

Bay- and *ortho*- ring annulated perylenediimides: Synthesis and their panchromatic absorption

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Herein, we report the synthesis of semi-coronenediimide (sCDI) and N-caprolactam pyrrolo-perylenediimide (pPDI) using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The reaction involves *in situ* removal of trimethylsilyl (TMS) group followed by a ring formation at the *ortho* and bay positions of perylenediimide (PDI). Both the molecules exhibit diverse photophysical properties. pPDI demonstrates panchromatic absorption with quenched fluorescence while sCDI displays blue-shifted absorption with high fluorescence quantum yield. The obtained sCDI has been structurally characterized.

Keywords: Semi-coronenediimide, pyrrolo-perylenediimide, panchromatic absorption, fluorescence

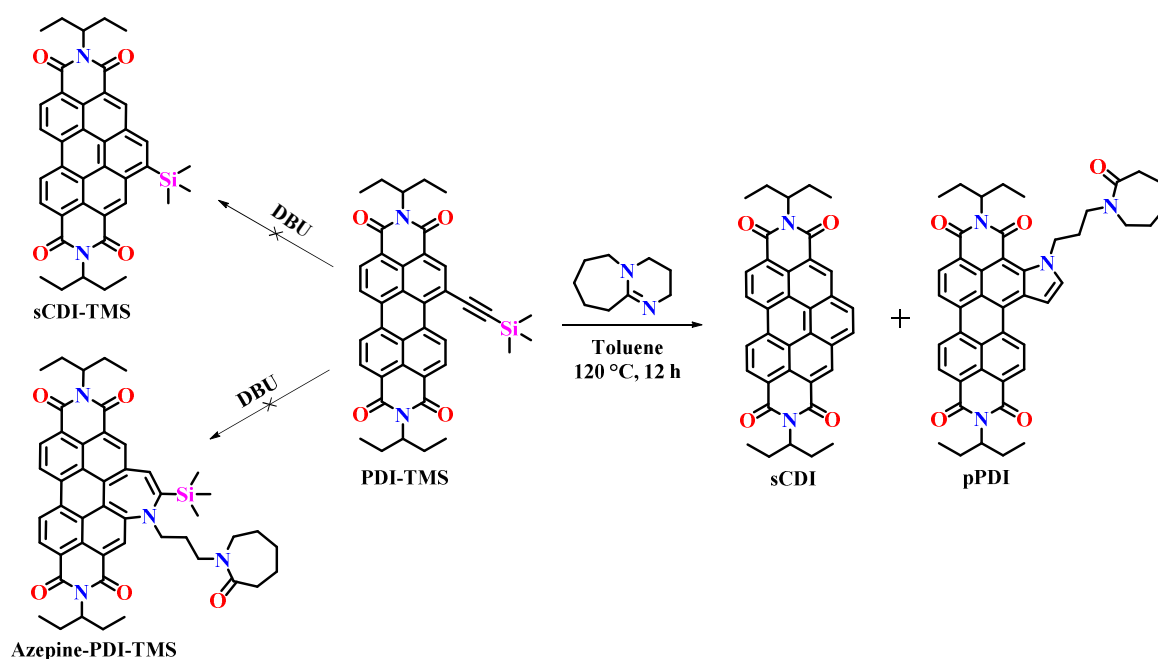
Perylene derivatives have emerged as an important class of functional dyes owing to their excellent photophysical characteristics, high thermochemical stability, flexible architecture and improved solubility¹. They have been successfully utilized in potential applications such as fluorescent solar collectors, photovoltaic cells, optical switches and lasers²⁻⁴. The aromatic core of perylene can be functionalized by diverse methodologies due to its robust and electronically tunable π -backbone. Recently, perylenediimides (PDIs) have evolved as materials of choice due to their electron-deficient nature and their application as n-type organic semiconductors. Core expansion of PDI on the shorter molecular axis leads to the formation of a new class of yellow chromophores, named coronenediimides (CDIs)⁵. CDIs have photophysical characteristics resembling both perylenediimide and coronene and have improved charge carrier abilities due to expanded aromatic core. Many synthetic methodologies like Diels-Alder reactions, photodriven cyclization, DBU-assisted cyclization of alkynes or Pd/DBU catalyzed cyclization have been employed for core expansion of PDI to get CDI with various substituents annulated to the bay positions⁶⁻⁹. We have recently reported the formation of 7-membered azepino-perylenediimide derivatives *via* nucleophilic participation reaction of DBU with the phenyl-alkynyl derivatives of PDI¹⁰. These derivatives displayed panchromatic absorption with excellent charge transfer transitions.

In the current work, we have utilized a similar methodology, employing ethynyl-trimethylsilane derivative as a reactant. Surprisingly, the reaction did not follow the expected path and led to the formation of two new PDI derivatives in a single-step synthetic procedure with diverse photophysical properties; N-heteroatom introduced 5-membered (pyrrolo) annulated derivative (**pPDI**) and a 6-membered (benzene) ring-annulated derivative (**sCDI**) (Scheme I). **sCDI** was highly fluorescent as compared to **pPDI** and one of the molecules shows intense absorption from visible to near-infrared region.

Results and Discussion

Synthesis

PDI¹¹, 1-bromo-perylenediimide (**PDI-Br**)¹² and 1-ethynyltrimethylsilyl-perylenediimide (**PDI-TMS**) were synthesized as per literature procedures, with minor modifications. In a typical procedure, PDI-TMS was dissolved in toluene and excess DBU was added. Reaction mixture was refluxed for 12 h. Thin layer chromatography revealed the formation of a less polar orange and a highly polar green fraction. Reaction mixture was purified by column chromatography using CHCl₃/hexane. The orange and green colour fractions were isolated in 22% and 14% yield, respectively. Complete synthetic and analytical details of all the molecules are provided in ESI.

Scheme I — Synthetic scheme for **sCDI** and **pPDI**

Characterization

^1H NMR spectrum of the orange fraction in CDCl_3 at room temperature indicated two clearly resolved doublets (H_c) and two singlets (H_a and H_b) in aromatic region for PDI core and four resolved signals (H_d , H_e , H_e and H_f) in the aliphatic region due to imide-substituted isopentyl group, with no trace of trimethylsilyl protons, as compared to the starting material. The absence of H_b proton signal in the ^1H NMR spectrum hints towards the cyclization of molecule and resembles to that of the reported CDI⁵ core. The reduced number of signals in ^1H NMR spectrum shows the symmetric nature of the molecule at the aromatic region (Figure 1). Two-dimensional NMR studies *i.e.*, COSY and HSQC along with ^{13}C NMR also validated the claim of ring formation at the bay positions. Further input was taken from APCI-HRMS analysis which confirmed the orange fraction as **sCDI** (ESI Figure).

The ^1H NMR spectrum of the green fraction in CDCl_3 at room temperature indicated two clearly resolved doublets (H_a and H_b) in aromatic region, apart from PDI core protons (H_c). The absence of a signal for H_a proton from PDI-TMS points toward the substitution at the *ortho*-position of PDI core. The shielded region shows signals for DBU frame-work protons which are similar to the caprolactam tail in the azepino-compound, with the disappearance of

proton resonances for trimethylsilyl group. The appearance of two additional signals around δ 7.6 (H_a and H_b) confirmed the formation of a product entirely different from the reported one (Figure 1). To elucidate the composition of the compound, high resolution mass spectrometry was performed which confirmed the presence of DBU moiety connected to the molecule. While going through the literature, we found that Li and coworkers have reported a heteroatom introduced pentacyclic ring formation on the naphthalenediimide in the presence of DBU and CuI ¹³. Taking a cue from this, we found that protons H_a and H_b are actually pyrrolic protons with coupling constants $J = 3.4$ Hz. This substantiated the formation of this 5-membered ring onto the *ortho*- position of PDI *via* Michael addition¹⁴ reaction followed by DBU ring opening. The green colour fraction was named as **pPDI**. When triisopropylsilyl ethynyl derivative of PDI was reacted with DBU, the reaction did not proceed which may be due to the bulkier nature of the TIPS group.

Single crystal X-ray analysis

Structural proof is imminent in further confirming the formation of products. After repetitive trials, suitable crystals of **sCDI** for the single crystal X-ray diffraction analysis were grown in chloroform and imidazole/hexane by solvent diffusion method. Solid

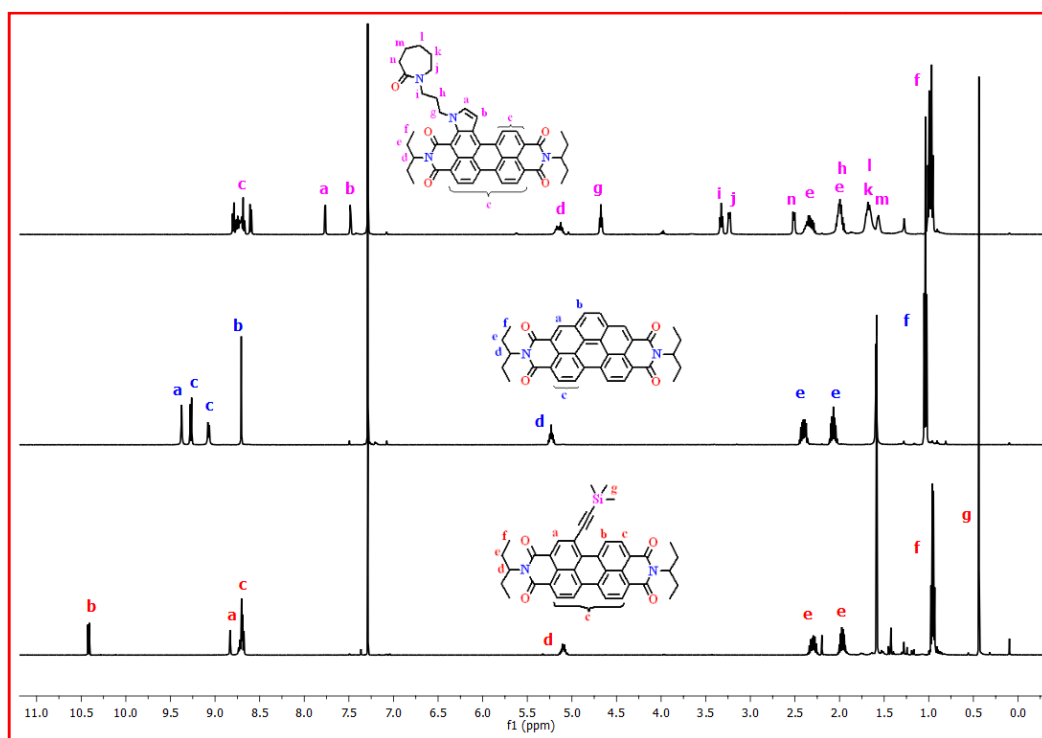


Figure 1 — ^1H NMR comparison of **PDI-TMS**, **sCDI** and **pPDI** in CDCl_3 at 298 K

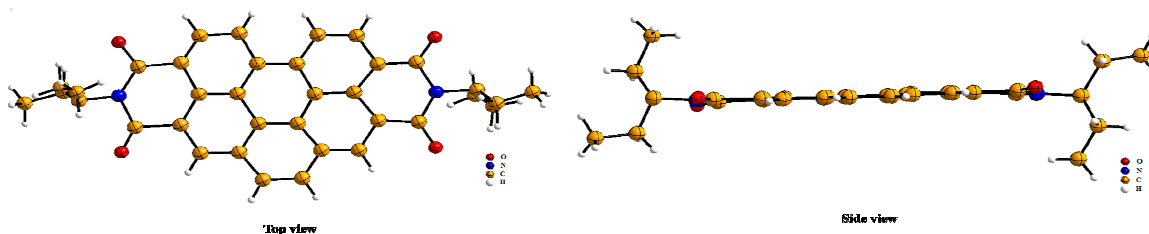


Figure 2 — Single crystal X-ray structure of **sCDI**. Solvent molecules were removed for clarity. CCDC 1565589

state structure revealed a perfectly planar core for the molecule **sCDI** (Figure 2). Unfortunately, **pPDI** did not yield quality single crystals for the diffraction studies.

Steady state absorption and emission studies

After successful characterization of the molecules, we set out to investigate their photophysical properties. Steady state absorption and emission spectra were recorded from dilute solutions in chloroform. **sCDI** displayed a hypsochromically shifted absorption spectrum in comparison to unsubstituted **PDI** (Figure 3 and Table I). However, this molecule retained the characteristic vibronic progression of parent **PDI**. The blue shift of **sCDI** is in line with the core-annulated **PDI** derivatives such as **CDI**.

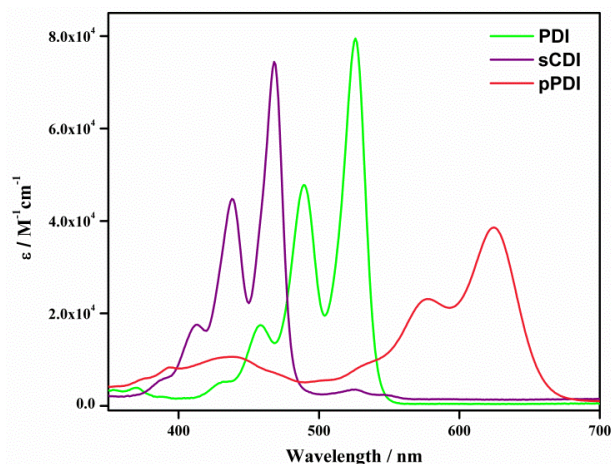


Figure 3 — Absorption profile of **sCDI** and **pPDI** in chloroform (10^{-6} M)

Table I — Absorption and emission details in chloroform

Compd	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	Φ	E_{red} (V)	E_{ox} (V)
PDI	526	79487	533	1	-0.67, -0.87	–
sCDI	468	74432	474	0.75	-0.83, -1.04	–
pPDI	625	38580	654	0.25	-0.70, -0.88	1.24

The most intriguing absorption features were observed for **pPDI**. This molecule exhibited panchromatic absorption covering the entire visible region. The absorption maxima showed huge red shift with respect to that of parent PDI. In addition, considerable band broadening was observed and sharp vibronic features of PDI were missing. This observed bathochromic shift in the absorption maxima can be attributed to the electron donating nature of the pyrrolic annulation along with an extended π -conjugation.

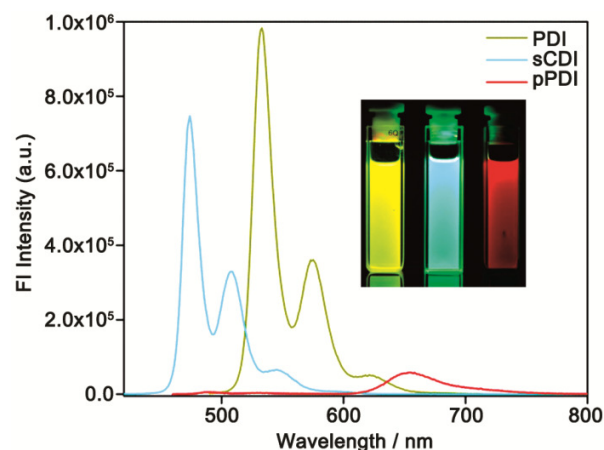
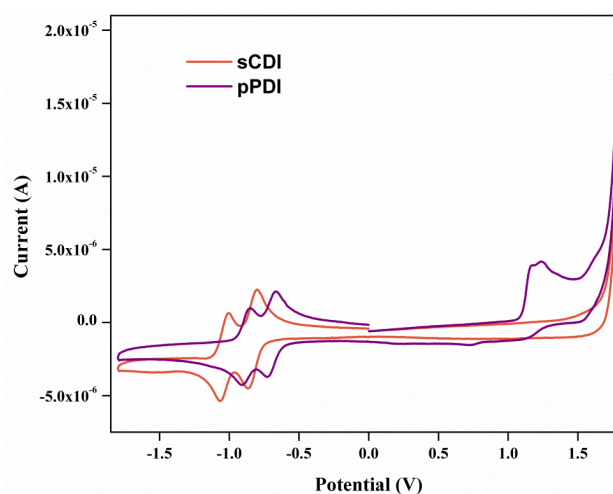
To gain further insight into the excited states of these molecules, emission studies were carried out from dilute solutions in chloroform. Interestingly, **sCDI** appeared to be highly fluorescent compared to **pPDI**. For **sCDI**, emission spectrum was a mirror image of absorption bands with emission maxima centered at 437 nm, which is in turn blue-shifted with respect to parent **PDI** (Figure 4 and Table I). From Figure 4, it can be seen that emission was quenched in case of **pPDI**. The quenching of fluorescence hints at possible intramolecular charge transfer in the excited state from electron-rich pyrrolic tail to electron-deficient PDI core. Quantum yields (Table I) were calculated with respect to unsubstituted **PDI**¹¹ having quantum yield = 1 by using the following formula:

$$QY = [QY_{\text{ref}} \times I \times A_{\text{ref}} \times \eta^2] / [A \times I_{\text{ref}} \times \eta_{\text{ref}}^2]$$

where, QY = quantum yield; ref = reference (**PDI**); A = Absorbance; I = integrated fluorescence intensity; η = refractive index of the solvent.

Electrochemical studies

Cyclic voltammetry (CV) experiments were carried out under continuous argon flow and a conventional three-electrode electrochemical cell was used. Glassy carbon working, platinum wire counter and SCE reference electrodes were used. All the measurements were carried out in dichloromethane solution with 0.1 M TBAP as the supporting electrolyte. All the spectra were recorded at a scan rate of 0.1 V/s. **sCDI** showed two reversible reductions at -0.83 V and -1.04 V vs. SCE (Table I and Figure 5). **pPDI**

Figure 4 — Emission profile of **sCDI** and **pPDI** in chloroform (10^{-6} M)Figure 5 — Cyclic voltammograms of **sCDI** and **pPDI** in dichloromethane using tetrabutylammonium hexafluorophosphate (TBAP) as a supporting electrolyte

undergoes two reversible reductions at -0.70 V and -0.88 V. In addition to this, an irreversible oxidation was also observed at 1.24 V, which further reflects the comparative electron-donating nature of the annulated pyrrolic ring.

Computational investigations

Computational investigations were carried out using DFT-B3LYP/6-31g(d,p) level using Gaussian 09 suite¹⁵ of programs. In case of **sCDI**, HOMO as

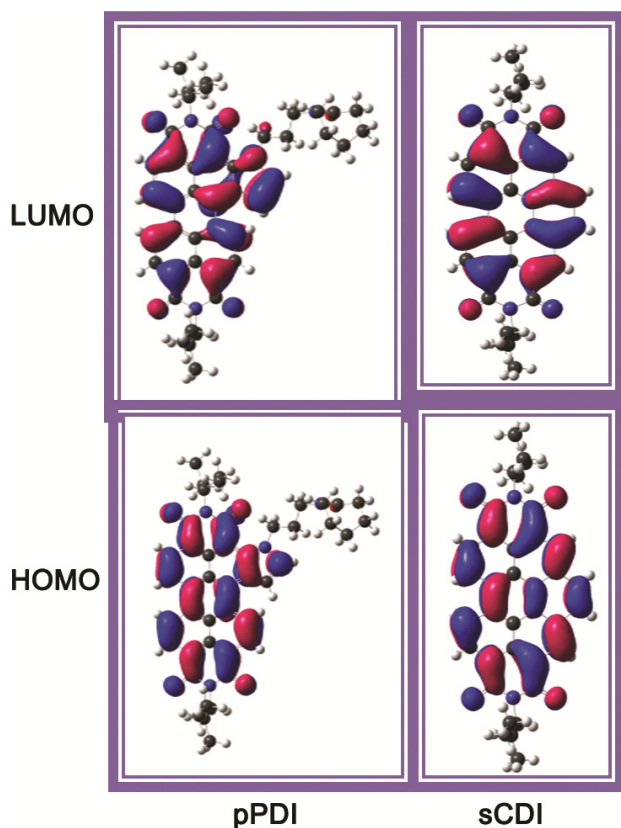


Figure 6 — DFT computed HOMO and LUMO for **sCDI** and **pPDI**

well as LUMO lie on extended-PBI aromatic framework. Similarly, **pPDI** also had frontier orbital contributions arising from entire extended π -backbone with the involvement of pyrrolic ring as well. However, ring opened-DBU tail does not contribute towards frontier orbitals as expected (Figure 6).

Conclusion

In summary, we have succeeded in obtaining *ortho*- and bay-fused perylenediimides namely N-caprolactam-pyrrolo-perylenediimide (**pPDI**) for the first time and semi-coronenediimide (**sCDI**) in a single pot reaction *via* a DBU-mediated synthesis. Solid state structural proof for **sCDI** confirms the planarity of its core and resulting in blue-shifted absorption along with bright emission. However, **pPDI** shows panchromatic absorption with diminished fluorescence due to a possible charge-transfer from the annulated pyrrole moiety. The current work highlights the versatility of the PDI framework for intriguing functionalization *via* simple synthetic manipulations. These new molecules have

the potential to be used for modern optoelectronic applications and further research in this direction is currently ongoing in our laboratory.

Supplementary Information

Supplementary information is available in the website <http://nopr.niscair.res.in/handle/123456789/60>.

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References

- Graser F & Hadicke E, *Leibigs Ann Chem* (1980) 483; (b) Naga Y & Misono T, *Dyes Pigm*, 5 (1984) 171; (c) Rademacher A, Maekle S & Langhals H, *Chem Ber*, 115 (1982) 2927; (d) Zollinger H, *Color Chemistry*, 2nd edn (VCH, Weinheim) (1991); (e) Würthner F, *Chem Commun*, (2004) 1564; (f) Huang C, Barlow S & Marder S R, *J OrgChem*, 76 (2011) 2386.
- Seybold G & Wagenblast G, *Dyes Pigm*, 11 (1989) 303; (b) Langhals H, *Nachr Chem Tech Lab*, 28 (1980) 716; (c) Schlettwein D, Worhrle D, Kaarmann E & Melville U, *Chem Mater*, 6 (1994) 3; (d) O'Neil M P, Niemczyk M P, Svec W A, Gosztola D, Gaines G L & Wasielewski M R, *Science*, 257 (1992) 63; (e) Gvishi R, Reisfeld R & Burshtein Z, *Chem Phys Lett*, 213 (1993) 338; (f) Wasielewski M R, *ChemSoc Rev*, 92 (1992) 435.
- Kohl C, Weil T, Qu J & Müellen K, *Chem Eur J*, 10 (2004) 5297; (b) Jones B A, Facchetti A, Wasielewski M R & Marks T J, *Adv Funct Mater*, 18 (2008) 1329; (c) Weiss E A, Ahrens B, Sinks L E, Gusev A V, Ratner M A & Wasielewski M R, *J Am Chem Soc*, 126 (2004) 5577; (d) Gao B, Lu C, Xu J, Meng F, Cui Y & Tian H, *Chem Lett*, 35 (2006) 1416.
- Jones B A, Facchetti A, Wasielewski M R & Marks T J, *J Am ChemSoc*, 129 (2007) 15259; (b) Würthner F, Saha-Möller C R, Fimmel B, Ogi S, Leowanawat P & Schmidt D, *Chem Rev*, 116 (2016) 962.
- Rohr U, Schlichting P, Böhm A, Gross M, Meerholz K, Brauchle C & Müllen K, *Angew Chem Int Ed*, 37 (1998) 1434; (b) Rohr U, Kohl C, Müllen K, Craats A V D & Warman J, *J Mater Chem*, 11 (2001) 1789; (c) Avlasevich Y, Müller S, Erk P & Müllen K, *Chem Eur J*, 13 (2007) 6555.
- Eversloh C L, Li C & Müllen K, *Org Lett*, 13 (2011) 4148.
- Yan Q, Cai K, Zhang C & Zhao D, *Org Lett*, 14 (2012) 4654; (b) Mao W, Zhang J, Li X, Li C & Tian H, *Chem Commun*, 53 (2017) 5052.
- Choi H, Paek S, Song J, Kim C, Cho N & Ko J, *Chem Commun*, 47 (2011) 5509; (b) Schmidt C D, Lang N, Jux N & Hirsch A, *Chem Eur J*, 17 (2011) 5289.
- Langhals H & Kirner S, *Eur J Org Chem*, 365 (2000) 380.
- Mishra R, Panini P & Sankar J, *Org Lett*, 16 (2014) 3994.
- Langhals H, Krötz O, Polborn & Mayer P, *Angew Chem Int Ed*, 44 (2005) 2427.
- Rajasingh P, Cohen R, Shirman E, Shimon L J W & Rybtchinski B, *J Org Chem*, 72 (2007) 5073; (b) Mishra R,

- Lim J M, Son M, Panini P, Kim D & Sankar J, *Chem Eur J*, 20 (2014) 5776.
- 13 Zhou C, Li Y, Zhao Y, Zhang J, Yang W & Li Y, *Org Lett*, 13 (2011) 292.
- 14 Bergmann E D, Ginsburg D & Pappo R, *Org React*, 10 (1959) 179; (b) Rossiter B E & Swingle N M, *Chem Rev*, 92 (1992) 771.
- 15 Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, Hratchian H P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery J A, Peralta J E, Ogliaro F, Bearpark M, Heyd J J, Brothers E, Kudin K N, Staroverov V N, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam J M, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas Ö, Foresman J B, Ortiz J V, Cioslowski J & Fox D J, *Gaussian 09*, Revision A. 02; Gaussian, Inc., Wallingford CT, (2009).