

Supporting Information

For

Dehydration in Water: Frustrated Lewis Pairs Catalyzed Directly

Allylization of Electron-Rich Arenes and Allyl Alcohols

Hua Zhang^{a,b}, Xiao-Yu Zhan^{a,b}, Yu Dong^{a,b}, Jian Yang^{a,b}, Shuai He^c, Zhi-Chuan Shi^c,
Xiao-Mei Zhang^a, Ji-Yu Wang^{*,a}

^aChengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, P. R. China.

^bUniversity of Chinese Academy of Sciences, Beijing 100049, P. R. China.

^cSouthwest Minzu University, Chengdu 610041, P. R. China.

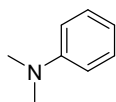
E-mail: Jiyuwang@cioc.ac.cn

Contents

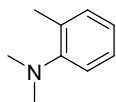
| | |
|-------------------------------------|----------|
| 1. General Information | S2-S4 |
| 2. Substrate of Synthesis | S4-S6 |
| 3. Typical Synthesis Procedure of 3 | S6 |
| 4. Characterization of 3 | S7-S25 |
| 5. X-Ray Analysis | S26 |
| 6. References | S27-S28 |
| 7. Copies of NMR Spectra | S29-S106 |

1. General Information:

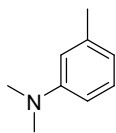
All template reaction experiments were carried out under atmospheric conditions. Thin layer chromatography was carried out in the ultraviolet light using a GF-254 silica gel plate. Column chromatography was carried out using 200-300 mesh silica gel. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 400 MHz on an Agilent spectrometer. CDCl_3 was used as solvent. Chemical shifts were referenced relative to residual solvent. Coupling constants (J) were reported in Hertz (Hz). HRMS were performed on a Thermo Scientific LTQ Orbitrap XL instrument. Melting points were measured with micro melting point apparatus. Tris(pentafluorophenyl)borane (energy chemical, 97%), 2,6-lutidine (kelong, 99%), N,N-dimethylaniline (**1a**, rhawn, 98%), 1,2,3-trimethoxybenzene (**1l**, bidepharm, 98%), 1H-indole (**1m**, bidepharm, 98%), 1-methyl-1H-indole (**1n**, adamas, 98%), 2-methyl-1H-indole (**1r**, bide, 98%), 2-phenyl-1H-indole (**1s**, adamas, 98%), 5-methoxy-1H-indole (**1t**, bidepharm, 98%), 6-chloro-1H-indole (**1u**, adamas, 98%), 5,6-dichloro-1H-indole (**1v**, bidepharm, 98%) were commercial available, and the N-substituted aromatic amines **1b-1e**, **1h-1k**^[1], N-cycloarylamines **1f-1g**^[2], **1o**^[3], **1p**^[4], **1q**^[5] and **2a-2r**^{[6], [7]} were prepared according to literature.



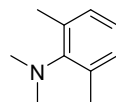
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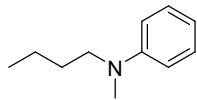
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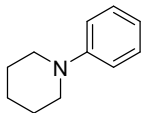
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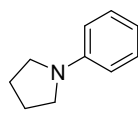
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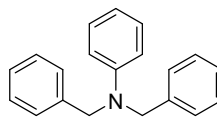
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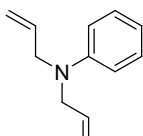
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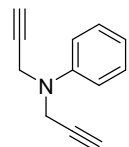
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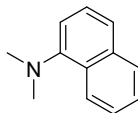
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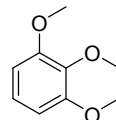
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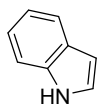
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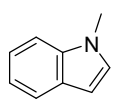
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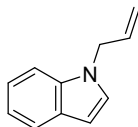
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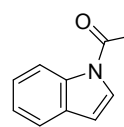
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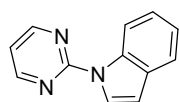
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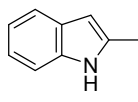
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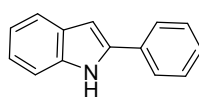
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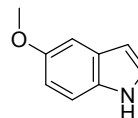
1q



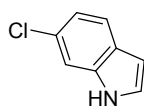
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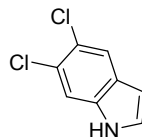
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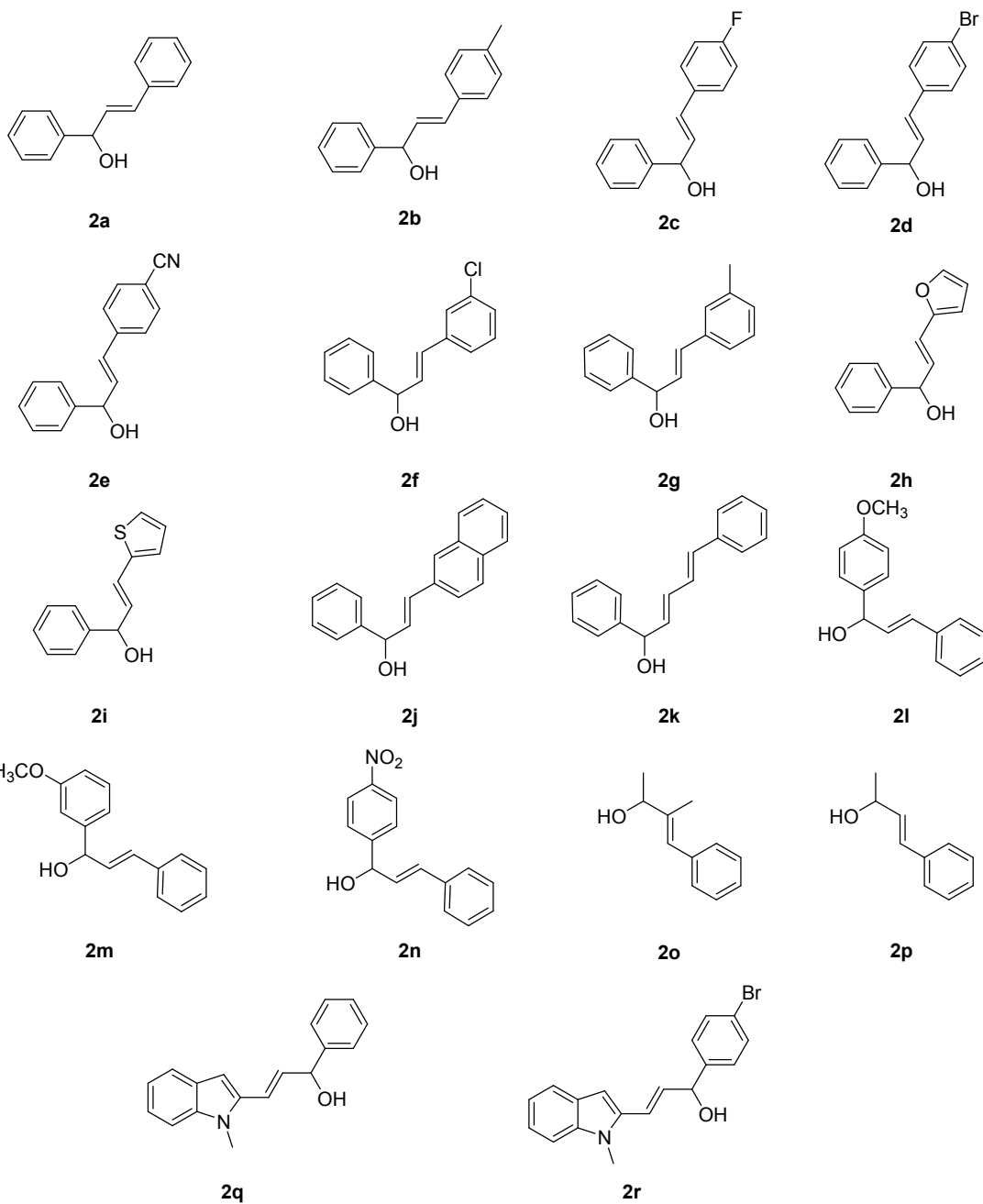
1t



1u

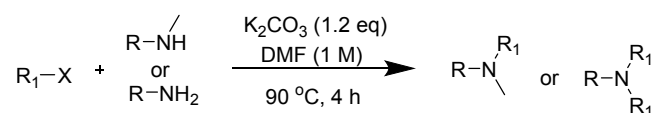


1v



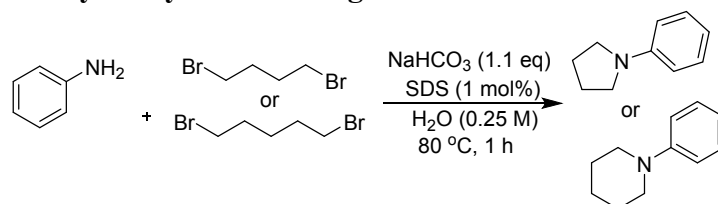
2. Substrate synthesis:

(a) Synthesis of N-substituted aromatic amines 1b-1e, 1h-1k^[1]



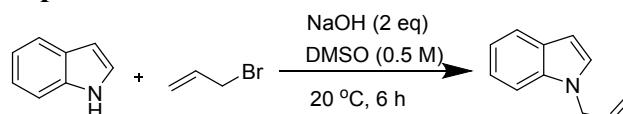
The experimental procedure for the synthesis of N-substituted aromatic amines (1b-1e, 1h-1k), please see: H. Shen, X. Zhang, Q. Liu, J. Pan, W. Hu, Y. Xiong and X. Zhu, Direct oxidative cyanation of tertiary amines promoted by in situ generated hypervalent iodine (III)-CN intermediate, *Tetrahedron Lett.*, 2015, **56**, 5628-5631.

(b) Synthesis of N-cycloarylamines 1f-1g^[2]



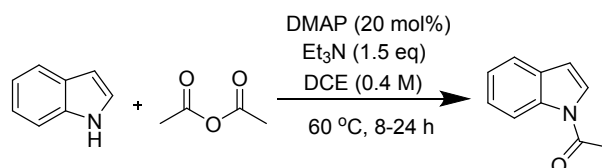
The experimental procedure for the synthesis of N-cycloarylamines (1f-1g), please see: X.-Z. Shu, Y.-F. Yang, Xiao-Feng Xia, K.-G. Ji, X.-Y. Liu and Y.-M. Liang, Platinum-catalyzed cross-dehydrogenative coupling reaction in the absence of oxidant, *Org. Biomol. Chem.*, 2010, **8**, 4077-4079.

(c) Synthesis of compounds 1o^[3]



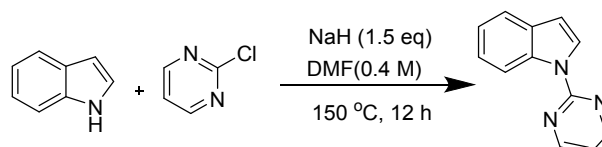
The experimental procedure for the synthesis of N-1-allyl-1H-indole (1o), please see: S. Olguín-Urbe, M. V. Mijangos, Y. A. Amador-Sánchez, M. A. Sánchez-Carmona and L. D. Miranda, Expedited Synthesis of Matrine Analogues through an Oxidative Cascade Addition/Double-Cyclization Radical Process, *Eur. J. Org. Chem.*, 2017, 2481-2485.

(d) Synthesis of compounds 1p^[4]



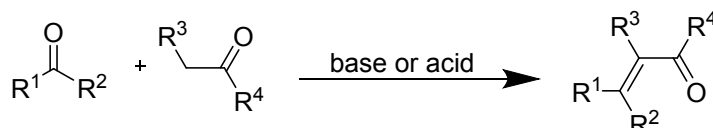
The experimental procedure for the synthesis of 1-(1H-indol-1-yl)ethan-1-one (1p), please see: Z.-L. Yan, W.-L. Chen, Y.-R. Gao, S. Mao, Y.-L. Zhang and Y.-Q. Wang, Palladium - Catalyzed Intermolecular C-2 Alkenylation of Indoles Using Oxygen as the Oxidant, *Adv. Synth. Catal.*, 2014, **356**, 1085-1092.

(e) Synthesis of compounds 1q^[5]

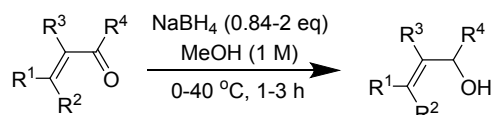


The experimental procedure for the synthesis of 1-(pyrimidin-2-yl)-1H-indole (1q), please see: M. Nishino, K. Hirano, T. Satoh and M. Miura, Copper-Mediated and Copper-Catalyzed Cross-Coupling of Indoles and 1,3-Azoles: Double C-H Activation, *Angew. Chem. Int. Ed.*, 2012, **51**, 6993-6997.

(f) Synthesis of compounds 2a-2r^{[6], [7]}

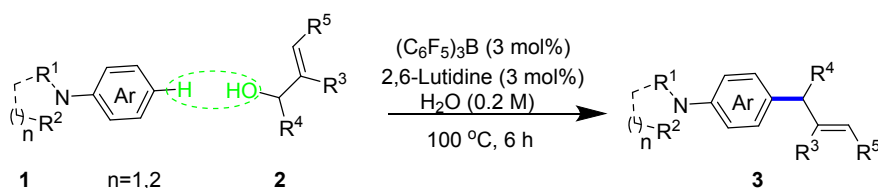


The experimental procedure for the synthesis of conjugated unsaturated ketones, please see: (a) B. Ding, Z. Zhang, Y. Liu, M. Sugiya and T. Imamoto, Chemoselective transfer hydrogenation of α , β -unsaturated ketones catalyzed by pincer-Pd complexes using alcohol as a hydrogen source, *Org. Lett.*, 2013, **15**, **14**, 3690-3693; (b) I. M. Ferreira, E. B. Meira, I. G. Rosset and A. L. M. Porto, Chemoselective biohydrogenation of α , β - and α , β , γ , δ -unsaturated ketones by the marine-derived fungus *Penicillium citrinum* CBMAI 1186 in a biphasic system, *Journal of Molecular Catalysis B: Enzymatic*, 2015, **115**, 59-65. (c) A. Sultan, A. R. Raza, M. Abbas, K. M. Khan, M. N. Tahir and N. Saari, Evaluation of silica-H₂SO₄ as an efficient heterogeneous catalyst for the synthesis of chalcones, *Molecules*, 2013, **18**, 10081-10094; (d) Z. Li, X. L. Chen, Y. J. Fu, W. Wang and M. Luo, A facile synthesis of trisubstituted alkenes from β -diketones and aldehydes with AlCl₃ as catalyst, *Res Chem Intermed.*, 2012, **38**, 25-35; (e) Y. H. He, Y. Hu and Z. Guan, Natural α -amino acid L-lysine-catalyzed Knoevenagel condensations of α , β -unsaturated aldehydes and 1, 3-dicarbonyl compounds, *Synthetic Communications*, 2011, **41**, 1617-1628; (f) Y. Ma, J. Li, J. Ye, D. Liu and W. Zhang, Synthesis of chiral chromanols via a RuPHOX-Ru catalyzed asymmetric hydrogenation of chromones, *Chem. Commun.*, 2018, **54**, 13571-13574.



The experimental procedure for the synthesis of conjugated unsaturated ketones, please see: W. Gladkowski, A. Skrobiszewski, M. Mazur, M. Siepka, A. Pawlak, B. Obmińska-Mrukowicz, A. Bialonska, D. Poradowski, A. Drynda and M. Urbaniak, Synthesis and anticancer activity of novel halolactones with β -aryl substituents from simple aromatic aldehydes, *Tetrahedron*. 2013, **69**, 10414-10423.

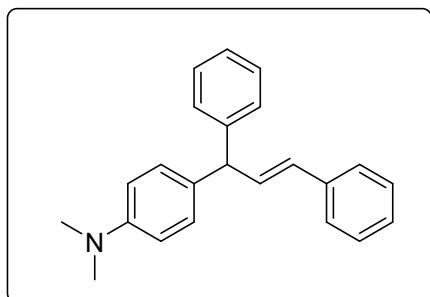
3. Typical Procedure for Synthesis of 3:



Add (C₆F₅)₃B (4.6 mg, 0.009 mmol), 2,6-lutidine (1 μ L, 0.009 mmol) and allyl alcohol (0.3 mmol) to the reaction tube and disperse immediately with water (1.5 ml). Afterwards, **compound 1** (0.3 mmol) were added. The solution was heated to 100 °C. The solution was kept at 100 °C for 6 h. Then the solution was diluted with saturated brine. Ethyl acetate extracted and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by column chromatography on silica gel using ethyl acetate/petroleum ether as eluent to give **3**.

4. Characterization of 3:

(E)-4-(1,3-diphenylallyl)-N,N-dimethylaniline (3a)^[8]



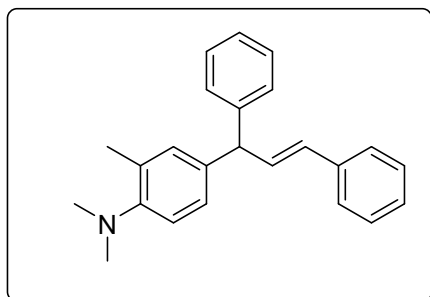
3a

White solid, m.p. 50-53°C, 87 mg, yield: 92%; $R_f = 0.30$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.45 (d, $J = 7.6$ Hz, 2H), 7.32 (dp, $J = 29.0, 8.2$ Hz, 8H), 7.19 (d, $J = 7.1$ Hz, 2H), 6.83-6.70 (m, 3H), 6.42 (d, $J = 15.8$ Hz, 1H), 4.89 (d, $J = 7.5$ Hz, 1H), 3.00 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.29, 144.25, 137.53, 133.38, 131.48, 130.83, 129.32, 128.69, 128.53, 128.44, 127.18, 126.33, 126.26, 112.78, 53.31, 40.79.

(E)-4-(1,3-diphenylallyl)-N,N,2-trimethylaniline (3b)



3b

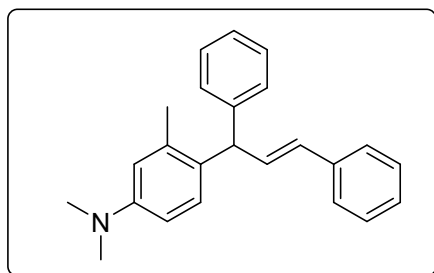
Colorless oil, 69 mg, yield: 68%; $R_f = 0.35$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.39 (dd, $J = 7.1, 1.5$ Hz, 2H), 7.37-7.17 (m, 8H), 7.08-6.95 (m, 3H), 6.68 (dd, $J = 15.8, 7.7$ Hz, 1H), 6.37 (d, $J = 15.8$ Hz, 1H), 4.83 (d, $J = 7.7$ Hz, 1H), 2.70 (s, 6H), 2.31 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 143.91, 137.50, 137.44, 133.02, 132.08, 131.36, 131.00, 128.63, 128.48, 128.42, 127.20, 126.45, 126.31, 126.30, 118.34, 53.68, 44.31, 18.48.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{26}\text{N}$ $[\text{MH}]^+$: 328.2060, found: 328.2056.

(E)-4-(1,3-diphenylallyl)-N,N,3-trimethylaniline (3c)



3c

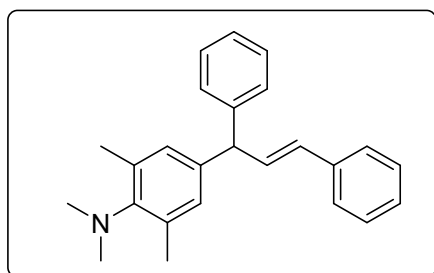
Colorless oil, 37 mg, yield: 38%; $R_f = 0.45$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.38 (d, $J = 7.3$ Hz, 2H), 7.36-7.26 (m, 4H), 7.26-7.17 (m, 4H), 7.07 (d, $J = 8.7$ Hz, 1H), 6.69 (dd, $J = 15.9, 6.8$ Hz, 1H), 6.61 (d, $J = 7.3$ Hz, 2H), 6.27-6.19 (m, 1H), 5.02 (d, $J = 6.8$ Hz, 1H), 2.95 (s, 6H), 2.28 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.27, 143.64, 137.62, 137.01, 133.33, 130.80, 129.88, 129.30, 128.87, 128.47, 128.29, 127.07, 126.27, 126.09, 114.97, 110.40, 49.71, 40.71, 20.31.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{26}\text{N}$ $[\text{MH}]^+$: 328.2060, found: 328.2063.

(E)-4-(1,3-diphenylallyl)-N,N,2,6-tetramethylaniline (3d)



3d

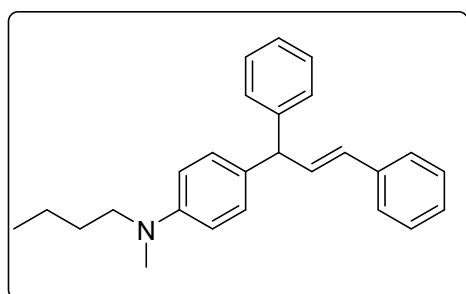
Colorless oil, 61 mg, yield: 60%; $R_f = 0.32$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.40-7.33 (m, 2H), 7.35-7.24 (m, 6H), 7.26-7.15 (m, 5H), 6.83 (s, 2H), 6.64 (dd, $J = 15.8, 7.8$ Hz, 1H), 6.34 (d, $J = 15.9$ Hz, 1H), 4.75 (d, $J = 7.8$ Hz, 1H), 2.78 (s, 6H), 2.23 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 143.84, 139.48, 137.42, 136.92, 132.96, 130.89, 128.76, 128.58, 128.45, 128.37, 127.16, 126.29, 126.25, 53.78, 42.51, 19.21.

HRMS (m/z): calcd for $\text{C}_{25}\text{H}_{28}\text{N}$ $[\text{MH}]^+$: 342.2216, found: 342.2218.

(E)-N-butyl-4-(1,3-diphenylallyl)-N-methylaniline (3e)



3e

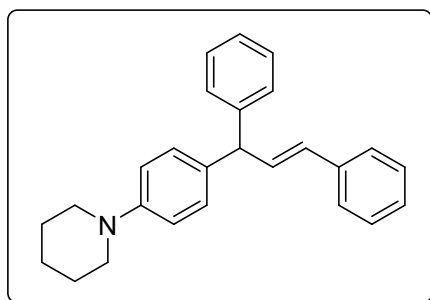
Colorless oil, 70 mg, yield: 66%; $R_f = 0.39$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36 (d, $J = 7.0$ Hz, 2H), 7.33-7.22 (m, 7H), 7.19 (tdd, $J = 7.2, 4.7, 2.3$ Hz, 3H), 7.07 (d, $J = 8.3$ Hz, 2H), 6.71-6.58 (m, 3H), 6.33 (d, $J = 14.5$ Hz, 1H), 4.79 (d, $J = 7.6$ Hz, 1H), 3.30-3.23 (m, 2H), 2.90 (s, 3H), 1.55-1.49 (m, 2H), 1.36-1.28 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 137.54, 133.43, 130.69, 129.29, 128.61, 128.42, 128.32, 127.05, 126.25, 126.14, 112.10, 53.26, 52.64, 38.31, 28.87, 20.33, 13.96.

HRMS (m/z): calcd for $\text{C}_{26}\text{H}_{30}\text{N}$ $[\text{MH}]^+$: 356.2373, found: 356.2378.

(E)-1-(4-(1,3-diphenylallyl)phenyl)piperidine (3f)



3f

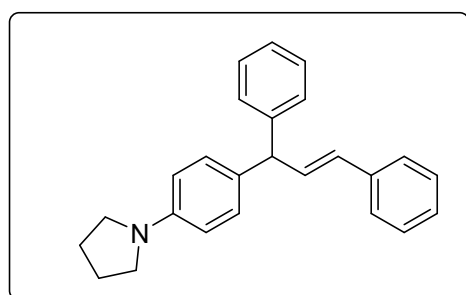
Colorless oil, 100 mg, yield: 94%; $R_f = 0.19$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42 (d, $J = 7.6$ Hz, 2H), 7.40-7.20 (m, 8H), 7.17 (d, $J = 8.2$ Hz, 2H), 6.96 (d, $J = 8.2$ Hz, 2H), 6.72 (dd, $J = 15.9, 7.5$ Hz, 1H), 6.39 (d, $J = 15.8$ Hz, 1H), 4.88 (d, $J = 7.4$ Hz, 1H), 3.18 (t, $J = 5.4$ Hz, 4H), 1.76 (p, $J = 5.6$ Hz, 4H), 1.62 (q, $J = 5.9$ Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 150.74, 144.07, 137.50, 134.13, 133.21, 131.01, 129.27, 128.72, 128.54, 128.45, 127.22, 126.34, 126.32, 116.59, 53.42, 50.80, 25.95, 24.33.

HRMS (m/z): calcd for $\text{C}_{26}\text{H}_{28}\text{N}$ $[\text{MH}]^+$: 354.2216, found: 354.2217.

(E)-1-(4-(1,3-diphenylallyl)phenyl)pyrrolidine (3g)



3g

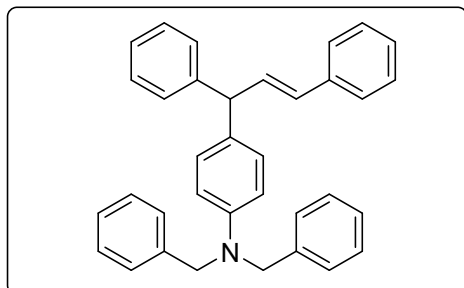
Colorless oil, 85 mg, yield: 83%; $R_f = 0.35$ (EtOAc/Petroleum ether 1:30)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.44-7.35 (m, 2H), 7.37-7.23 (m, 7H), 7.26-7.17 (m, 2H), 7.11 (d, $J = 6.5$ Hz, 2H), 6.70 (dd, $J = 15.8, 7.5$ Hz, 1H), 6.56 (d, $J = 6.6$ Hz, 2H), 6.36 (d, $J = 15.8$ Hz, 1H), 4.83 (d, $J = 7.5$ Hz, 1H), 3.36-3.22 (m, 4H), 2.05-1.95 (m, 4H).

¹³C NMR (101 MHz, CDCl₃): δ 146.59, 144.43, 137.61, 133.58, 130.70, 129.39, 128.65, 128.46, 128.34, 127.07, 126.29, 126.13, 111.70, 53.34, 47.70, 25.47.

HRMS (m/z): calcd for C₂₅H₂₆N [MH]⁺: 340.2060, found: 340.2057.

(E)-N,N-dibenzyl-4-(1,3-diphenylallyl)aniline (3h)



3h

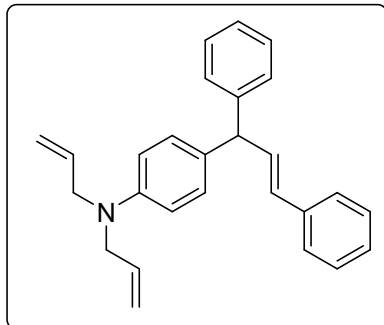
Colorless oil, 129 mg, yield: 93%; R_f = 0.32 (EtOAc/Petroleum ether 1:30).

¹H NMR (400 MHz, CDCl₃): δ 7.52-7.08 (m, 20H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.75-6.59 (m, 3H), 6.33 (d, *J* = 15.8 Hz, 1H), 4.77 (d, *J* = 7.7 Hz, 1H), 4.63 (s, 4H).

¹³C NMR (101 MHz, CDCl₃): δ 144.10, 137.48, 133.28, 130.73, 129.27, 129.20, 128.60, 128.44, 128.36, 127.10, 126.90, 126.26, 126.20, 54.47, 53.34.

HRMS (m/z): calcd for C₃₅H₃₂N [MH]⁺: 466.2529, found: 466.2533.

(E)-N,N-diallyl-4-(1,3-diphenylallyl)aniline (3i)



3i

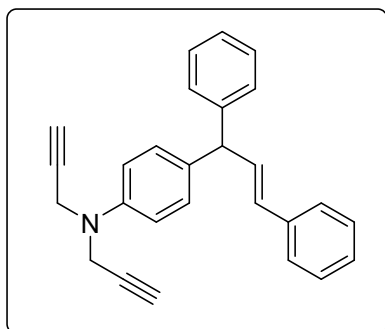
Colorless oil, 91 mg, yield: 83%; R_f = 0.51 (EtOAc/Petroleum ether 1:30).

¹H NMR (400 MHz, CDCl₃): δ 7.34 (d, *J* = 8.9 Hz, 2H), 7.32-7.20 (m, 6H), 7.16 (q, *J* = 7.1 Hz, 2H), 7.07-7.00 (m, 2H), 6.63 (q, *J* = 7.5 Hz, 3H), 6.32 (d, *J* = 14.6 Hz, 1H), 5.82 (ddd, *J* = 22.1, 10.1, 4.9 Hz, 2H), 5.20-5.08 (m, 4H), 4.76 (d, *J* = 7.6 Hz, 1H), 3.90-3.83 (m, 4H).

¹³C NMR (101 MHz, CDCl₃): δ 147.36, 144.28, 137.60, 134.23, 133.46, 131.18, 130.77, 129.27, 128.70, 128.51, 128.42, 127.15, 126.34, 126.24, 116.09, 112.44, 53.38, 52.89.

HRMS (m/z): calcd for C₂₇H₂₈N [MH]⁺: 366.2216, found: 366.2217.

(E)-4-(1,3-diphenylallyl)-N,N-di(prop-2-yn-1-yl)aniline (3j)



3j

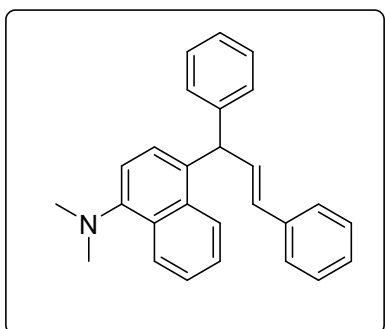
Colorless oil, 92 mg, yield: 85%; $R_f = 0.35$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42 (d, $J = 7.2$ Hz, 2H), 7.41-7.18 (m, 10H), 6.97 (d, $J = 8.6$ Hz, 2H), 6.72 (dd, $J = 15.8, 7.5$ Hz, 1H), 6.40 (d, $J = 15.8$ Hz, 1H), 4.89 (d, $J = 7.5$ Hz, 1H), 4.15 (d, $J = 2.4$ Hz, 4H), 2.29 (t, $J = 2.3$ Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 146.33, 143.89, 137.44, 134.80, 133.04, 131.13, 129.42, 128.72, 128.57, 128.50, 127.29, 126.41, 126.36, 115.86, 79.37, 72.79, 53.42, 40.55.

HRMS (m/z): calcd for $\text{C}_{27}\text{H}_{24}\text{N}$ $[\text{MH}]^+$: 362.1903, found: 362.1901.

(E)-4-(1,3-diphenylallyl)-N,N-dimethylnaphthalen-1-amine (3k)



3k

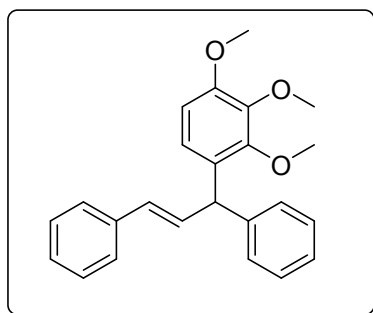
Colorless oil, 96 mg, yield: 88%; $R_f = 0.19$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.30 (d, $J = 8.3$ Hz, 1H), 8.00 (d, $J = 6.9$ Hz, 1H), 7.45-7.36 (m, 2H), 7.32 (d, $J = 7.2$ Hz, 2H), 7.30-7.20 (m, 7H), 7.18 (dd, $J = 10.1, 6.7$ Hz, 2H), 7.01 (d, $J = 7.8$ Hz, 1H), 6.78 (dd, $J = 15.9, 6.8$ Hz, 1H), 6.25 (d, $J = 16.0$ Hz, 1H), 5.57 (d, $J = 6.2$ Hz, 1H), 2.86 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 143.45, 137.46, 133.84, 133.09, 132.95, 131.64, 129.36, 128.98, 128.55, 128.51, 127.29, 126.49, 126.45, 126.37, 125.95, 124.88, 124.82, 124.66, 113.62, 49.98, 45.41.

HRMS (m/z): calcd for $\text{C}_{27}\text{H}_{26}\text{N}$ $[\text{MH}]^+$: 364.2060, Found: 364.2065.

(E)-(3-(2,3,4-trimethoxyphenyl)prop-1-ene-1,3-diyl)dibenzene (3l)



31

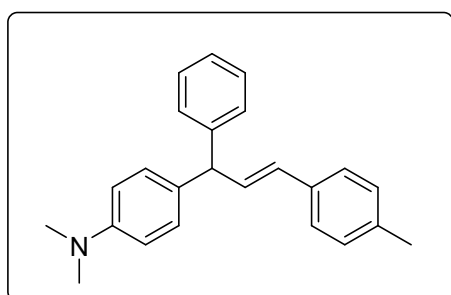
Colorless oil, 36 mg, yield: 33%; $R_f = 0.26$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36 (d, $J = 7.0$ Hz, 2H), 7.32-7.15 (m, 8H), 6.87 (d, $J = 8.6$ Hz, 1H), 6.71-6.61 (m, 2H), 6.28 (d, $J = 14.4$ Hz, 1H), 5.21 (d, $J = 8.9$ Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.64 (s, 3H).

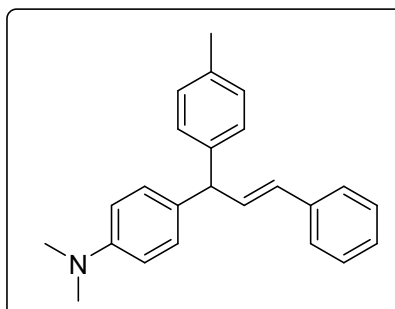
$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 152.46, 151.66, 143.84, 142.46, 137.45, 132.76, 131.15, 129.83, 128.57, 128.46, 128.25, 127.15, 126.25, 126.15, 123.49, 107.07, 60.77, 60.67, 55.95, 47.27.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{25}\text{O}_3$ $[\text{MH}]^+$: 361.1798, found: 361.1792.

(E)-N,N-dimethyl-4-(1-phenyl-3-(p-tolyl)allyl)aniline(3m1) and (E)-N,N-dimethyl-4-(3-phenyl-1-(p-tolyl)allyl)aniline (3m2)



3m1



3m2

Colorless oil, 90 mg, yield: 92%; 3m1:3m2=1:1, $R_f=0.21$ (EtOAc/Petroleum ether 1:30).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.44 (d, $J = 8.5$ Hz, 1H), 7.41-7.12 (m, 10H), 6.81-6.65 (m, 3H), 6.39 (dd, $J = 15.9, 10.6$ Hz, 1H), 4.86 (t, $J = 7.9$ Hz, 1H), 2.98 (d, $J = 1.6$ Hz, 6H), 2.39 (d, $J = 4.1$ Hz, 3H).

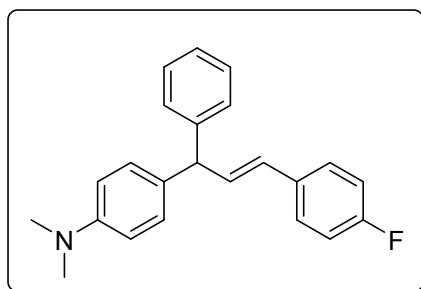
$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.17, 133.59, 132.38, 130.74, 130.70, 129.36, 129.31, 129.24, 129.16, 128.71, 128.57, 128.52, 128.42, 127.14, 126.34, 126.25, 126.23, 112.97, 112.94, 53.35, 52.97, 40.89, 40.88, 21.24, 21.11.

HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{26}\text{N}$ $[\text{MH}]^+$: 328.2060, found: 328.2063.

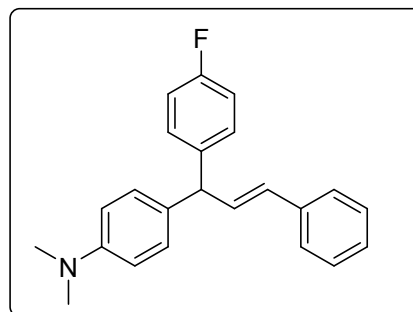
(E)-4-(3-(4-fluorophenyl)-1-phenylallyl)-N,N-dimethylaniline (3n1)

and (E)-4-(1-(4-fluorophenyl)-3-phenylallyl)-N,N-

dimethylaniline(3n2)



3n1



3n2

Colorless oil, 85 mg, yield: 86%; 3n1:3n2=1:1, R_f =0.39 (EtOAc/Petroleum ether 1:20).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36-7.11 (m, 7H), 7.09-7.01 (m, 2H), 6.99-6.87 (m, 2H), 6.67 (d, J = 6.7 Hz, 2H), 6.63-6.50 (m, 1H), 6.26 (dd, J = 15.8, 8.4 Hz, 1H), 4.75 (d, J = 8.6 Hz, 1H), 2.87 (d, J = 1.9 Hz, 6H).

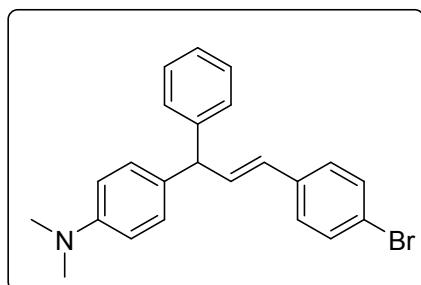
$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.30, 133.19, 133.17, 131.46, 130.99, 130.10, 130.02, 129.66, 129.28, 129.23, 128.63, 128.54, 128.44, 127.79, 127.71, 127.27, 126.32, 126.29, 115.45, 115.24, 115.03, 112.83, 53.28, 52.52, 40.75, 40.72.

HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{23}\text{FN}$ $[\text{MH}]^+$: 332.1809, Found: 332.1807.

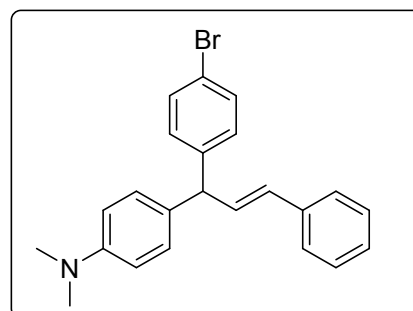
(E)-4-(3-(4-bromophenyl)-1-phenylallyl)-N,N-dimethylaniline (3o1)

and (E)-4-(1-(4-bromophenyl)-3-phenylallyl)-N,N-

dimethylaniline(3o2)



3o1



3o2

Colorless oil, 99 mg, yield: 85%; 3o1:3o2=1:1, R_f =0.29 (EtOAc/Petroleum ether 1:30).

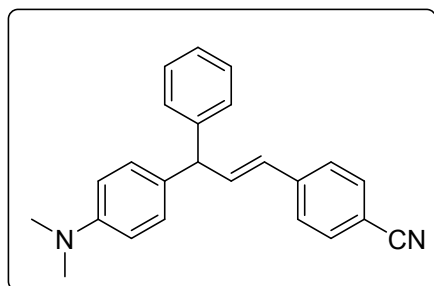
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.39 (dd, J = 13.7, 8.1 Hz, 3H), 7.31 (q, J = 7.4 Hz, 3H), 7.24 (dd, J = 8.4, 6.3 Hz, 3H), 7.16-7.02 (m, 3H), 6.74 (dd, J = 8.8, 3.2 Hz, 2H), 6.65 (ddd, J = 20.1, 15.8, 7.4 Hz, 1H), 6.31 (dd, J = 21.0, 15.8 Hz, 1H), 4.80 (dd, J = 13.3, 7.4 Hz, 1H), 2.94 (d, J = 1.2 Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 134.22, 132.64, 131.54, 131.43, 131.23, 130.41, 129.70, 129.27, 129.22, 128.59, 128.53, 128.44, 127.84, 127.31, 126.33, 126.31, 53.28, 52.69, 40.82, 40.77.

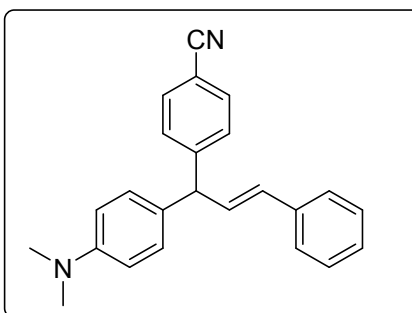
HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{23}\text{BrN}$ $[\text{MH}]^+$: 392.1008, Found: 392.1011.

(E)-4-(3-(4-(dimethylamino)phenyl)-3-phenylprop-1-en-1-

yl)benzointrile (3p1) and (E)-4-(1-(4-(dimethylamino)phenyl)-3-phenylallyl)benzointrile (3p2)



3p1



3p2

Colorless oil, 77 mg, yield: 76%; 3p1:3p2=5:2, $R_f=0.1$ (EtOAc/Petroleum ether 1:20).

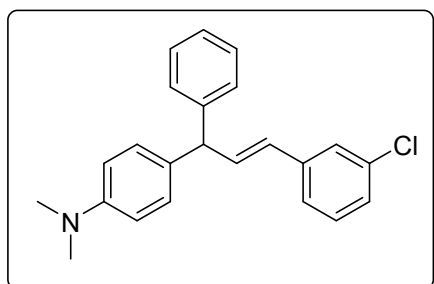
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.60-7.54 (m, 2H), 7.44-7.20 (m, 7H), 7.07 (t, $J = 9.0$ Hz, 2H), 6.84-6.78 (m, 1H), 6.71 (d, $J = 8.8$ Hz, 2H), 6.33 (dt, $J = 15.9, 1.8$ Hz, 1H), 4.84 (dd, $J = 7.6, 4.1$ Hz, 1H), 2.94 (d, $J = 2.7$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.95, 149.40, 143.40, 142.02, 137.57, 136.98, 132.32, 132.21, 132.07, 131.86, 131.67, 130.50, 129.75, 129.39, 129.34, 129.22, 129.19, 128.63, 128.57, 128.55, 128.52, 128.13, 127.52, 126.74, 126.49, 126.44, 126.32, 119.06, 112.77, 110.29, 110.05, 53.33, 53.28, 40.64, 40.58.

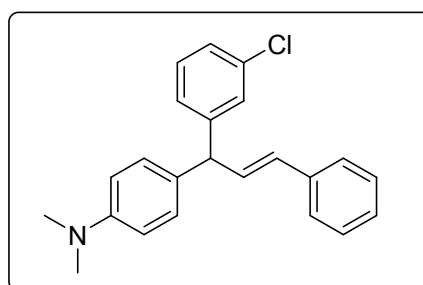
HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$ $[\text{MH}]^+$: 339.1856, Found:339.1860.

(E)-4-(3-(3-chlorophenyl)-1-phenylallyl)-N,N-dimethylaniline (3q1)

and (E)-4-(1-(3-chlorophenyl)-3-phenylallyl)-N,N-dimethylaniline(3q2)



3q1



3q2

Colorless oil, 79 mg, yield: 76%; 3q1:3q2=1:1, $R_f=0.39$ (EtOAc/Petroleum ether 1:20).

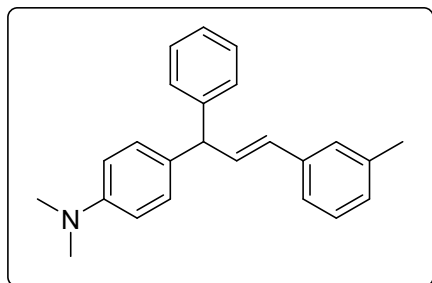
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.34-6.99 (m, 11H), 6.65 (d, $J = 8.6$ Hz, 2H), 6.63-6.51 (m, 1H), 6.24 (dd, $J = 27.4, 15.8$ Hz, 1H), 4.73 (dd, $J = 12.5, 7.5$ Hz, 1H), 2.86 (d, $J = 2.2$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 134.99, 132.48, 131.34, 129.69, 129.62, 129.56, 129.26, 129.23, 128.70, 128.61, 128.53, 128.46, 127.33, 127.05, 126.87, 126.43,

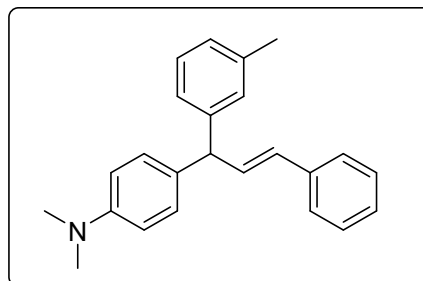
126.35, 126.20, 124.53, 112.85, 53.25, 53.02, 40.75, 40.70.

HRMS (m/z): calcd for C₂₃H₂₃ClN [MH]⁺: 348.1514, Found: 348.1511.

(E)-N,N-dimethyl-4-(1-phenyl-3-(m-tolyl)allyl)aniline (3r1) and (E)-N,N-dimethyl-4-(3-phenyl-1-(m-tolyl)allyl)aniline (3r2)



3r1



3r2

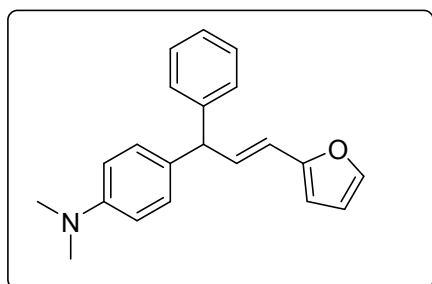
Colorless oil, 77 mg, yield: 78%; 3ab1:3ab2=3:2, R_f=0.22 (EtOAc/Petroleum ether 1:30).

¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, *J* = 7.4 Hz, 1H), 7.36-7.00 (m, 10H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.67 (ddd, *J* = 12.2, 7.5, 3.8 Hz, 1H), 6.34 (dd, *J* = 15.6, 12.7 Hz, 1H), 4.81 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.94 (s, 6H), 2.34 (s, 3H).

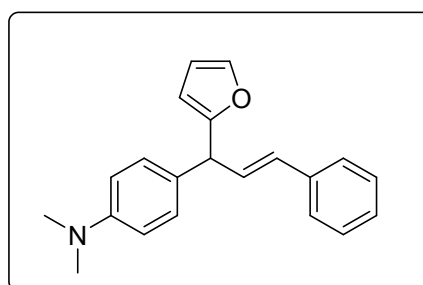
¹³C NMR (101 MHz, CDCl₃): δ 133.47, 133.16, 130.89, 130.69, 129.34, 129.28, 129.25, 128.65, 128.45, 128.37, 128.36, 128.26, 127.91, 127.08, 126.99, 126.30, 126.17, 125.68, 123.46, 112.85, 53.30, 40.78, 21.51, 21.38.

HRMS (m/z): calcd for C₂₄H₂₆N [MH]⁺: 328.2060, found: 328.2065.

(E)-4-(3-(furan-2-yl)-1-phenylallyl)-N,N-dimethylaniline (3s1) and (E)-4-(1-(furan-2-yl)-3-phenylallyl)-N,N-dimethylaniline (3s2)



3s1



3s2

Colorless oil, 64 mg, yield: 70%; 3s1:3s2=1:1, R_f=0.47 (EtOAc/Petroleum ether 1:20).

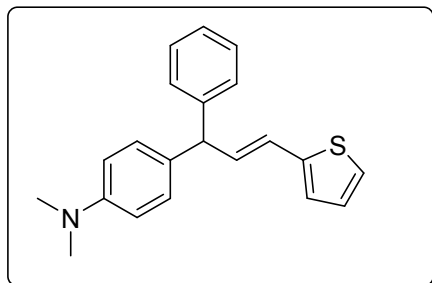
¹H NMR (400 MHz, CDCl₃): δ 7.40-7.10 (m, 8H), 6.85 (s, 2H), 6.60 (ddd, *J* = 26.9, 15.8, 6.8 Hz, 1H), 6.44-6.06 (m, 3H), 4.82 (dd, *J* = 14.4, 7.3 Hz, 1H), 2.96 (d, *J* = 1.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 152.96, 141.71, 141.55, 137.19, 131.15, 130.26, 129.49, 129.04, 128.61, 128.47, 128.43, 128.26, 127.33, 126.37, 126.34, 119.74, 111.19, 110.11, 107.13, 106.51, 53.08, 47.50.

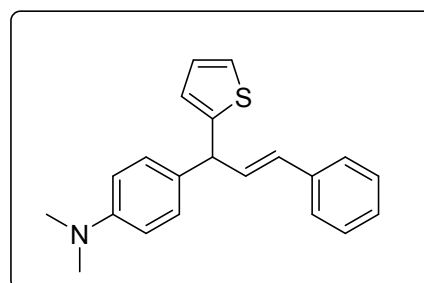
HRMS (m/z): calcd for C₂₁H₂₂NO [MH]⁺: 304.1696, found: 304.1698.

(E)-N,N-dimethyl-4-(1-phenyl-3-(thiophen-2-yl)allyl)aniline (3t1) and

(E)-N,N-dimethyl-4-(3-phenyl-1-(thiophen-2-yl)allyl)aniline (3t2)



3t1



3t2

Colorless oil, 64 mg, yield: 67%; 3t1:3t2=1:1, R_f=0.27 (EtOAc/Petroleum ether 1:30).

¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 7.7 Hz, 1H), 7.34 (q, *J* = 7.3 Hz, 2H), 7.30 – 7.12 (m, 5H), 7.02 – 6.87 (m, 2H), 6.79 – 6.73 (m, 2H), 6.72-6.54 (dd, *J* = 15.6, 7.0 Hz, 1H), 6.50-6.44 (dd, *J* = 15.8, 10.3 Hz, 1H), 5.04-4.82 (d, *J* = 6.9 Hz, 1H), 2.97 (s, 6H).

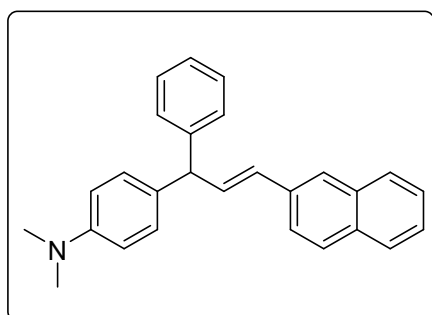
¹³C NMR (101 MHz, CDCl₃): δ 149.58, 149.31, 148.74, 143.93, 142.78, 137.29, 133.31, 132.72, 131.17, 130.63, 129.35, 128.91, 128.70, 128.53, 128.45, 127.33, 127.30, 126.74, 126.45, 126.32, 125.04, 124.85, 124.24, 124.16, 123.62, 112.80, 112.76, 53.10, 48.91, 40.76, 40.72.

HRMS (m/z): calcd for C₂₁H₂₂NS [MH]⁺: 320.1467, Found:320.1470.

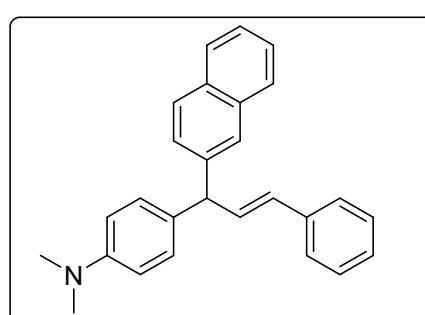
(E)-N,N-dimethyl-4-(3-(naphthalen-2-yl)-1-phenylallyl)aniline (3u1)

and (E)-N,N-dimethyl-4-(1-(naphthalen-2-yl)-3-phenylallyl)aniline

(3u2)



3u1



3u2

Colorless oil, 95 mg, yield: 87%; 3u1:3u2=1:1, R_f=0.18 (EtOAc/Petroleum ether 1:30).

¹H NMR (400 MHz, CDCl₃): δ 7.84 (q, *J* = 10.2, 7.8 Hz, 3H), 7.76-7.68 (m, 1H), 7.55-7.19 (m, 10H), 6.93-6.76 (m, 3H), 6.57-6.46 (d, *J* = 15.8 Hz, 1H), 5.06 (d, *J* =

7.4 Hz, 1H), 2.99 (d, $J = 1.8$ Hz, 6H).

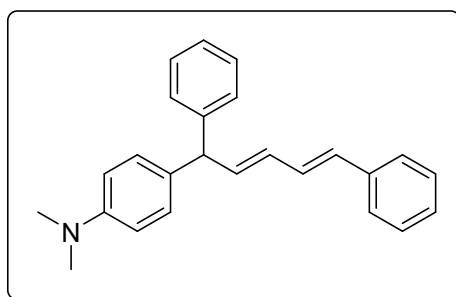
^{13}C NMR (101 MHz, CDCl_3): δ 149.27, 144.26, 141.79, 137.56, 135.05, 133.90, 133.73, 133.69, 133.64, 133.22, 132.88, 132.30, 131.73, 131.54, 131.19, 131.04, 129.51, 129.42, 128.76, 128.59, 128.51, 128.35, 128.14, 128.05, 127.96, 127.90, 127.71, 127.67, 127.60, 127.27, 126.78, 126.41, 126.35, 126.23, 126.03, 126.01, 125.68, 125.54, 123.81, 112.98, 112.96, 53.49, 53.44, 40.87, 40.85.

HRMS (m/z): calcd for $\text{C}_{27}\text{H}_{26}\text{N}$ $[\text{MH}]^+$: 364.2060, Found: 364.2062.

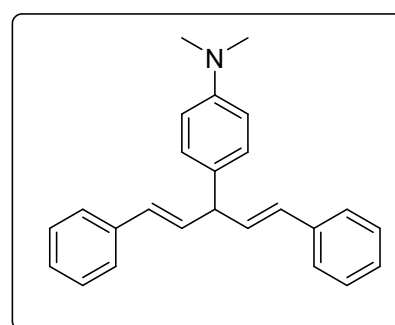
4-((2E,4E)-1,5-diphenylpenta-2,4-dien-1-yl)-N,N-dimethylaniline (3v1)

and 4-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-yl)-N,N-dimethylaniline

(3v2)



3v1



3v2

Colorless oil, 83 mg, yield: 81%; 3v1:3v2=3:1, $R_f=0.25$ (EtOAc/Petroleum ether 1:30).

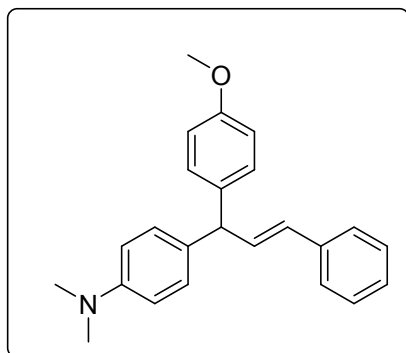
^1H NMR (400 MHz, CDCl_3): δ 7.47-7.23 (m, 10H), 7.23-7.09 (m, 2H), 6.95-6.72 (m, 3H), 6.53-6.15 (m, 3H), 4.80-4.36 (d, $J = 7.4$ Hz, 1H), 2.97 (d, $J = 5.1$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 144.14, 137.80, 137.55, 137.53, 132.57, 131.53, 131.33, 130.27, 129.30, 129.07, 128.85, 128.62, 128.60, 128.54, 128.42, 128.32, 127.89, 127.30, 127.19, 126.31, 126.25, 113.07, 53.25, 50.74, 40.94.

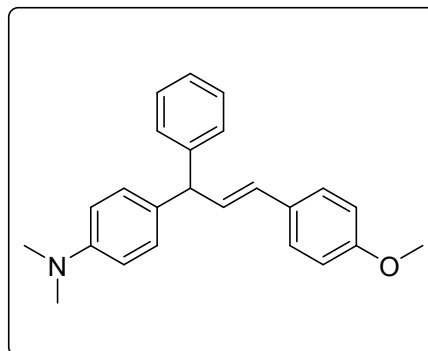
(E)-4-(1-(4-methoxyphenyl)-3-phenylallyl)-N,N-dimethylaniline (3w1)

and (E)-4-(3-(4-methoxyphenyl)-1-phenylallyl)-N,N-dimethylaniline

(3w2)



3w1



3w2

Colorless oil, 82 mg, yield: 80%; 3w1:3w2=1:1, $R_f=0.09$ (EtOAc/Petroleum ether 1:30).

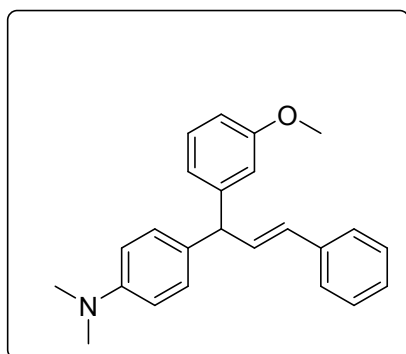
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.47-7.28 (m, 5H), 7.29-7.18 (m, 2H), 7.16 (d, $J = 8.2$ Hz, 2H), 6.89 (t, $J = 8.8$ Hz, 2H), 6.77 (d, $J = 8.3$ Hz, 2H), 6.72-6.55 (m, 1H), 6.36 (t, $J = 15.4$ Hz, 1H), 4.84 (t, $J = 8.1$ Hz, 1H), 3.83 (s, 3H), 2.97 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.16, 133.70, 131.26, 130.62, 130.25, 129.61, 129.33, 129.27, 128.68, 128.52, 128.40, 127.45, 127.14, 126.32, 126.20, 113.94, 113.82, 112.94, 55.32, 55.30, 53.33, 52.49, 40.87.

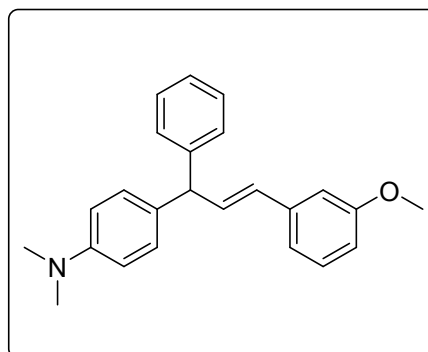
HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{26}\text{NO}$ $[\text{MH}]^+$: 344.2009, Found: 344.2012.

(E)-4-(1-(3-methoxyphenyl)-3-phenylallyl)-N,N-dimethylaniline (3x1)

(E)-4-(3-(3-methoxyphenyl)-1-phenylallyl)-N,N-dimethylaniline (3x2)



3x1



3x2

Colorless oil, 77 mg, yield: 75%; 3x1:3x2=1:1, $R_f=0.27$ (EtOAc/Petroleum ether 1:30).

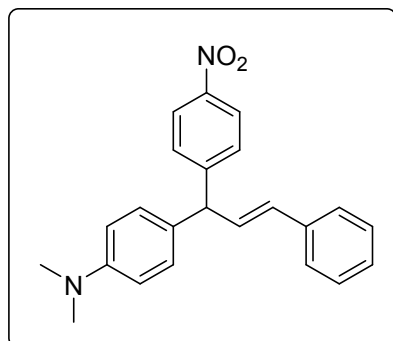
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.38 (d, $J = 7.1$ Hz, 1H), 7.36-7.17 (m, 5H), 7.12 (dd, $J = 8.9, 2.7$ Hz, 2H), 7.01-6.90 (m, 1H), 6.90-6.80 (m, 1H), 6.80-6.61 (m, 4H), 6.34 (t, $J = 15.4$ Hz, 1H), 4.81 (dd, $J = 12.5, 7.5$ Hz, 1H), 3.80-3.78 (s, 3H), 2.94 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 159.79, 159.67, 149.22, 145.89, 144.14, 139.00, 137.52, 133.68, 133.14, 130.85, 130.74, 129.42, 129.30, 129.29, 129.23, 128.64, 128.45, 128.38, 127.12, 126.30, 126.22, 121.12, 118.98, 114.63, 112.95, 111.48, 111.32, 55.21, 55.16, 53.32, 53.25, 40.77.

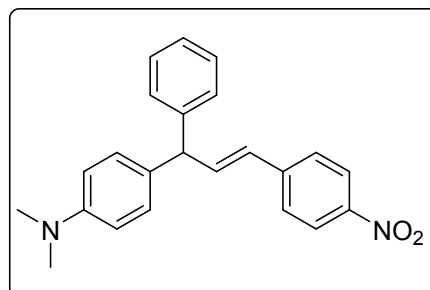
HRMS (m/z): calcd for C₂₄H₂₆NO [MH]⁺: 344.2009, found: 344.2013.

(E)-N,N-dimethyl-4-(1-(4-nitrophenyl)-3-phenylallyl)aniline (3y1)

and (E)-N,N-dimethyl-4-(3-(4-nitrophenyl)-1-phenylallyl)aniline (3y2)



3y1



3y2

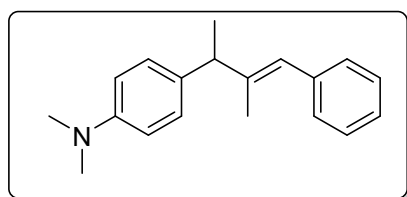
Colorless oil, 78 mg, yield: 72%; 3y1:3y2=2:3, R_f=0.28 (EtOAc/Petroleum ether 1:15).

¹H NMR (400 MHz, CDCl₃): δ 8.15 (dd, *J* = 8.6, 4.5 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.42-7.29 (m, 4H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.09 (t, *J* = 8.3 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 6.62 (dd, *J* = 15.9, 7.4 Hz, 1H), 6.37 (t, *J* = 16.7 Hz, 1H), 4.91 (d, *J* = 7.4 Hz, 1H), 2.94 (d, *J* = 1.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 152.08, 149.57, 149.43, 146.61, 146.46, 144.04, 143.27, 138.56, 136.91, 131.97, 131.53, 130.33, 129.62, 129.42, 129.24, 129.19, 128.98, 128.59, 128.56, 127.58, 126.74, 126.55, 126.34, 123.94, 123.66, 112.78, 112.77, 53.41, 53.10, 40.65, 40.59.

HRMS (m/z): calcd for C₂₃H₂₃N₂O₂ [MH]⁺: 359.1754, Found: 359.1758.

(E)-N,N-dimethyl-4-(3-methyl-4-phenylbut-3-en-2-yl)aniline (3z)



3z

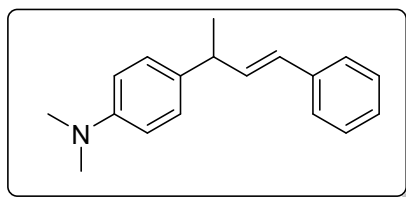
Yellow oil, 40 mg, yield: 51%; R_f=0.34 (EtOAc/Petroleum ether 1:30).

¹H NMR (400 MHz, CDCl₃): δ 7.36-7.23 (m, 4H), 7.22-7.09 (m, 3H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.46 (s, 1H), 3.50 (q, *J* = 7.1 Hz, 1H), 2.93 (s, 6H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.45 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 143.06, 138.74, 129.93, 129.29, 128.98, 128.13, 127.97, 127.96, 125.81, 124.09, 112.81, 47.51, 40.84, 19.64, 16.40.

HRMS (m/z): calcd for C₁₉H₂₄N [MH]⁺: 266.1903, found: 266.1905.

(E)-N,N-dimethyl-4-(4-phenylbut-3-en-2-yl)aniline (3aa)^[9]



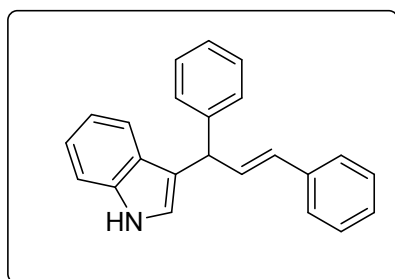
3aa

Yellow oil, 43 mg, yield: 57%; $R_f=0.31$ (EtOAc/Petroleum ether 1:30).

^1H NMR (400 MHz, CDCl_3): δ 7.35 (dd, $J = 8.3, 1.3$ Hz, 2H), 7.32-7.23 (m, 2H), 7.22-7.12 (m, 3H), 6.74 (d, $J = 8.7$ Hz, 2H), 6.41-6.35 (m, 2H), 3.57 (dt, $J = 7.2, 3.8$ Hz, 1H), 2.93 (s, 6H), 1.44 (d, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 137.81, 136.05, 129.05, 128.44, 128.42, 128.20, 127.88, 126.83, 126.10, 113.04, 41.54, 40.88, 21.23.

(E)-3-(1,3-diphenylallyl)-1H-indole (3ab)^[10]



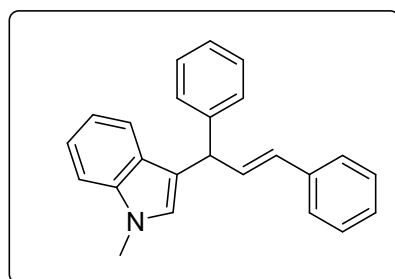
3ab

Yellow solid, m.p. 109-111°C, 79 mg, yield: 86%; $R_f = 0.13$ (EtOAc/Petroleum ether 1:20).

^1H NMR (400 MHz, CDCl_3): δ 7.85 (s, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.49-7.22 (m, 12H), 7.13 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 2.4$ Hz, 1H), 6.82 (dd, $J = 15.8, 7.4$ Hz, 1H), 6.54 (d, $J = 15.8$ Hz, 1H), 5.21 (d, $J = 7.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 143.50, 137.59, 136.72, 132.67, 130.64, 128.62, 128.61, 128.55, 127.29, 126.88, 126.51, 126.44, 122.76, 122.18, 119.97, 119.53, 118.66, 111.27, 46.30.

(E)-3-(1,3-diphenylallyl)-1-methyl-1H-indole (3ac)^[10]



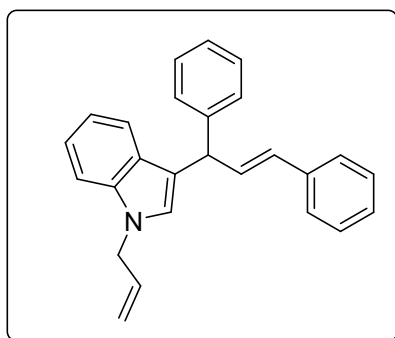
3ac

White solid, m.p. 116-117°C, 90 mg, yield: 93%; $R_f = 0.31$ (EtOAc/Petroleum ether 1:20).

¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.52-7.29 (m, 12H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.87 (q, *J* = 9.2, 7.9 Hz, 2H), 6.58 (d, *J* = 15.8 Hz, 1H), 5.25 (d, *J* = 7.4 Hz, 1H), 3.79 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 143.69, 137.64, 137.53, 132.85, 130.56, 128.63, 128.56, 127.51, 127.35, 127.28, 126.50, 126.45, 121.78, 120.09, 119.03, 117.17, 109.34, 46.31, 32.77.

(E)-1-allyl-3-(1,3-diphenylallyl)-1H-indole (3ad)



3ad

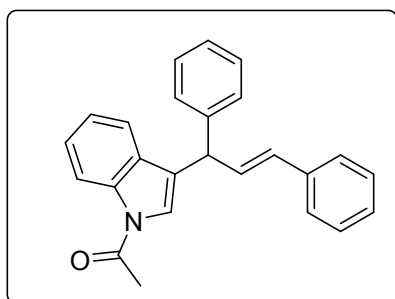
Yellow solid, m.p. 49-50°C, 90 mg, yield: 87%; *R_f* = 0.56 (EtOAc/Petroleum ether 1:15).

¹H NMR (400 MHz, CDCl₃): δ 7.49 -7.07 (m, 13H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.71 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.96 (ddd, *J* = 22.4, 10.5, 5.4 Hz, 1H), 5.20-5.02 (m, 3H), 4.66 (dt, *J* = 5.4, 1.7 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 143.49, 137.54, 136.86, 133.58, 132.71, 130.46, 128.49, 128.48, 128.41, 127.45, 127.14, 126.34, 126.33, 121.67, 120.06, 119.04, 117.46, 117.17, 109.59, 48.80, 46.25.

HRMS (m/z): calcd for C₂₆H₂₄N [MH]⁺: 350.1903, found: 350.1901.

(E)-1-(3-(1,3-diphenylallyl)-1H-indol-1-yl)ethan-1-one (3ae)



3ae

Yellow solid, m.p. 126-127°C, 60 mg, yield: 57%; *R_f* = 0.33 (EtOAc/Petroleum ether 1:20).

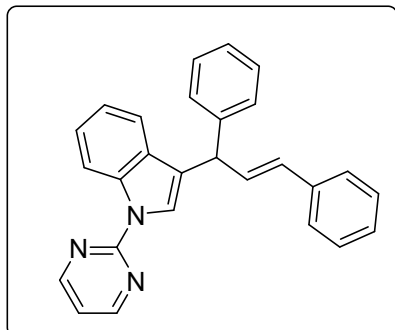
¹H NMR (400 MHz, CDCl₃): δ 8.45 (d, *J* = 8.2 Hz, 1H), 7.44-7.13 (m, 13H), 7.12 (s, 1H), 6.68 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.45 (d, *J* = 15.2 Hz, 1H), 5.05 (d, *J* = 7.3 Hz, 1H), 2.55 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 168.53, 141.75, 137.06, 136.38, 131.66, 130.83,

129.87, 128.73, 128.61, 128.45, 127.56, 126.93, 126.43, 125.33, 125.03, 123.52, 123.22, 120.08, 45.95, 24.08.

HRMS (m/z): calcd for C₂₅H₂₂NO [MH]⁺: 352.1696, found: 352.1699.

(E)-3-(1,3-diphenylallyl)-1-(pyrimidin-2-yl)-1H-indole (3af)



3af

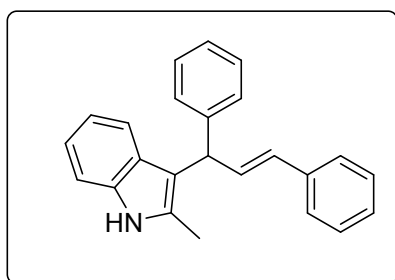
Yellow solid, m.p. 142-143°C, 85 mg, yield: 73%; R_f = 0.41 (EtOAc/Petroleum ether 1:20).

¹H NMR (400 MHz, CDCl₃): δ 8.81 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 4.8 Hz, 2H), 8.05 (d, *J* = 1.2 Hz, 1H), 7.40 (d, *J* = 11.8 Hz, 5H), 7.37-7.11 (m, 8H), 6.94 (t, *J* = 4.8 Hz, 1H), 6.78 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.48 (d, *J* = 14.6 Hz, 1H), 5.13 (d, *J* = 7.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 158.07, 157.69, 142.53, 137.39, 136.13, 131.74, 131.11, 130.48, 128.60, 128.56, 128.53, 127.30, 126.63, 126.44, 123.88, 122.71, 121.97, 119.91, 116.39, 115.88, 46.20.

HRMS (m/z): calcd for C₂₇H₂₂NO₃ [MH]⁺: 388.1808, found: 388.1805.

(E)-3-(1,3-diphenylallyl)-2-methyl-1H-indole (3ag)^[10]



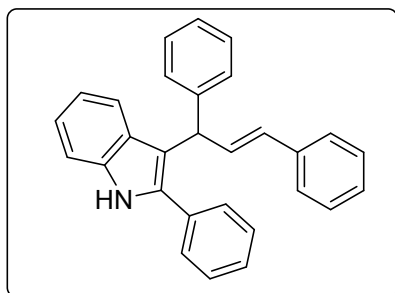
3ag

Yellow solid, m.p. 59-60°C, 81 mg, yield: 84%; R_f = 0.26 (EtOAc/Petroleum ether 1:10).

¹H NMR (400 MHz, CDCl₃): δ 7.77 (s, 1H), 7.44-7.34 (m, 5H), 7.35-7.25 (m, 5H), 7.27-7.18 (m, 2H), 7.16-7.08 (m, 1H), 7.05-6.97 (m, 1H), 6.87 (dd, *J* = 15.8, 7.2 Hz, 1H), 6.45 (dd, *J* = 15.9, 1.5 Hz, 1H), 5.18 (d, *J* = 5.9 Hz, 1H), 2.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 143.49, 137.58, 135.37, 132.21, 131.66, 130.61, 129.04, 128.52, 128.31, 128.28, 127.99, 127.12, 126.31, 126.13, 120.92, 119.43, 119.28, 112.86, 110.30, 45.10, 12.41.

(E)-3-(1,3-diphenylallyl)-2-phenyl-1H-indole (3ah) ^[10]



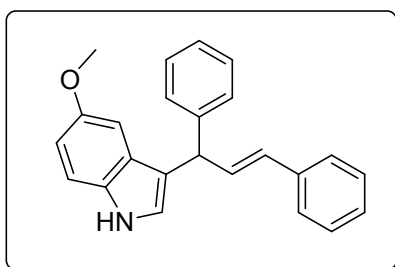
3ah

Yellow solid, m.p. 65-66°C, 106 mg, yield: 92%; $R_f = 0.25$ (EtOAc/Petroleum ether 1:10).

¹H NMR (400 MHz, CDCl₃): δ 8.06 (s, 1H), 7.57 (dd, $J = 7.5, 2.3$ Hz, 2H), 7.54-7.32 (m, 10H), 7.36-7.25 (m, 5H), 7.28-7.16 (m, 3H), 7.10-7.01 (m, 1H), 6.94 (dd, $J = 15.8, 7.3$ Hz, 1H), 6.46 (dd, $J = 15.8, 1.4$ Hz, 1H), 5.33 (d, $J = 7.2$ Hz, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 143.53, 137.55, 136.29, 135.64, 133.01, 132.32, 131.12, 128.86, 128.66, 128.50, 128.35, 128.32, 128.09, 127.96, 127.16, 126.37, 126.17, 122.16, 121.26, 119.75, 113.89, 110.99, 45.19.

(E)-3-(1,3-diphenylallyl)-5-methoxy-1H-indole (3ai) ^[10]



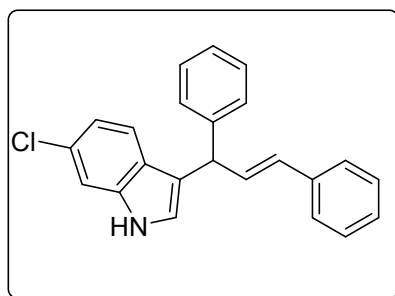
3ai

Yellow solid, m.p. 62-63°C, 81 mg, yield: 80%; $R_f = 0.25$ (EtOAc/Petroleum ether 1:10).

¹H NMR (400 MHz, CDCl₃): δ 7.90 (s, 1H), 7.42-7.18 (m, 12H), 6.91-6.81 (m, 3H), 6.74 (dd, $J = 15.8, 7.3$ Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 5.10 (d, $J = 8.7$ Hz, 1H), 3.73 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 153.79, 143.33, 137.52, 132.52, 131.83, 130.57, 128.53, 128.51, 128.45, 127.25, 127.18, 126.41, 126.33, 125.95, 123.48, 118.32, 112.15, 111.81, 101.83, 55.81, 46.24.

(E)-6-chloro-3-(1,3-diphenylallyl)-1H-indole (3aj) ^[11]



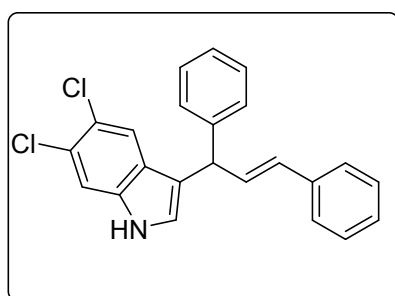
3aj

Yellow solid, m.p. 131-132°C, 80 mg, yield: 78%; $R_f = 0.58$ (EtOAc/Petroleum ether 1:7).

^1H NMR (400 MHz, CDCl_3): δ 7.94 (s, 1H), 7.40-7.17 (m, 12H), 6.99 (dd, $J = 8.5, 1.8$ Hz, 1H), 6.88 (dd, $J = 2.4, 1.0$ Hz, 1H), 6.70 (dd, $J = 15.8, 7.4$ Hz, 1H), 6.43 (d, $J = 15.8$ Hz, 1H), 5.08 (d, $J = 7.3$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 143.02, 137.32, 137.01, 132.11, 130.79, 128.53, 128.51, 128.42, 128.07, 127.29, 126.55, 126.32, 125.40, 123.24, 120.78, 120.21, 118.92, 111.04, 46.08.

(E)-5,6-dichloro-3-(1,3-diphenylallyl)-1H-indole (3ak)



3ak

Yellow solid, m.p. 125-126°C, 105 mg, yield: 93%; $R_f = 0.31$ (EtOAc/Petroleum ether 1:10).

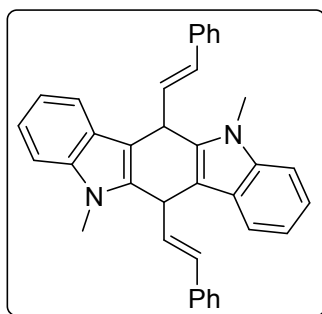
^1H NMR (400 MHz, CDCl_3): δ 8.00 (s, 1H), 7.46 (s, 1H), 7.42 (s, 1H), 7.39 – 7.34 (m, 3H), 7.33 – 7.31 (m, 3H), 7.30 – 7.28 (m, 2H), 7.26 – 7.20 (m, 2H), 6.91 (dd, $J = 2.4, 1.0$ Hz, 1H), 6.67 (dd, $J = 15.8, 7.3$ Hz, 1H), 6.42 (dd, $J = 15.8, 1.3$ Hz, 1H), 5.04 (d, $J = 8.5$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 142.65, 137.20, 135.40, 131.78, 131.00, 128.62, 128.57, 128.45, 128.44, 128.37, 127.40, 126.73, 126.58, 126.36, 126.00, 125.96, 125.91, 124.58, 123.52, 120.76, 118.56, 112.62, 45.87.

HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{18}\text{Cl}_2\text{N}$ $[\text{MH}]^+$: 378.0811, found: 378.0804.

5,11-dimethyl-6,12-di((E)-styryl)-5,6,11,12-tetrahydroindolo[3,2-

b]carbazole (3al)



3al

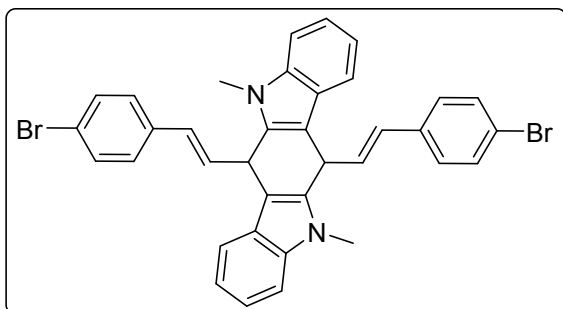
Yellow solid, m.p. 148-150°C, 27 mg, yield: 37%; $R_f = 0.54$ (EtOAc/Petroleum ether 1:20).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.74 (d, $J = 7.8$ Hz, 1H), 7.35 (m, 3H), 7.30-7.22 (m, 3H), 7.17 (m, 2H), 6.81 (d, $J = 15.7$ Hz, 1H), 6.27 (dd, $J = 15.7, 8.0$ Hz, 1H), 5.20 (d, $J = 7.8$ Hz, 1H), 3.83 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 137.95, 136.94, 135.83, 131.75, 130.20, 128.47, 127.37, 126.36, 125.91, 121.32, 119.24, 118.60, 109.09, 108.94, 37.26, 30.07.

HRMS (m/z): calcd for $\text{C}_{36}\text{H}_{30}\text{NNa}^+$ $[\text{M}+\text{Na}]^+$: 513.2301, found: 513.2306.

6,12-bis((E)-4-bromostyryl)-5,11-dimethyl-5,6,11,12-tetrahydroindolo[3,2-b]carbazole (3am)



3am

Yellow solid, m.p. 158-159°C, 29 mg, yield: 30%; $R_f = 0.51$ (EtOAc/Petroleum ether 1:20).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.70 (d, $J = 7.9$ Hz, 1H), 7.36 (dd, $J = 8.1, 6.1$ Hz, 3H), 7.28-7.20 (m, 1H), 7.21-7.10 (m, 3H), 6.70 (d, $J = 15.7$ Hz, 1H), 6.26 (dd, $J = 15.7, 7.8$ Hz, 1H), 5.18 (d, $J = 7.7$ Hz, 1H), 3.82 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 137.93, 135.77, 135.61, 132.41, 131.61, 131.57, 128.98, 127.84, 125.79, 121.48, 121.15, 119.37, 118.46, 109.18, 108.82, 37.09, 30.07.

HRMS (m/z): calcd for $\text{C}_{36}\text{H}_{28}\text{N}_2\text{Br}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 669.0511, found: 669.0518.

5. X-Ray Analysis

The X-ray quality crystals of **3af** were grown from ethyl acetate.

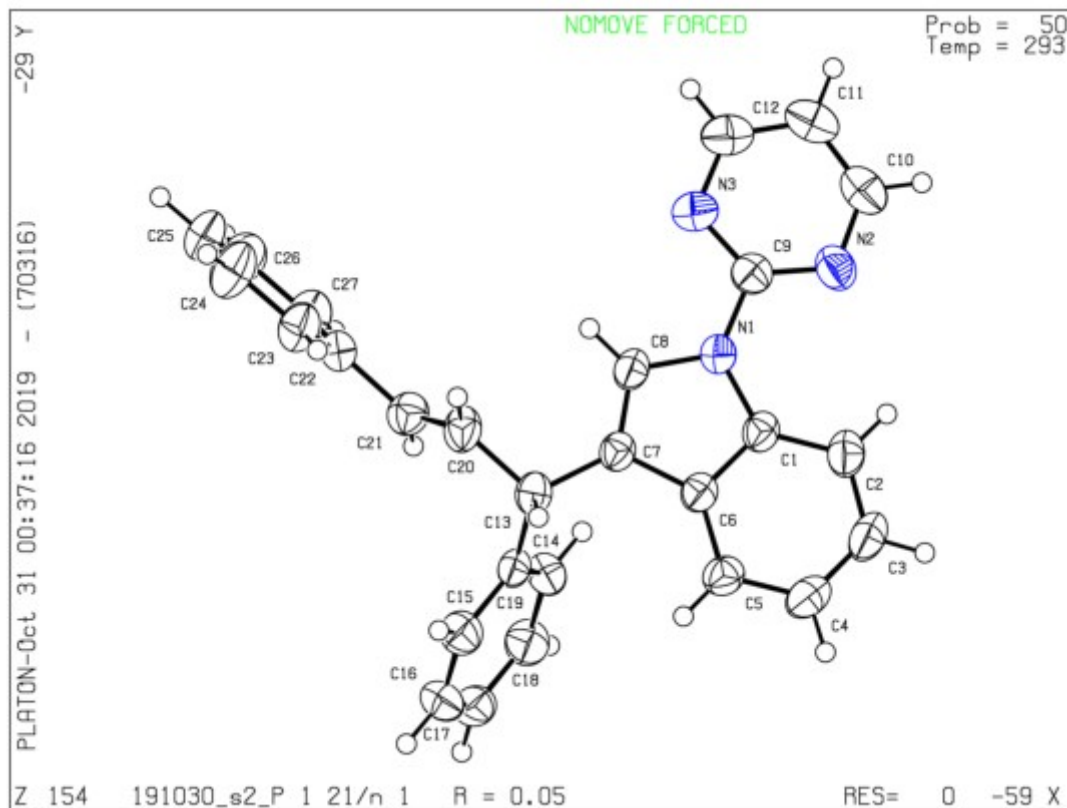


Figure S1. ORTEP Drawing of **3af** (CCDC)

The X-ray quality crystals of **3al** were grown from ethyl acetate and dichloromethane.

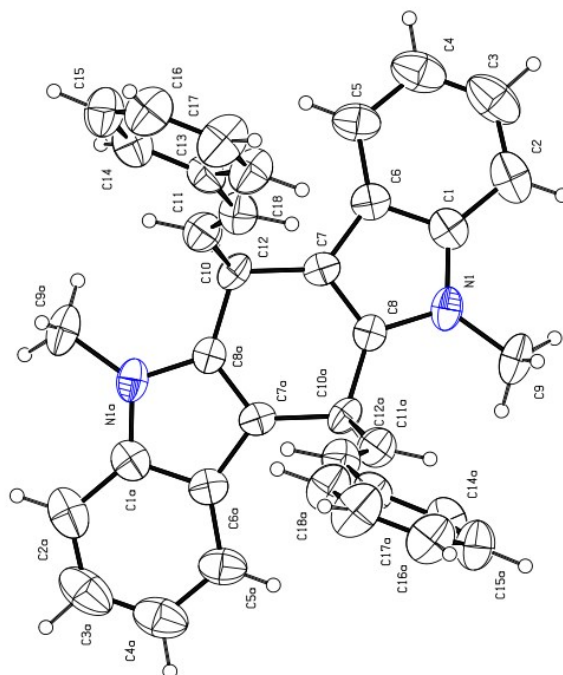


Figure S2. ORTEP Drawing of **3al** (CCDC)

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