13}C NMR spectrum of compound **2b** (126 MHz, solvent: $CDCl_3$)

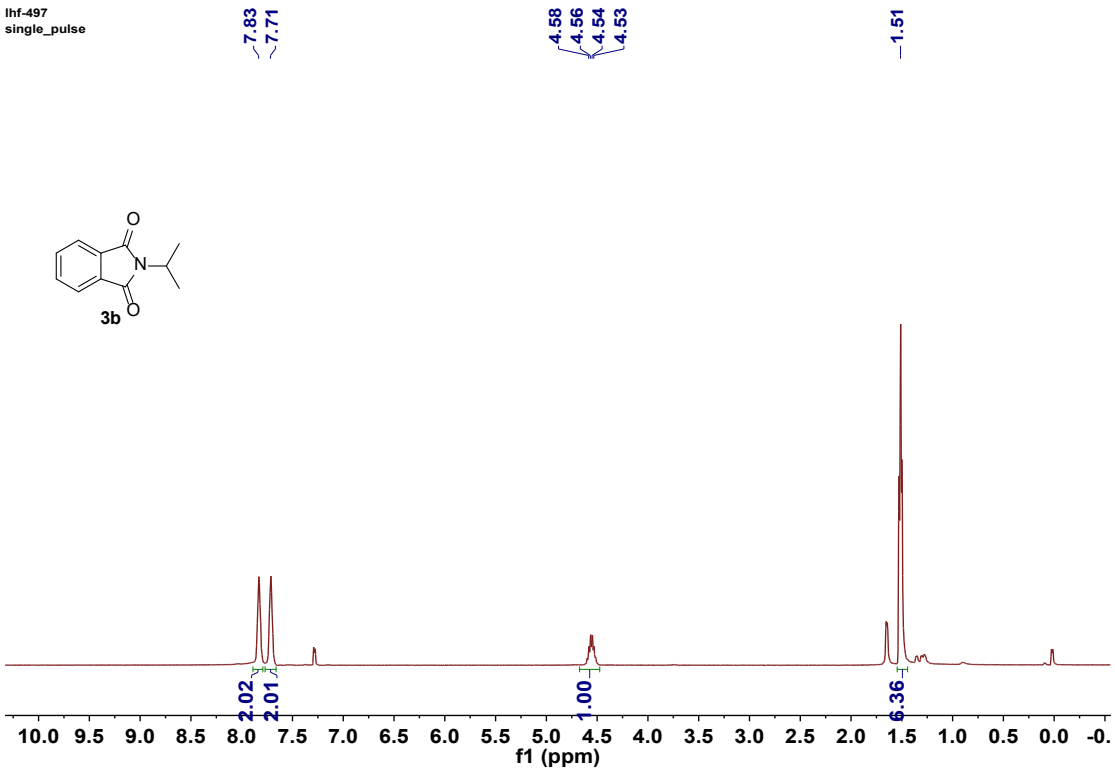


Figure S9. ^{1}H NMR spectrum of compound **3b** (400 MHz, solvent: $CDCl_3$)

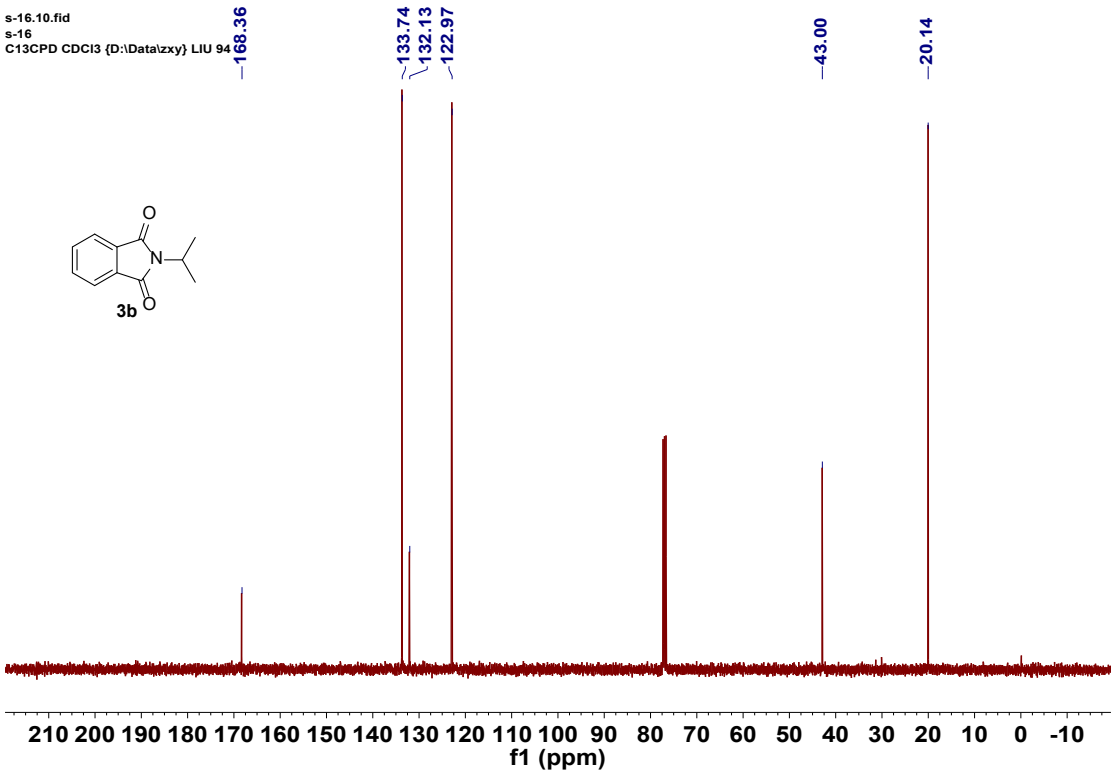


Figure S10. ^{13}C NMR spectrum of compound **3b** (101 MHz, solvent: $CDCl_3$)

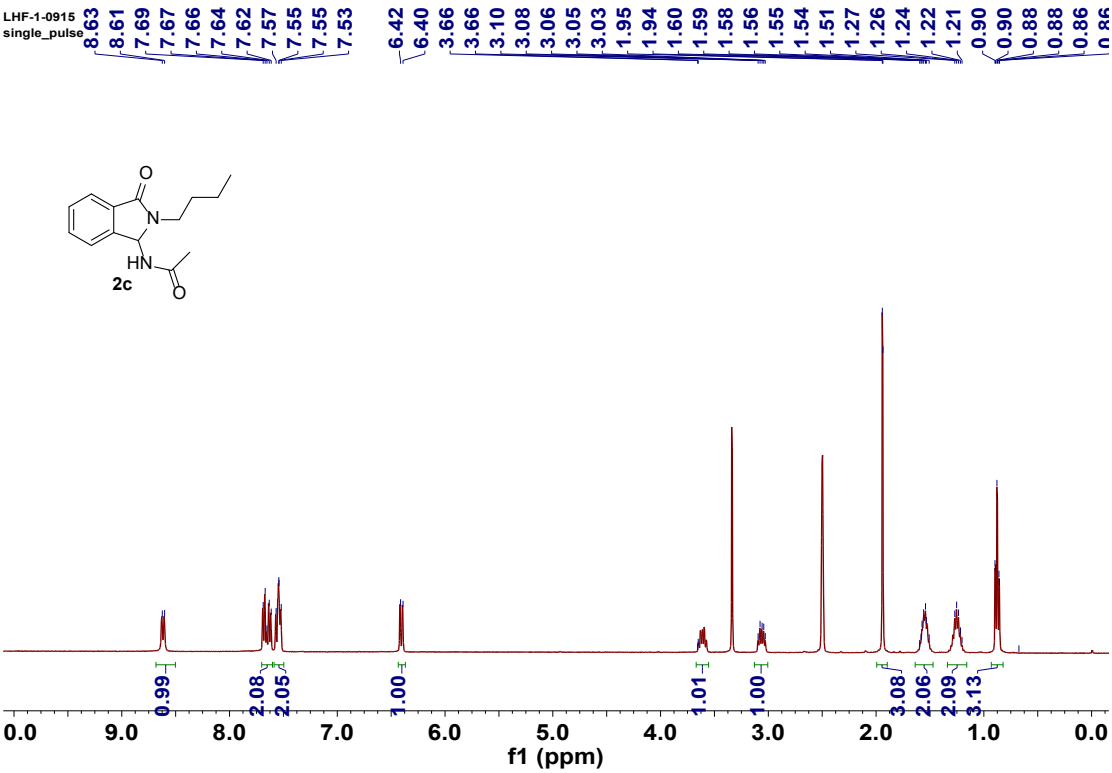


Figure S11. ^{1}H NMR spectrum of compound **2c** (400 MHz, solvent: DMSO-d_6)

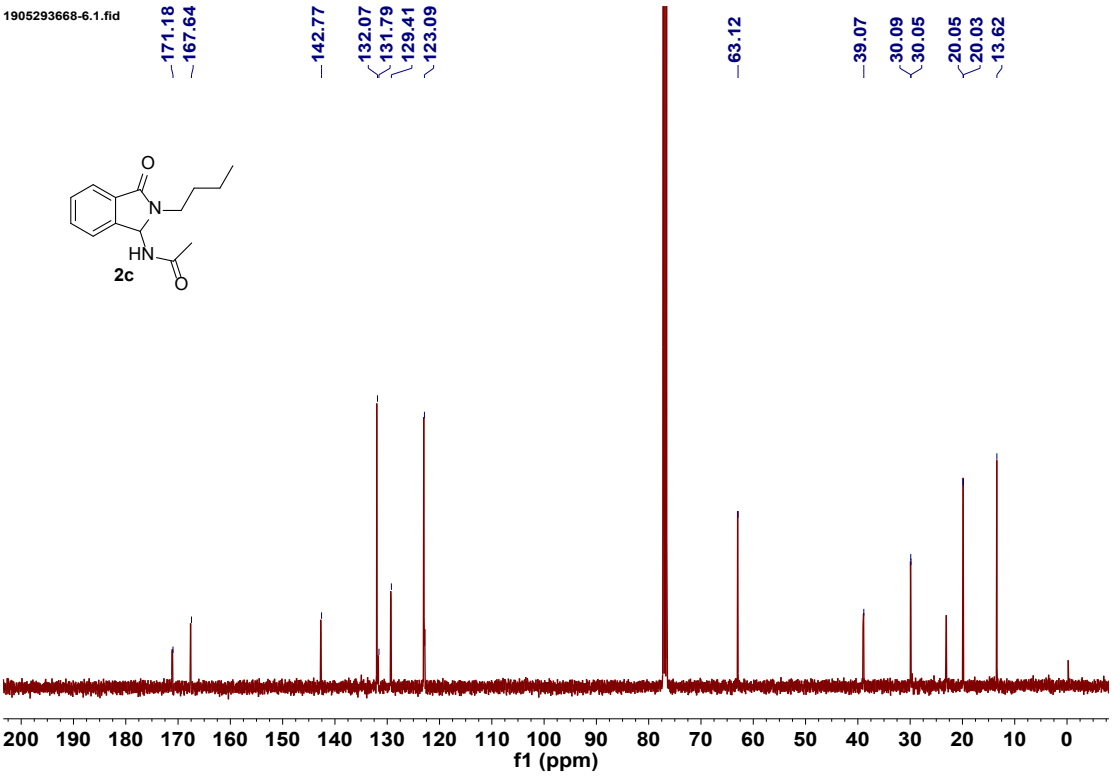


Figure S12. ^{13}C NMR spectrum of compound **2c** (101 MHz, solvent: $CDCl_3$)

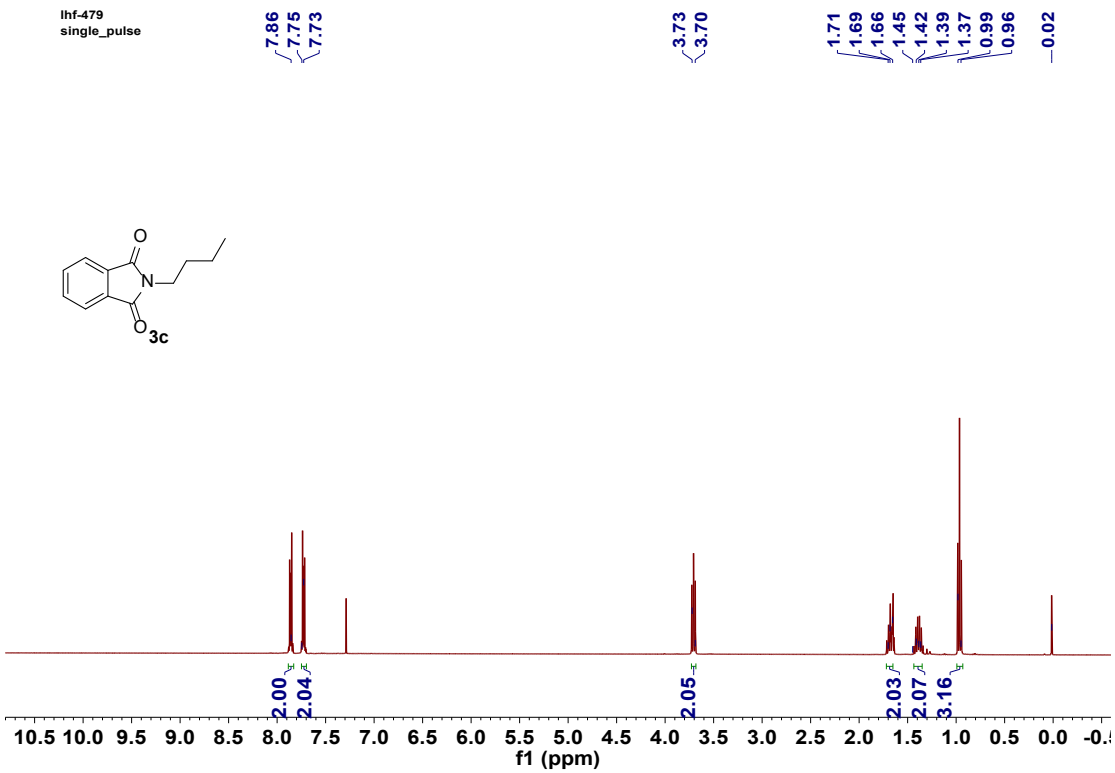


Figure S13. ^{1}H NMR spectrum of compound **3c** (400 MHz, solvent: $CDCl_3$)

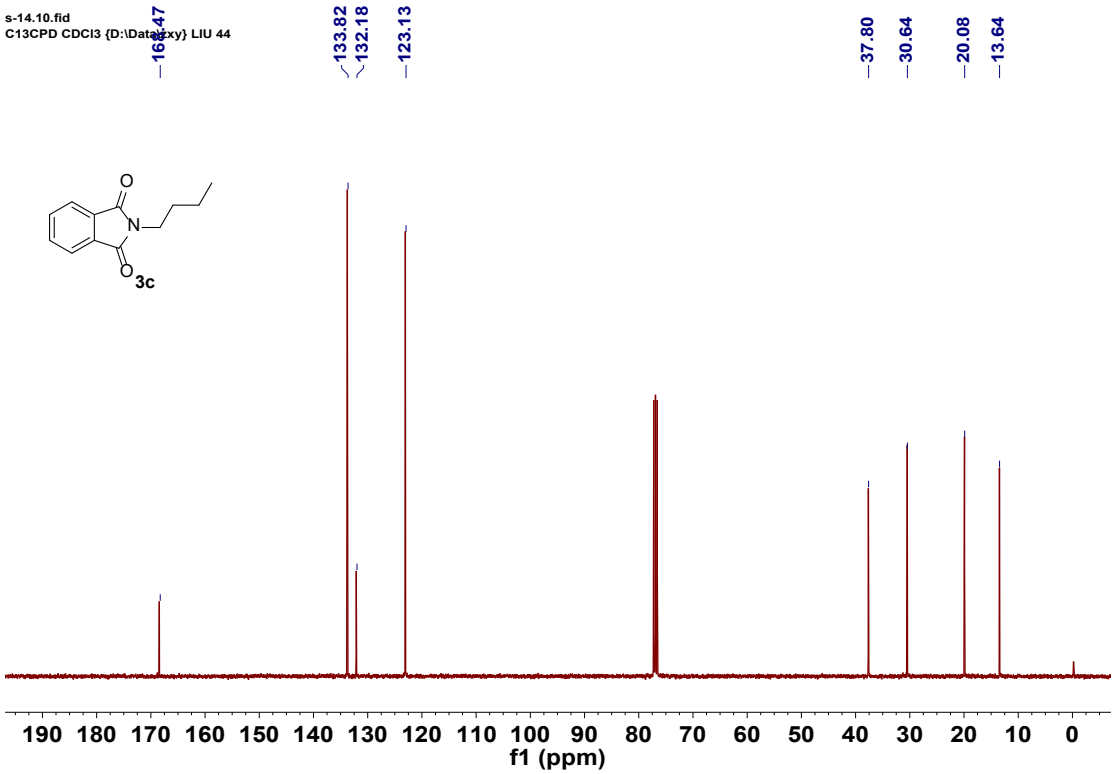


Figure S14. ^{13}C NMR spectrum of compound **3c** (101 MHz, solvent: $CDCl_3$)

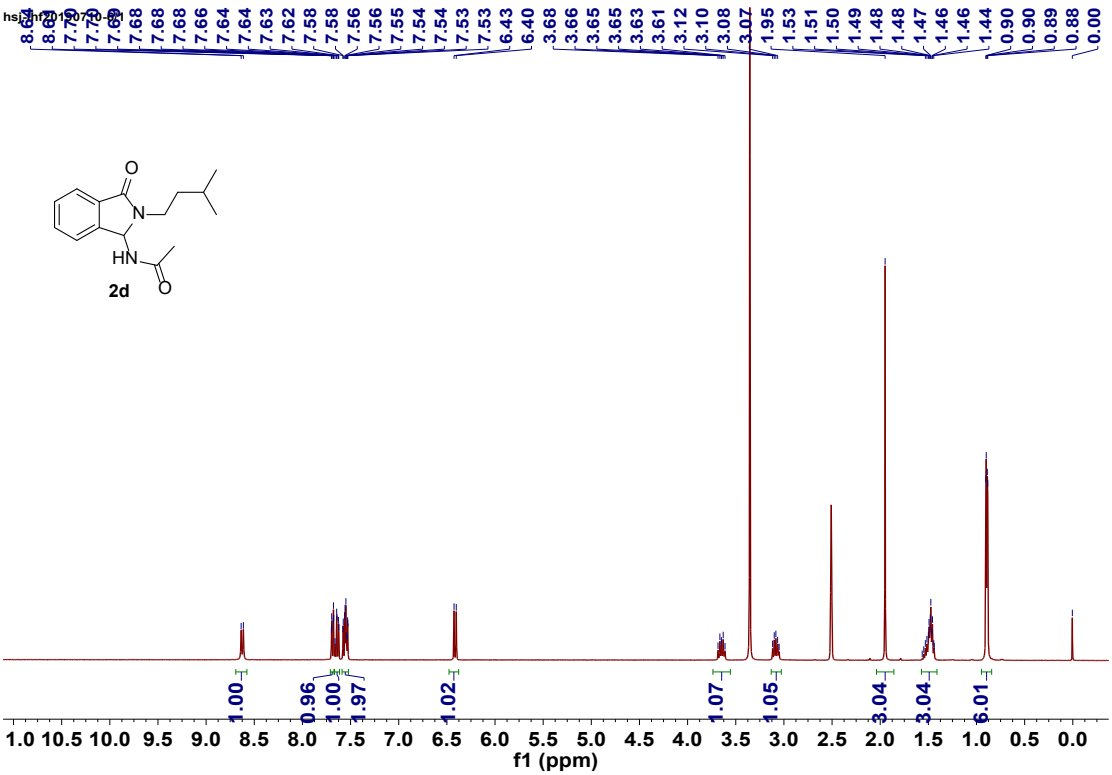


Figure S15. [1]H NMR spectrum of compound **2d** (400 MHz, solvent: DMSO-d_6)

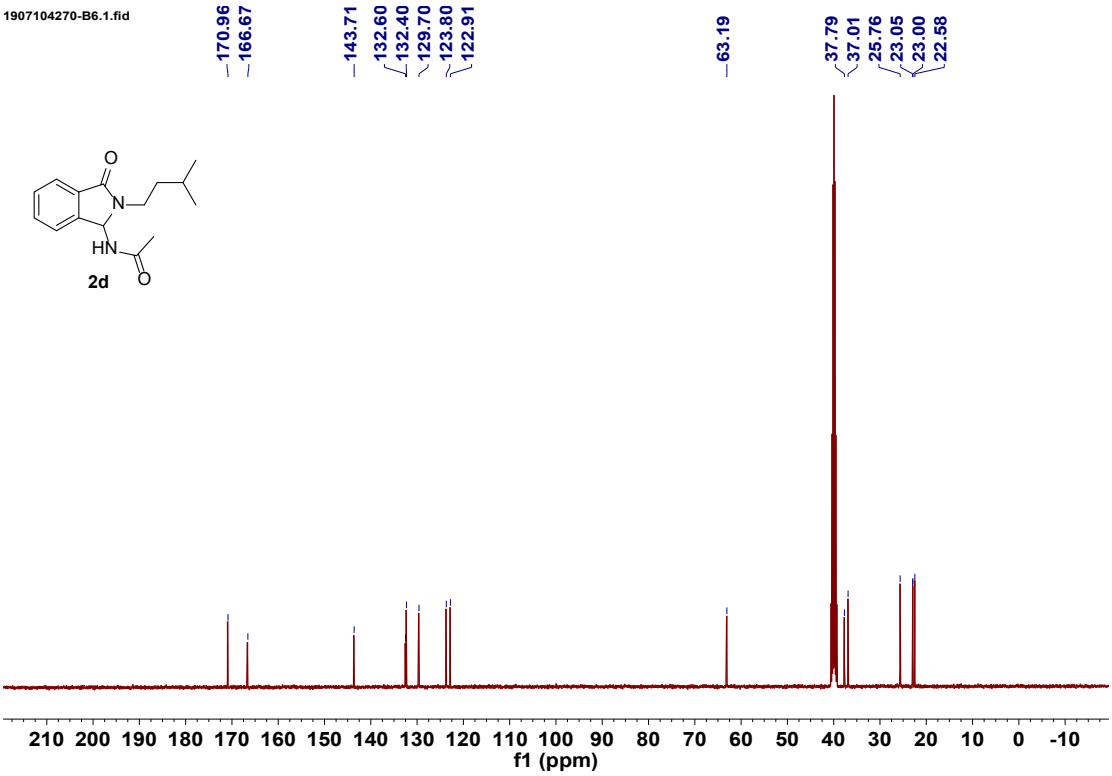


Figure S16. [13]C NMR spectrum of compound **2d** (101 MHz, solvent: DMSO-d_6)

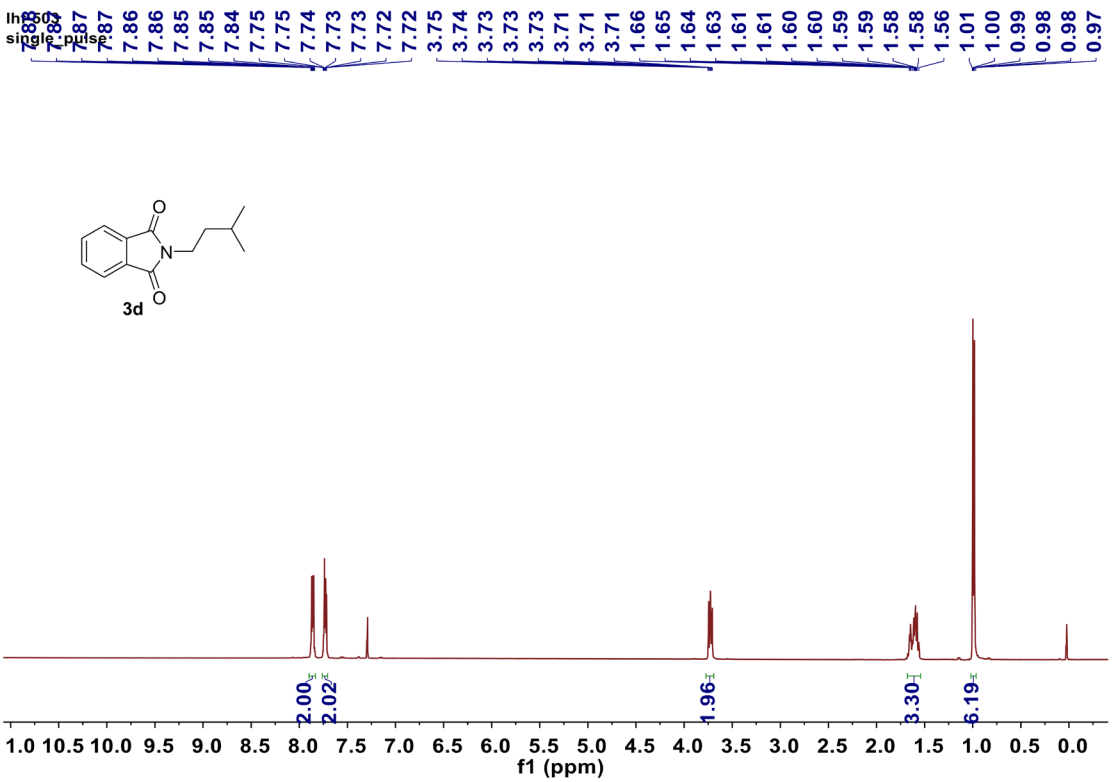


Figure S17. ^{1}H NMR spectrum of compound **3d** (400 MHz, solvent: $CDCl_3$)

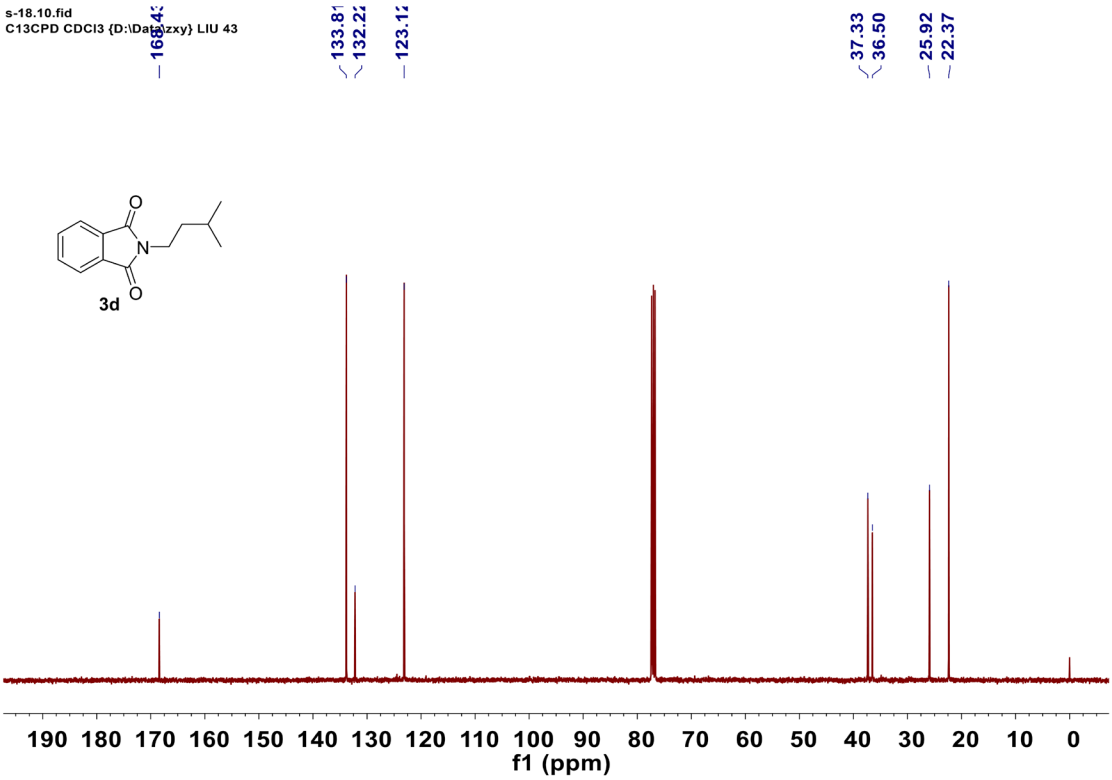


Figure S18. ^{13}C NMR spectrum of compound **3d** (101 MHz, solvent: $CDCl_3$)

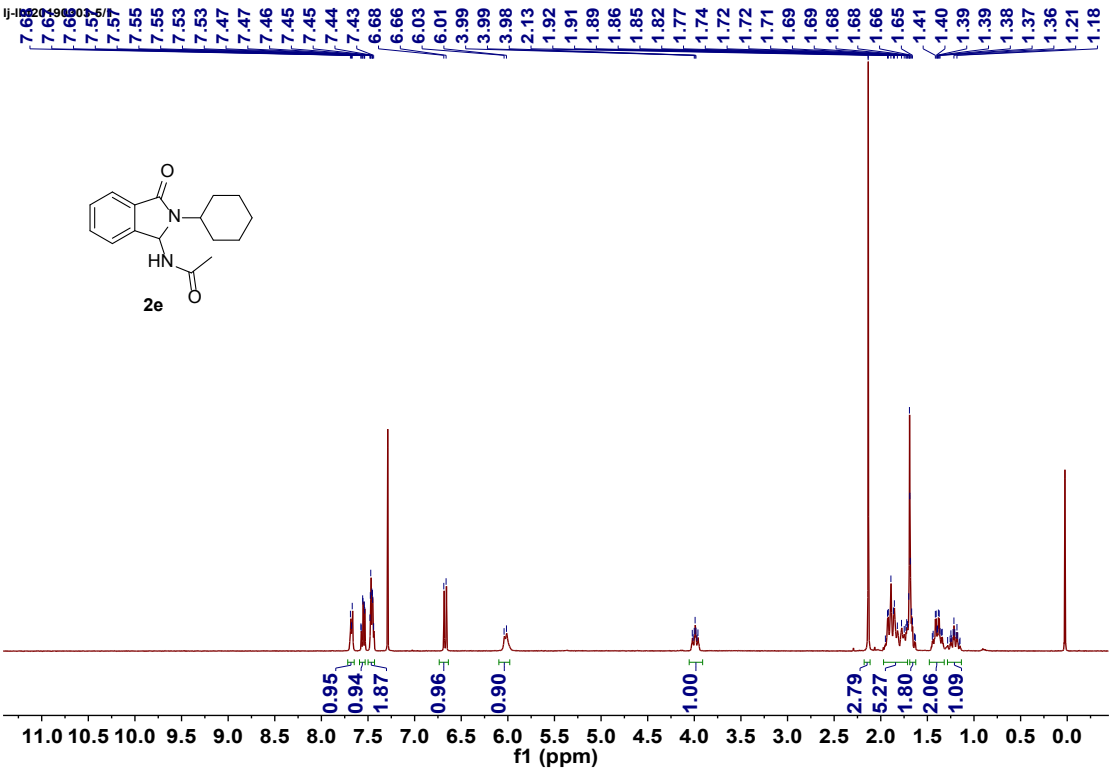


Figure S19. ^{1}H NMR spectrum of compound **2e** (400 MHz, solvent: $CDCl_3$)

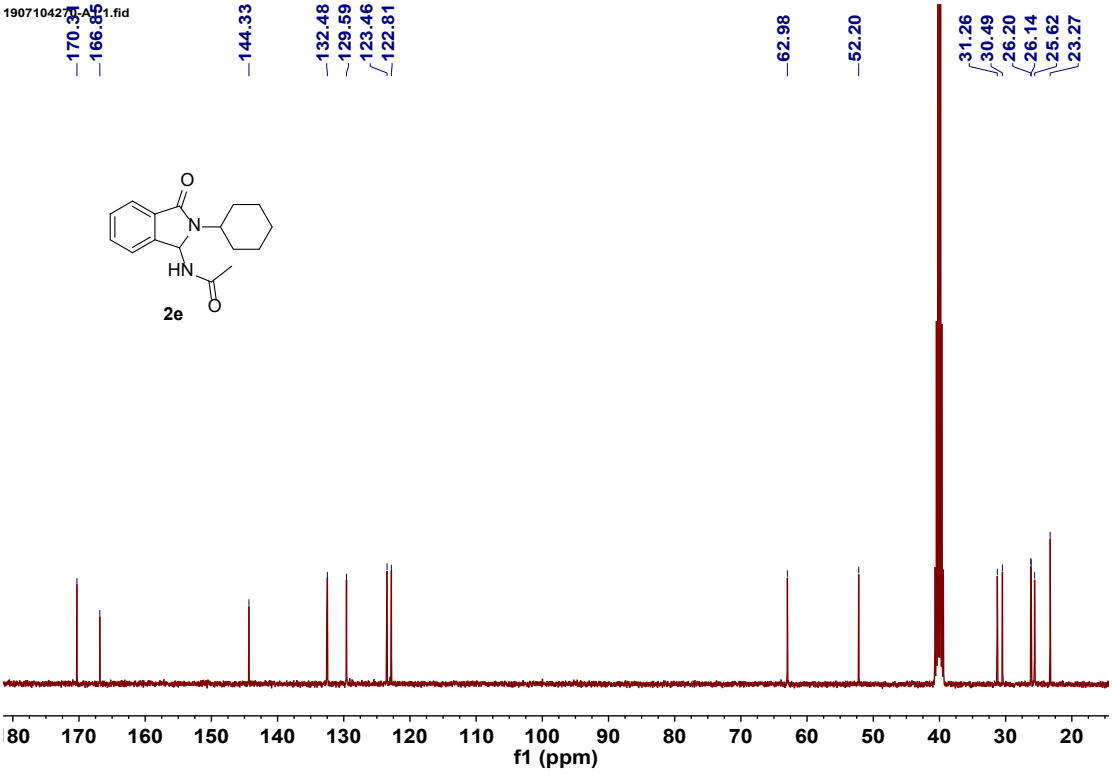


Figure S20. ^{13}C NMR spectrum of compound **2e** (101 MHz, solvent: DMSO-d_6)

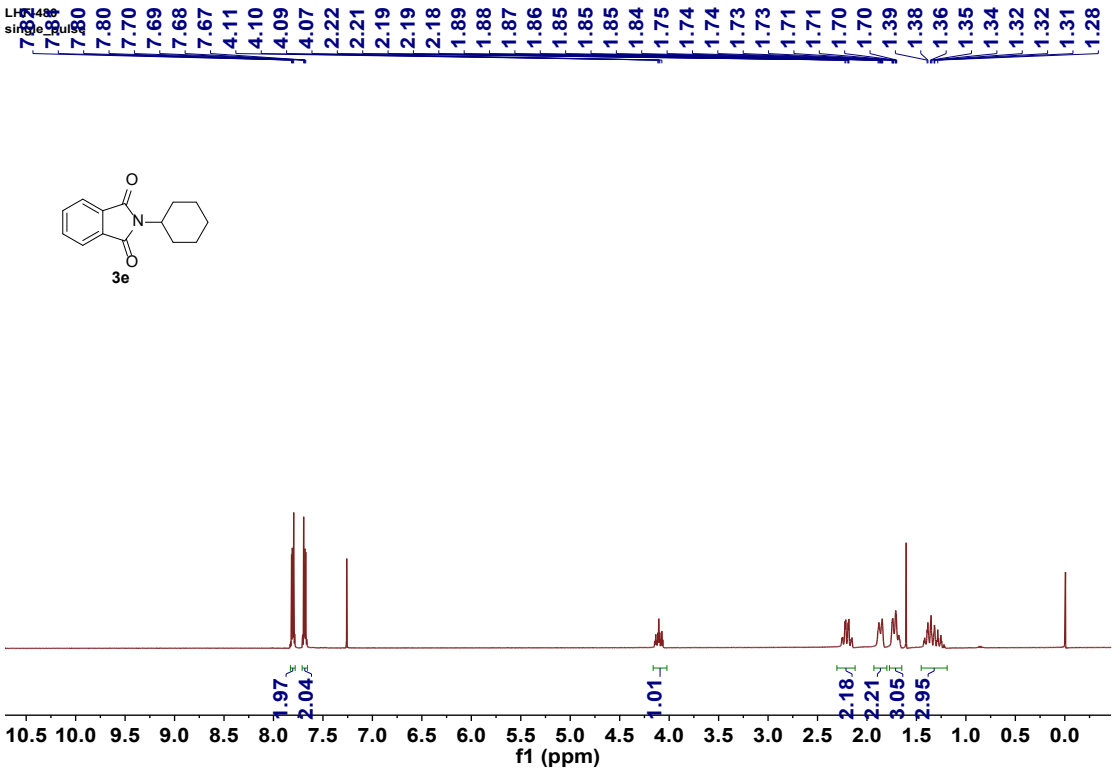


Figure S21. ^{1}H NMR spectrum of compound **3e** (400 MHz, solvent: $CDCl_3$)

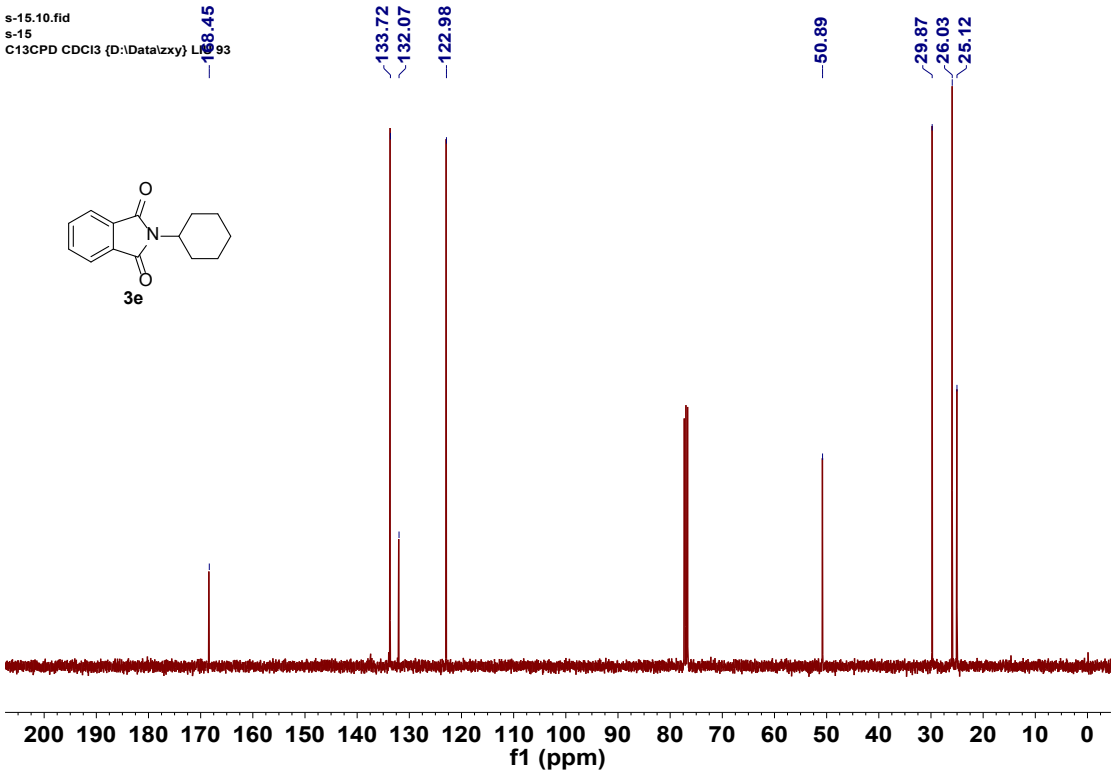


Figure S22. ^{13}C NMR spectrum of compound **3e** (101 MHz, solvent: $CDCl_3$)

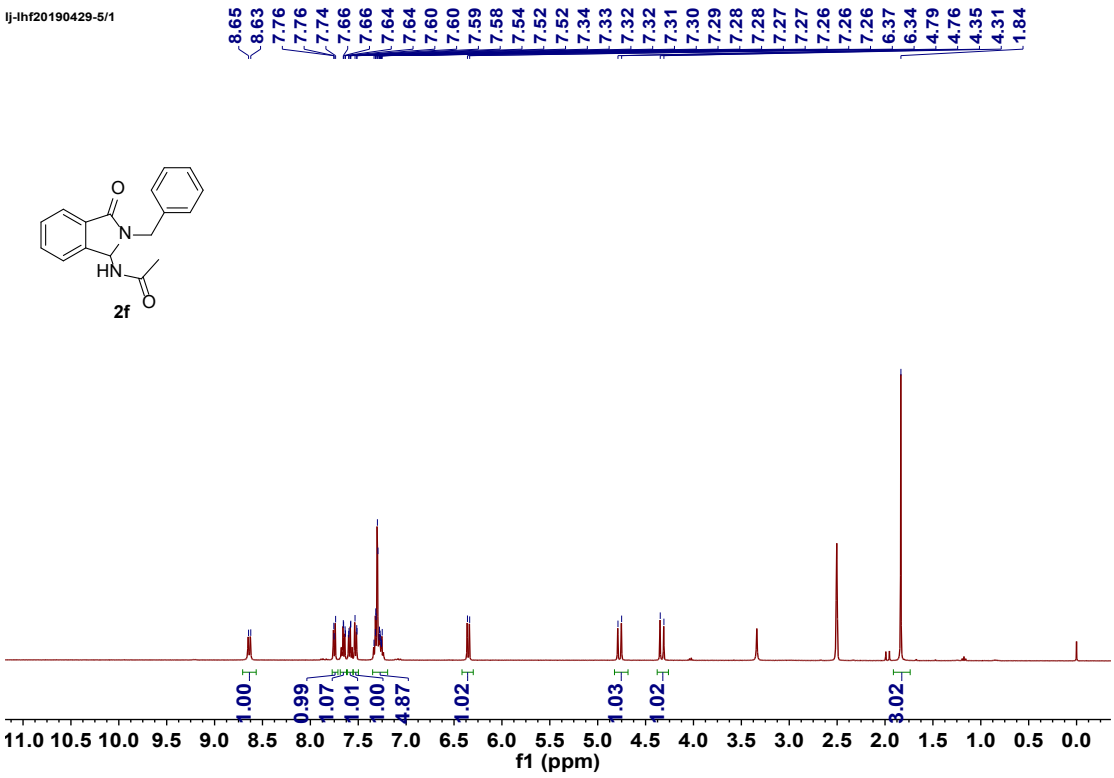


Figure S23. ^{1}H NMR spectrum of compound **2f** (400 MHz, solvent: DMSO-d_6)

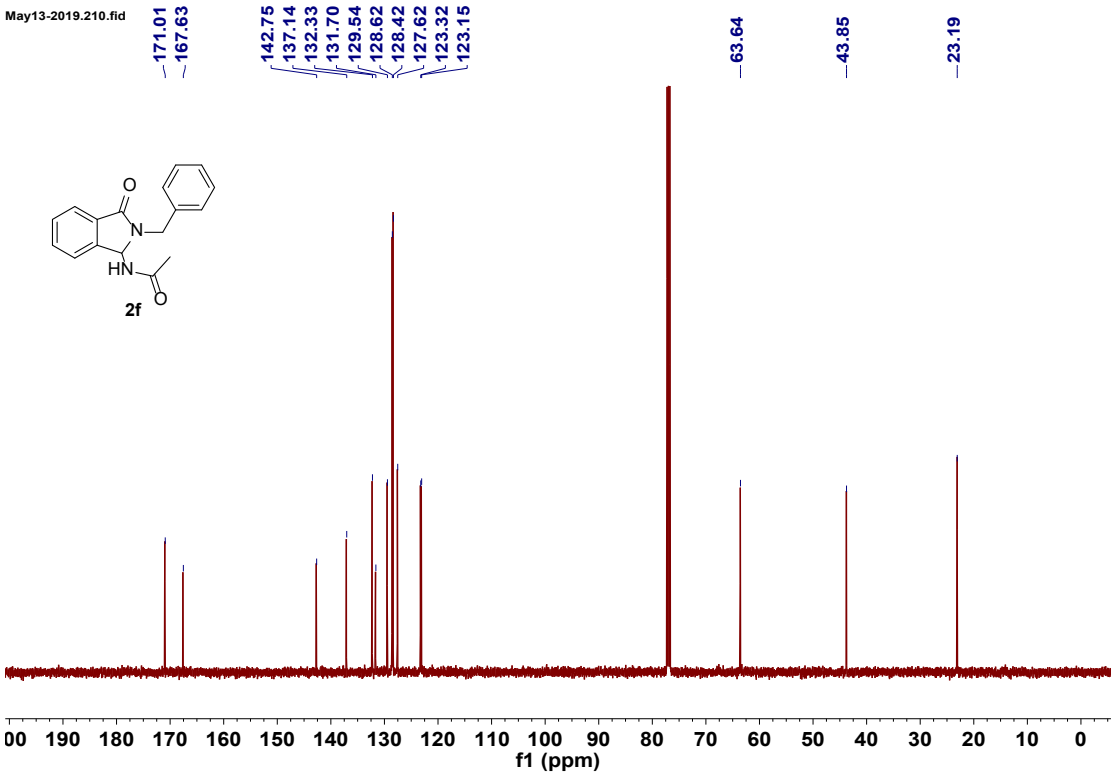


Figure S24. ^{13}C NMR spectrum of compound **2f** (126 MHz, solvent: $CDCl_3$)

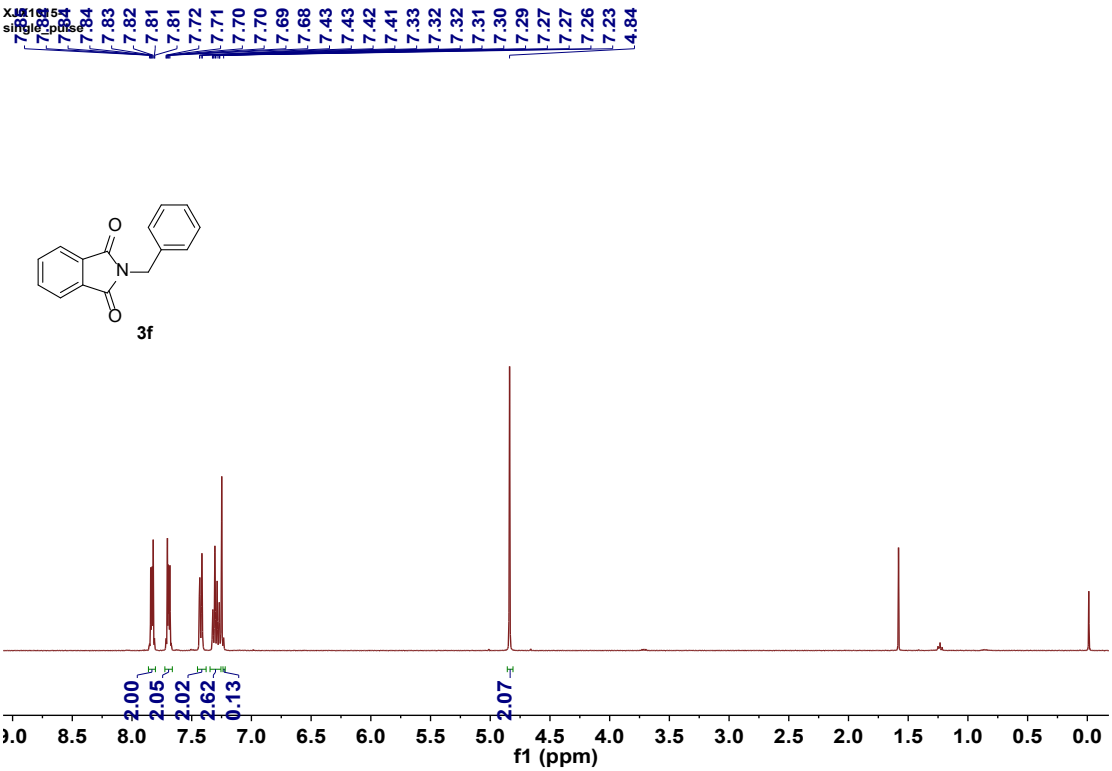


Figure S25. ^{1}H NMR spectrum of compound **3f** (400 MHz, solvent: $CDCl_3$)

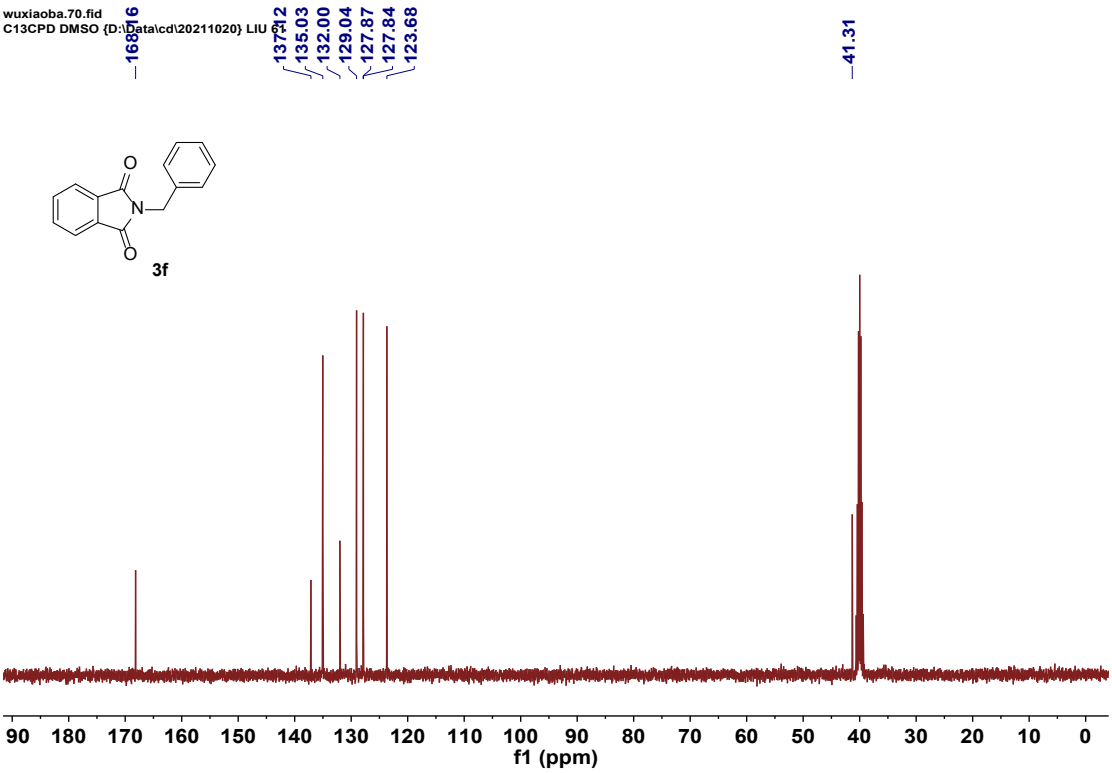


Figure S26. ^{13}C NMR spectrum of compound **3f** (101 MHz, solvent: DMSO-d_6)

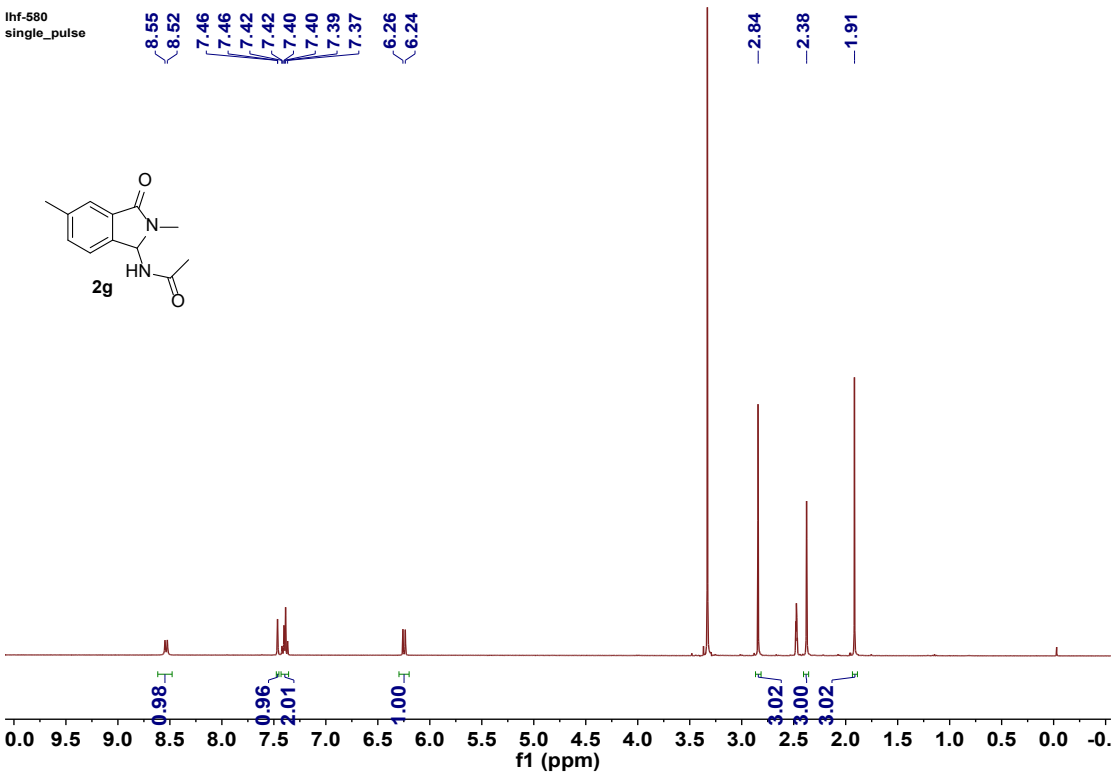


Figure S27. [1]H NMR spectrum of compound **2g** (400 MHz, solvent: DMSO-d_6)

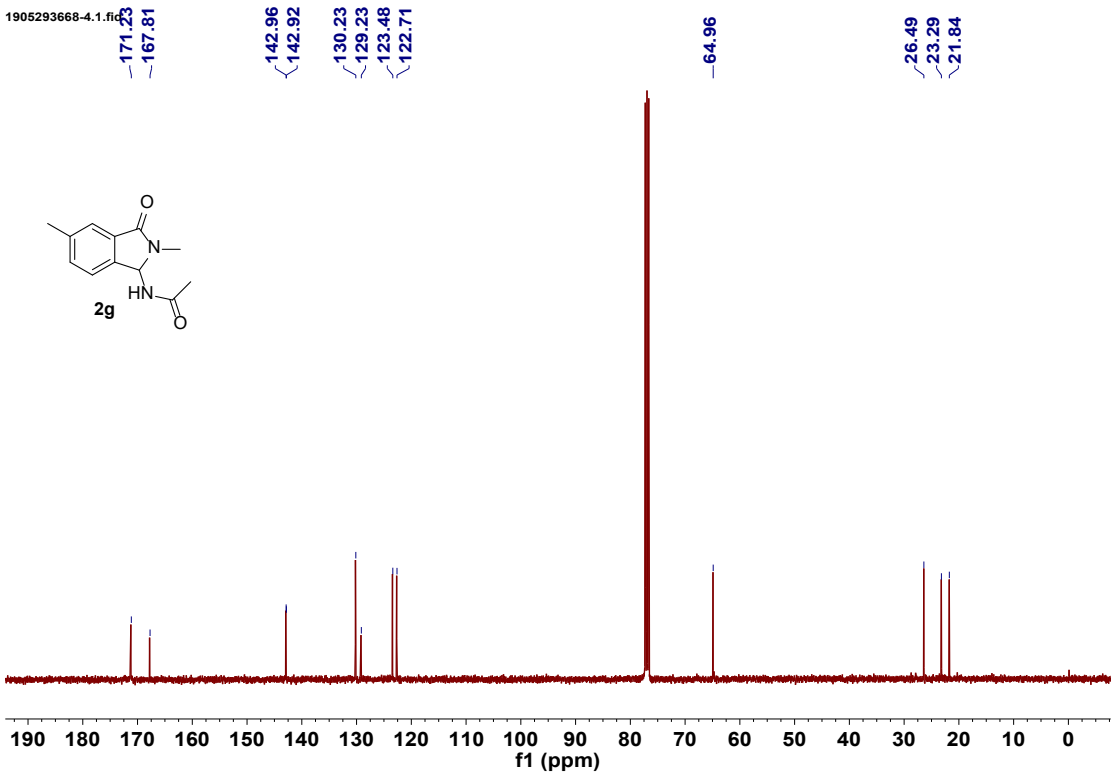


Figure S28. [13]C NMR spectrum of compound **2g** (101 MHz, solvent: $CDCl_3$)

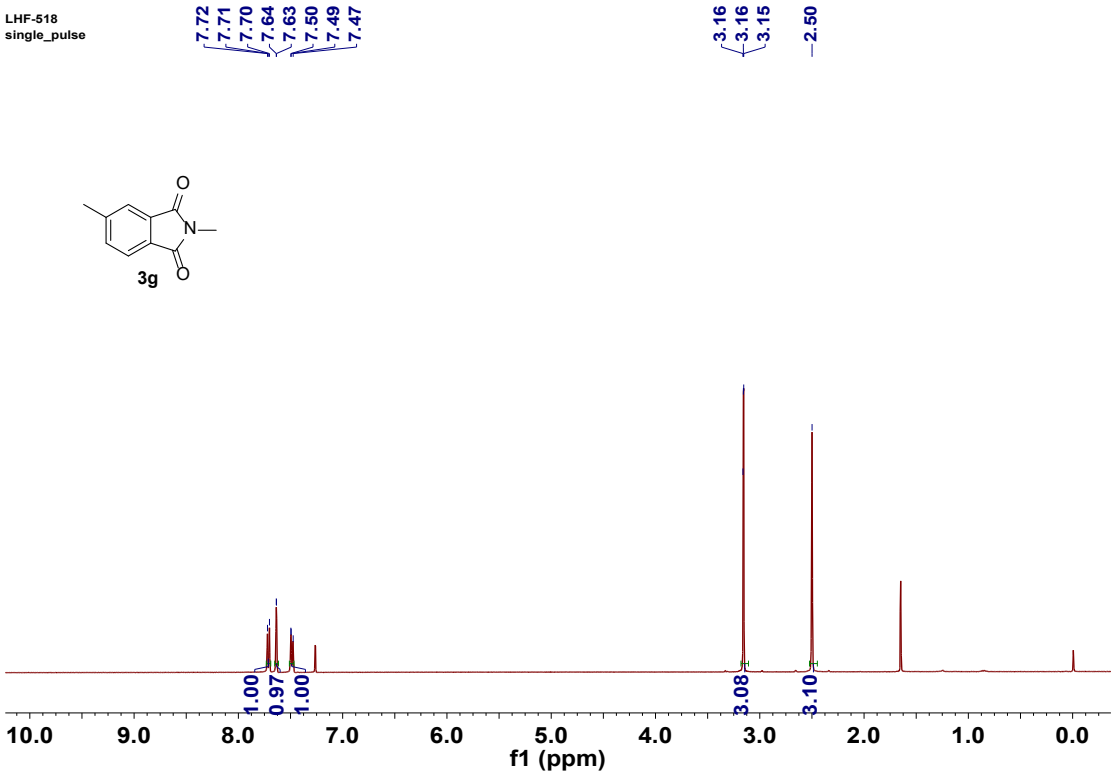


Figure S29. ^{1}H NMR spectrum of compound **3g** (400 MHz, solvent: $CDCl_3$)

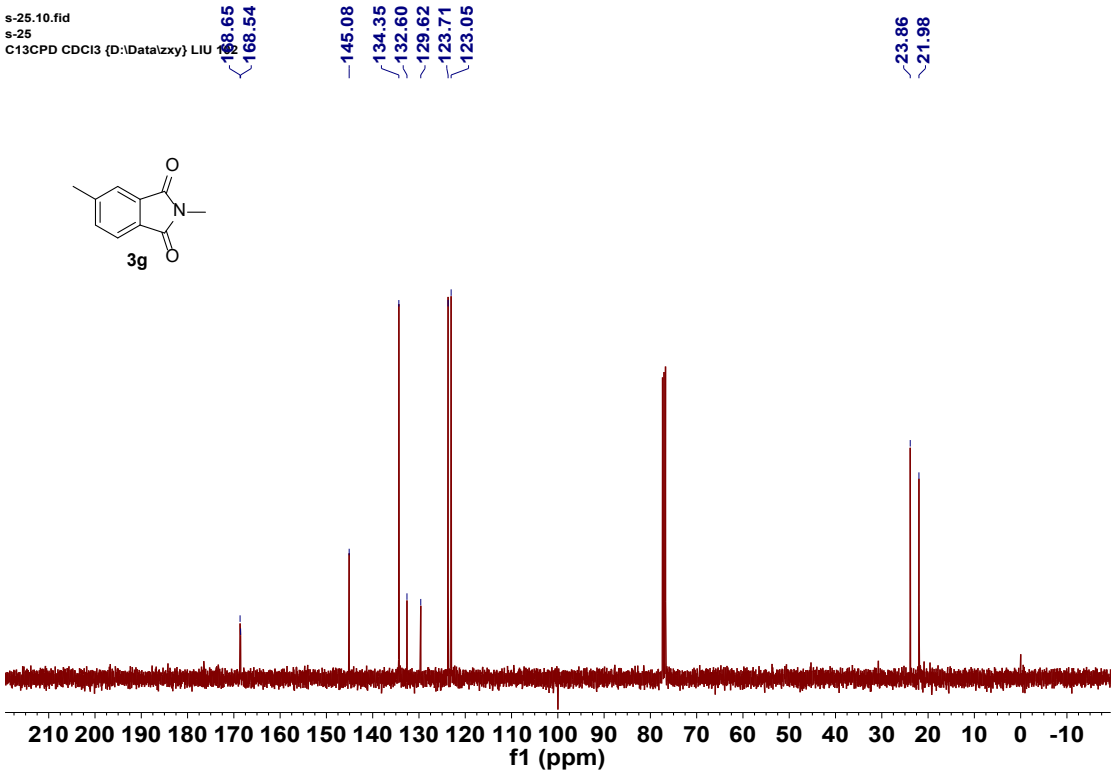


Figure S30. ^{13}C NMR spectrum of compound **3g** (101 MHz, solvent: $CDCl_3$)

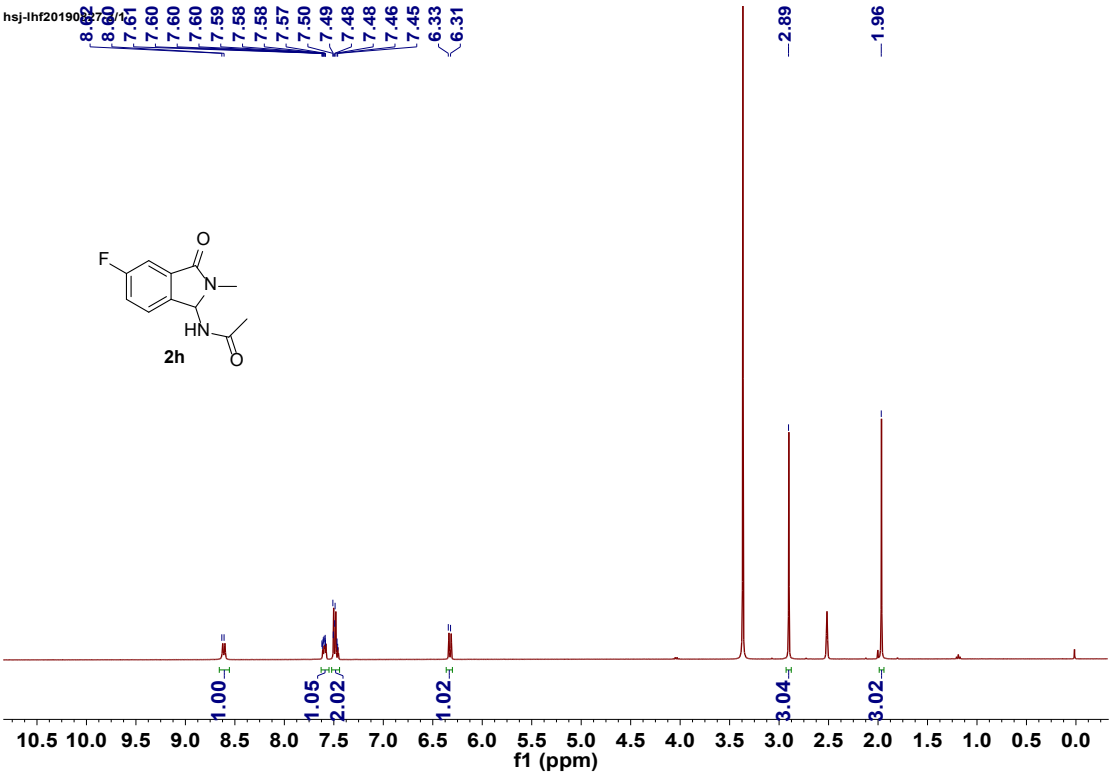


Figure S31. ^{1}H NMR spectrum of compound **2h** (400 MHz, solvent: DMSO-d_6)

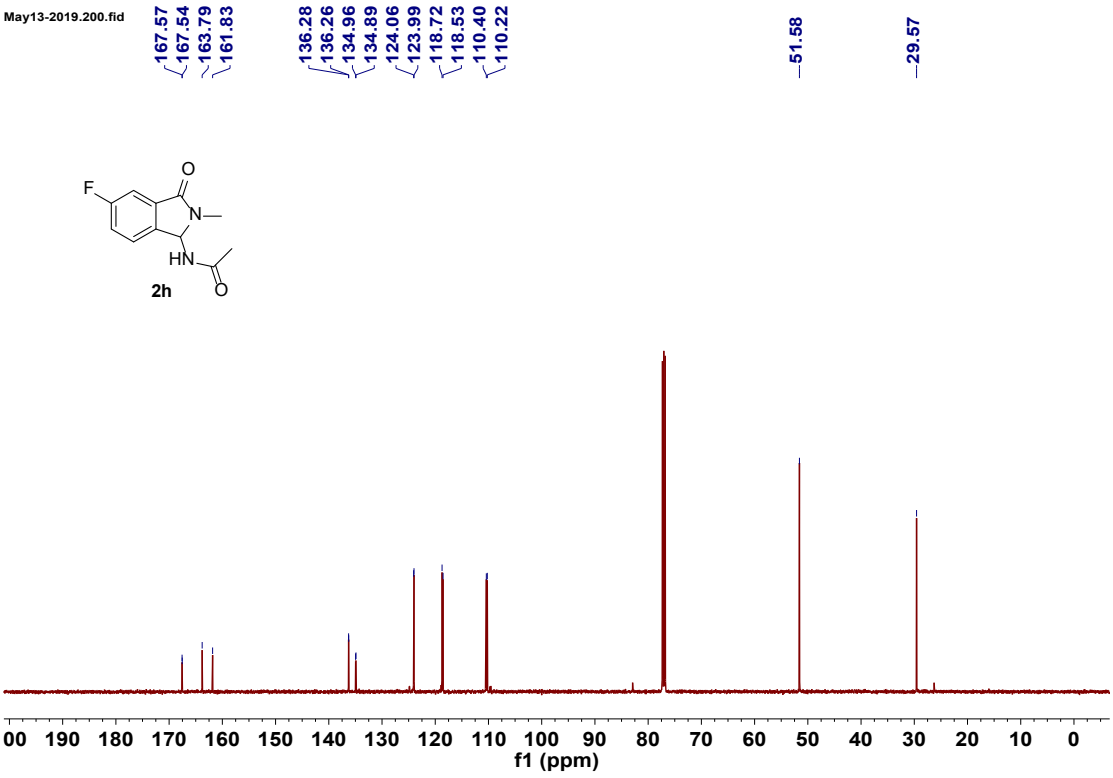


Figure S32. ^{13}C NMR spectrum of compound **2h** (126 MHz, solvent: $CDCl_3$)

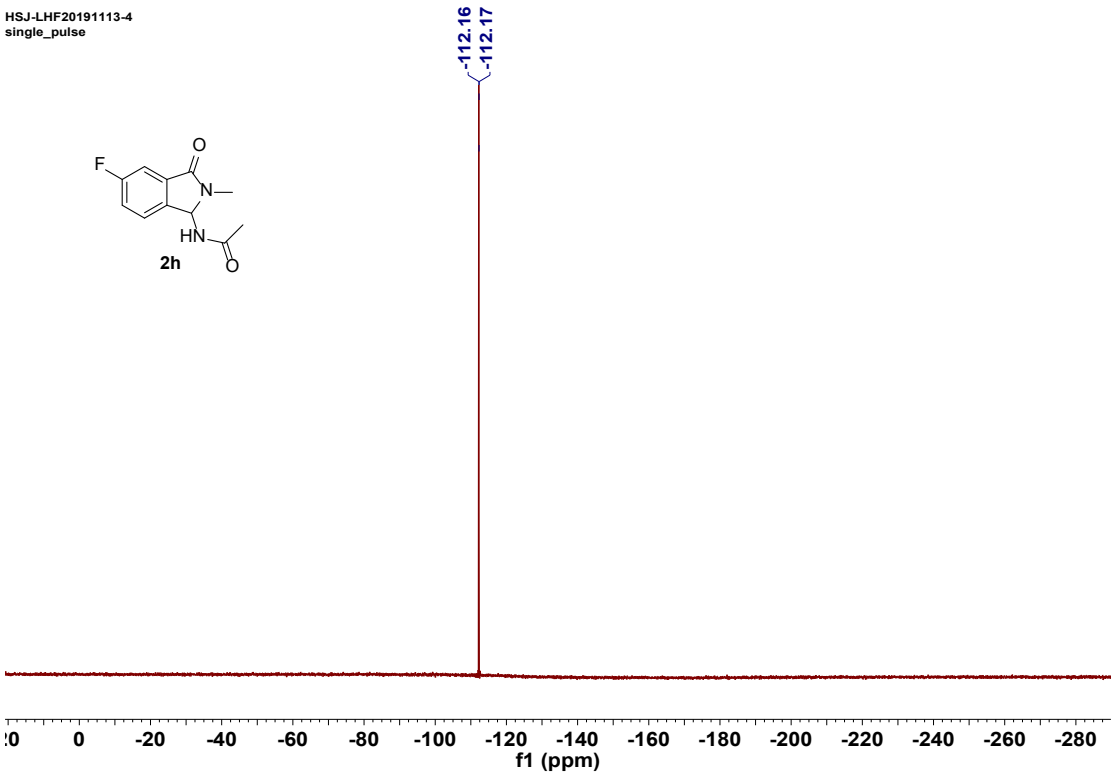


Figure S33. ^{19}F NMR spectrum of compound **2h** (376 MHz, solvent: DMSO-d_6)

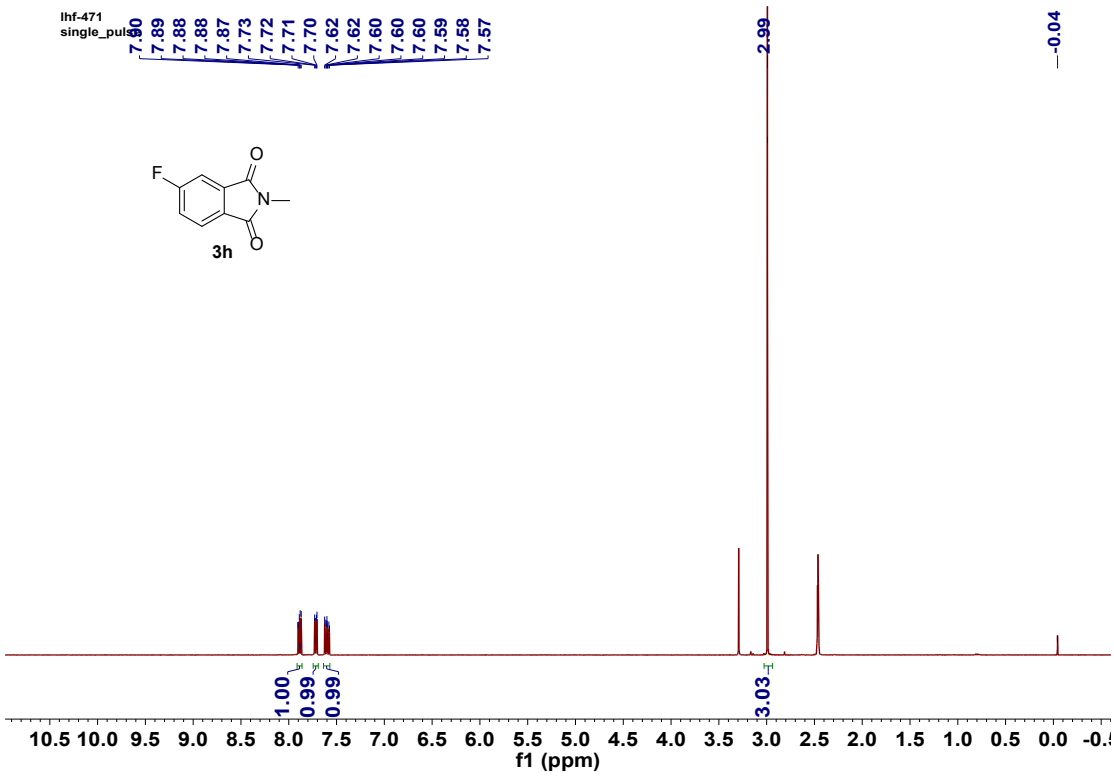


Figure S34. ^{1}H NMR spectrum of compound **3h** (400 MHz, solvent: DMSO-d_6)

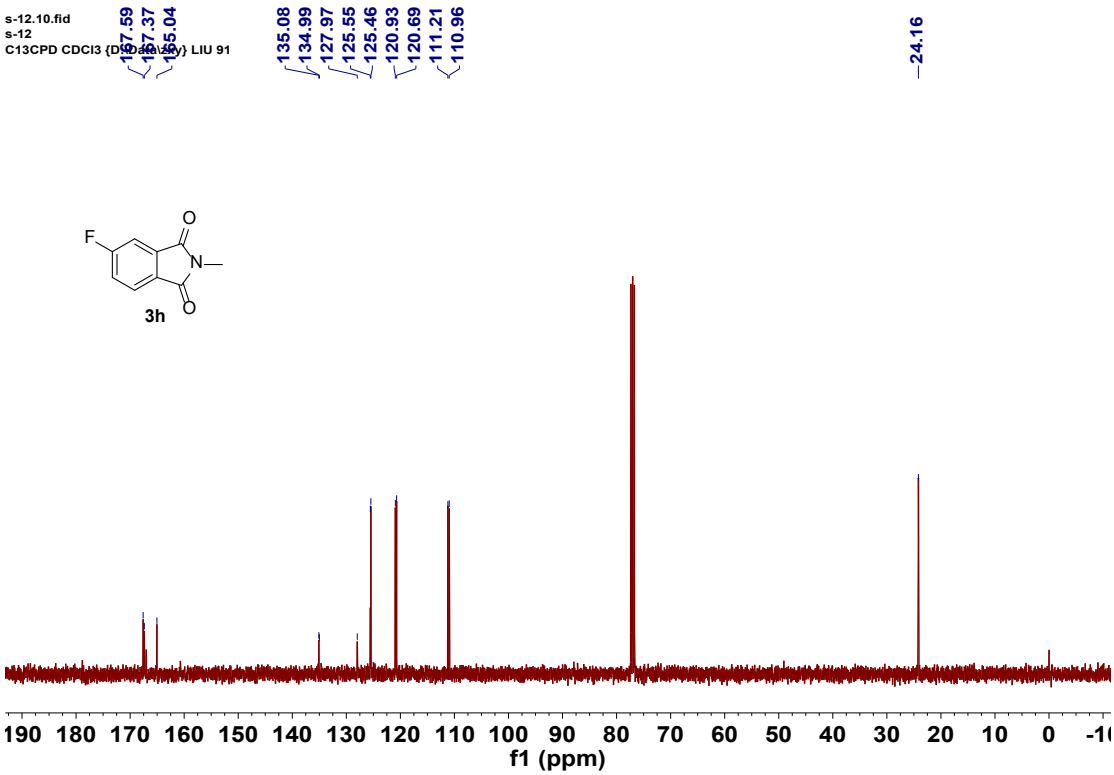


Figure S35. ^{13}C NMR spectrum of compound **3h** (101 MHz, solvent: $CDCl_3$)

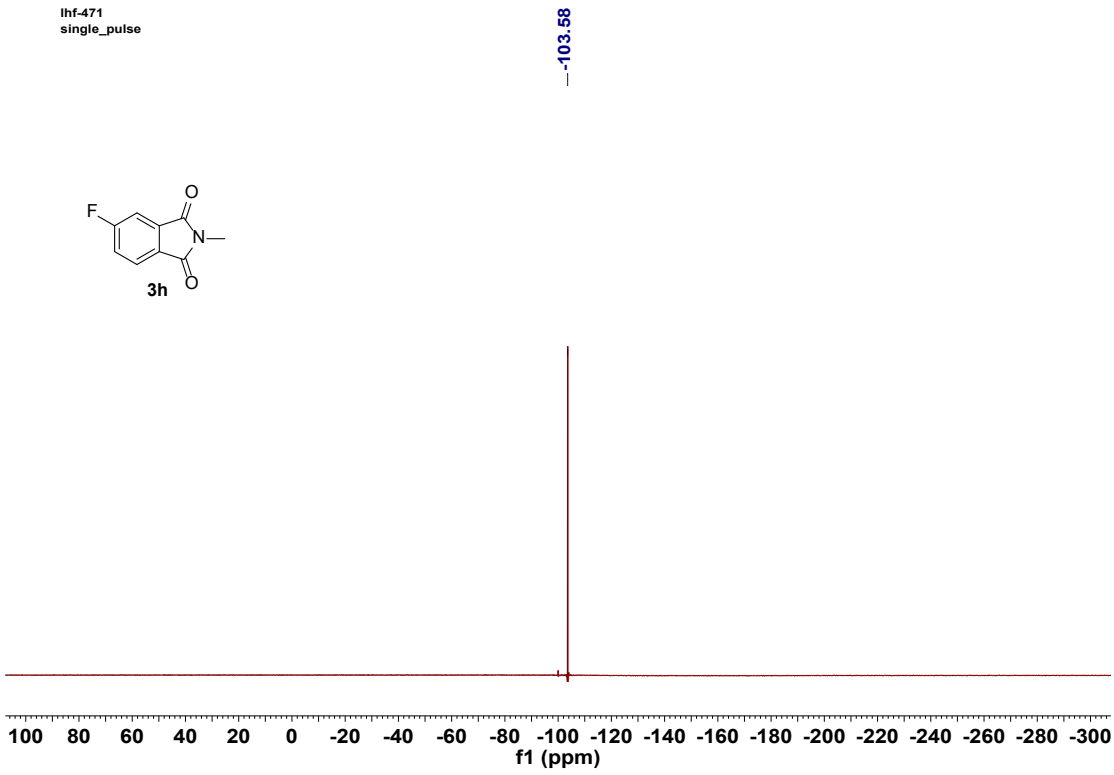


Figure S36. ^{19}F NMR spectrum of compound **3h** (376 MHz, solvent: DMSO-d_6)

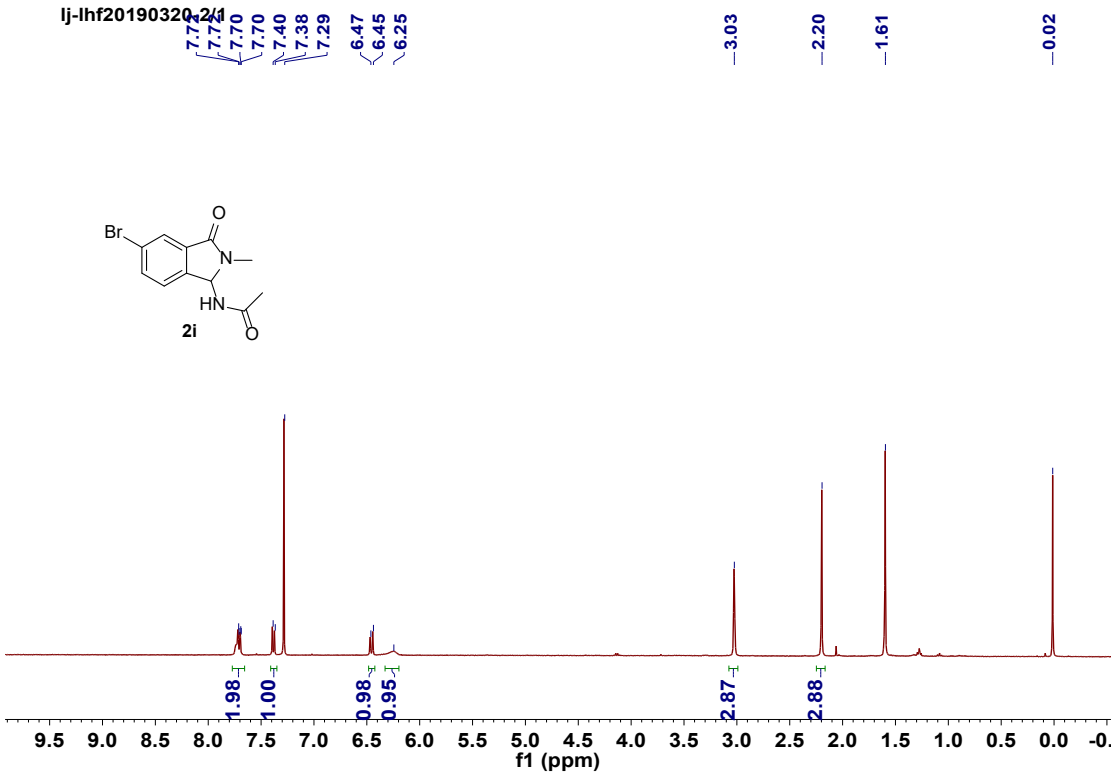


Figure S37. ^{1}H NMR spectrum of compound **2i** (400 MHz, solvent: $CDCl_3$)

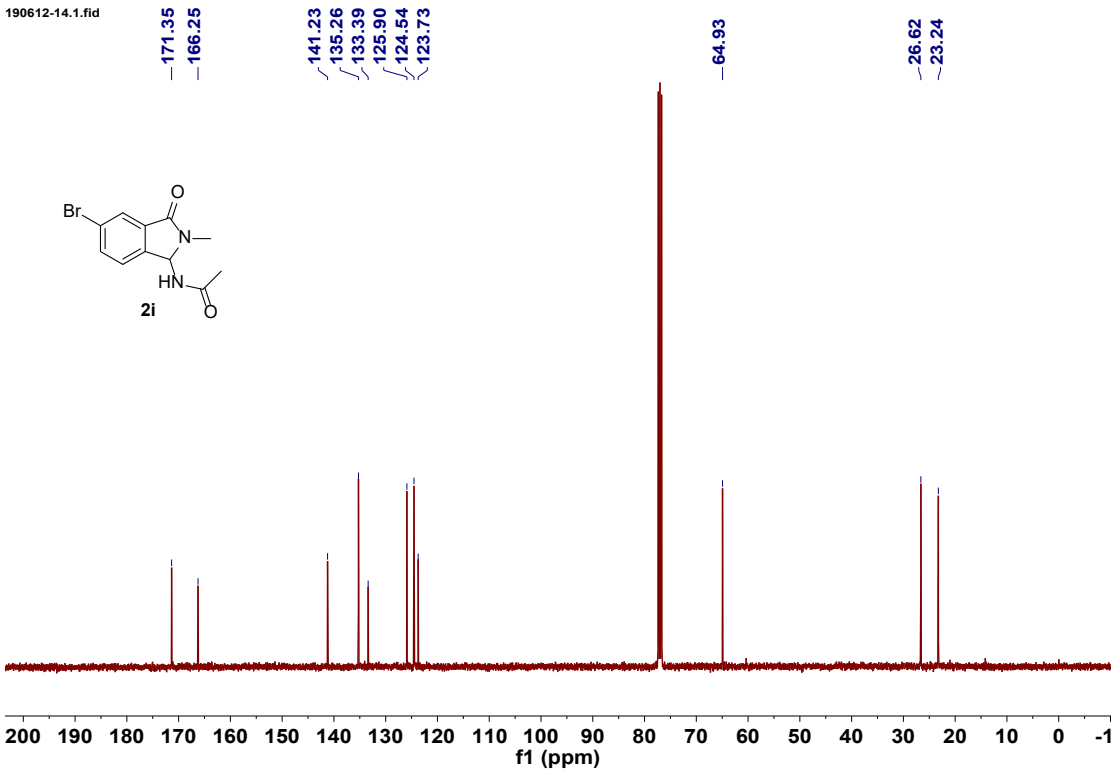


Figure S38. ^{13}C NMR spectrum of compound **2i** (101 MHz, solvent: $CDCl_3$)

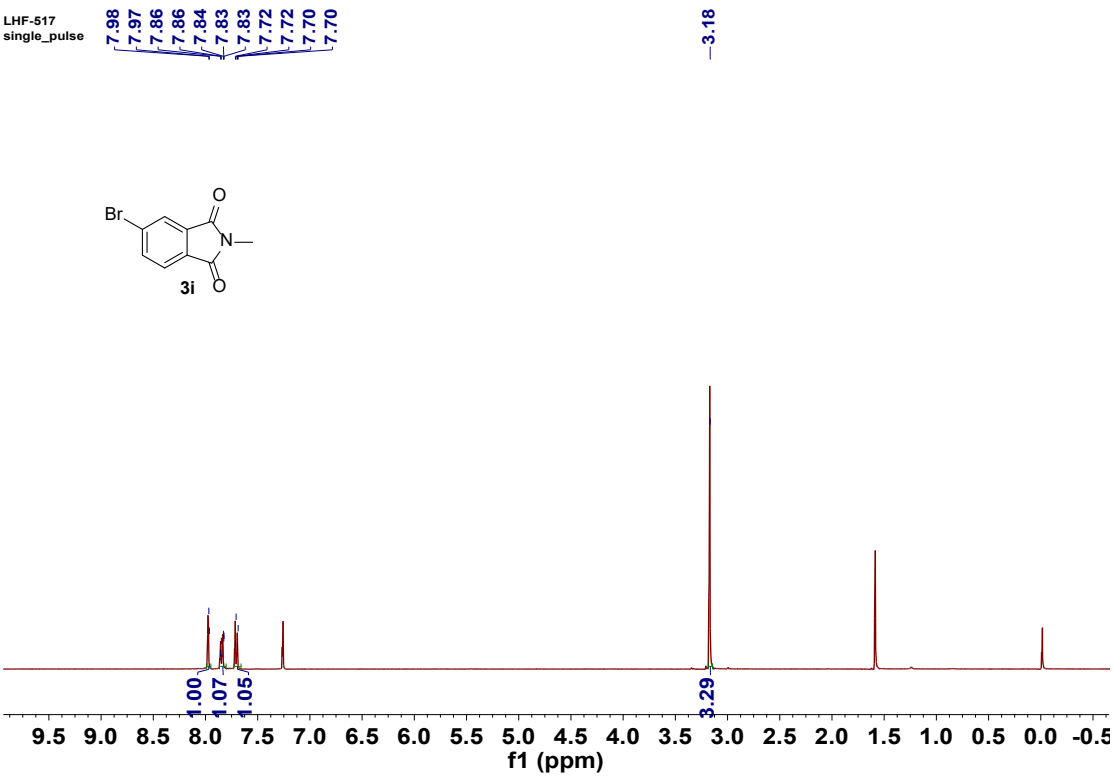


Figure S39. ^{1}H NMR spectrum of compound **3i** (400 MHz, solvent: $CDCl_3$)

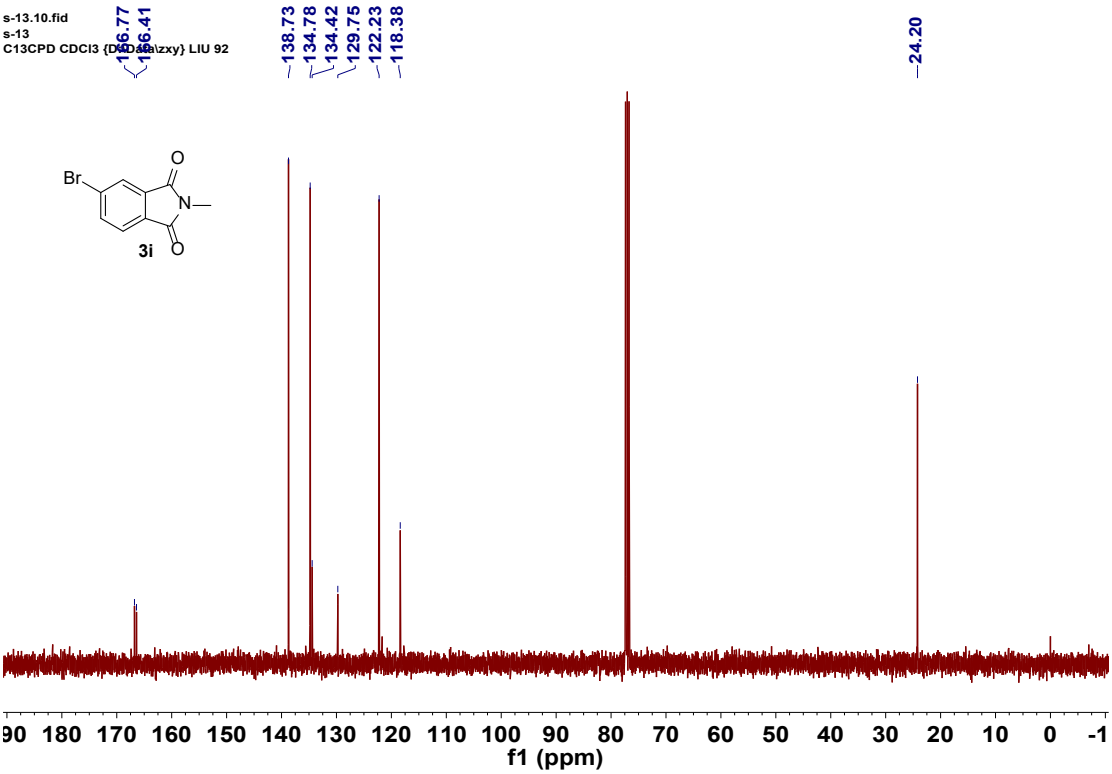


Figure S40. ^{13}C NMR spectrum of compound **3i** (101 MHz, solvent: $CDCl_3$)

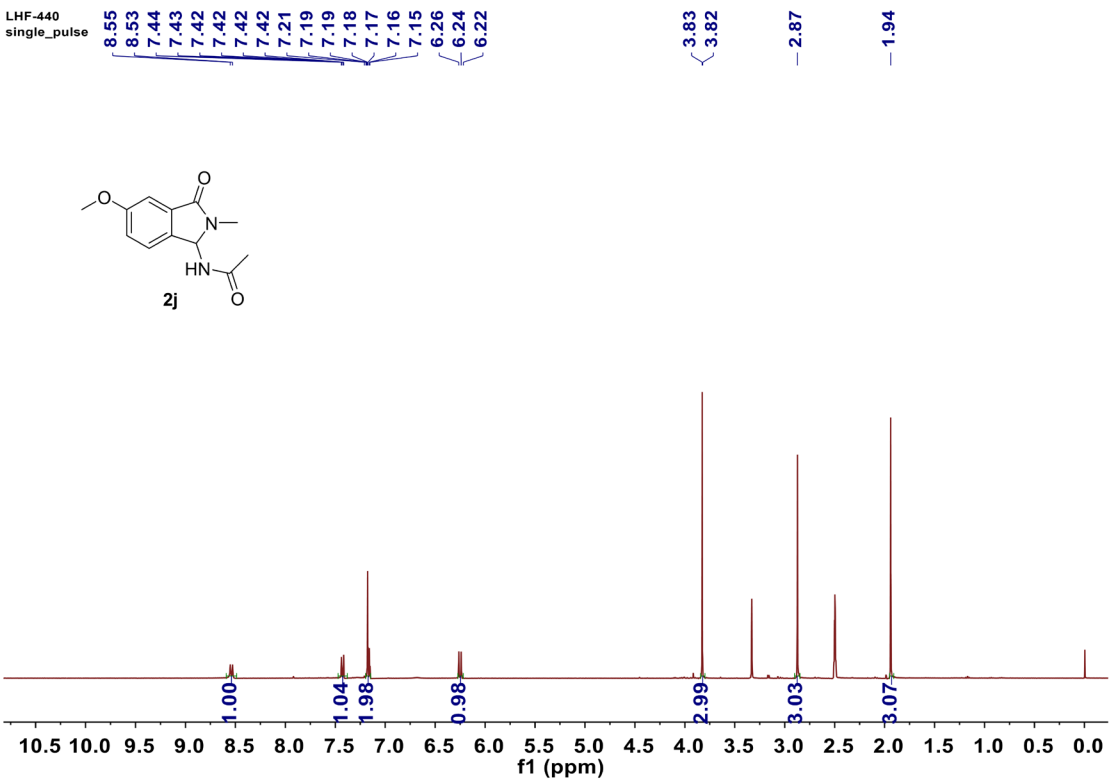


Figure S41. ^{1}H NMR spectrum of compound **2j** (400 MHz, solvent: DMSO-d_6)

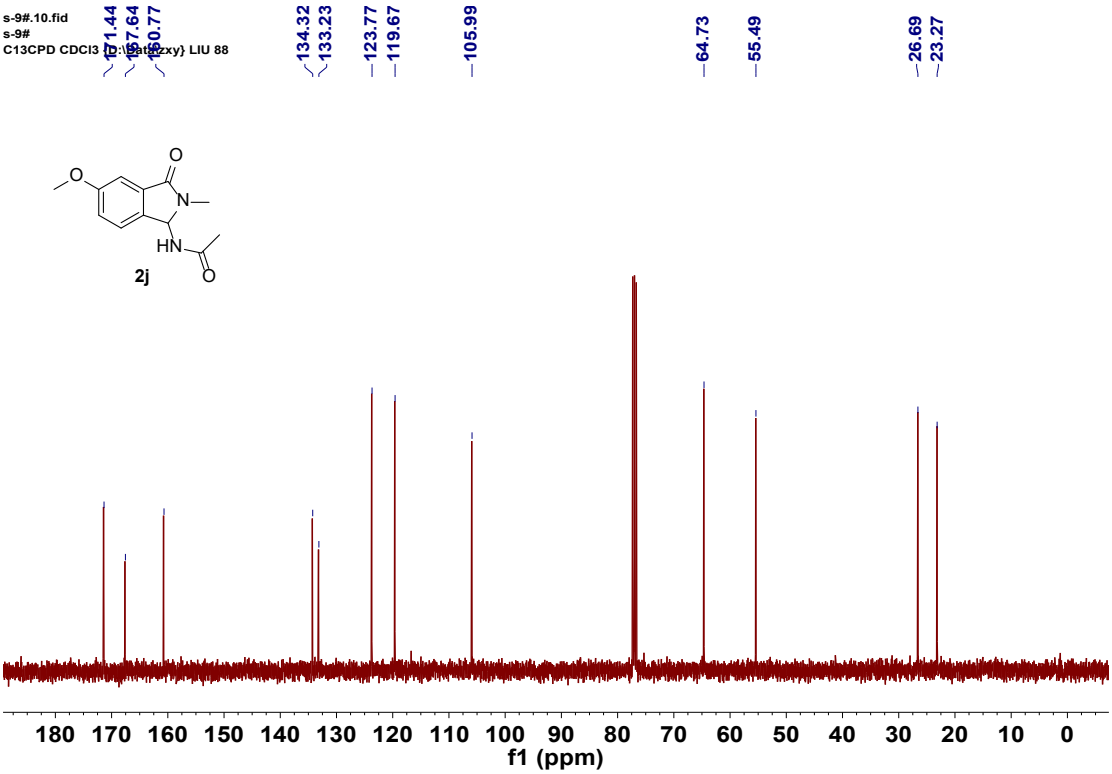


Figure S42. ^{13}C NMR spectrum of compound **2j** (101 MHz, solvent: $CDCl_3$)

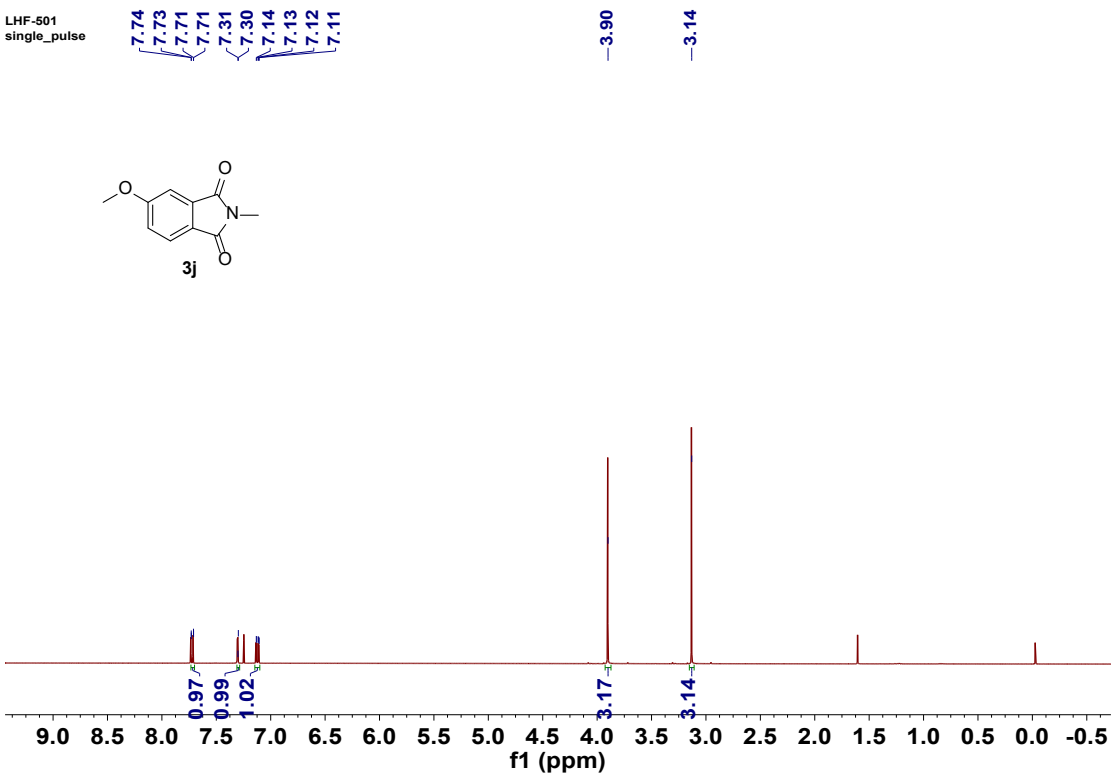


Figure S43. ^{1}H NMR spectrum of compound **3j** (400 MHz, solvent: $CDCl_3$)

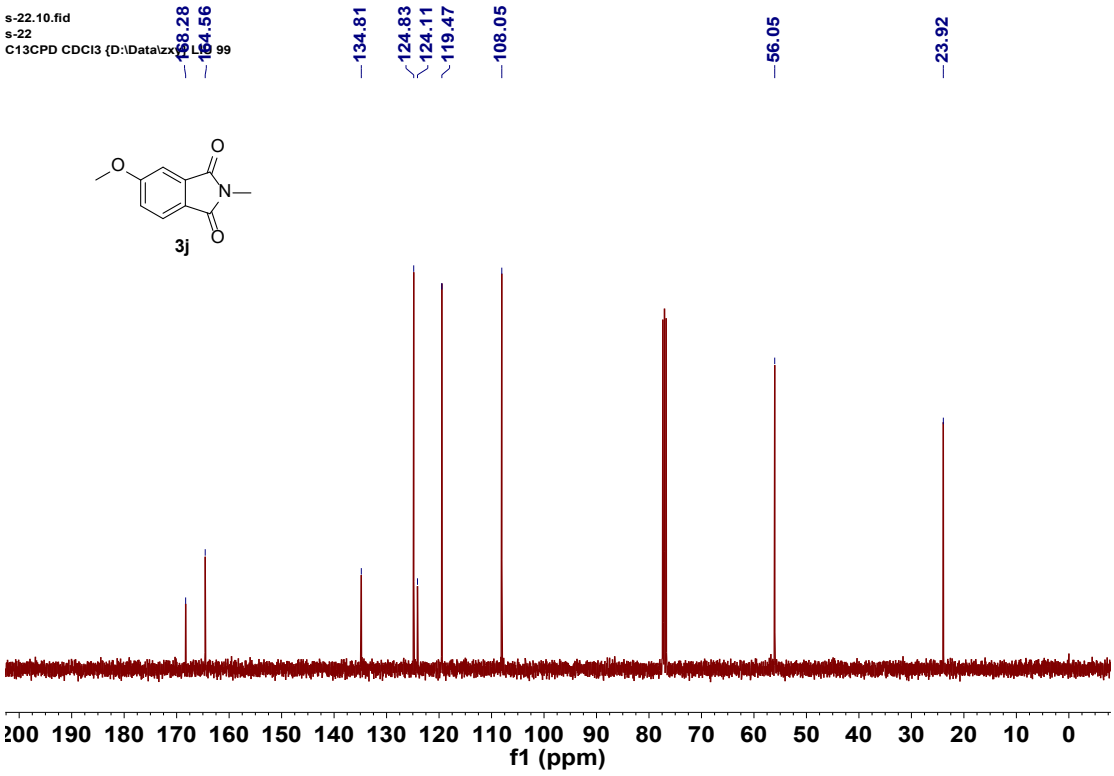


Figure S44. ^{13}C NMR spectrum of compound **3j** (101 MHz, solvent: $CDCl_3$)

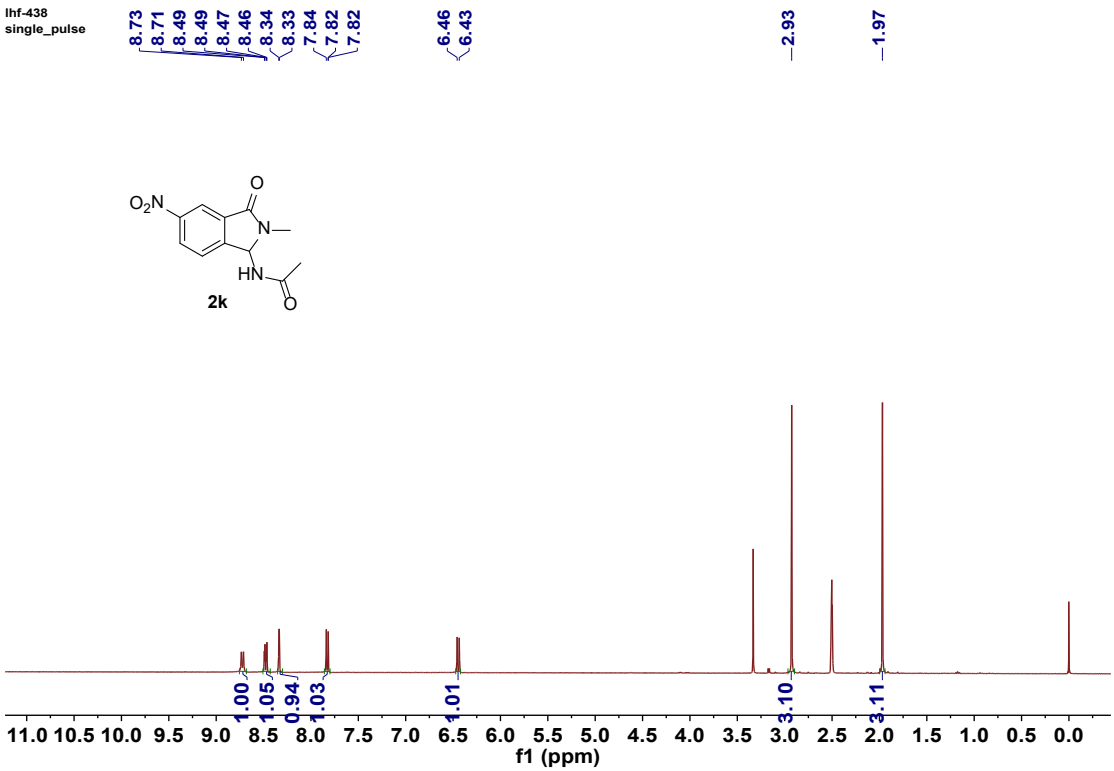


Figure S45. [1]H NMR spectrum of compound **2k** (400 MHz, solvent: DMSO-d_6)

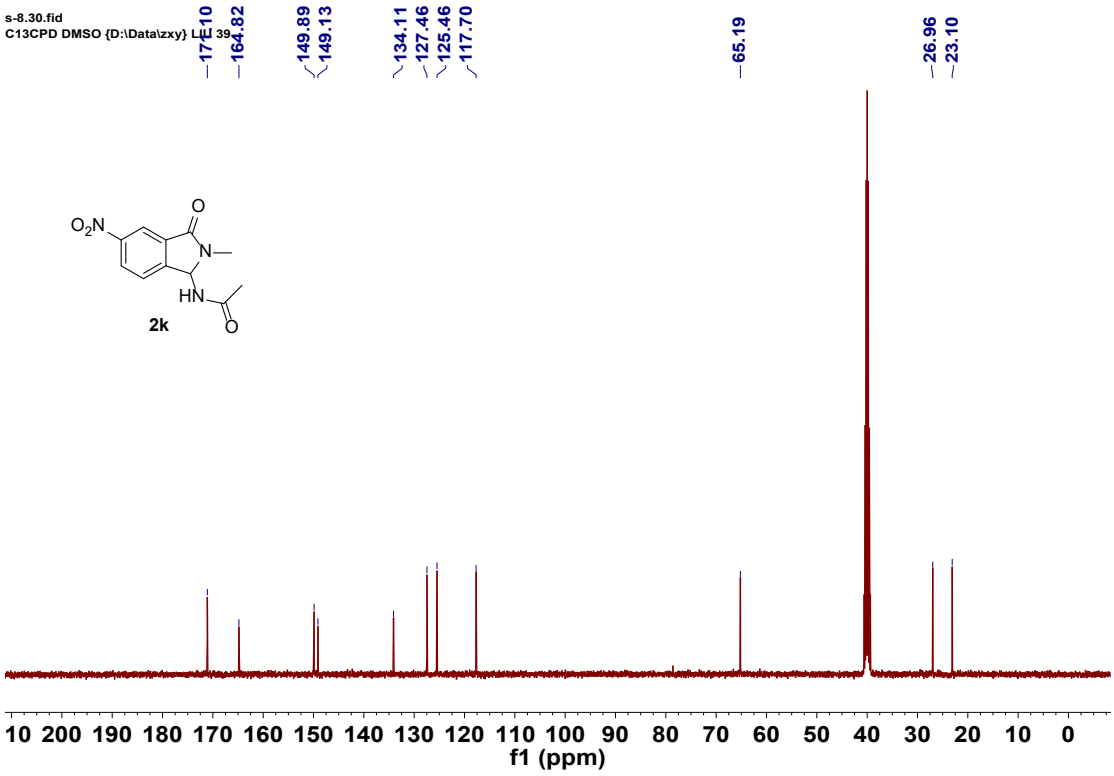


Figure S46. [13]C NMR spectrum of compound **2k** (101 MHz, solvent: DMSO-d_6)

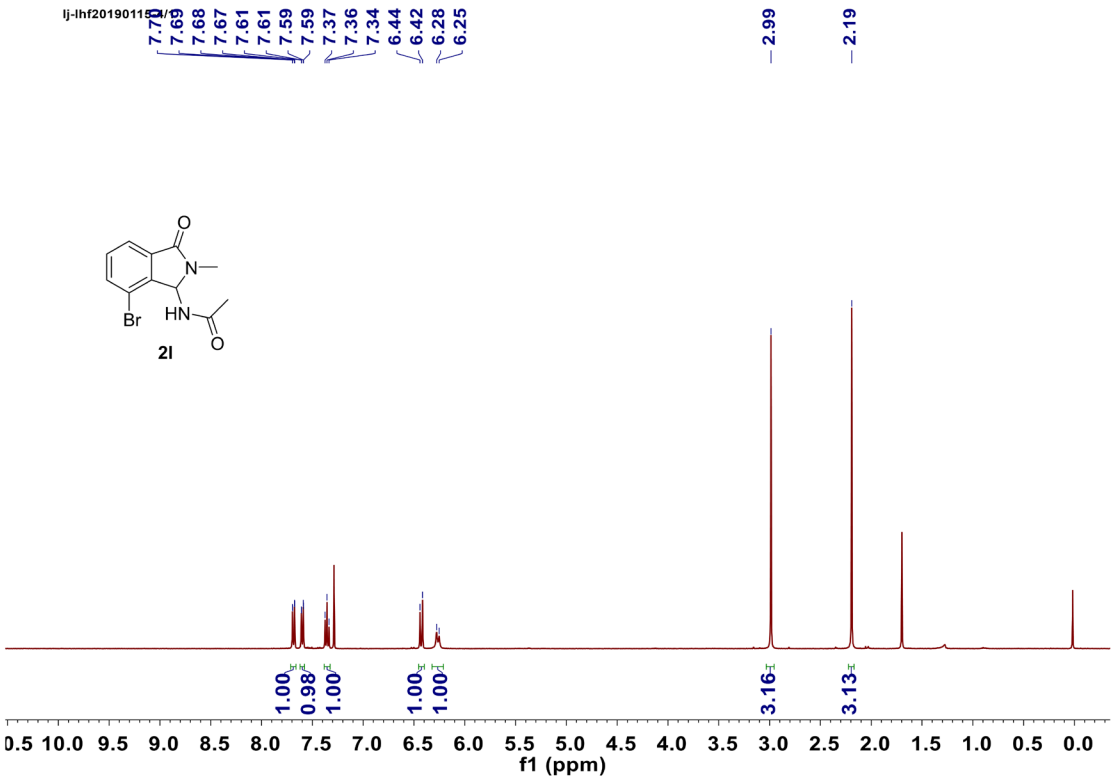


Figure S47. ^{1}H NMR spectrum of compound **2l** (400 MHz, solvent: $CDCl_3$)

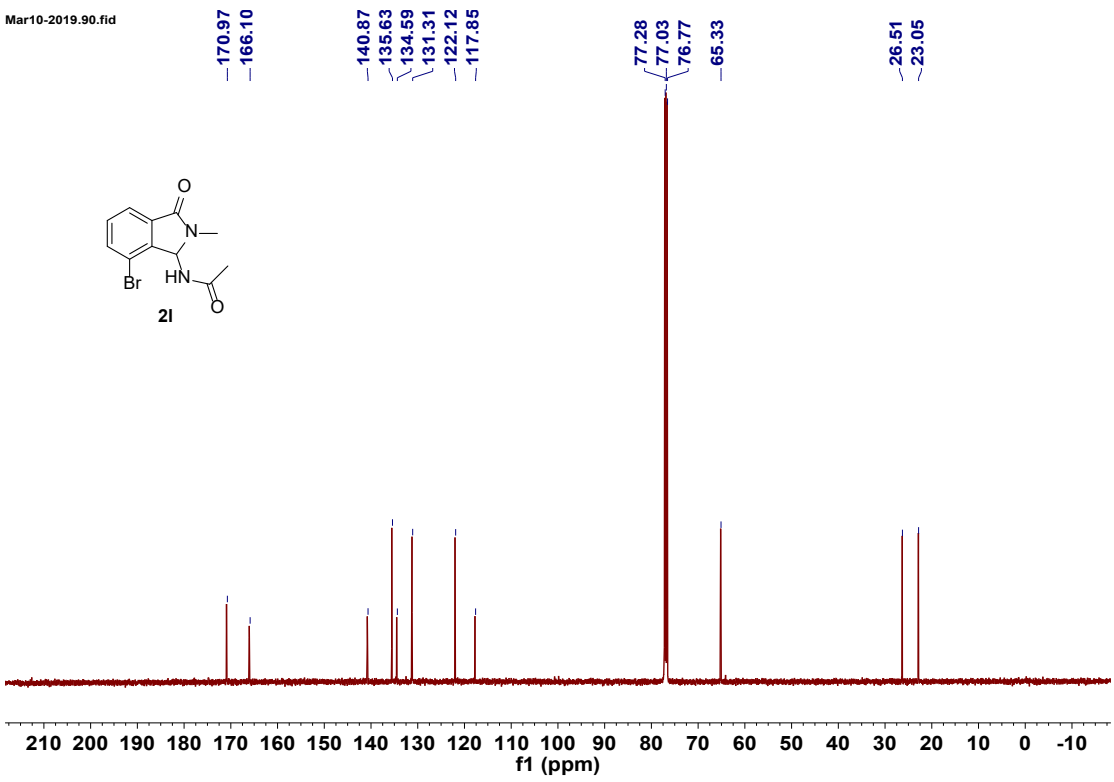


Figure S48. ^{13}C NMR spectrum of compound **2l** (126 MHz, solvent: $CDCl_3$)

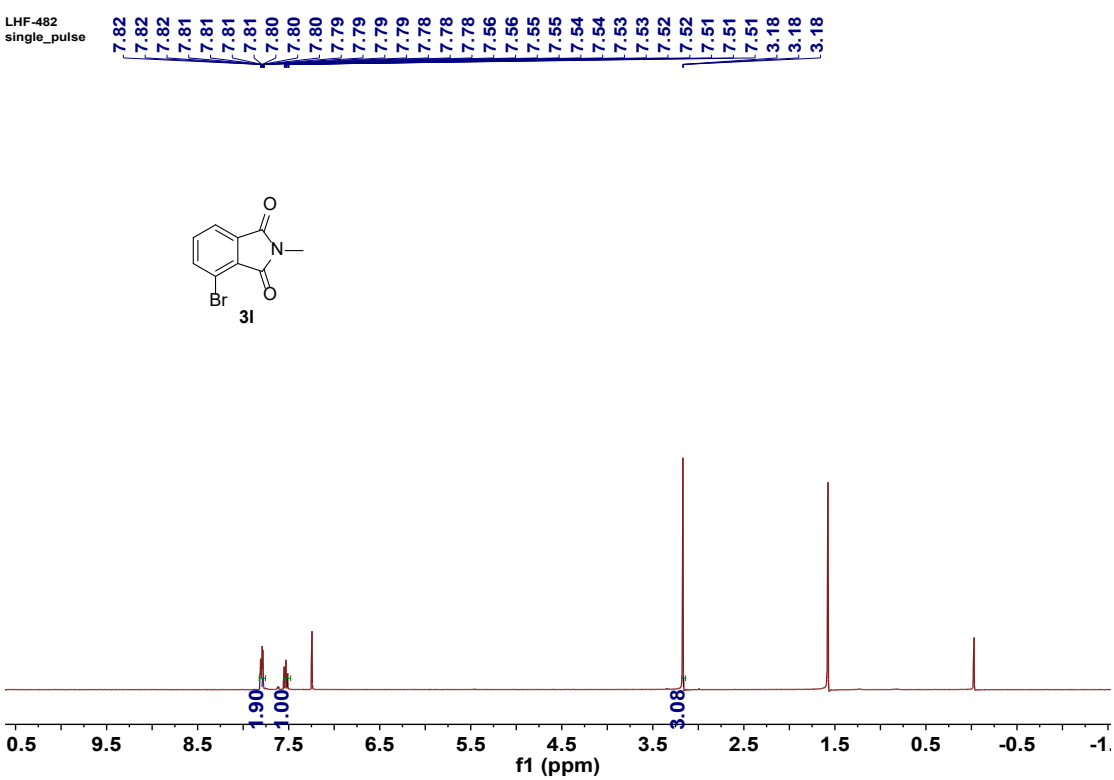


Figure S49. ^{1}H NMR spectrum of compound **3l** (400 MHz, solvent: $CDCl_3$)

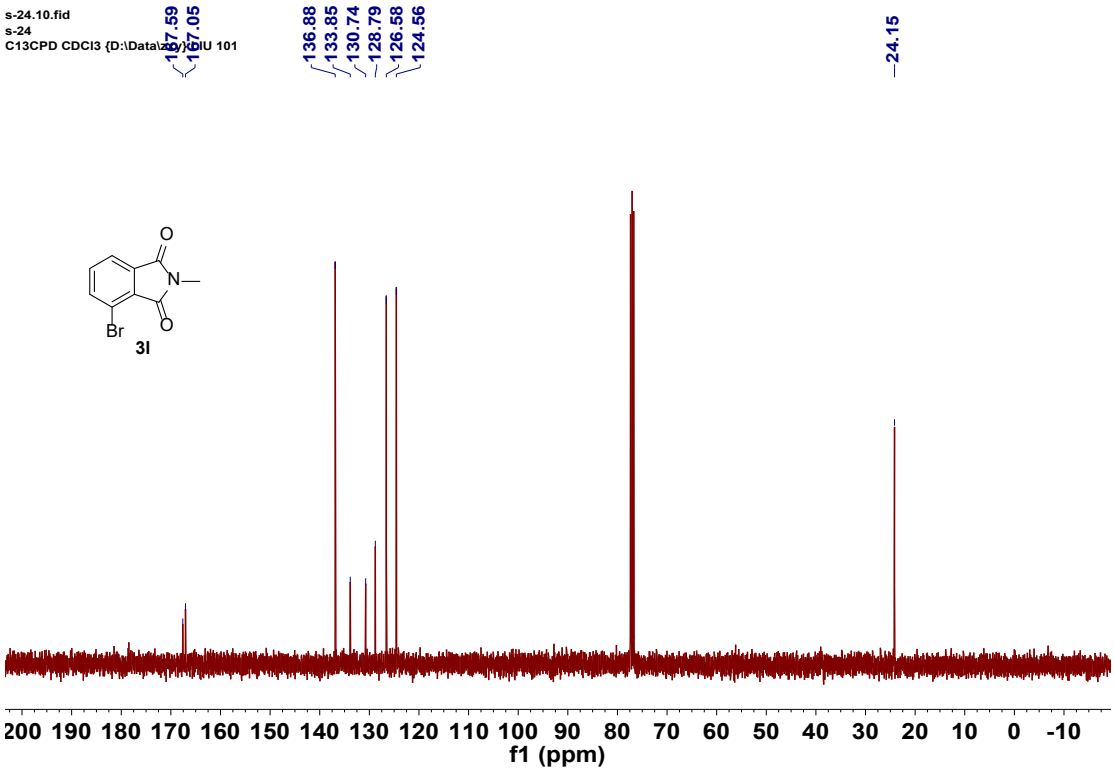


Figure S50. ^{13}C NMR spectrum of compound **3l** (101 MHz, solvent: $CDCl_3$)

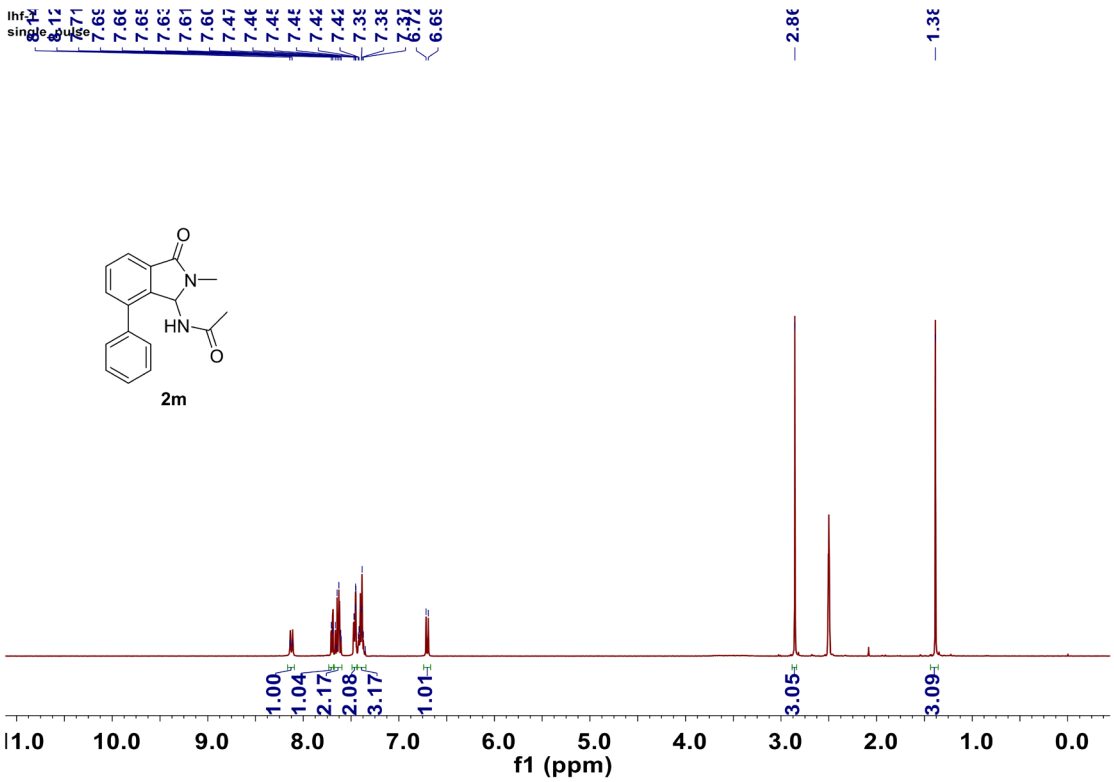


Figure S51. ^{1}H NMR spectrum of compound **2m** (400 MHz, solvent: DMSO-d_6)

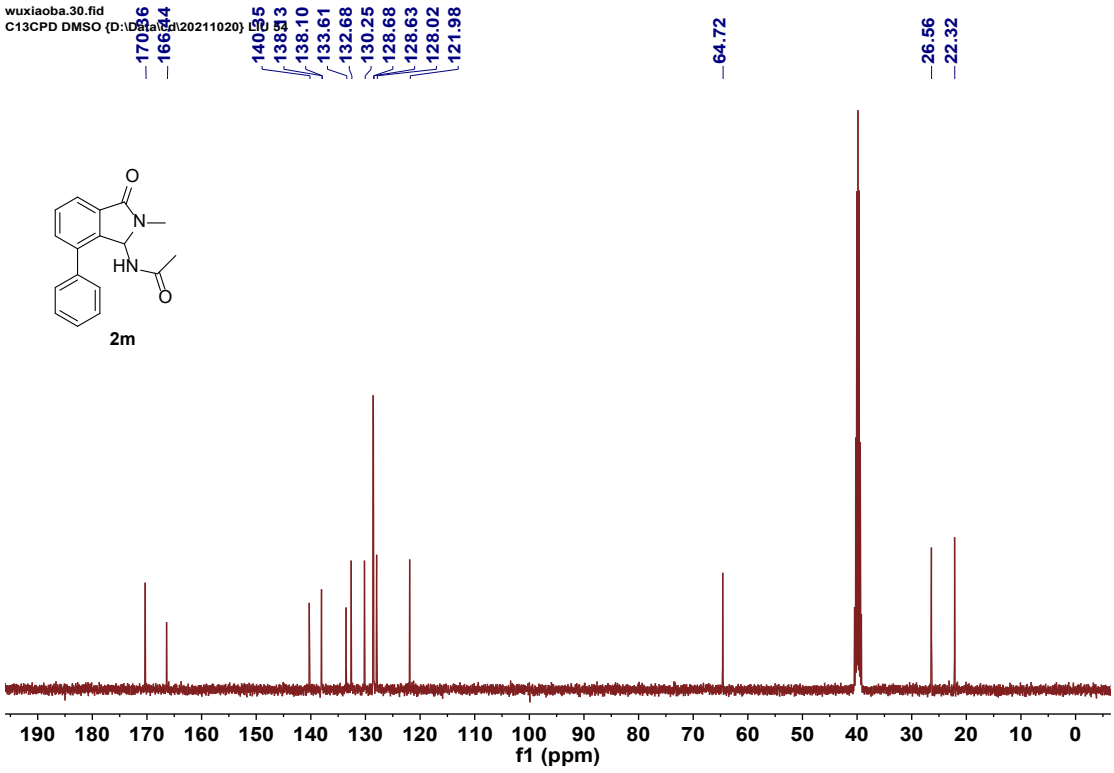


Figure S52. ^{13}C NMR spectrum of compound **2m** (101 MHz, solvent: DMSO-d_6)

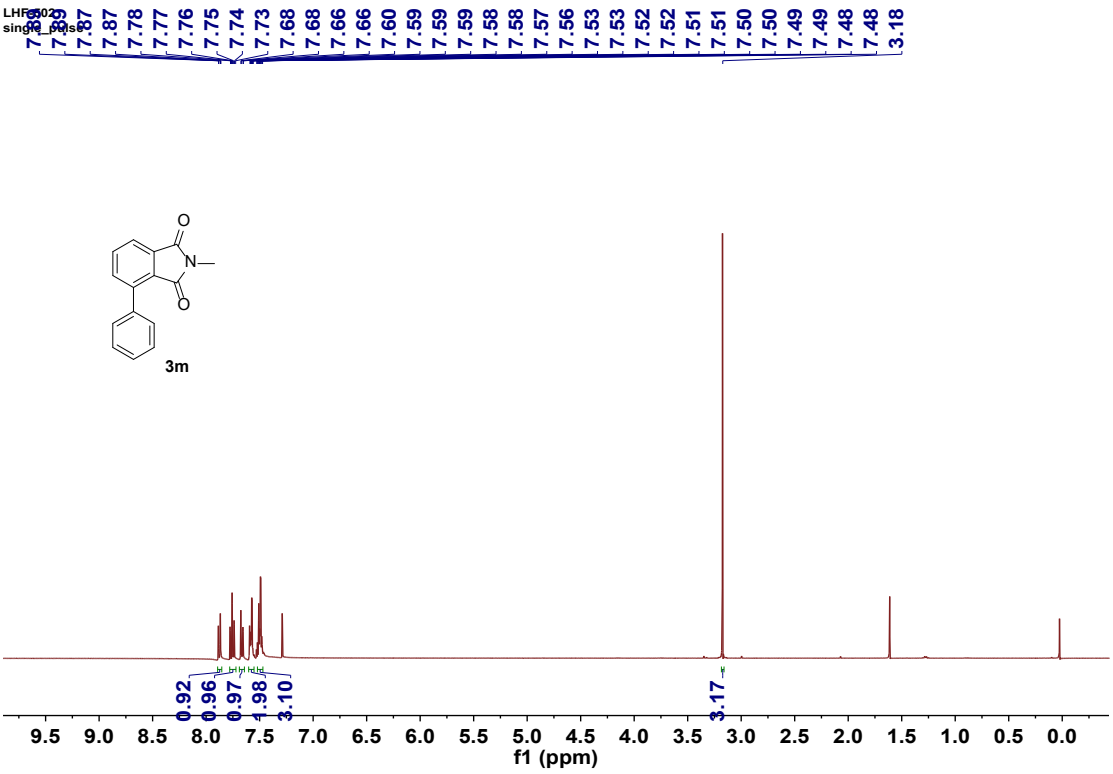


Figure S53. ^{1}H NMR spectrum of compound **3m** (400 MHz, solvent: $CDCl_3$)

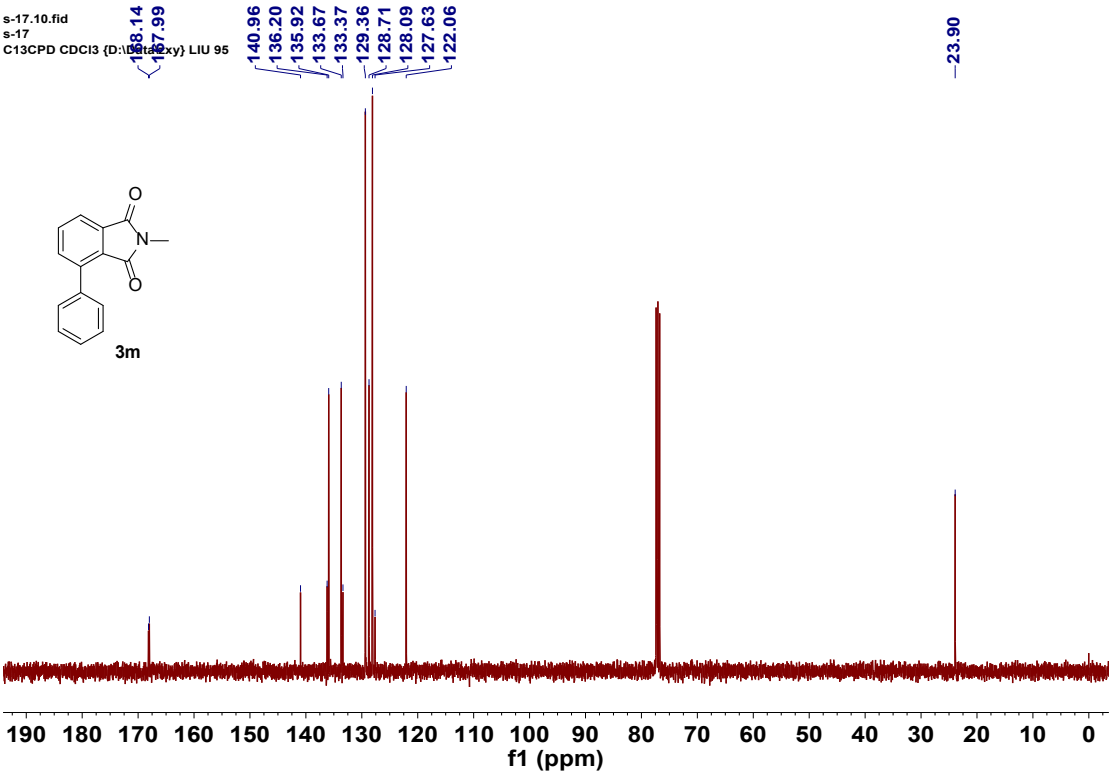


Figure S54. ^{13}C NMR spectrum of compound **3m** (101 MHz, solvent: $CDCl_3$)

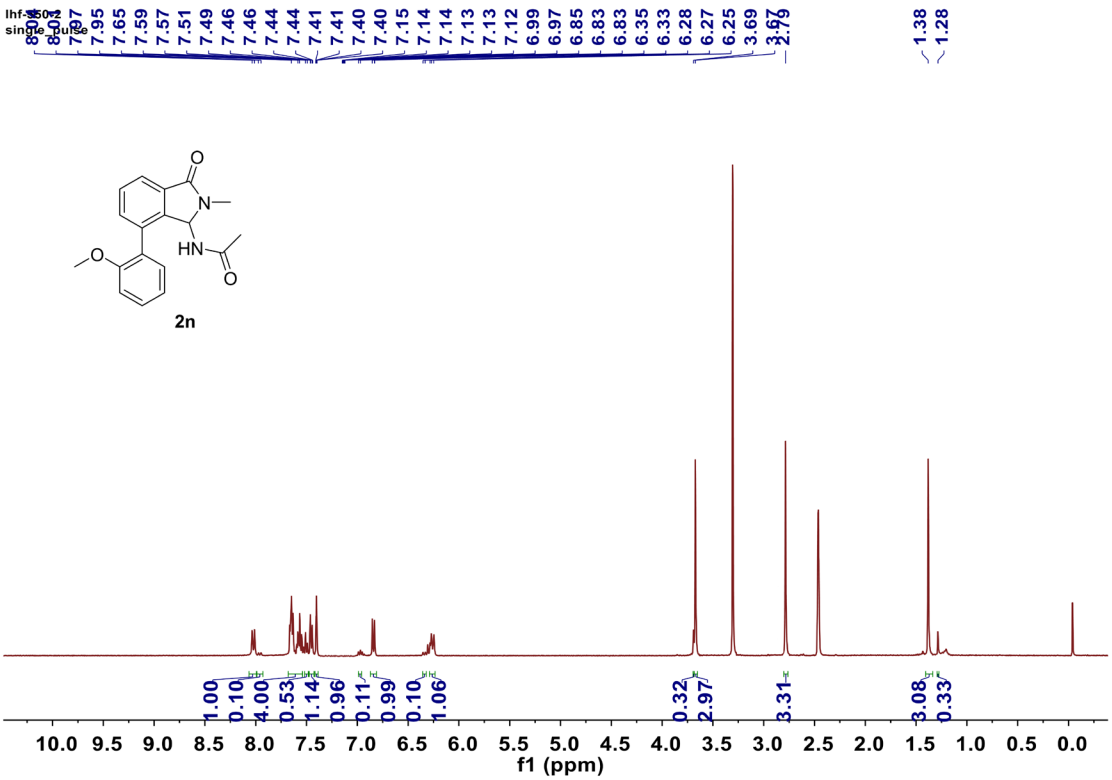


Figure S55. ^{1}H NMR spectrum of compound **2n** (400 MHz, solvent: DMSO-d_6) *d.r.* = 10:1

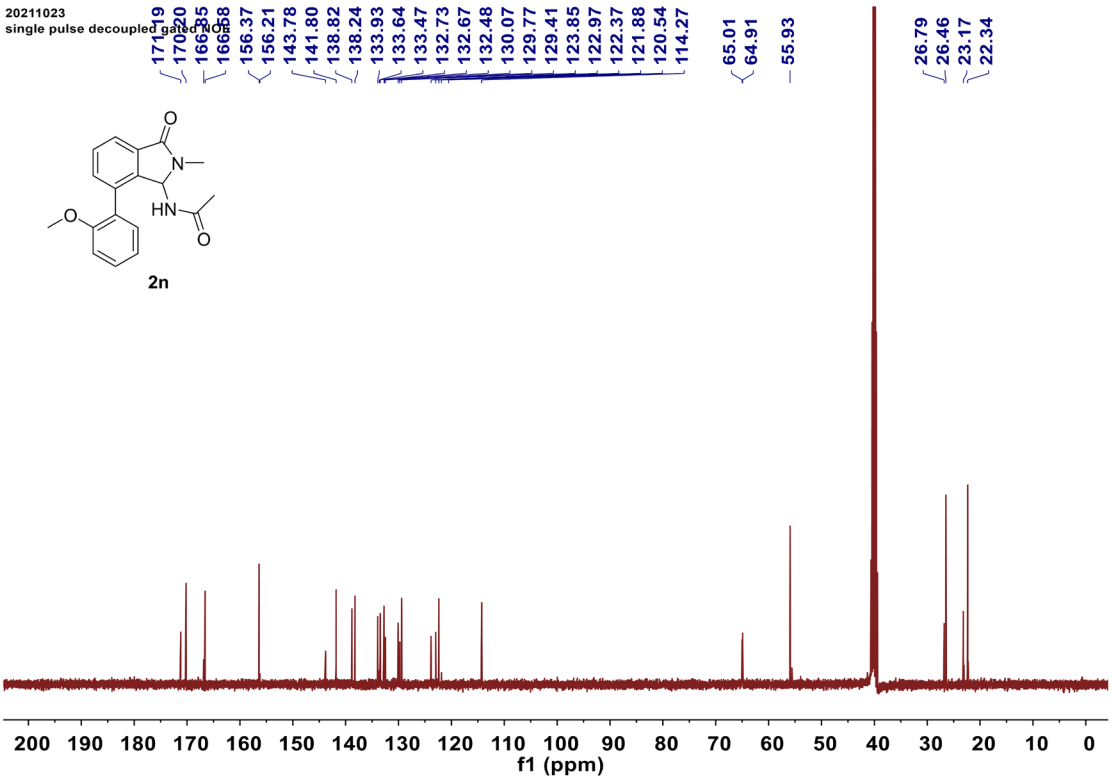


Figure S56. ^{13}C NMR spectrum of compound **2n** (101 MHz, solvent: DMSO-d_6)

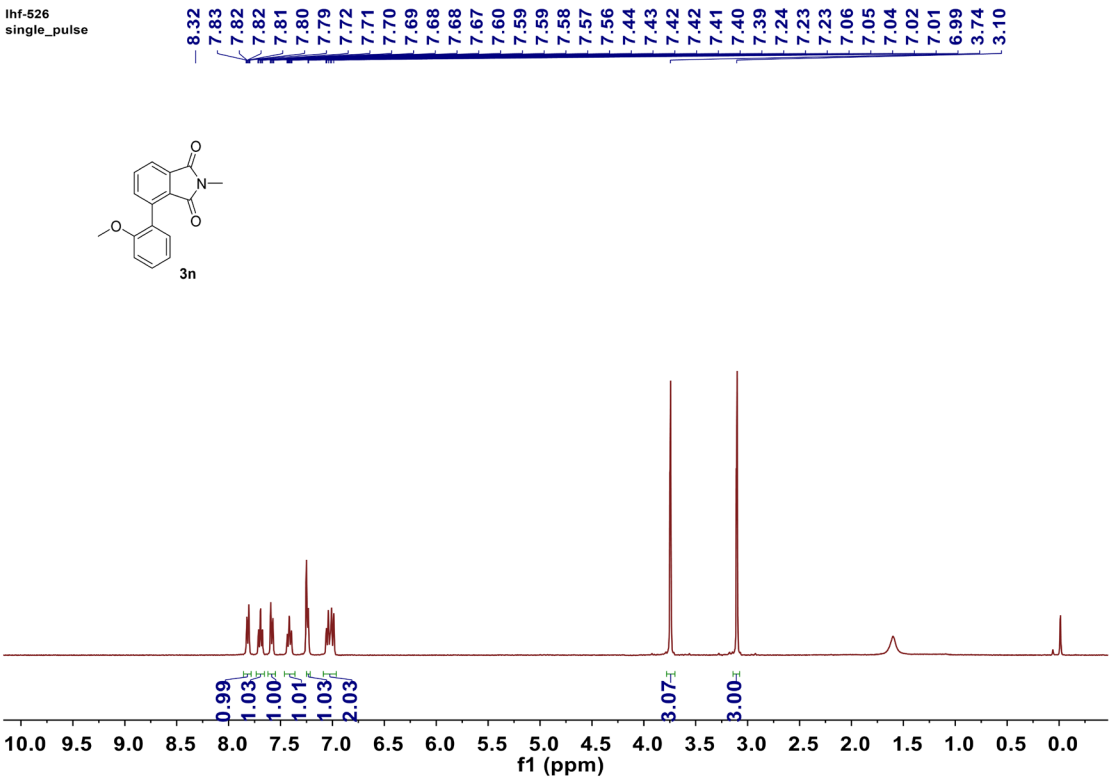


Figure S57. ^{1}H NMR spectrum of compound **3n** (400 MHz, solvent: $CDCl_3$)

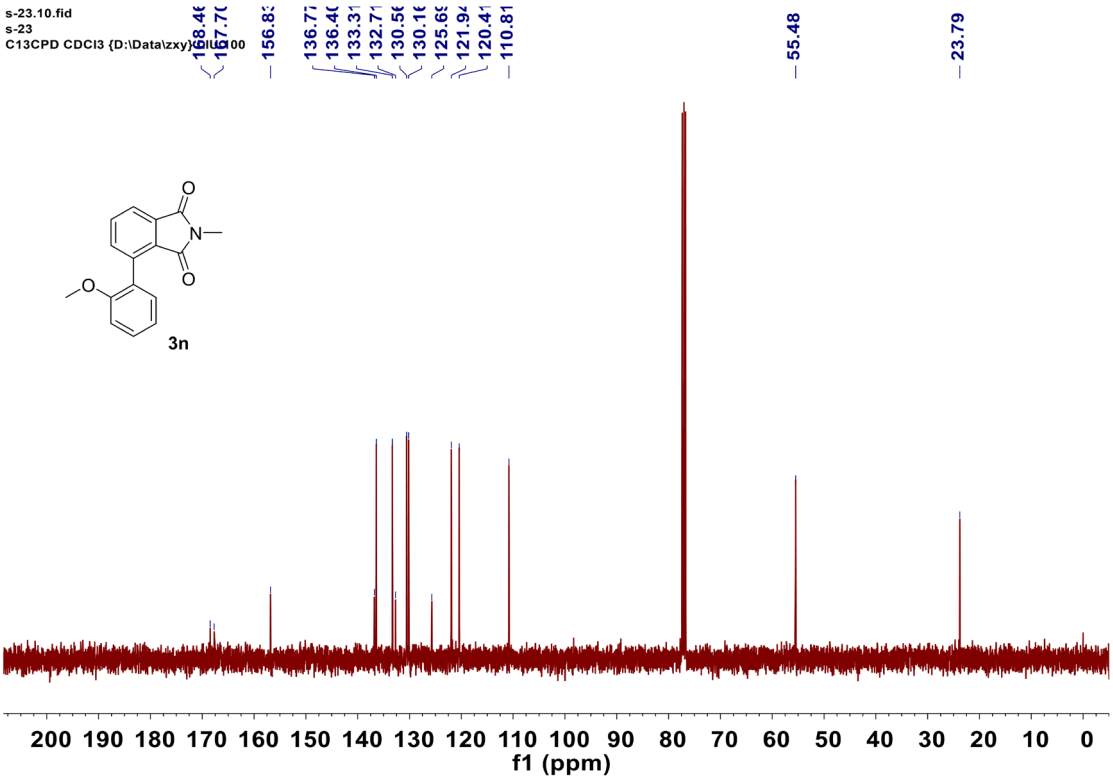


Figure S58. ^{13}C NMR spectrum of compound **3n** (101 MHz, solvent: $CDCl_3$)

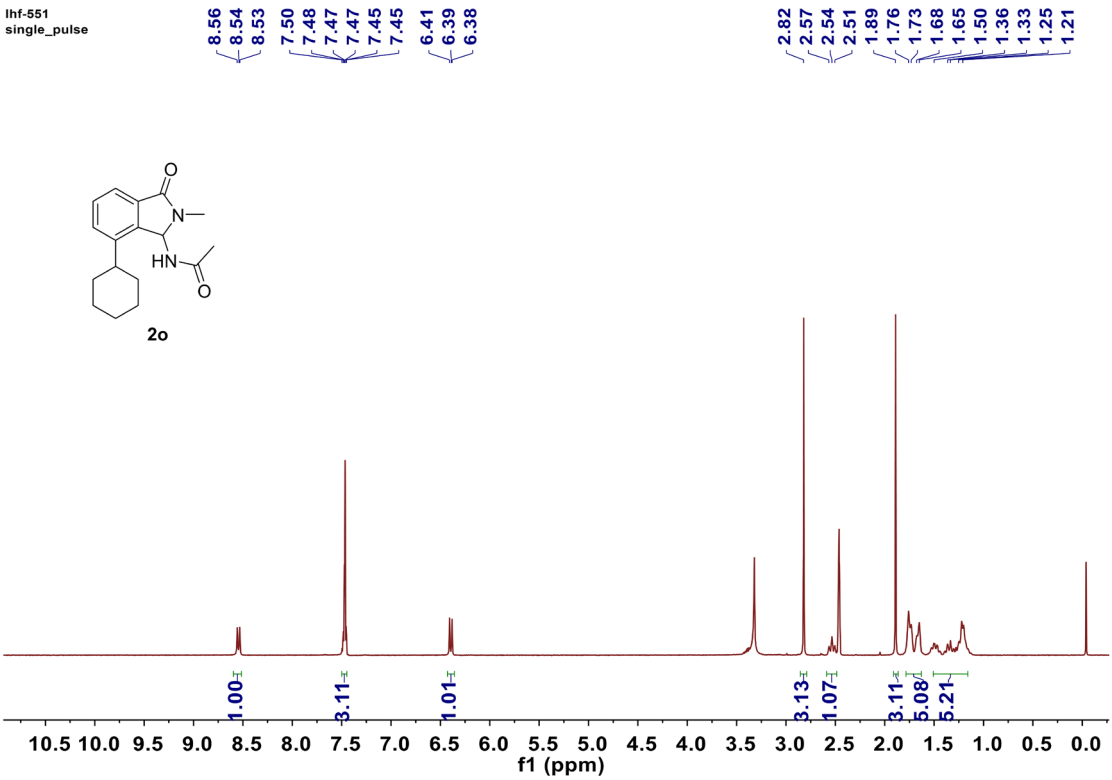


Figure S59. ^{1}H NMR spectrum of compound **2o** (400 MHz, solvent: DMSO-d_6)

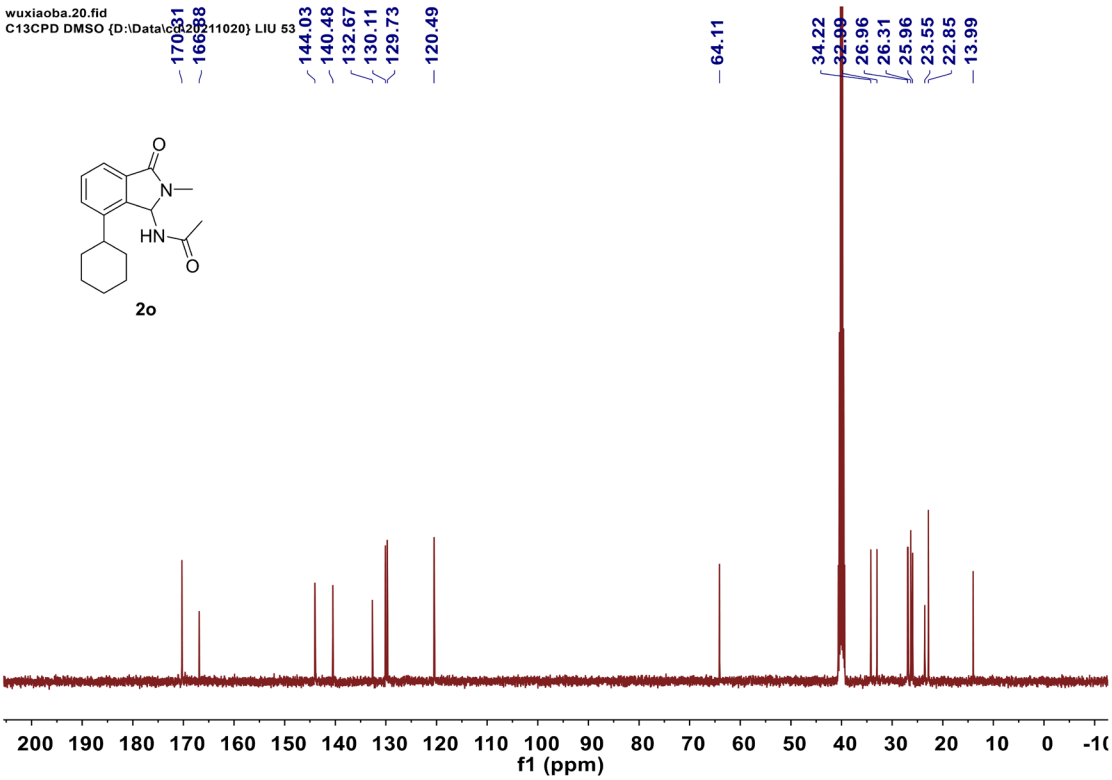


Figure S60. ^{13}C NMR spectrum of compound **2o** (101 MHz, solvent: DMSO-d_6)

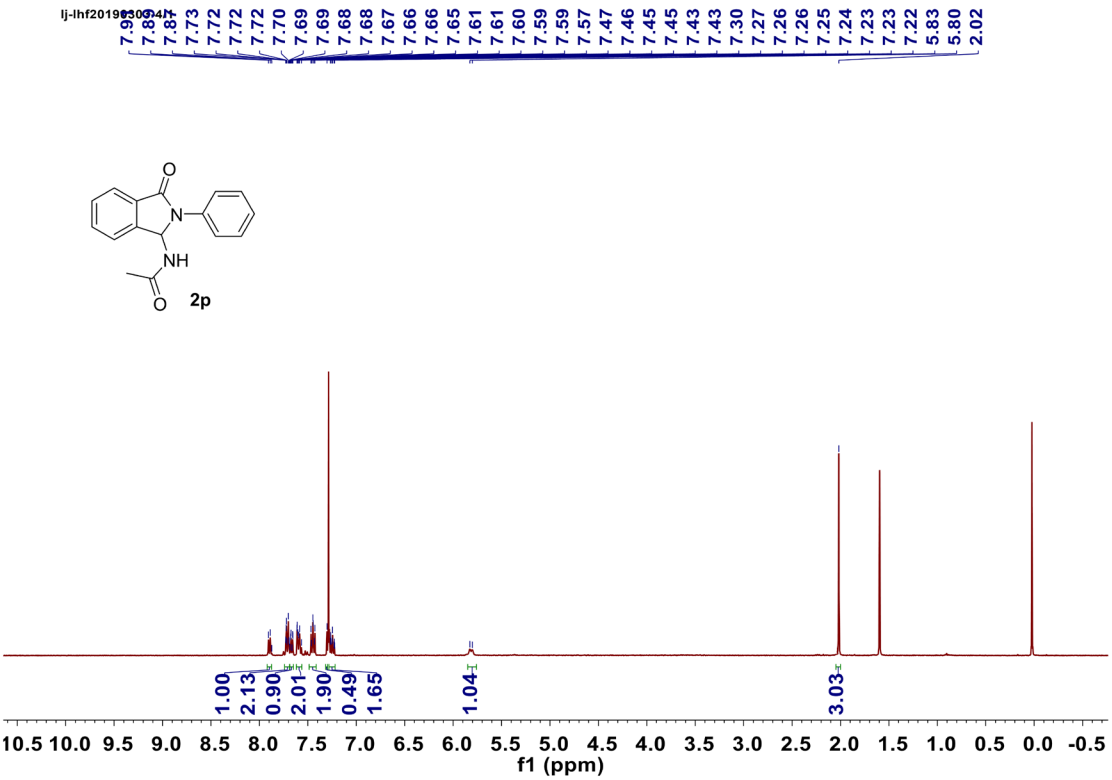


Figure S61. ^{1}H NMR spectrum of compound **2p** (400 MHz, solvent: $CDCl_3$)

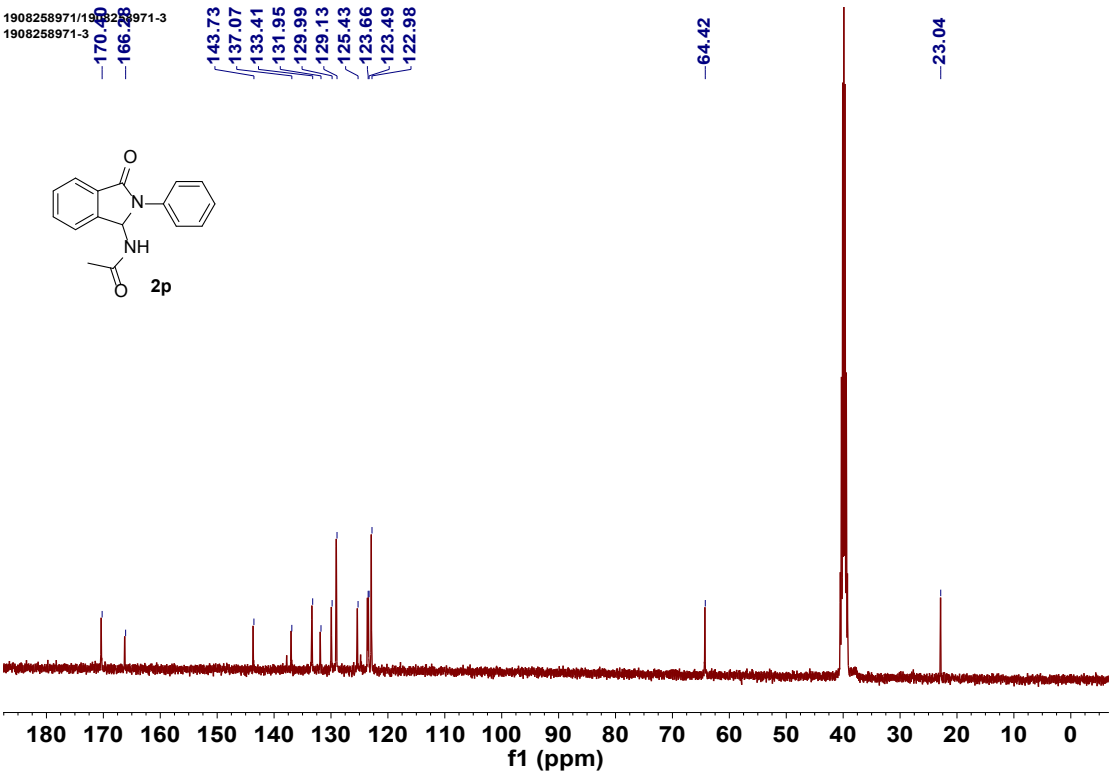


Figure S62. ^{13}C NMR spectrum of compound **2p** (101 MHz, solvent: DMSO-d_6)

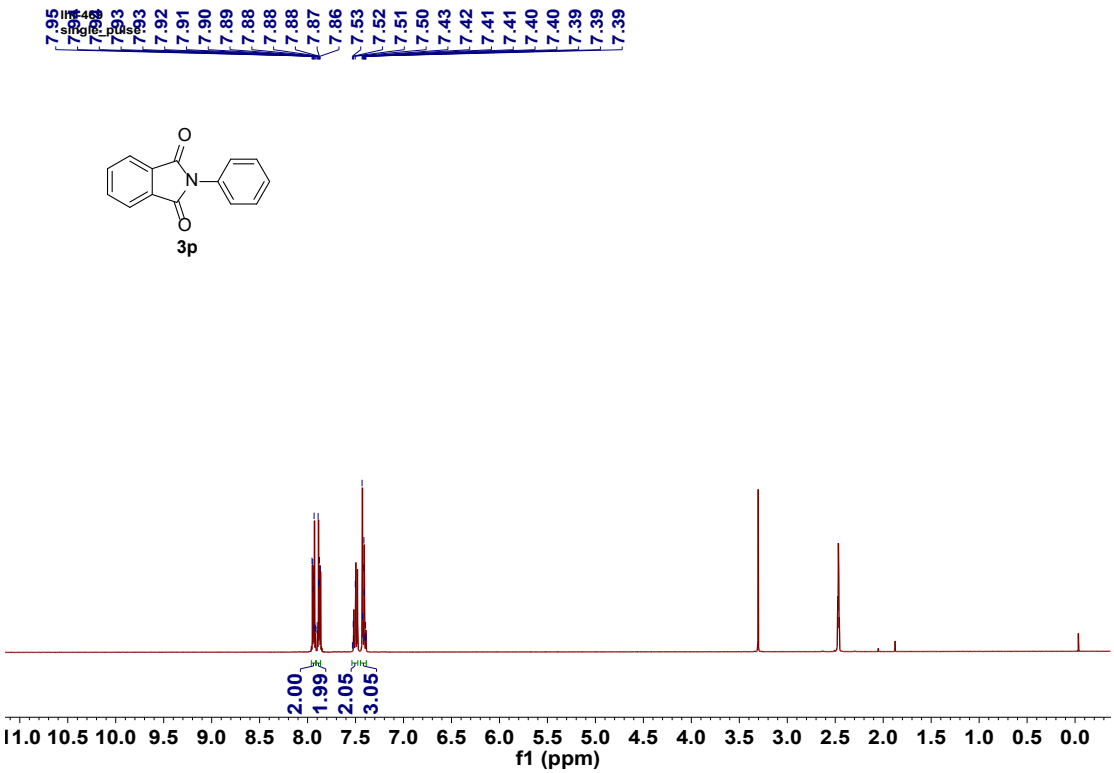


Figure S63. ^{1}H NMR spectrum of compound **3p** (400 MHz, solvent: DMSO-d_6)

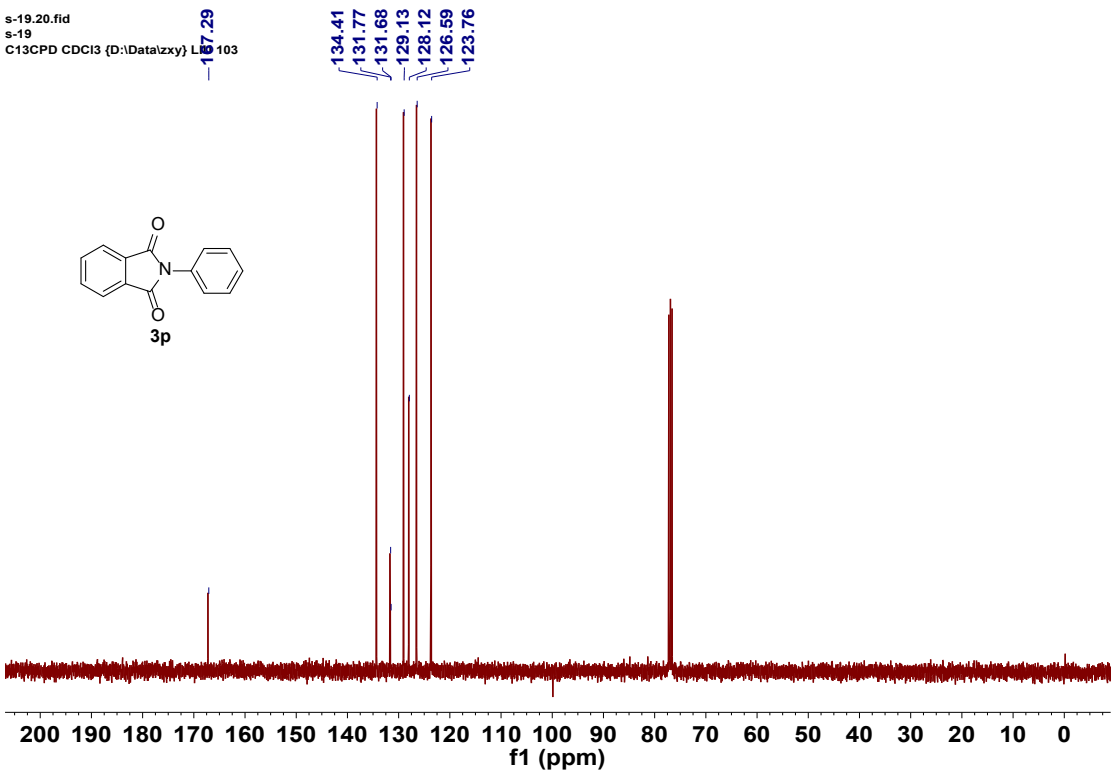


Figure S64. ^{13}C NMR spectrum of compound **3p** (101 MHz, solvent: $CDCl_3$)

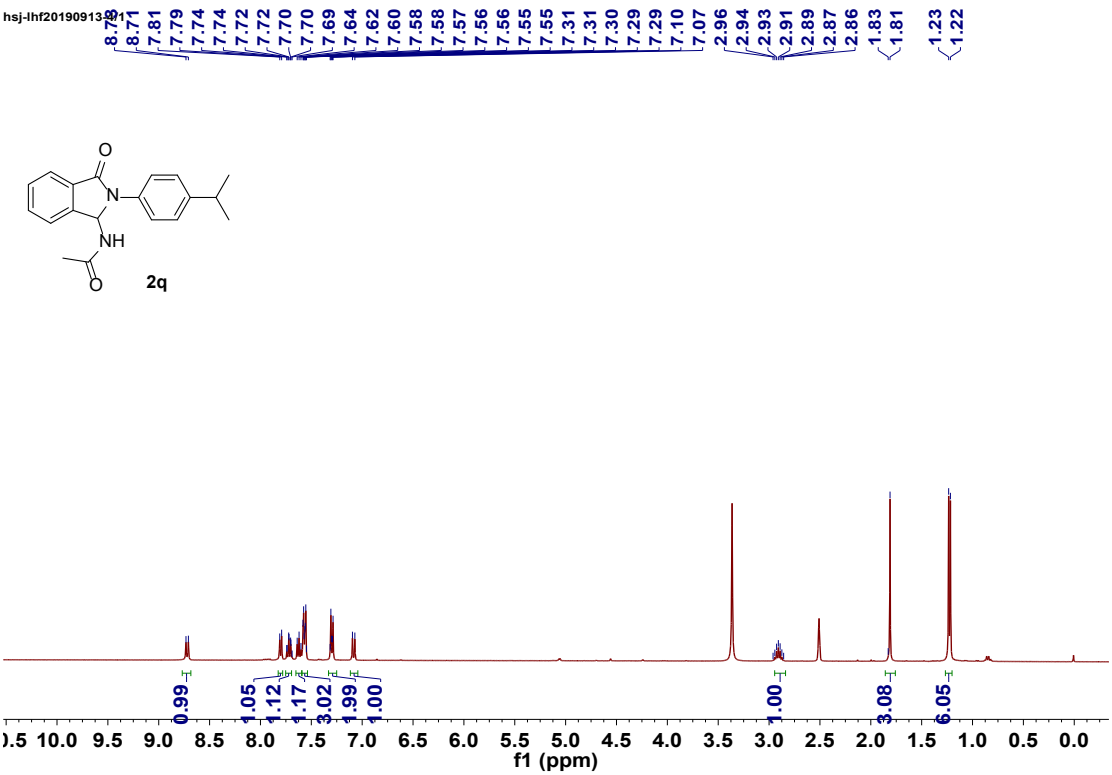


Figure S65. [1]H NMR spectrum of compound **2q** (400 MHz, solvent: DMSO-d_6)

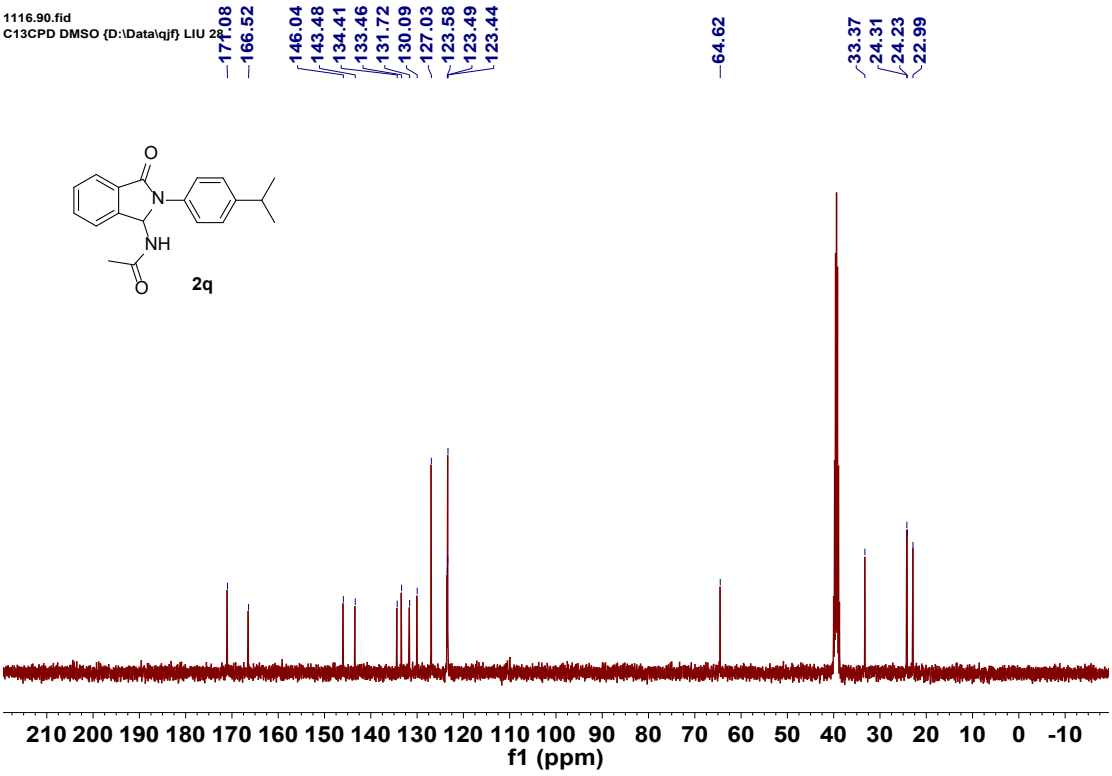


Figure S66. [13]C NMR spectrum of compound **2q** (101 MHz, solvent: DMSO-d_6)

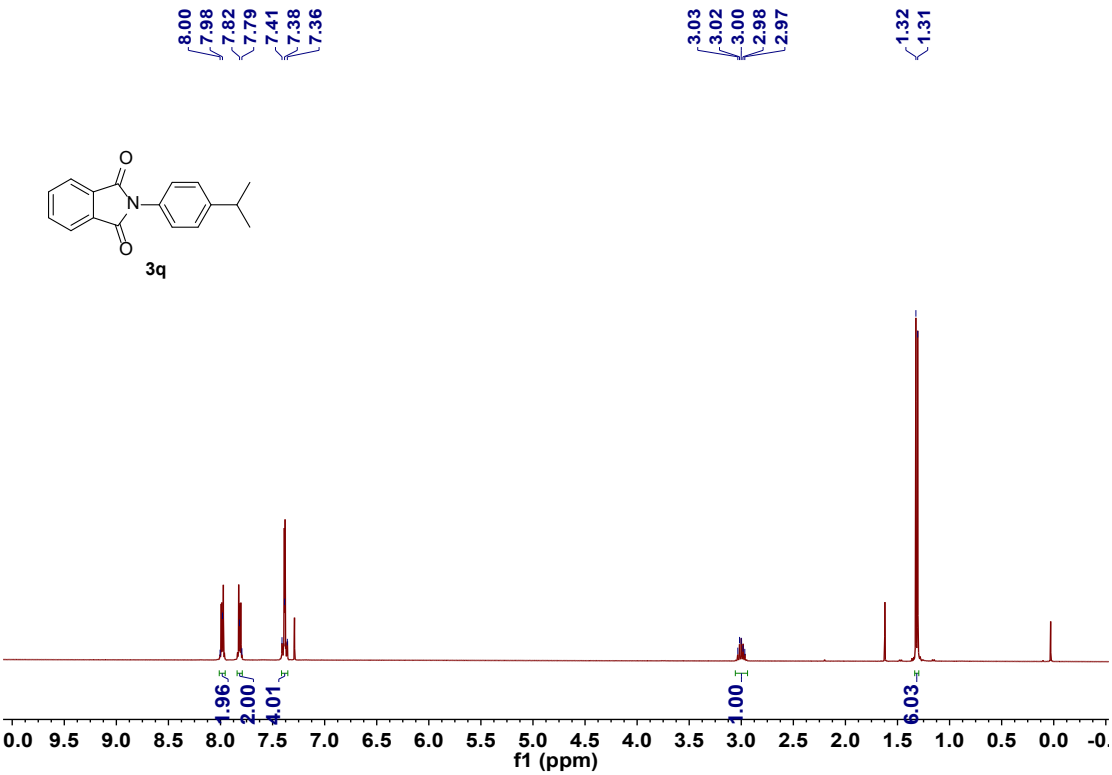


Figure S67. ^{1}H NMR spectrum of compound **3q** (400 MHz, solvent: $CDCl_3$)

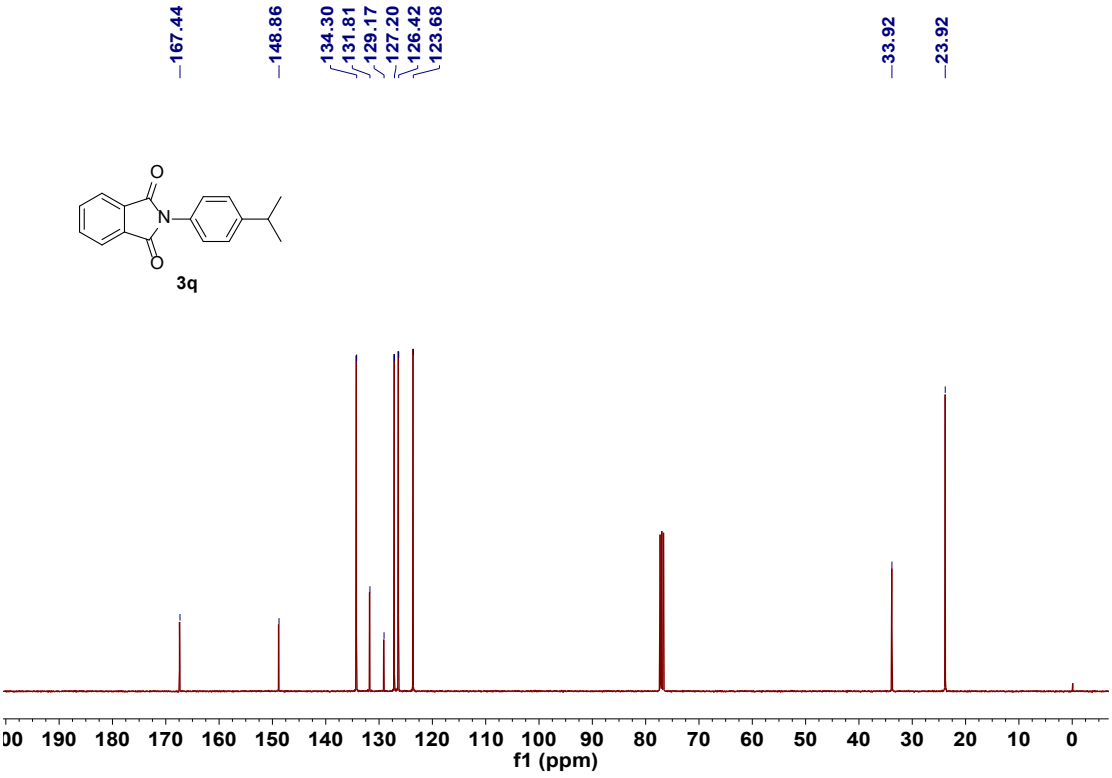


Figure S68. ^{13}C NMR spectrum of compound **3q** (101 MHz, solvent: $CDCl_3$)

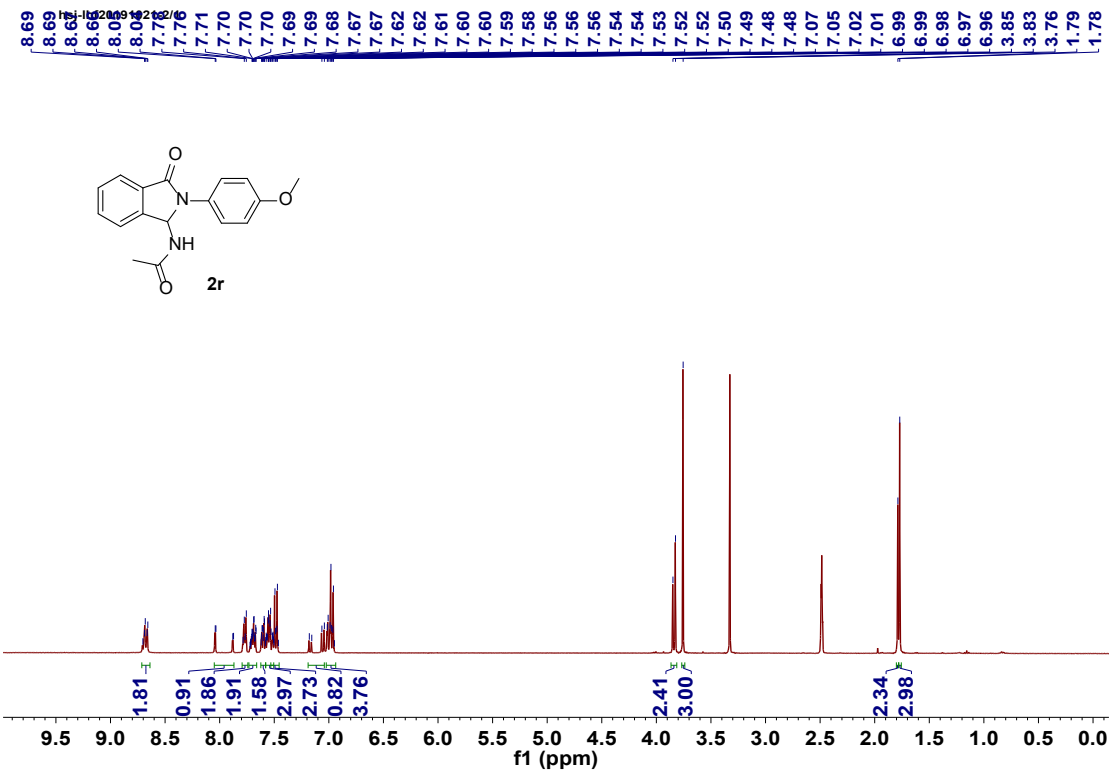


Figure S69. ^{1}H NMR spectrum of compound **2r** (400 MHz, solvent: DMSO-d_6) *d.r.* = 5:4

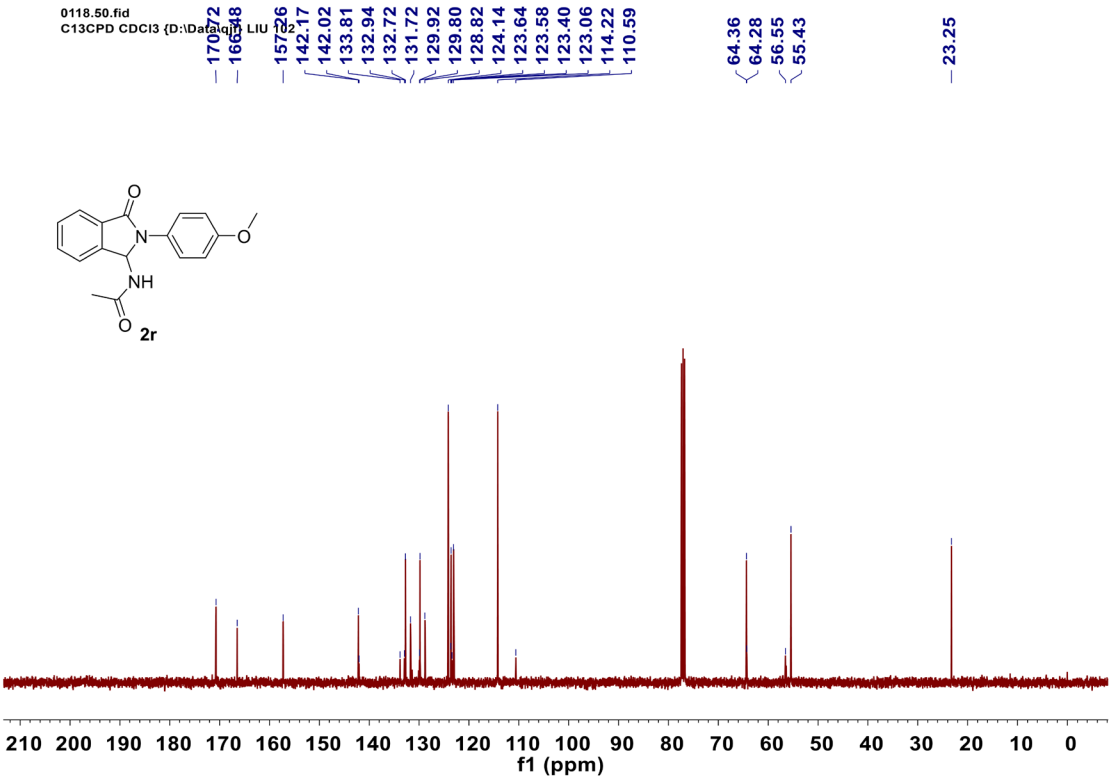


Figure S70. ^{13}C NMR spectrum of compound **2r** (101 MHz, solvent: $CDCl_3$)

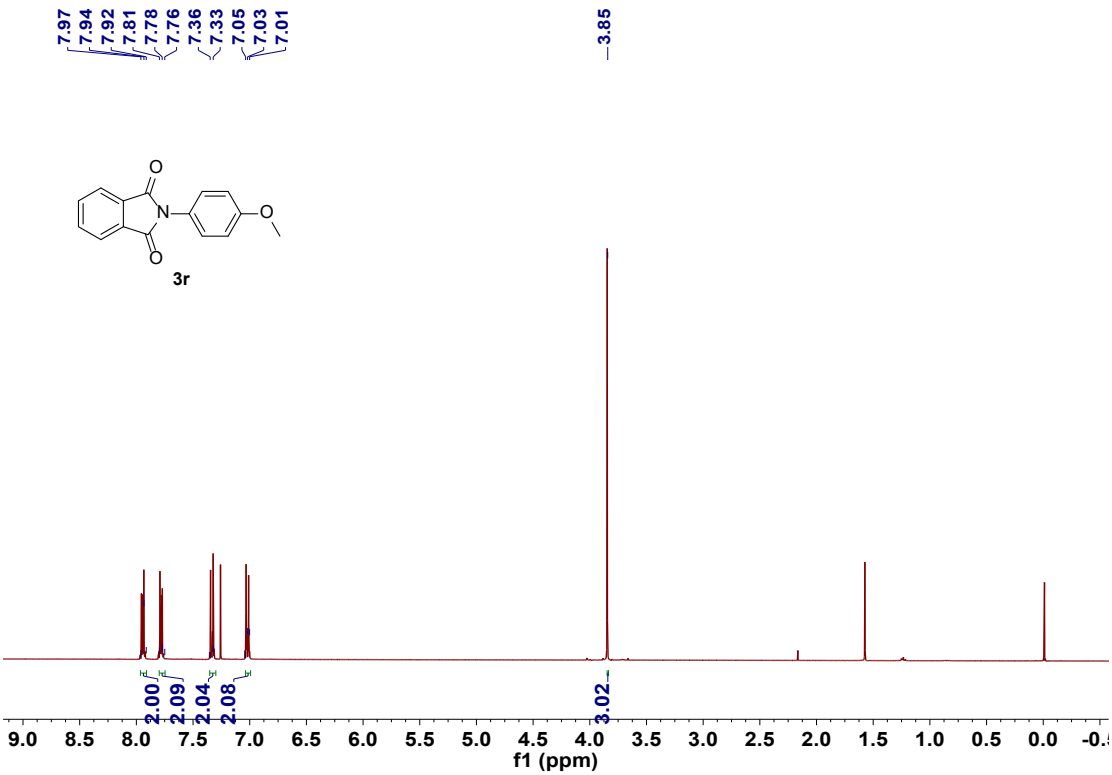


Figure S71. ^{1}H NMR spectrum of compound **3r** (400 MHz, solvent: $CDCl_3$)

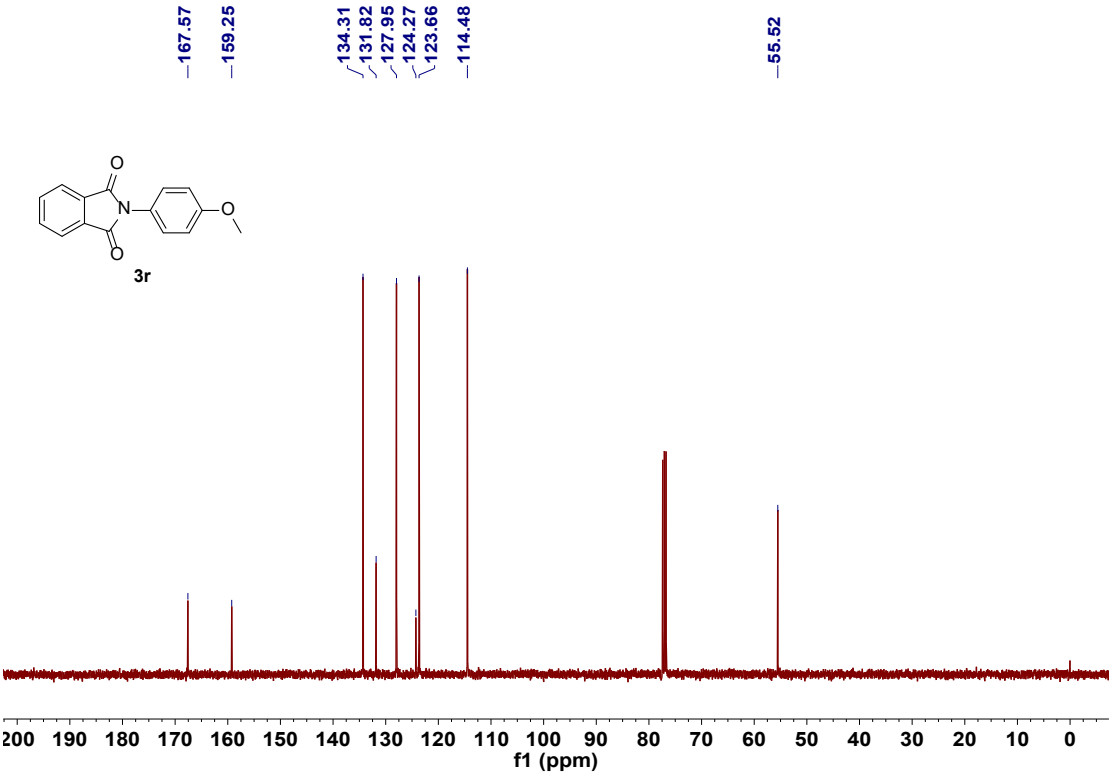


Figure S72. ^{13}C NMR spectrum of compound **3r** (101 MHz, solvent: $CDCl_3$)

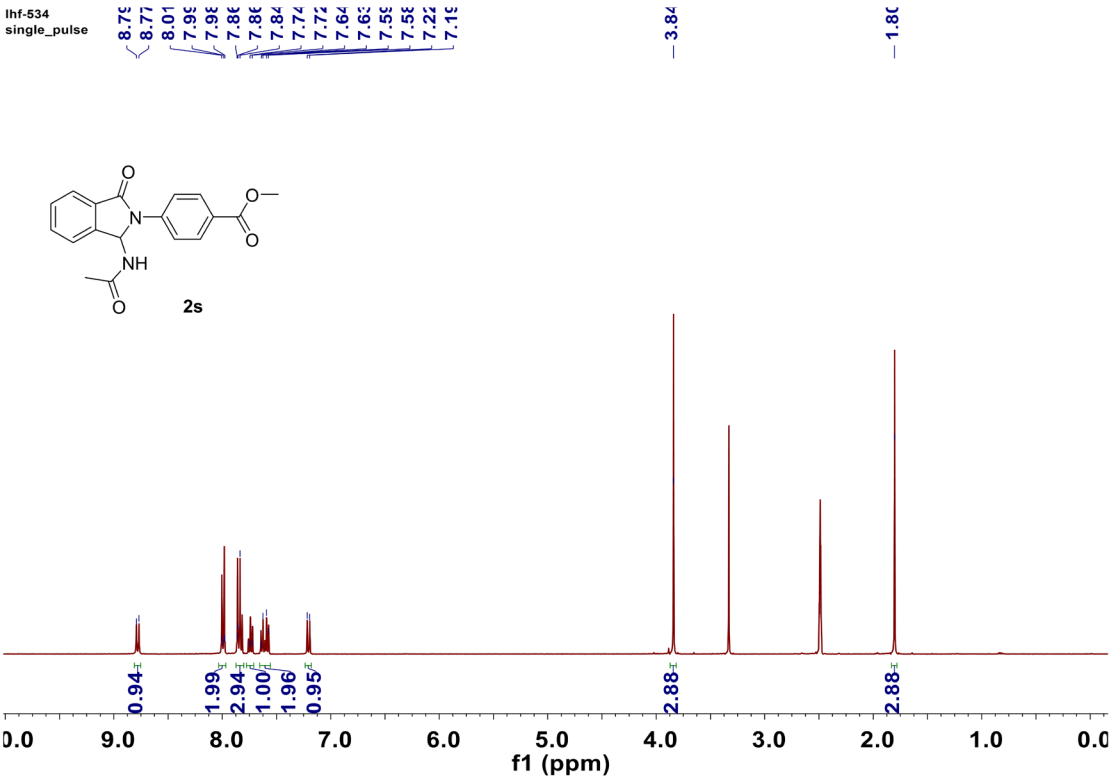


Figure S73. [1]H NMR spectrum of compound **2s** (400 MHz, solvent: DMSO-d_6)

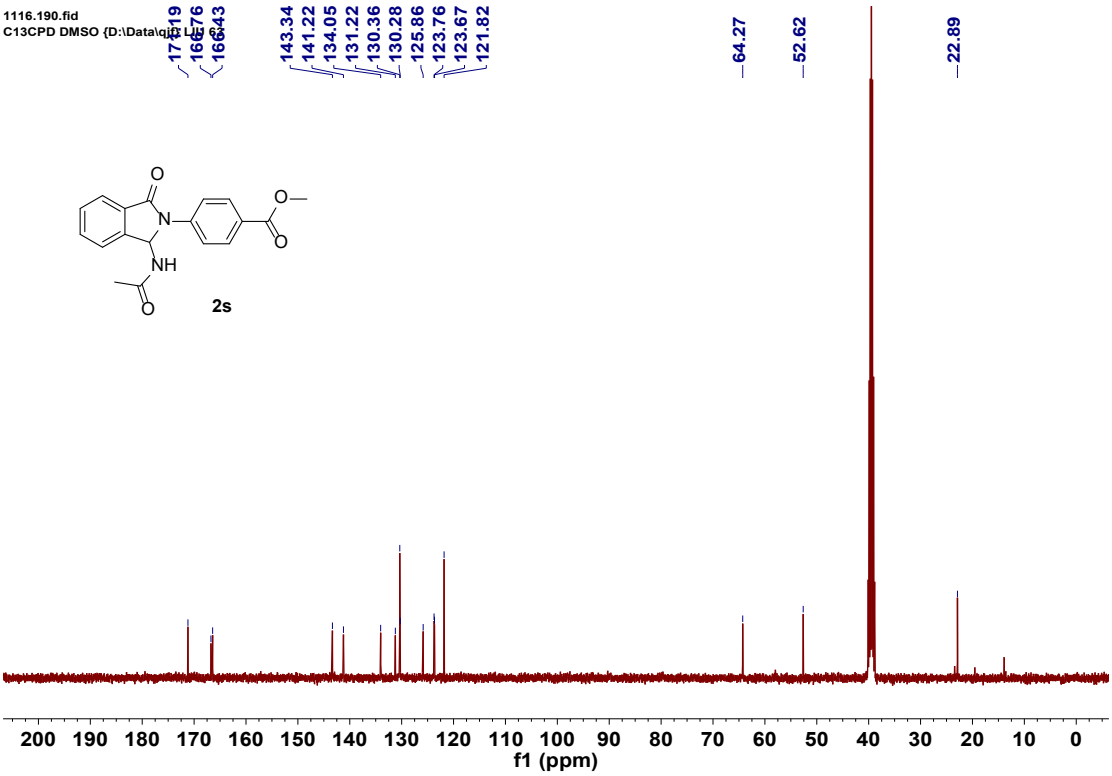


Figure S74. [13]C NMR spectrum of compound **2s** (101 MHz, solvent: DMSO-d_6)

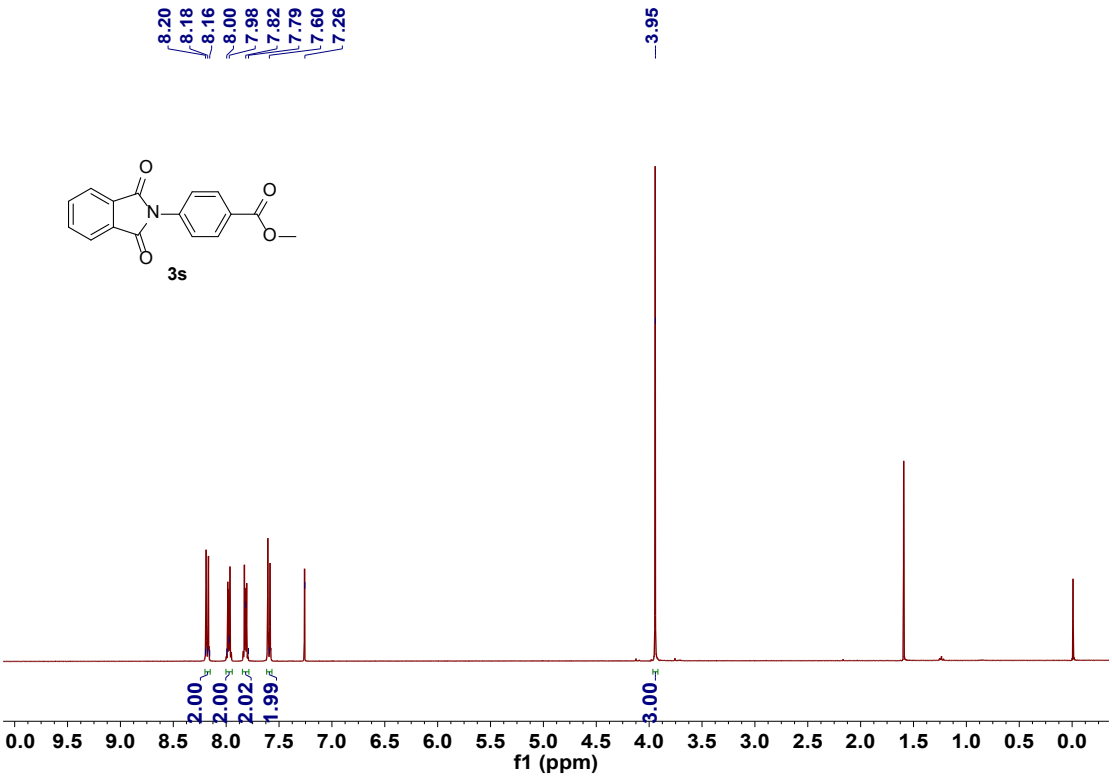


Figure S75. ^{1}H NMR spectrum of compound **3s** (400 MHz, solvent: $CDCl_3$)

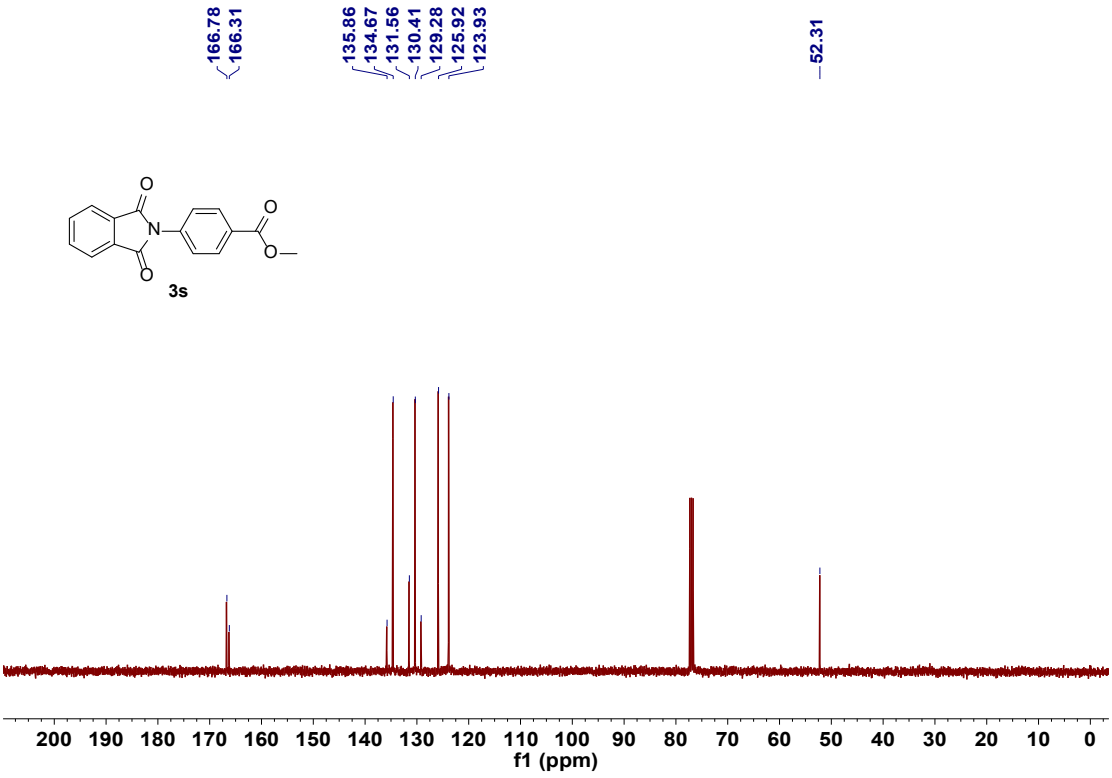


Figure S76. ^{13}C NMR spectrum of compound **3s** (101 MHz, solvent: $CDCl_3$)

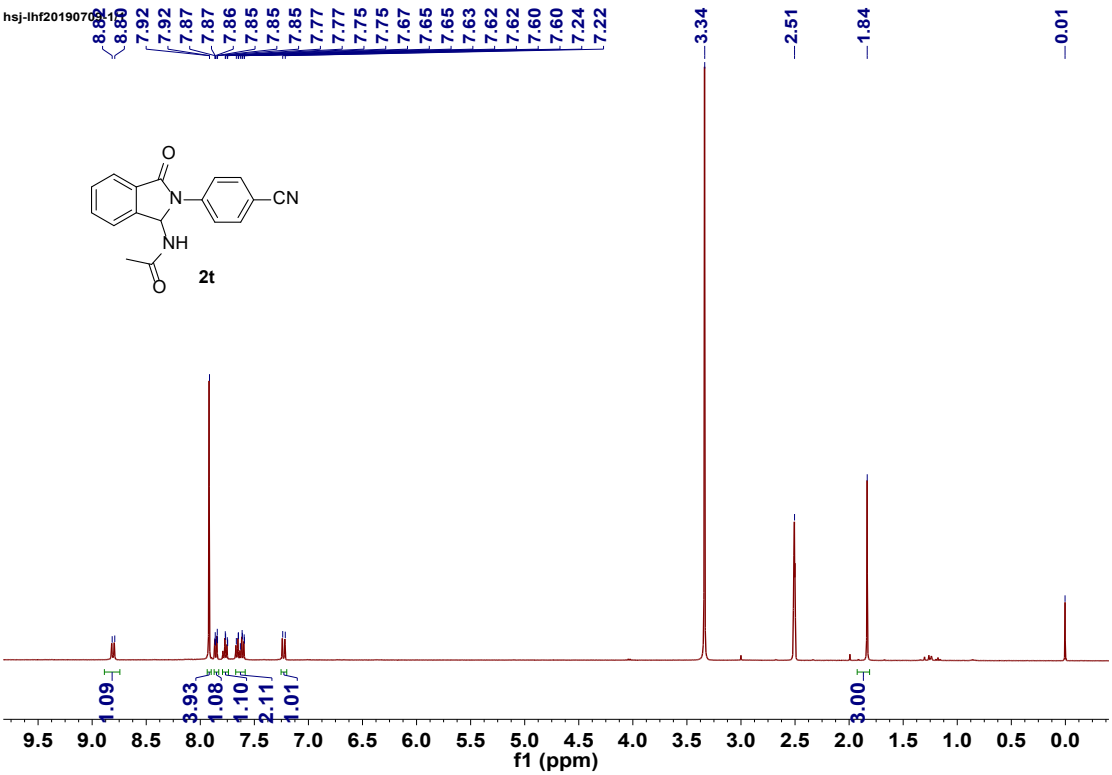


Figure S77. [1]H NMR spectrum of compound **2t** (400 MHz, solvent: DMSO-d_6)

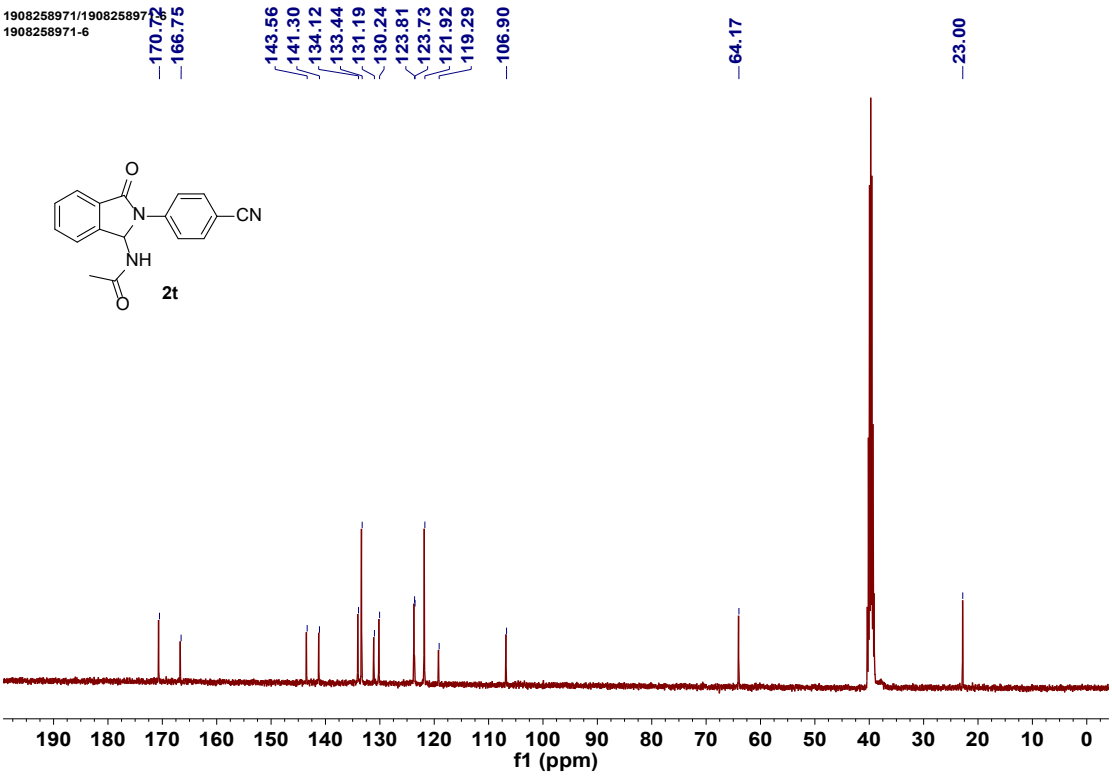


Figure S78. [13]C NMR spectrum of compound **2t** (101 MHz, solvent: DMSO-d_6)

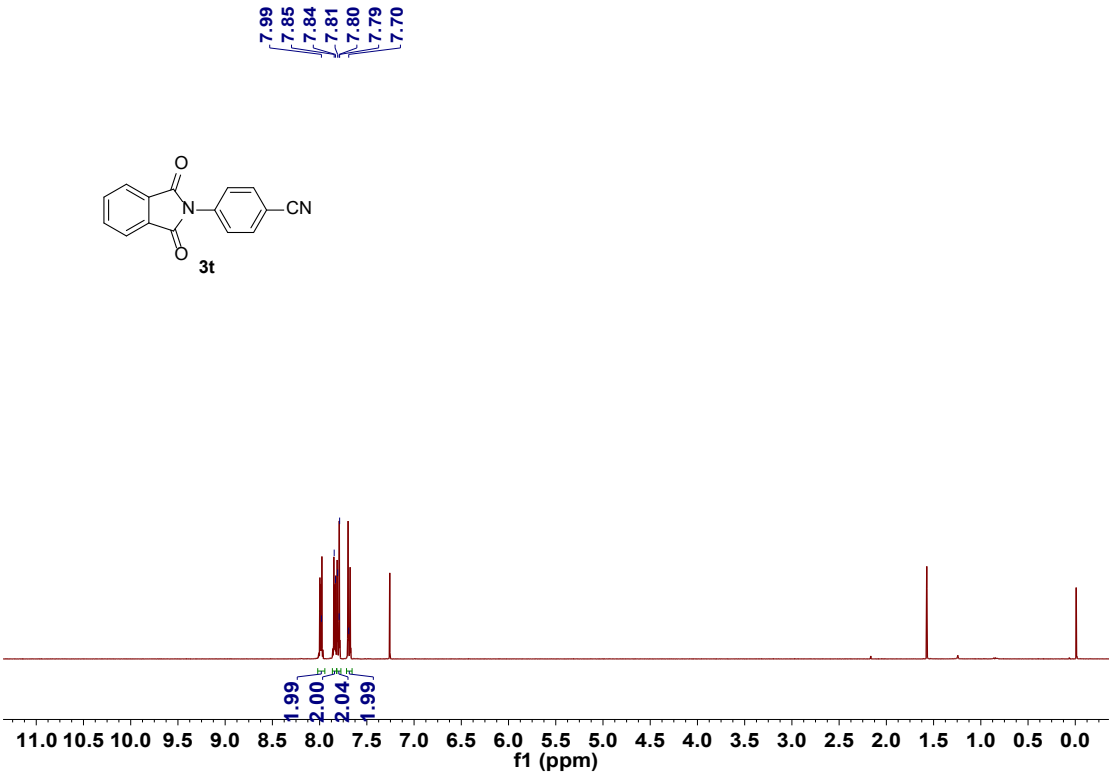


Figure S79. ^{1}H NMR spectrum of compound **3t** (400 MHz, solvent: $CDCl_3$)

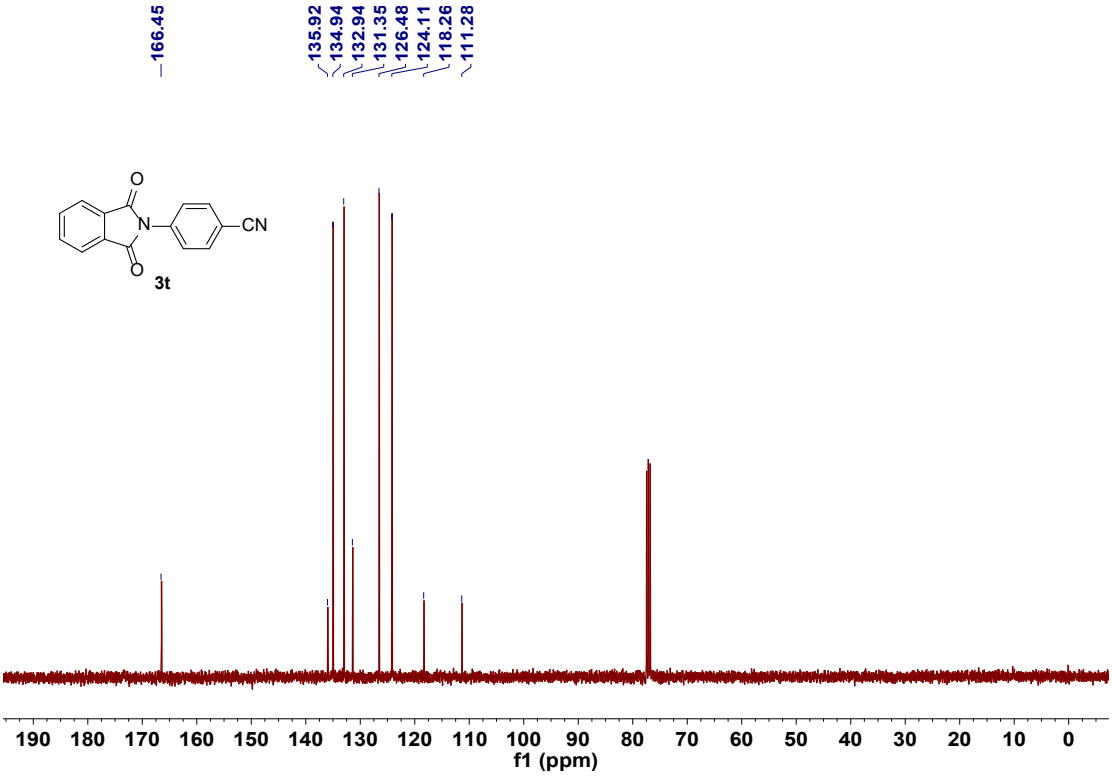


Figure S80. ^{13}C NMR spectrum of compound **3t** (101 MHz, solvent: $CDCl_3$)

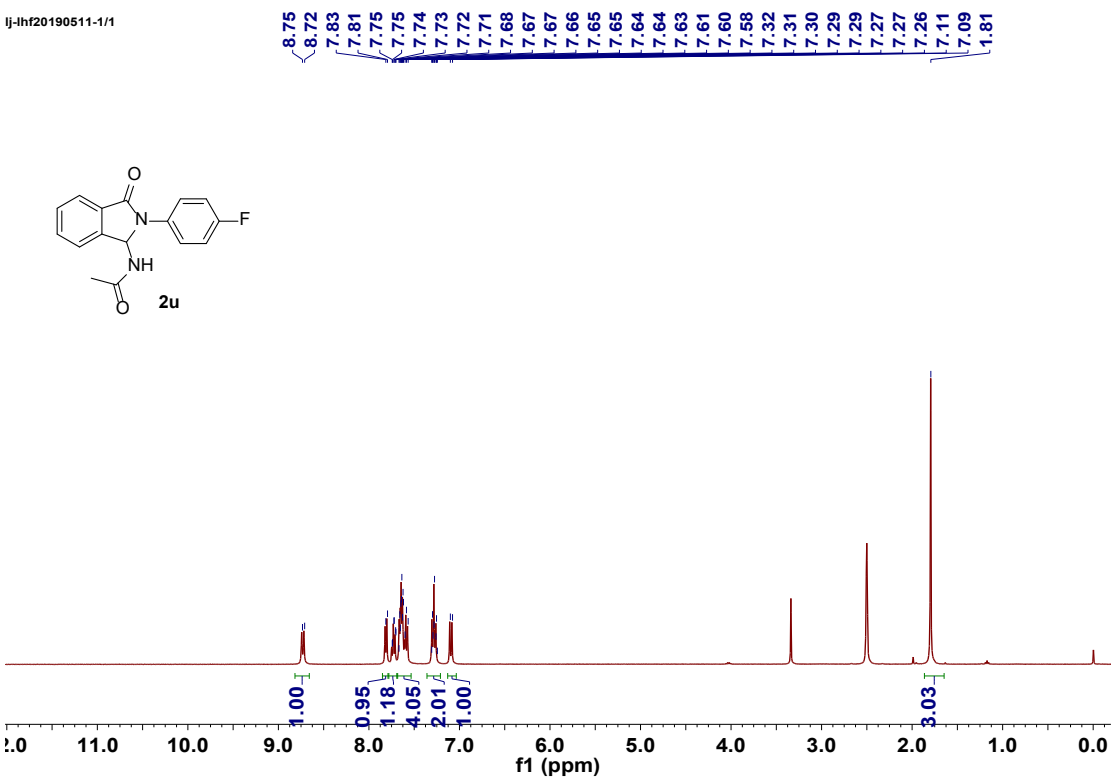


Figure S81. [1]H NMR spectrum of compound **2u** (400 MHz, solvent: DMSO-d_6)

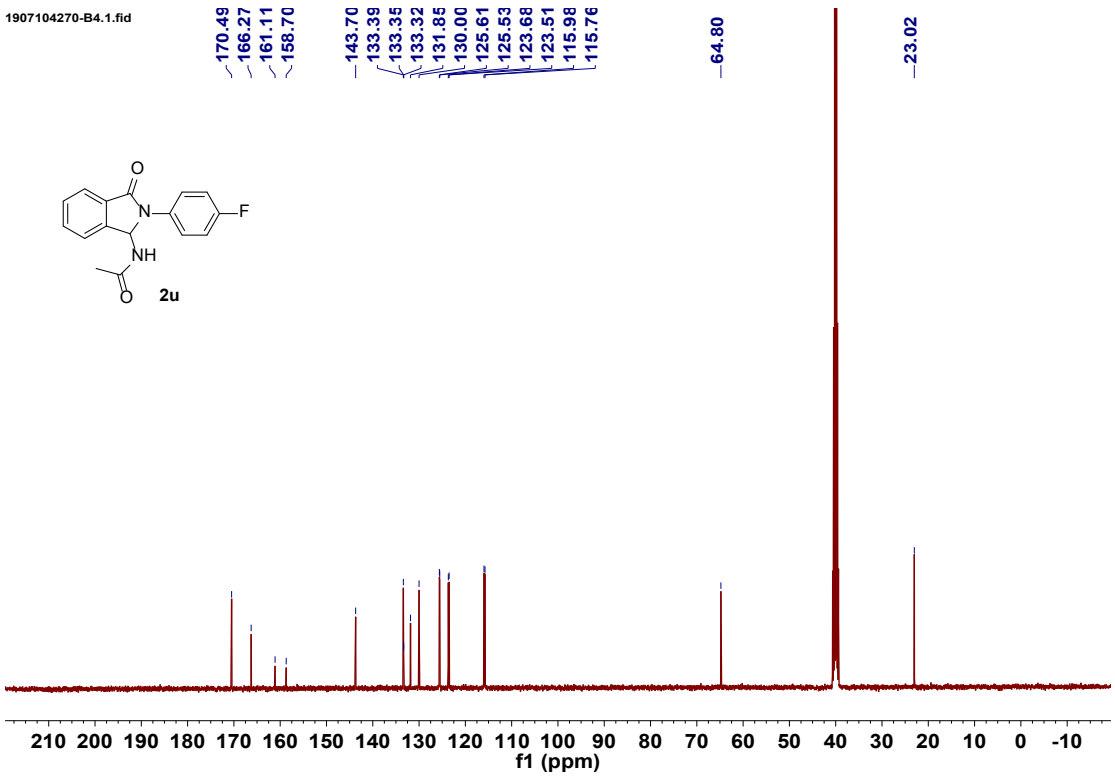


Figure S82. [13]C NMR spectrum of compound **2u** (101 MHz, solvent: DMSO-d_6)

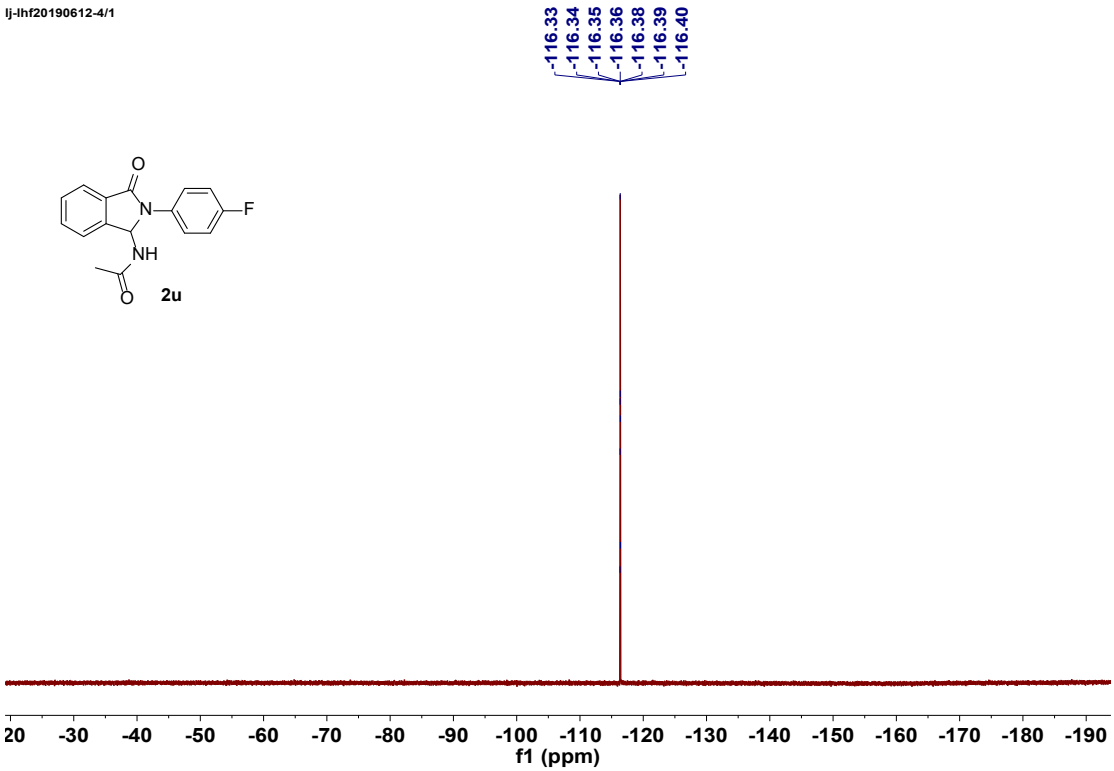


Figure S83. ^{19}F NMR spectrum of compound **2u** (376 MHz, solvent: $CDCl_3$)

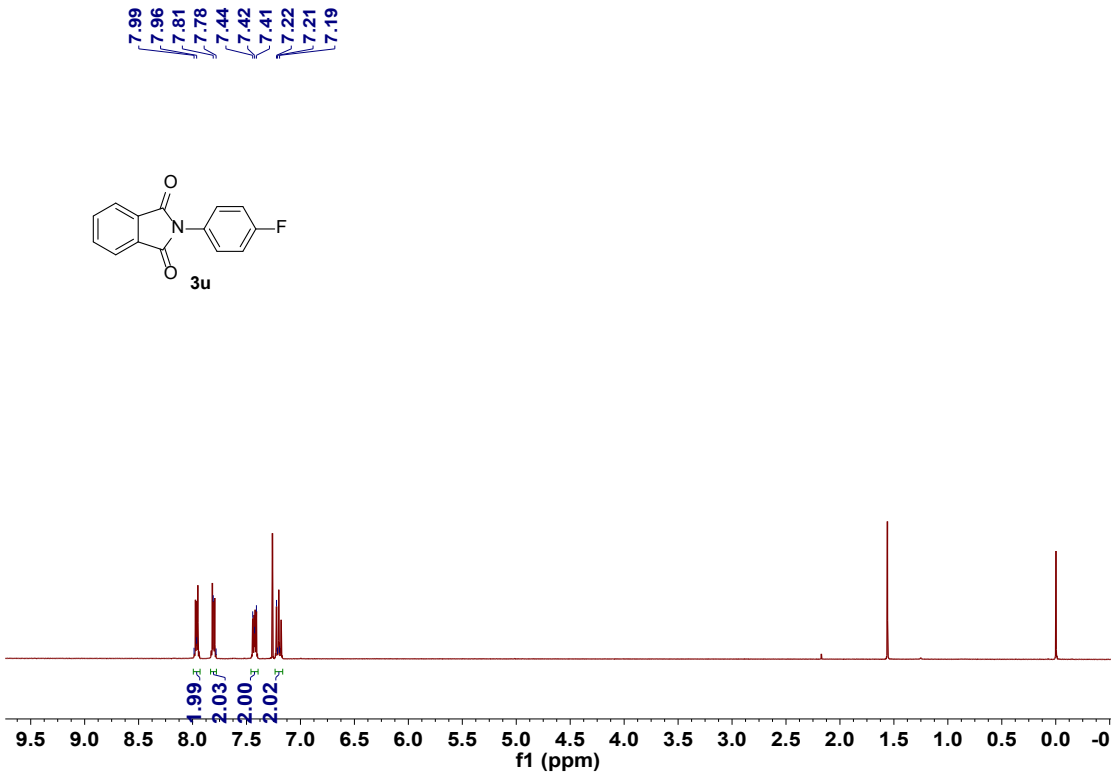


Figure S84. ^{1}H NMR spectrum of compound **3u** (400 MHz, solvent: $CDCl_3$)

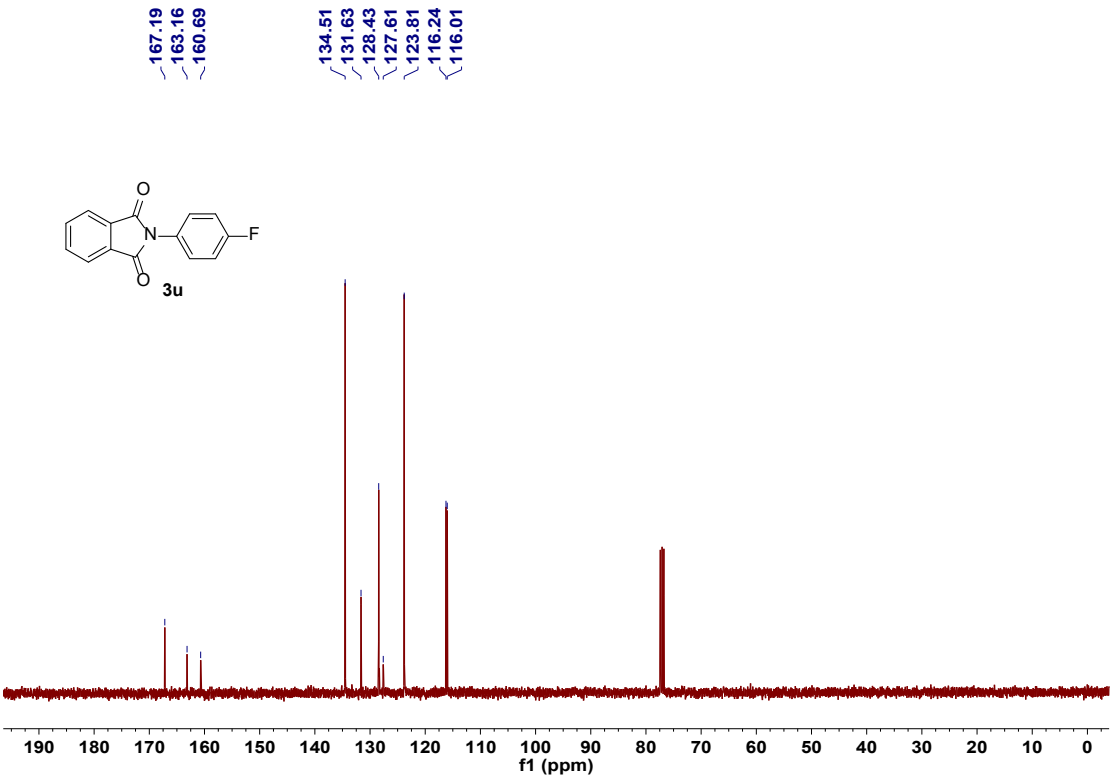


Figure S85. ^{13}C NMR spectrum of compound **3u** (101 MHz, solvent: $CDCl_3$)

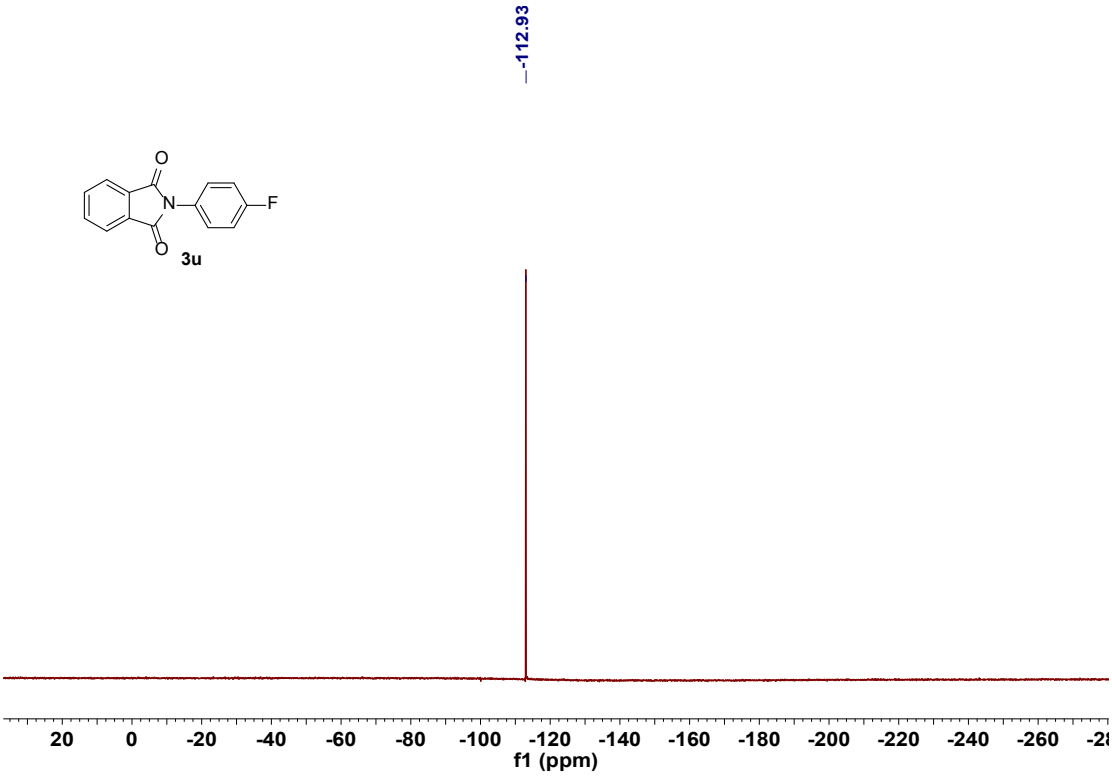


Figure S86. ^{19}F NMR spectrum of compound **3u** (376 MHz, solvent: $CDCl_3$)

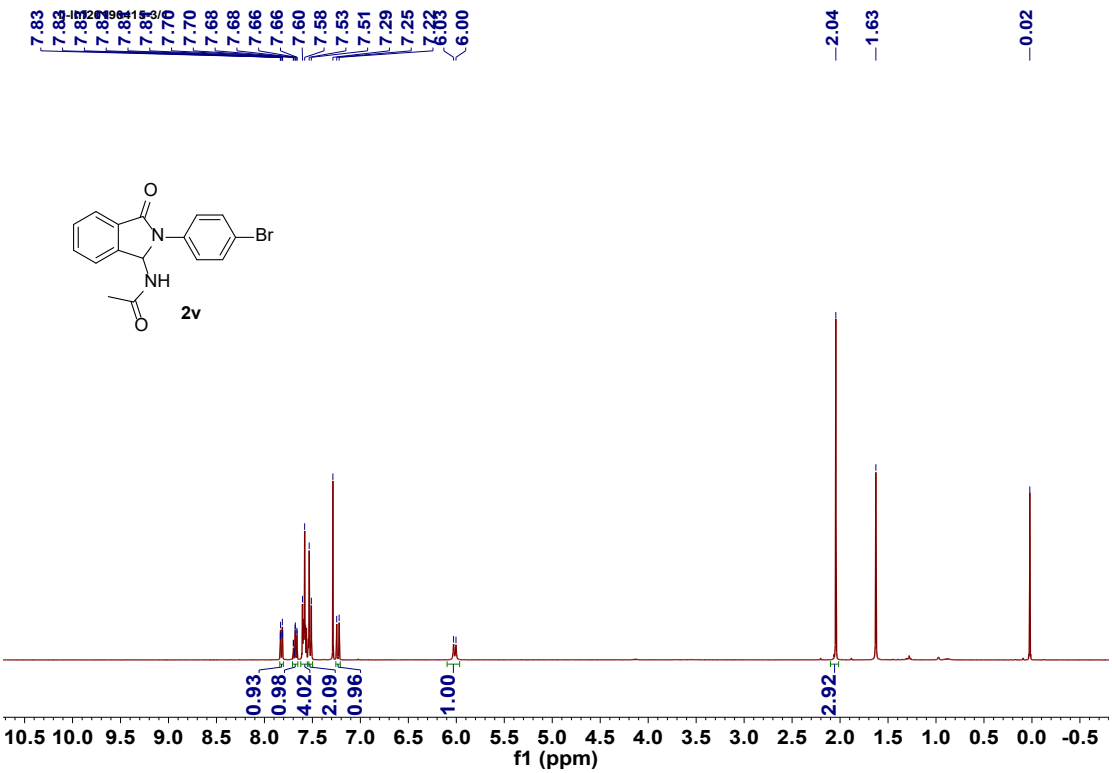


Figure S87. ^{1}H NMR spectrum of compound **2v** (400 MHz, solvent: $CDCl_3$)

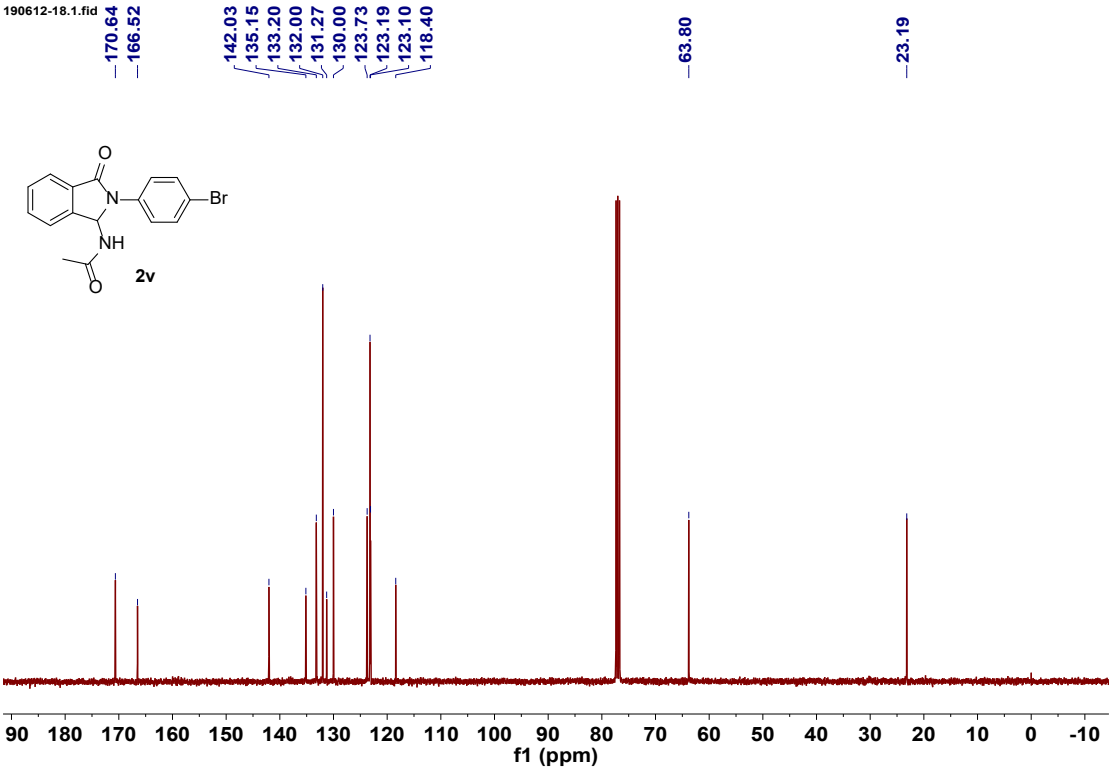


Figure S88. ^{13}C NMR spectrum of compound **2v** (101 MHz, solvent: $CDCl_3$)

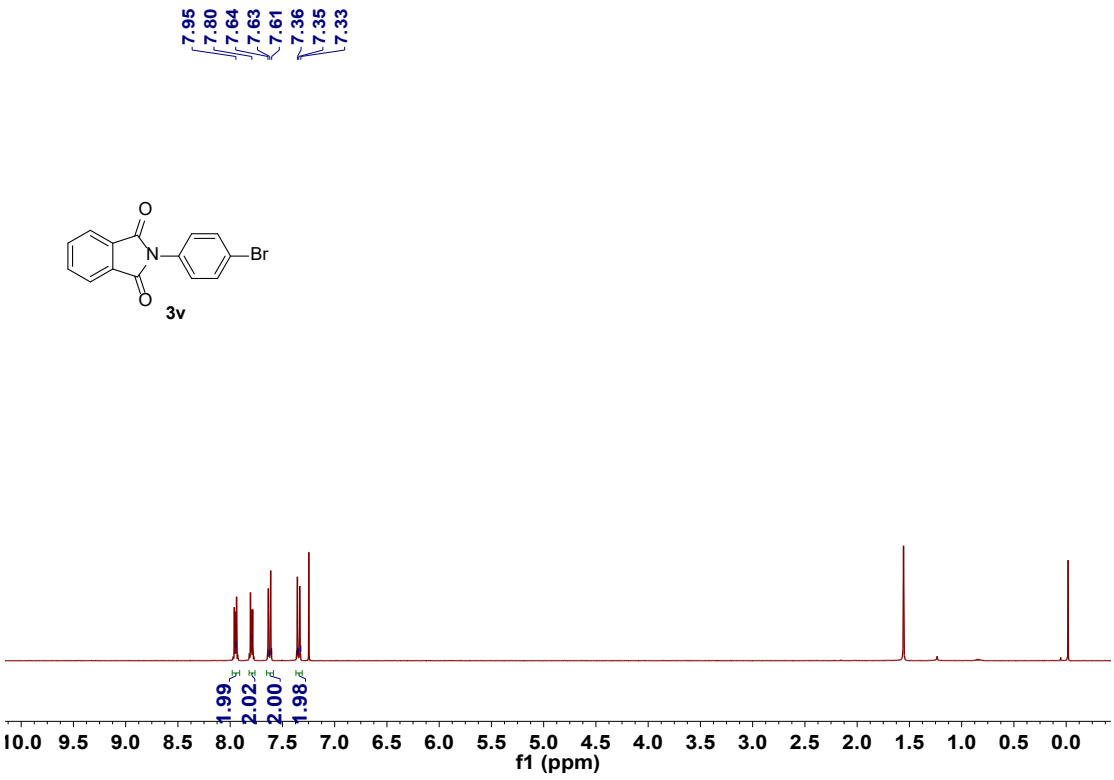


Figure S89. ^{1}H NMR spectrum of compound **3v** (400 MHz, solvent: $CDCl_3$)

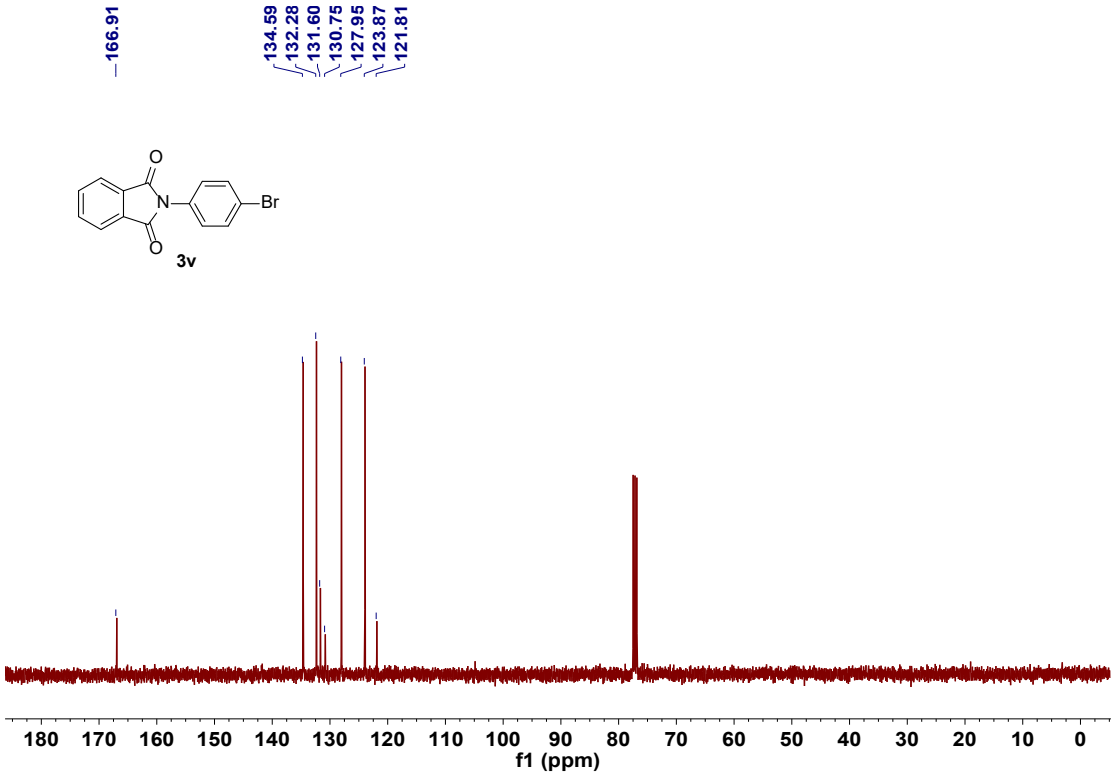


Figure S90. ^{13}C NMR spectrum of compound **3v** (101 MHz, solvent: $CDCl_3$)

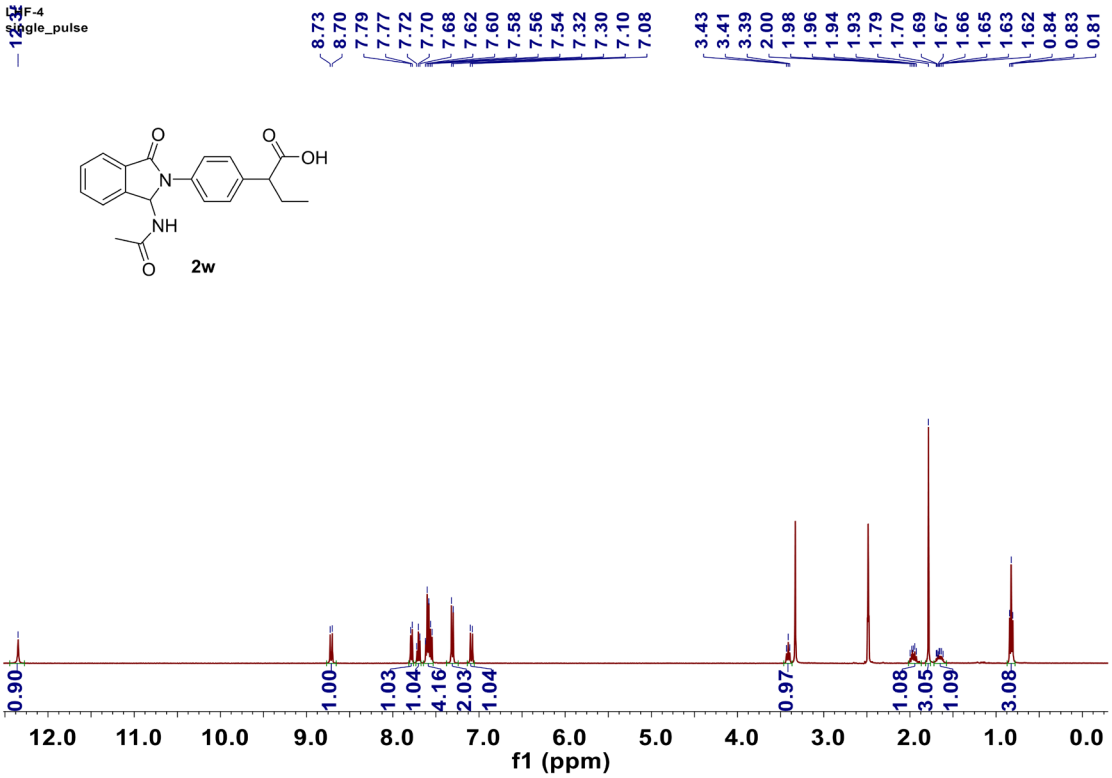


Figure S91. ^{1}H NMR spectrum of compound **2w** (400 MHz, solvent: DMSO-d_6)

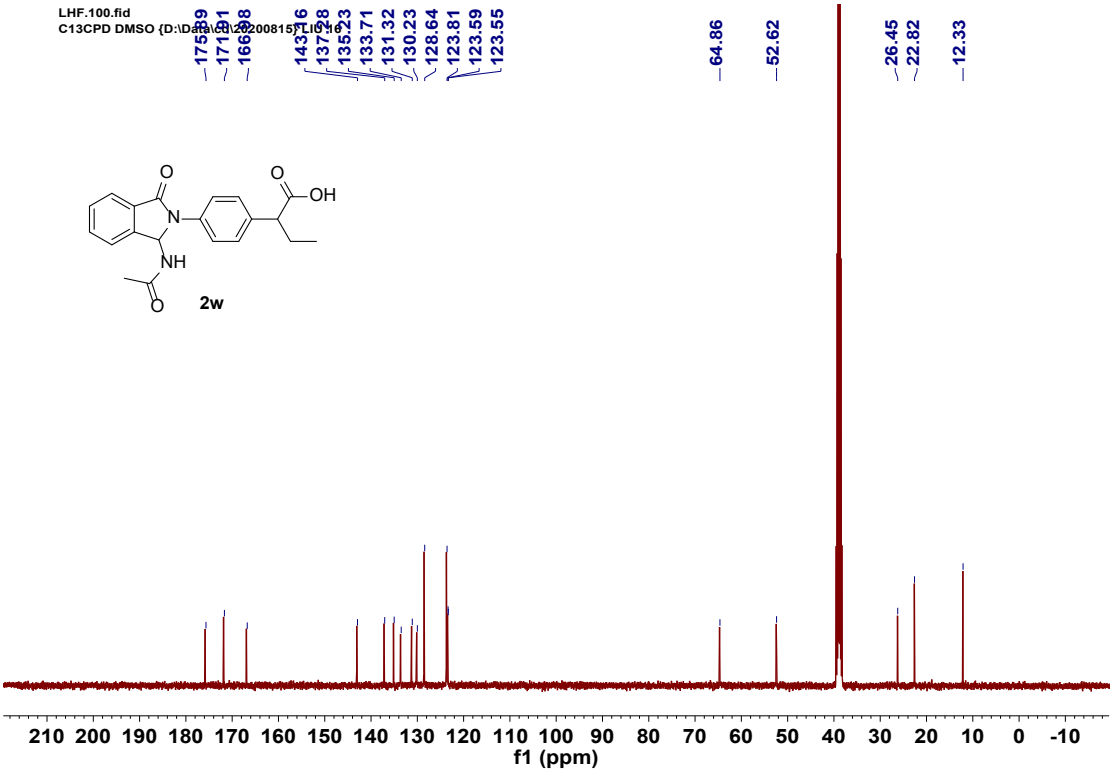


Figure S92. ^{13}C NMR spectrum of compound **2w** (101 MHz, solvent: DMSO-d_6)

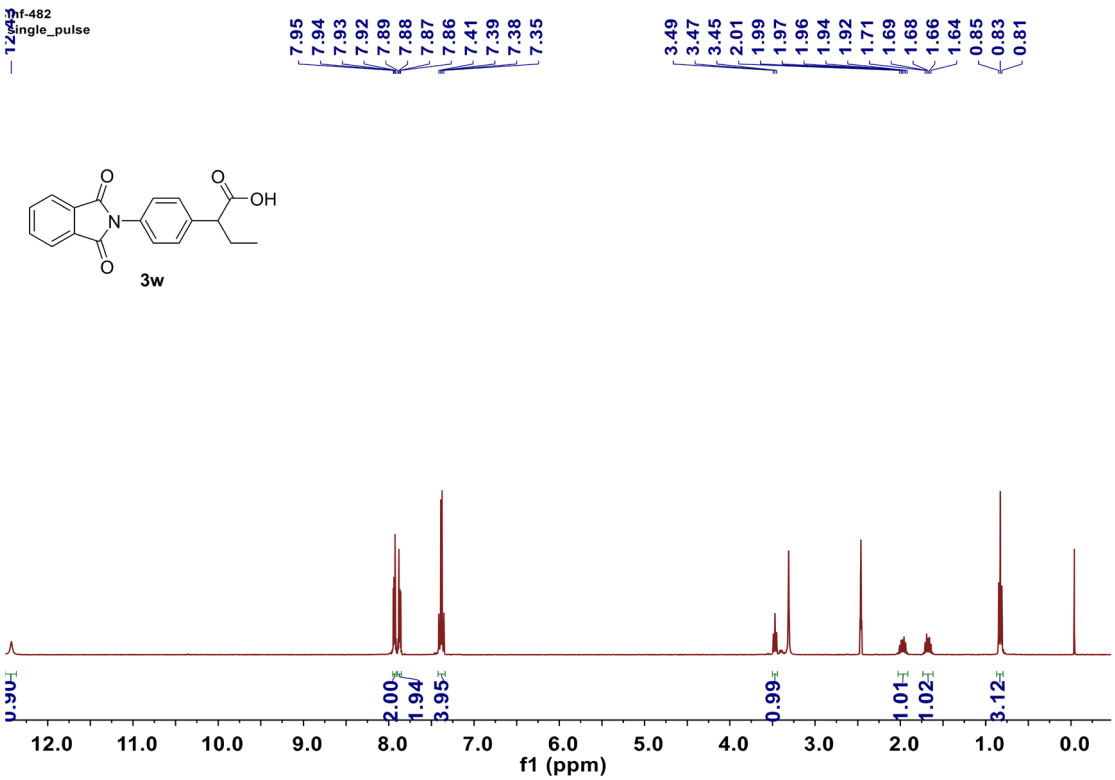


Figure S93. [1]H NMR spectrum of compound **3w** (400 MHz, solvent: DMSO-d_6)

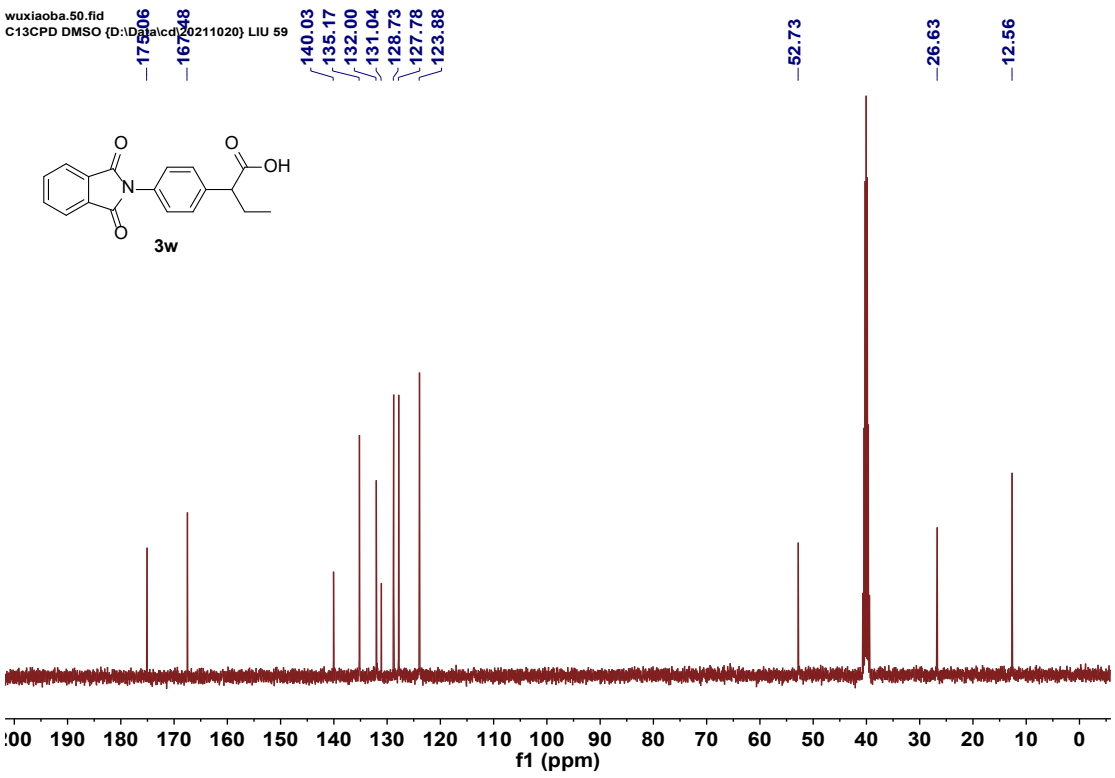


Figure S94. [13]C NMR spectrum of compound **3w** (101 MHz, solvent: DMSO-d_6)

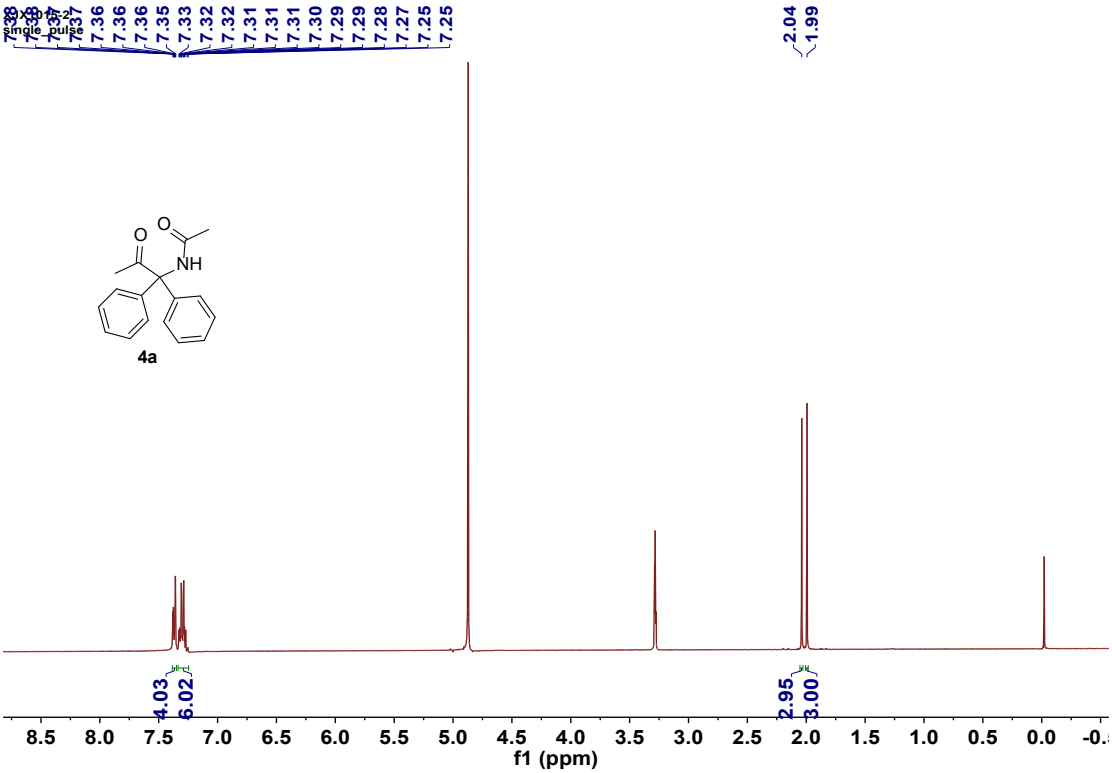


Figure S95. ^{1}H NMR spectrum of compound **4a** (400 MHz, solvent: MeOD)

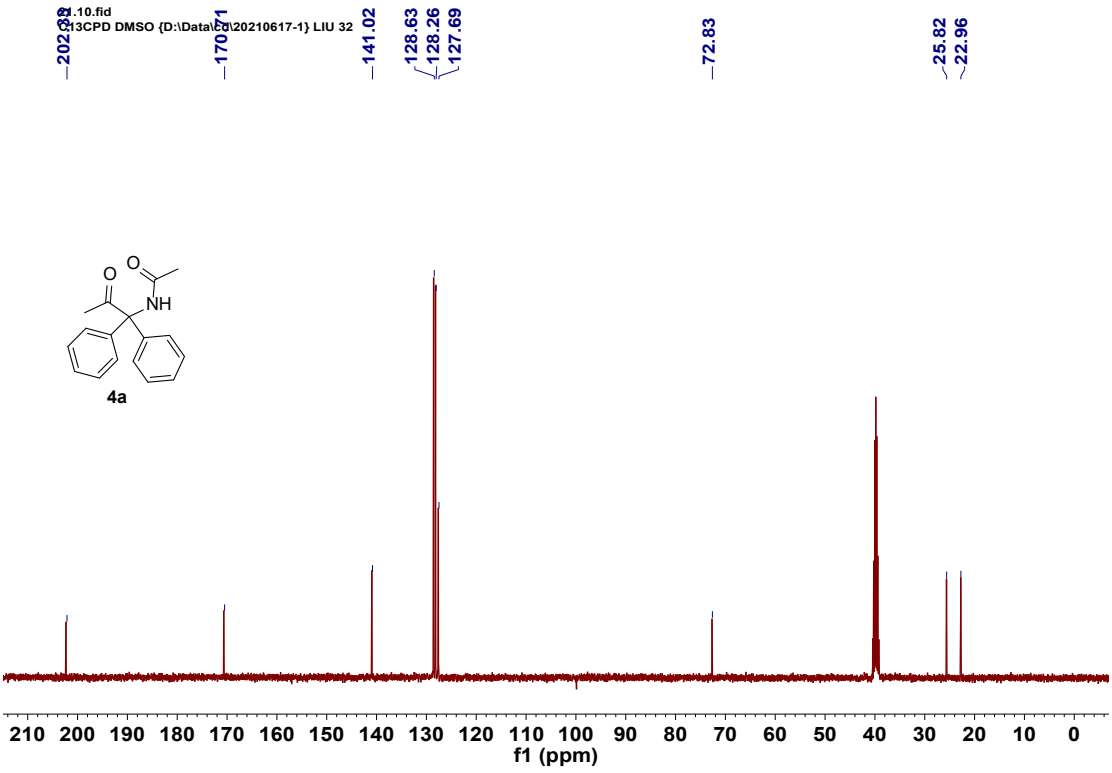


Figure S96. ^{13}C NMR spectrum of compound **4a** (101 MHz, solvent: DMSO-d_6)

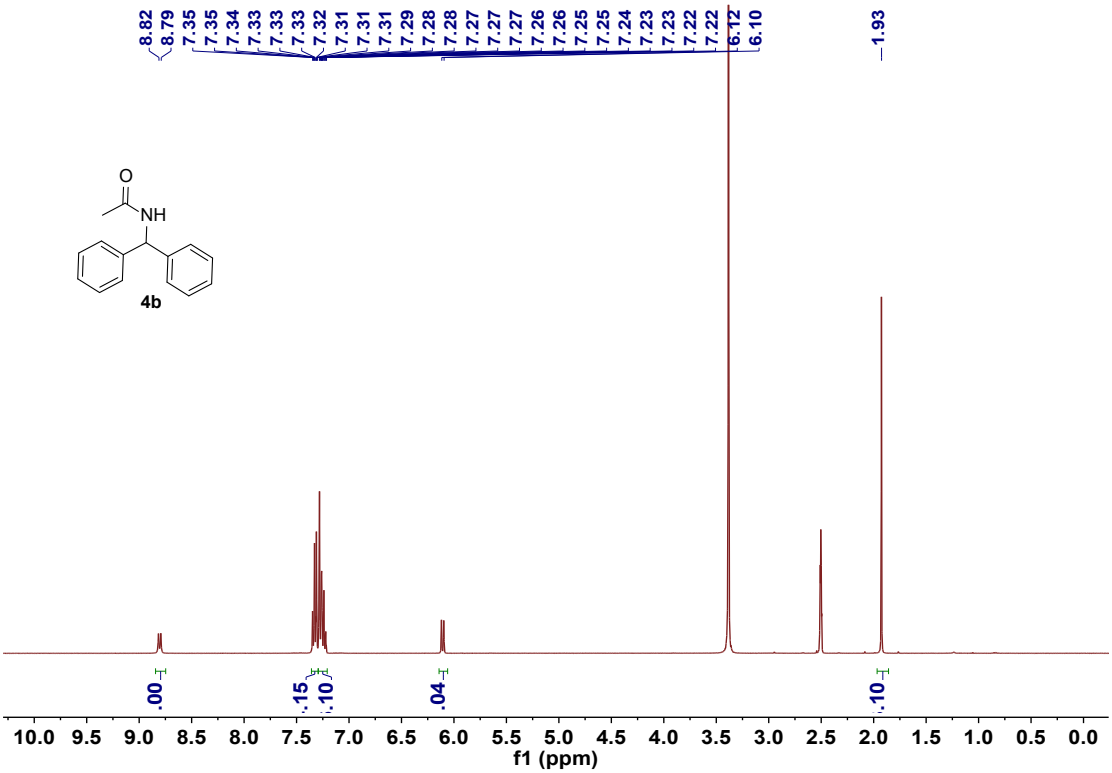


Figure S97. ^{1}H NMR spectrum of compound **4b** (400 MHz, solvent: DMSO-d_6)

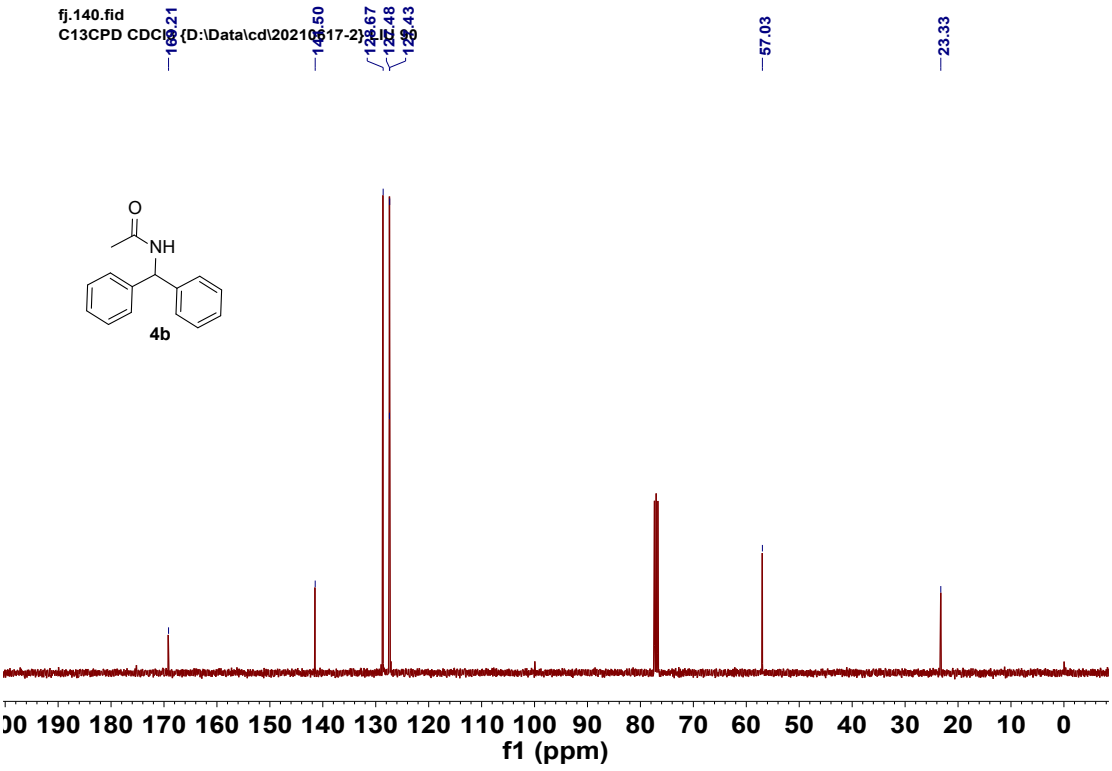


Figure S98. ^{13}C NMR spectrum of compound **4b** (101 MHz, solvent: $CDCl_3$)

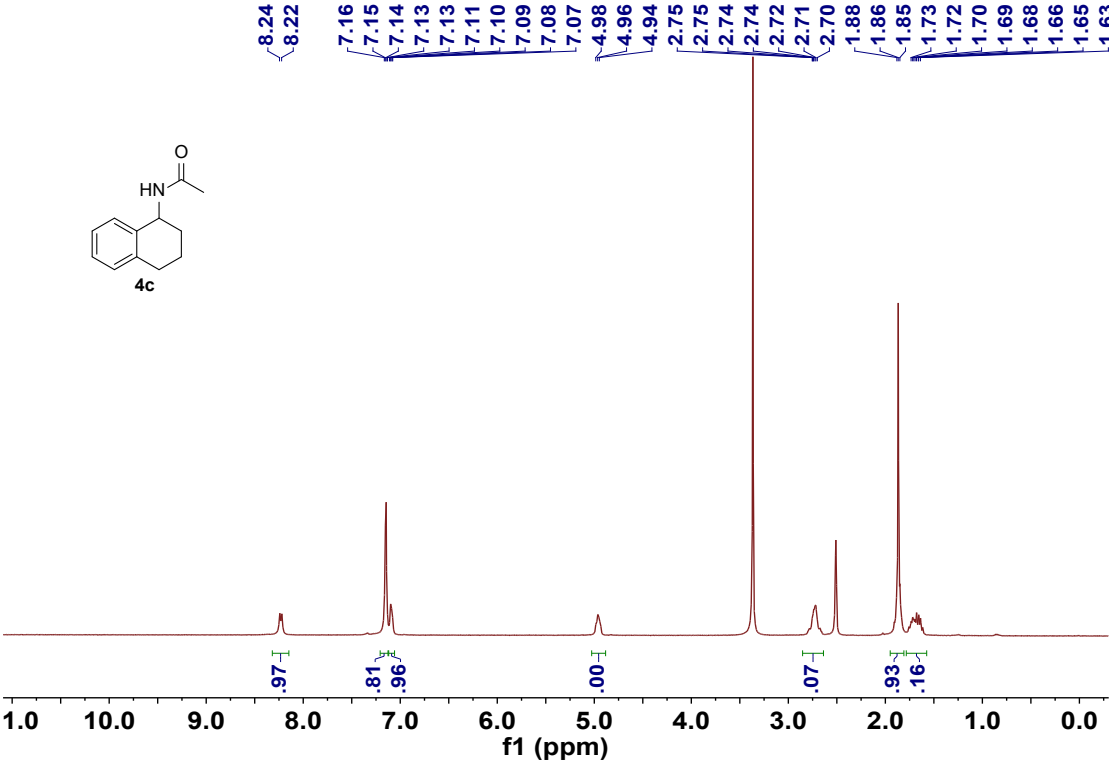


Figure S99. [1]H NMR spectrum of compound **4c** (400 MHz, solvent: DMSO-d_6)

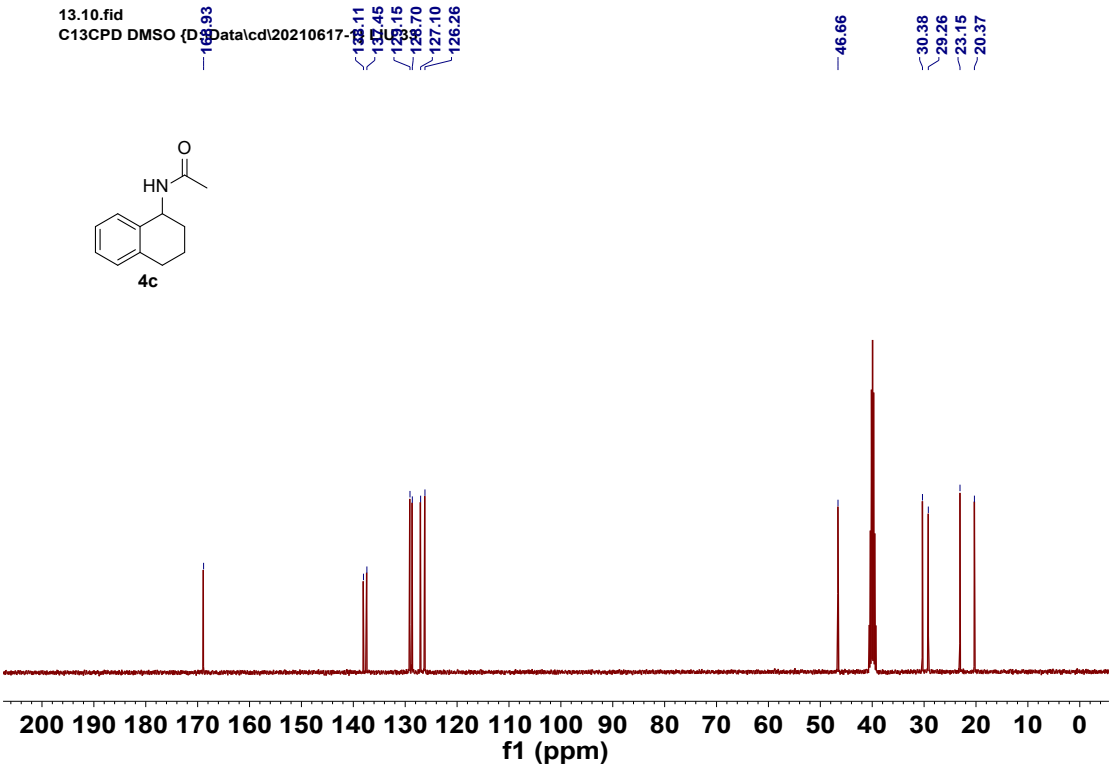


Figure S100. [13]C NMR spectrum of compound **4c** (101 MHz, solvent: DMSO-d_6)

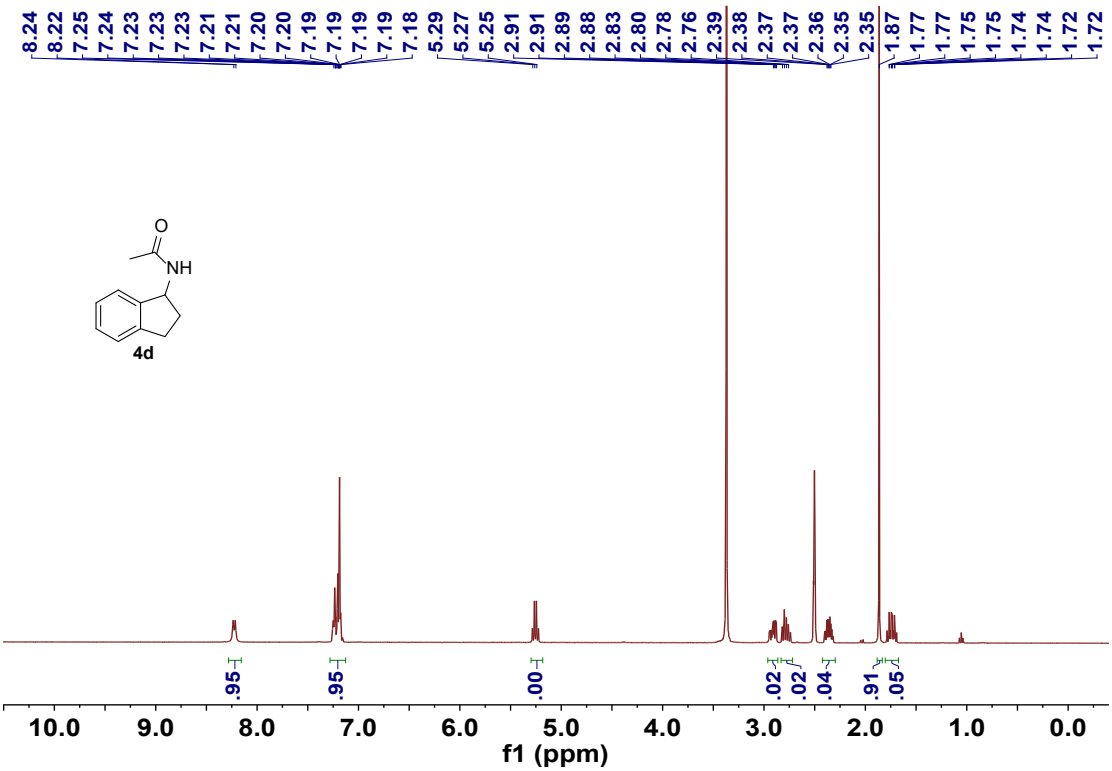


Figure S101. [1]H NMR spectrum of compound **4d** (400 MHz, solvent: DMSO-d_6)

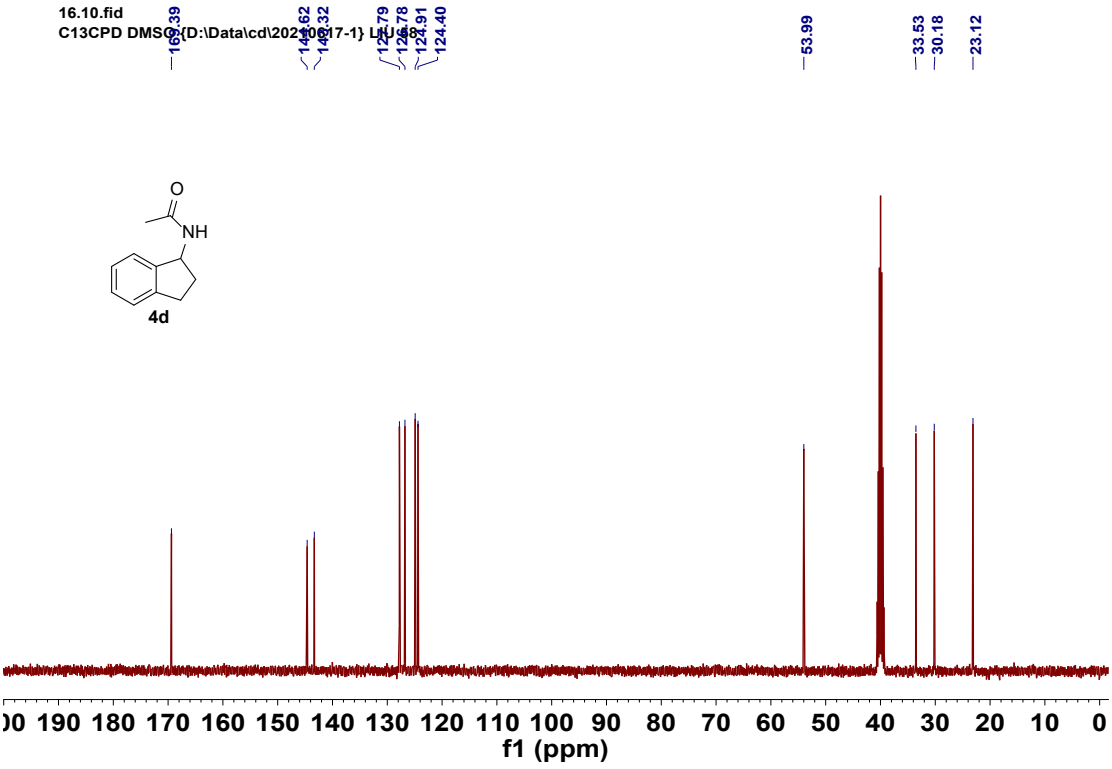


Figure S102. [13]C NMR spectrum of compound **4d** (101 MHz, solvent: DMSO-d_6)

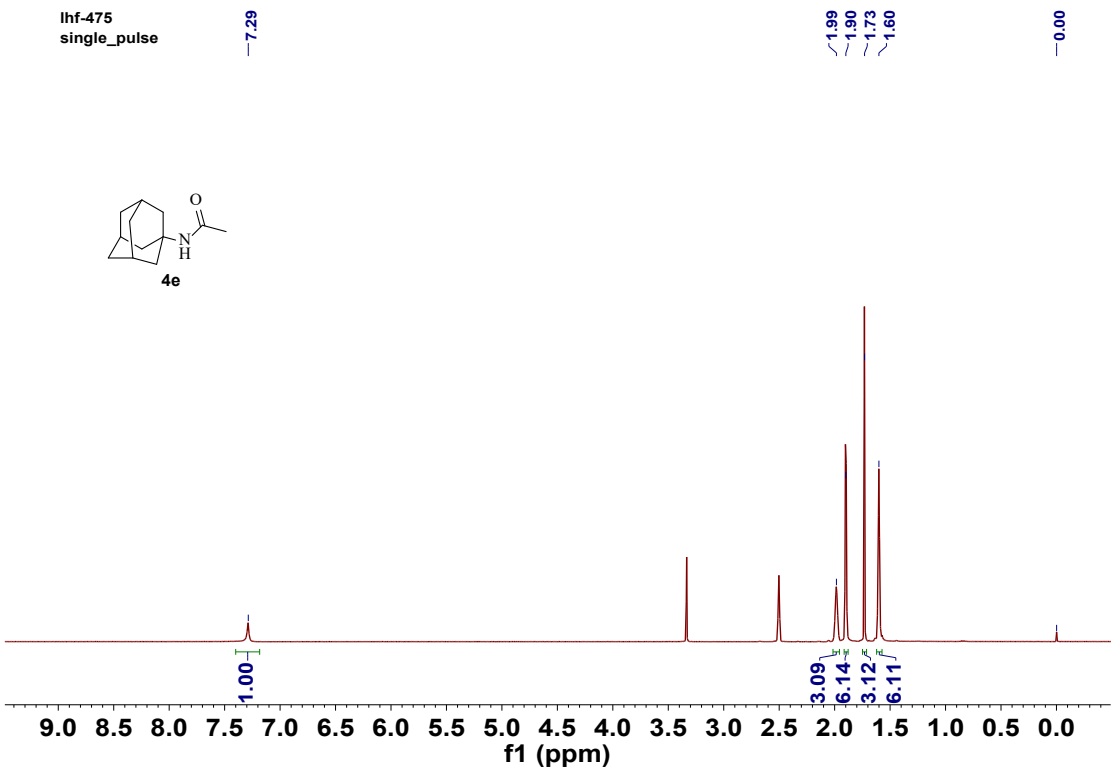


Figure S103. [1]H NMR spectrum of compound **4e** (400 MHz, solvent: DMSO-d_6)

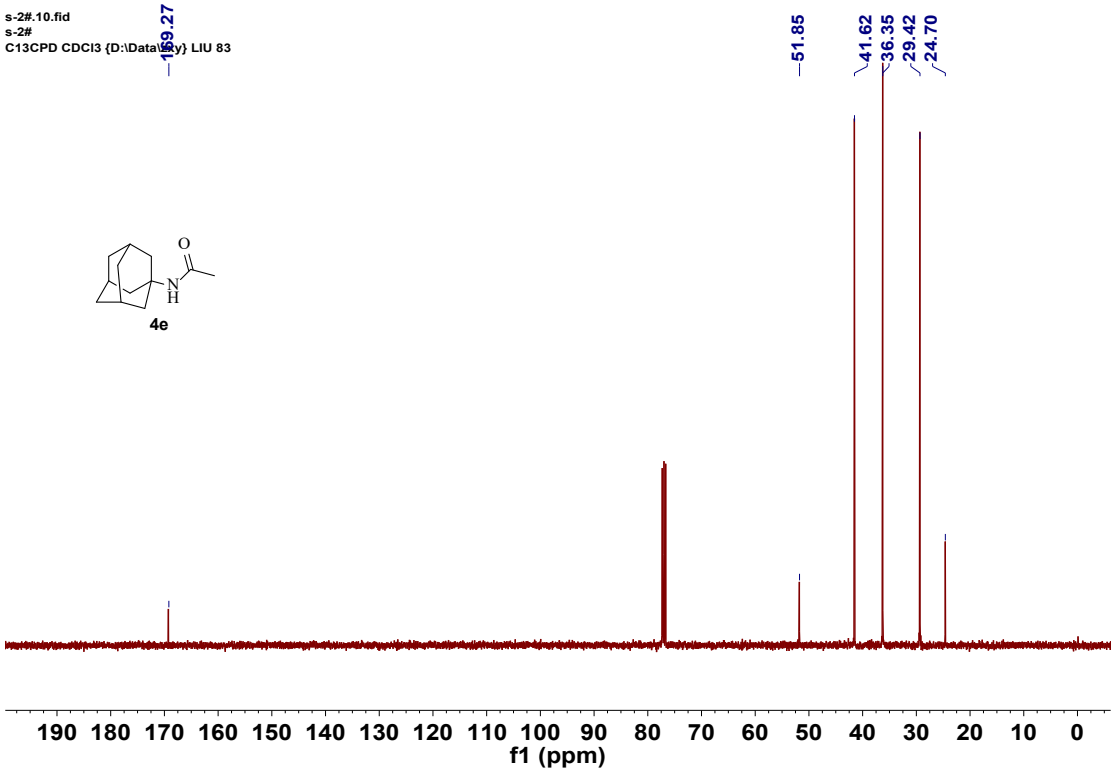


Figure S104. [13]C NMR spectrum of compound **4e** (101 MHz, solvent: $CDCl_3$)

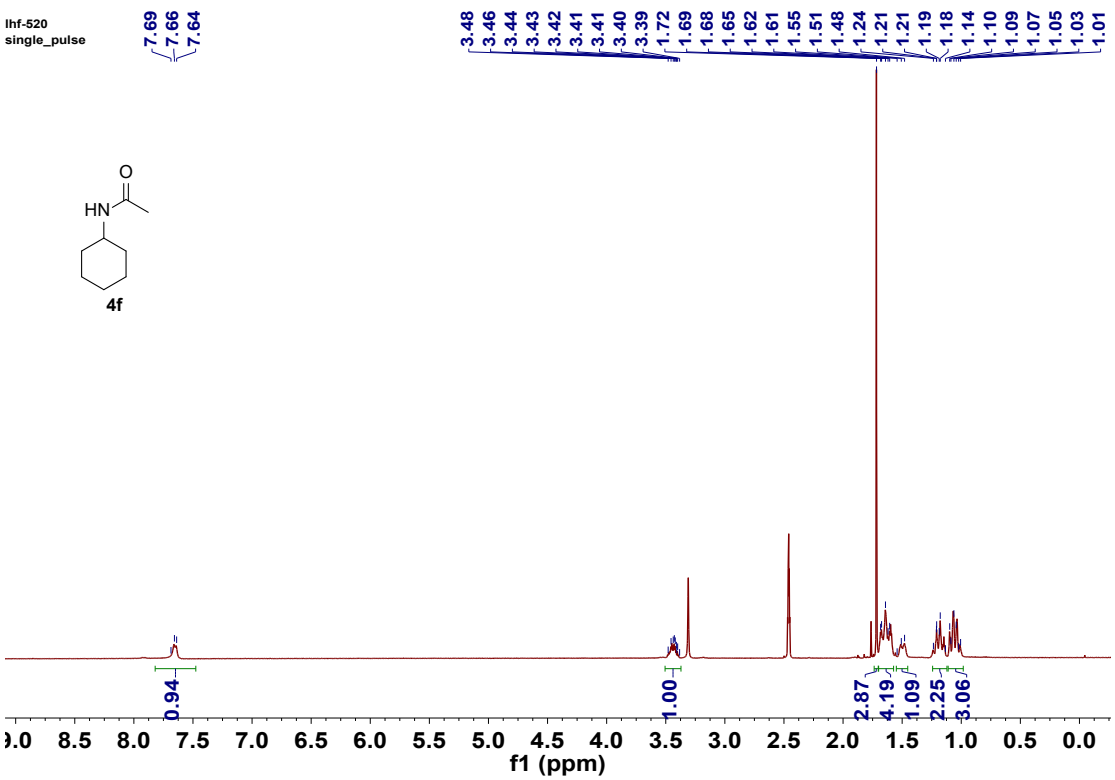


Figure S105. ^{1}H NMR spectrum of compound **4f** (400 MHz, solvent: DMSO-d_6)

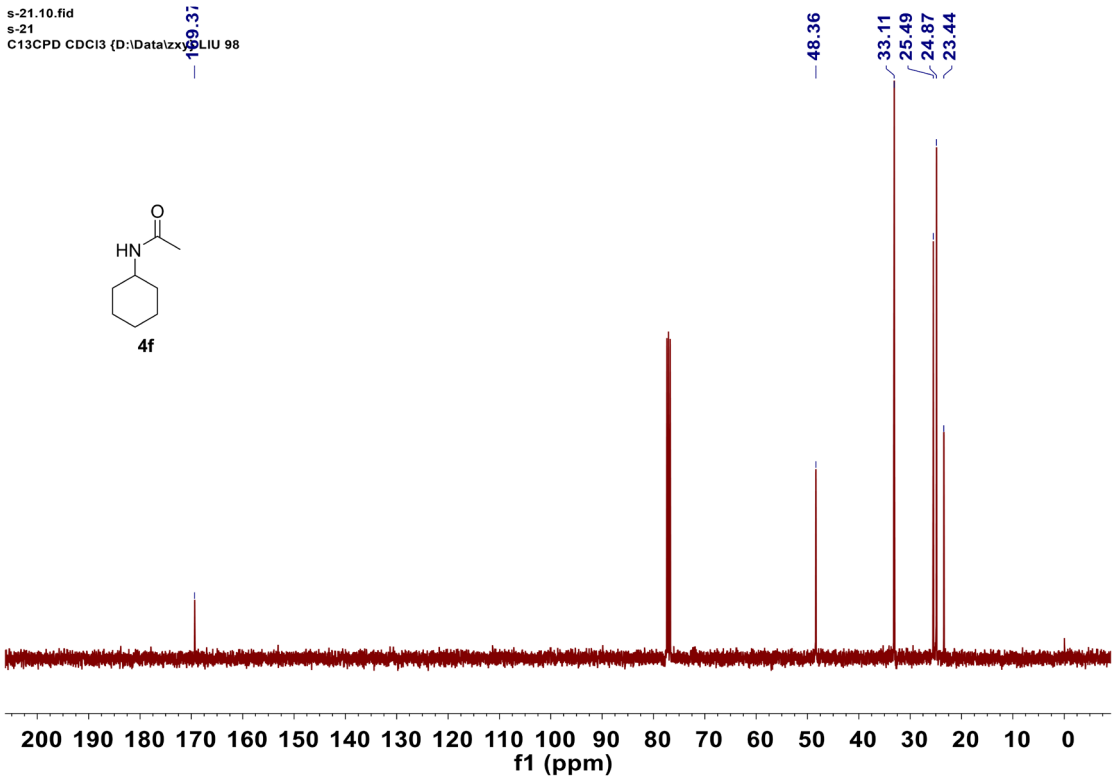


Figure S106. ^{13}C NMR spectrum of compound **4f** (101 MHz, solvent: $CDCl_3$)

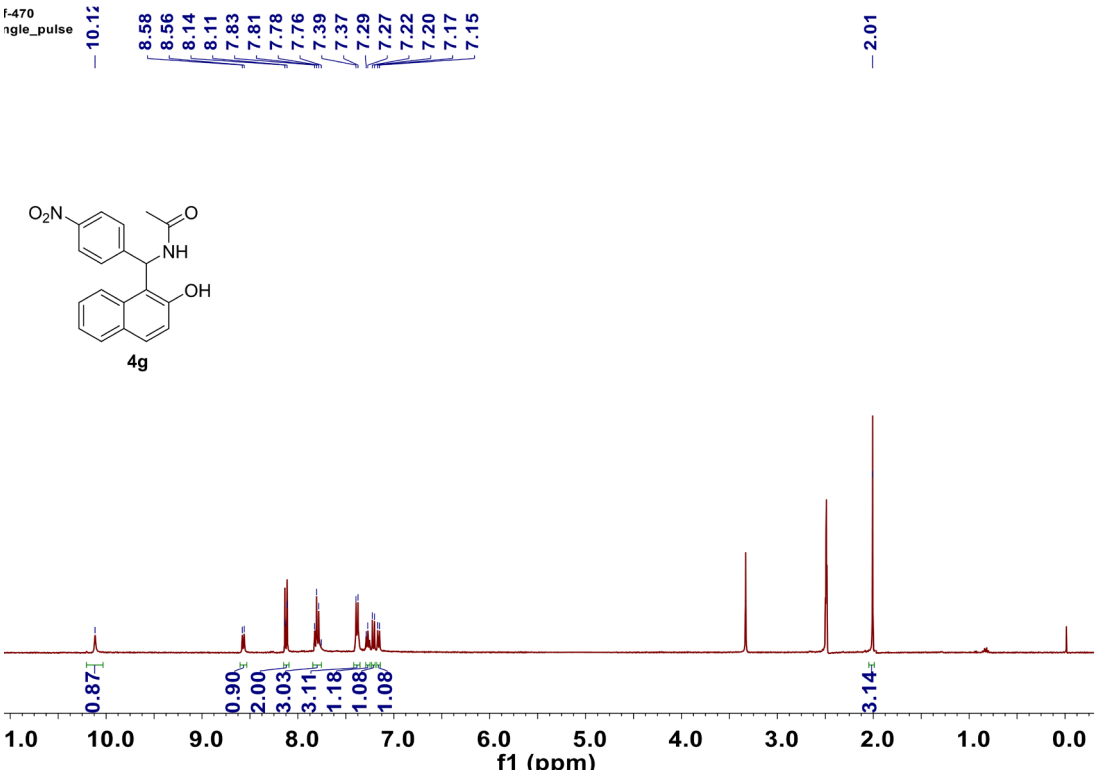


Figure S107. [1]H NMR spectrum of compound **4g** (400 MHz, solvent: DMSO-d_6)

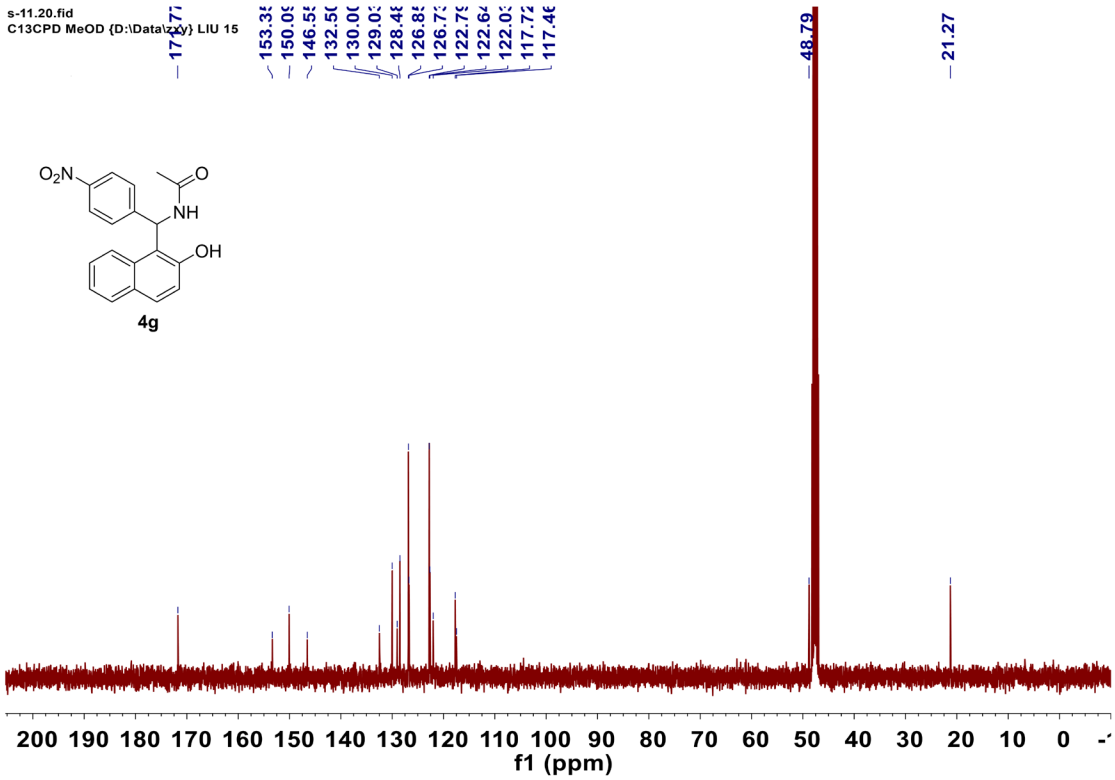


Figure S108. [13]C NMR spectrum of compound **4g** (101 MHz, solvent: MeOD)

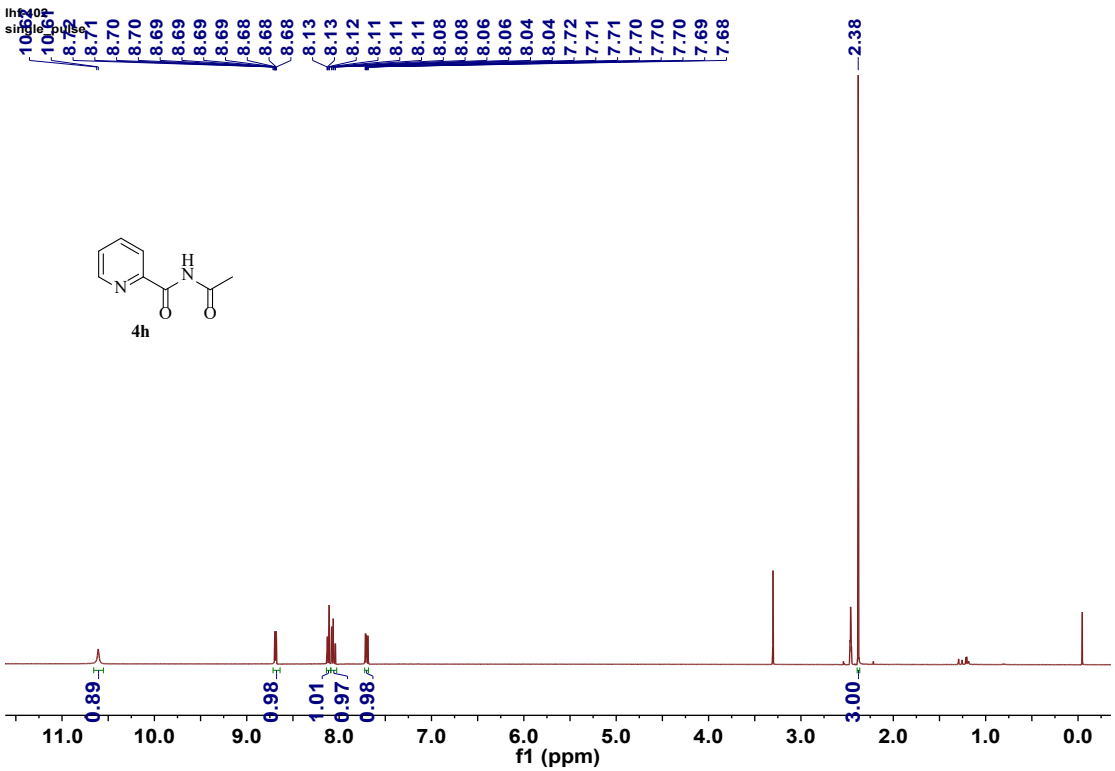


Figure S109. ^{1}H NMR spectrum of compound **4h** (400 MHz, solvent: DMSO-d_6)

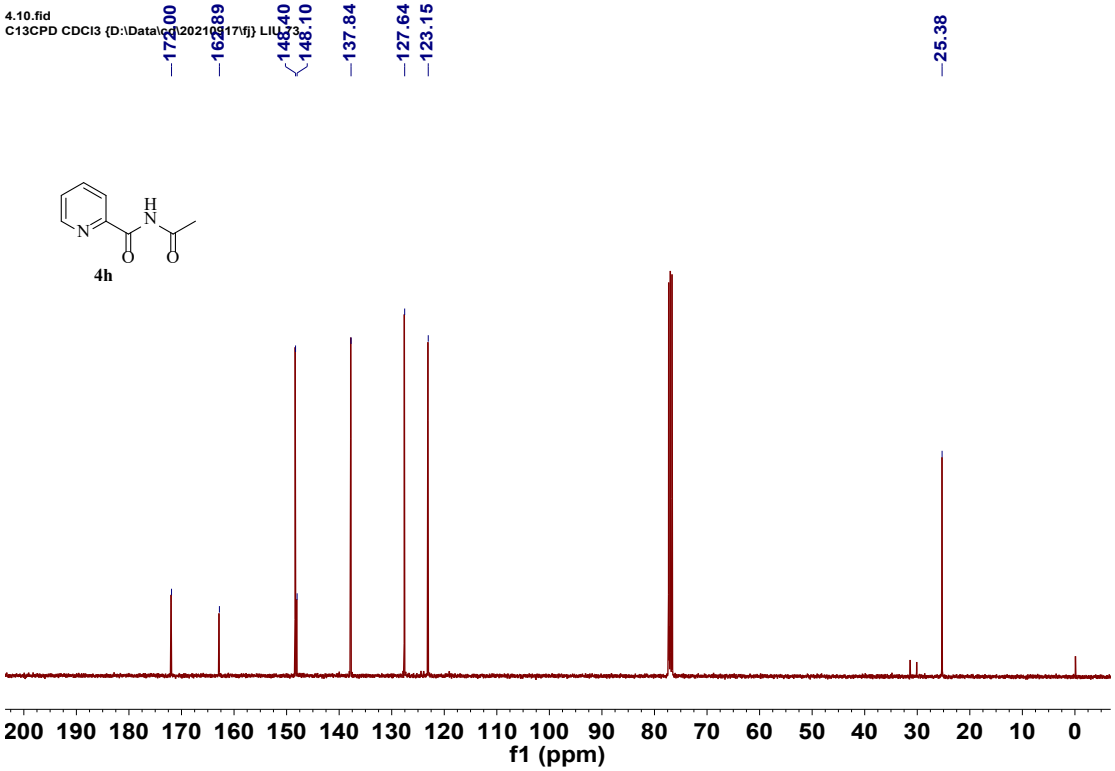


Figure S110. ^{13}C NMR spectrum of compound **4h** (101 MHz, solvent: $CDCl_3$)

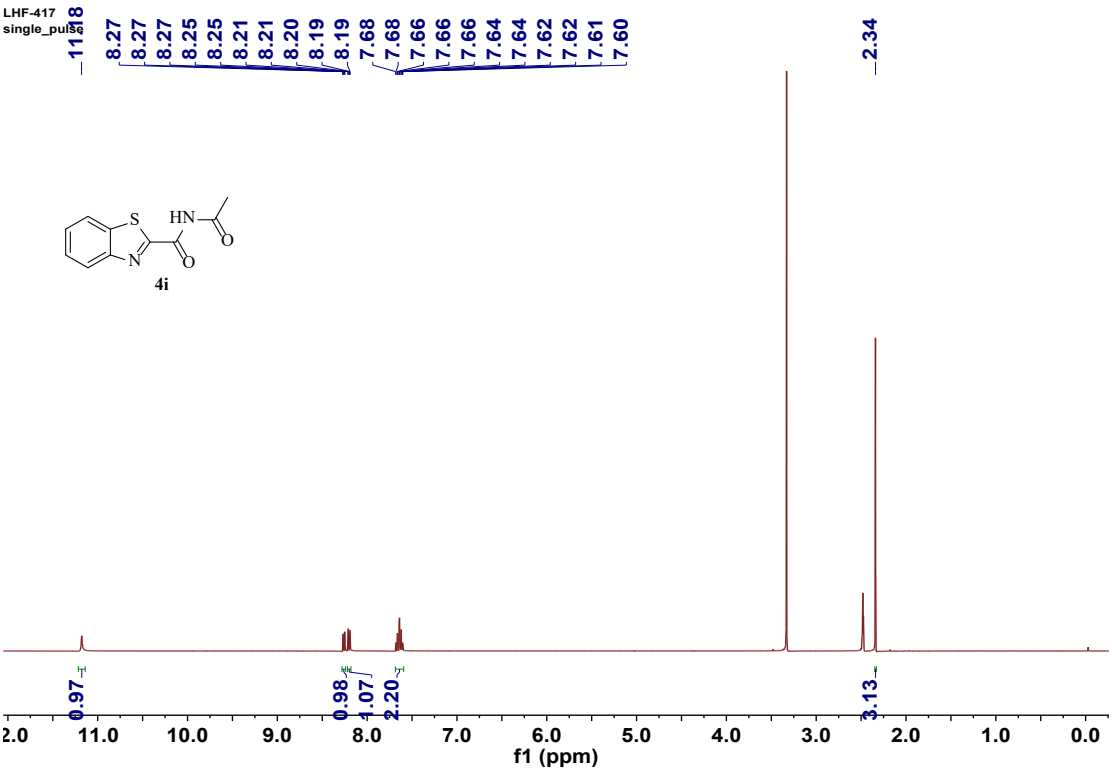


Figure S111. [1]H NMR spectrum of compound **4i** (400 MHz, solvent: DMSO-d_6)

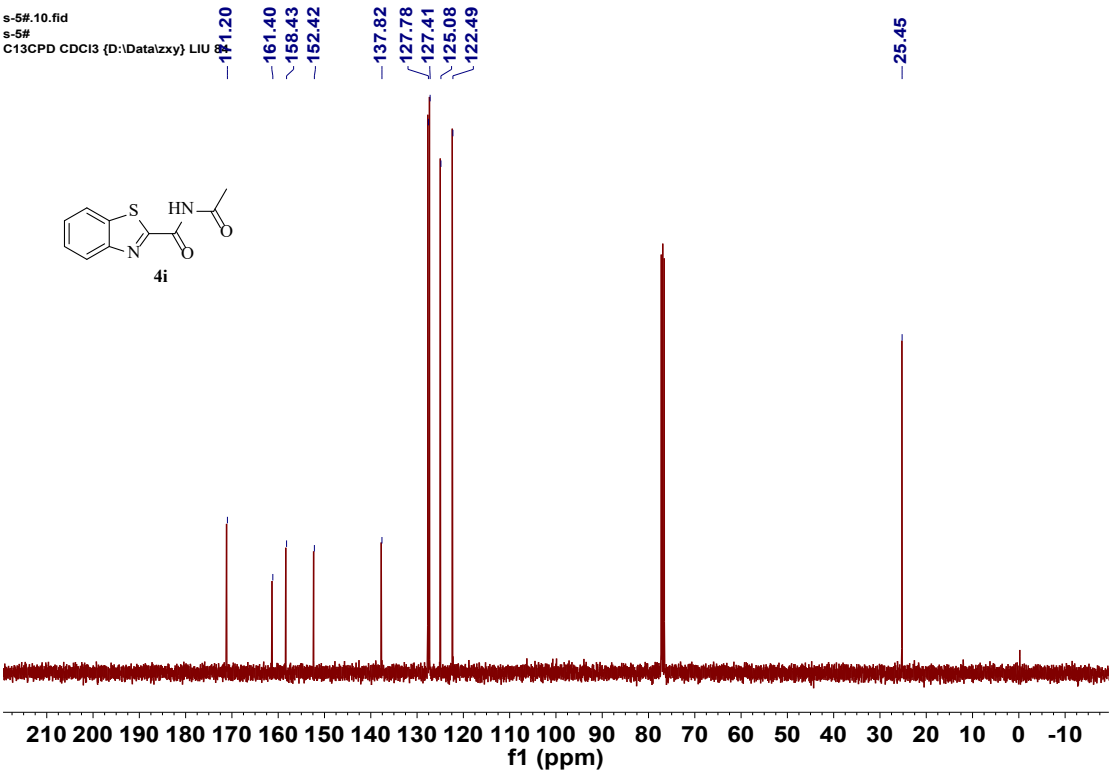


Figure S112. [13]C NMR spectrum of compound **4i** (101 MHz, solvent: $CDCl_3$)

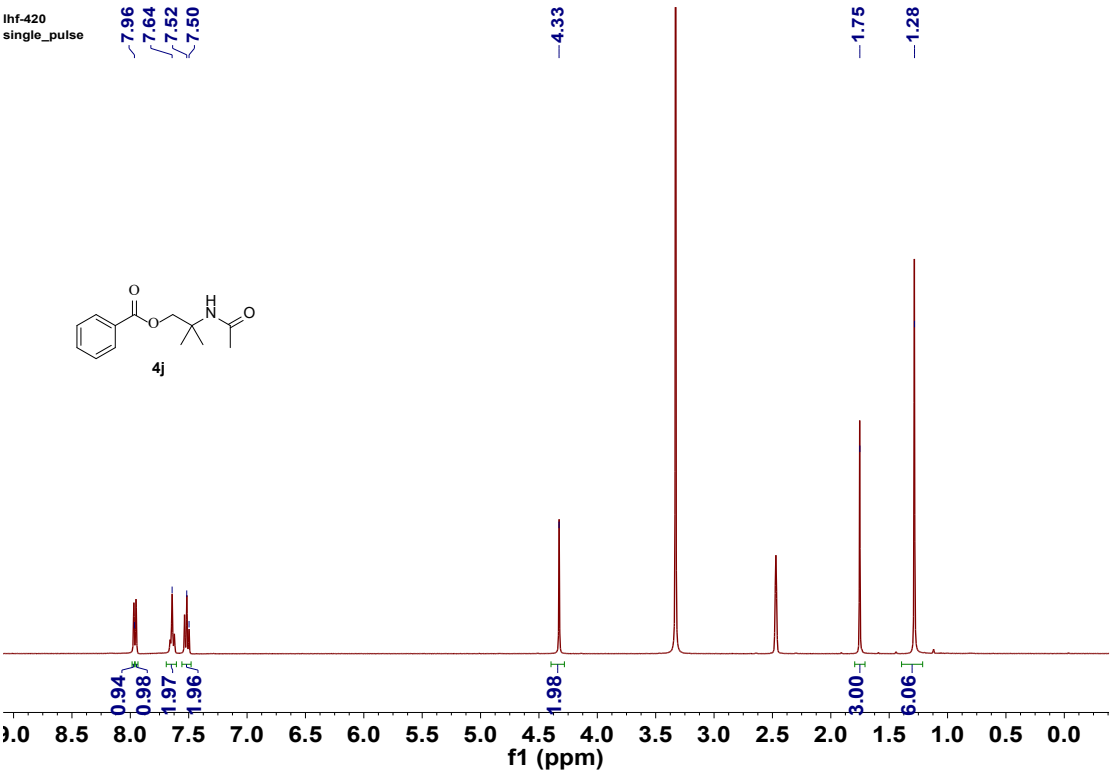


Figure S113. [1]H NMR spectrum of compound **4j** (400 MHz, solvent: DMSO-d_6)

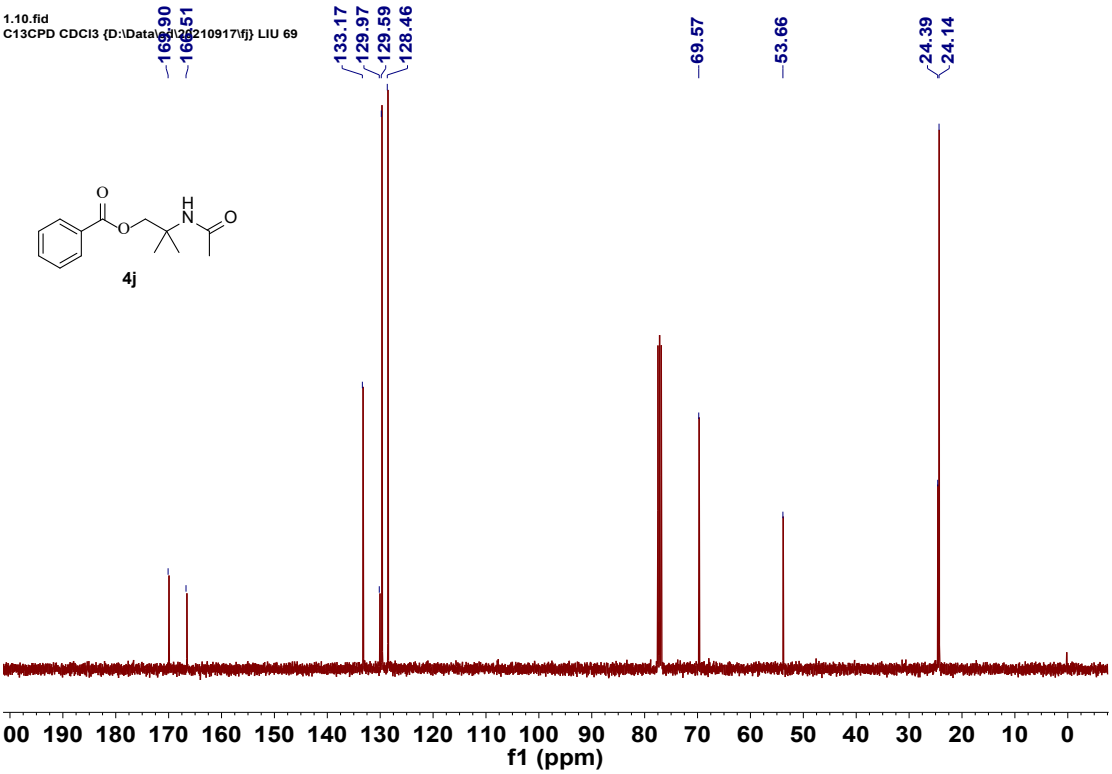


Figure S114. [13]C NMR spectrum of compound **4j** (101 MHz, solvent: $CDCl_3$)

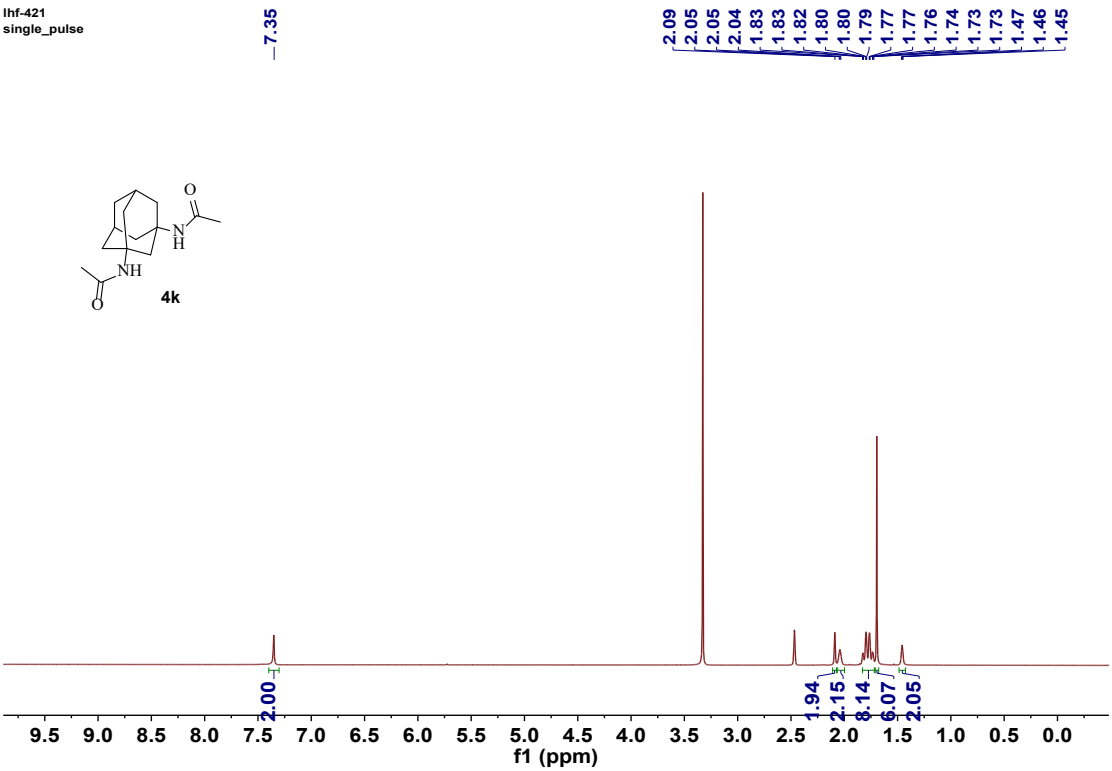


Figure S115. ^{1}H NMR spectrum of compound **4k** (400 MHz, solvent: DMSO-d_6)

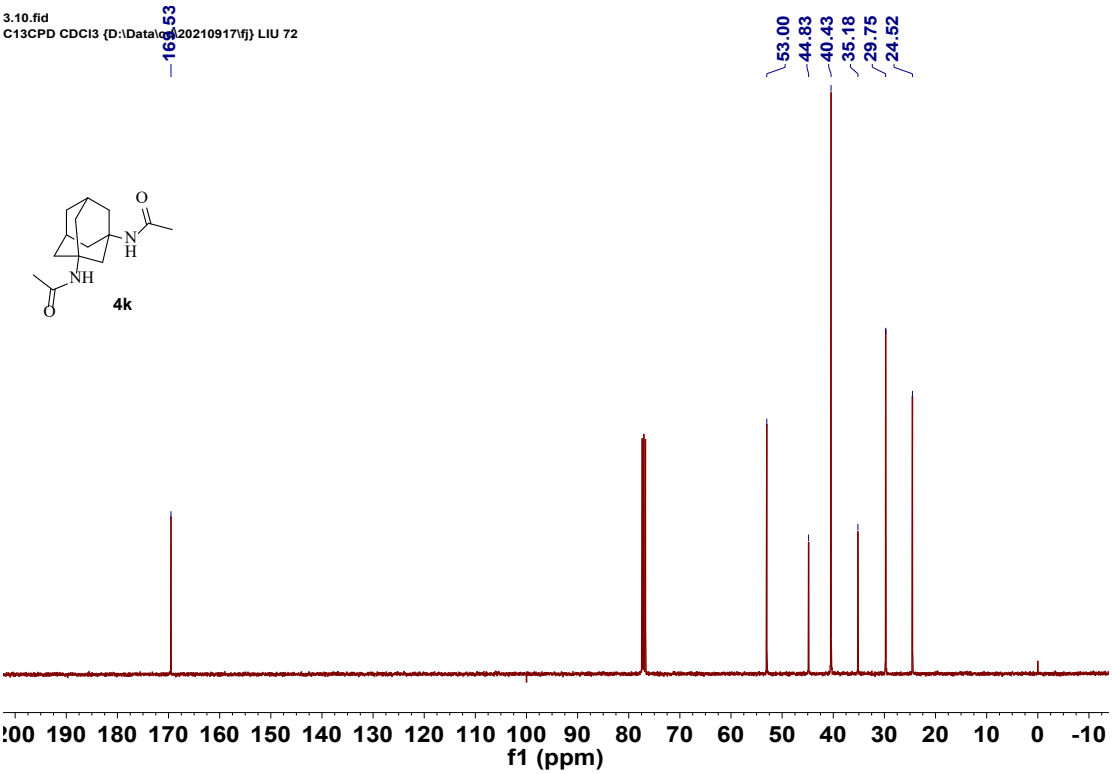


Figure S116. ^{13}C NMR spectrum of compound **4k** (101 MHz, solvent: $CDCl_3$)

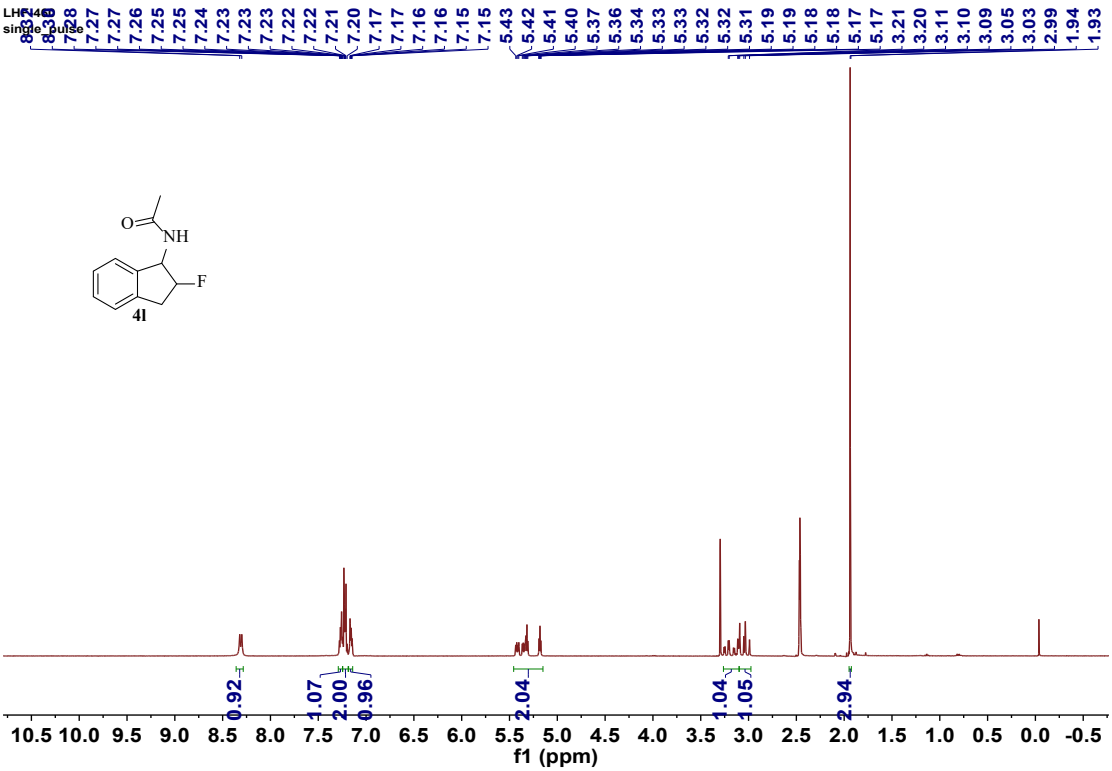


Figure S117. ^{1}H NMR spectrum of compound **4l** (400 MHz, solvent: DMSO-d_6)

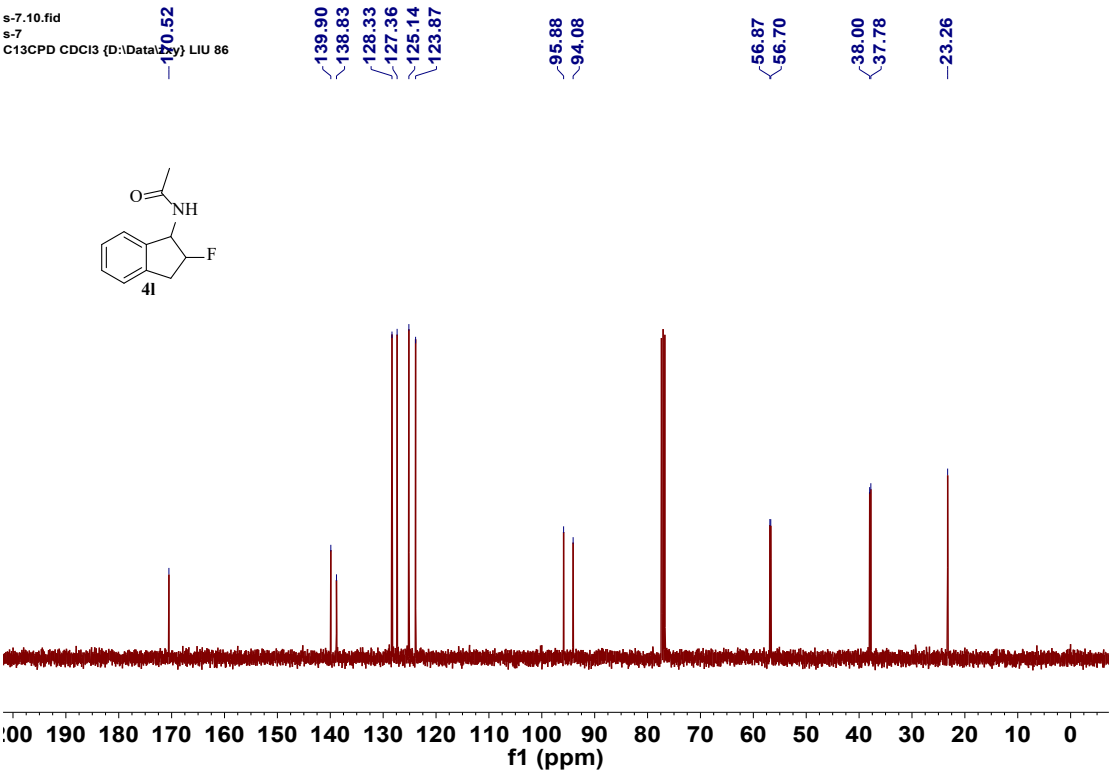


Figure S118. ^{13}C NMR spectrum of compound **4l** (101 MHz, solvent: $CDCl_3$)

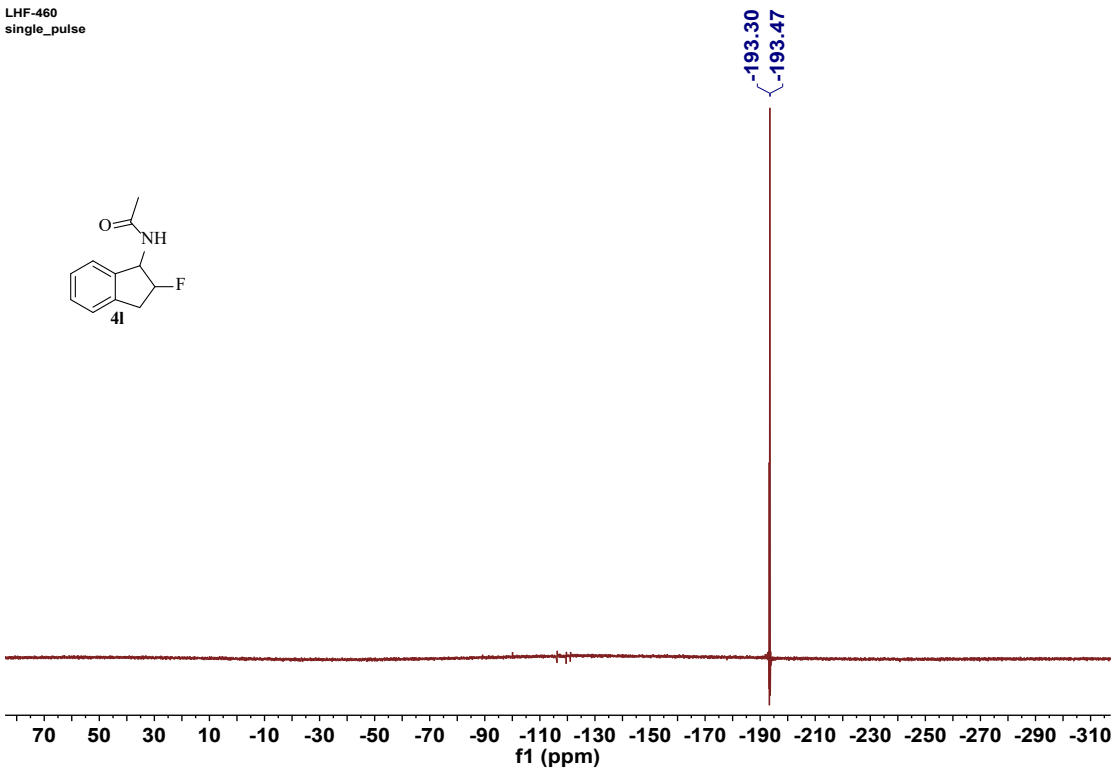


Figure S119. ^{19}F NMR spectrum of compound **4l** (376 MHz, solvent: DMSO-d_6)

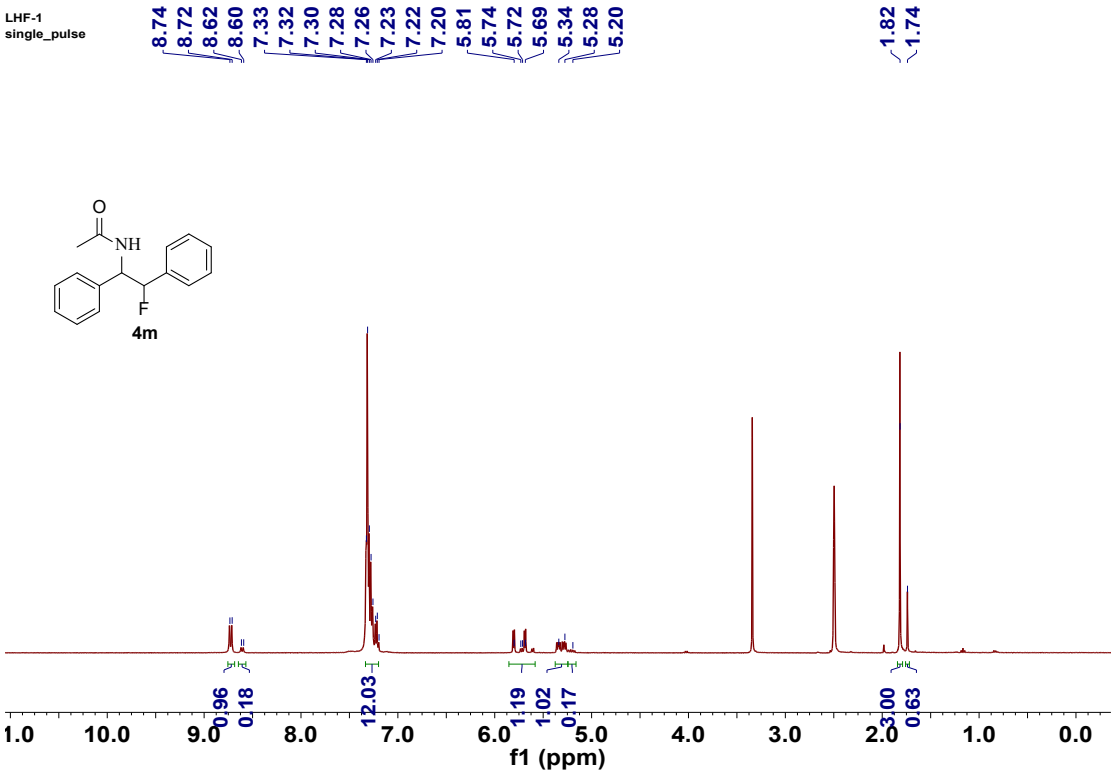


Figure S120. ^{1}H NMR spectrum of compound **4m** (400 MHz, solvent: DMSO-d_6) *d.r.* = 5:1

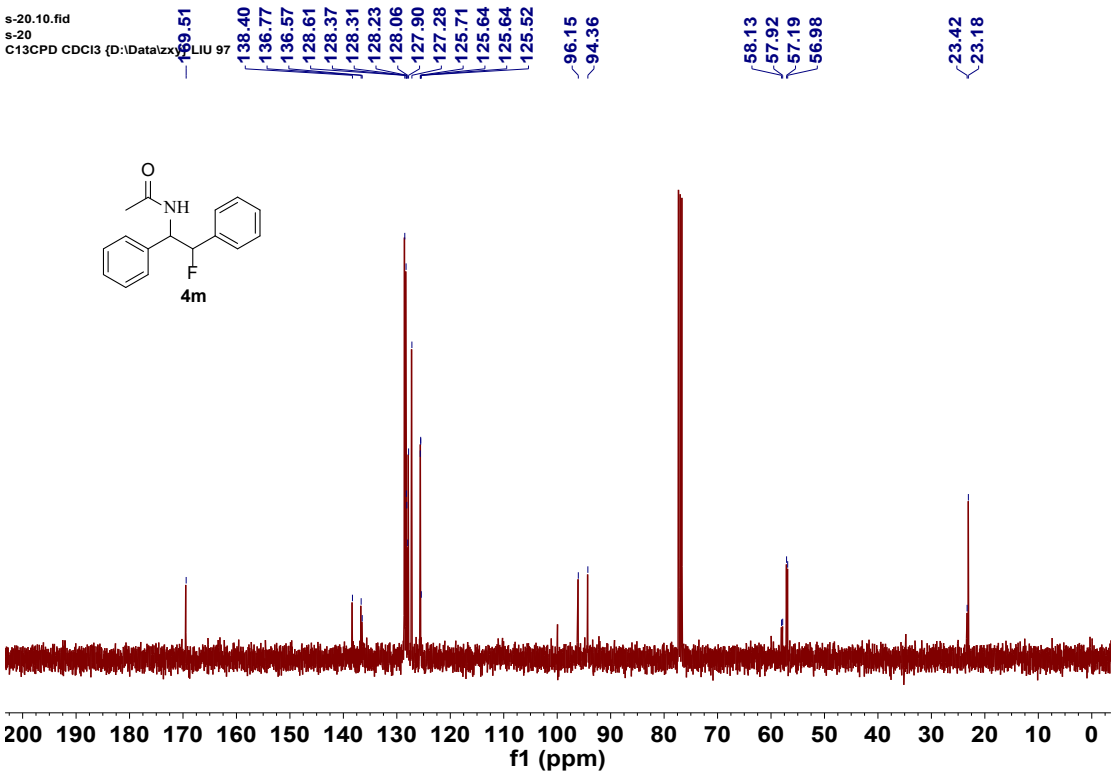


Figure S121. ^{13}C NMR spectrum of compound **4m** (101 MHz, solvent: $CDCl_3$)

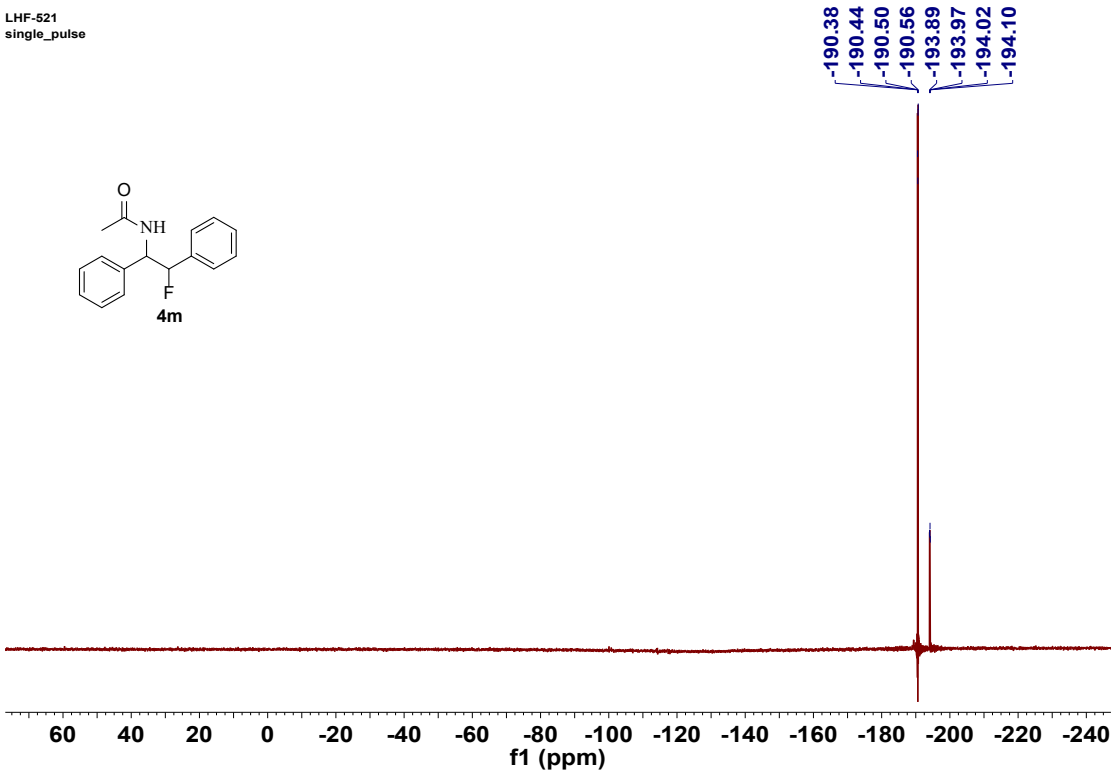


Figure S122. ^{19}F NMR spectrum of compound **4m** (376 MHz, solvent: $CDCl_3$)

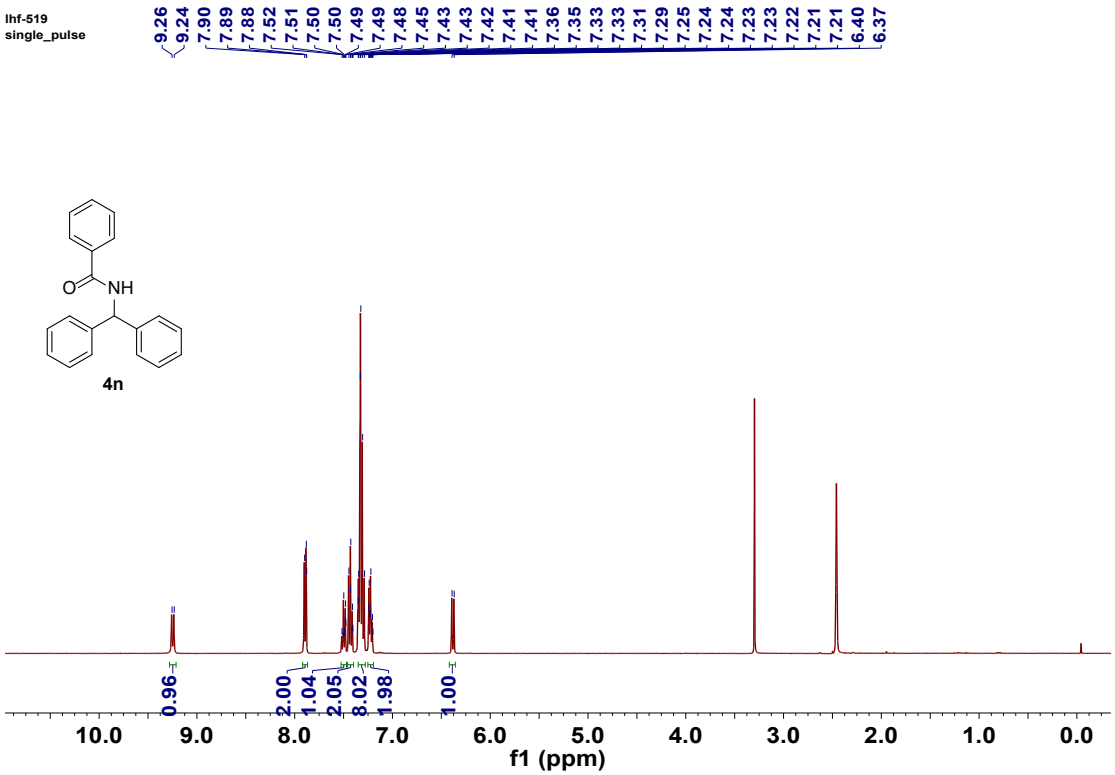


Figure S123. [1]H NMR spectrum of compound **4n** (400 MHz, solvent: DMSO-d_6)

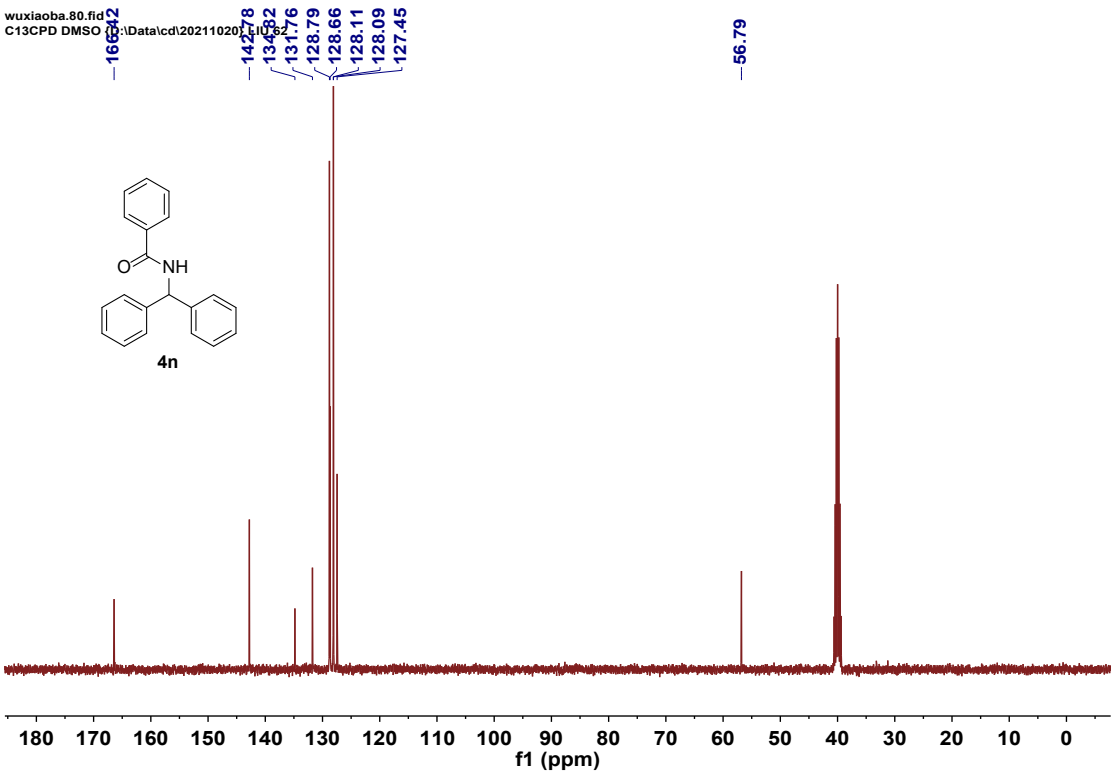


Figure S124. [13]C NMR spectrum of compound **4n** (101 MHz, solvent: DMSO-d_6)

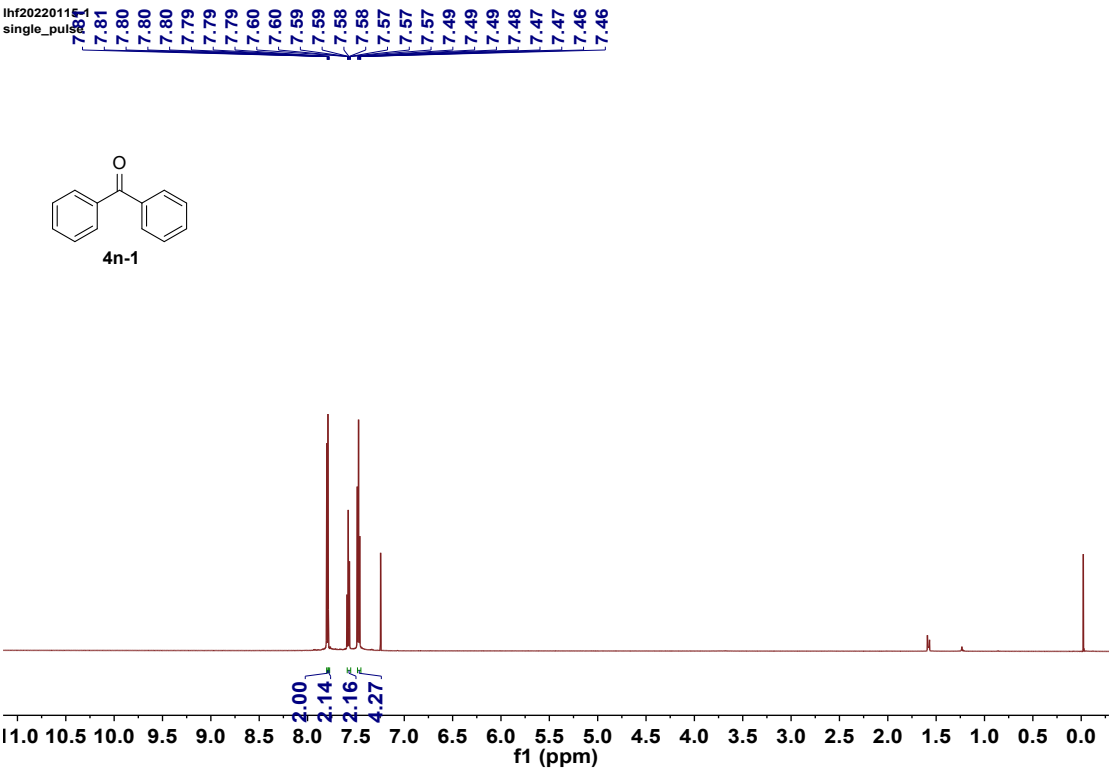


Figure S125. ^{1}H NMR spectrum of compound **4n-1** (600 MHz, solvent: $CDCl_3$)

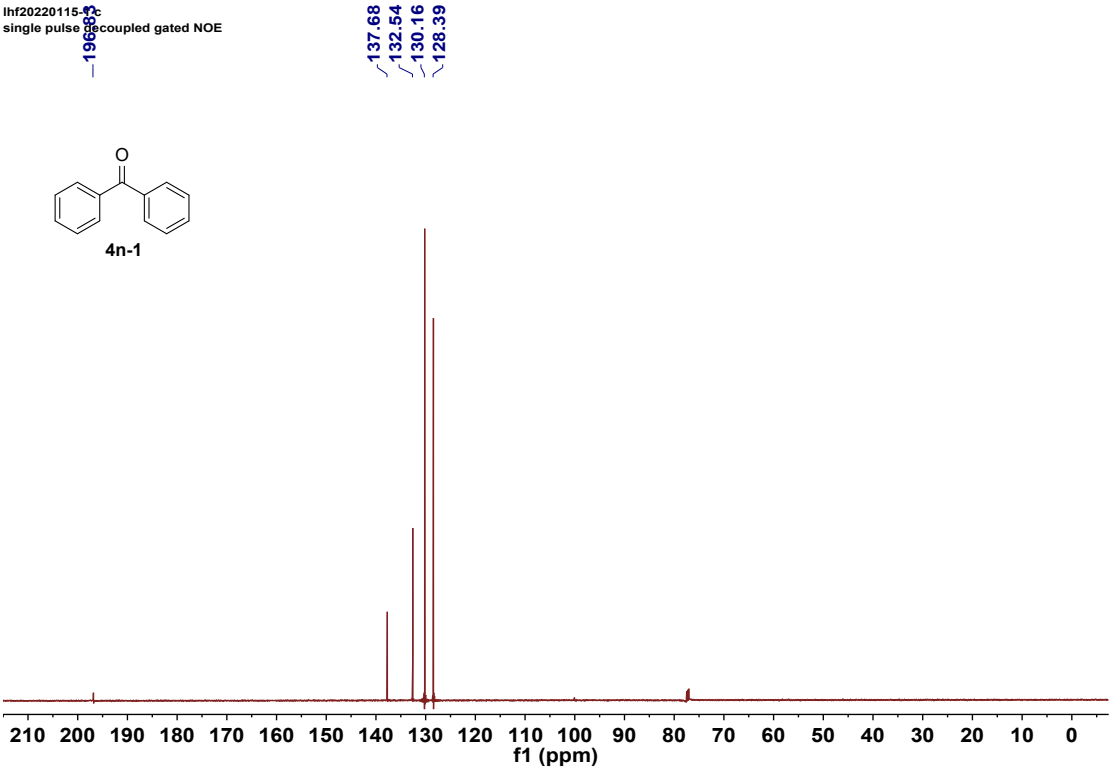


Figure S126. ^{13}C NMR spectrum of compound **4n-1** (151 MHz, solvent: $CDCl_3$)

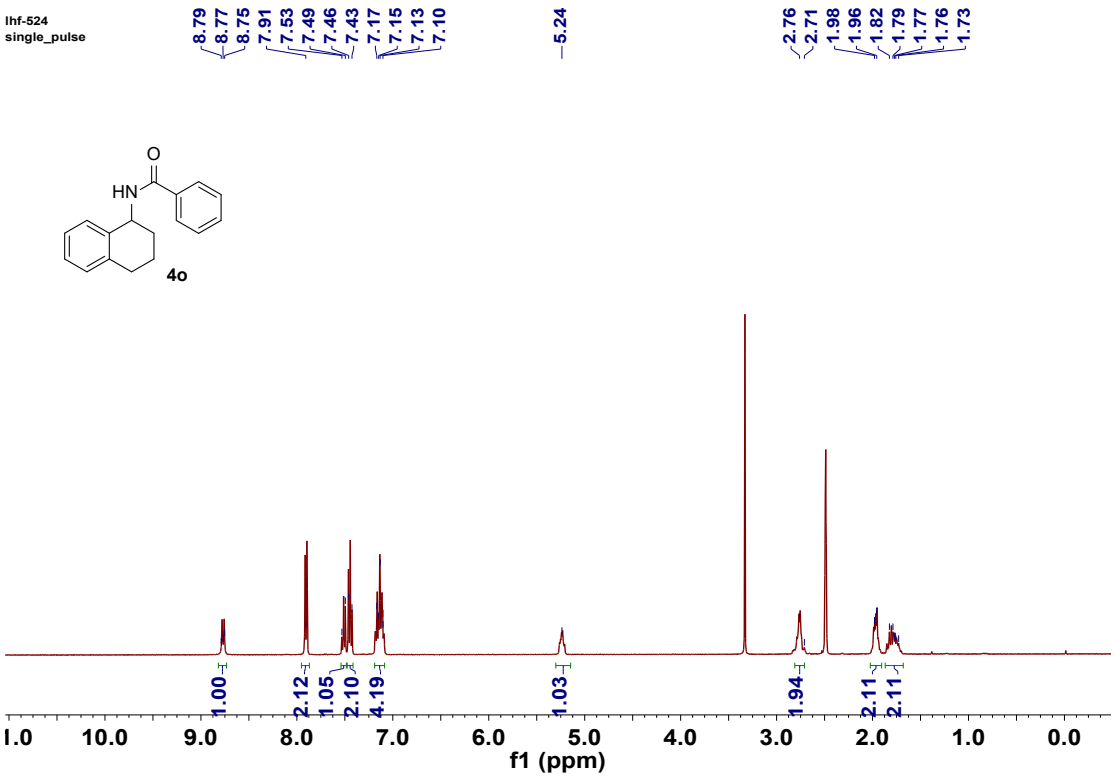


Figure S127. [1]H NMR spectrum of compound **4o** (400 MHz, solvent: DMSO-d_6)

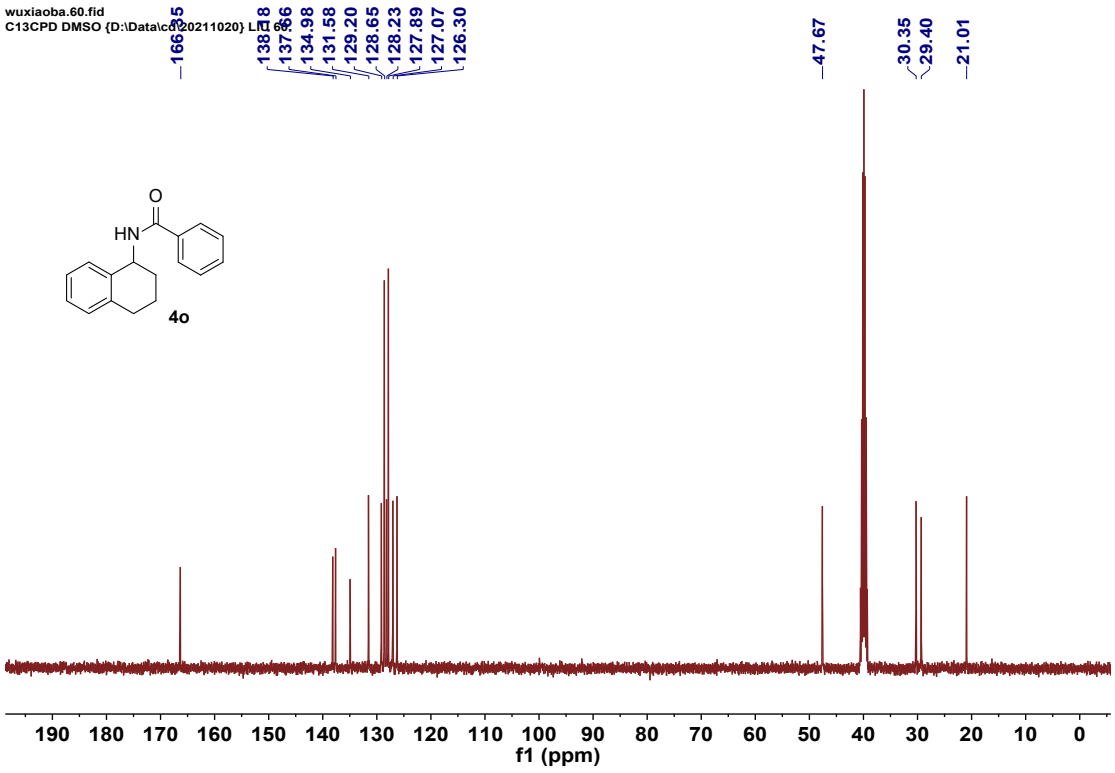


Figure S128. [13]C NMR spectrum of compound **4o** (101 MHz, solvent: DMSO-d_6)

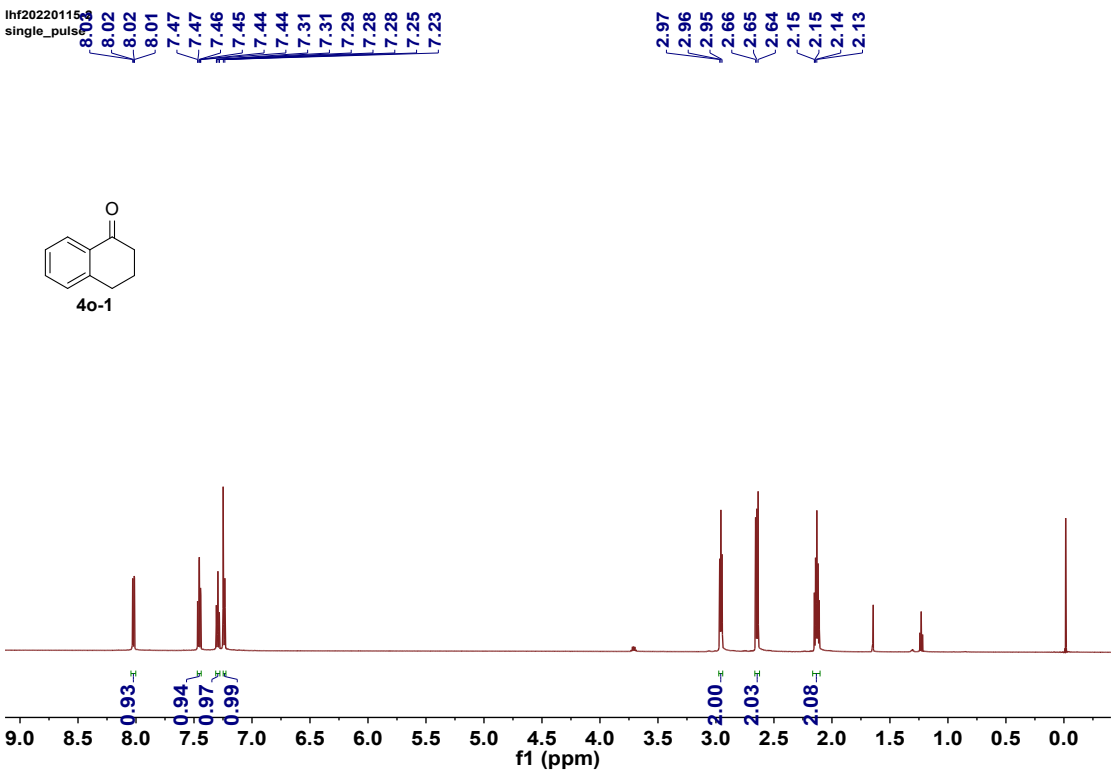


Figure S129. ^{1}H NMR spectrum of compound **4o-1** (600 MHz, solvent: $CDCl_3$)

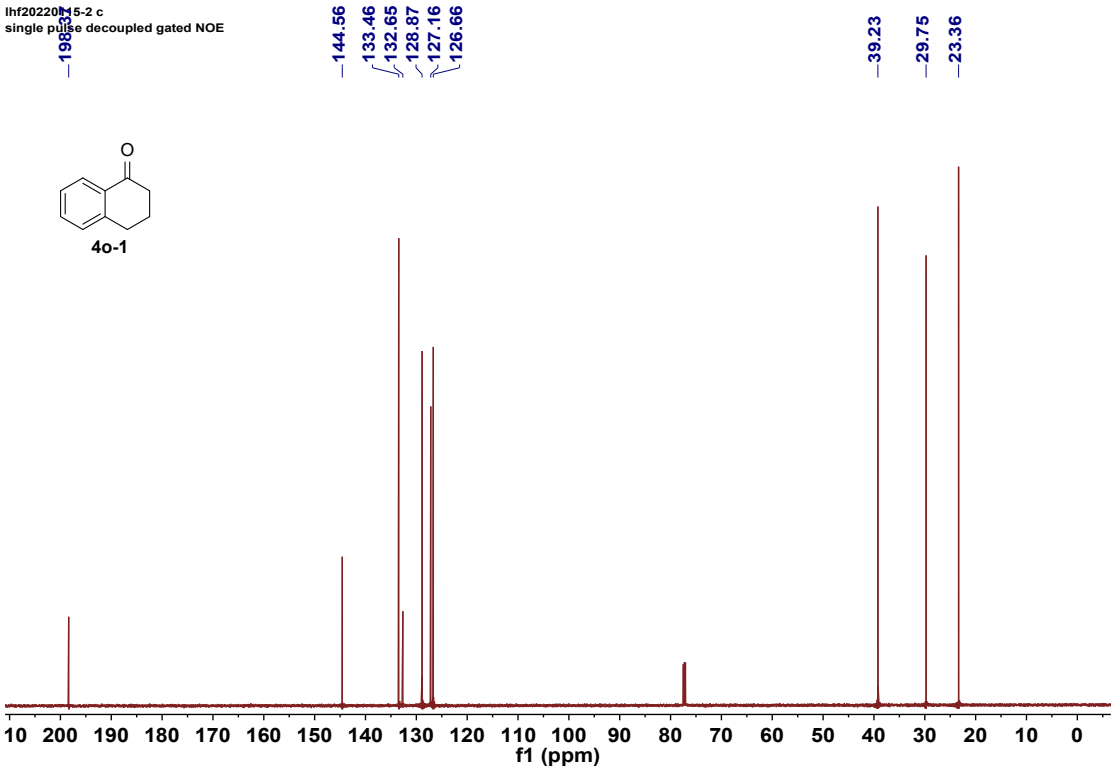


Figure S130. ^{13}C NMR spectrum of compound **4o-1** (151 MHz, solvent: $CDCl_3$)