Supporting Information for

Organocatalytic Activation of Isocyanides: *N*-Heterocyclic Carbene-Catalyzed Enaminone Synthesis from Ketones

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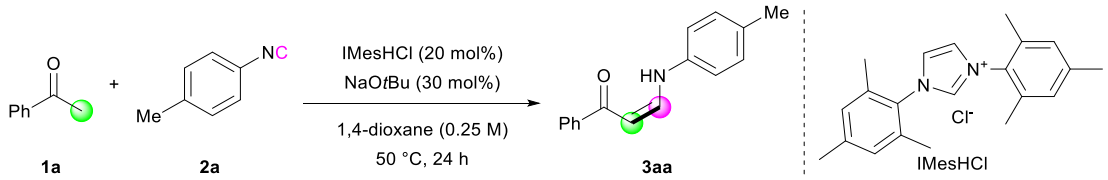
1. General Information

Unless otherwise noted, all reactions were performed in a 4mL screw-capped reaction vial. All anhydrous solvents were purchased from commercial suppliers and degassed with dry argon before use. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6, and the residue solvent signals were used as reference. Chemical shifts were reported in ppm, and coupling constants in Hz. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet). Unless otherwise note, all reagents and solvents as well as all starting ketones, benzyl bromide, **2b'**, and **2c** were purchased from commercial suppliers and used as received without further purification. Previously reported isocyanides (**2a**, **2b**, **2d**, **2e**, **2f**, **2g**, **2i**, and **2j**) were prepared from their corresponding amines by methods described in the literature,[1] and their identity was confirmed by comparison with reported data. New isocyanide **2h** was synthesized by a previously reported method, and its structure was confirmed by spectroscopic analysis.[1] The free carbene (IMes) was synthesized from the corresponding salt (IMesHCl), according to a previous method.[2] All enaminone products were purified by silica gel column chromatography (hexane/EtOAc with 3% NEt_3). We are grateful to the Organic Chemistry Research Center of Sogang University for HRMS-ESI analysis, the Korea Basic Science Institute (KBSI) for HRMS-EI analysis, and the Research Institute of Pharmaceutical Science (SNU) for single-crystal X-ray diffraction analysis.

2. Initial Experiment of (*Z*)-Enaminone Synthesis

Scheme S1. Reaction between **1a** and **2a**



IMesHCl (54.5mg, 0.16 mmol) and NaO*t*Bu (23.1 mg, 0.24 mmol) were charged in a 25 mL Schlenk tube under argon atmosphere. The tube was then sealed with a rubber septum, and 1,4-dioxane (1.6 mL) was added. The mixture was stirred for 5 min. at room temperature, and a solution of **1a** (93.5 µl, 0.8 mmol) and **2a** (95.6 µl, 0.8 mmol) in 1,4-dioxane (1.6 mL) was added via syringe. The mixture was stirred for 24 h at 50 ℃. After cooling to room

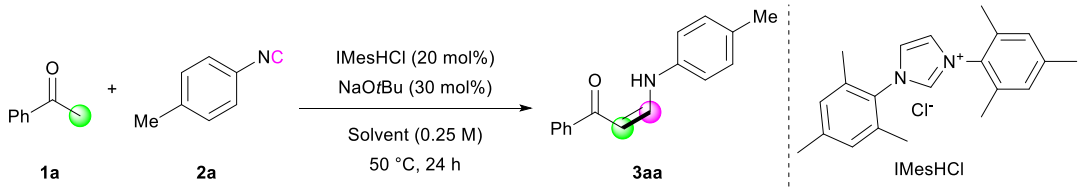
temperature, the volatiles were removed in vacuo and the remaining residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate) to afford **3aa** as a yellow solid (36.1 mg, 19 % yields).

3. General Procedure for the Synthesis of Enaminone (3)

IMesHCl (10.2mg, 0.03 mmol) and the base were charged in a 4 mL vial under argon atmosphere. The vial was then sealed with a Teflon-lined septum, and the ketone (0.2 mmol), aryl isocyanide (0.3 mmol), and DMA (2.4 mL) were added via syringe. The solution was stirred for the indicated time at 80 ℃. After cooling to room temperature, the volatiles were removed in vacuo and the remaining residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate in 3% triethylamine) to afford the corresponding enaminone.

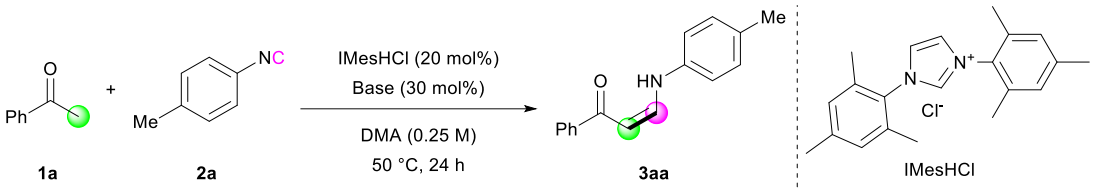
4. Optimization Tables

Table S1 – Solvent



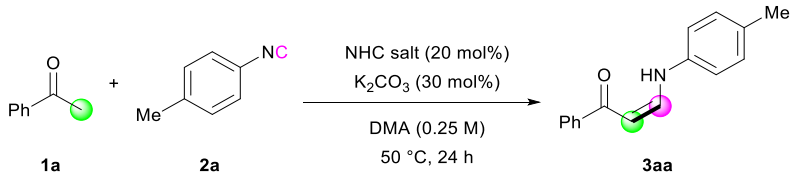
Entry	Solvent	Yield **3aa** (%)
1	1,4-Dioxane	30
2	MeCN	19
3	THF	35
4	Isopropyl acetate	25
5	DCM	13
6	1,2-DCE	Trace
7	Benzene	33
8	Toluene	36
9	*o*-Xylene	38
10	*p*-Xylene	32
11	Cyclohexane	32
12	Hexane	38
13	DMF	42
14	**DMA**	**43**
15	DMSO	40

Table S2 – Base



Entry	Base	Yield **3aa** (%)	Entry	Base	Yield **3aa** (%)
1	NaO*t*Bu	39	11	Cs_2CO_3	45
2	LiO*t*Bu	27	12	K_3PO_4	48
3	KO*t*Bu	37	13	K_2HPO_4	N. R.
4	NaOMe	45	14	KH_2PO_4	N. R.
5	LiHMDS	38	15	NaOAc	N. R.
6	KHMDS	32	16	CsOAc	30
7	NaH	45	17	TEA	N. R.
8	Li_2CO_3	N. R.	18	DIPEA	N. R.
9	Na_2CO_3	7	19	Pyridine	N. R.
10	K_2CO_3	45			

Table S3 – NHC Salt



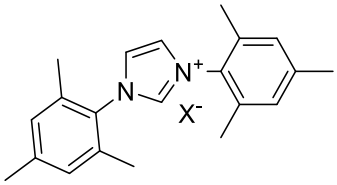
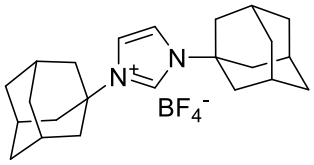
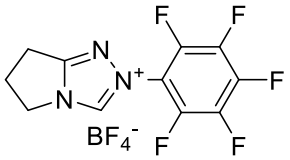
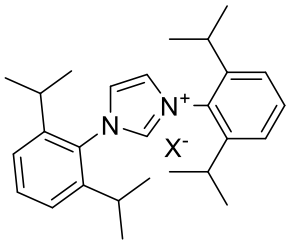
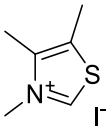
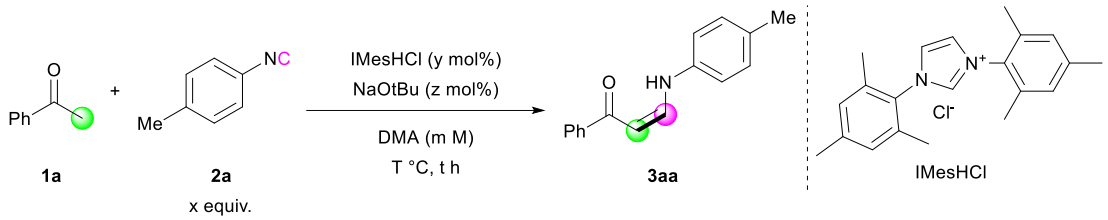
Entry	NHC Salt	X	Yield (%)	Entry	NHC Salt	Yield (%)
1		**Cl**	**45**	7		N. R.
2		BF_4	42			
3		PF_6	32	8		N. R.
4		Cl	N. R.			
5		BF_4	N. R.	9		N. R.
6		PF_6	N. R.			

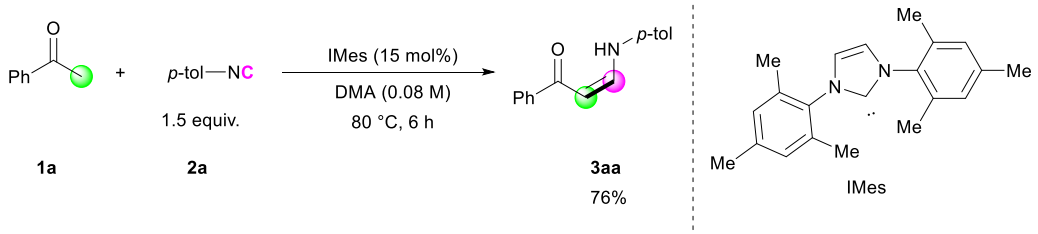
Table S4 – Equivalence & Time & Temperature



Entry	x	y	z	m	T	t	Yield **3aa** (%)
1	1.0	20	30	0.25	50	24	46
2	1.5	20	30	0.25	50	24	58
3	2.0	20	30	0.25	50	24	54
4	1.0	20	25	0.25	50	24	47
5	1.0	20	20	0.25	50	24	48
6	1.0	15	20	0.25	50	24	50
7	1.0	10	20	0.25	50	24	42
8	1.5	15	20	0.25	50	48	64
9	1.5	15	20	0.25	80	48	81
10	1.5	15	20	0.125	80	48	87
11	1.5	15	20	0.125	80	24	92
12	1.5	15	20	0.125	80	12	94
13	1.5	15	20	0.125	80	6	91
14	1.5	15	20	0.125	80	3	74
15	**1.5**	**15**	**20**	**0.083**	**80**	**6**	**93**

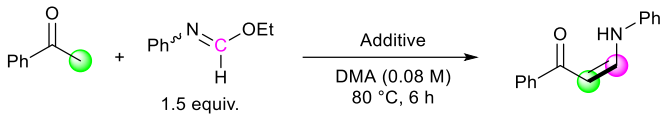
5. Experimental Procedures for the Control Experiments

Scheme S2. Reaction between **1a** and **2a** with IMes



IMes (9.1mg, 0.03 mmol) was charged in a 4 mL vial under argon atmosphere. The vial was then sealed with a Teflon-lined septum, and **1a** (23.4 µl, 0.2 mmol), **2a** (48 µl, 0.3 mmol), and DMA (2.4 mL) were added via syringe. The solution was stirred for 6 h at 80 ℃. After cooling to room temperature, the volatiles were removed in vacuo and the remaining residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate with 3% NEt_3) to afford the corresponding enaminone **3aa** in 76% yields.

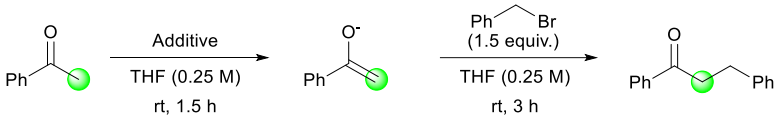
Scheme S3. Reaction between **1a** and **2b'**



1a **2b'** **3ab**

Additive (0.04 or 0.2 mmol) was charged in a 4 mL vial under argon atmosphere. The vial was then sealed with a Teflon-lined septum, and **1a** (23.4 µl, 0.2 mmol), **2b'** (44.5 µl, 0.3 mmol), and DMA (2.4 mL) were added via syringe. The solution was stirred for 6 h at 80 ℃. After cooling to room temperature, the volatiles were removed in vacuo and the remaining residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate with 3% NEt_3) to afford the corresponding enaminone **3ab**.

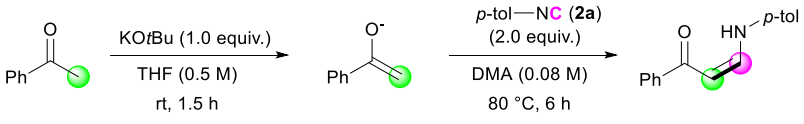
Scheme S4. Direct alkylation reaction with in-situ generated enolate anion



1a **1a'** **4**

Additive (0.5 mmol) and THF (2 mL) were charged in a 10 mL Schlenk tube under argon atmosphere, and the tube was then sealed with rubber septum. **1a** (58.3 µL, 0.5 mmol) was slowly added to the solution under argon flow at room temperature, and the solution was further stirred for 1.5 h at room temperature. Benzyl bromide (71.4 µL, 0.6 mmol) was added in the reaction mixture under argon flow, and the solution was further stirred for 3 h at room temperature. After the reaction was finished, the reaction mixture was diluted with ethyl acetate (10 mL), washed with aqueous sat. $NaHCO_3$ solution (10 mL) and brine (10 mL), dried with $MgSO_4$, and concentrated in vacuo. The crude mixture was analysed by ^{1}H-NMR using nitromethane as an internal standard.

Scheme S5. Reaction of **2a** with in-situ generated enolate anion

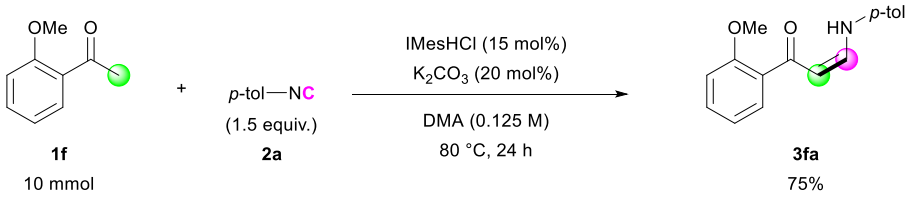


1a **1a'** **3aa**
55%

KO*t*Bu (56 mg, 0.5 mmol) and THF (1 mL) were charged in a 25 mL Schlenk tube under Ar atmosphere, and the tube was then sealed with rubber septum. **1a** (58.3 µL, 0.5 mmol) was slowly added to the solution under argon flow at room temperature, and the solution was further stirred for 1.5 h at room temperature. After removing all volatiles via manifold vacuum (white solid **1a'** was observed), **2b** (120 µL, 1.0 mmol), and DMA (6 mL) were added in the tube under argon flow. The solution was stirred for 6 h at 80 ℃. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 ml), washed with aqueous sat. $NaHCO_3$ solution (20 mL x 2) and brine (20 mL), dried with $MgSO_4$, and concentrated in vacuo. The crude mixture was purified by flash column chromatography (silica gel, hexane/ethyl acetate with 3% NEt_3) to afford the corresponding enaminone **3aa** in 55% yields.

6. Experimental Procedure for the Gram-Scale Reaction

Scheme S6. Gram-Scale Reaction of **1f** with **2a**



IMesHCl (511 mg, 1.5 mmol), K_2CO_3 (276 mg, 2.0 mmol), and DMA (80 mL) were charged in a 250 mL oven-dried round-bottom flask (RBF) under Ar atmosphere, and the flask was then sealed with rubber septum. **1f** (1.38 mL, 10 mmol) and **2a** (1.8 mL, 15 mmol) were added to the solution under argon flow, and the solution was further stirred for 24 h at 80 ℃. After reaction was finished, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (170 mL). The organic solution was washed with aqueous 5% LiCl solution (250 mL x 4) and aqueous sat. NaCl solution (250 mL), dried with $MgSO_4$ and concentrated in vacuo. The residual mixture was further purified by flash column chromatography (silica gel, hexane/ethyl acetate with 3% NEt_3) to afford the corresponding enaminone **3fa** in 75% yield.

7. Crystallographic Data of 3sa

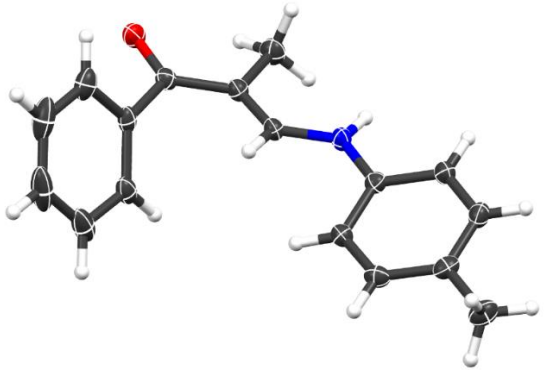


Figure 1. Solid-state structure of **3sa** at 50 % probability ellipsoids.

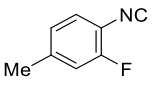
Single crystals of **3sa** were obtained by slow evaporation of sat. DMA solution of **3sa**, and one of them was chosen for the analysis by X-ray diffractometer.

Table S5 – Crystal data and structure refinement for **3sa**.

CCDC number	1503347
Empirical formula	$C_{17}H_{17}ON$
Formula weight	251.31
Temperature/K	101(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.39890(8)
b/Å	11.27072(15)
c/Å	19.0731(3)
α/°	90
β/°	92.0107(13)
γ/°	90
Volume/Å ^{3}	1374.71(3)
Z	4
ρ_{calc}g/cm^3	1.214
μ/mm^{-1}	0.587
F(000)	536.0
Crystal size/mm^3	0.289 × 0.148 × 0.031
Radiation	CuKα (λ = 1.54184)
2Theta range for data collection/°	9.116 to 152.968
Index ranges	$-7 \leq h \leq 5$, $-14 \leq k \leq 14$, $-23 \leq l \leq 23$
Reflections collected	16312
Independent reflections	2863 [R_{int} = 0.0287, R_{sigma} = 0.0191]
Data/restraints/parameters	2863/0/174
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1095
Final R indexes [all data]	R_1 = 0.0441, wR_2 = 0.1128
Largest diff. peak/hole / e.Å $^{-3}$	0.26/-0.27

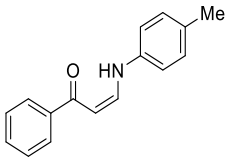
8. Spectroscopic Data

2-fluoro-1-isocyano-4-methylbenzene (**2h**)



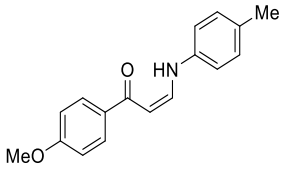
^{1}H NMR (499 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 10.2 Hz, 1H), 6.97 – 6.94 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.38, 157.12 (d, *J* = 255.9 Hz), 142.27 (d, *J* = 7.3 Hz), 127.44, 125.30 (d, *J* = 3.5 Hz), 116.98 (d, *J* = 18.1 Hz), 112.64 (d, *J* = 14.8 Hz), 21.36 (d, *J* = 1.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.26; HRMS-EI (m/z) $[M]^+$ calcd for C_8H_6FN, 135.0484; found: 135.0483.

(*Z*)-1-phenyl-3-(p-tolylamino)prop-2-en-1-one (**3aa**)



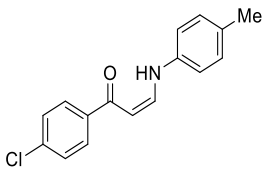
^{1}H NMR (499MHz, $CDCl_3$) δ 12.15 (d, *J* = 11.7 Hz, 1 H), 7.94 (d, *J* = 7.8 Hz, 2 H), 7.44 – 7.52 (m, 4 H), 7.15 (d, *J* = 8.3 Hz, 2 H), 7.02 (d, *J* = 8.3 Hz, 2 H), 6.00 (d, *J* = 7.8 Hz, 1 H), 2.33 (s, 3 H). Identity confirmed by comparing with reported literature.[3]

(*Z*)-1-(4-methoxyphenyl)-3-(p-tolylamino)prop-2-en-1-one (**3ba**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.08 (d, *J* = 11.8 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.45 (dd, *J* = 11.8 Hz, 7.9 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.95 (d, *J* = 7.9 Hz, 1H), 3.86 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.92, 162.50, 144.79, 138.10, 133.24, 132.18, 130.34, 129.38, 116.33, 113.74, 93.06, 55.49, 20.86; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{17}NNaO_2$, 290.1151; found: 290.1150.

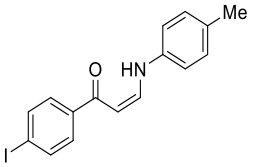
(*Z*)-1-(4-chlorophenyl)-3-(p-tolylamino)prop-2-en-1-one (**3ca**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (d, *J* = 12.3 Hz 1H), 7.87 (d, *J* = 6.7 Hz, 2H), 7.51 (dd, *J* = 11.4 Hz, 7.5 Hz, 1H), 7.42 (d, *J* = 6.7 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 5.95 (d, *J* = 7.5 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.38, 145.84,

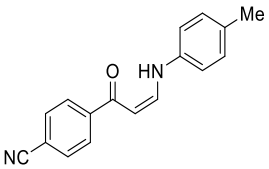
145.82, 137.79, 137.76, 133.85, 130.42, 128.78, 116.62, 93.00, 20.93; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{16}H_{14}ClNNaO$, 294.0656; found: 294.0658.

(*Z*)-1-(4-iodophenyl)-3-(p-tolylamino)prop-2-en-1-one (**3da**)



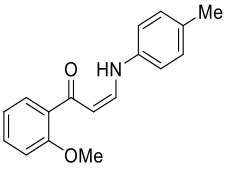
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.15 (d, *J* = 12.0 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 12.5 Hz, 7.7 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 5.93 (d, *J* = 7.7 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.70, 145.88, 138.80, 137.76, 133.88, 130.43, 128.97, 116.64, 98.82, 92.92, 20.92.; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{16}H_{15}INO$, 364.0913; found: 364.0913.

(*Z*)-4-(3-(p-tolylamino)acryloyl)benzonitrile (**3ea**)



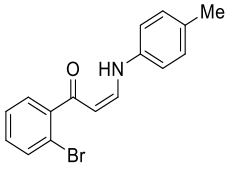
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.24 (d, *J* = 12.2 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.56 (dd, *J* = 12.6 Hz, 7.7 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 5.95 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.35, 146.76, 143.03, 137.39, 134.42, 132.41, 130.48, 127.82, 118.58, 116.87, 114.64, 93.10, 20.94; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{14}N_2NaO$, 285.0998; found: 285.0997.

(*Z*)-1-(2-methoxyphenyl)-3-(p-tolylamino)prop-2-en-1-one (**3fa**)



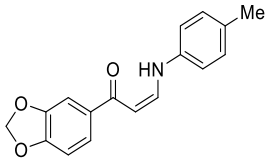
^{1}H NMR (499 MHz, $CDCl_3$) δ 12.05 (d, *J* = 12.6 Hz, 1H), 7.71 (dd, *J* = 7.6 Hz, 1.8 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.05 – 6.96 (m, 4H), 6.01 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.73, 157.67, 144.39, 138.15, 133.30, 131.96, 130.33, 130.19, 120.74, 116.47, 111.67, 98.48, 55.80, 20.87; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{17}NNaO_2$, 290.1151; found: 290.1152.

(*Z*)-1-(2-bromophenyl)-3-(p-tolylamino)prop-2-en-1-one (**3ga**)



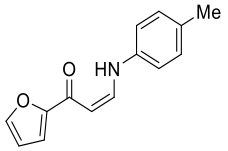
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.92 (d, *J* = 11.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.46 (dd, *J* = 12.5 Hz, 7.7 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 5.63 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.01, 145.51, 142.63, 137.69, 133.98, 133.63, 130.74, 130.41, 129.25, 127.38, 119.50, 116.76, 97.19, 20.92.; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{16}H_{14}BrNNaO$, 338.0151; found: 338.0152.

(*Z*)-1-(benzo[d][1,3]dioxol-5-yl)-3-(p-tolylamino)prop-2-en-1-one (**3ha**)



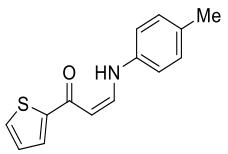
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.04 (d, *J* = 11.7Hz, 1H), 7.52 (d, *J* = 8.2Hz, 1H), 7.49 – 7.41 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H), 5.90 (d, *J* = 7.8 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.41, 150.60, 148.11, 145.00, 138.02, 134.14, 133.40, 130.37, 122.79, 116.42, 108.01, 107.63, 101.71, 93.04, 20.88; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{15}NNaO_3$, 304.0944; found: 304.0943.

(*Z*)-1-(furan-2-yl)-3-(p-tolylamino)prop-2-en-1-one (**3ia**)



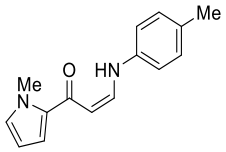
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.91 (d, *J* = 11.6 Hz, 1H), 7.53 (s, 1H), 7.45 (dd, *J* = 12.5, 7.8 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 3.4 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.51 (dd, *J* = 3.3, 1.5 Hz, 1H), 5.90 (d, *J* = 7.8 Hz , 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.96, 153.96, 145.30, 145.02, 137.84, 133.56, 130.36, 116.39, 113.97, 112.22, 112.20, 93.11, 20.88.; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{14}H_{13}NNaO_2$, 250.0838; found: 250.0836.

(*Z*)-1-(thiophen-2-yl)-3-(p-tolylamino)prop-2-en-1-one (**3ja**)



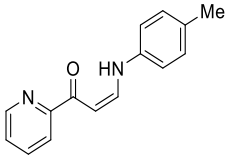
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (d, *J* = 11.6 Hz, 1H), 7.63 (d, *J* = 3.7 Hz, 1H), 7.54 (d, *J* = 4.9 Hz, 1H), 7.44 (dd, *J* = 12.5, 7.7 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.11 (t, *J* = 3.9 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 5.86 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.72, 146.44, 145.01, 137.88, 133.57, 131.46, 130.40, 128.90, 128.12, 116.37, 93.37, 20.89; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{14}H_{13}NNaOS$, 266.0610; found: 266.0610.

(*Z*)-1-(1-methyl-1H-pyrrol-2-yl)-3-(p-tolylamino)prop-2-en-1-one (**3ka**)



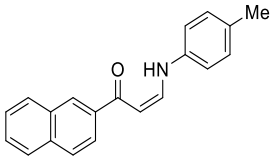
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (d, *J* = 11.9Hz, 1H), 7.29 (dd, *J* = 12.3, 8.1 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.86 - 6.82 (m, 1H), 6.76 (s, 1H), 6.14 - 6.10 (m, 1H), 5.79 (d, *J* = 8.1 Hz, 1H), 4.02 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.62, 142.89, 138.50, 132.54, 132.11, 130.27, 129.76, 116.04, 115.95, 107.76, 95.08, 37.68, 20.83.; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{15}H_{16}N_2NaO$, 263.1155; found: 263.1156.

(*Z*)-1-(pyridin-2-yl)-3-(p-tolylamino)prop-2-en-1-one (**3la**)



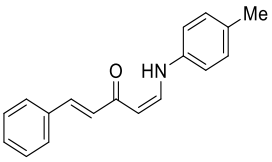
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.16 (d, *J* = 12.0 Hz, 1H), 8.66 (d, *J* = 4.1 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.60 (dd, *J* = 12.3, 7.7 Hz, 1H), 7.39 (dd, *J* = 7.7, 4.8 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.71 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.35, 155.40, 148.82, 146.35, 137.81, 137.04, 133.84, 130.40, 125.83, 121.76, 116.65, 92.93, 20.90.; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{15}H_{14}N_2NaO$, 261.0998; found: 261.0998.

(*Z*)-1-(naphthalen-2-yl)-3-(p-tolylamino)prop-2-en-1-one (**3ma**)



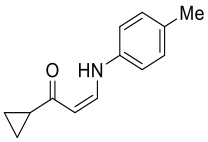
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.23 (d, *J* = 11.9 Hz, 1H), 8.45 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.16 (d, *J* = 7.8 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.74, 145.42, 137.95, 136.75, 135.05, 133.62, 132.95, 130.41, 129.47, 128.31, 128.12, 127.83, 127.72, 126.57, 124.10, 116.55, 93.61, 20.93; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{20}H_{17}NNaO$, 310.1202; found: 310.1204.

(1*E*,4*Z*)-1-phenyl-5-(p-tolylamino)penta-1,4-dien-3-one (**3na**)



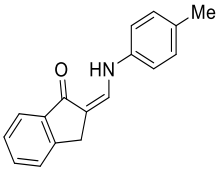
^{1}H NMR (499 MHz, $CDCl_3$) δ 12.18 (d, *J* = 12.3 Hz, 1H), 7.60 – 7.54 (m, 3H), 7.44 – 7.33 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 15.9 Hz, 2H), 5.50 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.07, 145.09, 139.47, 137.92, 135.64, 133.62, 130.40, 129.74, 128.94, 128.17, 127.86, 116.47, 97.83, 20.91;

(*Z*)-1-cyclopropyl-3-(p-tolylamino)prop-2-en-1-one (**3oa**)



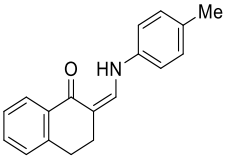
^{1}H NMR (499 MHz, $CDCl_3$) δ 11.56 (d, *J* = 10.9 Hz, 1H), 7.18 (dd, *J* = 12.4, 7.7 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.41 (d, *J* = 7.7 Hz, 1H), 2.29 (s, 3H), 1.83 – 1.78 (m, 1H), 1.05 – 1.02 (m, 2H), 0.85 – 0.81 (m, 2H); 13C NMR (75 MHz, CDCl3) δ 200.48, 142.57, 138.06, 132.86, 130.16, 115.94, 96.65, 20.70, 20.53, 9.89; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{13}H_{15}NNaO$, 224.1046; found: 224.1043.

(*Z*)-2-((p-tolylamino)methylene)-2,3-dihydro-1H-inden-1-one (**3pa**)



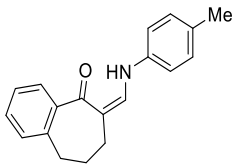
^{1}H NMR (499 MHz, $CDCl_3$) δ 11.35 (d, *J* = 11.3 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 3.66 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.32, 148.75, 141.02, 139.28, 138.16, 132.90, 132.16, 130.39, 127.21, 125.81, 122.94, 115.82, 107.75, 30.89, 20.87; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{15}NNaO$, 272.1046; found: 272.1048.

(*Z*)-2-((p-tolylamino)methylene)-3,4-dihydronaphthalen-1(2H)-one (**3qa**)



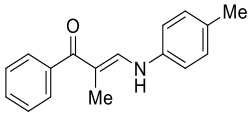
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.97 (d, *J* = 11.4 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.31 (m, 3H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 6.5 Hz, 2H), 2.68 (t, *J* = 6.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.55, 142.37, 142.08, 138.33, 135.32, 132.78, 131.90, 130.35, 127.98, 126.94, 126.67, 116.10, 104.83, 29.99, 27.86, 20.89.; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{18}H_{17}NNaO$, 286.1202; found: 286.1201.

(*Z*)-6-((p-tolylamino)methylene)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (**3ra**)



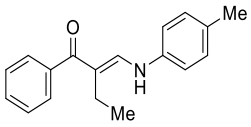
^{1}H NMR (499 MHz, $CDCl_3$) δ 12.01 (d, *J* = 11.6 Hz, 1H), 7.61 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.28 (d, *J* = 12.2 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 2.18 (t, *J* = 6.8 Hz, 2H), 1.95 (quint, *J* = 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.10, 143.03, 141.71, 138.93, 138.25, 132.84, 130.69, 130.31, 128.58, 127.49, 126.75, 116.15, 107.64, 31.01, 30.64, 28.11, 20.83; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO$, 300.1359; found: 300.1360.

(*E*)-2-methyl-1-phenyl-3-(p-tolylamino)prop-2-en-1-one (**3sa**)



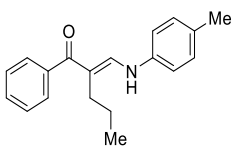
^{1}H NMR (499 MHz, DMSO-d_6) δ 8.96 (d, *J* = 13.1 Hz, 1H), 7.52 – 7.42 (m, 5H), 7.40 (d, *J* = 13.1 Hz, 1H), 7.06 (d, *J* = 8.3, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 2.20 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 194.83, 145.59, 141.37, 139.72, 131.58, 130.37, 130.10, 128.52, 116.26, 109.97, 20.67, 10.34; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{17}NNaO$, 274.1202; found: 274.1200.

(*E*)-1-phenyl-2-((p-tolylamino)methylene)butan-1-one (**3ta**)



^{1}H NMR (499 MHz, DMSO-d_6) δ 9.01 (d, *J* = 13.2 Hz, 1H), 7.50 – 7.40 (m, 5H), 7.32 (d, *J* = 13.2 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 2.48 (t, *J* = 7.3 Hz, 2H), 2.19 (s, 3H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 194.21, 144.40, 141.03, 139.29, 131.04, 129.88, 129.62, 128.04, 116.05, 115.80, 20.22, 16.75, 13.14; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{18}H_{19}NNaO$, 288.1359; found: 288.1358.

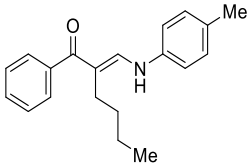
(*E*)-1-phenyl-2-((p-tolylamino)methylene)pentan-1-one (**3ua**)



^{1}H NMR (499 MHz, DMSO-d_6) δ 8.96 (d, *J* = 13.3 Hz, 1H), 7.50 – 7.42 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 2.46 (t, *J* = 7.3 Hz, 2H), 2.19 (s, 3H), 1.49 – 1.41 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H);

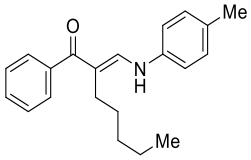
^{13}C NMR (75 MHz, DMSO-d_6) δ 194.52, 144.98, 141.10, 139.32, 131.07, 129.89, 129.62, 128.04, 115.87, 114.49, 25.16, 21.18, 20.19, 13.88.; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{21}NNaO$, 302.1515; found: 302.1517.

(*E*)-1-phenyl-2-((p-tolylamino)methylene)hexan-1-one (**3va**)



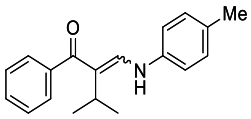
^{1}H NMR (499 MHz, DMSO-d_6) δ 8.94 (d, *J* = 13.2 Hz, 1H), 7.51 – 7.40 (m, 5H), 7.33 (d, *J* = 13.2 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 2.19 (s, 3H), 1.47 – 1.31 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 194.46, 144.79, 141.10, 139.33, 131.02, 129.86, 129.60, 128.04, 128.01, 115.85, 114.75, 30.39, 23.12, 22.23, 20.17, 14.14; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{20}H_{23}NNaO$, 316.1672; found: 316.1670.

(*E*)-1-phenyl-2-((p-tolylamino)methylene)heptan-1-one (**3wa**)



^{1}H NMR (499 MHz, DMSO-d_6) δ 8.94 (d, *J* = 13.2 Hz, 1H), 7.50 – 7.39 (m, 5H), 7.32 (d, *J* = 13.2 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.19 (s, 3H), 1.46 – 1.38 (m, 2H), 1.38 – 1.28 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 194.45, 144.76, 141.09, 139.32, 131.02, 129.87, 129.61, 128.02, 115.84, 114.77, 31.34, 27.77, 23.30, 22.27, 20.17, 14.06; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{21}H_{25}NNaO$, 330.1828; found: 330.1827.

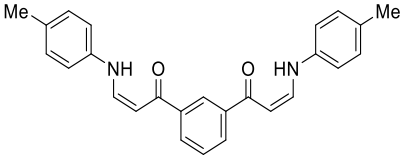
3-methyl-1-phenyl-2-((p-tolylamino)methylene)butan-1-one (**3xa**)



^{1}H NMR (499 MHz, DMSO-d_6) (*E*)-form (major): δ 8.91 (d, *J* = 13.2 Hz, 1H), 7.51 – 7.41 (m, 5H), 7.16 (d, *J* = 13.2 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 3.19 – 3.05 (m, 1H), 2.18 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H), (*Z*)-form (minor): δ 12.14 (d, *J* = 12.1 Hz, 1H), 7.68 (d, *J* = 12.1 Hz, 1H), 7.51 – 7.41 (m, 5H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.71 – 2.64 (m, 1H), 2.27 (s, 3H), 1.08 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 195.05, 143.97,

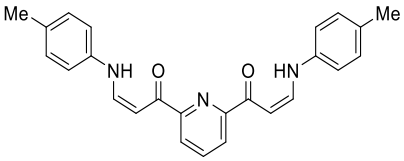
141.66, 139.44, 130.84, 129.85, 129.75, 128.21, 127.98, 118.84, 115.65, 25.10, 20.31, 20.20; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{21}NNaO$, 302.1515; found: 302.1515.

(2*Z*,2'*Z*)-1,1'-(1,3-phenylene)bis(3-(p-tolylamino)prop-2-en-1-one) (**3ya**)



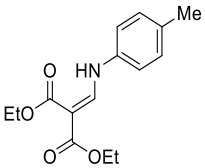
^{1}H NMR (499 MHz, $CDCl_3$) δ 12.18 (d, *J* = 12.4 Hz, 2H), 8.48 (t, *J* = 1.6 Hz, 1H), 8.07 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 12.4, 7.7 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 4H), 7.03 (d, *J* = 8.4 Hz, 4H), 6.07 (d, *J* = 7.8 Hz, 2H), 2.33 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.20, 145.78, 139.60, 137.86, 133.78, 130.42, 130.27, 128.80, 126.25, 116.63, 93.38, 20.91.; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{26}H_{24}N_2NaO_2$, 419.1730; found: 419.1732.

(2*Z*,2'*Z*)-1,1'-(pyridine-2,6-diyl)bis(3-(p-tolylamino)prop-2-en-1-one) (**3za**)



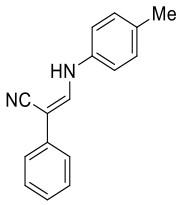
^{1}H NMR (499 MHz, $CDCl_3$) δ 12.18 (d, *J* = 12.4 Hz, 2H), 8.24 (d, *J* = 7.7 Hz, 2H), 7.98 (t, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 12.4, 7.7 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 4H), 7.05 (d, *J* = 8.0 Hz, 4H), 6.87 (d, *J* = 7.7 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.01, 154.27, 146.36, 137.97, 137.85, 133.93, 130.45, 123.60, 116.70, 93.00, 20.93; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{25}H_{23}N_3NaO_2$, 420.1682; found: 420.1684.

Diethyl 2-((p-tolylamino)methylene)malonate (**3Aa**)



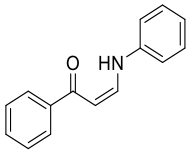
^{1}H NMR (499 MHz, $CDCl_3$) δ 10.97 (d, *J* = 13.7 Hz, 1H), 8.50 (d, *J* = 13.8 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). Identity confirmed by comparing with reported literature.[4]

(*Z*)-2-phenyl-3-(p-tolylamino)acrylonitrile (**3Ba**)



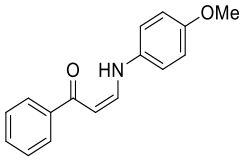
^{1}H NMR (499 MHz, DMSO) δ 9.61 (d, *J* = 12.9 Hz, 1H), 8.05 (d, *J* = 12.9 Hz, 1H), 7.50 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.25 (s, 3H). Identity confirmed by comparing with reported literature.[5]

(*Z*)-1-phenyl-3-(phenylamino)prop-2-en-1-one (**3ab**)



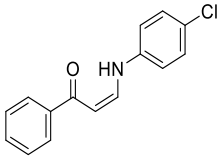
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.15 (d, *J* = 10.8 Hz, 1H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.56 – 7.44 (m, 4H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.04 (d, *J* = 7.8 Hz, 1H). Identity confirmed by comparing with reported literature.[6]

(*Z*)-3-((4-methoxyphenyl)amino)-1-phenylprop-2-en-1-one (**3ac**)



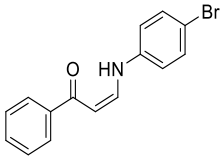
^{1}H NMR (499 MHz, $CDCl_3$) δ 12.20 (d, *J* = 11.9 Hz, 1H), 7.95 - 7.91 (m, 2H), 7.52 – 7.39 (m, 4H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.97 (d, *J* = 7.7 Hz, 1H), 3.79 (s, 3H). Identity confirmed by comparing with reported literature.[7]

(*Z*)-3-((4-chlorophenyl)amino)-1-phenylprop-2-en-1-one (**3ad**)



^{1}H NMR (499 MHz, $CDCl_3$) δ 12.14 (d, *J* = 11.6 Hz, 1H), 7.93 (d, *J* = 7.0 Hz, 2H), 7.54 – 7.42 (m, 4H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.05 (d, *J* = 7.9 Hz, 1H). Identity confirmed by comparing with reported literature.[7]

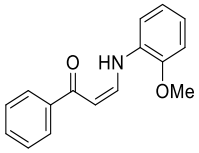
(*Z*)-3-((4-bromophenyl)amino)-1-phenylprop-2-en-1-one (**3ae**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.13 (d, *J* = 11.5 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.40 (m, 6H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.06 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.42, 144.47, 139.54, 139.11,

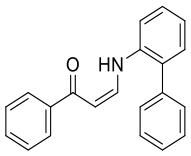
132.84, 131.92, 128.63, 127.48, 117.94, 116.25, 94.46; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{15}H_{12}BrNNaO$, 323.9994; found: 323.9991.

(*Z*)-3-((2-methoxyphenyl)amino)-1-phenylprop-2-en-1-one (**3af**)



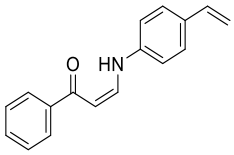
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.22 (d, *J* = 11.4 Hz, 1H), 7.97 (d, *J* = 7.1 Hz, 2H), 7.54 (dd, *J* = 12.7, 7.9 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.94 (dd, *J* = 12.9, 7.8 Hz, 2H), 6.06 (d, *J* = 7.8 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.82, 148.57, 143.70 (d, *J* = 3.8 Hz), 139.52, 131.47, 129.88, 128.43, 127.45, 123.59, 121.14, 113.32, 111.20, 94.19 (d, *J* = 3.8 Hz), 56.00 (d, *J* = 4.9 Hz**)**; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{16}H_{15}NNaO_2$, 276.0995; found: 276.0996.

(*Z*)-3-([1,1'-biphenyl]-2-ylamino)-1-phenylprop-2-en-1-one (**3ag**)



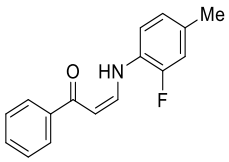
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (d, *J* = 10.9 Hz, 1H), 7.86 (d, *J* = 6.9 Hz, 2H), 7.61 – 7.31 (m, 11H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 5.97 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.64, 144.88, 144.86, 139.39, 138.01, 137.92, 132.18, 131.41, 129.35, 129.16, 128.80, 128.33, 128.13, 127.43, 123.74, 115.32, 94.48; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{21}H_{17}NNaO$, 322.1202; found: 322.1203.

(*Z*)-1-phenyl-3-((4-vinylphenyl)amino)prop-2-en-1-one (**3ah**)



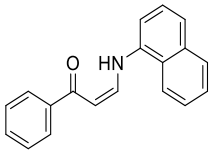
^{1}H NMR (499 MHz, $CDCl_3$) δ 12.19 (d, *J* = 11.9 Hz, 1H), 7.94 (d, *J* = 7.1 Hz, 2H), 7.55 – 7.43 (m, 4H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.04 (d, *J* = 7.8 Hz, 1H), 5.68 (d, *J* = 17.6 Hz, 1H), 5.20 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.12, 144.62 (d, *J* = 3.7 Hz), 139.80, 139.27, 136.02, 133.37, 131.73, 128.57, 127.74, 127.44, 116.40, 113.01, 94.06 (d, *J* = 3.7 Hz); HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{15}NNaO$, 272.1046; found: 272.1048.

(*Z*)-3-((2-fluoro-4-methylphenyl)amino)-1-phenylprop-2-en-1-one (**3ai**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.17 (d, *J* = 11.5 Hz, 1H), 7.95 (d, *J* = 7.1 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.09 (t, *J* = 8.2 Hz, 1H), 6.94 (t, *J* = 11.0 Hz, 1H), 6.93 (s, 1H), 6.07 (d, *J* = 7.8 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.18, 152.40 (d, *J* = 245.7 Hz), 144.61, 139.21, 134.30 (d, *J* = 6.9 Hz), 131.72, 128.53, 127.49, 126.36 (d, *J* = 11.0 Hz), 125.39 (d, *J* = 3.3 Hz), 116.86 (d, *J* = 18.6 Hz), 115.62 (d, *J* = 1.4 Hz), 94.46, 20.89; ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.9; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{16}H_{14}FNNa$, 278.0952; found: 278.0951.

(*Z*)-3-(naphthalen-1-ylamino)-1-phenylprop-2-en-1-one (**3aj**)



^{1}H NMR (499 MHz, $CDCl_3$) δ 13.08 (d, *J* = 11.0 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 6.8 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.74 (dd, *J* = 11.8, 7.7 Hz, 1H), 7.62 (t, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.45 (m, 4H), 7.31 (d, *J* = 7.6 Hz, 1H), 6.18 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.52, 146.32, 146.30, 139.35, 136.58, 134.45, 131.78, 128.61, 127.52, 126.84, 126.77, 125.92, 124.98, 124.29, 121.18, 111.16, 94.82; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{19}H_{15}NNaO$, 296.1046; found: 296.1047.

9. References

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(3) Katritzky, A. R.; Barcock, R. A.; Long, Q.-H.; Balsubramanian, M.; Malhotra, N.; Greenhill, J. V. *Synthesis* **1993**, *1993*, 233.

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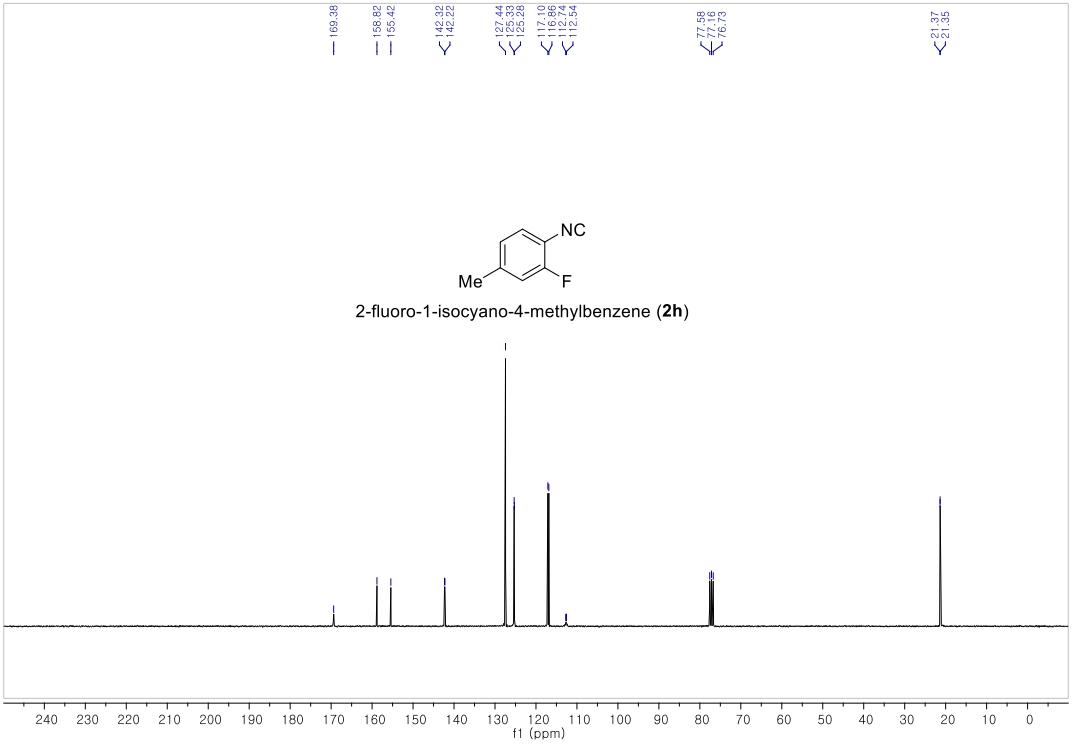
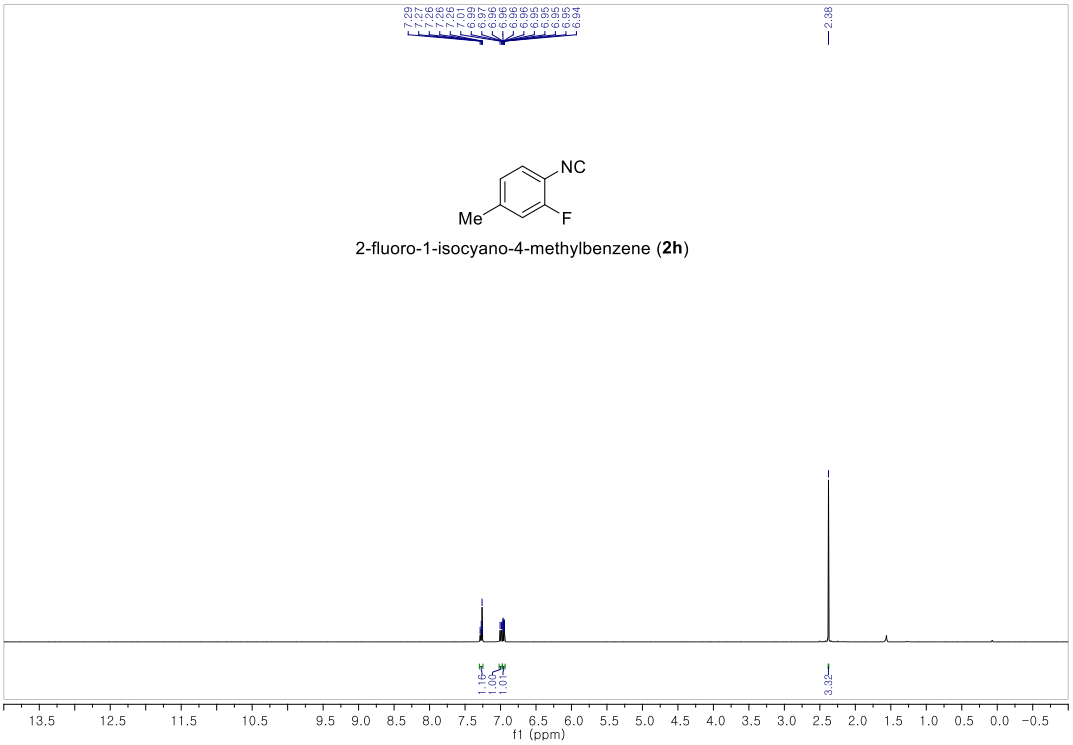
(6) Haak, E. *Eur. J. Org. Chem.* **2007**, *2007*, 2815.

(7) Yang, J.; Wang, C.; Xie, X.; Li, H.; Li, Y. *Eur. J. Org. Chem.* **2010**, *2010*, 4189.

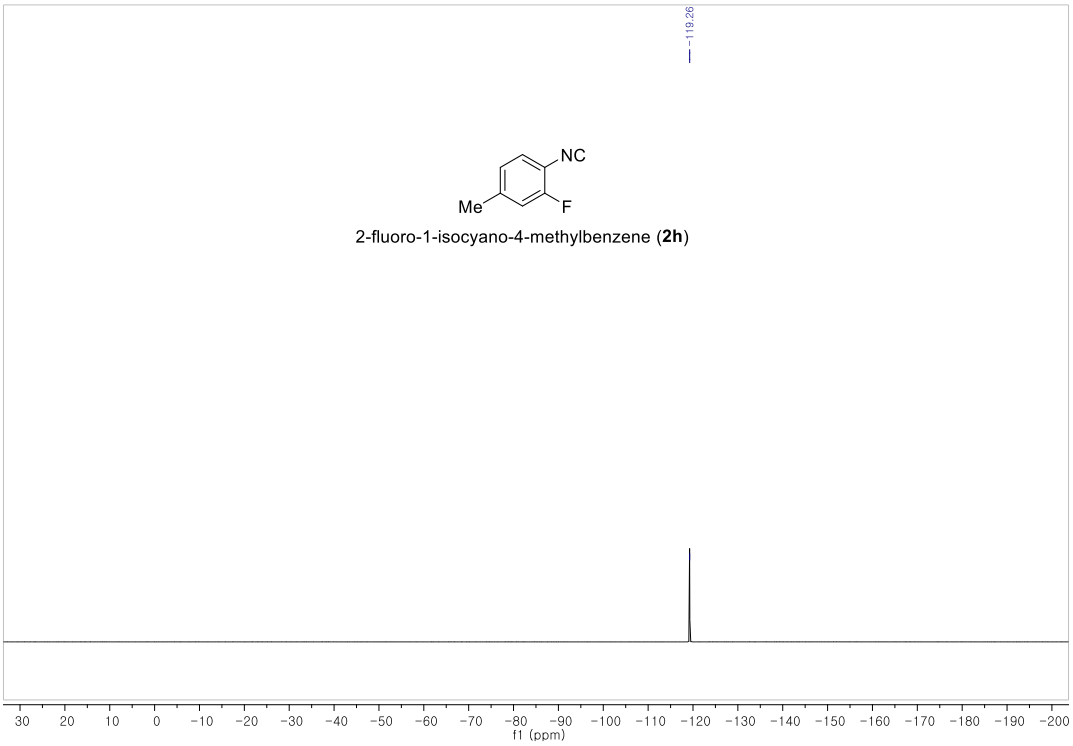
10. NMR Spectra



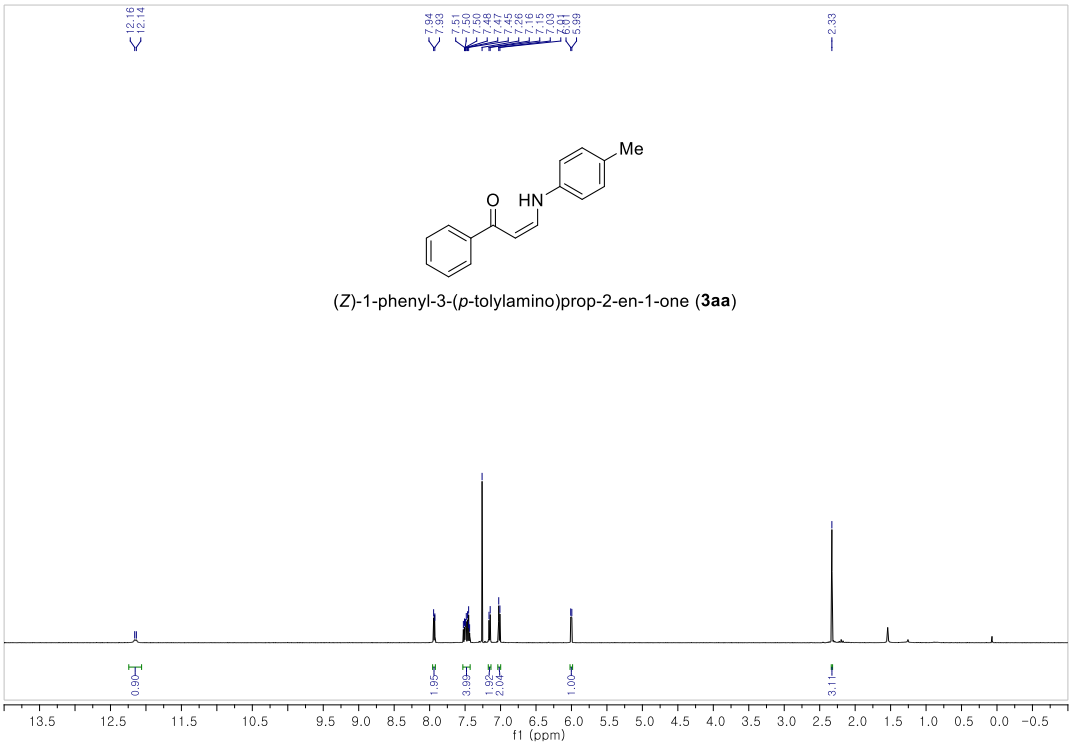
^{1}H NMR ($CDCl_3$, 499 MHz)



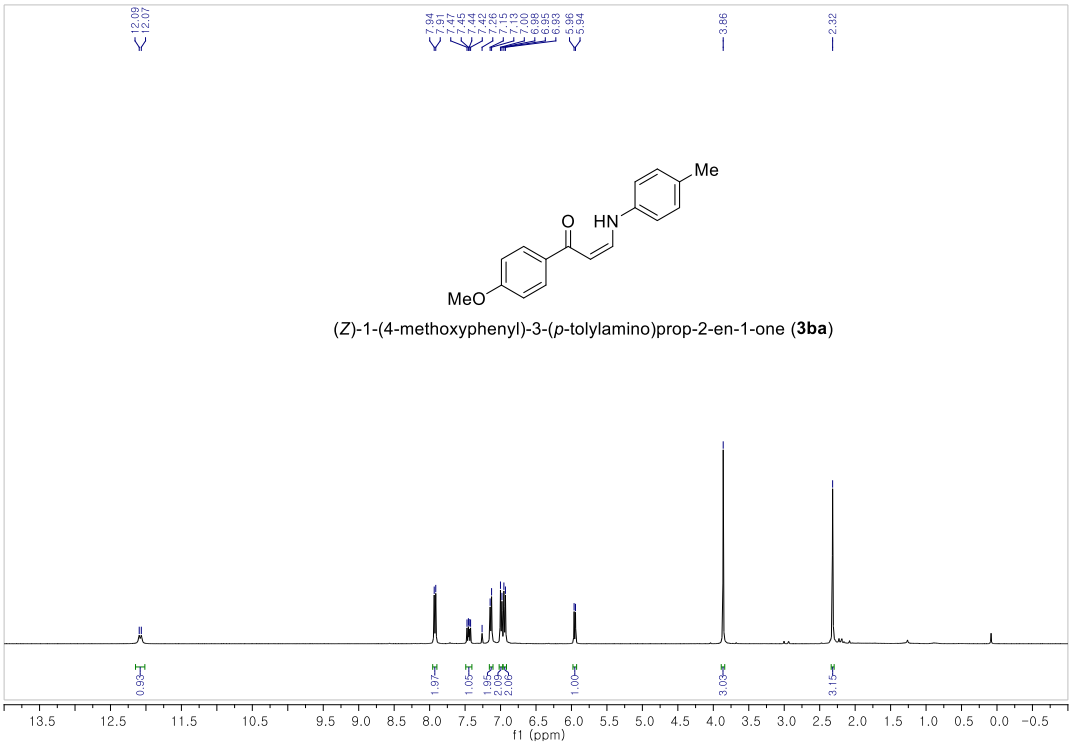
^{13}C NMR ($CDCl_3$, 75 MHz)



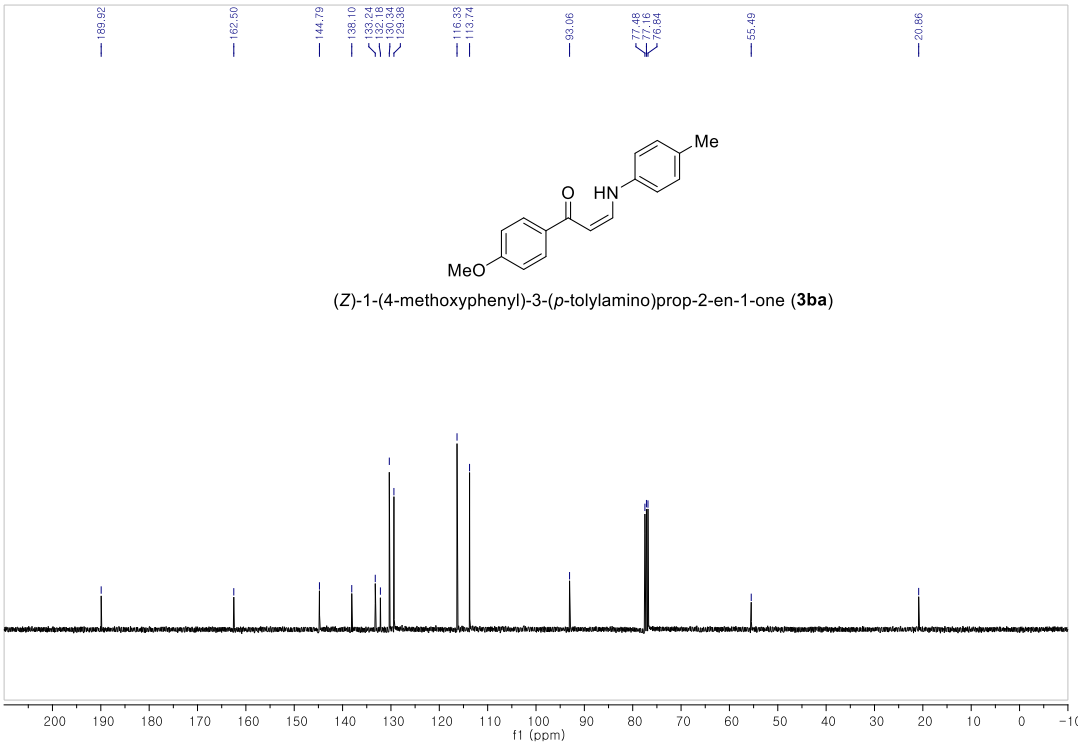
^{19}F NMR ($CDCl_3$, 376 MHz)



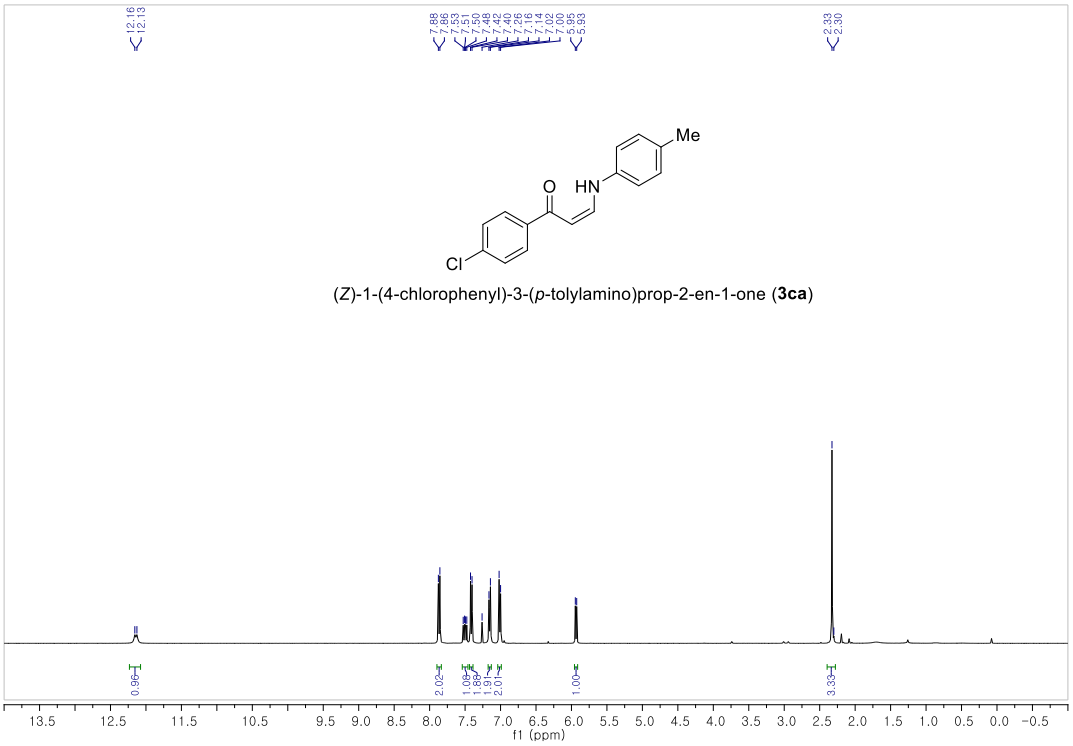
^{1}H NMR ($CDCl_3$, 499 MHz)



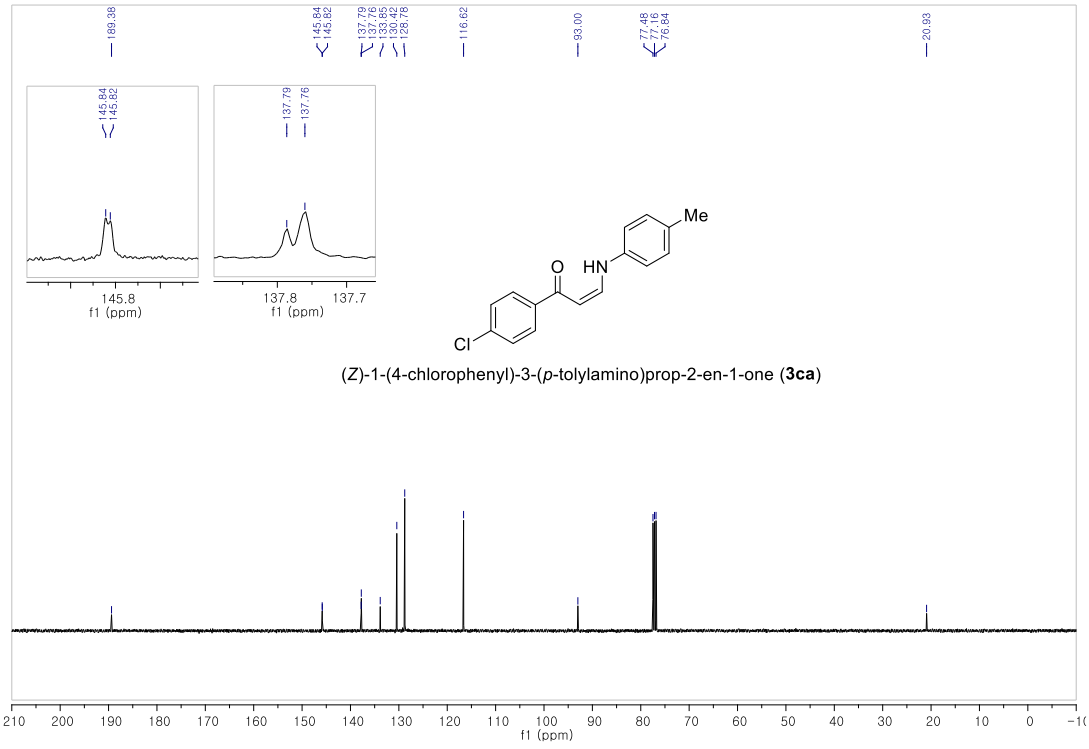
^{1}H NMR ($CDCl_3$, 400 MHz)



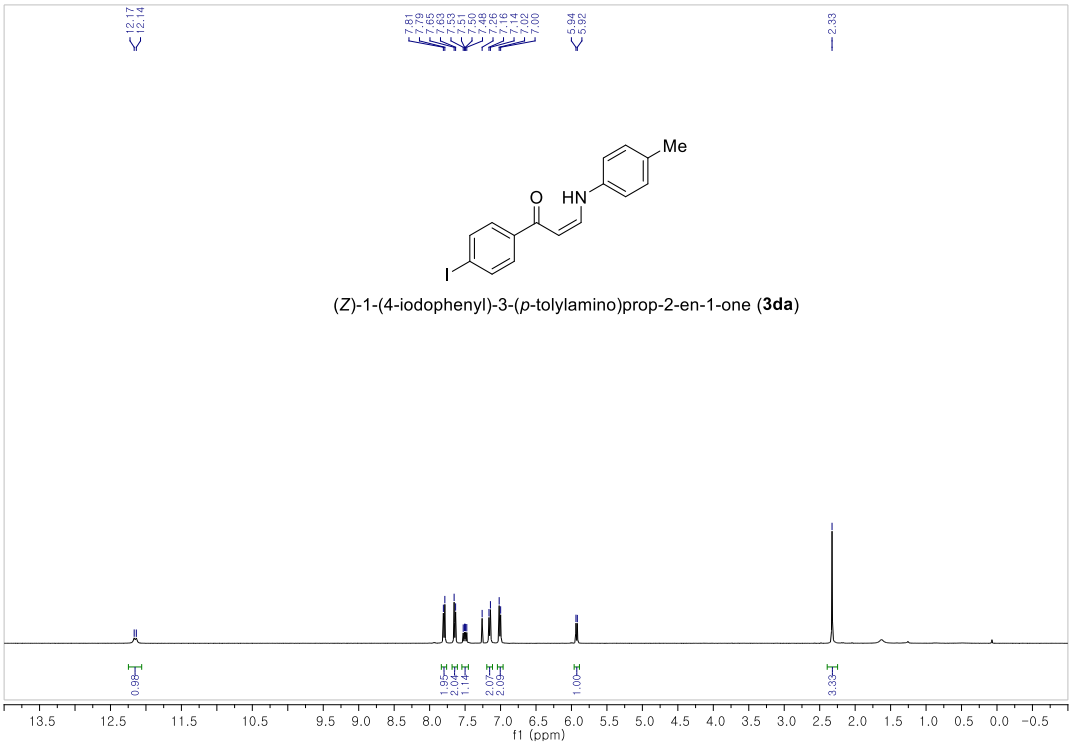
^{13}C NMR ($CDCl_3$, 101 MHz)



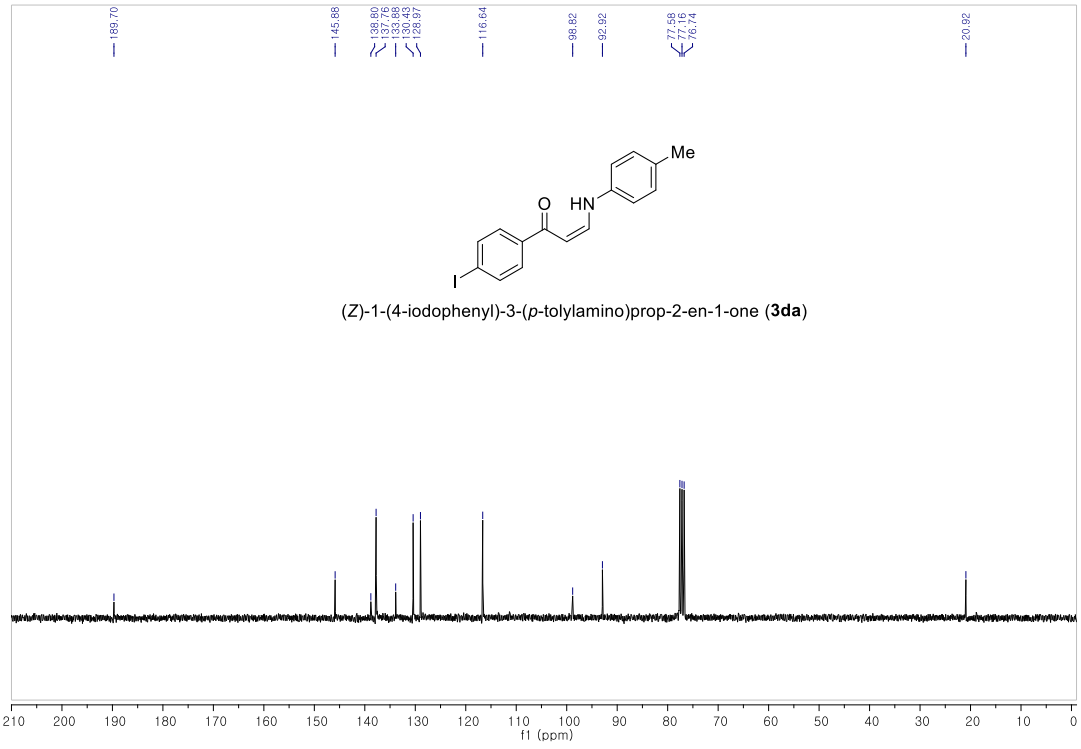
^{1}H NMR ($CDCl_3$, 400 MHz)



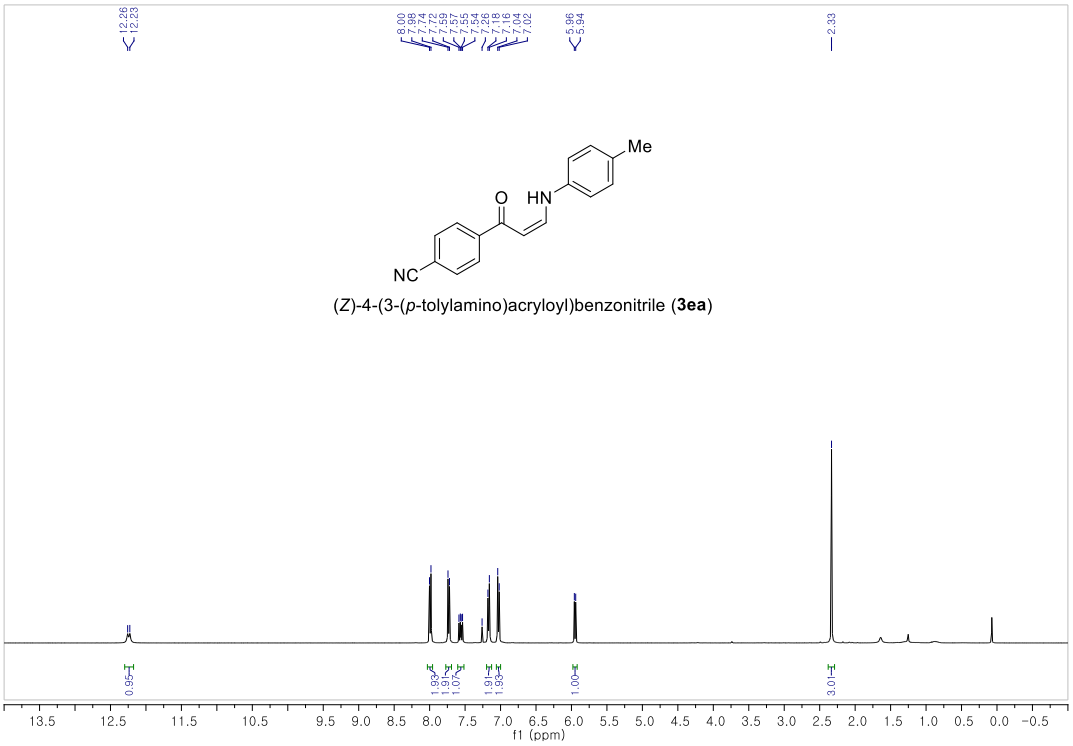
^{13}C NMR ($CDCl_3$, 101 MHz)



^{1}H NMR ($CDCl_3$, 400 MHz)

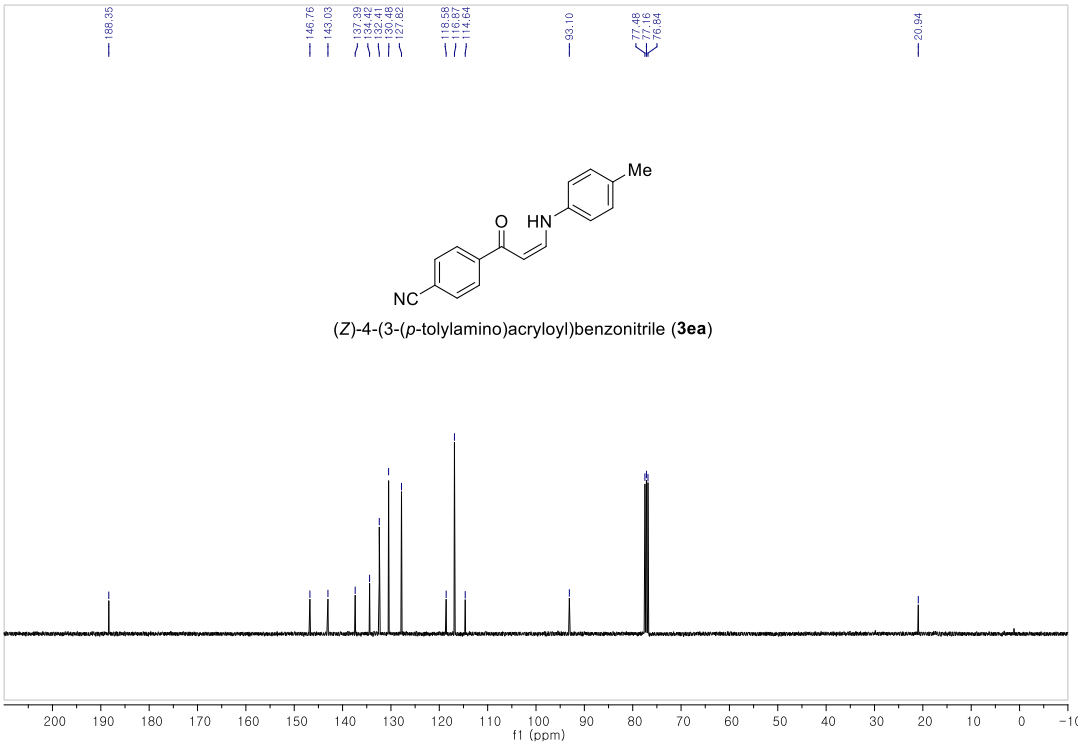


^{13}C NMR ($CDCl_3$, 75 MHz)



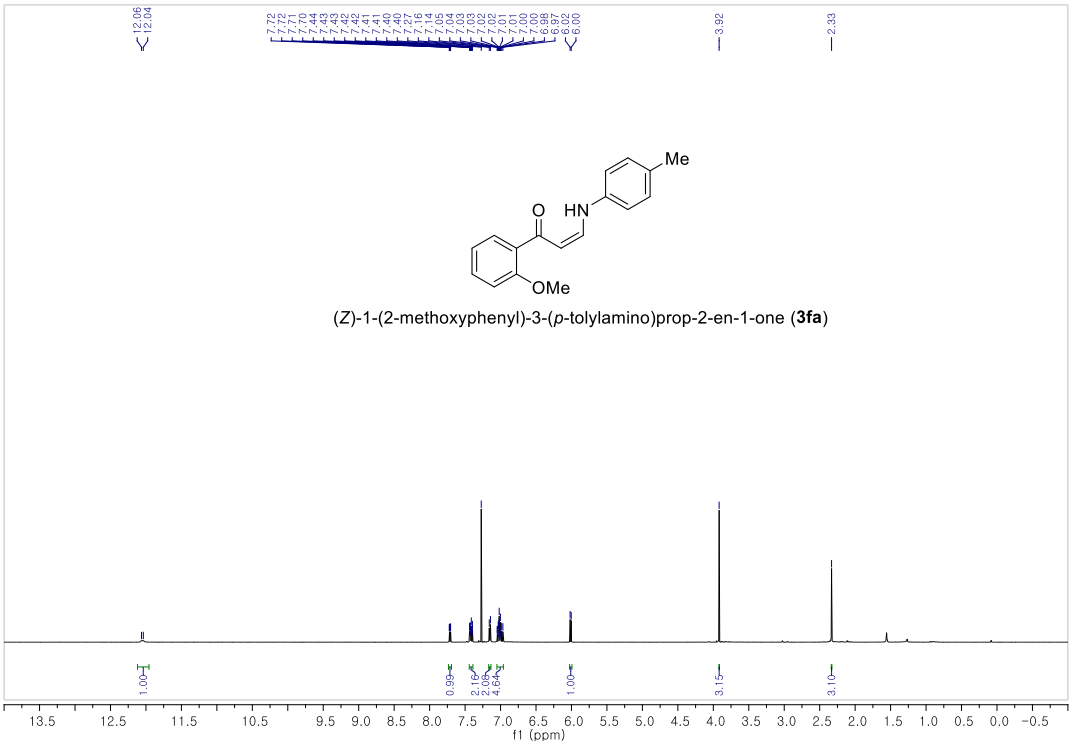
(*Z*)-4-(3-(*p*-tolylamino)acryloyl)benzonitrile (**3ea**)

^{1}H NMR ($CDCl_3$, 400 MHz)

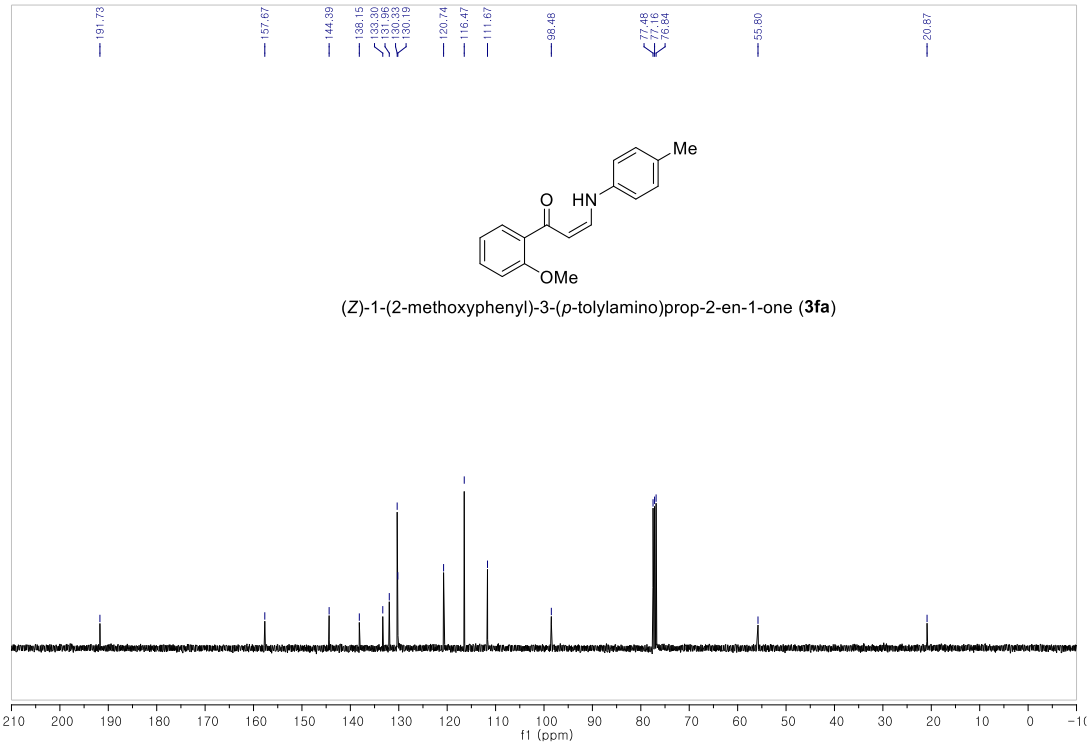


(*Z*)-4-(3-(*p*-tolylamino)acryloyl)benzonitrile (**3ea**)

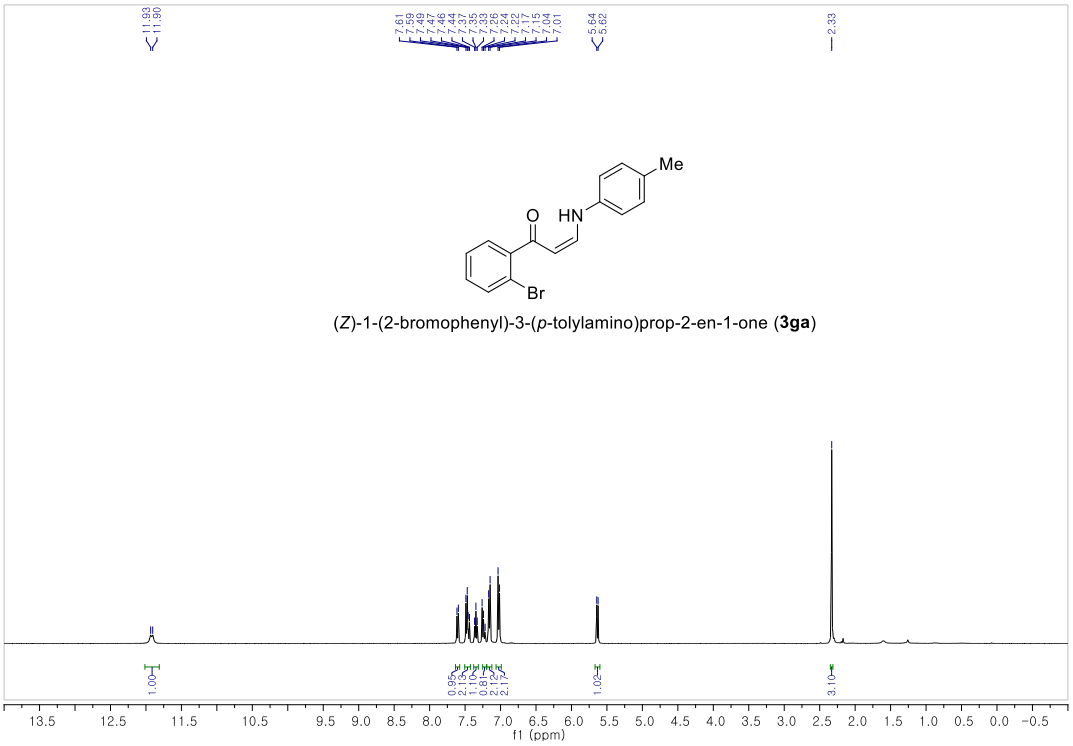
^{13}C NMR ($CDCl_3$, 101 MHz)



^{1}H NMR ($CDCl_3$, 400 MHz)

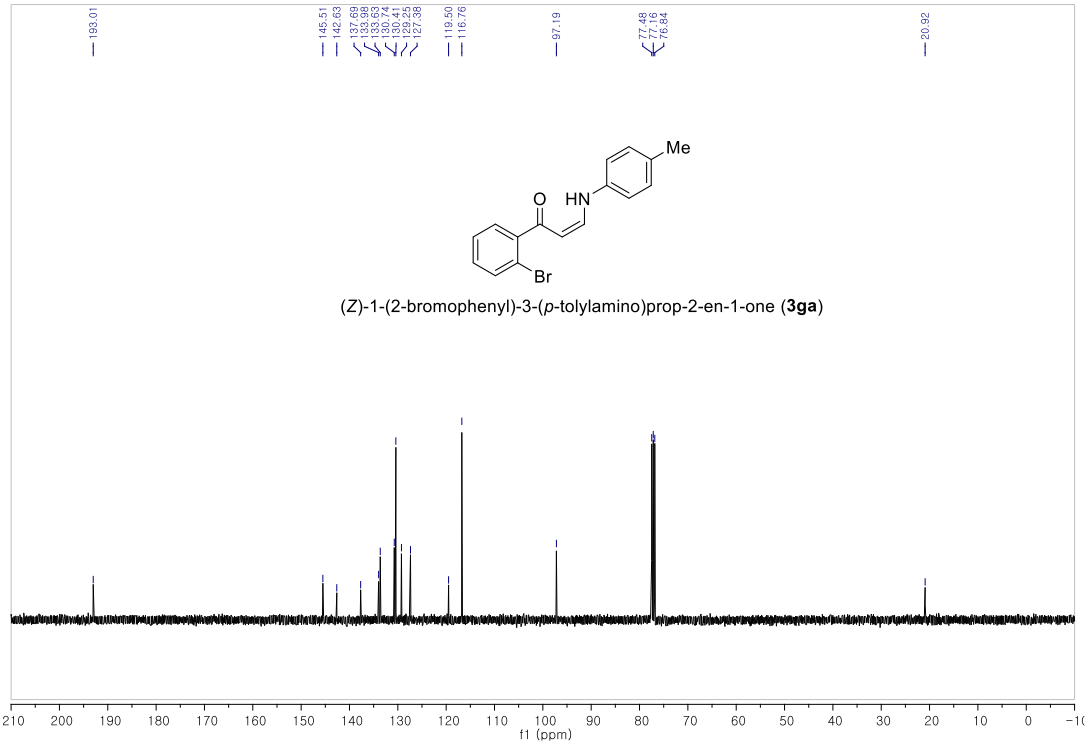


^{13}C NMR ($CDCl_3$, 101 MHz)



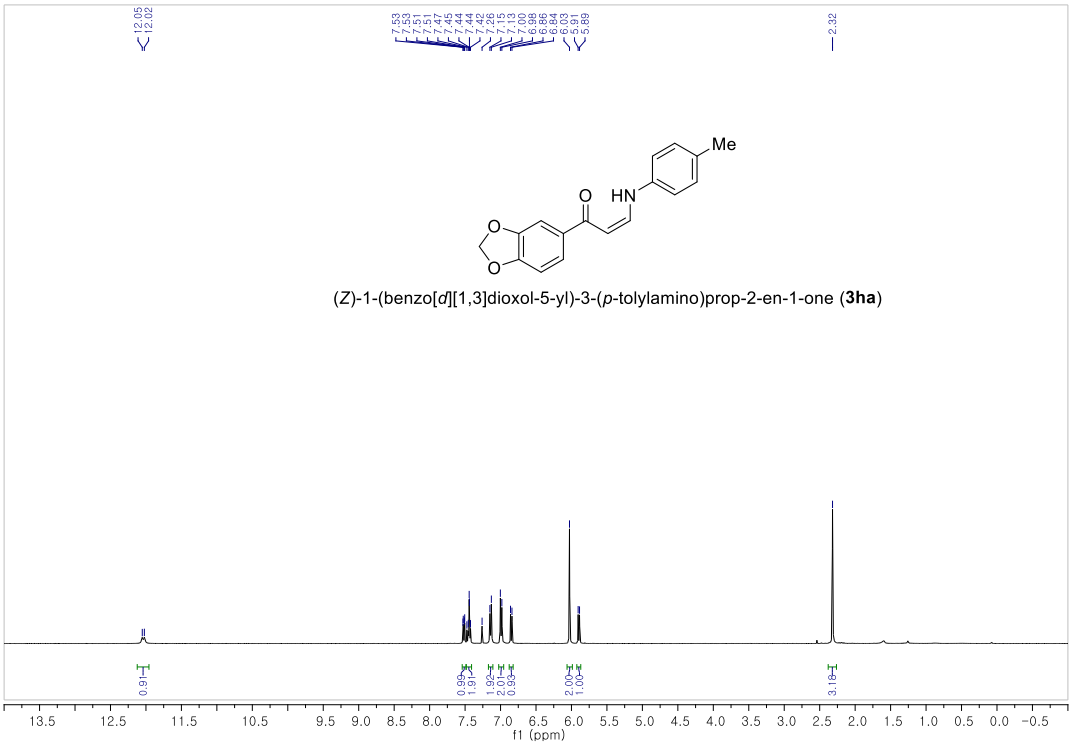
(*Z*)-1-(2-bromophenyl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ga**)

^{1}H NMR ($CDCl_3$, 400 MHz)



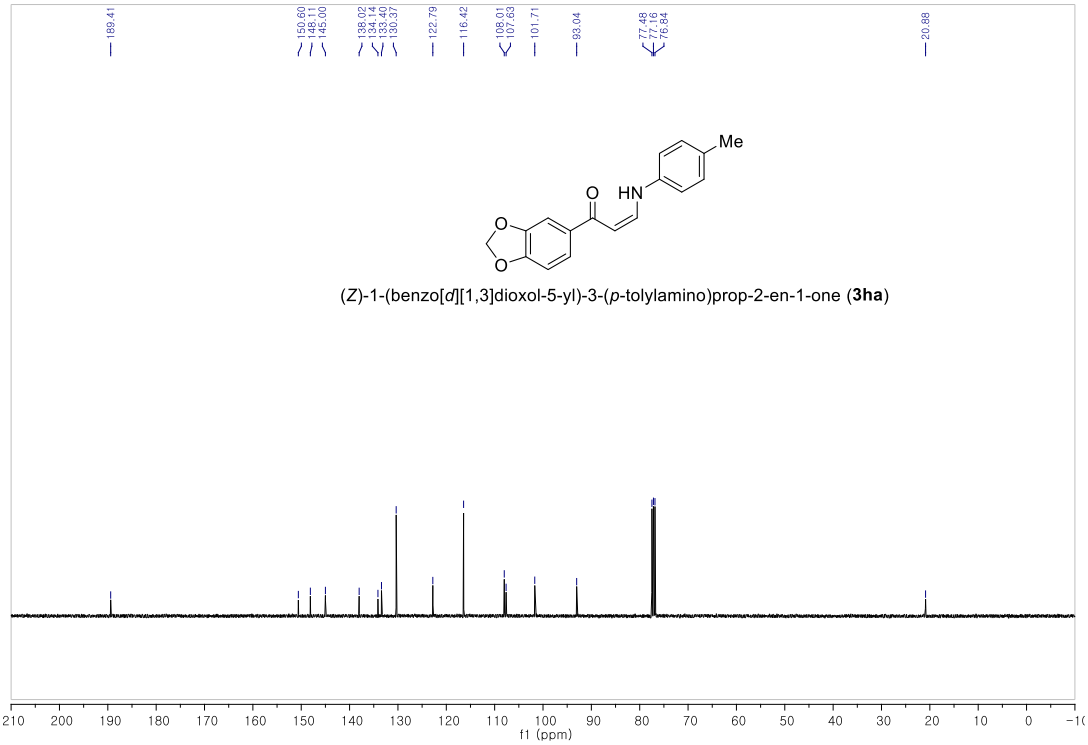
(*Z*)-1-(2-bromophenyl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ga**)

^{13}C NMR ($CDCl_3$, 101 MHz)



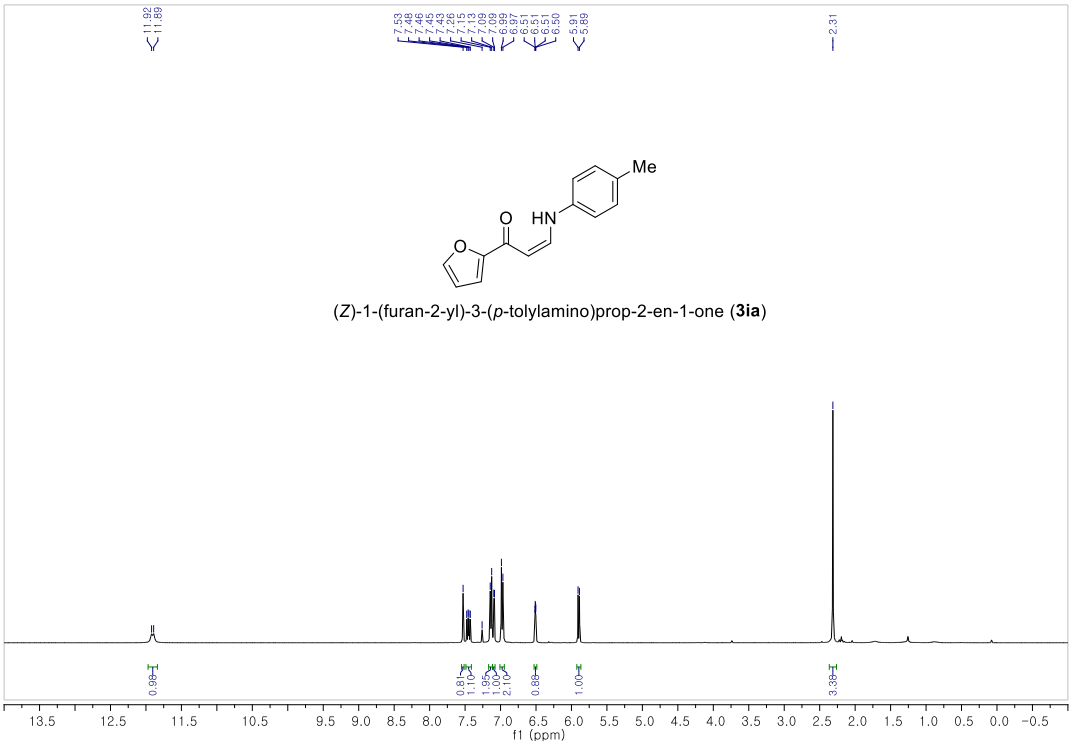
(*Z*)-1-(benzo[*d*][1,3]dioxol-5-yl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ha**)

^{1}H NMR ($CDCl_3$, 400 MHz)



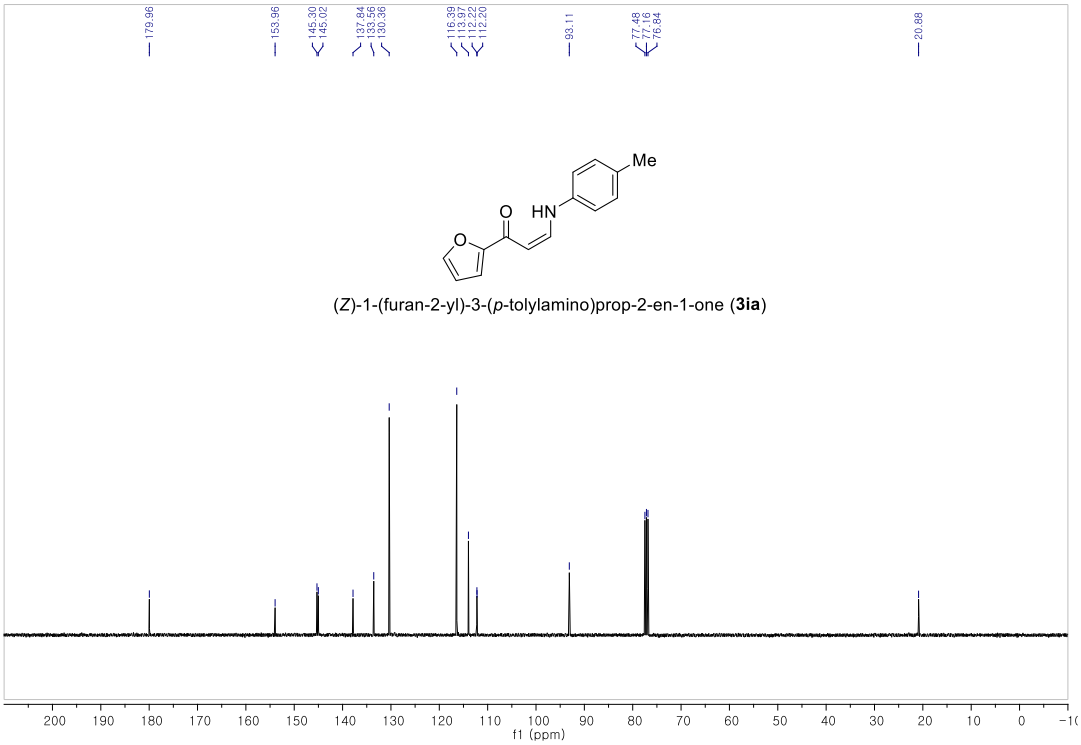
(*Z*)-1-(benzo[*d*][1,3]dioxol-5-yl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ha**)

^{13}C NMR ($CDCl_3$, 101 MHz)



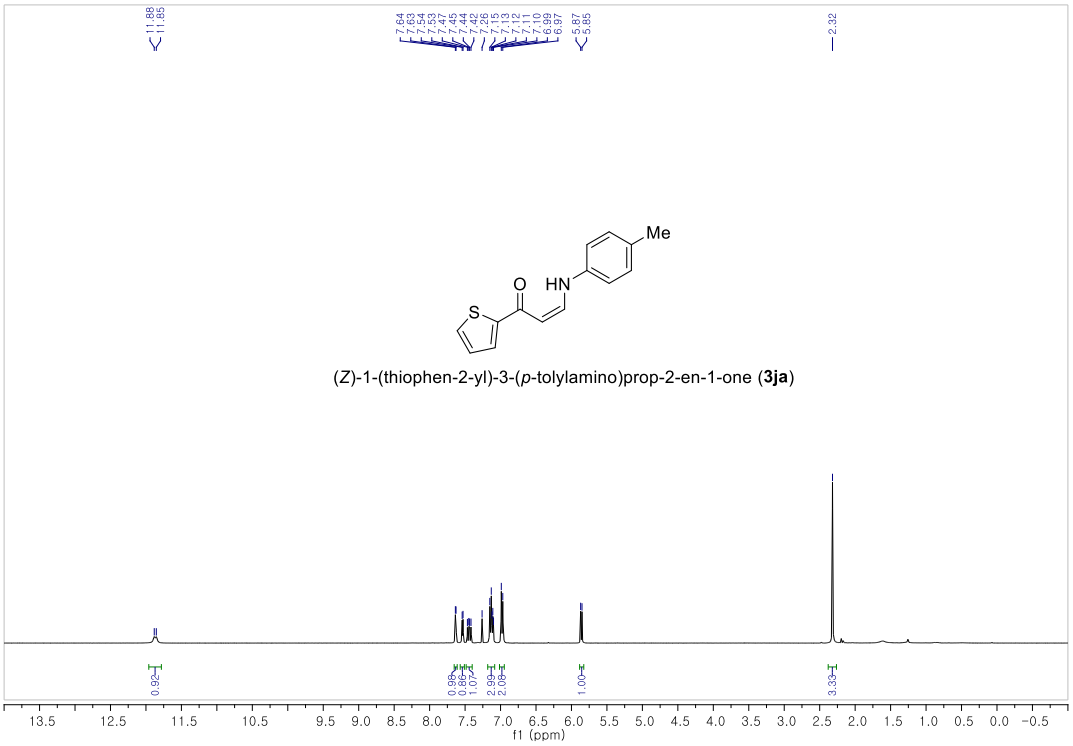
(*Z*)-1-(furan-2-yl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ia**)

^{1}H NMR ($CDCl_3$, 400 MHz)



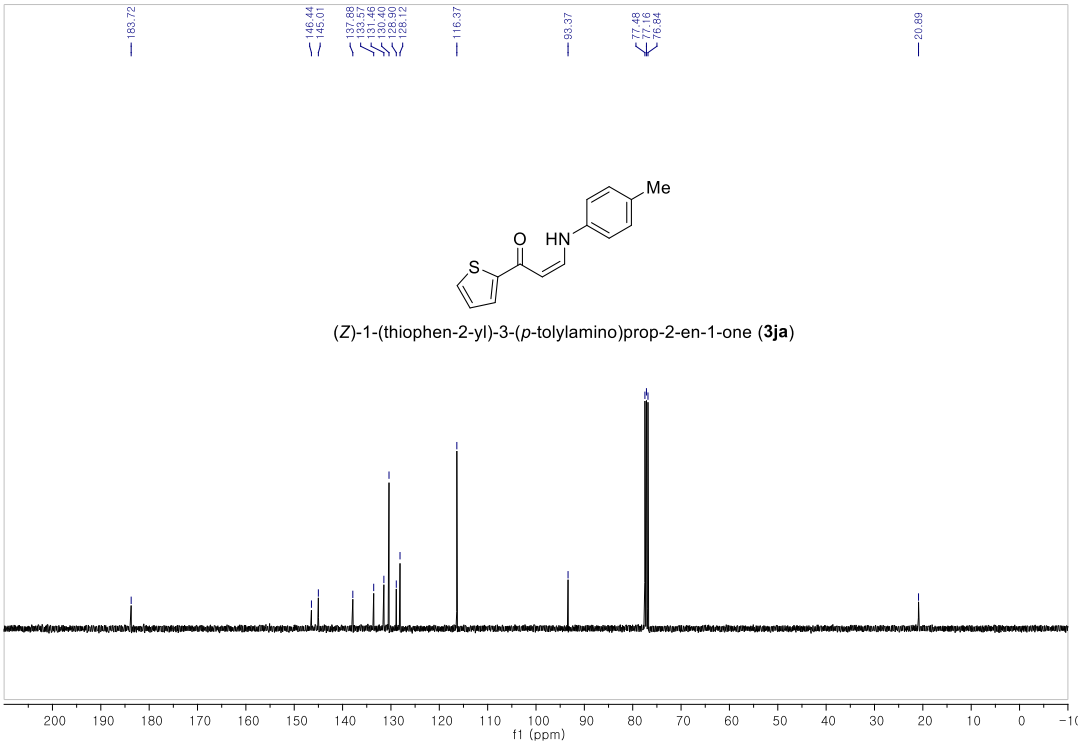
(*Z*)-1-(furan-2-yl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ia**)

^{13}C NMR ($CDCl_3$, 101 MHz)



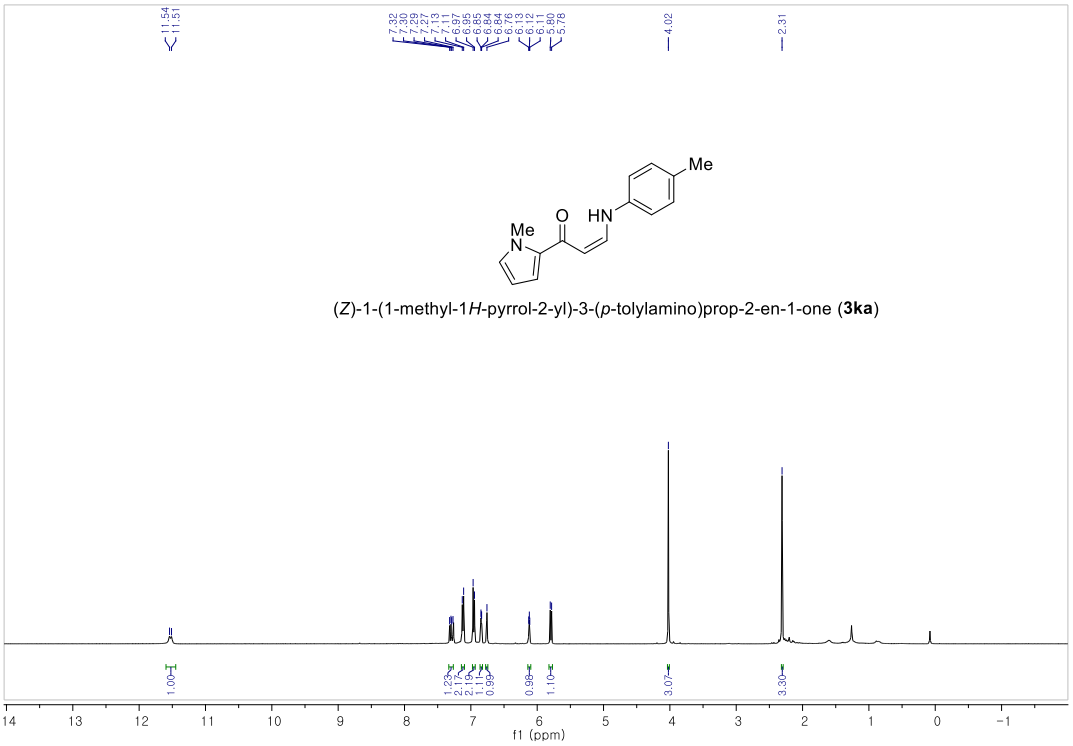
(*Z*)-1-(thiophen-2-yl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ja**)

^{1}H NMR ($CDCl_3$, 400 MHz)



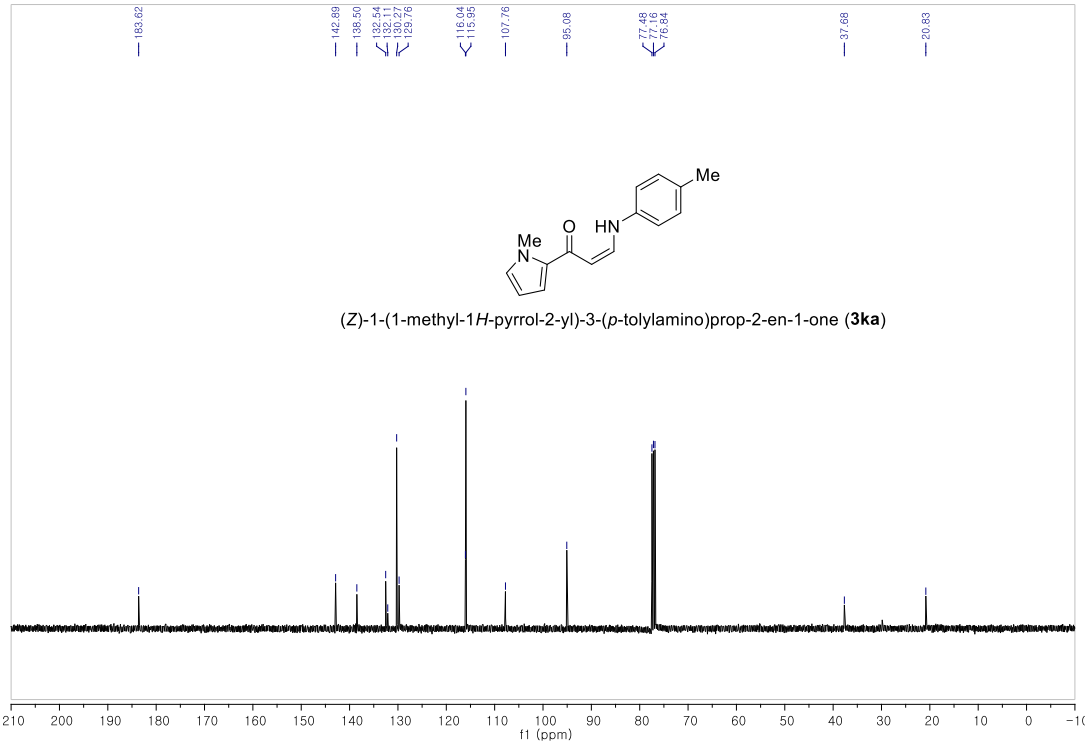
(*Z*)-1-(thiophen-2-yl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ja**)

^{13}C NMR ($CDCl_3$, 101 MHz)



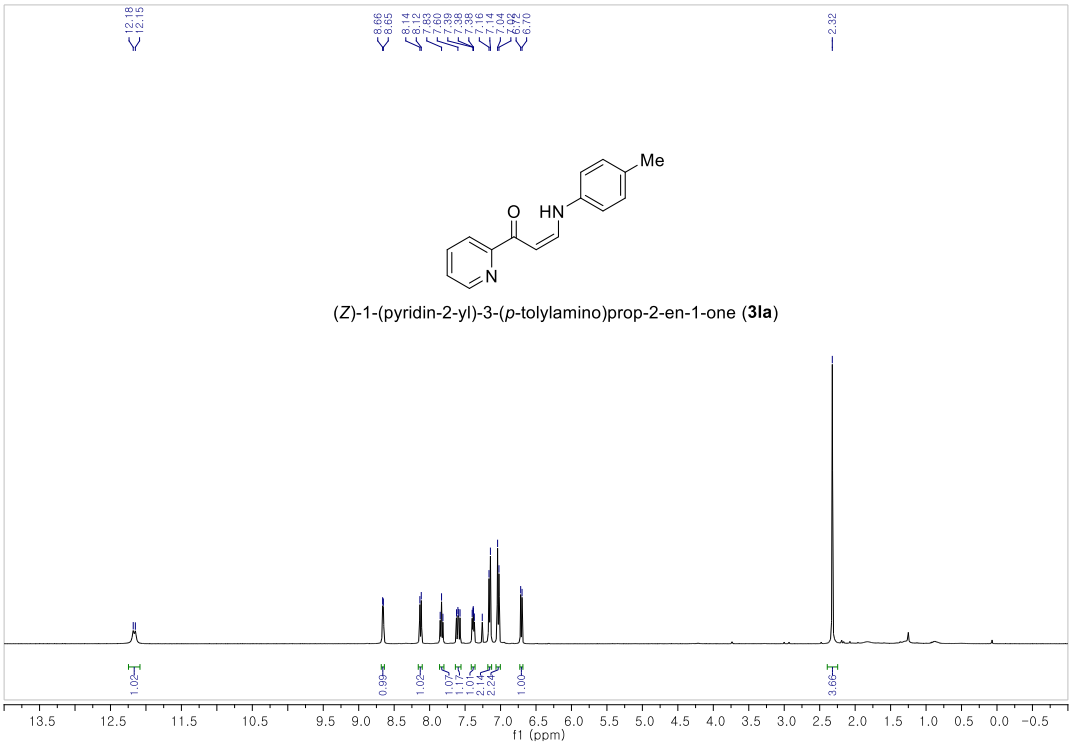
(Z)-1-(1-methyl-1*H*-pyrrol-2-yl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ka**)

^{1}H NMR ($CDCl_3$, 400 MHz)

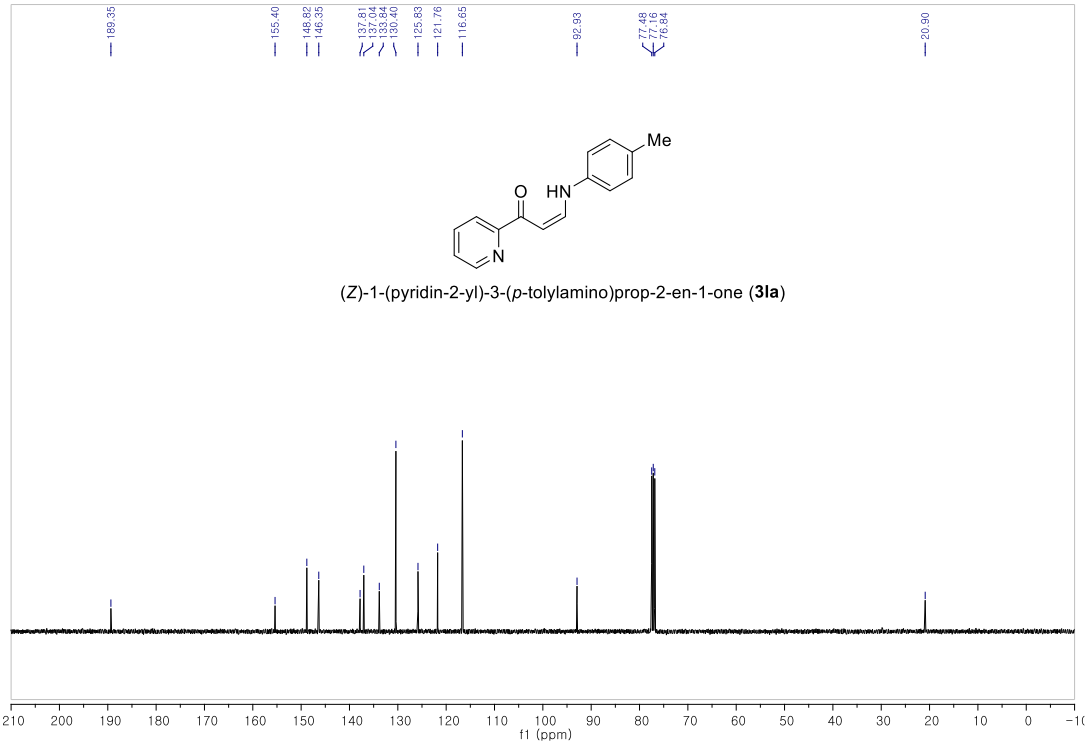


(Z)-1-(1-methyl-1*H*-pyrrol-2-yl)-3-(*p*-tolylamino)prop-2-en-1-one (**3ka**)

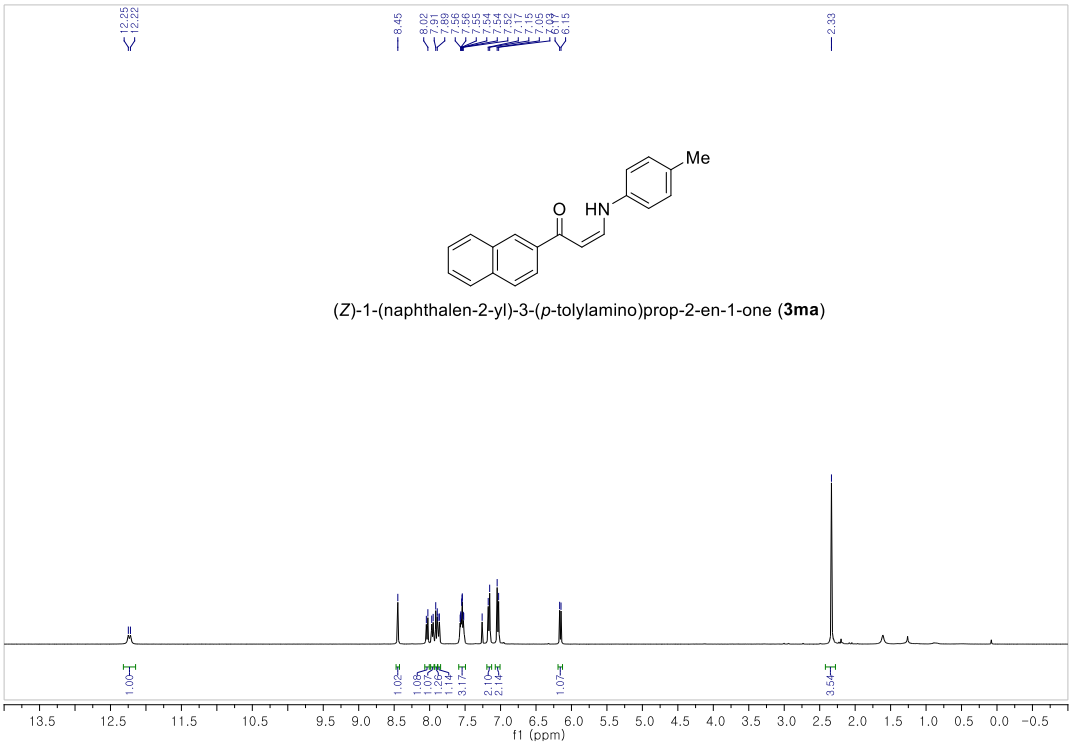
^{13}C NMR ($CDCl_3$, 101 MHz)



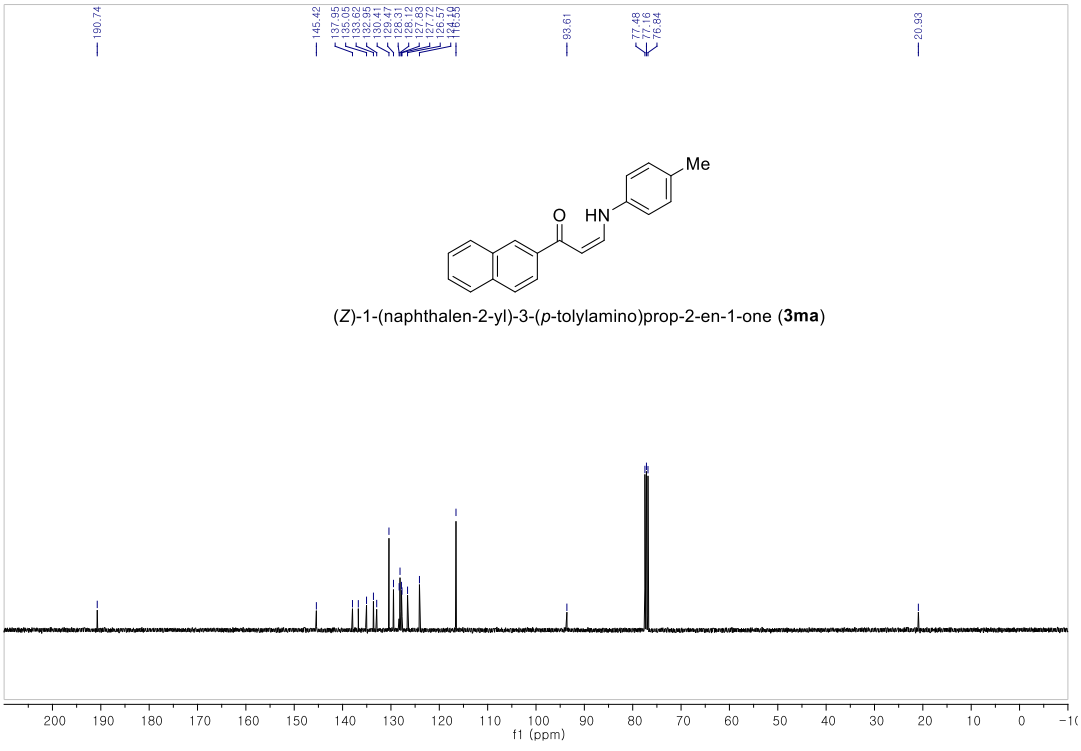
^{1}H NMR ($CDCl_3$, 400 MHz)



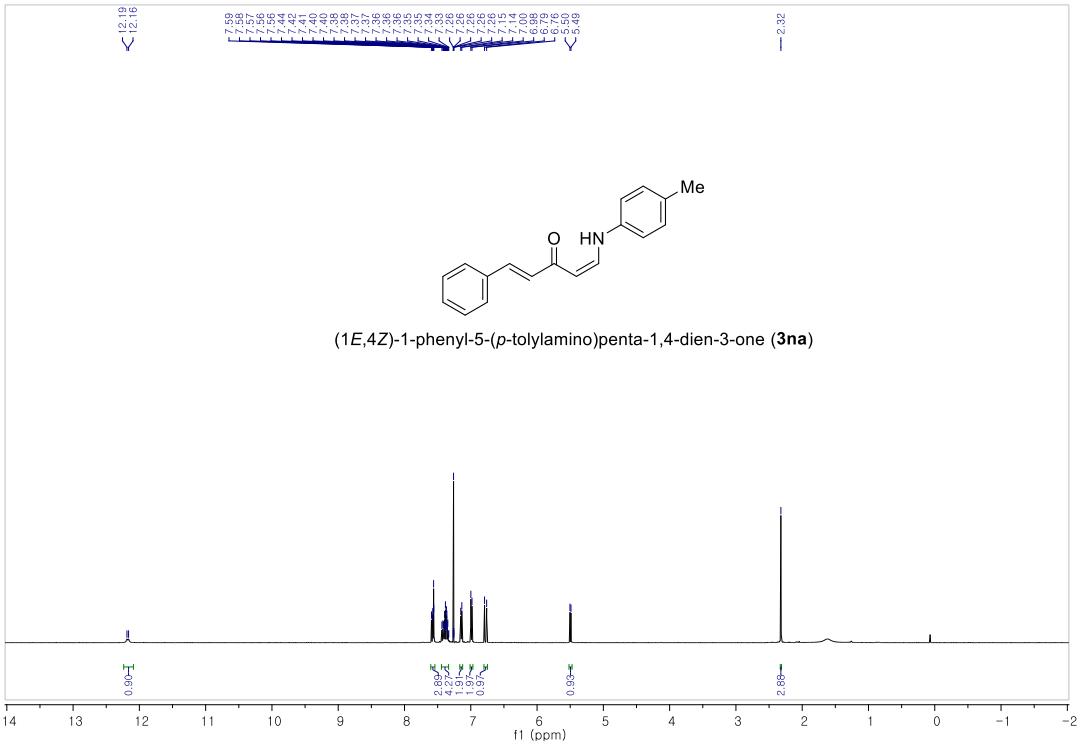
^{13}C NMR ($CDCl_3$, 101 MHz)



^{1}H NMR ($CDCl_3$, 400 MHz)

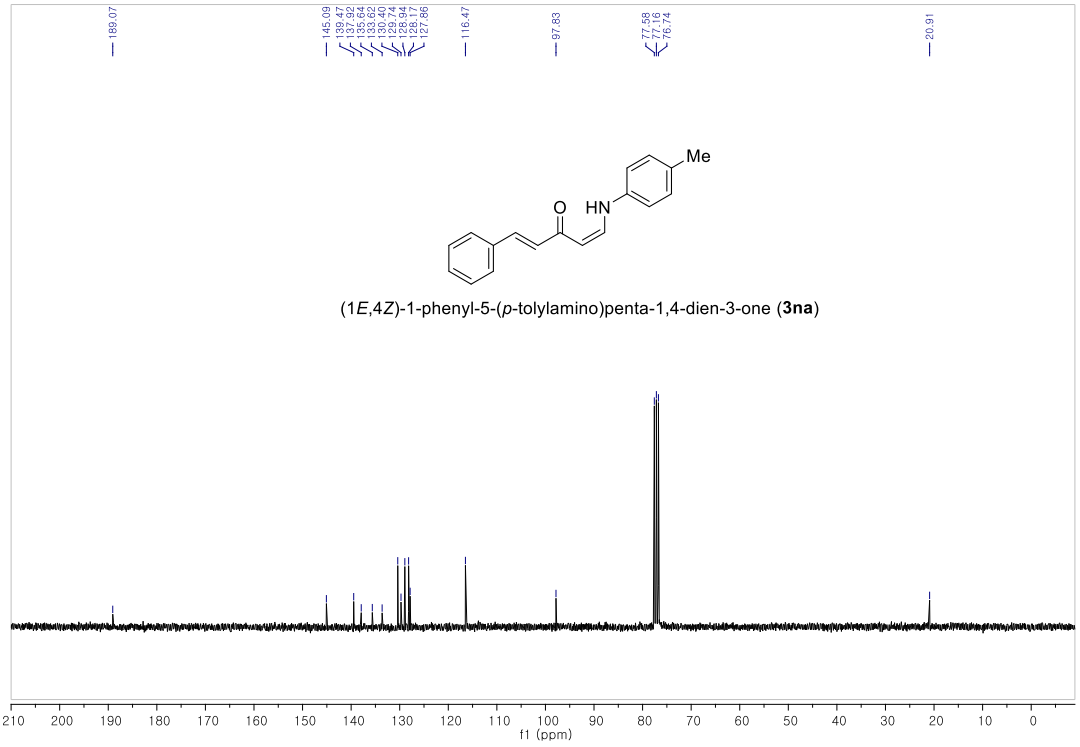


^{13}C NMR ($CDCl_3$, 101 MHz)



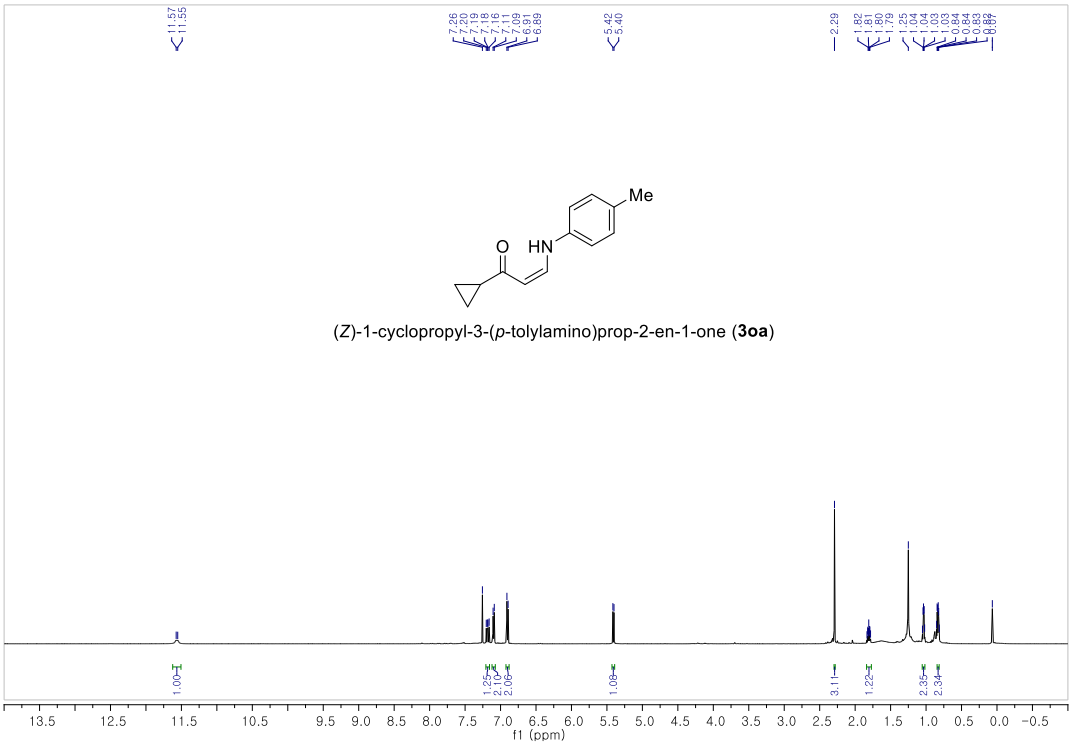
(1*E*,4*Z*)-1-phenyl-5-(*p*-tolylamino)penta-1,4-dien-3-one (**3na**)

^{1}H NMR ($CDCl_3$, 499 MHz)

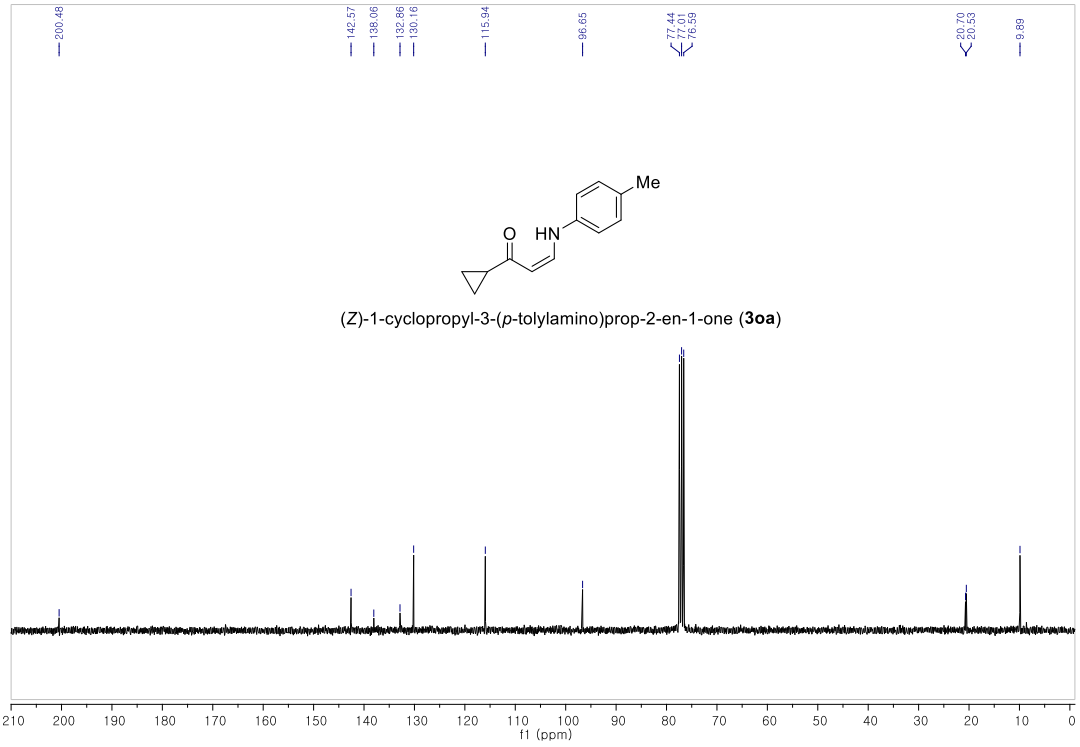


(1*E*,4*Z*)-1-phenyl-5-(*p*-tolylamino)penta-1,4-dien-3-one (**3na**)

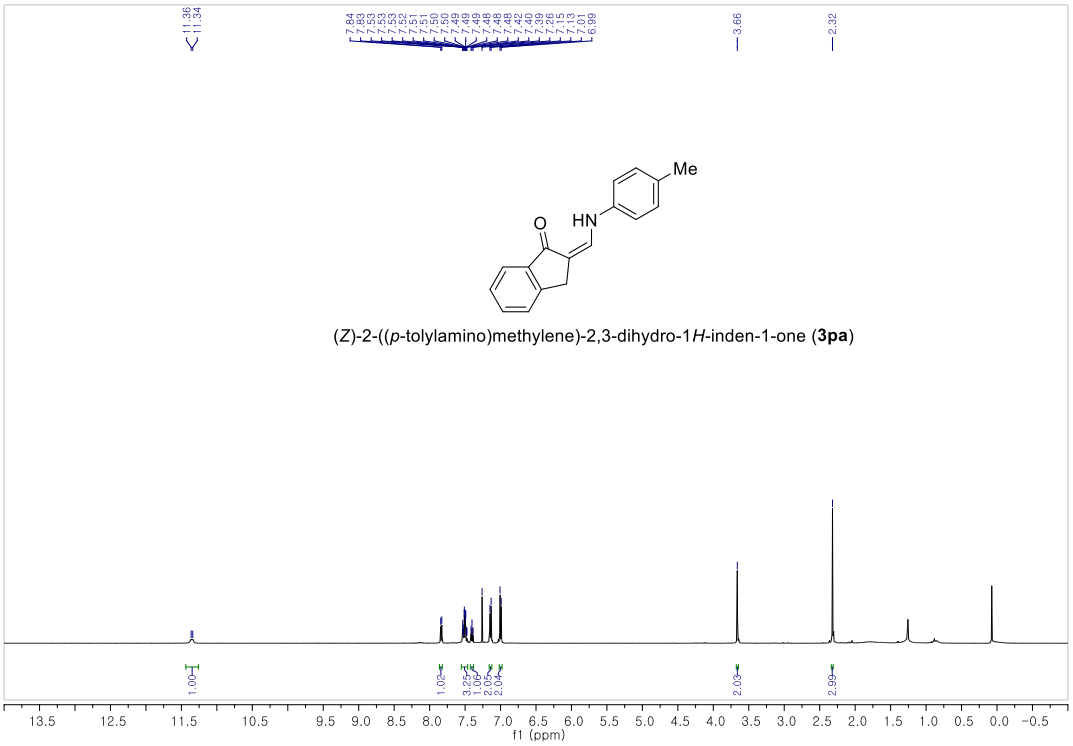
^{13}C NMR ($CDCl_3$, 75 MHz)



^{1}H NMR ($CDCl_3$, 499 MHz)

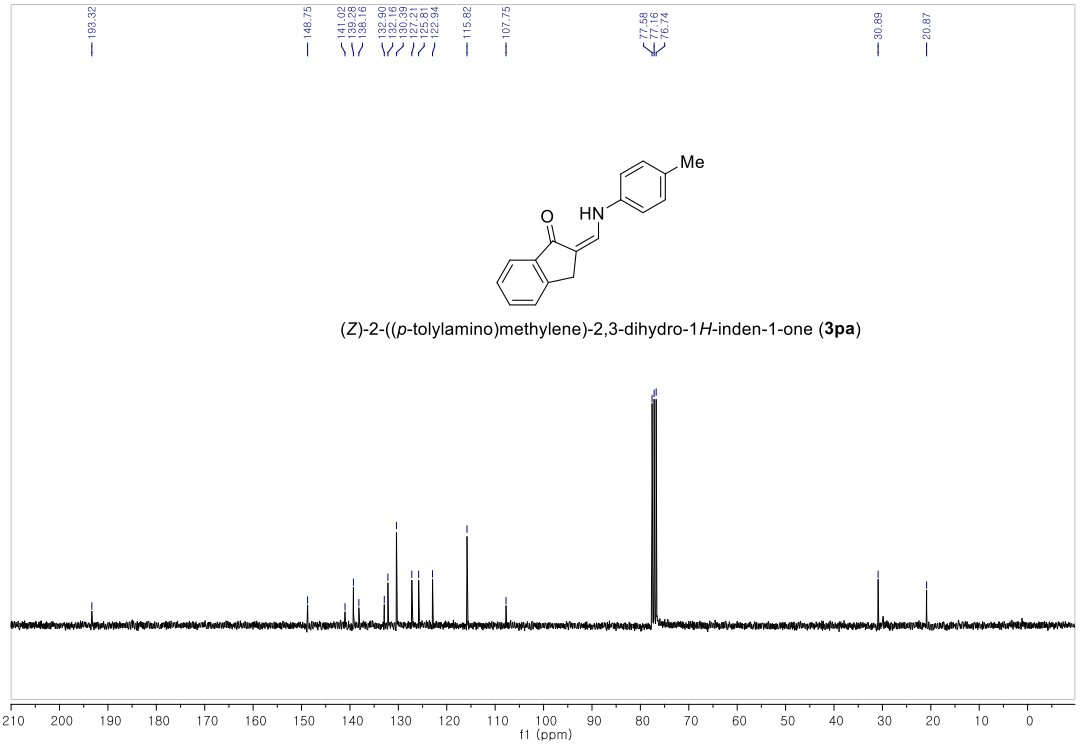


^{13}C NMR ($CDCl_3$, 75 MHz)



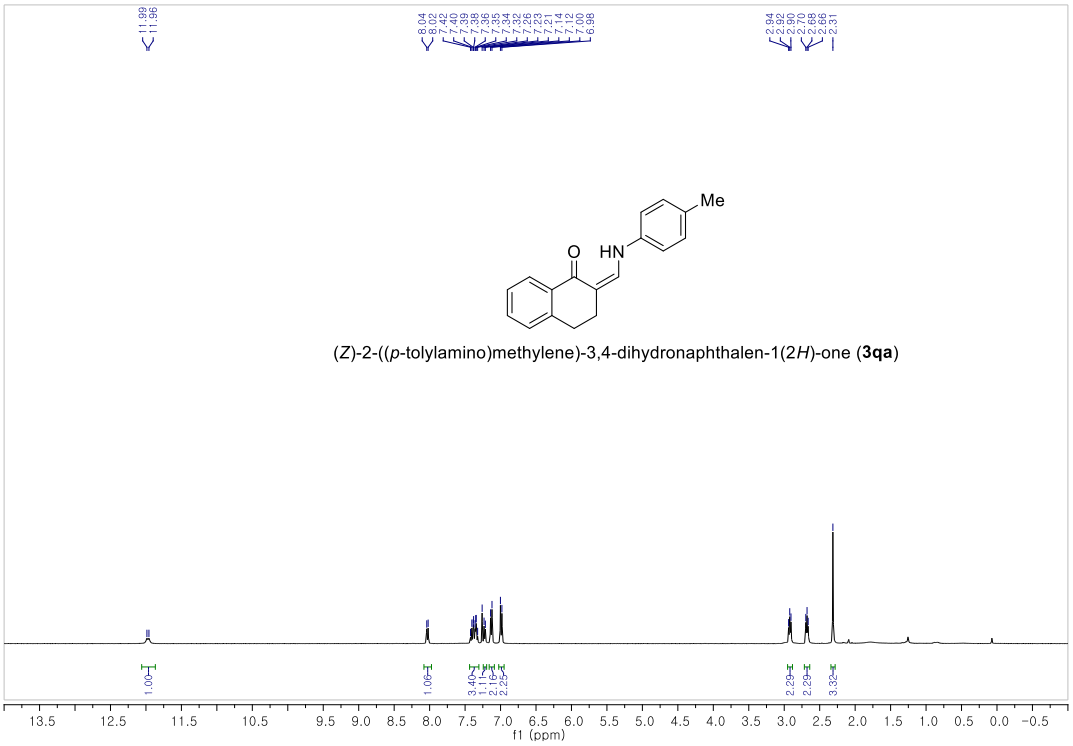
(*Z*)-2-((*p*-tolylamino)methylene)-2,3-dihydro-1*H*-inden-1-one (**3pa**)

^{1}H NMR ($CDCl_3$, 499 MHz)

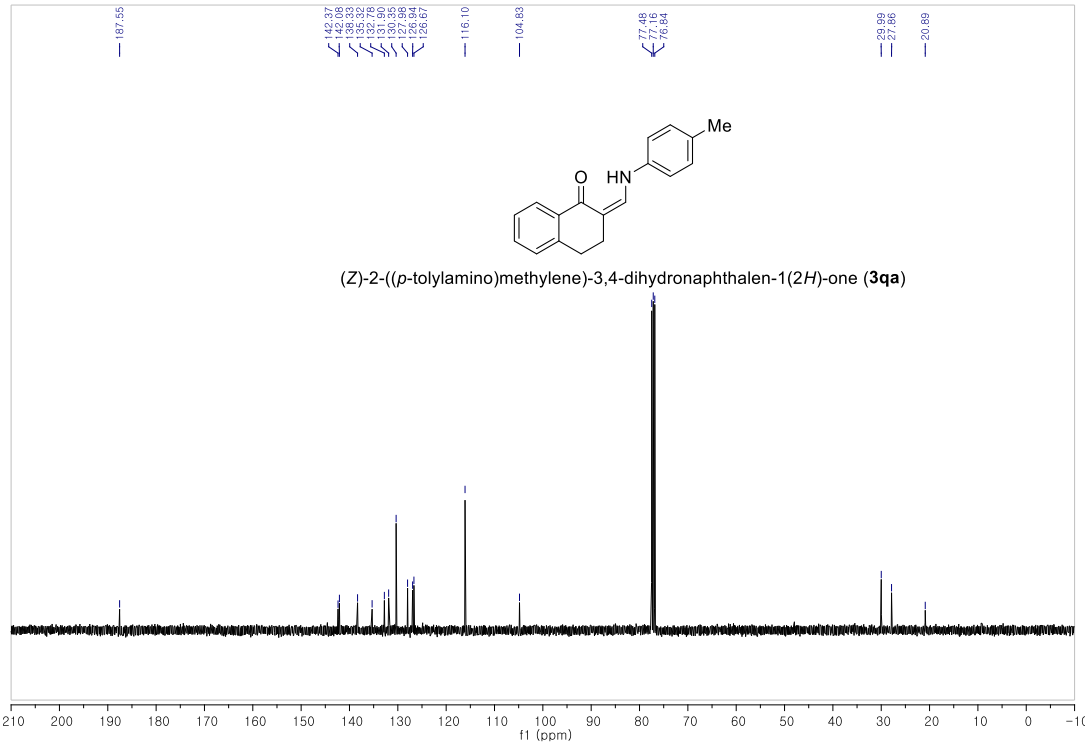


(*Z*)-2-((*p*-tolylamino)methylene)-2,3-dihydro-1*H*-inden-1-one (**3pa**)

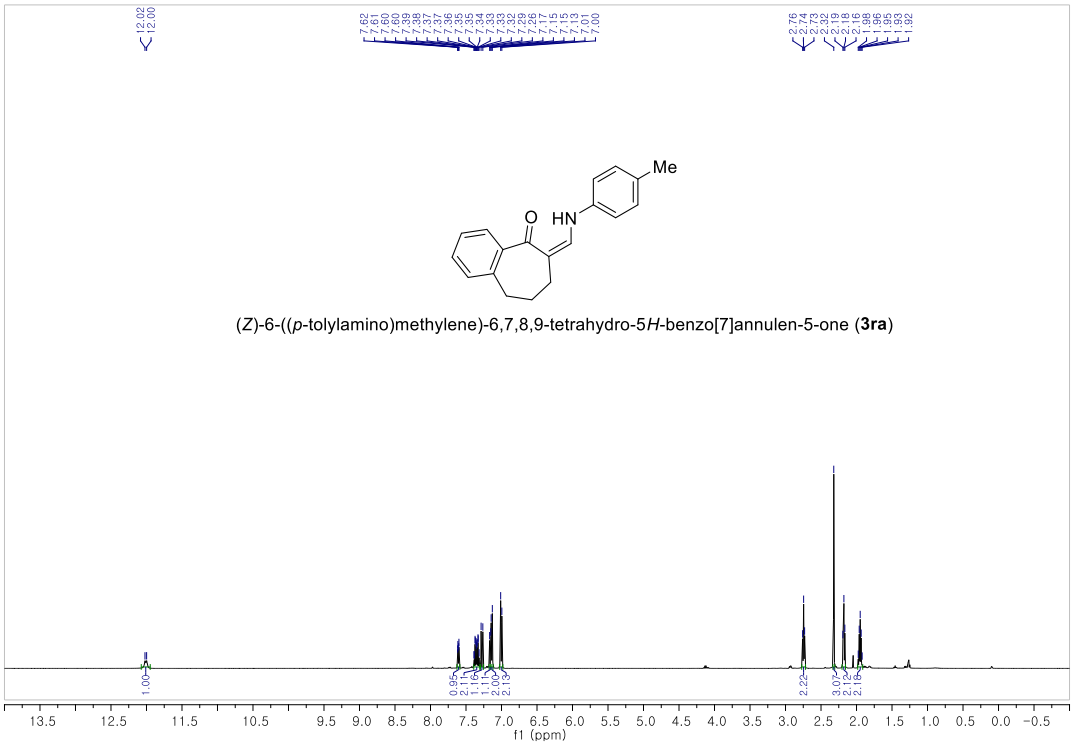
^{13}C NMR ($CDCl_3$, 75 MHz)



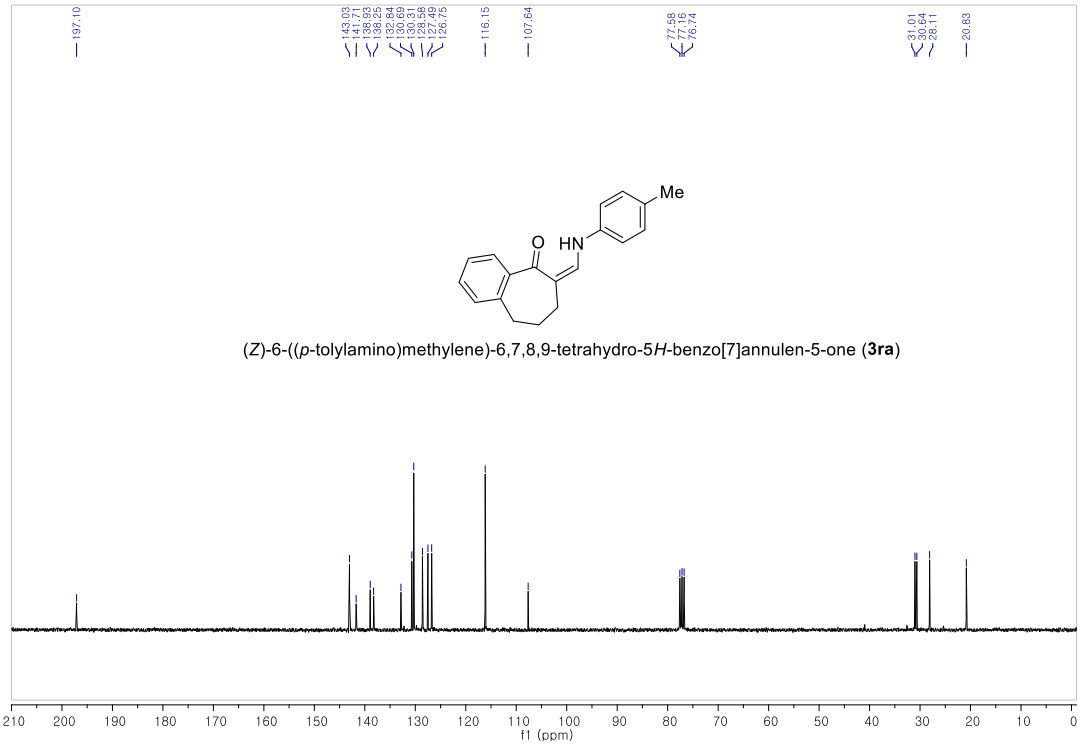
^{1}H NMR ($CDCl_3$, 400 MHz)



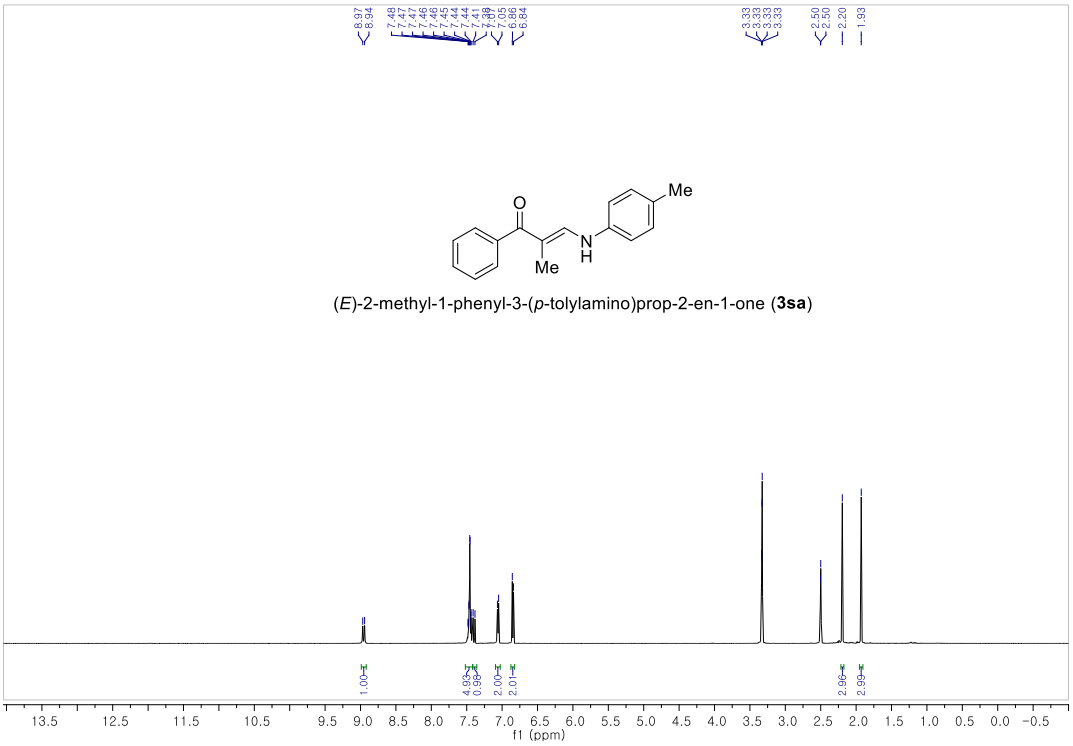
^{13}C NMR ($CDCl_3$, 101 MHz)



^{1}H NMR ($CDCl_3$, 499 MHz)

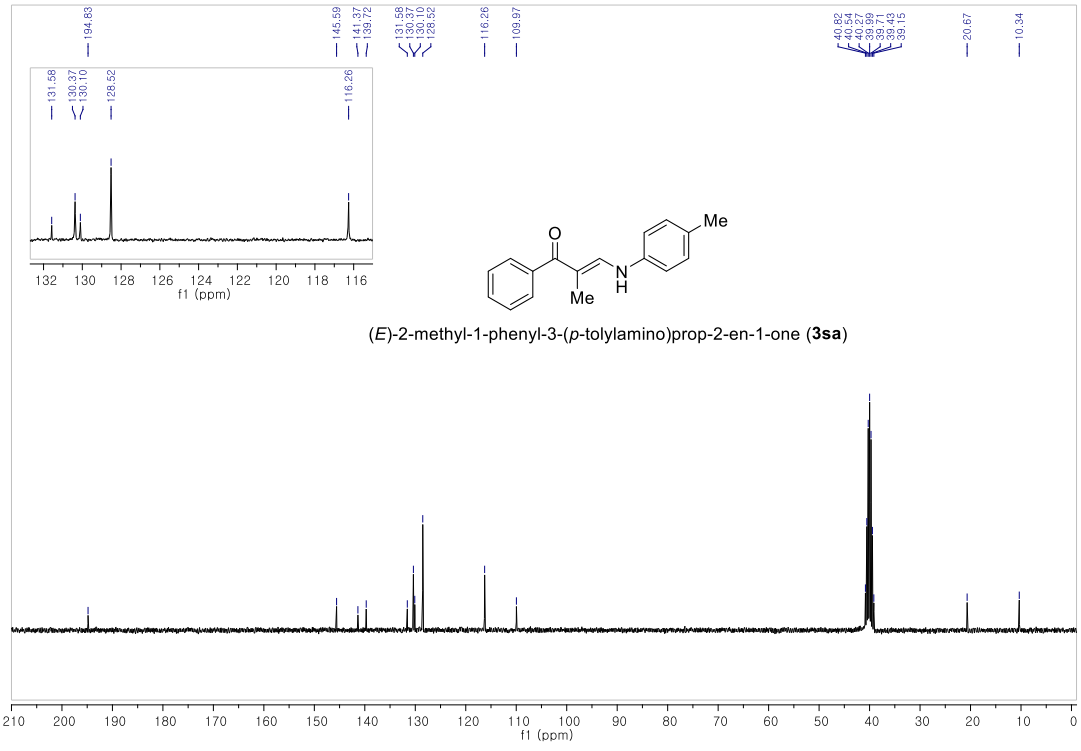


^{13}C NMR ($CDCl_3$, 101 MHz)



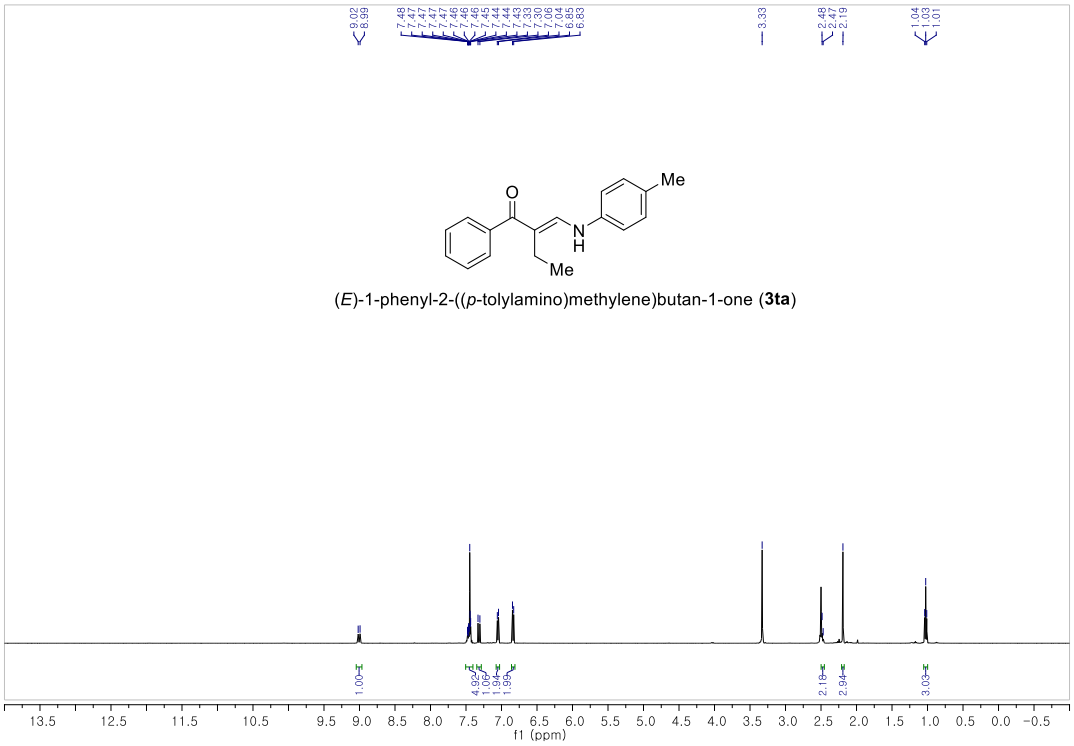
(*E*)-2-methyl-1-phenyl-3-(*p*-tolylamino)prop-2-en-1-one (**3sa**)

^{1}H NMR (DMSO-d$_6$, 499 MHz)

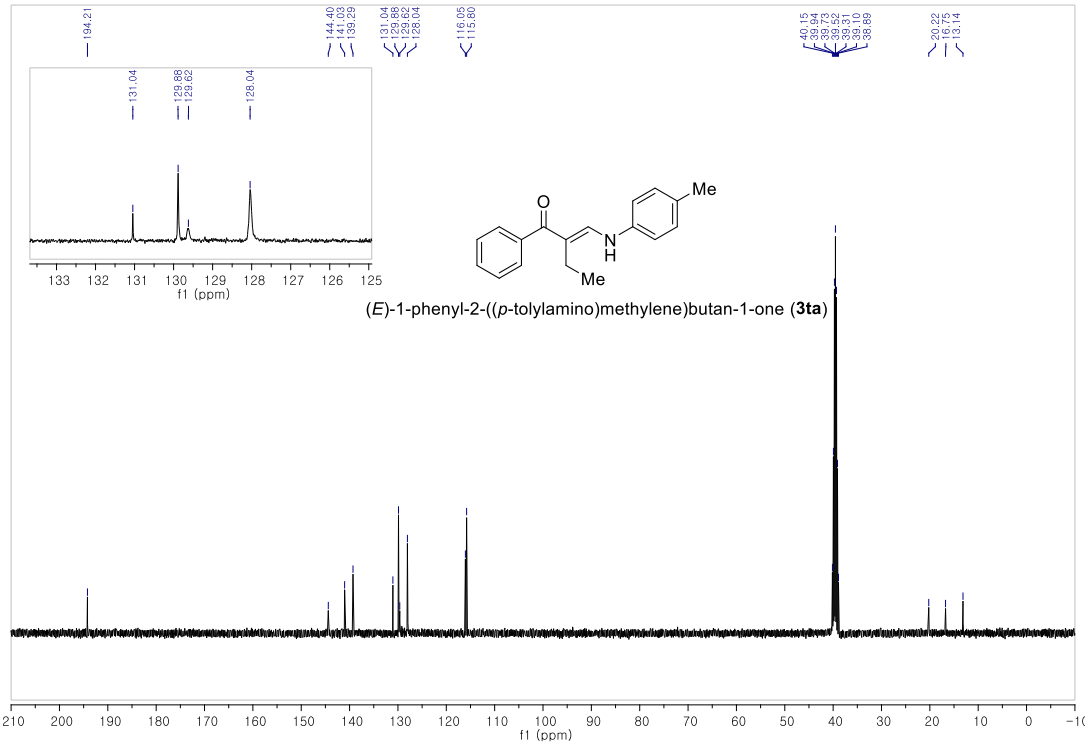


(*E*)-2-methyl-1-phenyl-3-(*p*-tolylamino)prop-2-en-1-one (**3sa**)

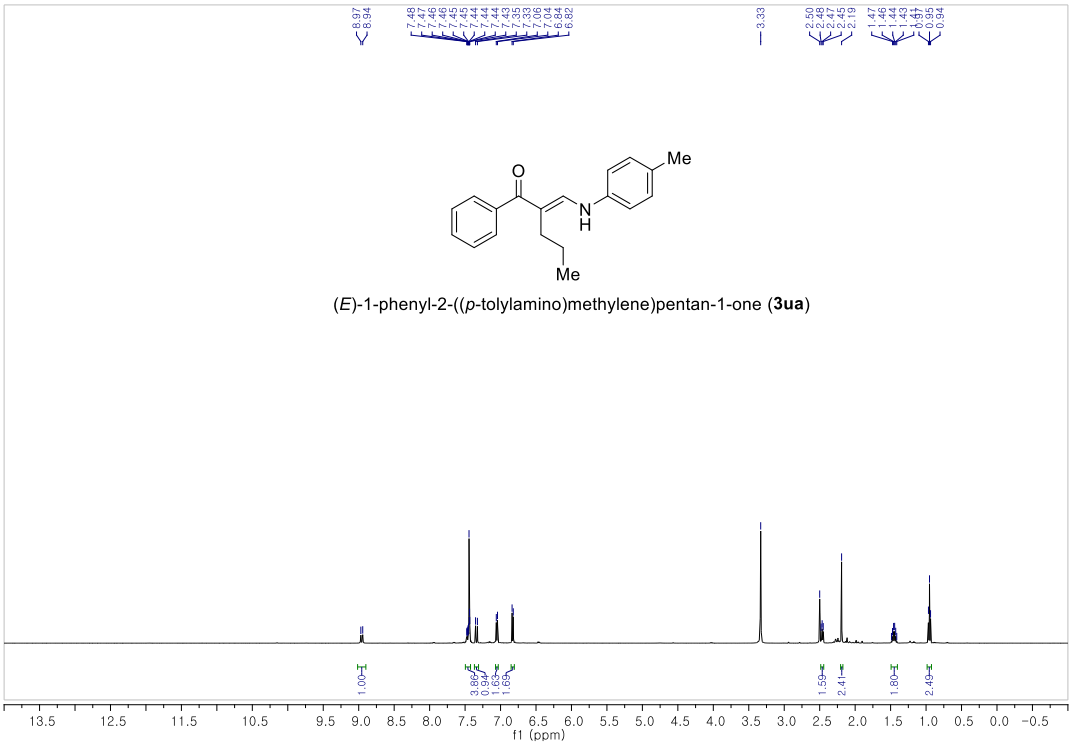
^{13}C NMR (DMSO-d$_6$, 75 MHz)



^{1}H NMR (DMSO-d$_6$, 499 MHz)

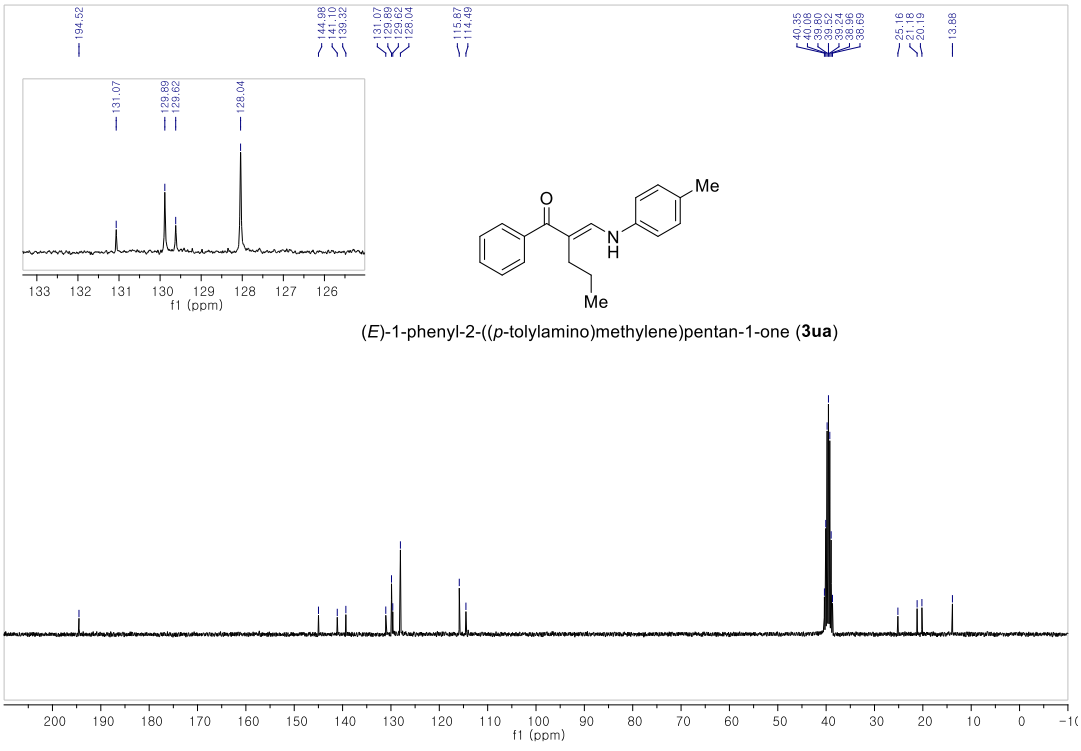


^{13}C NMR (DMSO-d$_6$, 101 MHz)



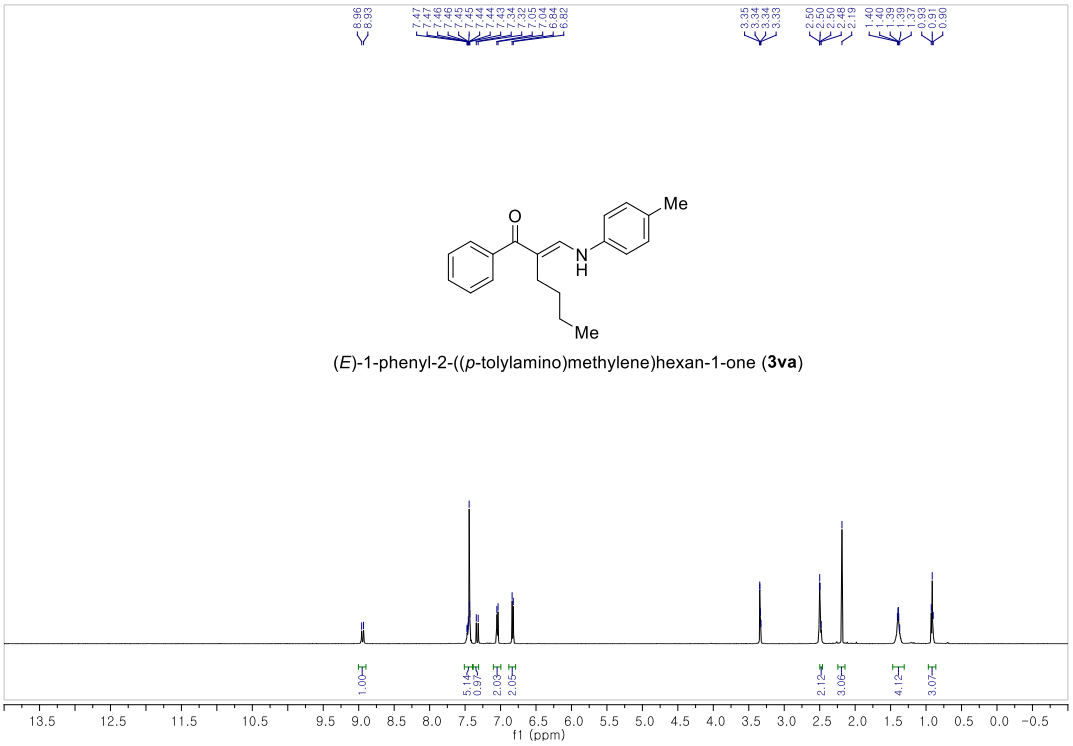
(*E*)-1-phenyl-2-((*p*-tolylamino)methylene)pentan-1-one (**3ua**)

^{1}H NMR (DMSO-d$_6$, 499 MHz)



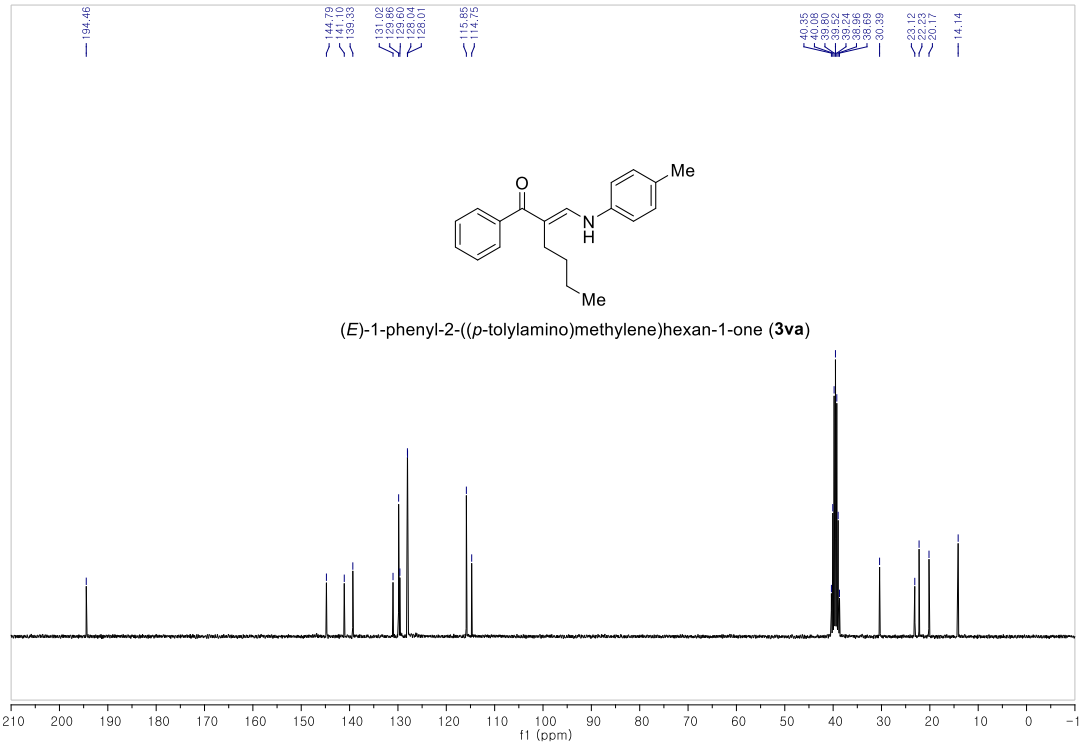
(*E*)-1-phenyl-2-((*p*-tolylamino)methylene)pentan-1-one (**3ua**)

^{13}C NMR (DMSO-d$_6$, 75 MHz)



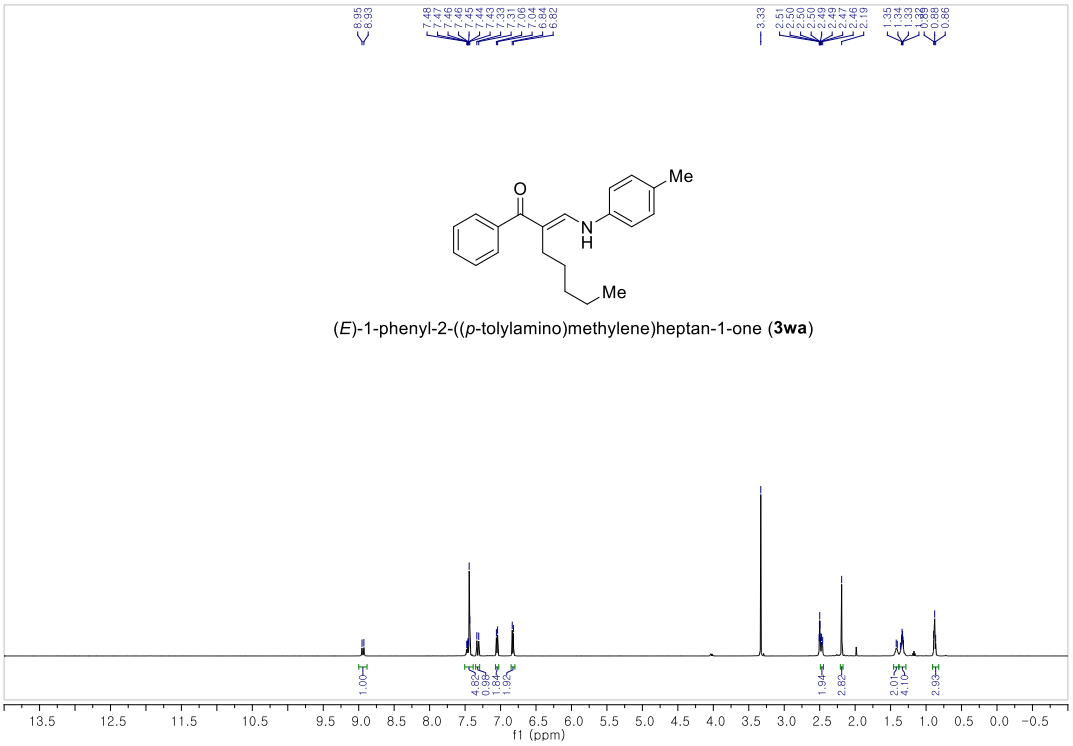
(*E*)-1-phenyl-2-((*p*-tolylamino)methylene)hexan-1-one (**3va**)

^{1}H NMR (DMSO-d$_6$, 499 MHz)

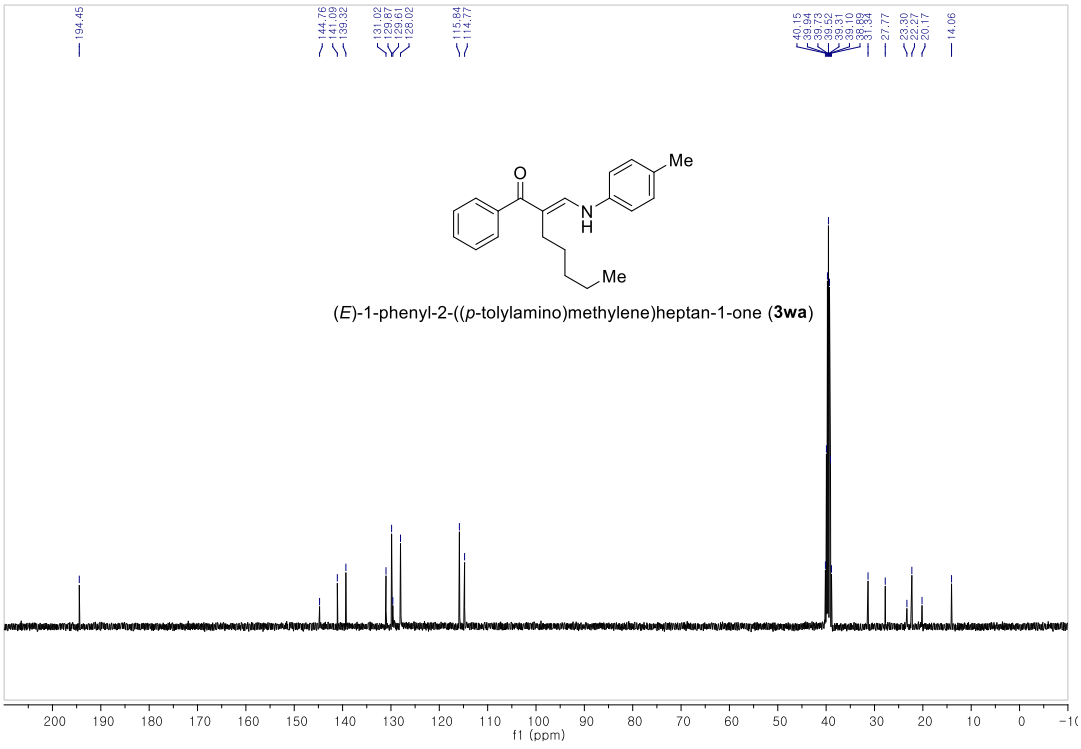


(*E*)-1-phenyl-2-((*p*-tolylamino)methylene)hexan-1-one (**3va**)

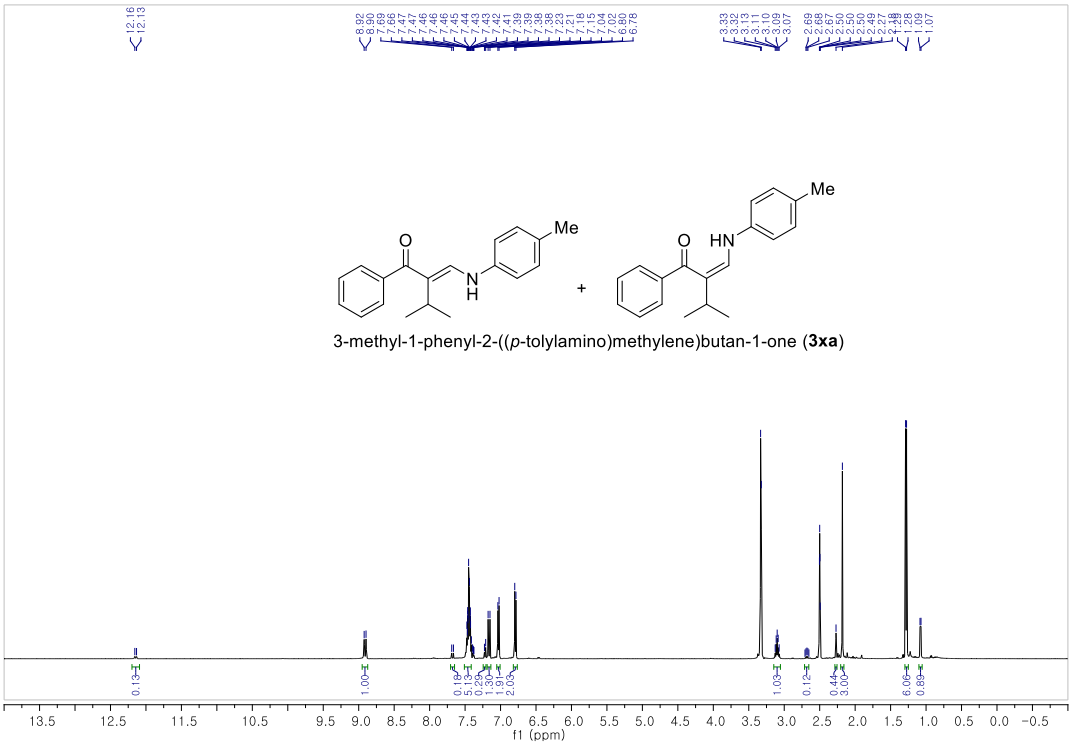
^{13}C NMR (DMSO-d$_6$, 75 MHz)



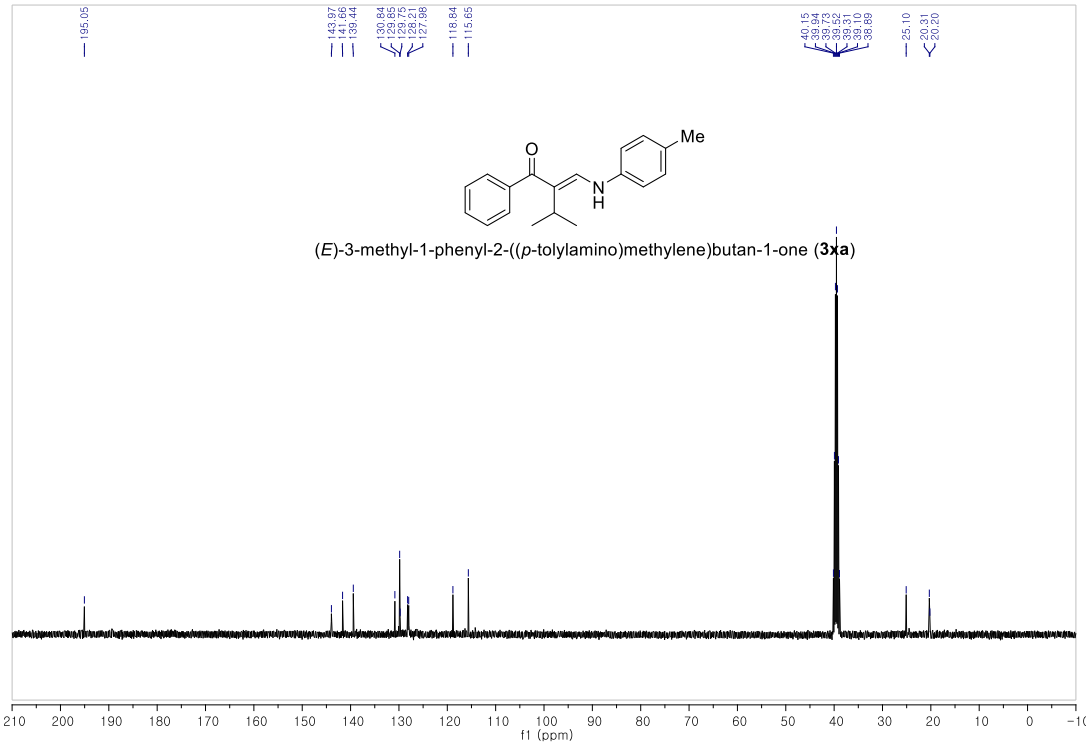
^{1}H NMR (DMSO-d$_6$, 499 MHz)



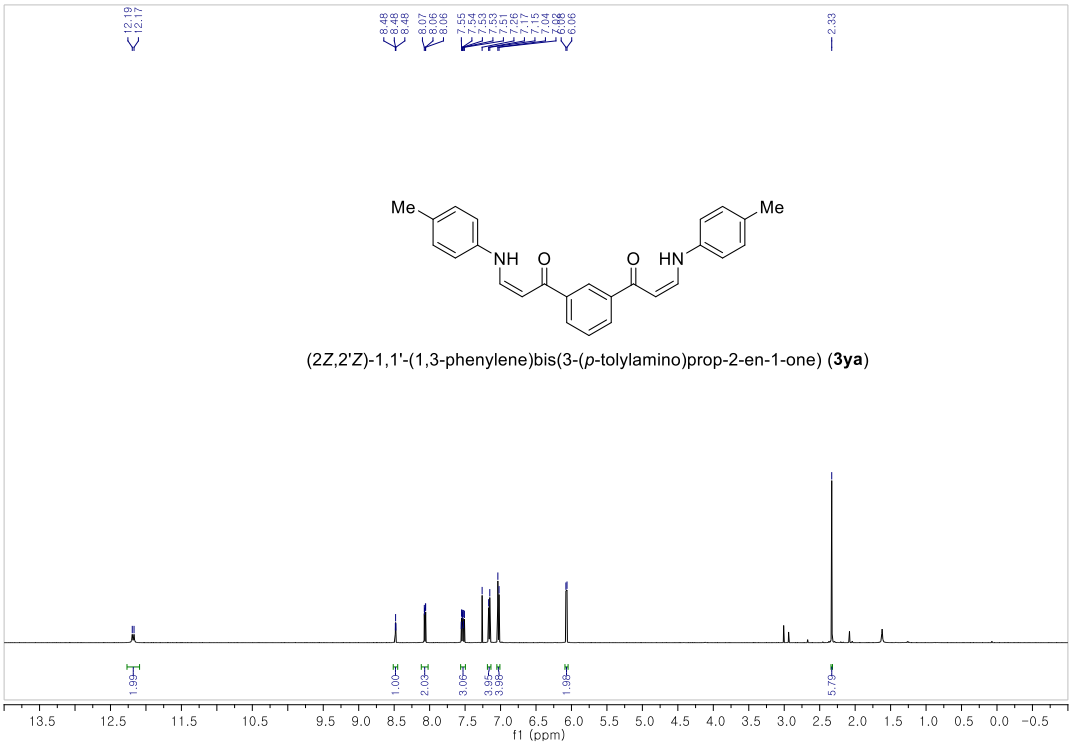
^{13}C NMR (DMSO-d$_6$, 101 MHz)



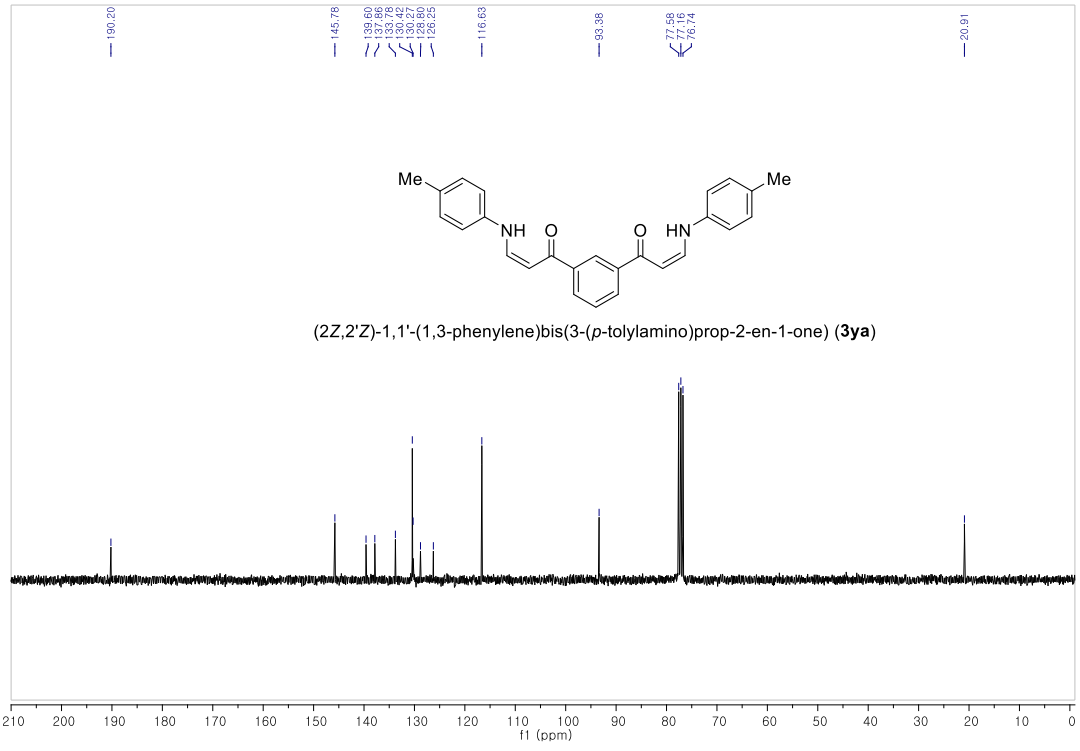
^{1}H NMR (DMSO-d$_6$, 499 MHz)



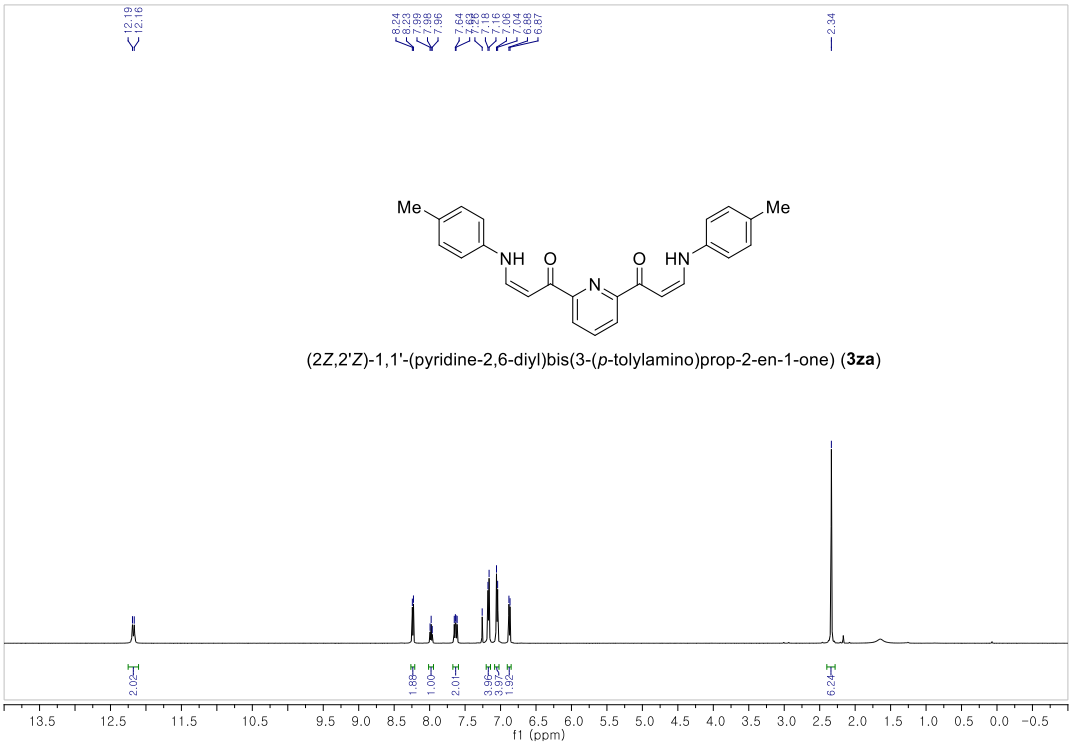
^{13}C NMR (DMSO-d$_6$, 101 MHz)



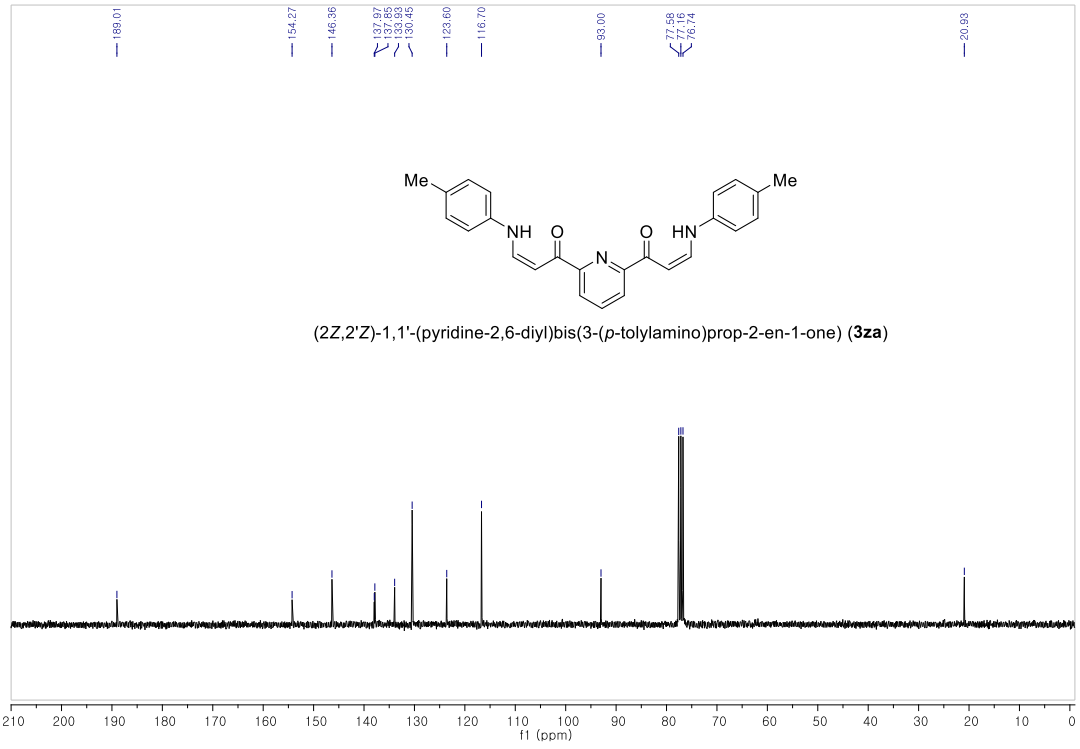
^{1}H NMR ($CDCl_3$, 499 MHz)



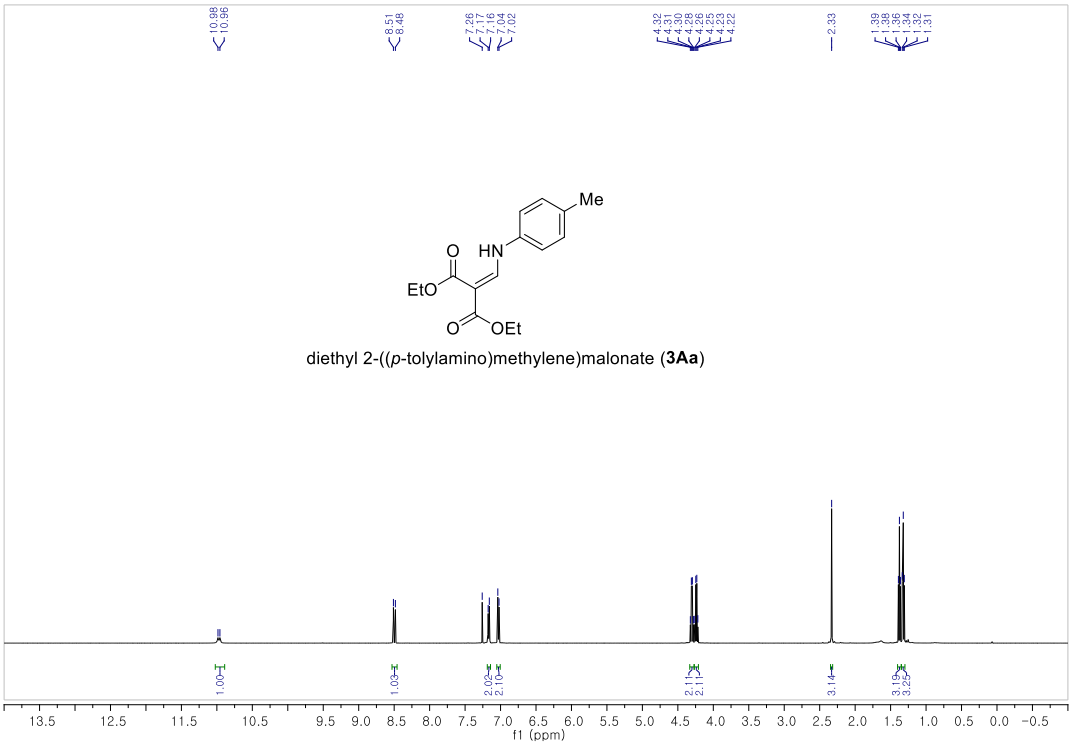
^{13}C NMR ($CDCl_3$, 75 MHz)



^{1}H NMR ($CDCl_3$, 499 MHz)

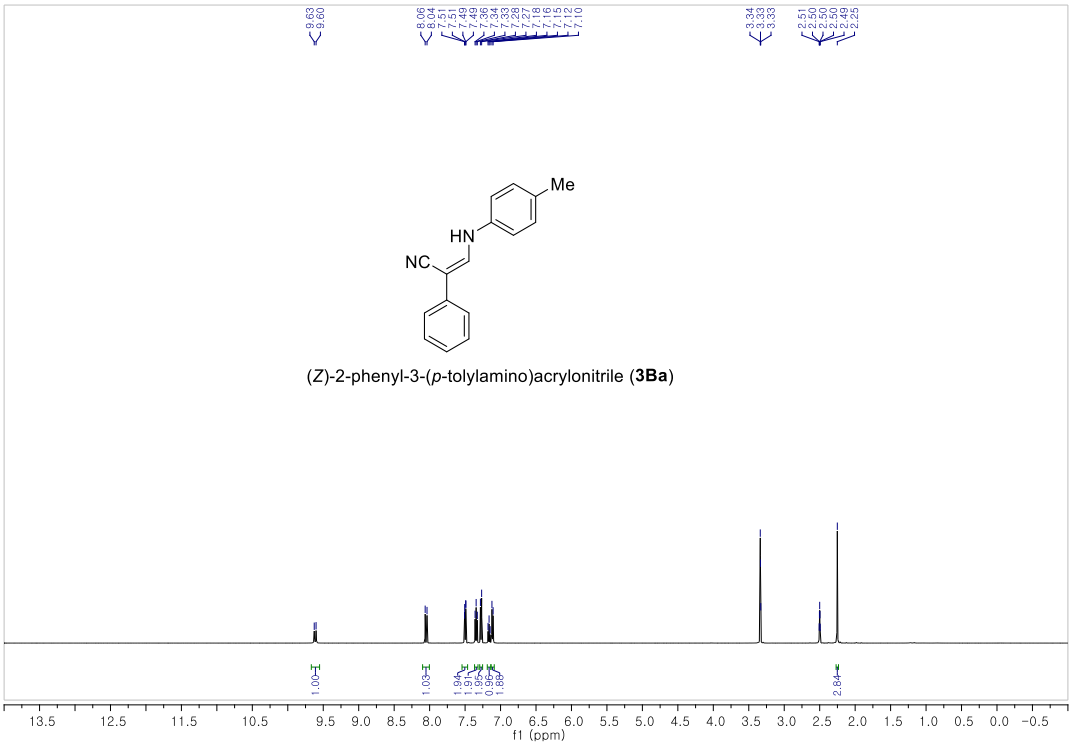


^{13}C NMR ($CDCl_3$, 75 MHz)



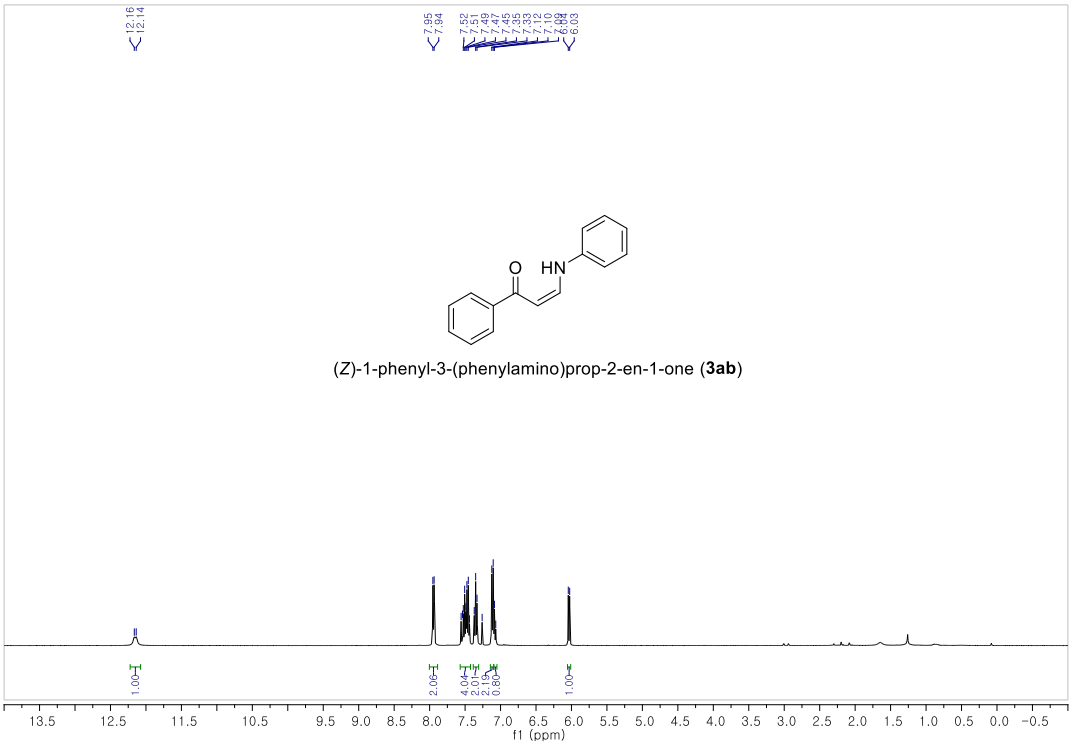
diethyl 2-((*p*-tolylamino)methylene)malonate (**3Aa**)

^{1}H NMR ($CDCl_3$, 499 MHz)



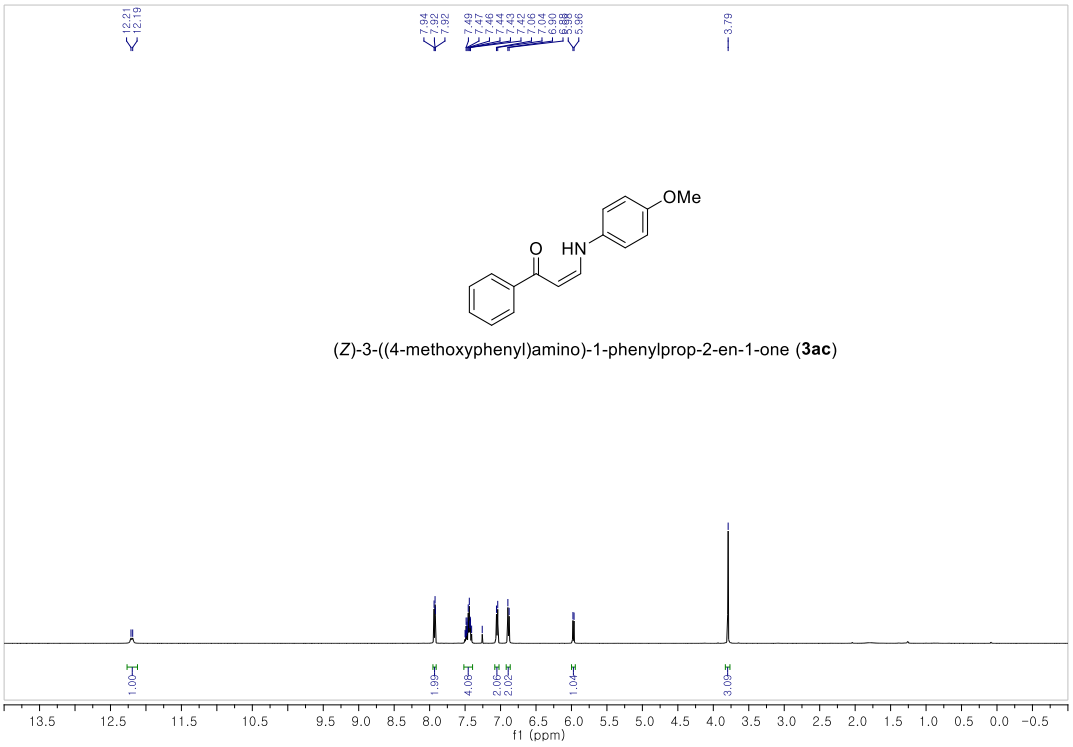
(*Z*)-2-phenyl-3-(*p*-tolylamino)acrylonitrile (**3Ba**)

^{1}H NMR (DMSO, 499 MHz)



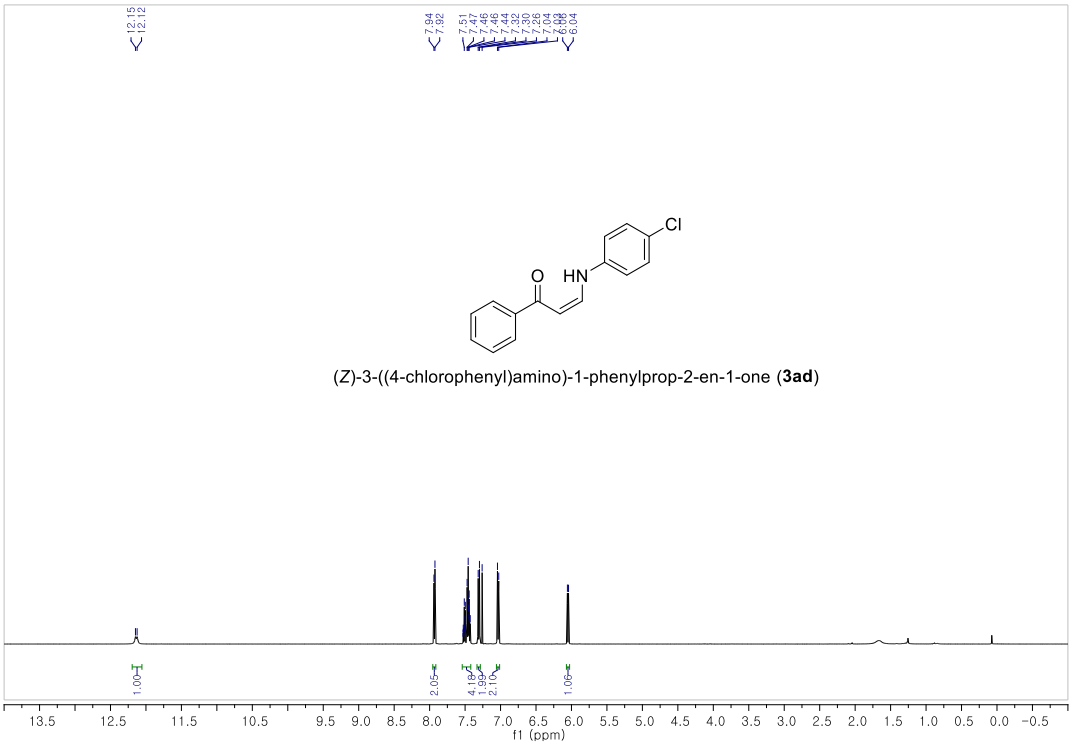
(*Z*)-1-phenyl-3-(phenylamino)prop-2-en-1-one (**3ab**)

^{1}H NMR ($CDCl_3$, 400 MHz)

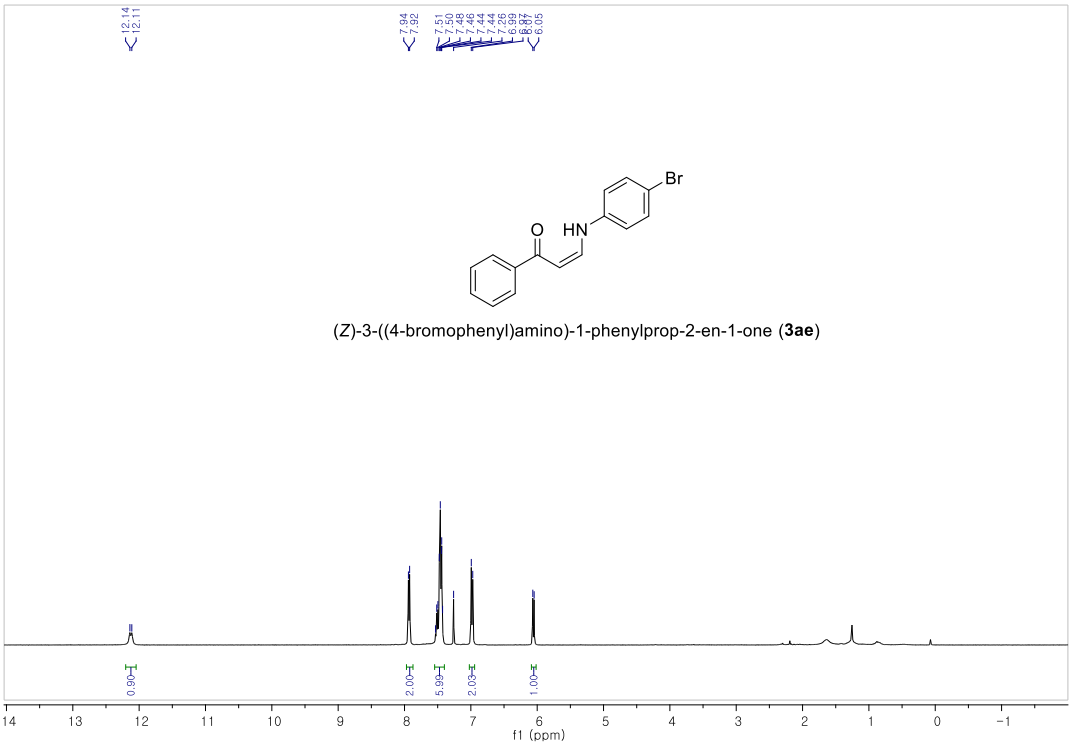


(*Z*)-3-((4-methoxyphenyl)amino)-1-phenylprop-2-en-1-one (**3ac**)

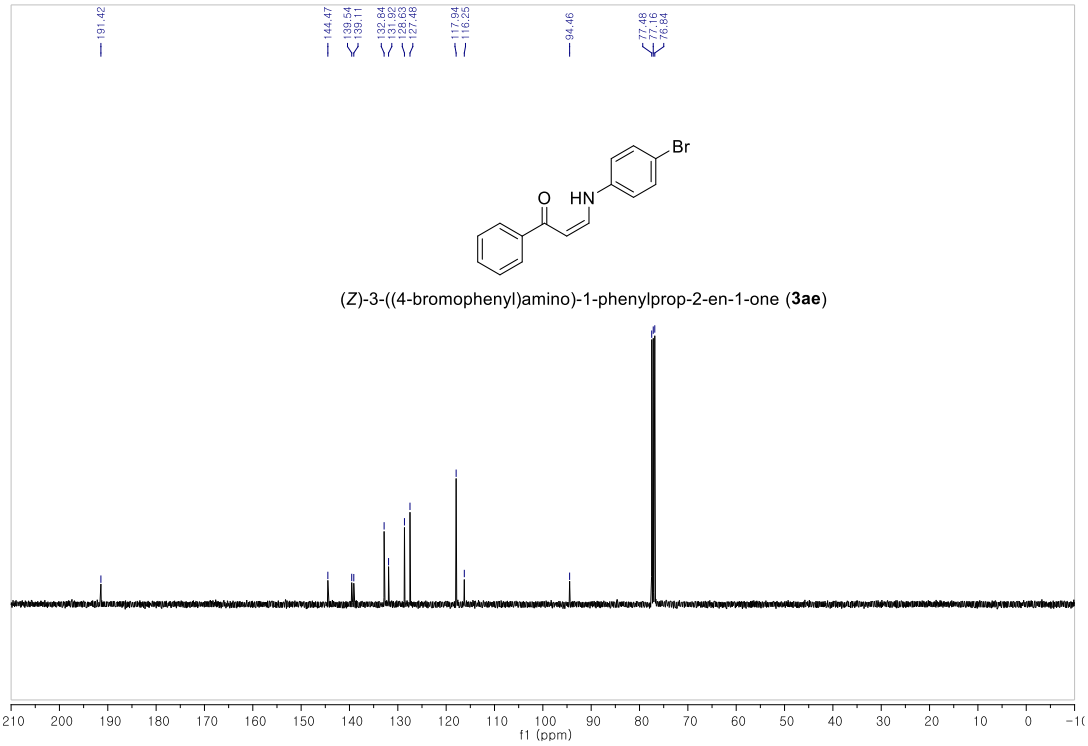
^{1}H NMR ($CDCl_3$, 499 MHz)



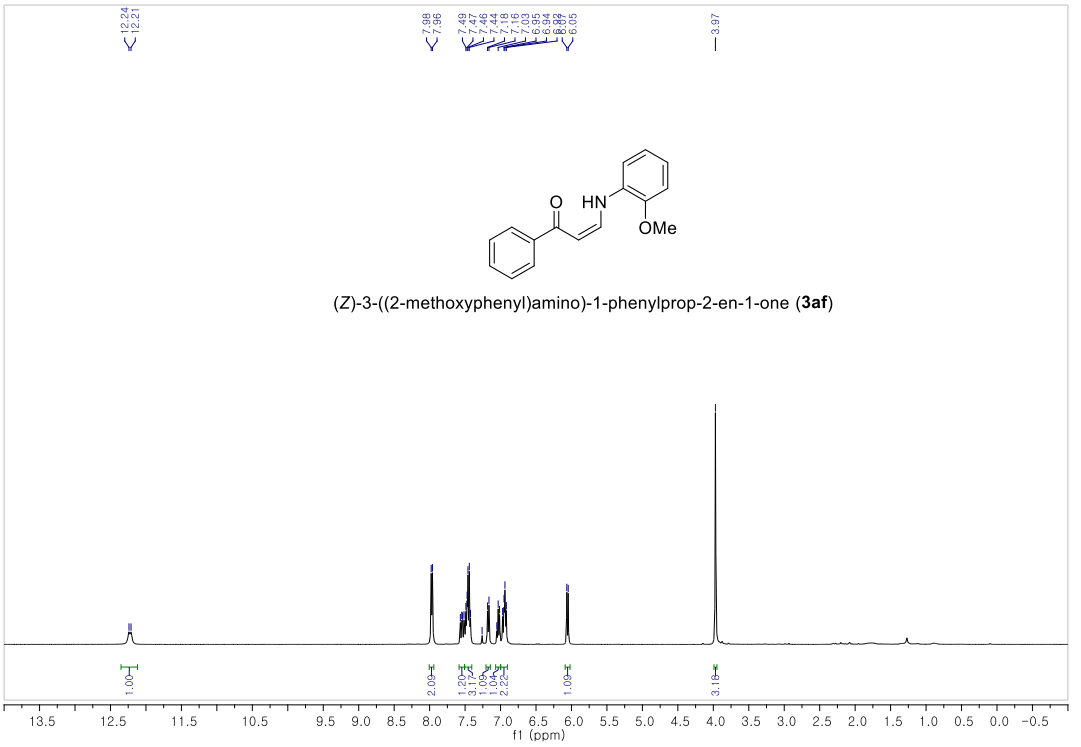
^{1}H NMR ($CDCl_3$, 499 MHz)



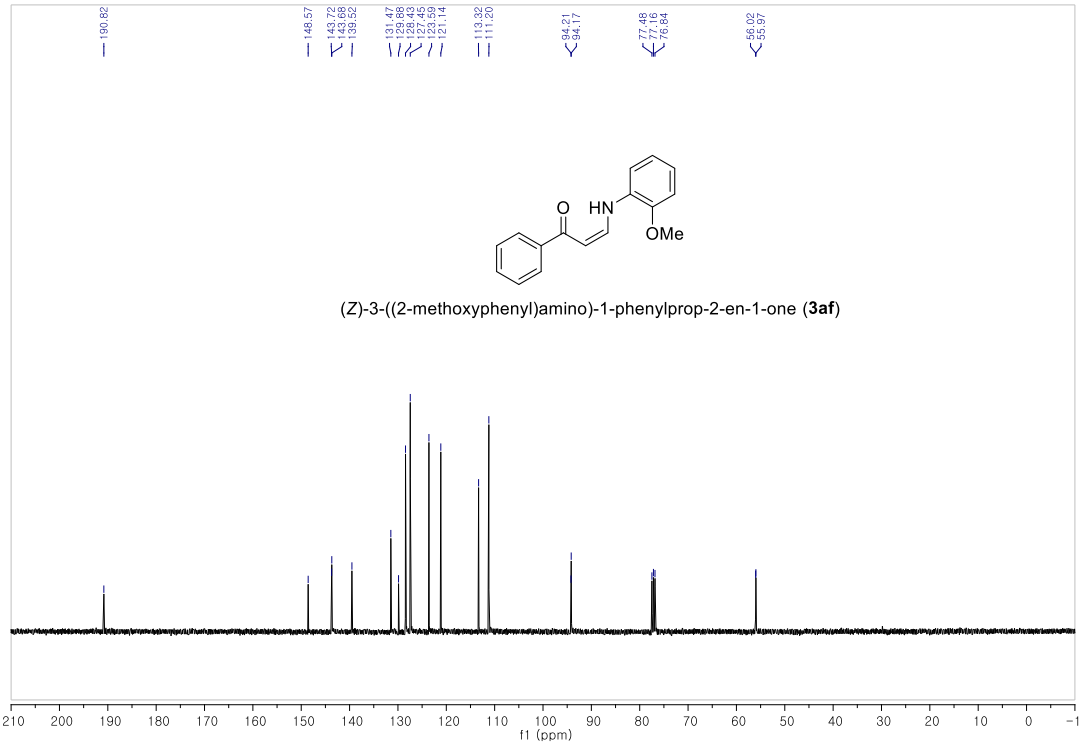
^{1}H NMR ($CDCl_3$, 400 MHz)



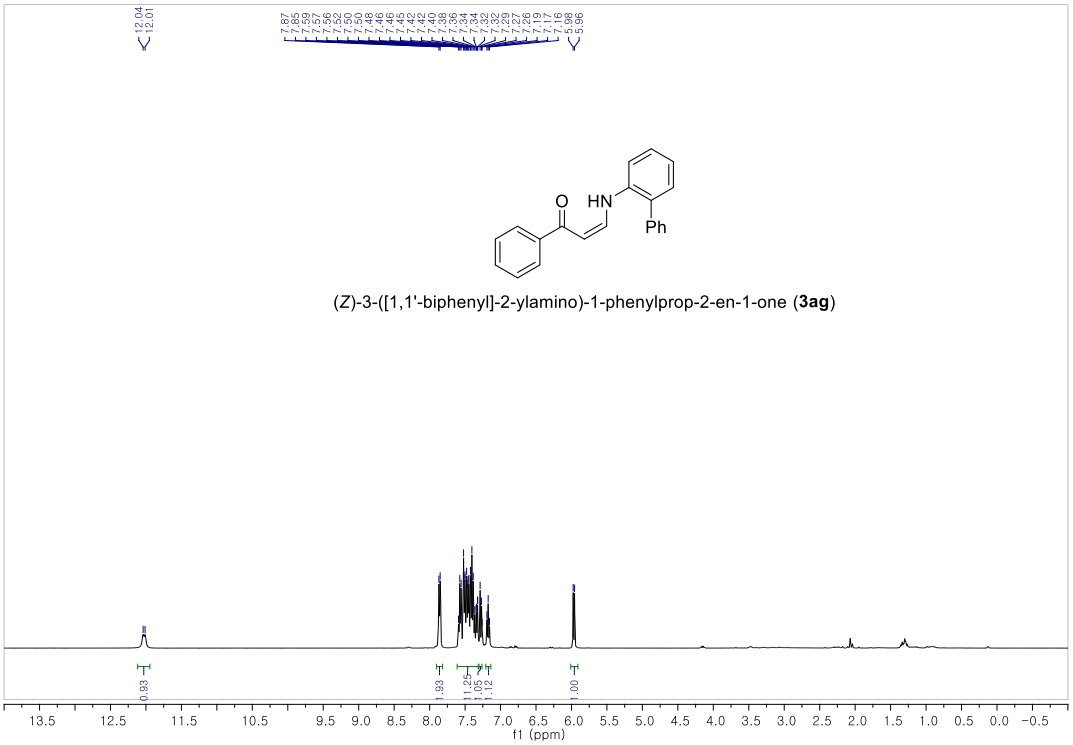
^{13}C NMR ($CDCl_3$, 101 MHz)



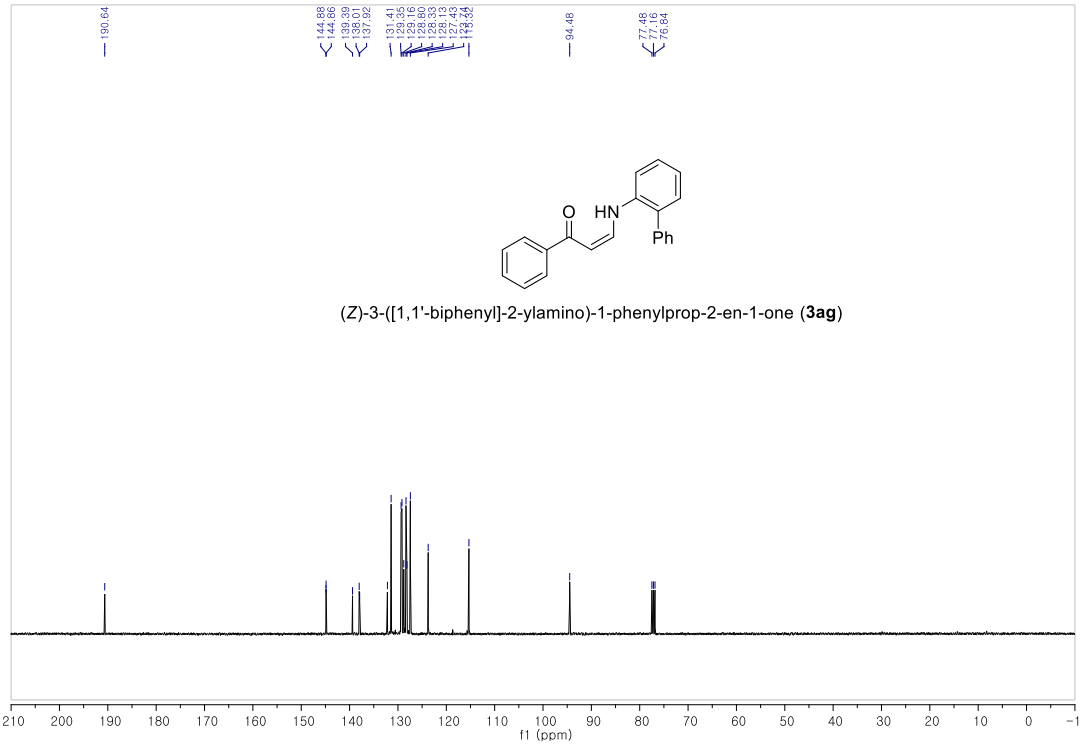
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

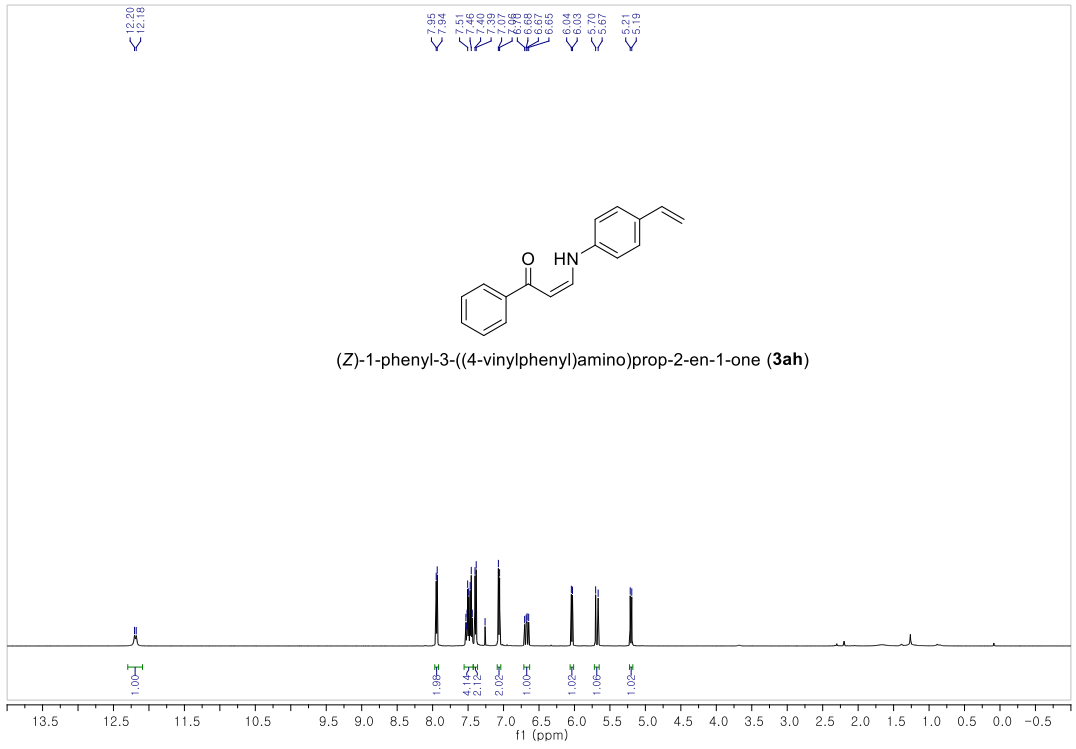


^{1}H NMR ($CDCl_3$, 400 MHz)



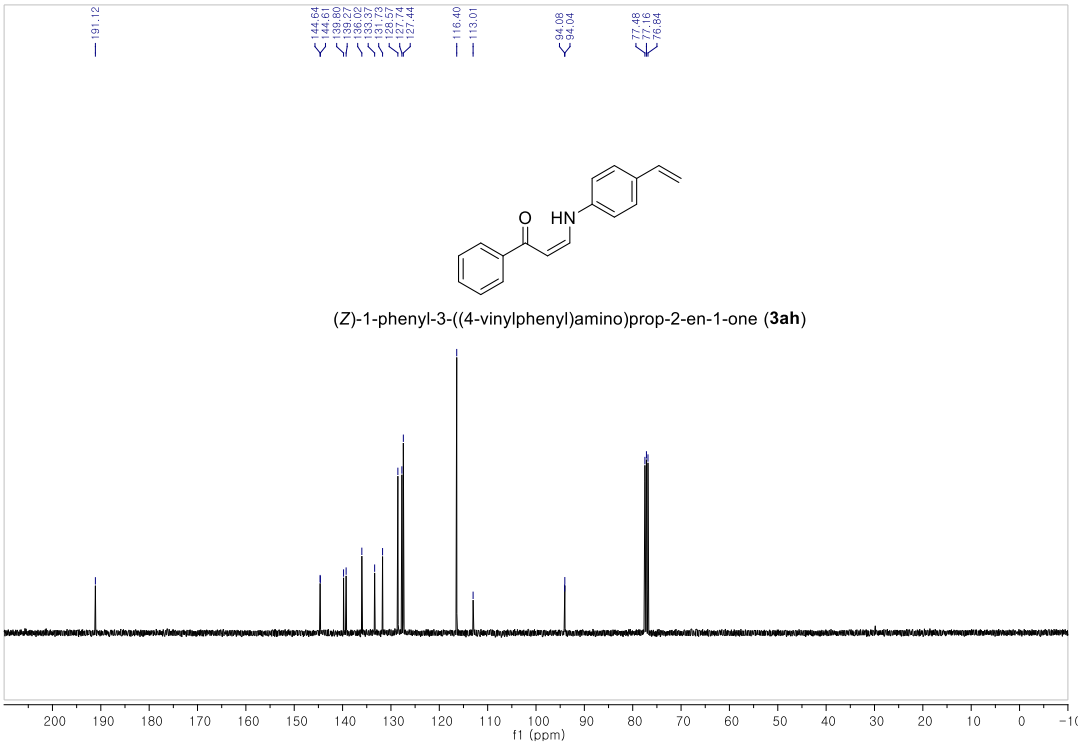
(*Z*)-3-([1,1'-biphenyl]-2-ylamino)-1-phenylprop-2-en-1-one (**3ag**)

^{13}C NMR ($CDCl_3$, 101 MHz)

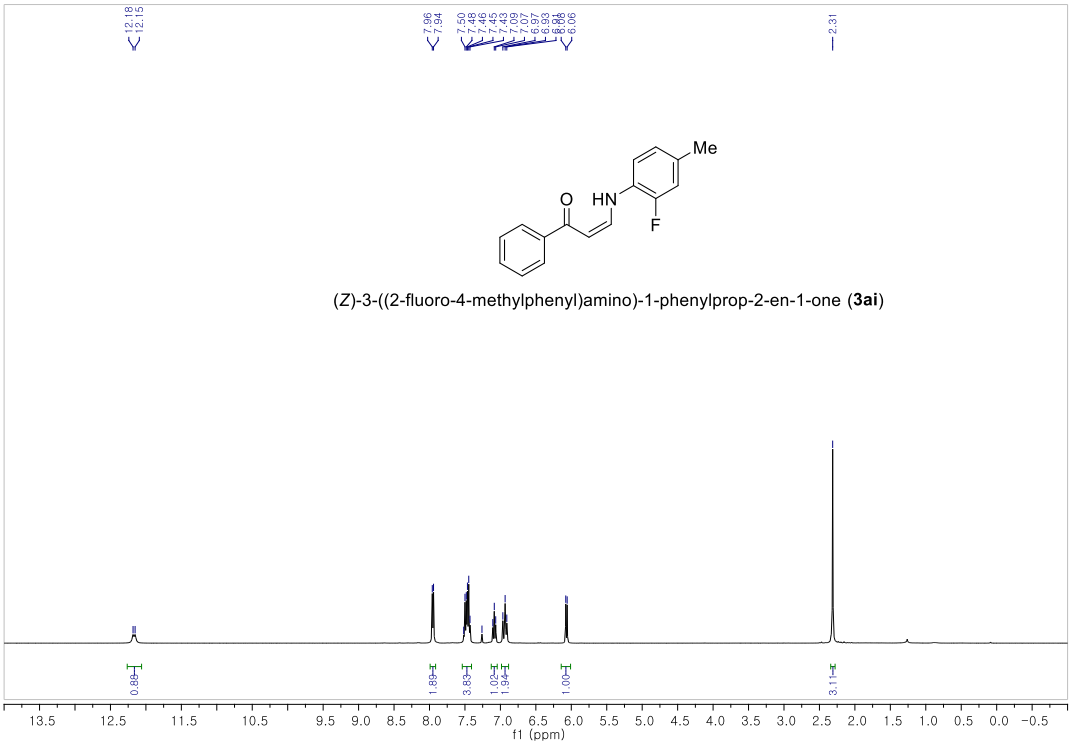


(*Z*)-1-phenyl-3-((4-vinylphenyl)amino)prop-2-en-1-one (**3ah**)

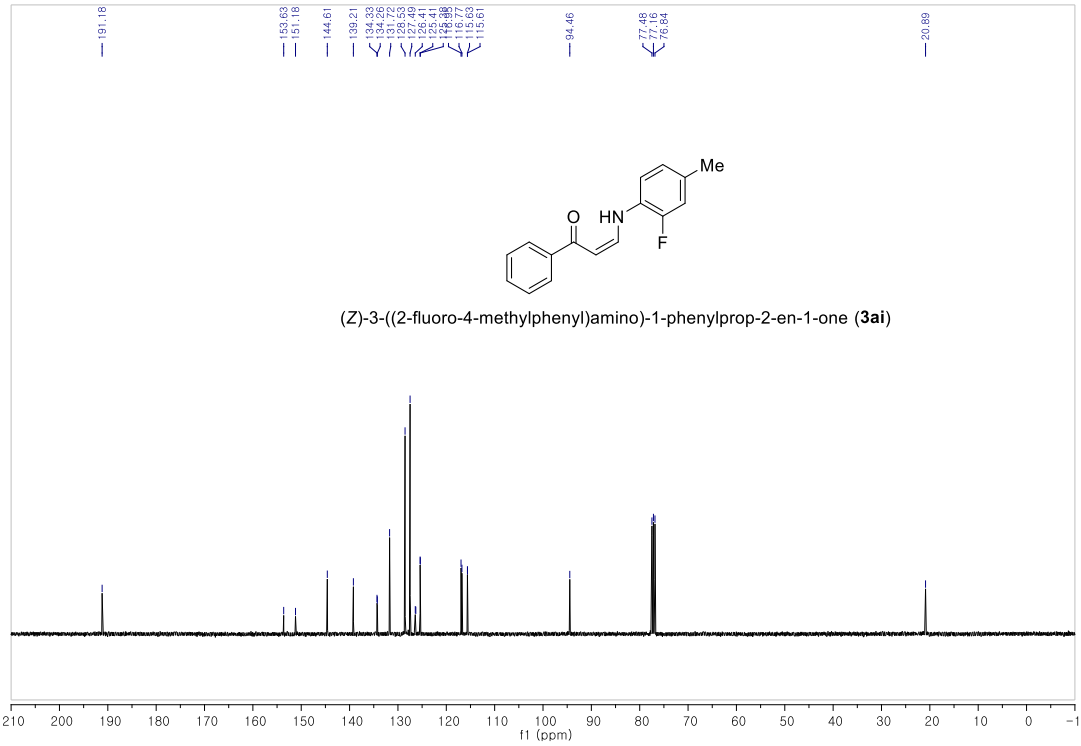
^{1}H NMR ($CDCl_3$, 499 MHz)



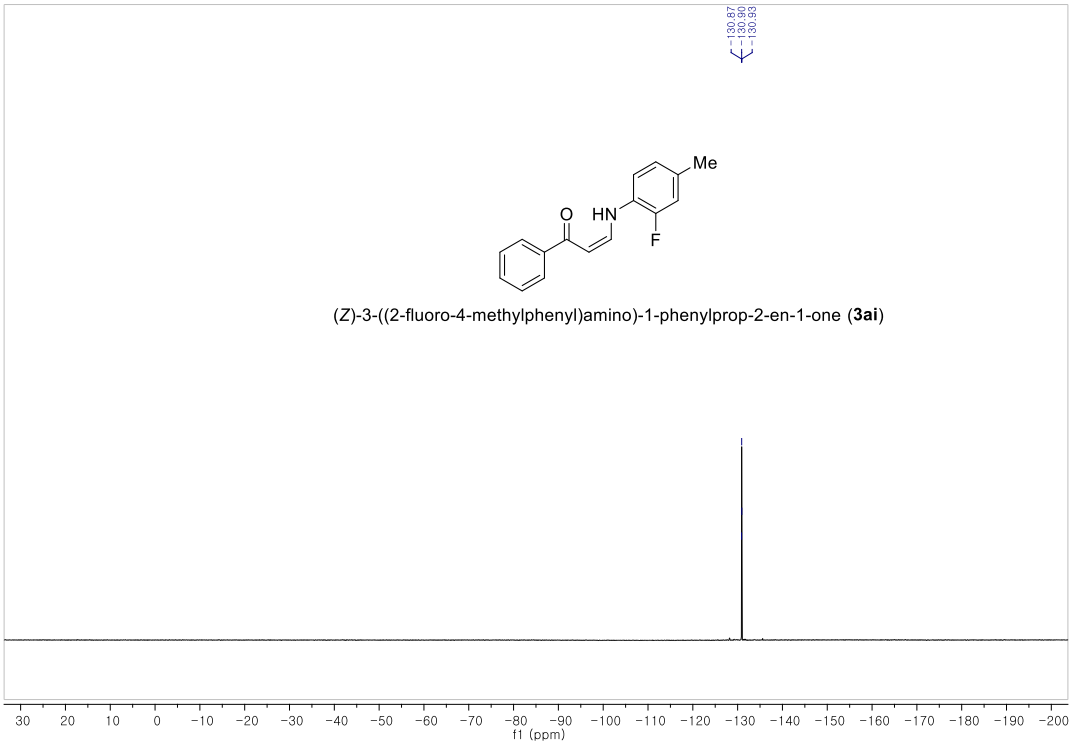
^{13}C NMR ($CDCl_3$, 101 MHz)



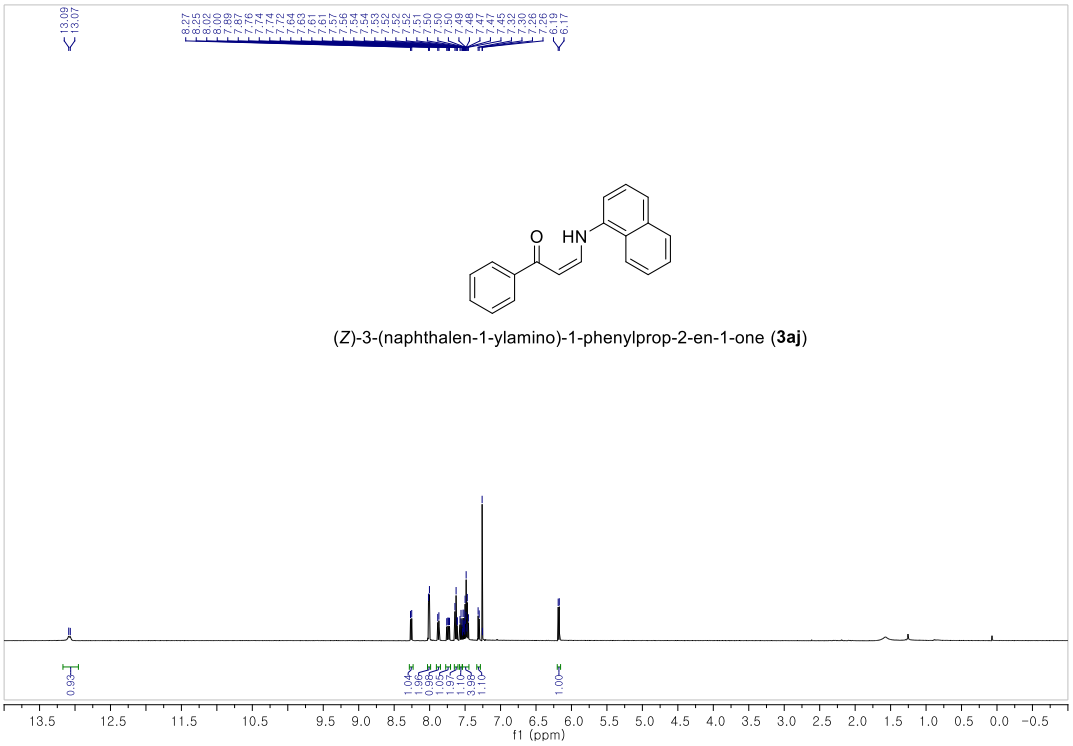
^{1}H NMR ($CDCl_3$, 400 MHz)



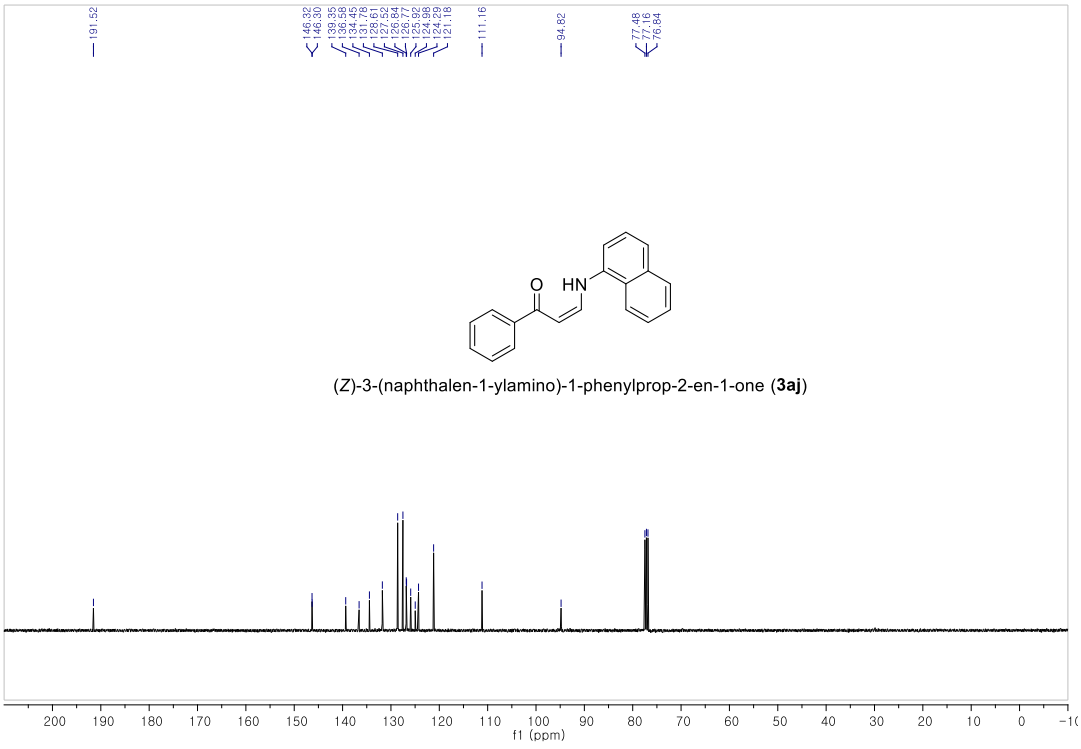
^{13}C NMR ($CDCl_3$, 101 MHz)



^{19}F NMR ($CDCl_3$, 376 MHz)



^{1}H NMR ($CDCl_3$, 499 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)