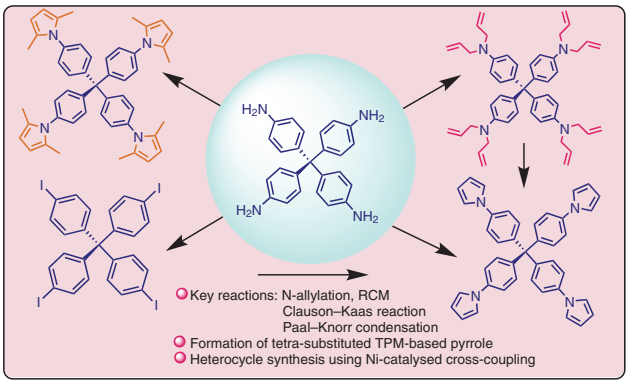
Tetraphenylmethane Derivatives Containing Nitrogen Heterocycles

Sambasivarao Kotha*
Deepshikha Singh

Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai, 400 076, India
srk@chem.iitb.ac.in



Received: 30.11.2023
Accepted after revision: 26.01.2024
Published online: 22.02.2024 (Accepted Manuscript), 26.03.2024 (Version of Record)
DOI: 10.1055/a-2274-5102; Art ID: SO-2023-11-0087-L

Abstract We disclose a useful approach to novel tetrahedral building blocks containing *N*-heterocycles. Pyrrole was introduced on to the tetraphenylmethane (TPM) core by employing the RCM strategy, Clauson–Kaas reaction, Paal–Knorr condensation, and Ullmann coupling as key steps. In addition, various heterocyclic derivatives of TPM were prepared using nickel catalysts. We also studied the photophysical properties of the synthesized TPM derivatives containing different peripheral substituents and found that they exhibit high quantum yields.

Key words aryl iodide, heterocycles, aromatization, tetraphenylmethane, cross-coupling

The high π-electron content of pyrroles makes them suitable donor units for the design of new materials. The synthesis of various types of pyrroles has attracted the attention of synthetic chemists in recent years for the development of organic semiconductors.[1] Since pyrrole is the most electron-rich five-membered heteroaromatic ring, it has found many applications in organic photovoltaics and organic field-effect transistors.[2,3] To generate new pyrrole building blocks,[4–6] functionalization reactions to link these pyrrole monomers to other aromatic units are required. We conceived new ways to incorporate pyrrole unit(s) on to the tetraphenylmethane core **1** (Figure 1).

Tetrahedral unit linking through an sp^3-hybridized carbon atom provides a sense of homo-conjugation, resulting in simultaneous mutual orthogonality and a high degeneracy of the molecular orbitals of the conjugated chains.[7,8] Hence, derivatives of tetraphenylmethane (TPM) hold promise for applications in gas capture and separation, catalysis, organic electronic devices, and sensors due to their high photoluminescence efficiency and excellent thermal stabilities.[9,10] TPM has gained importance in supramolecular networks, nanomaterials, and metal-organic framework (MOF) dendrimers, which are used in the solid state to adsorb gas molecules or volatile organic compounds.[11–15] Recently Zhang's group reported aromatic imides of TPM **2**, used in gas separation, showing their good gas-transport properties.[16] In addition, TPM-ethylene-based dendrimer **3** is widely used in the field of optoelectronic materials.[17] Moreover, porous organic polymers (POPs) **4**, containing the TPM core, has become attractive for capturing and storing carbon dioxide (CO_2) and radioactive iodine.[18] Dong and co-workers synthesized a self-decoupled porphyrin with a TPM-based tripodal platform **5** that is used for the mounting of molecules to metal surfaces (Figure 1).[19]

Tetraphenylmethane derivatives with an incorporated pyrrole represent an intriguing and essential group of *N*-heterocycles within this context. Although various methods have been attempted, there have been no reported instances of pyrrole combined with TPM. However, it has been proven that TPM serves as a valuable component and can be integrated into materials used for light emission or charge transportation by altering its peripheral substituents.[20] We report a convergent approach involving cross-coupling of TPM with various primary and secondary amines (pyrazole, 5-methoxyindole, 2,3-dimethylindole, triphenylmethane, spirobifluorene, 9,9′-terphenyldiamine, etc.) using nickel catalysts. In addition, we investigated the physical properties of the synthesized TPM-based compounds and determined their fluorescence quantum yields (Φ_f) in DMF solvent. The divergent routes to pyrrole-containing TMP derivatives start with a simple tetrahedral building block. A suitable TPM derivative containing amine or halide functionality is a useful starting point.

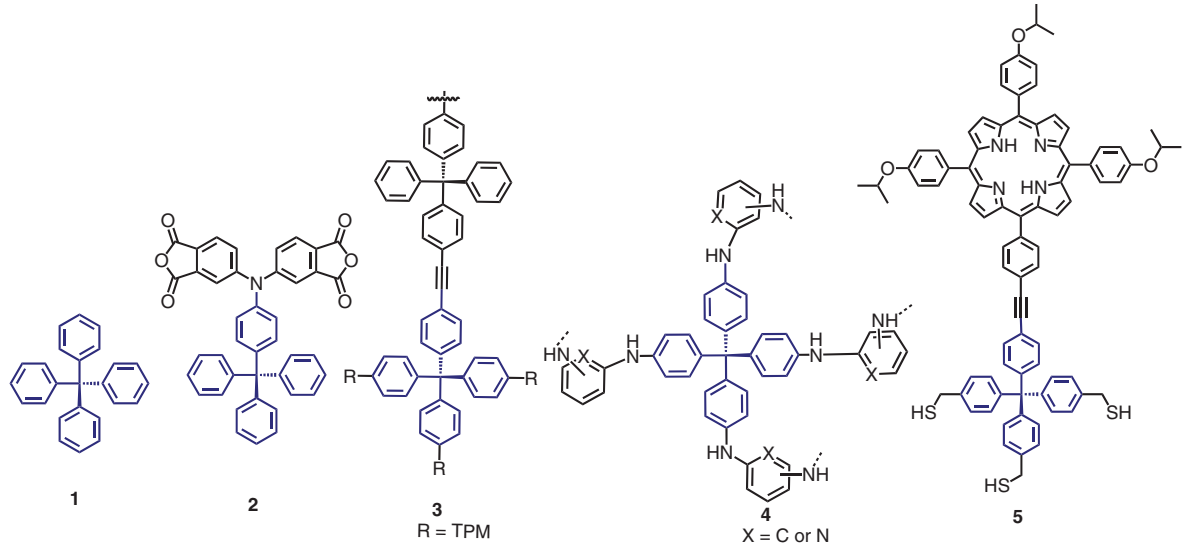
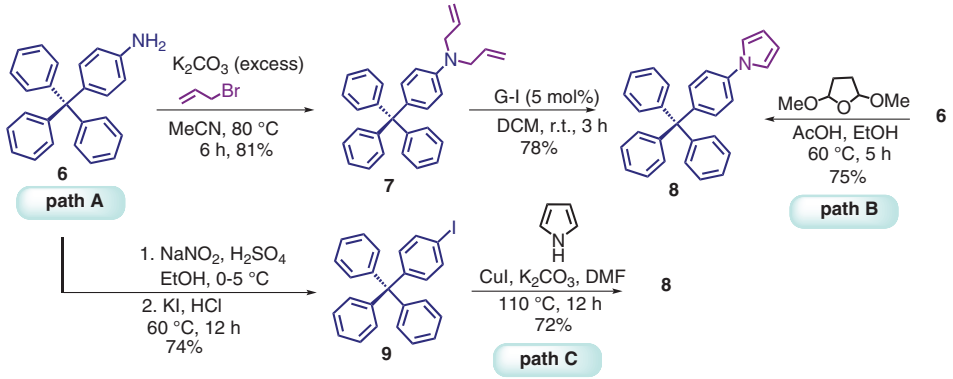


Figure 1 Useful nitrogen-containing tetraphenylmethane units

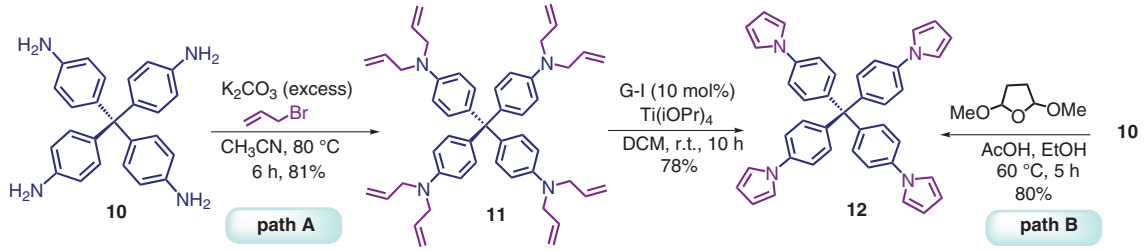
Here, we aim to synthesize mono- or tetra-substituted pyrroles *via* the involvement of RCM as a key step. As shown in Scheme 1, pyrrole formation was carried out in three different ways: (Path A) allylation of trityl aniline **6**, ring-closing metathesis (RCM) followed by aromatization using Grubbs first-generation catalyst (G-I) (5 mol%) in anhydrous DCM at room temperature for 3 h to give compound **8** in 78% yield; (Path B) Condensation reaction[21] involving 2,5-dimethoxy tetrahydrofuran with trityl aniline **6** (1.10 equiv) in acetic acid at 60 °C for 5 h, resulting in good conversion (75%). (Path C) Diazotization of **6** followed by subsequent iodination with KI to give the mono-iodo compound **9**, which underwent CuI-catalyzed cross-coupling reaction with pyrrole in anhydrous DMF at 110 °C for 12 h, resulting in the formation of compound **8** in 72% yield.

A simple and general methodology was developed to introduce a pyrrole moiety on to TPM. Similarly, tetra-amino compound **10** was employed to prepare tetra-pyrrole derivative via a RCM strategy (Path A) and a condensation reaction (Path B) to afford compound **12** in good yield (Scheme 2).

Along similar lines, the synthesis of symmetrical dimethyl substituted pyrroles such as **13** was achieved in good yield (76%) by condensation of amine **10** with an excess amount of 2,5-hexanedione in an acidic medium for 5 h at 60 °C (Scheme 3).[22] Due to the superior reactivity of iodides in comparison to other (pseudo)halides, we envisioned two pathways to generate tetrakis-(4-iodophenyl)methane (**14**) (Scheme 4). Initially, compound **10** undergoes a diazotization sequence followed by iodination. Alternatively, having prepared TPM, the use of bis(trifluoroacetoxy iodobenzene) and iodine in CCl_4 at 60 °C for 12 h also gave compound **14** in 42% good yield.[23–25] With tetraiodide derivative **14** in hand, the stage was set for the cross-coupling reaction.

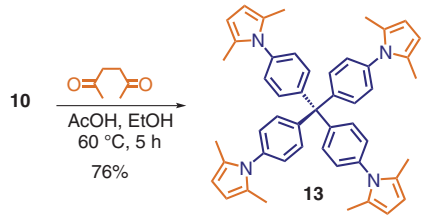


Scheme 1 Synthesis of pyrrole derivative **8** via RCM, Clauson–Kaas and Ullmann coupling



Scheme 2 Synthesis of tetrasubstituted TPM derivatives

The cross-coupling reaction proceeded smoothly in the presence of copper iodide (20 mol%), pyrrole (5.50 equiv), iodide derivative **14** (1.20 equiv), and mild base K_2CO_3, in anhydrous DMF at 110 °C for 12 h to give the target compound **12** (72%).

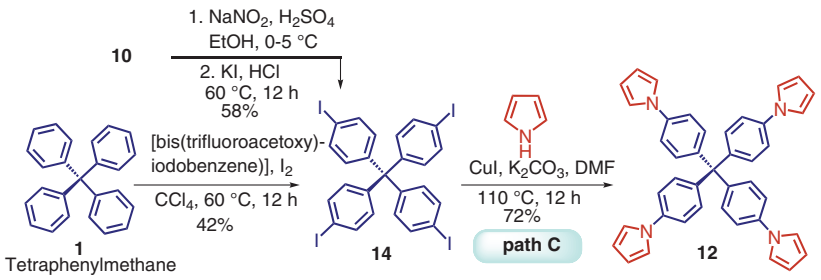


Scheme 3 Synthesis of **13** via Paal–Knorr condensation

In contrast, the copper-catalyzed coupling of aryl iodide **9** with indole **15** did not produce the cross-coupling product **16** (Table 1).[26,27] Control experiments were conducted to verify the involvement of the base, solvent, and the impact of coordinated ligands in the catalytic C–N cross-coupling process. Initially, we used $NiCl_2{\cdot}6H_2O$ as catalyst in the presence of K_2CO_3 for 24 h at 60 °C, but no desired compound was obtained (entry 1). The use of other Ni catalysts such as NiI, $Ni(COD)_2$, and $NiCl_2$·dme, resulted in low success, although a trace amount of product was isolated (<10%) in THF (entries 2–8). We also examined the introduction of ligands into the reaction mixture, but no improvement in the yield was observed when $NiCl_2$·dme/xantphos was used (entry 9). These catalytic systems did not work in ethanol and afforded no desired product in DMF-H_2O (entries 10 and 11). In addition, the utilization of 1,4-dioxane resulted in incomplete transformation into the product **16** (entry 12). Impurities were found when the reaction was conducted in CH_3CN/DMF (entry 13). Moderate yield was obtained when the reaction was performed for with $NiBr_2$·dme/dppf as catalyst and Cs_2CO_3 as base in toluene 12 hours at 110 °C (entry 14), and the yield increased to 82% when *t*-BuOK was used as base (entry 15).

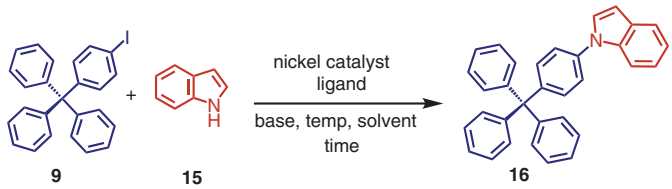
These reaction conditions allowed the coupling of a wide variety of substrates under relatively mild conditions, and a range of TPM derivatives[28,29] were prepared in good yield (74–83%; Table 2). The sequential coupling of pyrazole (**17**), 2,3-dimethylindole (**18**), 5-methoxyindole (**19**), and thiadiazole-2-amine (**20**) in combination with mono-iodo TPM was fruitful and generated compounds **25**–**28**, respectively, in appreciable yields (72–83%). Triphenylamine **21** and trityl aniline **22** were coupled successfully to give the products **29** and **30** in 78 and 81% yield, respectively. Considering the electron-rich nature of 4,4′-(9*H*-fluorene-9,9-diyl)dianiline (**23**), the amination reaction conditions successfully generated the desired product **31** in good yield (74%). A significant yield was also observed for the product **32** where the aromatic 4,4′-diamino-*p*-terphenyl (**24**) reacted efficiently with the mono-iodo derivative.

The photophysical properties of these highly fluorescent TPM derivatives were investigated by UV/Vis and fluorescence spectroscopy at room temperature with standard quartz cuvettes. Initially, the effect of solvent on fluorescence emission of pyrrole derivative **8** was studied in polar solvents (EtOAc, $CHCl_3$, ethanol, DCM, DMF, acetonitrile, THF) as well as nonpolar solvents (benzene, toluene and



Scheme 4 Efficient synthesis of TPM derivative **12**

Table 1 Optimization of Reaction Conditions



Entry	Cat.	Base	Solvent	*T* (°C)	*t* (h)	Yield (%)[a]
1	$NiCl_2{\cdot}6H_2O$	K_2CO_3	CH_3CN/DMF	60	24	NR
2	NiI	K_2CO_3	CH_3CN/DMF	90	24	NR
3	NiI	Cs_2CO_3	CH_3CN/DMF	90	24	NR
4	NiI	Cs_2CO_3	Toluene	110	20	NR
5	$Ni(COD)_2$	Cs_2CO_3	THF	60	24	<10
6	$Ni(COD)_2$	*t*-BuOK	THF	60	28	trace
7	$Ni(COD)_2$	KOH	DMF-H_2O	120	20	NR
8	$NiCl_2$·dme	NaO*t*-Bu	CH_3CN/DMF	10	20	NR
9	$NiCl_2$·dme/ xantphos	*t*-BuOK	Toluene	110	24	trace
10	$NiBr_2$·dme/ xantphos	*t*-BuOK	EtOH	60	24	trace
11	$NiBr_2$·dme /xantphos	*t*-BuOK	DMF-H_2O	130	24	NR
12	$NiBr_2$·dme/dppf	*t*-BuOK	1,4-dioxane	80	20	42
13	$NiBr_2$·dme/dtbpy	*t*-BuOK	CH_3CN/DMF	80	14	31
14	$NiBr_2$·dme/dppf	Cs_2CO_3	toluene	110	12	51
15	$NiBr_2$·dme/dppf	*t*-BuOK	toluene	110	12	82

[a] Chromatographically isolated yield. NR = no results

1,4-dioxane), with the polar aprotic solvent dimethyl formamide (DMF) being found to be most suitable (Figure 2).

The UV spectra of most of the substrates showed absorption maxima around 300 nm caused by the π-π* excitation of pyrrole fluorophores, as summarized in Table 3. The emission spectra were recorded by using the maximum absorption wavelength, and compounds **8**, **13**, **26**, and **30** showed a significant bathochromic shift in emission wavelength in the region of 400–500 nm (Figure 2; For excitation and emission spectra see the Supporting Information, pages 18–20). Using coumarin **30** dissolved in EtOH as a reference (quantum yield = 0.35) the calculated quantum yields (Φ_F) of the synthesized compounds were determined as shown in Table 3. Based on the calculated quantum yield of the compounds studied, **31** (90%) and **32** (88%) exhibited the strongest fluorescence.

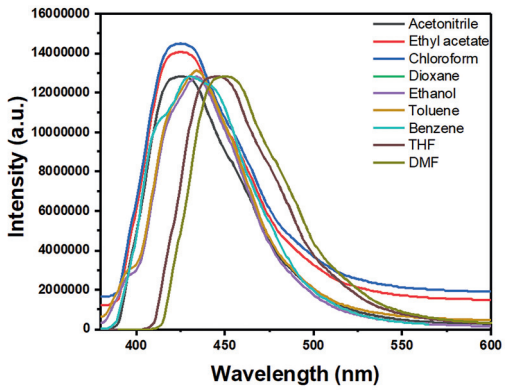
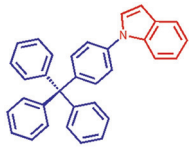
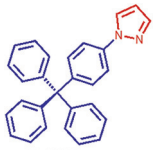
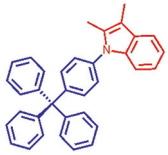
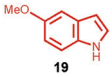
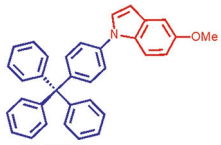
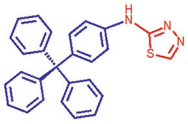
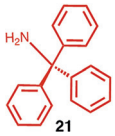
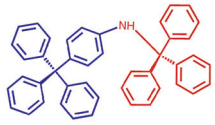
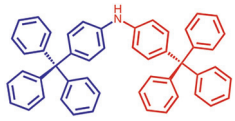


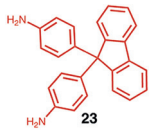
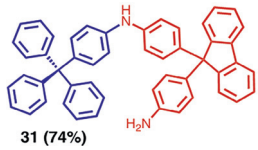
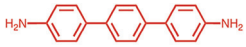
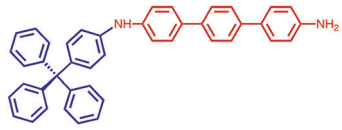
Figure 2 Effect of solvent on fluorescence emission of substrate **8**

In summary, we have presented a diversity-oriented strategy for incorporating different heterocycles, including pyrrole, pyrazole, and indole, into the TPM core. Our approach focuses on C–C and C–N bond formation, allowing for the synthesis of various carbocycles and heterocycles. The protocol we describe is straightforward to execute and makes use of readily accessible starting materials, enabling the efficient synthesis of valuable building blocks. The key steps in this process, which involve metathesis, Clauson–Kaas reaction, Paal–Knorr condensation, and Ullmann coupling, have been successfully employed to introduce a range of heterocycles into the TPM unit. We also assembled a family of tetrahedral molecules from cross-coupling of mono-iodo TPM and various primary and secondary amines, in the presence of inexpensive nickel catalysts, in good to excel-

lent yields. The compounds exhibited strong absorption and emission maxima in the 400–500 nm range with high fluorescence quantum yields (Φ_F) of 51–90% (Table 3). This synthetic procedure provides ample opportunities for the molecular engineering community to expand further.

Table 2 Cross-Coupled Tetraphenylmethane Derivatives[a]

Entry	Amine	Product	Yield (%)[b]
1	 15	 16 (82%)	82
2	 17	 25 (80%)	80
3	 18	 26 (73%)	73
4	 19	 27 (72%)	72
5	 20	 28 (83%)	83
6	 21	 29 (78%)	78
7	 22	 30 (81%)	81

Entry	Amine	Product	Yield (%)[b]
8	 23	 31 (74%)	74
9	 24	 32 (79%)	79

[a] Reaction conditions: Aryl iodide (1 equiv), amine (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), toluene (5 mL), 110 °C, 12 h.
[b] Chromatographically isolated yield.

Table 3 Quantum Yields of the TPM-Based Derivatives

Entry	Substrate	λ_{abs} (nm)	λ_{em} (nm)	Φ_F (%)[d]
1	**8**	310[a]	450	76
2	**12**	300[b]	370	87
3	**13**	300[a]	420	76
4	**25**	340[c]	400	51
5	**26**	330[b]	450	80
6	**28**	300[a]	390	77
7	**29**	310[a]	400	85
8	**30**	350[c]	455	87
9	**31**	280[a]	400	90
10	**32**	340[c]	395	88

[a] Compound was excited at λ_{ex} 280–310 nm in DMF.
[b] Compound was excited at λ_{ex} 320–330 nm in DMF.
[c] Compound was excited at λ_{ex} 340–350 nm in DMF.
[d] Quantum yield of product.

Reactions involving air-sensitive reagents or catalysts were conducted in anhydrous and degassed solvents. Dichloromethane (DCM) was distilled over P_2O_5. The commercial-grade reagents were used without further purification. All the reactions were monitored by thin-layer chromatography with alumina Merck plates using appropriate solvent systems. All the compounds were purified by column chromatography using silica gel (100–200 mesh) and the yields refer to the chromatographically isolated yield. The NMR spectral analysis was done using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in ppm (δ scale) and coupling constants (*J*) are reported in Hz. The standard abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet and multiplet signals, respectively. All NMR spectroscopic data were recorded with Bruker (AVANCE IIITM) 500 MHz and 400 MHz spectrometers. High-resolution mass spectrometric (HRMS) measurements were recorded with Bruker (Maxis Impact) or Micromass Q-ToF spectrometers. The melting points of unknown compounds were recorded with a Veego melting-point apparatus.

Allylation; General Procedure

Allyl bromide was added to a phenol derivative and K_2CO_3 suspension in acetonitrile (10–30 mL), and the reaction mixture was stirred at 80 °C for 3–6 h. Upon completion of the reaction (TLC monitoring), brine solution and EtOAc (3 × 20 mL) were added and the organic layer was separated and dried over anhydrous Na_2SO_4. The separated organic layer was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether and EtOAc as the eluent to afford the desired allyl compounds.

***N,N*-Diallyl-4-tritylaniline (7)**

Prepared according to the General Procedure for allylation with trityl aniline **6** (1.10 equiv), K_2CO_3 (3 equiv), allyl bromide (2.20 equiv), and acetonitrile (5 mL) at 80 °C for 6 h. The crude mixture was purified using column chromatography to give compound **7**.

Yield: 81% (149 mg obtained, starting from 150 mg); yellow oil; R_f = 0.45 (EtOAc/petroleum ether, 2%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 5.38 Hz, 12 H), 7.23–7.21 (m, 3 H), 7.04 (d, *J* = 8.28 Hz, 2 H), 6.63 (d, *J* = 6.34 Hz, 2 H), 5.93–5.87 (m, 4 H), 5.21 (t, *J* = 12.78 Hz, 4 H), 3.93 (d, *J* = 4.70 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.5, 146.7, 134.4, 132.0, 131.3, 127.4, 125.8, 116.3, 111.2, 64.2, 52.8.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{30}N$: 415.2380; found: 416.2380.

4,4′,4″,4‴-Methanetetrayl-tetrakis(*N,N*-diallylaniline) (11)

Obtained using compound **10** (1.10 equiv), K_2CO_3 (10 equiv), allyl bromide (6 equiv), and acetonitrile (10 mL) at 80 °C for 6 h.

Yield: 81% (75 mg obtained, starting from 50 mg of compound **10**); yellow oil; R_f = 0.45 (petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 8.95 Hz, 8 H), 6.55 (d, *J* = 8.77 Hz, 8 H), 5.88–5.83 (m, 8 H), 5.20–5.12 (m, 16 H), 3.88 (d, *J* = 4.88 Hz, 16 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 136.5, 134.7, 131.9, 116.1, 111.0, 61.5, 52.8.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{49}H_{57}N_4$: 701.7583; found: 701.7584.

G-I Mediated Pyrrole Formation (Path A); General Procedure

A stirred solution of RCM precursor **7** or **11** (1 equiv) in anhydrous DCM (10 mL) was degassed with nitrogen for 10 min and G-I (5–10 mol%) was added. The reaction mixture was then stirred at room temperature for 2–10 h. Upon completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography using 1–5% of EtOAc/petroleum ether as an eluent to deliver the pyrrole products **8** and **12**.

Clauson–Kaas Reaction (Path B); General Procedure

Amine (1 equiv), 2,5-dimethoxy tetrahydrofuran (1.25–4.60 equiv), and acetic acid (2–5 mL) were added to a 50 mL round-bottom flask and the reaction mixture was stirred at 60 °C for 3–6 h. TLC was used to monitor the progress of the reaction. Upon completion of the reaction, the mixture was cooled to room temperature and the product was extracted with ethyl acetate. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using an eluent (1–5% EtOAc/petroleum ether) to afford the pure products **8** and **12**.

Aryl-Amination (Path C); General Procedure

CuI (5–20 mol%) was added to a 50 mL round-bottom flask containing the aryl iodide substrate **9** or **14** (1.20 equiv), pyrrole (2.0–5.50 equiv) and K_2CO_3 (3–10 equiv) in DMSO (2–5 mL). The mixture was then heated at 120 °C for approximately 20 h until the starting material was consumed. The reaction mixture was washed with ethyl acetate and water. The organic layer was then washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the crude residue was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate as eluent.

Tetrakis(4-(1*H*-pyrrol-1-yl)phenyl)methane (8)

Reaction conditions (Path A): Compound **7** (100 mg, 1 equiv) in anhydrous DCM (10 mL) was degassed with nitrogen for 10 min, G-I (5 mol%) added at r.t. and the reaction was continued for 10 h. Yield: 78% (97 mg obtained from compound 7); white solid.

Reaction conditions (Path b): Trityl aniline **6** (100 mg, 1 equiv), 2,5-dimethoxy tetrahydrofuran (1.25 equiv) and acetic acid (2 mL), 60 °C, 5 h. Yield: 75% (92 mg obtained from compound **6**).

Reaction conditions (Path C): Aryl iodide substrate **9** (100 mg, 1.20 equiv), CuI (5 mol%), pyrrole (2.0 equiv), K_2CO_3 (3 equiv), DMF (2 mL), 110 °C, 12 h. Yield: 72% (72 mg from compound **9**).

White solid; mp 88–90 °C; R_f = 0.35 (2% petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.73 Hz, 1 H), 7.51 (s, 4 H), 7.48–7.43 (m, 3 H), 7.37 (d, *J* = 4.40 Hz, 10 H), 7.33 (s, 3 H), 7.32–7.28 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.7, 140.9, 132.7, 131.3, 127.8, 126.3, 126.0, 125.9, 123.5, 120.4, 120.0, 110.0, 65.0.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{24}N$: 385.3305; found: 385.3304.

Tetrakis(4-(1*H*-pyrrol-1-yl)phenyl)methane (12)

Reaction conditions (Path A): Compound **11** (200 mg, 1 equiv) in anhydrous DCM (20 mL) was degassed with nitrogen for 10 min, G-I (10 mol%) was added at r.t. and the reaction was continued for 10 h. Yield: 78% (129 mg obtained from compound **11**).

Reaction conditions (Path B): Trityl aniline **6** (200 mg, 1 equiv), 2,5-dimethoxy tetrahydrofuran (4.60 equiv) and acetic acid (5 mL), 60 °C, 5 h. Yield: 75% (183 mg obtained from compound **10**).

Reaction conditions (Path C): Aryl iodide substrate **14** (70 mg, 1.20 equiv), CuI (20 mol%), pyrrole (5.50 equiv), K_2CO_3 (10 equiv), DMF (5 mL), 110 °C, 12 h. Yield: 72% (40 mg obtained from compound **14**).

Viscous brown liquid; R_f = 0.56 (1% petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (s, 2 H), 7.72 (s, 2 H), 7.63–7.61 (m, 6 H), 7.42–7.41 (m, 3 H), 7.11 (m, 10 H), 7.07 (s, 4 H), 6.72 (d, *J* = 2.21 Hz, 1 H), 6.20 (d, *J* = 2.20 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 130.7, 129.1, 128.5, 125.5, 109.6, 60.5.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{33}N_4$: 581.2737; found: 581.2737.

Paal–Knorr Synthesis; Typical Procedure

Amine **10** (1.00 equiv), 2,5-hexanedione (2.60 equiv) and acetic acid (5 mL) were added to a 50 mL round-bottom flask and the reaction mixture was stirred at 90 °C for 6 h. TLC was used to monitor the progress of the reaction. Upon completion of the reaction, the mixture was cooled to r.t., the reaction was quenched with water, and the aqueous layer was extracted with EtOAc (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the product **13**, which was purified by silica gel column chromatography using eluent 1–5% EtOAc/petroleum ether.

Tetrakis(4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl)methane (13)

Reaction conditions: Amine **10** (90 mg, 1.00 equiv), 2,5-hexanedione (2.60 equiv), and acetic acid (5 mL), 90 °C, 6 h.

Yield: 76% (124 mg obtained from compound **10**); pale-yellow oil; R_f = 0.47 (1% petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.07 (m, 8 H), 5.81 (s, 2 H), 4.04 (q, *J* = 6.71, 13.6 Hz, 14 H), 2.11 (s, 24 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4, 137.3, 131.5, 128.6, 127.5, 105.9, 60.3, 20.9.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{49}H_{49}N_4$: 693.3879; found: 693.3879.

Aryl-Amination; General Procedure

$NiBr_2$·dme (5 mol%), dppf (10 mol%), and *t*-BuOK (2.50 equiv) were added to a previously dried two-neck round-bottom flask containing a magnetic bar. The mixture was dissolved in anhydrous toluene (5 mL) and stirred for 15 min under nitrogen at r.t. The aryl iodide **9** (1 equiv) was then added, followed by 15 min of further stirring at r.t. Finally, the amine (1.50–4.20 equiv) was added, and the reaction mixture was heated at reflux at 110 °C for 24 h in an oil bath. The reaction was monitored by alumina TLC until complete conversion was observed. The resulting mixture was cooled to r.t., diluted with EtOAc, and the solvent was then removed under reduced pressure. The residue was purified by silica gel column chromatography to give the desired products.

1-(4-Tritylphenyl)-1*H*-indole (16)

Aryl iodide **9** (50 mg, 1 equiv), indole **15** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were reacted at 110 °C for 24 h.

Yield: 82% (53.2 mg obtained from compound **9**); yellow oil; R_f = 0.47 (1% petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.74 Hz, 2 H), 7.25–7.24 (m, 7 H), 7.22–7.21 (m, 13 H), 6.96 (7.56 Hz, 2 H), 6.57 (d, *J* = 7.28 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.13, 137.2, 137.1, 133.1, 132.9, 132.1, 130.9, 128.14, 127.9, 123.3, 122.5, 121.3, 120.6, 110.7, 103.9, 66.3.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{35}H_{26}N$: 436.1987; found: 436.1986.

1-(4-Tritylphenyl)-1*H*-pyrazole (25)

Aryl iodide **9** (70 mg, 1 equiv), pyrazole **17** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were heated at 110 °C for 24 h.

Yield: 80% (64 mg obtained from compound **9**); white solid; mp 112–114 °C; R_f = 0.37 (2% petroleum ether/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (s, 2 H), 7.60–7.58 (q, *J* = 5.16, 11.66 Hz, 7 H), 7.47 (d, *J* = 6.76 Hz, 3 H), 7.40 (d, *J* = 5.76 Hz, 5 H), 7.21–7.17 (m, 3 H), 6.37 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.0, 134.2, 133.3, 131.9, 131.5, 131.4, 131.1, 130.9, 129.7, 128.5, 128.4, 127.7, 107.5, 73.6.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{23}N_2$: 387.1783; found: 387.1783.

2,3-Dimethyl-1-(4-tritylphenyl)-1*H*-indole (26)

Aryl iodide **9** (70 mg, 1 equiv), 2,3-dimethyl indole **18** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were heated at 110 °C for 24 h.

Yield: 73% (59 mg from compound **9**); brown sticky solid; R_f = 0.47 (2% petroleum ether/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50–7.48 (m, 1 H), 7.30–7.18 (m, 20 H), 7.13–7.09 (m, 2 H), 2.36 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.2, 135.3, 131.3, 128.0, 127.6, 127.5, 126.0, 121.0, 119.1, 118.0, 113.3, 110.1, 64.2, 11.6, 8.6.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{35}H_{30}N$: 464.2321; found: 464.2320.

5-Methoxy-1-(4-tritylphenyl)-1*H*-indole (27)

Aryl iodide **9** (95 mg, 1 equiv), 5-methoxy indole **19** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were heated at 110 °C for 24 h.

Yield: 72% (71 mg obtained compound **9**); colorless oil; R_f = 0.57 (2% petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 2 H), 7.24–7.21 (m, 20 H), 6.99 (t, *J* = 6.61 Hz, 1 H), 5.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 146.8, 137.6, 137.5, 137.3, 134.3, 134.18, 134.10, 134.01, 132.2, 130.1, 128.35, 128.2, 127.7, 127.5, 126.4, 123.5, 60.5, 53.5.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{28}NO$: 466.2353; found: 466.2352.

***N*-(4-Tritylphenyl)-1,3,4-thiadiazol-2-amine (28)**

Aryl iodide **9** (65 mg, 1 equiv), 1,3,4-thiadiazol-2-amine **20** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were heated at 110 °C for 24 h.

Yield: 83% (47 mg obtained from compound **9**); pale-yellow oil; R_f = 0.55 (1% petroleum ether/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (dd, *J* = 1.40 Hz, 7.82 Hz, 1 H), 7.26 (s, 6 H), 7.24–7.20 (m, 11 H), 6.96 (t, *J* = 7.58 Hz, 1 H), 6.57–6.55 (m, 1 H), 5.30 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.0, 147.2, 146.9, 132.3, 131.34, 131.31, 131.1, 127.8, 127.7, 127.6, 127.5, 126.3, 126.1, 126.0, 113.3, 63.4.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}N_3S$: 420.1455; found: 420.1456.

***N*,4-Ditritylaniline (29)**

Aryl iodide **9** (120 mg, 1 equiv), triphenyl amine **21** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were heated at 110 °C for 24 h.

Yield: 78% (121 mg obtained from compound **9**); colorless oil; R_f = 0.66 (1% petroleum ether/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.38 (d, *J* = 7.06 Hz, 2 H), 7.36–7.34 (m, 4 H), 7.33–7.32 (d, *J* = 3.73 Hz, 10 H), 7.31–7.28 (m, 10 H), 7.27 (d, *J* = 2.79 Hz, 4 H), 7.24–7.20 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.0, 146.9, 146.5, 145.6, 132.6, 131.3, 131.1, 131.0, 128.9, 128.4, 128.2, 128.1, 128.0, 127.7, 127.6, 127.4, 127.3, 127.0, 126.2, 126.1, 126.0, 64.7, 60.5.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{44}H_{36}N$: 578.2891; found: 578.2890.

Bis(4-tritylphenyl)amine (30)

Aryl iodide **9** (50 mg, 1 equiv), trityl aniline **22** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were heated at 110 °C for 24 h.

Yield: 81% (59 mg obtained from compound **9**); yellow sticky solid; R_f = 0.62 (1% petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.68 (m, 2 H), 7.59–7.52 (m, 2 H), 7.49 (t, *J* = 6.68 Hz, 2 H), 7.29–7.27 (m, 7 H), 7.26–7.23 (m, 15 H), 7.22–7.19 (m, 6 H), 6.70 (d, *J* = 8.56 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.2, 146.4, 132.6, 132.2, 131.2, 131.18, 131.15, 128.7, 128.6, 128.07, 128.05, 127.7, 127.5, 126.3, 126.2, 125.9, 115.2, 64.7, 64.4.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{50}H_{40}N$: 653.3083; found: 653.3082.

4-(9-(4-Aminophenyl)-9*H*-fluoren-9-yl)-*N*-(4-tritylphenyl)aniline (31)

Aryl iodide **9** (50 mg, 1 equiv), compound **23** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were heated at 110 °C for 24 h.

Yield: 74% (56 mg obtained from compound **9**); yellow oil; R_f = 0.57 (1% petroleum ether/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (t, *J* = 12.43 Hz, 2 H), 7.39 (t, *J* = 14.27 Hz, 2 H), 7.35 (dd, *J* = 2.44, 8.80 Hz, 15 H), 7.23 (m, 16 H), 7.28–7.27 (m, 7 H), 7.26–7.21 (d, *J* = 1.30 Hz, 6 H), 7.20 (s, 4 H), 7.08 (s, 1 H), 7.06 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7, 147.2, 146.9, 141.5, 139.9, 136.8, 133.3, 132.8, 132.6, 132.3, 131.7, 131.35, 131.31, 131.1, 130.9, 128.0, 127.8, 127.6, 127.5, 126.6, 126.1, 126.0, 125.8, 119.1, 113.3, 64.9, 64.3.

HRMS (ESI, Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{50}H_{39}N_2$: 667.3102; found: 667.3102.

N^4-(4-Tritylphenyl)-[1,1′:4′,1″-terphenyl]-4,4″-diamine (32)

Aryl iodide **9** (30 mg, 1 equiv), compound **24** (1.50 equiv), $NiBr_2$·dme (5 mol%), dppf (10 mol%), *t*-BuOK (2.50 equiv), and toluene (5 mL) were heated at 110 °C for 24 h.

Yield: 79% (31 mg obtained from compound **9**); yellow oil; R_f = 0.44 (1% petroleum ether/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.57 (t, *J* = 9.31 Hz, 2 H), 7.44–7.38 (m, 4 H), 7.30–7.27 (m, 3 H), 7.27–7.25 (m, 8 H), 7.22 (d, *J* = 5.96 Hz, 8 H), 7.19 (d, *J* = 5.96 Hz, 3 H), 7.14–7.09 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.2, 146.9, 146.5, 132.6, 132.3, 131.3, 131.2, 131.1, 130.6, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.39, 128.36, 128.30, 127.8, 127.7, 127.68, 127.62, 127.57, 127.51, 127.4, 127.2, 127.1, 126.8, 126.7, 126.38, 126.31, 126.2, 126.0, 125.9, 124.6, 124.1, 120.3, 1119.2, 113.3, 63.4.

HRMS (ESI, Q-ToF): *m*/*z* $[M + H]^+$ calcd for $C_{43}H_{35}N_2$: 579.2797; found: 579.2796.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgment

The authors gratefully acknowledge Prof. Anindya Dutta for helping in the photophysical studies, and the Department of Chemistry, IIT Bombay, for providing the facilities.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-2274-5102.

References

(1) Bulumulla, C.; Gunawardhana, R.; Gamage, P. L.; Miller, J. T.; Kularatne, R. N.; Biewer, M. C.; Stefan, M. C. *ACS Appl. Mater. Interfaces* **2020**, *29*, 32209.
(2) Zhang, X.; Richter, L. J.; DeLongchamp, D. M.; Kline, R. J.; Hammond, M. R.; McCulloch, I.; Heeney, M.; Ashraf, R. S.; Smith, J. N.; Anthopoulos, T. D.; Schroeder, B.; Geerts, Y. H.; Fischer, D. A.; Toney, M. F. *J. Am. Chem. Soc.* **2011**, *133*, 15073.
(3) Howard, J. K.; Rihak, K. J.; Hyland, C. J. T.; Bissember, A. C.; Smith, J. A. *Org. Biomol. Chem.* **2016**, *14*, 8873.
(4) Qiao, Y.; Zhang, J.; Xu, W.; Zhu, D. *J. Mater. Chem.* **2012**, *22*, 5706.
(5) (a) Han, X.; Huang, J.; Yuan, C.; Liu, Y.; Cui, Y. *J. Am. Chem. Soc.* **2018**, *140*, 892. (b) Liu, X.; Shi, X.; Liu, C.; Ren, Y.; Wu, Y.; Yang, W.; Alsaedi, A.; Hayat, T.; Kong, F.; Liu, X.; Ding, Y.; Yao, J.; Dai, S. *J. Phys. Chem. C* **2018**, *122*, 26337.
(6) Thomas, J. M. H.; Trewin, A. *J. Phys. Chem. C* **2014**, *118*, 19712.
(7) Zaręba, J. K. *Inorg. Chem. Commun.* **2017**, *86*, 172.
(8) Li, X.; Yu, Y.; Liu, Q.; Meng, Y. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3627.
(9) Liu, X. M.; He, C.; Huang, J.; Xu, J. *Chem. Mater.* **2005**, *17*, 434.
(10) Bai, D.-R.; Wang, S. *Organometallics* **2004**, *23*, 5958.
(11) (a) Ma, L.; Jin, A.; Xie, Z.; Lin, W. *Angew. Chem. Int. Ed.* **2009**, *48*, 9905. (b) Sengupta, S.; Sadhukhan, S. K. *Tetrahedron Lett.* **1999**, *40*, 9157.
(12) Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klock, C.; O'keeffe, M.; Yagh, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 4570.
(13) Pop, L.; Golban, M. L.; Hadade, N. D.; Socaci, C.; Grosu, I. *Synthesis* **2015**, *47*, 2799.
(14) Zaręba, J. K.; Białek, M. J.; Janczak, J.; Zoń, J.; Dobosz, A. *Cryst. Growth Des.* **2014**, *14*, 6143.
(15) Bauer, T.; Schlüter, A. D.; Sakamoto, J. *Synlett* **2010**, 877.
(16) Mao, H.; Zhang, S. *J. Mater. Chem. A* **2014**, *2*, 9835.
(17) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857.
(18) (a) Hu, X.; Wang, H.; Faul, C. F. J.; Wen, J.; Wei, Y.; Zhu, M.; Liao, Y. *Chem. Eng. J.* **2020**, *382*, 122998. (b) Lau, C. H.; Konstas, K.; Doherty, C. M.; Kanehashi, S.; Ozcelik, B.; Kentish, S. E.; Hill, A. J.; Hill, M. R. *Chem. Mater.* **2015**, *27*, 4756.
(19) Valášek, M.; Lindner, M.; Mayo, M. *Beilstein J. Nanotechnol.* **2016**, *7*, 374.
(20) (a) Zimmermann, T. J.; Müller, T. J. J. *Synthesis* **2002**, 1157. (b) Sengupta, S.; Sadhukhan, S. K.; Muhuri, S. *Synlett* **2003**, 2329. (c) Villa, M.; Ceroni, P.; Fermi, A. *ChemPlusChem* **2022**, *87*, e202100558.
(21) Rohit, K. R.; Meera, G.; Anilkumar, G. *J. Heterocycl. Chem.* **2022**, *59*, 194.
(22) Kim, B. H.; Bae, S.; Go, A.; Lee, H.; Gong, C.; Lee, B. M. *Org. Biomol. Chem.* **2016**, *14*, 265.
(23) Varala, R.; Seema, V.; Dubasi, N. *Organics* **2023**, *4*, 1.
(24) Suresh, P.; Pitchumani, K. *J. Org. Chem.* **2008**, *73*, 9121.
(25) Zhu, L.; Guo, P.; Li, G.; Lan, J.; Xie, R.; You, J. *J. Org. Chem.* **2007**, *72*, 8535.
(26) Liu, C. Z.; Wang, J. J.; Yang, B.; Li, Z.-Y.; Yan, M.; Liu, X.-M.; Hu, Z.-Y.; Liu, L.-T.; Li, Z.-T. *Chem. Commun.* **2023**, *59*, 11580.
(27) (a) Kotha, S.; Ganesh, T.; Ghosh, A. K. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1755. (b) Kotha, S.; Sreenivasachary, N. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1413. (c) Kotha, S.; Brahmachary, E. *Bioorg. Med. Chem. Lett.* **2002**, *10*, 2291. (d) Kotha, S.; Singh, K. *Tetrahedron Lett.* **2004**, *45*, 9607. (e) Kotha, S.; Manivannan, E.; Ganesh, T.; Sreenivasachary, N.; Deb, A. *Synlett* **1999**, 1621. (f) Kotha, S.; Enugurthi, B. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2719.
(28) Yeh, C.-H.; Lee, R.-. H.; Chan, L. H.; Lin, T.-Y. J.; Chen, C.-Ti.; Balasubramaniam, E.; Tao, Y. T. *Chem. Mater.* **2001**, *13*, 2788.
(29) Laliberté, D.; Maris, T.; Wuest, J. D. *Can. J. Chem.* **2004**, *82*, 386.